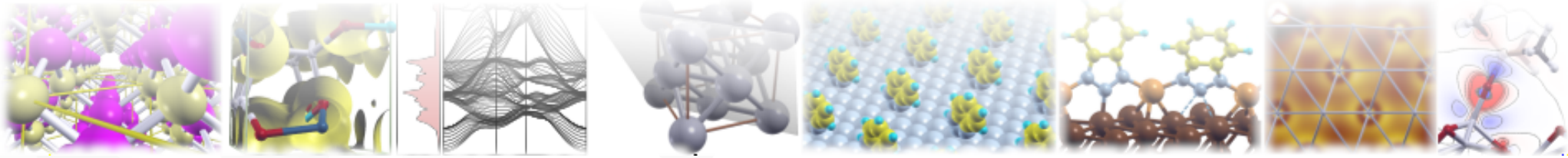
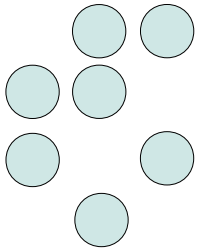
QUANTUMESPRESSO

September 15—20, 2019
Ljubljana, Slovenia

Summer School on Advanced Materials and Molecular Modelling



Chasing saddle points: the NEB method



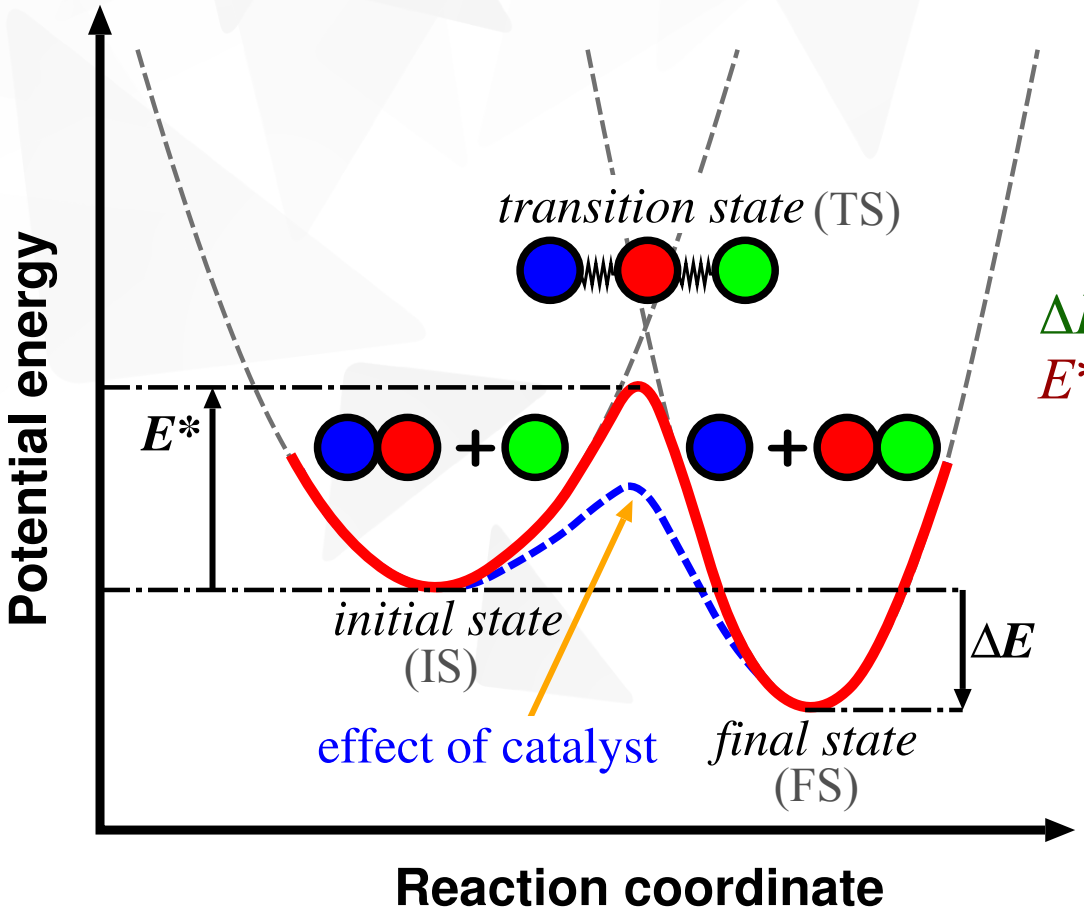
Anton Kokalj
Department of Physical and Organic Chemistry
Jožef Stefan Institute

(based on slides from previous QE schools + some new slides)

AK

Chemical reaction

- bond-breaking and bond-making → activated process
  (there is an energy barrier)



$\Delta E \equiv$ reaction energy → thermodynamics

$E^* \equiv$ activation energy → kinetics

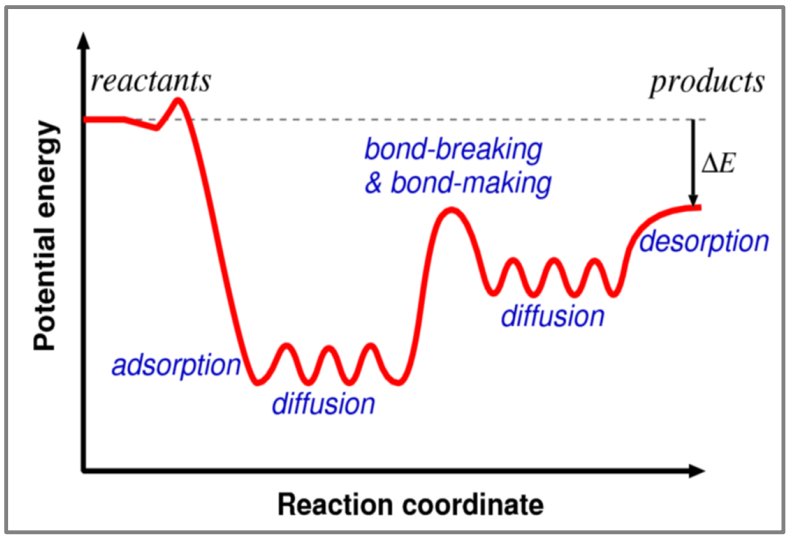
reaction rate constant:

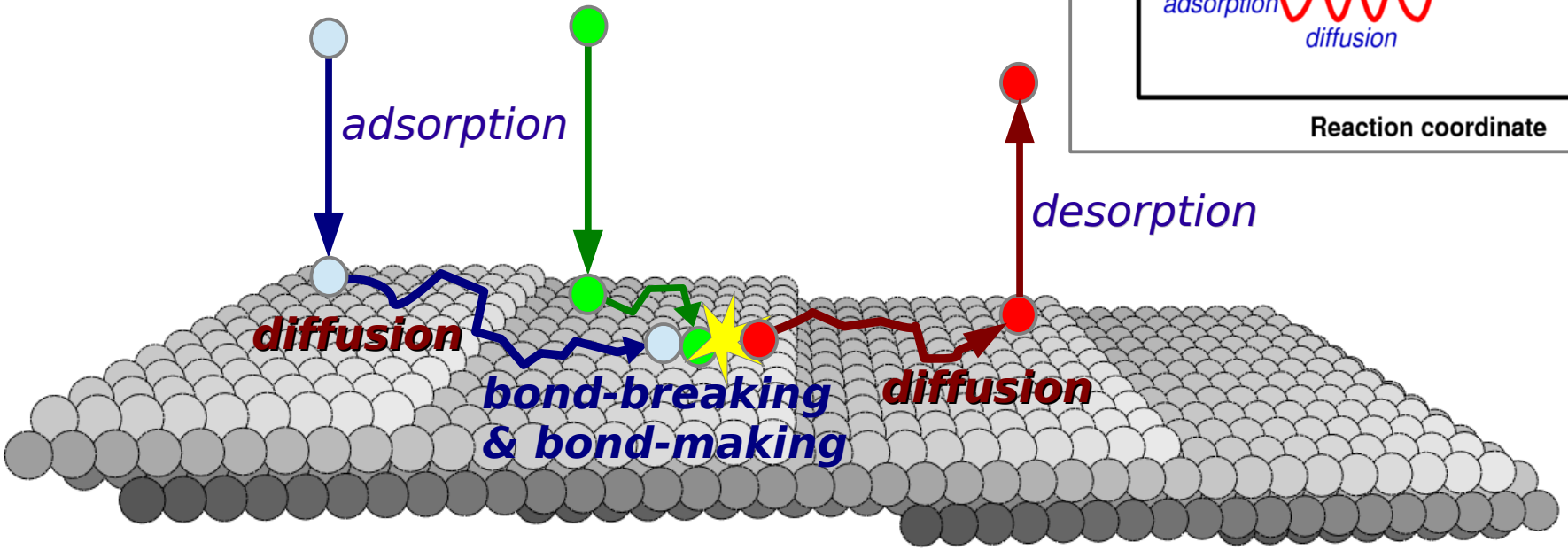
$$k = \nu \exp\left(-E^*/kT\right)$$

$$\nu = \frac{\prod_j^{3N} \nu_j^{\mathrm{IS}}}{\prod_j^{3N-1} \nu_j^{\mathrm{TS}}}$$

Heterogeneous catalysis

- Langmuir-Hinshelwood mechanism

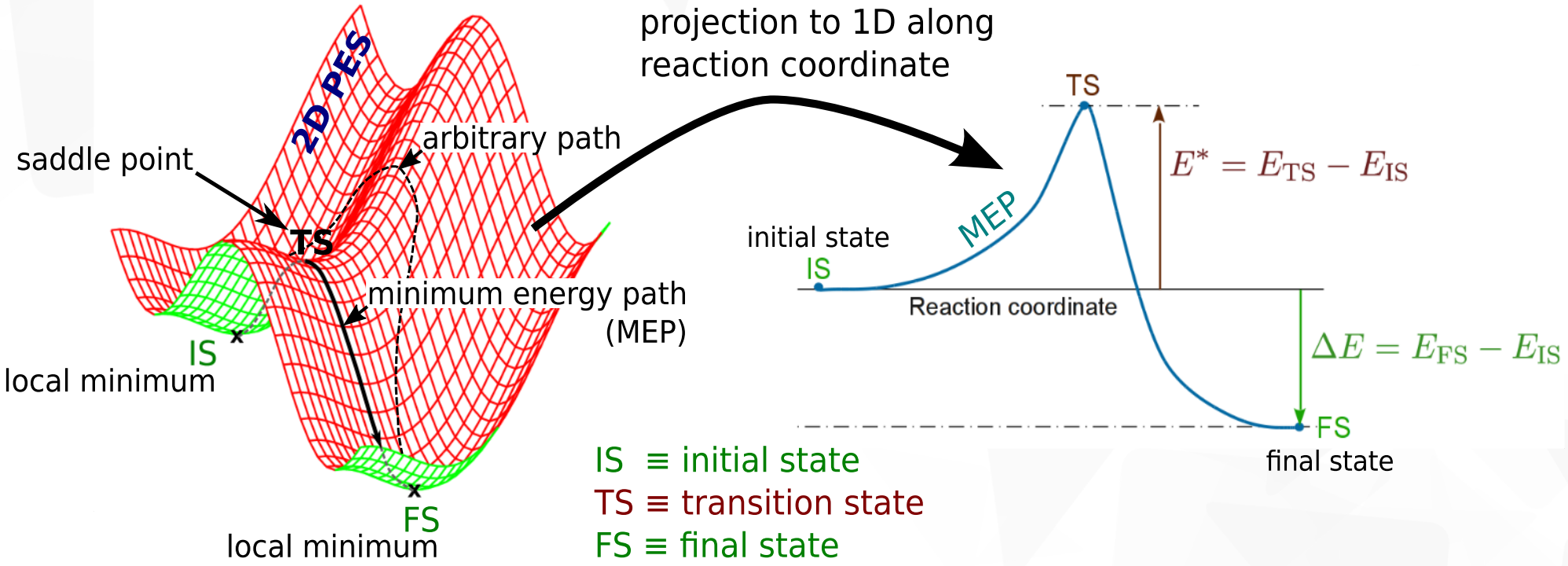




Elementary activated reaction step

- potential energy surface (PES) is highly multidimensional

(except for trivial examples)

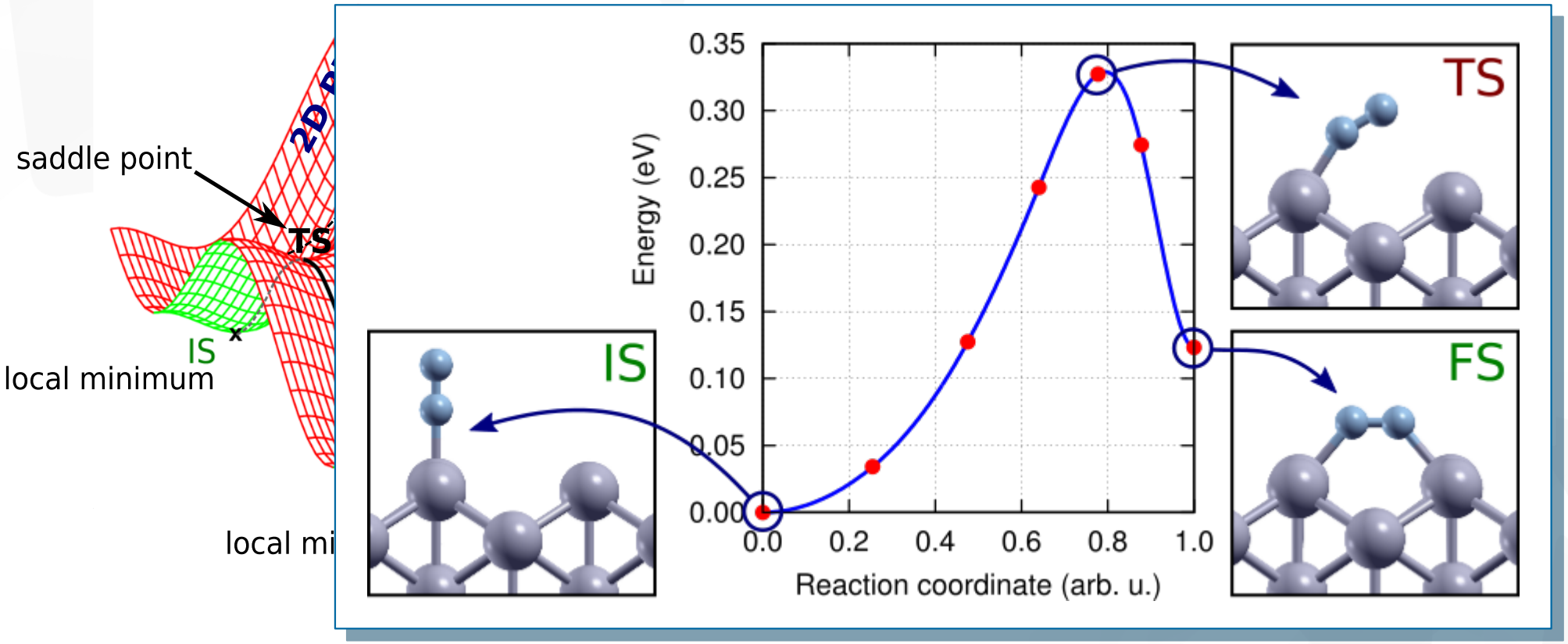


saddle points are unstable configurations and their location is a difficult talk

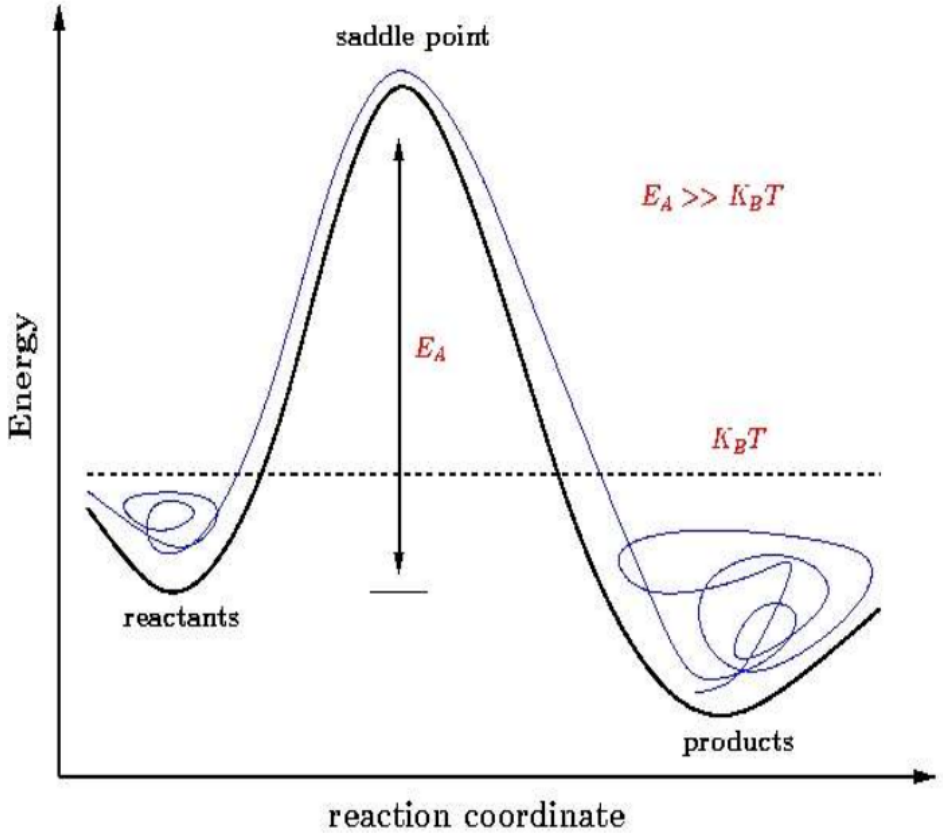
Elementary activated reaction step

- potential energy surface (PES) is highly multidimensional

(except for trivial examples)



Rare Events



The characteristic time scale of this transition process is:

$$t_{\text{jump}} \approx t_{\text{vib}} \cdot e^{\frac{E_A}{K_B T}}$$

Van't-Hoff - Arrhenius (1890)

(Remark: I often use E^* instead of E_A for activation energy)

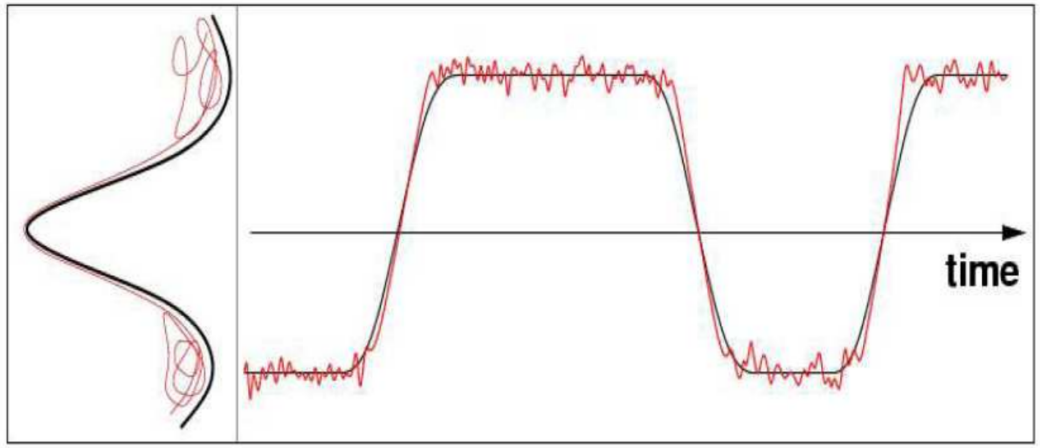
Rare Events

$$t_{\text{jump}} \approx t_{\text{vib}} \cdot e^{\frac{E_A}{K_B T}}$$

$$t_{\text{vib}} \approx 10^{-13} \text{ s}; \quad E_A \approx 0.75 \text{ eV}; \quad T = 300 \text{ K} \Longrightarrow t_{\text{jump}} \approx 1 \text{ s}$$

Assuming a time-step of one fempto-second, 10^{15} time steps of MD would be necessary to have a reasonable probability to observe ONE transition.

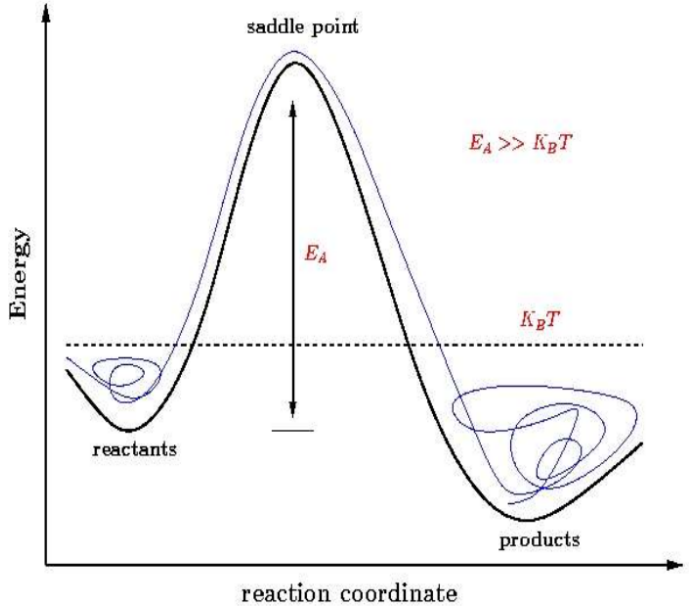
Nevertheless when the appropriate fluctuation occurs the process is extremely fast (a few fempto-seconds).



What is macroscopically perceived as a slow process is instead a rare event.

Rare Events

an alternative approach



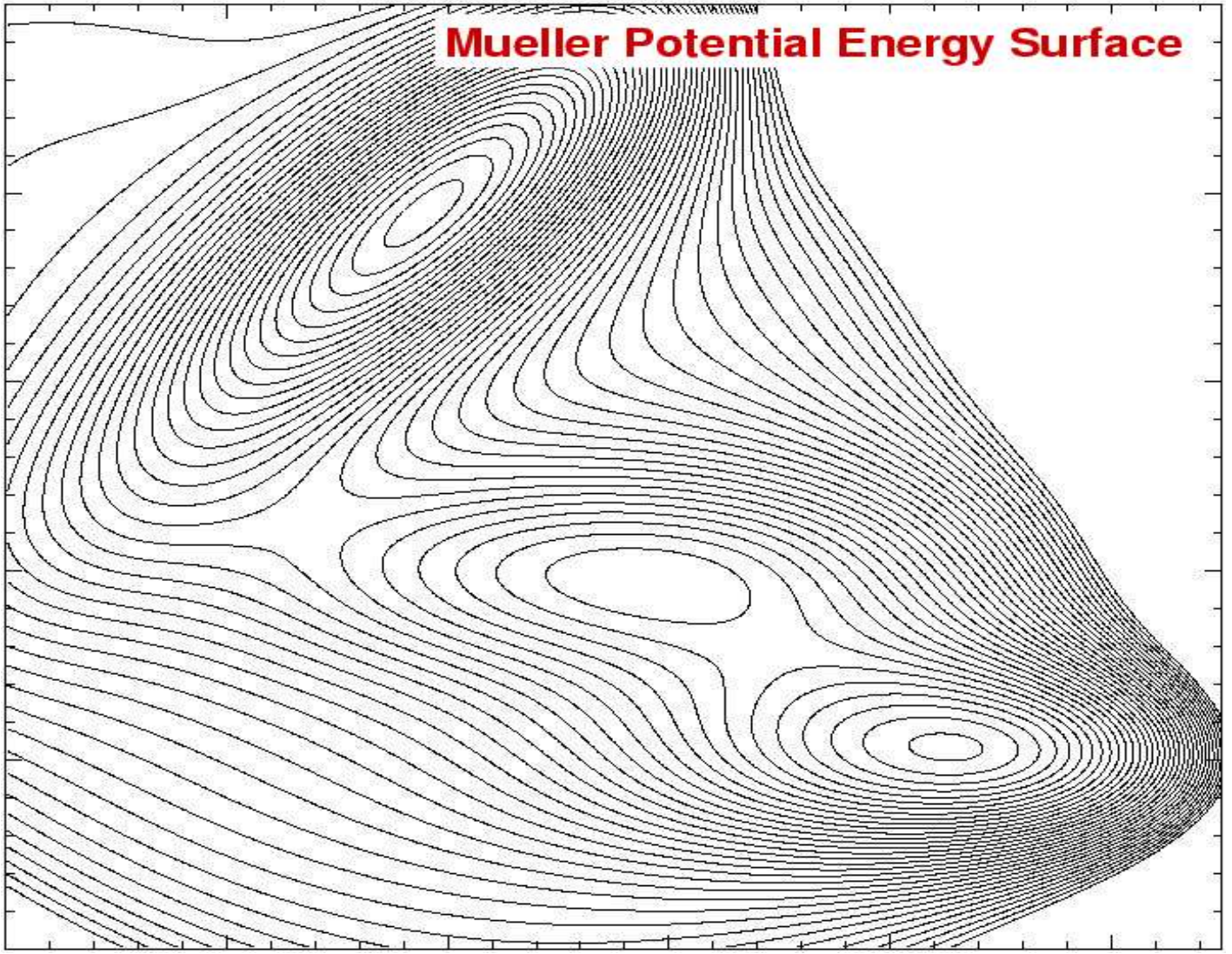
The transition probability can be estimated using equilibrium statistical mechanics. Once the saddle point has been located we can use harmonic Transition State Theory (hTST) to calculate the rate constants:

$$K_{\text{reactants} \longrightarrow \text{products}} = \mathcal{A} \cdot e^{-\frac{E_A}{K_B T}}$$

$$\mathcal{A} = \frac{\Pi_{i=1}^{3N} \ \nu_i^{reactants}}{\Pi_{i=1}^{3N-1} \ \nu_i^{saddle\ point}}$$

sbraccia@princeton.edu

saddle points in multidimensional systems: the Mueller PES



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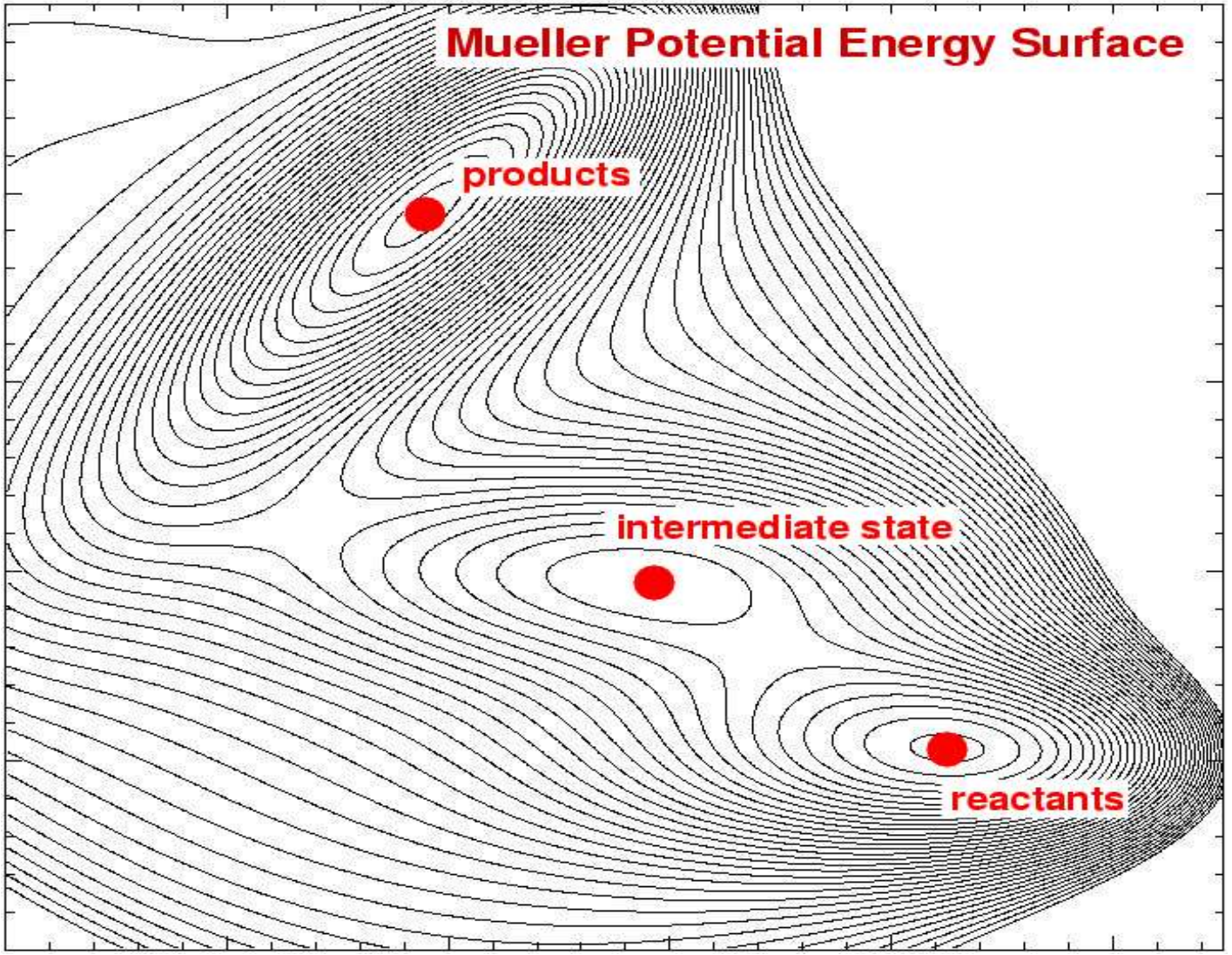

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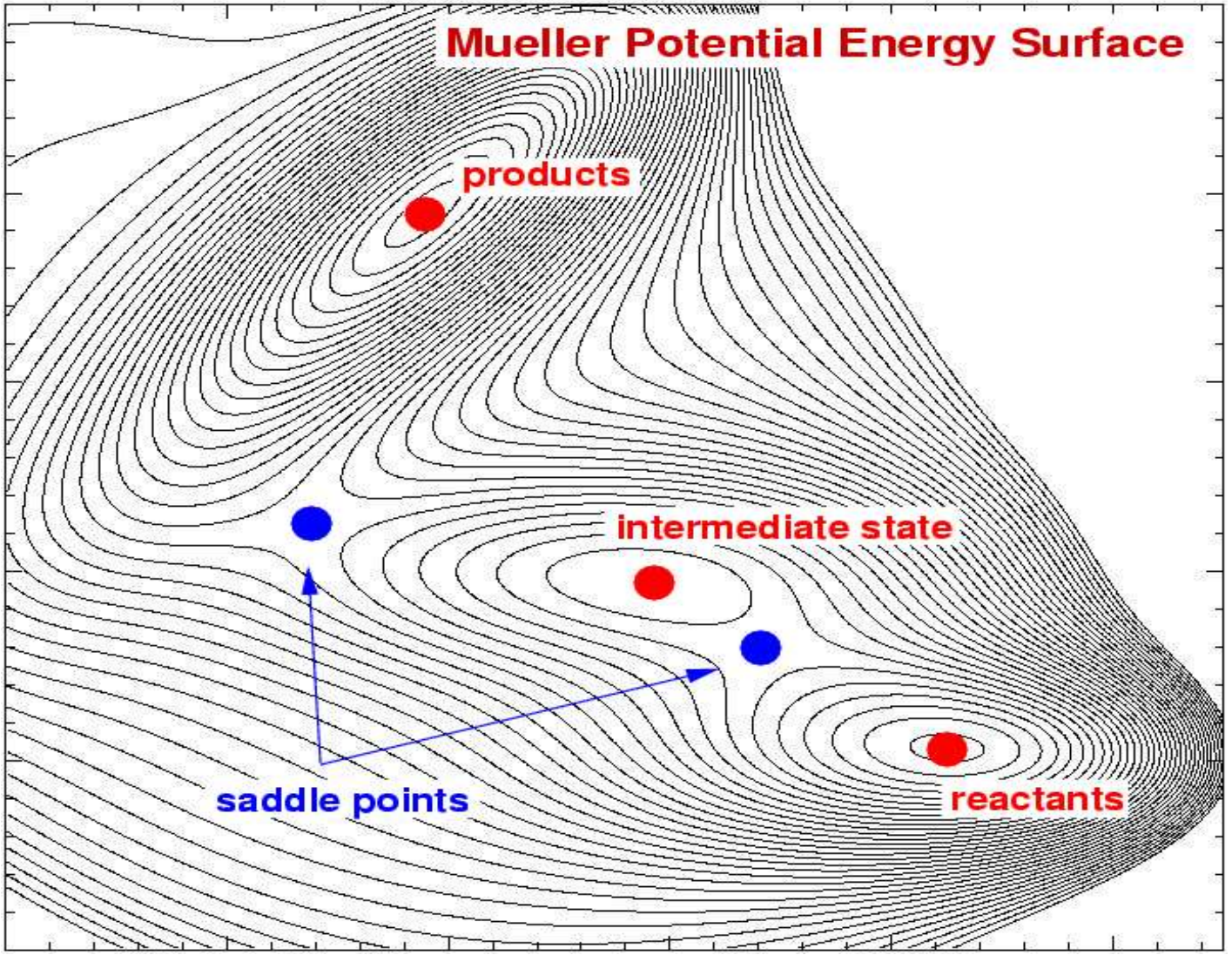

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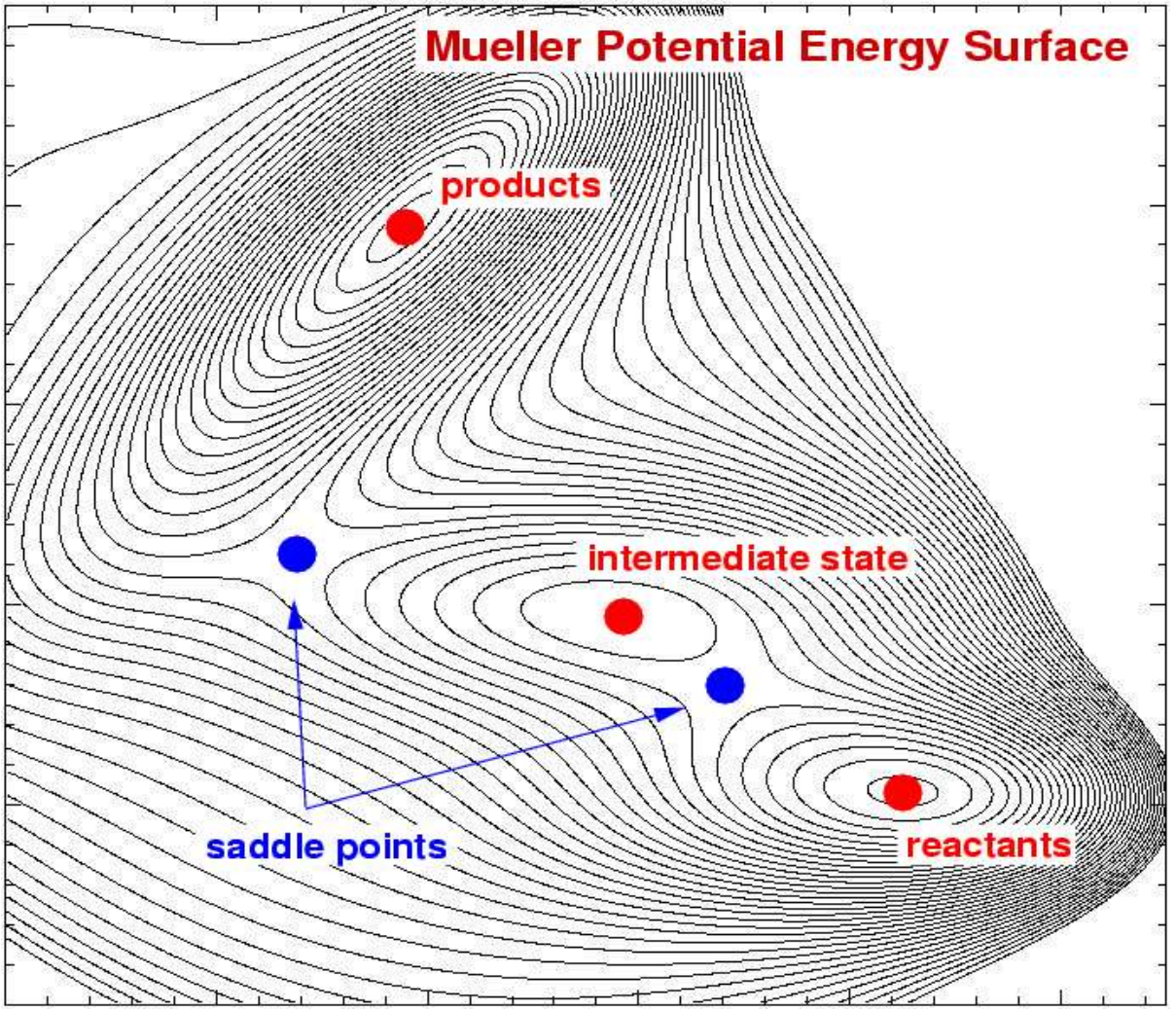

The path characterized by the "highest" transition probability, at zero temperature, is the Minimum Energy Path.

MEP: the components of the force orthogonal to the path are zero.

$$\nabla V(x(s)) - \tau(s)\ (\tau(s)|\nabla V(x(s))) = 0$$

normalised tangent

sbraccia@princeton.edu

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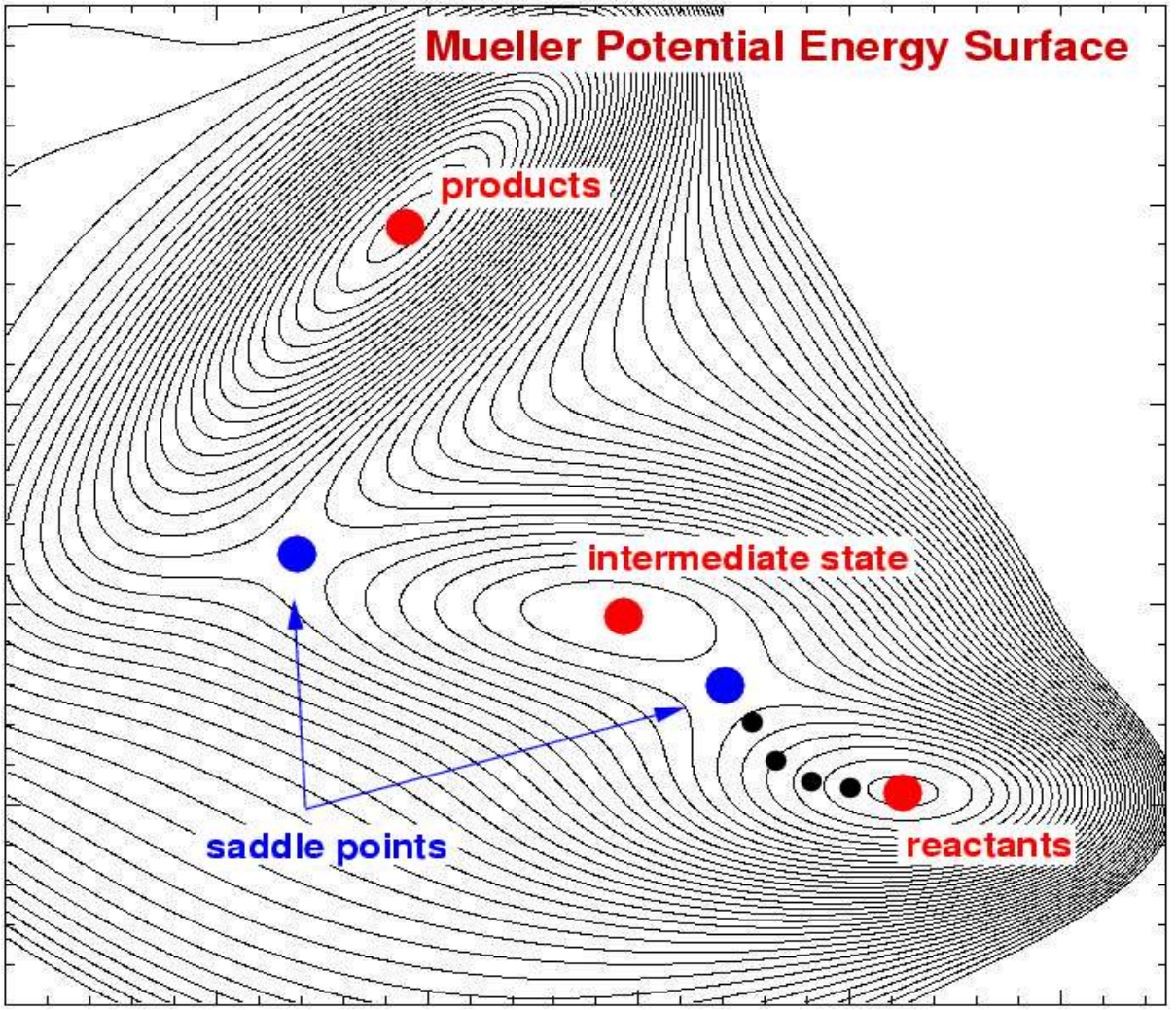

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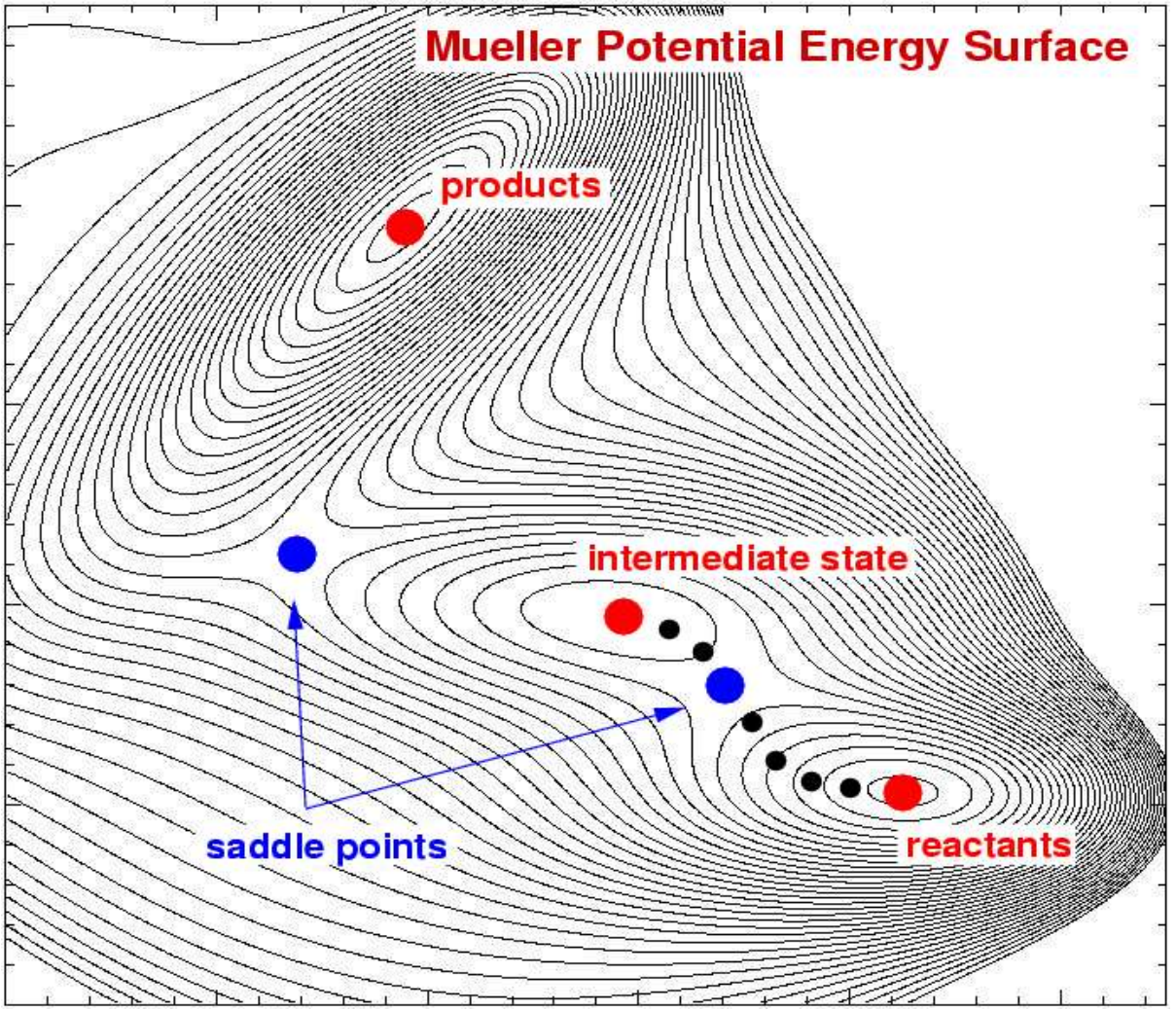

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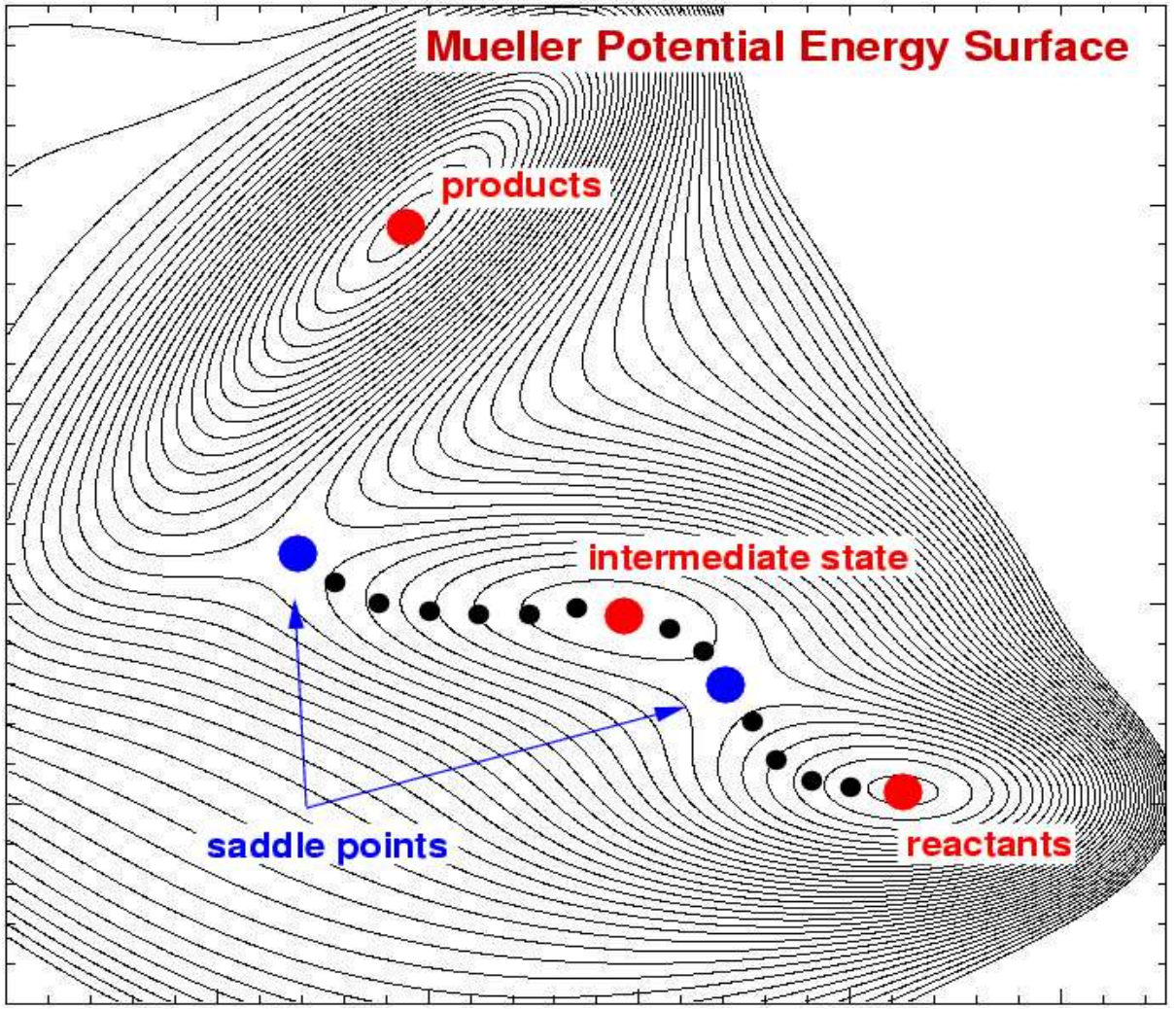

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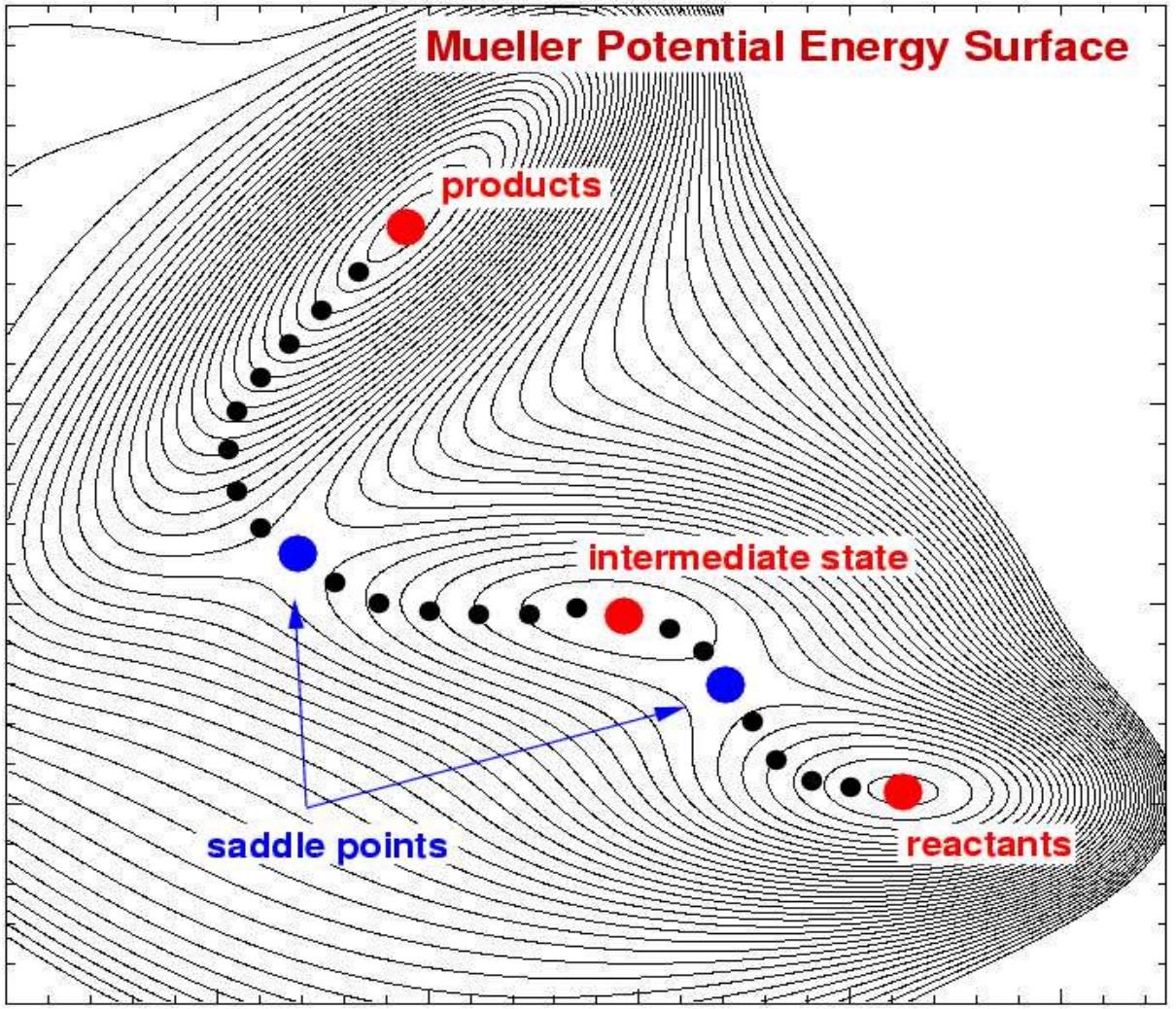


The path characterized by the "highest" transition probability, at zero temperature, is the Minimum Energy Path.

MEP: the components of the force orthogonal to the path are zero.

The MEP crosses the saddle points.

sbraccia@princeton.edu

how to locate the MEP

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

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

2) Orthogonal forces :

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

3) MEP condition :

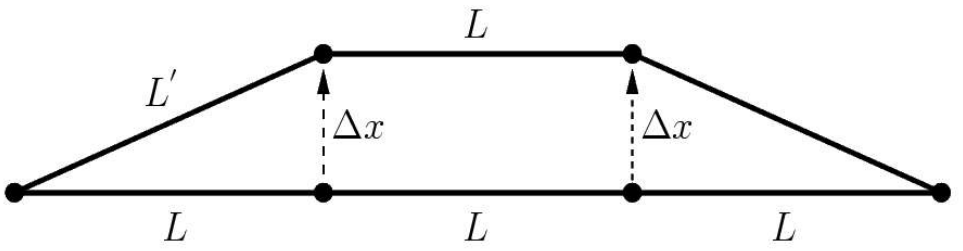
$$\| F(x_i)_\perp \| = 0$$

4) path dynamics
(steepest-descent) :

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

sliding down

The path dynamics does not preserve the inter-image distance (path's parametrisation):



$$L' = \sqrt{L^2 + \Delta x^2}$$

$$L' - L = L\left(\sqrt{1 + \frac{\Delta x^2}{L^2}} - 1\right) \sim \frac{1}{2}\frac{\Delta x^2}{L^2}$$

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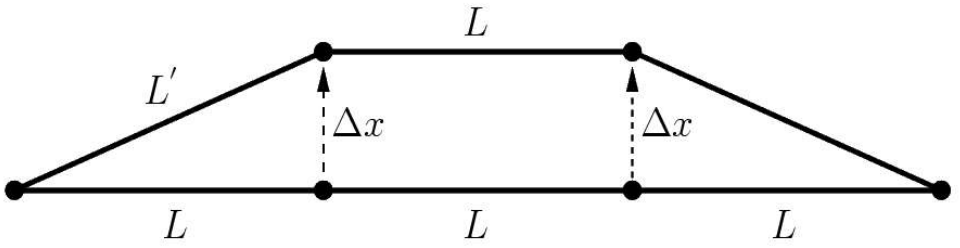

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Consequences:

1) Many images are required to represent the path.

2) The images can eventually slide down to the two minima.

Possible solutions :

1) NEB: the images are connected by springs. ⇦ this talk

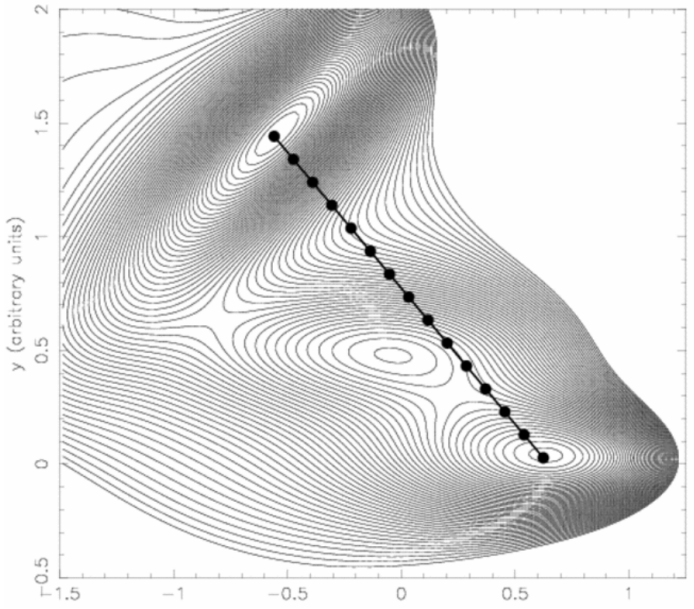
2) STRING: images are kept equispaced using Lagrange constraints.

Nudged Elastic Band method

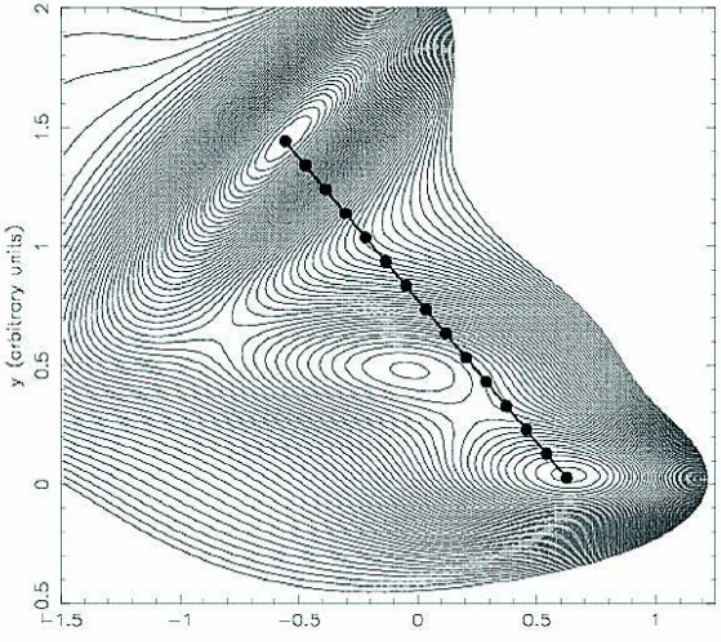
- Path is discretized into images
- Images are inter-connected by springs (these keep images "equidistant")
- Each image feels a true force and a force due to springs
- Spring forces are projected along the path and true forces orthogonal to the path

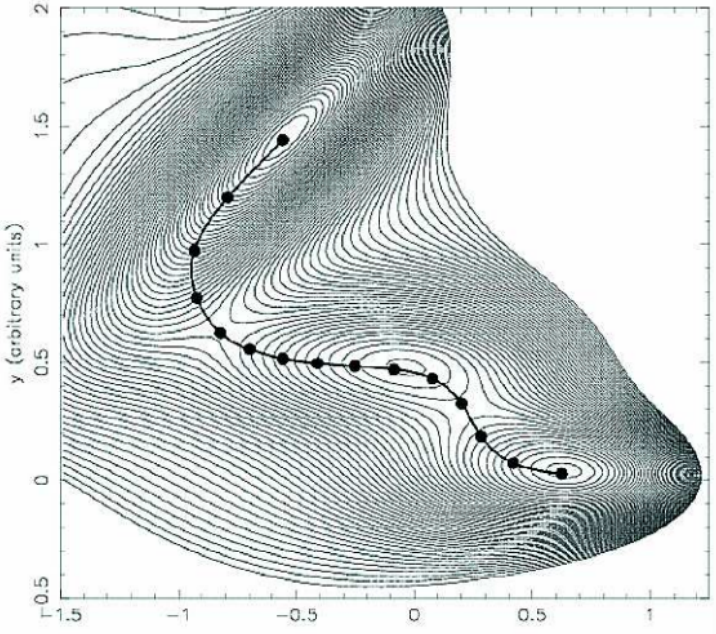
$$F(x_i) = -\left(\nabla V(x_i) - \tau_i \langle \tau_i | \nabla V(x_i) \rangle\right) \quad - \quad \tau_i \langle \tau_i | \nabla \frac{K_i}{2} (x_{i+1} - x_i)^2 \rangle$$

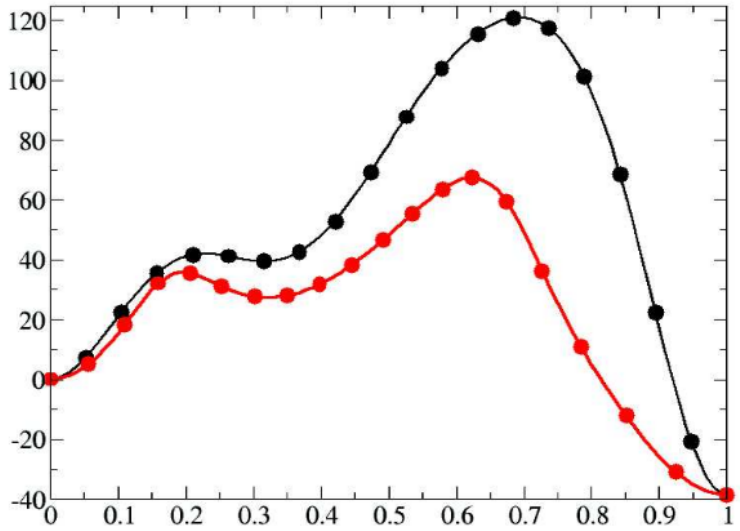
- Projections are defined by the path's tangent: **the tangent plays a crucial role !**



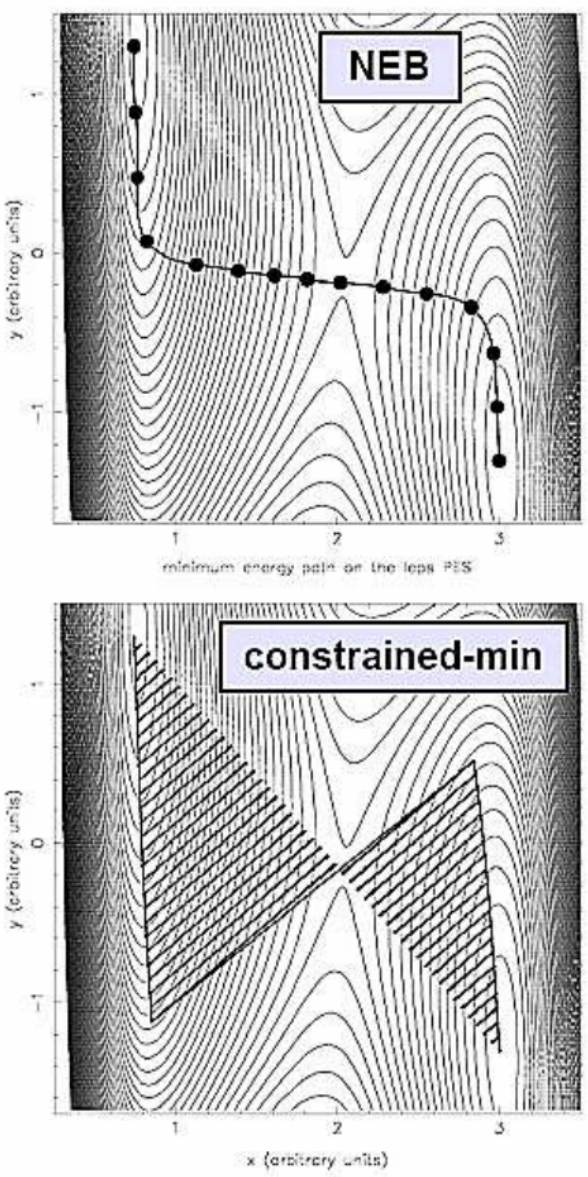
NEB on the Mueller PES

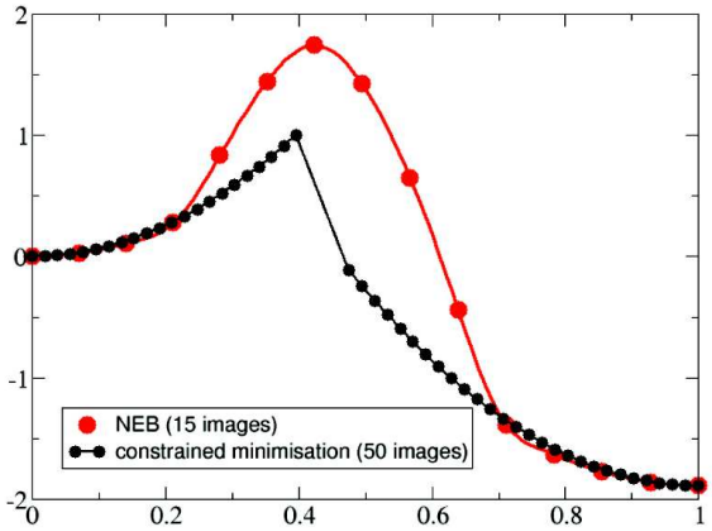






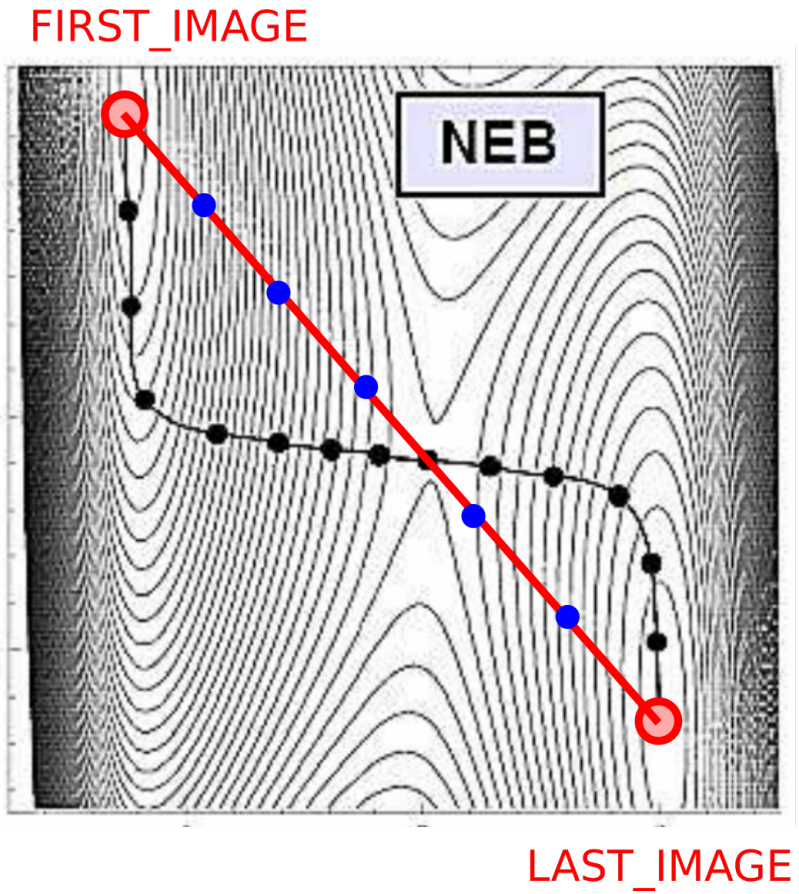
NEB vs constrained minimizations

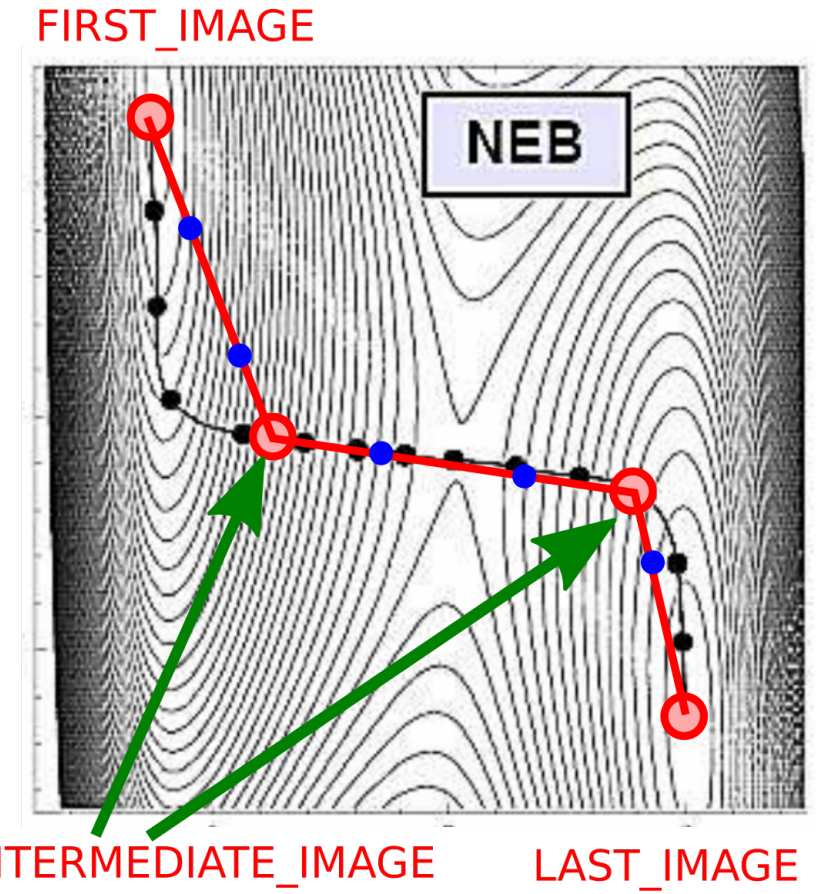




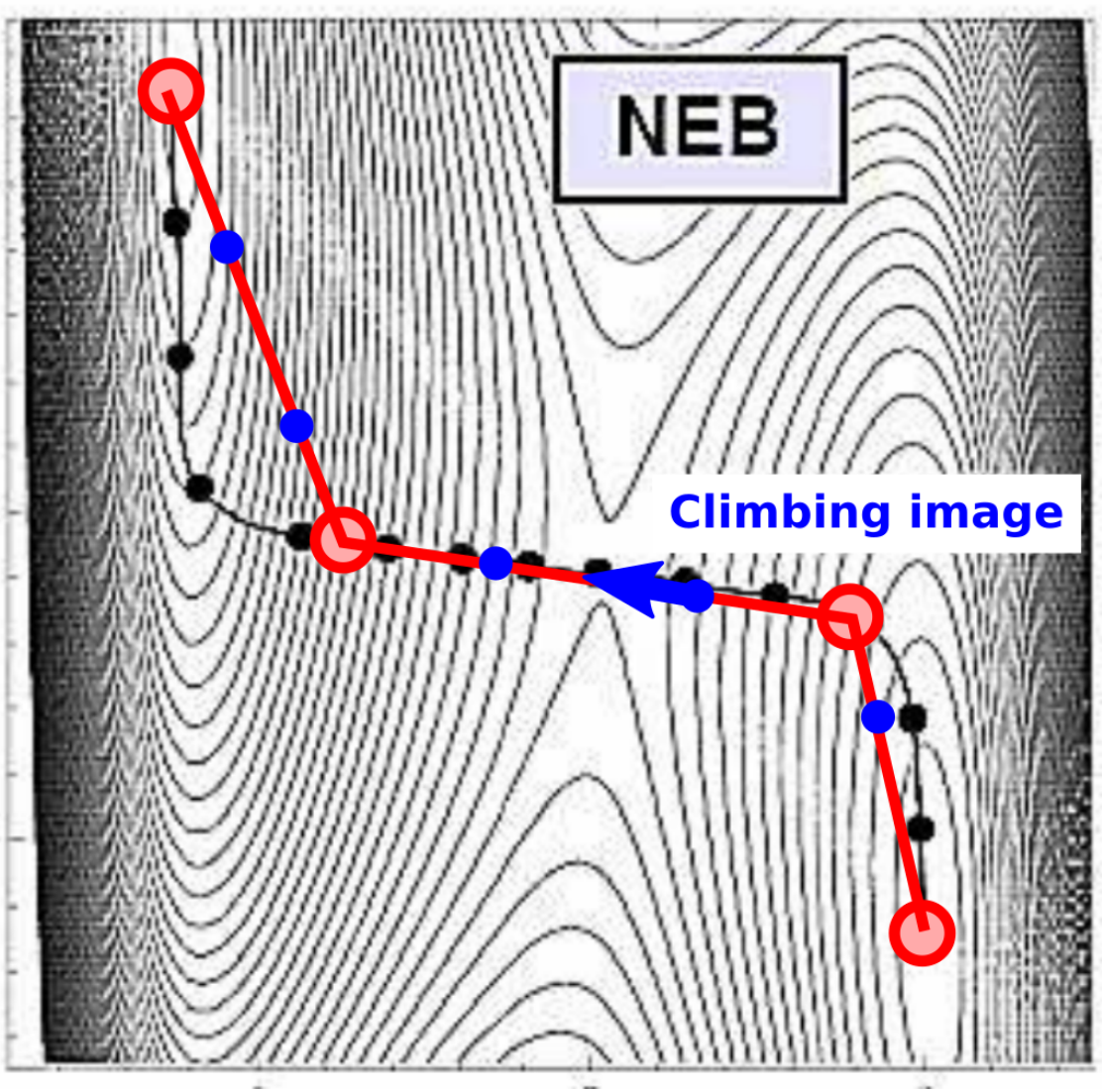
Constrained minimization is completely wrong in this case.

Specifying intermediate images





Climbing image NEB



NEB code and its input file

```
BEGIN
BEGIN_PATH_INPUT
&PATH
   ...
/
END_PATH_INPUT
```

NEB specification

```
BEGIN_ENGINE_INPUT
! pw.x  specific namelists and cards
&CONTROL
/
&SYSTEM
/
&ELECTRONS
/
CELL_PARAMETERS
   ...insert...
ATOMIC_SPECIES
   ...insert...
K_POINTS
   ...insert...
```

pw.x specification

```
BEGIN_POSITIONS
FIRST_IMAGE
ATOMIC_POSITIONS
   ...
INTERMEDIATE_IMAGE
ATOMIC_POSITIONS
   ...
LAST_IMAGE
ATOMIC_POSITIONS
   ...
END_POSITIONS
END_ENGINE_INPUT
END
```

specification of images

The QE program associated with the NEB method is `neb.x`.

For detailed description of the input file, see `INPUT_NEB.html`.

NEB code and its input file

The NEB input is specified via &PATH namelist. Important variables:

- num_of_images – number of images
- CI_scheme – do we want climbing-image NEB or not, possibilities:
  - 'no-CI' – climbing image is not used
  - 'auto' – climbing-image is used; the CI image is automatically the image with the highest energy
  - 'mannual' – climbing-image is (or climbing-images are) manually specified via CLIMBING_IMAGES card
- opt_scheme – type of optimization scheme ('broyden' = quasi-Newton Broyden method , 'quick-min' velocity Verlet type scheme)
- ds – time-step for CI_scheme = 'quick-min' (or optimization step length for CI_scheme = 'broyden')

Question: how many images should I use?
Answer: It depends, but usually inter-image distance in range of 1 to 2 Bohr should be OK (it is printed in the output).

That's all

Beware that NEB calculation is usually difficult to converge. Some experience is a plus.