Pt₃ and Pt₄ clusters on graphene monolayers supported on a Ni(111) substrate: Relativistic density-functional calculations

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(Received 13 April 2012; accepted 25 June 2012; published online 31 July 2012)

Density-functional theory including spin-orbit coupling and corrections for dispersion forces has been used to investigate the structural and magnetic properties of Pt₃ and Pt₄ clusters deposited on a graphene layer supported on a Ni(111) substrate. It is shown that the strong interaction of the Pt atoms with the Ni-supported graphene stabilizes a flat triangular and a slightly bent rhombic structure of the clusters. Pt atoms are located nearly on top of the C atoms of the graphene layer, slightly shifted towards the bridge positions because the Pt–Pt distances are larger than the C–C distances of the graphene sheet lattice-matched to the Ni support. The strong interaction with the substrate leads to a substantial reduction of both the spin and orbital moments of the Pt atoms, not only compared to the clusters in the gas-phase, but also compared to those adsorbed on a freestanding graphene layer.

The trends in the magnetic moments and in the magnetic anisotropy of the cluster/substrate complex have been analyzed and it is demonstrated that the anisotropy is dominated by the Ni support.

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I. INTRODUCTION

In a recently published series of papers we have used density-functional theory (DFT) to explore the structural and magnetic properties of small Ptₙ clusters in the gas phase¹ and supported on a freestanding graphene layer.² We have been able to show that free Pt clusters carry a magnetic moment and that strong relativistic effects lead to the formation of a large orbital moment and a large magnetic anisotropy energy (MAE). The spin-orbit coupling influences not only the magnetic, but also the structural properties of the clusters, leading to a preference for planar structures for clusters consisting of up to five Pt atoms, in contrast to scalar relativistic calculations predicting three-dimensional structures for trimers and tetramers.¹ Pt clusters bind only weakly to a freestanding graphene layer via one or two Pt atoms and preserve large spin and orbital moments and a substantial MAE.² In contrast isolated Pt atoms and Pt₂ dimers deposited on a graphene layer supported on a Ni(111) substrate are predicted to be non-magnetic. Although graphene binds to the Ni surface only very weakly by dispersion forces (included in our DFT approach by semi-empirical corrections), an adsorbed Pt atom or dimer binds much more strongly to the support and induces also a locally enhanced interaction between graphene and Ni leading to a substantial buckling of the ad-layer. The dimer on the graphene/Ni support is adsorbed in a flat configuration instead of an upright one on the freestanding graphene layer. While the isolated adatom and the flat dimer are non-magnetic, an upright dimer was found to be strongly magnetic.³

In the present work, we extend these investigations to Pt trimers and tetramers adsorbed on a graphene/Ni(111) support, motivated by the aim to find out whether for slightly larger clusters the large magnetic moments calculated for clusters in the gas phase or adsorbed on freestanding graphene layer persist or whether the influence of the Ni substrate is strong enough to completely quench the magnetic moment as for the adatom and the dimer. Our investigations are based on spin-polarized density functional theory including spin-orbit coupling (SOC) and semi-empirical dispersion corrections.⁴, ⁵

The fully relativistic approach permits to calculate the orbital moments and the MAE, the dispersion corrections provide an accurate description of the interaction between the graphene layer and the Ni substrate. The origin of the magnetic anisotropy and the contributions from the Pt clusters, the graphene layer and from the Ni substrate are analyzed in detail.

II. COMPUTATIONAL DETAILS

The electronic structure calculations and structural optimizations reported here are based on DFT as implemented in the Vienna ab initio simulation package VASP.⁶, ⁷ VASP is based on the projector augmented wave method⁷, ¹⁰ for describing the electron ion interactions. The basis set contained plane waves with a maximum kinetic energy of 500 eV. For electronic exchange and correlation effects the semi-local Perdew-Wang functional⁸ in the generalized-gradient approximation (GGA) and the spin-imperturbation proposed by Yosko et al.⁹ were used. DFT calculations do not account for van der Waals (dispersion) forces. Dispersion corrections have been computed using the semi-empirical force-field proposed by

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Grimme et al., Grimme’s DFT+d approach has been implemented in VASP code by Bućko et al., and applied to calculate the structures and binding energies of a large number of solids where dispersion forces play an important role. For graphene layers supported on metallic substrates this approach has been shown to be in good agreement with calculations using the computationally much more demanding random-phase approximation.

Spin-orbit coupling has been implemented in VASP by Kresse and Lebاقv, following the approach of Kleinman and MacDonald et al. Calculations including spin-orbit coupling have been performed in the non-collinear mode implemented in VASP by Hobbs et al. MAE’s have been calculated as (i) total energy differences from self-consistent calculations for different orientations of the magnetic moments and (ii) using the magnetic force theorem. The force theorem allows to calculate the MAE from the differences in the sum of the band energies from non-self-consistent calculations at a frozen potential and charge density.

The force theorem permits the elucidation of the electronic origin of the MAE via the decomposition of the MAE into contributions from the adsorbed cluster, the graphene layer and from the Ni substrate. Within this formalism, the MAE may be written as

$$\text{MAE} = \sum_{i} \sum_{m_l=-2}^{2} \int_{E_F}^{E_N} (E - E_F) \Delta n_{m_l}^i(E) dE,$$

where the sum is over all atoms in the supercell and over all angular momentum quantum numbers $m_l$. $E_q$ is the energy at the bottom of the valence band, and where

$$\Delta n_{m_l}^i(E) = n_{m_l}^i(E; \text{soft}) - n_{m_l}^i(E; \text{hard})$$

is the difference in the partial local density of states for electrons with quantum number $m_l$ at the site $i$ for soft- and hard-axis magnetization. The orbital anisotropy $\Delta \mu_L = \mu_{L}^{\text{soft}} - \mu_{L}^{\text{hard}}$ may be calculated in terms of the difference in the occupation of states with $m_l = \pm 2, \pm 1$, i.e., according to

$$\Delta \mu_L = 2 \mu_B \sum_{i} \sum_{m_l=1,2} \int_{E_F}^{E_N} \left[ \Delta n_{m_l}^i(E) - \Delta n_{m_l}^{i-1}(E) \right] dE.$$  

Note that a large contribution to the MAE requires a large value of $\Delta n_{m_l}^i(E)$, integrated over the valence band, irrespective of the value of $m_l$. A significant orbital anisotropy arises only if $\Delta n_{m_l}^i(E)$ is different for states with $m_l = \pm 1$ and/or $m_l = \pm 2$. One must also remember that the expression given for the orbital anisotropy is exact, whereas the force theorem leads only an approximate value for the MAE.

The results achieved with the force theorem are necessarily less accurate than those derived from total-energy differences. The determination of the partial contributions to the MAE from integrals over the difference in partial densities of state (DOS) involves a further approximation, because the plane wave components of the eigenfunctions have to be projected onto spherical waves within atomic spheres. A detailed comparative study of the impact of these approximations on calculations of the MAE has recently been published for Fe and Co adatoms on a Pt(111) surface. For all further computational details we refer to our previous work.

### A. Structural model

The graphene/Ni(111) complex was represented by a periodically repeated unit cell containing the graphene layer supported on a slab with four Ni layers, containing 48 C-atoms in the graphene layer and 24 Ni atoms per layer of the substrate. Repeated slabs are separated by 20 Å of vacuum, so that the interaction between the repeated images is negligible. The Brillouin zone was sampled using $6 \times 6 \times 1$ Γ-centered $k$-point mesh and using a Gaussian smearing of 0.02 eV. Electronic DOS were calculated using the tetrahedron method.

Pt trimers adopt a triangular structure in the gas phase and adsorbed on a free graphene layer. We have examined two possible configurations: one with the Pt$_3$ triangle parallel to the graphene sheet and a second one where the triangle is perpendicular to the surface and binds to graphene only via one of its edges (as on the free graphene layer).

For free Pt$_3$ clusters scalar relativistic calculations predict that the equilibrium structure is a tetrahedron, with a flat rhombus being only slightly higher in energy. If SOC is included, the planar structure is preferred. Upon adsorption on graphene the initially planar structure is distorted by a contraction along the long diagonal of the rhombus so that the two Pt atoms at its ends move to positions on top of C atoms, while the two atoms occupying the short diagonal move to a larger distance from the graphene layer. The resulting structure is a bent rhombus, intermediate between the planar and tetrahedral structures, both have been used as starting configurations in the present work. The adsorbate/graphene complex was relaxed (keeping the Ni substrate frozen as obtained from the standard GGA calculations) until the forces on all atoms were less than 25 meV/Å. Simultaneously, the electronic and magnetic degrees of freedom were relaxed until the change in total energy between successive iteration steps was smaller than $10^{-7}$ eV.

### III. RESULTS AND DISCUSSION

#### A. Pt trimers

The relaxed structures of triangular Pt$_3$ clusters with the Pt-plane parallel (a) or perpendicular (b) to the graphene layer are shown in Figure 1, the information on the adsorption energies and the relevant geometric parameters are compiled in Table I. A flat structure that allows a binding of all three Pt atoms with the graphene layer is lower in energy by 46 meV/Pt-atom than a perpendicular configuration where the cluster binds to the substrate only via one of its edges, as on a freestanding graphene layer. Of the two energies listed in Table I, $E_{ad}$ measures the adsorption energy of the cluster relative to the clean graphene/Ni(111) surface and the gas-phase Pt$_3$ cluster, whereas $E_{coh}$ measures the energy relative to the clean substrate and three isolated Pt atoms and hence accounts for the strength of the binding between the Pt atoms in the supported cluster. With $E_{ad} = -1.222$ eV/Pt-atom the binding of the cluster to the substrate is significantly weaker than...
for the dimer \((E_{\text{ad}} = -1.747 \text{ eV/Pt-atom})\), but because \(E_{\text{coh}}\) increases by 0.045 \text{ eV/Pt-atom} relative to the dimer and by 0.29 \text{ eV/Pt-atom} relative to the monomer the formation of a trimer is energetically favored.

The threefold symmetry of the cluster is broken by a minimal difference of 0.02 \text{ Å} in the Pt–Pt distances. The Pt atoms are located almost on top of the C atoms, slightly shifted towards the C–C bridge positions to admit for Pt–Pt distances of 2.639 \text{ Å} (increased by 0.139 \text{ Å} relative to the gas-phase cluster) which are larger than the C–C distances of 2.49 \text{ Å} in the graphene layer lattice-matched to the Ni(111) support. The strong binding of the Pt3 cluster to the substrate induces substantial distortions of the graphene layer. The Pt3 triangle sits in the center of an extended depression of the graphene layer, the buckling amplitude of graphene is 0.40 \text{ Å}. The C-atoms binding directly to the Pt atoms, however, are displaced outward relative to their neighbors but remain at a lower height than those at a large distance from the cluster.

In an upright triangle the Pt atoms forming the lower edge are again located close to on-top positions, slightly shifted towards the bridge (Pt–Pt distances of 2.646 \text{ Å}, substantially increased compared to 2.54 \text{ Å} in the upright cluster on graphene only). The Pt–C distances of the binding Pt-atoms are almost the same as for the flat triangle and only slightly increased by 0.024 \text{ Å} compared to a flat dimer. The deformation of the graphene layer and of the Ni support is similar to that induced by a flat Pt-trimer, but with larger buckling amplitudes.

The spin-moments calculated in a scalar-relativistic approach reflect the broken symmetry of the Pt3 triangles (see Figure 1). The spin-moments are only slightly changed if SOC is included, the magnetic structures for easy and hard magnetization directions are shown for both configurations in Figure 2. For the flat Pt trimer the easy magnetization direction is in-plane, the hard magnetic axis is perpendicular to the substrate. The spin and orbital moments per cluster are \(\mu_S = 0.556 \mu_B\) and \(\mu_L = 0.177 \mu_B\) for the easy and \(\mu_S = 0.568 \mu_B\) and \(\mu_L = 0.214 \mu_B\) for the hard magnetization direction, leading to negative spin and orbital anisotropies of \(\Delta \mu_S = -0.012 \mu_B\) and \(\Delta \mu_L = -0.037 \mu_B\). The spin moments in the top Ni layer vary for magnetization along the easy axis between 0.44 and 0.57 \(\mu_B\), i.e., they are reduced compared to their bulk value of 0.66 \(\mu_B\). The local distribution of the moments is similar to that reported for Pt adatoms and dimers on graphene/Ni(111), i.e., the lowest and largest values of the spin moment are found on the sites directly below the adsorbed Pt (see Figures 5 and 6 in Ref. 3). At a larger distance from the adsorbed cluster they converge to an intermediate value of 0.53 \(\mu_B\). The variation of the spin moments is already much smaller in the second Ni layer (between 0.60

### Table I

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Method</th>
<th>(E_{\text{ad}})</th>
<th>(E_{\text{coh}})</th>
<th>(d_{\text{Pt-Pt}})</th>
<th>(z_{\text{Pt-G}})</th>
<th>(z_{\text{G-Ni}})</th>
<th>(d_{\text{Pt-C}})</th>
<th>(b_C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat</td>
<td>DFT+d</td>
<td>-1.222</td>
<td>-3.607</td>
<td>2 \times 2.639, 2.637</td>
<td>2.35</td>
<td>2.18</td>
<td>2.08</td>
<td>0.40</td>
</tr>
<tr>
<td>Upright</td>
<td>DFT+d</td>
<td>-1.176</td>
<td>-3.561</td>
<td>2.646, 2.524, 2.495</td>
<td>2.36</td>
<td>2.18</td>
<td>2.08</td>
<td>0.55</td>
</tr>
</tbody>
</table>

\(E_{\text{ad}}\) and \(E_{\text{coh}}\) are given in \text{ eV/Pt-atom}, distances in \text{ Å}.
and 0.62 $\mu_B$) the moments are converged to the bulk value from the third layer onwards. The orbital moments of the Ni atoms vary between 0.030 and 0.062 $\mu_B$ in the first, between 0.043 and 0.045 $\mu_B$ in the second, and 0.049 and 0.056 $\mu_B$ in the third layer. The anisotropy of the Ni spin moments is very weak, the orbital moments are slightly reduced for perpendicular magnetization, varying only between 0.034 and 0.045 $\mu_B$ in the first layer. The average orbital anisotropy is $\Delta \mu_L = 0.010 \mu_B$ per Ni-atom. The MAE is 13.2 meV/cell or 0.089 meV/atom in the cluster/support complex (3 Pt, 48 C, and 96 Ni atoms). The contributions from cluster, graphene, and Ni support and the trends in the MAE with cluster size will be discussed below.

For the upright triangle the relativistic calculations initialized with the vector magnetic moment parallel to both the triangle and the graphene layer and parallel to the triangle, but perpendicular to the substrate converge to non-collinear stationary states are shown in Figures 2(c) and 2(d). In this case, we have calculated larger and positive spin and orbital anisotropies of $\Delta \mu_S = 0.046 \mu_B$ and $\Delta \mu_L = 0.058 \mu_B$. The reduction of the spin moments in the first Ni layer is smaller than below the flat Pt$_3$ cluster, varying between 0.47 and 0.65 $\mu_B$, and converge more quickly towards the bulk value. Orbital moments of the Ni atoms are only marginally influenced by the configuration of the adsorbed Pt-cluster. The MAE between these two states is 11.6 meV/cell or 0.078 meV/atom.

For a Pt$_3$ cluster supported on a freestanding graphene layer a flat configuration is unstable, it relaxes to an upright triangle bound via one of its edges. The stationary magnetic configurations are also at least weakly non-collinear. In the magnetic ground state the magnetization direction is parallel to the graphene layer, but oblique to the triangle and parallel to the C–C bonds of the substrate [see Figure 6(a) of Ref. 2]. The total spin and orbital moments of 0.70 $\mu_B$ and 0.50 $\mu_B$ are larger by about 0.1 $\mu_B$ than in the presence of the Ni-support.

### B. Pt tetramers

For a Pt$_4$ cluster the equilibrium configuration is an almost flat rhombus [see Figure 3(a)] with all four Pt atoms in or close to positions on top of C atoms in the graphene layer (the Pt atoms along the long diagonal are slightly shifted towards bridge positions). This configuration is only 9 meV/Pt-atom lower in energy than a trigonal Pt$_4$ pyramid with the Pt atoms forming the base located close to C atoms, slightly displaced towards the neighboring bridge positions [see Figure 3(b)].

The adsorption energy per atom is slightly reduced compared to the smaller clusters, but the binding energy per Pt atom is larger so the Pt$_4$ cluster is stable against decomposition into smaller Pt ensembles (see Table II).

The Pt$_4$ rhombus is composed of two equilateral triangles with Pt–Pt distances of 2.630 Å, it is slightly bent because the two atoms occupying the short diagonal lie about 0.04 Å higher than those at the long diagonal which are shifted at bit more from on-top towards bridge positions. The structure of the three-dimensional Pt$_4$ cluster is a flattened trigonal pyramid with an edge length in the basis of 2.76 Å, longer than the edges connecting the top atom with the basis with 2.60 Å. The three Pt atoms forming the basis are 2.072 Å above their binding C-atoms. The threefold symmetry of the pyramid might be broken, but the differences in the Pt–Pt distances are at the margin of the computational accuracy and there are no differences in the heights of the Pt atoms above the substrate and in the spin moments.

In both configurations the Pt$_4$ cluster is located in the center of a sink in the graphene layer, as for the smaller clusters. This depression originates from the fact that due to the relatively strong binding between the adsorbed Pt and the C atoms, the graphene layer is locally electronically not saturated. Hence the binding between graphene and the Ni substrate in this region is promoted not only by dispersion forces as in the absence of adatoms, but also acquires a weak covalent component. The buckling amplitude of the graphene layer of about 0.4 Å is the same for both configurations and the adsorption energy $E_{ad}$ and the Pt–Pt binding energy $E_{coh}$, and the Pt–Pt bond length $d_{Pt-Pt}$ of a Pt$_4$ tetramer on graphene/Ni(111) for flat and upright geometries. $z_{Pt,G}$ is the height of the (lower) Pt adatom above the average of the graphene-sheet. $z_{G,Ni}$ is the average distance between the graphene and the top Ni layers, $d_{Pt-C}$ the distance between the (lower) Pt and the nearest C atom. $b_c$ is the buckling amplitude of the graphene. Energies are given in eV/Pt-atom, distances in Å.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Method</th>
<th>$E_{ad}$</th>
<th>$E_{coh}$</th>
<th>$d_{Pt-Pt}$</th>
<th>$z_{Pt,G}$</th>
<th>$z_{G,Ni}$</th>
<th>$d_{Pt-C}$</th>
<th>$b_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat rhombus</td>
<td>DFT+d</td>
<td>-1.128</td>
<td>-3.806</td>
<td>5 × 2.63</td>
<td>2.37</td>
<td>2.16</td>
<td>2 × 2.07</td>
<td>0.42</td>
</tr>
<tr>
<td>pyramid</td>
<td>DFT+d</td>
<td>-1.119</td>
<td>-3.797</td>
<td>3 × 2.76</td>
<td>2.39</td>
<td>2.17</td>
<td>3 × 2.07</td>
<td>0.42</td>
</tr>
</tbody>
</table>

FIG. 3. Geometric structure of Pt$_4$ clusters. Cf. Fig. 1.
comparable to that induced by the smaller clusters. Further geometrical details are given in Table II.

The spin moments on the Pt atoms from scalar relativistic calculations are $2 \times 0.10$ and $2 \times 0.12 \mu_B$ for the rhombus and $3 \times 0.14$ and $0.10 \mu_B$ for the pyramid. If SOC is taken into account, the spin moments in the flat cluster with in-plane magnetization (this is also the easy axis) are only slightly reduced to $2 \times 0.090$ and $2 \times 0.081 \mu_B$, the orbital moments are $2 \times 0.039$ and $2 \times 0.023 \mu_B$ [see also Figure 4(a)]. The hard magnetic axis is out-of-plane. All local spin moments are reduced, but the orbital moments are reduced only on the sites along the long diagonal, but enhanced on the other two sites [see Figures 4(a) and 4(b)]. For the total cluster moments this leads to a substantial spin anisotropy of $\Delta \mu_S = 0.136 \mu_B$ and a very low orbital anisotropy of $\Delta \mu_L = 0.022 \mu_B$. The influence of the adsorbed cluster on the magnetic moments in the Ni layer is very similar to that reported for the smaller clusters, again we find an average modest orbital anisotropy of $0.01 \mu_B$ on the Ni atoms. The MAE of the cluster/substrate complex is $15.5$ meV/cell or $0.091$ meV/atom.

For the three-dimensional Pt$_4$ cluster the magnetic structure becomes strongly anisotropic if SOC is included. For the in-plane easy magnetization direction the threefold symmetry is broken, the spin moments on the three Pt atoms in the basal triangle are $2 \times 0.123$ and $0.114 \mu_B$, whereas the Pt-atom on the top of the cluster becomes almost non-magnetic with $\mu_S = -0.009 \mu_B$. With $2 \times 0.046$, $0.044$, and $0.002 \mu_B$ the distribution of the local orbital moments is very similar [see Figures 4(c) and 4(d)]. The hard magnetic axis is again out-of-plane, but the magnetic structure is slightly non-collinear, with the moments on the atoms in the basal plane slightly inclined towards the center of the pyramid. Both spin and orbital moments are smaller, leading to spin and orbital anisotropies of $\Delta \mu_S = 0.050 \mu_B$ and $\Delta \mu_L = 0.011 \mu_B$ which are much lower than for the flat cluster. This is also reflected in a lower MAE of $8.2$ meV/cell or $0.057$ meV/atom.

C. Trends in magnetic moments and anisotropy

It is interesting to confront the results for the magnetic properties of small Pt$_n$ clusters in the gas phase with those modified by the interaction with a support. The electronic configuration of a Pt atom is $5d^96s^1$, which should yield spin and orbital moments of $1 \mu_B$ each. DFT yields spin and orbital moments of $1.03$ and $1.09 \mu_B$, respectively. For a Pt adatom on a freestanding graphene sheet, the magnetism is completely quenched while an adatom on a Ni-supported graphene layer has very small spin and orbital moments which are slightly larger for out-of-plane (hard axis) magnetization (see Table III). For a gas phase dimer an easy magnetic direction has been found along the dimer axis, with spin and orbital moments which are much larger than for magnetization along the hard (perpendicular) direction. The stable configuration of a dimer on graphene is upright, perpendicular to the substrate and this is also the easy axis of magnetization—in agreement with the axial anisotropy of the free dimer. Spin and orbital moments are reduced and strongly anisotropic. If the graphene layer is supported on a Ni substrate, a flat Pt$_2$ dimer is lower in energy, and it is non-magnetic because magnetism is quenched by the much stronger binding to the substrate induced by the Ni support. An upright configuration exists as an excited state, the easy magnetic axis is again perpendicular to the substrate and parallel to the dimer axis, spin and orbital moments are further reduced compared to the same configuration on the free graphene layer (see Table III).

A Pt trimer in the gas-phase adopts a triangular configuration and has an in-plane easy axis. Spin and orbital moments are reduced compared to the dimer. The hard magnetic axis is perpendicular to the triangle, both spin and orbital moments are strongly anisotropic. On a free graphene sheet, the Pt$_3$ triangle is bound to the substrate only via one of its edges, resulting in an inhomogeneous distribution of the magnetic moments. Both spin and orbital components of the cluster moment are reduced by about 50% compared to the free cluster. The first excited magnetic state that determines the MAE is non-collinear with even slightly enhanced spin and orbital moments (details are given in Table III). On Ni-supported graphene a flat triangle is lower in energy, the easy magnetic axis is in plane, the hard one out of plane. The spin moment is reduced by the presence of the Ni support by about 20%, while the orbital moment is reduced by more than 50%. The spin moment is almost isotropic, the orbital moment is even slightly enhanced for magnetization along the hard direction.

The equilibrium structure of a Pt$_4$ tetramer is a flat rhombus, the magnetic ground state is antiferromagnetic. As no antiferromagnetic configuration could be found for the supported tetramer, it is more meaningful to choose the lowest ferromagnetic state as a reference. The lowest energy ferromagnetic state of Pt$_4$ is found at an energy of $2.89$ meV/Pt-atom above the ground state, this energy difference is lower than the MAE of the antiferromagnetic state of $4.35$ meV/Pt-atom. It has a spin moment of $2.62 \mu_B$ and an orbital moment of $1.42 \mu_B$. The easy magnetic axis is in plane, the hard axis perpendicular with a MAE of $8.72$ meV/Pt-atom. The spin moment of the cluster has a modest negative anisotropy, in
TABLE III. Spin and orbital moments $\mu_S$ and $\mu_L$, and spin and orbital anisotropies $\Delta\mu_S$ and $\Delta\mu_L$, of Pt$_n$ clusters, $n = 1$–4, in the gas phase (after Ref. 1), on a graphene layer (after Ref. 2), and on a graphene/Ni(111) support. All magnetic moments are given in $\mu_B$.

<table>
<thead>
<tr>
<th>System/structure</th>
<th>Magnetization direction</th>
<th>$\mu_S$</th>
<th>$\mu_L$</th>
<th>$\Delta\mu_S$</th>
<th>$\Delta\mu_L$</th>
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</thead>
<tbody>
<tr>
<td>Pt atom</td>
<td></td>
<td>1.03</td>
<td>1.09</td>
<td></td>
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<tr>
<td>Pt$_1$/graphene</td>
<td>Non-magnetic</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt$_1$/graphene/Ni</td>
<td>In plane$^a$</td>
<td></td>
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<tr>
<td>Pt$_2$ dimer</td>
<td>Axial$^b$</td>
<td>1.88</td>
<td>2.74</td>
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<tr>
<td>Pt$_2$/graphene</td>
<td>Out of plane$^a$</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Upright</td>
<td>In plane</td>
<td>0.60</td>
<td>0.53</td>
<td>0.70</td>
<td>1.17</td>
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<td>Pt$_2$/graphene/Ni</td>
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<tr>
<td>Flat</td>
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<tr>
<td>Pt$_3$/graphene</td>
<td>Out of plane$^a$</td>
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<td>Upright$^c$</td>
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<td>0.49</td>
<td>0.36</td>
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<td>Triangle</td>
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<td>Pt$_3$/graphene</td>
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<tr>
<td>Upright triangle</td>
<td>Non-collinear</td>
<td>0.73</td>
<td>0.53</td>
<td>$-0.03$</td>
<td>$-0.09$</td>
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<tr>
<td>Pt$_3$/graphene/Ni</td>
<td>In plane$^e$</td>
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<tr>
<td>Flat triangle</td>
<td>In plane</td>
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<td>0.21</td>
<td>$-0.01$</td>
<td>$-0.04$</td>
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<td>Pt$_4$/graphene</td>
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<td>0.96</td>
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<td>Rhombus (FM)</td>
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<td>Bent rhombus</td>
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<td>1.28</td>
<td>0.58</td>
<td>0.07</td>
<td>0.08</td>
</tr>
<tr>
<td>Pt$_4$/graphene/Ni</td>
<td>In plane$^e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bent rhombus</td>
<td>Perpendicular</td>
<td>0.21</td>
<td>0.10</td>
<td>0.13</td>
<td>0.12</td>
</tr>
</tbody>
</table>

$^a$Relative to graphene layer.
$^b$Relative to the dimer axis.
$^c$Excited configuration.
$^d$Relative to Pt$_3$ triangle.
$^e$Relative to Pt$_4$ rhombus.

contrast to the much larger positive orbital anisotropy.$^1$ Upon adsorption on graphene, the Pt$_4$ rhombus is bent about the short diagonal, the easy magnetic axis is in plane. Both spin and orbital moments are reduced by about 50% upon adsorption, both show a modest positive anisotropy (see Table III). On a graphene layer supported on Ni, the geometry remains similar, but the bending of the rhombus is strongly reduced. For in-plane magnetization spin and orbital moments are reduced to less than 25% of the values on a free graphene layer. For the hard magnetization direction both components are further reduced.

The MAE of Pt$_n$ clusters in the gas phase, supported on graphene and on graphene/Ni(111) are compiled in Table IV. For the clusters on the graphene/Ni support we have used both self-consistent total energy differences (TE) and the magnetic force theorem (FT) to determine the MAE and in addition we have estimated the contributions $\Delta E(i)$, $i = \text{Pt, C, Ni}$ from the Pt$_n$ cluster, the graphene layer and of the Ni support to the MAE from an integration over the projected partial DOS according to Eqs. (1) and (2). Note that since the partial DOS are based on a projection of plane wave onto spherical waves inside atom-centered

[Table IV]

<table>
<thead>
<tr>
<th>Pt$_n$</th>
<th>Gas-phase MAE(TE)</th>
<th>Pt$_n$/graphene MAE(TE)</th>
<th>Pt$_n$/graphene/Ni(111) MAE(TE)</th>
<th>MAE(FT)</th>
<th>$\Delta E(\text{Pt})$</th>
<th>$\Delta E(\text{gra})$</th>
<th>$\Delta E(\text{Ni})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_0$</td>
<td>13.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt$_1$</td>
<td>12.9</td>
<td>9.8</td>
<td>$-0.235$</td>
<td>0.026</td>
<td>0.394</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt$_2$ (upright dimer)</td>
<td>46.2</td>
<td>23.1</td>
<td>$-49.6$</td>
<td>$-18.4$</td>
<td>$-0.215$</td>
<td>0.027</td>
<td>0.568</td>
</tr>
<tr>
<td>Pt$_3$ (triangle)</td>
<td>15.2</td>
<td>5.2</td>
<td>$-13.2$</td>
<td>17.4</td>
<td>0.323</td>
<td>$-0.019$</td>
<td>0.548</td>
</tr>
<tr>
<td>Pt$_4$ (rhombus)</td>
<td>8.7</td>
<td>2.6</td>
<td>15.8</td>
<td>23.9</td>
<td>0.152</td>
<td>$-0.019$</td>
<td>0.932</td>
</tr>
</tbody>
</table>
FIG. 5. Differences $\Delta n_i(E)$ in the projected electronic densities of states of Pt/graphene/Ni(111) clusters for soft- and hard-axis magnetization [as defined in Eq. (2)] for Pt (black dashed lines), C (blue dotted lines), and Ni (red dotted-dashed lines) atoms. The full lines show the integrated contributions to the decomposed MAE from the Pt cluster, the graphene layer, and the Ni substrate, calculated according to Eq. (1) and using the same color code. (a) Isolated Pt-adatom, (b) upright Pt$_2$ dimer, (c) flat Pt$_3$ trimer, and (d) flat Pt$_4$ tetramer.

spheres,

$$\text{MAE}^\star(\text{FT}) = N_{\text{Pt}} \Delta E(\text{Pt}) + N_{\text{C}} \Delta E(\text{gra}) + N_{\text{Ni}} \Delta E(\text{Ni})$$

(4)

(where the $N_{\text{Pt}}$, $N_{\text{C}}$, and $N_{\text{Ni}}$ are the number of atoms in the Pt-cluster, the graphene layer and in the Ni surface) can differ from MAE(FT) derived from the force theorem and the total DOS and that MAE(FT) might be less accurate than MAE(TE).

For the gas-phase clusters we note a strong decrease of the MAE from the dimer to the tetramer, parallel to a decrease in the orbital anisotropy. Binding of the cluster to a graphene layer reduces the MAE by a factor of two for the dimer and by a factor of about three for the trimer and tetramer. However, one has to note that the binding of the cluster to the support via two Pt atoms only changes both the geometric and the magnetic structure.

The MAE of the clusters supported on the graphene/Ni(111) complex requires a more detailed analysis, because of the magnetism of both the adsorbed Pt cluster and the Ni support. A graphene-covered Ni(111) surface has a MAE of 13.8 meV/cell or 0.580 meV/surface-atom. An isolated Pt adatom is non-magnetic in the scalar-relativistic mode, but if SOC is included, the coupling to the magnetic substrate induces weak and slightly anisotropic spin and orbital moments leading to a slightly reduced MAE(TE) of 12.9 meV/cell. A calculation using the force theorem yields a value of MAE(FT) = 9.8 meV/cell, which illustrates the limitations of this approach. From the projected DOS we calculate contributions to the MAE of $-0.235$ meV/Pt-atom, $0.026$ meV/C-atom, and $0.394$ meV/Ni-surface-atom, together MAE$^\star(\text{FT}) = 10.46$ meV/cell. The very small contributions of the graphene layer to the MAE originate from very small induced magnetic moments on the C atoms, as discussed in more detail in Ref. 2. The $\Delta n_i(E)$ and the integrated contributions to the partial MAE’s are shown in Figure 5. They show that the leading contributions to the MAE come from states close to the Fermi energy, changes in the electronic DOS at larger binding energies caused by the re-orientation of the magnetization direction cancel upon integration.

For the metastable upright Pt$_2$ dimer on graphene/Ni we have calculated a large perpendicular MAE(TE) = $-49.6$ meV/cell of a magnitude comparable to that of a gas-phase dimer and larger than that of a dimer on a free-standing graphene layer. In this case the force theorem yields only a qualitative agreement for the MAE, probably because the re-distribution of the electronic charge upon re-orientation of the magnetization is too large, see Table IV. Nevertheless, the decomposition of the MAE is instructive: the MAE per Pt atom is about the same as for the isolated adatom and is dramatically reduced compared to a dimer in the gas phase or on graphene only, but the contribution from the Ni substrate changes sign such that the large negative MAE is caused mainly by the Ni substrate. Figure 5(b) shows that the differences in the projected Ni-DOS as a function of the magnetization direction are rather pronounced even at higher binding energies. The analysis of the partial DOS of the flat dimer shows that the stronger interaction between dimer and support is reflected by a broadening of both the Pt and Ni states.

For a Pt$_3$ trimer in the gas phase and absorbed in a flat configuration on graphene/Ni the easy magnetic axis is in-plane, the MAE’s are of comparable magnitude. However, the decomposition of the MAE yields contributions of $0.323$ meV, $-0.019$ meV, and $0.548$ meV per Pt, C, and Ni surface atom, adding to a value of $13.209$ meV/cell which is in good agreement with the total value. For a Pt$_4$ tetramer the easy magnetic axis is out-of-plane, the MAE is $10.46$ meV/cell.

For the metastable Pt$_2$ dimer on graphene/Ni we have calculated a large perpendicular MAE(TE) = $-49.6$ meV/cell of a magnitude comparable to that of a gas-phase dimer and larger than that of a dimer on a free-standing graphene layer. In this case the force theorem yields only a qualitative agreement for the MAE, probably because the re-distribution of the electronic charge upon re-orientation of the magnetization is too large, see Table IV. Nevertheless, the decomposition of the MAE is instructive: the MAE per Pt atom is about the same as for the isolated adatom and is dramatically reduced compared to a dimer in the gas phase or on graphene only, but the contribution from the Ni substrate changes sign such that the large negative MAE is caused mainly by the Ni substrate. Figure 5(b) shows that the differences in the projected Ni-DOS as a function of the magnetization direction are rather pronounced even at higher binding energies. The analysis of the partial DOS of the flat dimer shows that the stronger interaction between dimer and support is reflected by a broadening of both the Pt and Ni states.
agreement with the MAE from total-energy differences. The presence of the Pt trimer hardly affects the MAE determined by the Ni substrate. The MAE for the cluster on the free graphene layer is not directly comparable because it refers to entirely different magnetic structures. It is evident, however, that the presence of the magnetic support reduces the MAE per Pt-atom very strongly, from about 1.7 meV to 0.32 meV per Pt-atom.

For the tetramer, it is easier to compare the MAE’s because its geometric structure is always a rhombus: flat for the gas-phase cluster, bent about the short diagonal for the clusters adsorbed on graphene or graphene/Ni. The decomposition of the MAE yields contributions per Pt-atom of 2.18 meV, 0.65 meV, and 0.15 meV for the free cluster and those supported on graphene and graphene/Ni, decreasing roughly parallel to the total magnetic moment of the cluster ($\mu_B = 4.04, 2.01, 0.46 \mu_B$, respectively). The dominant contribution to the total MAE comes from the Ni substrate.

IV. CONCLUSIONS AND OUTLOOK

We have extended our investigations of Pt clusters on a graphene/Ni(111) support to trimers and tetramers. In both cases the clusters adopt a flat or nearly flat geometry, with the Pt atoms in positions slightly shifted from on-top of the C atoms towards bridge positions because of the mismatch between the Pt–Pt distances and the C–C distances lattice-matched to the Ni support. The flat geometry is stabilized by a much stronger binding of the Pt clusters to graphene/Ni(111) than to a freestanding graphene layer where the clusters are bound to the layer only via a Pt–Pt edge. For the Pt$_4$ cluster, however, the flat, slightly bent rhombus is only 9 meV/Pt-atom lower in energy than a trigonal pyramid. Due to the interaction with the adsorbate the C atoms in the graphene layer are locally electronically not saturated and this leads also to an enhanced interaction with the Ni support and a local deformation of the graphene sheet.

While for isolated adatoms and dimers the interaction with the support led to a complete quenching of the magnetism of the adsorbate, Pt trimers and tetramers are found to be magnetic, albeit with spin and orbital moments which are strongly reduced compared to the free clusters and also relative to those adsorbed on a freestanding graphene sheet. The reduction of the magnetic moments leads also to a very strongly reduced magnetic anisotropy of the Pt clusters. The analysis of the MAE shows that the magnetic anisotropy of the Pt$_n$/graphene/Ni(111) complex is dominated by the Ni support. Although the SOC is much stronger and the orbital moment is still larger for Pt than for Ni, the contribution to the MAE per Pt atom is lower than that per Ni atom at the interface with graphene. Only for the metastable upright Pt$_3$ dimer the spin and orbital moments on the Pt atoms are large enough to reverse the sign of the magnetic anisotropy of the graphene-covered Ni-substrate.

We expect that for larger Pt-clusters the strong interaction between the adatoms will stabilize three-dimensional cluster structures. However, in the case of the Pt$_4$ pyramid with a non-magnetic atom at the apex suggests that this will not lead to a stabilization of magnetism of the clusters. To create magnetic clusters of heavy elements with a strong SOC which can be expected to show a large magnetic anisotropy doping with strongly magnetic atoms could be an issue. At this point it is useful to recall earlier studies of the adsorption of adatoms and dimers on graphene. Recently Johll et al. studied the adsorption adatoms and dimers of Fe, Co, and Ni on graphene. Adatoms bind weakly in hollows, their spin moment is reduced by about 2 $\mu_B$ compared to the free atom, Ni adatoms are non-magnetic. Homonuclear dimers bind weakly in an upright position in the center of a hollow, with only very modest changes in the magnetic moment and bond length relative to the free dimers. The same conclusion holds also for heteroatomic dimers where the configuration with the atoms with more d electrons attached to graphene is found to be more stable. For heteroatomic dimers of a 3d atom with Pt the picture is more complex: for a Fe–Pt dimer upright configurations with the lower Pt atom bound in a top or bridge site and a magnetic moment of about 4 $\mu_B$ is most stable. Co–Pt and Ni–Pt dimers prefer to bind through the 3d atom to a hollow site, with magnetic moments of about 3 $\mu_B$ and 2 $\mu_B$, respectively. This means that relative to the free 3d atom, the magnetic moment of the dimer is in each case enhanced by about 1 $\mu_B$. The influence of SOC has not been investigated as yet, but mixed clusters combining one element with a large spin moment and one with a strong SOC seem to provide a way to create nanostructured clusters with a large magnetic anisotropy energy. We will follow this path in future research.

ACKNOWLEDGMENTS

Work at the Universität Wien has been supported through the VASP project.


