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LETTER TO THE EDITOR

Direct construction of a dividing surface of minimal flux for multi-degree-of-freedom systems that cannot be recrossed

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Abstract

The fundamental assumption of transition state theory is the existence of a dividing surface having the property that trajectories originating in reactants (resp. products) must cross the surface *only once* and then proceed to products (resp. reactants). Recently it has been shown (Wiggins *et al* (2001) *Phys. Rev. Lett.* **86** 5478; Uzer *et al* (2002) *Nonlinearity* **15** 957) how to construct a dividing surface in *phase space* for Hamiltonian systems with an arbitrary (finite) number of degrees of freedom having the property that trajectories only cross once *locally*. In this letter we provide an argument showing that the flux across this dividing surface is a minimum with respect to certain types of variations of the dividing surface.

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1. Introduction

Transition state theory provides a fundamental framework for computing chemical reaction rates. The original ideas are due to Wigner, Polanyi and Eyring, yet much work on different aspects of the subject continue to this day (see the recent reviews of [1, 2]). In recent years transition state theory has been shown to be much more widely applicable than just for problems in chemical reactions. It has been used in atomic physics [3], studies of the rearrangements of clusters [4], solid state and semi-conductor physics [5, 6], cosmology [7] and celestial mechanics [8].

The fundamental assumption of transition state theory is the existence of a dividing surface having the property that trajectories originating in reactants (resp. products) must cross the surface *only once* and then proceed to products (resp. reactants). The rate of the reaction from reactants to products (or vice versa) is proportional to the directional flux through the dividing surface. The construction of such a surface in specific systems, especially those with more than

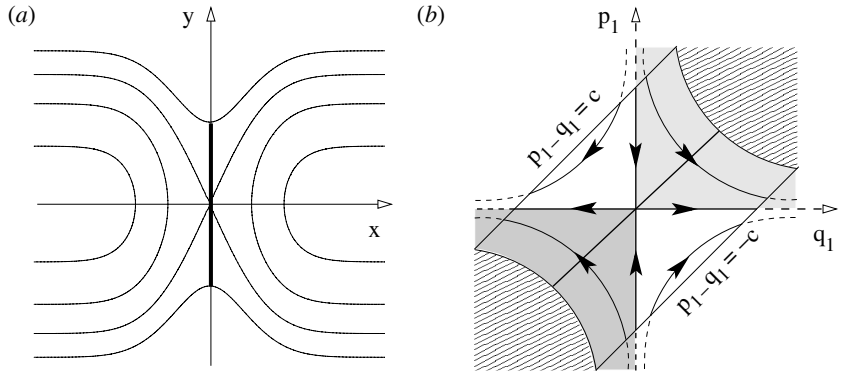

Figure 1. (*a*) Equipotentials and PODS (bold line) near a saddle. (*b*) Saddle plane (q_1, p_1) with projections of the $(2n-1)$-dimensional energy surface $H = E$ for $E > 0$ (all but the hatched region), the stable and unstable spherical cylinder (the p_1-axis and the q_1-axis), the NHIM (the origin), and the $(2n-2)$ spheres $p_1 - q_1 = 0$ (dividing surface). The light and dark grey regions are the projections of the energy surface volumes enclosed by the forward and backward reactive spherical cylinder $W_f(E)$ and $W_b(E)$, respectively. $p_1 - q_1 = \pm c$, $c > 0$, delimit the region of validity of the normal form.

two degrees of freedom (DOF), has posed extreme difficulties. The phenomenon of recrossing of a dividing surface gives rise to a larger value for the flux, which naturally inspires the idea of varying the dividing surface so that the flux is minimized, and it has lead to the subject of variational transition state theory, first proposed by Wigner [9], with recent developments discussed in [10, 11].

For systems with two DOF described by a Hamiltonian H of the simple type kinetic-plus-potential the problem of constructing a dividing surface with trajectories only crossing once and having minimum flux was solved during the 1970s by McLafferty, Pechukas and Pollak [12–15]. They considered the line segment in configuration space given by the projection of an unstable periodic orbit (the Lyapunov periodic orbit associated with a saddle point of the potential). Figure 1(*a*) shows this line segment which is referred to as a *repulsive periodic orbit dividing surface* (repulsive PODS) for simplicity in a symmetric potential (see the original references for the precise meaning of the term 'repulsive'). For fixed energy it connects two pieces of an equipotential surface and this way separates the reactant region (the part with $x < 0$ enclosed by the respective equipotential in figure 1(*a*)) from the product region (the part with $x > 0$ enclosed by the respective equipotential in figure 1(*a*)). The repulsive PODS solves the problem of (local) recrossings as there is no trajectory evolving from reactants to products (or vice versa) whose projection to configuration space is tangent to this line segment. After a reacting trajectory has crossed the repulsive PODS it has to leave the neighbourhood of the repulsive PODS before it can possibly recross it.

In order to understand, how the PODS theory can be generalized to systems with three and more DOF, it is necessary to recognize a PODS as a *phase space* object. We therefore rewrite the energy equation as

$$p_x^2 + p_y^2 = 2m(E - V(x, y)). \tag{1}$$

For (x, y) on the projection of the periodic orbit in figure 1(*a*) the equation in (1) defines a family of circles in (p_x, p_y) which shrink to points at the turning points of the periodic orbit. This means that the PODS is a 2-sphere. The periodic orbit, which has $p_x = 0$, can be considered as the equator of the PODS. It divides the PODS into two hemispheres, which have $p_x > 0$

and $p_x < 0$, respectively. The flux from $x < 0$ ('reactants') to $x > 0$ ('products') through the PODS in figure 1(a) is commonly written as

$$\mathcal{F}_E = \int \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}p_x\,\mathrm{d}p_y\,\delta(E-H)\delta(x-x_0)\,\Theta\,(p_x)\frac{p_x}{m}. \tag{2}$$

The step function $\Theta(p_x)$ effectively restricts the integral to one hemisphere of the PODS. Using Stokes' theorem it is not difficult to see that the flux in (2) is given by the action of the periodic orbit (p.o.), i.e.

$$\mathcal{F}_E = \oint_{\text{p.o.}} \boldsymbol{p}\,\mathrm{d}\boldsymbol{q}.$$

It is useful to point out that there is some confusion in terminology in the chemistry literature concerning the notion of 'transition state', which sometimes refers to the dividing surface (the PODS), and sometimes to the periodic orbit, which is an invariant manifold contained in the dividing surface. In the latter case, the phrase 'a trajectory crosses the transition state' refers to the intersection of the configuration space projections of the trajectory and the transition state. Note that a trajectory cannot cross an invariant manifold (in phase space). As we will see below in more detail, the loose use of the term transition state occasionally leads to confusion about how the dividing surface of minimal directional flux involves an invariant manifold. The configuration space picture, which is the starting point in the PODS construction by McLafferty, Pechukas and Pollak, breaks down, e.g. when a magnetic field is applied (or the Hamiltonian contains Coriolis terms due to rotations), i.e. when the Hamiltonian is no longer of the type kinetic-plus-potential. In this case the periodic orbit no longer projects to a line segment in configuration space. The study of this case, and in particular the generalization of PODS to three and more DOF, requires a phase space point of view.

Recently, it has been shown [16, 17] how to construct a dividing surface in *phase space* for Hamiltonian systems with an arbitrary (but finite) number of DOF having the property that trajectories only cross once locally. For this theory it is irrelevant whether the Hamiltonian has Coriolis terms or not. It is important to understand that periodic orbits do *not* play a role in constructing the dividing surface for more than two DOF due to dimensionality considerations. In this sense the PODS theory simply does not hold for more than two DOF. A fundamentally new geometrical object is required; a *normally hyperbolic invariant manifold* (NHIM), which reduces to a periodic orbit for two DOF. The seed of this idea can be found in [18, 19].

In this letter we give a geometrical argument demonstrating that the many DOF dividing surface realized in [16, 17] by a computational algorithm is indeed a surface of minimum directional flux, i.e. the directional flux increases if the dividing surface is varied. The dividing surface of [16, 17] is thus the optimal surface sought for in variational transition state theory. To begin we must first recall the elements of the general theory developed in [16, 17].

2. Dividing surface for multi-dimensional systems

In the general case of n DOF we consider an equilibrium point of saddle-centre-$\cdots$-centre type, i.e. the linearized vector field about the equilibrium point has one pair of real eigenvalues $\pm\lambda$ and $n-1$ imaginary eigenvalues $\pm\mathrm{i}\omega_k$, $k = 2, \ldots, n$, where without restriction of generality $\lambda, \omega_k > 0$. Equilibria of this type are characteristic for systems with a reaction-type dynamics, and they occur in all of the examples given in section 1. The transport is controlled by various high-dimensional manifolds which can be realized and computed through a procedure based on Poincaré–Birkhoff normalization. In fact, under general conditions (see [17] for the details), near a saddle-centre-$\cdots$-centre one can construct a sequence of local, non-linear, symplectic

transformations of the phase space coordinates that transform the Hamiltonian into

$$H = \lambda p_1 q_1 + \sum_{k=2}^{n} \frac{\omega_k}{2}(p_k^2 + q_k^2) + f_1(\mathcal{I}, q_2, \ldots, p_n, q_2, \ldots, q_n) + f_2(q_2, \ldots, p_n, q_2, \ldots, q_n) \tag{3}$$

up to any desired order. Here $(q_1, \ldots, q_n, p_1, \ldots, p_n)$ are canonical phase space coordinates, $\mathcal{I} = p_1 q_1$ and f_1, f_2 are at least of third order, i.e. they are responsible for the nonlinear term in the Hamiltonian vector field. Moreover f_1 has the property that it vanishes for $\mathcal{I} = 0$. (q_1, p_1) play the role of reaction coordinates. $(q_2, \ldots, q_n, p_2, \ldots, p_n)$ are the bath coordinates.

The importance of saddle-centre-$\cdots$-centre equilibria for reaction-type dynamics can be inferred from the topology of energy surfaces $H = E$. First consider the quadratic Hamiltonian given by the first part in (3) and write the energy equation as

$$E + \frac{\lambda}{4}(p_1 - q_1)^2 = \frac{\lambda}{4}(p_1 + q_1)^2 + \sum_{k=2}^{n} \frac{\omega_k}{2}(p_k^2 + q_k^2). \tag{4}$$

For $E < 0$ the left-hand side is positive for $p_1 - q_1 < -(-4E/\lambda)^{1/2}$ or $p_1 - q_1 > (-4E/\lambda)^{1/2}$. For a fixed $p_1 - q_1$ in either of these ranges the equation in (4) defines a $(2n-2)$-dimensional sphere S^{2n-2}. For $p_1 - q_1 = \pm(-4E/\lambda)^{1/2}$ the $(2n-2)$ spheres shrink to points. The energy surface thus appears as two disjoint *spherical cones* which correspond to 'reactants' and 'products', respectively. Increasing the energy to $E > 0$, the left-hand side of (4) is strictly positive. The formerly disjoint components merge and the energy surface becomes a *spherical cylinder* $S^{2n-2} \times \mathbb{R}$. Restricting to a sufficiently small neighbourhood by confining $p_1 - q_1$ to an interval $I = [-c, c]$ with $c > 0$ sufficiently small and with E sufficiently close to zero, the topological consideration remains true if the non-linear terms f_1 and f_2 are taken into account. Moreover, for a high but finite-order normal form, the error arising from neglecting the non-normalized 'tail' of the Hamiltonian can be made as small as desired by choosing the interval $[-c, c]$ sufficiently small and E sufficiently close to zero.

The importance of the normal form arises from the fact that it gives explicit expressions for all the manifolds which control the dynamics from reactants to products. For a fixed energy $E > 0$ the manifolds are the following.

- *The saddle sphere* $S^{2n-3}_{\mathrm{NHIM}}(E)$. On the energy surface $H = E$ the equation $p_1 = q_1 = 0$ defines a $(2n-3)$ sphere which we denote by $S^{2n-3}_{\mathrm{NHIM}}(E)$. It can be considered as a 'big saddle'. In fact, it is a so-called normally hyperbolic invariant manifold (NHIM) where normal hyperbolicity means that the expansion and contraction rates transverse to the manifold dominate those tangent to the manifold.
- *The forward and backward reactive spherical cylinders* $W_f(E)$ and $W_b(E)$. The saddle sphere has stable and unstable manifolds $W^s(E)$ and $W^u(E)$ which are iso-energetic, i.e. contained in the energy surface, and which are explicitly given by $q_1 = 0$ and $p_1 = 0$, respectively. These invariant manifolds have the topology of spherical cylinders $S^{2n-3} \times I$. Since they are of codimension 1 in the energy surface, i.e. they are of one dimension less than the energy surface, they act as impenetrable barriers. $W^s(E)$ and $W^u(E)$ each appear as two branches. We call the branch of $W^s(E)$, which has $p_1 > 0$, the *forward branch* $W^s_f(E)$ and the branch, which has $p_1 < 0$, the *backward branch* $W^s_b(E)$. Likewise, the forward branch $W^u_f(E)$ of $W^u(E)$ has $q_1 > 0$ and the backward branch $W^u_b(E)$ has $q_1 < 0$. We call the union of the forward branches, $W_f(E) := W^s_f(E) \cup W^u_f(E)$, the *forward reactive spherical cylinder*. Similarly, we call the union of the backward branches, $W_b(E) := W^s_b(E) \cup W^u_b(E)$, the *backward reactive spherical cylinder*. The significance of these spherical cylinders arises

from the fact that they enclose volumes of the energy surface which contain all forward and all backward reactive trajectories, respectively. All non-reactive trajectories are contained in the complement of these two volumes.

We define the dividing surface as follows.

- *The dividing surface* $S^{2n-2}_{\mathrm{ds}}(E)$: on the energy surface $H = E$ the equation $p_1 = q_1$ defines a $(2n-2)$ sphere which we denote by $S^{2n-2}_{\mathrm{ds}}(E)$. It is of codimension 1 in the energy surface. It divides the energy surface into two components: the reactant region $p_1 - q_1 > 0$ and the product region $p_1 - q_1 < 0$. The saddle sphere $S^{2n-3}_{\mathrm{NHIM}}(E)$ can be considered as the 'equator' of the dividing surface. It divides $S^{2n-2}_{\mathrm{ds}}(E)$ into two hemispheres: the *forward hemisphere* $B^{2n-2}_{\mathrm{ds,f}}(E)$, which has $p_1 = q_1 > 0$, and the *backward hemisphere* $B^{2n-2}_{\mathrm{ds,b}}(E)$, which has $p_1 = q_1 < 0$. $B^{2n-2}_{\mathrm{ds,f}}(E)$ and $B^{2n-2}_{\mathrm{ds,b}}(E)$ are topological $(2n-2)$ balls. Except for its equator, which is an invariant manifold, the dividing surface is everywhere transverse to the Hamiltonian flow as is easily seen from the equations of motions derived from the normal form Hamiltonian (3). This means that a trajectory, after having crossed the dividing surface, has to leave the neighbourhood of the dividing surface before it can possibly cross it again, i.e. the dividing surface *locally* is a 'surface of no return'.

An important advantage of the normal form coordinates is that dynamical issues related to flux and reactivity can be understood to a great extent from the projection to the plane of the reaction coordinates (q_1, p_1), see figure 1(*b*). Due to the constance of the saddle integral $\mathcal{I} = p_1 q_1$ trajectories project to hyperbolas. Forward reactive trajectories, which are enclosed by the forward reactive spherical cylinder $W_f(E)$, project to the first quadrant $q_1, p_1 > 0$. A forward reactive trajectory approaches the forward hemisphere $B^{2n-2}_{\mathrm{ds,f}}(E)$ of the dividing surface inside of the forward branch of the stable cylinder $W^s_f(E)$ whose 'interior' projects to the part of the first quadrant above the diagonal $p_1 = q_1 > 0$. After crossing the dividing surface, the trajectory leaves inside of the forward branch of the unstable spherical cylinder $W^u_f(E)$ whose 'interior' projects to the part of the first quadrant below the diagonal $p_1 = q_1 > 0$. While similar considerations hold for the backward reactive trajectories, non-reactive trajectories project to the second quadrant $p_1 > 0$, $q_1 < 0$ which corresponds to reactants or to the fourth quadrant $p_1 < 0$, $q_1 > 0$ which corresponds to products. Therefore reactive trajectories have $\mathcal{I} = p_1 q_1 > 0$ and non-reactive trajectories have $\mathcal{I} = p_1 q_1 < 0$.

3. Minimal flux property of the dividing surface

Consider at first the phase space volume form $\Omega = \mathrm{d}p_1 \wedge \mathrm{d}q_1 \wedge \cdots \wedge \mathrm{d}p_n \wedge \mathrm{d}q_n$, which in terms of the symplectic 2-from $\omega = \sum_{k=1}^{n} \mathrm{d}p_k \wedge \mathrm{d}q_k$ can be written as $\Omega = \omega^n/n!$. Let η be an energy surface volume form defined via the property $\mathrm{d}H \wedge \eta = \Omega$. Then the flux through a codimension 1 submanifold of the $(2n-1)$-dimensional energy surface $H = E$ is obtained by integrating over it the 'flux' form Ω' given by the interior product of the Hamiltonian vector field X_H with η [20], i.e.

$$\Omega' = \mathrm{i}_{X_H}\eta = \frac{1}{(n-1)!}\omega^{n-1}, \tag{5}$$

where $\mathrm{i}_{X_H}\eta(\xi_1, \ldots, \xi_{2n-2}) = \eta(\xi_1, \ldots, \xi_{2n-2}, X_H)$ for any $2n-2$ vectors ξ_k. The second equality in (5) is easily established on a non-critical energy surface, i.e. on an energy surface which contains no equilibria. The flux form Ω' is exact. In fact, the generalized 'action' form

$$\varphi = \sum_{k=1}^{n} p_k \,\mathrm{d}q_k \wedge \frac{1}{(n-1)!}\omega^{n-2}$$

has the property $\mathrm{d}\varphi = \Omega'$ and facilitates the use of Stokes' theorem to compute the flux. In the case of two DOF we simply have $\Omega' = \omega = \mathrm{d}p_1 \wedge \mathrm{d}q_1 + \mathrm{d}p_2 \wedge \mathrm{d}q_2$ and $\varphi = p_1\mathrm{d}q_1 + p_2\mathrm{d}q_2$. Since the dividing surface $S^{2n-2}_{\mathrm{ds}}(E)$ is a sphere, that is, a manifold without boundary, it follows from Stokes' theorem that the integral of Ω' over $S^{2n-2}_{\mathrm{ds}}(E)$ is zero. As in the case of PODS one has to distinguish between the directions in which the Hamiltonian flow crosses the dividing surface. Given a normal bundle over $S^{2n-2}_{\mathrm{ds}}(E)$ the direction can be specified by the sign of the scalar product between the normal vectors and the Hamiltonian vector field. This scalar product is strictly positive on one of the hemispheres of $S^{2n-2}_{\mathrm{ds}}(E)$, strictly negative on the other hemisphere and zero only at the equator of $S^{2n-2}_{\mathrm{ds}}(E)$, i.e. at the saddle sphere $S^{2n-3}_{\mathrm{NHIM}}(E)$, where the Hamiltonian vector field is tangent to $S^{2n-2}_{\mathrm{ds}}(E)$. Similarly, the flux form Ω' on $S^{2n-2}_{\mathrm{ds}}(E)$ vanishes nowhere on $B^{2n-2}_{\mathrm{ds,f}}(E)$ and $B^{2n-2}_{\mathrm{ds,b}}(E)$ and is identically zero on $S^{2n-3}_{\mathrm{NHIM}}(E)$. It is natural to take as the orientation of $B^{2n-2}_{\mathrm{ds,f}}(E)$ and $B^{2n-2}_{\mathrm{ds,b}}(E)$ the orientation they inherit from the dividing surface. Without restriction we may assume that the orientation of $S^{2n-2}_{\mathrm{ds}}(E)$ is such that Ω' is positive on the forward hemisphere $B^{2n-2}_{\mathrm{ds,f}}(E)$ and negative on the backward hemisphere $B^{2n-2}_{\mathrm{ds,b}}(E)$, i.e. Ω' and $-\Omega'$ can be considered as *volume forms* on $B^{2n-2}_{\mathrm{ds,f}}(E)$ and $B^{2n-2}_{\mathrm{ds,b}}(E)$, respectively. It follows from Stokes' theorem that the flux through the forward and backward hemispheres, $\int_{B^{2n-2}_{\mathrm{ds,f}}(E)} \Omega'$ and $\int_{B^{2n-2}_{\mathrm{ds,b}}(E)} \Omega'$, have the same magnitude but opposite sign and can be computed by integrating the action form φ over the saddle sphere: $\int_{B^{2n-2}_{\mathrm{ds,f}}(E)} \Omega' = -\int_{B^{2n-2}_{\mathrm{ds,b}}(E)} \Omega' = |\int_{S^{2n-3}_{\mathrm{NHIM}}(E)} \varphi|$. We call the positive quantity $\int_{B^{2n-2}_{\mathrm{ds,f}}(E)} \Omega'$ the *forward flux* and the negative quantity $\int_{B^{2n-2}_{\mathrm{ds,f}}(E)} \Omega'$ the *backward flux* through $S^{2n-2}_{\mathrm{ds}}(E)$.

We now show that the forward flux through $S^{2n-2}_{\mathrm{ds}}(E)$ is minimal. This can be stated as a variational problem and a result in this direction is obtained by MacKay [21] who proves that the integral $\int_C \varphi$ of the action form φ over codimension 2 submanifolds C of the energy surface is stationary with respect to variations of C if and only if C is invariant under the Hamiltonian flow. Since the saddle sphere $S^{2n-3}_{\mathrm{NHIM}}(E)$ is an invariant manifold, MacKay's result implies that the 'action' of $S^{2n-3}_{\mathrm{NHIM}}(E)$, $\int_{S^{2n-3}_{\mathrm{NHIM}}(E)} \varphi$, is stationary with respect to variations of $S^{2n-3}_{\mathrm{NHIM}}(E)$. MacKay considers arbitrary variations within the energy surface and this leads to an indefinite variational principle. In fact, in the context of transition state theory it is more useful to consider variations of the codimension 1 dividing surface $S^{2n-2}_{\mathrm{ds}}(E)$, which in a sense that will become clear below, imply variations of the codimension 2 saddle sphere $S^{2n-3}_{\mathrm{NHIM}}(E)$ in a smaller, more suitable class than in MacKay's case.

Consider at first the case of two DOF for which it is possible to visualize the energy surface $S^2 \times I$ in three-dimensional space as a nested set of 2-spheres parametrized along the interval I in radial direction. This is the so-called McGehee representation [22] which is shown in the first panel of figure 2. We consider a slight *generic, iso-energetic* deformation of the dividing surface $S^2_{\mathrm{ds}}(E)$ *that does not 'preserve' the saddle sphere* $S^1_{\mathrm{NHIM}}(E)$, i.e. $S^1_{\mathrm{NHIM}}(E)$ is not entirely contained in the deformed dividing surface, see figures 2(*c*)–(*e*). The deformation, which we denote by $\tilde{S}^2_{\mathrm{ds}}(E)$, is described mathematically as a graph over the dividing surface $S^2_{\mathrm{ds}}(E)$, and therefore $\tilde{S}^2_{\mathrm{ds}}(E)$ inherits the orientation of $S^2_{\mathrm{ds}}(E)$ (which is important because we want to preserve certain aspects of the directionality of the flux, to be described below). Since $\tilde{S}^2_{\mathrm{ds}}(E)$ is chosen to lie in the energy surface, it still separates the energy surface into two disjoint components like $S^2_{\mathrm{ds}}(E)$. Also like $S^2_{\mathrm{ds}}(E)$, the deformation $\tilde{S}^2_{\mathrm{ds}}(E)$ contains a circle $\tilde{S}^1(E)$ of points at which the Hamiltonian vector field is tangent to $\tilde{S}^2_{\mathrm{ds}}(E)$. This can be proven analytically, but intuitively it is easy to see from figure 2(*d*). $\tilde{S}^1(E)$ can be considered as the equator of $\tilde{S}^2_{\mathrm{ds}}(E)$; it divides $\tilde{S}^2_{\mathrm{ds}}(E)$ into forward and backward hemispheres $\tilde{B}^2_{\mathrm{ds,f}}(E)$ and $\tilde{B}^2_{\mathrm{ds,b}}(E)$ on which the flux form Ω' is strictly positive and negative, respectively. $\tilde{S}^1(E)$ can be considered as the deformation of $S^1_{\mathrm{NHIM}}(E)$ induced by the deformation of $S^2_{\mathrm{ds}}(E)$. It

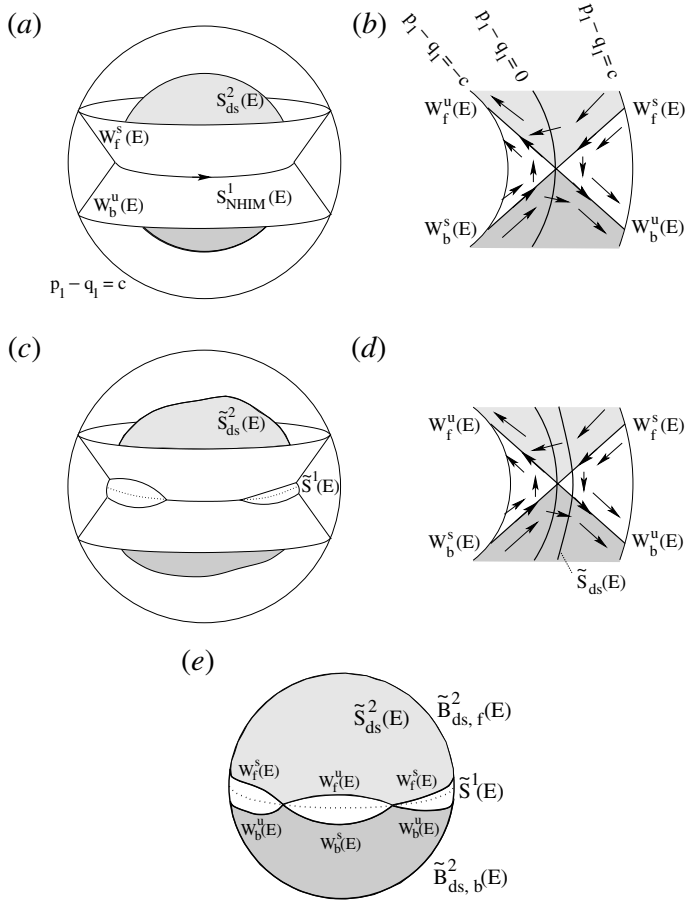

Figure 2. (*a*) McGehee representation of the dynamics and the geometry of the manifolds in an energy surface $H = E$ with $E > 0$ near a saddle-centre equilibrium point. The concentric spheres represent $p_1 - q_1 = c$ (outer sphere), $p_1 - q_1 = 0$ (dividing surface $S^2_{ds}(E)$, middle sphere), and $p_1 - q_1 = -c$ (inner sphere, not visible). The equator of the dividing surface is the periodic orbit $S^1_{NHIM}(E)$. $W^s_f(E)$, $W^u_f(E)$, $W^s_b(E)$ and $W^u_b(E)$ are the forward and backward branches of its stable and unstable cylinders ($W^s_b(E)$, and $W^u_b(E)$ are not visible). (*b*) Section of (*a*) with a plane of constant angle about the symmetry axis in (*a*). The arrows indicate the Hamiltonian vector field. Note that the vector field also has components out of this plane. (The energy surface $H = E$ contains no equilibrium points.) Trajectories in the white regions correspond to non-reactive trajectories. (*c*) A deformation $\tilde{S}^2_{ds}(E)$ of the dividing surface $S^2_{ds}(E)$ and its intersections with the stable and unstable manifolds of the Lyapunov periodic orbit $S^1_{NHIM}(E)$. The Hamiltonian vector field is tangent to $\tilde{S}^2_{ds}(E)$ along a circle $\tilde{S}^1(E)$ marked by a dotted line (not completely visible). (*d*) The same section as in (*b*) now also showing $\tilde{S}^2_{ds}(E)$ in this plane. The key point to note here is that $\tilde{S}^1(E)$ (the intersection of the circle where the vector field is tangent to $\tilde{S}^2_{ds}(E)$) moves into the white, non-reactive region. (*e*) $\tilde{S}^1(E)$ divides $\tilde{S}^2_{ds}(E)$ into two hemispheres $\tilde{B}^2_{ds,f}(E)$ and $\tilde{B}^2_{ds,b}(E)$. (The extra 'bubbles' shown in (*e*), that are not shown in (*c*), correspond to the intersection of $\tilde{S}^2_{ds}(E)$ with $W^s_b(E)$, and $W^u_f(E)$, which are not visible in (*c*).)

should be realized that in contrast to the case of $S^1_{NHIM}(E)$, the Hamiltonian vector field is not tangent to the deformation $\tilde{S}^1(E)$, i.e. $\tilde{S}^1(E)$ is not invariant under the Hamiltonian vector field ($\tilde{S}^1(E)$ is not a periodic orbit). It can be shown that if the deformation of $\tilde{S}^2_{ds}(E)$ is small enough then all points of $\tilde{S}^1(E)$ have $p_1 q_1 \leqslant 0$, i.e. they are contained in the complement of the

two volumes enclosed by the forward and backward reactive spherical cylinders $W_f(E)$ and $W_b(E)$. Again, intuitively this can be deduced from figures 2(*c*)–(*e*), where the essential point is seen in (*d*) where $\tilde{S}^2_{\rm ds}(E)$ protrudes into the white, non-reactive region. This is where the trajectories become tangent to $\tilde{S}^2_{\rm ds}(E)$, i.e., at some point on $\tilde{S}^2_{\rm ds}(E)$ trajectories 'bounce off'.

Consider the part of $\tilde{S}^2_{\rm ds}(E)$ which is contained in the forward reactive spherical cylinder $W_f(E)$ and marked by the light grey region in figure 2(*e*). The boundary of the light grey region corresponds to the intersection with the forward stable and unstable cylinder branches $W^s_f(E)$ and $W^u_f(E)$. The boundary is in general not a smooth manifold but it is homeomorphic to a circle S^1. It is possible to deform this piecewise smooth circle continuously onto the Lyapunov periodic orbit $S^1_{\rm NHIM}(E)$ without leaving the stable and unstable cylinders. Stokes' theorem implies that the difference between the integrals of φ along the piecewise smooth circle and the Lyapunov periodic orbit is given by the integral of Ω' over the region on the stable and unstable manifolds swept out in the deformation process. The flux form Ω' vanishes on the stable and unstable manifolds as its definition involves the interior product with the Hamiltonian vector field ('there is no flux through invariant manifolds'). It thus follows that the flux through the light grey part of $\tilde{B}^2_{\rm ds,\,f}(E)$ in figure 2(*d*) is equal to the flux through $B^2_{\rm ds,\,f}(E)$. Since the flux form Ω' is strictly positive on the complete hemisphere $\tilde{B}^2_{\rm ds,\,f}(E)$, the forward flux through $\tilde{S}^2_{\rm ds}(E)$ is larger than the forward flux through $S^2_{\rm ds}(E)$, and this completes the argument.

All the arguments above immediately carry over to systems with more than two DOF by simply adjusting the dimension of the involved manifolds. The essential geometric conditions and relations amongst the manifolds all hold.

The dividing surface of minimal forward flux is not unique, and this is the reason that we chose iso-energetic deformations that did not preserve the NHIM. For example, the equation $p_1 = aq_1$ with a (slightly) deviating from 1 again defines on the energy surface a $(2n-2)$ sphere which is a dividing surface and which has the same forward flux as $S^{2n-2}_{\rm ds}(E)$. We considered a *generic* deformation which is a deformation that changes the equator of $\tilde{S}^{2n-2}_{\rm ds}(E)$ such that it no longer coincides with the NHIM $S^{2n-3}_{\rm NHIM}(E)$. Non-generic deformations in this sense do not change the flux. Similarly, our dividing surface for two DOF coincides with a PODS in general only along its equator, i.e. at the Lyapunov periodic orbit, and this is what matters for the flux.

Transition state theory is a fundamental theory for calculating reaction rates in chemistry, and accordingly, there exists a vast amount of literature on this subject, most of which takes a configuration space rather than phase space oriented point of view, and this leads to the problems we mentioned in section 1. We therefore find it useful to relate the phase space geometry described above to the seminal work by Pechukas [18] as a representative example. Pechukas considers a quadratic potential with one saddle direction, for which it is easy to define a dividing surface and to find the NHIM: 'We set the reaction coordinate and momentum to zero, and then we have [...] an unstable 'molecule' that hangs around forever if nothing disturbs it' (p 288). This unstable 'molecule' is the NHIM and it is easy to see that setting the 'reaction coordinate' (the coordinate in the unstable direction of the potential saddle) and the corresponding momentum to zero defines on an energy surface, with energy larger than the energy of the saddle, a $(2n-3)$-dimensional invariant sphere where n is the number of DOF. The dividing surface is obtained by setting only the reaction coordinate (and not its momentum) to zero. For the system with a quadratic potential this defines a $(2n-2)$-dimensional sphere which contains the $(2n-3)$-dimensional NHIM. Due to the separability of a Hamiltonian with a quadratic potential, the NHIM and the transition state project to the same $(n-1)$-dimensional hypersurface in the n-dimensional configuration space. This 'degeneracy' is highly misleading (similar to the case of PODS) as in the projection to configuration space the distinction between

the NHIM and the dividing surface is obscured. The coincidence of the configuration space projections of the NHIM and the dividing surface does not mean that the NHIM divides the energy surface into two components. Although in the configuration space projection it looks as though a reactive trajectory would cross the NHIM, this is not true (in phase space).

The general theory developed in [16, 17] and in this letter implies that it is in general *not* possible to find a dividing surface free of local recrossings as a $(n-1)$-dimensional hypersurface in the n-dimensional configuration space (even not for systems of type kinetic-plus-potential if non-linear terms are taken into account). For example, except for the special case of two DOF, for which the NHIM is a Lyapunov periodic orbit, which projects to a one-dimensional object in the two-dimensional configuration space, the $(2n-3)$-dimensional NHIM projects for $n > 2$ generically to n-dimensional objects in the n-dimensional configuration space.

Finally, we note that it is important to realize that, as stated above, we work entirely in the neighbourhood of a saddle-centre-$\cdots$-centre equilibrium point. The normal form is used to prove that the phase space geometry in this neighbourhood is as we describe it. On the other hand, for kinetic-plus-potential Hamiltonians with two DOF the theory of PODS is used in a broader setting. For energies sufficiently high above the saddle-centre equilibrium, the normal form approximation might become invalid and the Lyapunov periodic orbit might undergo a bifurcation. This is the case in [23] where the Lyapunov periodic orbit becomes stable at a certain energy and, in a pitchfork bifurcation, gives birth to two new unstable periodic orbits. The PODS theory can then be applied individually to these new periodic orbits which coexist for higher energies and this leads to the notions of 'repulsive' and 'attractive' PODS which correspond to local minima and maxima of the flux. Similarly, bifurcations might occur in the case of more than two DOF, but the nature of these bifurcations is beyond existing theory. We therefore restrict ourselves to the neighbourhood of validity of the normal form (by choosing the energy sufficiently close to the energy of the saddle-centre-$\cdots$-centre).

4. Algorithm for computing the flux

Provided a *generic* non-resonance condition between the linear frequencies ω_k is fulfilled, the normal form Hamiltonian (3) assumes the simple form $H(\mathcal{I}, J_2, \ldots, J_n)$, where $J_k = (p_k^2 + q_k^2)/2$, $k = 2, \ldots, n$, are action variables associated with the bath coordinates. Like the saddle integral $\mathcal{I}$, the actions J_k are constants of the motion. Writing the flux form Ω' in terms of action–angle variables we obtain the result that the forward flux through the dividing surface is given by

$$\mathcal{F}_E = (2\pi)^{n-1}\mathcal{V}(E),$$

where $\mathcal{V}(E)$ is the volume in the space of the bath actions $(J_2, \ldots, J_n)$ enclosed by the contour $H(0, J_2, \ldots, J_n) = E$. In fact, the flux can be interpreted as the volume enclosed by a contour of constant energy E in the phase space of a reduced system with one dimension less than the complete system. In terms of the normal form coordinates, the reduced system is explicitly described by the invariant subsystem which has $q_1 = p_1 = 0$. The normally hyperbolic invariant manifolds are just the energy surfaces of this reduced system which is referred to as *activated complex* in the chemistry literature. The dimensionless quantity $\mathcal{F}_E/h^{n-1}$, where h is Planck's constant, is Weyl's approximation of the integrated density of states of the reduced system and can be interpreted as the number of 'transition channels'.

In the linear case, we have $H = \lambda\mathcal{I} + \sum_{k=2}^{n} \omega_k J_k$ and the energy surface $H = E$ encloses a simplex in $(J_2, \ldots, J_n)$ whose volume leads to the well-known result (see e.g. [20] for an

historical background)

$$\mathcal{F}_E = \frac{E^{n-1}}{(n-1)!} \prod_{k=2}^{n} \frac{2\pi}{\omega_k}$$

showing that the flux scales with E^{n-1} for energies close to the saddle energy. The normal form allows to include the non-linear corrections to this result to any desired order.

5. Conclusions

In this letter we have given a geometrical argument showing that the directional flux across the dividing surface for n DOF systems constructed in [16, 17] is a minimum, in the sense that the flux corresponding to forward reactive trajectories (which is equal in magnitude but opposite in sign to the flux corresponding to backward reactive trajectories) is a minimum. Hence it is the optimal dividing surface sought for by variational transition theory.

The key point for the construction of the dividing surface is the existence of a NHIM which exists on the energy surface near a saddle-centre-$\cdots$-centre equilibrium point and which mainly controls the dynamics nearby. The NHIM has the topology of a $(2n-3)$ sphere which can be considered as the equator of the dividing surface which is a $(2n-2)$ sphere. The NHIM divides the dividing surface into two 'hemispheres' which are open $(2n-2)$ balls. The hemispheres are transverse to the Hamiltonian flow. Hence the dividing surface is everywhere transverse to the Hamiltonian flow except for its equator (the NHIM) which is an invariant manifold. The NHIM can be considered as the energy surface of an invariant subsystem ('activated complex') with one DOF less than the complete system. The directional flux is the phase space volume enclosed by the energy surface of this reduced system.

The dividing surface is not unique. Any $(2n-2)$ sphere which contains the NHIM as its equator and which is transverse to the Hamiltonian flow except for its equator qualifies for a dividing surface. Nevertheless, all these dividing surfaces lead to the same flux. This makes it difficult (if not impossible) to compute a dividing surface from a variational principle of codimension 1 manifolds of the energy surface. Similarly, the NHIM appears only as an indefinite critical 'point' of the variational principle of codimension 2 manifolds of the energy surface of MacKay [21] which makes it practically infeasible to compute the NHIM from a variational principle. The normal form approach of [16, 17] is currently the only method to determine these manifolds and also to compute the flux for which we gave an algorithm in this letter.

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