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 [Henkelman and H. Jónsson, J. Chem. Phys. 113, 9978 (2000)]

For an image i in the nudged elastic band

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

where

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

and

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

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

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

and the total force on the image

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

where

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

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

0.2 CI-NEB

The climbing image (CI) NEB implementation follows that in [G. Henkelman, B. P. Uberuaga, and H. Joonsson. 113, 9901 (2000)] where after a few iterations the force on the maximum energy image (m) is given by

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

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