

# Chapter 6

## Conclusions and outlook

This thesis is focused on the modeling of the dynamics and quantum statistical thermodynamics of reactions in condensed phases. In particular the main topic is surface catalysis and photochemistry. Presently, this field of theoretical chemistry is at its very beginning, and consequently both numerical methods and physical models are to be developed. Efficient numerical methods are essential to drive the applications, for example because of the heavy scaling of density matrix calculations. For this reason, the third chapter of this thesis is almost exclusively on numerical methods. First, we studied the so called direct methods (see chapter 3), and combining the approaches of Refs.[81, 115] and Refs.[111, 107], we derived an efficient and stable integration scheme – the Faber polynomial method for density matrices. We compared this with other methods presently used, and found that it is very promising, especially for the computation of cw-spectra, for which we derived a special, numerically very robust series.

We applied the direct methods to the problem of surface scattering. Here, we have introduced the coupled channel density matrix (CCDM) method, which allowed us to introduce a two dimensional model for open system surface scattering. Consequently, we were able to make an interesting study of the possible scenarios that can appear in low energy scattering of vibrationally excited molecules impinging onto a metallic surface. We found that the experimentally observed strong vibrational

relaxation of H<sub>2</sub> ( $m = 1$ ) scattering from Cu(110) [39] is probably not only due to an electron hole mechanism, as suggested in [39], but must also have other sources. One possibility is the coupling of the H<sub>2</sub> vibrational coordinate to the coordinates neglected in our model (rotations, frustrated translations, surface phonons). Considering that the surface degrees of freedom cannot simply be discarded as indicates the quantitative disagreement of the experimental results with the full dimensional calculations done with the rigid surface model [142], the complete full dimensional modeling of the system or, alternatively the identification of the degrees of freedom which are essential to describe properly the dynamics is a really interesting challenge. Nevertheless, it is numerically extremely demanding. To make quantitative predictions for molecules scattering from metal surfaces, also proper *ab initio* potential energy surfaces should be used.

Nevertheless, this model study gives already basic reliable trends, and the methodology adopted should also be useful for other systems of interest in current theoretical surface science, ranging from surface catalysis to oxidization of metal surfaces. For example, the model introduced can be almost directly applied to the study of the vibrational excitation of NO scattering at Ag, where interesting experimental results are available [176, 177].

Straightforward extensions should allow the study of Rotationally Mediated Selective Adsorption (RMSA), and generally the coupling of molecular rotations to the surface degrees of freedom [178], or the molecular sticking in the physisorption well at very low temperatures [179]. As mentioned above a “final”, presently impossible goal is the dissociative dynamics of hydrogen with surface degrees of freedom taken into account. Another important step towards a quantitative description of the system is to replace the semiphenomenological relaxation rates by “*ab initio*” ones. Microscopic models accounting, *e.g.*, for the coupling between molecular vibrations and electron hole pairs in a substrate [163, 164, 165, 168] have been worked out, even if their inclusion in a large density matrix calculation of a scattering event is far from simple. Because of the numerical scaling problem, the direct methods will have to be replaced in favor of indirect propagation schemes to treat large realistic systems.

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Among these last methods, we have been working with the VWP method [95]. We have shown that this method is an adequate, general tool to deal with dissociative, dissipative problems, even when small probabilities are of interest, as shown in chapters 3 and 4. The two dimensional example given shows that the VWP scheme combines the advantages of the direct density matrix approaches (generality, accuracy) with those of the indirect wave packet methods (moderate memory requirements, potentially fast). For relatively probable events (in the order of a few percent) the method shows excellent numerical performance, thus suggesting to be useful also for surface scattering problems. Another challenge for the VWP method is to apply it to more complicated desorption processes, such as the so called DIMET, Desorption Induced by Multiple Electronic Transitions within a two mode model. In this case reexcitations are possible, and the same time the multi dimensionality requires the use of large grids. The latter fact rules out presently the use of a direct density matrix propagation, and the former challenges the VWP method because many coupled wave functions are required. Moreover, the coupling of the desorption coordinate with the surface modes was neglected so far, under the reasonable assumption of its weakness compared to the electronic dynamics. However, for complete quantitative predictions, it should be included in the model, complicating additionally the computational task. This could allow to have a more complete comparison with the experimental works done, for instance for NO/Pt [42, 130, 131, 41].

These applications require an improved integration scheme for the VWP equations of motion, and two directions of improvement are evident. First, considering that the general purpose integrator used is inefficient compared to schemes specifically designed for wave function or density matrix propagation, the use of more efficient integration schemes for the VWP equations of motion might enhance the CPU-time efficiency of the VWP approach. For example, propagators more suited to a MCTDH approach like [180], or generally more efficient ones [181] may be useful. Second, the equations of motion can be recast to a different form in order to reduce the problem of the “avoided crossings”.

Our goal is to make realistic modeling of reactions in condensed phases. We think that we have found some interesting methods to deal with large scale problems, our

calculations being the largest done up to now in the field of surface dynamics with environmental degrees of freedom taken into account. The presently exciting aspect of the work, as we tried to stress, is that it has opened an outlook over other applications and towards possible improvements in the direction of more complete and even larger systems simulations, hopefully aiming at a quantitative comparison with experimental results, that is presently missing for this kind of problems.