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 the so-called normal form coordinates [5,7] into the form

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

(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 \( \omega_k > 0 \), \( k = 1, \ldots, n \).

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

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

(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

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

(2)
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 as the “equator” of the diving surface. 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 \( q_0 \) 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]

\[
H = \frac{1}{2} \left[ \frac{\rho_1^2 + \rho_2^2 \cos^2 \phi}{\rho_1^2 \rho_2^2 \sin^2 \phi} J_1^2 + \frac{2 \cos \phi}{\rho_1^2 \sin \phi} J_1 J_2 \right. \\
\quad + \left. \frac{1}{\rho_1^2} J_2^2 + \frac{1}{\rho_1^2 + \rho_2^2} J_3^2 + p_1^2 + p_2^2 \right. \\
\quad + \left. \frac{p_1^2 + p_2^2}{\rho_1^2 \rho_2^2} \left( \rho_1 \rho_2 \rho_3 \left( \rho_1 + \rho_2 + \rho_3 \right) \right) + V(\rho_1, \rho_2, \phi). \tag{5}
\]

Here \((\rho_1, \rho_2, \phi)\) are Jacobi coordinates defined as

\[
\rho_1 = ||s_1||, \quad \rho_2 = ||s_2||, \quad s_1 \cdot s_2 = \rho_1 \rho_2 \cos \phi,
\]

where \(s_1\) and \(s_2\) are the mass-weighted Jacobi vectors (see Fig. 1)

\[
s_1 = \sqrt{\mu_1 (x_1 - x_3)}, \quad s_2 = \sqrt{\mu_2 (x_2 - \frac{m_1 x_1 + m_3 x_3}{m_1 + m_3})},
\]

computed from the position vectors \(x_k\) of the atoms and the reduced masses

\[
\mu_1 = \frac{m_1 m_3}{m_1 + m_3}, \quad \mu_2 = \frac{m_2 (m_1 + m_3)}{m_1 + m_2 + m_3}.
\]

The momenta \(p_1, p_2,\) and \(p_\phi\) in (5) are conjugate to \(\rho_1, \rho_2,\) and \(\phi,\) respectively, and \(J = (J_1, J_2, J_3)\) is the body angular momentum. The magnitude \(J_f\) of \(J\) is conserved under the dynamics generated by the Hamiltonian (5).

Let us at first consider a rigid molecule (i.e., the values of \(\rho_1, \rho_2,\) and \(\phi,\) are fixed). The body-fixed frame can then be chosen such that the moment of inertial 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

\[
H = \frac{1}{2} \left( \frac{J_1^2}{M_1} + \frac{J_2^2}{M_2} + \frac{J_3^2}{M_3} \right) \tag{8}
\]

FIG. 1. Definition of Jacobi coordinates for a triatomic molecule.
As the magnitude $J$ of $J$ 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 $J^2/(2M_1)$, 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]

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

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 $H = J^2/(2M_1) + \omega(q_0^2 + p_0^2)/2 + \text{h.o.t.}$ with the negative frequency

$$\omega = -\sqrt{M_2(M_2 - M_1)(M_3 - M_1)/M_1M_2M_3}.$$

Let us now consider a (flexible) triatomic molecule. For simplicity, we freeze $p_1$ and $p_2$ and consider the 2-degree-of-freedom system consisting of pure bending coupled with overall rotations. The potential $V$ is then a function of $\phi$ 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 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 $q = 0 \mod 2\pi, \dot{q} > 0$. Using the canonical pair $(\phi, p_\phi)$ 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 $p_\phi$. Near $\phi = \pi/2$, no transitions are possible from the

![FIG. 3. Potential $V$ as a function of the Jacobi coordinate $\phi$.](Image)

![FIG. 4. Poincaré surface of section for the Hamiltonian (5) with parameters $J = 0.2, \rho_1 = 1, \rho_2 = 2$ (see the text). Each picture is generated from a single trajectory of energy 0.0205625 in (a) and 0.0197526 in (b), respectively.](Image)
reactants region $p_0 > 0$ to the products region $p_0 < 0$ 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 $\phi$ near $0$ and $\pi$, respectively, coupled with rotations. For motions with the channel near $\phi = \pi/2$ being open, $p_0$ 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 $p_0 > 0$ and $p_0 < 0$. Globally, such transitions always occur in the present example when a trajectory passes close to the collinear configuration where $\phi$ is close to 0 or $\pi$. 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 $\omega_k$. This corresponds to the Hamiltonian restricted to the center manifold having a minimum. If all frequencies are negative, 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 $\omega_k$ 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 $\omega_k$, 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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