Definability of No-Return Transition States in the High-Energy Regime above the Reaction Threshold

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No-return transition states (TSs) defined in multidimensional phase space, where *recrossing* trajectories through the commonly used ''configuration'' TS pass only *once*, robustly exist up to a moderately high-energy regime above the reaction threshold, even when nonlinear resonances among the bath degrees of freedom perpendicular to the reaction coordinate result in local chaos. However, at much higher energy when global chaos appears in the bath space, the separability of the reaction coordinate from the bath degrees of freedom starts to lose locally. In the phase space near the saddles, it is found that the slower the system passes the TS, the more recrossing trajectories reappear. Their implications and mechanisms are discussed concerning to what extent one can define no-return TSs in the high-energy regime above the reaction threshold.

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Transition states (TSs) have provided us with great insights in understanding reaction rates not only in chemistry [1] but also in atomic physics [2], cluster physics [3], celestial mechanics [4], and biology [5]. The TS is defined as a dividing hypersurface through which reacting species pass only once on the way from the reactant to the product. One often defines the TS in the configuration space. However, this idea suffers from the recrossing problem and overestimates the reaction rates. One of the most outstanding questions to be addressed is to clarify in what circumstance such a no-return TS exists, which enables us to estimate the accurate reaction rates.

Recently, several remarkable developments have shed light on the passage mechanics through potential saddles of index one (equilibrium points with one negative Hessian eigenvalue). Theoretical studies on isomerization reactions of Lennard-Jones atomic clusters, that showed a decrease of local Lyapunov exponents in the regions of saddles compared with those in the potential well, implies dynamical regularity of passage near the potential saddle [6]. Experiments on the decomposition of vibrationally excited ketenes by Lovejoy *et al.* showed monotonical increases with quantized steps in the reaction rates as a function of energy above the threshold [7,8]. It was argued [9,10] that this indicates the existence of approximate invariants of motion in the TS.

The existence of no-return TSs was well established in 2 degrees of freedom (DOF) Hamiltonian systems. An unstable periodic orbit at the unstable equilibrium point (i.e., saddle point), that is an invariant of motion, gives rise to the so-called ''periodic orbit dividing surface (PODS)'' [11,12]. The generalization to many-DOF systems, however, has been unresolved until very recently [13]. The general procedure for extracting the no-return TSs from many-DOF phase space is described in detail in Ref. [2,14]. The crux is to generate a sequence of nonlinear canonical transformations in the region of the index one saddle that transforms the Hamiltonian into a normal form (a classical analog of the Dunham Hamiltonian in molecular spectroscopy). This construction provides us with a fundamentally new object, namely, the normally hyperbolic invariant manifold (NHIM), that takes the place of the PODS in many-DOF reacting systems. This building block enables us to define a robust no-return TS as a dividing hypersurface that decomposes the multidimensional phase space into the distinct regions of reactant and product. Moreover, the orbits that asymptotically approach to (leave from) the NHIM construct the stable (unstable) invariant manifolds, and form the boundary of the reaction paths in the phase space through which *all* reactive trajectories necessarily follow [15].

Up to the present, the versatility of the no-return TSs and the reaction paths in the phase space has been well examined in evaluating the accurate reaction rates in isomerization reactions of the 6-atom cluster [3,16] and HCN [17,18], ionization of a hydrogen atom in crossed electric and magnetic fields [2], and also the escape of asteroids from Mars [4]. However, most of the studies are only concerned with the low energy regime above the threshold (saddle point energy) where the passage dynamics is completely regular and the NHIM simply consists of unstable quasiperiodic orbits. The reaction rates in this energy regime monotonically increase in quantized steps with the energy of the system [7,8].

As the energy increases more above the threshold, nonlinear resonances start to take place among the bath DOF near the index one saddles. These can cease most of the invariants of action in the bath space. Nevertheless, nu-

merical evidences from the isomerization of 6-atom clusters [3,16] suggest that the NHIM and its stable or unstable manifolds still act as approximate invariants at such moderately high energies above the threshold. Furthermore, the robust existence of no-return TS enables us to evaluate the reaction rate quite accurately. As pointed out previously [19], this is due to the fact that the small denominator problem, which causes divergences of the perturbation expansion in the normal form calculation, can never be encountered by terms involving an imaginary frequency associated with the reactive DOF and the real frequencies of the bath DOF [20].

At much higher energies above the threshold, it was shown in the 6-atom cluster isomerization [3,16] that the no-return TS in phase space breaks down. Moreover, the experiments on ketene decomposition [7,8] revealed that the simple monotonic increase of the rates ceases in the high-energy regime. This indicates the destructions of the invariants of motion of the bath DOF and of the no-return TS. However, the general breakdown mechanisms of the concept of no-return TS have been yet one of the most outstanding unresolved problems. The purpose of the present Letter is to reveal in what circumstance nonlinear resonances among the bath DOF affect the existence of the no-return TS in the high-energy regime above the threshold. In particular, we demonstrate that the one-dimensional nature of the reaction coordinate, that decouples from the bath DOF up to moderately high energies, does not hold when global chaos arises in the bath space.

Our procedure is quite general, in principle, to any reacting systems in which the reactions are mediated through a potential saddle of index one at constant energy E. First, we expand a given N-DOF Hamiltonian system near the saddle as

$$H = E_0 + \sum_{i=1}^{N}\left(\frac{p_i^2}{2} + \frac{\omega_i^2 q_i^2}{2}\right) + \sum_{n=3}^{\infty} H_n, \qquad (1)$$

where E_0 is the energy of the saddle point, and H_n consists of terms of the nth degree in $(\mathbf{p}, \mathbf{q}) = (p_1, \ldots, p_N, q_1, \ldots, q_N)$. Here, (p_1, q_1) are the momentum and coordinate of the reactive normal mode, and those of the bath normal modes are denoted by $(\mathbf{p}_b, \mathbf{q}_b) = (p_2, \ldots, p_N, q_2, \ldots, q_N)$. Note that ω_1 is pure imaginary and ω_i is real for $i \geq 2$.

Next, we *formally* transform the Hamiltonian H to a "partial" normal form H' in which only the reactive DOF is normalized so that it is separated from the bath space [21].

$$H'(J_1', \mathbf{p}_b', \mathbf{q}_b') = E_0 + \omega_1 J_1' + \sum_{i=2}^{N}\left(\frac{p_i'^2}{2} + \frac{\omega_i^2 q_i'^2}{2}\right) + f_1(J_1', \mathbf{p}_b', \mathbf{q}_b') + f_2(\mathbf{p}_b', \mathbf{q}_b'), \qquad (2)$$

where

$$J_1' = \frac{1}{2\pi}\mathrm{Im}\int_{\mathrm{barrier}} p_1' dq_1' = i(p_1'^2/|\omega_1| - |\omega_1| q_1'^2)/2 \qquad (3)$$

is the imaginary "action" [22] of the new reactive mode (p_1', q_1'), and $(\mathbf{p}_b', \mathbf{q}_b') = (p_2', \ldots, p_N', q_2', \ldots, q_N')$ denote the new bath modes [23]. The functions f_1 and f_2 contain anharmonic terms in powers of the partial normal form variables $(\mathbf{p}', \mathbf{q}')$. In particular, f_1 is defined so that $f_1 = 0$ when $J_1' = 0$. Since the partial normal form does not involve the "angle" variable conjugated to J_1', the action variable J_1' is an invariant of motion. This ensures the existence of no-return TS if H can *actually* be transformed into Eq. (2). However the separability of the reactive DOF is not guaranteed when the energy becomes high. In the following, we scrutinize the validity of the transformation by monitoring the invariance of the action $J_1'(\mathbf{p}, \mathbf{q})$ along the dynamics of the *original* Hamiltonian H. We also analyze the role of resonances among the bath DOF for the persistence of no-return TS by projecting the original dynamics onto the new variables $[p_i'(\mathbf{p}, \mathbf{q}), q_i'(\mathbf{p}, \mathbf{q})]$ [3].

As an illustrative vehicle, we apply this to the following three-DOF Hamiltonian, which is regarded as a prototype of isomerization reactions,

$$H = \frac{p_1^2 + p_2^2 + p_3^2}{2} + a_1 q_1^2 + a_2 q_1^4 + \frac{\omega_1^2 q_1^2 + \omega_2^2 q_2^2}{2} + \sum_{i=0}^{2} e^{-\alpha_i (q_1 - q_{1i})^2}[\beta_i q_2^2 q_3^2 + \gamma_i q_1^2 (q_2^2 + q_3^2)]. \qquad (4)$$

The parameters are $a_1 = -35/75$, $a_2 = 2/1875$, $\omega_2 = 1$, $\omega_3 = 0.809$, $q_{10} = 2$, $q_{11} = -q_{12} = 14.1421$, $\alpha_0 = 1/16$, $\alpha_1 = \alpha_2 = 1$, $\beta_0 = 8$, $\beta_1 = \beta_2 = 1$, $\gamma_0 = 0.75$, and $\gamma_1 = \gamma_2 = 1$. The ratio between ω_2 and ω_3, approximately the golden mean, was chosen to avoid *linear* resonance. The imaginary frequency associated with q_1 at the saddle is estimated as $\omega_1 \simeq -0.924i$. The nonzero value of q_{10} aims at avoiding specific symmetry of the potential energy function in q_1. The Hamiltonian Eq. (4) is transformed to the partial normal form Eq. (2) up to the 15th order. The no-return TS in many-DOF phase space may, in general, bifurcate and migrate outward the remote regions from the saddle when E increases above the threshold as PODS does in two DOF systems [11]. In order to focus on the breakdown (not just bifurcation) of the no-return TS, the potential parameters are chosen such that the breakdown of the no-return property takes place *a priori* to the bifurcation of the no-return TS as E increases above the threshold.

In Fig. 1, we display the surface of section (SOS) of the NHIM defined by the condition $q_2' = 0$ and $p_2' > 0$. Note that the SOS should consist of a set of ellipses when the invariants of action exist for all the bath modes, resulting in the quantized monotonic increase of the reaction rate [7,8]. Here, two cases are shown: the case when most of the tori survive with some isolated stochastic layers [Fig. 1(a)], and the case when globally chaotic regions appear [Fig. 1(b)].

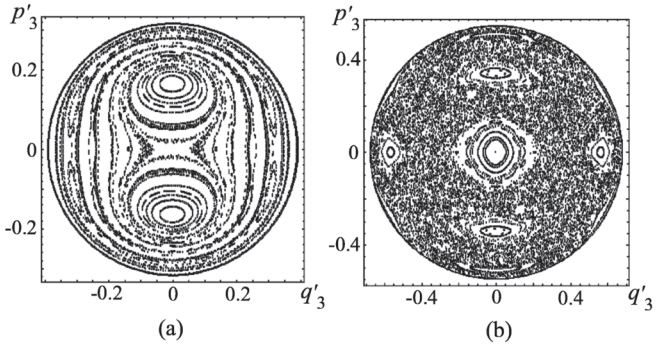

FIG. 1. The SOS on the NHIM displayed on the (q'_3, p'_3) plane: (a) $E = 0.05$ with some isolated stochastic layers, (b) $E = 0.15$ when global chaos emerges. The NHIM is represented by $\{(\mathbf{p}', \mathbf{q}')|p'_1 = q'_1 = 0, H'(J'_1 = 0, \mathbf{p}'_b, \mathbf{q}'_b) = E\}$.

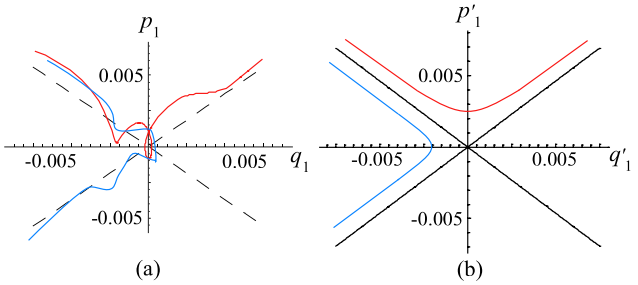

FIG. 2 (color online). Projections of representative recrossing orbits observed on the (p_1, q_1) plane onto the (p'_1, q'_1) plane at $E = 0.05$: (a) (p_1, q_1), (b) (p'_1, q'_1). The no-return TS in phase space is given by $\{(\mathbf{p}', \mathbf{q}')|q'_1 = 0, H'(J'_1 = p'^2_1/(2\omega_1), \mathbf{p}'_b, \mathbf{q}'_b) = E\}$.

In Fig. 2, a few representative recrossing trajectories obeying the original Hamiltonian H are shown at $E = 0.05$ on both the (p_1, q_1) and (p'_1, q'_1) planes. We can see how well the no-return TS persists robustly even when chaos exists locally on the bath space. The partial normal form "rotates" away the recrossing orbits on (p_1, q_1), in which the new action J'_1 actually behaves as a good invariant.

In the much higher energy regime above the threshold, it was found that the application of the Padé approximants to the series of partial normal form is crucial to confirm if the fluctuation in J'_1 arises from the finite truncation of the perturbation calculation, or from an inherent change of the underlying phase space structure.

Given a perturbation expansion of a physical quantity ξ (e.g., $\xi = q'_1, J'_1, p'_3$, etc.) in the partial normal form up to the kth order $\xi(\mathbf{p}, \mathbf{q}) = \sum_{j=0}^{k} \epsilon^j \xi_j(\mathbf{p}, \mathbf{q})$, where ξ_j denotes terms of jth power in $(\mathbf{p}, \mathbf{q})$ and ϵ^j keeps track of their power for $j = 0, \ldots, k$. The Padé approximant $\xi_{[n,m]}(\epsilon)$ with $n + m + 1 \leq k$ is a rational approximation to ξ defined by $P_n(\epsilon)/P_m(\epsilon)$, where $P_n(\epsilon)$ and $P_m(\epsilon)$ are polynomials of order n and m in ϵ, respectively, with coefficients depending on $(\mathbf{p}, \mathbf{q})$ [24]. In this Letter, we extrapolated all physical quantities in the partial normal form calculation by the Padé approximants with $n = m = 6$.

In Fig. 3, we show a few representative reactive trajectories obeying the original Hamiltonian H on the (p'_1, q'_1) plane with different J'_1 at the entrance to the saddle at $E = 0.15$. The Padé approximants of (p'_1, q'_1) show the existence of singularities in the partial normal form calculation (whose regions in the phase space have been considered as resonance regions [24]). The singularities are more pronounced as the trajectory is closer to the "NHIM" and its "stable and unstable invariant manifolds" with $J'_1 = 0$ predicted by Eq. (2). Moreover, the inset of Fig. 3 reveals that these trajectories cross the "stable or unstable manifolds" and, in particular, they recross the "no-return TS." The closer the trajectories are to the phase space regions of $J'_1 = 0$, the more energy should be distributed into the bath space because of energy conservation. This results in larger possibilities to yield stronger nonlinear resonances in the bath space.

To look deeper into the question of why the concept of no-return TS and the one-dimensional nature of the reaction coordinate are ruined in such a high-energy regime above the threshold, we compare the time evolution of the action J'_1 with the local Lyapunov exponents (LLEs) for the reactive and bath directions near the saddle. Figure 4(a) shows the Padé approximant of J'_1, and Fig. 4(b) displays the two largest LLEs λ_1 and λ_2, where λ_1 and λ_2 represents the instability along the reactive and bath directions, respectively. Here, LLEs were estimated for the reactive trajectory closest to the regions of $J'_1 = 0$ in Fig. 3 by using the Jacobian method [6]. Note that the large singular peaks of J'_1 appear when the value of λ_2 becomes comparable to λ_1. The sufficient condition for the existence of NHIM is that the absolute values of LLE along its normal directions are much larger than those along its tangential ones (termed as *normal hyperbolicity*) [25,26]. Instability of the dynamics on the NHIM is, thus, closely related to its structural stability. Figure 4 provides us with the first numerical evidence that the singularities of the action emerge, i.e., breakdown of the NHIM, when trajectories

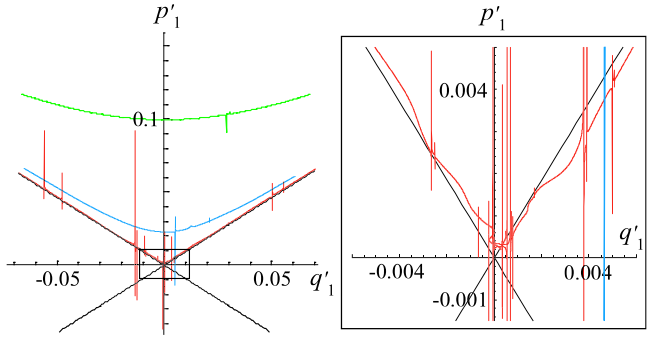

FIG. 3 (color online). Projections of representative reactive trajectories on the Padé approximants of the (p'_1, q'_1) at $E = 0.15$.

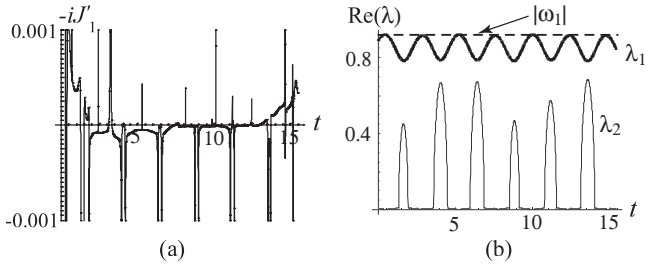

FIG. 4. Comparison between singularities of J_1' and LLEs for the trajectory closest to the regions of $J_1' = 0$ in Fig. 3: (a) The Padé approximant of $-iJ_1'$. (b) λ_1 and λ_2. The instantaneous values of LLEs are averaged over a time of 1 unit so that $\mathrm{Re}(\lambda_1)$ coincides with $|\omega_1'| = |\partial H'/\partial J_1'|$.

come near to the breakdown of normal hyperbolicity. The breakdown of NHIM by chaos in the bath space is a new phenomenon inherent to many-DOF systems.

In this Letter, we have examined the definability of no-return TS in the high-energy regime above the reaction threshold before the bifurcation of TS takes place [27]. When the energy above the saddle is not so high, we have confirmed the robust existence of no-return TS, i.e., the property of no-return persists even when chaos emerges among the bath modes. As the energy increases further, the no-return TS ceases to exist locally near the saddle because of strong chaos emerging in the bath space. These effects are strongly pronounced in those regions where the LLEs along the bath directions come nearer to the LLE along the reactive direction.

These observations lead us to the question: Is the concept of no-return TS ruined completely? A ''vague'' TS could be defined even when the no-return TS no longer exists in the mathematical sense. As energy increases above the saddles, the concept of no-return TS would initially break down in the local regions where the LLEs along the reactive and bath directions are comparable. Nevertheless, we could still define a vague TS using the other regions of the phase space (e.g., [24]) where the LLEs along the bath directions are smaller than those along the reactive one. Recently, it is shown that the NHIM exists even under the influence of an external noise [28].

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