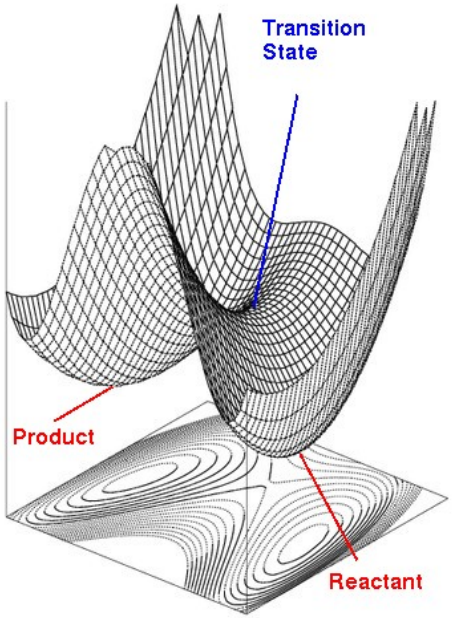
Review: Force reversed method[1] for locating transition states and a comparison to the Dimer method[2]

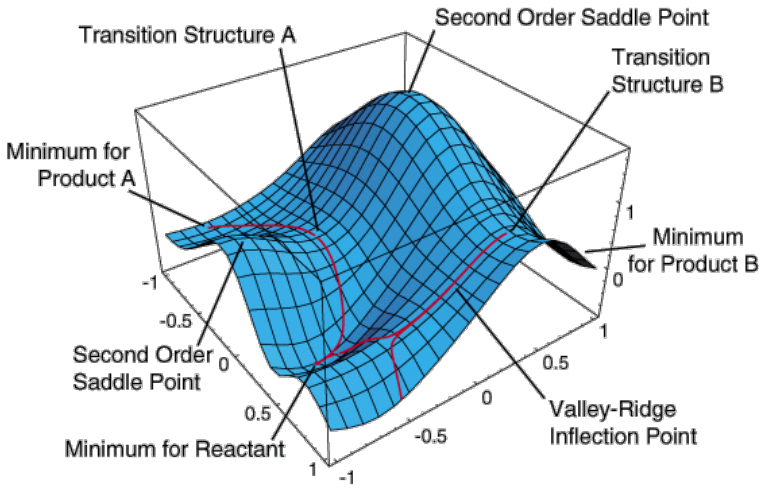


http://www.chm.bris.ac.uk/pt/harvey/jeremy.htm

By: Bryan Goldsmith
The Peters Group

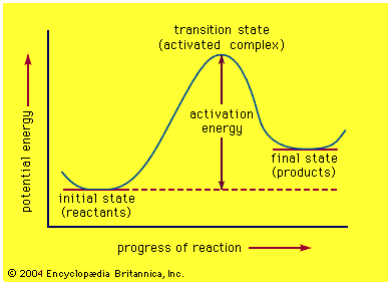
1. Keju Sun, Yonhui Zhao, Hai-Yan Su and Wei-Xue Li, Theo. Chem. Acc. (Accepted, August 17, 2011)
2. G. Henkelman and H. Jónsson, J. Chem. Phys. [**111**], 7010 (1999)

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"

- Discover reaction pathways
- Determine rate constants

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

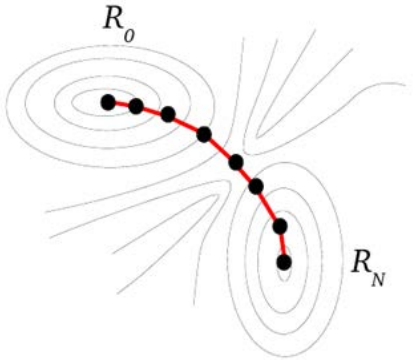
“Doubled-ended” searches
Saddle algorithm
Step-and-slide
Coordinate driving
Linear synchronous transit
Nudged elastic band

and others..

- 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



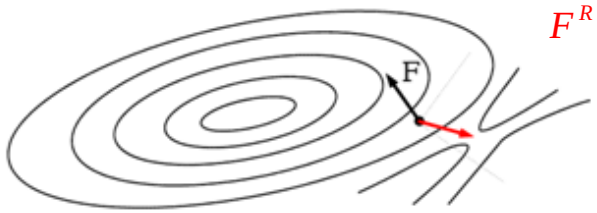
“Single-ended” searches
Newton Raphson
Cerjan-Miller
Dimer method
Force reversed method
Bofill-Anglada

and others..

- 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

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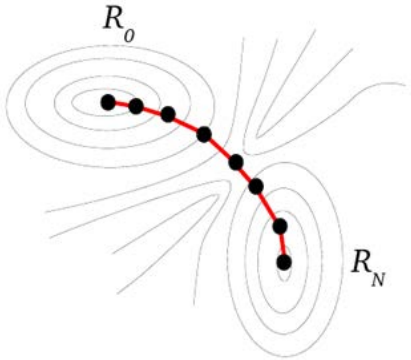

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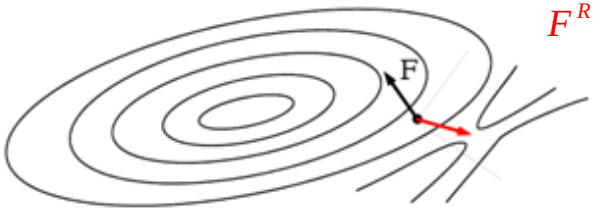

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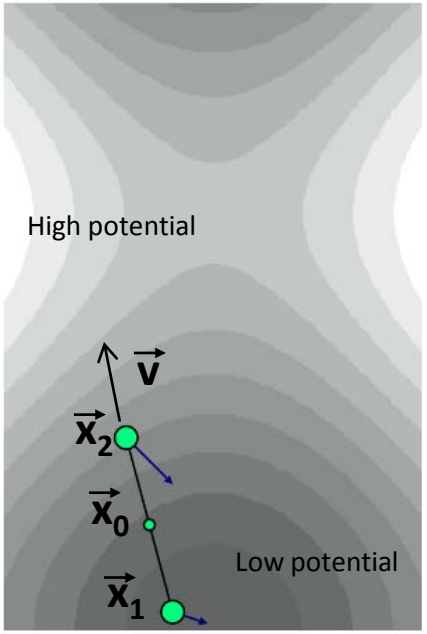
Dimer method

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



Local quadratic expansion around Dimer midpoint

$$E_{\text{Dimer}} = 2E(\vec{x}_0) + \frac{\Delta R^2}{4} \vec{v}^T H \vec{v} \qquad \Delta R = \left\| \vec{x}_1 - \vec{x}_2 \right\|$$

Dimer energy only depends on orientation vector, $\vec{v}$

E_{Dimer} is minimized when orientated along direction of the most unstable mode

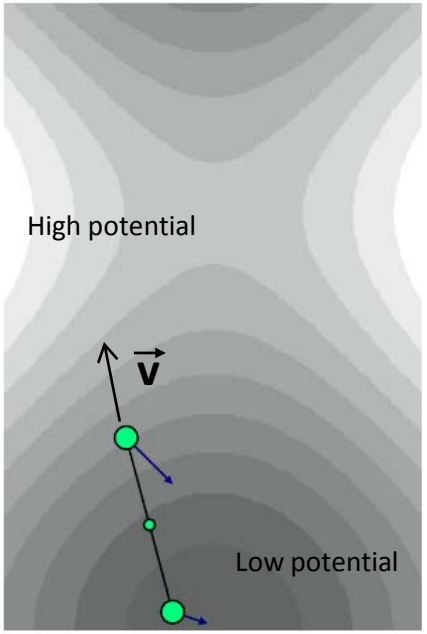
1. Munro and Wales, *Phys. Rev. B.* 59, 3969 (1999)

2. G. Henkelman and H. Jónsson, J. Chem. Phys. [**111**], 7010 (1999)

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



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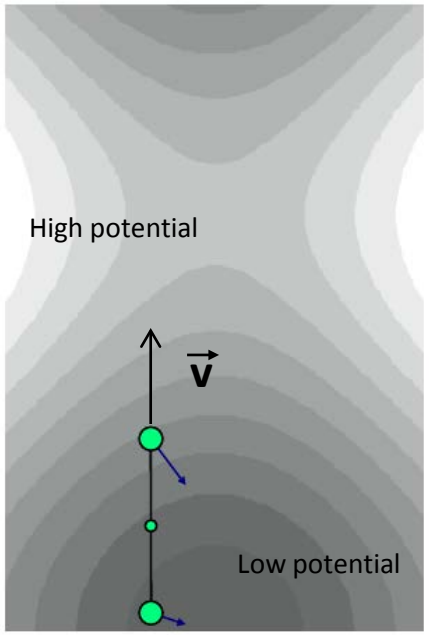

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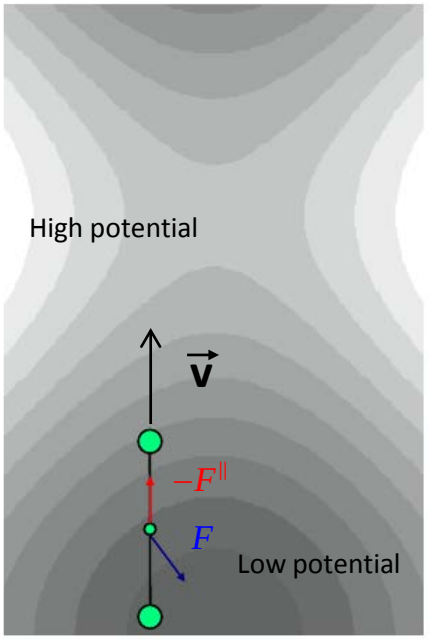

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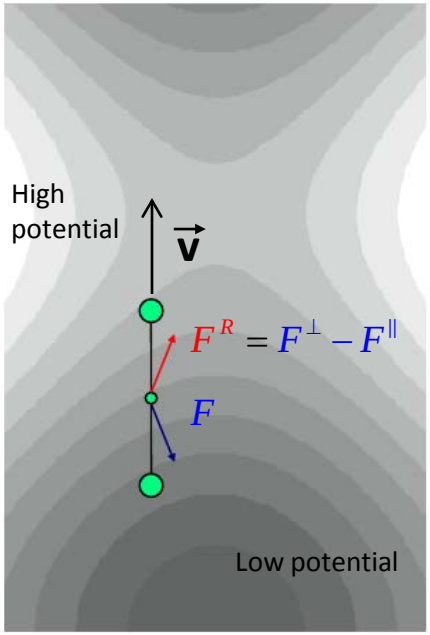

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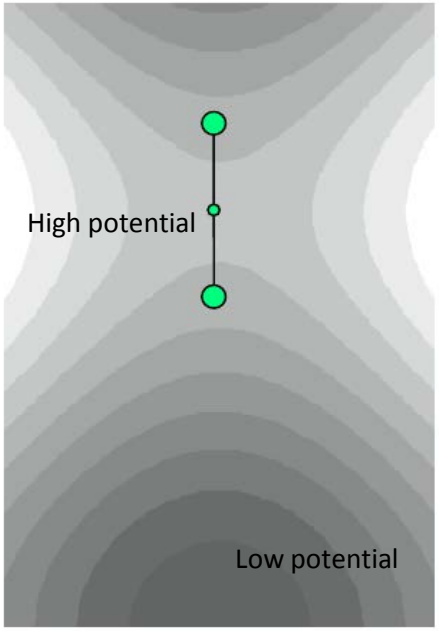


Repeat till converges to the transition state

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 Anglada[2] : work with a reduced set of coordinates to hone in on DOF of interest

Must follow the least stable mode

1. "Biasing a transition state search to locate multiple reaction pathways" B. Peters, W. Z. Liang, A. T. Bell, A. Chakraborty, J.Chem.Phys. 118, 9533 (2003)

2. Bofill, J. M.; Anglada, J. M. *Theoretical Chemistry Accounts* 205,463-472 (2001)

Force reversed method

Motivation

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

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

How it works (in words)

- Requires a 'rough' search direction, $\hat{\vec{R}}$

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

- Take a steepest ascent step toward the transition state

$\vec{P}_{j+1} = \vec{P}_j + \alpha_j \vec{F}_j^{R}$ where $\vec{P}_j$ is the configuration at iteration j

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

1. Keju Sun, Yonhui Zhao, Hai-Yan Su and Wei-Xue Li, Theo. Chem. Acc. (Accepted, August 17, 2011)

Primary force reversed (PFR) method

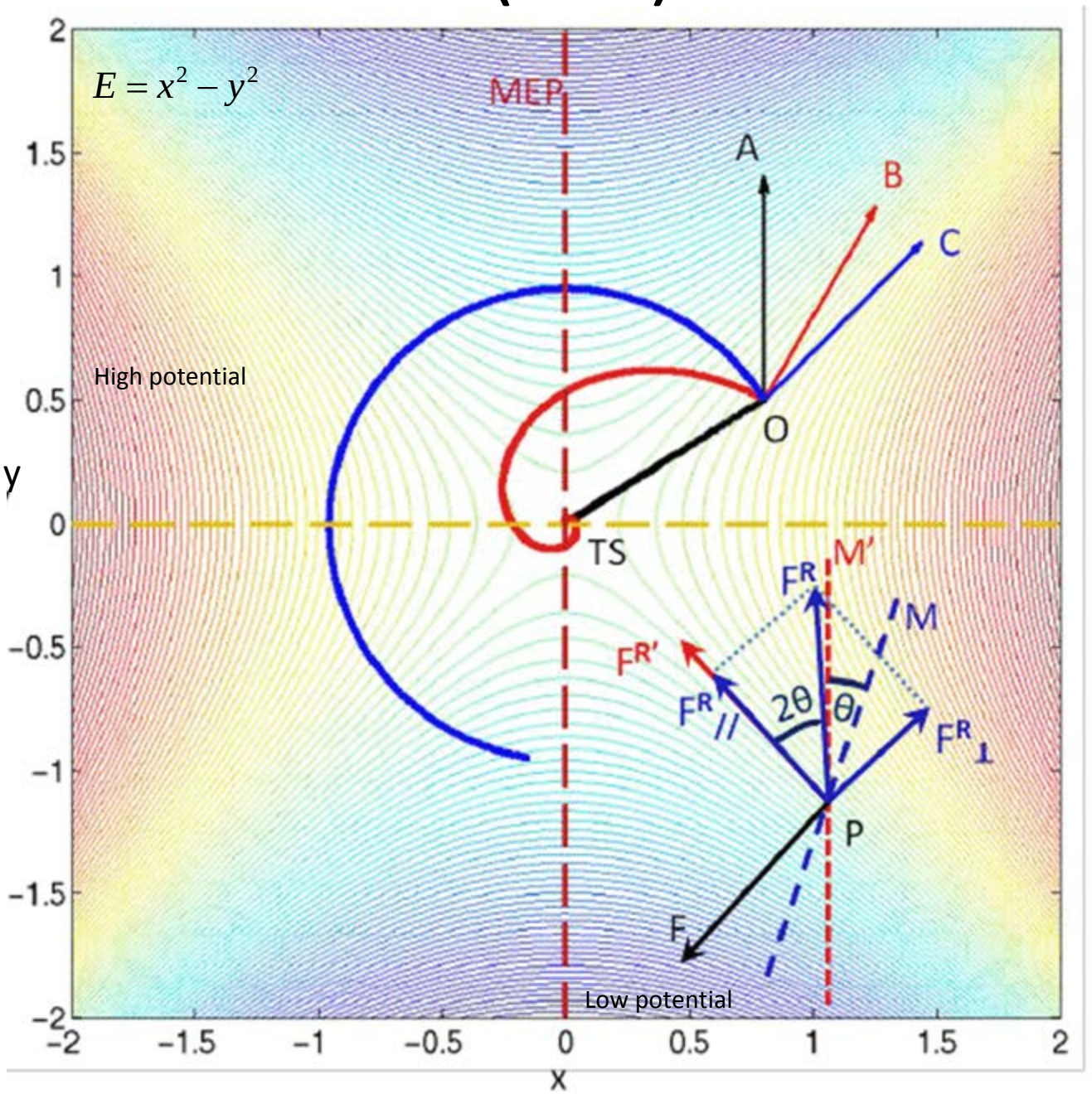
PM' = direction of minimum energy path

PM = guessed direction

θ = angle between PM’ and PM

Three trajectories from configuration **O**

θ < 45° for convergence (on this surface)



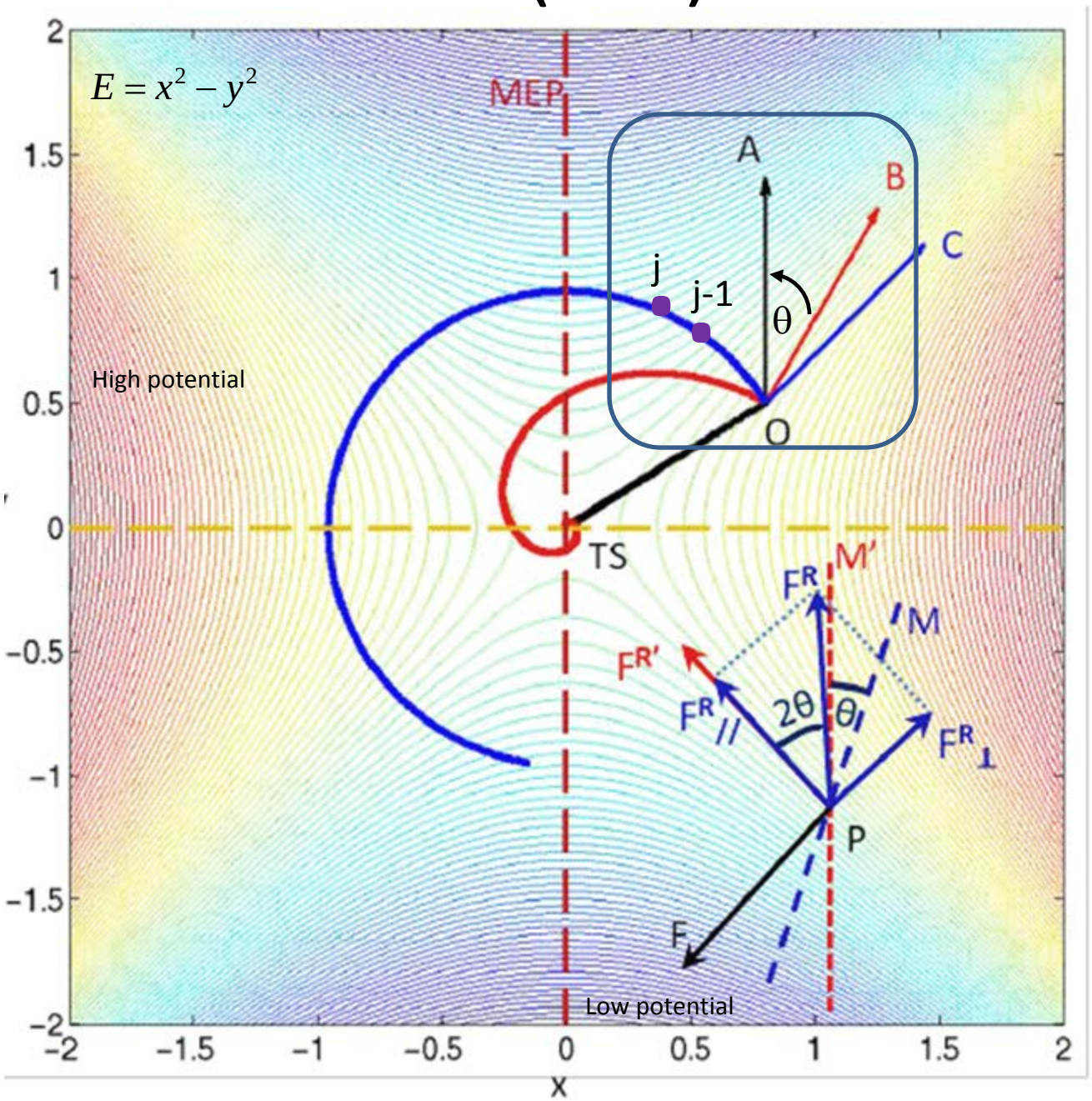
Enhanced force reversed (EFR) method

Convergence dependence on θ is an issue

Recognize that the spiral is in the direction of θ

Rotate search vector each iteration to decrease θ

$$\vec{R}_j = (\hat{\vec{F}}_j^{\vec{R}_{j-1}} - \hat{\vec{F}}_{j-1}) \cdot \left|\vec{R}_{j-1}\right|$$



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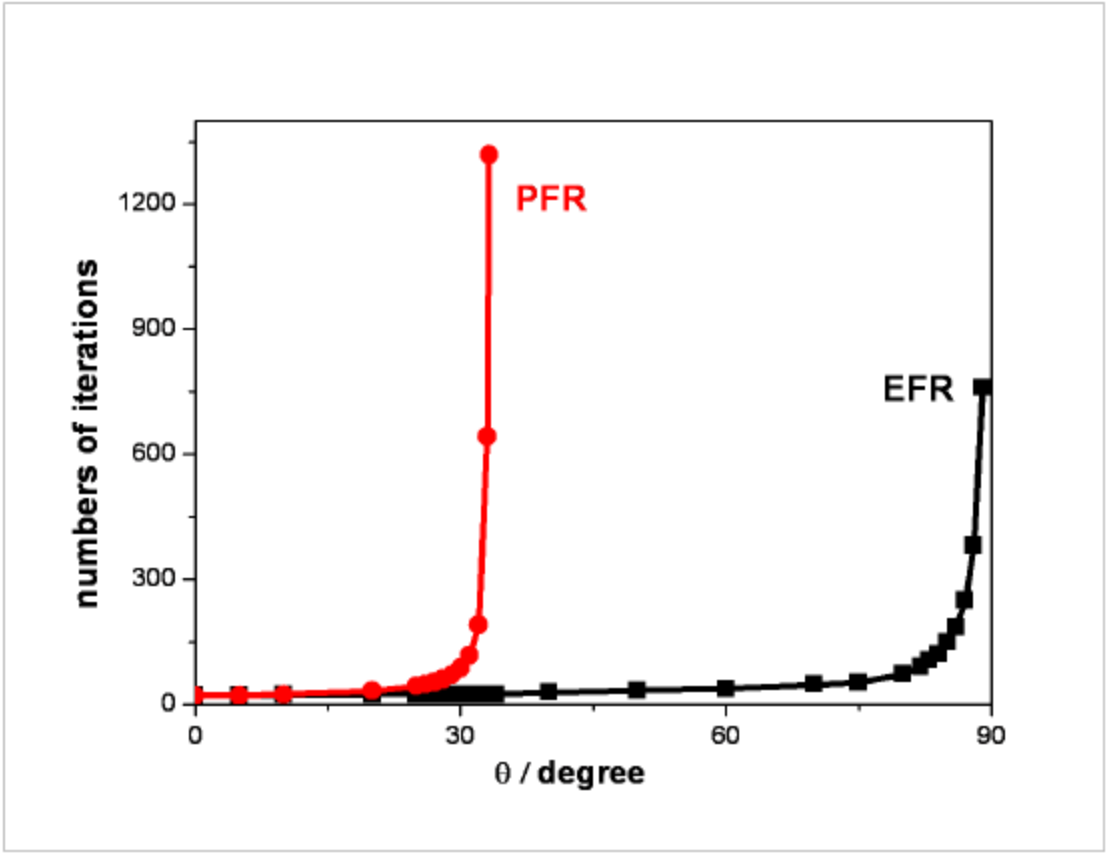


Pronounced differences for large deviations in θ

PFR versus EFR

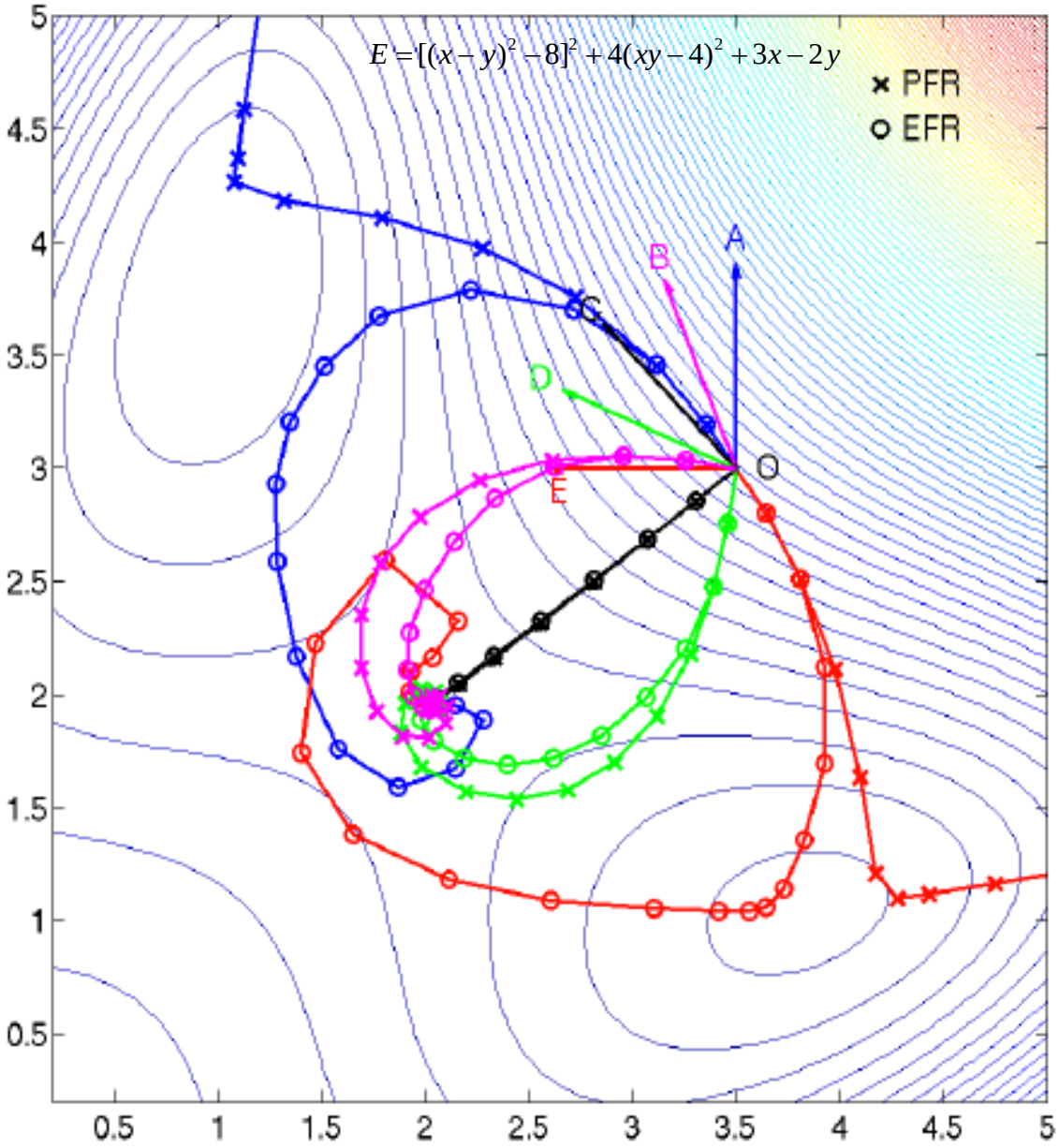
5 trajectories from point O
OA,OB,OC,OD,OE

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

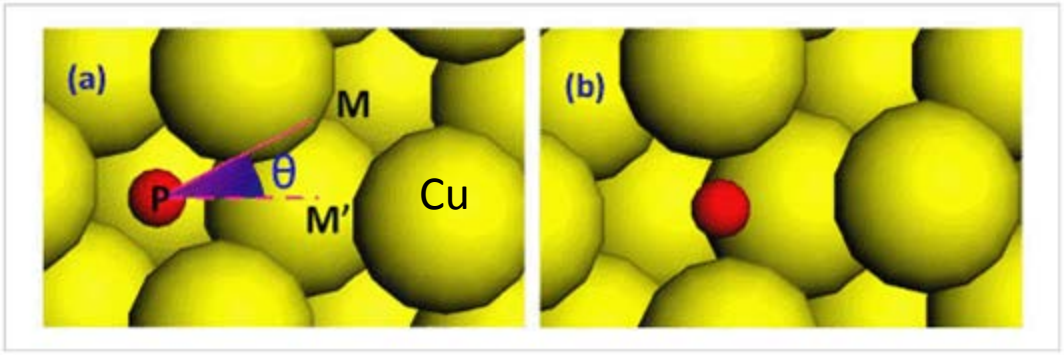


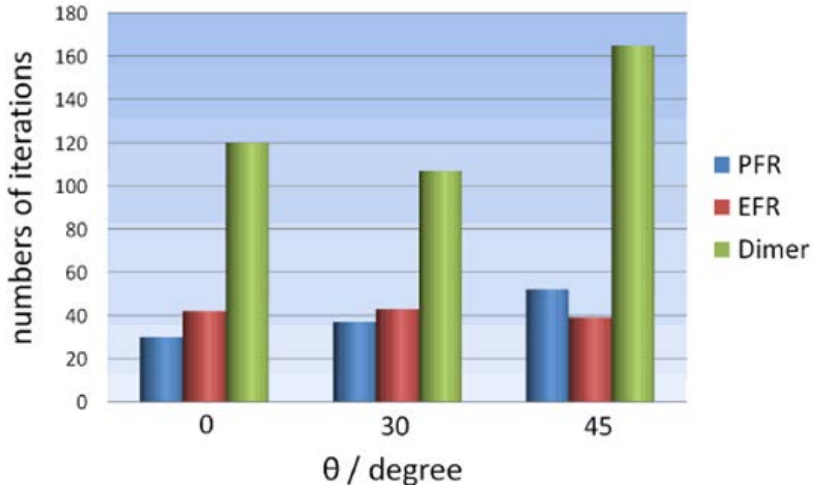
Oyxgen diffusion on Cu(111) surface

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



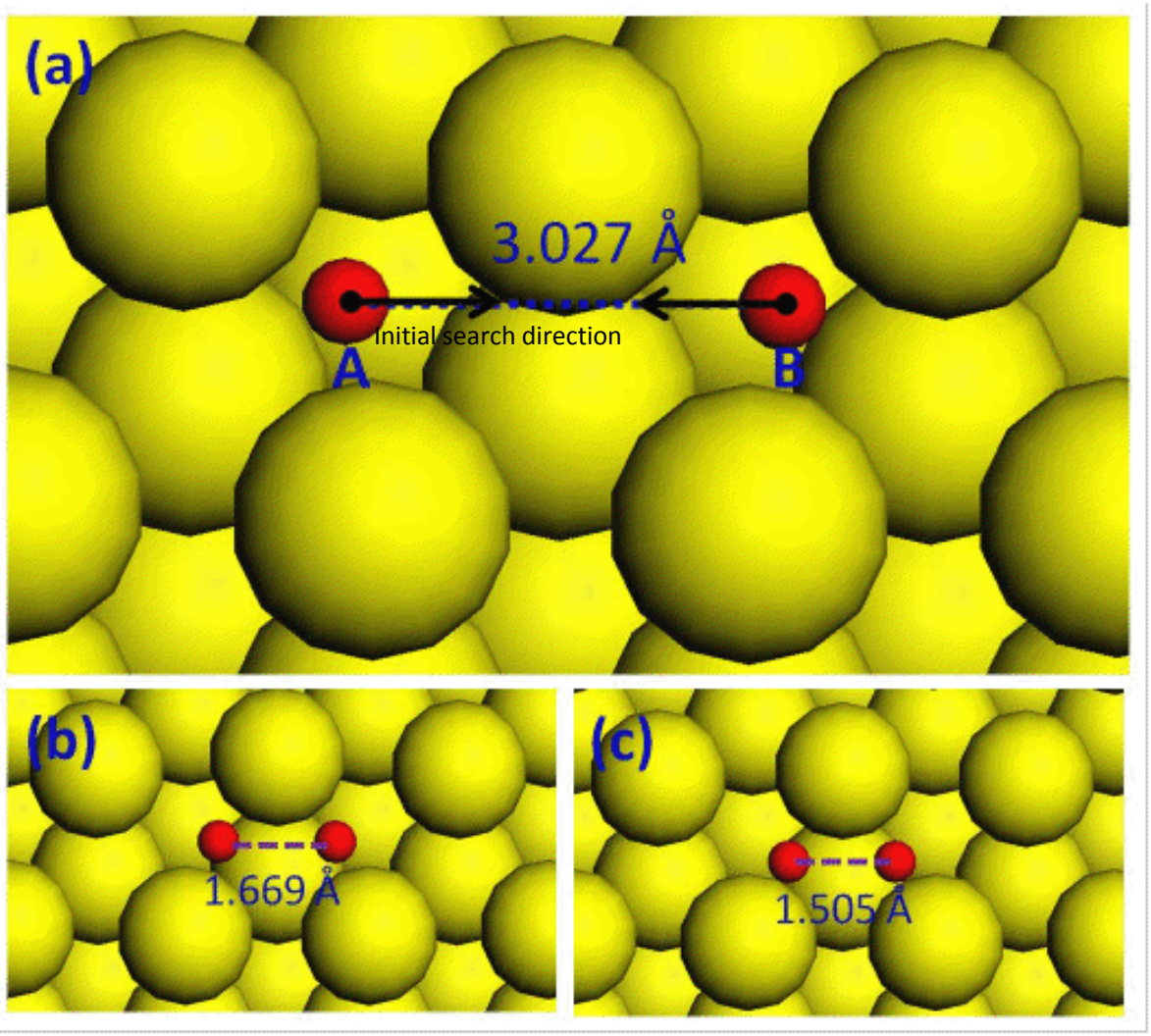


2-4 times faster than
Dimer method

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

Comparison to the Dimer method

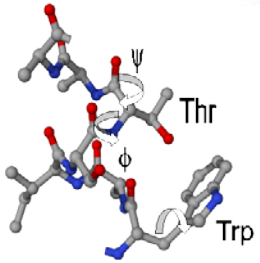
Dimer method	Enhanced force reversed method
Does not require Hessian calculation	Does not require Hessian calculation
Start from anywhere on PES	Start from anywhere on PES
Rotate Dimer to most unstable mode and reverse force	Rotate search direction toward MEP and reverse force
Two images	One image
Must follow the least stable mode	Doesn't follow MEP nor slowest ascent
Rediscovery problem	Rediscovery problem

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