

Transition state theory and rate estimates

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Part I:

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

Implementation:

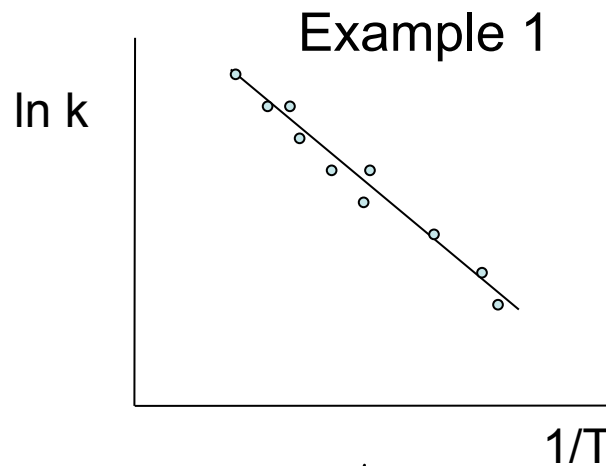
- The harmonic approximation to TST
- the effect of multidimensionality, entropy ...

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:

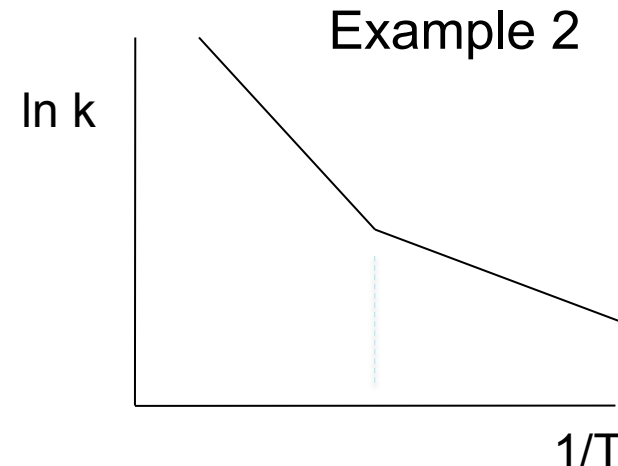
1. predict the mechanism and rate of transitions given information about the atomic structure and interaction between the atoms (such as DFT).
- and
2. analyze measurements of rates (typically Arrhenius plots) in terms of the atomic interactions and transition mechanism,



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

pre-exponential factor

activation energy



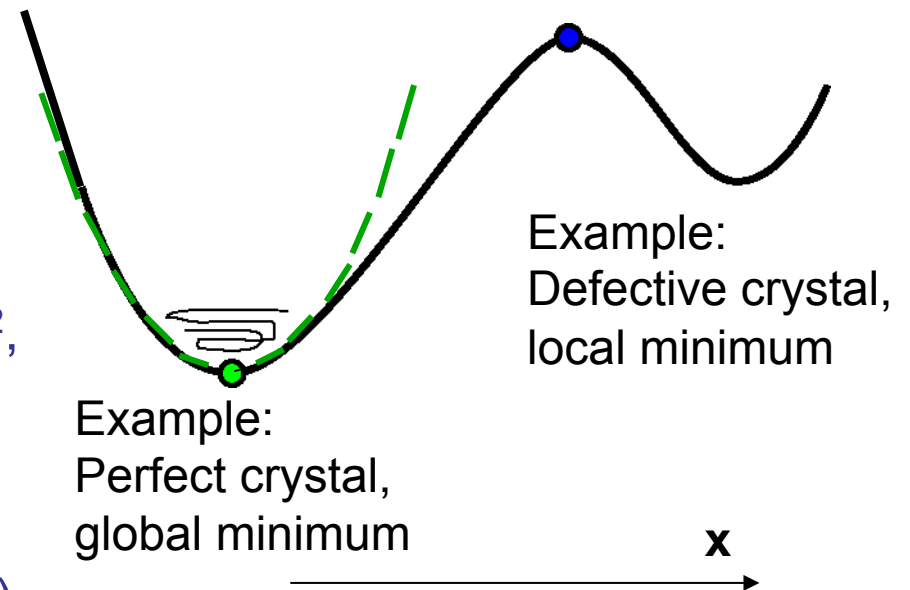
Crossover in mechanism,
entropy takes over at high T

Conventional approach to atomic simulations

Born-Oppenheimer (adiabatic) approximation:

1. Solve for the electronic degrees of freedom, $\mathbf{r}$, while keeping the nuclei fixed at coordinates $\mathbf{x}$.
Usually done with Kohn-Sham density functional theory (DFT) using approximate functionals such as PW91, PBE, RPBE, ...
Get energy surface, $V(\mathbf{x})$.

2. Solve for the motion of the nuclei. Usually with the classical approximation, $F=ma=m \, d^2x/dt^2$, sometimes using harmonic approximation (----)
 $V(\mathbf{x}) \sim \frac{1}{2}k_{sp}(\mathbf{x}-\mathbf{x}_{min})^2$.
(phonons, vibrational modes ...)

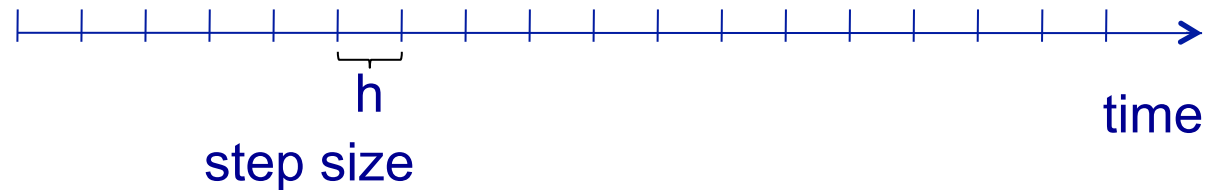


Straight forward approach

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 (finite difference approximation to $F=ma$):

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

where F is the force acting on the atom, $F_i = -\nabla_i V(x)$
and m is the mass of atom

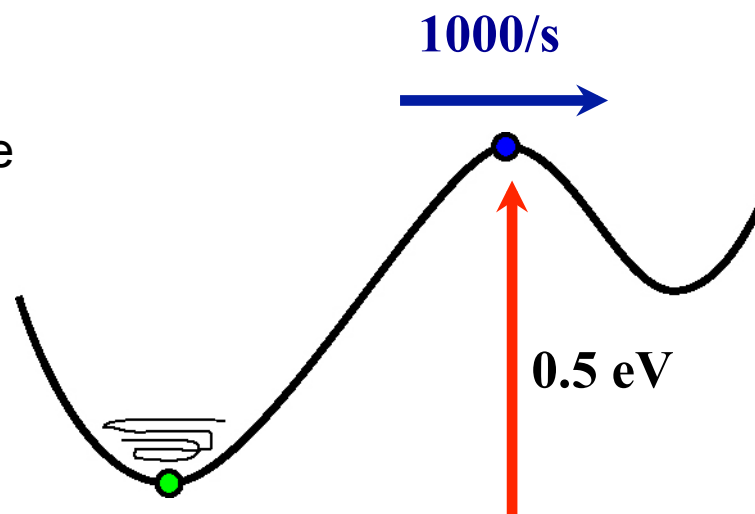
simple enough ...

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

Time scale problem:

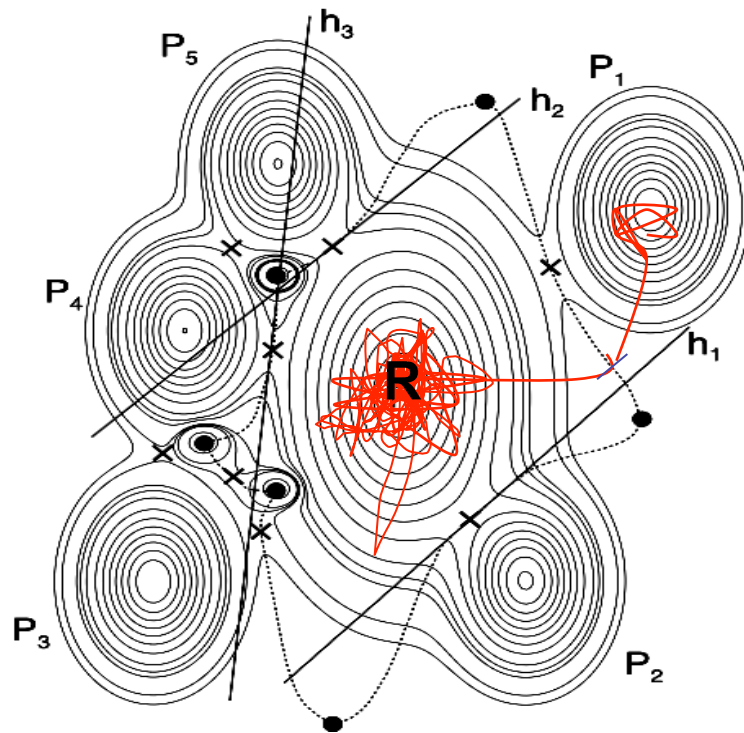
Most interesting transitions are *rare events* (i.e., much slower than vibrations).

- 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!



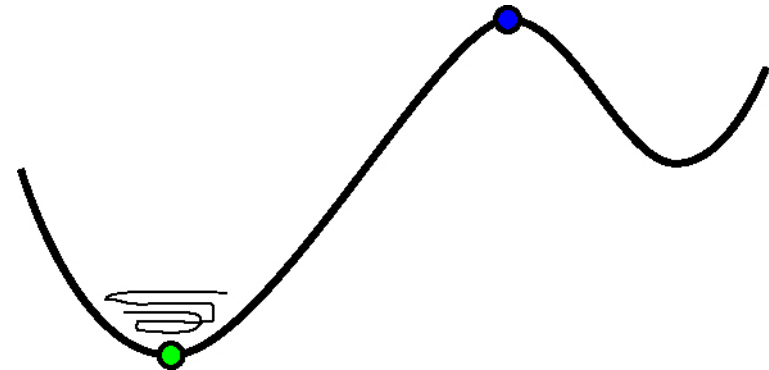
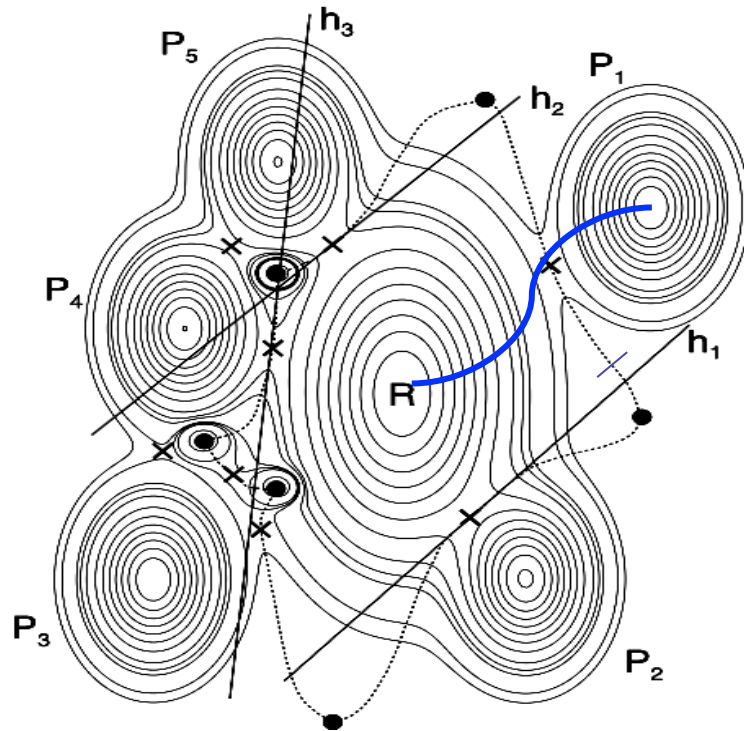
Need to take a long stroll on a 3N-dimensional **potential energy surface**, $V(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)$, where N is the number of atoms.

Given some initial state, **R**, want to find the rate of transitions and possible final states, **P₁**, **P₂** ...

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

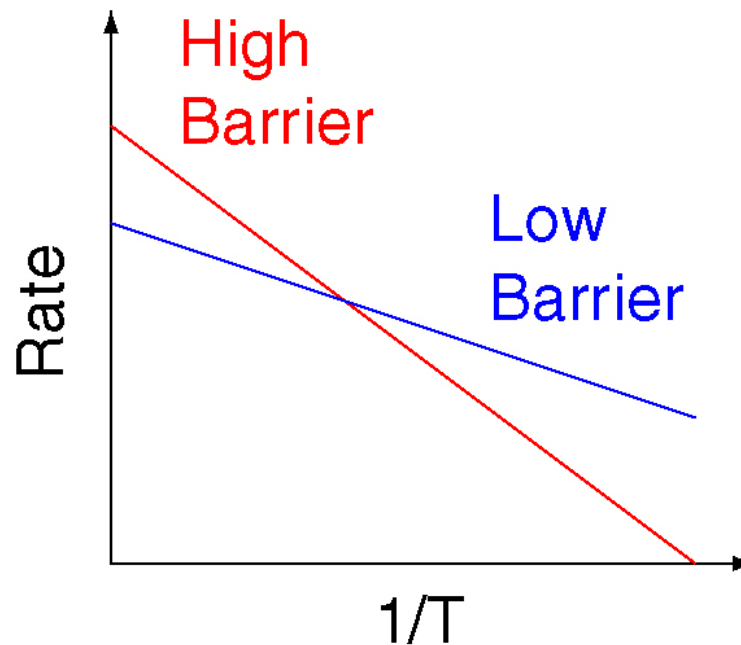
Systems of interest typically involve many degrees of freedom!

A one-dimensional picture of an energy barrier and two wells represents some path in the multidimensional space



Important to remember the high dimensionality!

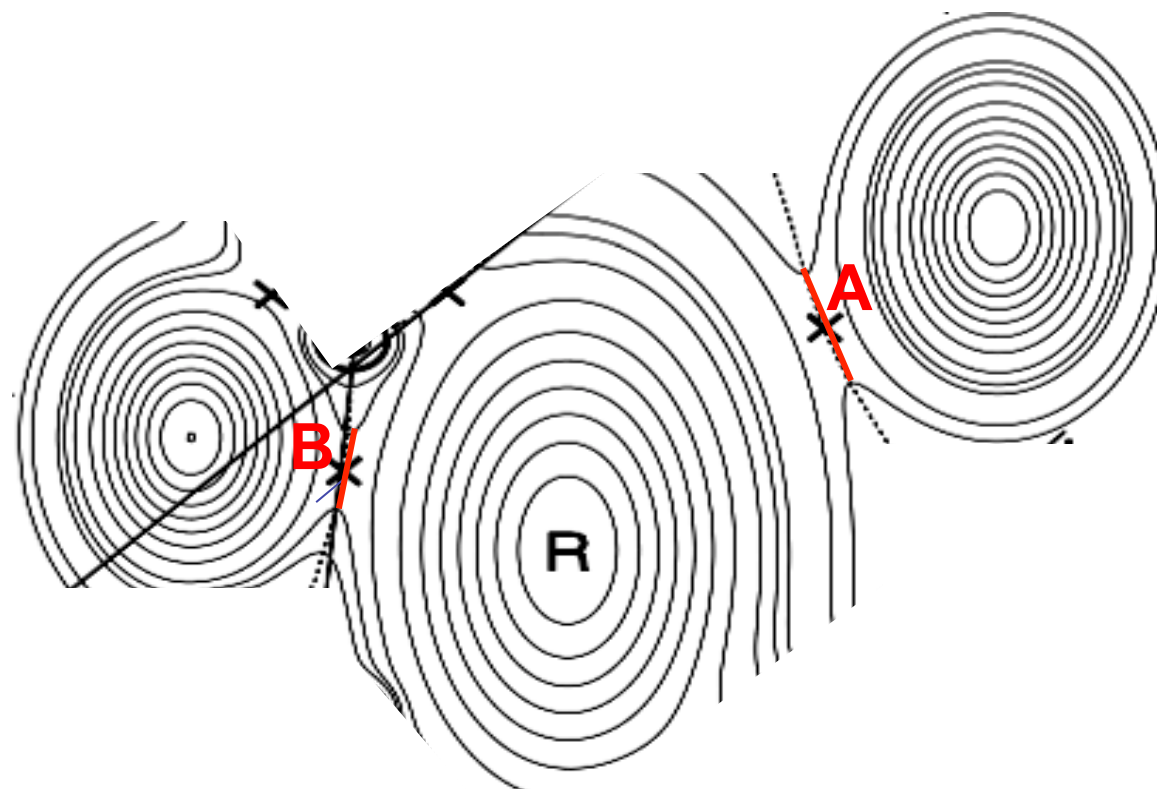
It is tempting to simply **heat up** the system to speed up the transition, but this is dangerous ...



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

Example: Diffusion of H_2O ad molecule on an ice surface
vs.
melting of the ice crystal (entropy takes over ...)

Example of energy landscape that could show crossover in mechanism as temperature increases



Compare two possible mechanisms (escape routes):

A has higher activation energy but wider mountain pass

B has lower activation energy but narrower mountain pass

How about just filling up the energy well?

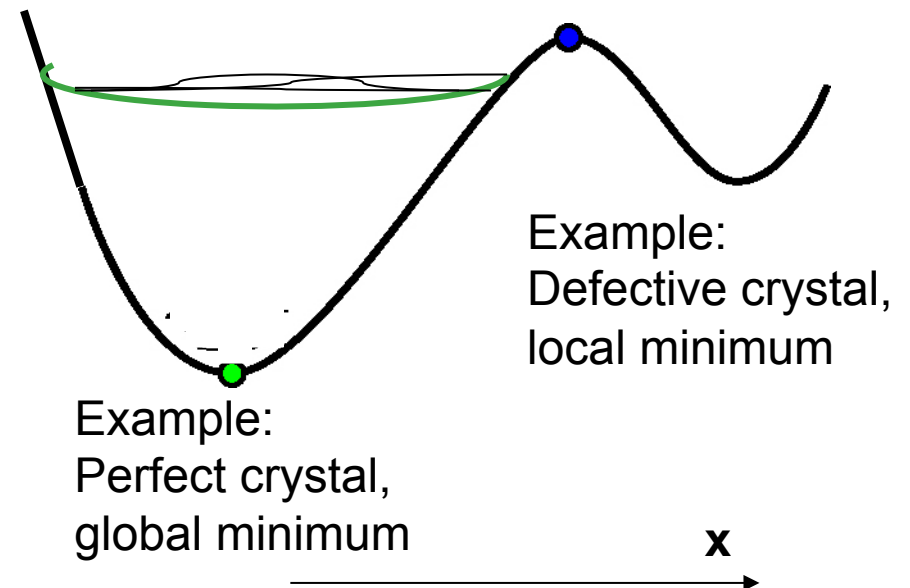
Apply a **bias** potential to make the potential well shallower

1. Accelerate the transitions out of the well by making it shallower, i.e. lowering the activation energy.
2. A critical issue is not to affect the energy surface in regions close to the barrier.

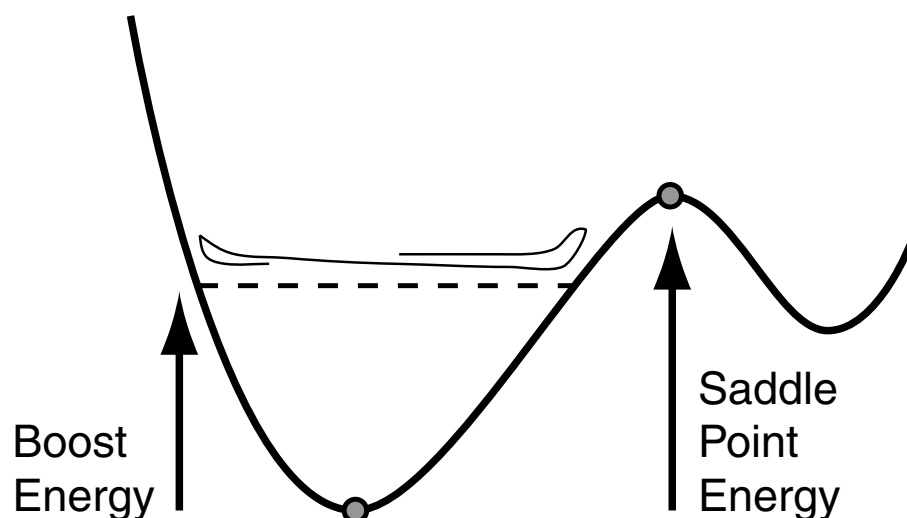
Many suggestions along these lines.

Most refined theory:

Voter's hyperdynamics method



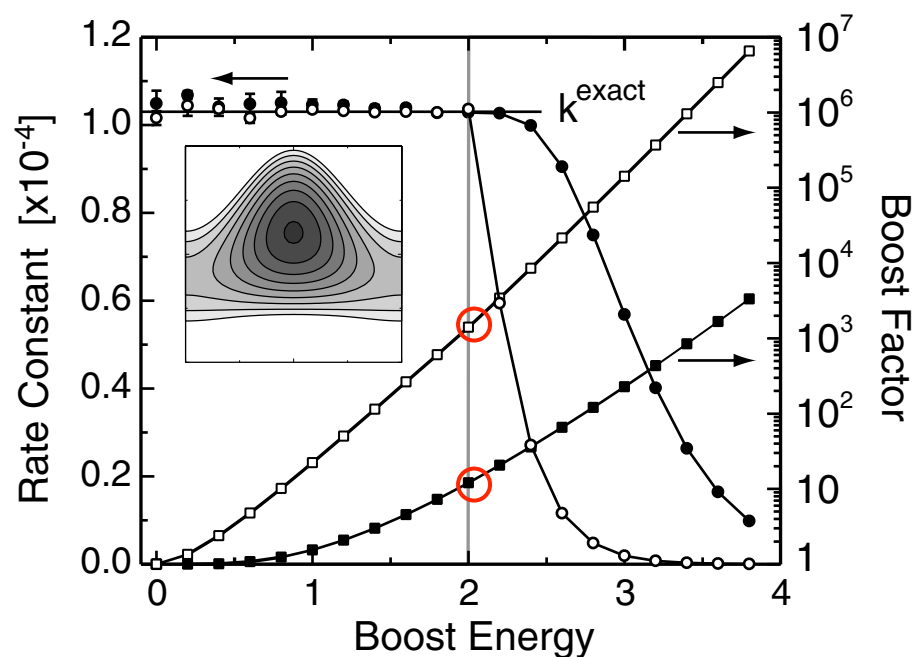
Try a flat bias potential applied to all degrees of freedom



This can give significant acceleration in **2** dimensions, but insignificantly for **10** dimensions. Why is that? (entropy ...)

Note: Dangerous to simply guess which degrees of freedom to boost ...

Easy to implement, simply check whether potential energy is below boosted energy, $V_{\min}$, then replace with boosted energy and zero force.



(Henkelman & Jónsson, JPC 2001)

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).

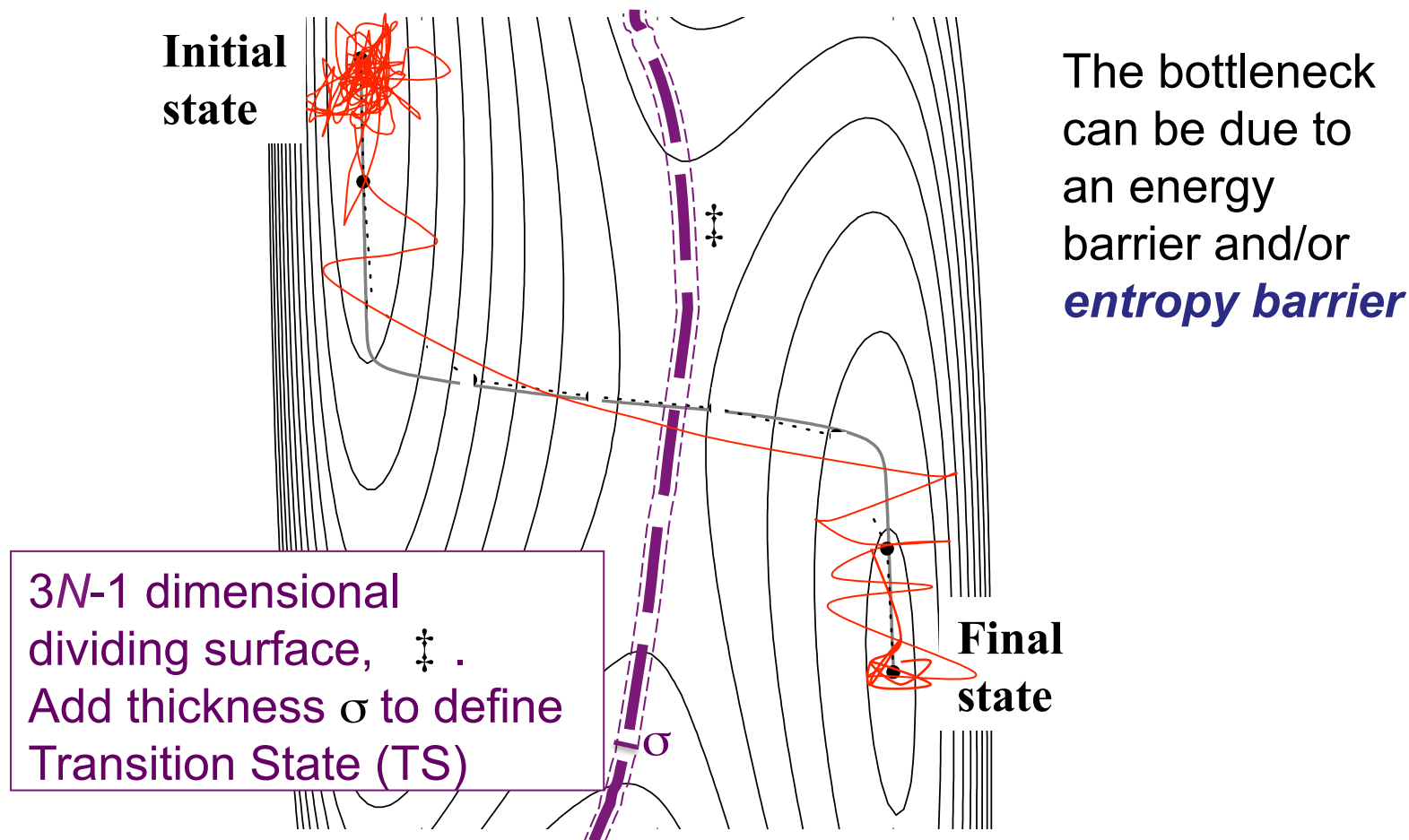
Keck, *J. Chem. Phys.* 1960.

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:



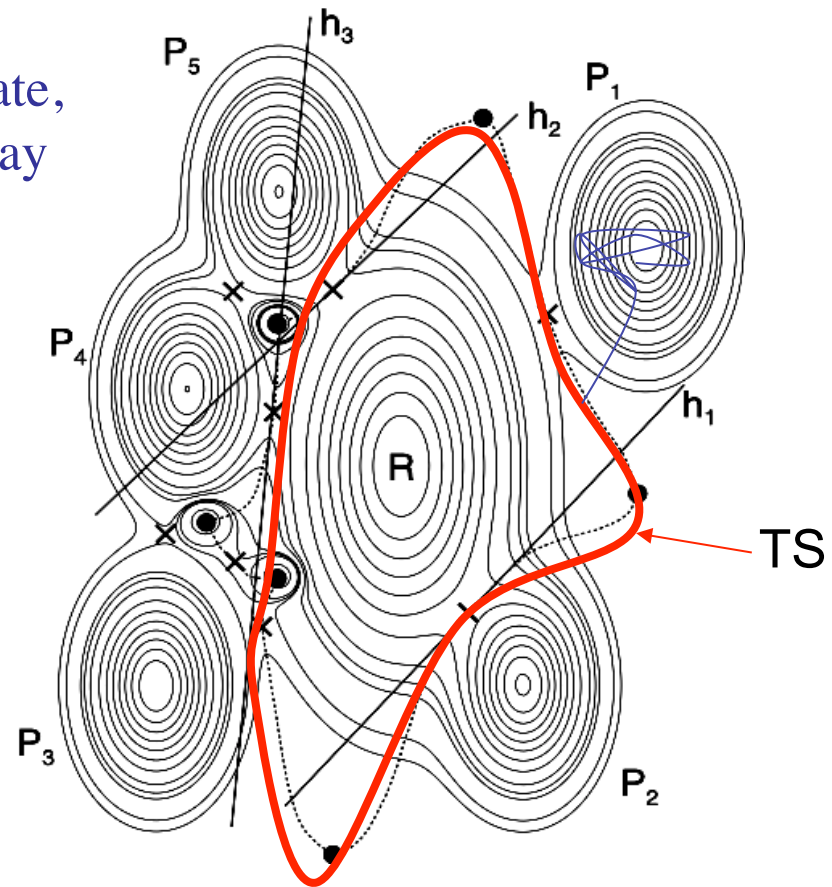
Basic Assumptions of Transition State Theory

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, $k_B T < \Delta E/5$*)
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).



Simple derivation of the TST estimate of a rate constant

First, review classical statistical mechanics:

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

Boltzmann distribution: Probability that $(\mathbf{x}, \mathbf{v})$ is in the range $\{\mathbf{x}, \mathbf{x} + d\mathbf{x}\}$ and $\{\mathbf{v}, \mathbf{v} + d\mathbf{v}\}$ is:

$$P(\mathbf{x}, \mathbf{v}) d\mathbf{x} d\mathbf{v} = A e^{-E(\mathbf{x}, \mathbf{v})/k_B T} d\mathbf{x} d\mathbf{v} \quad (A \text{ is a normalization constant})$$

This factorizes into:

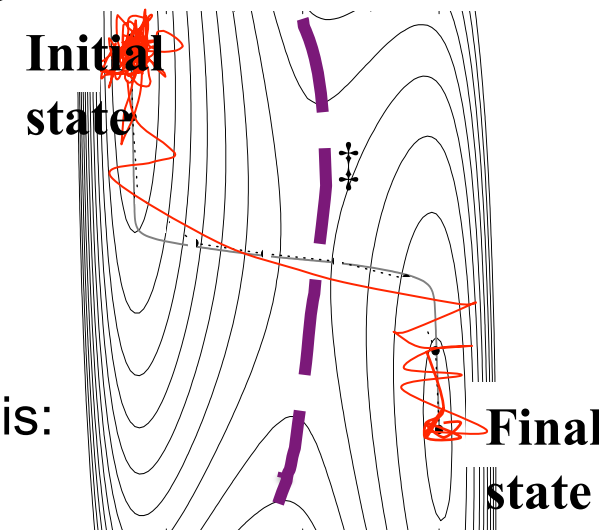
$$\underbrace{A_v e^{-\sum_i \frac{1}{2} m_i v_i^2 / k_B T} d\mathbf{v}}_{p_v(\mathbf{v})} \underbrace{A_c e^{-V(\mathbf{x})/k_B T} d\mathbf{x}}_{p_c(\mathbf{x})}$$

Given that the system is initially somewhere in R:

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

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

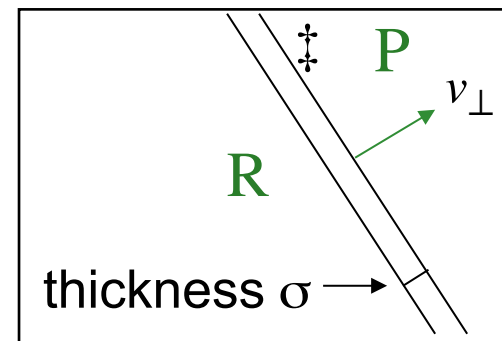
$$P_S = \frac{\int_S e^{-V(\mathbf{x})/k_B T} d\mathbf{x}}{\int_R e^{-V(\mathbf{x})/k_B T} d\mathbf{x}} \equiv \frac{Z_S}{Z_R} \quad \leftarrow \text{configuration integrals}$$



Simple derivation of the TST estimate of a rate constant

$$k^{\text{TST}} = (\text{probability of getting to TS}) \cdot (\text{flux out of TS})$$

Choose the dividing surface to be a **hyperplane**
 $ax+b=0$ particularly simple,
 (but, may not be good enough ...)



$$k^{\text{TST}} = P_{\ddagger} \frac{\langle v_{\perp} \rangle}{\sigma}$$

$$= \frac{\sigma \int_{\ddagger} e^{-V(\mathbf{x})/k_B T} d\mathbf{x}}{\int_R e^{-V(\mathbf{x})/k_B T} d\mathbf{x}} \frac{\langle v_{\perp} \rangle}{\sigma}$$

Maxwell:

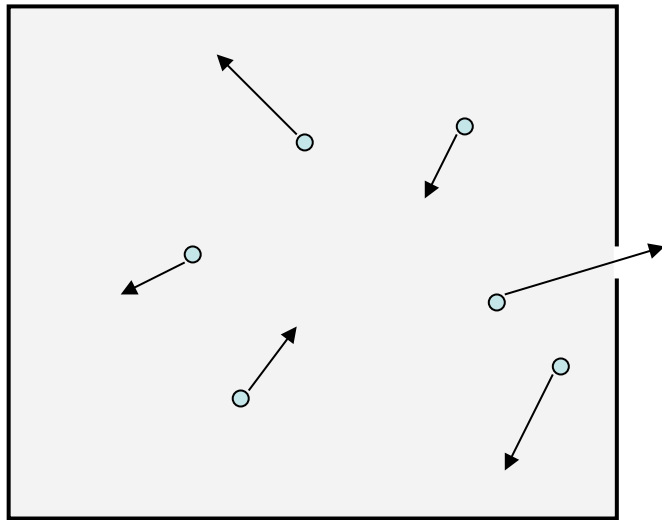
$$\langle v_{\perp} \rangle = \frac{\int_0^{\infty} v_{\perp} e^{-\frac{1}{2}\mu_{\perp} v_{\perp}^2 / k_B T} dv_{\perp} \int_{-\infty}^{\infty} e^{-\sum_i \frac{1}{2}\mu_i v_i^2 / k_B T} d\mathbf{v}}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\mu_{\perp} v_{\perp}^2 / k_B T} dv_{\perp} \int_{-\infty}^{\infty} e^{-\sum_i \frac{1}{2}\mu_i v_i^2 / k_B T} d\mathbf{v}} = \frac{\int_0^{\infty} v_{\perp} e^{-\frac{1}{2}\mu_{\perp} v_{\perp}^2 / k_B T} dv_{\perp}}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\mu_{\perp} v_{\perp}^2 / k_B T} dv_{\perp}} = \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}}$$

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

3N-1 dimensional
1 dimensional

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

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



No energy barrier here,
just an entropic bottleneck

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

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

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

ideal gas: $PV = Nk_B T$

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

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

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 $\mathbf{q}$ that satisfy

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

then the TST rate constant can be written as

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

here $\Theta[]$ is the Heavyside function
and

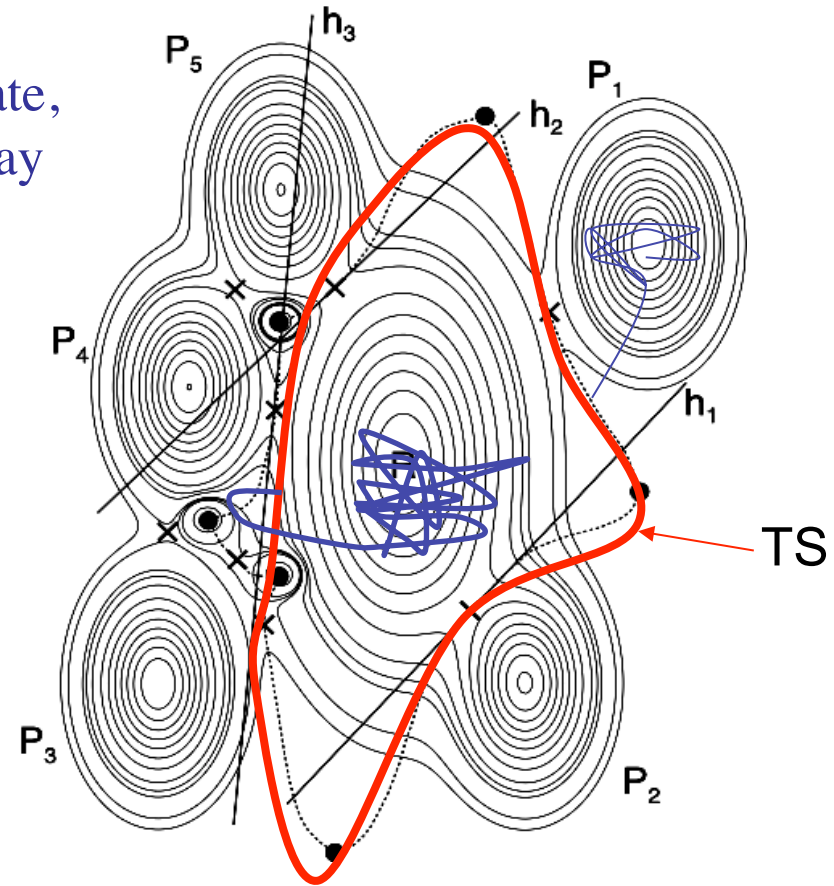
$$Q_R = \int d\mathbf{p} \int d\mathbf{q} e^{-H(\mathbf{p}, \mathbf{q})/k_B T}$$

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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.

- Can run short time scale dynamical trajectories starting at the TS to take recrossings into account - *dynamical corrections*
- $k^{\text{exact}} = \kappa k^{\text{TST}}$ where $0 < \kappa < 1$ and also to find the product state(s).

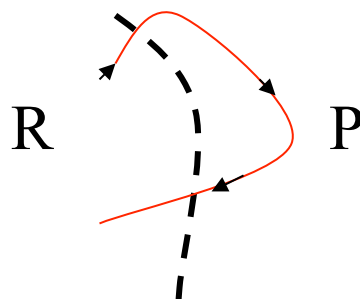


Variational principle for optimizing the choice of transition state

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

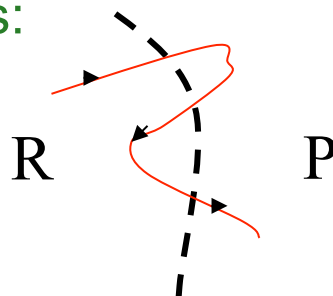
$$k^{\text{TST}} > k$$

One recrossing:



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

Two recrossings:



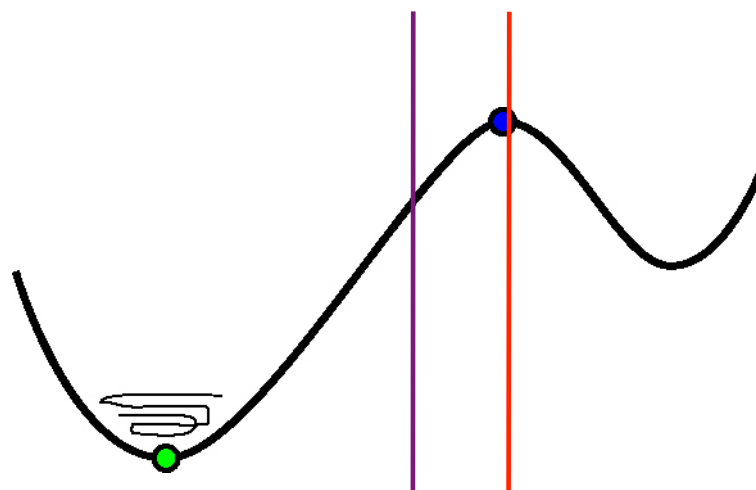
Should only count once, but gives two reactive events in TST estimate.

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

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

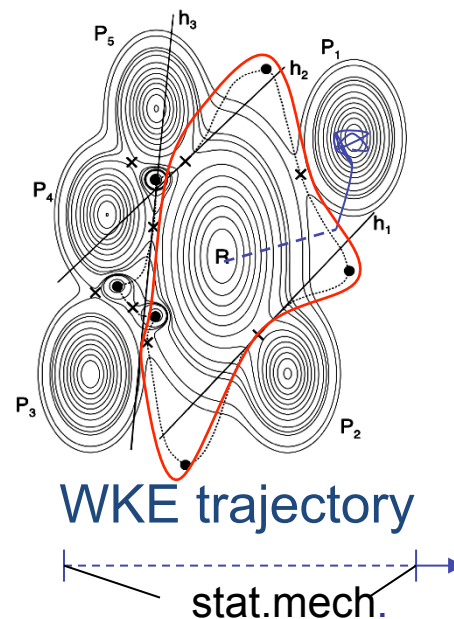
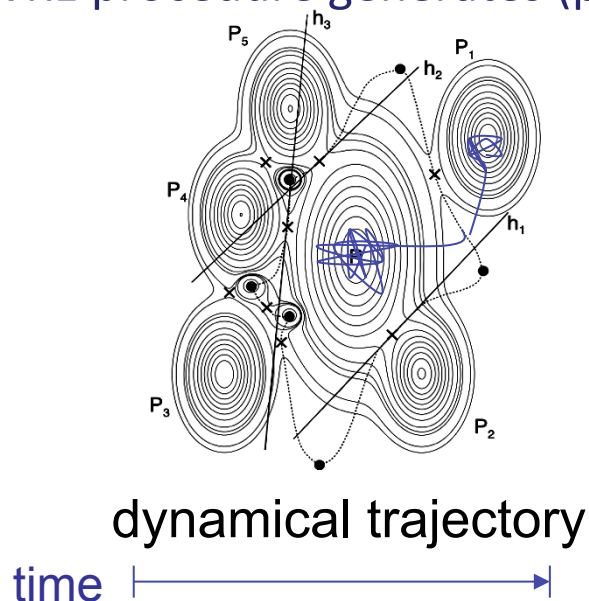
1. Find optimized transition state dividing surface using $k^{\text{TST}} > k^{\text{exact}}$

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

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

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



Part II:

Harmonic transition state theory (HTST): How to find first order saddle points?

Implementation of full, variational transition state theory:

- formulation in terms of the free energy of a hyperplanar dividing surface
- evaluate free energy difference from reversible work
- variational optimization by translating and rotating the hyperplane
- extension to a mosaic of hyperplanes to enclose the initial state

Application:

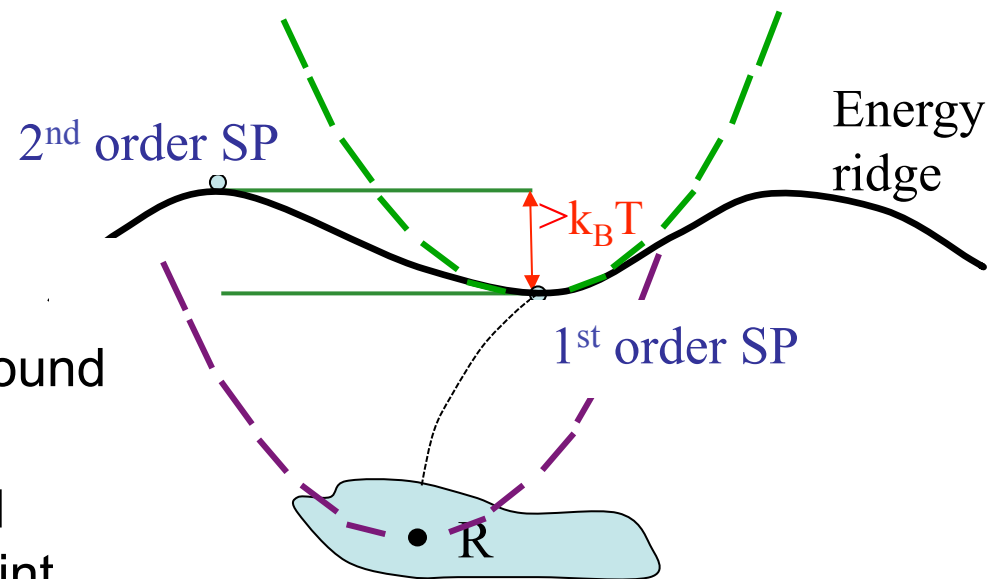
- 2-dimensional system representing a bond coupled to harmonic oscillator
- diffusion of an Al adatom on an Al(100) surface

HTST - Harmonic approximation to TST:

Good for solids at not too high T

Approximate the energy surface with second order Taylor expansions,

- (a) For reactant region expand around the local energy minimum,
- (b) For the transition state expand around the 1st order saddle point.



Works well when

- (1) energy of *second* order saddle points is significantly higher than $k_B T$ over the energy of *first* order saddle points, and
- (2) when the potential is smooth enough that a second order Taylor approximation to the PES is good enough in the region with large statistical weight.

Derivation of HTST: Expand PES around minimum in *normal mode* coordinate

Taylor expand PES around minimum and saddle point, use vibrational normal modes, q_i :

$$V_R(\mathbf{q}) \approx V_{\min} + \sum_{i=1}^{3N} \frac{1}{2} k_{R,i} q_{R,i}^2$$

$$V_{\ddagger}(\mathbf{q}) \approx V_{SP} + \sum_{i=1}^{3N-1} \frac{1}{2} k_{\ddagger,i} q_{\ddagger,i}^2$$

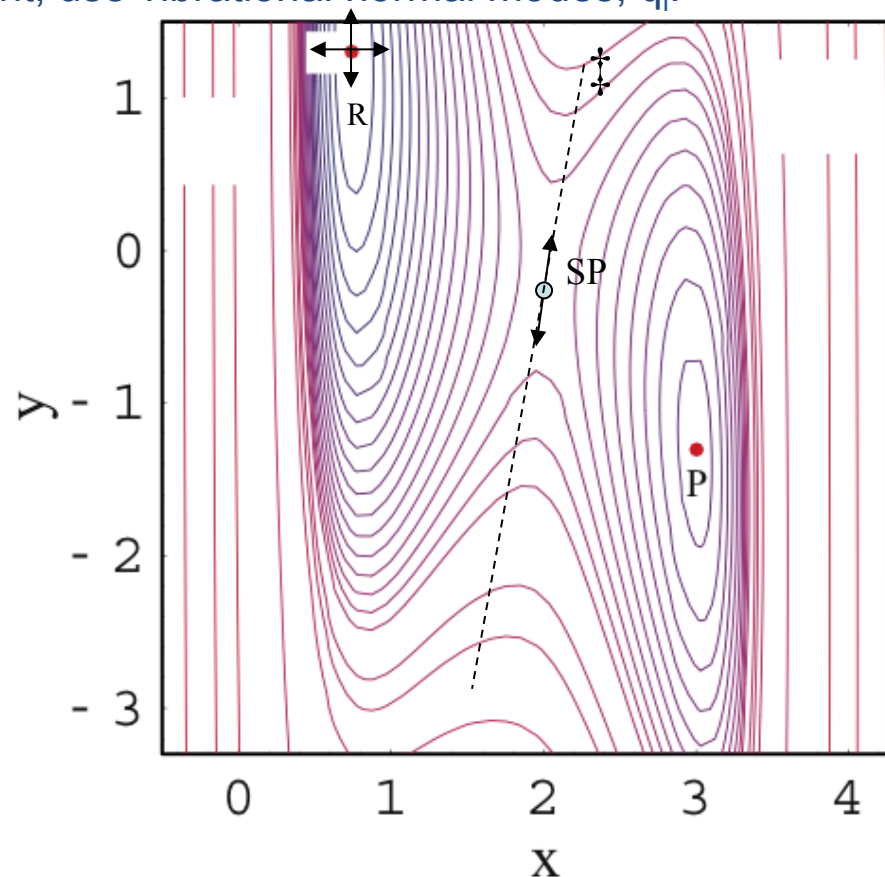
Plug into the expression for the rate constant:

$$\begin{aligned} k^{\text{HTST}} &= \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{\ddagger}}{Z_R} \\ &= \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{\int_{-\infty}^{\infty} e^{-\left(V_{SP} + \sum_{i=1}^{3N-1} \frac{1}{2} k_{\ddagger,i} q_{\ddagger,i}^2\right)/k_B T} d\mathbf{q}_{\ddagger}}{\int_{-\infty}^{\infty} e^{-\left(V_{\min} + \sum_{i=1}^{3N} \frac{1}{2} k_{R,i} q_{R,i}^2\right)/k_B T} d\mathbf{q}_R} \end{aligned}$$

Define: $\nu = \omega/2\pi = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$

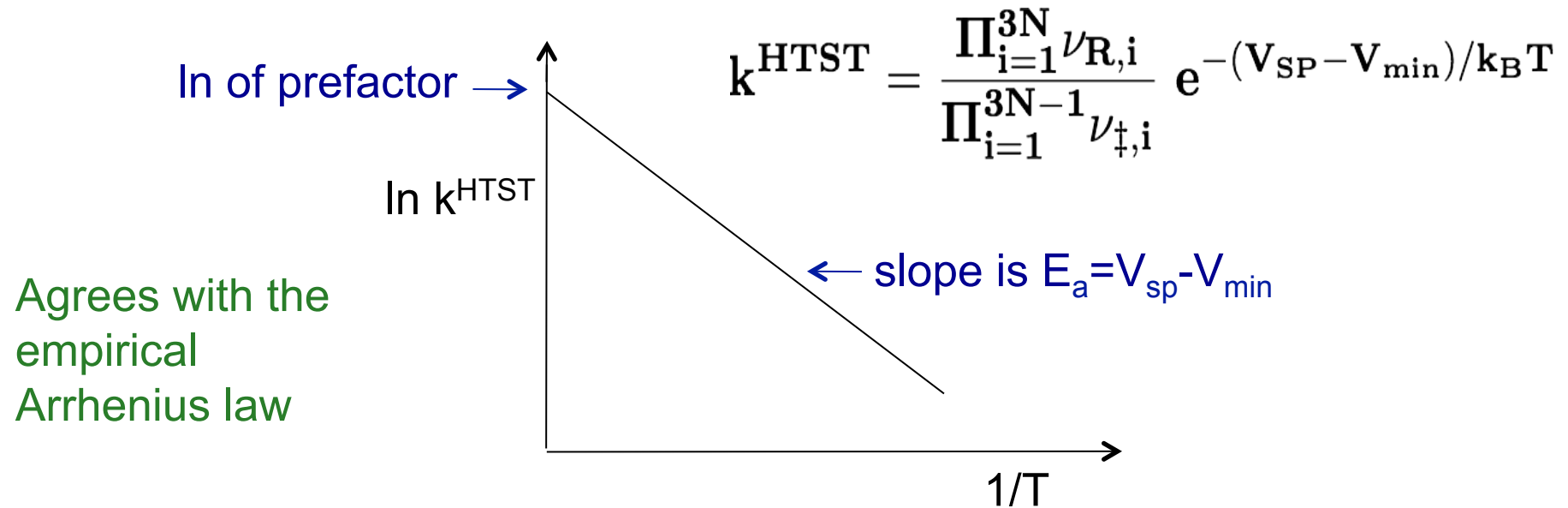
which gives:

$$k^{\text{HTST}} = \frac{\prod_{i=1}^{3N} \nu_{R,i}}{\prod_{i=1}^{3N-1} \nu_{\ddagger,i}} e^{-(V_{SP} - V_{\min})/k_B T}$$

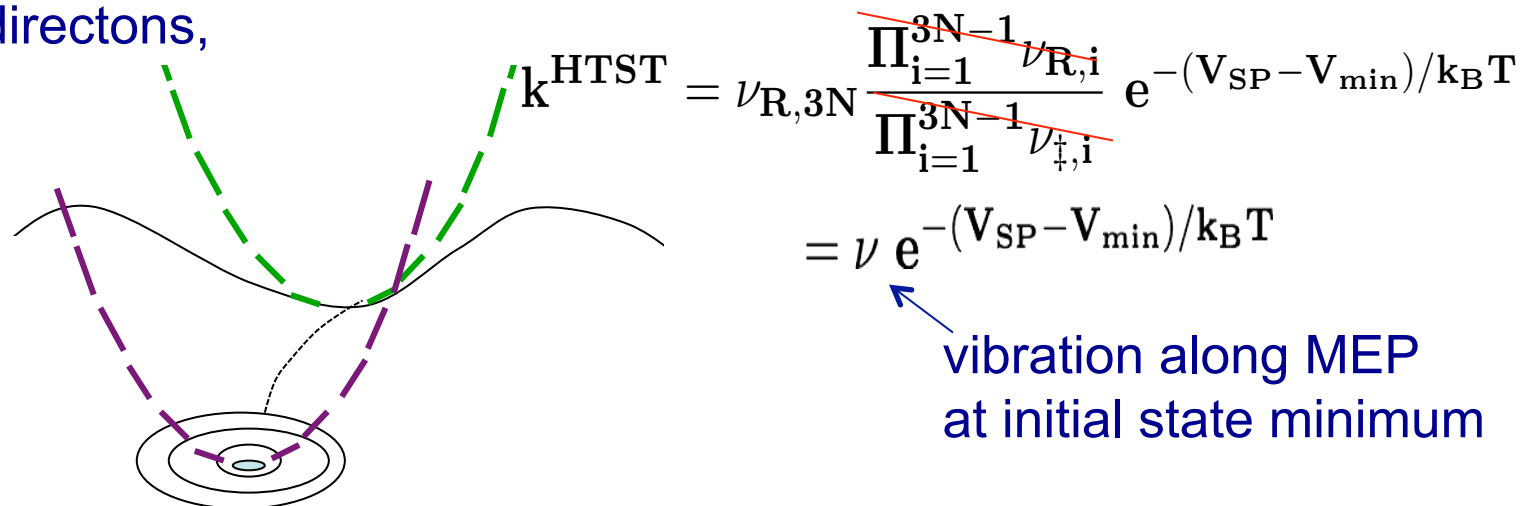


Agrees with the empirical Arrhenius law $k(T) = \nu e^{-E_a/k_B T}$

Interpretation of the expression for k^{HTST}

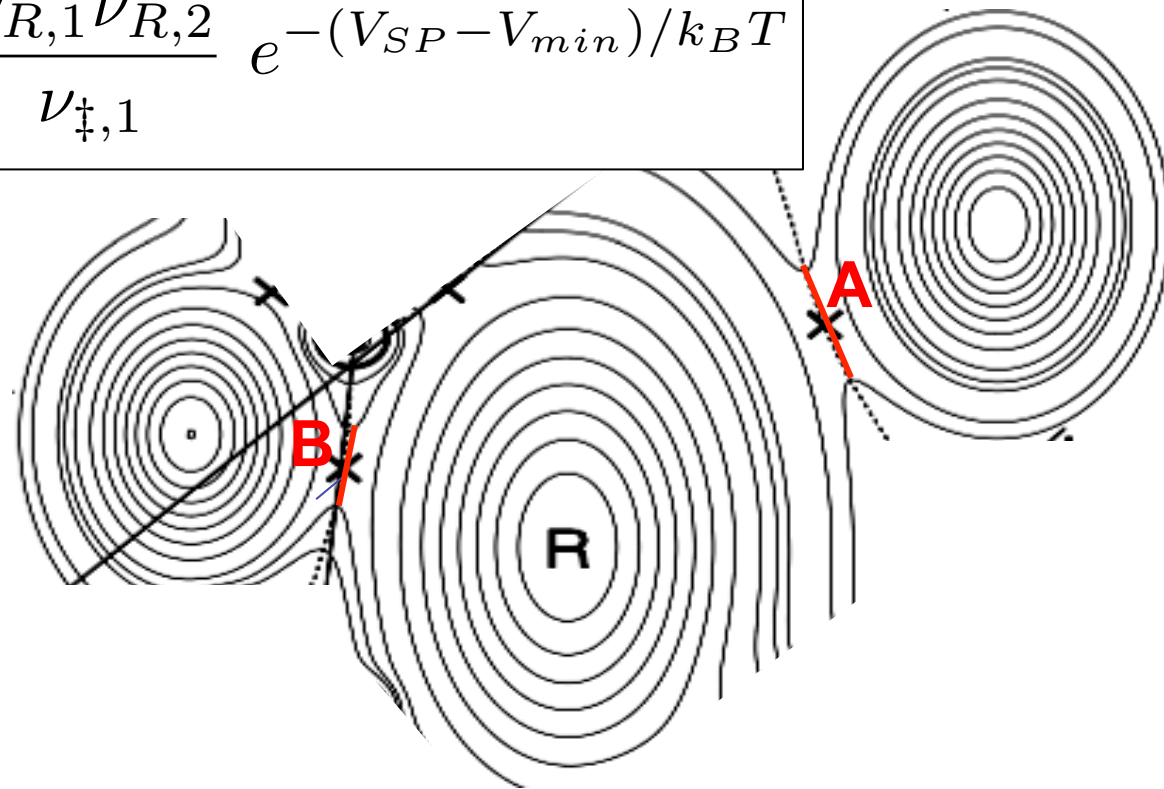


If the width of the energy valley is the same at the minimum and saddle point in all directions,



Back to the energy landscape with two escape channels

$$k^{HTST} = \frac{\nu_{R,1}\nu_{R,2}}{\nu_{\ddagger,1}} e^{-(V_{SP}-V_{min})/k_B T}$$



A has *larger* $V_{SP}-V_{min}$ but *lower* vibrational frequency at saddle point, $\nu_{\ddagger,1}$
B has *smaller* $V_{SP}-V_{min}$ but *higher* vibrational frequency at saddle point.

How about just filling up the energy well?

Apply a **bias** potential to make the potential well shallower

Can give significant acceleration in $k^{\text{HTST}} = \nu_{R,3N} \frac{\prod_{i=1}^{3N-1} \nu_{R,i}}{\prod_{i=1}^{3N-1} \nu_{\ddagger,i}} e^{-(V_{\text{SP}} - V_{\text{min}})/k_B T}$
2 dimensions, but insignificant for
10 dimensions. Why is that? (entropy ...)

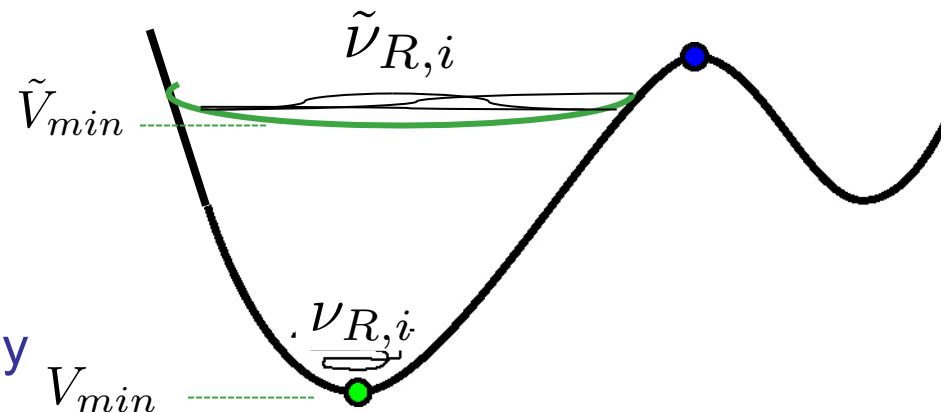
Rate of transitions is increased as $V_{\text{SP}} - V_{\text{min}}$ is made smaller.

But, at the same time the vibrational frequency is reduced.

If the vibrational frequency is reduced by

$$\frac{\nu_{R,i}}{\tilde{\nu}_{R,i}} = \frac{1}{5}$$

then the pre-exponential is decreased by
1/25 in a 2 dimensional system, but
 by **10^{-7}** in a 10 dimensional system!



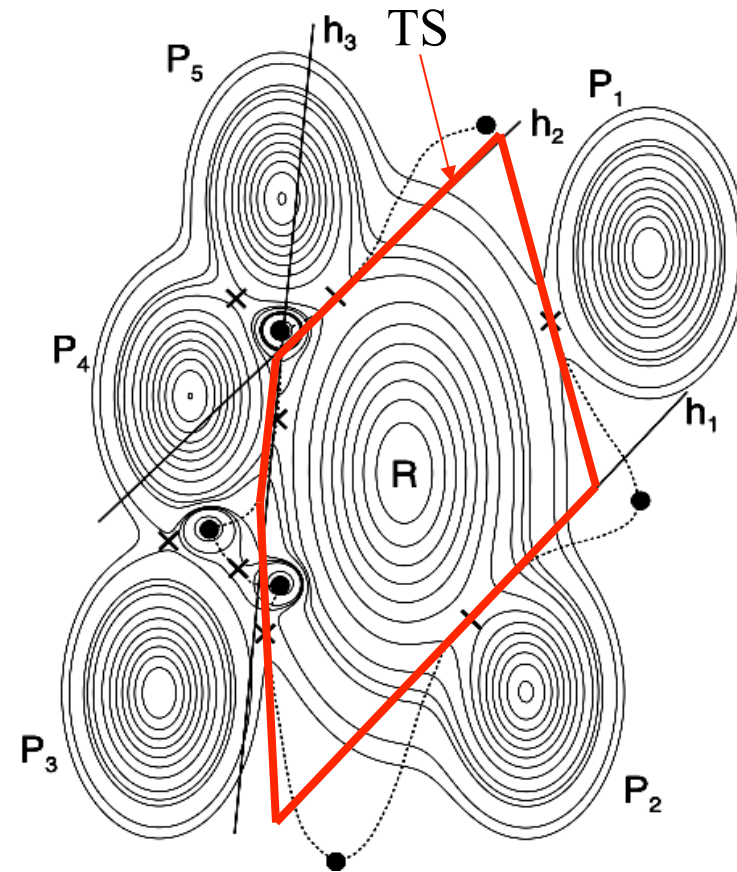
$$\frac{\tilde{k}}{k} = \left(\frac{\nu_{R,i}}{\tilde{\nu}_{R,i}} \right)^{3N} e^{\tilde{V}_{\text{min}} - V_{\text{min}}}$$

Harmonic TST involves a certain choice for the transition state dividing surface

- Need to find **all relevant saddle points** on the potential energy rim surrounding the energy basin corresponding to the initial state.
- The transition state is approximated as a set of hyperplanes going through the saddle points with the unstable mode normal to the hyperplane.
- For each hyperplanar segment:

$$k^{\text{HTST}} = \frac{\prod_{i=1}^D v_{R,i}}{\prod_{i=1}^{D-1} v_{\ddagger,i}} e^{-(V_{SP} - V_{\min}) / k_B T}$$

Temperature and entropy are taken into account within the harmonic approximation



HTST is typically many orders of magnitude faster than full TST!
But, need to find the saddle pts.

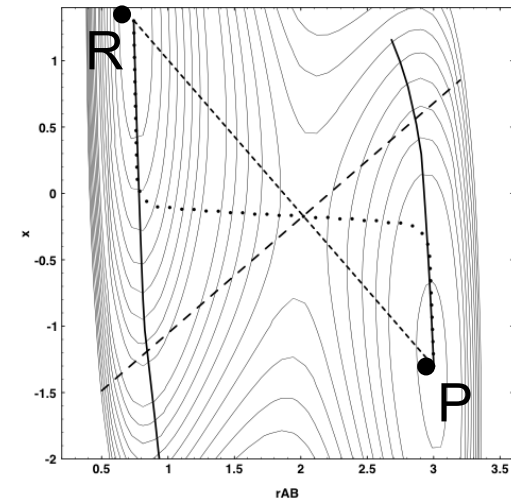
How to find the saddle point(s) ?

Methods for finding saddle points

Two categories:

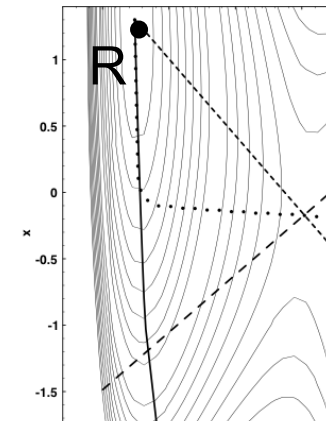
- A. Two point problem – both initial and final state minima are known.

Easier, can use info about final state minimum to guide the search



- B. One point problem – only initial state minimum is known.

Harder, can only use local info about the energy surface

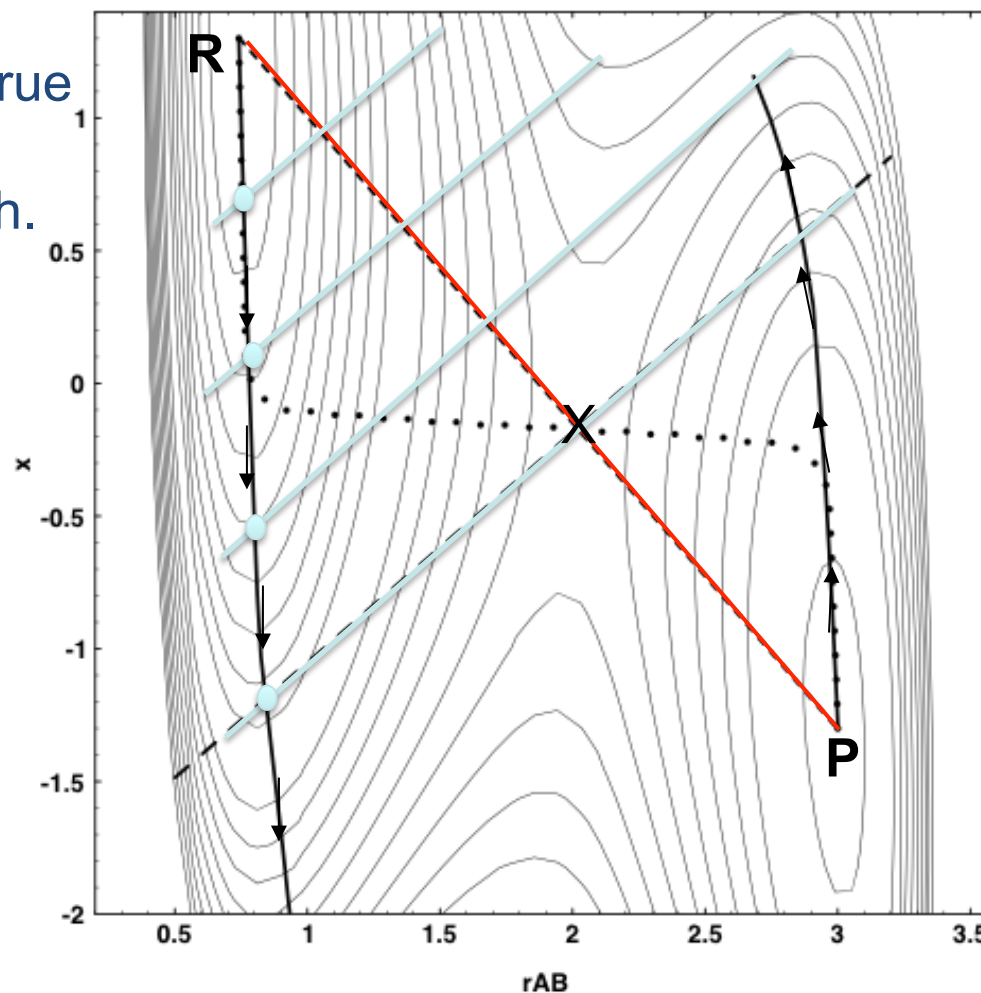


'Drag method' or 'Constrained Minimization'

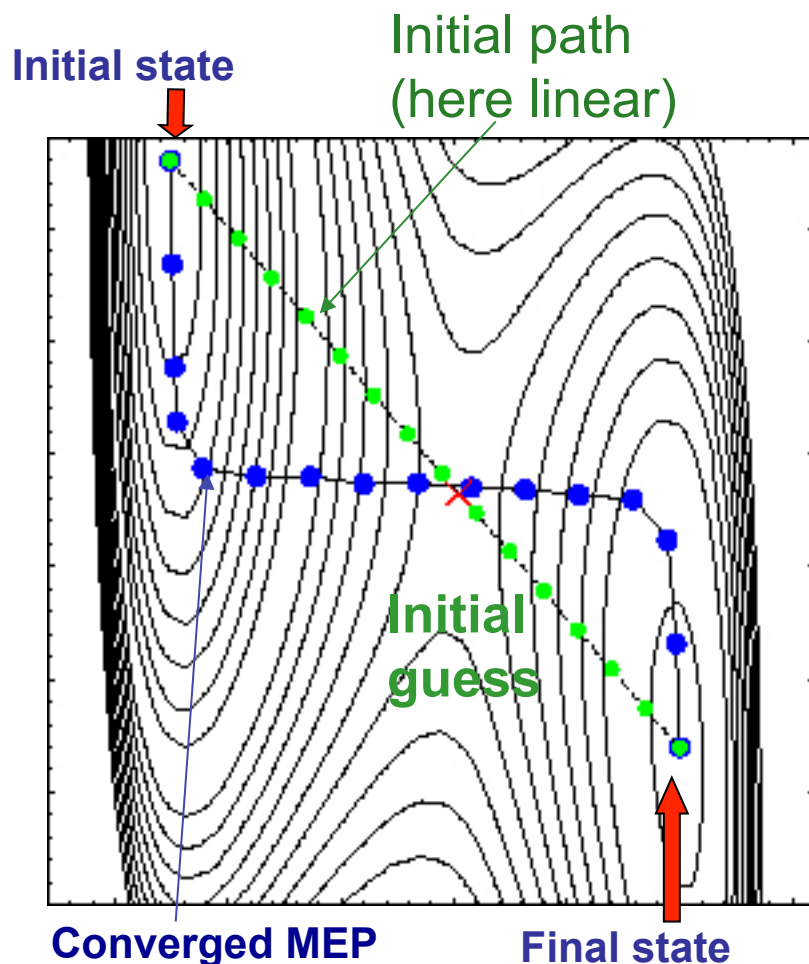
Given some (presumed) reaction coordinate (here linear interpolation between R and P, —), drag the system along that direction while relaxing all other degrees of freedom.

Can work, but fails when the true reaction coordinate differs significantly from the drag path.

Example: Even when the constraint hyperplane goes right through the SP, the relaxed position of the system is far from the saddle point!
Can lead to a discontinuous path and hysteresis (P to R gives different estimate than R to P).



Nudged Elastic Band (NEB) Method



Create several images (discretization pts.)

Effective force on each image

($\vec{R}$ here denotes atom coordinates, was $\vec{x}$ before):

$$\vec{F}_i^{nudged} = -\vec{\nabla}V(\vec{R}_i)|_{\perp} + (\vec{F}_i^s \cdot \hat{\tau}_{\parallel})\hat{\tau}_{\parallel}$$

tangent along current path

where the perpendicular force is

$$\vec{\nabla}V(\vec{R}_i)|_{\perp} = \vec{\nabla}V(\vec{R}_i) - (\vec{\nabla}V(\vec{R}_i) \cdot \hat{\tau}_{\parallel})\hat{\tau}_{\parallel}$$

and images are distributed with springs

$$\vec{F}_i^s \equiv k_{i+1}(\vec{R}_{i+1} - \vec{R}_i) - k_i(\vec{R}_i - \vec{R}_{i-1})$$

Estimate the tangent at each image using segment to adjacent image at higher energy.

Minimize all images simultaneously, in parallel. Typically 5 to 10 images.

(Mills, Jónsson & Schenter, *Surf. Sci.* 1995; Henkelman & Jónsson, *JCP.* 2000)

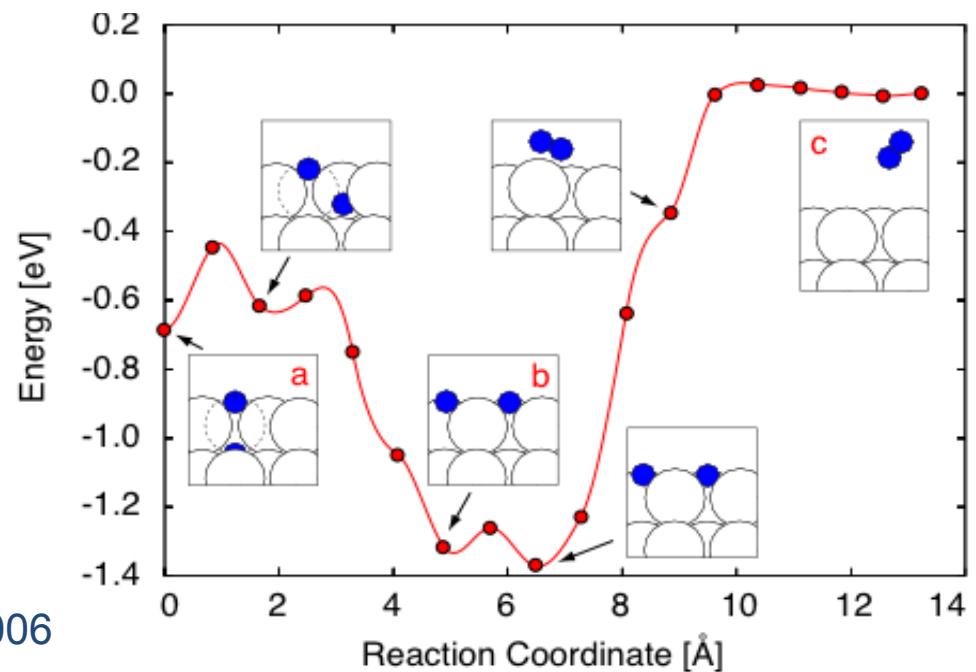
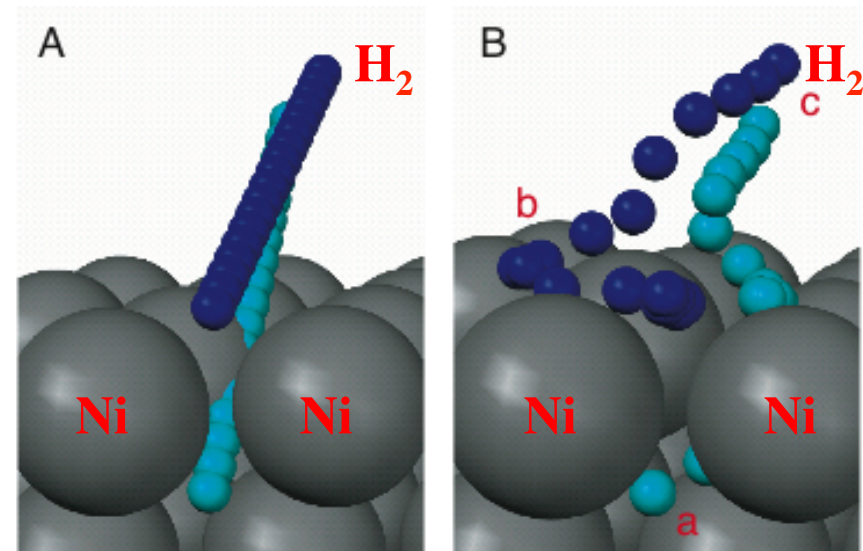
Use NEB with DFT calculations

Example 1:

Associative desorption of H_2 from Ni(111) starting with a subsurface and surface H-atom

Start up NEB assuming direct path for subsurface H-atom to attach to a surface H-atom

But, the MEP found shows that surface H-atom hops away. So, not H-H bond formation as subsurface H-atom moves up to the surface.



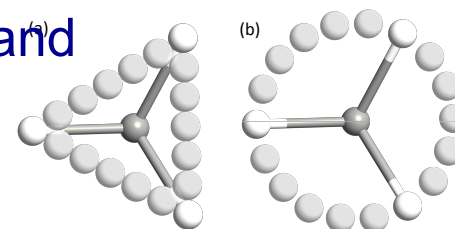
A better initial path for NEB calculations: IDPP

A recent development:

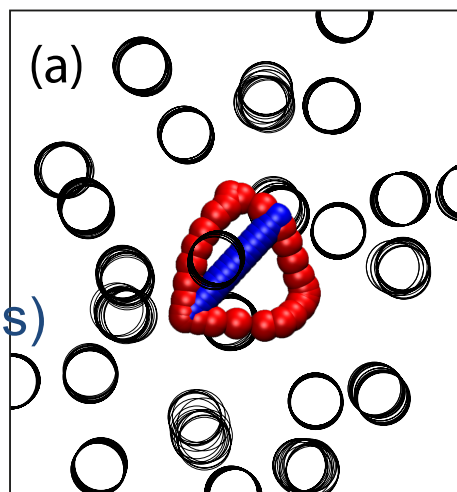
Interpolate pairwise distances in images between initial and final configurations, then fit coordinates of intermediate images to best satisfy the interpolated distances.

IDPP - image dependent pair potential.

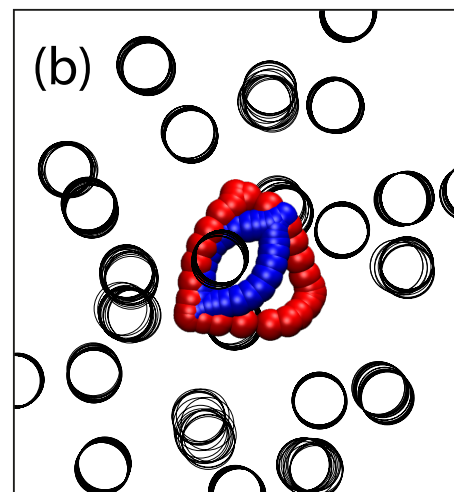
Can reduce SCF iterations since very close proximity of atoms is avoided, and saves atomic displacement iterations because the path is closer to MEP.



Exchange diffusion process in amorphous Silicon (DFT, 200 atoms)



Straight line interpolation
MEP

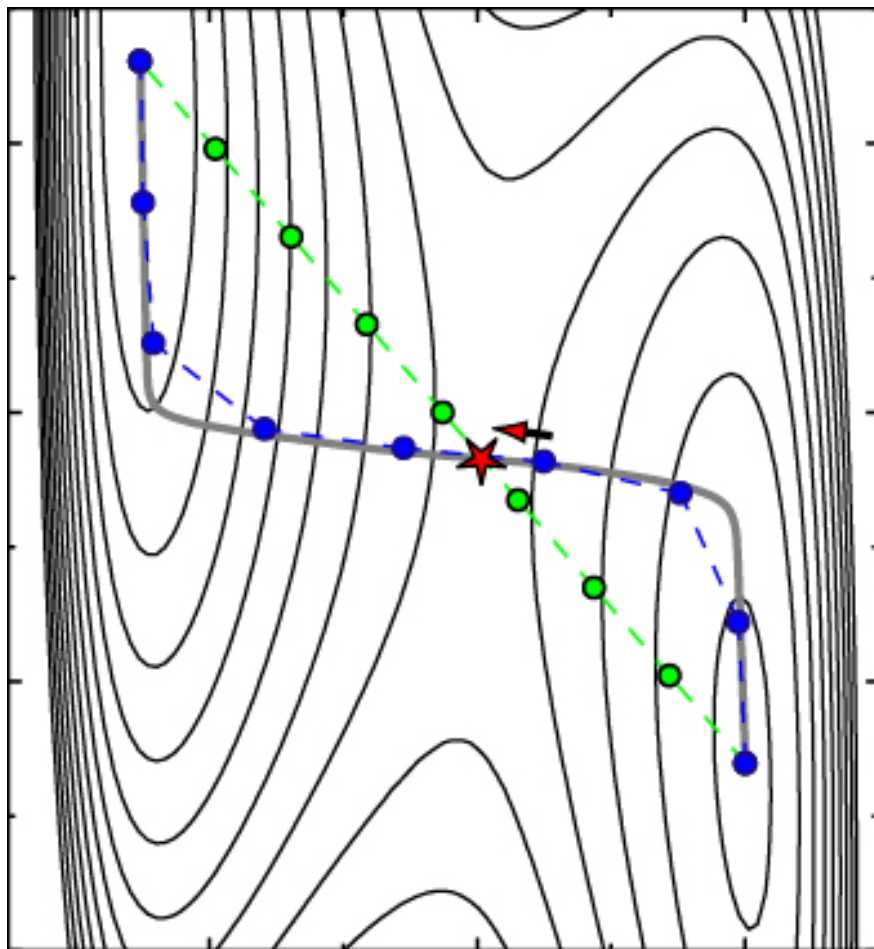


IDPP
MEP

Available in ASE (atomic simulation environment)

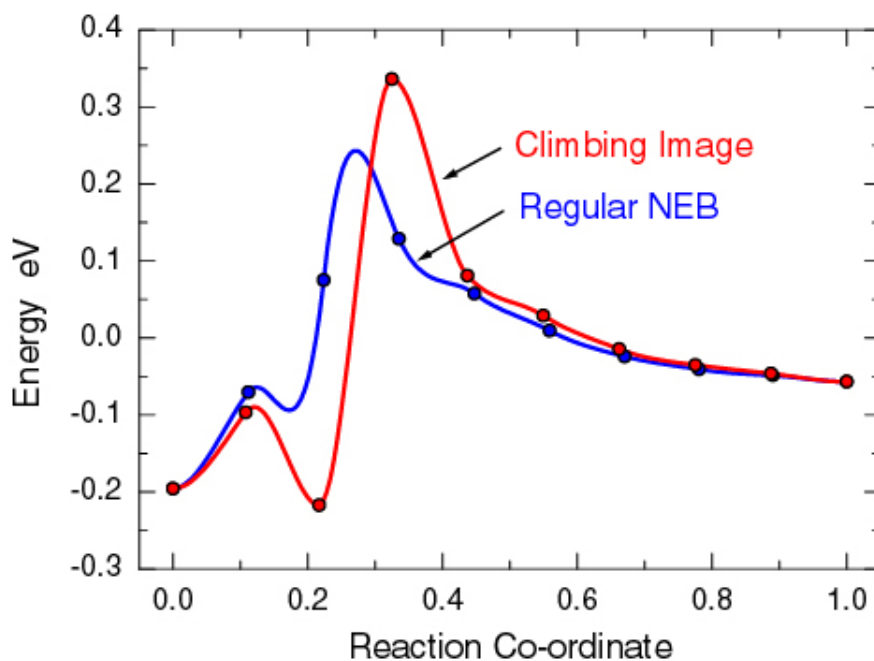
(S. Smidstrup, A. Pedersen, K. Stokbro and HJ, *JCP* 140, 214106 (2014))

Climbing image NEB (CI-NEB): Push the highest energy image up to converge on saddle point



The highest energy image is pushed up to the saddle point to give accurate estimate of the activation energy,

$$\mathbf{F}_{\text{CI}} = \nabla V(\mathbf{R}_i)|_{\perp} - 2\nabla V(\mathbf{R}_i)|_{\perp} \cdot \hat{\tau}_{||}$$



(G. Henkelman, et al., *J. Chem. Phys.* **113**, 9902 (2000))

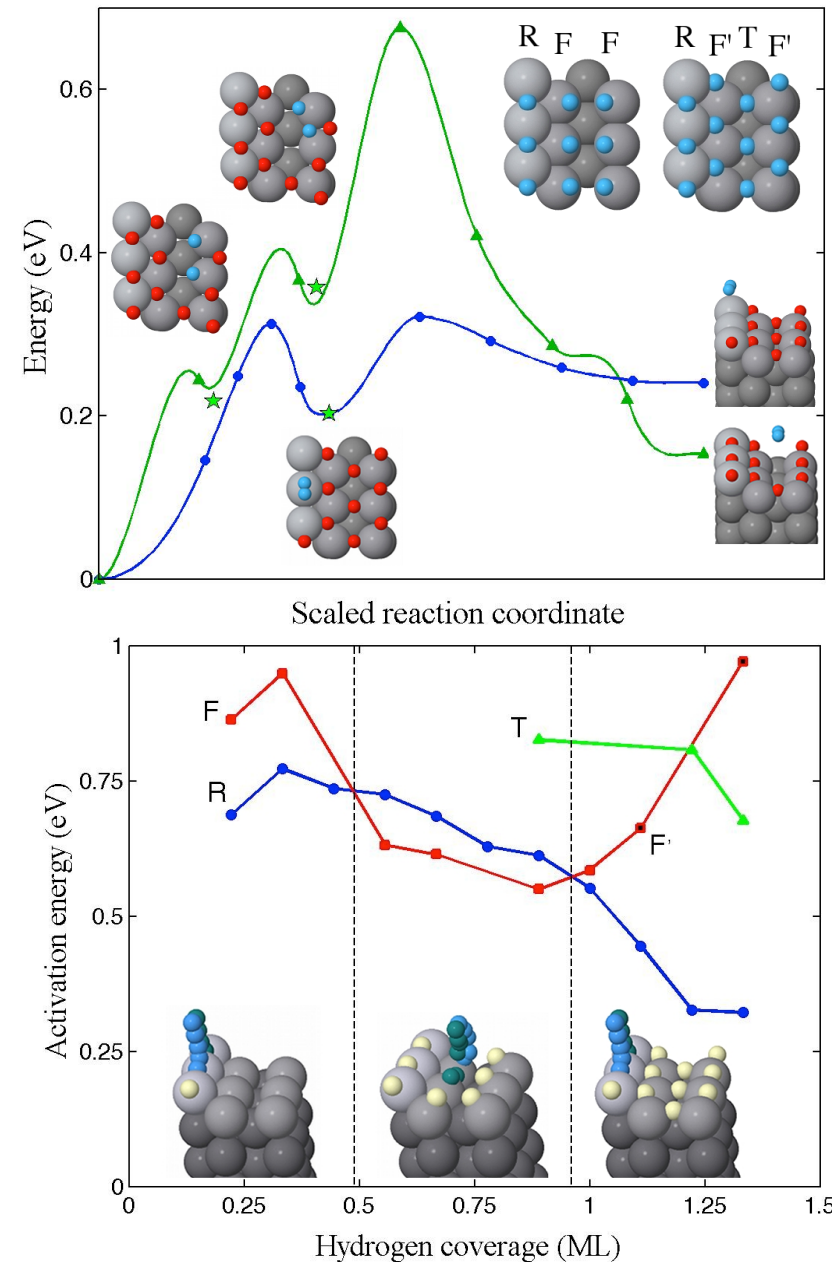
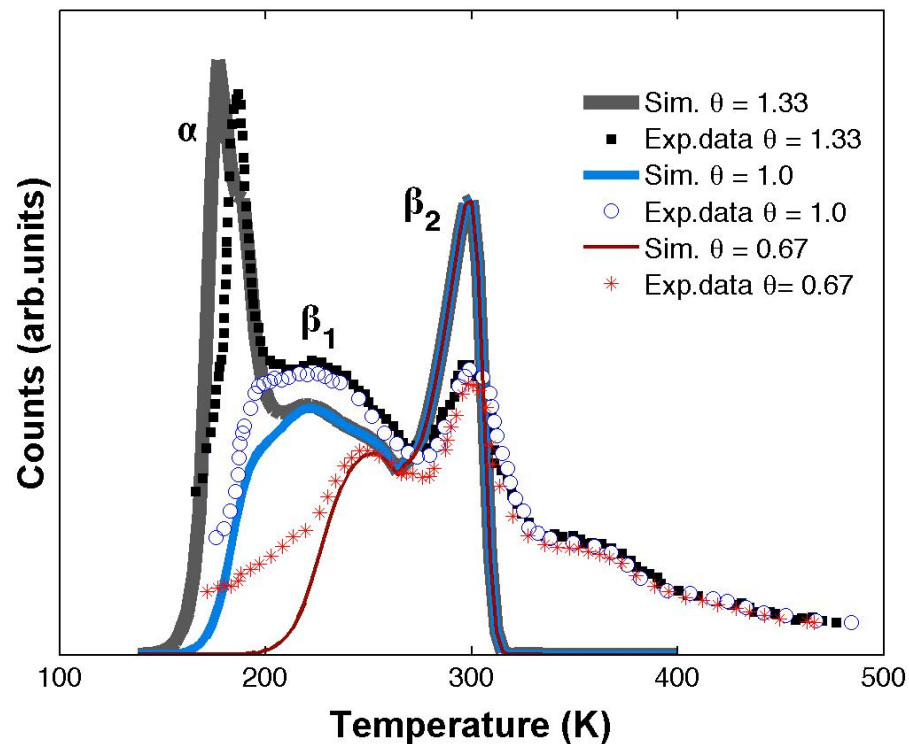
Use NEB with DFT calculations

Example 2:

Associative desorption of H_2 from $\text{Pt}(110)\text{-}2\times 1$ as a function of H-atom coverage.

Very strong coverage dependence!

(Guðmundsdóttir, Skúlason & HJ, *PRL* 2012)



Remarks on using the NEB Method

Cubic interpolation:

Important to use the force in the direction of the path as well as the energy at each image in the interpolation, gives a lot of info, in particular indications of intermediate minima (see appendix in *JCP* **113**, 9978 (2000)).

Divide and conquer:

If there is a hint of an intermediate minimum, then release the nearest Image and relax to converge to that minimum (if it exists). Then break up the path and calculate separately the two segments of the MEP.

Rotation and translation:

Six degrees of the system (at least) need to be frozen out. Otherwise, the system will do whatever it can to avoid the saddle point region.

In materials simulations with periodic boundary conditions, rotation is not a problem, but may need to remove translation of center of mass.

For clusters, remove also rotation using quaternions, see

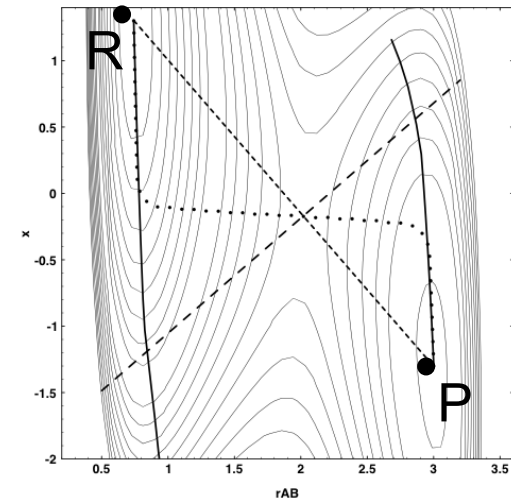
(Melander, Laasonen and Jónsson, *J. Chem. Theo. Comput.* 11, 1055 (2015)).

Methods for finding saddle points

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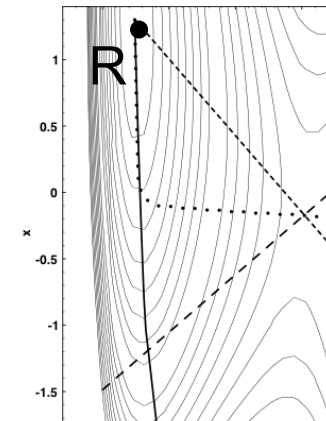
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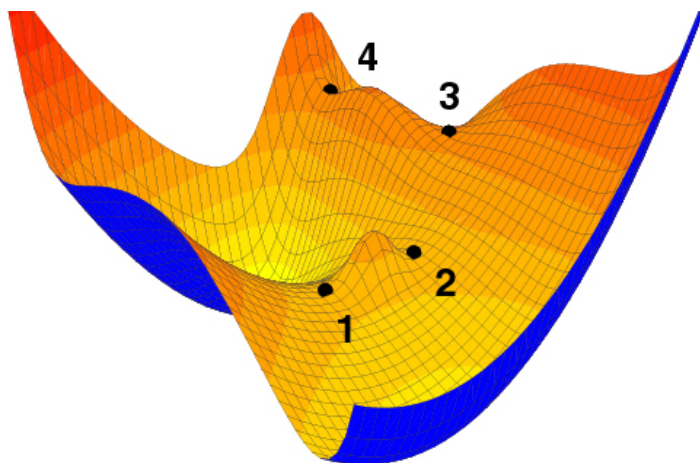
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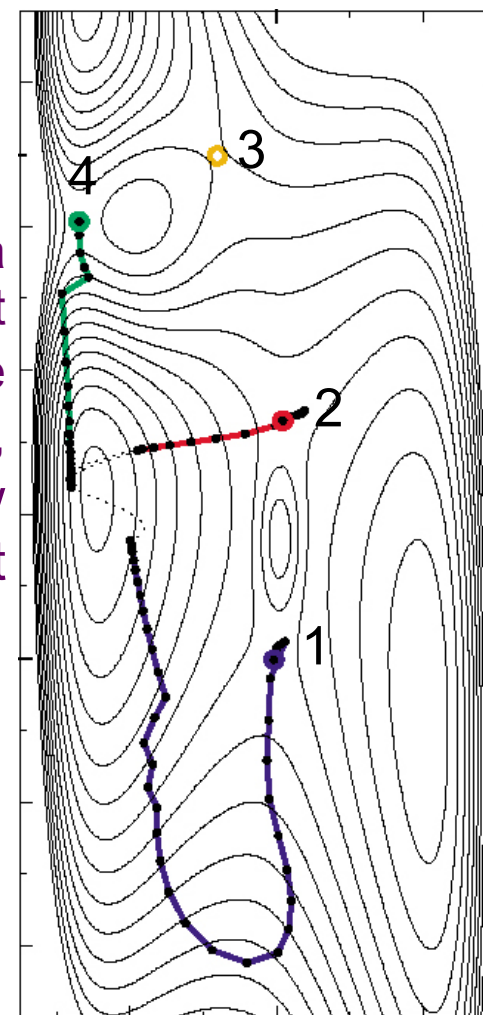


Minimum mode following method *(G. Henkelman and HJ, JCP 1999)*

Within HTST, need to find all the relevant saddle points on the energy rim surrounding the current state minimum.



Make a displacement from the minimum, then follow effective gradient



Transform the force by inverting the component along the minimum mode, $\hat{\mathbf{v}}_{i,min}$, of the Hessian (the matrix of second derivatives)

$$\mathbf{F}_{i,eff} = \mathbf{F}_i - 2(\mathbf{F}_i \cdot \hat{\mathbf{v}}_{i,min}) \hat{\mathbf{v}}_{i,min}$$

The direction along the minimum mode is found by minimizing the energy of a **dimer** (two replicas of the system, ) or by using the **Davidson** algorithm. No need to construct the Hessian matrix.

Use some minimization algorithm that only requires derivative of the objective function (not the objective function itself) and it will converge on a first order saddle point.

The force projection locally transforms a first order saddle point to a minimum.

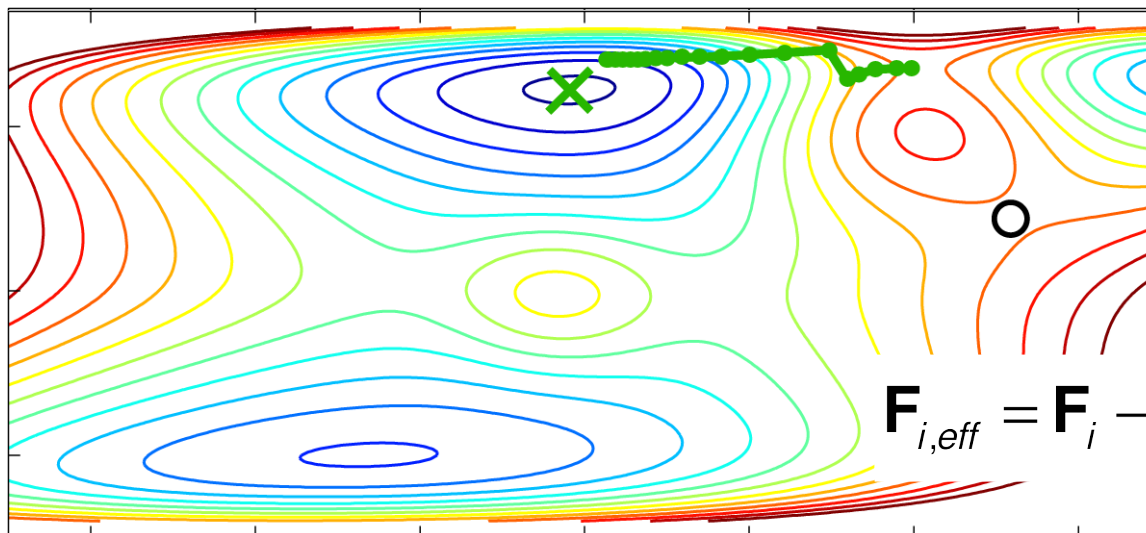
Use random initial displacement and then climb up the PES

Two phases:

1. When lowest eigenvalue of H is positive, move along minimum mode.
2. After lowest eigenvalue of H becomes negative, include also force perpendicular to the minimum mode.

Little or no bias from preconceived notion of the mechanism, perhaps displace under-coordinated atoms and their neighbors.

– Can discover unexpected mechanism and final state(s).



$$\mathbf{F}_{i,eff} = \mathbf{F}_i - 2(\mathbf{F}_i \cdot \hat{\mathbf{v}}_{i,min}) \hat{\mathbf{v}}_{i,min}$$

Beyond the harmonic approximation: Implementation of full TST

Evaluate

$$k^{TST} = \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{\ddagger}}{Z_R} \quad \text{where} \quad Z_S = \int_S e^{-V(\mathbf{x})/k_B T} d\mathbf{x}$$

for a hyperplanar dividing surface by evaluating free energy of the system confined to the hyperplane.

Free energy of hyperplanes

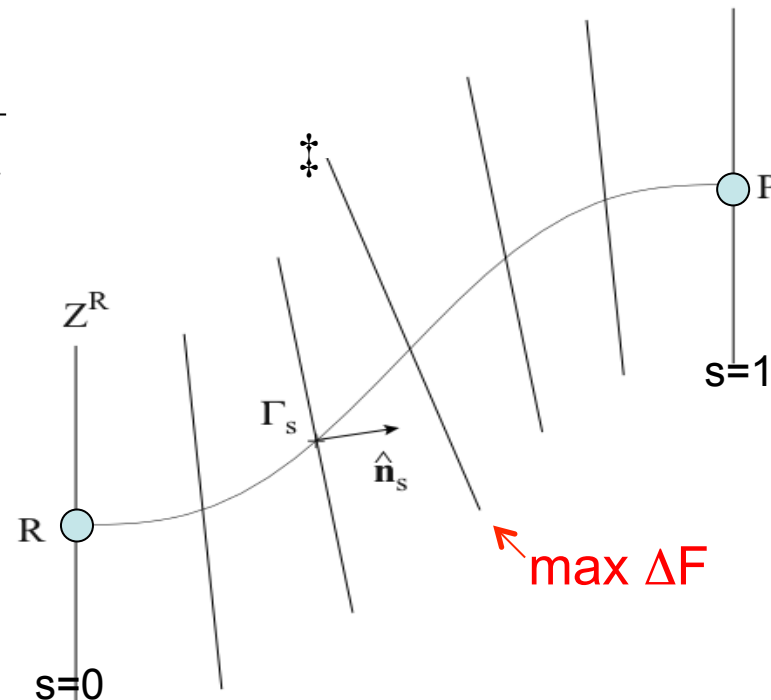
Rewrite the ratio of configuration integrals in terms of a **free energy difference, ΔF** , but then need to insert configuration integral for hyperplane in reactant region, Z_{H_R} , to get the units right

$$\begin{aligned} k^{\text{TST}} &= \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{\ddagger}}{Z_R} = \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{H_R}}{Z_R} \frac{Z_{\ddagger}}{Z_{H_R}} \\ &= \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{H_R}}{Z_R} e^{\frac{-\Delta F}{k_B T}} \end{aligned}$$

Given some path between the R and P minima, $\Gamma(s)$, construct a **progression of hyperplanes**.

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

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



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

Evaluate free energy change from reversible work

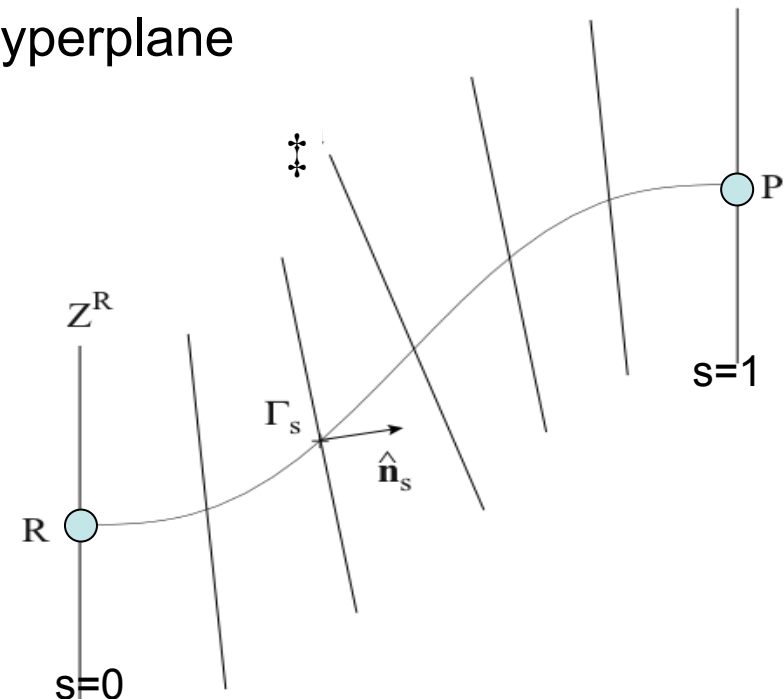
Sample the atomic coordinates and the forces within a hyperplane using Monte Carlo or Classical Dynamics (zero force comp. along the normal).

Obtain the average force $\mathbf{f}_n = \mathbf{f}(\mathbf{r}_s) \cdot \hat{\mathbf{n}}_s$ normal to the hyperplane and the 'torque' with respect to the point of intersection between the plane and the path, $\mathbf{R}_t = (\mathbf{r}_s - \mathbf{\Gamma}_s) \cdot \frac{d\hat{\mathbf{n}}_s}{d\theta}$

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

$$\Delta F = - \int_0^s \langle \mathbf{f}_n (1 - \mathbf{R}_t \frac{d\theta}{ds}) \rangle_{s'} ds'$$

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!



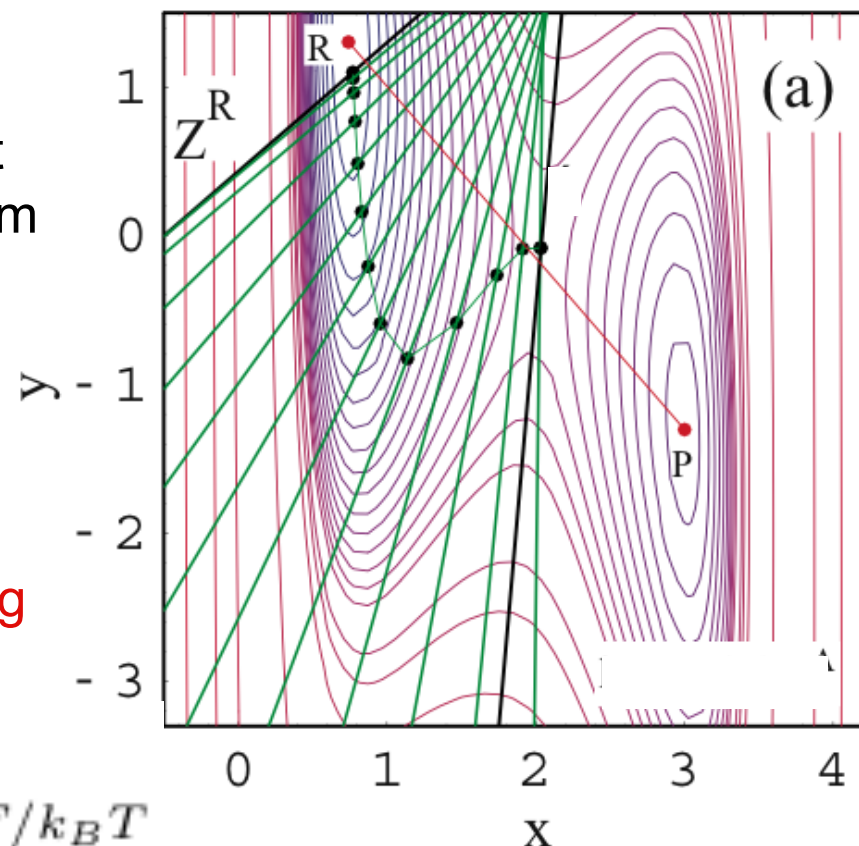
(Mills, Jónsson, Schenter: *Surf. Sci.* **324**, 305 (1995))

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

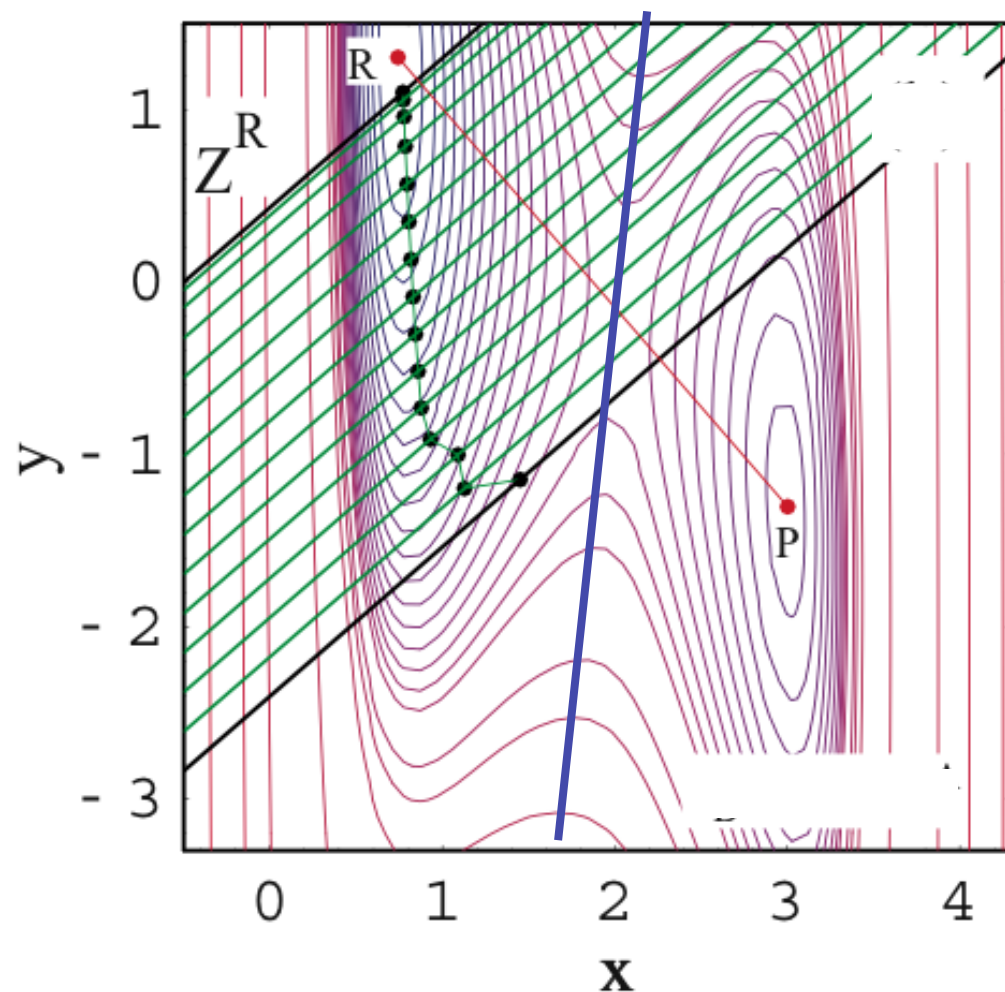


$$k^{RWTST} = \frac{\langle v_{\perp} \rangle}{2} \frac{Q^{Z^R}}{Q^R} e^{-\Delta F/k_B T}$$

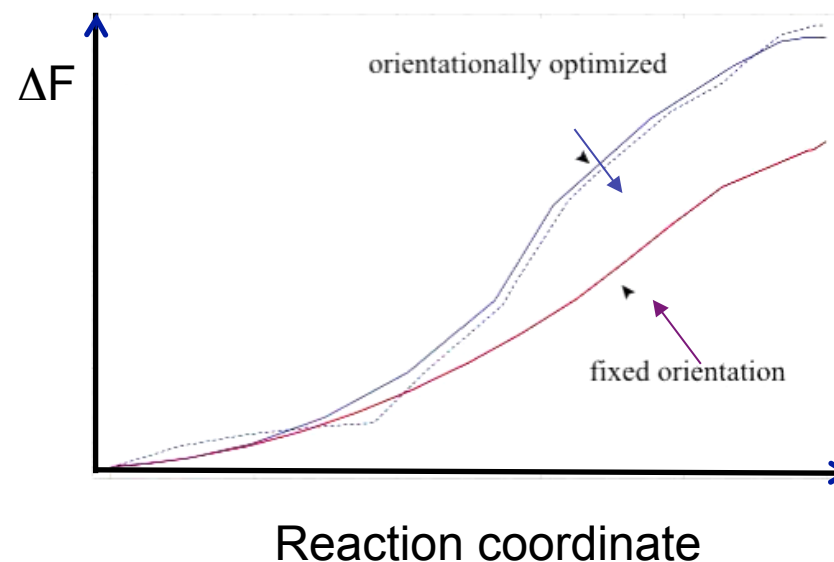
$$\Delta F = - \int_0^s \langle \mathbf{f}_n \left(\mathbf{1} - \mathbf{R}_t \frac{d\theta}{ds} \right) \rangle_{s'} ds'$$

(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 dof.



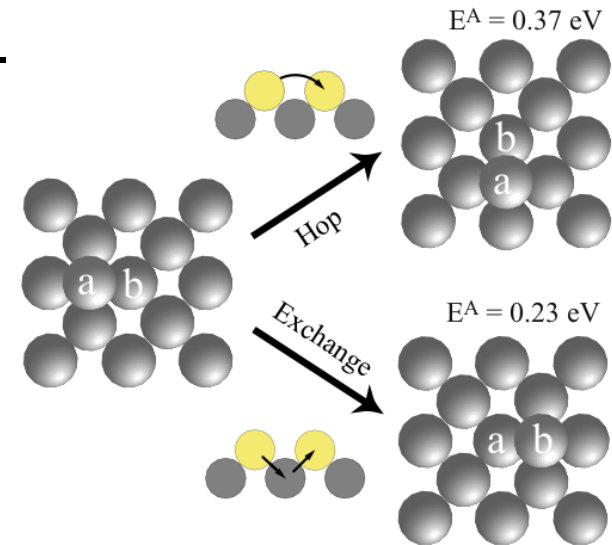
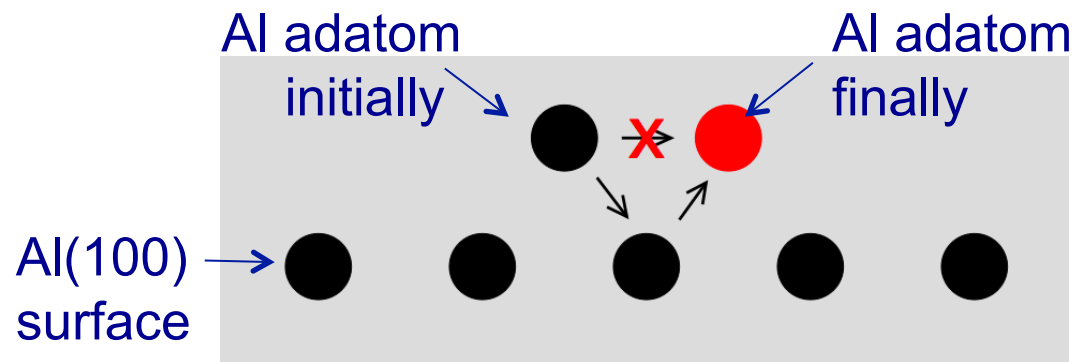
In a $3N$ -dimensional system, the optimization of the location of a dividing surface is a **one**-dimensional optimization, the optimization of orientation represents **$3N-1$** degrees of freedom – it is essential to optimize orientation! *Orientational optimization can reveal the transition mechanism.*

Important to *find* but not just *assume* the mechanism of transitions

An example of a surprise mechanism:

Al adatom diffusion on Al(100)

(see: Feibelman, *Phys. Rev. Lett.* **65**, 729 (1990)).



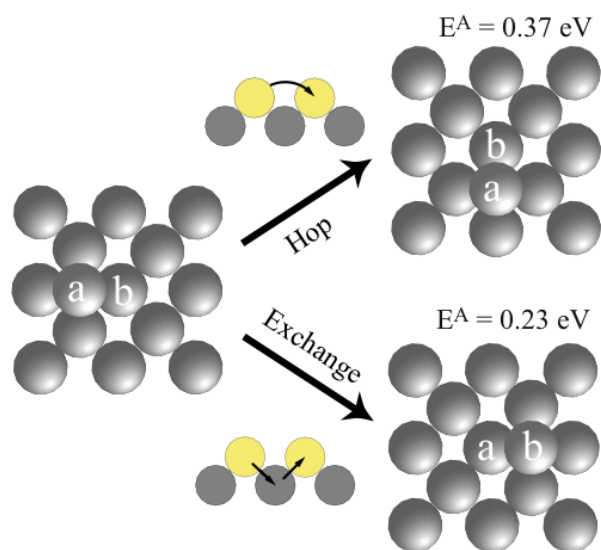
Another example of a surprise (explains re-entrant layer-by-layer growth):

Pt adatom descent from atop islands on Pt(111) near but not at kinks.

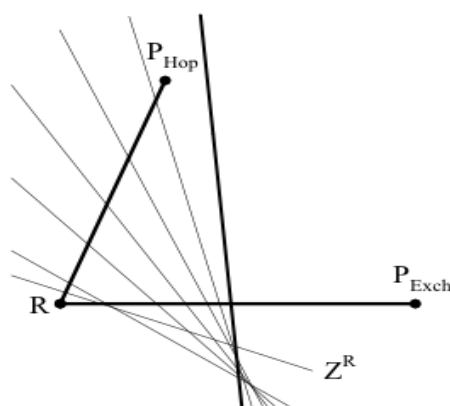
(see: Jónsson, *Annual Review of Physical Chemistry* **51**, 623 (2000))

Should not impose our preconceived notion of the mechanism of a transition,
but rather **learn about the mechanism from the calculation!**

Adatom diffusion on Al(100)

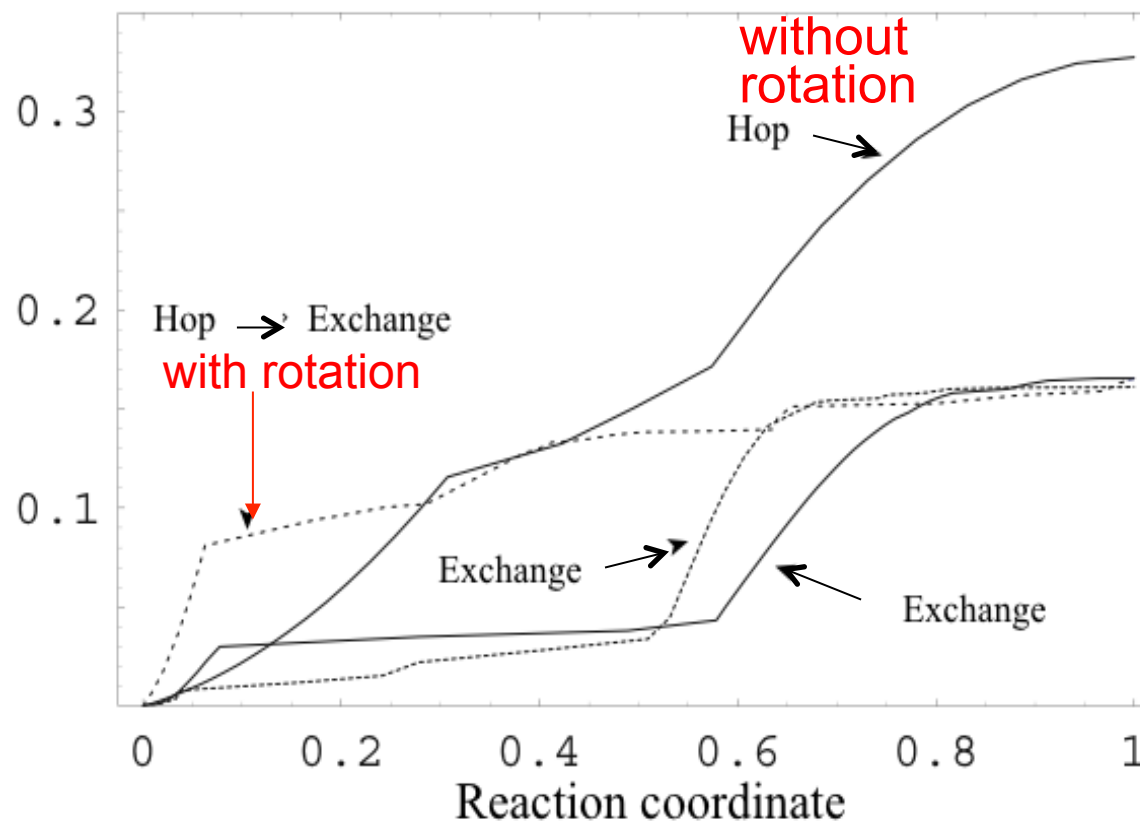


By rotational optimization of the hyperplane, the optimal mechanism can be found, even if the calculation is started from the wrong assumption.



Projection onto 2-D

$\Delta F(\text{eV})$



(G. Jóhannesson & HJ, JCP 2001)

Not good practice to simply pick some reaction coordinate and calculate a free energy barrier

If the goal is to learn from the simulation what the mechanism of The transition is, in addition to the rate

1. In general not known what the final state is
(example: final state is different for hop and exchange)
2. Dragging the system *slowly* along an assumed reaction coordinate while thermally averaging over other degrees of freedom in the system will *underestimate* the free energy barrier
since the system will slip along a coordinate orthogonal to the drag coordinate from the initial to final state, thus losing a contribution to the free energy estimate.
3. Dragging the system *fast* along an assumed reaction coordinate while thermally averaging over other degrees of freedom in the system will *overestimate* the free energy barrier
since the system will be pushed too far up in free energy before transferring from the initial state to the final state.

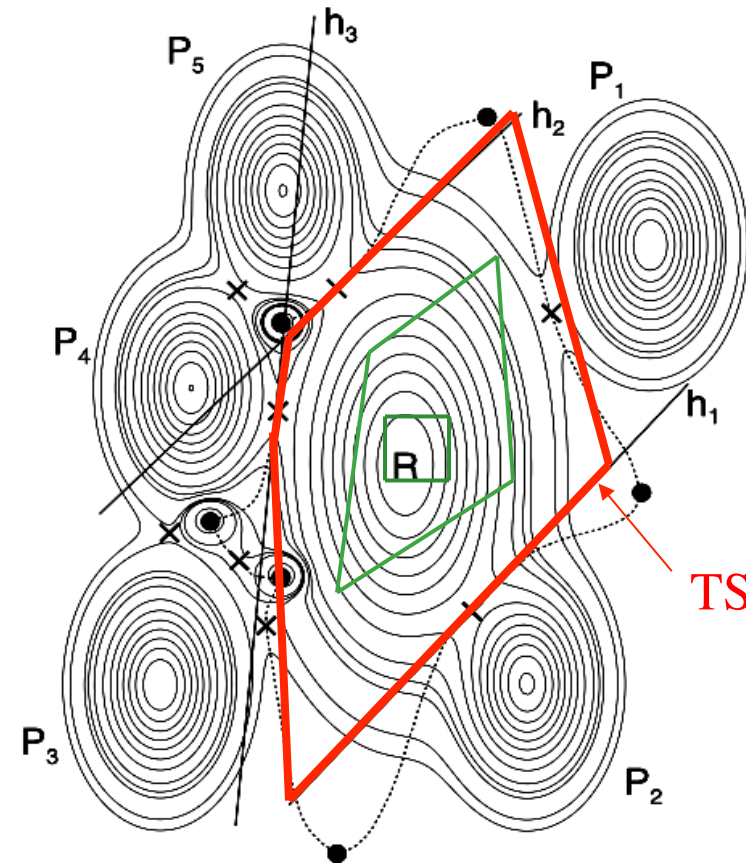
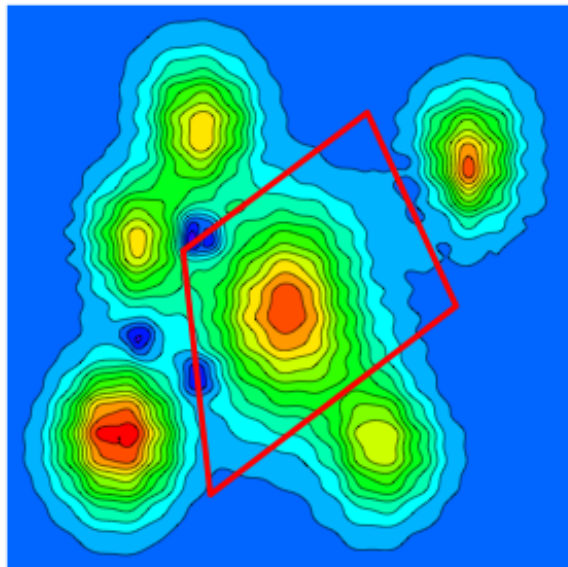
But, can be used to make nice graphics of an assumed reaction mechanism ...

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. Commun.* 2005

Ongoing quest ...

Some common **misconceptions** about TST

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.

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.