Dynamical Reaction Theory and Time Series Analysis

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Abstract. We provide an overview of the recent progress of the dynamical theory of reactions. After summarizing the conventional statistical reaction theory, we explain the basic concepts underlying the dynamical theory, i.e., normally hyperbolic invariant manifolds (NHIMs) and the Arnold web. Then, we go on to discuss the dynamical theory using these concepts. Here, we discuss the following three processes: (i) redistribution of energy among vibrational modes in the well, (ii) going over the potential saddle, and (iii) dynamical connection among multiple saddles. In particular, we focus our attention to those processes where limitations of the conventional statistical theory become manifest. We will also discuss time series analysis to extract dynamical information from molecular dynamics simulations involving multi-dimensional Hamiltonian systems.
Keywords: Phase Space Structures, Reaction Theory, Time Series Analysis.

1 Introduction

We will discuss global aspects of phase space structures in multi-dimensional Hamiltonian systems. In particular, we will focus our attention to the dynamical reaction theory from global view points. Starting from the the dynamical reaction theory, we will point possibility of chaotic itinerancy in reaction processes.

2 Phase Space Structures

Roughly speaking, the dynamical processes of reactions consist of the following three, i.e., redistribution of energy among vibrational modes in the potential well, going over the potential saddles, and their dynamical connection. For the redistribution of energy in the well, the Arnold web plays an important role. For the processes near the saddles, the concept of normally hyperbolic invariant manifolds (NHIMs) is crucial in defining the reaction coordinate. For the the dynamical connection, chaotic itinerancy becomes essential.

For each of the former two processes, perturbation approach is possible to construct the normal form. These normal forms offer basic understanding of the processes. For the distribution, the normal form describes how the vibrational modes exchange energy in the well. They are, in general, nonlinear modes with their frequencies dependent on their amplitudes. When nonlinear resonance takes place, the perturbation theory breaks down, and energy exchange among vibrational modes is enhanced dramatically there. In the action space, resonant regions constitute the network called the Arnold web. Therefore, properties of the Arnold web play an important role in our topics. For the processes of going over the saddle, the normal form theory is developed recently, which provides a mathematically sound foundation of the concept of transition states (TSs). The theory is based on the phase space structures called normally hyperbolic invariant manifolds (NHIMs). It enables us to define the boundary between the reactant and the product, and to single out the reaction coordinate, at least locally in the phase space near the saddles of index one. Thus, the dynamical theory of reactions is based on the studies of the above two, and on understanding how these processes are connected in the phase space.

3 Dynamical Reaction Theory

After reviewing these concepts, we discuss the following three subjects. First, we present existence of fractional behavior for processes in nonuniform Arnold webs[2][3]. Based on the fractional behavior, we cast doubt on the very existence of the concept of the reaction rate *constant*. We also discuss reaction processes under laser fields utilizing cooperative effects of laser fields and the Arnold web[4]. This offers a possibility of manipulating reaction processes by designing laser fields. Second, We discuss that the conventional idea of reaction coordinates is not valid when the condition of normal hyperbolicity is broken. These situations take place when the values of tangential Lyapunov exponents on the NHIMs become comparable to those of the normal exponents[1]. Third, we discuss intersections between stable/unstable manifolds emanating from the NHIMs in multi-dimensional Hamiltonian systems. We point out that these intersections constitute a network in the phase space, thereby enabling the chaotic itinerancy in Hamiltonian dynamical systems[5].

References

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