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Spin locking at the apex of nano-scale platinum tips

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Abstract

Nanostructures based on platinum, such as small clusters or STM-tips, often exhibit an atomistic structure that relies upon one or very few strongly under-coordinated platinum atoms. Here, we analyze a paradigmatic example, an apex atom on a pyramidal platinum cluster employing the density functional theory. We show that such a pristine platinum tip exhibits a spin polarization of the apex atom with a remarkable robustness. Due to a depletion of the projected density of states at the apex position, the apex-magnetization is efficiently locked to about $0.6\mu_B$.

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I. INTRODUCTION

Recent years have seen a significant amount of cross-fertilization between the research fields of spintronics and molecular electronics. And indeed, exploiting spin and charge at the same time could open a fascinating venue towards implementing *memory* (spin) and *logic* (charge) on the same device [1, 2]. For tailoring and controlling spin and charge transport through contacted nano-scale devices (molecules, atomic chains) it is necessary to achieve control over the device properties down to atomic scale. Therefore, a considerable effort in *Molecular Spintronics* is devoted to optimizing conditions so device properties become (1) reproducible and (2) well controlled.[3] The proper choice of the contact material is a central part of this endeavor, because on the atomic level contacts are invasive, in general, and must be considered to be a part of the device.

Here we report a result that is of relevance for the use of platinum as a nano-electrode material: due to the reduction of the coordination number a single platinum atom adsorbed on the bulk material exhibits a very strong tendency towards magnetism.

As is well known, platinum is an important material from the technological point of view. Besides being a commonly used electrode in catalytic chemistry, it has been employed in scanning tunneling microscopy measurements [4]. Also, platinum has been tested as contact material in *Molecular Electronics*, especially in break junction experiments [5, 6], since like gold it forms mono-wires when pulling the junction[7] even if bridged by small molecules [8]. However quite unlike gold, platinum has intriguing magnetic properties that may offer qualitatively new possibilities for contact design. They exist due to the proximity to a Stoner instability. While in the bulk form it is known to be non-magnetic, platinum develops super-paramagnetic behavior in the case of long mono-wires[9] and small nanoclusters.

Platinum electrodes have been studied by several authors [10–14] in theoretical transport studies of nano-wires and break-junctions. Fernández-Rossier *et. al* [10] showed that the finite magnetization of a short Pt chain survives even after attaching it to pyramid-like electrodes. It is thus clear, that the reduction of the coordination number from three-dimensional (12) to one-dimensional (2) is sufficient for a magnetic transition to take place – at least on the level of density-functional-theory, DFT, with conventional exchange-correlation functionals. The question, that we would like to address here is, whether a single apex-atom of such a pyramid by itself would be magnetic already. This would be an intermediate case

with a coordination number of three or four, depending on the specifics of the contact pyramid. We are motivated by the observation that such geometries are typical for applications of platinum as contact material in *Molecular Electronics*.

Our study suggests that already the single apex-atom is magnetic (on DFT-level). Moreover, we see that the magnetization invokes a kind of proximity effect, so that it enters the pyramid down to first and second neighbor distances. To the best of our knowledge, such a tip magnetization has not been reported yet. In the reference [12] the electrodes were modeled by infinite surfaces, and no finite magnetization seems to accumulate in the electrode volume. Thiess, *et al.* [13] used cluster-like electrodes in order to simulate a break-junction condition, yet the penetration of magnetization to the bulk was not reported by the authors.

Magnetism is treated in our work on DFT-level in the all-electron full-potential approach. We study platinum pyramids enforcing full-surface conditions by applying non-magnetic (*i.e.* non-polarized) boundary conditions on one of the faces and varying the total magnetization in the remaining volume. We observe that the tip magnetization decays from the apex towards the non-polarized bulk, spanning several atomic sites. The apex magnetization is insensitive to the details of the boundary conditions, indicating that the magnetization of the tip stems from the geometric quantum confinement.

Quantum confinement has been discussed as a possible agent to drive magnetic instabilities in itinerant electron systems before. We mention the 0.7 anomaly that can show up in the conductance of quantum point contacts [15, 16] It was explained as a consequence of a reduction of screening in the contact region due to the confined geometry. The loss of screening enhances electron interactions and thus can drive magnetic transitions, at least in principle.

Theoretical studies of the phenomenon approximate the electronic structure by a two dimensional jellium [17], which is appropriate for quantum-point contacts as realized in semiconductor technologies. By contrast, we demonstrate the phenomenon in a realistic three-dimensional system (corner of a Pt crystal) by using atomistic first-principles calculations. In the few-atom platinum clusters, the origin of spin magnetic moments can be attributed to the potential of the core, giving rise to localized $3d$ states with enhanced Coulomb interaction. Our claim is that the polarization survives also in the bulk limit, in regions of geometric confinement as tips, corners, necks or surface islands and corrugations.

We emphasize that the basic mechanism, quantum confinement and breakdown of screening, is not restricted to platinum and could apply to other metals close to magnetic transitions. So far, an intrinsic electrode magnetization was not reported for iridium [14] and palladium junctions [18, 19], mainly because electrodes were simulated by plain surfaces. We suspect, that it could exist, nevertheless, for the physical reasons outlined in this manuscript.

II. CALCULATION

We perform first-principles calculations based on spin-polarized density-functional theory. The exchange correlation (XC) functional used is Perdew-Burke-Ernzerhof [20]. The Kohn-Sham states are represented in an atom-centered basis set as implemented in the FHI-AIMS package [21] fully including all core electrons. Relativistic effects are included at the scalar level [22], essentially as a correction to the non-relativistic single-particle energies. The basis functions are numerical and strictly localized. The focus is on platinum clusters of pyramidal shape “cut” from the face-centered crystal of platinum, so that the axis points in the crystalline (111) direction. We use a family of pyramids of 11 atoms (3 layers), 18 atoms (4 layers, see figure 2, also attached as a Supplementary Material) and 33 atoms (5 layers) to be able to extrapolate finite-size effects. The nearest-neighbor spacing is 2.7749 Å. The threefold symmetry axis (111) of the pyramid is lifted by including ad-atoms.

In order to enforce a non-magnetic boundary on the face opposite to the apex (interface layer), the spin densities on the atoms of the interface layer are forced to vanish. We achieve this by using a variant of the constrained density functional theory according to the reference [23].

We add further remarks on technicalities: In principle, the constraint specification does not assure unique ground state spin density and the choice of initial density matrix is crucial for the convergence of magnetic systems. We have tested several initial spin configurations on the atoms and did not see evidence for inter-atomic coupling of anti-ferromagnetic character.

We substantiated the impact of limited basis set size in a small 11-atom pyramid without constrained magnetization density. The basis sets employed contained all the minimal set for each atom (all core and valence orbitals for a free atom) and additional functions (higher zeta, higher angular momentum and diffusive orbitals) grouped into hierarchically organized sets denoted as *light/tier1*, *light/tier2*, *tight/tier2*, etc, see reference [21] for a detailed description.

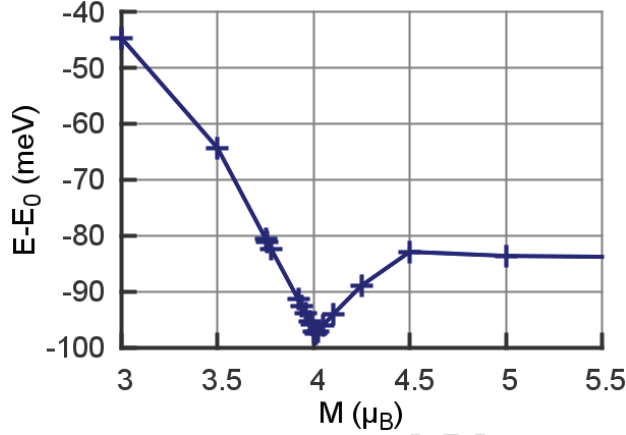


FIG. 1. Total energy of the 18-atom pyramid as a function of the total magnetization. Zero energy corresponds to the unpolarized solution.

For parameter sets *light/tier1*, *light/tier2*, *tight/tier1*, *tight/tier2*, the total magnetization does not differ more than a few percent. Therefore we employ the basic basis set *light/tier1* for most of the numerical results. This level is often denoted as double-zeta plus polarization in quantum chemistry literature. We further remark that larger basis sets involve extended orbitals, implying diffusion of constrained regions. For this reason, they are less suitable to a constrained density-functional study.

Size effects have minor impact on the accumulated spin. For the 11, 18, 33-atom pyramids we always find $M \approx 4\mu_B$ as the energy minimum, although the distribution of spin over layers changes, as the magnetization is allowed to relax deeper into the bulk of the pyramid.

We confirm the stability of the magnetic solution by checking against the LDA [24] and GGA+ U functionals [25]. In LDA, we obtain similar results to GGA, namely, the magnetic ground state for the pyramid, which survives also when constraints are imposed on the boundary. In simple terms, the GGA+ U introduces a penalty energy for fractional occupancy, rather than being a systematic cure of the flaws of semi-local exchange and correlation functionals. In the 11-atom pyramid,¹ we see only a small decrease of the apex magnetization from 0.69 to 0.60 μ_B , which we relate to the closing of the d shell.

² using $U = 2$ eV active on the 5d shell

III. RESULTS

Here we show results for a pyramid of 18 platinum atoms, as in figure 2. All physical quantities are calculated in DFT subject to a boundary condition of vanishing spin density on the pyramidal face opposite to the apex (see Methods for the details of our calculations).

Figure 1 displays dependency of the total energy on the magnetization of the 18-atom Pt-cluster. We find a minimum energy for $M \approx 4.01\mu_B$. Naturally, this corresponds to a magnetization spanning several atomic sites. To inspect the local behavior of spin density upon the variation of magnetization, we calculate the line density

$$\lambda(z) = \iint [n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})] dx dy \quad (1)$$

where $n_{\uparrow,\downarrow}(\mathbf{r})$ is the spin majority/minority electronic density. The z axis goes through the apex perpendicular to the interface layer. Figure 2 shows $\lambda(z)$ as z goes through the pyramid. Pink areas are regions of negligible spin-polarization. They are located outside the pyramid, as well as in the interstitials, giving rise to a ridge-valley picture. This reflects the fact that spin polarization is accumulated in the compact $5d$ orbitals, rather than in the overlapping sp orbitals. Interestingly, the ridges at $z = 0$ and 2.27\AA have constant height independent on the total magnetization. The entire variation of the magnetization is effectively restricted to the third layer (the third ridge starts from red (negative λ) to end up in green. Finally, the fourth layer is the constrained interface. Here only a small artefact of spin polarization appears³.

The ridge-valley structure allows unambiguous decomposition of magnetization to atomic layers - simply by integrating the line density between interstitials. The plot in figure 3 contains the layer magnetization divided by the number of atoms in the layer. Surprisingly, if the spin density is allowed to relax freely (i.e. switching off the constraint at the interlayer), the highest polarization is located in the layer next to the apex. If the constraint is applied, the magnetization decays towards the interface region as expected. Figure 3 demonstrates again that the apex is almost insensitive to the interface region (i.e. to the constraint). Change in the overall constraint is compensated in the deeper layers of the pyramid. The robustness of the apex indicates, that its magnetization is determined by quantum confinement, i.e. geometry of the tip.

³ Due to applying the constraint on the atomic Mulliken polarization and not on each orbital separately.

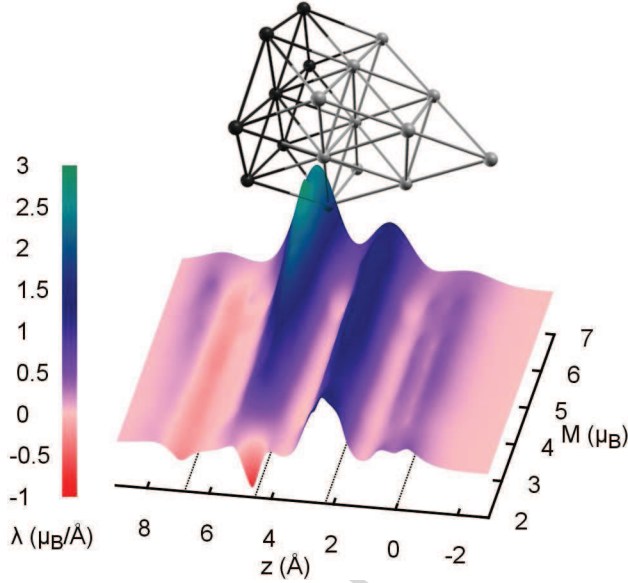


FIG. 2. Upper part: Ball-and-stick model[26] of the pyramid. The platinum atoms whose magnetization is constrained to vanish are darker. Lower part: Line spin density λ along the z axis of the 18-atom pyramid for magnetization varying between $M=2$ and $M=7 \mu_B$. Line spin density varies on the vertical axis and is color-coded for clarity. Atomic layers are positioned at $z = 0, 2.27, 4.53, 6.79 \text{ \AA}$ starting from apex and visualized by dashed lines in the horizontal plane.

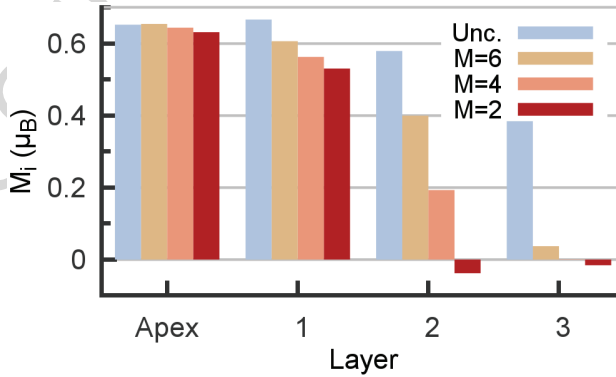


FIG. 3. Magnetic moment per atom in the layers 0-3 of the pyramid. Zero corresponds to the apex.

Finally, we demonstrate that the tight locking of apex magnetization may be understood as a consequence of depletion of apex density of states. Figure 4 presents the density of states of the 18-atom pyramid. The discrete spectrum has been convoluted with Gaussian smearing 0.05 eV, which roughly equals the average level spacing in the region of interest.

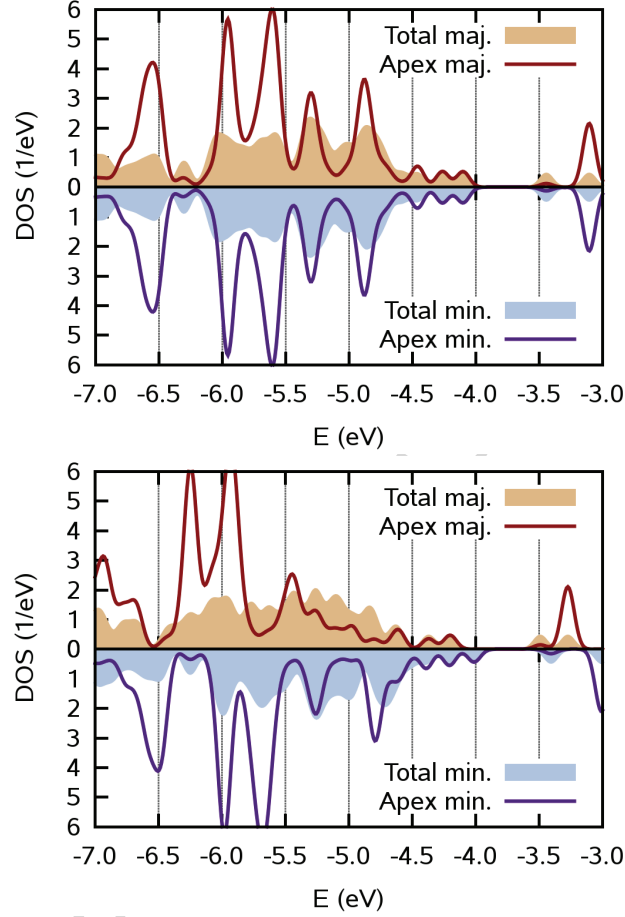


FIG. 4. Total and apex-projected density of states of the 18-atom pyramid. The total DOS has been divided by the number of atoms. The left plot presents an unpolarized solution, the right plot presents polarized $M = 4.01\mu_B$. Upper (lower) panel shows majority (minority) sector. The approximate chemical potential lies at $E = -4.89$ eV.

The chemical potential estimated as the average of highest occupied and lowest unoccupied single-particle energy level, is -4.89 eV. In the unpolarized case, the region below the electro-chemical potential, μ , shows higher spectral density, contributed mainly by the $5d$ orbitals. The chemical potential lies at the spectral resonance of a strong apex character. When allowing for (constrained) spin polarization, this spectral peak DOS is pushed to lower (higher) energies in the majority (minority) spin. At the same time, the apex density of states around the chemical potential is depleted. Hence, small deviations of the total magnetization can not be carried over in the apex region, since available single-particle states have little weight there.

IV. DISCUSSION

We discuss the possible impact of two approximations underlying our calculations.

Firstly, we recall that we have to rely upon approximate functionals for electronic exchange and correlation. Therefore, one expects that our results inherit typical artefacts of mean-field treatments. Such are related to underestimating quantum fluctuations so that broken-symmetry solutions are overemphasized. Still, we expect that the main features of our calculation survive also in the presence of quantum effects.

Quantum fluctuations of the spin are manifested in the Kondo effect which eventually leads to complete screening of the magnetic moment. Our main argument is that the observed magnetic moment, albeit localized, spans a few atomic sites, and has a relatively large magnitude, ($M \approx 4\mu_b$), which is not easily screened by the bulk electrons. Hence, one expects that a major fraction of the spin will persist down to lowest temperatures.

However, there is a suspicion that this case is slightly different from the commonly studied situation, where a transition-metal atom sits on top of a flat non-magnetic substrate (no pyramid). Magnetic ad-atoms such as Co exhibit Kondo effect [27] due to anti-ferromagnetic hybridization exchange with the paramagnetic host. In the case studied here, ferromagnetic-like instabilities at low-coordinated platinum atoms require ferromagnetic interactions (like Hund's rule exchange). Hence, the specific nature of quantum fluctuations calls for further investigations.⁴ We remark that the situation here bears similarity to the local moment formation observed in ferromagnetic atomic contacts [29]. Iron, cobalt and nickel are standard bulk ferromagnets whose magnetic moments reside in delocalized electronic states. Yet, as shown by Untiedt *et al.*, when short wires are formed between two electrodes, Kondo effect is at play. This signals that interaction of the moments in the wire region with the bulk electrons should have a considerable anti-ferromagnetic component.

Second, we have not been accounting for the spin-orbit interaction. Indeed, studies of

⁴ Tosatti *et al.* [28] have elaborated on the topic. They consider a nanoscale spin moment embedded in a metal close to a ferromagnetic transition. For them the spin is necessarily subject to a ferromagnetic exchange (interatomic direct Coulomb). The Coulomb-interaction competes with an anti-ferromagnetic exchange due to hybridization (kinetic, Kondo exchange). To our knowledge, the scenario when the ferromagnetic interaction prevades has not been observed yet.

platinum nano-structures suggest that a significant spin-orbit interaction could be present. For instance, Tosatti and coworkers [30] predicted colossal anisotropy of magnetization of infinite mono-wires.

To address the consequences of spin-orbit interactions for our results, we recall that the main effect of this interaction will be to fix the direction of a given magnetic moment. Hence it helps to decrease quantum fluctuations and will favor apex magnetism working into the direction of our claim.

V. CONCLUSIONS

We have demonstrated that platinum tips develop sizable magnetization ($4\mu_B$) even in the presence of a paramagnetic boundary. The spin density at the apex is effectively locked due to quantum confinement, manifesting itself in a local depletion of density of states. The magnetization per atom decays from the apex to the neighboring layers, mimicking a magnetic proximity effect.

The very presence of magnetization must be kept in mind whenever platinum electrodes are used in nano-scale transport studies. More generally, our results apply to a broader class of nano structures where, as we claim, low-coordinated platinum atoms drive a local magnetic instability. The unexpected deviation from the *normal metal* paradigm can have consequences important for molecular electronics and spintronics.

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Highlights

- Nano-scale platinum tips have an intrinsic magnetization
- Magnetism emerges despite the non-magnetic boundary of the cluster
- Quantum confinement efficiently locks the apex spin to $\approx 0.6\mu_B$