Summer course in Iceland, August 2010

Calculations of thermal rates

Overview of some theoretical approaches and methods for simulating thermally activated transitions (rare events), especially in and on the surfaces of solids.

Transition state theory (TST) for thermally activated transitions

Harmonic approximation to TST

Minimum energy paths – the NEB and CI-NEB methods

Adaptive kinetic Monte Carlo for simulating time evolution (EON)

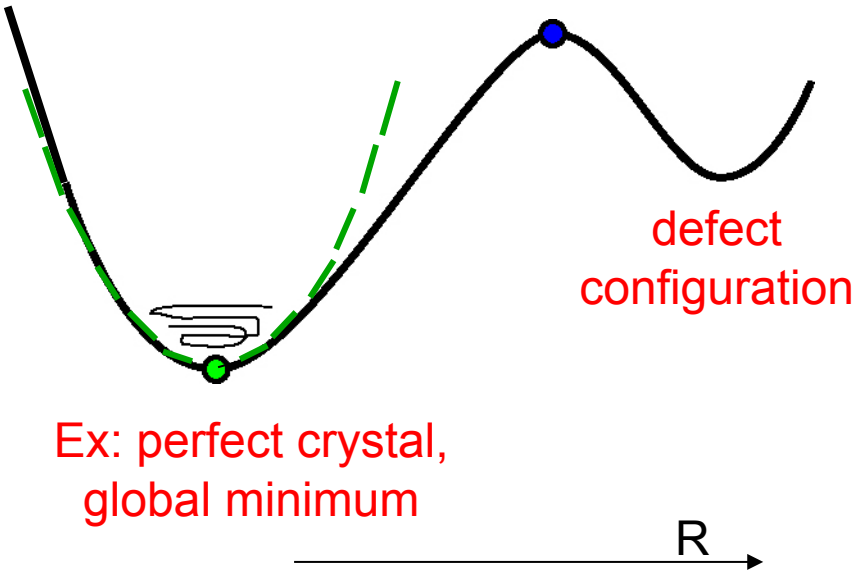
Tunneling rates obtained from harmonic quantum TST (HQTST)

Conventional approach to simulations of solids

Born-Oppenheimer (adiabatic) approximation:

1. Solve for the electronic degrees of freedom, **r**, while keeping the nuclei fixed at **R**.
   Usually done with density functional theory (DFT) using approximate functionals such as PW91 or RPBE.
   Get energy surface, E(R)

2. Solve for the motion of the nuclei. Usually with the classical approximation, F=ma, and within a harmonic approximation (----)
   $E(\mathbf{R}) \sim \frac{1}{2} k_{sp} (\mathbf{R}-\mathbf{R}_{min})^2$.



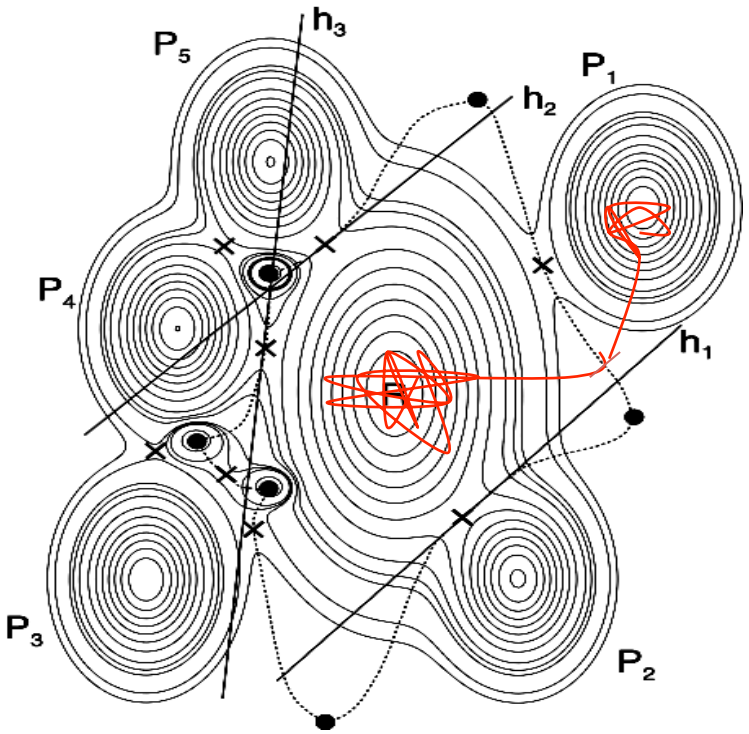
Second step in Born-Oppenheimer procedure:

II. Displacements of the atoms

Topics mentioned:

a. **Transition state theory (TST) for thermally activated transitions and WKE procedure**
b. **Harmonic approximation to TST (HTST) – easy to use with DFT**
c. **Minimum energy paths – the NEB and CI-NEB methods**
d. **Adaptive kinetic Monte Carlo for simulating time evolution**
e. **Tunneling rates obtained from harmonic quantum TST and WKB tunneling paths**

Simulate thermally activated transitions



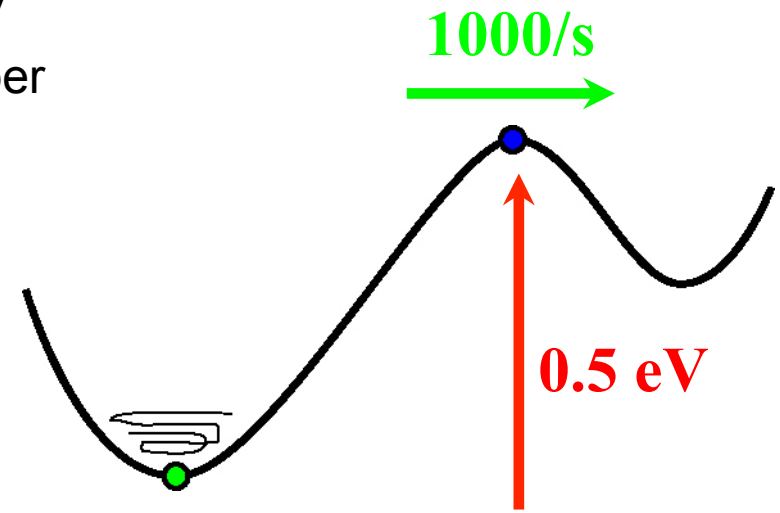
Need to take a stroll on a 3N-dimensional potential energy surface, $V(r_1,r_2, \ldots r_N)$, where N is the number of atoms, assuming Born-Oppenheimer approximation is valid.

For heavy atoms and high temperature use classical description, F=ma.
Otherwise, quantum mechanical.

Even for a classical system (where Newton is OK), a direct *dynamical* calculation of a thermal rate is *hard*

'Time scale problem':

- Most interesting transitions are rare events (i.e., much slower than vibrations). Typically there is a 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 - *fast!*
- A video of a direct classical dynamics simulation where each vibration spans a second in the video would would go on for more than a 100 years in between such reactive events - *no time for that!*

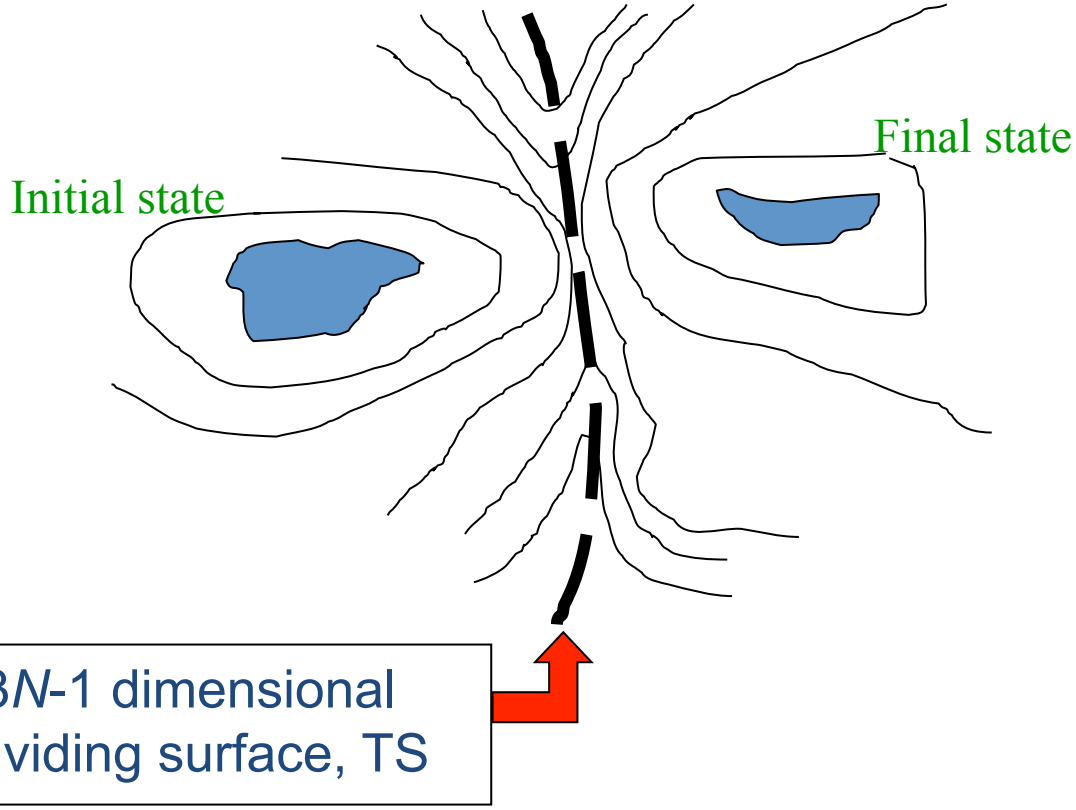


Cannot simply heat the system, the mechanism can change!

A ***statistical*** approach is needed

A. Transition State Theory (Wigner, Eyring 1930s)

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:



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

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

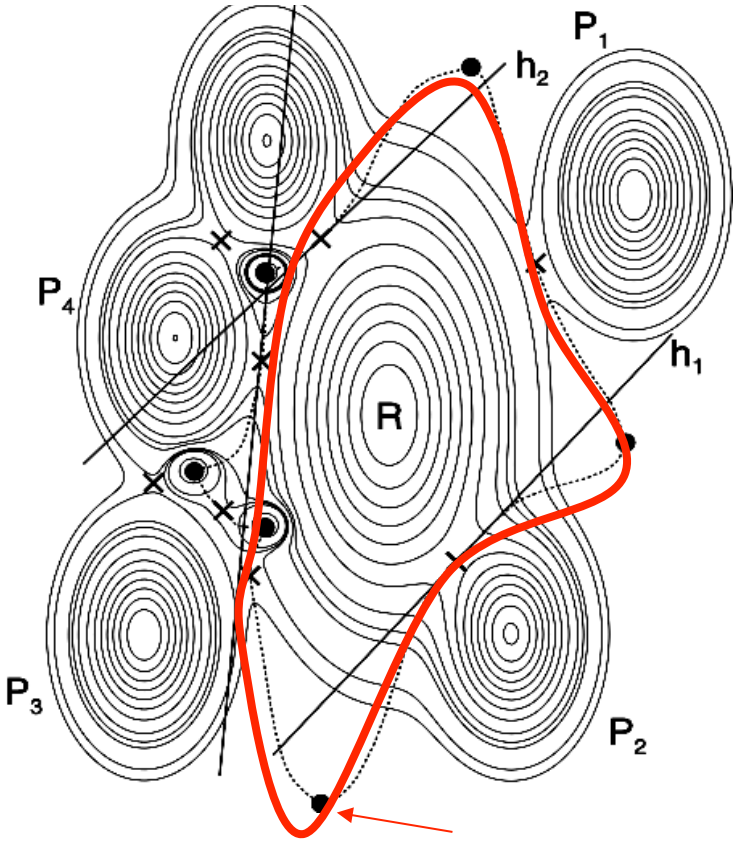
Transition State Theory

1. Born-Oppenheimer
2. Classical dynamics of nuclei (*need to extend to quantum systems…*)
3. Boltzmann distribution in R (*OK if slow enough*, $k_B T < E_a/5$)
4. No recrossings of TS *(often most serious, but can be fixed using trajectories)*

Note:

- TST gives the lifetime, $\tau=1/k$, of a given initial state - no knowledge of final state(s)
- Can run short time scale dynamics starting from TS to find the final state(s)
- Such trajectories can be used to take recrossings into account - *dynamical corrections*

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



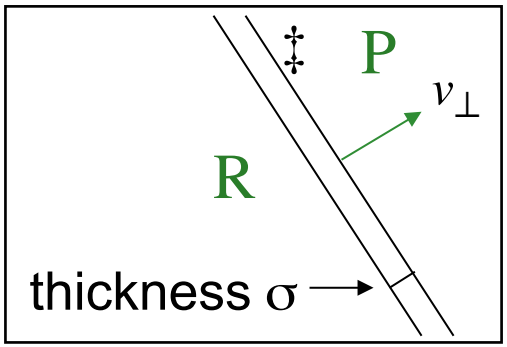
Need to create a TS dividing surface that encloses the initial state, R

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

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

configuration integrals

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



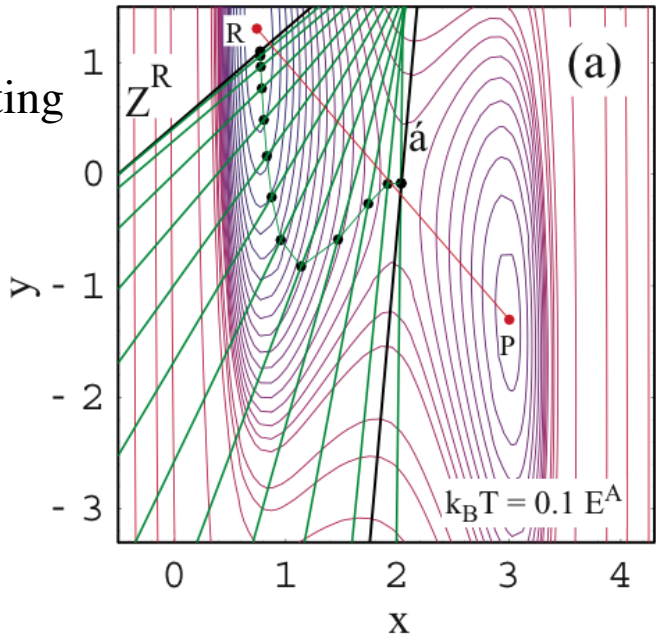
k^{TST} = (probability of being in TS) • (flux out of TS)

$$= \frac{\sigma \int_{\ddagger} e^{-V(\mathbf{x})/k_B T} d\mathbf{x}'}{\int_R e^{-V(\mathbf{x})/k_B T} d\mathbf{x}} \frac{\langle v_\perp \rangle_{TST}}{\sigma} = \sqrt{\frac{k_B T}{2\pi\mu_\perp}} \frac{Z_\ddagger}{Z_R}$$

Can write in terms of free energy difference found by integrating Reversible work in translating and rotating the hyperplane

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

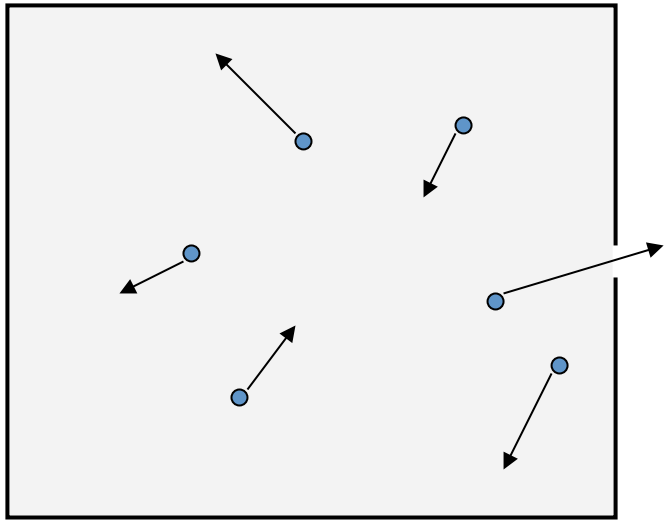
$$\Delta F(s) = -\int_0^s \langle F_n(1 - \kappa R_t) \rangle_{s'} ds',$$



Simple example:

Effusion of gas atoms through a small hole

No energy barrier, just entropic bottle neck



Box has volume, V; hole has area A

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

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 $r = \frac{PA}{\sqrt{2\pi m k_B T}}$

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

Could have many holes, leading to different containers

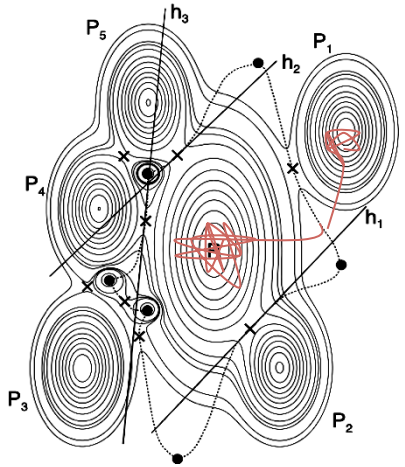
Wigner-Keck-Eyring (WKE)

two step procedure for finding the *exact* rate constant

1. Find optimal transition state dividing surface and obtain $t^{TST}=1/k^{TST}$
2. Run (short time) dynamics trajectories from the transition state to find product states and the dynamical correction, $k^{exact} = \kappa\, k^{TST}$

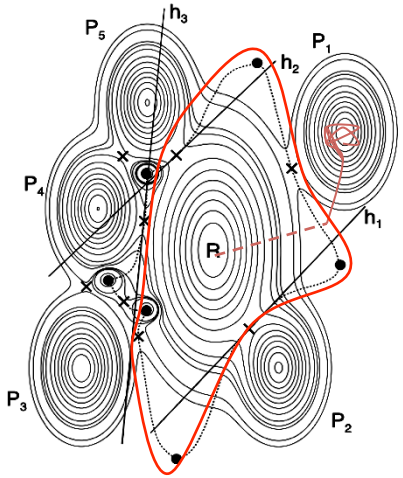
Note: Step 2 is hard unless a good job has been done in 1,
need to optimize the dividing surface!

Use WKE procedure to generate (pseudo) trajectories over long time scale



dynamical trajectory

time



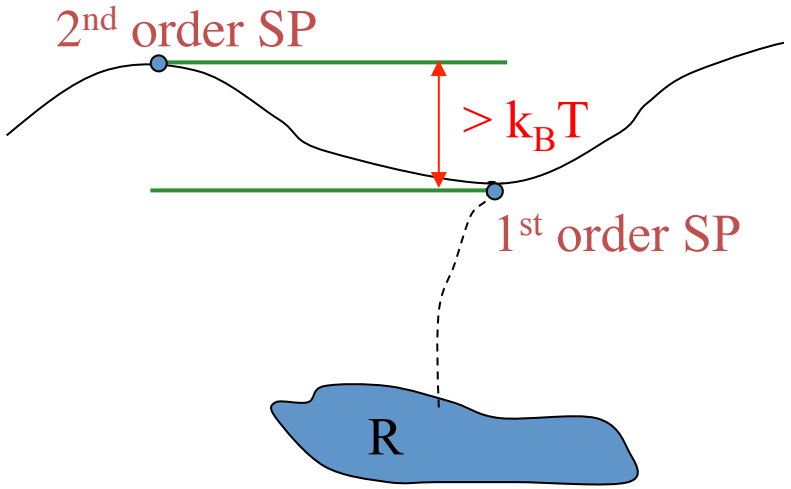
WKE trajectory

stat.mech.

b. Harmonic approximation to TST (HTST)

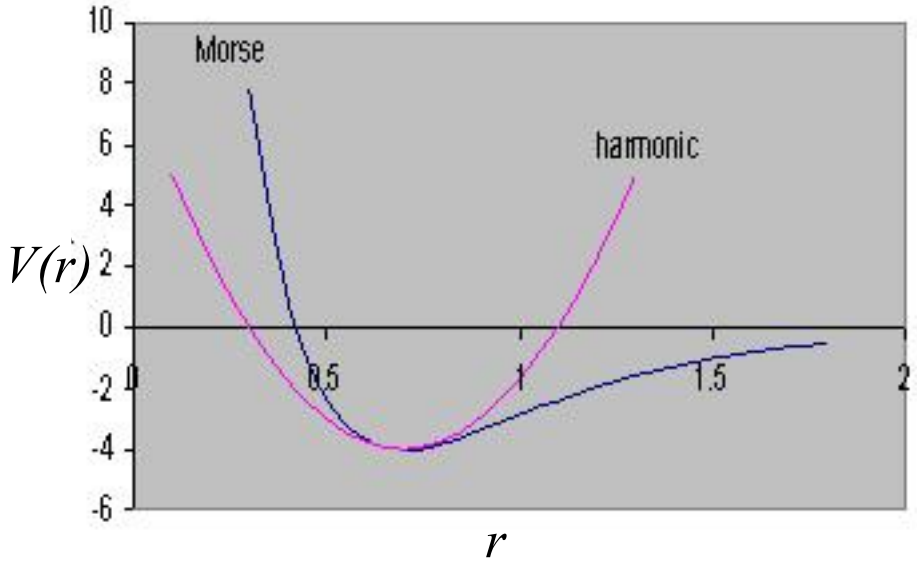
Typically a good approximation for solids (low enough temperature, but not too low).

OK 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:

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

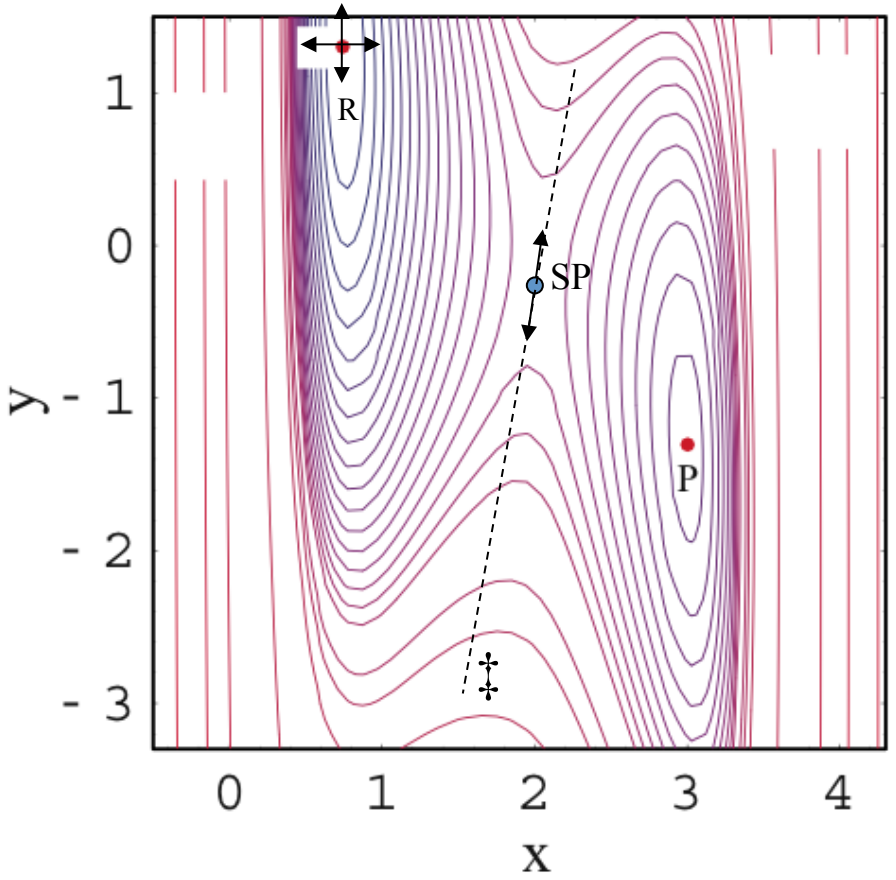


Derivation of HTST: Expand PES around minimum in *normal mode* coords.

Taylor expand PES around min and SP:

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

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



Plug into expression for rate constant:

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

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

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

which gives:

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

Agrees with the empirical Arrhenius law

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

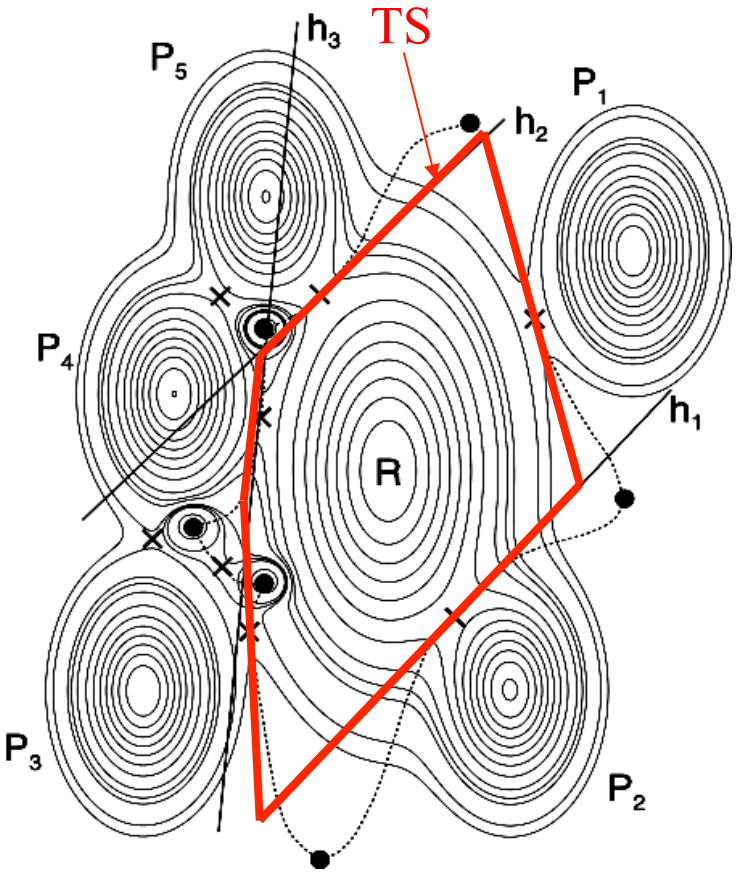
- Need to find **all relevant** saddle points on the potential energy rim surrounding the energy basin corresponding to the initial state.

- 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 saddle point region:

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

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



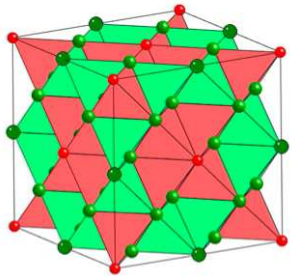
HTST is typically more than 10^3 faster than full TST!

But, the energy surface can be rough!

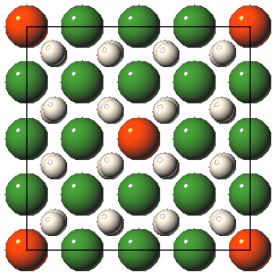
Example: Mg_7TiH_{16}

Initially, place H-atoms in center of each Td hole.

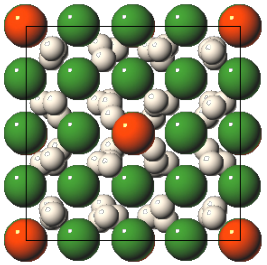
After relaxation, H-atoms have moved near the face between Td and Oh holes.



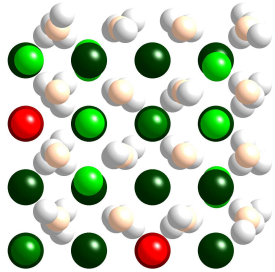
Td holes



H in Td center



H relaxed

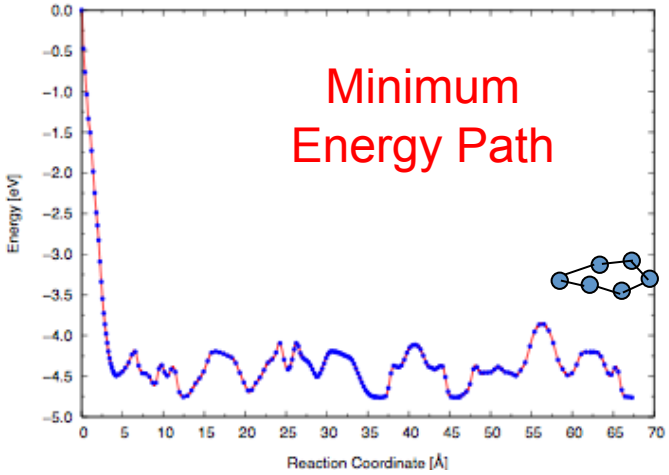


All atoms relaxed

At lowest energy minimum, some Mg atoms are displaced by 0.2 A from FCC, (best fit to X-ray data gives 0.1 A, *Moser, Noréus et al.*)

The structure is complex, multiple local minima on the energy surface,

see minimum energy path from regular → calcite structure to lowest energy str.



At room temperature, H-atoms can quantum mechanically delocalize over more than one local minimum (harmonic approximation not valid).

Overview: A few different approaches, with different amount of input

How much is known/assumed:	**Full sampling:**	**Harmonic approx:**
A. Initial state, final state and reaction coord. known:	Blue Moon (Ciccotti et al.)	Drag method (rediscovered much too often!)
B. Initial state and final state	Zero Tourque Path (Schenter, Mills &J) Trans. Path Sampling (Chandler et al.)	NEB, CI-NEB (Mills, Henkelman&J)
C. Only the initial state	OH-TST (J., B. & J) Parallel Replica (Voter)	Min.mode (dimer) (Henkelman & J.) TAD,Hyperdynamics (Voter)

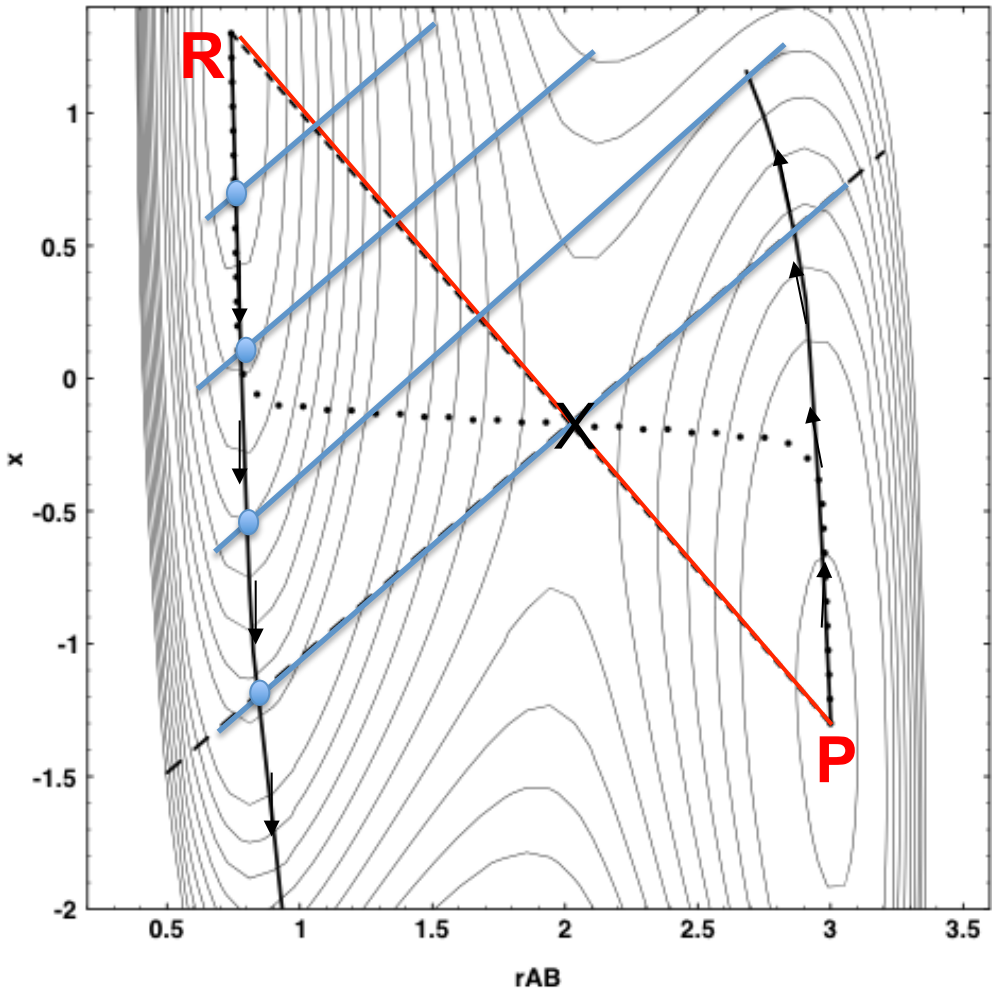
Drag method: Re-invented several times

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.

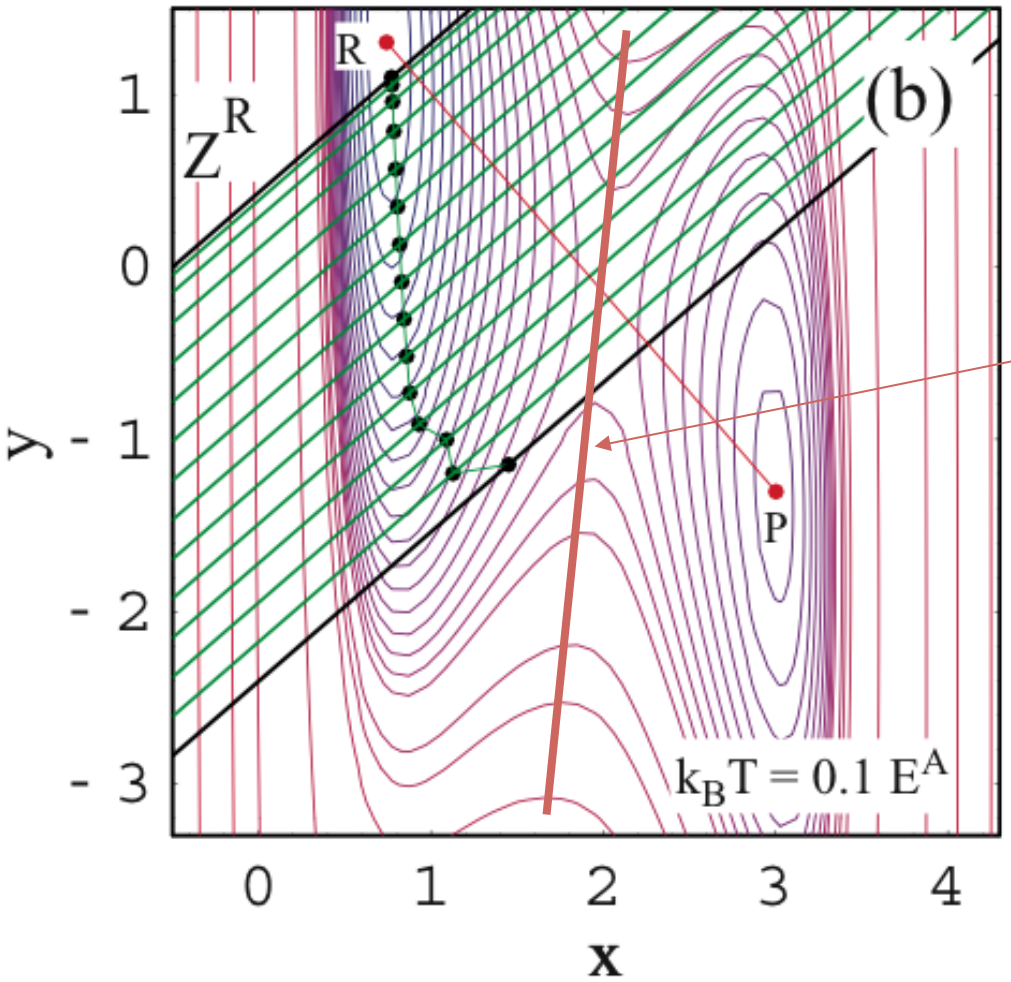
Can work, but fails when reaction coordinate differs from the drag path

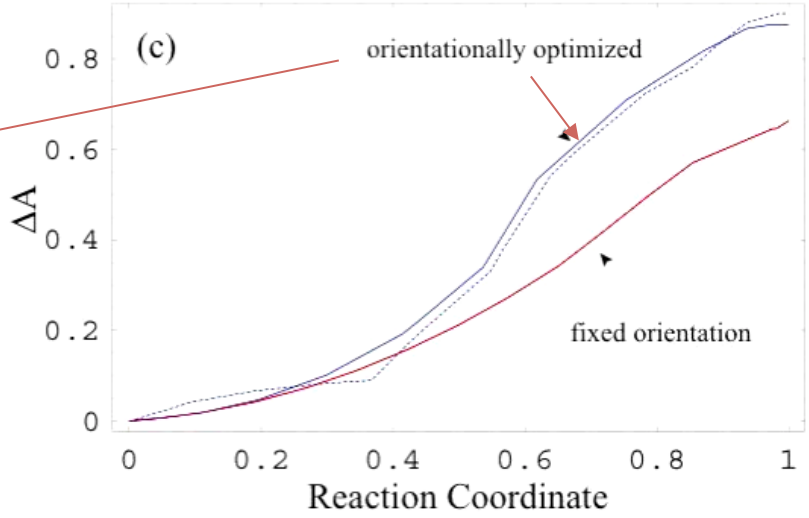
Can lead to a discontinuous path and hysteresis (P to R gives different estimate).

Even when the constraint hyperplane goes right through the SP, the relaxed position of the system is far from the SP!



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



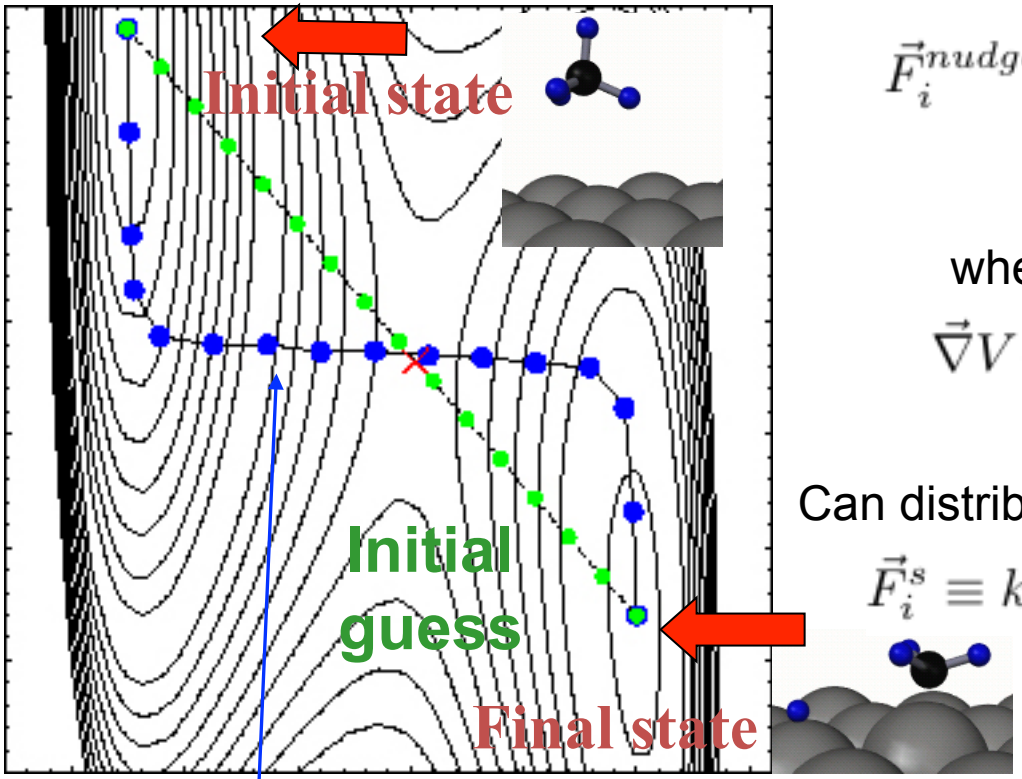


In a D-dimensional system, the optimization of the location of a dividing surface is a **one-**dimensional optimization, the optimization of orientation represents **D-1** degrees of freedom - essential to optimize orientation!

c. Find minimum energy paths using the NEB Method

Mills, Jónsson, Schenter Surf. Sci. 1995, H. Jónsson, G. Mills, and K.W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B.J. Berne, et al. (1998), p. 385

Distribute images (replicas) of the system along some path between initial and final state (ex. linear interpolation). Estimate tangent at each image from adjacent images.



Effective (nudged) force on each image:

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

tangent along path at image i

where the perpendicular component is

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

Can distribute images along the path with springs:

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

Get equally spaced images if the Same spring constant us used.

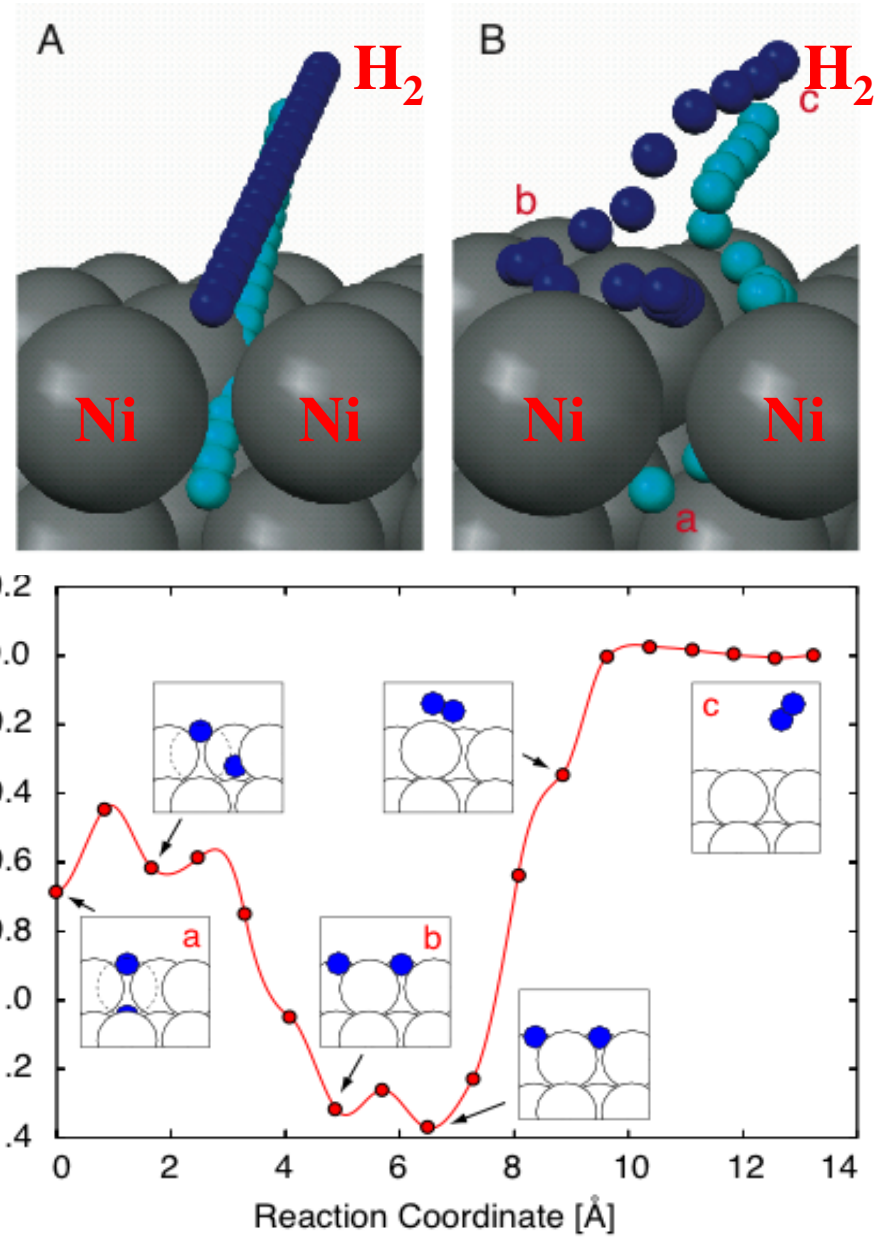
Use NEB with DFT calculations

Example 1:

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

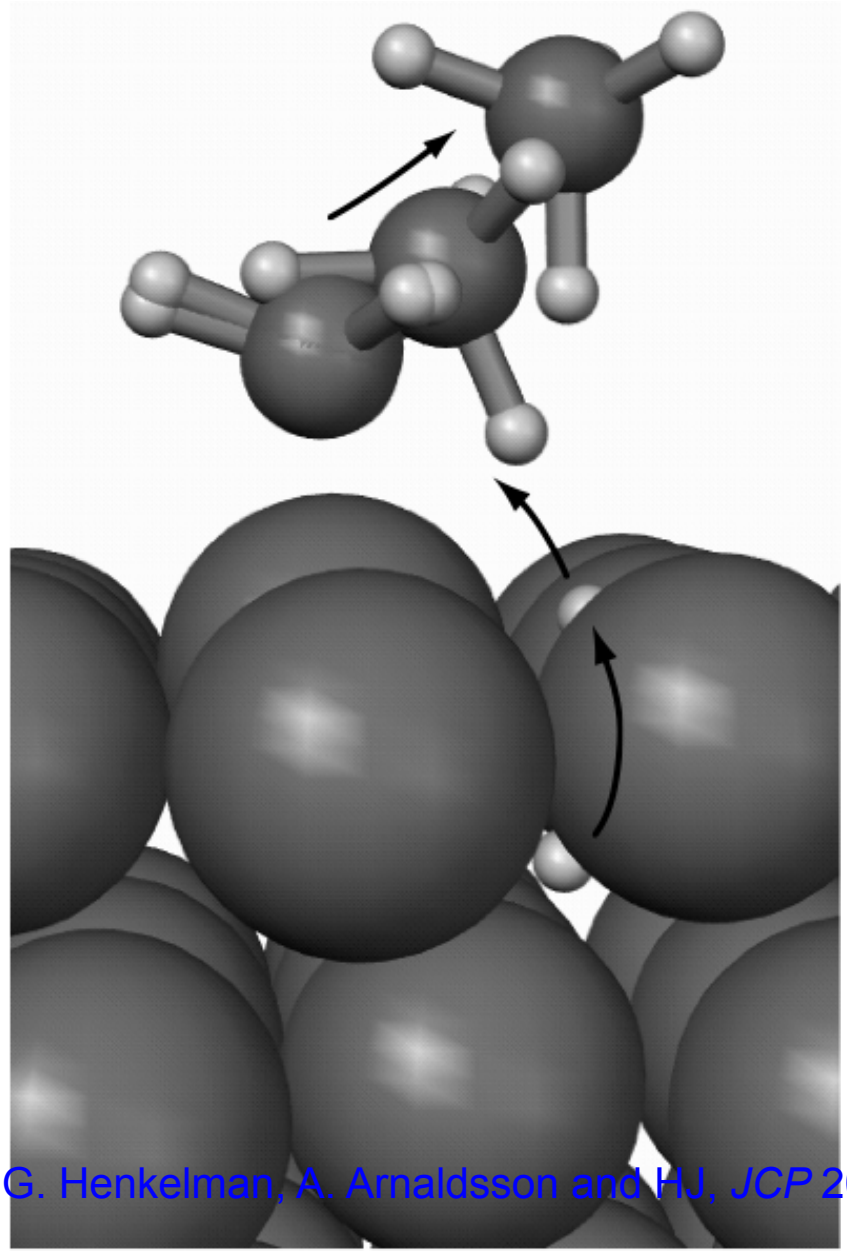
Start up NEB assuming direct path for subsurface H-atom to attach to a surface H-atom

But, the MEP found shows that surface H-atom hops away. So, not direct H-H binding



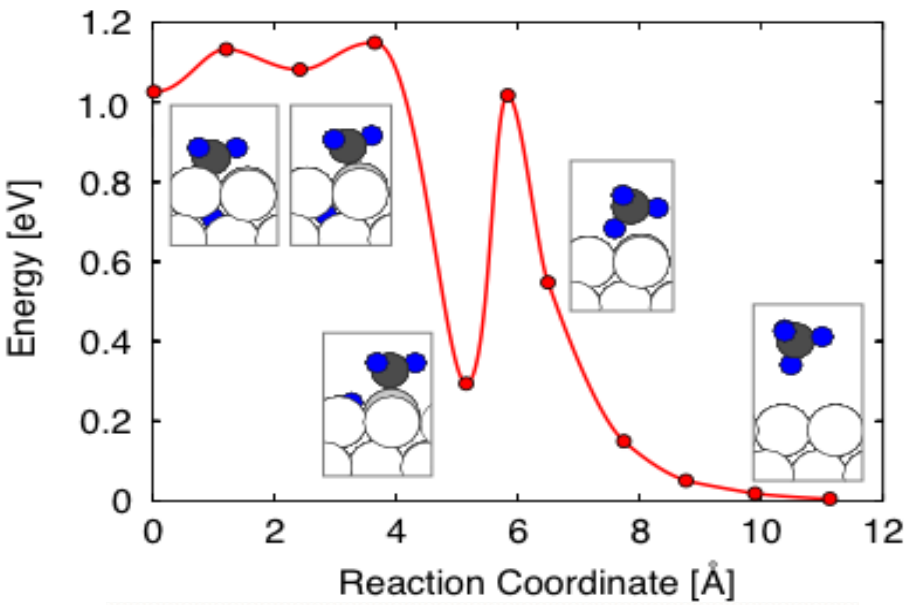
G. Henkelman, A. Arnaldsson and HJ, *JCP* 2006

Example 2: # Associative desorption of CH_4 from Ni(111), subsurface H

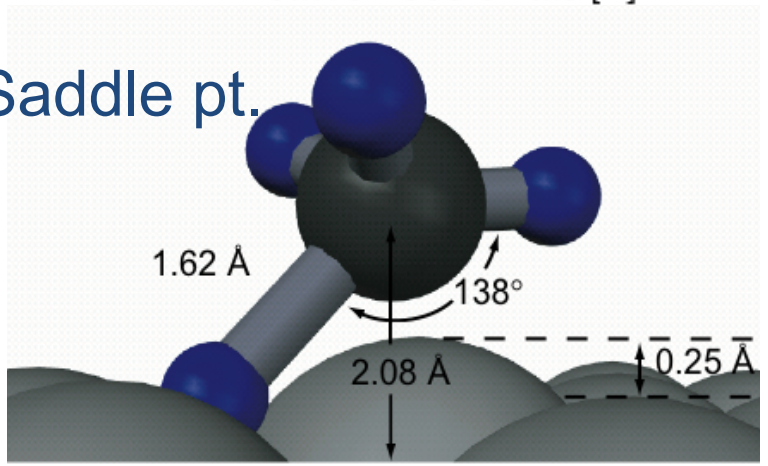


G. Henkelman, A. Arnaldsson and HJ, *JCP* 2006

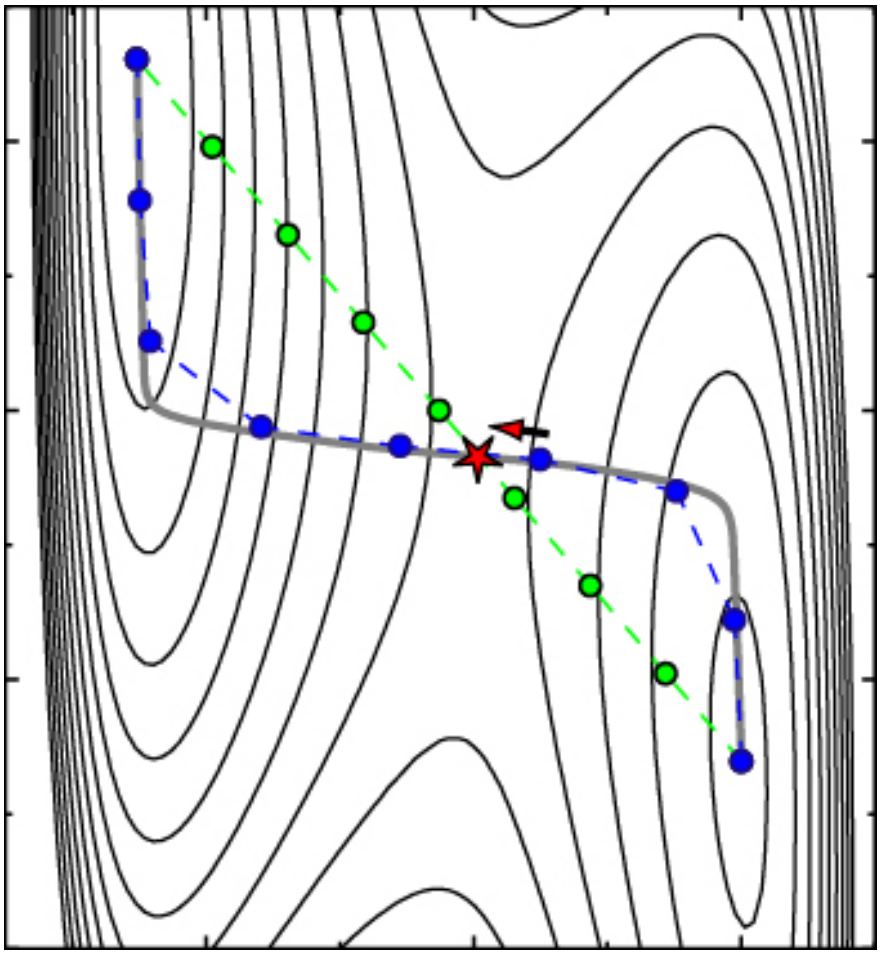
Same story as for H_2
no direct path with subsurface H



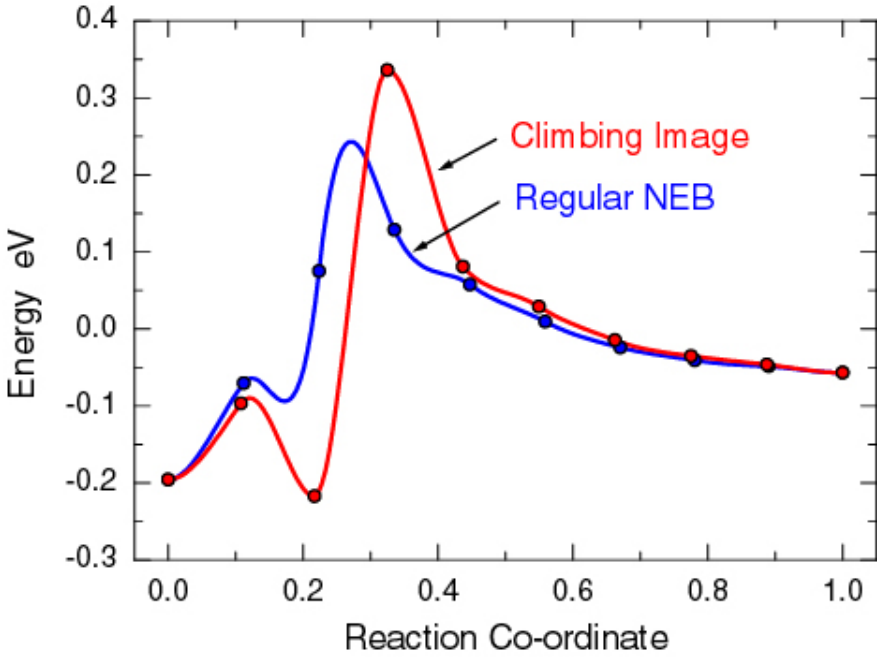
Saddle pt.



CI-NEB: Let the highest energy image converge on saddle point



The highest energy image in the elastic band is pushed up to the saddle point, gives more rigorous estimate of saddle point, needed for vibrational mode calculation



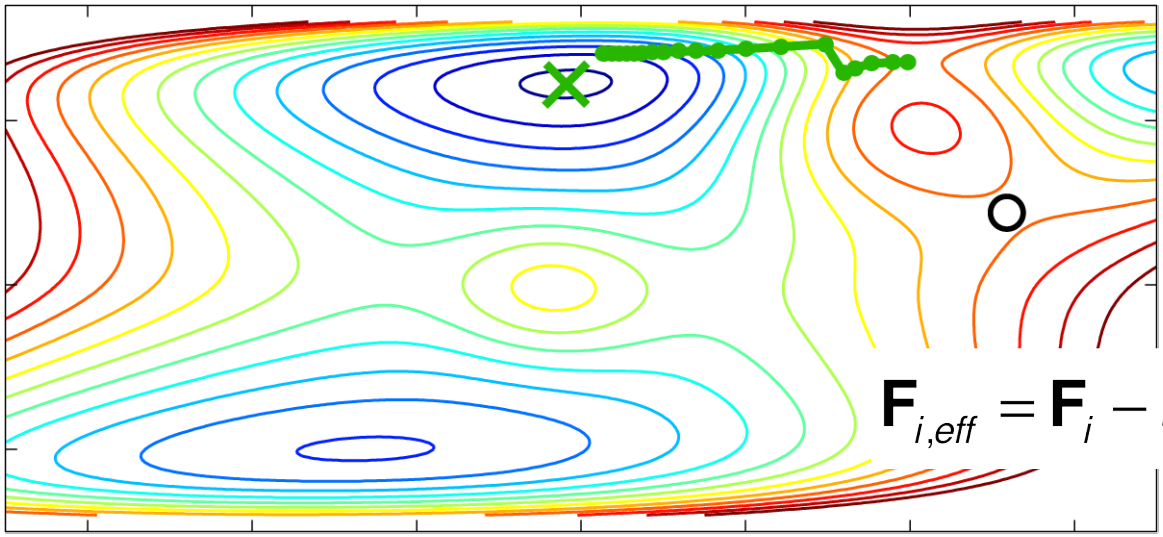
G. Henkelman, B.P. Uberuaga and HJ, *J. Chem. Phys.* **113**, 9902 (2000)

What if only the initial state minimum is known (not final state)?

Can climb up potential energy surface and home in on saddle pt. using the 'minimum-mode following' method

- Displace system using Gaussian random displacements
- Climb up guided by the Hessian's minimum-mode

  (Hessian is the matrix of second order derivatives of the energy)
- No bias from preconceived notion of the mechanism



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

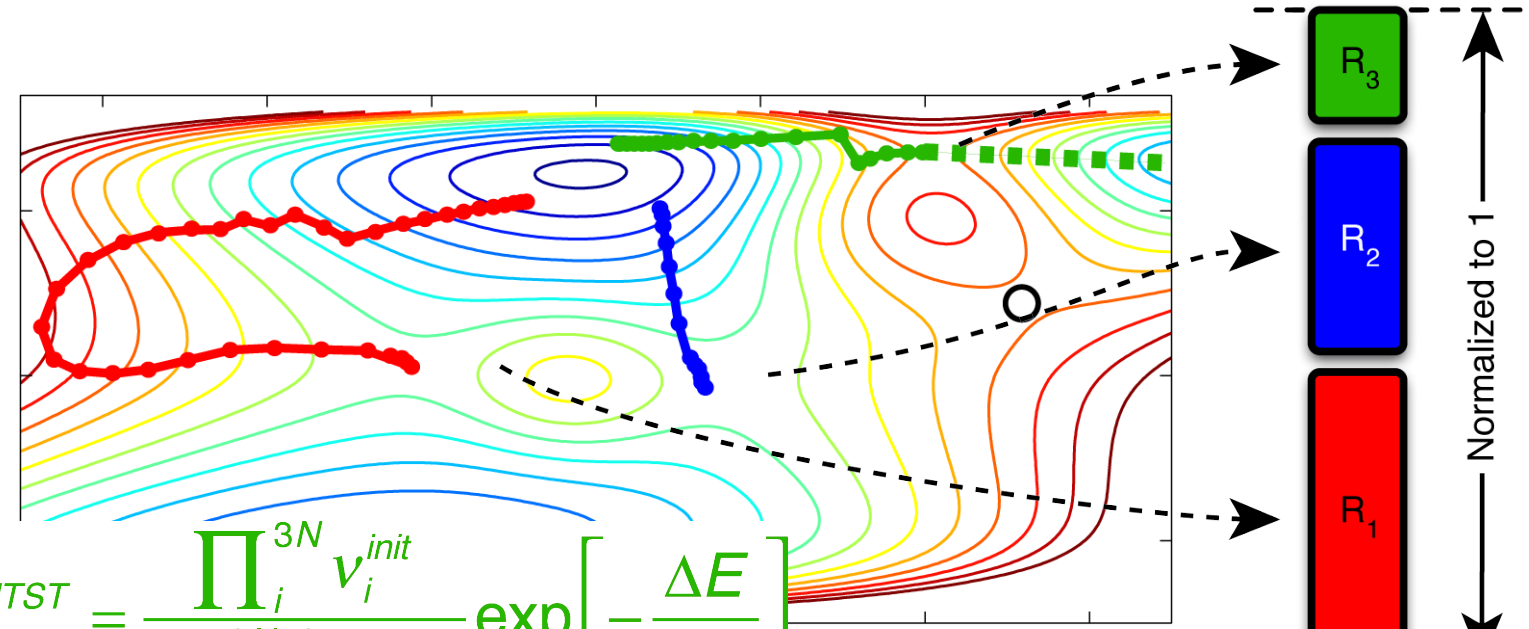
Ref: G. Henkelman and H. Jónsson, J. Chem. Phys. **111**, 7010 (1999)

C. Adaptive Kinetic Monte Carlo

Obtain a table of possible transitions from a given minimum:

- Locate adjacent Saddle Points
- Slide down PES, to determine product state (and check initial state)
- Estimate rate using HTST

Use random number to pick the next transition



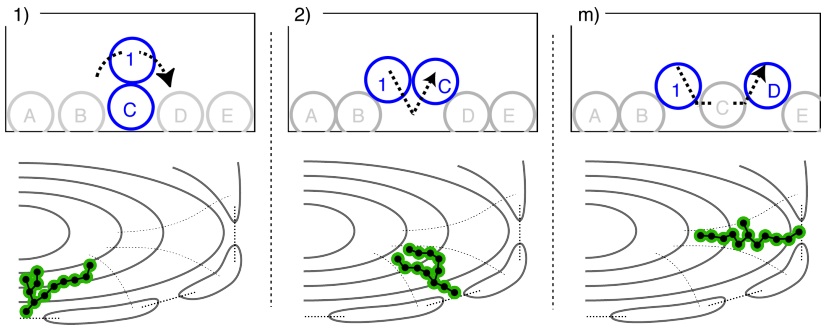
$$k^{HTST} = \frac{\prod_i^{3N} \nu_i^{init}}{\prod_i^{3N-1} \nu_i^{saddle}} \exp\left[-\frac{\Delta E}{k_B T}\right]$$

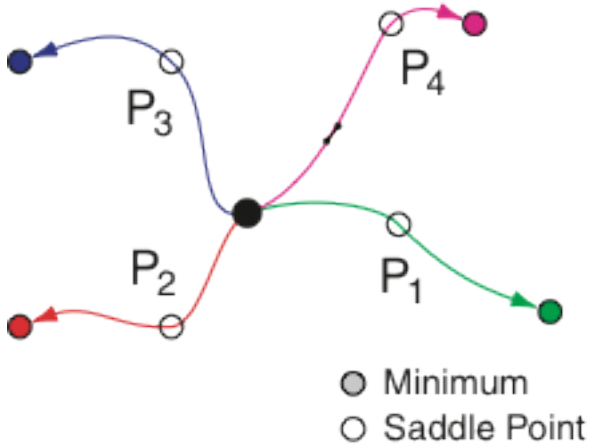
d. Adaptive Kinetic Monte Carlo

G. Henkelman and HJ, *JCP.* (2001)

1. Find low energy saddle points near the current minimum using multiple SP searches started at random (Gaussian distributed)
2. Find the prefactor, ν, from normal mode analysis and calculate the rate of each process $r_i = \nu\, e^{-\Delta E_i / k_B T}$
3. Use a random number to pick one of the transitions according to the relative transition rates
4. Advance system to the final state of the chosen process (trajectory or slide down)
5. Increment time by an amount $\Delta t = 1/\Sigma\, r_i$

Repeat 1 - 5 until the desired time interval has been reached



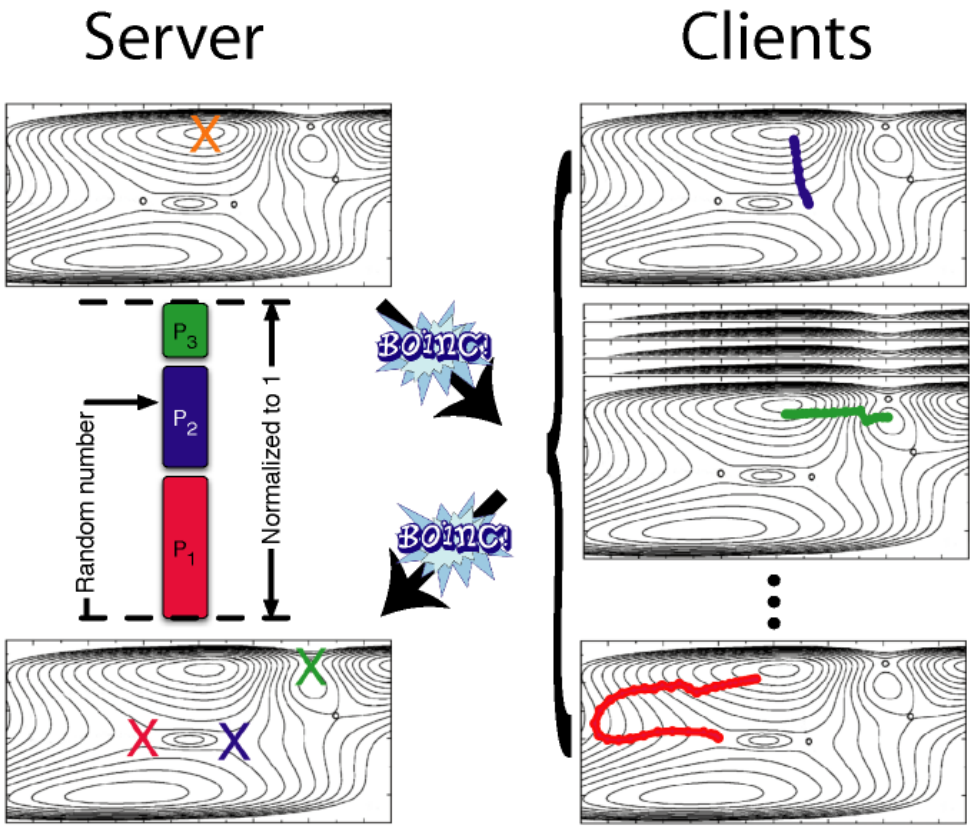


- No need to create a table of transitions and their rates *before* the simulation as in regular KMC

- Also, no need to assign atoms to lattice sites (defects, glass, …)

EON: Distributed computing software for AKMC

- Distribute saddle point searches over internet
  - Communication builds on BOINC
  - Communication and computation are not entangled
  - Client runs as stand-alone
- Atomic Forces
  - Can use DFT or potential functions for atomic forces
- Implementation
  - Client side C++
  - Server side Python



(Andreas Pedersen and H.J., *Mathematics and Computers in Simulation*,2009)

Several tricks to improve efficiency: Skipping path, coarse graining, recycling, …

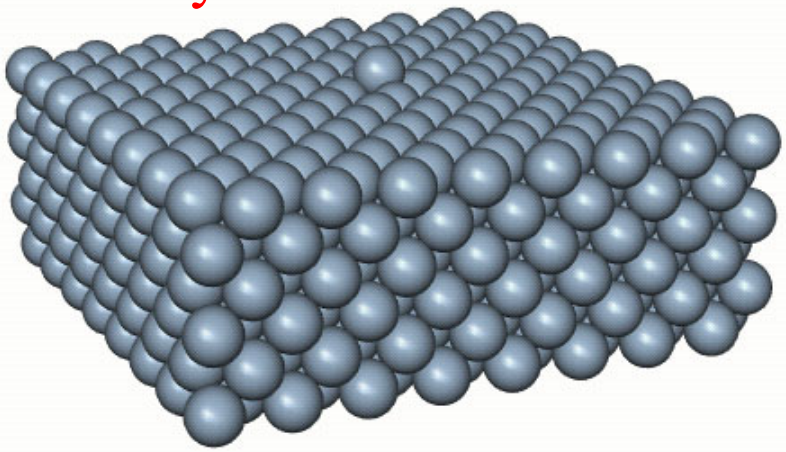
Examples: A. Multiple time-scale simulation of thin film growth

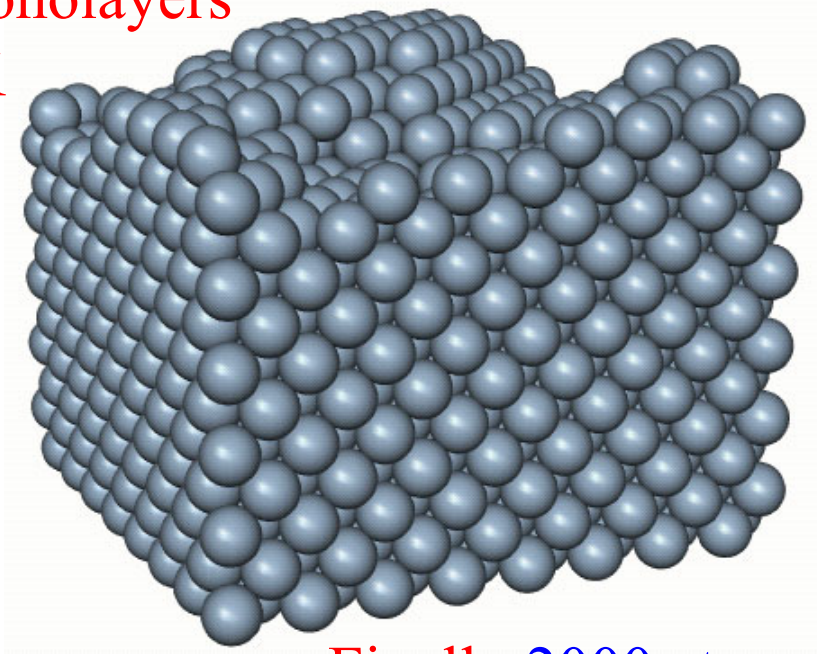
-Is the growing surface smooth or rough?

-What are the atomic scale processes that determine the morphology?

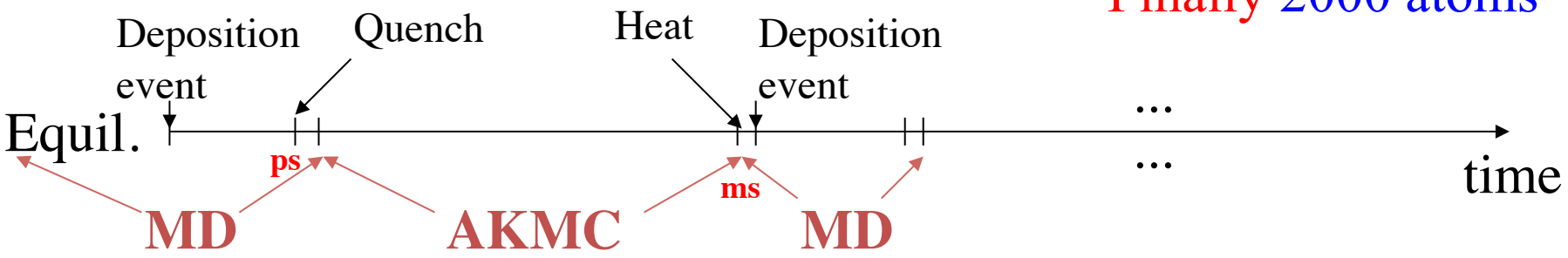
Simulation using EMT where 10 monolayers were deposited in 1 second, T=30 K

Initially 768 atoms



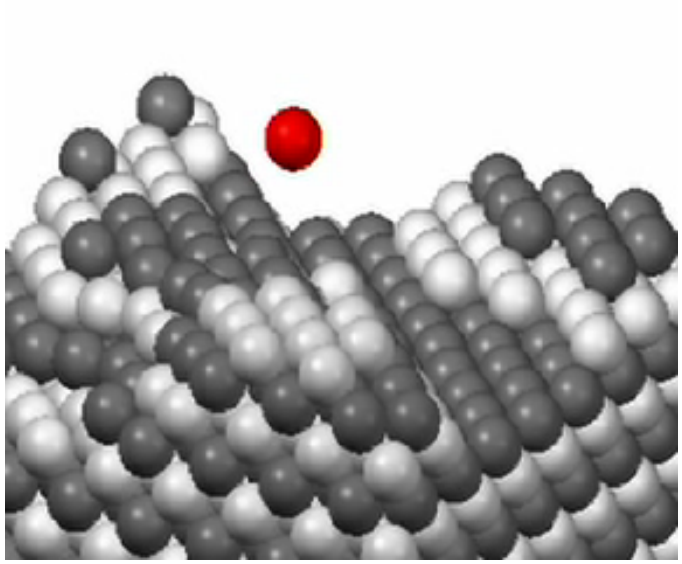


Finally 2000 atoms

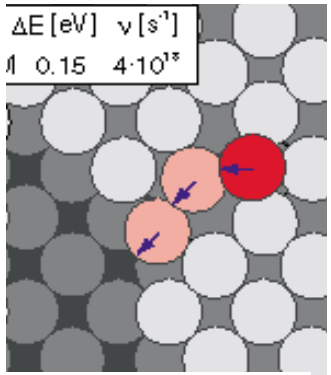


Simulate crystal growth from vapor (cont.)

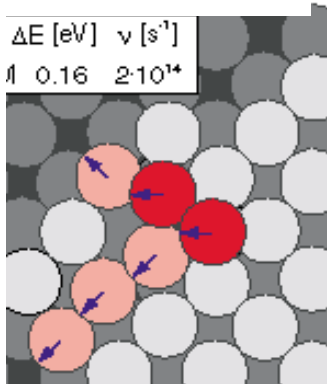
Deposition events (short time scale)
and
annealing events (long time scale)

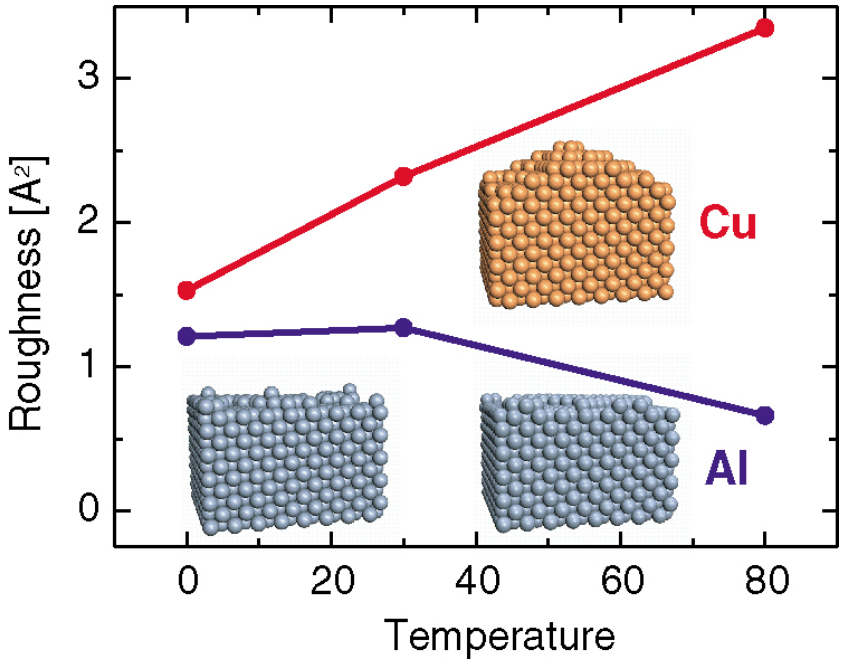


Many unexpected events were observed in Al growth simulations



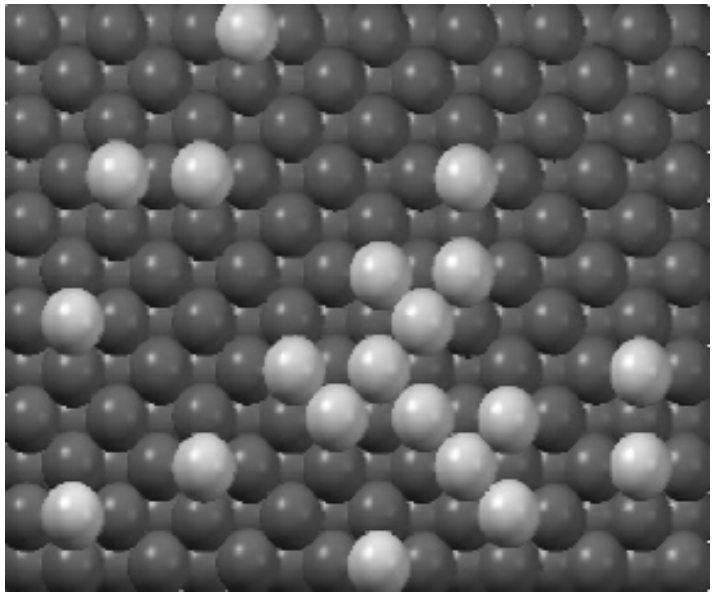
Most transitions involved concerted motion of multiple atoms

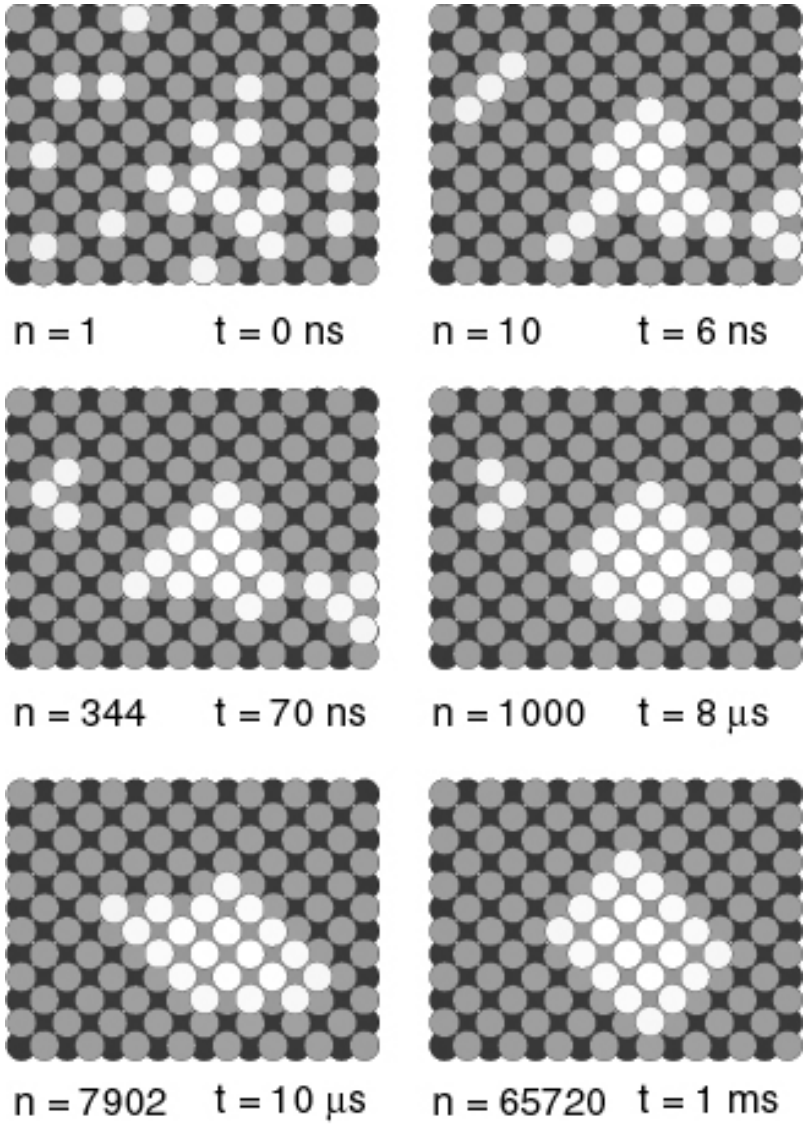




Example B:

Island formation of Al adatoms on Al(100) surface





Statistics

temperature: 300K
total transitions: 129,000
distinct transitions: 341
total time: 1 ms
dimer searches per step: 50
distinct processes per step: 26

Example 3: H-atom diffusion at a Σ5-Tilt GB in Al

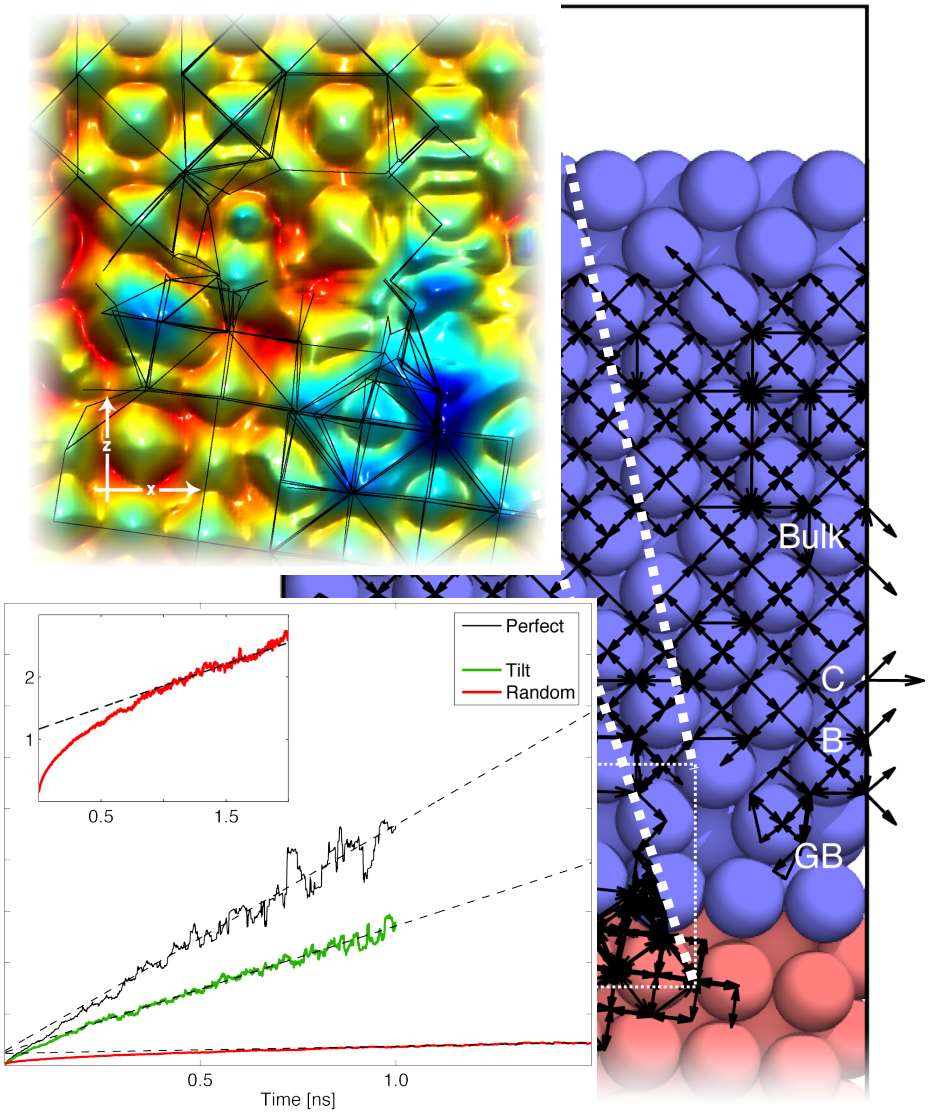
AKMC simulation using EMT potential

Long time ime evolution:
- Only a few paths go through the grain boundary

Effective potential Energy Surface:
- Projected onto xz-plane
  - Red high energy
  - Blue low energy
- Two low-energy basins within GB-region

Parallel-diffusivity decreases to one-half of the bulk value

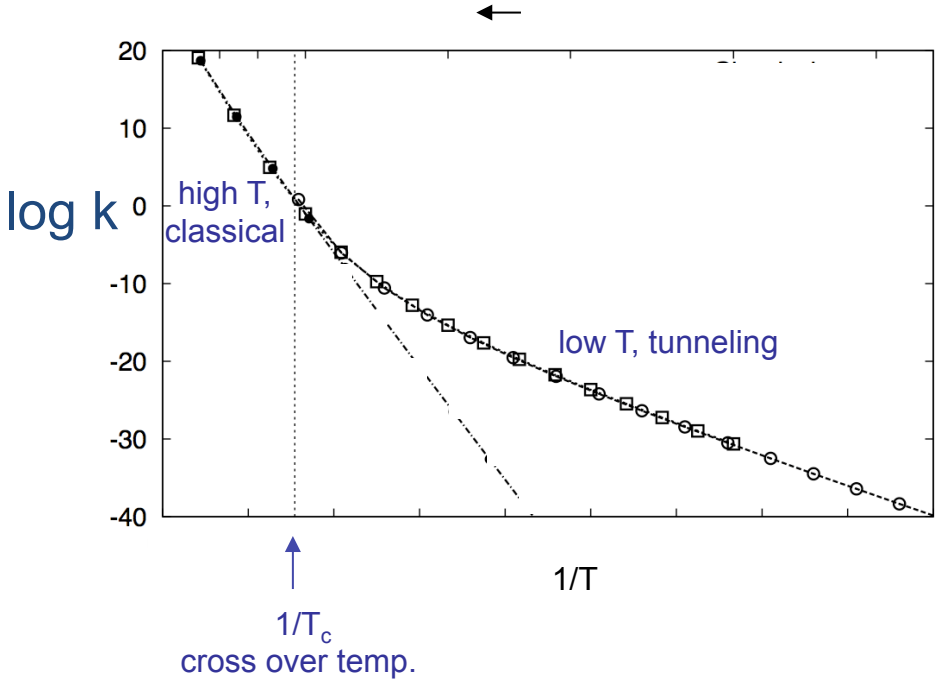
Trapping in the GB



A. Pedersen & HJ, Acta Materialia (2009)

e. Calculation of tunneling paths and rates in systems with many degrees of freedom

Estimate the rate of thermal transitions including tunneling as a possible transition transition mechanism



Becomes the dominant transition mechanism at low enough temperature

Can be important at room temperature if only light atoms are displaced appreciably

WKB semi-classical approximation

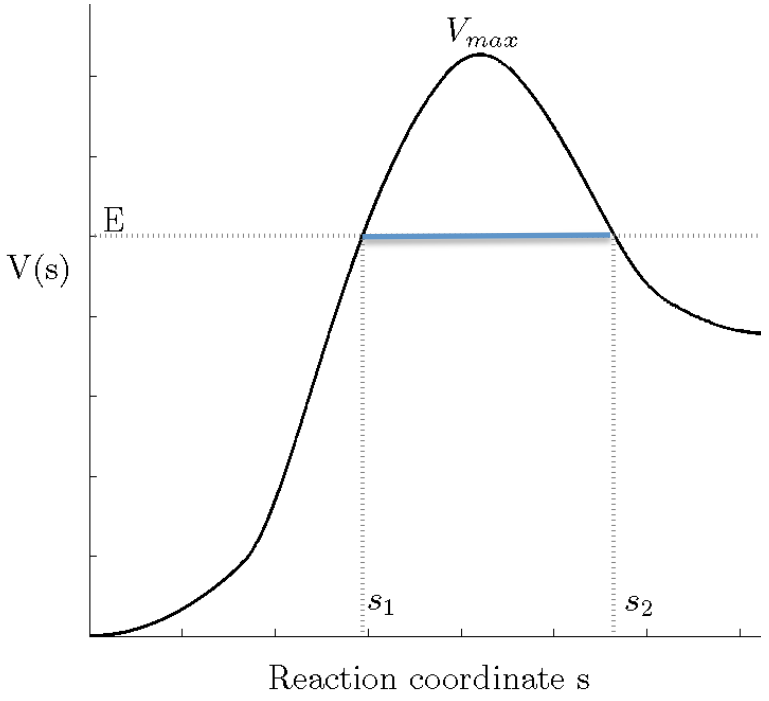
The effect of tunneling is included by multiplying the classical rate constant with a correction factor $k = \Gamma k_{cl}$

Transmission correction factor:

$$\Gamma(T) = \frac{\int_0^\infty P(E) e^{-\beta E} dE}{\int_{V_{\max}}^\infty e^{-\beta E} dE}$$

$$P(E) = \frac{1}{1 + e^{2\theta(E)}}$$

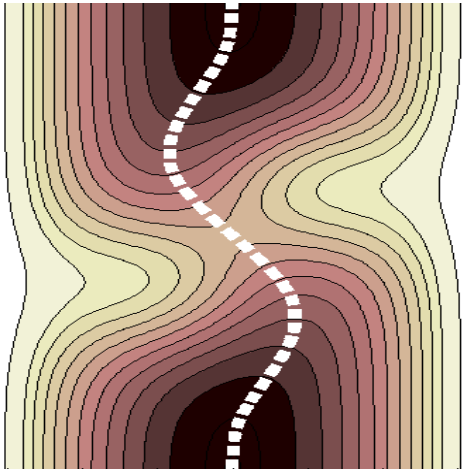
$$\theta(E) = \frac{1}{\hbar} \int_{s_1}^{s_2} \sqrt{2\mu(V(s) - E)} ds$$



Find optimal tunneling paths

- WKB: Find the path of lowest (imaginary) action – highest tunneling probability.

$$\theta(E) = \frac{1}{\hbar}\int_{s_1}^{s_2}\sqrt{2\mu(V(s)-E)}ds$$



- Based on similar procedure as in NEB
  - Distribute images of the system along the path and zeroing the perpendicular force derived from $\theta(E)$

Minimizing the action integral

$$\theta(\mathbf{R}) = \frac{1}{\hbar}\int_{s_1}^{s_2}\sqrt{2\mu(V(\mathbf{R})-E_c)}d\mathbf{R}$$

$$\xi_i \equiv \frac{1}{\hbar}\sqrt{2\mu(V(\mathbf{R}_i)-E_c)}$$

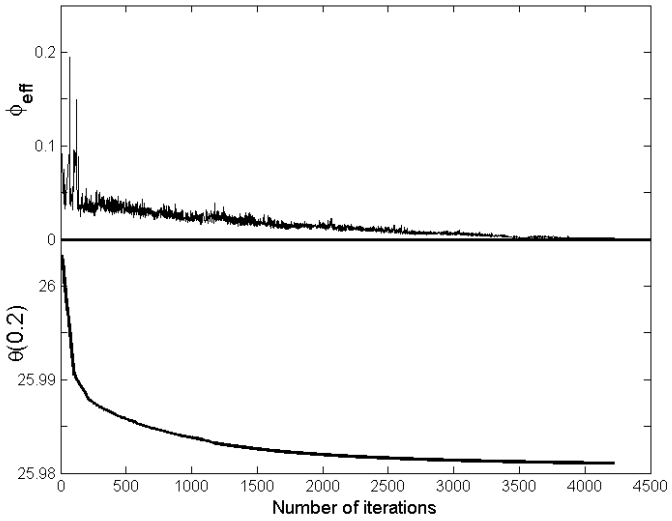
$$\theta(\mathbf{R}) \approx \frac{1}{2}\sum_{i=1}^{n}(\xi_i+\xi_{i-1})\,|\mathbf{R}_i-\mathbf{R}_{i-1}|$$

$$\boldsymbol{\phi}_j = -\frac{\partial\theta}{\partial\mathbf{R}_j} \qquad j=2,3,...,n-1$$

force in image j

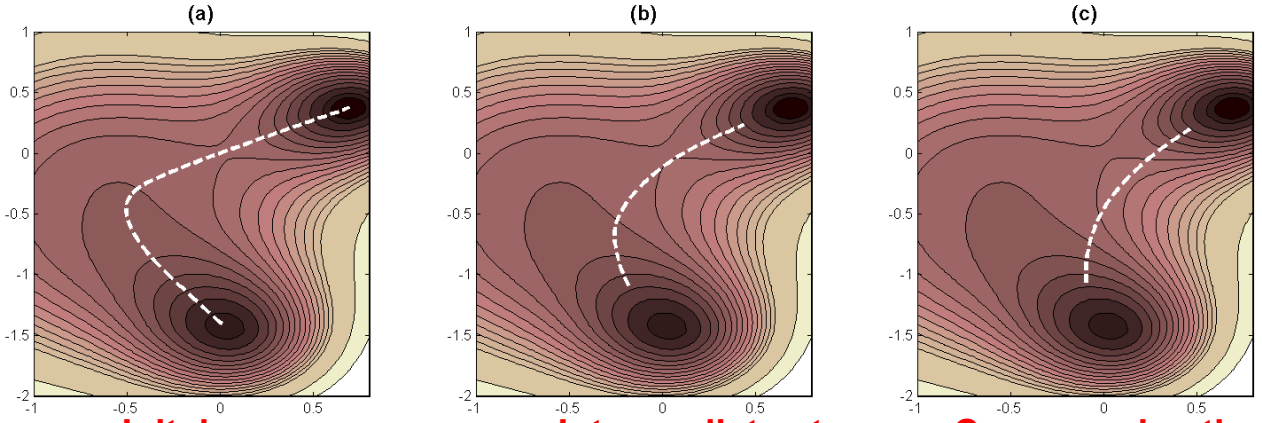
$$\boldsymbol{\phi}_j^{\text{eff}} = \boldsymbol{\phi}_j^{\perp} + k\left(|\mathbf{R}_{j+1}-\mathbf{R}_j| - |\mathbf{R}_j-\mathbf{R}_{j-1}|\right)\widehat{\tau}_j$$

$$\boldsymbol{\phi}_{0,n}^{\text{eff}} = \boldsymbol{\phi}_{0,n}^{sp} - (\boldsymbol{\phi}_{0,n}^{sp}\cdot\widehat{\mathbf{F}}_{0,n})\widehat{\mathbf{F}}_{0,n} + (V(\mathbf{R}_{0,n})-V_{1,2})\widehat{\mathbf{F}}_{0,n}$$



Force minimized to zero iteratively

End points made to converge to given energy (not fixed as in NEB)



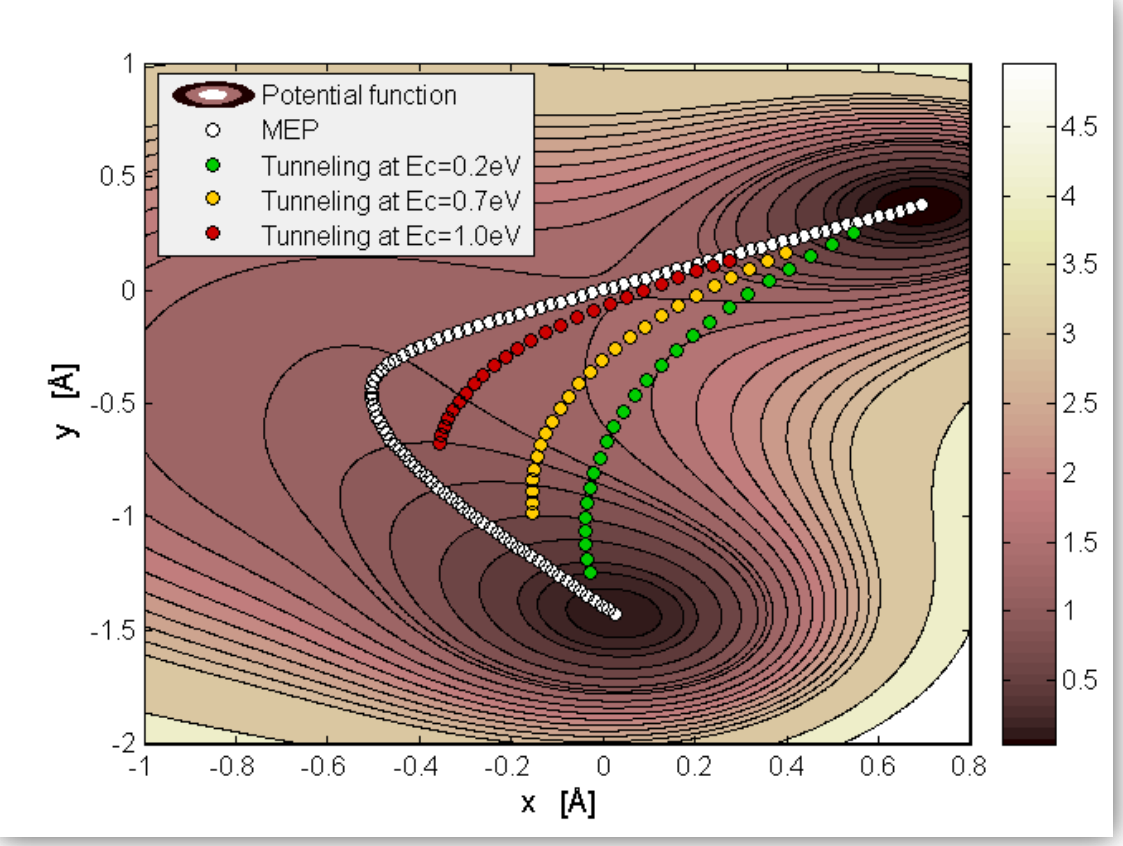
Inital guess

Intermediate step

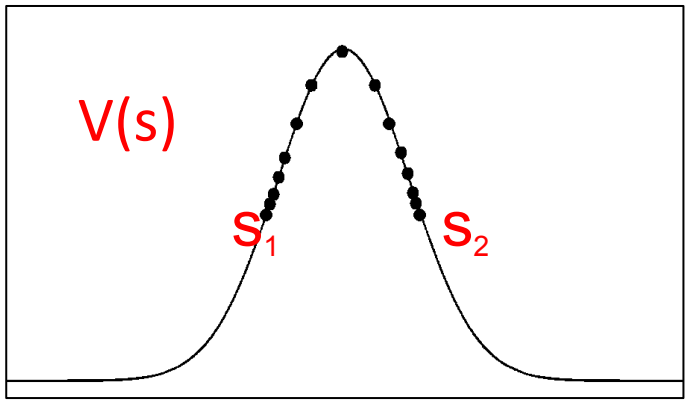
Converged path

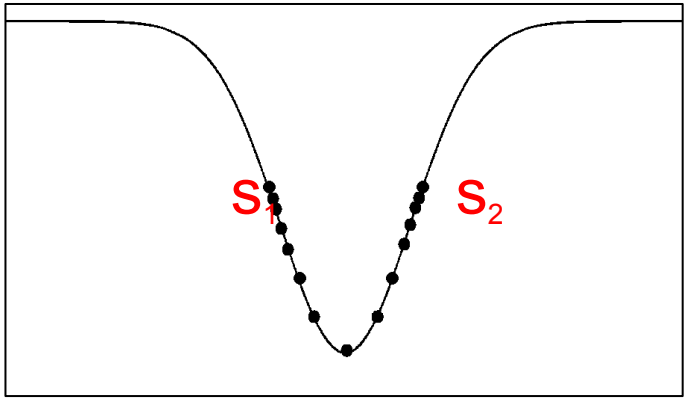
Tunnneling path ‘cuts corners’ compared with minimum energy path (MEP)

The wave function decreases exponentially in the classically forbidden region, so a narrower but higher energy barrier can give faster tunneling



Use harmonic approximation to relate an optimal WKB tunneling path to the thermal rate constant at a certain temperature ('instanton' theory)

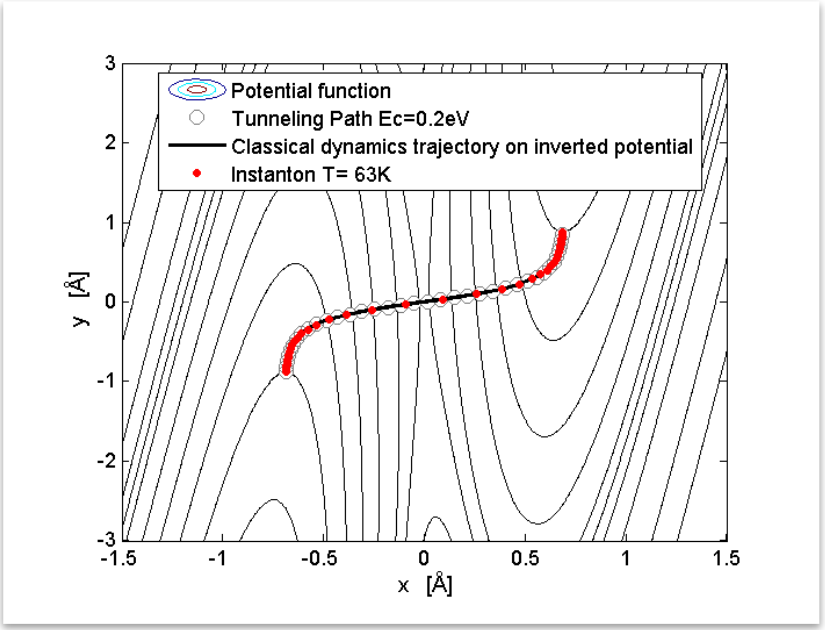




Time period:

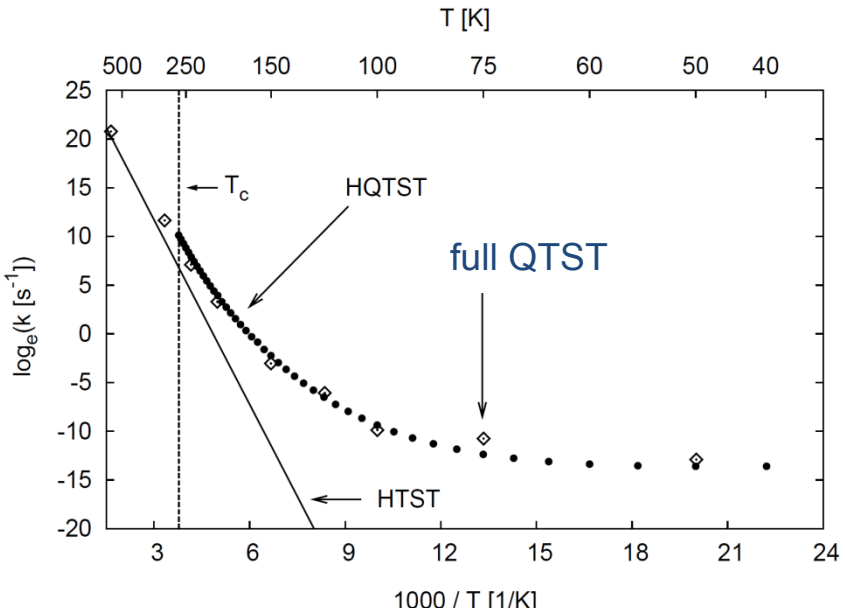
$$t = \beta\hbar = \frac{\hbar}{k_B T} \Rightarrow T = \frac{\hbar}{k_B t}$$

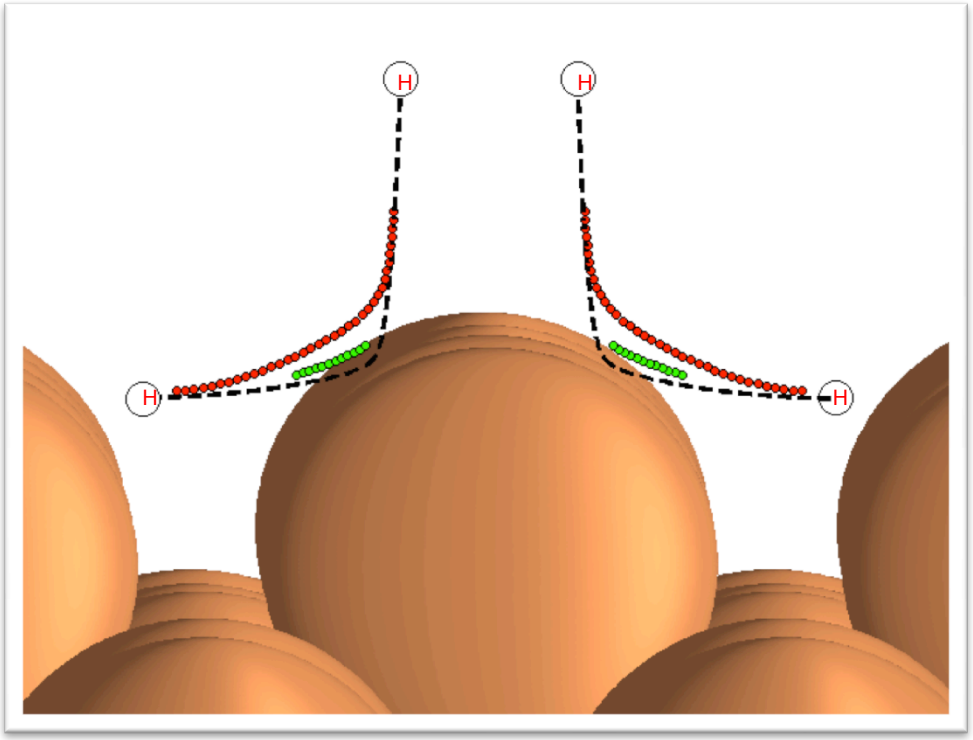
$$\Delta t = \frac{t}{P}$$



Example 1: H_2 adsorption from Cu(110) surface

- Multi dimensional system
- Here use potential function for testing against full QTST
  - 6 layers of 36 Cu atoms
  - 2 hydrogen atoms



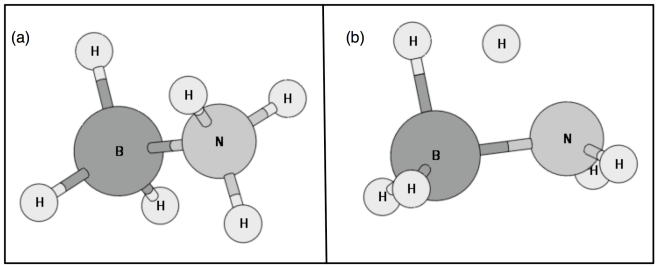


Even for this formation of a gas phase molecule, the harmonic approximation is very good.

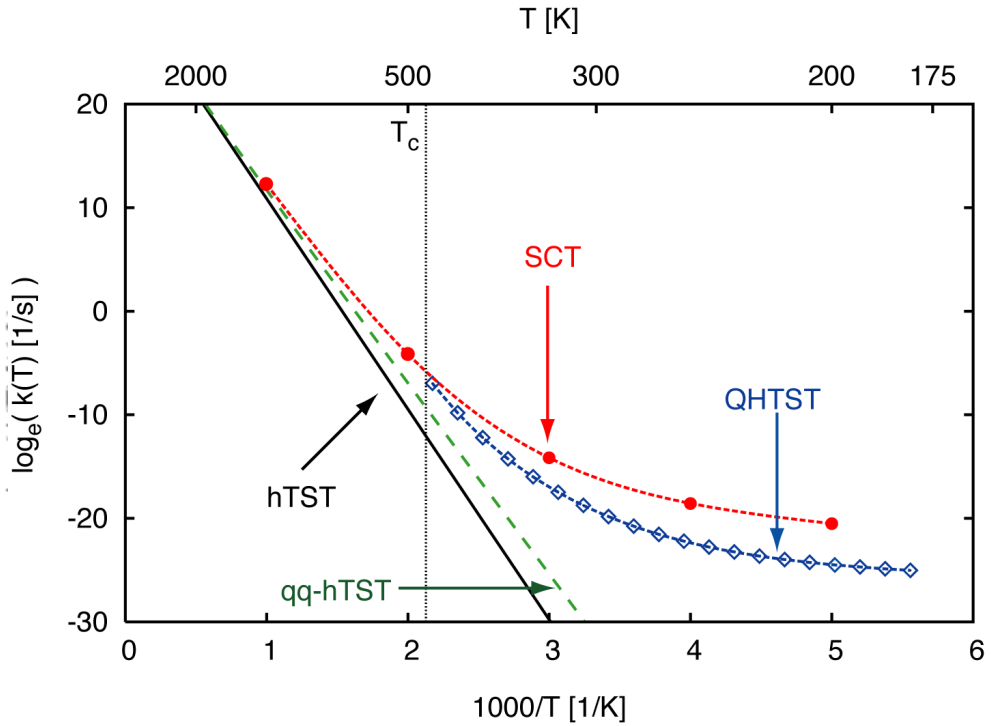
Example 2: Dehydrogenation of $BNH_{6(g)}$

Ammoniaborane, a candidate for hydrogen storage (Schenter, Gutowski, Abramov, …)

$$H_3BNH_{3(g)} \rightarrow H_2BNH_{2(g)} + H_{2(g)}$$



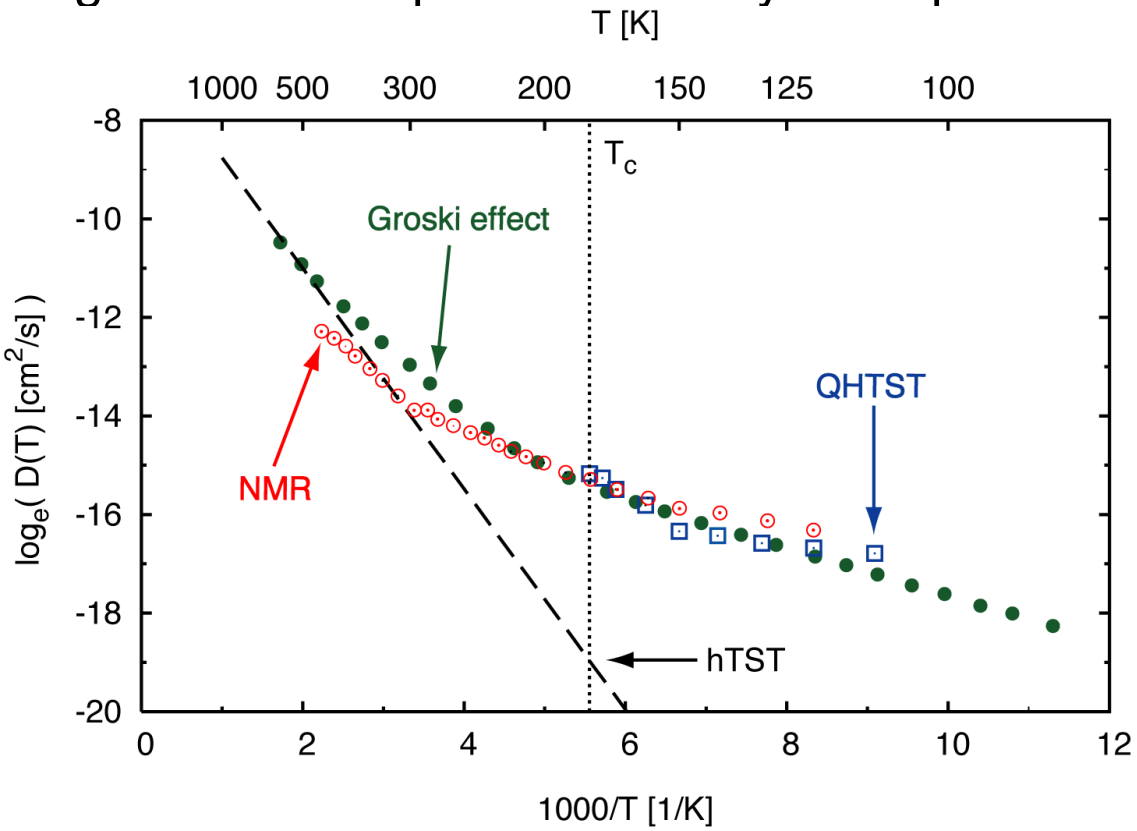
Calculate desorption of hydrogen, use the semi-empirical AM1 to evaluate atomic forces and up to 96 replicas at the lowest temperature



- Dominated by tunneling at room temperature.
- About 300 fold increase in rate at 370 K
- SCT overestimates the rate at low temperatures.

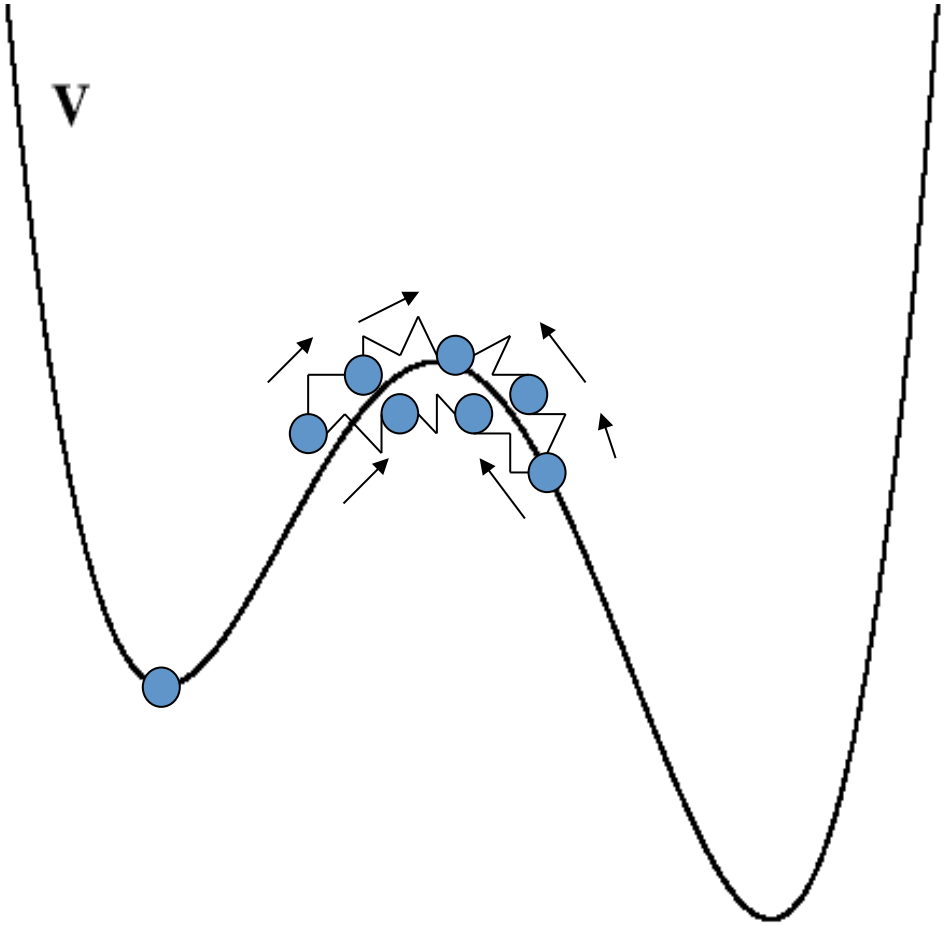
Example 3: Hydrogen diffusion in the BCC metal Ta

DFT calculations using PAW, PW91
16 Ta atoms, 1 H atom
Hops between adjacent tetrahedral holes
Up to 58 images used to represent the Feynman paths



Excellent agreement with experiments at low temperature *(no fitting!).*
Tunneling dominates at below room temperature.

Estimate when tunneling becomes important, find crossover Temperature, T_c



Ω: magnitude of imaginary frequency of unstable mode at saddle point

The temperature at which the spring constant in Feynman path integrals matches the curvature of the barrier is

$$T_c = \frac{\hbar \cdot \Omega}{2\pi \cdot k_B}$$

Gillan, *J. Phys. C* **20**, 3621 (1987)

At and below this temperature tunneling is the dominant transition mechanism.

Second step in Born-Oppenheimer procedure:

II. Displacements of the atoms

Topics mentioned:

a. **Transition state theory (TST) for thermally activated transitions and WKE procedure**
b. **Harmonic approximation to TST (HTST) – easy to use with DFT**
c. **Minimum energy paths – the NEB and CI-NEB methods**
d. **Adaptive kinetic Monte Carlo for simulating time evolution**
e. **Tunneling rates obtained from harmonic quantum TST and WKB tunneling paths**

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Andreas Pedersen - former Ph.D. student at UI, now research scientist

Jean-Claude Berthet – post-doc at UI (math)

Pavel Bessarab - Ph.D. student at UI

Kristinn Guðnason – M.S. student at UI (math)