

s-Electron Ferromagnetism in Gold and Silver Nanoclusters

Weidong Luo,^{*,†,‡} Stephen J. Pennycook,[‡] and Sokrates T. Pantelides^{†,‡}

Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, and Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Received July 12, 2007

ABSTRACT

Ferromagnetic (FM) ordering in transition-metal systems (solids, surface layers, nanoparticles) arises from partially filled d shells. Thus, recent observations of FM Au nanoclusters was unexpected, and an explanation has remained elusive. Here we report first-principles density-functional spin-polarized calculations for Au and Ag nanoclusters. We find that the highest-occupied level is highly degenerate and partially filled by s electrons with spins aligned according to Hund's rule. The nanoclusters behave like "superatoms", with the spin-aligned electrons being itinerant on the outer shell of atoms.

Ferromagnetism in bulk Fe, Co, and Ni originates from partially filled 3d shells. In contrast, transition metals in the 4d and 5d series do not exhibit FM ordering. The difference has been explained by the Stoner theory of itinerant electron magnetism.¹ A combination of large density-of-states at the Fermi energy, N_F , and a large Stoner exchange constant I is essential. The Stoner criterion is satisfied only in the 3d-series metals Fe, Co, and Ni,² where the high degree of localization of the partially filled 3d states at the Fermi energy is responsible for a sufficiently large N_F . Even then, the band broadening of the 3d states results in smaller magnetic moments than those for isolated atoms. For example, the magnetic moment of bcc Fe is $2.2 \mu_B$ per atom, reduced from $4 \mu_B$ in free Fe atoms.

Density-functional calculations have led to predictions that, in systems with reduced dimensionality like surface layers, nanowires, and nanoclusters, reduced coordination of the surface atoms can lead to increased N_F that can tip the Stoner criterion in favor of FM ordering.^{3–5} More specifically, FM ordering has been predicted for reduced-dimensionality systems made of elements from the 4d and 5d series and enhanced FM ordering has been observed for reduced-dimensionality systems made of Fe, Co, and Ni.⁶ In all cases, elements with partially filled d shells were considered. In a recent paper, Hong et al. predicted FM ordering in certain thicknesses of free-standing Pd multilayers and found that the ordering was triggered by the interior layers, not the surface layers.⁷ They attributed the effect to quantum confinement. Once more, the presence of partially filled d

shells is crucial to achieve FM ordering. The case of Au nanoparticles is particularly intriguing because the d orbitals are completely full and bulk Au is diamagnetic. Hori et al.^{8,9} reported that Au nanoparticles capped by a polymer exhibit ferromagnetism (the presence of transition-metal impurities with partially filled d shells was ruled out), whereas Crespo et al.¹⁰ reported that Au nanoparticles capped by tetraalkylammonium exhibit bulklike diamagnetic behavior. Because the nanoparticles are believed to interact weakly with the capping material, the data raise the question whether uncapped Au nanoparticles can indeed be ferromagnetic even though the d shells are completely full.

In this Letter, we report first-principles density-functional spin-polarized calculations and unveil the origin of FM ordering in Au nanoclusters. We find that in highly symmetric ("spherical") nanoclusters, the highest-occupied molecular orbital (HOMO) is entirely made up of Au 6s states of the Au atoms in the outer shell and is highly degenerate and partially filled. Spin alignment occurs in this s-like "shell orbital", very much the way it occurs in partially filled d orbitals in free transition-metal atoms, i.e., driven by Hund's rule. We now of course have a kind of "superatom" and the electrons are not confined to individual atoms but are actually itinerant in the outer shell so that an s-electron analog of the Hund's rule applies. Similar results obtain for Ag nanoclusters. In contrast, the same kind of calculations for Pt nanoclusters find that FM ordering is controlled by the partially filled d states in the usual way, and spin polarization generally occurs in many eigenstates of the Pt clusters.

Density functional theory^{11,12} as implemented in the Vienna ab initio simulation package (VASP)¹³ was employed to compute the electronic and spin-polarization properties of

* Corresponding author. E-mail: wdluo@ornl.gov.

[†] Department of Physics and Astronomy, Vanderbilt University.

[‡] Materials Science and Technology Division, Oak Ridge National Laboratory.

gold clusters. The (spin-polarized) generalized-gradient approximation (GGA)¹⁴ to the exchange-correlation functional was used. The electron–ion interaction of gold was described by the scalar relativistic projector augmented-wave (PAW) method.^{15,16}

We studied the electronic and magnetic properties of several “bare” gold clusters, using as initial configurations the low-energy structures determined by Häberlen et al.¹⁷ Clusters with two types of point group symmetry were considered. Three clusters with icosahedral symmetry (I_h), Au₁₃, Au₅₅, and Au₁₄₇, consist of one central atom and one, two, and three full shells of atoms, respectively. Six clusters with O_h symmetry, Au₆, Au₁₃, Au₁₉, Au₃₈, Au₄₄, and Au₅₅, can be viewed as parts cut from the bulk face-centered cubic gold crystal. For clusters up to 55 atoms, a cubic supercell of the size 20.4 Å ($5a_0$, a_0 being the lattice constant of bulk fcc gold) was constructed. For the Au₁₄₇ (I_h) cluster, the supercell size was increased to 28.56 Å ($7a_0$). These supercell sizes ensure that the separation between neighboring Au clusters is at least 12 Å so that the interaction between clusters is negligible. Only one k -point was needed for the supercell calculation. Because of the small energy level separations near the HOMO, we find that a small Gaussian smearing energy (0.01 eV) is required to obtain a magnetic moment in the clusters. Larger Gaussian smearing destroys the magnetic moment, implying the disappearance of magnetic moments at high temperatures.

The total energies associated with different magnetic states can be very similar to each other. As a result, sometimes a direct self-consistent electronic-structure calculation cannot reach the most stable magnetic state of a cluster. To accurately determine the magnetic moments of gold clusters, we used a constrained-polarization variation of density-functional theory. The total magnetic moment of a cluster is kept to a constant value (constrained) during the electronic self-consistency and atomic structural relaxation steps. For each cluster, a set of calculations are performed to obtain the total energy as a function of the total magnetic moment, from which the stable magnetic state of a cluster can be predicted. As an example, the total energy of the icosahedral Au₁₃ cluster as a function of its magnetic moment is shown in Figure 1. We clearly see that the Au₁₃ icosahedral cluster has a magnetic moment of 5 μ_B (the optimal total magnetic moments have integral values because the energy spectra of the clusters are discrete).

The spin polarization mechanism in Au clusters is similar to Hund’s rule in a transition metal atom with partially filled degenerate orbitals. The difference is that the spin polarization in Au clusters originates from the cluster’s HOMO levels, which are made up mostly by 6s orbitals, contrasting sharply with the partially filled d shells that become spin-polarized in free transition-metal atoms. Gold has a completely filled 5d shell and one 6s electron. The Fermi level of bulk gold metal cuts only through the 6s band, which is quite broad. Bulk gold is, therefore, nonmagnetic (actually weakly diamagnetic).

We first examine the electronic energy levels of an icosahedral Au₁₃ cluster when spin-polarization is *not* al-

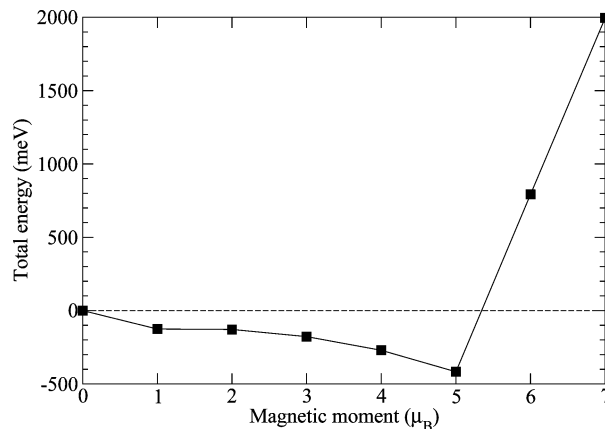


Figure 1. Determining the ground-state magnetic moment of icosahedral Au₁₃ cluster: total energy as a function of the total magnetic moment of the cluster.

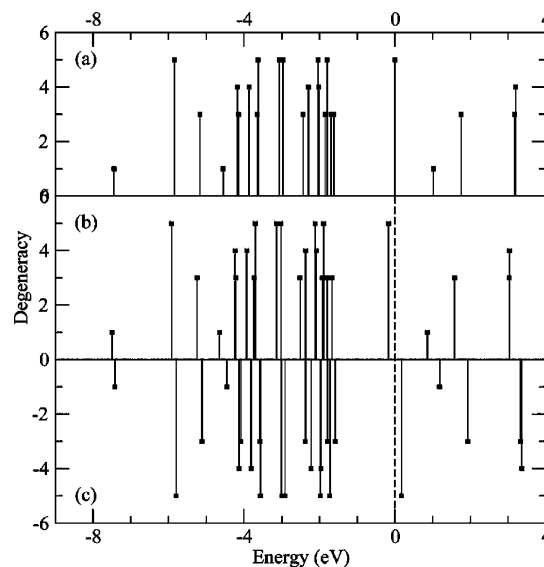


Figure 2. Degeneracy of energy levels in icosahedral Au₁₃ cluster: (a) no-spin polarization, 5-fold degenerate HOMO level is half-filled; spin polarization allowed, (b) majority spin, 5-fold HOMO level, and (c) minority spin, 5-fold LUMO level.

lowed. It is rather intriguing that the HOMO level has a 5-fold degeneracy (times 2 for spin), just like a d state in an atom, even though it is made of s orbitals centered on 12 Au atoms in the outer shell. Because only five electrons are available, the HOMO level is half occupied, as shown in Figure 2a. Because of the degenerate nature of the HOMO level, even a very weak exchange interaction can lower the total energy by polarizing the electrons. This is exactly what happens in the icosahedral Au₁₃ cluster if spin polarization is permitted in the DFT calculation. A configuration of five electrons with parallel spins in the majority-spin HOMO level of Au₁₃ (I_h) cluster results in the lowest energy, as shown in Figure 2b,c. Thus, the icosahedral Au₁₃ cluster acts like a “superatom” with half-filled HOMO levels due to a Hund’s rule effect similar to the half-filled 3d shells in Mn.

The spin density of icosahedral Au₁₃ cluster is shown as a contour plot in Figure 3. The integrated spin density within a sphere of radius R centered at the central Au atom of the

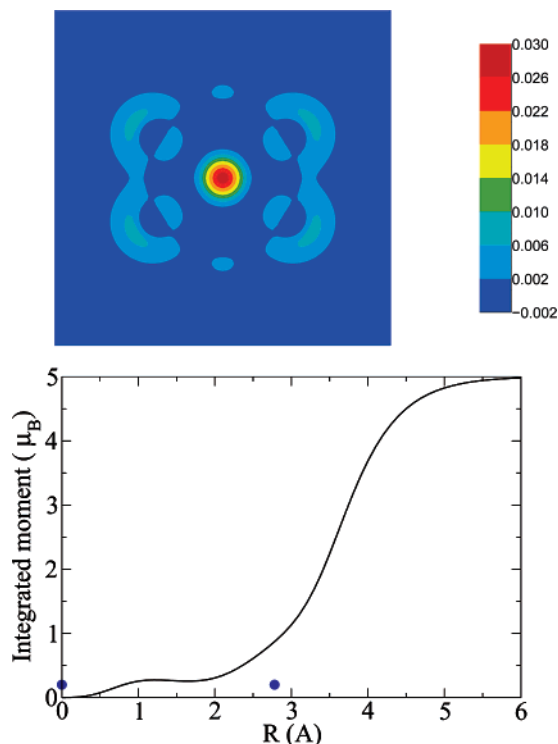


Figure 3. Spin density contour plot (unit: e/au^3) (top), and integrated spin density of icosahedral Au_{13} cluster (bottom), the positions of the center and the first shell gold atoms are marked.

cluster is also shown as a function of R . It is clear that the spin polarization occurs primarily on the outer-shell atoms.

It is informative to compare Au with its neighbors, such as Pt. A Pt atom has one less electron than a Au atom and the Fermi level in bulk Pt metal cuts through the 5d bands. The density-of-states at the Fermi energy, N_F , in bulk Pt is much larger than that of Au. Corresponding to the large N_F in bulk Pt, the energy level separations near the HOMO in the Pt_{13} (I_h) cluster are much smaller than the separations in Au_{13} (I_h) cluster. In the Pt_{13} (I_h) cluster, the HOMO level resulting from a nonpolarized calculation is only 2-fold degenerate and filled with two electrons (half filled), as shown in Figure 4a. However, the exchange interaction aligns electron spins among three energy levels near the HOMO, with level degeneracy of 3, 2, and 3, respectively. Thus, the degeneracy of the HOMO is not as crucial for magnetism as in Au clusters. The resulting magnetic moment of an icosahedral Pt_{13} cluster is much larger, $8 \mu_B$. This spin polarization mechanism can best be described as a Stoner mechanism as in bulk ferromagnetic metal, but with a larger effective N_F produced by low-coordination atoms as in surface layers.³

The magnetic moments of different Au clusters obtained from the present calculations are listed in Table 1. Also shown is the lowering of the total energy (ΔE) of each cluster due to the spin polarization (compared to the nonspin-polarized state). It is clear that the magnetic moments depend sensitively on the symmetry of the clusters. For the 13-atom and 55-atom clusters, the higher symmetry ones (I_h) have a higher level degeneracy in the outer shell orbital, thus larger magnetic moments due to the Hund's rule.

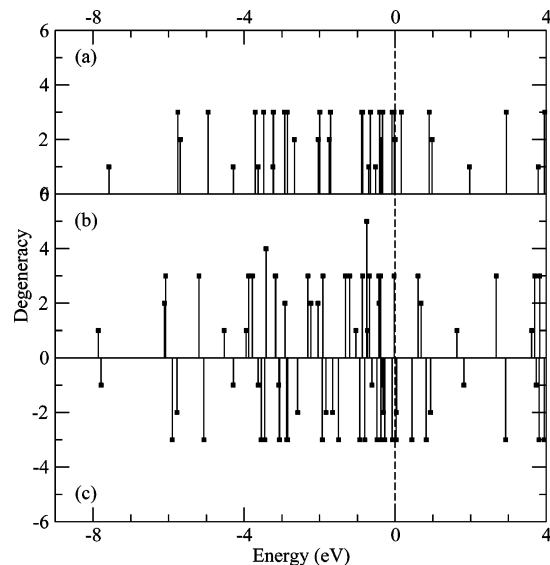


Figure 4. Degeneracy of energy levels in icosahedral Pt_{13} cluster: (a) no-spin polarization, 2-fold degenerate HOMO level is half-filled, spin polarization allowed, (b,c) parallel spin alignment across several energy levels, resulting in a total magnetic moment of $8 \mu_B$.

Table 1. Ground-State Magnetic Moments (μ) of Gold Clusters and Their Spin Polarization Energies (ΔE)

clusters	μ (μ_B)	ΔE (meV)
$\text{Au}_6 O_h$	2	-126.1
$\text{Au}_{13} I_h$	5	-417.1
$\text{Au}_{13} O_h$	1	-17.3
$\text{Au}_{19} O_h$	1	-19.5
$\text{Au}_{38} O_h$	4	-46.7
$\text{Au}_{44} O_h$	2	-23.2
$\text{Au}_{55} I_h$	3	-35.6
$\text{Au}_{55} O_h$	1	-4.5
$\text{Au}_{147} I_h$	1	-1.4

We also studied the magnetic properties of icosahedral Ag_{13} , Ag_{55} , Ag_{147} clusters and Ag_6 , Ag_{13} , Ag_{19} , Ag_{38} , Ag_{44} , Ag_{55} clusters with O_h symmetry. The magnetic properties of Ag clusters are very similar to the Au clusters because Ag is isoelectronic to Au. In particular, the ground-state magnetic moments of Ag clusters are the same as the corresponding Au clusters.

As the Hund's rule mechanism depends on the degeneracy of the HOMO levels, both the stable magnetic moments and the spin polarization energy (ΔE) are sensitive to the size and symmetry of individual clusters. We extracted the Hund's rule exchange coupling strength (J) of each Au cluster by the following relation:

$$\Delta E = -\frac{1}{4}Jn^2 \quad (1)$$

where n is the number of unpaired electron spins in the cluster. The extracted exchange coupling strength of each cluster is shown in Figure 5 as a function of the cluster size. Because the exchange energy originates from the differences of Coulomb energies between the HOMO electrons with

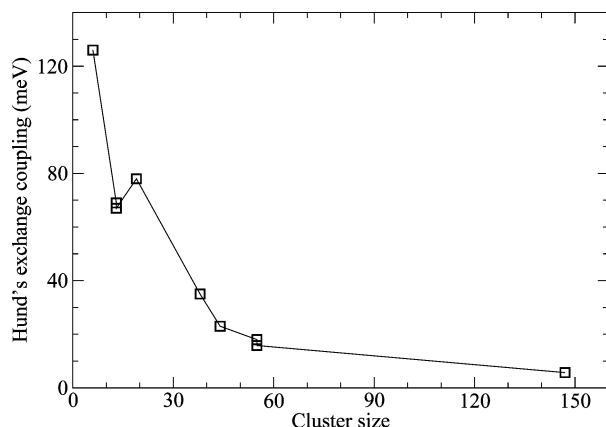


Figure 5. Hund's exchange coupling strength of different Au clusters.

different spin configurations. The exchange coupling strength decreases rapidly as the size of the Au cluster increases, as expected. It does remain finite, though small, for fairly large clusters and can, therefore, account for the observed value of $0.4 \mu_B$ for Au clusters of around 212 atoms.⁹

In summary, the formation of magnetic moments in noble-metal Au, Ag, and Pt nanoclusters was studied using density functional theory. Despite the filled d shells of gold and silver, nanoclusters of Au/Ag possess ground-state magnetic moments. High-symmetry Au and Ag nanoclusters behave like "superatoms" with Hund's rule exchange coupling among the outer-shell s electrons in the degenerate HOMO levels. In contrast to Au/Ag clusters, the magnetic moments of Pt clusters originate from partially filled 5d shells, and spin alignment occurs among many energy eigenstates of the clusters.

Acknowledgment. Research was sponsored in part by the DOE Office of Basic Energy Sciences, Division of Materials Sciences and Engineering and by the McMinn Endowment at Vanderbilt University. Computations were performed at the National Energy Research Scientific Computing Center.

References

- (1) Kübler, J. *Theory of Itinerant Electron Magnetism*; Oxford University Press: New York, 2000.
- (2) Janak, J. F. *Phys. Rev. B* **1977**, *16*, 255.
- (3) Blügel, S. *Phys. Rev. B* **1995**, *51*, 2025.
- (4) Reddy, B. V.; Khanna, S. N.; Dunlap, B. I. *Phys. Rev. Lett.* **1993**, *70*, 3323.
- (5) Cox, A. J.; Loudereback, J. G.; Apsel, S. E.; Bloomfield, L. A. *Phys. Rev. B* **1994**, *49*, 12295.
- (6) Billas, I. M. L.; Chatelain, A.; de Heer, W. A. *Science* **1994**, *265*, 1682.
- (7) Hong, S. C.; Lee, J. I.; Wu, R. *Phys. Rev. B* **2007**, *75*, 172402.
- (8) Hori, H.; Teranishi, T.; Nakae, Y.; Seino, Y.; Miyake, M.; Yamada, S. *Phys. Lett. A* **1999**, *263*, 406.
- (9) Yamamoto, Y.; Miura, T.; Suzuki, M.; Kawamura, N.; Miyagawa, H.; Nakamura, T.; Kobayashi, K.; Teranishi, T.; Hori, H. *Phys. Rev. Lett.* **2004**, *93*, 116801.
- (10) Crespo, P.; Litrán, R.; Rojas, T. C.; Multigner, M.; de la Fuente, J. M.; Sánchez-López, J. C.; García, M. A.; Hernando, A.; Penadés, S.; Fernández, A. *Phys. Rev. Lett.* **2004**, *93*, 087204.
- (11) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.
- (12) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.
- (13) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.
- (14) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (15) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.
- (16) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.
- (17) Häberlen, O. D.; Chung, S.-C.; Stener, M.; Rösch, N. *J. Chem. Phys.* **1997**, *106*, 5189.

NL071688H