

# Phase space barriers and dividing surfaces in the absence of critical points of the potential energy

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## Abstract

We consider the existence of invariant manifolds in phase space governing reaction dynamics in situations where there are no saddle points on the potential energy surface in the relevant regions of configuration space. We point out that such situations occur in a number of important classes of chemical reactions, and we illustrate this concretely by considering a model for transition state switching in an ion-molecule association reaction due to Chesnavich (J. Chem. Phys. **84**, 2615 (1986)). For this model we show that, in the region of configuration space relevant to the reaction, there are no saddle points on the potential energy surface, but that in phase space there is a normally hyperbolic invariant manifold (NHIM) bounding a dividing surface having the property that the reactive flux through this dividing surface is a minimum. We then describe two methods for finding NHIMs and their associated phase space structures in systems with more than two degrees-of-freedom. These methods do not rely on the existence of saddle points, or any other particular feature, of the potential energy surface.

## I. INTRODUCTION

Critical points of the potential energy surface have played, and continue to play, a significant role in how one thinks about transformations of physical systems<sup>1,2</sup>. The term ‘transformation’ may refer to chemical reactions such as isomerizations<sup>3–14</sup> or the analogue of phase transitions for finite size systems<sup>2,15,16</sup>. A comprehensive description of this so-called ‘energy landscape paradigm’ is given in ref. 2. The energy landscape approach is an attempt to understand dynamics in the context of the geometrical features of the potential energy surface, i.e., a configuration space approach. However, the arena for dynamics is phase space<sup>17–19</sup>, and numerous studies of nonlinear dynamical systems have taught us that the rich variety of dynamical behavior possible in nonlinear systems *cannot* be inferred from geometrical properties of the potential energy surface alone. (An instructive example is the fact that the well-studied and nonintegrable Hénon-Heiles potential can be obtained by series expansion of the completely integrable Toda system<sup>20</sup>.) Nevertheless, the configuration space based landscape paradigm is physically very compelling, and there has been a great deal of work over the past ten years describing *phase space signatures* of index one saddles<sup>21</sup> of the potential energy surface that are relevant to reaction dynamics (see, for example, refs 22–24). More recently, index two<sup>25–27</sup> and higher index<sup>28</sup> saddles have been studied.

The work on index one saddles has shown that, in *phase space*, the role of the saddle *point* is played by an *invariant manifold* of saddle stability type, a so-called normally hyperbolic invariant manifold or NHIM<sup>29,30</sup>. The NHIM proves to be the anchor for the construction of dividing surfaces that have the properties of no (local) recrossing of trajectories and minimal (directional) flux<sup>31</sup>. There is an even richer variety of phase space structures and invariant manifolds associated with index two saddles of the potential energy surface, and their implications for reaction dynamics are currently under investigation<sup>26</sup>. Fundamental theorems assure the existence of these phase space structures and invariant manifolds for a range of energy above that of the saddle<sup>30</sup>. However, the precise extent of this range, as well as the nature and consequences of any bifurcations of the phase space structures and invariant manifolds that might occur as energy is increased, is not known and is a topic of current investigation<sup>32</sup>.

While work relating phase space structures and invariant manifolds to saddle points on the potential energy surface has provided new insights and techniques for studying reaction

dynamics<sup>22-24</sup>, it certainly does not exhaust all of the rich possibilities of dynamical phenomena associated with reactions. In fact, recent work has called into question the utility of concepts such as the reaction path and/or transition state<sup>33-38</sup>. Of particular interest for the present work is the recognition that there are important classes of chemical reaction, such as ion-molecule reactions and association reactions in barrierless systems, for which the transition state is not necessarily directly associated with the presence of a saddle point on the potential energy surface (or even the amended potential, which includes centrifugal contributions to the energy<sup>39,40</sup>). The phenomenon of transition state switching in ion-molecule reactions<sup>41-43</sup> provides a good example of the dynamical complexity possible in such systems.

The lack of an appropriate critical point on the potential energy surface with which to associate a dividing surface separating reactants from products in such systems does *not* however mean that there are no relevant geometric structures and invariant manifolds in *phase space*. In this paper we discuss the existence of NHIMs, along with their stable and unstable manifolds and associated dividing surfaces, in regions of phase space that do not correspond to saddle points of the potential energy surface. After presenting a simple example motivated by Chesnavich's model for transition state switching in an ion-molecule association reaction<sup>43</sup>, we describe a theoretical framework for describing and computing such NHIMs. Like the methods associated with index one and two saddles, the method we develop for realizing the existence of NHIMs is based on normal form theory; however, rather than normal form theory for saddle-type equilibrium points of Hamilton's equations (which are the phase space manifestation of index one and two saddles of the potential energy surface), we use normal form theory for certain hyperbolic invariant tori. The hyperbolic invariant tori (and their stable and unstable manifolds) alone are not adequate, in terms of their dimension, for constructing NHIMs that have codimension one stable and unstable manifolds (in a fixed energy surface). However, by analogy with the use of index one saddles to infer the existence of NHIMs (together with their stable and unstable manifolds, and other dividing surfaces having appropriate dimensions), these particular hyperbolic invariant tori can likewise be used to infer the existence of phase space structures that *are* appropriate for describing reaction dynamics in situations where there is no critical point of the potential energy surface in the relevant region of configuration space.

Section II discusses our simplified version of Chesnavich's model for transition state switching<sup>43</sup>. For this 2 DoF system, we exhibit a NHIM (in this case, an unstable peri-

odic orbit) that is the rigorous dynamical manifestation of the minimal flux surface of variational transition state theory<sup>44–46</sup>. In Section III we describe a (time-dependent) normal form based approach for finding such NHIMs in phase space. In particular, we present two variations of the method. In Section III A we consider systems where (to leading order) the system can be separated into a two degree-of-freedom (DoF) subsystem and a collection of decoupled “bath modes”. We assume that there exists a hyperbolic periodic orbit in the 2 DoF subsystem, and show that this can be used to construct a hyperbolic torus for the full system. We then show that this hyperbolic torus implies the existence of a NHIM, with stable and unstable manifolds that are codimension one in the energy surface. Appropriate dividing surfaces can then be constructed using the NHIM and the normal form Hamiltonian. In Section III B we describe a method which requires knowledge of the appropriate hyperbolic invariant torus from the start. The advantage of the first method is that it is more intuitive and can exploit the considerable number of methods for locating hyperbolic periodic orbits in 2 DoF Hamiltonian systems. Method two is more general, but at present there are few techniques available for locating hyperbolic invariant tori of the appropriate dimension in general  $N$  DoF Hamiltonian systems that are *not* perturbations of integrable systems. Section IV concludes.

## II. A MOTIVATING EXAMPLE: VARIATIONAL TRANSITION STATE FOR A MODEL BARRIERLESS REACTION

### A. Introduction

The conventional approach to variational transition state theory (VTST) for barrierless reaction proceeds by minimizing the reactive flux with respect to variation of some reaction coordinate chosen *a priori*<sup>44–46</sup>. The value of the reaction coordinate so determined is therefore the location of a flux bottleneck, which is identified with the transition state for the particular association reaction. An invariant phase space characterization of such variationally determined dividing surfaces is highly desirable; for  $N = 2$  DoF, such transition states will presumably be associated with unstable *periodic orbit dividing surfaces* (PODS)<sup>47–49</sup>, or, more generally, with NHIMs ( $N \geq 2$  DoF)<sup>29,30</sup>.

### B. Model Hamiltonian

We consider a highly simplified model for a barrierless association reaction (cf. ref. 43). The system has 2 DoF: a radial coordinate  $r$ , identified as the reaction coordinate, and a coordinate  $s$  describing vibrations transverse to the reaction coordinate. The radial potential has the character of a long-range attractive ion-neutral interaction, while the potential transverse to the reaction coordinate is harmonic. The system is nonseparable by virtue of a dependence of the harmonic oscillation frequency on the coordinate  $r$ :

$$H = \frac{p_r^2}{2} + \frac{p_s^2}{2} - \frac{\alpha}{r^4} + \frac{1}{2}\omega(r)^2 s^2. \quad (1)$$

We take  $\omega(r)$  to have the form

$$\omega(r) = \omega_0 e^{-\beta r} \quad (2)$$

so that, for  $\beta > 0$ , the transverse vibration stiffens as  $r$  decreases.

A contour plot of the potential

$$v(r, s) = -\frac{\alpha}{r^4} + \frac{1}{2}\omega(r)^2 s^2 \quad (3)$$

for parameter values  $\alpha = 1$ ,  $\beta = 1$ ,  $\omega_0 = 8$  is shown in Fig. 1.

### C. Locating the bottleneck

For the 2 DoF Hamiltonian (1), we can compute the *action* of the transverse vibrational mode as a function of the coordinate  $r$  at fixed energy  $E$ :

$$I(r; E) = \left[ E + \frac{\alpha}{r^4} \right] \frac{1}{\omega(r)} = \left[ E + \frac{\alpha}{r^4} \right] \frac{e^{\beta r}}{\omega_0}. \quad (4)$$

As  $r$  decreases, there are two competing tendencies:

- Decreasing  $r$  increases the amount of energy in the oscillator degree of freedom, thereby tending to increase the action.
- Decreasing  $r$  increases the frequency  $\omega(r)$ , tending to decrease the action of the transverse mode.

The competition between these two trends can therefore result in the existence of a *minimum* in the action as a function of  $r$ : see Figure 2.

The minimum of the action as a function of  $r$  corresponds to an extremum of the sum of states (phase space area) or *flux* as a function of  $r$ , and hence is interpreted as a bottleneck. In the variational transition state approach, the transition state for association is then located at the value  $r = r^*$  corresponding to minimum flux. This bottleneck corresponds to an inner or “tight” transition state<sup>42,43</sup>.

### D. Intrinsic characterization of variational TS: PODS

The formulation of VTST outlined above for the model association reaction is unsatisfactory in that the minimum flux bottleneck so determined has no intrinsic dynamical significance. It is natural to seek a dynamical, phase space based characterization of the variational TS. For 2 DoF systems, transition states are identified as PODS<sup>47–49</sup>. The invariant object defining the TS is a hyperbolic (unstable) periodic orbit; the 1D periodic orbit forms the boundary of a 2D dividing surface on the 3D energy shell in phase space, which is the transition state. The minimal flux (local no-recrossing) property of the TS follows from the principle of stationary action<sup>50</sup>.

A search using the model potential (3) reveals the presence of a PODS in the vicinity of  $r \simeq r^*$  (the periodic orbit at  $E = 1$  is shown in Fig. 1)<sup>51</sup>. This PODS is the rigorous dynamical realization of the variational TS in this simple case.

### III. LOCATING NHIMS WHEN THERE ARE NO (RELEVANT) SADDLES ON THE POTENTIAL ENERGY SURFACE

In this section we describe two methods for locating NHIMs of the type discussed in the previous section. These methods are inherently phase space approaches, based on the existence of a hyperbolic invariant torus solution of Hamilton’s equations. Normal form theory for hyperbolic invariant tori can be used to provide “good coordinates” for computing explicit formulae for a NHIM, its stable and unstable manifolds, and dividing surfaces in the phase space vicinity of the hyperbolic invariant torus on which we base our method, in much the same way that it is used to compute similar objects associated with index one saddles of the potential energy surface<sup>22,24,52</sup>. A large literature for normal form theory associated with invariant tori of Hamilton’s equations has been developed over the past twenty years, see ref. 53 for an overview, and ref. 54 for a survey of the issues associated with bifurcation of tori in Hamiltonian systems. For our present purposes we use the results contained in ref. 55, which explicitly discusses the relevant normal form and also clarifies the issue of “hyperbolicity” of tori in Hamiltonian systems (concerning which there had previously been some confusion in the literature).

#### A. Method 1: a relevant 2 DoF subsystem can be identified at leading order

Consider a Hamiltonian of the following form:

$$H = \frac{p_r^2}{2} + \frac{p_s^2}{2} + V(r, s) + \frac{1}{2} \sum_{i=1}^{n-2} \omega_i (u_i^2 + v_i^2) + f(r, s, u_1, \dots, u_{n-2}, p_r, p_s, v_1, \dots, v_{n-2}) \quad (5)$$

where  $f(r, s, u_1, \dots, u_{n-2}, p_r, p_s, v_1, \dots, v_{n-2})$  is at least order 3, denoted  $\mathcal{O}_3(r, s, u_1, \dots, u_{n-2}, p_r, p_s, v_1, \dots, v_{n-2})$ . In general this term serves to couple all of the variables, but we have written the Hamiltonian in such a way that we can identify a clearly defined 2 DoF subsystem, on which we make the following assumption:

**Assumption:** The 2 DoF subsystem defined by the Hamiltonian:

$$\mathcal{H} = \frac{p_r^2}{2} + \frac{p_s^2}{2} + V(r, s), \quad (6)$$

has a hyperbolic periodic orbit, denoted  $\mathcal{P} = (r(t), s(t), p_r(t), p_s(t))$ .

To construct a NHIM for (5) we proceed as follows.

**Step 1: Transform the 2 DoF subsystem to normal form in a neighborhood of the periodic orbit.**

Following ref. 55, we can find an invertible transformation  $T_0$  (as smooth as the Hamiltonian) defined in a neighborhood of the periodic orbit

$$T_0 : (r, s, p_r, p_s) \mapsto T_0(r, s, p_r, p_s) \equiv (I, \theta, x, y) \quad (7a)$$

$$T_0^{-1} : (I, \theta, x, y) \mapsto T_0^{-1}(I, \theta, x, y) \equiv (r, s, p_r, p_s) \quad (7b)$$

such that the 2 DoF Hamiltonian takes the form:

$$K = \omega I + \lambda xy + \mathcal{O}_2(I) + \mathcal{O}_3(I, x, y), \quad (8)$$

where we can take  $\omega, \lambda > 0$ . Of course, nontrivial calculations are required in going from (6) to (8). In particular, after the hyperbolic periodic orbit is located, a time-dependent translation to “center” the coordinate system on the periodic orbit must be carried out; the resulting Hamiltonian is then Taylor expanded about the origin (i.e., the periodic orbit), a Floquet-type transformation constructed to make (to leading order) the dynamics in the normal direction to the periodic orbit constant (i.e.,  $\lambda$  is constant in (8)), then, finally, Hamiltonian normal form theory is applied to the result. Details of the methodology for carrying out this procedure for specific examples are described in refs 56,57. For the purposes of demonstrating the existence of a NHIM, we only need to know that such transformations can in principle be carried out.

**Step 2: Use the normal form transformation for the 2 DoF subsystem to rewrite (5).**

We use the normal form transformation of the 2 DoF subsystem to express (5) as follows:

$$\begin{aligned} \bar{H} = \omega I + \lambda xy + \frac{1}{2} \sum_{i=1}^{n-2} \omega_i (u_i^2 + v_i^2) \\ + F(u_1, \dots, u_{n-2}, v_1, \dots, v_{n-2}, I, \theta, x, y) + \mathcal{O}_2(I) + \mathcal{O}_3(I, x, y) \end{aligned} \quad (9)$$

where

$$\begin{aligned} F(u_1, \dots, u_{n-2}, v_1, \dots, v_{n-2}, I, \theta, x, y) = \\ f(r(I, \theta, x, y), s(I, \theta, x, y), u_1, \dots, u_{n-2}, p_r(I, \theta, x, y), p_s(I, \theta, x, y), v_1, \dots, v_{n-2}). \end{aligned} \quad (10)$$

**Step 3: Use Hamiltonian (9) to conclude the existence of a NHIM.**

Let

$$I = \frac{1}{2}(w^2 + z^2), \theta = \tan^{-1} \left( \frac{z}{w} \right). \quad (11)$$

We then rewrite (9) as

$$\begin{aligned} \mathcal{H} = & \lambda xy + \frac{\omega}{2}(w^2 + z^2) + \frac{1}{2} \sum_{i=1}^{n-2} \omega_i (u_i^2 + v_i^2) \\ & + F(u_1, \dots, u_{n-2}, v_1, \dots, v_{n-2}, I(w, z), \theta(w, z), x, y) + \mathcal{O}_2(I(w, z)) + \mathcal{O}_3(I(w, z), x, y). \end{aligned} \quad (12)$$

By construction,  $\mathcal{H}(0) = 0$ . Neglecting higher order terms in (12), we obtain:

$$\mathcal{H}_{\text{trunc}} = \lambda xy + \frac{\omega}{2}(w^2 + z^2) + \frac{1}{2} \sum_{i=1}^{n-2} \omega_i (u_i^2 + v_i^2). \quad (13)$$

If we set  $x = y = 0$ , then on the energy surface  $\mathcal{H}_{\text{trunc}} = h > 0$ ,

$$\frac{\omega}{2}(w^2 + z^2) + \frac{1}{2} \sum_{i=1}^{n-2} \omega_i (u_i^2 + v_i^2) = h > 0, \quad (14)$$

is a normally hyperbolic invariant  $2n-3$  sphere in the  $2n$ -dimensional space with coordinates  $(u_1, \dots, u_{n-2}, v_1, \dots, v_{n-2}, w, z, x, y)$ , having  $2n-2$  dimensional stable and unstable manifolds in the  $2n-1$  dimensional energy surface. The persistence theory for NHIMs implies that this manifold persists when the higher order terms are added for energies sufficiently close to  $h = 0$  (cf. ref. 30).

At this point we are in a position where normal form theory can be used on (12) to construct a new set of coordinates (the normal form coordinates) in which (12) assumes a particularly simple form that results in explicit formulae for the NHIM, its stable and unstable manifolds, and dividing surfaces between regions of the phase space corresponding to reactants and products. The normal form algorithm also provides the transformation from the original physical coordinates and its inverse, and this allows us to map these surfaces back into the original physical coordinates, as described in ref. 24.

**B. Method 2: A hyperbolic torus of dimension  $n-1$  can be located in an  $n$  DoF system.**

The advantage of method 1 is that it can make use of extensive prior work on locating periodic orbits, and determining their stability, in 2 DoF systems. In method 2 the

starting point is knowledge of the existence of a hyperbolic torus of dimension  $n - 1$  in the  $2n$ -dimensional phase space, with the frequencies on the torus satisfying a diophantine condition<sup>58</sup>. In this case, it follows from ref. 55 that an invertible transformation of coordinates, valid in a neighborhood of the torus, can be found where the system has the following form:

$$H = \omega_1 I_1 + \dots + \omega_{n-1} I_{n-1} + \lambda xy + \mathcal{O}_2(I_1, \dots, I_{n-1}) + \mathcal{O}_3(I_1, \dots, I_{n-1}, x, y). \quad (15)$$

Now let

$$I_i = \frac{1}{2}(u_i^2 + v_i^2), \theta_i = \tan^{-1} \left( \frac{v_i}{u_i} \right), i = 1, \dots, n - 1. \quad (16)$$

In terms of these coordinates the Hamiltonian (17) has the form:

$$\bar{H} = \frac{1}{2} \sum_{i=1}^{n-1} \omega_i (u_i^2 + v_i^2) + \lambda xy + \mathcal{O}_2(u_1^2 + v_1^2, \dots, u_{n-1}^2 + v_{n-1}^2) + \mathcal{O}_3(u_1^2 + v_1^2, \dots, u_{n-1}^2 + v_{n-1}^2, x, y) \quad (17)$$

We now proceed exactly as for method 1. Neglecting the terms in (17) of order 3 and higher gives:

$$\bar{H}_{\text{trunc}} = \frac{1}{2} \sum_{i=1}^{n-1} \omega_i (u_i^2 + v_i^2) + \lambda xy. \quad (18)$$

If we set  $x = y = 0$ , then on the energy surface  $\bar{H}_{\text{trunc}} = h > 0$ ,

$$\frac{1}{2} \sum_{i=1}^{n-1} \omega_i (u_i^2 + v_i^2) = h > 0, \quad (19)$$

is a normally hyperbolic invariant  $2n - 3$  sphere in the  $2n$ -dimensional space with coordinates  $(u_1, \dots, u_{n-1}, v_1, \dots, v_{n-1}, x, y)$  having  $2n - 2$  dimensional stable and unstable manifolds in the  $2n - 1$  dimensional energy surface. The persistence theory for NHIMs implies that this manifold persists when the higher order terms are added for energies sufficiently close to  $h = 0$ .

Method 2 relies on first finding an appropriate hyperbolic invariant torus, and in general the existence of this object will need to be verified numerically. There has been a great deal of activity developing such numerical methods in recent years. See, for example, refs 59–66.

Finally, it is also worth noting the difference between the  $h = 0$  limit for index 1 saddles on the potential energy surface compared with the torus case in phase space. In the former case the NHIM shrinks down to a point on the potential energy surface (i.e. configuration space), while in the latter case it shrinks down to a torus in phase space.

#### IV. SUMMARY AND CONCLUSIONS

In this paper we have exhibited a normally hyperbolic invariant manifold (NHIM<sup>30</sup>, in this case a PODS<sup>47-49</sup>, or unstable periodic orbit) defining a flux bottleneck in a simple model of an ion-molecule reaction, for which there is no associated critical point of the potential energy surface. We have also developed a theoretical framework for showing the existence of such NHIMs. Two methods were described that are in principle suitable for computing such phase space objects in the multidimensional case.

For index one saddles a software package has been developed that allows one to compute the normal form associated with the corresponding saddle-center-...-center stability type equilibrium point to high order for multi-dimensional systems, with control over the accuracy<sup>67</sup>. Accuracy is assessed by a battery of tests, and specifying an accuracy may affect the order of the normal form that can be computed as well as the dimensionality of the system that can be treated. In general, these issues must be analyzed on a case-by-case basis. Nevertheless, the normal form, and most importantly the transformation from the original physical coordinates and its inverse, allow us to realize the NHIM, its stable and unstable manifolds, and dividing surfaces between regions of the phase space corresponding to reactants and products. Moreover, flux through the dividing surfaces can be computed as an integral over the NHIM, and the normal form coordinates provide a natural way of selecting distributions of initial conditions of trajectories on the dividing surfaces to compute gap times<sup>14,68</sup>. It should be possible to develop similar software for computing normal forms associated with hyperbolic tori of the type discussed above, and one expects that the normal form will, similarly, allow one to realize phase space structures relevant to reaction dynamics as well as to compute fluxes and sample distributions of initial conditions.

This program has yet to be carried out, but the essential computational elements of the approach can be found in refs 56,57. Such capabilities would be very useful for the study of reaction dynamics in multimode systems exhibiting transition state switching, for example ref. 42.

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- <sup>1</sup> P. G. Mezey, *Potential Energy Hypersurfaces* (Elsevier, Amsterdam, 1987).
- <sup>2</sup> D. J. Wales, *Energy Landscapes* (Cambridge University Press, Cambridge, 2003).
- <sup>3</sup> D. Chandler, *J. Chem. Phys.* **68**, 2959 (1978).
- <sup>4</sup> B. J. Berne, N. DeLeon, and R. O. Rosenberg, *J. Phys. Chem.* **86**, 2166 (1982).
- <sup>5</sup> M. J. Davis and S. K. Gray, *J. Chem. Phys.* **84**, 5389 (1986).
- <sup>6</sup> S. K. Gray and S. A. Rice, *J. Chem. Phys.* **86**, 2020 (1987).
- <sup>7</sup> R. M. Minyaev, *J. Struct. Chem.* **32**, 559 (1991).
- <sup>8</sup> R. M. Minyaev, *Russ. Chem. Rev.* **63**, 883 (1994).
- <sup>9</sup> T. Baer and W. L. Hase, *Unimolecular Reaction Dynamics* (Oxford University Press, New York, 1996).
- <sup>10</sup> D. M. Leitner, *Int. J. Quantum Chem.* **75**, 523 (1999).
- <sup>11</sup> H. Waalkens, A. Burbanks, and S. Wiggins, *J. Chem. Phys.* **121**, 6207 (2004).
- <sup>12</sup> B. K. Carpenter, *Ann. Rev. Phys. Chem.* **56**, 57 (2005).
- <sup>13</sup> M. Joyeux, S. Y. Grebenshchikov, J. Bredenbeck, R. Schinke, and S. C. Farantos, *Adv. Chem. Phys.* **130 A**, 267 (2005).
- <sup>14</sup> G. S. Ezra, H. Waalkens, and S. Wiggins, *J. Chem. Phys.* **130**, 164118 (2009).
- <sup>15</sup> M. Pettini, *Geometry and Topology in Hamiltonian Dynamics and Statistical Mechanics* (Springer, New York, 2007).
- <sup>16</sup> M. Kastner, *Rev. Mod. Phys.* **80**, 167 (2008).
- <sup>17</sup> V. I. Arnold, *Mathematical Methods of Classical Mechanics*, vol. 60 of *Graduate Texts in Mathematics* (Springer, New York, Heidelberg, Berlin, 1978).

- <sup>18</sup> V. I. Arnol'd, V. V. Kozlov, and A. I. Neishtadt, in *Dynamical Systems III*, edited by V. I. Arnol'd (Springer, Berlin, 1988), vol. 3 of *Encyclopaedia of Mathematical Sciences*.
- <sup>19</sup> S. Wiggins, *Introduction to Applied Nonlinear Dynamical Systems and Chaos* (Springer-Verlag, 2003).
- <sup>20</sup> A. J. Lichtenberg and M. A. Lieberman, *Regular and Chaotic Dynamics* (Springer Verlag, New York, 1992), 2nd ed.
- <sup>21</sup> Consider a potential energy function  $V = V(q_1, \dots, q_n)$  that is a function of  $n$  coordinates  $\{q_k\}$ . (Coordinates describing translation and rotation are excluded.) At a non-degenerate critical point of  $V$ , where  $\partial V/\partial q_k = 0$ ,  $k = 1, \dots, n$ , the Hessian matrix  $\partial^2 V/\partial q_i \partial q_j$  has  $n$  nonzero eigenvalues. The *index* of the critical point is the number of negative eigenvalues.
- <sup>22</sup> T. Uzer, C. Jaffe, J. Palacian, P. Yanguas, and S. Wiggins, *Nonlinearity* **15**, 957 (2002).
- <sup>23</sup> T. Komatsuzaki and R. S. Berry, *Adv. Chem. Phys.* **123**, 79 (2002).
- <sup>24</sup> H. Waalkens, R. Schubert, and S. Wiggins, *Nonlinearity* **21**(1), R1 (2008).
- <sup>25</sup> D. Heidrich and W. Quapp, *Theor. Chim. Acta* **70**, 89 (1986).
- <sup>26</sup> G. S. Ezra and S. Wiggins, *J. Phys. A* **42**, 205101 (2009).
- <sup>27</sup> G. Haller, J. Palacian, P. Yanguas, T. Uzer, and C. Jaffé, *Comm. Nonlinear Sci. Num. Simul.* **15**, 48 (2010).
- <sup>28</sup> N. Shida, *Adv. Chem. Phys.* **130 B**, 129 (2005).
- <sup>29</sup> S. Wiggins, *Physica D* **44**, 471 (1990).
- <sup>30</sup> S. Wiggins, *Normally hyperbolic invariant manifolds in dynamical systems* (Springer-Verlag, 1994).
- <sup>31</sup> H. Waalkens and S. Wiggins, *J. Phys. A* **37**, L435 (2004).
- <sup>32</sup> C. B. Li, M. Toda, and T. Komatsuzaki, *J. Chem. Phys.* **130**, 124116 (2009).
- <sup>33</sup> L. P. Sun, K. Y. Song, and W. L. Hase, *Science* **296**, 875 (2002).
- <sup>34</sup> D. Townsend, S. A. Lahankar, S. K. Lee, S. D. Chambreau, A. G. Suits, X. Zhang, J. Rheinecker, L. B. Harding, and J. M. Bowman, *Science* **306**, 1158 (2004).
- <sup>35</sup> J. M. Bowman, *PNAS* **103**, 16061 (2006).
- <sup>36</sup> J. G. Lopez, G. Vayner, U. Lourderaj, S. V. Addepalli, S. Kato, W. A. Dejong, T. L. Windus, and W. L. Hase, *J. Am. Chem. Soc.* **129**, 9976 (2007).
- <sup>37</sup> B. R. Heazlewood, M. J. T. Jordan, S. H. Kable, T. M. Selby, D. L. Osborn, B. C. Shepler, B. J. Braams, and J. M. Bowman, *PNAS* **105**, 12719 (2008).

- <sup>38</sup> B. C. Shepler, B. J. Braams, and J. M. Bowman, *J. Phys. Chem. A* **112**, 9344 (2008).
- <sup>39</sup> L. Wiesenfeld, A. Faure, and T. Johann, *J. Phys. B* **36**, 1319 (2003).
- <sup>40</sup> L. Wiesenfeld, *Adv. Chem. Phys.* **130 A**, 217 (2005).
- <sup>41</sup> W. J. Chesnavich, L. Bass, T. Su, and M. T. Bowers, *J. Chem. Phys.* **74**(4), 2228 (1981).
- <sup>42</sup> W. J. Chesnavich and M. T. Bowers, *Prog. Reaction Kinetics* **11**, 137 (1982).
- <sup>43</sup> W. J. Chesnavich, *J. Chem. Phys.* **84**(5), 2615 (1986).
- <sup>44</sup> J. C. Keck, *Adv. Chem. Phys.* **XIII**, 85 (1967).
- <sup>45</sup> W. L. Hase, *Acc. Chem. Res.* **16**, 258 (1983).
- <sup>46</sup> D. G. Truhlar and B. C. Garrett, *Ann. Rev. Phys. Chem.* **35**, 159 (1984).
- <sup>47</sup> P. Pechukas, *Ann. Rev. Phys. Chem.* **32**, 159 (1981).
- <sup>48</sup> P. Pechukas, *Ber. Buns. Ges.* **86**, 372 (1982).
- <sup>49</sup> E. Pollak, *Periodic orbits and the theory of reactive scattering* (CRC Press, Boca Raton, 1985), vol. 3 of *Theory of Chemical Reaction Dynamics*, pp. 123–246.
- <sup>50</sup> C. Lanczos, *The Variational Principles of Mechanics* (Dover, New York, 1986).
- <sup>51</sup> The pods at energy  $E$  for the reversible Hamiltonian (1) is located by initiating trajectories with zero velocity on the equipotential line  $V = E$ . The initial position is varied until a self-retracing (periodic) orbit is obtained. For the 2 DoF system studied, this is a 1-parameter search.
- <sup>52</sup> S. Wiggins, L. Wiesenfeld, C. Jaffe, and T. Uzer, *Phys. Rev. Lett.* **86**(24), 5478 (2001).
- <sup>53</sup> H. W. Broer, G. B. Huitema, and M. B. Sevryuk, *Quasi-periodic motions in families of dynamical systems: order amidst chaos*, *Lecture Notes in Mathematics* (Springer-Verlag, New York, Heidelberg, Berlin, 1996).
- <sup>54</sup> H. Hanssmann, in *New advances in celestial mechanics and Hamiltonian systems* (Kluwer/Plenum, New York, 2004), pp. 109–121.
- <sup>55</sup> S. V. Bolotin and D. V. Treschev, *Regul. Chaotic Dyn.* **5**(4), 401 (2000).
- <sup>56</sup> A. Jorba and J. Villaneuva, *Physica D* **114**, 197 (1998).
- <sup>57</sup> A. Jorba, *Experimental Mathematics* **8**(2), 155 (1999).
- <sup>58</sup> W. M. Schmidt, *Diophantine Approximation*, vol. 785 of *Lecture Notes in Mathematics* (Springer, 1980).
- <sup>59</sup> L. Dieci, J. Lorenz, and R. D. Russell, *SIAM J. Sci. Stat. Comp.* **12**(3), 607 (1991).
- <sup>60</sup> L. Dieci and J. Lorenz, *SIAM J. Num. Anal.* **32**(5), 1436 (1995).
- <sup>61</sup> K. D. Etoh, R. D. Russell, and W. Sun, *App. Num. Math.* **32**(3), 273 (2000).

- <sup>62</sup> F. Gabern, W. S. Koon, J. E. Marsden, and S. D. Ross, *Physica D* **211**, 391 (2005).
- <sup>63</sup> F. Schilder, H. M. Osinga, and W. Vogt, *SIAM J. Appl. Dyn. Syst.* **4**(3), 459 (2005).
- <sup>64</sup> A. Haro and R. de la Llave, *Discrete Contin. Dyn. Syst.-Ser. B* **6**(6), 1261 (2006).
- <sup>65</sup> H. Dankowicz and G. Thakur, *Int. J. Bif. Chaos* **16**(5), 1491 (2006).
- <sup>66</sup> A. Jorba and E. Olmedo, *SIAM J. Appl. Dyn. Syst.* **8**(4), 1382 (2009).
- <sup>67</sup> The normal form software is available from <http://lacms.maths.bris.ac.uk/publications/software/index.html>.
- <sup>68</sup> E. Thiele, *J. Chem. Phys.* **36**(6), 1466 (1962).

### Figure captions

FIG. 1: Contour plot of the model potential of eq. (3). Parameter values  $\alpha = 1$ ,  $\beta = 1$ ,  $\omega_0 = 8$ . Superimposed on the potential contours is a PODS defining a “tight” transition state, computed at energy  $E = 1$ .

FIG. 2: Action  $I(E, r)$  (eq. (4)) as a function of  $r$ , computed at energy  $E = 1$ .

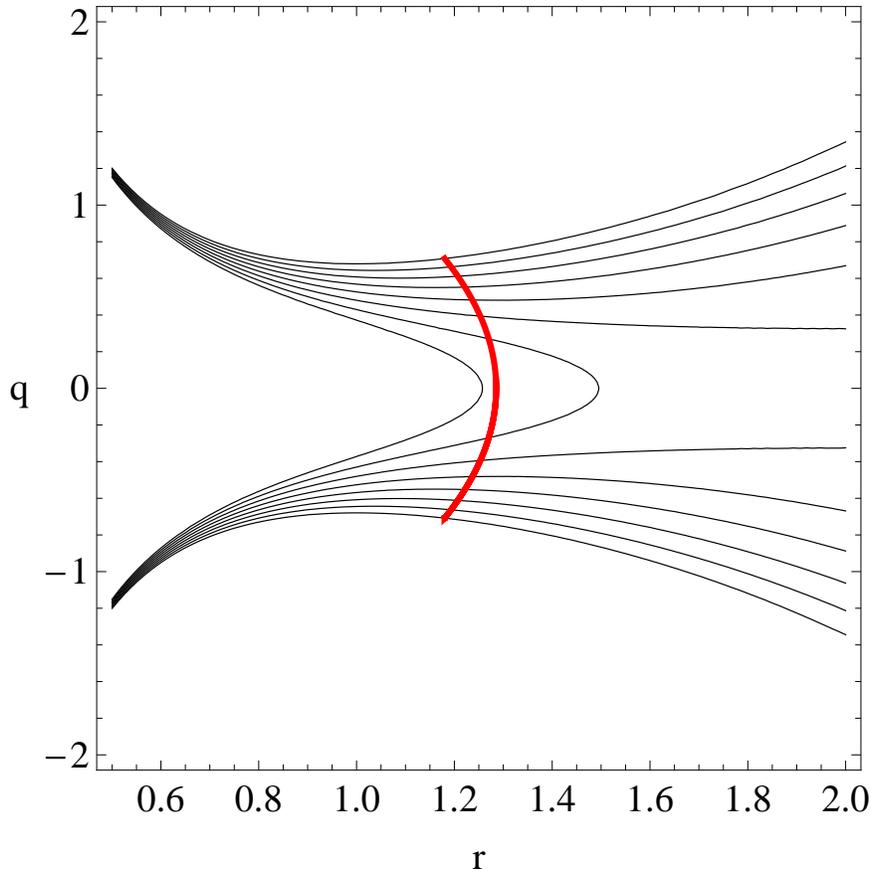


FIGURE 1

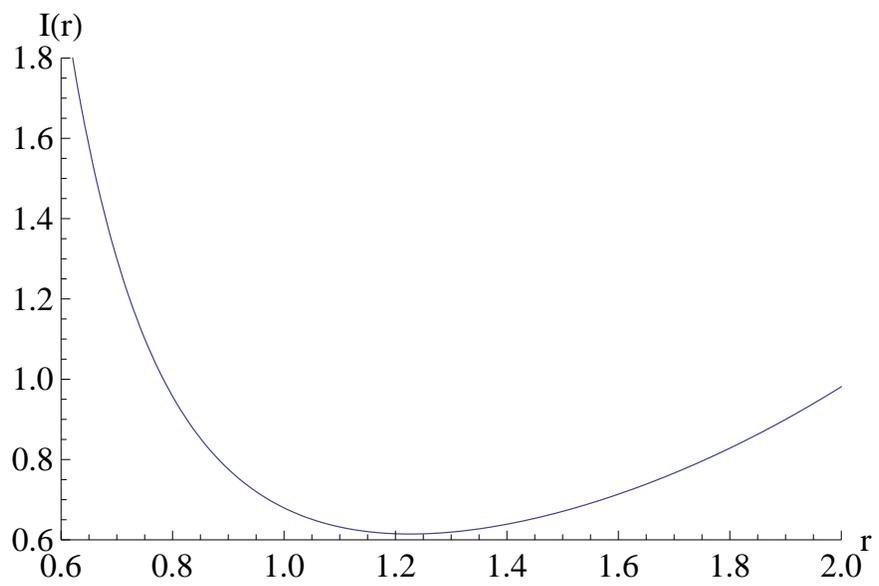


FIGURE 2