Lecture 2: HTST & minimum energy path calculations

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

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

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

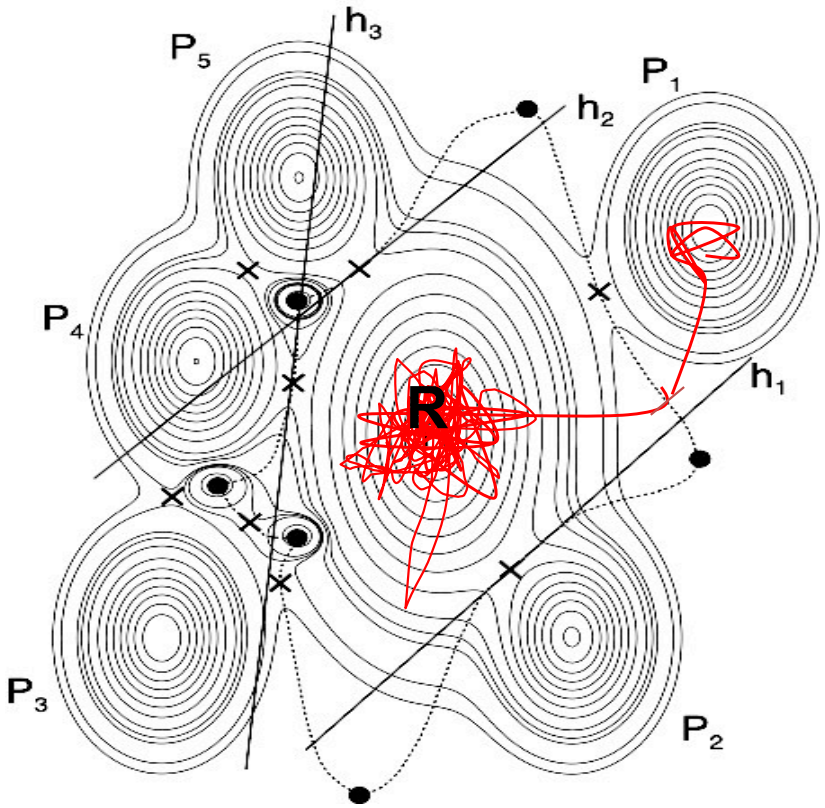
Second step in Born-Oppenheimer procedure:

Displacements of the atoms

Theoretical methods:

a. Transition state theory (TST) for thermally activated transitions and WKE two step procedure
b. Harmonic approximation to TST (HTST) – easy to use with DFT
c. Minimum energy paths – the NEB and CI-NEB methods
d. Saddle point searches without specifying a final state
e. Adaptive kinetic Monte Carlo for simulating long time evolution

Systems of interest involve many degrees of freedom!



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

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

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

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

Stationary points, steepest descent paths, minimum energy paths

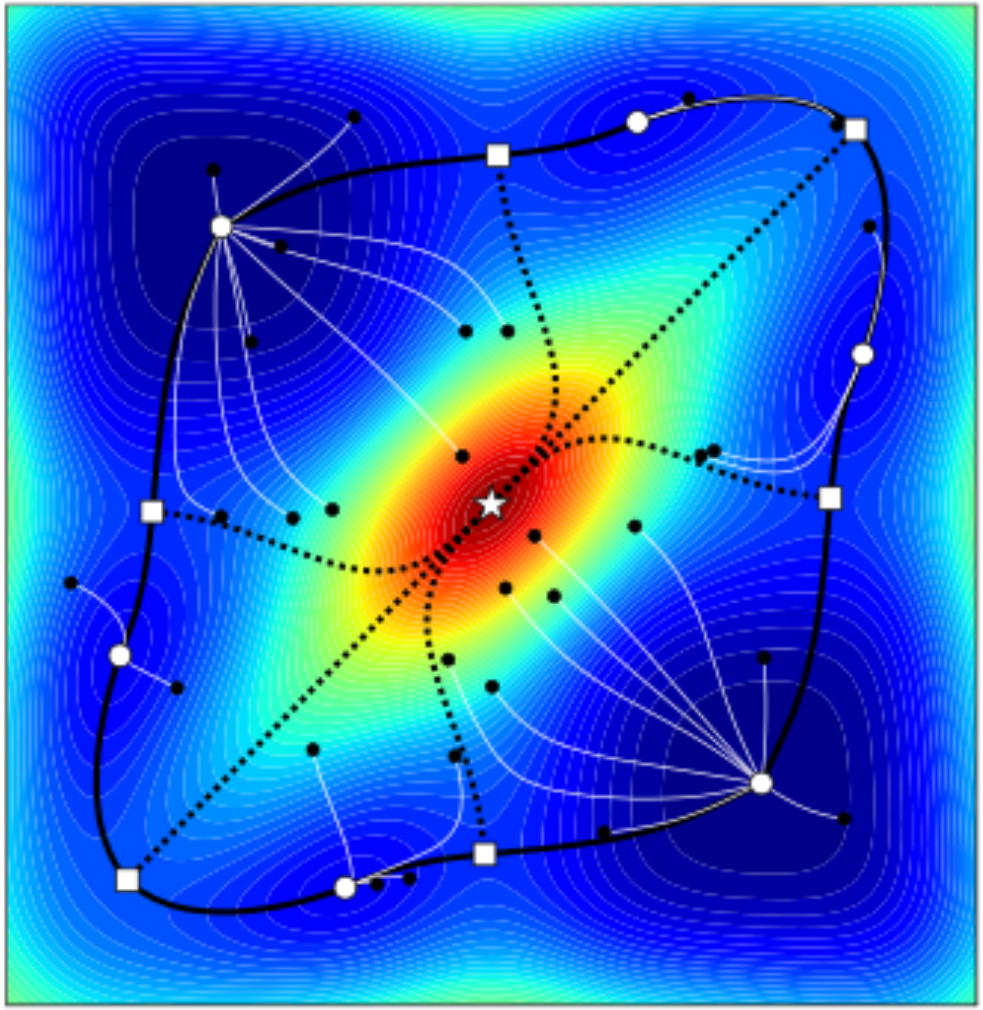


Figure Examples of steepest descent paths. The white symbols represent stationary points, the circles are minima, the squares are SP_1s and the star is a SP_2. The black circles are starting points for random SDPs (the white lines). The black lines are specific SDPs, the dotted ones are ridges while the solid ones are MEPs.

Gradient:

$$\nabla \mathbf{V}(\mathbf{x}) = \sum_{\mathbf{i}} \frac{\partial \mathbf{V}}{\partial \mathbf{x_i}} \hat{\mathbf{x}}_\mathbf{i}$$

At a stationary point:

$$\nabla \mathbf{V}(\mathbf{x}) = \mathbf{0}$$

minima, saddle points, …

Steepest descent path:

Follows the negative gradient at eath point

Minimum energy path (MEP):

steepest descent paths for which V is at a minimum in all directions perpendicular to the path

$$\nabla \mathbf{V} - (\nabla \mathbf{V} \cdot \hat{\tau})\hat{\tau} = \mathbf{0}$$

where $\hat{\tau}$ is unit tangent to the path

HTST - Harmonic approximation to TST:

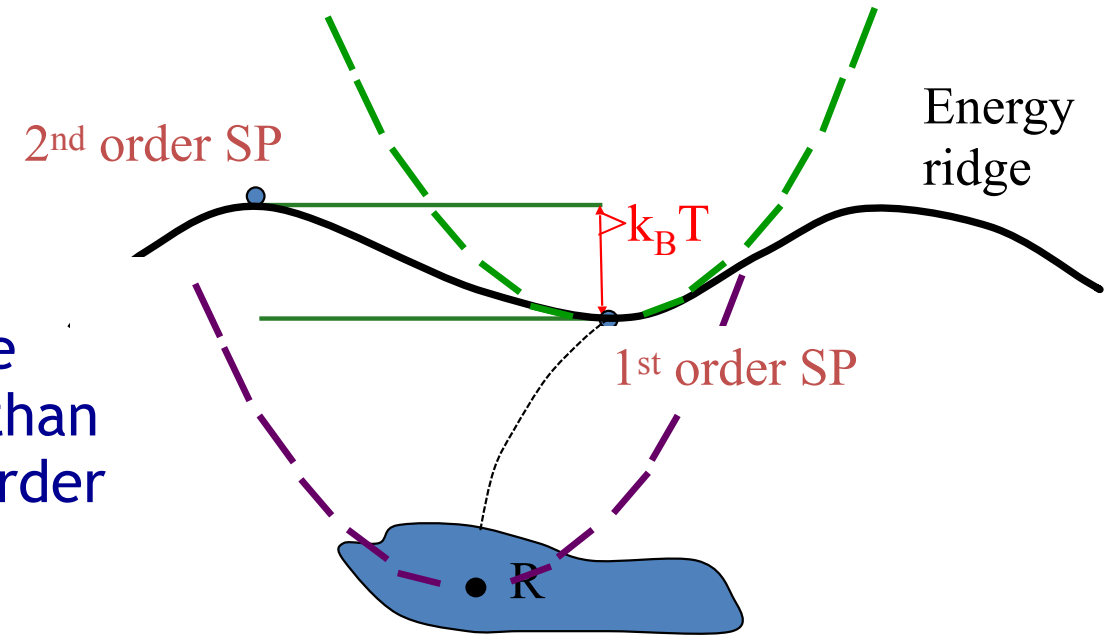
Good for solids at not too high T

Works well when

(1) energy of *second* order saddle points is significantly higher than $k_B T$ over the energy of *first* order saddle points,

and

(2) when the potential is smooth enough that a second order Taylor approximation to the PES is good enough in the region of large statistical weight.

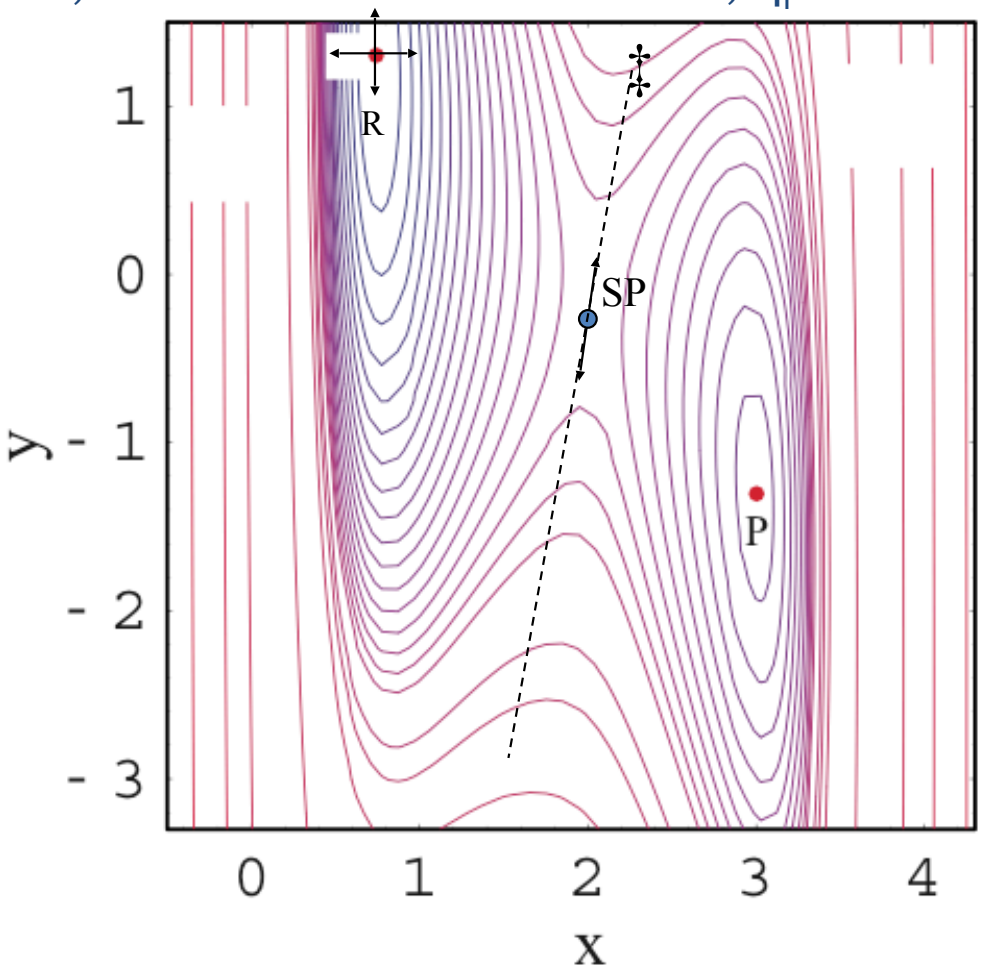


Derivation of HTST: Expand PES around minimum in *normal mode* coordinates

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

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

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



Plug into the expression for the rate constant:

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

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

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

Interpretation of the expression for k^{HTST}

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

ln of prefactor →

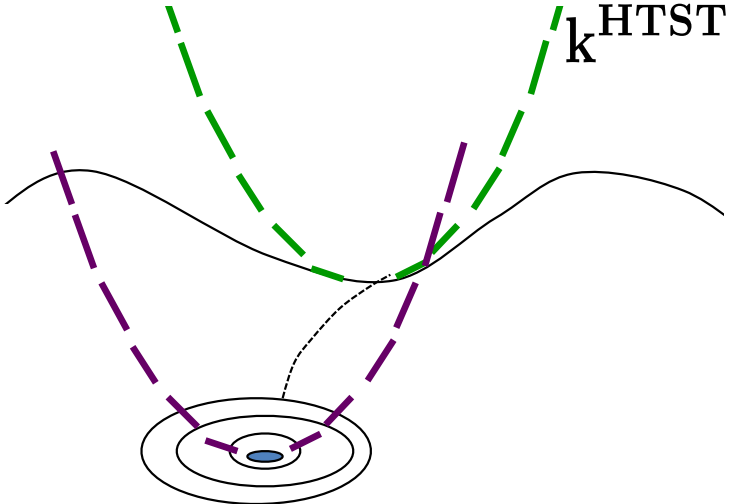
ln k^{HTST}

←slope is $E_a = V_{sp} - V_{min}$

1/T

Agrees with the empirical Arrhenius law

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



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

$$= \nu\, e^{-(V_{SP}-V_{min})/k_B T}$$

vibration along MEP at initial state minimum

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

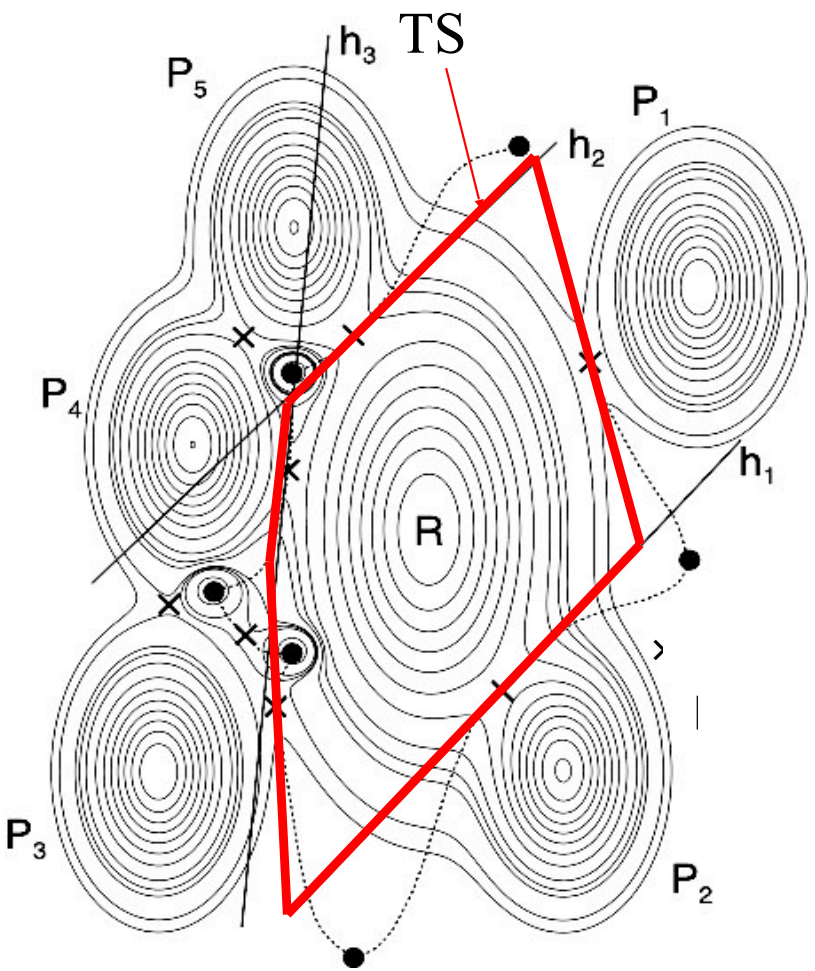
- Need to find **all relevant saddle points** on the potential energy rim surrounding the energy basin corresponding to the initial state.

- The transition state is approximated as a set of hyperplanes going through the saddle points with the unstable mode normal to the hyperplane.

- For each hyperplanar segment:

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

Temperature and entropy are taken into account within the harmonic approximation



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

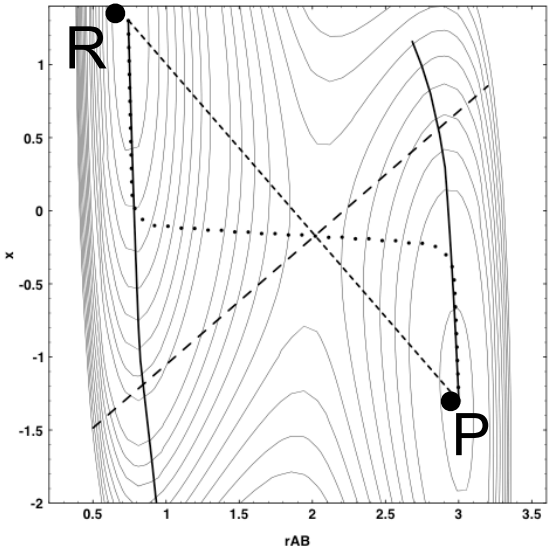
How to find the saddle point(s) ?

Methods for finding saddle points

Two categories:

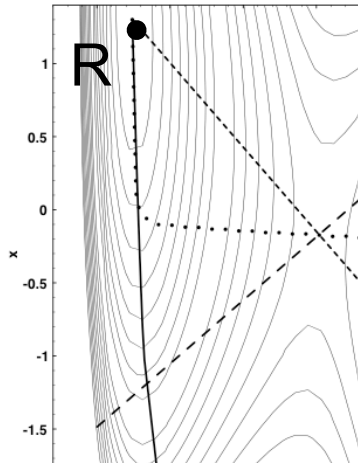
A. Two point problem – both initial and final state minima are known.

Easier, since info about final state minimum can guide the search



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

Harder, can only use local info about the energy surface



Second step in Born-Oppenheimer procedure:

Displacements of the atoms

Theoretical methods:

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e. Adaptive kinetic Monte Carlo for simulating time evolution

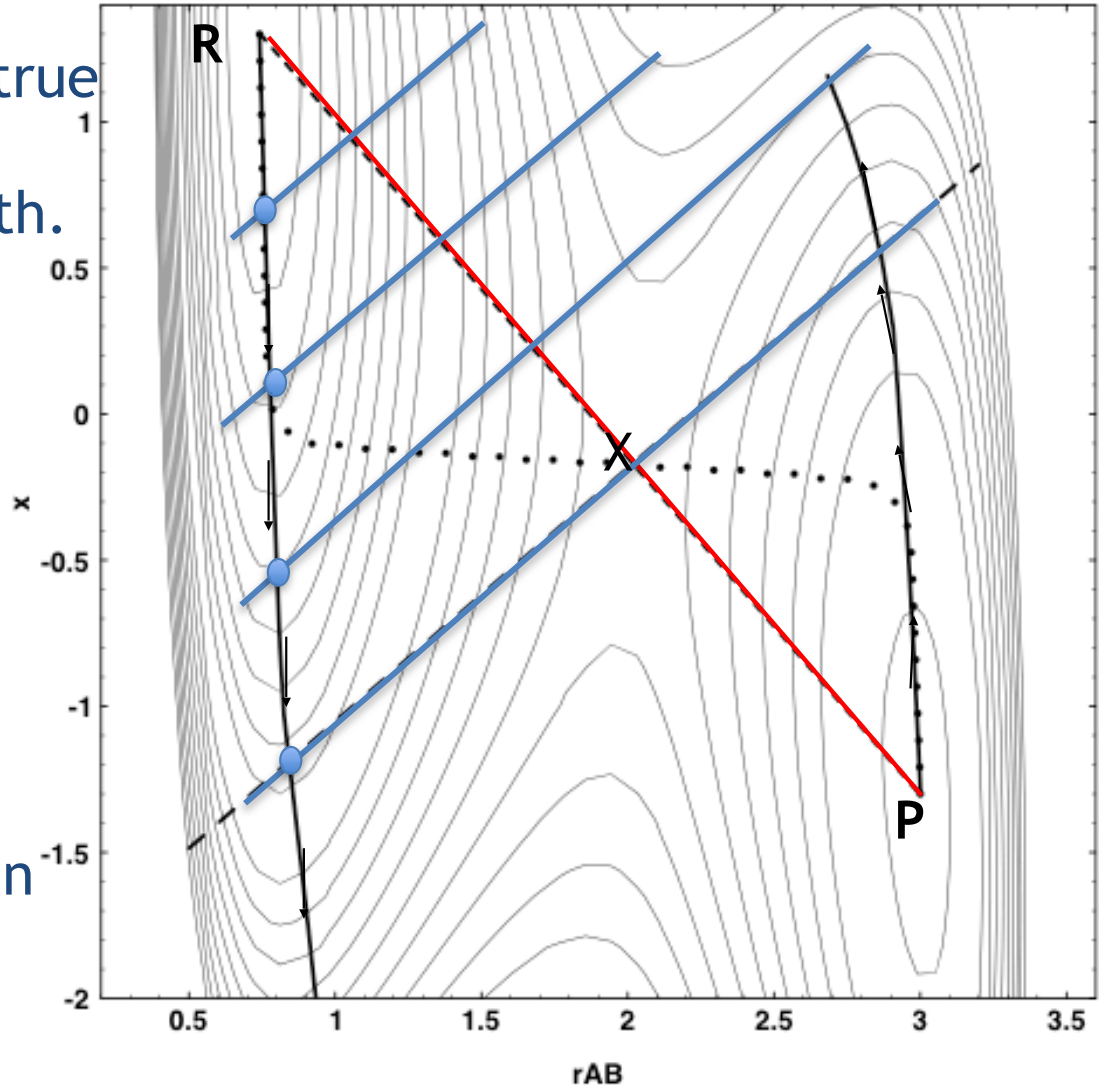
‘Drag method’ or ‘Constrained Minimization’

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

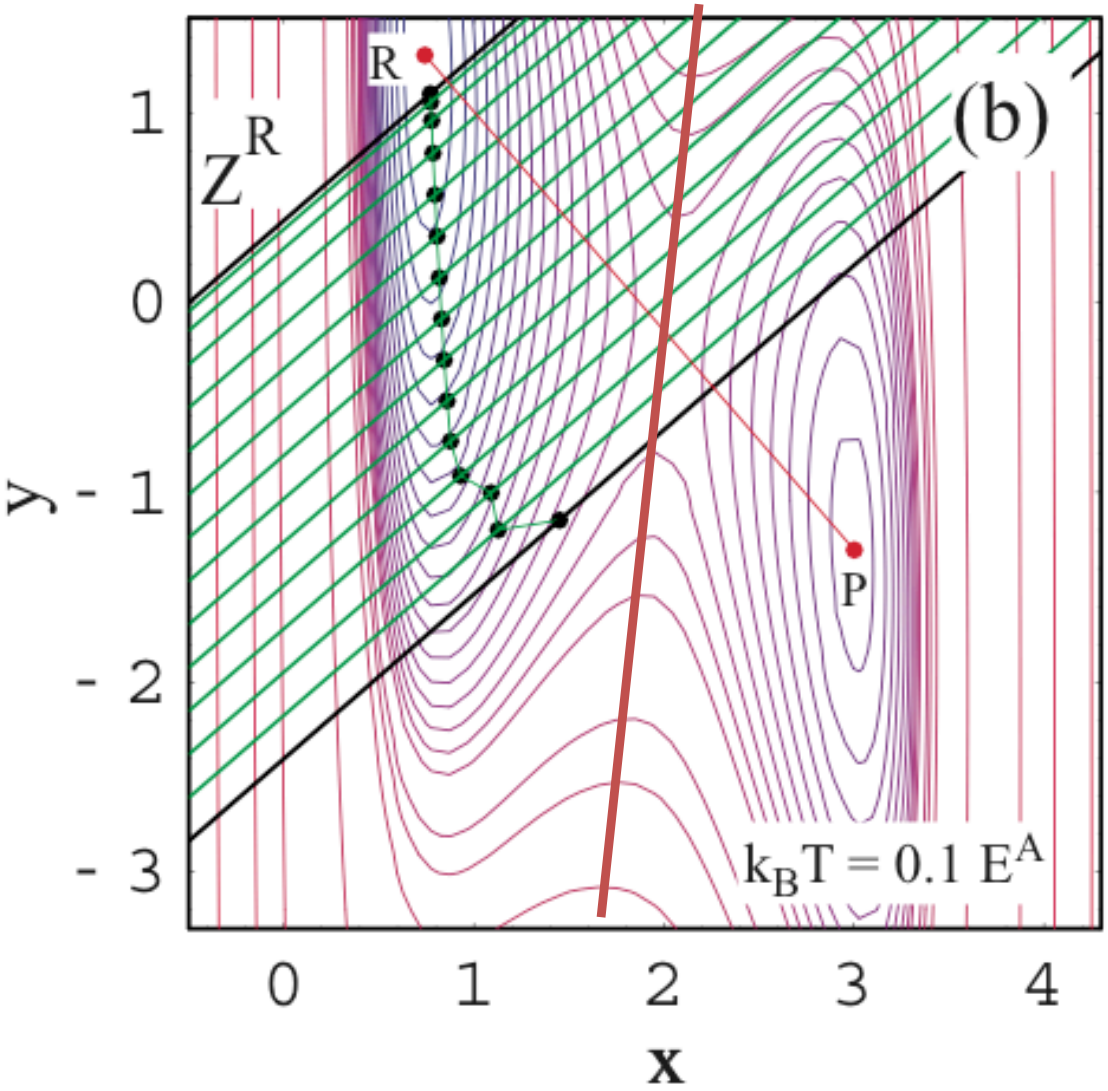
Can work, but fails when the true reaction coordinate differs significantly from the drag path.

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

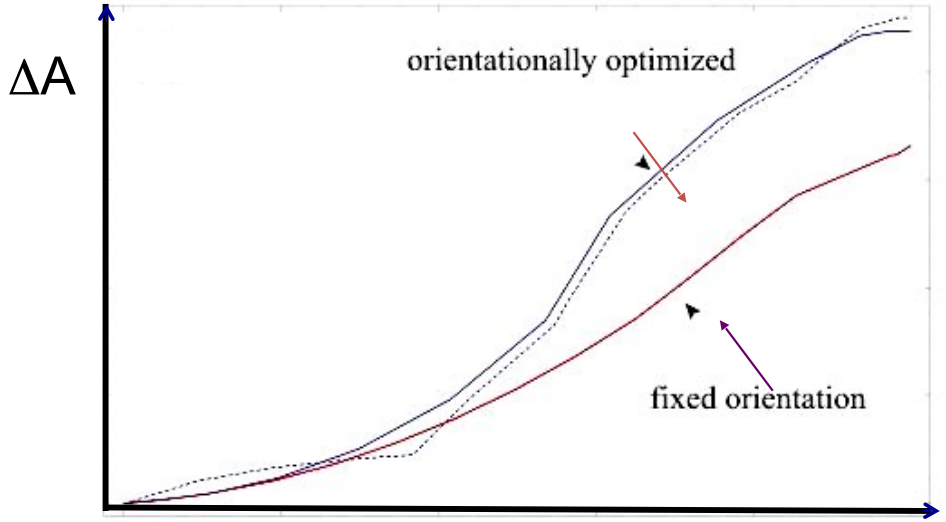
Can lead to a discontinuous path and hysteresis (P to R gives a different estimate than R to P).



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

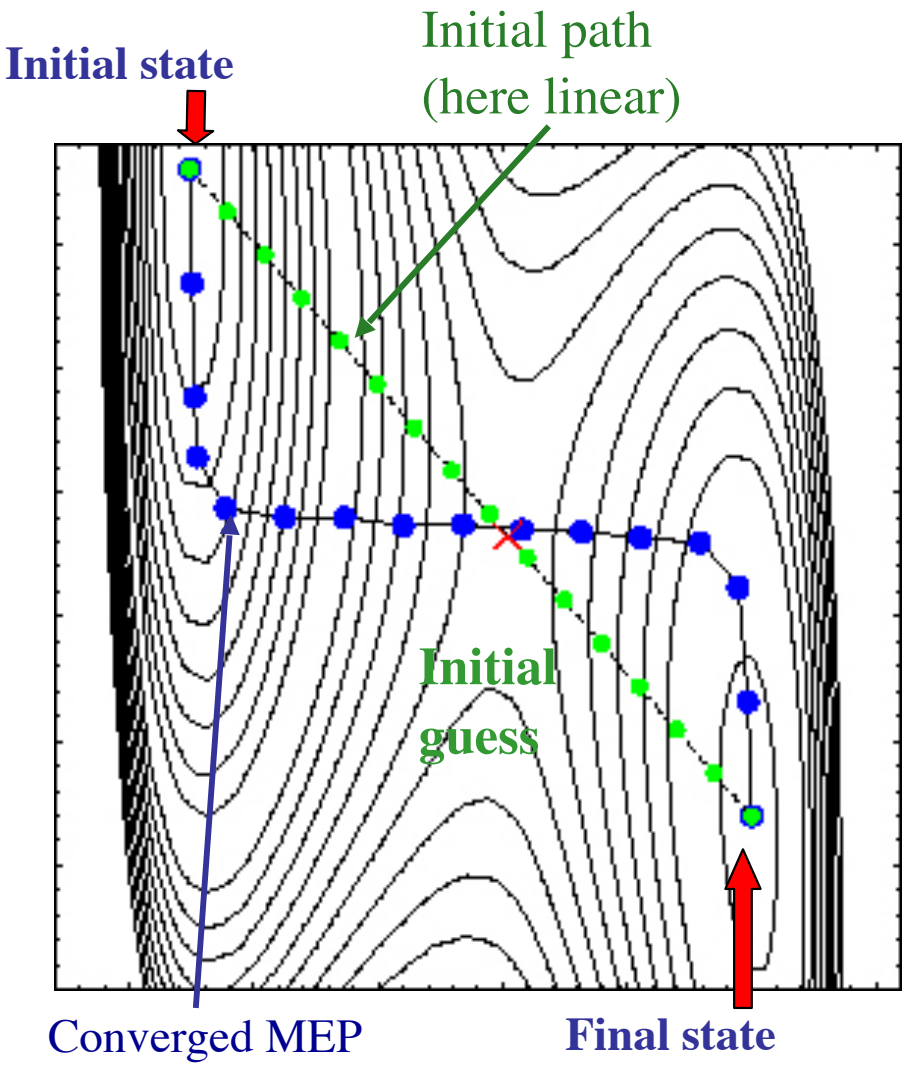


Not good to just pick some reaction coordinate and then average with respect to other degrees of freedom.



In a 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 – it is essential to optimize orientation! *Optimization of orientation can reveal the transition mechanism.*

Nudged Elastic Band (NEB) Method



Create several replicas of the system, 'images' (discretization points for the path)

Estimate the tangent at each image, $\hat{\tau}_{||}$ using line segment to adjacent image with higher energy.

Only the perpendicular component of the force acts on each image

$$\nabla V(\mathbf{x}_i)\big|_{\perp} = \nabla V(\mathbf{x}_i) - \left(\nabla V(\mathbf{x}_i)\cdot\hat{\tau}_{||}\right)\hat{\tau}_{||}$$

and the distribution of the images along the path is controlled by adding a spring force

$$\mathbf{F}_i^s = k_{i+1}\left(\mathbf{x}_{i+1}-\mathbf{x}_i\right) - k_i\left(\mathbf{x}_i-\mathbf{x}_{i-1}\right)$$

So the net force on an image becomes

$$\mathbf{F}_i^{NEB} = -\nabla V(\mathbf{x}_i)\big|_{\perp} + \left(\mathbf{F}_i^s\cdot\hat{\tau}_{||}\right)\hat{\tau}_{||}$$

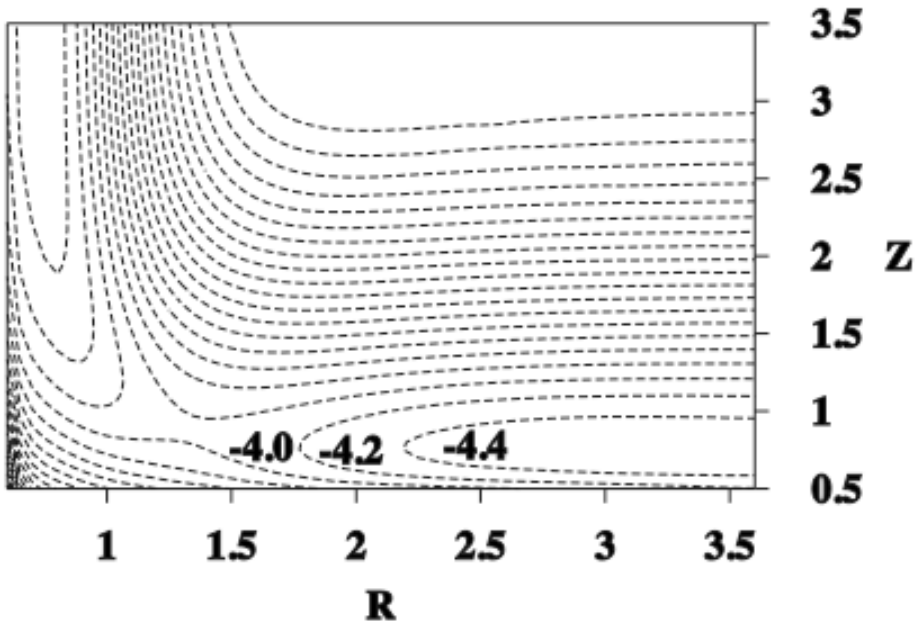
Adjust all images simultaneously, parallel computing.

*(Mills, Jónsson & Schenter, Surf. Sci. **324**, 305 (1995); Jónsson, Mills, Jakobsen, 1998). Review: V. Ásgeirsson and H. Jónsson, "Handbook of Materials Modeling. 1 Methods: Theory and Modeling" (Springer, 2018).*

Recall: H_2 adsorption/desorption from Cu(110) - get MEP using NEB

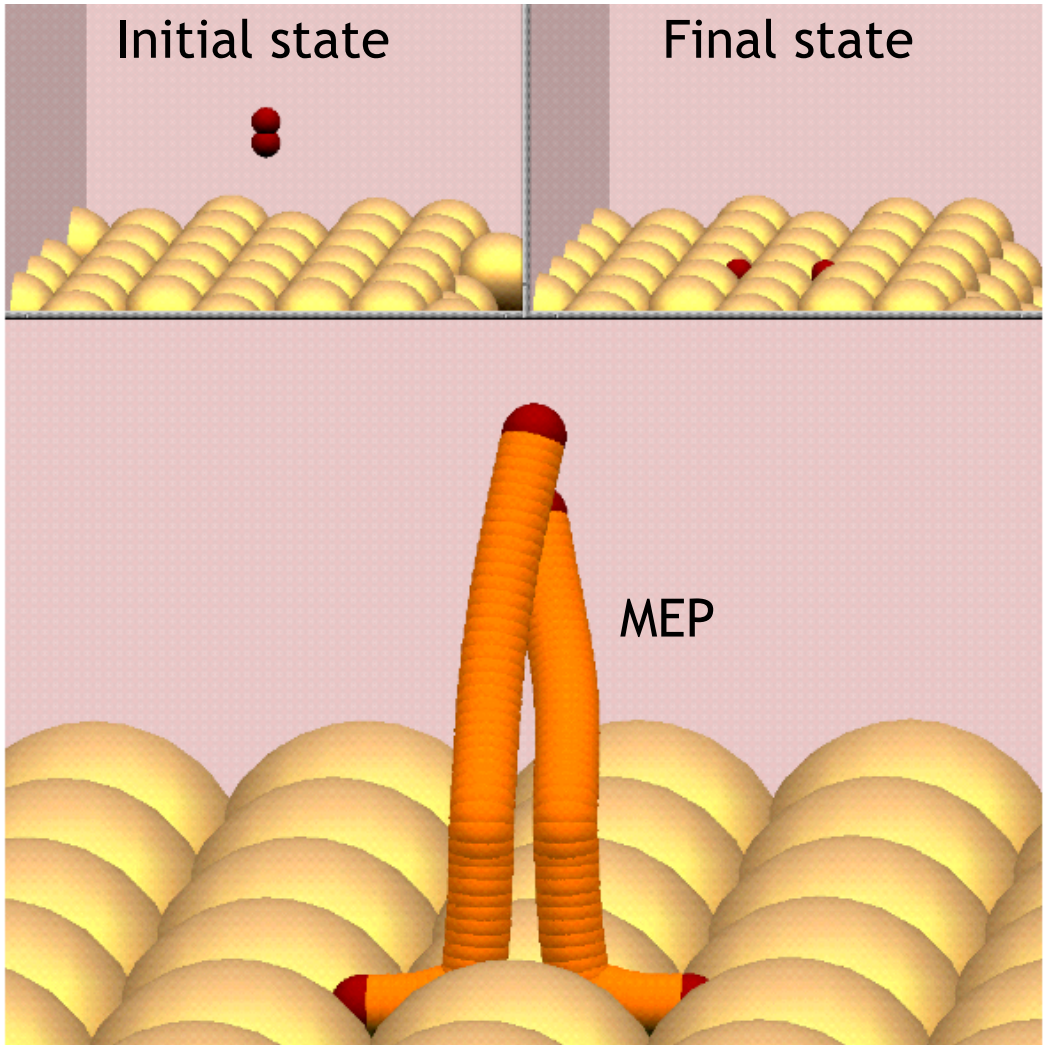
G. Mills and HJ, Phys. Rrev. Letters 1994

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



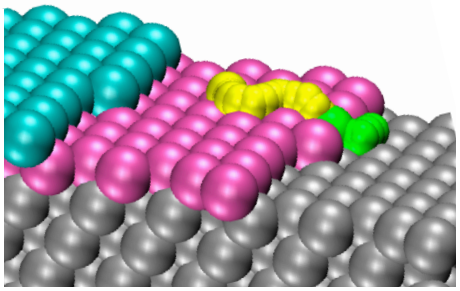
Evaluate the reversible work required to shift the system from reactants towards products to get ΔF

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

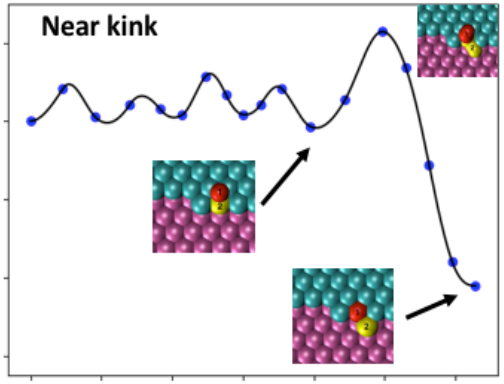


Example: Elementary processes in crystal growth

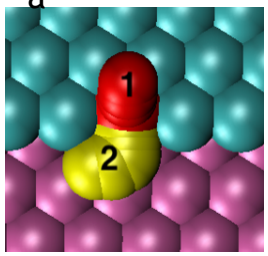
Unexpected temperature dependence observed in crystal growth for example Pt(111) growth (Poelsema et al.).



High temperature, T = 620 K: layer-by-layer growth
Intermediate temperature T = 425 K: multilayer growth
Low temperature, T = 275 K: **re-entrant** layer-by-layer growth

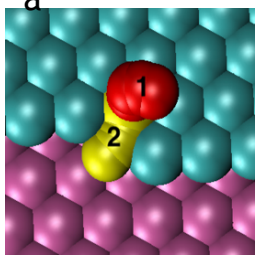


E_a = 0.45 eV



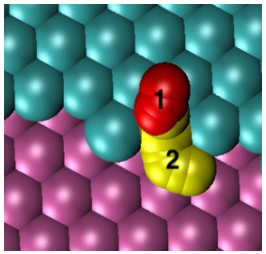
at straight edge

E_a = 0.38 eV



at kink

E_a = 0.15 eV



near kink

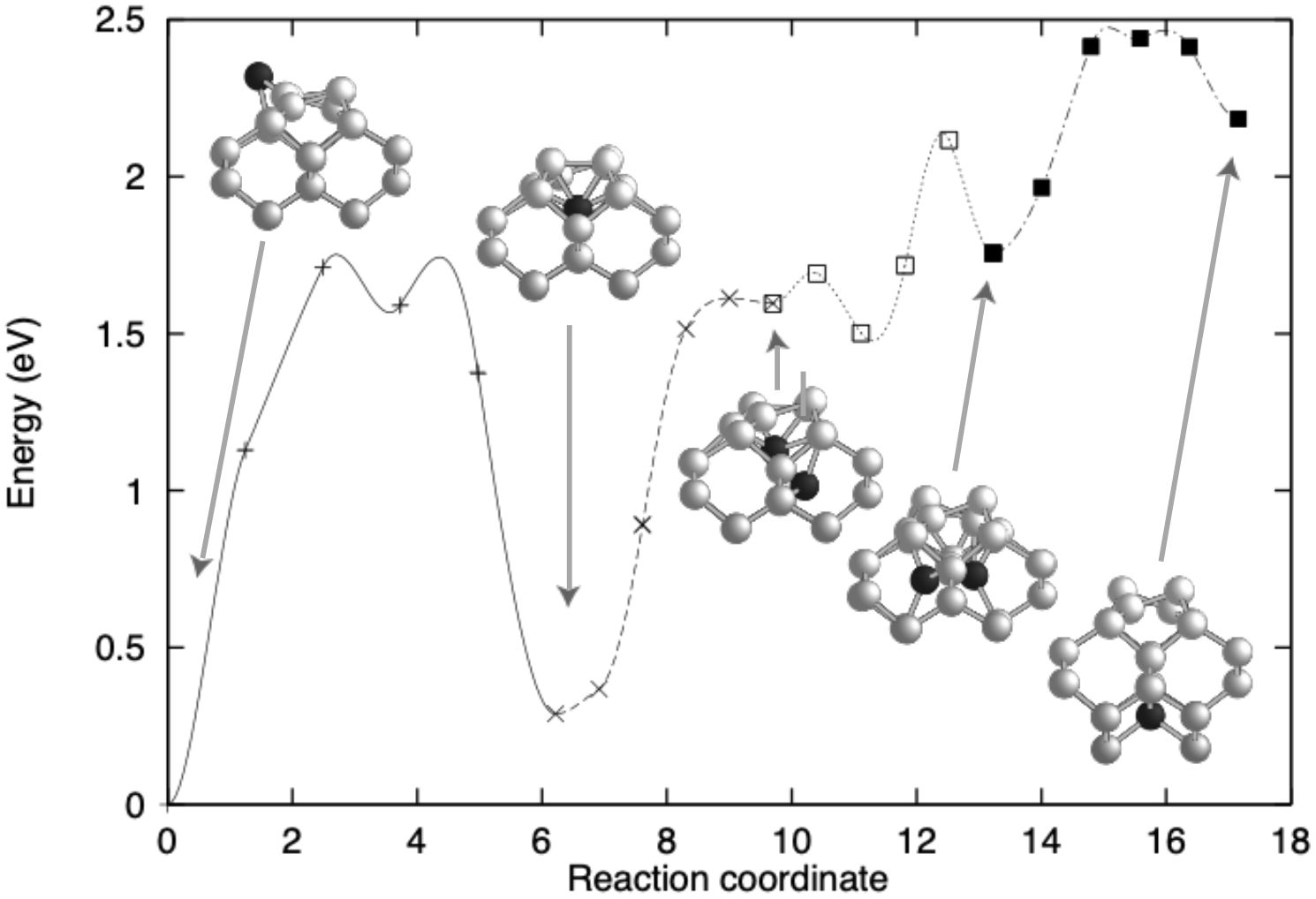
Lowest energy barrier for down stepping is ***near*** but not *at* kinks!

Leads to formation of more kinks.
Fractal islands at low temperature, T = 275 K

M. Villarba and HJ, Surf. Sci. 1995

Example: First use of NEB with DFT calculations

Migration of Ge atom into subsurface sites of Si(100).



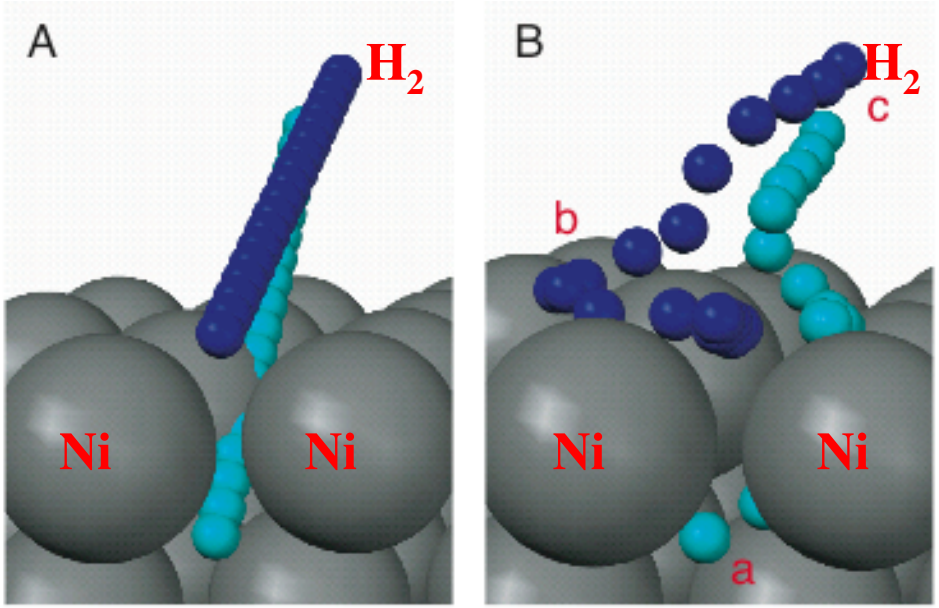
Blas Uberuaga *et al*. PRL 2000

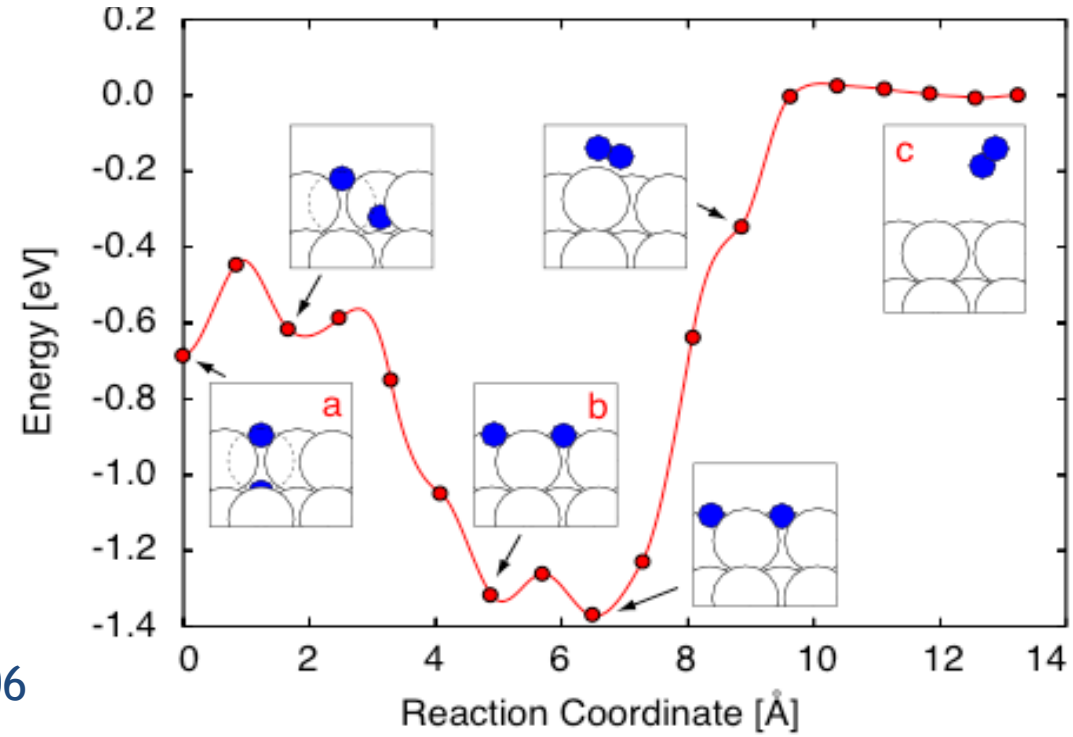
Example: Use NEB with DFT calculations

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

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

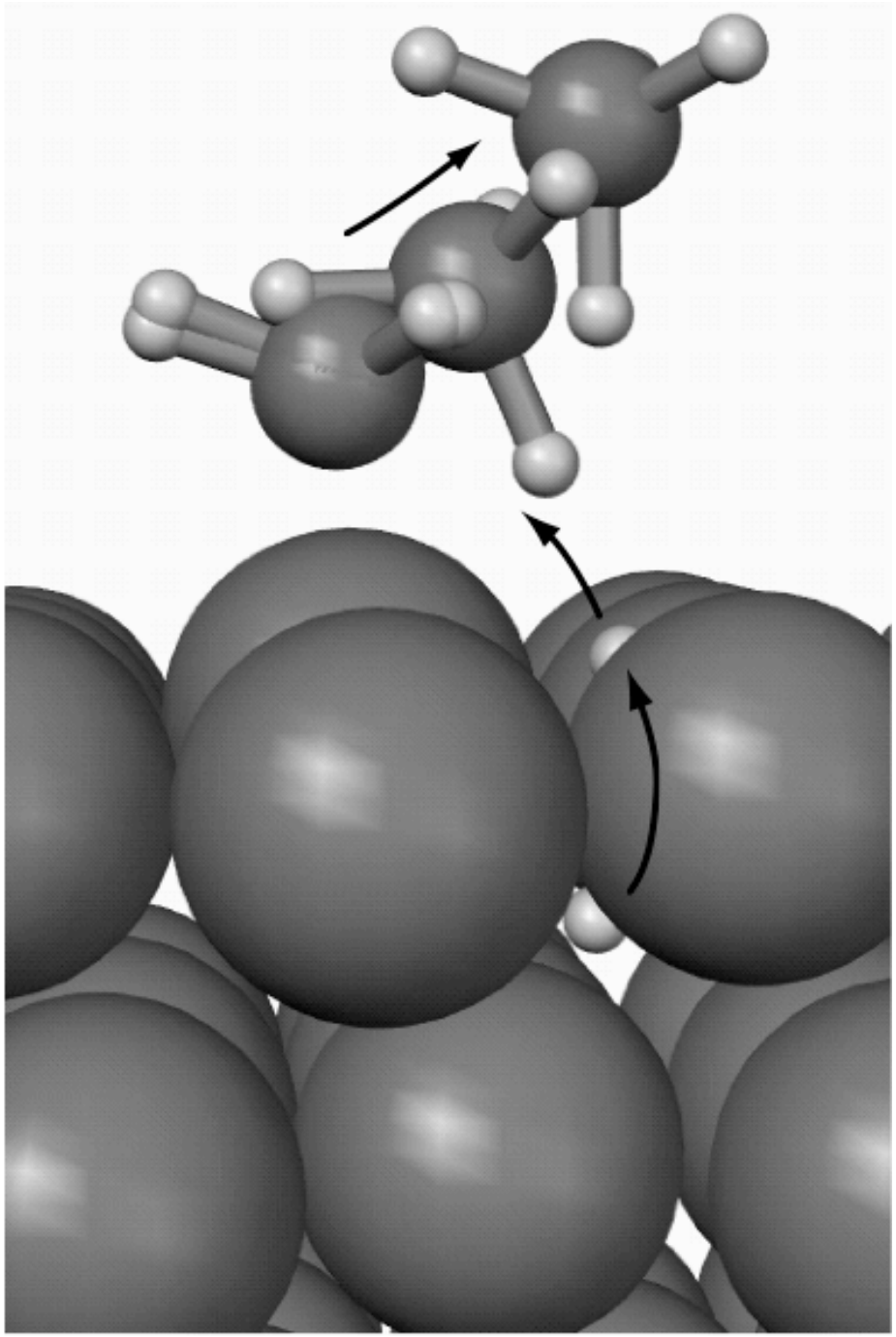
But, the MEP found shows that surface H-atom hops away. So, not H-H bond formation as subsurface H-atom moves up to the surface.



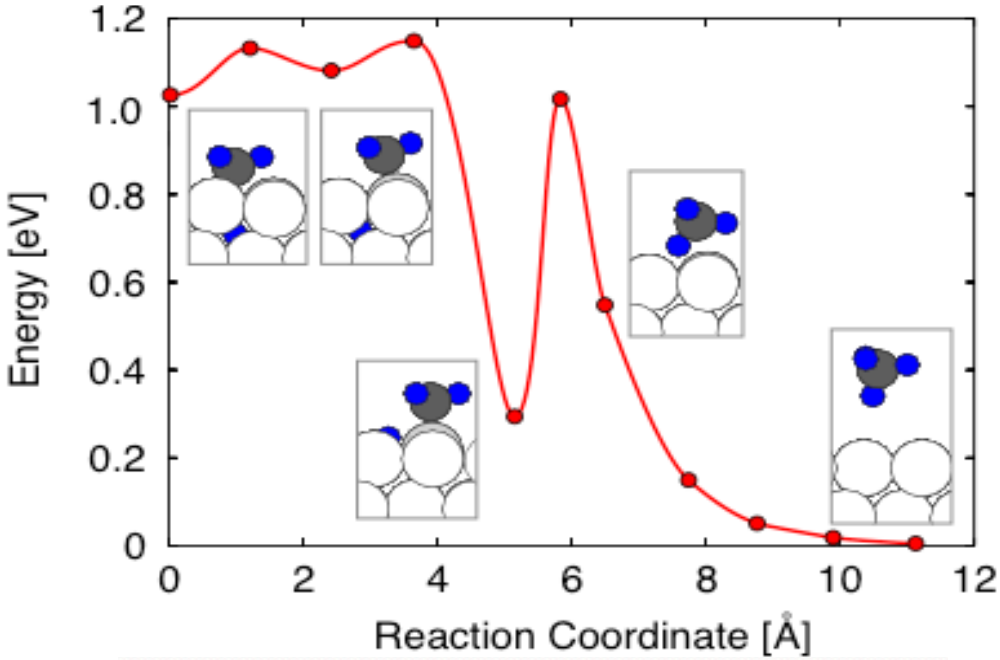


G. Henkelman, A. Arnaldsson and HJ, *JCP* 2006

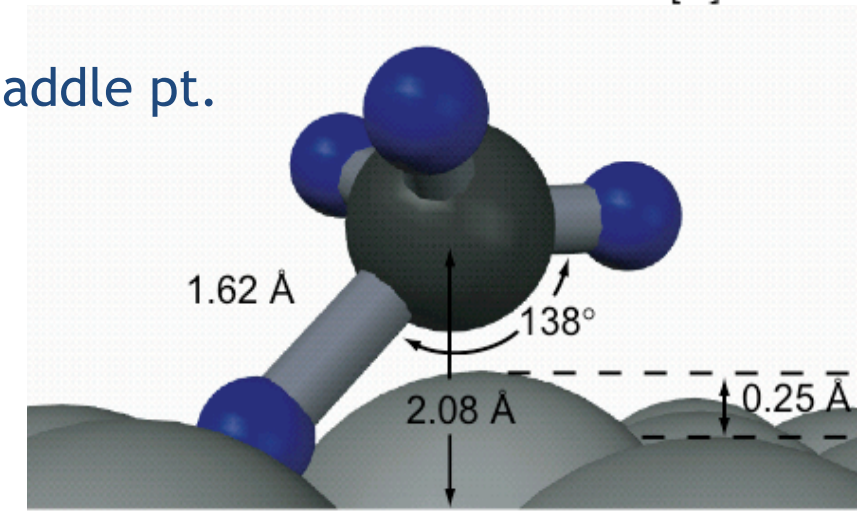
Example: Associative desorption of CH_4 from Ni(111), subsurface H



Same story as for H_2: no direct path for rxn. with subsurface H



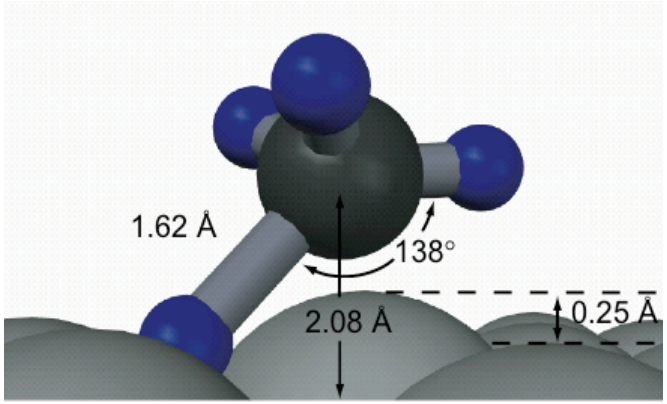
Saddle pt.



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

Then do the second step in WKE: Calculate trajectories starting at TS

After finding transition state (step 1 in WKE), do step 2, i.e. calculate dynamical trajectories (with DFT) starting from there to learn about the products, CH_4 in gas phase and bare Ni(111) surface.

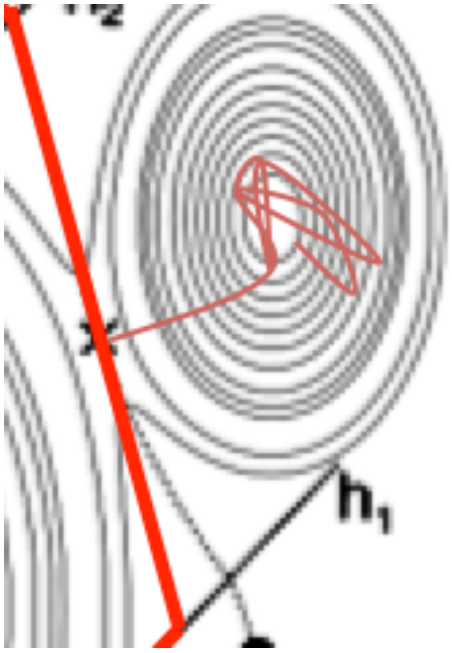


Find how much energy there is in the various degrees of freedom of the products:

Energy (eV)	Mode or subsystem
0.13	Ni(111) slab
0.50	CH_4 translation
0.03	CH_4 rotation
0.19	CH_4 vibration
0.85	Total in CH_4 and Ni(111) systems

Energy in each vibrational mode of CH_4

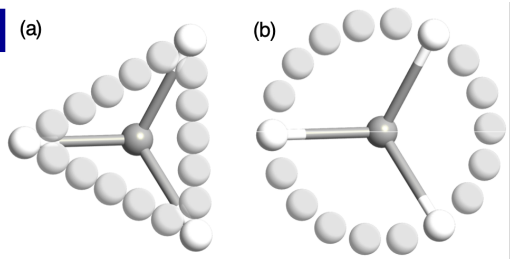
Energy (eV)	Mode Description	Frequency (cm^{-1})
0.021	$T2(\times 3)$ asymmetric stretch	3207
0.020	$A1(\times 1)$ symmetric stretch	3063
0.003	$E(\times 2)$ asymmetric deformation	1551
0.002	$T2(\times 3)$ asymmetric deformation	1324



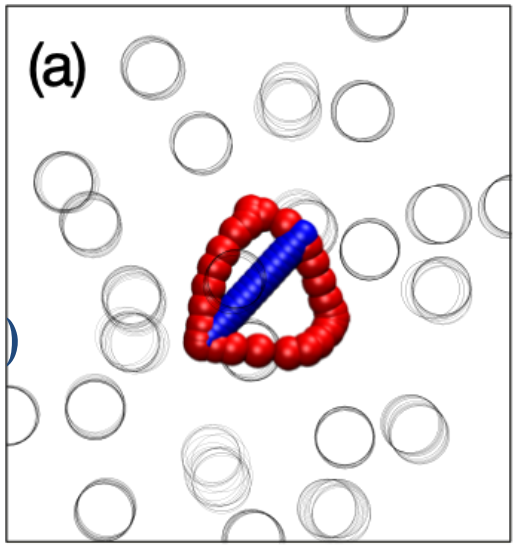
G. Henkelman, A. Arnaldsson and HJ, *JCP* 2006

A better initial path for NEB calculations: IDPP

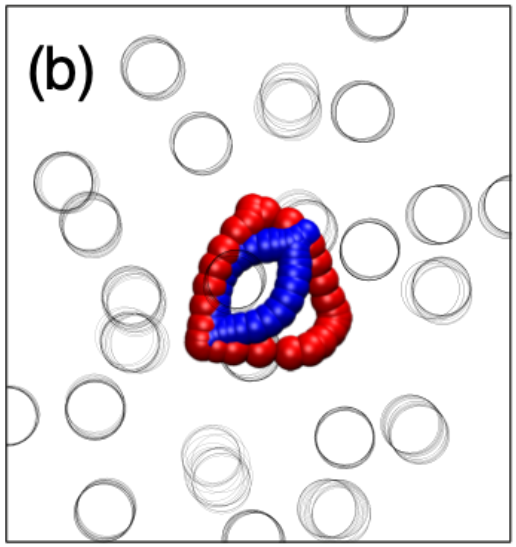
Interpolate pairwise distances in images between initial and final configurations, then fit coordinates of intermediate images to best satisfy the interpolated distances.
This generates **IDPP** - image dependent pair potential.
Can reduce SCF iterations since very close proximity of atoms is avoided, and saves atomic displacement iterations because the path is closer to MEP.



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



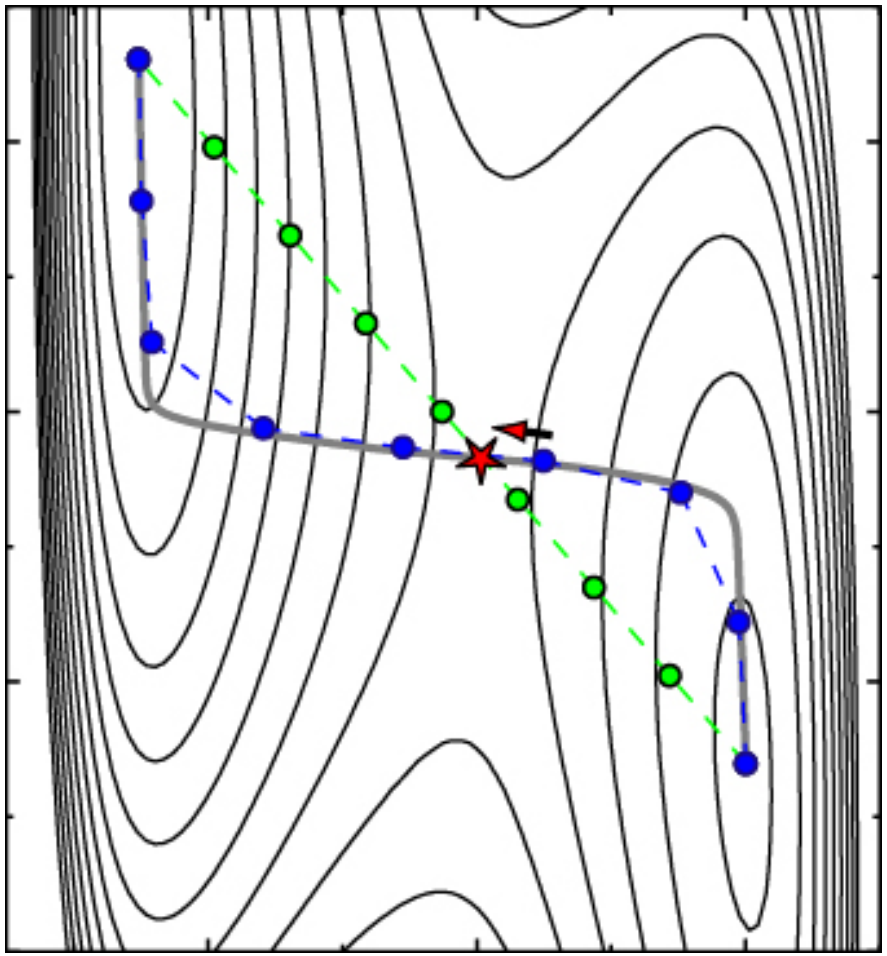
Straight line interpolation
MEP



IDPP
MEP

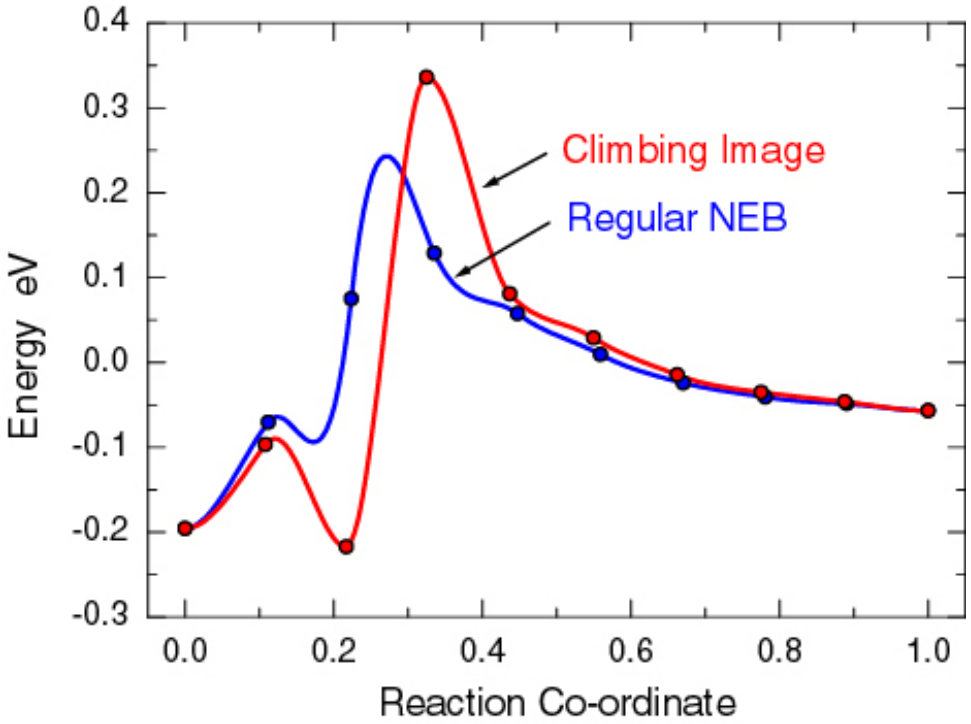
(S. Smidstrup, A. Pedersen, K. Stokbro and HJ, *JCP 140, 214106* (2014))

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



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

$$F_{CI} = \nabla V(R_{CI}) - 2\nabla V(R_{CI}) \cdot \tau_{||}\tau_{||}$$

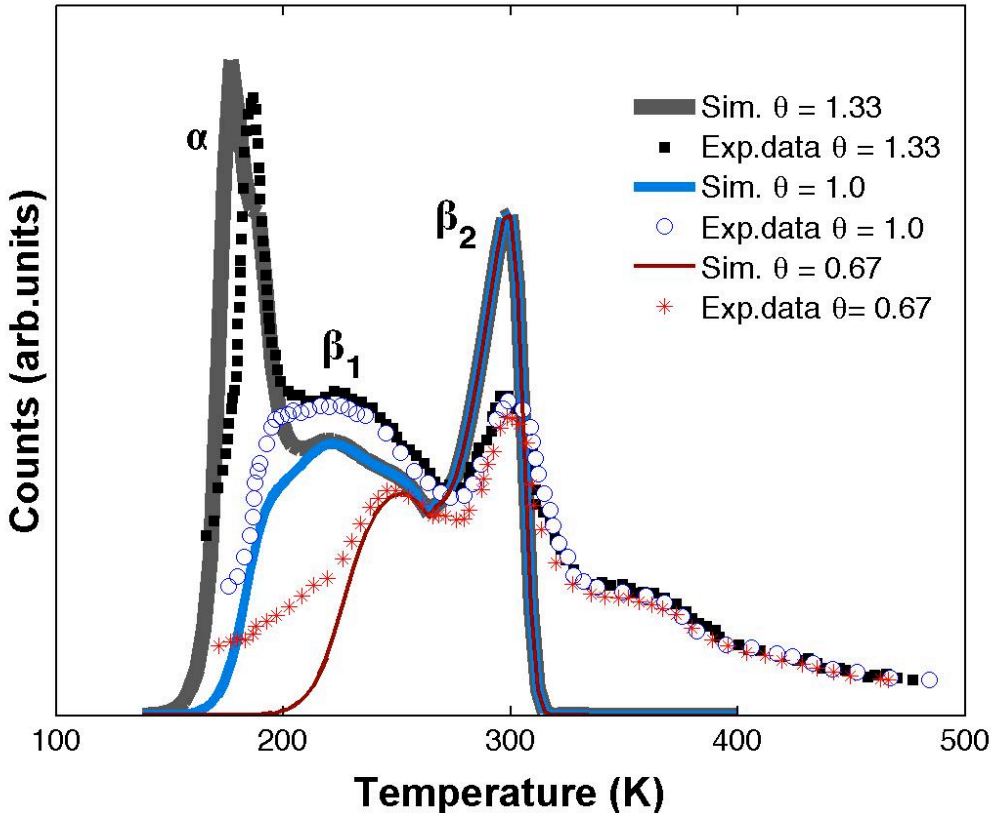


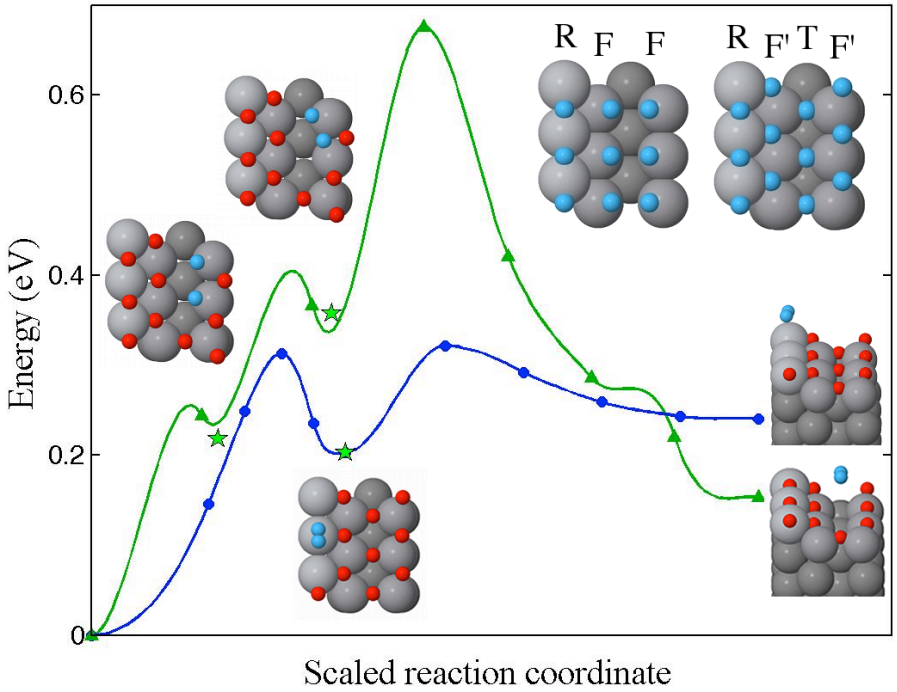
(G. Henkelman, B.P. Uberuaga and HJ, J. Chem. Phys. ***113****, 9902 (2000))*

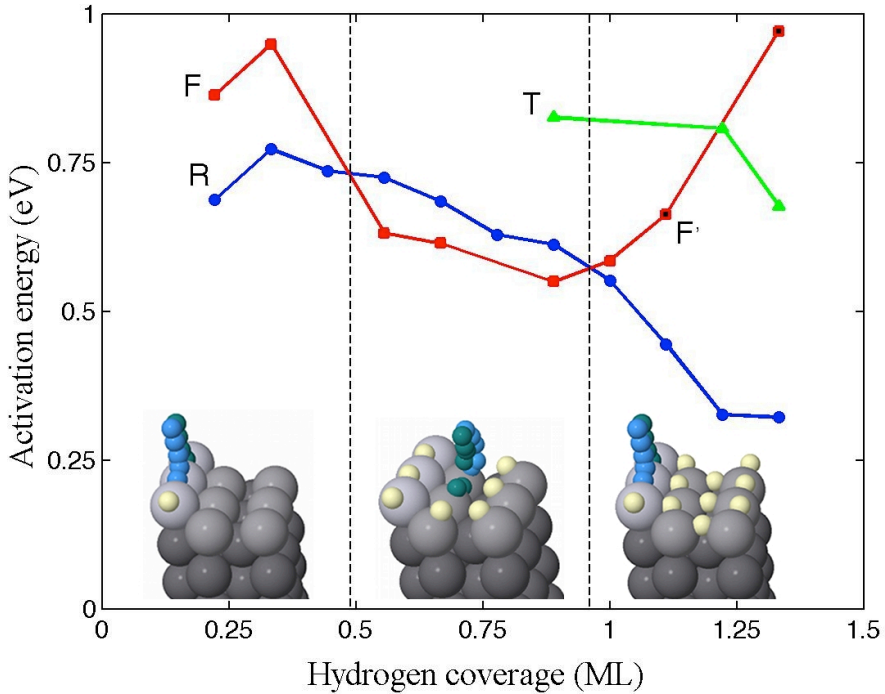
example: Hydrogen evolution reaction

Associative desorption of H_2 from Pt(110)-2x1 as a function of H-adatom coverage.
Very strong coverage dependence!

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







Remarks on using the NEB Method

Cubic interpolation of the energy:

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

Divide and conquer:

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

Rotation and translation:

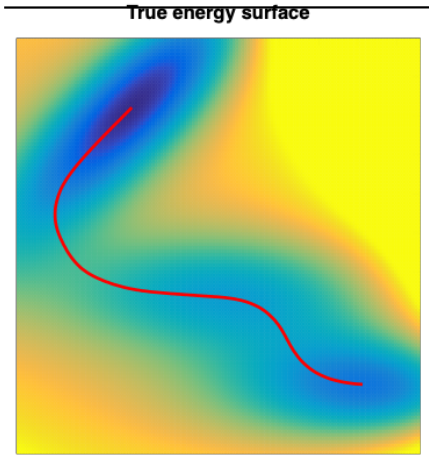
Six degrees of the system (at least) need to be frozen out. Otherwise, the system will do whatever it can to avoid the saddle point region.

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

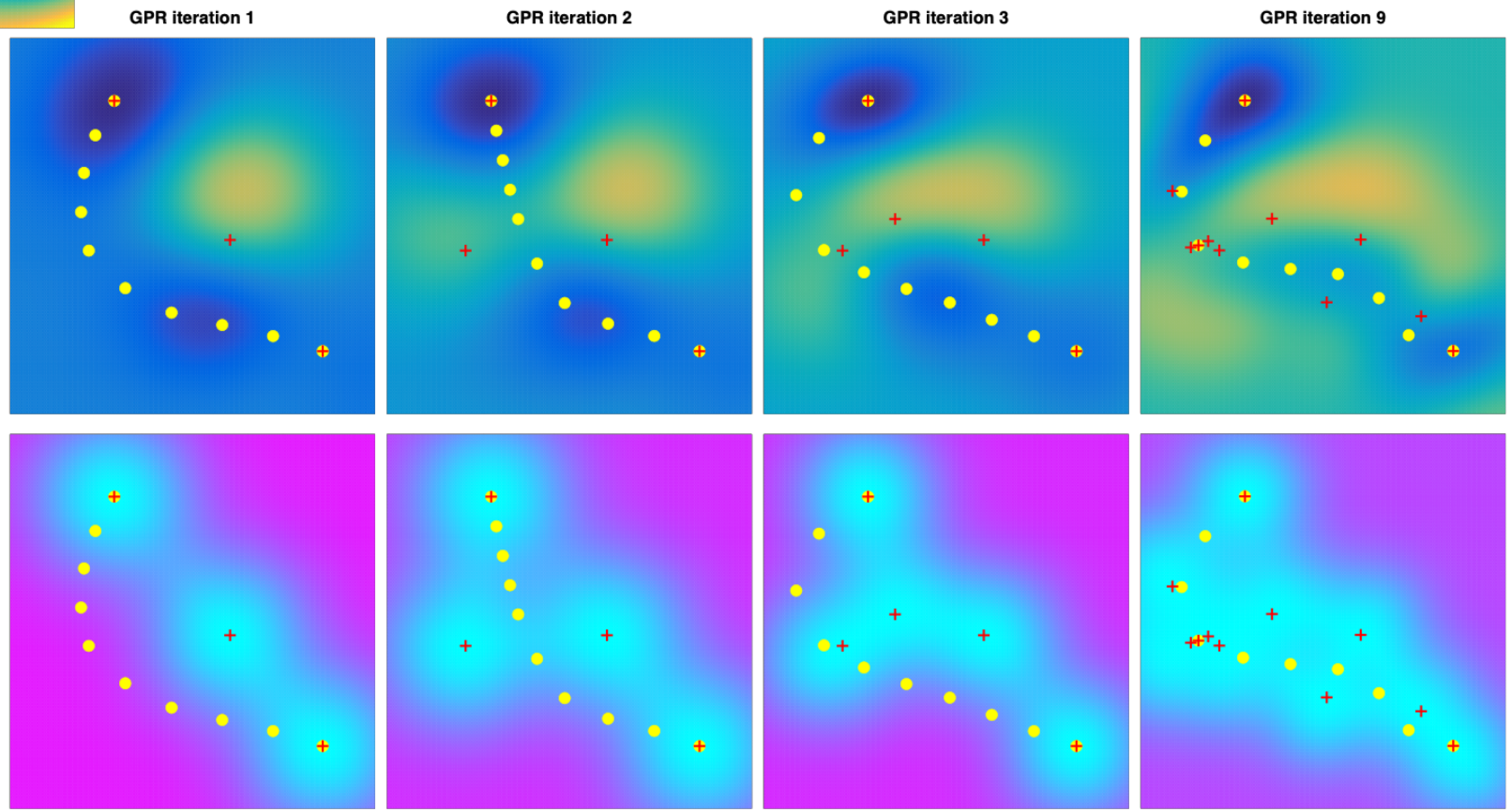
For clusters, remove also rotation using quaternions, see

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

Reduce computational effort by using machine learning



Use Gaussian Process Regression to interpolate and extrapolate to construct an approximate energy surface from the (DFT) calculated points.
Use uncertainty estimate to guide which calculation to carry out next.



O-P. Koistinen,F.B. Dagbjartsóttir V. Ásgeirsson, A. Vehtari and HJ, *JCP* 2017

Sampling MEPs to find the optimal one

Locally optimal MEP:

The NEB optimization usually brings the images to the MEP that is nearest to the initial path. But, this may not be the best path (i.e. the one with lowest activation energy).

Globally optimal MEP:

Genetic algorithm to search for the best MEP.
New intermediate configurations generated from two parent configurations using a heredity transformation.
Each intermediate local minimum found in NEB calculations added to the set.

(Emile Maras *et al.*
Comp. Phys. Commun. 205, 13 (2016)
and
Scientific Reports 7, 11966 (2017))