

Dynamics of molecular systems: from quantum to classical (in honor of Eli Pollak)

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Preface

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Although the Schrödinger equation in principle describes the behavior of molecular systems its straightforward application is limited to very few simple cases. In general, approximate methods are required. An additional complication in understanding the dynamics of molecular systems lies in the fact that molecules are most often not isolated but stay in constant interaction with their environment. This may lead to relaxation phenomena as well as decoherence but also to activation processes and subsequent reactions. It is the purpose of this special issue to present a timely overview of various methods that have been developed to understand the dynamics of molecular systems.

One fundamental issue in the description of the dynamics of complex systems is to develop an accurate, but still efficient, approximation to the quantum mechanical propagator. In this context particularly semi-classical formulations such as the initial value representation have been shown in various applications as powerful tools to capture even genuine quantum effects such as interferences and tunneling. In the last years substantial efforts have been devoted to better understand on the one hand their mathematical foundations. These activities also include alternative concepts as, e.g. Bohmian mechanics and coherent state formulations. On the other hand the description of the dynamics of dissipative systems has been pushed forward. While within a reduced formulation an exact expression for the density matrix exists within the path integral representation of quantum mechanics,

an explicit evaluation is not straightforward. In fact, several schemes have been derived, some of them from the path integral formulation, some of them from ab initio based concepts, to access the challenging regime of low temperatures and moderate system-reservoir interaction. Results provided by these approaches can be used as benchmarks to validate approximate methods. One important aspect of the dynamics in open systems is transport comprising transfer of charges in molecular aggregates and through contacts as well as energy transfer. Another one is the interaction with external fields which allow the control of the time evolution but may also be used as means to reveal the structure of surfaces in scattering scenarios.

The dynamics taking place on large time scales is particularly difficult to be accessed by quantum mechanical methods. A classical description though can shed light on long time aspects, in particular if the slow dynamics is governed by the motion of nuclei whereas all electronic degrees of freedom can be considered as fast. While (classical) molecular dynamics calculations considerably extend the time horizon they are still limited to time scales that may be too short for example to monitor the motion of a molecule in a solvent over a larger distance. Then more phenomenological approaches in terms of diffusion, Fokker-Planck and master equations may give insight into those mechanisms that are relevant for many processes, e.g. in surface diffusion or molecular biology.

This special issue is dedicated to Professor Eliahu Pollak on the occasion of his 60th birthday. Eli has always been an extraordinary scientist whose work has strongly influenced many of his colleagues and friends in particular those who had the opportunity and the pleasure to discuss and work with him. His contributions have had a lasting impact on several fields of non-equilibrium Statistical Mechanics and Chemical Physics. The topics covered in this special issue reflect a part of the broad scope of his interests.

Here we only want to highlight some of his main accomplishments. Transition State Theory (TST) of chemical reactions certainly is a central topic of Eli's research. In an early work with Phil Pechukas on microcanonical TST he emphasizes the role of unstable periodic orbits as constituents of the transition state long before their relevance for chaotic dynamics had become known. His paper on the equivalence of the Kramers rate for reactions in condensed media and canonical TST for an extended Hamiltonian system was a major breakthrough unifying seemingly opposite points of view. As a consequence Eli's Hamiltonian approach to reactions in condensed media led to the solution of the longstanding so-called Kramers turnover problem. Another central topic of Eli's research is the semi-classical limit of Quantum Theory. One of his contributions is a new version of quantum transition state theory applicable down to the temperature regime where

tunneling tends to dominate. He “derived” instead of “proposed with the help of intuition” the theory by replacing the asymptotic property of the reaction dynamics required in the exact formulation of the rate constant by that of a parabolic barrier. A fundamental problem in the semi-classical initial value representation of the quantum propagator has attracted Eli’s attention in the last years. For decades this type of representation, the best one known as the Herman–Kluk propagator, has been considered more as practical tool rather than a well-founded theory. Eli and co-workers introduced the concept of a correction operator and derived a semi-classical series expansion of the exact propagator, the zero-order term of which gives the standard Herman–Kluk result. This development not only led to a deeper mathematical understanding of initial value formulations, but allowed also for systematic improvements of the semi-classical results in various application including deep tunneling. Recently, he extended this approach to the dynamics of dissipative system as, e.g. the spin-boson problem.

As guest editors we express our thanks to the authors of this special issue as well as to the Editor Prof. Hofacker for his guidance and last but not least to Eli Pollak. We hope that he will enjoy his special issue.

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