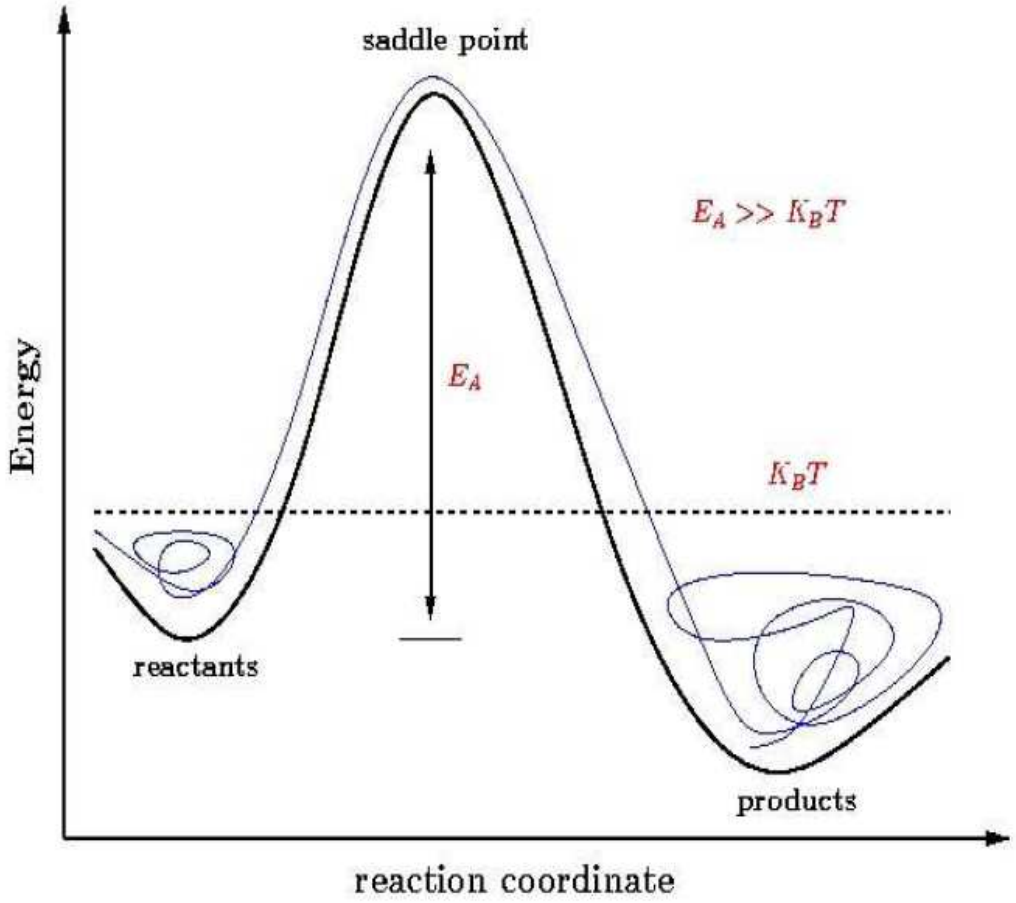
Rare Events and Nudged Elastic Band

Rare Events

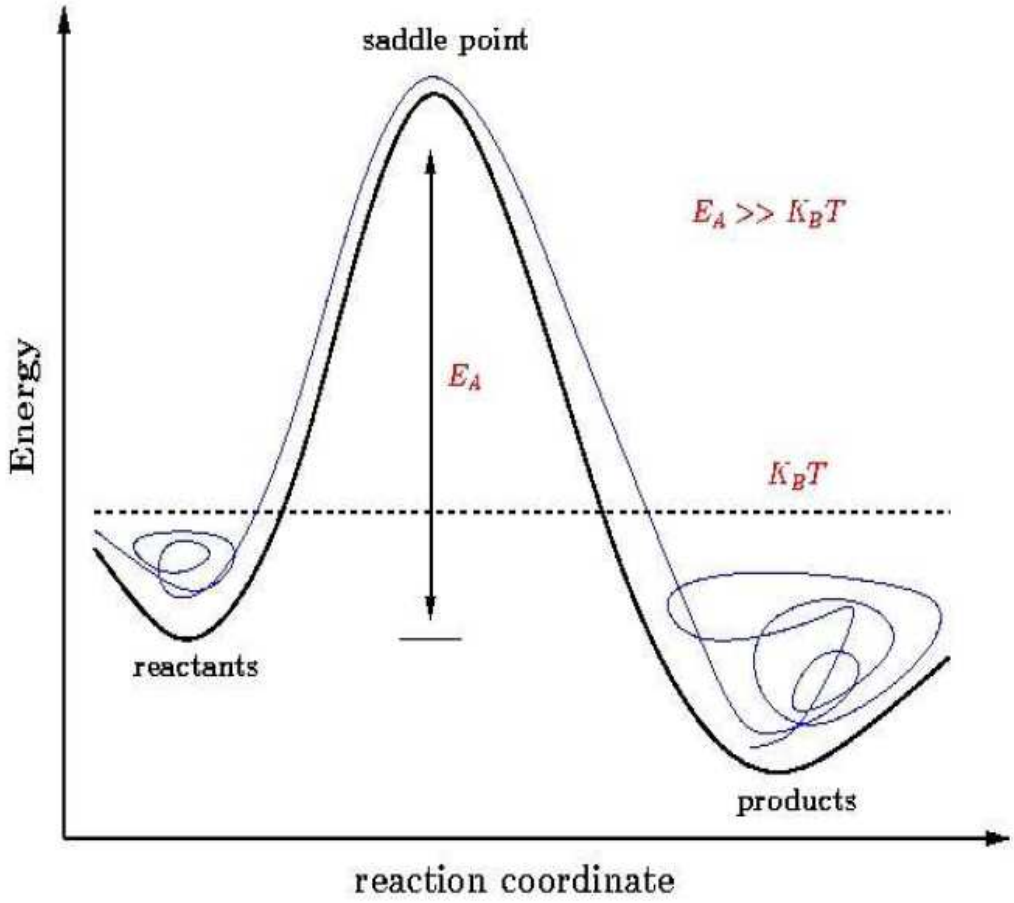


the characteristic time scale of this transition process is

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

Van't-Hoff - Arrhenius (1890)

Rare Events



the characteristic time scale of this transition process is

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

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

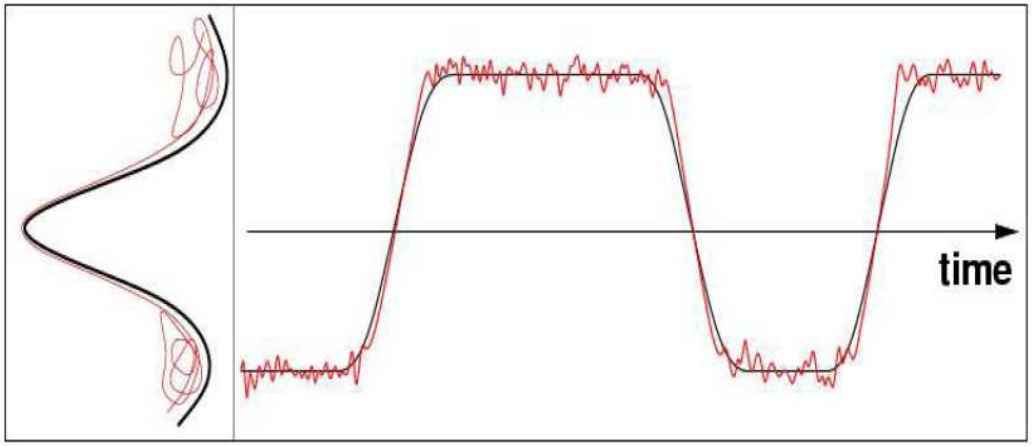
Rare Events

$$t_{jump} = t_{vib} \times e^{\frac{E_A}{K_B T}}$$

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

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.

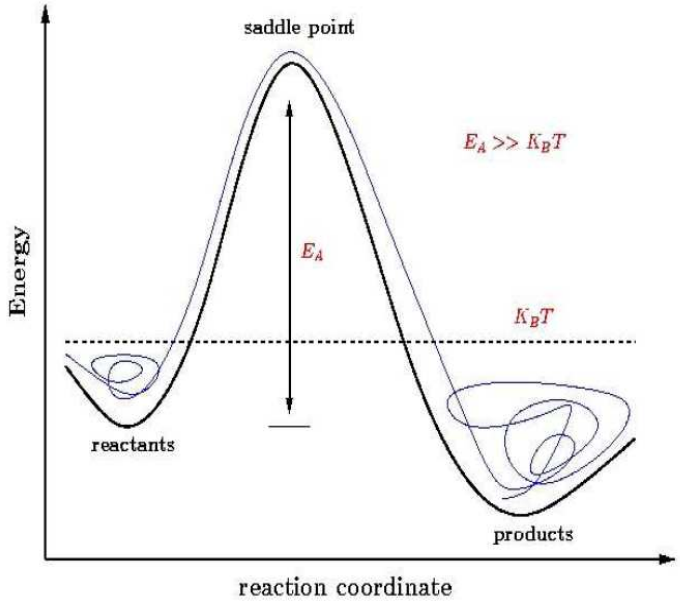
Nevertheless when the appropriate fluctuation occurs the process is extremely fast (a few fempto-seconds)



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.

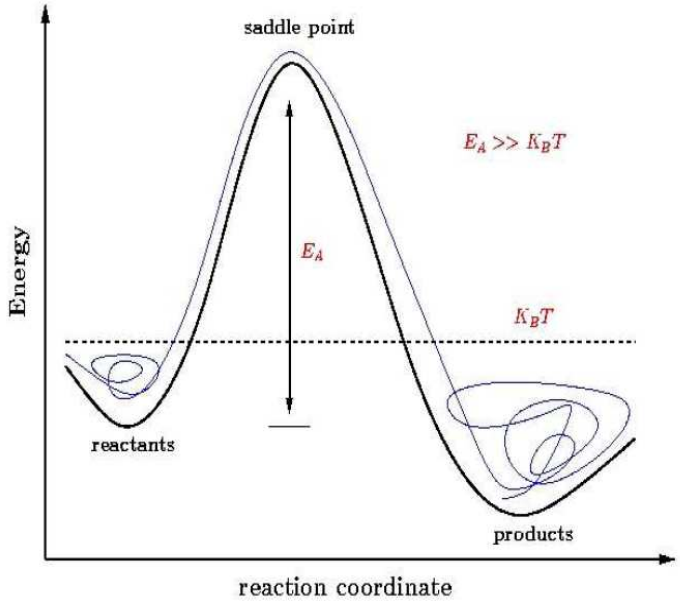
Once the saddle point has been located we can use harmonic Transition State Theory (hTST) to calculate the rate constants:

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

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

Rare Events

an alternative approach



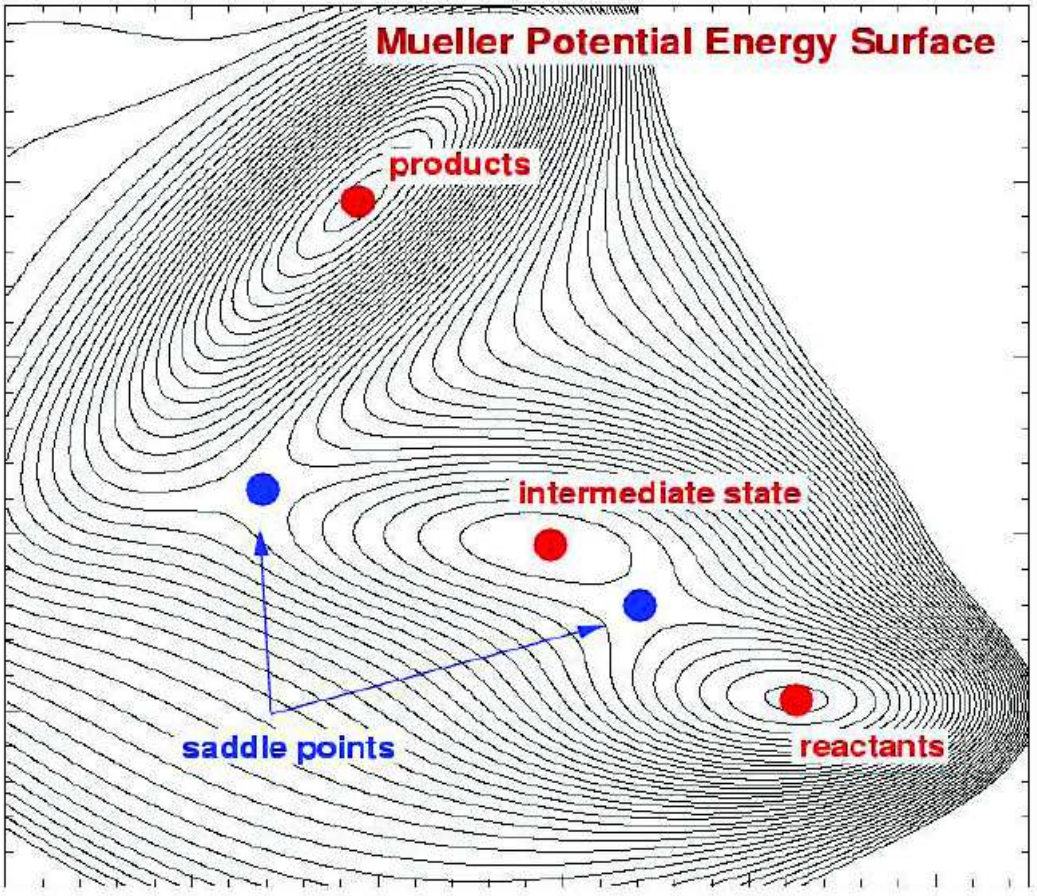
The transition probability can be estimated using equilibrium statistical mechanics.

Once the saddle point has been located we can use harmonic Transition State Theory (hTST) to calculate the rate constants:

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

Saddle points are unstable configurations and their location is a difficult task

Saddle points in multidimensions: the Mueller Potential

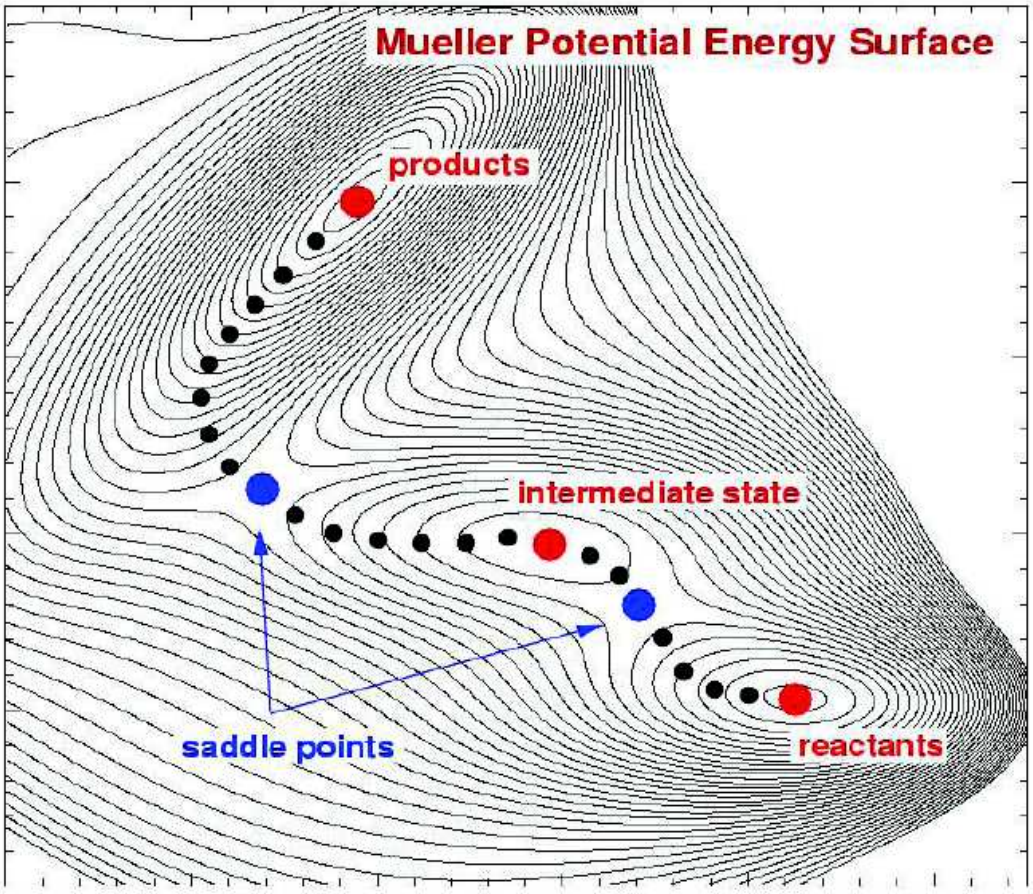


The path with the "highest" transition probability is the Minimum Energy Path.

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

$$-\left(\nabla V(x(s)) - \tau(s)\langle\tau(s)|\nabla V(x(s))\rangle\right) = 0$$

Saddle points in multidimensions: the Mueller Potential



The path with the "highest" transition probability is the Minimum Energy Path.

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

The MEP goes through the saddle point

Nudged Elastic Band method

Path discretization

$$\begin{aligned} s_i &\longrightarrow i * \delta s \\ x(s_i) &\longrightarrow x_i \\ \tau(s_i) &\longrightarrow \tau_i = \frac{x_{i+1} - x_i}{|x_{i+1} - x_i|} \end{aligned}$$

Orthogonal Forces

$$F(x_i) = -\left(\nabla V(x_i) - \tau_i \langle \tau_i | \nabla V(x_i) \rangle\right)$$

MEP condition

$$F(x_i) = 0$$

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

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

Nudged Elastic Band method

Path discretization

$$\begin{aligned} s_i &\longrightarrow i * \delta s \\ x(s_i) &\longrightarrow x_i \\ \tau(s_i) &\longrightarrow \tau_i = \frac{x_{i+1} - x_i}{|x_{i+1} - x_i|} \end{aligned}$$

Orthogonal Forces

$$F(x_i) = -\left(\nabla V(x_i) - \tau_i \langle \tau_i | \nabla V(x_i) \rangle\right)$$

MEP condition

$$F(x_i) = 0$$

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

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

However the images tend to "slide down" toward the end points...
Let us connect subsequent images by springs that only operate along the path

Nudged Elastic Band method

Path discretization

$$\begin{aligned} s_i &\longrightarrow i * \delta s \\ x(s_i) &\longrightarrow x_i \\ \tau(s_i) &\longrightarrow \tau_i = \frac{x_{i+1} - x_i}{|x_{i+1} - x_i|} \end{aligned}$$

Orthogonal + Spring Forces

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

MEP condition

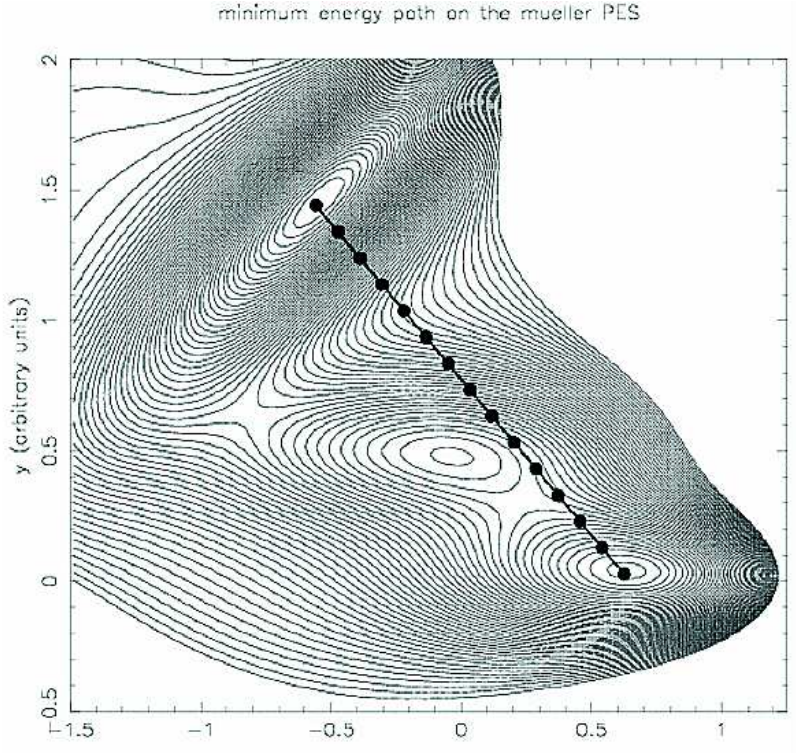
$$F(x_i) = 0$$

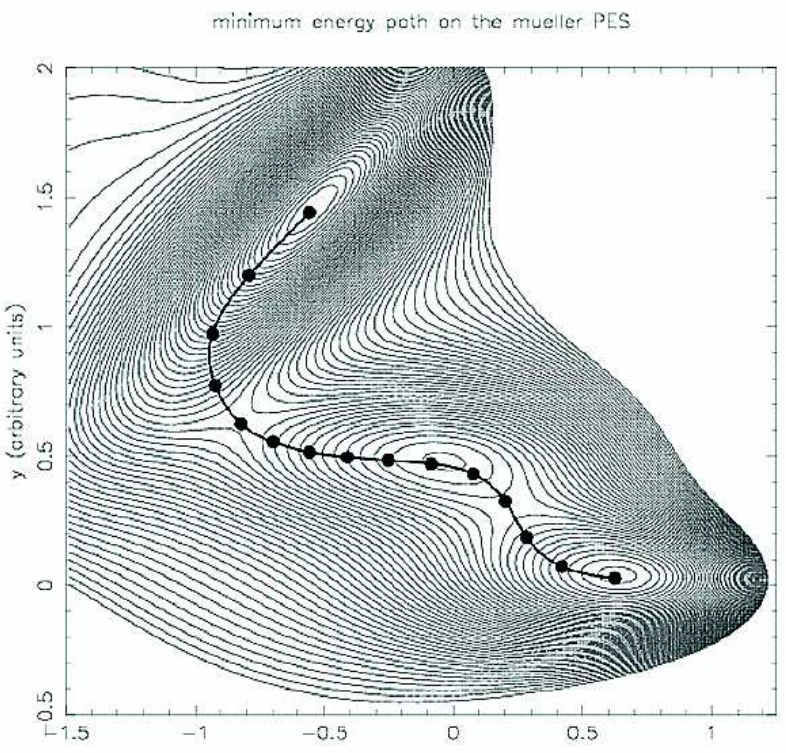
Path dynamics (steepest descent, quick-min, broyden)

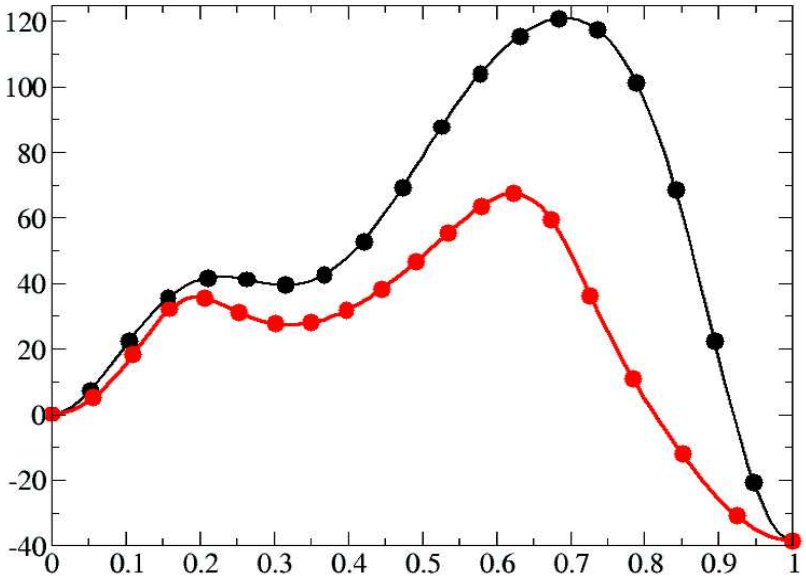
$$x_i^{k+1} = x_i^k + J^{-1} F(x_i)$$

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

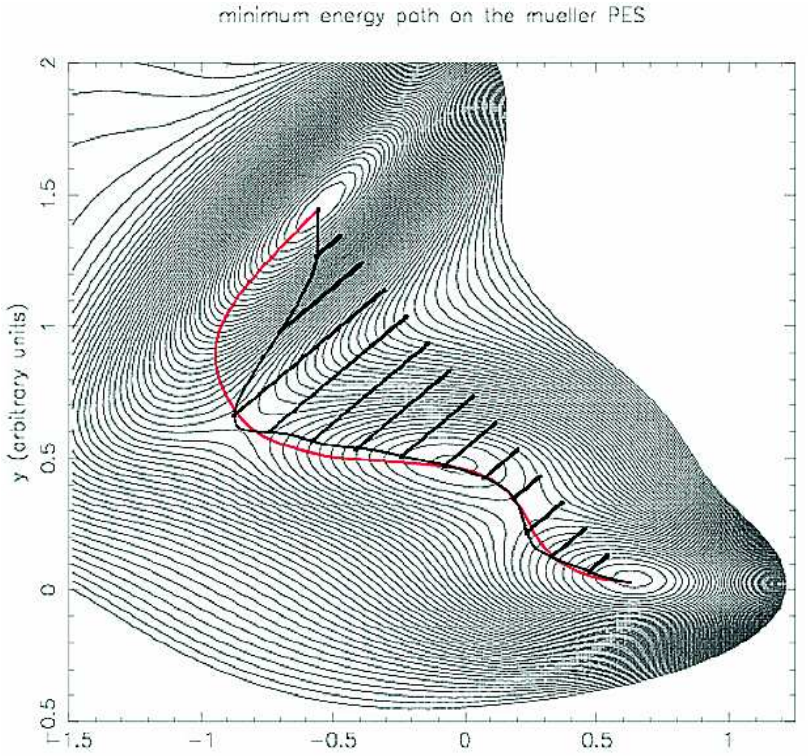
NEB on the Mueller PES

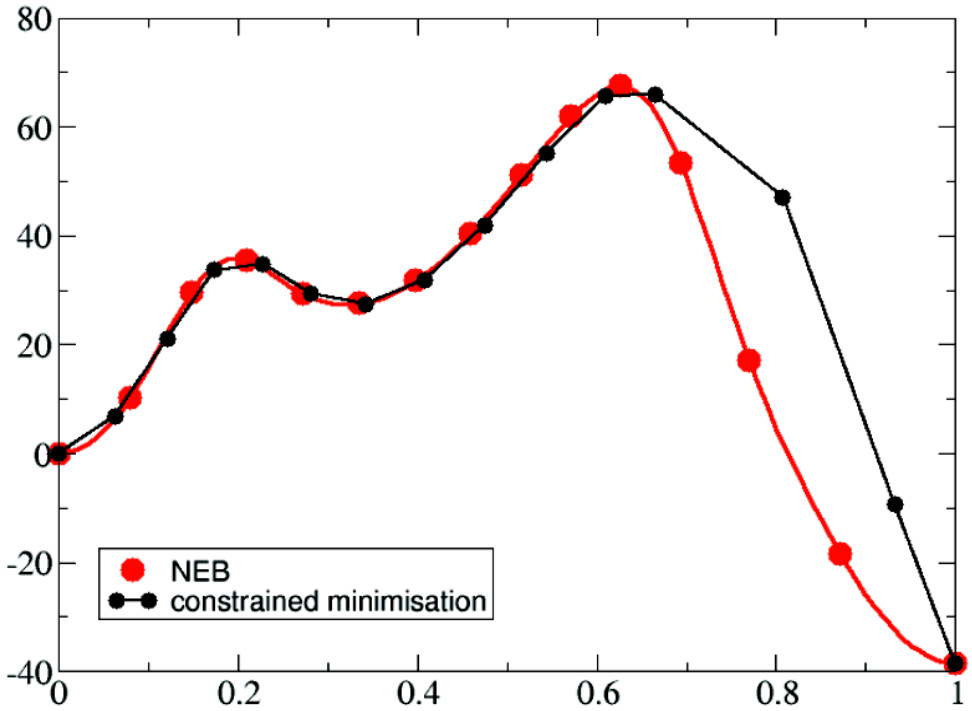






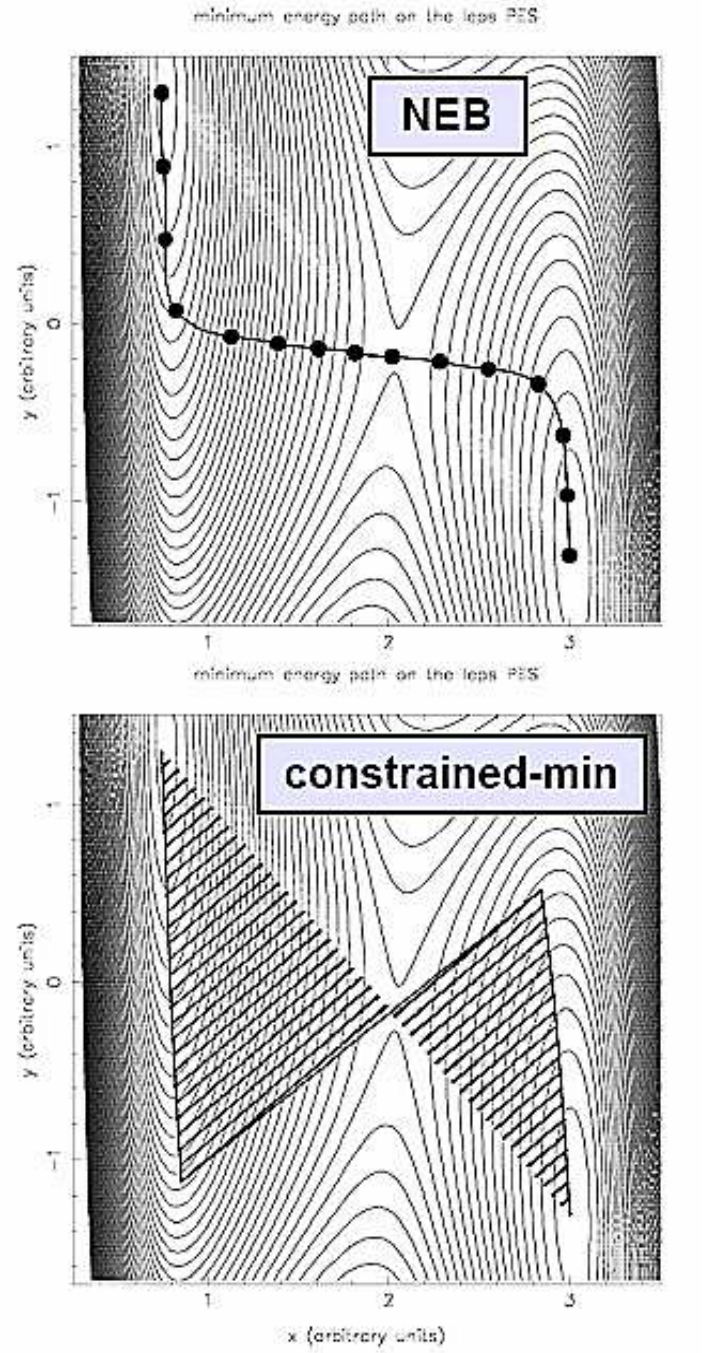
NEB vs constrained minimizations

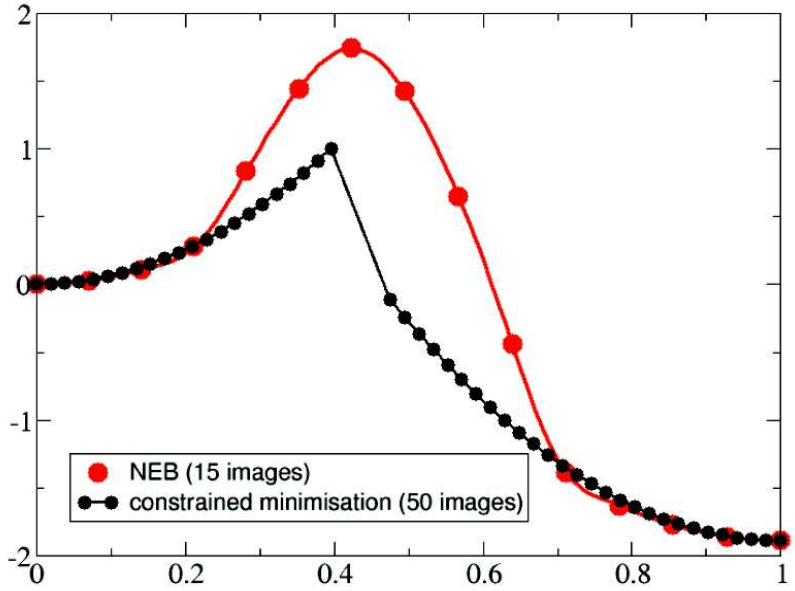




Constrained minimization does a good job in this case.

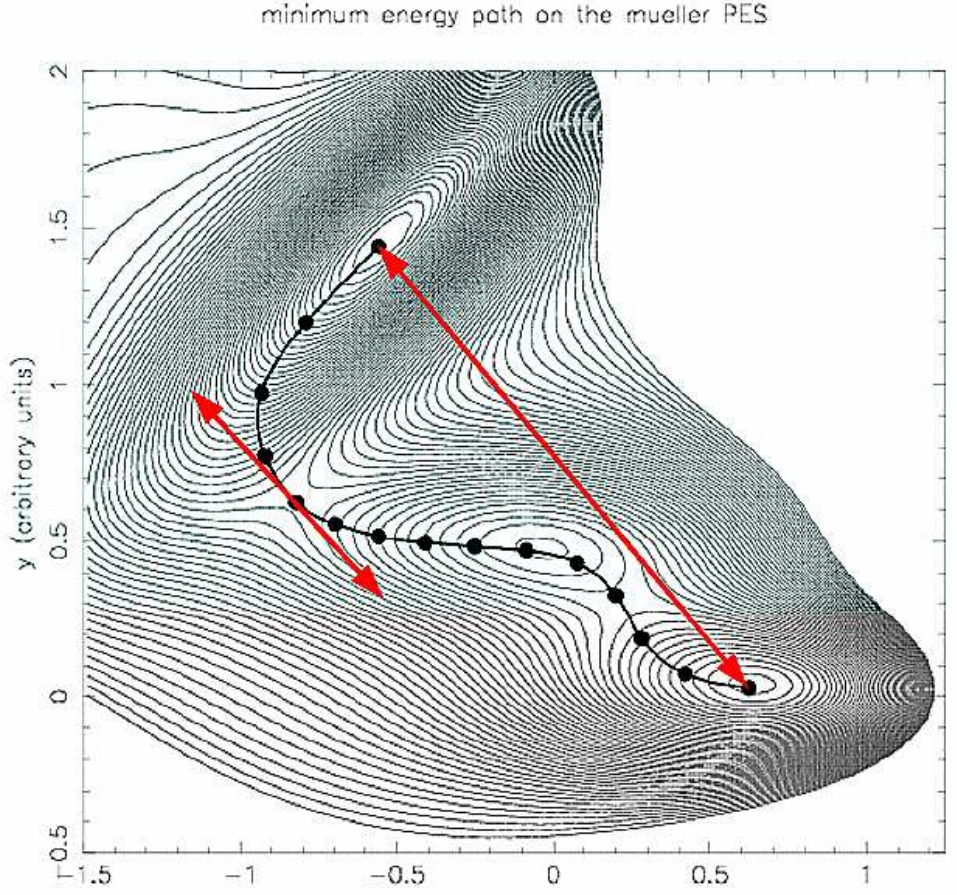
NEB vs constrained minimizations

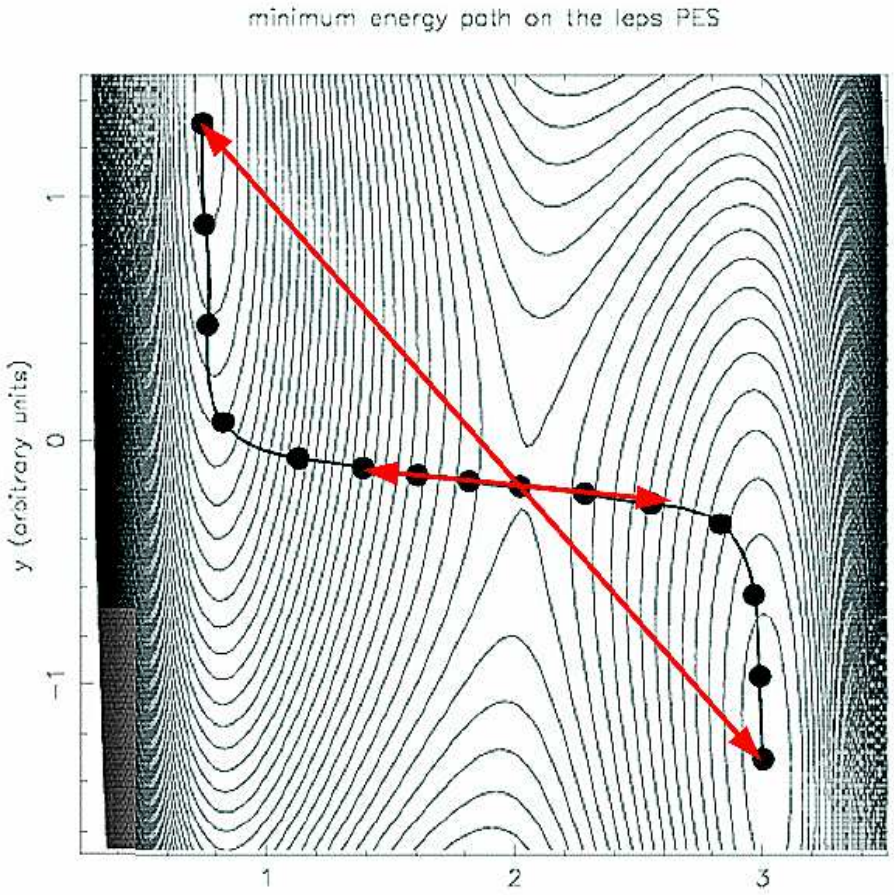




Constrained minimization is completely wrong in this case.

NEB vs constrained minimizations





NEB input variables

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

```
&CONTROL
   calculation = "neb"       <= mandatory
   nstep                     <= optional (0)
   ...
/
...
...
&IONS
   num_of_images             <= mandatory
   opt_scheme                <= optional {quick-min | sd | broyden | ...}
   CI_scheme                 <= optional {no-CI | auto | manual }
   first_last_opt            <= optional {.false. | .true.}
   ds                        <= optional {1.D0}
   k_max                     <= optional {0.1D0}
   k_min                     <= optional {0.1D0}
   path_thr                  <= optional {0.05D0 eV/A}
   ...
/
```

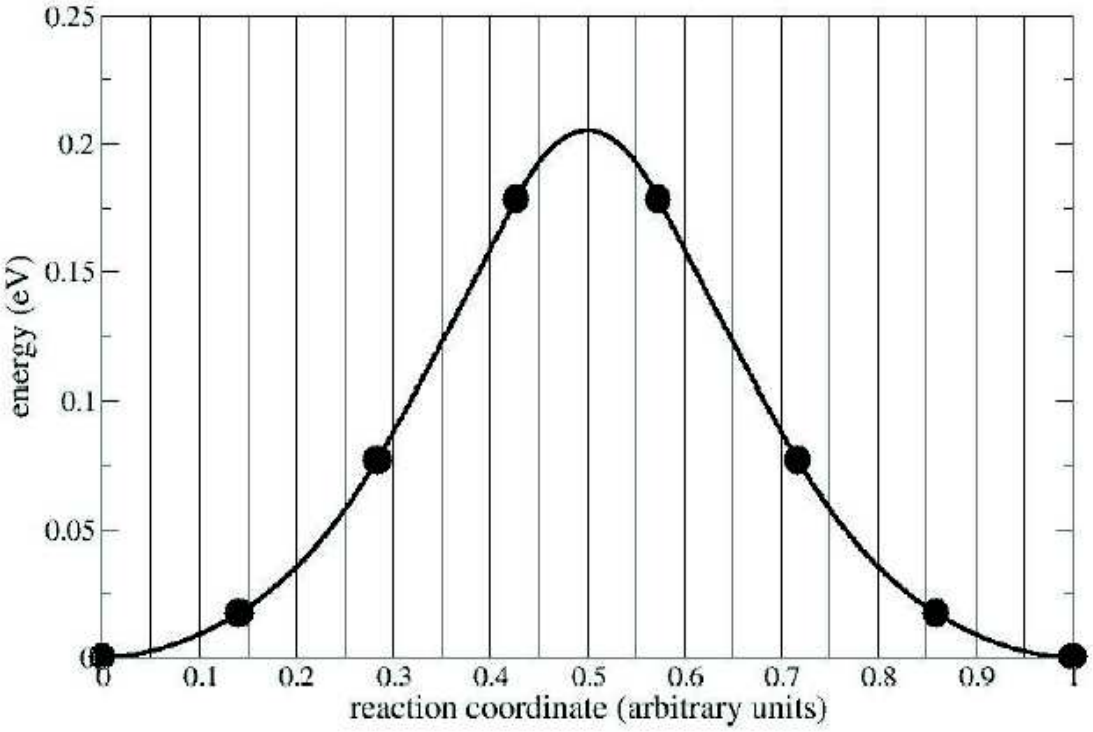
NEB input variables

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

```
ATOMIC_POSITIONS {  alat | bohr | angstrom | crystal   }
 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                                           <= 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
```

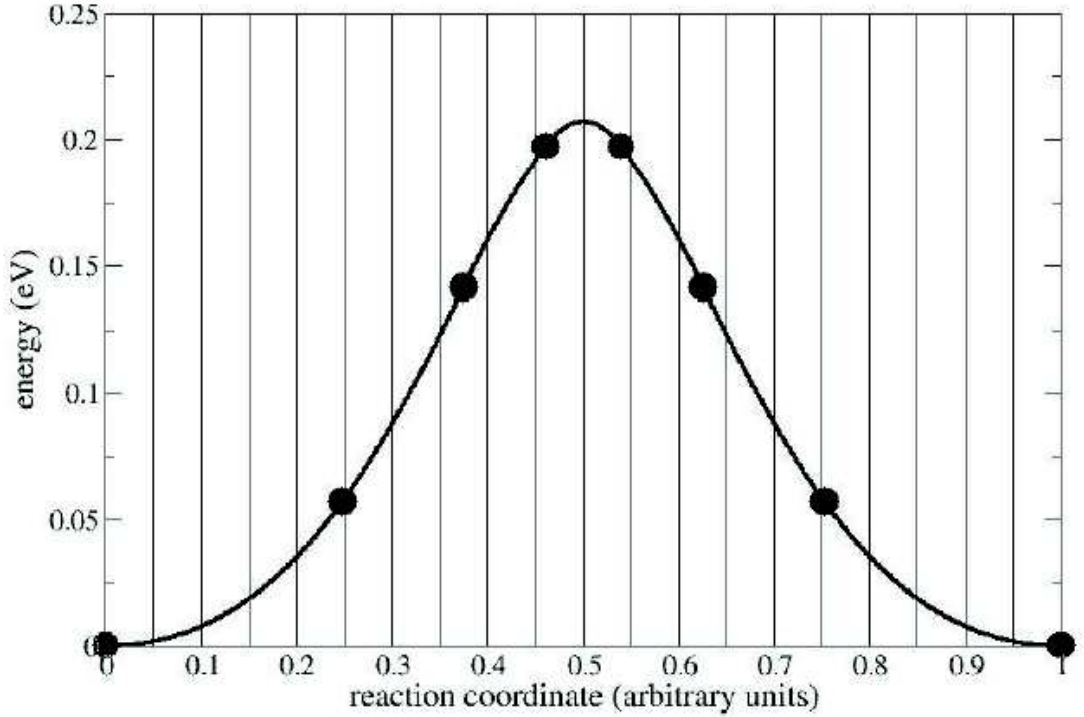
Example17: collinear proton transfer

plain NEB with 8 images



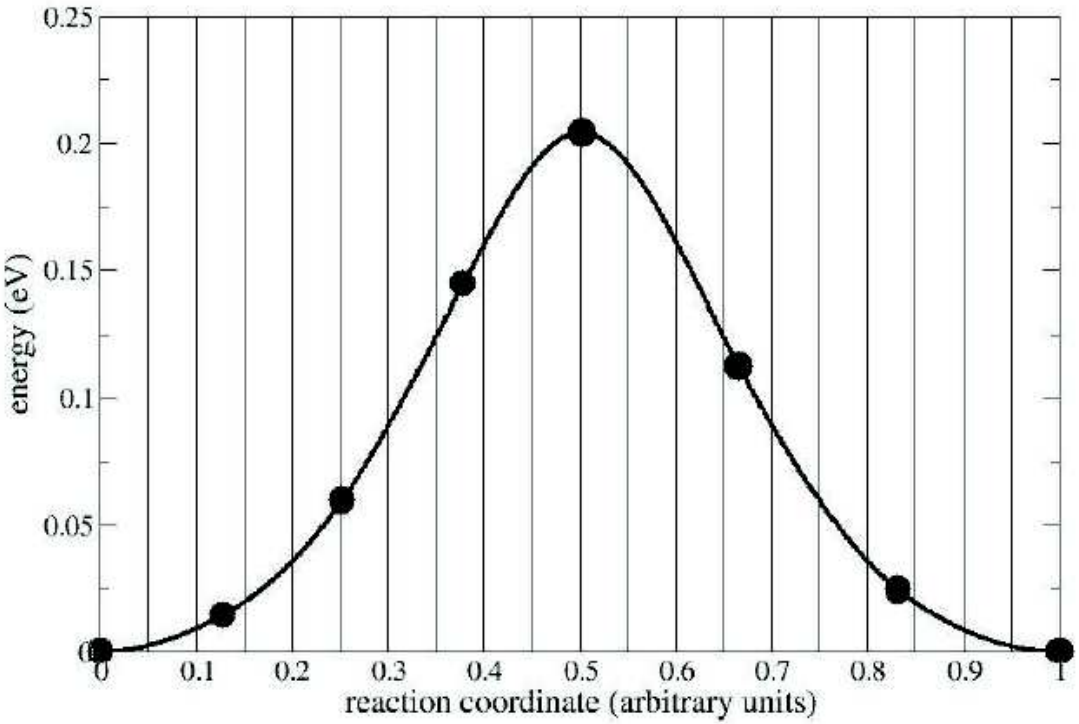
Example17: collinear proton transfer

variable elastic constants



Example17: collinear proton transfer

climbing image (manual on image 5)



THE END