Dynamical hierarchy in transition states: Why and how does a system climb over the mountain?

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How a reacting system climbs through a transition state during the course of a reaction has been an intriguing subject for decades. Here we present and quantify a technique to identify and characterize local invariances about the transition state of an *N*-particle Hamiltonian system, using Lie canonical perturbation theory combined with microcanonical molecular dynamics simulation. We show that at least three distinct energy regimes of dynamical behavior occur in the region of the transition state, distinguished by the extent of their local dynamical invariance and regularity. Isomerization of a six-atom Lennard–Jones cluster illustrates this: up to energies high enough to make the system manifestly chaotic, approximate invariants of motion associated with a reaction coordinate in phase space imply a many-body dividing hypersurface in phase space that is free of recrossings even in a sea of chaos. The method makes it possible to visualize the stable and unstable invariant manifolds leading to and from the transition state, i.e., the reaction path in phase space, and how this regularity turns to chaos with increasing total energy of the system. This, in turn, illuminates a new type of phase space bottleneck in the region of a transition state that emerges as the total energy and mode coupling increase, which keeps a reacting system increasingly trapped in that region.

The pervasive concept of the mechanism of the most common class of chemical reactions is that of a system moving on a single effective potential surface, typically in a space of $3N$-6 independent variables, for an N-body system, from one local minimum, the state of the reactants, across a saddle or transition state, to a second local minimum, that of the products. The concept of transition state or dividing surface was introduced by Eyring (1) and Wigner (2). If the system begins in thermal equilibrium, and if conditions justify assuming a quasiequilibrium between the reactants and systems crossing the transition state in the forward direction (i.e., toward the products) along the reaction coordinate q_1, then the apparatus of "transition-state theory" in any of several forms (1–12) can be invoked to evaluate the rate coefficient of the reaction. The greater part of the effort in using any of the specific methods is establishing the hypersurface dividing reactant from product so that it is as free as possible from the "recrossing problem." Such dividing surfaces have usually been defined in configurational space (1–8); Davis and Gray (13) first showed that in any Hamiltonian system with two degrees of freedom (dof), the transition state defined as the separatrix in *phase* space is always free from barrier recrossings. This analysis, however, has been limited to systems with only two dof; there has been no general theory yet for systems of higher dimensionality (14–17). Several recent developments, theoretical (18–23) and experimental (24, 25), have shed light on mechanics of passage through reaction bottlenecks. Indicative symptoms of a local regularity near reaction bottlenecks appeared in theoretical studies of small atomic clusters that compared local Liapunov functions and Kolmogorov entropies in saddle regions with those in other regions of potential surfaces (18–21). Experiments by Lovejoy *et al.* on decomposition of vibrationally excited ketene showed rates with quantized steps (24, 25). Marcus suggested that this could be a signature of existence of approximate invariants of motion in the transition state (26). "How does a complex system behave as it traverses the transition state?" and "What kinds of trajectories carry the system through?" are questions considerably more demanding than, for example, asking how the reaction rate depends on temperature.

It is these questions of microscopic mechanism that we address here, using isomerization of a six-atom cluster bound by pairwise Lennard–Jones forces as our illustrative vehicle. This was taken as typical of real systems of moderate size, because it has 15 internal (rotational + vibrational) dof. Fig. 1 shows the species' two stable structures, an octahedron (OCT) and a capped trigonal bipyramid (CTBP), and the energies of these structures and the saddles linking them. The crux of this approach is the application of Lie canonical perturbation theory (27) to generate a nonlinear coordinate transformation, from an arbitrary initial set of coordinates for the atoms of the reacting system into a new set in which the individual dof are as regular as possible, at the degree of expansion in perturbation theory one chooses to use.

The following results are the essential content of this report. (All results are given in the universal reduced units of the Lennard–Jones potential; energies, action, temperature, and time are, respectively, in units of the energy unit ε, Kps, K, ps.) Three distinct kinds of dynamical behavior occur in *quantitatively* identifiable energy regions above the transition state: (*i*) if the system has only a bit more energy than the absolute minimum required to traverse the saddle, $\sim 0.1\varepsilon$ above that saddle, and can go from reactant to product, then the action and frequency in each dof are well conserved in the region of the transition state, and each dof is fairly regular; we call this the *quasiregular region*; (*ii*) throughout a considerably wider range of energies, up to at least 0.5ε above a saddle, the one dof corresponding to the reaction coordinate in phase space remains rather regular and conserves its action and frequency with small bounds on the fluctuations of these quantities similar to those at $E = 0.1\varepsilon$, even when all the other dof have become chaotic, with large fluctuations in their action and frequency; this is the *semichaotic region*; and (*iii*) at still higher energies, the zone of regular behavior along the reactive dof shrinks to a size too small for the system to move about before being captured in either reactant or product state; this we term the *stochastic (fully developed chaotic) region*. These findings prove the picture that, up to moderately high energies, any system entering the neighborhood of the saddle point (or, more generally, approaching the *phase* space dividing hypersurface, suitably defined) with enough energy in the reactive dof to cross the hypersurface, then it certainly will do so, because that dof decouples from all the rest and retains both its action and frequency during transit (28–30).

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Abbreviation: dof, degrees of freedom.

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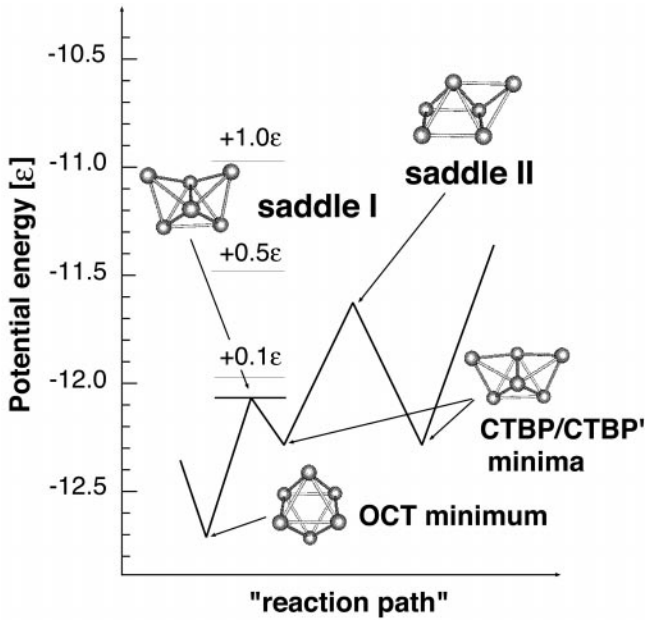


Fig. 1. Schematic picture of the potential energy surface of Ar_6. Capped trigonal bipyramid (CTBP)′ is a permutational isomer of the CTBP minimum neighboring on the octahedron (OCT) minimum. For argon, $\varepsilon = 121$ K.

This is a rigorous demonstration of the extent of persistence of the locally conserved action along the *phase*-space reaction coordinate, even in the sea of chaos, independent of the sample trajectory along which one evaluates its action and frequency; this was only a conjecture in our previous report, inferred from the energy dependence of the transmission coefficient (28). Without assuming any separation of time scales for individual modes of the system, we show how one can extract and visualize the stable and unstable invariant manifolds along the reaction coordinate in the phase space, to and from the hyperbolic point of the transition state of a many-body nonlinear system, just like that of a one-dimensional integrable pendulum. The most immediate and striking consequence of this analysis is that a new type of phase-space bottleneck emerges, which makes a reacting system increasingly trapped in the region of transition states as the total energy or temperature of the system increases, going from semichaotic into fully developed chaotic regions. This challenges the simple mechanisms one has supposed for a reacting system crossing a transition state, i.e., both the ballistic (or separable) and diffusive transitions.

Lie Canonical Perturbation Theory

The canonical perturbation approach we use to establish the coordinate system maximizing the local regularity in as many dof as possible is, in brief, the following. The Hamiltonian $H(\mathbf{p}, \mathbf{q})$ is expressed in a region around a saddle point of interest as an expansion in a small parameter ε, so that the lowest-order term or zero-th order Hamiltonian 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 $\mathbf{J}$ only and does not depend on the conjugate angle variables $\mathbf{\Theta}$. Then the maximum order of perturbation is chosen, in our case at second order. The first- and second-order terms of the Hamiltonian are expressed as sums of cubic and quartic terms in the normal coordinates of the system, and the three zero-frequency modes associated with translation of the center of mass are removed.

$$H(\mathbf{p}, \mathbf{q}) = \sum_{n=0} \varepsilon^n H_n(\mathbf{p}, \mathbf{q}), \quad [1]$$

$$= H_0(\mathbf{J}) + \sum_{n=1} \varepsilon^n H_n(\mathbf{J}, \Theta). \quad [2]$$

The requisite equations to solve are those that minimize the angle dependencies of the new Hamiltonian $\bar{H}$, thereby making the action variables $\bar{\mathbf{J}}$ as nearly constant as possible (27). If the $\bar{H}$ is obtained free from the angle $\bar{\mathbf{\Theta}}$ (at the order of the perturbative calculation performed), then

$$H(\mathbf{p}, \mathbf{q}) \overset{W}{\longrightarrow} \bar{H}(\bar{\mathbf{p}}, \bar{\mathbf{q}}) = \bar{H}(\bar{\mathbf{J}}) = \sum_{n=0} \varepsilon^n \bar{H}_n(\bar{\mathbf{J}}), \quad [3]$$

the new action and angle variables for the kth mode are expressed as

$$\frac{d\bar{J}_k}{dt} = \dot{\bar{J}}_k = -\frac{\partial \bar{H}(\bar{\mathbf{J}})}{\partial \bar{\Theta}_k} = 0, \quad [4]$$

$$\bar{J}_k = \text{constant}, \quad [5]$$

and

$$\dot{\bar{\Theta}}_k = \frac{\partial \bar{H}(\bar{\mathbf{J}})}{\partial \bar{J}_k} \equiv \bar{\omega}_k(\bar{\mathbf{J}}) = \text{constant}, \quad [6]$$

$$\bar{\Theta}_k = \bar{\omega}_k(\bar{\mathbf{J}})t + \beta_k, \quad [7]$$

where β_k is the arbitrary initial phase factor of the kth mode. From these, the equations of motion are derived (23) for the new coordinates $\bar{\mathbf{q}}(\mathbf{p}, \mathbf{q})$ and momenta $\bar{\mathbf{p}}(\mathbf{p}, \mathbf{q})$ to obey "$\bar{H}$";

$$\frac{d^2\bar{q}_k(\mathbf{p}, \mathbf{q})}{dt^2} + \bar{\omega}_k^2 \bar{q}_k(\mathbf{p}, \mathbf{q}) = 0, \quad [8]$$

and

$$\bar{p}_k(\mathbf{p}, \mathbf{q}) = \frac{\omega_k}{\bar{\omega}_k} \frac{d\bar{q}_k(\mathbf{p}, \mathbf{q})}{dt}, \quad [9]$$

where ω_k is the frequency associated with the normal coordinate, and the new frequency $\bar{\omega}_k (= \bar{\omega}_k(\bar{\mathbf{J}}) = \bar{\omega}_k(\bar{\mathbf{p}}, \bar{\mathbf{q}}))$ is independent of time t because the $\bar{\mathbf{J}}$ are constant.

This implies that, even though the motions look quite complicated in the $(\mathbf{p}, \mathbf{q})$ system, they can be reformulated as simple decoupled periodic and/or hyperbolic orbits in the $(\bar{\mathbf{p}}, \bar{\mathbf{q}})$ system. If, and only if, the approximate invariants $\bar{J}_k$ and $\bar{\omega}_k$ exist in a global (or at least local) region, can $\bar{q}_k(\mathbf{p}, \mathbf{q})$ and $\bar{p}_k(\mathbf{p}, \mathbf{q})$ be decoupled from one another, although they are functions of the coupled $\mathbf{p}$ and $\mathbf{q}$ obeying the original system Hamiltonian H. Lie canonical perturbation theory (27), which is based on Lie transforms, is the most powerful theory to establish these approximate invariants. The practical transformation W to the new coordinates proceeds by the method of "algebraic quantization" (22, 32), first by transforming from normal coordinates $\mathbf{q}$ and conjugate momenta $\mathbf{p}$ to "raising" and "lowering" operators in the customary way, and then expressing these in terms of action and the conjugate angle variables. We suppose here that the saddle is of rank 1, so that it has only one negative force constant, one imaginary frequency, and one imaginary action.

Local Invariancy Analyses About the Transition State

It is well known that the new transformed Hamiltonian $\bar{H}$ diverges if the system encounters (near-)resonance, and becomes meaningless (often called the "small-denominator problem"). It

is quite likely that the more dof, the more the global invariants through the whole system are spoiled, but the invariants of motion might survive within some locality in phase space, i.e., for a certain finite duration and/or in a limited set of dof. The local invariancy analyses we establish here can reveal the occurrence of such local invariants in the complexity of the dynamics. We use the action $\bar{J}(\mathbf{p}, \mathbf{q})$ and frequency $\bar{\omega}(\mathbf{p}, \mathbf{q})$ to monitor the extent of local invariance of motion along the course of the dynamical evolution obeying the *original* Hamiltonian $H(\mathbf{p}, \mathbf{q})$, even through a space where $\bar{H}$ might diverge.

We introduce a concept of "duration of regularity (τ)" for each mode of the system, at each ith order of perturbation; these are the residence times each mode remains close to its near-constant values of the variables, as determined by a chosen bound on the fluctuation $\Delta\bar{J}$ or $\Delta\bar{\omega}$; e.g., $\Delta\bar{J}$ for mode k, is

$$|\bar{J}_k^{i\text{th}}(\mathbf{p}(t+\tau), \mathbf{q}(t+\tau)) - \bar{J}_k^{i\text{th}}(\mathbf{p}(t), \mathbf{q}(t))| \leq \Delta\bar{J}. \qquad [10]$$

Near a stable fixed point it is well known that trajectories are regular or nearly so at low energies. Here, however, we deal with an unstable fixed point. At energies slightly above the energy of the saddle, virtually all the energy of the system must be put into potential energy as the system crosses the saddle, i.e., when the trajectory is that of a reaction. In that case, the motion of the system in the saddle region is governed essentially by the zero-order Hamiltonian and, even if this is not precisely so, the nonlinear terms of potential can be still regarded as small perturbations, for which perturbation theory should work well for any mode. The transition region is therefore almost regular for such energies. Simulations bear this out; Fig. 2 shows the probability distributions of the system's residence times in the zone of near-invariant action for several modes during the course of the reaction across saddle I at each order, at $E = 0.1\varepsilon$. If the system has only a bit more energy than the absolute minimum required to traverse the saddle and pass from reactant to product, then all the dof are fairly regular, and the action in each is well conserved *in the region of the transition state*. The higher the order of the perturbative calculation performed, the more the action is conserved along the negatively curved reactive mode 1, as it is in the other, nonreactive modes.

As the energy is increased more and more, to at least 0.5ε above the saddle energy, the actions of nonreactive modes show successively more variance and shorter durations of regularity as the calculation is refined to higher order. However, the higher the order of LCPT, the more the action in the mode of the reaction coordinate $\bar{J}_1(\mathbf{p}, \mathbf{q})$ stands out in bold relief as a near constant of motion for longer and longer times. Despite the much higher energy washing out any local regularity in the space of nonreactive modes, the system retains its invariant of the action along the reaction coordinate $\bar{q}_1(\mathbf{p}, \mathbf{q})$ as it does at $E = 0.1\varepsilon$ (see Fig. 3). Its associated frequency $\bar{\omega}_1(\mathbf{p}, \mathbf{q})$ also remains a rather good approximate classical invariant of motion near the saddle, even when the local frequencies of other modes are quite variable. Only very slow passages over the transition state spoil the invariant (31). At much higher energy, $\sim 1.0\varepsilon$, the probability of the system retaining invariance of its action diminishes even along the reaction coordinate at the second order, with a much larger escape rate from that fluctuation regime of the variables than at lower energies.

A Portrait of the Local Invariant Manifolds in $(\bar{\mathbf{p}}, \bar{\mathbf{q}})$ and Its Energy Dependence

How and where does the invariant of action distribute in the space $(\bar{\mathbf{p}}(\mathbf{p}, \mathbf{q}), \bar{\mathbf{q}}(\mathbf{p}, \mathbf{q}))$, and how is this spoiled in the region of the transition state with increasing total energy? Fig. 4 shows how the system distributes at $E = 0.1\varepsilon$ in the two-dimensional $(\bar{p}_2(\mathbf{p}, \mathbf{q}), \bar{q}_2(\mathbf{p}, \mathbf{q}))$ space while it retains its local, approximate invariant of action $\bar{J}_2^{2\text{nd}}(\mathbf{p}, \mathbf{q})$ for a certain locality, $\sim\Delta\bar{J} = 0.05$

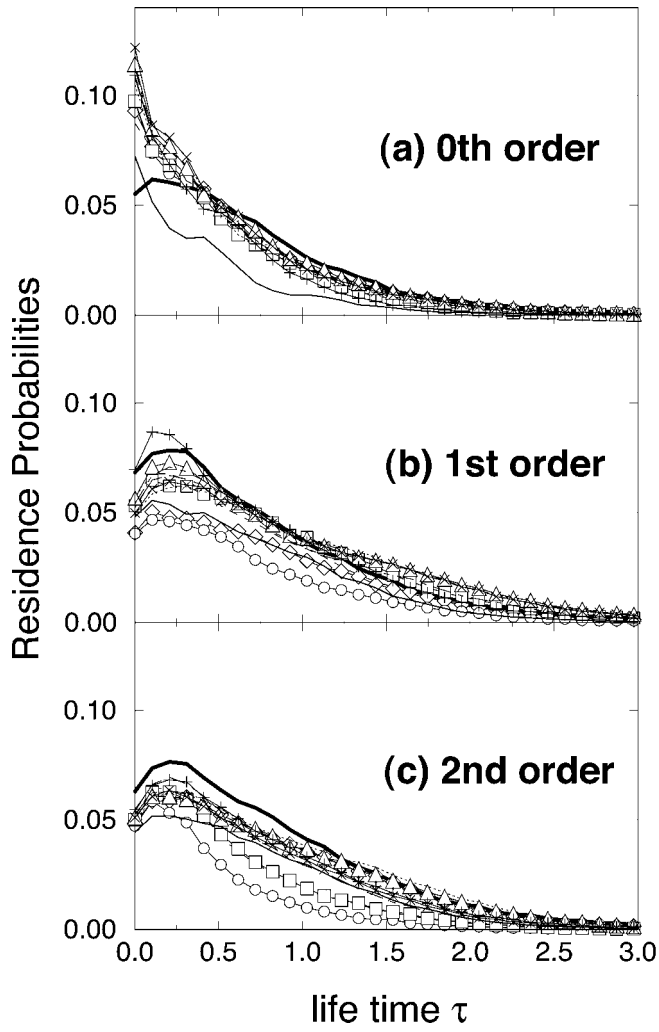


Fig. 2. The residence probabilities of the system residing in the zone of near invariants of action ($\Delta\bar{J} \leq 0.05$) during the course of the reactions at 0.1ε for saddle I at each order. The bold–solid line denotes the reactive mode 1 with imaginary frequency at each order, and the others are the nonreactive; dashed, ◇, filled ○, □, filled ◇, long-dashed, filled △, △, ○, dot-dashed, and solid lines denote 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12, respectively, in such an order that the frequencies, $0 < \bar{\omega}_2 \leq \bar{\omega}_3, \ldots, \leq \bar{\omega}_{12}$. The units of $\Delta\bar{J}_1^{i\text{th}}$ for the reactive mode 1 must be multiplied by a factor of an imaginary number i throughout this report.

and $\tau \geq 0.5$. The figure clearly tells us the existence of a local near-invariant of motion in this nonreactive dof, but it retains this constancy only at low energies, just slightly above the threshold. We refer to this as the quasiregular regime. As the energy increases, $\sim E \geq 0.5\varepsilon$, such invariant regions in the nonreactive dof totally disappear, i.e., all the nonreactive dof become chaotic. However, as shown by the strong correlation of $(\bar{p}_1(\mathbf{p}, \mathbf{q}), \bar{q}_1(\mathbf{p}, \mathbf{q}))$ in Fig. 5, even at $E = 0.5\varepsilon$, a significant amount of local invariance stands out in bold relief, associated with the reaction coordinate $\bar{q}_1(\mathbf{p}, \mathbf{q})$ at second order.

As the total energy of the system increases to high values, two things happen. The higher the energy, the narrower the zone of approximately invariant action around the origin of the coordinates, $\bar{q}_1(\mathbf{p}, \mathbf{q}) \cong \bar{p}_1(\mathbf{p}, \mathbf{q}) \cong 0$, and the smaller the residence probability in the zone of approximate local invariance. The system may recross the traditional dividing surface $S(q_1 = 0)$ before passing into the product or reactant region. We refer to the maximum distance attained in the conventional reaction coordinate q_1 away from the dividing surface between sequential

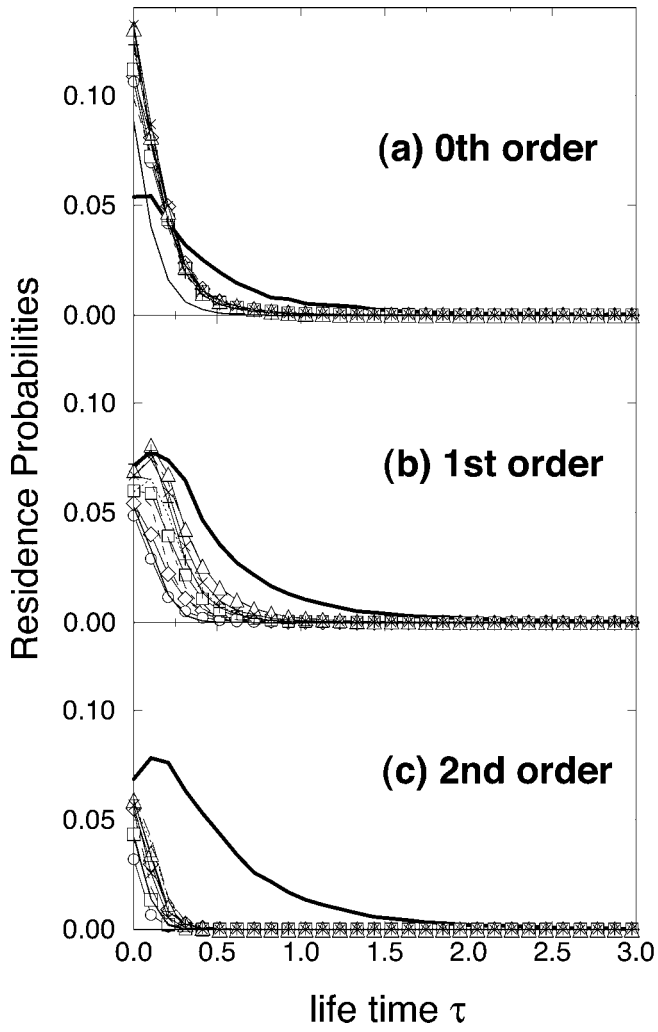


Fig. 3. The residence probabilities of the near invariants of action at 0.5ε. The other conditions and the meaning of each symbol are same as in Fig. 2.

crossings (prior to capture in reactant or product state as the "excursion regime"). The more the energy increases, the more the excursion regime of the system expands. But the excursion regime is the region in which the *new* action $\bar{J}_1(\mathbf{p}, \mathbf{q})$ should be conserved to rotate all the apparent recrossings in the q_1 away to single crossings or noncrossings in the $\bar{q}_1(\mathbf{p}, \mathbf{q})$ and predict the termini of the trajectories. That is, the more the total energy

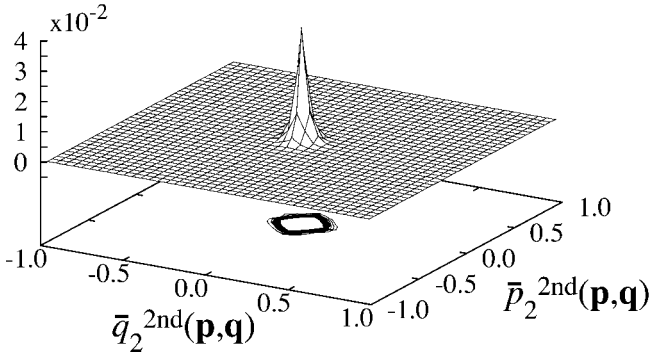


Fig. 4. The residence probability distribution in a local invariant of action on the two-dimensional ($\bar{p}_2^{2nd}(\mathbf{p}, \mathbf{q})$, $\bar{q}_2^{2nd}(\mathbf{p}, \mathbf{q})$) plane at $E = 0.1\varepsilon$ through saddle I: $\Delta\bar{J} = 0.05$ for durations $\tau \geq 0.5$.

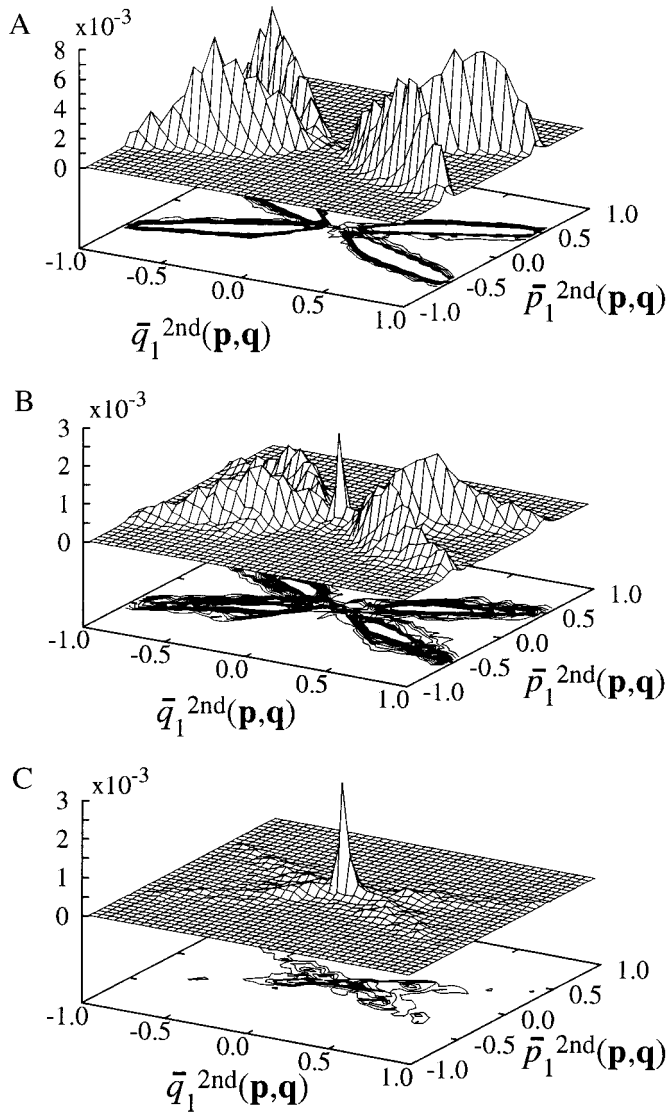


Fig. 5. The residence probability distribution of the local invariant on the ($\bar{p}_1^{2nd}(\mathbf{p}, \mathbf{q})$, $\bar{q}_1^{2nd}(\mathbf{p}, \mathbf{q})$) plane. The other conditions are same as in Fig. 4. (*a*) $E = 0.1$, (*b*) $= 0.5$, (*c*) $= 1.0\varepsilon$.

increases, the more the broadening of the excursion regime competes with the shrinkage of the region of local invariance of the action, in which the reaction coordinate $\bar{q}_1$ decouples from the others. The outcome of this competition to determine whether or when a dividing hypersurface $S(\bar{q}_1(\mathbf{p}, \mathbf{q}) = 0)$ is free from the recrossing problem can still be found in semichaotic region, $\sim E = 0.5\varepsilon$.

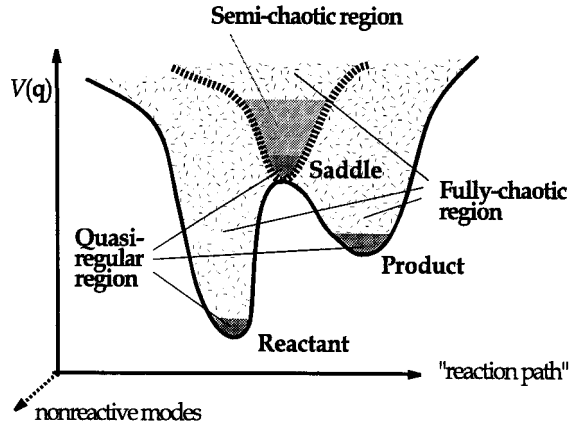
The clear "X" shapes of the two-dimensional contour maps of the figures at all three energies indicate that, without any explicit assumption of the separation of time scales associated with individual modes, as expected from Eqs. **8** and **9**, one can extract and visualize the stable and unstable invariant manifolds, at least in the region of the transition state, along the one-dimensional reaction coordinate $\bar{q}_1(\mathbf{p}, \mathbf{q})$ in many-body nonlinear systems. These figures should be contrasted with the corresponding diffuse contour maps in the conventional (p_1, q_1) plane (31).

The more striking and significant consequence is this; the rather "long-lived" approximate invariant $\bar{J}_1(\mathbf{p}, \mathbf{q})$, around the origin, $\bar{p}_1(\mathbf{p}, \mathbf{q}) \cong \bar{q}_1(\mathbf{p}, \mathbf{q}) \cong 0$, emerges with an increase of energy, even surviving at 1.0ε, despite the consequent high-

passage velocity through the saddle. Such a long-persistent invariant around that point could not be observed in the quasiregular region, 0.1ε. As shown in Eqs. **8** and **9**, if approximate invariants of action $\bar{J}_1$ and frequency $\bar{\omega}_1$ survive, the entire phase-space flow $(\bar{p}_1, \bar{q}_1)$ should be just like those of a one-dimensional integrable pendulum, and hence no any sharp spike should appear in the region where such invariants exist. The sharp spike around the origin $\bar{p}_1 \cong \bar{q}_1 \cong 0$ in the probability distribution of approximate constant of action $\bar{J}_1(\mathbf{p}, \mathbf{q})$ implies that slow passages through the reaction bottleneck tend to spoil the approximate invariant of frequency, and the system's reactive dof $(\bar{p}_1, \bar{q}_1)$ couples with the other nonreactive dof throughout the small region $\bar{p}_1 \cong \bar{q}_1 \cong 0$. The rather long residence in the region of constant $\bar{J}_1$ implies that the system is transiently trapped in the nonreactive space during the course of the reaction because of the mode–mode couplings that emerge with increasing total energy. These mode couplings are caused either by the restricted finite order of the perturbative calculation, or by the shrinkage of the convergence radius, even in an infinite-order calculation, to an extremely small size, outside of which the nonlinear couplings cannot be rotated away during the dynamical events. Whichever the reason, the picture emerges of a new type of phase space bottleneck caused by energy flows between reactive and nonreactive dof in some energy regime overlapping the semichaotic and fully developed chaotic regions. This phenomenon is generic, irrespective of the system and the order of LCPT we studied. In such an intermediate regime between these two energy regions, any simplistic picture, ballistic or diffusive, of the system's passage through transition states may be spoiled.

We point out here that with a residence time τ much shorter than that in Fig. 5 (with the same fluctuation bound), e.g., $\tau \leq 0.2$, a similar sharp spike exists at $E = 0.1\varepsilon$ around the origins, $\bar{p}_1^{\text{2nd}}(\mathbf{p}, \mathbf{q}) \cong \bar{q}_1^{\text{2nd}}(\mathbf{p}, \mathbf{q}) \cong 0$. This implies that the original Hamiltonian cannot completely be transformed to an exact integrable Hamiltonian at second-order in the LCPT calculation in the real situation at $E = 0.1\varepsilon$. However, as inferred (28) from the analysis of the transmission coefficients κ_c using the phase-space dividing hypersurface $S(\bar{q}_1^{\text{2nd}}(\mathbf{p}, \mathbf{q}) = 0)$, the system could be regarded as "fully" separable at 0.1ε in the region of the transition state because the transmission coefficient κ_c's value was evaluated to be 1.00000. In fact, Fig. 2 shows the actions in almost all of the nonreactive modes are retained as "approximately good" invariants at that low energy. This suggests that the different rates of energy exchange between the nonreactive dof and the reactive dof make the nonreactive *near-integrable* subset of modes contribute far less, and with less influence on the kinetics, than those modes in the *chaotic* subset. Recall that the RRKM theory postulates that the greater the number of dof that couple with the reactive mode, the slower the process of a specific mode gathering the energy required to react. If some nonreactive modes remain very regular, we might expect them to contribute nothing at all toward trapping the trajectory.

The high probabilities of near invariants of $\bar{J}_1(\mathbf{p}, \mathbf{q})$ and its associated $\bar{\omega}_1(\mathbf{p}, \mathbf{q})$, up to moderately high energies, through such a wide range in time and locality, imply that $\bar{p}_1(\mathbf{p}, \mathbf{q})$ and $\bar{q}_1(\mathbf{p}, \mathbf{q})$ are approximately decoupled from the other modes and can be used with considerable reliability to represent the local dynamics analytically. This proves the supposition of the existence of a multidimensional dividing hypersurface in the *phase* space, defined by the condition that the reactive coordinate $\bar{q}_1(\mathbf{p}, \mathbf{q}) = 0$, which is almost free of recrossing problems (28). Because of its momentum dependence and high degree of nonlinearity of the transformation, the dividing hypersurface is a rather abstract object. However, it is possible to graph distributions of projections of this hypersurface onto a few principal subspaces. Such projections can reveal the complexity of the recrossings over the saddle in the conventional configurational space (29, 30).



	Quasi-regular	Semi-chaotic	Fully-chaotic
Number of invariants of action	$\leq M$	~1	~0
Dynamical correlation between incoming & outgoing trajectories	Strong	Weak (But Non-Zero!)	None

Fig. 6. A universal dynamical hierarchy in the region of transition states.

Universal Dynamical Hierarchy in (First-Rank) Transition States

The results of this investigation indicate the existence of at least three distinct dynamical regimes in the region of a first-rank transition state, associated with approximate invariants of motion along the reactive coordinate $\bar{q}_1(\mathbf{p}, \mathbf{q})$ in the phase space (see Fig. 6). This is, as Hernandez and Miller first pointed out (33), because any arbitrary combination of modes cannot satisfy commensurability conditions to make an unstable mode mix with modes stable in that region. Thus this feature is generic for (first-rank) transition states irrespective of the system. From that point, finding a nonrecrossing reaction path in many-body phase space with its analytical solution of an equation of motion, even in a certain locality, is of considerable interest, as is establishing the extent to which the system reacts and evolves in a fully stochastic fashion or not.

In the lowest reaches of the energy above the saddle, all or almost all the dof of the system *locally* maintain approximate constants of motion in the region of the transition state, just as in the regions of energy minima. The dynamical correlation between incoming and outgoing trajectories through the transition state is quite strong, and the dimensionality of saddle crossings is essentially one, corresponding to the reactive mode $\bar{q}_1$ in the phase space. The staircase energy dependence of reaction rates and rate coefficients observed by Lovejoy *et al.* (24) for highly vibrationally excited ketene indicates that the transverse vibrational modes might indeed display approximate invariants of motion (26). We classify such a range of energy, corresponding to this behavior, as a *quasiregular* region.

As the energy increases, *almost* all of the near invariants are spoiled by chaotic motion and mode–mode coupling in the region of transition state because of innumerable resonances in the space of nonreactive modes. However, a few near invariants still survive in that sea of chaotic motions, specifically those associated with the reaction coordinate $\bar{q}_1(\mathbf{p}, \mathbf{q})$ during the course of crossings. This *semichaotic* region does not exist near potential minima but is inherent near (first-rank) transition states. In this region, the dynamical correlation between incoming and outgoing trajectories through the transition state becomes weak (but nonzero!), and the saddle crossings' dimensionality is $\simeq M - 1$ (M, total dimension of the system),

excluding the one dimension of $\bar{q}_1$, which determines the reaction path buried in the chaotic sea. In both quasiregular and semichaotic regions, a well-defined phase space dividing surface can be extracted, across which the longstanding ambiguity of the recrossing problem in transition state theories can be rotated away to yield unit transmission coefficients (28). This also indicates that semiclassical rate theory based on the locally conserved tunneling action (34) is likely to be effective at relatively high energies above the threshold, even if no good quantum number can be assigned in the nonreactive space in the transition state. Only if the energy is so high, in the *fully developed chaotic* region, that the trajectory can encounter places where the zone of quasiconstant action along the reaction coordinate is extremely small, does the reactive mode mix strongly with the other modes. At those energies, the reactive mode and all the others are effectively coupled together into a fully chaotic system.

This report sheds light on the nature of trapping of a reacting system in the region of transition states, and how it can affect the reaction rate; one should distinguish "apparent" and "true" trappings. In the former, although the system looks transiently trapped around a saddle, its reaction proceeds, independently, along the *nearly separable* reactive dof in *phase* space, but in the latter, the system not only looks trapped but also resists proceeding along any reactive dof one might choose, because of the nonvanishing mode couplings appearing between semichaotic and fully developed chaotic energy regimes.

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