Hill regions of charged three-body systems

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For charged 3-body systems, we discuss the configurations and orientations that are admissible for given values of the conserved total energy and angular momentum. The admissible configurations and orientations are discussed on a configuration space that is reduced by the translational, rotational and dilation symmetries of charged 3-body systems. We consider the examples of the charged 3-body systems given by the compound of two electrons and one positron and the helium atom (two electrons and a nucleus). For comparison, the well known example of the Newtonian 3-body system is discussed following the same scheme. The study is relevant for transition state theory as the bifurcations of the Hill regions can result from saddle-type equilibrium points in which case transition state theory could be used to study the transport from region to another.

This is joint work with Igor Hoveijn and Mohammad Zaman.

Phase-space geometry of the dissociation of van der Waals molecules

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The dissociation dynamics of van der Waals molecules such as HeI_2 can be described by a 4D mapping [1]. This mapping has a mixed phase space, i.e. regions of regular motion and chaotic motion coexist. The van der Waals complex is enclosed by 3D stable and unstable manifolds of the fixed point at infinity. The escape from this region is heavily influenced by the presence of the regular region due to long-trapped chaotic trajectories leading to a slow power-law decay [2]. We illustrate the phase-space geometry of the regular region by means of 3D phase-space slices [3,4] and in frequency space. Based on this it is possible to investigate the relevant mechanism of trapping for the van der Waals dissociation.

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Chaotic transition states on the monkey saddle

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Transition State Theory describes how a reactive system crosses an energy barrier that is marked by a saddle point of the potential energy. The transition from the reactant to the product side of the barrier is regulated by a system of invariant manifolds that separate trajectories with qualitatively different behaviour.

The situation becomes more complex if there are more than two reaction channels, or possible outcomes of the reaction. Indeed, the monkey saddle potential, with three channels, is known to exhibit chaotic dynamics at any energy. We investigate the boundaries between initial conditions with different outcomes in an attempt to obtain a qualitative and quantitative description of the relevant invariant structures.
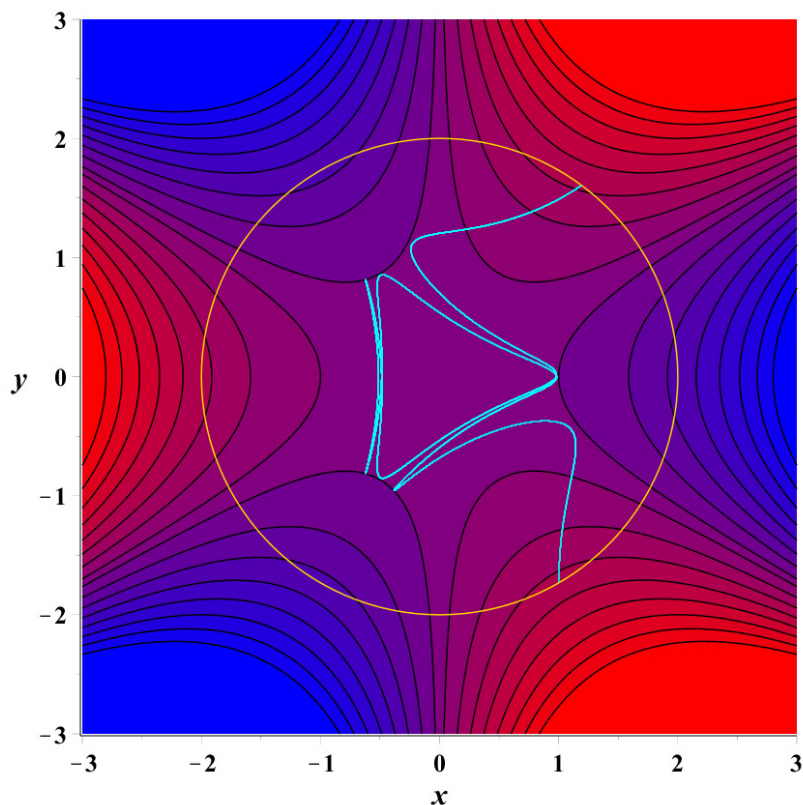
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Normal Forms in Singularity Theory for Geometric Classifications of Band Structures

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In this talk, we would like to present a normal form theory in Singularity Theory and its application to geometric classifications of band structures of crystals under various symmetries. One can think of this as a variation on a theme of normal form theory in Hamiltonian systems.

Geometry of bands plays important roles for transportation properties of crystals like, whether they are metals, insulators or topological insulators. Due to developments of technologies, it has become possible to observe and manipulate bands experimentally [1]. Given these developments, a natural question one may ask is whether it is possible to control transportation properties of crystals by manipulating their bands. To achieve that goal, it is important to understand geometry of band structures and what types of geometric changes occur if one changes system parameters.

In our previous study [2, 3], we studied geometric classification of bands in a neighborhood of a band crossing in a bulk of a crystal in case that either of time-reversal or space-inversion symmetry is broken in terms of singularity theory. In this classification, ones having a Weyl point compose the most generic class of codimension 0 and the other ones on verges of bifurcations compose classes of higher codimensions. When we control material properties by changing system parameters, not only the most generic class but also classes of higher codimension play an important role. By constructing a versal unfolding of a normal form of each class, we can obtain a comprehensive list of geometric changes that can happen if the normal form is perturbed smoothly.

In this talk, we extend our classification framework [2, 3] so that we can understand geometry of band structures and possible geometric changes under various symmetries. In a previous study, Golubitsky et al. [4] studied bifurcations of stationary solutions of dynamical systems under such symmetries in terms of equivariant singularity theory. In their equivariant singularity theory, it is assumed that:

1. Dimensions of source and target spaces of map germs under the classification are the same.

2. The same representation of a symmetry group acts on both of the source and target spaces.

On the other hand, in our classification, source space is a Bloch wavenumber space and target space is a set of traceless Hermite matrices and thus they have typically different dimensions and symmetry groups act on them through different representations. Therefore, our framework can be regarded as a generalization of their equivariant singularity theory. To apply our classification framework to systems with various symmetries, we develop a fully automated algorithm based on Comprehensive Gröbner Bases Systems. In this talk, we demonstrate our algorithm along with an example that appears under C_{3v} and time-reversal symmetries on a surface of a topological insulator such as Bi_2Se_3 [5].

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Transition state theory for driven systems with one or two rank-1 saddles

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The computation of reaction rates of driven systems using transition state theory and ensembles of trajectories requires the knowledge of a recrossing free time-dependent dividing surface to determine when a trajectory transitions from product to reactant. We present an efficient algorithm for this aim, consisting of three parts. In a first step, individual points on the dividing surface are computed with the binary contraction method [1] using Lagrangian descriptors. A smooth surface is obtained, in a second step, by interpolating the points using machine learning techniques, such as neural networks [2]. Finally, reaction rates are calculated by running a set of classical trajectories [3] or using the Floquet exponents of the transition state trajectory [4]. The method can be applied to systems with one or several degrees of freedom, and also allows for the consideration of friction and stochastic forces. Results are presented for a two- and three-dimensional model system describing a chemical reaction with a rank-1 saddle and for a system with two periodically oscillating barriers (see Fig. 1).
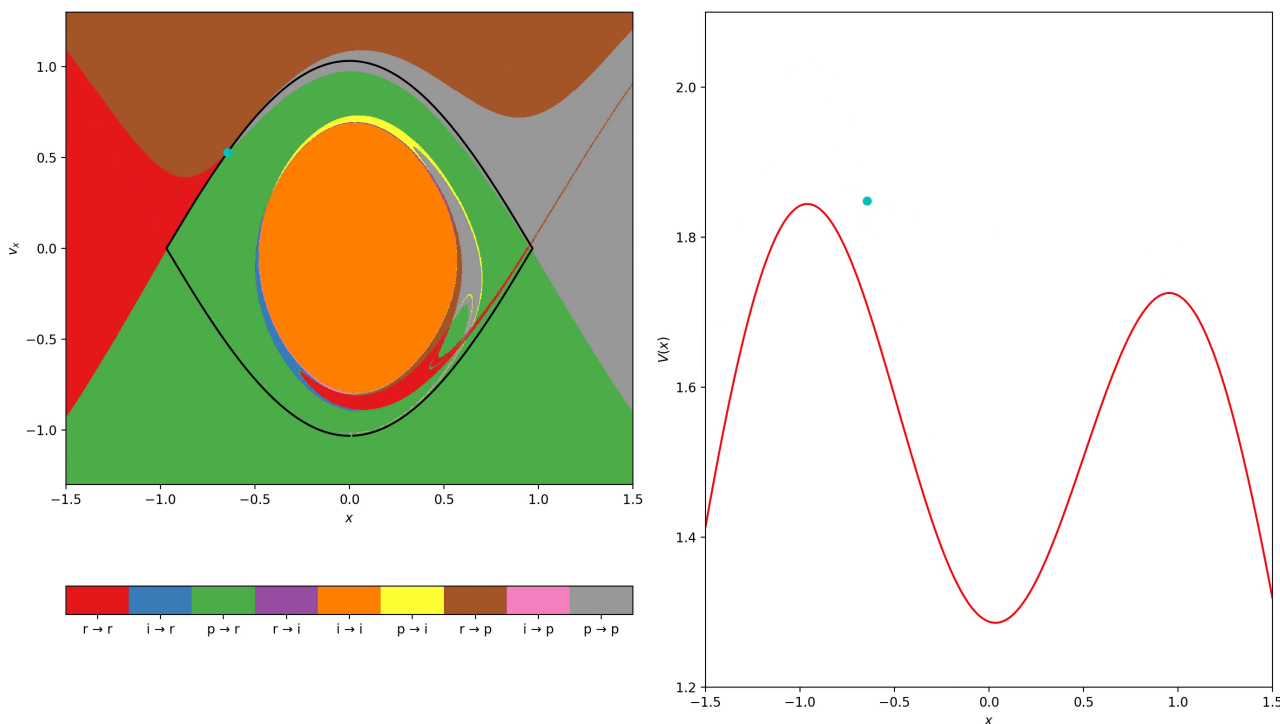
FIG. 1. Symbolic dynamics and transition state trajectory with r: reactant, i: intermediate, and p: product (left) and potential (right) at fixed time t for a one-dimensional system with two barriers periodically oscillating in height.

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Molecular Dynamics and Transition State Theory for the Solvated Isomerization Reaction LiNC/LiCN

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The calculation of reaction rates plays a central role in Chemistry. In gas phase reactions, the interaction with the environment is usually so small that it can be simply neglected. Consequently, one must solely solve the equations of motion for the system under study for a certain ensemble of initial conditions to determine the chemical rate. In condensed phase this task is much more demanding because then one must integrate not only the equations of motions for the system under study but also for the ingent number of particles that form the surrounding environment.

Transition State Theory (TST) provides a simple alternative to avoid the need of any time-consuming simulation. TST is able to (i) identify reactive trajectories, and (ii) compute reaction rates. This theory is based on the study of the so called "transition state" or "activated complex" that is formed when the reaction takes places, evolving from the reactants to the products. The transition state is an intermediate configuration that lives in the top of the energetic barrier that separates reactants and products, and acts as a bottleneck for chemical reactivity. The fundamental assumption of TST to be exact is the existence of a dividing surface that is free of recrossings, and that mus be crossed by all reactive trajectories only once. The identification of such a recrossing-free is a very challenging problem, specially when the systems is driven by colored noise of has many degrees of freedom.
In this talk, we will present all-atom molecular dynamics simulations to determine the reaction rate of the LiNC/LiCN molecular system in a bath environment. Then, we will revisit the dividing surfaces that exist for isolated systems (Periodic Orbit Dividing Surface, PODS, and Normally Hyperbolic Invariant Manifold, NHIM). Afterwards, we will present the time-dependent version of TST that has been developed over the last years. As we will demonstrate, our procedure is able to identify reactive trajectories uniquely and compute reaction rates without any numerical simulation. The accuracy of our calculations is demonstrated by adequately computing rates in chemical systems under the action of Markovian and non-Markovian friction, whose dynamics is described using the Langevin Equation and the Generalized Langevin Equation, respectively. The accuracy of the theory is assesed by accuratelly reproducing the all-atom simulations for LiNC/LiCN.

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Atomistic modelling of defects in nuclear graphite

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Nuclear graphite, is a synthetic graphite typically manufactured by isostatic pressure moulding. This material contains many interesting atomic and mesoscale structures. Recent TEM and Raman spectroscopy has shown that, in-plane boundaries between misaligned basal planes within the graphite crystallites occur. Also, sharp bends or kinks within a graphite crystallite are observed. Our previous work describes this "crazy paving" structure, which consists of nearly perfect slabs of graphite laminae, with nearly parallel c-axis. Each graphite slab has a random orientation about the c-axis. These slabs range in size from 100-1000 nm, with a thickness of ~30 nm.

Dynamical MD simulations are performed using a recent ReaxFF potential fitting, as well as, the AIREBO potential model. An existing geometric relaxation method is modified to construct these graphite "crazy paving" structures. The optimised structures show that the lowest energy interfaces comprise of 5, 6 and 7 carbon atom rings, giving formation energies in the region of 0.5-1.0 eV. The atomic structure of the boundary contains arm-chair graphite edges, a likely contributor to the D peak in Raman spectroscopy.

The motion of defects in these structures, occurs on timescales that are difficult to access with traditional MD. This is because the transition barriers are large, and so the timescale for diffusion can be micro-seconds or longer. In order to access longer timescales, some recent work using the Par-splice method is presented. This method runs many replicas of the same system in parallel and splices the trajectories together to produce a longer trajectory.

Transition state theory with time-dependent anharmonic barriers

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Classical transition state theory [1] has been extended to address chemical reactions across time-dependent barriers that are anharmonic. This resolves a challenge to the naive theory that necessarily leads to recrossings and approximate rates because it relies on a fixed dividing surface. We develop both perturbative [2, 3] and numerical methods for the computation of a time-dependent recrossing-free dividing surface for a model anharmonic system in a solvated environment that interacts strongly with an oscillatory external field [4]. This recrossing-free dividing surface moves attached to the so called *Transition State trajectory* (see Fig. 1).

We extend [5, 6] our previous work, which relied either on a harmonic approximation or on periodic force driving. We demonstrate that the reaction rate, expressed as the long-time flux of reactive trajectories, can be extracted directly from the stability exponents, namely, Lyapunov exponents, of the moving dividing surface. Comparison to numerical results demonstrates the accuracy and robustness of this approach for the computation of optimal (recrossing-free) dividing surfaces and reaction rates in systems with Markovian solvation forces. The resulting reaction rates are in strong agreement with those determined from the long-time flux of reactive trajectories.
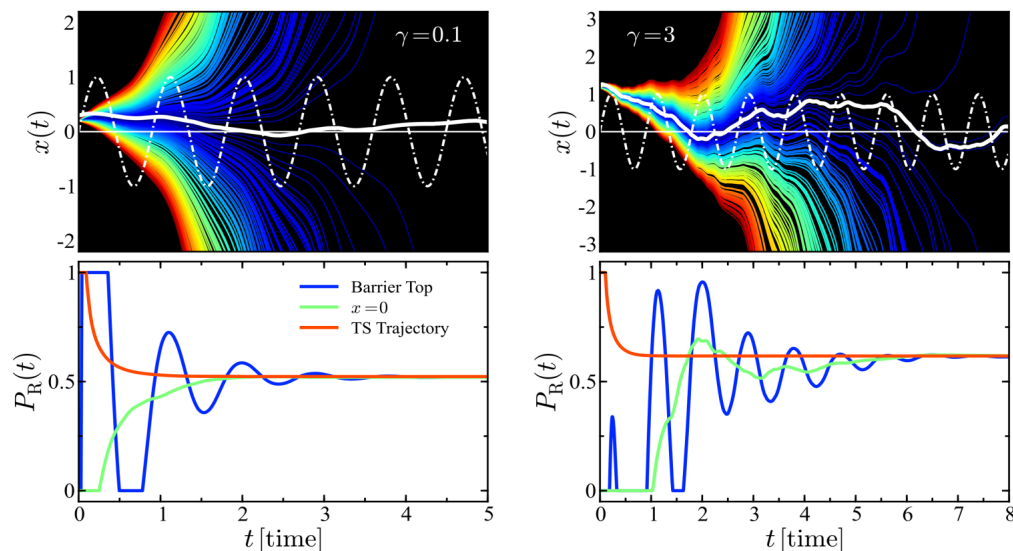
Fig 1: Time evolution of an ensemble of 250 trajectories for γ = 0.1 (top; left) and γ = 3 (top; right). Each trajectory is colored is identified along a color spectrum from blue (small) to red (large) according to the difference in the initial velocity [v(0) – V‡] with respect to the critical velocity V‡ that separates reactive from nonreactive trajectories. White curves indicate the locations of three dividing surfaces: the TS trajectory (thick), the instantaneous barrier top (dashed-dotted), and a static surface x = 0 (thin). Shown below are the respective reactant populations PR for each corresponding choice of the dividing surface, as computed from 105 trajectories. In all panels, the system parameters are σ = γ, Ω = 7, and ϵ = 1.

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