Classical and quantum reaction dynamics in multidimensional systems

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Joint work with

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- Steve Wiggins

→ Nonlinearity **21** (2008) R1-R118

Classical and quantum reaction dynamics in multidimensional systems

Transformations (like chemical reactions) are mediated by phase space "bottlenecks" (transition states)

Transition State Theory (Eyring, Polanyi, Wigner 1930s)

- Compute reaction rate from directional flux through 'dividing surface' in the transition state region

⇒ Computational benefits:

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Key problems and interests

- Dividing surface needs to have ‘no recrossing property’, i.e. it is to be crossed exactly once by all reactive trajectories and not crossed at all by non-reactive trajectories
- How to construct a dividing surface with these properties for multidimensional systems?
- Experiments indicate
  - transition states are more than merely a formal concept, but of physical significance
    - ‘supermolecules’ poised between reactants and products
  - the *dynamics* of reactions is important
    - violation of ergodicity assumptions (non RRKM behaviour; IVR)
- Understanding the mechanisms that govern reaction dynamics is a prerequisite for the control of chemical reactions
- How to formulate and realise a quantum version of transition state theory?

(see, e.g., E. Pollak & P. Talkner. (2005) Reaction rate theory: What it was, where it is today, and where is it going? *Chaos* **15** 026116)

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Classical Reaction Dynamics in Multidimensional Systems

Phase Space Conduits for Reaction

Phase Space Structures near a Saddle

Setup

Consider f-degree-of-freedom Hamiltonian system $(\mathbb{R}^{2f}(p_1,\ldots,p_f,q_1,\ldots,q_f),\omega=\sum_{k=1}^{f}\mathrm{d}p_k\wedge\mathrm{d}q_k)$ and Hamilton function $\mathcal{H}$.

Assume that the Hamiltonian vector field

$$\begin{pmatrix}\dot{p}\\ \dot{q}\end{pmatrix}=\begin{pmatrix}-\frac{\partial\mathcal{H}}{\partial q}\\ \frac{\partial\mathcal{H}}{\partial p}\end{pmatrix}\equiv J\,\mathrm{D}\mathcal{H}\,,\qquad J=\begin{pmatrix}0 & -1\\ 1 & 0\end{pmatrix}$$

has saddle-centre-. . .-centre equilibrium point ('saddle' for short) at the origin, i.e.

$$J\,\mathrm{D}^2\mathcal{H}\text{ has eigenvalues }\pm\lambda,\ \pm\mathrm{i}\omega_2,\ \ldots,\ \pm\mathrm{i}\omega_f,\qquad \lambda,\omega_k>0$$

Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

Simplest case

Consider Hamilton function

$$\begin{aligned} \mathcal{H} &= \tfrac{1}{2}p_x^2 - \tfrac{1}{2}\lambda^2 x^2 + \tfrac{1}{2}p_y^2 + \tfrac{1}{2}\omega_y^2 y^2 \\ &=: \mathcal{H}_x + \mathcal{H}_y \end{aligned}$$

- corresponding vector field is

$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = J\,D\mathcal{H} = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial p_x} \\ \frac{\partial \mathcal{H}}{\partial p_y} \\ \frac{\partial \mathcal{H}}{\partial x} \\ \frac{\partial \mathcal{H}}{\partial y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

- $\mathcal{H}_x$ and $\mathcal{H}_y$ are conserved individually,

$$\mathcal{H}_x = E_x \in \mathbb{R}, \quad \mathcal{H}_y = E_y \in [0, \infty), \quad \mathcal{H} = E = E_x + E_y \in \mathbb{R}$$

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Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

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Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

$E < 0$:

Rewrite energy equation $\mathcal{H} = E$ as

$$\underbrace{E + \frac{1}{2}\lambda^2 x^2 = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2}_{} \simeq S^2 \text{ for } x \in (-\infty, -\frac{\sqrt{-2E}}{\lambda}) \text{ or } x \in (\frac{\sqrt{-2E}}{\lambda}, \infty)$$

⇒ Energy surface

$$\Sigma_E = \{\mathcal{H} = E\}$$

consists of two disconnected components representing 'reactants' and 'products'

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⇒ Energy surface

$$\Sigma_E = \{\mathcal{H} = E\} \simeq S^2 \times \mathbb{R} \quad (\textit{spherical cylinder})$$

⇒ Σ_E bifurcates at $E = 0$ (the energy of the saddle) from *two* disconnected components to a *single* connected component

- Consider projection of Σ_E to $\mathbb{R}^3(x, y, p_y)$, i.e. project out

$$p_x = \pm\sqrt{2E - p_y^2 + \lambda^2 x^2 - \omega_y^2 y^2}$$

which gives two copies for the two signs of p_x

Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

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Linear vector field for $f = 2$ degrees of freedom

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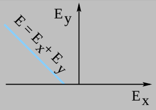
Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

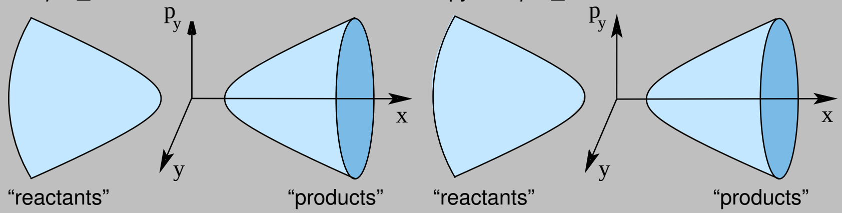
Σ_E for $E < 0$



$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

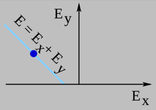
- Σ_E consists of two components representing reactants and products

copy with $p_x \geq 0$ copy with $p_x \leq 0$



Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E < 0$



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- all trajectories have $\mathcal{H}_x = E_x < 0$ and hence are non-reactive

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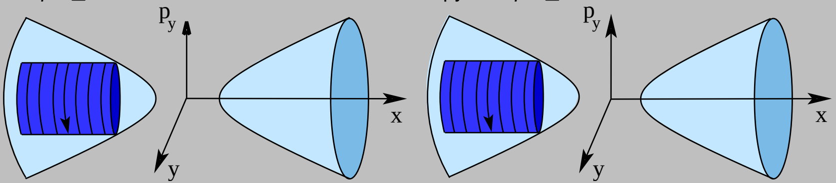
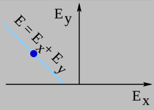


non-reactive trajectory on the side of reactants

Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E < 0$



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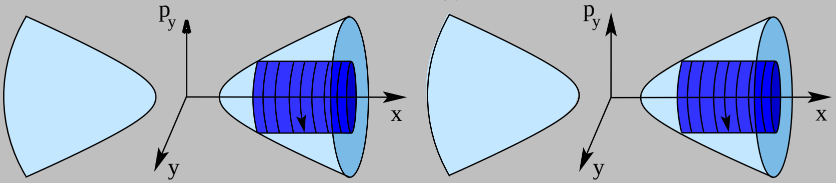
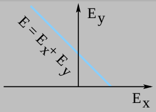


non-reactive trajectory on the side of products

Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



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- $\Sigma_E \simeq S^2 \times \mathbb{R}$

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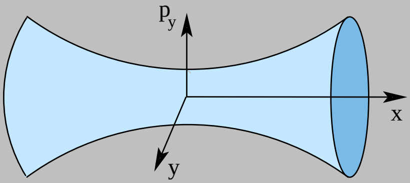

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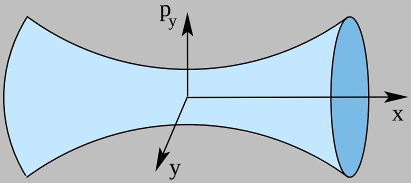
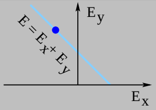


Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



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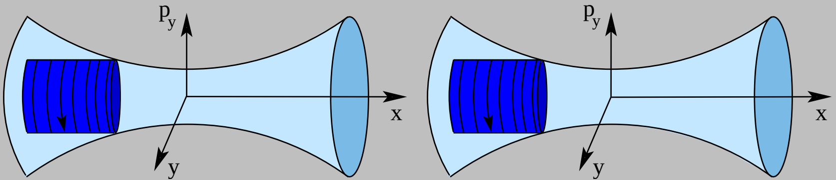

Non-reactive trajectory on the side of reactants

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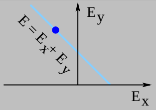
Phase Space Structures near a Saddle

Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



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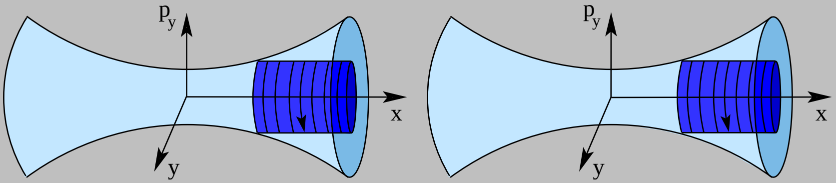

Non-reactive trajectory on the side of products

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Linear vector field for $f = 2$ degrees of freedom

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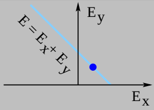

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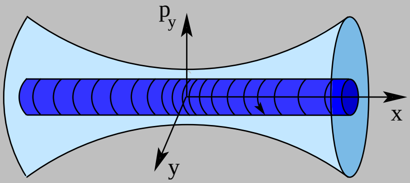
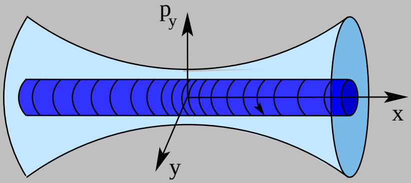


forward reactive trajectory

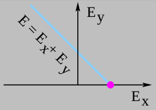
copy with $p_x \leq 0$



backward reactive trajectory

Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



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- Dynamical reaction paths have $\mathcal{H}_x = E_x = E$ (i.e. $\mathcal{H}_y = E_y = 0$)

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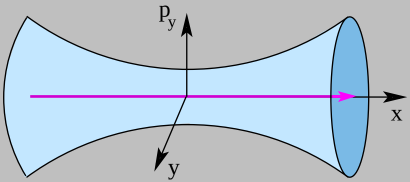

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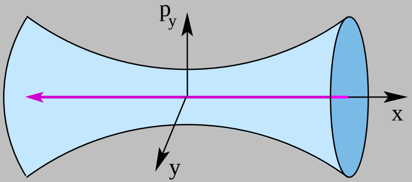

backward reaction path

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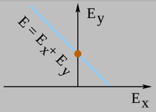
Linear vector field for $f = 2$ degrees of freedom

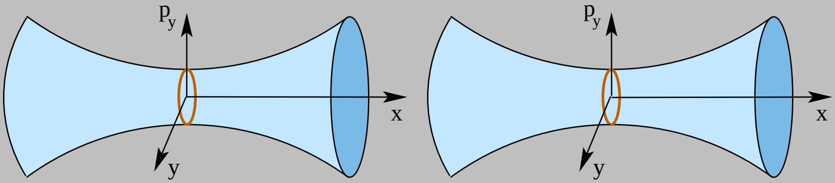
Σ_E for $E > 0$



$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

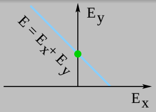
- Lyapunov periodic orbit $\simeq S^1$ has $\mathcal{H}_x = E_x = 0$ with $x = p_x = 0$

copy with $p_x \geq 0$ copy with $p_x \leq 0$



Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

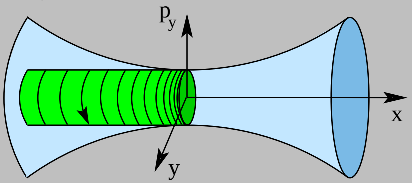
Σ_E for $E > 0$



$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

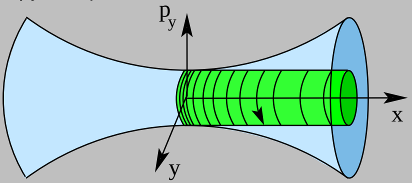
- Stable manifolds $W^s \simeq S^1 \times \mathbb{R}$ has $\mathcal{H}_x = E_x = 0$ with $p_x = -\lambda x$

copy with $p_x \geq 0$



reactants branch W_r^s

copy with $p_x \leq 0$



products branch W_p^s

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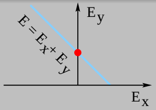
Phase Space Structures near a Saddle

Linear vector field for $f = 2$ degrees of freedom

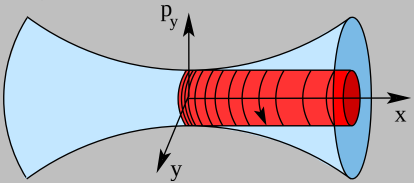
Σ_E for $E > 0$



$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

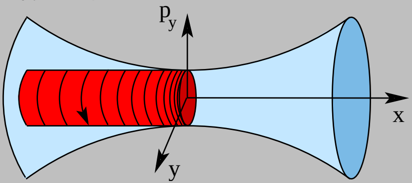
- Unstable manifolds $W^{\mathrm{u}} \simeq S^1 \times \mathbb{R}$ has $\mathcal{H}_x = E_x = 0$ with $p_x = \lambda x$

copy with $p_x \geq 0$



products branch $W^{\mathrm{u}}_{\mathrm{p}}$

copy with $p_x \leq 0$



reactants branch $W^{\mathrm{u}}_{\mathrm{r}}$

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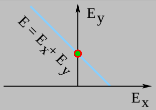
Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

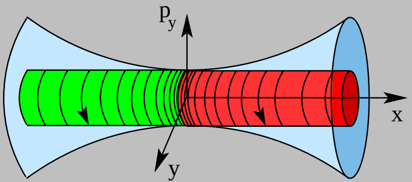
Σ_E for $E > 0$



$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

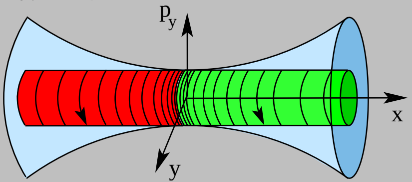
- *Forward* cylinder $W_r^s \cup W_p^u$ and *backward* cylinder $W_p^s \cup W_r^u$ enclose all the forward and backward reactive trajectories, respectively

copy with $p_x \geq 0$



forward cylinder

copy with $p_x \leq 0$

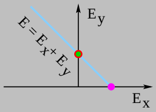


backward cylinder

Phase Space Structures near a Saddle

Linear vector field for $f = 2$ degrees of freedom

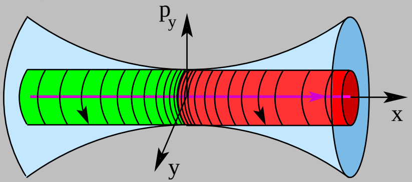
Σ_E for $E > 0$



$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

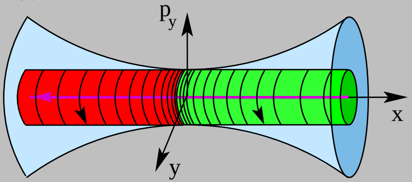
- Forward and backward dynamical reaction paths form the centreline of the forward and backward cylinders, respectively

copy with $p_x \geq 0$



forward reaction path

copy with $p_x \leq 0$

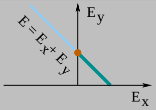


backward reaction path

Phase Space Structures near a Saddle

Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$

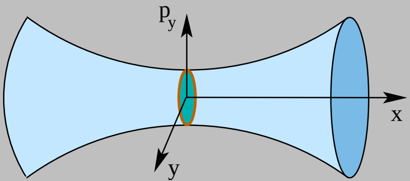


$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

- Dividing surface $\simeq S^2$ has $x = 0$,

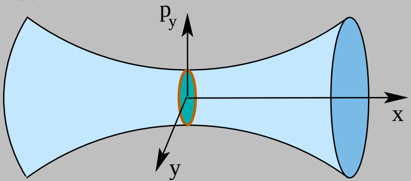
  Lyapunov periodic orbit $\simeq S^1$ forms its equator and divides it into two hemispheres $\simeq B^2$

copy with $p_x \geq 0$



forward hemisphere B_f^2

copy with $p_x \leq 0$



backward hemisphere B_b^2

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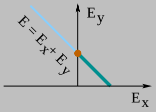
Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom

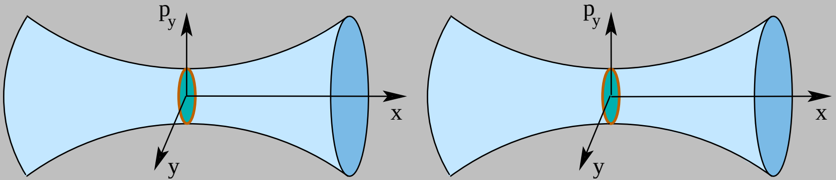
Σ_E for $E > 0$



$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

- Apart from its equator (which has $x = p_x = 0$) the dividing surface is transverse to the flow ($\dot{x} = p_x \neq 0$ for $p_x \neq 0$)

copy with $p_x \geq 0$ | copy with $p_x \leq 0$



forward hemisphere B_f^2 | backward hemisphere B_b^2

Phase Space Structures near a Saddle
General (nonlinear) case

- $f = 2$ degrees of freedom: dividing surface can be constructed from periodic orbit
  Periodic Orbit Dividing Surface (PODS) (Pechukas, Pollak and McLafferty, 1970s)
- How can one construct a dividing surface for a system with an arbitrary number of degrees of freedom? What are the phase space conduits for reaction in this case?

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Phase Space Structures near a Saddle
General (nonlinear) case

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- How can one construct a dividing surface for a system with an arbitrary number of degrees of freedom? What are the phase space conduits for reaction in this case?

Phase Space Structures near a Saddle

General (nonlinear) case; $E > 0$

	2 DoF	3 DoF	f DoF
energy surface	$S^2 \times \mathbb{R}$	$S^4 \times \mathbb{R}$	$S^{2f-2} \times \mathbb{R}$
dividing surface	S^2	S^4	S^{2f-2}
normally hyperbolic invariant manifold (NHIM)	S^1	S^3	S^{2f-3}
(un)stable manifolds	$S^1 \times \mathbb{R}$	$S^3 \times \mathbb{R}$	$S^{2f-3} \times \mathbb{R}$
forward/backward hemispheres	B^2	B^4	B^{2f-2}
“flux” form $\Omega' = d\varphi$	ω	$\frac{1}{2}\omega^2$	$\frac{1}{(f-1)!}\omega^{f-1}$
“action” form φ	$p_1 dq_1 + p_2 dq_2$	$(p_1 dq_1 + p_2 dq_2 + p_3 dq_3) \wedge \frac{1}{2}\omega$	$\sum_{k=1}^{f} p_k dq_k \wedge \frac{1}{(f-1)!}\omega^{f-2}$

Flux (rate): $N(E) = \int_{B^{2f-2}_{\text{ds; forward}}} \Omega' = \int_{S^{2f-3}_{\text{NHIM}}} \varphi$

Uzer et al. (2001) Nonlinearity **15** 957-992
H. W. & S. Wiggins (2004) J. Phys. A **37** L435
H. W., A. Burbanks & S. Wiggins (2004) J. Chem. Phys. **121** 6207
H. W., A. Burbanks & S. Wiggins (2005) Mon. Not. R. Astr. Soc. **361** 763

Phase Space Structures near a Saddle
General (nonlinear) case; construction of the phase space structures from normal form

- *locally*: decouple the dynamics in terms of Poincaré-Birkhoff normal form
  - Suppose generic non-resonance condition is fulfilled. Then, for each order N, there is a symplectic transformation $\Phi_{(N)}$ such that the transformed Hamiltonian $\mathcal{H}_{\mathrm{NF}}^{(N)} = \mathcal{H} \circ \Phi_{(N)}^{-1}$ truncated at order N is of the form
  $$\mathcal{H}_{\mathrm{NF}}^{(N)} = \mathcal{H}_{\mathrm{NF}}^{(N)}(I, J_2, \ldots, J_f) = \lambda I + \omega_2 J_2 + \cdots + \omega_f J_f + \text{h.o.t.}$$
  where
  $$\begin{aligned} I &= p_1 q_1 \equiv \tfrac{1}{2}(\tilde{p}^2 + \tilde{q}^2) && \text{“reaction coordinate”} \\ J_k &= \tfrac{1}{2}(p_k^2 + q_k^2) && \text{“bath coordinates”} \end{aligned}$$
  - phase space structures mentioned above can be explicitly constructed in terms of the normal form coordinates $(\mathbf{p}, \mathbf{q})$, and transformed back to the original coordinates using $\Phi_{(N)}^{-1}$
- *globally*: “globalise” manifolds by integrating them out of the neighbourhood of validity of the normal form

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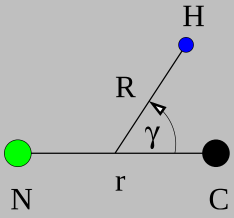
Example: HCN/CNH Isomerisation



3 DoF for vanishing total angular momentum:

Jacobi coordinates r, R, γ

Hamilton function

$$\mathcal{H} = \frac{1}{2\mu} p_r^2 + \frac{1}{2m} p_R^2 + \frac{1}{2} \left(\frac{1}{\mu r^2} + \frac{1}{mR^2} \right) p_\gamma^2 + V(r, R, \gamma)\,,$$

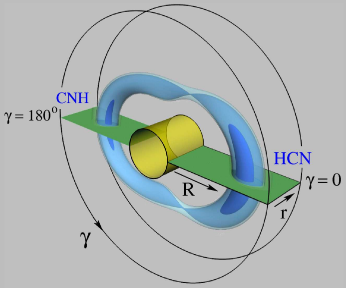
where

$$\mu = m_C m_N / (m_C + m_N), \quad m = m_H (m_C + m_N)/(m_H + m_C + m_N)$$

$V(r, R, \gamma)$: Murrell-Carter-Halonen potential energy surface

Example: HCN/CNH Isomerisation
Decoupling the dynamics

Iso-potential surfaces $V = const$.



saddle(s) at $\gamma = \pm 67°$

consider energy 0.2 eV above saddle

normal form to 16th order

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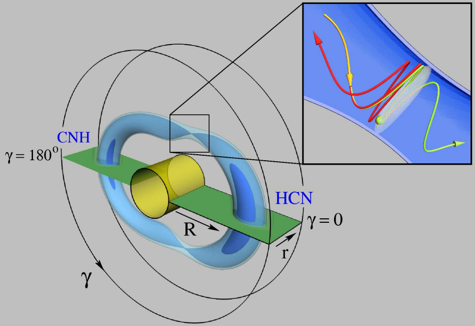

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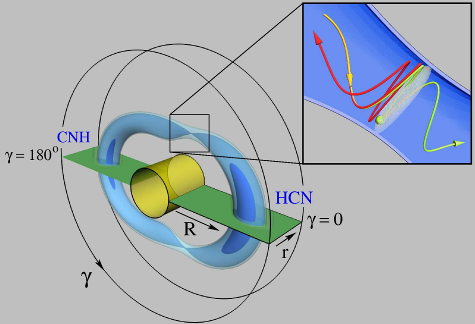

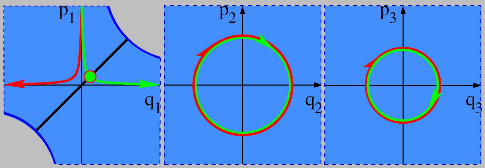

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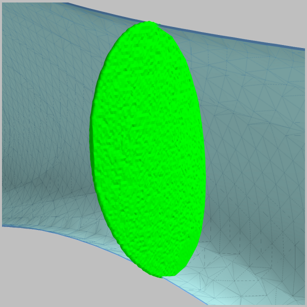
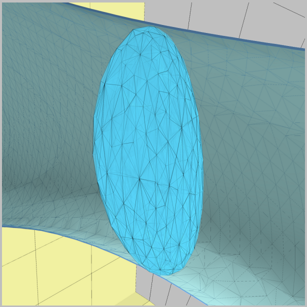
Example: HCN/CNH Isomerisation
Phase space structures

dividing surface S^4



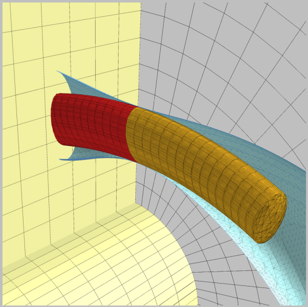
- transverse to Hamiltonian vector field
- minimises the flux

NHIM S^3



- *transition state* or *activated complex*

(un)stable manifolds $S^3 \times \mathbb{R}$



- phase space conduits for reaction

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- The stable and unstable manifolds of the NHIM(s) and the geometry of their intersections contain the full information about the reaction dynamics
- This allows one to study
  - complex reactions (rare events - how does a system find its way through a succession of transition states? global recrossings of the dividing surface?)
  - violations of ergodicity assumptions which are routinely employed in statistical reaction rate theories (can every initial condition react?)
  - time scales for reactions (classification of different types of reactive trajectories)
  - the control of reactions

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Global Recrossings and Rare Events

The role of homoclinic and heteroclinic connections

- Homoclinic connections

  orbits contained in the stable and unstable manifold of the same NHIM
- Heteroclinic connections

  orbits contained in the stable and unstable manifold of different NHIMs
- Heteroclinic cycles

  succession of heteroclinic connections

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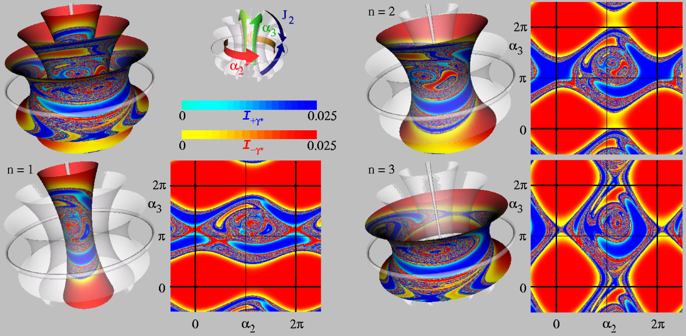
Example: HCN/CNH Isomerisation
Fibration of the NHIM and homoclinic and heteroclinic connections



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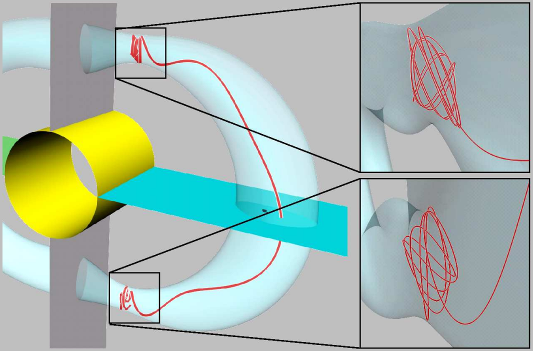
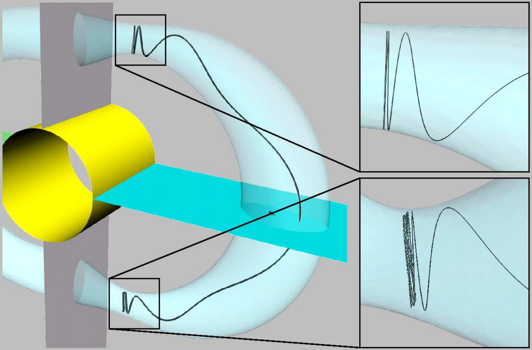
Example: HCN/CNH Isomerisation
Homoclinic and heteroclinic connections

Heteroclinic connection between invariant 2-tori in different NHIMs



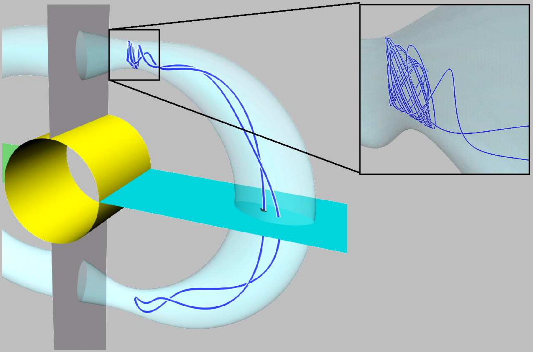
Example: HCN/CNH Isomerisation
Homoclinic and heteroclinic connections

Heteroclinic connection between invariant 2-torus and Lyapunov periodic orbit in different NHIMs



Example: HCN/CNH Isomerisation
Homoclinic and heteroclinic connections

Homoclinic connection to a *single* invariant 2-torus in a NHIM



Violations of ergodicity assumptions

Are all points in phase space reactive i.e. do they all, as initial conditions for Hamilton's equations, lead to reactive trajectories?

Theorem (Reactive Phase Space Volume) Consider a region M in an energy surface (e.g. the energy surface region corresponding to a potential well) with n exit channels associated with saddle equilibrium points. The energy surface volume of initial coniditions in M that lead to reactive (escape) trajectories is given by

$$\mathrm{vol}(M_{\mathrm{react}}) = \sum_{j=1}^{n} \langle t \rangle_{B_{\mathrm{ds};j}} N_{B_{\mathrm{ds};j}}$$

where

$\langle t \rangle_{B_{\mathrm{ds};j}}$ = mean residence time in the region M of trajectories starting on the j^{th} dividing surface $B_{\mathrm{ds};j}$

$N_{B_{\mathrm{ds};j}}$ = flux through j^{th} dividing surface $B_{\mathrm{ds};j}$

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H. W., A. Burbanks & S. Wiggins (2005) J. Phys. A **38** L759

H. W., A. Burbanks & S. Wiggins (2005) Mon. Not. R. Astr. Soc. **361** 763

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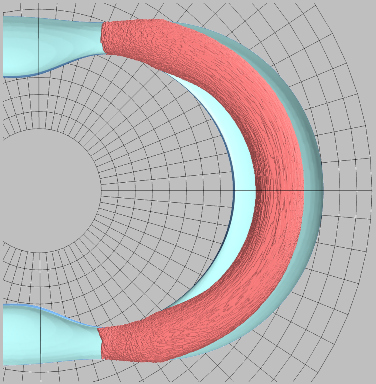
Example: HCN/CNH Isomerisation
Reactive phase space volumes



$$\frac{\mathrm{vol}(M_{\mathrm{HCN;\,react}})}{\mathrm{vol}(M_{\mathrm{HCN;\,total}})} = 0.09$$

only 9 % of initial conditions in the HCN well are reactive!

The procedure to compute vol(M_{react}) following from the theorem is orders of magnitudes more efficient than a brute force Monte Carlo computation

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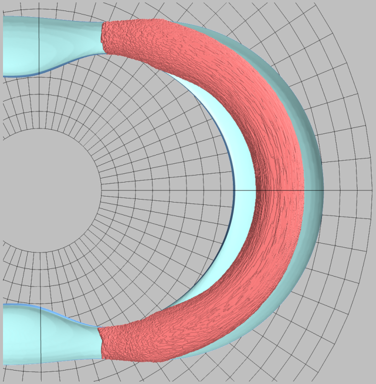
Example: HCN/CNH Isomerisation
Reactive phase space volumes



$$\frac{\mathrm{vol}(M_{\mathrm{HCN;\,react}})}{\mathrm{vol}(M_{\mathrm{HCN;\,total}})} = 0.09$$

only 9 % of initial conditions in the HCN well are reactive!

The procedure to compute vol(M_{react}) following from the theorem is orders of magnitudes more efficient than a brute force Monte Carlo computation

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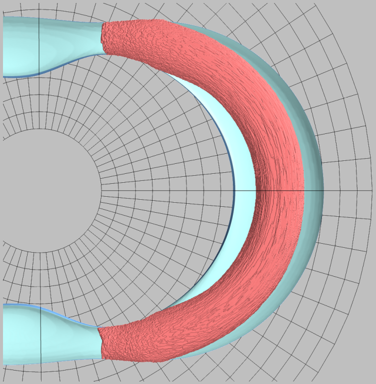

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The stable and unstable manifolds structure the reactive region into subregions of different types of reactive trajectories with a hierarchy of reaction time scales

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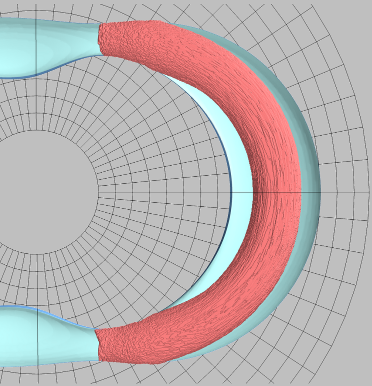
Reactive phase space subvolumes



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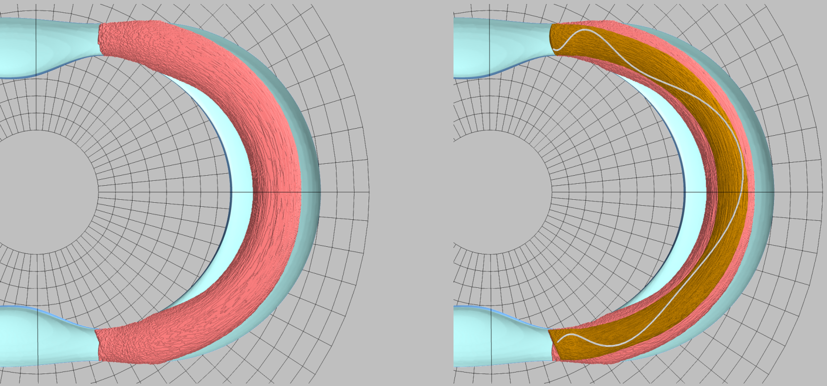

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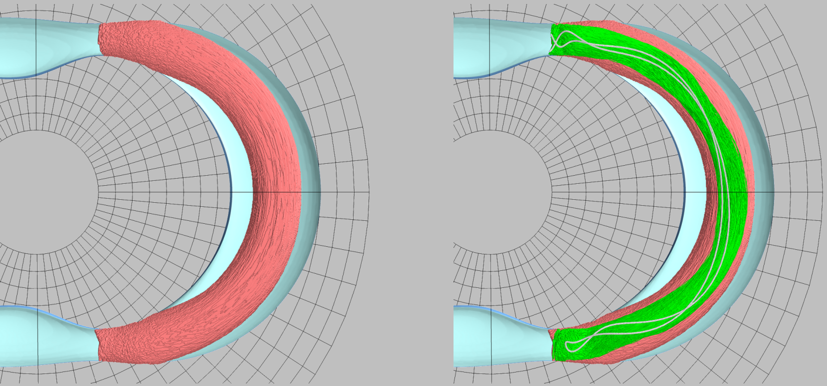

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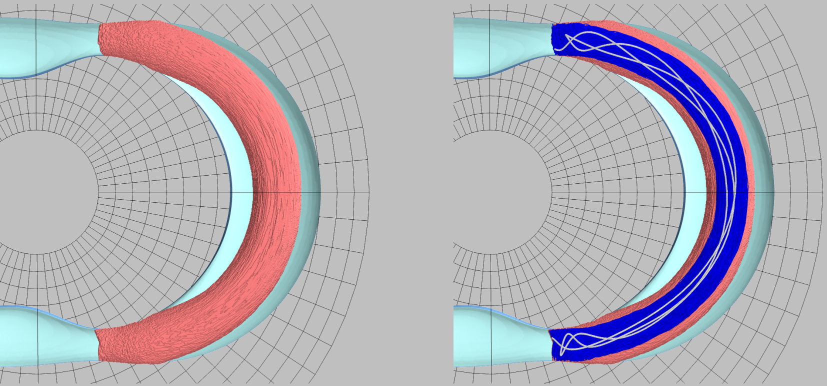

Quantum Reaction Dynamics in Multidimensional Systems

Quantum Transition State Theory

Quantum Transition State Theory

classical	quantum
Hamilton's equations	Schrödinger equation
$\dot{p} = -\frac{\partial \mathcal{H}}{\partial q}\,, \quad \dot{q} = \frac{\partial \mathcal{H}}{\partial p}\,, \quad (p,q) \in \mathbb{R}^{2f}$	$\widehat{H}\psi \equiv \left(-\frac{\hbar^2}{2}\nabla^2 + V\right)\psi = E\psi\,, \quad \psi \in L^2(\mathbb{R}^f)$

- Main idea: "locally simplify" Hamilton function/operator

symplectic transformations	unitary transformations
$\mathcal{H} \mapsto \mathcal{H} \circ \phi$	$\widehat{H} \mapsto U\widehat{H}U^{\star}$
(classical) normal form	quantum normal form

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Quantum normal form

- Quantum normal form is based on the symbol calculus (this leads to explicit algorithms like in the classical case)
- Suppose generic non-resonance condition is fulfilled. Then, for each order N, there is a unitary transformation $U_{(N)}$ such that the transformed Hamilton operator $\widehat{H}_{\mathrm{QNF}}^{(N)} = U_{(N)} \widehat{H} U_{(N)}^{*}$ resulting from truncating its symbol at order N is of the form

$$\widehat{H}_{\mathrm{QNF}}^{(N)} = H_{\mathrm{QNF}}^{(N)}(\widehat{I}, \widehat{J}_2, \dots, \widehat{J}_f),$$

  where

$$\begin{aligned} \widehat{I} &= -\mathrm{i}\hbar\left(q_1 \frac{\partial}{\partial q_1} + \frac{1}{2}\right) \\ \widehat{J}_k &= -\frac{\hbar^2}{2}\frac{\partial^2}{\partial q_k^2} + \frac{1}{2} q_k^2 \end{aligned}$$

- The elementary operators $\widehat{I}$ and $\widehat{J}_k$ have well known spectral properties

$$\sigma(\widehat{I}) = \mathbb{R}, \quad \sigma(\widehat{J}_k) = \{\hbar(n_k + \frac{1}{2}) \, : \, n_k \in \mathbb{N}_0\}$$

- This allows one to compute
  - cumulative reaction probabilities and quantum resonances
  - scattering and resonance wavefunctions (‘quantum bottleneck states’)

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Example: Coupled Eckart-Morse-Morse Potential

$$H = \frac{1}{2}(p_x^2 + p_y^2 + p_z^2) + \underbrace{V_{\mathrm{E}}(x) + V_{\mathrm{M};y}(y) + V_{\mathrm{M};z}(z)} + \underbrace{\epsilon\,(p_x p_y + p_x p_z + p_y p_z)}$$

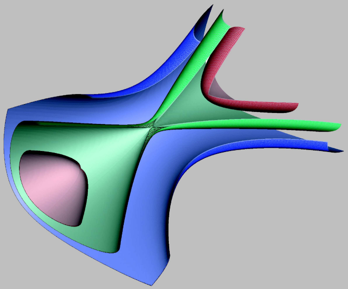
$$V_{\mathrm{E}}(x) = \frac{A\,\mathrm{e}^{ax}}{1+\mathrm{e}^{ax}} + \frac{B\,\mathrm{e}^{ax}}{(1+\mathrm{e}^{ax})^2}$$

'kinetic coupling'

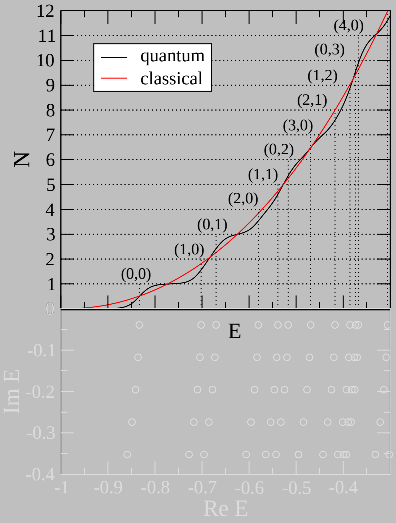
$$V_{\mathrm{M};y}(y) = D_y\left(\mathrm{e}^{(-2\alpha_y y)} - 2\mathrm{e}^{(-\alpha_y y)}\right)$$

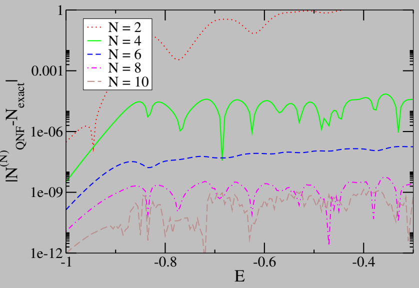
$$V_{\mathrm{M};z}(z) = D_z\left(\mathrm{e}^{(-2\alpha_z z)} - 2\mathrm{e}^{(-\alpha_z z)}\right)$$

Iso-potential surfaces:

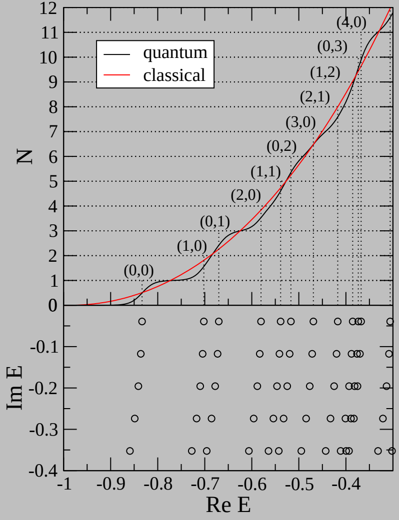


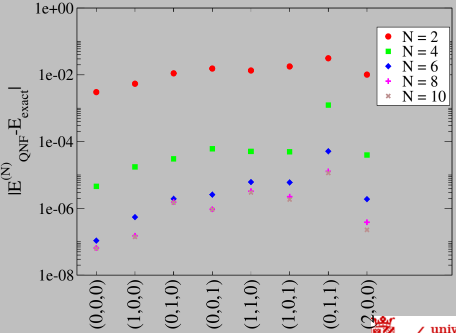
Example: Coupled Eckart-Morse-Morse Potential
Cumulative reaction probability





Example: Coupled Eckart-Morse-Morse Potential
Quantum resonances





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Outlook

- scattering and resonance states $\leftrightarrow$ classical phase space structures
- experimental observability of ‘quantum bottleneck states’
- state-to-state reactivities

Bibliography

- H.W., R. Schubert & S. Wiggins (2008) Nonlinearity **21** R1
- R. Schubert, H. W. & S. Wiggins (2006) Phys. Rev. Lett. **96** 218302
- H. W., A. Burbanks & S. Wiggins (2005) Phys. Rev. Lett. **95** 084301
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- H. W., A. Burbanks & S. Wiggins (2005) Mon. Not. R. Astr. Soc. **361** 763
- H. W. & S. Wiggins (2004) J. Phys. A **37** L435
- H. W., A. Burbanks & S. Wiggins (2004) J. Phys. A **37** L257
- H. W., A. Burbanks & S. Wiggins (2004) J. Chem. Phys. **121** 6207

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