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Rare Events & Nudged Elastic Band method

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and
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Bangalore, July 2006

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Potential Energy Landscape

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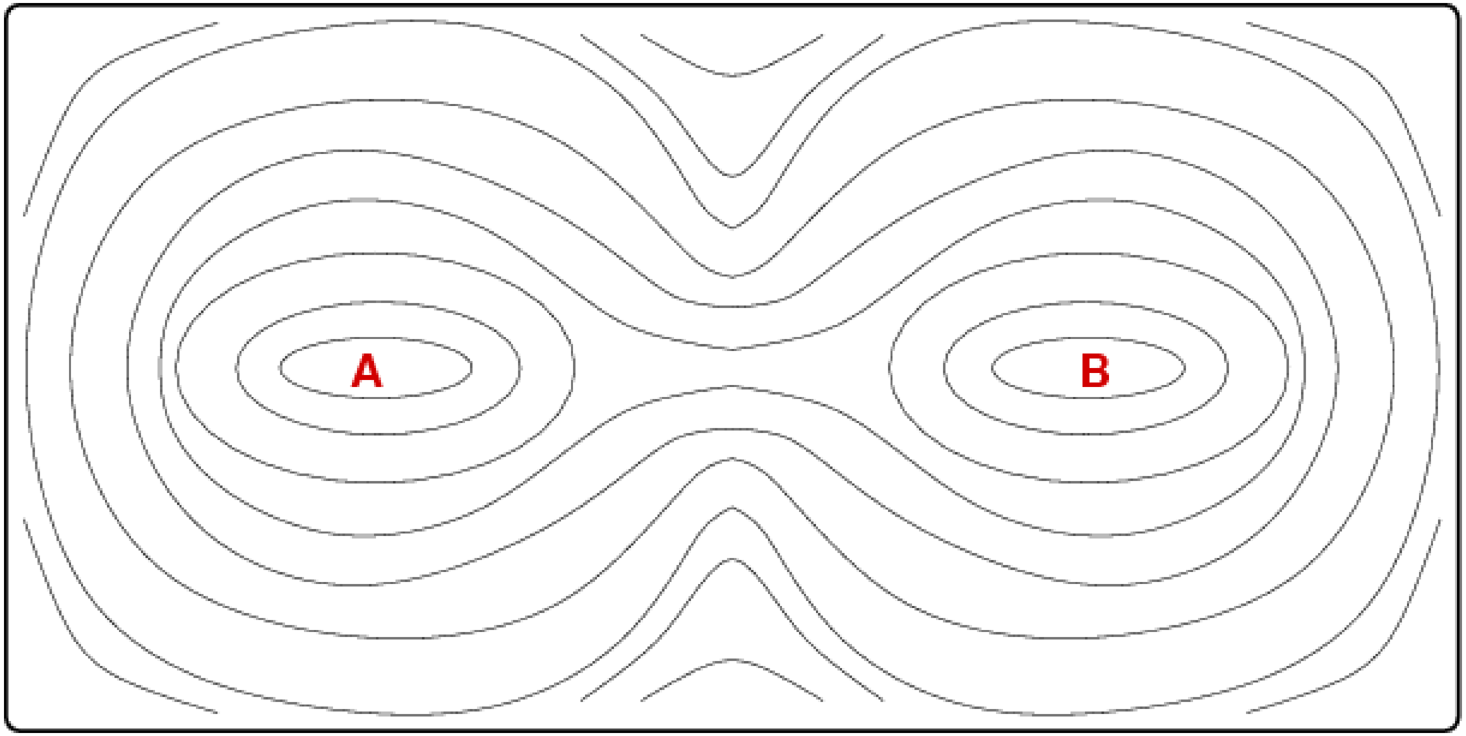
Let's consider a potential energy function (as defined in the lecture about dynamics) with two minima $\{q_A^{3N}\}$ and $\{q_B^{3N}\}$.

A two-dimensional example :



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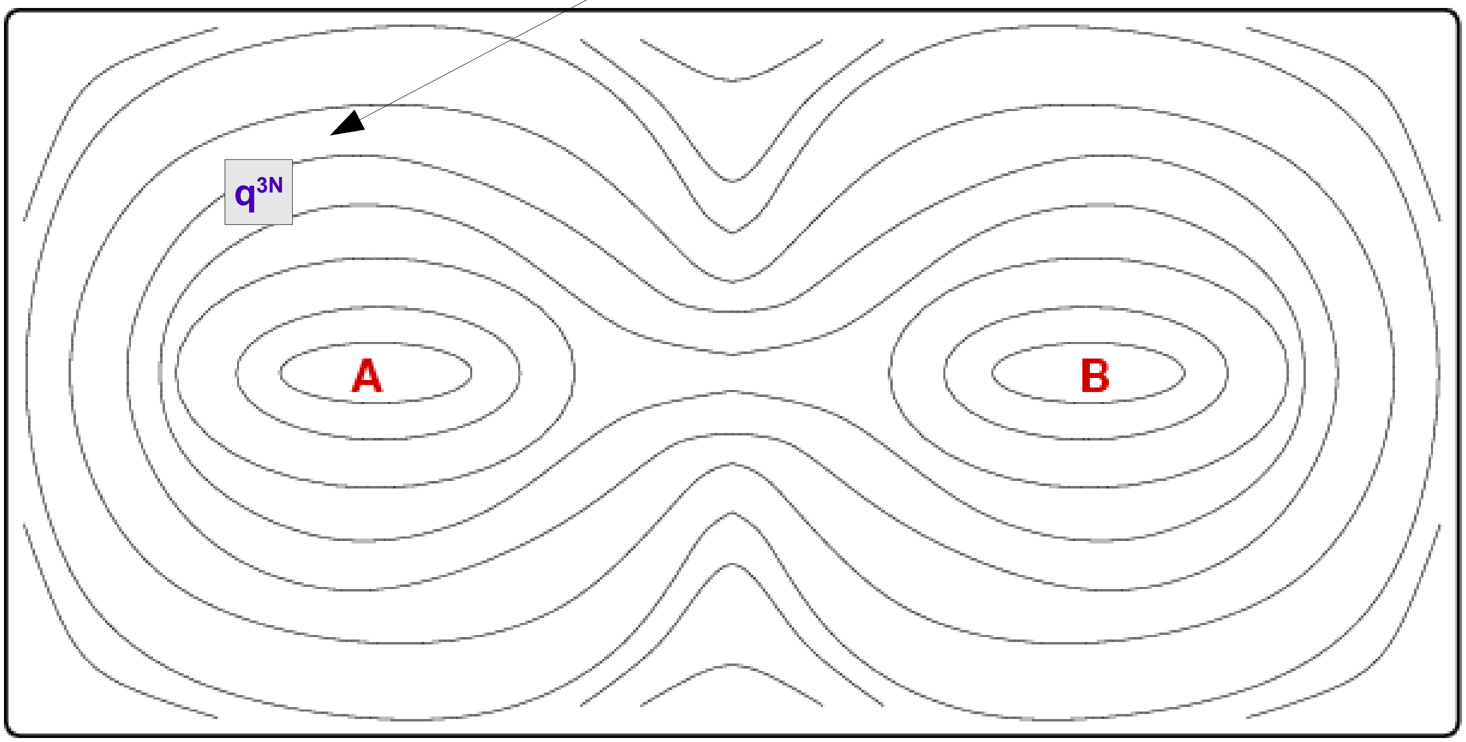
Potential Energy Landscape

The probability of finding the system in the neighbourhood of any configuration $\{q^{3N}\}$ is proportional to the Boltzmann factor computed at such configuration:

$$\mathcal{P}\left(q^{3N}\right) \sim \frac{\mathrm{e}^{-\beta U\left(q^{3N}\right)}}{\mathcal{Z}}$$



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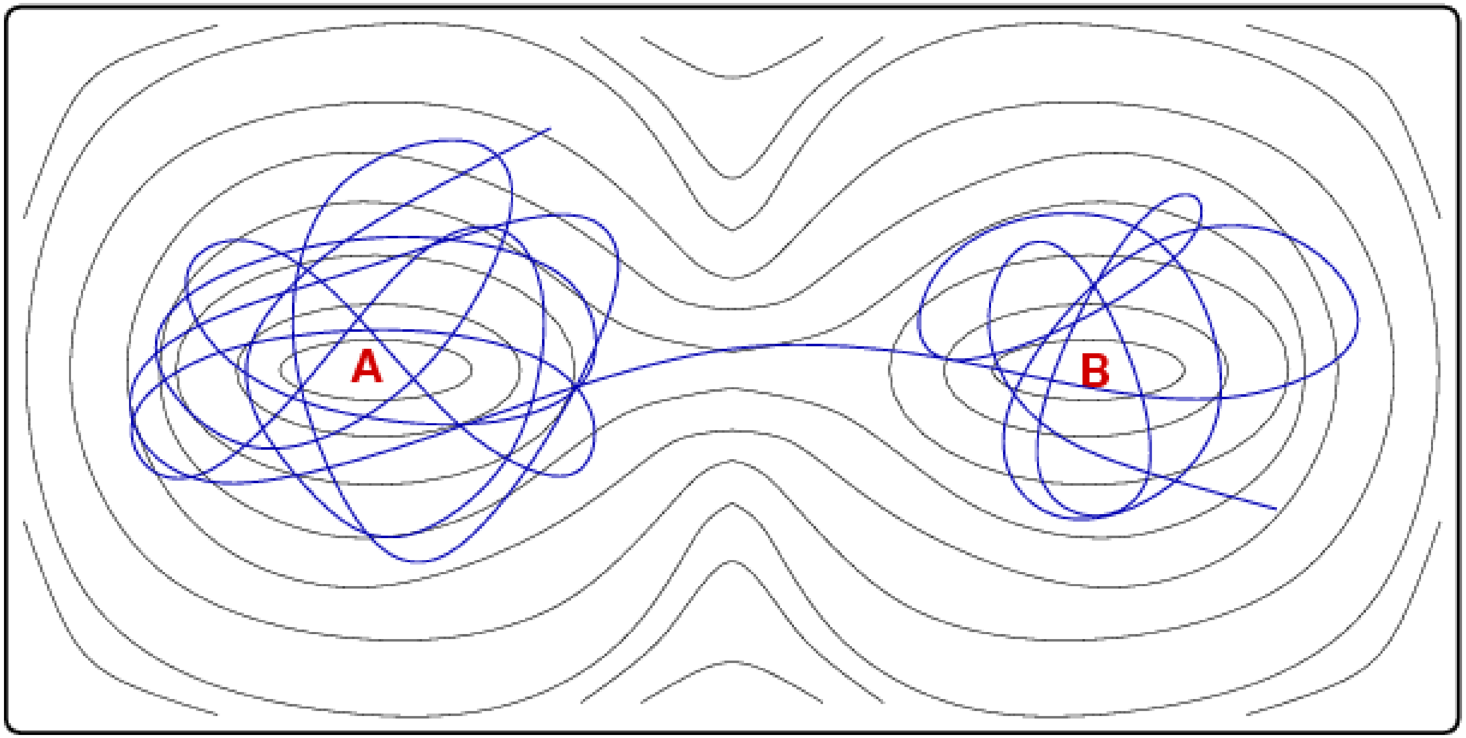
Dynamics in the Potential Energy Landscape

Equivalently (ergodicity) the relative time spent around a configuration $\{q^{3N}\}$ is proportional to the Boltzmann factor.

The system spends more time around configurations of low potential energy. Fluctuations are responsible for the transition between different minima.



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Phenomenology of rare events

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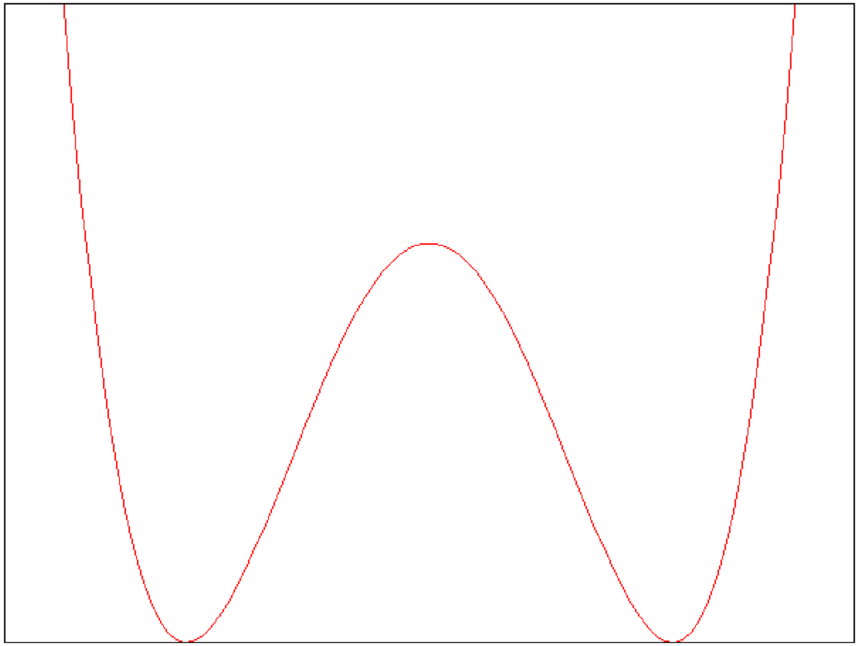
1-dimensional brownian motion in a double-well potential:

$$\mathrm{d}x(t) = -\nabla V\left(x(t)\right)\mathrm{d}t + \xi(t)$$



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Phenomenology of rare events

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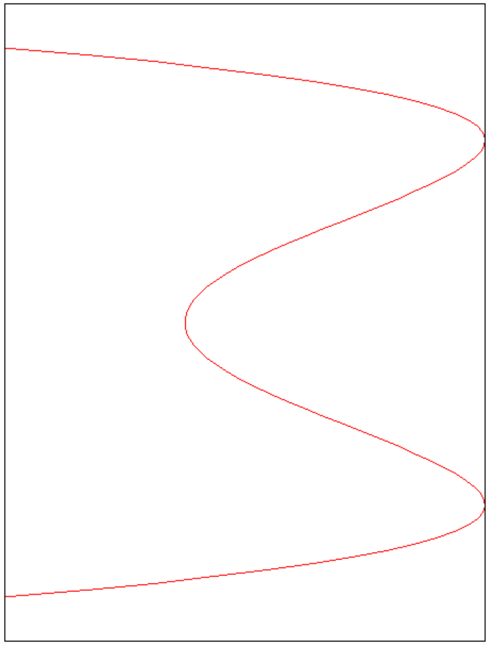
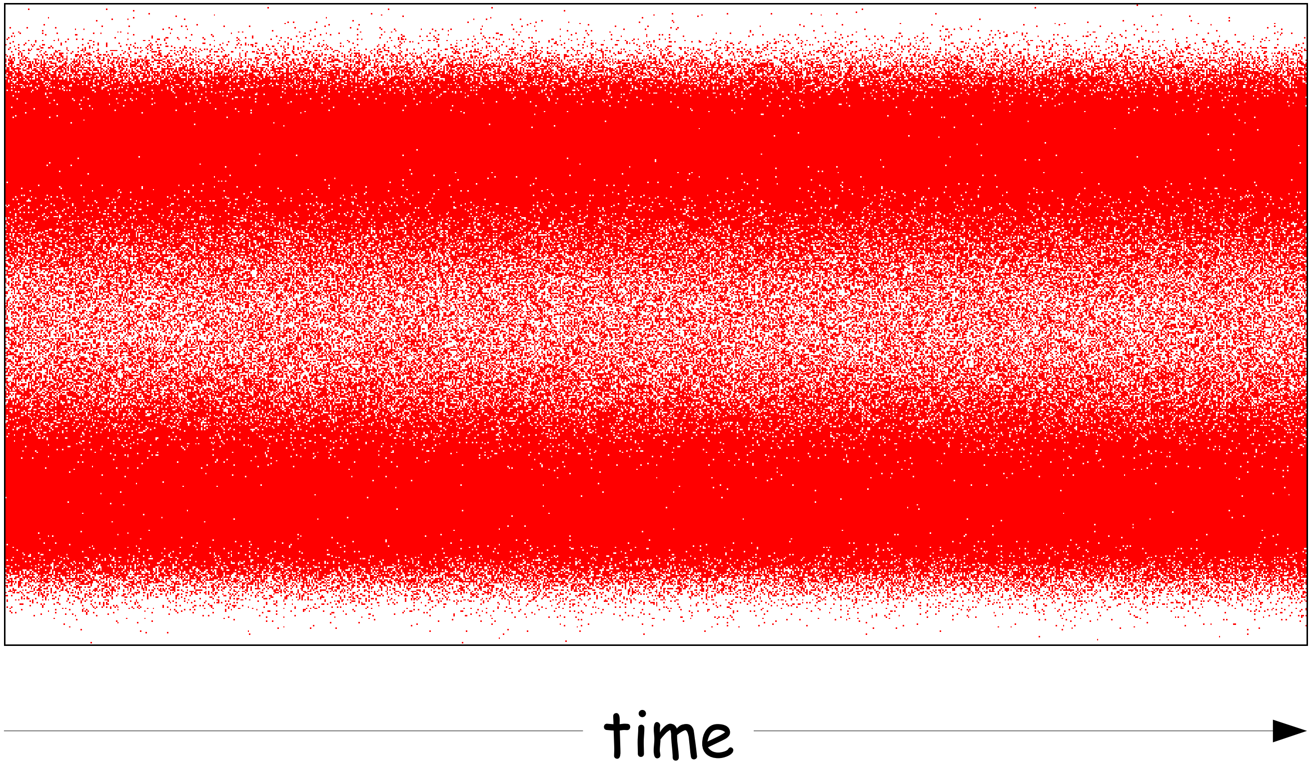
Brownian motion in a double-well potential at a temperature $K_BT \sim 0.5\ E_A$ (50% of the barrier height):

diffusive behaviour





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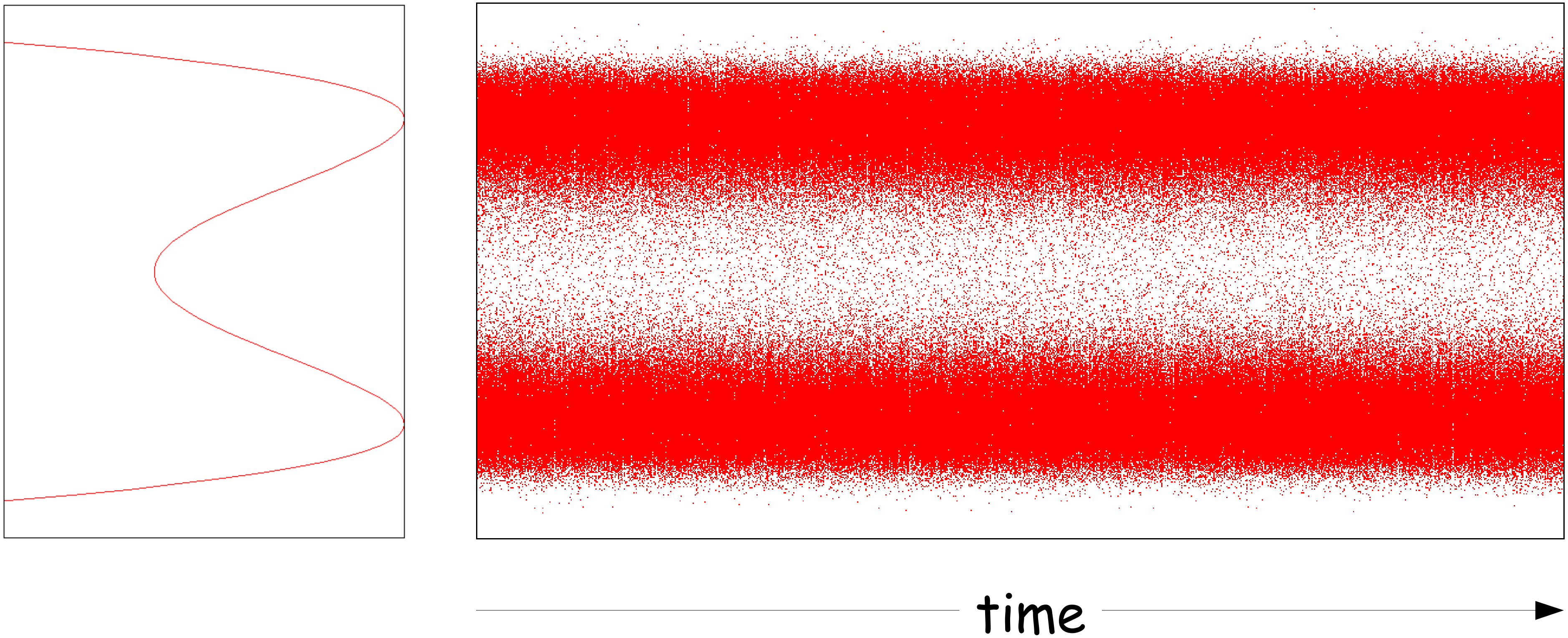
Phenomenology of rare events

Brownian motion in a double-well potential at a temperature $K_BT \sim 0.2\ E_A$ (20% of the barrier height):



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Phenomenology of rare events

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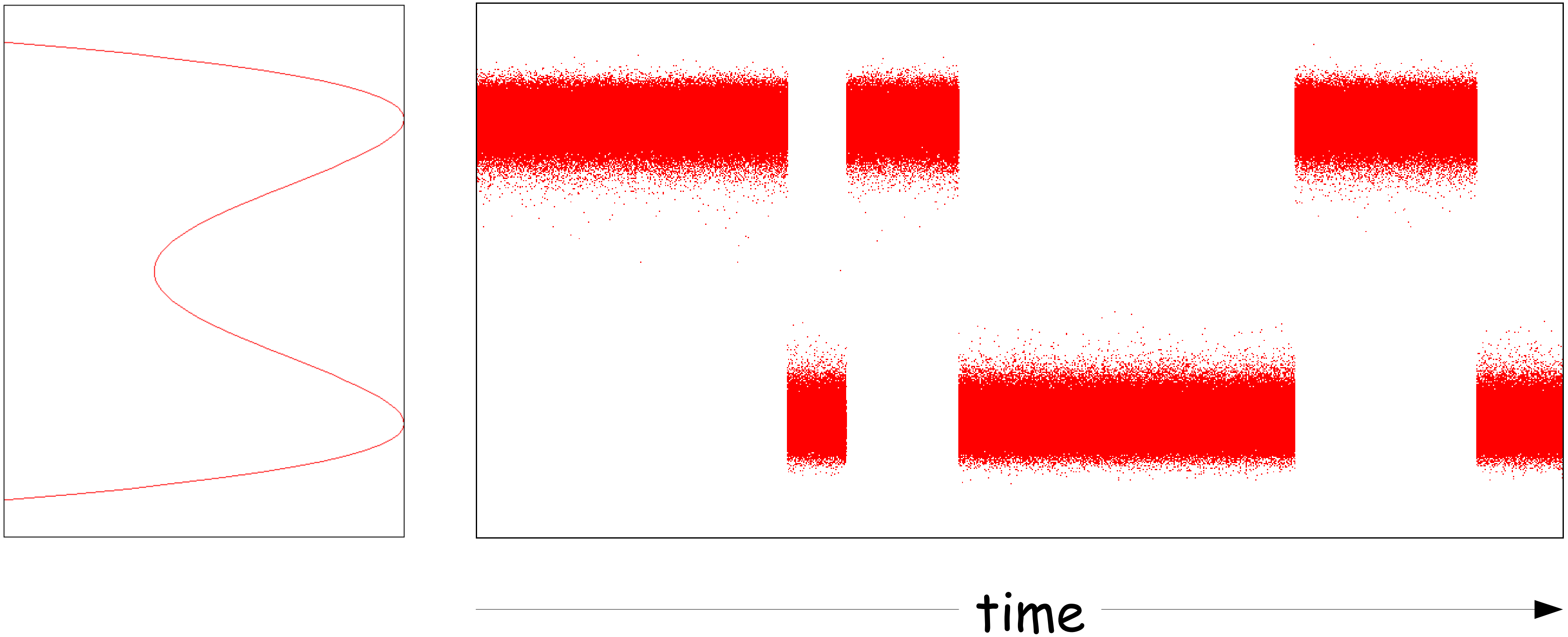
Brownian motion in a double-well potential at a temperature $K_B T \sim 0.08\ E_A$ (8% of the barrier height):

"instantonic" behaviour



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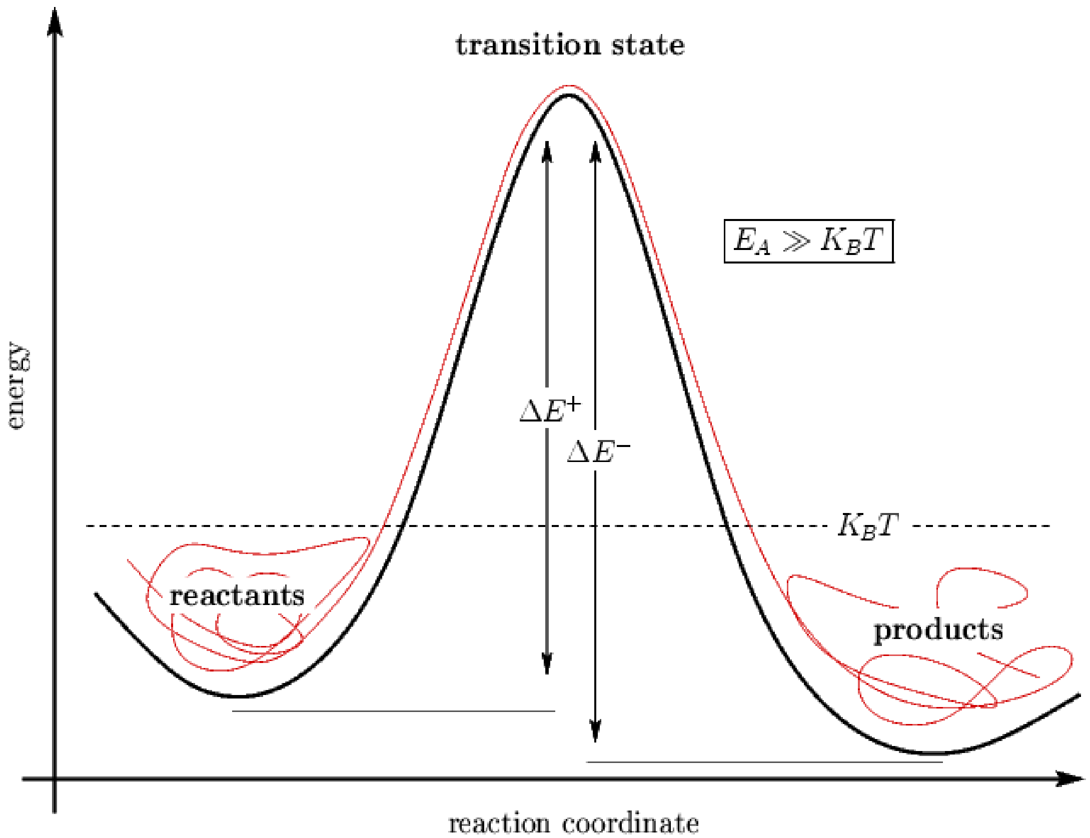
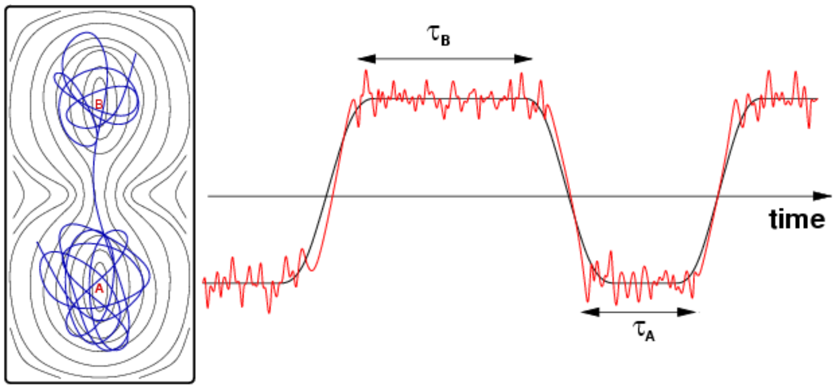
Phenomenology of rare events





$$\tau_A \sim e^{\beta \Delta E^+}$$

$$\tau_B \sim e^{\beta \Delta E^-}$$

$$\frac{\tau_A}{\tau_B} = e^{\beta (E_B - E_A)}$$

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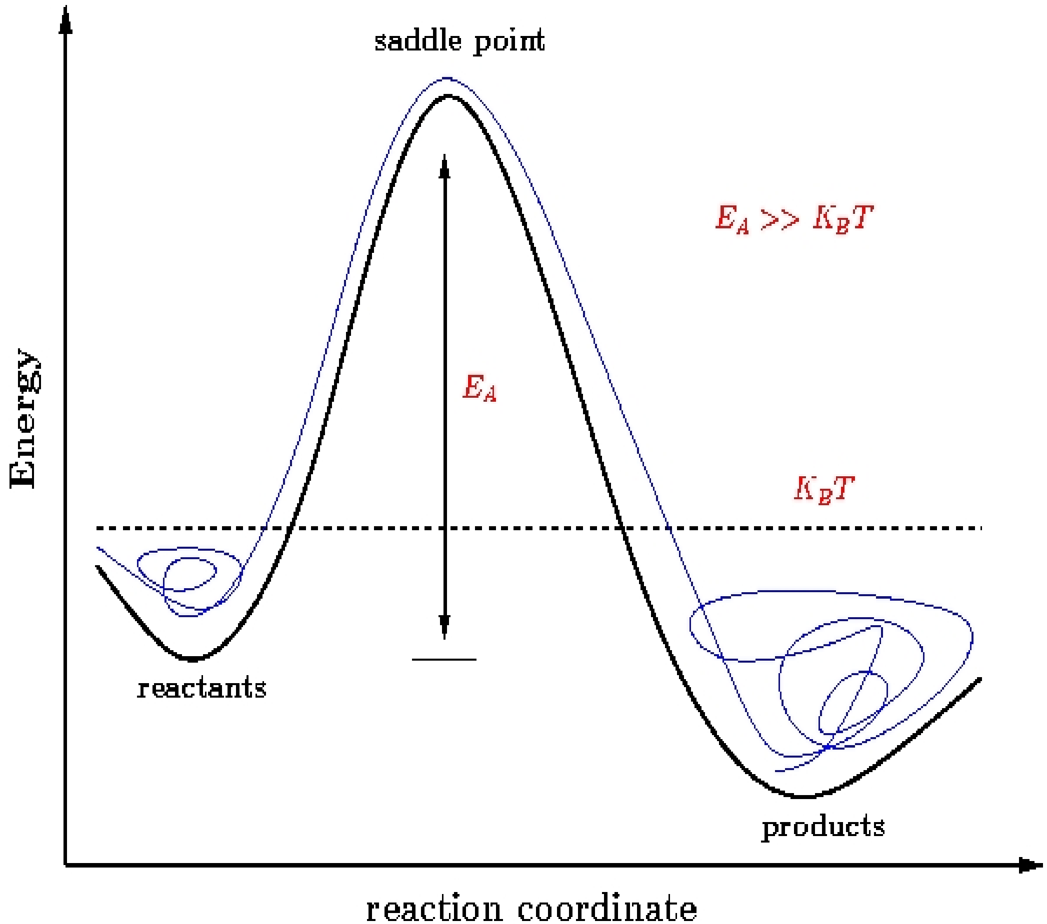
Study of rare events



What is the characteristic time scale of this transition process ?

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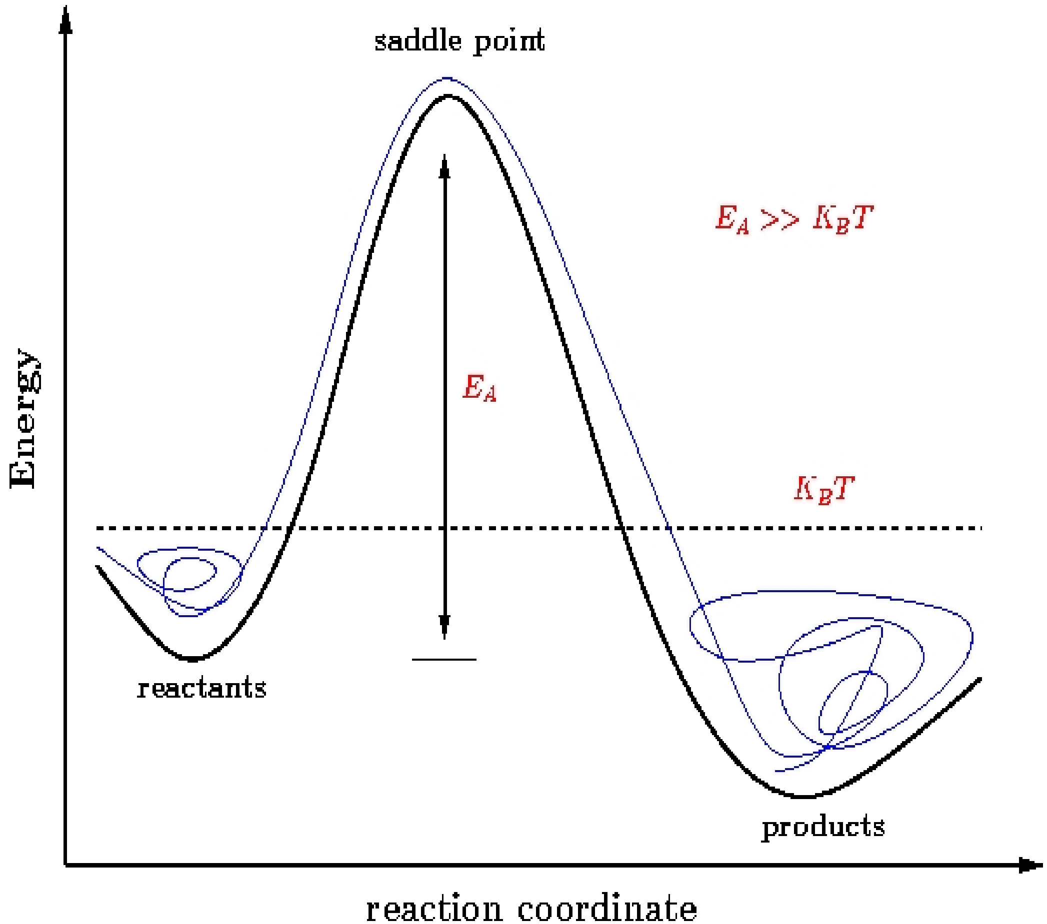
Study of rare events



What is the characteristic time scale of this transition process ?

Van't-Hoff - Arrhenius (1890)

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

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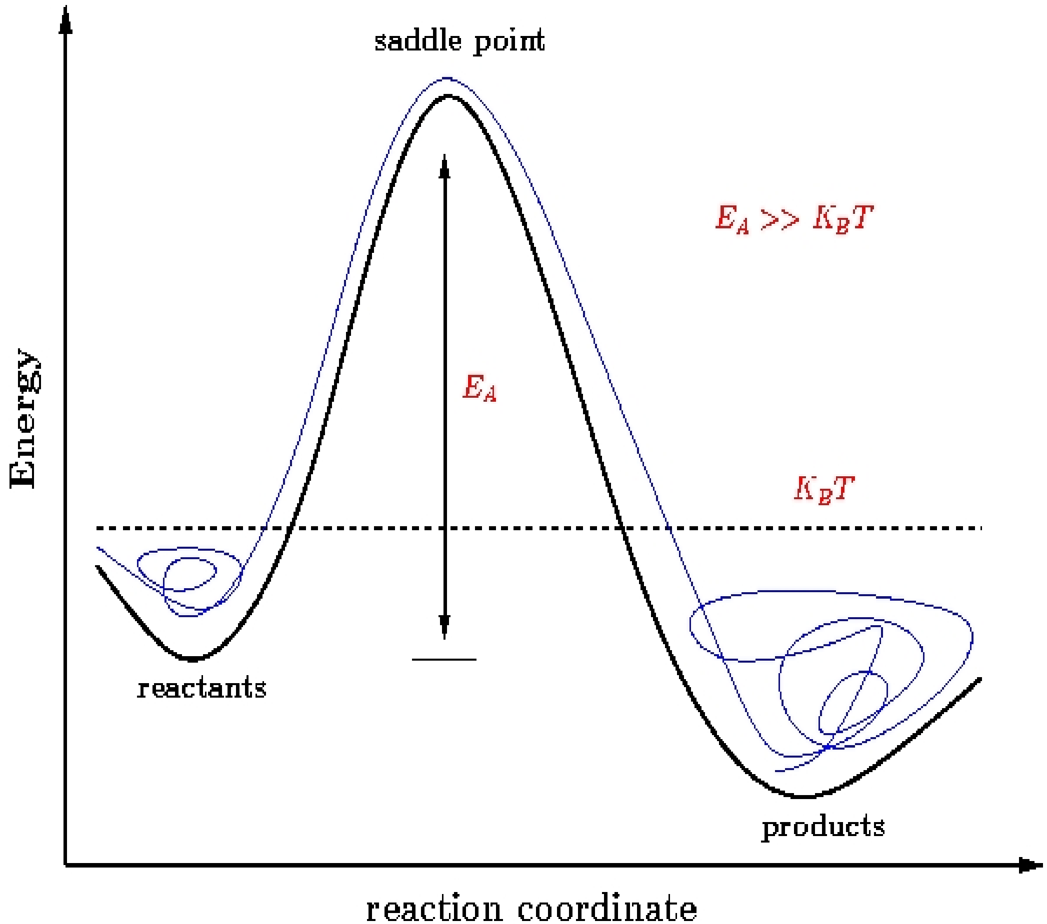
Study of rare events



What is the characteristic time scale of this transition process ?

Van't-Hoff - Arrhenius (1890)

E_A = 0.75 eV

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

t_{vib} ~ 10^{-13} s

T = 300 K

t_{jump} ~ 1 s

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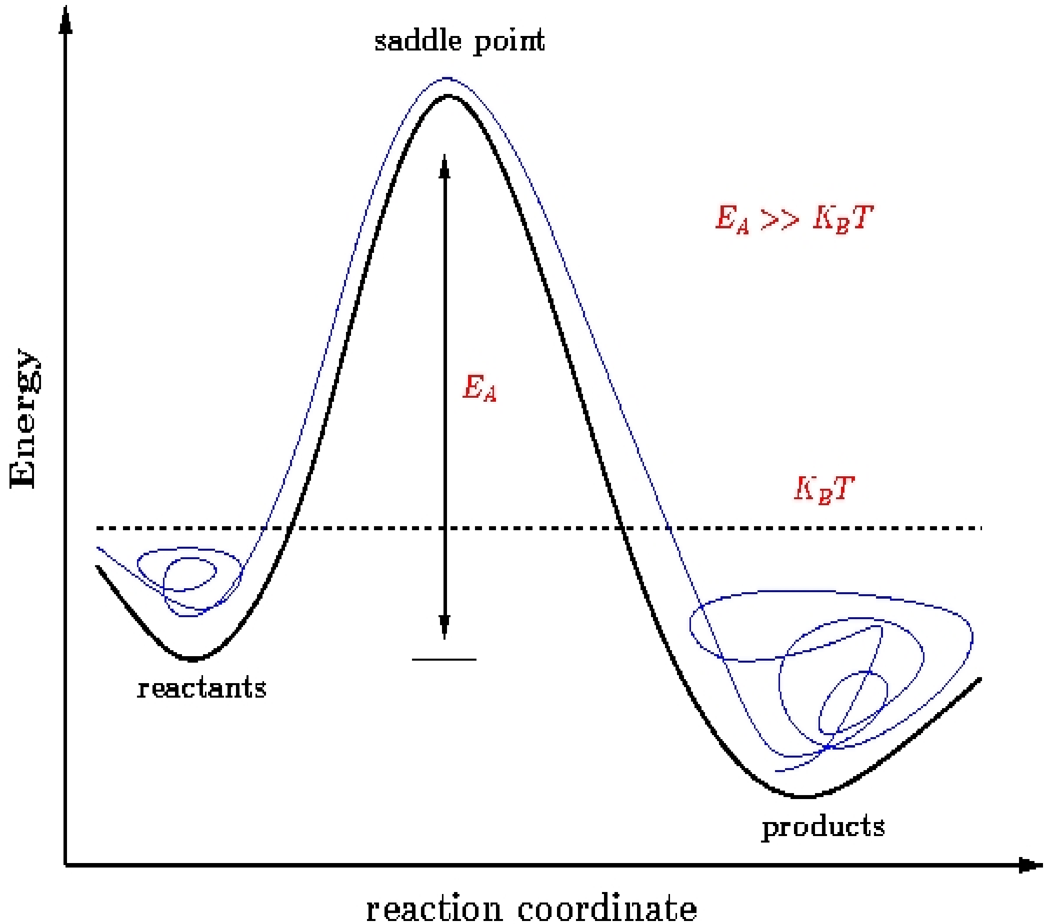

Assuming a time step of one femto-second, **~*10*[15] steps** of Molecular Dynamics are necessary to have a sizeable probability of observing at least a transition from reactants to products !

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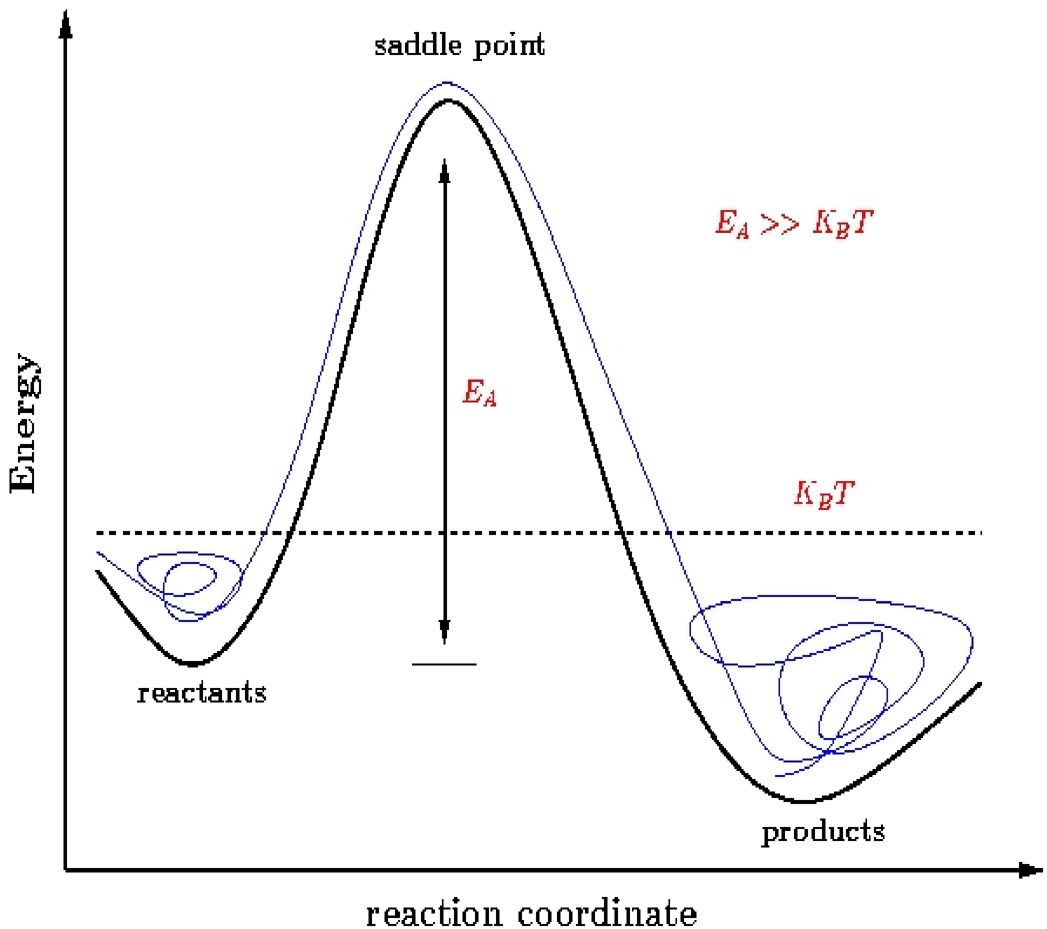
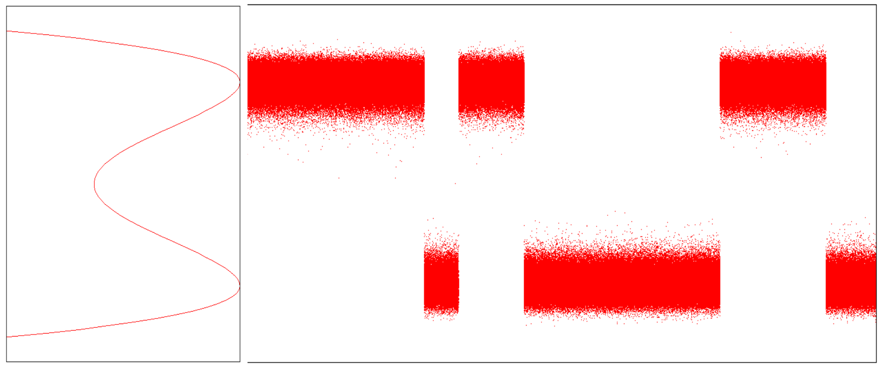
Study of rare events



Assuming a time step of one femto-second, ***~10^{15}* steps** of Molecular Dynamics are necessary to have a sizeable probability of observing at least a transition from reactants to products !

Nevertheless, when an appropriate fluctuation occurs, the process is extremely fast :

t ~ femto-seconds (10^{-15} s)



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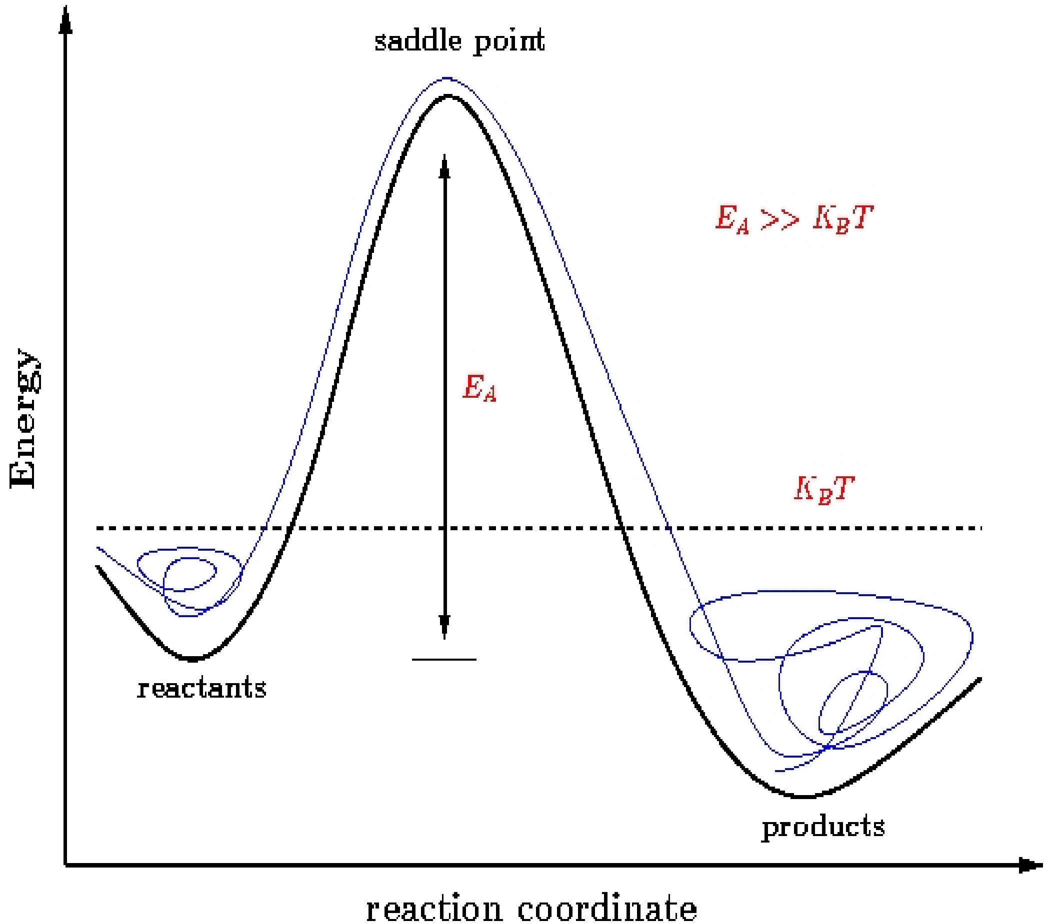
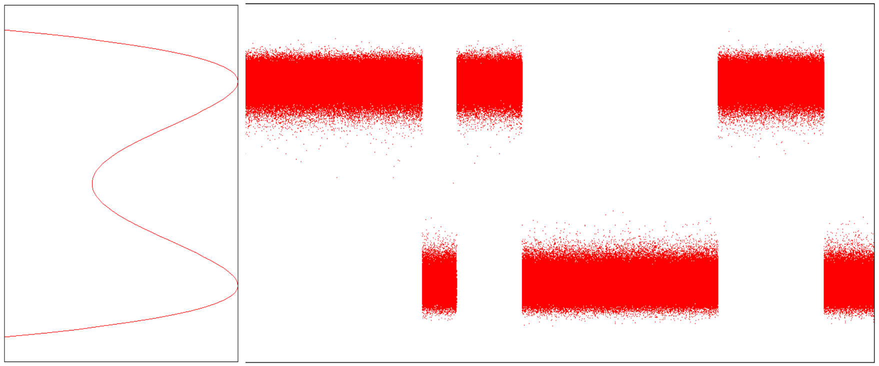
Study of rare events



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



The jumps are uncorrelated

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Study of rare events

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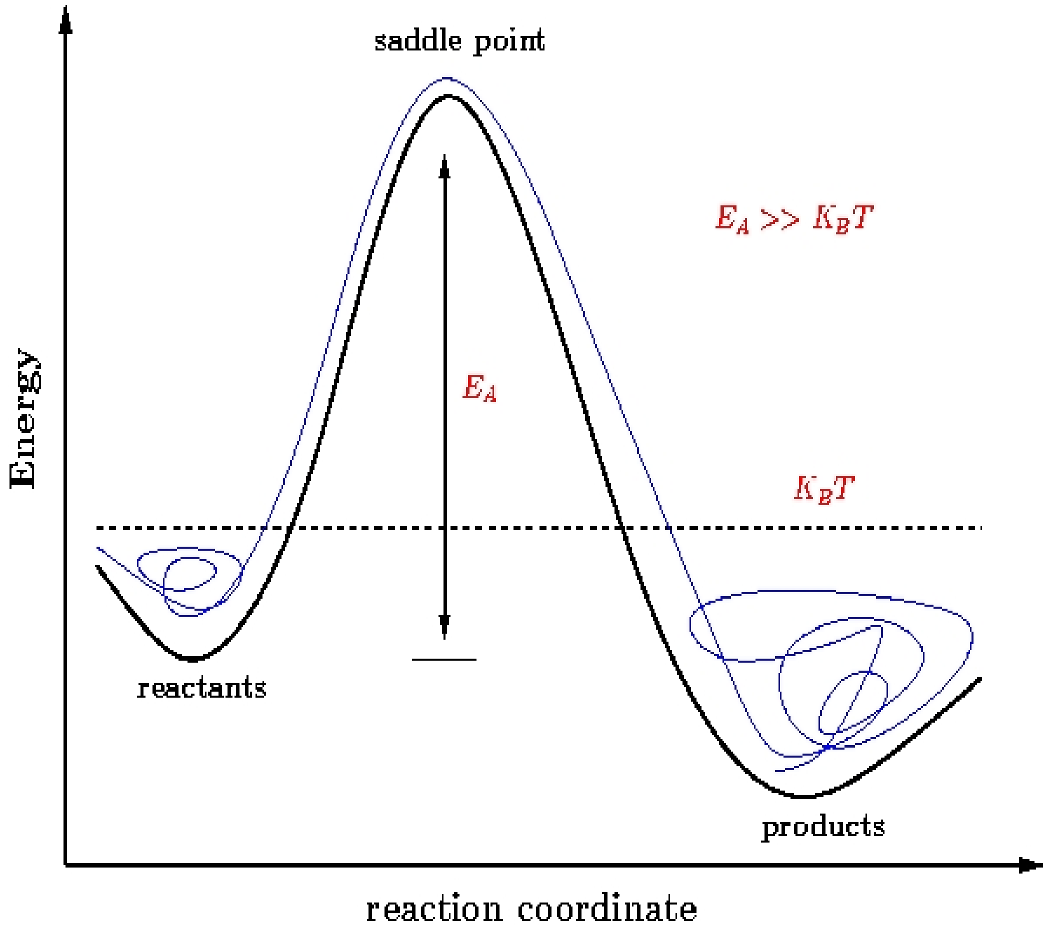

Alternative approach:

The transition rate can be estimated using equilibrium statistical mechanics:

- once the saddle point has been identified we can use harmonic **Transition State Theory** (**hTST**) to compute the rate constant:

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

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

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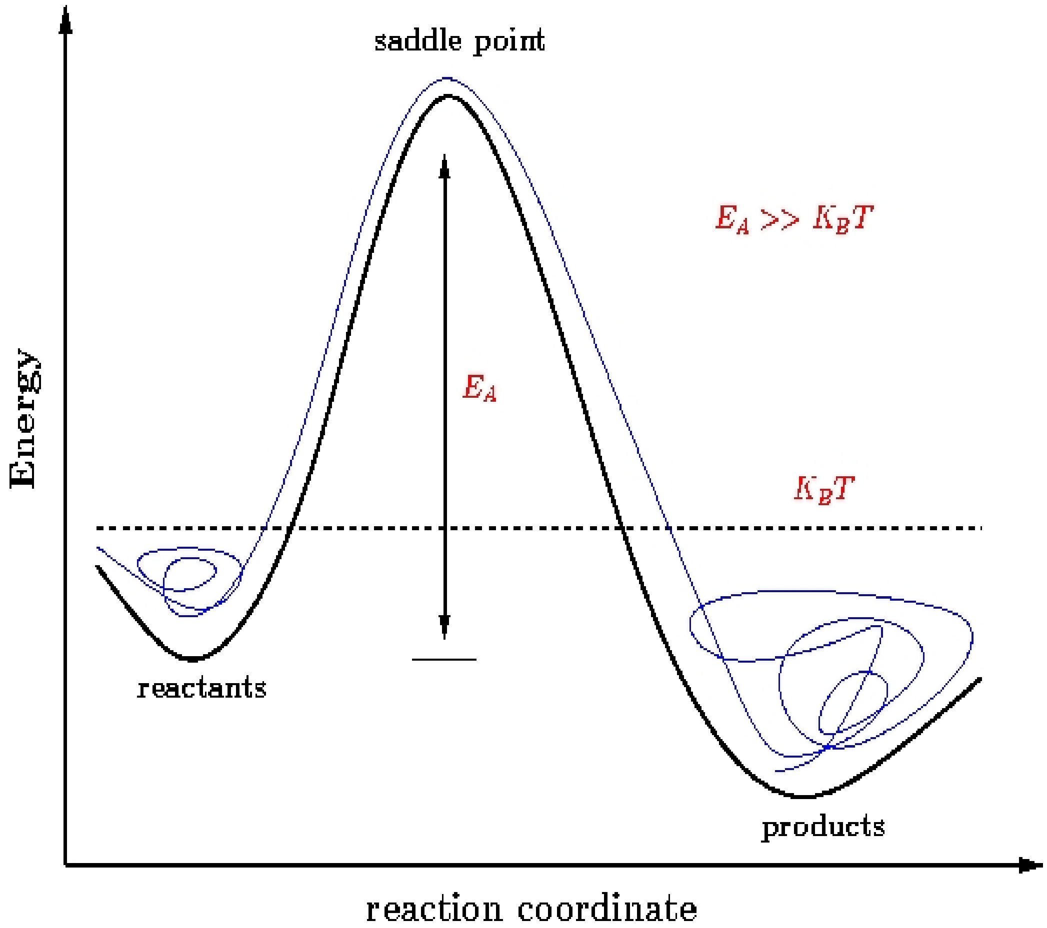
Study of rare events



The goal is locating all the relevant saddle points, but:

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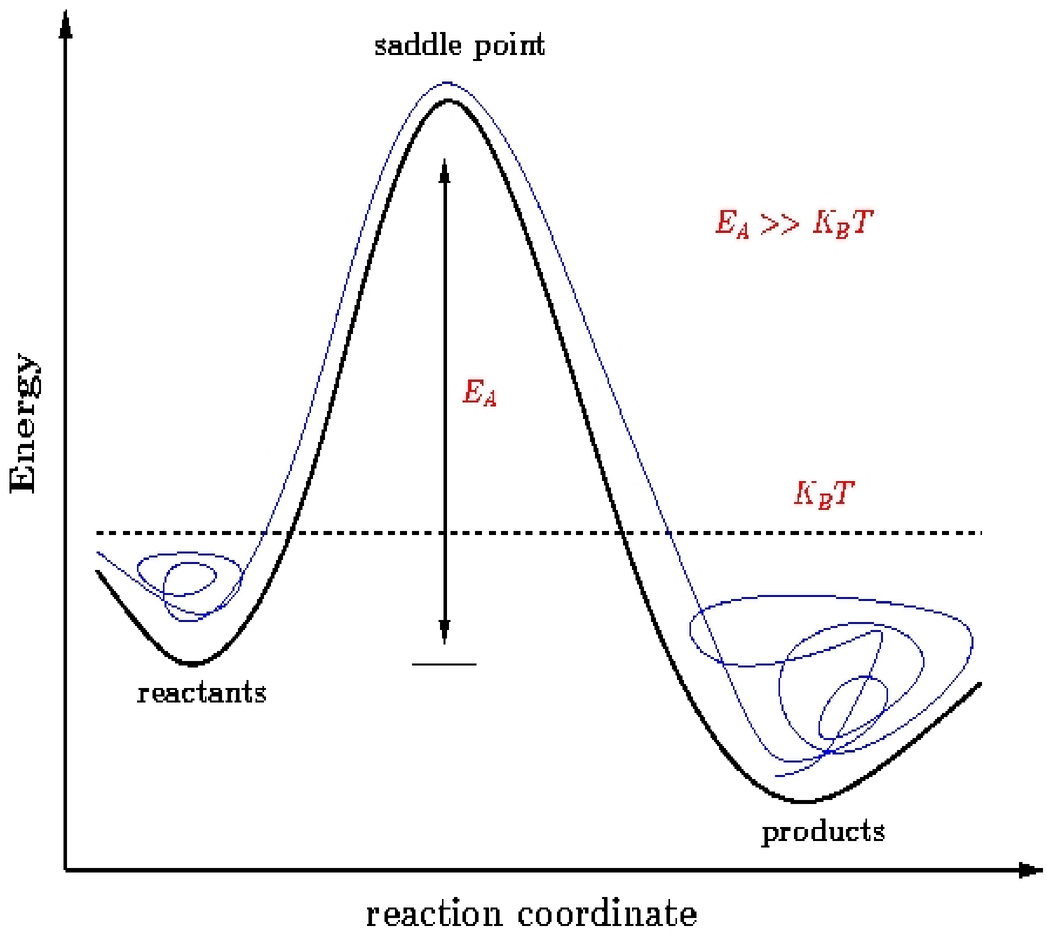
Study of rare events



The goal is locating all the relevant saddle points, but:

saddle points are unstable

their direct location is a rather difficult task

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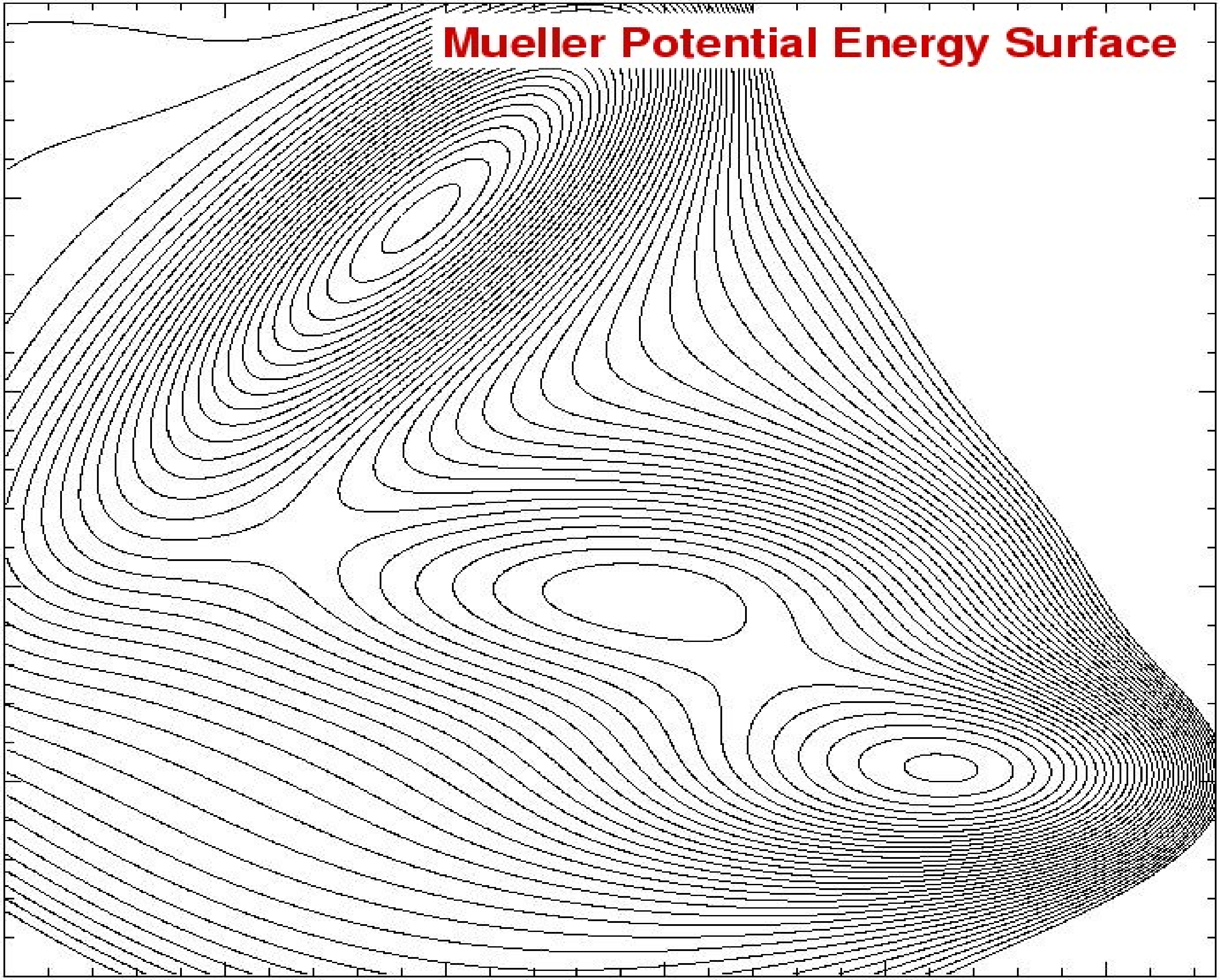
Saddle points in multidimensional systems: the Mueller PES



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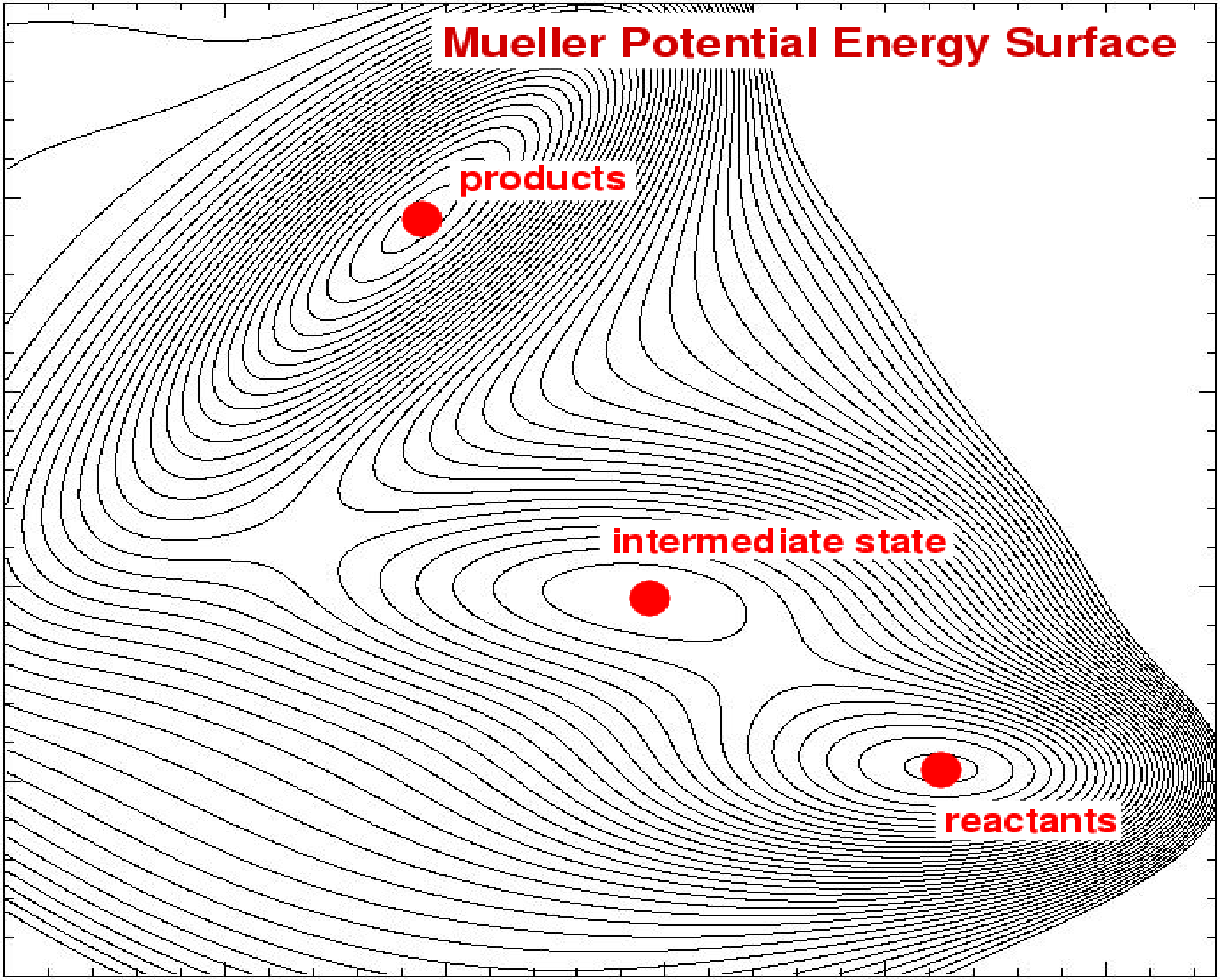

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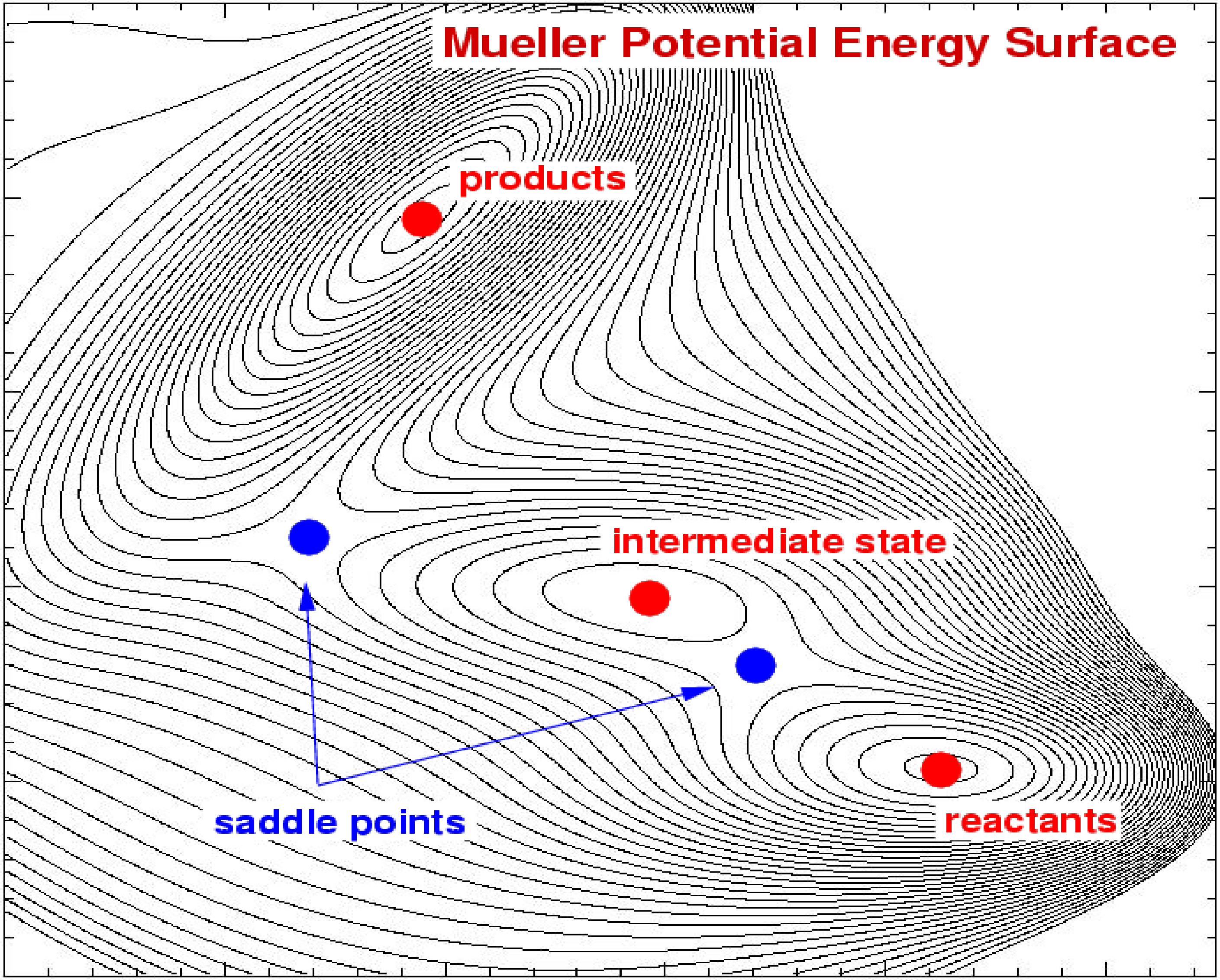

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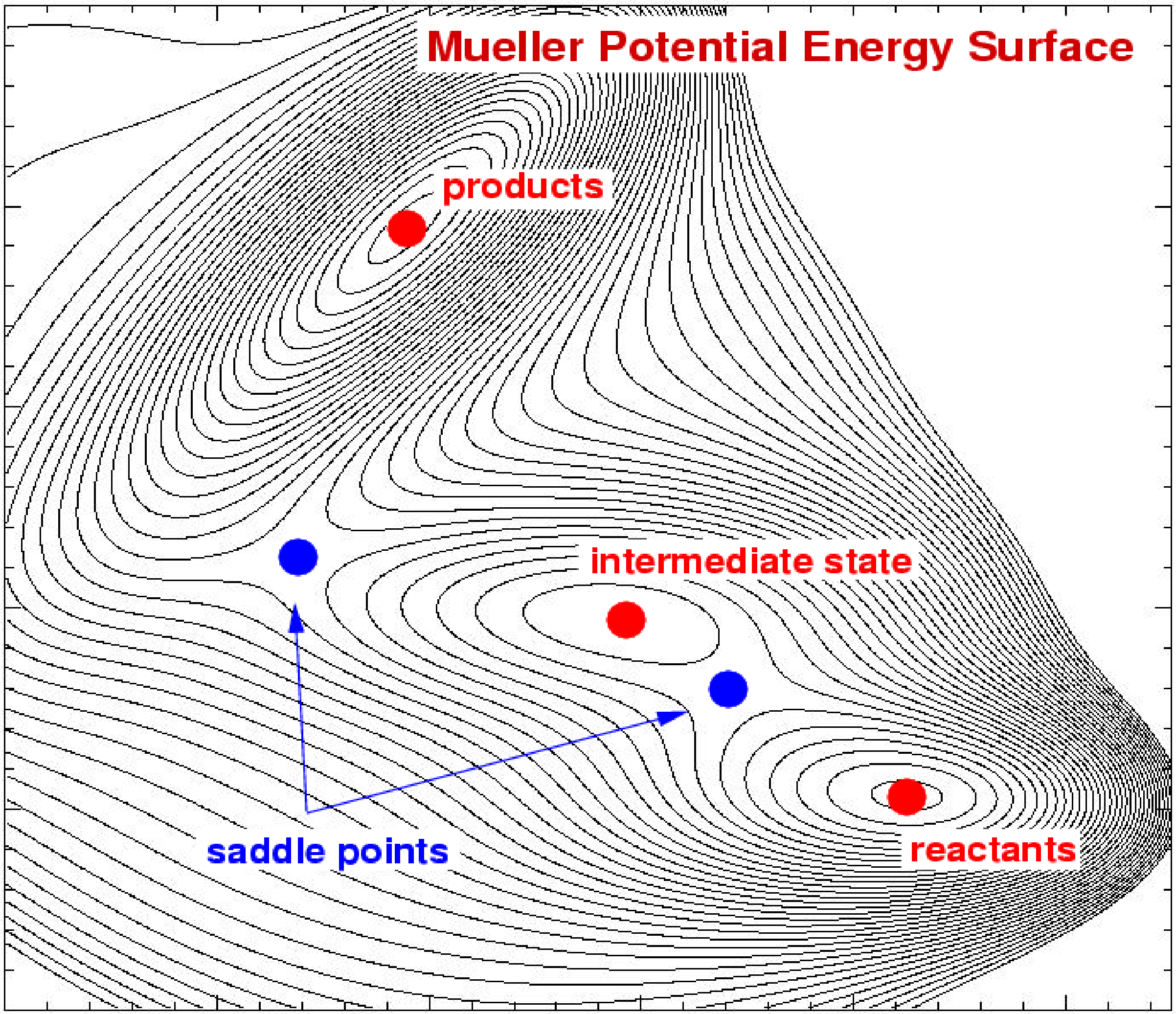

The path characterized by the "highest" transition probability, at zero temperature, is the Minimum Energy Path.

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

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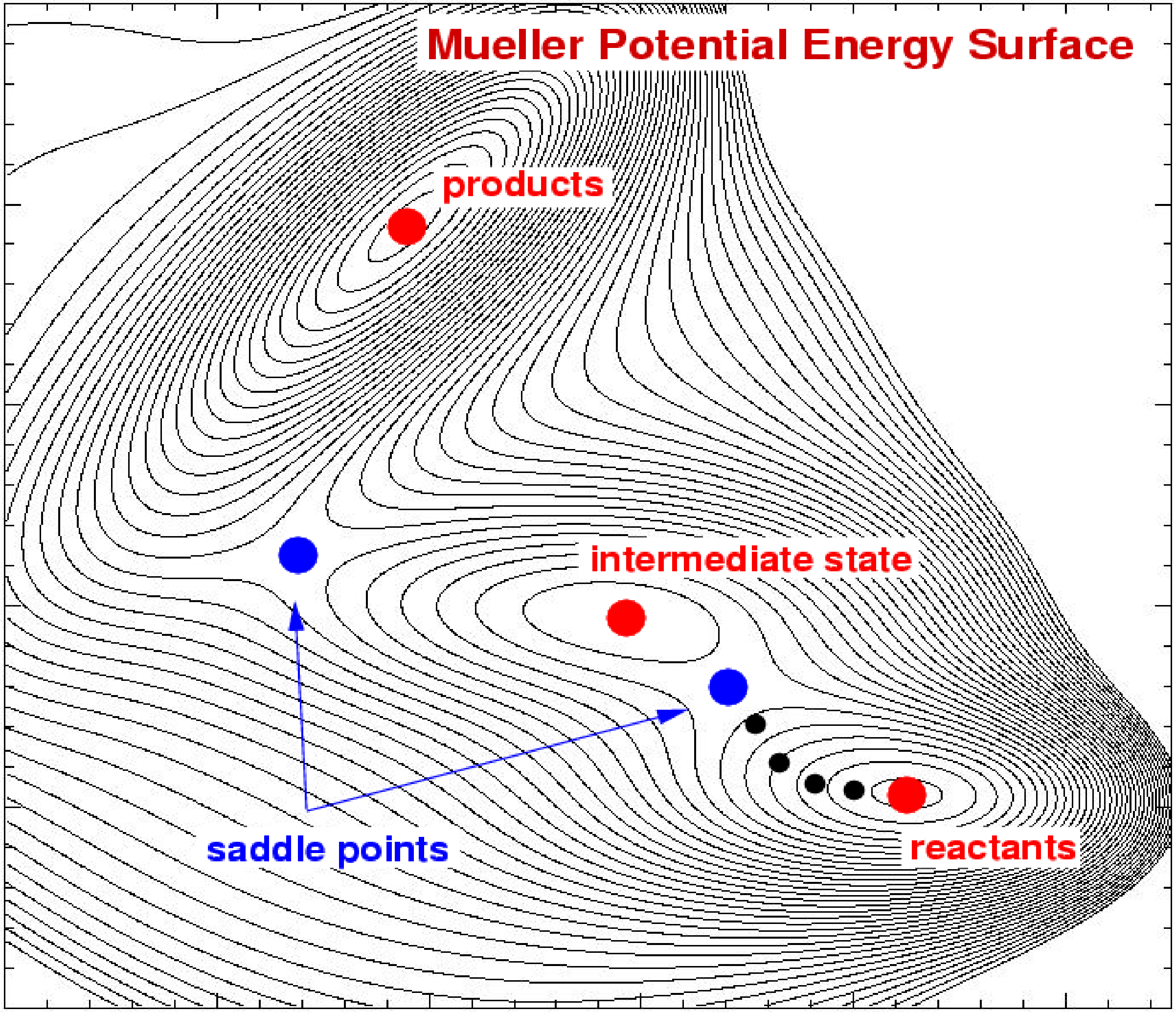

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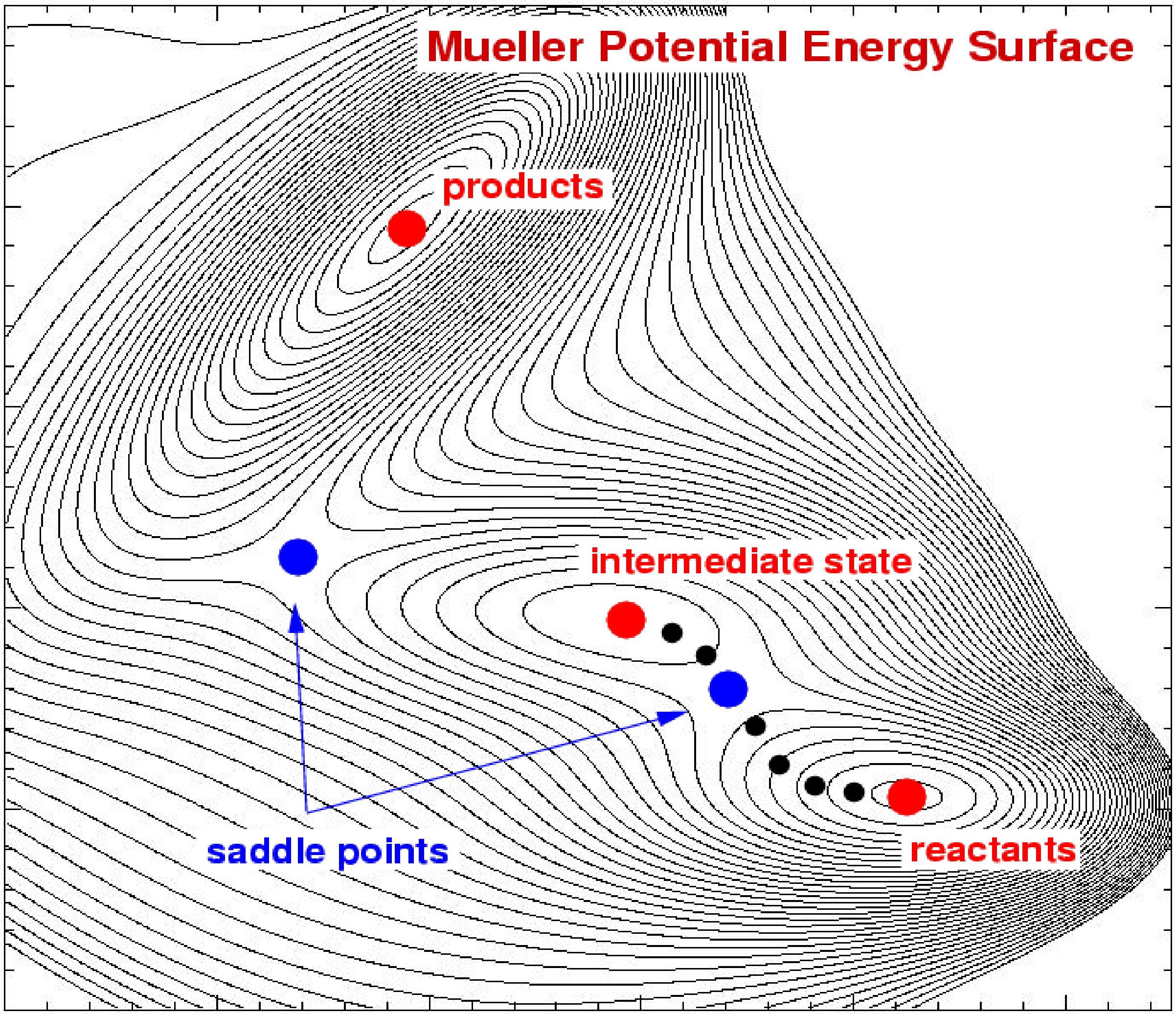

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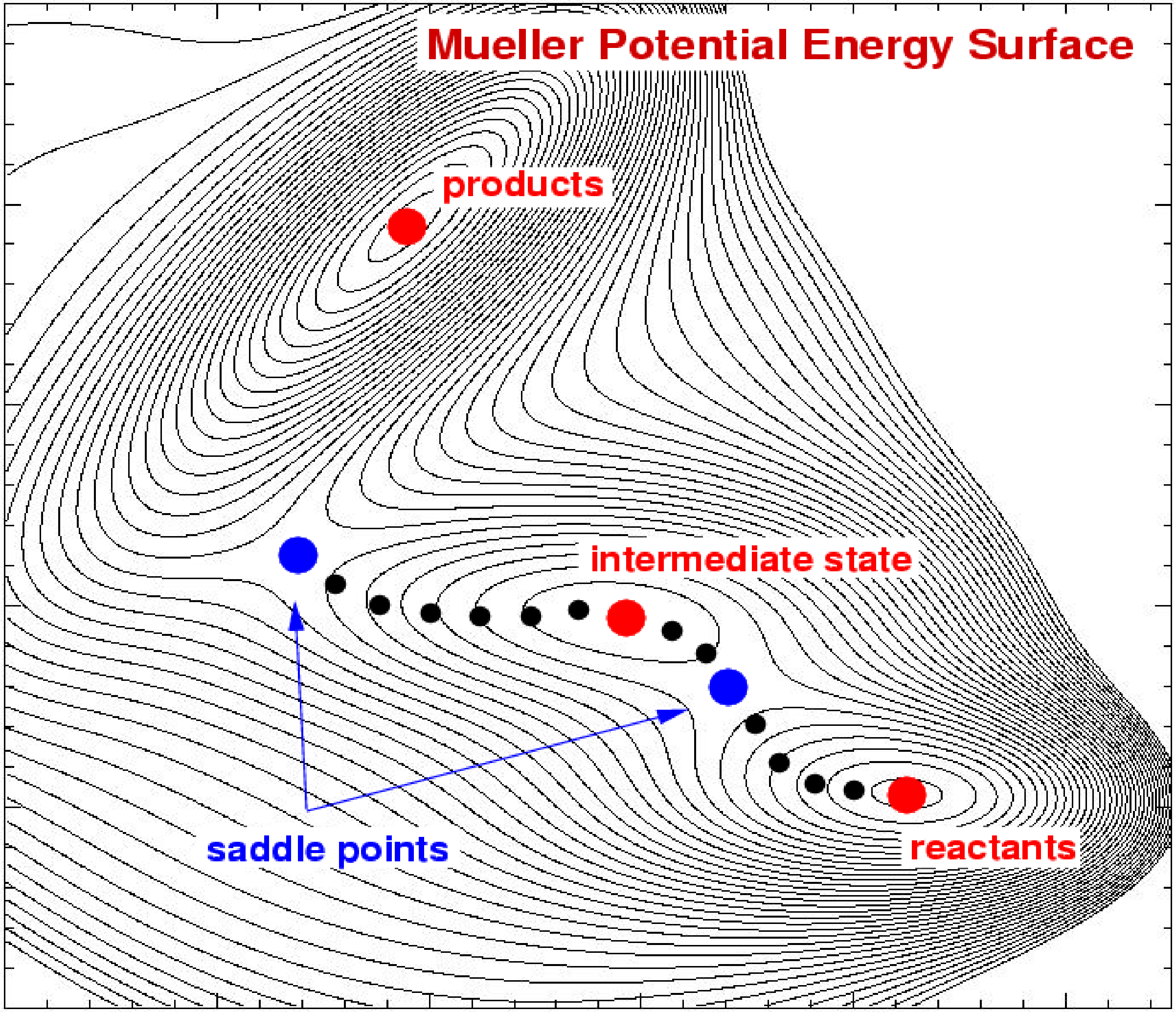

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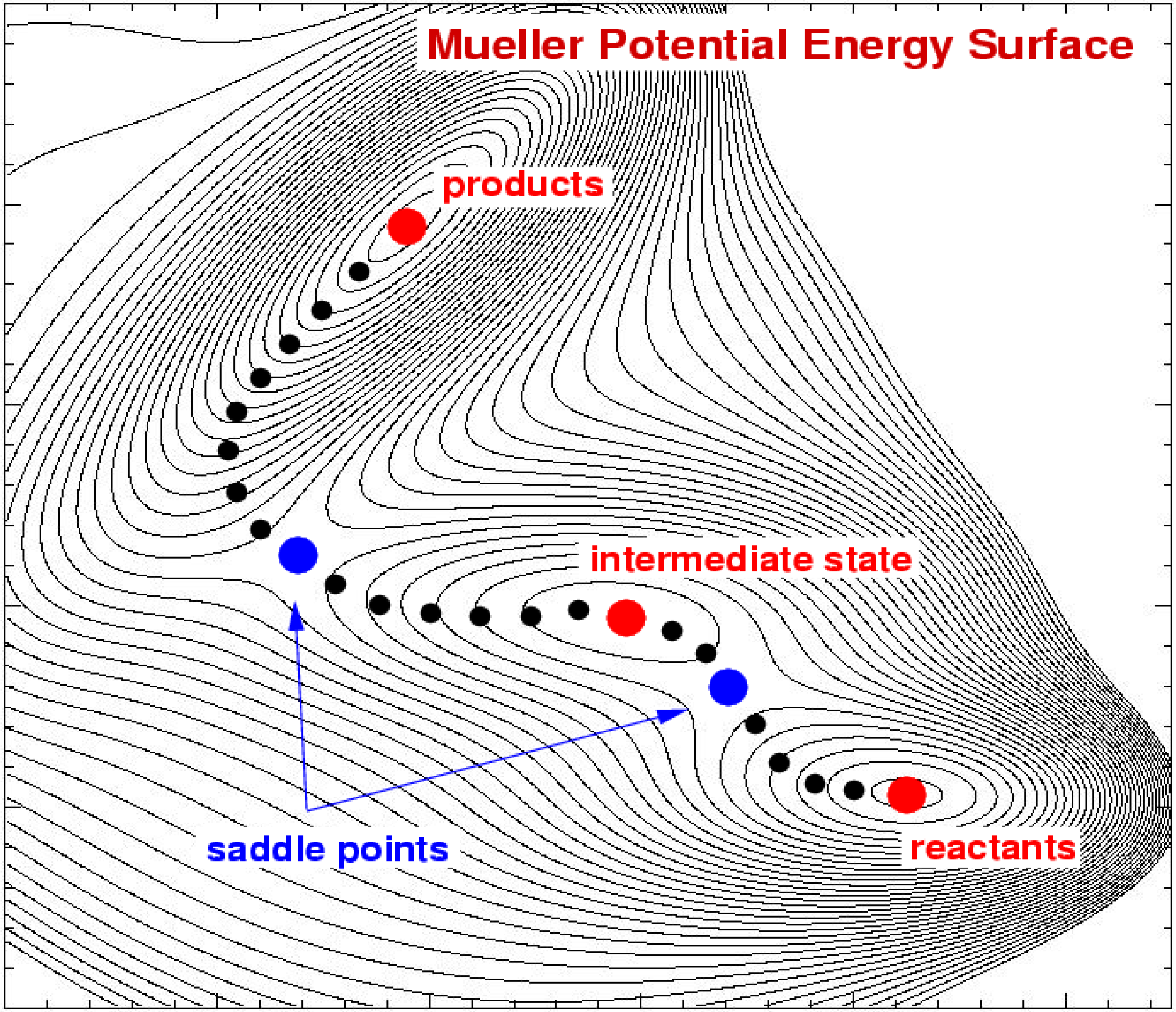

The path characterized by the "highest" transition probability, at zero temperature, is the Minimum Energy Path.

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

The MEP crosses the saddle points.

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How to locate the MEP

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

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

$$x(s) \longrightarrow x_i$$

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

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2) Orthogonal forces :

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

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4) path dynamics
(steepest-descent) :

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

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How to locate the MEP

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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 :

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

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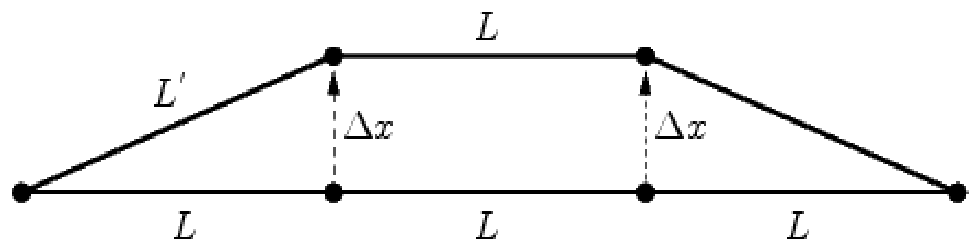
Sliding down

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



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

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

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Sliding down

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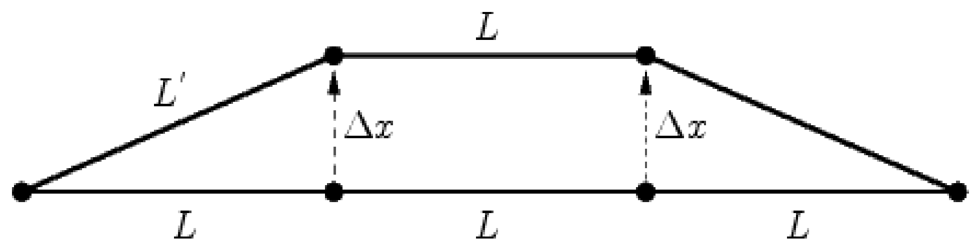
The path dynamics does not preserve the inter-image distance (path's parametrisation):

Consequences:

1) Many images are required to represent the path.



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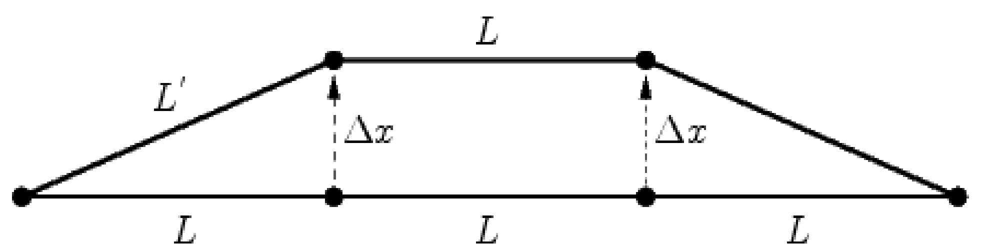
Sliding down

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

Consequences:

1) Many images are required to represent the path.

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



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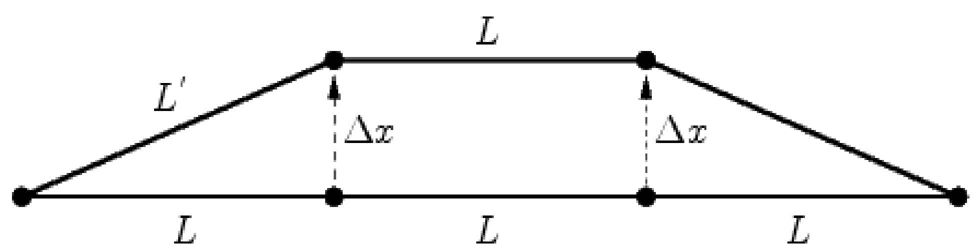

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Consequences:

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.

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

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Nudged Elastic Band method

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- Subsequent images of the chain are connected by springs (to enforce continuity).

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Nudged Elastic Band method

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- Subsequent images of the chain are connected by springs (to enforce continuity).

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

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Nudged Elastic Band method

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- Subsequent images of the chain are connected by springs (to enforce continuity).

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

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

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

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- Subsequent images of the chain are connected by springs (to enforce continuity).

- 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.

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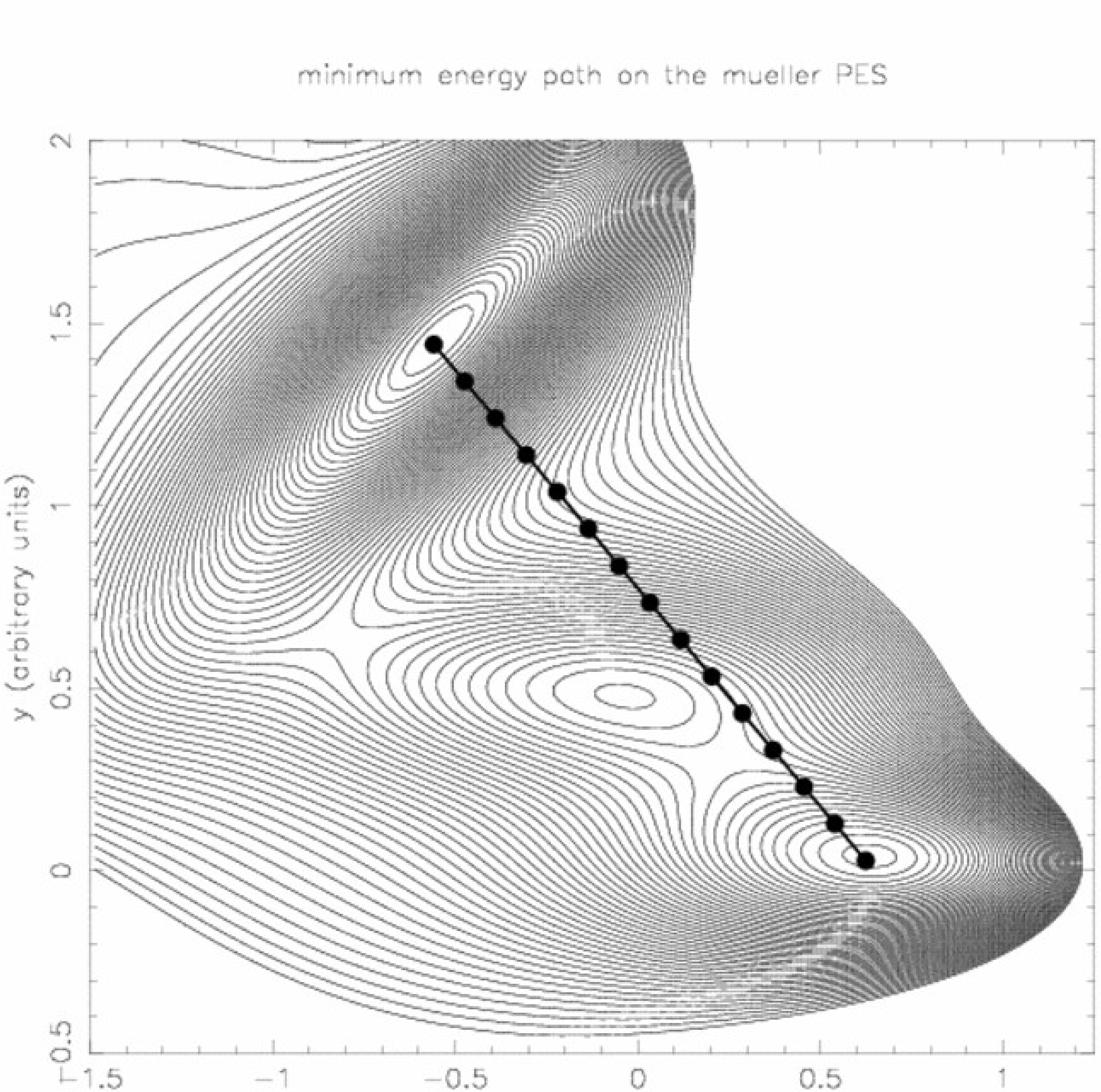
NEB on the Mueller PES



Initial guess: linear interpolation between the two end points.

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

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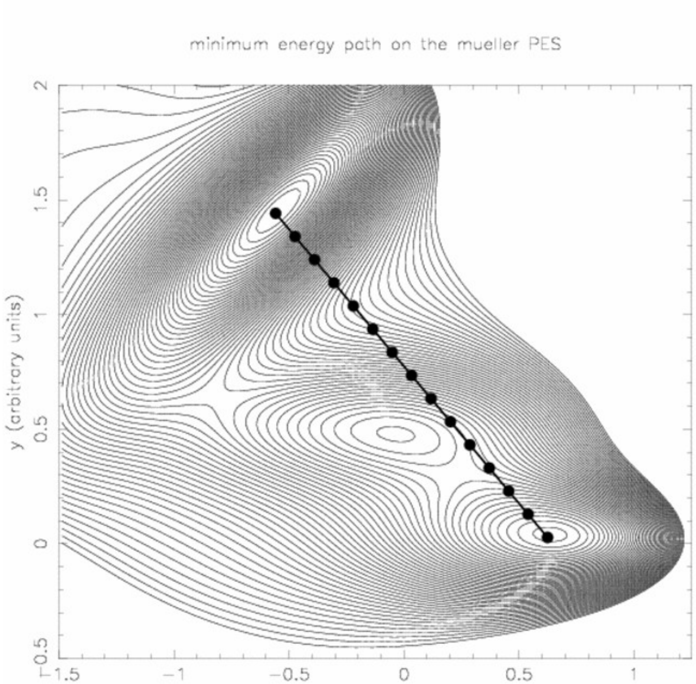
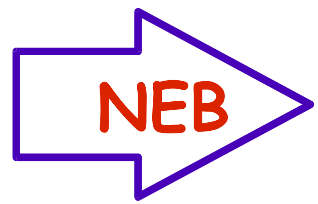
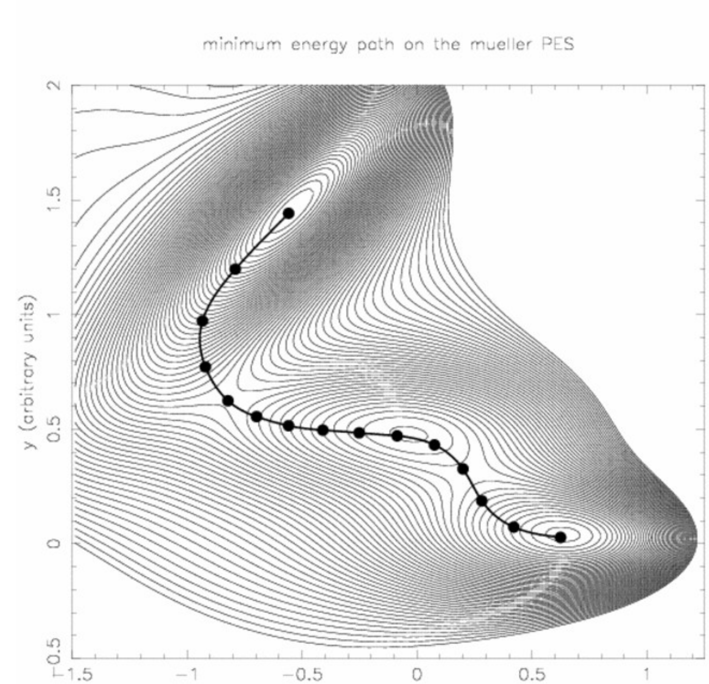
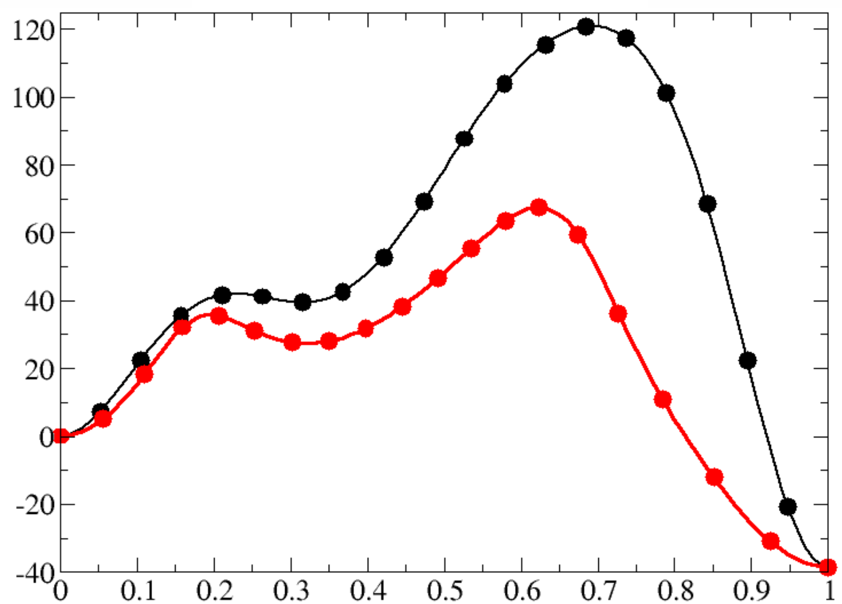
NEB on the Mueller PES









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Improvements

1) Higher resolution around the saddle point: variable elastic constants.

2) Accurate identification of saddle point: climbing image.

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Variable elastic constants

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- The user specifies the minimum (k_min) and the maximum (k_max) values of the elastic constants.

- Spring constants can be chosen so that springs are stiffer where the potential energy is higher (k_max > k_min): higher resolution around saddle points.

- The value of the elastic constant for each image x_i is obtained by interpolating between k_min and k_max:

$$k_i = \frac{1}{2}\left(k_{max} + k_{min} - (k_{max} - k_{min}) \cos\left(\pi \frac{(V(x_i) - V_{min})}{(V_{max} - V_{min})}\right)\right)$$

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Climbing image

A given image (x_i) can be made *"to climb"* up-hill the PES once the climbing direction is specified.
In the CI scheme the direction is given by the path's tangent.

$$F(x_{i_{max}}) = -\nabla V(x_{i_{max}}) + 2\,\tau_{i_{max}}\left(\tau_{i_{max}} | \nabla V(x_{i_{max}})\right)$$

- The image can be automatically chosen during the optimisation as the one with the highest energy (CI_scheme="auto").
- One or more images can be forced to climb (CI_scheme="manual").
- Climbing Image should be used after some optimisation steps.

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NEB: input variables

A detailed explanation of all the keywords can be found in the file Doc/INPUT_PW.

```
&CONTROL
  calculation = "neb"      <=  mandatory
  ...
  nstep                    <=  optional (0)
  ...
/
...
...
&IONS
  num_of_images            <=  mandatory
  CI_scheme                <=  optional (no-CI)
  opt_scheme               <=  optional (quick-min)
  ds                       <=  optional (1.0)
  first_last_opt           <=  optional (.FALSE.)
  k_max                    <=  optional (0.1)
  k_min                    <=  optional (0.1)
  path_thr                 <=  optional (0.05)
  ...
/
```

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NEB: input variables

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A detailed explanation of all the keywords can be found in the file Doc/INPUT_PW.

```
first_image                                          <=  mandatory
   X 0.0  0.0  0.0  { if_pos(1) if_pos(2) if_pos(3) }
   Y 0.5  0.0  0.0  { if_pos(1) if_pos(2) if_pos(3) }
   Z 0.0  0.2  0.2  { if_pos(1) if_pos(2) if_pos(3) }
intermediate_image 1                                 <=  optional
   X 0.0  0.0  0.0
   Y 0.9  0.0  0.0
   Z 0.0  0.2  0.2
intermediate_image ...                               <=  optional
   X 0.0  0.0  0.0
   Y 0.9  0.0  0.0
   Z 0.0  0.2  0.2
last_image                                           <=  mandatory
   X 0.0  0.0  0.0
   Y 0.7  0.0  0.0
   Z 0.0  0.5  0.2
```

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NEB: output

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Files in the working directory (./):

- `prefix.path` <= file containing data required to restart a NEB calculation
- `prefix.axsf` <= file containing the path in *xcrysden* format
- `prefix.xyz` <= file containing the path in *xyz* format
- `prefix.dat` <= file containing the reaction coordinate, the energy and the error of each image
- `prefix.int` <= file containing a cubic interpolation for the energy profile

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NEB: output

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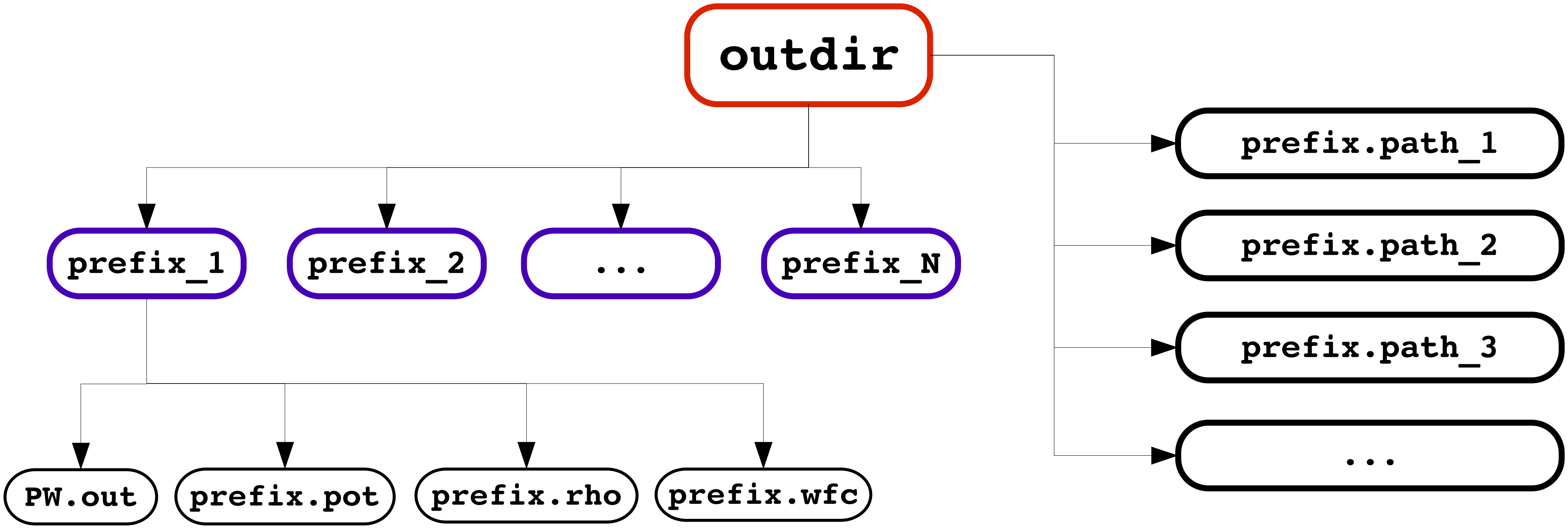

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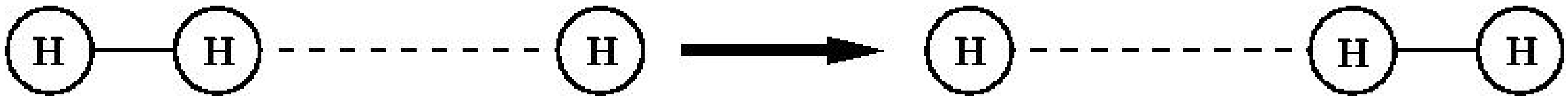
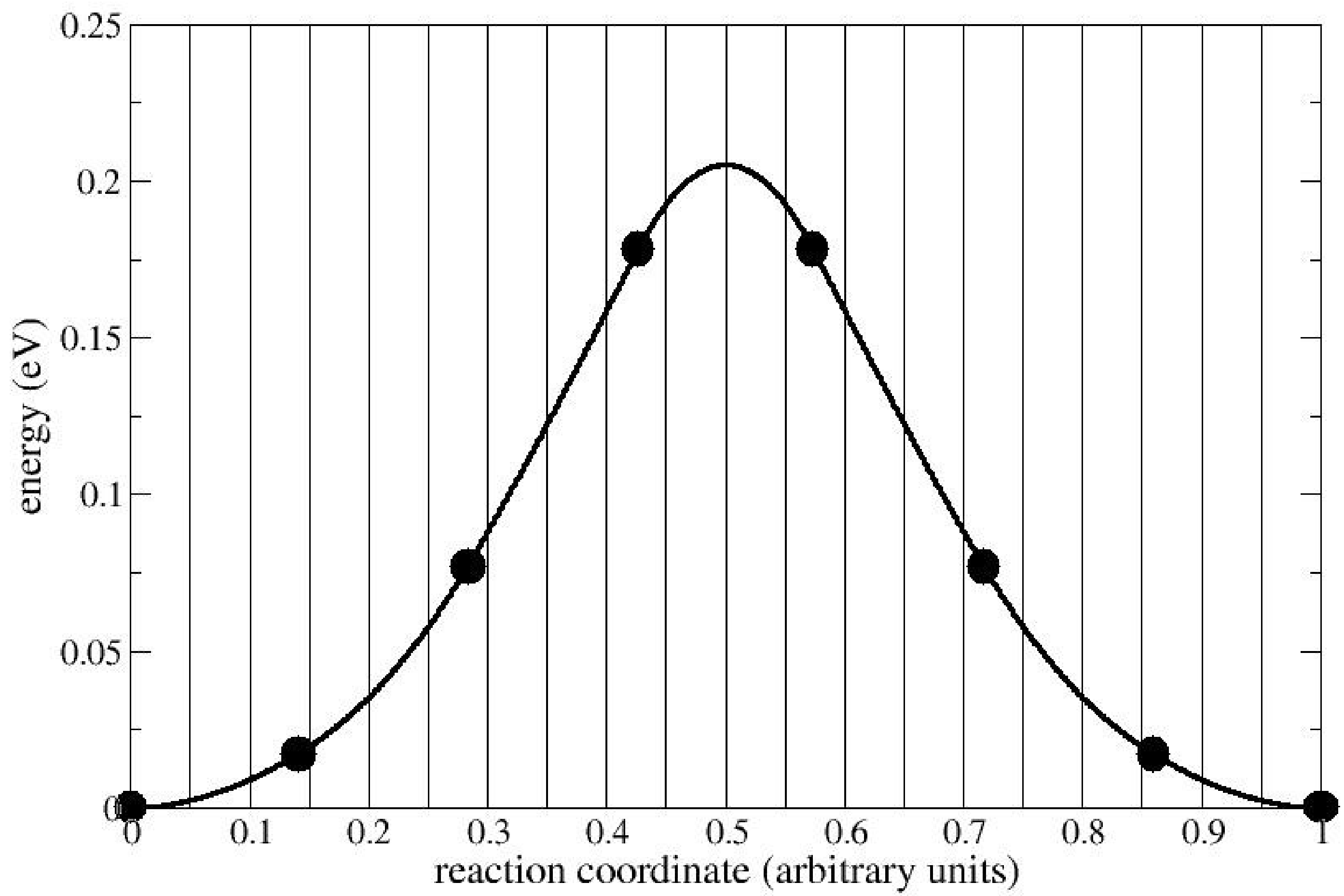
Example17: collinear proton transfer

plain NEB





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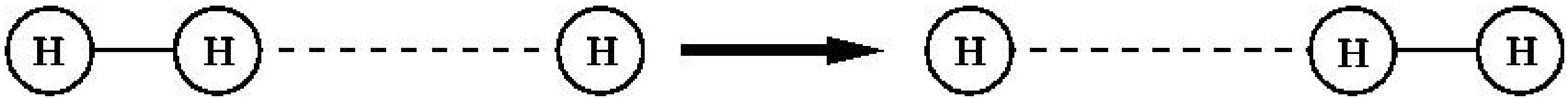
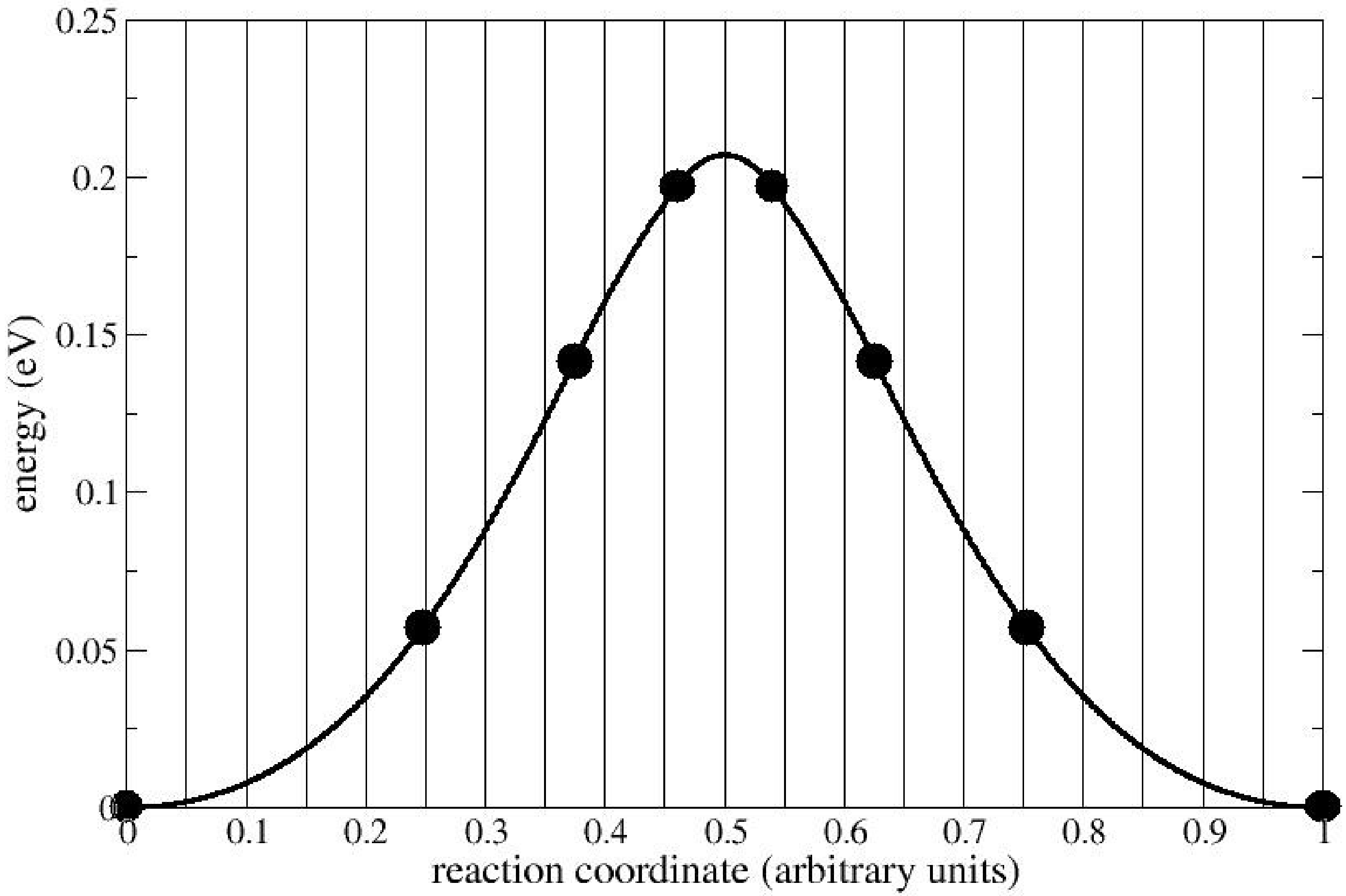
Example17: collinear proton transfer

variable elastic constants





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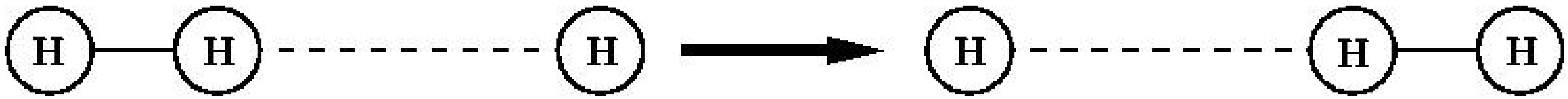
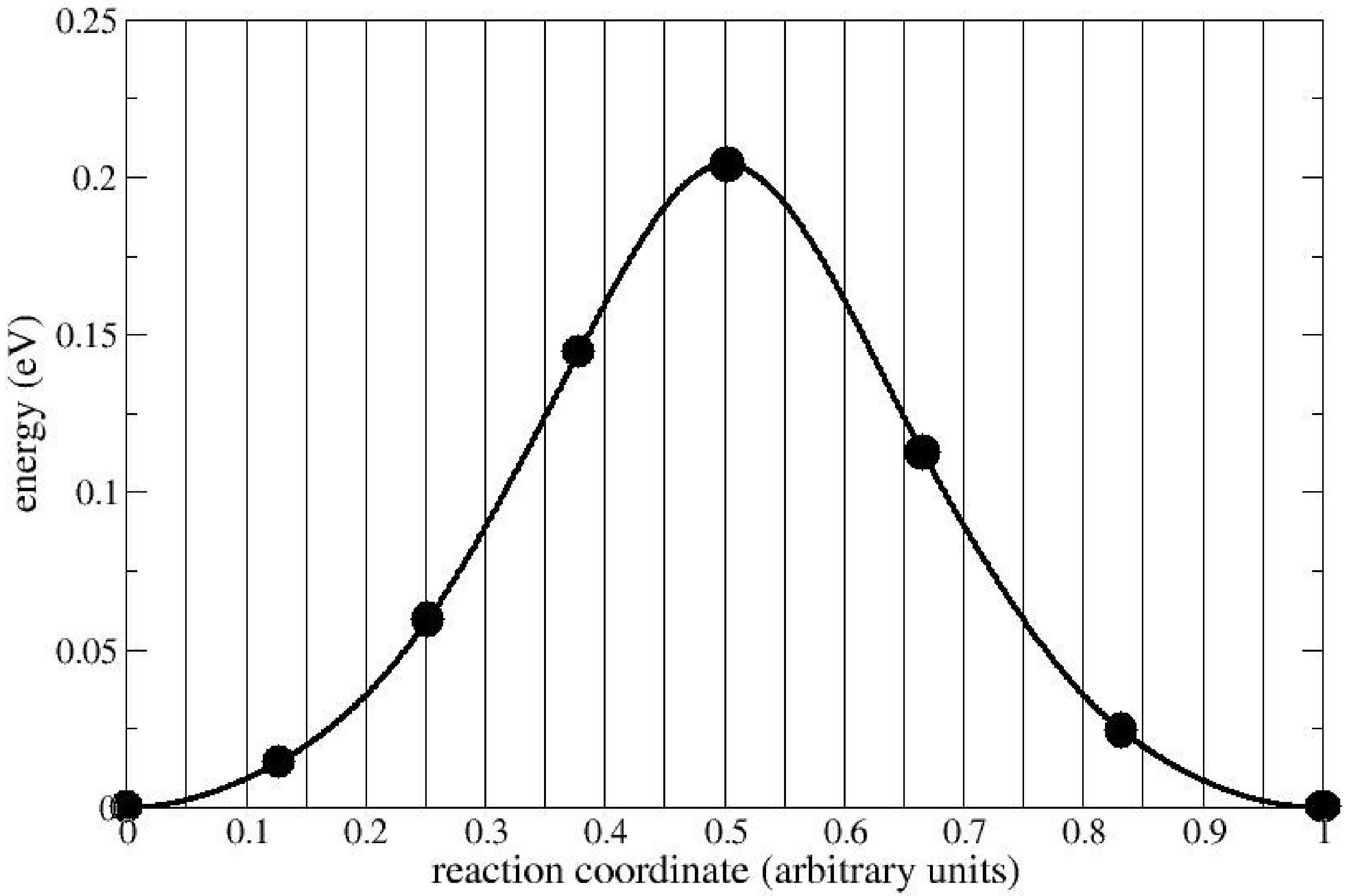
Example17: collinear proton transfer

climbing image (manual on image 5)





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Notes on parallel execution

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PWscf has two levels of parallelisation plus one specific for NEB:

1) R&G : wave-functions are distributed among the CPUs so that each CPU works on a subset of plane-waves. The same is done on real-space grid-points. By <u>default</u> all the CPUs are used for this <u>parallelisation</u> <u>scheme</u>. Example with 8 CPUs:

```
prompt> mpirun -np 8 pw.x -in input_file > output_file
```

2) k-points : k-points (when present) are distributed among pools of CPUs. Each pool can contain one or more CPUs. In this latter case *R&G* parallelisation is used within the pool. This scheme is selected by specifying in the command line the required number of k-points pools. Example with 8 CPUs and 2 k-points pools:

```
prompt> mpirun -np 8 pw.x -npool 2 -in input_file > output_file
```

3) NEB-images : NEB images are distributed among pools of CPUs. Within each image *R&G* and *k-points* parallelisation schemes can also be used. This scheme is selected by specifying in the command line the required number of images pools. Example with 8 CPUs, 2 k-points pools and 2 images pools:

```
prompt> mpirun -np 8 pw.x -npool 2 -nimage 2 -in input_file > output_file
```

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Notes on parallel execution

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R&G → ***k-points*** → ***NEB-images***

R&G

- High scalability of the memory usage.
- High intra-pool communication.
- Good work-load balance among CPUs.
- **Best choice. Bad scaling when number of plane-waves per CPU is very small.**

k-points

- NO scalability of the memory usage.
- Low inter-pool communication.
- Work-load among pools can result to be unbalanced.
- **Good when npool is a whole divisor of the number of k-points.**

NEB-images

- NO scalability of the memory usage.
- Extremely low inter-pool communication.
- Work-load among pools can result to be unbalanced.
- **Good for paths with several images.**