In this paper we unveil the geometrical template of phase space structures that governs transport in a Hamiltonian system described by a potential energy surface with an entrance/exit channel and two wells separated by an index-1 saddle. For the analysis of the nonlinear dynamics mechanisms, we apply the method of Lagrangian descriptors, a trajectory-based scalar diagnostic tool that is capable of providing a detailed phase space tomography of the interplay between the invariant manifolds of the system. Our analysis reveals that, the stable and unstable manifolds of two families of unstable periodic orbits (UPOs) that exist in the regions of the wells are responsible for controlling the access to the wells of trajectories that enter the system through the channel. In fact, we demonstrate that the heteroclinic and homoclinic connections that arise in the system between the manifolds of the families of UPOs characterize the branching ratio, a relevant quantity used to measure product distributions in chemical reaction dynamics.

Keywords: Phase space structure, Chemical reaction dynamics, Valley-ridge inflection point, Lagrangian descriptors.

I. INTRODUCTION

We study reaction dynamics on a model potential energy surface exhibiting post-transition state bifurcation in the vicinity of a valley ridge inflection (VRI) point. Our work can be viewed as a continuation and extension of the work in [1]. The potential energy surface (PES) has a high energy saddle point that represents the transition state (TS) and a lower energy saddle point that separates two potential wells. In between the two saddle points there is a VRI point. A schematic geometrical representation of the topography of such PES in the neighborhood of the VRI point is shown in Fig. 1 below and discussed in more detail in Section II. In the work carried out in [1], trajectories were initiated on a dividing surface in a region of the upper saddle point at a fixed total energy slightly above that of the saddle, with a value of momentum such that they approached the region of the lower saddle. In the process of evolution the trajectories crossed the region of the VRI and entered one of the potential wells. The trajectory based quantity of particular interest was relative number of trajectories entering each well, i.e. the branching ratio. In [1] the total number of trajectories computed was 61. The nature of the branching ratio is determined by the selectivity, as it is referred to in the chemistry literature. The PES considered in [1] was not symmetric in the sense that the two wells had different depths. Moreover, parameters in the PES could be varied in a way that slightly changed the location of the minima of the wells. It was observed that the branching ratio was sensitive to this change of parameters.

It was argued in [1] that an understanding of the dynamics underlying the branching ratio in such a PES and the mechanism underlying the nature of the selectivity required a phase space analysis, i.e. an analysis that explicitly considered the influence of the momentum of trajectories. This is particularly true when the underlying dynamics is nonstatistical, and the number of observations of organic reactions exhibiting nonstatistical behaviour is increasing yearly. An overview of many of these, as well as a guide to several reviews discussing the subject, is given in [1]. The importance of the understanding the dynamical mechanisms of selectivity was underlined by noting that control of selectivity is of essential importance for synthesis, especially if existing models used for analyzing the problem are incomplete or inapplicable.

In this paper we consider a symmetric version of the potential well studied in [1]. The symmetric version allows us to uncover the dynamical origin of the mechanism underlying selectivity in an unambiguous manner. This, again, highlights the necessity of a phase space perspective for understanding the dynamics. The phase space approach for analysing chemical dynamics is reviewed in [2], which contains an extensive guide to the literature. In this work, we will use three particular techniques of phase space nonlinear dynamics - Poincaré maps, Lagrangian descriptors and lobe dynamics.

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Poincaré maps [3, 4] allow us to reveal and analyze the KAM tori associated to the regular behavior displayed by the system. KAM tori are significant because they lead to trapping of trajectories. However, Poincaré maps provides an incomplete dynamical picture, since the regions where trajectories are chaotic appear in the Poincaré surfaces of section (PSOS) as a chaotic sea of random points, which are extremely difficult to interpret and completely obscure the intricate interactions (tangles) between the invariant stable and unstable manifolds. For this reason, we complement the analysis with Lagrangian descriptors (LDs) [5–7], which are a scalar trajectory diagnostic technique with the capability of revealing the stable and unstable manifolds and their intricate interactions through the formation of lobes. The resulting lobe dynamics provide us with a way to quantify phase space [8, 9] and form the basis of our understanding of selectivity.

The method of Lagrangian descriptors is a nonlinear dynamics technique that was first introduced a decade ago to analyze Lagrangian transport and mixing processes in Geophysical flows [5, 10]. The first definition of LDs relied on the computation of the arclength of trajectories of initial conditions as they evolve forward and backward in time [6, 10]. Since its proposal, this methodology has found a myriad of applications in different scientific areas. For instance, in the context of Geophysics, it has been used in Oceanography to plan transoceanic autonomous underwater vehicle missions by taking advantage of the underlying dynamical structure of ocean currents [11]. Also, it has been shown to provide relevant information for the effective management of marine oil spills [12]. Recently, this tool has also received recognition in the field of Chemistry, for instance in Transition State Theory [13–16], where the computation of chemical reaction rates relies on the knowledge of the phase space structures that separate reactants from products. Other applications of this tool to chemical problems include the analysis of isomerization reactions [17] and roaming [18, 19], the study of the influence of bifurcations on the manifolds that control chemical reactions [20], and also the explanation of the dynamical matching mechanism in terms of the existence of heteroclinic connections in a Hamiltonian system defined by Caldera type PES [21].

The contents of this paper are organized as follows. In Section II we describe the fundamental landscape characteristics of the potential energy surface defining the two DoF Hamiltonian model that we use in this work for the analysis of the phase space transport processes including the selectivity mechanism. Section III is devoted to providing a detailed description of the results obtained from the analysis of the nonlinear dynamics of the system. Finally, Section IV summarizes the conclusions of this paper. The reader can find in Appendix A a brief explanation of the method of Lagrangian descriptors, and how this technique can be applied to easily reveal the geometrical template of invariant manifolds and their intricate heteroclinic and homoclinic connections in the high-dimensional phase space of Hamiltonian systems.

The work in this paper is an extended and more detailed study of work begun in [22].

II. HAMILTONIAN MODEL FOR THE BRANCHING MECHANISM

In this section we present the fundamental characteristics of the Hamiltonian model with two degrees-of-freedom (DoF) that we study in this work. The potential energy surface (PES) that defines our Hamiltonian model is inspired in the analysis carried out in [1], where the influence of valley-ridge inflection points (VRIs) of the PES on the
selectivity (branching) mechanism observed in many organic chemical reactions is addressed. The topography of the PES introduced in [1] has an entrance/exit channel characterized by an index-1 saddle and two potential wells separated by an energy barrier determined by another index-1 saddle. The PES also has a VRI point between both saddles, where the intrinsic reaction coordinate of the system, i.e. the minimum energy path, bifurcates (or branches). It is thought in the Chemistry literature that this geometrical phenomenon observed in the vicinity of VRI points might play a relevant role in the determination of selectivity mechanisms, “guiding” the trajectories that enter the system through the channel towards any of the potential wells.

In this paper we use a simplified version of the PES from the one discussed in [1], where we assume that the energy landscape is symmetric with respect to the $x$-axis. Our Hamiltonian model has the classical structure of kinetic plus potential energy in the form:

$$H(x, y, p_x, p_y) = \frac{p_x^2}{2m_x} + \frac{p_y^2}{2m_y} + V(x, y) ,$$

(1)

where the PES is described by:

$$V(x, y) = \frac{8}{3} x^3 - 4x^2 + \frac{1}{2} y^2 + x(y^4 - 2y^2) .$$

(2)

In this work we assume that the mass in each DoF is $m_x = m_y = 1$. The potential energy function is symmetric with respect to the $y$ coordinate and has two wells separated by an index-1 saddle located at $(1, 0)$. Interestingly, the energy landscape has an entrance/exit channel determined by an index-1 saddle located at the origin, which has the highest energy among all the critical points on the PES. An illustration of the geometry of the PES described above is included in Fig. 2, and the location and energies of all the critical points is summarized in Table I. For completeness, the energy of the VRI point located on the $x$ axis at $(1/4, 0)$ is given by $V_I = V(1/4, 0) = -5/24$. It is important to note here that for a two degrees of freedom (DoF) Hamiltonian, wells of the PES are local minima and thus the Hessian matrix of the PES evaluated at these critical points has two pairs of imaginary eigenvalue (each eigenvalue in every pair has zero real part and imaginary part of equal magnitude but opposite sign with the other). On the other hand, index-1 saddles are critical point of saddle type, that is, the Hessian matrix evaluated at these critical points has two real eigenvalues of opposite sign.

The evolution of the Hamiltonian system in Eq. (1) takes place in a 4-dimensional phase space, and is determined by Hamilton’s equations of motion:

$$\begin{align*}
\dot{x} &= \frac{\partial H}{\partial p_x} = p_x \\
\dot{y} &= \frac{\partial H}{\partial p_y} = p_y \\
\dot{p}_x &= -\frac{\partial H}{\partial x} = 8x(1-x) + y^2 (2-y^2) \\
\dot{p}_y &= -\frac{\partial H}{\partial y} = y [4x (1-y^2) - 1] 
\end{align*}$$

(3)

Since the energy is conserved, dynamics is constrained to a three-dimensional energy hypersurface. It is important to remark here that, due to the symmetry of the PES in Eq. (2) with respect to the $x$ axis, which is a consequence of the potential being an even function of the $y$ coordinate, i.e. $V(x, y) = V(x, -y)$, the phase space structures in the phase space of the system are symmetric under a $180^\circ$ rotation about the origin in the $y$-$p_y$ plane. This symmetry plays, as we will show, a fundamental role for the explanation that the branching ratio for systems with this type of symmetric PES is unity. This means that, from all the incoming trajectories that visit for the first time during their evolution one of the potential wells, half of them go to the top well and the rest go to the bottom well.

### III. RESULTS

In this section we describe the results obtained in our analysis of the phase space transport and trapping mechanisms that take place in the model Hamiltonian. We will divide them into three cases, depending on the energy levels of the system:

**A. First case:** The energy is below that of the lower index-1 saddle and above that of the minima of the wells.
Figure 2. Potential energy surface given in Eq. (2). We have marked the relevant dynamical features of the energy landscape.

| Critical point     | x    | y    | Potential Energy (V) | Stability       |
|--------------------|------|------|----------------------|-----------------|
| index-1 saddle     | 0    | 0    | 0                    | saddle × center |
| index-1 saddle     | 1    | 0    | -4/3                 | saddle × center |
| Potential Well (A) | 1.107146 | 0.879883 | -1.94773            | center          |
| Potential Well (B) | 1.107146 | -0.879883 | -1.94773            | center          |

Table I. Location of the critical points of the PES.

B. **Second case:** The energy is below that of the upper index-1 saddle and above that of the lower index-1 saddle.

C. **Third case:** The energy is above that of the upper index-1 saddle.

The study of the dynamics is carried out by applying LDs in order to determine the geometry of the invariant stable and unstable manifolds of the unstable periodic orbits present in the system, and we also make use of the method of Poincaré maps for the analysis of the KAM tori that characterize the regular dynamics. All this analysis is done in the Poincaré surfaces of section (PSOS) given below:

\[
\begin{align*}
\Sigma_1(H_0) &= \left\{ (x, y, p_x, p_y) \in \mathbb{R}^4 \mid x = 0.05, p_x(x, y, p_x; H_0) > 0 \right\} \\
\Sigma_2(H_0) &= \left\{ (x, y, p_x, p_y) \in \mathbb{R}^4 \mid x = 1, p_x(x, y, p_x; H_0) > 0 \right\} \\
\Sigma_3(H_0) &= \left\{ (x, y, p_x, p_y) \in \mathbb{R}^4 \mid y = 0, p_y(x, y, p_y; H_0) > 0 \right\} \\
\Sigma_4(H_0) &= \left\{ (x, y, p_x, p_y) \in \mathbb{R}^4 \mid x = x_{well}, p_x(x, y, p_x; H_0) > 0 \right\}
\end{align*}
\]

(4)

where \(x_{well}\) is the \(x\) coordinate of the potential wells as shown in Table I. We briefly explain next the reasons for choosing the PSOS defined above. The first section, \(\Sigma_1(H_0)\), is taken at the entrance/exit channel and is used to understand the dynamical behavior of the trajectories that enter the system coming from infinity through the bottleneck associated to the upper index-1 saddle. On the other hand, sections \(\Sigma_2(H_0)\) and \(\Sigma_3(H_0)\) are used in order to analyze the regular dynamics governed by the KAM tori in the system and address well to well transport. Finally, the purpose of \(\Sigma_4(H_0)\) is to illustrate the bifurcation of the KAM tori family corresponding to the potential wells at a certain value of the energy of the system.
A. First case

The first case starts from the value of energy of the two stable equilibrium points until the presence of the index-1 saddle that separates the two wells. In this case, we have two stable equilibrium points that each of them, according the Lyapunov subcenter theorem [23–25], has at least two families of periodic orbits. In our case we have four families for the two wells. We see only two of these families in Poincaré sections (these sections are for positive values of momentum) because the other families have opposite sign of momentum and cannot appear in these sections.

We compare the panels A and B of Fig. 3 that correspond to lower and higher values of energy. Firstly, we studied the trapping and the phase space structure in the panel A of Fig. 3. We observe invariant curves around the stable periodic orbit of the upper well in $\Sigma_4(H_0)$ for a lower value of energy. These invariant curves represent the KAM invariant tori that exist, according to the KAM theorem [26–28], around the stable periodic orbits of the upper well. This means that there are many trajectories, that lie on these tori or they are in the regions between them, and they are trapped for ever. Notice that although in this figure we see the case for the upper well, the same happens for the case of the lower well due to the symmetry of the potential.

![Figure 3. Poincaré map calculated on the surface of section $\Sigma_4(H_0)$ for the system’s energy: A) $H_0 = -1.3$; B) $H_0 = -1.1$. The energy boundary is depicted as a magenta curve.](image)

Then we investigated the trapping and the phase space structure in the panel B of Fig. 3. We observe the appearance of another stable periodic orbit with invariant curves around it. This periodic orbit belongs to a family with period 2 that is appeared above the energy of the minima of the wells. This family is located in the region of the wells and this is the reason that we call it also as family of the wells. This family has two branches (it is a family with period 2), the one branch is close to the upper well and the other close to the lower well. The branch that is close to the upper well is represented by one point in the panel B of Fig. 3 and it has invariant curves around it. The same happens for the other branch close to the lower well. We see, that many trajectories are trapped for ever because they lie on these tori or they are in the regions between these invariant tori.

B. Second case

The second case corresponds to the interval of energy from the presence of the index-1 saddle that separates the two wells until the presence of the upper (entrance/exit) index-1 saddle. In this case, we have one index-1 saddle that separates the wells, according to the Lyapunov subcenter theorem [23–25] it has at least one family of periodic orbits. We studied the phase space structure and transport of trajectories from the region of the index-1 saddle that separates the two wells to the regions of the two wells.

In this case, we use two different Poincaré sections for every value of the energy. The Poincaré section $\Sigma_3(H_0)$ is appropriate in order to see the trapping and the restriction of the invariant manifolds in one small region. On the other hand, the other Poincaré section $\Sigma_2(H_0)$ is adequate in order to see the transport of trajectories from the region of the index-1 saddle that separates the two wells to the region of the two wells.
Firstly, we studied the phase space structure and trapping close to the family of the index-1 saddle that separates the two wells. The panel A of Fig. 4 displays the Poincaré map, superimposed with the stable (blue) and unstable (red) manifolds that have been extracted from the gradient of the scalar field generated by LDs. The energy of the system is \( H_0 = -0.2 \) and the Poincaré map has been computed on the surface of section \( \Sigma_3(H_0) \). Around the stable periodic orbits we see invariant curves that represent the KAM (Kolmogorov-Arnold-Moser) invariant tori ([26],[28],[27]) in the Poincaré section. These periodic orbits belong to the family of the wells. This means that there are trajectories that lie on these invariant tori or they are in the regions between these invariant tori. These trajectories are trapped in these regions forever. We observe the invariant manifolds of the unstable periodic orbits of the family of the index-1 saddle that separates the two wells are restricted in a small area close to the boundary of the forbidden region.

Now we want to see in detail the mechanism of transport trajectories from the region of the index-1 saddle that separates the two wells to the region of the two wells. In the panel B the energy of the system is the same as in the panel A (\( H_0 = -0.2 \)), but now the Poincaré map has been computed on the surface of section \( \Sigma_2(H_0) \). In the upper right and lower left corners of this figure we can still see the ordered regions around the stable periodic orbit of the family with period 2 of the wells as in the panel A. In the panel A we can clearly see only one family of the two families of the well due to the symmetry of the system for the section \( \Sigma_3(H_0) \) but for the section \( \Sigma_2(H_0) \) we can identify both of these families for each well. In the panel B we can observe two ordered regions that we don’t see in the panel A. These ordered regions correspond to the invariant curves around the stable periodic orbits of the other...
two families of the well in the central area of the panel B. These ordered regions do not cut the plane \( y = 0 \) and they cannot be seen in \( \Sigma_3(H_0) \). In this figure, we observe the invariant manifolds of the unstable periodic orbits of the index-1 saddle that separates the two wells to be extended until the region of the wells. We observe that many points are inside the lobes of the invariant manifolds and they are guided from the unstable invariant manifolds to the regions of the well. This explains the transport from the central region to the region of the wells. In addition, we see the symmetry of these invariant manifolds 180° with respect to the origin. This symmetry of the invariant manifolds gives us the information that the transport of the trajectories is symmetric. This means that the trajectories, that are transported to the wells, are guided equally from the unstable invariant manifolds of the unstable periodic orbits of the index-1 saddle that separates the wells to each region of two wells (50% of the trajectories to the one well and 50% to the other).

We increase the energy of the system at \( H_0 = -0.1 \) in order to study the trapping and the transport mechanisms for higher values of energy. We present these results in Fig. 4 C) and D) for the sections \( \Sigma_3(H_0) \) and \( \Sigma_2(H_0) \) respectively. In the panel C we observe except the invariant curves around the stable periodic orbit of the family of the wells and a new regular region. This region represents the KAM invariant tori around a stable periodic orbit of a family that is appeared for a value of energy (for energy \( H_0 = -0.152 \)) close to the energy of VRI. This family is initially unstable but it becomes stable (for energy \( H_0 = -0.15 \)) giving rise to two new families of unstable periodic orbits through a pitchfork bifurcation (for more details for this bifurcation see the appendix of [29]). We name these families as top unstable periodic orbits and bottom unstable periodic orbits because they are respectively at the regions of the top and bottom wells. The unstable (red) and stable (blue) invariant manifolds of these periodic orbits are restricted in a small area close to the boundary of the forbidden region. We observe that many points are inside the lobes of the invariant manifolds of the top and bottom unstable periodic orbits and they are guided from the unstable invariant manifolds to the regions of the well. This explains the transport from the central region to the region of the wells. In the panel D we observe (that corresponds to a value of energy after the bifurcation) a symmetry to the transport of trajectories from the region of the index-1 saddle that separates the two wells to the region of the two wells because of the symmetry (with respect to the origin) of the invariant manifolds of the top and bottom unstable periodic orbits. After the bifurcation we see that two unstable periodic orbits (top and bottom unstable periodic orbits) and not only one (unstable periodic orbits of the index-1 saddle that separate the wells), as in the case before the bifurcation, are responsible for the transport of the trajectories from the region of the index-1 saddle to the regions of the wells.

C. Third Case

In this subsection we will describe the dynamics of the Hamiltonian in Eq. (1) for energy \( H_0 = 0.1 \) above that of the upper index-1 saddle. This means that the bottleneck in the vicinity of the upper index-1 saddle is now open and therefore allows transport between the upper index-1 saddle, the wells and the lower index-1 saddle.

Our goal is to describe in detail the mechanisms of transport and trapping of the trajectories in our system. We can visualize the 3D potential energy surface with an exit channel and two potential wells in Fig. 5. Four different initial conditions in red, green, magenta and blue have been chosen, in order to determine the dynamical behavior. In black color are depicted the top and bottom unstable periodic orbits. We can easily come to conclusion that the dynamics is very difficult to be explained. The method of LDs can give us a way out of this by choosing the right lobes and study the lobe dynamics. More details about this will be given in Fig. 9 where the same initial conditions and colors have been used.

Firstly, we study the phase space structures and the trapping mechanisms. We observe in the panel A of Fig. 6 the invariant curves (that are denoted by the number 2) that represent the invariant tori in the Poincaré section \( \Sigma_2(H_0) \) around the stable periodic orbits of the families of the wells in the central area of the figure. These tori are inside the lobes of the unstable (red) and stable (blue) invariant manifolds of the upper and bottom unstable periodic orbits and they are restricted in a specific region at the top or bottom. This explains why the trajectories that lie on these tori, for example the trajectory in the lower right part of the panel B of Fig. 6, are in the top or bottom well regions and do not visit both wells. Tori that are represented by the invariant curves, denoted by the number 1, surround the stable periodic orbits of the family (with period 2) of the wells and they are not inside the lobes of the invariant manifolds. Trajectories on these tori visit both of the regions of the top and bottom well (see the upper right part of the panel B of Fig. 6). In the panel C of Fig. 6 we see, except the invariant curves around the stable periodic orbits of the families of the wells (as in the panel A), Invariant curves around the stable periodic orbits of the family that was born close to the energy of the VRI point, marked as 3 in Fig. 6) C). Trajectories on these tori visit both of the regions of the top and bottom wells, see the left part of Fig. 6 D).

Then, we investigate the mechanisms of transport of the trajectories in the phase space. For this reason, we depict the LDs (Fig. 7) that are calculated on the slice \( \Sigma_1(H_0) \). In the middle panel of Fig. 7 we present the unstable (red) and stable (blue) manifolds of the UPO associated to upper index-1 saddle, that controls the exit and entrance of
Figure 5. Dynamical evolution in forward time of four different initial conditions chosen on the surface of section $\Sigma_1(H_0)$, where the system’s energy is set to $H_0 = 0.1$. The boundary of the three-dimensional energy hypersurface is shown in blue, and the unstable periodic orbits that control the access of trajectories to the phase space regions corresponding to the potential wells of the PES are depicted in black.

The first initial condition $A$ corresponds to the one kind of trajectory behavior and the other initial conditions $B, B'$ to the other. The initial condition of the trajectory $A$ is in a lobe that is associated with the homoclinic intersections of the invariant manifolds of the UPO of the upper index-1 saddle (see the middle panel of Fig. 7). This means that the trajectories follow initially the unstable invariant manifold of the UPO of the upper index-1 saddle to the channel between the two wells. Then they are guided, through homoclinic intersections, from the stable invariant manifolds of the UPO of the upper index-1 saddle to the region of this periodic orbit and to the exit. Another example of this trajectory behaviour (except the trajectory $A$) is the trajectory 1 in Fig. 8. The initial conditions $B$ and $B'$ correspond to the second type of trajectory behaviour. The initial condition $B$ (or $B'$) is located in the lobe that is associated with a heteroclinic intersection of the unstable manifold of the unstable periodic orbit of the upper index-1 saddle with the stable invariant manifold of the top unstable periodic orbit (or the stable invariant manifold of the bottom unstable periodic orbit in the case of $B'$). This means that the trajectories begin from the region of the upper index-1 saddle and they follow the unstable invariant manifolds of the upper index-1 saddle until they start to follow, through a heteroclinic intersection, the stable manifolds of the top or bottom unstable periodic orbits to the region of the top or bottom well respectively (see the trajectories $B$ and $B'$ in the right panel of Fig. 7). The symmetric transport of trajectories is reflected by the symmetry (180° with respect to the point (0,0)) of the invariant manifolds of the unstable periodic orbits that are responsible for this transport (as we can see in the middle panel of Fig. 7). This means that there is a symmetry (180° with respect to the point (0,0)) between the lobes that are responsible to the transport from the entrance region to the region of the top wells (as the upper lobe in the middle panel of Fig. 7) and the lobes that are responsible to the transport from the entrance region to the region of the bottom well (as the lower lobe in the middle panel of Fig. 7). Two representative examples of this symmetry of the lobes are the initial conditions $B$ and $B'$ (in the middle panel of Fig. 7). The $B$ and $B'$ correspond to the transport from the entrance region to the region of the top well and to the transport from the entrance region to the region of the bottom well respectively.

Then we studied the secondary mechanisms (except the two basic mechanisms that we described above) of transport that we present in Fig 8. The initial conditions 2, 3 and 5 in the panel A of Fig. 8 correspond to three different secondary mechanisms of transport:

1. **First secondary mechanism**: This mechanism is responsible for the transport of trajectories from the region of bottom (or top well) to the region of the exit channel. In this mechanism the trajectories, that are located
Figure 6. Regularity behavior displayed by the Hamiltonian system through the KAM tori structures present in its phase space. The energy of the system is chosen as $H_0 = 0.1$. On panels A and C we show Poincaré maps superimposed with the stable (blue) and unstable (red) manifolds extracted from LDs using $\tau = 8$, and the sections used for the analysis of the dynamics are $\Sigma_2(H_0)$ for A) and $\Sigma_3(H_0)$ for C). On panels B and D, we depict the forward time evolution projected onto configuration space, of three different trajectories corresponding initial conditions labeled on panels A and C. Black curves represent the projections of the UPOs of the system. We also provide a detailed zoom of the regularity regions to illustrate the arrangement of the KAM islands, and for promoting a visual understanding of the tori, we include a three-dimensional representation of one of the torus.

in the region of the top or bottom well, follow the unstable invariant manifolds of the top or bottom unstable periodic orbits having heteroclinic intersections with the stable manifolds of the upper index-1 saddle. Then the trajectories through these heteroclinic intersection are guided from the stable manifolds of the unstable periodic of upper index-1 saddle to the region of the exit channel. The trajectory with initial condition 2 in the panel A of Fig. 8 is a representative example of this mechanism. The initial condition 2 is located in a lobe that is associated with the heteroclinic intersection of the unstable invariant manifold of the bottom unstable periodic orbit with the stable invariant manifold of the upper index-1 saddle. The trajectory is coming from the region of the bottom well and it moves to the exit channel (see the second part of the panel B of Fig. 8).

2. **Second secondary mechanism:** This mechanism is responsible for the transport of the trajectories from the
region of the top or bottom well to the region between the two wells and then again to the to the region of the top or bottom well. The trajectories follow initially the unstable invariant manifolds of the top or bottom unstable periodic orbits to the region between the two wells and through homoclinic intersections the trajectories follow the stable invariant manifolds of these periodic orbits again to the region of the top or bottom well. An example of a trajectory that have this behaviour is the trajectory with the initial condition 3 in the panel A of Fig. 8. The initial condition of this trajectory is located in a lobe that is associated with the homoclinic intersection of the invariant manifolds of the bottom unstable periodic orbit. The trajectory is coming from the region of the bottom well and it moves to the region between the two wells before it returns to the region of the bottom well (see the third part of the panel B of Fig. 8).

3. Third secondary mechanism: This mechanism is responsible for the transport of trajectories between the regions of the two wells (Inter-well transport). In this mechanism the trajectories that are located initially in the region of one of the two wells (top or bottom) follow the unstable invariant manifolds of the top or bottom unstable periodic orbits and through heteroclinic intersections, with the stable invariant manifolds of the bottom or top unstable periodic orbits, follow the stable invariant manifolds of the bottom or top unstable periodic orbits to the region of the other well. An representative example is the trajectory 5 (with the initial condition 5 in the panel A of Fig. 8). This trajectory has an initial condition in a lobe that is associated with the heteroclinic intersection of the unstable invariant manifold of the bottom unstable periodic orbit with the stable invariant manifold of the top unstable periodic orbit. The trajectory is coming from the region of the bottom well to the region of the top well (see the last part of the panel B of Fig. 8).

At this point it is important to note that the transport is symmetric to the origin and to the secondary lobes as well. That means that if we choose one initial condition in a lobe that visits the top well the symmetric initial condition will visit the bottom well. In order to confirm the symmetric dynamical behavior of our system we have chosen seven different initial conditions in the section $\Sigma_1(H_0)$ (panel A of Fig. 9), that we have evolved them in forward time (panel D) and shown as red (TB stands for trajectories that move from the top well to the bottom well, BT stands for trajectories that move from the bottom well to the top well), green (T stands for the trajectories that visit only the top well), magenta (None stands for the trajectories that don’t visit any of the wells) and blue (B stands for the trajectories that visit the bottom well) in Fig. 9. Notice that we focus only in the area where $y \in [0, 0.6]$ due to the symmetry to the origin. We underline the fact that if we choose one initial condition in a lobe that visits the top well the symmetric initial condition will be in a lobe in which the trajectories with initial conditions in this lobe will visit the bottom well. For example the red initial condition TB with the red initial condition BT. In this case the trajectory with the red initial condition TB visits the top and then the bottom well. If we choose the symmetric initial condition (180° with respect the origin) this initial condition will be located in a lobe in which all the trajectories in this lobe will visit the bottom and then the top well like the red initial condition BT in the panel A of Fig. 9. Other examples are the green and blue initial conditions. The trajectories with green initial conditions visit the top well. If
Figure 8. Lobe dynamics and evolution of trajectories analyzed from the interaction of the stable (blue) and unstable (red) manifolds of the system in a phase space region which corresponds to a zoom of Fig. 7. A) Invariant manifolds have been extracted from the gradient of LDs calculated on the PSOS $\Sigma_1(H_0)$ using $\tau = 8$ for the system’s energy $H_0 = 0.1$. We have selected different initial conditions, marked as yellow dots and labelled from 1 to 5 in order to probe the dynamical behavior of lobes. B) Trajectory evolution of the initial conditions in forward (blue) and backward (red) time, projected onto configuration space. The UPOs of the system are also depicted as black curves.

We choose the symmetric initial conditions ($180^\circ$ with respect the origin), these initial conditions will be located in lobes in which all the initial conditions correspond to trajectories that visit the bottom well such as the blue initial conditions in the panel A of Fig. 9. We note that the symmetric initial condition ($180^\circ$ with respect the origin) of the magenta initial condition, that corresponds to a trajectory that doesn’t visit any of the two wells, will be located in the same lobe and it will have the same trajectory behavior. This means that we don’t have symmetric lobes for trajectories which don’t visit any of the two wells.

We want to underline the fact that the size of the lobes is very important for the transport. An example of the influence of the size of the lobe to the transport is the initial condition 4 (in the panel A of Fig. 8). This initial condition is in a lobe that is associated with a heteroclinic intersection of the unstable invariant manifold of the bottom unstable periodic orbit and stable invariant manifold of the top unstable periodic orbit. This means that this trajectory should follow the mechanism of the third secondary mechanism. The trajectory 4 initially follows the unstable invariant manifold of the bottom unstable periodic orbit (if we integrate backward it goes to the region of the bottom well as we can see in the fourth figure of the panel B of Fig. 8 - as we expected from the mechanism) and then it is guided from the stable invariant manifold of the top unstable periodic orbit and it starts to approach the region of the top well (if we integrate forward it starts to move close to the region of the top well as we can see in the fourth panel of Fig. 8 - as we expected from the mechanism). Then the trajectory does not enter to the region of the top well (as we expected from the mechanism) but it exits through the channel between the two wells. This is because of the initial condition 4 of this trajectory is located in a very thin lobe and it has not enough time to follow the stable invariant manifold of the top unstable periodic orbit to the region of the top well in contrary with
Figure 9. Analysis of lobe dynamics, escape times and forward time evolution of trajectories for the system with energy \( H_0 = 0.1 \) on the surface of section \( \Sigma_1(H_0) \). A) Stable (blue) and unstable (red) manifolds extracted from the LD scalar field calculated using \( \tau = 8 \). We have marked initial conditions with circles of different colors in order to probe the system dynamics. The evolution of their trajectories, using the same color scheme, is shown in panel D). An explanation of the labels (T)-(B)-(TB)-(BT)-(None) is given in the main text of the paper; B) Forward escape time plot; C) Backward escape time plot; D) Trajectory evolution of the initial conditions selected in panel A), projected onto configuration space. We have also depicted with black curves the projections of the UPOs of the system.

IV. CONCLUSIONS

In this work we have studied, by means of applying the method of Lagrangian descriptors and using the classical approach of Poincaré maps, the phase space dynamics of a basic Hamiltonian system that could be used as a model of the selectivity (branching) mechanism in chemical reactions. Our analysis has shown that the heteroclinic and homoclinic intersections between the stable and unstable manifolds of the families of UPOs present in the system are responsible for the determination of selectivity as a phase space mechanism. In fact, the heteroclinic connections between the unstable manifold of the UPO associated to the index-1 saddle at the origin (located at the entrance channel) and the stable manifolds of the two new families of UPOs (created after bifurcation) are govern and control

the trajectory with the initial condition 5 that is located in a large lobe (see the panel A of Fig. 8 - we discussed it above as an example of the third secondary mechanism).

Now we will discuss the escape time of the trajectories and the influence of the size of lobes to this. In panel B of Fig. 9 we illustrate the exit times forwards in time. It is evident that the trajectories that escape faster belong to the lobe that doesn’t interact to any of the wells. Moreover the trajectories that escape slower belong to the lobes that visit both wells. This happens because these lobes are larger than the others and the trajectories are trapped for longer times inside them. In the panel C we present the exit times backwards in time, where it is clear that the trajectories that escape faster are the ones that are inside the unstable manifold of the UPO of the upper index-1.
the branching of trajectories. Moreover, these heteroclinic intersections guide trajectories that enter the system through the phase space bottleneck of the entrance channel towards one of the two potential wells, characterizing therefore the selectivity mechanism in this setup.

We studied the transport from the region of the wells to the exit. In this case the heteroclinic intersections between the unstable invariant manifolds of the unstable periodic orbits (top or bottom), that exist in the regions of the wells, with the stable invariant manifolds of the UPO of the upper index-1 saddle are responsible for this transport.

In addition, we investigated the transport from well to well. Two families of unstable periodic orbits (bottom and top), that exist in the regions of the wells, are responsible for the transport of trajectories from one well to the other. This is because of the heteroclinic connections between the unstable invariant manifolds of the top/bottom unstable periodic orbits with the stable invariant manifolds of the bottom/top unstable periodic orbits. This give us an extension of the selectivity of the trajectories in systems with an entrance channel and two potential wells.

Furthermore, we studied the mechanism which is responsible for the non-selectivity of any region of the wells from the trajectories that come from the entrance channel. This happens because many trajectories are inside the lobes of homoclinic connections between the unstable invariant manifolds and stable invariant manifolds of the unstable periodic orbits of the upper index-1 saddle.

Finally, we found that the size of the lobes between the invariant manifolds that are responsible for the transport plays important role to the transport and escape time of the trajectories.

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where “singular structures” that appear in the LD scalar field. is found between normally hyperbolic invariant manifolds (NHIMs) and their stable and unstable manifolds, and the works [30, 31], a rigorous theoretical foundation for this methodology is established, and a mathematical connection presented in [7], which relies on integrating along trajectories the phase space encoded in the initial conditions themselves. The simple and elegant idea behind LDs in order to provide a qualitative description of the system’s dynamics is to seed a given phase space region with initial conditions and integrate a bounded and positive quantity (an intrinsic geometrical and/or physical property of the dynamical space structure is to use trajectories, since these objects are its building blocks and the geometry of the underlying phase space is encoded in the initial conditions) across a time-dependent barrier: Self-similarity in the lagrangian descriptor and reactive basins, J Chem Phys 147, 064101 (2017).

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Appendix A: Lagrangian Descriptors

Consider a dynamical system with general time dependence:

$$\frac{dx}{dt} = v(x, t), \quad x \in \mathbb{R}^n, \quad t \in \mathbb{R}, \quad (A1)$$

where the vector field satisfies $v(x, t) \in C^r (r \geq 1)$ in $x$ and continuous in time. The natural way to explore phase space structure is to use trajectories, since these objects are its building blocks and the geometry of the underlying phase space is encoded in the initial conditions themselves. The simple and elegant idea behind LDs in order to provide a qualitative description of the system’s dynamics is to seed a given phase space region with initial conditions and integrate a bounded and positive quantity (an intrinsic geometrical and/or physical property of the dynamical system under study) along trajectories for a finite time. The definition of LDs that we use in this work follows the one presented in [7], which relies on integrating along trajectories the $p$-norm of the vector field of the dynamical system, where $p \in (0, 1]$ is a parameter chosen in advance. In this work, we will use for the simulations the value $p = 1/2$. In the works [30, 31], a rigorous theoretical foundation for this methodology is established, and a mathematical connection is found between normally hyperbolic invariant manifolds (NHIMs) and their stable and unstable manifolds, and the “singular structures” that appear in the LD scalar field.

Given a fixed integration time $\tau > 0$ and let $x_0 = x(t_0)$ be any initial condition of the system. We define the fixed-time integration LDs diagnostic calculated at time $t_0$ as:

$$M_p(x_0, t_0, \tau) = \sum_{k=1}^n \left[ \int_{t_0-\tau}^{t_0+\tau} |v_k(x(t; x_0), t)|^p dt \right], \quad (A2)$$

where $v_k$ is the $k$-th component of the vector field that defines the dynamical system in Eq. (A1). Notice that this
definition can be decomposed into its forward and backward integration parts:

\[
M_p^{(b)}(x_0, t_0, \tau) = \sum_{k=1}^{n} \left[ \int_{t_0 - \tau}^{t_0} |v_k(x(t; x_0), t)|^p \, dt \right],
\]

\[
M_p^{(f)}(x_0, t_0, \tau) = \sum_{k=1}^{n} \left[ \int_{t_0}^{t_0 + \tau} |v_k(x(t; x_0), t)|^p \, dt \right],
\]

where

The advantage of splitting function \(M_p\) into its forward and backward components is that forward integration highlights the stable manifolds of the dynamical system, while backward evolution recovers the unstable manifolds. Moreover, the combination of both forward and backward detects all the invariant manifolds simultaneously. This detection of invariant manifolds by means of locations at which the LD scalar field becomes non-differentiable has been mathematically quantified in terms of the notion of “singular structures” in the LDs plots, which are easy to recognize visually \([6, 7, 30, 31]\). Therefore, this approach allows us to easily extract the manifolds from the high values (ridges) attained by the gradient of the scalar function itself.

The methodology offered by LDs has thus the capability of producing a complete and detailed geometrical phase space tomography in high dimensions by means of using low-dimensional phase space probes to extract the intersections of the phase space invariant manifolds with these slices \([30–32]\). Any phase space slice can be selected and sampled with a high-resolution grid of initial conditions, and no information regarding the dynamical skeleton of invariant manifolds in high dimensions by means of using low-dimensional phase space probes to extract the intersections of the phase space invariant manifolds with these slices \([30–32]\). Any phase space slice can be selected and sampled with a high-resolution grid of initial conditions, and no information regarding the dynamical skeleton of invariant manifolds at the given slice is lost as the trajectories evolve in time. Moreover, this analysis does not rely on trajectories coming back to the chosen slice, as is required for Poincaré maps to work. In this respect, there is also another key point that needs to be highlighted which demonstrates the real potential of LDs with respect to other classical nonlinear dynamics techniques. Using LDs one can obtain all the invariant manifolds of the dynamical system simultaneously, and this comes with a tremendous save in the computational cost, since LDs are extremely simple and straightforward to implement.

In order to apply LDs for revealing the invariant manifolds in phase space, it is very important to remark the crucial role played by the integration time \(\tau\) in the definition of the method. The consequence of increasing the value for \(\tau\) is that richer and more intricate details of the underlying geometrical template of phase space structures are unveiled. This is the expected behavior, since an increase of the integration time would imply incorporating more information about the past and future dynamical history of trajectories in the computation of LDs. This means that \(\tau\) is intimately related to the time scales of the dynamical phenomena that occur in the model under consideration. This connection makes the integration time a problem-dependent parameter, and hence, there is no general “golden rule” for selecting its value for exploring phase space. One needs to bare in mind in this context that there exists a compromise between the complexity of the structures one would like to reveal from the application of the method in order to explain a certain dynamical mechanism, and the interpretation of the intricate manifolds displayed in the LD scalar output after the simulation is carried out. We will present an example regarding the importance of this property in the next section.

Since the Hamiltonian system we are dealing with in this work has an unbounded phase space, we need to be careful when applying LDs to reveal its invariant manifolds as trajectories can escape to infinity at a very fast rate or even in finite time. This issue is related to the fact that all initial conditions in the definition of LDs in Eq. (A2) are integrated for the same time \(t\), and this comes with a tremendous save in the computational cost, since LDs are extremely simple and straightforward to implement.

The total integration time is defined as:

\[
\tau_{x_0}^{\pm} = \min \left\{ \tau_0, |t^\pm|_{|x(t^\pm; x_0)| \notin R} \right\},
\]

where \(t^+\) and \(t^-\) are the times for which the trajectory leaves the interaction region \(R\) in forward and backward time, respectively. For this work we will define the interaction region as:

\[
R = \left\{ (x, y, p_x, p_y) \in \mathbb{R}^4 \left| x > -0.1 \right. \right\}
\]
which reflects the physical assumption that trajectories of the system escaping through the entrance/exit channel of the PES, characterized by the index-1 saddle at the origin, will never return.

We finish this appendix by illustrating how LDs can reveal the geometry of invariant manifolds with increasing complexity as the integration time parameter $\tau$ is increased. We do so by calculating LDs on the section $\Sigma_2(H_0)$ for the system with energy $H_0 = 0.1$, which is, as we have discussed, above that of the index-1 saddle at the origin. We carry out the computation by using the values $\tau = 4, 8, 16$ and the results obtained are shown in Fig. 10. On the left column we display the scalar field given by the LD diagnostic, and on the right column we demonstrate how the stable (blue) and the unstable (red) manifolds can be extracted from the gradient of the scalar field.

Figure 10. Lagrangian descriptors calculated on the surface of section $\Sigma_2(H_0)$, where the system’s energy is $H_0 = 0.1$, for three different values of the integration time. A) and B) correspond to $\tau = 4$; C) and D) use $\tau = 8$; E) and F) are for $\tau = 16$. In the right column we display the stable (blue) and unstable (red) manifolds extracted from the gradient of the LD scalar field.