Hydrogen dissociation on metal surfaces: A semi-empirical approach
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Summary

Many chemical and physical processes, for example in industry and also everyday life, happen on surfaces. One of the most important is reaction of a molecule on a surface in heterogeneous catalysis. Catalysis creates an alternative energy path to increase the speed and outcome of a reaction. There are many complexities to understand catalytic reactions. It is known that in the reaction mechanism for ammonia synthesis, the dissociation of nitrogen on the catalyst surface is the rate limiting step. The availability of accurate barriers for reactions of molecules on metal surfaces is of central importance to understanding and accurately calculating the rate of heterogeneously catalyzed processes.

Implementations of first principle methods provide availability of the chemically accurate calculation of barriers for gas phase reactions. However, for reactions of molecules on metal surfaces there is plenty of room for improvement. Density functional theory (DFT) using functionals at the generalized gradient approximation (GGA) or meta-GGA level, which can be used to map out potential energy surfaces (PESs) for molecule interacting with metal surfaces, is not yet capable of predicting reaction barriers for gas-phase reaction with chemical accuracy. Most recently, an implementation of the specific reaction parameter approach to DFT (SRP$-$DFT), adopted to molecule surface interactions, was proposed in which usually a single adjustable parameter in the density functional is fitted to reproduce an experiment that is particularly sensitive to the reaction barrier height for the specific system considered. The quality of the SRP density functional (SRP$-$DF) is tested by checking that the candidate SRP$-$DF for a system can also reproduce other experiments on the system, which differ from the experiment the functional was fitted to. This approach has provided accurate values of barrier heights for the dissociative chemisorption of H_2 on Cu(111), Cu(100), and also of CH_4 on Ni(111), Pt(111) and Pt(211) so

far. However, being semi-emprical and in need of validation, the SRP−DFT approach is not without problems.

In this thesis, the main aim is to provide an improved description of H_2 dissociative chemisorption on metal surfaces based on the semi-empirical SRP method in which the accuracy of exchange-correlation (XC) functionals is systematically improved in a semi-empirical and system specific way, by comparing the experimental data with theoretical results. The goal is to construct a database of reaction barriers with chemical accuracy for H_2 interacting with metal surfaces.

In Chapter 3, the aim is to extend the development of SRP density functionals, and the database, with a result for a weakly activated dissociative chemisorption reaction of H_2 with a transition metal surface. For this aim, a SRP−DF is developed, in which the SRP functional incorporates in the correlation part the revised version of the vdW-DF called vdW-DF2, for the dissociation of dihydrogen on Pt(111). The study has been performed using semi-empirical density functional theory and the quasi-classical trajectory (QCT) method. The validity of the QCT method is investigated by showing that QCT calculations on reaction of D_2 with Pt(111) closely reproduce quantum dynamics (QD) results for reaction of D_2 in its rovibrational ground state. The goal is to achieve a chemically accurate description of D_2 dissociation on Pt(111) with molecular beam simulations, while reproducing the experimental results at normal and off-normal incidence. In this chapter, an SRP-DF for H_2 on Pt(111) was obtained by adjusting the α parameter in the PBEα-vdW-DF2 functional until reaction probabilities computed with the QCT method reproduced sticking probabilities measured for normally incident D_2 with chemical accuracy. Reproducing the experimental data by using the SRP−DF functional and QCT calculations for off-normal incidence for $\theta_i = 30$ and $45°$, for which computed reaction probabilities show no dependence on the plane of incidence, confirms the quality of the SRP functional. We report that the minimum barrier height obtained for the reaction is -8 meV, in agreement with the experimental observation of no, or only a small energetic threshold to reaction. This value can be entered into a small, but growing database with barriers of reactions of molecules with metal surfaces, for which chemical accuracy is claimed.

In Chapter 4, the main focus is on the transferability of an SRP functional among chemically related systems. The SRP functional originally developed to describe chemisorption of dihydrogen on Cu(111) (called SRP48 functional) is tested here on dissociation of the same molecule on Ag(111),

with Cu and Ag belonging to the same group of the periodic table. In this chapter, we use the QCT method to compute molecular beam sticking probabilities and initial-state resolved reaction probabilities. To establish the appropriateness of the QCT method, we performed QD calculations for several rovibrational states, and compared with the QCT results. It is found that the QCT method reproduces the QD results very well. It is also found that the barrier heights in the SRP48 PES are higher than obtained with the PBE functional. Furthermore, we computed molecular beam sticking probabilities and compared with the available experimental results. The energy differences between the computed data and the spline interpolated experimental curve were in the range 2-2.3 kcal/mol. Thus, no chemical accuracy was achieved in our theoretical results. Our results show that the SRP48 functional is not transferable to H_2 dissociating on Ag(111) system, although Cu and Ag belong to the same group.

In Chapter 5, the main goal is to address the question whether the SRP−DF functional derived for dissociative chemisorption of H_2 on Pt(111) is transferable to H_2 reacting on Pt(211), which is relevant to heterogeneous catalysis. We use the SRP−DF functional, which was originally derived for the H_2 + Pt(111) system and is able to reproduce experiments on this system with chemical accuracy to model the reaction of H_2 on the stepped Pt(211) surface. We have performed molecular beam simulations with the QCT method using the BOSS model. The accuracy of the QCT method was assessed by comparison with QD results for reaction of the ro-vibrational ground state of H_2. The study shows that the theoretical results for sticking of H_2 and D_2 on Pt(211) are in quite good agreement with experiment, but uncertainties remain due to a lack of accuracy of the QCT simulations at low incidence energies, and possible inaccuracies in the reported experimental incidence energies at high energies. We also investigate the non-adiabatic effect of electron-hole pair excitation on the reactivity using the molecular dynamics with electron friction (MDEF) method, employing the local density friction approximation (LDFA). Only small effects of electron-hole pair excitation on sticking are found.

In Chapter 6, the focus is on two basic problems of the SRP−DFT methodology. The first problem is that sticking probabilities (to which SRP-DFs functionals are usually fitted) might show differences across experiments, of which the origins are not always clear. The second problem is that it has proven hard to use experiments on diffractive scattering of H_2 from metals for validation purposes, as dynamics calculations using a SRP−DF

may yield a rather poor description of the measured data, especially if the potential used contains a van der Waals well.

To address the first problem of the SRP−DFT approach, we have simulated three sets of measurements of sticking probabilities available for D_2 + Pt(111), using four different sets of molecular beam parameters. We compared these experiments on a one-to-one basis. We report that substantial differences exist between the three sticking probability curves measured for D_2 + Pt(111). We discuss the origin of the discrepancies between different experimental data and report the mean absolute deviations between the data of the experiments. We also discuss the question of which set of beam parameters can best be used to simulate a particular set of molecular beam experiments. We obtained that all three sets of experiments can be described with chemical accuracy using molecular beam parameters describing seeded molecular beams that are broad in energy. Performing simulations with different sets of molecular beam parameters also provides insight into under which conditions the experiments should agree with one another.

To address the second problem of the SRP−DFT approach, we performed diffractive scattering calculations comparing with experiments, using the SRP−DF. The theoretical results are shown and compared with experimental results for off-normal incidence for two incidence directions. Our results show that there are both quantitative and qualitative discrepancies between theory and experiments. Our study suggests that the SRP−DF for H_2 + Pt(111) may not yet be accurate enough to describe the diffraction in this system. The van der Waals well plays a role in the description of scattering of H_2 from Pt(111) and with the use of a PES exhibiting a van der Waals well, part of the scattering should be indirect. A similar study on H_2 scattering from Ru(0001) has shown that the agreement between experiment and theory with inclusion of a van der Waals well in the PES was improved by assuming a static surface disorder of metal surface. However, our results established that making this assumption will not improve the agreement between theory and experiment in the case of H_2 scattering from Pt(111).