

Chapter 1

Introduction

Physical processes and chemical reactions on surfaces are of fundamental interest both theoretically and for practical applications. Many scientific and technological fields are related to surfaces - *e.g.*, heterogeneous catalysis [1] and nanotechnology [2]. Therefore much scientific effort has been and is devoted to the understanding of these processes, both experimentally and theoretically.

In recent decades various theoretical methods for molecular wave packet dynamics of chemical reactions have been developed (see for example [3]), especially after the famous experiments of Zewail *et al.* [4, 5], in which the first real-time observations of chemical reactions on a fs time scale were achieved. Nevertheless, dynamics at solid surfaces are still a real challenge from a theoretical point of view. Although it is nowadays possible to perform highly accurate first principle electronic structure calculations for clean and adsorbate covered surfaces, the high dimensional many body interaction potentials which would be needed for *ab initio* surface dynamics are far beyond the limits set by the speed of modern computers. An often used strategy to circumvent this problem is therefore to freeze all internal degrees of freedom for the surface and to describe only the degrees of freedom belonging to the particle interacting with the surface, *e.g.* an adsorbate, in a first principles fashion. In this way quantum simulations of the dissociative adsorption of

H₂ on Pd [6] or Cu [7, 8] were performed in which all six degrees of freedom of a diatomic molecule relative to a non moving surface were accounted for. Besides substrate motion, also possible electronic excitations in the (metal) surface were neglected in these works (adiabatic approximation). This idealization which neglects the possibility to excite internal degrees of freedom of the substrate, will be called the “rigid” surface approach in this thesis. Similarly the term “non rigid” will be used for models for which in some way the internal degrees of freedom of a surface are included, irrespective of the level of sophistication. These degrees of freedom can be classified into two major parts: (i) the motion of the surface or bulk atoms [*i.e.*, the phonons] and (ii) the electronic degrees of freedom [*i.e.*, the possibility of electron-hole pair creation].

Although the “rigid” surface models are often very successful there are many effects related to the real “non rigid” nature of surfaces. For example the possibility of charge, phase and energy transfer between an adsorbate and the solid surface opens up dissipative channels which account for many different processes, some listed below, which can not be explained by a rigid surface model.

- (i) The thermal desorption of adsorbates: In the widely used experimental technique of thermal desorption spectroscopy (TDS [9]) the surface is progressively heated to higher and higher temperatures. The excited substrate phonons then couple to the adsorbate surface bond and thermal desorption of adsorbates occurs which is monitored.
- (ii) Vibrational relaxation of adsorbates: The lifetimes of vibrational excitations in adsorbed molecules are often by several orders of magnitude shorter than the lifetimes measured in the gas phase. This is a consequence of the sometimes very rapid energy transfer between an adsorbate and the surface [10]. For example, when a vibrationally excited adsorbate couples to the phonons of an insulator or semiconductor surface the vibrational relaxation time reduces from typically μs to ns. If the vibration couples to the electrons of a metal the lifetime becomes as

short as ps [10]. Even shorter lifetimes (fs) can result for electronically excited adsorbates.

- (iii) Sticking of gas phase atoms: It is a well known experimental fact that, depending on the temperature, gas phase atoms are sticking on surfaces. Since atoms have no energetically accessible internal degrees of freedom to redistribute the kinetic energy gained while approaching the surface, this can only be explained by an energy transfer to the surface.
- (iv) Temperature effects on dissociation and reaction of molecules: The dissociative adsorption of molecules is often the bottleneck of catalytic reactions on surfaces. Here a pronounced effect of the surface temperature on the dissociation rate can be found [11].
- (v) Reactions triggered by hot (surface) electrons: Many photoinduced surface reaction [12] or desorption processes [13] are initiated not by a direct coupling between the laser field and an adsorbate but by an indirect substrate mediated process in which initially surface electrons are excited by the laser.

This list could be continued. But after a vivid demonstration of the need for theoretical models which account for surface non rigidity, the question arises of how such models can be constructed.

A first step is often to introduce a reduced-dimensionality model by just freezing all neglected degrees of freedom and only leaving the important ones. Alternatively, one may resort to so-called system bath models. In the system bath models a few important degrees of freedom define the “system”, which is treated with rather high level of sophistication, while some or all other degrees of freedom are treated as a (heat) “bath” coupled to the system. There are many different types of these system bath models (for example a quantum mechanical system coupled to a classical bath) - some examples will be given in section 2.1.

The main subject of this thesis is to test several of these approximate methods to explore on the one hand their numerical feasibility and on the

other hand, if possible, their accuracy when compared with “exact” methods or with experimental results. Following the categorization of the dissipative channels on surfaces into two main groups, namely the excitation of phonons and the generation of electron-hole pairs, this thesis is also organized in two major sections.

In the first part (chapter 2) the influence of substrate vibrations on the sticking of gas phase atoms is examined for the H/Cu(100) system. In this chapter three different time-dependent wave packet methods, namely, reduced-dimensionality but “exact” wave packet propagation, the Time-Dependent-Self-Consistent Field (TDSCF) method, and the “mean-field” (Ehrenfest) mixed Quantum-Classical-Molecular-Dynamics (QCMD) scheme, are tested against each other and compared with classical trajectory results and with rigid surface calculations. Here the focus is solely on the surface vibrations although there are some indications that electron-hole pair creation might also contribute to the energy transfer for a hydrogen atom at a metal surface [14].

In the second part (chapter 3) the dissipative dynamics of an electron trapped inside an image potential in front of a Cu(100) will be simulated by means of the open quantum system Liouville-von Neumann equation (see for example [15]) and compared with rigid surface calculations and recent 2-Photon-Photoemission-Spectroscopy (2PPE) experiments [16, 17, 18]. In this case the transfer of phase and energy from the electron to the surface is mainly due to the creation of electron-hole pairs in the metal, or, more generally, due to the inelastic and elastic scattering of the image electron with the substrate electrons.

The physical systems will be explained in detail in the corresponding chapters. Here some general considerations are given in the following. In the system bath view for both cases the system is chosen to be a rather simple one, *i.e.*, a hydrogen atom and a single electron, respectively. Due to their light masses a quantum mechanically treatment of the H atom or the image charge electron is mandatory. In both cases the main physical effect, *i.e.*, the

sticking of the hydrogen atom or the relaxation of the electron back into the surface, can only be modeled in a non rigid surface approach. Although the system parts are rather simple, a simulation of the bath, the Cu(100) surface, in a first principle fashion is beyond reach for even the fastest modern computers. Therefore the focus of this thesis is on the strength and limitations of the different approximate methods used, and what can be learned from that about the underlying dynamics and for further improvements of these methods. An important goal of theory is also to achieve agreement with experimental data and thus contribute to a higher level of “understanding”. In the present thesis, very good agreement between theory and experiment has been achieved for the image potential state electron dynamics (see section 3.4). In the greater framework of the theory of non rigid surface dynamics the ultimate goal is to develop accurate methods appropriate for different systems, in which the energetics and (quantum) dynamics is treated entirely on an *ab initio* fashion, in analogy to the first principles rigid surface dynamics alluded to above [6, 7].

