Surface temperature and the dynamics of H2 on Cu(111)

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Chapter 1

Introduction

1.1 Heterogeneous catalysis

Through their modification of reaction pathways, catalysts are one of the cornerstones of life as we know it and are found in many shapes and sizes[1]. Be it in outer space, where we might find the origins of complex molecules on grains of dust[2], or inside a living cell, where complex organic structures push energetically unfavourable reactions towards products that sustain life[3]. Humanity has similarly employed catalysis and bends it to its own use through its widespread applications in industrial processes[4]. For example with steam reforming we are able to use methane and water to produce the hydrogen molecule, a process which under normal conditions is highly endothermic, i.e., costs a large amount of energy. This hydrogen can then be employed in the Haber-Bosch process, where it reacts with the inert nitrogen molecule to produce the very useful ammonia molecule[5]. We have also found ways of directly harvesting the energy out of these generated hydrogen molecules, converting the hydrogen back to water. Again catalysts are employed to aid in harvesting of the released energy for a large variety of applications[6]. What these applications all have in common is that while the reactant molecules are gaseous, or perhaps liquid, the catalysts are often (metallic) solids. This subtype of catalysis - heterogeneous catalysis, where the catalyst and the reactants exist in different phases of matter - is associated with the main topic of this thesis.

Chemical reactions generally occur in several elementary “steps”, even on the catalyst. One of these steps is often the slowest, due to unfavourable energetics or sterical effects. The breaking of the very stable N_2 triple bond is, for example, seen as the limiting step in the Haber-Bosch process[7–9]. Such a rate-limiting step is then particularly interesting for optimisation, as it would allow for a speed up of the entire reaction process. Similarly, by fine-tuning the catalyst and its environment, we would be able to more selectively produce one kind of product from a multi-step reaction process. On industrial scales, the focus would not just be on those catalysts that can most efficiently produce the desired product, but also on their stability, ease of production, and general economic costs associated with them.

In the field of theoretical surface science, in particular the subfield of heterogeneous catalysis, we aim to describe these rate-limiting elementary reaction steps to the best possible level using state-of-the-art theoretical methods. However, industrial catalysts are often complex structures of (metallic) nanoparticles, with many different sizes and crystal facets available, deposited on or in some form of supporting framework, and with a mix of molecules available that associate with the catalyst[10]. Therefore simplifications are often made, focussing on single crystal facets of the metallic catalyst, assuming (ultra-)low pressure of the reactant, or even assuming perfect, immobile surface slabs as a catalyst to describe single reactions as detailed as possible[11]. Likewise in this thesis, calculations are performed only for single (H_2) molecules reacting with a single crystal Cu(111) surface slab.

Metals as catalysts

As atoms cluster together to form solids their electronic orbitals will overlap and their electronic energy levels delocalise over the material. This forms bands of energy levels, either filled or empty, across the different energy levels, which are separated by “band gaps” where no energy levels exists. The Fermi-level, the (hypothetical) highest energy orbital still occupied by an electron, is found somewhere along this collection of bands and band gaps[12]. Everything below this Fermi-level in energy will mostly be filled with electrons, while everything above this level will be mostly empty energy levels.

Semi-conductors and insulators have Fermi-levels between two electronic bands, the lower energy valence band and the higher energy conduction band, which are separated by what is commonly known as *the* band gap[13]. In contrast metals form a special case of solids with a Fermi-level that is situated somewhere inside one of these electronic bands, completely lacking this band gap[12]. This makes metals excellent catalysts, as they can easily donate electrons out of, or accept electrons into, their electronic band structure with hardly any energetic cost involved.[14]

1.2 Hydrogen scattering from metal surfaces

The smallest, simplest, and easiest molecule to model for a gas-surface reaction is the hydrogen molecule (H_2). It consists of two protons and two electrons, which together form a relatively energetic single molecular bond. One, or both, of the atoms can also be substituted by the heavier deuterium (D) isotope, for which the nucleus consists of both a proton and a neutron. Outside its use as a lifting gas, coolant and especially as an energy carrier, H_2 is also an important reagent in many industrial and biological processes. The hydrogen molecule is also a key reagent in hydrogenation reactions performed in the petrochemical industry, in the synthesis of key industrial chemicals like methanol, and in the many biological processes of the living cell[15–18].

Although the basic mechanisms of the dissociative chemisorption of H_2 from metal surfaces have already been known for almost a century[19], the exact mechanisms governing selectivity, efficiency or even optimal catalytic particle design are still an open question today[20, 21]. Generally, experimental work is focused on most accurately describing the dissociation or scattering of the hydrogen molecules from single crystal surfaces under ultra-high vacuum (UHV) using either molecular beams (MB)[22–32] or through the inversion of the associative desorption experiments[28, 29, 33–37]. By carefully defining the MB, experimentalists are able to tune the distributions of the rotational and vibrational states of the H_2 inside the beam. The incidence energy normal to the surface can be adjusted by changing the angle of incidence of the beam and varying the nozzle temperature of the beam. Other MB work additionally relies on careful manipulation of the molecule using magnetic fields to obtain state-selective scattering probabilities, through a molecular spin-echo approach[23, 24]. Finally, by combining the associative desorption of H_2 with state-selective detection techniques, such as resonance-enhanced multi-photon ionisation (REMPI) and time-of-flight detection methods, experimentalists are able to investigate the relative dissociation rates of different rovibrational states at different incidence energies.

All these experimental results provide a treasure trove for the theoretician, who much prefers scattering from single well defined initial states to benchmark state-of-the-art theoretical methods. The tool that lies at the base of most theoretical approaches is density functional theory (DFT), which is used to solve the electronic part of the Schrödinger equation (See section 2.1.1). The results obtained from these DFT calculations provide the energy landscape, or potential energy surface (PES), brought about by the electrons of the system. This can in turn be used to investigate the motion of the nuclei over time. Here the exchange-correlation (XC)-density functional (DF) plays the vital role as

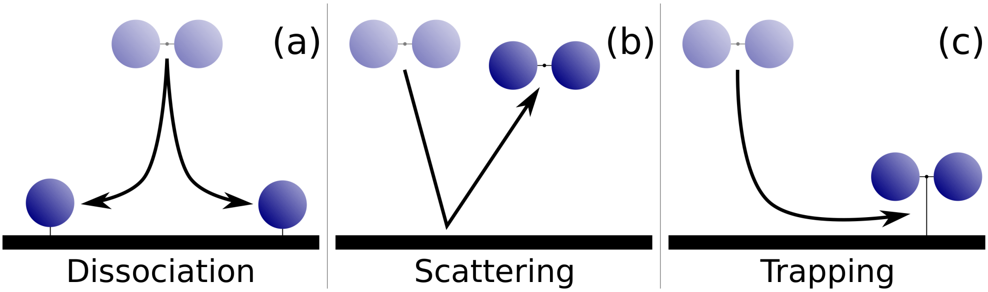

FIGURE 1.1: Most common outcomes for hydrogen interacting with a (metal) catalyst surface. (a) The molecular bond breaks and the molecule dissociates; (b) the molecule gets reflected away from the surface, with or without changes to its rovibrational energy and/or its parallel momentum; (c) the molecule sticks to the surface, but does not dissociate.

the unknown piece of an otherwise exact description of the electronic system. As this perfect XC-DF is unknown, it is left to the scientific community to find the most accurate description available. While many different techniques with varying computational costs exist to achieve the best approximation to this perfect XC-DF, I would like to highlight one approach which will be important in the future chapters of this work: the specific reaction parameter (SRP) approach to DFT[38, 39]. Here usually a linear combination of two XC-DFs is made, one overestimating and one underestimating an experimental observable, by fitting to the optimal fraction of the two DFs (see section 2.1.1). With this semi-empirical approach, accurate descriptions of some aspects of the system of interest can be achieved without applying very complicated XC-DFs.

Basics of hydrogen scattering

As the hydrogen molecule approaches the catalyst surface, one of three things can happen, depending on its normal incidence energy. One likely outcome will be the dissociation of the molecule, where the molecular bond breaks as the electrons of the metal fill the anti-bonding orbitals of the molecule, which results in each atomic hydrogen getting separately chemisorbed to the surface [see Fig. 1.1(a)]. Such a reaction can either happen direct or after scattering events, in which case the molecule “bounces” a few times on the surface before dissociating. Outside of the obvious location and energetic height of the reaction barrier, the general shape of the PES is also important. For instance, changes in the energy levels of the rotational and vibrational states of the molecule resulting from changes in the H-H interaction potential near the surface would allow for more, or less, of the molecule's internal energy to be used to surpass the reaction barriers[28, 29, 40].

Those molecules that do not react are generally scattered away from the surface, either immediately or after several "bounces", as illustrated in Fig. 1.1(b). Such an event includes not just energy exchange with the surface, which gets less and less likely as the mass mismatch between the hydrogen and the surface gets larger or the interaction time with the surface decreases, it can also result in energy exchange between the different degrees-of-freedom of the molecule itself[41]. At a quantum dynamical level, the scattering events can be rotationally, vibrationally, or rovibrationally elastic, if the rotational, vibrational, or the full rovibrational state does not change after scattering. If these states do change, the event is considered to be inelastic. Furthermore, the molecules can also be diffracted from the surface at specific angles, or diffraction orders[42], similar to X-rays or photons[43].

Finally, under some conditions it is also possible for the H_2 to get trapped on the surface without dissociating immediately [Fig. 1.1(c)]. For weak chemisorption (of H_2), this is paired with some electron transfer to the molecule's anti-bonding orbitals, but not enough to fully break the molecular bonds[44, 45]. In other cases no electron transfers occur at all, but the molecule could still experience the effects of a very weak (van der Waals) attraction to the surface, which is known as physisorption[46]. Often these trapped molecules will either dissociate as they lose energy to the surface, with or without diffusing towards better dissociation sites, or escape again from the surface. However, this dissociation process occurs over much longer time scales than is normally included in our calculations.

When investigating these systems using classical or quantum dynamical simulations, generally two important approximations are made: the Born-Oppenheimer (BO) approximation[47] and the static surface (SS) approximation. These together form what is commonly referred to as the BOSS approach[11, 39]. Furthermore, the surface is generally not only kept static, but also in its perfect crystal lattice structure.

Electron-hole pair excitations

The BO approximation is discussed in more detail in the section 2.1 of Chapter 2. It relies on the assumption that the electrons of an atom can instantaneously adjust themselves to any movement of the nucleus. In other words, one can find all the relevant energies for the system in two steps, first solving for just the electrons, with the nuclei held at different positions. The potential energies found for these positions can then be used to construct a PES, which is subsequently used to study the dynamics of just the nuclei.

The main problem with the BO approximation is the loss of any non-adiabatic effects, most importantly the effect of electron-hole pair excitations on the system. Unfortunately going beyond the BO approximation is currently still considered very challenging, and therefore outside the scope of this work. However, progress has been made to correct for the additional effects, such as electron-hole (e-h) pair excitations, on the dissociation reactions[48–54]. In these works a fictional (electronic) friction term is introduced to model the effects of these e-h pairs, using methods such as the local density friction approximation (LDFA)[50, 51] or the more advanced orbital dependent friction (ODF) method[49, 52–55]. Previous work with both the LDFA and the ODF have shown the effects to be very small for the H_2 on Cu(111) dissociation reaction[53].

Static surface approximation

The static surface approximation is in many ways based on a similar idea as the BO approximation. Due to the very large mass mismatch between a hydrogen atom and a (metal) surface atom, the forces between the two would (almost) entirely result into changes of the momentum of the hydrogen only. Such an imbalance in the changes in momentum would be especially large when the interaction time between the hydrogen and the surface is relatively short, allowing for little time for the hydrogen to equilibrate with the surface. Thus by assuming the surface to be static, one neglects any effect of energy exchange between the surface and the hydrogen molecule. Such an energy exchange could have effects not just on the probability for dissociation, but also for the final rovibrational state in scattering events, as the H_2 will only be able to change states due to internal energy redistributions.

With the SS approximation, the surface is (usually) assumed to be in its perfect crystal lattice structure. An expansion of this approach is the sudden approximation, where the surface atoms are still kept static, but now distorted from their ideal positions. By averaging over many different distorted surfaces one can then include the effect of the moving, distorted surface on the system, assuming the interaction time is short. However, great care should be taken that this selection of distorted surfaces properly represents the configurations one would expect for the system of interest. Sudden approximations have been applied, often with great success, to many different dissociation reactions. These include not just H_2 dissociation[56–59], but also the heavier CO_2 or CH_4 reactions[60–65].

Effects of surface temperature

Another effect closely linked with the sudden approximation is that of surface temperature effects. While some motion is always present in the surface due to zero-point energies, it is greatly increased with increasing surface temperatures. As the surface temperature increases, thermal surface distortions will also gain a greater magnitude, reducing the effectiveness of the perfect crystal approximations generally used in the BOSS approach. Furthermore, the higher surface temperatures will also lead to increased thermal expansion of the surface slab, which further reduces the perfect lattice approximations. As one would expect, these thermal surface atoms displacements will also affect the H_2 reactive scattering reactions. In particular, Bonfanti *et al.* have shown how displacements of surface atoms would not just affect the dissociation barrier energetically, but also geometrically[56, 58]. Such a change of the barrier would thus not only affect the dissociation probability of H_2, but will equally affect the scattering of the hydrogen and its final rovibrational state or diffraction order.

Over the years, several different models with varying ranges of computational costs and degrees of overall accuracy, have been proposed to include surface temperature effects. For H_2 in particular, such models include the effective Hartree potential by Dutta *et al.*[66, 67], the static disorder parameter by Manson and co-workers[68] and the static corrugation model (SCM)[57, 59]. Several similar methods have also been suggested for methane dissociation. Busnengo *et al.* introduced both reactive force-field methods, as well as the static distorted surface (SDS) model, and moving surface dynamics[63, 65, 69]. Jackson *et al.* also introduced statically distorted surfaces to model surface temperature effects, as well as a single degree-of-freedom to model the surface motion itself[62, 64], and a reduced density matrix approach, where the surface is modeled as a phonon bath[70, 71]. Using perhaps more general approaches, several studies have also been performed using either ring polymer molecular dynamics[72, 73] or high-dimensional neural network potential approaches[74–77].

The SCM in particular will be at the centre of this thesis. It relies on modifying the perfect crystal lattice PES of the BOSS model to include the effect of thermally distorted surface atoms through (relatively) simple pair potentials, which are obtained from fitting to first principles data. Furthermore, by keeping the surface static, but distorted, the SCM is computationally efficient, as we will see from Chapter 4 onward. However, as of yet, it has only been applied to the H_2 dissociation from a Cu(111) surface slab. Thus while the expressions are expected to be general enough for use with other (transition metal) surfaces, or diatomic molecules reacting with those, they have not been verified computationally. Neither have any parameters related to the SCM potential been determined for other systems than H_2/Cu. In addition, it also relies on accurate descriptions of the thermally distorted surface slabs to provide accurate results, which is an important topic in Chapter 3, as we will see.

1.3 Aim and scope of this thesis

As noted in the previous text, the inclusion of surface temperature effects has been a often revisited topic for surface scientists. Within this thesis I aim to further investigate these thermal effects for the well-studied reactive scattering of H_2 on Cu(111). Although this is one of the simplest systems available, theoretical models have been unable to accurately describe these surface temperature effects at a quantum dynamical level. Only recently have several models appeared that explicitly include all the degrees of freedom of just the hydrogen atoms. Using the static corrugation model (SCM), a solid theoretical database will be constructed of different experimental observables for the H_2/Cu(111) system, using both classical and state-of-the-art quantum dynamical approaches.

First in **Chapter 2**, the background of the techniques used throughout the thesis will be discussed, with a focus on quasi-classical dynamics (QCD) and the time-dependent wave packet (TDWP) approach to quantum dynamics (QD). Also outlined are the computations required to obtain several observables discussed throughout this work.

In **Chapter 3** a new approach to generate thermally distorted surface slabs for the SCM is introduced. It makes use of an embedded atom method (EAM) potential combined with molecular dynamics to generate a database of thermally distorted Cu(111) surfaces for a surface temperature of 925 K. D_2 dissociation results obtained using this EAM-SCM are compared to both those obtained from a random displacement (RD) approach based on the temperature dependent Debye-Waller factor, and previous experimental results. The validity of the EAM-SCM, and the sudden approximation, is further verified by comparing to results obtained from the EAM-based (classical) dynamic corrugation model (DCM), a modification of the SCM where surface motion is allowed during H_2 or D_2 interaction with the surface.

In **Chapter 4** the EAM-SCM, using the database of thermally distorted surfaces from the previous chapter, is implemented in a QD code based on the TDWP approach. To assess if the very small unit cell of the QD calculations is appropriate, several QCD calculations are performed where H_2 is constrained to a (1×1) unit cell, and compared to the results of the unrestricted hydrogen molecule. To find if a smaller subset of the distorted surface database can adequately represent the full surface QCD calculations, results of only a small subset of the database are compared to results obtained from the full database. This reduction in surface slabs used is required due to the computational costs of even single surface QD simulations. Next, QD calculations for the rovibrational ground state are compared to results obtained using the QCD approach. The differences between, or agreement of, these QCD and QD results would then highlight quantum effects relevant to both dissociation and scattering probabilities for this system. Finally, by reducing the number of surface atoms included in the SCM, the effect of only displacing one, three, or five closest surface atoms is compared to distorting the entire surface.

Chapter 5 expands on this comparison, including rovibrationally excited states and different methods of binning the final rovibrational state of the QCD calculations, and how this compares to those obtained from the QD. These results, for both the BOSS and SCM approaches, are also compared to recent associative desorption experiments.

Finally **Chapter 6** will take a closer look at the level of noise one can expect for TDWP calculations, and how this could influence comparisons to the experimental results. Cuts of the PES for different thermally distorted surface slabs are investigated to better explain how the inclusion of the thermal effects affect the geometry and height of the (lowest) reaction barrier of the system. The dissociation curves of Chapter 5 are subsequently used to calculate several observables, including simulated time-of-flight spectra, and rotational and vibrational efficacies, which can be more directly compared to available experimental work. These, together with the curves of the Chapter 5, will then also provide a solid set of results to compare to future studies.

1.4 Main results

This section will cover the main results discussed in each of the chapters of the thesis.

Chapter 3: Beyond the static corrugation model

A database of thermally distorted surface slabs of Cu(111) at a modelled temperature of 925 K is constructed using molecular dynamics and a highly accurate embedded atom method (EAM) approach[78]. These distorted slabs are implemented into the static corrugation model (SCM) and used to investigate the dissociation of D_2 on a Cu(111) surface slab at a QCD level for several initial rovibrational states of the molecule. Also included for comparison are

SCM results using the random displacement (RD) approach to SCM surface construction used in older studies[57, 59].

The SCM obtained dissociation curves and simulated time-of-flight spectra show increased widths compared to BOSS results where surface temperature effects are not included. This curve broadening of the SCM results is a characteristic effect, generally ascribed to surface temperature[79]. Dynamic corrugation model (DCM) results, which explicitly include a moving surface described by an EAM potential, also have almost perfect agreement with the EAM-SCM results. This strengthens the sudden approximation, one of the cornerstones of the SCM, and shows the minimal effect energy exchange has on the dissociation of D_2 on a thermally excited Cu(111) surface.

Surface configurations obtained from the EAM molecular dynamics are found to have a much broader distribution of surface atom displacements than configurations obtained from the bulk-like RD approach. This could be an explanation for the difference in saturation values we find between results of the EAM and RD generated surface slabs, although this has not been further explored. These displacement distributions of the EAM-SCM generated surface slabs also reveal a preference for D_2 (at lower incidence energies) to react with surfaces for which the surface atoms are displaced towards the bulk. Such an effect is not present for displacements parallel to the surface, or observed at all for results obtained with the RD-SCM.

Chapter 4: Quantum dynamical surface temperature effects on the dissociative chemisorption of H_2 from Cu(111)

As Chapter 3 has established the validity of the EAM approach to SCM and the limited effect of energy exchange on the dissociation reaction of D_2 on Cu(111), the EAM-SCM is now also used in TDWP QD simulations.

H_2 dissociation probabilities obtained using the QD-EAM-SCM approach were very similar to those obtained using the QCD-EAM-SCM approach, both when considering single surfaces or as an average over 104 different surface slabs. QD-BOSS and QCD-BOSS dissociation curves also agreed well with each other, although the QD results had clear fluctuations, attributed to imperfections of the PES.

Rovibrationally elastic scattering probabilities, however, show a clear disagreement between QD and QCD obtained results, in particular for the EAM-SCM results. Comparisons between the QD and QCD scattering probabilities for individual distorted surface slabs reveals slabs with very low reactivity as the biggest contributors to this difference, at least for the surface slabs considered. The clear difference between classical and quantum results highlights the importance of performing quantum dynamical simulations when trying to describe the H_2/Cu(111) system exactly. This difference becomes especially relevant when also including surface temperature effects, and when not only focusing on the dissociation reaction.

Finally, distorted surface configurations are considered where only one, three, or five surface atoms are in their distorted positions. It is found that five displaced surface atoms suffice to accurately describe the effect of the surface distortions on the dissociation curve. However, the general disagreement found between the QD and QCD scattering results is already clear when considering only one displaced surface atom. The good agreement between SCM results with a fully distorted surface and with only five surface atoms distorted can be well explained by the distance of the surface atoms from the incoming H_2. Only approximately the closest seven surface atoms are found within a region where the SCM potential significantly contributes to the total PES.

Chapter 5: The quantum dynamics of H_2 on Cu(111) at a surface temperature of 925 K: Comparing theory to experiments

Results obtained using the QD-EAM-SCM for the reactive scattering of H_2 from Cu(111) are now expanded to also include rovibrationally excited initial states. QCD-EAM-SCM results are also still considered, but expanded upon by adding the moving surface EAM-DCM approach.

Very good agreement is found between the dissociation curves of the QD- and QCD-EAM-SCM for the initially rovibrationally excited H_2, although some small differences are found for the higher initial vibrational states $\mathrm{v} = 1$. The moving surface QCD-EAM-DCM results also agreed well with both the static surface EAM-SCM approaches, as was also observed for D_2 in Chapter 3.

Some approaches to binning the final rovibrational state of the molecules scattered during the QCD trajectories were also tested. Little difference was found between either binning to the closest allowed rotational state, or using weights to only include that final rotational states that are allowed by quantum mechanics. Rounding down towards an allowed rotational state, however, vastly underestimated scattering results computed with QD, but only for those trajectories where the initial rotational state was equal to the lowest allowed state $(\mathrm{J} = 0, 1)$.

The QD and QCD dissociation curves were also directly compared to published experimental curves from Kaufmann *et al.* obtained from associative desorption measurements[37]. Unfortunately the methods of measuring these curves ensured there was a large amount of uncertainty in the saturation value of the experimental results. Nevertheless, EAM-SCM was shown to better describe the experimental curve onset than the BOSS approach, especially for the lower initial rovibrational states. A closer look at these onsets, however, also revealed a large amount of noise present in the QD results. This is believed to be primarily caused by the size of the time step (1.5 au) used in the split operator method when propagating the wave-packet in the calculations. Although this value was typical for most calculations performed in the past, it likely lead to significant noise when considering probabilities below 10^{-3}.

Chapter 6: The quantum dynamics of H_2 on Cu(111) at a surface temperature of 925 K: Comparing theory to experiments 2

As a direct continuation of Chapter 5, additional calculations are performed to investigate the effect of the time step of the SPO method on the noise in the dissociation curves. By reducing the time step by a factor 15 (to 0.1 au) for a single BOSS calculation, the error found in the curve is reduced by two orders of magnitude (to 10^{-5}). The noise still present in this reaction probability range is well below the levels found in the experimentally verified signal.

Cuts of the SCM PESs for several thermally distorted surfaces are also compared to the ideal lattice BOSS PES, with a focus on the reaction barrier on each cut. When including the surface temperature effects, the lowest reaction barrier on the bridge-to-hollow reaction site is found to move slightly towards a larger H−H distance, while at the same time moving a little closer to the surface.

To match the approach of previous studies, the dissociation curves of Chapter 5 are also fitted to several sigmoidal functions, which are subsequently used for the simulation of time-of-flight (ToF) spectra. These ToF spectra showed improved agreement with the experimental spectra of Kaufmann *et al.*[37] when using the EAM-SCM approach over the BOSS approach.

The fitting parameters of the sigmoidal function are directly compared to the experimental parameters and to each other. The inflection points of the QCD-EAM-SCM curves at different initial states are found to agree very well, slightly overestimating the experimental values, but displaying the same curvature. The width parameters of the EAM-SCM curves are found to be higher than those of the BOSS results across all initial states, yet both overestimated the value reported in the experiment[37]. This curve broadening due to surface temperature effects for the EAM-SCM has also already been observed for D_2 on Cu(111) as discussed in Chapter 3.

The rotational and vibrational efficacies, measures of the extent to which additional rotational and vibrational energy helps the molecule surpass the dissociation barrier, are calculated by determining the energy shift between the results of the rovibrational ground state and the excited states. Theory was found to not reproduce the negative rotational efficacy for lower rotational states with either the EAM-SCM or the BOSS approaches, although it captured this parameter well for the higher rotational energies. For the vibrational efficacies, the SCM reproduced experiment (slightly) better than the BOSS, especially when considering the QD results.

Finally the preference for the H_2 to react rotating either parallel to normal to the surface is investigated by calculating the rotational quadrupole alignment parameter. QD results are found to predict a larger preference for rotation parallel to the surface compared to QCD for lower initial rovibrational states, regardless of the BOSS or SCM approach used. This effect disappears, however, when higher initial rovibrational states are considered. In general, the SCM predicted a slightly smaller preference towards parallel rotation compared to the BOSS. This can be well explained by the distorted nature of the surface making exactly parallel rotation less favorable.

1.5 Outlook

As science progresses, new findings and unexpected results pave the way for new research. Thus it has also been for this thesis, where new results of this thesis, or new results released in the same time-frame allowed us to speculate a little on those topics that could be interesting for further study.

The SCM is shown to clearly affect not only the broadness of the dissociation curves of the H_2, but also the scattering probabilities. However, all the work so far has focused on surface slabs at the relatively high surface temperature of 925 K, which are easily described using classical dynamics for the motion of the surface atoms. Unfortunately, this regime is also ill-suited for comparisons with ultra-high vacuum beam adsorption experiments, which are typically performed on surfaces of much lower temperatures. Reducing the surface temperature of the classical dynamics is possible to a degree, however it will start deviating from an exact solution as this temperature dips below the Debye temperature of the surface. Under this Debye temperature zero-point energies and accurate distributions of the quantum mechanically allowed energy levels becomes important, and the surface can not be treated with classical dynamics. Instead other ways would have to be found to generate accurate surface slabs at low surface temperatures, not based purely on classical dynamics approaches. The effect these thermal surface distortions have on the reaction, based on the works in this thesis, are expected to be quite minor. Nevertheless, they could become more important when one wants to carefully consider specific state-to-state scattering probabilities and/or diffraction of the hydrogen molecule[23, 24].

Another, perhaps expected, future direction of the SCM itself would be expanding the model towards first other Cu lattices, and then eventually to other systems with metals surfaces or other diatomic molecules. As the SCM coupling potential itself only relies on (effective three-body) pair potentials, it should be directly transferable to other Cu lattices when considering H_2, although this has not yet been tested extensively to my knowledge. If the transferability to other copper surface facets is found to be insufficient, additional SRP48 DFT calculations could be easily included to aid in additional fitting to the same functional form. It is very unlikely that the general formulation of the potential would fail when different lattice configurations are involved. Fitting the SCM to other surfaces, or for other diatomics, would of course require new (DFT) calculations. Here an important consideration is the careful selection of surface slab configurations to include in the data-set, ensuring specific distortions are not oversampled. Again, it would be important to first investigate if the sudden approximation is applicable, by considering both the interaction time of the diatomic of choice with the surface, as well as the mass mismatch between the reactant and the surface atoms. If required, additional terms could be added to the potential to account for non-adiabatic effects, which would most likely be best modelled by electronic friction terms.

Other methods of including surface temperature effects have also seen developments, most notably the many variations of the high-dimensional neural network potential approaches (HD-NNPs). These approaches rely on a vast amount of parameters, fitted using machine learning techniques, which allows the NN to describe entire systems, including surface motion, as a single potential[80, 81]. An important topic in this field are the hyperparameters of the system; those parameters that generally have to be manually selected to help guide the machine learning process[82]. Nevertheless, methods do now exist to optimise these hyperparameters automatically[83]. Often additional terms are also used to aid in the fitting, enforcing symmetry through a variety of ways[84]. Although these NNs generally rely on physically motivated functions to describe the interaction between nodes, the nodes themselves will often still consist of fairly simple activation functions, requiring many nodes to construct the whole network. Neural networks are thus often unsuitable to perform any kind of extrapolation outside of the data-set it has been trained on, as its large amount of functions will all behave unexpectedly outside of their intended ranges. Although by carefully constructing these NNPs, some these extrapolation effects can be somewhat diminished[76]. Both these downsides, the extrapolation and the large amount of function evaluations, greatly affect the effectiveness of NNs when used in the quantum dynamics calculations as they were performed for this thesis. These QD calculations require evaluating the entire PES across the six degrees of freedom of the hydrogen molecule, which can result into up to 10^9 potential evaluations. Furthermore, including surface temperature using a sudden approximation also requires calculating tens to hundreds of PESs to obtain well converged average results.

This contrasts the workings of the SCM, which was designed with the eventual implementation into QD simulations as a primary goal. Its small selection of physically motivated functions to describe molecule-surface interactions, and the models ability to extrapolate (somewhat) outside of the training data provide an ideal basis for calculating the large amount of energies needed to construct a full 6D PES. However, with the recent progress regarding HD-NNPs and the endlessly growing computational power of modern machines, some time in the future NNs will inevitably catch up[85]. It is there that SCM should still provide a solid basis to both benchmark new techniques as well as provide a computationally cheap alternative to compare to. A more direct connection between the SCM and HD-NNPs could also be made, replacing the physically motivated coupling potential of the SCM with some form of an NNP instead. While some preliminary work has been performed on this approach, it has not been fully explored yet. Nevertheless, such a “fusion” of the SCM and NNPs would greatly reduce the computational speed of the model, one of the main advantages.

In a more general sense, the big focus on improving the accuracy of the exchange-correlation functionals pivotal for DFT calculations also provides opportunities for the development of better SCM (coupling) potentials. By “climbing Jacob’s ladder”[86], the model can move beyond the use of simple GGA functionals towards the more advanced meta-GGA or hybrid functionals, which could also improve the general applicability of such a newly fitted model. Nevertheless, computational costs should also be taken into account, as many surface distortions are first required to obtain an accurate expression of the SCM coupling potential.

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