Rare Events Summer School 2019

Lecture 1: Transition states and rate estimates

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Lecture 1. The *rare event* problem and transition state theory (TST)
- Transition states, dividing surfaces and reaction coordinates
- Recrossing corrections and the variational principle
- The WKE two step procedure for finding the mechanism and 'exact' rate
- Optimal hyperplanar TST

Lecture 2. Harmonic TST & minimum energy path calculations
- The harmonic approximation to TST (HTST)
- Methods for finding minimum energy paths, NEB and CI-NEB
- Variants and improvements on the NEB method
- Applications

Lecture 3. MMF method and adaptive kinetic Monte Carlo (AKMC)
- Methods for finding saddle points when only initial state is known, MMF
- Long time scale simulations using AKMC
- Coarse graining, recycling, distributed computing
- Applications

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in English 🇬🇧

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Rannsóknir Kennsla Stjórnun Ferilskrá

Sjá einnig:

Nýlegar greinar í vísindaritum

ELENA: Evrópuþjálfunarsamstarf um sundrun sameinda með rafeindum og vöxt nanóklasa

Slæður um virkjunarástandskenninguna og hraðareikninga

Slæður um skammtafræðilega hraðafræði, QTST

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Research | Teaching | Service | Brief CV

See also:

Recent articles in scientific journals

Notes, directions and problem set for summer school on Rare Events

Slides on transition state theory and rate estimates

Slides on quantum transition state theory, QTST

Rare Event Summer School, IISc Bangalore 2019

Lecture notes:

- Notes for lecture 1
- Notes for lecture 2
- Notes for lecture 3

Problem set 1 (calculations by hand):

- Problem set 1 for Sunday afternoon

Directions for setting up EON:

- Instructions for installing EON

Problem set 2 (calculations using EON on your laptop):

- Problem set 2 for Sunday afternoon

Files needed:

- Configuration file for a clean Al(100) slab
- Script for visualizing a minimum energy path found using NEB
- Script for doing AKMC calculations


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University of Iceland

10 000 undergraduate students

4 000 graduate students.

Eruption of a volcano under the a glacier, April 2010

Goal

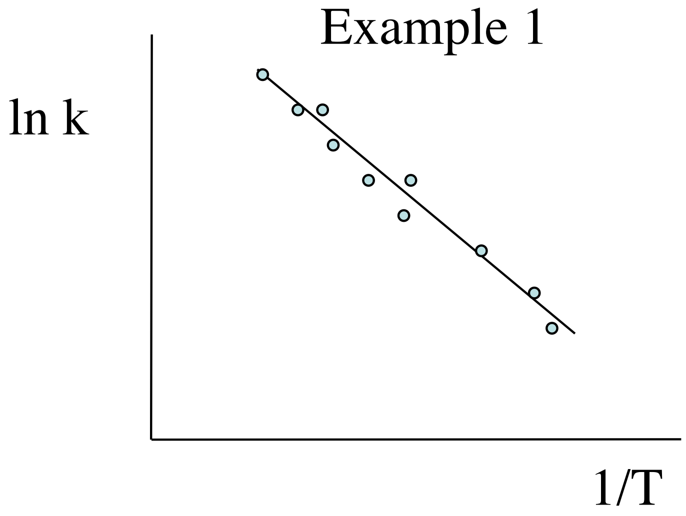
Characterize transitions that occur due to thermal energy in the system,
for example diffusion events, defect formation/migration, chemical reactions ...

Want to be able to:

1. predict the mechanism and rate of transitions given information about the atomic structure and interaction between the atoms (such as DFT).

or

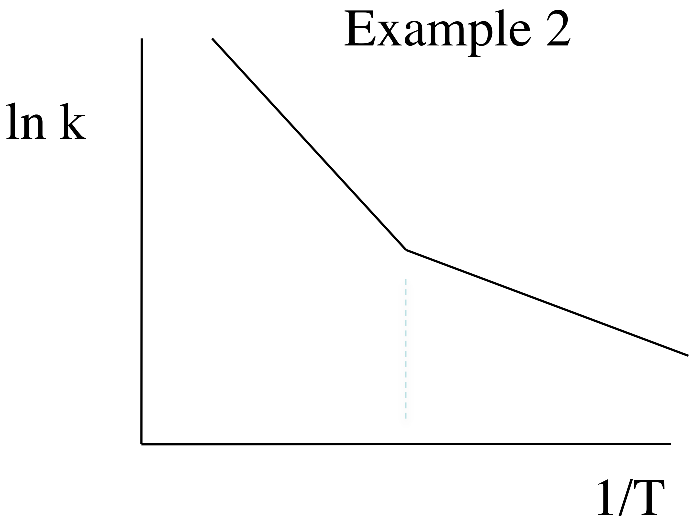
2. interpret measurements of rates in terms of the atomic interactions and transition mechanism, typically Arrhenius plots



$$k(T) = \nu e^{-E_a/k_B T}$$

ν: pre-exponential factor

E_a : activation energy



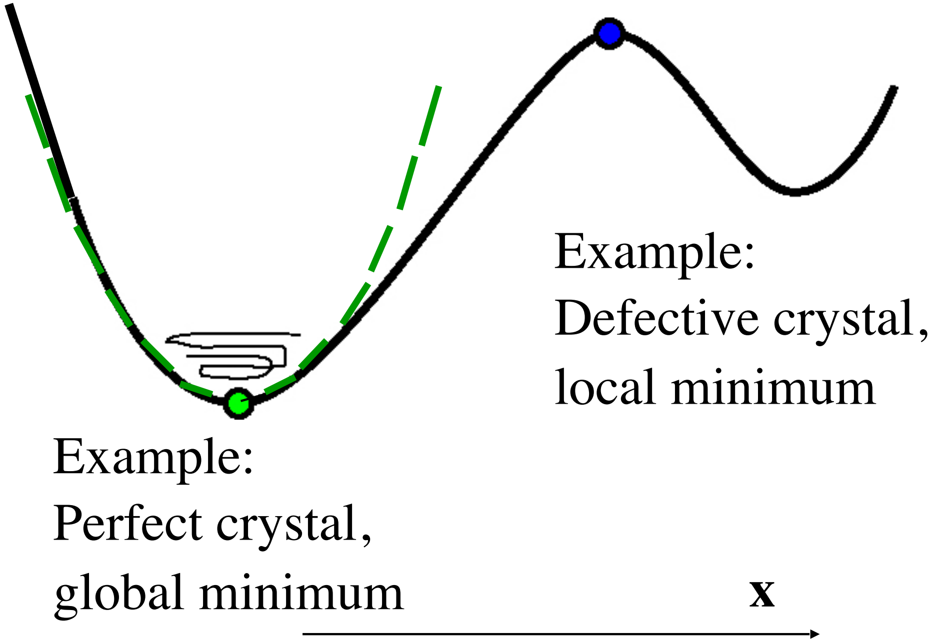
Crossover in mechanism

Conventional approach to atomic simulations

Born-Oppenheimer (adiabatic) approximation:

1. Solve for the electronic degrees of freedom while keeping the nuclei fixed at coordinates **x**.
   Usually done with Kohn-Sham density functional theory (DFT) using approximate functionals such as PBE, RPBE, PBE_{sol}, PBE_{mol}…
   Get energy surface, V(**x**).

2. Solve for the motion of the nuclei. Usually with the classical approximation, F=ma=m d^2x/dt^2, sometimes using harmonic approximation (----)
   $V(\mathbf{x}) \sim k_{sp}(\mathbf{x}-\mathbf{x}_{min})^2/2$



Example:
Defective crystal,
local minimum

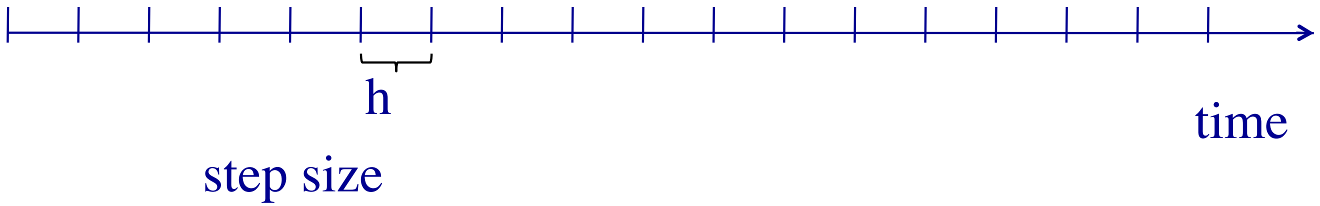
Example:
Perfect crystal,
global minimum

In principle, straight forward to simulate time evolution

Classical dynamics, (‘molecular dynamics’, MD)

For all but the lightest atoms and temperature well below room temperature, a classical description of the motion of the atoms is accurate enough.

Solve Newton eqns. of motion, F=ma, numerically by discretizing time



Verlet algorithm (using simple finite difference approximation of acceleration):

$$x(t+h) = 2x(t) - x(t-h) + h^2 F(x(t))/m$$

where F is the force acting on the atom,
and m is the mass of atom

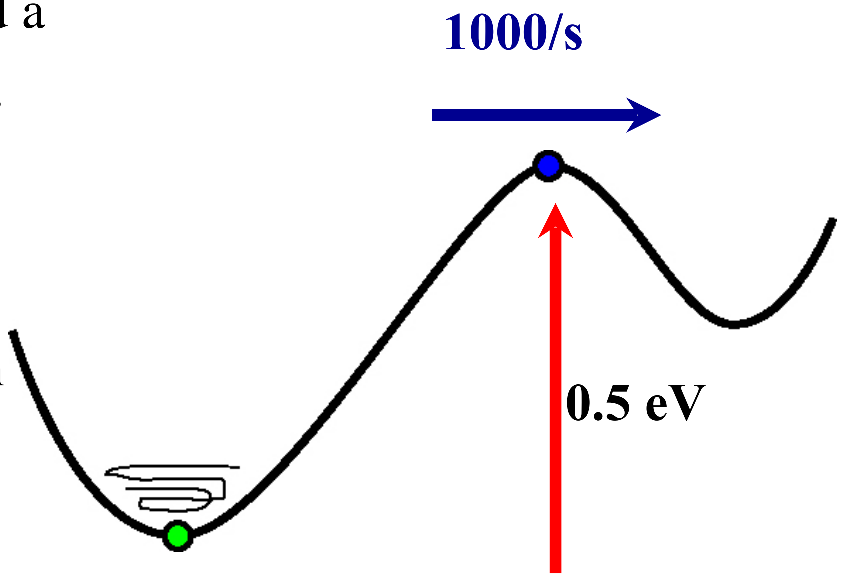
$$F_i = -\nabla_i V(x)$$

simple enough …

But, a direct dynamical simulation of a *thermally activated* process is in general *not* feasible

Time scale problem:

Most interesting transitions are *rare events* (i.e., much slower than vibrations).

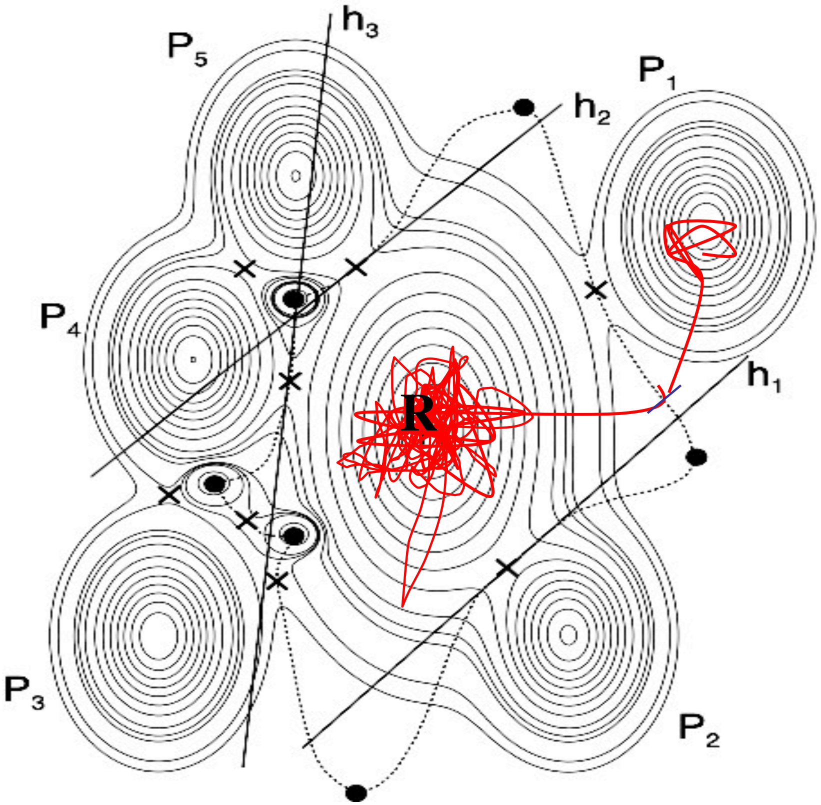


A transition with an energy barrier of 0.5 eV and a typical pre-exponential factor occurs 1000 times per second at room temperature *– fast on laboratory scale!*

A video of a direct classical dynamics simulation where each vibration spans a second in the video would go on for more than 100 years in between such reactive events *– slow on atomic scale!*

Typically there is a clear separation of time scales, and a ***statistical*** approach can be used

Systems of interest typically involve many degrees of freedom!



Maxima: filled circles
First order saddle points: x
Energy Ridge: dotted line
Solid straight lines: go through x

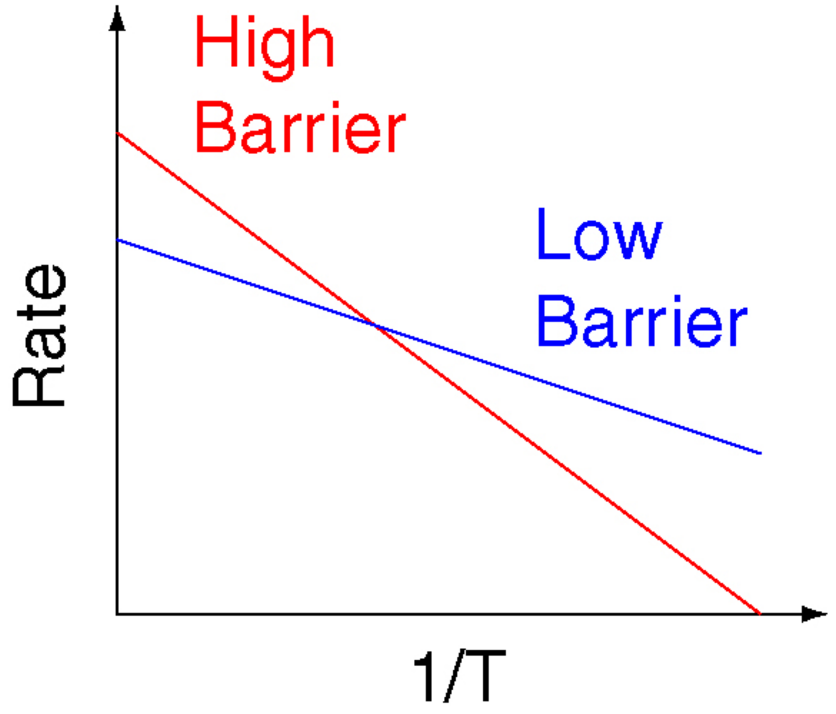
Need to take a long stroll on a 3N-dimensional **potential energy surface**, V($\mathbf{x}_1$,$\mathbf{x}_2$, … $\mathbf{x}_N$), where N is the number of atoms.

Given some initial state, **R**,
want to find the rate of transitions
and possible final states, **P_1, P_2 …**

Also, want to find the mechanism of the transitions (*how do the atoms move during a transition?*).

Note:

Dangerous to simply heat up the system to speed up the transition …



A crossover from one mechanism to another can occur as the temperature is increased.

Example: Diffusion of H_2O admolecule on an ice surface

vs.

melting of the ice crystal …

Transition State Theory (TST)

Also known as “Absolute Rate Theory” or “Activated Complex Theory”

Early pioneers:

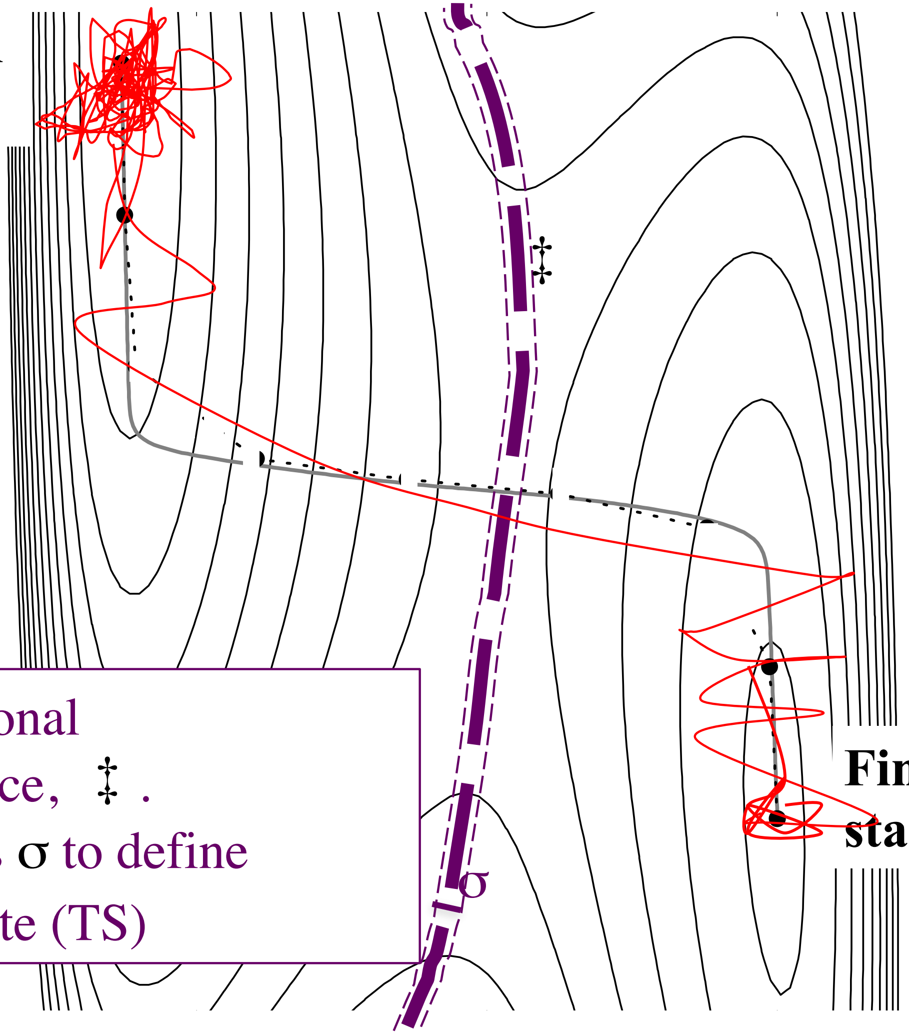
Pelzer & Wigner, *Z. Phys. Chem.* **B15**, 445 (1932*);*
Wigner, *Trans. Faraday Soc.* ***34,*** *29, (1937)*.
Eyring, *J. Chem. Phys.* **3**, 105 (1935).
Evans & Polyani, *Trans. Faraday Soc.* **31**, 857 (1935).

TST is a method for estimating the rate of **slow** transitions between states of a system due to thermal energy:

1. Gives an **approximation** to the rate constant, but
2. it possible to later calculate a correction to the TST estimate and obtain the **exact** rate using just short time scale simulations.

Transition State Theory (Wigner, Eyring 1930s)

Identify a 3N-1 dimensional dividing surface, that represents a **bottleneck** for going from the initial to a final state:



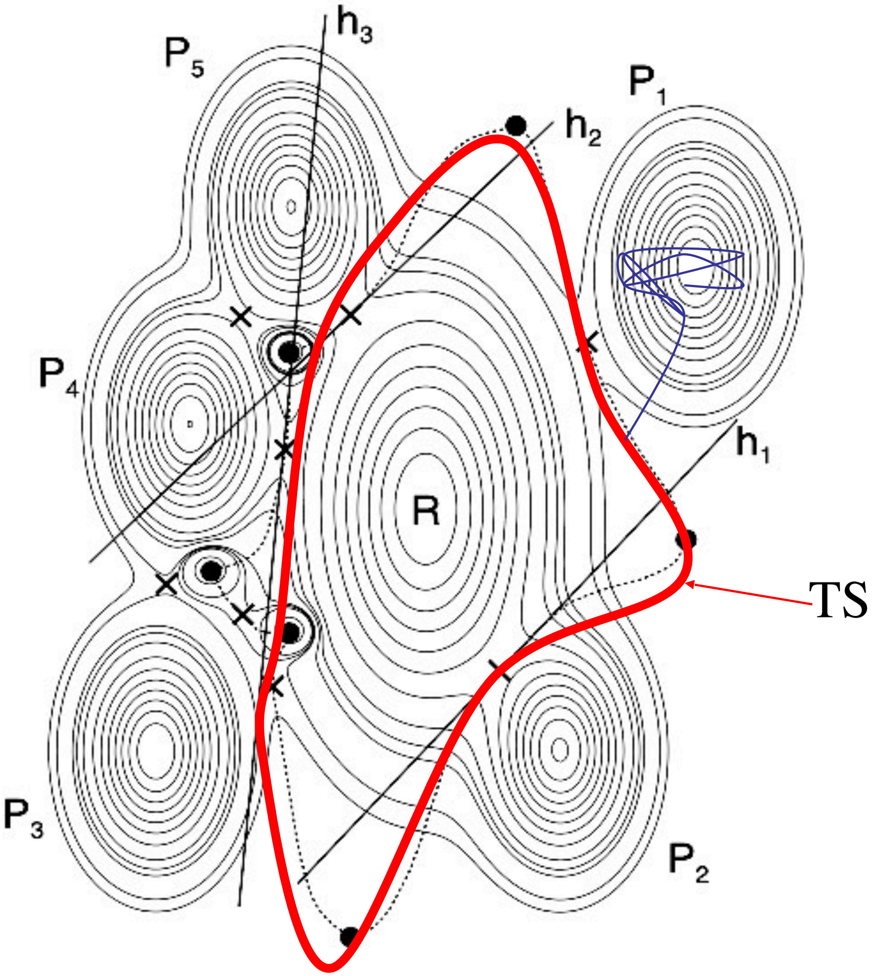
3N-1 dimensional dividing surface, ‡ .
Add thickness σ to define
Transition State (TS)

The bottleneck can be due to an energy barrier and/or ***entropy barrier***

Basic Assumptions of Transition State Theory

1. Born-Oppenheimer approximation (adiabatic)
2. Classical dynamics of nuclei (*can be extended to quantum systems …*)
3. Boltzmann distribution in initial state (*OK if slow enough*, $k_BT < \Delta E/5$)
4. No recrossings of TS, *(often weakest, but can be fixed using short trajectories)*.

   That is, if a trajectory reaches the TS and is heading away from the initial state, it will proceed to a product state and stay there for an extended time.



Note:

- The transition state should enclose the initial state to separate it from all possible product states.
- TST estimates the lifetime, τ, of the given initial state without knowledge of the product state(s).
- Can run short timescale dynamics to find product state(s).

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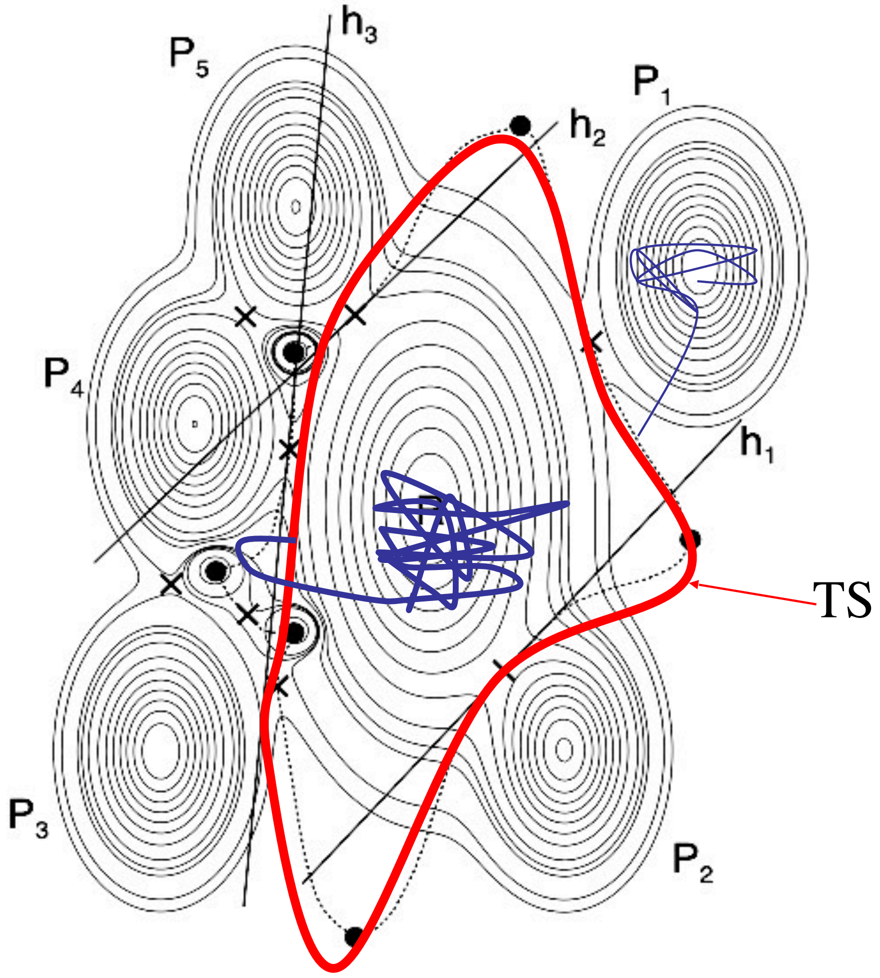


- Can run short time scale dynamic al trajectories starting at TS to take recrossings into account - ***dynamical corrections***
- $\mathbf{k}^{\mathbf{exact}} = \kappa\, \mathbf{k}^{\mathbf{TST}}$ where $0 < \kappa < 1$

  as well as to find the product state.

Simple derivation of the TST estimate of a rate constant

First, review classical statistical statistical mechanics:

Total energy of a conservative system: $E(x,v) = E_{kin} + E_{pot} = \sum_i \frac{1}{2} m_i v_i^2 \; + \; V(x)$

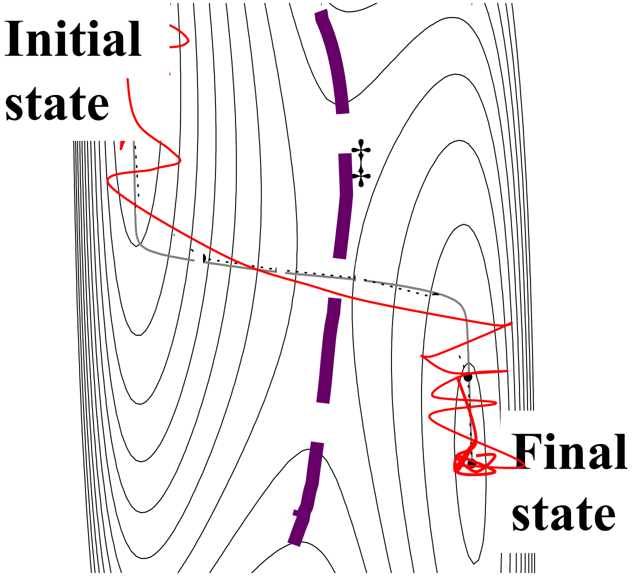
Boltzmann distribution: Probability that (x,v) is in the range {x,x+dx} and {v,v+dv} is:

$$P(x,v)dxdv = Ae^{-E(x,v)/k_BT}dxdv$$

(A is a normalization constant)

This factorizes into:

$$\underbrace{A_v\, e^{-\sum_i \frac{1}{2} m_i v_i^2 / k_B T}}_{p_v(\mathbf{v})} d\mathbf{v}\; \underbrace{A_c\, e^{-V(\mathbf{x})/k_BT}}_{p_c(\mathbf{x})} d\mathbf{x}$$



Given that the system is initially somewhere in R:

$$A_c = \frac{1}{\int_R e^{-V(\mathbf{x})/k_BT}\, d\mathbf{x}}$$

The probability of being in some subspace, S, of R is:

$$P_S = \frac{\int_S e^{-V(\mathbf{x})/k_BT} d\mathbf{x}}{\int_R e^{-V(\mathbf{x})/k_BT} d\mathbf{x}} \equiv \frac{Z_S}{Z_R}$$

configuration integrals

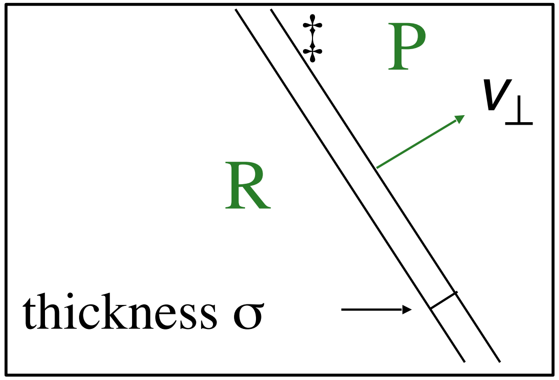
Simple derivation of the TST estimate of a rate constant (cont.)

k^{TST} = (probability of getting to TS) • (flux out of TS)

Choose the dividing surface to be a hyperplane

ax+b=0 particularly simple,

(but, may not be good enough ...)



$$k^{TST} = P_{\ddagger} \frac{< v_\perp >}{\sigma}$$

$$= \frac{\sigma \int_{\ddagger} e^{-V(\mathbf{x})/k_B T} d\mathbf{x}'}{\int_R e^{-V(\mathbf{x})/k_B T} d\mathbf{x}} \; \frac{< v_\perp >}{\sigma}$$

Maxwell:

$$< v_\perp > = \frac{\int_0^\infty v_\perp e^{-\frac{1}{2}\mu_\perp v_\perp^2 / k_B T} dv_\perp \int_{-\infty}^\infty e^{-\sum_{i'} \frac{1}{2}\mu_i v_i^2 / k_B T} d\mathbf{v}'}{\int_{-\infty}^\infty e^{-\frac{1}{2}\mu_\perp v_\perp^2 / k_B T} dv_\perp \int_{-\infty}^\infty e^{-\sum_{i'} \frac{1}{2}\mu_i v_i^2 / k_B T} d\mathbf{v}'} = \frac{\int_0^\infty v_\perp e^{-\frac{1}{2}\mu_\perp v_\perp^2 / k_B T} dv_\perp}{\int_{-\infty}^\infty e^{-\frac{1}{2}\mu_\perp v_\perp^2 / k_B T} dv_\perp} = \sqrt{\frac{k_B T}{2\pi\mu_\perp}}$$

3*N*-1 dimensional

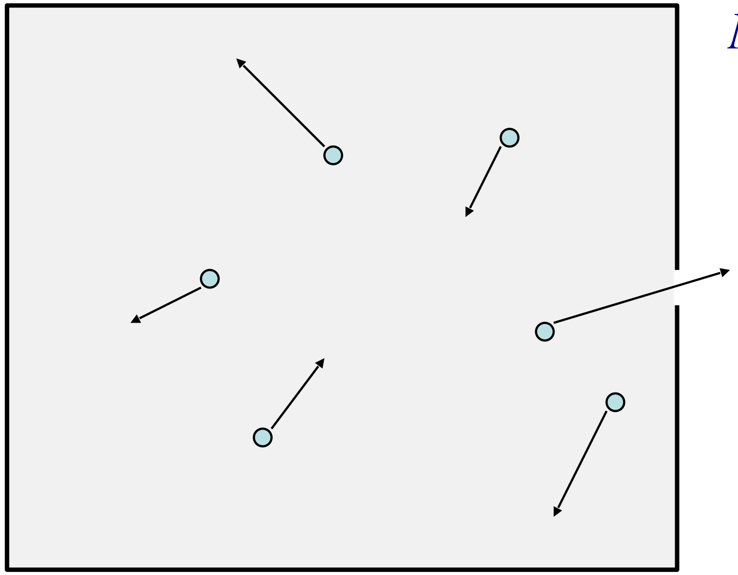
1 dimensional

So,

$$\boxed{k^{TST} = \sqrt{\frac{k_B T}{2\pi\mu_\perp}} \frac{Z_{\ddagger}}{Z_R}}$$

A simple example: Effusion of gas atoms through a small hole

Use
$$k^{TST} = \sqrt{\frac{k_B T}{2\pi\mu_\perp}}\frac{Z_\ddagger}{Z_R}$$
where
$$Z_s \equiv \int_S e^{-V(x)/k_B T} dx$$



Notation: V is volume of the box, A is area of the hole

$$Z_R = V \quad Z_\ddagger = A$$

So:
$$k^{\mathrm{TST}} = \sqrt{\frac{k_B T}{2\pi\, m}}\frac{A}{V}$$

ideal gas:
$$PV = N k_B T$$

gives:
$$k^{TST} = \frac{PA}{\sqrt{2\pi m k_B T N}}$$

No energy barrier here,
just an entropic bottle neck

Rate of effusion from TST:
$$r = N k^{TST} = \frac{PA}{\sqrt{2\pi m k_B T}}$$

Same result as kinetic theory of gases,

TST is exact in this case. No recrossings in the hole.

A more general choice of dividing surface

> *"The derivation can be made to look slightly less juvenile by introducing an obscure notation at this point"* (P. Pechukas, in *Dynamics of Molecular Collisions, Part B, edited by W. H. Miller (Vol. 2 of Modern Theoretical Chemistry) (Plenum, New York, 1976), Chap. 6.)*

Define the dividing surface subspace as the points ***q*** that satisfy

$$f(\mathbf{q}) = 0$$

then the TST rate constant can be written as

normal to dividing surface

$$\mathrm{k}^{\mathrm{TST}} = Q_R^{-1}\int d\mathbf{p}\int d\mathbf{q}\, e^{-H(\mathbf{p},\mathbf{q})/k_BT}\underbrace{\delta[f(\mathbf{q})]}_{\text{Ensures point is at dividing surface}}\underbrace{\left(\frac{\partial f(\mathbf{q})}{\partial \mathbf{q}}\cdot\frac{\mathbf{p}}{m}\right)}_{\text{normal component of velocity}}\underbrace{\Theta\left[\frac{\partial f(\mathbf{q})}{\partial \mathbf{q}}\cdot\mathbf{p}\right]}_{\text{ensures system is heading towards P at this point}}$$

here Θ[] is the Heavyside function

and

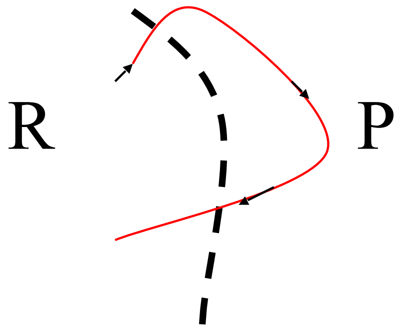
$$Q_R = \int d\mathbf{p}\int d\mathbf{q}\, e^{-H(\mathbf{p},\mathbf{q})/k_BT}$$

Variational principle for optimizing the choice of transition state

The neglect of recrossings, approximation 4, results in an overestimate of the transition rate in TST:

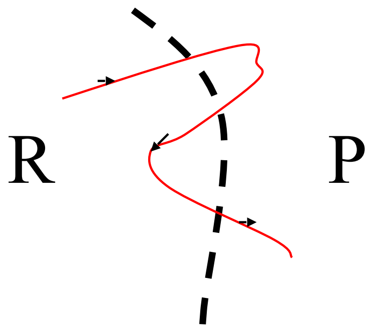
$\boxed{\mathbf{k^{TST} > k}}$

One recrossing:



Should not contribute to rate, but counts as one reactive event in TST.

Two recrossings:



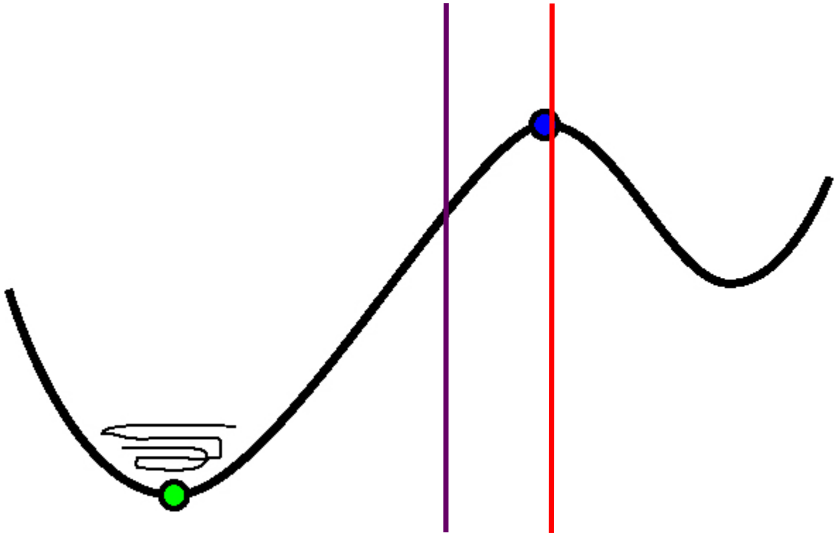
Should only count once, but gives two reactive events in TST estimate.

The optimal TS is the one that gives smallest estimate for $\mathbf{k^{TST}}$

This gives a **variational principle** that can be used to find the **optimal** choice of transition state.

(Keck, *J. Chem. Phys.* ***32****, 1035 (1960)*)

Both good and bad choices for the transition state can work, *in principle* ....



Less than optimal TS dividing surface. Many recrossings, $\kappa \ll 1$, need many short trajectories to identify product states and correct k^{TST}

Optimal TS dividing surface. Few recrossings, $\kappa \sim 1$, only need a few short trajectories to identify product states and correct k^{TST}

Use **Wigner-Keck-Eyring (WKE)** to generate reactive trajectories with much smaller computational effort than direct dynamics

---

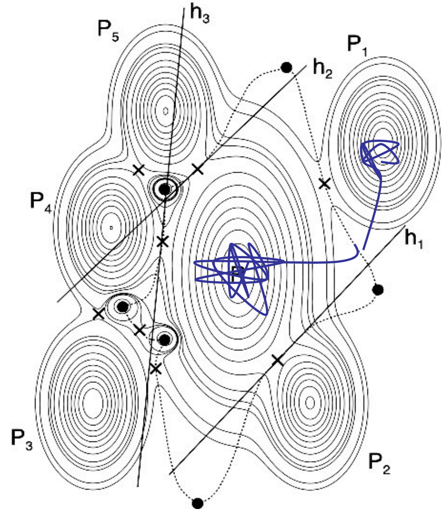
1. Find optimized transition state dividing surface using $\boxed{k^{TST} > k^{exact}}$

   For hyperplane $k^{TST} = \sqrt{\frac{k_B T}{2\pi\mu_\perp}}\,\frac{Z_\ddagger}{Z_R}$ where $Z_S = \int_S e^{-V(x)/k_B T}dx$

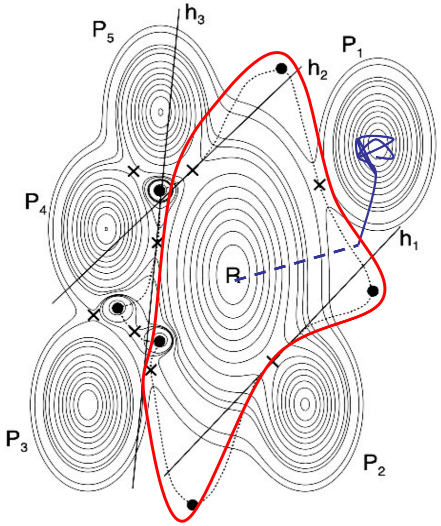
2. Run (short time) dynamics trajectories from the transition state to find product states and dynamical correction, $k^{exact} = \kappa\, k^{TST}$

Note: Step 2 is hard unless a good job has been done in 1, need to optimize the dividing surface.

WKE procedure generates (pseudo) trajectories over long time scale



dynamical trajectory



WKE trajectory

time

stat.mech.

Free energy of hyperplanes

Rewrite the ratio of configuration integrals in terms of a **free energy difference, ΔF,** but then need to insert configuration integral for hyperplane in reactant region, $\mathbf{Z_{H_R}}$ to get the units right

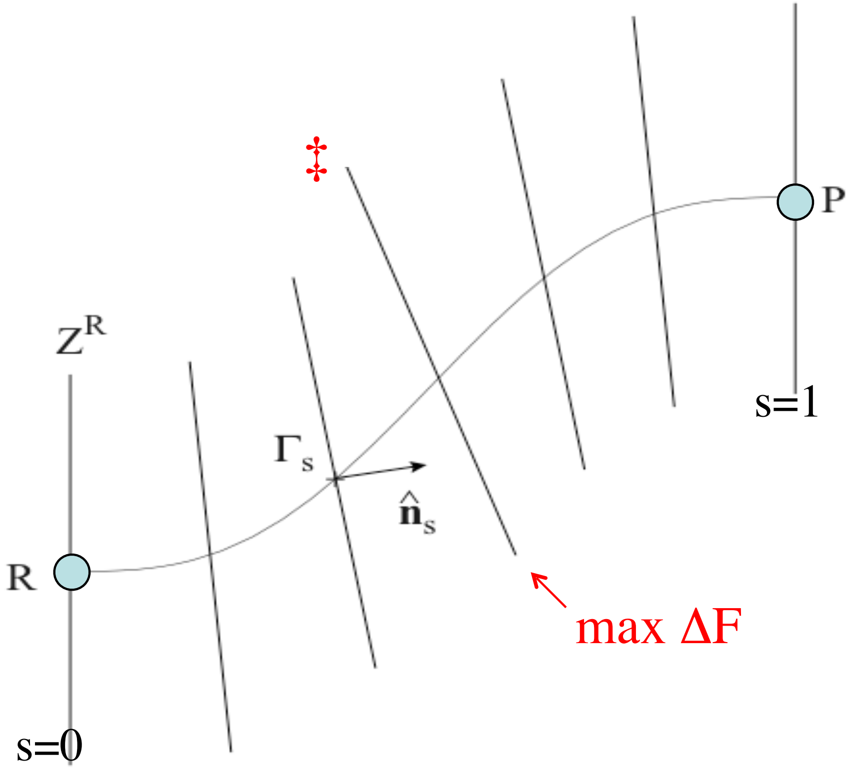
$$\mathbf{k^{TST}} = \sqrt{\frac{\mathbf{k_B T}}{\mathbf{2}\pi\mu_\perp}} \frac{\mathbf{Z_\ddagger}}{\mathbf{Z_R}} = \sqrt{\frac{\mathbf{k_B T}}{\mathbf{2}\pi\mu_\perp}} \frac{\mathbf{Z_{H_R}}}{\mathbf{Z_R}} \frac{\mathbf{Z_\ddagger}}{\mathbf{Z_{H_R}}}$$

$$= \sqrt{\frac{\mathbf{k_B T}}{\mathbf{2}\pi\mu_\perp}} \frac{\mathbf{Z_{H_R}}}{\mathbf{Z_R}} \mathbf{e}^{\frac{-\mathbf{\Delta F}}{\mathbf{k_B T}}}$$

Given some path between the R and P minima, Γ(s), construct a progression of hyperplanes.

Use thermodynamic integration to evaluate the free energy difference between initial hyperplane and subsequent hyperplanes

$$\mathbf{\Delta F} = \int_0^1 \mathbf{ds} \frac{\partial \mathbf{F}}{\partial \mathbf{s}}$$



A progression of hyperplanes from R to P.
The optimal TS dividing surface corresponds to maximum free energy, ‡

Evaluate free energy change from reversible work

Sample the atomic coordinates and the forces within a hyperplane using Monte Carlo or Classical Dynamics (zero force comp. along the normal).

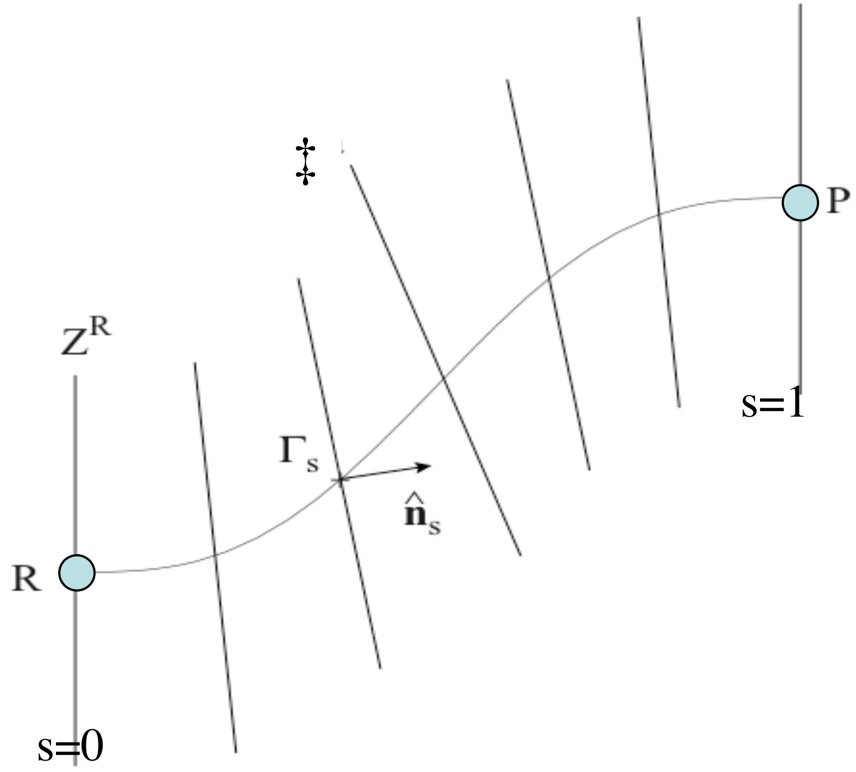
Obtain the average force $\mathbf{f_n} = \mathbf{f}(\mathbf{r_s}) \cdot \hat{\mathbf{n}}_\mathbf{s}$
normal to the hyperplane and the ‘torque’ with respect to the point of intersection between the plane and the path,

$$\mathbf{R_t} = (\mathbf{r_s} - \mathbf{\Gamma_s}) \cdot \frac{\mathbf{d\hat{n}_s}}{\mathbf{d}\theta}$$

The change in free energy is a sum of a contribution from the translation and a contribution from the rotation of the hyperplane

$$\mathbf{\Delta F} = -\int_0^{\mathbf{s}} < \mathbf{f_n}(\mathbf{1} - \mathbf{R_t}\frac{\mathbf{d}\theta}{\mathbf{ds}}) >_{\mathbf{s}'} \mathbf{ds}'$$

At each point along the path (for a given value of s), the orientation of the hyperplane should be adjusted to maximize the free energy (rotate against the torque). Orientational optimization without extra computations!

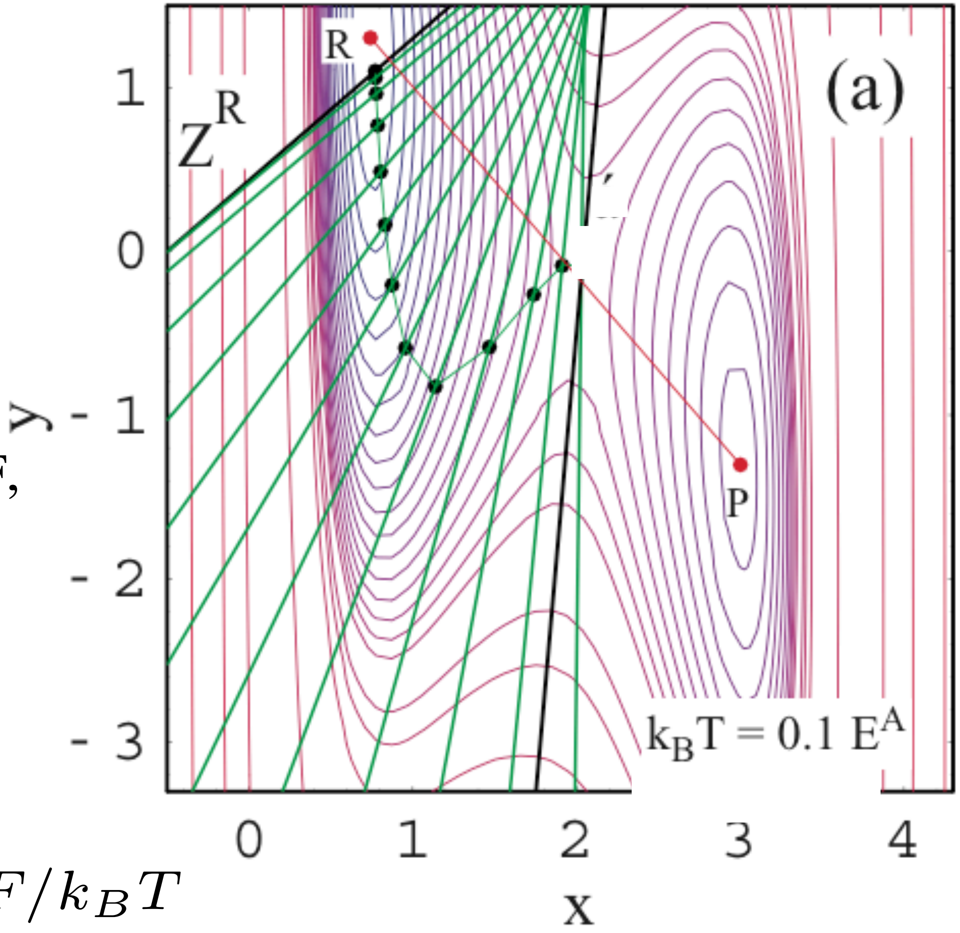


*(Mills, Jónsson, Schenter: Surf. Sci. **324**, 305 (1995))*

Implementation of variationally optimized TST using hyperplane

For **hyperplanar dividing surface**:
Want to find location and orientation that gives maximum free energy of the system when confined to the hyperplane.

Starting at the reactant, the free energy increase, ΔF, when moving towards product can be found by integrating the reversible work of translating and rotating the hyperplane

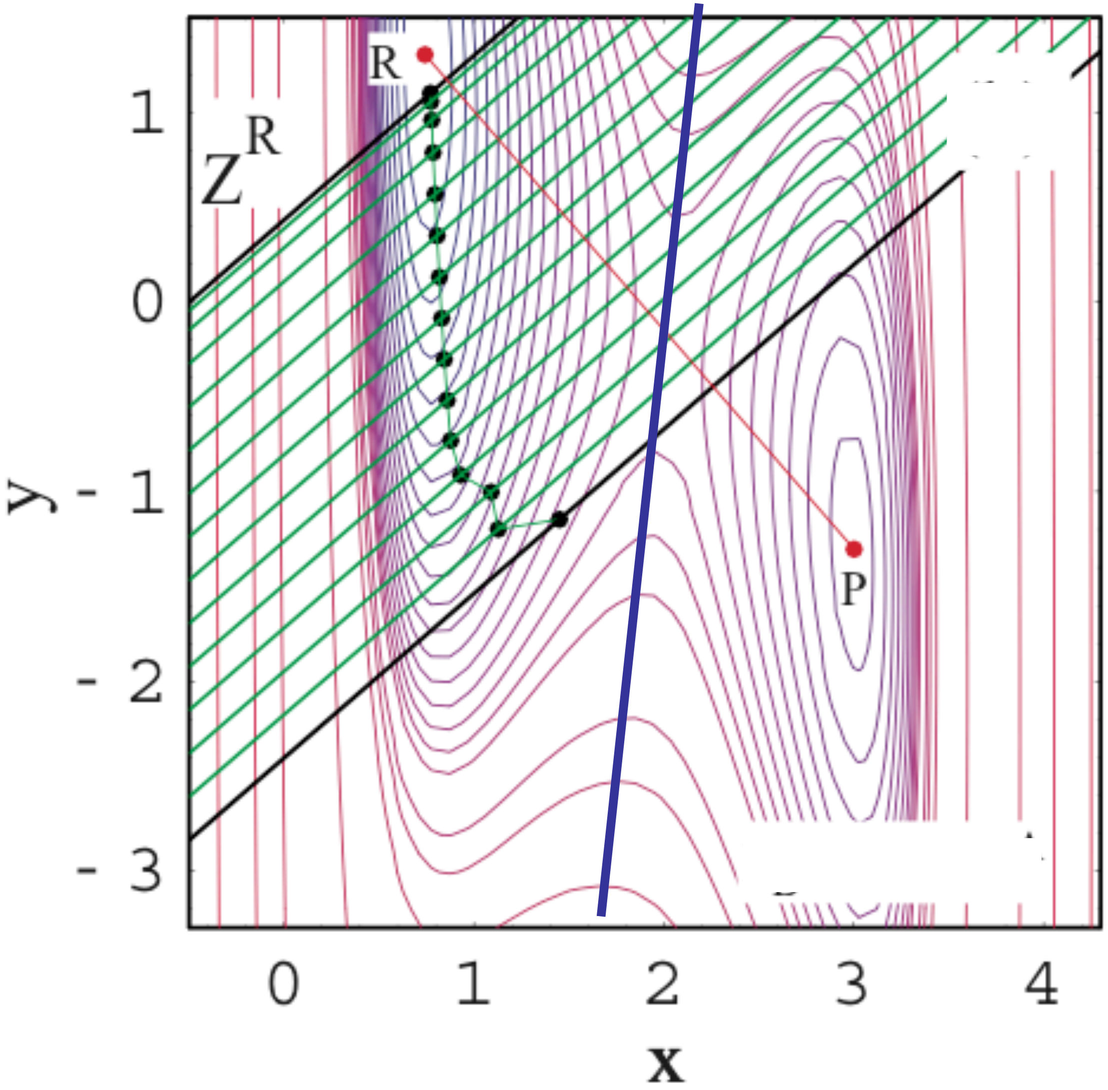


$$k^{RW-TST} = \frac{< v_\perp >}{2} \frac{Q^{Z^R}}{Q^R} e^{-\Delta F / k_B T}$$

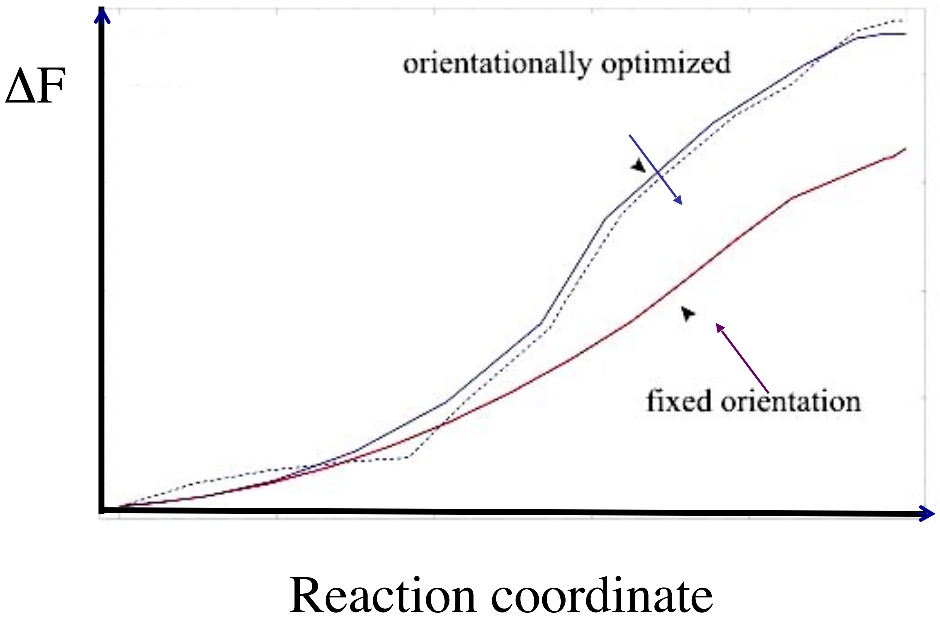
$$\mathbf{\Delta F} = - \int_{\mathbf{0}}^{\mathbf{s}} < \mathbf{f_n} (\mathbf{1} - \mathbf{R_t} \frac{\mathbf{d}\theta}{\mathbf{ds}}) >_{\mathbf{s'}} \mathbf{ds'}$$

(Jóhannesson and Jónsson, JCP 2001)

Need to be careful to **optimize orientation** as well as **location** of the TS dividing surface, else the free energy barrier can be underestimated.



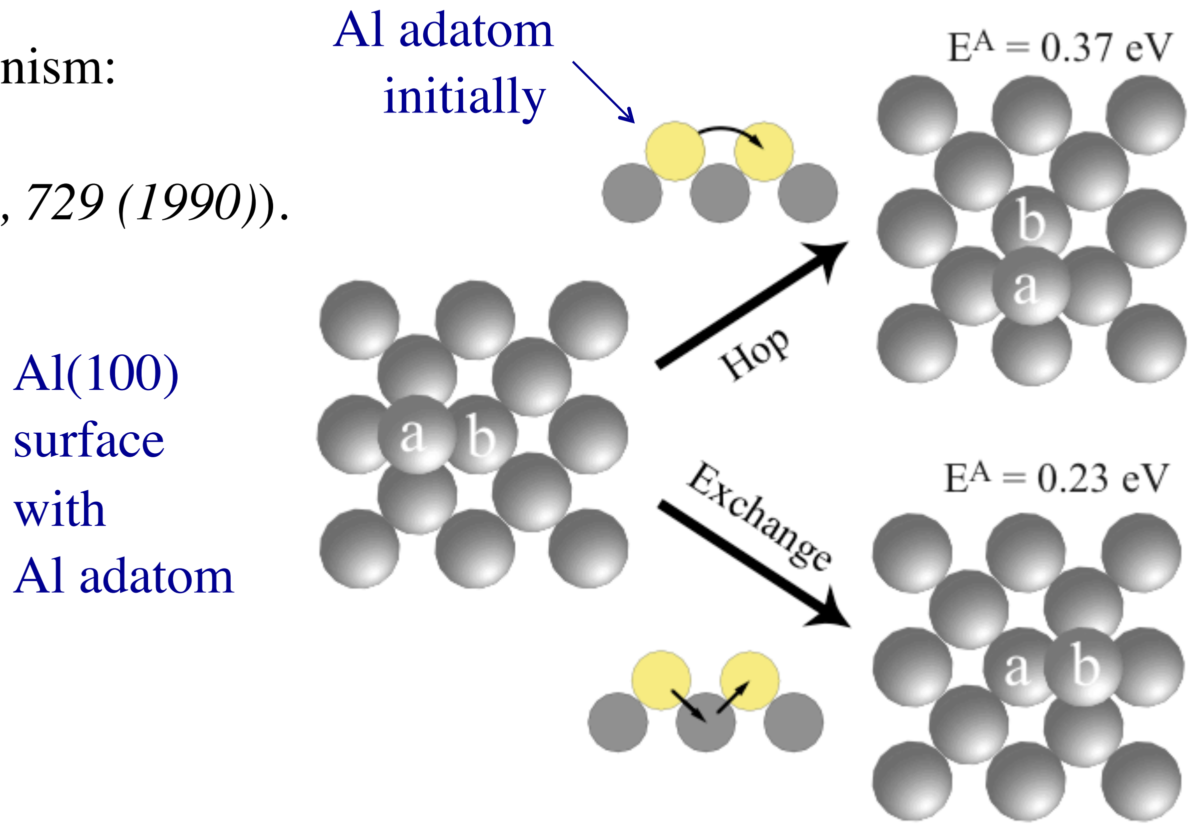
Not good to just pick some reaction coordinate and then average with respect to other degrees of freedom.



In a $3N$-dimensional system, the optimization of the location of a dividing surface is a **one-**dimensional optimization, the optimization of orientation represents **$3N$-1** degrees of freedom – it is essential to optimize orientation! *Orientational optimization can reveal the transition mechanism.*

Important to *find* rather than to *specify a priori* the mechanism of transitions

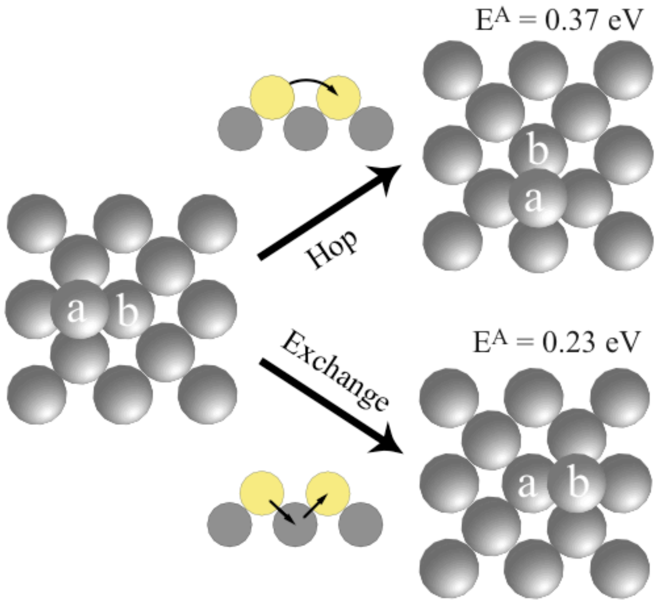
Classic example of a surprise mechanism:
Al adatom diffusion on Al(100)
(see: Feibelman, *Phys. Rev. Lett.* ***65**, 729 (1990)*).



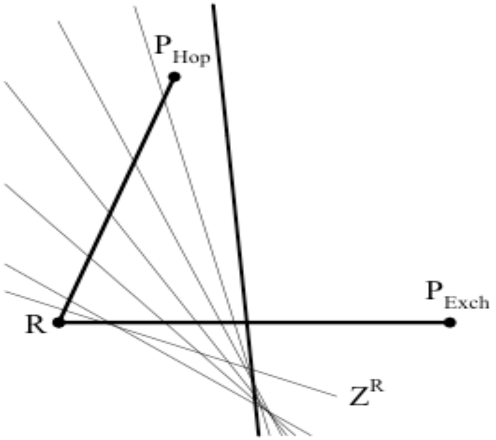
Another example of a surprise (explains re-entrant layer-by-layer growth):
Pt adatom descent from atop islands on Pt(111) near but not at kinks.
(see: Jónsson, *Annual Review of Physical Chemistry* ***51**, 623 (2000)*)

It is important not to impose a preconceived notion of the mechanism of a transition, rather **learn about the mechanism from the calculation**!

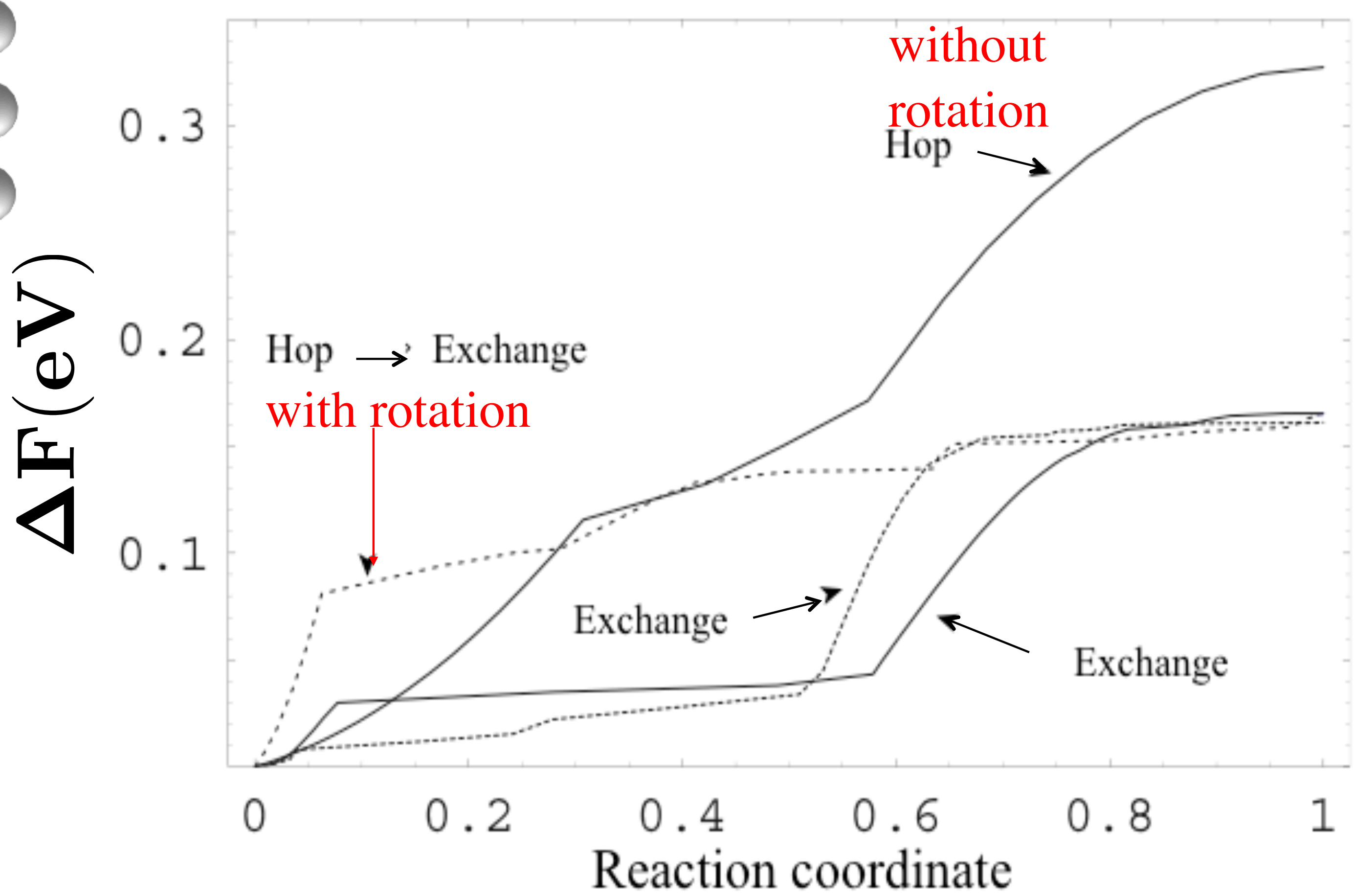
Adatom diffusion on Al(100)



By rotational optimization of the hyperplane, the optimal mechanism can be found, even if the calculation is started with the wrong assumption.



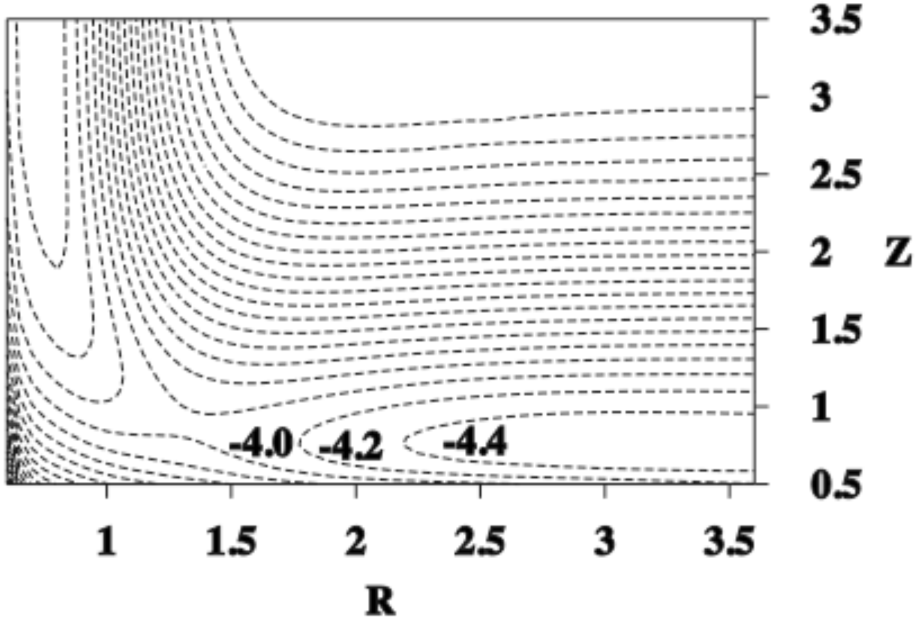
Projection onto 2-D

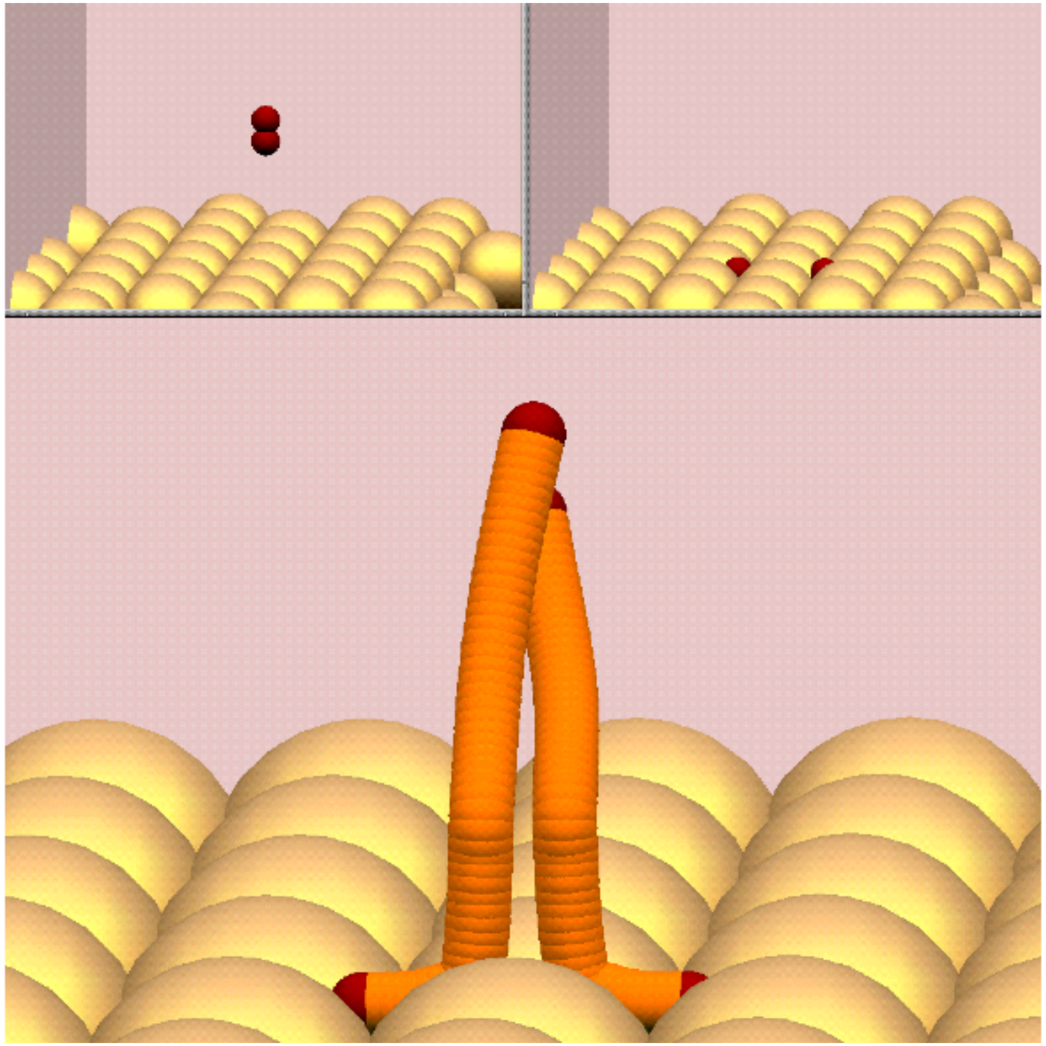


(*G. Jóhannesson & HJ, JCP 2001*)

Another example: H_2 adsorption/desorption from Cu(110)

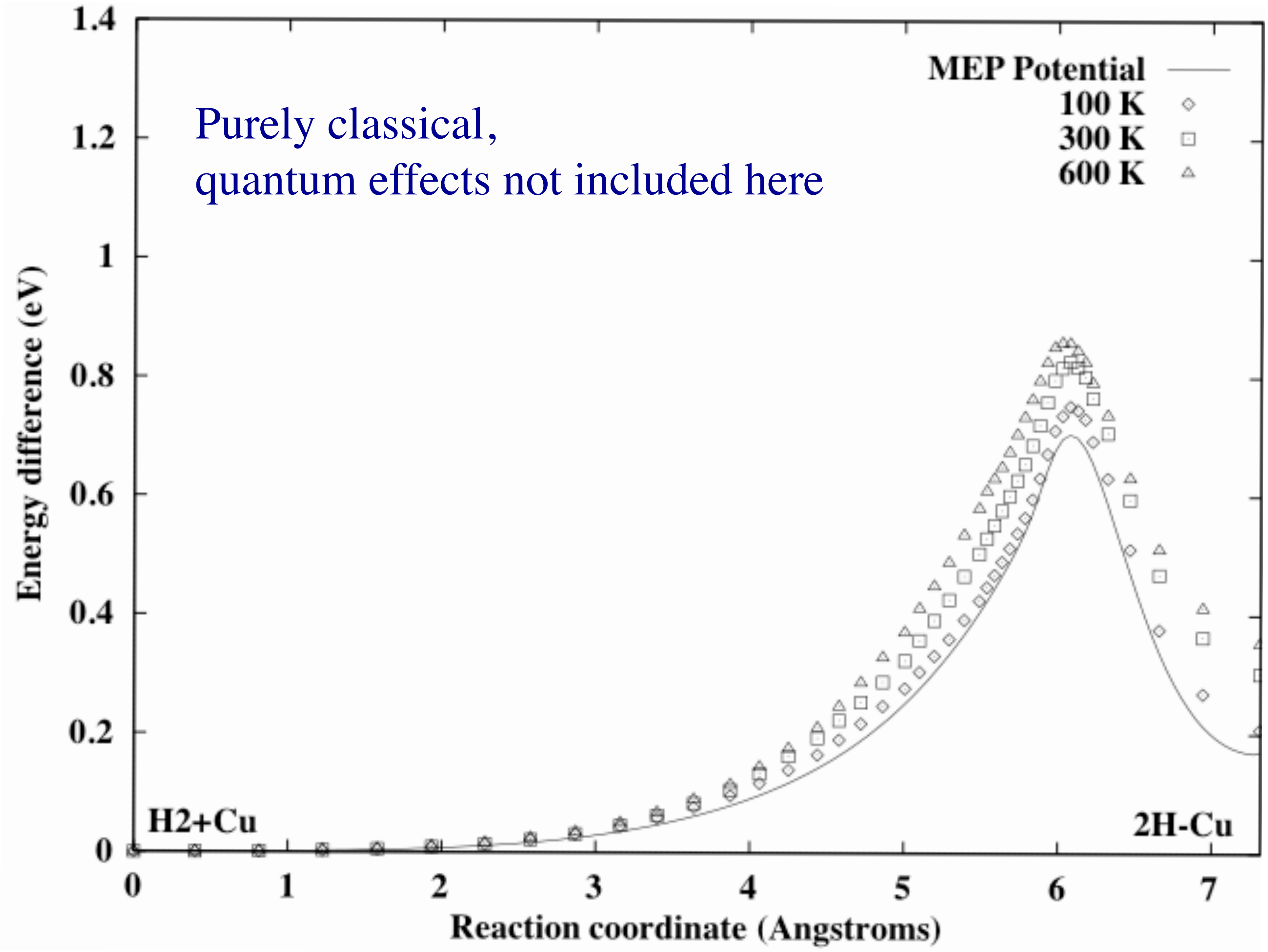
PES: Empirical potential of the EAM type where the H-Cu interaction is fitted to the LEPS potential of Depristo *et al*.





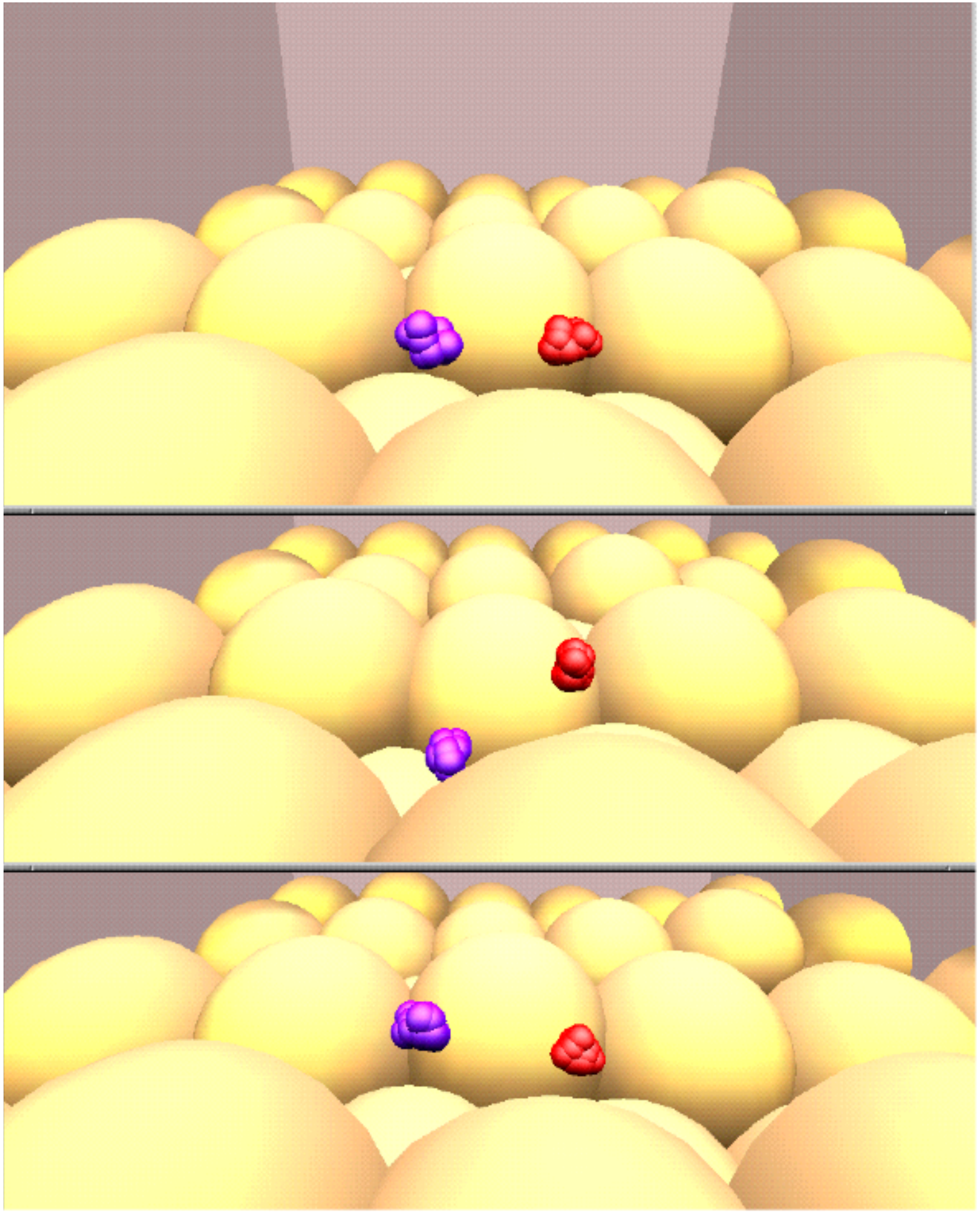
Evaluate the reversible work required to shift the system from reactants towards products to get ΔF

If H_2 comes from a gas with temperature equal to that of the surface, then TST applies!


Purely classical,
quantum effects not included here

Sampling of TS hyperplane for dissociative adsorption at T=600 K

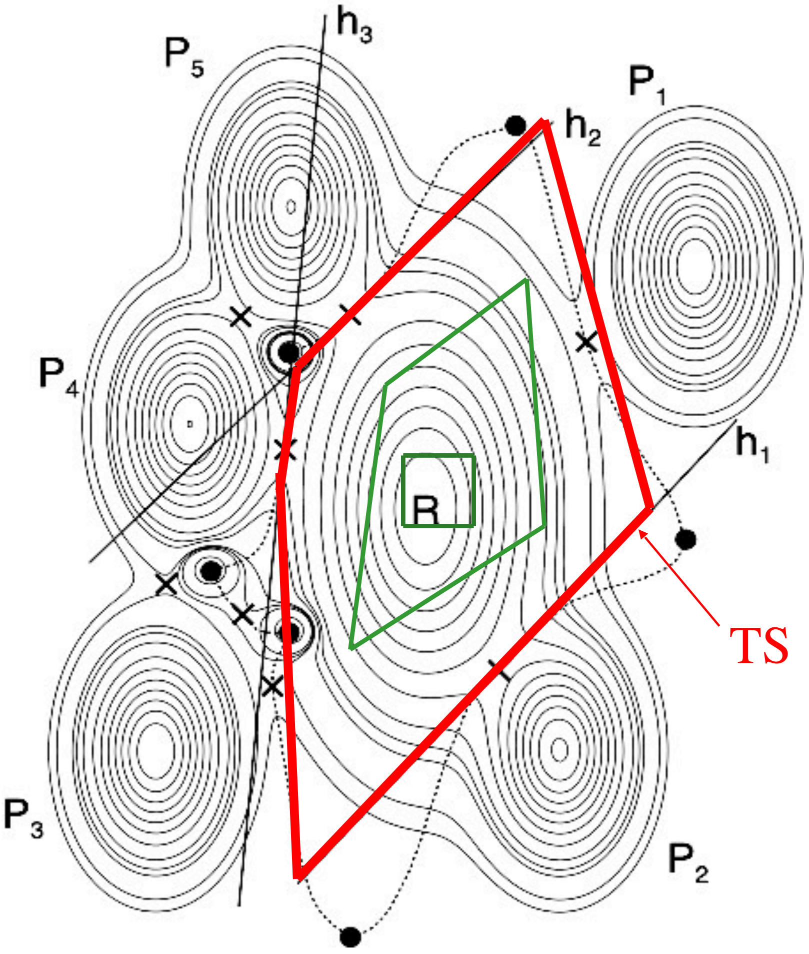
Three snapshots from thermal sampling of TS (which includes 5 degrees of freedom).
Only one of the 6 dof. of the H_2 molecule is constrained.

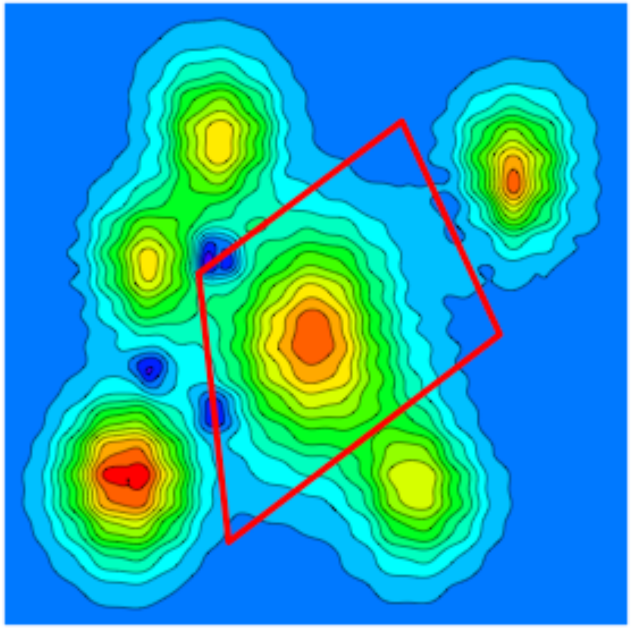


Challenge:
Parametrize and optimize a full dividing surface

Need to enclose the initial state.

One possibility: Use a mosaic of hyperplanar segments, and optimize orientation and placement of each one (as well as the number of segments).





T. Bligaard and HJ, *Comp. Phys. Comun.* 2005

Ongoing quest …

Correct or incorrect? (talk to your neighbor)

The transition state is a first order saddle point.

Transition state theory estimate of the rate constant is most accurate if there is a dip in the energy surface near the top of the potential energy curve (see picture in Atkins' P-Chem book).

Transition state theory can be used to estimate the rate constant only if the reaction mechanism is known.

Transition state theory assumes there is strong coupling to the heat bath so that a Boltzmann distribution of energy in each degree of freedom is maintained as the system climbs up the potential energy surface.