

Reactive and inelastic collisions

Transition states

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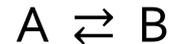
Subject of this talk

- I. Why bothering doing dynamics for molecular collisions?
 - a. General frame
 - b. Transition state theory

- II. How to do dynamics (or rather, how to try and hope to do dynamics)?
 1. Limits and capabilities
 2. Classical TS structure $n \leq 2$ degree of freedom
 3. Classical TS structure $n > 2$ degree of freedom
 4. Angular momentum, an incentive

Definition (*kind of*)

A general system transits from configuration/state A to state B, maybe reversibly:



The intermediate, which is supposed to separate A from B is a transition state:



It is the magic border which separates, assuming that such a border exists.

The following is often implied: If A reaches T*, it is supposed to continue onto B; if B reaches T*, it continues to A



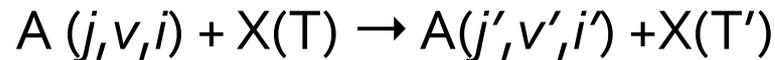
IN CHEMISTRY



j: rotation; v: vibration; i electronic state; T kinetic energy

Examples:

- Inelastic scattering:



All quantum number need not change. One is enough.

- Reactive scattering :



IN CHEMISTRY

- What is a chemical reaction?

Many things:

- Electron mediated:
 - $AB^+ + e^- \rightarrow A + B$ (dissociative recombination)
 - $A + B^- \rightarrow AB + e^-$ (associative detachment)

Extremely difficult theoretically: major role of electronic excited states, including molecular electronic Rydberg state (1 very excited electron). All Born-Oppenheimer type of approximations \pm senseless

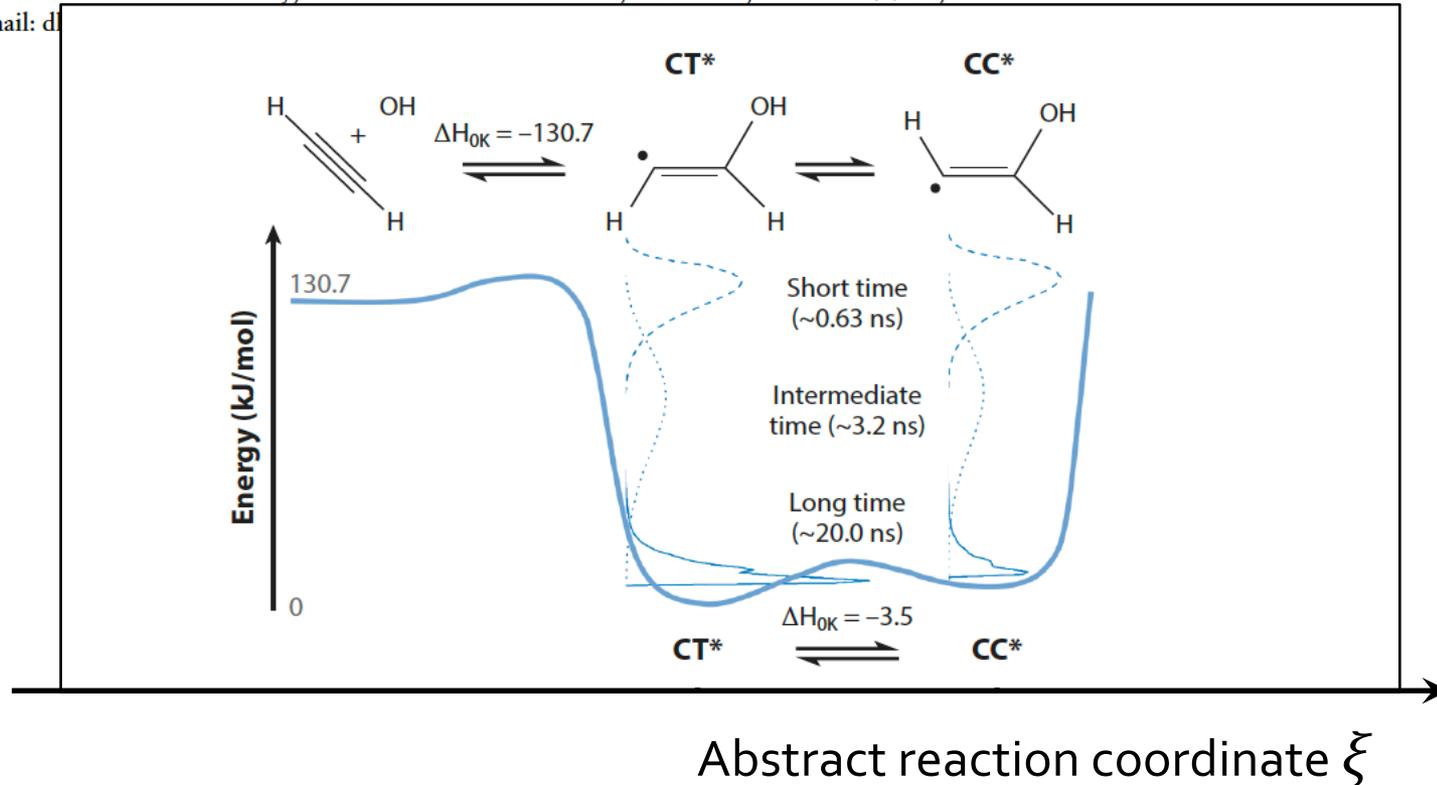
- Electron exchange, intersystem crossings (magnetic transitions, spin-flips)
 - $X_2 + H\bullet \rightarrow HX + X\bullet$
 - $CN\bullet + O\bullet \rightarrow CO + N\bullet\bullet$

Reaction Mechanisms on Multiwell Potential Energy Surfaces in Combustion (and Atmospheric) Chemistry

David L. Osborn

Combustion Research Facility, Sandia National Laboratories, Livermore, California 94550;

email: d

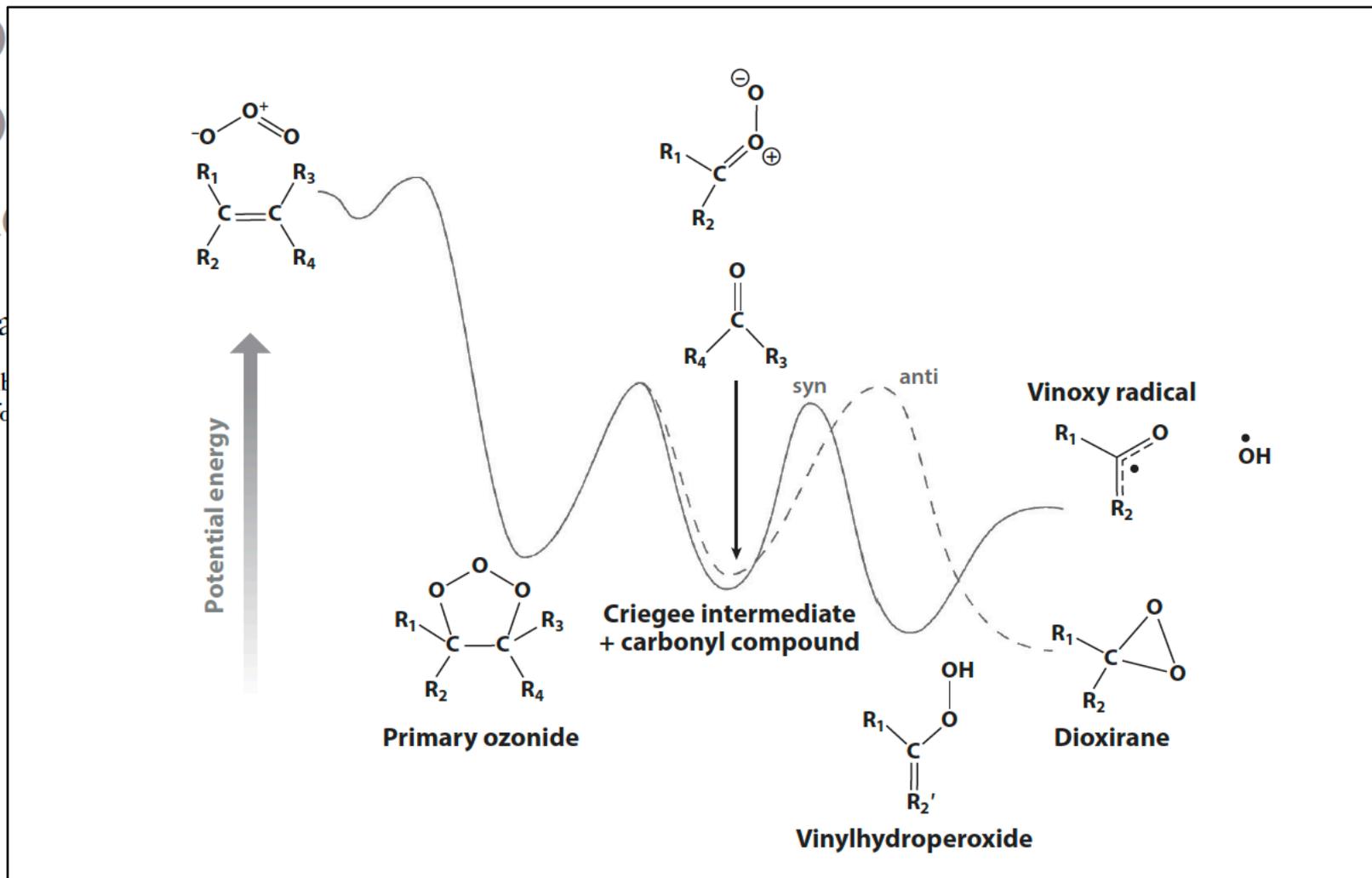


Criegee Intermediates: What

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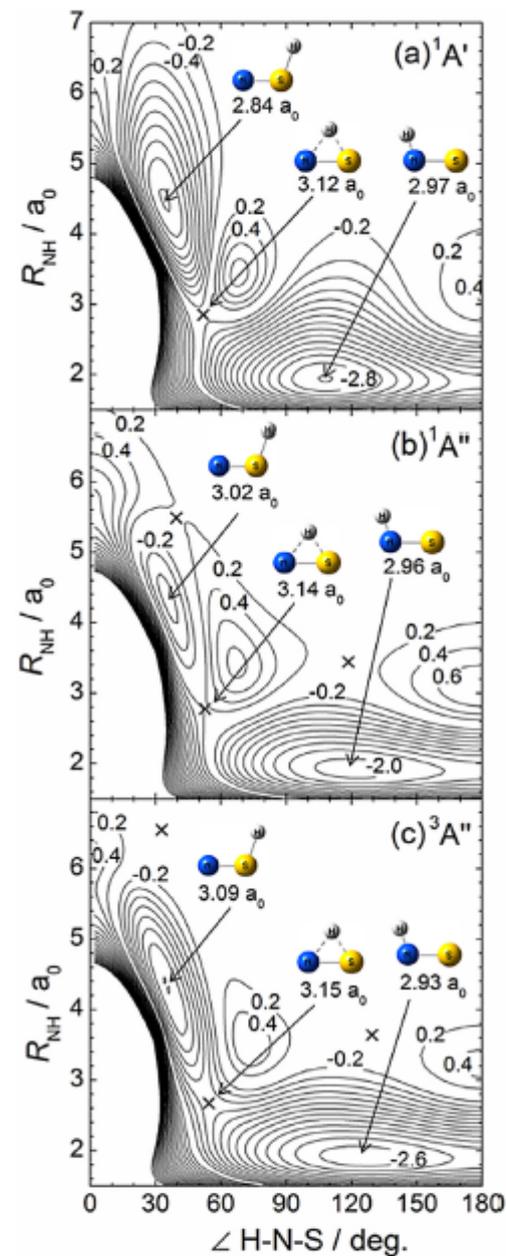
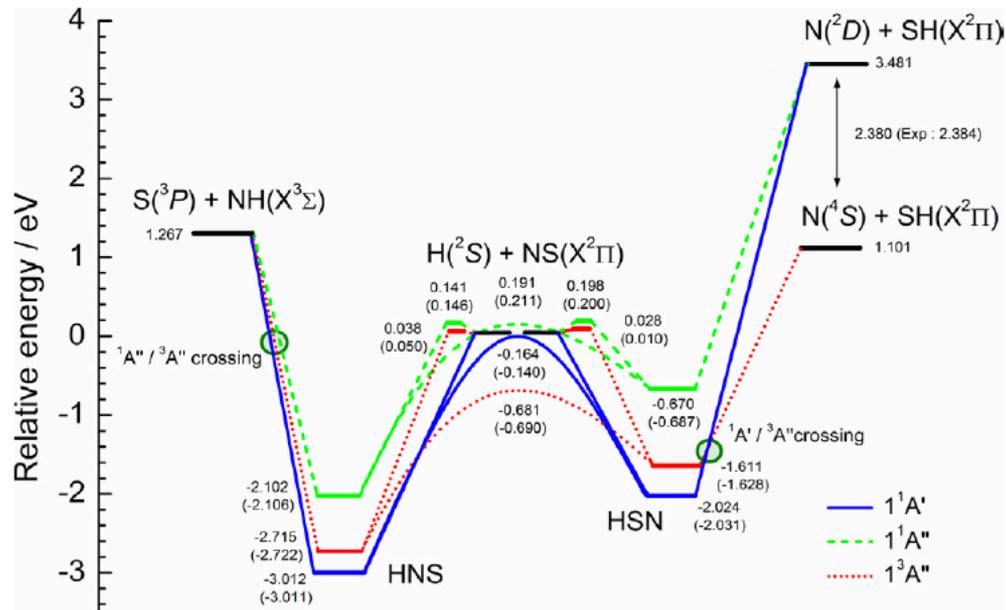
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Construction of global *ab initio* potential energy surfaces for the HNS system and quantum dynamics calculations for the $S(^3P) + NH(X^3\Sigma) \rightarrow NS(X^2\Pi) + H(^2S)$ and $N(^4S) + SH(X^2\Pi) \rightarrow NS(X^2\Pi) + H(^2S)$ reactions

Kazuma Sato, Toshiyuki Takayanagi*

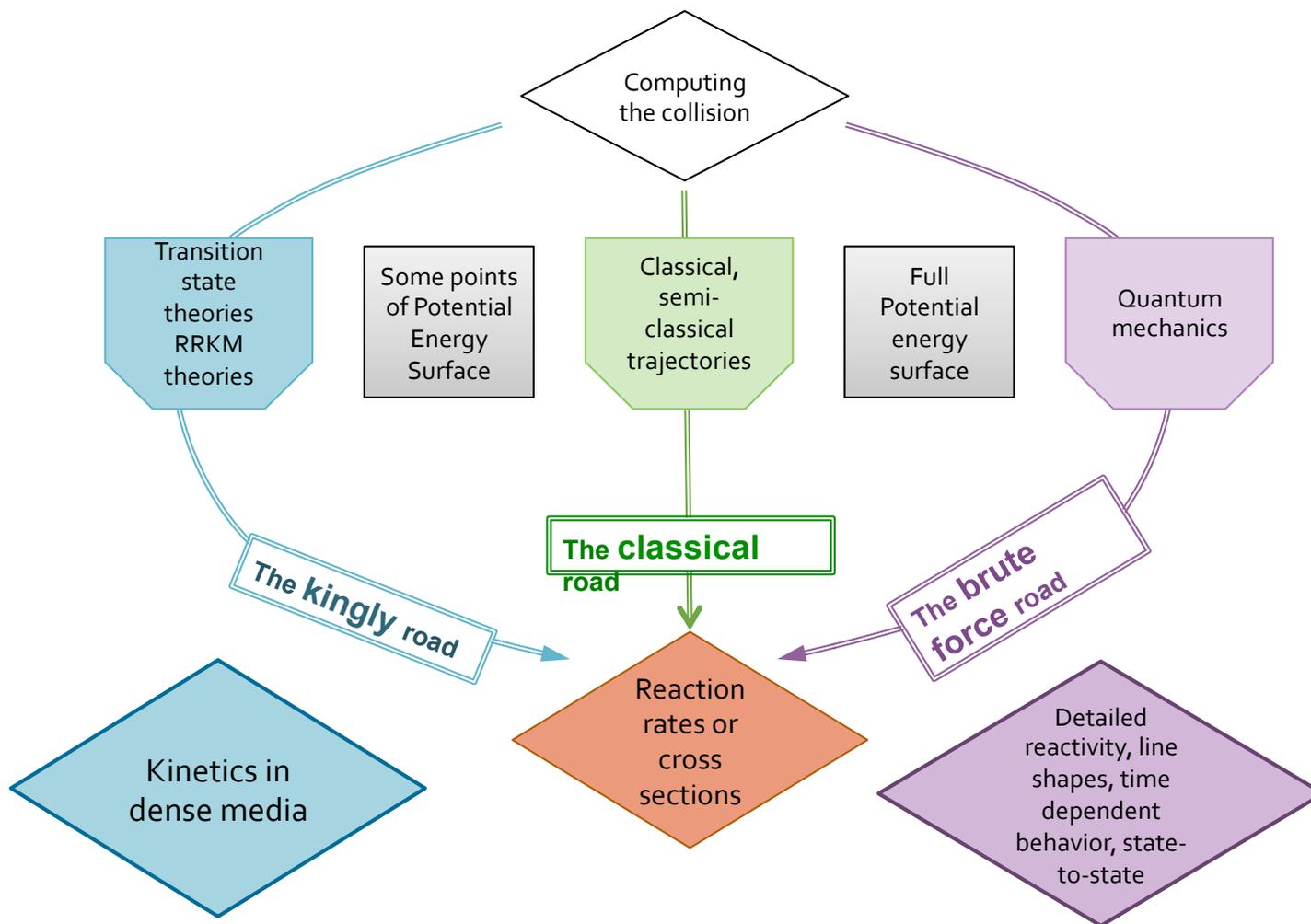
Department of Chemistry, Saitama University, 255 Shimo-Ogino, Sakura-ku, Saitama City, Saitama 338-8570, Japan



2. Contour maps of the three HSN potential energy surfaces plotted as a function of the H-N bond distance and the $\angle H-N-S$ angle with an optimized N-S bond distance. The zero energy is defined at the H+NS dissociation limit. The contours are spaced by 0.2 eV. For stationary point properties on these potential energy surfaces, see Table 1 for detail.

WHAT CAN WE DO WITH SUCH A
COMPLEX LANDSCAPE?

The usual pathways to compute transition rates



The thermochemical picture : TST, 1D

Microcanonical ensemble :
RRKM

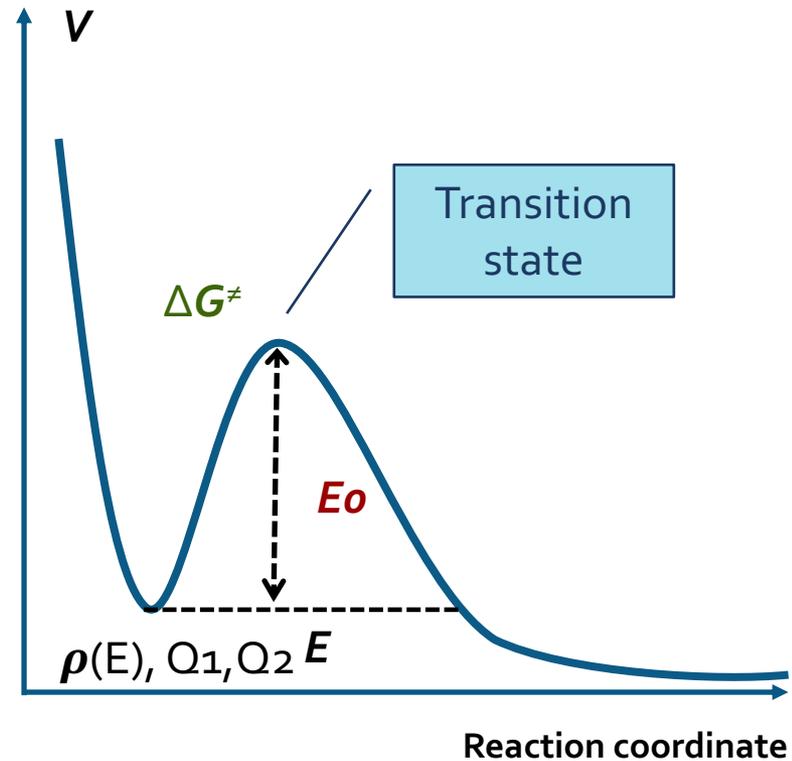
$$k(E) = \frac{N^\ddagger(E - E_0)}{b \rho(E)},$$

Canonical ensemble: Arrhenius-
Eyring

$$k_{\text{TST}}(\beta) = \frac{kT}{h} \frac{Q^\ddagger}{Q_1 Q_2} e^{-E\beta},$$

Extremely successful especially
so for very multidimensional
cases (ergodic hypothese)

Potential shape



When does TST fail?

- **Main cause : no mixing in phase space.** Time scales not long enough to have a uniform population in all the modes (or across whole phase space). (break down of the ergodicity)
- Mixing: Long enough time, high enough density (elastic collisions reshuffle the modes), fast IVR.
- More fundamentally: relevance of thermodynamics, existence of temperature, of one temperature

($T_{\text{internal}} = T_{\text{kinetic}}$, so called Local Thermodynamical Equilibrium)

- OK:
 - Our atmosphere, usual chemical reaction in the lab, in industry, in condensed phases
- Not OK:
 - Fast evolving physical parameters: no steady state: combustion in motors
 - Chemical rate slower than full physical equilibrium timescales: astrochemistry, high atmospheres
 - Very low T molecular physics, towards quantum molecular gases:
 $T_{\text{kin}} \neq T_{\text{rot}} \neq T_{\text{vib}}$ ($T_{\text{kin}} \sim \text{nK} - \mu\text{K}$, $T_{\text{vib}} = 0$)

One has to resort to dynamics

- Do we need **S**-matrix, cross sections, rates ?
 - $k(T) = \langle \sigma(E) p(E) \rangle_T$
 - Need to average $\sigma(E)$ over a strongly varying function of E .
- **Quantum dynamics:** Towards the full **S**(E) matrix

Really tough, for many reasons

- NOT because of the microcanonical formalism, nor the Hamiltonian, nor the PES
- BUT the size of the problem and the difficulty to do reactivity – no single best coordinate system, high demand on linear algebra
- Typically propagate $N \times N$ matrices representative of the Hamiltonian, $N \sim 10000$ or more (heavy atoms), thousands of time; millions of CPU hours, for 3-4 atoms.
- Only MCTDH represents (maybe) a breakthrough
 - Surely for bound problem
 - For scattering ?

Example of inelastic $\sigma(E)$

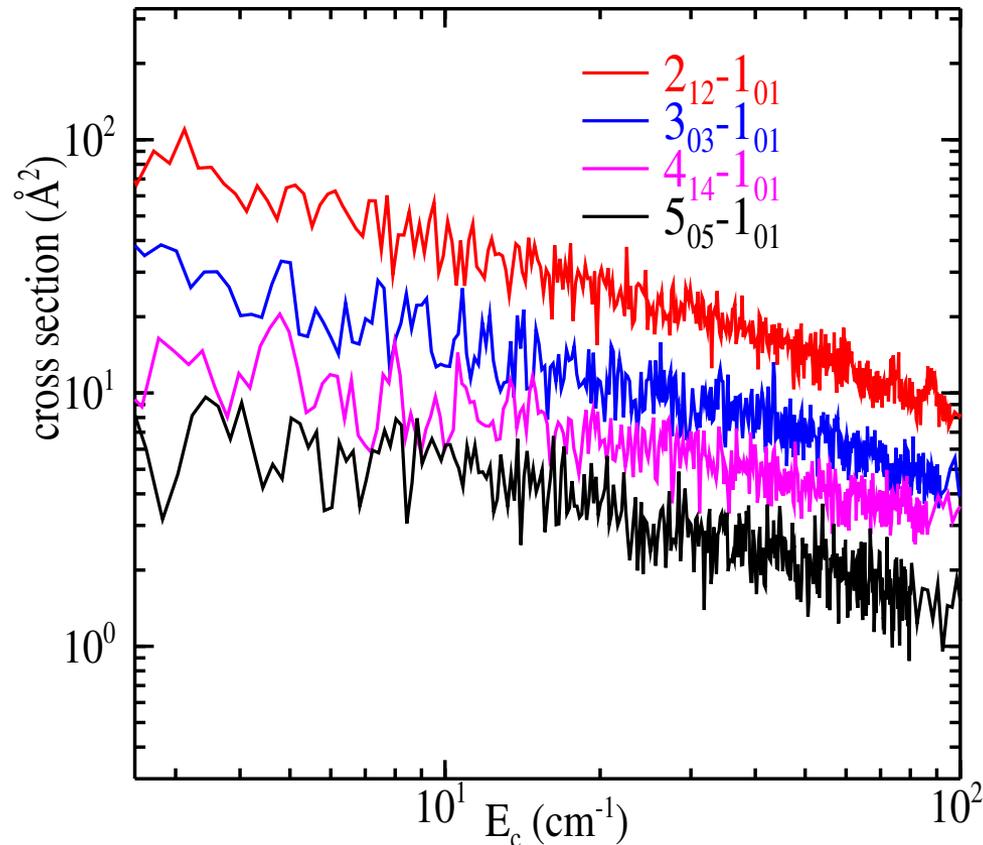
Collision $c\text{-C}_3\text{H}_2 - \text{He}$

Inelastic collisions,
rotational
deexcitation

CC computation,
"exact"

No numerical noise
at this scale

Ben Khalifa et al.
2020



WHY RESORT TO CLASSICAL DYNAMICS, HOW COULD IT OF HELP?

Lamp post paradox
we do not know (in advance) if classical dynamics is relevant,
but there is no way out.



WHY RESORT TO CLASSICAL DYNAMICS, HOW COULD IT OF HELP?

- Numerically doable in many dimensions, many degrees of freedom, any reasonable potential
- No real problem for computing either $\sigma(E)$ (micro-canonical sampling) or $k(T)$ (canonical sampling).
- Results not too bad for (better than an order of magnitude)
 - Main routes, large rates
 - Main internal energy distributions
- Results questionable or meaningless
 - Small probabilities
 - Internal degrees of freedom after collisions (so called state-to-state reactivity)
- Structure of phase space , use of TS

APPROXIMATIONS TOWARDS CLASSICAL DYNAMICS

- Hamiltonian classical dynamics & structure of phase space as seen from the point of view of chemical reactivity/scattering
 - **Guide to further dynamics**, to the various approximations or formalisms that one would like to try.
- One surface; Born – Oppenheimer everywhere valid
- We have the equation of motion (\neq nuclear physics, e.g.)
- Classical view point:
 - Usually time dependent picture
 - Symmetries
 - Space symmetries should be OK \leftarrow potential
 - Spin symmetries (ortho-para...) difficult
- Hamiltonian chaos is probably more a nuisance than a help ; do not focus on peculiar trajectories, only ensemble are relevant.

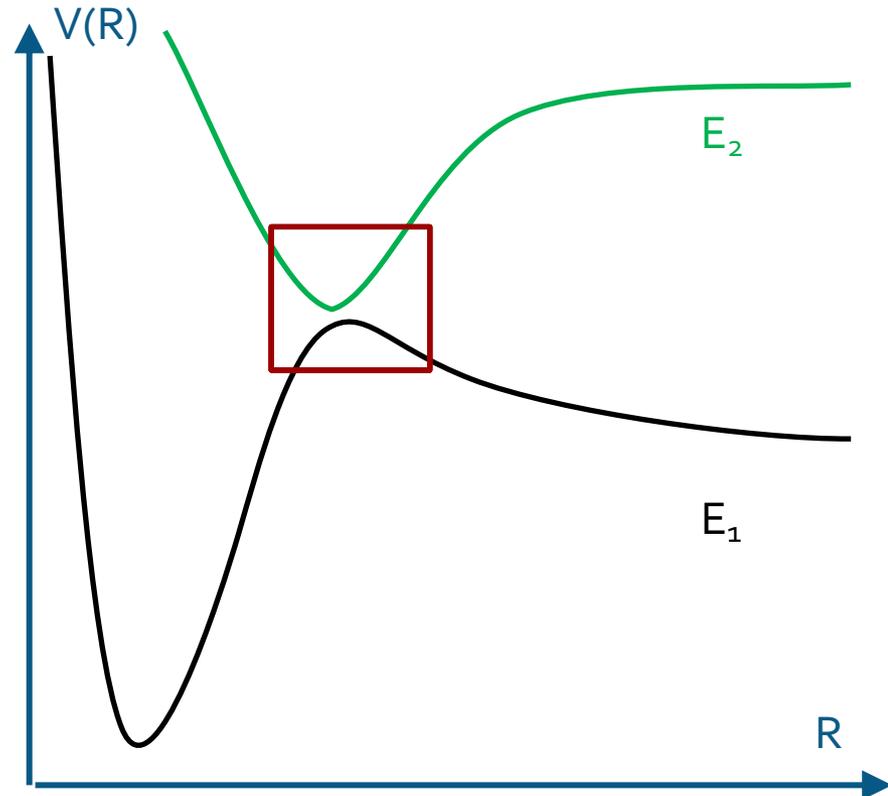
Describe dynamics

Full Hamiltonian (non relativistic, but ...) couples all bodies in the molecule:

$$H = T_{\text{electrons}} + V_{\text{el-el}} + V_{\text{el-nucl}} + V_{\text{nucl-nucl}} + T_{\text{nuclei}}$$

Procedure (in a nutshell)

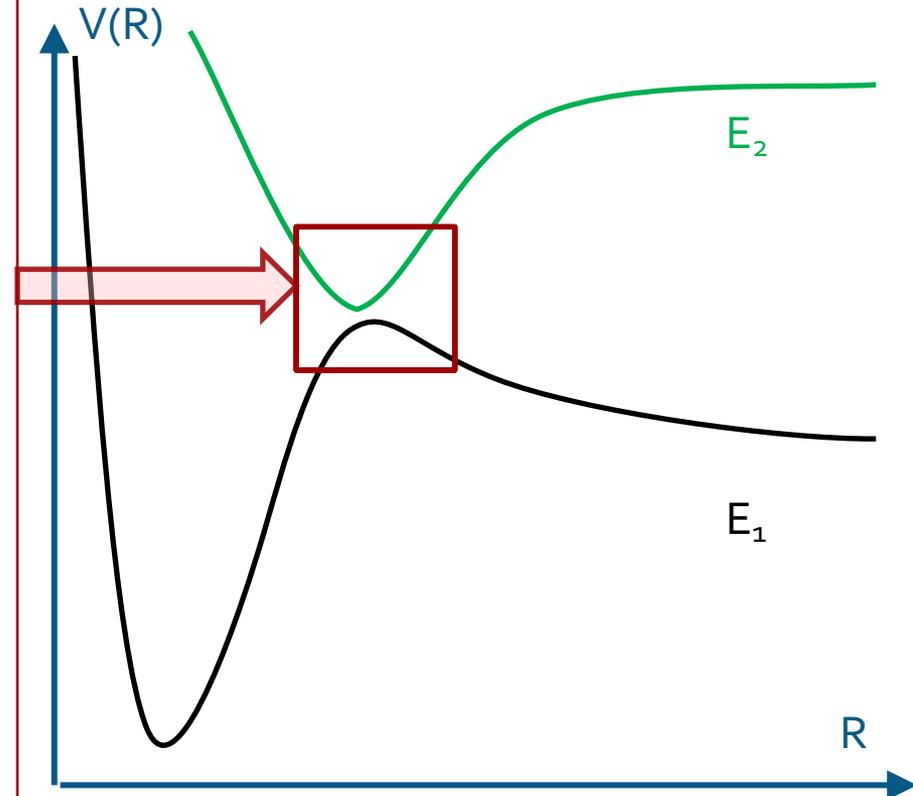
1. Clamp nuclei, solve for eigenvalues of $H \rightarrow E_i(R)$ ($R \in \mathbb{R}^n$)
2. Solve motion of nuclei on each of the E_i surface, mainly E_1
3. Then you get what you need, hopefully



Describe dynamics: fraught with difficulties.

In the avoided crossing regions:

- Nuclear and electronic frequencies comparable, adiabatic approximation questionable.
- Essence of many chemical reactions, especially with charge exchange (e- or proton)
- Landau-Zener usually not satisfactory: many crossings, multiple crossings ($n > 2$ surfaces) diabatic/adiabatic pictures difficult



Actual case, for transfer of rotational angular momentum

J. Loreau et al, 2020

Transfer of probability from rotational state $|\alpha\rangle$ to $|\alpha'\rangle$, via the solution of the time independent Schrödinger equation.

$$\begin{aligned}
 &-\frac{\hbar^2}{2\mu} \frac{d^2 \chi_\alpha}{dR^2} + \sum_{\alpha'} \langle \alpha' | V + \frac{\ell^2}{2\mu R^2} | \alpha \rangle \chi_\alpha(R) \\
 &= (E - \epsilon_{j_1 k_a k_c} - \epsilon_{j_2}) \chi_\alpha(R), \quad (2)
 \end{aligned}$$

Diagonalise the (2) matrix -> plot as a function of R.

Note that the 'crossings / anticrossings' are not separated, in space nor in energy.

This is the usual case.

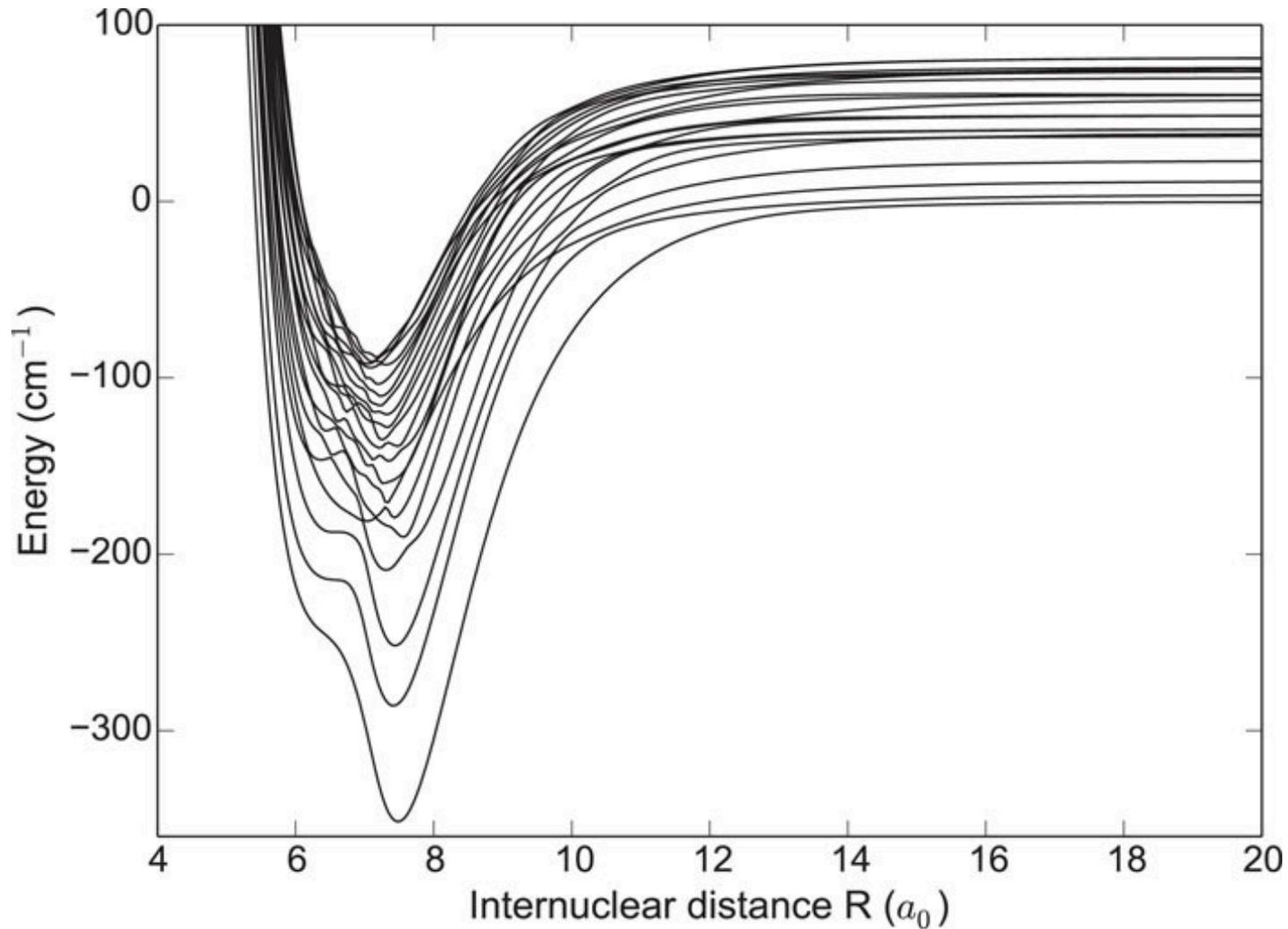


FIG. 1. Lowest adiabatic curves for para-H₂O—CO for $J = 0$.

Geometry....

DYNAMICAL SYSTEMS VIEW ON TRANSITION STATES

Recall : thermochemistry

Microcanonical ensemble :
RRKM

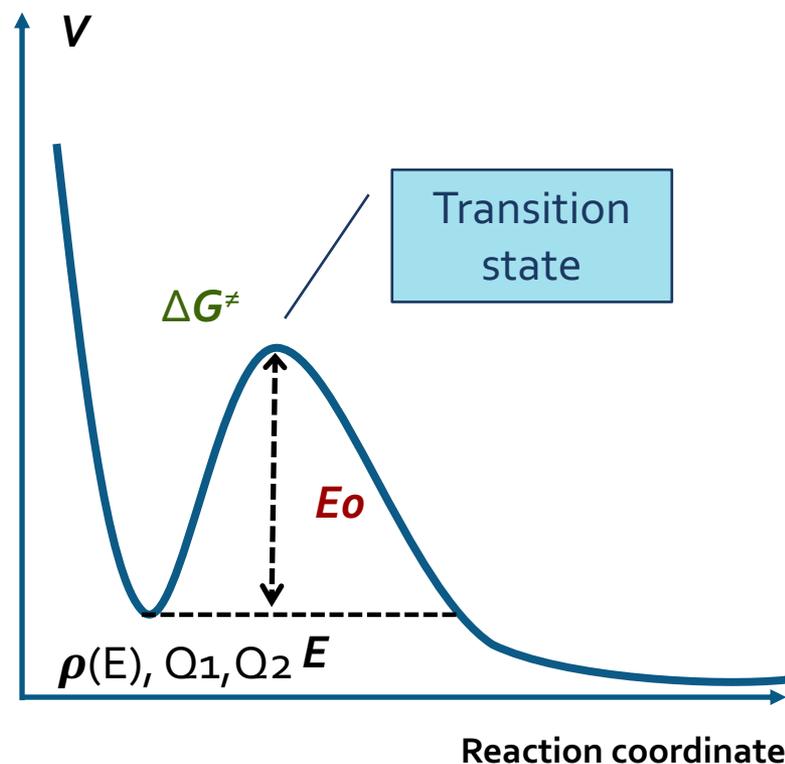
$$k(E) = \frac{N^\ddagger(E - E_0)}{b \rho(E)},$$

Canonical ensemble: Arrhenius-
Eyring

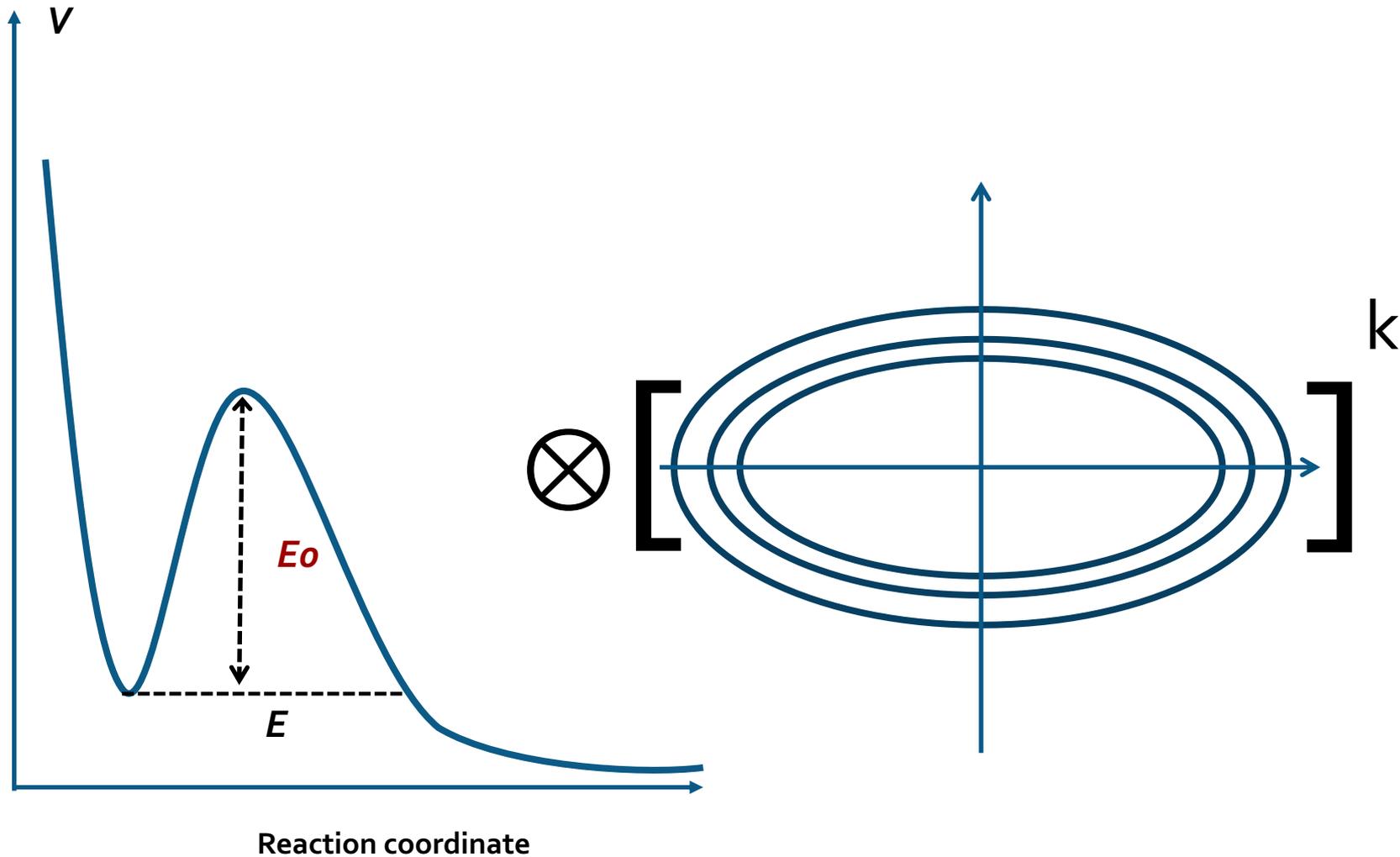
$$k_{\text{TST}}(\beta) = \frac{kT}{h} \frac{Q^\ddagger}{Q_1 Q_2} e^{-E\beta},$$

Extremely successful especially
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cases (ergodic hypothese)

Potential shape



Goal : $k+1$ -degrees of freedom

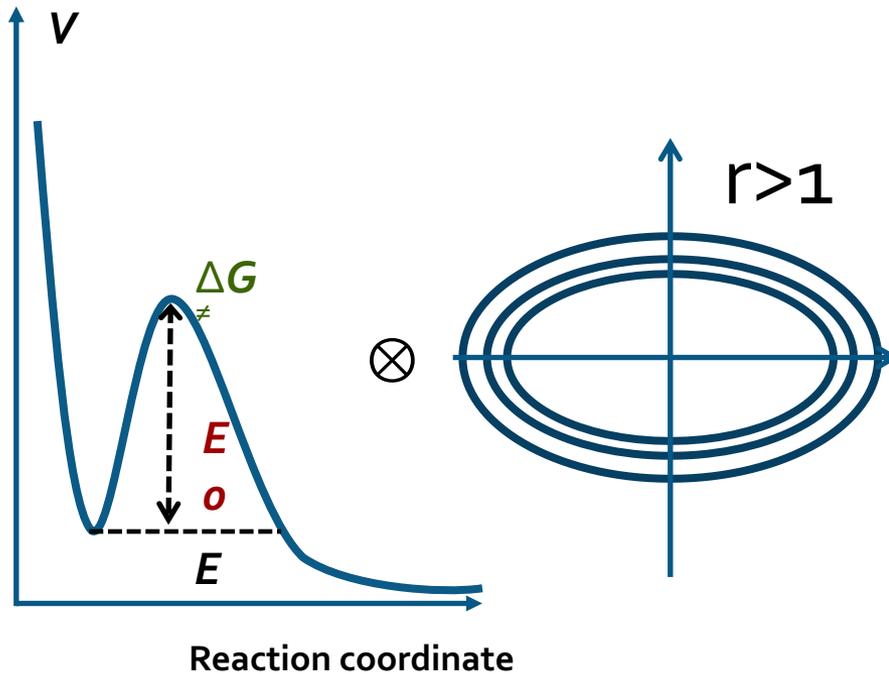


Hamiltonians, TS

Program:

1. $H(p_r, q_r)$, $r=1, n$; $x=(p_r, q_r)$.
 H independent of time (no time dependant electromagnetic field, no random forces or kicks).
2. Find critical (equilibrium) points : $\nabla H = 0$: $x=x^*$
3. Examine linear stability of the critical points via the eigenvalues of $\text{Hess}(H)$.
 - a. all eigenvalues imaginary by pairs $(\pm i\lambda_r)$: fully stable equilibrium ($\lambda_r > 0$, $\in \mathbb{R}$)
 - b. $n-1$ eigenvalues imaginary by pairs $(\pm i\lambda_r)$: 1 eigenvalue pair $\pm \lambda_1$ real ($\lambda_r > 0$, $\in \mathbb{R}$) \rightarrow we hope to define a TS, or a dynamical analog
 - c. $n-k$ eigenvalues imaginary by pairs $(\pm i\lambda_r)$: k eigenvalue pairs $\pm \lambda_{n-k}$ real.
 $k=2$, some theories ; $k>2$, unknown role, probably very minor
 - d. Other cases: $\pm \lambda_r \pm i\lambda_r$, or ($\lambda_r < 0$, $\in \mathbb{R}$) unknown role
 - e. Same as a-c, but one (>1 ??) pair of $\lambda=0$. Symmetry! Ex: rotation.

Goal : $k+1$ -degrees of freedom



- No overall distinction $r=1$ / $r>1$: only a local picture.
- The $r=1$ coordinates are 'reactive coordinates'
- The $r>1$ coordinates are 'bath coordinates'

DYNAMICAL SYSTEMS DESCRIPTION

- Very few cases fully explored,
- more than often too rudimentary.

- We go slowly: $k=0$, $k=1$, $k>1$ ($k+1$ degrees of freedom)

- Then time permitting, add rotation.

- Refs:
 - T. Komatsuzaki, 2000
 - S. Wiggins, LW et al., Phys Rev Lett 2001
 - **LW, Advances in Chemical Physics 2004**
 - S. Wiggins, H. Waalkens, 2004

- Many subsequent papers describe the geometry

n=1 : one dof system

- Phase space portrait, linearized motion

$$H_{lin} = \frac{1}{2}p_{\xi}^2 - \frac{1}{2}\lambda_{1,2}^2\xi^2$$

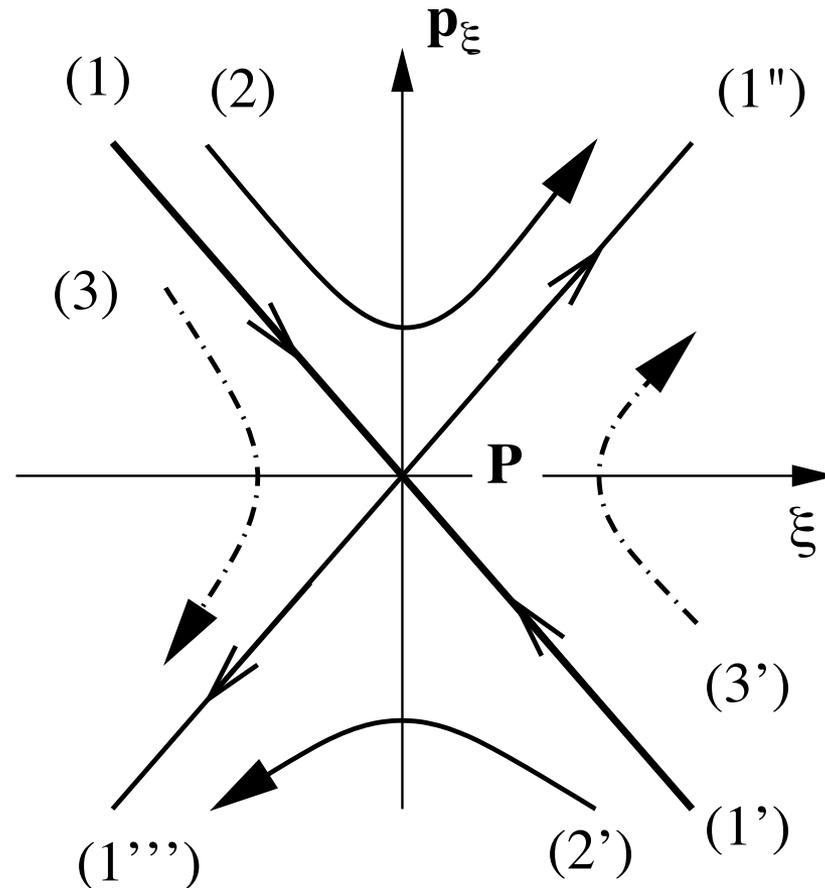
P unstable critical point

(1-1') stable manifolds

(2-2') stable manifolds

Trajectory (2-2') reactive

Trajectory (3-3') non reactive



n=1 : one dof system

- Phase space portrait, linearized motion

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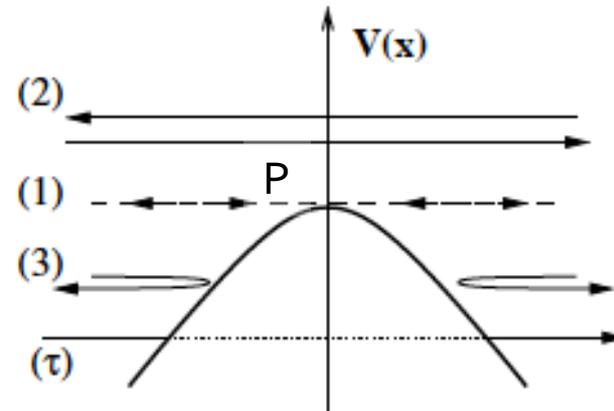
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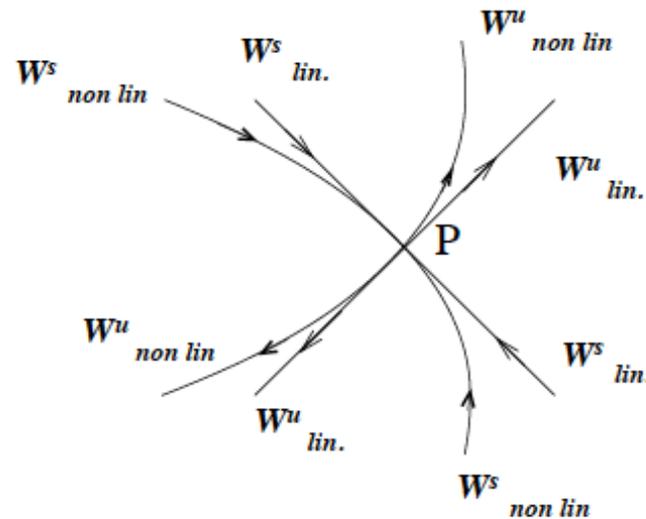
(2-2') stable manifolds

Trajectory (2-2') reactive

Trajectory (3-3') non reactive



Stable/unstable manifold theorem



$W^{u/s}$ is tangent to $W^{u/s}$ (linearized motion) at P . $W^{u/s}$ extend towards $T \rightarrow \pm\infty$. (not true for the center manifold, see below).
Normal form analysis and/or numerical integrations

$n=2$: two dof system

- Still easy, but need some thought.

- Dimensions.

TS has to be codim 1 in the energy level of phase space. In order to construct a barrier in phase space, the first step is to construct a manifold W that :

1. is made of a set of trajectories; W is said to be “invariant under the flow generated by the Hamiltonian H ”,
2. W is codimension 1 in the phase space ϕ or its restriction to a particular energy, $\phi(E)$. Point 2 means that (D is a dimension):

$D(W) = D(\phi) - 1 = 2$ or $D(W)(E) = D(\phi)(E) - 1 = 1$: W is a periodic trajectory

- W is NOT the TS: A TS has to be crossed by trajectories, hence not made of trajectories. We need the TS to be normal to the flow.

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(q_1, q_2)$$

Linearize around the critical point at origin

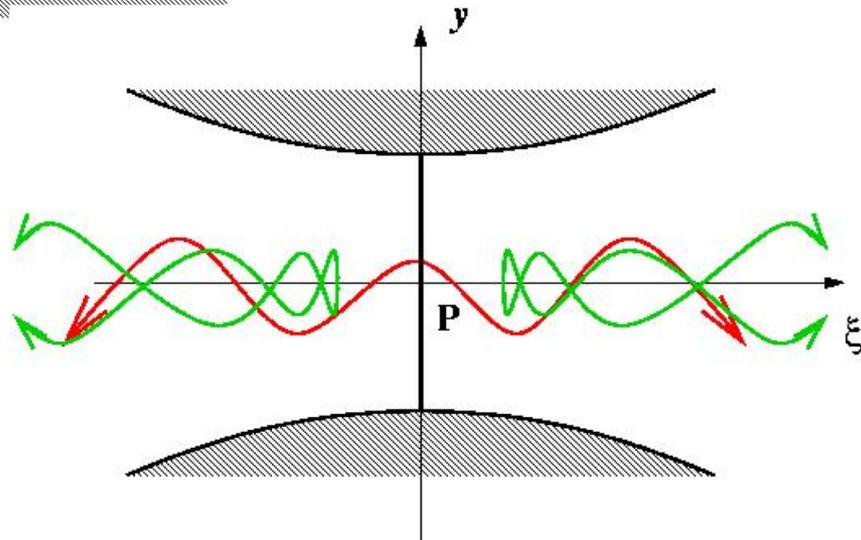
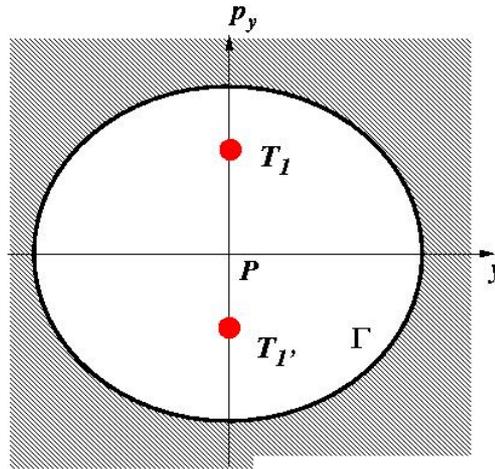
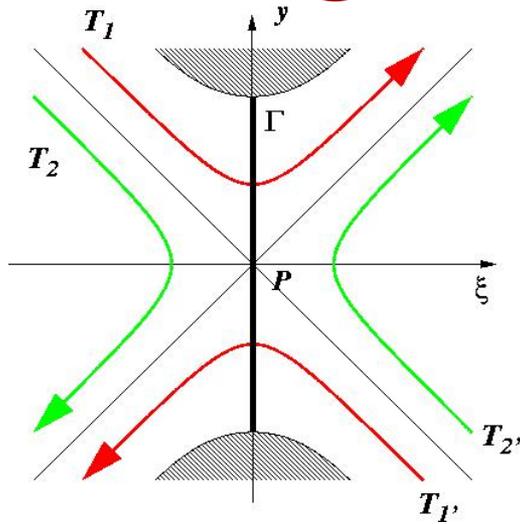
$$H = \frac{1}{2} (p_y^2 + p_\xi^2) + \frac{\omega^2}{2} y^2 - \frac{\kappa^2}{2} \xi^2 \quad .$$

Separate y from ξ

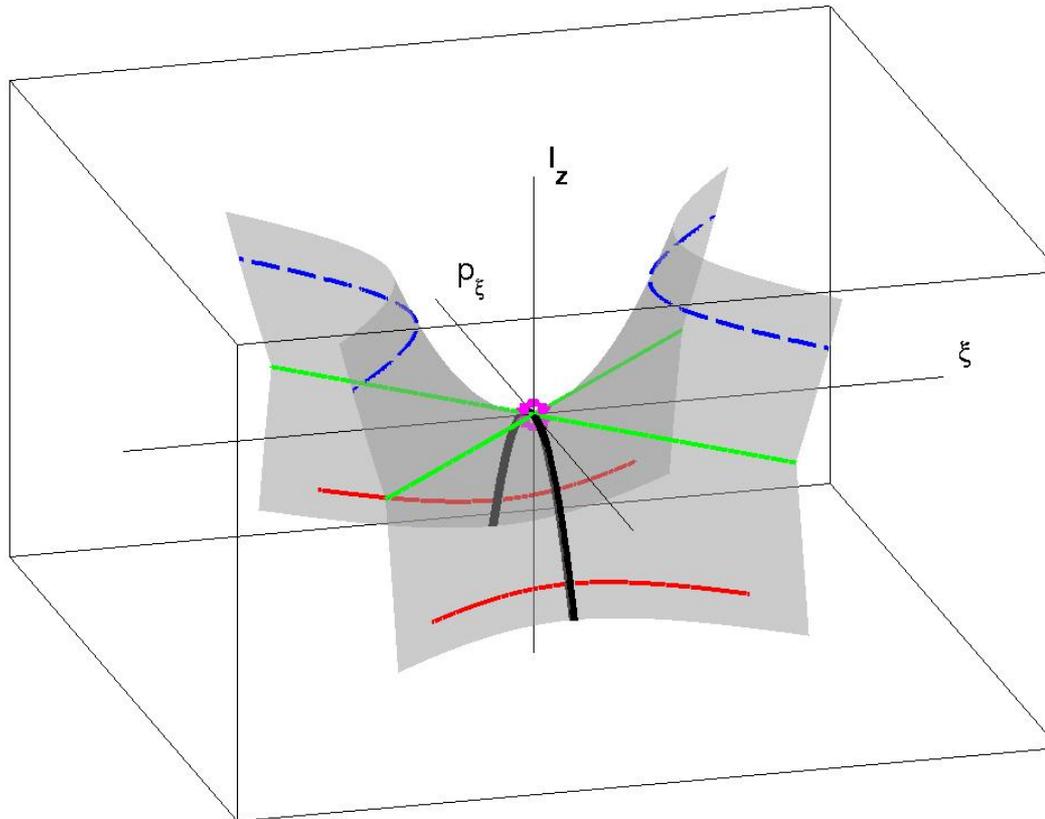
$$E = H = H(y) + H(\xi) = \omega_y I_y + H(\xi)$$

Phase space portraits

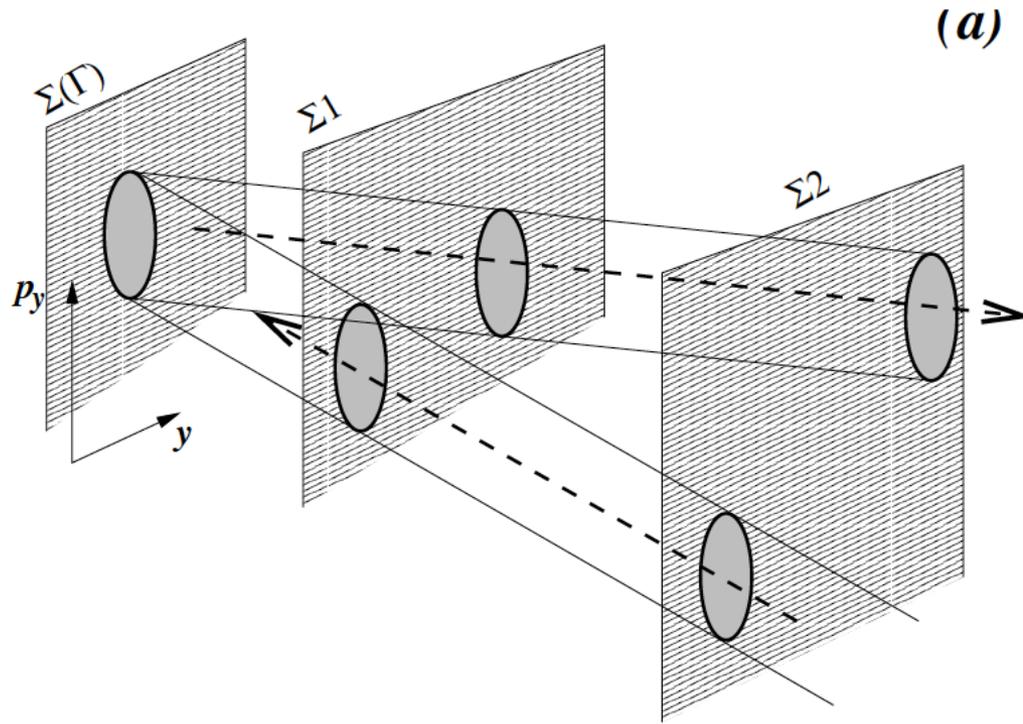
Configuration space image



Full energy level



Tubes



$n > 2$

- Dimensions.
TS has to be codim 1 in the energy level of phase space. In order to construct a barrier in phase space, the first step is to construct a manifold W that :
 1. is made of a set of trajectories; W is said to be "invariant under the flow generated by the Hamiltonian H ",
 2. W is codimension 1 in the phase space ϕ or its restriction to a particular energy, $\phi(E)$.
- W is NOT the TS: A TS has to be crossed by trajectories, hence not made of trajectories. We need the TS to be normal to the flow.

$n > 2$

- **W** is NOT the TS: A TS has to be crossed by trajectories, hence not made of trajectories. We need the TS to be normal to the flow.
- **W** must conduct trajectories: it has to be transverse to the TS, and asymptotic to ∂W by being made of stable/unstable manifolds built on ∂ TS.
- $n=2$ illustrates the point. $n=3$ is the general case (as far as I know)

n > 2

$$H = \sum_{i=1, n-1} \frac{1}{2} (p_{y_i}^2 + \omega_i^2 y_i^2) + \frac{1}{2} (p_\xi^2 - \kappa^2 \xi^2) \quad (27a)$$

To make contact with earlier papers and facilitate contact with perturbation theory, it is useful to make the following change of variables:

$$\begin{aligned} \eta &= \frac{1}{2\kappa} (p_\xi + \kappa \xi) \\ p_\eta &= \frac{1}{2\kappa} (p_\xi - \kappa \xi) \end{aligned}$$

and the Hamiltonian is written as

$$H = \sum_{i=1, n-1} \frac{1}{2} (p_{y_i}^2 + \omega_i^2 y_i^2) + \kappa^2 p_\eta \eta \quad (27b)$$

$$\eta = p_\eta = 0 / \xi = p_\xi = 0 \quad \text{NHIM} \quad (28a)$$

$$\eta = p_\eta \neq 0 / \xi = 0 \quad \text{Transition state} \quad (28b)$$

$$H = \sum_{i=1, n-1} \frac{1}{2} (p_{y_i}^2 + \omega_i^2 y_i^2)$$

$$H(I_1, \phi_1, I_2, \phi_2) = \omega_1 I_1 + \omega_2 I_2 \quad , \quad (29)$$

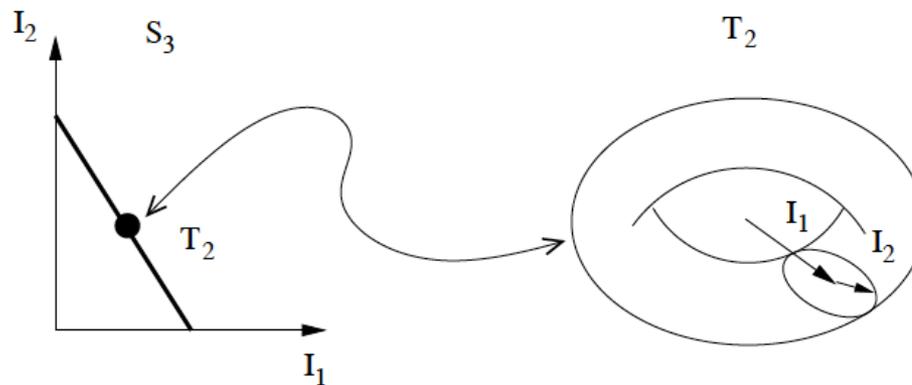


Figure 12: A scheme of the S_3 sphere, built with a foliation of tori. The straight line on the left panel is the image of equation (29).

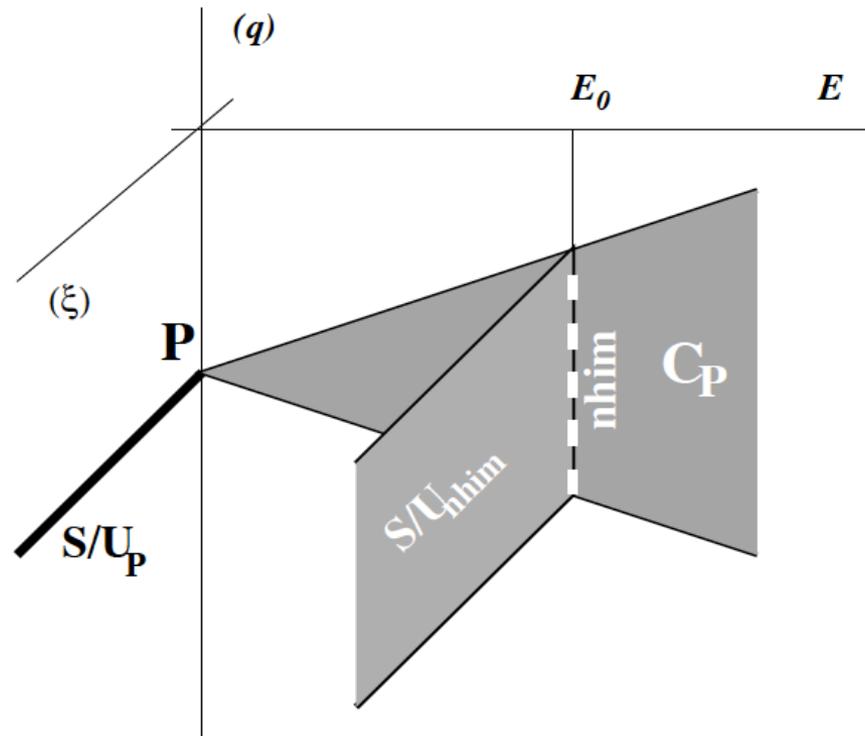
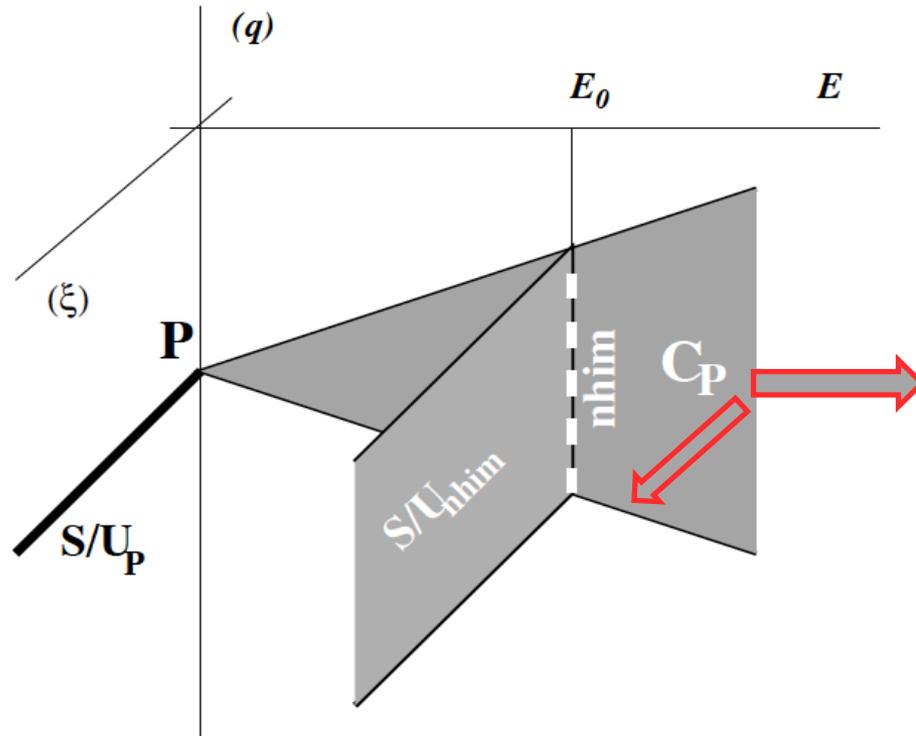


Figure 13: *The whole structure of the phase space in a nutshell...* P is the equilibrium point, E is the energy, (q) are the collective bath coordinates, (ξ) , the collective transition coordinates. The central manifold of P is C_P , the stable and unstable manifolds are indicated by S/U .



How does the center manifold bifurcate, what is the relevance of the bifurcation scheme is unknown

$n \geq 2$

- NHIM exist for $n \geq 2$, likewise TS as well as conduits in phase space
- Structuration of phase space nearby the TS, that extends towards $t \rightarrow \pm \infty$, at the expense of highly folded behaviour, at least in bound systems (homo-hetero clinic intersections)

- Several TS \rightarrow structuration of phase space via hetero-clinic intersections
- Quantum or semi classical TS difficult to define (Waalkens 2008)

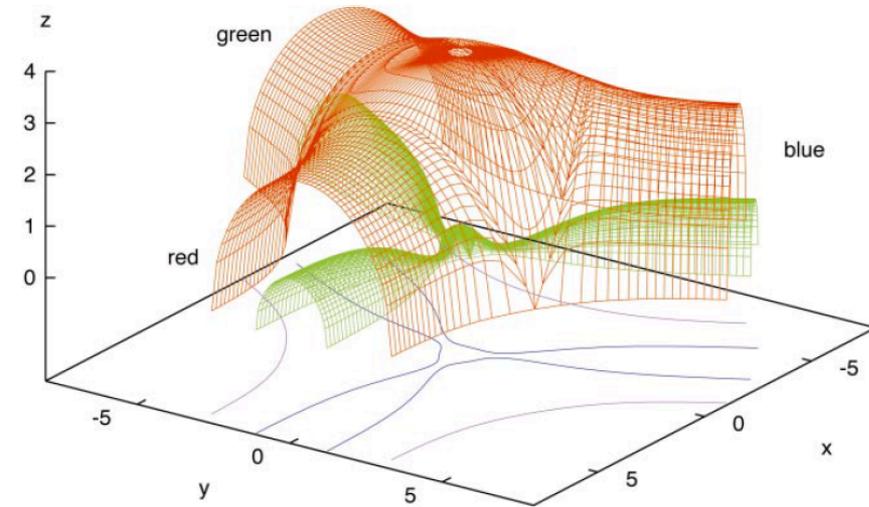
Now...

- Take advantage of the tubes :
 - Flow of probability
 - Currents 'easy' to compute (thanks to symplectic nature of Hamiltonian flow)
- Try and find semi-classical implications of the TS structuration
- Do not despair at the resonances in the wells regions
- Include angular momentum:
 - transport of rigid rotors
 - transport of flexible rotors, of collection of masses
 - No easy project !
- The full analysis at $r \rightarrow \infty$ is to be done; asymptotic points are non linear (possibly non-analytic) equilibrium points.

Conclusions

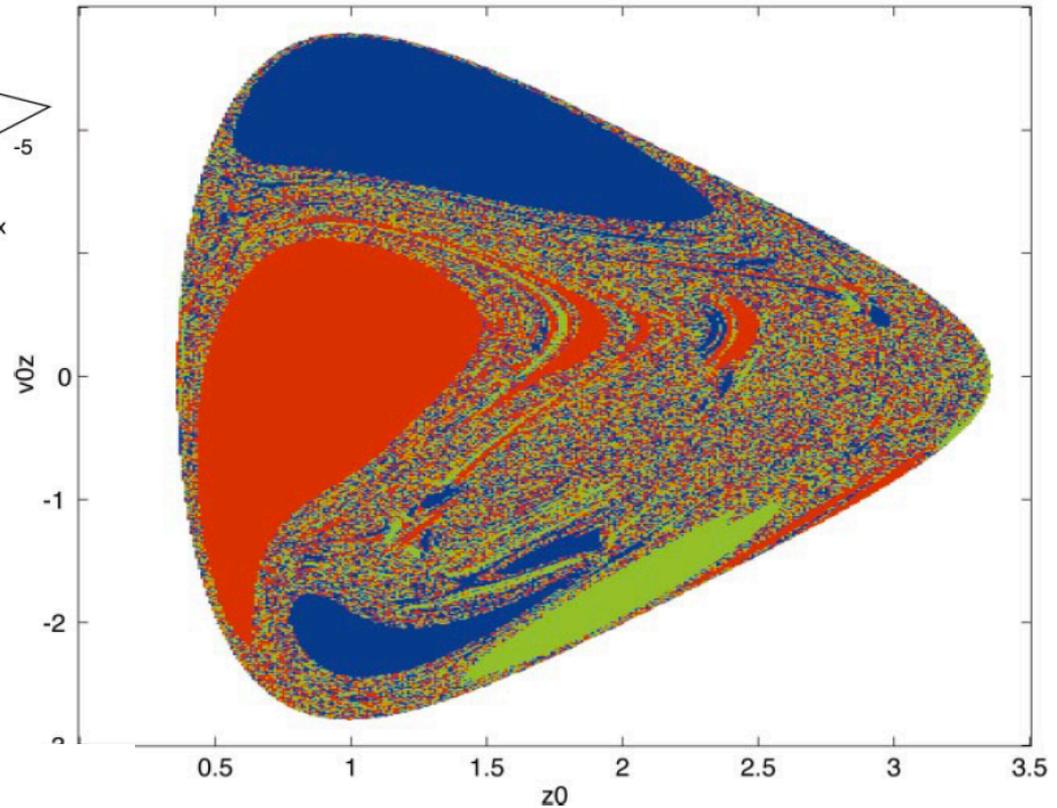
- How to take advantage of Hamiltonian geometry?
 - Classically
 - Semi-classically
- Open problems
 - Which are the relevant small parameters?
 - Where are the main difficulties, viewed from the side of physical chemists?
 - What are the expectations?

This is Hamiltonian mechanics!



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Topological aspects of chaotic scattering in higher dimensions

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