

Reaction Dynamics Through Kinetic Transition States

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The transformation of a system from one state to another is often mediated by a bottleneck in the system's phase space. In chemistry, these bottlenecks are known as transition states through which the system has to pass in order to evolve from reactants to products. The chemical reactions are usually associated with configurational changes where the reactants and products states correspond, e.g., to two different isomers or the undissociated and dissociated state of a molecule or cluster. In this Letter, we report on a new type of bottleneck which mediates kinetic rather than configurational changes. The phase space structures associated with such kinetic transition states and their dynamical implications are discussed for the rotational vibrational motion of a triatomic molecule. An outline of more general related phase space structures with important dynamical implications is given.

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Introduction.—Reaction-type dynamics is characterized by the property that a system spends long times in one phase space region (the region of the “reactants”) and occasionally finds its way through a bottleneck to another phase space region (the region of the “products”). The main examples are chemical reactions where the bottlenecks are induced by saddle points of the potential energy surface which arises from a Born-Oppenheimer approximation and determines the interactions between the constituent atoms or molecules involved in the reaction. The reactions are then characterized by configurational changes like, e.g., in an isomerization or dissociation reaction. In this case, the bottleneck is referred to a transition state. The main idea of transition state theory, which is the most frequently used approach to compute reaction rates, is then to define a surface in the transition state region and compute the rate from the flux through this so-called dividing surface. For getting the exact rate this way, it is crucial to define the dividing surface in such a way that it is crossed exactly once by reactive trajectories (trajectories that evolve from reactants to products) and not crossed at all by nonreactive trajectories (i.e., trajectories which stay in the reactants or products region). In the 1970s, it has been shown by Pechukas, Pollak, and others that, for systems with 2 degrees of freedom, such a dividing surface can be constructed from an unstable periodic orbit which gives rise to the so-called periodic orbit dividing surface [1,2]. It took several decades to understand how this idea can be generalized to systems with 3 or more degrees of freedom [3]. The object which replaces the periodic orbit is a so-called normally hyperbolic invariant manifold (NHIM) [4]. The NHIM not only allows for the construction of a dividing surface with the desired crossing properties, but it also has (like the unstable periodic orbit in the 2-degree-of-freedom case) stable and unstable manifolds

which have sufficient dimensionality to form separatrices that channel the reactive trajectories from reactants to products and separate them from the nonreactive ones [5]. In this Letter, we show that for systems which are not of the type “kinetic-plus-potential” there are saddle-type equilibrium points which either instead of the bottlenecks associated with configuration changes induce bottlenecks of a kinetic nature or, more generally, do not even induce bottlenecks but still give rise to NHIMs whose stable and unstable manifolds govern the dynamics near such equilibrium points.

The standard case.—For a system of the type kinetic-plus-potential (so-called natural mechanical systems [6]), saddle points of the potential lead to equilibrium points of Hamilton's equations near which the Hamiltonian can be brought through a suitable choice of canonical coordinates (so-called normal form coordinates [5,7]) into the form

$$H = E_0 + \frac{\lambda}{2}(p_0^2 - q_0^2) + \sum_{k=1}^n \frac{\omega_k}{2}(p_k^2 + q_k^2) + \text{h.o.t.}, \quad (1)$$

where $f = n + 1$ is the number of degrees of freedom and E_0 is the energy of the saddle of the potential. The quadratic part of the Hamiltonian (1) consists of a parabolic barrier in the first degree of freedom whose steepness is characterized by $\lambda > 0$ (the Lyapunov exponent) and n harmonic oscillators with frequencies $\omega_k > 0$, $k = 1, \dots, n$.

Let us ignore the higher order terms for a moment and rewrite the energy equation $H = E$ in the form

$$\frac{\lambda}{2}p_0^2 + \sum_{k=1}^n \frac{\omega_k}{2}(p_k^2 + q_k^2) = E - E_0 + \frac{\lambda}{2}q_0^2. \quad (2)$$

Then one sees that for $E > E_0$ (i.e., for energies above the energy of the saddle), each fixed value of the reaction

coordinate q_0 defines a $(2f - 2)$ -dimensional sphere S^{2f-2} . The energy surface thus has the topology of a “spherical cylinder”: $S^{2f-2} \times \mathbb{R}$. This cylinder has a wide-narrow-wide geometry where the spheres S^{2f-2} are “smallest” when $q_0 = 0$ (see [8] for a more precise statement). In fact, the $(2f - 2)$ -dimensional sphere given by setting $q_0 = 0$ on the energy surface $H = E > E_0$ defines a dividing surface which separates the energy surface into a reactants region $q_0 < 0$ and a products region $q_0 > 0$. All forward reactive trajectories cross it with $p_0 > 0$. All backward reactive trajectories cross it with $p_0 < 0$. The condition $p_0 = 0$ defines a $(2f - 3)$ -dimensional sphere which divides the dividing surface into the two hemispheres which have $p_0 > 0$ and $p_0 < 0$ and hence can be viewed as the “equator” of the diving surface. In fact, the equator is a NHIM [4]. It can be identified with the transition state: a kind of unstable “supermolecule” sitting between reactants and products [7,9]. The NHIM has stable and unstable manifolds $S^{2f-2} \times \mathbb{R}$. They thus have one dimension less than the energy surface $H = E$. They form the phase space conduits for reaction [10]. The NHIM is of central importance, because it dominates the dynamics in the neighborhood of the saddle. An important aspect of the theory of NHIMs is that they persist if the higher order terms in (1) are taken into account and the energy is not too far above E_0 [4]. The phase space structures above persist accordingly.

Kinetic transition states.—Let us now more generally consider the case of an equilibrium point of a Hamiltonian system which has one pair of real eigenvalues $\pm\lambda$ and n complex conjugate pairs of imaginary eigenvalues $\pm i\omega_k$, $k = 1, \dots, n$. By choosing normal form coordinates near such a so-called saddle-center-...-center equilibrium, the Hamiltonian assumes the form (1). In fact, this general case already formed the starting point in [3,5], and later works. It covers, e.g., applications of transition state theory to the ionization of hydrogen in a crossed field configuration which due to magnetic terms is not a natural mechanical system [11]. In all the studies based on the general starting point, it has so far been assumed that the frequencies ω_k are positive. The central point of this Letter is to report on what happens if we give up this assumption. To this end, let us for simplicity consider a system with $f = 2$ degrees of freedom with Hamiltonian function

$$H = E_0 + \frac{\lambda}{2}(p_0^2 - q_0^2) + \frac{\omega}{2}(p_1^2 + q_1^2) \quad (3)$$

with $\lambda > 0$ and $\omega < 0$. In this case let us rewrite the energy equation $H = E$ in the form

$$\frac{\lambda}{2}q_0^2 - \frac{\omega}{2}(p_1^2 + q_1^2) = \frac{\lambda}{2}p_0^2 + E_0 - E. \quad (4)$$

This is the same as (2), however with the role of q_0 and p_0 exchanged and $E - E_0$ replaced by $E_0 - E$. Accordingly for $E < E_0$, the right-hand side is positive for any p_0 and the energy surface has again the structure of a spherical

cylinder with a wide-narrow-wide geometry. The crucial difference to the standard case of positive frequencies in Eq. (2) is that the reaction coordinate is now p_0 instead of q_0 . The bottleneck is thus associated with kinetic rather than configurational changes. As the following example shows, such kinetic bottlenecks do indeed exist in many important applications.

Example: Rotational vibrational motion of triatomic molecules.—The Hamiltonian of a triatomic molecule is given by [12,13]

$$H = \frac{1}{2} \left[\frac{\rho_1^2 + \rho_2^2 \cos^2 \phi}{\rho_1^2 \rho_2^2 \sin^2 \phi} J_1^2 + \frac{2 \cos \phi}{\rho_1^2 \sin \phi} J_1 J_2 + \frac{1}{\rho_1^2} J_2^2 + \frac{1}{\rho_1^2 + \rho_2^2} J_3^2 + p_1^2 + p_2^2 + \frac{\rho_1^2 + \rho_2^2}{\rho_1^2 \rho_2^2} \left(p_\phi - \frac{\rho_2^2}{\rho_1^2 + \rho_2^2} J_3 \right)^2 \right] + V(\rho_1, \rho_2, \phi). \quad (5)$$

Here (ρ_1, ρ_2, ϕ) are Jacobi coordinates defined as

$$\rho_1 = \|\mathbf{s}_1\|, \quad \rho_2 = \|\mathbf{s}_2\|, \quad \mathbf{s}_1 \cdot \mathbf{s}_2 = \rho_1 \rho_2 \cos \phi,$$

where \mathbf{s}_1 and \mathbf{s}_2 are the mass-weighted Jacobi vectors (see Fig. 1)

$$\mathbf{s}_1 = \sqrt{\mu_1}(\mathbf{x}_1 - \mathbf{x}_3), \quad \mathbf{s}_2 = \sqrt{\mu_2} \left(\mathbf{x}_2 - \frac{m_1 \mathbf{x}_1 + m_3 \mathbf{x}_3}{m_1 + m_3} \right), \quad (6)$$

computed from the position vectors \mathbf{x}_k of the atoms and the reduced masses

$$\mu_1 = \frac{m_1 m_3}{m_1 + m_3} \quad \text{and} \quad \mu_2 = \frac{m_2(m_1 + m_3)}{m_1 + m_2 + m_3}. \quad (7)$$

The momenta p_1, p_2 , and p_ϕ in (5) are conjugate to ρ_1, ρ_2 , and ϕ , respectively, and $\mathbf{J} = (J_1, J_2, J_3)$ is the body angular momentum. The magnitude J of \mathbf{J} is conserved under the dynamics generated by the Hamiltonian (5).

Let us at first consider a rigid molecule (i.e., the values of ρ_1, ρ_2 , and ϕ are fixed). The body-fixed frame can then be chosen such that the moment of inertia tensor becomes diagonal with the principal moments of inertia $M_1 < M_2 < M_3$ ordered by magnitude on the diagonal. The Hamiltonian (5) then reduces to

$$H = \frac{1}{2} \left(\frac{J_1^2}{M_1} + \frac{J_2^2}{M_2} + \frac{J_3^2}{M_3} \right). \quad (8)$$

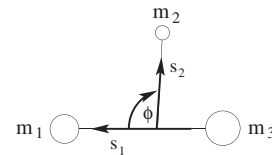


FIG. 1. Definition of Jacobi coordinates for a triatomic molecule.

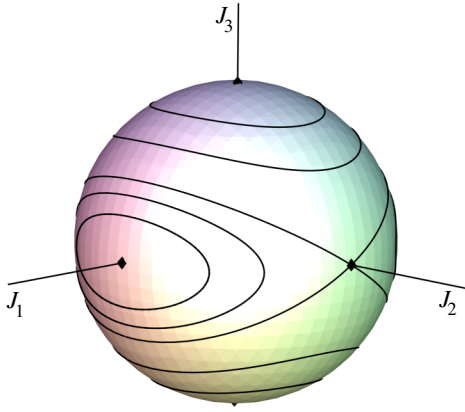


FIG. 2 (color online). Angular momentum sphere with contours of the Hamiltonian in (8).

As the magnitude J of \mathbf{J} is conserved, the angular momentum sphere $J_1^2 + J_2^2 + J_3^2 = J^2$ can be viewed as the phase space of the rigid molecule [13]. The solution curves of this 1-degree-of-freedom system are obtained from the level sets of the Hamiltonian H on the angular momentum sphere (see Fig. 2). The Hamiltonian H has local minima at $(J_1, J_2, J_3) = (0, 0, \pm J)$ of energy $J^2/(2M_3)$, local maxima at $(J_1, J_2, J_3) = (\pm J, 0, 0)$ of energy $J^2/(2M_1)$, and saddles at $(J_1, J_2, J_3) = (0, \pm J, 0)$ of energy $J^2/(2M_2)$. These correspond to the center equilibria of stable rotations about the first and third principal axes and the saddle equilibria of unstable rotations about the second principal axis, respectively. A possible choice of canonical coordinates (q, p) on the angular momentum sphere is [13]

$$J_1 = \sqrt{J^2 - p^2} \cos q, \quad J_2 = \sqrt{J^2 - p^2} \sin q, \quad J_3 = p. \quad (9)$$

Since $(J_1, J_2, J_3) = (J, 0, 0)$ [respectively, $(q, p) = (0, 0)$] is a maximum of the Hamiltonian, the normal form of the Hamiltonian at this equilibrium is $H = J^2/(2M_1) + \omega(p_0^2 + q_0^2)/2 + \text{h.o.t.}$ with the *negative* frequency $\omega = -\sqrt{M_2 M_3 (M_2 - M_1)(M_3 - M_1)}/M_1 M_2 M_3$.

Let us now consider a (flexible) triatomic molecule. For simplicity, we freeze ρ_1 and ρ_2 and consider the 2-degree-of-freedom system consisting of pure bending coupled with overall rotations. The potential V is then a function of ϕ only, and we choose it to be of the form shown in Fig. 3. This potential has two minima at $\phi = 0$ and $\phi = \pi$, which correspond to two different linear isomers which are separated by a barrier at $\phi = \pi/2$. This type of potential occurs, e.g., in the HCN/CNH isomerization problem [10]. We consider the equilibrium which for a given magnitude J of the angular momentum arises from the barrier at $\phi = \pi/2$ coupled with rotations about the first principal axis. In the absence of coupling between the bending and rotational degrees of freedom, we would expect from the discussion of the rigid molecule above that this equilibrium is a saddle

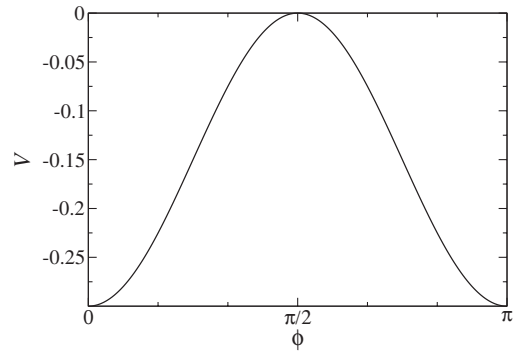


FIG. 3. Potential V as a function of the Jacobi coordinate ϕ .

center with a negative frequency $\omega < 0$. In fact, also in the presence of coupling between the bending motion and the rotation, this remains to be the case (at least for a moderate coupling strength). To illustrate the dynamical implication of this equilibrium, we use the canonical coordinates (q, p) defined in (9) on the angular momentum sphere $J_1^2 + J_2^2 + J_3^2 = J$ and construct a Poincaré surface of section with section condition $q = 0 \pmod{2\pi}$, $\dot{q} > 0$. Using the canonical pair (ϕ, p_ϕ) as coordinates on the surface of section, we obtain Fig. 4.

We see that, as expected, there appears to be a barrier associated with the momentum reaction coordinate p_ϕ . Near $\phi = \pi/2$, no transitions are possible from the

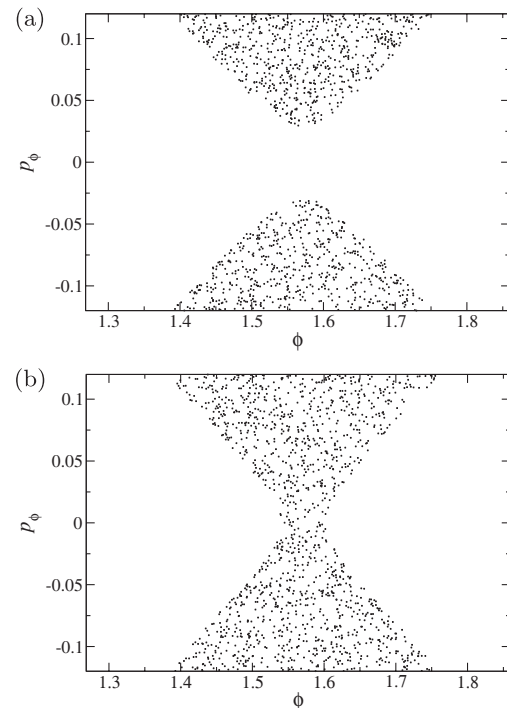


FIG. 4. Poincaré surface of section for the Hamiltonian (5) with parameters $J = 0.2$, $\rho_1 = 1$, and $\rho_2 = 2$ (see the text). Each picture is generated from a single trajectory of energy 0.0205625 in (a) and 0.0197526 in (b), respectively.

reactants region $p_\phi > 0$ to the products region $p_\phi < 0$ for energies *above* the energy of the saddle, whereas for energies *below* the energy of the saddle, transitions are possible. The rotational-vibrational motion of the triatomic molecule with the transition channel near $\phi = \pi/2$ being closed consists of unhindered bending motion between the two isomers associated with ϕ near 0 and π , respectively, coupled with rotations. For motions with the channel near $\phi = \pi/2$ being open, p_ϕ can switch sign near $\phi = \pi/2$, which corresponds to a trajectory bouncing back to the isomer it came from rather than switching to the other isomer. It is important to note that the saddle-center equilibrium studied here induces a *local* bottleneck for transitions between $p_\phi > 0$ and $p_\phi < 0$. *Globally*, such transitions always occur in the present example when a trajectory passes close to the collinear configuration where ϕ is close to 0 or π . This explains how a single trajectory can contribute points to the lower and the upper half in Fig. 4(a) even though the local channel near $\phi = \pi/2$ is closed.

More generally: Mixed positive and negative frequencies.—Near a saddle-center- \cdots -center equilibrium, the Hamiltonian of a system with $f = n + 1$ degrees of freedom can always be brought into the form (1). The NHIM at energy E is then obtained from the intersection of the center manifold of the equilibrium given by $q_0 = p_0 = 0$ and the energy surface $H = E$, i.e.,

$$\sum_{k=1}^n \frac{\omega_k}{2} (p_k^2 + q_k^2) + \text{h.o.t.} = E - E_0. \quad (10)$$

All studies on the geometric theory of reactions so far [14] concern the case of positive frequencies ω_k . This corresponds to the Hamiltonian restricted to the center manifold having a minimum. If all frequencies are negative, then the Hamiltonian restricted to the center manifold has a maximum. In this case, the NHIM is again a $(2f - 3)$ -dimensional sphere. However, as opposed to the case of positive frequencies, p_0 rather than q_0 is the reaction coordinate as discussed in the present example for $f = 2$. Also, the case of mixed signs of the ω_k occurs in many applications. It, e.g., also shows up in our example of the rotational-vibrational motion of a triatomic molecule if we take the other vibrational degrees of freedom into account which we for simplicity considered to be frozen. In the case

of mixed signs of the ω_k , the NHIM is not a sphere but a noncompact manifold. Although no bottleneck in the energy surface is induced in these cases, the NHIM has important dynamical implications, as it has stable and unstable manifolds which are of one dimension less than the dimension of the energy surface and hence form impenetrable barriers. This bears some similarities to the case of noncompact NHIMs that have recently been considered for rank 2 and higher rank saddles [15,16]. The study of the dynamical implications of saddle-center- \cdots -center equilibria with mixed positive and negative frequencies forms an interesting direction for future research.

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