TRANSITION STATE GEOMETRY NEAR HIGHER-RANK SADDLES IN PHASE SPACE

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Workshop on Dynamical Systems and Applications
BCAM, Bilbao (Spain), December 10th–11th (2013)
1 Rank-1 Saddles

2 Rank-\(m\) (\(m > 1\)) Saddles
   - Generalisation of the Transition State
   - Example: Ionization of the Helium Atom
1. Rank-1 Saddles

2. Rank-\(m\) \((m > 1)\) Saddles
   - Generalisation of the Transition State
   - Example: Ionization of the Helium Atom
Transition State Theory (TST) provides at the same time a simple way to compute reaction rates, and an intuitive understanding of the implied dynamical mechanism. It was started by E.P. Wigner around 1930.

The key idea is to define the TS in phase space, where (locally) a surface of no return can be defined.

The hypervolumes of initial conditions leading to products are identified, thus allowing a correct and explicit calculation of the corresponding reactive flux.
Need of Algorithms

- **Very precise determination** of the geometrical structures that play a role in the reaction.

- Calculation of **reaction rates** related to the flux through the Transition State.

- **Visualization strategies** for trajectories, periodic solutions, invariant tori, manifolds, TS, . . .
We start with a Hamiltonian system of the type:

\[ \mathcal{H} = \sum_{i=1}^{n-1} \frac{\omega_i}{2} (p_i^2 + q_i^2) + \lambda q_n p_n + f_1(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}, \mathcal{I}) + f_2(q_1, \ldots, q_{n-1}, p_1 \ldots, p_{n-1}) \]

where

- \((q_1, \ldots, q_n, p_1, \ldots, p_n)\) denote canonical coordinates;
- \(\mathcal{I} \equiv p_n q_n\);
- \(f_1, f_2\) are functions of order three, at least;
- \(f_1(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}, 0) = 0\).
The normally hyperbolic invariant manifold (NHIM) is the intersection of the central manifold of the origin with the energy surface given through:

\[ E = \sum_{i=1}^{n-1} \frac{\omega_i}{2} (p_i^2 + q_i^2) + \lambda q_n p_n \]

\[ + f_1(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}, I) \]

\[ + f_2(q_1, \ldots, q_{n-1}, p_1 \ldots, p_{n-1}) = h = C > 0. \]
The dynamics associated with $\mathcal{H}$ takes place on the energy surface of dimension $2n - 1$.

The normally hyperbolic invariant manifold associated with $\mathcal{H}$ is given through:

$$\mathcal{M}_h^{2n-3} = \left\{ (q_1, \ldots, q_n, p_1, \ldots, p_n) \mid q_n = p_n = 0, \right. $$

$$\sum_{i=1}^{n-1} \omega_i \frac{1}{2} (p_i^2 + q_i^2) + f_2(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1})$$

$$= h = C > 0 \right\}.$$

The NHIM acts as a multidimensional saddle and its dimension is $2n - 3$. 
The stable manifold of the NHIM is:

\[ W^s \left( \mathcal{M}_{h}^{2n-3} \right) = \left\{ (q_1, \ldots, q_n, p_1, \ldots, p_n) \mid q_n = 0, \right. \]
\[ \left. \sum_{i=1}^{n-1} \frac{\omega_i}{2} \left( p_i^2 + q_i^2 \right) + f_2(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}) = h = C > 0 \right\}. \]

The unstable manifold of the NHIM is:

\[ W^u \left( \mathcal{M}_{h}^{2n-3} \right) = \left\{ (q_1, \ldots, q_n, p_1, \ldots, p_n) \mid p_n = 0, \right. \]
\[ \left. \sum_{i=1}^{n-1} \frac{\omega_i}{2} \left( p_i^2 + q_i^2 \right) + f_2(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}) = h = C > 0 \right\}. \]

They are \((2n - 2)\)-dimensional objects which act as multidimensional separatrices.
The transition state for this system is obtained by taking $q_n = p_n$:

$$\mathcal{T} S_h^{2n-2} = \left\{ (q_1, \ldots, q_n, p_1, \ldots, p_n) \mid q_n = p_n, \right.$$ 

$$\sum_{i=1}^{n-1} \omega_i \frac{1}{2} (p_i^2 + q_i^2) + f_1(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}, p_n^2) + f_2(q_1, \ldots, q_{n-1}, p_1, \ldots, p_{n-1}) = h = C > 0 \right\}.$$ 

It has the following properties:

1. The trajectories crossing the transition state correspond to reactive trajectories.
2. The transition state is a “surface of no return” existing in the original Hamiltonian in fact.
3. The transition state is a sphere of dimension $2n - 2$.
4. All reactive particles must pass through the transition state.
Projection of a forward and backward reacting trajectory into the $q_n p_n$ plane
Normal Forms and Transition State Theory

Once the normal form is obtained we can compute analytically the expressions of the NHIM, its stable and unstable manifolds and the transition state in the original coordinates, let us say,

\[(Q, P) = (Q_1, \ldots, Q_n, P_1, \ldots, P_n)\]

in terms of the so-called “normal form” coordinates, let us say,

\[(q, p) = (q_1, \ldots, q_n, p_1, \ldots, p_n).\]

First we compute the direct change of coordinates, relating \((Q, P)\) with \((q, p)\).

- The NHIM is obtained by setting \(q_n = p_n = 0\);
- the stable manifold of the NHIM is obtained by setting \(q_n = 0\);
- the unstable manifold of the NHIM is obtained by doing \(p_n = 0\);
- the transition state results after making \(q_n = p_n\).
1 Rank-1 Saddles

2 Rank-$m$ ($m > 1$) Saddles

- Generalisation of the Transition State
- Example: Ionization of the Helium Atom
Equilibria with linearisation:

\[ \text{centre} \times \ldots \times \text{centre} \times \text{saddle} \times \ldots \times \text{saddle} \]

Is it interesting to apply the transition state theory to rank-\(m\) saddles?

1. The transition state as formulated with the standard theory does not separate the phase space conveniently.
2. It is not possible to apply the standard theory.
3. There are interesting examples in several fields.
Applications

- Celestial Mechanics:
  1. Three-body problems where one of the bodies is a gyrostat.
  2. Restricted full three-body problems (one of the primaries is a sphere and the other one is a triaxial ellipsoid).
  3. Elliptic Restricted Three Body Problem, around the periodic solutions $L_1$, $L_2$ and $L_3$ in the case that the linearisation is centre $\times$ saddle $\times$ saddle.

- Molecular Dynamics and Atomic Physics:
  1. Lennard-Jones potentials used to model molecular reactions with a high number of atoms.
  2. An atom subject to an electric field.
Elliptic Restricted Three Body Problem #1

(With Shinnosuke Kawai, Hokkaido University)

Elliptic restricted three-body problem in 3D:

After linearising around $L_1$, $L_2$ and $L_3$ and using symplectic Floquet theory to transform the periodic linear vector field into an autonomous linear vector field, the characteristic multiplier related to the periodic solutions are:

$$\text{centre} \times \text{centre} \times \text{saddle}$$

$$\text{centre} \times \text{saddle} \times \text{saddle}$$

$$\text{saddle} \times \text{saddle} \times \text{saddle}$$

It appears when handling cases where the eccentricity of the primaries is moderately high: useful for exoplanets, science missions around comets and asteroids, etc.
For each $L_i$ we have calculated 1600 monodromy matrices

1. Evolution of the NHIM according to the parameters of the problem: the eccentricity of the primaries $e_p$ and the mass ratio $\mu$.

2. How does the transition state and the related invariant manifolds behave when the saddles are of rank two?
The quadratic part of the Hamilton function is:

$$H_2 = \sum_{i=1}^{m} \frac{\omega_i}{2} (p_i^2 + q_i^2) + \sum_{i=m+1}^{n} \lambda_i q_i p_i$$

and the eigenvalues satisfy

$$0 \leq \lambda_{m+1} \leq \lambda_{m+2} \leq \ldots \leq \lambda_{n-1} < \lambda_n.$$
The spaces $E^c$, $E^s$ and $E^u$ are the usual linear invariant manifolds of $\mathbb{R}^n$ whose respective dimensions are $2m$, $n - m$ and $n - m$.

We define two linear spaces:

- $\hat{E}^s$ is the linear stable invariant manifold of dimension $n - m - 1$ spanned by the eigenvectors related to the eigenvalues $-\lambda_{m+1}, \ldots, -\lambda_{n-1}$.

- $\hat{E}^u$ is the linear unstable invariant manifold of dimension $n - m - 1$ spanned by the eigenvectors related to the eigenvalues $\lambda_{m+1}, \ldots, \lambda_{n-1}$.
The pseudo-unstable invariant manifold of the origin related to $\lambda_{n-1}$: maximal invariant subspace in which the norm of solutions grows, stays constant, or decays no faster than $e^{-\lambda_{n-1} t}$:

$$E_{\lambda_{n-1}}^u = E^c \times \hat{E}^s \times E^u.$$ 

The pseudo-stable invariant manifold of the origin related to $\lambda_{n-1}$: maximal invariant subspace in which the norm of solutions decays, stays constant, or grows no faster than $e^{\lambda_{n-1} t}$:

$$E_{\lambda_{n-1}}^s = E^c \times E^s \times \hat{E}^u.$$ 

Both spaces are $(2n - 1)$–dimensional.
Taking
\[ C = E_{\lambda_{n-1}}^s \cap E_{\lambda_{n-1}}^u = E^c \times \hat{E}^s \times \hat{E}^u \]
and
\[ \mathcal{E}_h = \left\{ (q_1, \ldots, q_n, p_1, \ldots, p_n) \mid H_2(q, p) = h > 0 \right\} \]
we define the linear pseudo normally hyperbolic invariant manifold (pseudo-NHIM) as:
\[ \mathcal{M}_{h}^{2n-3} = \mathcal{E}_h \cap C \]
\[ = \left\{ (q_1, \ldots, q_n, p_1, \ldots, p_n) \mid \sum_{i=1}^{m} \frac{\omega_i}{2} (p_i^2 + q_i^2) + \sum_{i=m+1}^{n-1} \lambda_i q_i p_i = h, \quad q_n = p_n = 0 \right\}. \]

It is unbounded.
Linear Pseudo-Stable and Pseudo-Unstable Manifolds of the NHIM

Its stable and unstable manifolds are $(2n - 2)$-dimensional and separate the phase space:

$$W^s \left( \mathcal{M}_{h}^{2n-3} \right) = \left\{ (q_1, \ldots , q_n, p_1, \ldots , p_n) \mid \sum_{i=1}^{m} \frac{\omega_i}{2} (p_i^2 + q_i^2) + \sum_{i=m+1}^{n-1} \lambda_i q_i p_i = h, \quad p_n = 0 \right\},$$

$$W^u \left( \mathcal{M}_{h}^{2n-3} \right) = \left\{ (q_1, \ldots , q_n, p_1, \ldots , p_n) \mid \sum_{i=1}^{m} \frac{\omega_i}{2} (p_i^2 + q_i^2) + \sum_{i=m+1}^{n-1} \lambda_i q_i p_i = h, \quad q_n = 0 \right\}.$$
We define it as:

\[ \mathcal{T}S^{2n-2} \left( \mathcal{M}_{h}^{2n-3} \right) = \left\{ (q_{1}, \ldots, q_{n}, p_{1}, \ldots, p_{n}) \mid \sum_{i=1}^{m} \frac{\omega_{i}}{2} (p_{i}^{2} + q_{i}^{2}) + \sum_{i=m+1}^{n-1} \lambda_{i} q_{i} p_{i} + \lambda_{n} q_{n}^{2} = h, \; p_{n} = q_{n} \right\}. \]

- Its dimension is \( 2n - 2 \).
- It is not an invariant manifold.
- It is unbounded and contains the NHIM \( \mathcal{M}_{h}^{2n-3} \).
Full Hamiltonian

Problem

- The nonlinear continuation of $W^s(M_{h}^{2n-3})$ and $W^u(M_{h}^{2n-3})$ cannot be done using the standard theory for NHIMs.

- The reason is that $M_{h}^{2n-3}$ is not bounded.

Solution

- We make a nonlinear continuation of $E^s_{\lambda_{n-1}}$ (resp. $E^u_{\lambda_{n-1}}$) in order to obtain the pseudo-stable (resp. pseudo-unstable) $W^{ps}(0)$ (resp. $W^{pu}(0)$) tangent to $E^s_{\lambda_{n-1}}$ (resp. $E^u_{\lambda_{n-1}}$) of dimension $2n - 1$ and of class $C\bar{r}$, where $\bar{r} = \min \{ [\lambda_n/\lambda_{n-1}] , r \}$ and the Hamiltonian $H$ is of class $C^r$.

- Both $W^{ps}(0)$ and $W^{pu}(0)$ are invariant manifolds.

- They are not unique but are tangent to $E^s_{\lambda_{n-1}}$ and $E^u_{\lambda_{n-1}}$, that are unique.
Nonlinear Pseudo-NHIM

If \( \tilde{\mathcal{E}}_h \) is the nonlinear energy surface (for fixed \( h > 0 \)), we define:

\[
W_h^{ps} = W^{ps}(0) \cap \tilde{\mathcal{E}}_h \quad \text{and} \quad W_h^{pu} = W^{pu}(0) \cap \tilde{\mathcal{E}}_h,
\]

which are of codimension 1 in \( \tilde{\mathcal{E}}_h \).

Then

\[
\tilde{\mathcal{M}}_h^{2n-3} = W_h^{ps} \cap W_h^{pu}
\]

is a smooth continuation of the surface \( \mathcal{M}_h^{2n-3} \) for \( h \) small enough.

\( \tilde{\mathcal{M}}_h^{2n-3} \) is the nonlinear pseudo-NHIM of dimension \( 2n - 3 \).

- It is not compact as it has \( n - m - 1 \) hyperbolic directions.
- The nonlinear TS is built in a similar way to the linear case.
1. **Rank-1 Saddles**

2. **Rank-\(m\) (\(m > 1\)) Saddles**
   - Generalisation of the Transition State
   - Example: Ionization of the Helium Atom
Initial Hamiltonian (three-body problem: the nucleus and two electrons):

\[
H = \frac{1}{2} \left( P_{\rho_1}^2 + \frac{P_{\phi_1}^2}{\rho_1^2} + P_{z_1}^2 \right) + \frac{1}{2} \left( P_{\rho_2}^2 + \frac{P_{\phi_2}^2}{\rho_2^2} + P_{z_2}^2 \right) - E(t)(z_1 + z_2) \\
- \frac{2}{\sqrt{\rho_1^2 + z_1^2}} - \frac{2}{\sqrt{\rho_2^2 + z_2^2}} \\
+ \frac{1}{\sqrt{\rho_1^2 + \rho_2^2 - 2 \rho_1 \rho_2 \cos(\phi_1 - \phi_2) + (z_1 - z_2)^2}}.
\]

The problem is of five degrees of freedom, and is autonomous if the electric field is chosen to be conservative.
Figure 8. The physical coordinates. The physical variables are chosen to be the cylindrical coordinates and corresponding momenta of each of the electrons. The presence of the electric field gives rise to a Stark barrier. To ionize classically the electrons must escape over this barrier (quantum-mechanically they can also ionize by tunnelling under the barrier). If the external electric field is taken to be constant the Hamiltonian system defining the problem is autonomous. The Stark barrier gives rise to a fixed point in the ten-dimensional phase space associated with the five degrees of freedom. This fixed point is a rank-two saddle. In other words, it has three stable or elliptic directions (central directions) and two unstable or hyperbolic directions. One of the unstable directions is associated with the non-sequential (or correlated) ionization (He → He\(^{2+}\) + 2 e\(^{-}\)) while the second unstable direction is associated with the non-sequential (or correlated) exchange (He\(^{+}\) + e\(^{-}\) (A) → He\(^{+}\) + e\(^{-}\) (B)).
Results

1. We have computed the normal forms to degree 12. Computing the local integrals, the errors are of the order of $10^{-10}$ within balls of radii $1/5$.

![Graph showing logarithm of error vs degree. The graph has a linear fit to the data.]

2. We have found the nonlinear transition state, the NHIM and the rest of structures (stable and unstable manifolds of the NHIM, periodic solutions and hyperbolic tori of dimensions 2 and 3).
Main idea for the projections: collect the unessential elliptic directions. Green (NHIM), yellow (TS), red/blue (stab./unst. manifold of NHIM).
Manifolds and Trajectories #2
Reactive and Nonreactive Trajectories

Two very close trajectories: the yellow solution reacts and the red one does not.
Almost identical initial conditions but yielding to different situations: (a) The two electrons ionise; (b) no electron ionises.
Electrons that Ionise and Electrons that Do Not Ionise

Seen in the physical space:

(a) (b) (c)
Another Example

(a) No ionisation. (b) Double ionisation.