Impenetrable Barriers in Phase-Space

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Dynamical systems theory is used to construct a general *phase-space* version of transition state theory. Special multidimensional separatrices are found which act as impenetrable barriers in phase-space between reacting and nonreacting trajectories. The elusive momentum-dependent transition state between reactants and products is thereby characterized. A practical algorithm is presented and applied to a strongly coupled Hamiltonian.

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Introduction.—Transition state theory (TST) was developed in the 1930s [1] as a way to determine absolute chemical reaction rates. An essentially thermodynamic picture emerged from the original research of Eyring [2] and this continued to be the dominant formulation of the theory for many decades. In parallel with Eyring's work, a dynamical picture was also being developed by Wigner [3] and this turns out to have considerable advantages. Not the least of these is that Wigner's formulation quickly leads to the recognition that the transition state (TS) is actually a general property of all dynamical systems, provided that they evolve from "reactants" to "products." The TS, therefore, is not confined to chemical reaction dynamics [4], but it also controls rates in a multitude of interesting systems, including, e.g., the rearrangements of clusters [5], the ionization of atoms [6], conductance due to ballistic electron transport through microjunctions [7], and diffusion jumps in solids [8]. Since transition state theory is fundamental for transformations in n degree-of-freedom systems, the work summarized here represents a general formulation of the nonlinear dynamics and geometry of classical reaction dynamics. It hinges on finding, for the first time, the dynamically exact higher-dimensional structures (separatrices, dividing surfaces) which regulate transport between qualitatively different states (reagents and products) in three or more degrees of freedom.

Stated succinctly, TST postulates the existence of a minimal set of states that all reactive trajectories must cross and which are never encountered by nonreactive trajectories. While the original idea of a TS was expressed as a dividing surface in *coordinate* space, Wigner recognized [9] that a rigorous treatment must seek dividing surfaces in *phase* space which separate reactants from products and which no trajectory passes through more than once. Enforcing this "no recrossing" requirement has been a major obstacle to applying TST in strongly coupled, multidimensional systems. Consequently, TST has remained a configuration-space theory that has further been confined to low dimensions for which the dividing surfaces can be found in practice.

The problem solved in this Letter is the construction of hypersurfaces of no return in the *phase-space* of strongly coupled, multidimensional systems. Our solution leads naturally to the multidimensional generalization of a saddle "point" and its associated separatrices.

Until very recently, neither theoretical understanding nor computing power was adequate to explore phase-space transport beyond the well-known two degrees-of-freedom ("2dof") limit [10]. However, with recent advances in dynamical systems theory [11], especially concerning normally hyperbolic invariant manifolds (NHIM) [12], the classical theory of chemical reactions can now be anchored rigorously in nonlinear dynamics. Indeed, this Letter makes explicit the long-sought classical structures that act as transition states in phase-space beyond 2dof. As we will show, the rigorous way to describe the notion of a "barrier" in phase-space is through invariant manifolds. "Invariance" signifies that trajectories starting on the manifold must remain on the manifold for the future and throughout the past. Hence, no trajectory can cross an invariant manifold. These manifolds, as indeed all other multidimensional structures in this Letter, become familiar objects when viewed in 2dof: For example, NHIM's reduce to none other than periodic orbits. Our treatment is general, and because it relies on recent advances in dynamical systems theory, we provide a "user's guide" which we then apply to a realistic system. The following review of 2dof systems will set the terms for extension to more degrees of freedom.

Lower-dimensional theory.—Current understanding of the transition state as a geometrical structure in 2dof systems has been greatly aided by the discovery [13] that projection of an unstable periodic orbit into configuration space defines a surface separating reactants and products and is therefore a "periodic orbit dividing surface" or PODS. In phase-space, the stable and unstable manifolds of this orbit partition the energy shell. This partitioning is invariant and separates the reactive and nonreactive dynamics. It is not generally recognized that the defining periodic orbit also bounds a surface in the energy shell.

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This surface partitions the energy shell into reactant and product regions and is not invariant. Defined in this way the surface is a surface of no return [6] and thus constitutes the phase-space transition state. It also provides an unambiguous measure of the flux between reactants and products [14–16]. These facts will be useful when we present the multidimensional versions of these structures.

Beyond 2dof, periodic orbits, and their stable and unstable manifolds [11], do not have the right dimensionality to partition the energy shell. Nevertheless, early insights [17] and recent numerical evidence from molecular dynamics calculations [5] suggest the existence of higher-dimensional structures with many of the regulatory features of the PODS, and it is precisely these phase-space structures which will be exhibited in this Letter.

Phase-space structure and the transition state for n-degree-of-freedom nonlinear Hamiltonians.—Consider an arbitrary Hamiltonian vector field, and suppose it has an equilibrium point at which the matrix associated with the linearization of the Hamiltonian vector field about the equilibrium point has eigenvalues $\pm i\omega_j$, $j = 1, \ldots, n-1$, and $\pm\lambda$. Moreover, assume that the submatrix corresponding to the imaginary eigenvalues is semisimple (i.e., the complexification is diagonalizable). Using Hamiltonian normal form theory [18], one can construct a sequence of local, nonlinear transformations of the coordinates that transform the Hamiltonian into

$$\begin{aligned} H = & \sum_{i=1}^{n-1} \frac{\omega_i}{2}\,(p_i^2 + q_i^2) + \lambda q_n p_n \\ & + f_1(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}, \mathcal{I}) \\ & + f_2(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}), \end{aligned} \tag{1}$$

up to arbitrarily high order where $(q_1, \ldots, q_n, p_1, \ldots, p_n)$ denote $2n$-dimensional canonical coordinates, $\mathcal{I} \equiv p_n q_n$ and f_1, f_2 are at least third order, i.e., they are responsible for the nonlinear terms in the Hamiltonian vector field, and $f_1(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}, 0) = 0$. This local result is valid in the neighborhood of the equilibrium point of center $\otimes \cdots \otimes$ center $\otimes$ saddle type [18]. However, once the phase-space structure is established locally, it can be continued numerically outside of the local region. In the energy domain, this continuation is valid up to the next bifurcation of phase-space structure.

The simplest n degree-of-freedom *linear* Hamiltonian system with a saddle,

$$H = \frac{1}{2}\sum_{i=1}^{n-1}(\,p_i^2 + \omega_i^2 q_i^2) + \frac{1}{2}\,p_\xi^2 - \frac{\kappa^2}{2}\,\xi^2 \tag{2}$$

(which consists of $n-1$ uncoupled linear oscillators and an uncoupled degree-of-freedom consisting of a saddle point) can be obtained from the linear part of (1) by a simple rotation in phase-space. In the language of reaction dynamics, the coordinates (ξ, p_ξ) are known as the reaction coordinates, whereas the remaining coordinates describe the "bath." In the ξ-p_ξ phase portrait, when the saddle is at the origin, trajectories are said to be reacting if ξ changes sign. We will show how to generalize this simple case to a fully nonlinear setting.

Returning to (1), the corresponding Hamiltonian vector field is given by

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} = \omega_i p_i + \frac{\partial f_1}{\partial p_i} + \frac{\partial f_2}{\partial p_i}, \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i} \\ &= -\omega_i q_i - \frac{\partial f_1}{\partial q_i} - \frac{\partial f_2}{\partial q_i}, \quad i = 1, \ldots, n-1, \\ \dot{q}_n &= \frac{\partial H}{\partial p_n} = \lambda q_n + \frac{\partial f_1}{\partial \mathcal{I}}\,q_n, \\ \dot{p}_n &= -\frac{\partial H}{\partial q_n} = -\lambda p_n - \frac{\partial f_1}{\partial \mathcal{I}}\,p_n, \end{aligned} \tag{3}$$

where the last two equations denote the motion in the reaction coordinates. The rest refer to dynamics in the bath modes.

A multidimensional saddle "point".—The dynamics occurs in the $2n$-1-dimensional energy surface given by setting H in (1) to be a positive constant h. If we set $q_n = p_n = 0$ in (3), then $\dot{q}_n = \dot{p}_n = 0$. Therefore $q_n = p_n = 0$ is a $2n$-2 dimensional invariant manifold. Its intersection with the $2n$-1-dimensional energy surface, denoted $\mathcal{M}_h^{2n-3}$, is given by

$$\begin{aligned} \mathcal{M}_h^{2n-3} = & \sum_{i=1}^{n-1} \frac{\omega_i}{2}\,(\,p_i^2 + q_i^2) \\ & + f_2(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}) \\ = & \; h = \text{const} > 0\,. \end{aligned} \tag{4}$$

Regardless of its stability properties, or the size of the nonlinearity, (4) is always an invariant manifold. Moreover, it is an example of a "normally hyperbolic invariant manifold" (NHIM) [12]. Normal hyperbolicity means that, under the linearized dynamics, the growth and decay rates of tangent vectors normal to the manifold (the "reaction") dominates the growth and decay of tangent vectors tangent to the manifold. Hence, NHIM's are higher-dimensional analogs of saddle points ("saddle spheres"). In our case the (q_n, p_n) coordinates describe the directions normal to (4). One key advantage of the structure of the normal form is that it separates, as much as possible, the dynamics normal to $\mathcal{M}_h^{2n-3}$ and the dynamics tangent to $\mathcal{M}_h^{2n-3}$.

Should the Hamiltonian be given in the form of (1), a preliminary local transformation is not required. The

manifold (4) is invariant regardless of the size of the nonlinearity. Moreover, it is also of saddle type with respect to stability in the transverse directions [19].

However, a key feature of NHIM's is that they persist under perturbation. Therefore, if we first need to obtain the form of (1) by applying normal form theory, then we are restricted to a sufficiently small neighborhood of the equilibrium point. In this case the nonlinear terms are much smaller than the linear terms. Therefore, (4) is a *deformed* saddle sphere (since the saddle-point dynamics decouple from the oscillatory dynamics at the linear level) and has $2n$-2 dimensional stable and unstable manifolds in the $2n$-1 dimensional energy surface [20]. Recent discoveries concerning regularity in complex reaction paths [5], anticipated by Miller [17] and executed by Hernandez and Miller [21], suggest that the decoupling of the reaction degree-of-freedom from the bath, and the reduction of complex reactive Hamiltonians to (1), is *general*.

Multidimensional separatrices.—Another advantage of computing the normal form is that the unstable and stable manifolds of $\mathcal{M}_h^{2n-3}$ are known explicitly:

$$W^u(\mathcal{M}_h^{2n-3}) = \Bigg\{(q_1,\ldots,q_n,p_1,\ldots,p_n) \;\Bigg|\; \sum_{i=1}^{n-1}\frac{\omega_i}{2}(p_i^2+q_i^2) + f_2(q_1,\ldots,q_{n-1},p_1,\ldots,p_{n-1}) = h = \text{const} > 0, p_n = 0\Bigg\}, \tag{5}$$

and $W^s(\mathcal{M}_h^{2n-3})$ is obtained by setting $q_n = 0$ instead of $p_n = 0$. Hence, the stable and unstable manifolds of the sphere have the structure of $\mathcal{M}_h^{2n-3} \times \mathbb{R}$ [22]. They act as invariant (impenetrable) boundaries between reactive and nonreactive trajectories, as can be seen by referring to (3) (see also [23]).

Multidimensional phase-space transition states.—Consider the hypersurface constructed by setting $q_n = p_n$. On the energy surface this gives

$$\sum_{i=1}^{n-1}\frac{\omega_i}{2}(p_i^2+q_i^2) + \lambda p_n^2 + f_1(q_1,\ldots,q_{n-1},p_1,\ldots,p_{n-1},p_n^2) + f_2(q_1,\ldots,q_{n-1},p_1,\ldots,p_{n-1}) = h = \text{const}. \tag{6}$$

This is a $2n$-2-dimensional surface that can be divided into two halves: $p_n > 0$ and $p_n < 0$. Each of these halves corresponds to a multidimensional surface: the $p_n > 0$ half corresponds to the surface that is crossed when the system passes from reactants to products and, consequently, is the multidimensional phase-space transition state. The boundary of this surface, given by $p_n = 0$, corresponds to the invariant manifold $\mathcal{M}_h^{2n-3}$, which is the NHIM. Its role is analogous to that of the orbit used to define the phase-space transition state in 2dof systems; that is, it bounds the multidimensional surface defining the phase-space transition state. Indeed, it acts as the PODS does in 2dof systems because by using Stokes' theorem, one can show that the flux through the transition state is equal to the flux through the boundary [24]. It can be proven that (6) is *locally* a surface of no return for the trajectories of Hamilton's equations given in (3). "Locally" means that there is a neighborhood of (6) that trajectories starting on (6) [except those starting on the $2n$-3 dimensional invariant manifold (4)] must leave before they can possibly reintersect (6).

Search algorithm for the transition state.—Our formalism enjoys the great advantage of boiling down to a practical algorithm:

(1) For a given Hamiltonian, find an equilibrium point for which the eigenvalues of the matrix associated with the linearization about the equilibrium point have the form described in Eq. (1).

(2) Transform the Hamiltonian to the normal form described above up to the desired degree of accuracy using a symbolic manipulator. The Hamiltonian is now in a new coordinate system that we will call the "normal form coordinates."

(3) Our arguments above show how to identify the transition state (6) and the higher dimensional analogs of the stable and unstable manifolds [22] that mediate the reaction in the normal form coordinates.

(4) These structures can be visualized in the original coordinates by using the inverse of the normal form transformation, which is computed symbolically along with the normal form transformation.

(5) Integrals of flux across the transition state can be computed in the normal form coordinates since the transformation between the original coordinates and the normal form coordinates is symplectic, hence volume preserving.

Field-induced ionization of a hydrogen atom.—In crossed electric and magnetic fields, the ionization of hydrogen atoms [25] over the so-called Stark saddle is regulated by an unusual phase-space transition state [6] in 2dof. We now apply our search algorithm to find the transition state in the full problem. The Hamiltonian in Cartesian coordinates scaled by the magnetic field is [6]

$$H = \frac{1}{2}(P_1^2+P_2^2+P_3^2) - \frac{1}{R} + \left[\frac{1}{2}(x_1P_2 - x_2P_1) + \frac{1}{8}(x_1^2+x_2^2) - \varepsilon x_1\right], \tag{7}$$

where $R = \sqrt{x_1^2+x_2^2+x_3^2}$. After translating the fixed point $x_s = -\varepsilon^{-1/2}$ to the origin, the Hamiltonian becomes

$$H = \frac{1}{2}(P_1^2 + P_2^2 + P_3^2) - \frac{1}{R} + \frac{1}{2}(x_1P_2 - x_2P_1) + \frac{1}{8}(x_1^2 + x_2^2) - \varepsilon x_1 - \varepsilon^{1/2}, \quad (8)$$

where $R = [(x_1 - x_s)^2 + x_2^2 + x_3^2]^{1/2}$ in the new coordinates. The eigenvalues of the matrix associated with linearization about the origin consist of two imaginary and one real pair, thereby making the origin center-center-saddle, appropriate for our methods. We seek a normal form expansion of the Hamiltonian up to a finite order N, namely $H = \sum_{n=2}^{N} H_n$ (where H_n denotes a homogeneous polynomial in six variables of degree n). Since the new origin is an equilibrium point, the first order terms vanish. The second order terms are

$$H_2 = \frac{1}{2}(P_1^2 + P_2^2 + P_3^2) + \frac{1}{2}(x_1P_2 - x_2P_1) + \left(\frac{1}{8} - \varepsilon^{3/2}\right)x_1^2 + \left(\frac{1}{8} + \frac{1}{2}\varepsilon^{3/2}\right)x_2^2 + \frac{1}{2}\varepsilon^{3/2}x_3^2. \quad (9)$$

Next we construct a real symplectic change of variables that brings (9) into the real normal form

$$H_2 = \mu x_1P_1 + \frac{\omega_1}{2}(x_2^2 + P_2^2) + \frac{\omega_2}{2}(x_3^2 + P_3^2). \quad (10)$$

For the calculation of the higher order terms we fix the electric field at the experimentally interesting value of $\varepsilon = 0.58$ [25]. In the normal form, the saddle variables (x_1, P_1) appear only as a product, as (1) requires. This expansion, the three-dimensional NHIM restricted to the energy surface (4), the four-dimensional stable and unstable manifolds restricted to the energy surface (5), and the transition state (6) can all be computed to arbitrarily high order, and then mapped back into the original coordinates via the inverse of the normal form transformation. The complete results will be reported elsewhere.

Finally, when we transform the Hamiltonian into action-angle variables, the resulting normal form is integrable to arbitrarily high accuracy (since the two oscillatory frequencies are nonresonant for $\varepsilon = 0.58$). This and other physical examples we researched (but omit for lack of space) explain why trajectories near the saddle are observed to be regular [5].

Conclusions and outlook.—In this Letter we have given the analytical and computational framework for analyzing phase-space transport in systems with three or more degrees of freedom when there is a single saddle point. When saddle points proliferate, each NHIM needs to be treated separately and the one with the minimum flux is the transition state.

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[19] This can be seen by examining (3). On $q_n = p_n = 0$ the transverse directions, i.e., q_n and p_n, are still of saddle type (more precisely, they grow and decay exponentially).
[20] At each point on the $2n$-3 dimensional NHIM there is an exponentially decaying and exponentially growing direction. The general theory of NHIM's tells us that this gives rise to $2n$-2 dimensional stable and unstable manifolds.
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