Chapter 4

Summary and conclusions

Several non rigid surface models were employed for two different simple test systems, namely the scattering of atomic hydrogen on Cu(100) and dynamics of electrons in image potential states on Cu(100). The first system/problem being a case study for the effect of substrate vibrations, the second for the influence of electron-hole pair creation. From the results, conclusions concerning the physical processes and the methodological aspects of non rigid surface dynamics can be drawn.

For the scattering of atomic hydrogen on Cu(100) the following can be said. In terms of "physics" one can conclude that for systems like gas phase hydrogen atoms approaching a Cu(100) surface, lattice phonons do matter despite of a large mass mismatch between the scatterers. Due to the lattice vibrations the hydrogen atom can actually stick in subsurface and adsorption sites. Nevertheless in the calculations presented here bulk absorption and reflection dominate for this system. A non-negligible amount of energy is released when the atom approaches the surface and the accelerated atom crashes into the substrate. Thereby a considerable amount of excitation of the surface oscillator(s) occurs, which influences the absorption and sticking dynamics. Since the energy transfer between hydrogen and copper is slow the H atom can travel as a "hot" atom for several ps and over long distances on the substrate before it finally absorbs or sticks. However, a full quantitative description of these processes needs probably the inclusion of electronic

friction which was neglected here.

In terms of methodological aspects the biggest surprise is how bad the mean-field approaches perform for quantitative predictions, while classical mechanics performs rather well. In the calculations presented here the QCMD and TDSCF methods get the effects of the substrate vibrations only qualitatively right, and can only account for overall trends. But there will be situations where the adsorbate behaves more quantum mechanically (*i.e.*, for less energetic projectiles and/or when tunneling becomes important) and where even only approximate quantum methods are to be preferred over classical ones.

For the image potential states dynamics on Cu(100) a surprisingly accurate simulation of energy and time resolved femtosecond two-photon-photoemission experiments was performed by means of the open quantum system Liouville-von Neumann equation. It could be demonstrated that a "non rigid" surface model is indispensable for such calculations. Considering the fact that this agreement could be reached within a rather simple one electron picture by using a carefully constructed model potential, one can hope to model even more complicated systems like surface reactions triggered by hot electrons or quenching processes due to creation of electron-hole pairs in a similar fashion. In this approach the (active) electron(s) and the nuclei would be treated on the same footing. This is different from the more traditional approach [12] where nuclear wave packets move on electronically adiabatic surfaces, with non adiabatic transitions induced between them by a laser field or the environment. Also, possible implications of the electron dynamics considered here, for quantum transport through nanostructures *e.g.* in molecular electronics, are quite obvious.

Concluding one can say that two examples for the importance of non rigid surface models for the simulation of dynamical processes at surfaces were given in this thesis. The future goal for theoreticians in this field should be in my view, to improve the methods available today further and thereby to built a toolkit consisting of different approaches for different physical systems,

which some day could lead to reliable predictive power usable for technical applications. These methods would then not only be useful for surface dynamics but also for more general situations of the "system plus bath" type such as chemistry in solution and solids, and biomolecules.