

University of Groningen

A formula to compute the microcanonical volume of reactive initial conditions in transition state theory

Waalkens, H.; Burbanks, A.; Wiggins, S.

Published in:
Journal of Physics A, Mathematical and General

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2005

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Waalkens, H., Burbanks, A., & Wiggins, S. (2005). A formula to compute the microcanonical volume of reactive initial conditions in transition state theory. *Journal of Physics A, Mathematical and General*, 38, L759-L768.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

LETTER TO THE EDITOR

A formula to compute the microcanonical volume of reactive initial conditions in transition state theory

H Waalkens, A Burbanks¹ and S Wiggins

School of Mathematics, Bristol University, University Walk, Bristol, BS8 1TW, UK

E-mail: H.Waalkens@bris.ac.uk

Received 6 September 2005, in final form 5 October 2005

Published 26 October 2005

Online at stacks.iop.org/JPhysA/38/L759**Abstract**

We present the formal proof of a procedure to compute the phase-space volume of initial conditions for trajectories that, for a constant energy, escape or ‘react’ from a multi-dimensional potential well with one or several exit/entrance channels. The procedure relies on a phase-space formulation of transition state theory. It gives the volume of reactive initial conditions as the sum over the exit/entrance channels where each channel contributes by the product of the phase-space flux associated with the channel and the mean residence time in the well of those trajectories which escape through the channel. An example is given to demonstrate the computational efficiency of the procedure.

PACS numbers: 45.20.Jj, 05.45.–a, 34.10.+x, 82.20.Db

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The problem of escape from a potential well where exit from the well is possible through channels that are associated with saddle points is a common problem in many areas of physics. In this letter, we prove a formula and present a procedure based on the formula that enables one to compute the phase-space volumes of initial conditions in the well that, for a fixed energy, lead to trajectories which escape from the potential well through any of these channels. We note that a similar result, the classical limit of the so-called *spectral theorem*, has been obtained by Pollak [1] in the context of molecular collisions (the spectral theorem relates time delays in collisions to the density of states; see [2] for the historical background). The implementation of our procedure relies on the recent development of a *phase-space* formulation of transition state theory based on general ideas from dynamical systems theory [3–8] and we therefore find it useful to provide a formal proof of the spectral theorem especially in this context.

¹ Present address: Department of Mathematics, University of Portsmouth, Lion Terrace, Portsmouth, P01 3HE, UK.

For energies slightly above the saddle, phase-space transition state theory, which is algorithmic in nature, solves the key problem of how to define and construct a dividing surface near a saddle point, which locally divides the energy surface into two disjoint components and which is free of local ‘recrossing’. These properties which are essential for rate computations will also play an important role in what follows.

In recent years, transition state theory has been recognized as a very fruitful approach whose applicability goes far beyond its origin of conception in chemistry. It has been used e.g. in atomic physics [9], studies of the rearrangements of clusters [10], solid state and semi-conductor physics [11, 12], cosmology [13] and celestial mechanics [14]. The results presented in this letter are of central interest for all of these areas as they open the way to study fundamental questions like the violation of ergodicity assumptions on the dynamics which are typically made in statistical approaches like Rice–Ramsperger–Kassel–Marcus (RRKM) theory [15].

Before we derive the formula for the volume of reactive initial conditions in a potential well, we recapitulate the building blocks of phase-space transition state theory.

2. Phase-space transition state theory

We start with an equilibrium point for Hamilton’s equations which is of saddle–centre–centre type (which we refer to as ‘saddle’ for short, in what follows). A detailed theory for phase-space transport associated with saddles has been developed in recent years [3–8]. For energies slightly above that of a saddle, on each $(2n - 1)$ -dimensional energy surface with n being the number of degrees of freedom, there exists an invariant $(2n - 3)$ -dimensional sphere S^{2n-3} of saddle stability type, which is significant for two reasons:

- It is the ‘equator’ of a particular $(2n - 2)$ -dimensional sphere, which we take as the *dividing surface*. The equator separates the dividing surface into two hemispheres which have the structure of open $(2n - 2)$ -dimensional balls. Except for the equator (which is an invariant manifold), the dividing surface is locally a ‘surface of no return’ in the sense that trajectories which have crossed the dividing surface must leave a certain neighbourhood of the dividing surface before they can possibly cross it again. For energies ‘sufficiently close’ to the energy of the saddle, the dividing surface satisfies the *bottleneck property*. This means that the energy surface has *locally* the geometrical structure of $S^{2n-2} \times I$ (i.e., $(2n - 2)$ -sphere \times interval where the interval corresponds to a so-called *reaction coordinate*) and the dividing surface divides the energy surface into two disjoint components. Moreover, the *only* way a trajectory can pass from one component of the energy surface to the other in the ‘forward’ direction is through one hemisphere and the only way to pass in the ‘backward’ direction is through the other hemisphere. The hemispheres are thus the gateways to the exit and entrance channels for the energy surface components. The fluxes through the forward and backward hemispheres are of equal magnitude and opposite sign so that the total flux through the dividing surface is zero. However, for our particular choice of dividing surface, the *directional* flux through each hemisphere is minimal in a sense made precise in [16].
- The $(2n - 3)$ -sphere is a *normally hyperbolic invariant manifold* (NHIM) [5]. Normal hyperbolicity means that the expansion and contraction rates of the dynamics on the $(2n - 3)$ -sphere are dominated by those transverse to it. The NHIM therefore has stable and unstable manifolds which in this case are $(2n - 2)$ -dimensional, having the structure of *spherical cylinders*, $S^{2n-3} \times \mathbb{R}$. Hence, they are of one dimension less than the energy surface and act as ‘separatrices’; they ‘enclose’ volumes of the energy surface. Their key dynamical

significance is that the only way that trajectories can pass through the dividing surface is if they are inside a particular region of the energy surface enclosed by the stable and unstable spherical cylinders.

For a system with two degrees of freedom, the NHIM is a periodic orbit. If this system is of type ‘kinetic-plus-potential’ the configuration space projection of the periodic orbit connects, for an energy slightly above the energy of the potential saddle, two branches of an iso-potential line and this is the basis for the construction of the so-called *periodic orbit dividing surface* (PODS) in the seminal work by McLafferty, Pechukas and Pollak [17–20].

For higher dimensions, the phase-space structures mentioned above can be computed via a procedure based on Poincaré–Birkhoff normalization [7, 8] which yields a nonlinear symplectic transformation of the original phase-space coordinates to new coordinates referred to as the *normal form coordinates*. The NHIM, the local parts of its stable and unstable manifolds and the dividing surface are simply given as normal form coordinate hyperplanes. The phase-space structures are then mapped into the original phase-space coordinate system by the inverse of the normal form transformation.

The phase-space structures, and techniques, are the key to analysing the problem of ‘escape’ or ‘reaction’ from a phase-space region. However, in order to use them, we must first derive a more general result.

3. A rigorous statement on volumes within the energy surface that are ‘swept out’ by trajectories

Let us consider an n degree-of-freedom Hamiltonian system (M, ω) where M is a $(2n)$ -dimensional manifold (the phase space) and ω is a symplectic 2-form. The Hamiltonian function, which is assumed not to depend on time, is H . The volume of a *phase-space region* is obtained by integrating over it the $(2n)$ -form $\Omega = \omega^n/n!$. Since energy is conserved under the dynamics, it makes sense to consider the volumes of regions in a single energy surface Σ_E . A differential form η to measure *energy surface volume* is a $(2n - 1)$ -form by which the phase-space volume form Ω can be decomposed according to $\Omega = dH \wedge \eta$ [21].

We want to derive a rigorous statement about how the integration of η over energy surface regions swept out by trajectories can be evaluated. The statement is phrased in a way that makes it directly applicable to the setting of transition state theory elucidated above.

Theorem 1. *Let S and S' be two $(2n - 1)$ -dimensional manifolds in M with S being a coordinate hyperplane $q_1 = 0$ of a canonical coordinate system $(p_1, \dots, p_n, q_1, \dots, q_n)$. Moreover, assume $\dot{q}_1 > 0$ in S which implies that S is transverse to the Hamiltonian flow. S' is arbitrary and may coincide with S . Let E be a regular value of H and Σ_E be the corresponding energy surface. Assume that $B \subset S \cap \Sigma_E$ is a $(2n - 2)$ -dimensional manifold which, under the map induced by the Hamiltonian flow, has a continuous image B' in $S' \cap \Sigma_E$. Assume that the corresponding orbit segments start on B and end on B' without having further intersections with B or B' . Then the energy surface volume of the set $M_{B \rightarrow B'}$, swept out by the orbit segments between B and B' , is given by*

$$\text{vol}(M_{B \rightarrow B'}) = \phi_B(t)_B, \quad (1)$$

with

$$\phi_B = \int_B \Omega', \quad \left(\Omega' = \frac{\omega^{n-1}}{(n-1)!} \right) \quad (2)$$

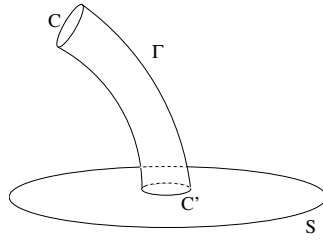


Figure 1. Sketch of a $(2n - 1)$ -dimensional manifold S and a two-dimensional closed manifold C in the $(2n)$ -dimensional phase space. The deformation of C consists of C' , which is the image of C in S under the inverse Hamiltonian flow, and Γ , which is swept over by letting the inverse Hamiltonian flow act on the boundary ∂C .

being the flux through B , and with

$$\langle t \rangle_B = \frac{\int_B t \Omega'}{\int_B \Omega'}, \quad (3)$$

being the average of the passage time $t : B \rightarrow \mathbb{R}^+$, which maps points in B to the times they require to reach S' under the Hamiltonian flow.

We start the proof of theorem 1 by the following generalization of a result by Binney, Gerhard and Hut [22]

Lemma 2. *Given the setting of theorem 1, there exists a sufficiently small phase-space neighbourhood of $M_{B \rightarrow B'}$ in which we can construct the canonical coordinates $(H, P_2, \dots, P_n, t, Q_2, \dots, Q_n)$ which are defined as follows. For a phase-space point in this neighbourhood, H is the energy at this point, $P_2, \dots, P_n, Q_2, \dots, Q_n$ are the coordinates $(p_2, \dots, p_n, q_2, \dots, q_n)$ of the image of this point in S under the inverse flow and t is the time it takes the point to reach S under the inverse flow.*

We first prove this result.

Proof (lemma 2). Since the Jacobian of the transformation $(p_1, p_2, \dots, p_n, q_2, \dots, q_n) \mapsto (H, p_2, \dots, p_n, q_2, \dots, q_n)$ which replaces p_1 by H has determinant \dot{q}_1 , and by our assumption $\dot{q}_1 > 0$ in S , it follows that $(H, p_2, \dots, p_n, q_2, \dots, q_n)$ are well-defined coordinates in S . Moreover, from the uniqueness of solutions of ODEs (Hamilton's equations in this case), it follows that a point in the volume swept out by letting the Hamiltonian flow act on S is uniquely determined by the coordinates $(H, p_2, \dots, p_n, t, q_2, \dots, q_n)$ where t is the time it takes the inverse flow to map the point back to S .

We now have to show that these coordinates are canonical, i.e. defining $\tilde{\omega} = dH \wedge dt + \sum_{k=2}^n dP_k \wedge dQ_k$ we have to show that, in the above neighbourhood, $\tilde{\omega} = \omega$. We thus have to prove that $\tilde{\omega} - \omega$ gives zero when we apply it to two arbitrary vectors in the tangent bundle of this neighbourhood, or equivalently, that the integral of $\tilde{\omega} - \omega$ over any small two-dimensional bounded manifold in this neighbourhood vanishes. Let us consider such a small two-dimensional manifold C , see figure 1. Since $d(\omega - \tilde{\omega}) = 0$ it follows from Stokes' theorem that the integral of $\omega - \tilde{\omega}$ over C is the same as the integral over any continuous deformation of C which has the same boundary ∂C as C . Consider the deformation shown in figure 1 which consists of a part C' which is the image of C in S under the inverse Hamiltonian flow and a part Γ which is the two-dimensional manifold swept out by letting the Hamiltonian flow act upon ∂C until ∂C reaches S . Since it is clear that the restrictions of ω and $\tilde{\omega}$ to C' coincide, it only remains to be shown that the restrictions of ω and $\tilde{\omega}$ to Γ coincide as well.

For a point in Γ , we choose two basis vectors u and v for the tangent space of Γ at this point. Since Γ is foliated by orbits we can choose u to be the Hamiltonian vector field at the point under consideration, i.e. $u = (\dot{p}, \dot{q})$. The vector v is obtained as the derivative of some phase-space curve $(p(\lambda), q(\lambda))$ which passes through this point, i.e. $v = (dp/d\lambda, dq/d\lambda)$. First we apply ω to (u, v) . This gives

$$\begin{aligned}\omega(u, v) &= \sum_{k=1}^n ((dp_k(u) dq_k(v) - dp_k(v) dq_k(u)) \\ &= - \sum_{k=1}^n ((\partial H/\partial q_k)(dq_k/d\lambda) + (\partial H/\partial p_k)(dp_k/d\lambda)) \\ &= -dH/d\lambda,\end{aligned}$$

where the last equality follows from the chain rule. Next we apply $\tilde{\omega}$ to (u, v) . This gives

$$\tilde{\omega}(u, v) = dH(u) dt(v) - dH(v) dt(u) + \sum_{k=2}^n (dP_k(u) dQ_k(v) - dP_k(v) dQ_k(u)).$$

Since H , and P_k and Q_k , $k = 2, \dots, n$, are conserved along trajectories with initial conditions in S , it follows that $dH(u) = dP_k(u) = dQ_k(u) = 0$, $k = 2, \dots, n$. Hence, $\tilde{\omega}(u, v) = -dH(v) dt(u)$, and using $dH(v) = dH/d\lambda$ and $dt(u) = 1$ we see that $\tilde{\omega}(u, v)$ agrees with $\omega(u, v)$ computed above. \square

Having proven the generalization of the result by Binney, Gerhard and Hut, we are now in a position to prove formula (1).

Proof (theorem 1). Recall that the energy surface volume form η is a $(2n-1)$ -form defined by $\Omega = dH \wedge \eta$ with $\Omega = \omega^n/n!$. The volume of $M_{B \rightarrow B'}$ is defined by $\text{vol}(M_{B \rightarrow B'}) = \int_{M_{B \rightarrow B'}} \eta$. According to the above, we have $\omega = \tilde{\omega}$ in a neighbourhood of $M_{B \rightarrow B'}$. It follows that $\Omega = dH \wedge dt \wedge dP_2 \wedge dQ_2 \wedge \dots \wedge dP_n \wedge dQ_n$ from which we can read off η to be $\eta = dt \wedge dP_2 \wedge dQ_2 \wedge \dots \wedge dP_n \wedge dQ_n$. Carrying out the integration in the direction of the flow, we get $\text{vol}(M_{B \rightarrow B'}) = \int_B t dP_2 \wedge dQ_2 \wedge \dots \wedge dP_n \wedge dQ_n$ where $t(E, P_2, \dots, P_n, Q_2, \dots, Q_n)$ is the time it takes the respective point in B to reach S' under the Hamiltonian flow. Since, in B we have $q_1 = 0$, and $P_k = p_k$ and $Q_k = q_k$, $k = 2, \dots, n$, it follows that the restriction of $dP_2 \wedge dQ_2 \wedge \dots \wedge dP_n \wedge dQ_n$ to B coincides with the restriction of $\Omega' = \omega^{n-1}/(n-1)!$ to B . We thus have $\text{vol}(M_{B \rightarrow B'}) = \int_B t \Omega'$ where, for a point in B , t is the time to reach its image in B' under the Hamiltonian flow.

As shown by MacKay [21], Ω' is the $(2n-2)$ -form to measure flux through co-dimension 1 submanifolds of non-critical energy surfaces. Since we assume the energy E under consideration to be non-critical, we can rewrite $\text{vol}(M_{B \rightarrow B'})$ according to $\text{vol}(M_{B \rightarrow B'}) = \phi_B \langle t \rangle_B$ where $\phi_B = \int_B \Omega'$ is the flux through B and $\langle t \rangle_B = \int_B t \Omega' / \int_B \Omega'$ is the mean passage time from B to B' . \square

4. Application to an example system

In order to illustrate how theorem 1 can be used to analyse the escape or reaction from a potential well, we apply it to the Müller–Brown potential energy surface [23, 24] which is a frequently used benchmark system in chemistry for testing algorithms in transition state theory (see e.g. [25–27]). The Hamiltonian function for this system is

$$H = \frac{1}{2}(p_x^2 + p_y^2) + V(x, y) \quad (4)$$

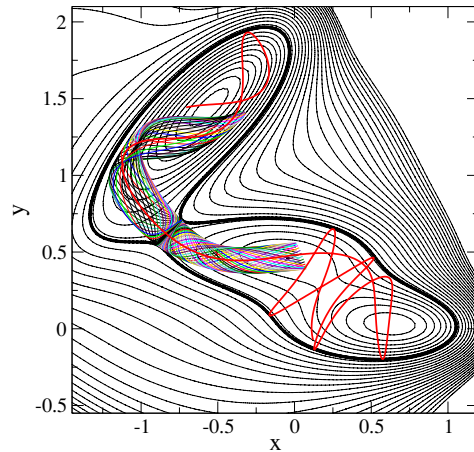


Figure 2. Iso-potential contours for the Müller–Brown surface. The bold contour is for energy $\Delta E = 3$ above the saddle at $(x, y) \approx (-0.82200, 0.62431)$. Shown also are local parts of the stable and unstable manifolds of the NHIM (a periodic orbit) and a segment of a trajectory that passes between the wells.

with the potential energy surface

$$V(x, y) = \sum_{k=1}^4 A_k \exp [a_k (x - x_k^0)^2 + b_k (x - x_k^0)(y - y_k^0) + c_k (y - y_k^0)^2], \quad (5)$$

where

$$\begin{aligned} A &= (-200, -100, -170, 15), & a &= (-1, -1, -6.5, 0.7), \\ b &= (0, 0, 11, 0.6), & c &= (-10, -10, -6.5, 0.7), \\ x^0 &= (1, 0, -0.5, -1), & y^0 &= (0, 0.5, 1.5, 1). \end{aligned} \quad (6)$$

Equipotentials for this surface are shown in figure 2. The surface has two wells: a deep well at the top and a shallow well with two local minima at the bottom. We want to use formula (1) to compute the volume of initial conditions in either potential well which for a fixed energy slightly above the energy of the saddle at $(x, y) \approx (-0.82200, 0.62431)$ can escape to the other well. In phase space, the two wells are separated by a dividing surface which we construct from the Poincaré–Birkhoff normalization procedure mentioned above. In a phase-space neighbourhood of the corresponding equilibrium point $(p_x, p_y, x, y) \approx (0, 0, -0.82200, 0.62431)$ of Hamilton's equations this yields a nonlinear transformation of (p_x, p_y, x, y) to normal form coordinates (p_1, p_2, q_1, q_2) . For the present system, which has two degrees of freedom, the dividing surface is a two-dimensional sphere that is given by the intersection of the normal form coordinate hyperplane $q_1 = 0$ with the energy surface Σ_E of the energy E under consideration [7].² The NHIM is an unstable periodic orbit; the Lyapunov orbit associated with the saddle. It separates the dividing surface into two hemispheres which are two-dimensional balls or discs. *Every* trajectory which passes from the top well to the bottom well has to cross one hemisphere. *Every* trajectory which passes from the bottom well to the top well has to cross the other hemisphere. These trajectories are enclosed by the stable and unstable manifolds of the NHIM which have the structure of cylinders whose configuration space projections are shown in figure 2.

² Note that in the present letter, we have adopted a convention for the normal form coordinates that is slightly different from the one in [7]. The systems are related by a simple symplectic rotation.

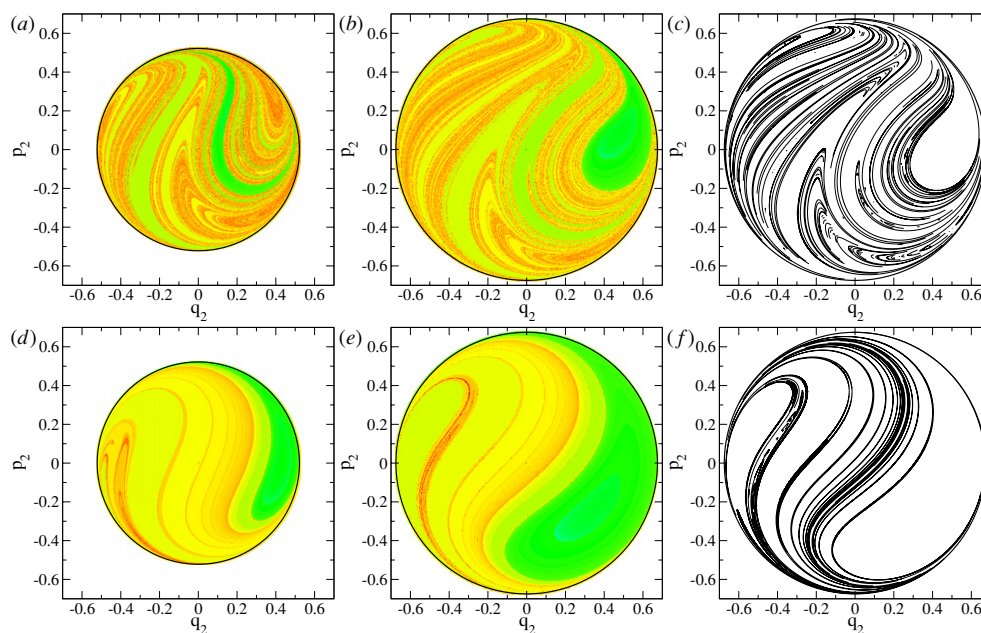


Figure 3. Contours of the residence times on the dividing surface hemispheres. The top (bottom) panels show the dividing surface hemisphere which corresponds to entrance to the lower (top) potential well of the Müller–Brown potential. The colours represent the residence times that trajectories started at the corresponding initial condition on the hemisphere spend in the corresponding well. The time increases from green to yellow to red on a standard hue scale. (a) and (d) are for energy $\Delta E = 3$ above the saddle energy, (b) and (e) are for energy $\Delta E = 5$ above the saddle energy. (c) and (f) show the intersection of the stable manifolds of the NHIM with the corresponding hemisphere for energy $\Delta E = 5$ above the saddle energy.

As a consequence of Liouville’s theorem on the conservation of phase-space volume [28], every trajectory (up to a set of measure zero) that enters a well through one hemisphere has to leave it at a later point in time through the other hemisphere. The reactive volume of either well is thus given by the volume swept out by trajectory segments with initial conditions on the corresponding hemisphere and endpoint on the other hemisphere. The NHIM’s stable and unstable manifolds partition the reactive regions into subregions that correspond to different types of reactive trajectories (see [29, 30] for a more detailed discussion). This is illustrated in figure 3 which shows the dividing surface hemispheres for energies $\Delta E = 3$ and $\Delta E = 5$ above the energy of the saddle. We parameterize the dividing surface hemispheres by the normal form coordinates (q_2, p_2) , and show the contours of the residence time (the time spent in the relevant well before the first exit of the well) for trajectories with initial conditions on these hemispheres. The residence times vary smoothly within the stripes and tongue-shaped patches appearing in figure 3. The boundaries of the patches correspond to the intersections of the hemispheres with the stable manifolds of the NHIM which are also shown in figure 3. The residence time is infinite on the boundaries. However, the divergence of the residence times is only mild. Upon approaching a boundary from the interior of a single patch the residence time diverges logarithmically. This is illustrated in figure 4 which shows a one-dimensional cut through one of the hemispheres in figure 3. The plateaus of the residence times in figure 4 correspond to different types of reactive trajectories. The singularities of the residence times at both ends of a plateau correspond to trajectories which are forward asymptotic in time to the NHIM (the periodic orbit). The magnifications in figure 4 show that the plateaus and

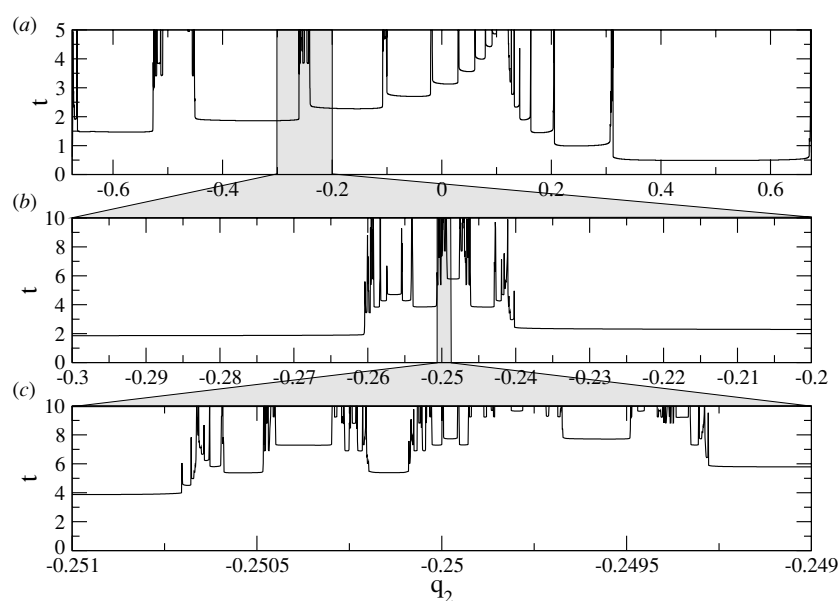


Figure 4. (a) Distribution of residence times along the line $p_2 = 0$ in figure 3(e). (b) and (c) show successive magnifications of a part of the graph in (a).

singularities form a self-similar structure which is well known from scattering theory. For a more detailed discussion of these structures, see [30].

Theorem 1 at first only applies to regions in the interior of the patches in figure 3. Utilizing standard arguments from integration theory it follows from the fact that the reactive volume of a well is finite that the integrals in equations (2) and (3) can be extended over a whole patch and also that the summation over the infinite number of patches converges. The summation over the patches gives the reactive volumes of a well as the product of the flux and the average total of the residence times of trajectories with initial conditions on the corresponding dividing surface hemisphere. In the case of two degrees of freedom where the NHIM is a periodic orbit, the flux is simply given by the action of the periodic orbit. For systems with more degrees of freedom the flux is given by a generalized action integral over the NHIM which is easily computed from the normal form [16]. The average residence time can be efficiently computed from a Monte Carlo integration [29, 30].

We apply the above procedure for energies $\Delta E = 3$ and $\Delta E = 5$ above the saddle and compare the results with a computationally expensive brute-force calculation in which we sample initial conditions (uniformly distributed with respect to the measure $\delta(E - H) dx dy dp_x dp_y$) on the entire energy surface components associated with the potential wells and integrate them in time until they either escape or reach a large cut-off time after which escape is very unlikely. Figure 5 shows the resulting survival probabilities $P(t)$, i.e. the normalized histogram of trajectories which stay in the well under consideration up to time t . The functions $P(t)$ saturate for large t at values P_∞ where $1 - P_\infty$ can be identified with the quotient of the reactive volume of a well and the total energy surface volume of that well. For each well, and for both studied energies, P_∞ is *not* equal to zero, indicating that the motions in the wells are not ergodic. This is further illustrated in figure 6 which shows the dynamics in terms of surfaces of section with the section condition $p_x = 0, \dot{p}_x > 0$. The ‘bottleneck’ of the energy surface due to the saddle is clearly visible (the wide-narrow-wide geometry near

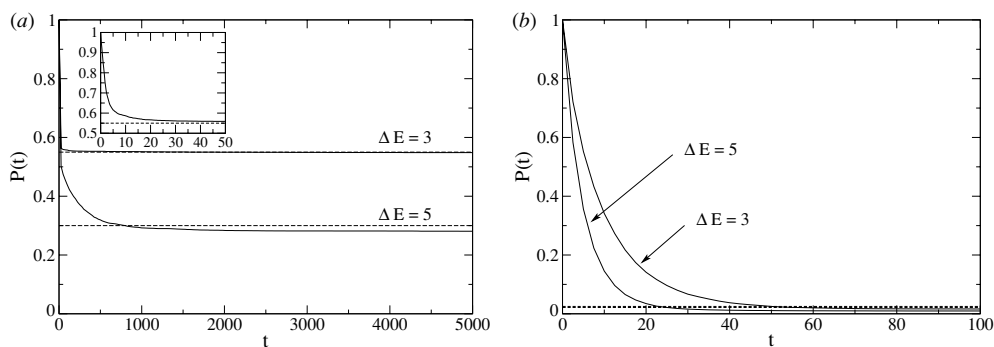


Figure 5. Survival probabilities for trajectories with initial conditions in the top well (a) and bottom well (b) of the Müller–Brown potential for energies $\Delta E = 3$ and $\Delta E = 5$ above the saddle. The inset in (a) shows a magnification of the survival probability graph for $\Delta E = 3$.

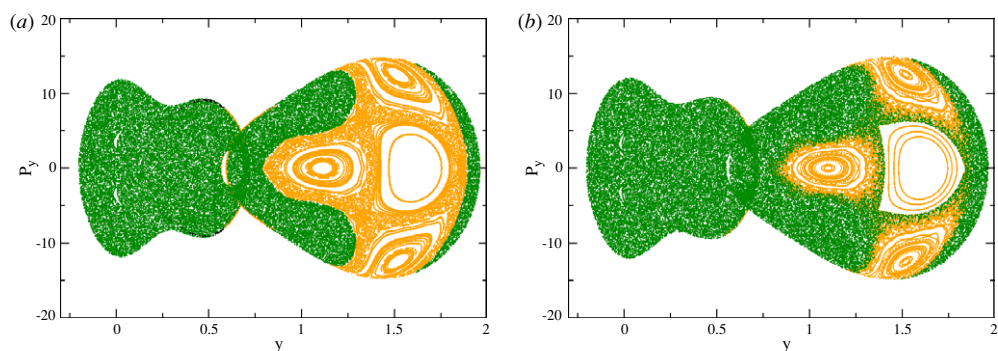


Figure 6. Poincaré surfaces of section for $p_x = 0, \dot{p}_x > 0$ for energies $\Delta E = 3$ (a) and $\Delta E = 5$ (b) above the saddle. Green dots mark reactive trajectories; orange dots mark non-reactive trajectories. The region to the left (right) of $y \approx 0.62431$ corresponds to the bottom (top) well of the Müller–Brown potential in figure 2.

$y \approx 0.62431$). The parts to the left and right of $y \approx 0.62431$ in figure 6 correspond to the bottom and top wells of the Müller–Brown potential, respectively. Reactive trajectories and non-reactive trajectories are marked green and orange, respectively. In agreement with the survival probability curves in figure 5, the surfaces of section in figure 6 indicate that the portion of reactive trajectories is much higher in the lower well than it is in the top well. It is worth mentioning that knowledge of the area of a region in the surface of section (occupied e.g. by reactive or non-reactive trajectories) alone is not sufficient to compute the volume of the corresponding three-dimensional region on the energy surface (see [22] for a thorough discussion of this issue).

For comparison, figure 5 also shows the values for the reactive volume computed from formula (1) as horizontal lines. In each case the computation of P_∞ using (1) is able to reproduce the results from the brute-force method with an error less than 2%.

5. Conclusions and outlook

We presented a method which enables one to compute the volumes of reactive initial conditions from the *exact* dynamics. It reduces the brute-force integration over the $(2n - 1)$ -dimensional

energy surface to a $(2n - 2)$ -dimensional integral over a dividing surface hemisphere which has a much simpler parametrization than the energy surface. As indicated in the example shown it opens the way to study fundamental questions in the context of the transition state theory, such as non-RRKM behaviour and memory effects. If several exit/entrance channels coexist, one has to apply the scheme illustrated in the example to each channel individually and sum over the resulting terms (1). The method has no limitations concerning the number of degrees of freedom nor on the type of Hamiltonian, which may have magnetic or Coriolis terms. For high-dimensional systems, the flux is also computed easily from the normal form [16]. Similarly, the mean passage time associated with an entrance channel can be obtained very efficiently from a Monte Carlo integration as we already demonstrated in applications to high-dimensional systems in celestial mechanics and chemistry [29, 30] for which we computed the phase-space structures mentioned earlier [8, 31].

Acknowledgments

We are grateful to A Biternas for providing us with the data that lead to the surfaces of section in figure 6. This work was supported by the Office of Naval Research, EPSRC and the Royal Society.

References

- [1] Pollak E 1981 *J. Chem. Phys.* **74** 6763
- [2] Brumer P, Fitz D E and Wardlaw D 1980 *J. Chem. Phys.* **70** 386
- [3] Wiggins S 1990 *Physica D* **44** 471
- [4] Wiggins S 1992 *Chaotic Transport in Dynamical Systems* (Berlin: Springer)
- [5] Wiggins S 1994 *Normally Hyperbolic Invariant Manifolds in Dynamical Systems* (Berlin: Springer)
- [6] Wiggins S, Wiesenfeld L, Jaffé C and Uzer T 2001 *Phys. Rev. Lett.* **86** 5478
- [7] Uzer T, Jaffé C, Palacià J, Yanguas P and Wiggins S 2002 *Nonlinearity* **15** 957
- [8] Waalkens H, Burbanks A and Wiggins S 2004 *J. Chem. Phys.* **121** 6207
- [9] Jaffé C, Farrelly D and Uzer T 2000 *Phys. Rev. Lett.* **84** 610
- [10] Komatsuzaki T and Berry R S 1999 *J. Chem. Phys.* **110** 9160
- [11] Jacucci G, Toller M, DeLorenzi G and Flynn C P 1984 *Phys. Rev. Lett.* **52** 295
- [12] Eckhardt B 1995 *J. Phys. A: Math. Gen.* **28** 3469
- [13] de Oliveira H P, Ozorio de Almeida A M, Damião Soares I and Tonini E V 2002 *Phys. Rev. D* **65** 083511
- [14] Jaffé C, Ross S D, Lo M W, Marsden J, Farrelly D and Uzer T 2002 *Phys. Rev. Lett.* **89** 011101
- [15] Steinfeld J I, Francisco J S and Hase W L 1989 *Chemical Kinetics and Dynamics* (Englewood Cliffs, NJ: Prentice Hall)
- [16] Waalkens H and Wiggins S 2004 *J. Phys. A: Math. Gen.* **37** L435
- [17] Pechukas P and McLafferty F J 1973 *J. Chem. Phys.* **58** 1622
- [18] Pechukas P and Pollak E 1977 *J. Chem. Phys.* **67** 5976
- [19] Pollak E and Pechukas P 1978 *J. Chem. Phys.* **69** 1218
- [20] Pechukas P and Pollak E 1979 *J. Chem. Phys.* **71** 2062
- [21] MacKay R S 1990 *Phys. Lett. A* **145** 425
- [22] Binney J, Gerhard O H and Hut P 1985 *Mon. Not. R. Astron. Soc.* **215** 59
- [23] Müller K and Brown L D 1979 *Theor. Chim. Acta* **53** 78
- [24] Müller K 1980 *Angew. Chem.* **19** 1
- [25] Olender R and Elber R 1996 *J. Chem. Phys.* **105** 9299
- [26] Elber R, Meller J and Olender R 1999 *J. Phys. Chem. B* **103** 899
- [27] Passerone D and Parrinello M 2001 *Phys. Rev. Lett.* **87** 108302
- [28] Arnold V I 1978 *Mathematical Methods of Classical Mechanics (Graduate Texts in Mathematics vol 60)* (Berlin: Springer)
- [29] Waalkens H, Burbanks A and Wiggins S 2005 *Phys. Rev. Lett.* **95** 084301
- [30] Waalkens H, Burbanks A and Wiggins S 2005 *Mon. Not. R. Astron. Soc.* **361** 763
- [31] Waalkens H, Burbanks A and Wiggins S 2004 *J. Phys. A: Math. Gen.* **37** L257