

# 学位論文の要約

題目 Applications of Real and Imaginary time Hierarchical Equations of Motion

(実時間と虚時間の階層方程式の実用)

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## 序論

The hierarchical equations of motion (HEOM) approach plays an important role in the study of open quantum dynamics. Its current formulation has been applied to various chemical and physical processes, for instance proton transfer reaction. Original studies are limited to the real time dynamics. Recently extension has been made to the thermodynamic problems. The so-called imaginary time HEOM serves as a powerful tool on the evaluation of various thermodynamic quantities.

### **Proton tunneling in a two-dimensional potential energy surface with a non-linear system–bath interaction: Thermal suppression of reaction rate**

We consider a proton transfer (PT) system described by a proton transfer reaction (PTR) coordinate and a rate promoting vibrational (RPV) coordinate interacting with a non-Markovian heat bath. While dynamics of PT processes has been widely discussed using two-dimensional potential energy surfaces, the role of the heat bath, in particular, in a realistic form of the system–bath interaction has not been well explored. Previous studies are largely based on a one-dimensional model and linear-linear system–bath interaction.

In the present study, we introduce an exponential-linear (EL) system–bath interaction, which is derived from the analysis of a PTR–RPV system in a realistic situation. This interaction mainly causes vibrational dephasing in the PTR mode and population relaxation in the RPV mode. Numerical simulations were carried out using the hierarchical equations of motion approach. We analyze the role of the heat bath interaction in the chemical reaction rate as a function of the system–bath coupling strength at different temperatures and for different values of the bath correlation time.

A prominent feature of the present result is that while the reaction rate predicted from classical and quantum Kramers theory increases as the temperature increases, the present EL interaction model exhibits opposite temperature dependence. The Kramers turn-over profile of the reaction rate as a function of the system–bath coupling is also suppressed in the present EL model, turning into a plateau-like curve for larger system bath interaction strength. Such features arise from the interplay of the vibrational dephasing process in the PTR mode and the population relaxation process in the RPV mode.

## **Probing photoinduced proton-coupled electron transfer process by means of two-dimensional electronic-vibrational spectroscopy**

We develop a detailed theoretical model of photo-induced proton-coupled electron transfer (PPCET) processes, which are at the basis of solar energy harvesting in biological systems and photovoltaic materials. Our model enables us to analyze the dynamics and the efficiency of a PPCET reaction under the influence of a thermal environment by disentangling the contribution of the fundamental electron transfer and proton transfer steps.

In order to study quantum dynamics of the PPCET process under an interaction with the non-Markovian environment, we employ the hierarchical equations of motion. We calculate transient absorption spectroscopy (TAS) and a newly defined two-dimensional resonant electronic-vibrational spectroscopy (2DREVS) signals in order to study the non-equilibrium reaction dynamics. Our results show that different transition pathways can be separated by TAS and 2DREVS.

Since we use the eigenstate representation of the system, it is also possible to improve the description of the reacting system by increasing the dimension of its configuration space and by introducing a more complex and structured system-bath interaction, for example, with the help of machine learning approaches. This provides a powerful tool to analyze the non-equilibrium reaction dynamics for rather complex PPCET reactions.

## **Imaginary-time hierarchical equations of motion for thermodynamic variables**

The partition function (PF) plays a key role in the calculation of quantum thermodynamic properties of a system that interacts with a heat bath. The imaginary-time hierarchical equations of motion (imHEOM) approach was developed to evaluate in a rigorous manner the PF of a system strongly coupled to a non-Markovian bath.

In this thesis, we present a more detailed discussion of imaginary-time HEOM (imHEOM). We also introduce an additional  $\beta$ -differentiated imHEOM (BD-imHEOM) that are obtained from the derivative of the elements of imHEOM with respect to inverse temperature  $\beta$ . We use both imHEOM and BD-imHEOM to evaluate the thermodynamic properties of not only the reduced system but also the system-bath interaction and the bath, in a numerically rigorous manner. In addition, we introduce the polyharmonic decomposition (PHD) method to construct both the imHEOM and the BD-imHEOM in a concise hierarchical structure that makes it possible to improve the numerical performance with high precision.

The capability of this formalism has been verified through numerical demonstrations. We have employed a spin-boson model and a  $2 \times 2$  transverse Ising model to clearly reveal the behavior of various quantities in a straightforward manner. Although this work has been restricted to an Ohmic form of the SDF, we note here that the PHD method imposes no restrictions on the SDF and could have broader applications. To make the present approach more useful, further computational efforts will have to be made to treat larger systems. For example, we can extend our imHEOM to the wave function based case by utilizing some other techniques. The scalability of all the above-mentioned approaches is the same as that of the typical Schrödinger equation, which incurs less computational cost than the density-matrix-based approach. We believe that the present results clarify the key features of quantum open dynamics system