Appendix: Overview of our methodology in "Regularity and Non-recrossing Paths in Transition States of Chemical Reactions"

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The crux of our method, Lie canonical perturbation theory, abbreviated as LCPT, is a classical version of Van Vleck perturbation theory. These theories *a priori* assume existence of M invariants of motion for the M-dimensional Hamiltonian systems in question. It is well known that with such methods, the new, transformed Hamiltonian diverges if the system encounters (near-)resonances, and becomes meaningless. However, we clarify in this work that LCPT is still powerful enough to reveal an invariant manifold even if almost action variables fail to maintain constants of motion. Rather, the method provides us with a new phase-space dividing surface free from recrossing up to moderately high energy. We briefly describe our method to construct a model Hamiltonian from any arbitrary autonomous Hamiltonian to which LCPT applies. We use an efficient technique, so-called algebraic quantization, to carry out the LCPT without any special mathematical manipulations and achieve a reformulated (classical) transition state theory by using the hyperbolic phase space orbit in the sea of chaotic motions of the other stable modes. At the end, we describe shortly three distinct levels of local dynamics in the transition state in terms of regularity of the dynamics, which have not been addressed previously.

APPENDIX A: LIE CANONICAL PERTURBATION THEORY (LCPT)

Canonical perturbation theories (*1*) transform $(\mathbf{p},\mathbf{q})$ to a new $(\bar{\mathbf{p}},\bar{\mathbf{q}})$ coordinate system so as to make the new Hamiltonian $\bar{H}(\bar{\mathbf{p}},\bar{\mathbf{q}})$ as close to integrable as possible. Lie canonical perturbation theory (LCPT) (*1*–*7*) is the most sophisticated theory among them, applicable to implementing higher-order perturbations and to treating systems with many degrees of freedom. The LCPT is based on Lie transforms, that is, the exponential of a Lie operator induces a canonical transformation: let L_w be the Lie operator associated with a generating function w,

$$L_w \equiv \{w,\} \tag{A1}$$

where $\{\}$ denotes the Poisson bracket. Then the transformation of an autonomous Hamiltonian H to a new Hamiltonian $\bar{H}$,

$$H(\mathbf{p},\mathbf{q}) \longrightarrow \bar{H}(\bar{\mathbf{p}},\bar{\mathbf{q}}) = \exp(L_w)H(\bar{\mathbf{p}},\bar{\mathbf{q}}) \tag{A2}$$

is canonical. We let H be an M-dimensional Hamiltonian expandable in ϵ (=strength of the perturbation) where the zeroth-order Hamiltonian H_0 is assumed to be integrable, e.g., a system of M harmonic oscillators. Such a zero-order system is a function of action variables $\mathbf{J}$ only, and does not depend on the conjugate angle variables $\mathbf{\Theta}$, so

$$H(\mathbf{p},\mathbf{q}) = \sum_{n=0}\epsilon^n H_n(\mathbf{p},\mathbf{q}), \tag{A3}$$

$$= H_0(\mathbf{J}) + \sum_{n=1}\epsilon^n H_n(\mathbf{J},\mathbf{\Theta}), \tag{A4}$$

$$= \sum_{k=1}^{M}\omega_k J_k + \sum_{n=1}\epsilon^n H_n(\mathbf{J},\mathbf{\Theta}), \tag{A5}$$

where ω_k is the fundamental frequency of the kth mode of H_0. Assuming the new Hamiltonian $\bar{H}$ and the generating function w are also expandable in ϵ, we substitute all H, $\bar{H}$, and w to Eq. A2 and determine the new Hamiltonian, at each order in ϵ, to be as a simple a form as possible by eliminating its dependencies on the new angle variables $\bar{\mathbf{\Theta}}$. (*1*, *3*, *7*) If the $\bar{H}$ is obtained free from the angle $\bar{\mathbf{\Theta}}$ (at the order of the perturbative calculation performed):

$$\bar{H}(\bar{\mathbf{p}},\bar{\mathbf{q}}) = \bar{H}(\bar{\mathbf{J}},\bar{\mathbf{\Theta}}) = \bar{H}(\bar{\mathbf{J}}) = \sum_{n=0}\epsilon^n\bar{H}_n(\bar{\mathbf{J}}), \tag{A6}$$

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

$$\frac{d\bar{J}_k}{dt} = \dot{\bar{J}}_k = -\frac{\partial\bar{H}(\bar{\mathbf{J}})}{\partial\bar{\Theta}_k} = 0, \tag{A7}$$

$$\bar{J}_k = constant \qquad (k = 1,2,3,\ldots,M), \tag{A8}$$

and

$$\dot{\bar{\Theta}}_k = \frac{\partial\bar{H}(\bar{\mathbf{J}})}{\partial\bar{J}_k} \equiv \bar{\omega}_k(\bar{\mathbf{J}}) = constant, \tag{A9}$$

$$\bar{\Theta}_k = \bar{\omega}_k(\bar{\mathbf{J}})t + \beta_k, \tag{A10}$$

where β_k is the arbitrary initial phase factor of the kth mode. From there, the equations of motion with respect to the new coordinates $\bar{\mathbf{q}}$ and momenta $\bar{\mathbf{p}}$ are obtained from the Hamiltonian equations of motion obeying $\bar{H}$;

$$\frac{d^2\bar{q}_k(\mathbf{p},\mathbf{q})}{dt^2} + \bar{\omega}_k^2\bar{q}_k(\mathbf{p},\mathbf{q}) = 0, \tag{A11}$$

and

$$\bar{p}_k(\mathbf{p},\mathbf{q}) = \frac{\omega_k}{\bar{\omega}_k}\frac{d\bar{q}_k(\mathbf{p},\mathbf{q})}{dt} \tag{A12}$$

where $\bar{\omega}_k (= \bar{\omega}_k(\bar{\mathbf{J}}) = \bar{\omega}_k(\bar{\mathbf{p}}, \bar{\mathbf{q}}))$ is independent of time t because the $\bar{\mathbf{J}}$ are constant through all t [Eq. (A7)]. The equations (A11) and (A12) tell us that even though the motions look quite complicated in the old coordinate system, they could be reformulated as simple decoupled periodic orbits in the phase space.

If one tries to regularize a general Hamiltonian globally, one almost surely encounters the problem that the (near-)commensurable conditions that an integer linear combination of fundamental frequencies vanishes identically at a given order ϵ^n,

$$\sum_{k=1}^{M} n_k \omega_k \leq O(\epsilon^n) \tag{A13}$$

(n_k is arbitrary integer), makes the corresponding new Hamiltonian diverge and destroys invariants of motion. (*1*) It is quite likely in many M-dimensional systems that the near-commensurable conditions densely distribute in the phase space, i.e., the occupation ratio of the M-dimensional tori in the phase space is negligibly small, and hence Eqs. (A11)-(A12) become meaningless. Here, however, we consider only approximately regular behavior in *local regions*, specifically saddles, where we find that such difficulties of fully-developed chaos for the full set of degrees of freedom only at quite high energies.

We first showed that, by monitoring the new action of the kth mode $\bar{J}_k(\mathbf{p}, \mathbf{q})$ along molecular dynamics (MD) trajectories obeying equations of motion of the original Hamiltonian $H(\mathbf{p}, \mathbf{q})$, one can detect whether the $\bar{q}_k$ mode tends to maintain an invariant of motion. If the $\bar{J}_k(\mathbf{p}, \mathbf{q})$ and its associated $\bar{\omega}_k(\mathbf{p}, \mathbf{q})$ exhibit near-constants of motion through a certain range in time and locality, it implies that $\bar{p}_k$ and $\bar{q}_k$ are approximately decoupled from the other modes, and represent the local dynamics analytically. Those quantities associated with a reactive mode exhibit such near-constants of motion up to a moderately high energy in the region of a saddle. Furthermore the dividing hypersurface, defined by the condition that the reactive coordinate in the transformed coordinates is zero, is almost free from recrossing problems.

APPENDIX B: THE REGIONAL HAMILTONIAN

Despite its versatility, LCPT has not been applied to many-degrees of freedom (DOF) realistic atomic/molecular systems. One of the two main difficulties is how one could handle the analytical derivative and integral calculations that appear successively in the LCPT procedure. The other is the near-impossibility of obtaining even moderately simple analytical expressions to describe the accurate (e.g., *ab initio*) potential energy surfaces in full. As shown for a variety of atomic/molecular clusters, the dynamical properties of multidimensional Hamiltonian systems are strongly nonuniform at low and moderate energies, depending on the local topography of their potential energy surfaces. (*8*, *9*)

We first expand the full $3N$-DOF potential energy surface about a chosen stationary point, i.e., minimum, saddle, or higher rank saddle. By taking the zeroth order Hamiltonian as a harmonic oscillator system, which might include some negatively curved modes, i.e., reactive modes, we establish the higher-order perturbation terms to consist of nonlinear, anharmonic couplings which we may express in arbitrary combinations of coordinates. Thus,

$$H = H_0 + \sum_{n=1}^{\infty} \epsilon^n H_n \tag{B1}$$

where

$$H_0 = \frac{1}{2} \sum_j (p_j^2 + \omega_j^2 q_j^2), \tag{B2}$$

$$\sum_{n=1}^{\infty} \epsilon^n H_n = \epsilon \sum_{j,k,l} C_{jkl} q_j q_k q_l \tag{B3}$$

$$+ \epsilon^2 \sum_{j,k,l,m} C_{jklm} q_j q_k q_l q_m + \ldots, \tag{B4}$$

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, 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. The frequency associated with an unstable reactive mode F and those of the other stable modes B are pure-imaginary and real, respectively. At any stationary point there are six zero-frequency modes corresponding to the total translational and infinitesimal rotational motions, and the normal coordinates of the infinitesimal rotational motions appear in the perturbation terms $H_n(\mathbf{q})$ $(n > 0)$. The contribution of the total translational motion is simply separated. We make no more mention of this. If one deals with a system whose total angular momentum is zero, one could eliminate the contributions of the total rotational motions from $H_n(\mathbf{q})$ $(n > 0)$ by operating with a suitable projection operator (*10*); at the stationary point it corresponds to putting to zero each normal coordinate and corresponding conjugate momentum representing the infinitesimal total rotational motion. For the sake of simplicity we focus on a $(3N\text{-}6)$-DOF Hamiltonian system with total linear and angular momenta of zero, so that the kinetic and potential energies are purely vibrational. For such a zeroth-order Hamiltonian $\omega_k \neq 0$ for all $k\ (= 1, 2, 3, \ldots, 3N - 6 (\equiv M))$, the associated action-angle variables of the stable modes B ($\omega_B \in \Re$: *real*) and the unstable mode F ($\omega_F \in \Im$: *imaginary*) are expressed as

$$J_B = \frac{1}{2\pi} \oint p_B dq_B = \frac{1}{2} \left(\frac{p_B^2}{\omega_B} + \omega_B q_B^2 \right), \tag{B5}$$

$$\Theta_B = \tan^{-1}\left(\frac{p_B}{\omega_B q_B}\right), \tag{B6}$$

and

$$J_F = \frac{1}{2\pi} Im \int_{barrier} p_F dq_F, \tag{B7}$$

$$= \frac{i}{2}\left(\frac{p_F^2}{|\omega_F|} - |\omega_F| q_F^2\right), \tag{B8}$$

$$\Theta_F = i \tanh^{-1}\left(\frac{p_F}{|\omega_F| q_F}\right), \qquad \omega_F \equiv -|\omega_F| i. \tag{B9}$$

Here the action associated with the reaction mode F, having first been postulated in the semiclassical transition state theory, (*11*–*13*) is purely imaginary and is connected with the barrier penetration integral in the semi-classical theory. It is easily verified (*14*) that any such set of variables $\mathbf{J}$ and $\mathbf{\Theta}$ is canonical, including those associated with the unbound mode F.

APPENDIX C: THE ALGEBRAIC QUANTIZATION METHOD

For practical LCPT calculations of the above Hamiltonians, a quite efficient method, called "algebraic quantization," has been developed. (*6*, *7*) This method first transforms $(\mathbf{p}, \mathbf{q})$ in Eqs. B2-B4 to $(\mathbf{a}^*, \mathbf{a})$ by the customary means:

$$a_k^* = \frac{1}{\sqrt{2}}(p_k + i\omega_k q_k), \quad a_k = \frac{1}{\sqrt{2}}(p_k - i\omega_k q_k), \tag{C1}$$

which are expressed in terms of the old action variable, the associated frequency J_k, ω_k, and time τ obeying Hamiltonian H_0 as

$$a_k^*(\tau) = \sqrt{\omega_k J_k} e^{i\Theta_k} = \sqrt{\omega_k J_k} e^{i(\omega_k \tau + \beta_k)}, \tag{C2}$$

$$a_k(\tau) = \sqrt{\omega_k J_k} e^{-i\Theta_k} = \sqrt{\omega_k J_k} e^{-i(\omega_k \tau + \beta_k)}. \tag{C3}$$

The cumbersome analytical calculations of Eqs. B4-B8 that appear in the LCPT calculations are then replaced by simultaneous algebraic, symbolic operations, thanks to the simple Poisson bracket rules for the $(\mathbf{a}^*, \mathbf{a})$,

$$\{a_j^*, a_k^*\} = \{a_j, a_k\} = 0, \quad \{a_j^*, a_k\} = i\omega_k \delta_{jk} \tag{C4}$$

where $\{\}$ and δ denote Poisson bracket and Kronecker delta, respectively. One simply substitutes (C1)-(C3) into (B1), to set up the simultaneous algebraic equations, which readily yield the desired dynamical quantities with the help of (C4). (*7*)

Finally, we obtain new transformed physical quantities $\bar{A}$, i.e., the new Hamiltonian $\bar{H}$, and new action $\bar{J}_k$, frequency $\bar{\omega}_k$, momentum $\bar{p}_k$, and coordinate $\bar{q}_k$ of the kth mode, in terms of the original $\mathbf{p}$ and $\mathbf{q}$ as

$$\bar{A} = \bar{A}(\mathbf{p}, \mathbf{q}) = \sum_{n=0} \epsilon^n \bar{A}_n(\mathbf{p}, \mathbf{q}). \tag{C5}$$

In the present work, we analyze $\bar{A}$ up to a (finite) ϵ^i order (i=0,1,2):

$$\bar{A}^{ith} = \bar{A}^{ith}(\mathbf{p}, \mathbf{q}) = \sum_{n=0}^{i} \epsilon^n \bar{A}_n(\mathbf{p}, \mathbf{q}) \tag{C6}$$

where no (near-) commensurable conditions were encountered at these orders during our LCPT procedure. The details of the computational recipe are given in (*7*).

To indicate the complexity of the transform, we show the expressions for $\bar{p}_1(\mathbf{p}, \mathbf{q})$ and $\bar{q}_1(\mathbf{p}, \mathbf{q})$ up to first order at saddle I of Ar_6(Here mode 1 is reactive and the others are non-reactive). The contributions of the original p_1 and q_1 in $\bar{p}_1^{ith}(\mathbf{p}, \mathbf{q})$ and $\bar{q}_1^{ith}(\mathbf{p}, \mathbf{q})$ are not necessarily large and almost all modes contribute to $\bar{p}_1^{ith}$ and $\bar{q}_1^{ith}(\mathbf{p}, \mathbf{q})$ for $i \geq 1$.

$$\bar{p}_1^{0th} = p_1, \tag{C7}$$

$$\begin{aligned}
\bar{p}_1^{1st} &= p_1 + 0.103353 p_1 q_1 + 0.097266 q_7 p_8 \\
&+ 0.084426 q_1 p_{10} + 0.079721 q_4 p_{11} - 0.075768 p_1 q_{10} \\
&- 0.070628 p_4 q_{11} + 0.067259 q_1 p_{12} - 0.061966 p_1 q_{12} \\
&+ 0.057190 q_5 p_{10} + 0.056576 q_6 p_{11} - 0.056558 p_7 q_8 \\
&+ 0.051195 q_{10} p_{12} - 0.048788 p_6 q_{11} - 0.044909 p_5 q_{10} \\
&- 0.044499 q_5 p_{12} + 0.039476 q_2 p_{12} + 0.038653 p_5 q_{12} \\
&- 0.038584 q_1 p_2 - 0.036376 p_{10} q_{12} - 0.035646 p_2 q_{12} \\
&+ 0.035423 p_2 q_2 - 0.032806 p_6 q_6 + 0.031813 p_3 q_3 \\
&- 0.031358 q_1 p_5 + 0.026383 p_7 q_7 + 0.025753 p_1 q_5 \\
&+ 0.025277 p_1 q_2 - 0.024068 p_{11} q_{11} + 0.019803 p_8 q_8 \\
&+ 0.017695 q_4 p_6 - 0.017171 p_9 q_9 + 0.016610 q_2 p_{10} \\
&- 0.014351 p_2 q_{10} + 0.010428 p_5 q_5 - 0.008864 p_4 q_6 \\
&+ 0.005637 q_2 p_5 - 0.003872 p_2 q_5 - 0.003792 p_{12} q_{12} \\
&+ 0.003657 p_4 q_4 - 0.002603 p_{10} q_{10} + 0.001701 q_3 p_9 \\
&- 0.001423 p_3 q_9,
\end{aligned} \tag{C8}$$

$$\bar{q}_1^{0th} = q_1, \tag{C9}$$

$$\begin{aligned}
\bar{q}_1^{1st} &= q_1 + 0.599212 q_7 q_8 - 0.559687 q_{11}^2 \\
&+ 0.412029 p_1^2 + 0.338508 q_7^2 + 0.328906 q_8^2 \\
&- 0.319091 q_6^2 + 0.310549 q_{10} q_{12} - 0.291435 q_9^2 \\
&+ 0.183270 q_3^2 + 0.170034 q_5 q_{10} + 0.162288 p_7 p_8 \\
&+ 0.152283 q_2^2 + 0.141216 p_2^2 + 0.136269 q_4 q_{11} \\
&- 0.130785 p_6^2 + 0.128438 q_6 q_{11} + 0.126825 p_3^2 \\
&+ 0.105180 p_7^2 + 0.101029 q_5^2 - 0.098218 q_5 q_{12} \\
&- 0.095949 p_{11}^2 - 0.090680 q_{12}^2 + 0.078946 p_8^2 \\
&+ 0.075768 q_1 q_{10} + 0.072618 q_4 q_6 - 0.068455 p_9^2 \\
&+ 0.061966 q_1 q_{12} + 0.059076 p_{10} p_{12} + 0.054028 q_2 q_{12} \\
&- 0.053049 p_1 p_2 - 0.051677 q_1^2 + 0.048960 p_5 p_{10}
\end{aligned}$$

$$
\begin{aligned}
&- 0.046850q_{10}^2 + 0.041571p_5^2 + 0.036248p_4p_{11} \\
&+ 0.035207p_4p_6 + 0.034517p_1p_{10} + 0.031050p_6p_{11} \\
&- 0.025753q_1q_5 - 0.025277q_1q_2 + 0.025194q_2q_{10} \\
&+ 0.024569q_4^2 - 0.023307p_5p_{12} - 0.022347p_1p_5 \\
&+ 0.021104p_1p_{12} + 0.015270p_2p_{12} - 0.015119p_{12}^2 \\
&+ 0.014577p_4^2 + 0.012340q_2q_5 - 0.010375p_{10}^2 \\
&+ 0.009008p_2p_{10} + 0.007034p_2p_5 + 0.003167q_3q_9 \\
&+ 0.001111p_3p_9 .
\end{aligned} \tag{C10}
$$

The new momenta and coordinates $\bar{p}_k(\mathbf{p},\mathbf{q})$ and $\bar{q}_k(\mathbf{p},\mathbf{q})$ have the following forms respectively,

$$
\bar{p}_k(\mathbf{p},\mathbf{q}) = \sum_j c_j \mathbf{p}^{2n-1}\mathbf{q}^m, \tag{C11}
$$

$$
\bar{q}_k(\mathbf{p},\mathbf{q}) = \sum_j d_j \mathbf{p}^{2n}\mathbf{q}^m, \tag{C12}
$$

where c_j and d_j denote the coefficient of the jth term, n, $m(\geq 0)$ are arbitrary integers, and $\mathbf{q}^m = q_1^{m_1}q_2^{m_2}q_3^{m_3}\cdots q_M^{m_M}(\sum_{j=1}^M m_j = m)$ etc. The new $\bar{p}_k(\mathbf{p},\mathbf{q})$ and $\bar{q}_k(\mathbf{p},\mathbf{q})$ maintain time reversibility. The units of $\bar{p}_k$ and $\bar{q}_k$ are $\epsilon^{1/2}$ and $m^{1/2}\sigma$, respectively. As we increase the order of LCPT to be evaluated, the total number of the terms rapidly increases. For example, $\sim$ 450 for $\bar{p}_1^{2nd}$ and $\bar{q}_1^{2nd}$.

APPENDIX D: REFORMULATION OF TRANSITION STATE THEORY

In the cases that saddle crossing dynamics has approximate invariants of motion associated locally with the reactive mode F in a short time interval but long enough to determine the final state of the saddle crossings, the $\bar{q}_F$ can be identified as a "good" reaction coordinate. This is because there is no means or force returning the system to the new dividing surface $S(\bar{q}_F = 0)$ even though the system may recross the original naive surface $S(q_F = 0)$. The reformulated microcanonical (classical) transition state theory(TST) rate constant k_{GTST} is obtained (7) as a thermal average of the one-way fluxes $j_+(= \dot{\bar{q}}_F(\mathbf{p},\mathbf{q})h(\dot{\bar{q}}_F(\mathbf{p},\mathbf{q})))$ across $S(\bar{q}_F = 0)$ over microcanonical ensembles constructed over a range of energies E.

$$
\begin{aligned}
k_{GTST}(E) &= \langle j_+ \rangle_E \\
&= \langle \dot{\bar{q}}_F(\mathbf{p},\mathbf{q})\delta\left[\bar{q}_F(\mathbf{p},\mathbf{q})\right] h\left[\dot{\bar{q}}_F(\mathbf{p},\mathbf{q})\right]\rangle_E, \\
&= \int_1 dq_1 dp_1 \ldots \int_N dq_N dp_N \\
&\times\ \delta\left[E - H(\mathbf{p},\mathbf{q})\right] \\
&\quad \dot{\bar{q}}_F(\mathbf{p},\mathbf{q})\delta\left[\bar{q}_F(\mathbf{p},\mathbf{q})\right] h\left[\dot{\bar{q}}_F(\mathbf{p},\mathbf{q})\right],
\end{aligned} \tag{D1}
$$

where $h(x)$ and $\delta(x)$, respectively, denote the Heaviside function and Dirac's delta function of x. The canonical form is also formulated straightforwardly.

If no approximate invariant of motion exists in the saddle region, $k_{GTST}(E)$ deviates from the (classically) exact reaction rate constant $k(E)$. Therefore one can introduce a new transmission coefficient κ_c, the deviation of the $k_{GTST}(E)$ from the $k(E)$:

$$
k = \kappa_c k_{GTST}. \tag{D2}
$$

We may use κ_c to estimate the barrier recrossing effect, as a measure of the extent to which the quasi-invariants of motion associated with the reactive mode, i.e., the local action and its local frequency, cease to be approximate invariants. Their nonconstancy reflects the degree of *fully-developed* chaos in which no invariant of motion exists, if the vibrational energy relaxation is fast enough to let us assume quasi-equilibration in the reactant's potential well.

In order to focus on how the recrossings over a given dividing surface contribute to κ_c, we estimate the time-dependent quantities $\kappa_c^{MD}(t; S(\bar{q}_F^{\rm ith} = 0))$ in terms of our MD trajectories defined by

$$
\kappa_c^{MD}(t; S(\bar{q}_F^{\rm ith} = 0)) = \frac{\langle j(t=0) h\left[\dot{\bar{q}}_F^{\rm ith}(\mathbf{p},\mathbf{q})\right]\rangle_E}{\langle j_+(t=0)\rangle_E} \tag{D3}
$$

where $j(t=0)$, and $j_+(t=0)$, respectively, denote the initial total, and initial positive fluxes crossing the ith order LCPT dividing surface $S(\bar{q}_F^{\rm ith}(\mathbf{p},\mathbf{q}) = 0)$. The origin of time t is taken to be zero when the system trajectory first crosses the given dividing surface. This equation should also tell us how the vanishing of the approximate invariants of motion of the reactive mode reflects on the κ_c.

APPENDIX E: DISTINCT CLASSES OF DYNAMICS IN THE TRANSITION STATE

We found, with the analysis afforded by the minimal-recrossing trajectories provided by the LCPT analysis, that there are at least three distinct energy regions above the saddle point energy that can be classified in terms of the regularity of saddle-crossing dynamics. Let us now articulate the distinctions among them.

Quasiregular region All or almost all the degrees of freedom of the system *locally* maintain approximate constants of motion in the region of the transition state. The saddle crossing dynamics from well to well is fully deterministic, obeying M-analytical solutions (see Eqs. A11-A12) for systems of M degrees of freedom. The dynamical correlation between incoming and outgoing trajectories from and to the transition state region is quite strong, and the dimensionality of saddle crossings is essentially one, corresponding to the reactive mode $\bar{q}_F$ in the $(\bar{\mathbf{p}},\bar{\mathbf{q}})$

space. Barrier recrossing motions observed over a naive dividing surface defined in the configuration space are *all* rotated away to no-return single crossing motions across a phase space dividing surface $S(\bar{q}_F(\mathbf{p},\mathbf{q}) = 0)$. If the vibrational energy relaxes fast enough to let us assume quasi-equilibration in the wells, the initial conditions $(\bar{\mathbf{p}}(0), \bar{\mathbf{q}}(0))$ of the system as it enters the transition state from either of the stable states can be simply sampled from microcanonical ensembles. One may then evaluate the (classical) exact rate constant, free from the recrossing problem. The staircase energy dependence observed by Lovejoy et al. (*15*) for highly vibrationally excited ketene indicates that the transverse vibrational modes might indeed be approximately invariants of motion. (*16*) We classify such a range of energy, in which the rate coefficient shows staircase structure, as corresponding to this quasiregular region.

Intermediate, semi-chaotic region Due both to significant (near-)resonances and to strong anharmonic mode-mode couplings emerging at these intermediate energies, *almost* all the approximate invariants of motion disappear, consequently inducing a topological change in dynamics from quasiregular to chaotic in the regions of saddle crossings. However at least one approximate invariant of motion survives during the saddle crossings, associated with the reactive coordinate $\bar{q}_F(\mathbf{p},\mathbf{q})$. This is due to the fact that an arbitrary combination of modes cannot satisfy the resonance conditions of Eq. A13 if one mode has an imaginary frequency, the reactive mode in this case, is included in the combination. The other frequencies associated with bath modes fall on the real axis, orthogonal to the imaginary axis in the complex ω-plane. That is,

$$\left| \sum_{k=1}^{M}{}^{\dagger} n_k \omega_k \right| \geq |\omega_F| > O(\epsilon^n) \qquad \text{(E1)}$$

for arbitrary integers n_k with $n_F \neq 0$, where $\Sigma^{\dagger}$ denotes the combination including the reactive mode. This was first pointed out by Hernandez and Miller. (*13*) In this region the dynamical correlation between incoming and outgoing trajectories to and from the transition state becomes weak (but non-zero!), and the saddle crossings' dimensionality is $\simeq M - 1$, excluding the one dimension of $\bar{q}_F$, in this region. If the associated imaginary frequency $\bar{\omega}_F(\mathbf{p},\mathbf{q})$ is approximately constant during a saddle crossing as the action $\bar{J}_F(\mathbf{p},\mathbf{q})$ is, the reaction coordinate $\bar{q}_F$ decouples from the Z-subspace composed of the other bath-DOF, in which the system dynamics is manifestly chaotic. The $\bar{q}_F$ dynamics is then represented analytically during saddle crossings, and a dividing surface $S(\bar{q}_F(\mathbf{p},\mathbf{q}) = 0)$ can still be extracted free from the barrier recrossings, even for saddle crossings chaotic in the bath modes. This class does not exist near potential minima, but is inherent associated with the transition state.

Stochastic (=fully-developed chaotic) region The system becomes subject to considerable nonlinearities of the potential energy surface at much higher energies, and the convergence radius becomes negligibly small for the LCPT near the fixed (saddle) point for the invariant of motion associated with the reactive coordinate $\bar{q}_F$. In this energy region, no approximate invariant of motion can be expected to exist, even in the passage over the saddle between wells. The saddle-crossing dynamics is entirely stochastic, with dimensionality essentially equal to the number of degrees of freedom of the system. Here it is probably not be possible to extract a dividing surface free from barrier recrossings. At these high energies above the lowest, presumably (but not necessarily) first-rank saddle, the system trajectories may pass over higher-rank saddles of the potential energy surface. These provides us with a new, untouched problem, i.e., what is the role of resonance in the imaginary ω-plane for the bifurcation? (This even arises in the degenerate bending modes for a linear transition state of a triatomic molecule.) With this, we encounter one of the related open subjects in statistical theories of many-DOF systems.

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