Magnetic Anisotropies of Late Transition Metal Atomic Clusters

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We analyze the impact of the magnetic anisotropy on the geometric structure and magnetic ordering of small atomic clusters of palladium, iridium, platinum, and gold. We have employed a noncollinear implementation of density functional theory where the spin-orbit interaction has been included self-consistently. The size of the clusters ranges from two to five, six, or seven atoms, depending on the element. Our results highlight the relevance of the spin-orbit interaction in the magnetic properties of small atomic clusters made of fourth- and fifth-row elements.

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Nanostructures of all kinds display a wealth of fascinating geometric, mechanical, electronic, magnetic, or optical properties. The exploding field of Nanoscience pretends to understand, handle, and tailor these properties for human benefit. Atomic clusters and chains, molecular magnets, and a number of organic molecules like for instance metallocenes indeed show novel magnetic behaviors, that include the enhancement of magnetic moments due to the reduced coordination and symmetry of the geometry [1], and a rich variety of new noncollinear magnetic structures that are absent in bulk materials [2].

Magnetism in small metallic atomic clusters (MAC) has been extensively studied both experimentally and theoretically along the past decade [3]. It is therefore somewhat surprising that, even though spin-orbit effects are expected to be enhanced in MACs of heavy elements, there are few published theoretical papers that include the spin-orbit interaction (SOI) in their simulations [4,5]. Further, the explicit effects of the SOI on the orbital magnetism and magnetic anisotropy (MA) have only been addressed for MACs of the light 3d Transition Metal elements, using either semiempirical approaches [6-9], or *ab initio* methods [10]. To the best of our knowledge, there are no *ab initio* studies of the impact of the SOI on the magnetism of the heavier 4d and 5d MAC [11]. This includes not only explicit calculations of the magnetic anisotropy energy (MAE), but also and more importantly, whether the SOI modifies the ground state and the lowest-lying (magnetic) states of a given cluster.

We present in this Letter a series of calculations of selected atomic clusters of 4*d*- and specially 5*d*-elements that show that the SOI is a key ingredient in any *ab initio* simulation of heavy transition metal MAC that should not be overlooked. These include Pd_n, Ir_n, Pt_n, and Au_n, with n = 2, 3, 4, and 5, and also Pd₆ and Au₆, Au₇. The rationale behind our choice is that 5*d* MAC are expected to have the largest MAEs; among all 5*d* elements, gold is monovalent and should display a simpler behavior; comparing the magnetic properties of gold MAC with those of its neighboring Pt and Ir elements should shed light on the possible trends; further, Pd is isoelectronic to Pt, and it is

important to check whether it displays similar magnetic behavior. We have found a number of interesting results. First, the SOI always alters slightly the geometry of MAC, therefore generalizing the results obtained for platinum [5] to other elements. Furthermore, the SOI can lead to qualitative changes in the atomic geometry in specific cases, as for example Ir₃ and Au₇. Second, the MA generated by the SOI has a strong impact on the magnetism of the lowestlying states of the clusters. The MA selects orientations that are typically parallel (PR) or perpendicular (PP) to specific bonds in each cluster. Thus, MA and tendency to ferromagnetic alignment conspire together for ferromagnetism, or frustrate each other, depending on the geometrical arrangements of the atoms in each cluster.

We have used the *ab initio* Troullier-Martins [12] pseudopotential code SIESTA [13]. We have added to this code a fully self-consistent and spin noncollinear implementation of the SOI as described in detail in Ref. [14]. This implementation has been tested satisfactorily in several bulk semiconductors and metals [14], some molecular magnets [15], a large number of atomic chains [16], and a good number of small metallic (in the present work) and intermetallic clusters [15] by now. We have crosschecked our results for Ir₂ and Pt_{2,3} with the plane wave, Vanderbilt pseudopotentials code Quantum ESPRESSO [17]. We have employed both LDA and GGA approximations [18,19] for all dimers and trimers to assess the reliability of our results, except for Ir₃. We have used LDA for larger MACs since LDA provides a slightly more accurate description of bulk Pd, Ir, Pt, and Au, including the magnetism of Pd [20]. We proved recently that the ground state and first excited isomers of Pd clusters are rather insensitive to the choice of correlation functional and pseudopotential [21]. We have found here that the MAE further enhances the consistency of LDA and GGA in Pd, Pt, and Ir MACs. In contrast, we confirm that the choice of functional is important for Au_n clusters [3], even after including the SOI. We have borrowed the atomic configuration for the pseudopotentials from Quantum ESPRESSO package's web page [17]. We have checked that they produce a correct description for the bulk phases and have also benchmarked with other choices of matching radii in the case of some Pd_n , Pt_n , and Ir_n MACs. We have included nonlinear core corrections for Pd to account for the effect of semicore states in the valence. We have used in all cases a very complete triple zeta doubly polarized basis set (three pseudo atomic orbital for s and d shells, and two for the unoccupied p shell), with long radii that provides a very accurate description of the structural and electronic properties of the corresponding bulk materials. We have explicitly tested and set tolerances in all parameters (density matrix, electronic temperature, real space grid, and forces) to achieve accuracies in the range 1-3 K. We have calculated the individual atomic spin moments \vec{S}_i using a Mulliken analysis, while to estimate the atomic orbital moments \vec{L}_i , we needed to compute previously the matrix elements of the orbital angular operator in the chosen pseudo atomic basis. We have taken between two and five different seeds both for the geometry and for the magnetism of each cluster, making a total of five to ten different initial configurations for each of the simulated clusters.

We discuss first the magnetic anisotropy of the dimers Pd_2 , Ir_2 , and Pt_2 , and Au_2 that we show in Figs. 1 (a1) through (d1) for LDA. We have found that GGA agrees with LDA in all the essential details [22]. Pd_2 shows a weak MAE of about 5 meV that favors an alignment perpendicular to the dimer axis at its equilibrium distance. This dimer displays a low to high orbital angular momentum transition at longer elongations, which swaps the MA to



FIG. 1 (color online). Calculated ground state energy *E*, spin moment per atom times the gyromagnetic ratio gS_i and orbital moment per atom L_i of (a1-a3) Pd₂, (b1-b3) Ir₂, (c1-c3) Pt₂, and (d1-d3) Au₂, as a function of interatomic distance for spins perpendicular (solid line) or parallel (dotted line) to the axis of the molecule. A different reference energy has been set for each dimer to provide for uniformity in the energy values. Figures (d2-d3) demonstrate that the moments of the gold dimer are exactly zero.

PR. In marked contrast to Pd₂, the spin moments of the isoelectronic Pt dimer show PR alignment at its equilibrium distance. The MAE is estimated as 100 meV or 35 meV, depending on whether LDA or GGA is used. The two electrons of a single Pd or Pt atom arrange in a high spin (S = 1) configuration, according to Hund's rule. We find that the impact of the SOI is larger for the Pt₂ dimer, where the spin moment is noticeably smaller than $2\mu_B$ and different for the two orientations, as shown in Fig. 1 (c2). For Ir_2 , the SOI also favors PR alignment, but the predicted MAE at the equilibrium distance of the dimer is of about 60 meV in the LDA approximation. The spin moment is twice larger than for Pt₂ and Pd₂ and is also slightly different for the two orientations. We have found that the two electrons in the gold dimer pair in a singlet state, and therefore this cluster does show zero MAE. Figures 1 (a3–d3) show the orbital moments of the different dimers. The atomic orbital moments align parallel to the spin moments, therefore spelling out that the $\hat{L} \cdot \hat{S}$ product favors ferromagnetic alignment of these moments. Notice that the orbital moments of Ir₂ and Pt₂ are similar, but much larger than those of Pd_2 . If we take these results as a rough guide for the anisotropy of bigger clusters, we expect a tendency to PP alignment for Pd MACs, while Pt and Ir clusters will prefer PR orientations. Before moving to bigger clusters, we note that a tendency to PP alignment is easily fulfilled for planar structures, while it leads to frustration (e.g., noncollinearity) if the geometry is three-dimensional; tendency to PR alignment, on the other hand, can only be fulfilled without frustration for linear geometries.

We pass now to discuss the geometry and magnetism of the ground state of the trimer MACs, that we show in Fig. 2. We find that Pd and Pt MACs form a triangle, while Ir arranges in a straight line, and Au₃ arranges as either a triangle (LDA) or a zigzag (GGA). The moments in Pd₃ actually align ferromagnetically in the plane of the triangle, in a forklike fashion. A closer look to this cluster reveals that the interatomic distances in the trimer are larger, and actually occur at the crossover length from PP to PR alignments in the dimer. This leads to a sort of magnetostrictive effect whereby one of the bonds becomes slightly longer than the other two, hence slightly distorting the equilateral triangle. The spin moments align perpendicular to that bond. Pt₃ is a perfect equilateral triangle, that shows no magnetostriction at all. The spin moments in platinum arrange in a forklike fashion in the plane of the triangle, as those in Pd₃, but now the moments are slightly noncollinear. Pd₃ and Pt₃ also share the first excited isomer, which shows out-of-plane anisotropy and ferromagnetic alignment, while the second one is a vortex for Pd₃, and shows out-of-plane antiferromagnetic alignment in the case of Pt₃. A rough estimate of the MAE for these two trimers can be made by taking the energy difference between the ground state and the first and second excited isomers, since they share the same geometry. This criterion yields MAEs of 25 and 35 meV for Pd and Pt, respectively,





FIG. 2. Equilibrium geometry and spin moments $g S_i$ in the ground state of the trimers (a) Pd₃, (b) Ir₃, (c) Pt₃, and (d) Au₃.

if we use the first state, and 60 and 90 meV when we use the second state. Interestingly, these estimates show similar values for the MAE of these two MACs, despite their different atomic weight. The PR MA in Ir₃ is strong enough to modify its geometry, stabilizing a linear structure instead of the triangle that is found when the SOI is not included. The first excited state in Ir₃ is a paramagnetic linear chain that has an excitation energy of 7 meV, while the second, that lies at a much higher energy of about 300 meV, is a triangle. Au₃ is weakly magnetic. LDA predicts a triangle with clear PP in-plane anisotropy which leads to a noncollinear state, while GGA yields a zigzag arrangement, with the spin moments also showing PP inplane anisotropy. The first excited state of LDA Au₃ is a triangle that shows out-of-plane PP anisotropy and has a MAE of 8 meV. GGA predicts smaller MAEs for gold than LDA, of the order of a few Kelvin [22].

We confirm that the atoms in the ground and first excited states of Pd_4 arrange as a tetrahedron [21,22]. On the contrary, all lowest-lying states of the fifth-row tetramers show planar geometries, as shown in Fig. 3 for the ground state clusters. Platinum tetramers form rhombuses, while the lowest-lying Ir₄ isomers are perfect squares. An exception is the second excited state of iridium, that is slightly bent in a sort of saddle. Gold displays a richer variety of lowest-lying planar structures. The tendency to both ferromagnetism and PP MAE in the Pd₄ MACs leads to strongly frustrated noncollinear states, with small energy differences among them. The ground state shows the magnetostrictive effect found in Pd₃, while the magnetic arrangements in the excited states precludes it. The ground state of the iridium and platinum tetramers shows in-plane MAE, where the atomic spin moments are aligned along one of the diagonals of the square or rhombus. Their first excited state display out-of-plane MA, on the contrary. The excitation energies of these lowest-lying states are of about 130 and 50 meV for Ir₄ and Pt₄, respectively. It₄ and Pt₄ MACs do not show magnetostrictive effects. The lowestlying states of gold clusters are paramagnetic, except for

FIG. 3. Equilibrium geometry and spin moments $g S_i$ in the ground state of the tetramers (a) Pd₄, (b) Ir₄, (c) Pt₄, and (d) Au₄.

the second one, that shows a ferromagnetic alignment with out-of-plane MA. The excitation energy of the first gold excited state is of 260 meV [22].

The lowest-lying states of the palladium, platinum, and iridium pentamers show fully 3-dimensional arrangements. Palladium MACs typically form triangular bipyramids. The ground and first excited state of Ir₅ are Cheops pyramids, while the second excited state is planar. The ground state of Pt₅ is also a Cheops pyramid, but the two first excited states are triangular bipyramids [22]. Gold pentamers are all planar; the ground state and first excited isomer displaying an arrangement reminiscent of the Olympics logo. The atomic spins in all Pd₅ states are ferromagnetically aligned and display the same clear tendency to PP MAE as in Pd₃ and Pd₄. This is to be contrasted to the case of platinum and iridium MACs, where the tendency to PR MAE can not be satisfied well in these 3-dimensional structures. This effect is specially acute for the Cheops geometry. The trade-off in this case between spin ferromagnetism and PR alignments gives rise here to small noncollinearities, as shown in Fig. 4. The spin moments in these two MACs lie in the basement's plane. They point along its diagonal for Pt₅, while for Ir₅, the moments are aligned parallel to the atomic bonds. The ground state of Au₅ is magnetic and displays in-plane MAE. The favored anisotropy is actually PP, which can not be satisfied, giving rise to a noncollinear arrangement that we show in Fig. 4. The first excited state of Au₅ shows out-of-plane anisotropy and has an excitation energy of only 4 K, revealing again the extreme softness of small gold MACs [22].

We comment finally on the behavior of a few MACs of larger size. The ground and first excited states of Pd_6 are square bipyramids. The SOI gives rise to small spin and angular moments in the ground state, that ceases to be paramagnetic. It is the first state, whose excitation energy is of 6 meV, which becomes paramagnetic. The ground state of Au_6 is degenerate. One of the states is a paramagnetic planar triangle while the other is a square bipyramid,



FIG. 4. Equilibrium geometry and spin moments $g S_i$ in the ground state of the pentamers (a) Pd₅, (b) Ir₅, (c) Pt₅, and (d) Au₅.

that has small (noncollinear) spin moments, see Figs. 5(a) and 5(b). Finally, we have found that the SOI stabilizes a planar atomic arrangement in Au₇. The ground state presents two degenerate magnetic configurations, with inplane and out-of-plane MAEs, that we show in Figs. 5(c) and 5(d). These again spell out the extreme softness of gold clusters [22].

To summarize, we have performed a theoretical analysis of the impact of the spin-orbit interaction in the magnetic properties of small clusters of Pd, Ir, Pt, and Au. We have found that the SOI modifies, slightly always and qualitatively in a few cases, the geometry of these clusters. More



FIG. 5. Equilibrium geometry and atomic spin moments $g S_i$ of the two degenerate ground states of Au₆ [(a) and (b)] and Au₇ [(c) and (d)].

importantly, the spin-orbit interaction gives rise to magnetic anisotropies. These sometimes enhances the tendency to ferromagnetic ordering, while other compete with it, yielding some noncollinear structures.

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