Ab initio studies of water at metal surfaces

Vassilev, P.D.

DOI: 10.6100/IR561293

Published: 01/01/2003

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Ab Initio Studies of Water at Metal Surfaces

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR AAN DE TECHNISCHE UNIVERSITEIT EINDHOVEN, OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF.DR. R.A. VAN SANTEN, VOOR EEN COMMISSIE AANGEWEZEN DOOR HET COLLEGE VOOR PROMOTIES IN HET OPENBAAR TE VERDEDIGEN OP DONDERDAG 23 JANUARI 2003 OM 16.00 UUR

DOOR

PETER D. VASSILEV

geboren te Sofia, Bulgarije
This research has been financially supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO). The work described in this thesis has been carried out at the Schuit Institute of Catalysis (part of NIOK, the Netherlands School for Catalysis Research), Eindhoven University of Technology, The Netherlands.
# Contents

<table>
<thead>
<tr>
<th>Contents</th>
<th>iiii</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Simulation Methodology</td>
<td>2</td>
</tr>
<tr>
<td>1.2 Objectives</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1 Water</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2 Water/Metal Interface</td>
<td>4</td>
</tr>
<tr>
<td>1.2.3 Hydroxyl–Water Coadsorption on Rh(111) Surface</td>
<td>6</td>
</tr>
<tr>
<td>2 Theoretical Background</td>
<td>7</td>
</tr>
<tr>
<td>2.1 Density Functional Theory</td>
<td>7</td>
</tr>
<tr>
<td>2.1.1 Schrödinger Equation and Born–Oppenheimer Approximation</td>
<td>7</td>
</tr>
<tr>
<td>2.1.2 Hohenberg-Kohn Theorems</td>
<td>8</td>
</tr>
<tr>
<td>2.1.3 Kohn–Sham Equations</td>
<td>9</td>
</tr>
<tr>
<td>2.2 Molecular Dynamics</td>
<td>9</td>
</tr>
<tr>
<td>2.2.1 General Definitions</td>
<td>9</td>
</tr>
<tr>
<td>2.2.2 Macroscopic and Microscopic States</td>
<td>10</td>
</tr>
<tr>
<td>2.2.3 Equation of Motion – Classical Motion of the Atoms</td>
<td>11</td>
</tr>
<tr>
<td>2.3 The VASP Program</td>
<td>11</td>
</tr>
<tr>
<td>2.3.1 Accuracy Considerations</td>
<td>12</td>
</tr>
<tr>
<td>3 Interpretation of the Results</td>
<td>13</td>
</tr>
<tr>
<td>3.1 Electronic Properties</td>
<td>13</td>
</tr>
<tr>
<td>3.1.1 Local (Projected) Density of States</td>
<td>14</td>
</tr>
<tr>
<td>3.1.2 COOP</td>
<td>14</td>
</tr>
<tr>
<td>3.1.3 Work Function</td>
<td>15</td>
</tr>
<tr>
<td>3.2 Structural and Dynamical Properties</td>
<td>15</td>
</tr>
<tr>
<td>3.2.1 Distribution Functions</td>
<td>15</td>
</tr>
</tbody>
</table>
CONTENTS

3.2.2 Velocity Autocorrelation Function and Vibrational Power Spectrum 16
3.2.3 Mean-Square Displacement and Diffusion Coefficient 16

4 Water Molecule and Water Dimer 17
4.1 Water Molecule: Computational Parameters 17
4.2 Water Molecule: Electronic Structure 18
4.3 Water Dimer 21
4.4 Summary and Conclusions 22

5 Liquid Water 23
5.1 Computational Details 23
5.2 Results and Discussions 24
  5.2.1 Enthalpy of Vaporization 24
  5.2.2 Radial Distribution Functions 25
  5.2.3 Self-Diffusion Coefficient 26
  5.2.4 Vibrational Power Spectrum 28
5.3 Summary and Conclusions 28

6 Water/Vapor Interface 29
6.1 Computational Details 29
6.2 Results and Discussions 30
  6.2.1 Density Profile Along the Surface Normal 30
  6.2.2 Mean-Square Displacement and Self-Diffusion 31
  6.2.3 Orientational Distribution of the Molecules 32
  6.2.4 Vibrational Power Spectrum 33
6.3 Summary and Conclusions 34

7 Adsorption of Water on Pt(111) and Rh(111) Surfaces 35
7.1 Computational Details 35
7.2 Results and Discussions 37
  7.2.1 Low Coverage Adsorption 37
  7.2.2 Bilayer of Water on Pt(111) and Rh(111) 41
  7.2.3 Electronic Structure Around the Fermi Level 42
  7.2.4 Water Bilayer in Vacuum 47
7.3 Summary and Conclusions 48

8 Water Bilayer on Rh(111): Structure 49
8.1 Computational Details 49
8.2 Accuracy of the Simulation 50
# CONTENTS

8.3 Results and Discussions ........................................... 53  
  8.3.1 Adsorption Energy ........................................... 54  
  8.3.2 Structure of the Bilayer ...................................... 54  
  8.4 Summary and Conclusions ....................................... 58  

9 Water Bilayer on Rh(111): Electronic Structure and Bonding 59  
  9.1 Computational Details ........................................... 59  
  9.2 Results and Discussions ......................................... 60  
    9.2.1 Electronic Structure and Electron Transfer Through the Interface ........................................... 60  
    9.2.2 Rhodium–Oxygen Interaction ................................ 62  
    9.2.3 Rhodium–Hydrogen Interaction .............................. 64  
  9.3 Summary and Conclusions ....................................... 66  

10 Liquid Water/Metal Interface 67  
  10.1 Computational Details ........................................... 67  
  10.2 Model of the Interface .......................................... 68  
  10.3 Results and Discussions ......................................... 72  
  10.4 Summary and Conclusions ....................................... 75  

11 Hydroxyl–Water Coadsorption on Rh(111) 77  
  11.1 Computational Details ........................................... 77  
  11.2 Results and Discussions ......................................... 78  
    11.2.1 Proton exchange rate ....................................... 79  
    11.2.2 Dynamical and Structural Properties ................... 81  
  11.3 Summary and Conclusions ....................................... 84  

12 Concluding Remarks .................................................. 85  

Bibliography ................................................................. 87  

A Comparison between different basis sets and density functionals 93  

Summary ................................................................. 97  

Samenvatting ............................................................... 99  

Acknowledgments .......................................................... 101  

Publications ............................................................... 103
CONTENTS

Curriculum Vitae 105
Chapter 1

Introduction

The structure and properties of liquid water and liquid water/metal interfaces are an important issue in electrochemistry and catalysis relevant to the description of numerous (electro–)chemical reactions. Not surprisingly, these systems have been the subject of many theoretical and experimental investigations [see for example Henderson (2002) and references therein]. Still there is a continued interest in the interpretation of the experimental results and in using various simulation methods at different levels of theory aiming at a better description of the processes in the system. Liquid water and water/metal interfaces were first modeled using “classical” molecular dynamics (MD) simulations. This technique relies on experimental results or previous theoretical calculations for the parameterization of the so–called classical interaction potentials. Most of the empirical water–water interaction potentials are essentially optimized to reproduce the experimentally observed properties of bulk water. However, the interpretation of the experimental data [Soper (2000) and references therein] may lead to quite distinct conclusions for the structure of liquid water.

An alternative way of modeling the interface is the first–principles molecular dynamics method based on the density functional theory, which does not require any input from experimental data. Recent publications of ab initio MD simulations have shown a good prediction of the structural and dynamical properties of bulk liquid water and different research groups have already considered the application of this technique for liquid water/metal interface. At present time there are several commonly used first–principles MD implementations, which can differ in their theoretical basis and in the choice of the so–called exchange–correlation functional.

The current work will first demonstrate that a specific ab initio compu-
tational approach, which is routinely used to study adsorption of molecules on transition metal surfaces, can be applied successfully to model bulk liquid water and the water/vapor interface. The investigation will then focus on modeling water at metal surfaces employing the same computational technique.

This thesis presents a systematic study of the properties of the water/metal interface, relating the results to the available experimental data and comparing with previous simulations. Of particular interest will be the interaction between the water molecules and the metal atoms. The electronic properties of the system will also be considered in view of recent experimental studies using scanning tunneling microscopy (STM). It will be shown that the presence of the metal substrate can give rise to local electronic states at the site of the oxygen atoms of the water molecules, explaining the apparent metallic conductivity of the interfacial water as deduced from the STM experiment. The hydroxyl–water coadsorption on a metal surface will also be considered, emphasizing the dynamics and the apparent diffusion of hydroxyl.

1.1 Simulation Methodology

The simulations of water and water/metal interface presented in this thesis are based on a computer implementation of the (electron) density functional theory (DFT). The \textit{ab initio} package VASP has been used throughout this work in combination with an in–house developed software for the analysis of the raw simulation data.

The accuracy and applicability of the results from DFT calculations depend on the choice of the exchange–correlation density functional. Commonly applied for modeling transition metals and adsorption processes on transition metal surfaces is the Perdew–Wang 91 (PW91) density functional and this is also the exchange–correlation functional used in the present work. A brief introduction to the density functional theory and the employed molecular dynamics technique is given in Chapter 2.

1.2 Objectives

The goal of this project is to gradually build knowledge of the interface emphasizing the local electronic properties and the determining factors for the structural and dynamical properties of interfacial water. This thesis covers three main areas of interest: water, water/metal interface, and hydroxyl–water coadsorption on the metal surface.
1.2. Objectives

1.2.1 Water

Water is perhaps the most important chemical substance and polar solvent. Numerous experimental investigations have considered the structure and properties of liquid water in view of its role in a variety of chemical, biochemical and electrochemical processes and it is also one of the most extensively studied subjects in the field of the MD simulations, including using \textit{ab initio} methods.\footnote{See Soper et al. (1997), Soper (2000) and references there in for experimental studies of the structure of liquid water using neutron diffraction and Draegert et al. (1966), Walrafen (1967), and Schiffer and Horning (1968) for infrared/Raman spectrometry on liquid water; Mills (1973) measured the self-diffusion of water in liquid water. Kuharski and Rossky (1985) performed a theoretical study of quantum effects of the hydrogen atoms, \textit{ab initio} MD simulations of liquid water were performed by Laasonen et al. (1993), Sprik et al. (1996), Silvestrelli et al. (1997), Silvestrelli and Parrinello (1999a), Krack and Parrinello (2000), and Boese et al. (2000), some comparing different exchange–correlation density functionals.}

One of the main conclusions from the \textit{ab initio} studies is that the so-called BLYP exchange-correlation density functional, proposed by Becke (1988) and Lee et al. (1988), gives the best description for bulk liquid water. However, the comparison between the density functionals reported by Sprik et al. (1996) did not include the PW91 density functional, which as mentioned above is preferred for transition metal surfaces. Furthermore, recent work of Hamman (1997) showed that simulations using the PW91 density functional result in good agreement between computed data and experiment for the sublimation energy and the volume of hexagonal ice Ih.

Since this work aims at describing the water/metal interface using density functional theory methods, several benchmark simulations were performed in order to assess the accuracy of the PW91 functional for water. In this thesis the single water molecule, water dimer and bulk liquid water are considered. The water monomer and dimer were studied by means of geometry optimizations and molecular dynamics simulations were performed to model liquid water at ambient conditions (Chapters 4 and 5).

The results of an \textit{ab initio} MD simulation of a water slab as a model for the liquid water/vapor interface are also presented (Chapter 6). The structure of liquid water/vapor interface has been studied quite intensively using experimental or theoretical methods.\footnote{See for example Goh et al. (1988) for experimental studies on the orientation of the water molecules at the water/vapor interface and Wilson et al. (1987), Matsumoto and Kataoka (1988), Townsend and Rice (1991), Lie et al. (1993), Yang et al. (1994), Taylor et al. (1996), and Sokhan and Tildesley (1997) for theoretical studies using classical interaction potentials.} Some of these studies however lead to different conclusions regarding the orientational distributions of the surface water dipole moment. In this thesis the orientational distribution at the water/vapor interface is investigated for the first time using \textit{ab initio} MD
methods in comparison with experimental data and classical MD simulations.

1.2.2 Water/Metal Interface

The water/metal interface is one of the main topics in this work. Computer simulations and experimental data have shown that water molecules next to a metal surface are arranged in several layers interacting through an extensive hydrogen–bond network.\(^3\) The strength of the metal–water and water–water bonds are believed to be comparable, making this system unique in the sense that it is characterized by a subtle interplay of adsorbate–adsorbate and substrate–adsorbate interactions. It has been suggested that both the water adsorption layer under ultra high vacuum conditions and the first water layer next to the surface at the liquid water/metal interface inherit the translational symmetry of the substrate with the molecules arranged in an ice–like structure. Experimental investigations have shown that on Pt(111) and Rh(111) surfaces water molecules adsorb forming hydrogen bonded clusters with a \(\left(\sqrt{3} \times \sqrt{3}\right)R30^\circ\) structure, although in the case of Pt(111) other phases have been observed as well. A model for the water adlayer on metal surfaces was proposed by Sass et al. (1981) and Doering and Madey (1982) (Fig. 1.1). This “bilayer” model consists of two sublayers: (i) water molecules from the first sublayer are chemisorbed on top of the metal atoms (Fig. 1.1, oxygens denoted with full circles), while (ii) molecules from the second sublayer, though still on top, are further away from the surface with one of their OH bond pointing away from the surface. The molecules from the two sublayers are bound together through hydrogen bonds.

In this thesis the results for the static structure and electronic properties of water molecules adsorbed at different coverages on Pt(111) and Rh(111) metal surfaces are presented (Chapters 7). Molecular dynamics simulations of water adsorbed on Rh(111) were performed using a larger unit cell in search of a better structural configuration of the adlayer (Chapter 8 and 9). Systems containing several layers of water adsorbed on Rh(111) surface modeling the

\(^3\) Very good introductions on this matter are given by Thiel and Madey (1987) and Henderson (2002). Computer simulations of the interface were performed by Benjamin (1996), Lee et al. (1984), Spohr (1989), Yeh and Berkowitz (1998), Halley et al. (1998), Izvekov et al. (2001), and Izvekov and Voth (2001). Experimental data on liquid water/metal surface by Russell et al. (1993), Toney et al. (1994, 1995), Iwasita and Xia (1996), and Ataka and Osawa (1998), some including studies of the potential dependence of the orientation of the water molecules at the interface. Experimental studies on chemisorbed water on Rh(111) or Pt(111) surface were performed by Zinck and Winberg (1980), Morgenstern et al. (1997), and Gibson et al. (2000), including STM imaging; a comparison between the properties of water adsorbed on Pt(111) and Rh(111) surfaces by Wagner and Moylan (1987).
1.2. Objectives

Figure 1.1: Perfect water bilayer on M(111) metal surface and the smallest surface unit cell $ABCD$. The substrate is represented through lines connecting the positions of the surface metal atoms. Full circles represent the oxygens from the first water sublayer, which is the closest to the surface, shaded circles represent the oxygens from the second sublayer. The hydrogen atoms are given with small circles.

liquid water/metal interface have also been considered (Chapter 10).

Using scanning tunneling microscopy (STM) Morgenstern et al. (1997) observed that the $\text{H}_2\text{O}$-bilayer adsorbed on Pt(111) surface appears as an elevation to the STM. The authors suggested that the bilayer possesses a metallic conductivity and supported their experimental data with first-principles results. These calculations, however, were performed using a model consisting of a single water molecule adsorbed on a Pt$_{10}$–cluster, which cannot account for the complete structure of the bilayer. In relation to the STM experiment and the apparent metallic conductivity of water bilayer, in this thesis the spatial distribution of the electron states around the Fermi level is also considered. These states may have implications for electron charge transfer processes through the interface and their spatial distribution is of significance in theoretical models for electron tunneling such as in the STM and electrochemical reactions.\footnote{For modeling of the process of electron tunneling and STM imaging see Tersoff and Hamann (1983, 1985); The theoretical description of electrochemical reactions and electron tunneling through water layers is discussed by Schmickler (1996), Benjamin (1996), Benjamin et al. (1997), Morgenstern et al. (1997), Hahn et al. (1998), Hong et al. (1998), Naaman et al. (1998), and Nitzan and Benjamin (1999).}
1.2.3 Hydroxyl–Water Coadsorption on Rh(111) Surface

The third subject covered in this thesis is the hydroxyl–water coadsorption on Rh(111) surface (Chapter 11). Hydroxyl adsorbed on transition metal surfaces plays an essential role in a number of surface-catalyzed chemical processes. For instance, it is a key intermediate in the hydrogen–oxygen reaction leading to water. Surface–bonded hydroxyl is probably of even greater importance in electrochemical processes, particularly when considered in an aqueous environment. Surface hydroxyl is commonly believed to be a precursor to surface oxidation and corrosion, as well as the oxidizing species in many electrocatalytic oxidation reactions, such as the carbon monoxide oxidation [see, e.g., Conway (1995) and Lipkowski and Ross (1998)].

The coadsorption of hydroxyl and water on a transition metal surface is one of the best illustrations for the potential of the ab initio molecular dynamics technique. It is known that the hydroxyl can take part in a proton exchange reactions with a neighboring water molecule:

\[
OH_{ad} + H_2O_{ad} \rightarrow H_2O_{ad} + OH_{ad}
\] (1.1)

The characterization of this system must include not only the process of an apparent hydroxyl transfer through the above bond–breaking mechanism, but also hydrogen–bond interactions between neighboring water molecules as well as interactions with the metal surface. The variety in the type and the strength of these interactions makes the description of this system using classical interaction potentials extremely difficult. In the ab initio MD approach the process of bond–breaking is naturally handled by the quantum–chemical electronic structure calculation and this type of simulations can easily cope with the complexity of the system. In this work the results of a density functional theory simulation of the hydroxyl–water coadsorption on Rh(111) surface are presented, emphasizing the dynamics and the apparent hydroxyl transfer on the surface.

\[\text{For experimental and theoretical studies see for example Fisher and Sexton (1980), Völlkening et al. (1999), Bedürftig et al. (1999), Michaelides and Hu (2001a,b), Wilke et al. (2000)}\]
Chapter 2

Theoretical Background

2.1 Density Functional Theory

This section presents a brief overview of the density functional theory (DFT). It is not the intention of this section to give a complete introduction to DFT, but rather to cover some basic definitions, which are relevant to the discussions of the simulation results. For more detailed information the interested reader is referred to Koch and Holthausen (2000), Payne et al. (1992), Vanderbilt (1990), Laasonen et al. (1993), and Kresse and Furthmüller (1996a,b).

2.1.1 Schrödinger Equation and Born–Oppenheimer Approximation

Most quantum chemistry calculations deal with the approximate solution of the time–independent non–relativistic Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

(2.1)

where $\hat{H}$ is the Hamilton operator, $\Psi$ is a many–particle wave function, and $E$ is a numerical value for the energy of the system. The set of wave functions $\{\Psi_i, i = 1, \ldots\}$, which are the solutions of this equation, represent the set of possible quantum states of the system with the wave function $\Psi_i$ containing all information for the state $i$.

The problem of solving the Schrödinger equation can be simplified by separating the electronic and the nuclear degrees of freedom. It is assumed that the electrons are moving much faster compared to the heavier nuclei and can be considered as moving in the field of fixed nuclei. This is known as the
Theoretical Background

Born–Oppenheimer approximation and the potential exerted on the electrons due to the nuclei is called *external potential*.

However, even in the framework of the Born–Oppenheimer approximation the solution of the Schrödinger equation is problematic for all but the simplest systems. An alternative approach to the wave function–based method was put forward by Hohenberg and Kohn (1964) in a report to *Physical Review*, illustrating the importance of the electron density.

### 2.1.2 Hohenberg-Kohn Theorems

The wave function obtained from a solution of the Schrödinger equation is not an observable, but its square $|\Psi|^2$ is related to the electron density $\rho(r)$. Hohenberg and Kohn (1964) proved that the *ground state* electron density is not just another quantity of this state, but it can also serve to uniquely identify the full many–particle system. In their paper they showed that if two external potentials $V_{\text{ext}}$ and $V'_{\text{ext}}$ give rise to the same ground state electron density $\rho_0(r)$, then $V_{\text{ext}}$ and $V'_{\text{ext}}$ can only differ by a constant. As a consequence, reversing the previous statement, the external potential, which in turn fixes $\hat{H}$, can be seen as a *functional* of $\rho_0(r)$ to within a constant. This means that the ground state electron density determines (at least in principle) the Hamiltonian $\hat{H}$, which determines the set of solutions/states $\{\Psi_i\}$, which determines all properties of the system.

$$\rho(r) \rightarrow \hat{H} \rightarrow \{\Psi_i\} \rightarrow \text{all properties}$$

(2.2)

In other words, the *ground state* electron density $\rho_0(r)$ can serve as a basic variable for the description of the system. All properties of the system can be seen as functionals of the ground state electron density and this relation forms the basis of the density functional theory.

Hohenberg and Kohn (1964) also showed that the ground state energy functional $E_0[\rho(r)]$ has a minimum value when the input density is the true ground state density $\rho(r) = \rho_0(r)$. This relation presents a way to search for the ground state electron density and the corresponding ground state energy value through a minimization of the energy functional $E_0[\rho(r)]$. However, the set of trial densities must be restricted to the so–called $N$-representable densities, i.e. only those which can be associated with a wave function (recall that the density $\rho$ is related to the square of the wave function $|\Psi|^2$).
2.1.3 Kohn–Sham Equations

One of the difficulties with the Hohenberg–Kohn scheme is that although the energy $E_0$ can be formally written as a functional of the ground state electron density, there is no known explicit expression for this functional. In their work Kohn and Sham (1965) suggested a different approach to this problem by introducing an artificial set of orthonormal (Kohn–Sham) one–electron orbitals, requiring that the density generated from the summation of the squared KS orbitals equals the ground state density. The next step is the introduction of the so–called exchange–correlation energy functional, which accounts (at least formally) for the quantum–chemical interaction between the electrons. In this definition the problem of minimizing the ground state energy functional is equivalent to solving a set of Schrödinger–like one–electron equations, also known as Kohn–Sham equations.

The exchange–correlation functional as defined by Kohn and Sham remains unknown, however there exist several approximations, for example the BLYP (Becke, 1988, Lee et al., 1988), the PW91 (Perdew, 1991), or the PBE (Perdew et al., 1996) exchange–correlation density functionals. The PW91 is extensively used throughout this thesis.

It is important to note that these functionals are not exact and they only approximate the true exchange–correlation density functional. This means that the area of applicability of different functionals may vary and it must be tested on the examples of known systems. In this thesis the accuracy of the PW91 density functional has been verified on the example of water dimer and liquid water.

2.2 Molecular Dynamics

Molecular dynamics is one of the main computational technique used in this thesis. The current section discusses briefly the foundations of this simulation method. A more in–depth view is given by Allen and Tildesley (1987) and Frenkel and Smit (1996).

2.2.1 General Definitions

Molecular dynamics (MD) is a computational method for calculating the time–dependent behavior of molecular systems in terms of microscopic properties. At this level of theory the state of the system is defined by the positions of the atoms and their velocities (momenta) and is also known as microscopic state. The set of all possible microscopic states, i.e. all possible coordinates
Theoretical Background

Figure 2.1: Schematic representation of the phase space and a trajectory generated during an MD simulation.

and velocities of the atoms, is called phase space. Equation of motion is a mathematical relation between the positions and other external parameters (masses, forces) allowing us to predict the next state of the system from the current state. The MD simulation technique is an iterative procedure modeling the time evolution of the system, i.e. the trajectory in the phase space, by solving the equation of motion (see also Fig. 2.1).

In essence the molecular dynamics method is a direct application of the Born–Oppenheimer approximation. It is assumed that the (rapid) motion of the electrons can be averaged out. This permits us to describe the system by only using the nuclear variables. [Note: The Car–Parrinello ab initio molecular dynamics method is an exception. In this technique the electronic degrees of freedom are included in an extended equation of motion of the system.]

2.2.2 Macroscopic and Microscopic States

It is important to differentiate between the microscopic state and the thermodynamic state of the system. The molecular dynamics method is a computer simulation of the system at the microscopic level. Although related to the microscopic states, the thermodynamic state is a macroscopic characteristic defined in terms of a small number of parameters, such as number of particles, temperature, pressure, etc. The relation between the microscopic (instantaneous) values of some property and the corresponding macroscopic value is subject of the statistical mechanics. The macroscopic value of a certain property is the average of the microscopic values corresponding to all possible states in the phase space accounting for the probability of finding the system in that state. This average value is called ensemble average and is also the observable value of the property.
As the molecular dynamics simulation generates a trajectory in the phase space, it is obvious that it may not include all possible states of the system. Nevertheless, one can always compute the average value of a property using this subset of states in the phase space (Fig. 2.1). The central assumption behind the molecular dynamics technique is that for a sufficiently long simulation this trajectory average will approach the ensemble average. This is also known as ergodic hypothesis.

2.2.3 Equation of Motion – Classical Motion of the Atoms

As mentioned above, the molecular dynamics method simulates the atomic motion in a many–particle molecular system by solving the relevant equation of motion. Most commonly Newton’s equation of motion is used, which is a “classical” mechanics equation of motion. This means that no quantum effects are included. It also requires a model for the interactions between the atoms, i.e. an expression for the forces acting on the atoms. The difference between the classical and ab initio molecular dynamics methods lies in the model used for the interactions. In the self–consistent ab initio MD, which is used in this work, the forces are computed from a quantum–chemical model of the system: for each configuration on the trajectory path (i.e. for each microscopic state of the system), the quantum–chemical problem for the electronic structure is being solved to obtain the forces. Note that even in that case the atomic motion is still “classical”, however the interaction potential is not.

2.3 The VASP Program

The Vienna Ab Initio Simulation Package (VASP) is a DFT-based program developed for systems with periodic boundary conditions. It uses a plane wave basis set for expanding the Kohn–Sham wave functions, which is a natural choice in view of the periodicity in the system. In this work Vanderbilt–type ultrasoft pseudopotentials (Vanderbilt, 1990, Kresse and Hafner, 1994) and the Perdew–Wang 91 (PW91) exchange–correlation density functional (Perdew, 1991) are used. The pseudopotentials, which are used for the description of the electron–ion interactions, and the plane wave basis set in relation to their application to study systems with periodic boundary conditions are extensively discussed by Payne et al. (1992), Vanderbilt (1990), and Laasonen et al. (1993). An introduction to the algorithms implemented in VASP is given by Kresse and Furthmüller (1996a,b).

The internal structure of the VASP program includes two main loops: (i) inner electronic loop and (ii) outer ionic loop. The inner loop is essentially
an implementation of a self–consistent algorithm for solving the Kohn–Sham equations. The total energy and the forces are also evaluated. The outer loop is concerned with the ionic movement and supports geometry optimization and molecular dynamics algorithms.

An essential difference of the molecular dynamics method implemented in VASP with the Car–Parrinello MD (Car and Parrinello, 1985) is that the electronic wave functions are not included in the equations of motion of the system. The electronic ground-state is computed self–consistently at each MD step.

2.3.1 Accuracy Considerations

A number of input parameters of the VASP program such as the size of the plane wave basis set, determined by the cutoff, the size of the unit cell, and the number of $k$-points sampling the so–called Brillouin zone, are of importance for the accuracy of the calculations. Most commonly one is interested in calculating the energy differences between particular systems/configurations. Provided that the same set of parameters is used, the relative differences in the total energies are not that sensitive compared to the absolute values.

In this work, whenever possible, the same set of parameters have been used for the evaluation of energy differences. One issue directly related to the estimated values for the adsorption (binding) energy, defined as the difference between the sum of the energies of the “clean” surface and the isolated molecule and the energy of a system consisting of water molecules adsorbed on the surface, is the energy of the reference water molecule in the “gas phase” (in this case in a large supercell). For some of the systems the reference water molecule was computed using a different (larger) unit cell compared to the unit cell used for the adsorption on the surface. This was done in order to minimize the interaction between the neighboring periodic images of the supercell. Another important effect is also the dependence of the total energy of the water molecule in vacuum on the cutoff for the plane wave basis set. This is due to the existence of large areas in the unit cell with presumably zero electron density - a situation which is poorly described using plane waves.

In Chapter 4 of this thesis several accuracy tests are presented using simple systems containing one water molecule and a water dimer in a cubic box. These results provide information on the proper computational setup for estimating the adsorption energies and for the MD simulations. Chapter 8 is also concerned with the accuracy of the molecular dynamics simulations comparing configurations obtained in the course of an MD run with more accurate static calculations.
Chapter 3

Interpretation of the Results

The VASP package itself does not provide ready-to-use tools for detailed electronic structure analysis or statistical analysis of the MD simulation results. However, the output generated by the program contains sufficient information for evaluating the properties of the system using external programs. The present Chapter provides a brief introduction of the properties considered in this thesis. A more detailed overview to the electronic properties of solids is given by Hoffmann (1988). The interpretation of MD simulation results in terms of structural and dynamical properties is discussed extensively by Allen and Tildesley (1987).

3.1 Electronic Properties

The density functional theory calculations are total energy calculations, i.e. one can obtain the total energy $E_0$ of the ground state of the system. As mentioned in Chapter 2, the Kohn-Sham (KS) orbitals were solely introduced as a practical approach to obtaining the electronic energy. Although the exact wave function is not known, it has been argued that the KS wave functions can also be used to describe the electronic properties of the molecules in a manner similar to the traditional molecular orbital approach (Koch and Holthausen, 2000, Baerends and Gritsenko, 1997, Politzer and Abbu-Awwad, 1998, Stowasser and Hoffmann, 1999, Kar et al., 2000, 2001). In this thesis the KS eigenfunctions have been used to analyze the electronic structure of the systems in terms of local density of states and bonding–antibonding properties in terms of crystal orbital overlap population (COOP) analysis.
3.1.1 Local (Projected) Density of States

The density of states is essentially the solid state equivalent of the molecular orbital (MO) energy level diagram. The so-called local density of states provides information on the contribution of local (atomic) orbitals to the relevant electron states, i.e. crystal/molecular orbitals. In the case of a water molecule adsorbed on a metal surface, which is the subject of this work, the local density of states can be used to identify the MO energy levels of the molecule among all electron states of the system. Naturally, an electron state is associated with a water MO only if at least one atomic orbital of the oxygen atom contributes to this state.

The decomposition of the delocalized one-electron Kohn-Sham wave functions, which are obtained from a self-consistent solution of the KS equations using a plane wave basis set, can be evaluated provided a set of projectors is chosen. In the implementation of VASP projection parameters (radii) are used to construct spherical harmonics-type projectors, which (through an appropriate choice of the radial component) are non-zero within spheres around the ion and vanish outside. The procedure, however, leaves some ambiguity in the choice of the radii of the spheres. Variations in the radii will affect not only the projection $C_{ln} = \langle Y_l | \phi_n \rangle$ of the wave function $\phi_n$ onto the projector $Y_l$, where $l$ is a composite index for the angular quantum number, but also the overlap integral between two projector–wave functions. Both the projections and the overlap integrals of the projectors play an essential role in the partitioning of the electrons of a molecule among the atoms and the bonds, as for example in the scheme proposed by Mulliken (1955). In particular this means that results for partial charges on atoms, and bond order estimations will depend on the choice of the radii. In spite of these limitations, this projection scheme can be applied for a qualitative determination of the local $s$-, $p$-, or $d$-character of the delocalized electron states and their eigenvalues (energies). In the present work the local (projected) density of states (LDOS) at a given site was calculated as the $|C_{ln}|^2$-weighted total density of states (plus augmentation part related to the pseudopotentials). In that scheme the total number of electrons is equal to the total density of states integrated up to the Fermi level multiplied by a factor of 2.

3.1.2 COOP

This thesis also makes use of a bonding–antibonding indicator of the interaction between two atoms $A$ and $B$ defined as the $(C_{Aln}^{*} C_{Bln} + C_{Aln} C_{Bln}^{*})^{-1}$-weighted DOS. This definition is applicable in the case when exactly one or-
bital on either of the two atoms is considered. The two projectors \( Y_{l,A} \) and \( Y_{l,B} \) are centered on \( A \) and \( B \), respectively. The above bonding–antibonding indicator is (qualitatively) equivalent to the crystal orbital overlap population (COOP) as defined in Hoffmann (1988), taking into account that the projections are complex numbers. The resulting curve represents the phase coherency between the projections and is positive in the bonding, negative in the antibonding, and zero in the nonbonding regions. The original definition of COOP in Hoffmann (1988) accounts also for the overlap integral of the atomic orbitals involved in the formation of the bond. In the case considered here - only two atomic orbitals, respectively two projectors \( Y_{l,A} \) and \( Y_{l,B} \) - the overlap integral is simply a multiplication factor. Since this work deals with a qualitative description of the bond between two atoms, the actual amplitude of the overlap is irrelevant, as long as it is positive. [Note that the projector–operators \( Y_{l,A} \) and \( Y_{l,B} \) can always be chosen, respectively oriented, in such a way, that the overlap is positive.] For this reason in the present work the above bonding–antibonding indicator will also be referred to as COOP.

3.1.3 Work Function

In the Kohn–Sham approach, the KS eigenvalues have no straightforward physical meaning. However, the eigenvalue of the highest occupied KS state, respectively the Fermi level of the system relative to the potential in the vacuum, equals the negative of the ionization energy, respectively the work function. Clearly, the exact work function is obtained only if the exact exchange–correlation density functional is used. Although in this work an approximate exchange–correlation functional is used, the estimated differences in the work function due to the changes in the surface dipole moment should still be reasonably accurate and informative (at least in a qualitative sense).

3.2 Structural and Dynamical Properties

3.2.1 Distribution Functions

The microscopic (i.e. atomic/molecular) structure of liquids and solids is often characterized in terms of distribution functions. In this thesis three types of distribution functions have been used: radial (pair) distribution function, distribution function along a line, and orientational distribution function. The radial distribution function (RDF) is the probability density of finding a pair of atoms of a given type at a given distance, relative to the probability density for a random distribution. The distribution function along a line (normally a
unit cell vector) gives the probability density of finding an atom of a certain type in a plane at a given height along the line. The orientational distribution function in this thesis is defined as the probability density of finding a given vector at an angle with a given axis. The vector of interest can be related to the connecting line between two atoms, for example the OH bond orientational distribution function. It can also be some other vector related to the geometry of the molecule, for example the dipole moment of the water molecule, defined as the bisector of the HOH angle.

3.2.2 Velocity Autocorrelation Function and Vibrational Power Spectrum

The (non-normalized) velocity autocorrelation function \( C_{vv}(t) = \langle v(t) \cdot v(0) \rangle \) measures the correlation between the velocities of a given particle at a time \( t \) and at some starting time \( t_s = 0 \). The Fourier transformed velocity autocorrelation function, also called vibrational power spectrum, is proportional to the density of the vibrational modes. In this thesis in some occasions the raw velocity autocorrelation function data is filtered using a Blackman window in order to smooth the spectrum. More information on this topic can be found in Allen and Tildesley (1987).

3.2.3 Mean–Square Displacement and Diffusion Coefficient

The mean–square displacement \( \text{MSD}(t) = \langle |r(t) - r(0)|^2 \rangle \) is a measure for the displacement of certain particle from its original location. A macroscopic characteristic for this process is the diffusion coefficient. The diffusion coefficient \( D \) can be computed using the Green–Kubo relation by integrating the velocity autocorrelation function

\[
D = \frac{1}{3} \int_0^\infty \langle v(t) \cdot v(0) \rangle dt \quad (3.1)
\]

or using the Einstein relation from the MSD

\[
2D = \frac{1}{3} \lim_{t \to \infty} \frac{d\langle |r(t) - r(0)|^2 \rangle}{dt} \quad (3.2)
\]

Strictly speaking the two relations are equivalent. In practice, however, the estimated values for \( D \) using equations 3.1 or 3.2 can deviate primarily due to short MD simulation times. The velocity autocorrelation function used in the Green-Kubo relation can have a long–time tail with a significant contribution to the integral value, while the Einstein relation is only valid at long times, when the MSD depends linearly on the time \( t \).
Chapter 4

Water Molecule and Water Dimer

As mentioned in Chapter 2, a number of input parameters of the VASP program are of importance for the accuracy of the calculations. In this Chapter simulations aimed at obtaining a satisfactory set of these parameters are presented using a single water molecule and a water dimer in a cubic box. The electronic structure of water molecule in the framework of the Kohn–Sham formalism is also examined in comparison with previous quantum–chemical calculations.

4.1 Water Molecule: Computational Parameters

To estimate the proper computational setup, a series of calculations was performed considering the dependence of the total energy and the optimized geometry of a water molecule on the dimensions of the (super)cell, the number of \( k \)-points, and the quality of the plane wave (PW) basis set. First the unit cell size was varied in the range of 8.0 to 15.5 Å while keeping the energy cutoff for the PW basis set constant at 500 eV. Only the \( \Gamma \)-point was used for the integration of the band energies. In this range of box sizes there was only a small (<0.01 eV) increase in the computed total energy. The final geometries of the molecule were practically the same with estimated differences in the O–H bond length and H–O–H bond angle being less than 0.002 Å and 0.3°, respectively. The convergence with respect to the number of \( k \)-points in the Brillouin zone was also tested using the same cutoff and a unit cell of side length \( L = 9.861 \) Å. [This unit cell size is also used for the simulation...
of bulk liquid water (see Chapter 5) and will be referred to as the bulk–MD unit cell. Switching from the Γ-point–only to a $3 \times 3 \times 3$ Monkhorst-Pack-type mesh (Monkhorst and Pack, 1976), corresponding to 8 irreducible $k$-points, resulted in a difference in the computed total energy of less than $1 \times 10^{-5}$ eV. The basis set dependence was evaluated by varying the energy cutoff $E_{\text{cut}}$ from 300 to 600 eV. The total energy converged to within 0.01 eV for $E_{\text{cut}}$ greater than 400 eV with no significant changes in the optimized geometry of the molecule for cutoffs above 325 eV. Additional comparative results between different density functionals and employing different basis sets are given in Appendix A.

In summary, the bulk–MD unit cell size of 9.861 Å, a Γ-point-only sampling of the Brillouin zone, and a cutoff of 400 eV are sufficient for an accurate description of a water molecule with no significant changes in the geometry for basis set cutoffs higher than 325 eV. The estimated O–H bond length of 0.973 Å and H–O–H angle of 104.7° are comparable to the results obtained by Sprik et al. (1996) using the BLYP functional and are in a reasonable agreement with the experimental values of 0.958 Å and 104.5°, respectively (Lide, 1993).

### 4.2 Water Molecule: Electronic Structure

This section discusses the Kohn–Sham wave functions and the applicability of the projection scheme introduced in Chapter 3 for single water molecule in a supercell. The symmetry and the bonding-antibonding properties of the Kohn–Sham eigenfunctions are examined in comparison with previous computational results.

The water molecule has $C_{2v}$ point group symmetry and it is convenient to consider the (canonical) molecular orbitals in terms of the symmetry-adapted linear combination of the atomic orbitals [only the occupied molecular orbitals are given adopting the symmetry notation for the MOs, see for example Doering and Madey (1982)]:

1. $1b_1 : 2p_z, O$
2. $3a_1 : c_6(2s_O) + c_7(2p_{x,O}) + c_8(1s_{H_A} + 1s_{H_B})$
3. $1b_2 : c_4(2p_y,O) + c_5(1s_{H_A} - 1s_{H_B})$
4. $2a_1 : c_1(2s_O) + c_2(2p_{x,O}) + c_3(1s_{H_A} + 1s_{H_B})$

In this work the origin of the Cartesian coordinate system is at the oxygen atom with the $x$-axis bisecting the HOH angle and the $z$-axis perpendicular to the plane of the molecule (see also Fig. 4.1). The conventional setting for
4.2. Water Molecule: Electronic Structure

Figure 4.1: Spatial distribution of the electron density corresponding to the Kohn–Sham molecular orbitals of water as computed with VASP (“top” and “side” views). The isosurfaces correspond to an electron density of $2^{-7} \times 10^{-1} \, \text{Å}^{-3}$.

As can be seen from Fig. 4.1 and 4.2, the spatial distribution of the electron density and the projections of the Kohn–Sham wave functions are in very good agreement with the expectations based on the symmetry group of the system and previous (Hartree-Fock) calculations (Neumann and Moskowitz,
Figure 4.2: Projections of the Kohn–Sham wave functions of a water molecule onto the oxygen s- and p-orbitals. The corresponding s-s and p-s COOP curves are given in the two panels on the right.

1968, Aung et al., 1968, Dunning, Jr. et al., 1972, Rosenberg and Shavitt, 1975, Thiel and Madey, 1987). The Kohn–Sham eigenstates possess the proper symmetry and display the correct ordering in eigenenergy. Only the highest–energy orbital, denoted as '(2b$_2$)', which is unoccupied and expected to have B2 symmetry, appears to have A1 symmetry (Fig. 4.2). However, as seen from the s-s and p-s COOP curves this orbital possesses the expected antibonding characteristics. The projections onto atomic orbitals other than the s- and p-orbitals of the oxygen and the s-orbitals of the hydrogens are negligible, as expected.

Note that the phase difference between the oxygen s- and the hydrogen s-projections (see the s-s COOP curve in Fig. 4.2), corresponding to the 3a$_1$ molecular orbital, appears antibonding, whereas the p-s phase coherency shows bonding character. This is in agreement with previous Hartree-Fock calculations [compare for example with the molecular orbital coefficients from Neu-mann and Moskowitz (1968), and Aung et al. (1968)] and is related to the partial nonbonding character of this MO. The 1b$_1$ orbital, which is primarily composed of the oxygen p$_z$-orbital, shows no indication of bonding or antibonding properties. The corresponding Kohn–Sham eigenfunction has no projections onto the s-spherical harmonics centered at either of the hydrogens (not shown), and hence this state is identified as the lone electron pair of the oxygen atom.

As seen in Fig. 4.2, the 2a$_1$ orbital is characterized by positive s-s and p-s COOP, while for the 3a$_1$, the s-s COOP is negative and the p-s is positive.
4.3 Water Dimer

For the $1b_2$ MO, the s-s COOP is zero, as expected, and there is only a p-s contribution to the bonding. Thus, the separate s-s and p-s COOP curves present a possibility to distinguish between the molecular orbitals of the water molecule in a qualitative way and can be used for the identification of the MO levels of water in a local density of states (LDOS) plot. These properties will be used in the chapters discussing the electronic structure of water adsorbed on metal surfaces.

In the chapters dealing with simulations of water adsorbed on the metal surfaces the importance of the electrostatic interactions between the molecules is discussed. It is obvious that this conclusions can only be drawn if the computed dipole moment of water agrees with the experiment. The computed dipole moment of 1.85 D using either a cubic or a hexagonal supercell with applied correction for the dipole–dipole interactions between the neighboring images of the supercell is in excellent agreement with the experimental value of 1.854 D (Lide, 1993) and the BLYP result of 1.87 D (Silvestrelli and Parrinello, 1999b).

4.3 Water Dimer

Except for the cutoff for the plane wave basis set which was varied, the simulations of the water dimer were performed using the computational settings estimated in section 4.1. The configuration under study corresponds to the trans-configuration with a plane of symmetry (see Fig. 4.3), which has been determined experimentally by Dyke et al. (1977).

In order to obtain the water dimer equilibrium geometry and dissociation energy, two series of calculations were carried out using the “accurate” cutoff of 400 eV and a reduced cutoff of 325 eV. The dissociation energy of the dimer (Table 4.1) was computed as the difference in the sum of the total energies of two single water molecules and the total energy of the dimer in the same
Table 4.1: Calculated O—O distance and binding energy of water dimer compared to the results using CCSD(T) (Klopper et al., 2000), BLYP (Sprik et al., 1996) and experiment (Curtiss et al., 1979, Dyke et al., 1977).

<table>
<thead>
<tr>
<th>$E_{cut}$/eV</th>
<th>$r$(O—O)/Å</th>
<th>$E_{dimer}$/kJ·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.88</td>
<td>2.88</td>
<td>23.5</td>
</tr>
<tr>
<td>325 eV</td>
<td>2.89</td>
<td>23.9</td>
</tr>
<tr>
<td>400 eV</td>
<td>2.91</td>
<td>21.0</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>2.95</td>
<td>18</td>
</tr>
<tr>
<td>BLYP</td>
<td>2.98</td>
<td>22</td>
</tr>
<tr>
<td>Experiment</td>
<td>2.98</td>
<td>22</td>
</tr>
</tbody>
</table>

unit cell using the same cutoff. The energies were corrected for dipole–dipole interactions between periodic images of the supercell as implemented in VASP. The O—O distance (Table 4.1) in the water dimer is in satisfactory agreement with estimated values based on the experimental data from Dyke et al. (1977) or the BLYP calculation of Sprik et al. (1996), and compares well to high-level ab initio coupled-cluster results of Klopper et al. (2000). Based on these results it is concluded that a cutoff of 325 eV is sufficient to obtain reasonable agreement between the equilibrium properties of water dimer predicted in this work and other theoretical and experimental results.

4.4 Summary and Conclusions

The PW91 exchange–correlation density functional in combination with the used pseudopotentials gives a reasonable description of single water molecule and water dimer using a cutoff for the plane wave basis set as low as 325 eV. Therefore, except for the MD of liquid water, the geometry optimization and the molecular dynamics simulations presented in the following chapters were performed using this setting. For the estimations of the enthalpy of vaporization of liquid water (Chapter 5) and the adsorption energies on the Rh(111) and Pt(111) surfaces (Chapter 7) the more accurate 400 eV cutoff has been used.

The size of the bulk–MD unit cell is large enough to avoid significant interactions between the neighboring periodic images. For this unit cell size only the Γ-point is sufficient for an acceptable description of the system. The computed gas–phase dipole moment of water molecule of 1.85 D is in excellent agreement with the experimental value and the BLYP results.
Chapter 5

Liquid Water

This Chapter deals with \textit{ab initio} molecular dynamics simulation of liquid water. The main goal of the simulation is to evaluate the accuracy of the Perdew-Wang 91 (PW91) exchange-correlation functional and the employed pseudopotential scheme for liquid water in comparison with classical MD, previous \textit{ab initio} MD, and experiment. Rather accurate parameters (i.e. cutoff for the plane wave basis set) have been used in order to minimize the effects of the computational setup on the results for the enthalpy of vaporization.

5.1 Computational Details

The \textit{ab initio} MD simulation of liquid water was carried out using a model of 32 molecules placed in a cubic box of size 9.861 Å, corresponding to the density $\rho = 0.998 \text{ g cm}^{-3}$ at ambient conditions. The cutoff for the plane waves was set to 400 eV and only the $\Gamma$-point has been used for the integration of the band energies. The time step was set to 0.5 fs. The starting configuration was obtained from an equilibrated classical MD simulation performed with the program MOLDY (Refson, 2000). The system was equilibrated for 1 ps followed by a statistical data collection for 3.5 ps. The average temperature during the microcanonical \textit{NVE} ensemble simulation was 307 K. For comparison, additional classical MD simulations were performed for systems containing 32, 64 and 128 water molecules using the SPC/E potential from Berendsen et al. (1987).\footnote{Dr. Christoph Hartnig performed the classical simulations with the SPC/E interaction potential using an MD simulation code provided in large parts by dr. E. Spohr.}

1Dr. Christoph Hartnig performed the classical simulations with the SPC/E interaction potential using an MD simulation code provided in large parts by dr. E. Spohr.
5.2 Results and Discussions

5.2.1 Enthalpy of Vaporization.

A thermodynamic property which is relatively easy to estimate from this simulation is the enthalpy of vaporization. The enthalpy $H$ of a thermodynamic system is given by the expression $H = U + pV$, where $U$ is the internal energy of the system and $p$ and $V$ are the pressure and the volume, respectively. The evaluation of $U$ from an MD run is straightforward by averaging the total energy of the system. The internal energy of the model liquid state (32 molecules in a box) was calculated in this way. Considering a system of classical particles, the internal energy $U$ can be expressed as a sum of the potential energy of the optimized (equilibrium) geometry and the averaged kinetic energy of the thermal movement $E_k$. Thus the averaged kinetic energy of a molecule at a temperature $T$ is $E_k = NkT/2$ and the gas occupies a molar volume $V_m$ as an ideal gas. For the purpose of evaluating the enthalpy of vaporization, the gas–phase water was considered as a gas of noninteracting molecules with $N = 9$ degrees of freedom (including translations). Following this scheme and taking the pressure $p = 1$ atm, the computed enthalpy of vaporization of liquid water is 39 kJ·mol$^{-1}$ (307 K), in satisfactory agreement with the experimental
5.2. Results and Discussions

Figure 5.2: Computed O—H radial distribution function (solid line) compared with the experimental data from Soper (2000) (dotted line) and Soper et al. (1997) (dashed line)

value of 43.9 kJ·mol$^{-1}$ (298 K) (Lide, 1993).

5.2.2 Radial Distribution Functions.

The radial distribution functions (RDF) of the three atom pairs, i.e. O—O, O—H, and H—H, were evaluated in comparison with the results from neutron diffraction data (Fig. 5.1, 5.2, and 5.3). The determination of the O—O pair distribution function based on neutron diffraction has been subject to a number of revisions due to experimental uncertainties, as discussed for example by Soper (2000). Most noticeable is the fact that the position and the shape of the first peak of the computed O—O RDF at 2.7 Å are in good agreement with the most recent experimental result, which displays a peak at around 2.75 Å. The pair radial distribution functions determined in previous $ab$ initio studies using BLYP and HCTH/120 density functionals were found [see Sprik et al. (1996), Boese et al. (2000)] to compare very well with the older experimental data from Soper et al. (1997), which are also shown on Fig. 5.1, 5.2, and 5.3. In an even more recent work using Car–Parrinello MD and the BLYP exchange–correlation density functional Izvekov and Voth (2002) reported also very good agreement between the computed and the most recent experimental results. It should be noted that the molecular structure obtained from the current
Liquid Water

Figure 5.3: Computed H—H radial distribution function (solid line) compared with the experimental data from Soper (2000) (dotted line) and Soper et al. (1997) (dashed line)

Simulation is more ordered compared to the experiment, resulting in a lower value of the first minimum in the RDF. The computed RDFs are in fact quite sensitive to the size of the unit cell. Silvestrelli and Parrinello (1999a) reported a significant improvement in the RDFs compared to experiment when the size of the model was increased from 32 to 64 deuterated water molecules. The shape of the O—H distribution function is also influenced by quantum effects of the hydrogen atoms, which are not taken into account in the present model [for a quantum mechanical study and the extent of quantum effects on the RDFs, see for example Kuharski and Rossky (1985)]. In conclusion, the computed radial distribution functions are in a reasonable agreement with the experiment and are not noticeably inferior to previous BLYP results using a similar setup.

5.2.3 Self–Diffusion Coefficient.

An important dynamic characteristic of a liquid is the self–diffusion coefficient $D$. As the oxygen atoms are much heavier than the hydrogen atoms, in the present work the motion of the oxygen atom is considered representative for the motion of the center of mass of the molecule. The self–diffusion coefficient can be computed using the mean–square displacement (MSD) or the velocity
autocorrelation function (see Chapter 3). The estimated values for the self-
diffusion coefficient are $0.8 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1}$ using the MSD of the oxygen atoms
(Fig. 5.4, $N=3$ directional degrees of freedom) and $1.2 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1}$ integrating
the oxygen velocity autocorrelation function. The difference in the results for
$D$ using the two definitions is due to the relatively short simulation time. It
is however more important to notice that the value of $D$ and the shape of the
MSD function implies a liquid–like behavior. Compared with the experimental
result of $2.30 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1}$ from Mills (1973) the computed value confirms the
reduced mobility of the molecules, which is related to the small size of the
unit cell. The value obtained using the BLYP functional for a system of
the same size, but using 32 deuterated water molecules, was reported $1.0 \times
10^{-9} \text{m}^2 \cdot \text{s}^{-1}$ by Silvestrelli and Parrinello (1999a) and $1.3 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1}$ by
Sprik et al. (1996). The influence of the size of the unit cell was demonstrated
by Silvestrelli and Parrinello (1999a), who reported an increase of $D$ by a factor
of around 2.5 for a system of 64 deuterated water molecules compared to 32.
This result also agrees with the classical MD simulations for models containing
32, 64 and 128 water molecules using the SPC/E potential. The computed self–
diffusion coefficients in this case are 1.8, 2.7 and $2.7 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1}$, respectively.

Assuming transferability of the results concerning the size of the system,
the estimated value obtained using PW91 is not only comparable to the
BLYP result, but both density functionals are in reasonable agreement
with experiment. Boese et al. (2000) computed a self–diffusion coefficient of
$2.7 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1}$ for a system of 32 molecules using the HCTH/120 density
functional. This result therefore appears to point to a mobility of the water
molecules, which is too high compared to experiment.
5.2.4 Vibrational Power Spectrum.

The vibrational properties of the system were computed from the Fourier transformation of the hydrogen velocity autocorrelation function (Fig. 5.5). The broad peak at 2900-3800 cm\(^{-1}\) corresponds to the intramolecular stretching, the bending vibrations are recognized at around 1600 cm\(^{-1}\). The broad peak in the region 400-1000 cm\(^{-1}\) represents intermolecular modes. These results agree well with the experimental infrared and Raman spectral data from Draegert et al. (1966), Schiffer and Horning (1968), and Walrafen (1967).

5.3 Summary and Conclusions

Accounting for the limitations of the model, all properties of liquid water – enthalpy of vaporization, radial distribution functions, mean–square displacement, self–diffusion, and vibrational power spectrum – are in reasonable agreement with the experimental data and previous \textit{ab initio} MD results. Therefore it is concluded that the PW91 exchange–correlation density functional in combination with the employed pseudopotentials can be used successfully for the description of liquid water.
Chapter 6

Water/Vapor Interface

This Chapter presents the results of the first *ab initio* MD simulation modeling the liquid water/vapor interface. The orientation of the molecules at the interface, the mean-square displacement and self-diffusion of water, and the vibrational characteristics of the system are considered in comparison with classical MD simulations and experiment.

6.1 Computational Details

The model for the water/vapor interface is based on a system containing a thin water slab. The model was constructed by taking a configuration from the equilibrated *ab initio* simulation of bulk water (Chapter 5) and placing it in a rectangular box obtained by doubling the original size in the z-direction. The resulting unit cell size is $9.861 \times 9.861 \times 19.723$ Å and contains 32 water molecules in a slab initially of a thickness of 9.861 Å and a vacuum region of the same size. For this simulation the accuracy of the calculation was reduced in favor of speed by lowering the energy cutoff for the plane wave basis set from 400 eV used in the simulation of bulk liquid water to 325 eV. As discussed in Chapter 4, the accuracy of the calculation should still be reasonable.

The equilibration of the system was performed in two stages: (i) an MD simulation run at 335 K for 1.4 ps, followed by (ii) a simulation at 300 K with Nosé thermostat for 1.5 ps. During these runs the water molecules, and particularly those at the surface, rearranged and the thickness of the water layer expanded slightly to about 10 Å. The statistical data collection was then performed for a period of 4 ps. The time step was set to 0.5 fs.

For comparison, additional classical MD simulations were performed for
Figure 6.1: Density distribution functions along the z axis perpendicular to the surface. The solid and dotted line correspond to the oxygen and the hydrogen distribution functions from a 4 ps ab initio MD simulation. The dashed line (zero shifted to 1) corresponds to the oxygen distribution function from a 250 ps classical MD simulation. All distribution functions are normalized to the bulk density. The preferred orientation of the water dipoles as concluded from the ab initio MD is shown on the right.

systems containing 32 and 128 water molecules using the SPC/E potential.¹

6.2 Results and Discussions

6.2.1 Density Profile Along the Surface Normal.

The limited size of the model does not allow a “real” bulk region in the middle of the slab. Therefore it is not possible to produce realistic data for the water density distribution along the surface normal (Fig. 6.1). The result is also strongly influenced by the reduced mobility of the molecules, as discussed below in connection to the MSD and self–diffusion. It should be pointed out however, that the ab initio oxygen distribution along the z axis perpendicular to the surface, agrees qualitatively with the result from a much longer classical MD simulation. The classical MD result, obtained using the same number of molecules, clearly shows the existence of layering in the model with two outer layers L1 and L3 and one inner layer L2. The observed maxima in the density profile correspond to the maxima obtained from the ab initio simulation. The presence of “gaps” in the ab initio oxygen distribution function is due to the

¹Dr. Christoph Hartnig performed the classical simulations with the SPC/E interaction potential using an MD simulation code provided in large parts by dr. E. Spohr.
6.2. Results and Discussions

Figure 6.2: Mean–square displacement (MSD) of the oxygen atoms normalized to the number of directional degrees of freedom $N$. The solid line represents the three dimensional ($N=3$) MSD of the oxygens in bulk water; dashed and dotted lines correspond to the two dimensional $xy$ ($N=2$) MSD and the one dimensional $z$ ($N=1$) MSD of the oxygens in water slab, respectively.

limited simulation time. However, the hydrogen distribution function indicates that the water molecules still interact via hydrogen bonds. It should be mentioned here that a classical molecular dynamics simulation of 4 ps, which is the length of the *ab initio* simulation, produces a similar density profile along the surface normal as the *ab initio* simulation.

6.2.2 Mean–Square Displacement and Self–Diffusion.

As seen from Fig. 6.2 presenting the computed $xy$ and $z$ components of the MSD of the oxygen atoms, only “cage movement” effects are observed, resulting in the small slope of the curve at longer times. This picture contradicts the conclusions in earlier (classical) MD simulations of Townsend and Rice (1991) and Taylor et al. (1996), who reported an increase of the self–diffusion coefficient in the surface transition zone compared to the bulk region. These simulations were performed using much larger systems containing 350 or more water molecules. The difference in the transport properties is a result of the combined effect of the small size of the MD unit cell in the current simulation and the number of molecules. Under these conditions the mobility of the molecules is highly reduced due to a space confinement and the imposed translational symmetry of the unit cell. This effect is much stronger for the two dimensional slab system compared to the three dimensional simulation of 32 bulk water molecules as the number of translational degrees of freedom is
effectively reduced.

6.2.3 Orientational Distribution of the Molecules.

It is generally accepted in the literature that the coupling between translational and rotational motions of water molecules in liquid water is weak. With this assumption, the orientational distribution functions of the molecules should not be affected by the limitations of the model to such an extent as the transport properties. To test the validity of this presumption, the results of classical MD simulations of water slabs containing 32 and 128 molecules were compared. Even for a system of 32 molecules and simulation time of 4 ps, the result qualitatively reproduces the molecular orientation computed for a system of 128 molecules with 5 ns simulation time, with an uncertainty in the maximum of the angular distribution of around 10°. This suggests that in spite of the relatively poor density profile obtained from a 4 ps simulation with 32 water molecules, the qualitative conclusions regarding the dipole orientation should still be valid.

To describe the orientation of the molecules one can define an angular variable $\theta$ between the dipole moment of a water molecule and the $z$ axis of the unit cell, which is also the axis perpendicular to the surface (Fig. 6.1). An angle of $\theta=90^\circ$ corresponds to an orientation of the dipole parallel to the plane of the surface. The water layer along the $z$ axis was divided in three (imaginary) sublayers each of a thickness of around 3.5 Å. The choice of the
positions of the dividing planes corresponds to the sublayers as observed from
the density profiles of both the classical and the \textit{ab initio} MD simulations. As
mentioned before, the middle sublayer is referred to as L2, and the two outer
sublayers as L1 and L3. L1 is the outer layer from the negative side of \( z \), and
L3 that from the positive side. In this definition the dipole moment of the
molecule points directly towards the vacuum region if \( \theta \) is 180\(^\circ\) for sublayer L1
and 0\(^\circ\) for sublayer L3. As can be seen from Fig. 6.3a, the results for L1 and
L3 are quite symmetric and the preferred orientation of the dipoles is towards
the “bulk” region. [Note: The probability density plot has been normalized to
unity; in this representation a random orientational distribution corresponds
to the line at \( y = 1 \).] The maximum probability is at an angle of 120\(^\circ\) with
the outward surface normal, which qualitatively agrees with the experimental
second–harmonic generation results from Goh et al. (1988). The current result
also agrees with most of the “classical” MD simulations studies (Matsumoto
and Kataoka, 1988, Townsend and Rice, 1991, Lie et al., 1993, Taylor et al.,
1996), although two studies reported a water dipole orientation parallel to the
surface (Wilson et al., 1987, Yang et al., 1994).

The intramolecular O–H bond orientation can be described by an angle
variable \( \phi \) between the bond and the surface normal in analogy with the
dipole moment orientation angle \( \theta \). The O–H orientational distribution func-
tion (Fig. 6.3b) indicates that about 20\% of the bonds point towards the bulk
at an angle of 160–180\(^\circ\) with the outward surface normal. Compared to the
result for the dipole moment, the O–H orientational distribution is not that
symmetric. It should be noted that the used normalization has the effect of
over-accentuating the deviations from the homogeneous distribution at an-
gles of around 0\(^\circ\) and 180\(^\circ\). This results in a much higher peak in the curve
for L1 around \( \phi = 0\(^\circ\) \), which in practice corresponds to a fraction of the O–
H bonds. The corresponding peak in the L3-curve is slightly shifted and is
around \( \phi = 160\(^\circ\) \).

\textbf{6.2.4 Vibrational Power Spectrum.}

As in the case of bulk liquid water, the vibrational power spectrum was
computed using the hydrogen velocity autocorrelation function (Fig. 6.4).
Compared to the bulk water, the peak at 3750–3800 cm\(^{-1}\) is strongly enhanced
due to free O–H groups at the surface. This feature is indeed expected on the
basis of the preferred orientation illustrated in Fig. 6.1 and is in agreement
with the experimentally observed peak at 3690 cm\(^{-1}\) by Du et al. (1993).
6.3 Summary and Conclusions

The MD simulation showed that the preferred orientation of the water molecules at the water/vapor interface is with the water dipole moment oriented towards the bulk liquid phase at an angle of $120^\circ$ with the outward surface normal, which is in agreement with the experimental data. The results from the two surfaces of the water slab lead to the same conclusion, suggesting that the MD simulation is long enough and the unit cell size and the size of the water slab itself are sufficient to avoid significant interactions between the molecules from the two surfaces and through the vacuum layer.

At the same time the simulation reveals some of the limitations of the model, particularly the reduced mobility of the molecules. This is an effect directly related to the size of the unit cell. Unfortunately this is unavoidable as the use of a larger unit cell containing more water molecules will result in a computationally very expensive simulation. However, the symmetry in the orientation of the water molecules dipole moments confirms the assumption that the reorientation of the molecules at the surface is affected to a much lesser degree compared to the transport properties. Together with the good performance of the PW91 exchange–correlation functional and the employed pseudopotentials for bulk liquid water this suggests that MD simulations of water adsorbed on metal surface could result in reasonable predictions of the orientation of the water molecules at the metal surface even if a relatively small unit cell is used.
Chapter 7

Adsorption of Water on Pt(111) and Rh(111) Surfaces

This Chapter deals with the properties of water molecules adsorbed on Rh(111) and Pt(111) at surface coverages of 1/12, 1/3, and 2/3 (bilayer). Two models for the bilayer were considered: in the first the molecules are arranged according to the original model of Doering and Madey, whereas in the second the water adlayer is flipped “upside-down”. This is of some interest to electrochemistry as several experimental studies of water/electrode interfaces have shown that the oxygen–electrode separation under electrochemical conditions can be controlled by the electric field on the electrode with the average molecular orientation changing from oxygen–down to oxygen–up. In the present work the adsorption energies, the polarization of the interface (work function), and the electronic structure in terms of local density of states are considered. The results for the spatial distribution of the electron states around the Fermi level of the metal are also presented. The interest in the spatial distribution of these states was motivated by the apparent metallic conductivity of water adsorbed on Pt(111) as seen from STM measurements.

7.1 Computational Details

The simulations were performed using M(111) slabs (M=Rh, Pt) consisting of 5 metal layers with water molecules adsorbed on both sides of the slabs in a centrosymmetric configuration with the center of symmetry in the middle of...
Figure 7.1: (a) Surface configuration of perfect water bilayer and the smallest surface unit cell $ABCD$. The substrate is represented through lines connecting the positions of the surface metal atoms. Full circles represent the oxygens of the first water layer (closest to the surface), shaded circles represent the oxygens of the second layer. Hydrogens are given with small circles. (b) Side view of perfect water bilayer. For clarity only part of the unit cell is shown. (c) Side view of a configuration derived from the original water bilayer by flipping the configuration shown in (b). $M_{||}$ and $M_{\perp}$ are the two surface atoms with adsorbed water molecules, $M_*$ is the “free” surface atom.

the slab. The surface unit cells were constructed using the bulk FCC lattice parameters of 3.85 and 3.99 Å for Rh and Pt, respectively, as computed with VASP. For the Rh(111) slabs this corresponds to surface unit cell vectors of length 4.71 Å for the small unit cell $(\sqrt{3} \times \sqrt{3}) R30^\circ$ ($ABCD$ in Fig. 7.1, 3 surface metal atoms) and 9.43 Å for the large unit cell $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ (12 surface metal atoms). For the Pt(111) slabs the surface unit cell vectors were 4.89 Å (only the small unit cell $(\sqrt{3} \times \sqrt{3}) R30^\circ$ was considered). The sizes of the unit cells along the $z$ axis, which is perpendicular to the metal surface, were 24.00 Å for the Rh(111) slabs (regardless of the size of the cell in the plane of the surface) and 24.90 Å for the Pt(111) slab.

The geometry optimizations were performed using a cutoff for the plane wave basis set of 325 eV. For the integration of the band energies a 5x5x1 Monkhorst-Pack-type mesh (Monkhorst and Pack, 1976) was used for the small surface unit cells and the $\Gamma$-point for the large unit cell. The electronic properties (work function, density of states) were evaluated using the optimized geometry and a cutoff of 400 eV and 7x7x1 and 3x3x1 Monkhorst-Pack-type meshes for the small and the large unit cells, respectively. For the s-, p-, and d-local density of states, the bands were projected onto spherical harmonics within spheres of radii of 1.50, 1.10, and 0.65 Å centered on the M
Table 7.1: Selected properties of water molecule in vacuum (W) and water adsorbed on M(111) surface (M=Pt, Rh) at different low coverages. $E_F$ is the Fermi level with respect to the average total electrostatic potential in the middle of the vacuum region, $\Delta \phi$ is the change in the work function compared to the clean metal surfaces, $\alpha$(H$_2$O) is the tilt angle between the water axis and outward surface normal, $\Delta z(M\|)$ is the displacement along the z axis of the substrate atom M$\|$ from the average plane of the other “free” surface atoms (positive value means displacement towards the vacuum). The KS eigenvalues are given relative to the lowest 2a$_1$ MO.

<table>
<thead>
<tr>
<th></th>
<th>W</th>
<th>1/12 Rh</th>
<th>1/3 Rh</th>
<th>1/3 Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ads}$, kJ/mol$^{-1}$</td>
<td>-</td>
<td>36.8</td>
<td>36.1</td>
<td>29.0</td>
</tr>
<tr>
<td>$E_F$, eV</td>
<td>-</td>
<td>-4.39</td>
<td>-4.35</td>
<td>-4.91</td>
</tr>
<tr>
<td>$\Delta \phi$, eV</td>
<td>-</td>
<td>-1.30</td>
<td>-1.34</td>
<td>-0.32</td>
</tr>
<tr>
<td>$E_F$-$E_{2a_1}$, eV</td>
<td>-</td>
<td>22.2</td>
<td>21.9</td>
<td>21.3</td>
</tr>
<tr>
<td>$E_{1b_1}$-$E_{2a_1}$, eV</td>
<td>18.2</td>
<td>17.2</td>
<td>17.1</td>
<td>17.1</td>
</tr>
<tr>
<td>$E_{3a_1}$-$E_{2a_1}$, eV</td>
<td>16.2</td>
<td>15.7</td>
<td>15.8</td>
<td>15.8</td>
</tr>
<tr>
<td>$E_{1b_2}$-$E_{2a_1}$, eV</td>
<td>12.3</td>
<td>12.3</td>
<td>12.3</td>
<td>12.3</td>
</tr>
<tr>
<td>O–H, Å</td>
<td>0.973</td>
<td>0.979</td>
<td>0.983</td>
<td>0.981</td>
</tr>
<tr>
<td>H–O–H, °</td>
<td>104.7</td>
<td>105.3</td>
<td>104.1</td>
<td>103.9</td>
</tr>
<tr>
<td>M$|$$-$O, Å</td>
<td>-</td>
<td>2.38</td>
<td>2.42</td>
<td>2.54</td>
</tr>
<tr>
<td>$\alpha$(H$_2$O), °</td>
<td>-</td>
<td>79</td>
<td>94</td>
<td>98</td>
</tr>
<tr>
<td>$\Delta z(M|)$, Å</td>
<td>-</td>
<td>+0.13</td>
<td>+0.07</td>
<td>+0.05</td>
</tr>
</tbody>
</table>

(M=Rh, Pt), O, and H atoms, respectively, as defined in VASP. The results of the projection scheme applied to single water molecule are discussed in detail in Chapter 4 of this thesis.

The computed density of states and band energies, including the Fermi energy, are given with respect to the total electrostatic potential in the middle of the vacuum region. This corresponds to a distance of around 7.5 Å from the metal surface. The work function is then the negative of the Fermi energy (Lang and Kohn, 1971, Fall et al., 1999).

7.2 Results and Discussions

7.2.1 Low Coverage Adsorption

This section discusses the results for the adsorption of water on Rh(111) and Pt(111) surfaces at 1/3 (Rh and Pt) and 1/12 (only Rh) coverages. For the 1/3 coverage the $\left(\sqrt{3} \times \sqrt{3}\right) R30^\circ$ surface unit cell ABCD was used with only the O$\|$ adsorption site being occupied (full circles on Fig. 7.1a). For the
Figure 7.2: Water adsorption on a Rh(111) surface at a coverage of 1/3. (a) LDOS of the oxygen atom from the water molecule (solid line) and of the underlying Rh atom (dot-dashed line, for clarity shifted by a value of 2 to the right). The integrated density of states (IDOS) for the O atom is given with a dashed line and the OH s-s and p-s COOP curves are given on the right. The Fermi level is represented with a horizontal dotted line. (b) Electron density corresponding to all KS-states with eigenvalues in the range of \([E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}]\] mapped onto a plane along the vector \(AC\) (see Fig. 7.1) and perpendicular to the surface. The isolines are defined as \(2^n \times 10^{-1} \, \text{Å}^{-3}\), \(n = -7, -6, \ldots, 2\), starting from the upper curve. The zero of the \(z\) axis, which is perpendicular to the surface, is in the middle of the 5-layer metal slab; the axes are given in Å.

1/12 surface coverage a four time larger \([2\sqrt{3} \times 2\sqrt{3} R30^\circ]\) unit cell was used, with one water molecule per surface per unit cell adsorbed on top of a Rh atom.

The results showed that the adsorption energies on the two metals are only slightly different and the adsorption energy is around 7 kJ·mol\(^{-1}\) more favorable in the case of Rh(111) compared to Pt(111) (see Table 7.1). The structural and electronic properties of water molecules adsorbed on Rh(111) and Pt(111) surfaces are similar, taking into account the difference in the atomic radii of the two metals. The orientation of the water molecules is approximately parallel to the surface of the substrate with the angle between the dipole of the molecule and the outward surface normal in the order of 79–98° in all three cases. From earlier studies, it was found that at low coverages the molecular axis of the water molecule is tilted at an angle of 30–70° with the outward surface normal [see for example Thiel and Madey (1987), Henderson (2002), Izvekov et al. (2001), and Izvekov and Voth (2001)]. The
7.2. Results and Discussions

Figure 7.3: Water adsorption on Pt(111) surface at a coverage of 1/3. (a) LDOS of the oxygen atom, of the underlying Pt and the OH s-s and p-s COOP curves. The definition of the lines corresponds to the one in Fig. 7.2a. (b) Electron density corresponding to all KS-states with eigenvalues in the range of \([E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}]\) mapped onto a plane along the vector \(AC\) (see Fig. 7.1) and perpendicular to the surface. The definition of the isolines is the same as in Fig. 7.2b; the axes are given in Å.

“Flat” orientation predicted in the present work is consistent with water–metal interaction through the 1b₁ MO of water. This MO is identified as the oxygen lone electron pair and in this configuration of the molecule on the surface is oriented along the surface normal. The interaction with the metal results in a broadening of the 1b₁ MO, while the spacing between the eigenvalues of the other occupied KS states does not vary with the type of the surface.

Note also the presence of a finite local density of states at the site of the oxygen atoms around the Fermi level of the metal (Fig. 7.2a and 7.3a). In this energy region the gas-phase water molecule does not possess electron states (compare Fig. 4.2). To verify that this is not a result of a fictitious overlap between the electron bands of the metal and the projector centered at the site of the oxygen, the spatial electron density which would correspond to all eigenfunctions within the energy interval of \([E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}]\) was computed. As seen in Fig. 7.2b and 7.3b, a p-type contribution to the electron charge density at the site of the oxygen center can be identified. [Note: The procedure used for computing the charge density implies that the eigenfunctions of all Kohn–Sham states within the specified energy interval are included in the charge density profile, regardless of whether they are actually occupied or not. Thus, the generated density also represents the properties
Adsorption of Water on Pt(111) and Rh(111) Surfaces

Table 7.2: Selected properties of water bilayer adsorbed on M(111) surface, M=Rh, Pt and a water bilayer in vacuum. $E_F$ is the Fermi level with respect to the average total electrostatic potential in the middle of the vacuum region, $\Delta \phi$ is the change in the work function compared to the clean surfaces, $\alpha(H_2O||)$ is the tilt angle between the dipole moment of the molecule with oxygen center $O_{||}$ and the outward surface normal, $\Delta z(X)$ is the displacement along the $z$ axis of the metal atom $X$ ($X=M_{||}$, $M_{\perp}$, $M_{\star}$, see also Fig. 7.1) from the average plane of all three surface atoms (positive direction is towards the vacuum). The KS eigenvalues are given relative to the lowest $2a_1$ MO.

<table>
<thead>
<tr>
<th></th>
<th>“up”/*Rh</th>
<th>“dwn”/*Rh</th>
<th>“up”/*Pt</th>
<th>“dwn”/*Pt</th>
<th>vac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ads}$, kJ·mol$^{-1}$</td>
<td>55.4</td>
<td>56.4</td>
<td>52.7</td>
<td>56.5</td>
<td>-</td>
</tr>
<tr>
<td>$E_{ads}$, kJ·mol$^{-1}$</td>
<td>2.4</td>
<td>3.4</td>
<td>1.5</td>
<td>5.3</td>
<td>-</td>
</tr>
<tr>
<td>$E_F$, eV</td>
<td>-2.13</td>
<td>-6.14</td>
<td>-3.41</td>
<td>-6.01</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta \phi$, eV</td>
<td>-3.56</td>
<td>0.45</td>
<td>-1.82</td>
<td>0.78</td>
<td>-</td>
</tr>
<tr>
<td>$E_F$–&lt;$E_{2a_1}$, eV</td>
<td>22.0</td>
<td>19.6</td>
<td>20.9</td>
<td>19.6</td>
<td>-</td>
</tr>
<tr>
<td>$E_{1b_1}$–&lt;$E_{2a_1}$, eV</td>
<td>17.5</td>
<td>17.6</td>
<td>17.5</td>
<td>17.6</td>
<td>17.7</td>
</tr>
<tr>
<td>$E_{3a_1}$–&lt;$E_{2a_1}$, eV</td>
<td>14.8</td>
<td>14.6</td>
<td>14.9</td>
<td>14.8</td>
<td>14.8</td>
</tr>
<tr>
<td>$E_{1b_2}$–&lt;$E_{2a_1}$, eV</td>
<td>12.0</td>
<td>12.0</td>
<td>12.1</td>
<td>12.1</td>
<td>12.0</td>
</tr>
<tr>
<td>$O_{</td>
<td></td>
<td>}$–H, Å</td>
<td>0.992</td>
<td>0.992</td>
<td>0.988</td>
</tr>
<tr>
<td>$O_{\perp}$–H$_p$, Å</td>
<td>1.011</td>
<td>1.017</td>
<td>1.005</td>
<td>1.002</td>
<td>1.021</td>
</tr>
<tr>
<td>$O_{\perp}$–H$_d$, Å</td>
<td>0.974</td>
<td>0.983</td>
<td>0.974</td>
<td>0.989</td>
<td>0.973</td>
</tr>
<tr>
<td>H–O$_{</td>
<td></td>
<td>}$–H, °</td>
<td>104.9</td>
<td>103.4</td>
<td>104.2</td>
</tr>
<tr>
<td>H–O$_{\perp}$–H, °</td>
<td>107.9</td>
<td>108.4</td>
<td>107.9</td>
<td>107.1</td>
<td>108.4</td>
</tr>
<tr>
<td>$M_{</td>
<td></td>
<td>}$–O$_{</td>
<td></td>
<td>}$, Å</td>
<td>2.63</td>
</tr>
<tr>
<td>$M_{\perp}$–O$_{\perp}$, Å</td>
<td>3.42</td>
<td>3.49</td>
<td>3.45</td>
<td>3.34</td>
<td>-</td>
</tr>
<tr>
<td>$M_{\perp}$–H$_d$, Å</td>
<td>-</td>
<td>2.51</td>
<td>-</td>
<td>2.35</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha(H_2O</td>
<td></td>
<td>)$</td>
<td>76</td>
<td>-</td>
<td>92</td>
</tr>
<tr>
<td>$\Delta z(M_{</td>
<td></td>
<td>})$, Å</td>
<td>+0.05</td>
<td>+0.02</td>
<td>+0.02</td>
</tr>
<tr>
<td>$\Delta z(M_{\perp})$, Å</td>
<td>-0.03</td>
<td>-0.02</td>
<td>-0.01</td>
<td>-0.03</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta z(M_{\star})$, Å</td>
<td>-0.02</td>
<td>0.00</td>
<td>-0.01</td>
<td>-0.02</td>
<td>-</td>
</tr>
</tbody>
</table>

of the states above the Fermi level.] As discussed in section 7.2.3, the spatial distribution of the charge density corresponding to the electronic states around the Fermi level is relevant to the processes of electron transfer through the interface.
7.2. Results and Discussions

7.2.2 Bilayer of Water on Pt(111) and Rh(111)

Water adsorbed at high coverages on metal surfaces forms a bilayer, which according to the model proposed by Doering and Madey (1982) is composed of two nonequivalent H$_2$O molecules: the first molecule, which is the closest to the surface (oxygen centers denoted with full circles in Fig. 7.1a), has its plane approximately in the plane of the surface with both hydrogens taking part in a hydrogen bond, while the second molecule (oxygen centers denoted with shaded circles) is perpendicular to the surface with one of the hydrogens dangling towards the vacuum and the other taking part in a hydrogen bond. In the present work two different configurations of the adsorbed bilayer were considered: (i) “up” configuration with the dangling H$_d$ atom pointing away of the surface (Fig. 7.1b), which is the original model of the bilayer as proposed by Doering and Madey (1982), and (ii) “down” configuration with the dangling H$_d$ atom pointing towards the surface (Fig. 7.1c). These configurations can be considered as two simplified models simulating different surface–oxygen separations. This is of some interest to electrochemistry as experimental studies have shown that the oxygen–surface separation can be controlled to some degree by the applied potential on the electrode (Toney et al., 1994).

The “up” and “down” configurations of the bilayer adsorbed on either Pt(111) or Rh(111) surfaces appear very similar in their computed adsorption energies $E_{ads}$ (Table 7.2). Interestingly, the data indicates that the “down” configuration is energetically more favorable than the “up” configuration, although the differences are very small. A comparison of the energy gain $E^\text{bilayer}_{ads}$ when an isolated water bilayer is adsorbed on the metal surfaces indicates that the interaction energy between the metal and the H$_2$O adlayer is weak. [This statement, however, will be partially revised later - see chapters 8 and 9 discussing the results of ab initio MD simulations using a larger unit cell.]

The alteration of the surface dipole between the “up” and “down” configurations has an effect on the Fermi level relative to the total electrostatic (ionic+electronic) potential in the middle of the vacuum region, respectively the work function. As can be expected the work functions of the “up” configurations (Table 7.2) are lower than the work functions of the clean 5–layer slab models of Rh(111) and Pt(111) of 5.23 and 5.69 eV, respectively, as computed
with VASP. The opposite effect is observed for the “down” configurations. These large changes in the work function (related to the surface dipole) and the relatively weak interaction of the bilayer with the metal surface indicates that the orientation of the H\textsubscript{2}O molecules at the metal surface may be controlled by the electric field on the electrode. This conclusion corroborates well with the potential dependences of the oxygen–surface separation, as determined experimentally using X-ray scattering [see for example the work of Toney et al. (1994)].

The electronic properties in terms of the spacing between the water MOs are also very similar to the case of an isolated water bilayer in vacuum (compare Fig. 7.4, 7.5, and 7.8; the isolated water bilayer is considered in section 7.2.4). Experimental UPS spectral measurements of molecular water adsorbed on Pt(111) and Rh(111) surfaces have shown that while the spacing between the 1b\textsubscript{2}, 3a\textsubscript{1}, and 1b\textsubscript{1} MOs of water adsorbed on Pt(111) is similar to the gas–molecule data, on Rh(111) the 3a\textsubscript{1} molecular orbital is shifted towards the Fermi level of the substrate (Wagner and Moylan, 1987). The current electronic structure calculations of a perfect water bilayer adsorbed on the metal surfaces could not reproduce this shift. Of all MO levels the relative position of the 3a\textsubscript{1} MO is perhaps the most dependent on the conformation of the bilayer. Within the present model, the degrees of freedom of the water bilayer are highly limited due to the imposed translational symmetry of the (relatively small) surface unit cell. This indicates that a more accurate structure of the bilayer may exist and should be searched for using a larger unit cell and employing ab initio molecular dynamics techniques. The same explanation can be suggested for the perhaps surprising result that in the present calculations the “down” configuration is slightly more stable than the “up” configuration. [The results of an ab initio MD simulations of water bilayer adsorbed on Rh(111) surface are presented in the Chapter 8.]

7.2.3 Electronic Structure Around the Fermi Level

The projections of the KS orbitals suggest that in spite of the elongated water–metal distances compared to the case of low coverage adsorption on the surface, the presence of a metal substrate still gives rise to a finite local density of states around the Fermi level at the site of the oxygen atoms (Fig. 7.4 and 7.5). From the electron density, corresponding to all electron states with KS eigenvalues in the range of [$E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}$], a p\textsubscript{2}-type contribution to the electron charge with the p-orbital oriented along the surface normal z can clearly be identified (Fig. 7.6). [This conclusion can also be verified by projecting the bands onto a p-type projector along the surface.
7.2. Results and Discussions

Figure 7.4: Water adsorption on a Rh(111) surface at a coverage of 2/3. LDOS of the two oxygen atoms O∥ and O⊥, of the underlying Rh∥ and Rh⊥ atoms and the set of OH s-s and p-s COOP curves. (a) configuration “up”, (b) configuration “down”. The definition of the lines corresponds to the one in Fig. 7.2a.

Note that the same p₂-type contribution to the charge density is present around the second water molecule which has its molecular plane perpendicular to the surface. In this configuration the lone electron pair of the central oxygen atom is along the plane of the surface. This interesting result is further explored by examining the spatial distribution of the electron states
around the Fermi level in an artificially created configuration with the water molecules partially rotated (see Fig. 7.7). The configuration (c) was created by taking the optimized structure for the “down” configuration and rotating the two water molecules in such a way that the planes of the molecules are no longer parallel nor perpendicular to the metal surface. Even in this configuration the electron density, corresponding to states around the Fermi level, resembles a $p_z$-type contribution with the $p$-orbital centered at the oxygen center and oriented approximately along the surface normal. This indicates that the finite density of states around the Fermi level of the metal and the corresponding spatial electron charge density distribution is to some degree independent of the orientation of the molecule, suggesting that is (primarily) related to metal–oxygen interactions, rather than metal–water interactions. The extent of mixing between the atomic states from the oxygen atom and the metal substrate appears to be primarily determined by the distance to the surface (compare the two molecules in the “up” configuration, Fig. 7.7a) and by the polarization of the surface (compare the spatial electron density of the “up” and the “down” configuration; note that in the “down” configuration the water molecules are further away from the surface compared to either of the molecules from the “up” configuration).

Traditionally, the processes of interfacial electron transfer between molecules or ions in the solution and the metal electrode is modeled in the framework of the surrounding solvent (most commonly water) considered as a simple dielec-
7.2. Results and Discussions

Figure 7.6: Water adsorption on M(111) surface, M= Rh, Pt, at coverages of 2/3. Electronic density corresponding to all KS-states in the energy range of $[E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}]$ mapped onto a plane along the vector AC (see Fig. 7.1) and perpendicular to the surface. (a) Rh(111), configuration “up”; (b) Pt(111), configuration “up”; (c) Rh(111), configuration “down”; (d) Pt(111), configuration “down”. The definition of the isolines is the same as in Fig. 7.2b; the axes are given in Å.

Electronic continuum (Marcus, 1956, 1965, 1993). Recent publications dealing with the electron tunneling phenomena through water layers have pointed out, that the full three dimensional structure of the solvent and the quantum properties of the electron have to be taken into account when describing processes of non-adiabatic electron transfer through the water/metal interface (Benjamin, 1996, Benjamin et al., 1997, Morgenstern et al., 1997, Hahn et al., 1998). The
finiite charge densities at the oxygens of electron states around the Fermi level confirm that the water molecules from the adlayer closest to the metal surface may play an active role in the electron transfer reactions and might not be considered as a simple dielectric medium. These results are also in agreement
7.2. Results and Discussions

Figure 7.8: Water bilayer in vacuum. LDOS of the two oxygen atoms O∥ and O⊥ (solid lines), integrated density of states (IDOS, dashed line) and the corresponding OH s-s and p-s COOP curves. The mid-point between the HOMO and the LUMO is given with a horizontal line.

with the experimental observations of Morgenstern et al. (1997), who reported that water adsorbed on Pt(111) appears as an elevation to the STM.

7.2.4 Water Bilayer in Vacuum.

In this section an isolated water bilayer is considered in comparison with the bilayer adsorbed on a metal surface. The current system can be seen as derived from the adsorption models for 2/3 water coverage on a metal surface by removing the substrate.

The presented structural and electronic properties are computed after a geometry optimization of an isolated bilayer as derived from the model for 2/3 surface coverage of Rh(111). During the optimization the bilayer retains the original configuration of the hydrogen bonds. The bilayer cannot break apart due to the imposed translational symmetry. The conformations corresponding to either “up” or “down” configurations of water bilayer adsorbed on the metal surfaces and the bilayer in vacuum differ by at most 2 kJ·mol⁻¹.

The optimized structural parameters of the isolated bilayer (Table 7.2) indicate that the bond length between the oxygen center O⊥ and the dangling hydrogen atom H_d remains the same as in the gas–phase water molecule, while all other OH bonds are elongated. In fact, the structural properties of the molecules from the isolated bilayer and the bilayer adsorbed on a metal surface (Table 7.2) are quite similar, except for the O⊥–H_d and O⊥–H_p bonds. The O⊥–H_p distance can be related to some extent to the conformation of the
bilayer and the unit cell size, which in turn determines the O$_{\perp}$–O$_{\parallel}$ distance. However, the O$_{\perp}$–H$_d$ in the adsorbed water bilayer varies depending on the configuration ("up" or "down"), which is probably due to interaction with the metal. [Note: The interaction between the bilayer and the metal surface is discussed in details in Chapter 9 of this thesis.]

Considering the electronic properties (Fig. 7.8), note that the 3a$_1$ KS molecular orbital (identified also from the COOP curves as discussed in Chapter 4) is split in two levels with a relative spacing of around 1.4 eV. This split agrees qualitatively with the experimentally observed broadening of the 3a$_1$ band for ice (Campbell et al., 1979, Abbati et al., 1979) and is also present in the case of the water bilayer being adsorbed on metal surfaces. The other molecular orbital with the same A1 symmetry (2a$_1$) in the current simulations appears also split, but to a much lower degree.

### 7.3 Summary and Conclusions

The ab initio density functional theory structural optimizations of molecular water adsorbed at low coverage on the (111) surfaces of Pt and Rh predict a "flat" orientation of the molecules with respect to the surface. The computed tilt angle between the water dipole moment and the outward surface normal is in the range of 79–98$^\circ$. This orientation is consistent with an interaction with the metal substrate through the 1b$_1$ lone electron pair of the oxygen atom.

In the framework of the model used in this simulation, the two configurations of water bilayer on the surface, which differ in the orientation of the molecules, display similar adsorption energies, while there are relatively large changes in the surface dipole moment. This indicates that in electrochemical conditions the orientation of water molecules could be controlled through the applied potential on the electrode. This is also in agreement with the experiment data. Comparing the "up" and "down" configurations, the intramolecular structural characteristics of the molecules are similar, except for the length of the "dangling" OH bond, which varies due to the interactions with the substrate.

The molecules adsorbed on the surface posses metallic–like conductivity related to mixing of local states of the oxygen atom with the electron bands of the metal substrate. The extent of this mixing appears to some degree independent of the orientation of the molecules.
Chapter 8

Water Bilayer on Rh(111): Structure

The geometry optimization calculations of the perfect–bilayer configurations presented in the previous Chapter showed that in spite of differences in the structure, the adsorption energies of the “up” and “down” structures are comparable. It was suggested that a larger unit cell may provide a better description of the system. This Chapter deals with a molecular dynamics simulation using a larger unit cell. The simulation aims at finding a more stable configuration of the water adlayer on the surface. The system can also be regarded as a simplified model for the first water layer at the liquid/water metal interface. The importance of the electrostatic interactions is discussed in view of the computed average orientation of the molecules.

8.1 Computational Details

The model employed in this simulation consists of a 3–layer Rh(111) slab with water molecules adsorbed on both sides of the slab. A \((2\sqrt{3} \times 2\sqrt{3})\) R30° surface unit cell (12 surface metal atoms) was constructed using the bulk FCC lattice parameters of 3.85 Å, as computed with VASP. This corresponds to surface unit cell vectors of length 9.43 Å (see Fig. 8.1). The size of the unit cell along the \(z\)-axis perpendicular to the metal surface was 19 Å.

For the electronic structure part, a cutoff of 325 eV was used for the plane wave basis set and the \(\Gamma\)-point was used for the integration of the band energies, except if stated otherwise (section 8.2). The molecular dynamics simulations
Figure 8.1: Surface configuration and unit cell. (a) top view, (b) side view. Rhodium, oxygen and hydrogen atoms are given in grey, black and white colors, respectively.

were performed using a time step of 0.5 fs at a mean temperature of 300 K. No constraints on the positions of the metal atoms or the geometry of the water molecules were applied. As discussed below, two different initial configurations were considered. Equilibration runs were performed starting from either of the initial configurations for 1.8 ps followed by statistical data collection for 1.8 ps. Thus, accounting for the fact that water was considered on both sides of the metal slab, the total length of statistical data is 7.2 ps and consists of four statistically independent blocks. [The time–evolution of the water adlayers on the two different surfaces of the slab are independent because the initial velocities of the atoms are assigned in a random way.]

8.2 Accuracy of the Simulation

In the previous study of water adsorbed on Rh(111) and Pt(111) (Chapter 7) fairly accurate 5–layer models for the surfaces were used. The goal of the present simulations is to search for a more stable configuration of the water adlayer using a larger unit cell and employing *ab initio* molecular dynamics. As this method is computationally expensive, in the present simulation the number of metal layers was reduced to 3. In view of computational efficiency, the simulation was performed using a Rh(111) slab. Rhodium is preferred compared to platinum as it has fewer (valence) electrons.

This section discusses the accuracy of the MD simulation comparing results
8.2. Accuracy of the Simulation

**Figure 8.2:** Schematic diagram of different computational models and the relevant accuracy tests. See also text.

obtained using the MD computational setup with the more accurate 5–layer data. For evaluating the accuracy, the “transition” from the 5–layer model to 3–layer model is considered as a two–step process (Fig. 8.2): (i) reduction of the number of the metal layers and (ii) increase in the size of the unit cell with (complementary) adjustment of the computational parameters (i.e. cutoff for the plane wave basis set and number of $k$–points).

**Step 1**

The first set of accuracy tests examines the dependence of the adsorption energies and the geometry characteristics of the “up” and “down” configurations as defined in Chapter 7 on the thickness of the metal slab (transition Step 1 in Fig. 8.2). The geometry optimization calculations of the 3–layer model were performed using the small \( \sqrt{3} \times \sqrt{3} \) R30° surface unit cell, a cutoff for the
Table 8.1: Selected properties of a perfect water bilayer adsorbed on Rh(111) surface computed using 3–layer (3L) and 5–layer (5L) models. See also text.

<table>
<thead>
<tr>
<th></th>
<th>“up”/5L</th>
<th>“up”/3L</th>
<th>“down”/5L</th>
<th>“down”/3L</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ads}$, kJ·mol$^{-1}$</td>
<td>55.4</td>
<td>50.2</td>
<td>56.4</td>
<td>51.0</td>
</tr>
<tr>
<td>$E_{bilayer}$, kJ·mol$^{-1}$</td>
<td>2.4</td>
<td>2.6</td>
<td>3.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Rh$</td>
<td></td>
<td>$–O$</td>
<td></td>
<td>$, Å</td>
</tr>
<tr>
<td>Rh$<em>{⊥}$–O$</em>{⊥}$, Å</td>
<td>3.42</td>
<td>3.42</td>
<td>3.49</td>
<td>3.48</td>
</tr>
<tr>
<td>Rh$_{⊥}$–H$_d$, Å</td>
<td>-</td>
<td>-</td>
<td>2.51</td>
<td>2.50</td>
</tr>
</tbody>
</table>

plane wave basis set of 350 eV and a $5 \times 5 \times 1$ Monkhorst-Pack-type mesh (Monkhorst and Pack, 1976). A more detailed description of the structures is given in Chapter 7. The adsorption energies (Table 8.1) are computed using as references an optimized 3–layer Rh(111) slab and a water molecule in a large supercell. Compared to the 5–layer calculations, the 3–layer models result in lower values for the adsorption energies. This can be attributed mainly to the small thickness of the metal slab, although other computational and numerical effects may have also influenced the results. [Note that the previous 5–layer simulations were performed with an even higher cutoff for the plane waves of 400 eV. The difference in the cutoff can also affect the energy of the reference water molecule in vacuum, which is computed using a different unit cell.] It is more important, however, that the interaction energy between the bilayer and the metal surface $E_{ads}$, as defined in Chapter 7, and the relative stability of the “up” and “down” configurations computed using the 3–layer models agree well with the 5–layer results. The rhodium–oxygen Rh$||$–O$||$ and Rh$_{⊥}$–O$_{⊥}$ and the rhodium–hydrogen Rh$_{⊥}$–H$_d$ distances computed using a different number of rhodium layers are also in very good agreement. It is therefore concluded that a model containing 3–layer metal slab can be used for an acceptable description of the “up” and “down” configurations of water adlayer on the surface. The difference in the adsorption energies between the 3–layer and the 5–layer models is regarded as a systematic error, which will not affect strongly the relative energies of the configurations obtained in the course of the MD simulation.

Step 2

The molecular dynamics simulations were performed using a twice larger $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ unit cell (Fig. 8.1a), a reduced cutoff for the plane wave basis set of 325 eV and only the $\Gamma$-point in the Brillouin zone. Using the MD unit
8.3. Results and Discussions

The present simulation consists of two sets of MD data starting from either the “up” or “down” perfect–bilayer configurations as determined in Chapter 7. The configurations differ in the orientation of the molecules and polarization of the interface. Throughout either of the simulations the water molecules stayed approximately on top of the metal atoms interconnected through hydrogen–bonds. The distribution functions evaluated using either of the simulation data sets were found to be comparable, indicating that the “up” and “down” initial configurations have evolved into similar final conformations. The statistical averages presented below are therefore computed using the two sets of cell and the MD computational parameters the estimated value for adsorption energy of the “up” configuration of the perfect bilayer is 50.4 kJ·mol$^{-1}$, which is in good agreement with the value computed using the smaller unit cell and the more accurate parameters. It is therefore concluded that the MD computational setup can be used for MD simulations in search for a more stable conformation of water adlayer on Rh(111) surface.

**Additional Accuracy Tests**

The above discussed accuracy tests consider only the perfect water bilayer configurations. These structures, however, are not truly representative for the conformations of the system obtained during the MD runs. In contrast to the perfect bilayer, the MD simulation results indicate a relaxation of the rhodium slab in terms of the positions of the Rh atoms along the surface normal (for more details see section 8.3.2). This was not observed in the perfect bilayer structures. An independent test of the accuracy in the domain of the MD simulation results was therefore carried out using six equally spaced in time configurations from the MD simulation data set. Of particular interest is the dependence of the total energy on the cutoff for the plane wave basis set and the number of $k$-points. Single point calculations were performed on the selected structures using a cutoff of 350 eV and $3 \times 3 \times 1$ Monkhorst-Pack-type mesh (Monkhorst and Pack, 1976). The relative differences in the total energies of the configurations obtained in the course of the MD simulation and using the more accurate settings are less than 0.33 eV per unit cell. [Note that the total energy per unit cell is on the order of 470 eV.] Accounting that there are 16 water molecules per unit cell adsorbed on both sides of the surface, this difference is equivalent to an error in the adsorption energy of water on the order of 2 kJ·mol$^{-1}$.
8.3.1 Adsorption Energy

This simulation aims at finding a more stable conformation of the water adlayer on the surface. The current section addresses the question if indeed a more stable configuration exists in the larger unit cell compared to the small unit cell. Using a (randomly) selected configuration from the MD data set a geometry optimization simulation of the structure was performed in order to estimate the adsorption energy at 0 K (which is the condition of the previous calculations). The adsorption energy of the resulting optimized structure is 64.7 kJ·mol$^{-1}$. This is around 14 kJ·mol$^{-1}$ higher than the values found for the perfect–bilayer structures using 3–layer model. Assuming transferability of this result to the more accurate 5–layer model, the estimated value for the adsorption energy of water adlayer on Rh(111) surface would be around 70 kJ·mol$^{-1}$. It has to be mentioned that the optimized structure may not represent the global potential energy surface minimum, i.e. the above value may be interpreted as a lower boundary to the adsorption energy for this system at 0 K. It is more important, however, that the geometry optimization performed using the larger unit cell resulted in a more stable structure compared to the small unit cell, as expected.

8.3.2 Structure of the Bilayer

The “up” and “down” configurations, which have different structural characteristics, were found to be comparable in their adsorption energies (Chapter 7). This indicates that the description of the structure of the bilayer should be given through a statistical interpretation of the MD results, rather than looking at a single (optimized) conformation. The structural properties of the system are first considered in terms of the number densities of the atoms along the surface normal $z$ (Fig. 8.3a). The oxygen distribution function reveals formation of a bilayer of water molecules with two distinct maxima and a tail towards the vacuum region. The integrated value of the first peak, which will be referred to as sublayer L1, equals 2.5 oxygen atoms per surface per unit cell, with the rest of 5.5 oxygen atoms per surface per unit cell being in the second sublayer L2. The reconstruction of the initial conformation of the bilayer adsorbed on Rh(111) results in a reduction of the number of close contacts between Rh and O atoms, which for the perfect “up” bilayer is four per surface per unit cell. [Note: The molecular dynamics simulation has been performed at an average temperature of 300 K, which is above the desorption
8.3. Results and Discussions

Figure 8.3: (a) Number densities of rhodium (dashed line), oxygen (solid line), and hydrogen atoms (dot-dashed line) along the surface normal. The zero of the surface normal is in the middle of the 3-layer metal slab. (b) Cross-section of the oxygen number density and the orientational distribution of the corresponding OH bonds. The isolines are defined as $2^n \times 10^{-1} \text{Å}^{-1}$, $n = -3, -2, ..., 3$, starting from the outer curve. The definition of the atoms corresponds to Fig. 8.1. The density plots are normalized to the total number of atoms of the corresponding type.

- temperature of around 180 K. However, desorption of water molecules from the surface does not occur in the course of the MD simulation due to the short simulation time and the small size of the system. The optimized structure, obtained in relation to the adsorption energy (section 8.3.1), also corresponds to a conformation of the bilayer with less than four water molecules in close contact with the surface - the number of oxygen atoms at a height above the surface in the range corresponding to the first peak L1 equals only three. An attempt to place a fourth water molecule at an oxygen–surface separation in the range of the first peak L1 resulted in a reconstruction during the geometry optimization of the bilayer (T=0 K) accompanied by a relocation of the “extra” water molecule towards the vacuum phase.

Considering the hydrogen distribution along the surface normal (Fig. 8.3a), note that there is a non-zero contribution of hydrogen number density at shorter distances to the metal surface compared to the oxygen. To explore further this result, the cross-section of orientational distribution of the OH bond with respect to the outward surface normal with the position of the corresponding oxygen center of the water molecules is considered (Fig. 8.3b). The distribution function reveals that water molecules from sublayer L1 have their OH bonds tilted away of the surface with a maximum in the angular
distribution function of around 70° (O₁H₁ₓ in Fig. 8.3b). These hydrogen atoms take part in hydrogen bonds with water molecules from L₂. In turn, water molecules from L₂ sublayer have one of their OH bonds approximately parallel to the surface (O₂H₂₂ and O₃H₃₁), while the other points either towards the metal (O₂H₂₁) or towards the vacuum (O₃H₃₂). Thus, the shoulder observed in the hydrogen distribution function along the surface normal at short hydrogen–surface distances originates from the H atoms from water molecules in the second (L₂) sublayer. Note that the peak corresponding to the “hydrogen–down” bond (O₂H₂₁) is enhanced compared to the “hydrogen–up” bond (O₃H₃₂), indicating that the movement of the H₂₁-type hydrogen atoms is to some degree restricted due to the presence of the metal.

The rhodium distribution function also appears broadened in the direction of the water adlayer. The origin of this broadening can be found in the rhodium number density distribution along the surface normal cross-section with the oxygen and hydrogen number densities (Fig. 8.4). The distribution plot clearly shows that the relaxation of the surface in terms of the position of the Rh atoms...
in the direction perpendicular to the surface is caused by the interaction with oxygen atoms from the first sublayer L1. In contrast to the results using the small unit cell (Chapter 7), the displacement of the Rh atoms in close contact with water molecules is on the order of 0.3 Å. This results in a separation between the oxygen atoms from L1 and the underlying Rh atoms on the order of 2.3 Å, which is shorter compared to the perfect–bilayer and is comparable to the low coverage results. Interestingly, the separation between the rhodium surface and the H$_{21}$-type atoms is on the same order of magnitude while there is no relaxation of the surface (compare Fig. 8.4 in the areas of the O$_1$ and H$_{21}$ atoms; the local configuration of O$_1$-type atom is characterized with the oxygen atom at a distance above the middle of the metal slab of around 4.7 Å. The underlying Rh atom is at a distance on the order of 2.4 Å. The corresponding distances of the H$_{21}$-type atom and the underlying Rh atom are 4.4 and 2.1 Å).

In summary, molecular water adsorbed on Rh(111) surface forms a bilayer–like structure which can be regarded as a superposition of the simple “up” and “down” structures found using the small unit cell. An indication of what is the determining factor for the orientation of the individual molecules can be found in the computed cross–section of the orientational distribution of the water dipole moment with the position of the oxygen center of the water molecule along the surface normal (see Fig. 8.5b). As seen from the figure, the dipole moment of the water molecules from L1 is at an angle with the outward surface normal in the order of 55–60°. The orientation of the dipole moment of the molecules from L2 varies between pointing towards the vacuum and towards the surface, with a preferred orientation towards the surface. The maximum in the angular distribution function is around 130°. However, the average orientation of the dipole moment computed accounting for all water molecules (L1+L2) is at an angle of 91° with the outward surface normal. This results in a very small contribution to the total surface dipole moment and this configuration is also the one which minimizes the long–range dipole–dipole repulsion. In conclusion, while the orientation of the molecules from L1, which are closer to the surface, is determined by the interaction with the metal substrate, the “driving force” for the orientation of the molecules from the second sublayer L2, i.e. those which are further away from the surface, is the electrostatic interaction with the L1 sublayer.

It has to be pointed out that an average orientation of the water molecule dipole moment around the plane parallel to the surface does not necessarily mean that there is no change in the surface dipole compared to the clean surface. [The electron charge transfer through the interface will be consid-
Figure 8.5: (a) Number densities of rhodium (dashed line), oxygen (solid line), and hydrogen atoms (dot-dashed line) along the surface normal. (b) Cross-section of the oxygen number density and the orientational distribution function of the dipole moment of the molecule with respect to the outward surface normal. The isolines are defined as $2^n \times 10^{-1} \text{Å}^{-1}$, $n = -2, -1, ..., 3$ starting from the outer curve. The definition of the atoms corresponds to Fig. 8.1. The density plots are normalized to the total number of atoms of the corresponding type.

The change in the work function compared to the clean Rh(111) surface is $\Delta \phi = -1.1 \text{eV}$ with fluctuations in the course of the MD simulation on the order of 0.5 eV. This value was estimated using the 6 reference configuration computed in relation with the accuracy tests.

8.4 Summary and Conclusions

The water adlayer adsorbed on Rh(111) surface forms a bilayer–like structure with two distinct peaks in the oxygen distribution function along the surface normal. The simulation revealed that a more stable conformation compared to the simple “up” and “down” structures can be found using a larger unit cell. The estimated value for the adsorption energy equals $70 \text{kJ\cdotmol}^{-1}$. While the orientation of the molecules in close contact with the surface is determined by the interaction with the substrate, the determining factor for the orientation of the molecules which are further away are the electrostatic interactions. This leads to an average orientation of the dipole moment of all water molecules approximately in the plane of the surface (in the absence of an external field).
Chapter 9

Water Bilayer on Rh(111): Electronic Structure and Bonding

The results of the MD simulation of water adlayer on Rh(111) surface presented in the previous Chapter showed that while the average orientation of the dipole moment of the molecules is parallel to the surface, the estimated change in the work function compared with the clean surface is around $-1.1 \, \text{eV}$. A change in the work function is related to a change in the surface dipole moment, respectively the electron charge density distribution function. The present Chapter investigates the electron charge transfer through the interface comparing the spatial distribution of the electron density of the substrate–adsorbate system with that of an isolated adlayer and a clean surface. The interaction between the water adlayer and the metal atoms is also examined, considering both rhodium–oxygen and rhodium–hydrogen interactions.

9.1 Computational Details

The results presented here were obtained using a 3–layer metal slab and a \((2\sqrt{3} \times 2\sqrt{3})\) \(\text{R}30^\circ\) surface unit cell (12 surface metal atoms). Single point calculations were performed using a cutoff for the plane wave basis set of 350 eV and $3 \times 3 \times 1$ Monkhorst-Pack-type mesh (Monkhorst and Pack, 1976). For the $s$-, $p$-, and $d$-local density of states, the KS bands were projected onto
spherical harmonics within spheres of radii of 1.50, 1.10, and 0.65 Å centered on the Rh, O, and H atoms, respectively, as defined in VASP.

9.2 Results and Discussions

9.2.1 Electronic Structure and Electron Transfer Through the Interface

As discussed in section 8.2, six equally spaced in time configurations were used to evaluate the error in the adsorption energy and assess the accuracy of the MD simulation. In the present Chapter the same configurations are used to evaluate the electronic properties of the system. The local density of states (LDOS) were calculated and the results for the averaged LDOS of all oxygen atoms and all surface Rh atoms using all six configurations are given in Fig. 9.1a. As discussed in Chapter 7, one of the indications that the small \( (\sqrt{3} \times \sqrt{3}) \text{R}30^\circ \) surface unit cell may not be sufficient for the description of the water bilayer adsorbed on the metal surface was the local density of states of the oxygen atoms, which in contrast with experiment displays five well-defined peaks. The average oxygen LDOS computed using the six MD configurations consists of three principal peaks. The detailed structure of the three peaks is revealed in Fig. 9.1b and 9.1c, presenting the LDOS data evaluated for two selected oxygen atoms \( O_{L1} \) and \( O_{L2} \) using one configuration. The two oxygen centers belong to the different sublayers L1 and L2, respectively,
9.2. Results and Discussions

Figure 9.2: Side view of a configuration of the bilayer of water adsorbed on Rh(111) surface (only three water molecules and the corresponding underlying rhodium atoms are given).

as defined in Chapter 8 (see also Fig. 9.2). The LDOS plots (Fig. 9.1b and c) indicate that the position and spacing between the energies of the local electron states vary between the adsorption sites, which is due to differences in the local chemical and electrostatic environment. The relatively broad peaks in the averaged LDOS plot are a superposition of otherwise well-defined electron states of water. The peak closest to the Fermi level in the averaged LDOS is composed of the \( 3a_1 \) and \( 1b_1 \) MOs. This data is in good (qualitative) agreement with the experimental UPS results from Wagner and Moylan (1987). Note also the finite local density of states around the Fermi level of the substrate at the site of the oxygen atoms. The current simulation data confirms the previously established result for an apparent conductivity of a water layer next to a transition metal surface.

As discussed in Chapter 8, the averaged orientation of the dipole moment of the water molecules is approximately in the plane of the surface. Nevertheless, the estimated difference between the work function of the substrate–adsorbate system and the clean surface is around \(-1.1\) eV. This means that the total surface dipole moment is altered upon adsorption of water molecules on the surface and this is due to a redistribution of the electron density. The electron charge transfer through the interface is illustrated in Fig. 9.3, presenting the so-called electron charge transfer function. The electron charge transfer function is defined as the electron density of the water–substrate system minus the sum of the electron densities of the isolated water adlayer and the “clean” metal substrate. In this case, the isolated water adlayer and the “clean” metal surface are in the same conformation as in the substrate–adsorbate system (no geometry optimizations). Based on this result it is concluded that there
is an electron charge transfer from the water adlayer towards the metal surface, which leads to an increase in the electron density in the interfacial area (compare the electron charge transfer function in Fig. 9.3c at heights of 3–4 and 4.5–7 Å above the middle of the metal slab).

### 9.2.2 Rhodium–Oxygen Interaction

The distribution functions obtained from the MD simulation showed that the Rh(111) surface is subject to relaxation in terms of the position of the Rh atoms along the surface normal. This section considers the interaction in view of the electronic structure and local density of states.

In order to assess the water–rhodium interaction, a configuration was selected from the MD simulation data set. A single point calculation was performed and the local densities of states were evaluated. The computed LDOS of an oxygen atom from a water molecule in the sublayer L1 is presented in the left panel of Fig. 9.4. The molecular orbitals were identified using the
9.2. Results and Discussions

Figure 9.4: Local density of states of the $O_{L1}$ oxygen atom (solid line) and the underlying Rh$_1$ rhodium atom (doted line) in the case of defect–free Rh(111) surface (left panel) and the defect Rh(111) surface with the underlying Rh$_1$ atom removed from the surface (right panel). The Fermi level of the substrate is presented with a horizontal dashed line. The LDOS in the left and right panels are aligned to match the positions of the $2a_1$ molecular orbitals.

COOP curves (not shown), as discussed in section 4.2. Note that the peak corresponding to the $1b_1$ eigenstate appears broader compared to the other molecular orbitals, suggesting that the interaction with the metal substrate is primarily through the $1b_1$ MO. This can be verified using a sample configuration derived from the original structure by removing the underlying rhodium atom (Rh$_1$ in Fig. 9.2), i.e. creating a defect in the rhodium surface. The local density of states of the resulting system (no geometry optimizations) were evaluated and the results for the $O_{L1}$ atom are presented in the right panel in Fig. 9.4. Comparing the defect–free and the defect LDOS data for the $O_{L1}$ atom, note the shift in the position of all eigenstates towards the Fermi level as well as the change in the spacing between the MOs. This indicates that the introduction of a defect on the surface at this specific site causes a modification of the chemical and electrostatic environment of the $O_{L1}$ water molecule. Recall that in the case of perfect bilayer, the spacing between the molecular orbitals was practically unaffected when the metal substrate was removed to create the isolated bilayer in vacuum. In the present case the interaction between the rhodium substrate and the water molecules from L1 through the $1b_1$ lone electron pair, which is shifted to lower eigenenergies, is significantly stronger. This conclusion corroborates well with the shortened oxygen–rhodium separation and the increase in the adsorption energy compared with the perfect bilayer (Chapter 8). The estimated increase in the adsorption energy was on the order of 14 kJ·mol$^{-1}$, while the number of close contacts between rhodium and oxygen is reduced. However, as discussed in
the next section, a model including only rhodium–oxygen interactions is too simplistic and cannot account for all interactions between the water layer and the metal surface.

9.2.3 Rhodium–Hydrogen Interaction

This section addresses the question of whether there is an interaction between the rhodium and the hydrogen atoms apart from steric effects. A detailed examination of the simulation results presented in the previous chapters can provide evidence for a possible attractive Rh–H interactions. For example, the geometry optimizations of the perfect bilayer models revealed that the “dangling” O⊥–H⊥ bond is elongated in the “down” configuration compared to the “up” configuration (Chapter 7). Note also that the “down” configuration is the configuration characterized with both 3a1 and 1b1 eigenenergies “overlapping” with the eigenenergies of the metal and thus the corresponding molecular orbitals are potential candidates for MO interactions with the substrate. Another example is the MD simulation (Chapter 8), and particularly the OH orientational distribution function. It was found that the peak in the angular distribution function corresponding to OH pointing towards the surface is more narrow compared to the peak for the OH pointing towards the vacuum. This indicates that the motion of the “hydrogen–down” H atoms is restricted to some degree, but does not provide any information on the origin of this effect. In principle restricted motion can be attributed to either space confinement (repulsion) or an attractive interaction with the substrate. In the present section it is argued that in the case of water chemisorbed on Rh(111) surface it is an attractive interaction between the rhodium and the hydrogen which is to be accounted for these effects. The discussion will first consider the electronic properties of the relevant water molecule (oxygen center O_L2, Fig. 9.2) and then will focus on analyzing the hydrogen motion in the course of the MD simulation.

An indication for bonding between the molecule and the surface can be obtained through an analysis of the electronic properties of the water molecule and the corresponding distribution of the electron charge. Comparing the clean surface with the substrate–adsorbate system, it is noted that there is an increase in the electron density in the region between the hydrogen atom H_2 and the underlying Rh_2, indicating formation of a bond between the two atoms (Fig. 9.3a). This data is further explored using the local electronic properties of the central O_H2 oxygen atom (Fig. 9.5). Following the same procedure introduced in the previous section, a defect in the rhodium surface is introduced by removing the underlying Rh_2 atom. The 1b1 MO is the lone electron pair
9.2. Results and Discussions

Figure 9.5: Local density of states of the O$_{L2}$ oxygen atom (solid line) and the underlying Rh$_2$ rhodium atom (doted line) in the case of defect–free Rh(111) surface (left panel) and the defect Rh(111) surface with the underlying Rh$_2$ atom removed from the surface (right panel). The Fermi level of the substrate is presented with a horizontal dashed line. The LDOS in the left and right panels are aligned to match the positions of the 2a$_1$ molecular orbitals.

of the O atom, however the 3a$_1$ is a “true” molecular orbital composed of oxygen and hydrogen atomic orbitals. This means that the interaction with the surface can potentially affect the stability of the molecule and the OH bonds in particular. The comparison of the local density of states of the oxygen atom indicates that in the defect–free system (Rh$_2$ present on the surface), both 3a$_1$ and 1b$_1$ MOs are broadened. In the present case however, the extent of the broadening is quite small compared to the O$_{L1}$ molecule (Fig. 9.4). This suggests that the interaction with the surface is much weaker compared to the interaction through the oxygen atoms.

In view of the above discussion, three different types of hydrogen atoms can be considered in the system: (a) “free” hydrogen atoms pointing towards the vacuum (H$_3$ in Fig. 9.2), (b) hydrogen atoms taking part in a hydrogen bond with a neighboring water molecule (H in Fig. 9.2), and (c) “free” hydrogen atoms pointing towards the surface (H$_2$ in Fig. 9.2). In search for a confirmation of the attractive interaction between the hydrogen and the rhodium atoms, the MD simulation data (see Chapter 8) is examined in terms of the vibrational power spectrum of the three types of hydrogen atoms. As seen in Fig. 9.6, the H$_3$–type atoms pointing towards the vacuum are characterized with a well defined peak in the power spectrum at around 3750 cm$^{-1}$. This peak is identified as the OH stretch vibration. The corresponding peak for the H$_2$–type atoms is much broader and shifted towards lower frequencies. This indicates that the respective OH bond is weakened compared to the OH bond pointing towards the vacuum and this is due to the presence of the metal.
Figure 9.6: Computed vibrational power spectrum of the hydrogen atoms: (a) “free” H atoms pointing towards the vacuum region (H₃ in Fig. 9.2), (b) H atoms taking part in hydrogen bonds with neighboring water molecules (H in Fig. 9.2), (c) “free” H atoms pointing towards the metals surface (H₂ in Fig. 9.2). The raw velocity autocorrelation data was filtered using a Blackman window in order to smooth the power spectrum.

[Note: The power spectrum is computed using four statistically independent blocks of MD data, as discussed also in Chapter 8, and is therefore regarded as quite representative for this system in its numerous conformations.] Based on this result it is concluded that there exists a weak attractive interaction between the hydrogen and the rhodium atoms.

9.3 Summary and Conclusions

The averaged local electronic density of states at the site of the oxygen atoms display three principal peaks, with the peak closest to the Fermi level being a superposition of 3a₁ and 1b₁ molecular orbitals of water. This result is also in good (qualitative) agreement with the experimental data. The analysis of the electronic structure indicates an electron charge transfer from the water molecules towards the surface, which results in the reduction of the work function of the system.

A rather interesting result is the existence of an attractive interaction between the surface rhodium atoms and the hydrogen atoms of the H₂O molecules from the second L2 layer. Although the interaction is relatively weak, the computed power spectrum indicates that it is sufficient to alter the dynamics of the hydrogen motion and should not be disregarded in a proper description of the system.
Chapter 10

Liquid Water/Metal Interface

This Chapter considers a model for the liquid water/metal interface and discusses its applicability and limitations. Molecular dynamics simulations starting from two different configurations are presented and the structure of the interfacial water is discussed in comparison with the results for the bilayer adsorbed on the metal surface (Chapter 8), experiment and previous classical and \textit{ab initio} MD results.

10.1 Computational Details

The \textit{ab initio} MD simulations were carried out using a 3-layer Rh(111) slab and a \((2\sqrt{3} \times 2\sqrt{3})\) R30° surface unit cell (12 surface metal atoms) with lattice surface vectors of 9.43 Å. The size of the unit cell in the direction perpendicular to the surface was set to 22.3 Å. Two different starting configurations were considered: The first configuration (i) was constructed using four perfect “up” bilayers as found for 2/3 water coverage of Rh(111) surface (Chapter 7) stacked on top of each other along the surface normal. For the second configuration (ii) a stack of four “down” perfect bilayer configurations was used. The two structures differ in the polarization of the interface. Equilibration MD runs with velocity scaling were performed for 1.5 and 2.8 ps starting from (i) and (ii), respectively. Statistical data collection was performed for 4.5 ps using either of the equilibrated configurations. The time step for the simulations at a mean temperature of 300 K was set to 0.5 ps. No constraints relating the positions of the metal atoms or the geometry of the molecules were applied. For the electronic structure part of the calculation a cutoff of 325 eV for the plane wave basis set and Γ-point for the integration of the band energies were applied.
10.2 Model of the Interface

The liquid water/metal interface has been studied extensively using classical molecular dynamics and experimental techniques. It has been shown that interfacial water inherits the translation symmetry of the substrate and the interface is characterized with formation of water layers extending up to about three molecular diameters from the surface [see for example Toney et al. (1994)]. In general the system can be modeled using either orthorhombic (orthogonal) or hexagonal unit cells. If a sufficiently large unit cell is used, the type of the unit cell should not matter for the simulation results as the periodic boundary conditions of a large unit cell will not affect to a great extent the structural properties of the system.

Using ab initio MD methods, it would be infeasible computationally to employ a large unit cell and the simulations are often limited to using relatively small unit cells. Restrictions apply not only to the size of surface area, but also to the thickness of the water adlayer. One of the problems related to the size of the unit cell is the imposed translational symmetry. In Chapters 5 and 6 of this thesis it was established that for bulk water and water slab small cubic, respectively orthorhombic unit cells result in a reduced mobility of the molecules, but the predicted orientational distribution at the liquid water/vapor interface is in reasonable agreement with experiment. A hexagonal substrate (metal surface), however, presents us with a new challenge. It is known that ice Ih forms a hexagonal crystal structure. An MD simulation employing hexagonal periodic boundary conditions can potentially result in a “frozen” structure, particularly in the case of small unit cells. This strongly suggests the use of unit cells which are large enough to “accommodate” both the interface and an adjacent bulk–like liquid water medium. Considering today’s computing resources, this goal can only be achieved if classical molecular dynamics techniques are employed. However, the ab initio MD simulations suggest that the electrostatic interactions play an important role in this system (Chapter 8). The electrostatic interactions are related to the polarizability of the molecules and the charge transfer, and although empirical schemes accounting for these effects have been developed, a preferred choice for the description of the system is the ab initio electronic structure calculation. Moreover, many of the classical interaction potentials include only a repulsive component for the metal–hydrogen interactions. In contrast, as discussed in Chapter 9, the ab initio calculations suggest that there exists a
10.2. Model of the Interface

(weak) attractive rhodium–hydrogen interaction.

Depending on the goal of the simulation and the properties being considered, one may prefer the classical MD schemes or the \textit{ab initio} method. This project aims at modeling the detailed microscopic and electronic structure of the water/metal interface. Therefore, in the present work \textit{ab initio} MD methods are employed. It is however acknowledged that this approach is not problem–free and the current Chapter considers the limitations of the \textit{ab initio} MD scheme and particularly those related to the type and size of the unit cell. [The accuracy of the used exchange–correlation density functional, pseudopotentials, and the 3–layer metal slab have already been discussed in the previous chapters.]

Several factors determine the choice of the simulation unit cell (type and size) while using an MD code employing three dimensional periodic boundary conditions. For example, a hexagonal unit cell satisfies the assumption that the water adlayer near the metal inherits to some extent the translational symmetry of the surface, but it is also possible to employ an orthorhombic unit cell which will also be consistent with the \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure. However, a hexagonal unit cell is a preferred choice compared with an orthorhombic unit cell as it does not introduce directional anisotropy. For this reason in the present work, the simulations of the (liquid) water/metal interface were performed using a hexagonal unit cell.

Considering the size of the unit cell in the direction perpendicular to the surface, water adlayers can be placed near one of the surfaces of the metal slab leaving a vacuum layer between the other surface (from the translational image in the neighboring cell) and the water slab. Alternatively, the size of the cell can be chosen in a way, that the volume enclosed between the original metal layer and the periodic image matches the volume of the water slab placed in between. In the latter case there are two water/metal interfaces per unit cell. Although the two–interface system may seem more attractive in view of the amount of statistical data collected from a single MD run, it is also the more difficult to perform. Because the volume needed to accommodate the water slab is not known in advance (the structure of the interfacial water can be subject to reconstruction compared to the bulk phase), the MD simulation should account for the pressure in the system using for example an \textit{NPT} ensemble. However, as the \textit{ab initio} MD simulations are computationally expensive and can be performed using only a small number of molecules, even an \textit{NPT} simulation may not result in a “true” bulk region in the middle of the water slab (recall that the experimental data suggests at least three water layers adjacent to the interface are affected by the presence of the metal
surface). Therefore in the present work the less demanding approach of “one interface per unit cell” was used employing four water layers near the metal surface and a thin vacuum layer between the molecules and the second metal surface.

As mentioned above, two starting conformations of the water slab, derived from the “up” and “down” perfect bilayer structures, were used. Initially the water layers were placed at separations of around 2.8 Å. In the course of the equilibration runs, these initial structures expanded into the vacuum (Fig. 10.1) to an estimated density of the water slab on the order of 0.85 g·cm$^{-3}$. This low density is attributed to the small unit cell and the reduced number of conformations of the slab. The expansion also implies that molecules from the water slab, which were originally adjacent to the vacuum layer may now interact with the other metal surface. This interaction will also contribute to the total energy of the system. It is therefore unreasonable to compare the relative stability (energies) of the structures obtained using the two different starting conformations as from the present results. However, because this “new” interface is four water layers apart from the “main” interface (Fig. 10.1) and only part of the molecules at the “new” interface interact with the metal surface, it is assumed that it will not affect strongly the properties of the original water/metal interface.

In contrast to the MD simulations of bilayer adsorbed on Rh(111) surface (Chapter 8), the “up” and “down” starting configurations followed different evolutionary paths in the course of present simulation. While the “up” configuration, which is characterized by the oxygen atoms being closer to the surface, retains its original conformation, the molecules in the “down” starting configuration are subject to reorientations. Comparing the distribution
functions along the surface normal (Fig. 10.1) and the spatial distribution functions (Fig. 10.2), note that the simulation starting from the “up” configuration results in well defined peaks corresponding to the oxygen and hydrogen atoms. This indicates a frozen ice–like structure. The evolution of the “down” configuration, which is characterized by the hydrogen atoms being closer to the metal atoms, meaning that initially the water molecules are weakly bonded to the surface, indicates a reconstruction of the water slab. The distribution functions display much broader peaks compared to the “up” structure with the final conformations being different from the initial structure (the orientation of the molecules will be considered in the next section). However, even this simulation could not reproduce the experimentally observed three layers structure of the interface with the peak corresponding to a fourth layer expected to vanish in a bulk–like phase. This can be attributed to the highly reduced mobility of the molecules due to space confinement and imposed translational symmetry - an effect, which was already observed for the water/vapor interface. In Chapter 6 it was shown that in spite of the reduced mobility of the molecules the orientational distribution of water at the water/vapor interface is still in reasonable agreement with experiment and previous classical MD simulations. It was concluded that a simulation of water/metal interface could in principle
produce acceptable results for the orientation of the molecules provided that the conditions of the simulation allow the molecules to reorient. While this is obviously not the case for the “up” configuration, the simulation starting from the “down” configuration results in a reorientation of the molecules and therefore can be regarded as liquid–like as far as the orientation of the molecules is concerned. For this reason in the next section these two simulations will be referred to as the “ice layer” and “liquid layer”, respectively. The disagreement with experimental data for the structure of water further away from the surface indicates that from the present results only the layers closest to the surface may be considered as meaningful. Therefore in the next section only the structure of the first two water layers at the “main” interface is examined with the rest of the water molecules regarded as a surrounding medium, which mimics to some degree the true bulk water environment.

10.3 Results and Discussions

As mentioned above, the two simulations display different distribution functions and orientations of the molecules with respect to the metal surface. The “up” starting configuration, which results in an ice–like structure, retains its original conformation. In this simulation, the structure of water at the interface resembles the perfect “up” bilayer with four oxygen atoms per unit cell in close contact with rhodium atoms (Fig. 10.3, the peak in the oxygen distribution function at around 4.8 Å from the middle of the metal slab) and other four further away (peak at around 5.7 Å). However, in contrast to the perfect bilayer, the rhodium surface is subject to relaxation in terms of the positions of the underlying metal atoms in the direction perpendicular to the surface. A relaxation of similar character is also observed for the simulation starting from the “down” configuration. In the latter case the number of oxygen atoms in close contact with metal atoms is around 2.2 per unit cell with the other 5.8 being in the second (broader) sublayer at around 5–7 Å above the middle of the metal slab. The layer at around 8–10 Å appears also broader in the “liquid layer” simulation compared to the “ice layer”. Using Car–Parrinello MD on water/Ag(111) interface Izvekov and Voth (2001) reported that the water layer closest to the surface displays only a single peak. The discrepancy between the present results and the Ag(111) results is attributed to the difference in the lattice constants of the two metals (3.85 and 4.09 Å FCC lattice constants for Rh and Ag, respectively). Although the surface “coverage” in the Rh and Ag simulations is comparable, in the present case a formation of a bilayer–like structures is forced due to the smaller distance between the top adsorption
10.3. Results and Discussions

Figure 10.3: (a) Number densities of rhodium (dashed line), oxygen (solid line), and hydrogen atoms (dot-dashed line) along the surface normal; \( z = 0 \text{ Å} \) is in the middle of the 3-layer slab. (b) Cross-section of the oxygen and the underlying rhodium atom number densities. For comparison the cumulative rhodium number density is also given in the left part of the subfigure, rotated on 90°. The isolines are defined as \( 2^n \times 10^{-1} \text{ Å}^{-2}, n = -2, -1, \ldots, 4 \), starting from the outer curve. (c) Cross-section of the hydrogen and the underlying rhodium atom number densities. The isolines are defined as \( 2^n \times 10^{-1} \text{ Å}^{-2}, n = -3, -2, \ldots, 4 \), starting from the outer curve.

sites of the surface. It has to be mentioned that the Ag(111) simulation of Izvekov and Voth (2001) could not reproduce the experimental data of a three layer structure of the interfacial water (Toney et al., 1994). Although layering is present in the current simulation, it must be acknowledged that the spacing between these layers may be too high. As mentioned above, this leads to a decrease in the density of the overlayer and is attributed to the limitations of the model due to the small unit cell. It is also possible that the result is influenced by the starting configurations and therefore the exact spacing between the layers situated at 4–6 and 8–10 Å remains an open question.

Considering the hydrogen distribution function (Fig. 10.3), note that in the “liquid layer” simulation the shortest Rh–H distance is also on the order of 2.3 Å, comparable to the Rh–O separation. The structure of the first overlayer in the “liquid layer” simulation is in fact similar to the structure of a single water bilayer adsorbed on the surface (Chapter 8). The cross section of the position of the central oxygen atom and the orientation of the OH bond indicates that the sublayer at 5–7 Å above the middle of the metal slab is in a way a mixture of “up” and “down” water molecules (Fig. 10.4). In contrast, the “ice layer” simulation displays only “up” configurations. This is also reflected in the dipole moment distribution functions (Fig. 10.5). The
Figure 10.4: Number densities of rhodium (dashed line), oxygen (solid line), and hydrogen atoms (dot-dashed line) along the surface normal: (a) “ice layer”, (b) “liquid layer”; z=0 Å is in the middle of the 3-layer metal slab. Cross-section of the oxygen number density and the orientational distribution of the corresponding OH bonds: (c) “ice layer”, (d) “liquid layer”. The isolines are defined as $2^n \times 10^{-1} \text{Å}^{-1}$, $n = -3, -2, ..., 3$, starting from the outer curve.

Figure 10.5: Number densities of rhodium (dashed line), oxygen (solid line), and hydrogen atoms (dot-dashed line) along the surface normal: (a) “ice layer”, (b) “liquid layer”. The z=0 Å is in the middle of the 3-layer metal slab. Cross-section of the oxygen number density and the orientational distribution function of the dipole moment of the corresponding molecule: (c) “ice layer”, (d) “liquid layer”. The isolines are defined as $2^n \times 10^{-1} \text{Å}^{-1}$, $n = -2, -1, ..., 3$ starting from the outer curve.
“ice layer” clearly indicates orientation of the water dipoles towards the water phase at an average angle with the outward surface normal on the order of 58 and 56° for the first (4–6 Å) and second (8–10 Å) adlayers, respectively. For the “liquid layer” the average angles are 85 and 81°, respectively. The latter closely resembles the result for a bilayer adsorbed on the surface. However, it is noticeable that compared to the single bilayer, in the present “liquid layer” simulation the structure of interfacial water is more rigid, resulting in the sharper peaks in the dipole moment distribution function cross-section with the position of the central oxygen atom. This indicates that the reduced mobility of the molecules at the interface is a combined effect of the interactions with metal atoms and water molecules from the second overlayer.

It has to be mentioned that the simulation results for Ag(111) reported by Izvekov and Voth (2001) indicate orientation of the dipole moment towards the water phase at a maximum in the distribution function of around 60°. In contrast, the result from the present “liquid layer” simulation suggests a small contribution of the water molecules to the total dipole moment. This is in agreement with earlier classical molecular dynamics studies (Spohr, 1989).

10.4 Summary and Conclusions

The \textit{ab initio} MD simulation showed that the dynamical properties of a model for the liquid water/metal interface may depend crucially on the choice of the starting configuration. The results can be considered representative only if the conditions of the simulation allow the molecules at the interface to reorient. A determining factor for the mobility of the molecules is the interaction with the metal surface and the second adlayer. The present “liquid layer” simulation confirms the previously established result concerning the importance of the electrostatic interaction for the structure of the interface. It is noticeable that the results of the MD simulation of a single bilayer adsorbed on the Rh(111) surface are in good agreement with the present results for the distribution functions of the adlayer closest to the surface. Both simulations indicate that around 2.2–2.5 oxygen atoms per unit cell (12 Rh atoms on the surface) are in close contact with metal atoms at a distance on the order of 2.3 Å. The relaxation of the metal surface in the present simulation supports the conclusion for interactions between the water molecules and the metal primarily through the oxygen atoms.
Liquid Water/Metal Interface
This Chapter presents an *ab initio* study of the structure and dynamics of surface bonded hydroxyl in an aqueous environment. The exchange rate and the apparent diffusion of OH on the surface through a Grotthus-like mechanism is discussed. The employed model has zero total charge, however the hydroxyl on the surface can be regarded as an OH$^{-}$ due to electron charge transfer from the metal to the 1$\pi$ orbital of the OH [see for example Koper and van Santen (1999)].

11.1 Computational Details

This simulation was performed using a 3–layer Rh(111) slab and one adlayer of OH/H$_2$O adsorbates. A $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ surface unit cell of length 9.43 Å was used, consistent with the bulk FCC lattice parameter for Rh of 3.85 Å as computed with VASP. The length of the unit cell along the $z$-axis perpendicular to the surface was 19 Å. Adsorbed layers of OH/H$_2$O were considered on both sides of the Rh(111) slab. The statistical results presented here are averaged data from the two surfaces.

The startup configuration of the simulation was created using a configuration from the previous molecular dynamics run of pure water layer on the Rh(111) surface in the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ surface unit cell (Chapter 8). One of the water molecules close to the surface was “stripped” off its two hydrogen atoms, leaving behind an oxygen atom. By doing this one takes advantage of the high activity of the oxygen on the surface to react with a neighboring H$_2$O
and produce OH. It has to be mentioned that the MD simulation of pure water on the Rh(111) surface keeps the oxygens from the water molecules approximately on top of the Rh atoms. Thus, the newly “created” oxygen atom in the startup configuration of the current simulation is also on top and probably more reactive compared to an oxygen adsorbed in the hollow or bridge sites.

The molecular dynamics simulation at a mean temperature of 310 K was performed using a time step of 0.5 fs. Although experimentally water desorbs at around 180 K, the H$_2$O/OH adlayer does not desorb during the MD simulation as the simulation time is very short. The high temperature of 310 K was chosen in order to speed up the equilibration of the system and to obtain acceptable statistical averages from the relatively short MD run. The equilibration of the initial configuration was performed for 1 ps followed by statistical data collection for 3.5 ps. A cutoff of 325 eV for the plane wave basis and only the Γ-point for the integration of the band energies were used.

11.2 Results and Discussions

The MD simulation showed that the O atoms on the surface, existing in the initial configuration, are short-lived. In the first stages of the equilibration run each of them reacted in less than 0.2 ps with a neighboring H$_2$O producing two OH on the surface:

\[ O_{ad} + H_2O_{ad} \rightarrow 2OH_{ad} \]  \hspace{1cm} (11.1)

Following this initial reaction the newly formed hydroxyls can take part in a chain of proton exchange reactions with a neighboring water molecule:

\[ OH_{ad} + H_2O_{ad} \rightarrow H_2O_{ad} + OH_{ad} \]  \hspace{1cm} (11.2)

Fig. 11.1 shows snapshots from the molecular dynamics simulation representing the course of events during a proton exchange between neighboring adsorption species. For clarity only the three adsorbed species involved in the process are shown. In the first stage 1→2 (Fig. 11.1) a proton is transferred from a water molecule to a neighboring hydroxyl. The proton hopping from H$_2$O to OH is along the hydrogen bond and is equivalent to an effective transfer of a hydroxyl in the opposite direction. This process can be reversed, restoring the OH in its initial position (configuration 1, Fig. 11.1), or can be continued (stage 2→3, Fig. 11.1), leading to a transfer of the OH to a third site. The latter suggests the possibility of an apparent diffusion of OH on the surface, which is not accompanied by any (long-range) mass transfer of H or O.
11.2. Results and Discussions

Figure 11.1: Subsequent configurations in the chain of proton exchange reactions between neighboring OH and H$_2$O leading to a change in the position of the hydroxyl. The Rh(111) surface is in the $xy$ plane.

11.2.1 Proton exchange rate

Similarly to the case of hydroxyl ions in liquid water (Tuckerman et al., 1995), the proton jump between neighboring oxygen adsorption sites resembles the Grotthus mechanism. However, as discussed below, on the surface the proton exchange rate is higher compared to the bulk phase. The dynamics of the hydroxyl migration on the surface is investigated using the following procedure for determining the OH adsorption site. At each MD step all of the hydrogens are assigned to the closest oxygen. This always results in at least one and at most two H centers assigned to any of the O centers at any time, i.e. after the initial reaction (11.1), the oxygen atom O$_{ad}$ is never restored on the surface. An oxygen atom with only one assigned H neighbor is identified as hydroxyl and its position is defined as the position of the central oxygen atom. This implies that the migration of the hydroxyl from one adsorption site to another will appear as a discontinuous jump in the displacement as a function of the time. As an example, the displacement of one of the hydroxyls is given in Fig. 11.2 (dotted line). Note that a number of proton jumps (for instance those around 1 ps and 1.5 ps) result in the migration of the OH to a
Figure 11.2: Displacement of the oxygen center of a selected hydroxyl from its original position as a function of time. Dotted line is the data from an assignment of the H centers to the closest O center. Solid line is after discarding the proton jumps resulting in short-lived (shorter than 21 fs) hydroxyl species at a particular adsorption site. The two lines overlap except in the regions of “unsuccessful” proton hops, which appear (dotted line) as a migration of the hydroxyl to a neighboring site followed shortly after by a migration back to the original site.

neighboring site, almost immediately followed by migration back to the original site. The life time of this short-lived OH adsorption species is on the order of the O–H stretch and H–O–H bend vibrational motion (the slower bend vibration has a frequency of 1600 cm$^{-1}$, corresponding to a period of around 21 fs, see Chapter 5). As it will be shown below, the local environment of the hydroxyls is characterized by shortened O–O distances. Correspondingly, the migration of the structural defect is accompanied by a rearrangement in the first coordination shell, which is a relatively slow process. This slower response of the environment is responsible for the existence of the short-lived hydroxyls, which can be viewed as an “unsuccessful” proton transfer due to an unfavorable geometry configuration of the new OH adsorption site. Although the proton hopping is relatively easy, the rate limiting step for the process of the migration of OH therefore remains the rearrangement of the local oxygen environment, as it is in bulk water (Tuckerman et al., 1995).

Tuckerman et al. (1995) showed that for a hydroxyl ion in bulk liquid water the proton exchange rate is less than 0.5 ps$^{-1}$. The present simulation of an adlayer of OH/H$_2$O on Rh(111) surface suggests the proton exchange rate is higher at the water/metal interface. In order to estimate the proton exchange rate the unsuccessful proton jumps as defined above are discarded.
Table 11.1: Proton exchange rate. \( t_{\text{min}} \) is the minimum lifetime of a hydroxyl, \( \nu \) is the corresponding frequency of a periodic process with a period of \( t_{\text{min}} \), ER is the estimated proton exchange rate as defined in the text.

<table>
<thead>
<tr>
<th>( t_{\text{min}}, \text{fs} )</th>
<th>( \nu, \text{cm}^{-1} )</th>
<th>( \text{ER, ps}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>9.1</td>
</tr>
<tr>
<td>10</td>
<td>( \approx 3300 )</td>
<td>6.4</td>
</tr>
<tr>
<td>15</td>
<td>( \approx 2200 )</td>
<td>3.5</td>
</tr>
<tr>
<td>21</td>
<td>( \approx 1600 )</td>
<td>3.0</td>
</tr>
<tr>
<td>26</td>
<td>( \approx 1300 )</td>
<td>3.0</td>
</tr>
<tr>
<td>30</td>
<td>( \approx 1100 )</td>
<td>2.8</td>
</tr>
<tr>
<td>40</td>
<td>( \approx 800 )</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Migration of a hydroxyl will only be considered if the new adsorption site has a lifetime longer than some given \( t_{\text{min}} \). In that way it is required that if a proton hopping takes place then the new configuration should last for at least one vibrational motion with a period of \( t_{\text{min}} \). For example for the stretch and bend vibrations of \( \text{H}_2\text{O} \) with frequencies of 1600 cm\(^{-1}\) and higher, which processes is being used as a criterion for the lifetime, the minimum time is \( t_{\text{min}}=21 \text{fs} \) (see also Fig. 11.2, solid line). As seen from Table 11.1 the proton hopping rate between neighboring sites is very high (9.1 ps\(^{-1}\)) if all proton jumps are considered. The actual proton exchange rate leading to a migration of OH estimated after discarding the unsuccessful H jumps is around 3.0 ps\(^{-1}\). Note that there is no dependence of the value of the exchange rate on the frequency \( \nu \) in the interval of 1600–1300 cm\(^{-1}\) (Table 11.1). This range corresponds to the gap in the frequencies between the fast O–H and H–O–H vibrational modes and the slow process of intermolecular O–O motion.

11.2.2 Dynamical and Structural Properties

The procedure for determining the OH adsorption site with \( t_{\text{min}}=21 \text{fs} \) described in the previous section was also applied for evaluating the diffusion coefficient and the structural properties. The (apparent) mean–square displacement (MSD) of hydroxyls was computed using the coordinates of the oxygen atom from OH as representative for the position of the entire group (Fig. 11.3). As can be seen from Fig. 11.3, while there is practically no mass transfer of O or H near the surface, the reaction between OH and \( \text{H}_2\text{O} \) leads to a well–pronounced migration of OH species with an apparent diffusion coefficient of around \( 3 \times 10^{-9} \text{m}^2\cdot\text{s}^{-1} \) (\( N = 2 \) directional degrees of freedom).

The MD simulation showed that the hydroxyls in an adlayer of OH/\( \text{H}_2\text{O} \)
Hydroxyl–Water Coadsorption on Rh(111)

Figure 11.3: Mean square displacement of hydroxyls (solid line), oxygens (dashed line) and hydrogens (long-dashed line); The data is normalized to the number of directional degrees of freedom $N=2$.

Figure 11.4: Local environment of the hydroxyl species.

are approximately lying in the plane of the surface, bonded with hydrogen bonds to the three closest neighbors as shown in Fig. 11.4. The oxygen atoms of all adsorbed species stayed approximately on top of the rhodium atoms. The local environment of the hydroxyl (central oxygen atom $O^*$) is described in terms of two different types of closest neighbors: (i) two “complexing” water molecules (oxygen center $O^c$) with an O–H bond pointing towards the hydroxyl and (ii) a third neighbor with oxygen center $O'$ (see Fig. 11.4). Occasionally one of these neighbors can be the second hydroxyl in the unit cell (around 11% of the simulation time not necessarily sequential), without destroying the
11.2. Results and Discussions

Figure 11.5: Unnormalized $O^* - O^c$ (solid), $O^* - O'$ (long-dashed), and $O - O$ (dashed) radial distribution functions. $O^*$, $O^c$, and $O'$ are the same as defined in Fig. 11.4 and $O$ denotes oxygen atoms which are not centers of OH.

Figure 11.6: Unnormalized $O^* - H$ (solid) and $O - H$ (long-dashed) radial distributions functions. $O^*$, $O^c$, and $O'$ are the same as defined in Fig. 11.4 and $O$ denotes oxygen atoms which are not centers of OH.

3 hydrogen–bonds. The results for the unnormalized radial distribution functions (RDF) (Fig. 11.5 and 11.6) show that $O^* - O^c$ distance of around 2.5 Å is shorter compared to the $O^* - O'$ distance or the $O - O$ separation between the water molecules on the surface. Correspondingly, the hydrogen bond between the hydroxyl and the complexing $\text{H}_2\text{O}$ is much shorter with an $O \cdots H$ distance of around 1.5 Å. It is therefore concluded that the chemisorbed OH can be
viewed as an OH(H$_2$O)$_2$ complex with different hydrogen–bonding properties compared to the other water molecules. [Note: The unnormalized RDF is defined as the probability density of finding an atom of a certain type around a given center at a distance $r$. It is essentially computed in the same way as the (normalized) RDF, except that no normalization factors are applied. This is due to the fact that the thickness and thus the density of the adsorption layer cannot be defined in an disambigous way.]

11.3 Summary and Conclusions

The results for the dynamical properties and the geometry of the hydrated hydroxyl suggest that within the adlayer of OH/H$_2$O on Rh(111) the basic structural unit representing the OH is the OH(H$_2$O)$_2$ complex composed of the OH itself and the two complexing H$_2$O molecules. Similarly to the case of a hydroxyl ion in bulk liquid water, a successful proton transfer, i.e. the migration of the OH, is determined by the motion of the oxygens and the rate–limiting step is the rearrangement of the oxygen centers. The proton exchange rate is around 3.0 ps$^{-1}$, which is higher compared to the 0.5 ps$^{-1}$ found for bulk phase.

The predicted dynamical properties, particularly the high frequency of proton jumps and the fast redistribution of OH on the surface, were computed under quite moderate temperature conditions of around 310 K. While there is no long–range mass transfer of oxygens or hydrogens, the apparent diffusion coefficient of OH on the surface is $3 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1}$. This result suggests that the transfer of OH considered in the light of the proton exchange reaction (11.2) may play a key role in (electro–)catalytic processes on the metal surfaces.
Chapter 12

Concluding Remarks

This thesis has dealt with computational modeling of liquid water and water/metal interfaces. It was shown that an *ab initio* simulation technique, which is commonly used for modeling adsorption processes on metal surfaces, can also provide an acceptable description of liquid water. The predicted properties are in reasonable agreement with previous *ab initio* calculations and experiment and the system displays the expected liquid-like behavior. Based on the results it is also concluded that a good balance between speed and accuracy has been achieved in the implementation of the *ab initio* method.

The advantage of the *ab initio* approach compared to the classical MD schemes is that it does not assume an explicit form of the interaction potentials, which in turn would require an input from experiment or previous calculations. However, it must be acknowledged that the first-principles MD calculations are not free of limitations. Space confinement and imposed translational symmetry of the small unit cells can result in reduced mobility of the molecules. This means that the predicted (self-)diffusion coefficients can be lower than the experimental values. Unfortunately performing *ab initio* MD simulations using larger models would be computationally too expensive. These limitations will apply in general to all *ab initio* MD schemes which are available at the present time.

However, the results presented in this thesis indicate that the reorientation of the molecules is affected to a much lesser degree by the size of the system than the transport properties. The MD simulation of water slab as a model for the liquid water/vapor interface indicates a preferred orientation of the surface water dipole moment towards the bulk phase. In contrast, at the water/metal interface the preferred orientation (in the absence of external field) is on average in the plane of the surface. The analysis of the simulation data for
Concluding Remarks

water/metal interface revealed the formation of bilayer–like structures. It was shown, however, that the microscopic characteristics of the bilayer are more complex compared to the original model proposed by Doering and Madey. It was also found that some of the OH bonds of the water molecules can point towards the metal surface. These conformations create the possibility for an interaction between the metal and the hydrogen atoms, which can potentially affect the stability of the water molecule.

An interesting result, which is in agreement with experiment, is that the water molecules next to the surface possess a metallic-like conductivity due to mixing of local states of the oxygen atoms with the electron bands of the metal substrate. This may be of importance for understanding electron transfer through the interface in, e.g., the scanning tunneling microscopy and electrode reactions.

The description of a variety of (electro-)chemical reactions requires modeling of processes of chemical bonds breaking and/or forming. While this would be extremely difficult to perform using classical interaction schemes, the \textit{ab initio} method can handle in a natural way the complexity of the problem. In this thesis the potential of the first–principles simulations was demonstrated on the example of hydroxyl/water coadsorption on Rh(111) surface, which system is also relevant to numerous oxidation reactions. The successful application of the \textit{ab initio} technique suggests that this kind of simulations will play a crucial role in modeling and understanding processes at the water/metal interfaces.
Bibliography


Appendix A

Comparison between different basis sets and density functionals

In this Appendix comparative calculations of the structural and vibrational properties of water molecule and water dimer in trans configuration are presented. The calculations were performed using the simulation packages Gaussian98, DMol, and VASP employing three different exchange–correlation functionals (PW91, BPW91, and BLYP). The presented data indicates that although the PW91 density functional and the plane wave basis set do not provide the best description of the system (the best agreement with experiment is attributed to BLYP), the results are in reasonable agreement with BLYP and experiment.

Figure A.1: OH bond length in single water molecule (Å)
Comparison between different basis sets and density functionals

Figure A.2: HOH bond angle in single water molecule (cm$^{-1}$)

Figure A.3: Assymetric stretch vibrational frequency of single water molecule (cm$^{-1}$)

Figure A.4: Symmetric stretch vibrational frequency of single water molecule (cm$^{-1}$)
Figure A.5: Bend vibrational frequency of single water molecule (cm\(^{-1}\))

Figure A.6: O–O distance in water dimer (Å)

Figure A.7: Stretch vibrational frequencies of water in water dimer (cm\(^{-1}\))
Comparison between different basis sets and density functionals

Figure A.8: Bend vibrational frequencies of water in water dimer (cm$^{-1}$)

Figure A.9: Intermolecular vibrational frequencies of water dimer (cm$^{-1}$)
Summary

Water is one of the most important chemical substances and polar solvents known to human kind. This thesis deals with the structure and properties of liquid water and water/metal interfaces. The systems are studied employing a computer implementation of the (electron) density functional theory.

Several benchmark simulations are performed in order to assess the accuracy of the \textit{ab initio} scheme. These calculations consider models for the pure bulk water system as well as the liquid water/vapor interface. It is shown that the Perdew-Wang 91 (PW91) exchange–correlation density functional can result in reasonable predictions of the properties of water. Accounting for the limitations of the models the computed structural properties in terms of radial distribution functions are in reasonable agreement with experiment and other molecular dynamics results. These simulations also reveal some of the limitations of the computational setup. Due to the limited size of the unit cells the systems display a reduced mobility of the molecules compared to the experimental data. Unfortunately this is unavoidable as due to the costliness of the \textit{ab initio} technique the use of larger unit cells would be computationally too expensive.

The main goal of this thesis is to investigate the electronic and structural properties of the water/metal interface and to compare with the available experimental data and previous simulations. It is shown that at low coverage water adsorbs with the plane of the molecule approximately in the plane of the surface. At high coverages the water adlayer forms a bilayer–like structure. The orientation of the molecules in close contact with the surface is primarily determined by the interactions with the surface. For the orientation of the molecules which are further away the determining factors are the interactions with the sublayer closest to the metal surface, including electrostatic interactions. It is found however, that in the absence of an external field the average orientation of the dipoles of \textit{all} molecules is in the plane of the surface. An interesting result is the existence of an attractive interaction between the surface (rhodium) atoms and the hydrogen atoms of the water molecules. Al-
though the interaction is weak, the computed power spectrum indicates that it is sufficient to alter the dynamics of the hydrogen motion and should not be disregarded.

Multilayers of water on Rh(111) surface as models for the liquid water/metal interface are also considered. The simulations showed that the dynamical properties of the system may depend on the choice of the starting configuration. The results of a molecular dynamics run can be considered representative for the liquid water/metal interface only if the conditions of the simulation allow the molecules at the interface to reorient. For such a system it was found that the structure of the adlayer closest to the surface resembles water bilayer.

The electronic properties of the system are also examined in view of recent experimental studies using scanning tunneling microscopy (STM). It is shown that the presence of a metal substrate can give rise to local electronic states at the site of the oxygen atoms. These properties explain the apparent metallic conductivity of the adlayer as deduced from the STM experiment.

The hydroxyl–water coadsorption on the metal surface is also considered in this work. Surface–bonded hydroxyl is of importance in numerous electrochemical processes, including surface oxidation and corrosion. In this thesis the structural properties and apparent diffusion of OH on the surface is investigated comparing with previous results for the hydroxyl ion in bulk liquid water. On the metal surface the basic structural unit representing the OH is the $\text{OH(H}_2\text{O)}_2$ complex composed of the OH itself and two complexing water molecules. The migration of the OH on the surface is realized through a process of proton hopping. Similarly to the case of hydroxyl ion in bulk liquid water, the rate–limiting step remains the rearrangement of the solvent environment. Nevertheless, the apparent diffusion of the OH on the surface is relatively high. These results indicate that the OH transfer on the surface may play a key role in (electro–)catalytic processes on metal surfaces.
Samenvatting

Water is één van de belangrijkste chemische verbindingen en polaire oplosmiddelen die de mensheid kent. Dit proefschrift handelt over de structuur en eigenschappen van vloeibaar water en metaal/water grensvlakken. De systemen worden bestudeerd met behulp van een computer implementatie van de (elektronen) dichtheidsfunctionaliteitheorie.

Verschillende testsimulaties zijn uitgevoerd om de nauwkeurigheid van de ab initio methode vast te stellen. Deze berekeningen beschouwen modellen voor zowel puur vloeibaar water, alsmede voor het grensvlak tussen vloeibaar water en waterdamp. Het blijkt dat de zogenaamde Perdew–Wang 91 (PW91) “exchange–correlation” dichtheidsfunctionaliteitgeef tot zeer redelijke voorspellingen van de eigenschappen van water. Rekening houdend met de beperkingen van de modellen, zijn de berekende structurele eigenschappen in de vorm van de radiële distributiefuncties in redelijke overeenstemming met experiment en andere moleculaire dynamica resultaten. Deze resultaten leggen echter ook een aantal beperkingen van de berekeningen bloot. Vanwege de beperkte grootte van de gebruikte eenheidscellen, laten de systemen een lagere mobiliteit van de moleculen zien in vergelijking met experimentele data.

Het voornaamste doel van dit proefschrift is de elektronische en structurele eigenschappen van het water/metaal grensvlak te bestuderen en deze te vergelijken met de beschikbare experimentele data en eerdere simulaties. Bij lage bedekkingsgraad blijkt water parallel aan het metaaloppervlak te adsorberen. Bij hogere bedekkingsgraad vormt de waterlaag aan het oppervlak een bilaag–achtige structuur. De oriëntatie van de water moleculen dichtbij het metaaloppervlak wordt voornamelijk bepaald door de interacties met het oppervlak. Voor de oriëntatie van de water moleculen die verder weg zitten zijn de interacties met de sublaag die het dichtstbij het metaaloppervlak zit, inclusief de elektrostatische interacties, de bepalende factoren. Echter,
in afwezigheid van een elektrisch veld, ligt de gemiddelde oriëntatie van de
dipolen van alle moleculen in het vlak van het oppervlak. Een interessant re-
resultaat dat we gevonden hebben is het bestaan van een attractieve interactie
between de oppervlakte (rhodium) atomen en de waterstof atomen van de wa-
termoleculen. Hoewel zwak, het berekende vibratiespectrum geeft aan dat de
interactie voldoende sterk is om de beweging van de waterstofatomen zodanig
tevveranderen, dat deze niet zomaar buiten beschouwing gelaten kan worden.

Meerdere waterlagen op een Rh(111) oppervlak zijn bestudeerd als model
voor het vloeibaar water-metaal grensvlak. De simulaties laten zien dat de
dynamische eigenschappen van het systeem kunnen afhangen van de keuze
van de beginconfiguratie. De resultaten van een moleculaire dynamica simulatie
kunnen alleen als representatief voor het vloeibaar water/metaal grensvlak
worden beschouwd, als onder de condities van de simulaties de water moleculen
aan het oppervlak zich kunnen heroriënteren. Voor een dergelijk systeem
blijkt, dat de structuur van de laag dichtbij het metaaloppervlak lijkt op die
van een water bilaag.

De elektronische eigenschappen van het systeem zijn ook bestudeerd in re-
latie tot recente experimentele studies met de Scanning Tunneling Microscoop
(STM). De aanwezigheid van het metaal substraat kan aanleiding geven tot
locale elektronische toestanden op de zuurstofatomen. Deze eigenschappen
verklaren de schijnbare metallic geleidingsvermogen van de laag zoals die
uit de STM metingen wordt afgeleid.

Tevens hebben we in dit proefschrift gekeken naar de co-adsorptie van
hydroxyl en water aan het metaaloppervlak. Hydroxyl gebonden aan het opp-
ervlak is een belangrijk intermediair in vele elektrochemische processen, zoals
oppervlakte oxidatie en corrosie. In dit proefschrift zijn de structurele eigen-
schappen en de diffusie van OH aan het oppervlak bestudeerd, in vergelijking
met eerdere simulatie resultaten voor het hydroxide ion in vloeibaar water.
Op het metaaloppervlak is de elementaire structuur van OH een OH(H2O)2
complex, bestaande uit OH en twee complexerende water moleculen. De mi-
gratie van OH over het oppervlak is het gevolg van een proton hopping pro-
ces. Vergelijkbaar met het hydroxide in bulk water, blijft de snelheidsbepa-
lende stap de herschikking van de omringende water moleculen. Niettemin
is de schijnbare diffusie van OH aan het oppervlak relatief snel. Deze resul-
taten geven aan dat OH overdracht aan het oppervlak van belang kan zijn in
(elektro–)katalytische processen aan metaaloppervlakken.
Acknowledgments

First of all I would like to thank prof. dr. Rutger van Santen for giving me the opportunity to work under his supervision on this project. I also thank prof. dr. Gert Jan Kramer for being my second promotor. Dr. Marc Koper is acknowledged for providing me with his extensive expertise in the field of water/metal interfaces and electrochemistry. Marc, thank you for all the very useful discussions without which this thesis would not have come out the way it is now.

I also thank dr. Frédéric Frechard for introducing me into the density functional theory and the VASP program. Dr. Christoph Hartnig is acknowledged for many discussions on the interpretation of the simulation results and the molecular dynamics technique in general.

I would also like to thank dr. Tonek Jansen for discussions on different occasions. All members of the Theory Group are acknowledged for the group meetings we have had throughout the years. The variety and the wide range of discussion topics have always been a source of new ideas for me.

The work on this thesis would not have been possible without the right working as well as social atmosphere in the Laboratory of Inorganic Chemistry and Catalysis at the TU/e, for which I am most grateful to all current and past members of the SKA group and the Theory Group in particular. Special thanks go to Vili and Paul for their friendship.
Publications


4. “Ab initio molecular dynamics simulation of water bilayer on Rh(111)”, Peter Vassilev, Marc T. M. Koper, and Rutger A. van Santen, to be published.
Curriculum Vitae

Peter Vassilev was born on the 27th of August 1973 in Sofia, Bulgaria. After finishing the National Natural Sciences and Mathematics High School with a specialization in Physics in 1991, he entered the university courses of the specialty of Chemistry at the Faculty of Chemistry, Sofia University “St. Kliment Ohridski”. In 1996 he completed the program of the specialization Chemical Physics and Theoretical Chemistry with a M.Sc. diploma work on “Correction for adsorption in single crystal X-ray analysis. Structure of Pb$_5$MoO$_8$”. Beginning of February 1997 he was appointed as a researcher at the Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Sciences. In October 1997 he joined the group of prof. dr. Rutger van Santen at the TU/e in Eindhoven, The Netherlands as an OIO (onderzoeker in opleiding) on the project “Ab Initio Studies of Water at Metal Surfaces”. Since October 2002 he is working as a researcher in the group of prof. dr. Evert Jan Baerends at the Vrije Universiteit in Amsterdam, The Netherlands.