Getting the electrons right for O2-on-metal systems

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1 Introduction

1.1 Heterogenous catalysis

Catalysis is one of the most vital and prevalent segments of chemistry[1]. From the growth of plant life[2,3] to the industrial production of fertiliser[1,4–6], from the aptly named catalyst in most modern fuel-based cars[7] to the production of the building blocks of life in outer space[8], catalytic processes occur all around us. Fundamentally, the presence of a catalyst in a chemical reaction will always speed up that reaction without the catalysis being altered or getting consumed by the chemical reaction[9].

This speedup can be achieved because a catalyst allows for a chemical reaction to occur via a different mechanism or pathway than would be the case without the presence of a catalyst[10]. A catalyst reacts with the reactants, i.e., starting chemicals, to form, bind, and stabilize the intermediate products. These intermediates convert into the final product of the chemical reaction, which is released, thereby regenerating the catalyst. This new pathway, though often more complex, is energetically more favourable, lowering the energy barrier to overcome for the reaction to occur. The entire process of consuming the reactants and regenerating the catalyst can be very fast, for an ideal catalyst very little of that catalyst is required to immensely speed up a chemical reaction[10].

The term catalysis was first used by Jöns Jakob Berzelius in 1835[11] to describe the acceleration of reactions by unchanged substances. The name comes from the Greek word “kataluein”, comprising of two terms “kata” translating to “down”, and “lyein” meaning “loosen”[11,12]. Although he was the first to use the term catalysis, Berzelius was not the first to describe the process of catalysis. It was Elizabeth Fulhame in 1794 who was the first to correctly describe the catalytic function of water in certain oxidation reactions[13]. The following centuries would, initially in conjunction with the Industrial Revolution, see a myriad of innovations and discoveries in the field of catalytic chemistry. Even now this work is still ongoing as chemists and chemical engineers try to find new and better catalysts to overcome modern challenges in chemistry, industry, and environmental science[14–22].

In general, catalysis is separated into three different categories. The first is homogenous catalysis, where the catalyst is dispersed in the same phase (gaseous, liquid, or solid) as the products and reactants of the reaction. The second category is heterogenous catalysis, where the phase of the catalysts is different from that of the products and the reactants. The third and final category is biocatalysis or enzymatic catalysis. This third category can in principle be seen as either homogenous or heterogenous depending on the type of biocatalyst or enzyme, but due to its distinctive nature from the other two types, it is generally treated as a separate category. The homogenous option may initially seem the most optimal choice for a catalyst, as it would facilitate the most efficient mixing of reactants and catalysts. However, it is often difficult to separate catalyst, reactant and product from each other. In heterogeneous catalysis, the catalyst is typically a solid compared to the liquid[23] or gaseous reactants and products. The different phases reduce the optimal mixing but it does facilitate easy separation of the catalysts from products and reactants.

Heterogenous catalysis is thus found in most industrial chemical production chains and processes[24,25]. Examples are the Haber-Bosch process for the production of ammonia (NH_3) for fertilizers[5,26], steam reforming where water (H_2O) and methane (CH_4) form hydrogen (H_2) gas and carbon monoxide (CO)[27–29], and the formation of more complex hydrocarbons (C_cH_h) from carbon dioxide (CO_2) and H_2 via the reverse water gas shift reaction[17,18,30–32] and the Fischer-Tropsch reaction[18,33–36]. For all these examples the optimal conditions typically involve high temperatures, high pressures, carefully constructed ratios of reactants and products, and (often) complex and expensive catalysts painstakingly optimised for these reactions. These complexities make it difficult to improve a catalyst for chemical reactions and its optimisation is often achieved on a trial-and-error basis. However, further improvements are paramount as an optimal catalyst can substantially reduce the temperatures or pressures needed to attain high chemical reaction rates. This will make production more efficient and reduce the enormous energy needs of the chemical industry. It is therefore of great scientific interest to try and understand the chemistry involved in heterogenous catalysis to ultimately achieve the ability to accurately predict the behaviour of a new or optimised catalyst based solely on its chemical composition, molecular structure, and morphology.

In this chapter the current scientific work in heterogenous catalysis is discussed, setting up the context and the relevance of this thesis. In the next section, the field of surface science will be discussed (Section 1.2.1), followed by some basics of surface structure (Section 1.2.2) and molecule-surface interactions (Section 1.2.3). Thereafter, an overview of experimental techniques is discussed. We will proceed with a discussion on how to control the molecular conditions (Section 1.2.4) and then show a brief overview of experimental techniques in surface science (Section 1.2.5). Against the backdrop of experiments the relevance and methods of theories and models in surface science are discussed (Section 1.2.6). After this, we are finally ready to discuss the scope of this work (Section 1.3) and to briefly summarise the results of this thesis (Section 1.4).

1.2 Surface science

In the study of heterogeneous catalysts, there are two major branches of academic science. The first is focused on understanding the catalytic performance under industrial, or *in situ*, conditions. This branch looks at macroscopic effects and conditions in the catalysis reaction[37,38]. The second branch, referred to as surface science, is focused on the fundamental chemical steps involved in the reaction on the catalyst-reactant interface, or surface. The chemical reaction steps involved on a surface are often a complex network of coupled elementary steps[24,39]. Fortunately, most heterogeneously catalysed processes are rate-limited by one of just a few elementary reaction steps[6]. For example, the dissociation of N_2 is the rate-limiting step in the Haber-Bosch process[5]. Thus, in surface science, we aim to optimise heterogeneous catalysis by developing an understanding of these rate-limiting steps. Contrary to the other branch, surface science requires the elimination of as many variables as possible to study the elementary reaction steps with as few unknown parameters as possible[40–45].

1.2.1 Study of the active component in heterogeneous catalysis

The first elimination of unknowns is achieved by restricting the surface science research to the active component of the catalysis. For heterogenous catalysis (often also for homogenous catalysis) the active component is typically a metal. This is because of the unique electronic structure of metals. This unique structure allows the metal to donate or accept electrons from reactants, intermediates, or products at low energetic “costs”[46]. Both the easy acceptation and donation of electrons, in turn, make it easier for chemical bonds to be either formed or broken for molecules that are close to or adsorbed on the metal surface, lowering barriers to reactions.

This unique electronic structure of metals is a result of the formation of the metal solid. In general, a metal solid forms when enough atoms have clustered and stay rigidly together. In the process, both their occupied and unoccupied electronic orbitals will start to overlap. The overlap causes the orbitals to get smeared out, or delocalised, over the clustered atoms. This will transform the initially distinct energy levels of an atom, or molecule, into larger energy bands. These energy bands are separated by areas where there are no defined energy levels, i.e., band gaps[47]. The energy bands that form can be either occupied, partially occupied, or unoccupied with electrons. The boundary where an energy band goes from occupied to unoccupied in a surface is generally referred to as the Fermi-level[48].

The Fermi-level of a solid surface can be positioned in a band gap, like with insulators or semiconductors, separating the energy bands into the highest occupied “valence” band and lowest unoccupied “conduction” band[49]. For both semiconductors and insulators exciting an electron to go from the valence to the conduction band, a so-called electron-hole-pair (ehp) excitation, takes a minimum energy equal to the size of the band gap. However, for metals, the Fermi-level is positioned inside an energy band, i.e., the band is only partially occupied. Thus, there is virtually no energetic cost for ehp excitation and the half-filled band makes it easy for the metal to exchange electrons with other compounds. It is this unique property of metals to freely “play” with the electrons that so often makes them the active component in a catalytic reaction[46].

1.2.2 Surface structure

The second unknown that needs to be understood is the structure of a metal (catalyst) surface. The structure of a surface can for instance influence the position of the Fermi-level of the surface, it can influence the locations on the surface where molecules can interact with the metal, and it influences where and how certain elementary steps in the reaction occur[50]. In the industrial applications of heterogenous catalysis the metal surface is often shaped by nanoparticles meaning the surface is complex with many types of surface facets, steps, corners kinks, and often defects. However, to properly study the effects of specific surface structures the surface of the metal catalyst needs to be very well-defined, i.e., the surface structure needs to be simple and described at atomic level precision. These types of metal surfaces are made by growing metal single-crystals that are cut and polished along the desired crystal axis to expose the right type of surface face[51]. These surface faces are characteristically defined by their Miller indices, for example for Cu(111) the Miller indices are (111) and they define the type of metal surface as a (111) face of a, in the case of Copper, face-centred cubic (FCC) cystal[52].

1.2.3 Surface interactions

At this point, it is relevant to briefly discuss what kind of interactions can occur at these well-defined metal surfaces. The basic interactions of a molecule with a metal and the general events that will occur when a molecule interacts with a surface are already known for some time[53,54]. However, the specifics of the exact mechanisms, interactions, selectivity, or efficiencies remain an open question to this day[39,45,55,56]. At present it is well understood that a molecule approaching a metal surface can largely end up doing one of two things. The molecule can either adsorb on the surface, or it can bounce back, i.e., scatter, from the surface. In turn, both scenarios can be redivided into subcategories.

There are generally three different subcategories of adsorption for molecules on metal surfaces. All three are characterised by different interactions with the metal surface. In the first option, "physisorption", the interaction between the molecule and metal is over the largest distance, i.e., it occurs when the molecule is furthest away from the surface. In physisorption, the interaction is not chemical. Thus, there is no exchange of electrons. At longer distances the interaction is governed by "Van der Waals" forces[57], or more specifically London-dispersion forces[57]. In simple terms, the London dispersion force is induced because electrons are not static in an atom, molecule, or metal surface. The movement of electrons induces an electric field which other electrons in the area will respond to. This results in electronic motion getting correlated over a larger distance. This correlation results in an attractive force between small and opposite dipoles induced in the electronic structure of the metal and adsorbing molecule. The physisorption of molecules on a metal surface is a rather weak interaction possessing a shallow potential well (see **Figure 1.1**).

The second and third subcategories of adsorption are chemical in nature, and in both electrons or electronic density, act to form chemical bonds between the molecule and the surface, and both are called chemisorption. In molecular chemisorption, the molecule forms a chemical bond with the surface without breaking any internal bond. This chemical bond forms as the orbitals of the molecule start overlapping with the energy bands lying close to the Fermi-level of the metal[42], allowing for easy electronic exchange between molecule and metal. The last subcategory of adsorption is dissociative chemisorption (DC). In such a scenario the anti-bonding orbitals of the molecule end up below the Fermi-level of the metal, thus chemical bonds in the adsorbing molecule are broken to facilitate energetically more favourable bonds with the metal surface[42]. These dissociative chemisorption reactions tend to result in the strongest form of interaction between the molecule (fragments) and the metal.

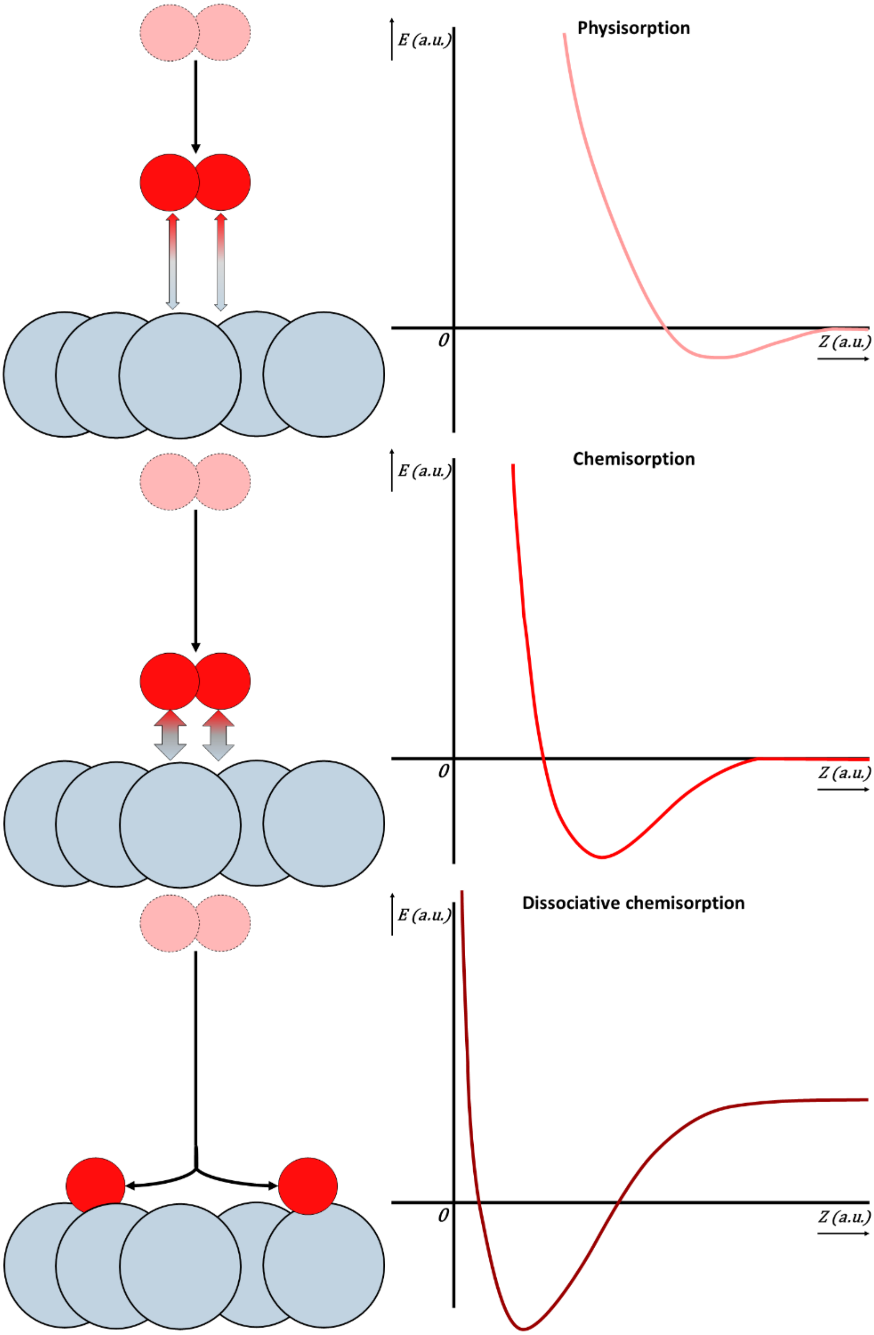

***Figure 1.1**: Schematic drawings of the three different simplified molecule-metal interaction types and their associated potential energy (E) as a function of the molecule-metal distance (Z), both in arbitrary units. All potentials are shown without additional barriers to interaction for visual and conceptual simplification.*

However, the attractive interactions are not always accessible for the approaching molecule and the molecule can be repelled from the surface, or sometimes the adsorption is not strong enough and the approaching molecule has too much internal energy and returns to the gas-phase. This results in scattering processes. Scattering can occur elastically when the molecule does not lose any internal energy when it bounces back to the gas-phase. Or, if the molecule does lose or gain some energy in the collision, the scattering is called inelastic[58]. Energy loss to, or gain from, the surface can happen via momentum transfer with the metal surface, excitation of electronic states in the metal, i.e., ehp excitations[59–61], or other more complicated, non-adiabatic, effects.

If the molecule is small enough a special type of scattering in the form of diffraction may occur[62]. This happens due to the interaction of the molecules with a periodic metal surface. Clean single crystal metal surfaces, as discussed in Section 1.2.2, possess repeating units. These periodic units will interact with the wavefunction of the approaching molecule (see Chapter 2) resulting in specific scattering patterns. This phenomenon is called diffraction and it is the same as how light diffracts on certain surfaces[63]. The larger, i.e., the heavier the molecule, the smaller its wave-function[64], thus the smaller this effect. We typically only observe diffraction patterns for electrons, H_2, He or other small molecules or ions.

The possibility of all of these occurrences makes the molecule-metal interactions complicated, because the occurrence of either adsorption or scattering does not exclude other events from occurring as well. Neither does adsorption need to be permanent: temporary adsorption can for example result in a form of inelastic scattering, and molecular chemisorption can be a precursor to dissociative chemisorption[65]. The combination of all these options means that even though the basic mechanisms for molecule-metal interactions are understood the complete detailed mechanical picture of all molecules interacting with metal surfaces is not known. In any system, any specific molecule with any (metal) surface will have their own, possibly unique, interactions with each other. The study of these interactions has therefore needed to develop into an enormous field of highly precise and systematic research.

1.2.4 Controlling reaction conditions

To ensure a clear picture of these complex interactions of metals and molecules in heterogeneous catalysis, the effect of many more unknowns besides the active components and surface structure needs to be eliminated. These include but are not limited to the temperature of the metal surface, the energy of the reactants, and additional molecules, or contaminations, that may influence the reaction. Moreover, any meaningful observations at the atomic scale needed to understand these complex mechanisms are very sensitive to even the smallest details. Therefore, most surface science experiments are done at ultra-high vacuum (UHV), i.e., at pressures smaller than 10^{-10} *mbar*, only slightly more than the gas pressures in the 'busy' parts of outer space. Not only does this high vacuum ensure there is very little contamination of unwanted chemical interactions, but it is also required for some measuring equipment to properly function.

The UHV conditions eliminate a lot of contamination and unwanted interactions but experiments still need to control the conditions of the molecules that interact with the metal. These days the introduction and conditioning of the molecules interacting with the metal is often achieved with molecular beam (MB) studies[66–71]. A MB is created by expanding a gas from a high-pressure room to a low-pressure room through a small nozzle. Due to this expansion, all molecules in the MB travel at roughly equal velocities in the same direction, undergoing very few collisions between them. The temperature of the nozzle (T_N) influences the rovibrational temperature of the beam[69], i.e., it determines the rotational and vibrational energy of the molecules in the MB. Similarly, T_N also influences the translational kinetic energy of the molecule, which in surface science is referred to as the incidence energy (E_i)[71].

However, often "seeding" is used to systematically influence the total E_i of the MB, without changing the rovibrational states as those can be kept constant with a constant T_N. Seeding is done by mixing the molecule of interest in a beam of inert (often noble) gases. A gas seeded with a lighter noble gas will travel faster, i.e., increase E_i, and a gas seeded with a heavier noble gas will travel slower. If only the normal component of the incidence energy, i.e., the component that is normal to the metal surface, influences the reaction of the molecule, i.e., if normal energy scaling (NES) holds[72], then the angle of the molecular beam (Θ) with the metal surface can also be altered to change the normal incidence energy ($E_i^{\perp}$) and thereby investigate the dependence of the reaction on this energy.

In some MB studies magnetic fields, electric fields or lasers can be used to further select or excite certain molecular states[73–76]. It must be noted that although MBs allow for great control of the reactive molecule, not all surface experiments use or require such setups. Sometimes the direct dosing of gasses is also a fine method of introducing a gas onto the metal surface[51,77,78], though this allows for far less exact control over the molecular states.

1.2.5 Surface science experiments

With almost all possible conditions, circumstances and variables covered, an experimentalist can work on observations and measurements. Below, a general overview of the most commonly used methods will be given. The aim is to form an idea of most of the experimental possibilities in surface science.

One of the most direct observables of the reaction of a molecule on a metal surface is the reaction probability. This can be measured in different ways but the most direct method of probing the reaction probability is by measuring the so-called "sticking probability" (S_0). S_0 can be measured by using a molecular beam and the King & Wells (K&W) method[69]. In principle, it is a very simple experimental setup. As the molecular beam enters the reaction chamber of the UHV setup it is initially bounced off a "flag". This flag is a metal plate placed inside the path of the MB (see Section 1.2.4). The flag blocks the molecules from reaching the metal surface and results in a certain base background pressure in the reaction chamber. This happens because the molecules are all scattered from the flag and end up bouncing around the reaction chamber, thus resulting in a certain pressure in the chamber. At a given time t' the flag is removed, thus the MB now impinges directly on the metal surface. A certain fraction of the molecules will stick to the metal surface whereas the rest will scatter off. This results in a drop in the background chamber pressure. S_0 is at this point nothing more than dividing the pressure drop over the old baseline pressure when the flag was still in place, thereby directly probing the probability that a molecule sticks to the metal surface[69]. The S_0 may reflect a combination of reactive and non-reactive sticking, depending on the type of surface interaction (see 1.2.3), surface temperature, surface structure, etc. Other experiments are required to probe what type of sticking has occurred. Although the K&W approach sounds simple enough, running such an experiment in practice is far from trivial.

Probing the type of molecule-surface interaction, or type of sticking, or indirectly probing sticking probabilities can also be done. For example, a technique that allows us to look at possible surface structures, and thus its distortion via adsorption, would be low energy electron diffraction (LEED)[42,79,80]. In LEED the periodic nature of a metal surface is used to study the diffraction of an electron beam. If the periodic structure is disturbed or altered by adsorbates then this shows in the diffraction pattern. Another technique using an electron beam would be Auger electron spectroscopy (AES)[81–89]. In AES the electron beam is used to excite core-shell electrons in atoms at the surface. These excited electrons leave an electron-hole behind, which will be filled with a higher-shell electron, and this releases energy in the form of either an X-ray photon or the excitation of a third electron from that atom. This third electron is referred to as an Auger electron and the emission energy of Auger electrons is unique to the atom and its chemical environment[81–83]. Beyond measuring the Auger electron the otherwise emitted X-ray photon can also be measured and shares its chemically unique properties with the Auger electron. Measuring these photons can be done with X-ray photon spectroscopy (XPS)[90–94]. XPS is usually more precise to the chemical environment of the atoms. It is common to use electron beams to excite the initial core-shell electron, however, X-rays can also be used[93]. Regardless, both techniques allow experimentalists to observe the type of chemical species on a surface and even its chemical environment. Both techniques can, with difficulty, also be used quantitatively[84–89,92,93] to determine the amount of adsorbed species which can then be used to estimate the sticking probabilities.

It is also possible to use mass spectrometers to study the desorption of material from the metal surface. This is a more indirect method of investigating sticking probabilities and is far more susceptible to other surface conditions and molecule-metal interactions as it inherently studies the product after the reaction[95]. However, desorption studies can still prove valuable with for example the use of transitions state theory[96] and well-defined reaction conditions.

One of the few techniques that can directly probe the surface on an atomic scale is scanning tunnelling microscopy or STM[97,98]. This method makes use of a phenomenon in quantum mechanics called “tunnelling” to sample the electronic densities at the surface. Electronic tunnelling occurs because, in the quantum mechanical description, an electron is delocalised, i.e., the wavefunction property of the electron (more in Chapter 2) means that the electron is spread over space with a given distribution. This spread can reach into potential barriers that are classically forbidden for the electron to reach. The probability of entering this classically-forbidden area decreases exponentially with the width of the potential barrier i.e., with the width of the vacuum gap between the tip of the STM and the surface. If the barrier is narrow the electron may tunnel through this barrier, as the electron is partially delocalised to the other side of the barrier. If a bias voltage is placed over the potential barrier, the tunnelling of the electrons will induce a small current that can be measured. This current is correlated to the width of the potential barrier, i.e., the distance between the microscope tip and surface[97–100]. This way the tip can scan a surface and probe the electronic density and its changes over the surface. Notably, the STM does not directly distinguish between atom or molecule types. The exact functioning of this technique is out of scope for this work and we refer the reader to Refs. [97–100] for more information. STM is a useful technique capable of directly probing the (electronic) structure of a surface, and any possible adsorbates, down to the atomic scale. Although the technique is still improving[101–107] an STM can only probe snapshots of the surface structure with substantial time differences between sequential snapshots. As a result, it does not form a complete picture of molecule surface interactions, i.e., any “movie” made with this technique has its image frames far apart in time.

All experiments described above looked at the reacting molecules or the surface directly. Studying the molecules that do not react, i.e., scatter, can also be informative in answering the fundamental questions of molecule-metal interactions. The outcomes of scattering events, though insightful, are far more dependent on the exact initial conditions of the scattering molecule[76,108]. Additionally, they usually probe the (electronic) structure of the surface in far greater detail than reactions generally will[76,109,110]. This makes the experimental studies even more involved than most reactive studies but also allows for far greater detail.

1.2.6 Theory in surface science

In the end, even experiments, like the ones described above, can still not tell the full story, and the full interaction between a molecule and surface can still not be completely observed directly. Experiments often probe average interactions or single snapshots. This is where theoretical surface science, or theoretical chemistry in general, plays a vital role. It may be possible to understand the fundamental interactions between different molecules or between molecules and metal surfaces by developing and applying accurate simulations to these problems. The ultimate goal of such simulations would be to predict the exact outcome of a chemical reaction based only on the conditions and the chemicals involved[111]. For now, this goal is still a little ambitious as the computational resources involved in simulations are extensive and full-dimensional quantum dynamics calculations for such large systems may even never be possible. Nevertheless, simulations can already be used to closely monitor the intricate interaction of molecules with each other and function as an instrumental tool in understanding the elementary reaction steps involved in heterogeneous catalysis.

For now, simulations and models in chemistry or surface science are not perfect and much work in the field of theoretical chemistry is currently being done to improve the accuracy of these models. Similarly to the framework of interactions of molecules and metals (see Section 1.2.3) the root of chemical simulations and models, i.e., the laws of physics, are known and well-understood for small systems. The difficulty arises from the increased complexity and the large number of degrees of freedom that arise in chemical systems. To model chemistry one has to model all the movements of the atomic nuclei and electrons. This is made even more complex as many, if not all, of the movements of the nuclei and electrons are coupled to each other. Moreover, the number of electrons and nuclei in the system increases rapidly as the chemical system grows larger[112]. On top of these difficulties, there is also the small inconvenience that the interaction of small particles is predominantly governed by quantum mechanics and not classical mechanics[112]. As a result, the computational costs of many chemical simulations, i.e., the time it takes to simulate a chemical reaction, quickly skyrockets[113–116] (see also Chapters 3, 4, and 5). Consequently, theoretical chemistry as a field has to constantly balance computational costs with accuracy.

The balancing act unavoidably comes with an inherent difficulty, namely, theoreticians need to know what approximation can be made without negatively affecting the accuracy of the model, put more simply, we need to know what we can get away with without ruining our results. In resolving this difficulty there are generally two major philosophies. The first is more "*a priori*", it seeks to understand the exact effects or faults of each approximation made in the underlying physics of the model. Thus, the physical understanding of the approximation is necessarily put above the eventual accuracy of the model. The second is more empirical in nature, where theoretical models are often tested and benchmarked against verifiable experimental results. Here the goal is to reproduce experimental results as closely as possible, sometimes at an unavoidable cost to the understanding of the physics of the model itself.

In surface science, both philosophies still have to deal with the fact that experiments like those described in Section 1.2.5 will need to be simulated. This could bring an unwantedly large scale to the chemical simulations that need to be performed. Luckily however, the general application of UHV technologies and the defining and elimination of unknowns in surface science experiments means that we can often compute results that can be compared to experiments by constructing aggregates of many different single, i.e., small, molecule-metal systems. Put differently, we need to simulate molecule-metal systems with the desired accuracy for many different starting conditions of molecules and metals based on experimental conditions and average over those results.

Still, directly and bluntly applying quantum mechanics to all the degrees of freedom in a chemical system is, usually, not a suitable method to compute observables. One of the first and more common, though not always allowed, approximations is to decouple the movement of the electrons and the nuclei. This approximation is called the Born-Oppenheimer approximation (BOA)[117], see also Chapter 2. Put simply, this approximation exploits the mass, and thus velocity, difference of the electrons and nuclei. It assumes that the light and nimble electron can quickly, or instantly, adjust its movement to any movement of the nuclei. Thus, any movement of the nuclei will not result in immediate electronic excitations[10,112,117–120]. Moreover, this allows us to treat the heavier nuclei classically, as their wavefunctions, see Chapter 2, are considerably less delocalised due to their high mass. This simplifies the problem. The electronic part of the system is still treated within quantum mechanics and this results in a potential energy for the movement of the nuclei. These nuclei can then be treated classically where the forces on the nuclei are governed by the potential energy.

This, however, does not diminish the complexity of the quantum mechanical nature of the electrons. In most of chemistry and especially most of surface science the electrons are modelled using density functional theory (DFT)[121]. The details of DFT are discussed in Chapter 2 but putting it briefly the electrons will not be treated by wavefunctions but with an electronic density functional, i.e., they will not be described by wavefunctions of all their own distinct coordinates but by their collective density[121]. Mathematically, the complete density functional (DF) is proven to exist, see Chapter 2, however, its exact form is not known[112,118,121,122]. Generally speaking, the terms that are not fully described are the electron exchange energy and the electron correlation energy[112,118,122]. These two terms are in most scenarios combined in the exchange-correlation (XC) DF. In this picture of DFT, the XC-DF is a small contribution to the total potential electronic energies[112,118,122]. It is, however, in these finer details that the focus for the majority of DFT-based theoretical chemistry lies[112,115,130–136,118,123–129]. There are many different approximations to the XC-DF[137–141], and many more are being developed. All these approximations come with their computational costs, errors, and (in)accuracies.

The approximations made in the XC-DF follow the common trend in theoretical chemistry: higher accuracy results in higher computational costs. In surface science, this is especially true as the metals in molecule-metal systems come with a high number of electrons that need to be simulated. Moreover, the inherent two-phased nature of the system means that the XC-DFs which will work well for the molecule often work less well for the metal and vice versa. Generally, the so-called "generalised gradient approximation" (GGA) approach (see Chapter 2) for the XC-DF has proven to be rather reliable for many molecule-metal interactions[56,124,129]. For many systems[129] the GGA seems to be the best compromise in the description of the highly delocalised electrons in the metal surface and the more localised electrons on the molecule whilst also being computationally affordable enough to simulate many different trajectories of the molecule impinging on the metal surface to accurately reproduce K&W or other MB studies[55,56].

1.3 Scope of this thesis

Theory in surface science has until recently been able to predominantly rely on the robust GGA framework for DFs: Specific reaction parameter (SRP) semi-empirical GGA DFs were able to describe certain molecule-metal systems within chemical accuracy, i.e., within *1 kcal/mol* of experimental results[55,56]. For example, the reactivities of H_2 + Cu (111)[135], H_2 + Pt(111)[142,143], H_2 + Pd(111)[144], H_2 + Ni(111)[127], CH_4 + Pt(111)[134], and several more[115,129] have all been described with (near) chemical accuracy by GGA DFs.

However, recent work[124,145] has shown that GGA DFs will not work for all types of molecule-metal systems. For instance, systems like HCl + Au(111)[124,125], O_2 + Al(111) (Chapters 3 and 4), O_2 + Cu(111) (Chapter 5), and NH_3 + Ru(0001)[124] have not yet been successfully described by theoretical models on the GGA-level of theory. In the same work, based on results for these and other systems, Gerrits *et al.*[124] suggested that GGA DFs will fail at, or have difficulty with, the correct description of molecule-metal reaction barriers if the charge transfer energy (E_{CT})[124] of the molecule-metal system is below *7 eV*. E_{CT} is defined as

$$E_{CT} = \phi - EA \qquad (1.1),$$

where ϕ is the energy required for an electron to be extracted from the metal surface, i.e., the work function of the metal surface[10], and *EA* is the electron affinity, which is the energy released by the molecule when an electron is attached to it[57]. In other words, E_{CT} is the energy needed for an electron to be transferred from a metal surface to a molecule, thus indirectly representing the likelihood of electron transfer occurring during the reaction of the molecule on a metal surface[124].

It is not yet fully understood why GGA fails for these specific $E_{CT} < 7\ eV$ systems. However, there are some possible similarities to the simulation of two molecules reacting with one another in the gas-phase[124], for which the GGA level of DFT has never been able to properly describe the reaction[146,147]. However, even though the problems in the gas-phase community have been better known for a longer time, there still seems to be no consensus on the cause of failure for GGA DFs[147–151]. Regardless of the cause, the gas-phase community has resorted to working with more accurate DFs in the form of so-called "hybrid" DFs[152,153].

Put simply, hybrid DFs admix a certain amount of exact exchange energy, i.e., Hartree-Fock (HF) exchange energy, to the exchange component of the XC part of a GGA DF[152], see Chapter 2. However, in Kohn-Sham DFT neither the exchange nor correlation contributions can be fully separated from one another[154]. The exchange component will contain a given amount of correlation interaction and *vice versa*. As a result, admixing in the exact HF-exchange energy is not necessarily straightforward and remains a process based on "*a priori*"-based educated guesses[152] or on trial-and-error[124].

The use of hybrid DFs is also difficult for metal surfaces as the large number of electrons and the use of plane waves (see Chapter 2 for more information) make the use of any fraction of exact exchange far more computationally expensive than the use of any regular GGA DF[155–157]. Lastly, the global exact exchange energy does not work well for metals due to the high delocalisation of electrons in a metal (Section 1.2.1), where the long-range interaction between electrons in the metal is generally screened by other electrons[158]. This means that a semi-local or fully local DF like GGA is generally more accurate in the description of the metal itself.

Regardless, Gerrits *et al.* showed that a screened hybrid DF adiabatically applied to the O_2 + Al(111) system, one of the more notorious systems with $E_{CT} < 7\ Ev$, resulted in considerable improvement of the reactivity over previously attained theoretical results[124]. Thus, it appears that similar to gas-phase calculations, the use of hybrid DFs, despite its difficulties, may resolve the current shortcoming of DFT in describing the more “difficult” molecule-metal systems to a large extent.

In this thesis, we aim to test and improve upon the application of screened hybrid DFs to more accurately describe the electrons and electronic structure in the “difficult” molecule-metal systems, like O_2 + Al(111) and O_2 + Cu(111). This entails testing a method to substantially reduce the computational costs of hybrid DFs based on a probable root cause of the error of GGA DFs(Chapter 3), and the alteration of the XC-DF with a better form of long-range electron correlation together with higher fractions of exact exchange for both O_2 + Al(111) (Chapter 4) and O_2 + Cu(111) (Chapter 5).

In these studies, compared to studies using the GGA the costs to compute the electronic structure of the molecule-metal system are balanced far more to the side of accuracy rather than computational efficiency. This ended up pushing the limits of current high-performance computing infrastructure to facilitate the electronic structure calculations necessary to test and verify these new DFs. Validation of the DF requires comparison to other theoretical work, i.e., benchmark studies, or experimental MB studies meaning that many different molecule-metal collisions would need to be simulated. This is done efficiently by constructing a PES using thousands of different DFT energies for different molecular geometries above the metal surface. The DFT data can then be interpolated using the corrugation-reducing procedure (CRP) to construct a continuous potential energy representation for every possible geometry of a molecule above and on a metal surface. With this PES the molecular reaction on the metal surface can then be computed using quasi-classical trajectory (QCT) dynamics calculations, i.e., single molecule-metal collision simulations. Hundreds of thousands of such trajectories are then aggregated to compute reaction probability curves that can be compared to other theoretical frameworks and experimental (reaction probability) results, mostly based on K&W experiments, to validate and test the accuracy of the screened hybrid DFs for the reactions studied.

1.4 Main results of the thesis and outlook

In the next few paragraphs the main results, conclusions, outlook, and contents of the following chapters are summarised. Before the main results are presented in Chapters 3-5, an inclusive overview of the theoretical models needed and employed in this work is provided in Chapter 2.

In Chapter 3, an extensive test of the non-self-consistent field (NSCF) screened hybrid DFT approach is shown. This approach computes NSCF-screened hybrid DFT energies based on self-consistent-field (SCF) GGA electronic densities. The chapter explores the accuracy of the NSCF-screened hybrid DF approach by implementing the NSCF HSE03-1/3x@RPBE DF for O_2 + Al(111). The molecular beam sticking probabilities (S_0) as well as a set of sticking probabilities for rotationally aligned O_2 are computed using quasi-classical trajectory (QCT) calculations, and analysed. The results show that the NSCF approach yields reaction probability curves that reproduce SCF results with near-chemical accuracy, suggesting that the NSCF approach can be used advantageously for exploratory purposes. An analysis of the potential energy surface and the barriers gives insight into the cause of the disagreement between the SCF and NSCF reaction probabilities and into the changes needed in theoretical modelling to further improve the description of the O_2 + Al(111) system. Additionally, an implementation of the hole model method to estimate reaction probabilities based on reaction barrier heights shows that the application of the hole model results in fair agreement with actual dynamic calculations. However, the hole model results in an increased slope of the reaction probability curve compared to the molecular dynamics, with a shift to lower or higher energies depending on whether the vibrational energy of the molecule is included in the initial energy of the molecule or not, indicating a sizable influence of dynamic effects on the O_2 + Al(111) reaction.

Chapter 4 continues with the work of O_2 on Al(111). So far the use of only a screened (N)SCF hybrid DF was not enough to ensure a highly accurate (i.e. chemically accurate) description of the DC of O_2 on Al(111). Previous work and Chapter 3 have shown that the onset of the S_0 curve was correctly described by the (N)SCF HSE03-1/3x DF, but the slope, or width, of the curve was not. Chapter 3 also discussed that the inclusion of non-local correlation in the DF may help to resolve this shortcoming. Therefore, in Chapter 4 the use of a non-local correlation DF combined with an increased fraction of exact exchange in the screened hybrid DF is tested. This is achieved by constructing another O_2 + Al(111) Born-Oppenheimer static surface (BOSS) PES, using the HSE06-1/2x-VdWDF2 DF, employing the corrugation reducing procedure (CRP), and using QCT calculations to compute the sticking probabilities. The resulting PES shows the presence of shallow Van der Waals wells in the entrance channel and the barriers to DC show slightly more corrugation and anisotropy compared to the previously used SCF HSE03-1/3x DF, but most barrier heights differ by less than *1 kcal/mol*. As a result, with the use of the HSE06-1/2x-VdWDF2 DF, the onset of the S_0 curve is somewhat better described than in previous work and the curve is broadened a little compared to the SCF HSE03-1/3x description, in improved agreement with experiment, but not more than seen for the NSCF approach as applied in Chapter 3. These results imply that if future theoretical methods aim to resolve the disagreement between theory and experiment then those methods would need to either result in radical changes in the PES or the shortcomings of the dynamical (BOSS) model need to be addressed. Both need to be achieved whilst keeping the computational demands of the applied method to feasible levels.

Lastly, to verify this new electronic structure approach for a different system, the computed sticking probabilities for O_2 + Cu(111) based on the same HSE06-1/2x-VdWDF2 screened hybrid Van der Waals DF are presented in Chapter 5. Also in Chapter 5, a six-dimensional BOSS PES was constructed using the CRP. This PES was used to perform QCT calculations to compute the sticking probabilities of O_2 + Cu(111). For the first time, DFT-based sticking probabilities are presented that underestimate the experimental sticking probabilities of O_2 + Cu(111), contrasting these results to the previous Chapters 3 and 4. While reproducing the experimental results would have been even more desirable, the fact that a DF which underestimates the measured sticking probabilities was found, means that a DF using a lower fraction of exact exchange will most likely describe the O_2 + Cu(111) system with high accuracy. Furthermore, the chapter shows evidence for the presence of both indirect and direct dissociative chemisorption. The indirect precursor-mediated mechanism occurs for low-incidence energy O_2. The mechanism is supplanted by a direct dissociative mechanism at higher incidence energies. Finally, the results suggest that the Cu surface temperature may also affect the dissociation mechanism, but this still needs further verification with a different theoretical framework that allows for the simulation of surface temperature.

The outlook from the fifth chapter for the O_2 + Cu(111) system, though far from trivial, is fairly bright. Broady speaking three things would need to be done to come to the highest standard and (presumably) highly accurate, description of the O_2 + Cu(111) system. The first is that surface motion and surface temperature need to be included in future modelling of this reaction. However, one should be careful, if this is done with an underlying DF based on the screened hybrid level then this must be done such that the number of required DFT calculations is kept to a minimum, to mitigate computational costs. This will likely exclude high dimensional neural network (HDNN) approaches previously used for, for instance, methane (CHD_3) on Cu(111), as that approach requires a large dataset to train the HDNN[123]. It may, therefore, be fruitful to test the dynamic surface corrugation (DCM) approach[159], previously successfully used for H_2 + Cu(111)[160]. The benefit of the DCM approach is that only a small number of DFT calculations will be needed to construct the O_2 + Cu coupling-potential required for the implementation of this approach. The second avenue is the inclusion of ehp excitation in the dynamical model. Multiple methods currently exist like LDFA or ODF and more advanced methods are being proposed[161]. Whichever method may be sufficient would first need to be tested. Notably, previous work of O_2 + Ag(111) seems to indicate that the LDFA will not have a substantial impact on the sticking results of O_2[162]. Regardless of the approach, it is again imperative that the amount of DFT calculations required for the approach is kept to a minimum. Last but not least is the search for the new, highly accurate, DF. This DF will likely have an exact exchange fraction somewhere between the HSE06-1/2x-VdFWD2 DF, i.e. 1/2, and the RPBE DF, i.e., *0*. The NSCF approach of Chapter 3 may come to mind to scan for new DFs with lower computational costs before committing again to highly costly SCF DFT calculations for a particular DF. These three avenues may, in principle, be explored in parallel as long as the final best-tested results of all three avenues are combined into one complete model.

As discussed above, for the O_2 + Al(111) system, the outlook is far less optimistic. It seems that any new screened hybrid DF would need to radically alter the PES to facilitate good agreement with the experiment, which is arguably unlikely, as discussed in greater detail in Chapter 4. Moreover, the high computational costs of the screened hybrid DF makes any higher-level DF an unlikely candidate to generate a new and complete PES. Lastly, Chapter 4 also presents compelling arguments that including surface motion and/or ehp excitation may represent unlikely candidate solutions to achieve further agreement with experiment, though these arguments still need to be validated. Such validation can best be done along similar lines as proposed for the O_2 + Cu(111) system above, i.e., use DCM for surface atom motion and test known ehp excitation modelling approaches. It may, however, be more fruitful for the O_2 + Al(111) system to proceed by finding ways to substantially lower the computational demands of the PES. Currently, the CRP requires a predefined DFT energy grid that is inefficient at (dynamically) sampling the interactions of a diatomic molecule with a metal surface. By making the sampling more efficient, and less rigid, the amount of DFT calculations needed to construct a complete PES may be reduced substantially. Additionally, an implementation of a fast and efficient machine learning algorithm, for example, based on a Δ-machine learning neural network approach[163], could also be used to generate a PES with a lower number of costly DFT calculations. Either way, reducing the costs of accurate PES generation may then allow for the use of new and computationally more expensive DFs. However, before such time, it remains unlikely that the BOSS DFT approach will be able to more accurately describe the O_2 + Al(111) system.