The interplay of structure and spin–orbit strength in the magnetism of metal–benzene sandwiches: from single molecules to infinite wires

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Abstract

Based on first-principles density functional theory calculations, we explore the electronic and magnetic properties of experimentally producible sandwiches and infinite wires made of repeating benzene molecules and transition-metal atoms of V, Nb, and Ta. We describe the bonding mechanism in the molecules and in particular concentrate on the origin of magnetism in these structures. We find that all the considered systems have sizable magnetic moments and ferromagnetic spin ordering, with the single exception of the V$₃$Bz$_4$ molecule. By including the spin–orbit coupling into our calculations we determine the easy and hard axes of the magnetic moment, the strength of the uniaxial magnetic anisotropy energy (MAE), relevant for the thermal stability of magnetic orientation, and the change of the electronic structure with respect to the direction of the magnetic moment, important for spin-transport properties. While for the V-based compounds the values of the MAE are only of the order of 0.05–0.5 meV per metal atom, increasing the spin–orbit strength by substituting V with heavier Nb and Ta allows one to achieve an increase in anisotropy values by one to two orders of magnitude. The rigid stability of magnetism in these compounds together with the strong ferromagnetic ordering makes them attractive candidates for spin-polarized transport applications. For a Nb–benzene infinite wire the occurrence of ballistic anisotropic magnetoresistance is demonstrated.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Conventional electronics based on charge transport is facing major challenges as the scale of electronic devices will reach physical limits where purely quantum phenomena, such as electron spin, may play a dominant role. Consequently, a new discipline of spintronics has emerged, focusing on processes where information is carried by the electron spin in addition to, or in place of, electron charge. The use of both charge and spin degrees of freedom is expected to enable revolutionary technologies due to ultra-high density magnetic recording, low energy consumption and short access times for reading and writing in spin-electronic devices [1–4].

An important class of representative magnetic materials which exhibit novel properties with promising applications in spintronics includes organometallic molecular magnets. In designing molecular magnets several basic requirements should be fulfilled: besides a ferromagnetic coupling of
local magnetic moments necessary for coherent transport, a significant thermal stability of magnetism is requested. A cornerstone quantity which is directly related to the stability of magnetism against quantum tunneling and thermal fluctuations is the magnetic anisotropy energy (MAE), the energy necessary to change the magnetization direction relative to real space coordinates. While in molecular magnets with a small number of magnetic ions and significant distances between them the dipolar contribution to the MAE can be safely neglected, spin–orbit coupling (SOC), which greatly increases in low-coordinated systems, is responsible for the anisotropy barrier.

Much experimental and theoretical effort has been devoted to understanding the spin dynamics and tunneling rates in organometallic molecular magnets [5]; however, surprisingly little attention has been paid so far to the first-principles calculations of their electronic and magnetic properties such as magnetic moments, spin coupling and magnetic anisotropies, which can be directly related to the measured quantities. Because of the need for an atomic scale description, *ab initio* density functional theory (DFT) is a driving force for spintronics, and, so far represents the most natural way towards basic understanding and the design of new spintronics materials. The flexibility and accuracy in describing elements from the whole periodic table by DFT results in an enormous predictive power, especially efficient when applied to organometallic compounds, where elements with properties of a completely different physical origin are involved.

Being still at a very early stage of development, the one-dimensional (1D) magnetic organometallic sandwiches represent an important class of novel organic molecular magnets, which have been suggested as ideal candidates for the smallest possible high-spin magnets, allowing an extremely high density data storage. Several experimental and theoretical studies have been performed on magnetic sandwiches formed by vanadium and benzene, $V_6B_{2m}$ (see [6–11] and citations therein). The EPR measurements on VBz (half-sandwich) and VBz$_2$ estimate magnetic moments of 1 $\mu_B$ [12]. Stern–Gerlach-type magnetic deflection experiments on $V_nB_{2m+1}$ ($n < 5$) complexes suggest an increase of magnetic moment with the number of V atoms in the molecule [13], indicating that the magnetic moments of the V atoms couple ferromagnetically. Synthesis, infrared spectroscopy [14] and electric dipole measurements [15] on MBz (half-sandwich) and MBz$_2$ (M = Nb, Ta) compounds have also been reported. Although these experiments have been carried out on molecules in the gas phase, magnetically similar and structurally stable molecules suitable for the use of deposition techniques on substrates in ultra-high vacuum atmosphere can be synthesized. Possible examples are the $\sigma$-donor/$\pi$-acceptor metal complexes such as bis($\eta^6$-arene) and bis[$\mu$-(arene$_2$:$\eta^6$:biphenyl)$_2$] molecules which can only be prepared by means of cocondensation techniques [16]. Concerning theoretical investigations of the magnetism in $V_nB_{2m+1}$ clusters, several applications in spintronics of these molecules have been recently suggested [17, 18].

In this paper, based on our *ab initio* full-potential DFT calculations, we present a complete and detailed picture of the electronic and magnetic properties of the $M_nB_{2m}$ ($M = V, Nb, Ta$) sandwiches and infinite wires [19, 20], obtained by an infinite repetition of the metal–benzene half-sandwiches. In particular, we concentrate on the values of the magnetic anisotropy energy barrier, a value of utter importance for technological applications. While most of the V-based complexes have a strong ferromagnetic ordering of the spins, they reveal quite small values of MAE. Substituting vanadium ions with the heavier magnetic Nb and Ta ones allows one to tune the spin–orbit strength, with consequent values of MAE two orders of magnitude larger, preserving strong ferromagnetic coupling of the spins. Moreover, due to the position of the Fermi level and significant spin–orbit splitting of the bands, infinite NbBz$_2$ wires are suggested to exhibit the recently proposed [21] ballistic anisotropic magneto-resistance (BAMR) effect, i.e. the change of the ballistic conductance upon changing the magnetization direction, which opens the vista for new device concepts in spintronics.

Most of the compounds considered in this paper have a magnetization which lies in the plane of the benzenes, perpendicular to the symmetry axis of the molecules ($z$) with negligible total energy variations as a function of spin rotation around the $z$-axis. This fact will make it difficult to stabilize the magnetism in these complexes against thermal fluctuations despite the fact that the energy needed to switch the magnetization direction from in-plane to the $z$-direction can be rather large. However, for the $V_nB_{2m+1}$, $V_nB_{2m}$ molecules and a Nb–Bz infinite wire, the magnetization direction points along the $z$-direction and the values of the uniaxial anisotropy are sizable. This suggests that a large subclass of the $M_nB_{2m}$ ($n = 1, 2, \ldots$) complexes has a magnetization which is bimodal in nature and may be applicable, for example, for data storage or as qubits for quantum information, owing to the rigid fixation of the spin moments in these compounds along the single axis in space. The latter properties in combination with the small size, transparent electronic structure and large magnetic moments make this subclass valuable for potential applications in future spin-electronics.

### 2. Method and computational details

The calculations were performed within the framework of density functional theory (DFT) using the generalized gradient approximation (GGA-PBE) [22] for the exchange–correlation potential. We employed a realization of the full-potential linearized augmented plane-wave method for truly one-dimensional systems (1D-FLAPW) [23], as implemented in the FLEUR code [24]. All the isolated molecules were calculated using unit cells repeated along the symmetry axis ($z$-axis) with a large spacing between molecules in order to exclude unwanted side effects on the electronic and magnetic structure due to interaction with the neighbors. The smallest distance between the closest atoms in two neighboring molecules was larger than 13.5 au in our calculations. The $z$-axis of the system cuts through the transition-metal atoms and the centers of gravity of the Bz molecules. The following muffin-tin radii were chosen: 2.4 au (V, Nb, Ta), 1.25 au (C) and 0.65 au (H). In the vacuum the wavefunctions were expanded into cylindrical basis functions with an angular expansion up to $m_{\text{max}} = 24$. Correspondingly, the charge density and potential were expanded up to $m_{\text{max}} = 48$. For
calculating the isolated molecules we used one $k$-point and for the infinite wires we used 8 and 16 $k$-points in one half of the Brillouin zone, respectively. The structures were relaxed with the basis functions cut-off parameter $k_{\text{max}}$ of 3.5 au$^{-1}$, and for calculations of the magnetic ground state at the relaxed positions converged values of the spin moments and total energies were achieved with $k_{\text{max}} = 3.6$ au$^{-1}$. As matter of convenience, throughout the paper we use the expression ‘Fermi energy’ not only to indicate the highest occupied state of an infinite metallic wire, but also to indicate the highest occupied orbital in single molecules, keeping in mind that for isolated molecules it loses the meaning of a chemical potential.

The magnetic anisotropy-induced energy barrier which needs to be overcome to change the magnetization direction from one which is lowest in energy (easy axis) to the energetically most unfavorable one (hard axis) is called the magnetic anisotropy energy (MAE). The MAE consists of two contributions: one due to classical dipole–dipole interaction of local magnetic moments and the other due to the spin–orbit coupling. For molecules with few magnetic centers and magnetic wires the dipolar interaction is very small, and the role of spin–orbit coupling becomes crucial, leading to huge values of orbital moments and magnetic anisotropy energy [29]. By including spin–orbit coupling in the total energy calculations we considered two possible symmetry-determined directions of the magnetization in the molecules: along the $z$-axis ($z$-case) and in the radial direction parallel to the planes of the benzenes ($r$-case), with the most energetically preferable axis being the easy axis. The MAE is defined as a total energy difference between these two configurations. For the molecules and wires considered in this paper, the dipolar contribution to the MAE amounts to not more than a tiny value of 0.01 meV per metal atom, with the $z$-axis as an easy axis. Therefore, we restrict our discussion in the following to the SOC part of the MAE. The variation of the MAE as a function of the $r$-axis in the plane of the benzenes normally contributes only a small fraction of the MAE value and is neglected. The magnetic anisotropy energy was obtained using the force theorem with the number of $k$-points up to 64, and the values of $k_{\text{max}}$ up to 4.0 au$^{-1}$, reaching convergence in the calculated values.

3. General remarks

The geometries of the considered molecules $V_nBz_{n+1}$ with $n = 1, 2, 3$ are shown in figure 1. Our calculations show that stable structures of the molecules are sandwiches with the metal atom above the center of gravity of Bz molecules, which was also found in other theoretical and experimental investigations (see [6, 13, 25] and citations therein). The geometry of the metal–benzene molecules was restricted to $C_{6v}$ symmetry, while all other structural parameters were relaxed. In general, spin polarization does not change the nonmagnetic equilibrium structural values by more than 1–2%. For all
sandwiches the planarity of the outer Bz molecules is broken with the planes of C and H hexagons parallel but slightly shifted relative to each other along the z-axis (the value of the shift ranges between 0.02 and 0.09 au, depending on the compound). For the V₂Bz₃ molecule we analyzed the changes in the electronic and magnetic structure due to rotations of the benzene molecules with respect to each other around the z-axis.

Structural optimization of the single benzene molecule yields the values of 2.625 au for the C–C bond length and 2.058 au for the C–H bond length, in perfect agreement with the values obtained with various methods and reported in [9]. While the changes in the C–H bond length due to the interaction with the transition-metal (TM) ions are negligible, the C–C distance in the benzene rings increases by at most 4.3% for the Ta infinite wire. As a function of the transition metal, the C–C bond length increases from 2.3% to 4.1% for half-sandwiches and from 3.4% to 4.3% for the infinite wires, going from V to Ta. Concerning the distance between the metal atoms and the centers of the closest carbon rings (M–C distance) in V-based molecules, a significant increase from the value of 3.075 au for the half-sandwich up to 3.622 au (19%) in the V₃Bz₄ molecule is observed, revealing a strong inhomogeneity as a function of the relative position of the V atom with respect to the center of the molecule. Changing the atomic number of the metal ion in the half-sandwiches and infinite wires results in the increase in the M–C distance by at most 2%, as compared to corresponding values for V.

In a simple picture the mechanism responsible for bonding in the molecules can be given on the basis of a schematic analysis of the orbitals of the metal atom (V, Nb, Ta) and benzene molecule, which can be classified in terms of the pseudo-angular momenta around the symmetry z-axis. Five d orbitals of the metal atom can be divided according to their symmetries into one dσ (dₓ²−ᵧ²), two dπ (dₓz, dᵧz), two dδ (dₓ²−y², dₓy). The six π-orbitals of Bz form one Lσr (π₁), two degenerate Lδr (π₂, π₂), (HOMO), two degenerate Lδl (π₃*, π₃*) (LUMO) and one Lδl (π₄) orbital. When Bz molecules and metal atoms are brought together, the HOMO and LUMO orbitals of Bz interact with the metal s, d orbitals of the same symmetry, and bonding occurs [26] (see also figure 1). Yasuike [27] explained the electronic structure of the VₙBzₙ₊₁ complexes based on a schematic orbital interaction diagram using extended Hückel or Hartree–Fock methods. We performed the DFT electronic structure calculations for these complexes with a side goal of checking the validity and limitations of the latter computational models.

In case of spin-polarized calculations, the calculated spin moments inside the muffin-tin spheres of carbon and hydrogen atoms constitute almost constant values of 0.01 µ_B and 0.001 µ_B, respectively. Therefore, further on we specify only the direction of the carbon local spin moments in the considered compounds.

Despite a great advantage of the DFT in predicting the trends in the properties of a large set of VₙBzₙ₊₁ complexes, we are well aware of the fact that in low-coordinated systems localized states develop, for which the common approximation to the exchange–correlation functional, the local density approximation (LDA) or the GGA, does not always provide reliable enough results. On the other hand, the molecules used in the context of spintronics or molecular electronics are typically attached to metallic leads. Electrons in the leads contribute by screening to the reduction of the Coulomb interaction in a molecule and the actual strength of the Coulomb interaction in this situation remains a subject of further investigations. The self-interaction correction of a singly occupied dσ state and the Coulomb interaction of localized states in molecules attached to the leads may be taken care of in the future by more reliable functionals, which are currently under scrutiny.

4. V–Bz molecules

We start with the study of the electronic and magnetic properties of the VₙBzₙ₊₁ sandwiches, paying special attention to the origin of magnetism in these compounds and its development with increasing number of V atoms in the complexes. The issue of stability is addressed and a possibility of experimental observation of magnetism in these compounds is discussed via evaluating the values of magnetic anisotropy. The insight into the physical properties of the V–Bz molecules which we provide in this section is important for understanding the trend in magnetic and electronic properties of the compounds with Nb and Ta ions, considered in the next section.

4.1. Half-sandwich VBz

In order to understand the bonding and formation of a magnetic moment in the VBz molecule, we take a look at the local densities of states (LDOS) for the nonmagnetic (NM) and spin-polarized (FM) cases at the optimized atomic positions, presented in figure 2 (left panel). In the NM case the nonbonding dσ orbital at the V site is situated at the Fermi level and accommodates one electron. The interaction between the LUMO orbitals of Bz and the dδ orbitals of the V atom results in two degenerate bonding δ states slightly lower in energy which accommodate four electrons located mostly at the V site. The overlap of the dσ orbitals of the V atom and Lδr (π₂, π₂) HOMO orbitals of Bz produces the next low-lying π-type states of the VBz molecule carrying four electrons located mostly at the C sites of the Bz ring. The interaction of the lowest Lσr (π₁) orbital of Bz with the 4s orbital of vanadium results in a low-lying σ state accommodating two electrons located mostly at the C sites of the Bz ring. The closest to the HOMO orbitals, the low-lying 1s benzene orbital, is not participating in the interaction with the metal ion. The charge density plots for the resulting states of the molecule are shown in figure 1, which illustrate the orbital character and bonding of the states.

The magnetic solution for this compound is lower in total energy than the nonmagnetic one by a large value of 0.491 eV. The spin-polarized LDOS displays a large exchange splitting of the states near the Fermi level (figure 2 (left panel)). This splitting is largest for the dσ state of V (located at the Fermi level in the nonmagnetic DOS). For the δ states, involved in the bonding, the exchange splitting is much smaller. Out of five electrons of V, three occupy spin-up (one at the dσ level and two at the two degenerate δ levels) and two occupy spin-down (two degenerate δ levels) states. This results in a total spin...
moment of $1 \mu_B$ for the system. Our calculations show that this spin moment is entirely located inside the muffin-tin sphere of the V atom ($1.09 \mu_B$). There is no significant exchange splitting of the low bonding states of the VBz molecule. The spin moments of the C atoms couple antiferromagnetically to the spin moment of the V atom.

4.2. Single sandwich VBz$\textsubscript{2}$

When two Bz molecules are placed at the same distance from V, as in the VBz$\textsubscript{2}$ molecule, the symmetry-adapted molecular $L(s, \pi, \delta, \phi)_{g,u}$ orbitals of the molecular complex Bz$\textsubscript{2}$ are produced from the orbitals of two Bz molecules. The atomic orbitals of V have $g$ symmetry and can interact only with the $L(s, \pi, \delta)_{g}$ orbitals of Bz$\textsubscript{2}$. According to the Hückel interaction scheme a nonbonding $d\sigma$ orbital occupies the Fermi energy with one electron. As a result of hybridization between the $\delta$ orbitals of V and the $(L\delta)_{g}$ orbitals of Bz$\textsubscript{2}$ two degenerate $\delta$ states lower in energy are created and accommodate four electrons. The overlap between the $\pi$ orbitals of V and $L\pi_{g}$ orbitals of Bz$\textsubscript{2}$ produces two $\pi_{g}$ bonding orbitals, while $L\pi_{u}$ $(\pi_{u})$ remain nonbonding (for the VBz$\textsubscript{2}$ sandwich the $\pi_{g}-\pi_{u}$ splitting is barely visible due to a large distance between the V atom and benzene molecules, as compared to the compounds with larger number of V atoms, discussed below). The basic features of the nonmagnetic LDOS (figure 2 (right panel) with corresponding plots of the orbitals in figure 1) reflect the Hückel-type interaction scheme for this compound [27]. As in the case of the half-sandwich VBz, the $d\sigma$ orbital with one electron is located at the Fermi level. Compared to the VBz LDOS, the doubly degenerate $\delta$ orbitals of the VBz$\textsubscript{2}$ molecule are situated much lower in energy. This suggests a different bonding of the $d\delta$ vanadium orbitals and $(L\delta)_{g}$ orbitals of the molecular complex Bz$\textsubscript{2}$.

The magnetic solution for this molecule is lower in total energy than the nonmagnetic one, with a difference in total energies $E_{NM} - E_{FM}$ of 0.459 eV. The spin-polarized LDOS of the VBz$\textsubscript{2}$ molecule (figure 2) reflects the main features of the VBz DOS. The largest exchange splitting occurs for the $d\sigma$ state, while the exchange splitting for the $\delta$ states is significantly quenched. The low-lying $\pi_{g}$, $\pi_{u}$, $s\sigma$, $Ls$ states of the molecule are almost not exchange split. The total spin moment of the VBz$\textsubscript{2}$ molecule constitutes the same value of $1 \mu_B$ as in the case of VBz. Furthermore, the spin moments inside the muffin-tin spheres of V, C and H are almost of the same values, as in the case of the VBz molecule, with antiferromagnetic coupling of the V and C local moments. Our value for the total magnetic moment agrees with the experimental average value of $0.8 \mu_B$, measured by Kaya and coworkers [13] for the VBz$\textsubscript{2}$ molecule at room temperature in the gas phase.

4.3. Double sandwich V$_2$Bz$_3$

When two outer Bz molecules are placed at the same distance from an inner Bz ring as in the V$_2$Bz$_3$ compound, symmetry-adapted molecular $L(s, \pi, \delta, \phi)_{g,u}$ orbitals of the molecular complex Bz$_3$ are created from the orbitals of two benzenes. The atomic orbitals of the V atoms and the molecular orbitals $L(s, \pi, \delta, \phi)$ of the central Bz have $g$-symmetry. Bonding molecular orbitals of V$_2$Bz$_3$ between V atoms and Bz molecules are formed due
to interactions of the orbitals with the same symmetry (e.g. g-orbitals). In general, the orbital interaction scheme for this complex becomes rather cumbersome.

The LDOS of this molecule are presented in figure 3 and corresponding charge density plots of the orbitals are shown in figure 1. The notations for the orbitals follow the same scheme as for VBz and VBz2. As a general observation, orbitals localized at the outer Bz rings (carrying u-index) are situated at higher energies than the corresponding orbitals of the inner Bz ring (carrying g-index). In the NM case nonbonding d\(_g\) and d\(_2\) orbitals are positioned at the Fermi energy, and slightly lower in energy there are two degenerate \(\delta_u\) orbitals arising from the hybridization between the d\(_g\) of V atoms and LUMO of the outer Bzs. Much lower in energy are two degenerate \(\delta_g\) orbitals reflecting strong hybridization between d\(_g\) of V atoms and LUMO of the inner Bz. Two \(\pi\)-hybrids, \(\pi_u\) and \(\pi_g\), are situated very deep in energy followed by a set of Ls- and \(\sigma\)-type orbitals.

Our calculations show that the V\(_2\)Bz\(_3\) molecule is magnetic, with a total energy difference between the FM and NM solutions (to which we refer below as \(E_{FM}\)) of 0.415 eV per metal atom. The AFM solution with opposite vanadium spins is by a tiny value of 3.0 meV per V atom higher in energy than the FM solution, suggesting that the magnetic order of the molecule can be easily influenced by effects such as thermal fluctuations and vibrations, above a threshold temperature \(T_0\) [28]. The total spin moment of the molecule of 0 \(\mu_B\) (AFM) and 2 \(\mu_B\) (FM) for these magnetic states should, in principle, result in an average value of 1.0 \(\mu_B\) for temperatures much larger than \(T_0\). This fact can explain an average value of 1.3 \(\mu_B\) for the complex, measured at \(T = 154\) K by Kaya and co-workers [13].

The spin moment value of 1.02 \(\mu_B\) inside the V muffin-tin sphere in both FM and AFM configurations is close to that of the VBz half-sandwich. In the FM case the spin moments of the C atoms are parallel to each other and opposite to the V spin moments. In the AFM case, the C spin moments in the outer Bzs are antiferromagnetically coupled to the closest V atom, while the C moment in the central Bz vanishes. Some authors [27] suggest that the induced carbon spin moment and its orientation with respect to the moments of V atoms could play a crucial role for the spin ordering of the latter ones. While the influence of the carbon spin moments on the magnetic ordering in the molecule is probably negligible, we performed a calculation, where we removed the central benzene from the complex, keeping the coordinates of all the other constituents constant. In this case, the total energy difference between the FM and AFM solutions \(E_{FM} - E_{AFM}\) (to which we refer below as \(E_{AF}\)) amounts to 22 meV per metal atom in favor of ferromagnetism. Thus the direct exchange between the V atoms favors ferromagnetism and the competition with antiferromagnetic super-exchange via the central benzene ring results in a small total \(E_{AF}\) value of 3.0 meV per metal atom for the V\(_2\)Bz\(_3\) sandwich.

The FM and AFM LDOS (figure 3) display large exchange splitting of the nonbonding V d\(_\sigma\) states: in both cases it reaches 2.5 eV. In the FM case the strongly bonding \(\delta_u\) orbitals show smaller exchange splitting than the \(\delta_g\) states, while the bonding low-energy \(\pi\), Ls and \(\sigma\) orbitals are not exchange split at all.

In order to understand the influence of the molecule’s conformation on the spin coupling in this sandwich we investigated the changes in the electronic and magnetic properties with respect to the rotation of the central benzene ring (figure 4) and \(\theta\)-distortion of the sandwich (figure 5).

In the first case we rotated only the atoms of the central benzene ring by an angle \(\theta\) around the \(z\)-axis and fixed all other atom positions. The total energy \(E_{\theta=0}\) (figure 4), shows a minimum at an angle of \(\theta = 30^\circ\) for both the FM and the AFM states. The significant energy gain of 50 meV suggests that the actual ground state might resemble a nontrivial angular orientation of the benzene in the molecules (indeed, the chirality of the complexes was reported in [6]). Quite surprisingly the energy difference \(E_{AF}\) between the FM and AFM solutions, which is one order of magnitude smaller than the total energy variation, does not display any significant changes. The same is true for the value of the magnetic anisotropy energy (MAE), which is in many systems extremely sensitive to the slightest deviations in the electronic structure.

In order to model contractions and elongations of the sandwiches we fixed all in-plane coordinates while the \(z\)-coordinate of all atoms was multiplied by a factor \(\alpha\) (the central benzene ring acts as a reference point). Such contractions and elongations along the \(z\)-axis result in large deviations of the total energies for the FM and AFM solutions, the energy...
difference $E_{AF}$, and the values of the MAE, as shown in figure 5. The total energy has its minimum in the unstretched case ($\alpha = 1$) and rises by large values of 50 meV upon contraction ($\alpha = 0.95$) and 250 meV upon elongation ($\alpha = 1.05$). The magnetic coupling is also strongly influenced. For an elongated sandwich ($\alpha > 1$) the antiferromagnetic super-exchange between the V atoms via the central benzene ring becomes even more pronounced and the energy difference $E_{AF}$ drops by almost half its value. Accordingly, the direct exchange between the V atoms dominates for a contracted molecule ($\alpha < 1.0$) and $E_{AF}$ increases by 4 meV in favor of ferromagnetism.

4.4. Triple sandwich $V_3Bz_4$ and $V_4Bz_5$

For the triple sandwich $V_3Bz_4$ we considered three possible magnetic configurations: $\uparrow\uparrow\uparrow$-ferromagnetic (FM), $\uparrow\downarrow\uparrow$-antiferromagnetic (AFM1), and $\uparrow\uparrow\downarrow$-antiferromagnetic (AFM2). The FM state is by 300 meV per V atom lower in energy than the nonmagnetic solution. Among the magnetic solutions, the total energy difference between the FM and AFM1 configurations of 4.1 meV per V atom favors the $\uparrow\downarrow\uparrow$ state, while the AFM2 $\uparrow\uparrow\downarrow$ state is by 1 meV (per V) higher in energy than the FM state. However, the energy barrier of 12.3 meV for the whole complex can be easily overcome due to thermal fluctuations, increasing the total spin moment of the system by occupying the excited high-spin FM state. This leads to an increase of the average value of the spin moment with increasing temperature, which was indeed observed experimentally [25].

In the FM case, the spin moments of the central and outer V atoms constitute 0.76 $\mu_B$ and 1.17 $\mu_B$, respectively, resulting in a total spin moment for the whole molecule of 3 $\mu_B$. The transfer of the spin density between V atoms indicates the delocalization of the $d_{z^2}$ electrons along the z-axis. The magnetic moments of the carbon atoms are antiparallel to the vanadium moments. For the $\uparrow\downarrow\uparrow$ configuration, the total spin moment of the system constitutes $1 \mu_B$, with an absolute value of 1.07 $\mu_B$ inside every V sphere, indicating a higher degree of electron localization on V sites. The moments of the outer carbons are opposite to the closest V spins, while the carbon moments in the two central rings of the complex vanish.

The LDOS for the NM, FM and AFM1 solutions are presented in figure 6, and the charge density plots of the marked orbitals (NM) are given in figure 1. Due to the rather complicated structure and small energetic resolution between the states, the LDOS is plotted in a smaller energy window compared to the previous complexes, and the lower HOMO orbitals (e.g. $\pi$) are not shown, but their charge density plots are given in figure 1.

From the charge density plots for the NM state we conclude that the bonding $\delta$ and $\pi$ molecular orbitals can be distinctly separated into three groups. The first group includes $\delta_u$ and $\pi_2$ orbitals representing the bonding orbitals of separate VBz (outside) and VBz2 (inside). The second nonbonding $u$-group, $\delta_u$ and $\pi_u$, is localized on the outer VBz and inner VBz2 parts of the molecule. The third g-type group is associated with the VBz2 part of the molecule and is responsible for the bonding in the molecule. Generally, the molecular orbitals associated with the central V atom are lying lower in energy than those of the outer V atoms.

For the NM case, the group of states close to the Fermi level includes $\delta_0$, $d\sigma_1$ and $d\sigma_2$ orbitals. For the $d\sigma_1$ ($d_{z^2}$-type), mainly located on the central V atom, the transition
The FM d for the AFM1 configuration due to antiparallel spin alignment. Contributions from all three V atoms, which is not the case exclusively on the outer V atoms. The σ splitting of 1.9 eV for both d states is clearly visible. At the same time, the d of charge density from the inner V to the outer ones is significantly smaller than the corresponding value of 1.9 eV for d states. A minus sign means that the magnetic (ferromagnetic) solution is lower in energy. The values of the spin moment μ are presented for the whole molecules. MAE stands for the magnetic anisotropy energy for the FM solution with the magnetization direction either perpendicular to the wire axis (r) or along the wire axis (z). All values are given in meV per V atom.

|          | VBz  | VBz2 | V2Bz3 | V3Bz4 | V4Bz5 | VBz∞ |
|----------|------|------|-------|-------|-------|------|
| EAF (meV)| 491  | 459  | 415   | 300   | 232   | 106  |
| EFM (meV)| —    | —    | 3     | +5    | 31    | 57   |
| μS (μB)  | 1    | 2    | 4     | 4     | 1∞    |      |
| MAE (meV)| 0.05(r) | 0.05(r) | 0.05(r) | 0.5(z) | 0.3(z) | 0.3(r) |

Figure 6. LDOS for the V3Bz4 molecule in the NM, FM and AFM1 configurations. Spin-up and spin-down channels are indicated by arrows. The charge density plots of the states for the NM case are presented in figure 1.

4.5. Magnetic anisotropy in VnBzm molecules

The magnetism of V–Bz complexes and its development with increasing number of V atoms is an interesting issue on its own. However, without an additional stabilizing factor this magnetism is difficult to observe experimentally, considering the scale of the energies involved, especially for smaller compounds. The technological application of the molecules is impossible without the spin moment of the molecule being coupled to the lattice, and violation of this will destroy such magnetic properties as half-metallicity or large magnetoresistance ratios [17].

The values of the MAE for the VnBzm compounds are presented in table 1. While for the smaller compounds the MAE is of the order of negligible 50 μeV per V atom, it increases by an order of magnitude for n > 2 accompanied by a change in the magnetization direction from r to z for large n. The value of 0.3 meV per V for an infinite VBz wire is close to that of 0.1 meV, reported in [30]. We conclude that magnetism in V–Bz molecules of any length can be stabilized only at very low temperatures, making their technological application rather questionable without applying a strong magnetic field from outside, despite their intriguing magnetism discussed before.

One way to increase the effective anisotropy barrier in V–Bz molecules could be in depositing the sandwiches on a substrate made of heavy elements, for instance, 5d transition metals. Such an approach was pioneered by Gambardella et al in [31] for monoatomic Co chains deposited on a Pt substrate, where a large MAE value leads to stabilizing the long-range ferromagnetic order. In this case the mechanism responsible for increase in the MAE lies in a spin polarization of the substrate atoms with a large spin–orbit interaction due to a large spin moment on the Co atoms [32]. For a VBz molecule, the spin moment of 1 μB of the V atom is effectively shielded from interacting with the substrate by the outer benzene rings and a significant spin polarization of the substrate atoms is unlikely. In addition, for spin-polarized transport applications [17] strong magnetism of the electrodes...
In this section we study the magnetic properties of benzene and transition-metal (TM) half-sandwiches and infinite wires for the 4d and 5d TMs Nb and Ta, which are isoelectronic to V. This choice is based on the experimental observation of Nb and Ta Bz-based compounds [14, 15], and the possibility to tune the spin–orbit strength in the molecules, without altering the electronic structure. We have performed nonmagnetic and spin-polarized calculations for the MBz half-sandwiches and considered for the infinite wires a ferromagnetic and antiferromagnetic ground state.

As seen in table 2, all three half-sandwiches are magnetic with large magnetization energies $E_M$, even for Ta with its extended 5d orbitals, and the smallest value of $E_M$ is obtained for the NbBz molecule. The main features in the electronic configuration of the molecules are preserved, going from V to Ta, with one unpaired electron occupying a nonbonding $\sigma$ orbital, as explained in detail for the VBz sandwich in section 4.1. While the total spin moment constitutes a constant value inside the muffin-tin sphere of the metal atom shows a significant reduction with increasing atomic number, from $0.94 \mu_B$ for V to 0.46 $\mu_B$ for Ta, reflecting the increasing spread from 3d to 5d orbitals.

Concerning the local densities of states (figure 7), the energetic ordering of the $\delta$ and $\sigma$ states, and the exchange splitting of these states near the Fermi level display a significant dependence on the metal ion. Essential for applications are the states near the Fermi level since they

### Table 2. Magnetism in V, Nb and Ta half-sandwiches and infinite wires.

|         | $E_M$ (meV) | $\mu_S$ ($\mu_B$) | $\mu_L(z)$ | $\mu_L(r)$ | $\Delta E$ (meV) | $\mu_S$ ($\mu_B$) | $\mu_L(z)$ | $\mu_L(r)$ | $\Delta E$ (meV) |
|---------|-------------|-------------------|------------|------------|-----------------|-------------------|------------|------------|-----------------|
| MBz     |             |                   |            |            |                 |                   |            |            |                 |                   |
| V       | –491        | 1.0 (1.09)        | 0.00       | 0.03       | 0.05(r)        |                   |            |            |                 |                 |
| Nb      | –378        | 1.0 (0.70)        | 0.00       | 0.05       | 0.38(r)        |                   |            |            |                 |                 |
| Ta      | –388        | 1.0 (0.46)        | 0.01       | 0.15       | 7.50(r)        |                   |            |            |                 |                 |
| MBz$_\infty$ |         |                   |            |            |                 |                   |            |            |                 |                   |
| V       | –110        | 1.00 (1.09)       | 0.00       | 0.00       | 0.02(r)        |                   |            |            |                 |                 |
| Nb      | –35.5       | 1.00 (0.66)       | 0.04       | 0.07       | 0.02(r)        |                   |            |            |                 |                 |
| Ta      | –11.2       | 0.68 (0.45)       | 0.05       | 0.09       | 0.03(r)        |                   |            |            |                 |                 |

Figure 7. Ferromagnetic LDOS for the half-sandwiches MBz (left panel) and infinite wires MBz$_\infty$ (right panel) for $M = V$, Nb and Ta. Spin-up and spin-down channels are indicated by arrows. The energetic positioning of the $\delta$ and $\sigma$ states strongly depends on the element. As compared to the DOS of the half-sandwiches, broadening of the sharp molecular states into disperse bands for the infinite wires can be seen.

is required, which is not the case for 4d and 5d transition-metal (TM) surfaces.

A different route to achieve significant anisotropy energies is to substitute the 3d vanadium atoms with heavier 4d or 5d transition metals. Recently, it was reported that in monoatomic chains of 4d transition metals giant values of MAE can be observed [29]. In monoatomic chains, however, the number of the nearest neighbors for a magnetic atom is reduced to a minimal value of two, resulting in enhanced magnetism with large spin moments. This is not necessarily the case for Bz-based compounds, where a strong interaction with large benzene molecules could, in principle, destroy the magnetism of the transition metals completely. In the next section we investigate this idea.

### 5. Metal–Bz molecules and metal–Bz$_\infty$ infinite wires with metal = V, Nb, Ta

In this section we study the magnetic properties of benzene and transition-metal (TM) half-sandwiches and infinite wires for the 4d and 5d TMs Nb and Ta, which are isoelectronic to V. This choice is based on the experimental observation of Nb and Ta Bz-based compounds [14, 15], and the possibility to tune the spin–orbit strength in the molecules, without altering the electronic structure. We have performed nonmagnetic and spin-polarized calculations for the MBz half-sandwiches and considered for the infinite wires a ferromagnetic and antiferromagnetic ground state.

As seen in table 2, all three half-sandwiches are magnetic with large magnetization energies $E_M$, even for Ta with its extended 5d orbitals, and the smallest value of $E_M$ is obtained for the NbBz molecule. The main features in the electronic configuration of the molecules are preserved, going from V to Ta, with one unpaired electron occupying a nonbonding $\sigma$ orbital, as explained in detail for the VBz sandwich in section 4.1. While the total spin moment constitutes a constant value of 1 $\mu_B$ for all half-sandwiches (table 2), its integrated value inside the muffin-tin sphere of the metal atom shows a significant reduction with increasing atomic number, from 1.09 $\mu_B$ for V to 0.46 $\mu_B$ for Ta, reflecting the increasing spread from 3d to 5d orbitals.

Concerning the local densities of states (figure 7), the energetic ordering of the $\delta$ and $\sigma$ states, and the exchange splitting of these states near the Fermi level display a significant dependence on the metal ion. Essential for applications are the states near the Fermi level since they
determine for example the spin-dependent transport properties, and can be tuned by a particular metal atom. While the value of the $\delta$- and $\sigma$-exchange splitting is quite large for V, it decreases for Nb and Ta—a consequence of a larger spread of the corresponding d orbitals. The same phenomenon is responsible for the relative positioning of the $\delta$ and $\delta$ states: a larger extent of the orbitals leads to a larger overlap of the metal and benzene orbitals with a stronger bonding, pushing the $\delta$ orbitals lower in energy with increasing atomic number.

The properties of the infinite wires, which are the limiting case of a very large number of the metal atoms in the molecules, together with the information for the half-sandwiches, on the other hand, provide an insight into the magnetism of complexes with increasing length. As can be seen from table 2, the magnetization energies and the spin moments differ significantly between MBz$_\infty$ wires and MBz half-sandwiches. While for the V wire the energy difference of 106 meV per metal ion in favor of magnetism is of the order of that for the half-sandwich, it drops by an order of magnitude for Nb and Ta, constituting small, but still sizable, values of 35.5 and 11.2 meV, respectively. This ensures us that, despite the large decrease in magnetization energy with increasing number of atoms in the Nb$_n$Bz$_{m}$ and Ta$_n$Bz$_{m}$ molecules, they will remain strongly magnetic even for very large $n$. In the infinite wires of Nb and Ta the values of the total and muffin-tin spin moments are significantly reduced compared to the VBz$_\infty$ wire, reflecting a more delocalized nature of the d orbitals of these transition metals.

The LDOS for the infinite wires (figure 7) reflect characteristic broadening of the sharp states in the DOSs for the half-sandwiches into bands. For example, the $\delta$ states of the single molecules correspond to strongly dispersive $\delta$ bands with two-peak structure in the DOS characteristic for 1D systems [29]. Among the two low-lying $Ls$ and $\pi$ groups of states the $Ls$ states show smaller dispersion, as they originate from states pointing in-plane, rather than along the chain axis. The $\sigma$ states are also very sharp, compared to $\delta$ states, reflecting their nonbonding nature and small overlap along the $z$-axis. With increasing nuclear number, the exchange splitting of the $\delta$ and $\sigma$ states decreases, in analogy to the single half-sandwiches, and the dispersion of the $\delta$ bands increases with their left edge in the DOS moving to lower energies, while the $\sigma$ band moves up in energy towards $E_F$. In contrast to finite molecules, which have a nonzero HOMO–LUMO gap and are of ‘insulating’ character, the infinite M–Bz wires are essentially metallic, with a nonzero density of states at the Fermi level, originating mainly from a $\delta$ band in the spin-down channel. The metallicity, more precisely, half-metallicity, of an infinite V–Bz wire was also theoretically predicted in [17, 30].

The importance of spin–orbit coupling in half-sandwich molecules and infinite wires with heavy 4d and 5d TMs of Nb and Ta is reflected in the values of the orbital moments $\mu_L$ (table 2), calculated for two different magnetization directions. For V compounds the absolute value of $\mu_L$ reaches 0.03 $\mu_B$ for a half-sandwich; for the Nb infinite wire it rises up to 0.07 $\mu_B$, and reaches as much as 0.15 $\mu_B$ for the Ta half-sandwich. The negative values of the orbital moments for most cases can be understood based on Hund’s rules. The values of the MAE also rise significantly when going from V to Ta, reaching a record value of 7.5 meV for the TaBz compound, which is two orders of magnitude larger than for VBz. For the infinite wires, the values of the anisotropy energy increase for V and Nb, while for TaBz$_\infty$ the value of the MAE drops compared to the TaBz molecule, but the value of 3.2 meV is still large. The easy axis of magnetization, with an exception of NbBz$_\infty$, lies in the plane of the benzenes for all the cases ($r$-case), and in general follows the rule that the direction of magnetization is that of the largest orbital moment, justified for 3d [33] and partly also applicable to 4d transition metals [29].

We conclude that substituting the vanadium ions in MBz compounds by heavier Nb and Ta ions, which can be synthesized experimentally [14, 15], preserves the large magnetization in these compounds with a pronounced tendency towards ferromagnetic arrangement of the spins. In addition, it would allow one to achieve much higher values of the magnetic anisotropy energy, making it possible to use these molecules for technological applications.

Another interesting effect of the spin–orbit coupling can be seen for the NbBz$_\infty$ infinite wire, and can be related directly to the recently proposed transport phenomenon of the ballistic anisotropic magnetoresistance (BAMR) [21]. In contrast to bulk materials, the mechanism of electronic transport changes drastically when going to the nanoscale. When the dimensions of the sample are smaller than the mean free path of the electrons, the transport is ballistic, rather than diffusive, and the conductance shows a step-like behavior with the applied voltage in units of $\frac{e^2}{h}$ for magnetic systems [34]. In recent experiments performed on Ni ballistic nanotransistors [35], a change of sign was found in the magnetoresistance obtained for the field parallel and perpendicular to the current. The BAMR has recently been experimentally demonstrated for Co nanocontacts in accordance to simple Co monowire band structure calculations [36]. The origin of this magnetoresistance anisotropy in the ballistic regime stems from the fact that the conductance, for example, in a perfect nanowire, depends on the number of bands $N(E_F)$ crossing the Fermi energy $E_F$: $G = N(E_F)\frac{e^2}{h}$. The crucial point behind the BAMR effect is that the number of bands at $E_F$ can depend on the magnetization direction via the spin–orbit interaction, which couples the orbital and spin moment, causing the projection of the latter to be different depending on the direction of magnetization.

It is important to realize, however, that the large desired values of the anisotropic magnetoresistance are a consequence not only of the electronic structure at the Fermi energy, but also of a large spin–orbit splitting of the bands. For a NbBz infinite wire, for example, a lucky combination of both occurs (figure 8). Significant spin–orbit splitting of the bands at the Fermi energy leads to a different number of states crossing the Fermi level for the two magnetization directions. In particular, the edge of the $\delta$ band at the $\Gamma$ point of the Brillouin zone for the spin-up channel occurs exactly at the Fermi energy $E_F$, and undergoes a spin–orbit induced splitting when the direction of magnetization is along the $z$-axis, so that one of the SO-split bands with negative orbital character [29] gets completely occupied and moves to lower energies. This is not the case for a magnetization pointing in the plane of the benzenes, when no spin–orbit splitting of the $\delta$ bands can be seen, with two of the degenerate $\delta$ bands crossing the Fermi energy. This
Figure 8. Calculated band structure of the infinite Nb–Bz wire in the 1D Brillouin zone. Left panel—band structure in the absence of the spin–orbit coupling, with spin-up and spin-down channels indicated by arrows; middle panel—band structure with spin–orbit coupling and the magnetization pointing along the \( z \)-axis; right panel—band structure with spin–orbit coupling and the magnetization in the planes of the benzenes. Note that the band structures in the middle and right panels are given on a different energy scale, as compared to the left panel, in the quarter of the 1D BZ.

allows one to manipulate the conductance in the system by an external magnetic field—an example of ballistic anisotropic magnetoresistance—which opens the road for many possible spin-dependent transport applications. In realistic systems, such as molecules sandwiched between two electrodes, which rarely serve as ideal electron injectors, the conductance of the whole system cannot be given any more by simple counting of the bands at the Fermi energy. The transport properties of the system will depend crucially on the coupling to the leads as well as on subtle details of the contact geometry. However, as follows from our calculations, for long Nb–Bz molecules and wires the importance of spin–orbit coupling for states around the Fermi energy could result in significant modulations of the overall conductance as a function of the direction of the applied magnetic field, irrespective of the specific contact geometry—an effect which could be observed experimentally.

6. Conclusions

In our extended first-principles study we shed light on the electronic and magnetic properties of metal–benzene sandwiches and infinite wires of V, Nb and Ta. We found that all the \( \text{V}_n\text{Bz}_m \) \( (n, m = 1, 2, 3, 4) \) molecules and the infinite wire \( \text{VBz}_\infty \) are magnetic with a large gain in total energy compared to the nonmagnetic solution. The magnetic ground state of all the molecules is ferromagnetic, with an exception of the \( \text{V}_3\text{Bz}_4 \) compound. The competition of the super-exchange mechanism between the metal atoms via the benzene molecules with the direct exchange between the metal ions results in small energy differences between the ferromagnetic and antiferromagnetic solutions for small \( n \). The rigidity of the magnetism was investigated with respect to the vibrations in the \( \text{V}_2\text{Bz}_3 \) compound. With increasing number of V atoms in the complexes the ferromagnetism becomes energetically more favorable, resulting in a monotonic increase of the total spin moment as a function of \( n \), as observed experimentally.

The values of the spin moments and their qualitative behavior as a function of the temperature are in good accordance with experiments as well.

We analyzed the stability of magnetism in V-based compounds by evaluating a crucial quantity, the magnetic anisotropy energy (MAE), which fixes the direction of the magnetization with respect to the lattice, making the technological application of the sandwiches possible. We find that for the molecules with \( n < 3 \) the values of MAE are of the order of tiny 50 \( \mu eV \) per metal atom, and rise with the number of V atoms up to 0.3 meV in the infinite wire. We show that in order to increase the effective anisotropy barriers in the sandwiches it is desirable to use heavy Nb and Ta metal ions isoelectronic to V. Going from a single half-sandwich to the infinite wires, the ferromagnetism in Nb–Bz and Ta–Bz compounds is preserved, while the values of MAE increase by one to two orders of magnitude. Moreover, strong spin–orbit coupling in these molecules can result in intriguing physical effects with major consequences for spin-polarized transport and spintronics applications. As an example, we demonstrate for a Nb–benzene infinite wire the possibility of ballistic anisotropic magnetoresistance.

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