Ψ_k Newsletter

AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

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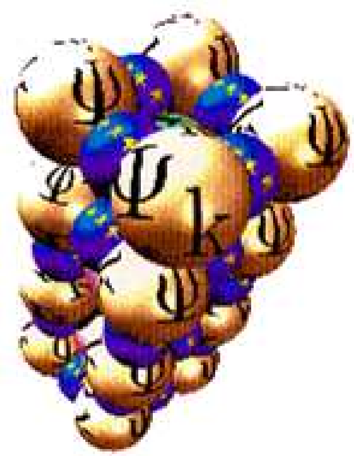

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Contents

1 Editorial

This summer issue of the Psi-k newsletter contains a number of abstracts and a scientific highlight review article. The latter is by Nicolae Atodiresei, Vasile Caciuc, Predrag Lazić and Stefan Blügel (Jülich, Germany) on ”Chemical and van der Waals Interactions at Hybrid Organic-Metal Interfaces”.

Please check the table of content for details.

Since this is the last Psi-k newsletter that I have edited, I would like to take this opportunity and thank everybody who has contributed to the newsletters over the past twenty years. All your efforts have been much appreciated. I have been especially grateful for all the scientific highlight articles and hope that they will continue to appear in the future editions. The latter are likely to change in due course and I wish all the best to whoever will deal with the future editions.

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2 Abstracts

Modelling the electronic structure and magnetic properties of LiFeAs and FeSe using hybrid-exchange density functional theory

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Abstract

The electronic structure and magnetic properties of LiFeAs and FeSe have been studied using hybrid exchange density functional theory. The total energies for a unit cell in LiFeAs and FeSe with different spin states including non-magnetic and spin-2 are calculated. The spin-2 configuration has the lower energy for both LiFeAs and FeSe. The computed anti-ferromagnetic exchange interactions between spins on the nearest (next nearest) neighbouring Fe atoms in LiFeAs and FeSe are approximately 14 (17) meV and 6 (13) meV respectively. The total energies of the checkerboard and stripe-type anti-ferromagnetic ordering for LiFeAs and FeSe are compared, yielding that for LiFeAs the checkerboard is lower whereas for FeSe the stripe-type is lower. However, owing to the fact that the exchange interaction of the next nearest neighbour is larger than that of the nearest one, which means that the collinear ordering might be the ground state. These results are in agreement with previous theoretical calculations and experiments. Especially the calculations for LiFeAs indicate a co-existence of conducting *d*-bands at the Fermi surface and *d*-orbital magnetism far below the Fermi surface. The theoretical results presented here might be useful for the experimentalists working on the electronic structure and magnetism of iron-based superconductors.

Solid State Communications 161 23 (2013)
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Electronic structure and exchange interactions in cobalt-phthalocyanine chains

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Abstract

The magnetic properties and electronic structure of cobalt phthalocyanine (CoPc, spin-$\frac{1}{2}$) molecular chains have been studied using density functional theory with a hybrid exchange functional, over a wide range of chain geometries. Our theoretical results for the exchange interactions in the known phases α-CoPc ($J/k_B \sim 85$ K) and β-CoPc ($J/k_B \sim 2$ K) are in quantitative agreement with recent magnetic measurements; we also find the computed exchange interaction agrees qualitatively with recent measurements by inelastic tunnelling spectroscopy on thin films. The computed exchange interactions are much larger than those in copper phthalocyanine (CuPc), and are predicted to rise to a maximum of $J/k_B \sim 400$ K when the molecules are face-on. The dominant exchange mechanism is expected to be super-exchange arising from the direct hopping between d_{z^2} orbitals.

Accepted in Physical Review B
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Antiferromagnetic-like coupling in the cationic iron cluster of thirteen atoms

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Abstract

We explore, within the density functional theory in the generalized gradient approximation to exchange and correlation, the map of spin isomers of the cationic Fe_{13}^{+} cluster in connection with recent X-ray magnetic circular dichroism spectroscopy experiments [M. Niemeyer *et al., Phys. Rev. Lett.* 2012, **108**, 057201] which observed an anomalous low magnetic moment per number of $3d$ holes in this cluster. We systematically explore the low-lying magnetic excitations and correlate them with structural rearrangements and stability indicators. We obtain the observed low magnetic moment per $3d$ hole as the ground state of Fe_{13}^{+} and we demonstrate that, as supposed by the experimentalists, the cluster undergoes a magnetic transition from a ferromagnetic-like configuration to an antiferromagnetic-like one upon ionization. We unravel this unexpected magnetic behavior showing that it is concomitant with a $\mathrm{T_h}$-deformation of the icosahedral structure together with the electronic filling of this particular iron cluster. The spin-orbit interaction preserves this magnetic configuration which is essentially due to the spin. Our computed magnetic anisotropy energy supports the experimental interpretation of the cluster as fluxional due to the very weak coupling of the magnetic moment to an easy axis.

(Submitted to Phys. Chem. Chem. Phys., DOI:10.1039/C3CP51377G.)
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The Microscopic Features of Heterogeneous Ice Nucleation May Affect the Macroscopic Morphology of Atmospheric Ice Crystals

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Abstract

It is surprisingly difficult to freeze water. Almost all ice that forms under mild conditions (temperatures > -40 °C) requires the presence of a nucleating agent - a solid particle that facilitates the freezing process - such as clay mineral dust, soot or bacteria. In a computer simulation, the presence of such ice nucleating agents does not necessarily alleviate the difficulties associated with forming ice on accessible timescales. Nevertheless, in this work we present results from molecular dynamics simulations in which we systematically compare homogeneous and heterogeneous ice nucleation, using the atmospherically important clay mineral kaolinite as our model ice nucleating agent. From our simulations, we do indeed find that kaolinite is an excellent ice nucleating agent but that contrary to conventional thought, non-basal faces of ice can nucleate at the basal face of kaolinite. We see that in the liquid phase, the kaolinite surface has a drastic effect on the density profile of water, with water forming a dense, tightly bound first contact layer. Monitoring the time evolution of the water density reveals that changes away from the interface may play an important role in the nucleation mechanism. The findings from this work suggest that heterogeneous ice nucleating agents may not only enhance the ice nucleation rate, but also alter the macroscopic structure of the ice crystals that form.

(Faraday Discuss., 2013, DOI:10.1039/C3FD00059A)

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Quantum simulation of low-temperature metallic liquid hydrogen

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Abstract

The melting temperature of solid hydrogen drops with pressure above ~65 GPa, suggesting that a liquid state might exist at low temperatures. It has also been suggested that this low-temperature liquid state might be non-molecular and metallic, although evidence for such behaviour is lacking. Here we report results for hydrogen at high pressures using *ab initio* methods, which include a description of the quantum motion of the protons. We determine the melting temperature as a function of pressure and find an atomic solid phase from 500 to 800 GPa, which melts at <200 K. Beyond this and up to 1,200 GPa, a metallic atomic liquid is stable at temperatures as low as 50 K. The quantum motion of the protons is critical to the low melting temperature reported, as simulations with classical nuclei lead to considerably higher melting temperatures of ~300 K across the entire pressure range considered.

(Nature Communications 4, 2064 (2013))
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On the Accuracy of van der Waals Inclusive Density-Functional Theory Exchange-Correlation Functionals for Ice at Ambient and High Pressures

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Abstract

Density-functional theory (DFT) has been widely used to study water and ice for at least 20 years. However, the reliability of different DFT exchange-correlation (xc) functionals for water remains a matter of considerable debate. This is partic- ularly true in light of the recent development of DFT-based methods that account for van der Waals (vdW) dispersion forces. Here, we report a detailed study with several xc functionals (semi-local, hybrid, and vdW inclusive approaches) on ice I*h* and six proton ordered phases of ice. Consistent with our previous study [Phys. Rev. Lett. **107**, 185701 (2011)] which showed that vdW forces become increasingly important at high pressures, we find here that all vdW inclusive methods considered improve the relative energies and transition pressures of the high-pressure ice phases compared to those obtained with semi-local or hybrid xc functionals. However, we also find that significant discrepancies between experiment and the vdW inclusive approaches remain in the cohesive properties of the various phases, causing certain phases to be absent from the phase diagram. Therefore, room for improvement in the description of water at ambient and high pressures remains and we suggest that because of the stern test the high pressure ice phases pose they should be used in future benchmark studies of simulation methods for water.

(Submitted to J. Chem. Phys. (July 2013))

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Space Charge Transfer in Hybrid Inorganic/Organic Systems

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Abstract

We discuss density functional theory calculations of hybrid inorganic/organic systems (HIOS) that explicitly include the global effects of doping (i.e. position of the Fermi level) and the formation of a space-charge layer. For the example of tetrauoro-tetracyanoquinodimethane (F4TCNQ) on the ZnO($000\bar{1}$) surface we show that the adsorption energy and electron transfer depend strongly on the ZnO doping. The associated work function changes are large, for which the formation of space-charge layers is the main driving force. The prominent doping effects are expected to be quite general for charge-transfer interfaces in HIOS and important for device design.

(Submitted to Phys. Rev. Lett. (June 2013))
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Scaling Laws for van der Waals Interactions in Nanostructured Materials

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Abstract

Van der Waals interactions play a fundamental role in biology, physics, and chemistry, in particular in the self-assembly and the ensuing function of nanostructured materials. Here we utilize an efficient microscopic method to demonstrate that van der Waals interactions in nano-materials act at distances greater than typically assumed, and can be characterized by different scaling laws depending on the dimensionality and size of the system. Specifically, we study the behavior of van der Waals interactions in single-layer and multi-layer graphene, fullerenes of varying size, single-wall carbon nanotubes, and graphene nanoribbons. As a function of nanostructure size, the van der Waals coefficients follow unusual trends for all of the considered systems, and deviate significantly from the conventionally employed pairwise-additive picture. We propose that the peculiar van der Waals interactions in nanostructured materials could be exploited to control their self-assembly.

(Accepted in Nat. Commun. (July 2013))
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Assessment and Validation of Machine Learning Methods for Predicting Molecular Atomization Energies

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Abstract

The accurate and reliable prediction of properties of molecules typically requires computationally intensive quantum-chemical calculations. Recently, machine learning techniques applied to *ab initio* calculations have been proposed as an efcient approach for describing the energies of molecules in their given ground-state structure throughout chemical compound space (Rupp *et al.*, Phys. Rev. Lett. **108**, 058301, 2012). In this paper we outline a number of established machine learning techniques and investigate the inuence of the molecular representation on the methods performance. The best methods achieve prediction errors of 3 kcal/mol for the atomization energies of a wide variety of molecules. Rationales for this performance improvement are given together with pitfalls and challenges when applying machine learning approaches to the prediction of quantum-mechanical observables.

(Accepted in J. Chem. Theory. Comp. (July 2013))

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Control of Intermolecular Bonds by Deposition Rates at Room Temperature: Hydrogen Bonds versus Metal Coordination in Trinitrile Monolayers

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Abstract

Self-assembled monolayers of 1,3,5-tris(4'-biphenyl-4"-carbonitrile)benzene, a large functional trinitrile molecule, on the (111) surfaces of copper and silver under ultrahigh vacuum conditions were studied by scanning tunneling microscopy and low-energy electron diffraction. A densely packed hydrogen-bonded polymorph was equally observed on both surfaces. Additionally, deposition onto Cu(111) yielded a well-ordered metal-coordinated porous polymorph that coexisted with the hydrogen-bonded structure. The required coordination centers were supplied by the adatom gas of the Cu(111) surface. On Ag(111), however, the wellordered metal-coordinated network was not observed. Differences between the adatom reactivities on copper and silver and the resulting bond strengths of the respective coordination bonds are held responsible for this substrate dependence. By utilizing ultralow deposition rates, we demonstrate that on Cu(111) the adatom kinetics plays a decisive role in the expression of intermolecular bonds and hence structure selection.

(Submitted to J. Am. Chem. Soc.)
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Adsorption structure determination of a large polyaromatic trithiolate on Cu(111): combination of LEED-I(V) and DFT-vdW

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Abstract

The adsorption geometry of 1,3,5-tris(4-mercaptophenyl)benzene (TMB) on Cu(111) is determined with high precision using two independent methods, experimentally by quantitative low energy electron diffraction (LEED-I(V)) and theoretically by dispersion corrected density functional theory (DFT-vdW). Structural refinement using both methods consistently results in similar adsorption sites and geometries. Thereby a level of confidence is reached that allows deduction of subtle structural details such as molecular deformations or relaxations of copper substrate atoms.

(Submitted to Phys. Chem. Chem. Phys.)

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Quantification of finite-temperature effects on adsorption geometries of π-conjugated molecules: Azobenzene/Ag(111)

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Abstract

The adsorption structure of the molecular switch azobenzene on Ag(111) is investigated by a combination of normal incidence x-ray standing waves and dispersion-corrected density functional theory. The inclusion of non-local collective substrate response (screening) in the dispersion correction improves the description of dense monolayers of azobenzene, which exhibit a substantial torsion of the molecule. Nevertheless, for a quantitative agreement with experiment explicit consideration of the effect of vibrational mode anharmonicity on the adsorption geometry is crucial.

(Physical Review B, **88**, 035421 (2013))

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Excited-state potential-energy surfaces of metal-adsorbed organic molecules from Linear Expansion Δ-Self-Consistent Field Density-Functional Theory (ΔSCF-DFT)

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Abstract

Accurate and efficient simulation of excited state properties is an important and much aspired cornerstone in the study of adsorbate dynamics on metal surfaces. To this end, the recently proposed linear expansion Δ Self-Consistent Field (leΔSCF) method by Gavnholt *et al.* [Phys. Rev. B **78**, 075441 (2008)] presents an efficient alternative to time consuming quasi-particle calculations. In this method the standard Kohn-Sham equations of Density-Functional Theory are solved with the constraint of a non-equilibrium occupation in a region of Hilbert-space resembling gas-phase orbitals of the adsorbate. In this work we discuss the applicability of this method for the excited-state dynamics of metal-surface mounted organic adsorbates, specifically in the context of molecular switching. We present necessary advancements to allow for a consistent quality description of excited-state potential-energy surfaces (PESs), and illustrate the concept with the application to Azobenzene adsorbed on Ag(111) and Au(111) surfaces. We find that the explicit inclusion of substrate electronic states modifies the topologies of intra-molecular excited-state PESs of the molecule due to image charge and hybridization effects. While the molecule in gas phase shows a clear energetic separation of resonances that induce isomerization and backreaction, the surface-adsorbed molecule does not. The concomitant possibly simultaneous induction of both processes would lead to a significantly reduced switching efficiency of such a mechanism.

(Journal of Physical Chemistry, **139**, 014708 (2013).)

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Multi-Doping of Si Cages: High Spin States beyond the Single-Dopant Septet Limit

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Abstract

Density-functional theory based global geometry optimization is employed to systematically scrutinize the possibility of multi-doping of hydrogenated Si clusters in order to achieve high spin states beyond the septet limit of a single-atom dopant. While our unbiased configurational search reveals that the previously suggested $Si_{18}H_{12}$ double hexagonal prism structure is generally too small to accommodate two dopants in magnetized state, the larger $Si_{24}H_{24}$ cage turns out to be suitable for such applications. For dimer dopants $M_2{}^+ = Cr_2{}^+$, $Mn_2{}^+$ and $CrMn^+$, the structural integrity of the host cage is conserved in the ground-state structure of corresponding $M_2{}^+@Si_{24}H_{24}$ aggregates, as is the unusually high spin state of the guest dopant, which in case of $Cr_2{}^+$ already exceeds the single-atom dopant septet limit by almost a factor of two. Moreover, the possibility of further increasing the cluster spin moment by encapsulating an even larger number of dopants into a suitably sized hydrogenated Si cage is illustrated for the example of a $(CrMn^+)_2@Si_{28}H_{28}$ aggregate with a total number of 18 unpaired electrons. These results strongly suggest multi-doping of Si clusters as a viable route to novel cluster-based materials for magneto-optic applications.

(Submitted to J. Phys. Chem. C, DOI: 10.1021/jp4057863)

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In Situ X-Ray Photoelectron Spectroscopy of Model Catalysts: At the Edge of the Gap

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Abstract

We present high-pressure x-ray photoelectron spectroscopy (HP-XPS) and first-principles kinetic Monte Carlo study addressing the nature of the active surface in CO oxidation over Pd(100). Simultaneously measuring the chemical composition at the surface and in the near-surface gas phase, we reveal both O-covered pristine Pd(100) and a surface oxide as stable, highly active phases in the near-ambient regime accessible to HP-XPS. Surprisingly, no adsorbed CO can be detected during high CO2 production rates, which can be explained by a combination of a remarkably short residence time of the CO molecule on the surface and mass-transfer limitations in the present setup.

(PRL 110, 117601, (2013))

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Coverage- and Temperature-Controlled Isomerization of an Imine Derivative on Au(111)

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Abstract

The isomerization behavior of photochromic molecular switches is strongly influenced by adsorption on metal surfaces. For (E)-3,5-di-tert-butyl-N-(3,5-di-tert-butylbenzylidene)aniline (abbreviated as TBI for tetra-tert-butyl imine), it is found that a layer adsorbed on Au(111) can undergo an isomerization from the trans to the cis and back to the trans configuration when continuously increasing the sample temperature and accordingly decreasing the sample coverage. The conformation and adsorption geometry of TBI are determined from near-edge X-ray absorption fine structure measurements in agreement with density functional theory calculations taking into account the van der Waals interaction between adsorbate and metal surface. The coverage- and temperature-controlled conformational transitions are reversible and are driven by the higher packing density of the less stable cis-isomer in combination with the low thermal activation barrier of the trans- to cis-isomerization typical for imine derivatives. This unexpected scenario is corroborated by thermal desorption and vibrational spectroscopy as well as scanning tunneling microscopy.

(J. Am. Chem. Soc., 2013, 135 (11), pp 4273C4281)
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First-principles thermodynamic screening approach to photo-catalytic water splitting with co-catalysts

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Abstract

We adapt the computational hydrogen electrode approach to explicitly account for photo-generated charges and use it to computationally screen for viable catalyst/co-catalyst combinations for photo-catalytic water splitting. The hole energy necessary to thermodynamically drive the reaction is employed as descriptor for the screening process. Using this protocol and hybrid-level density-functional theory we show that water oxidation on bare TiO_2 surfaces is thermodynamically more complex than previously thought. This motivates a screening for suitable co-catalysts for this half-reaction, which we carry out for Au particles down to the non-scalable size regime. We find that almost all small Au clusters studied are better suited for water photo-oxidation than an extended Au(111) surface or bare TiO_2 facets.

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3 SCIENTIFIC HIGHLIGHT OF THE MONTH

Review
Chemical and van der Waals Interactions at Hybrid Organic-Metal Interfaces

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Abstract

In this highlight we briefly review several of our recent theoretical studies focused on how the interplay between the chemical and the van der Waals interactions determines the bonding mechanism of several chemically functionalized π-conjugated organic molecules on non-magnetic and magnetic surfaces. In particular, we focus on the issue how to tailor the strength of the interaction between such π-conjugated organic molecules with a substrate of choice such that the nature of the molecular bonding has the specific features of the physisorption or chemisorption processes. Furthermore, we show how the precise control of these binding mechanisms allows us to design specific electronic and magnetic properties of hybrid organic-metallic interfaces.

1 Introduction

The intense research effort witnessed in the last decade to employ organic molecules as basic components in electronic devices triggered the development of the molecular electronics field [1] with the hope to become a viable alternative to the complementary metal-oxide-semiconductor (CMOS) technology to construct integrated circuits. Indeed, up to now the organic molecules clearly demonstrated their ability to be used as elementary functional units in devices as diodes [2], molecular switches [3], organic field-effect transistors [4, 5] or ultra-high-density memory circuits [6]. Despite of these impressive achievements, basic theoretical and experimental research is still required to close the technological gap between the CMOS and the molecular electronics.

Additionally, the use the spin degree of freedom in molecular-based devices extended the realm of molecular electronics to molecular spintronics [7]. For instance, single molecule magnets [8] were incorporated in supramolecular spin-valve devices [9] or magnetic molecules exhibit a spin-filter functionality of a magnetic surface [10]. Interestingly, the latter effect can be present even if the organic molecule is non-magnetic [11]. Overall, the field of molecular spintronics opens new exciting technological opportunities that are still to be explored [12].

2 Physisorption vs. Chemisorption Bonding Mechanism

2.1 Overview

The adsorption of an adsorbate (i.e., an atom, a cluster of atoms or a molecule) on a substrate implies two complementary aspects: (1) the change of the adsorbate's and substrate's electronic structure due to their mutual interaction in a degree determined by (2) the strength of the adsorbate–surface interaction which is quantitatively described by the adsorption energy E_{ads}[1]. In this respect, there are two main bonding mechanisms, namely *physisorption* and *chemisorption*. A schematic representation of the basic features displayed by the physisorption and chemisorption bonding mechanisms is depicted in Fig. 1.

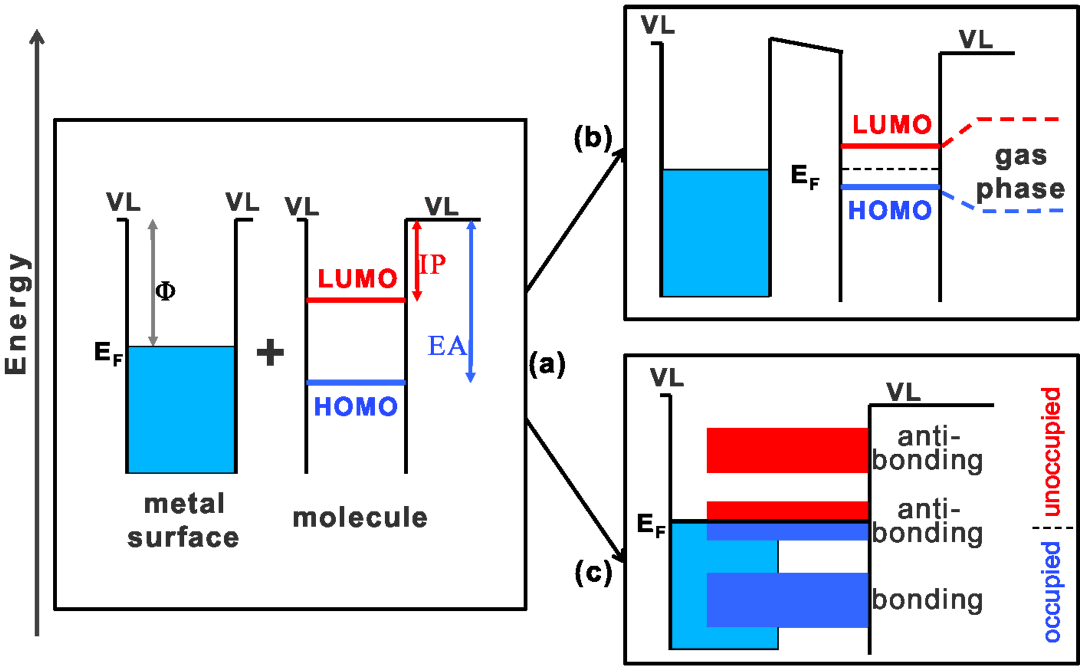

Figure 1: (a) Schematic illustration of the energy level alignment between a molecule and a surface of choice. Depending on the strength of the molecule-surface interaction, the adsorption process can be labelled as (b) physisorption or (c) chemisorption.

Initially, as shown in Fig. 1(a), the adsorbate (i.e., in our case a molecule) and the surface under consideration are well separated such that their electronic structure are aligned with respect to the vacuum level at infinity [13]. Then in the case of physisorption [see Fig. 1(b)], the gas-phase electronic structure of the adsorbate as well that of the surface are not significantly changed upon adsorption. In consequence, for a physisorbed molecule the concept of the molecular

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[1] The adsorption energy is defined as $E_{\text{ads}} = E_{\text{sys}} - E_{\text{surf}} - E_{\text{molec}}$, where E_{sys} is the total energy of the molecule–surface system while E_{surf} and E_{molec} denote the total energy of the clean surface and that of the molecule in the gas phase, respectively.

orbitals (MOs) obtained as a linear combination of the atomic orbitals of its atomic constituents is still a meaningful theoretical instrument that can be used to describe the molecular electronic structure. In this context, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) known also as frontier orbitals [14] are of a particular importance to rationalize the molecule–substrate interaction [15]. Additionally, it is important to note that a renormalization of the HOMO-LUMO gap can occur if a molecule is physisorbed on a polarizable surface due to the additional adsorbate–substrate image potential interaction [16–18]. From the energetic point of view, the molecule–surface interaction is relatively weak with an upper value of the adsorption energy of $\sim$ 0.1 eV while the adsorbate–substrate equilibrium distance is typically $\geq$3 Å. Importantly, the physisorption bonding mechanism is driven by the long-range dispersion-induced van der Waals (vdW) forces [19].

In contrast to physisorption, in the case of chemisorption the molecule and the substrate merge to form a new quantum mechanical system. As a consequence, for a chemisorbed system hybrid adsorbate–surface states are formed which can contain mixed electronic states without any resemblance to the states of the separated molecule and substrate [20,21]. From a methodological point of view, the formation of the new hybrid molecule–surface states can be seen as the result of the hybridization (i.e., mixing) process between the adsorbate and the surface electronic states. Historically, one of the first quantitative model used to describe this process is that proposed by Newns [22] on the basis of the Anderson impurity Hamiltonian [23], model referred to as Newns-Anderson (for a review see, for instance, Ref. [24]). In the Newns-Anderson model one can distinguish between the weak and strong chemisorption. A weak chemisorption process takes place when the adsorbate's electronic state of interest becomes a broad resonance due to its interaction with an extended and featureless *sp* band of the surface. On the contrary, the interaction between the molecule's energy level with a sharp $d(f)$ band induces the creation of the bonding and anti-bonding hybrid molecule–surface electronic states as depicted in Fig. 1(c).

From this perspective, the strong chemisorption in the Newns-Anderson model is very similar to the formation of bonding and antibonding combinations of the atomic orbitals to form MOs as described by the frontier molecular orbital theory [14]. In both weak and strong chemisorption bonding mechanisms, the hybridization of the molecular electronic states with those of the substrate are instrumental to obtain hybrid molecule–surface electronic states. It is worth to mention that for an optimal hybridization process two basic conditions must be fulfilled: (1) the molecule and substrate wavefunctions must have the appropriate symmetry to maximize the spatial overlap and (2) the overlapping electronic states must be close in energy to ensure a large energetic splitting between the bonding and antibonding hybrid states which in turn increases the stability of the molecule–surface system.

2.2 Theoretical Description

Nowadays the density functional theory (DFT) [25] is the theoretical tool of choice to investigate the structural and electronic properties of physical systems ranging from free atoms to complex systems such as single molecules or molecular layers on surfaces. While in principle exact for the ground-state properties, in practice DFT relies on the use of approximate exchange-correlation functionals such as the local density approximation (LDA) [26, 27] or the generalized gradient approximation (GGA) in various flavours (see, for instance, Refs. [28–31]). In particular, for the chemisorbed molecular systems the use of an approximate exchange-correlation functional leads to adsorption energies that are not chemically accurate [32].

As regarding the physisorbed molecular systems, a major shortcoming of the currently used semi-local GGA exchange-correlation functionals is the fact that they do not describe the long-range attractive van der Waals (London dispersion) interactions while LDA leads to binding in such physisorbed systems due to the exchange and not as a result of the correlation effects [33]. This failure is related to the intrinsic non-local character of the correlation effects responsible for the vdW forces, feature that is not captured in the commonly used local or semi-local approximations for the exchange-correlation energy functional. Nevertheless, these dispersion interaction can be included in DFT in a semi-empirical way as proposed, for example, by Grimme [34], Grimme *et al.* [35], Ortmann *et al.* [36], Tkatchenko and Scheffler [37] or Tkatchenko *et al.* [38]. This approach relies on the summing of atomic pairwise contributions of the form $-C_6^{ij}/R_{ij}^6$ containing the C_6^{ij} coefficient for the atomic pair ij in question separated by the distance R_{ij}. Additionally, a damping function is required to avoid near singularities at small inter-atomic distances (for more details see the previously mentioned references). One the other hand, starting from the adiabatic connection fluctuation dissipation (ACFD) theorem [39, 40], the non-local correlation effects have been included in the first-principles vdW-DF functional [41] and subsequent effort was devoted to improve its predictive power [42, 43]. So far, vdW-enhanced DFT calculations have been performed for various organic molecule–surface systems [44–47] or for the graphene (an extended π system) on several metal surfaces [48–51], to cite just few examples. Further details regarding the incorporation of the London dispersion interactions in DFT can be found in two recent Ψ_k highlights [52, 53].

3 Application to Molecular Electronics

An important goal in molecular electronics is to gain the ability to rationally tune the strength of the molecule–surface interaction to specifically modify the functionality of a molecule-based electronic device. In this respect, two different strategies can be adopted to systematically investigate this problem: (1) for a given substrate to modify the chemical structure of the molecule of interest through a chemical functionalization process (see, for instance, [21, 54, 55]) and (2) for the same molecule to vary the chemical nature of the substrate (see, for example, [56–58]).

The chemical functionalization process at the heart of the path (1) consists in the replacement of an atom or a group of atoms in a molecule through other atoms or group of atoms with a specific functionality (i.e., a functional group). A schematic illustration of this process viewed from the electronic structure point of view is shown in Fig. 2. More precisely, starting from benzene (C_6H_6) the replacement of a CH functional group by one N atom leads to pyridine (C_5H_5N) and through a further substitution one obtains pyrazine ($C_4H_4N_2$). The effect of this chemical functionalization of benzene is twofold: (a) by including a N atom in the aromatic ring the π character of HOMO is changed to σ and (b) the occupied π MOs such as π_1 are shifted to lower energies. Importantly, this energy shift increases with the number of N atoms ,i.e.,

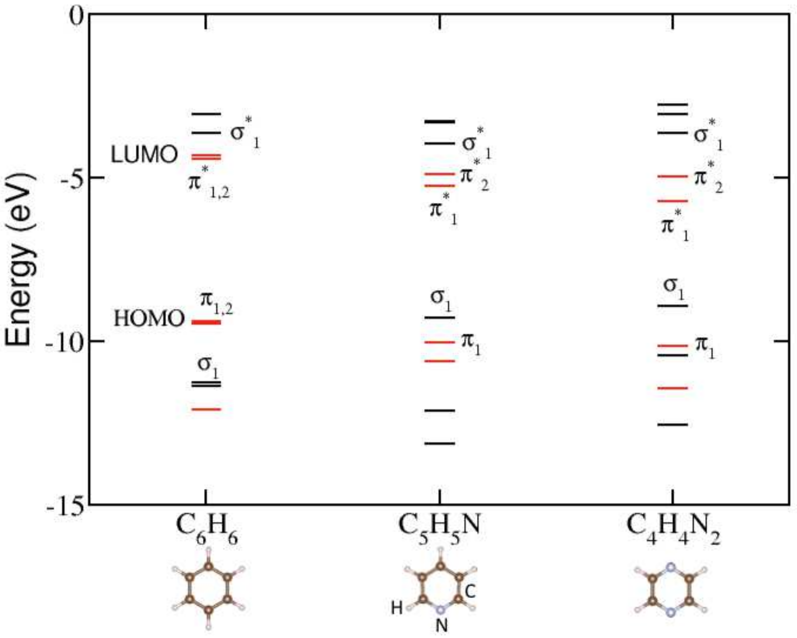

Figure 2: Energy level diagram for the planar π-conjugated benzene (C_6H_6), pyridine (C_5H_5N) and pyrazine ($C_4H_4N_2$) molecules in the gas phase. With respect to benzene, the presence of N in the aromatic ring (a) changes the character of the HOMO from π to σ and (b) gradually lowers in energy the HOMO-1 level with a π character by increasing the number of N atoms. Note that the HOMOs are aligned using the δSCF recipe in all three cases, i.e., $E_{\text{HOMO}} = E(N) - E(N-1)$, where $E(N)$ is the total energy of the neutral molecule while $E(N-1)$ represents the energy of the corresponding cation.

HOMO-1 and HOMO-2 of pyrazine are at lower energies as the similar MOs for pyridine.

We explored how the chemical functionalization of benzene with N atoms specifically determines the nature of the molecule–substrate interaction by investigating the bonding mechanism and the electronic structure of single benzene, pyridine and pyrazine molecules adsorbed flat on the Cu(110) surface [59]. On this substrate, the benzene is chemisorbed with its molecular plane parallel to Cu(110) [60, 61]. As regarding the pyridine, in a previous study [62] we have shown that this molecule is also chemisorbed on Cu(110) such that in the ground state it adsorbs with the aromatic ring via the N atom perpendicularly to surface. Nevertheless, when starting from a flat adsorption geometry like that in the case of benzene, the pyridine can preserve this flat geometry or it turns in an upright configuration, depending on its specific position on the Cu(110) surface [62].

This observation clearly emphasizes the importance of such flat adsorption geometries for a flat aromatic molecule like pyridine on a metal surface since they can be intermediate configurations on the adsorption path from the gas-phase to a metal surface. Therefore a similar flat adsorption configuration was considered also for the pyrazine molecule. The corresponding *ab initio* DFT simulations were carried out using the PBE exchange-correlation functional [28] and the London dispersion interactions were considered within the framework of the semi-empirical DFT-D2 [34] and the first-principles vdW-DF [41] methods.

	DFT		DFT-D2	
	d_{eq} (Å)	E_{ads} (meV)	d_{eq} (Å)	E_{ads} (meV)
Bz	2.43	-253	2.35	-492
Py	2.98	-108	2.43	-417
Pz	2.99	-36	2.59	-371

Table 1: The average equilibrium distances d_{eq} and the adsorption energies E_{ads} obtained for the benzene, pyridine and pyrazine molecules for a flat adsorption configuration on the Cu(110) substrate using the DFT and DFT-D2 relaxed geometries.

Table 1 summarizes the average equilibrium distances d_{eq} and the adsorption energies E_{ads} evaluated for these three π-conjugated molecules using the DFT and the DFT-D2 relaxed geometries. The main outcome of the DFT calculations is that the benzene is chemisorbed on Cu(110) while in a flat adsorption geometry the pyridine and pyrazine molecules are physisorbed with an average adsorption distance of $\sim 3\,\text{Å}$. In this regard, this picture changes significantly when the dispersion interactions are considered in the DFT calculations. More specifically, as expected, the inclusion of the vdW interactions leads to a a significantly smaller molecule–surface distance in the case of pyridine and pyrazine while it remains almost the same for the benzene molecule. A smaller DFT-D2 separation distance due to the inclusion of the long-range attractive dispersion interactions has a significant impact on the electronic structure of the adsorbed molecules.

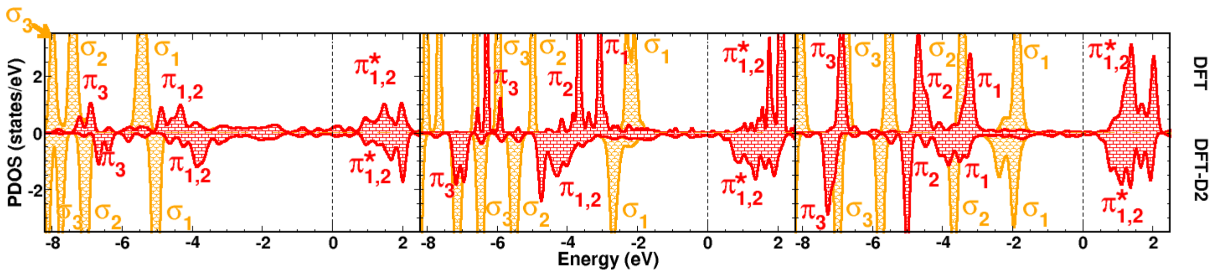

Figure 3: The DFT (upper figures) and DFT-D2 (lower figures) projected density of states (PDOS) of the benzene, pyridine and pyrazine molecules adsorbed flat on the Cu(110) surface. On this substrate the benzene is chemisorbed at the DFT level of the *ab initio* simulations such that the inclusion of the vdW interactions by means of the semi-empirical DFT-D2 method does not significantly change the electronic structure evaluated with DFT. On the contrary, in the case of pyridine and pyrazine, the inclusion of the dispersion interactions bring them closer to the Cu(110) substrate that leads to a stronger hybridization between the molecules p_z-orbitals and the Cu $d-$bands. (adapted after [59])

As shown in Fig. 3, the benzene electronic structure is not sensibly modified when the vdW interactions are taken into account. On the contrary, in the case of pyrazine the π_1 and $\pi^*_{1,2}$ PDOS features at the molecular site are significantly broader for the DFT-D2 relaxed geometry than for the DFT one. This implies that in a flat adsorption geometry pyridine becomes chemisorbed due to the London dispersion forces. Indeed, also the calculated adsorption energy E_{ads}^{DFT-D2} is lower than E_{ads}^{DFT}. A similar conclusion can be drawn for pyrazine where the vdW interactions significantly lowers its small DFT adsorption energy that implies that pyrazine binds to Cu(110) mainly via the dispersion interactions.

As already mentioned, a second modality to engineer the nature of the molecule–surface bonding mechanism is to modify the chemical reactivity of the substrate by studying the same molecule. Recently, we illustrated this possibility for annulene 1,3,5,7-cyclooctatetraene (C_8H_8, hereafter denoted as COT) [58]. This molecule is interesting since in the gas phase it has a non-aromatic tub conformation since it does not fulfil the Hückel's $4n+2$ rule for the π electrons of a planar aromatic molecule. However, when doubly charged it becomes planar and aromatic.

An interesting alternative route to induce aromaticity in COT is to make use of the hybridization process between its molecular electronic states and those of a surface of choice. This possibility is illustrated in detail in Fig. 4. Our *ab initio* simulations indicate that on the Au(111) surface the COT molecule preserves its tub geometry as in the gas phase and therefore on this substrate COT is physisorbed (a similar conclusion can be drawn from the analysis of the PDOS [58]). Indeed, the experimental and the simulated STM images are remarkably similar which emphasizes the validity of the previous conclusion. However, on the Ag(100) and the Cu(100) surfaces the COT molecule is chemisorbed and becomes flat. Also for these substrate the simulated STM images agree well with the experimental ones. Note that the adsorption energy is significantly stronger for COT on Cu(100) than on Au(111) that denotes a stronger molecule–substrate interaction in the former case. Therefore depending on reactivity of the underlying surface, one can tune the strength of the molecule–substrate interaction from physisorption to chemisorption.

4 Application to Molecular Spintronics

As in detail discussed in the previous section the physisorption is a weak interaction with no hybridization between molecular orbitals and the electronic states of the surface. On the contrary, characteristic for the chemisorption process is the strong molecule-surface interaction that leads to the creation of a new hybrid organic-metallic material due to a strong hybridization between atomic type orbitals that originally form the molecular orbitals and the electronic states of the surface. As a consequence, the electronic and magnetic properties of both molecule and metallic surface are drastically modified and in the most cases do not resemble the properties of the separated systems. In practice both physisorption and chemisorption processes can coexist within the same system as in the case of graphene on Ir(111) and Co/Ir(111) surfaces [49,63]. However, for certain molecule-metal systems the binding is dominated by physisorption [49, 58, 64] while for other hybrid systems the binding is driven by chemisorption [11,58,65]. Furthermore, in addition to physisorption and chemisorption processes a charge transfer between organic material and surface might occur that can specifically modulate the molecule-surface interaction [63,66].

A basic goal of the molecular electronics is to further take advantage of the electron spin degree of freedom by (i) incorporating specific spintronic functions within single molecular building blocks and (ii) using organics to modify the magnetic properties of magnetic substrates. For example, the most important factors that determine the functionality of a spintronic device are (1) the spin-polarized current injected from the hybrid interface and (2) the substrate magnetic

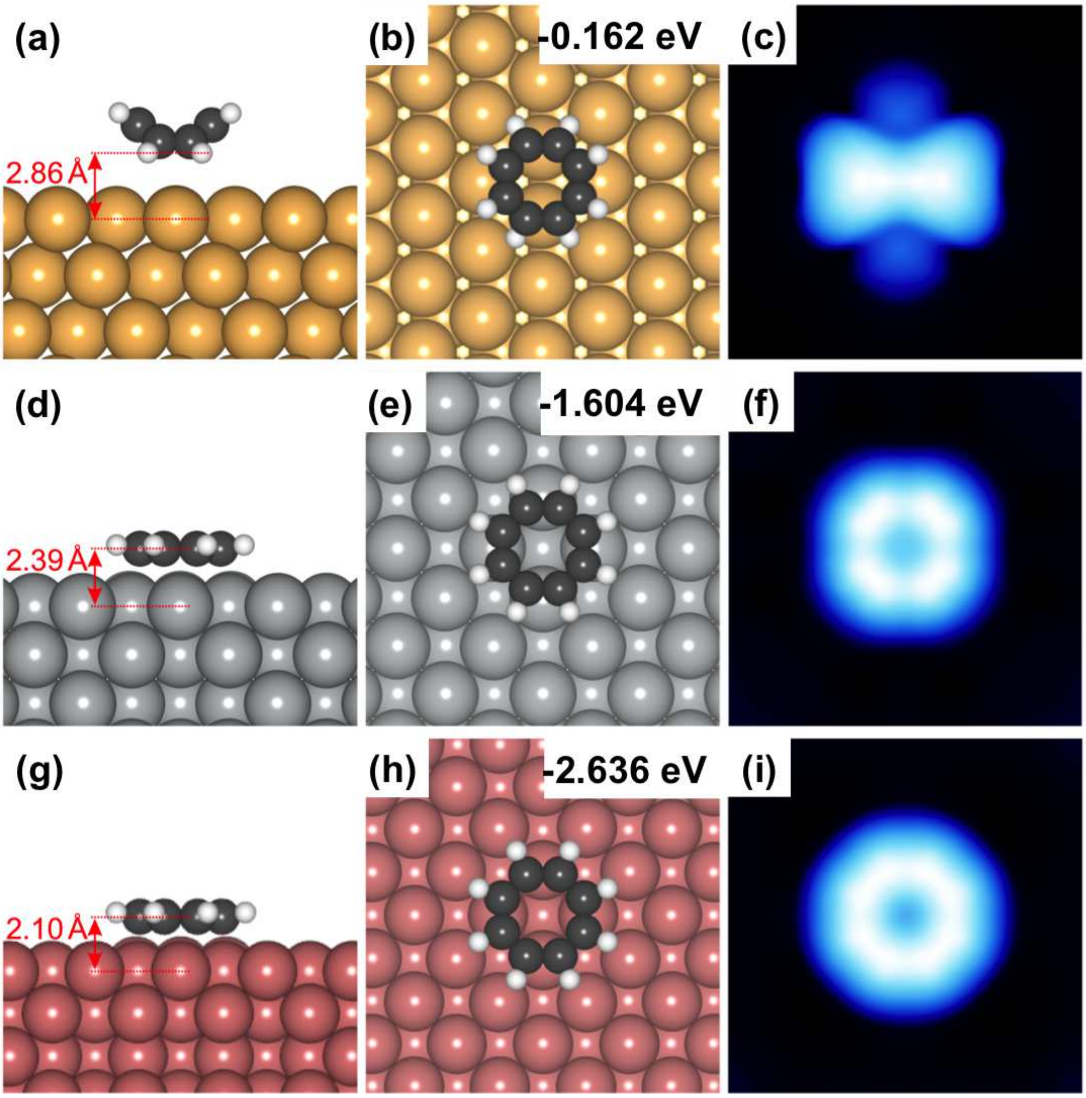

Figure 4: (left panel) Side views and (middle panel) top views of the adsorption geometries and (right panel) the theoretical STM maps obtained for the C_8H_8 (COT) molecule adsorbed on the Au(111) (top row), the Ag(100) (middle row) and the Cu(100) (bottom row) surfaces. On Au(111), COT exhibits a tub conformation as in the gas phase and thus the molecule is physisorbed on this surface. On the contrary, on the Ag(100) and Cu(100) substrates COT is chemisorbed and therefore it adopts a flat adsorption geometry. It is also worth to mention that the COT–surface adsorption distance significantly decreases starting from the Au(111) to Ag(100) and Cu(100) surfaces. Note also that the simulated STM images are in excellent agreement with the experimental STM maps shown in Ref. [58])

properties like magnetic exchange couplings, stability and direction of the magnetic moments of the metal atoms interacting with the organic material. More precisely, the spin-polarized current above the organic layer injected from the hybrid interface is one of the key factors that determine the efficiency of a spin-valve electronic device. Large efforts, see for instance [11, 65–67], are dedicated to understand how to manipulate the interface hybrid states in order to control the transmission of the spin information, i.e. to create an effective source of spin-polarized electrons at the interface.

In several recent studies performed in our group, we clearly demonstrated that the hybrid organic-metallic states rather than the intrinsic molecular spins are decisive in defining the spin-polarization across the hybrid interface [11, 65]. Moreover, the generality of our *ab initio* driven concept studies were clearly proven by spin-polarized scanning tunneling microscopy (SP-STM) experiments performed on $\pi-$conjugated organic materials like molecules [11, 66] and graphene [63] adsorbed on ferromagnetic surfaces.

In the following, we will remind how by adsorbing prototype $\pi-$conjugated organic molecules like cyclopentadienyl-type radicals onto a ferromagnetic substrate such as 2ML Fe/W(110), the magnetic properties of the hybrid system can be tailored by controlling the molecule-surface interaction, i.e. by chemically functionalizing the adsorbed organic molecules. As a result, the interface spin-polarization, the molecular magnetic moments and their spatial orientation can be finely tuned by using substituents with different electronegativities to the organic molecules which in turn lead to a different reactivity of the molecule towards the ferromagnetic surface.

As an instructive example, we can consider the adsorption of the hydrogenated and fluorinated cyclopentadienyl radicals (C_5H_5 and C_5F_5) onto the ferromagnetic 2ML Fe/W(110) surface. Compared to H atom, the F atoms have a significant higher electronegativity that leads to the formation of polar C-F bonds. Therefore, in the C_5F_5 radical the F atoms have a strong inductive electron withdrawal effect (i.e. the charge density is displaced from C towards F) and the $\pi-$conjugation is decreased as compared to C_5H_5 radical. Similar to the adsorption of pyridine and pyrazine on the Cu(110) substrate, the binding of C_5F_5 to the magnetic substrate is much weaker than the C_5H_5 molecule although both molecules C_5H_5 and C_5F_5 chemisorb on the 2ML Fe/W(110) surface, i.e. the adsorption energies are 2.040 eV for C_5F_5 and 2.515 eV for C_5H_5 [65].

The binding mechanism between the molecules (i.e., C_5H_5 and C_5F_5) and the 2ML Fe/W(110) substrate can be explained by using the spin-resolved local density-of-states (LDOS) of the molecule-surface systems shown in Fig. 5 and Fig. 6. As a general feature, the strong interaction between the organic molecules with the ferromagnetic surface leads to a spin-dependent hybridization. In particular, the spin-up p_z-atomic orbitals which originally form the π-molecular orbitals strongly hybridize with the majority d-states of Fe atoms creating hybrid organic-metal states with bonding and antibonding character. Interestingly, the hybrid antibonding states are situated around the Fermi energy while the hybrid bonding states are located at much lower energies (see also Fig. 7). On the contrary, in the spin-down channel, the p_z-atomic orbitals hybridize with the minority d-states of Fe atoms such that the hybrid bonding states appear well below Fermi energy while the hybrid antibonding states are located at high energies above Fermi energy (see Fig. 6). Therefore, characteristic for the complex organic-ferromagnetic sys-

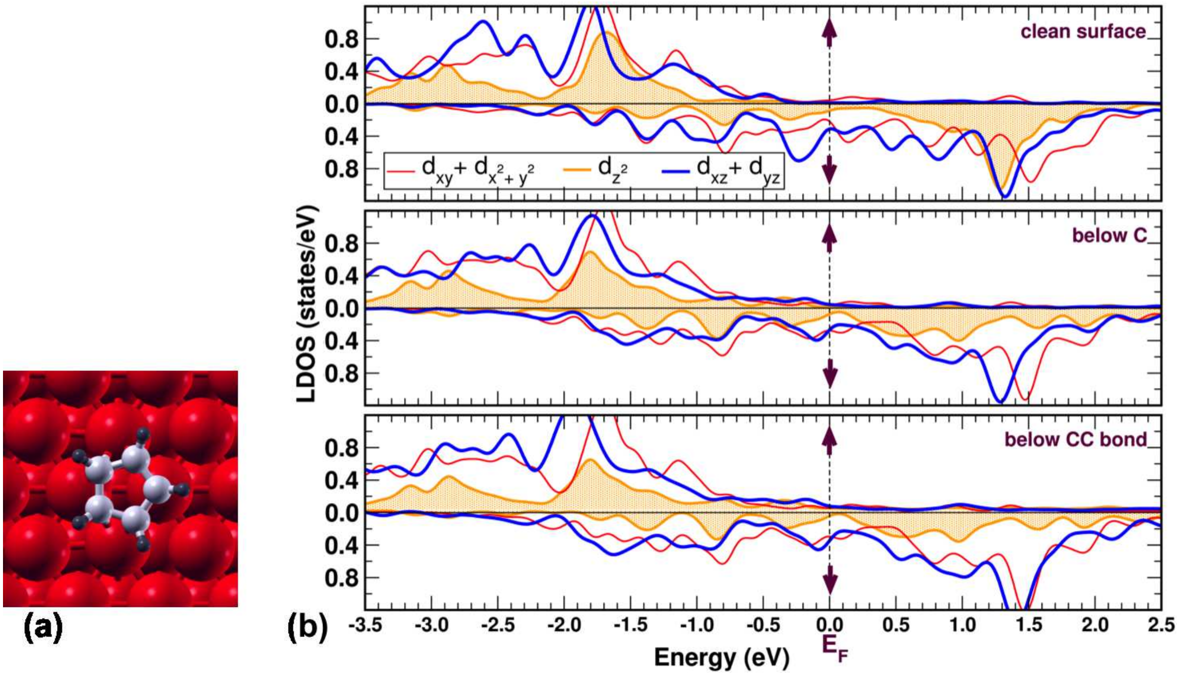

Figure 5: (a) Geometry (top view) of the C_5H_5 molecule adsorbed on the Fe/W(110) substrate. (b) The spin-resolved local density of states of an Fe atom of the clean surface (upper panel), an Fe atom below a C atom (middle panel) and an Fe atom below a CC bond (lower panel) of the C_5H_5 molecule show that the majority of electrons are in spin-up channel while the minority electrons are in spin-down channel. The strong molecule-metal hybridization leads to a change of the magnetic moments of the Fe atoms (e.g. 2.47 μ_B) binding to the C atoms as compared to the Fe atoms (e.g. 2.82 μ_B) of the clean surface [11, 65].

tems, the electronic states with large weight around the Fermi energy are in the spin-up channel at the molecular site and the spin-down channel at the clean surface site (Fig. 5 and Fig. 6).

Conceptually, the electronic structure formed at the organic molecule–ferromagnetic interface due to the spin-dependent hybridization resembles the $p_z - d$ Zener exchange mechanism [68] and is schematically depicted in Fig. 7. Furthermore, this exchange mechanism explains the spin-dependent electronic structure of other π-conjugated organic materials adsorbed on a ferromagnetic substrate, i.e., the adsorption of CoPc molecules on 2ML Fe/W(110) [66] or graphene on ferromagnetic Co/Ir(111) surface [63]. We note in passing that the Zener-type exchange mechanism [68] also describes the interaction of π-conjugated organic materials with ferromagnetic atoms as lanthanides for which a $\pi - f$ exchange mechanism occurs [69, 70].

Integrating the spin-resolved LDOS for the C_5H_5 molecule yields a very small magnetic moment of 0.003 μ_B which can be neglected and the molecule can be considered practically nonmagnetic. A very interesting feature is that upon adsorption, the fluorinated cyclopentadienyl radical C_5F_5 acquires a large magnetic moment (0.262 μ_B) oriented antiferromagnetically relative to the underlying magnetic substrate. As shown in Fig. 6 and schematically depicted in Fig. 7, the molecular magnetic moment in the C_5F_5 originates from the shift of the hybrid antibonding interface states above Fermi energy. It is important to note that the induced molecular magnetic moment is located mostly in the hybrid organic-metallic orbitals with $\pi(p_z)$-character at the

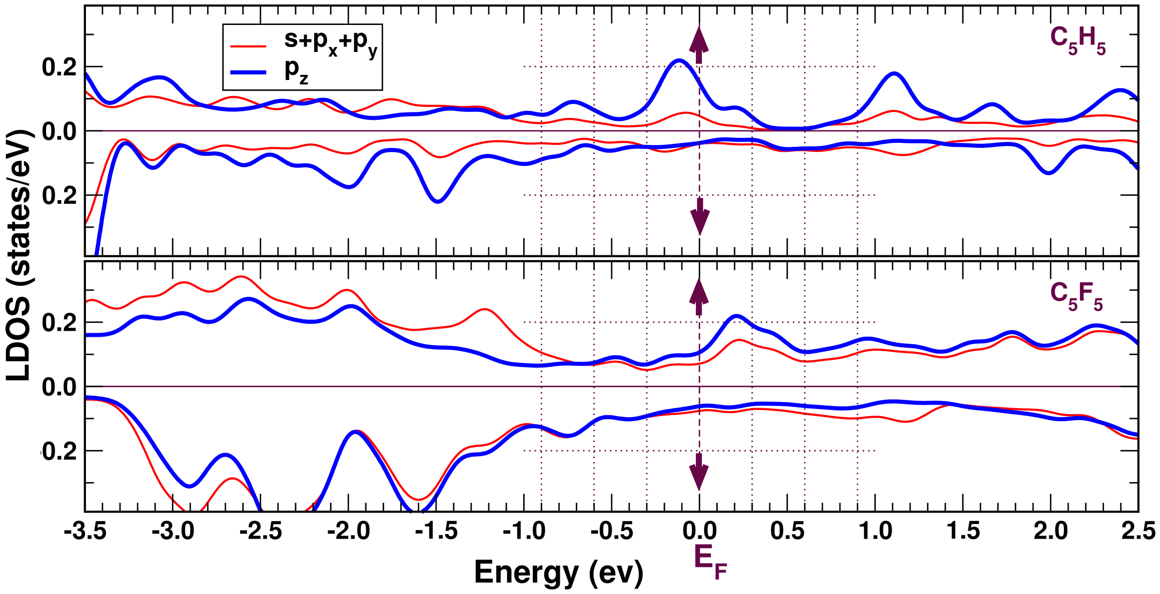

Figure 6: The spin-resolved local density of states of the C_5H_5 and C_5F_5 molecules adsorbed on the 2ML Fe/W(110) surface show broaden states as a result of a effective interaction with Fe atoms. In particular, a strong hybridization occurs only between out-of-plane orbitals (i.e., p_z of C and Fe d-orbitals with a z-component as d_{z^2}, d_{xz} and d_{yz}) while the in-pane orbitals slightly interact (i.e., s, p_x p_y of C and Fe d-orbitals as $d_{x^2-y^2}$ and d_{xy}). Interestingly, both adsorbed molecules show an energy-dependent spin-polarization. This implies that in a specific energy interval the number of spin-up and spin-down states is different and, as a consequence, the molecule has a net magnetization density that can be measured as a spin-contrast in SP-STM experiments [11, 66].

molecular site. Furthermore, as compared to the Fe atoms of the clean surface, the molecule-ferromagnetic metal interaction leads to a decrease of the magnetic moments of the Fe atoms directly binding to the C atoms. Interestingly, the decrease of the magnetic moments of these Fe atoms correlates with the increase of the substituient electronegativity, i.e., largest magnetic moment corresponds to the C_5H_5 while the smallest correspond to the C_5F_5 [65].

As already mentioned above, the spin-resolved LDOS of the adsorbed C_5H_5 and C_5F_5 molecules show an energy dependent spin-polarization which implies an unbalanced number of spin-up and spin-down hybrid interface states for a given energy interval below or above Fermi energy. In practice, this means that in a specific energy window the molecule has a net magnetization density that can be visualized as a magnetic contrast in SP-STM experiments [11, 66]. Fig. 8 shows that for an energetic window above Fermi energy ($[E_F + 0.3]$ eV) an inversion of the spin-polarization with respect to the ferromagnetic substrate occurs for both C_5H_5 and C_5F_5 molecules. This is also the case for the hydrogenated molecule (C_5H_5) for an energy interval below the Fermi level ($[E_F - 0.3]$ eV). In contrast, in the energy window $[E_F - 0.3]$ eV, the fluorinated molecule (C_5F_5) has the same spin-polarization as the ferromagnetic iron surface. To conclude, our results demonstrate that by a carefully choose of the molecular substituient and the bias voltage we can precisely control the spin-polarization above the molecular site, i.e., the spin orientation of the injected electrons above the hybrid interface.

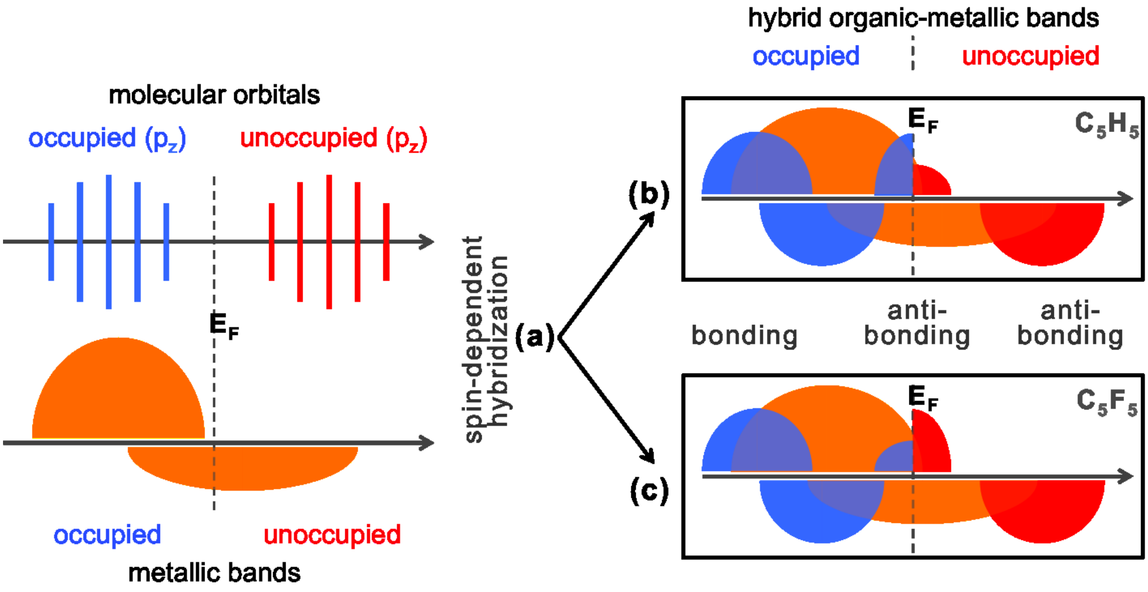

Figure 7: The general scheme used to explain the interaction between non-magnetic organic molecules and ferromagnetic surfaces. (a) Schematic drawings of the molecular orbitals (upper panel) and *d*-states of the ferromagnetic substrate (lower panel). (b, c) Due to a spin-dependent hybridization, the bonding states in both spin-up and spin-down channel appear at low energies well below Fermi level. The spin-up antibonding states are located in an energy window around the Fermi energy while the spin-down states appear at higher energies above Fermi energy. As an interesting characteristic, for the C_5H_5 molecule most of the hybrid antibonding states are situated below Fermi energy (see also upper panel in Fig. 6) while for the C_5F_5 most of these antibonding states are shifted just above Fermi energy (see also lower panel in Fig. 6) and lead to an induced magnetic moment at fluorinated molecular site.

In addition, by including the spin-orbit coupling (SOC) in our *ab initio* calculations we demonstrated that the magnetization direction of the hybrid organo-metallic interface can be manipulated by the adsorption of specific organic molecules. More precisely, the adsorbed hydrogenated molecules destabilize more the out-of-plane magnetization direction of the 2ML FeW(110) substrate as compared to fluorinated molecules which can enhance it [65]. The important message of these results is that in a spin-dependent STM experimental measurement, the magnetic contrast detected by a SP-STM tip with out-of-plane magnetization for the fluorinated molecules will be much larger as compared to that of a hydrogenated molecule.

To conclude this section, we have shown how the spin-polarization above an organic material adsorbed on a ferromagnetic substrate (i.e., the spin-polarized current injected from a hybrid interface) can be understood by performing *ab initio* simulations. Furthermore, by employing an appropriate chemical functionalization of the adsorbed organic molecule and by applying specific bias voltages we can precisely control the spin-polarization of the hybrid organic-ferromagnetic interface. As challenging theoretical outlook, a very important question which remain to be answered is how the magnetic properties like magnetic exchange couplings and spin-orbit interactions of the underlying magnetic substrate are modified due to the interaction with non-magnetic organic materials. Very recently, we demonstrated that the adsorption of π-conjugated

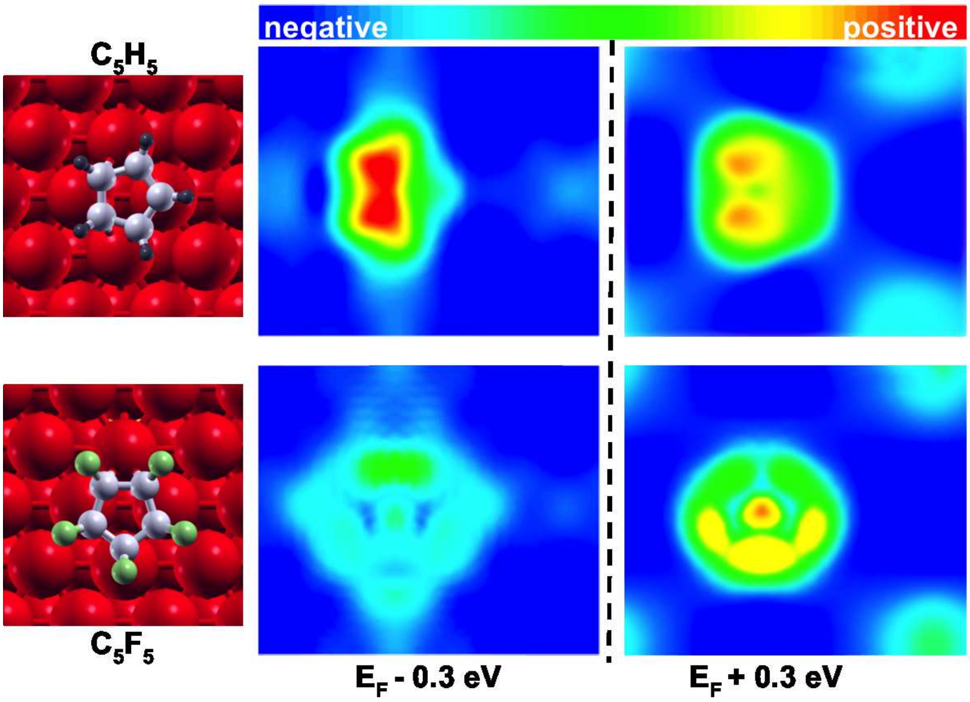

Figure 8: The simulated spin-polarization above the C_5H_5 and C_5F_5 molecules adsorbed on the 2ML Fe/W(110) surface for occupied ($[E_f - 0.3]$ eV) and unoccupied ($[E_F + 0.3]$ eV) energy intervals. The adsorbed C_5H_5 molecule shows an inversion of the spin-polarization with respect to the ferromagnetic substrate for energy intervals below and above Fermi level. On the contrary, the adsorbed C_5F_5 molecule shows an inversion of the spin-polarization with respect to the ferromagnetic substrate only for energy intervals above Fermi level and preserves the spin-polarization of the iron surface for energy intervals below Fermi level.

molecules on ferromagnetic surfaces mediates the creation of new local molecular magnetic units. More precisely, the organic-ferromagnetic interaction leads to a magnetic hardening effect, i.e., locally it increases the strengths of the magnetic exchange interactions of the magnetic atoms binding directly the molecule, stabilizes the magnetization direction and enhances the barrier for the magnetization switching with respect to the clean surface [71]. Even more interestingly, depending on the specific molecular structure and ferromagnetic substrate, a strong decoupling of the molecular mediated magnetic unit with respect to the magnetic electrode occurs (magnetic softening) and can be successfully used in building spintronic devices that work close to room temperature [12]. A detailed understanding and the precise control of the electronic effects responsible for the magnetic hardening and the magnetic softening effects induced by the adsorption of non-magnetic organic molecules on ferromagnetic substrates is the subject of future theoretical studies.

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