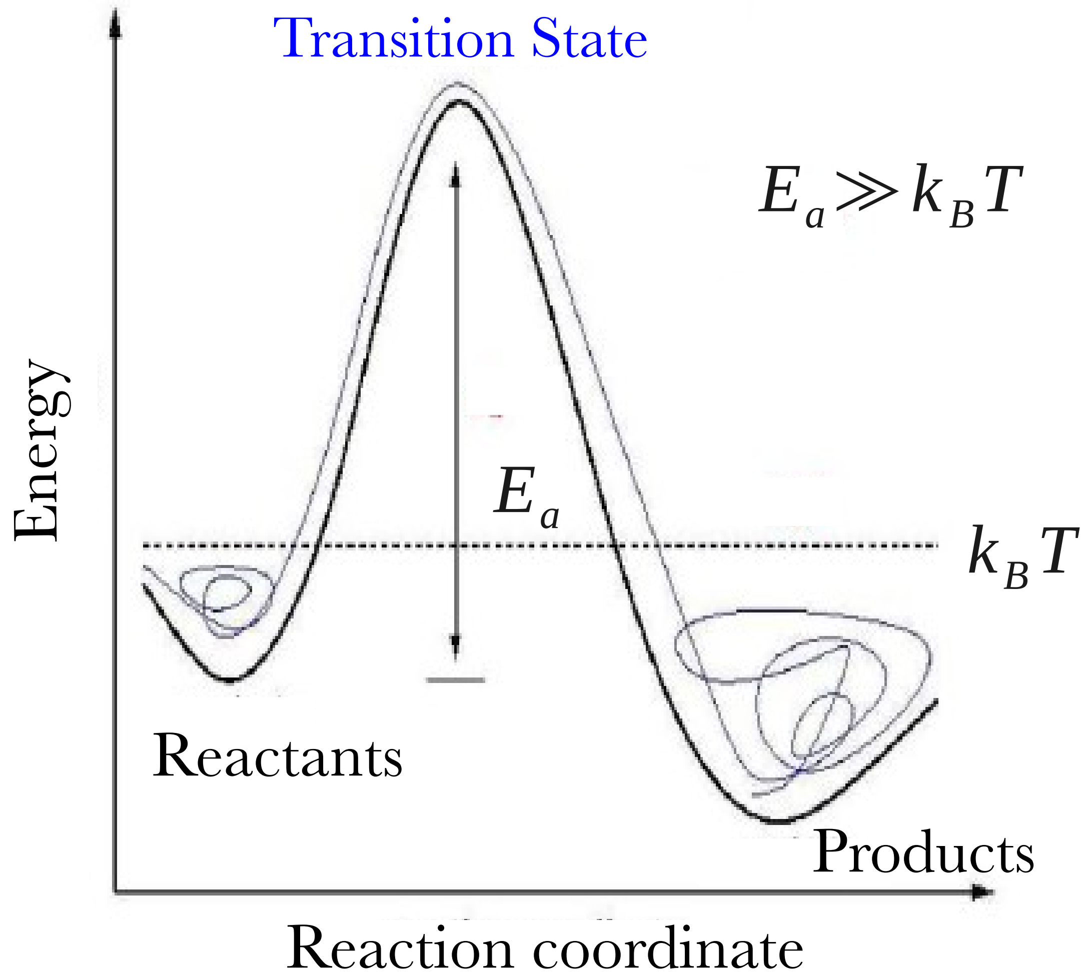
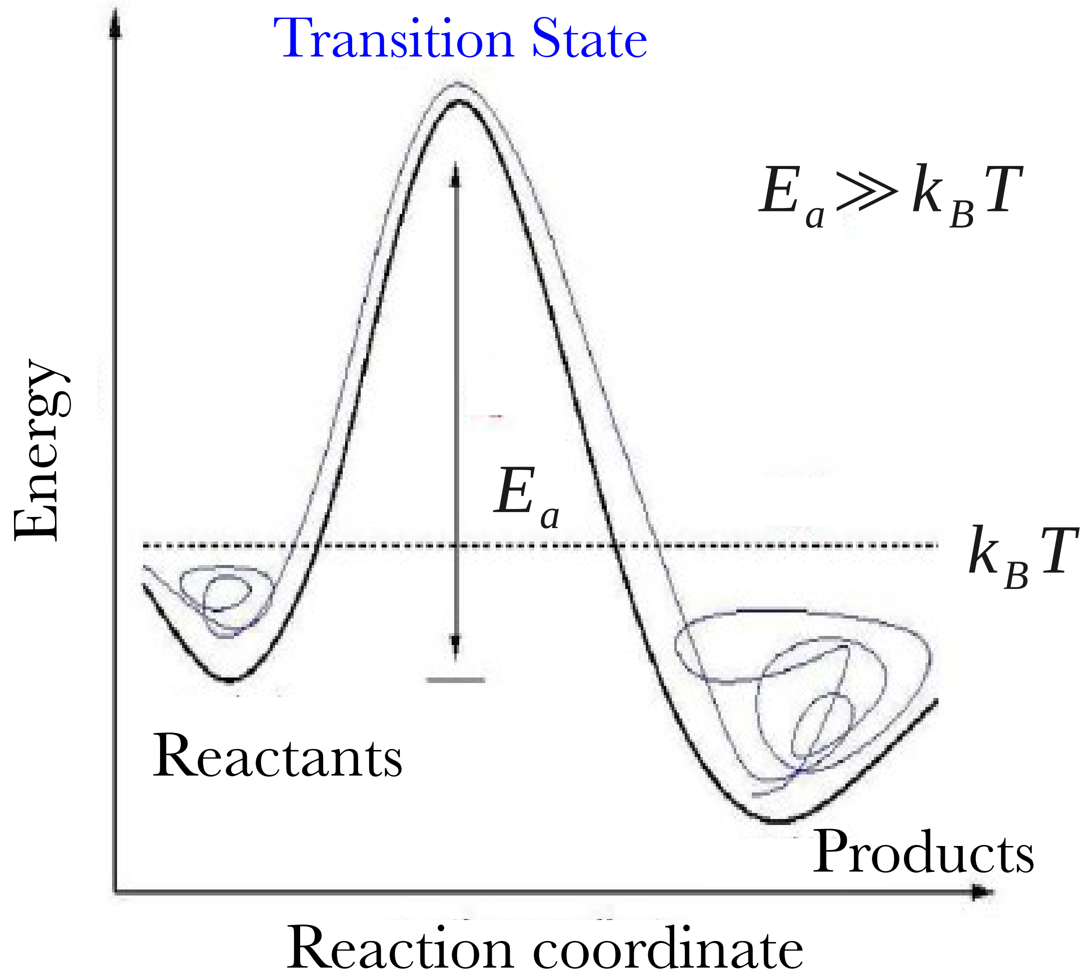
Rare events and Nudged Elastic Band method

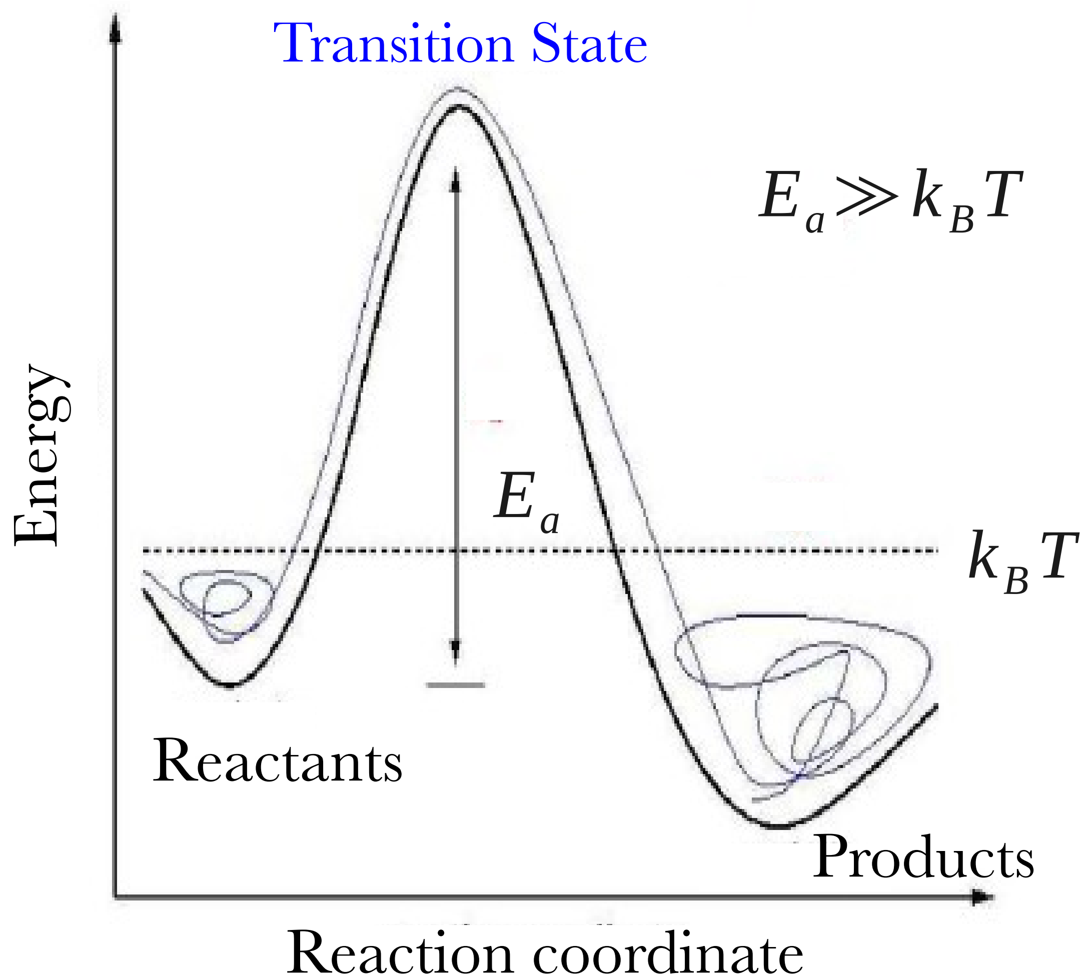
Simone Piccinin
CNR-IOM



Transition State
$E_a \gg k_B T$
Energy
E_a
$k_B T$
Reactants
Products
Reaction coordinate



(1) The system oscillates around the two minima $\tau_{vib} \approx \sqrt{\frac{m}{V''(q_{min})}}$



(1) The system oscillates around the two minima $\tau_{vib} \approx \sqrt{\frac{m}{V''(q_{min})}}$

(2) The system jumps from one minimum to another $\tau_{jump} \sim \tau_{vib}\, e^{\frac{E_a}{k_B T}}$

Van't-Hoff Arrhenius (1890)

$$\tau_{jump} \sim \tau_{vib}\, e^{\frac{E_a}{k_B T}}$$

$$\tau_{vib} \approx 10^{-13}\, s\,,\quad E_a \approx 0.75\, eV\,,\quad T = 300\, K\,,\quad \tau_{jump} \approx 1\mathrm{s}$$

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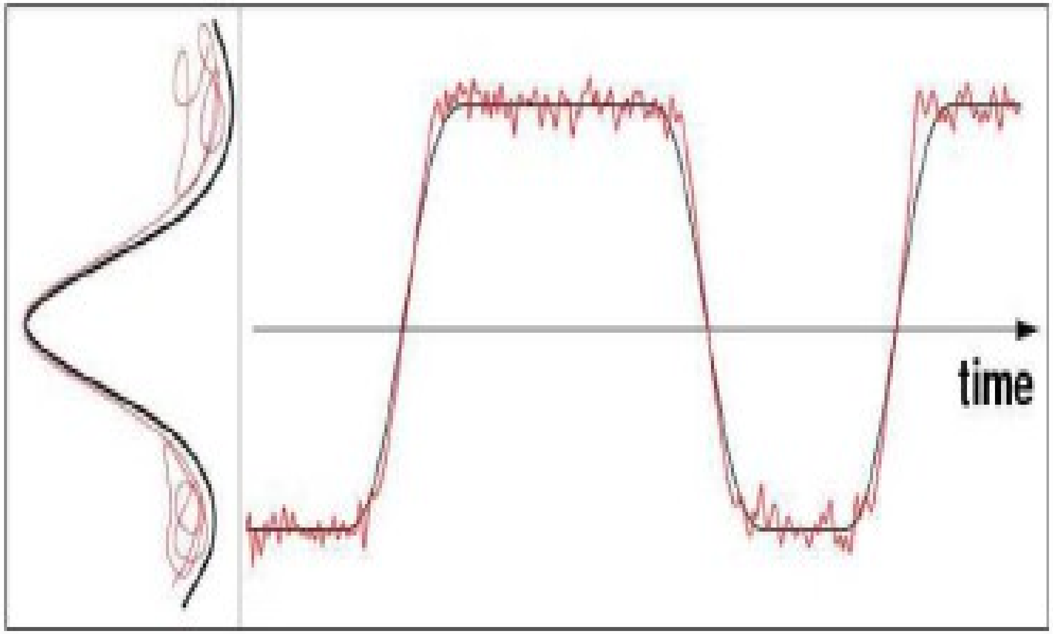

If the time step is about 1 fs then 10^{15} MD steps are necessary to have a reasonable probability to observe ONE transition !!

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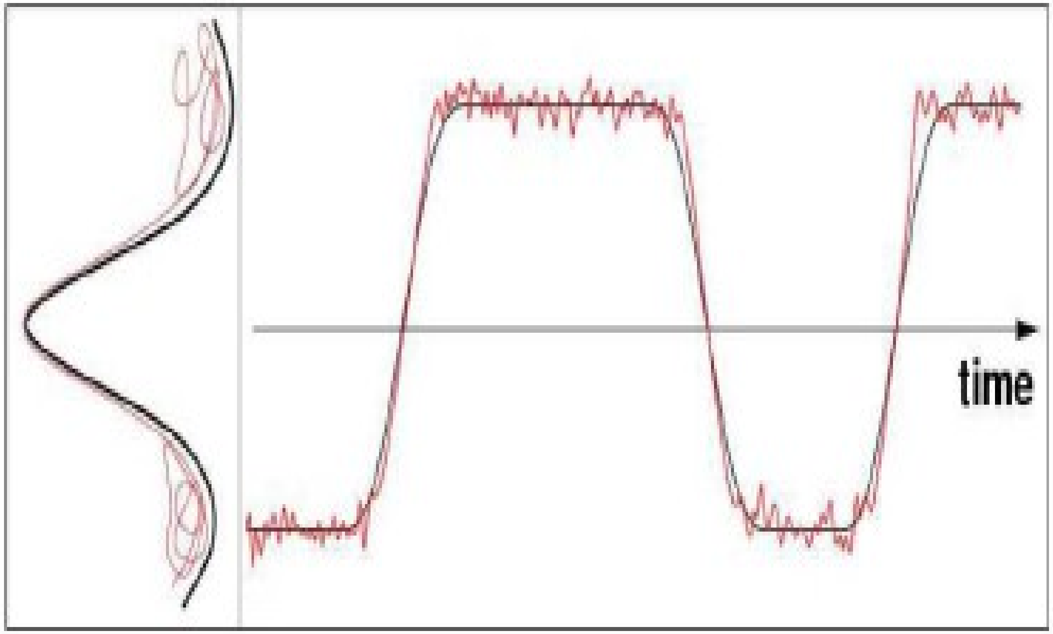

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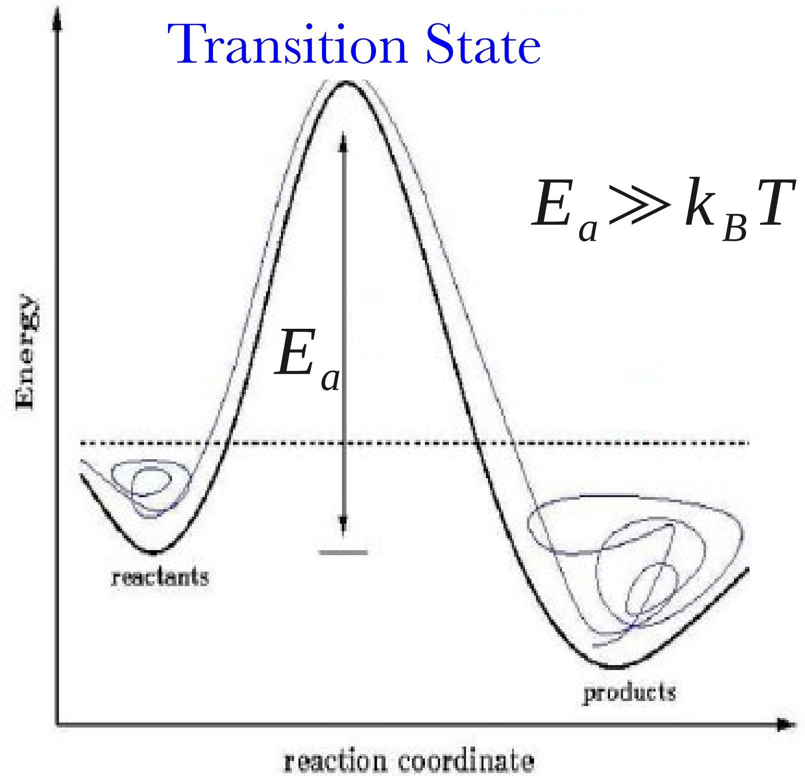
Macroscopically slow process … microscopically fast but rare events

These processes are called thermally activated process

EXAMPLES

- Diffusion processes at metal surfaces
- Dissociative adsorption of a molecule on a surface
- Diffusion of oxygen vacancies in oxides
- Contact formation between metal tip and a surface
- Atomic exchange processes at semiconductor interfaces
- ...

How do we simulate a rare event?



The transition probability can be estimated using equilibrium stat. mech.

Once the saddle point has been located we can use harmonic Transition State Theory to calculate the rate constant

$$K_{reactants \to products} = A\, \mathrm{e}^{-\frac{E_a}{k_B T}}$$

$$A = \frac{\prod_{i=1}^{3N} \nu_i^{reactants}}{\prod_{i=1}^{3N-1} \nu_i^{TS}}$$

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We need to find out E_a and A

- E_a is associated with a saddle point and finding the saddle point is a difficult task

- Criterion satisfied by the transition state: first derivative is zero, and second derivative is negative along one dimension and positive along all other dimensions

METHODS TO FIND SADDLE POINTS

- Constrained Minimization
  Simple, but in some cases it can land up with a wrong path

- Dimer Method
  Used when final state is not known

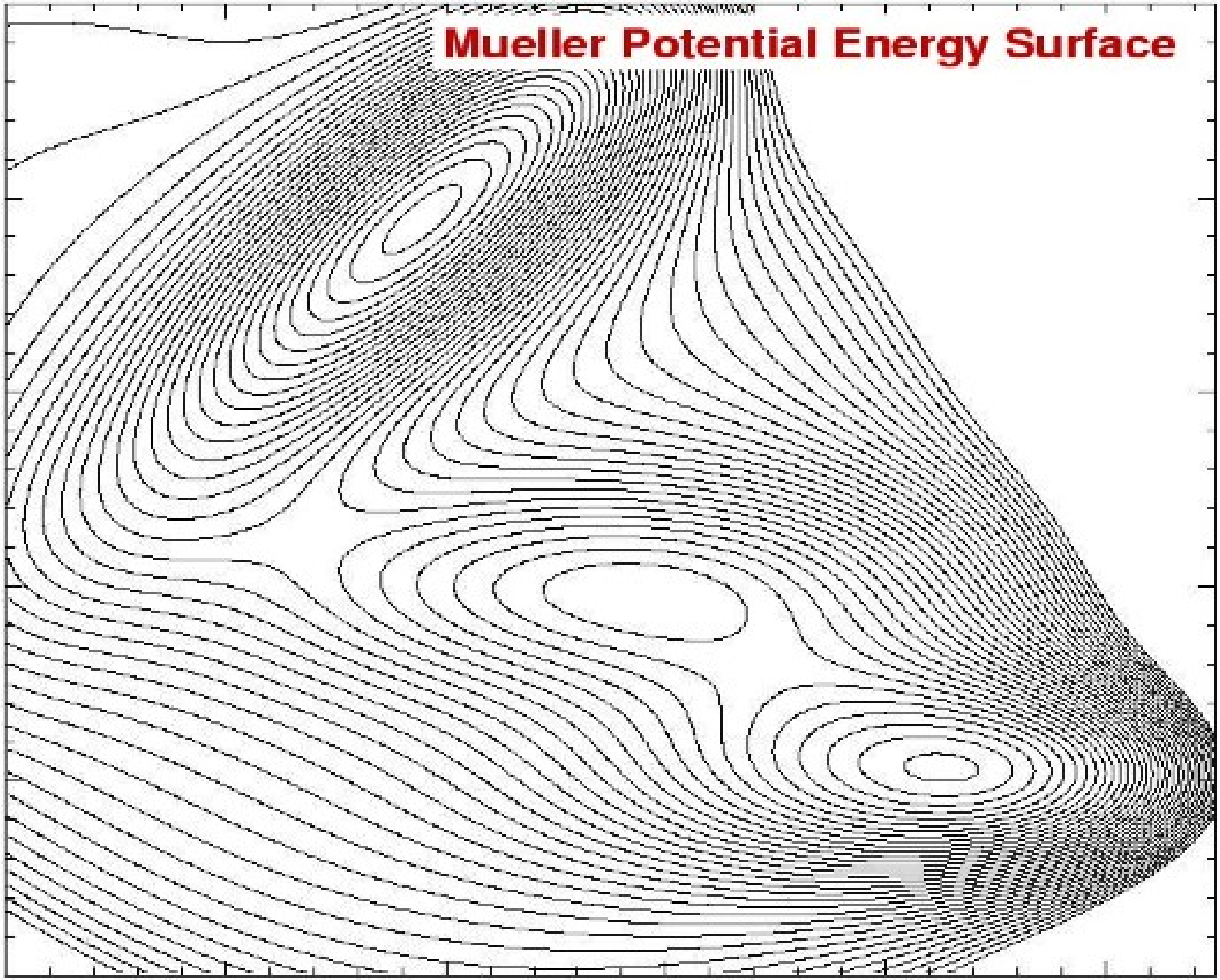
- Meta-dynamics (available in PLUMED)
  Requires the definition of suitable collective variables. One obtains directly the free energy surface in the subspace spanned by the CVs

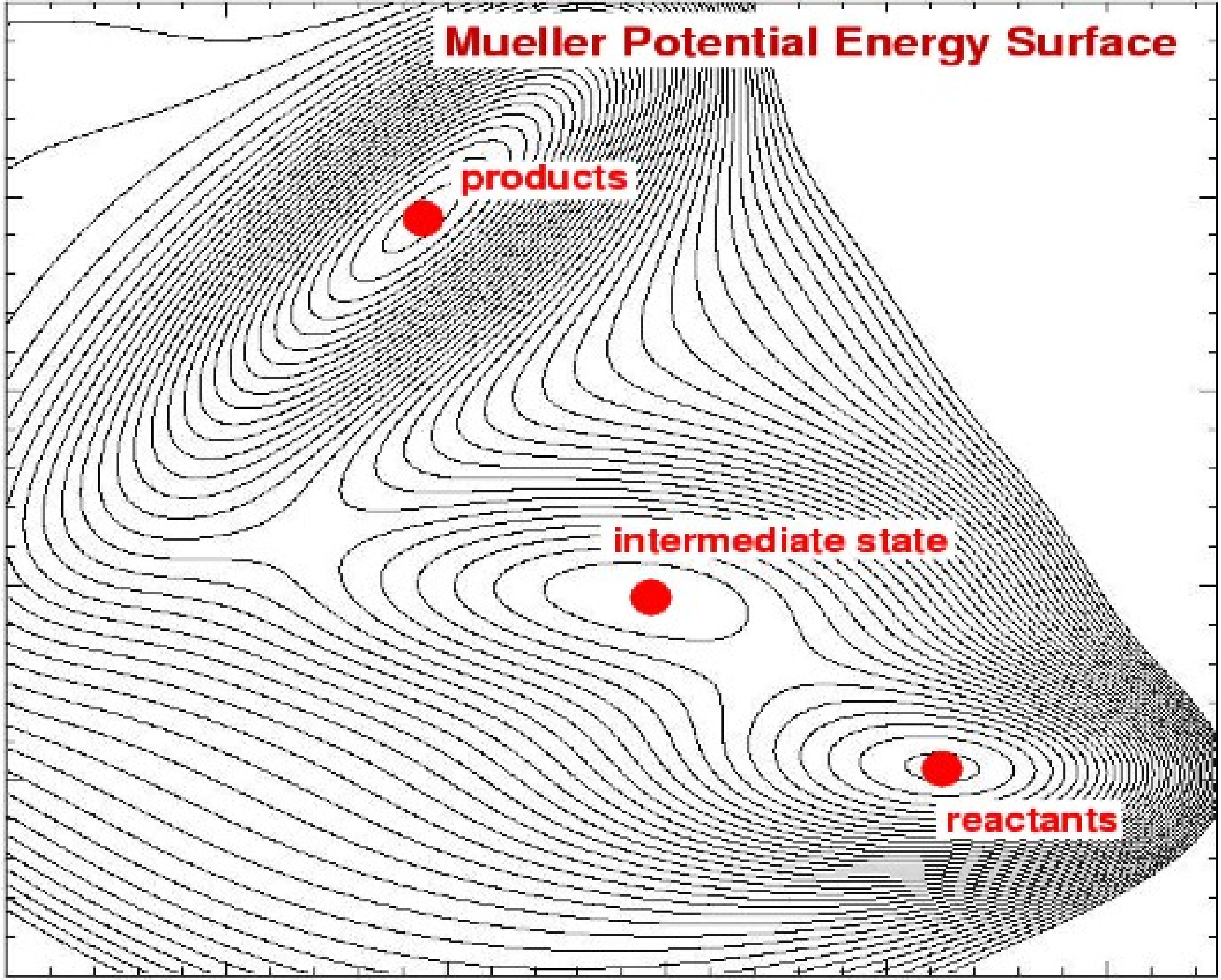
- Nudged Elastic Band (NEB)

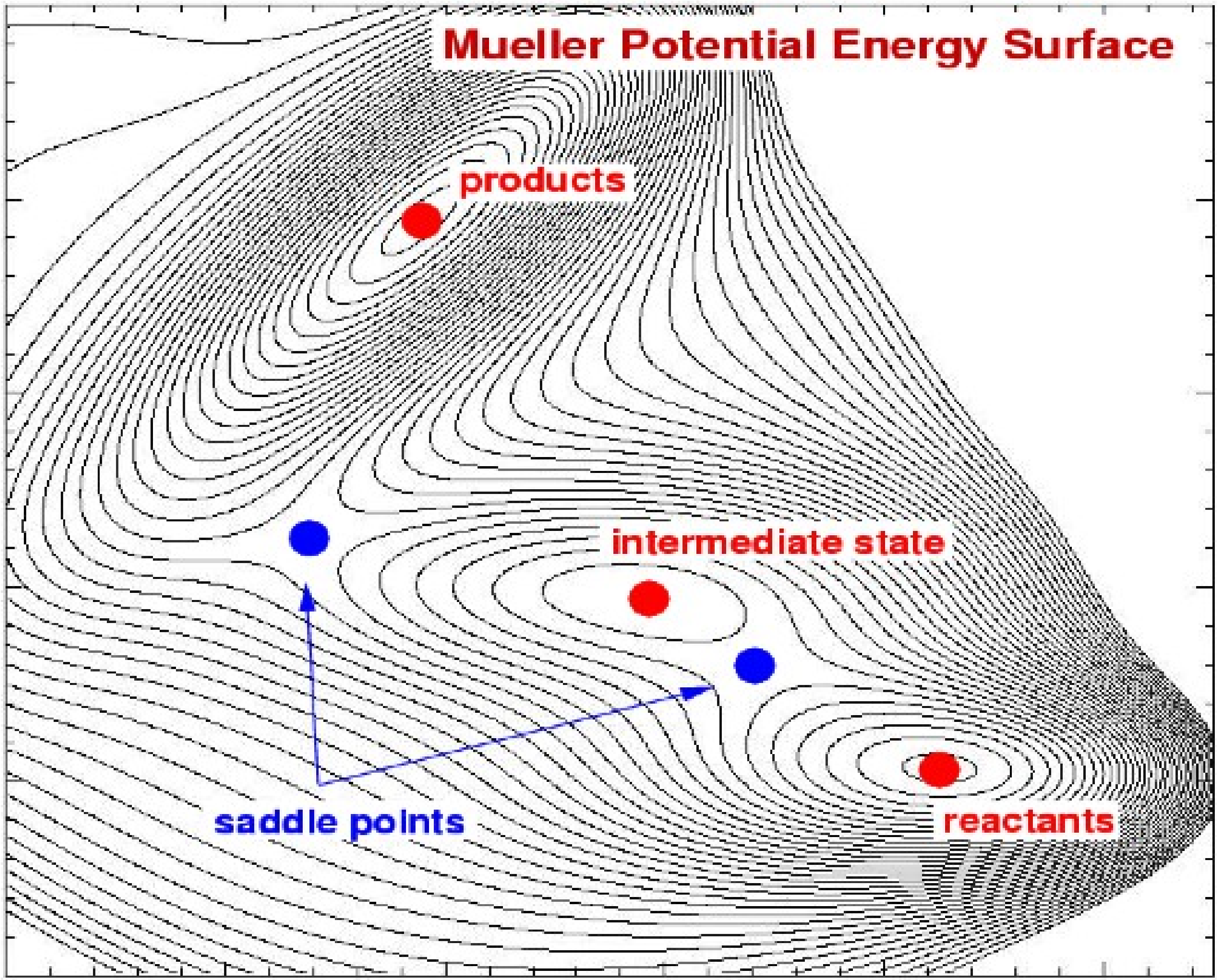
- ...

J. Chem. Phys. **111**, 7010 (1999)

Rep. Prog. Phys. **71,** 126601 (2008)


Mueller Potential Energy Surface


Mueller Potential Energy Surface
products
intermediate state
reactants


Mueller Potential Energy Surface
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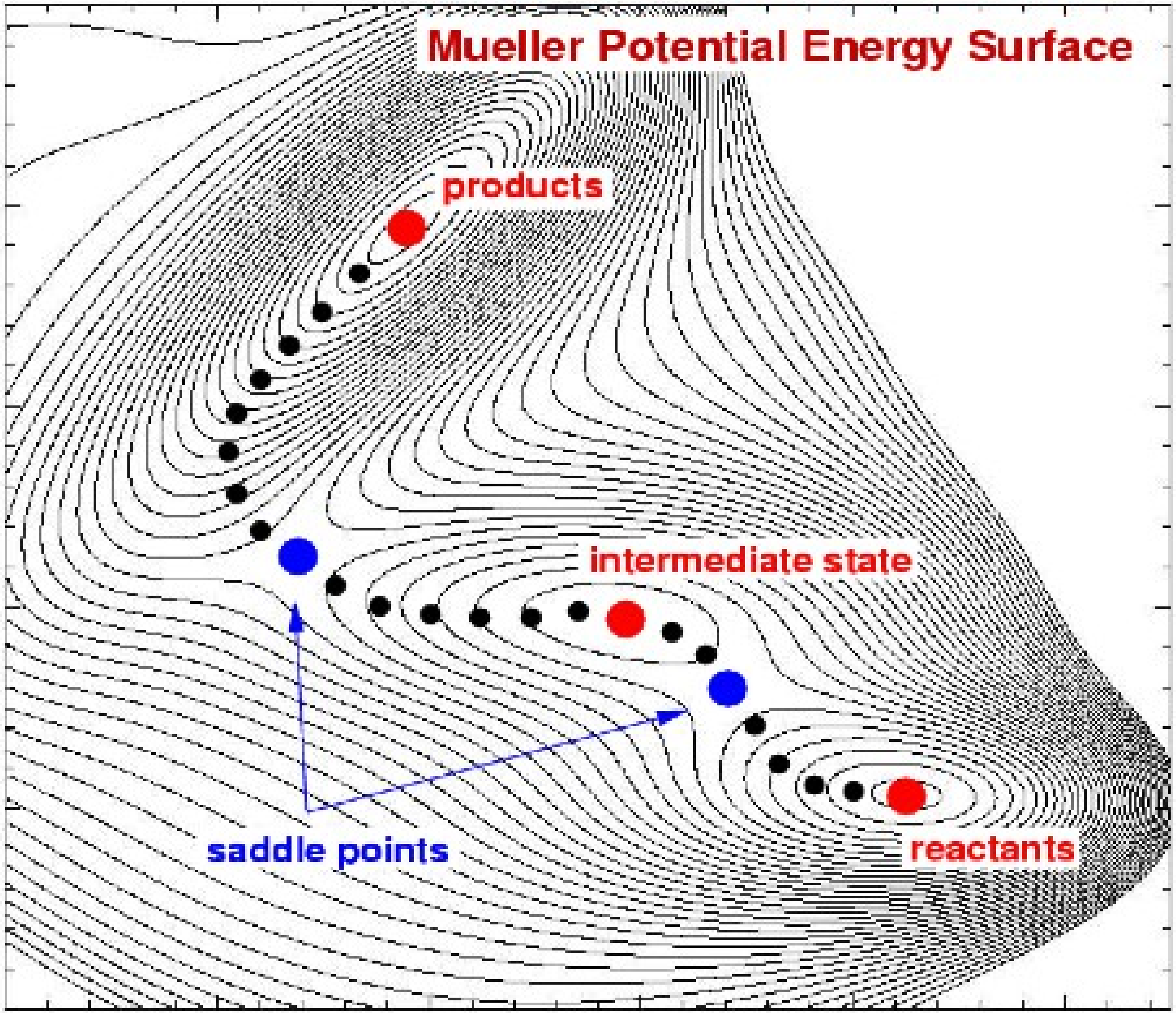

Mueller Potential Energy Surface
products
intermediate state
saddle points
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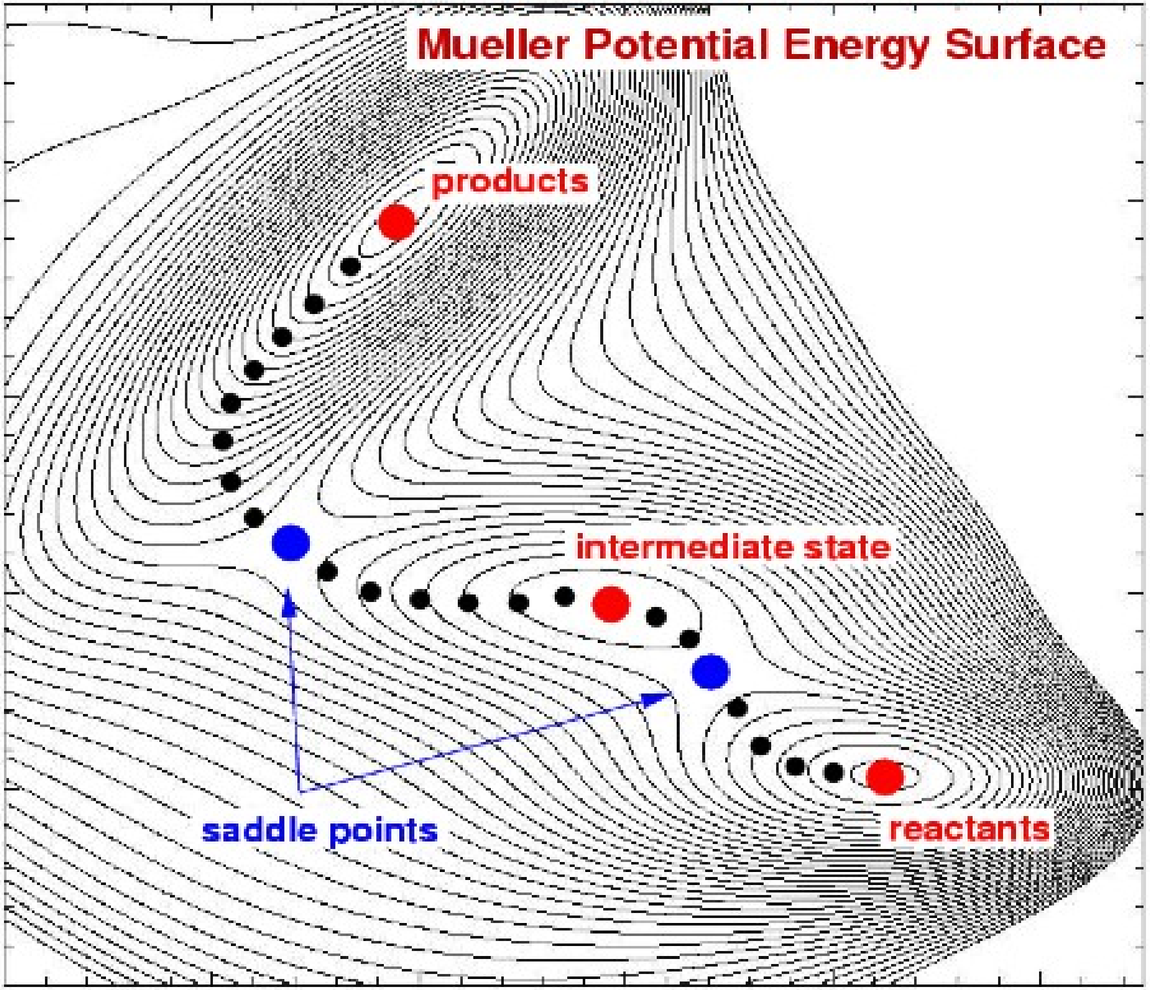
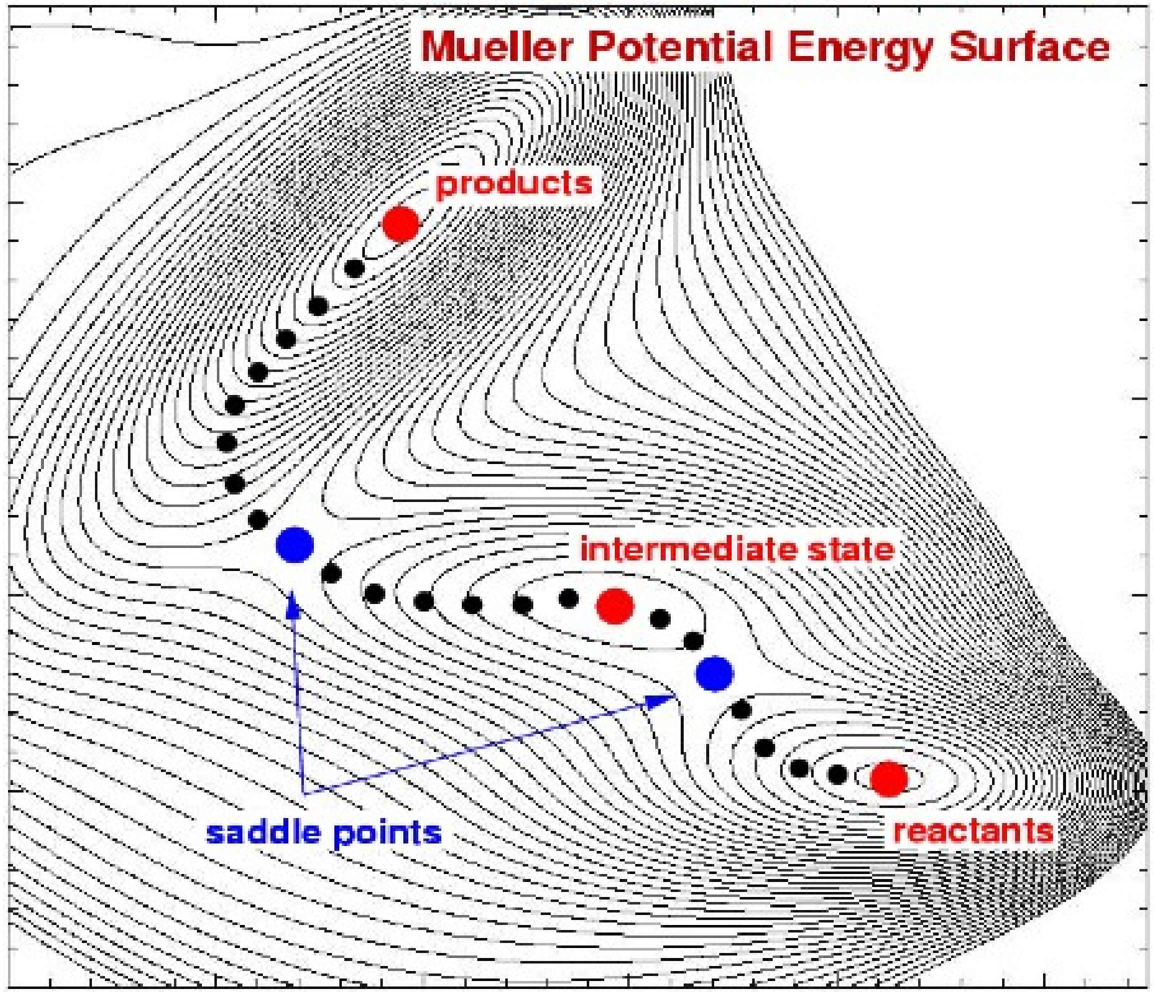


Minimum Energy Path (MEP) is the reaction path with the highest transition probability

The MEP goes through the saddle points



Minimum Energy Path (MEP): the components of the force orthogonal to the path are zero

$$\nabla E(\boldsymbol{R}_i)|_{perp} = -(\nabla E(\boldsymbol{R}_i) - \nabla E(\boldsymbol{R}_i).\boldsymbol{\tau}_i) = 0$$

Nudged Elastic Band method

1) Path discretisation
("chain of images") :

$$s \longrightarrow i \cdot \delta s$$

$$x(s) \longrightarrow x_i$$

$$\tau(s) \longrightarrow \tau_i = \frac{x_{i+1} - x_{i-1}}{|x_{i+1} - x_{i-1}|}$$

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$$F(x_i)_\perp = -\left[\nabla V(x_i) - \tau_i \; (\tau_i | \nabla V(x_i))\right]$$

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$$||F(x_i)_\perp|| = 0$$

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$$\| F(x_i)_\perp \| = 0$$

4) path dynamics
(steepest-descent) :

$$x_i^{k+1} = x_i^k + \lambda \, F(x_i^k)_\perp$$

5) Alternatively,
Broyden acceleration :

$$x_i^{k+1} = x_i^k + J^{-1} \, F(x_i^k)_\perp$$

Nudged Elastic Band method

- The path dynamics does not preserve the distance among images
- The images will tend to slide down towards the closest local minimum.
- Possible solutions:

1) NEB: connect images through springs (to keep them apart)

2) STRING: images are kept equispaced using Lagrange multipliers

Nudged Elastic Band method

• Subsequent images of the chain are connected by springs

• Each image feels forces due to external potential + springs.

• NEB idea [1,2]: elastic forces are projected along the path and external forces are projected orthogonally to the path.

• Projections are defined by the path's tangent: the tangent definition plays a crucial role.

[1] G.Mills and H.Jonsson, Phys. Rev. Lett. 72, 1124 (1994)

[2] G.Henkelman and H.Jonsson, J. Chem. Phys. 133, 9978 (2000)

Nudged Elastic Band method

Orthogonal + Spring Forces

$$F(x_i) = -(\nabla V(x_i) - \tau_i \langle \tau_i | \nabla V(x_i) \rangle) - \tau_i \langle \tau_i | \nabla \frac{K_i}{2}(x_{i+1} - x_i)^2 \rangle$$

MEP condition

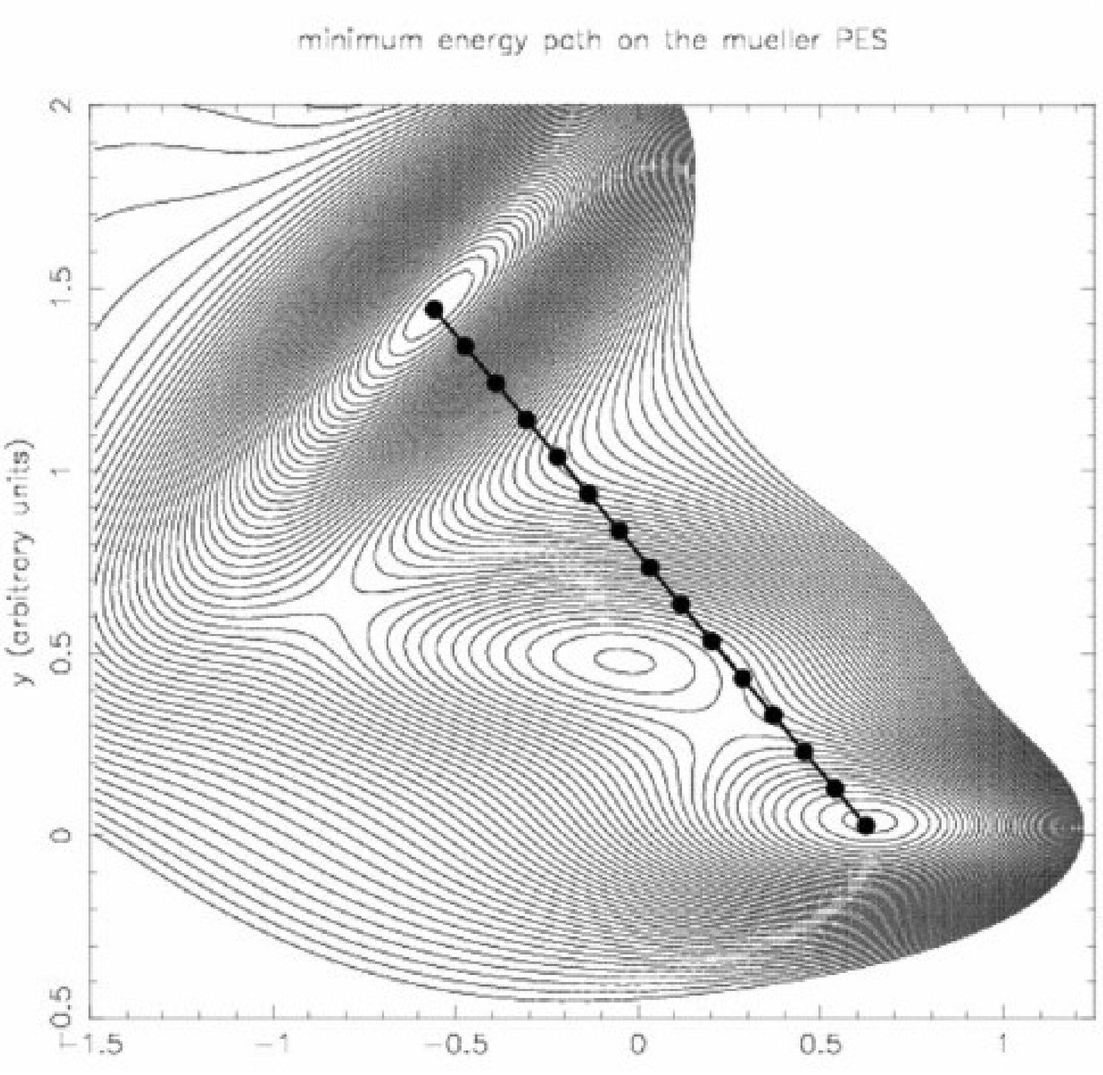
$$F(x_i) = 0$$

Path dynamics (steepest descent, quick-min, broyden)

$$x_i^{k+1} = x_i^k + J^{-1} F(x_i)$$

G.Mills and H.Jonsson, Phys.Rev.Lett. 72, 1124 (1994).
G.henkelman and H.Jonsson, J.Chem.Phys. 133, 9978 (2000).

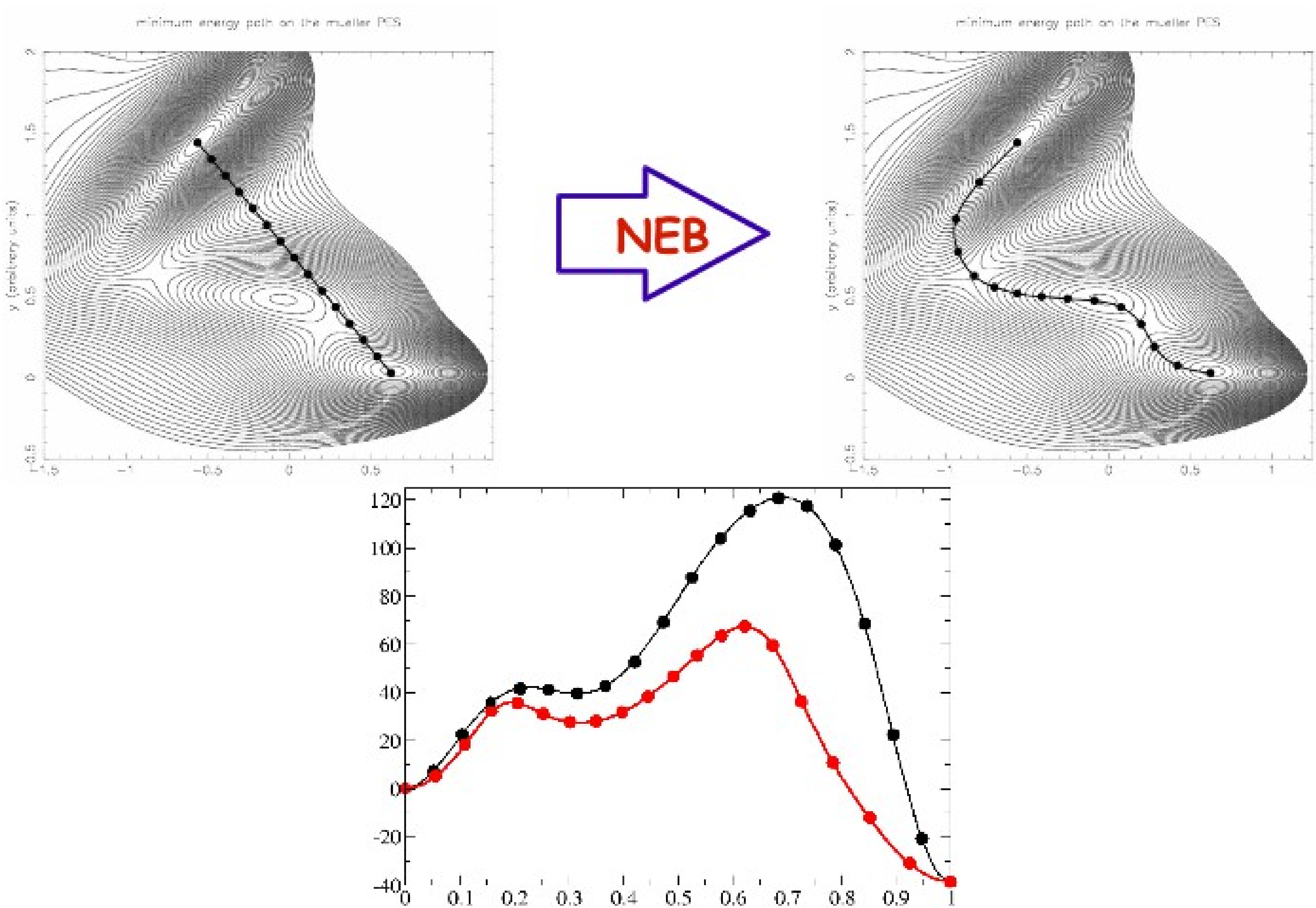
NEB on Mueller PES



Initial guess: linear interpolation between the two end points.

$$\vec{x}_i = \vec{x}_0 + \frac{i}{N}(\vec{x}_N - \vec{x}_0)$$

NEB on Mueller PES



Improvements

1) Accurate definition of the saddle point
Climbing Image

2) Higher resolution around the saddle point
Variable elastic constants

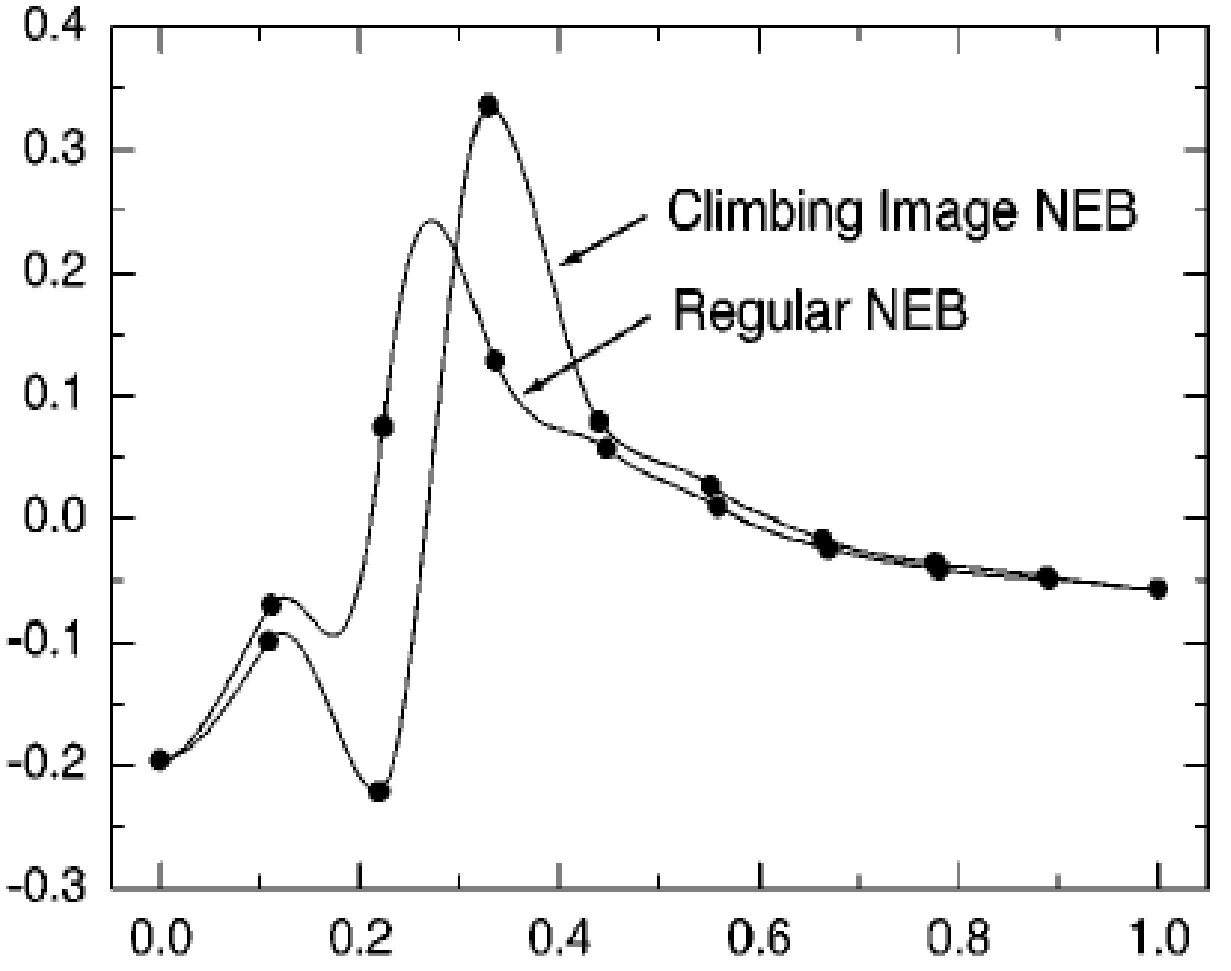
Climbing Image method

• Once we have located the MEP we need to find the TS

• We take the image with the highest energy, and let it "climb" the PES along the MEP, by inverting the force it experiences parallel to the MEP:

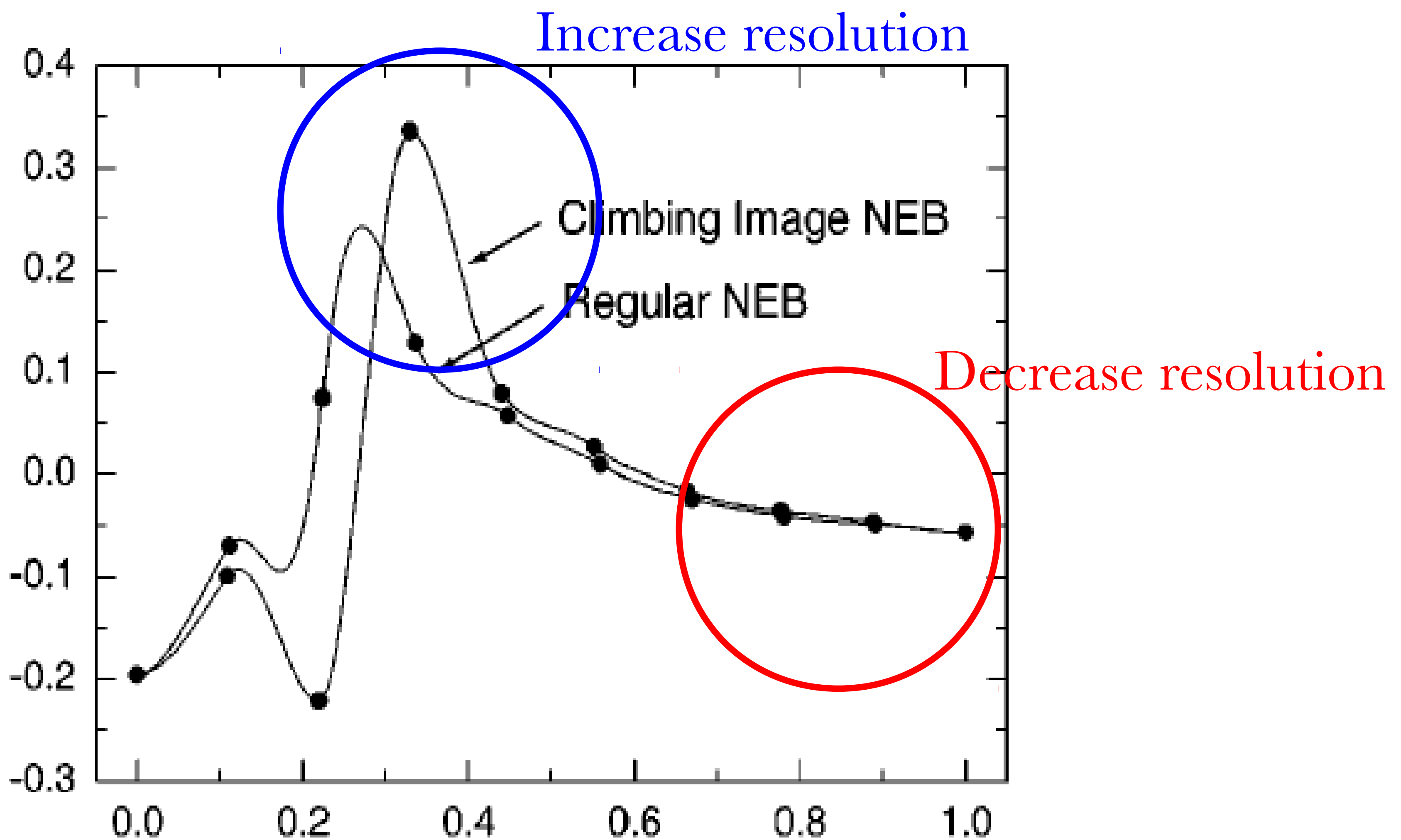
$$\boldsymbol{F}_{i_{max}} = -\left(\nabla E\left(\boldsymbol{R}_{i_{max}}\right) - \nabla E\left(\boldsymbol{R}_{i_{max}}\right)\big|_{||}\right) + \nabla E\left(\boldsymbol{R}_{i_{max}}\right)\big|_{||}$$

CI-NEB example



Dissociative adsorption of CH_4 on Ir(111)

NEB with variable spring constants



Dissociative adsorption of CH_4 on Ir(111)

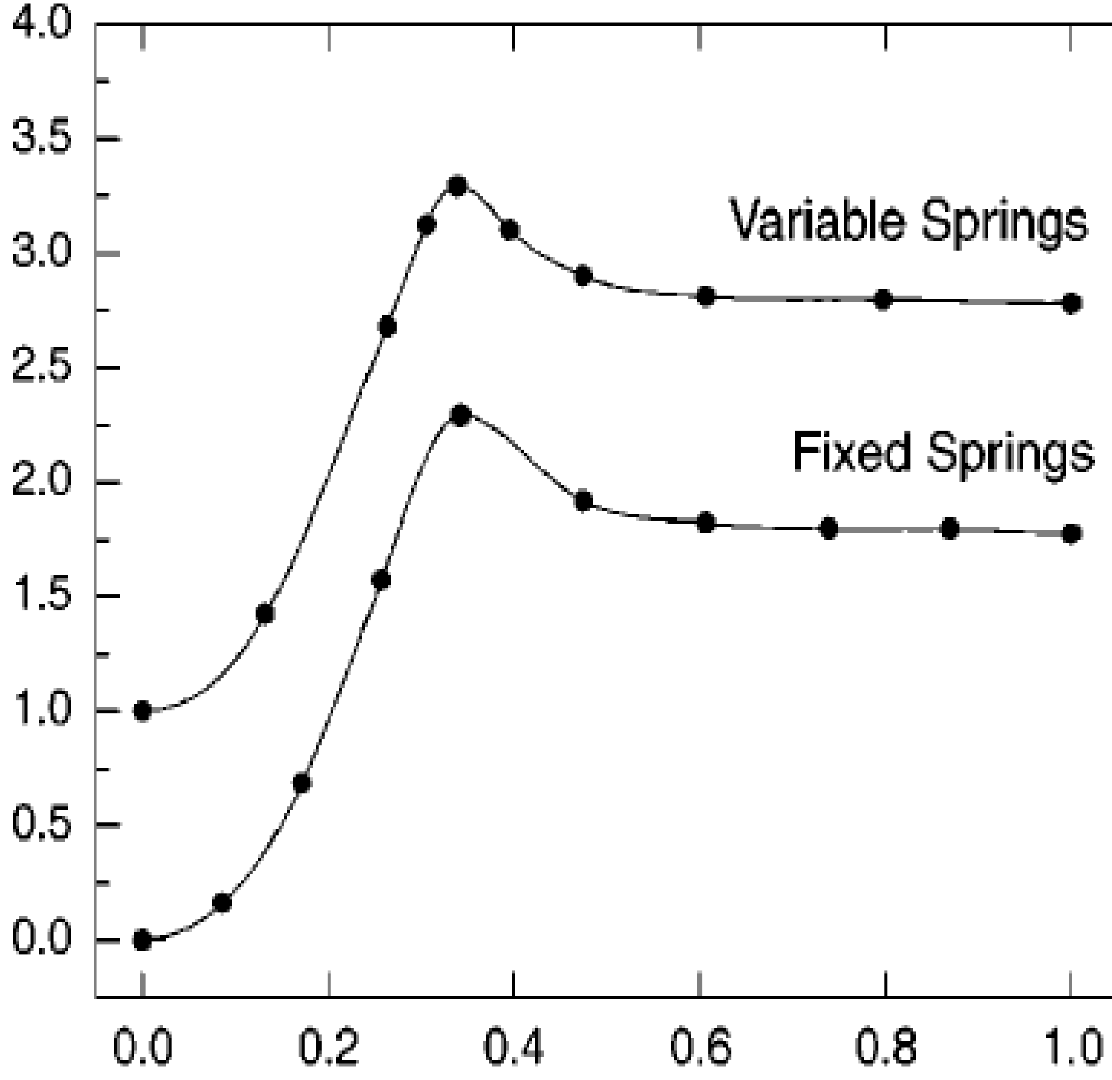
NEB with variable spring constants

Stiffer springs can be used near points of highest energy, thus increasing the resolution near the TS:

$$k_i = \frac{1}{2}(k_{max} + k_{min} - (k_{max} - k_{min})\cos\left(\Pi \frac{(E(\boldsymbol{R}_i) - E_{min})}{(E_{max} - E_{min})}\right))$$

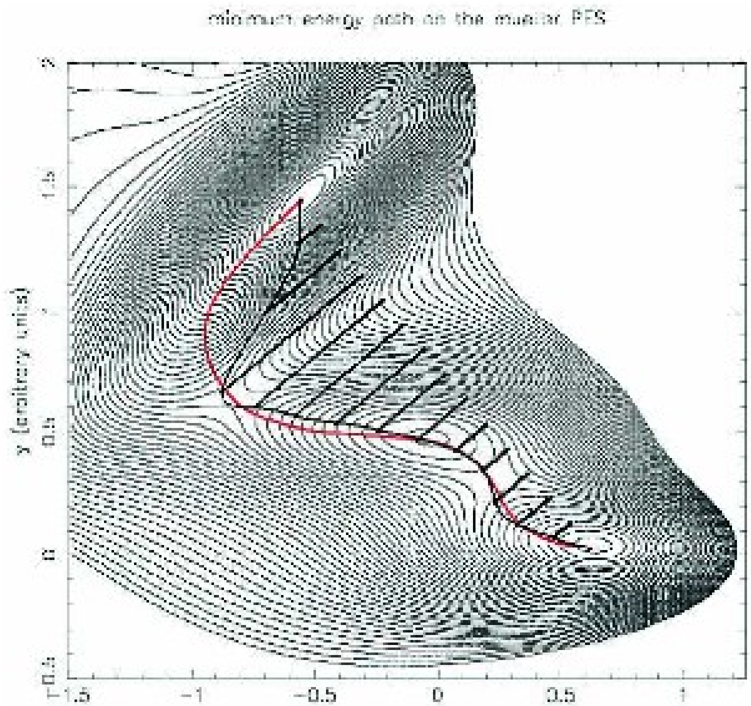
$$k_{i_{max}} = k_{max}$$

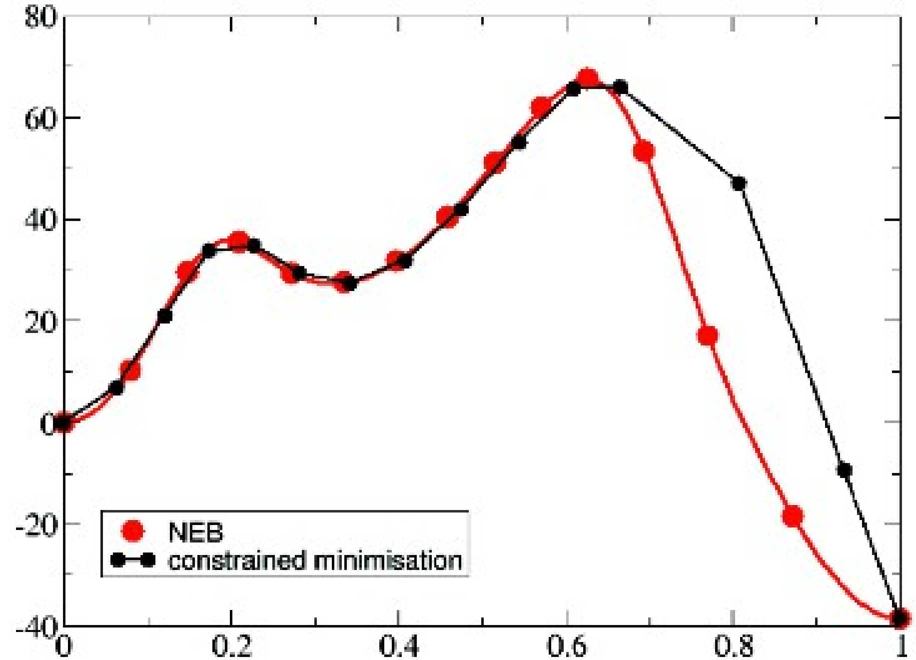
VARIABLE ELASTIC CONSTANTS example



Dissociative adsorption of H_2 on Si(100)

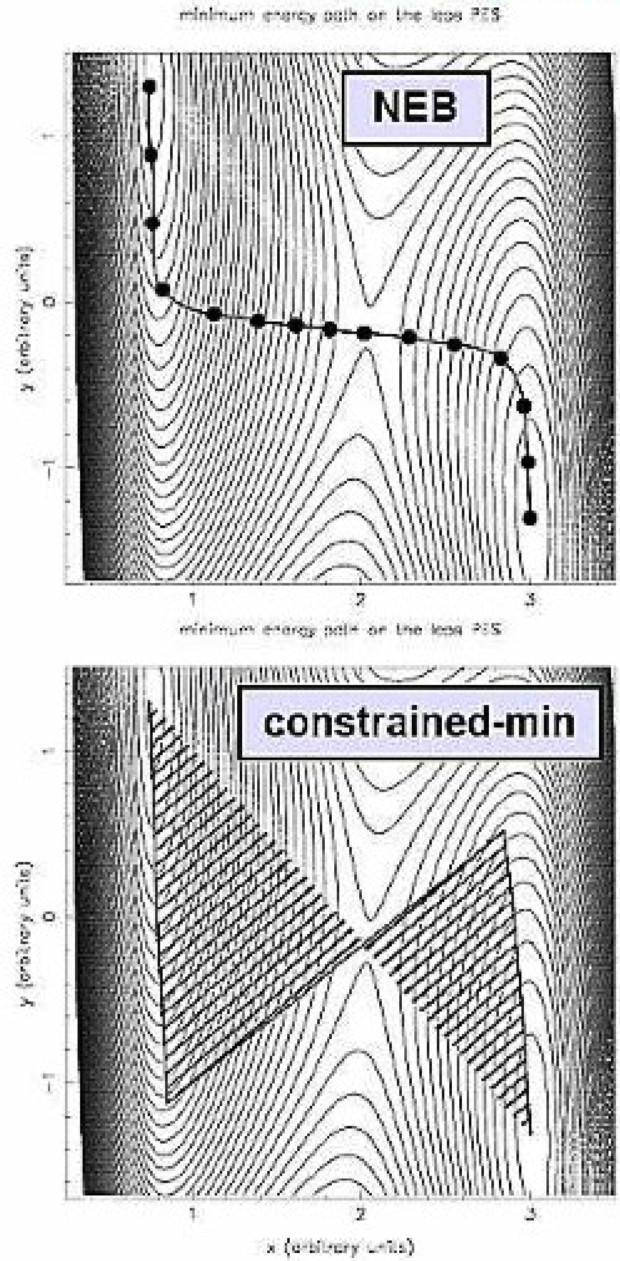
NEB vs constrained minimizations

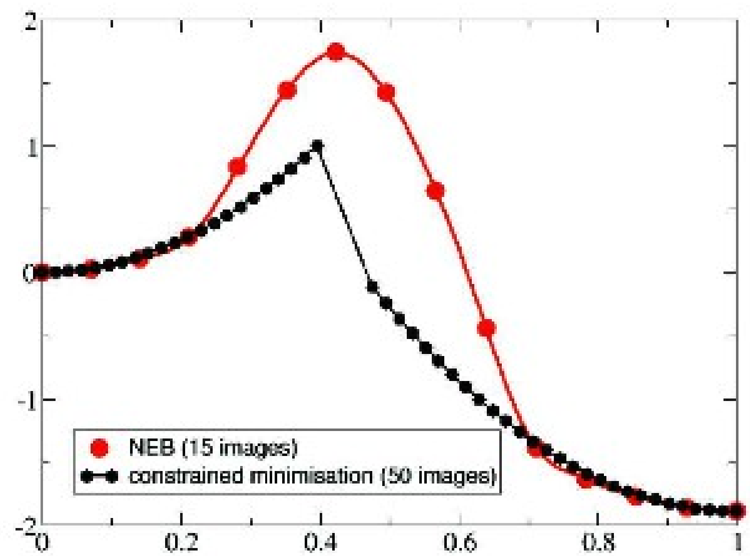




Constrained minimization does a good job in this case.

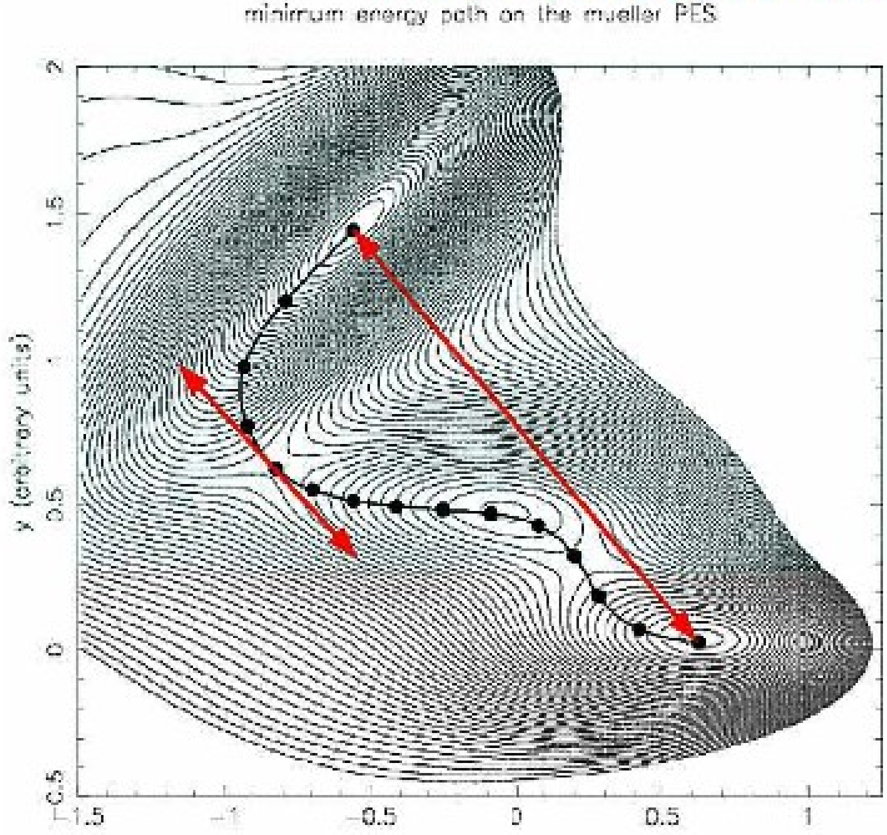
NEB vs constrained minimizations

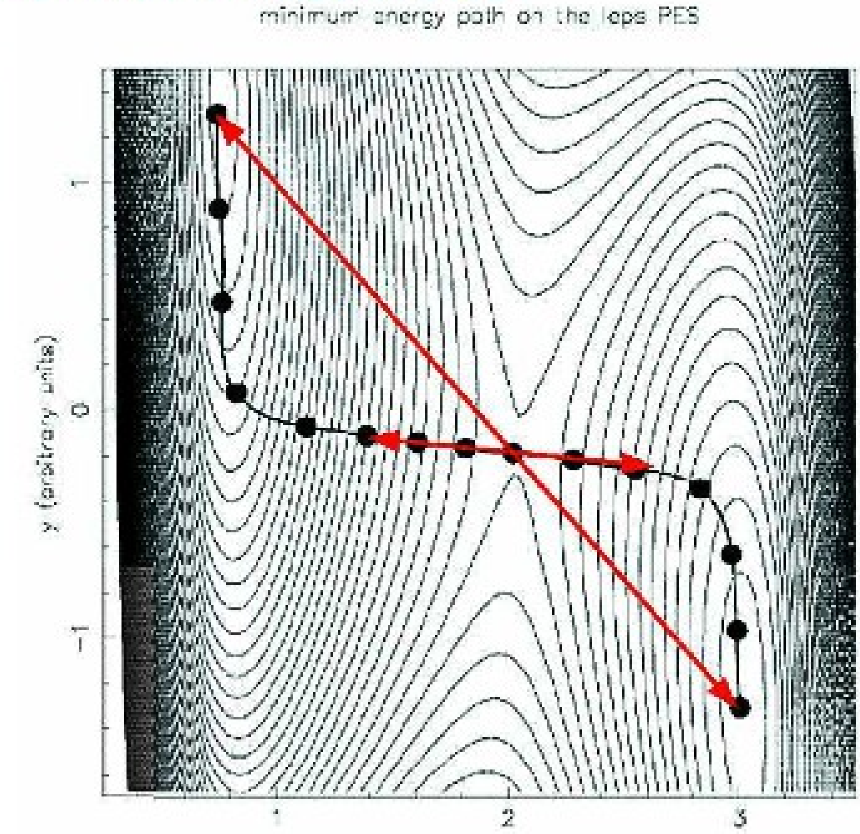




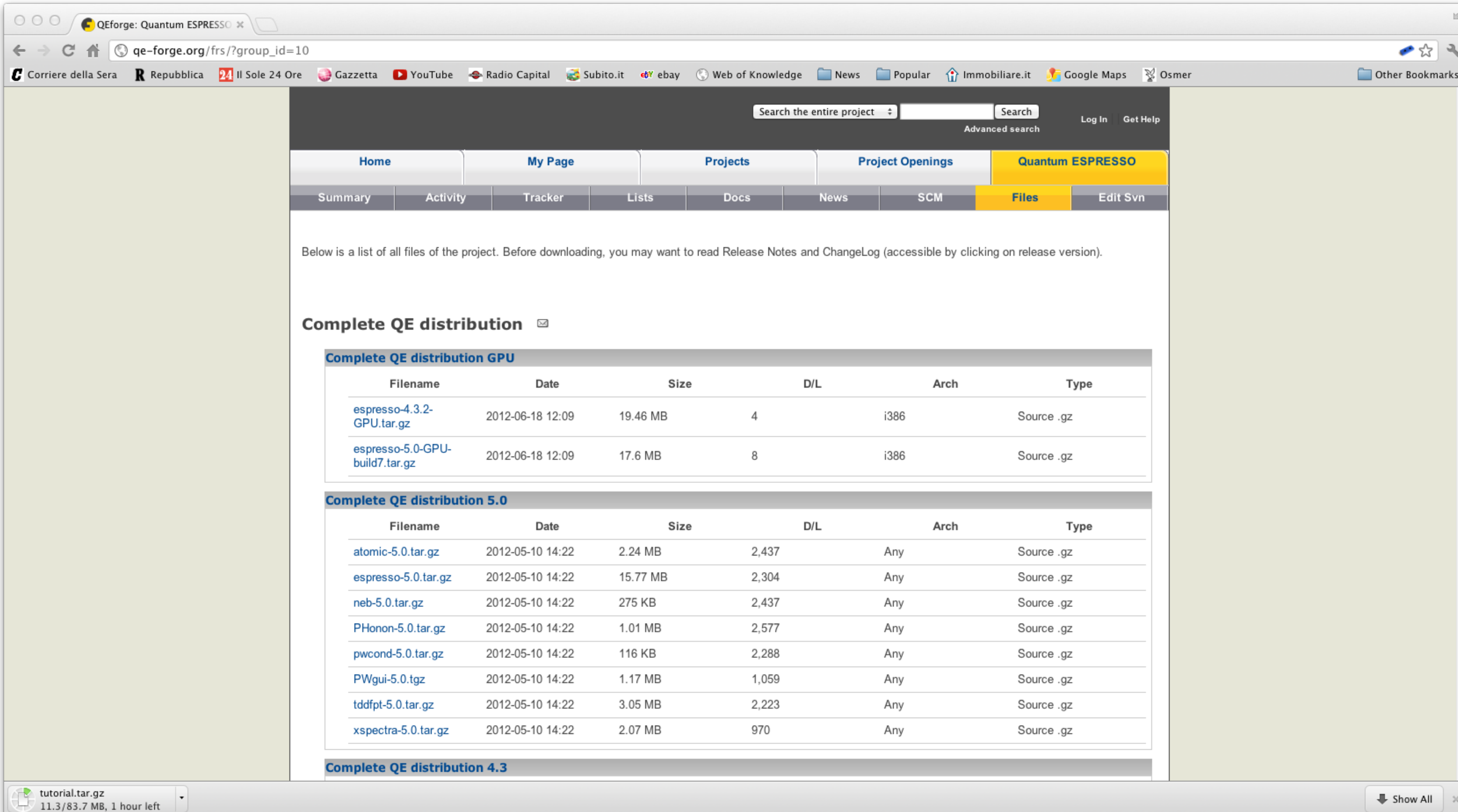
Constrained minimization is completely wrong in this case.

NEB vs constrained minimizations





NEB in Quantum-ESPRESSO



Below is a list of all files of the project. Before downloading, you may want to read Release Notes and ChangeLog (accessible by clicking on release version).

Complete QE distribution

Complete QE distribution GPU

Filename	Date	Size	D/L	Arch	Type
espresso-4.3.2-GPU.tar.gz	2012-06-18 12:09	19.46 MB	4	i386	Source .gz
espresso-5.0-GPU-build7.tar.gz	2012-06-18 12:09	17.6 MB	8	i386	Source .gz

Complete QE distribution 5.0

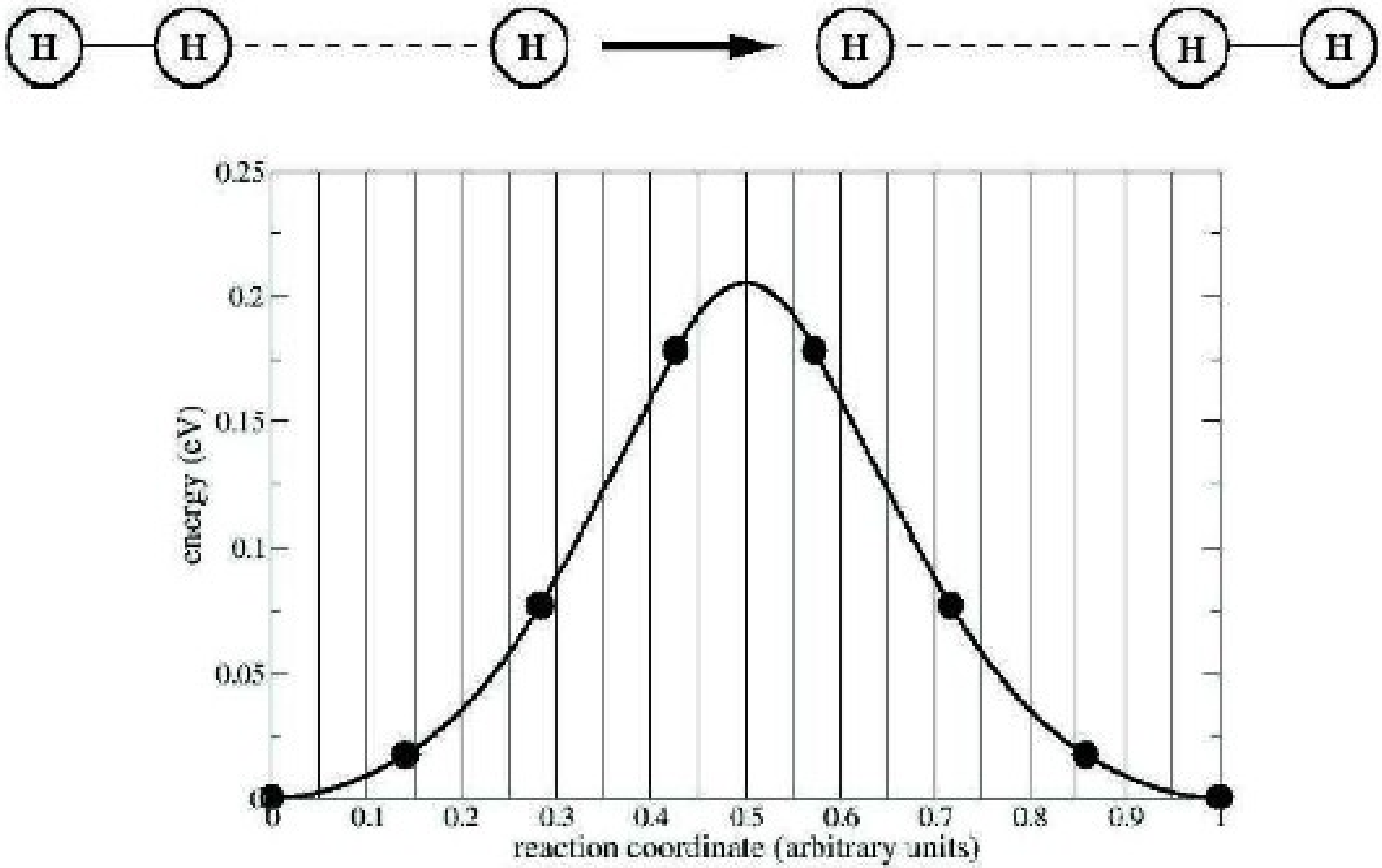
Filename	Date	Size	D/L	Arch	Type
atomic-5.0.tar.gz	2012-05-10 14:22	2.24 MB	2,437	Any	Source .gz
espresso-5.0.tar.gz	2012-05-10 14:22	15.77 MB	2,304	Any	Source .gz
neb-5.0.tar.gz	2012-05-10 14:22	275 KB	2,437	Any	Source .gz
PHonon-5.0.tar.gz	2012-05-10 14:22	1.01 MB	2,577	Any	Source .gz
pwcond-5.0.tar.gz	2012-05-10 14:22	116 KB	2,288	Any	Source .gz
PWgui-5.0.tgz	2012-05-10 14:22	1.17 MB	1,059	Any	Source .gz
tddfpt-5.0.tar.gz	2012-05-10 14:22	3.05 MB	2,223	Any	Source .gz
xspectra-5.0.tar.gz	2012-05-10 14:22	2.07 MB	970	Any	Source .gz

Complete QE distribution 4.3

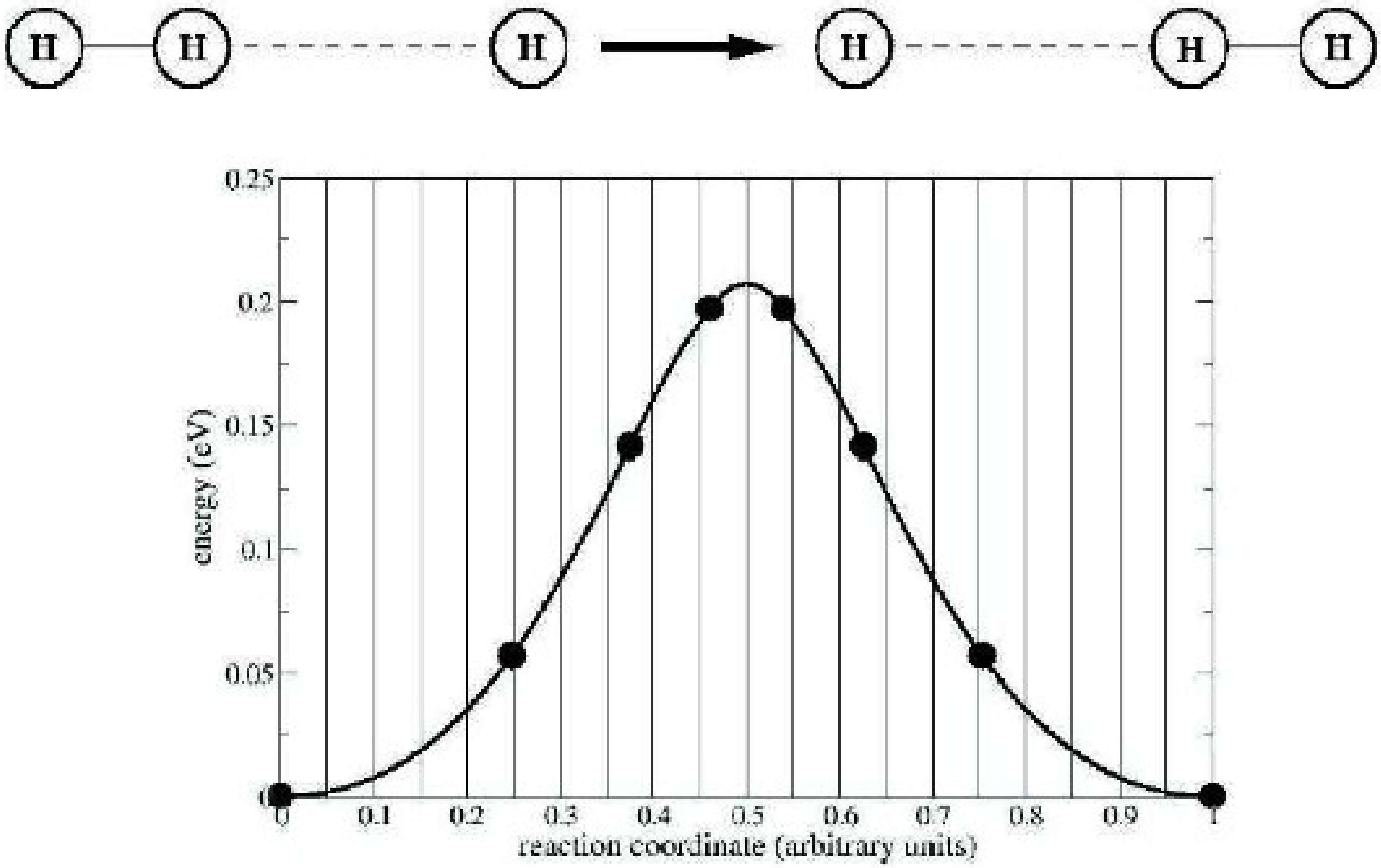
NEB in Quantum-ESPRESSO

- Determine IS and FS
- Guess an initial path, usually an interpolation between IS or FS
- Discretize the path into N images
- For each image perform an SCF calculations to obtain the forces
- Check whether MEP condition is satisfied
- If yes you are done
- If no then do path dynamics using steepest descent or Broyden until MEP conditions are satisfied
- Let the highest energy image climb to the TS

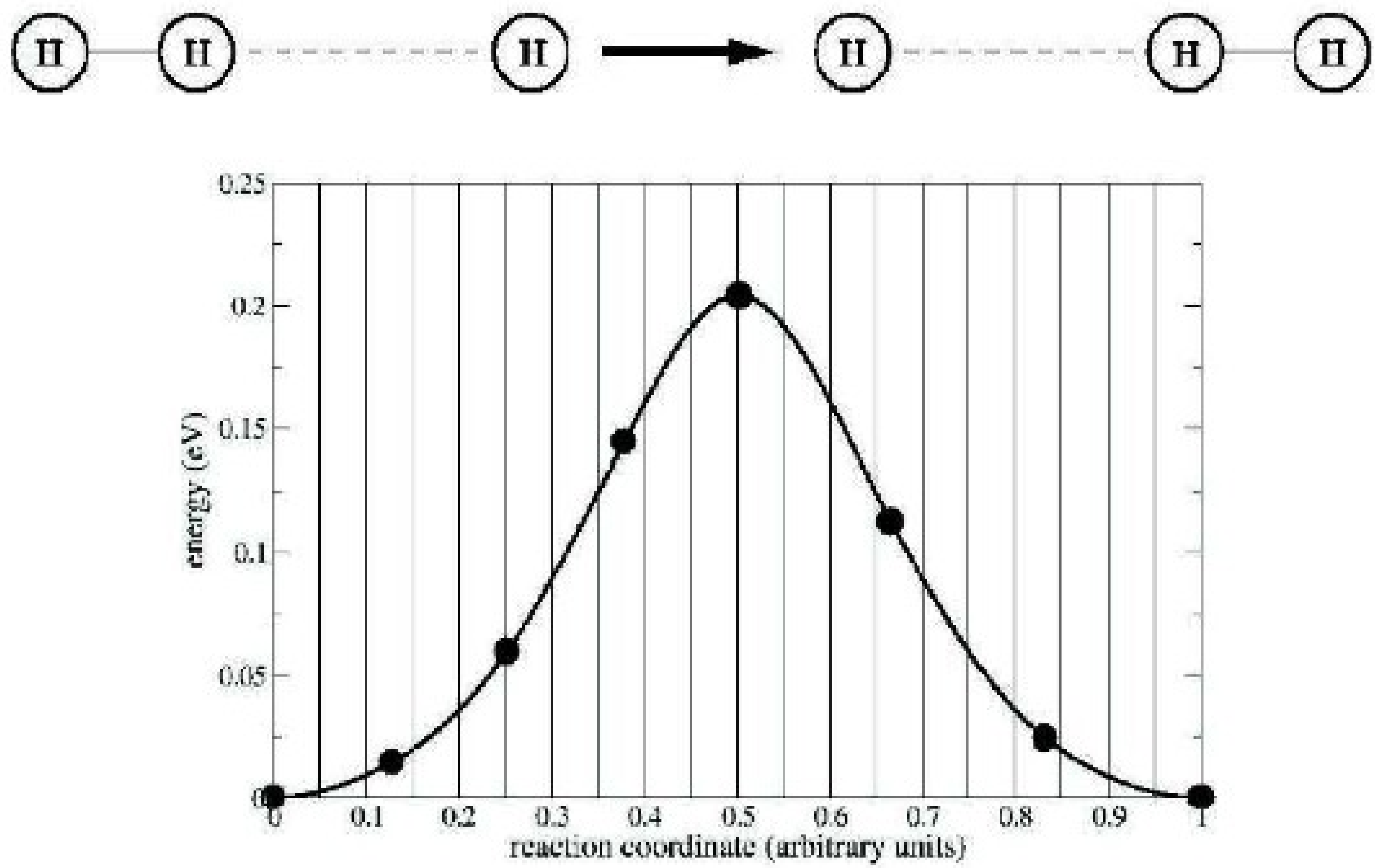
Example 1: collinear proton transfer
plain NEB with 8 images



Example 1: collinear proton transfer
variable spring constants



Example 1: collinear proton transfer
climbing image



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- Carlo Sbraccia, *Computer Simulations of Thermally Activated Processes*, Ph. D Thesis
- Lecture of Stefano de Gironcoli in Santa Barbara QE School
- Lecture of Prasenjit Ghosh in Bangalore QE School

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All figures & equations in this talk are taken from the above mentioned references

THE END