Classical and Quantum Reaction Dynamics in Multidimensional Systems

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Durham 12th July 2006

- "*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
- Transition State Theory (Eyring, Polanyi, Wigner 1930s): Construct a so called dividing surface in the transition state region and compute reaction rates from the directional flux through the dividing surface.
- The dividing surface needs to be a so called '*surface of no return*':
  - it has to be crossed *exactly once* by all reactive trajectories and not crossed at all by non-reactive trajectories

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Subject of the talk:

- How to construct a dividing surface with the desired properties?
- How to formulate a *quantum transition state theory*?

Applications:

- Chemical reactions (scattering, dissociation, isomerisation)
- Atomic physics (ionisation of Rydberg atoms in crossed fields)
- Condensed matter physics (atom migration in solids, ballistic electron transport through point contacts)
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Setup: Consider f-degrees-of-freedom Hamiltonian system with phase space $\mathbb{R}^{2f}(q_1,\dots,q_f,p_1,\dots,p_f)$ and Hamilton function H.

Assume that the Hamiltonian vector field has a saddle-centre-$\cdots$-centre equilibrium point ('saddle' for short) at the origin, i.e. an equilibrium point at which JD^2H has one pair of real eigenvalues $\pm\lambda$ and $f-1$ pairs of imaginary eigenvalues $\pm\mathrm{i}\omega_k$, $k=2,\dots,f$.

Firstly: Linear case

$$H=\sum_{k=1}^{f}\frac{1}{2}p_k^2-\frac{1}{2}\lambda^2q_1^2+\sum_{k=2}^{f}\frac{1}{2}\omega_k^2q_k^2$$

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Linear case for $E < 0$:

Rewrite energy equation $H = E$ as

$$E + \frac{1}{2}\lambda^2 q_1^2 = \underbrace{\sum_{k=1}^{f} \frac{1}{2} p_k^2 + \sum_{k=2}^{f} \frac{1}{2}\omega_k^2 q_k^2}$$

$$\simeq S^{2f-2} \text{ for } q_1 \in (-\infty, -\frac{\sqrt{-2E}}{\lambda})$$

$$\text{or } q_1 \in (\frac{\sqrt{-2E}}{\lambda}, \infty)$$

$\Rightarrow$ Energy surface Σ_E consist of two disconnected components (*spherical cones*) representing “reactants” and “products”

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$\Rightarrow$ Energy surface $\Sigma_E \simeq S^{2f-2} \times \mathbb{R}$

$\Rightarrow$ Σ_E bifurcates at $E = 0$ from two disconnected components to a single connected component

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3-Dimensional model of energy surface Σ_E for $f = 2$ and $E > 0$

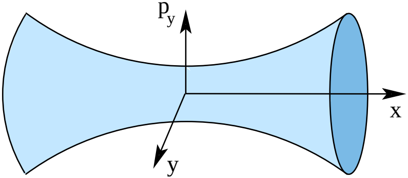
$$
\begin{aligned}
S^2 &= \text{nothern hemisphere} \cup \text{southern hemisphere} \cup \text{equator} \\
&= B^2 \cup B^2 \cup S^1
\end{aligned}
$$

$\Rightarrow$ Energy surface $\Sigma_E \simeq S^2 \times \mathbb{R} \simeq$ two solid cylinders $B^2 \times \mathbb{R}$ that are glued together along their boundaries $S^1 \times \mathbb{R}$

project the two solid cylinders to $\mathbb{R}^3(x, y, p_y)$

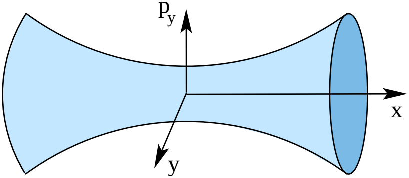
$$p_x = \pm\sqrt{E - \frac{1}{2}p_y^2 + \frac{\lambda^2}{2}q_x^2 - \frac{\omega^2}{2}q_y^2}$$

$p_x \geq 0$



"reactants" "products"

$p_x \leq 0$



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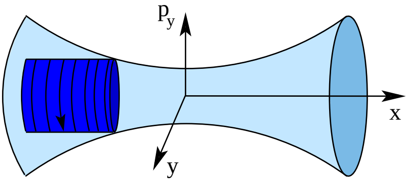
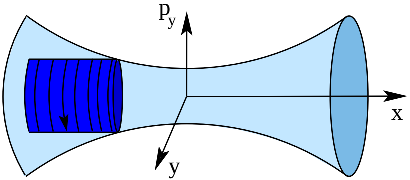
Nonreactive trajectories on the side of reactants

$p_x \geq 0$



$p_x \leq 0$



Nonreactive trajectories on the side of products

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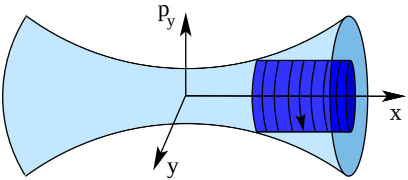
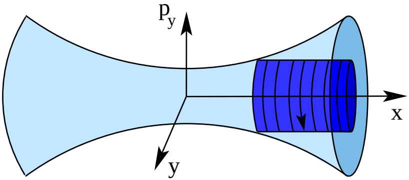


$p_x \leq 0$



Reactive trajectories

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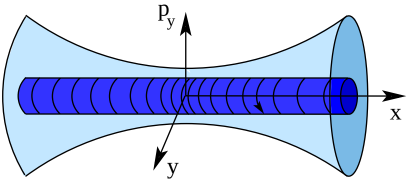
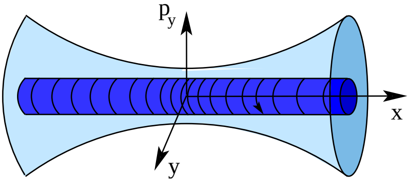


forward reactive

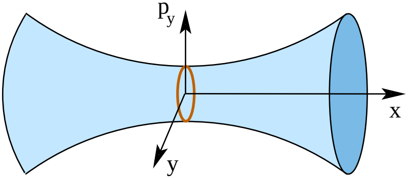
$p_x \leq 0$



backward reactive

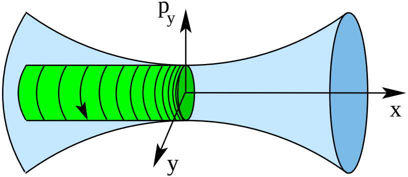
Lyapunov periodic orbit $\simeq S^1$

$p_x \geq 0$ $\qquad$ $p_x \leq 0$



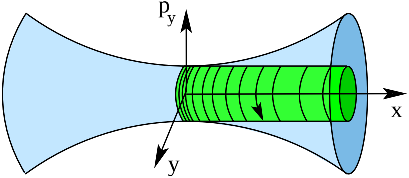
Stable manifolds $W^s \simeq S^1 \times \mathbb{R}$

$p_x \geq 0$



reactants branch W_r^s

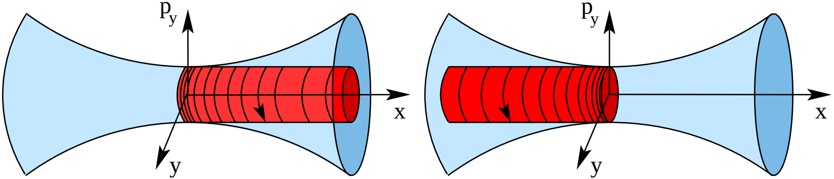
$p_x \leq 0$



products branch W_p^s

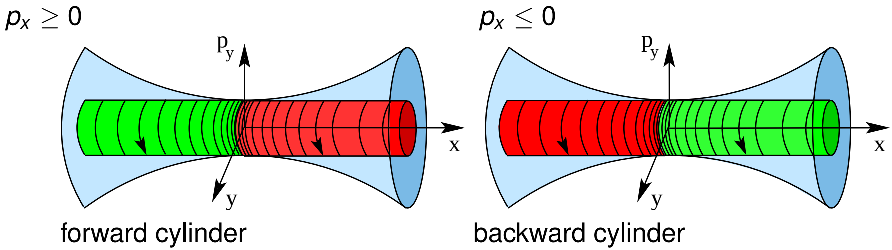
Unstable manifolds $W^u \simeq S^1 \times \mathbb{R}$

$p_x \geq 0$ $\quad$ $p_x \leq 0$



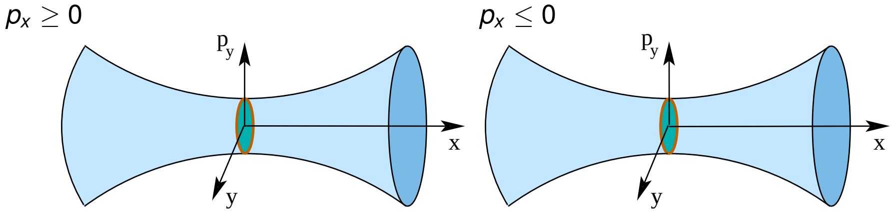
products branch W^u_p $\quad$ reactants branch W^u_r

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



Dividing surface S^2:

the Lyapunov periodic orbit forms the equator of the dividing surface



forward hemisphere B_f^2 backward hemisphere B_b^2

$\Rightarrow$ Periodic Orbit Dividing Surface PODS (Pechukas, Pollak, McLafferty 1970s)

Phase space structures for general case with $E > 0$

	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}
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	ω	$\frac{1}{2}\omega^2$	$\frac{1}{(f-1)!}\omega^{f-1}$
“action” form	$p_1 dq_1 + p_2 dq_2$	$(p_1 dq_1 + p_2 dq_2 + p_3 dq_3) \wedge \frac{1}{2}\omega$	$\sum_{k=1}^{f} p_k dq_k \wedge \frac{1}{(f-1)!}\omega^{f-2}$

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Unfold dynamics in terms of normal form

- locally:
  - nonlinear symplectic transformation to normal form coordinates $(\mathbf{p}, \mathbf{q})$
  - normal form coordinates provide explicit formulae for phase space structures mentioned above
  - given generic non-resonance condition:

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

where

$$I = p_1 q_1 \quad \text{“reaction coordinate”}$$
$$J_k = \tfrac{1}{2}(p_k^2 + q_k^2) \quad \text{“bath coordinates”}$$

- globally:
  “globalise” manifolds by integrating them out of the neighbourhood of validity of the normal form

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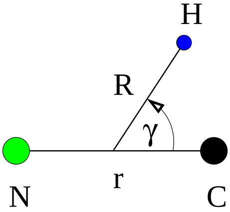
HCN Isomerisation

3 DoF for vanishing total angular momentum



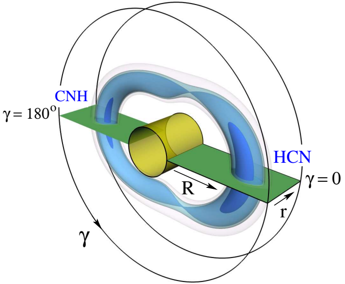
$$H = \frac{1}{2\mu} p_r^2 + \frac{1}{2m} p_R^2 + \frac{1}{2} \left(\frac{1}{\mu r^2} + \frac{1}{mR^2} \right) p_\gamma^2 + V(r, R, \gamma)$$

where

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

Unfolding the dynamics

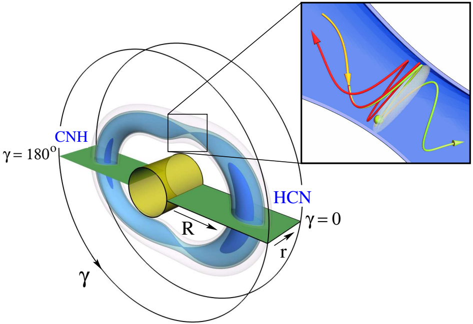
equipotential surfaces



saddle(s) at $\gamma = \pm 67^\circ$
consider energy 0.2 eV
above saddle

Unfolding the dynamics

equipotential surfaces



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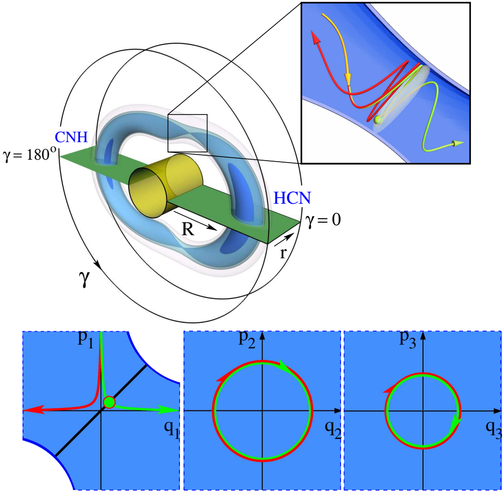

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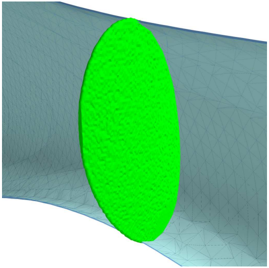
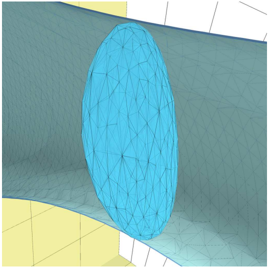
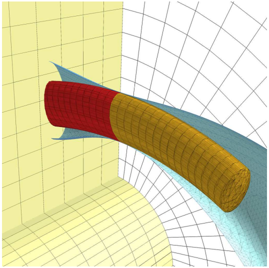
dividing surface S^4



NHIM S^3

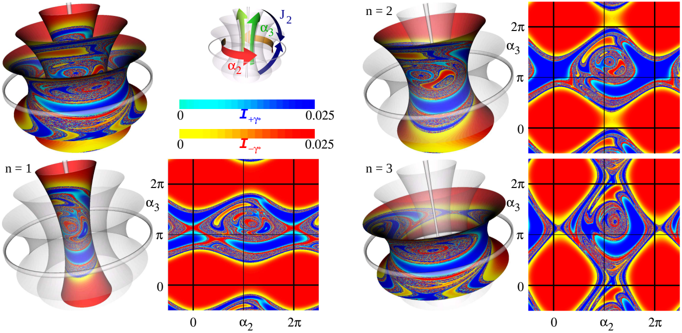


stable/unstable manifolds $S^3 \times \mathbb{R}$



Fibration of the NHIM

Homoclinic and heteroclinic connections



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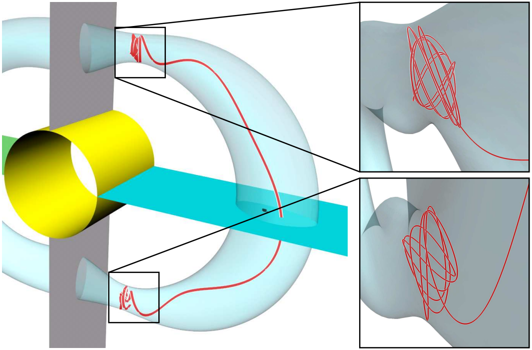
Homoclinic and heteroclinic connections



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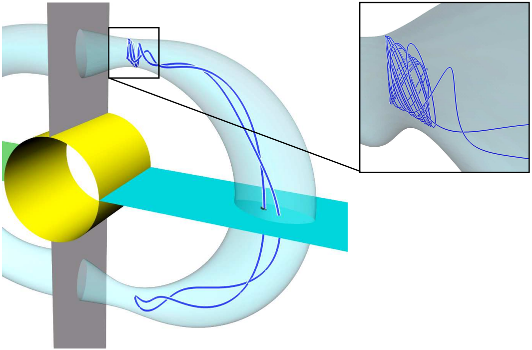
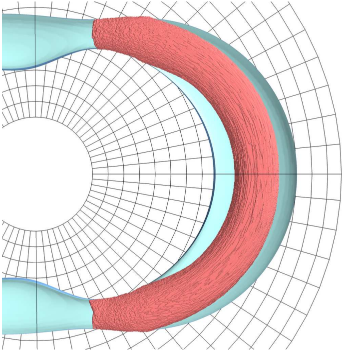
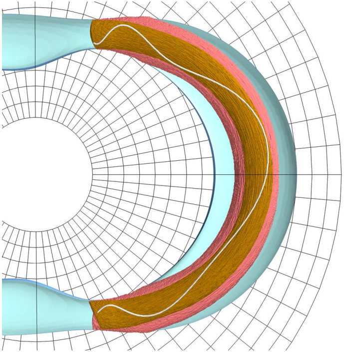


Reactive phase space volumes

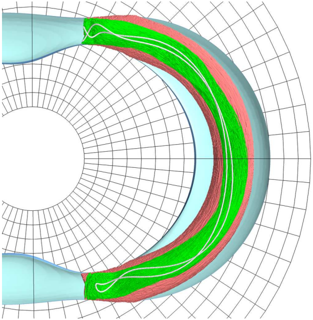


only 9 % of initial conditions are reactive!

Reactive phase space subvolumes



Reactive phase space subvolumes



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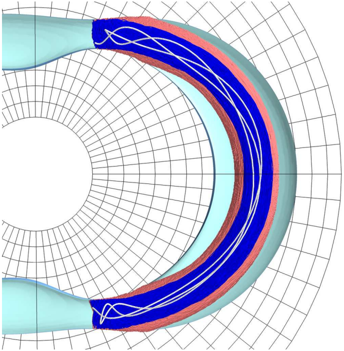

Quantum Normal Form

General idea: “unfold” local dynamics by approximating the original Hamilton operator by a ‘simpler’ Hamilton operator

Weyl calculus:

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

$$\widehat{A}\psi(q) = \frac{1}{(2\pi\hbar)^f} \int_{\mathbb{R}^{2f}} \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\langle q-q',p\rangle} A(\frac{q+q'}{2},p)\psi(q')\,\mathrm{d}q'\mathrm{d}p\,.$$

Examples:

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

Consider Hamilton operator $\widehat{H}$ whose symbol has expansion

$$H = E_0 + \sum_{s=2}^{\infty} H_s$$

with

$$H_s \in \mathcal{W}^s := \text{span}\{p^\alpha q^\beta \hbar^\gamma \;:\; |\alpha| + |\beta| + 2\gamma = s\}$$

and quadratic part

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

- Quantum normal form from conjugation by unitary operators

$$\widehat{H} =: \widehat{H}^{(2)} \to \widehat{H}^{(3)} \to \widehat{H}^{(4)} \to \cdots \to \widehat{H}^{(N)}$$

with

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

- choose $W_3, \ldots, W_N$ such that the symbol $H^{(N)}$ is up to order N a function of $I = p_1 q_1$, $J_k = \frac{1}{2}(p_k^2 + q_k^2)$, $k = 2, \ldots, f$, only
- it remains to quantise the powers of I and J_k. This leads to the recursion

$$\widehat{I^{n+1}} = \widehat{I}\widehat{I^n} - \widehat{I^{n-1}} n^2\hbar^2/4, \quad \widehat{J_k^{n+1}} = \widehat{J}_k\widehat{J_k^n} + \widehat{J_k^{n-1}} n^2\hbar^2/4$$

Result: $\widehat{H}^{(N)} = H_{\mathrm{QNF}}^{(N)}(\widehat{I}, \widehat{J}_2, \ldots, \widehat{J}_f)$

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- choose $W_3, \ldots, W_N$ such that the symbol $H^{(N)}$ is up to order N a function of $I = p_1 q_1$, $J_k = \frac{1}{2}(p_k^2 + q_k^2)$, $k = 2, \ldots, f$, only
- it remains to quantise the powers of I and J_k. This leads to the recursion

$$\widehat{I^{n+1}} = \widehat{I}\widehat{I^n} - \widehat{I^{n-1}} n^2\hbar^2/4, \quad \widehat{J_k^{n+1}} = \widehat{J}_k\widehat{J_k^n} + \widehat{J_k^{n-1}} n^2\hbar^2/4$$

Result: $\widehat{H}^{(N)} = H_{\mathrm{QNF}}^{(N)}(\widehat{I}, \widehat{J}_2, \ldots, \widehat{J}_f)$

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- Quantum normal form from conjugation by unitary operators

$$\widehat{H} =: \widehat{H}^{(2)} \to \widehat{H}^{(3)} \to \widehat{H}^{(4)} \to \cdots \to \widehat{H}^{(N)}$$

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Scattering states

eigenfunctions of $H^{(N)}_{\mathrm{QNF}}(\widehat{I}, \widehat{J}_2, \ldots, \widehat{J}_f)$ are products of the eigenfunctions of the harmonic oscillators $\widehat{J}_k$ and eigenfunctions of

$$\widehat{I} = -\mathrm{i}\hbar \left(q_1 \partial_{q_1} + \frac{1}{2} \right)$$

which are outgoing waves

$$\psi^{\text{out}}_{\text{react/prod}}(q_1) = \Theta(\mp q_1)|q_1|^{-1/2+\mathrm{i}I/\hbar}$$

and incoming waves

$$\psi^{\text{in}}_{\text{react/prod}}(q_1) = \frac{1}{\sqrt{2\pi\hbar}} \int \psi^{\text{out}\,*}_{\text{prod/react}}(p_1) \mathrm{e}^{\frac{\mathrm{i}}{\hbar} q_1 p_1} \, \mathrm{d}p_1$$

S-matrix

S-matrix is block diagonal with blocks

$$\begin{aligned} \psi_{\text{prod}}^{\text{in}} &= S_{n\,11}\,\psi_{\text{prod}}^{\text{out}} + S_{n\,12}\,\psi_{\text{react}}^{\text{out}} \\ \psi_{\text{react}}^{\text{in}} &= S_{n\,21}\,\psi_{\text{prod}}^{\text{out}} + S_{n\,22}\,\psi_{\text{react}}^{\text{out}} \end{aligned}$$

$$S_{\mathbf{n}}(E) = \frac{\mathrm{e}^{\mathrm{i}\left(\frac{\pi}{4} - \frac{I}{\hbar}\ln\hbar\right)}}{\sqrt{2\pi}}\Gamma\left(\frac{1}{2} - \mathrm{i}\frac{I}{\hbar}\right)\begin{pmatrix} -\mathrm{i}\mathrm{e}^{-\frac{\pi}{2}\frac{I}{\hbar}} & \mathrm{e}^{\frac{\pi}{2}\frac{I}{\hbar}} \\ \mathrm{e}^{\frac{\pi}{2}\frac{I}{\hbar}} & -\mathrm{i}\mathrm{e}^{-\frac{\pi}{2}\frac{I}{\hbar}} \end{pmatrix}$$

with I being implicitly defined by

$$H_{\text{QNF}}^{(N)}\big(I, \hbar(n_2 + 1/2), \dots, \hbar(n_f + 1/2)\big) = E$$

Cumulative reaction rate

Transmission probability of mode **n**

$$T_{\mathbf{n}}(E) = |S_{\mathbf{n}\,12}(E)|^2 = (1 + \mathrm{e}^{-2\pi \frac{I}{\hbar}})^{-1}$$

cumulative reaction probability

$$N(E) = \sum_{\mathbf{n}} T_{\mathbf{n}}(E)$$

Resonances

The S-matrix has poles at $I = -\mathrm{i}\hbar(n_1 + 1/2)$ for nonnegative integers n_1. These give the Gamov-Siegert resonances

$$H^{(N)}_{\mathrm{QNF}}\big(-\mathrm{i}\hbar(n_1 + 1/2), \hbar(n_2 + 1/2), \ldots, \hbar(n_f + 1/2)\big) = E$$

Example: coupled Eckart-Morse-Morse

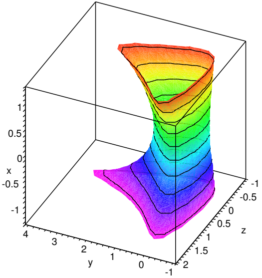
$$H = \frac{1}{2}(p_x^2 + p_y^2 + p_z^2) + V_{\mathrm{E}}(x) + V_{\mathrm{M};1}(y) + V_{\mathrm{M};2}(z) + \\ +\epsilon\,(p_x p_y + p_x p_z + p_y p_z) \qquad \text{(“kinetic coupling”)}$$

equipotential surface:

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

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

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



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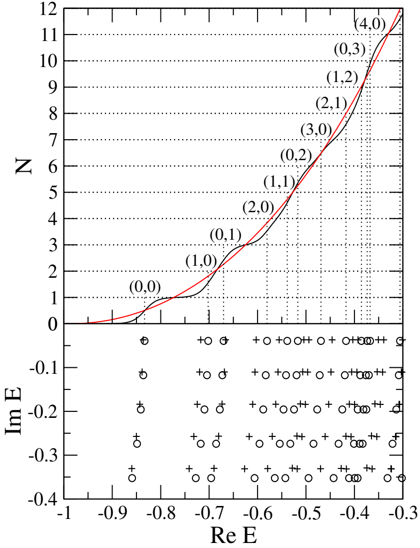
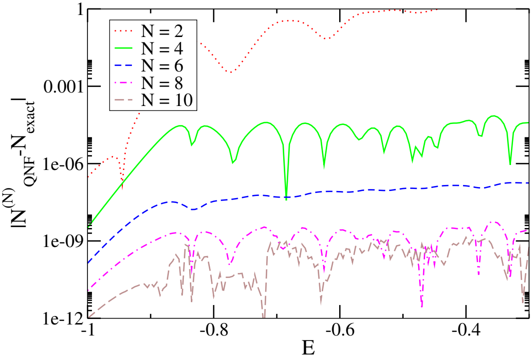
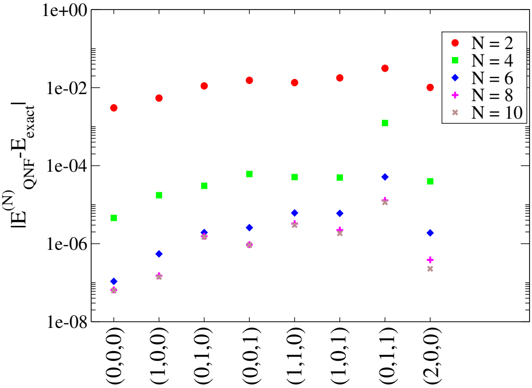
Cumulative reaction probability and resonances:



errors for cumulative reaction probability



errors for resonances



Conclusions

- reaction-type dynamics is controlled by high dimensional phase space structures:
  - NHIM (“activated complex”)
  - its stable and unstable manifolds
- they can be explicitly constructed from algorithms based on a Poincaré-Birkhoff normal form
- this opens the way to investigate key questions in reaction rate theory
- quantum normal form gives efficient procedure to compute resonances and reaction rates for high dimensional systems

Outlook

- scattering and resonance states $\leftrightarrow$ classical phase space structures (“quantum bottleneck states”; experimental observability)

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Collaborators:

Andrew Burbanks, Roman Schubert and Stephen Wiggins

Literature: (http://www.maths.bris.ac.uk/∼mazhw)

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