Chapter 7

Summary and Outlook

On the scale of typical bond length hydrogen (and its isotopes) behaves like a quantum particle. Thus, quantum effects, such as tunneling, are generally non-negligible in hydrogen atom transfer (HAT) reactions. This theoretical work is concerned with tunneling processes in HAT of small and polyatomic molecules, especially molecules with an intramolecular hydrogen bond. In order to account for the contortion of the molecule along large amplitude coordinates upon a tautomerization reaction, it is necessary to go beyond the harmonic approximation and consider anharmonic effects and the effects of mode coupling. In particular, the state-specific tunneling splittings of vibrational levels is addressed.

A theoretical description of tunneling requires the solution of the multidimensional Schrödinger equation. Approximate methods derived from semiclassical mechanics are investigated for this purpose. In semiclassical mechanics the propagation of a wave packet is described by classical trajectories, that are generated according to Newton's laws, with an associated phase factor, that only depends on properties of the classical trajectory alone. Semiclassical methods are promising tools, in principle, because they typically show a polynomial scaling with respect to the number of degrees of freedom(DOF), while quantum mechanical methods scale exponentially with the number of DOF.

In order to test the efficiency of semiclassical methods, one objective of the present work was the comparison of semiclassical methods with quantum mechanical exact results. In particular, two methods were considered that address the semiclassical determination of tunneling splittings. The first method was introduced in this work ([I]; cf. Sec. 3.2). It is an extension of an earlier approach by Makri and Miller [29], in which tunneling was considered to occur along pre-defined straight line paths. The new approach invokes trajectories that are propagated in the forbidden region (i.e., 'under the barrier'). The equations of motion for these trajectories were given by Takatsuka and Ushiyama [27, 28] (cf. Sec. 2.1.4). The present new method was applied to generic model PES (cf. Sec. 3.3.1

and 3.3.2) and to a PES of the hydroperoxyl anion [127] (cf. Sec. 3.3.3). It was shown that the new extended Makri-Miller model (EMM) accounts for cases of symmetric mode coupling with strong couplings, where the Makri-Miller model (MM) breaks down, i.e., the present EMM is superior to the ordinary MM [I] (cf. Fig. 3.5). Moreover, for the case of the HO_2^- anion, it was shown that the present EMM yields systematically better results than the MM.

The second method ([II]; cf. Sec. 4.1) was based on an application of the filter diagonalization method to semiclassical cross-correlation functions (cf. Sec. 4.1.3). Cross-correlation functions can be obtained semiclassically by adopting the semiclassical approximation to the quantum propagator [31, 32, 138] (cf. Sec. 2.3.2). Filter diagonalization is a high-resolution spectral technique that can circumvent the uncertainty principle of a discrete Fourier transform [136, 137]. In previous works [39], it was shown that tunneling splittings can be obtained by means of this method. This was attributed to the assumed quantum aspect that is introduced in a semiclassical propagation by using more than one wave packet. (For an infinite number of wave packets this is equivalent to a diagonalization of the Hamiltonian.) The present work lead to the conclusion that this assumption is in general unsound, i.e., the utilization of more than one wave packet does not include quantum effects into a semiclassical propagation [II] (cf. Fig. 4.3 and Fig. 4.5). Results for generic PES were presented (cf. Sec. 4.2). Moreover, the method is applied to a more realistic PES of 3,7-dichlorotropolone (cf. Sec. 4.2.2). The results concerning the semiclassical methods showed that the quantitative description of tunneling in HAT requires a quantum mechanical rather than a semiclassical treatment.

The second objective of this work was a description of tunneling in HAT for polyatomic molecules. To this end, the multi-configuration time-dependent Hartree (MCTDH) ansatz for the multidimensional wave function was employed [78, 25, 26]. This ansatz allows for a quantum propagation of a rather large number of degrees of freedom (DOF). However, like for a numerical exact quantum propagation on a product grid, the numerical effort for a MCTDH calculation still scales exponentially with respect to the number of DOF. Therefore, a selection of relevant DOF is necessary. Moreover, the PES has to be in product form for the MCTDH ansatz to be efficient. For this purpose, the Cartesian reaction plane (CRP) Hamiltonian [V] was introduced (cf. Chapter 5). In this approach, the potential energy surface (PES) is treated exactly on a well-defined plane that includes the minima and the transition state of the reaction; orthogonal DOF are treated by a second order Taylor expansion. The CRP Hamiltonian was derived as part of the present work [V] extending previous work of Ruf and Miller [42].

The tautomerization reaction of tropolone [TRN(OH)] was simulated by us-

ing the theoretical tools, MCTDH and CRP Hamiltonian (cf. Chapter 6). It was shown, by taking recent results of Tautermann *et al.* [114] into account, that the reaction plane covers the region of the configuration space that is relevant for the tautomerization reaction (cf. Sec. 5.1.2 and Fig. 5.3). It was found, that excitation of a particular vibrational mode, the reaction mode, promotes tunneling significantly (cf. Tab. 6.8 and Fig. 6.7). This mode is a superposition of in-plane normal mode vibrations with lowest frequency (cf. Fig. 6.4). A previous assignment of a so-called nascent tautomerization coordinate is shown to be in disagreement both with the stable limit theorem (Fukui *et al.* [68]) and with predictions of the present CRP ansatz. Moreover, the results suggest that transitions in the $1000 - 1700\,\mathrm{cm}^{-1}$ region may show significantly enhanced tunneling splittings as compared to the ground state (cf. Tab. 6.9). The OH stretch region was addressed in terms of a 12D model, based on resonance considerations concerning the modes that couple to the OH stretch (cf. Fig. 6.12). An analysis based on classical methods and semiclassical methods (power spectra and the Makri-Miller model), suggested, in particular, that so-called dynamical tunneling is responsible for the OH stretch splitting (cf. Sec. 6.2.5). The coupling mechanism was investigated by time-propagation of an appropriate wave packet. It was found that there is significant coupling of the OH stretch mode to the OH bend and reaction mode (cf. Sec. 6.2.6). Moreover, the coupling to the remaining modes is generally not negligible (cf. Fig. 6.16).

An isotopically substituted model of tropolone was also investigated in terms of a 4D model; tunneling splittings were found to be consistent with experimental results (cf. Tab. 6.8). The effect of symmetric chlorine substitution was discussed in terms of a minimal 3D model. Unlike expected from the the stable limit theorem, the tautomerization mechanism of the substituted compound, 3,7-dichlorotropolone, appears to be rather similar to that of tropolone, because the reaction mode geometry is similar.

Finally, some remarks concerning future investigations are given. The present work introduced an efficient and general means to construct multidimensional PES. The generality allows, in principle, for an application to HAT in different molecules than tropolone. Moreover, an extension to asymmetric PES is possible since the reaction plane can also be uniquely defined for an asymmetric system. The definition of reaction plane coordinates would then involve an additional orthogonalisation.

Concerning the present molecule, tropolone, the coupling of modes leading to the structured OH stretch band was studied in this work in terms of a time-dependent propagation of the local harmonic state corresponding to an OH stretch fundamental excitation. More detailed information about the mode couplings

could be obtained by resorting to non-linear spectroscopy [6]. This requires the computation of three-time dipole correlation functions. Thus, as a rough estimate, the numerical cost is squared when one time variable is fixed. Nevertheless, an application to a multidimensional system is probably possible, when non-linear spectroscopy is combined with high-resolution spectral techniques such as the filter diagonalization method (FDM). The FDM was discussed in the present work in the context of a semiclassical technique (cf. Section 4.1.3).

Moreover, there is growing interest in double or multi hydrogen transfer processes [121, 123, 12, 125, 126, 107]. In particular, such processes may show cooperative effects due to the coupling of the hydrogens. One may therefore hope that studies concerned with single hydrogen transfer, like the present one, may lead to a development of tools and methods that make a theoretical modeling and understanding of the more complicated double (or multi) hydrogen transfer processes possible.