Beyond the Born-Oppenheimer static surface model for molecule-surface reactions

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Chapter 1

Introduction

Chemical reactions convert some group of molecules, the reactants, into an other group of molecules, the products. It is then the job of a chemist to understand how and why these processes take place, at a fundamental level, in order to predict new chemical processes or improve existing ones. Fundamentally, a chemical process can be understood as a concerted movement of atoms constituting the reactants from their original arrangement to the arrangement making up the products. This concerted movement is governed by the interactions between these atoms. Figure 1.1 shows the total interaction between atoms, the potential energy, as a function of the arrangement of the atoms during their concerted movement from reactant state to product state (progress of reaction) in blue. Before the reactant can be converted into its product, it must generally first overcome a barrier in energy, where the interaction between atoms becomes more repulsive and an initial investment of energy is necessary. While this is sometimes understood as walking over a mountain, it is more accurate to compare it to walking through a mountain pass as movements of atoms in other directions than the concerted movement generally require even more energy. Once the chemical process is past the barrier, the invested energy is released again and can, in principle, be reused for other chemical processes. An example that should be well known to the general reader is lighting a campfire. First an initial energy source, heat, is added to wood

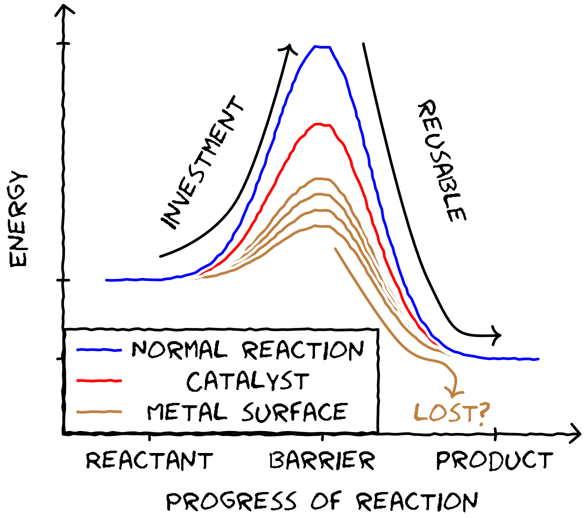

Figure 1.1: A schematic overview of the role of (heterogeneous) catalyis in chemical processes.

and O_2 in order to allow some of the atoms to rearrange into CO_2, H_2O and partially oxidated wood remains (e.g. ashes). The subsequently released energy can be reused to keep the wood burning. A simplified picture such as in figure 1.1 can not account for the complexity of burning wood and instead the total process can be broken down into a network of elementary reaction steps, which can no longer be further devided into smaller steps. These elementary reaction steps, which describe the conversion of specific reactants into products, are linked by providing their products as reactants for other elementary steps. Using the knowledge of these elementary reaction steps and their interconnection, a chemist can design a process in such a way that specific products are formed by choosing which, and the order in which, reactants are combined. Moreover, a chemist can use the understanding of these elementary reaction steps to determine the physical conditions for which they are more likely to commence than competing elementary reaction steps that do not yield the desired products. One such way is catalysis.

1.1 Heterogeneous Catalyis

In catalysis, an additional chemical substance, the catalyst, is added to reactants and interacts in such a way that the energy required to overcome the barrier of an elementary reaction step is changed. A special property of a catalyst is that it is found, in the same quantity, in both the reactants and the products, although it may only be regenerated after several elementary reaction steps and decay over time. This property means that instead of introducing a new elementary reaction step with different reactants and products, catalysis can be considered as modifying (several) elementary reaction steps. In Fig. 1.1 this is indicated in red, where the reactant and product energies remain the same, whereas the barrier has decreased. By selectively increasing and decreasing barrier heights of elementary steps, it is possible to 'guide' the reactants towards desired products.

Heterogeneous catalysis [1], where the catalyst is in a different phase than the products and reactants, is used on a large scale in industry [2]. The importance of heterogeneous catalysis in our current society can not be overstated. It is used in the electrolytic production of H_2 as well as in hydrogen fuel cells using that H_2. Gaseous exhaust fumes from car engines are ran past metal surfaces to convert the more toxic and environmentally burdening compounds to more acceptable ones [3]. One of the most influentual chemical processes, both on lives [4] and deaths [5], is the conversion of H_2 and N_2 to NH_3 in the heterogeneously catalysed Haber-Bosch process [6]. White [5] argues that up to 150 million deaths can be directly attributed to weapons manufactured that make use of NH_3 produced using the Haber-Bosch process. On the flip side, Erisman et al. [4] show that about half (48%) of the world's population in 2008 is sustained due to artifical fertilizers, again made from NH_3 resulting from the Haber-Bosch process. They expect the contribution of Haber-Bosch NH_3 to only grow. Moreover, they state that approximately 1% of the world's primary energy source is used for the Haber-Bosch process. This thoroughly motivates studying the underlying elementary reaction steps of these processes as a small improvement in the catalyst can, even with a tiny improvement, reduce energy consumption and polution, enormously in absolute amounts. In fact, Ertl and coworkers have already studied these elementary reaction steps experimentally, for which Ertl has been awarded the 2007 Nobel prize in chemistry [7].

1.2 Metal Surfaces as Catalysts for Molecules

A large group of effective catalysts for the conversion of small molecules consists of metal surfaces. Unlike for molecules, the electrons of a metal (surface) are delocalized and are thus more conveniently described according to their momuntum instead of position. This view of electrons is typically associated with a “physical” rather than “chemical” picture [8]. The quantum mechanical states of these electrons are grouped together in bands. What distinguishes a metal from other crystalline solids is the fact that at least on such band crosses the so-called Fermi level that separates occupied from unoccupied states.

Electrons of a molecule are more conveniently described by localized orbitals in a more chemical picture. It is exactly the fact that these two pictures meet that makes metal surfaces so interresting as a catalyst. The metal surface has electrons available that can be donated to the molecule at hardly any energetic cost and, likewise, can accept an electron from the molecule. These exchanges of electrons are what facilitates the lowering of the barrier in Fig. 1.1.

1.3 Interaction of Molecules with Metal Surfaces

The exact way in which a metal surface modifies the potential energy of molecules must be understood at a fundamental level in order to make accurate predictions for industrially relevent catalytic processes. To study these processes, it is necessary to design controlled experiments. A top-down approach starts from industrially relevant conditions, which makes it very challenging to disentangle the multitude of concurrently competing effects. The surface science approach to heterogeneous catalysis on the other hand is from the bottom up, where extremely simplified elementary reaction steps are studied and subsequently combined until the industrial conditions are reproduced. Ideally, both approaches can complement each other on the way towards understanding how to design better catalysis.

This thesis focusses on the bottom-up approach, starting from the Schrödinger equation [9] to understand specific elementary reaction steps. One way to study elementary reaction steps, like, e.g., dissociative chemisorption, which is often the rate limiting step in the Haber-Bosch process, is the study of molecular beam experiments [10–14]. These experiments study the fate of molecules that are prepared in a beam directed towards a (single crystal) surface.

1.4 Aim of this Thesis

The main topic of this thesis is the theoretical description of the reactive scattering of small molecules with transition metal surfaces beyond the Born-Oppenheimer static surface model. One particular goal is to obtain fundamental understanding of the processes governing the exchange of energy between molecules and metal surfaces by comparing simulations at different levels of theory both with each other and experimental results. Specifically, energy exchange beyond the Born-Oppenheimer approximation (facilitated by the lack of a band gap for electronic excitations in the metal surface) at the level of molecular dynamics with electronic friction (MDEF) is compared with experiments.

In Chap. 2 established theory that is commenly used for modeling molecular beam experiments is summarized. First, the theoretical background behind potential energy surfaces is described, followed by the quasi-classical trajectory method [15–17] for studying surface reactions. Afterwards, the generalized Langevin equation is introduced in order to model electronically non-adiabatic effects with a friction tensor [18–25]. This chapter concludes with details on how to compute electronic friction tensors using two different (sets of) approximations: the local density friction approximation (LDFA) [26–29] and the orbital dependent friction (ODF) method [18–25].

In Chap. 3 , the aim is to improve a previously developed Static Corrugation Model (SCM) [30] in order to describe reactive scattering at elevated surface temperatures. A large database of energies of surface atom displacements of a surface-adsorbate system is necessary for constructing and validating the improved SCM [31].

In Chap. 4 , the focus is on accurately describing electronically non-adiabatic effects for the reactive scattering of H_2 and D_2 on Cu(111) using electronic friction theory [24]. A continuous representation of the friction tensor is necessary in order to obtain the large amount of trajectories required for computing observables such as the dissociative chemisorption probability and rovibrationally (in)elastic scattering probabilities with sufficient statistical averaging.

In Chap. 5 , orbital-dependent friction (ODF) is used to model the reactive scattering of N_2 on Ru(0001) [25] as earlier both experimental and theoretical work by Luntz and coworkers [32, 33] had suggested that non-adiabatic effects may be extremely important for this system.

In Chap. 6 , the goal is to develop and compare machine learning models for continuous representations of electronic friction tensors, which account for symmetry properties of molecule-surface systems.

1.5 Main Results

This section summarizes the main scientific results obtained during the research that resulted in this thesis.

Chapter 3: An Improved Static Corrugation Model

The computationally efficient static corrugation model (SCM), which describes reactive scattering at elevated temperatures and is based on the sudden approximation, was improved by adding three-body interactions for H_2 on Cu(111). The improvement was achieved by making the parameters defining the model from Wijzenbroek and Somers

[30] linearly dependent on the H_2-bond distance and thus effectively including three-body effects. The three-body static corrugation model (SCM) was fitted using 15 113 configurations with either one or two surface atom displacements. At elevated surface temperatures of 900 K, both using 6-dimensional dynamics with the specific reaction parameter (SRP)48 density functional [16] in combination with the SCM or using [34] full dimensional dynamics (i.e. *ab-initio* molecular dynamics, AIMD) with SRP48 [35] accurately reproduces experimental reaction probabilities of associative desorption. Theory and experiment are not in agreement for molecules in the rovibrational ground state, which is attributed to the intrinsic, and not the extrinsic, curvature of the potential energy surface (PES) along the minimum energy path (MEP). Considering the sudden approximation made in the SCM, it can thus be concluded that surface motion is not important to obtain a chemically accurate description of those experiments for H_2 on Cu(111). It is, however, neccesary to take into account the change of the H_2-Cu(111)interaction potential due to Cu atoms being displaced from their equilibrium position at elevated temperatures.

Chapter 4: Testing Electronic Friction Models

Orbital-dependent friction (ODF) coefficients were computed for H_2 on a frozen Cu(111) surface to obtain 6×6 electronic friction tensors [24]. Good agreement was found between the newly calculated ones and the (by nowadays computational possibilities) very few reported ones by Luntz et al. [33] along a reaction path towards dissociation. The 21 independent elements of these tensors were subsequently fitted to construct a continuous neural network (NN) representation with symmetry adapted coordinates [36]. Electronic friction coefficients according to the local density friction approximation (LDFA) [26–29] were also calculated bases on the electron density of the clean Cu(111) surface by treating both hydrogen atoms as independent and continuously represented by a NN afterwards. MDEF simulations mimicking molecular beam experiments using both ODF and LDFA coefficients showed no significantly different H_2 dissociation probabilities compared to each other, and compared to simulations without electronic friction (i.e. within the Born-Oppenheimer static surface approximation). State-to-state scattering probabilities, on the other hand, are heavily affected by including electronic friction and also by whether ODF or LDFA is used as the friction model. Moreover, comparing the difference in initial and final kinetic energy for these simulations of state-to-state scattered molecules allows one to distinguish between the ODF and LDFA models. This suggests "fingerprint" experiments for validating inherent approximations of both models.

Chapter 5: Effect of Orbital-Dependent Friction

A continuous NN representation was obtained for ODF tensors of N_2 on Ru(0001). Molecular beam simulations using MDEF [17] were performed including the effects of elevated surface temperatures ($T_s = 575$K). Initial dissociative sticking probabilities for N_2 on Ru(0001) are approximately two times smaller when ODF is used as the friction model compared to LDFA, which also improves the agreement with the best currently available experimental data. Like for most other systems, LDFA yields the same results as simulations without electronic friction. Furthermore, considering the best estimates based on experimental data, ODF also improves the description of energy exchange with the surface. One of the main challenges for describing N_2 scattering from Ru(0001) is the correct description of the quenching of vibrational excitation. ODF was the only model that predicts enough vibrational quenching to fall within the experimentally determined bounds. Only when taking into account both surface motion and ODF was it possible to accurately reproduce experiments.

Chapter 6: Machine-Learning based Representations

First, a formalism is presented to describe symmetry properties of electronic friction tensors for molecules on frozen metal surfaces. Two methods result that allows these properties to be enforced on machine learning algorithms: an "*a priori*" and an "*a posteriori*" method. These methods can be seen as an extension to established methods used to obtain symmetry adapted potential energy surfaces. For symmetry adapted machine-learning based potential energy surfaces the neural network is presented with symmetry adapted coordinates or descriptors such that the neural network yields the same result for symmetry equivalent inputs. For tensors, it is necessary to also transform the outputs in a symmetry adapted way. In this chapter a comparison is made on how different symmetry adapted coordinates can affect the fitting accuracy and computational efficiency of neural-network-based machine learning models. The best result is obtained for an analytical "*a priori*" continuous representation when using "asymmetric" contributions. Another accurate method is to use a simple expression for mapping coordinates to a single unit cell and subsequently applying the "*a posteriori*" method to correct for the symmetry contraints. Also a method based on the work of Jiang and coworkers [21, 22] is shown to provide accurate fits, although discontinuities are found. Furthermore, two different ways to obtain tensors as an output from neural networks are compared. The elements of the tensor can either be obtained by assigning a unique neural network to each element, or by constructing a neural network with multiple outputs and subsequently arrange these outputs as a tensor. Positive definite tensors can be enforced by generating a lower triangular tensor that is subsequently squared. The best results are obtained for single neural networks with multiple outputs where positive definiteness is enforced.

1.6 Outlook

While the scientific results reported in this thesis are only a small step to fundamentally understand how to go beyond the Born-Oppenheimer static surface approximation, it paves the way for many further advances.

The newly improved static corrugation model (SCM) provides many new theoretical opportunities. Using a simple and physically meaningful analytical expression with few parameters, it might become possible to use the SCM for nuclear quantum dynamics. It is not clear what the effect of surface temperature would be in combination with quantum dynamics. These quantum dynamical calculations need a potential energy surface that does not contain any unphysical features such as very localized peaks in the second derivative [37, 38]. Moreover, an accurate description of the potential energy surface is also needed outside of the classically accesible region. Usually, high-dimensional neural networks, which is an alternative way to include the effect of surface displacements, contain small unphysical features and only accurately fit the clasically accesible region. Unlike high-dimensional neural networks, these are no issues for the SCM, although the accuracy of the fit is generally lower compared to neural networks. In combination with a sudden approximation, where multiple quantum dynamical calculations are performed for differently initialized surface displacements, the SCM can thus be used as a potential energy surface for wave-packet calculations [39] where surface temperature is taken into account quantum mechanically.

In order to obtain a potentially more accurate fit for the SCM, it is possible to replace the Rydberg-like potenial, which is used for the SCM in this thesis, with a low dimensional neural network fit. For such a low-dimensional fit it would be possible inspect if any of the aforementioned problems of high-dimensional neural networks are present, thus still allowing its use for quantum dynamics.

The current SCM does not allow for a description of the movement of surface atoms, which means that it does not account for energy transfer to the surface. Instead, only the effect on the movement of the absorbate due to displacements of the surface atom is taken into account. This effect could be trivially included by adding a “strain” potential which describes the interaction between surface atoms. Such an interaction is conveniently described using an embedded atom potential [40] and would allow for the description of surface motion without sacrificing the advantages of the SCM.

The large influence of ODF found for the dissociative chemisorption of N_2 on Ru(0001) is very important. Until now, electronic friction commonly based on LDFA for the simulation of molecular beam experiments has never been shown to significantly affect experimental observables. The results presented here show electronic friction can have such effects after all, although limitations on both the experimental and theoretical side prevent unequivocal verification of the importance of Beyond-Born-Oppenheimer effects for systems that are commenly considered as “weakly non-adiabatic”. This justifies further experimental and theoretical research in electronically non-adiabatic effects of molecular beam experiments and its connection to catalysis.

One of the major limitations for the verification of (ODF) electronic friction theory is the availability of specific experiments and the accuracy of currently available experimental data. While for theoretical modeling one can simply “switch off” the coupling between the electronic and nuclear system, this is option is not available for experiments. Therefore, it is neccesary to find observables which are mainly or at best only sensitive to non-adiabatic effects, and thus hardly or not at all affected by other theoretical shortcomings. The results from Chap. 4 enable the design of such an experiment. The energy loss during rovibrationally inelastic scattering of H_2 on Cu(111) turns out to be a “fingerprint” that is essentially independent of other state-of-the-art theoretical approximations like e.g. potential surfaces based on density functional theory (DFT).

Furthermore, there is now also new motivation for further improvements on theoretical modeling. In comparison to the many years of development of obtaining accurate PESs from DFT, there is hardly any systematic research on the effect of many of the approximations inherent to the use of electronic friction theory in practice. While some work on this topic is being done, and it is now possible for different groups to obtain comparable values for ODF tensors, this research is far from being complete.

The range of the chemical space that has been explored with the electronically non-adiabatic methods presented in this thesis is extremely small. Only N_2 on Ru(0001) and H_2 on Cu(111) are have been investigated here. Other researchers have also investigated H_2 on Pd [19, 23], CO on Cu(100) [19, 23, 41] and H_2 on Ag(111) [18, 21, 22]. For understanding the potential relevance of non-adiabatic effects in heterogeneous catalysis this is only a very first step - a much larger database including different molecules on different transition metal surfaces is required.

The continuous representation of electronic friction tensors has proven to be quite challenging. The machine learning models I present in Chap. 6 allows to obtain such a description using symmetry adapted coordinates. The asymmetric contributions neccesary to describe the symmetry correctly can so far not be obtained systematically. One way to obtain a “universal” solution could be to use embedded atom density based descriptors as symmetry adapted inputs for these models, as has recently been shown to be advantageous for potential energy surfaces [42]. These descriptors are defined as fictitious electron densities imposed on each atom in the system due to each other atom in the system. Specifically, these descriptors need to include angular contributions in the form of

$$x^{l_x} y^{l_y} z^{l_z}, \tag{1.1}$$

where x, y, and z are the Cartesian distances between two atoms in the system and l_i are integer parameters. It is then possible to define 8 partitions based on all combinations of the signs of x, y, and z. By taking each partition as an asymetric contribution, the correct symmetric continuous representation of (electronic friction) tensors is obtained for any system consisting of atoms.

Ultimately, a better understanding of the energy dissipation dynamics during chemical reactions on transition metal surfaces that are relevant for heterogeneous catalysis could be a first step towards reducing the energy consumption of chemical reactors used for industrial processes.

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