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UNDERSTANDING THE FORMATION OF SURFACE-SUPPORTED MOLECULAR NANOSTRUCTURES: ATOMISTIC SIMULATIONS

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To my family
There were only two fundamental forces to account for all natural phenomena: Love and Hate. While the first brought things together, the second caused them to part.

Empedocles (∼ 450 BC)
Abstract

In the rise of nanotechnology, *ab initio* simulations have established as an essential tool in studying matter at nanoscales. Nowadays, the fast growing of computer hardware allows computational techniques to research materials at some level inaccessible by experiment. Here the author presents, using state-of-the-art methods, five computer-aided works which are devoted to the understanding of molecular systems adsorbed on metal surfaces.

It is shown for the adsorption of the prototypical organic semiconductor PTCDA and 4,4’-diamino-p-terphenyl that on Au(111) the van der Waals interaction is crucial. Results from energy, geometry and electronic structure analyses compared with available experiments reveal a striking role of this interaction in determining the stability, structure, and electronics of the molecules upon adsorption.

On Cu(111), cyano-functionalized[7]helicene at low coverage forms chain-like structures oriented in some specific chirality-dependent direction. The direction is interpreted as a result of both the potential energy surface of isolated molecules at the surface and the hydrogen bonding, dipolar interactions among the molecules. The effect of Cu(111) on the intermolecular distance is also discussed.

The Ullmann coupling is a classic chemical reaction that has been experimentally investigated for over a century. A mechanism for this reaction is rationalized by means of DFT calculations. Before two phenyl groups recombine on Cu(111), they follow a non-trivial diffusion pathway to a structure in which they share the same surface bonding partner. Evolution of the electronic structure is discussed.

A limitation of two-dimensional supramolecular structures is their thermal and chemical stability. Much more stable structures can be pursued by exploiting covalent bonding between nano units, as a good example, the polymerizations of hexaiodo-substituted macrocycle cyclohexa-m-phenylene radicals. Resulting nanostructures are however significantly different on the three (111) coinage surfaces. It is shown by DFT and Monte Carlo simulations that the mobility and intermolecular reactivity play the key role for the polymer morphology on the surfaces.

Efficiency is practically important in computer simulation. For studying large systems a fully quantum mechanical description can be highly demanding, leading to the quest for some cheaper strategy. Quantum mechanics - molecular mechanics (QM/MM)
hybrid approaches have proved to be effective. However, the implementation of the classical electric polarization is still an open issue. A QM/MM scheme designed for physisorbed molecule-surface systems of polarized molecules on metal surfaces is presented. Nanostructures of 1-nitronaphthalene on Au(111) are chosen as test cases.
Zusammenfassung

Im Zuge der Entwicklung der Nanotechnologie haben sich *ab initio* Simulationen als fundamentales Werkzeug zur Untersuchung von Materie auf der Nanoskala etabliert. Die rasch wachsenden Möglichkeiten von Computer Hardware erlauben den Einsatz von Berechnungsmethoden, welche Informationen über Materie liefern können, die experimentell nicht zugänglich sind. Der Autor präsentiert im Folgenden fünf rechnergestützte Arbeiten, welche dem Verständnis der Absorption molekularer Systeme auf Metalloberflächen gewidmet sind.


Eine Limitation zweidimensionaler supramolekularer Strukturen ist ihre thermische und chemische Stabilität. Viel stablere Strukturen können durch Ausnutzung kovalenter Bindungen zwischen Nano-Einheiten erreicht werden, z.B. durch die Polymerisation von hexaiodo-substituierten makrozyklischen cyclohexa-m-phenylene Radikalen. Die resultierenden Nanostrukturen zeigen deutliche Unterschiede für die drei verschiedenen Münzmetaloberflächen. Mittels DFT und Monte Carlo Simulationen wird gezeigt, dass der Mobilität und der intermolekularen Reaktivität eine Schlüsselrolle für die Polymer-
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As this thesis also deals with methodological development I would like to thank Teodoro Laino for making the QM/MM package in CP2K easier to use, and for his personal insights for tackling the electrostatic problem presented in this thesis.

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## Methods

<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>LDA</td>
<td>Local density approximation</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
</tr>
<tr>
<td>GPW</td>
<td>Gaussian and plane wave</td>
</tr>
<tr>
<td>QM/MM</td>
<td>Quantum mechanics molecular mechanics</td>
</tr>
<tr>
<td>NEB</td>
<td>Nudged elastic band</td>
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<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
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## Organic substances

<table>
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<tr>
<td>PTCDA</td>
<td>$3,4,9,10$-perylenetetracarboxylic dianhydride</td>
</tr>
<tr>
<td>DATP</td>
<td>$4,4'$-diamino-p-terphenyl</td>
</tr>
<tr>
<td>TAPT</td>
<td>$2,4,6$-tris($4$-aminophenyl)-$1,3,5$-triazine</td>
</tr>
<tr>
<td>CHe</td>
<td>Cyano-functionalized[$7$]helicene</td>
</tr>
<tr>
<td>CHP</td>
<td>Hexaiodo-substituted macrocycle cyclohexa-$m$-phenylene</td>
</tr>
<tr>
<td>CHPR</td>
<td>CHP radical</td>
</tr>
<tr>
<td>NN</td>
<td>1-nitronaphthalene</td>
</tr>
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</table>

## Others

<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BO</td>
<td>Born-Oppenheimer</td>
</tr>
<tr>
<td>XC</td>
<td>Exchange-correlation</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy surface</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>SOMO</td>
<td>Singly occupied molecular orbital</td>
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<tr>
<td>DOS</td>
<td>Density of states</td>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
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<tr>
<td>PDOS</td>
<td>Projected DOS</td>
</tr>
<tr>
<td>LDOS</td>
<td>Local DOS</td>
</tr>
<tr>
<td>IS</td>
<td>Initial state</td>
</tr>
<tr>
<td>TS</td>
<td>Transition state</td>
</tr>
<tr>
<td>FS</td>
<td>Final state</td>
</tr>
<tr>
<td>vdw</td>
<td>van der Waals</td>
</tr>
<tr>
<td>HB</td>
<td>Hydrogen bonding</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Beiker-Ernzerhof</td>
</tr>
<tr>
<td>FK</td>
<td>Frenkel-Kontorova</td>
</tr>
<tr>
<td>1D</td>
<td>One-dimensional</td>
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<tr>
<td>2D</td>
<td>Two-dimensional</td>
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Chapter 1

Introduction

Nanotechnology - the study of manipulating matter on an atomic and molecular scale - has a great impact on physics, chemistry, biology, materials science, medicine, and engineering. It is currently a cutting-edge scientific research branch, an extremely fast growing interdisciplinary area with a huge potential of revolutionizing science and technology [1, 2]. Interest in nanoscale science probably emerges from the observation that the behavior of materials can change significantly from macroscale (bulk materials - larger than some \( \mu m \)) to nanoscale (clusters of atoms - smaller than 100 \( nm \)) dimensions [3]. For example, squeezing electrons of atoms into smaller spaces can change materials’ physical and chemical properties such as electronic spectra [4], magnetic moments [5], or chemical reactivity [6]. Furthermore, a quantitative understanding of atoms, groups of atoms, and molecules - the basic building blocks of nature - has been a fundamental but challenging question for scientists, and after all, for the quest for future technological applications.

One of the most demanding steps toward realistic applications in nanotechnology is the fabrication of nanostructures. Making and controlling matter at the nanoscale is a grand challenge for researchers. Today, miniaturized structures can be pursued by two widely used approaches, namely “top down” and “bottom up” [7, 8]. The former utilizes lithography-based techniques to manipulate materials, that is, “carving” larger structures to smaller ones; however, the implication of these technologies is inherently limited by the resolution of instruments (about 100 \( \text{Å} \)). The latter, arguably the most promising strategy, builds up nanostructures by using nano- or subnanoscale objects,
Introduction

i.e., atoms and molecules as starting blocks. It is clear that in the bottom-up approach two steps must be taken into account: synthesizing the nanobuilding blocks and assembling them together into predefined structures with desired properties [8]. While the first one can be done routinely since it is in a traditional domain of chemistry, the second one is a difficult task that bottom-up technologies must confront. Practically, we cannot fabricate nanoscale systems by moving individual atoms or molecules through an one-by-one (or step-by-step) fashion because that would be extremely time-consuming and also very expensive. We thus have to exploit their self-organization processes. Nowadays, intense research efforts are focused on comprehending and controlling the

![Figure 1.1: A dream come true of scientists or a nightmare of engineers?: Nanocars synthesized from organic molecules on Au(111). (From Ref. [9])](image)

self-assembly of organic molecules on surfaces. Foreseeable applications of such systems can be named, for example, nanoscale electronic and optoelectronic devices [10, 11] since organic molecules can be integrated as building components, or even nanovehicles (see Figure 1.1). Presently, the knowledge of the self-assembly of atoms or molecules (or both) on surfaces is mainly based on scanning probe microscopy (SPM) [8] such as scanning tunneling microscopy (STM) or atomic force microscopy (AFM). In spite of the fact that SPM tools, which usually have atomic resolution, allow us to characterize structures [12], study dynamics [13], manipulate magnetism [14],... many fundamental questions such as what happens in a molecule-substrate interface are currently not easy (if not possible) to address due to technological limitations. Computational science, on the other hand, appears to be an exquisite, progressively essential component in
materials research since it can provide us with the microscopic basis of many behaviors of matter observed by experiment, and notably, it is also able to help designing new materials [15, 16]. Thanks to more advanced numerical methods and increasingly powerful computing facilities, first principles calculations have enabled to describe processes occurring on surfaces in detail, even at a level that is not experimentally accessible.

In light of this circumstance, this thesis, motivated by a strong exchange of ideas with experimental groups, is devoted to a few theoretical aspects of the understanding of assembly of organic molecules on metal surfaces. The first goal of the author is to apply current understanding and computational tools to interpret some phenomena observed by experiment regarding the formation of molecular nanostructures on metal surfaces. The second goal is to develop a tool for modeling molecule/surface systems. The rest of this thesis is organized as follows:

Chapter 2 briefly reviews the up-to-date fundamental understandings of molecule-surface systems, addressing the adsorption and diffusion of atoms, molecules on surfaces, and the interaction among them.

Chapter 3 presents a short summary of the theoretical methods used in this work including density functional theory (DFT), and the nudged elastic band method (a technique for finding transition states).

In Chapter 4, we investigate the role of dispersion interactions in the adsorption of large molecules on surfaces with 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and amine-functionalized 4,4”-diamino-p-terphenyl (DATP) on Au(111) as representatives. By employing a drawback of standard DFT (not capturing van der Waals interactions), and comparing with results from a corrected density functional and available experiments, we show that dispersion interactions can always be important to the stability of these molecules on the surface.

A general aspect of surface self-assembly is that nanostructures result from a subtle competition between intermolecular and molecule-surface interactions. In Chapter 5, we demonstrate the importance of this interplay by studying the self-assembly of cyano-functionalized[7]helicene (CHe) on Cu(111). CHe is experimentally found to form chain-like structures on the metal surfaces. The intermolecular spacing is large compared to the equilibrium contact distance in vacuum predicted by DFT, however, upon adsorption the surface significantly modifies the potential energy between the molecules.
Chapter 6 gives a detailed description of the coupling process of phenyl radicals - the important intermediates in the prototypical Ullmann reaction - on Cu(111). Starting from single phenyl groups on the surface, through a non-trivial diffusion pathway, the reaction is completed after two phenyl groups find a state involving a “popping-out” surface atom which they simultaneously bind to. Results are compared with experimental evidence. The evolution of molecular orbitals along the reaction pathway is discussed.

Chapter 7 reports an application of the Ullmann reaction in fabricating nanostructures on metal surfaces. We investigate the formation of porous graphene - a graphene-like structure decorated with regular holes - from hexaiodo-substituted macrocycle cyclohexa-m-phenylene on the three (111) coinage metal surfaces as observed by STM. On Cu, the networks are dominated by open branched structures, on the Au surface a mixture of branched and small domains of compact network clusters are observed, and highly ordered and dense polyphenylene networks form on the Ag substrate. DFT calculations and Monte Carlo simulations show that different balances between diffusion and intermolecular coupling determine the observed branched and compact polyphenylene networks on the Cu and Ag surfaces, respectively, demonstrating that the choice of the substrate plays a crucial role in the formation of two-dimensional polymers.

Chapter 8 is devoted to a recent development of the quantum mechanics / molecular mechanics (QM/MM) hybrid techniques for molecule/surface systems. Efficiency is an important criterion in computational science. For very large systems, today’s computer power is practically not able to deal with by using demanding quantum mechanical methods. The QM/MM scheme takes advantage of quantum mechanical accuracy and molecular mechanical cost. The idea is that, for example, if interaction between adsorbed molecules and the substrate is electronically weak (physisorption) and we are only interested in the intermolecular interaction, we describe the molecules by QM, the surface by MM, and the molecule-surface contact by MM. Standard MM does not include the “image potential” between polarized molecules and metals surfaces, which can be important in certain cases. The aim of this chapter is to handle this problem.

And finally, Chapter 9 summarizes the whole content of the thesis and plots some perspectives.

The content reported in Chapters 4-8 is published (Chapters 4, 6 and 7), or to be published (Chapters 5 and 8) at the moment of handing in this thesis (with modifications with respect to the version being presented).
Chapter 2

Molecules at surfaces: An overview

When molecules are deposited on a surface, they can immediately be desorbed, or strongly stick to the surface and form some specific arrangement. The outcomes are governed by the subtle interplay between molecule-substrate and intermolecular interactions. Understanding intermolecular forces is essential for interpreting those phenomena. Thus, in this chapter we shall discuss some fundamental issues covering interactions in molecule-surface systems. In particular, we will address molecule-surface bonding types, the surface diffusion, surface-mediated intermolecular interactions, and chemical reactions of molecular systems upon adsorption.

2.1 Introduction

An intermolecular potential can be contributed by [17]: 1) classical interaction between the charge distributions in the system, 2) exchange-repulsion (as a result of the Pauli principle), 3) non-classical interaction stemming from correlated fluctuation of electrons in the system (known as the van der Waals (vdW) interaction), 4) induction originating from the distortion of the electron density of the molecule in response to the electric field produced by the surface, and 5) charge transfer between the two objects associated with the emergence of the chemical bonding (part of the induction contribution, but considered separately in some cases). When a molecule with some momentum hits a surface, it can be elastically reflected. The molecule can also lose energy to surface atoms by exciting them vibrationally or electronically, and then it is either inelastically
scattered back or bound to the surface with some strength if the lost energy is small or sufficiently large [18]. The adsorption of the molecule on the surface is either physisorption or chemisorption, depending on each contribution mentioned above. While physisorption is caused by the vdW interaction, chemisorption is associated with the formation of adsorbate-substrate chemical bonds. Needless to say, adsorption properties depend on the nature of the molecule and the substrate. At the surface, the molecule might have some kinetic energy to move around, it can also be decomposed. Alternatively, it can cooperate with other co-adsorbed molecules to form some stable structure.

Figure 2.1: Schematic illustration of surface processes of a molecule-surface system: the surface is exposed to a beam of molecules. Molecules can be adsorbed (energy $E_{\text{ad}}$), migrate (energy $E_{\text{m}}$), rotate (energy $E_{\text{r}}$), interact with each other (energy $E_{\text{i}}$), perform chemical reaction (energy $E_{\text{ac}}$), or form some ordered arrangement. Molecules can be modified both electronically and geometrically upon adsorption. These phenomena are consequences of the subtle interplay between the molecule-molecule and molecule-surface interactions. (Adapted from [19].)

Here, we review some of up-to-date understandings of the bonding and dynamic processes in molecule-surface junctions. The rest of this Chapter is organized as the following. In sections 2.2 and 2.3, we analyze two types of adsorption, physisorption and
chemisorption, under a simple scenario. Section 2.4 presents the diffusion of molecules at metal surfaces. Next, in section 2.5 we address some fundamental interactions between co-adsorbed molecules. Section 2.6 summarizes some semi-empirical rules in catalysis. Then, in section 2.7, we briefly discuss the effect on adsorbed molecules on the work function of the substrate. And finally, some concluding remarks presented in section 2.8.

2.2 Physisorption

In physisorption (or physical adsorption), the electronic structure of the adsorbates is hardly perturbed [20], and essentially, there is no charge transfer from adsorbates to substrates or vice versa [18]. This kind of adsorption usually refers to the vdW interaction. The origin of the dispersion interaction can be understood as follows. Let us consider a system of two He atoms. The fact is that each atom has a random, varying dipole moment due to the instantaneous fluctuation of electrons around the nucleus. The dispersion interaction arises from the coupling of these dipole moments, and the potential between the two atoms can be derived using perturbation theory. Briefly, at an instant one atom has dipole $\mathbf{p}_1$ that produces a field that induces a dipole $\mathbf{p}_2$ on the other atom. The perturbation Hamiltonian here is the dipole-dipole interaction which is

![Figure 2.2: Adsorption potential of Helium on several metal surfaces from theoretical calculations by Zaremba and Kohn [21].](image)

Figure 2.2: Adsorption potential of Helium on several metal surfaces from theoretical calculations by Zaremba and Kohn [21].
proportional to \( r^{-3} \), where \( r \) is the distance between the two atoms. As the permanent dipole moment of an atom is zero, the first-order contribution to the interaction energy is zero. Therefore, the second-order contribution, which is \( r^{-6} \) dependent, keeps the leading role. A full description can be found in Ref. [22].

The dispersion interaction between an adsorbate and a metal substrate can be described by the Lifshitz potential [23], \( V(z) = C/(z - z_0)^3 + O(z^{-5}) \), where \( z_0 \) is the reference-plane position, the order of \( z^{-5} \) is usually neglected. Please note that this potential differs from the dispersion potential of two atoms which is \( r^{-6} \) dependent, the \( V(z) \) potential can however be derived from the \( r^{-6} \) form by summing up all the contributions from surface atoms [24]. This attractive potential, in principle, leads to the collapse of the molecule to the surface. Nonetheless, when the adsorbate-substrate separation is small enough, wave-function overlap comes into action, and kinetic energy of electrons accordingly arises due to the orthogonality of the molecule’s and the surface’s orbitals as a consequence of the Pauli principle, making the system less stable. Therefore, a physisorption potential must consist of two parts: the long-range vdW attraction and the short-range Pauli repulsion [23].

Typical adsorbate-substrate spacing in physisorption is more than 3 Å, it is closely related to the so-called vdW radii of elements involved. The strength of physisorption depends on the polarizability and the number of atoms involved. The adsorption energy of “small” adsorbates such as single atoms can be of a few meV. For large molecules, this energy can be up to some eV as we shall see in the next parts of this thesis. Physisorption is weakly dimensional if the surface is less corrugated. For instance, the adsorption strength is less affected by the orientation of an adsorbate on a close-packed surface. This is especially the case for large adsorbed species. Small adsorbates tend to find positions on the substrate with the maximum number of neighboring surface atoms to maximize the interactions. Therefore, they are usually found at high coordination number regions such as hollow sites on the substrates [25].

### 2.3 Chemisorption

A more complicated kind of adsorption is chemisorption or chemical adsorption. In chemisorption, “real” chemical bonds (the bonds of chemical strength) are formed between the adsorbate and the substrate; it is thus expected that the electronic structure
of the molecule is significantly modified. To understand the formation of a molecule-surface chemical bond, it is helpful to start with the bonding in a hydrogen molecule.

Briefly, when two separate hydrogen atoms with ground states $\psi_{1s}^1$, $\psi_{1s}^2$ and identical energy $\epsilon_{1s}$ approach each other, they form a hydrogen molecule. According to the linear combination of atomic orbitals (LCAO) method, this molecule has two states [22]. One, called bonding state, with a symmetric combination of the two basis states has an energy lower than the sum of the energies of two isolated atoms. And one, called antibonding state, with an antisymmetric combination of the two basis states has an energy higher than the sum of the energies of two isolated atoms\(^1\). The significant contribution to the cohesion in the molecule here is the coupling between the two states, namely, $\langle \psi_{1s}^1 | H | \psi_{1s}^2 \rangle$, where $H$ is the Hamiltonian of the system.

For molecule-surface systems, we have a somewhat similar but rather intricate situation as many states from the adsorbate and from the substrate can be involved. Among many theoretical approaches devoted to the understanding of chemisorption [26], the so-called Newns-Anderson model is simple and able to provide physical essentials in chemisorbed systems [27]. It was first developed by Newns for the adsorption of hydrogen on metal surfaces [28] by using an early model originally proposed by Anderson for a bulk impurity [29]. According to this approach, one first constructs a connection between a state of the adsorbate $|a\rangle$ and the states of the substrate $|k\rangle$ by introducing the coupling matrix element $V_{ak} = \langle a | H | k \rangle$. Once the Anderson Hamiltonian of the bound system is established, the newly formed states can be unveiled by keeping track of the projection of the density of states on the molecular orbital. For metal surfaces, we have different circumstances. When the adsorbate state interacts with the $sp$ bands of the surface which are generally broad, its $\delta$-like DOS (in vacuum) is broadened into a Lorentzian shaped resonance, which is shifted with respect to the initial one; the broadening here is due to the finite time in the adsorbate state as electrons can hop in between the molecule and the surface. Owing to the fact that the $d$ bands are very narrow, the interactions between the molecular state and the $d$ metal states lead to bonding and antibonding states, like in the hydrogen molecule. Adsorption is called weak chemisorption if there is a single broadened resonance appearing in the one-electron spectrum, as in the former case, whereas it is called strong chemisorption if there are bonding and antibonding states, as in the latter case [27].

\(^1\)Bonding and antibonding terms here are inherently related to the cohesion in the molecule.
Needless to say, the adsorption strength is directly connected to the reactivity of metal substrates and the nature of adsorbates. A molecule can be adsorbed in different ways on different substrates. For instance, PTCDA chemically binds to Cu(111) and Ag(111) but physically to Au(111) [32]. A substrate can host different adsorbates in different manners. It is, for instance, clear that helium and oxygen are adsorbed on Cu(111) physically and chemically, respectively. In what follows, the factors determining the reactivity of a sd metal surface are addressed.

Hammer and Norskov, performing GGA-DFT calculations and borrowing the Newns-Anderson model investigating the adsorption of nonmetallic atoms on several metal surfaces, have shown that for transition metal surfaces the position of the $d$ bands, characterized by its center position $\epsilon_d$, is a possible indicator of the surface reactivity [30, 31, 33]. The first point, in their opinion, is that the strength of chemisorption depends mainly on the interactions between molecular states and the $d$ bands of the metal since the contribution from the $s$ bands is weak and can be considered to be
2.3 Chemisorption

approximately the same for a wide range of transition metals. When a molecular level couples to the itinerant $s$ states, it renders a bonding broadened shifted state. To a first approximation, this can be considered the same for all transition metals as they all have half-filled and very broad $s$ bands. The coupling between the molecular level and the $s$ bands is weak, nevertheless, it is the onset of the coupling to the $d$ bands. The second point is that a metal surface is more reactive if it the offset $\epsilon_d - \epsilon_F$, where $\epsilon_F$ is the Fermi level, is more positive. When the bonding state (resulted from the previous step) and $d$ metallic states form bonding and antibonding states, the antibonding state can be filled if it is located below $\epsilon_F$. If this state is shifted up through the Fermi energy and depopulated then the bonding becomes more pronounced; and the molecule-surface bonding is also stronger if the bonding state is more shifted down. As a result, the reactivity of transition metals decreases from left to right in the periodic table as the $d$ bands are increasingly filled (see Figure 2.4.a). Finally, for metals that have a similar $\epsilon_d$, the reactivity of the surfaces can be further evaluated through the coupling matrix elements. The reason here is that when a molecule is brought to a surface their states have to be orthogonal due to the Pauli repulsion, consequently giving rise to the kinetic energy. The repulsive strength on the other hand is approximately proportional to $V_{ad}^2$ (see Figure 2.4.b). Ag and Au, for instance, have nearly the same $\epsilon_d$, however, the coupling matrix element $V_{ad}$ between states of oxygen and gold is the larger due to the fact that $5d$ more extended than $4d$ and oxygen binds to Ag(111) more strongly. This is also a reason why gold is the noblest metal [34].

Additionally, the reactivity of a metal surface also depends on its geometric structure as chemisorption is usually found to occur at defected regions of the surface including steps, adatoms, reconstructions,... in several experiments [35]. This can be understood using the $\epsilon_d$ rule. Hammer and Norskov have pointed out that strain can lead to the shift of $\epsilon_d$ [30]. When surface atoms sustain tensile strain, the interatomic distance increases, the overlap between $d$ orbitals decrease, and then the band is less extended (as the atoms become more “isolated”), the $d$ band population remains unchanged due to the upshift of $\epsilon_d$. Similarly, for lower low-coordination regions like adatoms or steps the $d$ bandwidth is smaller and hence $\epsilon_d$ is higher. In other words, low-coordinated atoms are more chemically reactive.

Chemisorption is also determined by electronic properties of adsorbates. The chemical reactivity of an atom can be determined by its electron configurations. For molecules
Figure 2.4: Adsorption of oxygen on metal surfaces: (a) the correlation between the position of the $d$ band center ($\epsilon_d$, data presented here are for $4d$ metals) relative to the Fermi level and the adsorption energy; (b) the dependence of adsorption energy on the coupling matrix element squared $V_{ad}^2$ between oxygen 2$p$ and the metal $d$ states. (From Ref. [30])

it is more complicated and strongly depends on details of systems, for example, electron lone pairs of functional groups in functionalized molecules are important implications. Molecular frontier molecular orbitals - the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) - can directly contribute to the bonding. When a molecule and a metal surface are brought into contact, the molecular HOMO state cannot be higher than $\epsilon_F$. If the pre-adsorption molecular HOMO state is higher than $\epsilon_F$, it will be shifted down upon adsorption. If (pre-adsorption) molecular LUMO state is lower than $\epsilon_F$, the molecule can gain electron from the surface. In some cases, the overall charge transfer is roughly proportional to the difference between the chemical potential the surface and the one of the molecule, which is approximately the geometric mean of the HOMO and LUMO levels [36], and indeed, the chemical potential difference is a criterion for the reaction between two molecules [37]. To treat the chemical bonding between a molecule and a metal surface more seriously neighboring
levels of HOMO and LUMO need to be taken into account as they can, in principle, participate in the bonding [38].

Figure 2.5: Chemisorption vs Physisorption: Plot of desorption enthalpy versus number of carbons for alkanethiols and alkanes. Desorption enthalpy of alkanethiols from the physisorbed state is shown as (○) and from the chemisorbed state as (●). When the number of carbon atoms is large enough, physisorption comes to be dominant. (From Ref. [39])

Chemisorption strongly shows the site selectivity characteristic. Small molecules or functional groups of large molecules tend to find adsorption positions and molecular orientations that can facilitate the bonding with the substrate. Carbon monoxide (CO), for instance, is adsorbed on many metal surfaces in an upright fashion with C binding to a metal atom because its HOMO is localized on the C end. Molecule-surface chemical bonding always leads to a weakening of intramolecular bonds in the molecules as electronic (and geometric) properties of pre-adsorption molecules are modified. This can lead to the decomposition of adsorbed molecules if the bonding to the surface is too strong.

To this end, chemical bonding is certainly important for the adsorption of functionalized molecules on surface. The role of vdW interactions is, however, increasingly significant with respect to the size of molecules (number of atoms constituting). Experimental data presented in Figure 2.5 show a typical case of this trend, we shall also see again in Chapter 4 the role of dispersion forces in the stability of molecules on surfaces.
2.4 Surface diffusion

Owing to the fact that the substrate thermal energy can be associated with adsorbed species which experience a periodic substrate atomic lattice [40], the adsorbates can move from site-to-site, part-to-part on the surface. This is known as the thermal driven surface diffusion process of adsorbed atoms and molecules. To move the adsorbate from one site to another, the system must climb over a so-called migration energy barrier $E_m$ on the potential energy surface (we will see this surface again in the next chapter). Rotation of molecules might be entered in the diffusion process such that the system can seek the lowest barrier. The moving rate, or surface mobility, of adsorbed molecules is a crucial factor determining the nanostructures of molecular systems on surfaces and the reaction rate in heterogeneous catalysis [40, 41].

Clearly, environment temperature $T$ is salient to the diffusion rate. When $T \ll E_m/k_B$, adsorbed molecules can be immobile with respect to a practical time scale. If the diffusion takes place, it is driven by the molecule-surface energy exchange process. When a molecule jumps from one site to another one, it loses energy to the surface and remains at this site for a long time compared to the periods of the vibrational modes involved. The molecule will lose all of its memory of where it was from, its jumps are thus uncorrelated and the diffusion is a Makov process [40, 42]. The diffusion rate is approximately given by an Arrhenius expression $\Gamma = \nu \exp(-E_m/k_B T)$, where $\nu$ is the attempt frequency of about some $10^{13}$ depending on the properties of the potential energy surface (i.e, curvature,...). When $T \simeq E_m/k_B$ or $T \gg E_m/k_B$, $E_m$ is much less important or even comes to be trivial. Practically, molecules move freely or even are desorbed, therefore, the diffusion rate in this case becomes ill defined.

While the surface diffusion mechanism of atoms or simple molecules is well understood [43], it is still an open issue for the case of organic molecules as they have a large number of degrees of freedom and their interactions with surfaces are usually complex. The diffusion of adsorbed organic molecules can involve several processes such as molecular reorientation, conformation changing, molecule-surface bond-breaking and bond-forming, and so on. Therefore, it strongly depends on the details of molecule-surface chemical bonds (For example, see Figure 2.6). Not only anisotropic surfaces can restrict the motion of molecules [44, 19] but also isotropic surfaces do [13]. Molecules usually perform “short” jumps (i.e, from one site to a nearest neighboring site) but they carry
out “long” jumps (i.e., from one site to a second (or higher) nearest neighboring site) as well [44]. In additional, the surface diffusion rate is directly related to the bonding in the system. Physically adsorbed adsorbates are found to be mobile even at low temperatures [35, 45], whereas the mobility of adsorbed molecules can be reduced by chemical bonding to the surfaces [45, 46] but this is not always be the case [35, 47].

2.5 Adsorbate-adsorbate interactions on surfaces

At metal surfaces, molecules can interact with each other when they are well separated. On Cu(111), for instance, the attraction among adatoms is observed at distances of some nanometers [48], as caused by the double scattering of the surface-state electrons off the adatoms [48, 49]. This type of interactions is however very weak with the magnitude of fractions of meV, and the low temperature condition is consequently necessary for the observations. It is usually not considered in the practical fabrication of nanostructures.

At some shorter distance, there are four families of intermolecular interactions [30]:

a) Direct interactions caused by wave-function overlap.

b) Indirect interactions: adsorbates interact with each other through the substrate.

c) Elastic interactions: likewise, the interactions among adsorbed species due to
surface deformation.

d) Nonlocal electrostatic interactions.

Let us consider each family in some detail. In the first one, the interaction occurs when adsorbates are close enough such that the electron wave-functions between them start to overlap. The intermolecular force is attractive or repulsive depending on the electronic structure. For instance, if the interaction leads to the shift of states through the Fermi level (e.g., antibonding states are shifted up) then it can be attractive. It is however usually the case that the interaction is repulsive as dominated by the Pauli repulsion [30].

In indirect interactions, the lateral interaction is mediated by the substrate in such a way that the perturbation in the surface electronic structure caused by one adsorbate modifies the adsorption of others. A simple picture is that the bonding of an adsorbate makes the surface bonding partners more inert or reactive to another one, resulting in the repulsion or attraction between the two bodies [50]. Qualitatively, the adsorption of one molecule leads to the down-shift or up-shift of the center of the $d$ band, $\epsilon_d$, the adsorption of the others is accordingly changed [51].

In the third family - elastic interactions, surface atoms undergo rearrangements due to the interactions with the adsorbates. This can generally change the surface electronic structure, thereby modifying the bonding between two adsorbed bodies. This family is clearly related to the strain effect mentioned above.

The fourth family, in many aspects, is among the most important uses in fabricating non-covalently bonded nanostructures of organic species at surfaces. Electronic multipole interactions always exist among co-adsorbed molecules. Molecules with intrinsic dipole moments or surface-induced dipole moments due to the rearrangement of charges due to adsorption can interact with each other at distances of nanometers [52, 53]. Hydrogen bonding$^2$ and dipole-dipole interactions are typically favored in this family [41, 19].

For all the families considered above, intermolecular interactions are strongly influenced by surfaces. Even in family d) the intrinsic nonlocal electrostatic interactions among molecules can also be affected by the surfaces through image-potentials or a

---

$^2$According to Pauling [54] “under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond”
2.6 Heterogeneous catalysis

In heterogeneous catalysis, a surface changes the rate of a chemical reaction without being part of the products, i.e., it is the catalyst. In general, the surface can accelerate or decelerate the reaction depending on all the aspects we have considered: adsorption, diffusion and interaction of components involved. Similar to a surface diffusion step, a chemical reaction is a transition between two minima of a potential energy surface. Nevertheless, it is conceptually different, a chemical reaction leads to the change in chemical composition of the adsorbates.

The central interest here is the activation energy $E_a$, and the position of the transition state. Owing to the fact that the surface diffusion of reactants is part of the reaction [38], the migration barrier $E_m$ must be taken into account, if $E_a$ is not greater than $E_m$ then the actual reaction barrier is $E_m$. A very important finding in the study of chemical reactions is the so-called Bronsted-Evans-Polanyi principle which states that the activation energy depends linearly on the free energy released [56, 57], that is, $E_a = c_1 + c_2 \Delta G$ where $c_{1,2}$ are some (positive) constant. This semiempirical observation

charge transfer. Obviously, there is reciprocal relationship between the lateral and vertical interactions in a molecule-surface system. Adsorption changes the intermolecular interaction which in turn modifies adsorption. In other words, supramolecular nanostructures of molecules on surfaces are governed by the subtle interplay between molecule-surface (vertical) and molecule-molecule (horizontal) interactions.

Figure 2.7: Assembly of perylene tetra-carboxylic di-imide and melamine on a silver-terminated silicon surface by hydrogen bonding. (From Ref. [55])
has been proved to work in several cases [58] and can be helpful in designing catalysis systems. It has been suggested that the activation energy can be determined by the following factors [59]: the bonding competition effect, the local charge densities of reactants, the potential energy surface of the reactant on the surface. The first factor is understood as the indirect interaction between reactants (family b, previous section) where they weaken the bonding with the surface of their partners, the second one is a consequence of the Pauli repulsion (family b, previous section), and the last one is a result from the change in adsorption position of the reactants with respect to the surface.

The transition state position can be interpreted with the free energy difference, $\Delta G$. According to the so-called Hammond postulate [60], if $\Delta G > 0$ the transition state structure will closely resemble the reactants and be said to be early; oppositely, if $\Delta G < 0$ the transition state structure will closely resemble the product and be said to be late. This postulate, from a modeling point of view, can be useful in predicting what the transition state structure would be if the reactants and products are known.

In principle, both structural and electronic properties of substrates can affect the reaction rate, just like in the diffusion process of the reactants. Closely related to chemisorption, chemical reactions on surfaces are sensitive to specific sites and/or the strength of chemisorption. It is found that the decomposition of molecules occurs more easily at defective regions [61, 62]. It is also found that the dissociation of hydrogen molecule is associated with very low barriers on nickel and platinum surfaces but unlikely to occur on gold [33].

Today, besides traditional applications, heterogeneous catalysis is also used in nanotechnology. In particular, it is involved in the synthesis of low-dimensional polymers such as graphene nanoribbons [63]. This is an important application as it can open new opportunities in manufacturing novel electronics devices and many other applications.

### 2.7 Work function

Supported molecules can, as discussed above, in turn modify the properties of the substrate. Here, in the final issue we address the question of how adsorbed molecules change the work function of the supporting surface. The work function is the minimum energy required to remove an electron from the interior of a solid to a point immediately
outside the solid surface [64]. “Immediately outside” means a large distance on the atomic scale but small on the macroscopic scale. Sometimes, the work function of a material is expressed as the difference between the Fermi and vacuum levels (see Figure 2.8.b).

A key contribution to the work function is the effect of the dipole layer created by the “spilling out” of electrons at the surface [24, 65]. Upon adsorption, molecules can modify the electron density at the surface, and as a result, they change the surface dipole moment and eventually the work function of the substrate. Physisorbed molecules at a metal surface usually decrease the work function. This is due to the Pauli repulsion between the molecular and substrate electrons that decrease the surface dipole [66]. Chemisorbed molecules can, on the other hand, either increase or decrease the work function, depending on many contributions such as the molecular dipole moment, the (molecule-surface) charge transfer, the Pauli repulsion [67] which enhance or diminish the surface dipole moment.

Figure 2.8: Schematic representation of density distributions at a metal surface (a), and various energies relevant to a study of the work function. (From Ref. [65])

Studying the modification of the work function of a solid upon adsorption of organic molecules can provide the basis for technological applications. Transport of charge carriers across metal organic interfaces, for instance, can determine the performance of a device [68]. It is thus an important issue in organic electronics.
2.8 Summary

We have reviewed some key aspects of molecule-surface problems. There are two kinds of adsorption: physisorption and chemisorption; while the former is contributed by the vdW forces, the latter is associated with molecule-surface chemical bonds. As we shall see in this thesis, both kinds can be simultaneously present in a molecule-surface system, therefore, in most cases it will be problematic to classify a case purely in either category. The strength of molecule-surface chemical bonds depends on the chemical reactivity of the surface, which can be determined by the position of the \( d \) bands with respect to the Fermi level. The mobility of molecules on surfaces depends on the corrugation of the potential energy surface. Adsorbed molecules interact with each other directly or indirectly through the surface. The reaction enthalpy can be an important factor for evaluating the activation barrier and the position of the transition state in a chemical reaction. Finally, adsorbed molecules can modify the work function of supporting surfaces.
Chapter 3

Theoretical methods

Today, the fast development of computer hardware and computational algorithms allows us to access the quantum mechanical picture of materials at some level that is not experimentally reachable. The most powerful and widely used electronic structure technique to date is density functional theory which can deal with systems of thousands of electrons, e.g., nanotechnology systems. Here, we address some fundamentals of this method. We then introduce an approach determining the energy barrier of a chemical reaction, namely the climbing image nudged elastic band method. Other theoretical tools used in this thesis are also presented.

3.1 Introduction

Our understanding of the electronic structure of a material made up with $M$ nuclei and $N$ electrons is based on the solution of the (time-independent) Schrödinger equation [69]:

$$H\Psi(\{\vec{R}_i\}, \{\vec{r}_i\}) = E\Psi(\{\vec{R}_i\}, \{\vec{r}_i\}),$$

(3.1)

where the many-body wavefunction $\Psi(\{\vec{R}_i\}, \{\vec{r}_i\})$, which depends on the electron and nuclear coordinates $\{\vec{r}_i\}$\(^1\) and $\{\vec{R}_i\}$, describes the state of the system; and $E$ is the

\(^1\)Of course the wave function depends on the positions and spins of the $N$ electrons, however, in this Chapter spins will, for simplicity, not be explicitly indicated.
Theoretical methods

energy of the system. The Hamiltonian $H$ is given by:

$$H = T_e + T_I + V_{ee} + V_{el} + V_{II},$$

(3.2)

where (in atomic units)

$$T_e = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{\vec{r}_i}^2,$$

(3.3)

$$T_I = -\sum_{I=1}^{M} \frac{1}{2M_I} \nabla_{\vec{R}_I}^2,$$

(3.4)

$$V_{ee} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|},$$

(3.5)

$$V_{el} = -\sum_{i=1}^{N} \sum_{I=1}^{M} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|},$$

(3.6)

and

$$V_{II} = \sum_{I=1}^{M-1} \sum_{J=I+1}^{M} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}.$$  

(3.7)

Here, $m_e (M_I)$ and $-e (Ze)$ are the mass and the charge of electrons (nuclei); and $\hbar$ is the reduced Planck’s constant. The two first terms in $H$, $T_e$ and $T_I$, are kinetic operators, and the others are Coulomb potentials: the electron-electron, electron-nucleus, and nucleus-nucleus interactions. Mathematically, the equation (1.1) is very complicated and not analytically solvable even for the hydrogen molecule ion ($H_2^+$). The problem thus needs to be simplified. Owing to the fact that any nucleus is more than 1800 times heavier than an electron, the electronic motion is much faster. Therefore, solving the Schrödinger equation we can consider the nuclei as “fixed” in single arrangement, they act as an external potential applying on the electrons. Consequently, the wavefunction only explicitly depends upon the electronic coordinates. This approach is called the Born-Oppenheimer approximation. This adiabatic approximation allows to separate the wavefunction into electronic and nuclear components:

$$\Psi(\{\vec{R}_I\}, \{\vec{r}_i\}) = \Psi_0(\{\vec{R}_I\}, \{\vec{r}_i\})\chi(\{\vec{R}_I\}),$$

(3.8)
where \( \Psi_0(\{ \bar{R}_I \}, \{ \bar{r}_i \}) \) is the ground state wavefunction of the Hamiltonian \( H_{el} \) with all nuclear coordinates kept frozen:

\[
H_{el} = T_e + V_{ee} + V_{el} + V_{II}.
\] (3.9)

The corresponding electronic energy is nuclear coordinate dependent, \( E_{el} = E_{el}(\{ \bar{R}_I \}) \). Once the electronic wavefunction and energy are known, the nuclear wavefunction is determined by solving the Schrödinger equation for the nuclei:

\[
\left[ -\sum_{l=1}^M \frac{1}{2M_l} \nabla_{\bar{R}_l}^2 + E_{el}(\{ \bar{R}_I \}) \right] \chi(\{ \bar{R}_I \}) = E \chi(\{ \bar{R}_I \}),
\] (3.10)

\( E \) here is the total energy of the system that we wished to find, it implicitly depends upon the nuclear coordinates. \( \chi(\{ \bar{R}_I \}) \) provides information on the vibrational modes of the system.

The Born-Oppenheimer approximation greatly simplifies the electronic structure problems, however, the Schrödinger equation for electrons,

\[
H_{el} \Psi_n(\{ \bar{R}_I \}, \{ \bar{r}_i \}) = E_n \Psi_n(\{ \bar{R}_I \}, \{ \bar{r}_i \}),
\] (3.11)

is still extremely difficult to handle since electrons in a condensed matter system are interacting. Further approximations need to be made.

The Hartree-Fock method, for instance, adopts an approximation that the exact wave function of a system of \( N \) electrons can be approximated by a single Slater determinant of \( N \) spin orbitals. One of the major problems of this technique is that it does not capture full electronic correlation, thus calling for more advanced methods like post Hartree-Fock, these approaches in general can produce excellent results compared to experimental data \([70]\), they are however analytically and/or computationally demanding. As an example, if we have a grid of \( G = 10^3 \) points in space for each electron wave function, the number of values (or parameters) of the \( N = 10 \)-electron wave function to be calculated and stored is \( G^N = 10^{30} \) \([71, 72]\). Therefore, many-particle wavefunction strategies are not practically suitable for large systems.

Density functional theory (DFT), instead of examining many-body wavefunctions, considers the ground state electron density which uniquely determines the properties
of a system. Additionally, the electron density can be calculated from fictitious single-particle wavefunctions. DFT is thus extremely useful for systems of many electrons. One of the most important parts in DFT is the so-called exchange-correlation energy functional which is unfortunately unknown. In spite of the fact that the DFT community is still on the way searching for the best approximations for this functional, DFT has enjoyed an extraordinary success in calculating the electronic structure of molecules and solids [73].

As mentioned in the previous chapter, the surface diffusion process and chemical reactions of adsorbed molecules are connected to the transition of the system among minima on the potential energy surface. Molecular dynamics simulations might be useful, however, it is very difficult, or not affordable, to deal with the macroscopic time scale of physical phenomena. A widely used method in the study of surface diffusion or chemical reaction of molecules is the so-called nudged elastic band (NEB) method which can give an estimate of the energy barrier in such processes. Consisting of a series of geometry optimizations, this method is appropriate for present computer power.

The rest of this Chapter is organized as follows. In sections 3.2, 3.3, and 3.4 we shall discuss the Hohenberg-Kohn and Kohn-Sham formulations, the choice of the so-called basis functions, the use of pseudo-potentials, and the calculations of forces. In section 3.5, we shall study the basis of NEB. We shall also review the Tersoff-Hamann approximation which is used in producing scanning tunneling microscope (STM) data in section 3.6. Then, some methods for charge analysis are discussed in section 3.7. The slab model for surfaces in computer simulations and an introduction to the CP2K package are presented in sections 3.8 and 3.9, respectively.

### 3.2 Density functional theory

Since introduced in 1964-1965 by Hohenberg, Kohn, and Sham [74, 75], DFT has come to be a tremendous impact on electronic structure calculations in solid state physics and quantum chemistry. Unquestionably, this method can effectively deal with large systems in terms of computational cost and accuracy. The main idea behind this method is that rather than having to solve the many-body wavefunction problem, DFT handles a formulation of the ground state electron density.

The center of DFT is the Hohenberg-Kohn formulation [74] that reads: 1) The
3.2 Density functional theory

Ground state density $n(\vec{r})$ of an interacting electron system in some external potential $v_{\text{ext}}(\vec{r})$ uniquely determines this potential, up to a trivial additive constant\(^2\). The energy of the system can be defined through a universal functional of the electron density, $F[n]$, which is valid for any number of electrons $N$ and any external potential $v_{\text{ext}}(\vec{r})$, and minimized by the ground state density. Mathematically, the energy is written as

$$E[n] = F[n] + \int d\vec{r} v_{\text{ext}}(\vec{r}) n(\vec{r}),$$

where

$$F[n] = \langle \Psi | T_e + V_{ee} | \Psi \rangle = T[n] + U[n].$$

$F[n]$ plays the central role in this formulation, unfortunately, it is unknown. Kohn and Sham [75] have postulated that $F[n]$ can be written as:

$$F[n(\vec{r})] = T_0[n(\vec{r})] + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{\text{ex}}[n(\vec{r})],$$

where $n(\vec{r})$ is the electron density of a non-interacting electron system, which is given by a set of auxiliary one-electron orbitals:

$$n(\vec{r}) = \sum_{n} |\psi_n(\vec{r})|^2,$$

$T_0[n(\vec{r})]$ denotes the kinetic energy of a non-interacting electron system, which has a simple form:

$$T_0[n(\vec{r})] = \sum_{n} \langle \psi_n | -\frac{1}{2} \nabla^2 | \psi_n \rangle.$$

The second term in (3.14) is the Coulomb interaction separated out from the electron-electron interaction in $F[n(\vec{r})]$ (i.e, Hartree (classical Coulomb) energy). The last term of Equation (3.14), called the “exchange-correlation” energy\(^3\), is supposed to include many-body effects of an interacting electron system. Minimizing the energy functional $E[n(\vec{r})]$ with respect to $n(\vec{r})$ with the the number of electrons constrained to the constant

\(^2\)In the system of Hamiltonian (3.9), the external field is the potential caused by the nuclei and the additive constant is the nucleus-nucleus potential.

\(^3\)The “exchange” effect is due to the Pauli exclusion principle; the “correlation” effect is due to the motion of electrons correlated to minimize repulsive forces.
N through a Lagrange multiplier $\epsilon_n$ leads to a system of equations:

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\vec{r})\right] \psi_n(\vec{r}) = \epsilon_n \psi_n(\vec{r}),$$  \hspace{1cm} (3.17)

where the effective potential $v_{\text{eff}}$ (also called the Kohn-Sham potential) is

$$v_{\text{eff}}(\vec{r}) = v_{\text{ext}}(\vec{r}) + v_{\text{Hartree}}(\vec{r}) + v_{\text{xc}}(\vec{r}),$$  \hspace{1cm} (3.18)

where

$$v_{\text{Hartree}}(\vec{r}) = \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|},$$  \hspace{1cm} (3.19)

and

$$v_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{r})}.$$  \hspace{1cm} (3.20)

The Kohn-Sham formulation thus replaces a many-body problem by a single-electron problem which is much easier to solve. To this end, we have the energy of the system that is, in principle, the exact one because no approximations are made. Nevertheless, we still have an unknown component, $E_{\text{xc}}[n(\vec{r})]$, which is uninterestingly defined as the difference between $F[n(\vec{r})]$ and the two first terms in the left hand side of Equation (3.14). Kohn and Sham [75] proposed a scheme what is known as the local density approximation (LDA), in which, the exchange-correlation functional is given by:

$$E_{\text{xc}}^{\text{LDA}}[n(\vec{r})] = \int d\vec{r} \epsilon_{\text{xc}}(n) n(\vec{r}),$$  \hspace{1cm} (3.21)

where $\epsilon_{\text{xc}}(n)$ is the exchange-correlation energy per particle of a uniform electron gas of density $n$. LDA can provide good structural properties for solids [73]. However, it ignores corrections to the exchange-correlation energy at $\vec{r}$ due to the inhomogeneity of the electron density in materials, and then it also have drawbacks, for example, can fail to describe strongly correlated electron systems [73].

Another class of the exchange-correlation functional is the generalized gradient approximation (GGA), in which $E_{\text{xc}}$ also depends the local gradient of the electron density:

$$E_{\text{xc}}^{\text{GGA}}[n(\vec{r}), \nabla n(\vec{r})] = \int d\vec{r} F[n(\vec{r}), \nabla n(\vec{r})].$$  \hspace{1cm} (3.22)

GGA has proved to be an improvement over LDA (but it is not always the case!).
PBE density functional [76] is very popular in the GGA family, however, it still has disadvantages, for instance, it badly fails to capture the van der Waals interactions, as proved in the next chapter of this thesis. Therefore, the improvement of the density functional is still a big subject for the DFT community nowadays.

### 3.3 Basis sets

In the Kohn-Sham approach, the wave functions are expanded through a set of auxiliary functions (Kohn-Sham orbitals):

\[
\psi_n(\vec{r}) = \sum_{\nu} c_{vn} \varphi_{\nu}(\vec{r}),
\]

(3.23)

where \(K\) is the number of basis functions \(\varphi_{\nu}(\vec{r})\). There are two widely used classes: localized basis set and plane-wave basis set \((e^{ikr})\).

#### a) Gaussian basis set scheme:

The localized basis set class involves two kinds: Slater\((e^{-\alpha r}\), the Slater-type orbitals - STOs) and Gaussian\((e^{-\alpha r^2}\), the Gaussian-type orbitals - GTOs) functions. The STOs closely resemble the atomic orbitals of isolated atoms, however, this kind is not convenient to evaluate, for example, the Hartree energy. GTOs can tackle this problem. In the Gaussian basis set scheme, the basis functions are contracted Gaussian-type functions:

\[
\varphi_{\nu}(\vec{r}) = \sum_{i} d_{\nu i} g_i(\vec{r}),
\]

(3.24)

where constants \(d_{\nu i}\) are called contraction coefficients, \(g_i(\vec{r})\) are Gaussian primitive functions, \(L\) is the length of the contraction. The primitive functions are:

\[
g_i(\vec{r}) = A x^{l_x} y^{l_y} z^{l_z} e^{-\alpha_i r^2},
\]

(3.25)

where \(A\) is a normalized constant, \(\alpha_i\) is the orbital exponent, \(l_x, l_y, l_z\) are integers. Analogous to atomic orbital names which are based on the angular momentum number, the primitive function is called the s-type Gaussian function if \(l_x + l_y + l_z = 0\), the p-type Gaussian function if \(l_x + l_y + l_z = 1\), and so on. A common way to obtain the

---

4The Ref. [76] has been cited more than 16000 times so far.
contraction coefficients and orbital exponents \( \{d_i\} \) and \( \{\alpha_i\} \) in a contraction is to fit it to a Slater atomic orbital using a least square approach. In the self-consistent Kohn-Sham procedure, \( \{d_i\} \) and \( \{\alpha_i\} \) are kept fixed.

The simplest kind of the Gaussian basis set scheme is the minimal basis set denoted as STO-LG (usually, L=3-6), in which each Slater atomic orbital is described by one Gaussian contraction, it is also called a single zeta (SZ) basis set. Higher quality basis sets have two (double zeta - DZ), three (triple zeta - TZ), four (quadruple zeta - QZ),... contractions per atomic orbital. Once in molecules valence electrons need to be treated more seriously, we can use the so-called split-valance (SV) basis sets, in which more contractions are used to mimic valence orbitals than core orbitals. Basis sets with functions of higher angular momentum numbers are called polarization (P) functions (for describing the distortion of original atomic orbitals). To this end, DZP stands for “double zeta plus polarization” TZDP (or TZ2P) means “triple zeta plus double polarization” DZV designates basis set with “one contraction for core orbitals, and double contractions for valence orbitals”...

In this thesis, we employ the DZVP basis set for Cu, Ag, Au, and I, and TZV2P for H, C, N, and O [77].

The Kohn-Sham equation can be written as:

\[
HC = SCE, \tag{3.26}
\]

where the Kohn-Sham matrix \( H \) is:

\[
H_{\nu\mu} = \int d\vec{r} \varphi_{\nu}(\vec{r})(-\frac{1}{2}\nabla_r^2 + V_{KS}(\vec{r}))\varphi_{\mu}(\vec{r}), \tag{3.27}
\]

and the overlap matrix \( S^5 \):

\[
S_{\nu\mu} = \int d\vec{r} \varphi_{\nu}(\vec{r})\varphi_{\mu}(\vec{r}), \tag{3.28}
\]

The electron density is then determined by:

\[
n(\vec{r}) = \sum_{\nu\mu} P_{\nu\mu} \varphi_{\nu}(\vec{r})\varphi_{\mu}(\vec{r}), \tag{3.29}
\]

\(^5\)This can be calculated analytically with Gaussian basis sets.
where the density matrix element $P_{\nu\mu}$ is:

$$P_{\nu\mu} = \sum_{n=1}^{N} c_{n\nu} c_{n\mu}. \quad (3.30)$$

The Gaussian basis set scheme has its own advantages, for instance, good outputs can be achieved with moderate basis sets; it also allows to determine the Kohn-Sham matrix elements easily, and is highly computationally efficient. On the other hand, it also has some drawbacks, a notable problem is the so-called basis set superposition error (BSSE) [78]. BSSE is the energy error resulted from the incompleteness of localized basis sets. Consider a system of two molecules A and B the total energy of A(B) is lower than its actual one due to the basis functions of B(A). A widely used method to cancel the error is the counterpoise correction [78]. In brief, the counterpoise corrected interaction energy between A and B is [79]:

$$BSSE_{AB} = E_{A}^{AB} - E_{A}^{A} + E_{B}^{AB} - E_{B}^{B}, \quad (3.31)$$

where $E_{X}^{Y}$ stands for energy of system X with basis set Y, all are calculated in the bound geometry. BSSE corrections for systems of more than two objects, based on the counterpoise correction, can be found in Ref. [80]. We shall use these corrections for binding energy calculations presented in the next chapters.

b) Plane wave basis set scheme and pseudopotential:

In the plane wave basis set scheme, the Kohn-Sham orbitals can be written as:

$$\psi_{nk}(\vec{r}) = \frac{1}{\Omega} \sum_{\vec{G}} e^{i\vec{G}\vec{r}} c_{nk}(\vec{G}), \quad (3.32)$$

where $\Omega$ is the volume of the unit cell, $\vec{G}$ are reciprocal lattice vectors, and all the coefficients $c_{nk}(\vec{G})$ are the eigenstates of the Kohn-Sham equation:

$$\sum_{\vec{G}'} \left[ \frac{\hbar^{2}}{2m_{e}} |\vec{k} + \vec{G}'|^{2} \delta_{\vec{G},\vec{G}'} + V_{KS}(\vec{G} - \vec{G}') \right] c_{nk}(\vec{G}') = \epsilon_{nk} c_{nk}(\vec{G}). \quad (3.33)$$
The number of vectors $\vec{G}$ is practically determined by an energy cutoff $E_{\text{wave}}$:

$$\frac{1}{2} |\vec{G} + \vec{k}|^2 \leq E_{\text{wave}}. \quad (3.34)$$

The electron density is then given by averaging the results of all $\vec{k}$ in the first Brillouin zone ($1^{st} \text{BZ}$) and sum over all the occupied states:

$$n(\vec{r}) = \sum_{\vec{k} \in 1^{st} \text{BZ}} w_{\vec{k}} \left( \sum_n |\psi_{nk}|^2 \right), \quad (3.35)$$

where $w_{\vec{k}}$ denotes the weight of $\vec{k}$ in $1^{st} \text{BZ}$. This density can be expanded in plane waves:

$$n(\vec{r}) = \frac{1}{\Omega} \sum_{\vec{G}} \tilde{n}(\vec{G}) e^{i\vec{G} \cdot \vec{r}}, \quad (3.36)$$

where expansion coefficients $\tilde{n}(\vec{G})$ can be useful for calculating the Hartree energy and potential. Here, the number of $\vec{G}$ is practically determined by an energy cutoff $E_{\text{rho}}$:

$$\frac{1}{2} |\vec{G}|^2 \leq E_{\text{rho}}. \quad (3.37)$$

The advantages of the plane wave basis scheme are, for instance, plane waves are orthogonal, nuclear position independent, allows an easy calculation of the Hartree potential, numerically efficient through the use of fast Fourier transform, have only one parameter controlling the basis set size. Furthermore, it is a natural choice for periodic systems as they take inspiration from Bloch’s theorem. However, this scheme also have its own disadvantages. Notably, it is necessary to use a large number of plane waves to reproduce the rapid variation of the wave functions in the core region of atoms. A solution for this problem is the so-called “pseudopotentials”.

We know that properties of materials (mostly) depend upon the electrons in the outer shells of the atoms, or the valence electrons. It follows that a description of all-electron wave functions is computationally inefficient. The main idea of pseudopotentials is the nucleus and core electrons of an atom are replaced by a new potential experienced by valence electrons (and core electrons are kept “frozen” in the calculations). Within the core region, the valence wavefunctions are replaced by nodeless pseudowavefunctions. Reducing the number of electrons and substituting rapidly changing valance
wavefunction by smoother ones lead to a significantly smaller basis set size. Pseudopotentials can be built in different ways, however, a working pseudopotential should satisfy several conditions. For example, real and pseudo valance eigenvalues must be the same for a chosen prototype atomic configuration; real and pseudo atomic wavefunctions must be identical outside the “core” radius, $r_c$ [81].

The norm-conserving pseudopotentials of Goedecker, Teter, and Hutter (GTH) [82] are exploited throughout this thesis.

c) Hybrid Gaussian and plane-wave scheme: Although pseudopotentials can provide a big deal reducing the plane wave basis set size, the plane wave scheme still has problems [83], for instance, a large cutoff energy still required for several elements. Moreover, for open structures like surfaces, the same accuracy is needed in both atom-filled and empty regions of space (i.e, it cannot take advantage of vacuum to reduce the basis set size), hence, it is highly demanding of memory in plane-wave based DFT.

The idea of combining the Gaussian and plane-wave basis functions thus appears. This hybrid Gaussian and plane wave (GPW) method [83] can utilize the advantages of each basis set scheme, and the main idea lies on two representations of the electron density (3.29, 3.36). The expansion coefficients $\tilde{n}(\vec{G})$ satisfy that the density in the Gaussian and plane wave representations is the same, i.e, $n(\vec{r})_{\text{plane-wave}} = n(\vec{r})_{\text{Gaussian}}$. 

Figure 3.1: Pictorial representation of Coulomb potential, pseudo-potential ($V_{pp}$) and their wave functions: the rapidly varying “real” wave function is replaced by a nodeless pseudowavefunction.
While the Gaussian basis is employed to evaluate the Kohn-Sham matrix elements, the plane wave representation of the charge density is used to calculate the Hartree and exchange-correlation energy and potential efficiently. This dual presentation of the electron density can result in a scheme that, in terms of computational cost, linearly scales with the system size for calculating the total energy and the Kohn-Sham matrix. The approach provides a highly effective technique dealing with large systems.

### 3.4 Forces and geometry optimization

The total energy of a system, $E_{\text{total}} = E_{\text{total}}(\{\vec{R}_I\})$, is contributed by the ground state energy (1.19) and the ion-ion interactions $E_{II}$. In the Born-Oppenheimer approximation, the system moves on the 3M dimensional potential energy surface (PES). Practically, a geometry optimization process involves minimizing the 3M-variable function $E_{\text{total}}$. To search for a (local) minimum from a given geometry, we can evaluate the forces acting on each nucleus.

Equations (3.6) and (3.12) show that only external potentials experienced by electrons depend explicitly upon the nuclear coordinates. The force acting on nucleus $I$ is therefore given by:

$$
\vec{F}_I = -\frac{\partial E_{\text{total}}}{\partial \vec{R}_I} = -\int d\vec{r} n(\vec{r}) \frac{\partial V_{\text{ext}}}{\partial \vec{R}_I} - \frac{\partial E_{II}}{\partial \vec{R}_I},
$$

(3.38)

where the first term in the right hand side is known as the result of the Hellmann-Feynman theorem which reads

$$
\frac{dE_\lambda}{d\lambda} = \langle \psi_\lambda \mid \frac{\partial H}{\partial \lambda} \mid \psi_\lambda \rangle,
$$

(3.39)

where $\lambda$ is a continuous parameter. In Equation (3.38) $E_{II}$ is the interaction between nuclei (or ions) as given in Equation (3.7).

The optimization proceeds through a series of steps $\{\vec{R}_I\}_k \ k=1,2,3,..$ until the total force acting on each ion vanishes. There are ways to produce geometry in step $k+1$ from the one in step $k$, and the BFGS algorithm is used through calculations in this

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$^6$We can say ion-ion instead of nucleus-nucleus interactions in the pseudo-potential framework.

$^7$A minimum with a geometry “closest” to the given one is expected.
thesis, details can be found in Ref. [84].

3.5 Rare events and the nudged elastic band method

As mentioned above, the PES has different minima\(^8\) and the geometry optimization allows to obtain some local minimum. To move from one minimum (called the initial state (IS)) to another one (the final state (FS)), the system must overcome the (lowest) energy barrier between them\(^9\). Usually, this barrier is very much higher than the thermal fluctuation\(^{10}\) around those minima, the transition therefore rarely happens. This thermally driven process is called a \textit{rare event}.

Studying this family of problems one might think of treating the motion of the atoms using molecular dynamics (MD). However, the transition in practical applications is normally many orders of magnitude slower than atomic vibrations. For instance, a barrier of 1.0 eV can result in a time scale of seconds for the transition at room temperature while the oscillation period of the atoms is about $10^{-13}$ seconds. Consequently, it would take many years for conventional MD to probe the natural time evolution of such an event. Accordingly, the time scale problem is disastrous for direct MD simulations, thus calling for some more practical approach.

A method that can allow to obtain an accurate estimation of the transition rate is the so-called transition state theory (TST) [85, 86]. This purely statistical method considers the following assumptions: 1) In phase space there exists a hypersurface that divides space into a reactant region and a product region. This “dividing surface” is identified such that a reacting trajectory from TS to FS crosses the surface only one time, 2) The reaction rate is slow enough so that the IS and TS can be considered as being in thermodynamic equilibrium, then governed by the Boltzmann distribution, and 3) The Born-Oppenheimer approximation. It is important to note that the TST transition rate, \(k^{TST}\), is an upper limit for the true transition rate. \(k^{TST}\) depends upon IS, TS, and FS, and in the harmonic approximation to the IS and TS, it is given by

\(^8\)The number of minima increases exponentially against the number of atoms.

\(^9\)For example, chemical reactions, structural phase transitions,....

\(^{10}\)Thermal fluctuations, statistical mechanically, are random deviations of a system from its equilibrium.
\[ k^{TST} = \frac{\prod_{i}^{3M} \nu_{i}^{IS}}{\prod_{i}^{3M-1} \nu_{i}^{TS}} e^{-\frac{E^{TS} - E^{IS}}{k_B T}}, \tag{3.40} \]

where \( k_B \) is the Boltzmann constant, \( E^{IS} \) is the local potential energy minimum of IS, \( E^{TS} \) is the TS energy, and \( \nu_{i}^{TS, IS} \) are the corresponding normal mode frequencies. Those frequencies can be determined at zero temperature, however, the rate depends implicitly upon only the temperature in the exponential part. As the machinery of

Figure 3.2: Schematic illustration of the potential energy surface of a many-body system. The black curves indicate the minimal energy paths between minima A and B (C).

the transition is reflected by the TS (and IS and FS, however, they are already known and can be easily obtained by standard geometry optimization), the essential part here now is TS. Once TS is determined, the minimum energy path (MEP, or the reaction pathway) can be found by tracking down the gradient of the PES. The key property of the MEP is that the component perpendicular to the path of the force, \( \vec{F}_\perp \), at any point vanishes. This quantity can be viewed as the clue for the search of the MEP. So, how can we determine TS? The practical way employed in this thesis is presented in the following.

Suppose that a “proposed” reaction pathway, which is viewed a series of images (or “states”) with coordinates \( \vec{R}_i \) \( (i = 1, 2, 3, ..., N) \) as presented in Figure 3.3, is given. \( \vec{F}_\perp \)
can be evaluated by subtracting the total force by the parallel component:

\[
\vec{F}_{i\perp} = -\nabla V(\vec{R}_i)_{\perp} = -\nabla V(\vec{R}_i) - \left[-\nabla V(\vec{R}_i)\hat{\tau}_i\right] \hat{\tau}_i,
\]

(3.41)

where the normalized vector tangent to the MEP at point \(i\), \(\hat{\tau}_i\), is:

\[
\hat{\tau}_i = \frac{\vec{R}_{i+1} - \vec{R}_i}{|\vec{R}_{i+1} - \vec{R}_i|}.
\]

(3.42)

If \(\vec{F}_{i\perp}\) is nonzero, the corresponding \(\vec{R}_i\) is then adjusted until it vanishes. However, the convergence to the “expected” MEP is unlikely to be obtained since image \(i\) tends to “slide down” to some local minimum. In this context, the elastic interactions between adjacent images are introduced, as suggested in the so-called nudged elastic band (NEB) method [89]. According to this method, any image in between IS and FS is connected to each of its nearest neighbors by an imaginary spring with spring constant \(k\). However, this elastic band formulation has its own problems [90]: first, the component of spring force orthogonal to the path makes the band get pulled off the MEP, and second, the component of the true force (from the interactions between atoms in each image) parallel to the path causes the “down-sliding” problem. For those reasons, the force
acting on each image should consist of the parallel component of the spring force and the perpendicular component of the true force:

$$\vec{F}_i = \vec{F}^s_{i\parallel} - \nabla V(\vec{R}_i)_\perp,$$

(3.43)

where the first term is:

$$\vec{F}^s_{i\parallel} = k[(\vec{R}_{i+1} - \vec{R}_i - \vec{R}_i + \vec{R}_{i-1})_i]_i.\tag{3.44}$$

If the springs have the identical spring constant, the images converge on the MEP with equal spacing. The challenge here is that with a large number of images, it is likely that none of them lands at the saddle point.

The climbing image NEB (CI-NEB) method [91], a slightly modified version of NEB, can handle this problem. The idea is that the force acting on the image with the highest energy $i_{\text{max}}$ (which is supposed to be corresponding to the TS), given by:

$$\vec{F}_{i_{\text{max}}} = -\nabla V(\vec{R}_{i_{\text{max}}})_\perp + \nabla V(\vec{R}_{i_{\text{max}}})_\parallel,$$

(3.45)

is not affected by the spring forces. Rather, the inverse of the component of the true force parallel to the path is employed, allowing the image to climb up to the PES along the elastic band and slide down to the potential surface perpendicular to the path. In this way, the transition point can be achieved.

### 3.6 The Tersoff-Hamann STM theory

Since introduced by Binnig and Rohrer in 1981 [92], STM has been an extremely powerful tool widely used in surface science. The principle of STM is based on the concept of quantum tunnelling. A voltage difference between a conducting tip and a surface can give rise to a tunnelling current through the vacuum between them, which is given by (in atomic units):

$$I = 2\pi \sum_{\mu\nu} f(E_\mu)[1 - f(E_\nu + V)]|M_{\mu\nu}|^2\delta(E_\mu - E_\nu),$$

(3.46)
where $\mu(\nu)$ implies the tip (sample) states, $M_{\mu\nu}$ is the tunnelling matrix element between states $\mu$ and $\nu$, $f(E)$ denotes the Fermi-Dirac distribution, and $V$ stands for the bias.

According to Bardeen [93], the matrix element can be computed as

$$M_{\mu\nu} = -\frac{1}{2} \int_S S d\vec{S} (\Psi_{\mu}^* \nabla \Psi_{\nu} - \Psi_{\nu}^* \nabla \Psi_{\mu}),$$

(3.47)

where $S$ is a surface separating the tip and the sample. Here, the wavefunctions of the tips and the sample must be known. While the knowledge of the sample states can be obtained with *ab initio* calculations, it is difficult to know the exact wavefunction of the tip.

Tersoff and Hamann [94] have proposed an effective approach, in which the unknown electronic structure of the tip is replaced by a simple model. In particular, it is assumed that only atomic $s$-wavefunction of outermost tip atoms are present in the spherical tip of radius $R$. In the limit of the small applied bias (compared to the tip and sample work-functions), the current now can be rewritten as:

$$I \propto V \sum_{\nu} |\Psi_{\nu}(r_t)|^2 \delta(E_{\nu} - E_F) = V \rho(r_t, E_F),$$

(3.48)

where $r_t$ accounts for the height of the tip’s center with respect to the surface, and $\rho(r_t, E_F)$ denotes the local density of states at the Fermi level of the sample, which is the basic quantity imaged.

### 3.7 Charge analysis

Estimating partial atomic charges in a complex can provide useful information about the inter-atomic or intermolecular interactions. Here we present two charge analysis methods which are used in this thesis: Mulliken [95] and Bader [96] analyses.

In the Mulliken analysis, one first writes the total number of electrons as

$$N = \int d\vec{r} n(\vec{r}) = \sum_{\nu\mu} P_{\nu\mu} S_{\nu\mu} = \sum_{\nu} (\sum_{\mu} P_{\nu\mu} S_{\nu\mu}) = \sum_{\nu} Q_{\nu}.$$  

(3.49)

Each component $Q_{\nu}$ can be understood as the charge contributed by basis function $\varphi_{\nu}$. 
The net charge associated with a given atom, for example $A$, is given by

$$q_A = Z_A - \sum_{\nu \in A} Q_\nu,$$

where the notation $\nu \in A$ indicates all basis functions centered on atom $A$, $Z_A$ stands for the nuclear charge of the atom. The main disadvantage of this analysis is that in Equation (3.49) the overlap population (where $\nu$ and $\mu$ belong to two different atoms) is equally distributed between pairs of atoms, thus causing problems for systems of atoms of different electronegativities.

While the Mulliken method relies on the electronic wavefunctions, the approach by Bader is based on the electron density. The main idea of this method is that within a molecular space the electron density interpreted to belong to each atom (called “atomic volume”) in a molecule can be separated to the rest by a surface that satisfies the condition:

$$\nabla n(\vec{r}_s) \vec{n}(\vec{r}_s) = 0,$$

where $\vec{n}(\vec{r}_s)$ is vector normal to the surface at $\vec{r}_s$. Technically, the gradient (or the gradient vector field) of the density is essential. For a given point in the molecular space, the vector pointing in the direction of maximum increase in the density is part of one trajectory of $\nabla n(\vec{r}_s)$, which will last at a charge density maximum. Through the dividing surface, there is no flux in the gradient vector field, in other words, no trajectories cross these surfaces.

Of the two methods, the Bader analysis is practically more advantageous, because the charge density can be experimentally measured or theoretically calculated. Moreover, this method is also less dependent of the basis function used in \textit{ab initio} calculations. Therefore, the Bader analysis often proves to be more robust than the Mulliken or any other electronic orbital based analyses.

### 3.8 Slab model for surfaces

Periodic boundary conditions are routinely used in atomistic simulation to describe crystalline (but also disordered) systems [97]. In this thesis we shall deal with high-symmetry solid surfaces of face-centered cubic metals covered with adsorbates. Al-
though fcc metals (according to Wulff’s theorem) usually expose planes with a limited number of orientations, it is experimentally desirable to obtain a large area of the surface of interest, and this is obtained by cleaving a single crystal along a certain plane. The presence of a surface corresponds to breaking the crystal symmetry along the surface normal. From the point of view of modeling, one could think of taking advantage of the periodicity in two dimensions, but not the third, and to build codes that exploit periodic boundary conditions only in the parallel direction to the surface. Such codes, in principle, can exist, but it is more common to study a surface by a simulation program that applies periodic boundary conditions in all three dimensions, using the so-called periodic slab approach.

A surface is illustrated by a slab where the 2-dimensional periodicity is retained. The thickness of the slab is an important factor that needs to be adjusted from case to case. For example, a slab of 4-5 layers of atoms is good enough to reproduce the work function of an aluminum surface [98], but 24 layers are needed to obtained the surface states of a gold substrate [99]. Therefore, the choice of the slab thickness depends upon specific problems and theoretical methods. For electronic structure calculations in heterogeneous catalysis and surface assembly a thickness of 3-5 layers is practically relevant.

Figure 3.4: Schematic illustration of the slab model for a surface with periodic boundary conditions: the separation between the slab and its periodic replicas along the surface normal (the $z$ direction), $z_0$ must be large enough so that they do not interact with each other.
3.9 The CP2K package

All the DFT calculations presented in this thesis are carried out using the CP2K package [100]. It is a freely available (GPL) program, written in Fortran 95, to conduct simulations of solid states, liquid, molecular and biological systems at atomistic and molecular levels. This code offers many different methods such as GPW-DFT, classical pair and many-body potentials, semi-empirical Hamiltonians, quantum mechanics/molecular mechanics (QM/MM) hybrid schemes,... DFT using GPW implemented provides a great deal in assessing the electronic structure and energy of large systems (up to 700 atoms including metallic elements) - the subjects of this thesis.

Figure 3.5: Timings of a full wavefunction for liquid water samples against the system size with GPW-DFT implemented in QUICKSTEP of CP2K on a single Power4+ CPU using a DZVP/DZV basis: the sum of the linear scaling Kohn-Sham matrix construction (diamonds) and the cubic diagonalisation/DIIS based density matrix update (circles). The solid lines are single parameter fits using the ideal forms $a_1 N$ and $a_3 N^3$, triangles indicate the fraction of time spent in the Fast Fourier Transforms routines as part of the Kohn-Sham matrix constructions, whereas the dashed line is a fit using $a_{FFT} N \ln N$. The insert shows the same Kohn-Sham matrix construction data using linear axes. (From Ref. [100])
Chapter 4

Organic molecules at Au(111)

We show, by comparing density functional theory calculations with available experiments, that the van der Waals interaction is an extremely important component determining the properties of a prototypical molecule-surface system, the self-assembled hydrogen bonded network formed by PTCDA (3,4,9,10- perylenetetracarboxylic dianhydride) and DATP (4,4’-diamino-p-terphenyl) deposited on Au(111).

4.1 Introduction

As reviewed in Chapter 2, the driving forces leading to the formation of highly ordered molecular structures on single-crystal surfaces are the intermolecular and the molecule-substrate interactions [19]. Whereas in the absence of chemical reactions the formers are important but often rather weak, as in the case of hydrogen bonding or dipole-dipole interactions; substrate forces can vary in strength depending on the supporting surface and the adsorbed molecules, ranging from dispersive to strong chemical bonding. The rational design of molecular networks of technological interest relies on a deep knowledge of the relative role of such interactions, the structure and site-selectivity-based stability of the molecules adsorbed on the surface, the amount of electron transfer in the molecule-surface interface, the modification of the electronic structure induced by adsorption, and so on. Numerous experimental studies have demonstrated the feasibility of ordered two-dimensional organic networks on single crystal surfaces based on non-covalent interactions [19]. Both homo- [101, 102, 103] and hetero-molecular [55, 104]
networks have been realized with the ability to tailor the network structure through chemical design. In parallel, several theoretical works have addressed different issues concerning structure, stability and electronic properties of such self-assembled molecular networks on metallic surfaces. Hydrogen bonded networks, in particular, represent a challenge since the intermolecular bonding strength in this case is small, and the level of theory chosen should be accurate enough in order to be predictive concerning stability properties of such extended systems. Moreover, dispersion interactions may play a very important role, not only because they can lead to an overall increase of the adsorption energy, but also because they can modify the structure of the adsorbed layer, and eventually lead to a modification of the electronic nature of the molecule-surface bonding. Previous theoretical studies have, however, often neglected the effect of vdW interactions, since standard gradient corrected local density approximation schemes for DFT are not able to capture the dispersion forces [71].

There have been many attempts proposed to improve DFT calculations by implicitly introducing in the exchange-correlation functionals the nonlocal-correlations [71, 105]. However, those schemes are very computationally demanding for practical systems. There have also been further simpler and cheaper methods, in terms of methodology and computing cost, proposed by directly adding the vdW energy to the energy yielded by GGA. One of the most popular solutions recently adopted to include dispersion forces in the field of surface nano-science is the dispersion correction scheme by Grimme [106] which we shall call PBE-D (from the particular XC functional used) from now on. The semi-empirical character of this approach, as for other model schemes, calls for a convincing experimental verification (or falsification), case by case. For example, the experimental observation that for di(n-butyl)-quinacridone on Ag(110) both commensurate and incommensurate phases are experimentally observed has been rationalized with the help of PBE calculations and vdW corrections [107]. However, no change in the energy ranking and no evidence notwithstanding the experimental observation was found when not including dispersion corrections.

Here, we study the role of the vdW interaction in the adsorption of large organic molecules at a metal surface by performing extensive calculations within the framework of PBE and PBE-D, and comparing the results with detailed experimental data. We apply this approach for the first time to a hetero-molecular network, which is a bimolecular nanostructure of PTCDA and DATP as described below. Comparing our results
with the experiment at different levels: stability of single molecules and supramolecular structures, structural and electronic properties. We shall show that the subtle interplay between geometric (where the dispersion interaction directly plays a role) and electronic structure (where such an interaction only enters indirectly) eventually determines the experimental findings. The latter can not be explained without a dispersion corrected scheme, which (in spite of its phenomenological character) can be considered valid and predictive for this class of systems.

The rest of this Chapter is organized as follows. Section 4.2 describes the experimentally observed physical systems that serve as model structures in this work. In section 4.3 we introduce the Grimme correction to XC functionals. Next, in section 4.4, investigating adsorption properties of single molecules on Au(111) and comparing with available experimental data, we highlight the role of the vdw interaction to metal organic systems. Section 4.5 we address the stability of molecular molecular networks in the adsorption phase. Then in section 4.6, we compare again the efficiency of PBE and PBE-D by addressing the STM simulations compared with experiment. The modification of surface work-function upon the adsorption of molecules is discussed in section 4.7. And finally 4.8 presents concluding remarks.

4.2 Physical systems under study

There are many reasons why PTCDA is a model molecule in the organic semiconductor class [32]. For example, as an intensive dye molecule, it can be used in optoelectronic applications. PTCDA is a flat aromatic species, there exits overlap between the $\pi$-systems of neighboring molecules in its molecular crystal, thus can be exploited in studying the charge delocalisation effects. Additionally, nanostructures of this molecule exhibit interesting electronic properties on surfaces, e.g., there is a free-electron like two-dimensional band state confined to islands of PTCDA on Ag(111). PTCDA has both donor (H) and acceptor (O) sites to form hydrogen bonded systems. Besides, the molecule is easy to prepare and stable under experimental conditions. Tailoring low-dimensional structures (then electronics) to exploit unique electronic properties of PTCDA is therefore a desirable subject.

Recently, we have shown that a range of nanostructures of reduced dimensionality of PTCDA can be realized on Au(111) by mixing with a “foreign” hydrogen bonding
molecule, DATP, which we call the spacer [108], as presented in Figure 4.1. The purpose of using this spacer is to separate nanounits of pure PTCDA by hydrogen bonds between the anhydride ends of PTCDA and its amine groups. By using different DATP:PTCDA ratios $r_{DP}$ we obtain different structures of PTCDA. In particular, with $r_{DP} = 1$ a highly regular array of equally spaced individual PTCDA molecules stabilized by DATP spacers was achieved (Figure 4.1.c). With decreasing $r_{DP}$, various PTCDA rows were realized, and without the presence of DATP, we obtain a herringbone pattern of PTCDA.

![Figure 4.1: DATP and PTCDA (a and b, respectively): C(grey), H(white), N(blue), and O(red). Zero- and one-dimensional structures of PTCDA on Au(111) (c, d, e, f, and g) resulted from different PTCDA-DATP ratios: PTCDA in red and DATP in blue, array of equally spaced individual PTCDA molecules stabilized by DATP hydrogen-bonding spacer (c), single row PTCDA structure (d), alternate single-double PTCDA row structure (e), double row PTCDA structure (f), herringbone phase of PTCDA formed without DATP (Taken from Ref. [108]).](image)

The first case, $r_{DP} = 1$, is rather special because the corresponding structure resembles an array of quantum dots, thus offering some potential prospect in the applications of organic electronics. From a theoretical point of view, this system also provide an ideal test case for the aim of this chapter. As its relatively small unit cell is made up by only two molecules (plus surface atoms), it is computationally affordable within the DFT framework. Moreover, the two molecules in the unit cell are inherently different, we can exploit their difference in adsorption properties to obtain a systematic comparison between PBE and PBE-D formulations.
4.3 The Grimme dispersion correction

In the Grimme approach [106] the total energy $E_{PBE-D}$ (or $E_{DFT-D}$ in general, we use the PBE term in this specific case) is given by:

$$E_{PBE-D} = E_{KS-PBE} + E_{Disp}, \quad (4.1)$$

where

$$E_{Disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} C_{6}^{ij} \frac{R_{ij}}{R_{ij}^6} f_{dmp}(R_{ij}), \quad (4.2)$$

$$f_{dmp}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r-1)}}. \quad (4.3)$$

The $E_{KS-PBE}$ is the standard self-consistent Kohn-Sham energy within the PBE XC functional framework. The empirical dispersion correction, $E_{Disp}$, is made up by a number of components:

- $C_{6}^{ij}$ is the dispersion coefficient for atom pair $ij$, which is given by the geometric mean of single-atom coefficients: $C_{6}^{ij} = \sqrt{C_{6}^{i}C_{6}^{j}}$ where $C_{6}^{i}$ is the dispersion coefficient of atom $i$.

- $s_6$ is a global scaling factor depending of the density functional.$^1$

- $R_{ij}^6$ is the distance between atoms $i$ and $j$.

- $f_{dmp}(R)$ is a damping function which is used to avoid near-singularities at small $R$. $R_r$ is the sum of the vdW radii of atoms $i$ and $j$ and $d$ is a parameter chosen around 20.

- $N_{at}$ is the number of atoms.

All these parameters are fitted to *ab initio* data at a high level of theory. The $C_{6}$ coefficients for the vdW attraction are obviously of central importance in this approach. For C, N, and H we use the ones originally proposed by Grimme [106]. For Au, instead, no parameters were available$^2$. Keeping in mind the way $C_{6}^{ij}$ is defined, to derive the

$^1$This parameter is needed because the XC functional is re-parameterized

$^2$Our calculations were conducted in 2009. In 2010 Grimme published the data for gold. Thereafter several values of $C_{6}$ for gold were proposed, however, they are still controversial [109].
coefficients for Au, we follow a previous semi-classical study by Levi and Calvini [110] where interaction parameters between Au(110) and a fullerene $C_{60}$ are derived in the following way. First, the coefficient $C_3$ entering the $z^3$ interaction between the molecule and the surface is derived from the polarizability of fullerene using the Lifshitz formula (see Chapter 2); then, the same interaction is considered as the sum of pairwise vdW terms centered on the gold and carbon ions, with $C_{6}^{CAu}$ fitted in order to obtain the correct $C_3$. Strengthened by the fact that the structural properties of the rings facing the surface in the case of DATP and PTCDA are similar to the $C_{60}$ case, we derive $C_{6}^{Au}$ from $C_{6}^{CAu}$ using the geometrical mean formula, and used the resulting $C_{6}^{Au} = 17.29$ Jnm$^6$mol$^{-1}$ (or 299.86 a.u.) in our scheme, together with a typical vdW radius for gold (1.66 Å). Since this procedure was not obtained by ab initio fitting using the PBE-D functional, one could question whether this approach continues to be valid in presence of a damping function and of the DFT part of the functional. However, we verify in the next section that these parameters lead to an adsorption energy and geometry for PTCDA on Au(111) in excellent agreement with experiments. We thus decide to use these values throughout our calculations.

4.4 Single molecules at Au(111)

To understand surface-supported molecular systems, it is instructive to first have information about the adsorption of single molecules - the building blocks of supramolecular structures.

Adsorption positions of molecules are associated with high-symmetry sites on surfaces, for instance, on-top (right above a surface atom)... This is because of the relationship between the shape of the potential energy surface and the atomic positions, in particular, saddle points or minima of the potential energy surface are connected to the geometric symmetry of the atomic arrangement in the system. For molecules containing functional groups, the stable positions are usually correlated with the positions of these groups with respect to the surface, this is especially the case if chemisorption occurs. Moreover, planar aromatic molecules are often adsorbed in a flat-lying fashion [19]. To determine the most stable adsorption configurations for the DATP and PTCDA molecules on Au(111) we perform a series of geometry optimization starting from “adequate” guess configurations. Our models are obtained by placing PTCDA on
Au(111) such that all the carboxylic oxygen atoms\(^3\) are located at the on-top (bridge, hcp, fcc) positions. In the same fashion, DATP is located referring to the position of its N atoms. As the sizes of these molecules are commensurate with distances between surface atoms, they can be adsorbed in such a way that all carboxylic oxygen and nitrogen atoms can find favorable positions. We optimize these systems with both PBE and PBE-D schemes. The results from these methods are appallingly different. Now, we analyze energetic and geometric properties.

The adsorption energy, which is calculated in the BSSE scheme formulated by Equation (3.31) of the previous chapter, is presented in Table 4.1. Let us consider PTCDA first, the PBE adsorption energy of this molecule is almost zero. This result is unphysical because against experimental observations it shows that PTCDA cannot be adsorbed on Au(111). In contrast to PBE, PBE-D reproduces a very strong adsorption bonding of -1.92 eV. We note that this theoretical result shows full adequacy as the adsorption energy is in excellent agreement with the experimental one, namely -2.0 eV [111]. To this end, we can draw two conclusions: i) the PTCDA-Au(111) interaction is physisorption, thus verifying experimental suggestions [32], and ii) the PBE energy functional once again shows its deficiency of capturing the dispersion interaction. For DATP, the -0.37 eV PBE adsorption energy signals some chemical bonding between the amine groups and surface atoms. However, this adsorption cannot be strong enough to keep DATP on Au(111) in the time scale of interest at room temperature. The existence of this system may significantly be interpreted by the vdW forces as we notice that the molecule-surface bonding is vastly strengthened in our PBE-D calculations with a binding energy of -2.06 eV. So far, no detailed experiment has been done researching

\(^3\)Oxygen atoms that are bound to only one carbon atom.
Figure 4.2: Geometry of DATP and PTCDA on Au(111) from PBE and PBE-D calculations. a) high-symmetry sites on Au(111): H(hollow, green point), B(bridge, red point), and T(on-top, blue point). a) and d) respectively illustrate the most stable position of PTCDA and DATP where carboxylic oxygen and nitrogen atoms are located at on-top sites. Curly PBE geometries (b and e) are very different from relatively flat ones (c and f).

The adsorption properties of DATP on Au(111), we thus have no experimental data to examine the validity of our theoretical result. Nevertheless, taking the number of atoms constituted in PTCDA and DATP, and their similar lying adsorption geometry into account we can be confident that the dispersion contribution in the DATP-Au(111) system is reasonable. Therefore, the vdW interaction can always play a pivotal role in the adsorption of large organic molecules on metal surfaces with or without regarding to the presence of molecule-surface chemical bonds.

Geometric properties of these molecules on the gold substrate also exhibit a remarkable difference between the PBE and PBE-D schemes. Figure 4.2 displays the adsorption geometry of PTCDA and DATP. Obviously, in the PBE structure PTCDA has a bridge-like shape that would make the molecule less stable compared to its natural flat form. Dissimilarly, the molecule is relatively flat in the PBE-D structure as suggested by experiment [32]. Furthermore, the average height of carbon atoms with respect to the surface in the former is 3.60 Å which is far from the one of 3.15 Å in the latter and the experimental value of 3.25 Å [32]. The adsorption of PTCDA on Au(111) is practically not site-selectivity dependent, this is a typical physisorption system. For
DATP we also have the same trend, i.e, the molecule is flatter and closer to the substrate in the PBE-D calculation. The N-Au bond length in both schemes is about 2.8 Å which is between the covalent contact distance (2.18 Å) and the vdw contact distance (3.21 Å), explaining the somewhat small adsorption energy from the PBE calculation as discussed above.

It is noticeable that DATP is strongly deformed compared to its natural geometry (see Figure 4.1). This is because the molecule tends to arrange itself in such a way that the nitrogen atoms of the two terminal amine groups point toward surface atoms, thus facilitating the bonding to the surface through nitrogen electron lone-pairs. Additionally, due to strong vdw interactions and the Pauli repulsion the central ring of DATP becomes more parallel to the surface.

We have demonstrated, analyzing energetic and geometric properties, that the inclusion of dispersion forces is essential in the PBE exchange-correlation density functional for the present molecule-surface problems. In the following of this section, we explore electronic properties of the PTCDA-Au(111) and DATP-Au(111) systems.

Figure 4.3: PDOS of PTCDA and DATP in the gas (red curve) and adsorption (green and blue curves) phases (a,b); the electronic structure of the molecules is less affected by the surface in the PBE calculation. Induced charges from the PBE-D calculations (c,d); accumulation in pink and depletion in green with an iso-surface value of 0.0008 a.u (PTCDA) and 0.002 a.u (DATP)
Figure 4.3 shows the PDOS of the molecules in vacuum and on the surface. For PTCDA we can see that the HOMO state is located about 1.0 eV below the metallic Fermi level while the LUMO state is 0.4 eV above. Upon adsorption some molecular levels are broadened due to the interaction with surface electrons, they are only slightly shifted. Results from PBE-D calculations exhibit a larger broadening due to the molecule-surface closeness. Induced charges of the system presented in Figure 4.3 imply a strong Pauli repulsion in the region between the molecule and the surface as there is a large depletion portion in this region.

The electronic structure of DATP is strongly modified upon adsorption, especially in the PBE-D calculation. We notice that in the pre-adsorption HOMO of DATP is 0.1 eV higher than the Au(111) Fermi level. In the adsorption phase, the HOMO peak is 0.6 eV shifted down, as a result of the (weak) chemical bonds between the amine groups and surface atoms. Besides, the Pauli repulsion also plays a certain role in the change of the electronic structure.

4.5 Phase stability: an interpretation

The formation of molecular networks presented in section 4.2 is mainly due to the hydrogen bonding between neighboring molecules. Upon adsorption, PTCDA has both hydrogen bond acceptor (O) and donor (H) sites while the amine-functionalized DATP has only donor sites (H). DATP generally has acceptor sites, namely, nitrogen atoms which possess electron lone pairs. However, as described in the previous section, in the adsorption phase these nitrogen lone pairs point toward Au atoms, they are therefore sterically restricted to form intermolecular hydrogen bonds.

We now address the question arising concerning the stability of the mixed PTCDA-DATP structure with respect to other arrangements of DATP and PTCDA which could be experimentally observed under certain conditions. Three important observations can be drawn about the experimental findings (see Figure 4.4):

1. Structure 1 When the species are co-deposited, binary networks are observed and stabilized by NH⋯O hydrogen bonds, showing that at least for one of those species, homo-molecular lateral interactions are weaker (than the hetero-molecular one). This regular and extended rectangular pattern is characterized by a unit cell of $20.0 \times 17.5$
Å² containing two molecules.

2. **Structure 2** When only PTCDA is deposited, the typical herringbone structure stabilized by C-HO hydrogen bonds is obtained. This molecular network is characterized by a nearly rectangular unit cell of 19.5×12.9 Å² made up with two molecules.

3. **Structure 3** When DATP is deposited alone, a regular network is observed only with full monolayer coverage. This network is characterized by a parallelogram unit cell of 15.3 × 13.5 Å² × 79° consisting of two molecules.

From an experimental point of view, it is clear that **Structure 1** is energetically favorable as it is observed. To know how much **Structure 1** can be more stable than **Structure 2** and **Structure 3**, we calculate the binding energy for each case using the previously described protocol.

![Image of STM images and atomistic illustration](image)

**Figure 4.4:** Hetero- and homo-molecular networks: STM images (top panel) and atomistic illustration (bottom panel, not surface atoms included). Structure 1 represents the mixed phase which is stabilized by the hydrogen bonding between the ends of the molecules (highlighted by transparent yellow objects). Structure 2 represents the network of PTCDA alone which is stabilized by hydrogen bonding. Structure 3 represents the network of DATP alone which is experimentally observed only at the full-monolayer coverage, there is no hydrogen bonding among DATP molecules. Each network is characterized by a unit cell of two molecules.

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4 Owing to the effect of GGA on lattice parameter, in our model calculation we use a slightly larger unit cell of 20.6×17.9 Å².  
5 On Au(111), it is reasonable to set PTCDA and DATP in the molecular networks in such a way that functional group atoms of these molecules are placed at on-top positions, e.g., the most stable geometry of single molecules. Here we deal with the 3-body BSSE problems, the binding energy calculations are carried out in the scheme described in Chapter 2.
In Figure 4.5, from left to right we show isolated molecules adsorbed on the surface (a and b), the binary network and the homo-molecular DATP and PTCDA networks on Au(111) (c, d and e). Please note that for the periodic structures which contain two molecules per unit cell, the binding energies are given “per molecule” for consistency. Inspecting the equilibrium structures, we can confirm the hydrogen bonded nature of networks containing PTCDA (c, e, f, and g).

As should be clear from the diagram, the inclusion of vdW corrections not only determines the energy scale for molecular adsorption, but is also relevant in ranking

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6 Binding energy of each DATP seems to be unchanged from single molecules to the packed networks, showing that the lateral interactions are not completely repulsive. The (intermolecular) vdW interactions can play some role, this can cancel out the steric repulsion. In any case, the lateral DATP-DATP interactions here are within the accuracy of DFT
the strength of the lateral interactions for different networks. To clarify this point, we use the obtained binding energies to investigate the possibility of binary phases. Let us consider $N$ PTCDA and $N$ DATP molecules co-deposited on the Au(111) surface. We compare the following two possibilities (other intermediate cases are possible):

a) These molecules mix together and form the PTCDA-DATP binary network (Figure 4.5.c) composed by $N$ bimolecular unit cells.

b) No binary network is formed. $N$ PTCDA molecules aggregate together in $N/2$ unit cells of the homomolecular network (Figure 4.5.e). Moreover, DATP molecules can either remain isolated (Figure 4.5.a), or form some non-interacting disordered structures (at low) or aggregate together (at high coverage) and create the DATP-DATP monolayer containing $N/2$ unit cells (Figure 4.5.d).

Within the PBE-D scheme, in case (a), the binding energy of the whole system, which is the total binding energy of $(N + N)/2 = N$ bimolecular unit cells, the binding energy is $E(a) = -5.3N$ eV. In case (b), the energy is the sum of the binding energies of the PTCDA-PTCDA-Au(111) (Figure 4.5.e) and DATP-DATP-Au(111) (Figure 4.5.d) (or isolated DATP-Au(111)) systems, is $E(b) = -5.5N/2 - 4.15N/2 \simeq -4.83N$ (eV). The stability “difference” is $E(a) - E(b) = -0.47N$ eV, the mixed phase (case a) is accordingly always favored.

The PBE-D energy gain for forming a binary network is therefore 0.47 eV per molecular unit cell (two molecules). The same calculation in the PBE approximation would lead to a gain of 0.21 eV. In terms of Boltzmann factors and probabilities in the canonical ensemble, the enhancement of the difference within PBE-D corresponds to a dramatic increase in the probability ratio between the most favorable phase and the unfavored one, showing the relevant weight of vdW interactions in the relative importance of both phases. Note that our theoretical finding is in full agreement with the experimental observation that the binary network is always observed when both kinds of molecules are deposited on the metal surface. Moreover, in the presence of a 1:1 ratio of two species, the PTCDA homomolecular superstructures are never observed.

### 4.6 Bimolecular network: electronic structure

The PBE and PBE-D equilibrium structures of the bi-molecular network are shown in Figure 4.6. It is important to note that nitrogen atoms in the amine groups are 1.4
and 0.5 Å lower than the central ring of DATP in the PBE and PBE-D calculations, respectively. The twist angle of the DATP center ring is 21° (PBE) and 7° (PBE-D). Interestingly, these values are smaller than the corresponding ones in case of single DATP on Au(111), suggesting that the intermolecular hydrogen bonding increases the planar character of this molecule in presence of the surface. The vertical distortion of PTCDA (with respect to its planar geometry in vacuum) changes from 0.6 (PBE) to 0.2 Å (PBE-D). The PBE-D geometry shows that DATP is closer to the surface than PTCDA, which is not the case for PBE. Indeed, the role of vdW interactions here is to flatten the rings and allow for a more effective adhesion of the molecules.

![Figure 4.6: Geometry of PTCDA and DATP in the bi-molecular network (a) and PDOS onto the DATP central ring (b) from PBE and PBE-D calculations. In the PBE-D result DATP is flatter, the central ring is more parallel and closer to the surface, leading to a stronger broadening of molecular levels as depicted in (b).](image)

To have a direct comparison with experiment and an immediate description of the effect of geometry on the electronic structure of the system, we perform STM simulations using the Tersoff-Hamann approximation [94]. Within this approximation, as mentioned in Chapter 2, the integrated local density of states (LDOS) is proportional to the tunneling current, therefore we compare iso-surfaces of the LDOS (with a Gaussian convolution to mimic the finite size of the tip) to constant-current STM images.

Figure 4.7 shows topography maps for different sample biases. In general, the experimental apparent height of DATP is lower than the corresponding height of PTCDA for all biases. This is correctly reproduced by the PBE-D calculations. The apparent height difference between DATP and PTCDA, however, varies upon changing the bias, as an effect of the different region of the LDOS explored by the tunneling electrons. As shown in Figure 4.7, this is well reproduced (also quantitatively) within PBE-D, but not within PBE. The latter, indeed, shows (for $V_{\text{bias}} = 1.8$ V) a contrast inversion with
Figure 4.7: Experimental and simulated STM images and height profiles at various biases, PTCDA and DATP are respectively indicated by red and blue arrows.

respects to the experiment. Taking a closer look at a DATP molecule, the image of the central ring is closer to the experimental shape within PBE-D, reflecting the flattening effect of vdw interactions on large aromatic molecules with a non-planar gas-phase conformation. From all these considerations, we can conclude that PBE-D shows very good agreement with experiment while the PBE simulations fail in reproducing some of the most relevant features of the experimental STM images. We note that for $V_{bias} = +0.5$ V the experiment shows a clear broadening of the PTCDA signal, which was attributed to the LUMO of PTCDA. We observe a similar broadening also for $V_{bias} = +0.2$ V; the position of the LUMO in our calculations is in fact closer to the Fermi level with respect to the experiment (as a consequence of the reduced gap in standard GGA). But the inspection of the fine structure of the positive bias STM image confirms the experimental hypothesis.
Finally, we inspect the density of states (DOS) and we focus on the most dramatic difference between PBE and PBE-D results, that is, the rotation of the central ring of DATP. We project the total DOS onto the atomic states relative to the atoms of DATP central ring (Figure 4.6.b), and we notice a difference between PBE and PBE-D: the former shows a pronounced peak around $E = 1.8$ eV, which is not present when the ring is more planar due to the vdW corrections.

The agreement of the simulated STM images in the PBE-D approximation with experiment directly confirms that the ring reorientation induced by such a correction is realistic and underlines the importance of vdW in determining the equilibrium structure of weakly bound large organic adsorbates on single crystal surfaces. The observable difference in the projected DOS profile also stresses the effect that apparently tiny changes in the molecular structure can have on the electronic properties of the adsorbed system, as confirmed later on in the section about work function modifications.

### 4.7 Au(111) work-function modification

In addition to their use as templates, surface-supported organic nanostructures and monolayers are expected to find manifold applications in the next generation of low-cost electronic devices. Being able to make the transition “from structure to function” requires, however, a clear understanding of the properties of the organic-inorganic interface. Properties relevant for organic electronics devices include charge injection barriers and mobilities as well as the work function of the electrodes [112]. The work function of metals can be altered/tuned by covering the latter with an organic monolayer which can be used to improve device performances.

The effect of DATP-PTCDA coverage on the work function of Au(111) is investigated here. Technically, the procedure of work function calculation for a metal surface within a slab model is described in the work by Fall and coworkers [98]. As a test, we determine the work function of clean Au(111), which is 5.24 eV, showing excellent agreement with the experimental value of 5.26 eV [113]. The modification of the work function of several noble metal surfaces upon adsorption of PTCDA has been investigated in the literature. Experimentally, it is reported that the work function of PTCDA-covered Au(111) is reduced by 0.3 eV [114] or 0.4 eV [115] with respect to the clean surface. Recently, a PBE simulation of the PTCDA monolayer (Figure 4.5.e) has
led to a work function reduction of 0.34 eV [116]. Our result, which is presented in Figure 4.8 (top panel), is 0.3 eV (PBE) and 0.32 eV (PBE-D), in agreement with previous investigations. The results from PBE and PBE-D calculations for PTCDA monolayer

![Graph showing the electrostatic potential and electron density difference](image)

Figure 4.8: Electrostatic potential (top panel) and electron density difference (bottom panel) of the PTCDA(P)-DATP(D)-Au(111) system along the surface normal direction $z$. $z_0$ is the position of the outermost layer of Au(111).

are almost the same, although the distance of the molecules from the surface plane was found to quite different in the two cases (3.6 Å vs. 3.2 Å). In the case of the mixed DATP-PTCDA monolayer, there are unfortunately no experimental results to which we can refer. However, going from PBE to PBE-D we get an enhancement of the work function reduction, amounting to 0.4 and 0.6 eV, respectively. This is accompanied by an average height of the DATP atoms with respect to the first surface layer ions which reduces from 3.3 to 2.8 Å. This effect could find its origin either in an enhanced charge transfer (due to the closeness to the surface) and polarization (due to the more planar arrangement, favoring the ordering along $z$ of the induced dipole moment) of the DATP
molecules, or in the enhanced Pauli repulsion.

The bottom panel of Figure 4.8 shows the induced electron density integrated in planes parallel to the surface. The apparent effect of vdW interactions is the large redistribution of charge, which accounts for a large reduction of the surface dipole moment. More specifically, as the bi-molecular network is closer to the surface in the PBE-D calculation, electrons from Au(111) are more strongly pushed back to the surface (see black curve), leading to a larger induced electric dipole moment pointing upward (keeping in mind that the electron charge is negative). This dipole moment more strongly weakens the intrinsic dipole moment of the surface which points downward, then leading to a more noticeable decrease in the surface work-function as shown in the top panel.

4.8 Summary

In summary, we have presented a comprehensive study on supramolecular nanostructures of PTCDA and DATP on Au(111). With the help of a dispersion-corrected DFT scheme, we could establish the role of vdW interactions both in determining the exact equilibrium structure and the electronic properties of the adsorbate-substrate system. The effectiveness of the correction scheme appears evident when comparing simulated STM images (including the substrate) with the experimental ones. The relative heights of the two molecules comes out wrong within PBE, which is due to a wrong equilibrium geometry and subsequent inaccurate electronic density of states. Within the corrected PBE-D scheme, the molecules get flattened, the height differences change, and also the distances from the surface are adjusted accordingly. The latter point is crucial in affecting another important quantity in view of electronic device applications: the work function. We could observe substantial differences in the work function reduction between PBE and PBE-D: some of our predictions have presently no experimental counterpart and wait for further measurements to be confirmed. In conclusion, our computational results, which are in excellent agreement with experimental findings, provide convincing evidence that vdW corrected DFT, even in a simple form as in the Grimme scheme, should be used instead of “standard” DFT schemes when dealing with metal-supported supramolecular systems. We believe that this indication can help in the future in designing efficient and novel nanodevices obtained by self-assembly.
Chapter 5

Molecular chains at Cu(111)

We present a study on supramolecular structures of cyano-functionalized-[7]helicene (CHe) self-assembled on Cu(111). Experiments, conducted at ETHZ and the university of Basel, show that oriented, chain-like molecular nanostructures are observed at 77 K. Interestingly, homochiral chains grow in a direction that forms an angle of roughly -20° for M-CHe and +20° for P-CHe to a principal surface direction. Our ab initio simulations evince that this novel arrangement is resulted by the subtle interplay between the orientational and site-selectivity adsorption of CHe, the surface-induced electrostatic repulsion, and weak intermolecular hydrogen bonding. It is also suggested that the corrugation of the potential energy surface (PES) of CHe at Cu(111) can increase the intermolecular distance.

5.1 Introduction

In the fabrication of supramolecular structures on surfaces, hydrogen bonding plays an important role thanks to its selectivity and dimensional tuning abilities [19, 41]. Many two-dimensional (2D) hydrogen bonded networks have been addressed [19, 41, 55, 108] and most of them are related to aromatic molecules. A common feature of these molecules, for instance PTCDA (see Chapter 4), is that they are usually adsorbed on the noble metal surfaces in a flat-lying fashion, allowing the hydrogen bond donors and acceptors easily approach each other, thus facilitating the bonding.

Supramolecular architectures at surfaces of the helical species, a class of very fun-
damental molecules, also gain special attention. Helicity is a main element of chirality in molecules [117] and supramolecular helix-helix interactions are of utmost importance in biology [118]. Moreover, chiral surfaces keep an important role in various fields such as stereoselective chemical synthesis [119], and crystal growth [120]. The adsorption of [7]helicene on different surfaces has been investigated in our laboratory [12, 121, 122, 123], it is shown that nature of supporting surfaces can strongly modify the adsorption and geometry of this molecule. In particular, on Ni(100) at the saturated monolayer coverage the molecular helical axis is tilted about 43° with respect to the surface plane [123] whereas it is almost parallel to the surface normal on Cu(111) [12]. It is also found that long-range order of [7]helicene on Cu(111) is only observed at full monolayer coverage [122].

At low coverage, some chiral (or prochiral\(^1\)) species tend to form chain-like structures on substrates. The formation of 1D arrangements can be driven by π − π stacking [103, 125], and hydrogen bonding [124]. It is very common that the chain-like structures are homo-chirally constituted and oriented in some specific direction [126, 127]. While the homo-chiral property can be interpreted as a result of the “three-point contact” model [128, 129] or the coupling motif based on self-complementary helical aromatic units [103], the molecular chains’ orientation has not been quite well understood.

In this work, by introducing two cyano groups, we find that on Cu(111) CHe (Figure 5.1) can form ordered structures even at very low coverage, namely chain-like structures. Furthermore, the molecular chains grow along specific structure; while the so-called M-type (or M-CHe) assembles along a direction rotated -20° with respect to a principal (close packed) direction, the so-called P-type accumulates along a +20° direction. This shows that the supramolecular aggregation is controlled by the cyano groups and molecular chirality. To interpret this phenomenon, we perform density functional theory (DFT) calculations. We first determine the geometry of single molecules at the substrate, and then its adsorption PES. Combining these data with possible structures of the molecular chains in vacuum allows us to determine likely structures of the molecular chains. The molecular spacing is also discussed.

The rest of this Chapter is organized as follows. In section 5.2 the experimental

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\(^1\)Prochiral molecules: “Molecules of appropriately low symmetry, which are achiral as isolated gas-phase or solution-phase species, are described as prochiral if they become chiral when structurally constrained, for example by chemisorption on a surface.” [124].
observations on these systems are briefly presented. Section 5.3 investigates the adsorption properties of single molecules. Next, section 5.4 shows molecular chains in vacuum. In section 5.5, we interpret the chains upon adsorption. Finally, section 5.6 is some concluding remarks.

5.2 Experimental observations

Experimental observations are carried out for both P- and M-CHe on Cu(111). The molecules are deposited at room temperature, systems are subsequently cooled down to 77K. The results at near and full monolayer coverages have been reported in our previous work [130]; for coverage below 0.4 monolayer, chain-like molecular structures are formed at 77 K (see Figure 5.1). A notable observable geometric property is that these chains form an angle of about ±20° with the principal directions of the underlying copper substrate. In particular, the M-CHe molecular chains are oriented at an estimated angle of −20°, and interestingly, the one of +20° is not observed. Oppositely, only +20° directions are observed for P-CHe chains. Each molecule is identified by one lobe in the STM images, inspecting the apparent height profiles of the chains we find that the intermolecular distance is about 13.5 Å.

5.3 Single molecules at Cu(111)

As a first step towards understanding the 1D aggregations of M-CHe molecules (also the same for P-CHe) on Cu(111), we first study isolated molecules - the building block of the molecular chains - adsorbed on the surface using DFT calculations\(^2\). To mimic the substrate, we employ a slab made up with 4 layers of copper, 80 atoms each. The surface unit cell (22.26 × 20.56 Å\(^2\)) is large enough to neglect the interactions between the molecule and its periodic images. In geometry optimizations, only outermost surface atoms and the molecule are relaxed, others are kept fixed in the bulk positions.

Based on geometric considerations, upon adsorption CHe may have “upright standing” and “face-on lying” geometries. The latter can be expected to be predominant due to the considerable interaction between the delocalized \(\pi\)–system of the molecules.

\(^2\)Here we use the \textit{ab initio} scheme presented in Chapter 4.
Figure 5.1: M-CHe(a) and P-CHe(b). STM images are observed at low coverages of M-CHe (c, at 0.09 ML) and P-CHe(d, at 0.06 ML) on Cu(111) (at 1.3V, 20pA and 77 K), substrate principal and molecular growth directions are marked in blue and black lines, respectively. A P-CHe molecular chain (e) and its apparent height profile(f).

and the metallic surface as supposed by the adsorption of [7]helicene on Cu(111) [12]. Additionally, it has been shown that each cyano (-CN) functional group of adsorbed cyanides can strongly bind to a surface atom forming an anchoring point, as described in the adsorption of, for example, tetrafluoro-tetracyanoquinodimethane on Cu(111), tetracyanoethylene on Cu(100), hexaaazatriphenylene-hexacarbonitrile on
5.3 Single molecules at Cu(111)\cite{131, 132, 133}. From this consideration, we set up starting points for geometry optimizations. A procedure exploring a local PES of M-CHe on Cu(111) is presented in the next section. The stable geometries of M-CHe when it is adsorbed in the lying or standing fashion are depicted in Figure 5.2. In the lying structure a cyano group is remarkably bent down to a surface atom with respect to its nearest $\pi$-ring. As it is obvious, there is chemical bonding between M-CHe and the surface through a N-Cu bond of 2.1 Å. Induced charges shown in Figure 5.2.a-b also characterize a weak chemical bond. Figure 5.2.c shows the xy-integrated induced charges. There is a decrease in electron density of the molecule and an increase around the surface region, suggesting some charge transfer from M-CHe to Cu(111). The charge redistribution is a consequence of the N-Cu chemical bond and the Pauli repulsion. This might be the reason why the induced charge is more pronounced in the lying structure as one face of the molecule is nearly parallel to the surface. By calculating $\Delta N = \int_{z_0}^{z_c} \int_{L_y}^{L_y} \int_{L_x}^{L_x} \Delta \rho(x, y, z) dxdydz$ where $z_c$ is the midpoint of the two atoms in the N-Cu bond along $z$ direction and $L_v$ the vacuum region thickness, we find that the molecule loses 0.14 and 0.04 electrons to the surface in the lying and standing configuration, respectively. While a Bader population analysis yields a negligible charge transfer, a Mulliken analysis gives a 0.33 electron reduction in the molecule for both configurations.

The difference in the adsorption geometry leads to different binding energies, namely, -2.0 eV (lying) vs -1.4 eV (standing). This can be attributed to the dispersion interaction between flat lying aromatic molecules and Cu(111)\cite{47, 134} as the adsorption...
energy contribution from each benzene ring is about 0.5 eV. It is also important to emphasize, as pointed out in Chapter 4, that the VdW contribution to the binding of large molecules on surface is extremely important even for chemisorption systems [135], and it can be crucial to the structures of 3D (non-planar) molecules upon adsorption.

5.4 Molecular chains in vacuum

In what follows, we propose some structures of the molecular chains in vacuum mimicking possible arrangements of M-CHe in the molecular wires experimentally observed. Here, the geometry of singly adsorbed molecules is used to sample the PES. Non-trivially, each “unit cell” of the chain is made up with two molecules, allowing us to consider various structures of the chains. The total energy is inspected as a function of two coordinates: one describes the intermolecular distance between two any adjacent molecules along the chain direction (x), and the other designates the one along the direction orthogonal to the chain (y). Details on the these structures are provided in Figure 5.3.

Model 1) This model, shown in Figure 5.3.a, simulates a molecular chain made up with standing molecules, in which the helical axis of the molecules is parallel to the molecular chain direction, reminiscing of the wire-like structure of heptahelicene-2-carboxylic acid on a calcite surface [125]. Principal driving forces here, undoubtedly, are the $\pi - \pi$ stacking between aromatic residues that are mainly contributed by vdw interactions in the DFT description [106, 136]. The equilibrium intermolecular spacing in this model (more precisely, half of the translation vector size along the chain) amounts to 8.6 Å. Moreover, the lateral binding energy per molecule amounts only to -0.06 eV. Aromatic interactions might be important for supramolecular arrangements. Nevertheless, a 13.5 Å periodic spacing experimentally observed can result in a separation of more than 8 Å between two facing aromatic planes of two adjacent molecules, far beyond the typical interaction range of this type of about 3.0 Å [137]. Therefore, we can exclude this model from our considerations.

Model 2) Alternatively, CHe arranges such that cyano groups can participate in the bonding between molecules (Figure 5.3.b). The formation of this structure is mainly based on two anti-parallel CH⋯-NC hydrogen bonds. However, the hydrogen bonding of -0.16 eV is very much smaller than the difference between single adsorption energies
in the lying and standing configurations, i.e., 0.6 eV. Likewise, this structure is unlikely.

_Model 3_ The structure in Figure 5.3.c mimics a lying molecular chain, in which molecules are arranged in a “...head-tail-head-tail-...” fashion (“head” and “tail” stand for the surface-bound and non-surface-bound cyano groups, respectively). This structure is also stabilized by hydrogen bonding, specifically, two antiparallel CH···NC bonds. The optimum distance for this structure in vacuum is 10.3 Å and the corresponding
binding energy is -0.2 eV. This model is a good candidate for the experimental chains.

Model 4) This is a variation of Model 3, however, one molecule in the unit cell is rotated by 180° (see Figure 5.3.d), consequently, arranging molecules in a “...-head-head-tail-tail-...” order. The equilibrium spacing in this case is about 11 Å with a binding energy of -0.15 eV. The lateral displacement between the centers of the two molecules along the direction orthogonal to the chain is about 3.0 Å. This seems not to be a potential model for our experiment, based on the STM images.

Experimental investigations conducted among cyano substituent driven self- assemblies of porphyrins suggest that the cyano groups are involved in the binding in 2D patterns [138], and they play the decisive role in the formation of the molecular chains [139, 140]. On this basis, we firmly believe that these groups are connected with the chain direction in our systems. Furthermore, the hydrogen bonding magnitudes in Model 2,3,4 are almost equal. To this end, we can only conclude that the observed molecular chains is one of two arrangements, that is, Model 3,4, in which cyano groups can contribute to the bonding of the systems and in-chain molecules are adsorbed in the lying fashion. The remaining issue is that the equilibrium intermolecular distance in these models is well below the experimental value, thus calling for some role of the substrate to interpret the “repulsion” between molecules, or more precisely, the elongation of the “unit cell” in the chains.

5.5 Surface effect: an interpretation

Given the observed specific growth directions of the molecular lines, directionality in the adsorption of single molecules must be decisive. To gain the most stable structures of M-CHe upon adsorption as presented in section 5.3, we adopt the following for exploring the PES of the molecule upon adsorption. We assume that the surface atom positions are unchanged; the PES of M-CHe on Cu(111) thus depends, in principle, upon 50 × 3 coordinate components which determine the position of the molecule. The quantity of interest in this particular system is the adsorption direction of M-CHe and the bonding between a cyano group and a surface atom. Figure 5.4 shows α and δ (see the caption for definition) which are used to define the orientation and position of the molecule at the surface.

As expected, deep regions of the PES in both standing and lying configurations cor-
5.5 Surface effect: an interpretation

Figure 5.4: The PES (in eV) of M-CHe on Cu(111) in the standing (a) and lying (b) geometry when the molecule moves in a sextants circular sector (denoted by the transparent pink area in c). $\alpha$ is the lateral angle between a cyano group and a surface principal direction, $\delta$ is the lateral distance between the nitrogen atom in the cyano group and a surface atom. Calculations are carried out with all surface atoms kept fixed, cyano-connected carbon atoms xy-confined, and the rest free. b) shows the PES of the standing molecule, and c) shows the one of the lying molecule.

respond to a small $\delta$ (about 0.5 Å), meaning that preferable N-Cu bonds can form some anchoring point for the adsorption of the molecule. It is also important to note that the shape of the PES is strongly correlated with $\alpha$, i.e., the orientation of the molecule. In particular, for the lying geometry the favorable $\alpha$ is about 40° (or approximately $-20°$ with respect to another equivalent surface principal direction). For the standing case, an $\alpha$ angle of 45° brings in more stable structures (or $-15°$). Our DFT calculations evidently show that the molecule-surface bonding has a chiral character. Unfortunately, there is no available experimental data for the adsorption of single molecules. However, the chiral identification of single molecules has been reported for various systems [129, 141]; due to molecule-surface chemical bonding, adsorbed molecules can be oriented in a specific direction. Keeping in mind that the molecule under present investigation is M-CHe, if we change the chirality of the molecule (so P-CHe), the preference
of the molecular orientation must correspond to an $\alpha$ of about $+20^\circ$. The adsorption orientation of single molecules (characterized by $\alpha$) thus is the same with the molecular chain direction. The correlation between chirality and chain growth direction is consequently driven by the priority of local adsorption and, of course, intermolecular interactions (hydrogen bonding, ...).

Adsorption geometries of single molecules can significantly differ from the ones in a molecular chain [129]. Nonetheless, by considering possible (intermolecular) bonding sites of our molecules and the adsorption orientation ($\alpha$) of single molecules, we are convinced that the molecules in the chains cannot be significantly geometrically modified with respect to single cases. In Figure 5.5 we present a model for the directionality of our molecular chains. Suppose that in there is one molecule in a chain binding to surface site O. An adjacent molecule in the chain can bind to some potential binding surface sites A, B, C, D,... By considering $\alpha$ and $L/2$ of each site with respect to O, we can see that only site A can be in agreement with experimental data. And only Model 3 can be fit with the periodicity considered here.

It is also well recognized in several studies [52, 53, 142, 143] that adsorbed molecules equally charged or the formation of induced dipole moments at molecule-surface junctions can lead to long-range repulsive interactions between adsorbates on metal surfaces. However, the treatment of this electrostatic problem is not unique. For instance, it is suggested that the leading (repulsion) term decays as $1/r$ at some distance of $20-40$ Å [52], it is also believed that this term must decay as fast as $1/r^3$ described by the repulsion between parallel standing dipoles due to the image-charge screening [143]. The (standing) induced dipole moment can mainly be caused by chemical bonding [52] or the Pauli repulsion [142], surface-induced electrostatic forces can therefore be important components in the net interaction between coadsorbed organic molecules. For the system under study, following a description by Kohn and Lau [144] we estimate the induced moment along $z$ by using $\Delta P_z = \int_0^{L_x} \int_0^{L_y} \int_{z_0}^{z_0+L_z} \Delta \rho(x,y,z)(z-z_0) dx dy dz$ ($L_v$ denotes half of the vacuum thickness) which yields a result of $\Delta P_z = 5.3$ D. However, at the spacing of about 13.5 Å the magnitude of the dipole-dipole interaction in this case is just about 10 meV, thus unlikely responsible for the “repulsion” between molecules.

To have an explanation for the long intermolecular spacing, we now consider the effect of the potential energy when the intermolecular and molecule-surface interactions are simultaneously taken into account. In order to investigate the interplay between the
lateral interaction and the role of the substrate corrugation, it is interesting to resort to a model where the two contributions are separated as in the celebrated Frenkel-Kontorova (FK) model [145]. A full two-dimensional calculation of the PES of one adsorbed molecules would be necessary. The problem here, as shown in Figure 5.4, is that for each adsorption site different molecular orientations are possible, with different adsorption energies. Similarly, the lateral interaction between two molecules as computed in Figure 5.3 only focuses on particular mutual orientation, that can be relevant in relation to the experiments.

To simplify the analysis, we proceed in the following way. We have seen that a molecular chain will form along the 20° direction as discussed before. We consider the substrate corrugation along this direction by displacing a single molecule along the OA line in Figure 5.5, and at each position of the binding N atom, constraining the latter’s lateral position and minimizing the energy with respect to all other degrees of freedom. We thus obtain the substrate corrugation profile along the OA direction as shown in Figure 5.6.a.

This corrugation profile along the OA direction is called $V_s(x)$ and has a periodicity of 6.84 Å, with minima at the O point, at the A point and in the middle point in between. The corrugation of this profile is 0.16 eV.

The next ingredient is the pair interaction between two molecules. If the two
molecules are considered in vacuum, we obtain a line along \( \delta y = 0 \) in Figure 5.3, that we report in Figure 5.6.b.

Interestingly, the interaction curve \( V_l(|x_i - x_j|) \) is well fitted by a Morse potential plus a dipole-dipole interaction term with the dipole moment of the order of the computed dipole for this molecule. Now, we can use \( V_l \) and \( V_s \) as ingredients for a one-dimensional FK-like model, where the substrate corrugation, instead of being the traditional sinusoidal curve, is a highly anharmonic \( V_s \) profile we obtain via constrained optimization. We prepare chains of increasing size, and we find that by increasing the size of the chain it is possible to find solutions where large regions of the chain show molecules that are approximately at the distance of 13.67 Å, as dictated by the substrate. Such solutions, however, are always metastable with respect to the ones where the molecules have a distance of 10.7 Å as dictated by the lateral interaction \( V_l \).

It is possible to evaluate the effect of the chain length in the following way. We set an initial and a final state for a chain of \( N \) molecules: a state \( A \) where all molecules are at the distance of 13.67 Å and a state \( B \) where all molecules are at the distance of about 10.67 Å, the global minimum. We treat the problem with the \( V_l + V_s \) potential, and we seek a transition state in the reaction occurring between \( A \) and \( B \) with the NEB method. As shown in Figure 5.7.a, when the chain length is increased from \( N = 2 \) to \( N = 10 \) and to \( N = 20 \), the barrier for leaving the initial state increases to about 0.08
5.5 Surface effect: an interpretation

eV per molecule, an obstacle for the formation of a “compressed” more stable state, at least at low temperatures.

![Diagram](image)

Figure 5.7: a) Energy per molecule along the path between an extended and a compressed state for a chain of $N = 2, 10, 20$ molecules. b) Lateral interaction on the substrate for a molecular dimer with DFT calculations without and with energy optimization, compared with $V_s + V_l$ of the model above.

Although the emergence of the barrier can be seen as an indication that the chain length plays a role in the stabilization of the “expanded” state observed experimentally, the model above needs improvement since it postulates full separation between lateral and substrate interaction.

We recompute the full interaction between two molecules along the OA line using our ab initio method *in presence of the substrate* and we find that without optimization at each point, the system has a global minimum for the dimer at a distance of 13.67 Å as dictated by the substrate. Upon optimization, however, the shorter distance prevails and becomes the global minimum, as observed in Figure 5.7.b. The full DFT calculation, compared with the result of the FK potential separated in lateral and substrate term, shows some differences, namely a different profile of the potential around the global minimum and a slightly smaller separation between the two wells.

We can then subtract the previously computed substrate potential from the optimized curve depicted in Figure 5.7.a, and we find that the lateral potential, pruned by the substrate contributions, now presents a small barrier at $|x_i - x_j| = 11.5$ Å. Using the modified lateral potential in our FK model would not lead to a global minimum
for the average chain distance of 13.67 Å, but nevertheless would add stability to the
metastable state hindering the chain to “jump” into the solution where the molecules
lie at shorter distance. However, by repeating the full DFT calculation with the two
molecules translated by 3 Å along the substrate, we can not reproduce the same profile
of the lateral interaction when subtracting the correspondent substrate contribution.
This shows that the lateral and surface contributions can not be easily decoupled: the
interplay of hydrogen bonding, chemical interaction with the metal and electrostatic
forces hinders a treatment with simplified separated models. However, the indications
above strongly talk for a chain configuration at distance frozen in a metastable state
by the substrate corrugation, with a barrier to getting closer determined by the combi-
nation of chemical lateral and substrate effects.

5.6 Summary

We have presented a study on the nanostructures of CHe on Cu(111) at low coverage.
It is experimentally found that homochiral CHe assembles into chain-like structures,
and that molecular chains grow in a specific direction that forms an angle of roughly
$+20^\circ$ for the M-type and $-20^\circ$ for the P-type to the principal surface direction. Our
DFT calculations predict a “lying” adsorption geometry for CHe upon adsorption. The
calculated PESs show that single adsorbed CHe is oriented in a favorable direction;
together with proposed chains in vacuum, this accounts for the specific orientation of
the chains. For a CHe dimer at the surface, there are two notable minima on the
PES: one, much deeper, corresponding to an intermolecular distance of 10.7 Å, and
one corresponding to 13.67 Å. The FK model shows that the barrier between the two
minima increases if more molecules are added. Given that the chains are formed at
77 K, which might be too low to allow a transition from the second minimum to the
first one. This study provides an example of how important can be the influence of the
surface structure on molecular self-assembly.
Chapter 6

Phenyl-phenyl coupling at Cu(111)

The Ullmann reaction is one of the finest ways to connect two carbon units and plays an extremely important role in modern organic synthesis. There have been many experimental attempts to investigate elementary processes involved in this reaction at metal surfaces, it is however difficult to capture the atomistic picture of those processes. On the other hand, modern electronic structure calculation methods and new computer hardware can offer new insights into molecular systems at a level that is not reachable by present experimental techniques.

In this chapter, we address the coupling process of phenyl radicals - the important intermediates in the prototypal Ullmann reaction - on Cu(111) by using density functional theory and climbing image nudged elastic band calculations. Consistent with experiments, we prove that the fragments interact attractively already at relatively large distances. An intermediate state involving a “popping-out” surface atom is reached through a non-trivial surface diffusion path. The overall process of coupling to the final biphenyl state (with a barrier of 0.38 eV) is governed by a subtle electronic mechanism that reminds the concepts postulated by Hoffmann about the alignment of molecular frontier orbitals with the metallic Fermi level, $E_F$. Our results can be applied to more complex surface processes in the field of molecular self-assembly.

6.1 Introduction

The coupling reaction of halobenzenes to form biaryls catalyzed by copper was first introduced by Ullmann in 1901 [146]. Since these days, this class of chemical reactions
has been a highly interesting topic of catalysis, in terms of both basic understanding and applications. For over a century, it has inspired more than 400 schemes of synthesizing organic molecules [147]. Today, in the rise of nanotechnology it comes to be an influential tool to fabricate nanostructures [63, 148, 149].

Generally, this reaction consists of two steps (here Cu is the catalyst):

\[
\begin{align*}
C_6H_5I + 2Cu & \rightarrow C_6H_5Cu + CuI, \quad (1) \\
C_6H_5Cu + C_6H_5Cu & \rightarrow C_6H_5-C_6H_5 + 2Cu. \quad (2)
\end{align*}
\]

In the first step, (1), the C-I bond is broken, forming the intermediate compound, namely phenyl (C\(_6\)H\(_5\)). The reaction is completed after these phenyl groups couple.

Carried out on several metal surfaces, for various molecular coverages with different precursors (C\(_6\)H\(_5\)-X, X=I, Br and Cl), it has been studied intensively by means of various techniques. The step (1) of this reaction is usually activated by using thermal [150, 151], photon-stimulated [152] and electron-induced [153] treatments. Resulting phenyl groups, the important intermediates in the prototypal Ullmann coupling reaction, are stable on the metal surfaces over a certain range of temperatures, before forming biphenyl molecules in the step (2). The other products of the cleavage, the halogen atoms, diffuse around on the metal surfaces and are desorbed after the recombination of the phenyl groups. The range of temperatures for these processes strongly depends on the nature of substrates. For instance, at sub-monolayer coverages, the step (1) occurs at 175 K on Cu(111) [150, 151], at 200-250K on Au(111) [154] and below 200 K on Ag(111) [152]. By contrast, the biphenyl formation temperatures are higher on Cu(111) (over 300 K [150, 151]), and lower on Au(111) (165-180 K [154]) and on Ag(111) (110 K [155]).

In the recent years, among many fascinating applications that involve the Ullmann reaction, the surface-mediated synthesis of conjugated polymers has attracted particular interest. For instance, a method of synthesizing “porous” graphene\(^1\) with atomic precision [148], the synthesis of polyphenylene molecular wires [149], or the synthesis of nanoribbons\(^2\) have been reported [63]. This field of synthesis potentially offers new opportunities in nano-electronics.

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\(^1\) Porous graphene is modified graphene decorated with a regular array of holes that are terminated by hydrogen atoms. We will see this material again in the next chapter of this thesis.

\(^2\) Nanoribbons are thin strips of graphene or unrolled carbon nanotubes.
But this reaction is not all about one of the finest ways to link two carbon units. Phenyl and its relatives have also served as model molecules to investigate some of the most fundamental issues of surface science, namely surface-mediated interactions and intermolecular forces between molecules adsorbed on surfaces [35].

In spite of the fact that there are numerous experimental studies related to the Ullmann reaction, an understanding of the surface-mediated reaction mechanisms from an atomistic point of view is missing. The questions like “How does phenyl diffuse on Cu(111)?” or “What is actually underlying the formation of phenyl pairs on Cu(111)?” were open to date. Thanks to new advanced numerical methods and computing facilities, quantum mechanical simulations have enabled to describe catalytic reactions in detail, even at a level that is presently not accessible by experiments. It is therefore desirable to have a theoretical investigation collating with previous measurements. As a first step towards understanding the surface-mediated Ullmann reaction, here we investigate, using DFT and NEB calculations, the fundamental steps of the basic coupling between the phenyl groups on Cu(111). The cleavage of the C−X bond (X is a generic halogen atom), a precursor event, is not discussed in the present study. Our findings, concerning the surface diffusion process, the approaching of two phenyl groups and their recombination path to form biphenyl, are compatible with all available experimental data. Furthermore, we explain in detail the mechanism of the reaction and the electronic structure counterpart.

The rest of this chapter is organized as follows. Section 6.2 summarizes important experimental findings and the Hoffmann approach for the study of surface-supported chemical reactions. In section 6.3, we investigate the adsorption of a phenyl group on Cu(111). Section 6.4 presents the surface diffusion of this adsorbate. Sections 6.5 and 6.6 present the interaction between two adsorbed phenyl groups and the coupling between them. Finally, section 6.7 summarizes the content of this Chapter.

6.2 Experimental evidences and a theoretical approach

Among many experimental works devoted to the understanding of the mechanism of the Ullmann reaction on Cu(111), investigations by Xi and Bent [150, 151] are very instruc-
Routinely combining several techniques\(^3\) under an ultra-high vacuum condition they have shown that, at a submonolayer coverage, iodo benzene dissociates at 175 K, the resulting phenyl groups couple at some temperature higher than 300 K while the iodine remains adsorbed until temperatures above 900 K. They have also pointed out that the \(\pi\)-rings of the bi-phenyl products are almost co-planar and parallel to the substrate. However, they have not been able to draw a clear conclusion on the adsorption geometry of the phenyl mediate: whether it is parallel to the surface or tilts away with an angle of 30°. In another effort [156], White and coworkers have claimed, studying the same system at near-saturation coverages using the NEXAFS\(^4\) technique, that this angle is in the 43±5° range. This might suggest that intermolecular interactions can affect the adsorption geometry of phenyl groups. Insights into the the surface diffusion and intermolecular interactions of these groups are offered by the works of Weiss and coworkers [35, 157]. Using STM exploring a very low-coverage system, they have discovered that phenyl groups are mobile on Cu(111) even at a very low temperature (77 K); and that these groups tend to gather to form clusters, mostly pairs. The intermolecular interactions act as driving forces bringing phenyl together and ultimately promote reaction. Studying the problem of phenyl coupling on Cu(111), we borrow the idea from a pioneering work on the recombination of CH\(_n\)(n=1,2,3) fragments at metal surfaces by Hoffmann coworkers [38, 158]. For those C-C coupling reactions\(^5\), they have proposed a comprehensive scheme that it is, in their words,

"...conceptually advantageous to partition each coupling reaction and the energy barrier associated with it into four discrete steps..."

as pictorially presented in Figure 6.1. The first step deals with single reactants on the substrates, in particular, the adsorption and diffusion of the adsorbate are determined. The second step is to understand how two radicals interact with each other when they get close enough and ready to perform the coupling. Next, the third step describes the recombination between the two radicals. In the last step, the products of the reaction are desorbed from the surface. Accordingly, the overall activation energy for a surface-catalyzed chemical reaction is decided by the most costly process. This argument is

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\(^3\) Auger electron spectroscopy, high resolution electron energy loss spectroscopy, temperature-programmed reaction spectroscopy, and work function change measurements.

\(^4\) NEXAFS stands for near edge X-ray absorption fine structure.

\(^5\) This can, in principle, be generalized for any surface-mediated reaction.
6.2 Experimental evidences and a theoretical approach

Figure 6.1: Pictorial representation of the overall formation of phenyl from two phenyl groups on Cu(111): in step i) two isolated reactants diffuse around on the surface, then in step ii) when close enough they start to interact to each other and settle in a position where they are ready to couple, in step iii) the product is formed, it is desorbed in step iv).

important in searching the factor determining the reaction rate.

In this work, we employ DFT calculations within the PBE-D framework with the basis sets described in Chapter 3. The CI-NEB technique is exploited to investigate the rare events involved. The convergence threshold for the maximum force component in geometry optimizations is $10^{-4}$ hartree/bohr. The maximum force component for a band optimization is fixed to $3 \times 10^{-3}$ hartree/bohr. For the NEB simulations we guarantee an adequate separation between consecutive images (less than 1.0 Å) considering up to 16 images. To describe the substrate, we use a slab made up of three 8×6 copper layers with 48 atoms each (test calculations performed including an additional Cu layer revealed that adsorption energies, geometries and activation barriers do not change significantly). In order to avoid interactions between the slab and its periodic images along the direction of the surface normal a 25 Å vacuum region is added. The lateral size of
our unit cell is 17.8×15.4 Å², allowing to mimic a low molecular coverage condition, as reflected by available experiments; the lateral interaction energy among adsorbates and their periodic replicas was verified to be negligible. In all geometry optimizations two innermost surface layers are kept fixed at the bulk positions; the bulk lattice constant is fixed to the model equilibrium value (3.64 Å), consistent with the pseudo-potential in use. For calculations of the reactants in vacuum we use a spin-polarized scheme due to the presence of unpaired electrons; at the surface these electrons pair with Cu electrons, and spin-polarized and non-spin-polarized calculations are practically equivalent as revealed by test calculations. Therefore, all calculations with the surface involved are performed within the non-spin-polarized scheme.

6.3 Single phenyl group adsorbed on Cu(111)

![Figure 6.2: Phenyl and its two most stable structures on Cu(111): a) carbon atoms numbered, the SOMO, and mirror symmetry plane by the dashed line; b) and c) the stable geometries with relative energies; d) the induced charges (iso-surface value = 0.005 au) in the most stable configuration: accumulation (red) and depletion (blue).](image)

For convenience, we number the carbon atoms in phenyl from 1 to 6 (Figure 6.2). Phenyl, which is an open-shell system, possesses a singly occupied molecular orbital (SOMO); it can accordingly strongly bind to metal surfaces. From our calculations, this orbital is almost localized at the carbon atom numbered 1, thus determining the adsorption geometry of phenyl. As reported for the case of different coinage surfaces

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6From a molecular orbital point of view, the SOMO of phenyl is an unpaired sp² orbital of carbon C₁.
6.3 Single phenyl group adsorbed on Cu(111)

A remarkably observed feature is that the phenyl group, rather than oriented in a flat-lying fashion, is adsorbed in such a way that the π-ring is substantially inclined, making it possible to form a metal-carbon(M-C₁) σ-bond.

After optimizing several starting structures, we obtain the two most stable geometries of phenyl on Cu(111) (Figure 6.2.b-c). In the lowest energy configuration, C₁ is nearly located at a hollow site with the SOMO pointing towards a copper atom. The tilt angle of the phenyl plane with respect to the surface is 36°, in agreement with experiment and a recent theoretical study [159]. The Cu-C₁ bond-length, amounting to 2.04 Å, is very close to the covalent contact distance of 2 Å, giving a sign to a strong chemical bonding between phenyl and the surface. Upon adsorption, some of intramolecular geometric parameters of phenyl are significantly modified. Particularly, the C₁C₂ (C₁C₆) bond-length (1.43 Å) is 0.05 Å longer than the pre-adsorption correspondence, as a result of the fact that the formation of the Cu-C₁ bond makes the intra-molecular bonds weaker. The C₆C₁C₂ angle also varies from 126° (in vacuum) to 114° (on the substrate). Additionally, the π-ring is no longer completely planar as the C₄C₃C₂C₁ dihedral angle is about 1°. Concerning the second most stable structure, C₁ is located at a bridge site with the π-ring entirely in the plane. This geometry can be against the vdW interaction between phenyl and the surface. However, this might possibly be favorable for sp³ hybrid orbitals in carbon C₁. Here we do not go further in describing properties of this configuration. We shall see it again in the next section as it takes part in the surface diffusion process of phenyl.

To have a deeper insight into the adsorption of phenyl at Cu(111), we now analyze the electronic properties. As clearly shown in Figure 6.2 the induced charges upon adsorption mainly occur in the region around C₁ and its copper bonding partner. A pronounced accumulation of electrons in between these atoms implies a strong covalent character of the chemical bond. The pre-adsorption SOMO level of phenyl is 0.94 eV below the Fermi level of Cu(111), as a result there is a transfer of 0.35 electrons from the copper substrate to phenyl. A PDOS analysis, presented in a section below, also reveals a strong hybridization between the SOMO and metallic d-band states. These elucidate an adsorption energy of -1.8 eV of phenyl on Cu(111). This energy justifies the fact that phenyl is never desorbed from the surface at the temperature range of the reaction as experimentally observed.
6.4 Surface diffusion of phenyl

Assume that phenyl is initially located at a favorable position (Figure 6.2.c) where C_1 binds to Cu_0 as sketched in Figure 6.2.a. Since phenyl experiences a translational and rotational symmetry potential, there are many possibilities proposed for the diffusion mechanism. Because the system under study is strong chemisorption, it can reasonably be assumed that phenyl is likely to perform “short” jumps, i.e., from Cu_0 to one of adjacent surface atoms (Cu_{1-6}). For the sake of simplicity the present position of phenyl is called the initial state (IS), an equivalent position when phenyl completes a jump is called the final state (FS). As an initial guess for the NEB simulation of a reaction pathway, we adopt a linear interpolation of the nuclear coordinates between IS and FS.

![Figure 6.3: Phenyl binding to Cu_0 and migrating to one of the adjacent surface atoms which are in grey (a), direct transition requires a high activation energy, for example, a direct Cu_0-Cu_6 transition has a 0.40 eV migration energy (b). The indirect transition via an intermediate is energetically favorable (c).](image)

We first consider the Cu_0-Cu_6 transition (equivalent to Cu_0-Cu_5). Because direct transitions always bring in a complete C_1-Cu_0 bond breaking or a strong C_1-Cu bond distortion in the process, they require a very high activation energy as calculated (for example, see Figure 6.3.b). We notice that the difference in energy between the two most stable structures of phenyl on Cu(111) is small (Figure 6.2), if the transition between them needs some lower activation energy then a second most stable structure can act as an intermediate for Cu_0-Cu_6 transitions (which accordingly consist of at least two consecutive “small” steps). Figure 6.3 shows this mechanism for a Cu_0-Cu_6 transition which has an overall migration energy of about 0.1 eV. Please note that in the IS-IM step the C_1-Cu_0 bond is not completely broken, the transition state (TS) of
this step closely resembles IM which is not too much less stable than IS. This is the reason why the barrier in this case is very low compared to the ones of the direct cases. Owing to the fact that phenyl is still mobile on Cu(111) at a low temperature, our calculations agree well with experiment.

Direct Cu$_0$-Cu$_4$ and Cu$_0$-Cu$_2$ transitions are also energetically unfavorable. The rationale is similar to the Cu$_0$-Cu$_6$ case. Furthermore, these transitions are geometrically connected to a long move of phenyl which usually make phenyl pass some high energy meta-stable states.

Therefore, the indirect IS-IM-FS pathway can be viewed as the basic mechanism underlying the migration of phenyl between any two sites on Cu(111).

6.5 Phenyl-phenyl interaction on Cu(111)

On Cu(111), two adsorbates can interact with each other at a distance of some nanometers due to a surface-state band [49]. However the magnitude of this interaction is just of a few meV so that we do not consider it in this work.

Let us consider two well separate phenyl groups approaching each other, several geometries with both of them situated at the favorable position of single ones have almost the same energy but otherwise when they bind to two adjacent surface atoms (Figure 6.4.b-e). To this stage, by carefully optimizing all (reasonably) possible configurations we find that lower energies can only obtained if each of the adsorbates is in the single adsorption structure, signifying that adsorbate-substrate interactions are still decisive. Eventually, both of them stick to the same surface atom (Figure 6.4.f) and the global minimum of the two separate phenyl groups is reached.

In Figure 6.4.g we rationalize the variation of the total energy with respect to the C$_1$-C$_1$ distance$^7$. Clearly, the total energy on average decreases with respect to the distance, in agreement with the STM observation described above.

However, the most stable configuration (Figure 6.4.g) could be seen as counter-intuitive since two fragments share the same metal atom. First, as mentioned in Chap-

$^7$The C$_1$-C$_1$ distance is considered as a “reaction coordinate” for the phenyl-phenyl coupling reaction. The relative orientations of two phenyl groups are not clearly relevant. Moreover, the dashed line is of central interest since it represents the lowest energies when two phenyl groups bind to neighboring surface atoms and they are mostly located in a face-to-face fashion.
Figure 6.4: (a-f) some of optimized structures where both fragments are located at the energetically favorable of single ones: d indicates the C1-C1 distance, E indicates the energy relative to the lowest one. g) shows the energy against the C1-C1 distance: each red circle implies the energy and the distance of an optimized structure, the dashed line drawn merely for the configurations a-f. A (B) corresponds to structure f(b) and A’(B’) corresponds to structure f(b) with the substrate kept fix in the optimization.

ter 2 when a substrate atom is bound to one phenyl group, it can become more inert with respect to the other one, and the total adsorbate-substrate bonding might consequently be weakened. Second, the two phenyl groups are equally polarized by the surface, and the electrostatic repulsion come therefore to be likely. Third, we find that the shared surface atom is 0.6 Å lifted up from its initial equilibrium position, accordingly decreasing the surface cohesion. To resolve this paradox, we analyze two structures presented in Figures 6.4.b and 6.4.f which, for simplicity, we call structure B and structure A, respectively. Structure A is 0.3 eV more stable than structure B while the corresponding C1-C1 distance is 3.2 and 4.8 Å. Let us consider the following.

i) As the understanding of gas-phase systems would enrich the information about adsorption systems, we examine the interactions between two phenyl groups with their coordinates taken from structures A and B. Single point energy calculations reveal that the system of two close phenyl groups (we call A-vacuum) is 0.3 eV more stable than the other one (B-vacuum). The factor responsible for this difference is the wave function overlap between two groups. Figure 6.5.a shows the induced charges of these structures.
In the upper panel, no charge redistribution is yielded in B-vacuum, and the reason is that the C$_1$-C$_1$ distance of 4.8 Å is practically too large for orbital interactions. However, we can clearly see a modification of the electron density in the case of A-vacuum, despite a somewhat large C$_1$-C$_1$ distance of 3.2 Å, the wave function interference between two phenyl groups is thus already entered.

We further calculate the single point energies of the surface in structures A and B without the adsorbates. The popping out surface atom makes the cohesion of the surface 0.27 eV less stable. Thus, the total energy contribution from the dimer and from the surface is almost the same in both structures. Consequently, the difference is attributed to the adsorbate-substrate interactions.

ii) By relaxing structures A and B in such a way that all the surface atoms are kept frozen in their pre-adsorption positions (hence the shared atom in structure A is not allowed to move up), we obtain completely different results: structure A now (A’ in Figure 6.4) becomes less stable than B (B’ in Figure 6.4). Hence the shared copper atom is of central importance. This configures an intermediate situation between the bonding
of isolated phenyl groups to the surface and the final surface-supported biphenyl: in this intermediate set of distances, an additional source of electrons is necessary, represented by the popping out surface atom.

To be more specific we further analyze the electronic structure of (fully relaxed) structures A and B. In structure B, each phenyl is bound to a surface atom, just like in the single phenyl case (see Figures 6.2.d and 6.5.c). PDOS onto surface atoms and the phenyl dimer in Figure 6.5.e shows a hybridization between molecular orbitals and metallic states. It is however much more pronounced in structure A. The popping out Cu atom actively participates in the bonding with a “bridge” between the two C₁ carbon atoms. As revealed by Figure 6.5.e in the energy range of -4 $\div$ -2 eV, PDOS of the phenyl dimer and the atom closely resemble each other, i.e., the hybridization is more evident. Moreover, the metallic states in this case are more pushed down compared to in the case of structure B. The reason is, as mentioned in Chapter 2, that a surface atom becomes more chemically reactive when it is popping out. By further calculating the single point energy for structures A and B with only one phenyl group, we find that structure A is 0.1 eV less stable, however, the loss in stability of the surface alone due to the displacement the shared atom is 0.27 eV. It follows that the gain in bonding of a phenyl-Cu(111) junction due to the shared metal atom lifted is roughly 0.17 eV, and of a phenyl dimer is approximately 0.34 eV, consistent with energy difference in structures A and B. Therefore, the adsorption stability due to the lifting up of the shared atom can overcome the loss of coordination within the metallic surface. In other words, the local restructuring enhances the covalently bonded interactions between the adsorbates and the substrate. The net gain in energy upon closing up of the two fragments is an expression of the favorable balance between the loss of coordination and the enhanced reactivity of the out-of-plane copper atom. We note that a minor role could also be played by the attractive vdW interactions.

An issue is still missing in the description of the diffusion of the phenyl groups at the surface: if we consider two phenyl groups in structure B we have to understand how they could reach structure A. Obviously, they can not reach the final geometry by repeating the favorable diffusion pathway of phenyl on Cu(111) (section 6.4). For this case (the diffusion from structure B to structure A) we investigate only one pathway which consists of two small steps and obtain an overall barrier of about 0.09 eV.
6.6 Phenyl-phenyl coupling

We now discuss the final coupling step leading to the formation of an adsorbed biphenyl (Figure 6.1.iii). We set up a NEB calculation where the starting point is structure A (Figure 6.4.f). As the \( C_1-C_1 \) distance is quite large, using a linear interpolation as a guess for the NEB trajectory could result in a starting point too far from the optimal path. Therefore to obtain a reasonable guess, we perform a series of geometry optimizations constraining the \( C_1-C_1 \) separation from its initial value of 3.19 Å down to 1.50 Å. The FS configuration is then obtained by fully relaxing the last component of the constraint optimization series. Geometries obtained by this series of constraint calculations constitute the input for the NEB calculation.

![Diagram of reaction pathways and energy landscape](image)

Figure 6.6: Pictorial representation of the two reaction pathways mentioned in the text and the energy landscape: pathway_0 starts from the most stable geometry of pre-coupling phenyl groups and pathway_1 starts from a metastable state, the energy profile shows that pathway_1 cannot occur as the from the metastable geometry the system can easily reach the initial state of pathway_0. In other words, pathway_0 reflects coupling mechanism of the two phenyl groups.

The snapshots in Figure 6.6 (top panel) display pathway_0, which reveals that the
two reactants equally move toward each other along the reaction pathway. This can be viewed as a result of the nearly symmetric arrangement of the reactants about the surface normal crossing the shared copper atom. The tilt angle of the phenyl rings varies from 30° (IS₀) to 22° (TS₀) and 0° (FS₀) with the corresponding C₁-C₁ distance of 3.19, 2.34, and 1.49 Å. The simulation results show that the coupling of two phenyl fragments is strongly exothermic, i.e., the enthalpy of the system is decreased by 1.9 eV, according to the Hammond postulate (Chapter 2) TS₀ of this reaction closely resembles IS₀, consistent with the structural parameters above. Once the TS₀ is reached, the tilt angle and the total energy quickly decrease. The activation energy for this process is 0.38 eV, which is in line with the experimental finding that the onset temperature for the coupling is over 300 K, this low reaction barrier might be understood as a result of the similarity in geometry (and in the electronic structure) between IS₀ and TS₀. The energy barrier for the reverse pathway of 2.28 eV, which is much higher than the 1.3 eV adsorption energy of biphenyl on Cu(111), indicates that the biphenyl decomposition leading back to two reactants is unlikely: the molecule is rather desorbed than decomposed on the surface. By comparison, we find that in the gas phase the enthalpy gain with respect to the two separate radicals is 4.9 eV and the event is barrierless.

Is it possible that two separate phenyl groups can couple without visiting the most stable geometry (IS₀)? To address this question we perform a series of NEB calculations with several starting points (ISs) when the two reactants bind to two adjacent surface atoms and to the same surface atom⁸. A pathway with the lowest activation energy (0.29 eV), called pathway₁, is presented in Figure 6.6 (middle panel). However, we notice that the barrier for the system to move IS₁ to IS₀ is just 0.04 eV. Consequently if it was at IS₁ at a certain time, it would rather move to IS₀ than to FS₁. Armed with the fact that the two reactants are highly attractive on the surface and they can easily reach for their global minimum IS₀, we believe that the reactants do not directly couple when they bind to two neighboring surface atoms, alternatively, they should bind to the same copper atom, in the SI₀ configuration, before completing the recombination. Obviously, the attractive interactions between the two phenyl groups on the surface - the driving forces bringing the two reactants close together - are extremely important factors in determining the mechanism of biphenyl formation.

⁸Keep in mind that IS₀ is just one case when the two phenyl groups bind to the same surface atom.
Analyzing the electronic evolution of the system along the reaction pathway can provide further insight into reactant-substrate and reactant-reactant interactions. To this end, we inspect the frontier molecular orbitals (FMOs) for gas phase dimers in the same configurations of the adsorbed molecules in $I_{S_0}$, $T_{S_0}$ and $F_{S_0}$. Then we compute the projection of each state of the corresponding adsorbed systems $I_{S_0}$, $T_{S_0}$ and $F_{S_0}$ on the gas phase FMOs; we can thus extract the state with the closest character to the FMOs of the gas phase. Concerning $I_{S_0}$, the highest occupied molecular orbital

(HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecules in the gas phase (Figure 6.7) show the sigma-bonding ($\sigma$) and sigma-antibonding ($\sigma^*$) characteristics, respectively. On the surface, states with this character are both positioned below the Fermi level, $E_F$. This is also verified by the amount of charge that the reactants receive from the metal. In $T_{S_0}$, the $\sigma^*$ shape of the gas-phase LUMO seems to remain the same (compared to the one in $I_{S_0}$), however, states of the full system with this character rise in energy with respect to $E_F$, in correspondence to a back donation from the molecules to the substrate. Unlike the LUMO, the gas phase HOMO becomes a $\pi$ state with antibonding character ($\pi^*$), signaling the onset of the conjugation and of the biphenyl formation. States with the character of the $\sigma$-like gas-phase HOMO of $I_{S_0}$

Figure 6.7: a) FMOs (HOMO and LUMO) of the reactants in vacuum (top panel) and the states of the full system that show maximum projection on them (PHOMO and PLUMO) in $I_{S_0}$, $T_{S_0}$, and $F_{S_0}$. Energy is relative to $E_F$. b) Amount of charge gained by two phenyl groups in pathway from the Bader analysis.
in this stage (the TS$_0$ configuration) are thus pushed down to a much lower energy level. In FS$_0$ biphenyl is formed, the $\pi$-antibonding characteristic of the gas phase HOMO is unchanged. However the LUMO appears to be a $\pi$-state with bonding character ($\pi$) above $E_F$. The state with $\sigma^*$-LUMO of TS$_0$ is now pushed up to a higher energy region.

In many respects, this description is similar to the model for alkyl coupling on a metal surface proposed by Hoffmann [38]: along the reaction pathway, the C-C antibonding state (IS$_0$-LUMO) is pushed up above $E_F$, signaling a back-donation to the surface. However, from our calculations, in the TS$_0$, this antibonding state delocalized around $E_F$, and the reactants are still charged by 0.3 electrons (Figure 6.7.b).

### 6.7 Summary

Performing DFT and NEB calculations we have described the mechanism of diffusion of phenyl on Cu(111) and explained the experimentally observed low-temperature mobility. We analyzed the reaction process toward an intermediate state involving a bridging, “popping out” copper atom. Finally, we computed and discussed the final pathway leading to the formation of the planar biphenyl. With respect to the literature hypotheses about the overall activation energies, we found a lower barrier of 0.38 eV, which could in turn lead to a lower reaction temperature with respect to the experimentally observed, 300-400 K. Our results could be effected by the limitations of transition state theory or of the particular density functional approximation adopted here, and, similarly, the estimates about activation barriers derived from experimental desorption data are always problematic. More importantly, we found a viable mechanism through which in the reaction the presence of the Cu(111) surface promotes this fundamental reaction. Through the projection of the electronic ground state on selected molecular orbitals calculated in the gas phase, we verified the applicability of Hoffmann’s concepts about bonding and antibonding orbitals and their alignment with the metallic Fermi surface, and discovered that in this case the situation is more complex: when the reactants are far apart the HOMO and the LUMO involve, as expected, the bonding and antibonding orbitals built from the radical carbon atoms. As the reaction proceeds, the conjugation typical of biphenyl acquires importance; the bonding in the gas phase would be favored by a twist of one group with respect to the other; here instead, the surface allows the complex to adopt planar configuration; at the same time, the former
LUMO gets emptied as suggested by Hoffmann. In summary, we delivered a complete description of a simple yet still not understood reaction and we believe that the same conclusions can be applied to more complex systems of technological and fundamental interest.
Chapter 7

Polymer formation at surfaces

Understanding of surface mobility and coupling ability of reactants is the key factor to design structures of low-dimensional polymers on metal surfaces. In this Chapter we present, by combining experimental (scanning tunneling microscope) and theoretical (density functional theory - DFT, nudged elastic band - NEB, and Monte Carlo - MC) techniques, a study on surface-assisted assembly of the hexaiodo-substituted macrocycle cyclohexa-m-phenylene (CHP) toward covalently bonded polyphenylene networks on three (111) coinage metal surfaces. Experiment shows that room temperature (RT) dehalogenation of CHP on the surfaces leads to surface-stabilized CHP radical (CHPR) and co-adsorbed iodine atoms. Subsequent formation of covalently bonded molecular networks among CHPRs is thermally activated and found to proceed at different temperatures on the three surfaces. While a well defined and dense polyphenylene networks are formed on the silver surface, the networks are dominated by open branched structures are observed on the copper surface, on the gold surface the molecular structures are mixed by these features. DFT and NEB calculations reveal that the surface diffusion of CHPRs on Ag(111) is much more frequent than on Cu(111), in contrast to this, the coupling between them is easier on the copper surface. MC simulations prove that the different balance between diffusion and coupling determine the structures of molecular networks. Our results demonstrate that the choice of the substrate is crucial in the surface-mediated formation of two-dimensional (2D) polymers.
7.1 Introduction

Hydrogen bonding, surface metal coordination and aromatic coupling motifs are big deals in fabricating molecular nanostructures on surfaces [19, 41]. However, a common problem of supramolecular nanostructures built in those ways is, due to the comparably weak interaction energies, the poor thermal and chemical stability that would limit their uses in potential applications. The obvious requirement for more stable structures has recently led to great interest in covalently bonded 2D molecular networks [160]. Various proof-of-principle studies have demonstrated that different reactions readily proceed on surfaces, even though the reactants are confined to two dimensions [149, 161, 162]. However, despite the recent progress, the self-assembly organized growth toward extended and regular 2D covalent networks still defines one of the major challenges in surface chemistry. A partial explanation for this situation is related to the fact that the formation of covalent intermolecular bonds, in contrast to noncovalent bonding, is usually an irreversible process; therefore, molecules confined to covalent structures on surfaces are firmly anchored, and post-correction of defects or modification of morphology is usually not possible. Thus, to minimize defects in covalent networks and to steer the on-surface synthesis toward desired structures, a detailed understanding of the influence of adsorption energies, diffusion barriers, and lateral interactions of molecular precursors, all of which depend on the substrate atomic environment, symmetry, and chemical nature, is required. Up to the present day, however, there exists little experimental and computational insight into the role of the substrate in on-surface chemical routes toward 2D covalent networks.

In this Chapter, we present the impact of the substrate on the formation and connectivity of a 2D polymer. Recently, experimentalists in our lab have used a prototypical multidentate molecular precursor, namely, hexaiodo-substituted macro-cycle cyclohexa-m-phenylene (CHP), and exploit covalent intermolecular bond formation on the coinage metal surfaces Cu(111), Au(111), and Ag(111). On either surface, the adsorption of CHP at RT results in C-I bond cleavage, giving rise to the formation of surface-stabilized CHPRs and coadsorbed iodine atoms. Thermally activated CHPR-CHPR coupling is found to proceed at different temperatures on the three metals, notably at about 475 K (Cu), 525 K (Au), and 575 K (Ag). The morphology of the resulting polyphenylene networks differs significantly: On Cu(111), the growth of den-
dritic network structures with single-molecule-wide branches prevails; the Au surface promotes the evolution of small 2D network domains, and on the Ag(111) extended and well-ordered 2D networks emerge. Using density functional theory (DFT), nudged elastic band (NEB), and Monte Carlo (MC) calculations, we elucidate the nature of surface-stabilized CHPR (CHP radical), as well as the details of diffusion and reaction pathways. We find that on the copper substrate, diffusion of CHPR is hindered, while the coupling step is significantly promoted. On the silver surface, on the other hand, CHPR retains a high surface mobility but exhibit a low coupling affinity. We demonstrate that these differences are responsible for the formation of dendritic and 2D polyphenylene networks as observed on the copper and silver surfaces, respectively.

The rest of this Chapter is organized as follows. Section 7.2 summarizes major experimental findings. In section 7.3, we verify the dehalogenation process on Cu(111) by analyzing energetic properties and comparing experimental and simulated STM images. Section 7.4 represents the adsorption of CHPR on the copper and silver surfaces. Surface diffusion of CHPR on the two surfaces are addressed in section 7.5. Next, section 7.6 describes the coupling between two CHPRs. A MC explanation for the different shapes of the polymer networks is given in section 7.7. Finally, some discussions and concluding remarks are presented in sections 7.8 and 7.9.
7.2 Experimental observations

STM observations are conducted at different temperatures, exploring two basic chemical phenomena illustrated in Figure 7.1. At RT, where CHP is deposited at the metal surfaces, the dehalogenation process already occurs. Figure 7.2.a shows an overview STM image of CHP molecules adsorbed on Cu(111) that was held at this temperature. CHP agglomerates to small islands of a few molecules, which are distributed over the terraces. Individual molecules can only be spotted along the step edge. The inset in Figure 7.2.a shows a high-resolution STM image of CHP. A line profile analysis across the molecules yields a center-to-center distance of about 1.6 nm, which, in comparison with a theoretical CHPR-CHPR model, indicates that the CHPs are not covalently bonded under the applied experimental conditions. Around each CHP, bright spherical features can be discerned, which are distributed evenly around the molecules. The distance between these features is about 1.8 nm, which is significantly more than the value of the distance between two diametrically opposite CHP iodine atoms (1.5 nm). Furthermore, careful inspection of Figure 7.2.a shows that not all molecules are surrounded by such features and that some of the latter are “shared” by multiple molecules (see, e.g., the three islands marked by white circles). The position as well as the distribution of the spherical features thus suggest C-I bond cleavage upon adsorption of CHP on Cu(111) at RT\(^1\). On the silver and gold surfaces, line profile analyses also reveal that at RT separation of iodine atoms and CHPR are observed and CHPRs are yet to be connected.

The subsequent formation of covalently bonded networks is based on thermally activated aryl-aryl homocoupling. Figures 7.2.b-c summarize some experimental findings, which give strong evidence for covalent intermolecular bond formation. It is clear that coupled and uncoupled CHPR species as well as iodine atoms on the Cu(111) surface are observed at the same instant. A prominent domain of uncoupled radicals surrounded by iodine atoms is highlighted in the image (Figure 7.2.b, white circle). A line profile analysis of adjacent species reveals CHP-CHP distances of 1.24 and 1.56 nm (Figure 7.2.c), indicating that CHPR-CHPR coupling starts to occur at about 475 K on Cu(111). Different annealing temperatures to initiate intermolecular bonding on

\(^{1}\)This indicates that C-I bonds can be dissociated at some temperature lower than RT, thus, similar to the case of iodobenzene.
the other surfaces are also identified, that is, 525 K (Au) and 575 K (Ag). This implies that the nature of the surface plays an important role in intermolecular coupling. The morphology of the resulting polyphenylene networks are notably different: On the copper substrate, branched low-density clusters with single-molecule-wide branches prevail (Figure 7.2.d). On the other hand, on the gold surface the homocoupling of CHP leads to a mixture of branched and denser polyphenylene clusters as can be identified in Figure 7.2.e. Figure 7.2.f eventually shows that dense and highly ordered networks extend on the silver substrate.

### 7.3 C-I dissociation on Cu(111)

Gas phase CHP is a non-planar molecule. This can be seen as a consequence of the steric repulsion among some of hydrogen atoms constituted in CHP. Upon adsorption it becomes planar as revealed by our calculations. As mentioned above, experimental evidences suggest that CHP is decomposed into adsorbed CHPR and adsorbed iodine atoms at some temperature lower than RT as experimentally indicated. To verifying this
argument we perform DFT calculations\(^2\) and compare the experimental and simulated STM images.

![Figure 7.3: Adsorption of CHP on Cu(111) (a), adsorption of CHPR and six iodine atoms on Cu(111) (b) with the corresponding simulated STM image (c); configuration in (b) is about 5.0 eV more stable than the one in (a). CHPR surrounded by six Cu ad-atoms (d), the ad-atoms attached to CHPR (e) with the corresponding simulated STM image (f); configuration in (e) is 3.5 eV more stable than the one in (d). Experimental STM image (-2 V, 20 pA) of two CHP molecules on Cu(111) (g) with a model of the molecule overlaid and drawn to scale; detached iodine atoms (in light violet) that assemble around the surface-stabilized CHPRs. Energetic and geometric properties from calculations (a-f) show that only structure (b) and experimental observation are in agreement.](image)

The first hint for the dissociation of the C-I bonds in CHP on Cu(111) is that the \([\text{CHPR}+(6)\text{I}+\text{Cu}(111)]^3\) complex (Figure 7.3.b) is about 5.0 eV more stable than the one of \([\text{CHP}+\text{Cu}(111)]\) (Figure 7.3.a). Given that iodobenzene, which can be seen as a sub-unit of CHP, is decomposed into phenyl and iodine at some temperature 175 K \([150]\). Additionally, CHP and iodobenzene \([151]\) are adsorbed on Cu(111) in the

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\(^2\)All DFT calculations presented in this Chapter are carried out within the LDA framework. For these particular systems, we also carry out PBE-D calculations however LDA results are more “experimentally” favorable. The metal surfaces here are described by a slab of three layer of metal atoms, only the outer-most surface atoms are relaxed. The used unit cells are large enough to minimize the interaction between adsorbates and their periodic images.

\(^3\)The adsorption of CHPR on Cu(111) is described in the next section, I is adsorbed on the surface at a hollow site.
7.4 Adsorption of CHPR on Cu and Ag

same fashion, i.e., parallel to the surface. It can therefore be expected that the C-I bonds in CHP are broken already at some sub-RT. Moreover, the spacing between two diametrically opposite iodine atoms of CHP upon adsorption (Figure 7.3.a) amounts to 15.5 Å which cannot account for the distance of 1.8 nm experimentally observed. On the other hand, simulated results from the configuration with “detached” halogen atoms well agrees with the experimental data (Figures 7.3.b-c,g).

For the sake of completeness, we now show that the atom giving rise to each bright protrusion discerned in the STM images (Figures 7.2.a, 7.3.g) is an iodine atom rather than any other adatoms\textsuperscript{4}, and that there are no copper adatoms participating in the formation of the 2D polymers. Suppose that there exist surface ad-atoms, in contrast the iodine case, in the case of surface adatoms the “detached” ad-atom structure (Figure 7.3.d) is 3.5 eV less stable than the “attached” ad-atom one (Figure 7.3.e). Furthermore, copper ad-atoms are very mobile on Cu(111)\textsuperscript{5}. Accordingly, if there exist surface ad-atoms they are likely to be attached to CHPR, in the structure presented in Figure 7.3.e. Nevertheless, the simulated STM image of this structure (see Figure 7.3.f) is not experimentally favorable, the distance between two (centers of) the farthest bright protrusions of 1.53 Å is well below the experimental counterpart.

7.4 Adsorption of CHPR on Cu and Ag

We optimize several structures of CHPR on the two metal surfaces without considering the presence of the iodine atoms\textsuperscript{6}, the high symmetry geometry of CHPR allows us to choose its center as the reference point, i.e., it can be located at the on-top, bridge or hollow sites on the substrates. For each position of the CHPR center, we also consider different structures regarding the molecular rotation with respect to the surface. Some lowest energy cases are presented in Figure 7.4.

The most stable geometry is the same on both surfaces: at an on-top position, and each diameter (i.e., connecting two diametrically opposite carbons) of CHPR is 19° off

\textsuperscript{4}In fact, on a metal surface there can exist atoms of the same kind (or adatoms). In principle, these atoms can participate in the bonding of adsorbed molecules.

\textsuperscript{5}Our extra NEB-CI calculations within DFT show that the migration barrier of an iodine or a copper ad-atom is about 0.1 eV.

\textsuperscript{6}Iodine atoms in principle can affect the adsorption of CHPR, however the CHPR-M (M=Ag,Cu) covalent bonding is very much stronger than non-covalently bonded CHPR-I interactions.
Figure 7.4: Three lowest energy structures of CHP on the copper (a-c) and the silver (d-f) surfaces: energy is relative to the lowest one; atop, bridge, hollow sites indicate the position of the center of CHPR on the surface, and the surface atoms in gray are merely for guidance.

a) on-top; 0.0 eV  
b) bridge; 1.8 eV  
c) hollow; 2.0 eV

d) on-top; 0.0 eV  
e) bridge; 0.1 eV  
f) bridge; 0.2 eV

A significant difference between the two substrates in this case is that Ag(111) is considerably locally distorted while Cu(111) is almost unaffected. This can be understood as the following. Geometrically, the copper surface is commensurate with the (lateral) size of CHPR while the silver one is not comparable. More specifically, on the copper surface each of the six CHPR carbon atoms with dangling bonds can find one surface bonding partner such that the C-Cu bond length is close to the “best” one\(^7\) and the phenyl rings are tilted about 30° with respect to the surface, thus facilitating the carbon-metal bonds as mentioned in Chapter 6. On the silver surface the circumstance is very different due to a huge mismatch between the surface surface lattice and molecular size. The surface bonding partners of the six carbon atoms are lifted up by 0.7 Å from equilibrium positions. To elucidate this effect we optimize the

\(^{7}\)The C-Cu bond length in this case is similar to the one in a phenyl-Cu(111) system.
7.4 Adsorption of CHPR on Cu and Ag

CHPR-Ag(111) system with all substrate atoms kept fixed in their bare-surface positions. The resultant C-Ag bond length of 2.8 Å is notably larger than 2.3 Å - the one with the full optimization. We note that lifting a silver atom 0.7 Å from its equilibrium position on Ag(111) costs 0.46 eV while elongating the C-Ag bond in a phenyl-Ag complex from 2.3 to 2.8 Å requires 1.07 eV (see Figure 7.5). On this basis, it is likely that in the CHPR-Ag(111) system the six atoms are elevated in order to reduce the stretch of the C-Ag bonds.

Another notable difference is that the potential energy surface of CHPR on Ag(111) seems to be much flatter. Geometry optimizations show that the second lowest energy structure on Cu is much less stable than the lowest energy one (1.8 vs 0.0 eV) whereas they are almost the same on Ag (0.1 vs 0.0 eV). This can be understood as a consequence of, again, the lattice mismatch. Figure 7.5 indicates that for Cu(111) either the elevation of surface atoms or elongation of the C-Cu bonds needs a significant amount of energy. In the structure presented in Figure 7.4b some C-Cu bonds are deformed and two surface atoms elevated by 0.3 Å from the surface equilibrium positions. Dissimilarly, on Ag the low stability due to unfavorable C-Ag bonds and reduced surface cohesion seem remains the same from the lowest energy structure to the other one. This is an important element considering the mobility of CHPR on the surfaces, we shall come back to this detail in the next section.

We now estimate the adsorption energy of CHPR on the metal surface. Here we adopt a simple approximation, this energy is given by $E_{\text{ads}} = E_{\text{bound}} - E_{\text{separated}}$, where $E_{\text{bound}}$ is the lowest energy of CHPR on M(111), $E_{\text{separated}}$ is the total energy of the two individual systems, i.e., the surface-mimicking slab and CHPR held in the middle of the vacuum region. The adsorption energy amounts to -15 (-11) eV for the Cu(Ag) case, implying that CHPR is never desorbed. This also shows that CHPR is more stable on Cu(111).

The difference in adsorption energy (-15 vs -11 eV) between the two surfaces is mainly related to the local restructuring of the surface and the nature of the chemical bonds C-Cu and C-Ag in the systems. As pointed out in Chapter 2, the position of the $d$-band (more precisely, the band center) is an important factor determining the

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8Results in a) are obtained by optimizing the systems such that the height of the selected atom with respect to the surface is unchanged for each value of $h$. Likewise, in b) geometry optimizations were carried out with the C-M bond kept fixed at a length $d$. 
100 Polymer formation at surfaces

Figure 7.5: Energy vs the vertical displacement of an atom of Ag and Cu surfaces, $E_0 (h_0)$ denotes the energy (position) of the system (the atom) at equilibrium (a). Energy vs C-M bond length (M is a Cu or Ag atom) in the phenyl-M complex, $E_0 (d_0)$ denotes the energy (bond length) of the system (the C-M bond) at equilibrium.

Figure 7.6: Induced charges in the CHPR-Ag and CHPR-Cu systems (left panels): isosurface of 0.005 a.u, accumulation charges(red) and depletion charges(blue). PDOS onto the d-states of metal atoms (right panel): Ag-bound (also Cu-bound) stands for a surface atom binding to a carbon atom (C-bound), Ag-unbound (Cu-unbound) indicates an outer-most layer surface atom far-away from CHPR.
reactivity of $sd$ metal surfaces. It is clearly shown in Figure 7.6 that the copper $d$-band center is closer to the Fermi level (black curves), thus giving rise to stronger bonding to CHPR. Due to interaction with CHPR, the $d$-states of six bound copper atoms are shifted down while the ones of bound silver atoms are almost unchanged (blue curves). Induced charges (Figure 7.6) suggest orbital hybridization between CHPR and metal surface is also more pronounced in the copper case.

### 7.5 Surface diffusion of CHPR

To determine the diffusion mechanism of CHPR on the copper and silver surfaces, we perform NEB calculations, in which the images between two minima of the band are generated by linear interpolating these minimum energy coordinates. Assume that CHPR is initially located at its most stable position IS, i.e, the on-top$_1$ geometry on both surfaces (Figures 7.4.a, 7.4.d), then it moves to a nearest equivalent position FS, i.e., an adjacent on-top surface atom. Because of six strong chemical C-M bonds CHPR is unlikely to perform “long” jumps. Upon chemisorption, surface diffusion of large species is a generally complicated process. Taking a closer look at the symmetry of CHPR and the two (111) surfaces in the lowest energy configuration, we need to consider only one transition from one on-top surface atom to one of its six neighboring atoms\(^9\).

As mentioned in Chapter 2, there are possibilities of the migration resulting from the translation (and rotation) of CHPR on the substrates. CHPR is adsorbed on the surfaces in a face-to-face fashion, in which each unpaired $sp^2$ orbital of CHPR can practically interact with the Fermi sea. Because of this, it can be expected that in the migration process CHPR is not tilted up with respect to the surface plane. We first examine the direct translation assuming a translation of CHPR. This mechanism results in an activation energy of $3.5$ eV on Cu(111) and $0.9$ eV on Ag(111). The high migration energy in the copper case is possibly a direct consequence of the fact that all six C-Cu bonds are simultaneously strongly distorted in TS. In the silver case we also observe the same attribute (carbon-metal bonds become less energetically favorable), however, most “popping out” metal atoms are closer to their surface equilibrium position, leading

\(^9\)In fact there are two different groups of three equivalent atoms. However, the difference between hcp-hollow and bcc-hollow sites is negligible.
to a lower barrier compared to the copper case. We then investigate a more tricky

![Graph showing energy levels and reaction coordinate for diffusion of CHPR on Cu(111) and Ag(111)]

Figure 7.7: Diffusion of CHPR on Cu(111) and Ag(111): to migrate from one position IS (the most stable geometry, on-top) to another one FS (a nearest equivalent geometry) CHPR visits an intermediate state IM (the second most stable geometry, bridge). The two elementary steps are associated with the rotation of CHPR about an unbroken C-M (M=Cu, Ag) bond. The colored surface atoms are merely for guidance, arrows indicate rotational directions. The overall diffusion energy of CHPR is 2.2 and 0.8 eV on Cu(111) and Ag(111), respectively.

scenario where the molecular rotation (more precisely, the rotation of molecular center) is entered. This introduction leads to the involvement of some intermediate structure, like the case of phenyl on Cu(111) presented in Chapter 6. Of several diffusion routes, the most energetically feasible one is sketched in Figure 7.7. This migration pathway consists of two consecutive steps: from IS to an intermediate IM, and from IM to FS. In each step, the center of CHPR rotates about an unbroken C-M bond from the on-top position to the bridge position or vice versa. Our calculations reveal that the diffusion energy of CHPR on Cu now is 2.2 eV. TS in the IS→IM transition closely resembles the second lowest energy geometry of CHPR on Cu(111), leading to this lower activation
energy compared to 3.5 eV in the direct transition. On Ag we also obtain a slightly lower migration energy barrier of 0.8 eV.

To this end, CHPR is found to be obviously more mobile on the silver surface. Relatively low migration energy barriers (0.8-0.9 eV) and the less corrugated potential energy surface allow CHPR to move more frequently on Ag. This is an important argument considering the morphology of polymers on different surfaces as we shall see below.

### 7.6 CHPR-CHPR coupling

Now, we investigate the covalent intermolecular bond formation between two CHPRs on Cu(111) and Ag(111). In order to do that, the proper definition of the starting configuration is crucial. Similar to the study of phenyl-phenyl coupling presented in Chapter 6, we begin with some configurations in which two CHPRs start to interact with each other. IS is shown in Figures 7.8.a and 7.8.f, where two CHPRs are anchored to on-top\textsubscript{1} sites and separated by two atomic rows of the metal substrate. After collecting several possible reaction pathways, we find that the system always passes through IMs in which the two CHPRs bind to two adjacent surface atoms or a common metal atom. The final step of the reaction is given by covalent bond formation between the CHPRs. Note that in this FS the macrocycles of the CHPR-CHPR pair are both located on energetically favorable on-top\textsubscript{1} sites (Figures 7.8.e and 7.8.j). The NEB calculations reveal that intermolecular CHPR-CHPR coupling follows similar reaction pathways on Cu(111) and Ag(111), including diffusion steps toward IMs, and final covalent bond formation toward FS. However, inspection of the corresponding configurations and the energy diagrams of the reaction pathways depicted in Figure 7.8.k reveal striking differences between the two substrates. These differences, as discussed in the following, are related to a CHPR-induced surface restructuring and the matching of CHPR with respect to the metal surface lattice. Along the path from IS to FS, one CHPR performs a rotation around an unbroken C-metal bond, while the other one is is kept unmoved with respect to the surface atomic lattice. This mimics a diffusing molecule encountering and eventually binding to an “immobilized” network cluster (which, in this case, is represented by a single molecule). In our NEB calculations, in any transition only the minima are fixed, while the other images of the band are allowed to fully relax.
Figure 7.8: CHPR-CHPR coupling reaction pathway on the copper (a-e) and silver (f-j) with potential energy surface presented in (k). Colored surface atoms are merely for guidance: atoms in gray indicate the position of CHPR center and atoms in light violet indicate adjacent metal atoms or the same surface atom CHPRs bind to.
The initial step of the overall coupling process is determined by the diffusion of a “free” CHPR toward the first intermediate state IM₁ (Figures 7.8.b and 7.8.g) and is activated by significantly different energies, notably 2.2 eV on Cu(111) and 0.8 eV on Ag(111) (just like in the surface diffusion of isolated CHPR). The relative energy between IS and IM₁ for both surfaces is closely related to the position of the moving CHPR (in IM₁ it is at the bridge₁ position), if we compare this energy with the one in the single CHPR case we shall see that the interaction between two CHPRs is not noticeable to this end.

Further diffusion with small activation energies of 0.3 eV (Cu) and 0.1 eV (Ag) transfers the system toward the second intermediate state IM₂. On the silver surface, IM₂ is considerably more stable than IS, where the two CHPRs are well separated. The energy difference between the two configurations can be explained by the rearrangement of atoms in the outer-most metal surface layer when the two CHPRs bind to a common surface atom (Figure 7.8.h): in IM₂ the CHPR-induced surface restructuring is significant, and an elevation of 1.7 Å is DFT predicted for the “shared” surface atom and of 0.7 Å (or less) for the others directly binding to CHPRs. The effect of atomic elevation here is two-folded. On one hand, in IM₂ twelve surface atoms are lifted up while only eleven in IS. On the other hand, despite that in IM₂ the shared metal atom is significantly elevated, some of the others are moving down; moreover, the C-(shared)Ag bond length is similar to the free C-Ag bond length of the phenyl-Ag complex (2.0 Å, see Figure 7.5), and importantly, the shared atom becomes less coordinated to neighboring metal atoms, then eventually leading to stronger C-Ag bonds, reminiscing of a phenyl dimer on Cu(111) presented in Chapter 6. On the copper surface, the geometry of the CHPR-surface complex is nearly unaffected upon the transition from IS to IM₂. Moreover, because of the calculated distance between CHPR hydrogen atoms of only 1.8 Å intermolecular H···H repulsion results in a slightly higher energy of IM₂ (2.8 eV) as compared to IS (2.5 eV).

The following two steps toward CHPR-CHPR coupling again reveal important differences on the two surfaces: on Cu(111), intermolecular bond formation is essentially barrierless and readily occurs from IM₂ to IM₃, which reflects a favorable configuration and intermolecular distance for bond formation. However, inspection of the IM₃ shows that there is substantial stress on the CHPR-CHPR bond, and the system thus relaxes toward the favorable on-top₁ configuration in FS with an activation energy of 1.7 eV.
On Ag(111), on the other hand, the configuration and intermolecular distance between the two CHPRs in the IM\(_2\) state are obviously less favorable for intermolecular coupling. In the IM\(_2\) → IM\(_3\) transition, the moving CHPR rotates about a surface atom from the energetically favorable atop to a bridge site, requiring a significant amount of energy to pass a barrier of 1.8 eV. Here, in IM\(_3\) the two C-(shared)Ag bonds are strongly distorted; and this is, probably, the reason why IM\(_3\) is much less stable than IM\(_2\). Eventually, bond formation and relaxation to atop sites in FS proceed readily with a barrier of 0.2 eV.

The calculations thus strongly indicate that the difference between the two substrates with respect to 2D polymer formation is related to the favorable and less favorable matching of CHPR to the copper and silver surface lattices, respectively, and to the different chemical reactivities of Cu and Ag as discussed above.

### 7.7 Covalent network growth: MC simulations\(^{10}\)

To better understand the origin of the significantly different network morphologies, we use a generic MC process to simulate the diffusion and assembly of molecules on a hexagonal surface lattice. Briefly (Figures 7.9.a-c), a seed molecule fixed to the center of the lattice serves as nucleation site, and the subsequent growth of network clusters is based on iterative addition of CHPRs. The CHPRs are free to perform a random walk on the simulation grid; when they reach a possible binding site, their affinity to join the seed or a cluster is given by the coupling probability \(P\), which can be interpreted as the ratio between the reaction rate of the coupling step and the total number of events, that is, coupling and diffusion, according to \(P = \frac{\nu_{\text{coupl}}}{(\nu_{\text{coupl}} + \nu_{\text{diff}})}\), where \(\nu_{\text{coupl}}\) and \(\nu_{\text{diff}}\) denote the reaction rates for the coupling and diffusion steps, respectively. Very high or low coupling probabilities readily allow the following inference on the reaction rates for coupling and diffusion: \(P \approx 1\) if \(\nu_{\text{coupl}} \gg \nu_{\text{diff}}\) and \(P \approx 0\) if \(\nu_{\text{coupl}} \ll \nu_{\text{diff}}\).

Figures 7.9.d-f display simulated network clusters of 400 CHPRs by using coupling probabilities \(P = 1, 0.1,\) and \(0.01\), respectively. For a more quantitative description, a histogram showing the coordination number distribution of the CHPRs is appended below each cluster. In the growth regime corresponding to \(P \approx 1\), a diffusing molecule

\(^{10}\)by Oliver Gröning
Figure 7.9: Illustration of the MC process used for network growth simulations (top panel): a) A seed CHPR is fixed at the center of a hexagonal lattice (the arbitrarily defined (0,0) site) of a rhombic super cell; at the vertices of the seed, six equivalent coupling sites (in red) are defined. b) After performing a random walk a second CHPR visits the seed and binds to the latter with the coupling probability $P$. c) Once a CHPR couples to the seed (in this example at the (1,0) site) new occupation sites at the (2,1), (2,0), and (1,-1) grid points become available. d-f) Coupling probabilities of $P=1, 0.1,$ and 0.01, respectively, are used for the growth of clusters consisting of 400 CHPRs (in a 70×70 rhombic super cell); the corresponding coordination number distribution of the CHPRs in the cluster is given (bottom panels).
immediately sticks to the cluster when and where it hits the cluster. Note that this condition is equivalent to the classical diffusion-limited aggregation (DLA) model [163] that was applied to study metal-particle aggregation processes. As a consequence, characteristic branched “fractal-like” polyphenylene network structures with single-molecule-wide branches develop (Figure 7.9.d). By lowering the coupling probability by 1 order of magnitude, the evolution of denser network domains can be discerned (Figure 7.9.e). Eventually, compact network formation occurs for $P=0.01$ (Figure 7.9.f). Thus, by gradually increasing $\nu_{\text{diff}}$ and reducing $\nu_{\text{coupl}}$, denser network clusters emerge. This can readily be understood with simple reasoning: To promote the formation of compact structures, CHPRs must diffuse along the borders of islands and eventually occupy higher coordinated sites, a process that requires a high mobility and/or low coupling affinity of the reactants. However, it is equally important to notice that even under favorable growth conditions, defects discernible as “holes” in the clusters (Figures 7.9.e-f) occur. These defects arise when six CHPR units join at their meta positions to a circle. Because molecules are not allowed to cross over island borders, these defects persist in the clusters. These theoretical findings are in excellent agreement with experiment; “holes” with a characteristic star-shape pattern can easily be spotted within domains of the polyphenylene networks grown on Au(111) and Ag(111) (Figures 7.2.e-f). More importantly, the sequence of the presented cluster simulations is in excellent agreement with the polyphenylene-networks grown on Cu(111), Au(111), and Ag(111) (compare Figures 7.2.e-f and 7.9.e-f), which clearly points to different growth regimes for the covalent assembly of CHPRs on these surfaces.

### 7.8 Discussion

The difference in geometrical matching and chemical reactivity of Cu(111) and Ag(111) has noticeable implications on the energy diagram of the overall reaction pathway. On Cu(111), the initial diffusion process (2.2 eV) is the rate-limiting step. Once this barrier is overcome, the reaction is predicted to proceed spontaneously because the path toward intermolecular bond formation (IM$_3$) is essentially barrierless and the 1.7 eV required to relax the system is significantly lower than bond breaking (2.3 eV for IM$_3 \rightarrow$ IM$_2$) and backward diffusion (2.0 eV for IM$_2 \rightarrow$ IM$_1$). Therefore, the surface-mediated polymerization on Cu with hindered diffusion and favored coupling corresponds ideally
to the regime of diffusion-limited network formation, which explains why the branched clusters predicted by MC simulations for this growth regime are in excellent agreement with experimental observations on Cu(111). Conversely, on Ag(111) the energy diagram shows that CHPR coupling is the rate-limiting step: Once the initial diffusion barrier of 0.8 eV is overcome, the system readily reaches IM$_2$, and backward diffusion with individual barriers of 0.9 (IM$_2$ $\rightarrow$ IM$_1$) and 0.8 eV (IM$_1$ $\rightarrow$ IS) is favored over covalent bond formation (1.8 eV), leading to an overall increased mobility of the molecules.

Here, a few more comments on the experimental conditions are required. The discussed formation of polyphenylene networks is obviously based on the self-assembly of molecules deposited on a surface. For metal aggregation processes, it was shown that the growth conditions and thus the morphology of the resulting clusters can be addressed by varying the deposition rate and substrate temperature. Thus, to have unbiased conditions, our experimentalists used an identical and low deposition rate for all experiments reported here. Concerning temperature effects, we find no significant modifications of the network morphologies after performing the polymerization at different annealing temperatures. On the basis of the calculated energy diagram for CHPR-Cu(111), network growth is diffusion-limited and is thus not expected to change at higher temperatures. On the Ag surface, only at very high temperatures will the coupling probability increase. The barriers resulting from DFT reveal that diffusion-limited growth cannot be promoted by temperature.

A final important point in this discussion is the effect of coadsorbed iodine on the reaction mechanism. For verification, different sample preparation procedures were applied, in particular inducing the polymerization in a postannealing step or by immediately preparing the sample above the desorption temperature of iodine (not possible on Cu without the risk of surface degradation). Briefly, we find no evidence for iodine-induced network modification. This is consistent with previous findings on methyl radical coupling where the reaction pathways in the presence and absence of iodine remained unchanged [164]. These and our results thus suggest that the predominant effect of the halogen is to block surface sites and not to participate chemically in the coupling reaction. Collective electrostatic or indirect interaction effects mediated by the substrate might, however, contribute in reducing reaction barriers, which would require further theoretical investigation.
7.9 Summary

We have investigated the adsorption and self-assembly of CHP on (111) surfaces of coinage metals. In agreement with STM analysis, DFT calculations (performed for Cu(111)) show that the adsorption of CHP follows a dissociative pathway with selective C-I bond cleavage, resulting in coadsorbed iodine and the evolution of surface-stabilized CHP radicals. Subsequent covalent intermolecular bond formation between CHP radicals toward covalently bonded polyphenylene networks was investigated. DFT and NEB calculations unveil that the diffusion process is dominant on Ag(111) while intermolecular coupling is ruling on Cu(111). This was interpreted as a result of the difference in lattice constant (geometry) and chemical reactivity (electronic structure) between the two surfaces: the surface lattice of Cu(111) is more commensurate with the size of CHPR, and Cu(111) is also more reactive than Ag(111). MC simulations reveal that a high mobility (or low coupling affinity of the reactants) is a prerequisite for the growth of dense 2D polymer networks. All the simulations thus fully explain the experimental observations, that is, fractal-like structures on Cu(111) and extended, regular 2D networks on Ag(111), which can be envisaged for realistic applications such as nanofilter [165]. However, the simulations also clearly indicate that even under favorable growth conditions defects in the network clusters have to be expected, demonstrating that surface-supported 2D polymers based on irreversible reactions are inherently limited with respect to their structural perfection. Our results demonstrate that the substrate not only acts as a static support but that it is actively involved in all reaction steps and significantly influences the morphology of self-assembled covalently bonded nanostructures.
Chapter 8

An approach for the polarization effects in QM/MM calculations

An implementation of the classical polarization within a quantum mechanics / molecular mechanics (QM/MM) method, designed for physisorbed systems where metal surfaces are involved, is presented. While the molecules are dealt with by QM and the surfaces by MM, the molecule-surface interaction is described by a pairwise potential and electrostatic interactions. Here, the polarization is described through a set of varying Gaussian charges (centered at metal surface sites) which are induced by the charges of the supported molecules. The Gaussian charges are determined by a macroscopic condition that the potential is the same at each site of the metal surface [J. Chem. Phys., 102:511-524, 1995]. This implementation, based on the CP2K package, is built in a self-consistent fashion in which the induction charges and molecular charges mutually modify each other. A test system of 1-nitronaphthalene at Au(111) is discussed.

8.1 Introduction

For very large systems a full quantum mechanical description (such as DFT) can be computationally demanding. Classical simulation methods can be a solution, however, what they provide can be much less accurate. We thus have to search for new strategies like, for example, the quantum mechanics / molecular mechanics (QM/MM) hybrid scheme [166]. The QM/MM formulation is based upon the accuracy of QM and the
An approach for the polarization effects in QM/MM calculations

speed of MM; the main idea is that the simulated system is divided into two parts: one is treated with quantum mechanics (QM), and the other is treated with molecular mechanics (MM). Of course, we employ QM to study the part (of the system) directly related to the properties we want to investigate; as an example, for the interaction between a small molecule and a macromolecule, it is suitable treat the small molecule and the nearby part of the macromolecule quantum mechanically. The interactions between QM and MM regions are usually treated by MM. This formulation comes to be popular among simulation methods in biochemistry, biophysics [167], nevertheless, to our knowledge, it is applied for only a few organic/solid interfaces [168, 169].

For surface-assembly problems, adsorbates are usually the subjects of interest. In the QM/MM framework, if the molecule-surface interaction is not electronically strong (physisorption for instance), we can assign the solid surfaces as the MM part and molecules as the QM part. The standard way to describe molecule-surface interactions in this case is using some force field. Nonetheless, elementary force field methods do not (implicitly) capture a classical phenomenon: polarized molecules can interact with the charges in the metal surface that they induce, i.e., the image charge effect. Importantly, taking into account the polarization phenomenon in the MM region can lead to significant changes in simulation results [170, 171]. Finally, the image charges, in principle, can affect the structural and electronic properties of adsorbed molecules. It has been recently shown that an image-charge potential is a key factor determining the assembling behavior of organic molecules on metal surfaces [53, 143]. In the QM/MM formulation, the role of the image charges can be classically described as an external Coulomb potential applying on the QM region (molecules). And in turn, the modification in the molecular electronic structure (then molecular charge distribution) induces “new” image charges. It is therefore noticeable that these charges are variables in any molecular dynamics processes of the molecules. An approach for polarized charges is thus needed. Of several models of image charges for classical force field that have been addressed in literature [172, 173, 174], the Gaussian charge method developed by Siepmann and Sprik [172] meets this requirement.

This motivates us to treat the physisorption problem within a QM/MM approach in a more precise way. In this Chapter, we present an implementation of the polarization in QM/MM simulations applying for 1-nitronaphthalene(NN)-Au(111) interfaces. We adopt the Siepmann-Sprik scheme as a classical treatment for the charge polarization
8.2 The QM/MM formulation

In QM/MM calculations, the effective Hamiltonian of the system is given by:

\[ H = H_{\text{QM}} + H_{\text{MM}} + H_{\text{QM/MM}}, \]

(8.1)

where \( H_{\text{QM}} \) and \( H_{\text{MM}} \) are the Hamiltonians of the QM and MM regions, respectively; \( H_{\text{QM/MM}} \) denotes the interaction between the two.

The \( H_{\text{QM}} \) term is dealt with using \textit{ab initio} techniques, e.g., DFT. The \( H_{\text{MM}} \) term can be given by some standard force field, which has the following form [177, 178]:

\[ H_{\text{MM}} = H_{\text{MM, bonded}} + H_{\text{MM, non-bonded}}, \]

(8.2)

where \( H_{\text{MM, bonded}} \) describes the bonded parts of the region taking harmonic bond, angle and dihedral terms into account:

\[ H_{\text{MM, bonded}} = \sum_{\text{bonds}} \frac{k_b}{2} (R_{ij} - R_{ij}^{eq})^2 + \sum_{\text{angles}} \frac{k_\theta}{2} (\theta_{ijk} - \theta_{ijk}^{eq})^2 + \sum_{\text{dihedrals}} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)], \]

(8.3)

where the first (right hand side) term represents the energy between covalently bonded atoms, the second one describes the energy owing to the geometry of wavefunctions in covalent bonding; and the last one details the energy due to twisting a bond where \( \phi \) is the dihedral angle and \( V_n \) is the corresponding force constant, \( \gamma \) is the phase angle.

\( H_{\text{MM, non-bonded}} \) describes the non-bonded energy between all atoms pair considering van der Waals \( (A_{ij}) \), London \( (B_{ij}) \) and electrostatic (between partial atomic charges \( Q_i, Q_j \))
energies:

\[ H_{\text{non-bonded}}^{\text{MM}} = \sum_{j<i} \left( \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + Q_i Q_j \right). \] (8.4)

The complication of QM/MM methods is the coupling between QM and MM regions. This is especially the case when the QM/MM boundary crosses some covalent bond; for such a problem, some specific treatments such as “link atoms” [179] have been proposed. Here we address a simpler case, in which \( H_{\text{QM/MM}} \) in (1) contains all non-bonded contributions between them; it may be written as [180]:

\[ H_{\text{QM/MM}} = -N_{\text{QM}} \sum_i M_{\text{MM}} \sum_j Q_j \frac{1}{r_{ij}} + M_{\text{QM}} \sum_i M_{\text{MM}} \sum_j Z_i Q_j \frac{1}{R_{ij}} + M_{\text{QM}} \sum_i M_{\text{MM}} \sum_j \left( \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} \right), \] (8.5)

where \( N_{\text{QM}}, M_{\text{MM}} \) indicate the number of electrons, nuclei of the QM region, respectively; \( M_{\text{MM}} \) is the number of MM atoms, the first and second terms in the left hand side thus describe the electrostatic interaction between the two subsystems. The last term of (5) stands for dispersion interactions.

### 8.3 Electrostatic induction in metal surface systems

Let us consider a system of point charges located above a metal substrate. Suppose that the surface is an ideal conductor, then its dielectric constant is infinite, and at each \( \vec{r} \) point inside the metal the potential must, from a macroscopic point of view, be a constant [172]:

\[ V(\vec{r}) = \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} = V_0, \] (8.6)

where \( \rho(\vec{r}) = \rho_{\text{perm}}(\vec{r}) + \rho_{\text{ind}}(\vec{r}) \), \( \rho_{\text{perm}}(\vec{r}) \) is the “source” charge density inducing the charges \( \rho_{\text{ind}}(\vec{r}) \) in the metal, and constant \( V_0 \) is the potential applied on the metal.

In the approach by Siepmann and Sprik for a system of water molecules at metal surfaces [172], while the partial atomic charges of molecules are considered as point charges, the charge distribution at each metal site is given by a Gaussian function of width \( 1/(\eta \sqrt{2}) \)

\[ \rho_i(\vec{r}) = q_i (\pi \eta^2)^{3/2} \exp \left[-(\vec{r} - \vec{r}_i)^2 \eta^2 \right], \] (8.7)

where \( q_i \) are induced charge magnitudes to be determined and \( r_i \) is the coordinate of
Combining equations (8.6, 8.7) leads to:

\[ V_i + q_i \sqrt{\frac{2}{\pi} \eta} = V_0, \tag{8.8} \]

where the potential at site \( i \) is:

\[ V_i = \sum_a q_a \frac{\text{erf}(|\vec{r}_i - \vec{r}_a| \eta)}{|\vec{r}_i - \vec{r}_a|} + \sum_{j \neq i}^{\text{ind}} q_j \frac{\text{erf}(|\vec{r}_i - \vec{r}_j| \sqrt{2 \eta})}{|\vec{r}_i - \vec{r}_j|}. \tag{8.9} \]

This scheme has been expanded for periodic systems [181]. In Ref. [181], the potential given below is derived by combining an Ewald summation technique proposed by de Leeuw and Perram [182] and the electrostatics formulation of Siepmann and Sprik. Consider a system of \( n_g \) surface atoms (i.e., the number of Gaussian centers) and \( n_p \) point charges, the periodicity of the system is characterized by two orthogonal vectors \( \vec{a} \) and \( \vec{b} \). The potential at site \( j \) is:

\[
V_j = \sum_{i}^{n_p} q_i \sum_{k,l=-\infty}^{\infty} \frac{1}{r_{ijkl}} \text{erf}(r_{ijkl} \gamma) + \sum_{i}^{n_g} q_i \sum_{k,l=-\infty}^{\infty} \frac{1}{r_{ijkl}} \text{erfc}(r_{ijkl} \beta)
\]

\[
+ \frac{2}{ab} \sum_{i}^{n_p} q_i \sum_{k,l=-\infty}^{\infty} \int_{-\infty}^{\infty} dh \frac{1}{4 \pi^2 |k|^2 + h^2} \times \exp \left[ -\frac{(4 \pi^2 |k|^2 + h^2)(\alpha^2 + \eta^2)}{4 \alpha^2 \eta^2} \right] \cos(2 \pi \vec{k} \cdot \vec{r}_{ij,xy} + h z_{ij})
\]

\[
+ \frac{2}{ab} \sum_{i}^{n_g} q_i \sum_{k,l=-\infty}^{\infty} \int_{-\infty}^{\infty} dh \frac{1}{4 \pi^2 |k|^2 + h^2} \times \exp \left[ -\frac{(4 \pi^2 |k|^2 + h^2)(2 \alpha^2 + \eta^2)}{4 \alpha^2 \eta^2} \right] \cos(2 \pi \vec{k} \cdot \vec{r}_{ij,xy} + h z_{ij})
\]

\[
- \frac{2}{ab} \sum_{i}^{n_g} q_i \left[ \frac{\sqrt{\pi}}{\beta} \exp(-z_{ij}^2 \beta^2) + z_{ij} \pi \text{erf}(z_{ij} \beta) \right]
\]

\[
- \frac{2 \beta q_j}{\sqrt{\pi}} + \frac{\sqrt{2 \eta} q_j}{\sqrt{\pi}}.
\]

Here, \( 1/\alpha \) is the Ewald smearing parameter; \( \beta = \eta \alpha / (\eta^2 + 2 \alpha^2) \), and \( \gamma = \eta \alpha / (\eta^2 + \alpha^2) \); \( r_{ijkl} \) denotes the distance between atom \( i \) in cell \( (k,0) \) and atom \( j \) in cell \( (0,l) \) in the 2D
periodicity scheme, \( \overline{r}_{ij,xy} \) and \( z_{ij} \) stand for the \( xy \) and \( z \) components of the \( \overline{r}_{ij} \) between atoms \( i, j \) in the same cell, respectively. The \( \sum' \) notation implies that the \((0,0)\) cell is omitted from the sum.

### 8.4 Image charge contribution to the total energy

According to Siepmann and Sprik [172] and Reed et al. [181] the condition described in the previous section for obtaining image charges relies on a minimum principle about the total Coulomb energy of a system.

However, we shall first focus on the expression of the electrostatic energy within the QM/MM formalism of CP2K [175, 176], with some reformulation. Firstly, we recall the expression for a QM/MM total energy [176]:

\[
E_{\text{TOT}} = \frac{1}{2} \int \int \rho(r) \rho(r') \frac{1}{|r - r'|},
\]

(8.11)

where \( \rho = \rho_{\text{QM}} + \rho_{\text{MM}} \), and the total energy can be split into three terms which, neglecting the problem of neutrality and the introduction of background charge, are:

\[
E_{\text{QM}} = \frac{1}{2} \int \int \rho_{\text{QM}}(r) \rho_{\text{QM}}(r') \frac{1}{|r - r'|},
\]

(8.12)

\[
E_{\text{MM}} = \frac{1}{2} \int \int \rho_{\text{MM}}(r) \rho_{\text{MM}}(r') \frac{1}{|r - r'|},
\]

(8.13)

and

\[
E_{\text{QM/MM}} = \int \int \rho_{\text{QM}}(r) \rho_{\text{MM}}(r') \frac{1}{|r - r'|}.
\]

(8.14)

We note that this energy is equivalent to the energy of the “dynamical system” discussed in Ref. [181], namely the usual interaction energy, where \( \rho_{\text{QM}} \) is considered as classical point charges and MM part which is represented by image charges. Reed et al. derive the energy with respect to the image charges, set the result to a constant value, and this gives the linear system corresponding to the zero energy condition. The functional is derived with respect to the “QM” coordinates, and this gives the forces on the QM charges (point charges in this case). The image charge derivatives with respect to the coordinates are not considered, in view of a “Hellmann-Feynman principle” which is
not clearly stated in this case.

The main point of this section is the investigation of the energy and force terms: indeed papers on classical electrostatics [183] correctly point out that image charges implicitly depend on the position of real charges, and when computing the total energy of the system, namely the work done by bringing all charges to their final position and all metals to the prescribed potential, this dependence should be taken into account. This leads to a factor $\frac{1}{2}$ in the total energy, to the prescription of not considering the interaction energy among image charges (this is a consequence of the conductor condition of the metal) and even to a different sign in the energy related to the externally fixed potential of the conductor [184]. We shall show here that such modifications to the total energy are automatically taken into account within this scheme, and that the forces are correctly computed when the image charges are derived from a minimum principle.

We start from the simple case of a non-periodic system considered by Siepmann and Sprik. The extension to the periodic case, carried out by Reed et al. does not affect the following derivation.

We now rephrase some parts of the equation (8.14) in order to factorize the potential that must be set to zero on the image charge location.

The total electrostatic energy will include the interaction of the Gaussian charges, which also includes a term of interaction of each Gaussian with itself. This is a very important point. As also discussed in Ref. [181], this self-energy-like term must be included, because the charges are really gaussianly distributed, at variance with Ewald schemes where the smearing is only a mathematical tool to improve or reach convergence.

Therefore, the total energy of the system is

$$ U = U^{QM} + U^{MM} + U^{QM/MM}, \quad (8.15) $$

$$ U^{QM} = \frac{1}{2} \int dr \frac{\rho^{QM}(r)\rho^{QM}(r')}{|r - r'|}, \quad (8.16) $$

$$ U^{MM} = \frac{1}{2} \sum_{i,j; i \neq j}^{img} q_i(\rho^{QM}) q_i(\rho^{QM}) \text{erf}(|r_i - r_j| \eta) \frac{q_i^2 \eta}{|r_i - r_j|} + \sum_i \frac{q_i^2 \eta}{\sqrt{\pi}}, \quad (8.17) $$
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\[ U_{\text{QM/MM}} = \sum_i q_i(\rho^{\text{QM}}) \int dr \frac{\rho^{\text{QM}}(r) \text{erf} \left( |r_i - r| \sqrt{2\eta} \right)}{|r_i - r|}, \]  

(8.18)

we note that the electrostatic MM and QM/MM energies are the same \( E^{\text{MM}} \) and \( E^{\text{QM/MM}} \) in CP2K (and of course the QM energy). The condition of zero potential at each Gaussian charge site is obtained by

\[ \frac{\partial U}{\partial q_i} = 0 \quad \forall i, \]  

(8.19)

leading to

\[ V_i + \frac{q_i(\rho^{\text{QM}})\sqrt{2\eta}}{\sqrt{\pi}} = 0 \]  

(8.20)

and

\[ V_i = \int dr \frac{\rho^{\text{QM}}(r) \text{erf} \left( |r_i - r| \sqrt{2\eta} \right)}{|r_i - r|} + \sum_{j \neq i} \text{imag} q_j(\rho^{\text{QM}}) \text{erf} \left( |r_i - r_j| \eta \right). \]  

(8.21)

The second term in the right hand side of (8.21) stems from the interaction of the system of image charges. Note that the dependence of the image charges on the quantum density has been explicitly stated. We can easily see that the following equivalence holds:

\[ 0 \equiv \frac{1}{2} \sum_i q_i(\rho^{\text{QM}}) V_i = \frac{1}{2} E^{\text{QM/MM}} + E^{\text{MM}}. \]  

(8.22)

But since the left hand side is zero as \( V_i \equiv 0 \) by construction in the metal, so is the right hand side. Therefore the total energy of the system as computed in the QM/MM scheme, provided that the image charges satisfy the zero potential condition in the conductor, reduces to

\[ E = E^{\text{QM}} + E^{\text{QM/MM}} + E^{\text{MM}} \equiv E^{\text{QM}} + \frac{1}{2} E^{\text{QM/MM}}. \]  

(8.23)

The first question is thus answered: when the image charges are at self consistency, the two forms of the energy are equivalent, and the CP2K QM/MM energy can be used without modifications for computing the energy of the quantum/image charge system. Indeed, as stated by Equation (8.23), we discover that one half of the QM/MM energy counterbalances the full MM energy provided that the image charges are computed by
the condition (8.21, 8.22), namely the condition of zero potential at the metal lattice sites.

Concerning the forces, we have to derive with respect to the QM coordinates, and we have (in this formulation) a derivative of $\rho^{MM}(r)$ with respect to $r'$, a coordinate of the QM region, and $\rho^{MM}(r) = q_i(r') \times g(r - r_i)$ where $g$ is a Gaussian function. But in our formalism borrowed from Ref. [172], we can reduce the problem symbolically to the calculation of extra terms of the kind

$$\frac{\partial U}{\partial q_i} \delta q_i \delta \rho^{QM}.$$  \hspace{2cm} (8.24)

Each individual term of the kind (8.24) vanishes because of the condition (8.19); this means in practice, that the gradient of the QM/MM energy in its original form, neglecting the dependence of the image charges on the QM density, leads to the correct forces on the system.

## 8.5 Implementation

Here we propose an algorithm of including the polarized charges in QM/MM calculations (Figure 8.1):

1) Start with initial molecular and surface coordinates, and a trial of induction charges.

2) Optimize wavefunctions with QM/MM, calculate the partial atomic charges (or point charges) of molecules.

3) Calculate induction charges, check the convergence of these charges. If the convergence is not reached, go back to 2), otherwise go to 4).

4) Geometry optimization with QM/MM, check the convergence of forces. If the convergence is not reached, go back to 2), otherwise finish the run.

In step 1 we can assign an initial set of charges to the surface sites. Wavefunctions of the QM region are subsequently optimized in an external electric field caused by the MM charges. The calculation of partial atomic charges in step 2 is challenging: a fast and fairly accurate method is required. Once the point charges are known, we determine the Gaussian charges by solving equations (8.8, 8.9, 8.10), which in turns produce an electric field acting on the molecular system. This is self-consistent process is
controlled by a convergence criterion for induction charges, $\delta Q$. When it gets converged, the geometry optimization procedure is switched on in step 4. If the current geometry is not optimized, the program will go back to step 2.

In this work, we employ the QM/MM scheme implemented in the CP2K code [175, 176]. Our task is to provide the “input” of the code with the induction charges in each step of the wavefunction (and geometry) optimization.

### 8.6 Test system: 1-nitronaphthalene at Au(111)

Here we choose 1-nitronaphthalene (NN) at Au(111) for testing the performance of our implementation. NN is known to have a quite large dipole moment of about 5.0 D [185], and its nanostructures on Au(111) are well studied experimentally [186, 187, 188]. To model the surface-supported systems of NN, we employ the scheme sketched above. The molecular systems are fully described by DFT within the framework of PBE and
GPW. The surface, Au(111), is kept frozen in all calculations. The interaction between molecules and the substrate is given by

$$V_{mol-surf} = V_{BM-like} + V_{indc},$$  \hspace{1cm} (8.25)$$

where the first term in the right hand side resemble the Born-Mayer potentials and the second term implies the energy by polarized charges. The former, for a pair of atoms \((i, j)\), reads

$$V_{BM-like}^{ij} = A_{ij} e^{-R_{ij}/\rho} - \frac{C_{ij}^{6}}{R_{ij}^{6}} f_{dmp}(R_{ij}),$$  \hspace{1cm} (8.26)$$

where \(R_{ij}\) is the distance between atoms \(i\) and \(j\), \(\rho = 0.296\ \text{Å}\), \(A_{ij}\) and \(C_{ij}\) are taken from Ref. [189]. In the damping function,

$$f_{dmp}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_{c,ij} - 1)}},$$  \hspace{1cm} (8.27)$$

\(R_{c,ij}\) is the vdW radius sum of types \(i\) and \(j\), \(d = 20\) [106]. The reason for using this damping function is that with \(f_{dmp} = 1\) (i.e., the Born-Mayer potential) the NN-Au(111) separation is shorter compared to the one of a full DFT calculation; by introducing \(f_{dmp}\), we get a very good result (details provided below). Indeed, what we need is a well parameterized molecule-surface distance.

We first consider the adsorption of single NN on Au(111) by using full DFT calculations\(^1\). Our results show that NN is physisorbed on the surface, the distance between them is 3.26 Å close to the sum of vdW radii of C and Au (3.36 Å). We then perform geometry optimizations with the QM/MM scheme where the induction charge module is turned off. A 41.0 \times 41.7 Å\(^2\) rectangular unit cell of \(n\) Au layers \((n = 3 - 7)\) is considered. We find that the molecule-surface distance does not depend on \(n\), it is about 3.22 Å for all \(n\).

Then, we turn on the induction charge module and further optimize the structures of the systems resulted in the previous QM/MM calculations. To determine the partial atomic charges of NN, we employ the Mulliken population analysis, which produces a dipole moment, approximately given by \(|\vec{d}| = |\sum_{i} q_{i} \vec{r}_{i}|\), of about 4.0 D, which is slightly

\(^1\)Geometry optimizations are carried out with a 20.5 \times 20.7 Å\(^2\) rectangular unit cell of 4 Au layers and a single NN. Metal atoms are kept fixed.
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Figure 8.2: Single NN on Au(111): a) Atomistic representation and molecular dipole moment (in green). b) Electrostatic induction energy ($E_{\text{ind}}$, blue) and charge ($Q_{\text{ind}}$, red) vs. the number of surface layers $n$. c) For $n = 4$, energy of full DFT, QM/MM with (on) and without (off) the induction contributions vs. the molecule-surface separation. $E_0(h_0)$ is the energy (separation) at equilibrium. d) ($n = 4$) $E_{\text{ind}}, E_{\text{pc}}, E_{\text{dip}},$ and $E_{\text{pc} - \text{ind}}$ vs. the molecule-surface separation.

smaller than the one of 4.9 D determined from the electron density and ion charges. It appears that all the geometries are almost unchanged upon the introduction of the surface polarized charges. In Figure 8.2.a we show NN adsorbed on Au(111) and dipole moment $\vec{d}$. The position of this vector is determined by $\vec{r}_\pm = (1/Q_\pm) \sum_{i=1}^{n} \vec{r}_i q_i$, where $+q_i (-q_i)$ denotes positive (negative) partial atomic charges, and $+Q_i (-Q_i)$ denotes the sum of all $+q_i (-q_i)$. Figure 8.2.b shows the dependence of the induction energy, $E_{\text{ind}}$, and the total induction charge, $Q_{\text{ind}}$, on the number of metal layers. For $n \geq 3$, these qualities are unchanged (within a 0.3 meV and 0.001 e difference) with respect to the thickness of the surface. In fact, for some systems the electrostatic interaction energy is converged with two layers of metal atoms [172], or only three layers of metal are needed in describing the Gaussian charges [181]. Next, in Figure 8.2.c we compare the potential energy curves, when NN moves vertically on a substrate of 4 layers, in full DFT, and the QM/MM scheme presented above. It comes out that the induction energy makes the potential energy varying more quickly when NN is located above the equilibrium position and more slowly otherwise. However, the steepness of the QM/MM curves are
very different from the DFT one. Indeed, a “well-parameterized” classical pair potential for describing molecule-surface interactions would also be crucial, it is however beyond the goal of this Chapter.

Now, we introduce some energies. Firstly, $E_{\text{ind}}$ is the induction energy calculated in the QM/MM scheme proposed above, and is defined as the energy difference of the QM/MM calculations with and without induction charges for the same geometry. Secondly, $E_{\text{pc}}$ is the electrostatic energy between a point charge system (the atomic partial charges of NN in vacuum) and its image, regardless the interaction among its components (for example, interaction among charges of the same molecule), i.e., $E_{\text{pc}} = 1/2 \sum_{ij} q_i q_{j}^{\text{im}} / r_{ij}^{\text{im}}$, where $j^{\text{im}}$ denotes the image of $j$. Thirdly, $E_{\text{dip}}$ is the interaction energy between an electric dipole moment $\vec{d}$ and its image, $E_{\text{dip}} = -|\vec{d}|^2 / 16(z - z_0)^3$, where $z_0$ is mirror plane position chosen to be the outermost metal layer in the forthcoming calculations. And lastly, $E_{\text{pc-ind}}$, calculated in a QM/MM fashion in which the induction charges are directly replaced by the images of the point charges via a mirror plane, is the electrostatic interaction energy of the system due to the introduction of the image charges. Figure 8.2.d shows the dependence of these energies on the molecule-surface spacing for $n = 4$. Clearly enough, such energies coincide only when the molecule is far away from the surface. We notice that the macroscopic energy $E_{\text{pc}}$ and $E_{\text{pc-ind}}$ energies are almost identical, in agreement with the pioneering work by Siepmann and Sprik [172]. Around the equilibrium position ($z - z_0 = 3.22$ Å) we can see a significant difference between $E_{\text{ind}}$ and $E_{\text{pc}}$. So far we have not had any specific explanation for why the former is lower than the latter. It is also interesting to see that $E_{\text{dip}}$ is far below $E_{\text{pc}}$. What we can learn from this is that $E_{\text{dip}}$, a component in the multipole expansion of $E_{\text{pc}}$, cannot replace $E_{\text{pc}}$ in describing the “image charge” systems of sufficiently large molecules at metal surfaces.

Regarding the induction charge, with $n = 4$ we obtain a net charge of $-0.001e$ (see Figure 8.2.b) which is very close to the macroscopic value of zero. We thus decide to use four layers of gold in the remaining calculations. In Figure 8.3.a our results show that the magnitude of induction charges decreases quickly from the first (outermost) to the second layer (about one order) of the metal. In other words, the induction effect mainly occurs in the first layer. Furthermore, the charge distribution in this metal layer closely resemble the inverse of the NN dipole moment (see Figures 8.3.b and 8.2.a). On this basis, the image charges are nowhere near to the surface-mirror-symmetry position,
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Figure 8.3: Induction charges in a substrate of 4 layers: a) Magnitude of induction charges in layer 1-4. b) Charge distribution in the first layer. c) Charge distribution in the second layer. Rather than that they are located at (or around) the outermost layer of the substrate.

Figure 8.4: Hartree potential (iso-surface value of 0.003 a.u, red (+) and blue (-)) produced by: a) Induction charges and electrons+ions of the molecules (solid), and only electrons+ions of the molecule (transparent); b) Induction charges and point charges.

Finally, Figure 8.4.a shows the Hartree potentials of the QM/MM system with and without induction charges. It is clear that when the induction charges are taken into account, the (8.20) condition is held, the potential is accordingly screened. This is completely different from the induction charge free case, where the potential is nonzero in the metal. Figure 8.4.b shows the Hartree potential produced with point charges and induction charges. It appears to be similar to the potential produced by the QM/MM system when the induction charges are considered.
8.7 Summary

We have implemented a scheme for capturing precise image potentials of molecules physisorbed on metal surfaces within the QM/MM framework. This scheme combines a pioneering work by Siepmann and Sprik [172] expanded for periodic systems [181] for treating the polarization effect in a metal surface due to the presence of external point charges, and a QM/MM formulation [175, 176] implemented in the CP2K package [100]. It is designed for physisorbed systems where the supporting substrates are conductors. We deal with the molecules by QM and the surfaces by MM. The molecule-surface interaction is described by a standard potential (Lennard Jones, Born-Mayer,...), and electrostatic interactions due to the surface screening. The scheme is implemented in a self-consistent fashion in which the charge density of molecules calculated from QM determine the induction charges, which in turn, produce a potential acting on the molecules.

As a test, we consider a realistic problem of a NN molecule physisorbed on Au(111). It is found that a slab of 3-4 layers is good enough for the convergence of the induction energy and charges. By comparing the electrostatic energy of different considerations, it happens that this scheme reproduces a significant difference compared to classical point charge conventions. Furthermore, it can also produces the essential physics (screened potential). We are currently conducting tests for dimers and clusters of the same molecules to disentangle in the cases experimentally and theoretically described in Ref. [186] the role of lateral interactions and of the image charges in the long range ordering of such systems. Although more test cases need to be done, we expect that this strategy can be applied for the simulation of many practical systems, for example, biomolecules in a solvent (e.g., water) supported by metal surfaces.
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Chapter 9

Conclusions and outlook

In this thesis several aspects of molecular nanostructures built up on metal surfaces from a computer simulation point of view have been presented. In this chapter the major results are summarized.

A significant contribution to the adsorption of large molecules on metal surfaces is the dispersion interaction. We have shown, by means of DFT calculations combined with experimental data, that the bonding raised by this interaction can be as strong as -1.9 eV for physisorption (PTCDA on Au(111)). Even when the molecules form some chemical bond to the substrate, the van der Waals force can still be the key part of the molecule-surface interaction (DATP on Au(111)), and the main factor determining the molecular adsorption geometry (CHe on Cu(111)).

Upon adsorption, molecules, driven by molecule-substrate and intermolecular interactions, can assemble into noncovalently bonded (PTCDA and DATP on Au(111), and CHe on Cu(111)) or covalently bonded (Phenyl on Cu(111), and CHP on Cu(111) and Ag(111)) nanostructures. First, at near full surface coverage, the PTCDA-DATP network on Au(111) is stabilized by hydrogen bonding among constituent molecules. To maximize the stability of the assembly, PTCDA and DATP mix together forming a regular “lattice” which is energetically more favorable than when they are separate. On Cu(111), CHe at low coverage form some chain-like structures along some specific directions. This behavior is interpreted as a result of orientation-selectivity of single adsorbed molecules and hydrogen bonding among molecules. Interestingly, the intermolecular distance of the molecular chains is relatively large compared to the fa-
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Vorable range of hydrogen bonding. This geometric property explained by the so-called Frenkel-Kontorova model. Second, two phenyl groups adsorbed at Cu(111) can couple after a diffusion process, forming a biphenyl molecule. Unlike closed-shell systems like molecules previously considered, the phenyl groups can covalently interact with each other, resulting in a chemical bond between them, also showing that the C-C bond is more favorable than the C-Cu bond in the system. This mechanism is at the heart of the routine synthesizing nanostructures of CHP on the coinage (111) surfaces. The dehalogenation process happening at quite low temperatures is elucidated by comparison between experimental and simulated STM data. The difference in topography of CHPR structures on the surfaces is revealed as the diffusion and coupling abilities on CHPR on each substrate. DFT calculations show that the diffusion probability is higher than the coupling one on Ag(111), and this is opposite to what comes out on Cu(111). MC simulations show that the high diffusion rate leads to the formation of dense polyphenylene networks on Ag(111), and the high intermolecular coupling rate leads to the formation of open branched structures on Cu(111), as initially observed by STM.

Supported molecular systems in turn modify surface properties, the surfaces can be changed in work function (PTCDA-DATP on Au(111)) or locally restructured (phenyl on Cu(111), and CHPR on Ag(111)). Firstly, regarding molecule-surface interactions, PTCDA-DATP/Au(111) is a dispersion-interaction dominated system, the electrons of Au(111) is pushed back to the surface due to the Pauli repulsion, thus producing an electric dipole moment pointing out the surface, explaining why the covered surfaces have lower work-functions. Lastly, the phenyl dimer strongly binds to Cu(111) so that when they bind to the same metal atom, it is popping out in order to be more chemically reactive, satisfying the bonding to both phenyl groups. CHPR, on the other hand, also strongly binds to the copper and silver surfaces with six C-metal chemical bonds; unlike on Cu(111), the CHPR size is not commensurate with the surface lattice of Ag, six Ag atoms are accordingly moved out (from equilibrium) to strengthen all the Ag-bonds.

Finally, a scheme combining the QM/MM formulation and a treatment of polarization in metal surfaces was presented. This implementation was tested with a physisorbed system of NN on Au(111). To describe the image-charge screening potential, we performed the following procedure. First, using DFT calculations and a charge analysis, we obtained the atomic partial charges at the sites of the molecules (we called them
point charges). The value of the Gaussian-distribution charges in the metal induced by these point charges are determined upon requiring that the potential at every charge site of the metal is the same. The obtained Gaussian charges in turn produce an electric field acting on the molecules, leading to new point charges. This is a self-consistent process controlled by the convergence of the Gaussian charges. This procedure of course can also be part of geometry optimizations. Then, a test case of NN on Au(111) shows that this approach, which allows image charges to vary, can produce some remarkable differences compared to conventional considerations of the image potential.

An exciting aspect of nanoscience is the close interaction between experiment and theory. While experiment provides new physical phenomena, theory comes up with their microscopic origin. As an example, this thesis has been characterized by a deep interplay between simulations and corresponding experiments performed at EMPA and by external collaborators, or available in literature. Here, the present DFT-based works seek to find key factors governing the formation of molecular nanostructures at surfaces discovered by STM. In the end, the mutual enrichment between theory and experiment has appeared to be evident from the several cases illustrated. Learning from experiment, theory can also further develop and design experimental systems toward realistic applications. Nanotechnology is being in its early days. Studying fundamental physical phenomena occurring in molecule-surface systems is still an essential part in its development. We can only achieve the ultimate goal of nanotechnology - being able to control matter at nanoscale in simple, inexpensive and transferable ways - when a full understanding of all the processes involved is obtained. On this basis, intensive research efforts are needed; new insights and new computational strategies are a necessary part for the future of nanotechnology.
Bibliography


Curriculum Vitae

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Publications

This thesis is based on the following works:

- M. Treier, M.-T. Nguyen, N. V. Richardson, C. Pignedoli, D. Passerone, and R. Fasel,

- M.-T. Nguyen, C. Pignedoli, M. Treier, R. Fasel, and D. Passerone,
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- M.-T. Nguyen, C. Pignedoli, and D. Passerone,
  (Also selected for a simultaneous publication in the Virtual Journal of Nanoscale Science & Technology 22 (25) 2010.)

- M. Stöhr, S. Boz, M. Schär, M.-T. Nguyen, C. Pignedoli, D. Passerone, W. B. Schweizer, C. Thilgen, T. A. Jung, and F. Diederich,

- M.-T. Nguyen, et al.,
and theory,
to be submitted.

• M.-T. Nguyen, et al.,
An approach for the classical polarization in QM/MM hybrid calculations,
to be submitted.

The following works are not presented in this thesis:

• R. Erni, M. D. Rossell, M.-T. Nguyen, S. Blankenburg, D. Passerone, P. Hartel,
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hydrogenation reactions,

• M.-T. Nguyen, et al.,
On the stability of 1-nitronaphthalene clusters at Au(111),
to be submitted.