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Development of highly accurate density functionals for H₂ dissociation on transition metals

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2 Theory and methods

In this chapter the theory behind electronic structure calculations, the construction of potential energy surfaces (PESs), quasi-classical trajectory (QCT) calculations, and quantum dynamics (QD) calculations is introduced. The last section deals with the calculation of observables which can be used to compare to experimental observations.

Within the realm of quantum mechanics the wave function, usually denoted with the Greek letter Ψ , seems to take on the role of magical all-knowing oracle. There has been much discussion since its inception on whether the wave function is real object or a mathematical tool, and on whether it is a complete description of reality¹⁻³. These sort of musings on the deep mathematical nature of reality are, however, far beyond the scope of this thesis.

From here on it is presumed that everything that can be calculated about a particular particle or system is described by the (non-relativistic) time-dependent Schrödinger equation for coupled electron-nuclei dynamics^{4,5}. Throughout this chapter we shall assume that the Born-Oppenheimer approximation⁶ (BOA) has been made. In practice this means that in QD calculations we first need to solve the electronic structure problem to compute the ground state PES. After the PES is obtained the time-dependent Schrödinger equation for the nuclear dynamics can be solved. With a quasi-classical approach we can also solve Hamilton's equations of motion instead. Alternatively forces can be obtained on the fly from an electronic structure method, and used to solve Hamilton's equations of motion in direct dynamics calculations.

2.1 Electronic structure theory: density functional theory (DFT)

Calculating a PES for H_2 interacting with a metal surface in the static surface approximation involves solving the electronic problem for many different configurations of H_2 relative to the surface. DFT is a particularly efficient method for solving the electronic structure problem^{7,8}. DFT has its origin in the 1927 Thomas-Fermi model^{9,10}, which tries to evaluate the energy of a system using only the three dimensional electron density of a system, $n(\vec{r})$, as opposed to

the wave function of a system which depends on the coordinates of all particles in the system. The lack of a rigorous foundation of the Thomas-Fermi model and the large errors it produces for molecular calculations made it a rather crude tool, not suited for quantum chemistry¹¹.

Hohenberg and Kohn⁷ provided the rigorous foundation by showing that for a system of electrons in an external potential (i.e. the potential generated by the nuclei) the ground state wave function is a unique, although unknown, functional of the electron density $n(\vec{r})$. It was also shown that the exact ground state corresponds to the global minimum of the unknown functional of $n(\vec{r})$, which makes it possible to apply the variational principle to obtain the minimum energy and ground state electron density for a given approximation. Thus the evaluation of the energy density functional on an electron density which is not the ground state electron density will yield a higher energy than the ground state energy.

A difficulty in DFT arises in calculating the electrons' kinetic energy from $n(\vec{r})$, which is the main constituent of the total energy of the system. A solution to this problem was given by Kohn and Sham⁸ in the form of a fictitious system of non-interacting electrons in an effective external potential. The Kohn-Sham equations recast the many electron problem as a set of N single-electron equations:

$$\left[-\frac{\nabla^2}{2} + V_{KS}(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}) \quad (2.1)$$

In this equation and those below we will assume that atomic units are used. Here, $\phi_i(\vec{r})$ is the single particle orbital (or Kohn-Sham orbital) for a fictitious non-interacting system. The electron density can then be retrieved by summing over all Kohn-Sham orbitals.

$$n(\vec{r}) = \sum_{i=1}^N |\phi_i(\vec{r})|^2 \quad (2.2)$$

The first term in equation 2.1 represents the kinetic energy of the non-interacting electrons, and the second term is the Kohn-Sham potential, $V_{KS}(\vec{r})$. The Kohn-Sham potential is given by

$$V_{KS}(\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}), \quad (2.3)$$

in which $V_{ext}(\vec{r})$ is the external potential, $V_H(\vec{r})$ is the Hartree (Coulomb) potential, given by

$$V_H(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}', \quad (2.4)$$

and the exchange-correlation potential is given by

$$V_{xc}(\vec{r}) = \frac{\partial E_{xc}[n(\vec{r})]}{\partial n(\vec{r})}. \quad (2.5)$$

$V_{xc}(\vec{r})$ represents the error made by ignoring many-body effects by using the kinetic energy of the system of non-interacting electrons and the Coulomb potential. Although Hohenberg and Kohn⁷ proved that a universal exchange-correlation functional, E_{xc} , must exist, it is, presently, not known exactly. In any practical calculation it is therefore approximated. These approximations are discussed in section 2.1.1.

2.1.1 Exchange-correlation density functionals: LDA, GGA, meta-GGA

As discussed in section 2.1, the expression of the exact exchange-correlation functional is unknown. Many non-empirical density functionals have been constructed that recover some or all known exact constraints on the design of density functionals^{11,12}. Some notable examples are the PBE¹³, PBEsol¹⁴, RPBE¹⁵, B86b¹⁶, TPSS¹⁷, revTPSS¹⁸, and SCAN¹⁹ density functionals. In general semi-local approximations to the exchange-correlation functional, in a spin unpolarized framework, take the following form:²⁰

$$E_{xc}(n(\vec{r})) = \int d^3\vec{r} n(\vec{r}) \epsilon_{xc}(n(\vec{r}), \nabla n(\vec{r}), \tau(\vec{r})) \quad (2.6)$$

Here, $\nabla n(\vec{r})$ is the gradient of $n(\vec{r})$, and $\tau(\vec{r})$ is the kinetic energy density. Both $\nabla n(\vec{r})$ and $\tau(\vec{r})$ depend on $n(\vec{r})$. In equation 2.6 one can choose to only take into account $n(\vec{r})$, this is called the local density approximation (LDA)⁸. In the LDA the exchange-correlation energy is taken to be the exchange-correlation energy of the homogeneous electron gas of the same density as $n(\vec{r})$.

When one chooses to take into account not only $n(\vec{r})$ but also $\nabla n(\vec{r})$ this amounts to climbing Jacob's ladder²¹ one rung up to the generalized gradient approximation (GGA)^{13,15,22}. At the GGA level the exchange-correlation energy thus depends on both $n(\vec{r})$ and its gradient. When $n(\vec{r})$, $\nabla n(\vec{r})$ and $\tau(\vec{r})$ are taken into account in equation 2.6 one climbs another rung on Jacob's ladder²¹ towards a meta-GGA exchange-correlation density functional^{18,19}. Taking into

account higher orders in the expansion of $n(\vec{r})$ amounts to taking into account more and more information about the local environment of each point in the three dimensional $n(\vec{r})$. So far only one density functional has been reported that satisfies all known exact constraints on a exchange-correlation functional, namely the SCAN density functional¹⁹. Satisfying all known exact constraints is however no panacea for describing the interaction of H₂ with transition metal surfaces, as will be discussed in chapter 3.

Many different functional expressions have been put forward as exchange correlation functionals. The work presented in this thesis focuses on the construction of density functionals at the GGA level (see chapter 5) and the meta-GGA level (see chapters 3 and 6).

2.1.2 Non-local correlation

When an exchange-correlation functional is solely based on $n(\vec{r})$, $\nabla n(\vec{r})$ and/or $\tau(\vec{r})$ it is inherently (semi-)local. Such exchange-correlation functionals cannot describe long range electronic correlations such as Van der Waals interactions. As will be discussed in chapter 5, long range electronic correlation is also important in the description of the interaction of H₂ with transition metals.

So far, several methods have been proposed that introduce long range (non-local) correlation in DFT calculations²³. The simplest method is the DFT-D3 method by Grimme^{24,25} in which a pairwise potential is added based on C_6 coefficients computed using time-dependent density functional theory (TD-DFT). A more general approach to incorporating non-local correlation in DFT calculations is based on the Rutgers-Chalmers formulation of non-local correlation by Lundqvist et al.²⁶. One of the first generally applicable non-local exchange-correlation density functionals was the vdW-DF1 density functional proposed by Dion et al.²⁷, and its later revision vdW-DF2²⁸. Other implementations based on the same Rutgers-Chalmers formalism are the VV10²⁹ and rVV10³⁰ non-local exchange-correlation density functionals. The difference between the vdW-DF and VV10 based functionals is that the former consists of the local LDA correlation functional and a non-local correlation term, whereas the latter consists of a semi-local (beyond LDA) correlation functional plus a non-local correlation term.

The non-local term that is part of the vdW-DF and VV10 based non-local correlation functionals can be written as:

$$E_c^{\text{non-local}} = \int d\vec{r} n(\vec{r}) \left(\frac{\hbar}{2} \int d\vec{r}' \Phi(\vec{r}, \vec{r}') n(\vec{r}') + \beta \right). \quad (2.7)$$

Here $\Phi(\vec{r}, \vec{r}')$ is the kernel describing density-density interactions³¹. The parameter β is not present in the vdW-DF non-local correlation functionals and is taken to be $\beta = \frac{1}{32}(\frac{3}{b})^{\frac{3}{4}}$ in the VV10 group of non-local correlation functionals to ensure a zero non-local correlation energy for the homogeneous electron gas³². In the VV10 group of non-local correlation functionals the b parameter is optimized to avoid double counting of intermediate range correlation effects that might be present in the semi-local correlation functional that is part of the VV10 based correlation functionals.

In the context of plane wave DFT the method of Román-Pérez and Soler³¹ has allowed for the vdW-DF1²⁷, vdW-DF2²⁸, VV10²⁹ and rVV10³⁰ non-local correlation functionals to efficiently evaluate the double integral over $n(\vec{r})$ by use of an auxiliary function called the kernel which describes the density-density interactions. Note that apart from a convergence parameter C present in the integration kernel, only the vdW-DF1²⁷ non-local correlation functional is non-empirical²³. In the construction of the vdW-DF2²⁸, VV10²⁹ and rVV10³⁰ non-local correlation functionals at least one parameter is optimized to obtain better agreement with experimental observables.

2.1.3 The problem of obtaining accurate reaction barriers

Currently no first principles electronic structure method exists that can compute molecule-metal interaction energies and barrier heights to within chemical accuracy (1 kcal/mol³³). For the benchmark $\text{H}_2 + \text{Cu}(111)$ system diffusion Monte-Carlo (DMC) calculations underestimate the best available value for the reaction barrier height by 1.6 ± 1.0 kcal/mol³⁴. The description of O_2 scattering from Al(111) was greatly improved by dynamics calculations employing an embedded correlated wave function (ECW) method, but chemical accuracy was not yet reached³⁵.

In the absence of chemically accurate first principles methods describing the interaction of molecules with metals, validation of calculated barrier heights needs to be performed in relation to experimental measurements. However, a barrier height is not a direct observable. An alternative path to validating calculated results uses a dynamics method to compute a physical quantity that is an observable, such as the sticking probability as a function of the incidence energy. The sticking probability as a function of the incidence energy can be measured in supersonic molecular beam experiments³⁶. The fact that such experiments can probe the reactivity of specific, well-defined Miller index metal surfaces at low temperatures make such experiments suitable for validation of calculated barrier heights³³.

2.1.4 Specific reaction parameter approach to DFT

The specific reaction parameter (SRP) approach to DFT is a semi-empirical method, originally proposed by Truhlar and coworkers^{37,38}. Since the work presented in this thesis mostly focuses on reproducing molecular beam dissociative chemisorption experiments, the SRP method is applied by selecting a specific observable (here the zero coverage sticking probability, S_0) of an experiment. In the present context a SRP density functional (E_{xc}^{SRP}) is then constructed by taking a weighted average of a density functional (e.g. E_{xc}^{A}) that overestimates the sticking probability, and one density functional (e.g. E_{xc}^{B}) that underestimates the sticking probability for the system of interest³⁹.

$$E_{xc}^{\text{SRP}} = \alpha \cdot E_{xc}^{\text{A}} + (1 - \alpha) \cdot E_{xc}^{\text{B}} \quad (2.8)$$

Here α is the SRP mixing parameter. This approach allows for the construction of chemically accurate SRP density functionals for specific systems^{33,39-43}. A SRP density functional might be considered successful if it is fitted to reproduce one particular experiment, while also being able to describe another experiment on the same system the SRP density functional was not fitted to. Additionally, a SRP density functional can be considered transferable if it can reproduce experimental results for a system it was not fitted to, i.e. a molecular beam dissociative chemisorption experiment on the same molecule reacting with a different transition metal surface. Note that there exist also other approaches to creating a tunable density functional, one such example would be the PBE α density functional⁴⁴ in which α can be adjusted, as was done for $\text{H}_2 + \text{Pt}(111)$ ⁴⁰.

So far SRP density functionals fitted to reproduce molecular beam dissociative chemisorption experiments for H_2 and D_2 were shown to be transferable among systems in which H_2 interacts with different crystal faces of the same metal^{45,46}, but not with different metals^{47,48}. Transferability of SRP density functional among systems in which the same molecule interacts with different metals has only been reported for CH_4 dissociation on $\text{Ni}(111)$ ⁴² to CH_4 dissociation on $\text{Pt}(111)$ ⁴⁹. In chapters 5 and 6 it will be shown that this type of transferability can also be achieved for the reaction of H_2 and D_2 on low Miller index surfaces of transition metals, when using a non-local correlation functional such as vdW-DF1²⁷, vdW-DF2²⁸ or rVV10³⁰.

In equation 2.8 a weighted average is taken of two exchange correlation-functionals. In practice often only the exchange part of two density functionals is mixed in the creation of a SRP density functional. When creating SRP density functionals that incorporate a non-local correlation functional two expressions for the total exchange-correlation functional can be obtained, depending on whether the non-local correlation part stems from the vdW-DF or VV10 group

of non-local correlation functionals:

$$E_{xc}^{\text{SRP}} = \alpha \cdot E_x^{\text{A}} + (1 - \alpha) \cdot E_x^{\text{B}} + \overbrace{E_c^{\text{LDA}} + E_c^{\text{non-local}}}^{\text{vdW-DF non-local correlation}} \quad (2.9a)$$

$$E_{xc}^{\text{SRP}} = \alpha \cdot E_x^{\text{A}} + (1 - \alpha) \cdot E_x^{\text{B}} + \underbrace{E_c^{\text{semi-local}} + E_c^{\text{non-local}}}_{\text{(r)VV10 non-local correlation}}. \quad (2.9b)$$

2.1.5 Periodic DFT

Metal surfaces are often periodic. In this case it is advantageous to treat the metal surface as infinitely periodic in DFT calculations, since this naturally allows for performing calculations on only the atoms that are part of the repeating unit cell. Calculations using a finite metal slab would quickly spiral out of control with respect to computational cost due to the need to use large finite slabs in order to avoid 'edge' effects. An elegant way of introducing periodicity in DFT calculations is by applying Bloch's theorem⁵⁰, which applies to the solution of the Schrödinger equation of an electron in a periodic potential, and to the Kohn-Sham orbitals of equation 2.1. Bloch's theorem states that eigenfunction for an electron in a periodic potential can always be written as a plane wave multiplied with a periodic function which obeys the periodicity of the system

$$\phi_{i,\vec{k}}(\vec{r}) = u_k(\vec{r})e^{i\vec{k}\cdot\vec{r}}. \quad (2.10)$$

Here \vec{k} is a wave vector in the first Brillouin zone, and i is an index running over all Kohn-Sham orbitals. The function $u_k(\vec{r})$ is a function that obeys the same periodicity as the potential of the surface (\vec{R}), i.e. $u_k(\vec{r}) = u_k(\vec{r} + \vec{R})$. When expanding $u_{\vec{k}}(\vec{r})$ in a Fourier series (plane wave basis set) the Kohn-Sham orbitals can be written as

$$\phi_{i,\vec{k}}(\vec{r}) = N \sum_G c_{i,k}(\vec{G})e^{i(\vec{k}+\vec{G})\cdot\vec{r}}, \quad (2.11)$$

where N is a normalization constant, \vec{G} is a reciprocal lattice vector and $c_{i,k}(\vec{G})$ are the expansion coefficients.

In principle the Fourier expansion is exact, in practice a maximum kinetic energy cut-off is used for the plane waves in the basis set according to:

$$\frac{1}{2}|\vec{k} + \vec{G}|^2 \leq E_{\text{cut-off}} \quad (2.12)$$

Note that describing high energy core electrons using plane waves would require exceedingly high cut-off energies. To get around this problem one can replace the Coulomb potential set up by the bare nucleus and the core electrons by the potential of a pseudo atom. This pseudo atom would describe the nucleus, the core electrons, and the interactions between them, including relativistic effects^{51,52}. Pseudo potentials are constructed in such a way that the pseudo wave function is as smooth as possible within a cut-off radius r_c close to the nucleus while simultaneously yielding almost exactly the same real potential and wave function outside of r_c . Given that the wave function describing the core of the atoms is much smoother when using pseudo potentials, calculations can be carried out using a lower cut-off energy (see equation 2.12). For the work presented in this thesis two types of pseudo potentials have been used, namely Vanderbilt's ultrasoft pseudo potentials⁵¹ and the more general projector-augmented-wave potentials⁵³.

2.2 Constructing potential energy surfaces

Obtaining a continuous representation of the six dimensional PES of a diatomic molecule interacting with a surface of which the surface atoms are fixed in their ideal lateral positions can be achieved by applying the corrugation reducing procedure (CRP)^{54,55}. The CRP method is a rather efficient procedure to interpolate potential energies calculated on a grid and obtained from any electronic structure method. In the CRP method the molecule-surface PES is written as

$$V^{6D}(\mathbf{R}, \mathbf{r}) = I^{6D}(\mathbf{R}) + \sum_{i=1}^2 V^{3D}(\mathbf{r}_i), \quad (2.13)$$

where \mathbf{R} are the coordinates of the molecule, \mathbf{r}_i are the coordinates of the i^{th} atom belonging to the molecule, V^{3D} is the atom-surface potential evaluated for each atom, and I^{6D} is the so-called interpolation function. Subtracting the atomic potentials from the six dimensional potential ensures that I^{6D} is a smooth function that can readily be interpolated without performing an excessive amount of electronic structure calculations. The atom-surface potential is constructed in a similar way as the molecule-surface potential. The atom-surface potential is written as

$$V^{3D}(\mathbf{r}_i) = I^{3D}(\mathbf{r}_i) + \sum_j^N V^{1D}(\mathbf{r}_{ij}) \quad (2.14)$$

where I^{3D} is the three dimensional interpolation function that needs to be interpolated over the atomic coordinates \mathbf{r}_i , r_{ij} is the distance between atom i and surface atom j , and V^{1D} is a one dimensional corrugation reduction function. For V^{1D} one usually takes the Z dependence of the interaction of an atom normally incident on a top layer surface atom.

Applying the steps outlined in equations 2.13 and 2.14 reduces the corrugation of I^{6D} in the X, Y, θ and ϕ degrees of freedom with respect to V^{6D} ⁵⁴. The number of electronic structure calculations that need to be performed can be further reduced by taking into account the symmetry of the surface during the interpolation. The way this is achieved is by generating symmetry adapted basis functions for the interpolation using a Fourier expansion that obeys the correct wallpaper group symmetry of the surface⁵⁶. The way this is done specifically for the CRP PESs created for the work in this thesis has been documented in the PhD thesis of Wijzenbroek⁵⁷.

2.3 Nuclear dynamics

After a six dimensional (i.e. depending on the six degrees of freedom of the H₂ molecule are in relation to the metal surface) PES has been obtained, nuclear dynamics calculations can be performed either quasi-classically or quantum mechanically. Both methods can be used to calculate observables (see section 2.4) which in turn can be used to compare to experimental observations.

2.3.1 Quasi-classical trajectory method

In the quasi-classical trajectory method Newton's equations of motion are solved for the six degrees of freedom of the H₂ molecule moving on the six dimensional PES.

$$M_i \frac{d^2 \mathbf{R}_i}{dt^2} = -\nabla_i V^{6D}(\mathbf{R}_i) \quad (2.15)$$

Here i is the index that runs over the atoms in a diatomic molecule, and M_i is the mass of atom i . In all but chapter 4 the predictor-corrector method of Burlisch and Stoer⁵⁸ is used to integrate the equation of motion. Additionally, quasi-classical conditions are assumed⁵⁹ such that the quantum mechanical energies of impinging H₂ molecules in their initial rovibrational state are taken into account by imparting them to the molecule at time t_0 . The energies of the rovibrational states of the H₂ molecule are obtained by using the Fourier grid Hamiltonian (FGH) method⁶⁰.

The initial conditions of each trajectory are set up as follows. At the start of each trajectory the molecule is placed in the gasphase at $Z = Z_{\text{gas}}$, where

the potential does not depend on Z . The impact site in X and Y is randomly sampled, and an initial velocity vector for the center of mass of the molecule is constructed based on the chosen initial perpendicular and parallel translational energy (E_{\perp} and E_{\parallel} , respectively). The initial positions and momenta are further constrained by the vibrational quantum number ν , the rotational quantum number J and the magnetic rotational quantum number m_J . The orientation of the molecule with respect to θ and ϕ is chosen based on the rotational state. The initial angular momentum L is set by $L = \sqrt{J(J+1)}\hbar$ and the orientation of L is randomly sampled with the constraint $\cos\theta_L = m_J/\sqrt{J(J+1)}$. Here θ_L denotes the angle between L and the surface normal. The vibrational energy of a particular vibrational state is imparted to the molecule by randomly sampling positions and momenta obtained from a one dimensional classical dynamics calculations of the vibrating molecule of the same energy as the selected vibrational state.

Trajectories are considered to be reacted when the H-H distances becomes larger than some critical value r_c , and trajectories are considered to be scattered when Z becomes bigger than Z_{gas} and has a momentum away from the surface. For practical reasons there is a maximum propagation time t_{max} for all trajectory calculations. If neither reaction nor scattering has occurred the molecule is considered to be trapped. It should however be noted that when no energy is removed from the molecule during the trajectory, as is the case here, in principle no trapping should occur in the limit of an infinite simulation time. The reaction probability P_r is then calculated by dividing the number of reacted trajectories N_r by the total number of trajectories N_{total} .

$$P_r = \frac{N_r}{N_{\text{total}}} \quad (2.16)$$

The standard error in P_r , σ_{P_r} , can then be computed as

$$\sigma_{P_r} = \sqrt{\frac{P_r(1 - P_r)}{N_{\text{total}}}}. \quad (2.17)$$

Langevin equation with energy dissipation

In chapter 4 the Langevin equation is used instead of Newton's equations of motion in order to make it possible to carry out molecular dynamics calculations that incorporate electronic friction (MDEF). Dissipative effects due to electron-hole pair excitations in MDEF calculations have been described phenomenologically by coupling the six-dimensional H_2 molecule to a heat bath. The coupling is here realized by a (6×6) frictional tensor η , which accounts

for the effect of electron-hole pair excitations during the dynamics^{61–63}.

$$M_i \frac{d^2 \mathbf{R}_i}{dt^2} = -\nabla_i V^{6D}(\mathbf{R}_i) - \underbrace{\sum_{k=1}^N \eta_{ik} \frac{d\mathbf{R}_k}{dt}}_{\text{friction force}} + F_i^{\text{random}}(T) \quad (2.18)$$

Here η_{ik} is the frictional tensor element, and $F_i^{\text{random}}(T)$ is a temperature dependent random force. The temperature dependent random force is calculated as discussed in references^{62,63}, and is taken such that the fluctuation-dissipation theorem⁶⁴ can be taken into account⁶⁵

$$\langle F_i^{\text{random}}(t) F_j^{\text{random}}(t') \rangle = 2k_B T_{el} \eta_{ii} \delta_{i,j} \delta(t - t'). \quad (2.19)$$

In equation 2.19 k_B is the Boltzmann constant. In this way $F_i^{\text{random}}(T)$ is taken to be correlated to a Gaussian white noise distribution which is implemented as discussed in reference⁶², and vanishes for $T = 0K$. The electronic temperature T_{el} is taken to be equal to the surface temperature. Equation 2.18 is integrated using the Ermak-Buckholz propagator⁶⁶.

The local density friction approximation (LDFA) together with the independent atom approximation (IAA) is used to calculate the friction coefficients of equation 2.18^{67,68}. Molecular properties are thus neglected in this approach and the off-diagonal elements of the friction tensor as expressed in the Cartesian coordinates of the atoms are zero. As a consequence kinetical coupling between different degrees of freedom cannot be described in this model. Whether the LDFA is a valid approximation in combination with the IAA is still under debate^{69–71}, but it allows for a comparably simple incorporation of electronically non-adiabatic effects during the dynamics of H₂ reacting on transition metal surfaces^{62,63,67,69,72,73}.

2.3.2 Quantum dynamics

Six dimensional quantum dynamics (QD) calculations are performed by using the time-dependent wave packet (TDWP) method^{74–76} in order to solve the time-dependent nuclear Schrödinger equation:

$$i\hbar \frac{d\Psi(\vec{Q}; t)}{dt} = \hat{H}\Psi(\vec{Q}; t). \quad (2.20)$$

This is done using an in-house computer package^{77,78}. Here, $\Psi(\vec{Q}; t)$ denotes the nuclear wave function of H₂ at time t with \vec{Q} being the position vector. To describe motion in the six degrees of freedom of H₂ the following Hamiltonian

is used:

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2 - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{1}{2\mu r^2}\hat{J}^2(\theta, \phi) + V^{6D}(\vec{Q}). \quad (2.21)$$

Here, M and μ are the mass and reduced mass of H_2 , and $\hat{J}^2(\theta, \phi)$ is the angular momentum squared operator. A discrete variable representation (DVR)⁷⁹ is used to represent the wave packet in the Z, r, X and Y degrees of freedom and a finite basis representation (FBR)^{80,81} is used for the angular degrees of freedom. In order to transform the wave function from the DVR to the FBR and back, fast Fourier transforms⁸² and discrete associated Gauss-Legendre transforms^{80,81} are employed.

The initial wave packet is constructed as a product of a gas phase rovibrational eigenfunction of H_2 characterized by the quantum numbers ν, J and m_J ($\Phi_{\nu, J, m_J}(r, \theta, \phi)$) and a Gaussian wave packet with initial wave vector $\vec{k}_0 = (k_0^X, k_0^Y, k_0^Z)^T$ describing translational motion.

$$\Psi(\vec{Q}, t = 0) = \Phi_{\nu, J, m_J}(r, \theta, \phi)\psi(\vec{k}_0, t_0) \quad (2.22)$$

The initial translational motion is then described by the following wave function:

$$\psi(\vec{k}_0, t_0) = e^{i(k_0^X X_0 + k_0^Y Y_0)} \int_{-\infty}^{\infty} \beta(k_0^Z) e^{ik_0^Z Z_0} dk_0^Z \quad (2.23)$$

Here, $\beta(k_0^Z)$ is the initial Gaussian wave packet centered on Z_0 , which is defined through the width parameter σ and average momentum \bar{k} according to:

$$\beta(k_0^Z) = \left(\frac{2\sigma^2}{\pi}\right)^{-\frac{1}{4}} e^{-\sigma^2(\bar{k} - k_0^Z)^2} e^{i(\bar{k} - K_0^Z)Z_0}. \quad (2.24)$$

Here, σ is the width of the wave packet centered around the wave vector \vec{k}_0 . The width σ is chosen in such a way that most of the Gaussian wave packet is placed in a initial translational energy range of $E_i \in [E_{min}, E_{max}]$.

The wave function is propagated using the split operator (SPO) method⁸³ using a time step Δt . Reflections of the wave packet at large Z and r are avoided by the use of quadratic complex absorbing potentials⁸⁴, which permits the use of short grids in order to reduce the computational cost. The scattered wave packet is analyzed using the scattering matrix formalism⁸⁵. Scattering probabilities can then be obtained for the translational energy range present in the initial wave packet from the S -matrix elements. Subtracting the sum of the state-to-state scattering probabilities from unity yields the fully initial-state

resolved reaction probability.

$$P_r(\nu, J, m_J) = 1 - \sum_{\nu', J', m'_J, n, m} P_{scat}(\nu, J, m_J \rightarrow \nu', J', m'_J, n, m) \quad (2.25)$$

Here $P_{scat}(\nu, J, m_J \rightarrow \nu', J', m'_J, n, m)$ are the state-to-state scattering probabilities, and ν', J' and m'_J are the final vibrational, rotational and magnetic rotational quantum numbers. The quantum numbers for diffraction are denoted by n and m .

2.4 Computation of observables

2.4.1 Molecular beam sticking

Calculation of molecular beam sticking probabilities from fully initial-state resolved reaction probabilities involves averaging over the rovibrational state distribution according to the nozzle temperature T_n as well as over the velocity distribution of the molecules in the molecular beam. The probability to find H_2 with a velocity v in an interval $v + dv$ and in a particular rovibrational state at a given T_n is denoted by

$$P(v_0, \alpha, \nu, J, T_n)dv = \underbrace{Cv^3 e^{-(v-v_0)^2/\alpha^2} dv}_{P_{flux}(v_0, \alpha)} \times P_{int}(\nu, J, T_n)dv \quad (2.26)$$

where C is a normalization constant, v_0 is the stream velocity and α is the width of the velocity distribution. In equation 2.26 the reactivity of each state is weighted according to its Boltzmann weight as:

$$P_{int}(\nu, J, T_n) = \frac{g_N f(\nu, J, T_n)}{Z(T_n)} \quad (2.27)$$

with

$$f(\nu, J, T_n) = (2J + 1) \times e^{-(E_{\nu,0} - E_{0,0})/k_B T_{vib}} \times e^{-(E_{\nu,J} - E_{\nu,0})/k_B T_{rot}}. \quad (2.28)$$

Here, the factor g_N in equation 2.27 reflects the ortho/para ratio of hydrogen in the beam. For D_2 $g_N = 2/3$ ($1/3$) for even (odd) values of J , while for H_2 $g_N = 1/4$ ($3/4$) for even (odd) values of J . $Z(T_n)$ is the partition function, k_B is the Boltzmann constant, and $E_{\nu,J}$ is the energy of the rovibrational state characterized by the vibrational (ν) and rotational (J) quantum numbers. In equation 2.28 rotational cooling of the H_2 molecules due to the supersonic expansion is taken into account by setting the rotational temperature to $T_{rot} =$

$0.8 \cdot T_n$ ⁸⁶. Degeneracy averaged reaction probabilities are computed from fully initial-state resolved reaction probabilities as:

$$P_{\text{deg}}(E, \nu, J) = \sum_{m_J=0}^J (2 - \delta_{m_J,0}) \frac{P_r(E, \nu, J, m_J)}{2J+1}, \quad (2.29)$$

where $P_r(E, \nu, J, m_J)$ is the fully initial-state resolved reaction probability, with m_J being the magnetic rotational quantum number and E being the translational energy ($\frac{1}{2}mv^2$). Note that calculations are only performed for positive J and m_J , since given the rotational symmetry of the surfaces used in this thesis the sign of the angular momentum is unimportant. Molecular beam sticking probabilities can then be computed as a function of the parameters describing a molecular beam:

$$S_0(\langle E_i \rangle, T_N) = \sum_{\nu, J} \int P(v_0, \alpha, \nu, J, T_n) P_{\text{deg}}(E, \nu, J) dv. \quad (2.30)$$

Here, $\langle E_i \rangle$ is the average incidence energy, which can be computed from v_0 and α ; usually the sticking probability is simply written as $S(E_i)$ with the assumption that the reader knows that E_i then represents the average of E_i over the velocity distribution. A more exhaustive description of how molecular beam sticking probabilities can be computed can be found in ref.⁶²

2.4.2 Rotational quadrupole alignment parameters

The extent to which the reaction of H_2 with a transition metal surface depends on the alignment of the molecule relative to the surface normal can be calculated via the rotational quadrupole alignment parameter. The rotational quadrupole alignment parameter, $A_0^{(2)}(E, \nu, J)$, is computed from initial-state resolved reaction probabilities as follows:⁸⁷

$$A_0^{(2)}(E, \nu, J) = \frac{\sum_{m_J=0}^J (2 - \delta_{m_J,0}) P_r(E, \nu, J, m_J) \left(\frac{3m_J^2}{J(J+1)} - 1 \right)}{\sum_{m_J=0}^J (2 - \delta_{m_J,0}) P_r(E, \nu, J, m_J)}. \quad (2.31)$$

A positive value for $A_0^{(2)}(\nu, J)$ indicates a preference for reaction of molecules aligned parallel to the surface, a negative value indicates a preference for reactions of molecules aligned perpendicular to the surface, and zero means the reaction proceeds independent of the molecule's alignment

relative to the surface. Here the orientation refers to the angle θ between the H-H bond and the surface normal.

2.4.3 $E_{1/2}(\nu, J)$ parameters

Initial state-selected reaction probabilities can be obtained from H_2 associatively desorbing from metal surfaces by applying the principle of detailed balance⁸⁸ to associative desorption experiments^{86,89–91}. Typically the (unnormalized) state-resolved translational energy distributions of molecules desorbing from the surface is measured using resonance-enhanced multi-photon ionization (REMPI)^{46,86,89} combined with time-of-flight techniques. The state resolved distributions of desorbing molecules, $P_{\text{des}}(E, \nu, J)$, may be related to the degeneracy averaged initial-state resolved reaction probability, using:

$$P_{\text{des}}(E, \nu, J) \propto E e^{-\frac{E}{k_b T_s}} P_{\text{deg}}(E, \nu, J). \quad (2.32)$$

The extracted reaction probabilities are usually fitted to a sigmoid function, in most cases an expression involving the error function:

$$P_{\text{des}}(E, \nu, J) = \frac{A_{\nu, J}}{2} \left[1 + \text{erf} \left(\frac{E - E_0(\nu, J)}{W_{\nu, J}} \right) \right]. \quad (2.33)$$

Here, the $A_{\nu, J}$ values are the saturation values of the extracted degeneracy averaged reaction probabilities, and the effective barrier height ($E_0(\nu, J)$) is the incidence energy at which $P_{\text{deg}}(E, \nu, J)$ first becomes equal to $\frac{1}{2}A_{\nu, J}$. $W_{\nu, J}$ represents the width of the reaction probability curve.

In an associative desorption experiment the exact state-selective flux is usually not measured^{86,89–91}, meaning that the proportionality factor in equation 2.32 cannot be obtained directly. In the absence of a measured proportionality factor it is still possible to make a comparison between theory and experiment. Chapter 5 will detail four different methods that can be used to make such a comparison, namely the methods A1 and A2 in which normalized proportionality factors are obtained from a wholly experimental procedure, and methods B1 and B2 in which normalized reaction probabilities are extracted with reference to theory. Given that methods A2 and B2 apply to a specific associative desorption experiment for the $\text{H}_2 + \text{Au}(111)$ system and the particular experimental conditions for that experiment, only methods A1 and B1 will be briefly discussed here.

Method A1

Method A1 assumes that the effective barrier heights ($E_0(\nu, J)$) can be kept the same in the description of a molecular beam sticking experiment at a low surface temperature and an associative desorption experiment at a high surface temperature^{86,89}. When applying the principle of detailed balance the surface temperature dependence of $P_{deg}(E, \nu, J)$ is taken into account by allowing for larger $W_{\nu, J}$ parameters in the description of the associative desorption experiments^{92,93}. Next, the $A_{\nu, J}^{A1}$ parameters are determined assuming that they do not depend on the surface temperature by requiring that the measured molecular beam sticking probabilities can be computed as outlined in section 2.4.1. Generally the A parameters are taken to be independent of the initial rovibrational state, or to depend solely on the vibrational quantum number so that a fitting procedure can be followed with a properly constrained number of degrees of freedom. Method A1 was followed to extract initial-state resolved reaction probabilities in experiments on H₂ and D₂ desorbing from Cu(111)^{86,89,91}.

Calculated $E_{1/2}(\nu, J)$ parameters can then be defined as the translational energy at which the computed reaction probability becomes equal to half the experimental saturation value³⁹.

$$P_{deg}(E_{1/2}(\nu, J), \nu, J) = \frac{1}{2} A_{\nu, J}^{A1} \quad (2.34)$$

Method A1 is described in more detail in chapter 5.

Method B1

In method B1, the experimental sticking probability curve is normalized by equating the reaction probability at the maximum kinetic energy to which the experiment was sensitive ($E_{max}(\nu, J)$) to the calculated value at that translational energy^{90,91}.

$$P_{deg}(E_{1/2}(\nu, J), \nu, J) = \frac{1}{2} A_{\nu, J}^{B1} = \frac{1}{2} P_{deg}(E_{max}(\nu, J), \nu, J). \quad (2.35)$$

Note that the maximum translational energy to which the experiment is sensitive is usually not high enough to equal the absolute saturation value A of the reaction probability. However, as will be discussed in chapter 5, as long as $P_{deg}(E_{max}(\nu, J), \nu, J) \geq 0.9A$ the calculated $E_{1/2}(\nu, J)$ parameters will be underestimated by no more than 0.09 $W_{\nu, J}$.

2.4.4 Rovibrational state populations of H₂ and D₂ desorbing from Au(111)

The following expression is used to calculate state distributions of desorbing molecules:⁹⁰

$$N(\nu, J) = \int_0^{E_{\max(\nu, J)}} P_{\text{int}}(\nu, J, T_S) \sqrt{E} e^{-\frac{E}{k_B T_S}} P_{\text{deg}}(E, \nu, J) dE. \quad (2.36)$$

Here, E is the translational energy and T_S is the surface temperature. A comparison to experiment can be made by replacing $P_{\text{deg}}(E, \nu, J)$ in equation 2.36 with reported error function fits obtained experimentally⁹⁰. Note that it is critical for a valid comparison between theory and experiment that equation 2.36 is only integrated up to $E_{\max(\nu, J)}$. This is because the experimentally obtained error function fits for the reaction probability are only valid below $E_{\max(\nu, J)}$, and can yield reaction probabilities substantially bigger than one above $E_{\max(\nu, J)}$. Generally the obtained populations are normalized to the total $\nu = 0$ population according to:

$$N(\nu, J) = \frac{N(\nu, J)}{\sum_J N(\nu = 0, J)} \quad (2.37)$$

The ratio $\nu = 1 : \nu = 0$ can then be calculated as:

$$\nu = 1 : \nu = 0 = \frac{\sum_J N(\nu = 1, J)}{\sum_J N(\nu = 0, J)} \quad (2.38)$$

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