A Dynamical Propensity Rule for Transitions in Chemical Reactions†

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Received: March 12, 2002; In Final Form: July 9, 2002

A new dynamical propensity rule for transitions of a system crossing the barrier from one potential minimum to one another is derived from dynamical system theory. The rule is based on the existence of a no-return dividing hypersurface in the system's phase space in the vicinity of saddles of the multidimensional potential surface of a strongly coupled, chaotic system. We present numerical evidence of the rule's validity by applying it to the rearrangements of a cluster of six argon atoms.

I. Introduction

Transition state theories (TST),[1] first developed by Eyring[2] and Wigner[3] in the 1930s, have had great success in elucidating absolute reaction rates of not only chemical reactions but also of the evolution of other systems that pass from one stable state to another, e.g., the rearrangement of clusters[4−11] and the folding of proteins.[12,13] All of the various forms of TST postulate the existence of a dividing hypersurface, that is, the transition state (TS; generally, in principle a surface in phase space[3]) through which a reacting species should pass only once during the course of a reaction. However, few theories have clarified the physical conditions for the existence of such a no-return dividing hypersurface in either phase space or configurational space of a strongly coupled, multidimensional system. This is one of the most elusive aspects 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 "correction factor", called the transmission coefficient κ, to take into account that the system of interest actually makes more than one crossing of the surface presumed to be the desired dividing surface. It appears as if the system may return to the TS even several times along its reactive trajectory, contrary to the basic postulate of TST.

In the developments[14−19] of classical unimolecular reaction rate theories, there has been a great improvement of our understanding for the definability of such a general, no-return dividing hypersurface from the viewpoint of the geometrical structure of the phase space in chemical reactions. Davis and Gray[14] first showed in the late 1980s that in Hamiltonian systems with two degrees of freedom (dof), the 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[17] analyzed the predissociation of the van der Waals complex $He-I_2$ with three dof, i.e., the four-dimensional Poincaré section. They demonstrated, as predicted by Wiggins just previously,[18] that the occurrence of homoclinic tangency inherent to higher (>two) dimensional systems hampers the construction of the hypersurface dividing the bound complex reactant region from unbound trajectories. Toda[19] noticed that the homoclinic tangency leads to a bifurcation of the phase space reaction path with a transition between two topologically distinct chaos. Thus, the Davis−Gray separatrix transition state depends crucially on the Poincaré section having only two dimensions. No general *no-return* dividing hypersurface exists yet for systems of higher dimensionality. In other words, it is still an unresolved open problem of the circumstances that such a hypersurface should persist, if exists, or fall to ruin in the chaotic thermal bath of multidimensional systems.

With a focus on regularity of orbits in the vicinity of the unstable saddle points on potential energy surfaces, reactions in a-few-dof systems can be interpreted as occurring through cylindrical manifolds apart from the saddles.[20−22] Their approaches depend crucially on the existence of *pure* unstable periodic orbits in the nonreactive degrees of freedom in the region of the saddles; these unstable periodic orbits become spoiled whenever resonance exists among the nonreactive modes. 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 et al.[23−28] 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 et al.[29,30] 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.[31]

Recently, we showed,[6−11] using classical isomerization of a six-atom Lennard-Jones cluster, that a strongly coupled Hamiltonian system with several dof may exhibit at least three distinguishable energy regimes of dynamical behavior, so-called *quasiregular*, *semichaotic*, and *fully developed chaotic* regimes, in the region of a saddle. These are distinguished by the extent of the regularity of their dynamics. Up to energies high enough to make the system manifestly chaotic, approximate invariants

† Part of the special issue "R. Stephen Berry Festschrift".

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10.1021/jp025751x CCC: $22.00
Published on Web 08/20/2002

of motion associated with a reaction coordinate in the phase space imply a multidimensional dividing hypersurface that is free (or very nearly free) of recrossings in that regime, even in a sea of chaos. Our technique relies on the application of Lie canonical perturbation theory[32,33] (with algebraic quantization,[34−36] if necessary), a classical analogue of Van Vleck perturbation theory,[37] to the region of potential energy saddles. This method constructs a hyperbolic coordinate system with a dividing hypersurface in phase space that minimizes recrossings and apparent mode−mode mixing in the region. Hence, this provides us with the natural reformulation[6,35] of the conventional TST based on that hypersurface in multidimensional phase space and improves the predicted classical reaction rates of multidimensional systems. We presented a practical algorithm to visualize the dividing hypersurface in the multidimensional phase space of a given system[7,8] and illuminated[9,10] a new type of phase space bottleneck that emerges as the total energy increases, which keeps a reacting system increasingly trapped in the region of a saddle.

The earlier work of Wiggins[18,38] provides a firm mathematical framework for $N(>2)$-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 concepts of "saddle" and "separatrix" on a multidimensional phase space. However, a major technical obstacle preventing its implementation has been the lack of an algorithm for searching arbitrary NHIMs in realistic multidimensional systems. The algorithm we have developed from Lien canonical perturbation theory provides a way to compute a NHIM in the vicinity of arbitrary saddles. Very recently, Wiggins et al.[39] presented a mathematical condition for the robust persistence of the invariant of motion along the phase-space reaction coordinate in each order of perturbation. Uzer et al.[40] provided a fuller description of the (local) geometric structure of chemical reactions in multidimensional phase space and applied the Lie transformation to the vicinity of an unstable fixed point for a hydrogen in crossed electric and magnetic fields containing significant Coriolis interactions (a 3-dof system), which are neither fully kinetic nor fully potential, to compute its NHIM and the stable and unstable manifolds.

The purpose of this article is to establish a strong propensity rule for transitions of chemical reactions, based on the existence of a no-return dividing hypersurface in phase space, and to demonstrate the rule's validity by applying it to the rearrangements of a cluster of six argon atoms. This criterion should enable us to predict a priori whether the system climbs through the saddle to the product, or returns to its original state, and should reveal the physical foundation of why and how the system traverses the saddles from reactant to product states in multidimensional, strongly coupled, Hamiltonian systems.

II. Theory

Robust Persistence of a No-Return Phase Space Dividing Hypersurface in the Region of Saddles. Suppose that the Hamiltonian $H(\boldsymbol{p}, \boldsymbol{q})$ is expressed in a region around a saddle point of interest as an expansion in a small parameter ϵ, 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 $\mathbf{J}$ of H_0 only and does not depend on the conjugate angle variables $\boldsymbol{\Theta}$. The higher-order terms of the Hamiltonian are expressed as sums of cubic, quartic, etc. terms in the normal coordinates of the system, at its saddle.[41] For the sake of simplicity, we focus on a $(3N-6)$-dof Hamiltonian system with total linear and angular momenta of zero, so that the kinetic and potential energies are purely vibrational.[6]

$$H = H_0 + \sum_{n=1}^{\infty} \epsilon^n H_n \tag{1}$$

where

$$H_0 = \frac{1}{2}\sum_j (p_j^2 + \omega_j^2 q_j^2) = H_0(\boldsymbol{J}) \tag{2}$$

$$\sum_{n=1}^{\infty} \epsilon^n H_n = \epsilon \sum_{j,k,l} C_{jkl} q_j q_k q_l + \epsilon^2 \sum_{j,k,l,m} C_{jklm} q_j q_k q_l q_m + \ldots = \sum_{n=1}^{\infty} \epsilon^n H_n(\boldsymbol{J}, \boldsymbol{\Theta}) \tag{3}$$

Here, q_j and p_j are the jth normal coordinate and its conjugate momentum, respectively; ω_j and C_{jkl}, C_{jklm}, ... are respectively the frequency of the jth mode and 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 degree of freedom, "1", whose fundamental frequency ω_1 is pure imaginary, whereas the frequencies $\boldsymbol{\omega}_B$ of the other "bath" modes B are real.

An early insight by Hernandez and Miller[37] in their semiclassical theory based on Van Vleck perturbation theory and our recent numerical evidence[6−11] of a burial of local invariant of (classical) action associated with the phase-space reaction coordinate even in a strongly coupled, chaotic system implies that one can generally find a nonlinear, canonical transformations of the coordinates to transform nonintegrable Hamiltonian $H(\boldsymbol{p},\boldsymbol{q})$ into a new form:

$$\bar{H}(\bar{\boldsymbol{p}},\bar{\boldsymbol{q}}) = \bar{H}_0(\bar{\boldsymbol{J}}) + \sum_{n=1} \epsilon^n \bar{H}_n(\bar{J}_1, \bar{\boldsymbol{\xi}}_B) \tag{4}$$

in the vicinity of the saddles.[39] Here $(\bar{\boldsymbol{p}}, \bar{\boldsymbol{q}})$ is a new set of canonically transformed variables, $(\bar{\boldsymbol{J}}, \bar{\boldsymbol{\Theta}})$ denotes their action-angle variables, and $\bar{\boldsymbol{\xi}}_B$ represents those of bath modes $(\bar{\boldsymbol{J}}_B, \bar{\boldsymbol{\Theta}}_B)$, collectively. This is due to the fact that an arbitrary combination of modes cannot satisfy the resonance conditions if one mode has an imaginary frequency, included in the combination.

It is easily shown[11] that the equation of motion of the reactive mode "1" obeys the equation of motion of the original Hamiltonian H:

$$\ddot{\bar{q}}_1(\boldsymbol{p}, \boldsymbol{q}) - \frac{\dot{\bar{\omega}}_1}{\bar{\omega}_1}\dot{\bar{q}}_1(\boldsymbol{p}, \boldsymbol{q}) + \bar{\omega}_1^2 \bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = 0 \tag{5}$$

$$\bar{p}_1(\boldsymbol{p}, \boldsymbol{q}) = \frac{\omega_1}{\bar{\omega}_1}\dot{\bar{q}}_1(\boldsymbol{p}, \boldsymbol{q}) \tag{6}$$

where

$$\bar{\omega}_1 = \bar{\omega}_1(\boldsymbol{p}, \boldsymbol{q}) = \bar{\omega}_1(\bar{J}_1, \bar{\boldsymbol{\xi}}_B) = \frac{\partial \bar{H}(\bar{J}_1, \bar{\boldsymbol{\xi}}_B)}{\partial \bar{J}_1} \tag{7}$$

Here, $\dot{x}$ and $\ddot{x}$ represent the first and second derivatives of x with respect to time t. The $\bar{\omega}_1(\bar{J}_1, \bar{\boldsymbol{\xi}}_B)$ depends on time t only through bath modes $\bar{\boldsymbol{\xi}}_B(t)$ because $\bar{J}_1$ is independent of t by eq 4. The $\bar{\boldsymbol{\xi}}_B$-contributions to $\bar{\omega}_1$ emerge at $\mathcal{O}(\epsilon^2)$ in the vicinity of the saddles and, furthermore, are suppressed because of the nondivergent denominators involving one imaginary frequency

ω_1.[11] Our recent numerical analysis using a bundle of trajectories[10] showed that, even at a moderately high energy where almost all of the $\bar{\boldsymbol{J}}$ do not preserve their invariance except that $\bar{J}_1$, $\bar{\omega}_1^{2nd}(\boldsymbol{p}, \boldsymbol{q})$ tends to exhibit near-constant with a much smaller fluctuation than any of $\bar{\omega}_B{}^{2nd}(\boldsymbol{p}, \boldsymbol{q})$.

A Dynamical Propensity Rule for Transitions. Equation 5 corresponds to a one-dimensional pendulum whose length slowly changes, a well-used example to present the robust persistence of invariance of action under a sufficiently slow, small perturbation; this persistence is usually called "adiabatic invariance" (e.g., see the standard texts[33,42]). One thus can find an approximate analytical expression along $\bar{q}_1(\boldsymbol{p}, \boldsymbol{q})$ even in the region of a saddle where the system is strongly chaotic;[11] specifically

$$\bar{q}_1(\boldsymbol{p}(t), \boldsymbol{q}(t)) \simeq \frac{\alpha}{2} e^{|\bar{\omega}_1|t} + \frac{\beta}{2} e^{-|\bar{\omega}_1|t} \tag{8}$$

$$\alpha = \bar{q}_1(t_0) + \frac{\bar{p}_1(t_0)}{|\omega_1|}, \quad \beta = \bar{q}_1(t_0) - \frac{\bar{p}_1(t_0)}{|\omega_1|} \tag{9}$$

Here, constant coefficients α and β can be estimated from $\bar{q}_1(\boldsymbol{p}(t_0), \boldsymbol{q}(t_0))$, and $\bar{p}_1(\boldsymbol{p}(t_0), \boldsymbol{q}(t_0))$ at any arbitrary time t_0 in the region of the saddle.

These relations imply that, even though almost all dof are chaotic, the final state (and initial state) may be determined a priori. For example, 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 $\bar{q}_1 > 0$. Similarly, from only the phase space information at $t = t_0$ (the sign of β), one can infer whether the system on $S(q_1 = 0)$ at time t_0 has climbed from either stable state, i.e., reactant or product. The dynamical rule for (forward) transitions is thus derived as "if

$$\bar{q}_1(t_0) > -\frac{\bar{p}_1(t_0)}{|\omega_1|} \left(\bar{q}_1(t_0) < -\frac{\bar{p}_1(t_0)}{|\omega_1|} \right) \tag{10}$$

the system will go through to the product (return to the reactant)".

Transmission Coefficient κ. To elucidate how the "no-return" assumption for a given dividing surface, e.g., $S(q_1 = 0)$, would be spoiled, one has to estimate the transmission coefficient κ[43,44]

$$\kappa \equiv \lim_{t \to t_{long}} \frac{\langle j(t=0) h(q_1(t)) \rangle_E}{\langle j_+(t=0) \rangle_E} \tag{11}$$

in terms of microcanonical molecular dynamics (MD) simulations under an initial condition that the system distributes microcanonically at time $t = 0$ on the surface. Here $j(t = 0)$ and $j_+(t = 0)$ respectively denote the initial total and initial positive fluxes crossing the surface $S(q_1 = 0)$; $h(x)$ is the Heaviside function of x, and $\langle \rangle_E$ is the microcanonical ensemble at energy E. Often the value of the transmission coefficient κ has been taken as the value at a plateau that emerges after some interval long compared with the transit time. So far, *elaborate* MD simulations have been used to identify the final destination state of the system, either $q_1(t_{long}) > 0$ or $q_1(t_{long}) < 0$ after a long time t_{long}.

III. Results and Discussions

Now let us use eq 10 to elucidate the fate of each trajectory that starts on the surface $S(q_1 = 0)$, for which we estimated

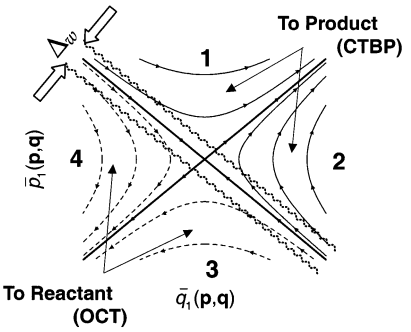

Figure 1. Schematic portrait of the stable and unstable invariant manifolds and the phase space flows on $(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}), \bar{p}_1(\boldsymbol{p}, \boldsymbol{q}))$.

coefficients α and β at $t = 0$. To obtain the functional forms of $\bar{q}_1(\boldsymbol{p}, \boldsymbol{q})$ and $\bar{p}_1(\boldsymbol{p}, \boldsymbol{q})$, we applied Lie canonical perturbation theory to the original Hamiltonian $H(\boldsymbol{p}, \boldsymbol{q})$ to generate a nonlinear canonical transformation from $(\boldsymbol{p}, \boldsymbol{q})$ to a new set $(\bar{\boldsymbol{p}}, \bar{\boldsymbol{q}})$ in which the individual dof are as regular as possible, up to second order. (In practice, we used the power of algebraic quantization,[34−36] quite efficient for the extension to higher order, as first developed by Fried and Ezra.[34]) We applied this to isomerization reactions in a simple cluster of six argon atoms bounded by pairwise Lennard-Jones (LJ) potentials, with total linear and angular momenta of zero.[6] This cluster has two kinds of potential energy minima, the octahedral (OCT) global minima with energy $E = -12.712\ \epsilon$ and the other, higher-energy capped trigonal bipyramid (CTBP) minima with energy $E = -12.303\ \epsilon$. There are two distinct kinds of first-rank saddles. Saddle I, for we present the analysis in this article, joins the OCT and the CTBP minima at energy $E = -12.079\ \epsilon$. In this report, we show the κ analysis over the saddle at three total energies, $E = 0.1$, 0.5, and 1.0 ϵ above the saddle point energy.

For analyses of the infrequent saddle crossings, we employed the Keck−Anderson method[45,46] to generate a microcanonical ensemble on $S(q_1 = 0)$. We generated 10 000 trajectories, which were found to be enough to yield statistical convergence in calculating κ. For the trajectory calculations, we used a fourth-order Runge−Kutta method with adaptive step-size control; the total energies in the MD calculations were conserved within $\pm 1 \times 10^{-6}\ \epsilon$ (all results are given in the universal reduced units of the LJ potential; energies, distance, momentum, and mass m are in units of ϵ, $m^{1/2}\sigma$, $m^{1/2}\sigma$ ps^{-1}, and argon atomic mass).

Phase Space Portrait in the Region of Saddles. Figure 1 shows a schematic portrait of the phase space flows (denoted by arrows) in the $(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}), \bar{p}_1(\boldsymbol{p}, \boldsymbol{q}))$ plane. Equation 10 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 $\bar{q}_1 = \bar{p}_1 = 0$, all of 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. Although the former and latter domains could be regarded respectively as "reactive" and "nonreactive" in elucidating the fate of reactions after the system leaving $S(q_1 = 0)$, all of the system trajectories classified in domains **2** or **4** do not cross through the phase-space dividing hypersurface $S(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = 0)$, i.e., simply not that of the reaction.

Table 1 classifies 10 000 system trajectories initiated on $S(q_1 = 0)$ into these four domains on the first, and second-order phase space planes $(\bar{p}_1^{ith}(\boldsymbol{p}, \boldsymbol{q}), \bar{q}_1^{ith}(\boldsymbol{p}, \boldsymbol{q}))$ at $E = 0.1$, 0.5, and 1.0 ϵ. In the table is shown that, if the incident momentum p_1 is positive (negative), i.e., going from OCT(CTBP) to CTBP(OCT) minima along the normal coordinate q_1, the system

TABLE 1: Classifications of 10 000 Trajectories Initiated on a Configurational Dividing Surface $S(q_1 = 0)$ into the Four Domains 1−4, Depending on the Signs of the Incident Momenta p_1, on the Phase-Space Planes $(\bar{p}_1^{ith}, \bar{q}_1^{ith})$ of the First and Second Orders at Three Distinct Energies 0.1, 0.5, and 1.0 ϵ[a]

	0.1 ϵ		0.5 ϵ		1.0 ϵ	
domain	first[a]	second	first	second	first	second
			$p_1(t=0) > 0$			
1	4890(3)	4897(0)	4729(15)	4734(3)	4553(18)	4580(19)
2	8(0)	4(0)	50(2)	47(1)	179(14)	141(4)
3	0(0)	0(0)	1(1)	2(0)	8(0)	8(4)
4	24(3)	27(0)	55(12)	67(11)	66(18)	75(25)
			$p_1(t=0) < 0$			
1	1(0)	0(0)	0(0)	3(0)	4(1)	3(3)
2	157(15)	166(4)	333(73)	337(49)	357(153)	368(129)
3	4888(10)	4900(2)	4699(21)	4725(14)	4576(30)	4591(21)
4	1(0)	0(0)	9(0)	7(0)	22(1)	29(0)

[a] The numbers in the parentheses denote the number of trajectories for which the propensity rule at the specified order fails to predict the final states; for example, 4729 trajectories are classified into the "reactive" domain **1** on $(\bar{p}_1^{1st}(\boldsymbol{p}, \boldsymbol{q}), \bar{q}_1^{1st}(\boldsymbol{p}, \boldsymbol{q}))$ plane, but 15 of the 4729 eventually went not to the product but to the reactant state. First and second indicate the order of the Lie perturbation method we performed.

tends to be classified mainly into the domain **1** (**3**) at all orders. The more the total energy increases, the more the system leaks into the other domains **2** and/or **4**. One can see the asymmetric character, depending on the direction of the reaction, of the classifications into the four phase space domains: when the incident p_1 is negative, the system leaks more into the other domain, i.e., **2**, from the domain **3**, than into the domains **2** and **4** from **1** when p_1 is positive. This is due to the fact that the density of states in the real reaction bottleneck; that is, the phase-space dividing hypersurface $S(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = 0)$ about saddle I is greater on the minus side than on the plus side along the q_1 axis.[7]

Now let us see how our dynamical propensity rule for the transitions can predict the fate of the reactions. Here, the numbers in the parentheses in the table indicate the number of trajectories for which the propensity rule fails to predict the correct final state at that order. At all of the three energies, the higher the order of the perturbation calculation, the better the rule predicts the reactions. At very high energies, ca. 1.0 ϵ, the rule evaluated at second order rather fails to predict the final state of the reactions. Note that the accuracies of the predictions depend on the direction of the reactions; that is, the numbers of the failure are significantly larger for the reaction from CTBP to OCT ($p_1 < 0$) than those from OCT to CTBP ($p_1 > 0$). This is also because of the distribution of the reaction bottleneck states, heavier on the OCT side along the q_1 axis: at the crossing $S(q_1 = 0)$ from CTBP to OCT, the system would be more likely to face the reaction bottleneck $S(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = 0)$ than at the same crossing from the other direction. In the latter case, at $q_1 = 0$, the system has passed the greater part of the distribution constituting the real $S(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = 0)$ and, hence, rarely returns to $S(q_1 = 0)$.[7] This implies that the fate of the reactions from CTBP to OCT depends more crucially on the accurate location of the $S(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = 0)$ than that from OCT to CTBP.

Figure 2 shows how eq 10 can predict the fate of trajectories that are *recrossing* over the configurational surface $S(q_1 = 0)$ on the *phase*-space planes $(\bar{p}_1^{ith}(\boldsymbol{p}, \boldsymbol{q}), \bar{q}_1^{ith}(\boldsymbol{p}, \boldsymbol{q}))$. This figure corresponds to $E = 0.5\ \epsilon$, where *most modes are strongly chaotic except* $\bar{q}_1(\boldsymbol{p}, \boldsymbol{q})$.[6] In the figures, the circle and triangle symbols denote the system trajectories having negative and positive incident momentum $p_1(t = 0)$ on the $S(q_1 = 0)$, and the open and filled, those whose final states were predicted

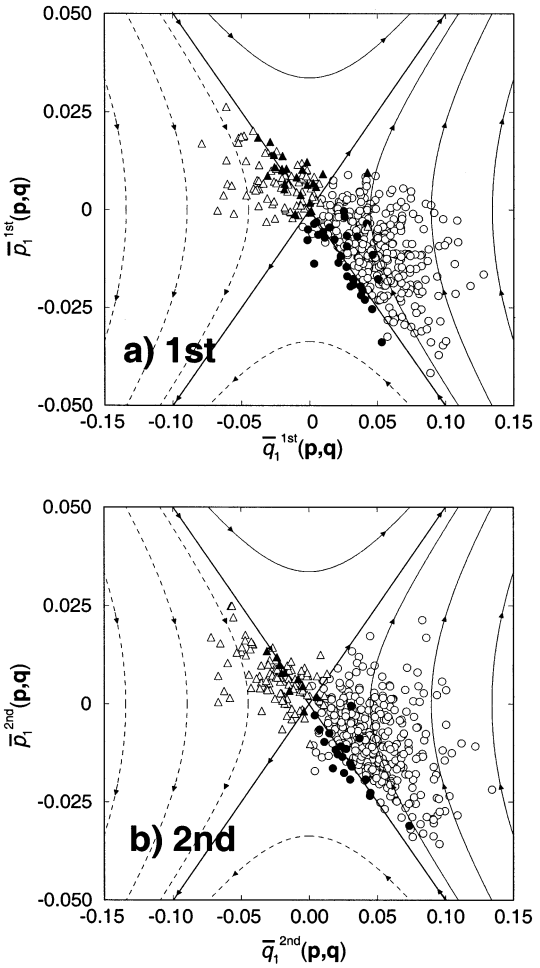

Figure 2. Distributions of the recrossing trajectories over $S(q_1 = 0)$ at time $t = 0$ on $(\bar{p}_1^{ith}(\boldsymbol{p}, \boldsymbol{q}), \bar{q}_1^{ith}(\boldsymbol{p}, \boldsymbol{q}))$ at $E = 0.5\ \epsilon$. (a) First and (b) second orders.

correctly and falsely by eq 10, respectively; for example, black circles classified in domain **3** are the trajectories crossing $S(q_1 = 0)$ from CTBP to OCT at $t = 0$ and are predicted to go into the reactant state, but their actual final states were product states. The recrossing trajectories that start on $S(q_1 = 0)$ mostly fall into domain **2** at each order, because of the asymmetric character of the reaction bottleneck $S(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = 0)$ along the q_1 axis.[7] Note that the fates of most recrossing trajectories can be predicted more accurately by eq 10 as the order of perturbation calculation increases, except just in the vicinity of the stable manifolds. In other words, except in a region very close to the approximate stable invariant manifolds, one may anticipate that the dynamical transition rule can well predict the fate of trajectories, even at energies so high that most modes are strongly coupled and strongly chaotic.

This leads us to introduce a small "sensitive band" along the approximate stable invariant manifolds, as depicted in Figure 1: if the system's trajectory lies in a small sensitive band defined by

$$-\frac{\bar{p}_1(t_0)}{|\omega_1|} - \Delta'_w < \bar{q}_1(t_0) < -\frac{\bar{p}_1(t_0)}{|\omega_1|} + \Delta'_w \qquad (12)$$

where $\Delta'_w (= \Delta_w / 2\sin(\tan^{-1}|\omega_1|))$, the final state of the reaction depends crucially on the accuracy of the approximate stable invariant manifolds, and one might have to determine the fate of such reactions using MD simulations.

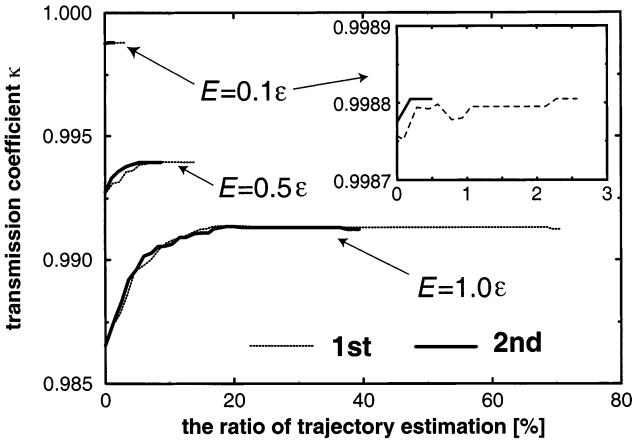

Figure 3. Transmission coefficients across the conventional dividing surface $S(q_1 = 0)$, κ, at $E = 0.1$, 0.5, and 1.0 ϵ.

Figure 3 shows the transmission coefficients κ across the configurational dividing surface $S(q_1 = 0)$ at $E = 0.1$, 0.5, and 1.0 ϵ, in which the fates of the reactions were estimated both by eq 10 and by direct MD simulations: if the system falls outside/inside a sensitive band, we estimated the final state by use of eq 10/direct MD simulations. In the figure, the sensitive band is set for each order by changing Δ_w from 0 to a number so large that the estimated κ's converge to those evaluated by the *full* MD estimation. Here, the abscissa gives the ratio of the number of those whose fates were estimated correctly by MD calculations to the total number of trajectories; that is, 0% implies that the fates of all of the reactions were estimated solely by eq 10 with Δ_w being zero. The ratios of the trajectory calculations in evaluating κ to yield the convergence to the exact values are 2.4%(1) and 0.6%(2) at 0.1 ϵ; 12.1%(1) and 7.1%(2) at 0.5 ϵ; and 69.2%(1) and 37.5%(2) at 1.0 ϵ. (The numbers in the parentheses are the orders of the perturbative calculations we performed.) At 0.1 ϵ, slightly above the saddle, the first- and second-order transition rules estimate κ to be 0.99876 and 0.99878, i.e., 99.995(7)% accuracy of that estimated by the *full* MD estimation. Even at a moderately high energy, ca. 0.5 ϵ, these order's rules provide us with κ to 99.9% accuracy. At much higher energies, ca. 1.0 ϵ or more, where the invariant of motion along the $\bar{q}_1(\boldsymbol{p}, \boldsymbol{q})$ is ruined in fully developed chaos, one might anticipate that the transition rule at any order would fail to yield κ to "good" accuracy. In other terms, even if one might find the *exact* invariant manifold locally at infinite order $\mathcal{O}(\epsilon^\infty)$, the recrossings should take place globally beyond the region where "local" recrossings can be eliminated by such canonical perturbation calculations.

IV. Conclusions and Outlook

In this article, we derived a strong dynamical propensity rule to predict the fate of a reaction. Our results strongly support the use of the concept of a single, nearly separable reactive degree of freedom in the system's *phase space*, a dof that is as free as possible from coupling to all of the rest of the dof in the region of the (first-rank) saddle even in a "sea" of high-dimensional chaos. This implies that most observed deviations from unity of the *conventional* transmission coefficient κ may be due to the choice of the reaction coordinate whenever the $\kappa < 1$ arises from the recrossings, and most transitions in chemical reactions must not take place in *fully*-stochastic fashion but in some predictable, dynamical fashion. If one carries out the backward calculations initiated with large momenta $\bar{p}_1(\boldsymbol{p}, \boldsymbol{q})$ on that dividing hypersurface $S(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = 0)$, one can reveal what kinds of initial conditions yield fast transitions from reactant to product.

The construction and accuracy of our propensity rule relies on the use of the perturbation calculation and the choice of the point about which to do the expansion of the potential. For a wide class of reactions regarded as occurring through a "potential barrier" as its reaction bottleneck (in a rough sense), the saddle point is the most reasonable choice. The great advantage of classical canonical perturbation calculation in the region of a saddle is to provide us with interesting *local* information about the original system at a finite low order up to which the perturbation series of the transformation is expected to be unaffected by the ultimate divergence arising from the characteristics of the whole phase space; the series presumably diverge for most realistic systems when the full, global set of interactions are taken into account. This "local" approach enabled us to present, for example, a first numerical evidence[6,9] of the robust persistence in the transition region of the invariants of motion associated with the reactive dof in the phase space, even while the other invariants with the nonreactive dofs are ever more quickly broken up as the total energy and the order of the perturbative calculation increase. This also gave us a first example[7] to visualize the phase space bottleneck of a multidimensional system whose degrees of freedom is much larger than 2 or 3. Very recently, the same algorithm was applied[40] for a three-mode system to compute a NHIM with its stable and unstable invariant manifolds. The NHIM (denoted here by $\mathcal{M}$) is expressed in terms of our notation by a set of all $(\boldsymbol{p}, \boldsymbol{q})$ satisfying both $\bar{q}_1 = \bar{p}_1 = 0$ and $\bar{H}_0(\bar{\boldsymbol{J}}_\mathbf{B}) + \sum_{n=1}\epsilon^n \bar{H}_n(\bar{\boldsymbol{J}}_\mathbf{B}, \bar{\boldsymbol{\Theta}}_\mathbf{B}) = E$ at a given total energy E, i.e.

$$\mathcal{M} = \{(\bar{q}_1, \bar{p}_1, \cdots, \bar{q}_N, \bar{p}_N) | \bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = \bar{p}_1(\boldsymbol{p}, \boldsymbol{q}) = 0, \bar{H}_0(\bar{\boldsymbol{J}}_B) + \sum_{n=1} \epsilon^n \bar{H}_n(\bar{\boldsymbol{J}}_B, \bar{\boldsymbol{\Theta}}_B) = E\} \quad (13)$$

The fundamental theorem on NHIMs ensures[18,38] that NHIMs, if they exist, survive under arbitrary perturbation with holding a property such 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 at a finite order perturbative calculation. Therefore, the robustness of the NHIM against perturbation (referred as to *structurally stable*[18,38]) may 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 finiteness of the order of the perturbative calculation can be regarded as a "perturbation".

Davis and Gray[14] first showed in a two-mode system the existence of dynamical bottlenecks to intramolecular energy transfer, that is, cantori buried in the reactant basin, which form partial barriers between irregular regions of phase space. This intramolecular bottleneck brought about multiply exponential decay on a wide range of time scales of the reaction, although the short-time decay is governed by an intermolecular bottleneck that divides the reactant region from scattering trajectories. Gillilan and Ezra[17] also observed a similar multiply exponential decay in a three-mode system, which makes us infer the existence of intramolecular bottlenecks. So far, there exists no general algorithm for locating arbitrary NHIMs, whereas 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. An analysis of pairwise local frequency ratios would be useful to search the intramolecular bottlenecks, at least, for 3-mode

systems.[47−49] However, it would be a very difficult task to deal with higher-dimensional systems.

The limitation of our present algorithm that applies a perturbative calculation to the region of saddles is that the resultant information is only *local* for the neighborhood of the saddle and there is no guarantee of whether all of the relevant recrossings of the reaction event are confined to such a locality. The higher the total energy of the system, the more the system may frequently recross a configurational dividing surface $S(q_1 = 0)$ and the longer the maximum excursion distances attained are in the coordinate q_1 away from the $S(q_1 = 0)$ before returning to it (prior to capture in reactant or product state). The *local* region in which the invariants of motion persist along the reactive dof should cover the excursion regime to predict the termini of the trajectories. That is, the more the total energy increases, the more the broadening of the excursion regime competes with the shrinkage of the region of local invariance of the action, evaluated by the perturbative method, in which *all* the apparent recrossings in the q_1 are rotated away to single crossings or noncrossings in the $\bar{q}_1(\boldsymbol{p}, \boldsymbol{q})$. (There is also a hidden perplexity of what time scale one should use to classify a trajectory as a "recrossing" versus a trajectory that contributes to establishing chemical equilibrium.) The outcome of this competition to determine whether or when a dividing hypersurface $S(\bar{q}_1(\boldsymbol{p}, \boldsymbol{q}) = 0)$ free from the recrossing problem can still be found in *semi-chaotic* region. However, as the total energy becomes much higher, such a regime of persistence of the local invariance calculated by any perturbative method should become extremely small, and most recrossing events should take place outside the local region of the saddle, in a *fully developed chaotic* region.[10] One might, nevertheless, anticipate that the stable and unstable invariant manifolds we extracted in the region of the saddle can be continued numerically through the rest of phase space.[50] This provides us with an essential clue to generalize separatrix theories to arbitrary multidimensional systems, which may shed light on how "local equilibrium" is established or spoiled in multidimensional reacting systems.

The development of the computer visualization of the higher dimensional structures of phase space is also highly demanding. The recent visualization[40] of a NHIM and the stable and unstable invariant manifolds was brought about by the projections of those onto the original space at a certain energy value where the system can be classified into the *quasiregular* region,[11] in which all actions persist approximately as the local invariants. Hence, the inverse of all of the transformed new coordinates and momenta into the original ones are straightforward. However, as the total energy increases, most actions become ruined; the exception is that of the reactive dof in the *semichaotic* region, and ultimately toward the *fully developed chaotic* region, where even it is spoiled. Here, the inverse of $(\bar{\boldsymbol{p}}, \bar{\boldsymbol{q}})$ into the original $(\boldsymbol{p}, \boldsymbol{q})$ should become rather problematic because of the divergence of most terms in the generating functions.

Acknowledgment. We acknowledge Professor Mikito Toda and Professor Stuart A. Rice for their continuous, stimulating discussions. We also thank Professor Stephen Wiggins for sending us their (p)reprint[40] with their recent progressive results[51] of the visualization of the NHIM and its stable and unstable invariant manifolds. T.K. acknowledges supports from the Japan Society for the Promotion of Science, Grant-in-Aid for Research on Priority Areas (A) "Molecular Physical Chemistry", and (C) "Genome Information Science" of the Ministry of Education, Science, Sports and Culture of Japan. R.S.B. acknowledges support from the National Science Foundation.

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