



Alexander von Humboldt
Stiftung/Foundation

FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT



POORMAN'S REVIEW ABOUT: CI - NUDGED ELASTIC BAND

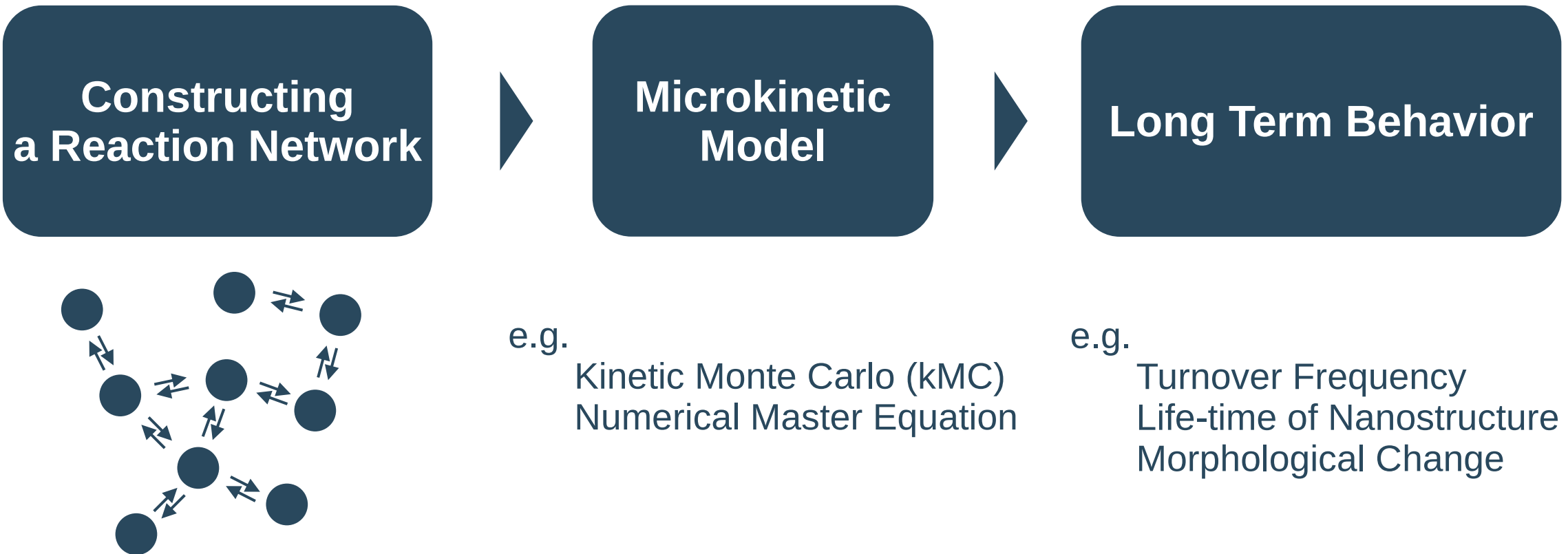
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Microkinetics Modeling

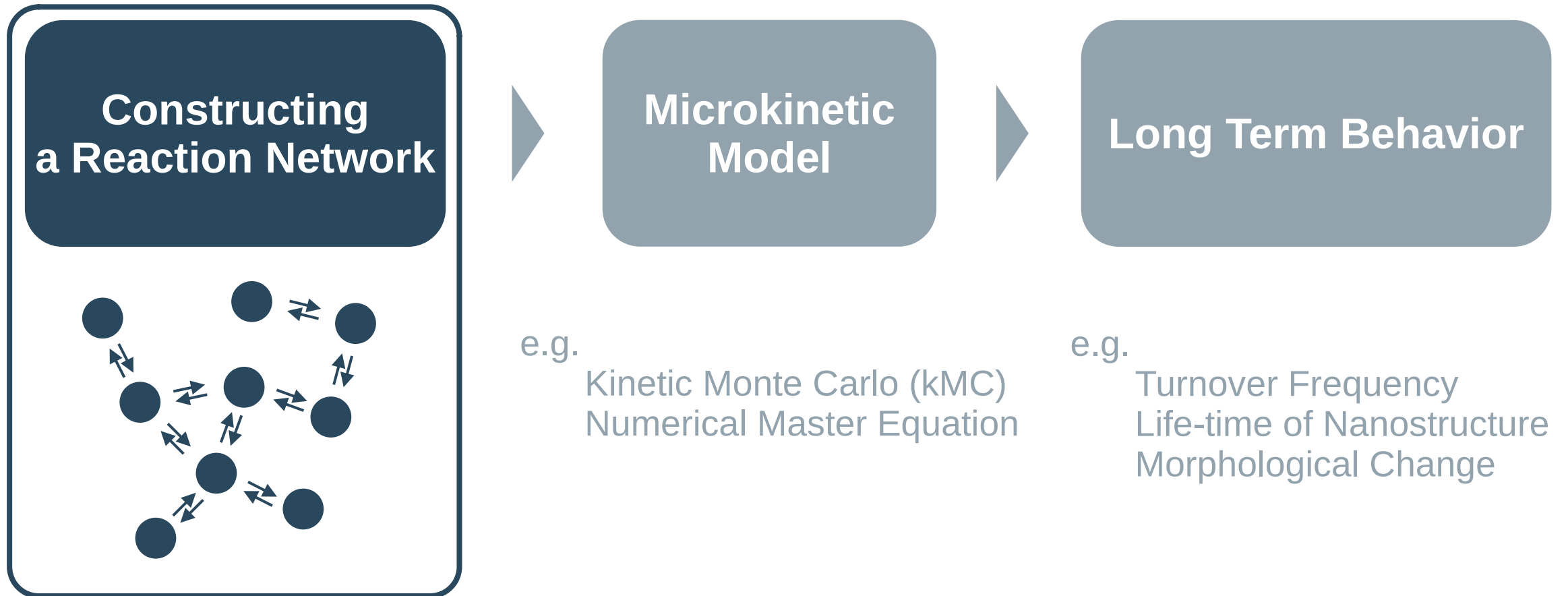
Typical approach studying long term behavior





Microkinetics Modeling

Typical approach studying long term behavior





Nudged Elastic Band Overview

What you have before NEB:

1) A pair of optimized metastable states

Obtained from some sampling
Handwritten

2) A potential energy surface (PES)

Classical force field (EAM)

Machine learned potential energy (MACE, GAP ...)





Nudged Elastic Band Overview

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What you get from NEB:

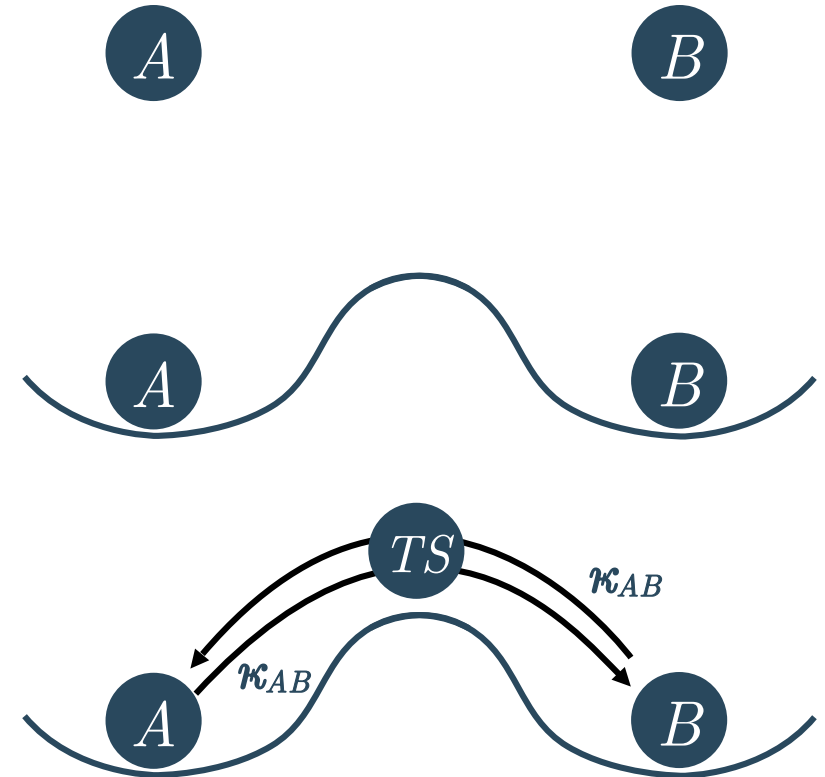
Transition State (TS) on the reaction path linking i,j

What you usually do with that TS:

Model the kinetic rate κ_{AB} , κ_{BA} (back-and-forth)

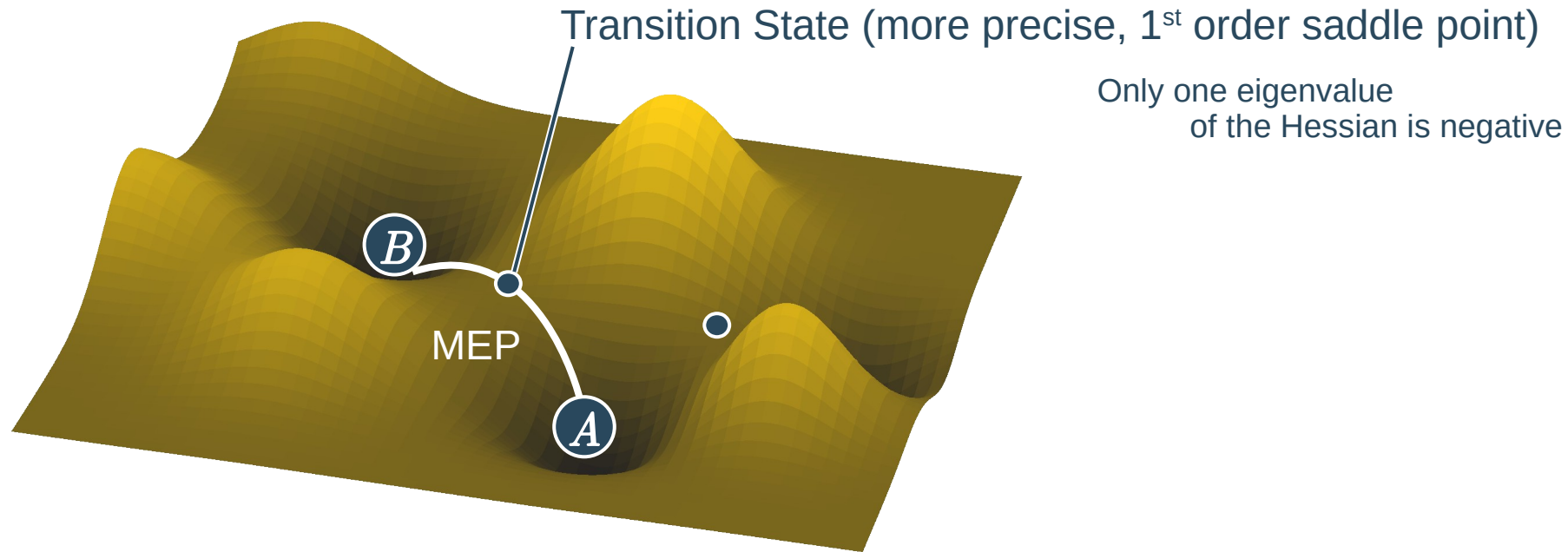
Usually simple Arrhenius form

$$\kappa = \nu \exp(-\Delta E_{\text{act}}/k_B T)$$





Nudged Elastic Band Overview

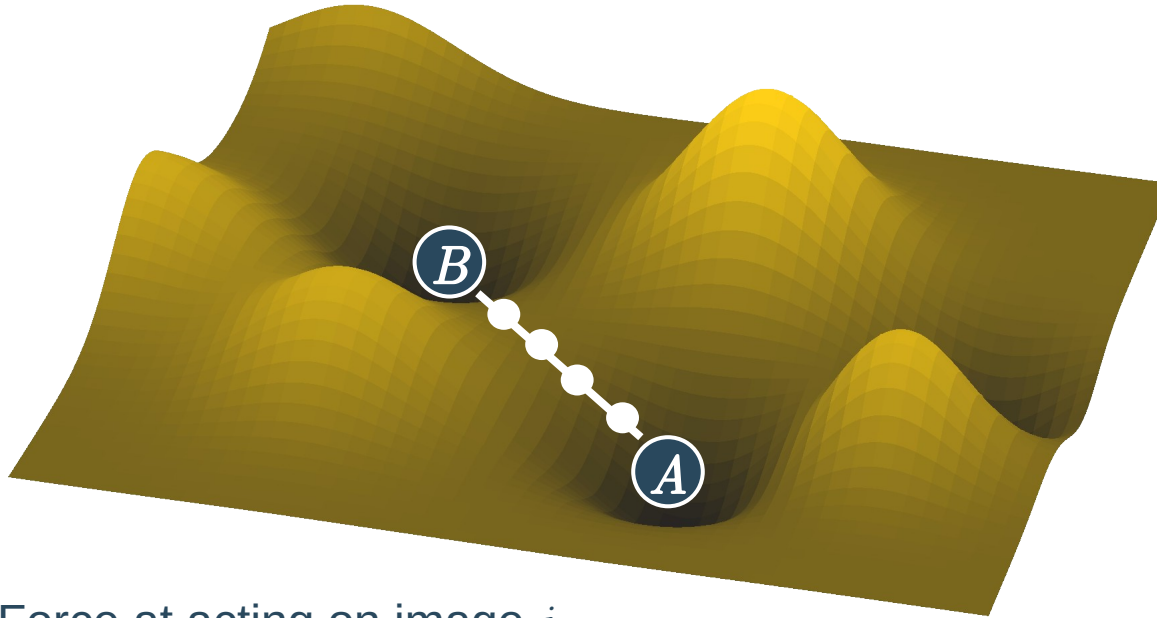


Potential Energy Surface V :
Practically $3N$ -Dimension $R_{0 < m \leq 3N}$
 N : Number of atoms free to move

Minimum Energy Path (MEP):
The most energetically favorable path linking A, B



Nudged Elastic Band Overview



Force at acting on image i

$$\mathbf{F}_i = -\nabla V(\mathbf{R}) + \mathbf{F}_i^{\text{band}}$$

$$\mathbf{F}_i^{\text{band}} = k (\mathbf{R}_{i+1} - \mathbf{R}_i) + k (\mathbf{R}_{i-1} - \mathbf{R}_i)$$

To get MEP:

1) Guess a path, typically straight line



2) Put some state-images in between



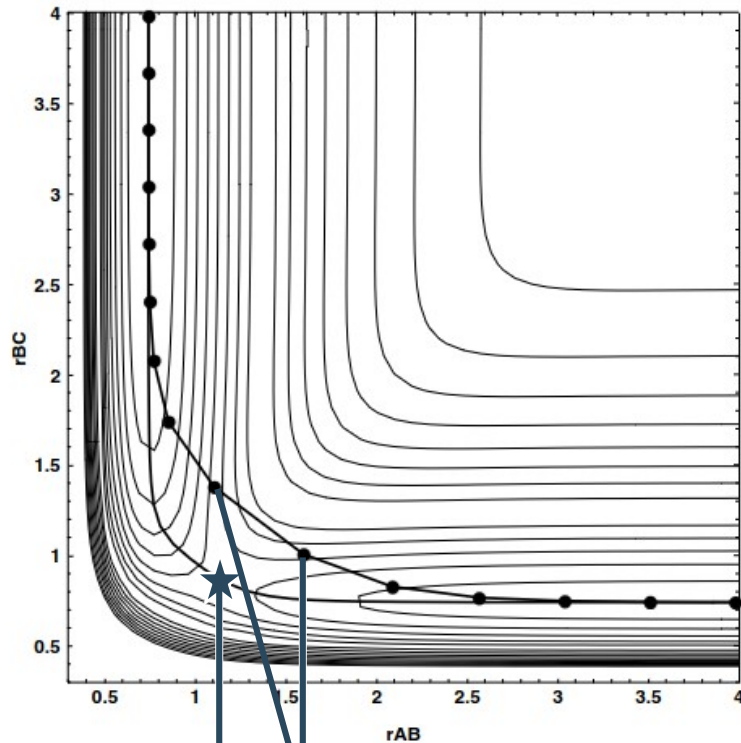
3) Put springs between the 'beads'
(Each spring has a spring constant k)



4) Optimize image-states on the band



Nudged Elastic Band Overview



From Elastic Band

Real Target

- i) The cuts the corner
- ii) It doesn't give the maximum along the band

To get MEP:

- ...
- 3) Put springs between the 'beads'
(Each spring has a spring constant k)



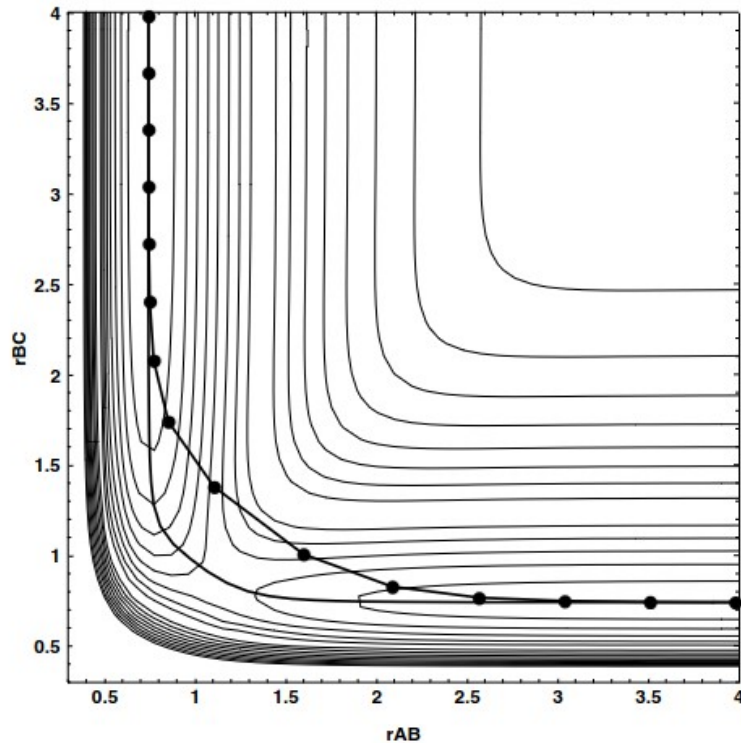
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Nudged Elastic Band Overview



To get MEP:

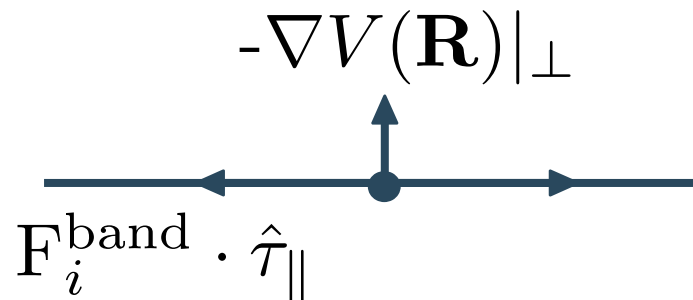
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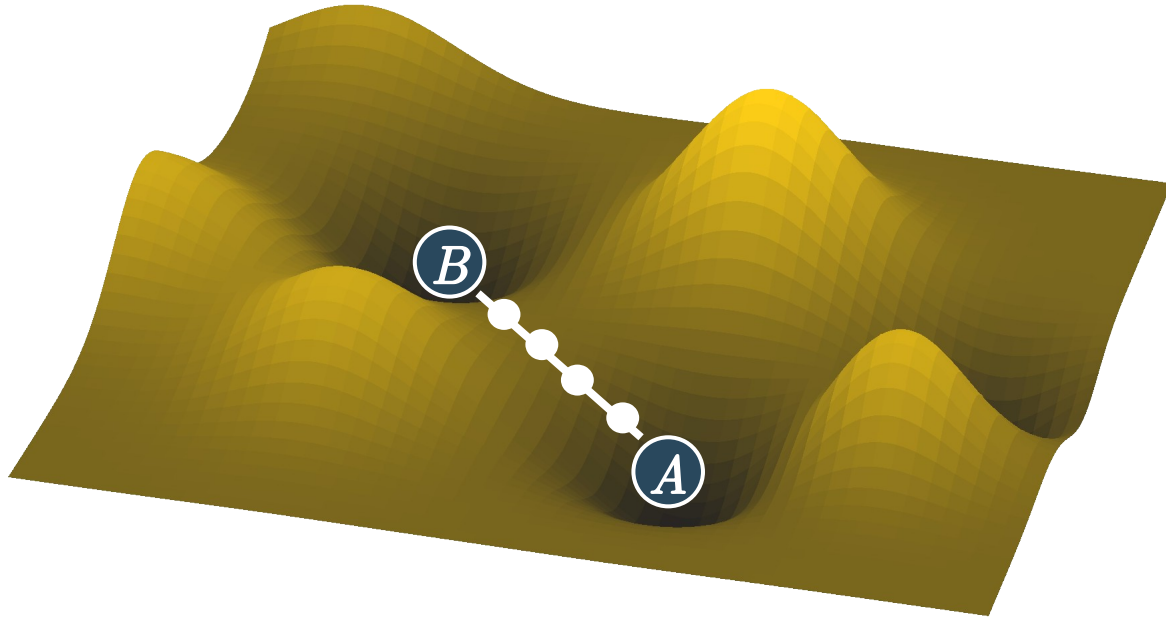
$$\mathbf{F}_i^{\text{NEB}} = -\nabla V(\mathbf{R})|_{\perp} + (\mathbf{F}_i^{\text{band}} \cdot \hat{\tau}_{\parallel}) \hat{\tau}_{\parallel}$$



Spring contributes only along the band
PES contributes perpendicular to the band



Climbing Image Nudged Elastic Band Overview



To get MEP:

- ...
- 3) Put springs between the 'beads'
(Each spring has a spring constant k)



Force acting on image i

$$\mathbf{F}_i^{\text{NEB}} = -\nabla V(\mathbf{R})|_{\perp} + (\mathbf{F}_i^{\text{band}} \cdot \hat{\tau}_{\parallel}) \hat{\tau}_{\parallel}$$

- 4) After a few NEB steps:

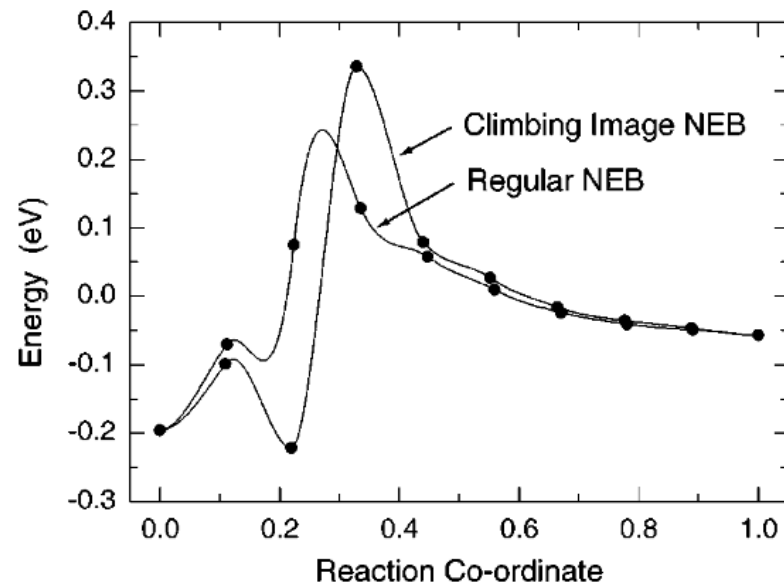
Special treatment for **the bead with highest energy**

$$\mathbf{F}_{i_{\max}}^{\text{ciNEB}} = -\nabla V(\mathbf{R}_{i_{\max}})|_{\perp} + \nabla V(\mathbf{R}_{i_{\max}})|_{\parallel}$$

- i) No effect from the band
- ii) Invert the force from PES along the band



Climbing Image Nudged Elastic Band Overview



Henkelman, G., Uberuaga, B. P., & Jónsson, H.
J. Chem. Phys. 113.22 (2000): 9901-9904.

To get MEP:

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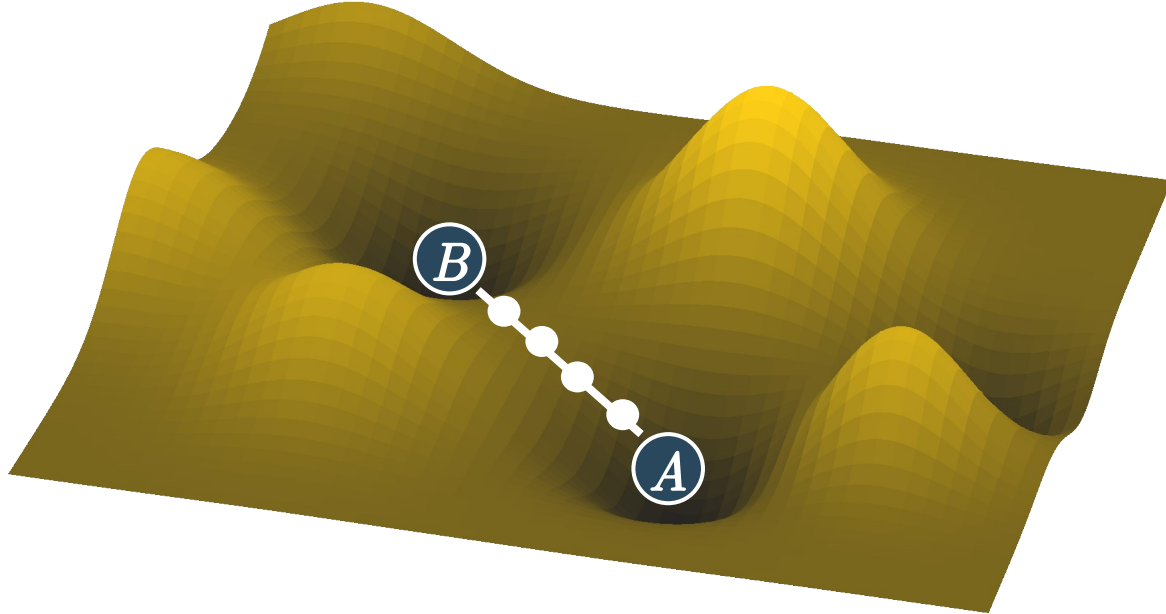
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Climbing Image Nudged Elastic Band Overview



When generating the initial guess of the band: Besides trivial interpolation of AB, here is a better way
Smidstrup, S., Pedersen, A., Stokbro, K., & Jónsson, H.
J. Chem. Phys., 140(21) (2014).

The band is a set of straight lines linking the beads!
How to estimate “tangential”/“perpendicular” direction
G. Henkelman and H. Jonsson,
J. Chem. Phys. 113, 9978 (2000)

To get MEP:

- ...
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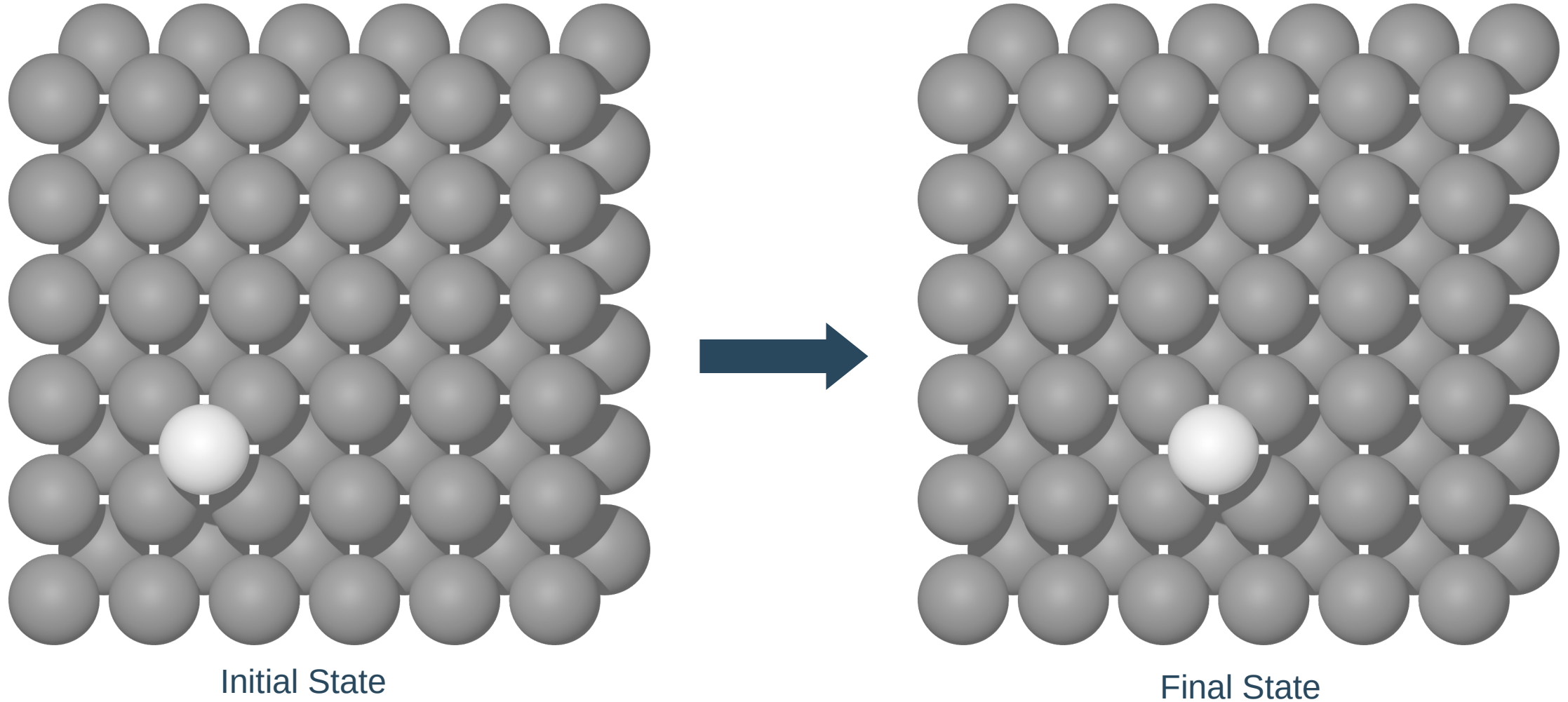
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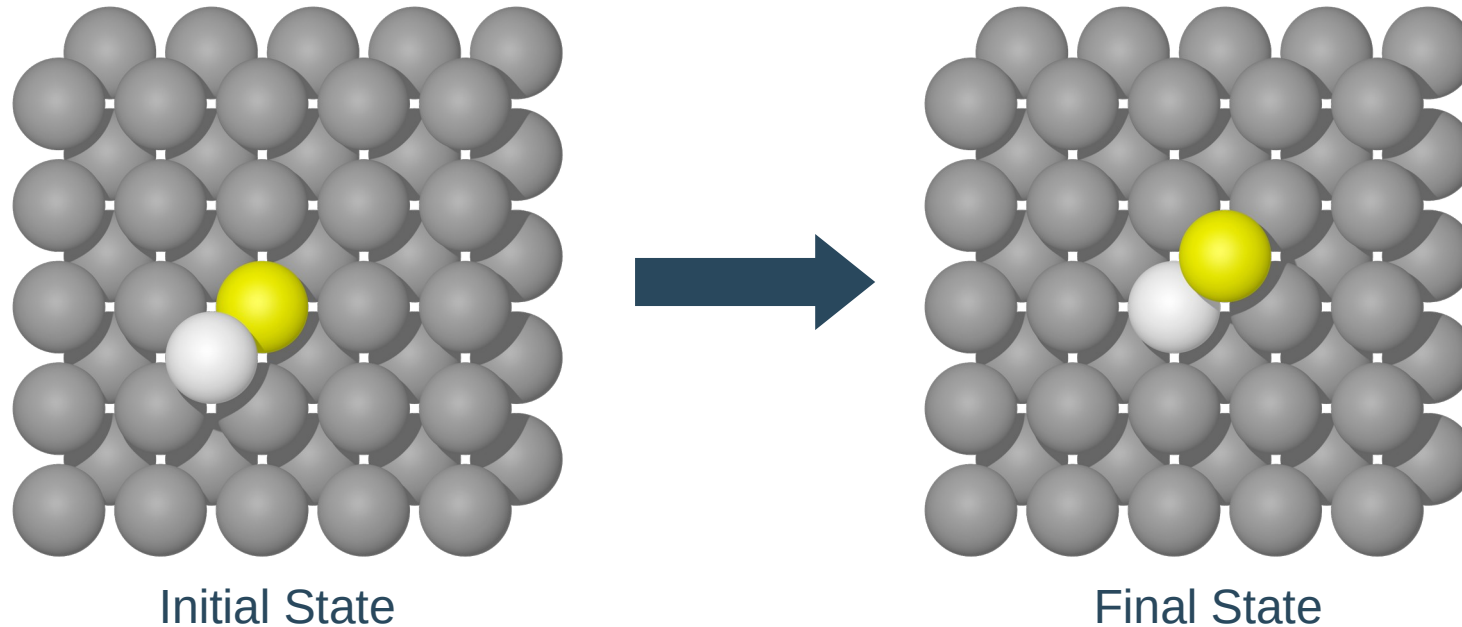
Demo Time Please Look at the Jupyter Notebook



The Simplest Example: Direct Hop of Adatom on FCC(100) Pd
With Classical Force Field (EAM)



Your Turn! Exercise 1: Exchange Terrace Diffusion



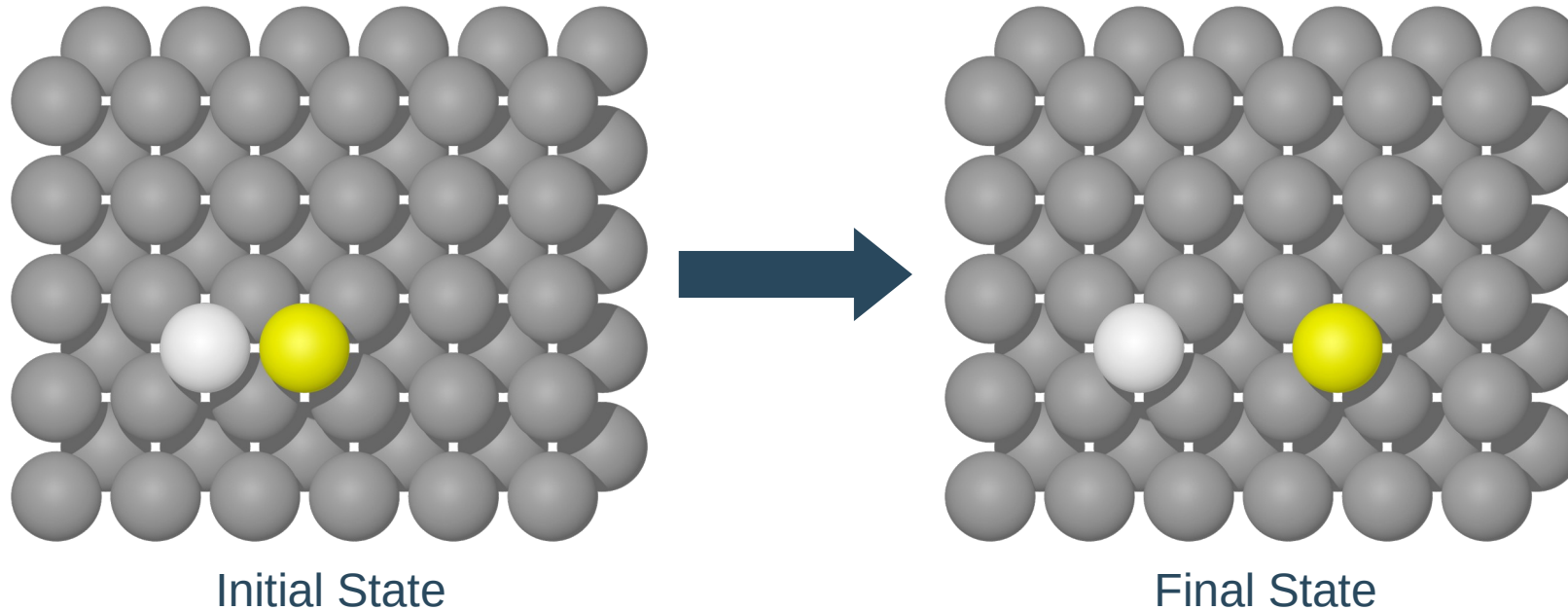
- Consider the exchange terrace diffusion on Pd(100) surface (all atoms shown are Pd)
- 1) Perform ciNEB and find the energy barrier and prefactors in both directions
 - 2) Plot the energy on the minimal energy pathway from ciNEB

CAUTION:

It is an exchange process, white atom is squeezing out the yellow atom.
NOT the white atom jumping to the diagonal site!

When you calculate the vibrational modes, which atoms should be included???

Your Turn! Exercise 2: Bond Breaking Direct Hop?



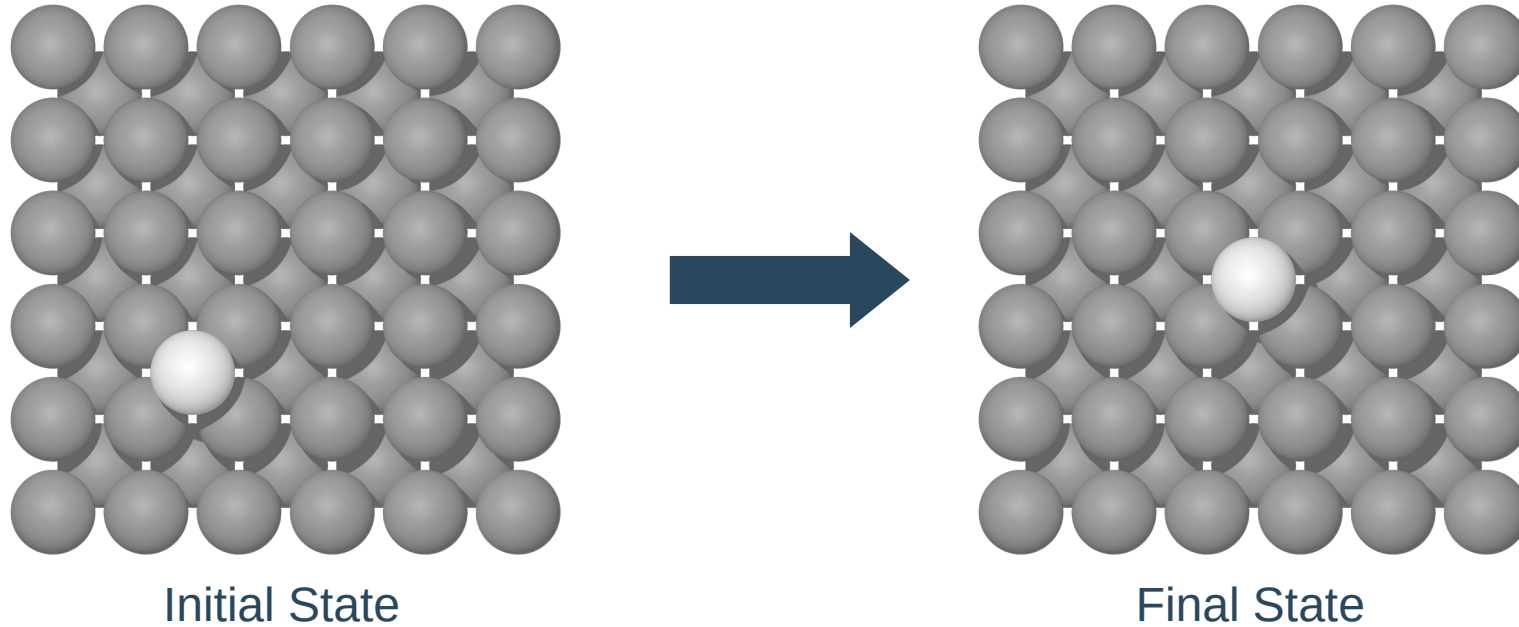
Consider the bond breaking process on Pd(100) surface (all atoms shown are Pd)

- 1) Perform ciNEB and find the energy barrier and prefactors in both directions
- 2) Plot the energy on the minimal energy pathway from ciNEB

CAUTION:

Take a closer look at the MEP plot.

Your Turn! Exercise 3: Hmmm



What about this process, if you perform ciNEB, take a closer look at the results.
Why is it not physical? How would you model this instead???



Footnote

Think about it again!

In general,

You want to calculate energy (construct PES) with a different force field /potential

What to do?

You may identify which atoms to include in the vibrational mode calculation

Do you want to do this identification by-hand every time?

Here the initial and final states are given, no matter they are physical or not

What structures / systems you are going to consider is up to you.

How you organize the work flow to generate these?

If you are choosing other tools instead of ASE, the idea of doing it is basically the same.

How you substitute each step with the tool(s) you choose?