Classical and Quantum Reaction Dynamics in Multidimensional Systems

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Joint work with

- Andy Burbanks
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Wigner's dynamical transition state theory: classical and quantum

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



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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



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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

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



- How to construct a dividing surface with the desired properties for multidimensional systems?
- Recent high resolution experiments allow one to probe in unprecendented detail both
 - transition states
 - 'supermolecules' poised between reactants and products (transition state theory is not merely a concept to compute a rate, but 'transition states' are objects of their own physical significance)
 - the dynamics of reactions
 - violation of ergodicity assumptions (non RRKM behaviour; IVR)
- Understanding the mechanisms that govern reaction dynamics is a prerequisite for the control of chemical reactions
- How to realise a quantum version of transition state theory which inherits the computational benefits of (classical) transition state theory, and as a local and therefore computationally inexpensive theory makes the computation of quantum reaction rates feasible for multidimensional systems

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

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Classical Reaction Dynamics in Multidimensional Systems

Phase Space Conduits for Reaction



Phase Space Structures near a Saddle

Setup

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

Assume that the Hamiltonian vector field

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

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

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



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

Simplest case

Consider Hamilton function

$$\mathcal{H} = \frac{1}{2}p_x^2 - \frac{1}{2}\lambda^2 x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2$$
$$=: \mathcal{H}_x + \mathcal{H}_y$$

corresponding vector field is

$$\begin{pmatrix} \dot{p}_{X} \\ \dot{p}_{Y} \\ \dot{x} \\ \dot{y} \end{pmatrix} = J \, \mathsf{D}\mathcal{H} = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial p_{X}} \\ \frac{\partial \mathcal{H}}{\partial p_{Y}} \\ \frac{\partial \mathcal{H}}{\partial x} \\ \frac{\partial \mathcal{H}}{\partial y} \end{pmatrix} = \begin{pmatrix} \lambda^{2} x \\ -\omega_{y}^{2} y \\ p_{X} \\ p_{Y} \end{pmatrix}$$

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

$$H_X = E_X \in \mathbb{R}, \quad H_y = E_y \in [0, \infty), \quad H = E = E_X + E_y \in \mathbb{R}$$
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Phase Space Structures near a Saddle Linear vector field for f = 2 degrees of freedom

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3

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

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

E < 0:

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

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

Energy surface

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

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

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⇒ Energy surface

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

- = Σ_E bifurcates at E = 0 (the energy of the saddle) from *two* disconnected components to a *single* connected component
- Consider projection of Σ_E to $\mathbb{R}^3(x, y, p_y)$, i.e. project out

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

which gives two copies for the two signs of p_{x}

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

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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

 Σ_E for E < 0



Σ_E consists of two components representing reactants and products



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

 Σ_E for E < 0



• all trajectories have $H_x = E_x < 0$ and hence are non-reactive



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

 Σ_E for E < 0



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

 Σ_E for E > 0



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



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

 Σ_E for E > 0



• Non-reactive trajectories have $H_x = E_x < 0$



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

 Σ_E for E > 0



• Non-reactive trajectories have $H_x = E_x < 0$



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

 Σ_E for E > 0



• Reactive trajectories have $H_x = E_x > 0$



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

$$\Sigma_E$$
 for $E > 0$



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



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

 Σ_E for E > 0



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



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

 Σ_E for E > 0



• Stable manifolds $W^{s} \simeq S^{1} \times \mathbb{R}$ has $\mathcal{H}_{x} = E_{x} = 0$ with $p_{x} = -\lambda x$



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

 Σ_E for E > 0



• Unstable manifolds $W^{u} \simeq S^{1} \times \mathbb{R}$ has $\mathcal{H}_{x} = E_{x} = 0$ with $p_{x} = \lambda x$



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

 Σ_E for E > 0



 Forward cylinder W^s_r ∪ W^u_p and backward cylinder W^s_p ∪ W^u_r enclose all the forward and backward reactive trajectories, respectively


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

 Σ_E for E > 0



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



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

 Σ_E for E > 0



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

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



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

 Σ_E for E > 0



• 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 $p_x \neq 0$)



Phase Space Structures near a Saddle General (nonlinear) case

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



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Quantum Transition State Theory Outlook

Phase Space Structures near a Saddle General (nonlinear) case; E > 0

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

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

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

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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 $\pm \lambda, \pm i\omega_2, \ldots, \pm i\omega_f, \lambda, \omega_k > 0$. Assume that the linear frequencies $(\omega_2, \ldots, \omega_f)$ are linearly independent over \mathbb{Q} . Then, for any given order, there exists a 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

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

where

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



- 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



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- 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



- 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
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Example: HCN/CNH Isomerisation



3 DoF for vanishing total angular momentum: Jacobi coordinates r, R, γ

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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

Quantum Transition State Theory Outlook

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



uantum Transition State Theory Outlook

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Classical and Quantum Reaction Dynamics in Multidimensional Systems

Example: HCN/CNH Isomerisation Phase space structures



- transverse to Hamiltonian vector field
- minimises the flux

- transition state or activated complex
- 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



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Global Recrossings and Rare Events

The role of homoclinic and heteroclinic connections

Homoclinic connections

orbits contained in the stable and unstable manifold of the same NHIM

Heteroclinic connections

orbits contained in the stable and unstable manifold of different NHIMs

Heteroclinic cycles

succession of heteroclinic connections

H. W., A. Burbanks & S. Wiggins (2004) J. Phys. A 37 L257

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Quantum Transition State Theory Outlook

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



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Example: HCN/CNH Isomerisation Homoclinic and heteroclinic connections

Heteroclinic connection between invariant 2-tori in different NHIMs





Example: HCN/CNH Isomerisation Homoclinic and heteroclinic connections

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





Example: HCN/CNH Isomerisation Homoclinic and heteroclinic connections

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





Violations of ergodicity assumptions

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

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

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

where

 $\langle t \rangle_{B_{ds;j}}$ = mean residence time in the region *M* of trajectories starting on the *j*th dividing surface *B*_{ds;j} *N*_{*B*_{ds;j}} = flux through *j*th dividing surface *B*_{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

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Quantum Transition State Theory Outlook

Example: HCN/CNH Isomerisation Reactive phase space volumes



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

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

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

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Outlool

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



Quantum Transition State Theory Outlook

Example: HCN/CNH Isomerisation Reactive phase space subvolumes




Quantum Transition State Theory Outlook

Example: HCN/CNH Isomerisation Reactive phase space subvolumes







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Quantum Transition State Theory Outlook

Example: HCN/CNH Isomerisation Reactive phase space subvolumes







Quantum Transition State Theory Outlook

Example: HCN/CNH Isomerisation Reactive phase space subvolumes







Example: Müller-Brown Potential Reactive phase space volumes

Example with f = 2 degrees of freedom

$$\mathcal{H} = \frac{1}{2}(p_x^2 + p_y^2) + V_{\rm MB}(x, y)$$



upper deep potential well

lower shallow potential well



Example: Müller-Brown Potential Reactive phase space volumes

Example with f = 2 degrees of freedom

$$\mathcal{H} = \frac{1}{2}(p_x^2 + p_y^2) + V_{\rm MB}(x, y)$$



Iso-residence times in the upper and lower well on the dividing surface hemispheres



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Example: Müller-Brown Potential Reactive phase space volumes

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Iso-residence times in the upper and lower well on the dividing surface hemispheres



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Example: Müller-Brown Potential Reactive phase space volumes

Iso-residence times along the line $P_2 = 0$



Iso-residence times in the upper and lower well on the dividing surface hemispheres



Quantum Reaction Dynamics in Multidimensional Systems

Quantum Transition State Theory



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Quantum Transition State Theory

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

Main idea: "locally simplify" Hamilton function/operator

symplectic transformations

 $\mathcal{H} \mapsto \mathcal{H} \circ \phi$

(classical) normal form

unitary transformations

 $\widehat{H} \mapsto U \widehat{H} U^{\star}$

quantum normal form

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Quantum Transition State Theory

classical	quantum
Hamilton's equations	Schrödinger equation
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Quantum Transition State Theory

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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

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

Examples:

$$\begin{array}{c|c} A & A \\ \hline J := \frac{1}{2}(p^2 + q^2) & \widehat{J} := -\frac{\hbar^2}{2}\frac{\mathrm{d}^2}{\mathrm{d}q^2} + \frac{1}{2}q^2 \\ I := pq & \widehat{I} := -\mathrm{i}\hbar(q\frac{\mathrm{d}}{\mathrm{d}q} + \frac{1}{2}) \end{array}$$



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	A	A
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2

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Examples:



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Theorem (Quantum Normal Form) Consider a Hamilton operator \hat{H} whose (principal) symbol has a saddle equilibrium point like in our classical setup, i.e. $J D^2 H$ 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

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

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

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- 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



- $\hat{H}_{\text{ONF}}^{(N)}$ is an operator function of the 'elementary' operators $\hat{l}, \hat{J}_k, k = 2, \dots, f$, whose spectral properties are well known
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classical

Taylor expansion of Hamilton function \mathcal{H} about critical point: $\mathcal{H} = \sum_{s=2}^{\infty} \mathcal{H}_s$ with

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

for saddle-centre-...-centre:

$$\begin{aligned} \mathcal{H}_2 &= \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f \\ I &= p_1 q_1, J_k = \frac{1}{2} (p_k^2 + q_k^2), \quad k = 2, \ldots, f \end{aligned}$$

successive symplectic transformations

$$\begin{split} \mathcal{H} &=: \mathcal{H}^{(2)} \to \mathcal{H}^{(3)} \to \ldots \to \mathcal{H}^{(N)} \\ \mathcal{H}^{(n)} &= \mathcal{H}^{(n-1)} \circ \phi_{\mathcal{W}_n}^{-1} \,, \quad \mathcal{W}_n \in \mathcal{P}_{\mathsf{Cl}}^n \end{split}$$



quantum

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quantum Taylor expansion of the symbol H of \hat{H} about critical point: $H = \sum_{s=2}^{\infty} H_s$ with $H_s \in \mathcal{P}^s_{\mathrm{dm}} = \mathrm{span}\{p^{\alpha}q^{\beta}\hbar^{\gamma}: |\alpha| + |\beta| + 2\gamma = s\}$



classical	quantum
Taylor expansion of Hamilton function ${\cal H}$	Taylor expansion of the symbol <i>H</i> 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
$\mathcal{H}_{s} \in \mathcal{P}_{cl}^{s} = span\{p^{lpha}q^{eta}: \ lpha + eta = s\}$	$H_{s} \in \mathcal{P}_{qm}^{s} = span\{p^{lpha}q^{eta}\hbar^{\gamma}: lpha + eta + 2\gamma = s\}$
for saddle-centrecentre:	for saddle-centrecentre:
$\mathcal{H}_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$	$H_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$
$I = p_1 q_1, J_k = \frac{1}{2} (p_k^2 + q_k^2), k = 2, \dots, f$	$I = p_1 q_1, J_k = \frac{1}{2} (p_k^2 + q_k^2), k = 2, \dots, f$



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



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classical	quantum
	^
Taylor expansion of Hamilton function ${\cal H}$	Taylor expansion of the symbol H of 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
$\mathcal{H}_{s} \in \mathcal{P}_{cl}^{s} = span\{ p^{lpha} q^{eta}: \ lpha + eta = s \}$	$H_{s} \in \mathcal{P}_{qm}^{s} = span\{p^{lpha}q^{eta}\hbar^{\gamma}: \ lpha + eta +2\gamma=s\}$
for saddle-centrecentre:	for saddle-centrecentre:
$\mathcal{H}_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$	$H_2 = \lambda I + \omega_2 J_2 + \ldots + \omega_f J_f$
$I = p_1 q_1, J_k = \frac{1}{2} (p_k^2 + q_k^2), k = 2, \dots, f$	$I = p_1 q_1, J_k = \frac{1}{2}(p_k^2 + q_k^2), k = 2, \dots, f$
successive symplectic transformations	successive unitary transformations
$\mathcal{H} =: \mathcal{H}^{(2)} ightarrow \mathcal{H}^{(3)} ightarrow \ldots ightarrow \mathcal{H}^{(N)}$	$\widehat{H} =: \widehat{H}^{(2)} \to \widehat{H}^{(3)} \to \ldots \to \widehat{H}^{(N)}$
$\mathcal{H}^{(n)} = \mathcal{H}^{(n-1)} \circ \phi_{\mathcal{W}_n}^{-1}, \mathcal{W}_n \in \mathcal{P}_{cl}^n$	$\widehat{H}^{(n)} = \mathrm{e}^{\frac{\mathrm{i}}{\hbar} \widehat{W}_n} \widehat{H}^{(n-1)} \mathrm{e}^{-\frac{\mathrm{i}}{\hbar} \widehat{W}_n}, W_n \in \mathcal{P}_{\mathrm{qm}}^n$



classical	quantum
for $s < n$: $\mathcal{H}_s^{(n)} = \mathcal{H}_s^{(n-1)}$	for $s < n$: $H_s^{(n)} = H_s^{(n-1)}$
$ \begin{split} &\text{for } s \geq n; \mathcal{H}_s^{(n)} = \sum_{j=0}^{\lfloor \frac{s-1}{n-1} \rfloor} \frac{1}{j!} [ad_{\mathcal{W}_n}]^j \mathcal{H}_{s-j(n-2)}^{(n-1)} \\ &\text{where } ad_{\mathcal{W}_n} := \{\mathcal{W}_n, \cdot\} \\ &\text{with Poisson bracket } \{A, B\}(\rho, q) = \end{split} $	
	$\frac{2}{\hbar}A(p,q)\sin\left(\frac{\hbar}{2}[\langle \overleftarrow{\partial}_{p}, \overrightarrow{\partial}_{q} \rangle - \langle \overrightarrow{\partial}_{p}, \overleftarrow{\partial}_{q} \rangle]\right)B(p,q)$ choose $W_{n}, n = 2, \dots, N$, such that $\{H_{2}, H_{n}^{(n)}\}_{M} = 0 (\text{i.e. } [\widehat{H}_{2}, \widehat{H}_{n}^{(n)}] = 0)$ from solving the homological equation $H_{n}^{(n)} = H_{n}^{(n-1)} + \{W_{n}, H_{2}\}$

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classical	quantum
for $s < n$: $\mathcal{H}_s^{(n)} = \mathcal{H}_s^{(n-1)}$	for $s < n$: $H_s^{(n)} = H_s^{(n-1)}$
$ \begin{split} &\text{for } s \geq n; \mathcal{H}_s^{(n)} = \sum_{j=0}^{\lfloor \frac{s-1}{n-1} \rfloor} \frac{1}{j!} [\text{ad}_{\mathcal{W}_n}]^j \mathcal{H}_{s-j(n-2)}^{(n-1)} \\ &\text{where } \text{ad}_{\mathcal{W}_n} := \{\mathcal{W}_n, \cdot\} \\ &\text{with Poisson bracket } \{A, B\}(\rho, q) = \end{split} $	for $s \ge n$: $H_s^{(n)} = \sum_{j=0}^{\lfloor \frac{s-1}{n-1} \rfloor} \frac{1}{j!} [Mad_{W_n}]^j H_{s-j(n-2)}^{(n-1)}$ where $Mad_{W_n} := \{W_n, \cdot\}_M$ 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 , $n = 2,, N$, such that



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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 $s \geq n$: $\mathcal{H}_{s}^{(n)} = \sum_{j=0}^{\left[\frac{s-1}{n-1}\right]} \frac{1}{j!} [\operatorname{ad}_{\mathcal{W}_{n}}]^{j} \mathcal{H}_{s-j(n-2)}^{(n-1)}$ where $\operatorname{ad}_{\mathcal{W}_{n}} := \{\mathcal{W}_{n}, \cdot\}$ with Poisson bracket $\{A, B\}(\rho, q) =$	for $s \ge n$: $H_s^{(n)} = \sum_{j=0}^{\left\lfloor \frac{s-1}{n-1} \right\rfloor} \frac{1}{j!} [Mad_{W_n}]^j H_{s-j(n-2)}^{(n-1)}$ where $Mad_{W_n} := \{W_n, \cdot\}_M$ with Moyal bracket $\{A, B\}_M(p, q) =$
$A(p,q)[\langle \overleftarrow{\partial}_{p}, \overrightarrow{\partial}_{q} \rangle - \langle \overrightarrow{\partial}_{p}, \overleftarrow{\partial}_{q} \rangle]B(p,q)$ choose $\mathcal{W}_{n}, n = 2, \dots, N$, such that	$\frac{2}{\hbar}A(p,q)\sin\left(\frac{\hbar}{2}[\langle \overleftarrow{\partial}_{p}, \overrightarrow{\partial}_{q} \rangle - \langle \overrightarrow{\partial}_{p}, \overleftarrow{\partial}_{q} \rangle]\right)B(p,q)$ choose $W_{n}, n = 2, \dots, N$, 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	



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 $s \ge n$: $\mathcal{H}_s^{(n)} = \sum_{j=0}^{\lfloor \frac{s-1}{n-1} \rfloor} \frac{1}{j!} [\operatorname{ad}_{\mathcal{W}_n}]^j \mathcal{H}_{s-j(n-2)}^{(n-1)}$ where $\operatorname{ad}_{\mathcal{W}_s} := \{\mathcal{W}_n\}$	for $s \ge n$: $H_s^{(n)} = \sum_{j=0}^{\lfloor \frac{s-1}{n-1} \rfloor} \frac{1}{j!} [Mad_{W_n}]^j H_{s-j(n-2)}^{(n-1)}$ where $Mad_{W_n} := \{W_n\}_{M_n}$
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 , $n = 2,, N$, 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
$\mathcal{H}_n^{(n)} = \mathcal{H}_n^{(n-1)} + \{\mathcal{W}_n, \mathcal{H}_2\}$	$H_n^{(n)} = H_n^{(n-1)} + \{W_n, H_2\}$





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Quantum normal form computation of the cumulative reaction probability

Scattering states are eigenfunctions of

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

i.e.

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

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



Quantum normal form computation of the cumulative reaction probability





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

$$N(E) = \sum_{n_{\text{scatt}}} T_{n_{\text{scatt}}}(E) = \sum_{n_{\text{scatt}} \in \mathbb{N}_{0}^{f-1}} \left[1 + \exp\left(-2\pi \frac{l_{n_{\text{scatt}}}(E)}{\hbar}\right) \right]^{-1}$$

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

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



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Quantum normal form computation of the cumulative reaction probability

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Example: Coupled Eckart-Morse-Morse Potential

$$H = \frac{1}{2}(p_x^2 + p_y^2 + p_z^2) + \underbrace{V_{\mathsf{E}}(x) + V_{\mathsf{M};y}(y) + V_{\mathsf{M};z}(z)}_{V_{\mathsf{E}}(x) = \frac{Ae^{ax}}{1 + e^{ax}} + \frac{Be^{ax}}{(1 + e^{ax})^2}} + \underbrace{\epsilon(p_x p_y + p_x p_z + p_y p_z)}_{\text{'kinetic coupling'}}$$
$$V_{\mathsf{M};y}(y) = D_y \left(e^{(-2\alpha_y y)} - 2e^{(-\alpha_y y)} \right)$$
$$V_{\mathsf{M};z}(z) = D_z \left(e^{(-2\alpha_z z)} - 2e^{(-\alpha_z z)} \right)$$

Iso-potential surfaces:





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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



Classical and Quantum Reaction Dynamics in Multidimensional Systems

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

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

to the lower half plane

Quantum resonances are obtained from complex Bohr-Sommerfeld quantization conditions

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

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

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Quantum resonances (Gamov-Siegert resonances) Husimi functions of resonance states in the saddle plane



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Example: Coupled Eckart-Morse-Morse Potential Quantum resonances



Classical and Quantum Reaction Dynamics in Multidimensional Systems

Periodic Orbit Formula for Cumulative Reaction Probability

$$n(E) := \frac{\mathrm{d}N(E)}{\mathrm{d}E} \approx n_0(E) + n_{\mathrm{osc}}(E)$$

where

 $n_0(E)$: Thomas-Fermi or Weyl term (corresponds to classical flux at energy *E*) $n_{osc}(E)$: sum over the fully resonant tori contained in the NHIM at energy *E*

More precisely, each q^{th} repetition of a resonant torus with frequencies $\Omega \sim \mu$ where $\mu \in \mathbb{N}_0^{\text{f}}$ coprime, contributes to $n_{\text{osc}}(E)$ a term

$$n_{\mu,q}(E) = \frac{2\pi}{\hbar^{(f+1)/2}} \frac{\lambda}{\sinh\left(\pi q \frac{|\mu|}{|\Omega|}\lambda\right)} \frac{\cos\left(q(2\pi\mu \cdot \mathbf{J}/\hbar - \pi\mu\alpha/2 - 2\pi|\mu|\lambda l_1/|\Omega|) + \pi\beta/4\right)}{q^{(f-3)/2}|\mu|^{(f-3)/2}|\Omega|^2 \sqrt{|\det K(\mathbf{J}^{\mu})|}}$$

where

- $\lambda = \frac{\partial H_0}{\partial I}(0, \mathbf{J})$ (stability index of resonant torus)
- α is the vector of Maslov indices (here $\alpha_k = 2$)
- *K* is the curvature tensor of the energy surface $\Sigma_E = \{\mathbf{J} : H_0(0, \mathbf{J}) = E\}$ (NHIM)
- β is the index of *K*

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Periodic Orbit Formula for Cumulative Reaction Probability

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Periodic Orbit Formula for Cumulative Reaction Probability Example: Eckart-Morse-Morse potential

Energy surfaces Σ_E with resonance lines μ_1/μ_2





Periodic Orbit Formula for Cumulative Reaction Probability Example: Eckart-Morse-Morse potential

Exact (dashed line) and periodic orbit approximation (solid line) of n(E) including resonant tori with $\mu_1, \mu_2 \le 3$





Summary

- reaction-type dynamics is controlled by high dimensional phase space structures:
 - NHIM ('activated complex')
 - its stable and unstable manifolds

which 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 leads to an efficient procedure to compute resonances and reaction rates for high dimensional systems

Outlook

- effect of rotation/vibration coupling on isomerisation problems (global effects of SO(3) reduction)
- experimental observability of 'quantum bottleneck states'
- state-to-state reactivity in complex reactions



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Funding



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