Chapter 2

Dynamics simulation of many-body systems

This chapter will give an overview of 'state of the art' to describe polyatomic systems as accurate as possible. Since fully quantum descriptions of systems including more than four atoms are not possible for the time being [21], some approximations have to be applied for the investigation of many-body systems. A detailed description of all the possible methods would go beyond of the scope of this work, so only short résumés are given to describe the advantages and disadvantages of each method. While in this work classical dynamics simulations were performed, and their advantages and disadvantages will become clear in chapter 7.7, the *ansatz* will already be constructed to include more accurate methods.

2.1 Classical Molecular Dynamics

In classical molecular dynamics simulations, the classical Newton equations of motion are integrated numerically for the atoms included in the system. This results in *trajectories*, which describe the path of the objects through space, thus the nuclei are evolving corresponding to classical mechanics. As a first order approximation, classical MD allows to predict the dynamics of large many-body systems, since the computational effort only scales polynomial (see section 5.1), compared to exponential scaling for exact quantum solutions. MD simulations were used to investigate for example activated rate processes with limitation to slow molecular

evolution or for calculating the energy flow between solute and solvent [24]. There are different limitation for classical MD. Obviously no quantum effects are included like zero-point motion, tunneling, quantization or decoherence. These effects may play an important role, for example for investigations including light atoms like hydrogen or simulations at low temperatures. In addition to these drawbacks arising from the classical mechanical treatment of the atoms, there will be further limitations by the second concept the method is based on, the Born-Oppenheimer- or adiabatic approximation. It is assumed that the electrons adjust to the motion of the nuclei instantaneously, while the nuclei evolve on an adiabatic potential energy surface, which can be calculated 'on the fly', at each time step. Now processes, which include transitions between the states or potential energy surfaces of the systems, can not be described correctly by classical MD. Examples for such processes, in which the Born-Oppenheimer-approximation breaks down, are electron transfer reactions, energetic collisions, predissociation or to some extent nonradiative relaxation in large molecules or condensed media, as long as nonadiabatic transitions have to be included.

Classical MD simulations were performed on systems like $H+Cl(Ar)_n$ by Schmidt and Gerber [38] including Monte Carlo methods, the sputtering from solid argon including energy dispersion in the solid [44].

2.2 Quantum-classical Dynamics

One possibility to overcome the limitations of pure classical dynamics is to treat only few important degrees of freedom (DOF) of the system quantum mechanically and most of them classically as 'bath' modes. This ansatz includes a certain separability of the quantum and classical parts[21]. Additionally, the classical and quantum motions have to be self-consistent: the motions of the nuclei may induce electronic (quantum) transitions, followed by a change in the potential energy or the forces acting on the classical particles. Different approaches are used to describe the dynamics of the system accurately, including non-adiabatic transitions, for example the Ehrenfest (mean-field) approach, surface hopping or the classical separable potential method.

2.2.1 Mean-field approach

The classical limit of the time-dependent self-consistent field method TDSCF is called Ehrenfest or mean-field approach. Here the total wave function is separated to a part belonging to the fast (quantum) particles and a slow (classical) particle wave function. The motion of the particles will interact by their average fields, so the fast particles will move in the mean field of the slow particles and vice versa. For example, the classical motion will be described including the forces of each (weighted) potential energy surface and including forces due to the transitions between adiabatic states via non-adiabatic coupling.

This method will be appropriate for systems including only small coupling between the different DOF, while stronger coupling will lead to decoherence and thus the mean-field approach is not valid anymore. In addition, if the classical motion can take place on two sufficiently different potential energy surfaces, which would lead to a divergence of the trajectories, the average potential will not be appropriate to describe the situation. Multiconfigurational and Configuration Interaction TDSCF will overcome some of these disadvantages by a different way of factorizing the wavefunction, but since this method is not applied here the interested reader should refer to [24, 25, 21] and references cited within.

2.2.2 Classical separable potential method

The principal idea behind the classical separable potential method CSP is to obtain the potentials by classical trajectories and then perform a quantum simulation with TDSCF wave functions. Thus, the separation of the wavefunction into a classical and quantum part is avoided and the effort of solving the multidimensional differential equations is reduced.

A scheme of CSP simulations is given in [21] by Jungwirth and Gerber: First the initial conditions of the classical trajectories are determined by mapping the initial wave function on the classical coordinates and momenta, using the Wigner distribution. Classical trajectory propagation follows and the CSP potentials are evaluated for each mode, by this replacing the multidimensional integrals of the TDSCF method with a summation over weighted trajectories, thus reducing the computational effort. Finally quantum propagations of the modes are performed to describe the dynamics of the system.

One problem lies in the not strictly conversation of energy, which can be overcome by using a configuration interaction extension to this method CI-CSP. Now interactions between the modes will be included. CI coefficients are allowed to evolve in time and the most important of these terms are determined by classical trajectory simulations, using the fact that modes, which are strongly correlated will show this behaviour both in classical and quantum mechanics. The CSP method is applicable to weak quantum systems, and the method was used to describe systems like HCl in Ar clusters [31] or the quantum dynamics of iodine in rare gas clusters [32].

2.3 Surface hopping

In systems with several converging potential energy surfaces, non-adiabatic coupling may play an important role in the course of the dynamics. The surface hopping method invented by Tully in 1971 [26, 27] can be used to implement the non-adiabatic transitions in the dynamic simulations of a system. The basic concept can be described as follows: classical trajectories are simulated, usually on an adiabatic state. In regions with two or more potential energy surfaces converging, the probability of 'hops' from one surface to another is calculated, by this introducing non-adiabatic transitions. After the 'hopping event', either the trajectory on the 'new' state is traced or a set of new trajectories, following the now occupied different adiabatic surfaces, weighted with a factor complementary to the hopping probability.

This method will be explained more detailed, because most of the informations necessary to implement this method can be derived from the simulations already performed in this work.

The method is not restricted to an adiabatic basis or to a special propagation method. For example Gersonde and Gabriel combined a 'classical path' method with nonadiabatic transitions described by surface hopping [29]. As an example the method used by Gerber et al is taken. A set of different systems was simulated successfully, like HCl, F_2 or Cl in rare gas matrices. The nuclei are propagated classically. The potential surfaces of the system are calculated 'on the fly', meaning that the system Hamiltonian is diagonalized at each time step, corresponding to a particular configuration of the nuclei, generating the adiabatic potential surfaces $W_i(\mathbf{R})$ and the corresponding adiabatic electronic states $\phi_i(\mathbf{r}, \mathbf{R})$. Since the trajectories $\mathbf{R}(t)$ are functions of time we can replace the dependence of \mathbf{R} by a dependence of time. The electronic wave function of the system can be expanded in this adiabatic basis:

$$\Psi(\mathbf{r},t) = \sum_{j} c_j(t)\phi_j(\mathbf{r},t)$$
(2.1)

and propagated according to the Schrödinger equation.

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = H_{el}(\mathbf{r}, \mathbf{R}) \Psi(\mathbf{r}, t)$$
(2.2)

The coefficients can be derived, using the equation of Tully:

$$i\hbar\dot{c}_k(t) = c_k(t)W_k(\mathbf{R}) - i\hbar\sum_j c_j(t)\dot{\mathbf{R}}(t)\mathbf{d}_{jk}(\mathbf{R})$$
(2.3)

The nonadiabatic couplings $\mathbf{d}_{jk}(\mathbf{R})$ are defined as

$$\mathbf{d}_{jk}(\mathbf{R}) = \int \phi_i(\mathbf{r}, \mathbf{R}) \nabla_R \phi_j(\mathbf{r}, \mathbf{R}) \, d\mathbf{r}$$
(2.4)

By integration of equation 2.3, the populations of each state $|c_i(t)|^2$ can be determined.One possibility to decide if a 'hop' is occurring is to compare $|c_i(t)|^2$ with a random number $0 < \lambda < 1$. To conserve the energy after a hopping event, the momenta of the nuclei have to be adjusted. Another problem lies in the treatment of the phase, see equation 2.4, which is not determined after the switch from one potential energy surface to another. Coker et al leave the phase fixed [73], Gerber and Krylov developed a method including a 'gauge' constraint, to keep the geometrical phase of the wave function fixed [48]. While the applicability of the surface hopping algorithm has been shown for different systems [75, 26, 48, 45]. A good review is given by Kuntz [30].

Summarizing, different methods of describing the dynamics of many-body systems are available. Quantum-classically simulations will treat the nuclei classically, and different methods can be used to implement quantum effects like nonadiabatic transitions, which plays an essential role in the course of the solid state dynamics.