A generalized solid-state nudged elastic band method

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Characterizing reaction pathways and kinetics in solids

nudged elastic band method

solid-state nudged elastic band
rare event problem

Problem:

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<thead>
<tr>
<th>Time Scale</th>
<th>Description</th>
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<td>ps</td>
<td>dynamics simulations</td>
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<td>thermally activated reaction dynamics</td>
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<tr>
<td>μs</td>
<td>experimental time scales</td>
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$\Delta E$
rare event problem

Problem:

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$\Delta E \sim 0.5$ eV at 300K

Rate $\sim 1$/ms

$\sim 10^{12}$ force evaluations

DFT force evaluation $\sim$ mins
Transition State Theory

\[
k^{TST} = \frac{1}{Q_{\text{initial}}} \left\langle e^{-\hat{H} / k_B T} \dot{s} \delta(s - s^*) \Theta(\dot{s}) \right\rangle
\]

Probability

\[
k^{TRUE} = \kappa k^{TST}
\]
Transition State Theory

Rate from harmonic transition state theory

\[ Rate = \frac{\Pi \nu_i}{\Pi \nu_j^\dagger} \cdot e^{-\frac{\Delta E}{k_B T}} \]

\[ k^{TST} = \frac{1}{Q_{\text{initial}}} \left\langle e^{-\frac{\hat{H}}{k_B T}} \dot{s} \delta(s - s^*) \Theta(\dot{s}) \right\rangle \]

probability
forward flux

generally true for solids and surface chemistry
but wish were always true:

1) Smooth
2) Continuous
3) “large” system curvatures
Nudged elastic band method (NEB)

(find saddle points on a potential energy surface)

NEB force on image i

\[ F_{i}^{\text{NEB}} = F_{i}^{\perp} + F_{i}^{\text{sll}} \]

Projected gradient forces

\[ F_{i}^{\perp} = F_{i} - (F_{i} \cdot \hat{\tau}_{i})\hat{\tau}_{i} \]

Tangential spring forces

\[ F_{i}^{\text{sll}} = k(|R_{i+1} - R_{i}| - |R_{i} - R_{i-1}|)\hat{\tau}_{i} \]

Sheppard et al. JCP 128, 134106 (2008)
Nudged elastic band method (NEB)

(find saddle points on a potential energy surface)

NEB force on image $i$

$$F_{i}^{\text{NEB}} = F_{i}^{\perp} + F_{i}^{\text{sl}}$$

Projected gradient forces

$$F_{i}^{\perp} = F_{i} - (F_{i} \cdot \hat{\tau}_{i})\hat{\tau}_{i}$$

Tangential spring forces

$$F_{i}^{\text{sl}} = k(| R_{i+1} - R_{i} | - | R_{i} - R_{i-1} |)\hat{\tau}_{i}$$

Climbing image

$$F_{i}^{\text{CI}} = F_{i} - 2(F_{i} \cdot \hat{\tau}_{i})\hat{\tau}_{i}$$

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Nudged elastic band method (NEB)

(find saddle points on a potential energy surface)

\[ F_{i}^{\text{NEB}} = F_{i}^{\perp} + F_{i}^{\text{ssl}} \]

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Tangential spring forces

\[ F_{i}^{\text{ssl}} = k(|R_{i+1} - R_{i}| - |R_{i} - R_{i-1}|)\hat{\tau}_{i} \]

Climbing image (find saddle points on a potential energy surface)

\[ F_{i}^{\text{CI}} = F_{i} - 2(F_{i} \cdot \hat{\tau}_{i})\hat{\tau}_{i} \]
Nudged elastic band method (NEB)

(finding saddle points on a potential energy surface)

connect initial and final state with “n” interpolated configurations

Calculate energy/gradient of all images

Find up-winding tangent

$\hat{\tau}_i$

solve NEB force projections

$F_{i,NEB} = F_{i}^{\perp} + F_{i}^{sll}$

Step along NEB force

optimize($F_{i,NEB}$)

Sheppard et al. JCP 128, 134106 (2008)
The good:
finds the saddle point quantitatively
Robustly finds the minimum energy path
(with variable resolution of the MEP)
reaction coordinate changes dynamically

The bad:
Two-ended search method
Only finds the local saddle point
Only works well for smooth landscapes

The Ugly:
Based on force projections
No object function
due to lack of object function (ill defined Hessian)
Examples of good systems

Pd cluster rolling on MgO

Energy [eV]

Scaled Reaction Coordinate

Reaction coordinate [Å]

Xu et al. PRL 95, 146103 (2005)
Sheppard et al. JCP 128, 134106 (2008)

CH₄ desorption on Ni(111)

Henkelman et al. JCP 124, 044706 (2006)

H diffusion on TiO₂

Hydrogen diffusion along (001) (arbitrary units)

Li et al. JACS 130, 9080 (2008)
Periodic boundary conditions

Simulating solids

Cost of empirical potential

\[ \sim N^2 \]

\sim 34 \text{ million atoms to model } 1\text{cm}^3

Cost of DFT

\[ \sim N_e^3 \]
two types of variables

Atomic degrees of freedom

position of the atoms
\[ R_i \]
change in position
\[ dR = R' - R \]
Forces on atoms
\[ F_i = -\frac{\partial E}{\partial R_i} \]

Periodic representation

definition of the cell
\[ h = \begin{pmatrix} h_{1x} & 0 & 0 \\ h_{2x} & h_{2y} & 0 \\ h_{3x} & h_{3y} & h_{3z} \end{pmatrix} \]
change in the cell
\[ \varepsilon = h^{-1} \cdot (h' - h) \]
force on the cell
\[ \Omega \sigma = \Omega (\sigma_{CAUCHY} + P \cdot I) \]
Volume of cell
\[ \Omega = \text{det}(h) \]
Drag methods

regular NEB always minimizing stress

(works if reaction coordinate is local)

Caspersen and Carter *PNAS*, **102** 6738, (2005)
rapid nuclear motion (RNM)

(works if reaction coordinate is concerted motion)
Treat all degrees of freedom

all degrees of freedom

Position

\[ \mathbf{R} = \{h,R_i\} \]

d change in position

\[ \mathbf{dR} = \{J\varepsilon,dR_i\} \]

Forces

\[ \mathbf{F} = \{\varpi\sigma/J,F_i\} \]

Weighting of cell and atomic degrees of freedom

Invariant to doubling the cell
Treat all degrees of freedom

**Position**

\[ \mathbf{R} = \{ h, R_I \} \]

deck in position

\[ d\mathbf{R} = \{ J\varepsilon, dR_I \} \]

**Forces**

\[ \mathbf{F} = \{ \Omega \sigma / J, F_I \} \]

**Weighting of cell and atomic degrees of freedom**

Invariant to doubling the cell

\[
\begin{align*}
\text{Atomic distance} & : dR \\
\text{Cell distance} & : \varepsilon \\
\text{Jacobian to modify cell distance} & : J \varepsilon \Rightarrow J \sim \sqrt{n}
\end{align*}
\]

Independent of units
Treat all degrees of freedom

all degrees of freedom

Position

\[ \mathbf{R} = \{ h, R_i \} \]

change in position

\[ \text{dR} = \{ J\varepsilon, \text{dR}_i \} \]

Forces

\[ \mathbf{F} = \{ \Omega\sigma / J, F_i \} \]

Weighting of cell and atomic degrees of freedom

Invariant to doubling the cell \( J\varepsilon \Rightarrow J \sim \sqrt{n} \)

Independent of units

Units

\[
\begin{array}{ll}
\text{dR}_i & \text{distance} \\
F_i & \text{energy/distance} \\
\varepsilon & \text{dimensionless} \\
\Omega\sigma & \text{Volume*pressure} = \text{energy} \\
J\varepsilon & \text{distance} \\
\Omega\sigma / J & \text{energy/distance}
\end{array}
\]
Treat all degrees of freedom

all degrees of freedom

Position

\[ \mathbf{R} = \{ h, R_i \} \]

change in position

\[ d\mathbf{R} = \{ J \varepsilon, dR_i \} \]

Forces

\[ \mathbf{F} = \{ \Omega \sigma / J, F_I \} \]

Weighting of cell and atomic degrees of freedom

Invariant to doubling the cell

\[ J \varepsilon \Rightarrow J \sim \sqrt{n} \]

Independent of units

\[ J = \left( \frac{\Omega}{n} \right)^{1/3} \sqrt{n} \]

ok under range of values

\[ \theta_i = 2 \tan^{-1} \left( \frac{\nu_I}{\nu^*} \right) \]
rock-salt to wurtzite in CdSe

a) atom dominated

initial (rock salt)

4.06 Å

9.08 Å

4.38 Å

4.22 Å

9.36 Å

4.06 Å

final (wurtzite)

4.38 Å

8.75 Å

11.49 Å

8.75 Å

b) cell dominated
Reaction coordinate dominated by motion of atoms

- Initial state
- Final state

Energy/atom (meV):
- -60
- -40
- -20
- 0
- 20
- 40
- 60

NEB

SS-NEB

RNM

Initial state

Final state

Saddle

15 meV

13 meV

RNM

SS-NEB

NEB

Reactor coordinate dominated by motion of atoms
Reaction coordinate dominated by motion of cell

![Graph showing energy changes with initial and final states in SS-NEB, RNM, and NEB methods.](image)

12 meV
16 meV
energy/atom (meV)

initial state
final state

SS-NEB
RNM
NEB

reaction coordinate dominated by motion of cell
Size consistency (cell dominated path)

- Energy / atom (meV)
- Distance / $\sqrt{N}$ (Å)

Transition state

Atoms / cell:
- 8
- 32
- 72
- 128

Human readable text:

Size consistency (cell dominated path)

- Energy / atom (meV)
- Distance / $\sqrt{N}$ (Å)

Transition state

Atoms / cell:
- 8
- 32
- 72
- 128
Concerted mechanism to nucleation
Nucleation
Transition states in CdSe via DFT

Functional: PW91
Energy Cutoff = 455 eV
KPOINTS = 10 X 10 X 10 Monkhorst-Pack mesh
Conclusions:

SS-NEB is a robust saddle point finding method containing both atomistic and periodic degrees of freedom.


Can be adapted to any code where Energy, Force, and a Stress tensor are calculated:

VASP: (vtst extension) http://theory.cm.utexas.edu/vtsttools/code/
TSASE: (python wrapper for VASP and LAMMPS)
   http://theory.cm.utexas.edu/henkelman/code/tsase.php

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