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Hydrogen dissociation on metal surfaces: A semi-empirical approach

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Citation

Nour Ghassemi, E. (2019, September 19). *Hydrogen dissociation on metal surfaces: A semi-empirical approach*. Retrieved from <https://hdl.handle.net/1887/76855>

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Issue Date: 2019-09-19

CHAPTER 2

Theoretical Background

In this chapter we provide the background that is required for the following chapters. The diatomic molecule interacting with an ideal static surface model is discussed. A brief description of density functional theory (DFT) is presented followed by methods for construction of potential energy surfaces. Methods for dynamics calculations on H₂-surface systems and for computing properties from the results of dynamics calculations are described.

2.1 Modelling the molecule surface interaction

The interaction between a molecule and a surface is fully described by the Schrödinger equation [1] as :

$$\hat{H}_{tot}\psi(\vec{r}, \vec{R}) = E_{tot}\psi(\vec{r}, \vec{R}), \quad (2.1)$$

in which E_{tot} is the total energy and $\psi(\vec{r}, \vec{R})$ is the wave function, depending on all the electronic coordinates $\vec{r}$ and the nuclear coordinates $\vec{R}$. $\hat{H}_{tot}$ is the Hamiltonian that describes both the electronic and nuclear motions. The electronic Hamiltonian is composed of kinetic energy term of the electrons ($\hat{T}_e$) and electrostatic potentials (V),

$$\hat{H}_e = \hat{T}_e + V_{ee} + V_{nn} + V_{ne}, \quad (2.2)$$

so that the total Hamiltonian is given

$$\hat{H}_{tot} = \hat{T}_n + \hat{H}_e, \quad (2.3)$$

where $\hat{T}_n$ is the kinetic energy of the nuclei (with mass M_j) in atomic units, given by

$$\hat{T}_n = \sum_{j=1}^M \frac{-1}{2M_j} \nabla_{\vec{R}}^2. \quad (2.4)$$

Note that throughout this chapter we will use atomic units. The kinetic energy of the electrons is given by

$$\hat{T}_e = \sum_{i=1}^N -\frac{1}{2} \nabla_{\vec{r}}^2. \quad (2.5)$$

V_{ee} is the electron-electron (repulsive) interaction potential

$$V_{ee} = \sum_{i=1}^N \sum_{k>i}^N \frac{1}{|\vec{r}_i - \vec{r}_k|}, \quad (2.6)$$

V_{nn} is the nuclear-nuclear (repulsive) interaction potential with atomic numbers Z

$$V_{nn} = \sum_{j=1}^M \sum_{k>j}^M \frac{Z_j Z_k}{|\vec{R}_j - \vec{R}_k|}, \quad (2.7)$$

and V_{ne} is the nuclear-electron (attractive) interaction potential

$$V_{ne} = \sum_{j=1}^M \sum_{i=1}^N \frac{-Z_j}{|\vec{r}_i - \vec{R}_j|}. \quad (2.8)$$

In the framework of the Born-Oppenheimer (BO) approximation [2], the ground state potential energy surface (PES) arises from solving the electronic Schrödinger equation for the problem by the partition of the problem into electronic and nuclear degrees of freedom (DOFs),

$$\hat{H}_e \psi_e(\vec{r}; \vec{R}) = (\hat{T}_e + V_{ee} + V_{nn} + V_{ne}) \psi_e(\vec{r}; \vec{R}) = E_e(\vec{R}) \psi_e(\vec{r}; \vec{R}), \quad (2.9)$$

and

$$\hat{H}_n \psi_n(\vec{R}) = [\hat{T}_n + E_e(\vec{R})] \psi_n(\vec{R}). \quad (2.10)$$

This approximation allows us to write the full wave function in a separable form :

$$\psi(\vec{r}, \vec{R}) = \psi_e(\vec{r}; \vec{R}) \psi_n(\vec{R}), \quad (2.11)$$

where $\psi_e(\vec{r}; \vec{R})$ is the corresponding electronic wave function that parametrically depends on all nuclear coordinates $\vec{R}$, and $\psi_n(\vec{R})$ is the nuclear wave function. In Equation 2.9, E_e is the electronic energy of the system (for the ground state, this is the lowest value) which depends on the nuclear positions. For this thesis we neglect the surface atom DOFs and the molecule interacts with the frozen ideal surface. $E_e(\vec{R})$ will be referred to as the potential energy surface (PES) for the ground electronic state. The most efficient electronic structure method to solve the electronic Schrödinger equation for the molecule-surface interaction in an approximative but still accurate way is density functional theory (DFT). It will be the subject of the next section in this chapter.

2.2 Density functional theory

To obtain the potential energy for a particular configuration, which needs to be done for many configurations to map out a PES, an electronic structure method is needed. The problem in electronic structure calculations arises when the system is described by a high dimensional many-electron wave function. To solve this problem, a much simpler three dimensional quantity, *i.e.*, the electron density $n(\vec{r})$ is used to replace the high-dimensional many-body wave function [3]. The electron density in a system with N electrons depends on only three DOFs and the computational cost of the method scales as N^3 instead of N^m for the wave function based methods, with $m \geq 4$.

Hohenberg and Kohn [3] showed that for any system of interacting particles in an external potential $V_{ext}(\vec{r})$, the electron density is uniquely determined, in other words, the ground state wave function is a unique functional of the density $n(\vec{r})$. Furthermore, they showed that a universal functional for the energy $E[n(\vec{r})]$ can be defined in term of the density. The exact ground state corresponds to the global minimum value of this functional. This makes it possible to use the variational principle to obtain the minimum energy and the ground state electronic density. All physical information about the system is given by $\hat{H}_e$ and according to the theorem, there is a one-to-one correspondence between $\hat{H}_e$ and the ground state electronic density. Therefore, from the Hohenberg and Kohn theorem, the energy is a functional of the electron density,

$$E_e[n(\vec{r})] = \hat{T}_e[n(\vec{r})] + V_{ee}[n(\vec{r})] + V_{ne}[n(\vec{r})] = F_{HK}[n(\vec{r})] + V_{ne}[n(\vec{r})]. \quad (2.12)$$

F_{HK} is the Hohenberg and Kohn functional which is universal and independent of the system. $V_{ne}[n(\vec{r})]$ is the system dependent term and is called the external potential. We note that in practice V_{nn} is also added to the electronic Hamiltonian, even though this just adds a constant to the value of the energy for a specific configuration of the nuclei. F_{HK} is unknown and approximation is needed to express it. It is very useful to separate F_{HK} in three different contributions as

$$F_{HK} = \hat{T}_e[n(\vec{r})] + E_H[n(\vec{r})] + G_{XC}[n(\vec{r})], \quad (2.13)$$

in which $E_H[n(\vec{r})]$ is the Hartree interaction of the electrons, given by

$$E_H[n(\vec{r})] = \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}', \quad (2.14)$$

$G_{XC}[n(\vec{r})]$ is a functional that contains quantum mechanical many-body effects and it is unknown. Here, in the Hohenberg and Kohn theorem $\hat{T}_e[n(\vec{r})]$ is the kinetic energy of the electrons.

Kohn and Sham [4] developed a practical way to avoid problems with calculating the kinetic energy from the electronic density. They proposed a fictitious system consisting of non-interacting electrons in an effective external potential (the Kohn-Sham potential V_{KS}). The many-electron problem can be reformulated as a set of N single-electron equations referred to as the Kohn-Sham equations,

$$\left[-\frac{\nabla^2}{2} + V_{KS}(\vec{r})\right]\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}). \quad (2.15)$$

ϕ_i is the single particle orbital or Kohn-Sham (KS) orbital obtained for an fictitious non-interacting system and yields the electron density of the original system

$$n(\vec{r}) = \sum_{i=1}^N |\phi_i(\vec{r})|^2. \quad (2.16)$$

The first term on Equation 2.15 yields the kinetic energy of the non-interacting electrons, $\hat{T}_S$. The total kinetic energy of the system $\hat{T}_e$ can be separated in a non-interacting contribution $\hat{T}_S$ and an unknown component $\hat{T}_C$ that contains correlation through many-body effects. This component is also a functional of the electron density and together with G_{XC} forms the well-known exchange-correlation (XC) functional $E_{XC} = G_{XC} + \hat{T}_C$. This name comes from the fact that it contains the exchange interaction due to the Pauli exclusion principle and many-body electron-electron correlation. This unknown XC functional is approximated in particular calculations and its approximations will be discussed in the Section 2.2.1. The total energy functional 2.12 can be rewritten with respect to these definitions as

$$E_e[n(\vec{r})] = \underbrace{\hat{T}_s[n(\vec{r})] + E_H[n(\vec{r})] + V_{ne}[n(\vec{r})]}_{\text{known}} + \underbrace{E_{XC}[n(\vec{r})]}_{\text{unknown}}. \quad (2.17)$$

Minimizing this energy functional is done through the solution of the single particle Kohn-Sham equations (Equation 2.15). The Kohn-Sham potential in Equation 2.15 is given by

$$V_{KS}[n(\vec{r})] = V_{ext}[n(\vec{r})] + V_H[n(\vec{r})] + V_{XC}[n(\vec{r})]. \quad (2.18)$$

Here, V_{ext} is the external potential from the nuclei,

$$V_{ext} = \sum_{j=1}^M \frac{Z_j}{|\vec{r} - \vec{R}_j|}, \quad (2.19)$$

V_H is the Hartree potential, given by

$$V_H[n(\vec{r})] = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}', \quad (2.20)$$

and V_{XC} is the exchange-correlation potential, given by

$$V_{XC}[n(\vec{r})] = \frac{\delta E_{XC}[n(\vec{r})]}{\delta n(\vec{r})}. \quad (2.21)$$

All these functional derivatives that enter in the Kohn-Sham equation depend on the density, and therefore on the KS orbitals. The Kohn-Sham equations are solved self-consistently.

2.2.1 The exchange-correlation functional

The quality of DFT depends on the form of the unknown XC functional E_{XC} . The simplest approximation for the XC functional was proposed in the paper of Kohn-Sham [4] and it is called the local density approximation (LDA), where the XC functional is written as,

$$E_{XC}^{LDA}[n(\vec{r})] = \int n(\vec{r}) \epsilon_{XC}^{LDA}(n(\vec{r})) d\vec{r}, \quad (2.22)$$

where ϵ_{XC}^{LDA} is the XC energy per electron of the homogeneous electron gas (HEG) with the electron density $n(\vec{r})$. In the LDA, the XC energy of a system depends locally on the electron density. ϵ_{XC}^{LDA} is usually separated into exchange and correlation contributions

$$\epsilon_{XC}^{LDA}(n(\vec{r})) = \epsilon_X^{HEG}(n(\vec{r})) + \epsilon_C^{LDA}(n(\vec{r})). \quad (2.23)$$

There is an exact solution for the exchange energy in the HEG, and it is given by

$$\epsilon_X^{HEG}(n(\vec{r})) = -\frac{3}{4} \left(\frac{3n(\vec{r})}{\pi} \right)^{\frac{1}{3}}. \quad (2.24)$$

However, the correlation energy is not known analytically and needs to be approximated. The accurate calculation of the correlation part is possible

based on Quantum Monte Carlo data by Ceperley and Alder [5]. Several popular approximations for the LDA correlation functional are given in references [6–8]. Although LDA functionals are simple, they work rather well in simulating many bulk and surface systems. For systems which have an electron density far away from the HEG, *i.e.* systems with strongly varying densities, LDA usually does not perform very well. This is the case for molecules and for the interaction of a molecule with a metal surface, for which LDA does not describe barriers to dissociation accurately, so that for various strongly activated H₂-metal surface systems no or only a very small barrier to dissociation is found [9, 10].

A more advanced level of XC functionals is formed by the generalized gradient approximation (GGA) XC functionals [11, 12]. In the GGA, the XC energy not only depends on the electron density, but also on the gradient of electron density $\nabla n(\vec{r})$, *i.e.*:

$$E_{XC}^{GGA}[n(\vec{r})] = \int n(\vec{r}) \epsilon_{XC}^{GGA}(n(\vec{r}), \nabla n(\vec{r})) d\vec{r}. \quad (2.25)$$

Such a functional is often called a semi-local functional, because of the added density gradient dependence. The XC energy E_{XC}^{GGA} is split into an exchange and a correlation contribution, E_X^{GGA} and E_C^{GGA} , respectively, as for the LDA. The exchange part of E_{XC}^{GGA} is always expressed as

$$E_X^{GGA}[n(\vec{r})] = \int n(\vec{r}) \epsilon_X^{HEG}(n(\vec{r})) F_X(s) d\vec{r}, \quad (2.26)$$

where $F_X(s)$ is generally called the exchange enhancement factor, which is commonly written as a function of the reduced density gradient s :

$$s = \frac{|\nabla n(\vec{r})|}{2(3\pi^2)^{\frac{1}{3}} n^{\frac{4}{3}}(\vec{r})}. \quad (2.27)$$

s is dimensionless due to the exponent of the density in the denominator. We note that all traditional GGA functionals exploit an equation like Equation 2.26 to express the exchange part of the XC energy, so that Peverati and Truhlar [13] used this expression to define the GGA. However, Peverati and Truhlar also defined a non-separable gradient approximation (NGA), in which the electron density and its gradient is employed to represent both exchange and correlation in a non-separable term [13, 14]. This new kind of functional approximation includes both exchange and correlation in a

non-separable way by a new functional type that has the form of a non-separable gradient enhancement of HEG exchange; it also includes a more conventional correlation term [13].

Many different GGA functional forms exist. The functional significantly improves over LDA results in many cases, and it is relatively accurate for a large range of systems. The most famous and most used functional in the surface science community is the PBE [15] functional. The exchange enhancement factor for the PBE XC functional is given by:

$$F_X(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa}, \quad (2.28)$$

where κ and μ are derived from physical constants (not semi-empirical parameters). Another functional frequently used for gas-surface systems is RPBE [16], in which the exchange enhancement factor is given by:

$$F_X(s) = 1 + \kappa \cdot (1 - e^{-\mu s^2 / \kappa}). \quad (2.29)$$

Unfortunately, for molecules interacting with metals the GGA is not always very accurate. For instance, for such systems, it is observed that often RPBE yields too high reaction barriers, while the PBE functional is too attractive (yields too low barriers) at the same time, but mixing these two functionals can provide the required accuracy for the system [17]. Implementation and references for a large number of other GGA functionals can be found in Ref. [18]. Construction of new GGA functionals is still an active research field in the surface science community.

The next step upward from the GGA level on "Jacob's ladder" proposed by Perdew and Schmidt [19] is the meta-generalized gradient approximation (meta-GGA), which depends on the kinetic energy density and /or the Laplacian of the density in addition to the gradient of the density. This functional provides the opportunity of a better incorporation of exact quantum mechanical constraints, and in many cases a somewhat higher accuracy can be achieved compared to GGA results. Popular meta-GGA functionals are TPSS [20] and revTPSS [21]. The additional variable in the meta-GGA functional yields an advantage for surface science, by allowing a better distinction between molecules and solids [21].

The next step on the ladder is the "hyper-GGA" level, in which exact Hartree-Fock exchange is added into the GGA functional to improve it. A well-known hybrid functional in the molecular chemistry community is

B3LYP [19, 22, 23] which gives very good descriptions for energetic and structural properties of isolated molecular systems. In spite of the good performance of hybrid functionals in molecular chemistry, they are not so common in solid state physics and surface science, especially for molecule-metal systems. The evaluation of the exact exchange functional for metals in which electrons are de-localized, is computationally very costly and difficult to achieve for molecule-surface interaction where the goal is to obtain a full PES [24–26].

An important limitation of all local or semi-local (*i.e.*, up to meta-GGA level) functionals is that they can not describe long range electronic correlations (which give rise to long range interactions), such as van der Waals (vdW) interaction. Various methods have been proposed to overcome this problem, some more or some less applicable to problems involving metals surfaces. A popular approach is adding a pairwise potential based on C_6 coefficients computed from time-dependent density functional theory (TD-DFT) in the DFT-D3 method by Grimme *et al.* [27]. C_6 coefficients obtained from the mean-field ground state electron density in other methods have been reported by Tkatchenko and Scheffler [28]. Very significant progress was achieved by introducing the non-local correlation density functional vdW-DF, which has been reported by Dion *et al.* [29]. Since then, further refinements of vdW-DF functional provided very satisfying results for many systems [30–32] and other functionals have been reported by improving over the original vdW-DF functional, by either changing the exchange functional, the correlation functional or both. The computational method of Román-Pérez and Soler [33] has allowed the vdW-DF [29] and vdW-DF2 [34] correlation functional to be evaluated efficiently.

Specific reaction parameter density functional

The so-called specific reaction parameter (SRP) approach to DFT is a semi-empirical approach to optimizing the unknown XC functional, which in its original version was developed by Truhlar and co-workers [35] for reactions in the condensed phase. This approach is based on fitting one or a few parameters in the XC functional to a set of experimental data. The functional is optimized for describing a specific reaction, then the fitted functional is tested against at least one other set of experimental data for the same system. Diaz *et al.* [17] applied an implementation of this approach to a gas-surface reaction by fitting a weighted average of two GGA functionals

to one set of experimental data, which is very sensitive to minimum barrier height, for $\text{H}_2 + \text{Cu}(111)$. It has been shown that this new semi-empirical functional is able to reproduce a large range of experimental data for the $\text{H}_2 + \text{Cu}(111)$ [17] system within chemical accuracy, and is transferable to H_2 interacting with another crystal face of the Cu metal, *i.e.*, $\text{Cu}(100)$ [36]. In this thesis, our main focus lies on this method and we apply the SRP methodology to our selected systems. In the next chapters we discuss more about how SRP density functionals are derived and can be transferable from one system to another system.

2.3 Density functional theory for periodic systems

A metal surface is infinite but periodic. When performing calculations on a molecule interacting with a metal surface, it is necessary to take into account the periodicity of the surface to avoid edge effects. DFT is very suitable for representing an infinite surface. For a periodic system, the potential of the system should represent this periodicity. In solid state physics, the Bloch theorem [37] applies to the solution of the Schrödinger equation of an electron in a periodic potential. This theorem says that an eigenfunction for an electron in a periodic potential can be written as a plane wave multiplied with a periodic function with the same periodicity as the potential. Therefore, to build the periodicity into the DFT calculation a periodic basis set can be used. Based on the Bloch theorem the eigen-states, in this case the KS orbitals, can be written as

$$\phi_{i,k}(\vec{r}) = u_k(\vec{r})e^{i\vec{k}\cdot\vec{r}}, \quad (2.30)$$

where $\vec{k}$ is a wave-vector in the first Brillouin zone and $u_{i,k}$ is a function with the same periodicity ($\vec{R}$) as the potential,

$$u_{i,k}(\vec{r}) = u_{i,k}(\vec{r} + \vec{R}). \quad (2.31)$$

By expanding $u_{i,k}$ in the plane wave basis set (Fourier series), the KS orbitals can be written as

$$\phi_{i,k} = N \sum_G c_{i,k}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}}, \quad (2.32)$$

where $\vec{G}$ is a reciprocal lattice vector, $c_{i,k}(G)$ is an expansion coefficient and N is a normalization factor.

When performing the actual calculations, the number of plane waves that represent the wave function can not be infinite. The size of the basis set is specified by the maximum kinetic energy $E_{cut-off}$. In Equation 2.32, the plane wave $e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$ is included in the basis set if:

$$\frac{1}{2}|\vec{k} + \vec{G}|^2 \leq E_{cut-off}. \quad (2.33)$$

To determine a suitable $E_{cut-off}$ one should perform several calculations with increasing $E_{cut-off}$ to ensure that the property of interest (*e.g.*, energy) is converged with respect to $E_{cut-off}$. Also in the calculations, continuous sampling of the first Brillouin zone is computationally problematic and it has to be sampled by a discrete (and finite) number of grid points (the *k*-points). A particularly useful scheme for generation of *k*-points grids that will be used in this thesis, was devised by Monkhorst and Pack [38].

The plane wave basis has some advantages. First, they are orthogonal and easy to use to control the completeness of the basis set. Also, they are independent of the atomic positions so with plane waves, there is no basis set superposition error. Furthermore, a computational advantage arises from the fact that a fast algorithm exist to operate with them and convert the wave function between real space and momentum space (fast Fourier transforms (FFTs)). The use of plane waves as a basis set also has some downsides. To represent core electron orbitals, which are rapidly varying functions due to their localization close to the nucleus, and also valence electron orbitals very close to nuclei, which can assume a highly-oscillating behaviour, a prohibitively large number of plane wave is necessary. However, core electrons described by these wave functions do not participate in the interaction with the other atoms, since the rearrangement of the valence electrons is mainly responsible for bonding. Therefore, it is possible to remove these electrons and replace them by effective potentials named pseudopotentials. The name of pseudopotentials comes from the fact that the strong Coulomb potential of a bare nucleus is replaced with a softer potential of a pseudo-atom. The pseudo-atom includes nuclei, core electrons and interaction among them including relativistic effects.

The pseudopotential can be constructed in such a way that the potential and resulting pseudo-wave functions are as smooth as possible inside the cut-off radius r_c close to the nucleus and that they are almost exactly the

same as the real potential and wave function outside the cut-off radius. In the pseudopotential approach, the pseudo-wave functions are smoother than the corresponding all electron wave functions which oscillate rapidly in the core region, while they reproduce the all electron wave functions beyond a distance from the nucleus r_c . Ultrasoft pseudopotentials were introduced by Vanderbilt (1990) [39]; these allow calculations to be performed with a low cutoff energy. A more general approach is provided by the projector-augmented waves (PAW) method [40, 41], which also allows for calculation of all-electron observables and which is used in the calculations presented in this thesis.

In plane wave DFT, there is periodicity in three dimensions in contrast to the two dimensional periodicity of the surface. To tackle this problem, a supercell approach [42] is used to treat molecule on surface systems, which actually have 2D periodicity. A large vacuum space is introduced along the dimension perpendicular to the surface so that the unit cell is partitioned into regions of solid (slab) and vacuum [43]. The slab [44] is periodic in the directions parallel to the surface and contains enough atomic layers in the direction perpendicular to the surface to converge the molecule-surface interaction energy. To minimize the artificial interaction between periodic images (interaction between the slab and its periodic image) a thick enough vacuum space is needed. In the construction of the supercell all these factors should be taken into account to keep the computational cost (number of atoms) as low as possible, while still obtaining accurate results.

2.4 Construction of potential energy surfaces

In the previous section we described the electronic structure methods that provide the data that one needed to obtain the PES on which the nuclear motion is propagated. A continuous PES is needed to solve the Schrödinger equation for nuclear motion, Equation 2.10. To obtain a continuous PES, the approach is to perform a number of DFT single point calculations for a set of selected configurations of the system and then interpolate them using some sort of fitting scheme. For the PES of a diatomic molecule interacting with a frozen metal surface a rather efficient interpolation method is available, which was proposed by Busnengo *et al.* [45, 46] and is called the corrugation reducing procedure (CRP). The CRP method will be used as an interpolation method through out this thesis and will be described here.

The main problem in the interpolation of the molecule-surface potential near to a surface is that it is highly corrugated, *i.e.*, a large variation in the potential exists when a small change happens in the molecular coordinates. The idea behind the CRP method is to reduce this corrugation to a manageable level. It is known that the interaction of the individual atoms with the surface causes most of the corrugation in the potential. Therefore, the CRP interpolation method, for example for H_2 interacting with a surface, reduces the corrugation near the surface by subtracting the H atom-surface interactions from the total interaction to obtain a smoother function. Then the interpolation is carried out of the smoother function and the H-surface potential is added back to obtain the final full 6D potential. First let us define the coordinate system of a H_2 molecule on a surface. As mentioned in Section 1.2.1, the geometry of the H_2 molecule relative to the surface can be described by the motion of (the center of mass (COM) of) the H_2 molecule in three dimensions ($(X, Y, Z) \equiv R$), and the internal motion of the molecule ($(r, \theta, \phi) \equiv q$), *i.e.*, the interatomic distance r , the angle between the molecular axis and the surface normal θ , and the angle ϕ between the projection of the molecular axis on the surface and the X axis, respectively. In the CRP method, the six-dimensional (6D) PES is written as

$$V^{6D}(\vec{R}, \vec{q}) = I^{6D}(\vec{R}, \vec{q}) + \sum_{i=1}^2 V_i^{3D}(\vec{r}_i), \quad (2.34)$$

in which V^{6D} is the full 6D PES of the H_2 /surface system and I^{6D} is the so-called 6D interpolation function of the H_2 /surface system, which still depends on the center of mass coordinates ($\vec{R}$) with respect to the surface and the internal coordinates of the H_2 molecule ($\vec{q}$). V_i^{3D} is the three-dimensional (3D) PES of the H/surface system, with $\vec{r}_i$ the vector representing the coordinates of the i th H atom with respect to the surface. For the interpolation of the 3D H/surface system PES, the CRP is again applied using

$$V_i^{3D}(\vec{r}_i) = I_i^{3D}(\vec{r}_i) + \sum_j^N V^{1D}(R_{ij}), \quad (2.35)$$

where I_i^{3D} is the 3D interpolation function describing the H/surface system, and N is the number of surface atoms to take into account in the summation. The interaction of a hydrogen atom with a single surface atom is represented by a one-dimensional (1D) function V^{1D} depending on the distance between

the hydrogen atom i and surface atom j (R_{ij}). The V^{1D} function reduces the corrugation of V_i^{3D} .

The first step in this procedure is to calculate the DFT points for a grid of geometries. To reduce the computational cost, it is very useful to include the most symmetric molecular configurations. This is because a periodic lattice is considered and additional symmetry is usually present in the form of mirror planes and rotation axes. Furthermore, in the case of a homonuclear diatomic molecule, or when the molecule is above a high symmetry site of the surface, even more symmetry can be present. Therefore, several symmetric X, Y positions are selected and for each of these positions several orientations (θ, ϕ) are chosen. Finally for each set of (X, Y, θ, ϕ) , a grid of (r, Z) values is chosen. The DFT calculations are performed for each $(X, Y, Z, r, \theta, \phi)$ geometry. Then the CRP approach is applied to these DFT points. The 3D potentials of each atom of the molecule are subtracted from the 6D molecule-surface potential points. The remaining interpolation function I^{6D} is smooth enough to use standard numerical interpolation methods to interpolate it. In this step typically the 6D problem is decoupled into four two-dimensional (2D) interpolation steps [47]. For each calculated (X, Y, θ, ϕ) configuration, 2D cubic splines interpolation method is used to interpolate the calculated (r, Z) grid of energy points. Once the interpolated values of (r, Z) grid points are obtained, the (θ, ϕ) interpolation for each (X, Y) combination is carried out. Usually a Fourier interpolation method is used with basis functions (sines and cosines) incorporating the symmetry of the system. Finally, the interpolation is performed for the remaining (X, Y) coordinates. In this step a symmetry adapted Fourier expansion or 2D periodic cubic splines can be used. After interpolating the interpolation function the 3D potentials are again added to obtain the continuous 6D potential.

In the CRP scheme, the individual 3D atom potentials have to be calculated. They are obtained in a similar way as the 6D PES. First the DFT values are obtained for a grid of positions of the H-atom (X, Y, Z) . The 3D PES is also corrugated and its corrugation is reduced by subtraction of the 1D pair potentials. Then the 3D interpolation function can be interpolated using 3D cubic splines. The interpolation is performed in two steps. First, for each calculated (X, Y) configuration, 1D cubic spline interpolation is performed to interpolate the calculated (Z) grid of energy points. Then a Fourier interpolation is performed in the (X, Y) coordinates, using symmetry adopted sine and cosine functions. For V^{1D} the spline interpolation

of the interaction of the H atom above $X = 0, Y = 0$ is used.

2.5 Molecular dynamics

Once the 6D PES is constructed one can perform the dynamics calculations either classically or quantum mechanically. Computing the dynamical properties gives us the opportunity to understand and compare to the experimental measurements.

2.5.1 Quasi-classical dynamics

The classical trajectory calculations are performed by solving Newton's equations of motion for the 6 molecular DOFs as

$$M_i \frac{d^2 R_i}{dt^2} = -\nabla_i V^{6D}(R_i, R_j), \quad i \neq j \quad (2.36)$$

where i, j are the indexes of the atoms in the diatomic molecule. To integrate the equations of motion, different propagators exist and can be used, such as the (velocity) Verlet propagator [48], the Beeman propagator [49], etc.

The Quasi-classical trajectory (QCT) method usually gives more accurate results for H_2 -surface reactions than the purely classical method because in a QCT calculation the initial vibrational zero point energy (ZPE) is modelled using an ensemble of initial conditions for the internal motion of the molecule that forms a classical microcanonical distribution [50]. The vibrational states of the molecule are calculated using the Fourier grid Hamiltonian (FGH) method [51]. In the QCT calculations based on the CRP interpolated PES, Hamilton's equations of motion are integrated with the predictor-corrector method of Bulirsch and Stoer [52].

At the beginning of each trajectory calculation the initial conditions have to be set, *i.e.*, the initial positions, and velocities of the particles. In modeling H_2 dissociation on a surface, the molecule is initially positioned far away from the surface, where the potential does not yet depend on Z . The molecule with a particular velocity towards the surface corresponds to the perpendicular incidence energy $E_{\perp}$. The impact site on the surface is chosen randomly and, if off-normal incidence is considered, a velocity vector is set up according to the parallel incidence energy $E_{\parallel}$, the polar incidence angle θ_i , and the azimuthal incidence angle ϕ_i .

Reaction or scattering probabilities, for each initial incidence energy and initial rovibrational state (E_i , ν_i and j_i) are calculated as an average over molecular initial conditions (position of the molecular center of mass over the surface unit cell, molecular orientations and orientation of the initial angular momentum vector) where these initial conditions of the H_2 molecule are selected using a standard Monte Carlo method. To obtain m_j resolved reaction probabilities, the initial angular momentum L of the H_2 molecule is fixed by $L = \sqrt{j(j+1)}\hbar$ and its orientation is chosen randomly with the constraint $\cos(\theta_L) = m_j/\sqrt{j(j+1)}$, where θ_L is the angle between the angular momentum vector and the surface normal.

After the propagation over a certain number of time steps, the trajectories are analyzed to determine whether a specific outcome has been reached. When the interatomic distance of the molecule reaches a particular value, the molecule is considered to have reacted. When the distance between the molecule and the surface becomes larger than a certain value where no interaction is present, the molecule is considered to have scattered. The molecule is considered to be trapped if neither outcome has occurred.

The reaction probability P_r can be obtained from

$$P_r = \frac{N_r}{N_{total}}, \quad (2.37)$$

where N_r is the number of reacted trajectories and N_{total} is the total number of trajectories. Certain observables such as molecular beam sticking probabilities or degeneracy averaged reaction probabilities can be computed using the QCT method.

2.5.2 Quantum dynamics

For the quantum dynamics (QD) calculations, a time-dependent wave packet (TDWP) method [53] was used, where the time dependent Schrödinger equation is solved to generate scattering and reaction probabilities. The wave packet is represented in a discrete variable representation (DVR) [54] for Z, r, X, Y and a finite basis representation (FBR) [55, 56] has been used to describe the angular DOFs. Fast Fourier transforms [57] and discrete associated Gauss-Legendre transforms [55, 56] were used to transform the wave function from FBR space to DVR space, and *vice versa*. The wave packet is propagated in time using the Split Operator method [58]. The

initial wave packet, which is placed far away from the surface on a specular grid (sp), where the interaction with the surface is negligibly small, is written as a product of a Gaussian wave packet to describe motion perpendicular to the surface, plane waves to describe motion parallel to the surface, and a rovibrational wave function describing the initial state of the molecule according to

$$\psi_0(X, Y, Z, r, \theta, \phi) = \phi_{\nu,j}(r) Y_{jm_j}(\theta, \phi) \frac{1}{\sqrt{A}} e^{ik_0^{X,Y} \cdot \mathcal{R}} \int dk^Z \beta(k_0^Z) \frac{1}{2\pi} e^{ik_0^Z Z}. \quad (2.38)$$

Here $\phi_{\nu,j}(r)$ and $Y_{jm_j}(\theta, \phi)$ are, respectively, the vibrational and rotational eigenfunction of the H_2 molecule in the gas phase with vibrational, rotational and magnetic rotational quantum number ν , j and m_j . The initial parallel motion of the wave packet along X and Y is described by $\frac{1}{\sqrt{A}} e^{ik_0^{X,Y} \cdot \mathcal{R}}$, in which A is a normalization factor (the surface area of the unit cell), $k_0^{X,Y}$ is the initial parallel momentum and $\mathcal{R}$ is the position vector (X, Y) . The wave packet describing motion in the Z direction is a function of the initial momentum k_0^Z and is Gaussian shaped and centered on Z_0 :

$$\beta(k_0^Z) = \left(\frac{2\sigma^2}{\pi} \right)^{1/4} e^{-\sigma^2(\bar{k}-k_0^Z)^2} e^{i(\bar{k}-k_0^Z)Z_0}. \quad (2.39)$$

Here $\bar{k}$ is the average momentum in Z and σ is a half width parameter. To ensure that the wave packet moves towards the surface with a range of translational energies, $\bar{k}$ is chosen to be negative. When the wave packet enters the region where it interacts with the surface, it is transferred from the specular grid to the regular grid using a projection operator formalism [59, 60]. The part of the wave packet which returns from the surface, is analyzed using the scattering amplitude formalism [61–63] at Z_∞ where the molecule and surface (in principle) no longer interact and is integrated over time to obtain the state-to-state scattering S-matrix elements for all open vibration, rotation and diffraction channels. Beyond Z_∞ or large r , optical potentials [64] are used to adsorb the reacted part of the wave packet and the reflected part of the wave packet.

Scattering probabilities as a function of energy were obtained from S-matrix elements over the entire range of energies present in the wave packet. The fully initial state resolved reaction probability is defined as 1 minus the

sum of the scattering probabilities:

$$P_r(\nu, j, m_j) = 1 - \sum_{\nu', j', m'_j, n, m} P_{scat}(\nu, j, m_j \longrightarrow \nu', j', m'_j, n, m), \quad (2.40)$$

where $P_{scat}(\nu, j, m_j \longrightarrow \nu', j', m'_j, n, m)$ are the state to state scattering probabilities. $\nu(\nu')$, $j(j')$, $m_j(m'_j)$ ss are the initial(final) vibrational, rotational and magnetic rotational quantum number, respectively, and n and m are the quantum numbers for diffraction. For more details about this method see Ref. [65].

2.5.3 Computation of observables

Initial state resolved reaction probabilities

Initial state resolved reaction probabilities $P_{deg}(E; v, j)$ are obtained by degeneracy averaging the fully initial state resolved reaction probabilities $P_r(E; v, j, m_j)$ according to

$$P_{deg}(E; v, j) = \frac{\sum_{m_j=0}^{m_j=j} (2 - \delta_{m_j,0}) \cdot P_r(E; v, j, m_j)}{2j + 1}, \quad (2.41)$$

where P_r is the fully initial state-resolved reaction probability, δ is the Kronecker delta, and ν , j and m_j are the initial vibrational, rotational and magnetic rotational quantum number of the H_2 molecule, respectively.

Molecular beam sticking probabilities

In order to make a meaningful comparison of computed reaction probabilities with measured sticking probability results, we have performed simulations of the molecular beam conditions, used in the experiments. For this one has to take into account two things. First, the initial state resolved reaction probabilities should be averaged over all rovibrational states which have a significant population in the molecular beam. Second, it is necessary to consider the spread of incidence energies present in the molecular beam. Therefore we need to compute the molecule's monoenergetic reaction probabilities $P_{mono}(E_i, T_n)$, which depend on the collision energy E_i and on the

nozzle temperature T_n , and thus, on the rovibrational state populations. The monoenergetic reaction probability can be written as :

$$P_{mono}(E_i, T_n) = \sum_{\nu, j} F_B(\nu, j; T_n) P_{deg}(E_i; \nu, j), \quad (2.42)$$

where $P_{deg}(E_i; \nu, j)$ is the monoenergetic initial state-resolved reaction probability and $F_B(\nu, j; T_n)$ is the Boltzmann weight of the (ν, j) state. The factor $F_B(\nu, j; T_n)$ is given by:

$$F_B(\nu, j; T_n) = (2j+1)e^{[-E_{vib}(\nu, j)/k_B T_n]} \times e^{[-E_{rot}(\nu, j)/0.8k_B T_n]} \times N(j), \quad (2.43)$$

where $N(j)$ is the normalization factor which takes into account the correct nuclear spin statistics for hydrogen and is given by :

$$N(j) = \frac{w(j)}{\sum_{\nu', j' \equiv j \pmod{2}} (2j' + 1) e^{[-E_{vib}(\nu', j')/k_B T_n]} \times e^{[-E_{rot}(\nu', j')/0.8k_B T_n]}}. \quad (2.44)$$

In Equation 2.44, the summation runs only over the values of j' which have the same parity as j . Furthermore, E_{vib} and E_{rot} are the vibrational and rotational energy of the rovibrational state, respectively, and k_B is the Boltzmann constant. Because there are three parallel nuclear spin states and only one anti-parallel spin state for H_2 , for the molecular beam at thermal equilibrium at high temperature (room temperature or higher), which is the usual case in the experiments, a ratio between ortho (odd j)- and para-hydrogen of 3:1 is expected. At very low temperature, it is expected that only the $\nu = 0$ and $j = 0$ rovibrational state is occupied. Therefore, the molecular beam in the thermal equilibrium should consist of pure para-hydrogen at very low temperature. However, the conversion of ortho- to para-hydrogen is very slow and does not happen on the time scale of the experiment. The H_2 is then either (vibrationally or rotationally) cooled or heated by the nozzle, but without the possibility of a nuclear spin flip. Therefore, the 3:1 ortho-para ratio in the $N(j)$ factor ($w(j)$) is, for practical purposes, independent of the nozzle temperature. For $H_2(D_2)$, $w(j)$ is equal to $1/4(2/3)$ for even j values, and $3/4(1/3)$ for odd j values.

In the Equations 2.43 and 2.44, the experimental rotational distributions can be described by a rotational temperature T_{rot} , which is assumed to be lower than the nozzle temperature ($T_{rot} = 0.8T_n$) [66, 67]. Once the

monoenergetic reaction probabilities have been computed, one can compute reaction probabilities convoluted over the incidence energy or velocity distribution of the experimental molecular beam, according to the expression [68] :

$$P_{beam}(T_n) = \frac{\int_{\nu_i=0}^{\nu_i=\infty} f(\nu_i; T_n) P_{mono}(E_i; T_n) d\nu_i}{\int_{\nu_i=0}^{\nu_i=\infty} f(\nu_i; T_n) d\nu_i}, \quad (2.45)$$

where $E_i = 1/2Mv_i^2$, v_i being the velocity of the molecule, and $f(\nu_i; T_n)$ the flux weighted velocity distribution for a nozzle temperature T_n given by:

$$f(\nu_i; T_n) d\nu_i = C v_i^3 \exp[-(v_i - v_s)^2 / \alpha^2] d\nu_i. \quad (2.46)$$

In this equation, C is a constant and T_n is the nozzle temperature used in the corresponding molecular beam experiment. Furthermore, the parameter v_s is the stream velocity and α is the parameter that characterizes the width of the velocity distribution. Note that the parameters C , v_s and α again parametrically depend on the nozzle temperature. The parameters can be obtained by fitting the experimental time-of-flight (TOF) spectra, using the Levenberg-Marquardt algorithm [69], to

$$G(t; T_n) = c_1 + c_2 v^4 \exp[-(v - v_s/\alpha)^2], \quad (2.47)$$

where c_1 and c_2 are constants. In Equation 2.47, v is taken as L/t where L is the length of the flight path.

Vibrational efficacy

The vibrational efficacy is used to investigate how efficiently vibrational energy can be used to promote reaction relative to translational energy. It can be computed by

$$\eta_\nu(P) = \frac{E_i^{\nu=0,j}(P) - E_i^{\nu=1,j}(P)}{E_{vib}(\nu=1, j) - E_{vib}(\nu=0, j)}, \quad (2.48)$$

where $E_{vib}(\nu, j)$ is the vibrational energy corresponding to a particular state of the gas-phase molecule and $E_i^{\nu,j}(P)$ is the incidence energy at which the the initial state-resolved reaction probability becomes equal to P for H_2 (D_2) initially in its (ν, j) state. In evaluating Equation 2.48 j is typically taken as 0.

Diffraction probabilities

To study diffraction, a quantum phenomenon, quantum dynamics calculations should be performed. In the diffractive scattering process, the molecule's translational momentum parallel to the surface can only change by discrete amounts. In order to compare with the experimental diffraction probabilities [70], as we will see in Chapter 6, the rovibrationally elastic diffraction probabilities are computed by

$$P_{nm}(\nu, j, m_j) = \sum_{m_j''=-j}^j P_{scat}(\nu, j, m_j \rightarrow \nu' = \nu, j' = j, m_j'' = m_j, n, m), \quad (2.49)$$

where P_{nm} is the rovibrationally elastic probability for scattering into diffraction state denoted by the n and m quantum numbers. These probabilities are degeneracy averaged by

$$P_{nm}(\nu, j) = \sum_{m_j=0}^j (2 - \delta_{m_j 0}) P_{nm}(\nu, j, m_j) / (2j + 1). \quad (2.50)$$

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