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Research paper

A new type of dynamical matching in an asymmetric Caldera potential energy surface

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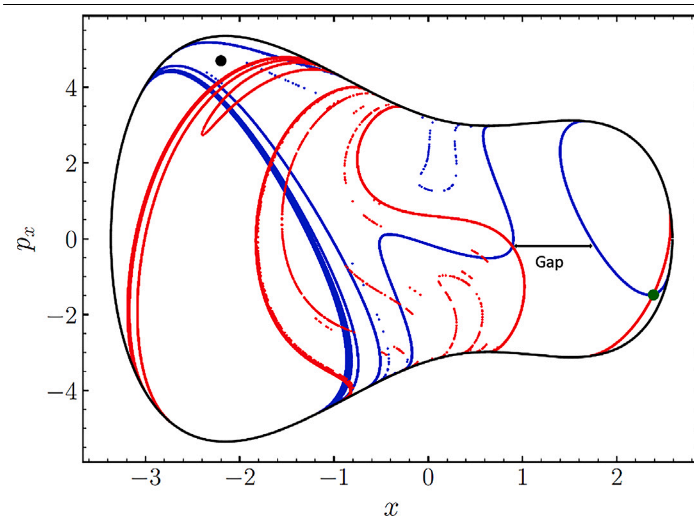
HIGHLIGHTS

- Asymmetric Caldera potential energy surface.
- Influence of asymmetry on dynamical matching.
- Influence of asymmetry on the trapping of trajectories.
- Periodic orbit dividing surfaces and dynamical matching.
- Influence of asymmetry on heteroclinic connections.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated the trajectory behavior associated with the upper index-1 saddles of an asymmetric Caldera potential energy surface. We have found a new type of dynamical matching, and revealed the origin of this trajectory behavior through the use of dividing surfaces and Lagrangian descriptors.

1. Introduction

Potential energy surfaces (PES) have proved to be pivotal in enabling a theoretical understanding of chemical dynamics. By constructing these surfaces through, for instance, interpolation [1,2], free energy direct dynamics sampling [3], or modeling of qualitative behaviors [4], underlying mechanisms of reactions can be exposed [5]. In particular,

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Caldera type PES are characterized by a central minimum surrounded by a relatively flat region and four index-1 saddles (two with high values of energy and two with lower values of energy). The higher energy saddles control entrance to the Caldera region (and are therefore associated with reactants in the chemical context) and the lower energy saddles control exit from the Caldera region (associated with products) [4,6]. Caldera PES have been used to describe many organic chemical reactions, such as the vinylcyclopropane-cyclopentene rearrangement [7,8], the stereomutation of cyclopropane [9], the degenerate rearrangement of bicyclo[3.1.0]hex-2-ene [10,11] or 5-methylenebicyclo[2.1.0] pentane [12]. In those studies the Caldera PES have been symmetric with respect to the simultaneous interchange of the higher energy saddles and the lower energy saddles. These studies have revealed a dynamical phenomenon that has come to be realized to be of importance in organic chemical reactions, and been termed "dynamical matching" (see [6,13]). This phenomenon is characterized by the feature that *all* trajectories that enter the Caldera by crossing the region of the higher energy saddles evolve straight across the Caldera and exit through the region of the opposite lower energy saddle. This happens for both of the higher energy saddles as a result of the symmetry of the PES. It has been reported that dynamical matching may be broken in a symmetric Caldera PES in two cases. One is if the PES is symmetrically stretched in one coordinate direction (see [14–16]) and the other if the critical points of the PES undergo a pitchfork bifurcation, as described in [17,18]. This latter work highlights the fact that the original caldera PES has four index one saddles that control entrance to and exit from the Caldera region. Certainly more, or fewer, index one saddles is a possibility in applications. Our approach would provide a guide for the analysis of such systems, but it ls likely that new phase space transport mechanisms would be possible. We also remark that we do not know of a specific molecular reaction that exhibits the type of dynamical matching that we describe in this paper. Nevertheless, our results may provide insight into interpreting experimental results in situations where dynamics resembling dynamical matching occurs, but the saddle point number and configuration of the PES is different from the original Caldera PES. In this paper we investigate the phenomenon of dynamical matching for an asymmetric Caldera PES and show that fundamentally different dynamical phenomena may occur as a result of the asymmetry. The paper is organized as follows. In Section 2, we describe our model, followed by the results (Section 3) and closing with our conclusions (Section 4).

2. Model

In this section we describe the model under study. The potential takes the form

$$V(x,y) = c_1(x^2+y^2) + c_2 y - c_3(x^4+y^4-6x^2y^2) + c_4 x, \tag{1}$$

which is the symmetric Caldera potential [6], with the addition of the term $c_4 x$ which breaks the horizontal symmetry. Here (x,y) pairs give the position in Cartesian coordinates. In this paper, we set $c_1 = 5, c_2 = 3, c_3 = -0.3$ (as in [13,14]) and $c_4 = 2.5$. This form of Caldera (one central minimum with two upper saddles to correspond to high values of energy and two lower saddles to correspond to lower values of energy) is maintained for values $c_4 \in [0,3]$. In order to emphasize the effects of asymmetry, the value $c_4 = 2.5$ near the extreme end of this range is chosen.

The addition of a kinetic term yields the Hamiltonian

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

where p_x and p_y are the momenta conjugate to x and y respectively, and we take $m = 1$. The equations of motion can be directly computed from the Hamiltonian.

This potential has a similar topography (see Fig. 1) to the symmetric Caldera potential (see [13,14]) except for the non-existence of symmetry with respect to the $x = 0$ axis. It is characterized by a central minimum and four index-1 saddles around it (see for example [6,13–16]). In Table 1, we give the positions of the equilibrium points of our system, as shown in Fig. 1.

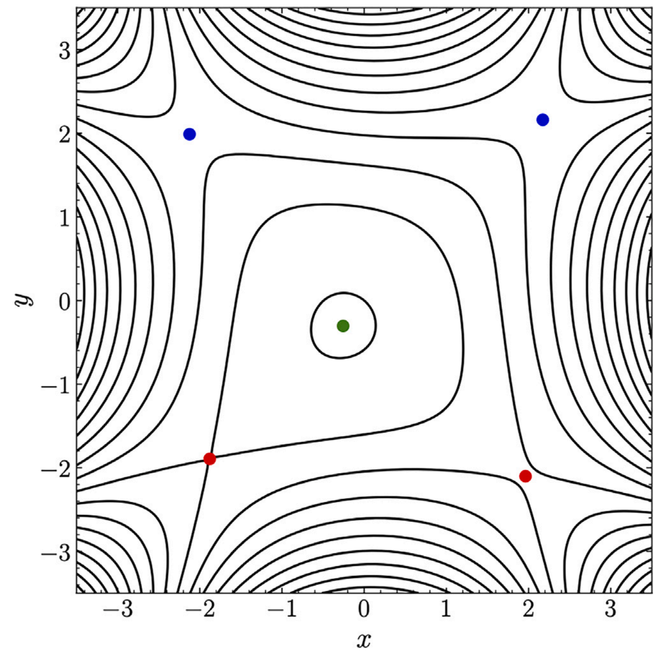

Fig. 1. The contours of an asymmetric case of the Caldera potential (1) for $c_1 = 5, c_2 = 3, c_3 = -0.3, c_4 = 2.5$. The equilibria are plotted as blue points (upper saddles), red points (lower saddles) and a green point (central minimum).

Table 1
Stationary points of the asymmetric Caldera potential for $c_1 = 5, c_2 = 3, c_3 = -0.3$ and $c_4 = 2.5$.

Critical point	x	y	E
Central Minimum (CM)	−0.256	−0.304	−0.77
Upper Right Saddle (URS)	2.173	2.161	32.41
Upper Left Saddle (ULS)	−2.125	1.989	21.67
Lower Right Saddle (LRS)	1.963	−2.101	19.63
Lower Left Saddle (LLS)	−1.880	−1.894	10.01

3. Results

In this section, we will describe a new type of dynamical matching that we have detected in an asymmetric Caldera PES. The upper saddles (blue points in Fig. 1) correspond to the reactants and the lower saddles (red points in Fig. 1) to the formation of products. In the symmetric case of the Caldera we have dynamical matching for trajectories emanating from the regions of both upper saddles. In this paper we will analyze a different type of dynamical matching occurring in the asymmetric Caldera PES.

In the Caldera PES we use periodic orbit dividing surfaces (PODS) in order to monitor the entrance in to and exit out from the Caldera. The dividing surfaces are phase space objects of one dimension less than the energy surface (see for example [19–22]). These surfaces play an important role in transition state theory [23,24] with applications in chemical reaction dynamics [23,24] and dynamical astronomy [25]. These phase space objects can be constructed in Hamiltonian systems with two degrees of freedom (as in our case) using the classical algorithm of [26–30] described in [19–21]. The generalization of the construction of these surfaces in Hamiltonian systems with three degrees of freedom has also been done recently [31–33].

In the symmetric case of the Caldera PES, we have two types of behavior for trajectories with initial conditions on the PODS associated

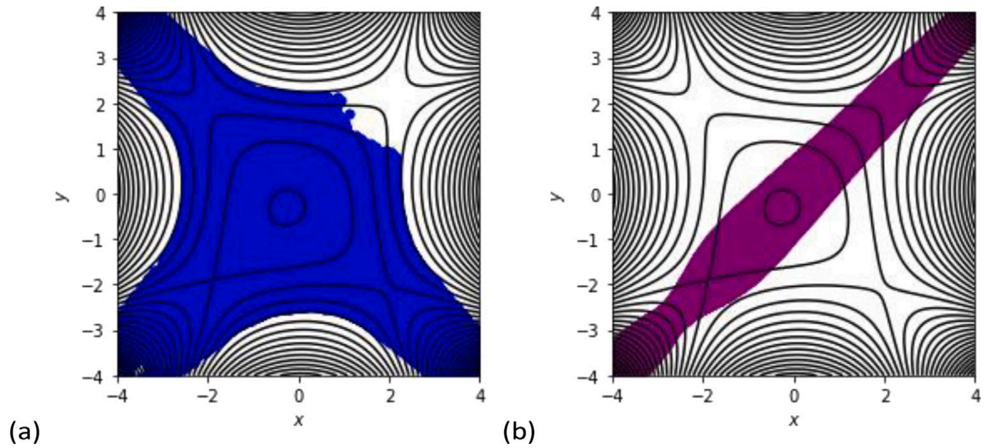

Fig. 2. The evolution of the trajectories (in the configuration space) that are initiated on the periodic orbit dividing surfaces associated with the upper left saddle [that is represented by a blue color—panel (a)] and the upper right saddle [that is represented by a purple color—panel (b)] for the energy value $E = 36$.

with the unstable periodic orbits (UPOs) of the upper saddles. The first type is dynamical matching which was described above. The second type is the trapping of trajectories in the central area of the Caldera for a time interval before they exit through any region of a saddle of the Caldera (see [14–16]). These two behaviors do not coexist in the symmetric case of the Caldera for a fixed value of energy. The phase space mechanism responsible for the type of trajectory behavior is the existence or absence of heteroclinic intersections between the unstable invariant manifolds of the UPOs of upper saddles and the stable invariant manifolds of the UPOs of the central area of the Caldera (see for example [14–16]).

In the asymmetric Caldera PES studied here, we take a uniform sample of 16,000 initial conditions on the PODS associated with the UPOs of the upper saddles for the value of energy $E = 36$ (which is higher than the energy corresponding to the upper saddles). Then we integrate these initial conditions in order to investigate the trajectory behavior associated with this upper saddle. As we can see in Fig. 2, we have the existence of the two types of trajectory behavior simultaneously for the same value of energy. The first type corresponds to the trajectories that are initiated on the dividing surfaces associated with the UPOs of the upper right saddle (URS). The second type corresponds to the trajectories that are initiated on the dividing surfaces associated with the UPOs of the upper left saddle (ULS). This means that we observe for the first time a new type of dynamical matching, which occurs only on one side of the Caldera PES and not on the other.

In order to probe the phase space transport mechanism responsible for this behavior, we used the method of Lagrangian descriptors (LDs) (see the books [34,35] and references therein) in our Caldera-type Hamiltonian system (see [15,16] for the computation of LDs in a Caldera-type system). Using the LDs, we computed the unstable and stable invariant manifolds in the Poincaré section $y = 2$ with $p_y > 0$ for $E = 36$ (see Fig. 3). We choose this section to investigate the behavior of the invariant manifolds of the UPOs of the upper saddles. We see in Fig. 3 that the phase space mechanism for this new type of dynamical matching consists of the coexistence of two phase space mechanisms of the first and second types of trajectory behavior. This is the origin of this new type of dynamical matching.

We observe in Fig. 3 that there is a gap between the unstable invariant manifolds of the UPOs associated with the URS and the stable invariant manifolds of the central area. The unstable invariant manifolds guide the trajectories away from the region of the periodic orbit, but also away from the region of the central area of the Caldera. This can be confirmed by the fact that a trajectory corresponding to an initial condition close to the region of the UPO of the URS (like the green point in Fig. 3) exhibits the first type trajectory behavior [see Fig. 4(a)] indicating the phenomenon of dynamical matching.

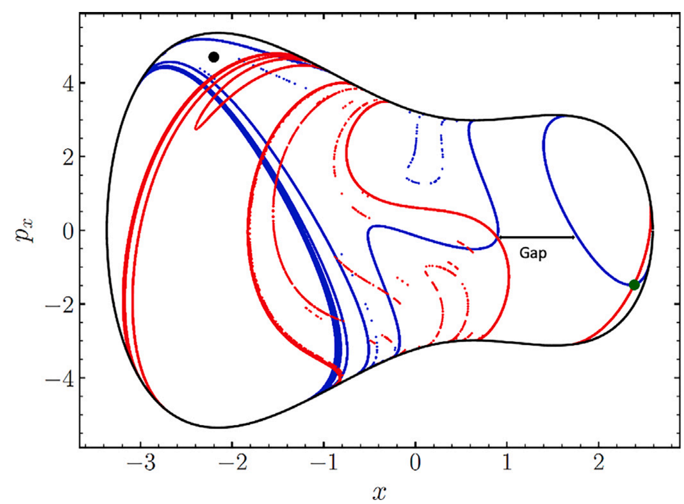

Fig. 3. The invariant manifolds in the 2D slice $y = 2$ with $p_y > 0$, for value of energy $E = 36$. The stable invariant manifolds and the unstable invariant manifolds are demonstrated by blue and red colors. The invariant manifolds are extracted from the gradient of the LDs using $\tau = 4$ for the integration time. The green and black points represent two different initial conditions of trajectories. The time evolution of these trajectories is presented in Fig. 4.

In addition, we see in Fig. 3 that there is an interaction (many heteroclinic intersections) between the unstable invariant manifolds of the UPOs associated with the ULS and the stable invariant manifolds of the central area. This means that many trajectories follow the unstable invariant manifolds of the UPOs associated with the ULS and they are trapped inside the lobes between the heteroclinic intersections. Then they follow the stable invariant manifolds to the central area. An example of this behavior is the trajectory corresponding to the black point in Fig. 3. In Fig. 4(b), we see that this trajectory coming from the region of the ULS is trapped in the central area of the Caldera. The trajectories, that are trapped in the central area of the Caldera, are guided away from the center by the unstable invariant manifolds of the central area, and to the exits from the Caldera (see cases II and III of [13] or the second part of transport in [36]). This can be confirmed by the trajectory corresponding to the black point in Fig. 3 [see Fig. 4(b)].

4. Conclusions

We studied the behavior of trajectories that are initiated at the region of the upper index-1 saddles of an asymmetric Caldera potential

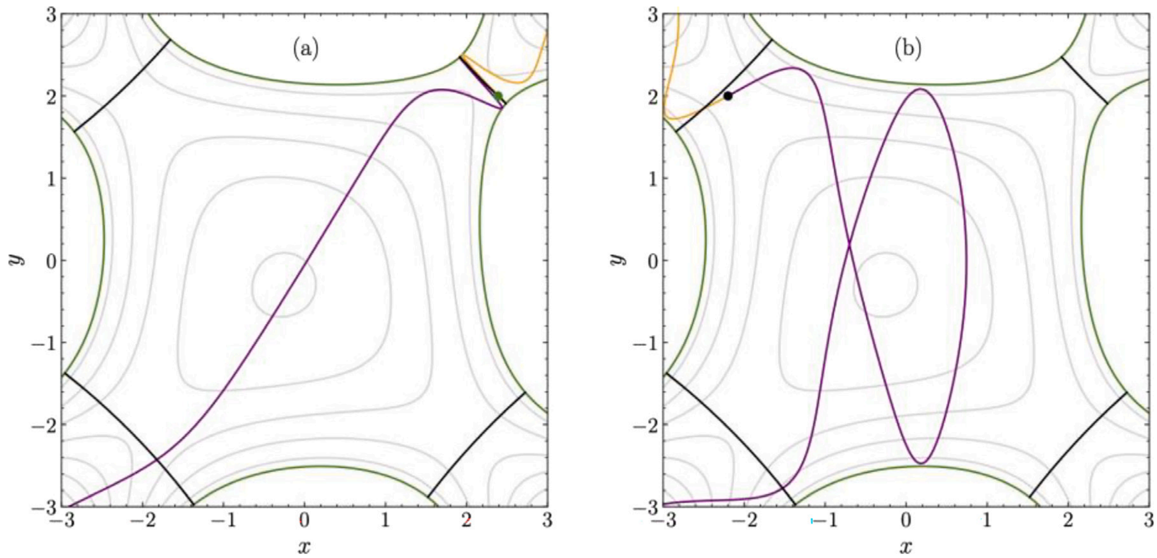

Fig. 4. (a) The forward (purple color) and backward in time (orange color) evolution in the (x, y) configuration space of the trajectory with initial conditions corresponding to the green point in Fig. 3. (b) Similar to (a) but for the trajectory with initial conditions corresponding to the black point in Fig. 3. In both panels the periodic orbits corresponding to each saddle are marked as black lines.

energy surface. We found a new type of dynamical matching, for which we have the coexistence of dynamical matching and trapping in the central area of the Caldera potential energy surface for the trajectories that come from the region of the upper saddles. This is because of the coexistence of two phase space mechanisms of transport. These mechanisms are based on the interaction or the gap between the unstable invariant manifolds of the unstable periodic orbits of the upper saddles and the stable invariant manifolds of the central area.

CRediT authorship contribution statement

M. Katsanikas: Conceptualization, Methodology, Investigation, Computations, Figure preparation, Visualization, Writing – original draft, Writing – review & editing. **M. Hillebrand:** Conceptualization, Methodology, Investigation, Computations, Figure preparation, Visualization, Reviewing and editing. **Ch. Skokos:** Conceptualization, Methodology, Investigation, Visualization, Reviewing and editing, Funding acquisition. **S. Wiggins:** Conceptualization, Methodology, Investigation, Visualization, Writing – original draft, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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