Review: Force reversed method\textsuperscript{1} for locating transition states and a comparison to the Dimer method\textsuperscript{2}

By: Bryan Goldsmith
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1. Keju Sun, Yonhui Zhao, Hai-Yan Su and Wei-Xue Li, Theo. Chem. Acc. (Accepted, August 17, 2011)
Searching phase space

Local geometry optimization is easy
- Walk down hill
- Positive definite Hessian, $\vec{v}^T H \vec{v} > 0$
- Use a Quasi-Newton Raphson Method

What if we want to find saddle point?

Transition state:
“maximum along the minimum energy path connecting two minima”

Problem of dimensionality
If you can go in 3N-6 different directions, how do you find the one that leads to the transition state?
Brief overview of TSS methods

“Doubled-ended” searches
Saddle algorithm
Step-and-slide
Coordinate driving
Linear synchronous transit
Nudged elastic band

- Can’t be used for unknown mechanisms
- Can find minimum energy path (MEP)

Nudged elastic band
- Given two minima, find the path with the lowest maximum
- Series of replicas connected by springs
- Does not require Hessian

“Single-ended” searches
Newton Raphson
Cerjan-Miller
Dimer method
Force reversed method
Bofill-Anglada

- Can find unexpected transition states

Mode-following
- Follow negative eigenvalue (unstable mode) to the saddle point
- Reverse the component of the force in the direction of the unstable mode

\[
F^R = F^\perp - F^\parallel
\]

Usually requires knowledge of Hessian
### Brief overview of TSS methods

#### “Doubled-ended” searches
- Saddle algorithm
- Step-and-slide
- Coordinate driving
- Linear synchronous transit
- Nudged elastic band

#### “Single-ended” searches
- Newton Raphson
- Cerjan-Miller
- **Dimer method**
- **Force reversed method**
- Bofill-Anglada

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**Nudged elastic band**
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**Mode-following**
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\[ F^R = F^\perp - F^\parallel \]
**Dimer method**

**Dimer**: pair of images of the system displaced with a fixed small distance.

Local quadratic expansion around Dimer midpoint:

\[ E_{\text{Dimer}} = 2E(\vec{x}_0) + \frac{\Delta R^2}{4} \vec{v}^T H \vec{v} \quad \Delta R = \|\vec{x}_1 - \vec{x}_2\| \]

Dimer energy only depends on orientation vector, \(\vec{v}\).

\[ E_{\text{Dimer}} \] is minimized when orientated along direction of the most unstable mode.

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Dimer method

How it works

- Replicate the system to form the Dimer
- Rotate the Dimer to lowest energy orientation
- *Reverse* the force along Dimer orientation vector
- Translate Dimer using the effective force
Dimer method

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Repeat till converges to the transition state
Why use the Dimer method?

Advantages

Does not require Hessian calculations
- Can be applied to planewave DFT calculations
- Higher level ab initio theories where second derivatives are unavailable
- Applicable to large systems

Can be initiated anywhere on the PES
- Start near a minimum energy basin or for guessed transition states
- Find unexpected reaction mechanisms

Problems

Rediscovery of previously found saddle points
- Peters et al. ¹: bias potentials as discovered to prevent rediscovery of known saddle points
- Bofill and Anglada²: work with a reduced set of coordinates to hone in on DOF of interest

Must follow the least stable mode

Force reversed method

Motivation

- Develop an efficient transition state searching algorithm
  Use one image (Dimer method uses 2)
  $\longrightarrow$ Less force calculations per iteration

- Be compatible with plane-wave DFT calculations (VASP)

How it works (in words)

- Requires a ‘rough’ search direction, $\hat{R}$

- Reverse the force along search direction
  $$\vec{F}^R = \vec{F}^\perp - \vec{F}^\parallel = \vec{F} - 2(\vec{F} \cdot \hat{R})\hat{R}$$

- Take a steepest ascent step toward the transition state
  $$\vec{P}_{j+1} = \vec{P}_j + \alpha_j \vec{F}^R_j$$
  where $\vec{P}_j$ is the configuration at iteration $j$

  $$\alpha_j = 1.5e^{-\beta_j/2}\alpha_{j-1}$$
  and $\beta_j$ is the angle between $\vec{F}_j$ and $\vec{F}_{j-1}$

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Primary force reversed (PFR) method

$PM'$ = direction of minimum energy path
$PM$ = guessed direction

$\theta$ = angle between $PM'$ and $PM$

$\theta < 45^\circ$ for convergence (on this surface)

Three trajectories from configuration $O$

$E = x^2 - y^2$
Enhanced force reversed (EFR) method

Convergence dependence on $\theta$ is an issue

Recognize that the spiral is in the direction of $\theta$

Rotate search vector each iteration to decrease $\theta$

$$\overrightarrow{R}_j = (\hat{F}_j - \hat{F}_{j-1}) \cdot |\overrightarrow{R}_{j-1}|$$
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Pronounced differences for large deviations in $\theta$
PFR versus EFR

5 trajectories from point O
OA, OB, OC, OD, OE

3 converge for PFR
OB, OC, OD

All converge for EFR

Doesn’t follow MEP nor slowest ascent
- Useful as the reaction coordinate of interest may be off of the MEP

\[ E = [(x-y)^2 - 8]^2 + 4(xy-4)^2 + 3x - 2y \]
Oxygen diffusion on Cu(111) surface

Model O diffusion from fcc hollow site to a neighbor hcp hollow site
- 5 layer slab with 9 atoms per layer
- Oxygen and metal atom in top three layers are relaxed

Initial State

Transition State

2-4 times faster than Dimer method
Dimer Optimizer: L-BFGS
PFR/EFR Optimizer: Steepest descent
O$_2$ dissociation on Cu(111) surface

Fig. 8 (Colored on line) O$_2$ dissociation on the Cu(111) surface at the final state (a), the transition state (b), and the initial state (c). The black arrows show the searching direction. The yellow and red balls are Cu and O atoms, respectively.

EFR: 26 iterations
Dimer: 156 iterations
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<th><strong>Enhanced force reversed method</strong></th>
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<tr>
<td>Rotate Dimer to most unstable mode and reverse force</td>
<td>Rotate search direction toward MEP and reverse force</td>
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Author’s claim force reversed method is similar or even more efficient than Dimer method
Conclusion

Many good transition state searching algorithms already exist (e.g. NEB, Dimer, Cerjan-Miller eigenvector following, Growing string)

Yet new algorithms are still under development
Goal: Find TS in large systems efficiently

Force reversed method is another useful tool available to VASP users

Some future work: Exploit Bofill’s reduced landscape algorithm to:
1) Prevent rediscovery of known transition states
2) Find transition states involving bond breaking/making with precision