An introduction to Transition State Theory

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If this rough document comes into your hands you should know that it was developed by the authors mentioned on the front page, and was presented at a winter school at Han-sur-Lesse, Belgium in December 2006. However, the material is based on a large number of publications, all cited in the text in the relevant places. The document will most likely be in constant development over the next few years. If your interested in the newest version contact Roar Olsen at r.a.olsen@chem.leidenuniv.nl. At the moment you're free to use it as an introductory text to transition state theory. If you plan to use it for teaching purposes, please ask for permission first. Any feedback, whether used individually or in a context of a course, will be greatly appreciated.

What is Transition State Theory (TST)?

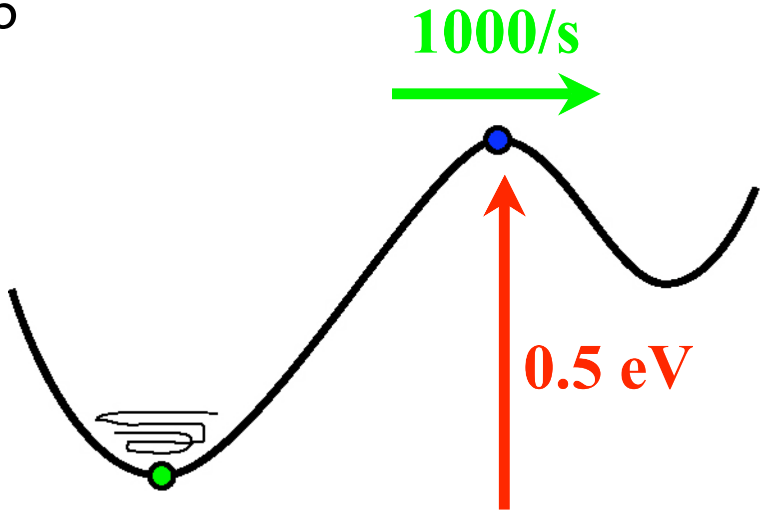
- TST started its life as “Absolute Rate Theory”, has also been known as “Activated Complex Theory”
- Due to:
  Pelzer & Wigner, *Z. Phys. Chem.* **B15**, 445 (1932)
  Eyring, *J. Chem. Phys.* **3**, 105 (1935)
  Evans & Polyani, *Trans. Faraday Soc.* **31**, 857 (1935)
- A method to calculate the *thermal* rate of change ($\mathbf{k}^{TST}$) in a system

Why TST?

Want to be able to study the time evolution of a system undergoing atomic rearrangements and bond breaking (diffusion, catalysis, growth, pattern formation, etc) using calculations based on, for example, density functional theory (DFT).

Time scale problem:

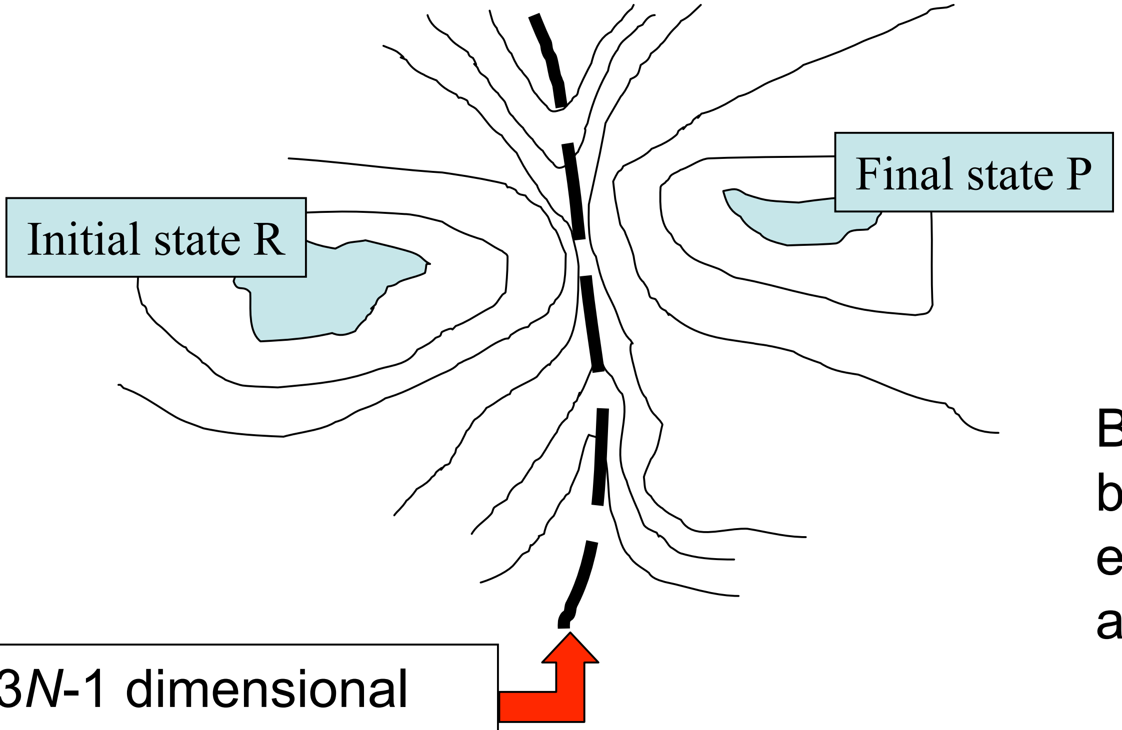
- Most interesting transitions are rare events (ie, much slower than vibrations). Typically there is clear separation of time scales!
- A transition with an energy barrier of 0.5 eV and a typical prefactor occurs 1000 times per second at room temperature. A direct classical dynamics simulation would require 10^{12} force evaluations and thousands of years of CPU time to cover the average time period between such events.



Cannot simply heat the system, the mechanism can change!

Main ideas of TST

Identify a 3*N*-1 dimensional dividing surface, a Transition State (TS), that represents a **bottle neck** for going from an initial to a final state:



3*N*-1 dimensional dividing surface, TS

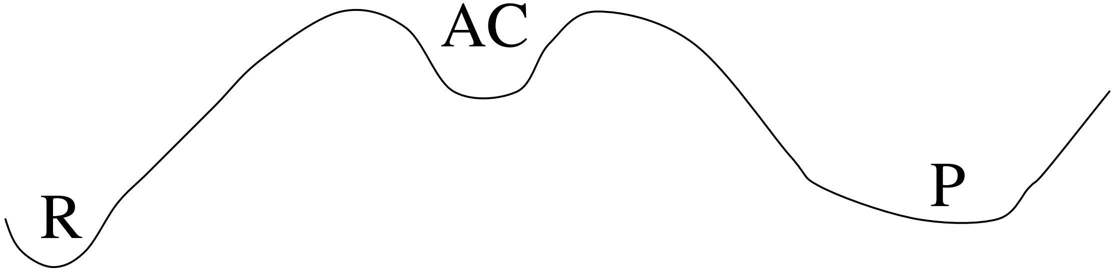
Bottle neck can be due to an energy barrier and/or entropy

k^{TST} = (probability of being in TS) • (flux out of TS)

Mahan, *J. Chem. Education* **51**, 709 (1974):

> "In view of [its] success, it is unfortunate that the theory [TST] does not enjoy a better understanding and confidence among non-specialists. Some of this difficulty can be traced to the rather unconvincing derivations of the [TST] expression for the rate constant which are found in many physical chemistry texts and monographs on chemical kinetics."

Not much seems to have changed since then, despite the article by Mahan in 1974. See, for example Atkins, "Physical Chemistry", 6th and 7th edition.



Why this lecture series?

- Lack of good introductory texts on TST (if you know of one or find one, please let me know!)
- This makes it difficult for a beginner to access the primary TST research literature
- My goal is to provide a bridge to the primary TST literature starting from a point of no prior knowledge of TST

In about 6 hours I will cover:

2-3 hours

- why TST? (this I’ve just told you)
- ingredients (Schrödinger equation, Born-Oppenheimer approximation, classical/quantum, statistical mechanics)
- a simple derivation of TST, and a simple example
- harmonic TST
- variational TST, corrections due to recrossing, free energy of a dividing surface, systematic optimization of a dividing surface, thermodynamic integration, reversible work

2-3 hours

- path integrals, propagator, quantum statistical mechanics
- quantum TST (QTST), harmonic, centroid, full

1 hour

- methods for Saddle Point (SP) and reaction path searching

OK! Let's get started!!!

The ingredients

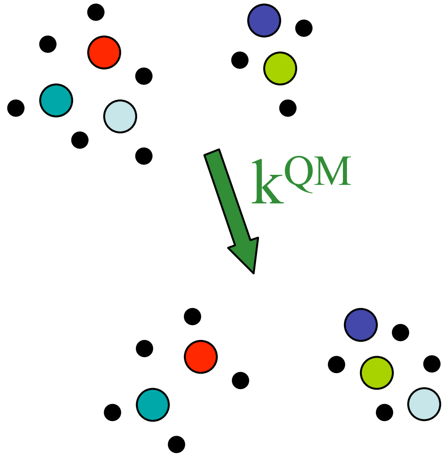
The exact rate of change from Quantum Mechanics (QM)?

Simple! Just solve the time-dependent Schrödinger equation, right?

$$i\hbar \frac{\partial \Psi(\mathbf{R}_n,\mathbf{R}_e,t)}{\partial t} = \hat{H}_{\mathrm{tot}} \Psi(\mathbf{R}_n,\mathbf{R}_e,t)$$

$$\hat{H}_{\mathrm{tot}} = \hat{K}_n + \hat{K}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne}$$

In principle exact (under the assumption that the time-dependent Schrödinger equation does indeed govern the evolution of the system). However, almost always computationally intractable!



$$\Psi(\mathbf{R}_n,\mathbf{R}_e,t) = \sum_{\mu} \chi_{\mu}(\mathbf{R}_e;\mathbf{R}_n)\psi_{\mu}(\mathbf{R}_n,t)$$

$$i\hbar \frac{\partial \psi_{\nu}}{\partial t} = \left[\hat{K}_n + \hat{V}_{nn}\right]\psi_{\nu} + \sum_{\mu} \left\langle \chi_{\nu} \middle| \hat{K}_e + \hat{V}_{ee} + \hat{V}_{ne} \middle| \chi_{\mu} \right\rangle \psi_{\mu} + \sum_{\mu} C_{\nu\mu}\psi_{\mu}$$

$$C_{\nu\mu} = \sum_i \frac{1}{m_i}\left[\left\langle \chi_{\nu} \middle| \nabla_i \middle| \chi_{\mu} \right\rangle \nabla_i + \frac{1}{2}\left\langle \chi_{\nu} \middle| \nabla_i^2 \middle| \chi_{\mu} \right\rangle\right]$$

Now make the Born-Oppenheimer approximation

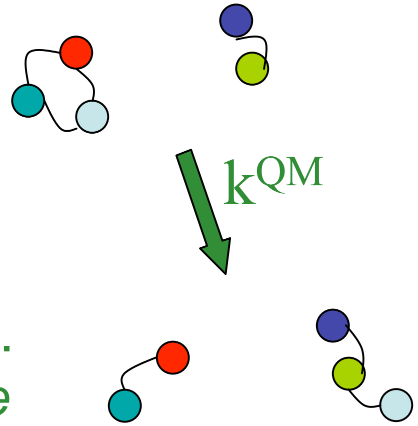
$$C_{\nu\mu} = 0$$

and assume the electronic problem is solved by

$$\hat{K}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne}\left|\chi_\nu(\mathbf{R}_e;\mathbf{R}_n)\right\rangle = \varepsilon_\nu(\mathbf{R}_n)\left|\chi_\nu(\mathbf{R}_e;\mathbf{R}_n)\right\rangle$$

then

$$\boxed{i\hbar\frac{\partial\psi_\nu(\mathbf{R}_n,t)}{\partial t} = \left[\hat{K}_n + \varepsilon_\nu(\mathbf{R}_n)\right]\psi_\nu(\mathbf{R}_n,t)}$$



Electronic and nuclear degrees of freedom decoupled.

The electrons are “gone”. The nuclei move on a *single* Potential Energy Surface (PES), $\varepsilon_\nu(\mathbf{R}_n)$.

After this separation life becomes “easier”. The electronic problem can be solved at any level we choose - *ab initio*, DFT, semi-empirical model potentials, etc. The nuclear dynamics doesn’t really care how the PES has been obtained (but the resulting rate of change of course depends on how good a job was done on the PES). However, given a PES, the corresponding (wrong) rate of change can be obtained exactly by solving the time-dependent nuclear Schrödinger equation.

You have just seen that one *can* go beyond Born-Oppenheimer in a QM description of the nuclear dynamics. However, in TST we *never* attempt to do this.

The first (of the four) assumptions of TST is that the nuclear dynamics takes place on a *single* PES!

Exercise:

TST can not treat systems where there is a change in the electronic state during the reaction.

Why is this?

Difficult to answer at the moment, since we've not fully outlined TST. But you should keep this question in mind in the following and try to answer it as often as you can! (Assuming you don't get it right the first time…)

At which level should the nuclear dynamics be treated?

$$m_i \frac{d^2\mathbf{R}_i(t)}{dt^2} = -\nabla_i \varepsilon_\nu(\mathbf{R}_i)$$

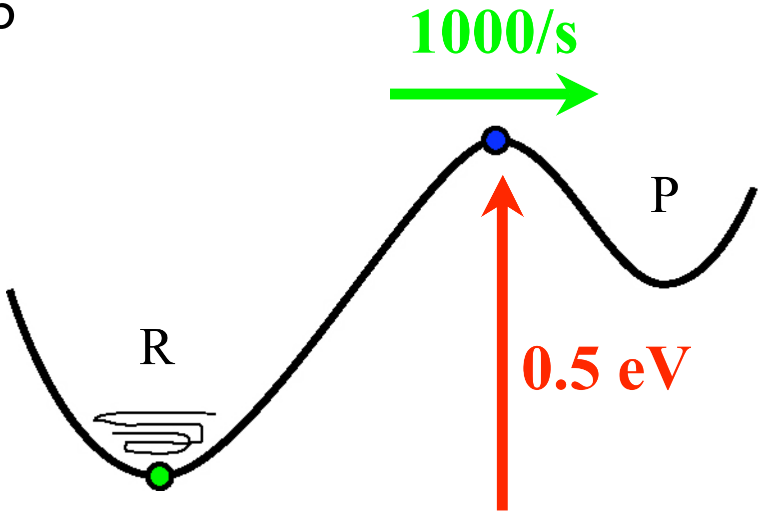
The traditional TST developed in the 1930s. Thus, the second (of the four) assumptions in TST is that classical mechanics can be used to treat the nuclear dynamics.

$$i\hbar \frac{\partial \psi_\nu(\mathbf{R}_n,t)}{\partial t} = \left[\hat{K}_n + \varepsilon_\nu(\mathbf{R}_n)\right]\psi_\nu(\mathbf{R}_n,t)$$

If the dynamics is treated at this level we are doing QTST. This is a more recent development.

Now is a good moment to return to the time scale problem mentioned in the introduction:

- Most interesting transitions are rare events (ie, much slower than vibrations).
- A transition with an energy barrier of 0.5 eV and a typical prefactor occurs 1000 times per second at room temperature. A direct classical dynamics simulation would require 10^{12} force evaluations and thousands of years of CPU time to cover the average time period between such events. We cannot simply heat the system, the mechanism can change!



- However, we are saved by the fact that there typically is a clear separation of time scales! For each attempt to reach the TS, a large number of collision will have happened in the reactant (sub)system. This suggests that we can “forget” about explicit dynamics, turn to statistical mechanics and do ensemble averaging!

We need to decide which ensemble to use:

- Microcanonical ensemble, $\Omega(N,V,E)$:
  Useless for our purposes! The total energy is constant, and this implies that we can only average over internal states with the same total energy. This is actually what is done when doing classical trajectory calculations. And we have very good reasons for not wanting to do this!
- Canonical ensemble, $Q(N,V,T)$:
  This is the one we'll use. We can then use "the Boltzmann" to calculate the probability of finding our system with a given total energy *E* through e^{-E/k_BT}. Of course, for this to be valid we need to assume thermal equilibrium!

  > The third (of the four) assumptions in TST is that there (formally) must be thermal equilibrium in the reactant valley.

- Grand canonical, $\Xi(V,T,\mu)$ and isothermal-isobaric, $\Delta(N,T,p)$:
  Exercise: Can these two ensembles be use to build TST? If yes, why, and what would happen to the calculated rate? Would one of the ensembles give a more accurate result? If no, why not?

A simple derivation of TST

Total energy of system:

$$E(\mathbf{x},\mathbf{v}) = E_{kin} + E_{pot} = \sum_i \frac{1}{2} m_i v_i^2 + V(\mathbf{x}) \qquad \left[V(\mathbf{x}) \equiv \varepsilon_\nu(\mathbf{R}_n)\right]$$

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:

$$P(\mathbf{x},\mathbf{v})\,d\mathbf{x}\,d\mathbf{v} = A\,e^{-E(\mathbf{x},\mathbf{v})/k_BT}\,d\mathbf{x}\,d\mathbf{v}$$ (A is some normalization)

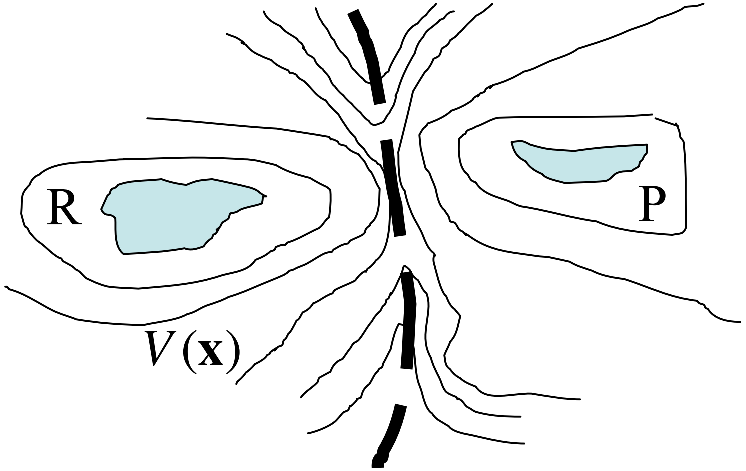
This factorizes into:

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

Given that the system is initially somewhere in R:

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

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

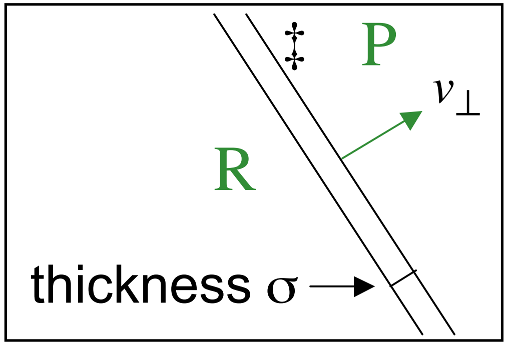


The probability of being in some subspace, S, of R is:

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

configuration integrals

A hyperplane ax+b=0 is a particularly simple (but not necessarily good) choice for the dividing surface



k$^{\mathrm{TST}}$ = (probability of being in TS) • (flux out of TS)

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

$$\langle v_\perp \rangle = \frac{\int_0^\infty v_\perp e^{-\frac{1}{2}\mu_\perp v_\perp^2/k_BT}\,dv_\perp \int_{-\infty}^\infty e^{-\sum_{i'}\frac{1}{2}\mu_i v_i^2/k_BT}\,d\mathbf{v}'}{\int_{-\infty}^\infty e^{-\frac{1}{2}\mu_\perp v_\perp^2/k_BT}\,dv_\perp \int_{-\infty}^\infty e^{-\sum_{i'}\frac{1}{2}\mu_i v_i^2/k_BT}\,d\mathbf{v}'} = \frac{\int_0^\infty v_\perp e^{-\frac{1}{2}\mu_\perp v_\perp^2/k_BT}\,dv_\perp}{\int_{-\infty}^\infty e^{-\frac{1}{2}\mu_\perp v_\perp^2/k_BT}\,dv_\perp} = \sqrt{\frac{k_BT}{2\pi\mu_\perp}}$$

3*N*-1 dimensional!

So, $\boxed{\mathrm{k}^{\mathrm{TST}} = \sqrt{\frac{k_BT}{2\pi\mu_\perp}}\,\frac{Z_\ddagger}{Z_R}}$

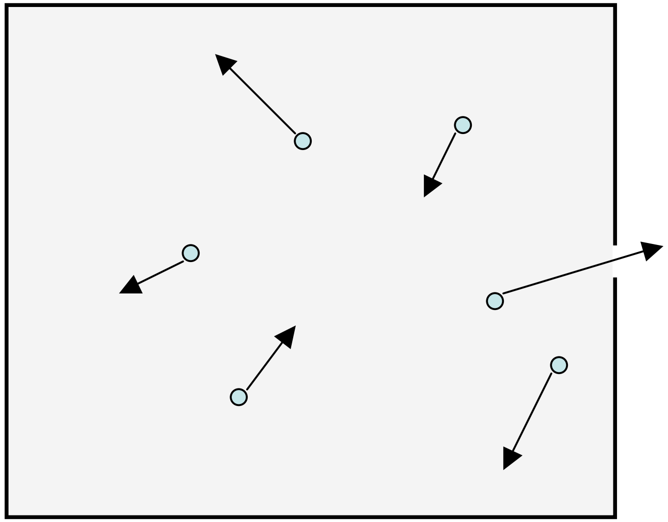
1 dimensional!

That was painless, huh?

A simple example

Effusion of gasatoms through a small hole.

No energy barrier, just entropic bottle neck.



Box has volume, V; hole has area A

So, $Z_R = V, Z_{\ddagger} = A$

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

ideal gas: $PV = N_m k_B T$

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

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

Same result as kinetic theory, TST is exact in this case!

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” (Pechukas)

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

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

then the TST rate constant can be written as

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

here Θ[] is the Heavyside function and

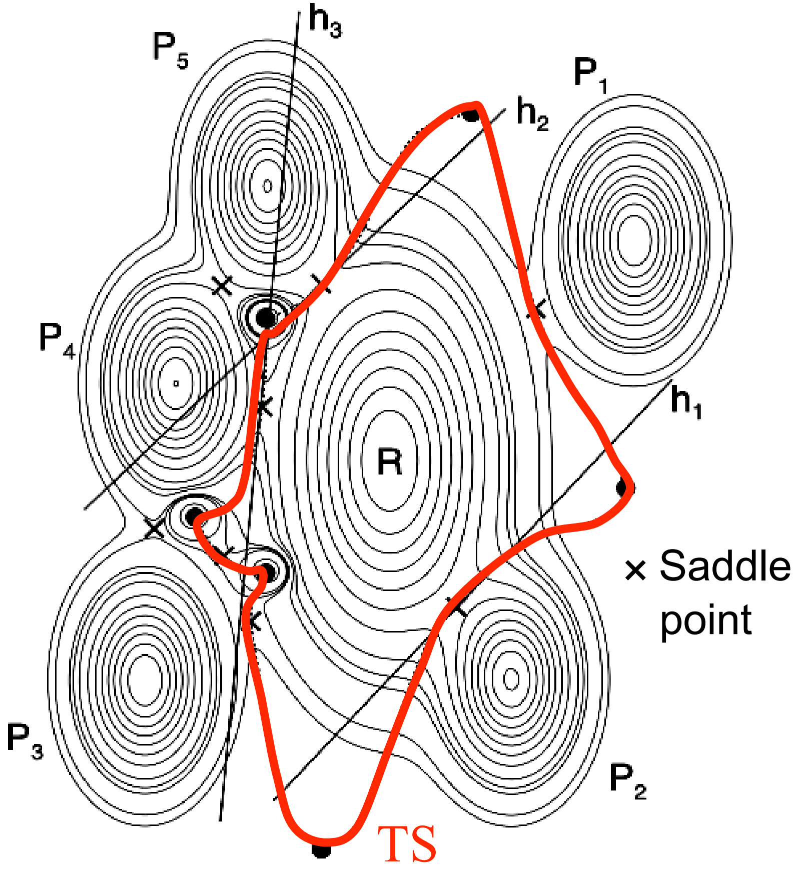
$$Q_R = \int d\mathbf{p}\int d\mathbf{q}\, e^{-H(\mathbf{p},\mathbf{q})/k_BT}$$

A short summary and some comments

The TST assumptions:

1. Born-Oppenheimer
2. Classical dynamics of nuclei
3. Boltzmann distribution in R, OK if slow enough, $k_B T < E_a/5$
4. No recrossings of TS, most serious

Need to create a dividing surface that encloses the initial state



Note:

- TST gives the lifetime, $t=1/k^{TST}$, of a given initial state - no knowledge of final state(s).

  Need to run (short time) dynamics starting from TS to find the final state(s).

- Such trajectories can be used to take recrossings into account - dynamical corrections:

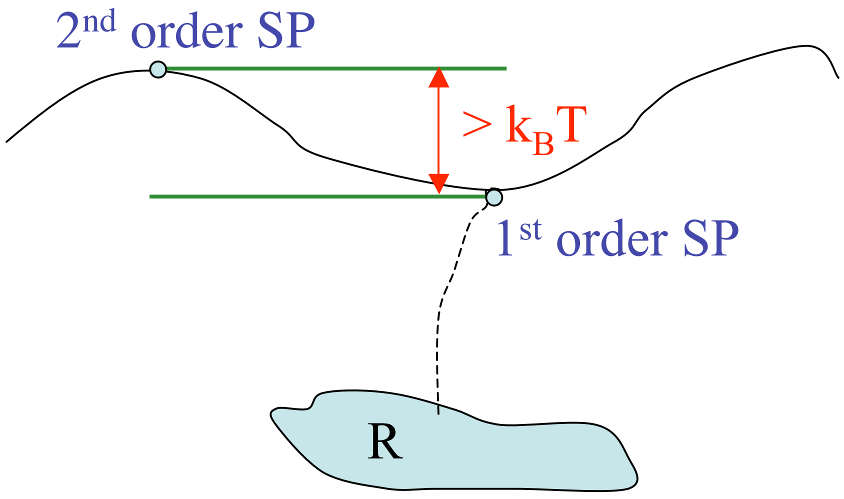
  $k^{exact} = \kappa\, k^{TST}$

  More on this later.

Harmonic TST
(HTST)

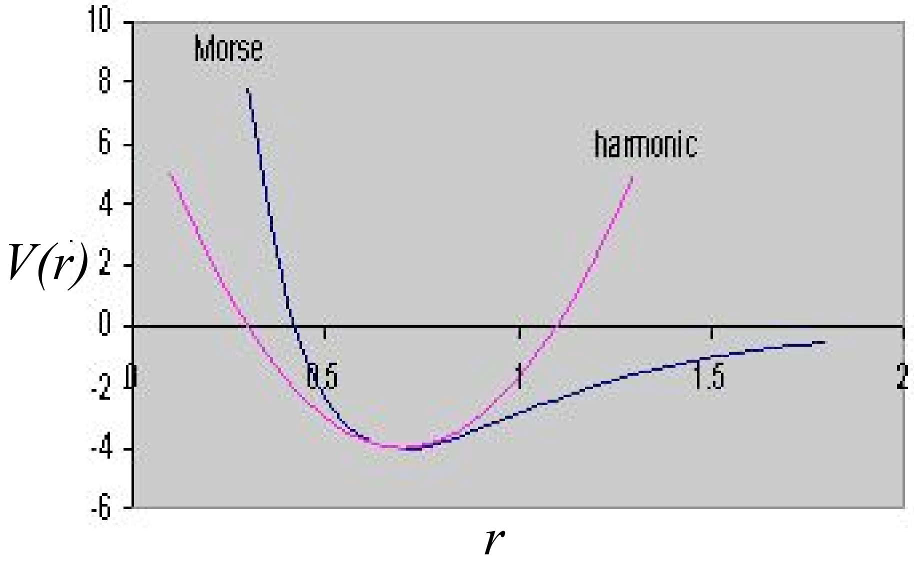
Good approximation for many solids at low temperature

When energy of second order saddle points is much higher than $k_B T$ over the energy of first order saddle points and 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.



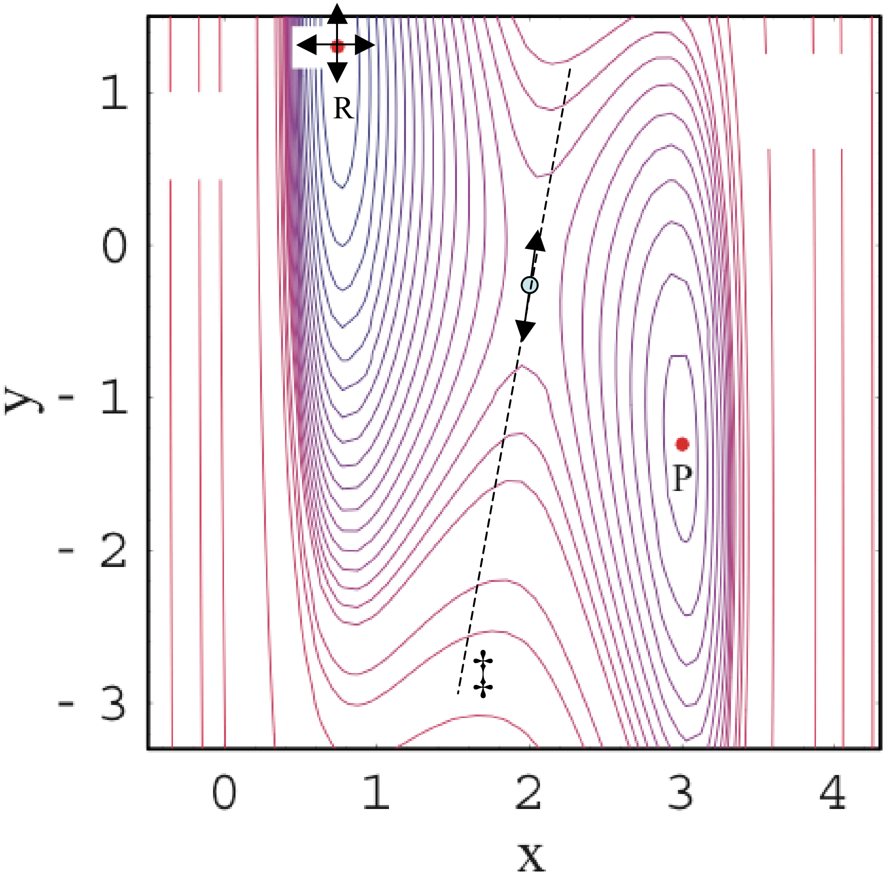
Analogous to the standard approximation for diatomic molecules:

$$V(r) \approx V(r_0) + \frac{1}{2}k\left(r - r_0\right)^2$$



Taylor expand PES around minimum, find normal modes:

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



Taylor expand PES around SP:

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

Then, the TST rate constant becomes:

$$\mathrm{k}^{\mathrm{HTST}} = \sqrt{\frac{k_B T}{2\pi\mu_\perp}}\, \frac{Z_\ddagger}{Z_R}$$

$$= \sqrt{\frac{k_B T}{2\pi\mu_\perp}}\, \frac{\displaystyle\int_{-\infty}^{\infty} e^{-\left(V_{SP} + \sum_{i=1}^{3N-1} \frac{1}{2} k_{\ddagger,i}\, q_{\ddagger,i}^2\right)/k_B T}\, d\mathbf{q}_\ddagger^{'}}{\displaystyle\int_{-\infty}^{\infty} e^{-\left(V_{\min} + \sum_{i=1}^{3N} \frac{1}{2} k_{R,i}\, q_{R,i}^2\right)/k_B T}\, d\mathbf{q}_R}$$

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

which finally gives:

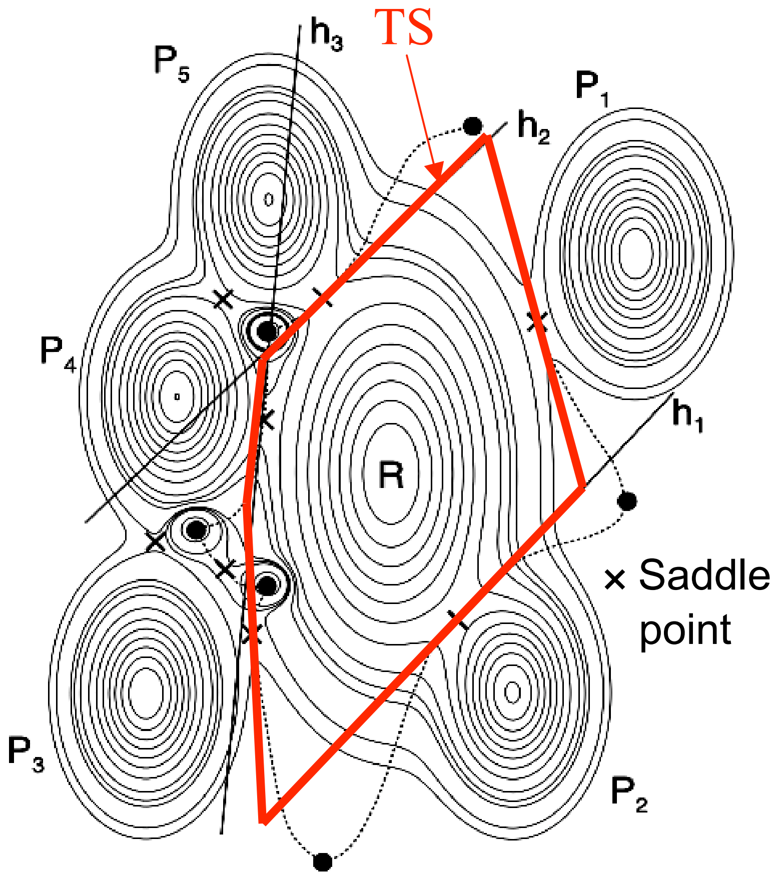
$$\boxed{\mathrm{k}^{\mathrm{HTST}} = \frac{\prod_{i=1}^{3N} \nu_{R,i}}{\prod_{i=1}^{3N-1} \nu_{\ddagger,i}}\, e^{-(V_{SP} - V_{\min})/k_B T}}$$

Agrees with the empirical Arrhenius law

- 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, and a second order Taylor approximation to the PES at minimum and saddle points is used.
- For each saddle point region:

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

Temperature and entropy are taken into account within the normal mode approximation



HTST is more than 10^3 faster than full TST! (to be discussed later)

Simple, approximate correction for quantum effects in HTST

Use quantum mechanical partition function for each vibrational mode instead of the classical one **and** a zero-point corrected activation barrier. Corrects reasonably well for zero-point-energy effects, but not tunneling.

Note: A simple zero point energy correction where only

$$E_a = V_{SP} - V_{\min}$$

is replaced with

$$E_a = \left(V_{SP} + \sum_{i=1}^{D-1} \frac{h\nu_{\ddagger,i}}{2} \right) - \left(V_{\min} + \sum_{i=1}^{D} \frac{h\nu_{R,i}}{2} \right)$$

and classical partition functions used, is typically not a good approximation when calculating the rate of thermal transitions!

Henkelman *et al.*, *J. Chem. Phys* **124**, 044706 (2006)

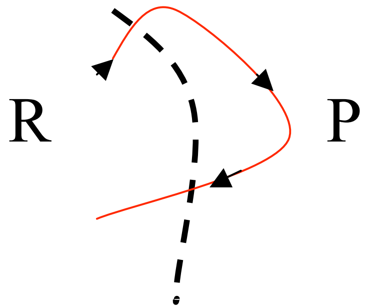
Variational TST

Neglect of recrossings results in an overestimate of the transition rate in TST:

$$k^{TST} > k$$

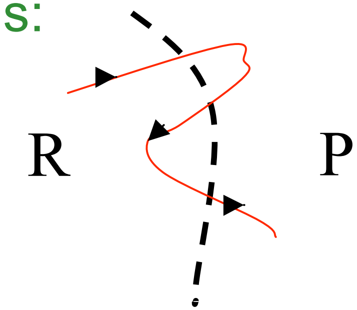
This gives a **variational principle** that can be used to find the dividing surface that provides the **optimal** transition state.

One recrossing:



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

Two recrossings:



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

The optimal TS is the one that gives smallest estimate for k

Keck, *J. Chem. Phys.* **46**, 4211 (1967)
Shui, Appelton & Keck, *J. Chem. Phys.* **56**, 4266 **(**1972)

Wigner-Keck-Eyring (WKE)

two step procedure for finding the exact rate constant:

- Find optimal transition state dividing surface and obtain k^{TST} (i.e., find the TS giving the lowest rate)
- Run (short time) dynamics trajectories from the transition state to find the dynamical correction factor, gives:

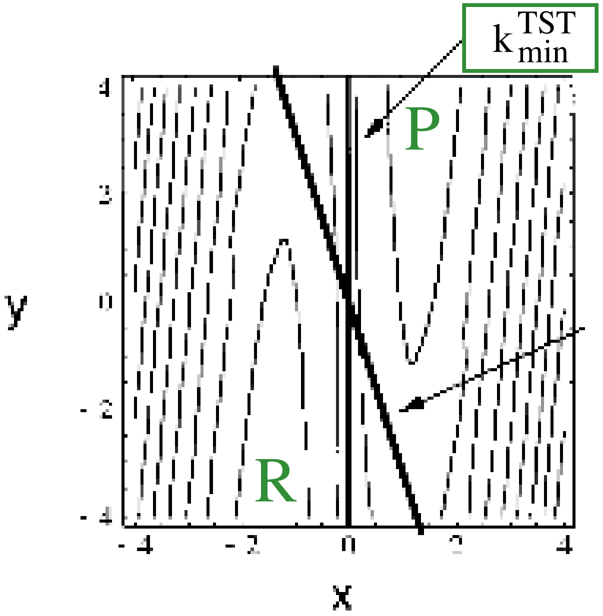
$$k^{exact} = \kappa\, k^{TST}$$

Note: the second step is hard unless a good job has been done in the first. Need to optimize the TS!

Keck, *J. Chem. Phys.* **46**, 4211 (1967)
Shui, Appelton & Keck, *J. Chem. Phys.* **56**, 4266 **(**1972)

Optimization of the TS

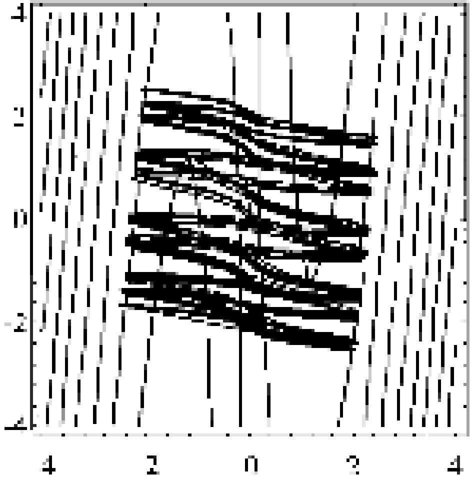
An Example: Symmetric Eckart barrier coupled to harmonic oscillator



$$V(x,y) = V_0 \cosh^{-2}\left(\frac{1}{2}ax\right) + \frac{1}{2}m\omega^2\left(y - Cx\right)^2$$

Run dynamics at some temperature starting at different planar dividing surfaces and evaluate k^{TST} and $k^{exact} = \kappa k^{TST}$

Get large number of recrossings, trapped trajectories - resonances



Still, k^{TST} is found to be only a factor of 2 too large for the optimal planar TS at $k_BT=0.1V_0$. Optimal planar TS found to be $x=0$. At higher T, $k_BT=0.3V_0$, the optimal TS makes a 70^o angle with the x=0 axis.

Interesting observation:

The optimal TS is not the dividing surface that gives the smallest number of recrossings.

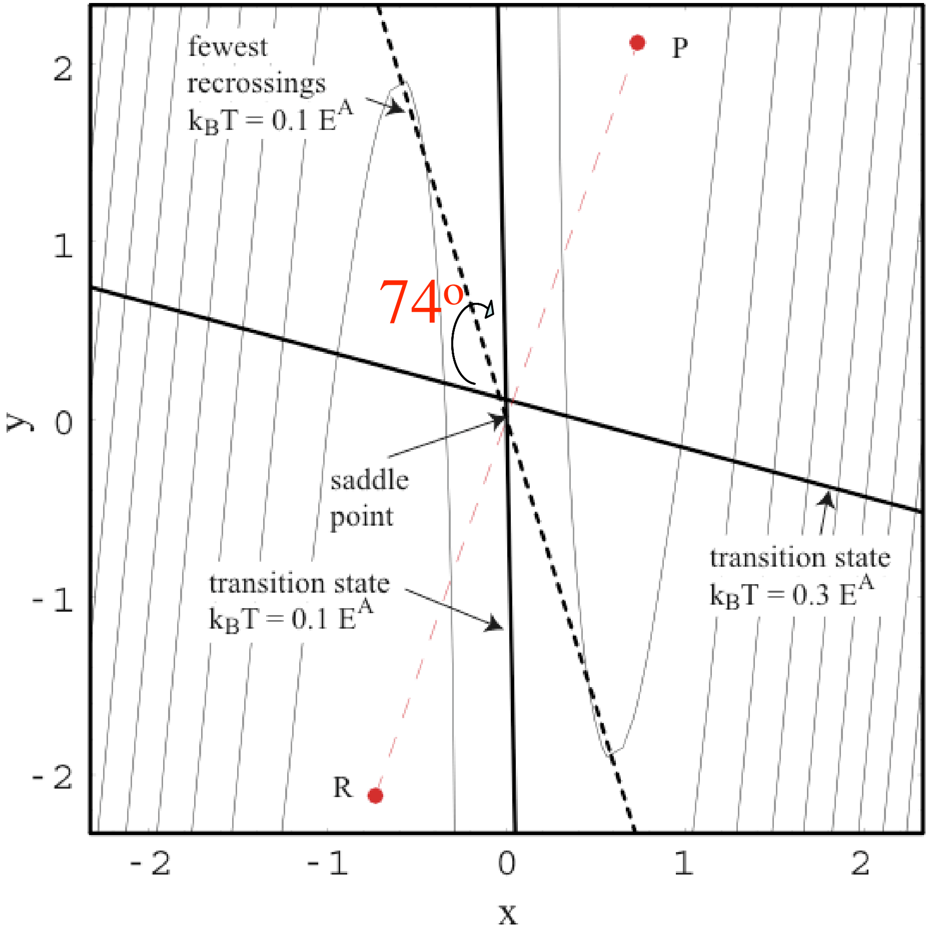
Makarov & Metiu, *J. Chem. Phys.* **107**,7787 (1997)

Can define the free energy, ΔF, of the dividing surface with respect to a reference state. For two locations, 1 and 2, of the hyperplanar dividing surface, get partition functions Q_1 and Q_2 and define
$\Delta F = -k_B T \ln(Q_2 / Q_1)$

Then, $k^{TST} \sim e^{-\Delta F/kT}$

To minimize k^{TST} need to find the dividing surface that corresponds to maximum free energy (use eg RW-TST or OH-TST)

Applied to Eckart problem, → gives results very close to min{k^{TST}} results of Makarov & Metiu



Jóhannesson & Jónsson, *J. Chem. Phys.* **115**, 9644 (2001)

Reversible work TST
(thermodynamic integration)
RW-TST

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

The free energy difference, ΔF, can be found by integrating the reversible work involved in moving a dividing surface from R to TS along the minimum energy path.

Simplest to use a progression of hyperplanes (but the Blue Moon method of Ciccotti *et al.* allows the use of curved surfaces, more general and more complex)

$$\mathrm{k}^{\mathrm{RWTST}} = \frac{\langle|v_\perp|\rangle}{2}\frac{Q_{Z_R}}{Q_R}\frac{Q_\ddagger}{Q_{Z_R}}$$

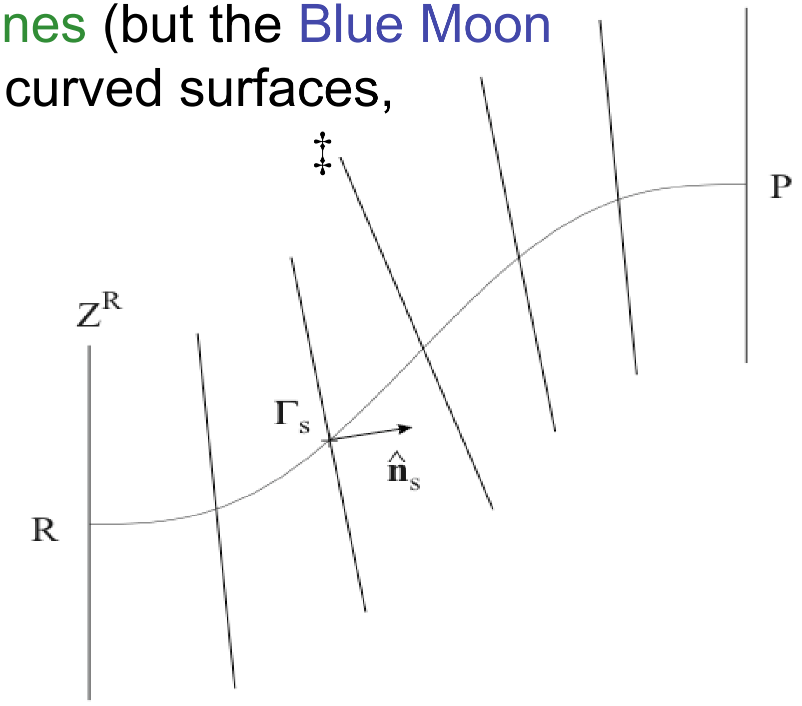
$$\mathrm{k}^{\mathrm{RWTST}} = \frac{\langle|v_\perp|\rangle}{2}\frac{Q_{Z_R}}{Q_R}e^{-\frac{\Delta F}{k_B T}}$$

$$\Delta F = -\int_0^s \langle F_n(1-\kappa R_t)\rangle_{s'}\,ds'$$

$$F_n = F(\mathbf{r}_\mathbf{s})\cdot\hat{\mathbf{n}}_s$$

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

$$\kappa = \frac{d\theta}{ds}$$



Need to integrate over both translation and rotation of hyperplane

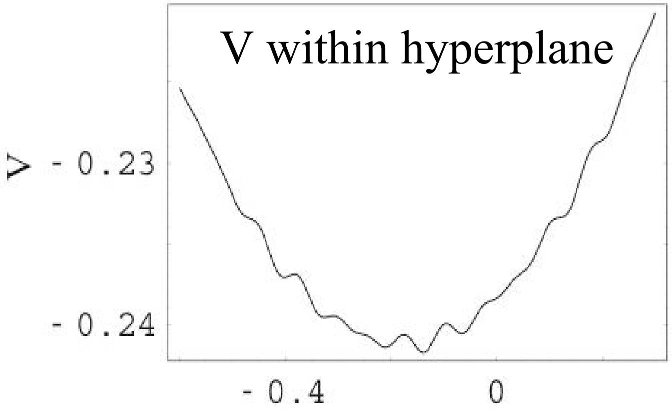
Mills, Jónsson & Schenter, *Surf. Sci.* **324**, 305 (1995)

In order to find free energy difference, calculate translational and rotational force acting on the hyperplane. Carry out Monte Carlo or Molecular Dynamics sampling of the probability distribution within the hyperplane, then thermally average

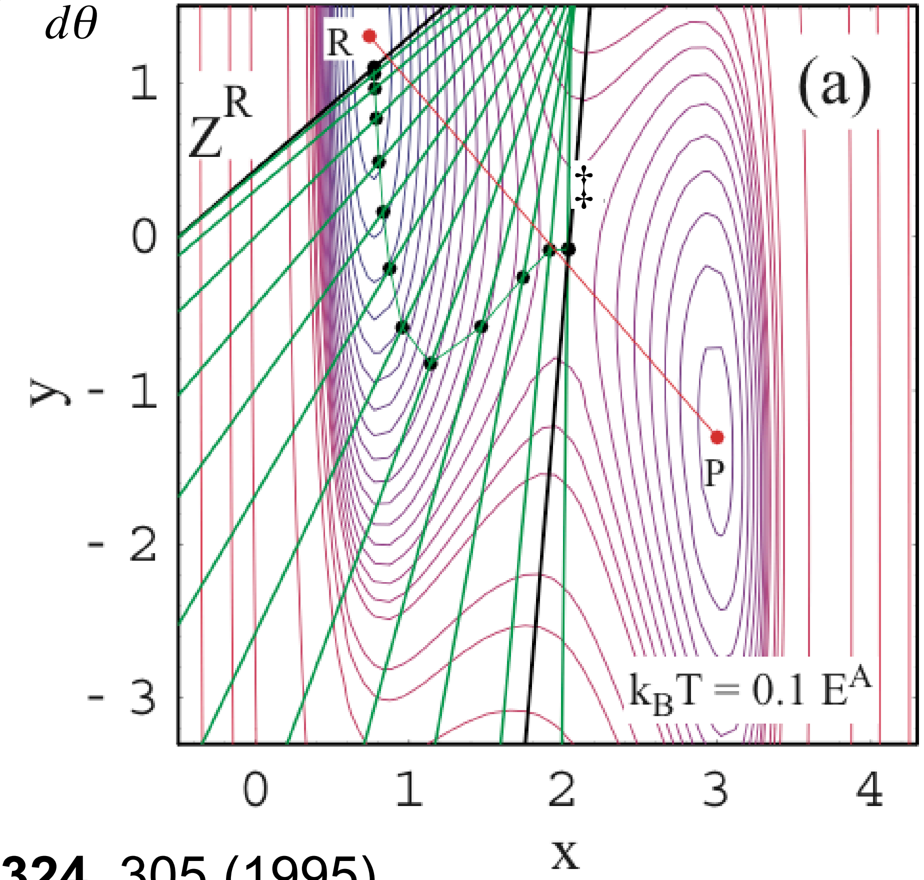
Translational force $F_n = F(\mathbf{r}_s)\cdot\hat{\mathbf{n}}_s$

Rotational force $F_r = F_n\kappa\left(\mathbf{r}_s - \Gamma_s\right)\cdot\dfrac{d\hat{\mathbf{n}}_s}{d\theta}$

from each point in the hyperplane

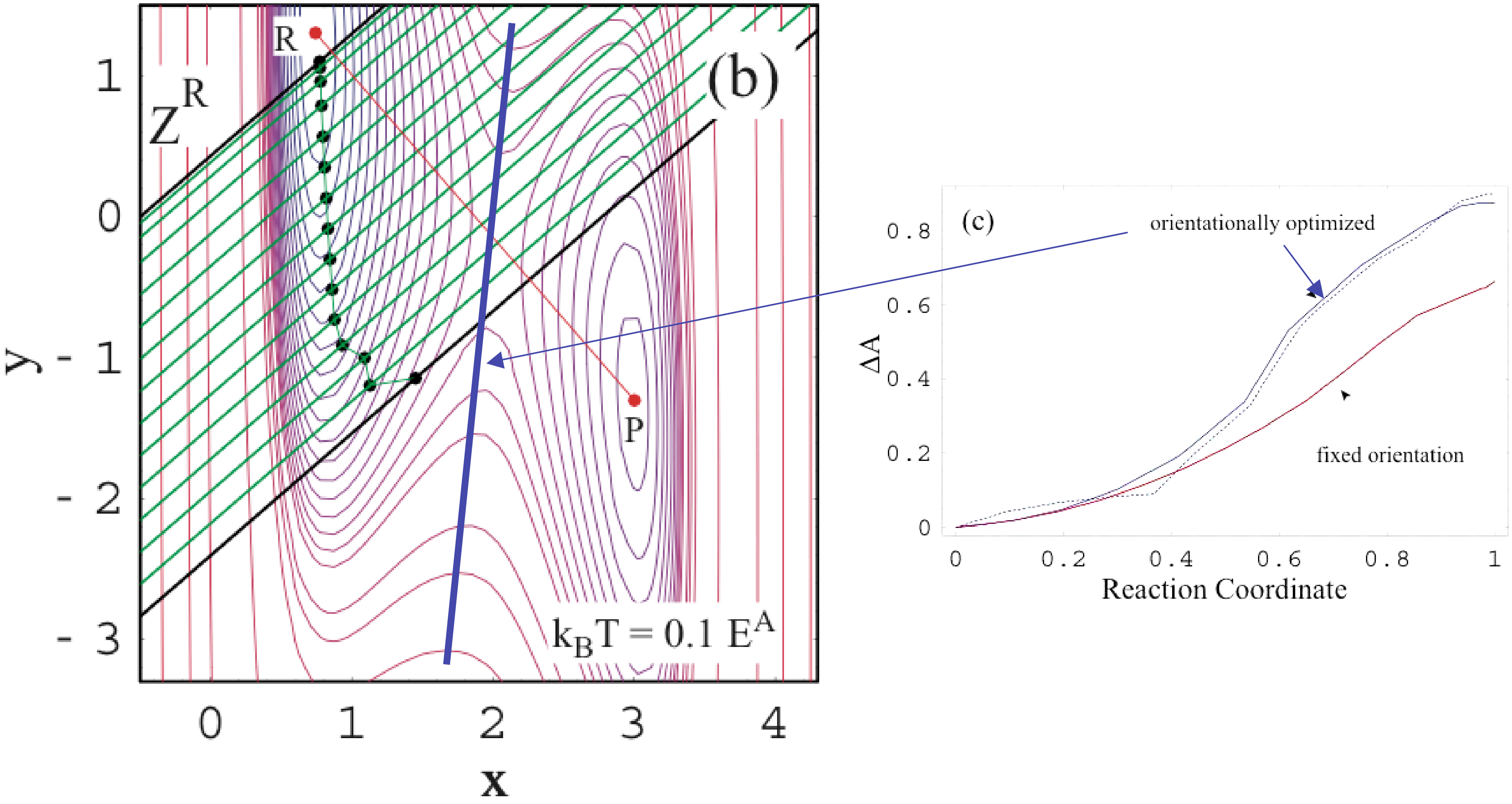


The energy landscape within the hyperplane can have multiple bumps as long as sampling can be carried out



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

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



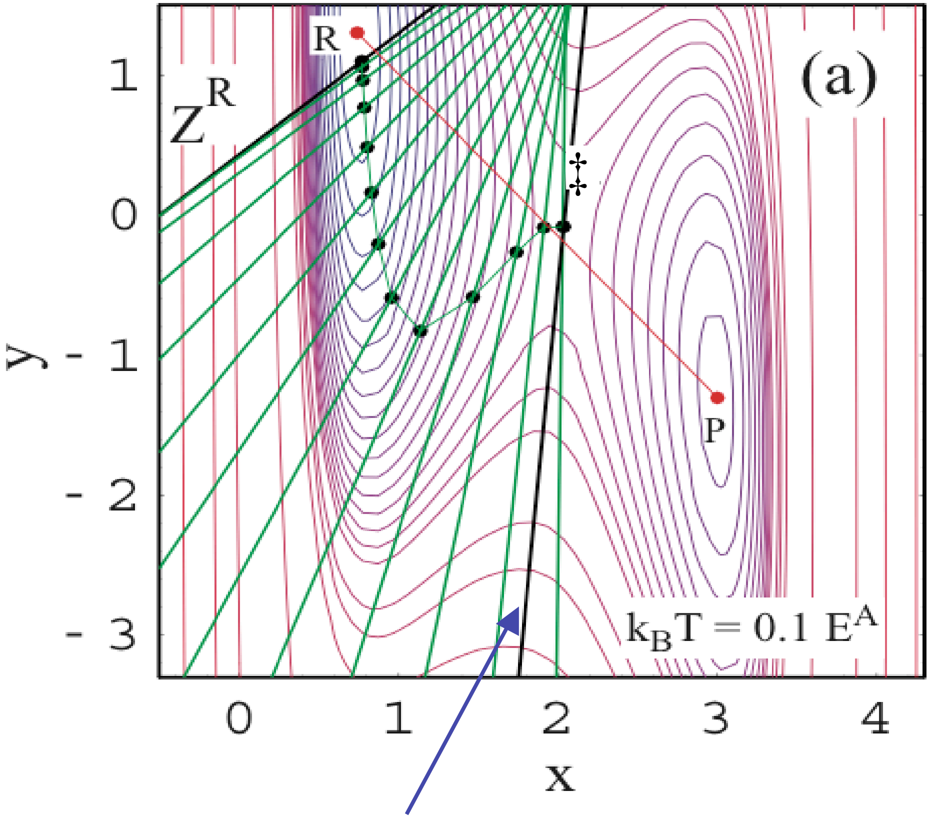
In a 3*N*-dimensional system, the optimization of the location of a dividing surface is a **one**-dimensional optimization, the optimization of orientation represents **3*N*-1** degrees of freedom - essential to optimize orientation!

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

Optimal hyperplanar TST
OH-TST

Jóhannesson & Jónsson,
J. Chem. Phys. **115**, 9644 (2001)

Instead of constructing a path of some sort, start with the hyperplane in the reactant region and let it move uphill in free energy against the translational force acting on it and let it rotate against the rotational force acting on it until the max free energy plane is found,



Optimal hyperplanar dividing surface

i.e., the plane for which

$<F_n> = 0$ and

$<F_r> = 0$.

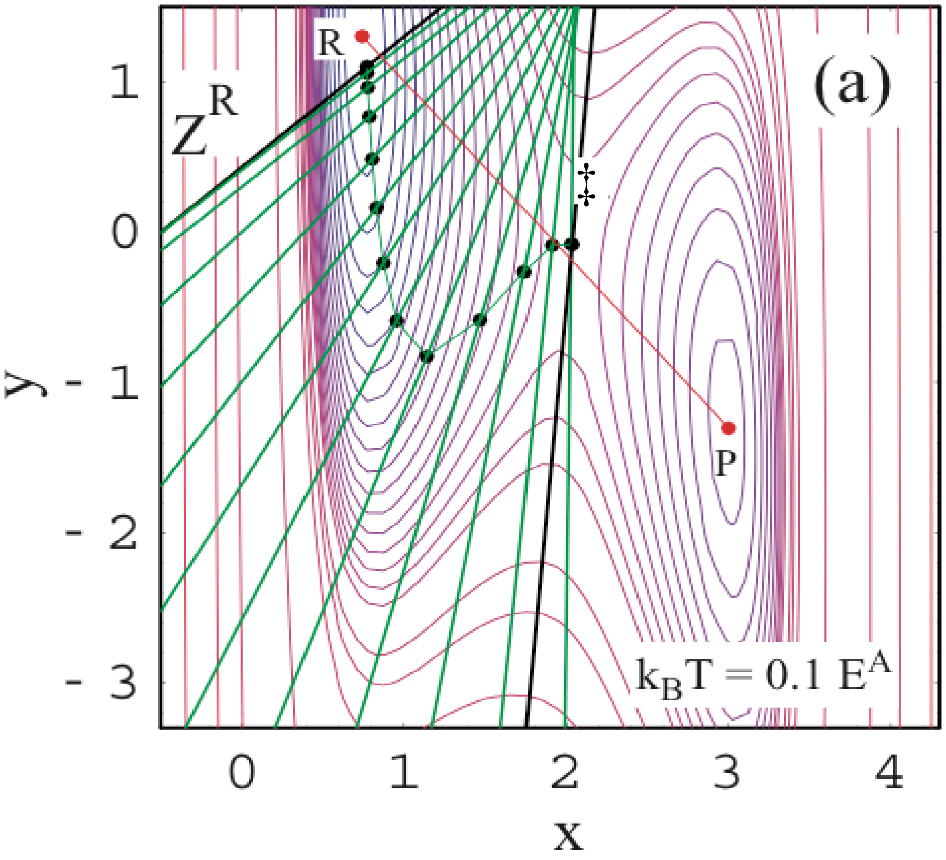
Can use any minimization method that only requires the gradient of the object function,
For example ‘quickmin’ or conjugate gradient method.

By integration over the ‘trajectory’ of hyperplanes, get ΔF.

Jóhannesson & Jónsson, *J. Chem. Phys.* **115**, 9644 (2001)

The normal to the optimized hyperplane gives the reaction coordinate at the TS, i.e., shows which atoms are moving, how much and in which direction.

By allowing the hyperplane to rotate, different transition mechanisms are sampled. The method can, therefore, reveal a new and unexpected transition mechanism.



Jóhannesson & Jónsson, *J. Chem. Phys.* **115**, 9644 (2001)

The OH-TST method is, apparently, the first method developed to systematically optimize a dividing surface with respect to more than one degree of freedom.

Previous implementations of variational TST compared different dividing surfaces by simply carrying out a full TST calculation for each one.

Imagine finding the minimum energy configuration of more than 100 atoms by moving them by hand without the knowledge of the force acting on the atoms. This is analogous to optimizing the dividing surface without having the force on the dividing surface. It shows how the free energy of the dividing surface can be maximized by displacing and reshaping the dividing surface.

Jóhannesson & Jónsson, *J. Chem. Phys.* **115**, 9644 (2001)

How can the TS be represented and optimized in studies of realistic systems (with many degrees of freedom)?

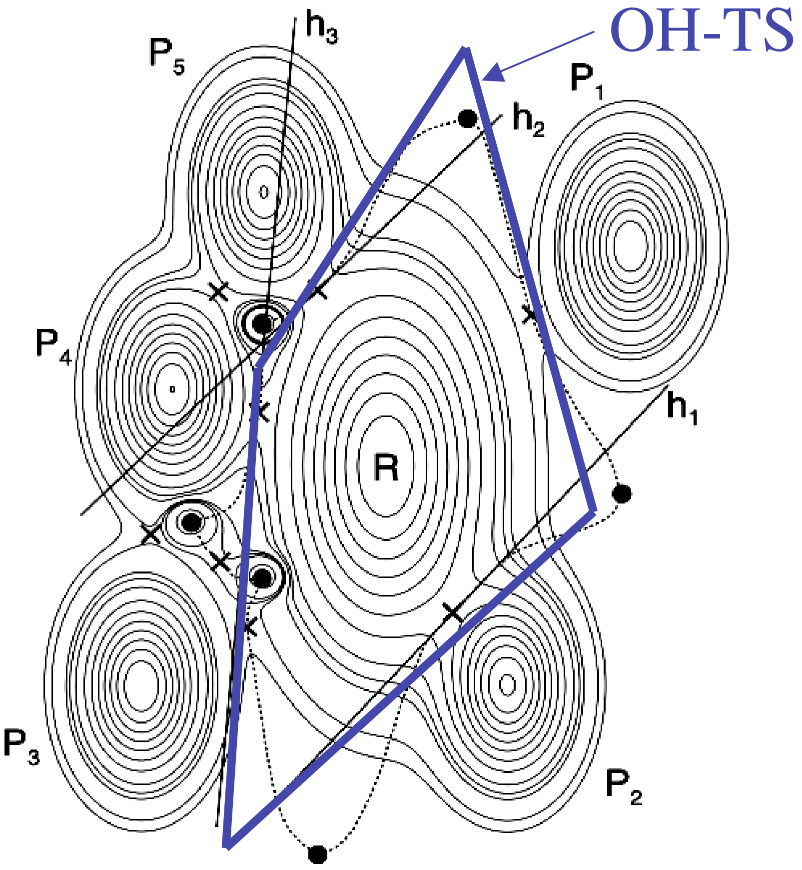
One possibility: Piecewice hyperplanar representation

OH-TST:

Maximize free energy of each hyperplanar segment (minimize k^{TST}) both with respect to position and orientation, get $\Delta F_1, \Delta F_2$, ...

Reveals transition mechanism:

The normal to a hyperplanar segment shows which atoms are moving and in which way at the bottle neck for that reaction channel.



Or use curved surfaces and variationally optimize shape as well as location?

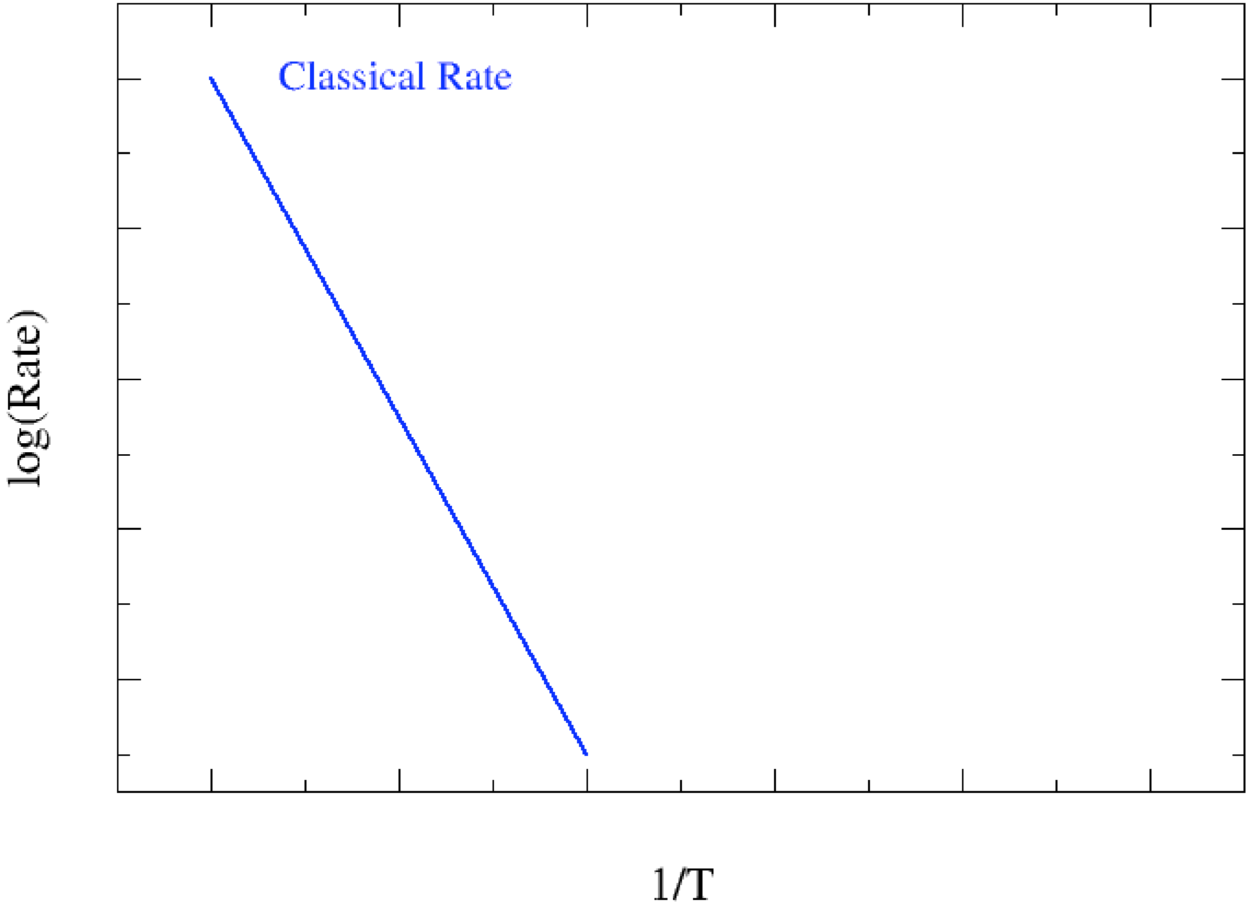
Jóhannesson & Jónsson, *J. Chem. Phys.* **115**, 9644 (2001)
Bligaard & Jónsson, *Comp. Phys. Commun.* **169**, 284 (2005)

A short summary of classical TST

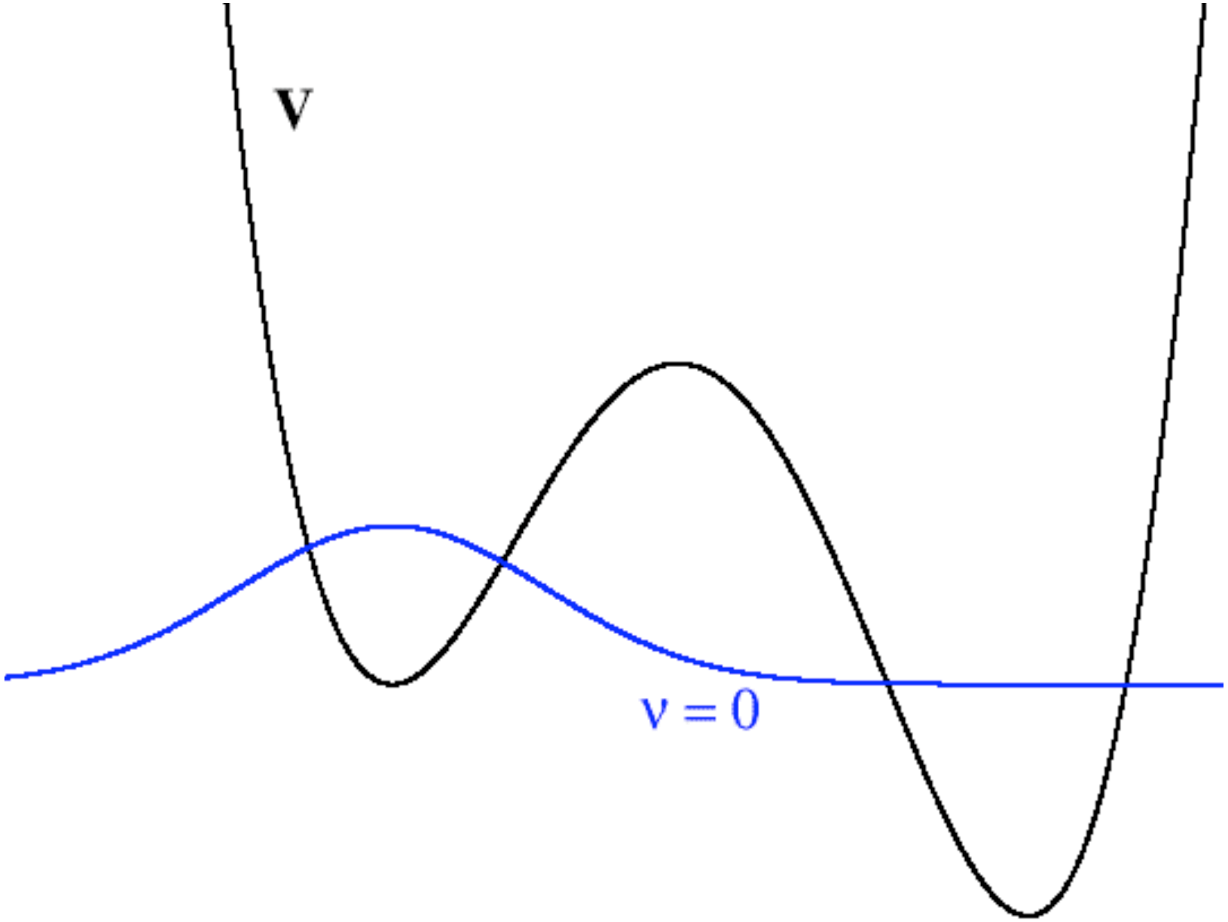
- If possible, use harmonic TST. More than 10^3 faster than variational TST
- In the two-step Wigner-Keck-Eyring (WKE) procedure, the exact rate constant of a transition is found by (1) finding a TS and evaluating k^{TST}, then (2) running short time trajectories to obtain the dynamical correction factor, $k^{exact} = \kappa\, k^{TST}$.
- In order to be able to do step (2) efficiently, the TS needs to be good - important to variationally optimize TS in step (1)!!!
- The TS can be optimized systematically by evaluating the force acting on it (obtained from the thermally averaged force on the system confined to the dividing surface). In the case of a hyperplanar TS, the translational and rotational force on the hyperplane can easily be evaluated and used in some optimization algorithm to find the hyperplane of maximum free energy, giving the optimal hyperplanar TS.

Why Quantum TST (QTST)?

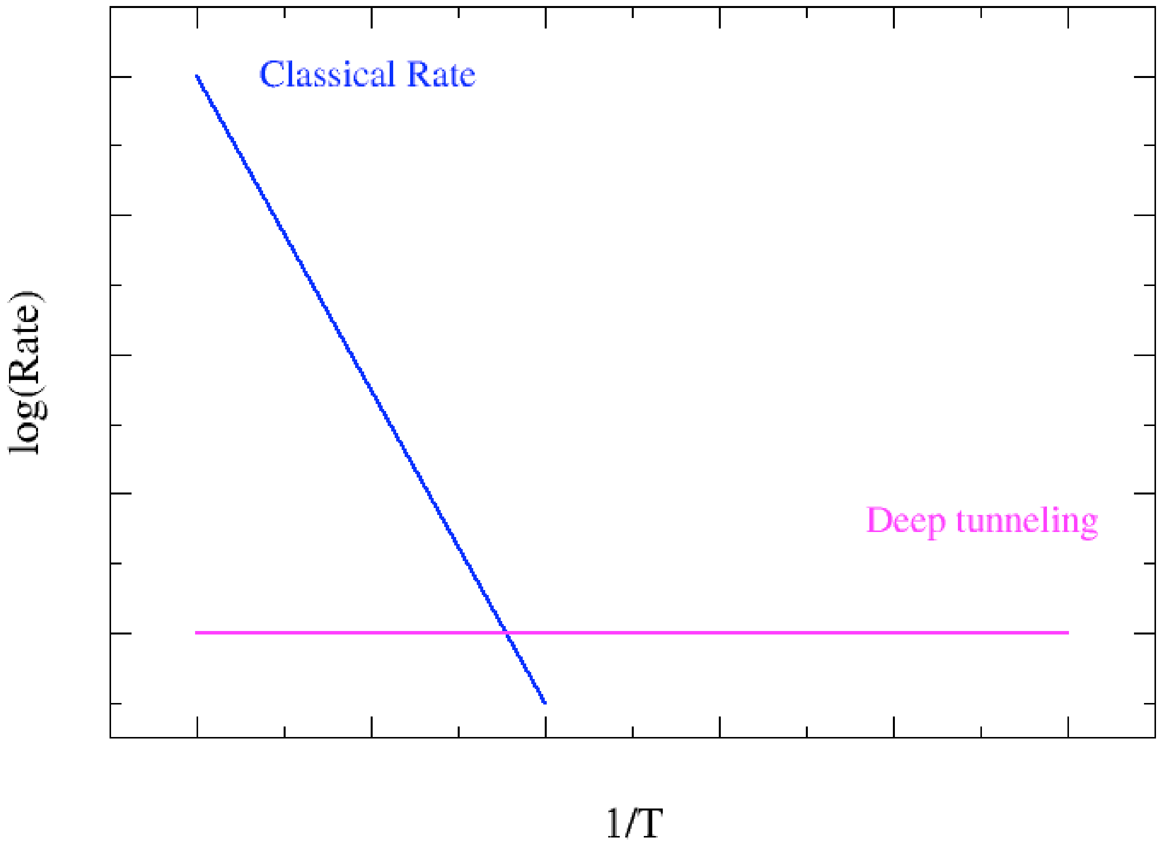
Classical temperature dependence of rates



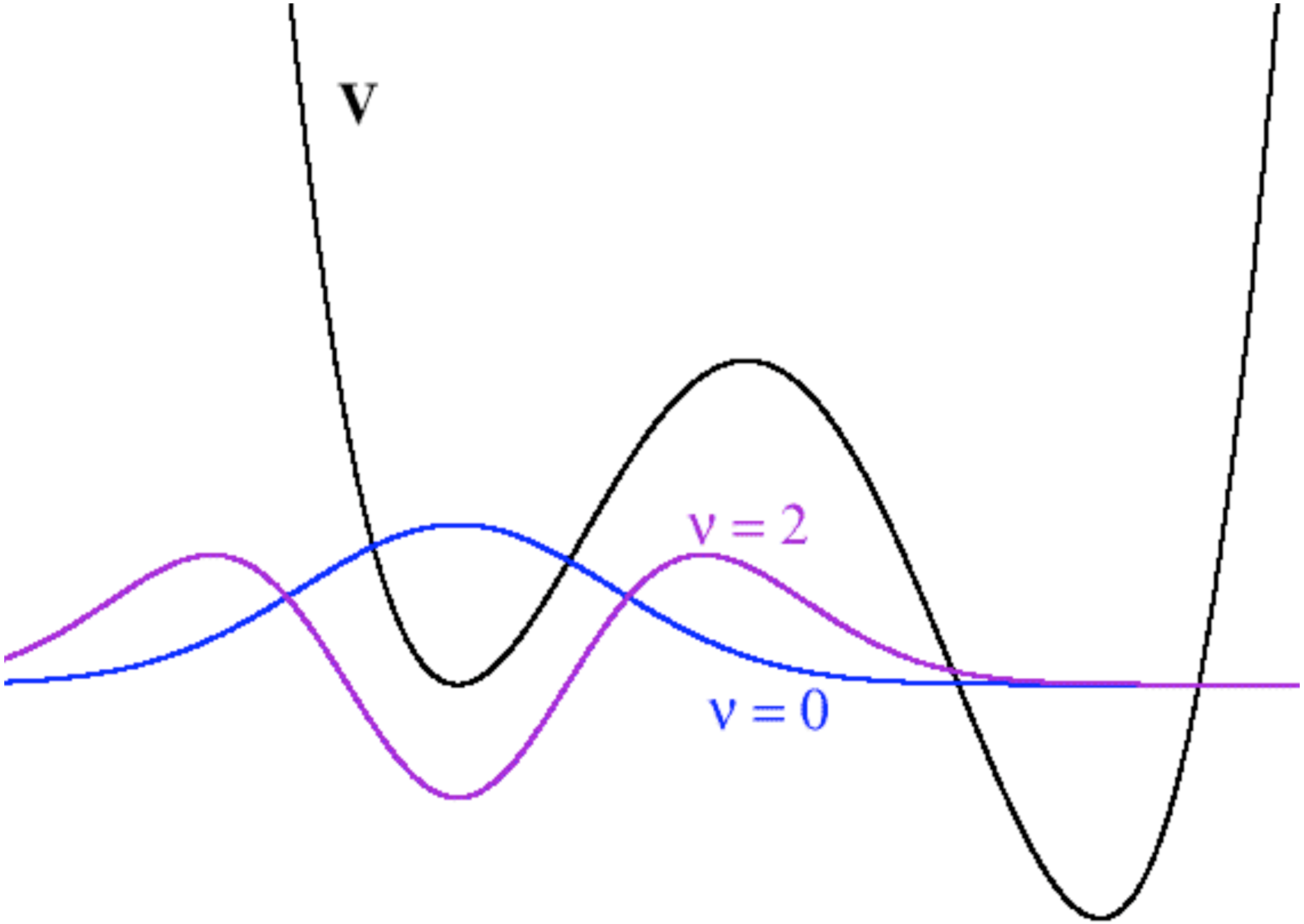
Ground state tunneling



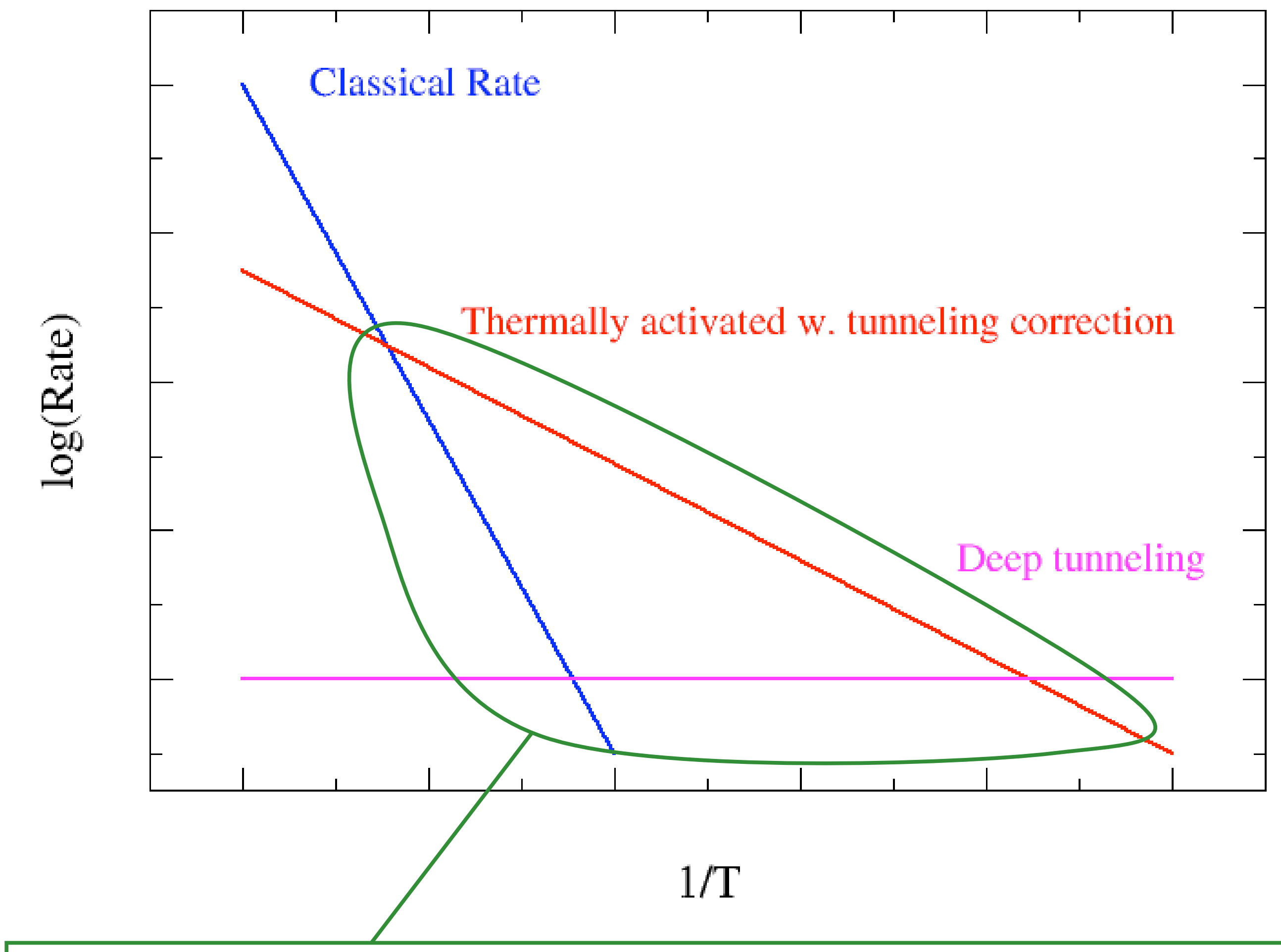
Ground state tunneling



Excited state tunneling



Excited state tunneling



We want to access this region! Need to include quantum tunneling effects. Can be done in an elegant manner by using the path integral formulation of Feynman.

Path integrals and quantum statistical mechanics

Thirty-one years ago, Dick Feynman told me about his \`sum over histories' version of quantum mechanics. \`The electron does anything it likes', he said. \`It goes in any direction at any speed, forward or backward in time, however it likes, and then you add up all the amplitudes and it gives you the wave-function.’ I said to him, \`You're crazy'. But he wasn't.

F.J. Dyson

In H. Woolf (ed.), *Some strangeness in the proportion*, p.376. Published by Addison-Wesley, 1980.

A formal solution to the Schrödinger equation

$$i\hbar \frac{\partial \Psi(\mathbf{x},t)}{\partial t} = \hat{H}\,\Psi(\mathbf{x},t)$$

is given by

$$\Psi(\mathbf{x}_f,t) = U(\mathbf{x}_f,t;\mathbf{x}_i,0)\Psi(\mathbf{x}_i,0)$$

$$U(\mathbf{x}_f,t;\mathbf{x}_i,0) = \left\langle \mathbf{x}_f \middle| e^{-\frac{i\hat{H}t}{\hbar}} \middle| \mathbf{x}_i \right\rangle$$

where *U* is known as the propagator.

$$Q = Tr\, e^{-\frac{\hat{H}}{k_B T}}$$

Using the energy eigenbasis it is easy to see that this is indeed the well-known partition function:

$$\hat{H}\left|n\right\rangle = E_n\left|n\right\rangle, \left\langle n \middle| n' \right\rangle = \delta_{nn'}\,, \sum_n \left|n\right\rangle\left\langle n\right| = 1$$

$$Q = Tr\, e^{-\frac{\hat{H}}{k_B T}} = \sum_n \left\langle n \middle| e^{-\frac{\hat{H}}{k_B T}} \middle| n \right\rangle = \sum_n \left\langle n \middle| n \right\rangle e^{-\frac{E_n}{k_B T}} = \sum_n e^{-\frac{E_n}{k_B T}}$$

If we now use the position eigenbasis to evaluate the partition function:

$$\langle \mathbf{x} | \mathbf{x}' \rangle = \delta(\mathbf{x} - \mathbf{x}')\,,\ \int d\mathbf{x} |\mathbf{x}\rangle\langle\mathbf{x}| = 1$$

$$Q = \int d\mathbf{x} \langle \mathbf{x} | e^{-\frac{\hat{H}}{k_B T}} | \mathbf{x} \rangle = \int d\mathbf{x}\, \rho_{\mathbf{xx}}$$

$$\rho_{\mathbf{xx}} = \langle \mathbf{x} | e^{-\frac{\hat{H}}{k_B T}} | \mathbf{x} \rangle$$

and compare to

$$U(\mathbf{x}_f, t; \mathbf{x}_i, 0) = \langle \mathbf{x}_f | e^{-\frac{i\hat{H}t}{\hbar}} | \mathbf{x}_i \rangle$$

we see that

$$\rho_{\mathbf{xx}} = U(\mathbf{x}, -\frac{i\hbar}{k_B T}; \mathbf{x}, 0)$$

So, doing quantum statistical mechanics is the same as doing quantum mechanics in imaginary time with closed paths (and an performing an extra integration)!

Now let's evaluate the evolution operator by splitting the propagation into *P* steps, ε=*t/P:*

$$U(\mathbf{x}_f,t;\mathbf{x}_i,0)=\int\cdots\int\prod_{n=1}^{P-1}d\mathbf{x}_n\left\langle\mathbf{x}_f\right|e^{-\frac{i\hat{H}\varepsilon}{\hbar}}\left|\mathbf{x}_{P-1}\right\rangle\left\langle\mathbf{x}_{P-1}\right|e^{-\frac{i\hat{H}\varepsilon}{\hbar}}\left|\mathbf{x}_{P-2}\right\rangle\cdots\left\langle\mathbf{x}_1\right|e^{-\frac{i\hat{H}\varepsilon}{\hbar}}\left|\mathbf{x}_i\right\rangle$$

If

$$\hat{H}=\frac{\mathbf{p}^2}{2\mu}+V(\mathbf{x})$$

it is convenient to introduce a complete set of momentum eigenstates when evaluating each part of the propagator:

$$\left\langle\mathbf{x}_n\right|e^{-\frac{i\hat{H}\varepsilon}{\hbar}}\left|\mathbf{x}_{n-1}\right\rangle=\frac{V}{(2\pi\hbar)^{3N}}\int d\mathbf{p}\left\langle\mathbf{x}_n|\mathbf{p}\right\rangle\left\langle\mathbf{p}\right|e^{-\frac{i\hat{H}\varepsilon}{\hbar}}\left|\mathbf{x}_{n-1}\right\rangle=$$

$$\frac{V}{(2\pi\hbar)^{3N}}\int d\mathbf{p}\left\langle\mathbf{x}_n|\mathbf{p}\right\rangle\left\langle\mathbf{p}|\mathbf{x}_{n-1}\right\rangle e^{-\frac{i\varepsilon}{\hbar}\left(\frac{\mathbf{p}^2}{2\mu}+V(\mathbf{x}_{n-1})\right)}=$$

$$\frac{1}{(2\pi\hbar)^{3N}}\int d\mathbf{p}\,e^{\frac{i}{\hbar}\mathbf{p}\cdot(\mathbf{x}_n-\mathbf{x}_{n-1})}e^{-\frac{i\varepsilon}{\hbar}\left(\frac{\mathbf{p}^2}{2\mu}+V(\mathbf{x}_{n-1})\right)}\quad;\quad\left\langle\mathbf{x}|\mathbf{p}\right\rangle=\frac{1}{\sqrt{V}}e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{x}}$$

$$\left\langle\mathbf{x}_n\right|e^{-\frac{i\hat{H}\varepsilon}{\hbar}}\left|\mathbf{x}_{n-1}\right\rangle=\left(\frac{\mu}{2\pi i\varepsilon\hbar}\right)^{\frac{3N}{2}}e^{\frac{i\varepsilon}{\hbar}\left[\frac{\mu}{2}\frac{(\mathbf{x}_n-\mathbf{x}_{n-1})^2}{\varepsilon^2}-V(\mathbf{x}_{n-1})\right]}$$

Use this to evaluate the full propagator and we get

$$U(\mathbf{x}_f,t;\mathbf{x}_i,0)=\int\cdots\int\prod_{n=1}^{P-1}d\mathbf{x}_n\left(\frac{\mu}{2\pi i\varepsilon\hbar}\right)^{\frac{3NP}{2}}e^{\sum_{n=1}^{P}\frac{i\varepsilon}{\hbar}\left[\frac{\mu}{2}\frac{\left(\mathbf{x}_n-\mathbf{x}_{n-1}\right)^2}{\varepsilon^2}-V(\mathbf{x}_{n-1})\right]}$$

With the following definitions

$$\frac{\left(\mathbf{x}_n-\mathbf{x}_{n-1}\right)}{\varepsilon}\to\dot{\mathbf{x}}(t)$$

$$V(\mathbf{x}_{n-1})\to V\left(\mathbf{x}(t)\right)$$

$$\sum_{n=1}^{P}\varepsilon\to\int_0^t dt$$

$$\int D\,\mathbf{x}(t)\equiv\lim_{P\to\infty}\int\cdots\int\prod_{n=1}^{P-1}d\mathbf{x}_n\left(\frac{\mu}{2\pi i\varepsilon\hbar}\right)^{\frac{3NP}{2}}$$

the final result for the propagator has become

$$U(\mathbf{x}_f,t;\mathbf{x}_i,0)=\int D\,\mathbf{x}(t)\,e^{\frac{i}{\hbar}\int_0^t dt\left\{\frac{1}{2}\mu\dot{\mathbf{x}}^2(t)-V\left(\mathbf{x}(t)\right)\right\}}=\int D\,\mathbf{x}(t)\,e^{\frac{i}{\hbar}S\left(\mathbf{x}(t)\right)}$$

This is the very elegant path integral formulation of quantum mechanics developed by Feynman

$$U(\mathbf{x}_f,t;\mathbf{x}_i,0)=\int D\mathbf{x}(t)\,e^{\frac{i}{\hbar}\int_0^t dt\left\{\frac{1}{2}\mu\dot{\mathbf{x}}^2(t)-V(\mathbf{x}(t))\right\}}=\int D\mathbf{x}(t)\,e^{\frac{i}{\hbar}S(\mathbf{x}(t))}$$

It is a lot more intuitive than it looks at first sight! Take ***all*** possible paths starting at $\boldsymbol{x}_i$ and ending at $\boldsymbol{x}_f$, evaluate the classical action S for ***all*** these paths, weight them by ***same*** “factor” $e^{iS(\mathbf{x}(t))/\hbar}$ and sum them up. That’s it! No path is more important than another!

Exercise:
How does the Feynman path integral formulation approach the classical limit? How does this compare to the traditional the quantum mechanical formulation?

Useful reading:
Feynman & Hibbs, *Quantum Mechanics and Path Integrals*, McGraw-Hill, New York, 1965.
Trotter*, Proc. Am. Math. Soc.* **10**, 545 (1959)
Suzuki, *Prog. Theor. Phys.* **46**, 1337 (1971)

Now, how does quantum statistical mechanics looks in the path integral wrapping? We just showed that

$$U(\mathbf{x}_f,t;\mathbf{x}_i,0)=\int D\,\mathbf{x}(t)\,e^{\frac{i}{\hbar}\int_0^t dt\left\{\frac{1}{2}\mu\dot{\mathbf{x}}^2(t)-V(\mathbf{x}(t))\right\}}=\int D\,\mathbf{x}(t)\,e^{\frac{i}{\hbar}S(\mathbf{x}(t))}$$

The canonical partition is then given by

$$Q=\int d\mathbf{x}\left\langle\mathbf{x}\right|e^{-\frac{\hat{H}}{k_BT}}\left|\mathbf{x}\right\rangle=\int d\mathbf{x}\,U(\mathbf{x},-i\tau;\mathbf{x},0)=\int D\,\mathbf{x}(\tau)\,e^{-\frac{S_E(\mathbf{x}(\tau))}{\hbar}}$$

$$\tau=\frac{\hbar}{k_BT}$$

Only closed paths
$\boldsymbol{x}_f=\boldsymbol{x}_i=\boldsymbol{x}$

1 integration more than the propagator!

with

$$S_E(\mathbf{x}(\tau))=\int_0^{\frac{\hbar}{k_BT}}d\tau\left\{\frac{1}{2}\mu\dot{\mathbf{x}}^2(\tau)+V(\mathbf{x}(\tau))\right\}$$

Let’s have a look at the discrete Euclidean action S_E:

$$S_E\left(\mathbf{x}(\Delta\tau)\right) = \sum_{n=1}^{P} \Delta\tau \left[\frac{\mu}{2}\frac{(\mathbf{x}_n - \mathbf{x}_{n-1})^2}{(\Delta\tau)^2} + V(\mathbf{x}_{n-1})\right]$$

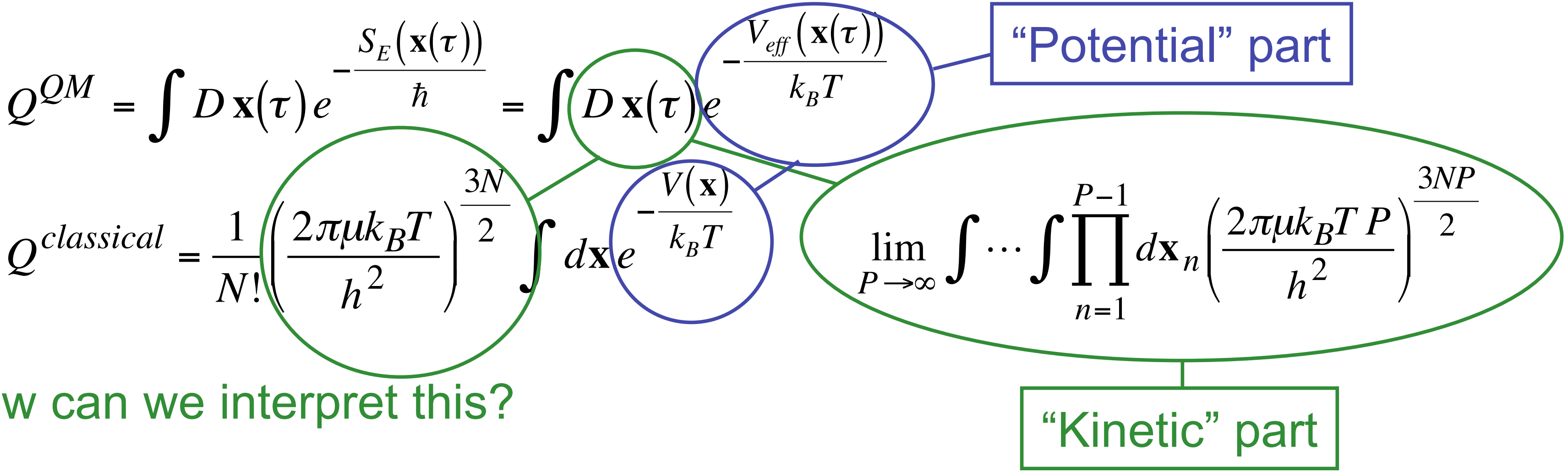
With

$$\Delta\tau = \frac{\hbar}{k_B T\, P}$$

we can rearrange the terms in the Euclidean action to get

$$S_E\left(\mathbf{x}(\Delta\tau)\right) = \frac{\hbar}{k_B T} \underbrace{\sum_{n=1}^{P}\left[\frac{1}{2}k_{sp}(T)\left(\mathbf{x}_n - \mathbf{x}_{n-1}\right)^2 + \frac{V(\mathbf{x}_{n-1})}{P}\right]}_{V_{eff}} \quad ; \quad k_{sp}(T) = \mu P\left(\frac{k_B T}{\hbar}\right)^2$$

Now, compare the quantum mechanical and classical canonical partition functions



$$Q^{QM} = \int D\,\mathbf{x}(\tau)\, e^{-\frac{S_E(\mathbf{x}(\tau))}{\hbar}} = \int D\,\mathbf{x}(\tau)\, e^{-\frac{V_{eff}(\mathbf{x}(\tau))}{k_B T}}$$

$$Q^{classical} = \frac{1}{N!}\left(\frac{2\pi\mu k_B T}{h^2}\right)^{\frac{3N}{2}} \int d\mathbf{x}\, e^{-\frac{V(\mathbf{x})}{k_B T}}$$

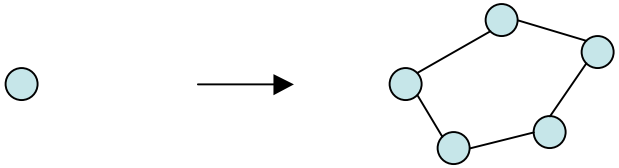
$$\lim_{P\to\infty} \int\cdots\int \prod_{n=1}^{P-1} d\mathbf{x}_n \left(\frac{2\pi\mu k_B T\, P}{h^2}\right)^{\frac{3NP}{2}}$$

“Potential” part

“Kinetic” part

How can we interpret this?

- Statistical mechanics of a quantum particle is mathematically equivalent (isomorphic) to classical statistical mechanics of a distribution of images of the particle connected with springs with stiffness proportional to T^2 (temperature) and P (the number of images)



$$k_{sp}(T) = \mu P\left(\frac{k_B T}{\hbar}\right)^2$$

- Instead of the potential surface, work with an effective potential

$$V(\mathbf{x}) \rightarrow V_{eff}\left(\mathbf{x}_0, \mathbf{x}_1, \ldots, \mathbf{x}_P = \mathbf{x}_0\right) = \sum_{n=1}^{P}\left[\frac{1}{2} k_{sp}(T)\left(\mathbf{x}_n - \mathbf{x}_{n-1}\right)^2 + \frac{V(\mathbf{x}_{n-1})}{P}\right]$$

- How can this be used to calculate rates of change including quantum quantum effects?
- But first we should determine at which temperature quantum effects become important

The classical to quantum transition occurs when the restoring force of the springs becomes smaller than the potential force due to small displacements around the classical saddle point:

$$T_c = \frac{\hbar\Omega}{2\pi\, k_{sp}}$$

Where Ω is the magnitude of the imaginary frequency at the classical saddle point.

Gillan, *J. Phys. C: Solid State Phys.* **20**, 3621 (1987); *Phys. Rev. Lett.* **58**, 563 (1987); *Philos. Mag. A* **58**, 257 (1988)

Instanton Theory
(HQTST)

Miller, Callan, Coleman,
Benderskii, Makarov, and more

A harmonic approximation to the effective potential, V_{eff}, at the initial state minimum and the saddle point (the instanton) leads to the “instanton” or harmonic quantum transition state theory:

$$\mathrm{k}^{\mathrm{HQTST}} = \frac{1}{Q_R} \cdot \sqrt{\frac{\mu k_B T P \sum_{n=1}^{P} \left(\mathbf{x}_{n+1} - \mathbf{x}_n\right)^2}{2\pi\hbar^2}} \cdot \frac{k_B T P}{\hbar \left| \prod_j' \nu_j \right|} \cdot \exp\left(- \frac{V_{eff}\left(\mathbf{x}_{ins}\right)}{k_B T} \right)$$

frequencies of vibrational modes at instanton

Leave out zero mode

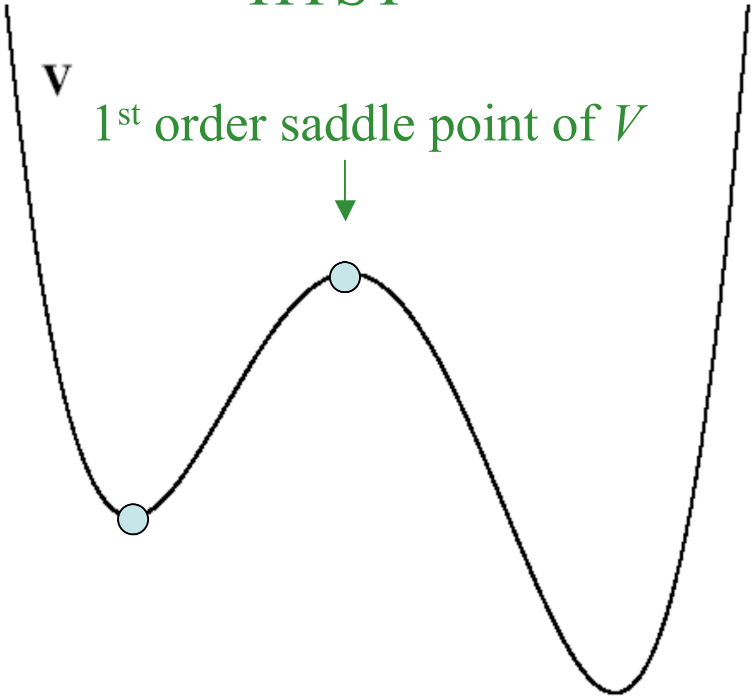
Compare to classical harmonic TST:

$$\mathrm{k}^{\mathrm{HTST}} = \frac{1}{Q_R} \frac{1}{\prod_{i=1}^{3N-1} \nu_{\ddagger,i}} e^{-\frac{V_{SP}}{k_B T}}$$

Miller, *J. Chem. Phys.* **62**, 1899 (1975)
Callan & Coleman, *Phys. Rev. D* **16**, 1762 (1977)
Benderskii & Makarov, many papers early 1990s.

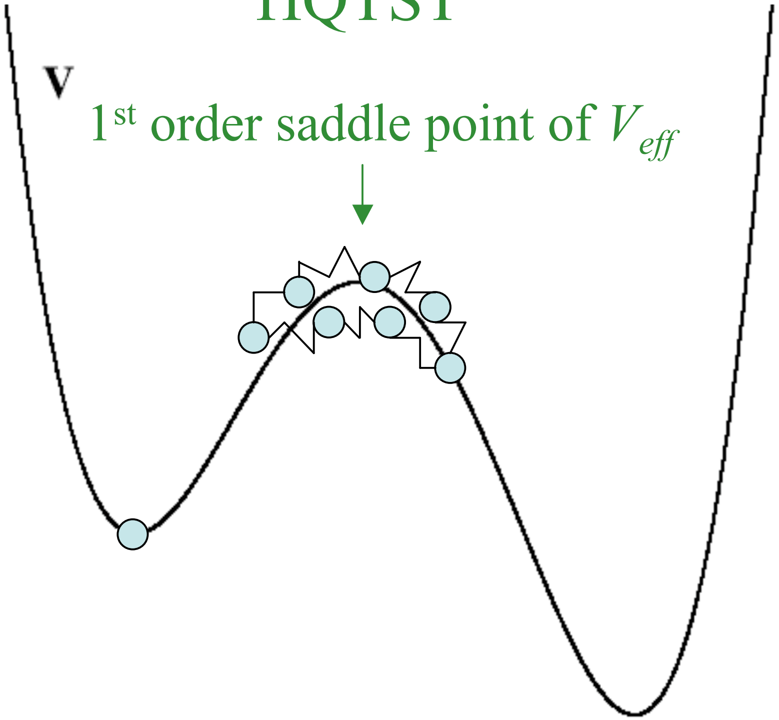
The instanton versus the classical saddle point:

HTST



1st order saddle point of V

HQTST



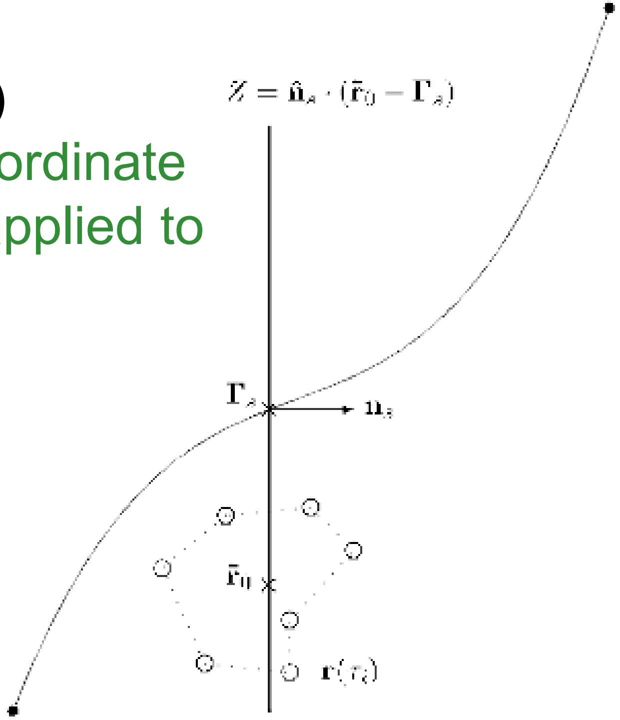
1st order saddle point of V_{eff}

Variational Centroid methods (VCs)

Gillan, Voth, Chandler, Miller, Mills, Jónsson, Schenter, and more

The quantum TS is defined in terms of a (3*N*-1) dimensional dividing surface in the classical coordinate space, where the transition state constraint is applied to the centroid, of the Feynman paths

$$\tilde{\mathbf{x}}_{cen} = \frac{1}{P}\sum_{i=1}^{P}\mathbf{x}_i$$



VCs involve either finding an optimal quantum TS or evaluating the reversible work required to shift the system [where the centroid is confined to a (3*N*-1) dimensional surface] from reactants towards products. They are analogous to their classical counterparts discussed earlier.

Gillan, *J. Phys. C: Solid State Phys.* **20**, 3621 (1987); *Phys. Rev. Lett.* **58**, 563 (1987); *Philos. Mag. A* **58**, 257 (1988)
Voth, Chandler, Miller, *J. Chem. Phys.* **91**, 7749 (1989)
Voth, *Chem. Phys. Lett.* **170**, 289 (1990); *J. Phys. Chem.* **97**, 8365 (1993)
Messina, Schenter & Garret, *J. Chem. Phys.* **98**, 8525 (1993); **99**, 8644 (1993)
Mills, Jónsson & Schenter, *Surf. Sci.* **324**, 305 (1995)

Reversible
Action-space Work QTST
(RAW-QTST)

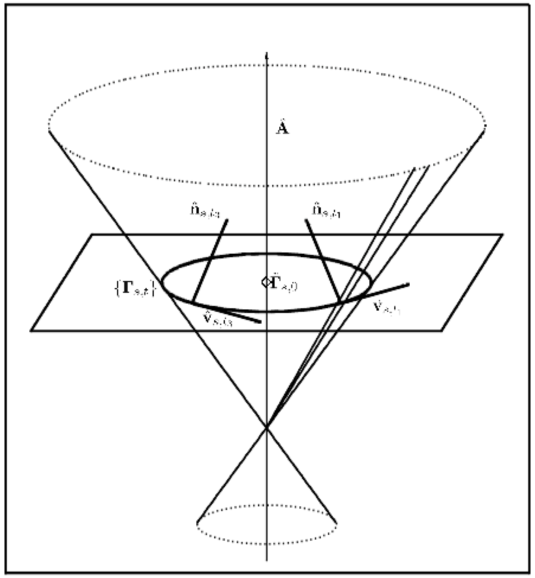
Mills, Schenter, Makarov & Jónsson

Chem. Phys. Lett. 278, 91 (1997)

The (discrete) Euclidean action

$$S_E\left(\mathbf{x}(\Delta\tau)\right) = \frac{\hbar}{k_B T}\sum_{n=1}^{P}\left[\frac{1}{2}k_{sp}(T)\left(\mathbf{x}_n - \mathbf{x}_{n-1}\right)^2 + \frac{V(\mathbf{x}_{n-1})}{P}\right]$$

defines an 3*NP* dimensional action-space. The quantum TS is defined as a 3*NP*-1 dimensional cone in the action-space of all closed Feynman paths with *P* images



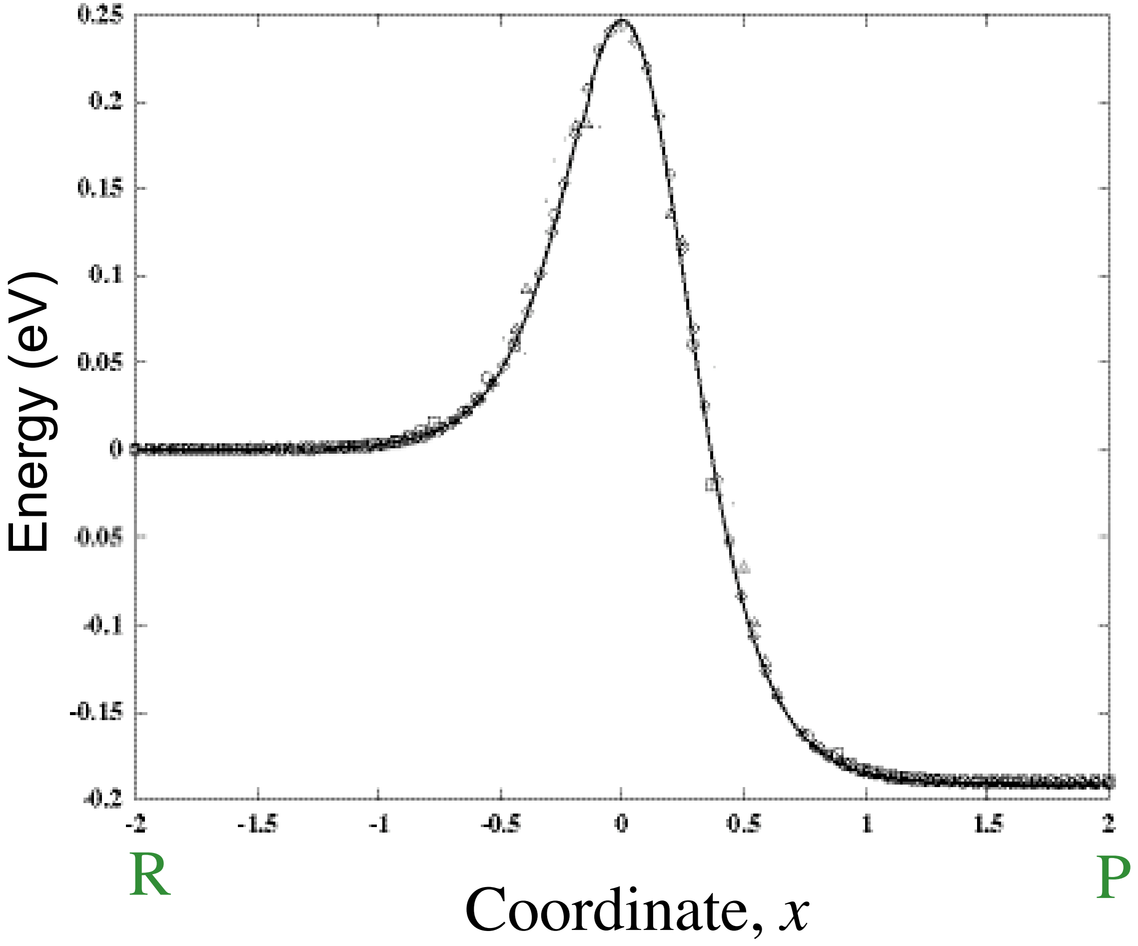
RAW-QTST involves evaluating the reversible work required to shift the system confined to a cone from the reactants towards products. It is analogous to the classical OH-TST.

An example:
Asymmetric Eckart Barrier

Mills, Schenter, Makarov & Jónsson

Chem. Phys. Lett. 278, 91 (1997)

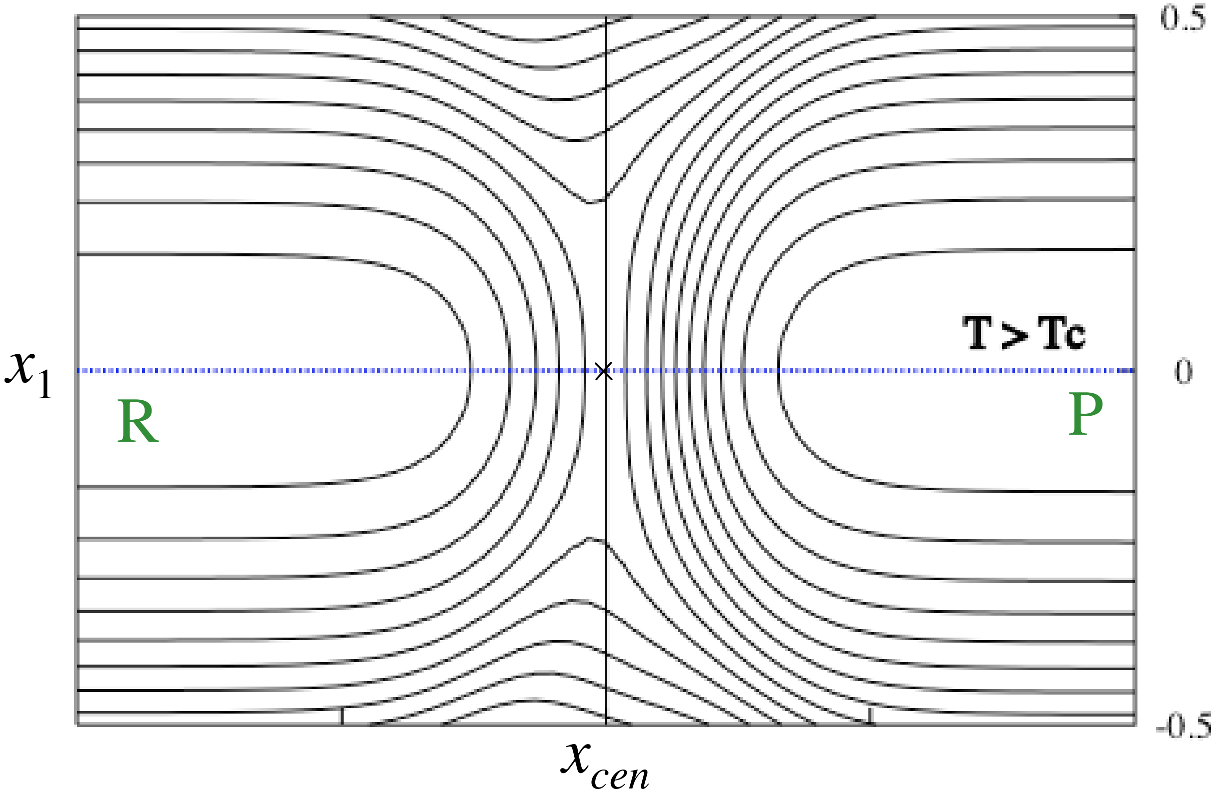
The asymmetric Eckart barrier



Isosurfaces of the effective potential, the action surface:

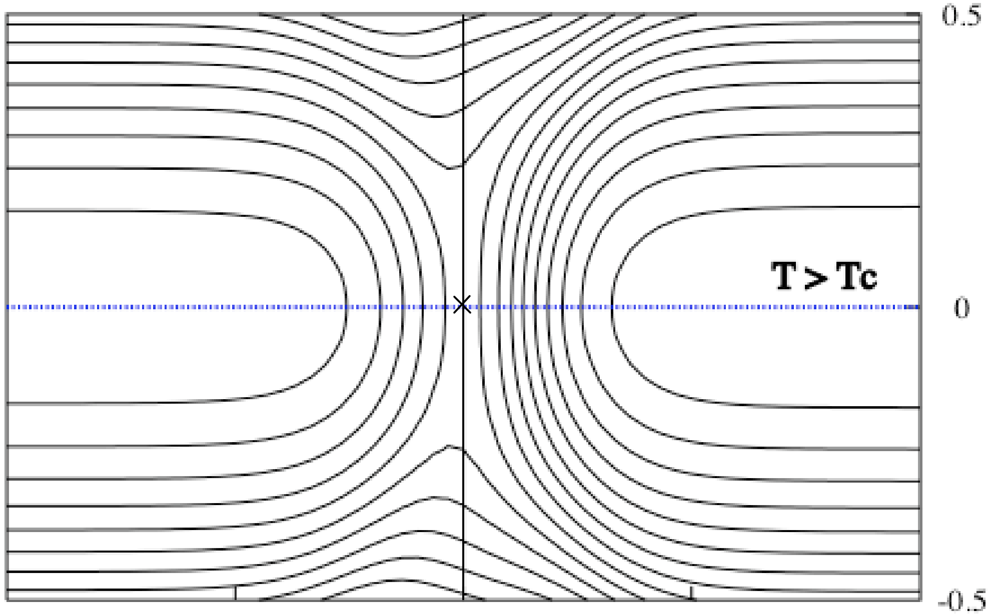
Consider Feynman paths of the form $\mathbf{x}(\tau) = x_{cen} + x_1 \sin(2\pi k_B T \tau / \hbar)$, (only two Fourier components)

Contour plot shows the value of the effective potential as a function of (x_{cen},x_1)



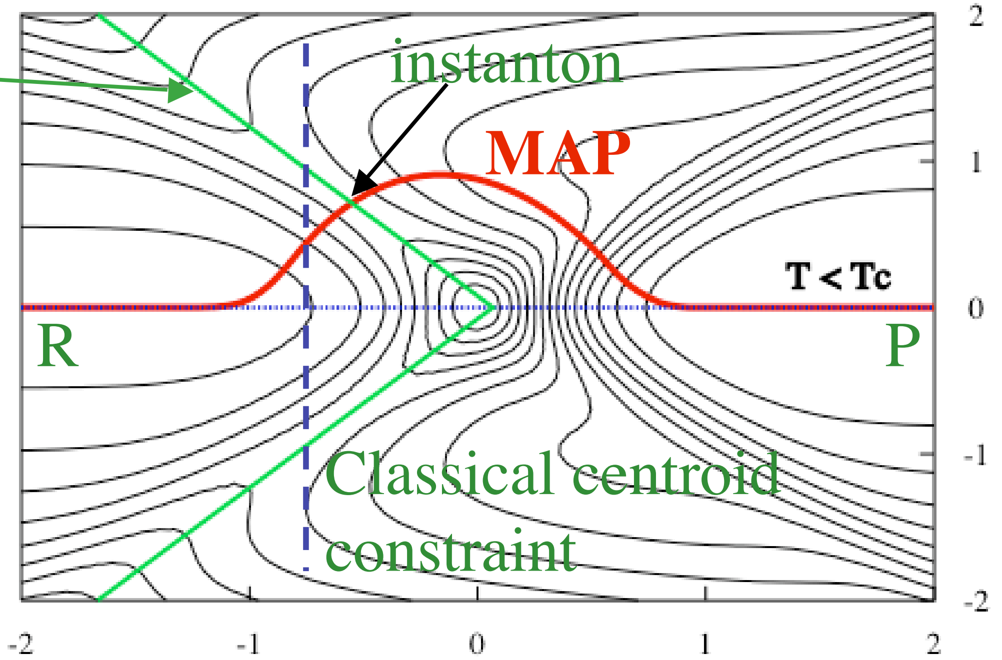
At high T, T>T$_c$, quantum delocalization (non-zero x$_1$) increases the effective potential

At high T, $T>T_c$, the Minimum Action Path (MAP) coincides with the Minimum Energy Path (MEP)

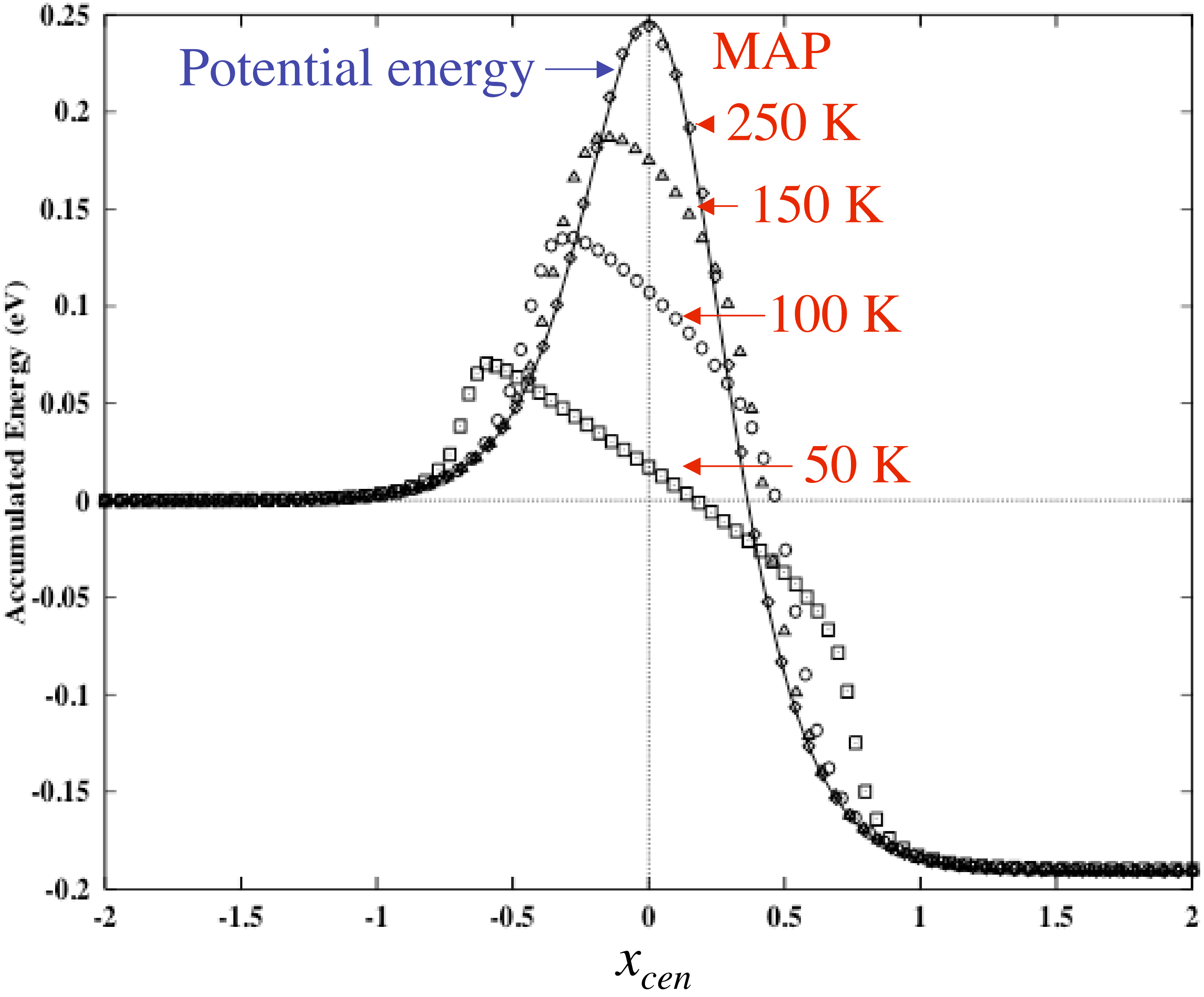


TS: conical dividing surface

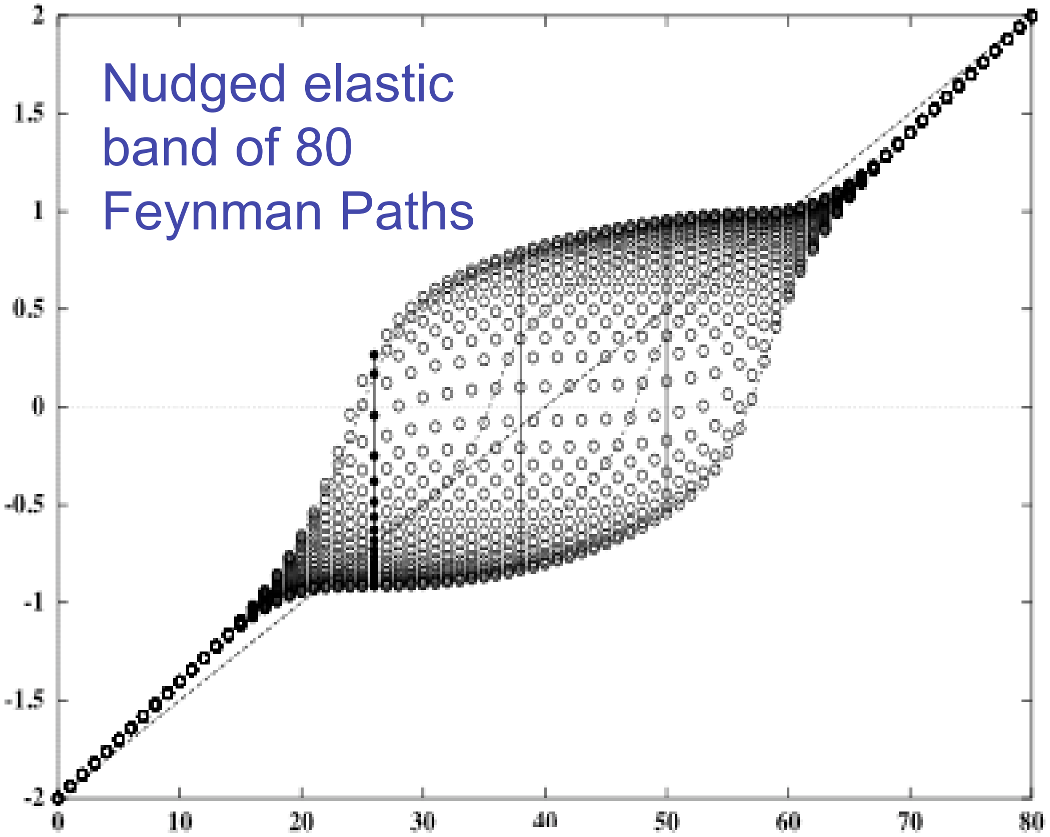
At low T, the MAP involves quantum delocalization (tunneling)



Compare the MAP with the MEP



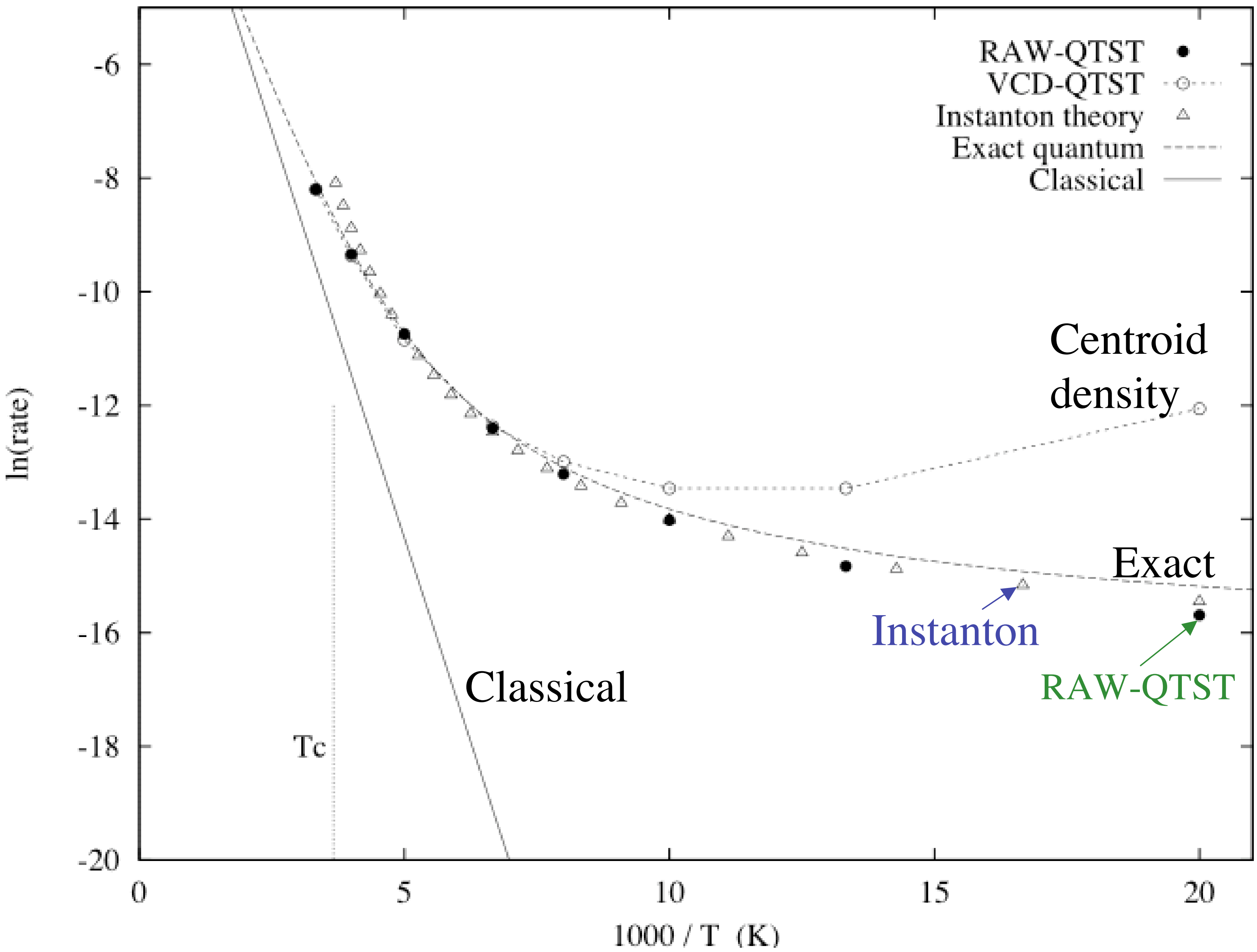
Sequence of closed Feynman paths along the MAP going from initial to final state



Nudged elastic band of 80 Feynman Paths

Final state

Initial state

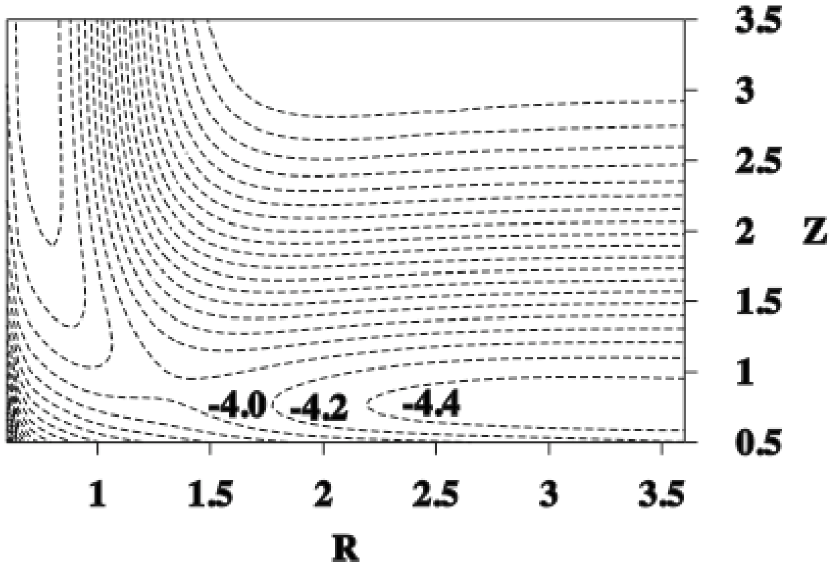

RAW-QTST
VCD-QTST
Instanton theory
Exact quantum
Classical
Centroid density
Exact
Instanton
RAW-QTST
Classical
Tc
ln(rate)
-6
-8
-10
-12
-14
-16
-18
-20
0
5
10
15
20
1000 / T (K)

Another example: Adsorption/desorption of H_2 on Cu(110)

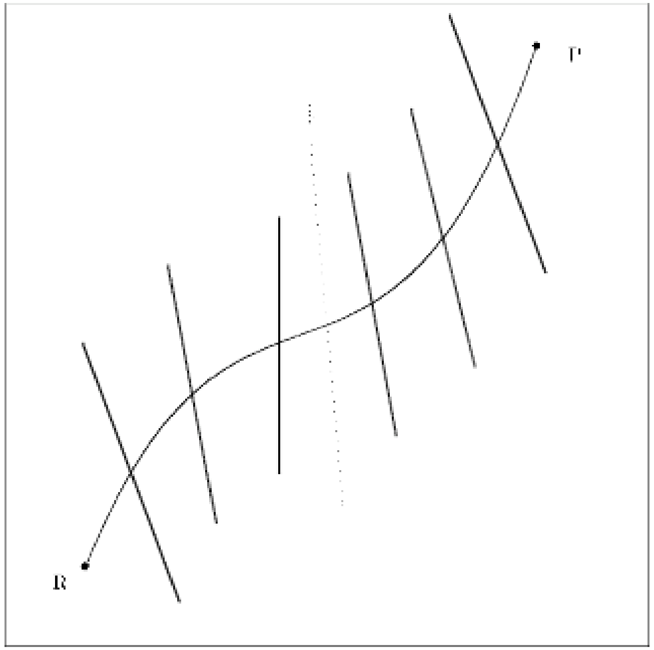
Mills, Jónsson & Schenter

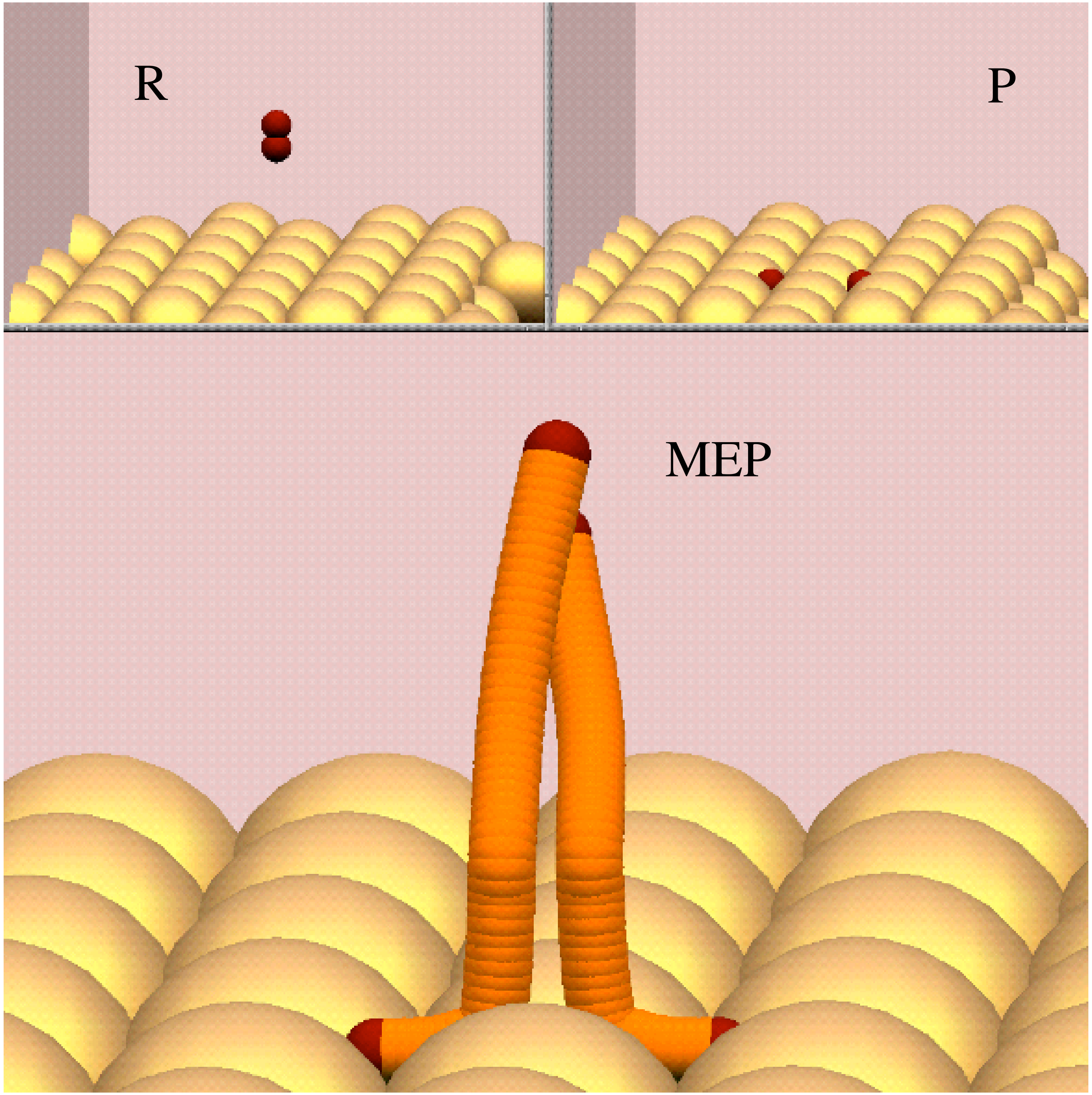
Surf. Sci. **324**, 305 (1995)

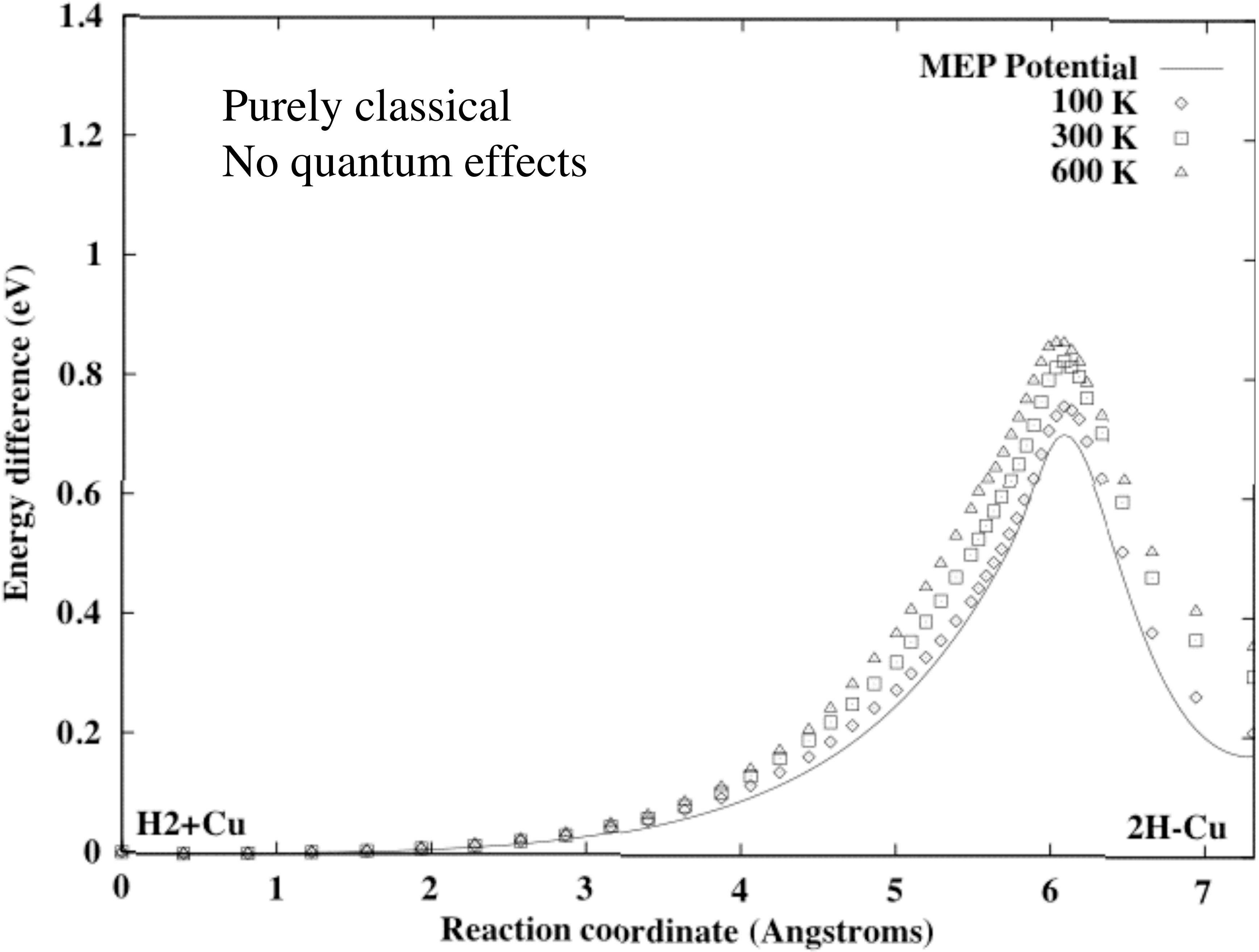
PES: Empirical potential of the EAM type where the H-Cu interaction is fitted to the LEPS potential of Depristo *et al.*



Method: Evaluating the reversible work required to shift the system [where the centroid is confined to a (3N-1) dimensional surface] from reactants towards products



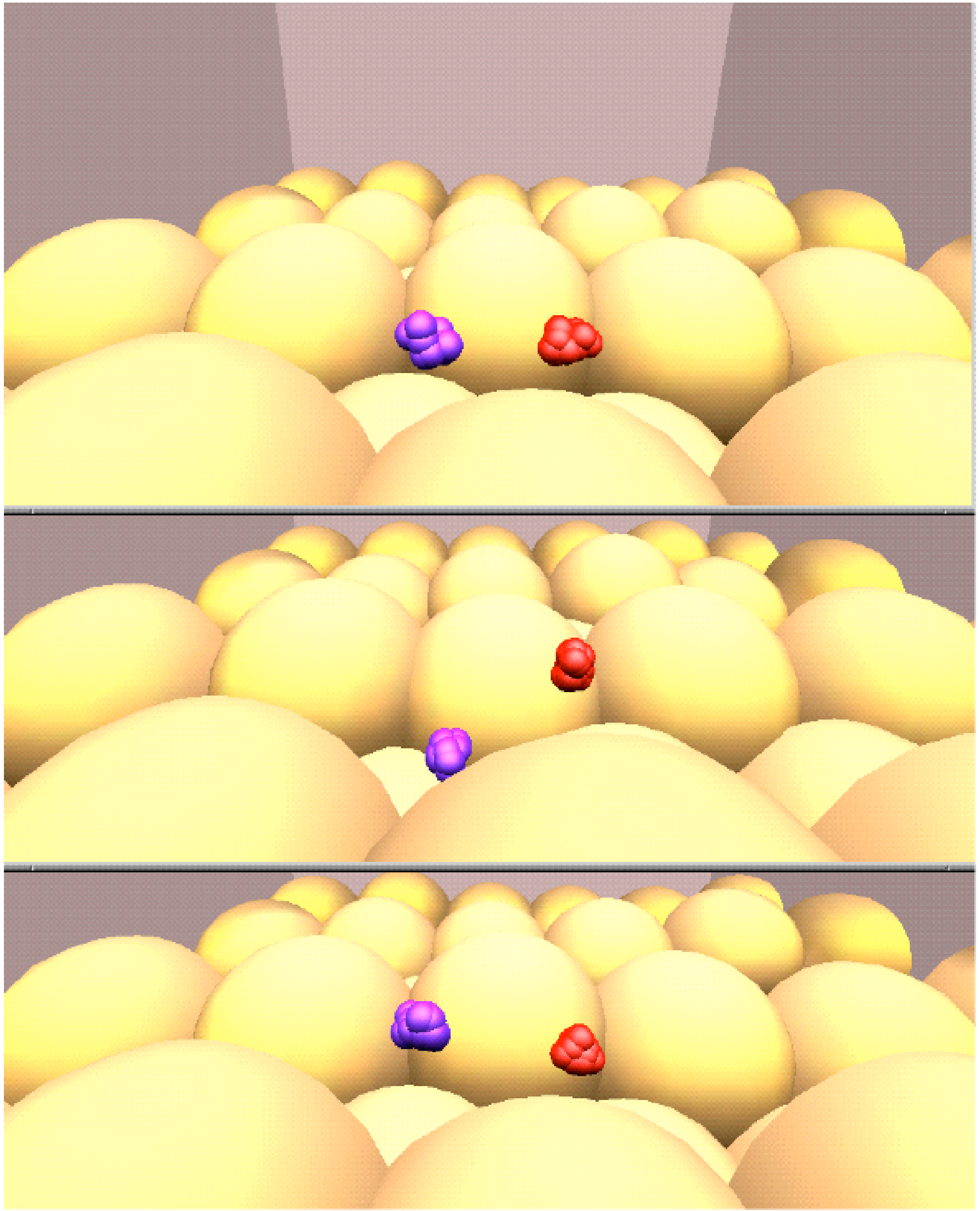

R
P
MEP

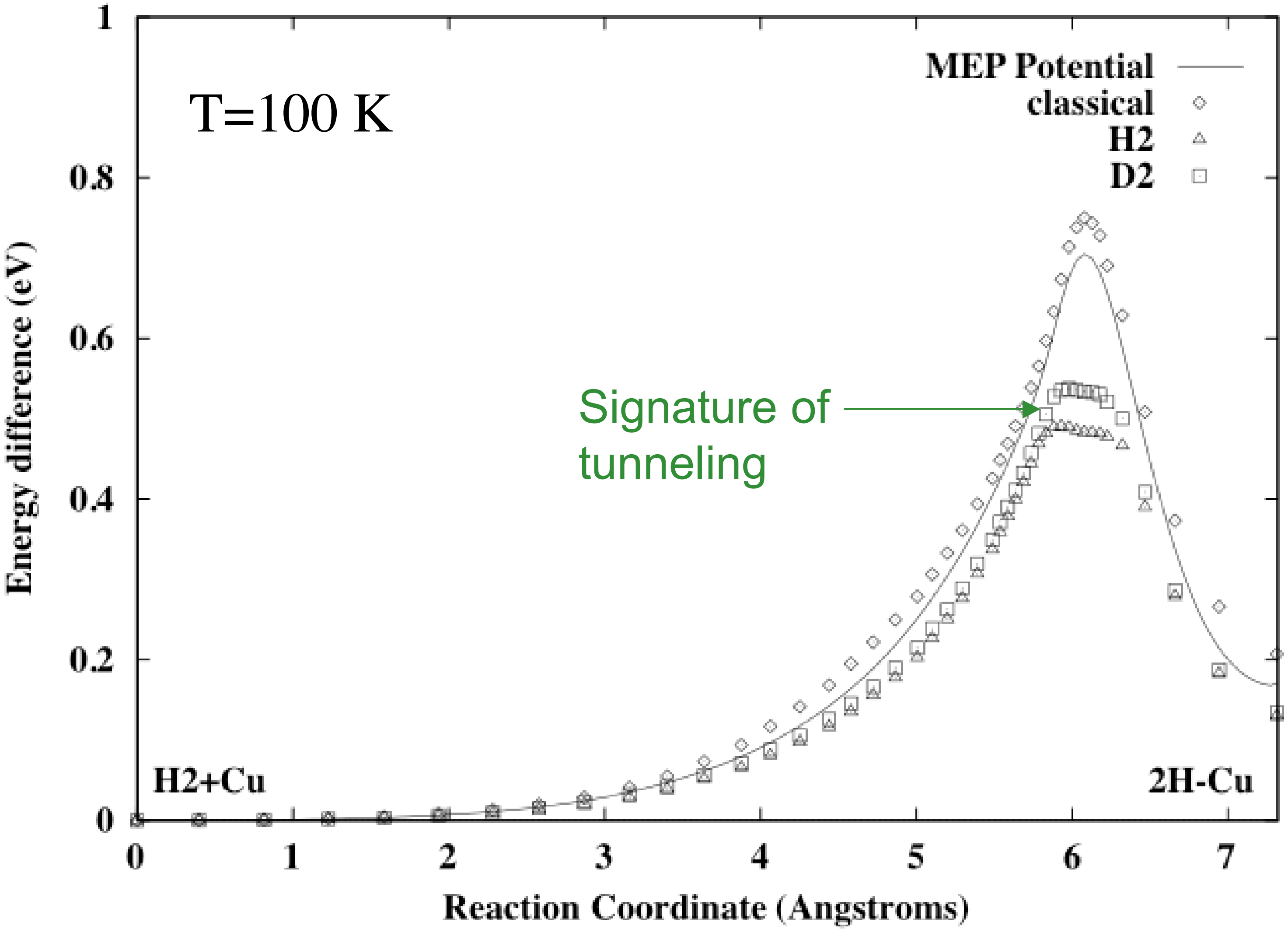


Purely classical
No quantum effects

Transition state for dissociative adsorption at T=600 K

Three snapshots from thermal sampling of TS (which includes 5 degrees of freedom)

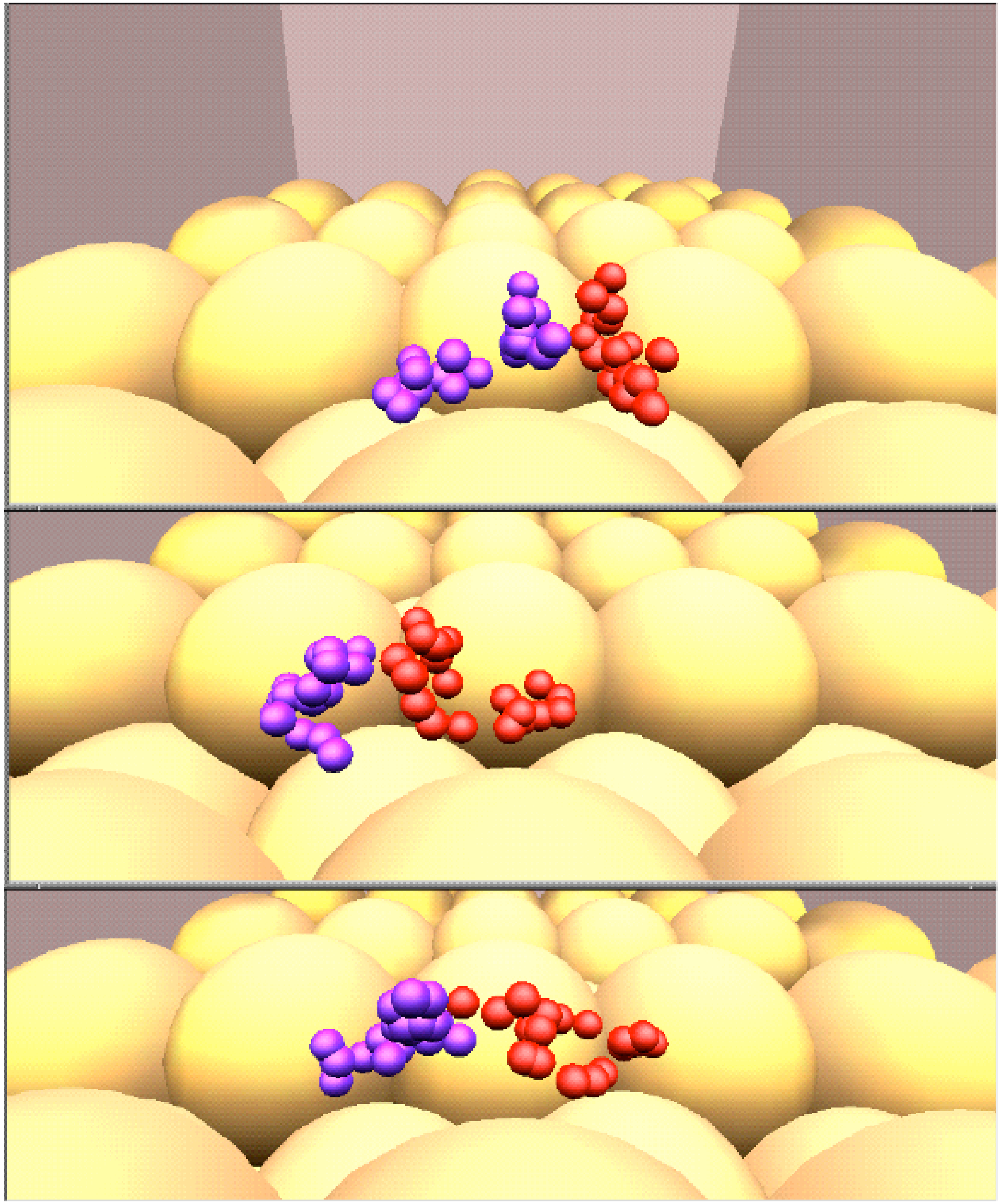


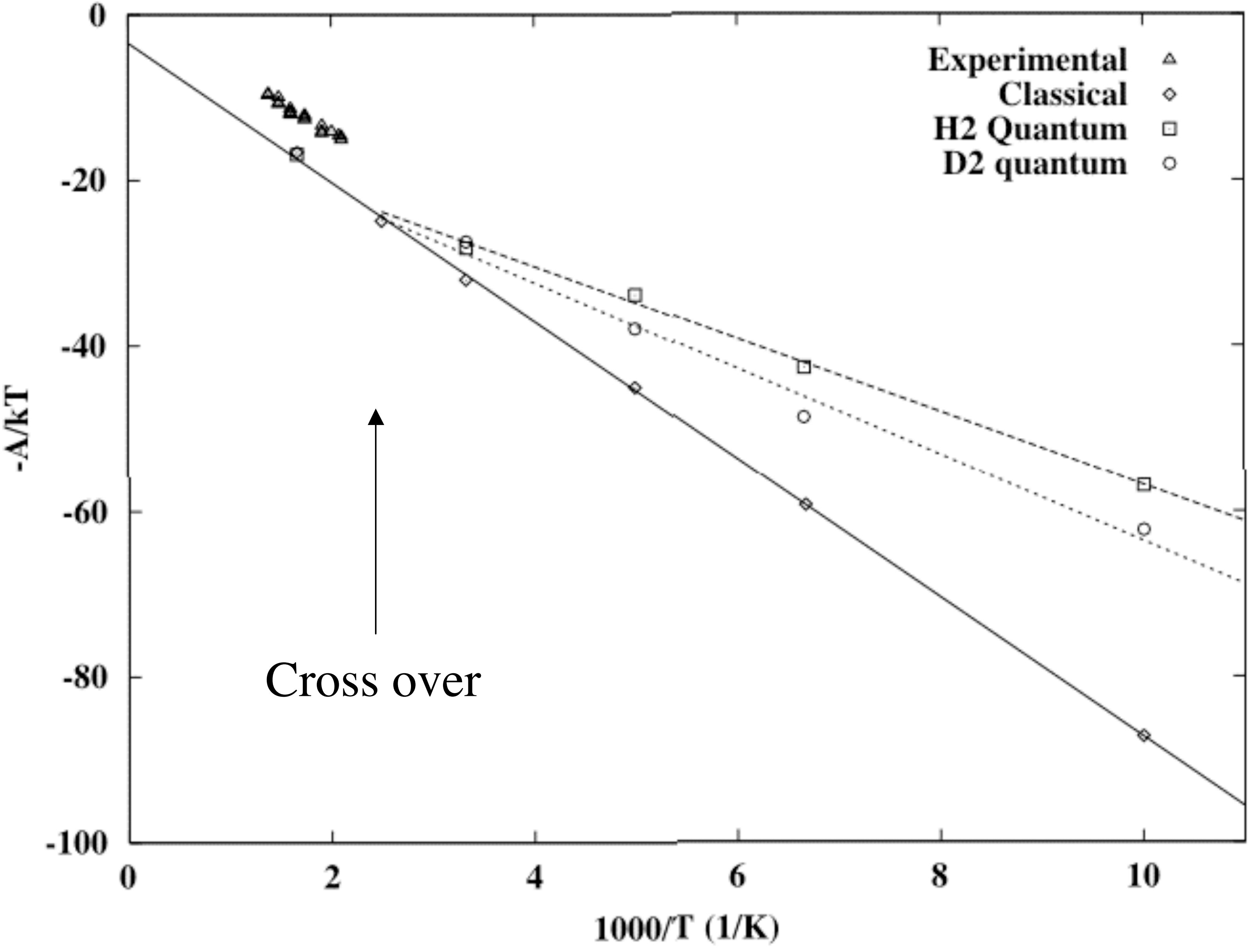


Signature of tunneling

Transition state at T=100 K, Strong quantum effects

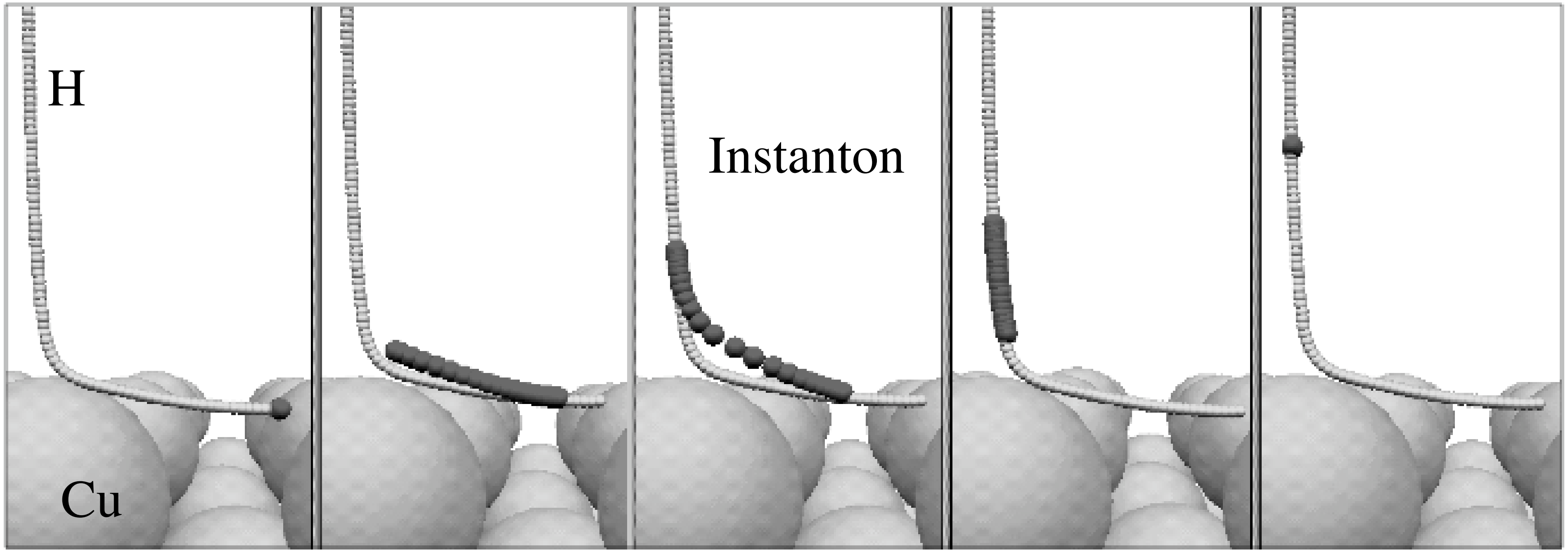
Three snapshots from thermal sampling of TS (which includes 5 degrees of freedom)




0
-20
-40
-60
-80
-100
-A/kT
0
2
4
6
8
10
1000/T (1/K)
Experimental △
Classical ◇
H2 Quantum □
D2 quantum ○

Cross over

T = 100 K: Minimum action path for H_2 adsorption/desorption from Cu(110)



(only one of the two H-atoms is shown)

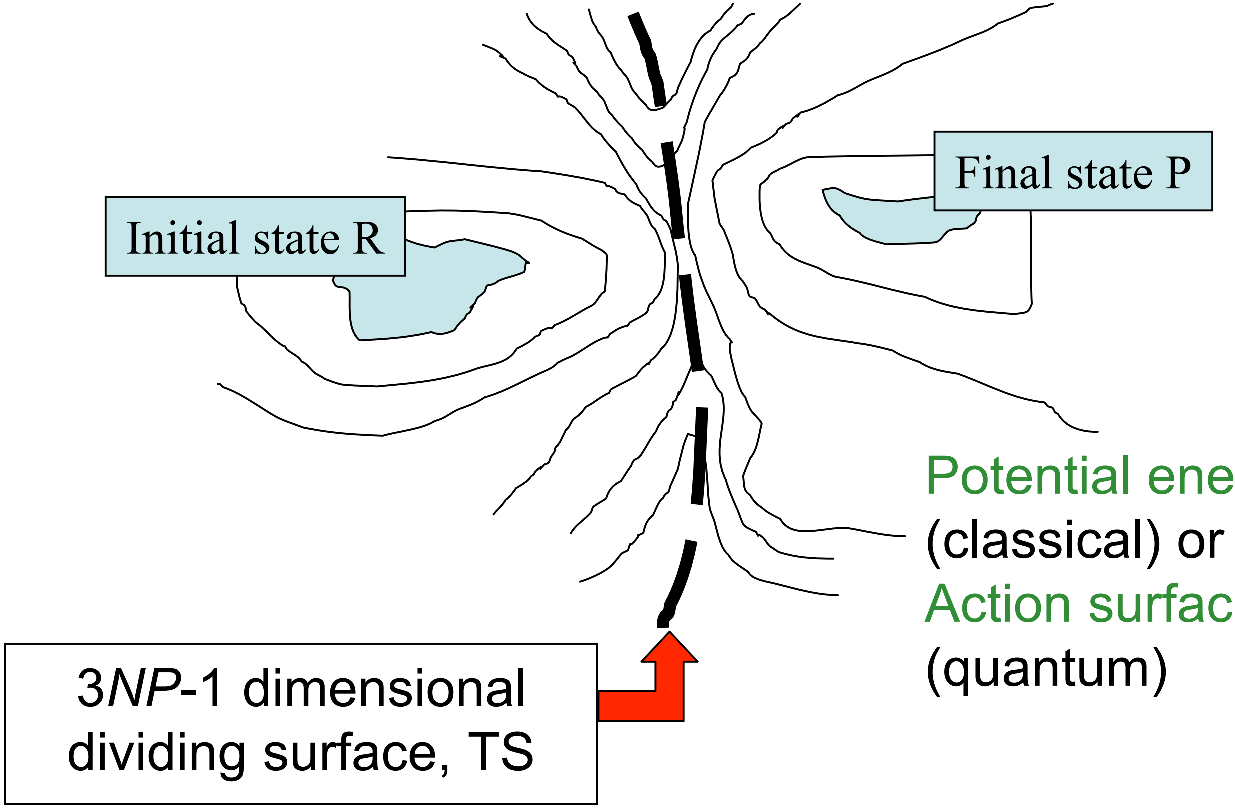
Your tool box

Hierarchy of methods for finding transition rates

	Full sampling	Harmonic approximation
Classical	Variational TST: Need to find the optimal 3N-1 dimensional dividing surface or do reversible work calculations	Harmonic TST: Need to find all relevant saddle points on the rim surrounding the initial state and a normal mode analysis
Quantum	VCs: Find optimal quantum TS using centroid constraint RAW-QTST: Do reversible work calculations with V_{eff}	Harmonic QTST: Find the instanton and its vibrational frequencies

Main ideas of (Q)TST

Identify a $3NP-1$ ($P>1$:quantum, $P=1$:classical) dimensional dividing surface, a Transition State (TS), that represents a **bottle neck** for going from an initial to a final state:



Initial state R

Final state P

$3NP-1$ dimensional dividing surface, TS

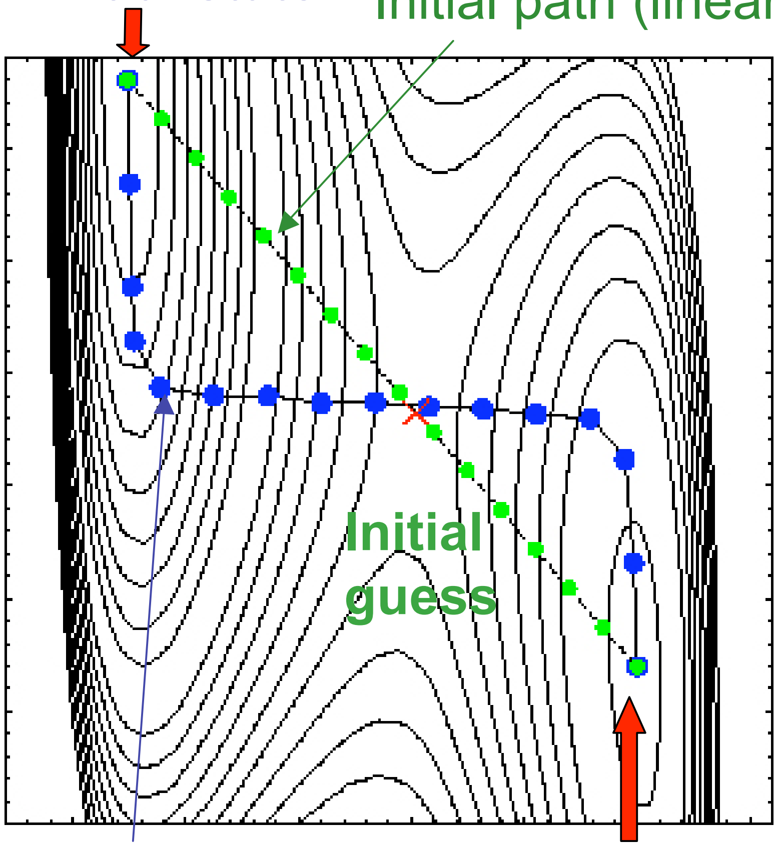
Potential energy surface (classical) or Action surface (quantum)

k^{TST} = (probability of being in TS) • (flux out of TS)

Saddle point and reaction path searching

Chain of state methods (multiple images)

Nudged Elastic Band (NEB) Method



Initial state

Initial path (linear)

Initial guess

Relaxed path (MEP)

Final state

Spring force between images of system:

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

Effective force on each image:

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

tangent along path

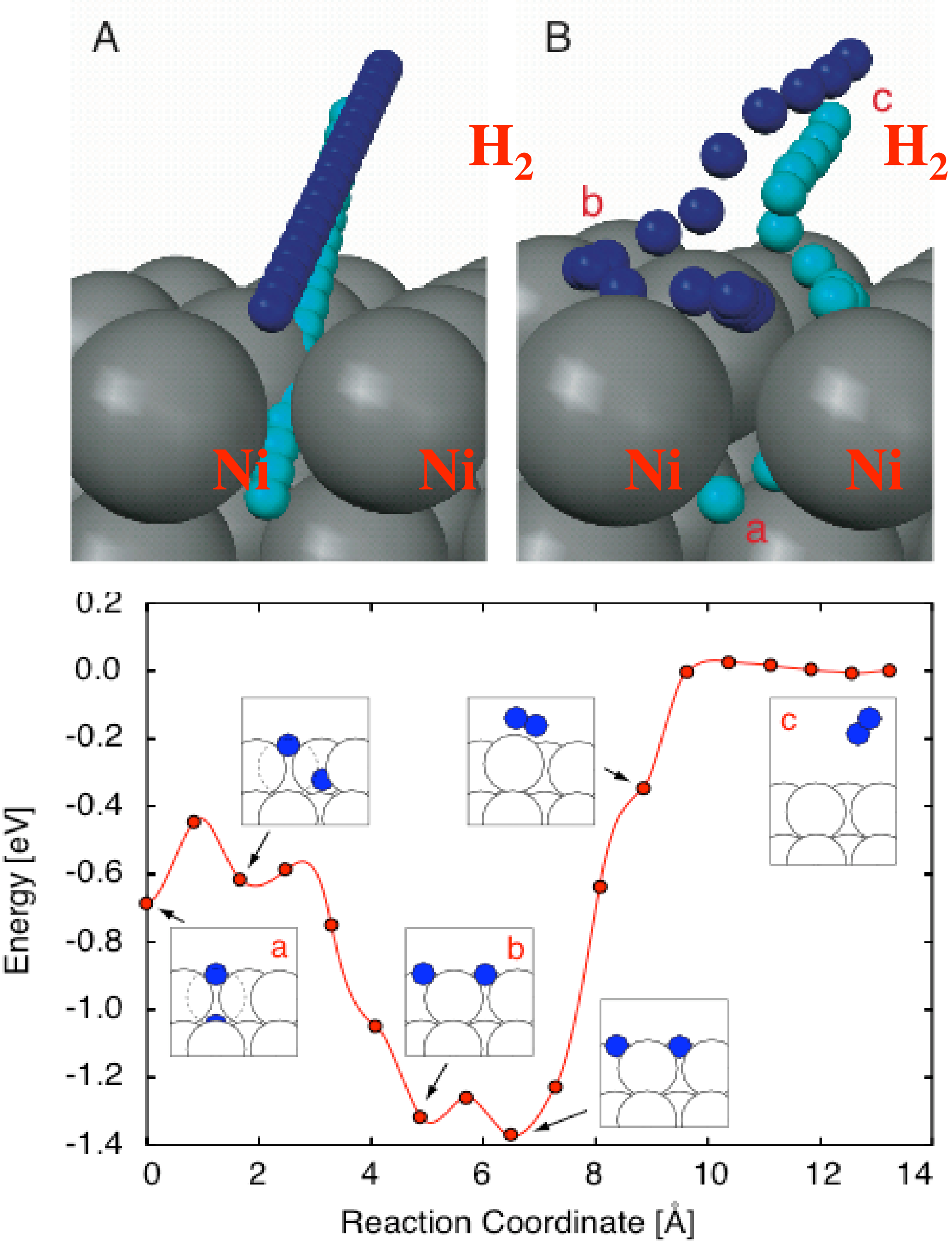
where the perpendicular force is

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

Mills, Jónsson & Schenter, *Surf. Sci.* **324**, 305 (1995)
Henkelman & Jónsson, *J. Chem. Phys.* **113**, 9978 (2000)

An example:

Associative desorption of H_2 from Ni(111) starting with a suburface 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 direct association!

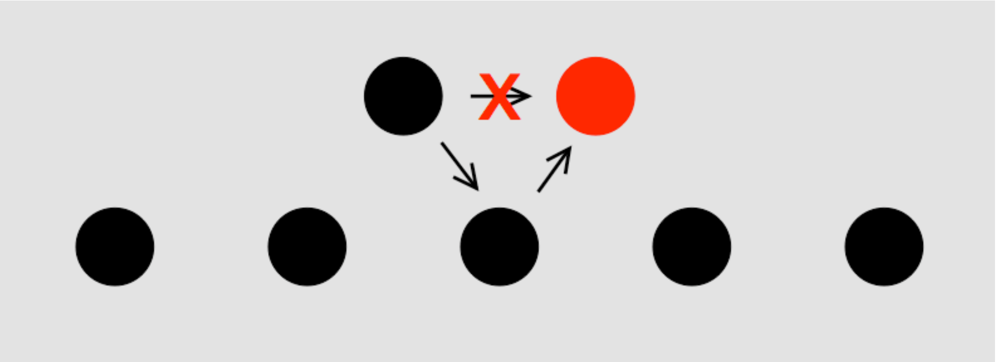
Min-mode and all mode methods (single image):

A comparison of methods for finding saddle points without knowledge of the final states

Olsen, Kroes, Henkelman, Arnaldsson & Jónsson,
J. Chem. Phys. 121, 9776 (2004)

Why bother?

- We obviously want to be able to locate saddle points! How else could we study the details of a chemical reaction?
- And: Feibelman, *Phys. Rev. Lett.* ***65***, *729 (1990)*



Do not always want to impose our prejudice on which direction the saddle point search should take! NEB will get this wrong unless you start with the correct final state (while OH-TST will work)

In the next 30 minutes:

- Some methods that will do the job
- The model test systems
- Which method is the better one?
- The stuff you should remember
- and what should be done next?

Some methods that will do the job

- Modified Newton-Raphson, all mode following methods
  - RFO with exact Hessian (2nd derivative matrix)
  - RFO with approximate Hessian
- Minimum mode following methods
  - Lanczos
  - Dimer
- Hybrid RFOs, a combination of all mode and minimum mode following methods

An all mode following method: Rational Function Optimization

- $$V(\mathbf{x}_{\text{new}}) - V(\mathbf{x}_{\text{old}}) = \frac{\mathbf{g}^t \Delta\mathbf{x} + \frac{1}{2}\Delta\mathbf{x}^t \mathbf{H} \Delta\mathbf{x}}{1 + \Delta\mathbf{x}^t \mathbf{S} \Delta\mathbf{x}}$$

- $$\Delta x_i = -\frac{g_i}{\lambda_i - \gamma_i}$$ (Eigenvector following)

$$\mathbf{S} = \begin{bmatrix} \gamma_1 & 0 & . & . \\ 0 & \gamma_2 & . & . \\ . & . & . & 0 \\ . & . & 0 & \gamma_n \end{bmatrix}$$

$\{\lambda_i, \mathbf{v}_i\}$ eigenpairs of $\mathbf{H}$

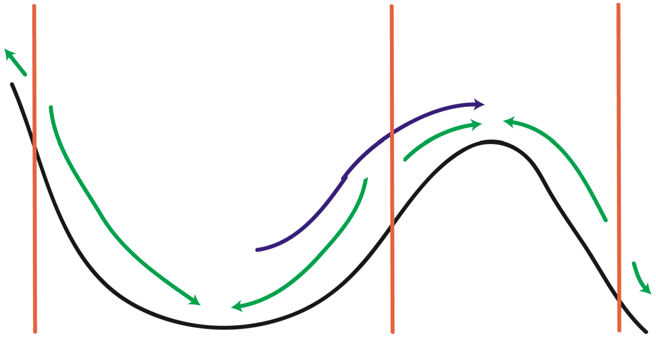
$$\Delta\mathbf{x} = \sum_{i=1}^{n} \Delta x_i \mathbf{v}_i \;, \; \mathbf{g} = \sum_{i=1}^{n} g_i \mathbf{v}_i$$

Rational Function Optimization

- A simple example:

$$\Delta x_i = -\frac{g_i}{\lambda_i} \text{ for } \gamma_i = 0$$

Well-known Newton-Raphson
Steps to closest extremal point



- Our choice:

$$\Delta x_i = -\frac{g_i}{\lambda_i - \gamma_i} \;,\; \lambda_1 - \gamma_1 < 0 \;,\; \lambda_i - \gamma_i > 0 \text{ for } i > 1$$

A PES walker that moves uphill along the lowest eigenmode and downhill along all other modes

Actually: $\lambda_i - \gamma_i = \frac{1}{2} d_i \left[|\lambda_i| + \sqrt{\lambda_i^2 + 4 g_i^2} \right], \; d_1 = -1, \; d_{i \neq 1} = 1$

The Hessian within RFO

- Exact Hessian available (for the moment we don't care how it is obtained)
- Calculate an approximate Hessian based on the gradient and step vectors:

$$\Delta \mathbf{x} = \mathbf{x}_{\text{new}} - \mathbf{x}_{\text{old}}, \; \Delta \mathbf{g} = \mathbf{g}_{\text{new}} - \mathbf{g}_{\text{old}}$$

$$\mathbf{H}_{\text{new}} = \mathbf{H}_{\text{old}} + \Delta \mathbf{H}$$

$$\Delta \mathbf{H}^{\text{Powell}} = \frac{(\Delta \mathbf{g} - \mathbf{H}_{\mathbf{old}} \Delta \mathbf{x}) \bullet \Delta \mathbf{x}^{t} + \Delta \mathbf{x} \bullet (\Delta \mathbf{g} - \mathbf{H}_{\mathbf{old}} \Delta \mathbf{x})^{t}}{\Delta \mathbf{x}^{t} \bullet \Delta \mathbf{x}}$$

$$- (\Delta \mathbf{g} - \mathbf{H}_{\mathbf{old}} \Delta \mathbf{x})^{t} \bullet \Delta \mathbf{x} \frac{\Delta \mathbf{x} \bullet \Delta \mathbf{x}^{t}}{(\Delta \mathbf{x}^{t} \bullet \Delta \mathbf{x})^{2}}$$

The Hessian within RFO

$$\Delta\mathbf{H}^{\text{Bofill}} = \phi^{\text{Bofill}}\Delta\mathbf{H}^{\text{SR1}} + (1-\phi^{\text{Bofill}})\Delta\mathbf{H}^{\text{Powell}}$$

$$\Delta\mathbf{H}^{\text{SR1}} = \frac{(\Delta\mathbf{g}-\mathbf{H}_{\mathbf{old}}\Delta\mathbf{x})\bullet(\Delta\mathbf{g}-\mathbf{H}_{\mathbf{old}}\Delta\mathbf{x})^{t}}{(\Delta\mathbf{g}-\mathbf{H}_{\mathbf{old}}\Delta\mathbf{x})^{t}\bullet\Delta\mathbf{x}}$$

$$\phi^{\text{Bofill}} = \frac{[(\Delta\mathbf{g}-\mathbf{H}_{\mathbf{old}}\Delta\mathbf{x})^{t}\bullet\Delta\mathbf{x}]^{2}}{[(\Delta\mathbf{g}-\mathbf{H}_{\mathbf{old}}\Delta\mathbf{x})^{t}\bullet(\Delta\mathbf{g}-\mathbf{H}_{\mathbf{old}}\Delta\mathbf{x})][\Delta\mathbf{x}^{t}\bullet\Delta\mathbf{x}]}$$

A minimum mode following approach: Using Lanczos to find minimum mode

Instead of calculating the full Hessian matrix at each geometry step the following steps can be used to obtain the lowest eigenpair:

1. $$\mathbf{q}_k = \frac{\mathbf{r}_{k-1}}{\beta_{k-1}}$$
$$\mathbf{u}_k = \mathbf{H} \bullet \mathbf{q}_k \quad (*)$$
$$\mathbf{r}_k = \mathbf{u}_k - \beta_{k-1}\mathbf{q}_{k-1}$$
$$\alpha_k = \mathbf{q}_k^t \bullet \mathbf{r}_k$$
$$\mathbf{r}_k = \mathbf{r}_k - \alpha_k \mathbf{q}_k$$
$$\beta_k = \left\|\mathbf{r}_k\right\|$$

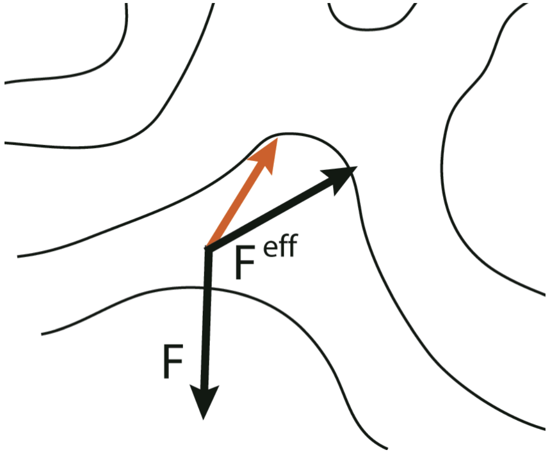
1a. $$\mathbf{u}_k = \frac{\mathbf{g}(\mathbf{x}_k) - \mathbf{g}(\mathbf{x}_{\text{current}})}{\delta x_{\text{L}}}$$
$$\mathbf{x}_k = \mathbf{x}_{\text{current}} + \delta x_{\text{L}} \mathbf{q}_k$$

2. $$\mathbf{T}_j = \begin{bmatrix} \alpha_1 & \beta_1 & & \\ \beta_1 & \alpha_2 & . & \\ & . & . & \beta_{j-1} \\ & & \beta_{j-1} & \alpha_j \end{bmatrix}$$

3. Diagonalize $\mathbf{T}_j$: $\{\lambda_1, \mathbf{v}_1\}$ of $\mathbf{H}$

Stepping with minimum mode

Only minimum eigenmode known, can not do eigenvector following as in the RFO case, but:



$$\mathbf{F}^{\text{effective}} = \begin{cases} -(\mathbf{F} \bullet \mathbf{v}_1)\mathbf{v}_1 & \text{if } \lambda_1 > 0 \\ \mathbf{F} - 2(\mathbf{F} \bullet \mathbf{v}_1)\mathbf{v}_1 & \text{if } \lambda_1 < 0 \end{cases}$$

determines the direction of the walk, and

$$\Delta\mathbf{x} = -\frac{\mathbf{F}^{\text{effective}}}{C},\ C \text{ is curvature along } \mathbf{F}^{\text{effective}}$$

Another minimum mode approach: Using a dimer to find minimum mode

- Two images of the system (the dimer) can be used to find the lowest eigenvector and eigenvalue, since

$$V_D = V(\mathbf{x}_1) + V(\mathbf{x}_2)$$

is minimized when the dimer is oriented along the lowest eigenvector!

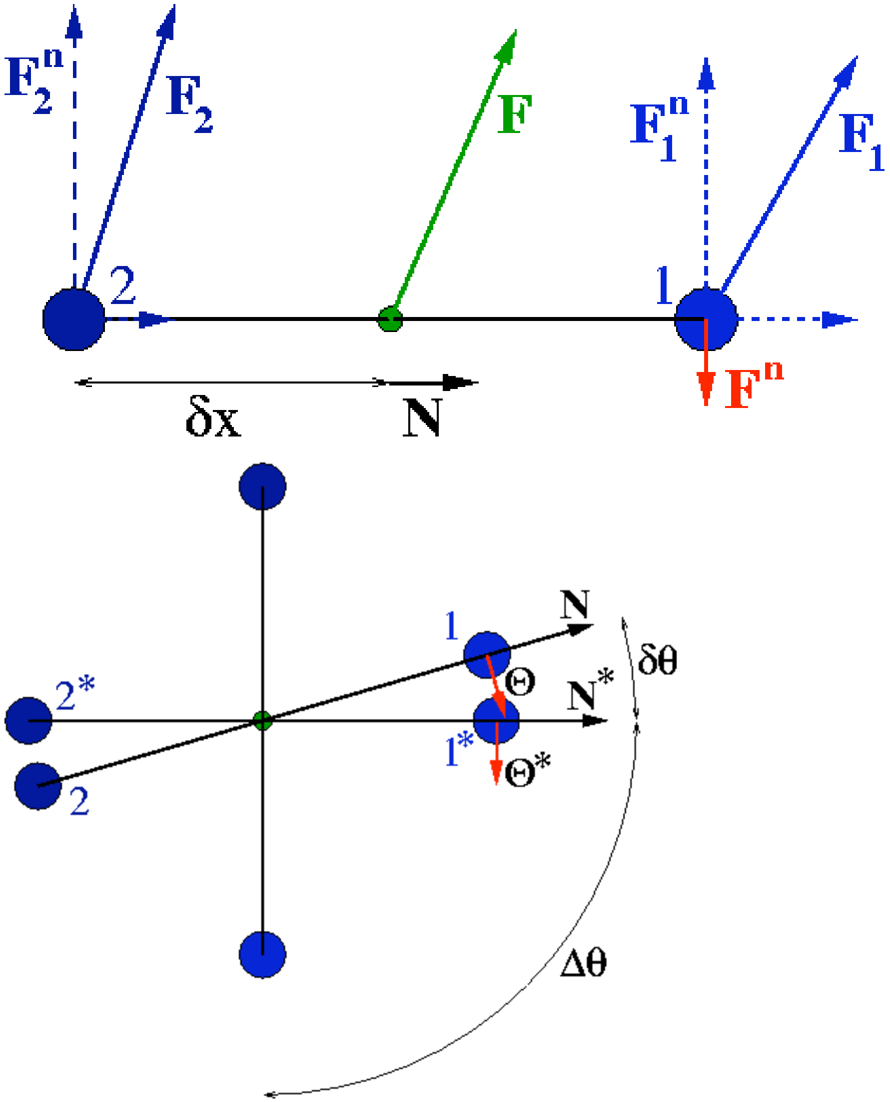
- The dimer: $\mathbf{x}_1 = \mathbf{x} + \delta x_D \mathbf{N}$

$$\mathbf{x}_2 = \mathbf{x} - \delta x_D \mathbf{N}$$

- Stepping is done as for the Lanczos method

Dimer details

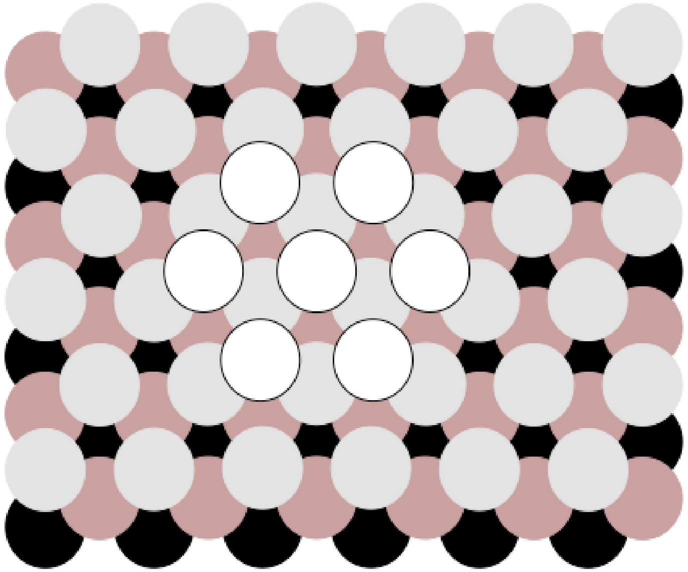
1. $\mathbf{x}_1 = \mathbf{x} + \delta x\mathbf{N}, \mathbf{x}_2 = \mathbf{x} - \delta x\mathbf{N}; \quad \mathbf{F}, \mathbf{F}_1$
2. $\mathbf{F}_2 = 2\mathbf{F} - \mathbf{F}_1; \quad \mathbf{F}_i^n = \mathbf{F}_i - (\mathbf{F}_i \bullet \mathbf{N})\mathbf{N}$
3. $\mathbf{F}^n = (\mathbf{F}_1^n - \mathbf{F}_2^n)/\delta x; \quad \Theta = \mathbf{F}^n / \left\|\mathbf{F}^n\right\|$
4. $\mathbf{N},\Theta \xrightarrow{\delta\theta} \mathbf{N}^*,\Theta^*$
5. $\mathbf{x}_1^* = \mathbf{x} + \delta x\mathbf{N}^*, \mathbf{x}_2^* = \mathbf{x} - \delta x\mathbf{N}^*; \quad \mathbf{F}_1^*$
6. $\mathbf{F}_2^* = 2\mathbf{F} - \mathbf{F}_1^*; \quad \mathbf{F}_i^{*n} = \mathbf{F}_i^* - (\mathbf{F}_i^* \bullet \mathbf{N}^*)\mathbf{N}^*$
7. $\mathbf{F}^{*n} = (\mathbf{F}_1^{*n} - \mathbf{F}_2^{*n})/\delta x$
8. $F = (\mathbf{F}^{*n} \bullet \Theta^* + \mathbf{F}^n \bullet \Theta)/2$
9. $F' = (\mathbf{F}^{*n} \bullet \Theta^* + \mathbf{F}^n \bullet \Theta)/\delta\theta$
10. $\Delta\theta = -\frac{1}{2}\arctan\left(\frac{2F}{F'}\right) - \delta\theta/2$



Hybrid RFOs

- In convex region (all Hessian eigenvalues positive) only use the lowest eigenmode and step like the Lanczos and Dimer methods
- Outside convex region use the step as calculated by the RFO method

Model systems



6 layer slab, each layer 56 atoms
7 atoms island on top of the slab
Parameters chosen for Pt(111)

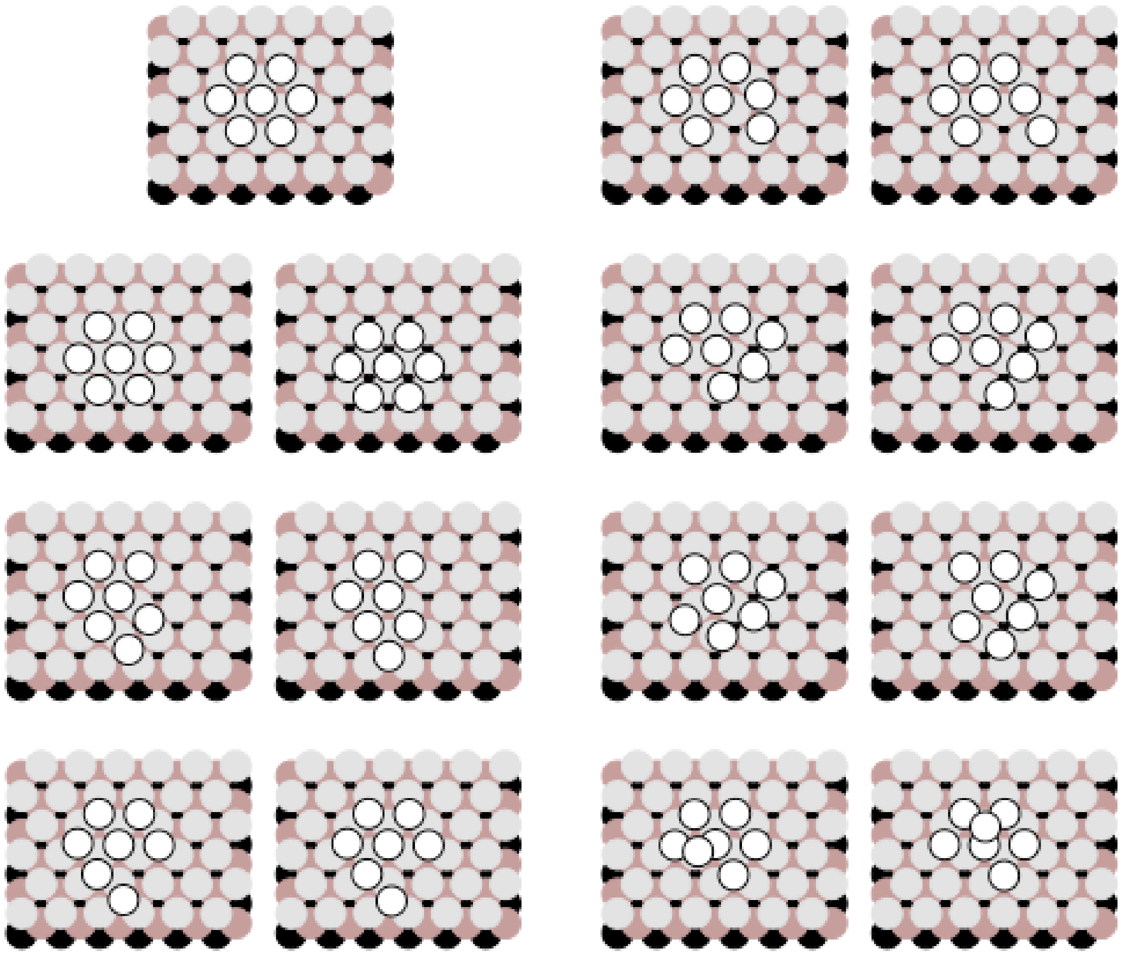
- 175 atoms free to move, 525D PES
- 7 atoms free to move, 21D PES
- 1 atom free to move, 3D PES

$$V(r) = D_e\left(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\right)$$

$$\alpha = 1.6047\ \mathring{\mathrm{A}}^{-1},\quad r_0 = 2.8970\ \mathring{\mathrm{A}}$$

$$\mathrm{D_e} = 0.7102\ \mathrm{eV}$$

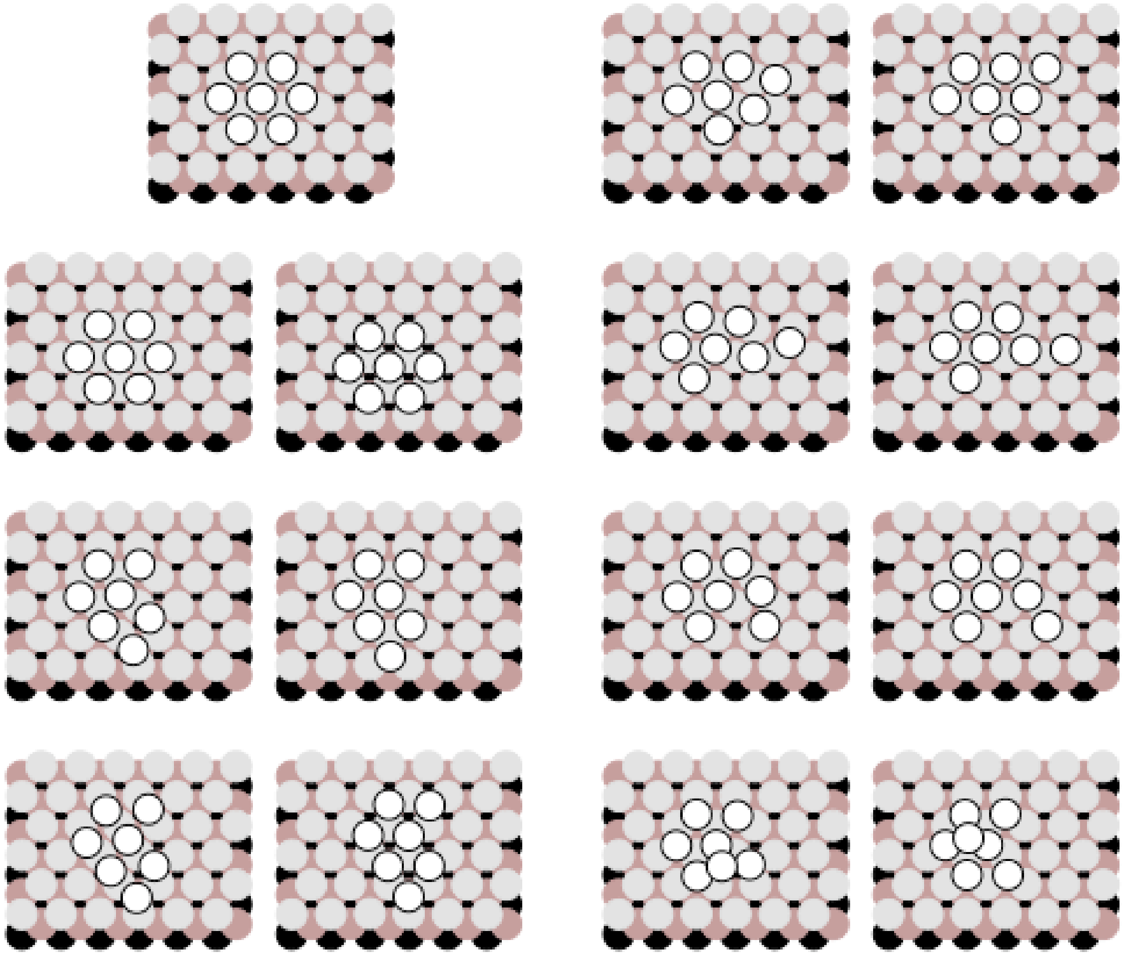
21D PES: Saddles and final states



Search results for the 21D PES

Method	$\Delta x^{max,ran}$	n^{TS}	n	$< f >$	$< s >$
Lanczos 3 iterations	0.4, 0.3	94	342	190.7	38.9
Dimer 1 rot + max rot F	0.3, 0.3	95	259	176.8	46.9
RFO, exact	0.5, 0.3	59	470	11.9	
Hybrid RFO, exact	0.5, 0.3	68	458	12.1	
RFO, Bofill	0.2, 0.1	10	500	47.8	
exact initial **H**	0.2, 0.1	13	497	36.8	
exact initial **H**	0.2, 0.3	60	402	73.9	
Hybrid RFO, Bofill	0.2, 0.1	10	492	50.1	
exact initial **H**	0.2, 0.1	35	470	39.1	
exact initial **H**	0.2, 0.3	65	289	71.9	

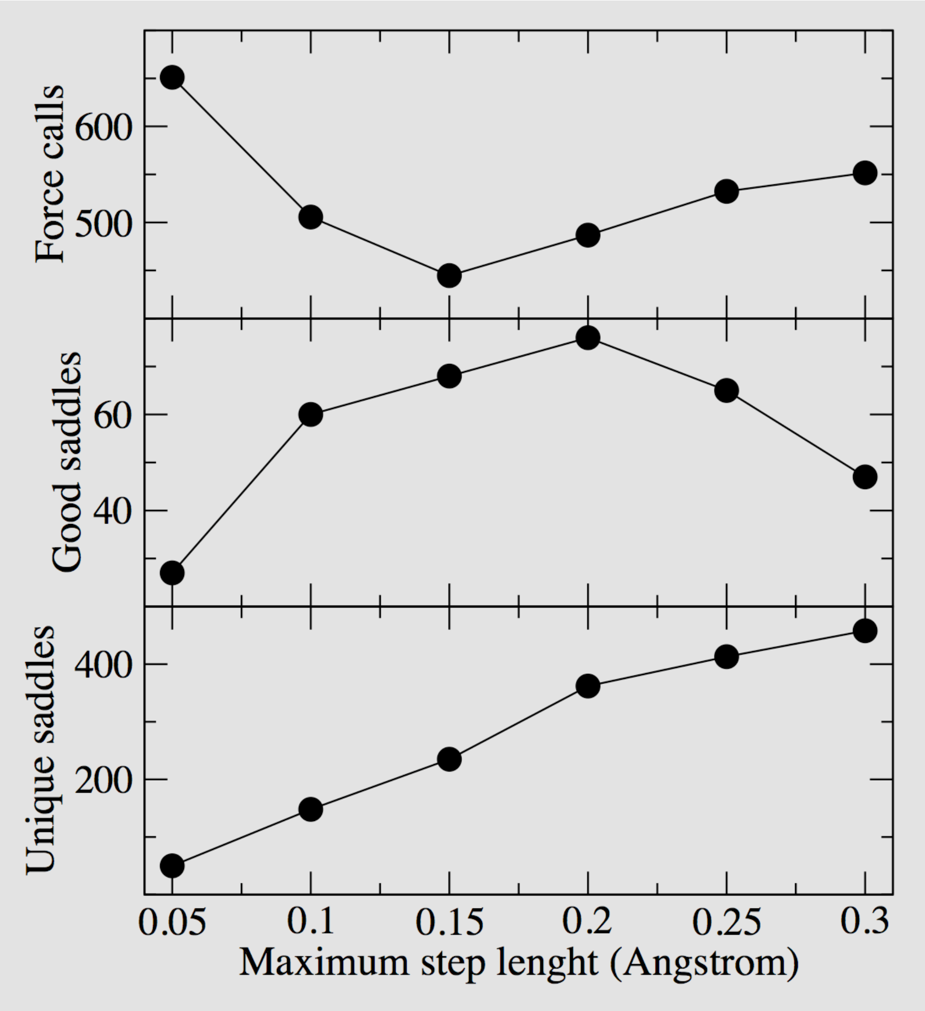
525D PES: Saddles and final states



Search results for the 525D PES

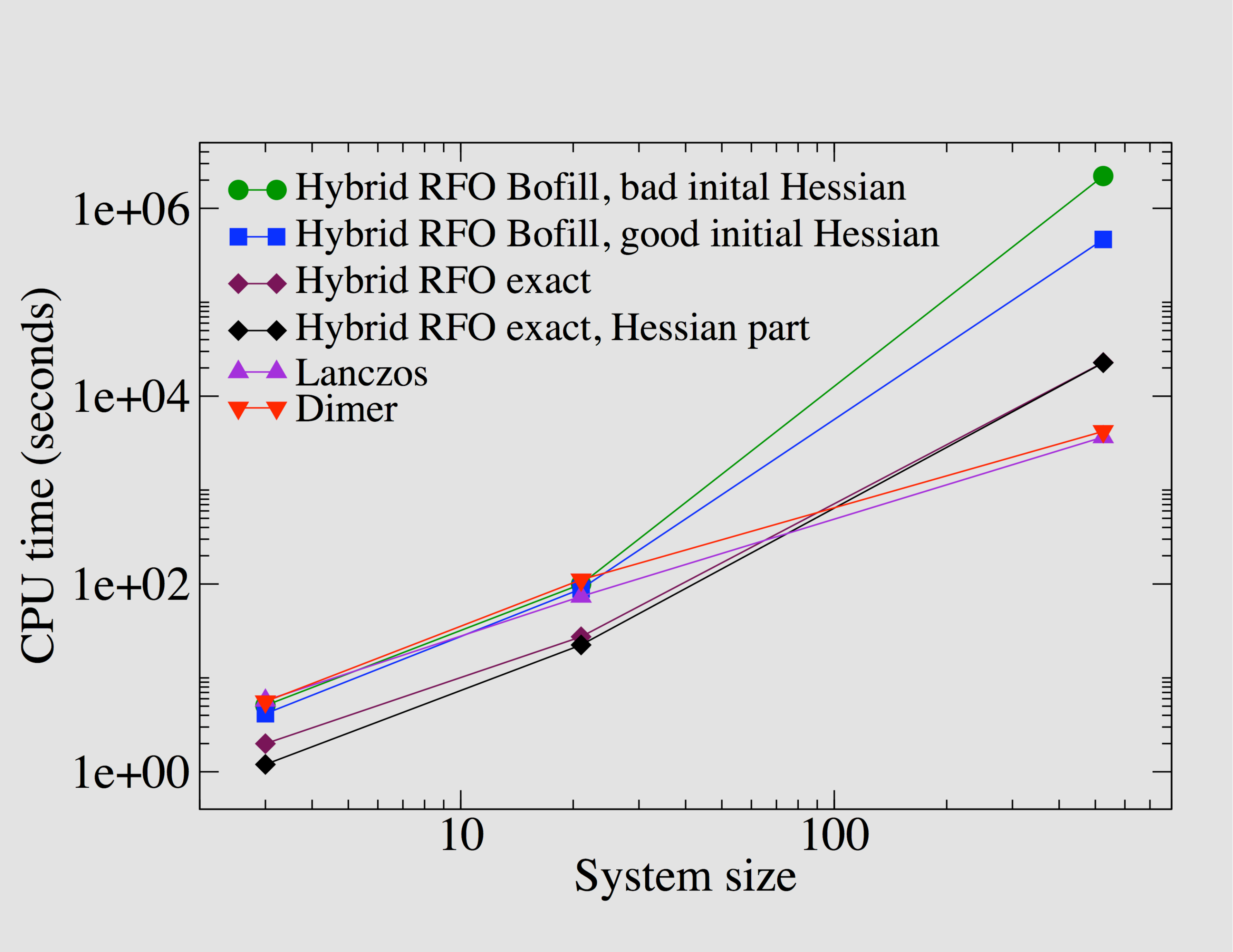
Method	$\Delta x^{max,ran}$	n^{TS}	n	< f >	< s >
Lanczos					
4 iterations	0.5, 0.3	86	210	372.1	72.7
Dimer					
1 rot + max rot F	0.15, 0.3	78	276	335.1	87.8
RFO, exact	0.5, 0.3	45	413	19.1	
Hybrid RFO, exact	0.5, 0.3	58	411	17.1	
RFO, Bofill	0.2, 0.1	16	353	1286.6	
exact initial **H**	0.2, 0.1	10	432	342.6	
exact initial **H**	0.1, 0.3	27	474	539.2	
Hybrid RFO, Bofill	0.2, 0.1	17	294	1224.3	
exact initial **H**	0.2, 0.1	15	380	291.4	
exact initial **H**	0.1, 0.3	30	406	465.2	

The most important parameter: Maximum step length



- 525D PES
- Dimer method
- 1 rotation

Computational effort



What you should remember…

	Cheap force		Expensive force	
System size	Lowest Saddles	All Saddles	Lowest Saddles	All Saddles
Small / Medium	(H)RFO exact	Minimum mode or (H)RFO exact	(H)RFO Bofill	Mininum mode or (H)RFO Bofill
Large	Minimum mode	Minimum mode	Minimum mode or (H)RFO Bofill	Minimum mode

and this, too…

- Minimum mode: Limit iterations
- Use “standard” minimum mode settings
  Just as easy to used as traditional RFOs
- Control searches by maximum step length
  and starting position

…what still needs to be done

- Third order search algorithms
- Combine interpolation and search methods
- How does the different methods handle noise?
- Repeat comparison for a more “chemical” system
  Are there inherent differences between solid state and gas phase chemistry PES walking?

Exercises

- TST can not treat systems where there is a change in the electronic state during the reaction.
  Why is this?
- Can the grand canonical and isothermal-isobaric ensembles be use to build TST? If yes, why, and what would happen to the calculated rate? Would one of the ensembles give a more accurate result? If no, why not?
- Can you argue why a simple zero point energy correction where $E_a = V_{SP} - V_{\min}$ is replaced with

  $$E_a = \left(V_{SP} + \sum_{i=1}^{D-1} \frac{h\nu_{\ddagger,i}}{2} \right) - \left(V_{\min} + \sum_{i=1}^{D} \frac{h\nu_{R,i}}{2} \right)$$

  and classical partition functions used, is typically not a good approximation when calculating the rate of thermal transitions?

- How does the Feynman path integral formulation approach the classical limit? How does this compare to the traditional the quantum mechanical formulation?