The Geometry of Classical and Quantum Transition State Theory

Holger Waalkens

Johann Bernoulli Institute for Mathematics and Computer Science
University of Groningen

Joint work with

Andy Burbanks
Roman Schubert
Steve Wiggins

See also

Charles Jaffe
Thomas Bartsch
Fabio Revuelta

Reaction-Type Dynamics in Dynamical Systems

- ‘Transformations’ are mediated by phase space bottlenecks
  - phase space consists of disjoint regions in which system remains for long times
  - there are rare - but important - events where the system finds its way through a phase space bottleneck connecting one such region to another

For Example, in Chemistry

- Evolution from reactants to products through ‘transition state’

“*On the way from reactants to products, a chemical reaction passes through what chemists term the transition state – for a brief moment, the participants in the reaction may look like one large molecule ready to fall apart.*”

from R. A. Marcus. *Skiing the Reaction Rate Slopes.* Science **256** (1992) 1523

university of groningen

Reaction-Type Dynamics in Dynamical Systems

- ‘Transformations’ are mediated by phase space bottlenecks
  - phase space consists of disjoint regions in which system remains for long times
  - there are rare - but important - events where the system finds its way through a phase space bottleneck connecting one such region to another

For Example, in Chemistry

- Evolution from reactants to products through ‘transition state’

“*On the way from reactants to products, a chemical reaction passes through what chemists term the transition state – for a brief moment, the participants in the reaction may look like one large molecule ready to fall apart.*”

from R. A. Marcus. *Skiing the Reaction Rate Slopes.* Science **256** (1992) 1523

university of groningen

Reaction-Type Dynamics in Dynamical Systems

- ‘Transformations’ are mediated by phase space bottlenecks
  - phase space consists of disjoint regions in which system remains for long times
  - there are rare - but important - events where the system finds its way through a phase space bottleneck connecting one such region to another

For Example, in Chemistry

- Evolution from reactants to products through ‘transition state’

“*On the way from reactants to products, a chemical reaction passes through what chemists term the transition state – for a brief moment, the participants in the reaction may look like one large molecule ready to fall apart.*”

from R. A. Marcus. *Skiing the Reaction Rate Slopes*. Science **256** (1992) 1523

university of groningen

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

- Compute reaction rate from directional flux through ‘dividing surface’ in the transition state region
  - 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
- Computational benefits:
  - compute rate from flux through a dividing surface rather than from integrating trajectories, i.e. use ‘local’ rather than ‘global’ information

university of groningen

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

- Compute reaction rate from directional flux through 'dividing surface' in the transition state region
  - 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
- Computational benefits:
  - compute rate from flux through a dividing surface rather than from integrating trajectories, i.e. use 'local' rather than 'global' information

university of groningen

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

- Compute reaction rate from directional flux through ‘dividing surface’ in the transition state region
  - 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
- Computational benefits:
  - compute rate from flux through a dividing surface rather than from integrating trajectories, i.e. use ‘local’ rather than ‘global’ information

university of groningen

Classical and quantum reaction dynamics in multidimensional systems

Applications

- Chemical reactions (scattering, dissociation, isomerisation, protein folding)

  Many, many people

- Atomic physics (ionisation of Rydberg atoms in crossed field configurations)

  S. Wiggins, L. Wiesenfeld, C. Jaffé & T. Uzer (2001) Phys. Rev. Lett. **86** 5478

  H. Cartarius, J. Main & G. Wunner (2009) Phys. Rev. A **79** 033412

- Condensed matter physics (atom migration in solids, ballistic electron transport)

  G. Jacucci, M. Toller, G. DeLorenzi & C. P. Flynn (1984) Phys. Rev. Lett. **52** 295

  B. Eckhardt (1995) J. Phys. A **28** 3469

- Celestial mechanics (capture of moons near giant planets, asteroid motion)

  C. Jaffé, S. D. Ross, M. W. Lo, J. Marsden, D. Farrelly & T. Uzer (2002) Phys. Rev. Lett. **89** 011101

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

- Cosmology

  H. P. de Olivieira, A. M. Ozorio de Almeida, I. Danmião Soares & E. V. Tonini (2002) Phys. Rev. D **65** 083511

ersity of
ingen

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,

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

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,

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

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

Simplest case

Consider Hamilton function

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

- corresponding vector field is

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

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

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

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

$E < 0$:

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

$$\underbrace{E + \frac{1}{2}\lambda^2 x^2 = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2}$$

$$\simeq S^2 \text{ for } x \in (-\infty, -\frac{\sqrt{-2E}}{\lambda})$$

$$\text{or } x \in (\frac{\sqrt{-2E}}{\lambda}, \infty)$$

$\Rightarrow$ Energy surface

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

consists of two disconnected components which represent the 'reactants' and 'products'

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

$E < 0$:

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

$$\underbrace{E + \frac{1}{2}\lambda^2 x^2 = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2}$$

$$\simeq S^2 \text{ for } x \in (-\infty, -\frac{\sqrt{-2E}}{\lambda})$$

$$\text{or } x \in (\frac{\sqrt{-2E}}{\lambda}, \infty)$$

$\Rightarrow$ Energy surface

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

consists of two disconnected components which represent the 'reactants' and 'products'

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

$E > 0$:

$$\underbrace{E + \frac{1}{2}\lambda^2 x^2 = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2}_{\simeq S^2 \text{ for all } x \in \mathbb{R}}$$

⇒ 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

$E > 0$:

$$\underbrace{E + \frac{1}{2}\lambda^2 x^2 = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2}_{\simeq S^2 \text{ for all } x \in \mathbb{R}}$$

$\Rightarrow$ Energy surface

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

$\Rightarrow$ 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

$E > 0$:

$$\underbrace{E + \frac{1}{2}\lambda^2 x^2 = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2}_{\simeq S^2 \text{ for all } x \in \mathbb{R}}$$

$\Rightarrow$ Energy surface

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

$\Rightarrow$ 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

$E > 0$:

$$\underbrace{E + \frac{1}{2}\lambda^2 x^2 = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2}_{\simeq S^2 \text{ for all } x \in \mathbb{R}}$$

$\Rightarrow$ Energy surface

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

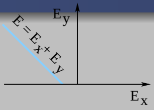
$\Rightarrow$ Σ_E bifurcates at $E = 0$ (the energy of the saddle) from *two* disconnected components to a *single* connected component

- 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

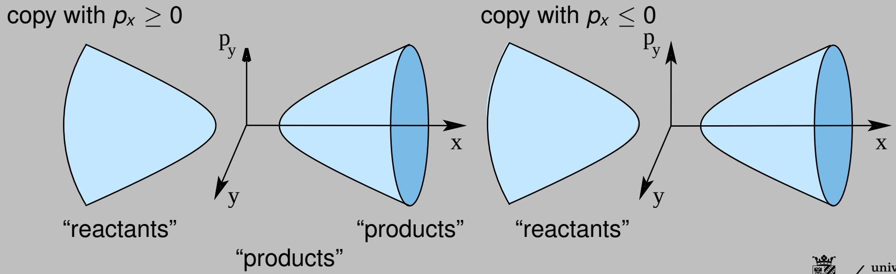
Phase Space Structures near a Saddle
Linear vector field for $f = 2$ degrees of freedom



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

Σ_E for $E < 0$

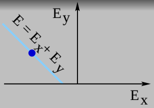
- Σ_E consists of two components representing reactants and products



university of groningen

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

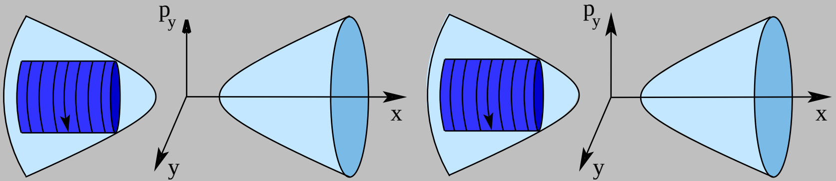
Σ_E for $E < 0$



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

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

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



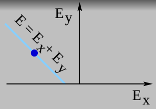
non-reactive trajectory on the side of reactants

university of groningen

Phase Space Structures near a Saddle

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

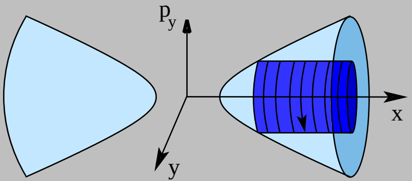
Σ_E for $E < 0$



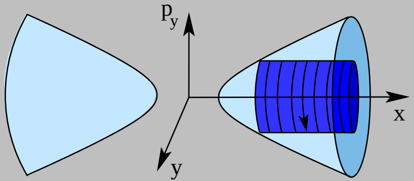
$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

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

copy with $p_x \geq 0$

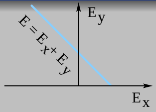


copy with $p_x \leq 0$



non-reactive trajectory on the side of products

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

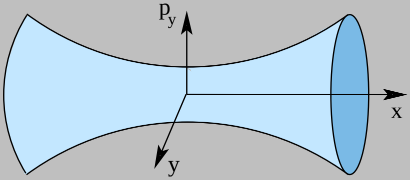


$$\begin{pmatrix} \dot p_x \\ \dot p_y \\ \dot x \\ \dot y \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

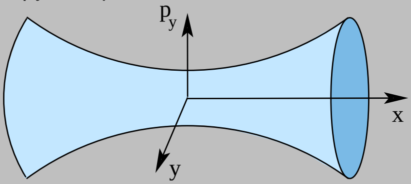
Σ_E for $E > 0$

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

copy with $p_x \geq 0$

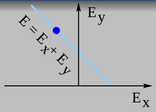


copy with $p_x \leq 0$



university of groningen

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

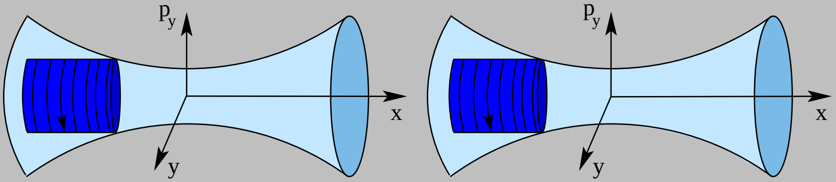


$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

Σ_E for $E > 0$

- Non-reactive trajectories have $\mathcal{H}_x = E_x < 0$

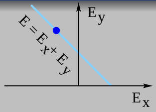
copy with $p_x \geq 0$ copy with $p_x \leq 0$



Non-reactive trajectory on the side of reactants

university of groningen

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

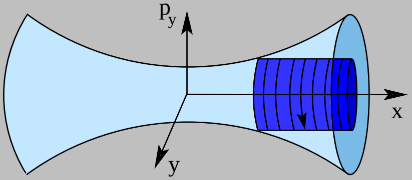


$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

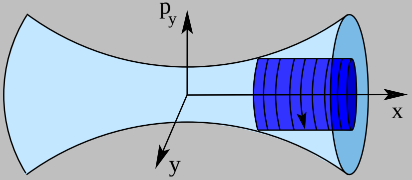
Σ_E for $E > 0$

- Non-reactive trajectories have $\mathcal{H}_x = E_x < 0$

copy with $p_x \geq 0$



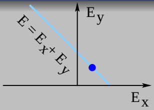
copy with $p_x \leq 0$



Non-reactive trajectory on the side of products

university of groningen

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

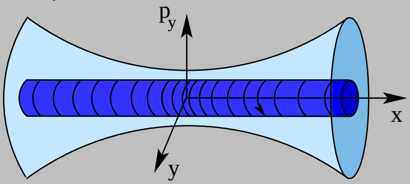


$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

Σ_E for $E > 0$

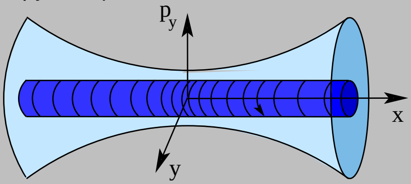
- Reactive trajectories have $\mathcal{H}_x = E_x > 0$

copy with $p_x \geq 0$



forward reactive trajectory

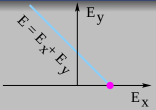
copy with $p_x \leq 0$



backward reactive trajectory

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

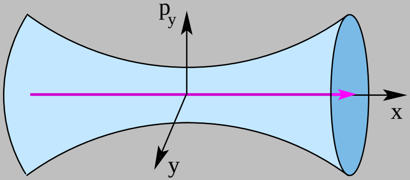
Σ_E for $E > 0$



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

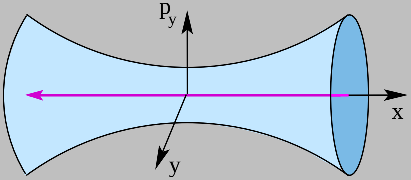
- Dynamical reaction paths have $\mathcal{H}_x = E_x = E$ (i.e. $\mathcal{H}_y = E_y = 0$)

copy with $p_x \geq 0$



forward reaction path

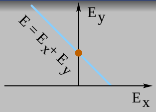
copy with $p_x \leq 0$



backward reaction path

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

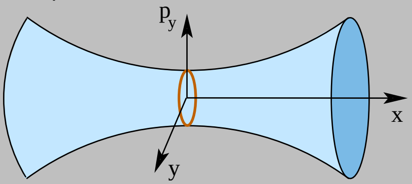
Σ_E for $E > 0$



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

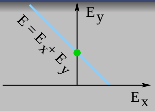
- Lyapunov periodic orbit $\simeq S^1$ has $\mathcal{H}_x = E_x = 0$ with $x = p_x = 0$

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



university of groningen

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

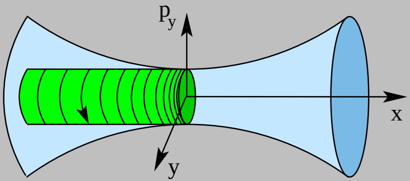


$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

Σ_E for $E > 0$

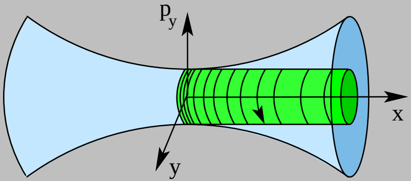
- Stable manifolds $W^s \simeq S^1 \times \mathbb{R}$ has $\mathcal{H}_x = E_x = 0$ with $p_x = -\lambda x$

copy with $p_x \geq 0$



reactants branch W^s_r

copy with $p_x \leq 0$

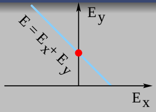


products branch W^s_p

university of groningen

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

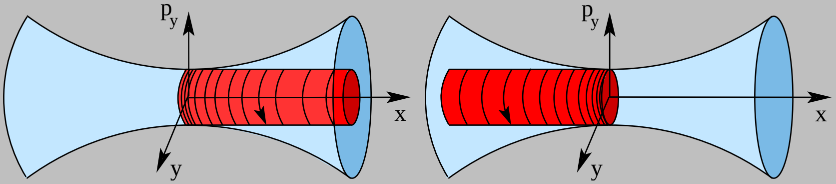
Σ_E for $E > 0$



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

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

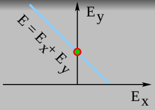


products branch $W^{\mathrm{u}}_{\mathrm{p}}$ reactants branch $W^{\mathrm{u}}_{\mathrm{r}}$

Phase Space Structures near a Saddle

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

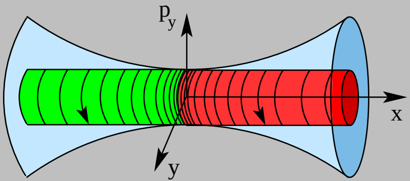
Σ_E for $E > 0$



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

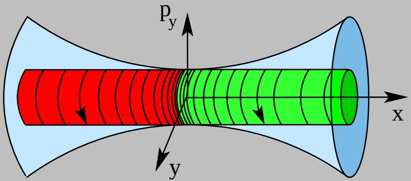
- *Forward* cylinder $W_r^s \cup W_p^u$ and *backward* cylinder $W_p^s \cup W_r^u$ enclose all the forward and backward reactive trajectories, respectively

copy with $p_x \geq 0$



forward cylinder

copy with $p_x \leq 0$

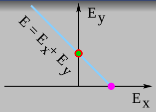


backward cylinder

university of groningen

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

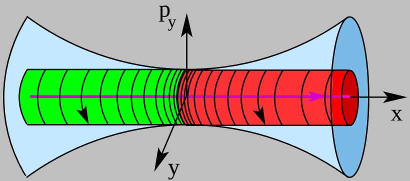
Σ_E for $E > 0$



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

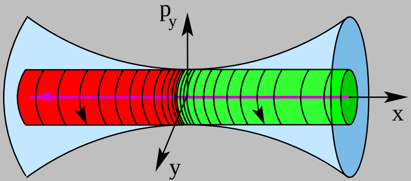
- Forward and backward dynamical reaction paths form the centreline of the forward and backward cylinders, respectively

copy with $p_x \geq 0$



forward reaction path

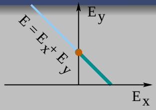
copy with $p_x \leq 0$



backward reaction path

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

Σ_E for $E > 0$

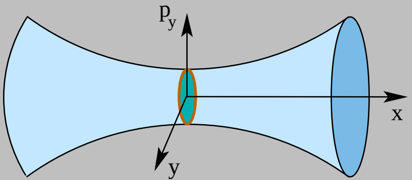


$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

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

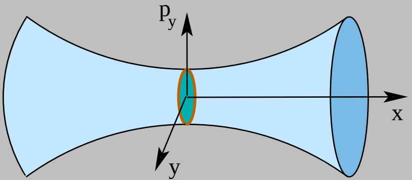
  Lyapunov periodic orbit $\simeq S^1$ forms its equator and divides it into two hemispheres $\simeq B^2$

copy with $p_x \geq 0$



forward hemisphere B_f^2

copy with $p_x \leq 0$



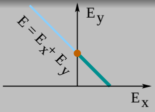
backward hemisphere B_b^2

university of groningen

Phase Space Structures near a Saddle

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

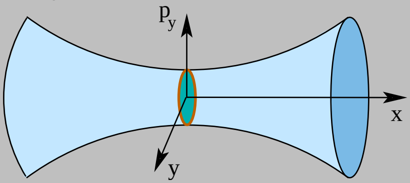
Σ_E for $E > 0$



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

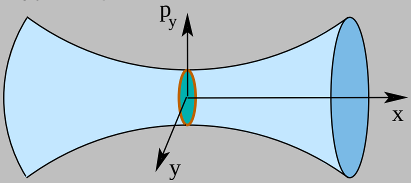
- Apart from its equator (which has $x = p_x = 0$) the dividing surface is transverse to the flow ($\dot{x} = p_x \neq 0$ for $p_x \neq 0$)

copy with $p_x \geq 0$



forward hemisphere B_f^2

copy with $p_x \leq 0$



backward hemisphere B_b^2

university of groningen

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?

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?

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

R. MacKay (1990) Phys. Lett. A **145** 425
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

Phase Space Structures near a Saddle

General (nonlinear) case; construction of the phase space structures from normal form

Theorem (Normal Form) *Consider a Hamiltonian vector field with a saddle equilibrium point like in our setup, i.e.* $J\,D^2\mathcal{H}$ *has eigenvalues* $\pm\lambda, \pm\mathrm{i}\omega_2, \ldots, \pm\mathrm{i}\omega_f$*,* $\lambda, \omega_k > 0$*. Assume that the linear frequencies* $(\omega_2, \ldots, \omega_f)$ *are linearly independent over* $\mathbb{Q}$*. Then, for any given order, there exists a local, nonlinear symplectic transformation to normal form (NF) coordinates* $(P, Q) = (P_1, \ldots, P_f, Q_1, \ldots, Q_f)$ *in which the transformed Hamilton function, to this order, assumes the form*

$$\mathcal{H}_{NF} = \mathcal{H}_{NF}(I, J_2, \ldots, J_f) = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f + h.o.t.\,,$$

where

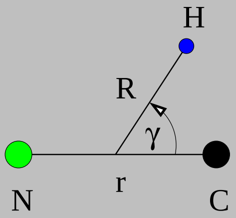
$$I = P_1 Q_1\,, \quad J_2 = \frac{1}{2}(P_2^2 + Q_2^2)\,, \quad \ldots\,, \quad J_f = \frac{1}{2}(P_f^2 + Q_f^2)\,.$$

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

Comments

- The NF proves the regularity of the motions near transition states
- The NF gives explicit formulae for the phase space structures that control reaction dynamics
- The phase space structures can be realised in the NF coordinates (P, Q) and mapped back to the original coordinates (p, q) using the inverse of the NF transformation
- The NF gives a simple expression for the flux in terms of the integrals $I, J_2, \ldots, J_f$
- The NF transformation can be computed in an algorithmic fashion
- In general the NF transformation does not converge but has to be truncated at a suitable order
- The NF is of local validity. Unbounded phase space structures like the NHIM's stable and unstable manifolds have to be extended from the neighbourhood of validity of the NF by the flow corresponding to the original vector field

Example: HCN/CNH Isomerisation



3 DoF for vanishing total angular momentum:

Jacobi coordinates r, R, γ

Hamilton function

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

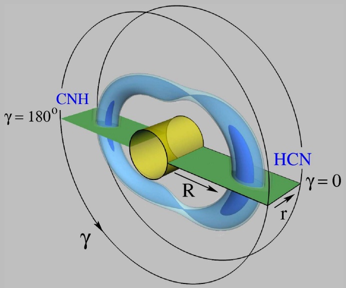
where

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

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

Example: HCN/CNH Isomerisation
Unfolding the dynamics

Iso-potential surfaces $V = const.$



saddle(s) at $\gamma = \pm 67^\circ$

consider energy 0.2 eV above saddle

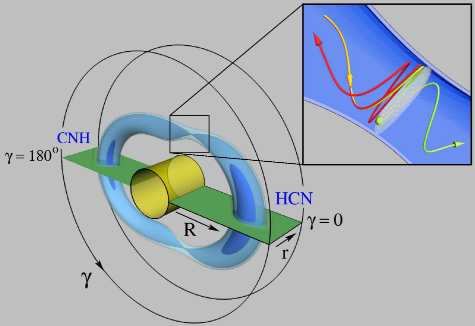
normal form to 16$^{\mathrm{th}}$ order

H. W., A. Burbanks & S. Wiggins (2004) J. Chem. Phys. **121** 6207

university of groningen

Example: HCN/CNH Isomerisation
Unfolding the dynamics

Iso-potential surfaces $V = const.$



saddle(s) at $\gamma = \pm 67^\circ$

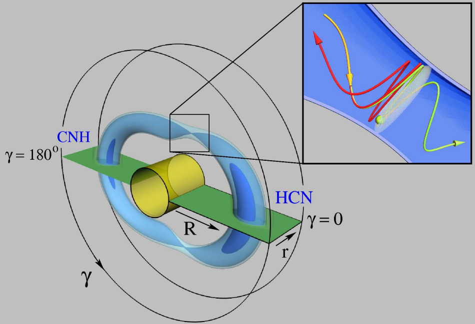
consider energy 0.2 eV above saddle

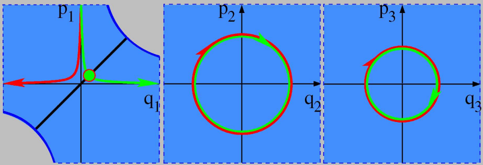
normal form to 16th order

H. W., A. Burbanks & S. Wiggins (2004) J. Chem. Phys. **121** 6207

Example: HCN/CNH Isomerisation
Unfolding the dynamics

Iso-potential surfaces $V = const.$





saddle(s) at $\gamma = \pm 67^\circ$

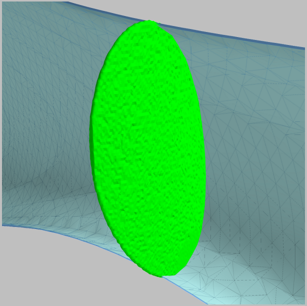
consider energy 0.2 eV above saddle

normal form to 16^{th} order

H. W., A. Burbanks & S. Wiggins (2004) J. Chem. Phys. **121** 6207

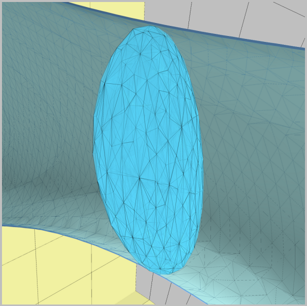
Example: HCN/CNH Isomerisation
Phase space structures

dividing surface S^4



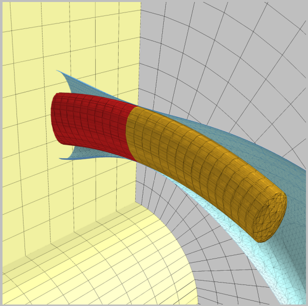
- transverse to Hamiltonian vector field
- minimises the flux

NHIM S^3



- *transition state* or *activated complex*

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



- phase space conduits for reaction

- 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

university of groningen

- 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

university of groningen

- 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

- 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

- 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

university of groningen

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 $B_{\mathrm{ds};j}$

H. W., A. Burbanks & S. Wiggins (2005) Phys. Rev. Lett. **95** 084301

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

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

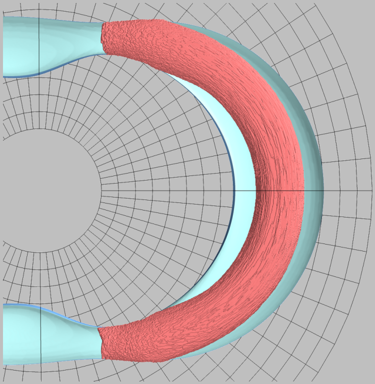
$\langle t \rangle_{B_{\mathrm{ds};j}}$ = mean residence time in the region M of trajectories starting on the j^{th} dividing surface $B_{\mathrm{ds};j}$

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

H. W., A. Burbanks & S. Wiggins (2005) Phys. Rev. Lett. **95** 084301

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

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!

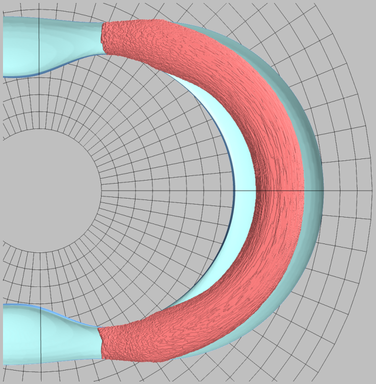
The procedure to compute $\mathrm{vol}(M_{\mathrm{react}})$ following from the theorem is orders of magnitudes more efficient than a brute force Monte Carlo computation

H. W., A. Burbanks & S. Wiggins (2005) Phys. Rev. Lett. **95** 084301

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

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 $\mathrm{vol}(M_{\mathrm{react}})$ following from the theorem is orders of magnitudes more efficient than a brute force Monte Carlo computation

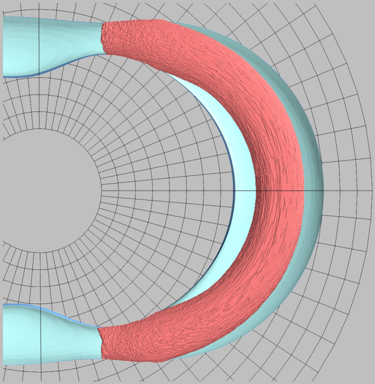
H. W., A. Burbanks & S. Wiggins (2005) Phys. Rev. Lett. **95** 084301

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

university of groningen

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 $\mathrm{vol}(M_{\mathrm{react}})$ following from the theorem is orders of magnitudes more efficient than a brute force Monte Carlo computation

H. W., A. Burbanks & S. Wiggins (2005) Phys. Rev. Lett. **95** 084301

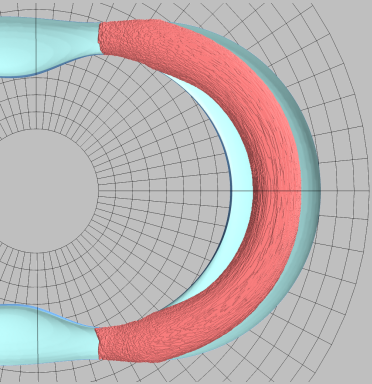
H. W., A. Burbanks & S. Wiggins (2005) J. Phys. A **38** L759

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

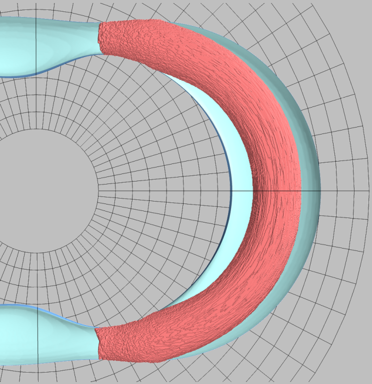
university of groningen

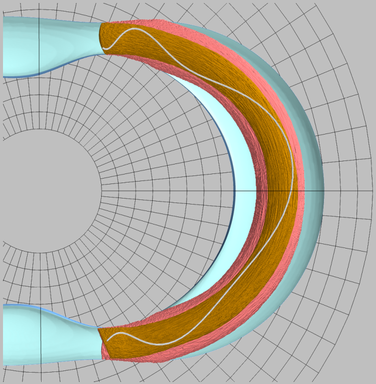
The stable and unstable manifolds structure the reactive region into subregions of different types of reactive trajectories with a hierarchy of reaction time scales

Example: HCN/CNH Isomerisation
Reactive phase space subvolumes

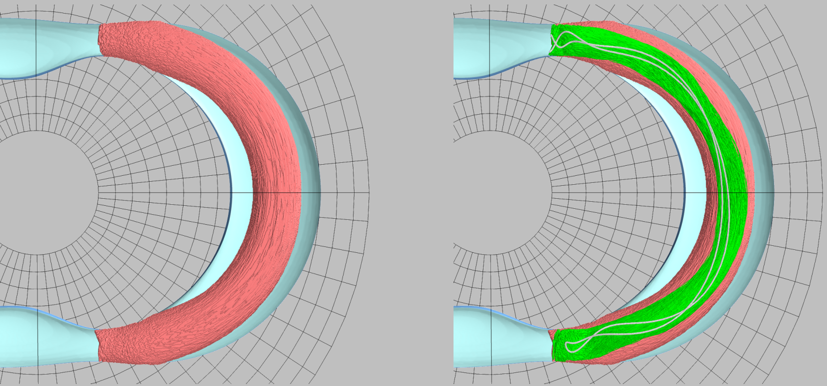


Example: HCN/CNH Isomerisation
Reactive phase space subvolumes



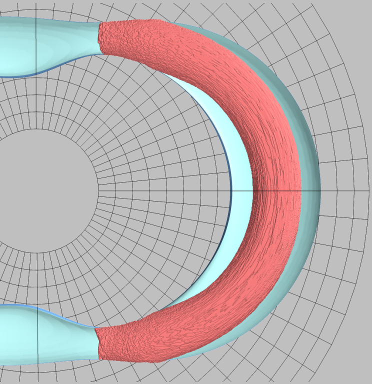


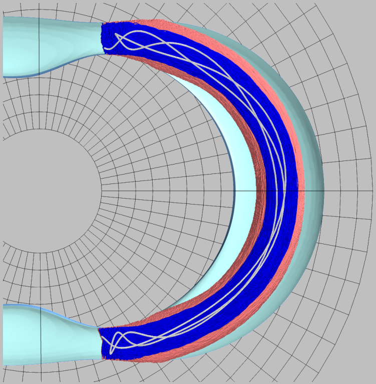
Example: HCN/CNH Isomerisation
Reactive phase space subvolumes



university of groningen

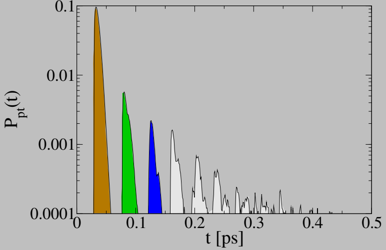
Example: HCN/CNH Isomerisation
Reactive phase space subvolumes





Example: HCN/CNH Isomerisation
Reactive phase space volumes

Reaction time distribution



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

R. Schubert, H. W. & S. Wiggins (2006) Phys. Rev. Lett. **96** 218302

H.W., R. Schubert & S. Wiggins (2008) Nonlinearty **21** R1-R118

university of groningen

Quantum Transition State Theory

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

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

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

R. Schubert, H. W. & S. Wiggins (2006) Phys. Rev. Lett. **96** 218302

H.W., R. Schubert & S. Wiggins (2008) Nonlinearty **21** R1-R118

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

R. Schubert, H. W. & S. Wiggins (2006) Phys. Rev. Lett. **96** 218302

H.W., R. Schubert & S. Wiggins (2008) Nonlinearty **21** R1-R118

university of groningen

Systematic quantum-classical correspondence from Weyl calculus

Weyl calculus:

operator $\widehat{A} \leftrightarrow$ phase space function A (symbol)

$$\widehat{A} = \frac{1}{(2\pi\hbar)^f} \int_{\mathbb{R}^{2f}} \overline{A}(\xi_q, \xi_p) \widehat{T}(\xi_q, \xi_p) \, \mathrm{d}\xi_q \mathrm{d}\xi_p \leftrightarrow A(\hbar, q, p) = \mathrm{Tr}(\widehat{T}(q,p)\widehat{A}) \,,$$

where

$$\widehat{T}(q,p) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\langle p, \widehat{q}\rangle + \langle q, \widehat{p}\rangle)}$$

Examples:

A	$\widehat{A}$
$J := \frac{1}{2}(p^2 + q^2)$	$\widehat{J} := -\frac{\hbar^2}{2}\frac{\mathrm{d}^2}{\mathrm{d}q^2} + \frac{1}{2}q^2$
$I := pq$	$\widehat{I} := -\mathrm{i}\hbar(q\frac{\mathrm{d}}{\mathrm{d}q} + \frac{1}{2})$

Systematic quantum-classical correspondence from Weyl calculus

Weyl calculus:

operator $\widehat{A} \leftrightarrow$ phase space function A (symbol)

$$\widehat{A} = \frac{1}{(2\pi\hbar)^f} \int_{\mathbb{R}^{2f}} \overline{A}(\xi_q, \xi_p) \widehat{T}(\xi_q, \xi_p) \, \mathrm{d}\xi_q \mathrm{d}\xi_p \leftrightarrow A(\hbar, q, p) = \mathrm{Tr}(\widehat{T}(q,p)\widehat{A}) \,,$$

where

$$\widehat{T}(q,p) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\langle p, \widehat{q}\rangle + \langle q, \widehat{p}\rangle)}$$

Examples:

A	$\widehat{A}$
$J := \frac{1}{2}(p^2+q^2)$	$\widehat{J} := -\frac{\hbar^2}{2}\frac{\mathrm{d}^2}{\mathrm{d}q^2} + \frac{1}{2}q^2$
$I := pq$	$\widehat{I} := -\mathrm{i}\hbar(q\frac{\mathrm{d}}{\mathrm{d}q} + \frac{1}{2})$

university of groningen

Systematic quantum-classical correspondence from Weyl calculus

Weyl calculus:

operator $\widehat{A} \leftrightarrow$ phase space function A (symbol)

$$\widehat{A} = \frac{1}{(2\pi\hbar)^f} \int_{\mathbb{R}^{2f}} \overline{A}(\xi_q, \xi_p) \widehat{T}(\xi_q, \xi_p) \, \mathrm{d}\xi_q \mathrm{d}\xi_p \; \leftrightarrow \; A(\hbar, q, p) = \mathrm{Tr}(\widehat{T}(q,p)\widehat{A}) \, ,$$

where

$$\widehat{T}(q,p) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\langle p, \widehat{q} \rangle + \langle q, \widehat{p} \rangle)}$$

Examples:

A	$\widehat{A}$
$J := \frac{1}{2}(p^2 + q^2)$	$\widehat{J} := -\frac{\hbar^2}{2}\frac{\mathrm{d}^2}{\mathrm{d}q^2} + \frac{1}{2}q^2$
$I := pq$	$\widehat{I} := -\mathrm{i}\hbar(q\frac{\mathrm{d}}{\mathrm{d}q} + \frac{1}{2})$

university of groningen

Systematic quantum-classical correspondence from Weyl calculus

Weyl calculus:

operator $\widehat{A} \leftrightarrow$ phase space function A (symbol)

$$\widehat{A} = \frac{1}{(2\pi\hbar)^f} \int_{\mathbb{R}^{2f}} \overline{A}(\xi_q, \xi_p) \widehat{T}(\xi_q, \xi_p) \, \mathrm{d}\xi_q \mathrm{d}\xi_p \leftrightarrow A(\hbar, q, p) = \mathrm{Tr}(\widehat{T}(q,p)\widehat{A}) \, ,$$

where

$$\widehat{T}(q,p) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\langle p, \widehat{q}\rangle + \langle q, \widehat{p}\rangle)}$$

Examples:

A	$\widehat{A}$
$J := \frac{1}{2}(p^2+q^2)$	$\widehat{J} := -\frac{\hbar^2}{2}\frac{\mathrm{d}^2}{\mathrm{d}q^2} + \frac{1}{2}q^2$
$I := pq$	$\widehat{I} := -\mathrm{i}\hbar(q\frac{\mathrm{d}}{\mathrm{d}q} + \frac{1}{2})$

Quantum Normal Form

Theorem (Quantum Normal Form) *Consider a Hamilton operator $\widehat{H}$ whose (principal) symbol has a saddle equilibrium point like in our classical setup, i.e. $J\,D^2H$ has eigenvalues $\pm\lambda, \pm i\omega_2, \ldots, \pm i\omega_f$, $\lambda, \omega_k > 0$. Assume that the linear frequencies $(\omega_2, \ldots, \omega_f)$ are linearly independent over $\mathbb{Q}$. Then, for any given order, there exists a unitary transformation $U^{(N)}$ such that*

$$U^{(N)}\widehat{H}U^{(N)\star} = \widehat{H}^{(N)}_{QNF} + \widehat{R}^{(N)}$$

where

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

and $R^{(N)}$ is of order $N+1$, i.e. $R^{(N)}(\epsilon p, \epsilon q, \epsilon^2\hbar) = O(\epsilon^{N+1})$

R. Schubert, H. W. & S. Wiggins (2006) Phys. Rev. Lett. **96** 218302

H.W., R. Schubert & S. Wiggins (2008) Nonlinearty **21** R1-R118

Quantum Normal Form

Comments

- $\widehat{H}^{(N)}_{\mathrm{QNF}}$ is an operator function of the 'elementary' operators $\widehat{I}$, $\widehat{J}_k$, $k = 2, \ldots, f$, whose spectral properties are well known
- This allows one to compute
  - quantum reaction probabilities (i.e. the analogue of the classical flux) and quantum resonances (i.e. the quantum lifetimes of the activated complex)
  - scattering and resonance wavefunctions ('quantum bottleneck states') which are localised on the classical phase space structures
- Like the classical normal form the quantum normal form can be computed in an algorithmic fashion

Quantum Normal Form

Comments

- $\widehat{H}^{(N)}_{\mathrm{QNF}}$ is an operator function of the 'elementary' operators $\widehat{I}$, $\widehat{J}_k$, $k = 2, \ldots, f$, whose spectral properties are well known
- This allows one to compute
  - quantum reaction probabilities (i.e. the analogue of the classical flux) and quantum resonances (i.e. the quantum lifetimes of the activated complex)
  - scattering and resonance wavefunctions ('quantum bottleneck states') which are localised on the classical phase space structures
- Like the classical normal form the quantum normal form can be computed in an algorithmic fashion

Quantum Normal Form

Comments

- $\widehat{H}^{(N)}_{\mathrm{QNF}}$ is an operator function of the 'elementary' operators $\widehat{I}$, $\widehat{J}_k$, $k = 2, \ldots, f$, whose spectral properties are well known
- This allows one to compute
  - quantum reaction probabilities (i.e. the analogue of the classical flux) and quantum resonances (i.e. the quantum lifetimes of the activated complex)
  - scattering and resonance wavefunctions ('quantum bottleneck states') which are localised on the classical phase space structures
- Like the classical normal form the quantum normal form can be computed in an algorithmic fashion

university of groningen

Quantum Normal Form

Comments

- $\widehat{H}^{(N)}_{\text{QNF}}$ is an operator function of the 'elementary' operators $\widehat{I}$, $\widehat{J}_k$, $k = 2, \ldots, f$, whose spectral properties are well known
- This allows one to compute
    - quantum reaction probabilities (i.e. the analogue of the classical flux) and quantum resonances (i.e. the quantum lifetimes of the activated complex)
    - scattering and resonance wavefunctions ('quantum bottleneck states') which are localised on the classical phase space structures
- Like the classical normal form the quantum normal form can be computed in an algorithmic fashion

Sketch of the Quantum Normal Form Computation

classical	quantum
Taylor expansion of Hamilton function $\mathcal{H}$	Taylor expansion of the symbol H of $\widehat{H}$
about critical point: $\mathcal{H} = \sum_{s=2}^{\infty} \mathcal{H}_s$ with	about critical point: $H = \sum_{s=2}^{\infty} H_s$ with
$\mathcal{H}_s \in \mathcal{P}_{\mathrm{cl}}^s = \mathrm{span}\{p^\alpha q^\beta : \lvert\alpha\rvert + \lvert\beta\rvert = s\}$	$H_s \in \mathcal{P}_{\mathrm{qm}}^s = \mathrm{span}\{p^\alpha q^\beta \hbar^\gamma : \lvert\alpha\rvert + \lvert\beta\rvert + 2\gamma = s$
for saddle-centre-...-centre:	for saddle-centre-...-centre:
$\mathcal{H}_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$	$H_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$
$I = p_1 q_1,\, J_k = \frac{1}{2}(p_k^2 + q_k^2)\,, \quad k = 2, \ldots, f$	$I = p_1 q_1,\, J_k = \frac{1}{2}(p_k^2 + q_k^2)\,, \quad k = 2, \ldots, f$
successive symplectic transformations	successive unitary transformations
$\mathcal{H} =: \mathcal{H}^{(2)} \to \mathcal{H}^{(3)} \to \ldots \to \mathcal{H}^{(N)}$	$\widehat{H} =: \widehat{H}^{(2)} \to \widehat{H}^{(3)} \to \ldots \to \widehat{H}^{(N)}$
$\mathcal{H}^{(n)} = \mathcal{H}^{(n-1)} \circ \phi_{\mathcal{W}_n}^{-1}\,, \quad \mathcal{W}_n \in \mathcal{P}_{\mathrm{cl}}^n$	$\widehat{H}^{(n)} = \mathrm{e}^{\frac{i}{\hbar}\widehat{W}_n} \widehat{H}^{(n-1)} \mathrm{e}^{-\frac{i}{\hbar}\widehat{W}_n}\,, \quad W_n \in \mathcal{P}_{\mathrm{qm}}^n$

university of groningen

Sketch of the Quantum Normal Form Computation

classical	quantum
Taylor expansion of Hamilton function $\mathcal{H}$ about critical point: $\mathcal{H} = \sum_{s=2}^{\infty} \mathcal{H}_s$ with	Taylor expansion of the symbol H of $\widehat{H}$ about critical point: $H = \sum_{s=2}^{\infty} H_s$ with
$\mathcal{H}_s \in \mathcal{P}_{\mathrm{cl}}^s = \mathrm{span}\{p^\alpha q^\beta : \|\alpha\| + \|\beta\| = s\}$	$H_s \in \mathcal{P}_{\mathrm{qm}}^s = \mathrm{span}\{p^\alpha q^\beta \hbar^\gamma : \|\alpha\| + \|\beta\| + 2\gamma = s$
for saddle-centre-...-centre:	for saddle-centre-...-centre:
$\mathcal{H}_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$	$H_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$
$I = p_1 q_1,\ J_k = \frac{1}{2}(p_k^2 + q_k^2), \quad k = 2, \ldots, f$	$I = p_1 q_1,\ J_k = \frac{1}{2}(p_k^2 + q_k^2), \quad k = 2, \ldots, f$
successive symplectic transformations	successive unitary transformations
$\mathcal{H} =: \mathcal{H}^{(2)} \to \mathcal{H}^{(3)} \to \ldots \to \mathcal{H}^{(N)}$	$\widehat{H} =: \widehat{H}^{(2)} \to \widehat{H}^{(3)} \to \ldots \to \widehat{H}^{(N)}$
$\mathcal{H}^{(n)} = \mathcal{H}^{(n-1)} \circ \phi_{\mathcal{W}_n}^{-1}, \quad \mathcal{W}_n \in \mathcal{P}_{\mathrm{cl}}^n$	$\widehat{H}^{(n)} = \mathrm{e}^{\frac{i}{\hbar}\widehat{W}_n} \widehat{H}^{(n-1)} \mathrm{e}^{-\frac{i}{\hbar}\widehat{W}_n}, \quad W_n \in \mathcal{P}_{\mathrm{qm}}^n$

university of groningen

Sketch of the Quantum Normal Form Computation

classical	quantum
Taylor expansion of Hamilton function $\mathcal{H}$ about critical point: $\mathcal{H} = \sum_{s=2}^{\infty} \mathcal{H}_s$ with	Taylor expansion of the symbol H of $\widehat{H}$ about critical point: $H = \sum_{s=2}^{\infty} H_s$ with
$\mathcal{H}_s \in \mathcal{P}_{\mathrm{cl}}^s = \mathrm{span}\{p^\alpha q^\beta : \lvert\alpha\rvert + \lvert\beta\rvert = s\}$	$H_s \in \mathcal{P}_{\mathrm{qm}}^s = \mathrm{span}\{p^\alpha q^\beta \hbar^\gamma : \lvert\alpha\rvert + \lvert\beta\rvert + 2\gamma = s$
for saddle-centre-. . . -centre:	for saddle-centre-. . . -centre:
$\mathcal{H}_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$	$H_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$
$I = p_1 q_1,\ J_k = \frac{1}{2}(p_k^2 + q_k^2)\,, \quad k = 2, \ldots, f$	$I = p_1 q_1,\ J_k = \frac{1}{2}(p_k^2 + q_k^2)\,, \quad k = 2, \ldots, f$
successive symplectic transformations	successive unitary transformations
$\mathcal{H} =: \mathcal{H}^{(2)} \to \mathcal{H}^{(3)} \to \ldots \to \mathcal{H}^{(N)}$	$\widehat{H} =: \widehat{H}^{(2)} \to \widehat{H}^{(3)} \to \ldots \to \widehat{H}^{(N)}$
$\mathcal{H}^{(n)} = \mathcal{H}^{(n-1)} \circ \phi_{\mathcal{W}_n}^{-1}, \quad \mathcal{W}_n \in \mathcal{P}_{\mathrm{cl}}^n$	$\widehat{H}^{(n)} = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\widehat{W}_n} \widehat{H}^{(n-1)} \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\widehat{W}_n}, \quad W_n \in \mathcal{P}_{\mathrm{qm}}^n$

university of groningen

Sketch of the Quantum Normal Form Computation

classical

Taylor expansion of Hamilton function $\mathcal{H}$

about critical point: $\mathcal{H} = \sum_{s=2}^{\infty} \mathcal{H}_s$ with

$$\mathcal{H}_s \in \mathcal{P}_{\mathrm{cl}}^s = \mathrm{span}\{p^\alpha q^\beta \, : \, |\alpha| + |\beta| = s\}$$

for saddle-centre-. . . -centre:

$$\mathcal{H}_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$$

$$I = p_1 q_1 ,\, J_k = \tfrac{1}{2}(p_k^2 + q_k^2) \,, \quad k = 2, \ldots, f$$

successive symplectic transformations

$$\mathcal{H} =: \mathcal{H}^{(2)} \to \mathcal{H}^{(3)} \to \ldots \to \mathcal{H}^{(N)}$$

$$\mathcal{H}^{(n)} = \mathcal{H}^{(n-1)} \circ \phi_{\mathcal{W}_n}^{-1} \,, \quad \mathcal{W}_n \in \mathcal{P}_{\mathrm{cl}}^n$$

quantum

Taylor expansion of the symbol H of $\widehat{H}$

about critical point: $H = \sum_{s=2}^{\infty} H_s$ with

$$H_s \in \mathcal{P}_{\mathrm{qm}}^s = \mathrm{span}\{p^\alpha q^\beta \hbar^\gamma \, : \, |\alpha| + |\beta| + 2\gamma = s$$

for saddle-centre-. . . -centre:

$$H_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$$

$$I = p_1 q_1 ,\, J_k = \tfrac{1}{2}(p_k^2 + q_k^2) \,, \quad k = 2, \ldots, f$$

successive unitary transformations

$$\widehat{H} =: \widehat{H}^{(2)} \to \widehat{H}^{(3)} \to \ldots \to \widehat{H}^{(N)}$$

$$\widehat{H}^{(n)} = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\widehat{W}_n} \widehat{H}^{(n-1)} \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\widehat{W}_n} \,, \quad W_n \in \mathcal{P}_{\mathrm{qm}}^n$$

university of groningen

Sketch of the Quantum Normal Form Computation

classical	quantum
Taylor expansion of Hamilton function $\mathcal{H}$	Taylor expansion of the symbol H of $\widehat{H}$
about critical point: $\mathcal{H} = \sum_{s=2}^{\infty} \mathcal{H}_s$ with	about critical point: $H = \sum_{s=2}^{\infty} H_s$ with
$\mathcal{H}_s \in \mathcal{P}^s_{\text{cl}} = \text{span}\{p^\alpha q^\beta : \|\alpha\| + \|\beta\| = s\}$	$H_s \in \mathcal{P}^s_{\text{qm}} = \text{span}\{p^\alpha q^\beta \hbar^\gamma : \|\alpha\| + \|\beta\| + 2\gamma = s$
for saddle-centre-...-centre:	for saddle-centre-...-centre:
$\mathcal{H}_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$	$H_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$
$I = p_1 q_1,\, J_k = \frac{1}{2}(p_k^2 + q_k^2)\,, \quad k = 2, \ldots, f$	$I = p_1 q_1,\, J_k = \frac{1}{2}(p_k^2 + q_k^2)\,, \quad k = 2, \ldots, f$
successive symplectic transformations	successive unitary transformations
$\mathcal{H} =: \mathcal{H}^{(2)} \to \mathcal{H}^{(3)} \to \ldots \to \mathcal{H}^{(N)}$	$\widehat{H} =: \widehat{H}^{(2)} \to \widehat{H}^{(3)} \to \ldots \to \widehat{H}^{(N)}$
$\mathcal{H}^{(n)} = \mathcal{H}^{(n-1)} \circ \phi^{-1}_{\mathcal{W}_n}\,, \quad \mathcal{W}_n \in \mathcal{P}^n_{\text{cl}}$	$\widehat{H}^{(n)} = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\widehat{W}_n} \widehat{H}^{(n-1)} \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\widehat{W}_n}\,, \quad W_n \in \mathcal{P}^n_{\text{qm}}$

university of groningen

Sketch of the Quantum Normal Form Computation

classical	quantum
for $s < n$: $\mathcal{H}_s^{(n)} = \mathcal{H}_s^{(n-1)}$	for $s < n$: $H_s^{(n)} = H_s^{(n-1)}$
for $s \geq n$: $\mathcal{H}_s^{(n)} = \sum_{j=0}^{[\frac{s-1}{n-1}]} \frac{1}{j!} [\mathrm{ad}_{\mathcal{W}_n}]^j \mathcal{H}_{s-j(n-2)}^{(n-1)}$	for $s \geq n$: $H_s^{(n)} = \sum_{j=0}^{[\frac{s-1}{n-1}]} \frac{1}{j!} [\mathrm{Mad}_{W_n}]^j H_{s-j(n-2)}^{(n-1)}$
where $\mathrm{ad}_{\mathcal{W}_n} := \{\mathcal{W}_n, \cdot\}$	where $\mathrm{Mad}_{W_n} := \{W_n, \cdot\}_M$
with Poisson bracket $\{A, B\}(p, q) =$	with Moyal bracket $\{A, B\}_M(p, q) =$
$A(p,q)[\langle \overleftarrow{\partial}_p, \overrightarrow{\partial}_q \rangle - \langle \overrightarrow{\partial}_p, \overleftarrow{\partial}_q \rangle] B(p,q)$	$\frac{2}{\hbar} A(p,q) \sin\left(\frac{\hbar}{2} [\langle \overleftarrow{\partial}_p, \overrightarrow{\partial}_q \rangle - \langle \overrightarrow{\partial}_p, \overleftarrow{\partial}_q \rangle] \right) B(p,q)$
choose $\mathcal{W}_n$, $n = 2, \dots, N$, such that	choose W_n, $n = 2, \dots, N$, such that
$\{\mathcal{H}_2, \mathcal{H}_n^{(n)}\} = 0$	$\{H_2, H_n^{(n)}\}_M = 0$ (i.e. $[\widehat{H}_2, \widehat{H}_n^{(n)}] = 0$)
from solving the homological equation	from solving the homological equation
$\mathcal{H}_n^{(n)} = \mathcal{H}_n^{(n-1)} + \{\mathcal{W}_n, \mathcal{H}_2\}$	$H_n^{(n)} = H_n^{(n-1)} + \{W_n, H_2\}$

university of groningen

Sketch of the Quantum Normal Form Computation

classical	quantum
for $s < n$: $\mathcal{H}_s^{(n)} = \mathcal{H}_s^{(n-1)}$	for $s < n$: $H_s^{(n)} = H_s^{(n-1)}$
for $s \geq n$: $\mathcal{H}_s^{(n)} = \sum_{j=0}^{[\frac{s-1}{n-1}]} \frac{1}{j!} [\mathrm{ad}_{\mathcal{W}_n}]^j \mathcal{H}_{s-j(n-2)}^{(n-1)}$	for $s \geq n$: $H_s^{(n)} = \sum_{j=0}^{[\frac{s-1}{n-1}]} \frac{1}{j!} [\mathrm{Mad}_{W_n}]^j H_{s-j(n-2)}^{(n-1)}$
where $\mathrm{ad}_{\mathcal{W}_n} := \{\mathcal{W}_n, \cdot\}$	where $\mathrm{Mad}_{W_n} := \{W_n, \cdot\}_M$
with Poisson bracket $\{A, B\}(p, q) =$ $A(p,q)[\langle \overleftarrow{\partial}_p, \overrightarrow{\partial}_q \rangle - \langle \overrightarrow{\partial}_p, \overleftarrow{\partial}_q \rangle] B(p,q)$	with Moyal bracket $\{A, B\}_M(p, q) =$ $\frac{2}{\hbar} A(p,q) \sin\left(\frac{\hbar}{2} [\langle \overleftarrow{\partial}_p, \overrightarrow{\partial}_q \rangle - \langle \overrightarrow{\partial}_p, \overleftarrow{\partial}_q \rangle] \right) B(p,q)$
choose $\mathcal{W}_n$, $n = 2, \ldots, N$, such that	choose W_n, $n = 2, \ldots, N$, such that
$\{\mathcal{H}_2, \mathcal{H}_n^{(n)}\} = 0$	$\{H_2, H_n^{(n)}\}_M = 0$ (i.e. $[\widehat{H}_2, \widehat{H}_n^{(n)}] = 0$)
from solving the homological equation	from solving the homological equation
$\mathcal{H}_n^{(n)} = \mathcal{H}_n^{(n-1)} + \{\mathcal{W}_n, \mathcal{H}_2\}$	$H_n^{(n)} = H_n^{(n-1)} + \{W_n, H_2\}$

university of groningen

Sketch of the Quantum Normal Form Computation

classical	quantum
for $s < n$: $\mathcal{H}_s^{(n)} = \mathcal{H}_s^{(n-1)}$	for $s < n$: $H_s^{(n)} = H_s^{(n-1)}$
for $s \geq n$: $\mathcal{H}_s^{(n)} = \sum_{j=0}^{[\frac{s-1}{n-1}]} \frac{1}{j!}[\mathrm{ad}_{\mathcal{W}_n}]^j \mathcal{H}_{s-j(n-2)}^{(n-1)}$	for $s \geq n$: $H_s^{(n)} = \sum_{j=0}^{[\frac{s-1}{n-1}]} \frac{1}{j!}[\mathrm{Mad}_{W_n}]^j H_{s-j(n-2)}^{(n-1)}$
where $\mathrm{ad}_{\mathcal{W}_n} := \{\mathcal{W}_n, \cdot\}$	where $\mathrm{Mad}_{W_n} := \{W_n, \cdot\}_M$
with Poisson bracket $\{A, B\}(p, q) =$	with Moyal bracket $\{A, B\}_M(p, q) =$
$A(p,q)[\langle \overleftarrow{\partial}_p, \overrightarrow{\partial}_q \rangle - \langle \overrightarrow{\partial}_p, \overleftarrow{\partial}_q \rangle] B(p,q)$	$\frac{2}{\hbar} A(p,q) \sin\left(\frac{\hbar}{2}[\langle \overleftarrow{\partial}_p, \overrightarrow{\partial}_q \rangle - \langle \overrightarrow{\partial}_p, \overleftarrow{\partial}_q \rangle]\right) B(p,q)$
choose $\mathcal{W}_n$, $n = 2, \dots, N$, such that	choose W_n, $n = 2, \dots, N$, such that
$\{\mathcal{H}_2, \mathcal{H}_n^{(n)}\} = 0$	$\{H_2, H_n^{(n)}\}_M = 0$ (i.e. $[\widehat{H}_2, \widehat{H}_n^{(n)}] = 0$)
from solving the homological equation	from solving the homological equation
$\mathcal{H}_n^{(n)} = \mathcal{H}_n^{(n-1)} + \{\mathcal{W}_n, \mathcal{H}_2\}$	$H_n^{(n)} = H_n^{(n-1)} + \{W_n, H_2\}$

Sketch of the Quantum Normal Form Computation

classical	quantum
for $s < n$: $\mathcal{H}_s^{(n)} = \mathcal{H}_s^{(n-1)}$	for $s < n$: $H_s^{(n)} = H_s^{(n-1)}$
for $s \geq n$: $\mathcal{H}_s^{(n)} = \sum_{j=0}^{[\frac{s-1}{n-1}]} \frac{1}{j!} [\mathrm{ad}_{\mathcal{W}_n}]^j \mathcal{H}_{s-j(n-2)}^{(n-1)}$	for $s \geq n$: $H_s^{(n)} = \sum_{j=0}^{[\frac{s-1}{n-1}]} \frac{1}{j!} [\mathrm{Mad}_{W_n}]^j H_{s-j(n-2)}^{(n-1)}$
where $\mathrm{ad}_{\mathcal{W}_n} := \{\mathcal{W}_n, \cdot\}$	where $\mathrm{Mad}_{W_n} := \{W_n, \cdot\}_M$
with Poisson bracket $\{A, B\}(p, q) =$	with Moyal bracket $\{A, B\}_M(p, q) =$
$A(p,q)[\langle \overleftarrow{\partial}_p, \overrightarrow{\partial}_q \rangle - \langle \overrightarrow{\partial}_p, \overleftarrow{\partial}_q \rangle] B(p,q)$	$\frac{2}{\hbar} A(p,q) \sin\left(\frac{\hbar}{2} [\langle \overleftarrow{\partial}_p, \overrightarrow{\partial}_q \rangle - \langle \overrightarrow{\partial}_p, \overleftarrow{\partial}_q \rangle] \right) B(p,q)$
choose $\mathcal{W}_n$, $n = 2, \ldots, N$, such that	choose W_n, $n = 2, \ldots, N$, such that
$\{\mathcal{H}_2, \mathcal{H}_n^{(n)}\} = 0$	$\{H_2, H_n^{(n)}\}_M = 0$ (i.e. $[\widehat{H}_2, \widehat{H}_n^{(n)}] = 0$)
from solving the homological equation	from solving the homological equation
$\mathcal{H}_n^{(n)} = \mathcal{H}_n^{(n-1)} + \{\mathcal{W}_n, \mathcal{H}_2\}$	$H_n^{(n)} = H_n^{(n-1)} + \{W_n, H_2\}$

Sketch of the Quantum Normal Form Computation

classical	quantum
$\Rightarrow \quad \mathcal{H}^{(N)} = \mathcal{H}_{\text{CNF}}^{(N)} + \mathcal{R}^{(N)}$	$\Rightarrow \quad \widehat{H}^{(N)} = \widehat{H}_{\text{QNF}}^{(N)} + \widehat{R}^{(N)}$
where $\boxed{\mathcal{H}_{\text{CNF}}^{(N)} = \mathcal{H}_{\text{CNF}}^{(N)}(I, J_2, \ldots, J_f)}$	where $\boxed{\widehat{H}_{\text{QNF}}^{(N)} = H_{\text{QNF}}^{(N)}(\widehat{I}, \widehat{J}_2, \ldots, \widehat{J}_f)}$
(and $\mathcal{R}^{(N)}$ is remainder term of order $N+1$)	(and $R^{(N)}$ is remainder term of order $N+1$)

R. Schubert, H. W. & S. Wiggins (2006) Phys. Rev. Lett. **96** 218302

H.W., R. Schubert & S. Wiggins (2008) Nonlinearty **21** R1-R118

university of groningen

Sketch of the Quantum Normal Form Computation

classical	quantum
$\Rightarrow \quad \mathcal{H}^{(N)} = \mathcal{H}^{(N)}_{\text{CNF}} + \mathcal{R}^{(N)}$	$\Rightarrow \quad \widehat{H}^{(N)} = \widehat{H}^{(N)}_{\text{QNF}} + \widehat{R}^{(N)}$
where $\boxed{\mathcal{H}^{(N)}_{\text{CNF}} = \mathcal{H}^{(N)}_{\text{CNF}}(I, J_2, \ldots, J_f)}$	where $\boxed{\widehat{H}^{(N)}_{\text{QNF}} = H^{(N)}_{\text{QNF}}(\widehat{I}, \widehat{J}_2, \ldots, \widehat{J}_f)}$
(and $\mathcal{R}^{(N)}$ is remainder term of order $N+1$)	(and $R^{(N)}$ is remainder term of order $N+1$)

R. Schubert, H. W. & S. Wiggins (2006) Phys. Rev. Lett. **96** 218302

H.W., R. Schubert & S. Wiggins (2008) Nonlinearty **21** R1-R118

Quantum normal form computation of the cumulative reaction probability

Scattering states are eigenfunctions of

$$\hat{H}_{\text{QNF}} = H_{\text{QNF}}(\hat{I}, \hat{J}_2, \ldots, \hat{J}_f),$$

i.e.

$$\hat{H}_{\text{QNF}}\, \psi_{(I,n_{\text{scatt}})} = H_{\text{QNF}}(I, \hbar(n_2 + \frac{1}{2}), \ldots, \hbar(n_f + \frac{1}{2}))\, \psi_{(I,n_{\text{scatt}})},$$

where $I \in \mathbb{R}$ and $n_{\text{scatt}} \in \mathbb{N}_0^{f-1}$ and

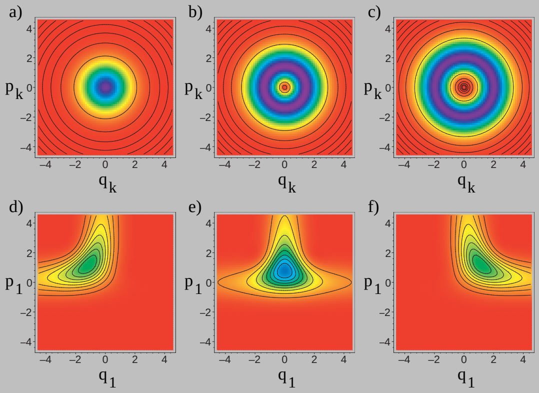
$$\psi_{(I,n_{\text{scatt}})}(q_1, \ldots, q_f) = \psi_I(q_1)\psi_{n_2}(q_2)\cdots\psi_{n_f}(q_f)$$

with quantum numbers $n_{\text{scatt}} = (n_2, \ldots, n_f) \in \mathbb{N}_0^{f-1}$

Quantum normal form computation of the cumulative reaction probability

centre planes
(q_k, p_k),
$k = 2, \ldots, f$

saddle plane
(q_1, p_1)



Quantum normal form computation of the cumulative reaction probability

A scattering state $\psi_{(I,n_{\text{scatt}})}$ has transmission probability

$$T_{n_{\text{scatt}}} = \left[1 + \exp\left(-2\pi\frac{I}{\hbar}\right)\right]^{-1}$$

Cumulative reaction probability

$$N(E) = \sum_{n_{\text{scatt}}} T_{n_{\text{scatt}}}(E) = \sum_{n_{\text{scatt}}\in\mathbb{N}_0^{f-1}} \left[1 + \exp\left(-2\pi\frac{I_{n_{\text{scatt}}}(E)}{\hbar}\right)\right]^{-1},$$

where $I_{n_{\text{scatt}}}(E)$ is determined by

$$H_{\text{QNF}}\left(I_{n_{\text{scatt}}}(E), \hbar(n_2+1/2), \ldots, \hbar(n_f+1/2)\right) = E$$

Quantum normal form computation of the cumulative reaction probability

A scattering state $\psi_{(I,n_{\text{scatt}})}$ has transmission probability

$$T_{n_{\text{scatt}}} = \left[1 + \exp\left(-2\pi \frac{I}{\hbar}\right)\right]^{-1}$$

Cumulative reaction probability

$$N(E) = \sum_{n_{\text{scatt}}} T_{n_{\text{scatt}}}(E) = \sum_{n_{\text{scatt}} \in \mathbb{N}_0^{f-1}} \left[1 + \exp\left(-2\pi \frac{I_{n_{\text{scatt}}}(E)}{\hbar}\right)\right]^{-1},$$

where $I_{n_{\text{scatt}}}(E)$ is determined by

$$H_{\text{QNF}}\left(I_{n_{\text{scatt}}}(E), \hbar(n_2 + 1/2), \ldots, \hbar(n_f + 1/2)\right) = E$$

university of groningen

Example: Coupled Eckart-Morse-Morse Potential

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

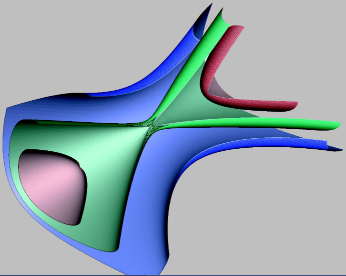
$$V_{\mathrm{E}}(x) = \frac{A\,\mathrm{e}^{ax}}{1+\mathrm{e}^{ax}} + \frac{B\,\mathrm{e}^{ax}}{(1+\mathrm{e}^{ax})^2}$$

'kinetic coupling'

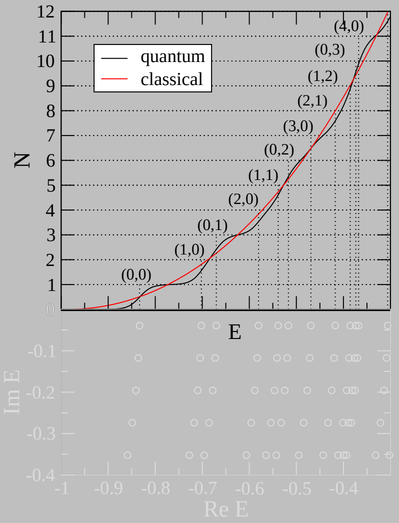
$$V_{\mathrm{M};y}(y) = D_y\left(\mathrm{e}^{(-2\alpha_y y)} - 2\mathrm{e}^{(-\alpha_y y)}\right)$$

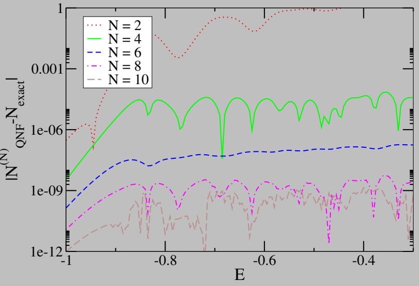
$$V_{\mathrm{M};z}(z) = D_z\left(\mathrm{e}^{(-2\alpha_z z)} - 2\mathrm{e}^{(-\alpha_z z)}\right)$$

Iso-potential surfaces:



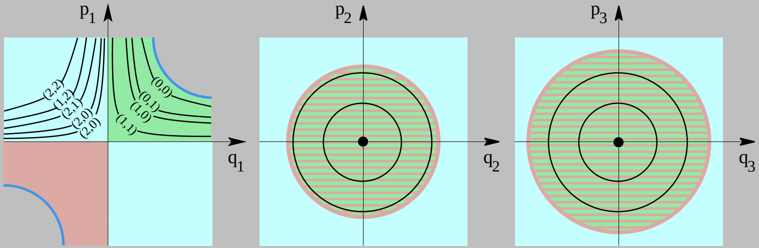
Example: Coupled Eckart-Morse-Morse Potential
Cumulative reaction probability





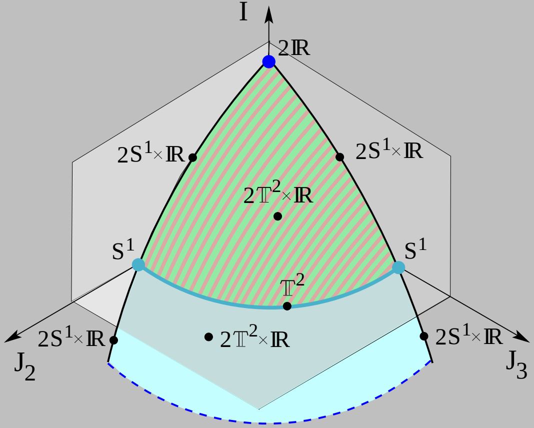
Example: Coupled Eckart-Morse-Morse Potential
Cumulative reaction probability

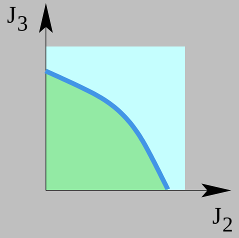
Cumulative reaction probability $N(E) \approx$ 'number of open transmission channels at energy E'



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

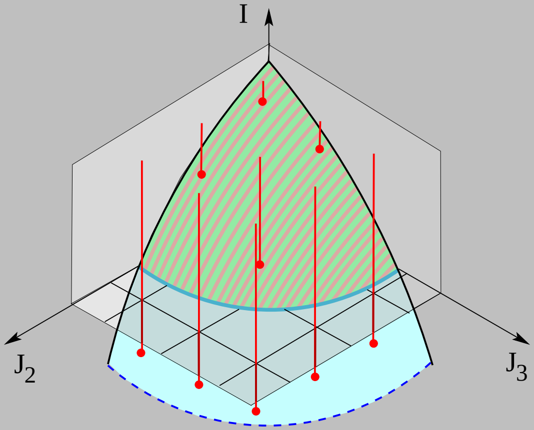
Cumulative reaction probability $N(E) \approx$ integrated density of states of the activated complex to energy E

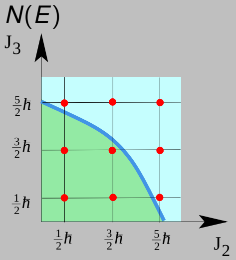




Example: Coupled Eckart-Morse-Morse Potential
Cumulative reaction probability

Cumulative reaction probability $N(E)$ = integrated density of states of the activated complex to energy E





university of groningen

Quantum resonances (Gamov-Siegert resonances)

Heisenberg uncertainty relation prohibits the existence of an invariant subsystem analogous to the classical case in quantum mechanics

Wavepackets initialised on the (classical) activated complex decay exponentially in time. This is described by the resonances.

Formal definition of resonances: poles of the meromorphic continuation of the resolvent

$$\widehat{R}(E) = (\widehat{H} - E)^{-1}$$

to the lower half plane

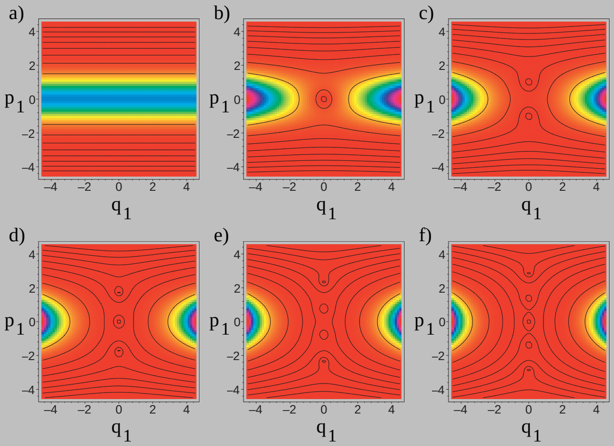
Quantum resonances are obtained from complex Bohr-Sommerfeld quantization conditions

$$E_{(n_1, n_2, \dots, n_f)} = H_{\mathrm{QNF}}^{(N)}(I_{n_1}, J_{n_2}, \dots, J_{n_f})$$

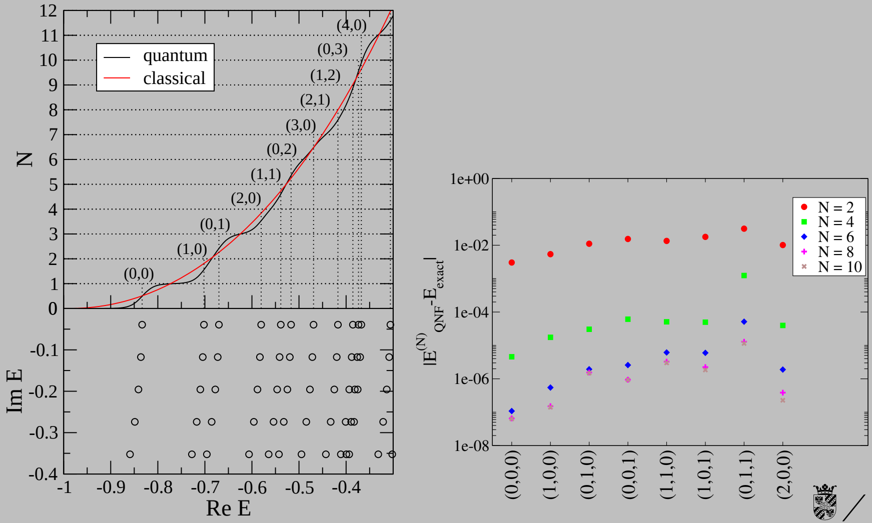
$$I_{n_1} = -\mathrm{i}\hbar(n_1 + \tfrac{1}{2}), \quad J_{n_2} = \hbar(n_2 + \tfrac{1}{2}), \dots, J_{n_f} = \hbar(n_f + \tfrac{1}{2}), \; n_1, \dots, n_d \in \mathbb{N}_0$$

Quantum resonances (Gamov-Siegert resonances)

Husimi functions of resonance states in the saddle plane



Example: Coupled Eckart-Morse-Morse Potential
Quantum resonances



university of groningen

Outlook

- more general bottlenecks/transition states
- going beyond (quantum) normal forms