



Kickoff meeting
Georgia Institute of Technology
Atlanta, Georgia, USA
May 4th, 2017

Organizing Committee

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Contents

Introduction	1
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Agenda	2
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Talk Abstracts

- Obtaining exact transition state theory rates without perturbation theory by Rigoberto Hernandez 3
- Dividing surfaces of multi-dimensional driven systems by Jörg Main 4
- Molecular Dynamics and Transition State Theory for the Solvated Isomerization Reaction LiNC/LiCN by Rosa Mar ía Benito 6
- The Fokker-Planck equation for LiCN isomerization by Thomas Bartsch 8
- Frequency analysis of the laser driven nonlinear dynamics of HCN by Florentino Borondo 9
- Single and double ionization of Mg by electron impact by Jonathan Dubois 10
- Normally Hyperbolic manifolds in quasi-periodic systems by Rafael de la Llave 12

- Hyperbolic periodic orbits in nongradient systems and small-noise-induced metastable transitions by Molei Tao 13
- Computation of power expansions of Poincaré maps by Angel Jorba 15
- Computation of invariant manifolds related to hyperbolic fixed points of Poincaré maps by Marc Jorba-Cusco 16

Poster Abstracts

- A Neural Network Approach to Time-Dependent Dividing Surfaces by Philippe Schraft 17
- Transition State Theory for a driven spin system by Robin Schuldt 18

Introduction

The School of Mathematics at the Georgia Institute of Technology hosts the kickoff meeting for the European Union RISE grant “Stability and Transitions in Physical Processes (TraX).” The project aims at linking mathematicians, physicists and chemists to identify the universal mechanisms behind dynamical transition processes. The collaborative project is coordinated by the School of Mathematics of Loughborough University, and involves the Department of Mathematics of the University of Barcelona, the Institut de Mathematiques de Marseille (CNRS / Aix Marseille University), the Physics Department of the Polytechnic University of Madrid, the Chemistry Department at the Universidad Autónoma of Madrid and the Physics Department at the University of Stuttgart. The third country partners are Georgia Institute of Technology, represented by the School of Mathematics and the School of Physics and Johns Hopkins University, represented by the School of Chemistry. More information about his meeting available at <http://traxkickoff.gatech.edu>.

Our sponsors



Agenda

We will convene at the School of Math in Skiles 005 at 8 am.

8:30-9:00 – Welcome by Dean Goldbart

9:00-9:30 - Rigoberto Hernandez

9:30-10:00 - Jörg Main

10:00-10:30 - Rosa María Benito

10:30-10:45 - Coffee break/ Poster session

10:45-11:15 - Thomas Bartsch

11:15-11:45 - Florentino Borondo

11:45-12:15 - Jonathan Dubois

12:15-1:45 - Lunch at First Place, on campus.

1:45-2:15 - Rafael de la Llave

2:15-2:45 - Molei Tao

2:45-3:00 - Coffee break/ Poster session

3:00-3:30 - Angel Jorba

3:30-4:00 -Marc Jorba-Cusco

4:00-5:00 –Poster session

4:00-7:00 - Steering committee meeting, in Skiles 114

8:00 - Dinner in the city.

Obtaining exact transition state theory rates without perturbation theory

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The rates of chemical reactions (or any activated process) are by definition determined by the flux of reactants (or initial states) that end up as products (or final states). Through the last hundred years of studies on reaction rate theory, it has become clear that this can be equated to the flux through any surface that divides reactants from products as long as only those trajectories that end up as products are included in the flux. Transition state theory (TST) ignores this last clause. It thereby overestimates the rate if any of the trajectories recross the dividing surface. However, its advantage is that it replaces a dynamical calculation with a geometric one. Through the variational principle or perturbation theory, however, one can construct non-recrossing dividing surfaces that lead to exact rates. These approaches are limited by the nature of the search space of surfaces and the reference dividing surface, respectively. We have recently discovered that the Lagrangian descriptor can be used to resolve the dividing surface directly [1]. We will further show the accuracy of the approach for barrierless reactions, model reactions, ketene isomerization and LiCN isomerization [2].

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- [1] A. Junginger and R. Hernandez, *J. Phys. Chem. B*, **120**, 1720 (2016).
[2] G. T. Craven and R. Hernandez, *Phys. Rev. Lett.* **115**, 148301 (2015).

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Dividing surfaces of multi-dimensional driven systems

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Dynamics between reactant and product basins are typically mediated by a rate-determining barrier at which a dividing surface can be attached. The transition state theory rate is the cumulative instantaneous flux through the transition state divided by the reactant population. It is exact only if it is free of recrossings at long time. This picture becomes more complicated as soon as the barrier position is time-dependent because its motion necessarily gives rise to recrossings across the fixed dividing surface. In one-dimensional systems, a non-recrossing time-dependent dividing surface can be attached to the so-called transition state trajectory which is a special unstable trajectory that always remains at the barrier top. We present the extension of the transition state trajectory formalism to systems with additional bath degrees of freedom. We demonstrate the general construction of this hypersurface in phase space using a minimization procedure of Lagrangian descriptors and apply it to a two-degree of freedom system with time-dependent model potential

$$V(x, y, t) = E_b \exp\left(-a [x - \hat{x} \sin(\omega_x t)]^2\right) + \frac{\omega_y^2}{2} \left[y - \frac{2}{\pi} \arctan(2x) \right]^2. \quad (1)$$

The dynamics simulation of particle ensembles provides a numerical demonstration that our dividing surface is recrossing-free and, therefore, leads to exact transition state theory rates [1]. The method should be applicable to, e.g., time-dependent molecular reactions or spintronic devices driven by tailored external fields or thermal noise.

[1] M. Feldmaier, A. Junginger, J. Main, G. Wunner, and R. Hernandez, *Phys. Rev. A*, submitted.

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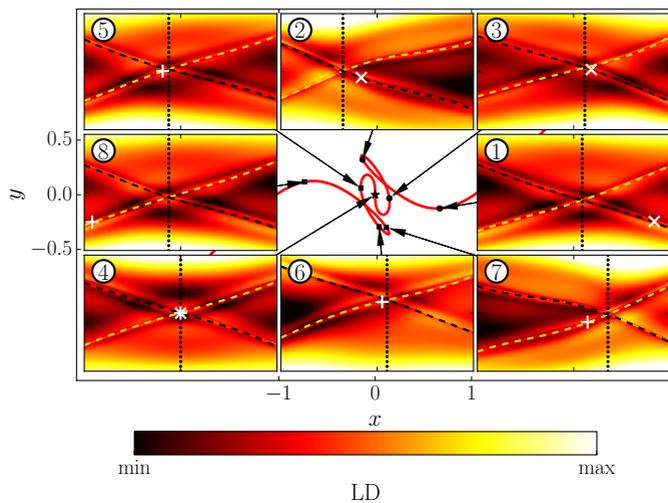


FIG. 1. Illustrative trajectory of a reactive particle undergoing multiple oscillations in the saddle region. Color maps of the Lagrangian descriptor surface at eight selected points (x, v_x) along the reaction coordinate are shown at fixed values of the bath coordinates (y, v_y) .

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. 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. This time-dependent TST is based on the identification of the phase space objects that act as separatrices for chemical reactivity. These structures, which are invariant manifolds, are attached to the transition state trajectory, a very particular trajectory that remains randomly moving or jiggling in the vicinity of the barrier top for all times. 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

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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 assessed by accurately reproducing the all-atom simulations for LiNC/LiCN.

The Fokker-Planck equation for LiCN isomerization

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The Fokker-Planck equation describes the time-evolution of the probability distribution in phase space of a stochastically driven system. It can be formulated as an eigenvalue problem in which the eigenvalues identify the time scales in the equilibration of the system.

Atomistic simulations of the isomerization dynamics of LiCN in an argon bath [1, 2] indicate that the system possesses a clear separation of time scales and an exponential approach to equilibrium even at high temperatures, where the thermal energy is comparable to or higher than the isomerization barrier. An analysis of the eigenvalues and corresponding eigenfunctions of the Fokker-Planck equation could explain why this is so. I will present preliminary results along these lines.

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- [1] P. L. García-Müller, F. Borondo, R. Hernandez, R. M. Benito: *Phys. Rev. Lett.* **101** (2008) 178302.
[2] P. L. García-Müller, R. Hernandez, R. M. Benito, F. Borondo: *J. Chem. Phys.* **137** (2012) 204301.

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Frequency analysis of the laser driven nonlinear dynamics of HCN

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We present at the conference a study the vibrational dynamics of a model for the HCN molecule in the presence of a monochromatic laser field. The variation of the structural behavior of the system as a function of the laser frequency is analyzed in detail using the smaller alignment index, frequency maps, and diffusion coefficients. It is observed that the ergodicity of the system depends on the frequency of the excitation field, especially in its transitions from and into chaos. This provides a roadmap for the possibility of bond excitation and dissociation in this molecule.

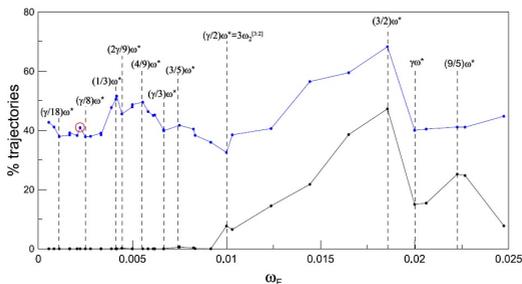


FIG. 1. Fraction of dissociative (black circles) and chaotic (blue circles) trajectories as a function of the laser frequency, ω_F . All peaks and valleys are found to be correlated with resonances between ω_F and $\omega^* = \omega_{1,2}^{[1:1]}$, as indicated by the labels, except for the case of the peak encircled in red, where the resonance condition corresponds to $\omega_F = (2/3)\omega_2^{[3:2]}$.

[1] A. Lopez-Pina, J. C. Losada, R. M. Benito, and F. Borondo, J. Chem. Phys. **145**, 244309 (2016).

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Single and double ionization of Mg by electron impact

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We consider electron impact-driven single and double ionization of magnesium in the energy range of 10 to 100 eV. Figure 1 schematically shows trajectories of the electrons during a double ionization of magnesium by electron impact. The impact electron (black), is sent, with an impact energy ϵ_0 , in the direction of a target, an atom Mg with its two outer shell electrons.

We use a Hamiltonian model to compute the cross sections associated with single and double ionization processes. We compare these cross sections with the experimentally measured ones [2]. The impact electron is labeled by $k = 0$, and the two outer shell electrons of Mg are labeled by $k = 1, 2$. The Hamiltonian of the system is

$$H = \sum_{k=0}^2 \left(\frac{|\mathbf{p}_k|^2}{2} - \frac{2}{\sqrt{|\mathbf{r}_k|^2 + a^2}} + \sum_{j>k} \frac{1}{\sqrt{|\mathbf{r}_k - \mathbf{r}_j|^2 + b^2}} \right). \quad (1)$$

Our classical Hamiltonian model of these (e,2e) and (e,3e) processes sheds light on their total cross sections and reveals the underlying ionization mechanisms. Two pathways are at play in single ionization: delayed and direct. During the direct ionization, the collision between the impact electron and one of the inner electrons causes immediate ionization. During the delayed ionization, the impact electron excites the atom, and the ionization occurs by chaotic diffusion. In contrast, only the direct process is observed in double ionizations, ruling out the excitation-autoionization channel. We observe two double ionization processes: Two-Step 1 (TS1) and Two-Step 2 (TS2) mechanisms. During the TS1 mechanism, the impact electron collides with only one of the inner electrons. The double ionization is caused by a second collision between the two inner electrons. During the TS2 mechanism, the impact electron collides with both of the inner electrons. We provide evidence that the TS2 mechanism predominates over the TS1 mechanism, in agreement with experiments [3].

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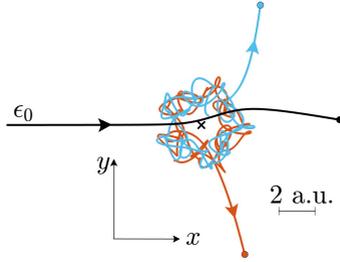


FIG. 1. Trajectory of each of the three electrons in configuration space during the double ionization of a target by electron impact. The impact electron is shown in black; the two electrons of the target, in red and blue. The position of the ionic core is shown by the cross.

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 [2] P. McCallion, M. B. Shah, and H. B. Gilbody, *J. Phys. B: At. Mol. Opt. Phys.*, **25**, 1051-1060 (1992).
 [3] C. Li, E. M. S. Casagrande, A. Lahmam-Bennani, and A. Naja, *J. Phys. B: At. Mol. Opt. Phys.* 45, 135201 (2012).

Normally Hyperbolic manifolds in quasi-periodic systems

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We present efficient numerical algorithms to compute quasiperiodic solutions and their invariant manifolds in quasiperiodic systems.

The algorithms are backed up by a-posteriori theorems that ensure their validity.

We have implemented these algorithms and have empirically discovered some phenomena that happen in the boundary of normally hyperbolic systems. Systems can lose normal hyperbolicity by *bundle collapse*: The Lyapunov exponents remain bounded away from zero, but the distance between the stable and unstable bundles goes to zero. We have found that this global bifurcation presents universal scaling relations.

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- [HdlL06a] À. Haro and R. de la Llave. Manifolds on the verge of a hyperbolicity breakdown. *Chaos*, 16(1):013120, 8, 2006.
- [HdlL06b] À. Haro and R. de la Llave. A parameterization method for the computation of invariant tori and their whiskers in quasi-periodic maps: numerical algorithms. *Discrete Contin. Dyn. Syst. Ser. B*, 6(6):1261–1300, 2006.
- [HdlL06c] A. Haro and R. de la Llave. A parameterization method for the computation of invariant tori and their whiskers in quasi-periodic maps: rigorous results. *J. Differential Equations*, 228(2):530–579, 2006.

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Hyperbolic periodic orbits in nongradient systems and small-noise-induced metastable transitions

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We consider how stochastic perturbations introduce new behaviors to differential dynamical systems. More specifically, we quantify how small white noises induce transitions between metastable states. Via maximizing transition probability characterized by Freidlin-Wentzell large deviation theory [1], it can be shown that these transitions utilize structures in certain deterministic systems, which may or may not be the original system with noise removed.

In gradient systems (i.e., reversible thermodynamics), metastable transitions were known to cross separatrices at saddle points. We investigate nongradient systems (which may no longer be reversible), and demonstrate a very different type of transitions that cross hyperbolic periodic orbits. Numerical tools for identifying such periodic orbits and computing the transition paths are described.

Below is an example, which is sheared Allen-Cahn SPDE on 2-torus

$$\phi_t = \kappa \Delta \phi + \phi - \phi^3 + c \sin(2\pi y) \partial_x \phi + \sqrt{\epsilon} \eta.$$

Figure 1 and 2 illustrate a hyperbolic periodic orbit in this system, which bifurcated from a saddle point as c increases, and a numerically obtained metastable transition.

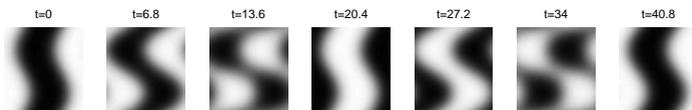


FIG. 1. Snapshots of a hyperbolic periodic orbit in sheared Allen-Cahn.

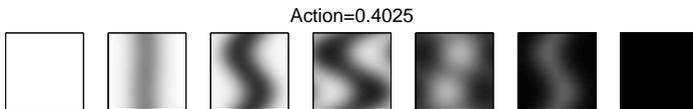


FIG. 2. A transition path that locally maximizes the transition probability, which crosses the separatrix at a point on a periodic orbit.

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- [1] Freidlin M.I., Wentzell A.D. (2012) Random Perturbations of Dynamical Systems. Springer, Berlin Heidelberg.

Computation of power expansions of Poincaré maps

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In this presentation we will introduce a computational technique (jet transport) to compute high order power expansions of Poincaré maps with respect to initial data and/or parameters. The method is based on the use of automatic differentiation techniques and we will show that it is efficient enough to be carried out even with extended precision arithmetic. As applications, we mention the are the effective computation of normal forms, centre manifolds and stable/unstable manifolds of periodic orbits.

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Computation of invariant manifolds related to hyperbolic fixed points of Poincaré maps

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Let $\mathcal{U} \subset \mathbb{R}^n$ be an open set and $f : \mathcal{U} \mapsto \mathbb{R}^n$ a diffeomorphism. Assume we have a method to compute, numerically, the image of a given point as well as its derivatives up to some degree. Then, we can use the parametrization method to compute parametrization of geometrical objects which are invariant under the dynamics induced by f . The idea is to solve, degree by degree, an invariance equation which depends on the inner dynamics on the desired object.

In this talk we will see how, using Jet transport, we can compute 1-D and 2-D invariant manifolds associated to a totally hyperbolic periodic orbit of a Hamiltonian system with two degrees of freedom and periodic time dependence. Specifically, we will explain how to compute the invariant manifolds of a fixed point of a suitable Poincaré map.

In this context, Jet transport becomes crucial. Jet transport is used here to get the derivatives of the Poincaré map at the fixed point and to perform, in a rather efficient way, composition of homogeneous polynomials.

Illustrative examples will be presented. We will discuss how a small ratio between the weak and strong eigenvalue brings a remarkable effect of propagation of errors. A solution for this problem is to use extended precision arithmetic.

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A Neural Network Approach to Time-Dependent Dividing Surfaces

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In a dynamical system, the transition between reactants and products is typically mediated by a barrier whose properties determine the corresponding rate. The latter is the flux through an appropriate dividing surface (DS) between these two regions and it is exact only if it is free of recrossings. For time-independent barriers, the DS can be attached to the top of the corresponding saddle point of the potential energy surface, and in time-dependent systems, the DS is a moving object itself. The precise determination of reaction rates, e. g. using transition state theory, requires the actual construction of a DS for a given saddle geometry which is, in general, a demanding methodical and computational task, especially in high-dimensional systems. Such complex, time-dependent, global, and recrossing-free DSs can be constructed as smooth and continuous hypersurfaces using neural networks, see Fig. 1. In this approach, the neural network uses the bath coordinates and time as input and it is trained such that its output provides the exact position of the DS along the reaction coordinate. A huge advantage of this procedure is that, once the neural is trained, the complete dynamics of the DS as well as a precise distinction between reactants and products is available for all possible system configurations, for all times, and with only little computational effort.

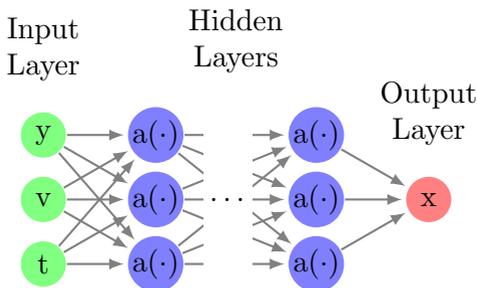


FIG. 1. Sketch of a simple feedforward neural network.

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Transition State Theory for a driven spin system

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As spintronics recently became a topic of interest, so did the general properties of spins. The basic process of spin flips seems closely related to that of a chemical reaction. An investigation of general transition dynamics with methods of Transition State Theory seems promising. As a general approach for spin systems, the Gilbert equation with damping

$$\dot{\mathbf{m}}(t) = \gamma(-\mathbf{m} \times \mathbf{H} + \alpha(\mathbf{m} \times \dot{\mathbf{v}})), \quad (1)$$

gives a semiclassical description of the respective magnetization dynamics. The included potential \mathbf{H} depends on the environment and external influences. The pinned layer model seems to offer for a potential, which allows two stable spin orientations that can be interpreted as up- and down-states. To allow for spin flips, a second order equation for the dynamics is needed. We present a model for a driven spin system, its properties and its investigation with methods of transition state theory and Lagrangian descriptors.

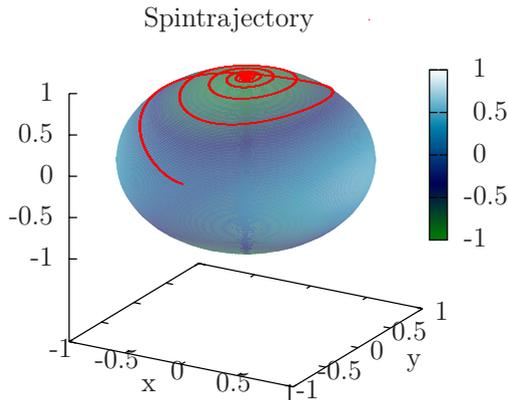


FIG. 1. Spin trajectory on the potential surface in coordinate-space.

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