CHAPTER 2

REGULARITY IN CHAOTIC TRANSITIONS ON TWO-BASIN LANDSCAPES

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I. INTRODUCTION

Let us begin with a simple, but still unresolved question, that is, "Why can a reacting system climb through the saddle from a basin to one another?" Figure 1 schematically shows representative reactive and nonreactive, saddle crossing trajectories that were initiated from the reactant well. Although both trajectories have sufficient total energy larger than the saddle point energy, one will climb
through the product well but the other will go back to the original, react well. This implies for classical systems that the condition for the react systems to possess a total energy larger than the saddle point energy is necessary and not sufficient. Then, what are the necessary and sufficient conditions for a reacting system to climb through from one basin to another? This is one of the central issues we want to focus on in the present chapter.

Dynamics on two-basin potential energy surfaces has been extensively explored in the context of chemical reactions over the past several decades [14]. Transition state theories (TST), first developed by Eyring [3] and Evans and by Wigner [5] in the 1930s, have had great success in elucidating absolute reaction rates of chemical reactions. All the various forms of (classical) TST is based on two fundamental assumptions:

**No-Return Assumption.** A dividing hypersurface—that is, the transition state (TS)—exists (generally in phase space) through which a reacting species should pass only once on the way from the reactants to the products before being “captured” in the products. Note that this implicitly requires the hypersurface can decompose the space into two distinct regions: reactant and product. This, in turn, implies that for Hamiltonian systems with $n$ degrees of freedom, the TS must be of co-dimension one—that is, $(2n - 2)$ dimension—on the $(2n - 1)$-dimensional equi-energy hypersurface of the chosen $2n$-dimensional phase space $\mathbb{R}^{2n}$ [15].

**Local Equilibrium Assumption.** There exists a quasi-equilibrium between the reactant and a system crossing the TS from the reactant to the product. This precise representation was taken from an insightful article on the observability of the invariant of motion in the transition state by Marcus [16]: The motions along the reaction coordinate at the transition state wa.
postulated in the original TST to be one-dimensional, translational
motions. This implies that the reactive degree of freedom is assumed to
be dynamically separable from the other degrees of freedom at the
transition state. Although many literatures have often described to assume
the quasi-equilibrium as "occurring between the reactant and the TS
itself," rigorously speaking, there is no source to yield a quasi-equilibrium
between the reactant and a dynamically separable, elusive state. In the
other words, the reacting systems move about "ergodically" within the
reactant well more quickly than finding en route to the TS. (Readers will
see in this chapter that this is a generic consequence inherent to the
first-rank saddles up to moderately high energies if the TS is defined not
in the configurational space but in the phase space.)

However, few theories have clarified the physical conditions needed to
validate these fundamental assumptions—that is, the necessary and sufficient
additions to use this description for a reacting species climbing through the
dele from the reactant to the product well. This is one of the most elusive
pects in justifying the application of TST to a multitude of reacting systems.
In practice, one has often defined the TS in configurational space with an ad hoc
section factor, called the transmission coefficient $\kappa$, to take into account that
the system of interest actually makes more than one crossing of the
surface presumed either to be the desired dividing surface or one that
the system finds en route to the TS without moving about "ergodically" in the
actant well.

In the developments [17–24] of classical unimolecular reaction rate theories,
there has been a great improvement of our understanding of the definability of
such a general, no-return dividing hypersurface from the viewpoint of the
dynamical structure of the phase space in chemical reactions. Davis and Gray
[7] first showed in the late 1980s that in Hamiltonian systems with two degrees
of freedom (DOFs), a TS always free from recrossings can be defined as the
separatrix in the Poincaré section formed by taking the union of segments of the
stable and unstable manifolds, and the transport across the TS is interpreted as
mediated through the turnstile lobes bounded by two homoclinic intersection
points. Gillilan and Ezra [20] analyzed the predissociation of van der Waals
complex He–I with three DOFs—that is, the four-dimensional Poincaré section.
They demonstrated, as predicted by Wiggins [21], that the occurrence of
homoclinic tangency inherent to higher-dimensional systems (> two) hampers
the construction of the hypersurface dividing the bound complex reactant region
from unbound trajectories. Toda [22–24] noticed that the homoclinic tangency
leads to a bifurcation of the phase-space reaction path with a transition between
two topologically distinct chaotic regimes. Thus, the Davis–Gray separatrix
transition state depends crucially on the Poincaré section having only two
dimensions. No general, no-return dividing hypersurface has been found yet for systems of higher dimensionality. In other words, it is still an unresolved open problem to determine the circumstances in which such a hypersurface would persist, if it exists, or would be mined in the chaotic thermal bath of multidimensional systems.

Focusing on regulation of trajectories in the vicinity of the saddle points on potential energy surfaces, several theoretical and experimental developments have shed light on mechanics of passage through the region of a potential saddle for higher-dimensional systems. Indicative symptoms of local regularity near the saddles appeared in theoretical studies of small atomic clusters by Berry and co-workers [25–31] that compared local Liapunov functions and Kolmogorov entropies in saddle regions with those in other regions of potential surfaces. Evidence appeared also in experiments by Lovejoy and co-workers [32,33] on decomposition of vibrationally excited ketene that showed rates with quantized steps; Marcus suggested that this could be a signature of existence of approximate invariants of motion in the TS [16].

De Leon and co-workers [34–37] established an elegant reaction theory for a system with two DOFs, the so-called reactive island theory to mediate reactions through cylindrical manifolds apart from the saddles. Their original algorithm depends crucially on the existence of pure unstable periodic orbits in the nonreactive DOFs in the region of the saddles and did not extend to systems with many DOFs.

Recently, Komatsuzaki and Berry revealed [38–45] using classical isomerization of a 6-atom Lennard-Jones cluster that at least three distinct energy regimes of dynamical behavior, so-called quasi-regular, semi-chaotic, and fully developed chaotic regimes, exist in the region of a saddle of strongly coupled, many particle Hamiltonian systems. These are distinguished by the extent of regularity of their dynamics. Up to energies high enough to make the system manifestly chaotic, approximate invariants of motion associated with a reaction coordinate in the phase space imply a multidimensional dividing hypersurface that is free from recrossings occurring in that regime even in a sea of chaos. Their technique relies on the application of Lie canonical perturbation theory [46,47] (with algebraic quantization [48–50], if necessary), a classical analog of Van Vleck perturbation theory [51,52], for the region of potential saddles. This provides us with the natural reformulation [38,39] of the conventional TST based on that hypersurface in multidimensional phase space, which gives us better classical reaction rates of multidimensional systems. They presented a practical algorithm to visualize the dividing hypersurface in the multidimensional phase space of a given system [40,41], illuminated a new type of phase space bottleneck that emerges as the total energy and mode-coupling increase, which keeps a reacting system increasingly trapped in the region of a saddle [42,43], and established a strong propensity rule and corresponding
formula for transitions of chemical reactions which enables us to predict \emph{a priori} whether the system climbs through the saddle to the product or returns to its original state [45].

The earlier work of Wiggins [21,53] provides a firm mathematical framework for many-dimensional phase space transport, based on the notion of a normally hyperbolic invariant manifold (NHIM) and its stable and unstable manifolds as the appropriate generalization of the concept of “saddle” and “separatrices” on a multidimensional phase space. However, the major technical obstacle preventing its implementation has been the lack of an algorithm for searching arbitrary NHIMs in realistic multidimensional systems. As shown by Komatsuzaki and Berry, Lie transforms provide one of the most powerful techniques to extract a NHIM at least in the region of saddles from many-dimensional phase space. Recently, Uzer et al. [54] applied the Lie transformation to the vicinity of a saddle for a hydrogen atom in crossed electric and magnetic fields containing significant Coriolis interactions (a 3-DOFs system) and provided a detailed description of the (local) geometric structure of chemical reactions in multidimensional phase space. Wiggins et al. [15] presented a mathematical foundation of the robust persistence, in each order, of the invariant of motion along the phase-space reaction coordinate.

In this chapter, we briefly survey our recent findings on the mechanism for a reacting species to climb through the saddle and its relevance to the underlying geometric structure of the phase space. We focus on describing the concept, sacrificing mathematical rigor. (Readers can refer to our recent review article [41] for the mathematical description and also the articles by others [55–58] in this volume of \emph{Advances in Chemical Physics}.) In another article in this volume [59], one of the authors reviews several kinds of strange, cooperative dynamical behavior observed through structural transitions on multibasin landscapes for liquid water and proteins and discusses how such a regulatory structure through a “reaction bottleneck” may be generic irrespective of the size of the systems and “ruggedness” of potential energy surfaces.

II. DYNAMICAL REGULARITY IN THE REGION OF SADDLES

Suppose that Hamiltonian \( H(p,q) \) is expressed in a region around a saddle point of interest as an expansion in a small parameter \( \epsilon \), so that the zero-order Hamiltonian \( H_0 \) is regular in that region; specifically, it is written as a sum of harmonic-oscillator Hamiltonians. Such a zero-order system is a function of action variables \( J \) of \( H_0 \) only, and it does not depend on the conjugate angle variables \( \Theta \). The higher-order terms of the Hamiltonian are expressed as sums of
cubic, quartic, and so on, terms in the normal coordinates of the system, a saddle [9,38,39].

\[
H = H_0 + \sum_{n=1}^{\infty} e^n H_n
\]

\[
H_0 = \frac{1}{2} \sum_j \left( p_j^2 + \omega_j^2 q_j^2 \right) = H_0(\mathbf{J})
\]

\[
\sum_{n=1}^{\infty} e^n H_n = \epsilon \sum_{j,k,l} C_{jkl} q_j q_k q_l
\]

\[
+ e^2 \sum_{j,k,l,m} C_{jklm} q_j q_k q_l q_m + \cdots = \sum_{n=1}^{\infty} e^n H_n(\mathbf{J}, \Theta)
\]

Here, \( q_j \) and \( p_j \) are the \( j \)th normal coordinate and its conjugate momentum, respectively; \( \omega_j \) and \( C_{jkl} \), \( C_{jklm} \), \ldots are, respectively, the frequency of the \( j \)th mode, the coupling coefficient among \( q_j \), \( q_k \), and \( q_l \) and that among \( q_j \), \( q_k \), \( q_l \), and \( q_m \), and so forth. We denote hereinafter a reactive DOF, "1", whose fundamental frequency \( \omega_1 \) is pure imaginary, while the frequencies \( \omega_n \) of the other "bath" modes \( B \) are real. An early insight by Hernandez and Miller [60] in their semiclassical theory based on Van Vleck perturbation theory and recent classical chemical reaction theory based on Lie canonical perturbation theory by Komatsuzaki and Berry [38–45] show that there robustly exists an invariant of (classical) action associated with the phase-space reaction coordinate buried in a sea of chaos for strongly coupled many-body systems in the region of the first-rank saddles. This is due to the generic fact that an arbitrary combination of modes cannot satisfy the resonance conditions if one mode has an imaginary frequency, included in the combination, that is,

\[
\left| \sum_{k=1}^{n} n_k \omega_k \right| \geq |\omega_1| > O(e^n)
\]

for arbitrary integers \( n_k \) with \( n_1 \neq 0 \). This implies that one can generally find a nonlinear, canonical transformations of the coordinates to transform nonintegrable Hamiltonian \( H(\mathbf{p}, \mathbf{q}) \) into a new form:

\[
\tilde{H}(\tilde{\mathbf{p}}, \tilde{\mathbf{q}}) = \tilde{H}_0(\tilde{\mathbf{J}}) + \sum_{n=1}^{\infty} e^n \tilde{H}_n(\tilde{J}_1, \tilde{\xi}_n)
\]

in the vicinity of the saddles up to arbitrarily high order [15,44,45,54]. Here \( (\tilde{\mathbf{p}}, \tilde{\mathbf{q}}) \) are new canonical variables, \( (\tilde{\mathbf{J}}, \tilde{\Theta}) \) their action-angle variables, and \( \tilde{\xi}_n \)
sents those of bath modes \( (\mathbf{J}_B, \mathbf{\Theta}_B) \), collectively. The phase-space reaction
lineate \( \hat{q}_1 \) and momentum \( \hat{p}_1 \) obeys
\[
\ddot{q}_1(p, q) + \frac{\dot{\omega}_1}{\omega_1} \dot{q}_1(p, q) = \Gamma, \quad \ddot{p}_1(p, q) = \frac{\partial H}{\partial q_1}(p, q)
\]  
(6)

\( \Gamma \) is region of any first-rank saddle [44], where
\[
\Gamma = \frac{\dot{\omega}_1}{\omega_1} \dot{q}_1(p, q) = \omega_1(J_1, \xi_{\mathbf{g}}) = \frac{\partial H(J_1, \xi_{\mathbf{g}})}{\partial J_1}
\]  
(7)

d \( \dot{\xi}_t \) represent the first and second derivatives of \( x \) with respect to time \( t \). The
\( J_1, \xi_{\mathbf{g}}(t) \) depends on time \( t \) only through bath modes \( \xi_{\mathbf{g}}(t) \) because \( \dot{J}_1 \) is

...
Figure 2. The projections of a reactive, "recrossing" trajectory onto the configurational space and the phase space (see text for details).

Figure 3. The projection of a nonreactive "recrossing" trajectory onto the configuration space and the phase space (see text for details).
We derived a dynamical propensity rule for transitions as follows: From Eq. (6), one can derive an approximate analytical form for \( \bar{q}_1(p, q) \) [44,45]:

\[
\bar{q}_1(p(t), q(t)) = \frac{\alpha}{2} e^{\int_0^t |\bar{a}(r)| dr} + \frac{\beta}{2} e^{-\int_0^t |\bar{a}(r)| dr}
\]

\[
\approx \frac{\alpha}{2} e^{\int_0^t |\bar{a}(r)| dr} + \frac{\beta}{2} e^{\int_0^t |\bar{a}(r)| dr}
\]

\[
\alpha = \bar{q}_1(t_0) + \frac{\bar{p}_1(t_0)}{|\alpha_1|}, \quad \beta = \bar{q}_1(t_0) - \frac{\bar{p}_1(t_0)}{|\alpha_1|}
\]

where constant coefficients \( \alpha \) and \( \beta \) can be estimated from \( \bar{q}_1(p(t_0), q(t_0)) \) and \( \bar{p}_1(p(t_0), q(t_0)) \) at any arbitrary time \( t_0 \) in the region of the saddle. This enables us to predict a priori whether the system climbs through the saddle to the product, or returns to its original state, and tell us the physical foundation of why and how the system traverses the saddles from reactant to product states; if the trajectories have crossed a configurational dividing surface \( S(q_1 = 0) \) at time \( t_0 \) with \( \alpha > 0 \), the final state has already been determined at “the time \( t_0 \) when the system has just left the \( S(q_1 = 0) \)” to be a stable state directed by \( \bar{q}_1 > 0 \) (let us denote that state as the product state). Similarly, from only the phase-space information at \( t = t_0 \) (the sign of \( \beta \)), one can infer whether the system on \( S(q_1 = 0) \) at time \( t_0 \) has climbed from either stable state—that is, reactant or product.

The dynamical propensity rule for (forward) transitions is derived as

\[
\text{"If } \bar{q}_1(t_0) > -\frac{\bar{p}_1(t_0)}{|\alpha_1|} \quad \text{then } \bar{q}_1(t_0) < -\frac{\bar{p}_1(t_0)}{|\alpha_1|} \quad \text{the system will go through to the product (return to the reactant)."
\]

III. GEOMETRIC ASPECTS OF THE PHASE SPACE

Figure 4 shows a schematic portrait of the phase space flows (denoted by arrows) in the \( (\bar{q}_1(p, q), \bar{p}_1(p, q)) \) plane and the caricature of the corresponding

![Figure 4](image-url)
Figure 5. The distributions of the recrossing trajectories over configurational surface $S(q_1 = 0)$ at time $t = 0$ on the phase-space planes $(p_{1\text{th}}(p, q), q_{1\text{th}}(p, q))$ at $E = 0.5e$, where most modes are strongly chaotic—except $q_1(p, q)$. (a) First and (b) second orders: The circle and triangle symbols denote the system trajectories having negative and positive incident momenta $p_1(t = 0)$ on the $S(q_1 = 0)$, and the open and filled symbols denote those whose final states were predicted correctly and falsely by Eq. (11), respectively [45].

trajectories on the potential energy surfaces. Eq. (11) tells us that if one divides the phase space into four domains using the stable and unstable invariant manifolds to and from the unstable fixed point $q_1 = p_1 = 0$, all the system trajectories classified at any time (e.g., $t = 0$), into the domains 1 and 2 should eventually go into the product state, and those classified into the domains 3 and 4 go into the reactant state. While the former and latter domains could be regarded, respectively, as “reactive” and “nonreactive” in elucidating the fate of reactions after the system leaves $S(q_1 = 0)$, all the system trajectories classified in domain 2 or domain 4 never cross through the phase-space dividing hypersurface $S(q_1(p, q) = 0)$; that is, these trajectories do not correspond to reactions.

Up to moderately high energy ($\sim 179\%$) of the activation barrier for reactant $\rightarrow$ product in the $\text{Ar}_g$ isomerization reaction, the rates of most trajectories can be predicted more accurately by Eq. (11) as the order of perturbation calculation increases, except just in the vicinity of the (approximate) stable invariant manifolds (e.g., see Fig. 5), and that the transmission coefficient $\kappa$ observed in the configurational space can also be reproduced by the dynamical propensity rule without any elaborate trajectory calculation (see Fig. 6). Our findings indicate that almost all observed deviations from unity of the conventional transmission coefficient $\kappa$ may be due to the choice of the reaction coordinate whenever the $\kappa$ arises from the recrossings, and most transitions in chemical
Figure 6. The transmission coefficients across the conventional dividing surface $S(\eta = 0)$, $\kappa$, at $E = 0.1, 0.5$, and $1.0\text{eV}$ above the saddle point energy. The activation barrier height is about $0.633\text{eV}$. The rates of the reactions were estimated both by Eq. (11) and by direct molecular dynamics (MD) simulations: if the system falls outside/inside a sensitive band defined vertical to the (approximate) stable invariant manifolds on the $(\bar{p}_1, \bar{q}_1)$ plane, we estimated the final state by use of Eq. (11)/direct MD simulations. In the figure, the sensitive band is set for each order by changing the size of the band from 0 to a number so large that the estimated $\kappa$'s converge to those evaluated by the full MD estimation. Here, the abscissa gives the ratio of the number of those whose rates were estimated correctly by MD calculations to the total number of trajectories; that is, $0\%$ implies that the rates of all the reactions were estimated solely by Eq. (11). The ratios of the trajectory calculations in evaluating $\kappa$ to yield the convergence to the exact values are $2.4\%(1), 0.6\%(2)$ at $E = 0.1\text{eV}$; $12.1\%(1), 7.1\%(2)$ at $0.5\text{eV}$; and $69.2\%(1), 37.5\%(2)$ at $1.0\text{eV}$. (The numbers in the parentheses are the orders of the perturbative calculations we performed.) [Reprinted with permission from Ref. 45. Copyright © 2002, American Chemical Society.]

reactions must not take place in **fully stochastic** fashion but in some predictable, dynamical fashion.

Then, how can one "capture" the global aspects of the phase-space geometry from the geometric structure of the phase space in that local region? One can find an essential clue from an insightful classical theory for isomerization reactions composed of two DOFs, so-called reactive island theory (RIT) developed by De Leon, Marston, Mehta, and Ozorio de Almeida [34–37] (see also Ref. 55).

Let us begin with the following system with two DOFs, which we shall henceforth call a 2-DOFs system, in this case with a Hamiltonian for a double-well potential:

$$H = \frac{1}{2} (p_1^2 + p_2^2) - q_1^2 + q_1^4 + q_2^2$$  \hspace{1cm} (12)
where there is no coupling between reactive DOF \((p_1, q_1)\) and the other bath DOFs \((p_2, q_2)\). Now, consider the following two Poincaré sections \(\Sigma_{q_1}^+\) and \(\Sigma_{q_1}^-\):

\[
\Sigma_{q_1}^+ = \{(p, q) | q_2 = q_2^0, p_2 > 0\}
\]

(13)

\[
\Sigma_{q_1}^- = \{(p, q) | q_1 > q_1^0, q_1^0 = 0, p_1 > 0\}
\]

(14)

Here, \(q^1\) is the position of the saddle point in \(q_1\), and \(q_1^0\) and \(q_2^0\) are some fixed values of \(q_1\) and \(q_2\), respectively. The geometrical structure of the stable and unstable invariant manifolds \(W^-_A(E)\) and \(W^+_A(E)\) is the direct product of the one-dimensional circular space \(S_1^A\) composed of \(q_2\) and \(p_2\) on the three-dimensional equienergy hypersurface embedded in the phase space \(\mathbb{R}^4\) and the linear space \(\mathbb{R}^1\) associated with the unbound, reactive degree of freedom \(q_1\)—that is, two-dimensional cylindrical topology. As interpreted from Fig. 7, all the "reactive" crossing trajectories occur through the interior of the cylinder whose boundary consists of the stable and unstable invariant manifolds \(W^-_A(E)\) and \(W^+_A(E)\). (Note that the system is bounded by an equienergy hypersurface in the phase space at total energy \(E\).) If the system resides on the boundary of the cylinder, it never crosses the saddle although it approaches asymptotically to the unstable periodic orbit at the unstable fixed point, referred as to \(\tau(E)\) hereinafter, in the infinite future or past. If and only if the system resides interior of the cylinder, can it cross through the saddle.
However, we lose the concept of reaction itself for systems being integrable because all the "reactive" trajectories eternally rotate between regions A and B and can never be "captured" by either A or B. Figure 8 shows the corresponding Poincaré section structures when the two modes are weakly coupled each other. Under the perturbation, it is well known that the unstable and stable invariant manifolds $W^u_\mathcal{A}(E)$ and $W^s_\mathcal{A}(E)$ in the phase space no longer connect smoothly, but generically intersect each other with a finite angle on $\Sigma^+_\mathcal{q}$, resulting in a tangled structure due to the infinite number of the intersections between $W^u_\mathcal{A}(E)$ and $W^s_\mathcal{A}(E)$ at homoclinic points on that surface of section [47]. (This intersection occurring between one-dimensional "curves" arising from the two-dimensional invariant cylinders $W^s_\mathcal{A}(E)$ and $W^u_\mathcal{A}(E)$ on the two-dimensional Poincaré section $\Sigma^+=_{\mathcal{q}}$ is generically zero-dimensional (i.e., point) and referred to as homoclinic point, because it connects outgoing and incoming "curves" of the topologically same hyperbolic, unstable fixed point.) As $W^s_\mathcal{A}(E)$ and $W^u_\mathcal{A}(E)$ extend away from the unstable periodic orbit at the unstable fixed point, their initial intersections across the $\Sigma^+=_{\mathcal{q}}$ may give rise to an overlap between them on that section. Note that $W^s_\mathcal{A}(E)$ and $W^u_\mathcal{A}(E)$ never overlap themselves, and the areas closed by them on $\Sigma^+=_{\mathcal{q}}$ are conserved as the same because each reaches the same unstable periodic orbit in the infinite past and future.

Invariant tori $\Omega^s_{\mathcal{A}}(E)$ and $\Omega^u_{\mathcal{A}}(E)$ may exist in the phase space, resulting in librational motions within the potential well and rotational motions across the saddle, respectively, although their measure of the phase space should depend
on both the strength of nonlinear coupling among modes and total energy $E$. The invariant cylinder manifolds $W^+_A(E)$ and $W^-_A(E)$ wander about in a sea of chaos (between these invariant tori) in an indefinite complicated fashion. However, the manner in which the cylinders overlap one another in the phase space mediates the reactions: All the reactive trajectories from $A$ to $B$ are mediated through the interior of the cylinder, the so-called reactive island (RI), bounded by the stable invariant manifold $W_A^+(E)$ from the unstable periodic orbit at the unstable fixed point, $\tau(E)$. Similarly, all the back reactions from $B$ to $A$ are mediated through the interior of the RI bounded by the unstable invariant manifold $W_A^-(E)$.

A very insightful picture is shown in Fig. 9 of the RIs at a Poincaré surface of section with the corresponding "semi-global" dynamics in region A. In the figure, $\Pi_A^+$ and $\Pi_A^-$ represent the regions that contain the set of all points $(p_1, q_1)$ on the $\Sigma^+_A$ within the RIs bounded by $W_A^+$ and $W_A^-$, respectively. (Hereinafter, for the sake of simplicity, we omit any notation of their $E$ dependence, although they all depend on total energy $E$.) The overlap "hatched" region is denoted by

![Figure 9. Schematic picture of the reactive island structure on $\Sigma^+_A$ and the corresponding dynamics in the reaction coordinate $q_1$. See text for detail discussions. (Reprinted with permission from A. M. Ozorio de Almeida, N. De Leon, M. A. Mehra, and C. C. Marston, Physica D 46, 265 (1990). Copyright © 1990, Elsevier Science Publishers, North-Holland.)](image-url)
\( \Pi_\Lambda = \Pi_\Lambda^+ \cap \Pi_\Lambda^- \). The consequent semi-global dynamics belonging to each region on the Poincaré section \( \Sigma_{\eta}^+ \) composed of overlapped two RIs can be well interpreted as follows:

A: All \( B \to A \) trajectories (passing from \( B \) to \( A \)) which will be "captured" in \( A \) (\( \sim \) at least more than one oscillation in \( q_1 \)) must go through the interior of \( \Pi_\Lambda^+ - \Pi_\Lambda^- \).

B: All \( B \to A \) trajectories which will go back to \( B \) immediately (\( \sim \) in one oscillation in \( q_1 \)) must go through the interior of \( \Pi_\Lambda^- \).

C: All \( A \to B \) trajectories which had temporarily been "captured" in \( A \) (\( \sim \) at least more than one oscillation in \( q_1 \)) must go through the interior of \( \Pi_\Lambda^+ - \Pi_\Lambda^- \).

D: All \( A \to B \) trajectories which were originally initiated from the unstable periodic orbit \( \tau(E) \) as \( t \to -\infty \) without returning to \( A \) must lie along the part of the boundary of \( \Pi_\Lambda^+ \) within the interior of \( \Pi_\Lambda^- \).

E: All trajectories which had temporarily been "captured" in \( A \) (\( \sim \) at least more than one oscillation in \( q_1 \)) and will be asymptotic to \( \tau(E) \) without visiting \( B \) must lie along the part of the boundary of \( \Pi_\Lambda^- \) exterior to \( \Pi_\Lambda^+ \).

F: Homoclinic trajectories asymptotic to \( \tau(E) \) as \( t \to \pm \infty \) lie on the intersection of the boundary of \( \Pi_\Lambda^+ \) and \( \Pi_\Lambda^- \).

G: \( B \to A \) trajectories which will be asymptotic to \( \tau(E) \) as \( t \to \infty \) without returning to \( B \) must lie along the part of the boundary of \( \Pi_\Lambda^- \) within the interior of \( \Pi_\Lambda^+ \).

H: All trajectories which will be "captured" in \( A \) (\( \sim \) at least more than one oscillation in \( q_1 \)) which were initiated from \( \tau(E) \) as \( t \to -\infty \) without visiting \( B \) must lie along the part of the boundary of \( \Pi_\Lambda^- \) exterior to \( \Pi_\Lambda^+ \).

I: All trajectories temporarily captured in \( A \) that are neither pre-, post-reactive to \( B \) nor asymptotic to \( \tau(E) \) must lie in a region exterior to both \( \Pi_\Lambda^+ \) and \( \Pi_\Lambda^- \), \( I_\Lambda = \Pi_\Lambda^+ \cup \Pi_\Lambda^- \) (of course, it is possible for the system belonging to \( I_\Lambda \) to enter the interior of \( \Pi_\Lambda^- \) and go through to \( B \)).

The stable and unstable invariant cylinders intersect this section infinitely often, preserving each area bounded by the closed curve of \( W_\Lambda^- \) and \( W_\Lambda^+ \), although it will become indefinitely deformed due to their homoclinic tangles. However, one of the most striking consequences deduced from the analyses of the initial intersection of the invariant cylinder manifolds at a certain Poincaré section defined in region \( A \) is this: If and only if the system lies in the interior of \( \Pi_\Lambda^- - \Pi_\Lambda^- \), the system can climb through from \( A \) to \( B \) whenever wandering in the region of \( A \) for at least more than one oscillation in \( q_1 \).

Figure 10 shows a representative trajectory passing through the two Poincaré sections \( \Sigma_A \) and \( \Sigma_B \) defined in both the regions of \( A \) and \( B \), where \( \Sigma_A = \Sigma_A^+ \).
Figure 10. A representative reactive trajectory intersecting two Poincaré sections $\Sigma_A$ and $\Sigma_B$ defined in both the regions of $A$ and $B$ through the reactive island at $q_1 = 0$. Note that the passing through the interior of $\Pi^{-}_A - \Pi_A$ will never occur in that direct back reaction on $\Sigma_A^+$ after passing through the interior of $\Pi_A$, although it is depicted so for the sake of simplicity. [Reprinted with permission from A. M. Ozorio de Almeida, N. De Leon, M. A. Mehta, and C. C. Marston, *Physica D* 46, 265 (1990). Copyright © 1990, Elsevier Science Publishers, North-Holland.]

(Eq. (14)) and $\Sigma_B = \{(p, q)| q_i = q_i^0 (< q_1 = 0), p_1 < 0\}$. Note here that $W_A^-$ may intersect with $W_A^+$ or $W_B^+$, but it never does with $W_B^-$ and $W_A^-$ itself, and all the reactions will occur through the interior of the invariant cylinders. By assuming that successive intersections of the reactive islands will eventually cover both surfaces of section (faster than a characteristic time scale of the reaction), a simple first-order kinetics can be formulated, taking into account the direct back reaction (recrossing motion within one oscillation in $q_1$):

$$
\begin{align*}
I_B^A & \rightarrow \Pi_B^A \rightarrow \Pi_A^B \rightarrow I_A^B, \\
I_A^A & \rightarrow \Pi_A^B \rightarrow \Pi_A^B \rightarrow I_A^B, \\
\Pi_A^B & \xrightarrow{\gamma_B} \Pi_B^A
\end{align*}
$$

(15)

where $I_A^A$ and $I_B^B$ are the regions exterior to $\Pi_A^+$ and $\Pi_B^-$, respectively, and each rate constant $\alpha$, $\beta$, $\gamma$ is, respectively,

$$
\begin{align*}
\alpha_A &= \frac{\text{Area}(\Pi_A^+ - \Pi_A^-)}{\text{Area}(I_A^A)} \quad (16) \\
\beta_A &= \frac{\text{Area}(\Pi_A^+ - \Pi_A^-)}{\text{Area}(\Pi_A^A)} \quad (17) \\
\gamma_A &= \frac{\text{Area}(\Pi_A)}{\text{Area}(\Pi_A^A)} = 1 - \beta_A \quad (18)
\end{align*}
$$

Similar equations hold for $\alpha_B$, $\beta_B$, and $\gamma_B$. 
Then, the population kinetics can be written with respect to the "mapping time" $n$:

\[
\begin{align*}
\Pi_A(n) &= \alpha_A \Gamma_A(n-1) + \gamma_A \Pi_B(n-1) \\
\Gamma_A(n) &= (1 - \alpha_A) \Gamma_A(n-1) + \beta_A \Pi_B(n-1) \\
\Pi_B(n) &= \alpha_B \Gamma_B(n-1) + \gamma_B \Pi_A(n-1) \\
\Gamma_B(n) &= (1 - \alpha_B) \Gamma_B(n-1) + \beta_B \Pi_A(n-1)
\end{align*}
\]

The population of A can be obtained as $N_A(n) = \Pi_A(n) + \Pi_A(n)$ and the asymptotic (exponential) decay rate of $N_A(n)$, $k^{RI}$, is given by

\[
k^{RI} = -\ln|\lambda^{max}| \tag{19}
\]

Here $\lambda^{max}$ is the eigenvalue with the largest norm, which can be obtained by diagonalization of the above discretized master equation (the corresponding, continuous master equation formulation with respect to the real time domain can be found in Ref. 36).

De Almeida et al. [34] applied the RIT to the following 2-DOFs Hamiltonian:

\[
H = \frac{1}{\mu}(p_1^2 + p_2^2) + 4q_2^2(q_1^2 - 1) \exp(-\nu q_2) + \nu [1 - \exp(-\nu q_2)]^2 \tag{20}
\]

where $\mu = 8.0$, $\nu = 2.3$, $\lambda = 1.95$, and $D = 10.0$. The point $q_1 = 0$ corresponds to the saddle point, and the potential energy surface is symmetric with respect to the reaction coordinate $q_1$. Figure 11 shows the RI structure on $\Sigma_A^\alpha$ at three distinct energies above the saddle point energy. Note that, as the total energy becomes higher above the barrier, the system undergoes more direct back reactions (the area of the overlap region between $\Pi_A^\alpha$ and $\Pi_A^\alpha$ increases) and the population of A becomes more "oscillatory" in converging to an equilibrium value. On the other hand, at a total energy just slightly above the barrier, there exists no overlap region between the first intersections of the cylinder manifolds bounded by $W_A^\alpha$ and $W_A^\alpha$, resulting in no direct back reaction occurring in one oscillation in $q_1$ as Fig. 12A $\rightarrow$ Fig. 12B.

These observations coincide with our naive intuition that we have had no means to quantify so far; that is, the closer is the total energy to the energy barrier, the more difficult it becomes for the system that has passed through the saddle to go back to the original state due to the "dissipation" of the energy accumulated for climbing in the reactive DOF $(p_1, q_1)$ to the "bath." This indicates that there exists one possible diagnosis to address the question, "What is the condition that enables us to assume local equilibrium in the reactants, in
Figure 11. Reactive island structures on the Poincaré section $\Sigma_A$ at $q_0^A = 1/\sqrt{2}$ and the kinetic data for the symmetrical Hamiltonian in Eq. (20) at an excess energy of $\Delta E = 3.0$ (upper), $\Delta E = 1.0$ (middle), and $\Delta E = 0.2$ (bottom). (A) The reactive island structure. (B) The population decay results of A using three different methods: trajectory calculation by preparing 4000 points uniformly distributed above the barrier and mapping them numerically (solid line), RTT (dashed line), and “purely random” (PR) model that does not explicitly take into account direct back reaction—that is, ignoring the overlap region of the direct back route (dotted line). At $\Delta E = 0.2$, $\Pi_A^+$ and $\Pi_A^-$ denote the next intersections of $\Pi_A^+$ and $\Pi_A^-$, respectively. $\Pi_A^+$ ($\Pi_A^-$) denotes the overlap region between $\Pi_A^+$ and $\Pi_A^-$, resulting from the next intersection of $\Pi_A^+$, and $\Pi_A^-$ denotes the overlap region between $\Pi_A^-$ and $\Pi_A^-$. $\Pi_A^+$ and $\Pi_A^-$ yields two and three oscillations in $q_1$ prior to return to B after crossing the saddle from B to A. [Reprinted with permission from A. M. Ozorio de Almeida, N. De Leon, M. A. Mehta, and C. C. Marston, *Physica D* 46, 265 (1990). Copyright © 1990, Elsevier Science Publishers, North-Holland.]
Figure 12. Caricatures of the cylinders as they wind about the phase space volume. All the surfaces and volumes are embedded in four-dimensional phase space $\mathbb{R}^4$. (A) The cylinders $W^+_B$ and $W^-_A$ overlap one another at $\Sigma^+_B$, resulting in direct back reactions. (B) These two cylinders do not overlap one another. [Reprinted with permission from N. De Leon, J. Chem. Phys. 96, 285 (1992). Copyright © 1992, American Institute of Physics.]

In terms of the topological character of the reactive islands on the Poincaré surface of section defined in the reactant domain?

If the coupling between the two modes is sufficiently strong, $W^+$ and $W^-$ will be discontinuous on the Euclidean mapping plane $\Sigma^+_B$, because they cannot avoid crossing the mapping plane before intersecting it again [34]. This implies that the turnstile transition state developed by Davis and Gray in terms of surface of section $\Sigma^+_B$ for a 2-DOF reacting system may be very difficult to apply, in practice, for strongly coupled, 2-DOF systems. On the other hand, the RIT usually requires only the first few intersections of $W^+$ and $W^-$ from the unstable periodic orbit $\tau(E)$ at the Poincaré section “perpendicular to” the reaction coordinate. These intersections will give rise to discontinuous island structures, and hence RIT may be more applicable, in practice, at least for a general class of systems with 2 DOFs.

Why has this elegant reaction theory not been applied to general reactive systems with many DOFs? It was because their algorithm depends crucially on finding pure unstable periodic orbits in the nonreactive degrees of freedom. As pointed out previously [44], it is always possible to find this regulatory object in
any 2-DOFs system irrespective of the kind of system and the value of total energy the system possesses, because there is no source to yield resonance by a single imaginary-frequency mode and a single real-frequency mode. Systems of many DOFs are no longer integrable in the saddles except at energies just slightly above the threshold energy because of resonances amongst the nonreactive modes that spoil any unstable, regular, periodic orbits.

Readers may easily notice that the application of Lie transforms to the vicinity of the first rank saddles [49] has a great potential for revisiting this classic theory that enables us to capture the semi-global, multidimensional substructure in a sea of chaos. Figure 13 shows the phase space portrait of an N degrees of freedom (N-DOFs) Hamiltonian in the region of the first-rank saddles at the quasi-regular regime where almost all actions behave as approximate invariants. In this energy regime, the geometric structure of the stable and unstable invariant manifolds $W^{-}_\mathcal{A}$ and $W^{+}_\mathcal{A}$ is the direct product of the $(2N-2)$-dimensional spherical space $S^{2N-2}$ composed of the $(N-1)$-uncoupled bath modes $(\tilde{q}_k(p,q), \tilde{q}_k(p,q))$ ($1 < k < N$) and the interval $\mathbb{R}^1$ associated with the unbound, reactive DOF. As discussed by Uzer et al. [54], this leads to $(2N-2)$-dimensional, stable and unstable, invariant spherical cylinder manifolds $S^{2N-3}_E \times \mathbb{R}^1$ on the $(2N-1)$-dimensional equienergy hypersurface at total energy $E$ in the $2N$-dimensional phase space $\mathbb{R}^{2N}$.

The trajectories inside these spherical cylinders look like “regular flows,” and their projections onto a two-dimensional space spanned by any two bath modes $\tilde{q}_k(p,q)$ result in a Lissajous figure as depicted in Fig. 2.6a in Ref. 44. As the total energy increases, the bath DOFs no longer retain their invariants of action and they become coupled with one another. However, as shown previously [38-45] as far as belonging to the semi-chaotic energy regime, the reactive DOF $\tilde{q}_1(p,q)$ can be well uncoupled from all the other chaotic, bath DOF. Here, one might regard $W^{-}_\mathcal{A}(E)$ and $W^{+}_\mathcal{A}(E)$ as $(2N-2)$-dimensional, stable and unstable, invariant “deformed” spherical cylinders on the equienergy hypersurface. The trajectories inside these “deformed” spherical cylinders look like “chaotic flows,” and their projections onto a two-dimensional space spanned by any two bath modes $\tilde{q}_k(p,q)$ result in a chaotic dynamics as depicted in Fig. 2.6b in Ref. 44.
Recently, Wiggins et al. [15] provided a firm mathematical foundation of the robust persistence of the invariant of motion associated with the phase-space reaction coordinate in a sea of chaos. The central component in RIT that is, unstable periodic orbits, are naturally generalized in many DOFs systems in terms of so-called normally hyperbolic invariant manifold (NHIM). The fundamental theorem on NHIMs, denoted here by $\mathcal{M}$, ensures [21,53] that NHIMs, if they exist, survive under arbitrary perturbation with the property that the stretching and contraction rates under the linearized dynamics transverse to $\mathcal{M}$ dominate those tangent to $\mathcal{M}$. Note that NHIM only requires that instability in either a forward or backward direction in time transverse to $\mathcal{M}$ is much stronger than those tangential directions of $\mathcal{M}$, and hence the concept of NHIM can be applied to any class of continuous dynamical systems. In the case of the vicinity of saddles for Hamiltonian problems with many DOFs, the NHIM is expressed by a set of all $(\mathbf{p}, \mathbf{q})$ satisfying both $\ddot{q}_1 = \ddot{p}_1 = 0$ and $\hat{H}_0(\dot{\mathbf{J}}_B) + \sum_{n=1} e^n \hat{H}_n(\dot{\mathbf{J}}_B, \dot{\Theta}_B) = E$, that is,

$$\mathcal{M} = \{(\ddot{q}_1, \ddot{p}_1, \ldots, \ddot{q}_N, \ddot{p}_N) | \ddot{q}_1(\mathbf{p}, \mathbf{q}) = \ddot{p}_1(\mathbf{p}, \mathbf{q}) = 0, \hat{H}_0(\dot{\mathbf{J}}_B) + \sum_{n=1} e^n \hat{H}_n(\dot{\mathbf{J}}_B, \dot{\Theta}_B) = E\}$$

with $(2N - 3)$ dimensionality on the $(2N - 1)$-dimensional equienergy hypersurface. One of the big differences between the unstable regular periodic orbits RIT requires and NHIM is that the motions inside the NHIM can even be chaotic (although a straightforward extension of the concept of unstable periodic orbits to $n$ degrees of freedom systems should possess $n$ unstable, regular, periodic orbits), and the NHIMs retain their invariance robustly against perturbation with the stable and unstable invariant manifolds. So, at a wide range of energies above the barrier, the RIT can be generalized and applied, in principle, to a wide class of chemical reaction systems with many DOFs; if one brings about the backward calculations (to the reactant domain) initiated from the interior of the phase space bounded by the NHIM at the saddle, one may reveal what kinds of initial conditions one must prepare to obtain fast transitions from the reactant to the product.

IV. KRAMERS–GROTE–HYNES THEORY REVISITED

Two approaches to overcome the recrossing problem have been variational TST [8,10,61], which optimizes a configurational dividing surface by minimizing the number of recrossings, or by (generalized) Langevin formalism of Kramers [6] and Grote and Hynes [11], which regards the recrossings as arising from
“(molecular) friction” by the “bath” DOFs. Zwanzig [62] proved that the following class of Hamiltonians, that is,

\[ H(p, q) = \frac{p_1^2}{2\mu} + V(q_1) + \sum_{i=2}^{n} \left[ \frac{p_{Bi}^2}{2m_i} + \frac{m_i\omega_i^2}{2} \left( q_{Bi} - \frac{c_i q_1}{m_i\omega_i^2} \right)^2 \right] \]  (22)

can be reformulated by a generalized Langevin formalism,

\[ \mu \ddot{q}_1 = -\frac{\partial V}{\partial q_1} - \mu \int_0^t \dot{q}_1(t') \zeta(t - t') dt' + R(t) \]  (23)

\[ \langle R(0)R(t) \rangle = k_B T \zeta(t) \]  (24)

where, for example

\[ \zeta(t) = \sum_{l=1}^{n} \frac{c_l^2}{m_l\omega_l^2} \cos \omega_l t \]  (25)

Here, \( q_1, p_1 \) are the “system” coordinate and momentum; and \( q_{Bi}, p_{Bi} \) are the \( i \)th “bath” variables with mass \( m_i \) and frequency \( \omega_i \). \( c_i \) is the coupling constant of the \( i \)th “bath” oscillator with the “system.” \( \mu \) is the mass of the “system” and \( k_B \) Boltzmann constant, and the average \( \langle \rangle \) is over the “thermal bath” at temperature \( T \).

van der Zwan and Hynes [63] and later Pollak [64] showed that the reaction rate of the Grote–Hynes formulation with the reaction coordinate \( q_1 \) is exactly equivalent to that of the transition state theory if the reaction coordinate is chosen as an unstable normal coordinate \( \bar{q}_1 \) composed of the total system \(- “system q_1,” \) “bath \( q_{Bi} \)” (see also Fig. 14).

However, their arguments have been often criticized because of the simplicity of its Hamiltonian class (it’s integrable!). Our recent findings suggest that nevertheless their equivalence arguments may be made much more general and applicable to a wider range of Hamiltonian classes, even when the system is almost chaotic. This stimulates us to reconsider a fundamental question of what constitutes the “thermal bath” for reacting systems. One may anticipate that reactions take place along a ballistic path composed of the total system in the thermal fluctuation, at least, in the region of saddles. The “thermal bath” for reactions, simply defined thus far is all the rest of the atoms or molecules except the reacting system, does not necessarily retard the reactive trajectories; rather, such a “bath” might control and assist the reactants to climb and go through the saddles. In the context of protein folding, Plotkin and Wolynes [65] addressed how the inclusion of the other degrees of freedom into the reaction coordinate is essential for obtaining the optimal dividing surface for protein folding. Still, the
questions, “What is the dynamical role of water molecules surrounding the protein system?” [66,67] and “What should be regarded as the system and the thermal bath during the dynamical evolution of structural transitions?” have been nontrivial, open subjects in many disciplinary fields in sciences.

V. STOCHASTICITY OF SADDLE CROSSINGS

The classical canonical perturbation calculation at the region of a saddle provides us with interesting local information of the original system at a finite low order up to which the series of the transformation are expected to be less affected by the ultimate divergence arising from the characteristics of the whole phase space. The local region in which the invariants of motion persist at least along the reaction coordinate should cover an entire saddle region that the system explores prior to being “captured” in either reactant or product state, in order to predict the termini of the trajectories. In other terms, energy regimes in which all or most of all the recrossing events occur within such a locality can be classified into quasi-regular, or semi-chaotic regimes. The more the total energy increases, the more the broadening of the excursion regime competes with the shrinkage of the “convergence radius” in which an approximate invariant of the action exists at least for the phase-space reaction coordinate. It is expected that, in an extremely high-energy regime, most recrossing events would take place outside of the “region of invariance” and the saddle crossing motions are entirely stochastic in
nature, irrespective of any choice of reaction coordinate, and dynamical correlation between outgoing and incoming trajectories to and from the saddle is completely lost. Such an energy regime may be regarded as stochastic (= fully developed chaotic) regime [38]. However, there is no mathematical framework yet that shows how the breakup of the normal hyperbolicity for the NHIMs affects the crossing trajectories over the region of the saddles. Komatsuzaki and Berry found [42,43] that the approximant of the NHIM at a finite order implies that a reacting system be substantially trapped as the total energy of the system increases from the “semi-chaotic” regime. It may lead a conjecture that a “vague NHIM” makes a reacting system increasingly trapped as vague tori do [68,69]. A new mathematical foundation is apparently required to inquire further into the question. Note, in addition, that, especially at high energies, the system may also pass over higher-rank saddles, and we encounter many new, untouched subjects—for example, definability of transition state and the role of resonance in the imaginary \( \omega \)-plane for the bifurcation.

VI. CONCLUDING REMARKS AND FUTURE PROSPECTS

The robust existence of a skeleton composed of a NHIM and its spherical invariant cylinders in the phase space should play their essential roles not only to help us understand the physical origin of observed nonstatistical, dynamical behavior but also to provide us with a new scope to control chemical reaction dynamics in terms of geometrical feature of the phase space. Here, let us articulate some of the subjects we have to confront in the immediate future:

1. It is ensured that the NHIMs, \( \mathcal{M} \), if they exist, survive under arbitrary perturbation to maintain the property that the stretching and contraction rates under the linearized dynamics transverse to \( \mathcal{M} \) dominate those tangent to \( \mathcal{M} \). In practice, we could compute the \( \mathcal{M} \) only approximately with a finite-order perturbative calculation. Therefore, the robustness of the NHIM against perturbation (referred to as structurally stable [21,53]) is expected to provide us with one of the most appropriate descriptions of a “phase-space bottleneck” of reactions, if such an approximation of the \( \mathcal{M} \) due to a finite order of the perturbative calculation can be regarded as a “perturbation.” One of the questions arising is, “How can the NHIMs composed of a reacting system in solutions survive under the influence of solvent molecules?” (This is closely relevant to the subject of how the “system” and “bath” should be identified in many-body systems.)

2. In two-mode [17] and three-mode [20] systems it was shown that dynamical bottlenecks exist to intramolecular energy transfer; that is, cantori are buried in the reactant basin, which form partial barriers between irregular regions of phase space. This brought about multiply
exponential decay on a wide range of time scales of the reaction. There exists no general algorithm for locating arbitrary NHIMs, while the stable and unstable manifolds of some of them may represent the multidimensional generalization of the partial barrier associated with a periodic orbit approximant to a cantorus [70]. An analysis of pairwise local frequency ratios would be useful to search the intramolecular bottlenecks, at least, for 3-mode systems [71–73]. However, it would be a very difficult task to deal with higher-dimensional systems.

3. One can visualize the NHIM and its stable and unstable invariant manifolds by the projections of those objects onto the original space by inverting all the transformed new coordinates and momenta into the original ones in the quasi-regular region, in which all actions persist approximately as the local invariants. However, although the motions inside the NHIM and its invariant manifolds can be chaotic in the semi-chaotic region, the inverse of $(\tilde{p}, \tilde{q})$ into the original $(p, q)$ should become rather problematic because of the divergence of most terms in the generating functions. The partial normalization in which Lie transform applies only to the reactive DOF is required to capture these abstract invariant objects in the original coordinate space in the semi-chaotic region.

4. There exists no mathematically rigorous framework for describing the mechanism of the breakup of NHIM. There exists only a conjecture that a "vague NHIM" might act as a new bottleneck in the phase space transport [42,43].

5. The computer algorithm for Lie canonical transformation technique has not been improved essentially after Dragt and Finn [74,75]. It would be almost impossible to apply this beyond a few tens DOFs even to a fairly low order by using modern computational facilities. In this regard, the development of a means for coarse-graining multimode systems to a reduced set of DOFs is quite a challenge for further applications to rugged, multibasin dynamics [76].

6. There are great potentialities to explore multibasin chemical reaction theory based on the geometric structure of the phase space for multibasin transitions: By identifying each first-rank (and higher-rank if necessary) saddle linking the distinct energy minima (or lower-rank saddle), one can apply a Lie transform to the regions in the vicinity of each fixed point and extract the normally hyperbolic invariant manifolds (NHIM) and its stable and unstable invariant manifolds from the state space. The intersection phenomena between the stable cylinder approaching one NHIM associated with one saddle and the unstable cylinder departing from another NHIM with another saddle can tell us how a bundle of trajectories
passing through different saddles are dynamically correlated. In the case of gas-phase multibasin reactions, to elucidate the mechanism of the intersection provides us with a clue to establish the control of sequential chemical reactions. Consider a system of $n$ DOFs. The NHIM is a topologically $(2n - 3)$-dimensional ("deformed" in the semi-chaotic regime) sphere, $S_{E}^{2n-3}$, and the stable and unstable invariant manifolds are the $(2n - 2)$-dimensional ("deformed" in the semi-chaotic regime) spherical cylinder topologies, $S_{E}^{2n-3} \times \mathbb{R}^1$, on the $(2n - 1)$-dimensional equienergy hypersurface at total energy $E$ in the phase space $\mathbb{R}^{2n}$. The dimensionality of an intersection manifold (if it exists for $n > 2$) is $2n - 3$. It is expected that there would be strong dependency on the initial condition "interior of NHIM" to bring the system either to another NHIM or back to the same NHIM. That is, to understand the skeleton of the phase space composed of the cylinder invariant manifolds provides us with not only a new insight to control the dynamical correlations but also the rigorous reaction pathways of multibasin chemical reactions [77–79].

These are some of several challenging, but very fascinating, subjects for the forthcoming future for two-basin chemical reactions.

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