

0.1 Original NEB

Nudged elastic band (NEB) approaches to locating transition states are efficient alternatives to evaluating the PES on a uniform grid over some coordinates of interest. The implementation in *autodE* follows that in [*J. Chem. Phys.*, 2000, **113**, 9978]

For an image i in the nudged elastic band

$$\boldsymbol{\tau}_i = \begin{cases} \boldsymbol{\tau}_i^+ & \text{if } V_{i-1} < V_i < V_{i+1} \\ \boldsymbol{\tau}_i^- & \text{if } V_{i+1} < V_i < V_{i-1} \\ \boldsymbol{\tau}_i^+ \Delta V_i^{max} + \boldsymbol{\tau}_i^- \Delta V_i^{min} & \text{if } V_{i-1} < V_{i+1} \\ \boldsymbol{\tau}_i^+ \Delta V_i^{min} + \boldsymbol{\tau}_i^- \Delta V_i^{max} & \text{if } V_{i+1} < V_{i-1} \end{cases} \quad (1)$$

where

$$\begin{aligned} \boldsymbol{\tau}_i^+ &= \mathbf{x}_{i+1} - \mathbf{x}_i \\ \boldsymbol{\tau}_i^- &= \mathbf{x}_i - \mathbf{x}_{i-1} \end{aligned} \quad (2)$$

and

$$\begin{aligned} \Delta V_i^{max} &= \max(|V_{i+1} - V_i|, |V_{i-1} - V_i|) \\ \Delta V_i^{min} &= \min(|V_{i+1} - V_i|, |V_{i-1} - V_i|) \end{aligned} \quad (3)$$

and \mathbf{x}_i are the coordinates of image i . The spring force is

$$\mathbf{F}_i^s|_{\parallel} = (k_i |\mathbf{x}_{i+1} - \mathbf{x}_i| - k_{i-1} |\mathbf{x}_i - \mathbf{x}_{i-1}|) \hat{\boldsymbol{\tau}}_i \quad (4)$$

and the total force on the image

$$\mathbf{F}_i = \mathbf{F}_i^s|_{\parallel} - \nabla V(\mathbf{x}_i)|_{\perp} \quad (5)$$

where

$$\nabla V(\mathbf{x}_i)|_{\perp} = \nabla V(\mathbf{x}_i) - \nabla V(\mathbf{x}_i) \cdot \hat{\boldsymbol{\tau}}_i \hat{\boldsymbol{\tau}}_i \quad (6)$$

and finally $\hat{\boldsymbol{\tau}} = \boldsymbol{\tau}_i / |\boldsymbol{\tau}_i|$.

0.2 CI-NEB

The climbing image (CI) NEB implementation follows that in [*J. Chem. Phys.*, 2000, **113**, 9901] where after a few iterations the force on the maximum energy image (m) is given by

$$\mathbf{F}_m = -\nabla V(\mathbf{x}_m) + 2\nabla V(\mathbf{x}_m) \cdot \hat{\boldsymbol{\tau}}_i \hat{\boldsymbol{\tau}}_i \quad (7)$$

which is the force due to the potential along the band being inverted.