I-Q Theoretical Studies on Dynamical Foundation of Chemical Reactions and Proteins

Recent experimental developments in single molecule spectroscopy have shed light on the distinct nonergodic features and the heterogeneity of the state space and non-Markovian process of biomolecules. This project focuses on the dynamical foundation of chemical reactions, *i.e.*, why and how the reacting systems climb through the saddle, and on the developments of new time series analyses to extract the dynamical information regarding the underlying state space structure from single molecule time series.

I-Q-1 Dynamical Hierarchy in Transition States of Reactions

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Recent theoretical developments[1–4] in chemical reactions have greatly improved our understanding of the definability of the no-return dividing hypersurface and the reaction path along which all reacting species follow. We present a partial normalization procedure of Lie canonical perturbation theory to elucidate the phase space geometry of the transition state in the multidimensional phase space for a wide range of energy above the threshold. State selectivity and dynamical correlation along the evolution of reactions are also discussed.

References
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I-Q-2 Definability of No-Return Transition States in High Energy Regime above Reaction Threshold

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No-return transition states (TSs) defined in multidimensional phase space, where *recrossing* trajectories through the commonly used "configuration" TS pass only *once*, robustly exist up to moderately high energy regime above the reaction threshold even when nonlinear resonances among the bath degrees of freedom perpendicular to the reaction coordinate result in local chaos. However, at much higher energy when global chaos appears in the bath space, the separability of the reaction coordinate from the bath degrees of freedom ceases to hold locally. In the phase space near the saddles, it is found that the slower the system passes the TS, the more recrossing trajectories reappear. Their implications and mechanisms are discussed concerning to what extent one can define no-return TSs in high energy regime above the reaction threshold.

I-Q-3 Wavelet Analysis and Arnold Web Picture for Detecting Energy Transfer in a Hamiltonian Dynamical System

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Our motivation is to understand how, in chemical reactions, the reaction coordinate effectively gains dynamical energy from the other degrees of freedom (*i.e.*, bath coordinates) avoiding thermalization of the redistributed energy. In such a system, the phase space structure should be not homogeneous; *i.e.*, the system is never ergodic. In this study, we introduce a way to capture the inhomogeneity of the phase space and to monitor energy transfers among their partial degrees of freedom in nonergodic systems using wavelet analysis and a picture of the Arnold web. First, we examine several simple energy transfer processes, *i.e.*, a motion on a resonance line, between resonance lines, and around a resonance junction in a simple three-degree-of-freedom (DOF) system and show how the elemental processes of the intramolecular vibrational energy redistribution (IVR) are detected by our tools. We especially note that the structure of the higher order resonance of the system can be detected by wavelet analysis and motion in the action space. Next, we analyze a reaction process in a simple Hamiltonian system of 3 DOF with a double-well potential, *i.e.*, a system with a transition state of the center-saddle-center type, and detect energy transfers in the reactive process. The aim of the study is to propose a way to characterize the inhomogeneity of the phase space, *e.g.*, the reactive doorway, which leads to controllability of the chemical reaction by light, *i.e.*, control of the reaction by selectively preparing an initial state in the reactive doorway by optical excitation.

I-Q-4 Foundation and Limitations of Statistical Reaction Theory

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We study the foundation and limitations of the statistical reaction theory. In particular, we focus our attention to the question of whether the rate *constant* can be defined for nonergodic systems. Based on the analysis of the Arnold web in the reactant well, we show that the survival probability exhibits two types of behavior: one where it depends on the residential time as the power-law decay and the other where it decays exponentially. The power-law decay casts a doubt on definability of the rate *constant* for nonergodic systems. We indicate that existence of the two types of behavior comes from sub-diffusive motions in remote regions from the primary resonances. Moreover, based on the analysis of non-stationary features of the trajectories, we can understand how Normally Hyperbolic Invariant Manifolds (NHIM) is connected with the Arnold web. We propose that the following two features play a key role in understanding the reactions where ergodicity is broken, i.e., whether the Arnold web is nonuniform and how the NHIM is connected with the Arnold web.

I-Q-5 Bifurcation of Transition States in Many-Degrees of Freedom Chemical Reactions: Non-Collinear H_2+H Exchange Reaction

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A new method is presented to scrutinize the bifurcation of no-return transition states (TSs) at potential saddles for many degrees of freedom (dof) systems. The bifurcation can give rise to a short-lived intermediate state at the saddle resulting in the overestimation of the reaction rate from the TS. As an illustrative example of the method, the H_2+H exchange reaction is investigated. It is shown that the new action variable of bath dof defined in the multidimensional phase space also serves as a bifurcation control parameter for the no-return TS besides the total energy. This enables us to determine analytically when and how the no-return TS is ruined through the bifurcation. The definability of no-return TSs after the occurrence of bifurcation above the reaction threshold is also discussed.

I-Q-6 Fractional Behavior in Nonergodic Reaction Processes of Isomerization

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We present numerical manifestation of fractional behavior in reaction processes for a prototype model of three-degree-of-freedom (3DOF) isomerization. Survival probability in the well exhibits two distinct ranges of time scale: One when it decreases in time with power-law and the other when it does exponentially. Trajectories with power-law decay exhibit $1/f$ spectra and sub-diffusion in action space, and those with exponential decay do Lorentzian spectra and normal diffusion. The existence of these two types of behavior is explained based on nonergodicity on the network of nonlinear resonances (Arnold web) in the well, and connection between the saddle and the Arnold web. Implications of the fractional dynamics are discussed in terms of Maxwell's demon in molecules.

I-Q-7 Mechanism of Fast Energy Exchange between Two NO Vibrations in a Short Lifetime Path of O(1D)+N_2O→NO+NO: Analyses by the Normal Form Theory

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Normal form theory is applied to analyze classical dynamics of a short lifetime path in the reaction O(^{1}D) + N_2O → NO + NO, which was found to exhibit efficient energy exchange between the vibrational modes in spite of the short lifetime of the reaction intermediate as shown in our previous paper [S. Kawai *et al.*, *J. Chem. Phys.* **124**, 184315 (2006)]. The normal form procedure simplifies the analysis of the dynamics near the saddle point by significantly reducing the number of coupling terms in the Hamiltonian. By assessing the contribution of the remaining coupling terms, we reduce the system to a subsystem of two degrees of freedom, which describes the basic mechanism of the energy transfer near the saddle. The motion of the subsystem preserves the "normal mode picture" in spite of its high energy. Then the vibrational energy, which is initially localized in the new NO bond, is transferred to the old NO bond through the beat between the symmetric and antisymmetric stretching modes. Moreover, the period of the "beat" between the two normal modes is short enough for the energy transfer to take place near the saddle. Thus, the essence of the efficient energy transfer is explained by the robust preservation of the "normal mode picture" and the relatively large difference between the frequencies of the two modes.

I-Q-8 Topographical Complexity of Multidimensional Energy Landscapes

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A new scheme for visualizing and quantifying the

complexity of multidimensional energy landscapes and multiple pathways is presented employing Principal Component (PC)-based disconnectivity graphs and the Shannon entropy of relative `sizes' of superbasins. The PC-based disconnectivity graphs incorporate a metric relationship between the stationary points of the system, which enable us to capture not only the actual assignment of the superbasins but also the size of each superbasin in the multidimensional configuration space. The landscape complexity measure quantifies the degree of topographical complexity of a multidimensional energy landscape and tells us at which energy regime branching of a main path becomes significant, making the system more likely to be kinetically trapped in local minima. The path complexity measure quantifies the difficulty encountered by the system to reach a connected local minimum by the path in question, implying that the more significant the branching points along the path are the more difficult it is to end up with the desired local minimum. As an illustrative example, we apply this analysis to two kinds of small model protein systems exhibiting a highly frustrated, and an ideal funnel-like energy landscape.

I-Q-9 A New Scheme to Construct Multidimensional Effective Free Energy Landscape from Single Molecule Time Series

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The questions "How can one learn from an ensemble of short single molecule time series about the underlying multidimensional free energy landscape or, in general, state space?" and "How can one differentiate molecular memory along several reaction paths, if it exists?" are among the most important and central subjects for analyzing single molecule time series. Here we present a concept of local ergodic state (LES) to explore free energy landscape picture. We introduce a working hypothesis on a given single molecule time series concerning LES: if LES exists, a unique distribution (not necessarily Gaussian) function for the observable can be assigned for the LES. To assign LESs from single molecule time series, we focus on the hierarchy of time scales, $t_{cor} \ll t_{eq} \ll t_{obs} \ll t_{esc}$, where t_{cor} is the time scale of the system to possess dynamic memory, t_{eq} the time scale to be "equilibrated" within each LES, t_{obs} the observation time, and t_{esc} the time scale of the system to escape from a LES to the other LES on multidimensional free energy landscape. Our methodology naturally leads to a free energy landscape whose topography depends on which time scale the system experiences the underlying landscape. For example two metastable states will be unified as one if the time scale of observation is longer than the escape time scale for which the system can visit mutually these two states. We present our recent analyses on time series of the end-to-end distance of 46-bead model protein.