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Tuning Chemical and Optical Properties of Nanomaterials: From Extended Surfaces to Finite Nanoclusters

Zahra Hooshmand Gharehbagh
TUNING CHEMICAL AND OPTICAL PROPERTIES OF NANOMATERIALS: FROM EXTENDED SURFACES TO FINITE NANOCCLUSTERS

by

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ABSTRACT

Modifying the electronic and optical properties of surfaces and nanostructures are in the forefront of surface science. This dissertation’s focus is on this problem. The first part is on the adsorption of functionalized naphthalene molecules on Cu(111) surface. The results show that changing the functional group results in modification of charge redistribution at the interface of molecule and surface and the electronic structure of Cu changes. The second part discusses the new Moiré structure of h-BN on Rh(111) induced by intrinsic carbon impurities of Rh single crystals. We found that these impurities intercalate between h-BN and Rh(111) with new local properties such as charge transfer from Rh and C atoms to h-BN such as appearance of new states in the BN. The third part is about the study of CO super lattice structure at $\frac{1}{2}$ML when adsorbed on Pd(111). By considering all the possible overlayer structures and using several different functionals, we found that two structures can be made by CO adsorbents and all the other structures convert to one of these two. The fourth part is on the electronic and optical properties of ligated Ag$_{44}$ nanoclusters. Using DFT and TDDFT calculations we show that when the pH level of a solvent is changed, the protecting ligands deprotonate and their interaction with each other as well as the metal core varies and the new peaks in absorption spectrum arise from electron rich deprotonated ligands. The final part is on the adsorption of planar molecules on MoS$_2$. We found that the isomers of di-iodobenzene adsorb with same strength on MoS$_2$ and it is the symmetry of frontier orbitals that identifies their different behavior. Also the adsorption and dissociation of benzenethiol on MoS$_2$ was studied and the results show that benzenethiol dissociates only in the presence of defects and heals the structure.
“A scientist in her laboratory is not a mere technician: she is also a child confronting natural phenomena that impress her as though they were fairy tales.”

—Marie Curie
To my father & my mother:

“Ajdar Hooshmand and Sakineh Zaali”

&

In the memory of my late grandmother:

“Leyla Mohammadi”
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CHAPTER 1: INTRODUCTION

Surface chemistry has drawn tremendous attention for several reasons. The surface of a solid is an interface of solid and gas or solid and liquid. Therefore the description of phenomena at the surface of materials is a challenging task. On a metal surface, the chemical reactions on the surface and electronic modifications are unique in the sense that the metal surfaces provide semi-infinite source of electrons at the Fermi level. The surface can act as a template to grow molecular layers, facilitate pattern formation and/or chemical reactions, each of which involve several steps of physical and chemical interactions between the surface and the molecule or atom specie (adsorbate). The adsorption of an adsorbate or alloying of a surface may lead to change in the electronic properties of the material. Understanding the phenomena happening in this scale then provides a guideline to engineer the properties of material for desired applications.

When the adsorbate reaches a surface electrostatic interaction between the two results in its adsorption. This adsorption is divided into two categories: Physisorption and Chemisorption.

When an adsorbate is physisorbed, it is weakly bound to the surface. The electronic structure of the surface and the adsorbate remain the same as what it was before their interaction. Both surface and adsorbate possess a specific electronic structure which defines their properties. Strictly speaking these properties are defined by orbital structure and charge distribution in the species. In the case of physisorption the hybridization between the orbitals of the surface and adsorbate is very small and therefore their electronic structure remains unperturbed. However, there should still be some kind of interactions which causes adsorption. This is the realm of long range van der Waals (vdW) and dipole-dipole interactions.
For chemisorption the situation is completely different. The hybridization between adsorbate and surface is very strong and the adsorbate binds strongly to the surface by making covalent bonds. The electronic structure of both parts is affected and differs from what it was before the interaction.

Interestingly it was shown that when molecules are deposited on the surface, they can form patterns and self-assembled structures [1]. This structure formation happens at high coverages where the interaction among the adsorbates become as important as interaction between the adsorbate and the surface. The self-assembly of molecules is also interesting since several factors are available to tune the final structure but more importantly because it provides samples of long range ordered structures with physisorption or chemisorption of molecules.

The idea of self-assembled structures was inspired by the DNA structure, whose detection by Scanning Tunneling Microscopy (STM) revolutionized our understanding of life and all the inherent characteristics in the body. But more precisely it also led to several striking ideas which brought new strategies to modify the properties of artificial material by asking if such self-assemblies can happen on surfaces? And if so, what changes may be observed in the molecule or the surface? Several self-assembled structures have been studied since then which show that these structures can be formed on metal surfaces, displaying intriguing structural and electronic properties. If the molecules are weakly bound, the pattern is usually formed by H bond among the adsorbates. The vDW interaction between molecules and surface is the dominant factor in their binding to the surface. This frequently results in planar networks of molecules. On the other hand, if the interactions are strong, the adsorbates may form covalent bonds with the surface and result in completely different structures from that resulted from H bond formed patterns. The shape, size,
functional properties and composition of adsorbates can be controlled to produce the desired networks.

In reality the surface of a solid is not perfect. There are several kinds of impurities including, steps and kinks, vacancies or adatoms (by adatom we mean any atom which exist on top of the surface, either thermally extracted from steps or kinks or deposited on the surface). These factors tremendously affect the interaction of adsorbate with surface in general and more specifically the pattern formation or self-assembly of deposited molecules. One such important result is when molecules and adatoms interact and form covalent bonds. In a real system, atoms on the surfaces diffuse and find other atoms or dissolve into the bulk. However the covalent bond formation
between these atoms and molecules stabilizes them and this becomes the building block of metal coordinated structures. It is worth mentioning that although the interaction between metal atom and the molecule(s) is covalent, the vdW interactions play an important role in the orientation of adsorbed molecules. The adatoms are adsorbed on high symmetry points of the surfaces and the networks usually reflect the symmetry of the substrate.

From application point of view especially in catalysts, self-assembly of molecules around a metal atom is very important. In fact it was shown by Sykes et al. [2] that single atom alloys (SAA) show higher activity than their bulk or surface counterparts. The H₂ molecule was adsorbed and dissociated on Pd atom and it was dispelled on Cu surface which was the host alloy. Designing single atom catalysts not only is beneficial regarding the limited amount of resources but also gives the possibility to reduce the number of unwanted reactions and consequently increase the selectivity of catalyst. When looking into the hybridization between the orbitals of atom and molecules, this also means that we can design structures in which specific orbitals are selected to be involved in reaction.

Transition metals are specifically important in this regard since they have several oxidation states. One way to modify their oxidation state is to modify the functionality of the molecules which make covalent bond with metal center, i.e. the electronic structure of both molecule and metal atom are altered. When there is no adatom the formation of well-ordered structure of adsorbates is driven by inter-molecular interactions, especially at very high coverages while in low coverage, the role of the substrate is more important.
Another factor to modify the self-assembled structures is the inherent impurities in the near surface areas of substrate. An example of such structures is the self-assembly of borazine on metal surfaces at high temperatures which gives rise to the formation of hexagonal boron nitride (h-BN). Depending on the underlying substrate the h-BN could be highly or slightly corrugated. The insulator layer decouples the interaction between adsorbates with metal surface and is usually used as template to grow nanoparticles or to immobilize atoms and trap molecules. The segregation of impurities in the near surface areas of the metal modifies the electronic structures “locally” and changes the charge distribution on the h-BN. As a result its interaction with adsorbates are modified. For example, formation of h-BN on top of Rh(111) a long range ordered corrugated Moiré structure is formed. The carbon impurities in the Rh single crystal affect this structure by change in the charge distribution on h-BN. The carbon atoms intercalate in the regions between Rh and BN and the charge transfer from Rh and C to BN forms permanent dipoles which results in the increase of work-function of h-BN.

Figure 1.2. Moiré structure of h-BN/Rh(111) with carbon impurities at the interface of Rh(111) and h-BN.
Figure 1.3. Up: The simulated absorption spectrum of ligated Ag44 clusters for deprotonated and dimerized ligands at pH 13 and 7. The inset shows the experimental spectrum [3]. Down: Two of excitations obtained from Kohn-Sham wave functions for pH 13 and 7. The lowest panel shows the charge transfer for each excitation. See chapter 6 for detailed discussions.

As mentioned before, one important effect of adsorbed molecules on adatoms is their role in stabilizing the adatoms. This is also applicable to nanoparticles. When the size of nanoparticle is very small, the nanoparticles tends to combine with other nanoparticles and form bigger structures. Adsorption of molecules on the other hand, not only protects the size of the structure, it also provides an ingredient to modify electronic and optical properties of these systems by modifying the interactions among molecules and the metal nanoparticle. When the size of these protected nanoparticles is reduced to less than 2nm, they are called nanoclusters. One way to tune their electronic and optical properties is change in the functionality of the protecting molecules. This
can be achieved by varying the pH level of the solution in which the nanoclusters are prepared. We could show that the deprotonation of molecules at higher pH levels changes the absorption spectrum of a small silver nanocluster which was protected by thiol groups.

The understanding of these properties needs solving the physical problem at the electronic structure level. The interesting electronic or optical properties of a system emerge from the interactions among electrons. The question then is: how can we unravel the mechanisms behind these properties? The first step to answer this question is to construct the Hamiltonian of the system of study. This Hamiltonian should be material-specific, i.e., it should be distinguished from the Hamiltonian of another system. The next step is to find the eigenvalues by solving the Hamiltonian. This may seem a straightforward task however finding solutions to this equation without considering approximations is formidable owing to its many-body nature. The approximations are thus used to first find the ground state of the Hamiltonian which is used further for calculations of observables. The most widely used approximation in computational chemistry and physics is Density Functional Theory which provides a frame work to deal with the density of electrons. This theory is the basis of thousands of research done in last few decades in materials science. In its original form though it was not applicable to realistic systems and a number approximations were made before it could give tangible results.

The goal of this thesis is to address the local electronic structural changes in a system as a result of molecular adsorptions, impurities, pH level variation and pattern formation. The premise is that the structural and electronic properties of material can be described in terms of chemical bond formation and charge rearrangements. A variety of problems are addressed in this dissertation which allow us to examine the effect of local electronic structural changes on a range of material
properties. All systems investigated in this study are motivated by experimental data, whose rationalization has been one of the goals of the research. The results of this work are obtained by means of state of the art computational approaches based on density functional theory. The dissertation is organized as follows:

Chapter 2 introduces the theoretical background on the many body problem. It presents the formalism behind density functional theory and a summary of the approximations used for its application to the systems studied in this thesis. The shortcomings of this theory in description of long range order vdW interactions are described and the methods for inclusion of these interactions are introduced. The ab-initio thermodynamics approach to calculate zero point energies of pattern is described and the methods to estimate the charge of atoms and the reaction barriers are explained. For excited states description the time dependent density functional theory is necessary. As in the case of density functional theory for ground state calculations, this theory also need approximations to be solved. A brief description of some of these approximations can be found at end of this chapter.

Chapter 3 describes an ab initio study of adsorption of functionalized Naphthalene molecule on Cu(111). The adsorption of single molecules on the surface and on the adatom indicate that the molecules in general tend to stay 3Å away from the surface and the competition between vdW interactions and covalent bond between molecule and Cu results in tilted binding of molecules to the surface and to the adatom.

Chapter 4 explains the effect of impurity in the Rh(111) on the Moiré structure of h-BN. In this chapter I show that carbon impurities as detected in XPS measurements intercalate between Rh and BN and change the charge distribution on the h-BN. A variety of concentrations are
considered and the one with that matches experimental observations is determined. I could also show that at this specific concentration new states appear in the B and N atoms in the regions above impurities. The result of this modification in morphology of h-BN/Rh(111) structure is also reflected in the increased work function of the system.

Chapter 5 is dedicated to the super lattice structure of CO molecules on the Pd(111) surface at 1/2ML. Based on \textit{ab initio} and vibrational frequency calculations two stable structures are found. My results show that the barrier for converting one of structures to the other one is very small which explains the STM results of coexisting two structures at this coverage.

Also by repeating all calculations with a set of popular DFT functionals for describing electron exchange-correlation, I could show that the results are independent of the choice of the functional. Moreover the inclusion of vdW interactions did not affect my results.

Chapter 6 describes my first principle studies of ligated Ag$_{44}$ nanoclusters. My results for excitations calculations as well as the numerical simulations of absorption spectrum show that at low pH the protecting ligands dimerize and at high pH they are deprotonated. This deprotonation modifies the excitation map and gives rise to new peaks in absorption spectrum.

Chapter 7 provides the adsorption and reaction of small planar molecules on MoS$_2$ monolayer. In this chapter I showed that the adsorption of di-iodobenzene isomers on MoS2 monolayer is determined by symmetry rather than adsorption strength. I also found that on a defect laden MoS2, the benezenethiol molecule adsorbs strongly and heals the defects with benzene as the final product while on pristine-MoS2, the reactions are feasible if only there are pre-adsorbed atomic H on the surface.

Chapter 8 presents the main conclusions of this dissertation.
CHAPTER 2: THEORETICAL METHODS

2.1 Introduction

One of the most profound discoveries in the history of science happened when the electronic structure of atoms was described by Niels Bohr in 1923. Following this discovery the quantum mechanics was developed in which it enabled the description of some experimental phenomena like: photoelectric effect which was not compatible using the classical description of matter. The heart of quantum mechanics is the Schrödinger Equation (SE) \[4\] which gives the total energy of a quantum mechanical system using the following equation:

\[
\hat{H}\Psi(\vec{r}, t) = E\Psi(\vec{r}, t)
\] (2.1)

\(\hat{H}\) is the Hamiltonian operator consisting of the kinetic and potential interaction energies and \(E\) is the total energy of the system. The configuration, state, of the system at each given space \((r)\) and time \((t)\) is described by \(\Psi(r, t)\), the wave function. Although this equation has well defined solutions to problems such as harmonic oscillator or a particle in a box, solving it for practical purposes such as describing the electronic structure of material is formidable. In the following we will lay out the reasons for such difficulty and give a summary of one of the most-used methods in quantum chemistry and solid state physics, named Density Functional Theory (DFT) [5,6]. Afterwards, we will cover all the other calculations methods used in this thesis. Since DFT is the basis of all the simulations presented in this thesis, we will start with this method.
2.2 **Schrödinger Equation of electronic system**

Let’s consider a collection of atoms, such as a molecule, \( \text{CO}_2 \). To obtain the electronic properties for this system, we need to solve the following SE:

\[
\hat{H} = -\frac{\hbar^2}{2M} \sum_{i=1}^{M} \nabla_i^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i} U(r_i, r_j) + \sum_{A=1}^{M} \sum_{B<A}^{M} U(R_A, R_B) \tag{2.2}
\]

Eq. (2.2) consists of: the kinetic energy of nuclei (ions), the kinetic energy of individual electrons, the Coulomb potential interaction between nuclei and electrons as well as the Coulomb potential interaction between nuclei and electrons themselves. This equation is in general time-dependent. However, to obtain the electronic structure of the system, we need to find its minimum energy or **ground state (GS)**. Since GS is not time-dependent, Eq. (2.2) reduces to time-independent SE. To solve this problem for a system of \( N \) electrons and \( M \) ions, we should note that this equation has 3\( N + 3M \) dimensions. Therefore it is very difficult, if not impossible, to solve it for practical purposes. The first approximation used to simplify this equation was introduced by Born and Oppenheimer in 1927 [7]. Since the mass of nuclei is much heavier than that of an electron (~1800 times!), it means that electrons are moving much faster than nuclei and therefore they will respond to changes much more rapidly than nuclei. This brings two simplifications to SE:

1. The first and the last terms in Eq. (2) can be neglected.
2. The wave function could be divided to an ionic and an electronic parts.

In another words, using BO approximation one can consider electrons moving in the potential field of fixed ions. Therefore eq. (2.2) will reduce to the following equation:

\[
\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i} U(r_i, r_j) \right] \Psi_{\text{elec}} = E_{\text{elec}} \Psi_{\text{elec}} \tag{2.3}
\]

The sum of interaction energy among the nuclei (last term in eq. (2.2)) and \( E_{\text{elec}} \) gives the total energy of the system. However, even with this approximation, solving eq. (2.3) is formidable.
because this equation is a many-body problem due to electron-electron interaction term \((U(r_i, r_j))\).

In another words, the individual electron wave function cannot be determined without simultaneously considering the individual electron wave functions associated with all the other electrons. The main question therefore is what observable related to wave function can be estimated by solving SE? To answer this, it is important to note that, the quantity that can be measured (observed) is not wave function rather it is the “probability” that the \(N\) electrons, in any order, are in a set of particular coordinates. This probability is equal to:

\[
P = \Psi^*(r_1, ..., r_N)\Psi(r_1, ..., r_N)
\]  

(2.4)

\(\Psi^*\) is the complex conjugate of wave function. This is very close to the density of electrons at a particular position in space, \(n(r)\):

\[
n(r) = 2\sum \psi_i^*(r)\psi_i(r)
\]  

(2.5)

The summation includes all the occupied states and the coefficient 2 comes from Pauli Exclusion Principle. So in fact this quantity is giving the probability of finding electrons at specific coordinates. Therefore, the electron density has lots of information about the system of study. But most importantly it decreases the equation of a function of \(3N\) coordinates to the one with only 3 coordinates. To GS is obtained by minimizing the energy with respect to density. The main task therefore is to find the correct density and solves the KS equation with correct results for practical purposes.
2.2.1 Thomas-Fermi approximation

To understand what the importance of DFT is, it is necessary to go over the methods that were used before that. One of the most famous and widely used methods in quantum chemistry is Thomas-Fermi approximation [8,9]. This approximation is also based on electron charge density. In this approach one considers atoms as homogeneous gas of electrons distributed around the nuclei. In another words electrons are not interacting and they are moving in the external field of frozen nuclei. This assumption gives the following relation between electron’s density and Fermi energy (The integral to obtain electron density is solved in momentum space):

\[
n(\vec{r}) = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \varepsilon_F^{\frac{3}{2}} \tag{2.6}
\]

Using this density the kinetic energy is:

\[
T_{TF}[n(\vec{r})] = C_s \int d^3 r \ n^\frac{5}{3}(\vec{r}), \quad \tag{2.7}
\]

with

\[
C_s = \frac{3}{10} \left(\frac{3\pi^2}{2}\right)^2 \tag{2.8}
\]

The total energy of electrons can be written as:

\[
E_{TF}[n(\vec{r})] = C_s \int d^3 r \ n^\frac{5}{3}(\vec{r}) + \frac{1}{2} \int d^3 r \int d^3 r' \ \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int d^3 r n(\vec{r}) v_{ext}(\vec{r}). \quad \tag{2.9}
\]

The second and third terms are electron-electron and electron-ion Coulomb interaction terms, respectively. By minimizing this functional the GS is obtained. The physical constraint to solve this equation come from the fact that the density which minimizes eq. (2.9) should result in total number of electrons:

\[
\int d^3 r \ n(\vec{r}) = N \quad \tag{2.10}
\]
The minimization over eq. (2.9) by variational method results in following relation between external potential and that of kinetic energy of electrons and repulsion interaction among them:

\[
\frac{5}{3} C_s n(\bar{r})^2 + v_{\text{ext}}(\bar{r}) + \int d^3r \frac{n(\bar{r})}{|\bar{r} - \bar{r}'|} - \mu = 0
\]  

(2.11)

\(\mu\) is the chemical potential of electrons.

For decades scientists were playing with this equation to obtain GS energy and they never asked the question: Is there something exact that the right-hand side of Thomas-Fermi equation is trying to approximate? Answering this question by Hohenberg and Kohn in mid-1960s was the beginning of development of DFT based on two fundamental mathematical theorems proved by Hohenberg and Kohn [5].

### 2.2.2 The first Hohenberg-Kohn Theorem

The first Hohenberg-Kohn theorem states that: The ground state energy from Schrödinger equation is a "unique" functional of the electron density.

This theorem can be proved by contradiction. Let’s suppose that we have a system with density of \(n(\bar{r})\) in an external field \(V_{\text{ext}}(\bar{r})\). The ground state energy of this system is \(E_0\) which is identified by Hamiltonian \(\hat{H}\):

\[
E_0 = \langle \Psi | \hat{H} | \Psi \rangle
\]  

(2.12)

If \(n(\bar{r})\) is not uniquely determined by \(V_{\text{ext}}\), this means that there could be another external potential, \(V_{\text{ext}}'(\bar{r})\) that will give the same density \(n(\bar{r})\) and gives the ground state energy as \(E_0'\) identified by the Hamiltonian \(\hat{H}'\):
\[ E_0' = \langle \psi' | \hat{H}' | \psi' \rangle \]  

(2.13)

Since \( E_0 \) and \( E_0' \) give the ground state this means that:

\[ E_0 < \langle \psi' | \hat{H}' | \psi' \rangle \]  

(2.14)

and

\[ E_0' < \langle \psi | \hat{H} | \psi \rangle \]  

(2.15)

Adding both sides of equations (2.14) and (2.15) the following inequality is obtained:

\[ E_0 + E_0' < \langle \psi' | \hat{H}' | \psi' \rangle + \langle \psi | \hat{H} | \psi \rangle \]  

(2.16)

Replacing the first and second terms of the right hand side of above inequality with eq. (2.12) and eq. (2.13) we can rewrite eq. (2.16) as:

\[ E_0 + E_0' < E_0 + E_0' \]  

(2.17)

This inequality is a contradiction which means that the assumption is not correct. In another words there is a one by one correspondence between external potential and electron density. Therefore having the electron density the external potential can be identified uniquely and vice versa. The unique representation of \( V_{\text{ext}} \) by \( n(\vec{r}) \) has a very important result: by having electron density all the properties of ground-state are determined. All the components of Hamiltonian are functional of electron density. However this theorem says nothing about what the density functional should be. The second Hohenberg-Kohn theorem gives answer to this question.
2.2.3 The second Hohenberg-Kohn Theorem

The second Hohenberg-Kohn theorem states that: The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.

Let’s consider the total energy of a system of N interacting electrons as $E$:

$$ E[n(\vec{r})] = T[n(\vec{r})] + V_{\text{ext}}[n(\vec{r})] + V_{\text{ee}}[n(\vec{r})] $$  \hspace{1cm} (2.18)

where $T[n(\vec{r})]$ is the total kinetic energy, $V_{\text{ext}}[n(\vec{r})]$ is the external potential and $V_{\text{ee}}[n(\vec{r})]$ is the electron-electron interaction energy. The first and last terms are only functional of electron density and the external potential can be uniquely identified by electron density $n(\vec{r})$. The ground state energy $E_0$ corresponds to the ground state density, $n_0(\vec{r})$. For any other state with total energy of $\tilde{E}$ with corresponding density $\tilde{n}(\vec{r})$ the following inequality holds:

$$ \tilde{E} > E_0 $$  \hspace{1cm} (2.19)

or

$$ T[\tilde{n}(\vec{r})] + V_{\text{ext}}[\tilde{n}(\vec{r})] + V_{\text{ee}}[\tilde{n}(\vec{r})] > E_0 $$  \hspace{1cm} (2.20)

This inequality indicates that the “true” density functional is the one that minimizes total energy and gives ground state of the system. This provides a prescription for finding the electron density.

2.3 Kohn-Sham Equations

Kohn and Sham presented the equations of a system of “fictitious” non-interacting particles in which their total density is the same as the total density of the original system [6]. This
equation satisfies the Hohenberg-Kohn theorems. To deeply understand the importance of this simplification, we will start by writing the SE of this new system:

$$\left\{ -\frac{1}{2} \nabla^2 + V_s(\vec{r}) \right\} \phi_j(\vec{r}) = \epsilon_j \phi_j(\vec{r}) \quad (2.21)$$

Which represents the Schrödinger equation of a non-interacting system. $V_s(\vec{r})$ is the potential of the single “fictitious” particles and $\phi_j(\vec{r})$ is the corresponding single-occupied wave function of the particles. These wave functions are KS wave functions and not the ones of the real many-body system. These new non-interacting particles are also fermions and they satisfy Pauli’s exclusion principle so the density of this system will be:

$$n(\vec{r}) = \sum_{j=1}^N |\phi_j(\vec{r})|^2 \quad (2.22)$$

This density is the same as the GS density of the real system. To find the KS potentials we will go back to the result obtained in Hohenberg-Kohn second theorem for a system of N interacting electrons:

$$E[n(\vec{r})] = T[n(\vec{r})] + V[n(\vec{r})] + V_{ee}[n(\vec{r})] \quad (2.23)$$

In which $T[n(\vec{r})]$ is the total potential energy. The second term is:

$$V[n(\vec{r})] = \int n(\vec{r}) V_{ext}(\vec{r}) d^3r \quad (2.24)$$

The last term consists of two parts:

$$V_{ee}[n(\vec{r})] = E_H[n(\vec{r})] + E_{XC}[n(\vec{r})] \quad (2.25)$$

$E_H[n(\vec{r})]$ is the classical electrostatic Hartree potential:

$$E_H[n(\vec{r})] = \frac{\int \rho(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (2.26)$$

and $E_{XC}[n(\vec{r})]$ is unknown. The GS energy can be obtained using vibrational method:
\[
E_{GS}[n(\vec{r})] = \frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})} \bigg|_{n=n_{GS}} = \frac{\delta T[n(\vec{r})]}{\delta n(\vec{r})} \bigg|_{n=n_{GS}} + V_{ext}[n(\vec{r})] + \frac{\delta E_H[n(\vec{r})]}{\delta n(\vec{r})} \bigg|_{n=n_{GS}} + \frac{\delta E_X[n(\vec{r})]}{\delta n(\vec{r})} \bigg|_{n=n_{GS}}
\]

For a non-interacting system:

\[
E_{GS}[n(\vec{r})] = \frac{\delta T[n(\vec{r})]}{\delta n(\vec{r})} \bigg|_{n=n_{GS}} + V_s(\vec{r})
\]

Substituting eq. (2.28) in eq. (2.27) the GS energy equals:

\[
V_s(\vec{r}) = V_{ext}[n(\vec{r})] + V_H[n(\vec{r})] + V_{XC}[n(\vec{r})]
\]

with

\[
V_H[n(\vec{r})] = \frac{\delta E_H[n(\vec{r})]}{\delta n(\vec{r})} \bigg|_{n=n_{GS}}
\]

and

\[
V_{XC}[n(\vec{r})] = \frac{\delta E_{XC}[n(\vec{r})]}{\delta n(\vec{r})} \bigg|_{n=n_{GS}}
\]

Therefore KS potential is the sum of original external potential, the classic Hartree potential and the unknown exchange-correlation potential. This also indicates that having that last piece of information about \(V_{XC}\) can provide the set of self-consistent equations that finally gives the Hamiltonian and GS energy of the original system using the non-interacting electrons, i.e. all the physical properties of a system in GS. It is important to notice that these equations are based on two theorem which provide guidelines to find the global minimum of system, GS, by self-consistently finding the GS density and therefore this is where DFT is limited in its power to describe physical properties of systems. It is “only” accurate for GS properties and not excited states.

The self-consistent KS equations can be solved iteratively by following these steps:

Step 1: Pick an initial guess for the electron density, \(n(\vec{r})\).

Step 2: Calculate \(V_H\) and \(V_{XC}\) using equations (2.30) and (2.31).
Step 3: Solve the KS equation to obtain wave function, \( \phi_i(\vec{r}) \) and using that the corresponding new electron density, \( n_{\text{new}}(\vec{r}) \).

Step 4: If new electron density is the same as initial guess, the calculation will stop. Otherwise follow steps 1-3 until convergence is achieved. Figure 2.1 shows a flow chart of self-consistent DFT calculations.
2.4 **Exchange-Correlation Functional**

The most important difficulty in solving KS equations is exchange-correlation term which its exact form is unknown. This energy is the difference between the exact value of the GS energy with that of the Hartree energy and the kinetic energy coming from non-interacting picture. Having the exact exchange-correlation functional, makes it possible to solve the system of $N$ interacting electrons in the external field by mapping from DFT to SE. However, owing to its unknown form the approximations are used widely with efficiency and low computational cost. While there are several approximations, we discuss only the two most used ones: the local density approximation and the generalized-gradient approximation functionals.

2.4.1 **The Local Density Approximation**

The local density approximation (LDA) assumes that the exchange-correlation energy experienced by each electron at point $\vec{r}$ is the same as that of a homogeneous electron gas with the same electron density. Using this approximation the exchange energy and potential are calculated exactly as:

$$E_x = \int \rho(\vec{r}) V_x d\vec{r}$$  \hspace{1cm} (2.32)

and

$$V_x = -\left(\frac{81}{64}\right)^{\frac{1}{3}} \frac{1}{\rho^{\frac{4}{3}}}(\vec{r}) = -\frac{0.4582}{r_s}$$  \hspace{1cm} (2.33)

$r_s$ is the effective radius of the sphere with density $n(\vec{r})$ and is defined as:

$$\frac{4}{3} \pi r_s^3 = \frac{1}{n}$$  \hspace{1cm} (2.34)
Calculations of the correlation energy $E_C$ and potential $V_C$ is a difficult many-body problem. However, there are approximations to do so. Various approximations such as Vosko-Wilk-Nusiar (VWN) [10], Perdew-Zunger (PZ) [11] have been made to calculate the correlation energy. For example, the (PZ) approximation is widely used which presents the correlation potential as:

$$V_C = \begin{cases} 
-0.1423(1 + 1.0529\sqrt{r_s} + 0.3334r_s)^{-1} & \text{if } r_s \geq 1 \\
-0.048 + 0.0311\ln r_s + 0.002r_s\ln r_s - 0.0116r_s & \text{if } r_s < 1 
\end{cases}$$

Despite its simplicity, LDA performs very well by calculating lattice parameters that are usually $1-2\%$ larger than experimental value. It fails, however, in a number of predictions including: the magnetic properties, the electronic structure of strongly correlated systems, the dissociation energy of molecules and the adsorption energy of atoms and molecules on solid surfaces.

### 2.4.2 The Generalized-Gradient Approximation

As mentioned before, LDA considers the local density as that of a homogeneous gas. To take into account the inhomogeneity of electrons density one needs to include the gradient and/or higher derivatives of density with respect to space. The first attempt in this direction was proposed by Kohn and Sham as gradient expansion approximation (GEA) [6]. However, this approximation resulted in worse failures than LDA.

To solve this problem a variety of exchange-correlation functionals have been proposed in which the exchange-correlation energy has the following form:

$$E_{XC} = \int F_{XC}[\rho(\vec{r}), \nabla \rho(\vec{r}), \nabla^2 \rho(\vec{r}), ...]d\vec{r}$$

(2.36)
This approximation in general is called generalized-gradient approximation (GGA) in which not only the exchange-correlation energy is a functional of electron density at $\mathbf{r}$, but also it is functional of charge variations at each point of space $\mathbf{r}$. GGA functionals have been calculated using two different strategies. The first known as *ab initio* approach, starts with the derivation of theoretical expression for $F_{XC}$. It then requires the functional to satisfy some or all known properties of the $E_{XC}$. The second strategy, known as an empirical approach is based on fitting all the parameters of $F_{XC}$ to reproduce a large number of known experimental values. There are many variations for first one such as LYP [12], PW91 [13] and PBE [14].

Although generally GGA improves the results obtained by LDA by predicting better energy gap for semiconductors and insulators as well as that of binding energies, bond lengths and angles, it still overestimates lattice constants of solid structures. Another shortcomings of both LDA and GGA is that because the non-locality of electrons is not fully taken into account, both approximations don’t capture the long range interactions.

### 2.5 van der Waals interactions in DFT

As mentioned in previous section, the long-range interactions are not fully described in LDA and GGA because of their local built-in nature. These approximations do not take into account the non-locality of electrons. What does this mean?

The distribution of electrons in atoms is a dynamic process rather than static. Even at very low temperatures the electrons are fluctuating. As a result of this mobility there are instantaneous creations of electric multipoles at one part of the system which consequently induce multipoles at
another part of the system. The interaction between these multipoles is attractive and is known as van der Waals (vdW) or dispersion interactions. This interaction can exist even if there is no chemical bond between interacting parts. One very famous example of this kind of adsorption is the adsorption of Benzene on metallic surfaces.

To take into account this non-local interactions many approximations have been proposed. In this section we will briefly describe these methods and their mathematical basics.

2.5.1 The dispersion-corrected density functional theory

In this method the total energy of the system consists of two different parts: (1) the total energy obtained from DFT calculations (LDA or GGA) and (2) the vdW interaction energy:

\[ E_{tot} = E_{tot}^{DFT} + \sum_{i=1}^{N} \sum_{j=j+1}^{N} E_{ij}^{vdW} \]  \hspace{1cm} (2.37)

The second term is defined as:

\[ E_{ij}^{vdW} = \sum_{n=6}^{\infty} s_n f_n(r_{ij}) \frac{C_n^{ij}}{r_{ij}^6} \]  \hspace{1cm} (2.38)

Where \( s_n, C_n^{ij} \) and \( f_n \) are scaling factors, pairwise interaction coefficients and damping functions, respectively. \( i \) & \( j \) indices represent atoms \( i \) and \( j \) and \( r_{ij} \) is the distance between them. The most widely used methods based on this approximation are: DFT-D2, DFT-D3 and TS.

2.5.2 DFT-D2

This method was proposed in 2006 by Grimme et al. [15] and adds vdW energy in the following form to \( E^{DFT} \):
\[
E_{ij}^{vdW} = \sum_{n=6}^{\infty} s_n f_n(r_{ij}) \frac{C_{ij}^6}{r_{ij}^6}
\] (2.39)

\( s_6, f_6 \) and \( r_{ij}^6 \) are scaling factor, damping function to avoid the divergence at short distance and the distance between atoms \( i \) & \( j \), respectively. \( f_6(r_{ij}) \) is given by:

\[
f_6(r_{ij}) = \frac{1}{1 + e^{-d(r_{ij}/R_{ij} - 1)}}
\] (2.40)

In this formalism, \( d = 20 \) and \( R_{ij} \) is the sum of atomic vdW radii of atoms \( i \) & \( j \). To calculate \( C_{ij}^6 \), the coefficient of individual atoms \( i \) & \( j \) are calculated from atomic ionization potentials and static polarizabilities separately and then give \( C_{ij}^6 \) as:

\[
C_{ij}^6 = \sqrt{C_{ij}^6 C_{ij}^6}
\] (2.41)

These coefficients are computed for a list of atoms corresponding to each DFT functional in [15].

Although DFT-D2 works very well in producing accurate binding energies between molecules as well as atoms, it does not work very well for extended systems since it is independent of system. A newer version of this method was proposed by Grimme et al. in 2010 [16] which addresses these issues, known as DFT-D3.

### 2.5.3 DFT-D3

The new version of DFT-D2 [16] calculates vdW energy as:

\[
E_{ij}^{vdW} = s_6 f_6(r_{ij}) \left( \frac{C_{ij}^6}{r_{ij}^6} \right) + s_8 f_8(r_{ij}) \left( \frac{C_{ij}^8}{r_{ij}^8} \right)
\] (2.42)

In this formalism \( f_n(r_{ij}) \) is chosen as:
\[ f_s(r_{ij}) = \frac{1}{1 + 6 \left( \frac{r_{ij}}{s_n R_{ij}} \right)^{-\alpha}} \quad (2.43) \]

\[ s_n \text{ and } \alpha \text{ in eq. (2.43) are empirical parameters. } R_{ij} \text{ is the cutoff radius of atoms } i \& j. \]

To calculate \( C_{n}^{ij} \) at first a large number of \( C_{6}^{AB} \) coefficients of atoms A and B are calculated based on their polarizabilities in their hybrid compounds. Then \( C_{6}^{ij} \) coefficients are obtained by interpolation of these coefficients as a function of coordinates. The higher orders of \( C_{n}^{ij}: C_{8}^{ij}, C_{10}^{ij}, \ldots \) coefficients are computed recursively from the value of \( C_{6}^{ij} \). Since for \( n > 8 \), the DFT-D3 results do not improve, the approximation is truncated on \( n = 8 \). The \( R_{ij} \) values which are the inter-nuclei values of pairs of atoms \( i \& j \) are pre-calculated for atoms with atomic number of \( Z = 1 \sim 94 \) by authors of this method.

### 2.5.4 Tkatchenko-Scheffler method

Another approach to address the issues of DFT-D2 was proposed by Tkatchenko and Scheffler (TS) in 2009 [17]. This method uses the same correction terms of DFT-D2 except that the pair coefficient is scaled with respect to its value of pairing of free atoms:

\[ C_6^{ii} = \left( \frac{V_{eff}^i}{V_{free}^i} \right)^2 C_{free}^{ii} \quad (2.44) \]

\( V_{eff}^i \) is the effective Hirschfeld-partitioned volume and \( V_{free}^i \) is the free atom volume:

\[ V_{free}^i = \frac{\int r^3 w_i(\vec{r}) \rho(\vec{r}) d^3 \vec{r}}{\int r^3 \rho_{free}^i(\vec{r}) d^3 \vec{r}} \quad (2.45) \]

In which \( w_i(\vec{r}) \) is the Hirschfeld-partitioned weight for the atom \( i \) and is calculated as:
\[ w_i(\vec{r}) = \frac{\rho_i^{\text{free}}(\vec{r})}{\sum_j \rho_j^{\text{free}}} \]  

(2.46)

\( \rho(\vec{r}) \) and \( \rho_i^{\text{free}}(\vec{r}) \) in eq. (2.45) are the charge density of the system of study and that of free atom \( i \) where the origin of \( \vec{r} \) is on atom \( i \).

The relation between \( C_6^{ij} \) and coefficient of individual atoms \( i \) & \( j \) is given by:

\[
C_6^{ij} = \frac{2c_i^{i}C_6^{ij}}{\left(\frac{\alpha_j}{\alpha_i}\right)C_6^{ii} + \left(\frac{\alpha_i}{\alpha_j}\right)C_6^{jj}}
\]  

(2.47)

with \( \alpha_i \) as the static polarizability of atom \( i \).

Similar to DFT-D2 and DFT-D3 a damping function is introduced to avoid the divergence of the vdW energy at small distances which determines the range of dispersion corrections:

\[
f_6(r_{ij}, R_{ij}) = \frac{1}{1 + e^{-d(R_{ij} - s_R)}}
\]  

(2.48)

\( R_{ij} \) is the sum of vdW radii of atoms \( i \) & \( j \), \( d \) & \( s_R \) are free parameters determined to be 20 and 0.94 respectively in order to produce the best corrections for PBE functionals.

### 2.5.5 van der Waals Density Functional

This method [18-21] is the only method that uses a vdW exchange-correlation functional to take into account the vdW interaction into DFT calculations. In another words, despite DFT-D2, DFT-D3 and TS, it does not include dispersion corrections based on external parameters. Rather it uses an exchange-correlation functional defined as:

\[
E_{XC} = E_X^{GA} + E_C^{LDA} + E_C^{nl}
\]  

(2.49)
What this formalism provides is a combination of all the correlations for all ranges. The last term which is fully non-local correlation energy is given by:

\[
E_C^{nl} = \frac{1}{2} \int d^3r_1 d^3r_2 n(\mathbf{r}_1) \phi(q_1, q_2, \mathbf{r}_{12}) n(\mathbf{r}_2)
\]  

(2.50)

\(\phi(q_1, q_2, \mathbf{r}_{12})\) is a universal kernel and its definition for different classes of vdW-DF methods can be found in literature. The first and second terms in eq. (2.49) are the exchange energy evaluated using GGA functional and the local correlation energy obtained using LDA.

Although this method is more expensive than DFT-D and TS methods, it improves the values of lattice parameter and binding energies as a result of more accurate approach in considering the non-local interactions.

### 2.5.6 optB88-vdW

The optimized-Becke88 vdW functional (optB88) [21] is a functional with exchange factor of:

\[
F_x^{B88} = 1 + \frac{\mu s^2}{1 + \beta \text{sarcsinh}(cs)}
\]  

(2.51)

In this equation, \(s\) is the reduced gradient density and it is given by:

\[
s = \frac{\left|\nabla n(\mathbf{r})\right|}{2(3\pi^2)^{3/4}n(\mathbf{r})^{3/2}}
\]  

(2.52)

the parameters \(c, \mu\) and \(\beta\) are defined as:

\[
c = 2^{4/3}(3\pi^2)^{1/3}, \quad \beta = \frac{9\mu}{2c} \left(\frac{6}{\pi^2}\right)^{1/3}, \quad \mu \cong 0.2743
\]  

(2.53)
The optB88 functional has the $\mu/\beta$ and $\mu$ as 1.2 and 0.22 respectively. This modification gives binding energies that are significantly improved with respect to B88. However, similar to vdW-DF it is computationally expensive since all the parameters should be updated during calculations.

2.6 DFT calculations for extended systems

Even with exact exchange-correlation functional it is very difficult to solve KS equations for real systems because there are infinite number of electrons in the system. Therefore finding solutions based on symmetry to reduce the size of the system of study is crucial. This is where Bloch’s theorem allows us to solve the problem.

2.6.1 Bloch’s theorem

In solid state physics the crystal structures possess symmetry which allows one to break them down to the smallest unit cell that can fill the whole space and give the bulk structure of a crystal. If geometrically one can do so in real space, then using Fourier transformation a simple behavior is obtained in frequency, energy, space (reciprocal lattice). In another words, each electronic state (wave function in quantum mechanics) represents the state of an electron in a periodic external potential in which this periodicity comes from the periodicity of atomic structure. The mathematical presentation of such wave function is the product of a plane-wave ($\exp(i\vec{k} \cdot \vec{r})$) and a function $u$ with the periodicity of solid lattice:
\[ \psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}) \]  \hspace{1cm} (2.54)

\( u_{n,\mathbf{k}}(\mathbf{r}) \) can be expanded into basis sets using plane-waves whose wave vectors are reciprocal lattice vectors:

\[ u_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \]  \hspace{1cm} (2.55)

Substituting (2.55) in (2.54) we get:

\[ \psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \]  \hspace{1cm} (2.56)

Since \( u_{n,\mathbf{k}}(\mathbf{r}) \) has the periodicity of the lattice, it is identical to the function at \( \mathbf{r} + \mathbf{R} \):

\[ u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n,\mathbf{k}}(\mathbf{r}) \]  \hspace{1cm} (2.57)

or

\[ \psi_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{r}} \psi_{n,\mathbf{k}}(\mathbf{r}) \]  \hspace{1cm} (2.58)

This is called Bloch’s theorem [22]. This theorem allows one to have a problem of finite number of electrons rather than a system with infinite number of electrons. To apply this theorem to non-periodic systems such as alloys, systems with vacancy or surfaces, we need to build periodic models and use the perspective unit cell. This unit cell is called supercell.

### 2.6.2 k-point Sampling

Using Bloch’s theorem there could be infinite number of \( \mathbf{k} \) vectors which give the same wave function. Since reciprocal lattice is also periodic it can be considered as a collection of unit cells in energy space. This unit cell is called Brillouin Zone (BZ). The whole energy space can be reproduced by translation of \( \mathbf{k} \) vectors of BZ. Therefore if we solve the KS equations at certain \( k- \)
points we can have reasonable results for the unit cell. The set of these $k$ points is called $k$-point sampling. The BZ is sampled by equally spaced mesh points which is called Monkhorst and Pack method [23]. The accuracy of calculation is dependent on the density of mesh points. In practice one needs to test the accuracy of calculations for different number of $k$-points until the increase in the density of mesh points does not affect the energy of system, i.e. convergence is achieved.

2.6.3 Plane wave basis sets

To solve equation (2.54) we need to find a solution for $u_{n,k}$ to have a full solution for the system of study. To do so, the $C_{n,k+\vec{g}}$ coefficients should be accurately identified. These coefficients are proportional to the reverse of $\frac{1}{|\vec{k}+\vec{g}|}$. Therefore by increasing $|\vec{k}+\vec{g}|$ the coefficients will decrease. This means that the expansion of $u_{n,k}$ in terms of $C_{n,k+\vec{g}}$ coefficients can be truncated at a certain value of $|\vec{k}+\vec{g}|$. The kinetic energy, on the other hand, is proportional to $|\vec{k}+\vec{g}|^2$. Thus truncation in terms of coefficients expansion means a cutoff for kinetic energy:

$$E_{\text{cut}} \geq \frac{1}{2} |\vec{k}+\vec{g}|^2$$  \hspace{1cm} (2.59)

Using plane wave basis sets the KS equation can be written as:

$$\Sigma_{\vec{g}'} \left[ \frac{1}{2} |\vec{k}+\vec{g}|^2 \delta_{\vec{g},\vec{g}'} + V_{\vec{g},\vec{g}'}^{\text{eff}} \right] c_{i,\vec{k}+\vec{g}'} = \varepsilon_i c_{i,\vec{k}+\vec{g}'}$$  \hspace{1cm} (2.60)

The effective potential in second term of this equation is:

$$V_{\vec{g},\vec{g}'}^{\text{eff}} = \int V_{\text{ext}}^{\text{eff}} e^{i(\vec{g}-\vec{g}') \cdot \vec{r}} d^3\vec{r}$$  \hspace{1cm} (2.61)

To find the eigenvalues and eigenstates of eq. (2.60) we need to diagonalize the matrix whose number of elements re determined by the kinetic energy cutoff. Consequently the
coefficients $C_{n, \bar{k}+\bar{g}}$ will be obtained. Similar to $k$-point sampling the cutoff energy must be tested before doing the actual calculations for bigger systems. This cutoff energy changes from an atom type to another type. The cutoff energy is determined by convergence in calculations, i.e. the total energy does not change by varying the kinetic energy.

2.7 **Pseudopotential Approximation**

So far by introducing some approximations the SE for a real system is doable by solving it for a decreased number of electrons rather than infinite number of electrons of a real system. Even so we are left with huge number of electrons. For a real systems simulations we deal with at least 20 atoms in the unit cell. This means that we have to deal with hundreds of electrons in the unit cell. This problem by far is very difficult to solve. To further reduce the number of electrons it is important to know which electrons are involved in interactions.

In an atom there are two kinds of electrons: 1. Core electrons, 2. Valence electrons. Core electrons form the inner-shells of an atom and are strongly bound to nucleus. To involve these electrons in chemical interactions, one needs to separate them from core levels. This requires a huge amount of energy. In another words these electrons are not active. The outer-shell electrons which fill the highest energy levels of an atom, are valence electrons and are weakly bound to nuclei. These electrons are close to Fermi level and they are responsible for forming bonds and making interactions with electrons of neighbor atoms. This classification simplifies the problem of solving KS equations by a huge amount. Instead of dealing with all the electrons we can only solve equation for valence electrons. The other computational benefit of excluding core electrons
comes from the fact that the wave functions in core region have lots of oscillations. Mathematically this means that we need a huge amount of plane waves whose superposition accurately describes this region. This requires a huge amount of computational resources. To overcome this problem the pseudopotential approximation was developed by Phillips [24] and Yin et al [25]. In this approximation the atoms are divided into two regions of core and valence in which a weaker potential is replaced by the strong potential in core region named pseudopotential. The wave functions in this region are pseudo-wave functions. The boundary conditions requires that both wave function and its derivative be continuous at the boundary of core and valence regions. This means:

Pseudo-wave function of core region should match wave function of valence region a boundary.

The pseudo-wave function must be smooth and node-less in the boundary as a requirement of continuity of both regions wave-functions in the boundary. This boundary is called cutoff region. DFT, however, needs correct charge density to give correct values for observables. Therefore one should get correct charge density in the core region using pseudo-wave functions. This condition is called norm-conserving: inside the core region the total charge density generated by pseudo-wave functions must be identical with that generated by true wave functions. The potential who satisfies norm-conserving condition is called norm-conserving pseudopotential.

This condition does not work very well for some atoms such as C, O and N and some transition metals. It produces hardness of pseudopotential which means that a large plane wave basis set is required. To avoid this problem, Vanderbilt proposed a method for relaxing norm-conserving pseudopotentials so that it yields soft pseudopotential and smooth pseudo-wave functions. This method is called ultra-soft pseudopotential (USPP) [26]. Using this method there
will be charge loss because it is not constrained with norm-conserving condition. The charge loss is restored by an augmented charge which is determined as the difference between pseudo-wave function and true wave function of atoms.

In 1994 Blochl introduced the projected-augmented-wave method (PAW) [27] for high accuracy first principle calculations. This method is equivalent to all-electrons method. After reformulation of method in 1999 by Kress and Joubert [28], the PAW method became widely used. This reformulation uses a transformation operator that can map the true wave function onto pseudo-wave functions. After solving KS equations using pseudo-wave functions, the operator constructs real wave functions and observables are calculated. Thus the accuracy of this method is the same as all-electrons method.

2.8 Structural Relaxations

Within DFT and all the approximations introduced so far, the GS of a system with frozen nuclei can be determined. To find the minimum energy configuration one also needs to obtain the configuration of ions that minimizes the total energy of system, i.e. the ionic GS configuration. To obtain this result the force acting on ions should be zero. If forces are known methods such as conjugated gradient algorithm can be used to find their GS. This procedure is called structural relaxation.

DFT calculations does not directly provide the forces acting on ions. The theorem that gives these forces is called Hellmann-Feynman theorem [29] which gives forces as:

\[ \vec{F}_A = -\nabla_A E = -\nabla \langle \psi |\hat{H}| \psi \rangle = -\langle \psi |\nabla_A \hat{H}| \psi \rangle \]  \hspace{1cm} (2.62)
In another words the forces on the ions at their GS are the expectation values of the gradient of GS Hamiltonian.

When performing DFT calculations on real systems, usually there is a threshold for relaxation process. This force is mostly given in eV/Å or Ry/Bohr. Throughout this thesis there will be several places where the threshold of force acting on atoms is specified. This simply means that the calculation will stop as soon as the forces acting on atoms in all directions are smaller than the given threshold value.

2.9 Ab-initio Thermodynamics

The calculations performed by DFT gives the GS of a many-body system at zero temperature. The realistic condition, however, happens at non-zero temperatures. Even at zero temperature, ions (atoms) are not frozen and they vibrate. Although DFT gives correct results for GS, to cover the energy of a system at a non-zero temperature (T) and pressure (P) one needs to calculate free energy rather than total energy. Gibbs free energy as a function of T & P can be employed to achieve this purpose. This method is known as ab-initio thermodynamics (TD) [30-32]. Using this method the stability of a solid structure is evaluated.

Let us consider a surface (denoted as “sur”) covered by adsorbates (denoted by “ads”). The free energy of this surface, \( \gamma \) is defined as:

\[
\gamma = \frac{1}{A} (G_{ads/sur} - \mu_{sur} - \mu_{ads})
\]  

(2.63)
$A$ is the surface area exposed to adsorbate(s), $N$ is the number of adsorbates and $\mu_{\text{sur}}$ and $\mu_{\text{ads}}$ are chemical potentials of surface and adsorbate, respectively. The Gibbs free energy for this system is given by:

$$G_{\text{ads/sur}} = E_{\text{ads/sur}}^{\text{total}} + F_{\text{ads/sur}}^{\text{vib}} + PV$$  \hspace{1cm} (2.64)

$E_{\text{ads/sur}}^{\text{total}}$ is the total GS energy obtained from DFT and $F_{\text{ads/sur}}^{\text{vib}}$ gives the vibrational energy of the system at finite temperature as:

$$F_{\text{ads/sur}}^{\text{vib}} = \int d\omega \left[ \frac{1}{2} \hbar \omega + k_B T \ln \left( 1 - e^{-\frac{\hbar \omega}{k_B T}} \right) \right] \sigma(\omega)$$  \hspace{1cm} (2.65)

$\sigma(\omega)$ is the phonon density of states and $k_B$ is the Boltzmann constant. The last term in equation (2.64) is very small for a solid (in the order of $10^{-10}$) and can be neglected. The vibrational energy of atoms in a solid at $T=0$ K is:

$$F_{\text{vib}} = \sum_i \frac{1}{2} \hbar \omega_i$$  \hspace{1cm} (2.66)

This term is also called zero point energy (ZPE). To calculate the chemical potential for surface and adsorbate the following relation is used:

$$\mu_{\text{Gas}}(T, p) = \bar{\mu}_{\text{Gas}}(T, p_0) + k_B T \ln \left( \frac{p}{p_0} \right)$$  \hspace{1cm} (2.67)

In this equation, $p$ is variable, $p_0$ is the ambient pressure (1 atm) and $\bar{\mu}_{\text{Gas}}$ are obtained for $p_0 = 1$ atm from experimental entropy and enthalpy taken from thermochemical table. This definition is based on an ideal gas. By substituting eq. (2.64) and eq. (2.65) in eq. (2.63), the temperature and pressure dependence energy can be calculated which provides information on the stability of the systems under pressure in non-zero temperatures.
2.10 Bader Charge Analysis

In so many cases the charge transferred among interacting atomic species, provides useful insight on the nature of bonding. However as discussed before, the main basis for solving KS is charge density which is a continuous quantity and is not an observable. Therefore to find the amount of charge transferred among atoms, a definition of atom based on charge density is required. Richard Bader proposed a model named “Atoms In Molecules” (AIM) [33] to estimate the space of an individual atom by a 2D zero flux surface on which the charge density is a minimum perpendicular to this surface. These regions are called Bader volumes. The mathematical condition to be satisfied is:

\[ \nabla n(\vec{r}).\hat{n}(\vec{r}) = 0 \]  \hspace{1cm} (2.68)

\( \hat{n}(\vec{r}) \) is the unit vector of the 2D surface and \( \nabla n(\vec{r}) \) gives the gradient vector field of charge density. Through an iterative procedure the product of \( \nabla n(\vec{r}) \) and \( \hat{n}(\vec{r}) \) are calculated until the gradient of the produced trajectory satisfies the above condition. Bader’s method not only provides a tool to visualize atoms in molecules, it also gives information on the transferred charge or multipole moments of interacting atoms. The total charge of each atom is estimated in Bader volume.

In recent years, an algorithm has been developed by Henkelman et al. [34] which implements Bader analysis in DFT calculations. This algorithm uses a grid-based calculations to obtain total charge of an atom. To achieve accurate results a fine grid should be used to avoid cusps at core region and provide correct number of valence electrons.
2.11 Tersoff-Hamann Model for Simulations of Scanning Tunneling Microscopy

In several chapters of this thesis we have simulated the Scanning Tunneling Microscopy (STM) image of the system under study to validate our results compared to experimental data. These simulations were performed using a method named Tersoff-Hamann (TH) [35,36] model. In this section a brief description of this method and its basis is introduced.

The invention of scanning tunneling microscopy (STM) [37-39] has profoundly affected our understanding of the structure of material. STM provides information on the atomic structure of surfaces. The low-temperature STM is very useful in studying the local electronic properties of a surface. The basic concept behind STM imaging is a tunneling current between the probing device, STM tip, and the sample. Upon applying a voltage the tip moves on the surface without touching it. The flowing current therefore is generated by tunneling of electrons between tip and sample which is a pure quantum mechanical concept. To understand and simulate STM, the knowledge on both tip and sample are important. However it is very difficult to access right model for tip experimentally. Moreover, when performing STM to get insight into the atomic structure of sample, the electronic structure of tip is not of interest and therefore we need a model that can give reasonable approximation without directly considering the structure of tip.

The first model to simulate STM image was proposed by Bardeen in 1961 [40]. This model uses a non-interacting approach between tip and sample and is reasonable for low voltage STM measurements. The tip and sample are described by separate wave functions $\Psi_T$ and $\Psi_S$, respectively and the tunneling current is calculated as their overlap:

$$I_{S\rightarrow T} = \frac{4\pi e}{\hbar} \sum_{\nu\mu} f(E^S_{\mu} - E^T_{\nu}) [1 - f(E^T_{\nu} - E^S_{\mu})] |M_{\mu\nu}|^2 \delta(E^T_{\nu} - E^S_{\mu} - eV)$$

(2.69)
\[ I_{T \rightarrow S} = \frac{4\pi e}{\hbar} \sum_{\nu \mu} f(E^S_\nu - E^T_\nu)[1 - f(E^S_\mu - E^T_\mu)]|M_{\mu\nu}|^2 \delta(E^T_\nu - E^S_\mu - eV) \quad (2.70) \]

Equations (2.69) and (2.70) give the tunneling current from tip to sample and vice versa. The net tunneling current is given by the difference between them:

\[ I = \frac{4\pi e}{\hbar} \sum_{\nu \mu} \left[ f(E^S_\nu - E^T_\nu) - f(E^T_\mu - E^S_\mu) \right]|M_{\mu\nu}|^2 \delta(E^T_\nu - E^S_\mu - eV) \quad (2.71) \]

The summation goes over all single states \( \mu \) and \( \nu \) of sample and tip. \( f(E^S_\nu - E^T_\nu) \) and \( f(E^T_\mu - E^S_\mu) \) are Fermi-Dirac distribution function of occupied states and \( M_{\mu\nu} \) are tunneling matrix elements which is given by:

\[ M_{\mu\nu} = \frac{\hbar^2}{2m} \int [\bar{\psi}_\mu \nabla \psi^*_\nu - \bar{\psi}^*_\nu \nabla \psi_\mu] dS \quad (2.72) \]

This integral is performed on the separation surface between tip and sample’s defining volumes.

To get rid of tip’s states in the equation above, TS model considers tip as a locally spherical potential with s-wave functions centered at \( \vec{R}_T \). The regular wave function describing such potential is a Bessel function of the second type:

\[ \psi^T_\nu(\vec{r} - \vec{R}_T) = C k_0^T(\kappa |\vec{r} - \vec{R}_T|) = C e^{-\kappa|\vec{r} - \vec{R}_T|} \quad (2.73) \]

\( C \) is the normalization constant and \( \kappa \) is given by:

\[ \kappa = \frac{2mE}{\hbar^2} \quad (2.74) \]

Using the wave function in eq. (2.72) the tunneling elements of Bardeen’s formulation are as:

\[ M_{\mu\nu}(\vec{R}_T) = -\frac{\hbar^2}{2m} \int_{\Omega_T} \left[ k_0^T(\kappa |\vec{r} - \vec{R}_T|) \nabla^2 \psi_\nu^T(\vec{r} - \vec{R}_T) \right. \\
- \left. \left. \psi_\nu^T(\vec{r} - \vec{R}_T) \nabla^2 k_0^T(\kappa |\vec{r} - \vec{R}_T|) \right] d\vec{r} \quad (2.75) \]

Since the tip’s wave function decays in the sample, one can use the vacuum Schrödinger equation to solve it:
\[(\nabla^2 - \kappa^2)G(\vec{r} - \vec{R}_T) = \delta(\vec{r} - \vec{R}_T)\]  

(2.76)

with \(G(\vec{r} - \vec{r}')\) as the Green function of the vacuum:

\[G(\vec{r} - \vec{R}_T) = \frac{\kappa}{4\pi \epsilon C} \psi^T(\vec{r} - \vec{R}_T)\]

(2.77)

The equation (2.75) then simplifies to:

\[M_{\mu\nu}(\vec{R}_T) = -\frac{2\pi e}{\kappa m} \psi^\nu(\vec{R}_T)\]

(2.78)

This result is the core of TH model. It states that if tip is symmetric around a point \(\vec{R}_T\), the tunneling matrix element is directly proportional to the sample’s wave function at \(\vec{R}_T\). Using this result the tunneling current is:

\[I(\vec{R}_T, V) = \frac{16\pi^3 \epsilon^2 e^3}{\kappa^2 m^2} n^T \int_0^{eV} \text{den}_s(\vec{R}_T, E_F^S + \epsilon)\]

(2.79)

\(n^T\) is a constant in this model owing to tip’s s-type nature in this model and \(n_S\) is:

\[n^S(\vec{R}_T, \epsilon) = \sum \delta(E^S_{\mu} - \epsilon) |\psi^S_{\mu}(\vec{R}_T)|^2\]

(2.80)

Eq. (2.79) shows that the current is proportional to the integral over all the states at tip’s center with energies ranging in the interval of Fermi energy and its shift by applied bias voltage (eV). Using DFT calculations we can calculate the partial charge density of the system within the range of applied bias voltage.

Although TH model provides a simple and valuable framework for STM simulations, it is limited only to the cases that all the tip wave functions other than s-wave function are neglected. If the geometry of tip is more complicated other extensions should apply to its formulations.
2.12 Reaction Barriers Calculations: Nudged Elastic Band Method

In the studying of the chemical reactions and/or their feasibility calculations of the reaction barriers are of great importance. At zero temperature the atoms in a system possess a configuration so that the total energy of the system is in a local minimum. At finite temperatures, though, the atoms start to move while their motion is around their equilibrium position. This causes atoms to move along the path that corresponds to the lowest energy maximum. This path is called minimum energy path (MEP).

For a reaction the path starts from one local minimum which is defined by initial state (IS) and ends at another local minimum called final state (FS). The system moves along this path going through several meta-stable states with energies higher than the energy of IS and FS. The state with highest energy is called transition state (TS). Mathematically such point on the energy landscape is called saddle point. The energy cost to move from IS to TS is called energy barrier. In this thesis the energy barriers have been calculated using a method named Nudged Elastic Band (NEB) method [41]. NEB method is used when both initial and final states are known.

If IS and FS of a system are known, using elastic band method a series of images according to the linear interpolation are generated between these two states. The images are connected by artificial springs to the neighboring images. Let’s consider these states as \((R_0, R_1, R_2, \ldots, R_N)\) where \(R_0\) is the initial image and \(R_N\) is the final image. While IS and FS are kept fixed, the energy of all the other images are minimized such that the neighboring images are equidistant from each other. The energy of images can be expressed as:

\[
S(R_1, R_2, R_3, \ldots, R_N) = \sum_{i=1}^{N-1} E(R_i) + \sum_{i=1}^{N} \frac{k}{2} (R_i - R_{i-1})^2
\]  

(2.81)
$E(R_i)$ is the potential energy of image $i$ and $k$ is the spring constant connecting it to the neighbor images. Once the energies of individual images are minimized, the MEP can also be determined. Therefore not only this method provides the configuration of TS and consequently the energy barrier of the specific reaction energy, it also give insight into energy landscape. The strength of NEB method comes from two problems inherited in elastic band method:

1. When MEP is curved, the elastic band pulls the image away from MEP as a result of the elasticity force of springs between images which is perpendicular to the path. This is defined as corner-cutting problem.
2. Since the initial and final states are fixed, the images in between move towards the fixed end points. This results in the reduction of number of images around the saddle point. The force component causing this problem is the parallel component of interatomic force. This is defined as down-sliding problem.

To avoid these problems a new force is introduced:

$$F_{i}^{\text{NEB}} = -\nabla E(R_i)_\bot + F_i^{\text{spring}} \cdot \hat{t}_i \hat{t}_i$$ (2.82)

The first term in this equation is the perpendicular force component coming from the gradient of the energy:

$$F_{i}^{\bot} = \nabla E(R_i) - \nabla E(R_i). \hat{t}_i \hat{t}_i$$ (2.83)

The parallel force is the result of connecting springs:

$$F_{i}^{\parallel} = k(|\vec{R}_{i+1} - \vec{R}_i| - |\vec{R}_i - \vec{R}_{i-1}|)$$ (2.84)

The main important ingredient in this formulation is the unit vector $\hat{t}_i$. This vector is the tangent vector at image $i$ and is calculated by bisecting the two unit vectors from image $i \rightarrow i + 1$ and $i - 1 \rightarrow i$:
\[ \hat{t}_i = \frac{\vec{R}_{i+1} - \vec{R}_i}{|\vec{R}_{i+1} - \vec{R}_i|} + \frac{\vec{R}_i - \vec{R}_{i-1}}{|\vec{R}_i - \vec{R}_{i-1}|} \] (2.85)

and is normalized as:

\[ \hat{t}_i = \frac{\hat{t}_i}{|\hat{t}_i|} \] (2.86)

Figure 2.2. An illustration of force components through elastic band method along with the nudged forces components. Figure is taken from Ref [42].

This definition ensures that images are kept equidistant from each other. On the other hand the corner-cut problem is solved since the nudging force compromises the pulling away of images from curved MEP. However, if the energy change is high between successive images, NEB might
still not lead to the convergence in optimizing the MEP. The solution to this case is a function with a slight modification in the original NEB force (eq. (2.82)): a small increase in the perpendicular component of spring force while reducing its parallel component. This equation is defined as:

$$F^\text{NEB}_i = -\nabla E(R_i) + F^\parallel_i \hat{\tau}_i \hat{\tau}_i + f(\phi_i) \{F^\parallel_i - F^\parallel_i \hat{\tau}_i \hat{\tau}_i\}$$

(2.87)

$f(\phi_i)$ is a switching function which smoothly turns on the perpendicular component of spring force:

$$f(\phi_i) = \frac{1}{2} (1 + \cos(\pi \cos(\phi_i)))$$

(2.88)

with

$$\cos(\phi_i) = \frac{(\vec{R}_{i+1} - \vec{R}_i)(\vec{R}_i - \vec{R}_{i-1})}{[(\vec{R}_{i+1} - \vec{R}_i)][(\vec{R}_i - \vec{R}_{i-1})]}$$

(2.89)

In an implementation of NEB by Henkelman et al. [41] a new tangent vector is defined for the slow-converging or non-converging cases:

$$\hat{\tau}_i = \begin{cases} \hat{\tau}_i^+ & \text{if } E_{i+1} > E_i > E_{i-1} \\ \hat{\tau}_i^- & \text{if } E_{i+1} < E_i < E_{i-1} \end{cases}$$

(2.90)

with

$$\hat{\tau}_i^+ = \vec{R}_{i+1} - \vec{R}_i$$

(2.91)

$$\hat{\tau}_i^- = \vec{R}_i - \vec{R}_{i-1}$$

(2.92)

In fact the new tangent vectors are between image $i$ and its neighbor image with higher energy.

If image $i$ is in minimum, i.e. both neighbors are higher in energy, or in a maximum, i.e. both neighbors are lower in energy, the equation (2.156) modifies to:

$$\hat{\tau}_i = \begin{cases} \hat{\tau}_i^+ \Delta E^\text{max}_i + \hat{\tau}_i^- \Delta E^\text{min}_i & \text{if } E_{i+1} > E_i > E_{i-1} \\ \hat{\tau}_i^+ \Delta E^\text{min}_i + \hat{\tau}_i^- \Delta E^\text{max}_i & \text{if } E_{i+1} < E_i < E_{i-1} \end{cases}$$

(2.93)

where
The new tangent vectors are weighted averages of the vectors defined in equations (2.91) and (2.92). The intermediate images are optimized according to a force-based optimization method. Some of the commonly used ones include: Steepest-Descent (SD) [43], Quick-min (QM) [44], Conjugated Gradient (CG) [43] and Limited-memory Broyden-Fletcher-Goldfrab-Shanno (LBFGS) routines. Once the projection of forces are known, a convergence criteria is identified and the optimization is employed to move images along the reaction path.

2.13 Climbing Image Nudged Elastic Band Method

Climbing-Image (CI) NEB [45] is a modification to the regular NEB calculations, the modification comes from turning the spring force off for the image with highest energy. As a result this image climbs to the saddle point. Therefore only the force coming from interatomic interactions is inverted. Subsequently the image maximizes its energy along the band while minimizing it on all the other directions. After convergence, this image will be in exact saddle point. Since the spring force is not acting on this image, it will have unequal spacing with images on either side of it. It is important to note that to have time-efficient CI-NEB calculations, one needs to start with some regular NEB calculations to both have an estimate of reaction co-ordinates around the saddle point as well as having the highest energy image closer to the saddle point. If initially the calculations start with CI-NEB, the convergence process takes much longer especially
if the maximum energy image is far from the saddle point. Figure (2.3) presents the comparison of the obtained MEP for CH$_4$ dissociative adsorption on Ir(111) using both NEB and CI-NEB.

All the barriers calculated in this thesis were performed using regular NEB at first and after identifying the MEP, the CI-NEB calculations were carried out.

Figure 2.3. DFT calculations of the minimum energy path for CH$_4$ dissociative adsorption on the Ir(111) surface. The regular NEB results in a low resolution of the barrier, and the interpolation gives an underestimate of the activation energy. The climbing image NEB brings one of the images right to the saddle point and gives the activation energy precisely with insignificant additional computational effort. Image and caption are from Ref [45].
2.14 Time-Dependent Density Functional Theory

So far we have learnt that standard DFT refers to the GS of materials. The important output to be calculate for GS is the GS density of electrons. Then the total energy and forces acting on atoms in material are obtained. Within GS-DFT calculations the reaction barriers, atomic charges and ZPEs are estimated. However standard DFT is limited in the sense that it deals with GS properties, i.e., the properties independent of time with lowest energy of system. So many of physical properties of materials, though, are time dependent and belong to excited states of materials. In another words we need to describe the time-dependent observables of material. Time-Dependent DFT (TDDFT) goes beyond limitation of GS-DFT by solving time-dependent-SE (TDSE) as a functional of density of electrons. TDDFT describes “driven systems”. What is a driven system and how TDDFT describes it?

A driven system is the one exposed to some kind of time-dependent external field such as a laser pulse. The TDSE is consisted of following terms:

\[
\frac{i\partial}{\partial t} \Psi(\vec{r}, t) = \hat{H}(t)\Psi(\vec{r}, t)
\]  

(2.96)

with

\[
\hat{H}(t) = T_e[n(\vec{r})] + V_e[n(\vec{r})] + \sum_{j=1}^{N} \sum_{a} - \frac{Z_a e^2}{|\vec{r}_j - \vec{R}_a|} + \sum_{j=1}^{N} \vec{n}_j \vec{E}(t)\cos(\omega t)
\]

(2.97)

In this case the external potential is the sum of third and fourth terms in equation (2.97).

It is important to know what happens if a molecule or solid is irradiated with a laser: The particles of system may come out which is ionization (if electrons are coming out) and dissociation (if ions are separated from system). If electrons are excited by adsorption of laser energy (excitation), after a while they will de-excite to lower energies and a photon will be generated.
These are some kinds of phenomena of interest which are not in the realm of GS-DFT calculations. Adsorption spectrum, photon spectrum as a result of interaction of system in a given $\omega$ are some observables that are obtained by solving TDSE.

TDDFT is in spirit very similar to GS-DFT, i.e., the density is the important object to be determined. However the electrons orbitals are time dependent and so is the electron density. As mentioned at the beginning of this section the external potential consists of a static term (electron-ion interaction) and a time-dependent term (the applied external potential). Similar to GS-DFT, the BO approximation is deeply embodied in TDDFT calculations. In another words, even in the presence of a time dependent external potential, the ions are kept fixed. However, despite GS-DFT the problem starts from an initial state, $\Psi(t_0) = \Psi_0(\vec{r}_1, ..., \vec{r}_N)$, which is determined in a previous step and the task is to describe its propagation in time, $\Psi(\vec{r}, t)$ when exposed to a time-dependent external potential. As a result of having a time-dependent state, the density of electrons is also time dependent:

$$n(\vec{r}, t) = N \int d^3r_2 ... \int d^3r_N |\Psi(r_1, ..., r_N, t)|^2$$  \hspace{1cm} (2.98)

The time-dependent KS equation is represented by:

$$i \frac{\partial}{\partial t} \phi_j(\vec{r}, t) = (-\frac{\nabla^2}{2} + v_s(\vec{r}, t))\phi_j(\vec{r}, t)$$ \hspace{1cm} (2.99)

where the time dependent single particle potential is:

$$v_s(\vec{r}, t) = V_{\text{ext}}[n(\vec{r}, t)](\vec{r}, t) + \int \left(\frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|}\right) d^3r' + V_{\text{xc}}[n(\vec{r}, t)](\vec{r}, t)$$ \hspace{1cm} (2.100)

The second term is time-dependent Hartree potential and the last term should be identified by some approximations. The solution to this equation is not following the same routine as GS-DFT. In another words it is not self-consistent calculations. Starting from the initial state, the time-
dependent potential is applied to the system and for the time of propagation the time-dependent density is calculated. After having density, the quantity of interest can be obtained. However similar to DFT there is a one to one correspondence between external potential and density. This was proved by Runge and Gross (RG) in 1984 [46].

2.14.1 One-to-One Correspondence

Let’s consider N non-relativistic electrons in a time-dependent external potential. The RG theorem states that “the densities $n(\vec{r}, t)$ and $n'(\vec{r}, t)$ evolving from a common initial state $\Psi(t = 0)$ under the influence of two potentials $V_{\text{ext}}(\vec{r}, t)$ and $V'_{\text{ext}}(\vec{r}, t)$ in which both are expandable about the initial time 0, eventually differ if the potentials differ by more than a purely time-dependent ($\vec{r} = \text{independent}$) function”. This can be written as:

$$\Delta V_{\text{ext}}(\vec{r}, t) = V_{\text{ext}}(\vec{r}, t) - V'_{\text{ext}}(\vec{r}, t) \neq c(t) \quad (2.101)$$

The starting point to this theorem is the current density. First we will show that current densities corresponding to time-dependent density of electrons differ. The current density is given by:

$$j(\vec{r}, t) = N \int d^3r_2 \ldots \int d^3r_N \text{Im}\{\Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N, t)\overline{\Psi'}(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N, t)\} \quad (2.102)$$

Using the continuity principle we have:

$$\frac{\partial n(\vec{r}, t)}{\partial t} = -\vec{\nabla}.j(\vec{r}, t) \quad (2.103)$$

At $t = 0$ the equation of motion for the difference of the two current densities is:
This means that for two Taylor-expandable potentials that differ by more than a time-dependent constant, the corresponding currents are different. This proof establishes a one-to-one correspondence between current densities and external potentials.

Now using the last term in eq. (2.104) we extend this to densities by taking the gradient of both sides:

$$\frac{\partial}{\partial t} \{ n(\vec{r}, t) - n'(\vec{r}, t) \}_{t=0} = -\nabla \cdot \{ n_0(\vec{r}) \nabla \nabla (V_{\text{ext}}(\vec{r}, t) - V'_{\text{ext}}(\vec{r}, t)) \}_{t=0} \quad \text{(2.105)}$$

The time derivative of external potentials difference is non-zero. Therefore if the divergence is also non-zero, the densities must differ. Since the potentials differ by more than a time-dependent constant, the theorem is proved.

### 2.14.2 Linear Response Theory

Linear Response (LR) TDDFT [47] is applicable under the assumption that the external potential is so small that we can use time-dependent perturbation theory to solve the time-dependent KS equation:

$$\hat{H}(t) = \hat{H}_0 + \delta \hat{V}(t) \quad \text{(2.106)}$$

At $t = 0$ the second term is zero and the time dependent Hamiltonian reduces to the static Hamiltonian. Using interaction picture, the wave functions in eq. (2.96) are transformed to:
\[ |\Psi_i(t)\rangle = e^{iH_0 t}|\Psi(t)\rangle \]  \hspace{1cm} (2.107)

and the operators are presented as:

\[ \hat{O}_i = e^{iH_0 t}\hat{O}_se^{-iH_0 t} \]  \hspace{1cm} (2.108)

One can write the wave functions in interaction picture as following in terms of GS wave functions:

\[ |\Psi_i(t)\rangle = |\Psi_0\rangle - i \int_0^t dt'\delta V_i(t')|\Psi_0\rangle + O(\delta V_i(t)^2) \]  \hspace{1cm} (2.109)

Since the applied potential is very small and we are in perturbation regime, all the terms with higher orders are neglected. Therefore wave functions are linearly dependent to time-dependent perturbation term. Using equation (2.104) the expectation value of any operator can be calculated:

\[ \langle \hat{O}(t) \rangle = \langle \Psi_i(t)|\hat{O}_i|\Psi_i(t)\rangle = \langle \hat{O}_0 \rangle - i \int_0^t dt'\langle \Psi_0|[\hat{O}_i, \delta \hat{V}_i(t')]|\Psi_0\rangle \]  \hspace{1cm} (2.110)

The response of the operator is defined as its variation with respect to perturbation term.

By considering the operator in the equation above as density operator, its expectation value gives the time-dependent density. The density operator is defined as:

\[ \hat{n}(\vec{r}) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i), \quad n(\vec{r}) = \langle \Psi|\hat{n}(\vec{r})|\Psi\rangle \]  \hspace{1cm} (2.111)

Using this definition the time-dependent perturbation operator is re-written as:

\[ \delta \hat{V}(\vec{r}, t) = \delta V(\vec{r}, t)\hat{n}(\vec{r}) \]  \hspace{1cm} (2.112)

This helps us to have the perturbation term as a multiplicative one-dimensional operator. By plugging the eq. (2.112) in eq. (2.110) the response of density is given by:

\[ \delta n(\vec{r}, t) = \int_0^\infty dt' \int d^3r'\chi(\vec{r}t, \vec{r}'t')\delta V(\vec{r}'t') \]  \hspace{1cm} (2.113)

with
\[
\chi(\vec{r}, t, \vec{r}', t') = \frac{\delta n(\vec{r}, t)}{\delta V(\vec{r}', t')} = -i \Theta(t - t') \langle \Psi_0 | [n_1(\vec{r}, t), n_1(\vec{r}', t')] | \Psi_0 \rangle
\]  

(2.114)

This equation is called the density-density response or susceptibility. \(\Theta(t - t')\) is step function and is zero for \(t < t'\). Calculations of susceptibility as the linear response of density with respect to time-dependent potential is the central object of Linear-Response (LR) theory.

Using time-dependent single particle KS relation, the eq. (2.113) is modified to:

\[
\delta n_{KS}(\vec{r}, t) = \int_0^\infty dt' \int d^3 r' \chi_{KS}(\vec{r}, \vec{r}, t') \delta V_{KS}(\vec{r}', t')
\]  

(2.115)

and

\[
\chi_{KS}(\vec{r}, t, \vec{r}', t') = \left( \frac{\delta n_{KS}(\vec{r}, t)}{\delta V_{KS}(\vec{r}', t')} \right)_{V_{KS} = V_{KS}[n_0](\vec{r})}
\]  

(2.116)

Since we are in LR regime, this means that the time-dependent part of each term in \(V_{KS}\) is linearly related to potential’s expansion in time. Therefore the exchange correlation potential can be written as:

\[
V_{XC}[n(\vec{r}, t)](\vec{r}, t) = \int dt' \int d^3 r' \left( \frac{\delta V_{XC}[n(\vec{r}, t)](\vec{r}, t)}{\delta n(\vec{r}', t')} \right) n_{1}(\vec{r}', t')
\]

(2.117)

The subscript “1” indicates that it is the perturbed term proportional to the first order of perturbation potential. By substituting eq. (2.100) and eq. (2.117) in eq. (2.116) one gets:

\[
n_1(\vec{r}, t) = \int dt' \int d^3 r' \chi_{KS}(\vec{r}, t, \vec{r}', t')[\delta V_{1}(\vec{r}', t')] + \int dt'' \int d^3 r'' \left( \frac{\delta(\vec{r} - \vec{r}'')}{|\vec{r} - \vec{r}'|} f_{XC}(\vec{r}', t', \vec{r}'', t''') \right) n_1(\vec{r}'', t''')
\]

(2.118)

Subsequently one can rewrite the equation above in terms of susceptibility and get:
\[
\chi(\vec{r}, t, \vec{r}', t') = \chi_{KS}(\vec{r}, t, \vec{r}', t') + \int dt'' \int d^3r'' \chi_{KS}(\vec{r}, t, r'', t'') \frac{\delta(t''-t'')}{|r''-r'|} + \int d\tau_1 \int d\tau_2 f_{XC}(\vec{r}_1, \vec{r}_2, \tau_1, \tau_2) \chi(\vec{r}_1, \vec{r}_2, \tau_1, \tau_2) \]

(2.119)

In frequency space this equation is:

\[
\chi(\vec{r}, \vec{r}', \omega) = \chi_{KS}(\vec{r}, \vec{r}', \omega) + \int d^3r_1 \int d^3r_2 \chi_{KS}(\vec{r}, \vec{r}_1, \omega) \frac{1}{|\vec{r}_1-\vec{r}_2|} + f_{XC}(\vec{r}_1, \vec{r}_2, \omega) \chi(\vec{r}_1, \vec{r}_2, \omega) \]

(2.120)

This is the main TDDFT-LR equation and gives the total susceptibility of system in the presence of a time-dependent perturbation. The KS susceptibility is given by:

\[
\chi_{KS}(\vec{r}, \vec{r}', \omega) = 2 \lim_{\eta \to 0} \sum_q \left\{ \frac{\xi_q(\vec{r})}{\omega - \omega_q + i\eta} - \frac{\xi_q^*(\vec{r})}{\omega + \omega_q + i\eta} \right\} \]

(2.121)

When \(\omega\) matches the energy difference between two levels in the system, the response function \(\chi\) blows up which means that it has a pole. This energy difference is hidden in the values of \(\omega_q\):

\[
\omega_q = \varepsilon_i - \varepsilon_j
\]

(2.122)

and

\[
\xi_q(\vec{r}) = \phi_i^*(\vec{r}) \phi_j(\vec{r})
\]

(2.123)

\(\varepsilon_i\) and \(\phi_i(\vec{r})\) are KS eigenenergy and states. If there is no perturbation, i.e., no Hartree-XC effects, the eq. (2.120) reduces to susceptibility of GS-KS system and the transitions are the single-particle KS transitions of GS. The presence of kernel shifts the transitions to the true values. Each transition determined by the poles of susceptibility are related to the absorption intensities. This is also called oscillator strengths and is directly affected by the kernel, i.e., different XC functionals may lead to different strengths in absorption spectrum. In the next section, we show how susceptibility is related to absorption spectrum.
2.14.3 Absorption Spectrum

The interaction between light (electromagnetic fields) and matter can be expressed in terms of Maxwell’s equations [48]:

\[ \nabla \cdot \vec{D} = n_f, \quad \vec{B} = \epsilon \vec{E}, \quad \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \]  \hspace{1cm} (2.124)

\[ \nabla \cdot \vec{B} = 0, \quad \vec{B} = \mu \vec{H}, \quad \nabla \times \vec{H} = \vec{j}_f + \frac{\partial \vec{D}}{\partial t} \]  \hspace{1cm} (2.125)

\( \vec{D} \) is the electric displacement and is connected to electric field by a complex coefficient named permittivity. The same is true for \( \vec{B} \) and \( \vec{H} \). In the case of a non-magnetic material \( \mu = 1 \). One of the most important characteristics of a material is its permittivity:

\[ \epsilon = \epsilon' + i\epsilon'' \]  \hspace{1cm} (2.126)

The real part of eq. (2.126) shows the oscillations of field inside the material while its imaginary part shows its decay. Light in a material can be propagated, adsorbed or reflected. Each of these phenomena depends on the internal properties of that specific material when interacting with a characteristic frequency. The electric permittivity is, on the other hand, related to susceptibility by:

\[ \epsilon = (1 + 4\pi \chi)\epsilon_0 \]  \hspace{1cm} (2.127)

What this equation means is that permittivity \( \epsilon \) embodies a measure of the response of material to an external potential which has the same definition provided in previous section for \( \chi \). Therefore the absorption spectrum of material which is defined by its permittivity, is obtained by having the electric susceptibility. This spectrum as discussed before has peaks when the frequency of the light matches that of the energy difference between two energy levels.
2.14.4 Casida Equation

In section (2.14.3) we showed that the total susceptibility can be obtained in terms of $\chi_{KS}$ if the kernel is known. The first matrix representation of LR-TDDFT was derived by Casida in 1995 [49] and 1996 [50]. Casida showed that the true excitation frequencies $\Omega_i$ of a system and the strength of these excitations can be obtained from eigenvalues and eigenvectors of the following matrix equation:

$$ RF_i = \Omega_i F_i $$  \hspace{1cm} (2.128)

with

$$ R_{qq'} = \omega_q^2 \delta_{qq'} + 4\sqrt{\omega_q \omega_{q'}} \int d^3 r \int d^3 r' \phi_q(r) f_{HXC}(r, r', \Omega_i) \phi_{q'}(r') $$ \hspace{1cm} (2.129)

and the oscillator strength of each transition in the interacting system is given by:

$$ f_i = \frac{2}{3} \Omega_i (|\langle \Psi_0 | \hat{x} | \Psi_i \rangle|^2 + |\langle \Psi_0 | \hat{y} | \Psi_i \rangle|^2 + |\langle \Psi_0 | \hat{z} | \Psi_i \rangle|^2) $$ \hspace{1cm} (2.130)

Eq. (2.130) is also known as dipole moments equation. In another words the strength of each transition is dictated by dipole moment of transition from state $\Psi_0$ to $\Psi_i$. It is important to mention that the matrix formulation presented by Casida is only valid for discrete spectra and therefore it is mostly used to describe excitations in finite systems. To have a description of excitations in extended systems, one can write eq. (2.120) in momentum space for an extended system. The derivation of this formalism is not in the scope of this thesis and can be found in literature.
CHAPTER 3: ADSORPTION OF FUNCTIONALIZED NAPHTHALENE MOLECULES ON Cu(111)

3.1 Introduction

Organic molecules on metal surfaces can serve as building blocks of self-assembled networks with promising applications in areas such as heterogeneous catalysts, electronic devices, optoelectronics, etc. [51-59]. The molecules self-assemble and form well patterned structures either by interactions between adjacent molecules [60-87] or by coordination around a metallic center[65,74,75,77,88-110]. The metallic center (adatom), on the other hand, either is an atom from substrate which is thermally generated [65,74,75,77,88,91,95,97,98,100,101,105-107,109], usually from edge, step or kink sites, or is deposited on the surface at a fixed temperature [88-90,92-96,99,101-105,108-110]. The adatom then serves as a charge reservoir to stabilize molecules and in the situation that molecules are symmetric and the concentration of adatoms is enough, this leads to formation of well-patterned structures with an array of organized adatoms. The patterns are tunable based on the size and functionality of molecule [75,89,92,93,96,97,103], underlying surface [74,93,101,106,109] or adatom specie [95,110]. Thus structures are a result of molecule-adatom, molecule-molecule and molecule-substrate interactions.

While experimental studies have proven that single atoms could be catalytically more active than its nanoparticle or surface counterparts with even higher selectivity such as single atom alloys (SAA) [2], at high temperatures the atoms either dissolve to host surface or form clusters which again results in loss of activity. In this regard, organic molecules are best candidates to stabilize these atoms due to their high stability and facile preparations. That is why surface coordination structures have attracted tremendous interest for catalytic purposes simply because not only the
less amount of material is used as catalyst without losing its efficiency at high temperature but also due to the possibility to tune the charge accumulation on atomic centers in contact with the functional group of molecule. Therefore, the change of functional group in coordinated structure of molecules may result in change of the oxidation state of the desired adatom which is the key factor in selectivity of catalytic atomic centers. Although the formation of surface coordination patterns, need two or more symmetric molecules, the first step to fully understand these systems is studying of a single molecule adsorption. With this in mind, we have used van der Waals (vdW) corrected Density Functional Theory (DFT) calculations on adsorption of a group of functionalized Naphthalene molecules with varying functional groups on the Cu(111) surface to answer the question: how functional group affects the geometric and electronic properties of adsorption? To avoid the steric effects between different functional groups, each molecule carries only one functional group including: N, CN (cyanide, polar), NC (isocyano, polar), NH2 (amine, polar), COH (aldehyde, polar) and COOH (carboxyl, polar), each with one or more lone pairs and with the order of polarity as: COOH > COH > NH2 > NC > CN > N. In this regard, the role of functional group is studied in detail. Furthermore using our results, we give an estimation of vdW and covalent interactions in the bonding of each molecule to the surface/adatom. We also demonstrate how introducing a single atom leads to great changes in charge accumulation and consequently binding of molecules.
3.2 Calculation Methods

The calculations in this paper were performed using DFT [5,6] by employing the projector-augmented wave (PAW) [27,28], plane wave basis set and the supercell method as implemented in the Vienna Ab-initio Simulation Package (VASP) [111]. The exchange-correlation interaction of electrons was described by generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhoff (PBE) functional [112]. To include long range order interactions we have used optB88-vdW functional [21] for the systems of molecule adsorption on Cu(111). In the case of adding Copper atom onto the slab, for time purposes, we have used DFT-D3 correction [16]. The kinetic energy cutoff was set to 500 eV. Our supercell consists of 5 layers of Cu(111) slab with optimized lattice parameter of 3.63 Å with all layers allowed to relax. A k point sampling of 15×15×15 mesh centered at the zone center was used corresponding to a unit cell of Cu bulk structure. The slab and its periodic image were separated by 20 Å. In the case of optB88 functional all the structures were relaxed until forces acting on each atom was smaller than 0.03 eV/Å. This value was set to 0.01 eV/Å when using DFT-D3 method.

All binding energies (BE) were calculated by:

\[ BE = E_{\text{slab+mol}} - E_{\text{slab}} - E_{\text{mol}} \]  \hspace{1cm} (3.1)

In which \( E_{\text{slab+mol}} \) is the total energy of the coupled system of slab and molecule, \( E_{\text{slab}} \) is the total energy of the clean slab and \( E_{\text{mol}} \) is the total energy of each molecule in gas phase.

To estimate the effect of adsorption of molecules on the charge distribution, the charge difference was calculated using:

\[ \Delta \rho = \rho_{\text{slab+mol}} - \rho_{\text{slab}} - \rho_{\text{mol}} \]  \hspace{1cm} (3.2)
\( \rho_{slab+mol} \) stands for total charge density of the coupled system of slab and molecule, \( \rho_{slab} \) is the total charge density of the relaxed slab after adsorption of molecule and \( \rho_{mol} \) is the total charge density of adsorbed molecule on the slab to give the charge density difference as a result of adsorption of molecule.

3.3 Results and Discussions

3.3.1 Molecular and Electronic Structure of Molecules

Fig. 3.1 shows the structure of a Naphthalene and functionalized molecules. The HOMO and LUMO of each molecule is displayed in this figure. The first observation is that functionalizing Naphthalene changes the distribution of highest and lowest molecular orbitals, i.e. the charge distribution changes. This change is less for isoquinoline which N atom is in the ring.

Figure 3.2 shows the comparison of DOS of each molecule in gas phase with that of Naphthalene. Introducing all the functional groups, except N which is in the ring, results in new states in the HOMO-LUMO gap which increases the probability of hybridizations between the states of these molecules with that of Cu.
Figure 3.1. Naphthalene (middle) and six functionalized molecules. The functional group name is written besides each molecule. Color code of atoms: C (black), N (blue), O (red) and H (green). The HOMO and LUMO of naphthalene (middle) and each single molecule in gas phase are displayed in blue and red, respectively. The isosurface is set to 0.009 Bohr$^3$. 
Figure 3.2. Molecular orbitals of Naphthalene and functionalized molecules in gas phase. The fermi energy is set in the middle of HOMO and LUMO and is shown with dashed line.

### 3.3.2 Adsorption of Single Molecules on the Cu(111) Surface

The adsorption of each single molecule on the Cu(111) surface was studied for all the symmetric adsorption sites and the ones with highest adsorption energies are shown in Fig. 3.3. Table 3.1. summarizes the structural and energetic properties of each structure. The end of the molecule with functional group tilts towards the surface to form bond with Cu atom while the other end moves away from the surface.
In fact there are two contributions to adsorption: 1) the covalent interaction between the functional group and the underlying metal atom(s), 2) the vdW interaction between the backbone of molecule and the surface. Varying the functional group leads to not only change in the preferred adsorption site for the molecule but also the change of tilt angle of the backbone. Therefore the energies of adsorption as well as the charge rearrangements couldn’t be discussed without taking both interactions into account.

Figure 3.3. Top view and side view of single molecules adsorbed on the Cu(111). The dashed line shows the horizontal as the origin where tilt angles were calculated. Color code: Orange: Cu, Black: C, Green: H, Blue: N, Red: O.
Table 3.1. The list of functional groups, binding energies and structural properties of each molecule after adsorption on Cu(111).

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Functional Group</th>
<th>Binding Energy (eV)</th>
<th>Bond Length (Å)</th>
<th>Tilt Angle (°)</th>
<th>Distance from Surface (Å)</th>
<th>Δh of Cu atom (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>N</td>
<td>-1.21</td>
<td>2.17</td>
<td>12.39</td>
<td>3.08</td>
<td>0.16</td>
</tr>
<tr>
<td>b</td>
<td>CN</td>
<td>-1.23</td>
<td>2.08</td>
<td>1.24</td>
<td>3.18</td>
<td>0.17</td>
</tr>
<tr>
<td>c</td>
<td>NC</td>
<td>-1.92</td>
<td>1.98</td>
<td>2.02</td>
<td>2.96</td>
<td>0.22</td>
</tr>
<tr>
<td>d</td>
<td>NH₂</td>
<td>-1.49</td>
<td>2.24</td>
<td>9.01</td>
<td>3.29</td>
<td>0.16</td>
</tr>
<tr>
<td>e</td>
<td>COH</td>
<td>-1.27</td>
<td>2.16</td>
<td>9.89</td>
<td>3.32</td>
<td>0.10</td>
</tr>
<tr>
<td>f</td>
<td>COOH</td>
<td>-1.35</td>
<td>2.25</td>
<td>5.90</td>
<td>3.16</td>
<td>0.07</td>
</tr>
</tbody>
</table>

As stated in Table 3.1, the molecules backbone remains almost 3Å away from the surface. This is the minimum energy distance required by molecules vdW interactions with Cu(111). However when the functional group is added, it facilitates the covalent bond formation between Cu atom of the surface and the group. This interaction brings the molecule closer to the surface. As a result of competition between these two interactions, the molecules tilt from their planar orientations. If the functional group possess a longer and flexible structure, this reduces the tilt angle (as in the case of CN, NC and COOH groups) while if it is short and/or in the molecular ring, this tilt will be maximum (as observed for N). The strong bond between molecules and Cu moves the bonding copper higher than its stable height. The results of change in the vertical distance of Cu atom with respect to clean surface are listed in Table 3.1.
The correlation between BE of individual molecules with tilt angle, bond length, Δh of binding Cu atom from the surface or the separation distance between backbone and the surface are studied to see if the BE is linearly changing with either of these quantities. These plots show that while for the strongest binding among group (NC) there is a well-defined pattern between these quantities, the pattern cannot be generalized to all the molecules, rather it is a combination of all the quantities that contribute to adsorption energies of molecules. In fact, each of these quantities are representative of either vDW or covalent contribution strength in binding. However, these contributions are also related to the number of lone pairs on functional groups, the length of functional group and the polarity of that specific group. For example, the change in height of bonding Cu atom with respect to that of an atom from the clean surface is a result of covalent binding with molecule.

Figure 3.4. Bar charts of binding energies and Δh of binding Cu atom, tilt angle, bond length and molecules distance from Cu(111).
Figure 3.5. Charge density redistribution of the coupled molecule and metal surface with (a-f) representing the Naphthalene molecules with N, CN, NC, NH$_2$, COH and COOH, respectively. The blue (red) represent charge depletion (accumulation). The isosurface is set to 0.02 Bohr$^3$.

The charge redistribution between molecule and metal surface is calculated and plotted in Fig 3.5. This figure shows that the charge depletion and accumulation is most pronounced around the functional group and binding atom. The charge accumulation is in the middle of the bond while on the surface the depletion is very high close to molecule end. This distribution shows that molecules form strong covalent bonds with Cu. Our results show that the charge redistribution is the highest for isocyano-naphthalene, which also has the highest adsorption energy on the surface. The redistribution of charge in the organic molecule-metal interface is the key subject in the molecular devices. Moreover the strong charge redistribution in the region between functional group end of molecule and metal surface is reflected in the elongation of the functional group. For example in the case of NC functional group the triple bond between N and C elongates by 0.05 Å which shows the weakening of the bond between N and C.
Figure 3.6. Projected density of states (PDOS) of bonding Cu atom with molecule. (a-f) are as listed in Table 3.1.

Fig. 3.6. shows the projected density of states for coupled systems of molecule and Cu(111). Since the adsorption of molecules are in z direction, the respective z valence orbitals of binding Cu atom and functional group are plotted. The results of PDOS indicate that the interaction between functional group and Cu leads to strong hybridization between their orbitals. For each
molecule this is also accompanied by a charge transfer from surface to molecule. This charge is calculated using Bader analysis and summarized in table 3.2.

Table 3.2. Bader net charge on the bonding molecules after adsorption on Cu(111).

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Net Charge on the molecule (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.15</td>
</tr>
<tr>
<td>CN</td>
<td>0.19</td>
</tr>
<tr>
<td>NC</td>
<td>0.11</td>
</tr>
<tr>
<td>NH2</td>
<td>0.13</td>
</tr>
<tr>
<td>COH</td>
<td>0.16</td>
</tr>
<tr>
<td>COOH</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Impact of Functional Group on the Electronic Properties of Cu Atom Adsorption of single molecules change the electronic structure of Cu atom. This is the key point for having a framework to design Cu catalysts for practical purposes. Previously the electronic structure of meal surfaces was studied by Stamenkovic et al. [113] by changing the Pt alloys compositions. The change in d-band of these alloys was considered as the main factor in analyzing their electronic structure. This was based on the d-band center model of Hammer and Norskov [114] and has proven to be useful in understanding bond formation and trends in reactivity of transition metals.
The d-band model is an approximate description of the bond formation at a transition metal surface. When an adsorbate reaches to a transition metal element, its s and p states couple with d states and form bonding and anti-bonding bonds. The strength of the bond of adsorbate on the metal atom is determined by the energy of the anti-bonding states relative to Fermi level. These states are always higher in energy than d-states, therefore the energy of the d-states relative to the Fermi level is a good first indicator of the bond strength between adsorbate and metal. This means that the higher energy of the anti-bonding states and the stronger bonds are a reflection of the higher position of the energy of d states relative to the Fermi level. This provides a basis on the fundamental insights into the design of catalysts since the understanding of the interaction between adsorbate and metal is the first step towards determining the reaction process. Stamenkovic et al. [113] showed that the adsorption energy of O on Pt alloys in linearly correlated with d-band center of alloy.

In a similar process one can study the modifications in the electronic structure of transition metal by changing the functional group. For our systems we have calculated the d-band center of binding Cu atom to functional group. The obtained values are summarized in Table 3.3.

Using the projected density of states the d-band center is calculated using following formula:

$$\epsilon_d = \frac{\int_{-\infty}^{\infty} ED_d(E - E_F) dE}{\int_{-\infty}^{\infty} D_d(E - E_F) dE}$$

(3.4)

$E$ is the energy of electrons in d-state, $D_d$ is the density of electrons in d-band states relative to the Fermi level.

The absolute value of energy of d-band center is the highest for isocyano group. Each group results in different values for d-band center relative to that of clean surface. This indicates that the
binding of adsorbates on the Cu atom coordinated by NC group will be the highest and is different from that of clean Cu. Another result from this data is that on the surface of Cu, the adsorption of single molecules of this study leads to similar modifications for some groups: the d-band-center is almost the same for Cu atom attached to isoquinoline or cyano-naphthalene.

Table 3.3. d-band center values of Cu atom attached to functionalized naphthalene molecules with functional groups listed above.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>d-band center of Cu (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-1.86</td>
</tr>
<tr>
<td>CN</td>
<td>-1.87</td>
</tr>
<tr>
<td>NC</td>
<td>-2.17</td>
</tr>
<tr>
<td>NH2</td>
<td>-1.75</td>
</tr>
<tr>
<td>COH</td>
<td>-1.75</td>
</tr>
<tr>
<td>COOH</td>
<td>-1.66</td>
</tr>
</tbody>
</table>

3.3.3 Adsorption of Single Molecules on Cu adatom

On a metal surface, there are defects such as steps, kinks, vacancies or adatoms. While depositing molecules on the surface, the organic layer inter-diffuses with metal adatoms, also called as metal centers, and form covalent bond. In fact this, as mentioned before, is the building block of single atom catalysts or organic electronic devices and provides an elegant strategy for
supramolecular Nano-structures. To simulate this bonding a Cu atom has been added to a threefold hollow site on the Cu(111) surface and the adsorption of each molecule is studied in the presence of adatom. As discussed for adsorption of molecules on the bare Cu(111) surface, the backbone of interacting molecules tends to stay 3 Å away from metal surface because of vdW interactions between π-conjugated molecule and the metal surface. In this sense, the backbones of adsorbed molecules tilt towards the surface which is the opposite of the molecules adsorption on the bare surface. Such tilt comes from the extra height originated by adatom. The adsorption energies and tilt angles as well as the vertical distance of molecules from surface are listed in Table 3.4.

Table 3.4. The list of functional groups, binding energies and structural properties of each molecule after adsorption on Cu adatom. The negative sign of tilt angle shows the tilt towards the surface.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Functional Group</th>
<th>Binding Energy (eV)</th>
<th>Bond Length (Å)</th>
<th>Tilt Angle (°)</th>
<th>Distance from Surface (Å)</th>
<th>∆h of Cu adatom (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>N</td>
<td>-2.18</td>
<td>1.97</td>
<td>-1.92</td>
<td>3.15</td>
<td>0.046</td>
</tr>
<tr>
<td>b</td>
<td>CN</td>
<td>-2.33</td>
<td>1.90</td>
<td>-5.19</td>
<td>3.10</td>
<td>0.059</td>
</tr>
<tr>
<td>c</td>
<td>NC</td>
<td>-2.73</td>
<td>1.86</td>
<td>-5.18</td>
<td>3.07</td>
<td>0.070</td>
</tr>
<tr>
<td>d</td>
<td>NH₂</td>
<td>-2.29</td>
<td>2.03</td>
<td>-6.95</td>
<td>3.03</td>
<td>0.045</td>
</tr>
<tr>
<td>e</td>
<td>COH</td>
<td>-2.17</td>
<td>1.95</td>
<td>-3.32</td>
<td>3.00</td>
<td>0.051</td>
</tr>
<tr>
<td>f</td>
<td>COOH</td>
<td>-2.18</td>
<td>1.97</td>
<td>-4.83</td>
<td>3.00</td>
<td>0.038</td>
</tr>
</tbody>
</table>
The charge redistribution between molecule and the surface becomes very strong when the adatom is added. The adatom provides a huge amount of charge which polarizes the backbone of molecules. Such interactions lead to strong dipole interactions between the backbone and metal surface and increases the work function of the respective region. This also shows how a single atom serves as a charge reservoir and makes strong bonds with interacting molecules.
Figure 3.8. Charge density redistribution of the coupled molecule and metal surface with (a-f) representing the Naphtalene molecules with N, CN, NC, NH$_2$, COH and COOH, respectively. The blue (red) represent charge depletion (accumulation). The isosurface is set to 0.002 Bohr$^3$.

The transferred charge from Cu to molecules are calculated using Bader method. The molecules become charged as a result of interaction with Cu adatom and Cu(111) substrate.

Table 3.5. Bader net charge on the molecules after binding with Cu adatom.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Net Charge of molecule (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.24</td>
</tr>
<tr>
<td>CN</td>
<td>0.28</td>
</tr>
<tr>
<td>NC</td>
<td>0.25</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>0.17</td>
</tr>
<tr>
<td>COH</td>
<td>0.28</td>
</tr>
<tr>
<td>COOH</td>
<td>0.25</td>
</tr>
</tbody>
</table>
3.3.4 Impact of Functional Group on the Electronic Properties of Cu Adatom

Similar to what was discussed and calculated in section 3.3.3, the d-band center of Cu adatom is obtained in adjacent of different functional groups. The results of this calculations are summarized in Table 3.6. A similar trend is obtained for adatom. The values are not compared because of different functionals used for calculations.

Table 3.6. d-band center values of Cu adatom attached to functionalized naphthalene molecules with functional groups listed above.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>d-band center of Cu adatom (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-1.72</td>
</tr>
<tr>
<td>CN</td>
<td>-1.79</td>
</tr>
<tr>
<td>NC</td>
<td>-2.10</td>
</tr>
<tr>
<td>NH2</td>
<td>-1.67</td>
</tr>
<tr>
<td>COH</td>
<td>-1.65</td>
</tr>
<tr>
<td>COOH</td>
<td>-1.68</td>
</tr>
</tbody>
</table>
3.4 Summary and Conclusions

The adsorption of six functionalized naphthalene molecules on Cu are studied using DFT calculations. Changing functional group results in different charge distributions on molecules. When adsorbed on the Cu(111) surface, the molecules bind to surface via two interactions: the vdW interaction coming from the backbones of molecules with surface and the covalent interaction among functional group and Cu atom. This results in different geometries of adsorption for each molecule and the bond strength varies as well. Adsorption of molecules on Cu(111) shows that the molecules backbone incline to stay 3 Å away from surface while at the same time the functional group brings it close to the surface. As a result all the molecules bind tilted to the surface. When studying the adsorption with Cu adatom on the surface, the tilt angle reduces since having adatom introduces enough space between molecules backbone and substrate.

To study the effect of functional group on the electronic structure of metal atom, the d-band center was calculated. This results show that the d-band center of Cu atom/adatom binding to functional groups varies for each system. Therefore the electronic structure of Cu can be tuned only by change in functional group. Our findings can establish an approach for design of single atom catalysts.
CHAPTER 4: IMPURITY INDUCED NEW MOIRÉ STRUCTURE OF h-BN ON Rh(111)

4.1 Introduction

Single sheet of graphene (C-C) and hexagonal boron nitride (h-BN) are ideal prototypes of two dimensional materials. Both structures possess a honeycomb lattice structure with strong sp² in plane hybridizations. However there are distinct differences between the two: the π-derived electrons in graphene are delocalized and as a result it is a semiconductor. For this reason its transport properties are of interest [115,116]. In the case of h-BN the situation is completely different: the electrons are localized on N atoms and therefore there is a large band gap in this system. One of the major applications emerging from this wide band gap is using the single layer of h-BN on metallic substrates as a decoupling layer to study the unperturbed or less perturbed electronic structures of molecules for fundamental understanding or to grow nanoparticles [117]. Several other applications are listed for h-BN in catalysis due to its inert structure namely selective dehydrogenation of propane to propene [118].

The electronic properties of h-BN are tunable either by structural modifications or by doping. Both methods have been extensively studied. However there are difficulties in applying these methods: the structural modifications usually induce defects and therefore deteriorates the electronic properties. Chemical doping on the other hand is difficult to control.

So far the fabrication of vdW hetero-stacks consisting of h-BN and graphene is mainly done by mechanical transfer or exfoliation. The problem is induced defects which affects the performance of device. More importantly this technique is not scalable and therefore it is not applicable for mass productions. If the structures are grown in vertical stacks by chemical vapor
deposition an active surface should be present to provide the situation for this growth. However as mentioned before h-BN is catalytically inert and as soon as the surface is covered with it the decomposition of ethylene or methane to produce graphene is inhibited.

Recently an approach is used by [119] to produce a new structure of h-BN-graphene on Rh(111) substrate. Depending on the amount of carbon dissolved in the near-surface region of Rh(111) two structures were grown: for low carbon amount the pure h-BN and for intercalated carbon a phase called IC-h-BN is observed. The amount of carbon can be controlled and the electronic properties are tuned by change in the structure of h-BN. It is therefore essential to understand the properties of this new phase and how intercalation of carbon rings lead to such changes in electronic structure of h-BN/Rh(111). Herein we provide fundamental insight into the (a) the structure of new phase as well as a brief study on the structure of pure h-BN/Rh(111) and (b) the electronic and chemical properties of the new phase while providing information on the possible concentrations of carbon in the observed experimental structure.

This chapter is organized as follows: in the next section the calculation methods used for this study are explained. Then the structure of h-BN/Rh(111) has been discussed and compared to previous theoretical and current experimental data. The structure of new phase is obtained by examining a range of carbon concentrations to verify the experimental structure. We have studied the electronic structure by an extensive analysis on the density of states and charge transfer calculations.
4.2 Calculation Methods

Simulations were performed using Density Functional Theory (DFT) [5,6] employing the projector-augmented wave (PAW) [27], plane-wave basis set, and the supercell method as implemented in the Vienna Ab-initio Simulation Package (VASP) [28,111]. The exchange-correlation interaction of electrons are described by the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhoff (PBE) functional [112]. The cutoff for kinetic energy of plane-wave expansion is set to 500 eV. To include dispersion correction DFT-D3 [16] is used. The supercell consists of a three-layer, 12×12, Rh(111) slab constructed with optimized lattice parameter of 3.79 Å and a 13×13 monolayer of h-BN with bond length of 1.46 Å and a vacuum of 20 Å to separate the slab and its normal periodic images. The total number of atoms in unit cell varies between 601 atom for h-BN/Rh(111) system to 658 atoms for IC-h-BN/Rh(111) system with 5 carbon rings at each corner of every other rim area. We sample the Brillouin Zone with one point at the zone center. For simulation of hexagonal carbon rings intercalated underneath the BN rim areas (two such areas exist, one closer to the Rh(111) surface than the other), we place the rings under every other rim area, selecting the one in which carbon will be further away from the Rh(111) substrate. These carbon rings (1-5) furthermore form a triangle, i.e. the 1-5 membered rings exist at the corner of a triangle. An example of the supercell of simulation is shown in Figure 4(c). To find the lowest energy of configuration of rings on top of Rh(111) substrate, we have simulated the systems with the rings at all high symmetry points in a manner that either the center of these rings is placed on the FCC, HCP, TOP or Bridge sites or one of carbon atoms in the ring is exactly placed on these high symmetry points. We relaxed all structures until all components of
the force acting on each atom were smaller than 0.01 eV/Å. All the atoms were allowed to relax in all directions while the bottom layer of Rh(111) substrate was fixed for all calculations.

The STM images were simulated by using the Tersoff and Hamman [35,36] method, i.e. the tunneling current at low voltage is assumed to be proportional to the local density of states (LDOS) around the Fermi level at the position of the tip apex. In our calculations, the simulated topological STM image is approximated to be the local density of states (LDOS) isosurface with value of $10^{-6}$ e/Å³ contributed from all states in the energy range of -0.005 eV to 0.005 eV ((i.e. within 5.0 meV of the Fermi level). For simulations of STM and calculations of DOS the Brillouin Zone is sampled by 3×3×1.

To calculate the charge transfer among different components of the system the Atoms In Molecules (AIM) method of Bader [33] is used as implemented in Henkelman algorithm [120,121]. The charge difference between the structures of new phase with that of pure h-BN/Rh(111) is calculated using:

$$\rho_{\text{diff}} = \rho_{\text{IC-hBN/Rh(111)}} - \rho_{\text{hBN/Rh(111)}}$$

(4.1)

In which the $\rho_{\text{IC-hBN/Rh(111)}}$ is the total charge density of the new phase and $\rho_{\text{hBN/Rh(111)}}$ is the charge density of pure h-BN/Rh(111) system.
4.3 Results and Discussions

4.3.1 Structure of h-BN/Rh(111)

Boron nitride (BN) has been grown on several transition metals. Its structure is formed self-assembly on these surfaces using borazine precursors at high temperatures. Borazine possess the same structure of Benzene with C atoms substituted by B and N successively. At high temperatures borazine is dehydrogenated and different islands of rings diffuse on the transition metal surfaces and form single layer of BN. The importance of BN on transition metal surfaces arises from its highly ordered structure which acts as a strong decoupling insulating layer. Its structure on Rh(111) is particularly interesting owing to its corrugation on Rh(111) which results from two major reasons: 1) the lattice mismatch between h-BN and Rh(111) and 2) the strong interaction of h-BN and underlying Rh substrate. The highly regular structure is also known as a nanomesh with regions of highly interacting BN atoms with Rh(111) which subsequently have the lowest distance to underlying Rh and areas of weakly interacting regions which form tent-like structure. The whole BN monolayer though remains intact owing to its strong ionic structure. In an extensive study by Blaha et al. [122] it was shown that an stable monolayer of h-BN forms when B is on fcc and N is on top sites of Rh(111) and the nanomesh consists of a $(13 \times 13)$ superstructure of h-BN on a $(12 \times 12)$ substrate of Rh(111). Since there is lattice mismatch between BN and Rh(111) the successive adsorption sites of B and N differs from this optimum and results in repulsion of these regions from Rh(111). Therefore the corrugation appears on the monolayer. This corrugated structure is used to grow nanoparticles [117] but more importantly to trap and immobilize molecules or ions because of in plane dipole moments which act as trapping centers for molecules [123-126].
To study the new phase of h-BN on Rh(111) we started with the structure of pure h-BN. Figure 4.1 (a) shows the corrugated structure formed by h-BN on Rh(111) along with the sample model for IC-h-BN with 3 rings. The unit cell of each structure is identified with solid lines. Different regions of this structure are named in Figure 4.6(a). These areas are characterized by the distance of B atoms from Rh(111) in these regions. BN monolayer is adsorbed on Rh(111) as a result of vdW and covalent interactions and the bond length between B-N is in the range of 1.43 Å to 1.48 Å with the periodicity of the structure as 3.2 Å which is in agreement with experimental measurements [119,127]. The lattice mismatch between h-BN and Rh substrate is calculated to be 7.6% using the following formula:

\[ m = \frac{n_1 d_{BN}}{n_2 d_{Rh}} - 1 \]  

(4.2)

where \( n_1 \) comes from \((n_1 \times n_1)\) h-BN superstructure, \( n_2 \) from \((n_2 \times n_2)\) of Rh(111) substrate, \( d_{BN} \) is the lattice parameter of h-BN overlayer and \( d_{Rh} \) is \( a_{Rh}/\sqrt{2} \) where \( a_{Rh} \) is the lattice parameter of fcc Rh(111) structure.
Figure 4.1. (a) The corrugated structure of h-BN on Rh(111), (b) the same as (a) with three carbon rings at corners of one rim area. (c) The top view of (b) with simulation unit cell in solid lines. Different colors are used based on height difference of B and N from Rh(111) substrate. Color code: Rh: grey, N: yellow, orange and red and B: light blue, navy and dark blue.

4.3.2 The Geometrical Structure of New Phase

The new phase of h-BN/Rh(111) is observed with a long range order structure as obtained in LEED measurements. XPS measurements on the other hand shows the presence of C in its structure [119]. Based on following three reasons it is assumed that carbon accumulates under rim areas:

1. At high temperatures if there are any other molecules consisting of carbon will leave the surface.
2. The strong interaction in the depression regions among BN and Rh(111) makes it highly unlikely for extra elements to accumulate under these regions.
3. The strong ionic bond between B and N is unlikely to be broken by a substituted element 
but also point contact STM measurements show that the BN monolayer remains intact, i.e., 
there is no broken bond on the monolayer.

Figure 4.3(a) shows the STM image of new phase structure along with that of h-BN/Rh(111). The 
original Moiré structure observed in STM image of h-BN/Rh(111) is altered and disconnects the 
continuity in rim areas by dividing these regions to higher and lower triangles. Therefore it is 
possible that only one of rim areas are affected when the impurities are dissolved near surface area. 
To verify this assumption we placed carbon atoms in the form of hexagonal rings under the rim 
area with highest edge distance from Rh(111). Although it has not been tested in this study, it has 
been shown theoretically that for number of carbon atoms more than N≥6 the impurities form as 
islands rather than chains and these islands have lower energies when they are a combination of 
symmetric hexagons [128].

The results show that carbon rings grow next to each other with their centers adsorbed on 
top of Rh atoms. This is also in accordance with growth of graphene on Rh(111) which 
theoretically is predicted to grow with the carbon atoms sitting on the bridge sites of Rh(111) 
[129]. Moreover, as the number of rings grow the orientation of islands with respect to each other 
reflects the three-fold symmetry of underlying substrate. Figure 4.3 shows the configuration of 
these rings with respect to each other for a range of 1-5 rings. In addition, the islands are corrugated 
when 2 or more of them are combined to form islands. The corrugation arises from lattice 
mismatch between Rh and graphene and has been previously observed [129].
Figure 4.2. Top view of C rings configuration with respect to each other for concentrations of 1-5 rings. For visualization purposes the BN monolayer is removed.

Figure 4.3. (a) The side view of h-BN/Rh(111) and (b-f) IC-h-BN/Rh(111) with 1-5 rings. The rings are corrugated as a result of lattice mismatch between graphene and Rh(111).
Besides the above mentioned structural properties, the results of our simulations represent other differences in the Moiré structure of h-BN/Rh(111) with respect to that of h-BN/Rh(111) in two distinct ways:

1. The height in the rim areas are modulated. As the number of rings has been increased this modulation becomes stronger. As a consequence, this change in the height of one of rim areas affects the extent of depression region.

2. The interaction among carbon rings and Rh(111) as well as the rings with BN results in small lateral displacements of B and N atoms from their original adsorption sites in h-BN/Rh(111). This gives rise to the height modulation as discussed in 1.

For the systems of our study the height modulation changes with number of rings as depicted in Figure 4.4.

To verify our results with that obtained from experiments we have simulated the STM image of obtained structures. This is discussed in next section.
4.3.3 *Simulations of Scanning Tunneling Microscopy*

When measured experimentally, the STM image of the new phase of h-BN/Rh(111) shows distinct regions: a hexagon region which is assumed to belong to previous depression regions of h-BN/Rh(111), a triangle region with bright protrusions and a dark triangle. The hexagons are surrounded by these triangles. The simulated STM image of studied structures with 1-5 rings are presented in Figure 4.6. While the regions observed experimentally are obtained also for lower concentrations of carbon in our simulations (1 and 2 rings), the distinction between dark and bright triangles becomes more clear when the number of rings are increased to 3, 4 and 5. We should however mention that based on STM results only, we cannot assign the new phase to our structure because of limitations embodied in the applied simulation method (See section 2.11). Another
important conclusion from STM simulations is the accuracy of model used in here: The agreement between experiment and simulations proves that the former depression areas remain unchanged and only one of rim areas are affected. Also experimentally a decrease in the area of depression regions is observed which is in accordance with height modulations in the BN above the rings. Since in this model the carbon rings intercalate between h-BN and Rh(111), in the rest of this chapter we will refer to new phase as intercalated-h-BN/Rh(111) (IC-h-BN/Rh(111)).

Figure 4.5. The STM images of new phase of h-BN on Rh(111): (a) High-resolution image of the IC-h-BN Moiré pattern where the respective areas are denominated (U = 5 mV, I = 5 pA), taken from Ref [115]. (b-f) Simulated STM image of the structures with 1-5 carbon rings at each corner of bright triangles.
4.3.4 Electronic Structure Calculations

4.3.4.1 Density of States

As mentioned before the inhomogeneity in the Moiré structure of h-BN/Rh(111) and IC-h-BN/Rh(111) is a reflection of inhomogeneity of interactions. As a result of this variation one can expect the spatial variations in electronic structure. To verify this assumption, we have examined the spatial density of states of IC-h-BN/Rh(111) and compared it with respective areas in h-BN/Rh(111). For this purpose the structure of IC-h-BN Moiré pattern is divided to three regions: the first region is hexagon area which is the former depression region on h-BN. The second region is dark triangles which based on our calculations is the same as original rim area without modifications. The third region is the bright triangle which is the modified rim area with intercalation of carbon rings. The regions are as displayed in Figure 4.7 (a).

The DOS of B and N atoms in hexagons along with that of DOS of depression region in the h-BN unit cell are presented in Figure 4.7. Comparing the results of DOS, there is not a significant difference in the position of peaks. This is also in agreement with the fact that depression regions are not modified. Looking at the states very close to Fermi level (Fig 4.8(e-h)), the reduction in the states is observable. Although BN is a wide gap insulator, the states inside gap are a result of strong hybridizations between Rh and BN monolayer.

For dark triangle regions the DOS shows no significant change with respect to rim area of h-BN/Rh(111). The only change is a reduction in the intensity. The gap around Fermi level remains unchanged with no states appearance in the gap. Figure 4.8 displays the comparison between DOS of dark triangle of new phase and rim of h-BN/Rh(111).
Figure 4.6. Density of states contributed by B and N atoms in the valley region of h-BN/Rh(111) and that of Hexagon regions for structures with 3-5 rings. (a-d) shows the DOS for a wide energy range while (e-h) shows this DOS for small energy intervals around $E_F$.

Figure 4.7. DOS of B and N atoms in the region of dark triangle of new phase with that of rim areas of h-BN/Rh(111).
Next, the DOS of B and N atoms in bright triangle is compared with DOS of rim area in h-BN/Rh(111). While for structures with 1 and 2 carbon rings at the corners of bright triangle, no noticeable change in DOS is observed, for structures with 3-5 carbon rings there are new states appeared in the energy gap around Fermi level. For 5 carbon rings concentration, as shown in Figure 4.9, the gap disappears. Therefore the intercalation of carbon rings modifies the electronic structure of the h-BN.

Figure 4.8. (a-d) DOS contributed by N and B atoms in bright triangle regions of new phase with that of rim areas of h-BN/Rh(111). (e-g) The same as (a-d) for states very close to Fermi level.
Figure 4.9. Total DOS of BN in h-BN/Rh(111) compared with DOS of BN in IC-h-BN/Rh(111) with 3-5 rings. The inset in (a) shows the dz/dV measurements results on the position of bright triangle. The figure is taken from Ref [119].

To assign the experimental results to the simulated structures, the DOS of bright triangles are compared with experimental results of dz/dV spectra on the bright triangle which shows two new unoccupied states around 2 eV and 5 eV. For the concentrations of carbon considered in this study, the only structure with new states above Fermi level close to the ones in dz/dV is the one with 5 rings (See Figure 4.10). The new states are indicated by arrows. Therefore the experimental Moiré structure has more agreement with the model system of 5 carbon rings. Since we have not
considered higher concentrations of carbon, it can be concluded that the concentration of rings should be at least 5.

### 4.3.4.2 Bader Charge Analysis and Charge Difference Calculations

To further investigate the differences between h-BN/Rh(111) and IC-h-BN/Rh(111) we have analyzed the charge transfer between different elements of systems and calculated the charge density difference to identify the change in the charge configuration as a result of carbon intercalation.

Table 4.1. summarizes net charge of atoms for structures with 1-5 rings with respect to h-BN/Rh(111). The results of Bader analysis show that the charge will transfer from Rh substrate as well as C atoms to N the net charge on B atoms reduces with respect to B atoms of h-BN/Rh(111). Since the net charge increases by increase in number of rings, it is assumed that this charge transfer to N atoms is mostly on the regions above carbon rings.

Table 4.1. Bader charges difference between respective elements of new phase and that of h-BN/Rh(111). The subscript (0) refers to the charge difference with respect to the structure with no C impurities.

<table>
<thead>
<tr>
<th>Structure</th>
<th>∆Q(Rh)₀</th>
<th>∆Q(N)₀</th>
<th>∆Q(B)₀</th>
<th>∆Q(C)₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>1C</td>
<td>+2.54</td>
<td>+0.95</td>
<td>-0.34</td>
<td>-3.14</td>
</tr>
<tr>
<td>2C</td>
<td>+3.72</td>
<td>+0.55</td>
<td>+0.27</td>
<td>-4.53</td>
</tr>
<tr>
<td>3C</td>
<td>+4.2</td>
<td>-0.04</td>
<td>+1.01</td>
<td>-5.16</td>
</tr>
<tr>
<td>4C</td>
<td>+4.45</td>
<td>-0.11</td>
<td>+2.4</td>
<td>-5.82</td>
</tr>
<tr>
<td>5C</td>
<td>+5.13</td>
<td>-0.89</td>
<td>+2.17</td>
<td>-6.40</td>
</tr>
</tbody>
</table>
The side view of results for charge difference calculations shows a charge depletion on Rh layers as well as both hexagon and dark triangles while there is charge accumulation on bright triangles. The top view of the charge difference in the structure with 5 rings shows that the charge distribution will differ in new phase and thus one can expect that the chemical properties are modified. The most important concept is the modified in plane dipolar rings which are proved to be the trapping center for molecular moieties. As a result the interaction of dipolar rings are modified. In the next section we will provide more evidence on the effect of local changes on the potential energy of BN Moiré structure on Rh(111).

Figure 4.10. (a-c) Charge difference plots between IC-h-BN/Rh(111) and h-BN/Rh(111) for structures with 3-5 rings intercalation under rim areas; (d) top view of charge difference for structure with 5 rings. The excess in charge is plotted in red and the lack of charge is shown in green. The isosurface is set to $4 \times 10^{-5}$ e/Bohr$^3$. 
4.3.5 The Effect of Impurity on Chemical Properties of h-BN/Rh(111)

4.3.5.1 Local Variations of Work Function

In general the work function of a metal is defined as the minimum energy required to take an electron from metal to infinity. This energy is needed to overcome two parts contributed to the energy of an electron in the metal. The first one arises from the existence of dipole layer in the surface of metal. The charge in the surface of the metal with $z$ as the normal to the surface, is not zero. Rather the charge of dangling bonds in the surface leaks beyond the termination point of the geometrical surface ($z=0$). The existence of this charge pushes the electrons back and a dipole layer forms on the surface. Therefore if an electron should be removed from metal, it should go through this change in its potential energy. The second contribution comes from chemical potential of an electron. Inside a solid surface the energy of an electron is lowered by amount of chemical potential, $\mu$ as a result of chemical bonding. Therefore to remove an electron from the required work function should be equal to the sum of chemical potential and potential energy change of electrons when going through the dipole layer in the surface.

When an electron is removed from a solid it induces polarization in it resulting in an attractive Coulomb interaction. In the case of a metal, the induced positive charge lies in the same distance from metal surface as the distance of electron outside of it. This charge induced inside the metal surface is called image charge and the attractive potential energy is named as image potential. In principle this potential is felt by electrons for a maximum distance of 3-4 Å away from surface and it vanishes at vacuum level, again in accordance the definition of with work function.
On a real surface there are several defects such as vacancies or step sites which the electrostatic potential felt by an electron is different from that of an ideal surface. This means that for a traveling electron parallel to the surface of a metal, there will be modulations in charge density and therefore the work function of the electron changes locally. This can be further extended to the definition of work function of a Moiré structure such as h-BN/Rh(111) or IC-h-BN/Rh(111). The modulations in the structure is a reflection of interaction strength between the monolayer and underlying substrate. In another words the electrostatic potential is modulating with the same periodicity of the Moiré structure. Therefore taking an electron away from different regions of this structure requires varying amount of energy.

To calculate the variations of work function in h-BN/Rh(111) and IC-h-BN/Rh(111) at first the electrostatic potential of the system is calculated. This is called $V_{loc}$ in this work. The work function then is defined as:

$$\phi = V_{loc}(x, y) - E_F$$  \hspace{1cm} (4.3)

To obtain the $V_{loc}$ in vacuum level the variations of local potential are calculated with respect to the normal to the surface (z-direction, here). Having the value of $z = vac - level$, the average potential as a function of $(x, y)$ is calculated:

$$V_{loc}(x, y) = \int V(x, y, z)dz$$  \hspace{1cm} (4.4)

To identify how accumulation of C impurities changes the electronic properties of the Moiré structure, the vacuum level is identified and the variations are calculated at that specific height. Figure 4.12 shows the results of this simulation for impurities with concentrations of 1-5 rings at each corner of bright triangle.
The simulations results show an increase in the local work function of respective areas of IC-h-BN/Rh(111) compared to that of h-BN/Rh(111). While the work function modulates by 290 meV for h-BN/Rh(111), this modulation increases to 320 meV for a structure with 5 rings in the corners. This increase can be assigned to the increase or rearrangement of the surface dipoles which happens when there is a charge transfer from substrate to dipole layer as it was also shown by Bader analysis. In the case of new phase, the carbon rings which are electron rich can also contribute to this charge transfer.

As a result of increase in the surface dipole layer, the work function increases, i.e. the removal of electrons requires higher energies since the electrons should also go through the potential energy created by the surface dipoles.

Figure 4.11. Local variations of work function for (a) h-BN/Rh(111) and (b-f) IC-h-BN/Rh(111) with 1-5 carbon rings at each corner of bright triangles. The units are in ‘eV’.
One implication of this increase in work function is that the charge transfer from IC-h-BN/Rh(111) to an adsorbate decreases.

4.4 Summary and Conclusion

Using first principles calculations the Moiré structure of h-BN on Rh(111) and its new phase in the presence of carbon impurities was studied. The results of new phase show that the carbon intercalates under the rim areas of h-BN over Rh(111). These impurities are in the form of carbon ring islands with their center located on top of Rh atoms underneath. This also leads to height modulations of h-BN. The new phase structure was studied with 1-5 carbon rings at each corner of rim area and the simulation of STM image for each structure shows that the ones with 3-5 rings are closer to experiment. To investigate the modification in electronic properties the DOS of different regions were calculated. Our results show that the areas of BN with closest distance the states are almost unmodified. The reduction in the intensity of these regions is in agreement with smaller size of these areas in new phase. The regions with carbon rings underneath, on the other hand show strong modifications in DOS. Our results show that new states appear for structures with 3 and 4 rings in the gap of BN and the gap disappears when the number of rings are increased to 5. Above Fermi level two new states are also obtained for this concentration which are also observed in experiment. The chemical properties variations show itself in an increase of work function of the new phase when compared to original structure. This increase is explained as a result of charge transfer to h-BN which creates dipoles and modifies the in-plane dipole rings. These results show that the local change in structure results in novel chemical properties.
CHAPTER 5: CO ADSORPTION ON Pd(111) AT 0.5ML

5.1 Introduction

CO adsorption on the Pd(111) surface is an interesting topic not only because of fundamental interest but also because Pd is widely used as an industrial catalyst. Despite extensive efforts in understanding the adsorption of CO on Pd(111) with almost all available surface science techniques [130-141] and state-of-the-art theoretical and computational methods [139,142-146], it is surprising that the overlayer structure at ½ monolayer (ML) coverage is still not well characterized, with contradictory information coming from different experimental and theoretical works. On the other hand, adsorption structures of CO on Pd(111) at low and high coverages are well understood. For example, there is agreement that for coverages less than 1/3ML, there is no ordered structure, rather CO molecules are found to adsorb on three-fold hollow (TFH) sites [131,147,148]. Between 1/3ML and ¾ML, however, several ordered structures have been reported [133]. At 1/3ML coverage, a \((\sqrt{3} \times \sqrt{3})R30^\circ\) overlayer with CO molecules occupying FCC hollow sites is found [130]. This site assignment is not surprising, since at such low coverages the interaction between CO and the metal surface is the dominant factor that determines the binding site. At ¾ML coverage, however, intermolecular interactions become important and the overlayer structure assumes a (2×2) structure with (three) CO molecules adsorbed on the top and the FCC and HCP hollow sites. The above adsorption sites and overlayer structures of molecules have been confirmed experimentally [131] and with density functional theory (DFT) based calculations [131,142,149].
At ½ML coverage, interactions of CO molecules with both the metal surface and amongst themselves (intermolecular) become equally important which makes the understanding of the overlayer structure more complex and have led to contradictory interpretations by different research groups. Results from Low Energy Electron Diffraction (LEED) experiments [131,133] are in agreement that the structure is c(4×2)-2CO. However, there is no such consensus on the nature of the binding sites. Infra-Red Reflection-Absorption Spectroscopy (IRAS) measurements propose adsorption at the bridge sites (Bridge-Bridge) [131,132,134], while photoelectron diffraction [135], High Resolution X-ray Photoelectron Spectroscopy (HR-XPS) and High Resolution Electron Energy Loss Spectroscopy (HR-EELS) [136] point to the involvement of only FCC and HCP (FCC-HCP) hollow sites [135,136]. At the same time, Scanning Tunneling Microscopy (STM) study of Rose et al. [138] showed the coexistence of two islands at ½ML CO coverage on Pd(111) in which binding sites assignment for each island, based on the appearance of protrusions, concluded simultaneous presence of both Bridge-Bridge and FCC-HCP occupancies. On the other hand, High Resolution Core Level Shift Spectroscopy (HRCLS) combined with DFT based calculations by Martin et al. [139] concluded that at this coverage the CO molecules adsorb on a mixture of FCC-Bridge and HCP-Bridge sites.

The question thus remains: is the bridge site involved in the c(4×2)-2CO structure on Pd(111)? We address this question by carrying out first principles calculations based on DFT of the overlayer structure of CO on the Pd(111) surface at ½ML coverage. We show that indeed two possible combinations of adsorption sites exist: the first consists of CO molecules adsorbed on equal mixture of FCC and HCP hollow sites (FCC-HCP) and the second consists of CO molecules adsorbed on sites located between the FCC hollow and the bridge sites (FCC-Bridge Hybrid).
In the next section, calculation details are provided. In section 3 we discuss the results from this study in view of those from previous experimental and theoretical results.

### 5.2 Calculation Method

The calculations in this study include those of the system total energy, adsorbate vibrational frequencies, and simulation of STM images. Some details for each are given below.

#### 5.2.1 Total energy calculations

We performed DFT [5,6] calculations employing the projector-augmented wave (PAW) [28,150], plane-wave basis set, and the supercell method as implemented in the Vienna Ab-initio Simulation Package (VASP) [151]. We described the exchange-correlation interaction of electrons by the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhoff (PBE) functional [152]. We set the cutoff for kinetic energy of plane-wave expansion at 500 eV. Our supercell consists of a five layers of Pd(111) slab constructed with optimized lattice parameter of 3.94 Å, with CO molecules adsorbed on one side of the slab and a vacuum of 20 Å to separate the slab and its normal periodic images. We sampled the Brillouin zone with a uniform 18×18×18 and 9×11×1 mesh centered at the zone center corresponding to a unit cell of bulk Pd and the Pd(111) surface (see Fig. 1), respectively. We relaxed all structures until all components of the force acting on each atom were smaller than 0.001 eV/Å.
To estimate the role of van der Waals (vdW) interactions in determining the adsorption sites at \( \frac{1}{2} \)ML coverage, calculations were also performed by using the optB88-vdW [21] functional. For testing purpose, some of the calculations were repeated with PW91 [13] functional as well.

For all optimized structures (obtained after ionic-relaxation) the binding energy (BE) is calculated by:

\[
BE = E_{\text{slab+adsorbate}} - E_{\text{slab}} - 2 \times E_{\text{adsorbate}}
\]

(5.1)

in which \( E_{\text{slab+adsorbate}} \) is the total energy of the system consisting of the Pd(111) slab and CO, \( E_{\text{slab}} \) represents the total energy of the clean Pd(111) slab and \( E_{\text{adsorbate}} \) gives the total energy of the CO molecule in gas phase. The binding energies are then averaged over the number of CO molecules in the unit cell.

5.2.2 Calculations of vibrational frequencies

We calculated vibrational frequencies of the system by using the finite difference method in which atoms are displaced by 0.01 Å along each direction of the three Cartesian coordinates. The forces on the atoms so generated are calculated using Hellmann-Feynman theorem. From the obtained forces, the Hessian matrix was constructed and diagonalized using the Phonopy code [153]. A scaling factor of 1.02 was applied to obtain frequencies so that the calculated C-O stretch frequency in gas phase equals the experimental value of 2170 cm\(^{-1}\) [154].
5.2.3 Simulation of STM images

We simulated STM images [155] by using the Tersoff and Hamman [35,36] method, i.e. the tunneling current at low voltage is assumed to be proportional to the local density of states (LDOS) around the Fermi level at the position of the tip apex. In our calculations, the topological STM image is approximated to be the LDOS isosurface with value of $10^{-6}$ e/Å³ contributed from all states in the energy range of -0.1 eV to 0.00 eV (i.e. within 0.1 eV of the Fermi level).

5.3 Results and Discussions

5.3.1 Testing the reliability of DFT functional

Previous body of work [156-163] suggests that DFT does not always predict correctly the adsorption site for CO on close-packed transition metal surfaces. We tested the case of 1/3ML coverage of CO on Pd(111) because we are aware from experiments that at this coverage CO molecules form the $(\sqrt{3} \times \sqrt{3})$R30° overlayer occupying the FCC hollow sites [131]. We considered the three high symmetry adsorption sites, i.e. the FCC and HCP hollow sites and the top site, and verified that the most preferable adsorption site is the FCC. This result implies that the PBE functional is reliable and appropriate for our model system. We also tested the case of a single CO on Pd(111) and found that CO prefers to bind on the FCC site and the energy difference between FCC and HCP sites is 20 meV, which is in excellent agreement with the results of Mitsui et al. [148].
5.3.2 CO Overlayer Structure on Pd(111) at $\frac{1}{2}$ ML

Fig. 5.1 shows all surface unit cells of CO on Pd(111) at $\frac{1}{2}$ML coverage forming c(4×2)-2CO overlayers that we have considered in this study. After ionic relaxations (results of which are summarized in Table 5.1), these structures convert to either one of the following: the “FCC-HCP” structure with equal mixture of the FCC and the HCP adsorption sites (Fig. 5.2a) and the “FCC-Bridge Hybrid” structure with both CO molecules binding to the sites located between the FCC and bridge sites (Fig. 5.3a). The average binding energy of the CO molecule in the FCC-HCP and FCC-Bridge Hybrid structures are -1.84 eV, -1.77 eV, respectively. The small difference in the
binding energies suggests a slight preference of FCC-HCP over FCC-Bridge Hybrid. We found no imaginary vibrational frequency for the obtained structures suggesting their dynamical stability. The results presented herein after are obtained with the PBE functional of DFT. Usage of the PW91 [13] and the optB88-vdW [21] functionals led to preference for similar binding sites as with PBE but with a slight difference in binding energy of CO molecules, as listed in Table 5.2.

5.4 Discussion

5.4.1 FCC-HCP binding sites

The FCC-HCP is one of the structures of c(4×2)-2CO on Pd(111) that was suggested from analysis of experimental data [135,138] and shown theoretically to be the lowest energy one for ½ML coverage [139,142,143,164]. Our ionic relaxations of several different starting structures also result in FCC-HCP as the final structure (see Table 5.1). The relaxed FCC-HCP structure shown in Fig. 5.2a displays a tilted geometry which is further elaborated in Fig. 5.2b. More quantitatively, we find the
Table 5.1. The final binding sites obtained after ionic relaxation of the possible initial c(4×2)-2CO configurations shown in Figure 1, using the PBE and optB88-vdW functionals.

<table>
<thead>
<tr>
<th>Initial Configuration</th>
<th>Final Configuration (PBE)</th>
<th>Final Configuration (optB88-vdW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Bridge-Bridge</td>
<td>FCC-HCP</td>
<td>FCC-HCP</td>
</tr>
<tr>
<td>(b) Bridge-FCC</td>
<td>FCC-HCP</td>
<td>FCC-HCP</td>
</tr>
<tr>
<td>(c) Bridge-HCP</td>
<td>FCC-HCP</td>
<td>FCC-HCP</td>
</tr>
<tr>
<td>(d) HCP-HCP</td>
<td>FCC-HCP</td>
<td>FCC-HCP, FCC-Bridge Hybrid</td>
</tr>
<tr>
<td>(e) FCC-HCP</td>
<td>FCC-HCP</td>
<td>FCC-HCP</td>
</tr>
<tr>
<td>(f) FCC-FCC</td>
<td>FCC-Bridge Hybrid</td>
<td>FCC-Bridge Hybrid</td>
</tr>
<tr>
<td>(g) TOP-TOP</td>
<td>FCC-Bridge Hybrid</td>
<td>FCC-Bridge Hybrid</td>
</tr>
<tr>
<td>(h) FCC-TOP</td>
<td>FCC-HCP</td>
<td>FCC-HCP</td>
</tr>
<tr>
<td>(i) HCP-TOP</td>
<td>FCC-HCP</td>
<td>FCC-HCP</td>
</tr>
<tr>
<td>(j) Bridge-TOP</td>
<td>FCC-HCP</td>
<td>FCC-Bridge Hybrid</td>
</tr>
</tbody>
</table>

CO molecules, in fcc and hcp sites, to be tilted with angles of 3.18° and 3.23°, respectively, with respect to the surface normal. In its simulated STM image (Fig. 5.2c), the protrusions appear in a periodic arrangement at the vertices and near the center (Fig. 5.2c) of a rectangular unit cell with dimension of 4.82×5.57Å. Because STM captures electronic properties at few angstroms away from the surface and the molecules, the tilted binding of CO results in appearance of protrusions adjacent to the positions of molecules as obtained by Rose et al. [138] who concluded that CO molecules occupy bridge sites (bridge-bridge structure) with spatially equal distance between them. However, such structural assignment was found to be unstable in our calculations. We find
the average binding energy of CO to be -1.85 eV, in agreement with previous theoretical results [139,142,143].

![Figure 5.2. FCC-HCP structure: (a) Top view of structure with c(4×2)-2CO unit cell, (b) side view showing the tilt angles of the CO molecules and C-Pd bond-lengths when adsorbed on FCC and HCP sites and (c) simulated STM image.](image)

**5.4.2 Bridge-Bridge binding sites**

The Bridge-Bridge geometry in which both CO molecules are on bridge sites is one of the suggested c(4×2)-2CO structure [131,132,137,138] (shown in Fig. 5.1a). This assignment was made largely because the frequency of the reported CO stretching mode [131,132,137], in the range of 1880-2000 cm⁻¹, was assigned to two-fold coordinated sites based on single molecule vibration frequencies [131] and the similarity of its geometric structure and STM image [138].

With force threshold of 0.01 eV/Å, we could obtain this structure with CO binding energy of -1.76 eV. This structure was also previously reported as one of relaxed structures at ½ML [139,142,143,145,164].

However, our calculation of the vibrational frequencies for the bridge-bridge structure showed the existence of modes with imaginary frequencies, indicating the instability of the structure. Indeed,
by further optimizing to a force threshold of 0.001 eV/Å, CO molecules on the bridge sites were found to move to TFH sites, and next form the FCC-HCP structure.

Table 5.2. Calculated binding energies (in eV) and C-O stretch frequencies (in cm\(^{-1}\)) on Pd(111) at ½ML obtained using different DFT functionals. (\(^a\)Ref [139], \(^b\)Ref [143], \(^c\)Ref [142], \(^d\)Ref [146])

<table>
<thead>
<tr>
<th>Functional</th>
<th>FCC-HCP</th>
<th>FCC-Bridge Hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>-1.84</td>
<td>-1.77</td>
</tr>
<tr>
<td>PBE with ZPE Correction (eV)</td>
<td>-1.78</td>
<td>-1.71</td>
</tr>
<tr>
<td>PW91</td>
<td>-1.85(^c)</td>
<td>-1.76</td>
</tr>
<tr>
<td>optB88-vdW</td>
<td>-1.92</td>
<td>-1.86</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C-O stretch frequency (cm(^{-1}))</th>
<th>PBE</th>
<th>PW91</th>
<th>optB88-vdW</th>
</tr>
</thead>
<tbody>
<tr>
<td>1910, 1842</td>
<td>1917, 1852(^a)</td>
<td>1924, 1856</td>
<td></td>
</tr>
<tr>
<td>1928, 1858(^b)</td>
<td>1914, 1847</td>
<td>1923, 1857</td>
<td></td>
</tr>
<tr>
<td>1906, 1850(^c)</td>
<td>1929, 1859</td>
<td>1944, 1874</td>
<td></td>
</tr>
</tbody>
</table>

5.4.3 **FCC-BRIDGE Hybrid binding sites**

The FCC-Bridge Hybrid adsorption geometry of c(4×2)-2CO on Pd(111) found in the present work has not been proposed or reported previously. This structure is similar to Bridge-Bridge
discussed earlier, except that in this structure the CO molecules bind neither at the bridge site nor at the FCC site but between these two sites with C-Pd bond lengths of 2.00 Å and 2.30 Å and 2.06 Å. The relaxed FCC-Bridge Hybrid geometry is shown in Fig. 5.3a and 3b and the CO binding energy of -1.77 eV is listed in Table 5.2. As in the FCC-HCP case, CO binds here tilted with respect to the surface normal (Fig. 3b) with an angle of 2.58° for both sites. Our simulated STM image of this structure (Fig. 3c) shows the zig-zag rows of protrusions similar to those also seen in experiments [138]. The problem is that the zig-zag rows in our calculations are apparently in the direction perpendicular to those in the experimental STM images [138] (in which the structure was assigned as FCC-HCP).

Despite this discrepancy and further verifications required, the FCC-Bridge Hybrid structure reported here could potentially be the one that produces the zig-zag rows in experimental STM images. This is because the distances between the protrusions in the rows found in the experimental STM images appear to be very similar to those between the titled CO molecules in FCC-Bridge Hybrid structure proposed here. Note that our STM simulations do not take into account the effect of tip and temperature which may account for some of the differences. Note also that our calculated barrier for transition from the FCC-Bridge Hybrid structure to FCC-HCP is 20 meV while the reverse transition barrier is 117 meV. These values indicate that FCC-Bridge Hybrid structure may convert to FCC-HCP while the reverse transition is not favorable which is in accordance with the
results of Ref [138] in which the structure with protrusions as obtained for FCC-HCP occurs more frequently.

Figure 5.3. FCC-Bridge Hybrid structure: (a) Top view of structure with c(4×2)-2CO unit cell, (b) side view with tilt angles of molecules and C-Pd bond-lengths on FCC-Bridge.

This also suggests that LEED experiment [131], performed in high temperature, was done with the FCC-HCP c(4×2) overlayer structure.

5.4.4 FCC-BRIDGE and HCP-BRIDGE binding sites

FCC-Bridge and HCP-Bridge are the two structures recently suggested by Martin et al. [139] largely because at ½ML the XPS spectra has two distinct peaks, whose intensities display a 1:3 ratio, for the Pd 3d_{5/2} component confirming the existence of two types of Pd atoms upon CO exposure. Combined with experimental results, their DFT calculations show the possibility of existence of four structures at ½ ML coverage: Bridge-Bridge, FCC-HCP, FCC-Bridge and HCP-Bridge. However only Bridge-Hollow structures satisfy the 1:3 ratio observed experimentally in which 1 Pd atom is coordinated with 2 (bridge bonded) CO molecules and 3 Pd atoms are
coordinated with 1 (TFH bonded) CO molecule. They obtained binding energies of FCC-Bridge and HCP-Bridge structures are -1.76 eV and -1.75 eV, respectively. Based on this assignment, their measured IR frequency (a strong peak at 1959 cm$^{-1}$ and a weaker peak at 1864 cm$^{-1}$) has the best agreement with their calculated vibrational frequencies for HCP-Bridge structure (1957 cm$^{-1}$ and 1862 cm$^{-1}$). Thus they have concluded that at ½ML coverage the Bridge-Hollow structures are the experimentally observed ones.

On the contrary, we find phonon instabilities for the FCC-Bridge structure obtained with a force threshold of 0.04 eV/Å or larger (0.05 eV/Å used by Martin et al. [139]). The CO molecule at bridge sites, relaxes to the HCP site to form FCC-HCP structure once the force threshold is smaller than 0.04 eV/Å. HCP-Bridge structure was not obtained for the above mentioned force thresholds since the CO molecule at the bridge site was found to move to the FCC site on ionic relaxation.

It is also worth noting that the suggested structures based on 1:3 ratio of Pd types in Martin et al. [139] are in contradiction with XPS result of Surnev et al. [136] in which a 1:1 ratio is observed between two types of Pd atoms (2 Pd atoms are coordinated with CO molecule adsorbed on the hollow site and 2 other Pd atoms are coordinated with 2/3 CO molecule adsorbed on the other hollow site), confirming that FCC-HCP structure is the geometry of CO molecules at ½ML coverage on Pd(111). On the other hand, the shifts of Pd 3d$_{5/2}$ components in XPS spectra with respect to the Pd bulk component, realized by Martin et al. [139], are very close to the shifts observed for (2×2)-3CO structure at almost ¾ML coverage obtained by Surnev et al. [136] in which a 1:3 ratio can be observed between two kinds of Pd atoms. The similarities of the shifts and the ratio between two types of surface Pd atoms in the two experiments suggest the possibility
of CO coverage of Martin et al. experiment [139] to be closer to $\frac{3}{4}$ML, resulting in (2×2)-3CO structure, not (4×2)-2CO as reported. Our obtained structures (FCC-HCP and FCC-Bridge Hybrid) have a ratio of 1:1 between the two types of surface Pd as obtained in Ref [136].

5.4.5 About CO stretch vibrational frequencies

C-O stretch vibrational frequencies were often used to describe or identify overlayer structure and adsorption sites [131-134,137] on Pd(111). In the c(4×2)-2CO overlayer, because of the presence of two molecules per surface unit cell, two types of CO stretching modes are present: symmetric and antisymmetric, as described in Ref. [142]. We found that the corresponding frequencies for FCC-HCP are 1910 cm$^{-1}$ and 1842 cm$^{-1}$, respectively, and for FCC-Bridge Hybrid are 1924 cm$^{-1}$ and 1856 cm$^{-1}$, respectively, as summarized in Table 2. The reported experimental frequencies are 1936 cm$^{-1}$ [131], 1920 cm$^{-1}$ [132], 1950 cm$^{-1}$ [134] and 1959 cm$^{-1}$ [139]. As discussed above, our calculations show that the FCC-HCP structure is the most stable and is the only structure in full accord with experimental features. Our calculated stretch frequency of 1906 cm$^{-1}$ for C-O for the FCC-HCP structure is similar to that in previous theoretical works [142,164]. On the other hand, the calculated C-O symmetric stretch frequency of 1924 cm$^{-1}$ for FCC-Bridge Hybrid structure is close to results of Ref [132]. The higher stretch frequency of this structure relative to FCC-HCP is also in line with the fact that the latter is more stable than the former.
5.5 Conclusion

In this work [165] we have examined the characteristics of several possible overlayer structures of CO on Pd(111) at ½ML coverage to bring some consensus in the ongoing debate on the adsorption site/s. We find two structures with equal mixtures of CO to provide good agreement with existing experimental data: FCC-HCP and a FCC-Bridge Hybrid. More importantly, we do not find the bridge site to be the preferred one at ½ML coverage: the Bridge-Bridge, Bridge-TOP, FCC-Bridge and HCP-Bridge structures are found to relax to FCC-HCP. Additionally, the FCC-FCC and TOP-TOP configurations relax into a new structure which we call FCC-Bridge Hybrid. Our calculated STM image of the FCC-HCP structure is in good agreement with one of the experimental STM images [138] which we believe was incorrectly assigned previously to the structure in which both CO molecules bind to the bridge sites. Our proposed FCC-Bridge Hybrid structure is very interesting as it produces zig-zag STM images resembling those seen in experimental STM images albeit not in full agreement with the orientation of those in the experiments. Furthermore, the transition barrier for FCC-Bridge Hybrid to FCC-HCP is found to be small (20 meV) and the reverse barrier to be relatively large, pointing to the FCC-HCP as the most stable structure. This conclusion is also in qualitative agreement with experiments according to which the FCC-HCP structure is found more frequently in the STM images. We also found that inclusion of vdW interactions in the calculations did not have significant effect on our conclusions.
CHAPTER 6: ELECTRONIC AND OPTICAL PROPERTIES OF Ag\textsubscript{44}(MNBA)\textsubscript{2}

6.1 Introduction

The notable optical properties of the thiol-protected Ag nanoclusters (NCs) \[3,166-179\], nanoparticles stabilized by organic ligands with diameter in the order of 2nm, have recently drawn tremendous attention of the community due to several reasons. It was found that these systems, synthesized much later than their Au “cousins”,\[167\] have rather different optical properties as compared to the same sized Au NCs \[172,173,180,181\]. In particular, the electronic and optical properties of one of such systems, [Ag\textsubscript{44}(SR)\textsubscript{30}]\textsuperscript{4+} (S stands for thiolate and R represents the ligand), with very stable closed electronic shell structure \[182\], identified by single crystal X-ray diffraction \[172,173\], has been extensively studied in the last years. Importantly, this system has a multi peak broad absorption spectra \[166\], which might be used in different optical applications. It has been also shown that the optical properties of [Ag\textsubscript{44}(SR)\textsubscript{30}]\textsuperscript{4+} can be tuned by substituting Ag\textsubscript{12} core of Ag\textsubscript{44} NC with Au\textsubscript{12} \[173\], changing the head groups of capping ligands \[166,174,178\] or even by changing the length of the ligands \[174\]. However, such tuning does not necessarily require the direct substitution of metal cluster or its stabilizing ligands. Rather, it was experimentally proved that protonation of ligands also causes the change in optical absorption spectrum. This phenomena was observed after lowering pH of the solution for [Ag\textsubscript{44}(SPhCOOH)\textsubscript{30}]\textsuperscript{4+} NCs, that resulted in formation of COOH…HOOC dimer interactions between neighboring clusters \[172\]. Recently, it has also been shown that altering pH level of the solution causes changes in optical spectrum of [Ag\textsubscript{44}(MNBA)\textsubscript{30}]\textsuperscript{4+} NC (MNBA=5-mercaptop-2-nitro benzoic acid) \[3\]. Optical absorption spectrum was measured at pH=13 and pH=7 and
displayed dramatic changes when the pH is lowered: At pH=13 the absorption spectrum showed multiple peaks at 857 nm, 652 nm, 553 nm, 483 nm and 392 nm. However, when pH was lowered to 7, the peak at 392 nm was broadened and the peak at 652 nm was blue shifted by 27 nm while the peak at 857 vanished completely. On the other hand, the vibrational spectroscopy showed the involvement of hydrogen bonds in the NC when pH was lowered. Therefore it was proposed that at low pH (pH=7), the neighboring ligands could form dimers either by direct interactions between COOH…HOOC groups or via water molecules. However, when the pH is increased to 13, the carboxylate groups are deprotonated and the interaction between MNBA ligands change. Therefore presence or absence of dimerization affects the configuration of ligands with respect to each other as well as Ag$^{44}$ core which then changes the electronic and optical properties of NC. Results of a model (DFT) calculations [3] with one MNBA dimer coupled to Ag$^{44}$ suggest that the strong hydrogen bonds between carboxylate groups are rather strong. However, using this model, there is no full understanding of the electronic and optical properties of this system and therefore the origin of the change in optical absorption spectrum as a result of deprotonation at higher pH is not fully understood. The question thus remains: what is a possible reason for such a change in the absorption spectrum when pH increases from 7 to 13?

In this context, we have performed DFT based calculations to understand the excitation spectrum of [Ag$^{44}$(MNBA)_{30}]^{4-} in the case of different configurations of MNBA ligands: dimerized and deprotonated. Namely, we have used three different dimerized MNBA ligands (See Fig. 1) to study the electronic properties of Ag$^{44}$ NCs by means of Density Functional Theory (DFT) simulating both pH=7 and pH=13 when: (1) the ligands are dimerized and adsorbed on Ag$^{44}$ (pH=7) and (2) when the H from carboxylate group is removed to simulate deprotonation of ligands at pH=13. To
test the reliability of this model, the optical absorption spectrum is also simulated by DFT and TDDFT [46] calculations and the transitions resulting in main features of experimental absorption spectrum are identified. While DFT has been used to predict the ground state properties of Ag NCs [173,183-186], the calculations of optical properties are defined by the excited states. Using our model system, the simulations of absorption spectrum by DFT calculations, fail to reproduce the main features of the experimental results [3], while TDDFT gives result which are in good agreement with experiment.

This chapter is organized as follows. In Section (2), we give details of the used computational and theoretical methods. In Section (3), results on the electronic properties of the systems are presented. Section (4) includes results of the optical properties of the NCs. Finally, in Section (5) we give our conclusions.

6.2 Computational details

6.2.1 Electronic structure calculations

The relaxation of systems were done by using DFT [5,6] by employing the projector-augmented wave (PAW) pseudopotentials [27,28], with the plane-wave basis set and the supercell method as implemented in the Vienna Ab-initio Simulation Package (VASP) [111]. For the exchange-correlation potential we have used the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhoff (PBE) [112] functional. To include the long-range interactions, DFT-D3 [16] correction was employed. The kinetic energy cutoff was set to 400 eV with k-point sampling at
the Gamma point. The periodic image of the NCs were separated by 30 Å. The structures were relaxed until the force components acting on each atom were smaller than 0.01 eV/Å. To estimate the effect of deprotonation of dimers on the charge density redistribution of Ag$_{44}$, we have calculated the change of the charge of the total system using:

$$\Delta \rho = \rho_{Ag_{44}+Dimer} - \rho_{Ag_{44}} - \rho_{Dimer} \quad (6.1)$$

where $\rho_{Ag_{44}+Dimer}$ stands for the total charge density of the coupled Ag$_{44}$ and molecular dimer system, $\rho_{Ag_{44}}$ is the total charge density of the relaxed Ag$_{44}$ cluster after the adsorption of the dimer, and $\rho_{Dimer}$ is the total charge density of the adsorbed molecular dimer on the Ag$_{44}$.

To study details of the transfer of the electronic charge between the components of the system, we have used the topological Atoms in Molecules (AIM) Bader approach [33] as implemented in the Henkelman algorithm [120,121].

### 6.2.2 Transition Contribution Maps

Traditionally, one can analyze the spectral features of a system using an electron-hole pair-by-pair method. However, in a system with many atoms those features could arise from several transitions. Therefore, instead of using transition-by-transition method, one can use transition contribution maps (TCM) as described in Ref [187]. These maps present a weighted sum of several transitions to analyze the spectral features corresponding to a variety of transitions. In detail, the TCMs are two-dimensional (2D) plots of the transition probabilities (proportional to squares of the transition
dipole moments) with vertical axis displaying the energy of unoccupied \((E_u)\) states while the horizontal axis shows the energy of the occupied \((E_o)\) states. The dipole moments are then, presenting the ‘contribution intensity’. In summary it can be written as:

\[
M^{TCM}(E_o, E_u) = \Sigma_{ij} |d_{ij}|^2 f_{ij}(E_o, E_u)
\]  

(6.2)

where \(d_{ij}\) is the dipole moment and,

\[
f_{ij}(E_o, E_u) = \left(\frac{\sqrt{2\pi}\sigma}{e}\right)^{-2} e^{-\frac{(E_o - E_i)^2 + (E_u - E_j)^2}{2\sigma^2}}
\]  

(6.3)

is a 2D Gaussian broadening function with width \(\sigma = 0.01\) eV.

This method has been previously used to analyze the absorption spectra for other nanoclusters [173,185] and nanoparticles [188]. These maps could be combined with other analysis methods such as partial or projected density of states [173,185,188] to identify the characteristics of measured transitions.

Using this approach the transition contribution maps (TCMs) of the single MNBA molecule, Ag\(_{44}\) bare nanoparticle and coupled molecule-nanoparticle structures at pH=7 (when MNBA molecules form dimer) and at pH=13 (when MNBA molecules are deprotonated) are calculated by using the KS wave functions generated by the Quantum Espresso code [189]. We have combined our results with partial charge density of each transition.

6.2.3 Absorption Spectrum simulation

Using Kohn-Sham (KS) wave functions obtained as described in previous section the absorption spectrum is calculated. To obtain this spectrum, one can begin with calculations of the charge
susceptibility \( \chi_{\bar{G}\bar{G}'}(\vec{k}, \omega) \) that can be found from the following equation:

\[
\chi_{\bar{G}\bar{G}'}(\vec{k}, \omega) = \chi_{KS\bar{G}\bar{G}'}(\vec{k}, \omega) + \sum_{\bar{G}_1, \bar{G}_2} \chi_{KS\bar{G}\bar{G}_1}(\vec{k}, \omega) \left\{ v_{\bar{G}_1}(\vec{k}, \omega) \delta_{\bar{G}_1 \bar{G}_2} + f_{v_{\bar{G}_1}(\vec{k}, \omega) \delta_{\bar{G}_1 \bar{G}_2}} \right\} \chi_{\bar{G}_2\bar{G}_1}(\vec{k}, \omega),
\]

where \( \chi_{KS\bar{G}\bar{G}'}(\vec{k}, \omega) \) is the Kohn-Sham (KS) susceptibility, \( v_{\bar{G}_1}(\vec{k}, \omega) \delta_{\bar{G}_1 \bar{G}_2} \) and \( f_{v_{\bar{G}_1}(\vec{k}, \omega) \delta_{\bar{G}_1 \bar{G}_2}} \) are the Coulomb potential and the exchange-correlation (XC) kernel. The last equation is given in the frequency-momentum representation for the general case of extended (periodic) systems with \( \bar{G} \) being the reciprocal vectors (in our case, one has only one k-point \( \vec{k} = 0 \)).

The KS susceptibility can be calculated as:

\[
\chi_{KS\bar{G}\bar{G}'}(\vec{k}, \omega) = \frac{1}{V} \sum_{\vec{k}} \sum_{j,l=1}^{\infty} \frac{f_{\bar{k}+\vec{k}'-l\bar{k}+\vec{k}'\omega}}{\omega + \epsilon_{\bar{k}+\vec{k}'} - \epsilon_{\bar{k}+\vec{k}'} + i\eta} \int d^3 r \varphi_{j\bar{k}'}^{0*}(\vec{r}) e^{-i(\vec{k}+\vec{G})\vec{r}} \varphi_{l\bar{k}+\vec{k}'}^{0}(\vec{r}) \quad (6.5)
\]

\[
\times \int d^3 r' \varphi_{l\bar{k}+\vec{k}'}^{0*}(\vec{r}') e^{i(\vec{k}+\vec{G})\vec{r}'} \varphi_{j\vec{k}'}^{0}(\vec{r}'),
\]

where \( \epsilon_{\bar{k}+\vec{k}'} \) and \( \varphi_{j\vec{k}'}^{0}(\vec{r}') \) are the DFT KS eigen-energies and eigen-functions and \( f_{\bar{k}+\vec{k}'} \) the corresponding level occupancy.

Next, from \( \chi_{\bar{G}\bar{G}'}(\vec{k}, \omega) \) one can calculate the dielectric function (in the real-space representation) as:

\[
e^{-1}(\vec{r}, \vec{r}', \omega) = \delta(\vec{r} - \vec{r}') + \int d^3 r'' \frac{\chi(\vec{r}'', \vec{r}', \omega)}{|\vec{r} - \vec{r}''|}. \quad (6.6)
\]
Finally, imaginary part of the macroscopically- (spatially-) averaged last function gives the absorption spectrum of the system. This formalism was used to obtain both the TDDFT and DFT absorption spectra (putting $v_{\vec{G}_1}(\vec{k}, \omega)\delta_{\vec{G}_1\vec{G}_2} + f_{XC\vec{G}_1\vec{G}_2}(\vec{k}, \omega) = 0$ in Eq.(2) in the last case).

6.3 **Results and discussion**

6.3.1 **Structure of model dimers and Ag$_{44}$**

Figure 7.1 shows the dimer models used to analyze the effect of molecule-molecule interaction. The first model as depicted in Figure 7.1(a) is the dimerized model of two quasi-planar MNBA molecules coupled via COOH…COOH hydrogen bond. In this model, the O-H…O bond angle is 178.48°, very close to the planar bond, which leads to a separation of 12.6 Å between S atoms and results in very strong H bond between two COOH groups. Figure 1(b) shows the second model with S atoms brought closer to each other, resulting in Hydrogen bond formation between carboxylate groups. In this case, the COOH groups form almost planar configuration. In the third model (Fig 1(c)) the O-H…O bonding is mediated by water molecules and each water molecule forms two Hydrogen bonds which leads to very strong dimer structures. Table 6.1 summarizes the averaged hydrogen bond lengths and angles for each dimer model in the gas phase.

The isolated Ag$_{44}$ part of the system has icosahedral symmetry with total number of 38 atoms in the shell, leaving only 6 atom in the core, as shown in Fig 7.2. The analysis of frontier orbitals of this cluster shows that its LUMO charges are located on outer shell atoms that makes them very reactive (Fig 7.2(b)).
Table 6.1. Averaged hydrogen bond lengths and angles for the three dimer models in the gas phase shown in figures 2(a-c).

<table>
<thead>
<tr>
<th>Model</th>
<th>O-H…O Bond length (Å)</th>
<th>∠OHO (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer Model 1</td>
<td>1.56</td>
<td>178.48</td>
</tr>
<tr>
<td>Dimer Model 2</td>
<td>1.60</td>
<td>165.98</td>
</tr>
<tr>
<td>Dimer Model 3</td>
<td>1.61</td>
<td>169.91</td>
</tr>
</tbody>
</table>

Figure 6.1. (a-c) MNBA dimer models used in the paper along with the HOMO and LUMO charges of each one shown in green and orange colors, respectively. The isosurface is set to 0.008 Bohr⁻³.
Figure 6.2. (a) HOMO and (b) LUMO charge distributions of the isolated Ag\textsubscript{44} NC with the icosahedral symmetry. The isosurface is set to 0.008 Bohr\textsuperscript{3}.

6.3.2 Electronic Structure of Ag\textsubscript{44}(MNBA)\textsubscript{2}

Upon adsorption of molecular dimers on Ag\textsubscript{44} (dimerized system), the hydrogen bond lengths and angles change with respect to the isolated dimers as a result of the interaction between the ligands and the metal cluster. The average hydrogen bond length and angles are 1.66 Å and 164.18°, respectively, which are in the range of strong hydrogen bonds. Deprotonation (deprotonated system), on the other hand, results in the absence of hydrogen bonds in the case of models 1 and 2 while in model 3 a few hydrogen bonds remain after deprotonation. The unsaturated oxygens of the deprotonated carboxylates make bond with Ag atoms of the Ag\textsubscript{44} and breaks one out of four bonds of Ag to NC in models 1 (Figure 3(d)) and 3 (Figure 3(f)). Such interactions brings the backbone of bonding molecules closer to the metal core and leads to change of the configuration of capping ligands with respect to each other and Ag\textsubscript{44}. While this increases the interaction between ligands backbone with Ag\textsubscript{44}, the absence of hydrogen bonds in models 1 and 2 and the presence of fewer hydrogen bonds in model 3, result in the decrease of binding energy in all three systems.
when deprotonated. This decrease is less in model 3 because even after deprotonation of carboxylate groups, the water molecules form strong hydrogen bonds with oxygen atoms of this group and therefore the highest molecule-nanoparticle binding energy for both dimerized and deprotonated structures takes place in the systems of model 3. This implies that in the solution, the hydrogen bonding is mediated by water molecules rather than being a result of direct interactions between the carboxylate groups. The increase in the number of hydrogen bonds, then, results in higher binding energy of ligands with respect to two other model systems. Table 6.2 summarizes binding energies, bond lengths and bond angles for each of dimerized and deprotonated systems of study (supporting info of Ref[3]).

To understand the effect of deprotonation on the electronic structure of NCs, the charge density redistribution in the cases of different models were calculated. Figs 6.3(a-c) show the charge difference for dimerized ligands on Ag₄₄ and Figs 6.3(d-f) in the absence or presence of fewer hydrogen bonds. For the dimerized ligands on Ag₄₄, the main charge accumulation and depletion occur around the area of the bonding of Ag atom(s) to S atom of MNBA. The accumulation of charge takes place mostly in the midst of Ag and S atoms, indicating a covalent bond formation. However, for deprotonated ligands, the strong interaction of unsaturated oxygen atom charges from the carboxylate group as well as the ligand backbone charges with the ones of Ag₄₄, result in strong charge depletion on Ag₄₄ and higher polarization of ligands.

The amount of transferred charge from Ag₄₄ to ligands was calculated by using Bader analysis and the results are shown in Table 6.3. As it follows from this Table, the charge transfer from Ag₄₄ to capping ligands is larger in the case of deprotonated systems, and is reflected in the change of the optical properties of NCs in high (pH=13) and low (pH=7) acidic environment. This trend is
consistent with charge redistribution analysis in which the depletion of charge on Ag$_{44}$ and accumulation of charge on ligands increases significantly upon deprotonation. When ligands are deprotonated, the unsaturated O charge from the carboxylate group also gets an electron from Ag$_{44}$, while for dimerized system the electron transfer happens mainly between the thiol group and Ag$_{44}$ subsystems.

Table 6.2. Binding energies, averaged Ag-S bond lengths and hydrogen bonds of systems as shown in Figure 6.3(a-e).

<table>
<thead>
<tr>
<th>Model</th>
<th>Binding Energy (eV)</th>
<th>Ag-S bond length (Å)</th>
<th>O-H…O bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimerized Model 1</td>
<td>-1.16</td>
<td>2.42</td>
<td>1.66</td>
</tr>
<tr>
<td>Deprotonated Model 1</td>
<td>-0.61</td>
<td>2.50</td>
<td>-</td>
</tr>
<tr>
<td>Dimerized Model 2</td>
<td>-1.60</td>
<td>2.54</td>
<td>1.62</td>
</tr>
<tr>
<td>Deprotonated-Model 2</td>
<td>-0.84</td>
<td>2.55</td>
<td>-</td>
</tr>
<tr>
<td>Dimerized Model 3</td>
<td>-2.04</td>
<td>2.57</td>
<td>1.69</td>
</tr>
<tr>
<td>Deprotonated Model 3</td>
<td>-1.83</td>
<td>2.50</td>
<td>1.85</td>
</tr>
</tbody>
</table>
Table 6.3. Bader charge of systems as shown in Figure 5(a-e).

<table>
<thead>
<tr>
<th>Model</th>
<th>Transferred Bader Charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimerized Model 1</td>
<td>0.98</td>
</tr>
<tr>
<td>Deprotonated Model 1</td>
<td>2.17</td>
</tr>
<tr>
<td>Dimerized Model 2</td>
<td>0.85</td>
</tr>
<tr>
<td>Deprotonated-Model 2</td>
<td>1.88</td>
</tr>
<tr>
<td>Dimerized Model 3</td>
<td>0.98</td>
</tr>
<tr>
<td>Deprotonated Model 3</td>
<td>2.12</td>
</tr>
</tbody>
</table>
Figure 6.3. Charge density redistribution due to molecule-nanoparticle coupling in cases of dimerized (a-c) and deprotonated (d-f) Ag$_{44}$(MNBA)$_2$ NCs for three different dimer models as shown in Fig. 1(a-c). Green and red colors represent charge depletion and accumulation respectively. The isosurfaces are set to 0.002 Bohr$^3$.

6.3.3 Optical Properties of Ag$_{44}$(MNBA)$_2$

Since using model 3, the binding energy for dimerized and deprotonated systems has the highest value, as discussed in previous section, the optical properties of Ag$_{44}$(MNBA)$_2$ are analyzed using this system. In this section, we present the results of KS-TCMs. The TCM approach is a powerful approach that has been also previously used to identify the optical transitions in NCs and nanoparticles [173,185,188].

For single MNBA molecule, there are few strong peaks in the TCM (Fig. 6.4(a)). For bare Ag$_{44}$, on the other hand, TCM exhibits multiple strong peaks close to the HOMO level, as well as a set
of peaks with transition energies of around 3.2-6 eV (Fig. 6.4(b)). As a result of coupling between the MNBA ligands and Ag\textsubscript{44}, several other peaks appear in both dimerized and deprotonated systems (most of the new peaks are different in these two types of systems, Figs. 6.4(c) and 6.4(d). In particular, wide transition energy (E\textsubscript{u}-E\textsubscript{o}) range \(\sim\)3.2-6 eV in bare Ag\textsubscript{44} is enhanced in both systems (see Figs. 6.4(b-d), where these excited states are marked by yellow circles). However, this energy range is broader for dimerized system which is in agreement with experimental data. The position of this transition range is almost the same for the isolated Ag\textsubscript{44} and the coupled Ag\textsubscript{44}-molecule structures which indicates that these transitions in coupled systems correspond mostly to the inter-cluster excitations. The charge density calculation for this transition support this conclusion (Figs. 6.4(c-d)).
Figure 6.4. KS TCMs for (a) single MNBA molecule, (b) bare Ag$_{44}$ nanoparticle, (c) dimerized (MNBA)$_2$ on Ag$_{44}$ (pH=7) and (d) deprotonated (MNBA)$_2$ on Ag$_{44}$ (pH=13) at different resonance energies. All KS energies are given with respect to the HOMO energy.
At the next step, we have identified the charge densities of the occupied and unoccupied states of some of the strongest transitions for single MNBA molecule and Ag$_{44}$ nanoparticle. These charge densities are shown at the bottom of Figs 6.5(a-e) and the corresponding transition points are marked with green circles. The strongest transition in MNBA corresponds to a transition from HOMO-5 to LUMO. In the case of Ag$_{44}$, the higher energy transitions (Figs 6.5(b, c)) mainly involve charge transitions from corner atoms to edge atoms. However for lower energy transitions (Figs 6.5(d, e)), the charge transfers take place mainly between core atoms.
Figure 6.5. Individual optical transitions of single MNBA molecule and Ag_{44} nanoparticle and the corresponding charge transitions from occupied to unoccupied states (shown at the bottom of each diagram). The charge of occupied and unoccupied states are displayed in dark purple and blue colors, respectively. The isosurface is set to 0.003 Bohr^{3}. The related transition is marked with a green circle.
Figs 6.6 and 6.7 show the transitions corresponding to observed peaks in the experimental absorption spectrum of the Ag$_{44}$(MNBA)$_{30}$ at pH=13 and pH=7, respectively. The experimentally-observed transition of each marked point is shown as the inset in Figs 6.6 and 6.7. At both pH levels of 7 and 13, there is a peak at about 392 nm. This peak corresponds to broad transition energy range between 3 eV and 6 eV. The charge density calculations at this energy range also shows these transitions mainly take place on the Ag atoms. This is even more pronounced in the case of dimerized systems. The main difference between the two experimental absorption spectra at pH=7 and pH=13 is the new small peaks at 483 nm and 553 nm. The identified charge transitions corresponding to these peaks take place from capping ligands to Ag$_{44}$. Since, as it was mentioned before, at higher pH the carboxylate group of MNBA are deprotonated, one gets a change of the ligands configuration with respect to Ag$_{44}$ in this case. Also, as it was shown at section 3, the charge distribution in the coupled system is significantly affected by deprotonation. As a result, the excess charge on the oxygen atoms of carboxylate group gives rise to the new peaks at higher pH. [3]. The corresponding transition for each peak is marked with dark yellow circles.
Figure 6.6. Transition contribution map of the deprotonated system (pH=13). The corresponding charge transitions between occupied and unoccupied states are shown at the bottom of each diagram. The isosurface is set to 0.003 Bohr$^{-3}$. The inset of each figure represents experimental absorption spectrum of Ag$_{44}$(MNBA)$_{30}$. 
Finally, in order to understand the absorption experimental data for Ag\textsubscript{44}(MNBA)\textsubscript{30}, we have calculated the absorption spectrum of Ag\textsubscript{44}(MNBA)\textsubscript{2} using both DFT and TDDFT and compared our results with experiment. The calculated results are displayed in Figure 6.8, where we have also included the experimental spectra as inset. The experimental positions of absorption peaks are marked with dotted lines on simulated spectra for comparison between energy peaks of experiment and the ones obtained in theory.
As it follows from Fig 6.8, five distinct peaks are present in the experimental spectrum of the system when in the deprotonated case (corresponding to pH=13) at the following frequencies: 392 nm (3.16 eV), 483 nm (2.58 eV), 553 nm (2.25 eV), 652 nm (1.9 eV) and 857 nm (1.45 eV). The DFT results for the absorption spectrum of Ag₄₄(MNBA)₂ at pH=13 show only three dominant peaks at 620 nm (1.99 eV), 740 nm (1.68 eV) and 890 nm (1.39 eV), and strongly red-shifted absorption spectrum as compared to the experimental results (Fig. 8(a)). At pH=7, the experimental absorption spectrum have only two dominant peaks at pH=7: 329 nm (3.16 eV) and 625 nm (1.98 eV). Similar, to the pH=13 case, the DFT cannot reproduce the position of the peaks correctly (Fig. 8(b)). Therefore, the DFT results cannot reproduce the main features of the absorption spectrum of the two systems above. Namely, 1) the DFT spectrum is significantly red-shifted and 2) it does not show all the peaks, most notably 652 nm and 857 nm peaks in the pH=13 case. Therefore, to correct the theoretical absorption spectrum we applied the TDDFT approach [46].

The TDDFT absorption spectrum demonstrates five distinct peaks at pH=13 at the following energies: 450 nm (2.76 eV), 500 nm (2.48 eV), 570 nm (2.18 eV), 730 nm (1.70 eV) and 880 nm (1.41 eV), which is in much better agreement with the experimental data, except probably the 652 nm peak, for which one has TDDFT 730 nm shoulder (top Fig. 6.8). At pH=7, the agreement of the TDDFT result with the experiment is also much better. In particular, the TDDFT is capable to reproduce the wide spectral area around 400nm and the second peak at 620nm, though the approach gives also two extra peaks at 480nm and 720nm with a relatively small height. Therefore, the TDDFT correction shifts the DFT closer to the experimental curve and reproduces. Due to the used (PBE) approximation for the TDDFT XC potential and an used simplified model (in
particular, with two instead of thirty molecules), our TDDFT absorption spectrum is still somewhat red-shifted (~0.4eV) as compared to the experimental data, though the shift is much less than in the DFT case. Such a shift was also reported for thiol-protected silver NCs in Ref. [173], where the same approximation for the TDDFT XC potential was used.

6.4 Conclusion

Using DFT and TDDFT approaches, the electronic and optical properties of model systems of Ag$_{44}$(MNBA)$_2$ were analyzed and the results were compared to experimental results of Ag$_{44}$(MNBA)$_{30}$ structure. Namely, two different models were used: with MNBA ligands forming a dimer (simulating the pH=7) and with deprotonated ligands (simulating the pH=13). Our results show that for all the proposed dimer models, the deprotonation of ligands (pH increase) leads to substantial modification of the configurations of the ligands-metal NC system and as a result of their electronic and absorption spectra. We demonstrate that the TDDFT results for the absorption spectra is in much better agreement with the experimental data as compared to the DFT ones. Detailed calculations of the TCM shows that new peaks in the absorption spectrum are related to the charge transfer between the NC and molecular (electron rich in the deprotonated case) subsystems. As our results suggest, one can use change of the pH of the solution to tune the optical properties of the MNBA-decorated silver nanoparticles.
Figure 6.8. (a) Simulated absorption spectrum of Ag$_{44}$(MNBA)$_2$ at deprotonated (corresponding to pH=13) and (b) dimerized (corresponding to pH=7), using DFT and TDDFT. The dotted lines represent the position of experimental peaks. The experimental results for Ag$_{44}$(MNBA)$_{30}$ [3] are displayed as inset for comparison.
CHAPTER 7: ADSORPTION AND REACTION OF PLANAR MOLECULES ON SINGLE LAYER MoS$_2$

7.1 Introduction

Single layer MoS$_2$ is of great interest for a wide variety of applications because of its low dimensional structure and striking electronic and optical properties [190,191]. The basal plane (of pristine MoS$_2$) is very inert since all S and Mo bonds are saturated. In this sense the basal plane is a suitable ground for the physisorption of molecules particularly those that are planar. The weak interaction between the molecule and MoS$_2$ could lead to molecular structure formation. Furthermore, molecules such as hydrogen could lead to the creation of sulfur vacancies which would make the MoS$_2$ surface reactive. At the same time planar molecules such as benzene thiol could heal sulfur vacancies when adsorbed on this two-dimensional material. In this chapter I summarize some of the results that I have obtained for the adsorption and reaction of two planar molecules that were also the subject of experimental examination in our research collaborators’ laboratories.

In a recent experiment done by Dowben et al. the adsorption of di-iodobenzene on single crystal MoS2 was studied [192]. The intensity ratio of iodine to molybdenum was measured as a function of exposure for different isomers of the molecule. These data show that while for Ortho (1,2-) and Para (1,4-) di-iodobenzene the ratio remains almost zero, for Meta (1,3-) this ratio increases with exposure. Fig. 7.1 shows the results of this experiment. To understand what can cause such different trend, the adsorption characteristics of the three isomers are studied on single layer MoS2. Some preliminary results are summarized in this chapter.
On the other hand, edges of two-dimensional materials and defects are expected to be chemically active and therefore they can act as catalyst for a number of reactions such as hydro-desulfurization. Hydro treating processes are reductive hydrogen treatments of fossil fuel applied to upgrade and clean up oil resources to reduce the emission of environmentally harmful compounds and to sustain a better exploitation of low-grade crude oil. However defects are the major traps or scattering centers of charge carriers, leading to a relatively low mobility and current level in Field–Effect Transistors (FET) [193]. Therefore, healing of defects is also of great importance for electronic applications. The adsorption of benzene-thiol (BT) on MoS$_2$ could provide insight into reaction mechanisms on MoS$_2$ that could lead to the healing of defects. While the results of first section of this chapter are only provided for pristine MoS$_2$ (in the 2H phase), for the second section both pristine and defect-laden monolayers are considered. The chapter is organized as follows: in the next section the calculation methods of simulations are described. This is followed by a summary of the results of di-iodobenzene adsorption on MoS$_2$, which in turn is followed by the results for the energetics of adsorption and dissociation of BT on MoS$_2$.

### 7.2 Computational details

The relaxation of systems in this paper are done using DFT [5,6] by employing the projector-augmented wave (PAW) [27,28], plane wave basis set and the supercell method as implemented in the Vienna Ab-initio Simulation Package (VASP) [111,151]. The exchange-correlation interaction of electrons are described by generalized gradient approximation (GGA) in the form of
Perdew-Burke-Ernzerhoff (PBE) [112] functional. To include long range order interactions both DFT-D3 [16] correction and opt-B88 functional [20,21] are used. The kinetic energy cutoff is set to 500 eV with k point sampling at Gamma point. The periodic image of MoS$_2$ slab is separated by 14 Å. The structures are relaxed until force acting on each atom was smaller than 0.01 eV/Å.

The defect-laden structure is constructed by removing one Sulfur atom from pristine MoS$_2$. The adsorption energy of di-iodobenzene isomers, BT and its dissociated parts are obtained by:

$$E_b = E_{mol+MoS_2} - E_{mol} - E_{MoS_2}$$  \hspace{1cm} (7.1)

in which the $E_{mol+MoS_2}$ is the total energy of adsorbed specie on MoS$_2$, $E_{mol}$ is the total energy of molecule in gas phase and $E_{MoS_2}$ is the total energy of pristine and defect-laden MoS$_2$. The reaction energies are calculated as the energy difference between final products and initial structures.

Figure 7.1. intensity ratio of iodine to Molybdenum as a function of exposure for 1,2-di-iodobenzene (red), 1,3- di-iodobenzene (black) and 1,4- di-iodobenzene (blue). [192]
7.3 Results and Discussions

7.3.1 Adsorption of Di-iodobenzene on MoS$_2$

7.3.1.1 Adsorption Energies

The structure of three di-iodobenzene isomers along with MoS$_2$ are presented in Fig. 7.2. The adsorption of all three isomers were studied on high symmetry points of MoS$_2$ for all the possible configurations and the total energies were calculated for each one. The structures of 1, 2-di-iodobenzene on MoS$_2$ are shown in Fig. 7.3. For other two isomers similar configurations were considered.

Figure 7.2. Three isomers of di-iodobenzene: (a) 1, 2-di-iodobenzene (Ortho), (b) 1, 3-di-iodobenzene (Meta) and (c) 1, 4-di-iodobenzene (Para). Color code: Black: C, Pink: H and Purple: I.
The highest adsorption energy of di-iodobenzene isomers on MoS$_2$ is obtained for the structure with the center of benzene ring on top of a sulfur atom. The final structures are shown in Fig. 7.4. All three isomers are adsorbed with equal adsorption energies with a distance of 3.5 Å away from...
MoS$_2$. The results of binding energy and height shows that the isomers are weakly bounded to MoS$_2$. The adsorption energies for different adsorption configurations are summarized in Table 7.1.

The equal strength of binding of isomers on MoS2 gives rise to the question that what can be the origin of different I/Mo ratio of these molecules as observed in [192]. In order to answer this question, at first step, the electron affinity of molecules were calculated. Electron affinity of a system is defined as the energy needed to add an electron to it. For molecules this electron goes to lowest unoccupied orbital (LUMO). The energy is then obtained as:

$$\chi = E_{Vac} - E_{LUMO}$$  

(7.2)

The obtained values show a very small difference in the electron affinity of molecules with no specific trend, suggesting that this cannot be the origin of difference in the interaction of 1,3-diiodobenzene with that of 1,2- and 1,4-di-iodobenzene. The values of electron affinity are listed in Table 7.2.
Table 7.1. Adsorption energies of di-iodobenzene isomers on MoS2. The configurations (a-f) are shown in Fig. 7.3.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Adsorption Energy (eV) 1,2-di-iodobenzene</th>
<th>Adsorption Energy (eV) 1,3-di-iodobenzene</th>
<th>Adsorption Energy (eV) 1,4-di-iodobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-0.78</td>
<td>-0.72</td>
<td>-0.77</td>
</tr>
<tr>
<td>b</td>
<td>-0.81</td>
<td>-0.81</td>
<td>-0.81</td>
</tr>
<tr>
<td>c</td>
<td>-0.88</td>
<td>-0.77</td>
<td>-0.87</td>
</tr>
<tr>
<td>d</td>
<td>-0.79</td>
<td>-0.88</td>
<td>-0.87</td>
</tr>
<tr>
<td>e</td>
<td>-0.76</td>
<td>-0.79</td>
<td>-0.76</td>
</tr>
<tr>
<td>f</td>
<td>-0.80</td>
<td>-0.77</td>
<td>-0.79</td>
</tr>
</tbody>
</table>

Table 7.2. Calculated electron affinity of di-iodobenzene isomers.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>E(LUMO)</th>
<th>E(Vac)</th>
<th>Electron Affinity (X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-di-iodobenzene</td>
<td>-2.28</td>
<td>0.175</td>
<td>2.46</td>
</tr>
<tr>
<td>1,3-di-iodobenzene</td>
<td>-2.18</td>
<td>0.188</td>
<td>2.38</td>
</tr>
<tr>
<td>1,4-di-iodobenzene</td>
<td>-1.94</td>
<td>0.188</td>
<td>2.13</td>
</tr>
</tbody>
</table>
7.3.2 Frontier Orbitals Analysis

In the next step, the frontier orbitals (states close to the Fermi level) of isolated isomers and MoS2 as well as coupled structures were analyzed. Fig. 7.5 (a-f) shows the HOMO and LUMO of isomers and (g,h) shows the highest occupied and lowest unoccupied bands of MoS2. All three isomers have $\pi$-conjugated electron distributions within benzene ring in the HOMO. When adsorbed on MoS2 the interaction between the frontier orbitals determines the adsorption strength and orientation. Therefore a comparison of these orbitals before and after coupling of isomers gives insight into the mechanism of adsorption.

Figure 7.5. Frontier orbitals of di-iodobenzene isomers and MoS2. Red and Blue represent HOMO and LUMO respectively. The isosurface is set to 0.005 e/Bohr$^3$. 

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For coupled systems the highest (lowest) occupied (unoccupied) bands were also extracted and plotted in Fig. 7.6. While the adsorption of 1, 2-and 1, 4-di-iodobenzene molecules do not affect the HOMO of molecules and that of MoS2, this is different in the case of 1, 3-di-iodobenzene. The HOMO of 1, 3-di-iodobenzene is strongly affected by MoS2 and the \( \pi \) bond in benzene ring is broken (Figure 7.6(b)). This is the origin of why 1, 3-di-iodobenzene adsorbs different than the two other isomers and indicates that symmetry of isomer plays the role rather than its binding strength.

Figure 7.6. Partial charge density of highest occupied band of di-iodobenzene isomers on MoS2. The top and middle plots show the side and top view of structures. The bottom plots show the HOMO of isomers in gas phase. The benzene ring of molecules in gas and adsorbed phase are highlighted with a circle. In (a) 1, 2-di-iodobenzene and (c) 1, 4-diodobenzene the \( \pi \) bonds are preserved and connected to each other by green arrows. The isosurface is set to 0.005 e/Bohr\(^3\).
7.3.3 Adsorption and Dissociation of Benzenethiol on Pristine and Defect-Laden MoS$_2$

7.3.3.1 Adsorption Energies

The adsorption energies of BT and its dissociated parts on pristine MoS$_2$ (p-MoS$_2$) and defect-laden MoS$_2$ (d-MoS$_2$) with both DFT-D3 and optB88 functionals are summarized in Table 7.3. The obtained results show the same trend using both functionals. Since the calculations by opt-B88 are much more expensive than DFT-D3, for the rest of calculations DFT-D3 results have been used. The final structures of adsorbed species on pristine MoS$_2$ and defect-laden MoS$_2$ are displayed in Figs. 7.7 and 7.8.

Table 7.3. The adsorption energies of BT and its dissociated parts obtained using optB88 vdW-functional and DFT-D3 corrections.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Adsorption Energy (eV)</th>
<th>Adsorption Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>optB88</td>
<td>DFT-D3</td>
</tr>
<tr>
<td>C$_6$H$_5$SH</td>
<td>-0.77</td>
<td>-0.77</td>
</tr>
<tr>
<td>C$_6$H$_5$S</td>
<td>-0.80</td>
<td>-2.76</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>-1.22</td>
<td>-0.59</td>
</tr>
<tr>
<td>H</td>
<td>1.72</td>
<td>-0.11</td>
</tr>
</tbody>
</table>
As shown in Figure 2 for p-MoS$_2$ and d-MoS$_2$, BT adsorbs horizontally on MoS$_2$ with almost same adsorption energies for both of MoS$_2$ monolayers, indicating that presence of S defects on MoS$_2$ does not affect the adsorption of BT on MoS$_2$. However, if H from thiolate group of BT is detached, the adsorption energies increase dramatically on d-MoS$_2$ and C$_6$H$_5$S fills the vacancy site and heals the present defect. The results also show that while the adsorption of atomic H on p-MoS$_2$ is endothermic, it is exothermic on d-MoS$_2$.

Figure 7.7. Top and side view of (a) C$_6$H$_5$SH, (b) C$_6$H$_5$S and (c) C$_6$H$_5$ on p-MoS$_2$. 
7.3.3.2 Reaction Energies

To obtain the possible reactions of BT on pristine and defect-laden MoS2 monolayers, the reaction energies for are calculated. Table 7.4. summarizes the energy values for all of reactions.

Since pristine MoS$_2$ is inert (there are no dangling bonds on the surface), BT physisorbs rather than chemisorption. Reaction energy calculations show that the only possible reaction on pristine
MoS$_2$ is dissociation of BT to Benzene and H$_2$S molecule in gas phase leaving MoS$_2$ without defects. However such reactions are only possible if there are H atoms adsorbed on MoS$_2$. If such atomic hydrogens exist on the MoS$_2$, they will remove S from MoS$_2$, while adsorption of BT fills the vacancy and Benzene will desorb from Surface.

In the presence of defects, BT dissociation on MoS$_2$ is favorable, leading to healing of defects and desorption of Benzene. The vacancy provides charge and acts as active site for C$_6$H$_5$S. This suggests that using BT not only results in healing of defects, but also, hydro-desulfurization of BT happens if defects are on the MoS$_2$. Since the difference in adsorption energies of C$_6$H$_5$S on pristine and defect-laden MoS$_2$ is 1.91 eV, the contribution of vibrations (in the order of a few meV), is negligible.
### Table 7.4. Reaction energies of BT on p-MoS2 and d-MoS2.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>On Pristine MoS2</strong></td>
<td></td>
</tr>
<tr>
<td>$C_6H_5SH/P$-$\text{MoS}_2 \rightarrow C_6H_5S/P$-$\text{MoS}_2 + H/\text{MoS}_2$</td>
<td>3.25</td>
</tr>
<tr>
<td>$C_6H_5SH/P$-$\text{MoS}_2 + H/\text{MoS}_2 \rightarrow H_2S(g) + C_6H_5/P$-$\text{MoS}_2$</td>
<td>0.14</td>
</tr>
<tr>
<td>$C_6H_5SH/P$-$\text{MoS}_2 + H^*/P$-$\text{MoS}_2 \rightarrow H_2S(g) + C_6H_5(g) + MoS_2$</td>
<td>1.44</td>
</tr>
<tr>
<td>$C_6H_5SH/P$-$\text{MoS}_2 + 2H^*/MoS_2 \rightarrow H_2S(g) + C_6H_6(g) + MoS_2$</td>
<td>-3.66</td>
</tr>
<tr>
<td><strong>On Defect Laden MoS2</strong></td>
<td></td>
</tr>
<tr>
<td>$C_6H_5SH/d$-$\text{MoS}_2 \rightarrow C_6H_6(g) + P$-$\text{MoS}_2$</td>
<td>-2.47</td>
</tr>
<tr>
<td>$C_6H_5SH/d$-$\text{MoS}_2 \rightarrow H/P$-$\text{MoS}_2 + C_6H_5S/d$-$\text{MoS}_2$</td>
<td>1.33</td>
</tr>
<tr>
<td>$C_6H_5SH/d$-$\text{MoS}_2 + H^*/P$-$\text{MoS}_2 \rightarrow H_2S(g) + C_6H_5(g) + MoS_2$</td>
<td>1.43</td>
</tr>
</tbody>
</table>
Using vdW corrected DFT calculations the adsorption of three di-iodobenzene isomers and benzenethiol on MoS2 were studied.

In the first part the adsorption of isomers give the same binding strength on MoS2. The experimental results, on the other hand, show that 1, 3-diiodobenzene behaves quite differently from 1, 2-and 1, 4-diiodobenzene. The electron affinity of all three molecules were calculated and the obtained results showed no specific trends to verify experimental data. However the analysis of frontier orbitals shows that the frontier orbitals of 1, 3-diiodobenzene is strongly affected by interactions with MoS2 while the frontier orbitals of two other isomers remain unchanged. Our results show that symmetry is the identifying factor in adsorption mechanism of di-iodobenzene isomers rather than adsorption strength.

On the second part the adsorption and dissociation energetics of benzenethiol on pristine and defect-laden MoS2 was studied. Using two different functional for vdW interactions, we found that results have the same trend with higher energies obtained by optB88. Moreover, we show that benzenethiol is weakly adsorb on pristine MoS2 while remaining flat and the reactions of its dissociations are endothermic. If there are pre-adsorbed H atoms on the surface, the reaction is exothermic with H2S and benzene as final products. On the defect-laden MoS2, the benzenethiol rotates and binds vertically to defect site, healing the defect and leaves pristine MoS2 and benzene as final products in an exothermic reaction.
CHAPTER 8: CONCLUSION

This dissertation has investigated the structural, chemical and optical properties of nanostructures when modified by adsorbates and discussed the super structure of small molecules on transition metal surfaces in medium coverage of adsorbate based on first principles and the density functional theory calculations.

In chapter 3 using six different groups: N, CN, NC, NH2, COH and COOH, the adsorption of functionalized naphthalene molecule on Cu(111) was studied. I showed that altering the functional group not only changes the covalent and vdW interactions of adsorbed molecule with surface and adatom but also changes the electronic structure of the bonding surface atom and adatom. These results are relevant to design of single atom catalysts while the reaction center is modified by changing functional group.

In chapter 4 a new phase of h-BN Moiré structure on Rh(111) was studied. This new structure was obtained by intercalation of carbon impurities under specific regions of BN. I showed that the carbon atoms form islands of hexagonal rings and grow in a manner that their center is on top of Rh atoms. The transferred charge from Rh and C to BN creates dipoles that increases work function of the new phase. These results also help establish that it is the changes in the local environment induced by trapping of the carbon rings and subsequent modifications in surrounding bond lengths and geometrical arrangement that lead to electronic structural changes and hence to novel local chemical properties.

In chapter 5, using density functional theory based calculations I evaluates the structural and vibrational properties of the c(4×2) overlayer structure of CO on Pd(111), with all possible highly symmetric adsorption sites. My results show that the CO molecules prefer to adsorb either
only on the hollow (FCC or HCP) sites or only at sites which are located in-between the bridge and the FCC sites and that there is no stable overlayer structure in which the molecule binds only at the bridge sites or combination of bridge and hollow sites. The stretch frequency of CO molecules in each structure was calculated and compared to the experimental results.

In chapter 6, density functional theory (DFT) and Time-Dependent DFT studies of the effects of deprotonation of MNBA ligands on the electronic structure and optical properties of Ag$_{44}$ nanoparticle was investigated. The obtained results for the excitation energies of the system at low pH demonstrate that the optical absorption spectrum of Ag$_{44}$(MNBA)$_2$ is defined by transitions that have a mixed Ag-to-Ag and Ag-to-ligand character, while increase in the level of pH gives rise to new peaks which are mostly contributing from ligand-to-Ag transitions. TDDFT results capture the main features of the experimental data and indicate the crucial role of deprotonation on the optical properties of Ag$_{44}$ NC at higher pH.

In Chapter 7, the adsorption of two different planar molecules were studied. The first one was the adsorption of di-iodobenzene isomers on MoS2 to test the effect of symmetry vs. registry. Our results show that while all three isomers bind with same strength to MoS2, the 1, 3-diiodobenzene reacts differently and the $\pi$ bonds of benzene rings broke. The second molecule was benzenethiol and its adsorption and dissociation was studied on pristine and defect-laden MoS2. While BT does not bind on pristine MoS2 I binds strongly to defect site on defect laden MoS2, healing defects and leaving benzene as final product.

The results obtained in this dissertation promise to be relevant for the experimental and theoretical design of functional materials.
Title: CD adsorption on Pd(111) at 0.5ML: A first principles study
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APPENDIX B: LIST OF PUBLICATIONS


**In Preparation**


**Z. Hooshmand**, D. Le, Volodymyr Turkowski and T. S. Rahman, "**Electronic structure and optical properties of Ag44(MNBA)2 nanoclusters: an ab initio study**"

**Z. Hooshmand**, D. Le, and T. S. Rahman, "**Towards understanding of the surface coordination: The impact of functional group on the electronic structure of coordination center**"

D. Le, **Z. Hooshmand**, T. S. Rahman "**Effect of hydrogen adsorption on the structure of the basal plane of MoS2**"

**Z.Hooshmand**, D. Le and T. S. Rahman “**Reshaping the edges of MoS2 single layer: Interaction with H**”
LIST OF REFERENCES


