# Chapter 1

# Introduction

## 1.1 Motivation

Hydrogen bonds are of fundamental interest in chemistry and biology [1], because they contribute to the structure and function of many molecules. For instance, the structure of macromolecules, such as DNA and proteins, is determined by hydrogen bonding, and steps of enzymatic reactions rely on the formation and breaking of hydrogen bonds. Such reactions often include the hydrogen atom transfer (HAT) between a hydrogen donor and acceptor site. HAT is ubiquitous in chemistry and the understanding of its properties has drawn considerable attention [2, 3, 4, 5]. In particular, time-resolved non-linear spectroscopy has emerged as a powerful tool for the investigation of its reaction dynamics [4, 5, 6].

The de Broglie wave length of a hydrogen with kinetic energy equal to typical vibrational energies is of the same order of magnitude as lengths of chemical bonds. Thus, in general, quantum effects are non-negligible in HAT. For instance, a hydrogen may *tunnel through* a barrier [7]. The impact of *tunneling* on HAT ranges from tautomerization reactions of triatomics and polyatomics [8] to enzymatic reactions [9]. An important experimental tool for the identification of tunneling effects is isotope substitution.

The invariance of the Hamiltonian of an isolated molecule with respect to permutations of identical atoms gives rise to symmetrically equivalent minima [10]. The tunneling between such symmetrically equivalent minima is *coherent* [8] and leads to a splitting of energy levels. Coherent tunneling was observed for molecules possessing intra-molecular hydrogen bonds. Prototypical molecules are malonaldehyde and tropolone [8]. Both were addressed by means of microwave spectroscopy and high-resolution IR spectroscopy [11]. In particular, it was found that tunneling splittings are *state-specific*, i.e., there are certain vibrational modes of the molecule that either promote, suppress, or have no effect on

the tunneling splitting. Coherent tunneling was also found for molecules having two or more intramolecular hydrogen bonds [12, 13]. Especially, evidence for coherent tunneling in the hydrogen bond network of calix[4]arenes was established [13] by using nuclear magnetic resonance (NMR) spectroscopy [14].

If the system size is increased (i.e., there are many internal degrees of freedom (DOF) or there is coupling to the environment) or if the minima have an energy bias then tunneling becomes *incoherent* and can be characterized by a temperature dependent rate of conversion [8]. The most significant effect of incoherent tunneling is the deviation of the rate from the Arrhenius law for low enough temperatures. Incoherent tunneling was found by using NMR spectroscopy, e.g., for porphyrine and naphthazarin [8]. Moreover, incoherent tunneling was found to contribute significantly to enzyme catalysis [9]. The cis-trans isomerization of formic acid in rare gas matrices is also subject to incoherent tunneling [15]. A rather strong dependence of the tunneling rate on the host atoms (Ar, Kr, Xe) was found.

Theoretically, an isolated polyatomic molecule (or macromolecule) constitutes a many particle system, where the electrons and nuclei interact via the Coulomb forces. The time-evolution is governed by the Schrödinger equation of quantum mechanics [16]. The large proton-electron mass ratio, $m_p/m_e \approx 1836$, allows for an adiabatic separation of electronic and nuclear motion [17]. This *Born-Oppenheimer separation* leads to the concept of potential energy surfaces (PES). The nuclear Hamiltonian consists of the kinetic energy of the nuclei plus the PES. Excitations of electrons give rise to different PES. For certain nuclear configurations these PES may come close to each other and the Born-Oppenheimer separation breaks down [18].

Near a certain stable configuration of the nuclei (a minimum or saddle point), when the Born-Oppenheimer separation is valid, the nuclear motion can be described by the harmonic approximation. In this approximation there are certain modes of vibration, where a single mode behaves as a one-dimensional harmonic oscillator [19]. If the amplitudes of vibrations get larger, non-harmonic effects are non-negligible. In particular, there is a non-vanishing coupling among vibrational modes. If energy is initially stored in a certain vibration of a special bond, then this energy is distributed among the other modes during the course of time. This general effect of a multidimensional anharmonic systems is called intramolecular vibrational energy redistribution (IVR) [20, 21, 22].

The experimental findings and theoretical considerations suggest that a reliable numerical simulation of HAT in polyatomic molecules (or macromolecules) requires the treatment of many coupled DOF. The numerical effort for an numerically exact solution of the Schrödinger equation scales exponentially with respect

to the number of DOF. In contrast, the numerical solution of Newton's (or Hamilton's) equation of motion only scales linearly with the number of DOF. In particular, the dynamics of macromolecules can be addressed by classical molecular dynamics techniques [23]. However, if quantum effects, such as tunneling, are significant a classical simulation is inappropriate.

The inclusion of quantum effects into a simulation that is based on classical (or classical-like) trajectories is one of the ultimate goals of modern computational chemistry. Several approaches have been discussed in the literature; a recent overview can be found in Ref. [24]. Several approaches rely on *semiclassical mechanics*, a mathematically well-defined approximation to quantum mechanics. The essential finding is, that quantum effects, such as tunneling and interference, can be described by associating complex phases to classical trajectories, where the phases depend solely on properties of the classical trajectory.

Alternatively, efficient propagation techniques have been developed that are heading towards a direct solution of the Schrödinger equation by means of a restricted ansatz for the wave function [25, 26]. These techniques are currently applicable to systems of moderate size (say, 1 to 25 DOF), when the full-dimensional PES is known.

## 1.2   Objective

The present work pursues two objectives. The first objective is a comparison of semiclassical and quantum mechanical exact results concerning state-specific tunneling splittings. The determination of state-specific tunneling splittings is a rather precise test for any theory of tunneling. In particular, two different approximate semiclassical methods are examined. The first method is based on the work of Takatsuka *et al.* [27, 28]. This method accounts for tunneling by means of trajectories that are propagated in the classically forbidden region (i.e., "under the barrier"). In earlier, related approaches, tunneling was assumed to occur along predefined paths, for instance, straight lines in the widely used Makri-Miller model [29]. The new method is an intuitive extension that is founded on the multi-dimensional extension of Wentzel-Kramers-Brillouin (WKB) theory [16, 30]. So far, the new method was not applied to the case of state-specific tunneling. Thus, a detailed investigation should unveil advantages and disadvantages of the method. The requirement of a comparison with quantum mechanical exact results confines the analysis to few DOF.

The second semiclassical method was considered to be a hybrid quantum-semiclassical approach. Semiclassical correlation functions can be obtained by performing wave packet propagations based on the semiclassical approximation

to the quantum mechanical propagator [31]. Several types of semiclassical propagators exist; special interested was drawn by those propagators that rely on the propagation of Gaussians (so-called *coherent states*), because these propagators are numerically convenient to handle [32, 33]. In particular, the propagator of Herman and Kluk [34] is widely used. This propagator was inspired by the frozen Gaussian method of Heller [35]. The essential idea is to resemble the propagation of a wave packet by propagating many Gaussians along classical trajectories. Mandelshtam [36] proposed to analyze semiclassical cross-correlation functions by high-resolution spectral techniques, such as harmonic inversion [37, 38]. A cross-correlation function relies on the correlation of two or more wave packets. It was argued that this can be viewed as being intermediate between an exact quantum mechanical diagonalization and a pure semiclassical propagation. And the extraction of tunneling splittings was demonstrated for simple analytical models [39]. This work takes up the idea, analyzing first the *reason* why tunneling splittings can be obtained by a semiclassical propagation and then investigates the application to a realistic anharmonic system.

The second objective of this work is the description of coherent tunneling in intra-molecular HAT of polyatomic molecules by means of numerical simulations. A prominent example for such a reaction is the tautomerization of tropolone [TRN(OH)],



(R1)
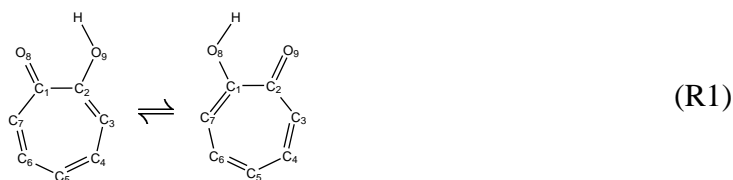
Tunneling splittings corresponding to the tautomerization reaction of such molecules are state-specific (see above) and the intra-molecular hydrogen bond introduces a considerable anharmonic coupling into the PES. It was pointed out [40], that the HAT in TRN(OH) [and similar molecules] is accompanied by a significant reorganization of heavy atoms. A similar conclusion was drawn for malonaldehyde [41]. This important observation was termed *heavy atom tunneling* [40]. Moreover, vibrational enhancement of HAT in TRN(OH) reveals features of similar processes in enzymatic reactions [40]. Thus, with certain restrictions, polyatomics, such as TRN(OH), may be considered as a reasonable test case for larger systems.

The comparison of semiclassical and exact results (Objective no. 1) showed that a *quantitative* treatment requires a quantum rather than a semiclassical approach. To this end, the multi-configuration time-dependent Hartree (MCTDH) approach [25, 26] is employed. For this approach to be efficient, a product representation of the PES is necessary. Moreover, the anharmonicity of a PES with

two minima hampers a full-dimensional treatment, i.e., it is necessary to select relevant DOF. Both requirements are achieved by using the *Cartesian-Reaction-Plane Hamiltonian* (CRP) approach. This approach was derived as part of this work and is a variant of the related approach by Ruf and Miller [42]. The PES is treated exactly on the so-called *reaction plane* [43] and a second order Taylor expansion is used for the orthogonal DOF. The input necessary for a construction of the PES can be obtained by quantum chemistry calculations [44, 45, 46].

Using the considered approaches, the state-specific tunneling of TRN(OH) is analyzed. In particular, the findings of Redington *et al.* [47] concerning the tautomerization mechanism are discussed in terms of the newly developed CRP approach. Furthermore, the coupling mechanism hidden underneath the OH stretch band, that is expected to be dominated by Fermi resonances of the OH stretch local mode with other modes [48], is addressed.

## 1.3 Outline

A brief discussion of basic theoretical concepts is given in Chapter 2. More specific discussions are paged out to the corresponding Chapters. Chapter 3 and 4 are both concerned with semiclassical mechanics.Chapter 3 introduces and tests the newly developed method that is based on the work of Takatsuka *et al.* [27, 28] (see above). The theoretical foundation of the theory is multidimensional WKB theory (cf. Section 2.1). Moreover, the multidimensional WKB theory facilitates a general understanding of state-specific tunneling and is therefore of particular importance for the present work.

In Chapter 4 the hybrid quantum-semiclassical approach [36] is discussed (see above). In this approach, tunneling is described by purely real-valued trajectories by means of a semiclassical approximation to the quantum mechanical propagator (cf. Sec. 2.3.2). Furthermore, the filter diagonalization method is introduced.

The second objective is addressed in Chapter 5 and 6. Chapter 5 introduces the newly developed CRP approach. In particular, the similarities and differences to the Cartesian-Reaction-Surface (CRS) of Ruf and Miller [42] is detailed. An application to the tautomerization of tropolone (TRN) is given in Chapter 6. A 12D model is constructed and analyzed in terms of the well-established multi-configuration time-dependent Hartree approach (cf. Sec. 2.3.1). Additionally, a semiclassical investigation is given.

In Chapter 7 the work is summarized and an outlook for future investigations is given.