Classical and Quantum Reaction Dynamics in Multidimensional Systems

Holger Waalkens (Groningen University)

A system displays reaction type dynamics if its phase space possesses bottleneck type structures. Such a system spends a long time in one phase space region (the region of `reactants'), and occasionally finds its way through a bottleneck to another phase space region (the region of `products'), or vice versa. In Hamiltonian systems such bottlenecks are induced by equilibrium points of saddle-center-...-center type ('saddles' for short).

The main approach to compute reaction rates is Transition State Theory which has its origin of conception in chemistry where it was invented by Wigner, Eyring and Polanyi in the 1930's. The main idea here is to compute the reaction rate from the flux through a dividing surface placed in the bottleneck (or in chemical terms `transition state') region. In order not to overestimate the rate the dividing surface needs to have the so-called `no-recrossing' property which means that it is crossed exactly once by reactive trajectories and not crossed at all by nonreactive trajectories. The construction of such a dividing surface has posed a major problem in Transition State Theory since its invention. In the first part of my talk I will discuss in detail the phase space structures which govern the dynamics `across' saddles, and how they can be computed from a normal form. This implies the construction of a dividing surface without recrossing. In fact, such a dividing surface is `spanned' by a normally hyperbolic invariant manifold (NHIM) whose stable and unstable manifolds moreover form the phase space conduits for the reaction. The NHIM can be viewed as the mathematical manifestation of the transition state as an unstable invariant subsystem poised between reactants and products.

In the second part of my talk I will discuss the quantum mechanics of reactions, and the role that the classical phase space structures play for these. This relationship can be studied in terms of a quantum normal form. The two main quantum imprints of the transition state are the quantization of the so-called cumulative reaction probability (the quantum analogue of the classical flux) and quantum resonances which describe the decay of wavepackets initialized on the transition state. The quantum normal form can be formulated as an explicit algorithm which, when implemented on a computer, leads to a very efficient method to compute both cumulative reaction probabilities and quantum resonances.

The talk summarizes joint work with Roman Schubert and Stephen Wiggins from Bristol University.