From Oxygen to Oxide: First-Principles Study of Some Key Aspects

Behrooz Razaznejad

Department of Applied Physics
CHALMERS UNIVERSITY OF TECHNOLOGY
GÖTEBORG UNIVERSITY
Göteborg, Sweden 2003
From Oxygen to Oxide: First-Principles Study of Some Key Aspects
BEHROOZ RAZAZNEJAD
ISBN 91-7291-279-0

© BEHROOZ RAZAZNEJAD, 2003

Doktorsavhandlingar vid Chalmers tekniska högskola
Ny serie nr 1961
ISSN 0346-718X

Applied Physics Report 03-8

Department of Applied Physics
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone +46 (0)31-772 8426

Cover: Schematic picture illustrating the different stages in aluminum oxidation. From top left: (i) Charge-density plot for an oxygen molecule adsorbed on the (111) facet of an aluminum surface. (ii) Schematic picture of an oxygen island on aluminum surface. (iii) 3D visualization of the surface-state electron density for the relaxed (001) surface of the metastable κ-alumina.

Chalmersbibliotekets reproservice
Göteborg, Sweden 2003
ABSTRACT

Having important technological applications and interesting fundamental science aspects, oxidation of aluminum has received impressive attention. Technologically, the main reason for the great interest is the fact that the oxide film which forms on aluminum protects the surface against further oxidation and corrosion. From a fundamental point of view, the simple electronic structure of aluminum makes it a prototype system for oxidation. A close interplay between theoretical studies and experiments has provided a proper atomic-scale explanation to many key aspects of aluminum oxidation. However, there are still some unsettled issues, which remain to be solved in the future.

This thesis is a theoretical study of some key aspects of aluminum oxidation. On one hand, adsorption of diatomic molecules on the (111) surface of aluminum, forming the initial stage of aluminum oxidation, is elucidated. On the other hand, a new one-dimensional electron gas (1DEG) is predicted and characterized on the surface of the metastable κ-alumina. First-principles density-functional-theory (DFT) calculations, using the plane-wave pseudopotential method, make the basis for our study and are used as inputs for phenomenological models.

The main objective of the adsorption study is to provide a proper explanation of the sticking behavior and a deeper understanding of molecular chemisorption. The sticking behavior is accounted for in a diabatic charge-transfer model, based on electronically excited states, calculated from first-principles. The latter is achieved by developing a new DFT-extended ΔSCF method. Molecular intermediates are predicted for several diatomic molecules, e.g., O₂, NO and CO, revitalizing concepts as chemical hardness and molecular asymmetry. Such molecular states are apt for molecular trapping, molecular flipping, and abstraction. The latter has been confirmed experimentally for O₂ on Al(111) and explains the huge separation (≥ 80 Å) between thermally adsorbed O-atoms on the same surface. These concerted experimental observations and theoretical studies demonstrate the virtue of electron-structure-trend analysis.

The materials-theory prediction of an 1DEG on the (001̅) surface of κ-alumina is made on the basis of DFT calculations. Furthermore, the Peierls metal-insulator instability of this 1DEG is characterized by means of a tight-binding model, with DFT calculations as input parameters. It is concluded that this 1DEG is metallic over a temperature range of [1,800] K and exhibits a high electrical conductivity, which should make it a very interesting manifestation of a 1DEG.

**Keywords:** density functional theory, plane waves, adsorption, oxidation, potential-energy surface, molecule-surface interaction, one-dimensional electron gas, Peierls instability
LIST OF PUBLICATIONS

This thesis consists of an introductory text and the following papers:

I Adiabatic Potential-Energy Surface of O$_2$/Al(111): Rare Entrance-Channel Barriers but Molecularly Chemisorbed State Apt for Abstraction
Y. Yourdshahyan, B. Razaznejad, and B. I. Lundqvist

II Adiabatic Potential-Energy Surfaces for Oxygen on Al(111)
Y. Yourdshahyan, B. Razaznejad, and B. I. Lundqvist

III Dissociative Adsorption of NO upon Al(111): Orientation Dependent Charge Transfer and Chemisorption Reaction Dynamics
A. J. Komrowski, H. Ternow, B. Razaznejad, B. Barenbak, J. Z. Sexton, I. Zoric,
B. Kasemo, B. I. Lundqvist, S. Stolte, A. W. Kleyn, and A. C. Kummel

IV Initial Sticking of O$_2$ Modeled by Charge Transfer
A. Hellman, B. Razaznejad, I. Zoric, Y. Yourdshahyan, and B. I. Lundqvist

V Trends in Adsorption of Diatomic Molecules on the Al(111) Surface
B. Razaznejad, A. Hellman, and B. I. Lundqvist

VI Hard-Material Prediction of One-dimensional Electron Gas
B. Razaznejad, C. Ruberto, P. Hyldgaard, and B. I. Lundqvist

VII Prediction of a Robust Hard-Material One-Dimensional Electron Gas
B. Razaznejad, C. Ruberto, P. Hyldgaard, and B. I. Lundqvist

VIII Potential-Energy Surfaces for Excited States in Extended Systems
A. Hellman, B. Razaznejad, and B. I. Lundqvist
Scientific publications not included in this thesis:

**Density-Functional Bridge Between Surfaces and Interfaces**

**Goldstone Tensor Modes**
JHEP **9902** (1999) 001.

My contributions to the included publications are the following:

I The project was initiated by YY who started the initial calculations. I have performed half of the calculations, and most part of the analysis, with suggestions and comments from the other authors. The manuscript has been written jointly.

II Same as above, except for an additional section on on-surface diffusion of oxygen atoms, which was provided by YY.

III I started the collaboration with experimentalists, performed all the theoretical calculations and most part of the theoretical analysis, with contributions and comments from BL. The paper has been written jointly.

IV I participated in setting up the diabatic sticking model, making the analysis and conclusions, and also writing the paper. Most part of the calculations have been performed by AH.

V I have performed all the adiabatic calculations, and have participated in making the analysis and conclusions. Most part of the paper has been written by me.

VI The project was initiated by the calculations performed by CR. However, the study of phase-transitions was suggested by PH. I have performed all the calculations and analysis and written most part of the paper, with suggestions, comments, and contributions from the other authors, especially from PH.

VII Same as above.

VIII I have participated in setting up the project, making the analysis and conclusions, and also writing the manuscript. The calculations have been performed by AH.
## Contents

1 **Introduction** 1

2 **Initial Stage of Aluminum Oxidation:** 5  
   **Adsorption of Diatomic Molecules**  
   2.1 **Gas-Surface Dynamics:**  
      Adiabatic versus Diabatic Descriptions 8  
   2.2 **General Description of Sticking** 12  
   2.3 **The Adiabatic Representation** 14  
      2.3.1 **O₂** Dissociation on the Al(111) surface 16  
      2.3.2 **NO** dissociation on the Al(111) surface 18  
      2.3.3 Trend Study 19  
   2.4 **The Diabatic Representation** 20  
      2.4.1 **O₂** Dissociation on the Al(111) surface 24  
      2.4.2 Trend Study 27

3 **Intermediate Stage of Aluminum Oxidation:** 29  
   **Diffusion of Oxygen Atoms**  
   3.1 Clean Aluminum Surface: Test-laboratory for DFT Calculations 31  
   3.2 Abstractive Chemisorption 32  
   3.3 Single-O-Atom Adsorption 33  
   3.4 Island Formation and Diffusion 34

4 **Final Stage of Aluminum Oxidation:** 39  
   **Oxide Formation**  
   4.1 The Metastable \( \kappa \)-Alumina 40  
   4.2 One-Dimensional Electron Gas on The Surface of \( \kappa \)-Alumina 41  
   4.3 Metal-Insulator Peierls Transition 43

5 **Theoretical Methods** 47  
   5.1 **Total Energy Calculations:** The Ground State 47  
      5.1.1 Pre-DFT Theories 48  
      5.1.2 Density Functional Theory 50
5.2 Electronic Excited States ........................................ 57
  5.2.1 Electronically Excited States in DFT ................. 57

6 Conclusions and Outlook ............................. 59

Acknowledgments ........................................ 63

Bibliography .............................................. 65

A The Semiclassical Master Equation .................. 75

B Solutions of the SSH Hamiltonian ................. 79
  B.1 The two-band case ($Q = 2$) ....................... 80
  B.2 The four-band case ($Q = 4$) .................... 81
  B.3 The two-band case ($Q = 8$) .................... 81
Surfaces bear directly on all aspects of our daily life. Some effects of surfaces, such as friction, are macroscopic and encountered physically or through observations everyday, while others are microscopic, controlling catalytic activities and the behavior of electronic devices. The latter has attracted unfathomable amount of research activities worldwide. The knowledge and technology that have come as a result of this research area is what ignited the industrial revolution in nanotechnology and continues to drive the international economy. Computers, flat-panel displays, calculators, watches, and color-TV sets all contain microchips and are examples of surface science in action. The accumulated experience in microscopic surface science has in recent years expanded research possibilities in diverse areas such as biotech, materials science, and environmental science. Not only have improved air-pollution detectors and more efficient medicines come out as a result of these research activities, but they have also deepened our knowledge of atomic scale properties of surfaces. Needless to say, surface science is growing as a research area and also entering other more remote science disciplines. This thesis tries to shed light on a very important phenomena in surface science, namely the oxidation of metal surfaces.

During the years solid-state physics has undergone a very interesting development. A major goal has been to derive atomistic quantum-mechanical descriptions of the macroscopic properties of a solid, such as stability, reactivity, elasticity, specific heat, electrical conductance, optical response and magnetism. Due to the vast number of atoms in condensed matter, about $10^{23}$ in $1 \text{ cm}^3$, however, this is a difficult task. In order to make such a large number of atoms accessible to a theoretical description, efficient theories based on general and physically sound concepts have to be developed. One such method is the Density Functional Theory (DFT), which during the recent decades has become the most spread tool for theorists to study problems related to solid-state physics. DFT allows us to study the ground-state electronic structures of systems consisting of a large number of atoms with a use-
ful accuracy, without any initial information other than the number of atoms and their charges. The common applications concern stability, structure, bond nature, and compressibility of solids and vibration properties of molecules, respectively. It is also very useful for studying the energy landscape for surface processes, such as adsorption of atoms and molecules on metal surfaces. Without powerful computers, however, the application of DFT would be limited to a few simple problems. A combination of manageable and accurate theories, efficient algorithms, and fast computers now makes it possible to study many interesting and complex phenomena, such as metal-surface oxidation, which is a key subject of this work.

For almost any metal, a surface that is exposed to gaseous oxygen forms an oxide film. Famous exceptions are the noble metals, like gold. Often this can be an unwanted process. For instance, corrosion of materials in, e.g., automobiles, easily comes into one’s mind when thinking about oxidation of metal surfaces. However, under controlled conditions, oxidation has an enormous practical importance. For instance, thin oxide films that are formed as a result of the direct interaction between the gaseous oxygen and metal surfaces, are widely used as catalysts, sensors, dielectrics, and corrosion inhibitors. For the latter purpose, certain metals including aluminum and rhodium are used, as they form protective oxide layers which passivate their surfaces, inhibiting further oxidation and corrosion.

To understand this is the main motivation for studying the oxidation of aluminum. In addition, aluminum is abundant on earth, and the simple but yet versatile electronic structure of the aluminum surface makes it a model system for oxidation. Despite large amounts of scientific effort over the years, the microscopic mechanisms governing the onset, promotion, and termination of aluminum oxidation are largely unknown. The unique features of the Al(111) surface were for the first time described by Gartland in 1977. Since then there have been many attempts to understand the key steps in the oxidation process, including dissociative adsorption of the O₂ molecule on the surface, migration of the oxygen atoms on the surface and into the bulk, and formation of the stoichiometric aluminum oxide (Al₂O₃). These attempts have raised several controversial issues within each of the different stages of aluminum oxidation.

The initial stage of this process, which basically concerns dissociation of oxygen molecules and adsorption of oxygen atoms on the bare surface, is one of the common model systems for molecule-surface interactions and dynamics. As a scientific problem it has been picked up and left unsolved many times by prominent scientists. Today, when surface science has reached the level of detailed quantitative comparisons between theory and experiment, it might seem surprising that in such comparisons there are still some unsettled key dynamics issues, highlighted in this Thesis. The most puzzling observation concerns the dissociative sticking probability. For thermal molecules, it is very low, $s_0 \approx 10^{-2}$. With increasing translational energy of the incoming oxygen molecule the sticking probability grows successively to a value near unity.²

The first theoretical explanation of the measured sticking probability is given in this Thesis. This is achieved by proposing a model, which combines knowledge
from different areas of physics and chemistry. In this model the charge-transfer concept is identified as the key ingredient in the dissociation process, and the motion of the molecule is described along the diabatic potential energy surface. The latter is obtained by developing a new method, which is based on DFT and can be used to account for excitations in physical systems of many kinds. The robustness of our O₂ sticking model is tested and generalized by supplementary trend studies of F₂, NO, CO₂, and N₂ adsorption.

The intermediate stage of aluminum oxidation has also attracted large amounts of experimental and theoretical work. It involves formation, growth, and motion of oxygen islands on the surface. Most interesting are the scanning-tunneling-microscope (STM) results on the fate of the oxygen atoms after dissociation and formation of the oxygen islands. Results in early STM experiments have once been given the remarkable interpretation that after the dissociation of a thermal molecule the two oxygen atoms on the Al(111) surface should be separated by at least 80 Å.³, ⁴ This has been shown theoretically impossible,⁵ and the dilemma is resolved by the experimental observation that dissociation occurs via abstraction, i.e. the emission of one oxygen atom.⁶ The abstraction mechanism is given theoretical support by our adiabatic calculations.⁷, ⁸ The idea is that, in its approach to the surface, at some stage, the O₂ molecule is oriented perpendicular to the surface or is making a small angle to the normal. One of the oxygen atoms should be adsorbed near the point of impact, while the other atom should be repelled or transfer along the surface over a large distance and even leave the surface. This abstraction alone cannot account for the growing oxygen islands, however. To identify all the mechanisms, responsible for the latter observation, remains as a challenge for future studies.

The final stage of aluminum oxidation includes the penetration of adsorbed oxygen atoms into sublayer sites and formation of the oxide film. Experimentally it has been observed that oxide starts to form at a coverage of 0.2 monolayer of chemisorbed oxygen and at the border of oxygen islands.³, ⁴ In addition, diffusing surface aluminum atoms, chemisorbed oxygen atoms, and oxidic oxygen coexist on the surface. For the oxide formation one proposed mechanism is the place-exchange mechanism, during which the chemisorbed oxygen atom and the underlying aluminum atom change places. The activation barrier for this process is huge, however, requiring large amounts of energy.³, ⁴, ⁸, ⁹ Whether the place-exchange process occurs or whether there are other mechanisms promoting the oxide formation is not elucidated here. Under atmospheric pressure and at room temperature, Al₂O₃ forms a vitreous or ”glassy” structure. Although it does not show any apparent long-range ordering, the oxide has some local short-range structure.

There are quite a number of different stable and metastable phases of aluminum oxide. In the Thesis the (00̅1) -surface structure of the metastable χ phase is studied. It is seen that this surface is aluminum terminated with the Al atoms lying in zigzag lines on the surface. The electronic structure of the surface indicates that each zigzag Al chain has the character of a one-dimensional electron gas (1DEG), predicting a 1DEG system that extends the list of 1DEG systems with one having interesting properties for future applications.
1 Introduction

The Thesis is organized as follows. In Chapter 2 the initial stage of aluminum oxidation is discussed. The focus is on the adiabatic versus diabatic descriptions of gas-surface reactions in general and $\text{O}_2/\text{Al}(111)$ system in particular. The most important result is the proposed diabatic charge-transfer model, stimulating the development of a simple method for excitation potentials, which accounts for the experimentally observed sticking behavior of $\text{O}_2$ and similar diatomic molecules on the $\text{Al}(111)$ surface.

Chapter 3 gives a detailed discussion of the intermediate stage of aluminum oxidation. The focus is the abstraction mechanism for the $\text{O}_2/\text{Al}(111)$ system, which explains the huge spatial separation of the chemisorbed oxygen atoms at low coverage. The experimental observation of this mechanism together with our theoretical support are discussed in detail. The chapter is ended with some speculative ideas to explain the island formation, which are interesting for future studies.

The final stage of aluminum oxidation is given in Chapter 4. Although this stage is discussed in some detail, the focus is on the predicted 1DEG on the $(00\bar{1})$ surface of $\kappa$ alumina. The metal-insulator phase transition for this system is also discussed.

The theoretical methods used in the Thesis to perform the electronic structure calculations are given in Chap.4. These include DFT for the ground-state calculations, and our extended DFT method to deal with excitations. Finally, Chapter 5 gives a summary of the present work and an outlook for future studies.
The dissociative adsorption of molecules on surfaces contains many interesting physical and chemical phenomena, which have captured the interest of many researchers. One important reason for this interest is the fact that gas-surface reactions have many technical applications, such as corrosion, microelectronics, heterogeneous catalysis, and environmental techniques. Another reason is the strive for fundamental understanding of fascinating processes occurring at the thin interface between atomic, molecular, and solid state physics. In recent years, the appearance of powerful computers and better algorithms, together with the advancement of theoretical models, has made it possible to study more complex and realistic gas-surface systems and even compare the results with the experimental findings. Today it should be possible to follow the behavior of the molecule approaching a surface and understand the true dynamical processes. This understanding might include new physical phenomena and reaction channels.

A molecule colliding with a metal surface can become trapped in a potential well, referred to as adsorption, or scatter directly back into the gas phase. In addition, the molecule can dissociate either directly or by passing an intermediate trapped state. This molecular state might be either a physisorption or a chemisorption state. Physisorption is the weakest form of bonding to a solid surface, an attraction due to the interaction between the dipolar quantum mechanical fluctuations of the induced molecule and surface dipole moments. Hence, a molecule trapped in a physisorption potential well is only slightly perturbed from its gas phase structure. Chemisorption arises when a chemical bond is created between the molecule and the surface. In this case, the strong interactions with the metal will alter the molecular electron structure. Typically, in these states there is a charge transfer between the metal and the molecule. Therefore, during the transition from the physisorption state to the chemisorption state, the electronic structure of the molecule-metal entity is changed.
2 Initial Stage of Aluminum Oxidation:
Adsorption of Diatomic Molecules

The molecule-surface interactions might break the molecular bond, leading to dissociation of the molecule. One mechanism behind the dissociation process is that electrons from the surface are transferred to the antibonding orbitals of the molecule. After dissociation, the atomic fragments might diffuse along the surface or into the substrate. The molecule can however hit the surface and fly back to the gas-phase without being trapped or dissociated at the surface.

A realistic description of reactions at surfaces needs to account for three levels:
(i) A large piece of the multi-dimensional potential-energy surface (PES) has to be calculated, i.e. one from which the forces on all the participating atoms can be determined. Density-Functional-Theory (DFT) calculations are the best known tools to obtain PES’s, and in fact they are the only rather reliable means to handle extended systems from first-principles. However, the present generation of implemented functionals represents approximations to the unknown correct functional, with their shortcomings. As a matter of fact, the huge inhomogeneity provided by the surface can give very unfavorable conditions for their applicability, and it can be argued that surfaces, with their multitude of accurate experimental tools, are important to drive the development of improved functionals. Although the calculation of the PES’s is a hard task and, as mentioned above, still involves a number of inaccuracies, the PES’s are always needed for further theoretical calculations.
(ii) As soon as a sufficiently accurate PES of relevant nuclear degrees of freedom is obtained, the dynamics of the nuclei moving along the PES has to be studied, e.g., by calculating molecular trajectories. This has been done in various approaches from classical trajectories in molecular dynamics calculations to fully quantum-mechanical treatments. For heavy atoms the quantum effects can be neglected and a molecular-dynamics treatment is sufficient.
(iii) The statistics of the dynamics requires a proper treatment. This can be achieved by taking averages over a sufficiently high number of trajectories of particles and wavepackets in classical and quantum treatments, respectively. In our study we focus on point (i).

The most studied case of a gas-surface reaction is the dissociation dynamics of hydrogen molecules on transition metals. One reason for this is the simplicity of the H_2 molecule. Another is its common occurrence in technologically important processes. The first model system, on which Gross et al. applied six-dimensional quantum mechanics, is the adsorption of H_2 on Pd(100). These investigations show surface corrugation to have a big influence on the reaction dynamics, giving steering and steric effects. Furthermore, the energy-dependent sticking behavior of the H_2 molecule is determined. In these studies the electronic excitations are neglected, which is justified, due to the low exothermicity of adsorption of hydrogen molecules on metal surfaces. That electron-hole pair excitations are indeed negligible as a dissipation channel for hydrogen molecules on transition and noble metal surfaces, such as Cu(111), are shown by Brivio et al. This does not need to be true for other more complex molecule-surface systems, however.

In this report we study the dissociative sticking of less simple diatomic molecules, namely F_2, O_2, NO, CO, and N_2, on the simpler Al(111) surface. As de-
scribed in this and the next chapters, there are many reasons for studying these particular systems. The oxidation of metal and semiconductor surfaces plays a central role in heterogeneous catalytic oxidation, e.g., in car exhaust catalysis. The choice of the Al(111) surface is based on its simple electron structure from the theoretical point of view. There exist also a number of puzzling experimental discoveries about the sticking behavior of O$_2$ adsorption on the Al(111) surface. The most remarkable and important experimental results concern the initial sticking probability and the possible existence of a precursor state (physi- or chemisorbed). The experimental studies$^{1,2}$ show that the initial dissociative sticking probability for thermal molecules is very low, $S_0 \approx 10^{-2}$. With increasing kinetic energy of the incoming O$_2$ molecules the sticking probability increases quickly (see Fig. 2.1). In conventional terms, this is an indication of an activated dissociative sticking process.$^{21}$ It has also been reported$^2$ that vibrational excitation of the oxygen molecule enhances the sticking. The results mentioned above might appear a little strange for such an exothermic process (the energy gain for the formation of Al-O bonds is estimated to be about 5 eV per O atom$^{22}$).

To determine whether the dissociation process is a precursor-mediated or a direct process, one can measure the temperature dependence of the initial sticking coefficient. The experimental study by Österlund et al.$^2$ shows no such dependency.

**Figure 2.1:** The initial sticking probability of O$_2$ on Al(111), at normal incidence, as a function of translational energy $E_t$. Open and closed symbols represent experiments with ground-state and mixed ground-state and vibrationally excited O$_2$ molecules, respectively.
which indicates that the process is a direct one. It also indicates that the energy dissipation to the phonon bath of the aluminum surface is of minor importance in activation of the dissociation. However, a recent experimental study\textsuperscript{23} shows a surface-temperature dependence for the sticking coefficient. The existence of such a precursor state is still an open question. It is worth mentioning that the experimental method used in the study by J. Yates \textit{et al.}\textsuperscript{23} suffers from a drawback, as the measurement of the initial sticking coefficient in their method requires approximately 0.15 monolayer chemisorbed oxygen on the surface, which is clearly not the "initial" sticking coefficient.

The fact that surface science still has unsettled key dynamics issues on the prototype reaction between the O\textsubscript{2} molecule and the Al(111) surface is of course disturbing. The main objective of this chapter is to put forward and explain the mechanisms involved in the initial stage of aluminum oxidation, i.e. the adsorption of the O\textsubscript{2} molecule on the Al(111) surface. It has been shown, by our\textsuperscript{7,8,24} and other studies,\textsuperscript{25,25–30} that an adiabatic account cannot provide the basic explanation of the observed sticking behavior. One has then to search for non-adiabatic sources. In this process, however, the adiabatic calculations are of great importance for setting up and understanding the non-adiabatic processes. In addition, the adiabatic calculations have illustrated some new features of the adsorption process, such as the possible molecular chemisorption state, charge-transfer anticipating harpooning, steering effects, and abstraction, i.e. the dissociative decay by emission of one neutral O atom.\textsuperscript{†} Hence, both adiabatic and non-adiabatic processes should be considered in order to fully understand the initial stage of aluminum oxidation. During this study it has become clear that a trend study involving adsorption of different diatomic molecules is of great value in the understanding of oxygen adsorption. For this reason the oxygen study is complemented with those for other diatomic molecules, such as NO, CO, N\textsubscript{2}, which does not only clarify many aspects of oxygen adsorption but also sheds light on many other gas-surface reaction phenomena.

The chapter is organized as follows. In sections 2.1 and 2.2 a general description of gas-surface reaction and dissociative sticking are given. Some important concepts, like gas-surface dynamics, sticking probability, and PES’s, are discussed in some detail. In section 2.3 the adiabatic picture for oxygen dissociation is put forward and compared to the one for other diatomic molecules such as NO, CO, and N\textsubscript{2}. In section 2.4 a diabatic representation is suggested and the sticking behavior of the oxygen studied and compared to some other molecules, as in the adiabatic case.

### 2.1 Gas-Surface Dynamics: Adiabatic versus Diabatic Descriptions

Due to the enormous number of degrees of freedom, the dynamics of surface reactions is not exactly solvable. In order to make a theoretical study of the adsorption

---

\textsuperscript{†}The abstraction mechanism is discussed in detail in the next chapter.
2.1 Gas-Surface Dynamics: Adiabatic versus Diabatic Descriptions

processes of atoms and molecules at surfaces possible, appropriate approximations are needed. In most studies of slow-moving molecules, the motions of the nuclei and the electrons are decoupled. Due to the differences in masses, the nuclei appear static to the electrons and, hence, the electrons generate a potential which governs the nuclear motion. This approximation, which is called the Adiabatic or Born-Oppenheimer approximation, neglects excitations of the electronic system by nuclear motion.

In order to fully understand the adiabatic approximation, one has to study the general spinless Hamiltonian of the whole system with $N$ nuclei of mass $M$ and $n$ electrons. This can formally be written as

$$\hat{H} = \hat{T}_n(\mathbf{R}) + \hat{H}_e, \quad (2.1)$$

where

$$\hat{T}_n(\mathbf{R}) = -\frac{\hbar}{2M} \sum_N \nabla^2_{R_N} \quad (2.2)$$

is the operator of the kinetic energy of the nuclei, and

$$\hat{H}_e = \hat{T}_e(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{ne}(\mathbf{r}, \mathbf{R}) + \hat{V}_{nn}(\mathbf{R}). \quad (2.3)$$

The coordinates of the electrons and nuclei are $\mathbf{r}$ and $\mathbf{R}$, respectively. The terms in $\hat{H}_e$, from left to right, are the kinetic energy of the electrons, the Coloumb electron-electron interaction, the Coloumbic energy between the electrons and the nuclei, and the Coloumbic nucleon-nucleon interaction. Already at this point, it is interesting to note that the electronic matrix elements of the nuclear kinetic energy operator $\hat{T}_n$ can be considered infinitesimally small, because of the mass ratio between electrons and nuclei. This will lead to the separation of $\hat{T}_n$ and $\hat{H}_e$, as discussed in the following.

To solve the time-dependent Schrödinger equation ($i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$), the wavefunctions $\Psi(\mathbf{r}, \mathbf{R}, t)$ can be expanded in a suitable basis set of electronic wavefunctions \{\phi_k(\mathbf{r}, \mathbf{R})\}, according to

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_k \chi_k(\mathbf{R}, t) \phi_k(\mathbf{r}, \mathbf{R}), \quad (2.4)$$

where $\chi_k(\mathbf{R}, t)$ can be considered as time-dependent coefficients. The Schrödinger equation can then be rearranged into a system of coupled equations of the form

$$\hbar \frac{\partial \chi_k}{\partial t} = (\hat{T}_n + \hat{V}_{nn}) \chi_k + \sum_j \left< \phi_k | \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne} + \hat{V}_{nn} | \phi_j \right> + \hat{K}_{kj} \chi_j, \quad (2.5)$$

where the coupling operators $\hat{K}_{kj}$ between electronic and nuclear motions, given by

$$\hat{K}_{kj} = -\frac{\hbar}{2M} \sum_N \left( 2 \left< \phi_k | \nabla_{R_N} \phi_j \right> \nabla_{R_N} + \left< \phi_k | \nabla_{R_N}^2 \phi_j \right> \right), \quad (2.6)$$

9
2 Initial Stage of Aluminum Oxidation:
Adsorption of Diatomic Molecules

depend of the velocities $\frac{\hbar \nabla R_N}{M}$ of the nuclei and the derivative of the electronic states with respect to nuclear position. The first term of the coupling operator $\hat{K}_{kj}$ contains $\nabla R_N$, which causes transitions between electronic states with different angular momenta.\textsuperscript{31}

The Born-Oppenheimer approximation implies that the off-diagonal matrix elements $\hat{K}_{kj}$, which give rise to transitions between different electronic states, can be neglected for slow-moving molecules. In the adiabatic representation, the electronic basis functions $\{\phi_k(\mathbf{r}, \mathbf{R})\}$ are chosen such that the electronic part is diagonalized, i.e.

\[
< \phi_k | \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{e-n} | \phi_j > = \delta_{kj} < \cdots > ,
\]

where $\delta_{kj}$ is the Kronecker delta. The basis functions chosen in the adiabatic representation are referred to as the stationary states or the so-called adiabatic states.

The Schrödinger equation can then be separated into a stationary electronic part and a time-dependent nuclear part:

\[
\hat{H}_e \phi_k(\mathbf{r}, \mathbf{R}) = \varepsilon_k(\mathbf{R}) \phi_k(\mathbf{r}, \mathbf{R}) \quad \text{(2.8)}
\]

\[
[\hat{T}_n + \varepsilon_k(\mathbf{R})] \chi_k(\mathbf{R}, t) = -\frac{\hbar}{i} \frac{\partial \chi_k(\mathbf{R}, t)}{\partial t} . \quad \text{(2.9)}
\]

As discussed earlier, the electronic ground state energy $\varepsilon_k(\mathbf{R})$ constitutes the multi-dimensional PES’s of the surface reaction. Using the adiabatic states leads to the so-called noncrossing rule, which states that two PES’s with the same symmetry may not cross.\textsuperscript{31} It is important to emphasize that the noncrossing rule is a mathematical construction, caused by choosing a particular set of basis functions and not a law of nature.\textsuperscript{31}

Technically, in the adiabatic approximation one solves Eq. (2.8) to obtain the PES $\varepsilon_k(\mathbf{R})$ and then studies the motion of the nuclei on this PES by solving Eq. (2.9). This procedure may not always be adequate, since tunneling of electrons or excitation to non-ground state PES’s might occur. As mentioned in the beginning of this section, the adiabatic approximation is a good approximation for slow-moving adsorbates, i.e. if the interaction potentials do not change rapidly during the surface reaction. This is due to the fact that the coupling terms $\hat{K}_{kj}$ depend on the nuclear velocities and can be neglected for slow-moving particles.

This is a good approximation in many physical process, but there exists a large number of experiments that suggest the existence of non-adiabatic steps.\textsuperscript{30,32,33} The non-adiabatic treatment according to Eq. (2.5) is a formidable task, however. A diabatic description can, in particular as it relies on reasonable physical conditions, thus be useful. A formal approach may use the diabatic representation. The main idea behind the diabatic representation is that in some molecule-surface reactions,\textsuperscript{25,34} when the molecule is in an excited state, one cannot separate the motions of the electrons and the nuclei, but one has to take into account the transitions between the different electronic states along the minimum energy path. In such a representation the off-diagonal matrix elements of the electronic part of the Hamiltonian ($\hat{K}_{kj}$) do not vanish any more and transition between different electronic states may appear.
To describe different electronic states, diabatic states are introduced. Their calculation is not straightforward and the choice of the diabatic states is not unique. Due to these difficulties, a diabatic description normally needs much empirical input in order to achieve good numerical results. In this thesis a new method is introduced to obtain diabatic states theoretically from first-principles. This method is based on an extension of density-functional-theory (DFT) and will be discussed in detail in Chapter 5.

![One-dimensional potential energy curve of Lennard-Jones.](image)

**Figure 2.2:** One-dimensional potential energy curve of Lennard-Jones.

To describe the dissociation of O\textsubscript{2} on the Al(111) surface, both adiabatic and non-adiabatic descriptions have been put forward. The adiabatic and diabatic descriptions of a gas-surface interaction can be visualized by a one-dimensional classical potential energy curve (PEC), shown in Fig. 2.2 and introduced by Lennard Jones.\cite{35} His motivation was to describe the dissociation of H\textsubscript{2} on metal surfaces. The curves in Fig. 2.2 give the total energy of the system as a function of the reaction coordinate, which is the distance z of the particle from the metal surface. The curve labeled (1) shows the PEC for the molecule-surface interaction. The minimum of this curve corresponds to a physisorbed molecular state at the surface. The physical reason behind this minimum is the competition between attractive van der Waals forces and the repelling forces due to the overlap between the molecule and surface-electron orbitals. Curve (2) is the energy-potential curve for the interac-
ation between two widely separated atoms and the surface. The minimum of this curve represents the two atoms being adsorbed at the surface. For the dissociation to occur, the molecule must make a transition from (1) to (2) at K. This is a region where non-adiabatic processes may occur. If the transition at K occurs adiabatically, the crossing is avoided and the interaction follows the dashed line. Physically, this means that the molecules, at each distance from the surface, have enough time to rearrange their electronic system to the surrounding and the transition occurs before the crossing is reached. This could give rise to an activation barrier between the two potential minima. In this case the dissociation is said to be activated and the sticking should increase with increasing kinetic energy of the incoming molecules. However, if the barrier does not exist, the adiabatic process happens spontaneously, i.e. all impinging molecules stick to the surface independent of their initial kinetic energies. In a non-adiabatic process, the system follows curve (1) beyond the crossing and at some point makes a sudden transition to the dash-dotted PEC, which is the adiabatic ground-state described by curve (2) plus an e-h pair excitation. The relaxation to the ground-state may be realized by the emission of a photon or, more likely, by a decay without radiation.

Although the Lennard-Jones model could describe many features of the dissociation process for H\textsubscript{2} on a metal surface, it does not take into account one important issue. When the molecule makes a transition from curve (1) to (2) its bond length is increased by a large amount, a feature that is not included in the one-dimensional Lennard-Jones model. To overcome this problem one extends the one-dimensional potential-energy curve to at least a two-dimensional PES, where the PES is often displayed as a function of the molecular center of mass distance (Z) from the surface and the molecular bond length (R). To fully understand the dynamics of dissociation of diatomic molecules at surfaces, one has to calculate a six-dimensional PES. This is however an almost impossible task, and one calculates just some two-dimensional cuts through this six-dimensional PES.\footnote{A large part of the theoretical study in this report has been based on the careful and accurate calculation of large pieces of the multi-dimensional PES of diatomic molecules on Al(111).}

### 2.2 General Description of Sticking

For a molecule to be trapped at a surface, it must give up some of its energy to the surface. This energy transfer, also called dissipative process, gives rise to either excited lattice vibrations, which has been extensively studied for gas-surface collisions under various conditions,\textsuperscript{36,37} or excited electronic states of the surface, such as electron-hole excitations or spin waves. To quantify the concept of the energy transfer, one usually calculates the \textit{energy loss probability} \( P_\varepsilon(E) \) (The probability that a molecule having initial energy \( \varepsilon \) loses the energy \( E \) to the surface during one passage through the potential well) and also the microscopic \textit{sticking coefficient} \( s(\varepsilon) \)
at zero-temperature limit as an integral of $P_e(E)$ over the energy transfer $E$,

$$s(\varepsilon) = \int_{\varepsilon}^{\infty} P_e(E)dE.$$ \hspace{1cm} (2.10)

Energy conservation implies that, if there is minimum in the PES with a depth of an energy larger than $E$, then the particles leaving energy $E$ to the substrate will stick to it. \(^8\) Hence, the sticking probability tells us how many of the incident particles that are trapped at the surface. It does not only depend on the energy, but also on external parameters, such as the surface temperature, the angle of incidence, and the internal degrees of freedom of the molecule. \(^9\)

When the temperature of our adsorbate-substrate system is not zero, thermally averaged physical quantities have to be defined. Then the adsorption of molecules at surfaces depends on the temperature and one defines the thermal sticking coefficient $s(T)$. This quantity gives the average sticking probability of a gas in thermal equilibrium at temperature $T$. Under the condition of detailed balance, the thermal sticking probability is given by the following equation

$$J_{\text{MB}}^{\text{out}} = s(T)J_{\text{MB}}^{\text{in}},$$ \hspace{1cm} (2.11)

where $J_{\text{MB}}^{\text{out}}$ and $J_{\text{MB}}^{\text{in}}$ are the Maxwell-Boltzmann distributed fluxes of incoming and outgoing particles, respectively. Equation (2.11) shows that the assumption of detailed balance asserts adsorption and desorption to be the same dynamical process, one the time-reverse of the other. In situations where the lattice is strongly perturbed or the adsorption process releases a big amount of energy (exothermic process) making the process irreversible, this assumption can be disputed, however.

There are many different sticking mechanisms that one has to distinguish between. The two general paradigms of sticking are the direct and the precursor-mediated sticking processes. In the first case the molecule might even dissociate through some intermediate states, but the life-times of the molecule in these intermediate states are so short that the molecule does not have time to reside in any of them. In the second case there exist some stable molecular states near the surface and the molecule can be trapped in some of these states for a long time when impinging on the surface. This means that in precursor-mediated sticking the molecule can eventually thermalize in the molecular states and lose memory of the initial sticking conditions. As a result the sticking will be determined by the surface temperature rather than by dynamical variables. One can distinguish between these two mechanisms by measuring the sticking coefficient as a function of surface temperature, noticing that a precursor is required for a temperature dependence. In the case of $O_2$ dissociation on the Al(111) surface there are controversial experimental results about the existence of a precursor-mediated state.\(^2,23\)

\(^8\) In the case of a molecule, it can be trapped at the surface either as a molecule or as separated atomic fragments.

\(^9\) With internal degrees of freedom we mean the rotational, vibrational, and electronic degrees of freedom. In the oxygen dissociation on Al(111) surface it has been reported\(^32\) that these internal degrees of freedom play an important role in the dissociation.
As discussed in the beginning of this section, the internal degrees of freedom have a major role in the adsorption dynamics. In particular, these are the vibrational and rotational degrees of freedom for the molecule. The effect of molecular vibrations on dissociation is evident if molecular beams with the same translational energy but at different temperatures show different dissociation probabilities. This was first shown for the H$_2$/Cu(111) system by Hayden and Lamont$^{38}$ and has an important effect in the case of O$_2$ dissociation on Al(111) surface.$^2$ The rotational degrees of freedom are important in the dissociation process, if some rotational states are more likely to overcome the dissociation barrier. There have been some suggestions$^5$ that molecular orientation must be considered in order to explain the low value of the sticking coefficient for O$_2$ dissociation on the Al(111) surface.

To measure the sticking coefficient, one uses, e.g., molecular-beam experiments. These beams are formed by expanding a gas that flows through a nozzle. The translational energy of the beam can be controlled by changing the temperature of the nozzle. This has, however, some unwanted side-effects, since the population of the vibrational states also changes, when changing the temperature. There exist some experimental methods, such as Raman pumping, where one can selectively overpopulate a particular internal state. A much simpler method to distinguish between the translational degrees of freedom and the internal ones, is to seed the gas under study with another gas that has a different molecular mass. The molecules in the gas of interest are slowed down with a heavier seed gas and speeded up with the lighter seed gas. The translational and the internal degrees of freedom can be distinguished by comparing the result of dissociation for a pure beam with that of a seeded one.

### 2.3 The Adiabatic Representation

The O$_2$/Al(111) system has been confronting the surface science with a number of puzzles. Especially interesting for theoreticians has been the fact that a proper understanding of the initial sticking has been lacking, until now. As mentioned earlier, molecular beam experiments suggest that the dissociative adsorption is activated with a minimum entrance-channel energy barrier of 100-200 meV. Such an activation barrier could in principle be seen in an adiabatic description, using DFT calculations with state-of-the-art functionals. Similar studies on simpler molecule/metal systems, e.g., H$_2$ dissociation on Cu(111),$^{13-19}$ have shown that an adiabatic description is adequate to account for the observed sticking behavior. Furthermore, such calculations are of key importance for further theoretical studies and illustrate the power of DFT for the study of gas-surface reactions. To assess how much can be accounted for in an adiabatic description, extensive first-principles DFT calculations of the multi-dimensional PES of O$_2$ on Al(111) are performed and presented in this Thesis.

Since there might exist different complex trajectories for the O$_2$ molecule ap-
proaching the surface, the work of mapping the PES should be done in a systematic way. There exist some preliminary LDA\textsuperscript{39} and some GGA calculations\textsuperscript{29} for some cuts in the PES, which imply that the oxygen molecule should dissociate without any activation barrier. These studies have been performed only for geometries with the molecule parallel to the surface and can be used for comparisons. In this work we use different versions of GGA for different reasons.\textsuperscript{**} On one hand, the LDA seems to be inaccurate in describing our system. On the other hand, there have been indications of different results with different GGA versions in the very sensitive region of the outer tails of the substrate electron states. The PES mapping, presented here, includes also non-parallel configurations of the oxygen molecule relative the surface, as these seem to be important for the dynamics.

To increase the understanding, it is natural and valuable to look for trends. From a theoretical standpoint, trend studies are easy, in principle. For instance, on can change to molecular neighbors of $\text{O}_2$, e.g., NO. Thereby one has a case with a stronger intramolecular bond. Furthermore, the weakly bond shallow intermediate molecular state predicted by our calculations on $\text{O}_2$/Al(111) might cause some experimental difficulties. Both the local experimentalists and we have in this situation decided to speed up the process by trend analysis. By going from $\text{O}_2$ to NO the number of electrons per molecule is reduced by one unit, which for the free molecule means a reduced number of antibonding electrons, i.e. an increased bond order, and an increased dissociation energy (from 0.4 eV for $\text{O}_2$ to 2 eV for NO). Yet there are great similarities, such as $\text{O}_2$ and NO having similar weights and both being magnetic ($S = 1$ and $\frac{1}{2}$, respectively).

On the Al surface, the bonding can be analyzed in terms of intermolecular bonds, i.e. chemisorption of the constituting atoms, and intramolecular bonds.\textsuperscript{40} It is natural to expect the intramolecular bond on Al(111) of NO to be stronger than that of $\text{O}_2$. To simplify an experimental identification of such a molecular intermediate state, total-energy calculations on NO/Al(111) are also performed in this Thesis.

In addition, understanding the catalytic reduction of nitride monoxide (NO) is of great technological importance. One of the most common and important processes in which one tries to reduce the discharge of nitride monoxide is the car exhaust catalysis. This is due to the fact that NO is one of the strongest oxidizing agents, which can affect air pollution with detrimental effects on global environment. In recent years more stringent air quality regulations have been imposed on automobile manufacturers, which make a detailed understanding of the catalytic reduction of NO even more urgent. To reduce the emission of noxious nitrogen oxides, a number of catalysts, such as Rh, Pd, and Pt, are used in the automotive industry. The adsorption and reactivity of NO on metal surfaces is also important from a fundamental point of view.

The adiabatic trend study is extended by calculating the PES’s for the molecular

\textsuperscript{**}We have used the following functionals: PW91, PBE, revPBE and RPBE. In most parts of the work the first version of GGA (PW91) has been used. Since the other functionals are believed to give more accurate results for molecule/surface systems some of the calculations have been used with these new functionals. The differences in the results are found to be of minor importance.
neighbors of NO, i.e. CO and N₂, on the Al(111) surface. Although CO and N₂ have similar weights as O₂ and NO, their electronic structures are very different. Being “closed-shell” molecules, charge transfer is not a key ingredient in the molecule-surface reaction. As will be discussed later, the adiabatic picture is adequate in describing the sticking behavior and the theoretical and experimental results agree very well.

2.3.1 O₂ Dissociation on the Al(111) surface

The presented adiabatic study includes a thorough investigation of the energetically most favorable entrance channel, an extensive mapping of the multi-dimensional PES, and analysis of the local density of states (LDOS) for the oxygen molecule and the Al(111) surface.

In order to examine the minimum energy path, a damped molecular dynamics method (DMD) is utilized. In this method the PES is mapped in a sequence of configurations \( \mathbf{R}_i \) and from it the forces \( \mathbf{f}_i \) on each atom are calculated. The atoms are propagated by action of these forces for a short time (\( \approx 1 \) fs) to a new configuration \( \mathbf{R}_{i+1} \), for which the PES is calculated. This procedure is repeated until an allowed variation in the forces is reached. Figure 2.3 summerizes the result of these calculations for different orientations of the O₂ molecule with its center of mass (CM) over top, fcc, bridge, and hcp sites.

The DMD calculations show (i) the energetically most favorable entrance channel to be over fcc site, in agreement with SLDA calculations, 39 (ii) energy-barriers to be present in the entrance channel only for some rare conditions (gray circles in Fig. 2.3), without statistical significance, and (iii) the fate of the dissociated O-atoms to be at two adjacent fcc sites, 0.8 Å above the Al surface layer, independent of the initial configurations. The latter result is in agreement with very recent STM results 41 but in contradiction with slightly older ones. 4

In addition to the above-mentioned results, the mapping of two-dimensional PES’s (Fig. 2.4 is an example of such a two-dimensional PES) reveals the existence of a metastable molecular state for the tilted configurations (\( \theta \neq 90 \)). Observation of this molecularly chemisorbed state should not be much harder than the cases of O₂ on Pt(111), 42 and Ag(100), 43 utilizing a He-cooled substrate. This molecular intermediate is apt for molecular trapping and abstraction ††. The latter has been reported for, the F₂/Si system. 44

Calculating LDOS’s is essential in understanding the nature of the dissociation mechanism and the existence of the molecular states. The LDOS of the oxygen molecule near the surface, in the surface-parallel configuration, indicates a down-shift of the minority-spin \( \pi^- \) molecular orbital (MO) resonance, already at \( Z \approx 3.0 \) Å above the aluminum surface. Hence, the \( \pi^- \) MO, which is unfilled in the free molecule, becomes partially filled. This implies electron transfer to this orbital with a concomitant reduction of the spin-magnetic moment. Since this orbital is an anti-

†† The abstraction mechanism is detailed in Chapter 3, when discussing the on-surface oxygen-atom diffusion.
bonding orbital, its down-shift leads to a weakened intra-molecular bond and the
dissociation of the oxygen molecule.

Figure 2.3: Schematic figures for relaxation of an $O_2$ molecule with parallel orientation
($\theta = 90^\circ$) on Al(111) (small and large circles represent O and Al atoms, respectively). The
symbols v and h indicate $\phi = 0^\circ$ and $90^\circ$, respectively. The upper row shows the definition
of our coordinates ($Z$, $d_{O-O}$, $\theta$ and $\phi$). The PEC's along the reaction path are also plotted
for each configuration. The last channel is the only one with an activation barrier, which is
marked with small gray circles for the $O_2$ molecule.

Such a charge-transfer is important in the dissociation of electronegative mole-
cules like Cl$_2$ on alkali metals.\(^{45}\) Since the $O_2$ molecule has a much lower vertical
electron affinity than Cl$_2$, and since the Al(111) surface has a larger work function
than the alkali metals, the charge-transfer occurs only in regions much closer to the
surface, which means that the simple image picture breaks down. This makes the
$O_2$/Al(111) system much more complicated. A thorough analysis of the LDOS for
2 Initial Stage of Aluminum Oxidation:
Adsorption of Diatomic Molecules

Figure 2.4: Cuts through the six-dimensional PES of O$_2$ with bond length $d_{O-O}$, a distance $Z$ above the Al(111) surface on fcc site. The molecule-surface angles $\theta$ are (a) 90° and (b) 0°. The numbers in the equipotential contours are the energy values in eV measured from the energy of totally separated O$_2$ and Al(111) surface.

the oxygen molecule near the molecular chemisorption state reveals that the existence of such a molecular state can be traced back to an electronic Hund’s-rule spin effect that for the very inequivalent O atoms of the non-parallel O$_2$ close to the Al surface is stabilizing the metastable molecularly chemisorbed state. So, a local symmetry breaking causes a spatial spin polarization, which results in a shifted antibonding MO resonance and a strengthened intramolecular bond. For O$_2$ parallel to the surface, on the other hand, the constituting atoms are equivalent, and this mechanism is missing. Thus, the antibonding MO resonance has a more efficient filling, which leads to a direct dissociation of the oxygen molecule.

2.3.2 NO dissociation on the Al(111) surface

Concerted experimental and theoretical studies of NO dissociation on the Al(111) surface$^{46}$ point at a complex dynamics. There are some expected features, such as charge-transfer and molecular chemisorbed states, and novel ones, such as molecular flipping and oxygen-selective abstractive chemisorption.

Molecular-beam experiments show the initial thermal sticking probability to be low for low incident energy, and to grow radically with increasing impingement energy. This behavior of the thermal sticking coefficient resembles the one measured for O$_2$ dissociation on the same surface.$^2$ In addition, it is observed that oriented NO molecules for N end-on collisions exhibit higher sticking probability. Hence, molecular asymmetry for NO highly affect the sticking behavior. However, the most surprising experimental observation is made by Auger electron spectroscopy, showing more adsorbed oxygen than nitrogen at low coverages and on stepped surfaces.
2.3 The Adiabatic Representation

As for O₂, our calculated adiabatic PES’s fail to describe the sticking behavior of NO correctly. However, they indicate the existence of a molecularly chemisorbed state, identified as having a “NO²⁻” electron configurations. Such molecular states for the side-on and N end-on configurations turn to be important to explain the two other experimental observations, mentioned above. In a simple proposed model, the picture that emerges for the NO dissociation is the following: (i) Charge transfer is most efficient for the N end-on orientation for the NO molecule. (ii) Dissociation is unlikely to occur for this channel, since the saddle point for dissociation is at an inaccessibly long bond-length (> 2 Å) and energetically above the vacuum level. (iii) The energy barrier for dissociation is lowered (about 1.6eV) to a value of about 0.4 eV upon a rotation of the NO molecule to an orientation with the molecular axis parallel to the surface (the side-on orientation). (iv) However, the barrier for dissociation with a saddle point at the smallest bond length (1.7 Å) is for an O end-on orientation. Hence, the simplified picture is that the NO molecule approaches the Al(111) surface in the N end-on orientation, initiating charge transfer and the dissociation process, it is stuck in a molecular precursor state and then rotated to the side-on or O end-on orientation and dissociated. The rotation of the molecule during the dissociation process might cause abstractive dissociation near step edges.

2.3.3 Trend Study

The biggest difference between CO and N₂ compared to O₂ and NO is their electronic structures. The former molecules are chemically hard, i.e. they have a large HOMO-LUMO gap. Furthermore, their ground-state is spin compensated. In contrast, the O₂ and NO molecules have open-shell orbitals, which according to Hund’s spin-rule have magnetic groundstates (S=1/2 for NO and S=1 for O₂). This has important ramifications concerning the charge transfer processes being the key process in the molecule-surface interaction. This in turn makes the adiabatic representation adequate in describing the sticking behavior of the CO and N₂ molecules, while for O₂ and NO a diabatic model is presented and discussed in the following sections. Computationally, the difference in the electronic structures for the studied molecules is essential. As NO and O₂ are magnetic molecules, the calculations performed for obtaining the PES cuts are done spin-polarized for O₂ and NO. The spin-polarized calculations are more time consuming and much harder to converge. However, when all the molecules are close to the Al surface, the magnetic moment goes to zero, so spin-polarization effect is important far outside the surface.

Another important issue that concerns the binding of the molecule to the surface is the ordering of the energy levels of σ and π characters. For homonuclear molecules (O₂ and N₂) the binding σₚ orbitals, both spin up and spin down, are lower in energy than the binding πₚ orbitals. For the heteronuclear molecules (NO and CO), on the other hand, the ordering between these two orbitals is reversed. As the binding σₚ orbital is active in chemisorption, NO and CO exhibit stronger binding to the surface than O₂ and N₂.

The calculated adiabatic PES’s for CO and N₂ have some interesting features,
and show that electronic structure of the adsorbate is essential for energy barriers, molecularly adsorbed states, and dissociation. For the CO molecule the PES for the parallel case shows an energy barrier in the entrance channel with a height of 0.3 eV followed by a shallow physisorbed molecular state, a CO neutral state, with a depth of 0.1 eV. After this molecular state, which might be difficult to observe experimentally, the PES is repulsive. In the perpendicular case with the C atom down the PES is similar to the PES for the parallel case, but the position of the molecular state is shifted down, which makes it an "CO\(^-\)" state, and it is 0.4 eV deeper. In the latter case the binding \(\sigma\) orbital of the CO molecule is shifted down in energy and couples strongly to the Al surface electrons. The PES in the perpendicular case with the O atom down is totally repulsive. For the \(\text{N}_2\) molecule there is no molecular state and the PES is totally repulsive in both the parallel and the perpendicular cases.

According to our calculated adiabatic PES’s the \(\text{O}_2\) and NO molecules should stick to the Al(111) surface, independent of their initial kinetic energy, while CO and \(\text{N}_2\) do not interact with the surface. The latter fact that the initial sticking is zero for CO and \(\text{N}_2\), for low and moderate kinetic energies, agrees well with experimental findings.\(^{47}\) Although the experimentally observed sticking behavior of CO and \(\text{N}_2\) is reconciled in the adiabatic representation, it fails to account for the sticking behavior of \(\text{O}_2\) and NO. The rationale for this is that for the latter molecules, which are open-shell molecules, the charge transfer from the surface to the antibonding molecular orbitals is the key ingredient in the dissociation process. Here, non-adiabatic processes with transition between different electronic states should occur. Hence, one should go beyond the adiabatic representation and consider even non-adiabatic processes. This is the main objective of the next section, where a model based on the diabatic representation of the PES’s is introduced which not only explains the experimentally observed sticking behavior for \(\text{O}_2\) and NO but also makes the connection between the adiabatic and diabatic representations more clear.

### 2.4 The Diabatic Representation

The adiabatic calculations, described in the previous section, highlights many interesting gas-surface reaction channels for the \(\text{O}_2/\text{Al}(111)\) system, such as harpooning, molecularly chemisorbed state, and abstraction. Harpooning, i.e. charge-transfer from the electronic states of the substrate to the antibonding \(\pi^+\) resonance of the \(\text{O}_2\) molecule is identified as the key process for the dissociation event of diatomic molecules on simple sp-band metals, such as aluminum. To fully account for the charge-transfer process, two physically important effects should be considered: (i) As the molecular affinity level is downshifted due to the image potential \(U_{\text{im}}\) according to

\[
U_{\text{im}} = \frac{-e^2}{16\pi\varepsilon_0(z - z_{\text{im}})},
\]

(2.12)
where $z_{im}$ is the image plane, it will at some point cross the Fermi level of the surface and make an electron transfer feasible. It is important to note that the image potential, given in Eq. (2.12), breaks down at $z_{im}$. To avoid this singularity of the asymptotic expression, the image potential should be adjusted to a saturated form at the vicinity of the image plane, e.g., the one given by Jennings. (ii) At the same time, due to overlap effects between the electronic states of the molecule and those of the substrate, the width of the affinity level is broadened. This makes the life-time of the unoccupied affinity level (the hole) shorter as the molecule approaches the surface and thereby increases the probability for electron transfer. The two effects, described above, are illustrated in Fig. 2.5 and incorporated in a charge-transfer model referred to as the Nørskov-Newns-Lundqvist model. This model was originally employed on alkali/metal reactions for a quantitative description of the observed photon and exoelectron emission spectra.

The broadening of the affinity level can be described in the time-independent Anderson-Newns model. In this model the Hamiltonian is given by

$$H = H_{\text{subs}} + H_{\text{ads}} + H_{\text{coupling}}$$

(2.13)

Here $H_{\text{subs}}$, $H_{\text{ads}}$, and $H_{\text{coupling}}$ are the Hamilton operators that describe the substrate, the adsorbate, and the coupling between the adsorbate and the substrate, respectively. Assuming that only one level of the adsorbate is active in the bonding, which is the case for the interaction between the hydrogen atom and a metal surface, the different terms in Eq. (2.13) can be written as

$$H_{\text{subs}} = \sum_{k,\sigma} E_{k,\sigma} c_{k,\sigma}^{\dagger} c_{k,\sigma} = \sum_{k,\sigma} E_{k,\sigma} n_{k,\sigma},$$

$$H_{\text{ads}} = \sum_{\sigma} (\epsilon_{a,\sigma} c_{a,\sigma}^{\dagger} c_{a,\sigma} + \frac{1}{2} U n_{a,\sigma} n_{a,-\sigma}),$$

and

$$H_{\text{coupling}} = \sum_{k,\sigma} (V_{a,k} c_{a,\sigma}^{\dagger} c_{k,\sigma} + \text{H.C.}).$$

Here $E_{k,\sigma}$ and $\epsilon_{a,\sigma}$ represent the energy levels of the substrate states $|k, \sigma>$ and the adsorbate state $|a, \sigma>$, respectively (\(\sigma\) being the spin degree of freedom), and $c_{k,\sigma}^{\dagger}$ ($c_{k,\sigma}$) and $c_{a,\sigma}^{\dagger}$ ($c_{a,\sigma}$) their corresponding creation (annihilation) operators. The operators $n_{k,\sigma} = c_{k,\sigma}^{\dagger} c_{k,\sigma}$ and $n_{a,\sigma} = c_{a,\sigma}^{\dagger} c_{a,\sigma}$ are the number operators for the substrate states $|k, \sigma>$ and adsorbate level $|a, \sigma>$, respectively. The quantity $U$ describes the effective Coulomb interaction on the adatom and

$$V_{ak} = V_{ka}^{\dagger} = \langle a | H | k \rangle$$

(2.14)

\(^{1}\)In our calculations, the image plane is defined to be 0.94 Å in front of the jellium edge, which is positioned half a lattice distance (1.20 Å) out from the outermost surface nucleus of the Al(111) surface.
is the coupling matrix element. This Hamiltonian is solved approximately by replacing the two-body operator $n_{\alpha\sigma}n_{\alpha-\sigma}$ by an effective one-body operator, according to

$$n_{\alpha\sigma}n_{\alpha-\sigma} \sim <n_{\alpha\sigma}> n_{\alpha-\sigma} + <n_{\alpha-\sigma}> n_{\alpha\sigma} <n_{\alpha\sigma}> n_{\alpha-\sigma},$$

(2.15)

which is called the Hartree-Fock approximation. It is then shown that the adsorbate resonance width $\Delta(z)$ for this model can be written as

$$\Delta(z) = \pi \sum_k |V_{ak}|^2 \delta(\varepsilon(z) - \varepsilon_k),$$

(2.16)

where $\delta(\varepsilon)$ is the Dirac delta function. It is interesting to mention that the resonance width, given in Eq. (2.16), decays exponentially with increasing $z$. The rationale for this is that the both the substrate, $|k, \sigma>$, and adsorbate states, $|a, \sigma>$, have exponentially decaying wavefunctions.

The one-dimensional PEC’s of Fig. 2.2 illustrate the adiabatic and non-adiabatic filling of the affinity level. In the adiabatic picture the affinity level is filled continuously and the molecule follows the PEC, represented by a dashed line in Fig. 2.2. The rationale for this is that the electronic system, in the adiabatic picture, is always in thermal equilibrium. In the diabatic picture, the affinity level of the molecule will remain empty even after crossing the Fermi level of the surface, and the molecule follows the upper diabatic PEC of Fig. 2.2. In this case, the electron transfer occurs instantaneously, which leads to such non-adiabatic processes as surface chemiluminescence or exoelectron emission.

It was mentioned earlier that the adiabatic picture, where the affinity level of the molecule is filled continuously, does not explain the observed sticking behavior of $O_2$ on Al(111). Since sticking is a dynamic phenomenon, non-adiabatic sources should be searched for. In order to model the charge transfer process in a diabatic picture, we use a one-dimensional master equation, originally suggested by Langreth and Nordlander and later used by Hellberg et al. to describe the charge transfer in the $Cl_2/K$ system. This equation is derived using the time-dependent Newns-Anderson model. Neglecting back donation of electrons from the molecule to the substrate, i.e. considering the tunneling process to be irreversible, and using the semiclassical trajectory approximation, the master equation can be written as

$$\frac{d}{dt}n_-(t) = \tau_{res}^- f(E^A(z(t)))[1 - n_-(t)].$$

(2.17)

Here $n_-(t)$ is the electron population of the molecular affinity level, $f(E)$ is the Fermi-distribution function, and

$$E^A(z(t)) = V_{molecule-metal}^-(z(t)) - V_{molecule-metal}^+(z(t))$$

(2.18)

is the difference between the diabatic PES’s. The resonance tunneling $\tau_{res}^-$ is modeled as

$$\hbar \tau_{res}^- = 2\Delta_0 \exp(-\alpha_{res}|z|) \frac{\rho(E)}{\rho(E_F)},$$

(2.19)

A simple derivation of this master equation is given in Appendix A.
where $\rho$ is the bulk density of states, and $\Delta_0$ and $\alpha_{\text{rez}}$ are two parameters that describe the resonance width as a function of the CM distance.

![Diagram](image)

**Figure 2.5:** A schematic picture illustrating the shift and broadening of the molecular affinity level as a function of distance to the surface $z$. Far outside the surface, the shift is described by the image potential $U_{\text{im}}$, which together with a Jenning’s correction\(^4^8\) describes the shift close to the surface.

There are several assumptions behind the expression, given in Eq. (2.17). These include: (i) The presented model is a one-dimensional (1D) model, where the trajectory of the impinging molecule is approximated by a 1D trajectory ($r(t) = z(t)$). The molecule might be involved in a variety of motions, like translate, rotate, vibrate, temporarily stay in a molecularly chemisorbed state, as the one identified for the O$_2$ and NO molecules in the adiabatic picture, and undergo abstraction. All of these processes involve all degrees of freedom of the molecule and should be taken into account in an extended model. Our model does not take into account this multitude of dynamics in the "inner reaction zone", but focuses on how to get there. (ii) The tunneling rate is assumed to have exponentially decaying dependence on the distance $z$ to the surface. As mentioned earlier, this point is justified by the fact that the wavefunctions of the surface states and the molecular affinity level are exponentially decaying and the matrix elements of this wavefunctions define the tunneling rate. (iii) The occupation numbers $n_e(t)$ are represented by expectation values referring to a macroscopic ensemble of the molecules scattered against the surface. Thus the fractional occupancy of the molecular affinity level $n_e(t)$ should be interpreted as an ensemble average of the occupation.$^{5^3}$

In order to calculate the sticking probability from Eq. (2.17), it is further assumed that the impinging molecule will stick to the surface as soon as one surface electron has been transferred to its affinity level. Such an assumption implies that the
initial sticking probability $s_0$ is equivalent to the population of the ionized molecules and mathematically given by

$$s_0 = n_-(t \to \infty). \quad (2.20)$$

For several molecules, such as $O_2$ and NO, multi-electron tunneling processes are important. For these molecules, quite a number of other events can happen, after the first tunneling event. A second electron can tunnel, which brings the molecular ion to propagate on the diabatic molecule-surface PEC. This is interesting, as our adiabatic DFT calculations have shown the existence of metastable "$O_2^{-2}\$" and "$NO^{-2}\$" chemisorption states.\textsuperscript{8,46} Although the multi-electron tunneling processes together with a more accurate dynamics of the impinging molecule are important in the dissociation processes as a whole and should be included in an extended model, the focus of the following sections is our simplified model study, as it is able to account for the trends in the sticking behavior for diatomic molecules of the Al(111) surface.

### 2.4.1 $O_2$ Dissociation on the Al(111) surface

In any diabatic study of gas-surface systems, diabatic PES’s are required as a first step. In our charge-transfer model, described in the previous section, the most important PES’s for the $O_2$/Al(111) system include the $O_2$/Al(111)-PES and one for $O^-$/Al(111)$^+$, as the sticking is initiated by this first charge-transfer that brings the system from the former PES to the latter one. In this way the modelling of the diabatic PES’s comes into focus. In this thesis two approximate PES accounts are given.

The $O^-$/Al(111)$^+$ PES is modelled by the image potential, where the Jennings saturated form\textsuperscript{48} is included in the vicinity of the image plane. The other PES is much more difficult to obtain. The adiabatic DFT calculations, presented previously, accounts in principle for this PES far outside the surface, where charge-transfer is negligible. However, as the molecule approaches the surface the overlap between the molecular orbitals and those of the surface makes charge transfer inevitable. To computationally prevent this in adiabatic DFT calculations is not an easy task. Here we present two different methods for obtaining the neutral $O_2$/Al(111)-PES. The first one is based on the Thomas-Fermi theory\textsuperscript{56,57} and the other is a new ACSCF-method within DFT that we have developed to calculate diabatic PES’s in different gas-surface system by introducing electron-hole (e-h) pairs. Both the Thomas-Fermi theory and the other method are described in detail in chapter 5.

The $O_2$/Al(111) potential for a chemically inert oxygen molecule consists of the weak but long-ranged van der Waals attraction $V_{vdW}$ and a repulsive part $V_R$ due to the overlap between the Bloch electron states of the metal surface and the valence electrons of the oxygen molecule. At large separation between the $O_2$ molecule and the Al(111) surface there is only the van der Waals interaction. The asymptotic form

24
of it for an atom or molecule outside the surface is

\[ V_{vdW}(Z) = \frac{C_3}{(Z - Z_0)^3}, \]  

(2.21)

where \( Z \) is the distance between the molecular CM and the Al(111) surface, \( C_3 \) is the van der Waals coefficient, and \( Z_0 \) is the van der Waals reference-plane position. The van der Waals interaction is orientation dependent. This effect can cause an impinging molecule to be aligned in a specific orientation with great importance for molecular trapping or abstraction, i.e., give a steering effect. The small anisotropy \( \S \) is not included in our diabatic model, but in all the calculations the oxygen molecule is assumed to approach the surface in a perpendicular orientation. The standard DFT with the existing LDA and GGA approximations fails to account for the van der Waals energy. This is not a failure of DFT itself, but a failure of these approximations due to their local or semilocal nature. In order to formulate any van der Waals density functional, the exchange-correlation energy should be improved so that it accounts for the truly nonlocal dependencies. Recently, a new approximate van der Waals density functional has been proposed, from which the parameters \( C_3 \) and \( Z_0 \) are calculated to be 1.47 eV/Å² and 0.29 Å, respectively.

![Figure 2.6](image)

Figure 2.6: The diabatic (dashed lines) and adiabatic (solid line) PES’s calculated with the

\( \S \)This anisotropy is estimated to be about 7 meV between the parallel and the perpendicular oxygen molecule at a CM distance of 3.5 Å from the surface."
The origin of the repulsive part $V_R$ of the O$_2$/Al(111) potential is the Pauli principle, which implies that the occupied wavefunctions of the surface and the adsorbate should be orthogonal to each other when they start overlapping. This in turn makes the wavefunction of the system to oscillate more, which adds to the kinetic energy. The same principles make the basis of the Thomas-Fermi theory,\textsuperscript{56,57} where the kinetic energy is given as a functional of the total charge density of the system (see chapter 5). Hence, in our first attempt to model the repulsive kinetic-part of the potential $V_R$, the Thomas-Fermi functional with the von Weizsäcker correction\textsuperscript{60} is utilized\textsuperscript{¶}. In order to obtain the charge density of the O$_2$/Al(111) system in a neutral state, first the charge density of a free Al(111) surface and a free and neutral oxygen molecule are calculated using the standard ground-state DFT with the GGA approximation for the exchange-correlation effects. The density used in the Thomas-Fermi functional is the superposition of these two charge densities. The result of the calculated PES’s using the Thomas-Fermi theory is illustrated in the insert of Fig. 2.6.

In order to use our $\Delta$SCF method to obtain the diabatic PES’s, the molecular orbitals of the oxygen molecule that are involved in the charge transfer process should be identified. Our ground-state DFT calculations, clearly illustrate that the $2p_{x,y}$-derived minority-spin $\pi_p^-$ resonance, which is empty in the free oxygen molecule, is involved in the charge transfer process. Already at $Z = 3.0$ Å this orbital gets partially filled. This implies electron transfer to this orbital, with a concomitant reduction of the spin-magnetic moment. Due to its antibonding character, the intramolecular bond weakens. Up to two electrons can be transfered to this orbital and close to the surface it is totally occupied. To account for the repulsive part of the neutral O$_2$/Al(111) potential in our $\Delta$SCF method, the $\pi_p^-$ resonance should be kept empty at all separations. This is achieved by introducing electron-hole pairs in the system, as discussed in chapter 5. The hole is placed in the $\pi_p^+$ resonance of the oxygen molecule, while the extra electron is smeared out on the electronic states of the Al(111) surface. In this method only integer values of holes can be introduced into the system. This puts restriction on the region, where the diabatic potentials can be calculated. For the O$_2$/Al(111) system, this implies that the repulsive part of the neutral potential can be accounted for only when the $\pi_p^-$ resonance is totally filled, i.e. two electrons have been transfered to this orbital. As this is the case in some region close to the surface, the total O$_2$/Al(111) is obtained by matching the calculated repulsive part to the attractive van der Waals part. The obtained diabatic PES’s are illustrated in Fig. 2.6. To determine more precisely the curve crossing between the neutral O$_2$/Al(111) potential and the O$_2^-$/Al(111)$^+$ potential, the repulsive part of the latter is also calculated using our $\Delta$SCF method. This is then matched to the image potential and illustrated in Fig. 2.6. For completeness the adiabatic PES is also included in this figure.

\textsuperscript{¶}The functional form for the kinetic energy of the Thomas-Fermi theory including this correction is also given in chapter 5
Having obtained the diabatic PES’s for the O$_2$/Al(111) system, the master equation, introduced in the previous section, is used to calculate the sticking probability. The experimental sticking data together with our calculated sticking probability are given in Fig. 2.7. The calculated sticking is based on the diabatic PES’s obtained from the $\Delta$SCF method. Similar sticking behavior is obtained using the Thomas-Fermi potentials, though with different values for the physical parameters, such as the life-time of the $\pi_p^*$ resonance of the oxygen molecule. To reproduce the experimental sticking data a physically more reasonable value for the $\pi_p^*$ resonance life-time is used in the $\Delta$SCF calculations compared to those of Thomas-Fermi.

Our calculated sticking behavior has a S-shaped energy dependency and a low value at thermal energies, despite the lack of a energy barrier in the adiabatic entrance channel. The physics behind this is the competition between time-scales, that of nuclear motion against the electronic one, which is the key ingredient in the model. Although the electron tunneling time might be comparable to the nuclear-time motion in the ”outer reaction zone”, it is much shorter in the ”inner reaction zone”. Hence, in the latter region, the electron tunneling occurs much faster than the motion of the nuclei, with a transition to the negative-ion potential as a result. The neutral molecules that reach the ”inner reaction zone” will in this way stick to the surface. The argument given above implies that a temporary energy barrier is set up for the molecule with a heigh that depends on the initial translation energy of the oxygen molecule.

### 2.4.2 Trend Study

Charge transfer initiates also the dissociation process for the NO molecule on Al(111). This is evident from the adiabatic calculations, as the antibonding $2\pi^+$ orbital of NO is shifted down in energy and filled as the molecule approaches the surface. Hence, a similar diabatic study as the one for O$_2$, detailed in the preceding section, should be worthwhile. In contrast to the O$_2$ case, there is a molecular asymmetry of the hetronuclear molecule NO that affects the sticking in several ways with effects on electron overlap and molecular dynamics. The adiabatic calculations exhibit a high energy activation barrier for the O end-on orientation, but an energetic favorization of the N end-on orientation, which should be the orientation considered in our one-dimensional diabatic trend study. However, to fully account for the observed sticking behavior, a three-dimensional model is required, which is not included in this thesis.

The sticking behavior of NO in the N end-on configuration, calculated in our diabatic picture is plotted in Fig. 2.7. Like in the O$_2$, case the calculated sticking has an S-shaped behavior, in agreement with the experimental data. The failure of the adiabatic picture and the success of the diabatic one in describing the sticking behavior is explained in the basis of a competition between the electron-tunneling process and the nuclear motion, for molecules with intermediate values of intramolecular strengths. This is indeed the case for O$_2$ and NO. Another important observation is the non-zero value of the sticking behavior of NO in the limit of zero
initial translational energy. This result reflects an important aspect of the nature of molecular orbitals. As the NO molecule has a stronger intra-molecular bond than the O₂ molecule, the curve crossing between diabatic PES’s occurs further in for NO than O₂, making charge-transfer to be more active for slow-moving molecules.

![Figure 2.7: sticking behavior for O₂ (left) and NO (right) on the Al(111) surface, obtained experimentally (open circles) and theoretically (solid line), using a one-dimensional diabatic model.](image)

For chemically hard molecules N₂ and CO, the change in electronic structure upon approach to the surface is negligible. This is due to the strong intramolecular coupling in these molecules, which makes charge transfer almost inactive in the molecule-surface reaction. Hence, making a distinction between the adiabatic and diabatic descriptions for these molecule-surface reactions has less meaning and the calculated adiabatic PES’s fully account for the observed sticking behavior, i.e. zero sticking at low and moderate translational energies.
Chemisorption of molecules on metal surfaces can be associative, dissociative, or abstractive, i.e., the whole molecule can adsorb on the surface, it can dissociate into separated fragments forming surface-adsorbate bonds on the surface, or one part of the molecule can leave the surface. Dissociative adsorption plays an important role in many surface reactions, including those in heterogeneous catalysis, etching, chemical vapor deposition, and corrosion. For a diatomic molecule, dissociative chemisorption occurs only if it is an exothermic process, i.e., if the energy obtained in forming two surface-adsorbate bonds is sufficient to account for the one needed to cleave the diatomic bond. In this case the dissociated fragments can either end up directly into nearby sites or reach their equilibrium sites first after a transfer over some lattice constants, depending on, e.g., the surface corrugation. If the barrier to diffusion is large compared to thermal energies, one would expect to observe mostly isolated pairs of atoms in the limit of low coverage. A contrast is found in the example of a diatomic molecule that hits the surface with its axis more or less perpendicular to the surface, leaving one of the atoms on the surface, while the other one is repelled and ejected into the gas phase. Such a dissociation scenario is called abstractive chemisorption and has been reported for several systems, e.g., halogens on the Si(111) surface or Br$_2$ on the Pt(111) surface.

Being chemisorbed on the surface, the atomic fragments might start to form islands on the surface, as the adsorbate coverage increases. Although the initial chemisorption mechanism does not influence the island-formation process itself, it might have great effect on the shape and growth rate of the islands. So does surface corrugation, which has puzzling consequences in the O$_2$/Al(111) system.

For this system there exist some conflicting experimental results on the fate of
the oxygen atoms after dissociation. Results in early scanning-tunneling microscope (STM) experiments at 300K were initially given the interpretation that after dissociation of a thermal molecule the two O atoms on the Al(111) surface should become separated by at least 80 Å at low coverage (below approximately 0.04 monolayer (ML)). The atoms are also found randomly distributed on the surface, that is, there is no correlation between two neighboring oxygen atoms. The given explanation of this observation is in terms of the so-called “hot-adatom” mechanism. In such a mechanism the energy released during adsorption is transformed to kinetic energy, causing non-thermal motion of the adsorbed oxygen atoms along the surface. Molecular dynamics simulations based on this idea, using first-principles data, do not confirm the presence of a large transient mobility of oxygen atoms on the Al(111) surface, as proposed in the STM analysis. The reason for this is the large diffusion energy barrier for oxygen atoms on the Al(111) surface (~1 eV), which makes the oxygen atoms immobile on the surface at room temperature. In the same STM study it has been observed that, as the coverage is increased to 0.21 ML, the number of islands containing more than one adatom grows more rapidly than expected. This observation seems to be in contradiction to the first one, i.e. wide separation of uncorrelated and immobile atomically adsorbed oxygen atoms. A number of theoretical and experimental works have addressed these two observations, in order to explain them in a consistent mechanistic picture and to understand the intermediate stage of aluminum oxidation, i.e. diffusion of the adsorbed oxygen atoms both on the surface and into the substrate in order to start the oxide formation.

The above-mentioned experimental observations on the fate of adsorbed oxygen atoms on the Al(111) surface would be rather astonishing, if compared to recent studies of oxygen dissociation on other metals. For other closed-packed surfaces, such as Pt(111) and Pd(111), the adsorbed oxygen atoms are found to be adsorbed in stable fcc sites separated by a maximum distance of 8 Å. On the more open Cu(110) surface, the distance between the individual oxygen atoms is found to be mostly 5 and 10 Å, whereas it is concluded that oxygen atoms remain in neighboring sites after dissociation on Rh(110). Apart from the case of Al(111), the only system illustrating higher separation between the adsorbed oxygen atoms is adsorption of O₂ on Ag(100), with on-surface O-O distances of typically 20 Å.

The wide separation of the uncorrelated adsorbed oxygen atoms at low coverage has recently been explained in a new laser/STM experiment in terms of abstractive chemisorption. At a translational energy of 0.5 eV, chemisorption of oxygen is documented to give both abstraction of neutral oxygen atoms, uncorrelated atomically adsorbed oxygen atoms, and correlated ones in neighboring fcc sites as end products. The existence of correlated atomically adsorbed oxygen atoms on neighboring fcc sites has also been confirmed in another STM study. Theoretical supports for the abstraction mechanism are provided by our studies. The fact that the fcc site is the chemisorption site for the adsorbed oxygen atom on the surface has been verified both experimentally and theoretically. The chemisorption energy is found to be about 7.4 eV/atom with respect to the free oxygen atom, the location about 0.8 Å above the surface-atom layer, and the diffusion barrier for single oxygen atoms...
3.1 Clean Aluminum Surface: Test-laboratory for DFT Calculations

Applying the single-atom abstraction mechanism to the O₂/Al(111) system adds to the confusion on the observed oxygen-island growth. In the simplest view of atom abstraction, the atom that adsorbs to the surface remains bound at the point of impact due to the large diffusion energy barrier.⁴⁻⁹ So, while atom abstraction can explain the observation of single atomically adsorbed oxygen on the surface, it does not allow for the rapid growth in island size as the coverage increases. To understand island formation in the O₂/Al(111) system several studies have employed Monte-Carlo (MC) methods, including different modifications of the dissociative mechanisms and assumptions about diffusion barriers.⁶⁵⁻⁶⁷ However, to fully account for the experimental observations by means of MC- or other phenomenological models, the energetics of the key processes, such as diffusion barriers, should be calculated from first-principles. As mentioned in the previous chapter the predictive power of first-principles DFT calculations has been tested for many atom/surface reactions with great satisfaction. Thus, such a study would facilitate the understanding of oxygen nucleation and diffusion on the Al(111) surface, which is the main subject of our work discussed in this chapter.

This chapter is organized as follows: first the clean Al(111) surface is treated. This is important, as it makes the basis for all further studies of aluminum oxidation. The focus is then shifted to the abstraction mechanism. Both experimental observations and our theoretical support for this mechanism are discussed in detail. The chapter is rounded off with some aspects of island formation and diffusion.

### 3.1 Clean Aluminum Surface: Test-laboratory for DFT Calculations

The starting point for all calculations on the Oxygen/Al(111) system is to construct the Al(111) surface and test the robustness of the DFT method by calculating the physical parameters of the substrate, e.g., the surface energy (σ) and the structural parameters for bulk aluminum, such as the lattice constant, the bulk modulus, and the cohesive energy. The structural parameters are calculated to a = 4.04 Å for the lattice constant, B = 72.5 MPa for the bulk modulus, and E₉coh = 3.5 eV for the cohesive energy. The achieved values compare well with those using similar methods and also those obtained from experiments.⁷⁴⁻⁸¹

For a surface calculation in the slab geometry, it is important to reduce errors due to quantum-size effects,⁸² which should give a dependence of the results on the number of Al layers. The surface energy is given by

\[ \sigma = \frac{1}{2} (E_{\text{slab}}(n) - nE_{\text{bulk}}), \]  

(3.1)

where \( E_{\text{slab}}(n) \) is the total supercell energy for a slab with \( n \) Al layers and \( E_{\text{bulk}} \) the total bulk energy of one Al layer. The latter is obtained from

\[ E_{\text{bulk}} = E_{\text{slab}}(n) - E_{\text{slab}}(n-1). \]  

(3.2)
Quantum size effects are negligible, when the obtained value for the surface energy is fully converged with respect to the number of Al layers in the slab. Our calculated surface-energy value \( \sigma = 0.808 \text{ J/m}^2 \) is the converged value of six Al layers, in excellent agreement with 0.82 J/m\(^2\) and 0.81 J/m\(^2\) from a similar calculation\(^{83}\) and experiment,\(^{81}\) respectively.

Another key physical parameter is the workfunction for the clean Al(111) surface, essential for both sticking and island formation. Our calculated value (4.18 eV) compares well with other theoretical and experimental studies.\(^{84,85}\)

### 3.2 Abstractive Chemisorption

As mentioned in the beginning of this chapter, the long-standing issue of wide separation of uncorrelated adsorbed O atoms is resolved. Our DFT calculations\(^8\) in combination with still more recent STM and resonantly enhanced multiphoton ionization experiments\(^6\) provide an explanation by revitalizing and establishing the abstraction view. That abstraction could occur for the \( \text{O}_2/\text{Al}(111) \) reaction is evident in our calculated adiabatic PES for a nonparallel oxygen molecule (Fig. 2.4), discussed in detail in the previous chapter. The adiabatic PES calculations do not only show the growing bond length \( (\text{d}_{\text{O-O}}) \) of a molecule that gets over the dissociation barrier but also a growing CM coordinate (Z). The nonparallel orientation and the strong chemisorption of a single oxygen atom, discussed in the previous sections, implies that one oxygen atom should stay on the surface and the other one leave, i.e. abstraction.\(^6,86\)

In order to have conditions for abstractive chemisorption, the oxygen molecule should hit the surface with its axis more or less perpendicular to it. So for impinging oxygen molecules, anisotropy really matters. Thermal molecules in a gas appear with equal weights on all orientations. A particular direction, such as the parallel direction, thus has a low statistical weight. In the region close to the surface, however, there are steering effects that might favor some orientation. The steering effect works for a slow-moving molecule, which has enough time to adapt its orientation to the minimum energy path. For higher energies, the impinging molecule is too fast for such a reorientation mechanism to work.

Two sources for alignment of impinging thermal and subthermal oxygen molecules into a perpendicular orientation are van der Waals and directional chemisorption forces, the latter expressed as an angle (\( \theta \)) dependence of the PES. The van der Waals forces are weak but dominating for a molecule far outside the surface. The anisotropy in the asymptotic form of the van der Waals energy makes the perpendicular orientation energetically favorable compared to the other orientations by several meV.\(^*\) This slight anisotropy, which is comparable to thermal energies and energies calculated with GGA, might steer the incoming thermal and subthermal oxygen molecule to approach the surface in the perpendicular orientation.

\(^*\)The calculated van der Waals energy, at for instance \( Z = 3.5 \text{ Å} \), is \(-42\) and \(-49\) meV for parallel and perpendicular \( \text{O}_2 \), respectively.
3.3 Single-O-Atom Adsorption

The total mapping of the PES implies that for given CM position of the molecule the parallel orientation is energetically most favorable. However, for the molecule to change its orientation from, e.g., the perpendicular to the parallel orientation, there exists an energy barrier for all the CM distances.\(^8\) In addition, the calculated Hellmann-Feynman forces on the individual oxygen atoms indicate a rotation of the molecular axis towards the perpendicular orientation for the molecules approaching the surface with an angle (\(\theta\)) between the molecular axis and the surface normal that is less or equal to 30°. Such molecules are apt for abstraction at dissociation. That the steering effect works for slow-moving molecules and that it is important for the abstraction channel can be seen in the experimental data obtained by Komrowski et al.\(^6\) Their data shows that at an \(O_2\) incident energy of 0.8 eV about 60% of the impinging \(O_2\) molecules undergo the abstraction channel, while 30% are dissociated normally, resulting in adatom pairs adsorbed on the surface. Furthermore, the normal dissociation channel is found to be dominating at higher energies.

This abstraction channel is exothermic by about 2.4 eV, the bond energy of a free oxygen molecule being 5.11 eV and the chemisorption energy of oxygen atom being 7.55 eV, according to experimental data. In the predicted abstraction the outer oxygen atom is expected to end up as a neutral atom far outside the surface at adiabatic or near-adiabatic conditions. Inspection of the projected LDOS shows it to attain a \((2p)\) configuration already at a CM distance of 1.6 Å and at a bond length of 1.8 Å, i.e., when the atom is 2.5 Å outside the surface layer.

As mentioned in the introduction to this chapter, the experimental studies in Ref. 6 clearly confirm our prediction about the existence of the abstraction channel for the \(O_2/Al(111)\) system. It also report on the simultaneous existence of uncorrelated atomically adsorbed oxygen atoms and correlated ones in neighboring fcc sites.\(^3, 4, 6\) Accordingly, at intermediate translational energies, a predominant fraction of the chemisorption events follow an abstraction mechanism, which provides a realistic explanation of the observation of single chemisorbed oxygen atoms. The experimental observations of the abstraction channel and the existence of singles and pairs of oxygen atoms as end products are fully consistent with our theoretical study and have important ramifications.

3.3 Single-O-Atom Adsorption

Although the abstraction mechanism provides a satisfactory explanation for the experimentally observed wide separation of adsorbed oxygen atoms on the Al(111) surface, it cannot alone explain the rapid growth of the oxygen islands. To understand this observation the key issues are the chemisorption site, the chemisorption energy, and the diffusion energy barriers for single oxygen atoms as well as oxygen islands. Postponing the latter study to the next section, here the kinetics of single oxygen diffusion is discussed.

Generally speaking, there is agreement in the literature about the chemisorption site, the chemisorption energy, and the diffusion energy barrier for a single oxygen
atom on the Al(111) surface. For instance, DFT calculations\(^9\) show the oxygen chemisorption site on Al(111) to be in the three-foldly coordinated fcc position, the distance from the surface layer to be 0.86 Å, and the chemisorption energy to be 5.0 eV/atom with respect to the free oxygen molecule, which means a chemisorption energy of 7.55 eV/atom (\(E_b = 5.11\ eV\)) with respect to the free oxygen atom. This is a very strong chemisorption energy, which makes the adsorbed oxygen atoms immobile on the surface. These results have been calculated within the local-density approximation (LDA), using GGA non-selfconsistently for the total energy, the so-called post-GGA. The main objective of our study for single-oxygen chemisorption on the Al(111) surface is to find out whether improved methods, including use of GGA, change the picture of single oxygen chemisorption on the Al(111) surface and also to test our method and generated potentials on a well-known system. Our calculated results are 0.74 Å and 7.375 eV/atom for the chemisorption position and energy with respect to the free oxygen atom, respectively. The diffusion energy barrier is calculated by mapping the PES along the diffusion path. Obviously the fcc hollow site is found to be the chemisorption site and the diffusion energy barrier is calculated to be 0.72 eV.

In our calculations, mentioned above, the Al(111) surface is allowed to relax. When moving the oxygen atom from the fcc site over the bridge site into the hcp site, the surface atoms reconstruct in order to minimize the total energy. The energy lowering, caused by surface reconstruction, is in the magnitude of several meV. Our calculated diffusion barrier (0.72 eV) is compared to the reported STM result of 1.0-1.1 eV\(^3\). The STM value is measured in the temperature range 350-530 K and is described by the authors to be in the 10-20% range of the adsorption energy, which could explain why it differs from our calculated value.

### 3.4 Island Formation and Diffusion

One of the key phenomena in the oxidation process, which still lacks a proper atomistic understanding, is the formation of oxygen islands. In order to study the dissociative chemisorption of \(O_2\) on the Al(111) surface at 300 K, Brune et al.\(^3,4\) have by STM found that the number of oxygen islands that contain more than one adatom increases more rapidly than expected. Different explanations have been addressed in several Monto-Carlo simulations,\(^65-67\) including one that explains the rapid growth of oxygen islands in terms of the abstraction mechanism as the only operative dissociation mechanism.\(^65\) However, in order to fit the experimental data, two modifications are proposed: (i) The dissociation probability is higher at sites next to preexisting chemisorbed O adatoms, and (ii) the abstracted O atom is permitted to make a hop in the direction of a preexisting, nearby O adatom.\(^65\) Although result that comes out is satisfactory, a total understanding of the island formation of oxygen on the Al(111) surface cannot be claimed until the model assumptions have been further tested by experiment and first-principles calculations.

In order to study the island-formation process by means of first-principles cal-
3.4 Island Formation and Diffusion

culations, we employ DFT on the energetics of the adsorbed oxygen atoms on the Al(111) surface. Since the objective of this study is to consider islands that contain more than two adatoms, a 4×4 slab geometry consisting of six Al and five vacuum layers is chosen. Two main processes have been studied, i.e. the effect of oxygen coverage on the dissociation probability, and the effect of surrounding environment on the diffusion energy-barriers of adsorbed oxygen atoms.

For an oxygen molecule to dissociate on the Al(111) surface electrons should be transferred from the surface states to the antibinding π* resonance of the oxygen molecule.8 In the adiabatic picture (section 2.3) one of the key ingredients governing the dissociation process is the workfunction of the Al(111) surface. An increase of the workfunction reduces the dissociation probability, if all other parameters are assumed to be fixed. In agreement with other theoretical calculations,87 made for oxygen coverages larger than 0.25 ML, and experiments,1,88,89 our calculated workfunction for coverages smaller than 0.25 ML also exhibits an increasing trend with increasing coverage. This is due to the significant electron transfer from the substrate to the adatom, as the adsorbed oxygen atom obtains an "O2−" electron configuration. The increase of the workfunction with coverage, if all other physical parameters remain unchanged, implies that the sticking probability decreases with coverage. The decrease of the sticking as a function of coverage has recently also been observed experimentally.90 However, to fully understand the sticking behavior as a function of coverage, the change in the local electronic environment due to the preexisting chemisorbed oxygen should be taken into account. Considering such local effects is a complicated problem and is not discussed here.

Before investigating the change in oxygen diffusion energy-barriers as a function of coverage, the energetics and geometric structures of oxygen-islands should be studied. Since our calculations show, in agreement with earlier studies,9,87 that the fcc hollow site is the energetically most favorable adsorption site, only oxygen atoms adsorbed on the fcc site are considered. To determine the shape of the oxygen islands, total energies have been calculated for islands containing N oxygen atoms (N = 3, 4, and 5), having all possible configurations. The result is shown in Fig. 3.1, which shows the most stable structure to be compact islands. Furthermore, the binding energy as a function of coverage is also calculated. This is given by

\[
E_b(\theta) = -\frac{1}{N}(E_{O,Al} - E_{Al} - NE_O),
\]

where N is the number of oxygen atoms in the island, \(E_{O,Al}\) is the total energy for the O/Al(111) system, \(E_{Al}\) is the surface energy, and \(E_O\) is the energy of a free oxygen atom. The binding energy is seen to increase with increasing coverage, indicating that attractive forces act between the adsorbed oxygen atoms, making island-formation energetically favorable. The same conclusion has been made in other theoretical studies,9,87 where only coverages bigger than 0.25 ML have been considered.
Figure 3.1: Energy differences between all possible structures of oxygen islands, containing three, four, and five oxygen atoms. The binding energy per O adatom as a function of oxygen coverage is also illustrated in the top right corner.

To understand the effect of the surroundings on the diffusion energy-barriers, the diffusion pathways from nearest neighbor sites to the next nearest neighbor sites have been mapped for the cases of N-atom-islands, where N = 2, 3, 4, 5. The result is illustrated in Fig. 3.2. As compact islands are energetically very stable, the diffusion barrier for an oxygen atom leaving an island increases with increasing island-size. Furthermore, the diffusion-barriers from next nearest neighboring sites to neighboring sites is around 0.8 eV, i.e., equivalent to the diffusion barrier for single O atom diffusion (~ 0.72 eV), making a single hop of an oxygen atom between the two sites improbable. Hence, it can be concluded that island formation is not due to the diffusion of single O adatom on the Al(111) surface.

For some metal-on-metal growth, e.g., Al on Al(111) surface, it is realized that a collective motion of atom-dimers on the surface reduces the diffusion barriers along the surface and is one of the important processes in island-formation. To investigate this possibility the diffusion pathway for an oxygen-oxygen dimer has been mapped and the result is shown in Fig. 3.3. The diffusion barrier for such a collective motion is 1.58 eV. As the calculated binding energy for an oxygen-oxygen dimer (~ 0.21 eV) on the surface is too small, the collective motion of oxygen-
The on-surface diffusion energy-barriers for an oxygen atom leaving an oxygen island, containing different number of oxygen atoms.

As discussed in the previous section, our theoretical first-principle calculations do not corroborate the experimental findings by Brune et al.\textsuperscript{3,4} about the rapid growth of the oxygen islands. Although the puzzle for on-surface oxygen diffusion still remains, our results clarify many important aspects and put the confusion on a much higher and more interesting level.

There exist a number of speculative ideas that could explain the experimental observation about single atom abstraction and island formation in a consistent way.
One such, is the trapping of slow moving oxygen molecules in a physisorbed molecular state, moving parallel to the surface rather freely. These molecules should dissociate upon hitting a preexisting adsorbed oxygen atom and contribute to the island growth. According to our calculation, presented in the previous section, there exists a physisorbed molecular state 3.2 Å outside the surface with a depth of 100 meV and frustrated translational vibration in the order of 3.2 meV. A simple estimate shows that the life-time for such a molecular state is about $10^{-4}$ s, which is enough to make the mechanism, mentioned above, to work.
Final Stage of Aluminum Oxidation: Oxide Formation

When oxygen encounters a metal surface, oxygen atoms can penetrate down to the metal bulk, initializing the oxide formation. The creation of subsurface oxygen is a key step on the pathway to corrosion. The motion of oxygen past a layer of metal atoms makes room for additional oxygen at the surface, leading to greater oxygen uptake. This phenomenon has been observed experimentally.\textsuperscript{92, 93} In the experimental study by Brune \textit{et. al.},\textsuperscript{3, 4} which is of considerable importance for the field of surface-reaction dynamics, the first oxide is observed at 0.2 ML, when the chemisorbed oxygen islands reach a certain critical size. This implies that on-surface diffusing aluminum atoms, chemisorbed oxygen atoms, and oxidic oxygen coexist on the surface. It is also observed that the 3D oxide process starts at the edges of oxygen islands, and that it continues growing, leading to the formation of oxide grains on the surface.\textsuperscript{3, 4}

One proposed mechanism is the place-exchange mechanism. It promotes oxide formation at the edges of oxygen islands. During this process, one oxygen atom at the edge of the 2D oxygen island and the underlying aluminum atom change their places. Our first-principles calculations indicate that the activation barrier for this process is huge, however, requiring a large amount of energy. However, during the dissociative chemisorption of the O\textsubscript{2} molecule, the energy release is about 10 eV.\textsuperscript{8, 9, 87} This amount of energy will heat up the underlying lattice locally. As a result the activation barrier might be lowered. Whether the place-exchange mechanism occurs or whether there are other processes promoting the oxide formation is issues that call for further elucidation.

Finally the whole surface will be covered with oxide grains, starting the formation of a thin oxide film.\textsuperscript{3, 4} The oxide formation is a very fast process. However, after forming a thin oxide film the rate of oxidation drops to a very low value. In the case of aluminum, the thin oxide film, which forms at room temperature, protects
the surface against further oxidation and corrosion. This corrosion inhibition is the main technical reason for studying the oxidation of aluminum.

An early explanation of the formation of a protective oxide layer has been given by Mott and Cabrera. In this model the driving force for the formation of the oxide layer is an electric field over the (thin) oxide layer that manages to pull a metal ion across the film. The rationale for the existence of such an electric field is the fact that atomically chemisorbed oxygen, on the "vacuum side" of the thin film, is negatively charged. This is indeed the result of the adiabatic calculations, presented in the previous section. In the Mott-Cabrera model it is given in terms of the energy difference between the Fermi energy of the metal and the affinity level of oxygen. According to the model, the oxide film stops growing when the electric field becomes too small to be able to pull ions across the film. Although the oxide layer passivation is accounted for in the Cabrera-Mott model, an atomic scale study is still lacking.

In this chapter a brief review of the different phases of alumina in general and the metastable \(\kappa\) alumina in particular is given. The focus is our prediction of a one-dimensional electron gas (1DEG) on one of the surfaces of \(\kappa\)-alumina. The electronic properties of this system together with a possible metal-insulator transition are also elucidated.

## 4.1 The Metastable \(\kappa\)-Alumina

Under atmospheric pressure and at room temperature \(\text{Al}_2\text{O}_3\) forms a vitreous or "glassy" structure. Although the oxide does not show any apparent long-range ordering, it has some local short-range structure. The rationale for this is the very low saturation thickness (20-30 Å) of the oxide that inhibits further oxidation. The oxide-film growth is different on different metals. On Zn the oxide grows pseudo-morphically, i.e. it adopts its lattice parameter to the one of the substrate, while on Fe and Cu ordered overlayer oxide structures are observed. Compared to the crystalline oxide structure, the vitreous one is thermodynamically less stable. Hence, a crystalline structure will be formed, upon heating or other excitations.

Aluminum does not exist as a free metal in nature. It is, however, found in aluminum hydroxides, which are common in nature. These include: "Gibbsite" \(\alpha\)-\(\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}\), "Boehmite" \(\alpha\)-\(\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}\), and "Diaspore" \(\beta\)-\(\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}\). All of these phases of aluminum oxides end up as \(\alpha\)-\(\text{Al}_2\text{O}_3\) upon thermal treatment. The \(\alpha\)-phase is stable for temperatures from absolute zero to its melting temperature (\(~1000\) K). It is a material of high technological significance, such as in electronics (epitaxial growth of Si on sapphire), as a packing material, as a dielectric, as a laser-host material (Cr-doped \(\alpha\)-\(\text{Al}_2\text{O}_3\)), as an insulator for nuclear reactors, and so on. The wide range of technical applications is thanks to the hardness, abrasion resistance, mechanical strength, corrosion strength, and the good electrical insulation of \(\text{Al}_2\text{O}_3\).

Beside the stable \(\alpha\) phase, there exists a number of different metastable phases of alumina, e.g., the \(\kappa\) phase. Despite their metastability, the transition aluminas,
4.2 One-Dimensional Electron Gas on The Surface of $\kappa$-Alumina

with transition temperature above 500° K, have received an impressive attention. Not only retaining good thermomechanical and electrical resistances, they have also high surface area, fine particle size, and catalytic activity. Upon thermal heating, as the different phases transform to each other and end up in the stable $\alpha$ phase, an understanding of the intermediate metastable aluminas is essential. Therefore, the transition aluminas have been studied extensively during the last years. So far the majority of the research has been experimental, aimed at characterizing the transformation mechanisms, surface structure, chemical reactivity, and crystal structure of the different metastable phases. However, such experimental studies have been hampered by the metastability, poorly developed crystallinity, and difficulty of obtaining pure-phase samples. As a result, there is little known about the structure of almost all metastable alumina phases.

One of the metastable phases, which has received considerable attention, is the $\kappa$ phase. It has many interesting and important technical applications, e.g., in wear-resistant coatings on cemented-carbide cutting tools. The earliest experimental work to determine the structure of bulk $\kappa$-$\text{Al}_2\text{O}_3$ was performed during a study of the transition aluminas.\textsuperscript{95, 96} As a step in the thermal treatment, leading finally to the $\alpha$ phase, a transition alumina, which was arbitrarily given the name $\kappa$-$\text{Al}_2\text{O}_3$, was observed. The crystal structure was determined much later. In the 1980s it was shown that the $\kappa$ phase has a primitive orthorombic structure.\textsuperscript{97} Theoretically, the structure of the $\kappa$ phase was determined by Yourdshahyan et al.,\textsuperscript{98} employing DFT and using the supercell method. This was the first time that first-principle methods have been applied to the structure determination of such a complex system. In similar studies\textsuperscript{99, 100} the surface electronic structure of $\kappa$-$\text{Al}_2\text{O}_3$ has been investigated, revealing new features of ion-surface stability and electronic structure, such as the existence of a one-dimensional electron gas on one of the surfaces. This is the main theme of the following sections.

4.2 One-Dimensional Electron Gas on The Surface of $\kappa$-Alumina

Upon cleavage of bulk $\kappa$-$\text{Al}_2\text{O}_3$ perpendicular to its main axis, two different surfaces are created, namely the (001) and (00$\bar{1}$) surfaces. The most stable termination of the $\kappa$(001)/(00$\bar{1}$) occurs in the middle of an Al layer.\textsuperscript{99, 100} The (001) surface exhibits a huge inward relaxation (-117\%) of the surface Al atoms, making this surface O terminated. This is due to the open structure of the crystal. On the other hand, the inward relaxation of the Al atoms at the (001) surface is much smaller (-74\%), making this surface Al terminated. By studying the geometric structure of the latter surface, it is observed that the Al atoms are lying in zigzag lines along the [100] direction. The distance between two adjacent Al lines is 8.4 Å, while the Al-Al distance within the line is 2.4 Å. Due to the charge asymmetry in bulk $\kappa$-$\text{Al}_2\text{O}_3$ there exists an excess of electrons at the (00$\bar{1}$) surface, compared to an ideal ionic situation. The calculated bandstructure $E(k)$ of the chain clearly shows a parabolic form
along the [100] direction and is almost flat along the [010] direction. A calculation of the effective mass of this band along [100] yields a value of $1.4 \cdot m_e$ at the Fermi energy, where $m_e$ is the electron mass. From this calculation the Fermi wavevector $k_F$ is estimated to $k_F = \frac{\pi}{a}$, where $a$ is the distance between two Al atoms along the chain. To understand the localization of the surface-state electrons, the 3D charge density profile is calculated and plotted in real space, as shown in Fig. 4.1. The surface state is clearly localized around the surface Al atoms, which gives it the character of a pseudo-1D electron gas along the [100] zigzag surface Al line.

![Figure 4.1: 3D visualization of the surface-state electron density for the relaxed k-Al2O3(001) surface at Fermi energy. Large balls are O atoms and small ones are Al atoms.](image)

Today, there is a broad range of candidates for a one-dimensional electron gas (1DEG) with interesting electron-electron interaction effects and future applications. This is due to the advances in syntethic chemistry and semiconductor fabrication technology. The most notable 1DEG is the carbon nanotube (CNT), which was discovered by Iijima in 1991. Carbon nanotubes are formed by rolling up a hexagonal lattice of carbon atoms to a cylindrical shape. Depending on how the graphite layer is rolled up, two different types of CNT appear, one metallic and one semiconducting. Experimentally, Carbon nanotubes are produced by the carbon arc-technique and by laser vaporization of cobolt-nickel doped graphite.

Other interesting manifestations of 1DEG systems include inorganics (MX chains, the platinocyanate chain compound K$_2$Pt(CN)$_4$Br$_{0.3}$H$_2$O, and the charge-density-wave compounds NbSe$_3$ and K$_{0.3}$MoO$_3$), organics (trans-polyacetylene (TPA), the charge-transfer salt TTF-TCNQ, and the Bechgaard salts, and metallic edge states). The organic quasi-1D systems have many important future technological applications, e.g., in light-emitting devices, in organic transistors, in sensors, as corrosion inhibitors, and much more.

It is well-known that the metallic behavior characteristic of 1D metals breaks down below some critical temperature, associated with a structural transition, called
the Peierls transition, * of the conducting chains of atoms. An energy bandgap appears at the Fermi energy with semiconducting behavior as a result. The critical temperature varies dramatically between the above-mentioned “traditional” 1D materials. For the inorganic systems the transition temperature is around 200 K. For CT salts it is around 60 K, and for the trans-polyacetylene it is far above room temperature. This effect is responsible for making polyacetylene and most other polymers insulating except upon special difficult doping. The CNT is the only existing 1D system that remains metallic even at 0 K. However, it has a complex band structure, as the 1DEG is coupled to other metallic states. Our predicted 1DEG on the surface of κ-alumina does not only provide a much simpler 1DEG realization compared to CNT, but it is also metallic over a much wider temperature range than most existing realizations of 1DEG, as discussed in the following.

### 4.3 Metal-Insulator Peierls Transition

In 1D metallic systems (linear chains), as the temperature is lowered, metallic behavior is not maintained as in normal 3D metals, but semiconducting behavior occurs. This phenomenon was suggested by Peierls in 1955,† and is referred to as the Peierls instability. The physics for such an instability is the competition between the elastic energy and the electronic energy of the system. The structural deformation creates an energy bandgap at the Fermi energy ($E_F$), lowering the electronic energy in the system. Upon deformation of the 1D structure, the elastic energy of the system grows, which puts an upper limit on the deformation and hence the energy bandgap. Peierls also suggested that such a deformation occurs at a wavevector equal to $G = 2k_F$. Figure 4.2 illustrates the effect of the Peierls distortion on the bandstructure for a one-dimensional metal with an electron gas filling all conduction band orbitals out to the wavevector $k_F$.

Such periodic lattice distortions have been observed experimentally in many anisotropic compounds. The ultimate model case is the quasi 1D polymer trans-Polyacetylene (TPA). This polymer consists of weakly coupled chains of CH units, with alternating double (shorter) and single (longer) bonds between the C atoms. Furthermore, the polymer is insulating at room temperature, with an energy bandgap of 1.8 eV. In 1979 Su, Schrieffer, and Heeger introduced a tight-binding model, referred to as the SSH model, in order to study TPA. They were able to assign both the bond alternation and energy bandgap to the Peierls instability in the system. Their theoretical study is based on a variational approach, where the total energy of the system is given as a functional of the lattice displacement †. If the functional has a minimum, different from zero, corresponding to a $\frac{2\pi}{k_F}$-periodic configuration, then there is a Peierls instability.

---

*This will be detailed in the next section
†When introducing the temperature, one should study the Gibbs free energy instead of the total energy. This is due to the fact that for non-zero temperatures, there is an entropy effect that contributes to the total energy.
Figure 4.2: Peierls instability for a half filled band. Electrons with \( k \) near the Fermi surface have their energy lowered by a lattice deformation.

In order to fully understand the Peierls instability within the model, as discussed briefly above, one has to start with the SSH Hamiltonian. This Hamiltonian, which is a one-electron Hamiltonian with electron-phonon interaction explicitly included, can be written as

\[
H = H_{e-e/ph} + H_{ph},
\]

where

\[
H_{e-e/ph} = \sum_{n,s} t_{n+1,n}(c^\dagger_{n+1,s}c_{n,s} + c^\dagger_{n,s}c_{n+1,s}),
\]

\[
H_{ph} = \sum_n \left[ \frac{p^2}{2M} + \frac{K_{eff}}{2}(u_{n+1} - u_n)^2 \right],
\]

with \( u_n \) being the displacement of the \( n \)th atom, \( p_n \) its conjugate momentum, \( M \) the mass of the zig-zag Al-line and \( c^\dagger_{n,s} / c_{n,s} \) the fermionic creation/annihilation operators. The electron-phonon interaction is included in the hopping integral \( t_{n+1,n} \) which can to first order be expanded around \( u_{n+1} = u_n = 0 \), giving

\[
t_{n+1,n} = t_0 - \alpha(u_{n+1} - u_n).
\]

There are three model parameters which have to be determined, namely the electronic bandwidth \( t_0 \), the electron-lattice coupling constant \( \alpha \), and the effective spring constant \( K_{eff} \). This Hamiltonian can be solved in \( k \) space \(^1\), yielding the eigenenergies of the system. Depending of how much of the conducting band is filled, different solutions are obtained. In the case of TPA half of the conducting band is filled,

\(^1\)The details are given in the Appendix
leading to a two-band solution. From the eigenenergies the Gibbs free energy can be obtained as a functional of the displacement coordinate \((u)\). In order to evaluate the critical temperature, the bond alternation and the energy bandgap for the Peierls instability, the Gibbs free energy functional is minimized with respect to \(u\).

In the case of TPA, i.e. when half of the conducting band is filled, an analytic expression is given for the critical temperature \((T_c)\) and the energy bandgap \((E_g)\), namely$^{108,109}$

\[ E_g \sim k_B T_c = \xi 2t_0 \pi \exp\left( -\frac{\pi Kt_0}{4\alpha^2} \right). \]  

(4.5)

This expression depends strongly on the effective spring constant \(K_{\text{eff}}\) but mostly on the electron-lattice coupling constant \(\alpha\). Thus an accurate determination of these two parameters is essential to obtain a reasonable value for the critical quantities.

The Peierls distortion, occurring within the model, can be viewed as a result of spontaneous symmetry breaking. At high enough temperatures, the phonon elastic energy dominates. As the temperature is lowered, the electron-phonon coupling, which is the term in the Hamiltonian that breaks the symmetry spontaneously, becomes comparable to the phonon elastic energy, leading to a structural distortion. As is the case in systems with a spontaneous symmetry breaking, the Hamiltonian retains its translational symmetry, while the ground state exhibits a structural distortion, breaking the translational symmetry.

The SSH model can be used to study the Peierls instability in our system, consisting of zigzag Al atoms on the surface of \(\kappa\)-alumina. However, it should be adapted to our surface-physics problem. This is achieved by considering the following:

(i) The underlying oxide affects the electronic properties of the 1D chain. To account for this the electronic bandwidth \(t_0\) and the electron-phonon coupling \(\alpha\) are estimated using DFT calculations for the whole system, i.e. the Al chain and the underlying oxide.

(ii) The chemical potential \(\mu\) of the 1D Al chain must, of course, be equal to the 3D one of the entire oxide surface. However, it can effectively be calculated exactly as in the original SSH model, i.e. so that the number of electrons in the Al chain is conserved. The underlying surface has a large energy gap between the surface state and the bulk-type conduction band $^\S$. As this energy gap makes the Fermi-distribution function to completely vanish at the conduction band and room temperature, the number of electrons transferred into and out of the surface-state thus remains negligible and surface-state electron conservation applies.

(iii) As our 1D system lies on the surface of \(\kappa\)-alumina, the Peierls instability should be searched for as a result of the competition between the surface-electronic energy and the surface-phonon elastic energy. In such a model, a soft phonon mode, referred to as the longitudinal Rayleigh mode, causes the Peierls distortion. In order to account for such surface phonons, a phenomenological phonon model is proposed and the effective spring constant \(K_{\text{eff}}\) is then estimated by means of DFT calculations.

$^\S$ Using our calculated bandstructure results, this energy gap is estimated to be 3.5 eV.
(iv) Finally, in accordance with the value of \( k_F \), an eight-band analysis is employed to solve our surface-SSH model. In contrast to the two-band model, discussed above, there is no analytic expression for the Gibbs free energy and hence the critical temperature. These quantities are evaluated numerically.

The conclusion of our calculations is that the critical temperature \( T_c \) is much smaller than 1K. The low value of \( T_c \) and the simplicity of the band structure make our system a good candidate for studying electron-electron correlations, e.g., Luttinger liquid (LL) theory, transport through grain boundary, and interacting nonlinear transport effects.

Finally, the limitations of the SSH model should be mentioned. This model works when the energy bandgap is small compared to the bandwidth and the correlation length much larger than the lattice constant. Furthermore, explicit Coloumb interactions are missing and the phonons are treated classically. The former effect is, however, partially included by using screened values for \( t_0 \) and \( \alpha \).
Theoretical Methods

5.1 Total Energy Calculations: The Ground State

The inhomogeneous electron gas, which plays an important role in today’s solid-state research, is defined to be a set of interacting electrons moving quantum-mechanically in the potential field of a set of atomic nuclei. The latter are considered to be static (the Born-Oppenheimer approximation). The theory of inhomogeneous electron gas originates from the statistical theory of Thomas and Fermi. In this theory, the relations from the homogeneous electron gas are used locally in the inhomogeneous charge cloud, existing in atoms, molecules, and solids. Such a local assumption naturally requires the electron density to vary slightly over a characteristic electron wave length. Although the Thomas-Fermi theory provides a quick and often good first orientation for many important questions, e.g., trends of the energetics, its validity cannot be assessed easily and further improvements are difficult to make. The rationale for this is that the Thomas-Fermi theory is derived phenomenologically and not as approximation to an exact formulation of electron theory. Other approaches for studying the many-electron systems include the Hartree and Hartree-Fock approximations (HFA). The Hartree-Fock theory provides reasonable results in many cases, but it does not have the computational speed needed. This is still more true, when the accuracy of HFA is improved by including so called configuration interactions (CI). However, there is another approach for studying the electronic properties of many-electron systems - Density Functional Theory (DFT) - which over the last thirty years or so has become the most useful method of choice for the solution of such problems. The Thomas-Fermi method can be considered as the simplest version of this theory.

Since all the work done here is based on DFT, we just give a brief introduction to the Thomas-Fermi, Hartree, and Hartree-Fock theory. The main part of this chapter involves DFT and various approximations that have been used in implementing it.
5 Theoretical Methods

5.1.1 Pre-DFT Theories

The total energy and the electronic structure of a solid can be obtained by solving the stationary many-body Schrödinger equation, *which can be written as*

\[ \hat{H}\Psi = E\Psi. \]  \( \text{(5.1)} \)

Here \( \Psi = \Psi(r_1s_1, r_2s_2, \cdots, r_Ns_N) \), where \( r_i \) are the spatial degrees of freedom and \( s_i \) are the spin degrees of freedom, is the N-body wave function and

\[ \hat{H} = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - Ze^2 \sum_{\mathcal{R}} \frac{1}{|r_i - \mathcal{R}|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \right) \]  \( \text{(5.2)} \)

is the Hamiltonian. Here the terms from left to right are the kinetic energy of the electrons, the Coloumb interaction energy between the electrons and the lattice atoms, and the Coloumbic electron-electron interaction. Solving Eq. (5.1) analytically is impossible even for \( N = 2 \) and one has to come up with some physically simplifying ideas. One approach is to give an approximation for the many-body wavefunction \( \Psi \), which makes Eq. (5.1) easy to solve. The easiest approximation, which is called the Hartree approximation, is to put

\[ \Psi(r_1s_1, r_2s_2, \cdots, r_Ns_N) = \psi_1(r_1s_1)\psi_2(r_2s_2) \cdots \psi_N(r_Ns_N), \]  \( \text{(5.3)} \)

where the \( \psi_i \) are a set of N orthonormal one-electron wavefunctions. Putting this ansatz into Eq. (5.1), one obtains the following set of equations for each one-electron wavefunction

\[ -\frac{\hbar^2}{2m} \nabla_i^2 \psi_i(r) + U^{\text{ion}}(r)\psi_i(r) + U^{\text{ee}}(r)\psi_i(r) = \epsilon_i\psi_i(r). \]  \( \text{(5.4)} \)

Here \( U^{\text{ion}}(r) \) is as in Eq. (5.2) and

\[ U^{\text{ee}}(r) = -e \int d\mathbf{r}' \rho(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \]  \( \text{(5.5)} \)

with

\[ n(\mathbf{r}') = -e \sum_i |\psi_i(\mathbf{r}')|^2. \]  \( \text{(5.6)} \)

The set of equations (5.4) can be solved self-consistently by first guessing a form for the density \( n(\mathbf{r}) \). A new \( n(\mathbf{r}) \) is then calculated from the calculated wavefunctions. The disadvantage with the Hartree approximation is that it treats all the electrons in the solid as independent electrons. This means that the Hartree approximation does not take into account such effects as exchange and correlation.

*There are many good text-books written on this subject. This section is mainly based on Ref. 124.*
To improve upon the Hartree approximation, one can use the fact that the wavefunction for fermions should be antisymmetric w.r.t. exchange of two coordinates, i.e.

\[ \Psi(r_1, s_1, \ldots, r_i, s_i, \ldots, r_{N_s}, s_{N_s}) = -\Psi(r_1, s_1, \ldots, r_j, s_j, \ldots, r_{N_s}, s_{N_s}) \]  

(5.7)

The first approximation for the wavefunction to accomplish this effect is to write the N-body wavefunction as a determinant of one-electron wavefunctions,

\[ \Psi(r_1, s_1, \ldots, r_{N_s}, s_{N_s}) = \begin{vmatrix} \psi_1(r_1, s_1) & \psi_1(r_{N_s}, s_{N_s}) \\ \vdots & \vdots \\ \psi_N(r_1, s_1) & \psi_N(r_{N_s}, s_{N_s}) \end{vmatrix} \]  

(5.8)

Putting the ansatz above into Eq. (5.1), gives the following nonlinear differential equations

\[
\begin{aligned}
- \frac{\hbar^2}{2m} \nabla^2 \psi_i(r) &+ U_{\text{ion}}(r) \psi_i(r) + U_{\text{ee}}(r) \psi_i(r) \\
+ \sum_j \int d' V_j(r, r') \psi_j(r') \delta_{s_is_j} &= \varepsilon_i \psi_i(r).
\end{aligned}
\]

(5.9)

In the equation above, which is called the Hartree-Fock equation, we have

\[
V_j(r, r') = -\frac{e^2}{|r - r'|} \psi_j^*(r') \psi_j(r).
\]

(5.10)

Comparison of the Hartree and Hartree-Fock equations clearly shows that the latter equation is much more difficult to solve than the first one. This is due to the nonlinear term (\( \int d' V_j(r, r') \psi_j(r') \)). This term is called the exchange term and it arises from the Pauli repulsion.

The Hartree-Fock approximation is not the end of the story. There exist another effect, called the correlation effect, which is not present in the Hartree-Fock equation. It arises from the fact that in quantum mechanics the motion of one electron is correlated with that of the other electrons. To include this effect in the many-body Schrödinger equation, one could write the many-body wavefunction as a combination of many Slater determinants, as in configuration-interaction (CI) approximations. Usually the correlation energy is smaller than the exchange energy, however, and can be neglected as a first approximation.

To solve the Hartree-Fock equation is a hard task, due to its non-linear nature. It is therefore very attractive to have a method in which the density \( n(r) \) can be obtained directly from the potential \( v(r) \), by-passing the wave functions. This is the achievement of the Thomas-Fermi theory, which uses the uniform electron gas relations locally to the inhomogeneous many-electron system.

The starting point of this theory is to write the total electronic energy as a functional of the charge density \( n(r) \). Inspecting the Hamiltonian, given in Eq. (5.2), yields an expression for the total energy as

\[
E[n(r)] = \int t(n(r)) dr + \int n(r) V_N(r) dr + \int n(r) n(r') V_{e-e}(r, r') dr dr',
\]

(5.11)
where
\[ V_N(r) = -Z \sum R \frac{1}{|r - R|} \] (5.12)
is the electron-nuclear potential,
\[ V_{e-e} = \frac{1}{2|r - r'|} \] (5.13)
is the Coloumb interaction energy between the electrons, and \( t(n(r)) \) is the kinetic energy density for the electrons. Applying the local assumption to the mean charge density for a uniform electron gas and using the Pauli exclusion principle, it is shown that the kinetic energy density \( t(r) \) only depends on the charge density as
\[ t(n(r)) = c_k [n(r)]^{5/3}, \text{ where } c_k = \frac{3h^2}{10m} \left( \frac{3}{8\pi} \right)^{2/3}. \] (5.14)
The energy expression, given in Eq. (5.11), evidently depends only on the electron density and the given nuclear potential energy \( V_N \). Minimizing this expression with respect to the charge density \( n(r) \) under the condition that the total number of electrons \( N \) is the integral of the charge density, will provide us the ground state energy and density of the system.

Although the original Thomas-Fermi theory is much simpler than the Hartee method, specially for very large systems, it does not take into account the exchange and correlation effects. These terms can of course be incorporated into the original Thomas-Fermi framework by using the local assumption and applying relations derived from the uniform electron gas. There exist various corrections to allow in an approximate manner for the effects of exchange, correlation, and density gradients. One such is the von Weizäcker correction, \(^{60}\) where the correction to the kinetic energy functional \( t(n(r)) \) is given by
\[ \delta t(n(r), \nabla n(r)) = \frac{1}{72} \left( \frac{\hbar^2}{8\pi^2m} \right) \frac{|
abla n(r)|^2}{n(r)}. \] (5.15)
This leads to improved results, but the improvements are not consistent. The difficulty in testing the validity of the Thomas-Fermi theory and also improving it in a consistent manner, has led to the search for a firm and exact theoretical foundation for dealing with interacting electronic systems in terms of the density \( n(r) \). One very elegant approach to this is DFT, which is the main subject of the following sections.

### 5.1.2 Density Functional Theory

From previous section it is easy to see that the electron structure of a solid is uniquely determined by the external potential \( v(r) \) and the number of electrons \( N \). This potential acts on the \( N \) electrons and the properties of the system are governed by \( v(r) \). In 1964 Hohenberg and Kohn\(^{125}\) showed that the external potential can be replaced in
5.1 Total Energy Calculations: The Ground State

this role by the charge density \( n(\mathbf{r}) \) of the \( N \) electrons. They also showed that except for an additive constant the replacement is unique. Since the charge density also fixes the number of electrons \( N \), it follows that the whole system can be described by the charge density. This was a first attempt to describe the effects of exchange and correlation in an easy way for an electron gas in a given external field.

The main idea behind DFT is to write the total groundstate energy of the system as a functional of the charge density in the following way:

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

(5.16)

where the second term describes the interaction of the electrons with an external potential \( v_{\text{ext}}(\mathbf{r}) \). The remarkable thing about this equation is that the functional \( F \) only depends on the charge density and not on the external field. The actual groundstate energy \( E \) and density \( n(\mathbf{r}) \) are then obtained by minimizing the energy functional \( E[n] \) in Eq. (5.16) with respect to variations in \( n(\mathbf{r}) \), subject to the constraint of constant particle number \( N \).

There exist different possible representations of the functional \( F[n] \). An explicit form for the functional \( F \) is given by the Kohn-Sham representation, in which the functional \( F \) is written as

\[
F[n] = T[n] + \frac{1}{2} \int n(\mathbf{r}) v_c(\mathbf{r} - \mathbf{r'}) n(\mathbf{r'}) d\mathbf{r} d\mathbf{r'} + E_{XC}[n],
\]

(5.17)

where

\[
n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2,
\]

(5.18)

with \( \psi_i(\mathbf{r}) \) being the one-particle eigenfuctions. The functional \( T[n] \) is the kinetic energy of independent electrons, i.e. electrons without mutual Coulomb repulsion, in their groundstate, and can be written as

\[
T[n] = \sum_{i=1}^{N} \int \frac{\hbar^2}{2m} |\nabla \psi_i(\mathbf{r})|^2 d\mathbf{r}.
\]

(5.19)

The second term in Eq. (5.17) is the Coulomb energy with \( v_c(\mathbf{r}) = \frac{1}{|\mathbf{r}|} \). The functional \( E_{XC}[n] \) is the so called exchange-correlation energy. The physical effects included in \( E_{XC} \) are of both a potential and kinetic energy character, i.e. a negative potential energy due to the Pauli principles (the exchange effect), a negative potential energy due to the Coulomb repulsion (the correlation effect) and a positive correlation contribution to the kinetic energy due to the uncertainty and Pauli principles.

To obtain the groundstate energy and density \( n(\mathbf{r}) \), we can minimize the functional given in Eq. (5.17) w.r.t. the \( \{\psi_i(\mathbf{r})\} \). This is equivalent to minimizing the energy-functional \( E[n] \) w.r.t. \( n(\mathbf{r}) \) and gives us the following one-particle Schrödinger equations with an effective potential \( V_{\text{eff}} \), i.e.

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}} \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad i = 1 \cdots N,
\]

(5.20)
where

\[
V_{\text{eff}}(\mathbf{r}) = \int v_c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') d\mathbf{r}' + v_{\text{ext}}(\mathbf{r}) + \frac{\delta E_{\text{XC}}[n]}{\delta n}.
\]

From the discussion above we see that in the DFT formalism one can replace the N-body Schrödinger equation with N one-particle Schrödinger equations. This is a huge simplification for solving the many-body problem. The price for this simplification is that one has to come up with some physically relevant approximations for the exchange-correlation energy (see the discussion in the next section).

To obtain an explicit form for the exchange-correlation energy, one can turn on the electron-electron interaction adiabatically. This means that one introduces a coupling constant \( \lambda \), which varies from 0 to 1, connecting a non-interacting system with a physical one. The many-body Hamiltonian for the system can then be written as

\[
H_\lambda = T + v_{\text{ext}}(\mathbf{r}) + \lambda v_{ee} + v_\lambda,
\]

where we have introduced a new external potential \( v_\lambda \) to have a constant charge density when varying the coupling constant \( \lambda \).\(^{128}\) The exchange-correlation energy can then be written exactly as an integral over the coupling constant, \(^{128}\) i.e.

\[
E_{\text{xc}} = \frac{e^2}{2} \int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n_{\text{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}),
\]

where

\[
n_{\text{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) = n(\mathbf{r}') \int_0^1 d\lambda [g_{\lambda}(\mathbf{r}, \mathbf{r}', \lambda) - 1].
\]

The function \( g_{\lambda}(\mathbf{r}, \mathbf{r}', \lambda) \) is the pair correlation function in the system with the density \( n(\mathbf{r}) \). The physical meaning of the function \( n_{\text{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) \) is that this function represents the charge density of an exchange-correlation hole that the electron creates around it. The exchange-correlation hole originates from the Pauli principle and the repulsive Coulomb interaction, which both reduce the probability of an electron to be near another one. The hole has a charge equal to that of an electron but different in sign. The exchange-correlation energy can be defined as the interaction between the electron and its exchange-correlation hole.

There can be said many things about the exchange-correlation hole. One important condition that the exchange-correlation hole should satisfy is the so-called sum rule, which can mathematically be written as\(^{128}\)

\[
\int d\mathbf{r}' n_{\text{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) = -1.
\]

This condition originates from the definition of the pair correlation function. The second important observation is that the exchange-correlation energy only depends on the spherical average of the exchange-correlation hole. Eq. (5.23) is exact but its evaluation for an arbitrary nonuniform system presents a virtually impossible task.
The Exchange and Correlation Energy

From the first section in this chapter we see that exchange and correlation are two effects illustrating the Pauli principle and Coloumb repulsion effects, respectively. The most natural and easiest way to obtain the energy due to these two effects in the DFT-formalism is the local density approximation (LDA). The assumption behind this approximation is that the exchange-correlation energy density $\varepsilon_{\text{XC}}(r)$ per electron in the system at a point $r$ in space is equal to the same quantity in a homogeneous electron gas with the same density at the same point. The exchange-correlation energy can be written as

$$E_{\text{XC}}[n] = \int \varepsilon_{\text{XC}}(r)n(r)dr,$$

where $\varepsilon_{\text{XC}}(r)$ is equal to the charge density of a homogeneous electron gas at the point $r$. This equation illustrates that the most important property of the LDA is that the exchange-correlation energy is local. This means that LDA ignores the inhomogeneous effects in the electron density. Thus, the LDA can be used when the charge density does not vary much in space. Unfortunately, many physical systems such as atoms, molecules and solids, have a strongly varying density, and one would expect that the LDA is not a good approximation. Actually, the LDA gives overestimated molecular bonds and cohesive energies in most cases. However, this approximation has been applied to many real systems and in several cases the results have been more accurate than the expectations have suggested. The reason for this success is that the correlation energy in the LDA satisfies a number of exact sum rules. The LDA can be considered to be a first order approximation. The natural improvement is to let the XC-energy not only be a function of the charge density but a function of the charge density $n(r)$ and its gradient $\nabla n(r)$. In such a gradient approximation the XC-energy can be written as

$$E_{\text{XC}}[n] = \int \varepsilon_{\text{XC}}(n(r))n(r)dr + \int B_{\text{XC}}(n(r))|\nabla n(r)|^2 dr,$$

where the function $B_{\text{XC}}(n)$ is obtained by means of the density-density response function of a homogeneous electron gas. Unfortunately, the original Eq. (5.27) does not satisfy the sum rule (5.25). Starting with Langreth-Mehl, a series of improved gradient corrections have been proposed. Such approximations are called the generalized gradient approximations (GGA). For many calculations of the properties of materials, such as the binding energy and the lattice constant, the semilocal GGA gives better results than the local LDA.

There exist different GGA-functionals with their successes and failures. The functionals that we have used include the Perdew-Wang-91 (PW91), the Perdew-Burke-Erzenhof (PBE) functional, and two revised versions of the PBE functional (revPBE and RPBE). The PW91 functional is constructed to satisfy as many exact conditions as possible. The PBE functional is essentially the same as the PW91 functional, but it has a simpler functional form, fewer parameters and does not satisfy all the conditions that PW91 does. The construction of the revised version of
the PBE functional (revPBE) is based on a softening of the criteria used in the construction of the PBE functional, that is the Lieb-Oxford criterion,\textsuperscript{137} which gives a lower bound for the exchange-correlation energy. The RPBE functional fulfills this criterion but differs from PBE and revPBE in the functional form of the exchange-correlation energy. It has been reported that these functionals give rather different chemisorption energies.\textsuperscript{136} The RPBE functional seems to be the most reliable one for the molecule-surface calculations. The following table shows the changes in the Pd lattice constant (a), the chemisorption site (Z), the bond length (b) and the chemisorption energy ($E_{chem}$) for the CO/Pd(111) system.\textsuperscript{136} The table shows that

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PW91</th>
<th>PBE</th>
<th>revPBE</th>
<th>RPBE</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3.89</td>
<td>3.99</td>
<td>3.99</td>
<td>4.01</td>
<td>4.02</td>
<td>3.89</td>
</tr>
<tr>
<td>Z</td>
<td>1.85</td>
<td>1.93</td>
<td>1.93</td>
<td>1.95</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>1.19</td>
<td>1.19</td>
<td>1.19</td>
<td>1.19</td>
<td>1.19</td>
<td>1.13</td>
</tr>
<tr>
<td>$E_{chem}$</td>
<td>-2.74</td>
<td>-2.07</td>
<td>-1.94</td>
<td>-1.64</td>
<td>-1.65</td>
<td>-1.47</td>
</tr>
</tbody>
</table>

the lattice constant (a), the chemisorption site (Z) and the bond length (b) are almost independent of the choice of exchange-correlation functional. The LDA gives smaller values for these parameters than GGA. On the other hand the value of the chemisorption energy depends strongly on the choice of exchange-correlation functional. It is clear from the table that LDA is not accurate enough when studying adsorbate-metal systems. Among the different GGA functionals the revised versions of PBE (revPBE and RPBE) prove to be the best candidates for giving accurate chemisorption energies.

**Plane Waves**

So far we have discussed the DFT-formalism and have noted that this formalism reduces the problem of solving the many-body Schrödinger equation to that of solving one-particle Schrödinger equations in a consistent manner. This is a huge simplification, but it still remains a formidable task to solve these one-particle Schrödinger equations for an infinite number of non-interacting electrons interacting in the potential of an infinite number of nuclei. To overcome these difficulties, one can use periodic systems and apply Bloch’s theorem to the electronic wavefunctions.

Bloch’s theorem says that in a periodic lattice the wavefunction of each electron can be written as

$$\psi_i(\mathbf{r}) = u_i(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}),$$  \hspace{1cm} (5.28)

where the function $u_i(\mathbf{r})$ has the symmetry of the crystal lattice. The theorem makes it possible to calculate a finite number of electronic wavefunctions instead of an infinite number. However, each wavefunction should be calculated in an infinite number
of \( k \)-points, since the wave-vector spectrum is continuous and infinite. To reduce the problem one uses periodic systems (supercells), that obey periodic boundary conditions, which makes the wave-vector spectrum to become discrete, but still infinite. To make the spectrum finite, one samples \( k \) points and introduces a cutoff energy, which means that one just take into account wave vectors corresponding to an energy less than the cutoff energy. This approximation is valid since it has been shown that the wave vectors with small kinetic energy are more important than those with large kinetic energy. This approximation leads to an error in the calculated physical quantities and raises the question of convergence. To make sure that the calculated physical quantities are reliable, one has to do a convergence test w.r.t. the cutoff energy and the \( k \) point sampling. The question of convergence differs between different systems, such as bulk and slab systems. For bulk calculations it is enough to ensure that the total energy is converged w.r.t. the two criteria mentioned above. In slab calculations, on the other hand, there is another factor which plays an important role in the accuracy of the results, that is the size of the slab geometry (number of atom and vacuum layers). Hence, in slab calculations, one has to perform a convergence test w.r.t. the size of the slab geometry in addition to the convergence tests done in bulk calculations.

**Pseudopotential Approximation**

The previous section implies that using a plane-wave basis simplifies the computation. However, to perform an all-electron calculation would require an extremely large number of plane waves. To overcome this problem a pseudopotential (PP) approximation is introduced. This approximation is based on the fact that most physical properties of solids depend more on the valence electrons than on the core electrons. In the pseudopotential approximation one introduces a weak pseudopotential for the valence electrons that includes the effect of the core electrons and the strong core potential and acts on a set of pseudo wavefunctions rather than the true valence wavefunctions. The pseudopotential is constructed so that the pseudo wavefunctions have the same scattering properties as the real valence wavefunctions outside the cutoff radius \( r_c \), but are smooth inside.\(^\dagger\) This is illustrated in the figure below. To construct a pseudopotential we perform an all-electron calculation for a free atom, solving the Kohn-Sham equations with a full potential, and obtain all the Kohn-Sham orbitals. For each angular momentum \( l \), we choose some of these orbitals to be the valence orbitals and the rest to form the core. Then we choose a cutoff radius \( r_c \), for each angular momentum channel, so that the valence orbitals do not have any nodes outside \( r_c \).\(^\ddagger\) The pseudo wavefunctions are constructed to coalesce with the valence wavefunctions outside \( r_c \) and to be smooth inside. The pseudopotential is then calculated by using a potential that generates the chosen

\(^\dagger\) The real valence wavefunctions have large oscillations in the core region. It is necessary to keep them orthogonal to the core wavefunctions. In the pseudopotential approximation the core electrons are missing and the pseudo wavefunctions can be smooth in the core region.

\(^\ddagger\) In the simplest version, the same cutoff radius can be chosen for each angular momentum.
Figure 5.1: An illustration of the pseudopotential (dashed line) and the all-electron potential (solid line) and their corresponding wavefunctions. Whereas the two potentials are matched outside the core region, inside the core region the pseudopotential is finite and the all-electron potential diverges. This property of the pseudopotential gives smooth pseudo wavefunctions in the core region.

pseudo orbitals. Since the whole procedure is $l$-dependent, the pseudopotential is also $l$-dependent and has the following general form

$$V_{NL} = \sum_{lm} |lm > V_l < lm|,$$  \hspace{1cm} (5.29)

where $|lm >$ are spherical harmonics and $V_l$ is the pseudopotential for angular momentum $l$.

There are different types of pseudopotentials.\cite{138} In the norm-conserving pseudopotentials the pseudo wavefunctions are constructed so that their norms are conserved. This condition is necessary for the pseudo wavefunctions to produce the same charge density as the true valence orbitals. The first attempt to construct such pseudopotentials has been done by Hamann, Schlüter and Chiang (HSC).\cite{139} It has been shown that the norm-conserving condition not only fixes the charge density problem but also improves the accuracy of the pseudopotential. These pseudopotentials are semi-local, in the sense that they are local in the radial variable but non-local in the angular dependency:

$$V_{HSA} = V_{loc}(r) + \sum_l |lm > V_l < lm|.$$

These PP’s are not efficient to implement in a plane-wave-based method. A high implementation efficiency became possible, when Kleinman and Bylander\cite{140} showed how to cast a semi-local pseudopotential into a fully non-local separable form. In 1990, Vanderbilt proposed a method to construct non-local pseudopotentials directly without using the Kleinman and Bylander method. Vanderbilt’s pseudopotential, called ultra-soft pseudopotential (USPP), circumvents the norm constraint by intro-
ducing a generalized orthogonality condition, which makes the pseudo wavefunctions really smooth in the core region. This new method for constructing smooth pseudopotentials paved the way for a huge development in this area. In this work we use ultrasoft pseudopotentials of the Vanderbilt type for oxygen, nitrogen, and aluminum.

5.2  Electronic Excited States

As mentioned in the beginning of this chapter, the standard DFT is formulated for the electronic ground-state of a many-electron system, and fails to account for electronically excited states. It has, however, some limited but exact results on excited states, as the Hohenberg-Kohn theorems can be applied to excited states that have the lowest energy, in each given overall symmetry.¹²⁸,¹⁴¹ There are several attempts to extend the standard DFT to take into account electronically excited states. These include the GW approximation,¹⁴²–¹⁴⁴ Görtling-Levy perturbation theory,¹⁴⁵–¹⁴⁷ time-dependent DFT (TDDFT),¹⁴⁸–¹⁵⁰ and ΔSCF.¹²⁸,¹²⁹,¹⁴¹,¹⁵¹ Although the above mentioned theories look very promising in accounting for electronically excited states within simple systems, such as atoms and molecules, they fail to do so for more complex systems, e.g., gas-surface systems. In the following we propose a simple and intuitive method to study electronically excited states in some dynamical processes. The method can be considered as a generalization of the original ΔSCF, replacing the HFA or its natural extensions with DFT framework.

5.2.1  Electronically Excited States in DFT

In the standard interpretation of DFT, detailed in the previous sections, the set of KS energy parameters \( \epsilon_i \), defined in Eq. (5.20), have no physical meaning except for the highest occupied one, which represents the ionization energy.¹⁴¹ Although the KS-orbitals in the standard DFT are only introduced to make the minimization procedure of the energy functional given in Eq. (5.17), they can be considered to describe non-interacting electrons in an exchange-correlation potential and can be used to define an electronic configuration. As such, the KS-orbitals account for bond formation, charge-transfer, and other physically important effects.

Having obtained the ground-state KS-orbitals, by solving the equations (Eq. (5.20)), a certain excitation into the system can be introduced in a natural and intuitive way by utilizing the concept of electron-hole (e-h) pairs, i.e. charge-transfer between occupied and unoccupied KS-orbitals. In order to create such e-h pairs, i.e. change the occupancies of the KS-orbitals by unity, occupation numbers \( n_i \) are assigned to each KS-orbital \( \psi_k \), with \( n_i = 0 \) representing an empty orbital (a hole) and \( n_i = 1 \) an occupied one. Using the occupation numbers, the charge density given in Eq. (5.18) is modified to

\[
n(r) = \sum_{i=1}^{\infty} n_i |\psi_i(r)|^2,
\]

(5.31)
and the charge density of the excited configuration becomes

$$\tilde{n}(r) = \sum_{i=1}^{\infty} n_i |\tilde{\psi}_i(r)|^2. \quad (5.32)$$

Here the new set of KS-orbitals $\tilde{\psi}_i(r)$ describe the electronically excites system, calculated in a self-consistent way with $n_i = 0$ form some $i \leq N$, and where KS-orbitals $\psi_r(r)$ that are unoccupied in the ground-state now are included ($n_f = 1$).

This electronically excited charge density is used to construct the potential and set up new KS equations, which are solved self-consistently with the only restriction of keeping the hole fixed in the affected KS-orbital $\psi_f(r)$. In solving these KS equations, all the effects from the excitation are dealt with self-consistently, as the constructed potential depends on excited KS orbitals $\tilde{\psi}_i(r)$. The energy of the electronically excited system is evaluated in the usual minimization procedure for the energy functional given in Eq. (5.17), with the electron density of the excited system as the input.

Technically, some minor problems are encountered, as the method is applied to extended systems, e.g., gas-surface system. For a finite system, like an atom or a molecule, e-h pairs are introduced easily, as each fully occupied orbital has only one energy level. For extended systems, on the other hand, the identification of the relevant KS orbitals and introduction of e-h pairs becomes complicated due to the densely packed KS orbitals and their corresponding energy levels. This is accomplished by utilizing the confinement supercell method, with its discrete sampling of $k$-space, together with a thorough analysis of the local density of states.
Conclusions and Outlook

The goal of this thesis is to elucidate various aspects of aluminum oxidation in general and the initial stage in particular. The complexity of the oxidation process has forced us to consider the different stages separately and develop new theoretical methods and concepts. For the initial stage, the importance of non-adiabatic processes and the power of trend studies is demonstrated, as it has deepened our understanding of the oxidation process and shed light on many physical phenomena. Studying the final stage of the oxidation process, the oxide has also led us to the prediction of a one-dimensional electron gas on the surface of the metastable κ-aluminum oxide. It is fascinating that a phenomenon that has so many industrial applications provides us with problem settings that calls for a better understanding of new fundamental physics.

For the adsorption of oxygen on the surface, both adiabatic and non-adiabatic descriptions have been put forward. Many concepts, such as harpooning, exoelectrons, surface chemiluminescence, spin flipping, and abstraction, have been introduced, which indicates that already this early stage of oxidation may have many intricate features.

An important issue in understanding the initial stage of aluminum oxidation is the very low initial thermal dissociative sticking probability of oxygen. A traditional activation barrier in either the entrance or the exit channel has earlier been the suggested explanation to this observation. Our extensive mappings of the adiabatic O₂/Al(111) potential-energy hypersurface show barriers to be absent in the exit channel and present in the entrance channel only for some rare conditions, without statistical significance. As our adiabatic calculations thus show ground-state DFT to be insufficient to account for the observed energy dependence of the sticking probability, we have taken a step beyond the adiabatic ground-state DFT to include non-adiabatic effects and developed a new method to deal with excited states. On the basis of the calculated excited states for the O₂/Al(111) system a non-adiabatic model is constructed that looks very promising in describing the sticking behavior...
correctly. In order to test the robustness of our non-adiabatic model the study of oxygen adsorption on Al(111) is augmented with similar calculations for adsorption of other diatomic molecules on the same surface. Based on these studies, a general framework is proposed to describe trends in the sticking behavior of diatomic molecules on a simple sp-band metal, such as the Al(111) surface. Although our sticking model looks promising, a complete understanding of the initial stage of aluminum oxidation should include a fully dynamical multi-dimensional description with dissipation. This remains as a challenge for future theoretical studies, however.

Our DFT-based method to deal with electronically excited states finds applications in other areas as well. Most interesting examples include photodissociation of dimers, exoelectron emission and chemiluminescence in gas-surface reactions. Although there exist more sophisticated methods to extend the standard DFT to incorporate electronically excited states, e.g., time-dependent DFT, our "DSCF" method is very attractive, as it provides a simple and intuitive alternative for describing excitations. Therefore, its full applicability and limitations should be explored in the near future and its accuracy compared to the existing methods.

Another issue in the initial stage of aluminum oxidation is the existence of an intermediate molecularly adsorbed state, still a matter of discussion. Based on separate and independent measurements of the sticking probability and its surface temperature dependence, the dissociation of oxygen on the (111) surface of aluminum has been reported as both a direct one and one mediated by a molecular precursor. Such intermediate molecular states are evident for several molecules in our adiabatic trend study on the adsorption of diatomic molecules on the Al(111) surface, and should be searched for experimentally. For the O$_2$ molecule, however, the intermediate molecular state is calculated to be weakly bound, which might cause some experimental difficulties. There are also conflicting results concerning the fate of the oxygen atoms after dissociation, with such candidates as short-range diffusion, long-range transfer, and abstraction, i.e. dissociative decay by emission of one oxygen atom. The adiabatic PES for oxygen on Al(111) is of key importance to assess these phenomena.

To understand the oxidation process, successive adsorption, diffusion, and aggregation of oxygen on the aluminum surface have to be described. The structure, energetics, and bonding of surface and subsurface layers of O on Al at different coverages have also to be characterized. The theoretical works done to assess these phenomena are sparse, which makes a first-principles study very valuable in understanding the oxidation of aluminum. Although extensive mappings of the energetics of oxygen on the surface are presented in this thesis, a proper explanation of the observed oxygen islands remains as a challenge for future studies. Here a theoretical study, bridging the atomic-scale DFT calculations and model studies by, e.g., Kinetic-Monto-Carlo (KMC) simulations, could be very worthwhile. A proper theoretical explanation of the initial oxide formation is also lacking, as a large number of atoms is required to model this process. Such a study is beyond the practical limit of existing first-principles methods, however.

In the other limit of aluminum oxidation, there is the surface film of aluminum
oxide, exhibiting a variety of stable and metastable phases. As mentioned in the beginning, a new 1DEG is predicted on a metastable alumina surface and characterized. Here extensive DFT calculations make the basis of our prediction, and a phenomenological model is introduced to study the metal-insulator phase transition in this system. The latter is essential in convincing the experimentalists to grow the surface and measure on it. From a Luttinger-liquid perspective, the predicted 1DEG should be very interesting, as it should exist in a much broader temperature interval than any other suggested manifestation of the 1DEG.

One-dimensional systems are of great importance in nanoscience and technology. Today, there exists a number of one-dimensional systems with interesting future applications, such as rechargeable batteries, light-emitting devices, transistors, sensors, and much more. Scientifically, these systems are important in understanding electron-electron interaction effects in low dimensions and have attracted large amounts of theoretical work. Our predicted one-dimensional system adds to the existing systems. In addition, our system provides a much better one-dimensional electron gas compared to the existing ones, as it has a simple bandstructure and is metallic over a wider temperature range. An experimental verification of this system should be of great interest for future applications and studies.

As a final remark, it is noted that all the included studies concern electron-electron interaction effects under different conditions and in different dimensions. For molecule-surface systems, electron-electron interactions are essential in breaking the molecular bond, as they provide the necessary non-adiabatic channels to dissipate the energy. What is viewed as three-dimensional overlap between the electronic states of the adsorbate and the substrate in formation of the molecule-surface bond is viewed as a propensity for tunneling in the time-dependent adsorption process, resulting in sticking. Surplus heat has then to be dissipated. In 1D systems, where our predicted 1DEG makes an excellent candidate, on the other hand, electron-electron interactions play a decisive role in the behavior of the 1DEG. However, the reduced dimensionality calls for new descriptions of these effects, for instance those observed in photoemission spectra. Here Luttinger-liquid theory proves to be the best candidate.
There is certainly a number of people who has made this thesis possible and mentioning them by name is only a very small token of thanks for their contributions.

Bengt Lundqvist, it is my great pleasure to thank you for providing such a friendly atmosphere, for your encouragement and advice. You manage to strike the perfect balance between providing direction and encouraging independence. I am deeply grateful for your understanding and support, when I wanted to go to Milan to pursue a career in Fashion Design, and when I came back to finish my thesis. Per Hyldgaard, thank you for acting as my second supervisor, and for always being around to answer my questions. Our discussions have been a great source of inspiration! Igor Zorić, thank you for your advice and never-ending ideas. I would probably have been lost in my theories, had it not been for you to remind me of “reality”. Anders Hellman, Carlo Ruberto, and Yashar Yourdshahyan, you have been such good friends and collaborators! Not only have you helped me to reach this point, but you have also provided a great deal of fun moments. Thank you! Many thanks to all members of the Materials and Surface Theory group, past and present, for contributing to the pleasant atmosphere. Ing-Britt Bengtson, Camilla Eriksson, and Margaretha Lövgren, I am indebted to you for taking care of various administrative issues. Kristian, Erik, Tobias, and Martin, I am grateful for your sincere support and friendship. Ania, my adorable girlfriend, thank you for everything. You have meant more for the completion of this thesis than you can imagine. And last, but certainly not least, my mother Nahid and my brother Reza, thank you for your uncompromising support and encouragement throughout my studies, and for helping me to reach my goals.

Göteborg, March 2003,
Behrooz Razaznejad
Bibliography


[41] M. Schmid, G. Leonardelli, R. Tschelieβnig, A. Beidermann, and P. Varga, 
L355-L362.


2603.


[83] D. Sigel, private communications.


The Semiclassical Master Equation

The starting point of the semiclassical master equation is the time-dependent Newns-Anderson Hamiltonian,\(^5^4\) which can be written as

\[
H(t) = \sum_{k,\sigma} \varepsilon_k c^\dagger_{k,\sigma} c_{k,\sigma} + \sum_{\sigma} \varepsilon_{a,\sigma}(t) c^\dagger_{a,\sigma} c_{a,\sigma} \\
+ \sum_{k,\sigma} (V^\dagger_{a,k}(t) c^\dagger_{k,\sigma} c_{a,\sigma} + V_{k,a}(t) c^\dagger_{a,\sigma} c_{k,\sigma}) \\
+ U(t) c^\dagger_{a,\sigma} c_{a,\sigma} c^\dagger_{a,\sigma} c_{a,\sigma}. \tag{A.1}
\]

Here \(\varepsilon_{k,\sigma}\) and \(\varepsilon_{a,\sigma}(t)\) represent the energy levels of the substrate states \(|k, \sigma\rangle\) and the adsorbate level \(|a, \sigma\rangle\), respectively (\(\sigma\) being the spin degree of freedom), and \(c^\dagger_{k,\sigma}(c_{k,\sigma})\) and \(c^\dagger_{a,\sigma}(c_{a,\sigma})\) their corresponding creation (annihilation) operators. The operators \(n_{k,\sigma} = c^\dagger_{k,\sigma} c_{k,\sigma}\) and \(n_{a,\sigma} = c^\dagger_{a,\sigma} c_{a,\sigma}\) are the number operators for the substrate states \(|k, \sigma\rangle\) and adsorbate level \(|a, \sigma\rangle\), respectively. The quantity \(U\) describes the effective Coulombs interaction in the adsorbate level. In the Hartree-Fock approximation, the last term can be omitted by making the following replacement

\[
\varepsilon_{a,\sigma}(t) \to \varepsilon_{a,\sigma}(t) - U <n_{a,\sigma}>. \tag{A.2}
\]

This is a good approximation if the fluctuation of the opposite spin \((-\sigma)\) is small or if \(U\) is small compared to the electronic bandwidth of the substrate. Using the Heisenberg’s equations of motion and suppressing the spin index for simplicity, the operators \(c^\dagger_a\) and \(c^\dagger_k\) satisfy the following equations

\[
i \frac{\partial c_a}{\partial t} = \varepsilon_a(t) c_a(t) + \sum_k V_{a,k}(t) c_k(t) \tag{A.3}
\]

and

\[
i \frac{\partial c_k}{\partial t} = \varepsilon_k c_k(t) + V_{k,a}(t) c_a(t). \tag{A.4}
\]

75
Before solving the above equations, two approximations should be made. In the first
one the matrix elements $V_{a,k}(t)$ are written as

$$V_{a,k}(t) = V_{a,k}u(t), \quad \text{(A.5)}$$

where $u(t)$ is a parametrized function independent of $a$ and $k$. In the second approx-
imation, it is assumed that the chemisorption function, $\Delta(\omega)$, given by

$$\Delta(\omega) = \pi \sum_k |V_{a,k}|^2 \delta(\omega - \varepsilon_k), \quad \text{(A.6)}$$

where $\delta(\varepsilon)$ is the Dirac delta function, is independent of energy. Solving Eq. (A.4),
using the two approximations, and inserting the solution into Eq. (A.3), yields the
following equation of motion for $c_a(t)$

$$i \frac{dc_a}{dt} = [\varepsilon_a(t) - i\Delta(t)]c_a(t) + \sum_k V_{a,k}u(t)c_k(t_0) \exp(i\varepsilon_k(t_0 - t)). \quad \text{(A.7)}$$

Integrating this equation, assuming that the substrate is in thermal equilibrium, i.e.

$$< c_k^\dagger(-\infty)c_K(-\infty) > = f(\varepsilon_k, T), \quad \text{(A.8)}$$

where $f(\varepsilon_k, T)$ is the Fermi distribution function at temperature $T$, using that the
occupation number of the adsorbate level is given by

$$< n_a(t) > = < c_k^\dagger(t)c_k(t) >, \quad \text{(A.9)}$$

and that the cross terms $< c_k^\dagger(-\infty)c_K(-\infty) >$ vanish, yields the following equation
for the ensemble average of the occupation number for the adsorbate level

$$< n_a(t) > = < n_a(-\infty) > \exp[-2 \int_{-\infty}^t \Delta(t) dt]$$

$$+ \frac{1}{\pi} \int_{-\infty}^{\varepsilon_F} f(\varepsilon, T) |A(\varepsilon; t, -\infty)|^2. \quad \text{(A.10)}$$

The first term is the memory term, which describes the irreversible process of decay
of the initial state. This term can be neglected, as it is decaying exponentially. The
second term is the production term, where $A$ is the occupation probability amplitude
given by

$$A(\varepsilon; t, -\infty) = \int_{-\infty}^t \sqrt{\Delta(t')} \exp\{i\varepsilon t' - \int_{t'}^t [i\varepsilon_a(s) + \Delta(s)] ds\} \, dt'. \quad \text{(A.11)}$$

In order to obtain a classical master equation, the occupancy of the adsorbate level,
given in Eq. (A.10), is differentiated w.r.t. $t$, which leads to the following master
equation

$$\frac{d < n_a(t) >}{dt} = 2\Delta(t)N(1 - < n_a(t) >) - 2\Delta(t)(1 - N) < n_a(t) >, \quad \text{(A.12)}$$
where

\[
N = \int_{-\infty}^{E_F} f(\varepsilon, T) \rho_a(\varepsilon) d\varepsilon,
\]

(A.13)
is the equilibrium occupancy and \(\rho_a(\varepsilon)\) is the density of states of the adsorbate level. Two assumptions are made to derive the classical master equation: (i) that the \(\varepsilon_a(t)\) and \(\Delta(t)\) vary slowly in time, and (ii) the tunneling time is smaller than the scattering time.

Finally, it is noted that the probability of the occupation \((P_{n_a}(t))\) of the adsorbate level is related to its occupation number \((n_a(t))\) by

\[
<n_a(t)> = \int_{-\infty}^{E_F} P_{n_a}(t) \rho_a(\varepsilon) d\varepsilon,
\]

(A.14)

which gives the following master equation for the occupation probability

\[
\frac{dP_{n_a}(t)}{dt} = 2\Delta(t) f(\varepsilon, T)(1 - P_{n_a}(t)) - 2\Delta(t)(1 - f(\varepsilon, T)) P_{n_a}(t).
\]

(A.15)
The first term describes the charge-transfer from the substrate to the adsorbate level, while the second term describes the back-donation of charge and is neglected for our sticking study (compare to Eq. (2.17)).
APPENDIX B

Solutions of the SSH Hamiltonian

The SSH Hamiltonian can be written as

\[ H = H_e + H_{e-\text{ph}} + H_{\text{ph}}, \]  

(B.1)

where

\[ H_e = t_0 \sum_{n,s} (c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s}), \]

\[ H_{e-\text{ph}} = -\alpha \sum_{n,s} (u_{n+1} - u_n)(c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s}), \]

and

\[ H_{\text{ph}} = \sum_n \frac{K}{2} (u_{n+1} - u_n)^2, \]

where \( u_n \) is the displacement of the \( n \):th atom, \( c_{n,s}, (c_{n,s}^\dagger) \) the fermionic creation (annihilation) operators, and \( t_0, \alpha, \) and \( K \) are parameters. According to Peierls theorem,\(^{120} \) the strongest instability occurs for a charge-density wave of wavevector \( G = 2k_F \). Hence, the displacement coordinates \( u_n \) are considered to be \( u_n = u \cos(2k_F na) \), where \( a \) is the lattice spacing. This makes \( H_{e-\text{ph}} \) invariant under spatial translations \( \frac{m\pi}{k_F}, m = \pm 1, \pm 2, \cdots \) and the total Hamiltonian can be diagonalized in the reduced zone \([−k_F, k_F]\). In order to do this, the fermionic operators \( c_{n,s} \) are Fourier transformed in the reduced zone \([−k_F, k_F]\) according to

\[ c_{k\gamma} = \frac{(-i)^\gamma}{\sqrt{N}} \sum_n e^{-ina(k+2\pi\gamma)}c_n, \quad \gamma = 0, \cdots, Q - 1, \]

(B.2)

where \( \frac{1}{Q} \) gives the filling of the conducting band. Here, only \( Q = 2, 4, \) and \( 8 \) are considered, corresponding to \( \frac{1}{2}, \frac{1}{4}, \) and \( \frac{1}{8} \)-filled bands, respectively. The
rationale for this is that the SSH Hamiltonian was originally studied for a 1/2-band, while our predicted 1DEG has a 1/8-filled conducting band. Inverting the relations given in Eq. (B.2) and using the fact that $u_n = u \cos(2k_F n a)$ under Peierls distortion, the Hamiltonian can be written as

$$H = \sum_{k,\alpha,\beta} c_{k\alpha}^\dagger \Gamma_{k,Q} c_{k\beta} + H_{ph}(u),$$  \hspace{1cm} (B.3)$$

where

$$\Gamma_{k,Q} = \begin{pmatrix}
\varepsilon_{k,0} & \Delta_{k,0} & \cdots & 0 & \Delta_{k,Q-1} \\
\Delta_{k,0} & \varepsilon_{k,1} & \cdots & 0 & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & \cdots & \varepsilon_{k,Q-2} & \Delta_{k,Q-2} \\
\Delta_{k,Q-1} & 0 & \cdots & \Delta_{k,Q-2} & \varepsilon_{k,Q-1}
\end{pmatrix},$$  \hspace{1cm} (B.4)$$

and $H_{ph}(u)$ is given below for each specific case ($Q = 2, 4, \text{and } 8$). The $\varepsilon_{k,\gamma}$ are the eigenvalues for $H_e$ and $\Delta_{k,\gamma}$ are the coupling terms between two adjacent bands. The latter terms arises from the electron-phonon coupling term in the Hamiltonian. Furthermore the energy eigenvalues $\varepsilon_{k,\gamma}$ and the coupling terms $\Delta_{k,\gamma}$ are such that $\varepsilon_{k,\alpha} = -\varepsilon_{k,Q+\alpha}$ and $\Delta_{k,\alpha} = -\Delta_{k,Q+\alpha}$, where $\alpha = 0, \cdots, \frac{Q-1}{2}$. Since the matrix $\Gamma$ is symmetric, there should exist a unitary transformation $U$, which diagonalizes $\Gamma$. Putting $\tilde{c}_{k\gamma} = U c_{k\gamma}$, the Hamiltonian takes the form

$$H = \sum_{k,\gamma} E_{k,\gamma} \tilde{n}_{k\gamma} + H_{ph}(u).$$  \hspace{1cm} (B.5)$$

The $E_{k,\gamma}$ are the eigenvalues of the full Hamiltonian, describing the bands $\gamma$ with electron-phonon coupling, and $\tilde{n}_{k\gamma} = \tilde{c}_{k\gamma}^\dagger \tilde{c}_{k\gamma}$ is the number operator for the band $\gamma$. The fermionic operators $\tilde{c}_{k\gamma}^\dagger / \tilde{c}_{k\gamma}$ are the collective modes of the system.

The explicit expressions for $H_{ph}(u)$, the eigenenergies $\varepsilon_{k,\gamma}$ and $E_{k,\gamma}$, and the coupling terms $\Delta_{k,\gamma}$, in each of the three considered cases ($Q = 2, 4, \text{and } 8$) are given below.

### B.1 The two-band case ($Q = 2$)

- The eigenenergies $\varepsilon_{k,\gamma}$:

$$\varepsilon_{k,0} = -\varepsilon_{k,1} = -2t_0 \cos(ka)$$

- The coupling terms $\Delta_{k,\gamma}$:

$$\Delta_{k,0} = 4\alpha u \sin(ka)$$
The eigenenergies $E_{k,\gamma}$:

\[
E_{k,0} = 2t_0 \sqrt{1 + (4z^2 - 1) \sin^2(ka)}
\]

\[
E_{k,1} = -2t_0 \sqrt{1 + (4z^2 - 1) \sin^2(ka)}
\]

where $z = \frac{au}{t_0}$.

The phonon Hamiltonian $H_{ph}$:

\[
H_{ph} = 2NKu^2
\]

**B.2 The four-band case ($Q = 4$)**

- The eigenenergies $\epsilon_{k,\gamma}$:
  \[
  \epsilon_{k,0} = -\epsilon_{k,2} = -2t_0 \cos(ka)
  \]
  \[
  \epsilon_{k,1} = -\epsilon_{k,3} = 2t_0 \sin(ka)
  \]

- The coupling terms $\Delta_{k,\gamma}$:
  \[
  \Delta_{k,0} = -\Delta_{k,2} = au(\cos(ka) - \sin(ka))
  \]
  \[
  \Delta_{k,1} = -\Delta_{k,3} = -au(\cos(ka) + \sin(ka))
  \]

- The eigenenergies $E_{k,\gamma}$:
  \[
  E_{k,0} = -E_{k,2} = -\sqrt{2t_0^2 (1 + z^2) \left[ 1 + \sqrt{1 - f^2(z) \sin^2(ka)} \right]}
  \]
  \[
  E_{k,1} = -E_{k,3} = -\sqrt{2t_0^2 (1 + z^2) \left[ 1 - \sqrt{1 - f^2(z) \sin^2(ka)} \right]}
  \]

where $f(z) = \frac{1-z^2}{1+z^2}$ and $z = \frac{au}{t_0}$.

- The phonon Hamiltonian $H_{ph}$:
  \[
  H_{ph} = \frac{1}{2} NKu^2
  \]

**B.3 The two-band case ($Q = 8$)**

- The eigenenergies $\epsilon_{k,\gamma}$:
  \[
  \epsilon_{k,0} = -\epsilon_{k,4} = -2t_0 \cos(ka)
  \]
  \[
  \epsilon_{k,1} = -\epsilon_{k,5} = -2t_0 \cos(ka + \frac{\pi}{4})
  \]
  \[
  \epsilon_{k,2} = -\epsilon_{k,6} = 2t_0 \sin(ka)
  \]
  \[
  \epsilon_{k,3} = -\epsilon_{k,7} = 2t_0 \sin(ka + \frac{\pi}{4})
  \]
• The coupling terms $\Delta_{k,\gamma}$:

\[
\begin{align*}
\Delta_{k,0} &= -\Delta_{k,4} = \alpha u \left( \sin(ka + \frac{\pi}{4}) - \sin(ka) \right) \\
\Delta_{k,1} &= -\Delta_{k,5} = -\alpha u \left( \sin(ka + \frac{\pi}{4}) - \cos(ka) \right) \\
\Delta_{k,2} &= -\Delta_{k,6} = \alpha u \left( \cos(ka + \frac{\pi}{4}) - \cos(ka) \right) \\
\Delta_{k,3} &= -\Delta_{k,7} = -\alpha u \left( \sin(ka) + \cos(ka + \frac{\pi}{4}) \right)
\end{align*}
\]

• The eigenenergies $E_{k,\gamma}$:

In this case it is not possible to obtain an analytic expression for the eigenenergies $E_{k,\gamma}$, but they are solved for numerically.

• The phonon Hamiltonian $H_{ph}$:

\[
H_{ph} = \frac{K N u^2}{2} \left( 1 - \frac{1}{\sqrt{2}} \right)
\]