Collinear versus non-collinear magnetic order in Pd atomic clusters

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We present a thorough theoretical assessment of the stability of non-collinear spin arrangements in small palladium clusters. We generally find that ferromagnetic order is always preferred, but that antiferromagnetic and non-collinear configurations of different sorts exist and compete for the first excited isomers. We also show that the ground state is insensitive to the choice of atomic configuration for the pseudopotential used and to the approximation taken for the exchange and correlation potential. Moreover, the existence and relative stability of the different excited configurations also depends weakly on the approximations employed. These results provide strong evidence on the transferability of pseudopotential and exchange and correlation functionals for palladium clusters as opposed to the situation found for the bulk phases of palladium.

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INTRODUCTION

The magnetic properties of free-standing atomic clusters of 3d TM elements have been intensively scrutinized during the last two decades. Two different but related phenomena have specifically been discussed and essentially unravelled. The first is the modification of local magnetic moments as compared with the values found in bulk materials. The second is the competition between the possible ferromagnetic, antiferromagnetic and non-collinear arrangements of the local spins, as well as its interplay with the geometry of the nanostructure. In the case of ferromagnetic elements like Fe, Co and Ni, the increase of the average cluster magnetic moment can be easily explained in terms of the reduced atomic coordination in the low-dimensional regime, with oscillations associated to structural (symmetry) changes. The case of antiferromagnets like Cr and Mn is much more complex. Atoms of these elements may display large magnetic moments, since they have a large number of d-holes susceptible to be polarized. On the other hand, clusters of these atoms may display tiny average magnetizations due to the tendency of their atomic moments to align in antiparallel directions. The structure plays also a fundamental role in the magnetic behavior of these clusters, since it may originate magnetic frustration. A conventional example of magnetic frustration in a classical spin system appears when atoms positions form triangular motifs. The studies of these classical systems show that magnetic frustration frequently leads to non-collinear configurations of the local spin moments. The latest theoretical studies reported in the literature show that non-collinear arrangements of quantum spins also appear as the ground or as some of the first isomers of clusters of 3d atoms, including not only Cr and Mn, but also Fe, Co and Ni.

All materials made of 4d TM elements are paramagnets, in contrast to those of the 3d row. A natural question thus arises of whether small clusters of 4d elements may show low-lying magnetic states of collinear or even non-collinear nature. Bulk palladium, being a paramagnet in the brink of becoming a ferromagnet, presents one of the most intriguing and controversial magnetic behaviors in nature. It is therefore not surprising that the very few experimental and theoretical studies published so far try to clarify whether Pd clusters of given sizes are magnetic or not, and what is the order of magnitude of their average magnetic moment. From the experimental side, most of the reports agree that only very small clusters have a net magnetic moment, with the exception of Shinohara and coworkers, who found noticeable magnetic moments at the surface of Pd particles as big as 79 Å. From the theoretical side, there is also consensus that very small Pd clusters are indeed magnetic. Futschek et al. have studied recently small Pd clusters using Density Functional Theory (DFT) in the collinear framework, within a fixed-moment mode. They have found that multiple spin isomers exist for each cluster size with very small energy differences. Interestingly, some of these competing isomers present ferromagnetic order, while others display antiferromagnetic alignments, with possible frustration. Although Pd has tendency to ferromagnetic order, this fact strongly points out to the possible existence of non-collinear magnetic structures, as a mechanism to release the frustration and competition between the different magnetic solutions.

We report in this article a thorough Ab initio study of the magnetic behavior of small palladium clusters Pd_N, with N ranging from 3 to 7. We have performed a simultaneous optimization of the geometric and magnetic degrees of freedom fully allowing for non-collinear spin arrangements. A debate exists currently on the accuracy of the Local Density Approximation (LDA) versus the Generalized Gradient Approximation (GGA) for the determination of the magnetic behavior of low-
Theoretical Details

We have performed our calculations using the code SIESTA. SIESTA is a DFT method that employs linear combination of pseudoatomic orbitals as basis set. The electronic core is replaced by a nonlocal norm-conserving Troullier-Martins pseudopotential that may include nonlinear core correction terms. The code allows to perform, together with the electronic calculation, structural optimization using a variety of algorithms. It also allows to simulate non-collinear spin arrangements both in the LDA and in the GGA approximations.

In the present calculation, we have also used a variety of pseudopotentials to test their effect on free-standing clusters and their corresponding transferability. We have generated three different pseudopotentials using LDA. The first (LDA1) was built with the electronic configurations $5s^1$, $5p^6$ and $4d^9$, and core-corrections matching radius $r_c = 2.00$ a.u.; the second (LDA2) was identical to LDA1, but with $r_c = 1.2$ a.u.; the third had a closed-shell atomic configuration ($5s^0$, $5p^6$ and $4d^{10}$) and $r_c = 1.2$ a.u. We have also generated two GGA pseudopotentials with electronic configuration $5s^1$, $5p^6$ and $4d^9$, and $r_c = 2.0$ or 1.2 a.u. (GGA1 and GGA2, respectively). In all five cases, the cutoff radii of the s, p and d orbitals were taken at 2.30, 2.46 and 1.67 a.u., respectively. We have described valence states by a double-$\zeta$ polarized basis set (e.g.: two different radial functions for s and d orbitals and a single one for p orbitals). We have taken an energy cutoff of 150 Ry to define the real space grid for numerical integrations, but we checked that higher cutoffs did not alter the results. We have carried out the structural optimization using a conjugate gradient algorithm, where we have set the tolerance for the forces at 0.003 eV/Å, with eventual double-checks using 0.001 eV/Å.

Results

We have found that the five pseudopotentials provide similar results when applied to an isolated palladium atom, being the eigenvalues of the ground state and different excited states slightly better reproduced with LDA1 and GGA1 (both had $r_c = 2.00$ a.u.). However, we have observed that they give rise to different magnetic behaviors when applied to the bulk fcc material. We first remind that palladium has a paramagnetic ground state with a lattice constant of 3.89 Å. Moreover, the latest simulations show that LDA predicts a paramagnetic ground state with a lattice constant of about 3.85-3.91 Å, in agreement with experiments, while GGA predicts the ground state to be ferromagnetic, with a much larger lattice constant of about 4.0 Å and a magnetic moment of about 0.4 $\mu_B$. The fact that LDA provides a slightly better description of the ground state of bulk hcp has been stressed recently by Alexandre and co-workers. Our LDA1 pseudopotential gives a ferromagnetic ground state with $M \approx 0.54 \mu_B$, while LDA2 and LDA3 predict the ground state to be paramagnetic, as it should. Finally, both GGA pseudopotentials lead to a ferromagnetic ground state with $M \approx 0.48 \mu_B$. On the other hand, all LDA approximations give a lattice constant equal to 3.90 Å. In contrast, both GGA pseudopotentials predict it to be equal to 4.01 Å. We note here that the fact that all LDA pseudopotentials predict the same lattice constant for the ground state regardless of its magnetic nature also happens with fcc iron, where LDA predicts the same ground state energy and lattice constant for the paramagnetic, antiferromagnetic and ferromagnetic Low Spin states. These results highlight the lack of transferability of the different pseudopotential and the sensitivity with the exchange and correlation functional used to describe the ground state of bulk palladium.

It is therefore of great importance to assess whether the same difficulties apply to the case of the atomic clusters considered here. As we shall discuss below, atomic palladium clusters are much more insensitive to the choice of pseudopotential and exchange and correlation functional. We shall show that the ground state is the same for the different approximations used here, in stark contrast to the case of the bulk material. Further, a large portion of the low-lying excited states are reproduced by all approximations.

Notice that we have not kept fixed the magnetic moment in our simulations of the Pd$_N$ clusters, but rather have allowed it to vary freely during the non-collinear iterative selfconsistency process, in contrast to previous authors. Moreover, while we can not rule out that we may have missed low lying solutions, we have endeavored to minimize this risk by feeding a large variety of non-collinear seeds for each cluster. This effort has allowed us to find a rich and complex family of metastable
TABLE I: Binding energy of the ferromagnetic clusters in meV/atom.

| N  | LDA1  | LDA3  | GGA1  | Ref.[18] | Ref.[19] |
|----|-------|-------|-------|----------|----------|
| 3  | 1.755 | 1.326 | 1.289 | 1.203    | 1.250    |
| 4  | 2.293 | 1.942 | 1.769 | 1.628    | 1.675    |
| 5  | 2.502 | 2.168 | 1.933 | 1.766    | 1.805    |
| 6  | 2.721 | 2.401 | 2.110 | 1.919    | 1.949    |
| 7  | 2.791 | 2.452 | 2.155 | 1.953    | 1.985    |

TABLE II: Inter-atomic distances of the ferromagnetic clusters in Angstrom.

| N  | LDA1  | LDA3  | GGA1  | Ref.[18] | Ref.[19] |
|----|-------|-------|-------|----------|----------|
| 3  | 2.49  | 2.49  | 2.56  | 2.52    | 2.52    |
| 4  | 2.57  | 2.59  | 2.64  | 2.61    | 2.61    |
| 5  | 2.61  | 2.63  | 2.70  | 2.65    | 2.64    |
| 6  | 2.62  | 2.64  | 2.70  | 2.66    | 2.66    |
| 7  | 2.64  | 2.66  | 2.72  | 2.68    | 2.70    |

solutions, that was absent in previous works. We finally note that we have repeated all calculations with the pseudopotentials LDA1, LDA3 and GGA1.

We have found that all clusters, except Pd$_6$, share the same collinear magnetic ground state, with a total spin of 2 $\mu_B$, in agreement with previous authors [18, 19]. The geometry of the ground state and the average interatomic distance of the Pd$_N$ clusters is displayed in Fig. 1, where we show that these range from 2.55 Å in Pd$_3$ to 2.71 Å for Pd$_7$. We have written the binding energies of the different clusters in Table I. The table shows that GGA1 gives slightly smaller values than LDA1 and LDA3, as otherwise expected. Moreover, the binding energies predicted by GGA1 are very similar to those obtained by Kumar, who also used the GGA (within an ultrasoft pseudopotentials, plane wave code) and by Futschek et al., who used the all-electron VASP code, but did not state the approximation employed.

We should stress that all the tested pseudopotentials provide the same ground state, in stark contrast to the situation that arose for the bulk material. Moreover, we have found very similar inter-atomic distances for all Pd$_N$ clusters, as shown in Table II. The table shows that GGA1 predicts slightly longer distances than LDA1 or LDA3, as otherwise. These distances also agree with those obtained by Kumar and Futschek within a range of 1 per cent.

The Pd$_6$ cluster displays a behavior different from the rest, and therefore we discuss it separately. Futschek and coworkers [19] found that Pd$_6$ was also ferromagnetic in contrast to Kumar et al. [18], who predicted it to be paramagnetic. We have found that both states are nearly degenerate, with the paramagnetic solution being slightly more stable. Further, we have found that the relative energy of the two solutions show a strong dependence with inter-atomic distance. Fig. (2) shows that there is a level crossing when the bonds are elongated by just 1 per cent from the equilibrium distance. The close proximity between the equilibrium distance and the level crossing distance explains the sensitivity of these results with respect to slight differences in the simulations and the discrepancies between Kumar and Futschek [18, 19]. Additionally, we have been unable to find non-collinear or antiferromagnetic solutions for this cluster.

In contrast, and independently of the pseudopotential or approximation used, the rest of the clusters show a rich variety of antiferromagnetic and non-collinear solutions. Most of these solutions, though not all, exist for all LDA1, LDA3 and GGA1. We have also found that, whenever they exist, the relative order of the different solutions is maintained, and the size of the atomic moments is very similar. These facts strengthen our belief that Pd atomic clusters are much more insensitive to the pseudopotential and approximation employed than bulk Pd. It is also reassuring that most of the collinear solutions have been identified in previous calculations [19] (e.g.: AF1 for Pd$_4$ and Pd$_5$ and AF2 for Pd$_7$).

The non-collinear solutions found can be classified into those that release antiferromagnetic frustration and therefore have lower excitation energy than the AF solution (NC1 and NC2 in Pd$_4$, shown in Table III and Fig. 3), and radial or quasi-radial solutions, that resemble the hedgehogs found in low dimensional theories of classical or quantum antiferromagnets [28]. Hedgehogs in these theories do not release frustration but rather are

\[ \text{FIG. 2: Energy difference of the Ferromagnetic state and the Paramagnetic one for the Pd}_6 \text{ clusters as a function of the average inter-atomic distance. We have taken the energy of the paramagnetic ground state as the zero of energy. Distances are measured in units of the equilibrium distance of the cluster. The vertical dashed line indicates the theoretical interatomic distance of bulk palladium in the GGA1 approximation.} \]
TABLE III: Different solutions obtained for the Pd$_N$ clusters. We provide the absolute values of the atomic magnetic moments, the total magnetic moment in the cluster $\bar{\mu}$ (both in units of $\mu_B$) and the excitation energy per atom (in meV). For $N=5$ and 7, the first two values of the atomic moments correspond to the axial sites, whereas the last ones correspond to the planar sites.

| N=3  | LDA1                      | LDA3                      | GGA1                      |
|------|---------------------------|---------------------------|---------------------------|
|      | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) |
| Ferro. | (0.67×3) 2 0 | (0.67×3) 2 0 | (0.67×3) 2 0 |
| NC1  | (0.35, 0.24, 0.24, 0.35) 0.25 9 | (0.25, 0.28, 0.28, 0.25) 0.03 10 | (0.29, 0.29, 0.29, 0.29) 0 12 |
| NC2  | (0.32, 0.32, -0.32, -0.32) 0 26 | (0.32, 0.32, -0.32, -0.32) 0 30 | (0.29, 0.29, -0.29, -0.29) 0 25 |
| AF1  | (0.41, 0, -0.41, 0) 0 40 | (0.31, 0, -0.31, 0) 0 31 | (0.38, 0, -0.38, 0) 0 36 |
| Para. | (0×3) 0 68 | (0×3) 0 34 | (0×3) 0 75 |
| N=4  | LDA1                      | LDA3                      | GGA1                      |
|      | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) |
| Ferro. | (0.50×4) 2 0 | (0.50×4) 2 0 | (0.50×4) 2 0 |
| NC1  | (0.29, 0.29, 0.29, 0.29) 0 12 | (0.29, 0.29, 0.29, 0.29) 0 12 | (0.29, 0.29, 0.29, 0.29) 0 12 |
| NC2  | (0.35, 0.24, 0.24, 0.35) 0.25 9 | (0.25, 0.28, 0.28, 0.25) 0.03 10 | (0.29, 0.29, 0.29, 0.29) 0 12 |
| AF1  | (0.32, 0.32, -0.32, -0.32) 0 26 | (0.32, 0.32, -0.32, -0.32) 0 30 | (0.29, 0.29, -0.29, -0.29) 0 25 |
| AF2  | (0.41, 0, -0.41, 0) 0 40 | (0.31, 0, -0.31, 0) 0 31 | (0.38, 0, -0.38, 0) 0 36 |
| Para. | (0×4) 0 59 | (0×4) 0 59 | (0×4) 0 59 |
| N=5  | LDA1                      | LDA3                      | GGA1                      |
|      | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) |
| Ferro. | (0.43, 0.43, 0.38×3) 2 0 | (0.40×5) 2 0 | (0.42, 0.42, 0.39×3) 2 0 |
| AF1  | (0, 0, 0.43, - 0.43, 0) 0 22 | (0, 0, 0.33, - 0.33, 0) 0 19 | (0, 0, 0.39, - 0.39, 0) 0 19 |
| AF2  | (0, 0, -0.24, 0.24, 0) 0 27 | (0, 0, 0.44, - 0.22, 0) 0 22 | (0, 0, 0.27×3) 0 28 |
| Para. | (0×5) 0 41 | (0×5) 0 41 | (0×5) 0 55 |
| N=6  | LDA1                      | LDA3                      | GGA1                      |
|      | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) |
| Ferro. | (0.33×6) 2 0 | (0.33×6) 2 0 | (0.33×6) 2 0 |
| Para. | (0×6) 0 -13 | (0×6) 0 -12 | (0×6) 0 -4 |
| N=7  | LDA1                      | LDA3                      | GGA1                      |
|      | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) | Local moments  \(\bar{\mu}\) |
| Ferro. | (0.19, 0.19, 0.32×5) 2 0 | (0.21, 0.21, 0.31×5) 2 0 | (0.20, 0.20, 0.32×5) 2 0 |
| AF1  | (-0.36, 0.36, -0.33, -0.22, 0.22, 0.32, 0) 0 9 | (-0.32, 0.32, -0.30, -0.20, 0.20, 0.30, 0) 0 8 | (-0.32, 0.32, -0.30, -0.20, 0.20, 0.30, 0) 0 8 |
| AF2  | (0.0, -0.36, 0.23, 0.23, 0.36, 0) 0 14 | (0.0, -0.29, -0.20, 0.20, 0.29, 0) 0 8 | (0.0, -0.32, -0.21, 0.21, 0.32, 0) 0 12 |
| Radial | (0.27, 0.27, 0.18×5) 0 22 | (0.24, 0.24, 0.12×5) 0 14 | (0.24, 0.24, 0.17×5) 0 20 |
| Para. | (0×7) 0 24 | (0×7) 0 24 | (0×7) 0 33 |

excitations over the antiferromagnetic ground state. We also find that these radial states have a higher energy than the antiferromagnetic solution, and therefore do not release frustration.

Notice that the antiferromagnetic and non-collinear solutions can be reached at temperatures of the order of room temperatures (25 meV). Therefore, any measurement of the magnetization performed at room temperature should find a thermal average of all those states, many of which have a tiny magnetic moment. It should not be surprising that such a measurement gives a small net moment.

We finally discuss the relationship between magnetism and equilibrium interatomic distances. We have found that these are essentially the same regardless of the magnetic state for the largest clusters (\(N=5-7\)), the smallest ones showing slight variations of less than 0.04 Å, but only within the LDA solutions. We have additionally analyzed the relative stability of the different solutions as a function of the interatomic distance. To this aim, we plot in Fig. 4 the energy per atom of the low-lying excited states of the Pd$_5$ cluster, relative to the ground state energy, as a function of an uniform volume expansion, obtained using GGA1. The figure shows that no crossover takes place, apart from the nearly-degenerate AF1 and AF2 solutions, that cross at an expansion of about 4%. Moreover, the relative energy differences are essentially preserved and the local magnetic moments kept constant, except for the AF2 and radial solutions, where they slightly change (by about 10%).

**CONCLUSIONS**

To summarize, we have studied the geometry and magnetic properties of the ground state and lowest lying iso-
mers of small palladium clusters Pd$_N$, with $N$ ranging from 3 to 7. Our results confirm that the ground state is indeed collinear or paramagnetic. We have found a rich variety of non-collinear low-lying isomers, some of which efficiently release frustration, while other (hedgehog-like solutions) do not. All these solutions should contribute to the room temperature magnetic behavior of the clusters, probably rendering small measured magnetic moments. We have finally found that simulations of atomic clusters are rather insensitive to the choice of the pseudopotential and to the approximation used for the exchange and correlation potential.

To provide a rough explanation of this contrasting behavior, we first note that GGA and LDA provide results that are quantitatively very similar in most cases, including bulk palladium. GGA provides results that are qualitatively different from LDA for bulk palladium because this material sits right at the edge of the paramagnetic-ferromagnetic transition, actually tilted slightly towards the paramagnetic side. Therefore, bulk palladium falls slightly short of fulfilling Stoner’s criterion. GGA and LDA are mean field approximations. Hence, they tend to overestimate magnetic properties. This error is partly compensated by LDA, that predicts usually lower magnetic moments than GGA. Consequently, LDA predicts the correct ground state for bulk palladium, while GGA provides a ground state that is slightly tilted towards the magnetic side of the phase diagram. Hence, LDA and GGA predict quantitatively similar, but qualitatively different results for the magnetic properties of this material. Atomic Pd clusters are strongly magnetic, with the exception of Pd$_6$. Therefore, all these approximations predict quantitative and qualitative similar results for those clusters.

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