# The Multi-dimensional Quantum Dynamics of Hydrogen and Proton Transfer Processes

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Quantum effects play an important role in the dynamics of many chemical reaction processes. Tunneling strongly enhances the reaction rate of hydrogen transfering reactions. Ultrafast non-adiabatic transitions due to conical intersections of the potential energy surfaces frequently determine the course of photochemical reactions. Several other examples could be quoted. Due to the multi-dimensional nature of these processes, their accurate theoretical description posts a considerable challenge. Here the multi-configurational time-dependent Hartree (MCTDH) approach provides an essential tool facilitating accurate multi-dimensional quantum dynamics simulations.

Hydrogen-transfering gas-phase reactions are important in atmospheric and combustion chemistry and play a key role for the fundamental understanding of elementary chemical reaction processes. Important examples are reactions of methane with atoms (e.g., H, O, Cl, F) or small molecules (e.g., OH). Tunneling can increase the thermal rate constant of such reactions by an order of magnitude already at room temperature. In recent work, the thermal rate constant of the $H+CH_4 \rightarrow H_2+CH_4$ reaction could be accurately calculated by quantum dynamics calculations. These calculations were based on high level electronic structure calculations, obtained a full 12-dimensional potential energy surface by Shepard interpolation of the ab initio results, and employed the MCTDH approach for the quantum dynamics simulations. As a result, first principle based theoretical predictions could be obtained with an accuracy which can rival the accuracy of the available experimental data.

The present talk will introduce the MCTDH approach and discuss basic concepts of quantum dynamical simulations of chemical reaction processes focusing on a quantum transition state concept. Studying the $H+CH_4$ example, the importance of quantum effects will be discussed. Results of accurate theoretical calculations will be compared with experiment and with different approximate theories. To complete the discussion, also an example were tunneling effects have wrongly been postulated to be important, the dissociative desorption of $N_2$ on a Ru-surface, will be presented.

Proton transfer is another area of chemistry where tunneling is of fundamental importance. The quantum nature of the proton dynamics strongly influences, for example, the vibrational states of molecules with intra-molecular hydrogen bridges. Molecules with symmetric hydrogen bridges show characteristic tunneling splittings of their vibrational levels. In the present talk, the malonaldehyde molecule will be discussed as a example. Rigorous full 21-dimensional quantum dynamics results will be presented and the multi-dimensional nature of the proton transfer process will be highlighted.