Finding NHIM: Identifying High Dimensional Phase Space Structures in Reaction Dynamics using Lagrangian Descriptor

CHAMPS
Chemistry and Mathematics in Phase Space

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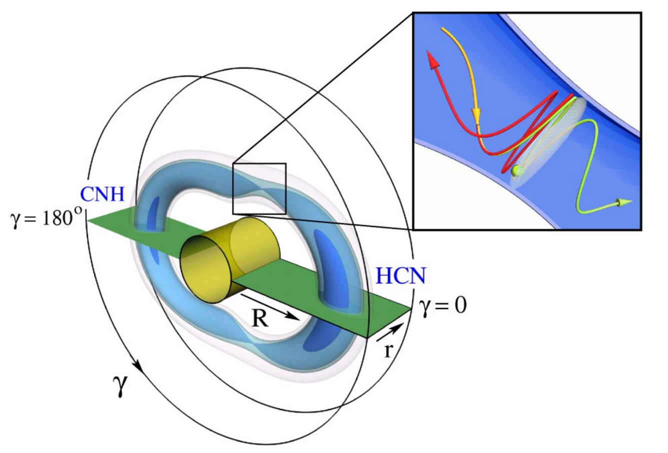
1. Motivation and goal



Shown here is the equipotential surface for the three degrees-of-freedom HCN/CNH isomerization along with example trajectories that cross to HCN side and stay on the CNH side. The potential energy is in terms on Jacobi coordinates (r, R, γ) and low (high) equipotential values are mapped to dark (light) blue color. Adapted from Ref. [1].

The phase space structures — such as the dividing surface (shown as the white translucent surface), normally hyperbolic invariant manifold, its stable and unstable manifolds — associated with the barrier between the two sides form the skeleton of the reaction dynamics.

Our objective is to identify the high dimensional phase space structures using an isoenergetic two-dimensional surface.

2. Benchmark system: 3 degrees-of-freedom decoupled Hamiltonian

When the "reactive" and "non-reactive" coordinates are decoupled as presented in Ref. [2], the 3 DoF quadratic Hamiltonian is given by

$$H(q_1,p_1,q_2,p_2,q_3,p_3) = \underbrace{\frac{\lambda}{2}\left(p_1^2 - q_1^2\right)}_{H_r} + \underbrace{\frac{\omega_2}{2}\left(p_2^2 + q_2^2\right)}_{H_{b_1}} + \underbrace{\frac{\omega_3}{2}\left(p_3^2 + q_3^2\right)}_{H_{b_2}}, \quad \lambda,\ \omega_2,\ \omega_3 > 0$$

For a fixed energy $H(q_1,p_1,q_2,p_2,q_3,p_3) = h$, the dividing surface is defined by $q_1 = 0$ and given by

$$\frac{\lambda}{2}p_1^2 + \frac{\omega_2}{2}\left(p_2^2 + q_2^2,\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2,\right) = H_r + H_{b_1} + H_{b_2} > 0, \quad H_r > 0,\ H_{b_1}, H_{b_2} \geqslant 0.$$

The two hemispheres ($p_1 > 0$ and $p_1 < 0$) "meet" at $p_1 = 0$ along

$$\mathcal{M}(h) := \frac{\omega_2}{2}\left(p_2^2 + q_2^2,\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2,\right) = H_{b_1} + H_{b_2} \geqslant 0,$$

which is a *normally hyperbolic invariant manifold* (NHIM) of geometry $\mathbb{S}^3$.

The stable and unstable manifolds of the NHIM are

$$\mathcal{W}^{u/s}(\mathcal{M}(h)) := \Big\{(q_1,p_1,q_2,p_2,q_3,p_3) \mid q_1 = p_1/q_1 = -p_1, \frac{\omega_2}{2}\left(p_2^2 + q_2^2\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2\right) = H_{b_1} + H_{b_2} > 0\Big\}.$$

3. Benchmark system: 3 degrees-of-freedom coupled Hamiltonian

Consider the symplectic transformation

$$C = \begin{pmatrix} 0_{3\times3} & I_{3\times3} \\ -I_{3\times3} & J_{3\times3} \end{pmatrix},$$ where $0_{3\times3}, I_{3\times3}, J_{3\times3}$ are the zero, identity, and the unit matrix, respectively.

This transformation applied to (1) gives a 3 degrees-of-freedom coupled Hamiltonian

$$\mathcal{H}(x,p_x,y,p_y,z,p_z) = \frac{\lambda}{2}\left[(-x+p_x+p_y+p_z)^2 - p_x^2\right] + \frac{\omega_2}{2}\left[(-y+p_x+p_y+p_z)^2 + p_y^2\right] + \frac{\omega_3}{2}\left[(-z+p_x+p_y+p_z)^2 + p_z^2\right]$$

For a fixed energy $\mathcal{H}(x,p_x,y,p_y,z,p_z) = h$, the dividing surface is defined by $p_x = 0$ and given by

$$\frac{\lambda}{2}\left[(-x+p_y+p_z)^2\right] + \frac{\omega_2}{2}\left[p_y^2 + (-y+p_y+p_z)^2\right] + \frac{\omega_3}{2}\left[p_z^2 + (-z+p_y+p_z)^2\right] = h.$$

On the dividing surface, the NHIM is defined by $-x+p_x+p_y+p_z = 0$ that is $p_y + p_z = x$, and given by

$$\mathcal{M}(h) := \frac{\omega_2}{2}\left[(x-p_z)^2 + (x-y)^2\right] + \frac{\omega_3}{2}\left[p_z^2 + (x-z)^2\right] = h.$$

Next, in the coupled coordinates, the stable and unstable manifolds of the NHIM are given by

$$\mathcal{W}^{u/s}(\mathcal{M}(h)) := \Big\{(x,p_x,y,p_y,z,p_z) \mid x = p_y + p_z / x = 2p_x + p_y + p_z, \frac{\omega_2}{2}\left((-y+p_x+p_y+p_z)^2 + p_y^2\right) + \frac{\omega_3}{2}\left((-z+p_x+p_y+p_z)^2 + p_z^2\right) = h\Big\}.$$

4. Method of Lagrangian descriptor

Consider a general dynamical system

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

where $\mathbf{v}(\mathbf{x},t) \in C^r$ $(r \geq 1)$ in $\mathbf{x}$ and continuous in time. Developed in Refs. [3, 4], the Lagrangian descriptor for an initial condition $\mathbf{x}_0 = \mathbf{x}(t_0)$ at time t_0 and for an integration time τ is

$$M_p(\mathbf{x}_0, t_0, \tau) := \int_{t_0-\tau}^{t_0+\tau} \sum_{i=1}^{n} |\dot{x}_i(t;\mathbf{x}_0)|^p \, dt$$

where $p \in (0,1]$ and $\tau \in \mathbb{R}^+$ are freely chosen parameters, and the overdot symbol represents the derivative with respect to time. We will use $p = 0.5$ and $\tau = 10$ in this study.

5. Lagrangian descriptor and invariant manifolds: 3 DoF decoupled Hamiltonian

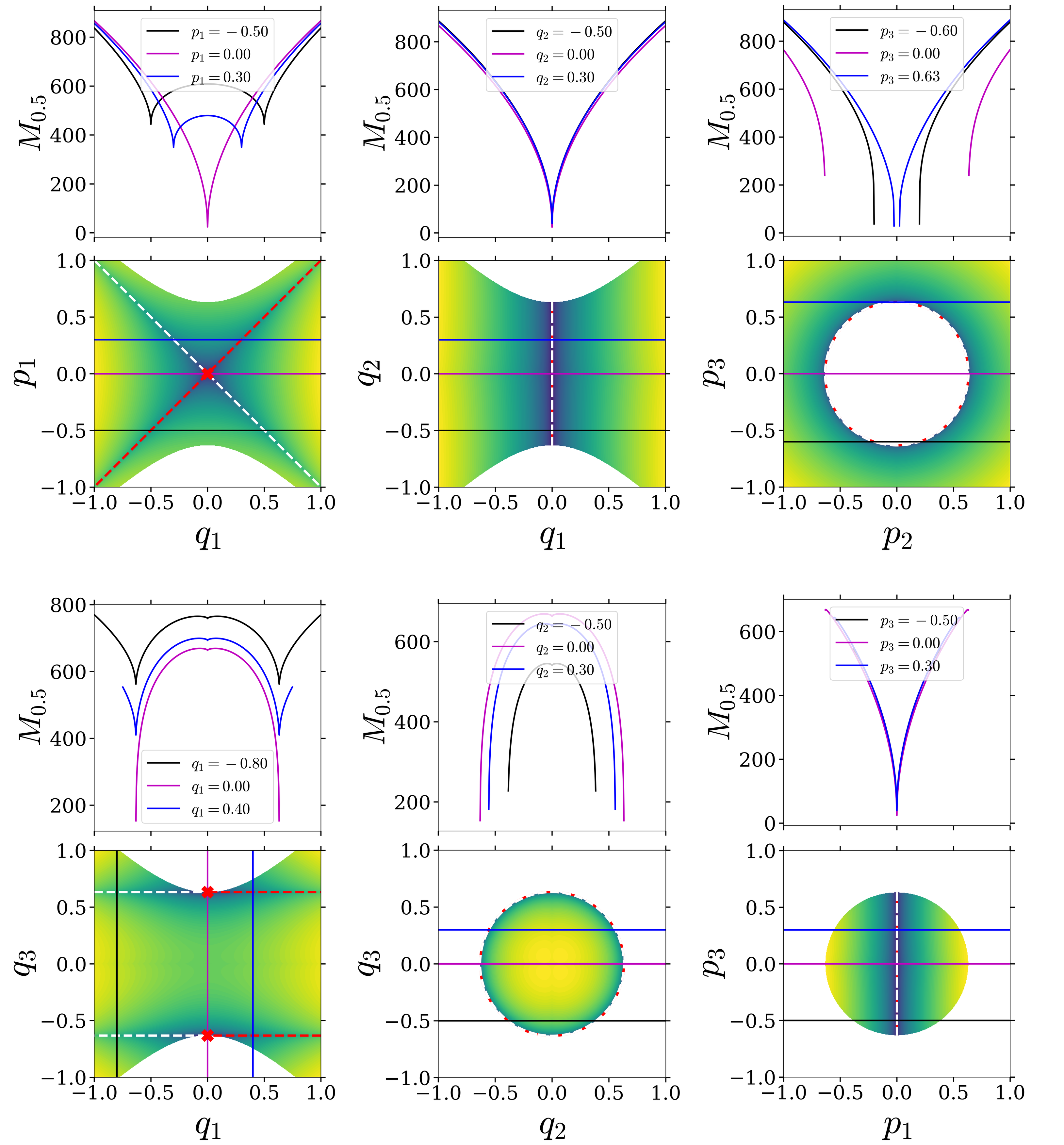
For example, the intersection of the isoenergetic two-dimensional surface

$$U^+_{q_1p_1} = \{(q_1,p_1,q_2,p_2,q_3,p_3) \mid q_2 = 0, p_2 = 0, q_3 = 0, \dot{q}_3 > 0 : p_3(q_1,p_1,q_2,p_2,q_3;h) > 0\},$$

with the NHIM (1) becomes

$$\mathcal{M}(h) \cap U^+_{q_1p_1} = \{(q_1,p_1,q_2,p_2,q_3,p_3) \mid q_1 = 0, p_1 = 0, q_2 = 0, p_2 = 0, q_3 = 0, \dot{q}_3 > 0 : p_3(q_1,p_1,q_2,p_2,q_3;h) > 0\}.$$

which is a point at the origin $(0,0)$ shown in the left most Lagrangian descriptor plot in the panel below.



6. Lagrangian descriptor and invariant manifolds: 3 DoF coupled Hamiltonian

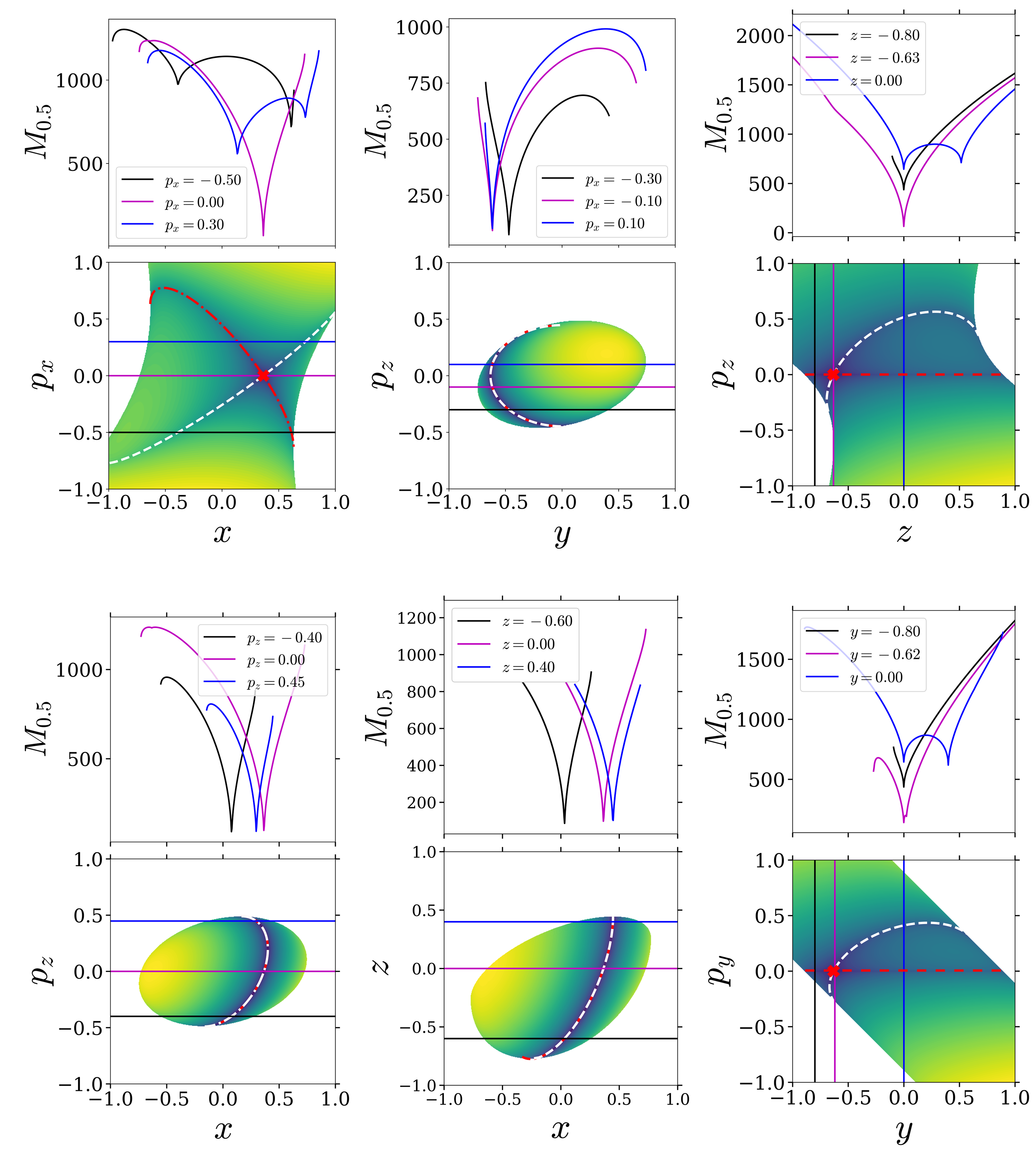
For example, the intersection of the isoenergetic two-dimensional surface

$$U^+_{xp_x} = \{(x,p_x,y,p_y,z,p_z) \mid y = 0, z = 0, p_y = 0, p_z(x,p_x,y,p_y,z;h) > 0 : \dot{z}(x,y,z,p_x,p_y,p_z) > 0\},$$

with the NHIM (1) becomes

$$\mathcal{M}(h) \cap U^+_{xp_x} = \Big\{(x,p_x,y,p_y,z,p_z) \mid y = 0, z = 0, p_y = 0, p_x = 0, p_y + p_z = x, \frac{\omega_2}{2}\left((x-p_z)^2 + x^2\right) + \frac{\omega_3}{2}\left(p_z^2 + x^2\right) = h, \dot{z}(x,p_x,y,p_y,z,p_z) > 0 : x > 0\Big\}.$$

which is a point on the line $p_x = 0$ shown in the left most Lagrangian descriptor plot in the panel below.



Minima and singular features in Lagrangian descriptors on isoenergetic two-dimensional surfaces identify the NHIM and its invariant manifolds' intersection with the surfaces. Based on this proof of concept, we are now turning our focus towards more realistic molecular systems.

References

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[3] A. M. Mancho, S. Wiggins, J. Curbelo, and C. Mendoza, "Lagrangian Descriptors: A Method for Revealing Phase Space Structures of General Time Dependent Dynamical Systems." *Communications in Nonlinear Science and Numerical*, vol. 18, pp. 3530–3557, 2013.

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