Density-Functional Theory for practitioners - Lecture 6

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(Developed by Patrick Rinke and Milica Todorović)

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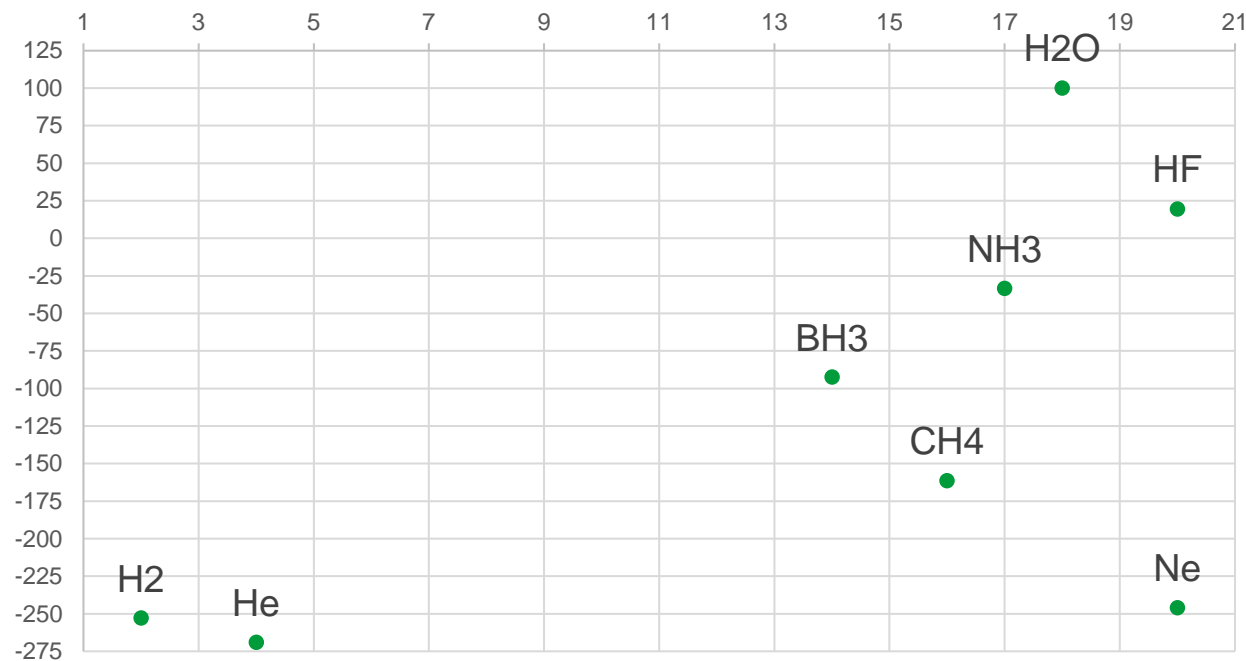**Aalto University**
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Revision

At your table, reflect on all the tutorials:

- What did you find particularly instructive and illuminating about the tutorial exercises?

- What was difficult and could be improved?

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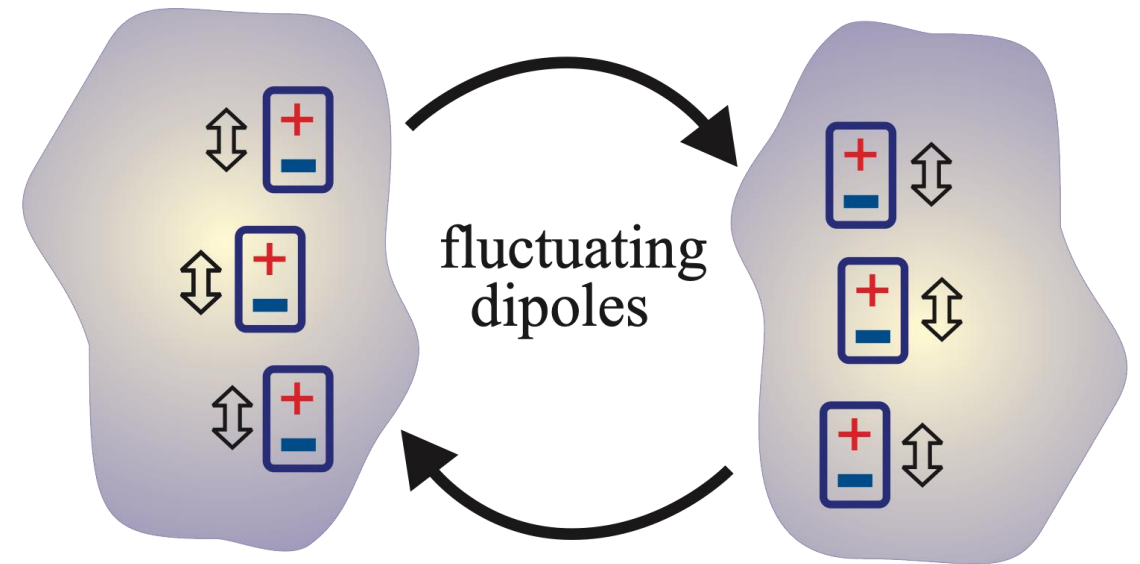# House keeping – Hydrogen, Halogen and dispersion bonds

Molecular weight vs. boiling temperature

Zero point motion creates fluctuating dipoles. Those induce and couple to new fluctuating dipoles.

fluctuating dipoles
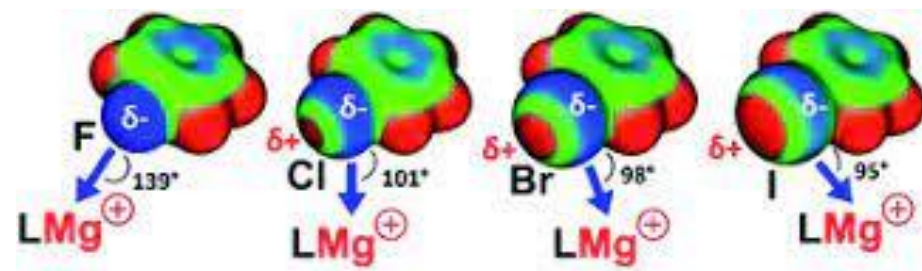
increasing halogen σ-hole

Learning outcomes

After completion of this class you

- are familiar with Transition State Theory.

- have a first understanding of Nudged Elastic Band method.

This lesson

Must know	Should know	Nice to know
Transition state theory	Arrhenius equation	Climbing Image-NEB (CI-NEB) method
Nudged elastic band (NEB)	Diffusion in DFT	The strength and weakness of NEB

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What we can simulate

Atomic structures

Vibrations and phonons

Electronic properties

Molecular Dynamics

What we can simulate

Atomic structures

Vibrations and phonons

Electronic properties

Molecular Dynamics

What we cannot simulate yet

Phase transitions

Conformational rearrangements

Reactions

Diffusion

What we cannot simulate yet
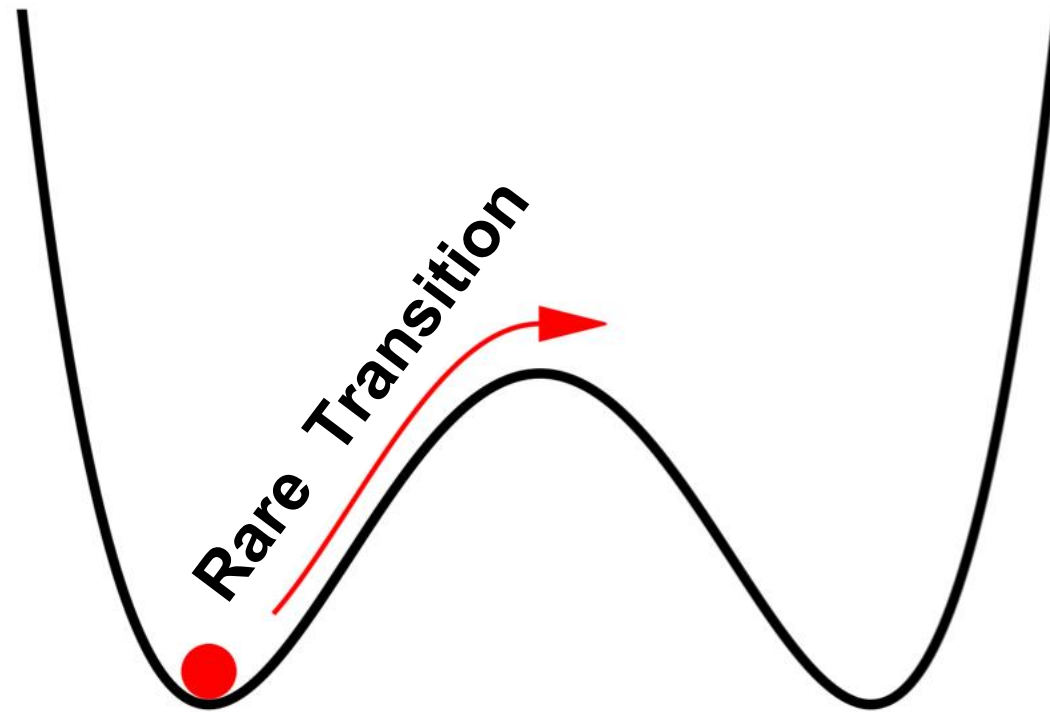
Phase transitions

Conformational rearrangements

Reactions

Diffusion

Why are they difficult to simulate?

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Rare events

Rare Transition

The typical MD step ~ **fs** (10^{-15} s)

If one MD step takes 1second to run,
then simulating a 1 second process would take
32 million years !

Need new methods !

Chemical Reactions

Chemical reactions are complicated and influenced by many factors:

Concentration   Electromagnetic radiation

Pressure   Catalyst

Surface area

Temperature

Solution

How can we predict reaction rates?

Arrhenius equation

Activation Energy

$$k = Ae^{\frac{-E_a}{RT}}$$

Pre-exponential factor

Reaction rate can be calculated by Arrhenius equation

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Arrhenius equation

Activation Energy

$$k = Ae^{\frac{-E_a}{RT}}$$

Pre-exponential factor

Reaction rate can be calculated by Arrhenius equation

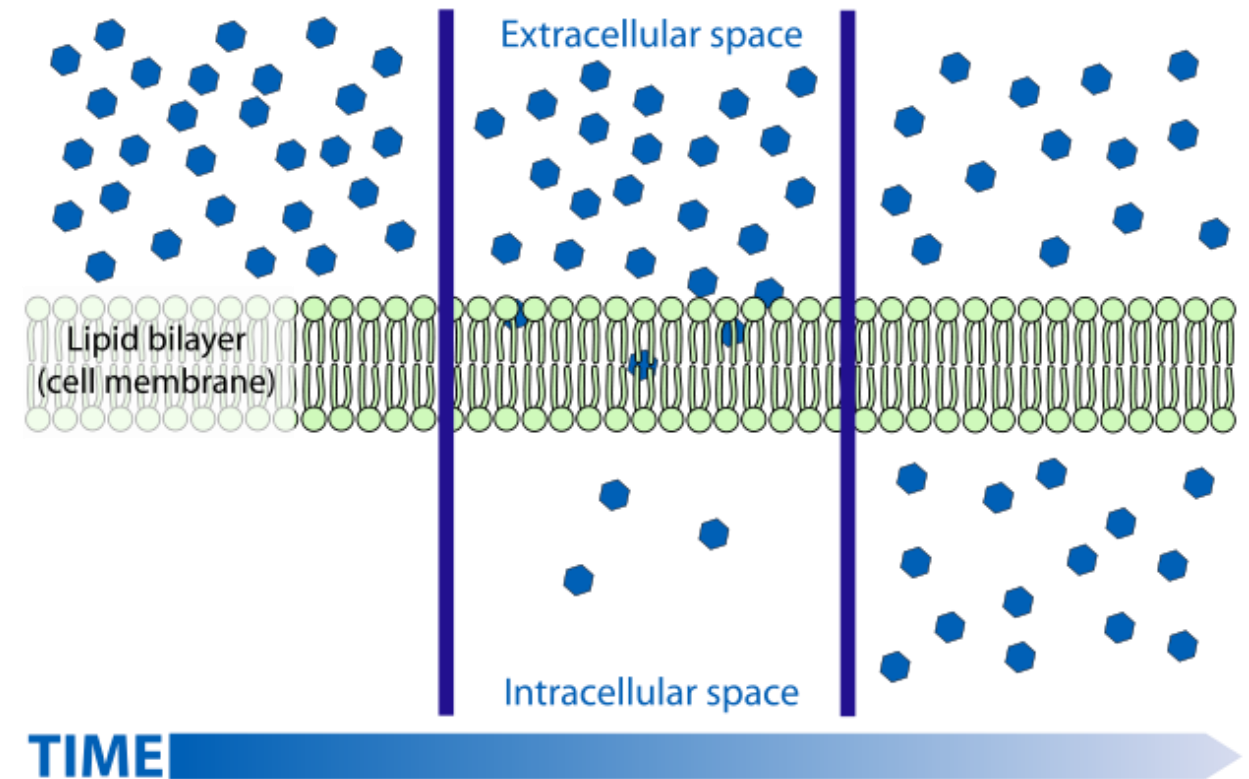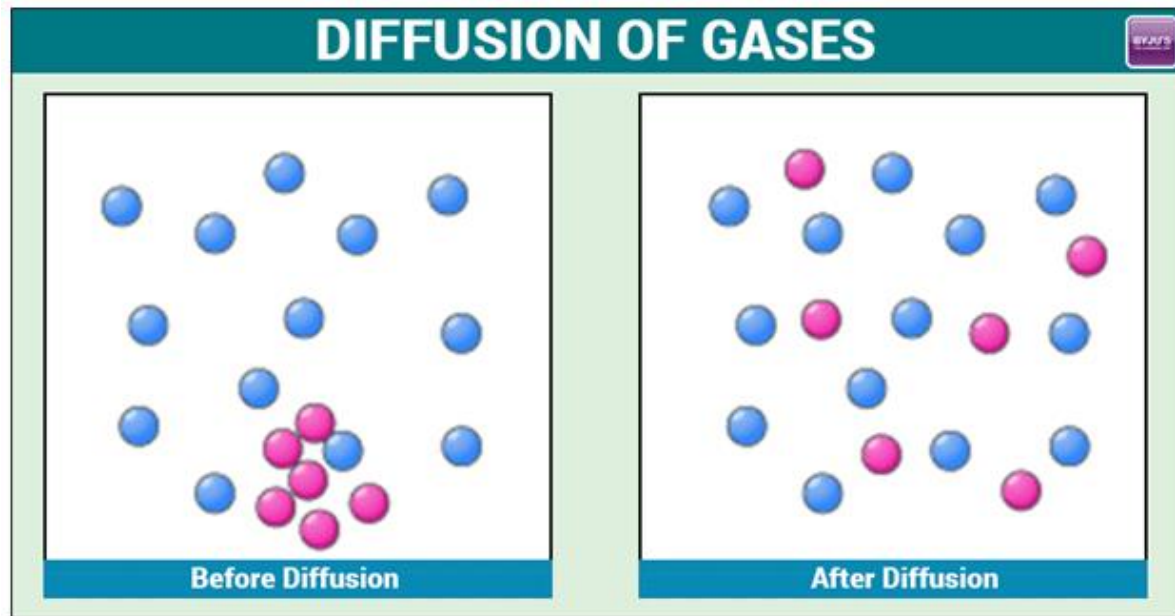The equation is quite a general equation for activated processes

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Arrhenius equation

Activation Energy

$$k = Ae^{\frac{-E_a}{RT}}$$

Pre-exponential factor

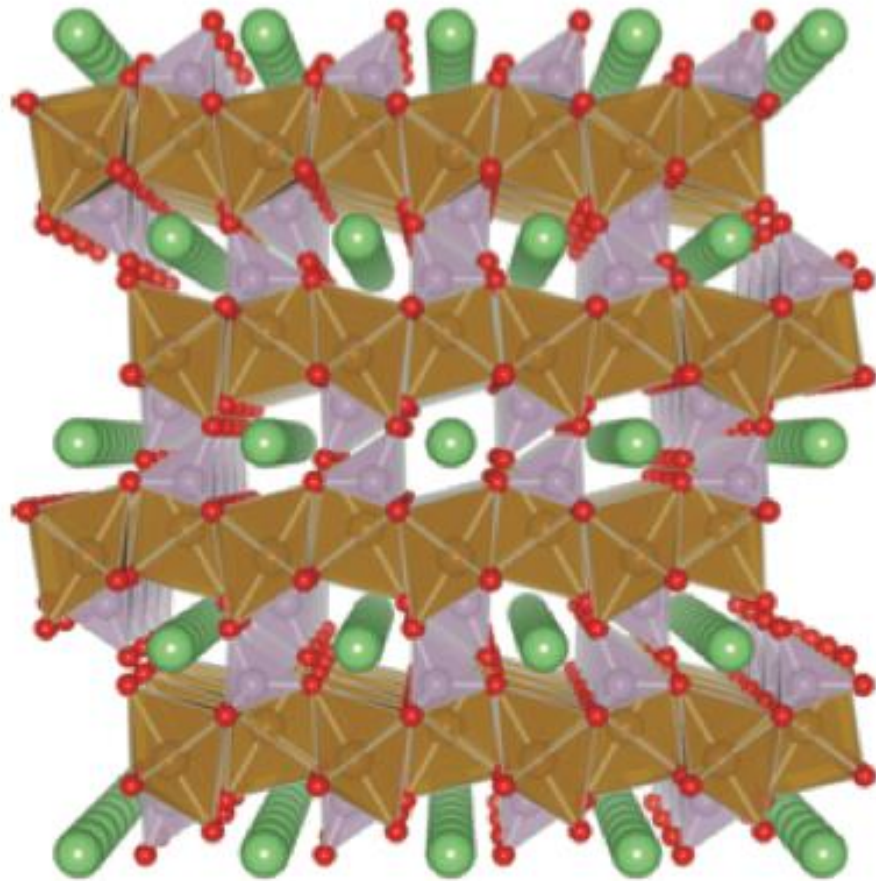We can get **A** and **E$_a$** by using transition state theory !

Diffusion in general

DIFFUSION OF GASES

Before Diffusion — After Diffusion

Extracellular space

Lipid bilayer (cell membrane)

Intracellular space

TIME

Diffusion is net movement of anything (e.g., atom, ions, molecules) from a region of higher concentration to a region of lower concentration.

Diffusion is driven by a gradient in concentration.

Diffusion in DFT

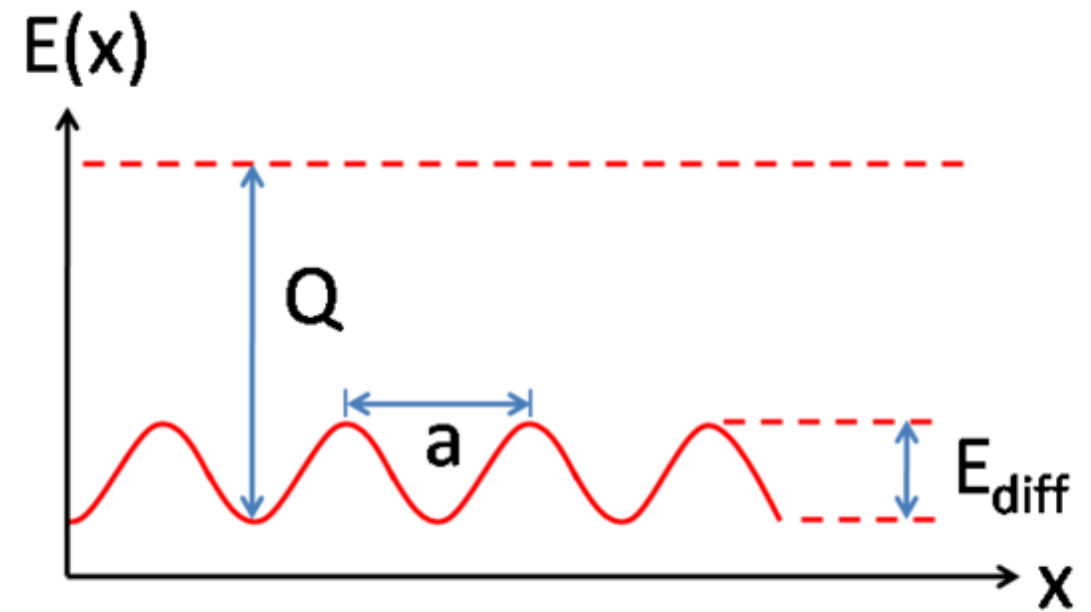Using DFT we can study the diffusions of an atom or few atoms on surfaces or in bulk systems
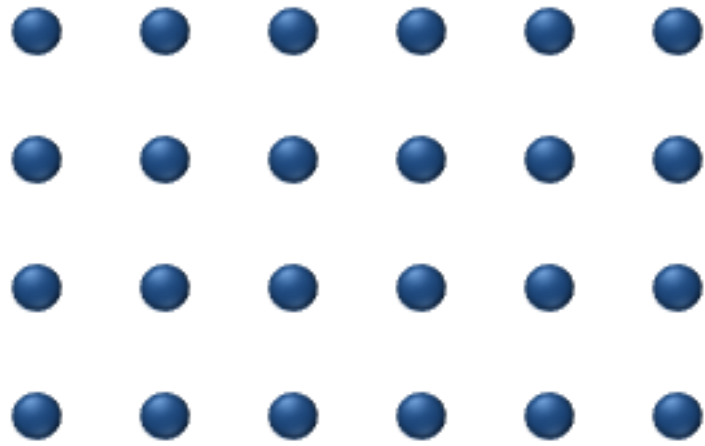

Li$^+$ diffusion path in LiFePO$_4$

Pt$_4$ diffuses on MgO (100) surface

Malik *et al*, Nano Letters, 2010

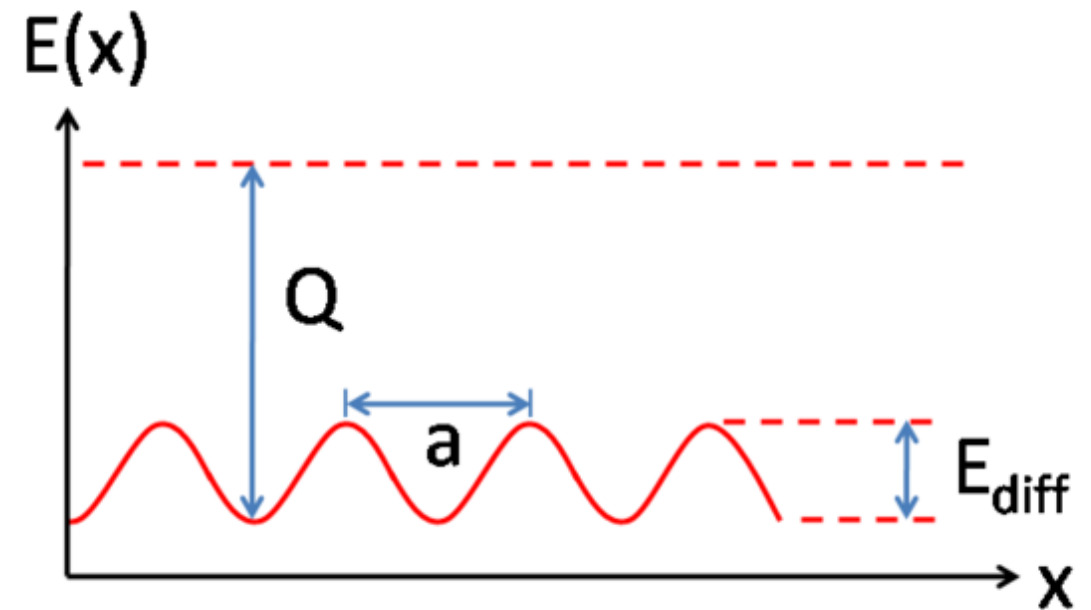**Aalto University**
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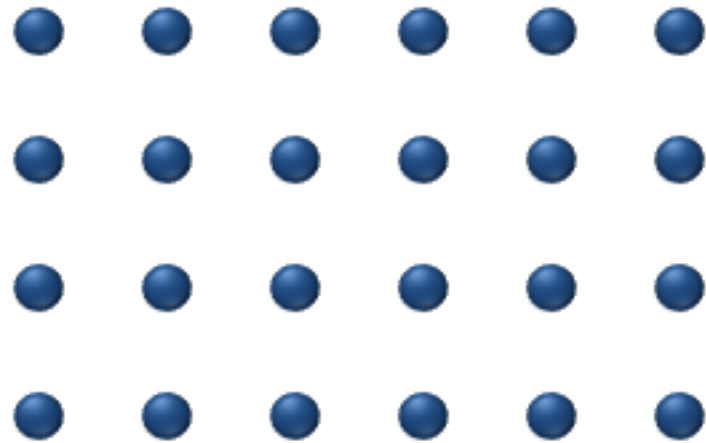
Diffusion rate

Potential energy barrier

$$\Gamma = \nu e^{\frac{-E_{diff}}{k_B T}}$$
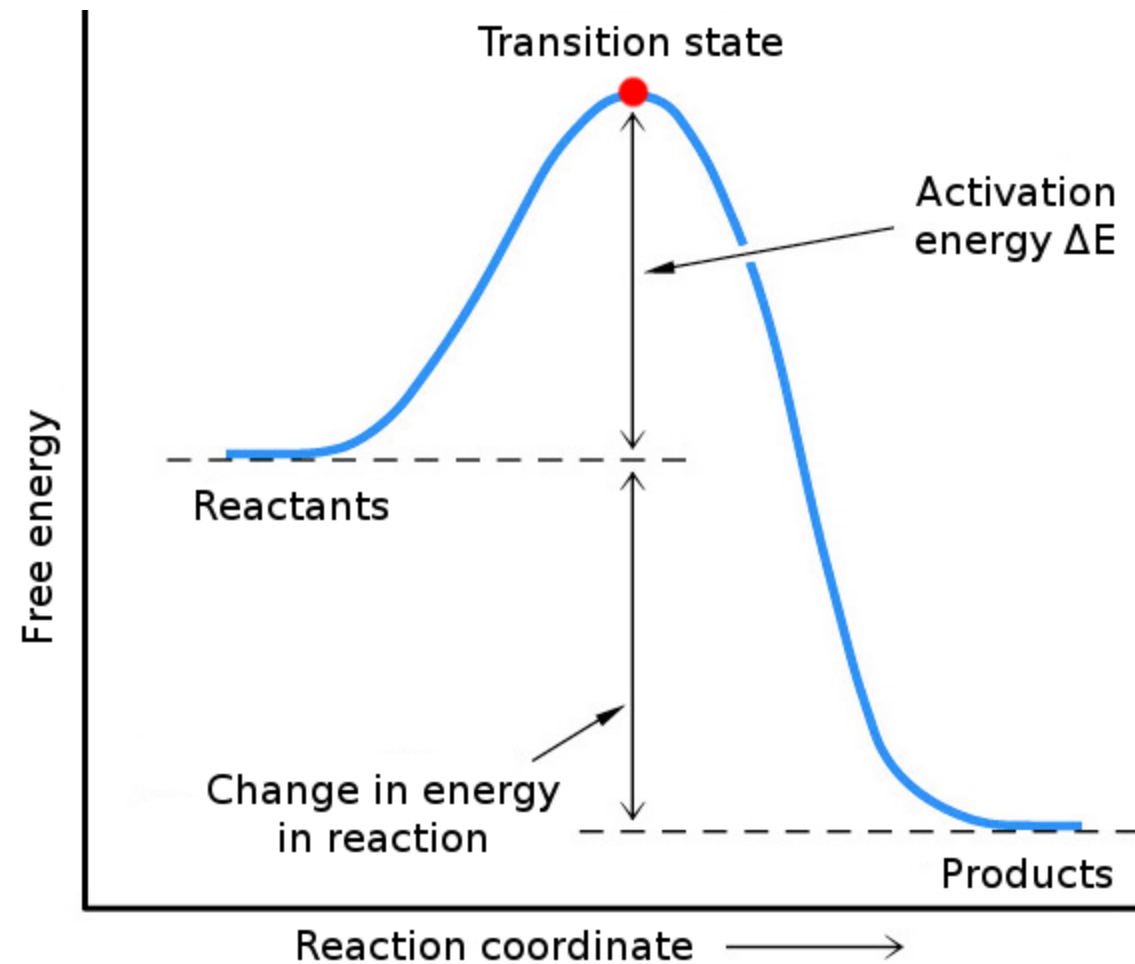
Attempt frequency

Diffusion rate

$$\Gamma = \nu e^{\frac{-E_{diff}}{k_B T}}$$

We can get ν, $\mathbf{E_{diff}}$ by using transition state theory !

Activation energy

Reaction rate in Transition State Theory depends on the activation energy ΔE

Transition State Theory (TST)

TST relies on two basic assumptions:

⭐ The rate is slow enough that a **Boltzmann distribution** is established and maintained in the reaction state.

⭐ A dividing surface of dimensionality **D-1** can be identified such that a reacting trajectory going from the initial state to the final state **only crosses** the dividing surface **once**.
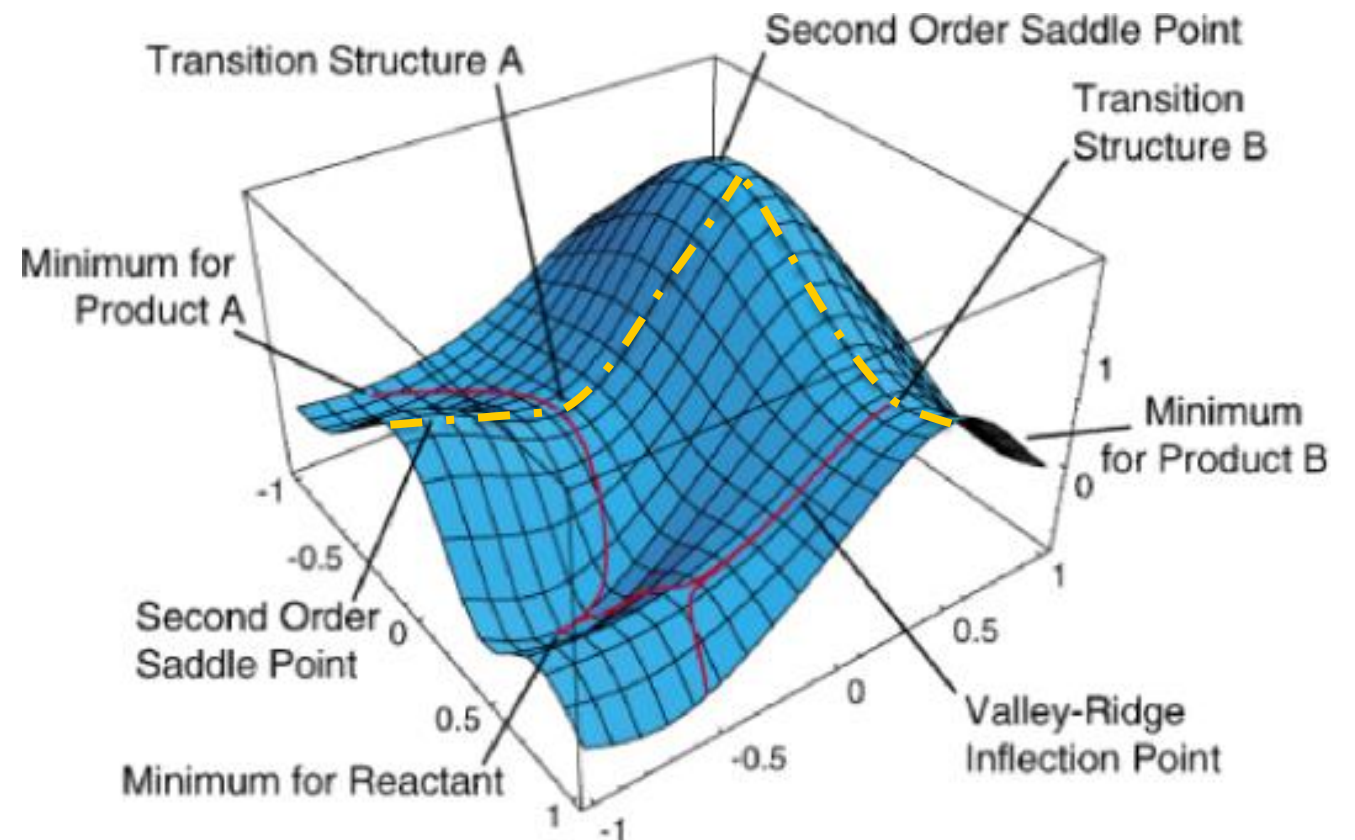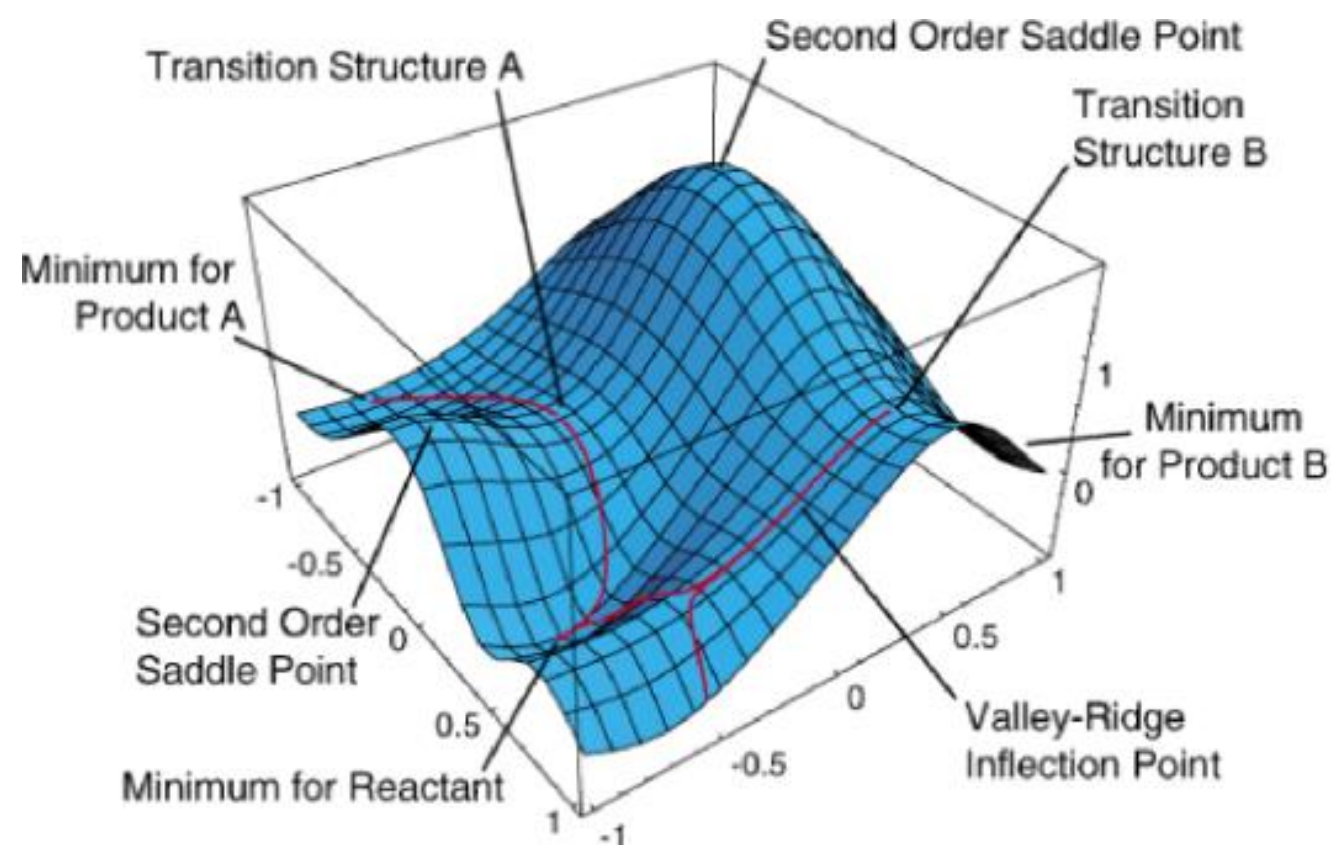

2D PES example → **1D** line of potential ridge

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Key concepts in TST
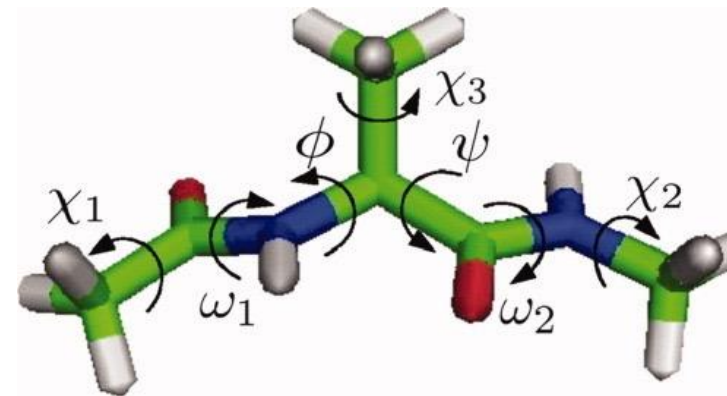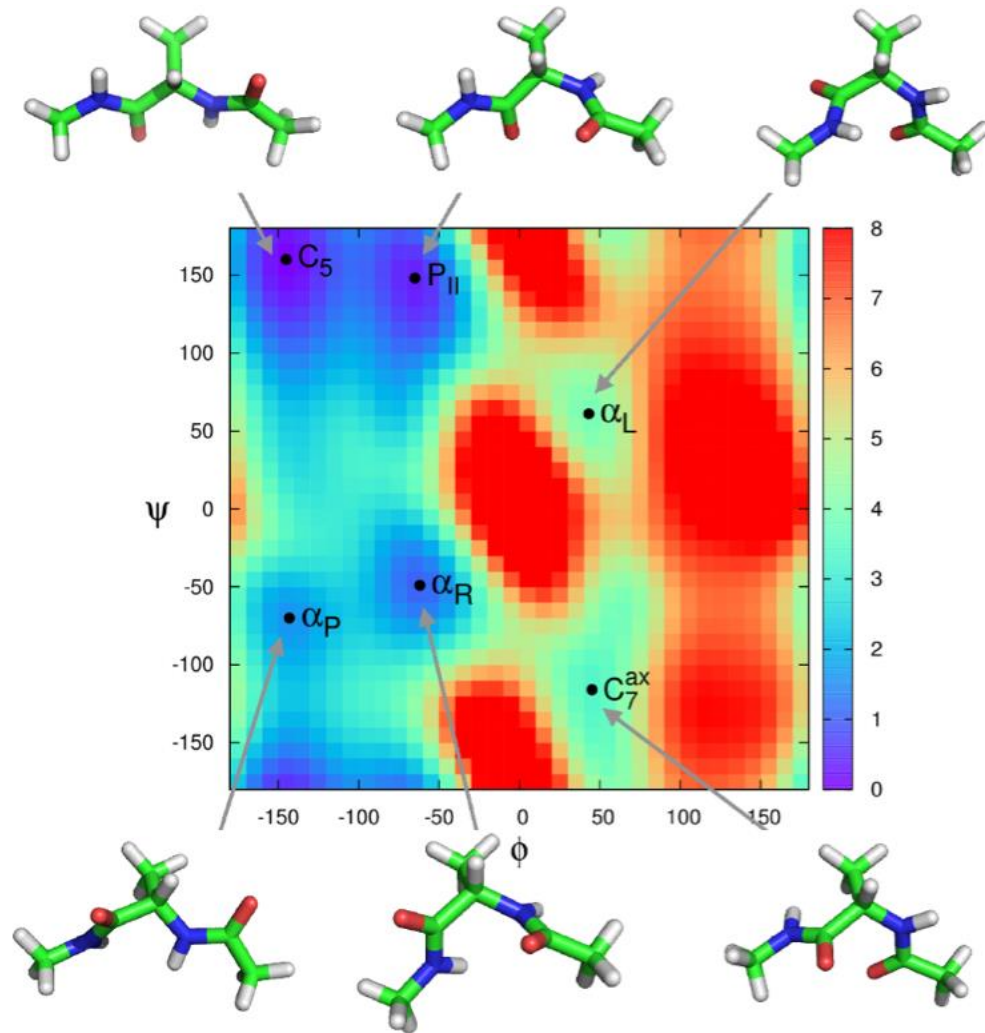
Potential Energy Surface

Minimum Energy Path

Transition state

Potential Energy Surface

A **potential energy surface (PES)** describes the **energy** of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms.
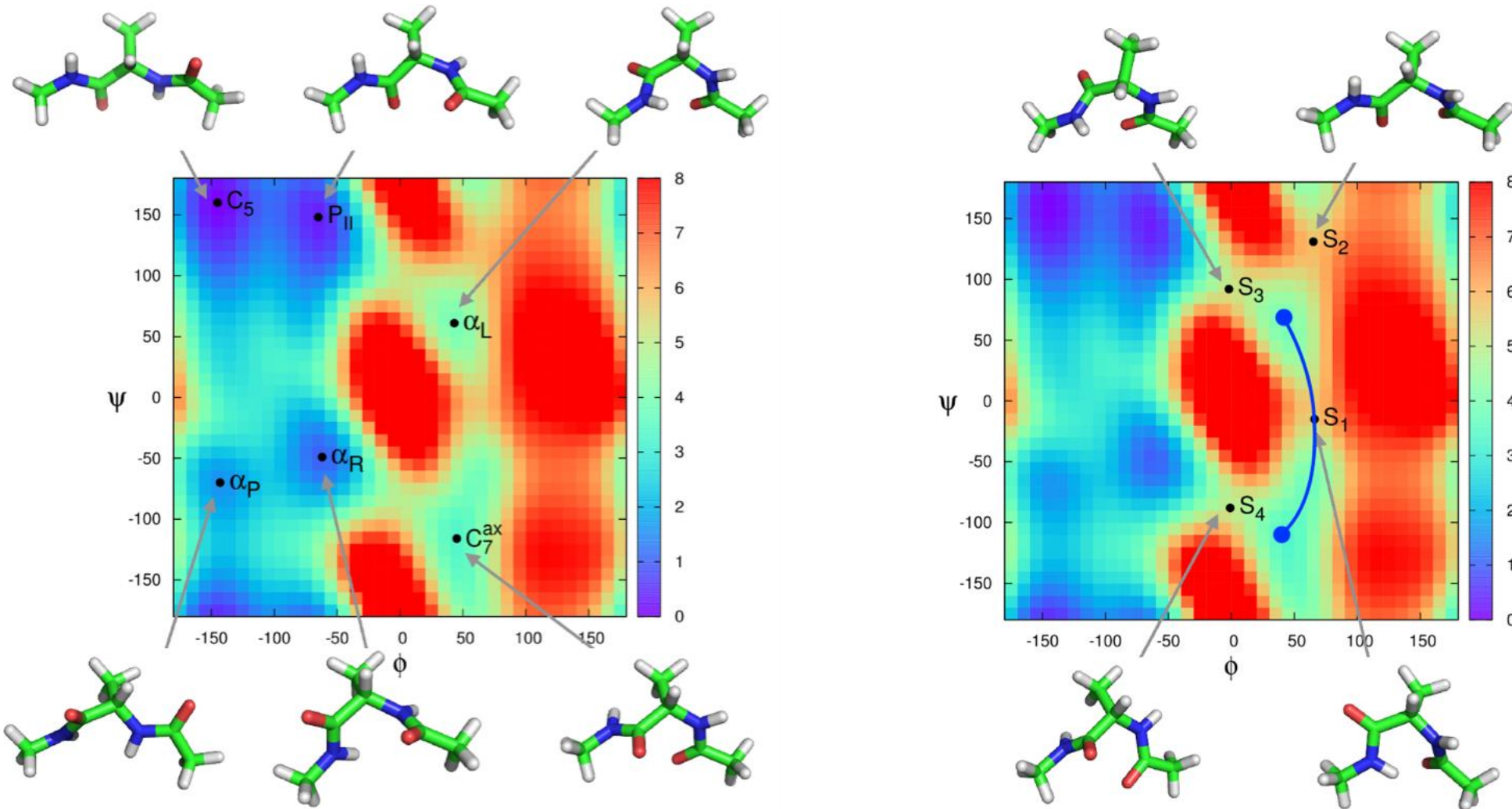

Alanine dipeptide

Jaillet et al., J. Comput. Chem. 32 3464-3474 (2011)

Potential Energy Surface

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Jaillet et al., J. Comput. Chem. 32 3464-3474 (2011)

Minimum Energy Path and Transition state

⭐ **Minimum Energy Path (MEP)**
- a lowest energy path from reactants to products (from one stable configuration to another)

⭐ The potential energy maximum along the MEP is called
- **transition state (TS)**.
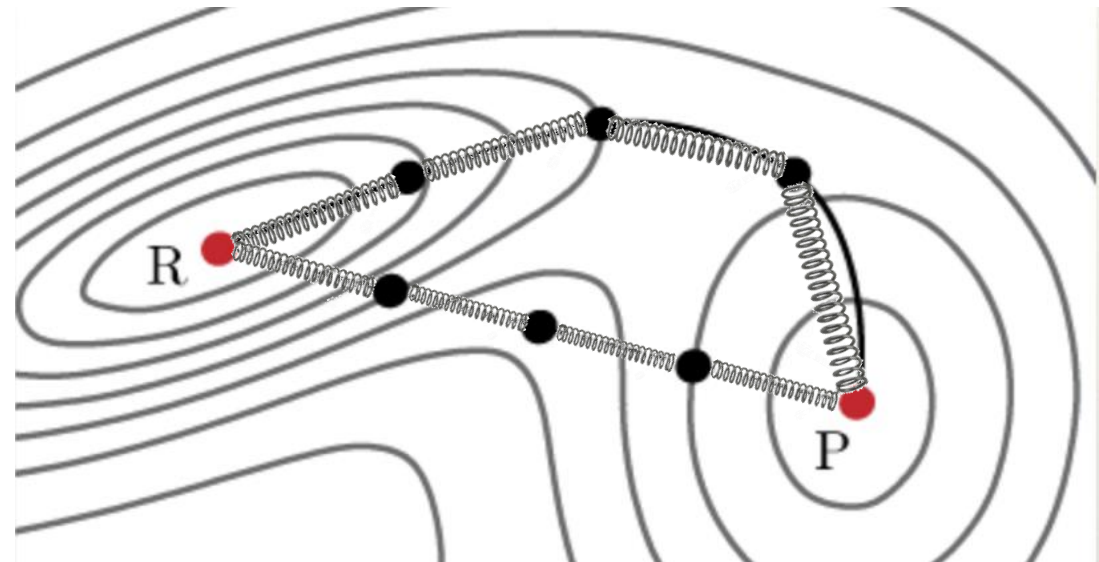

● Minima
● Saddle Points
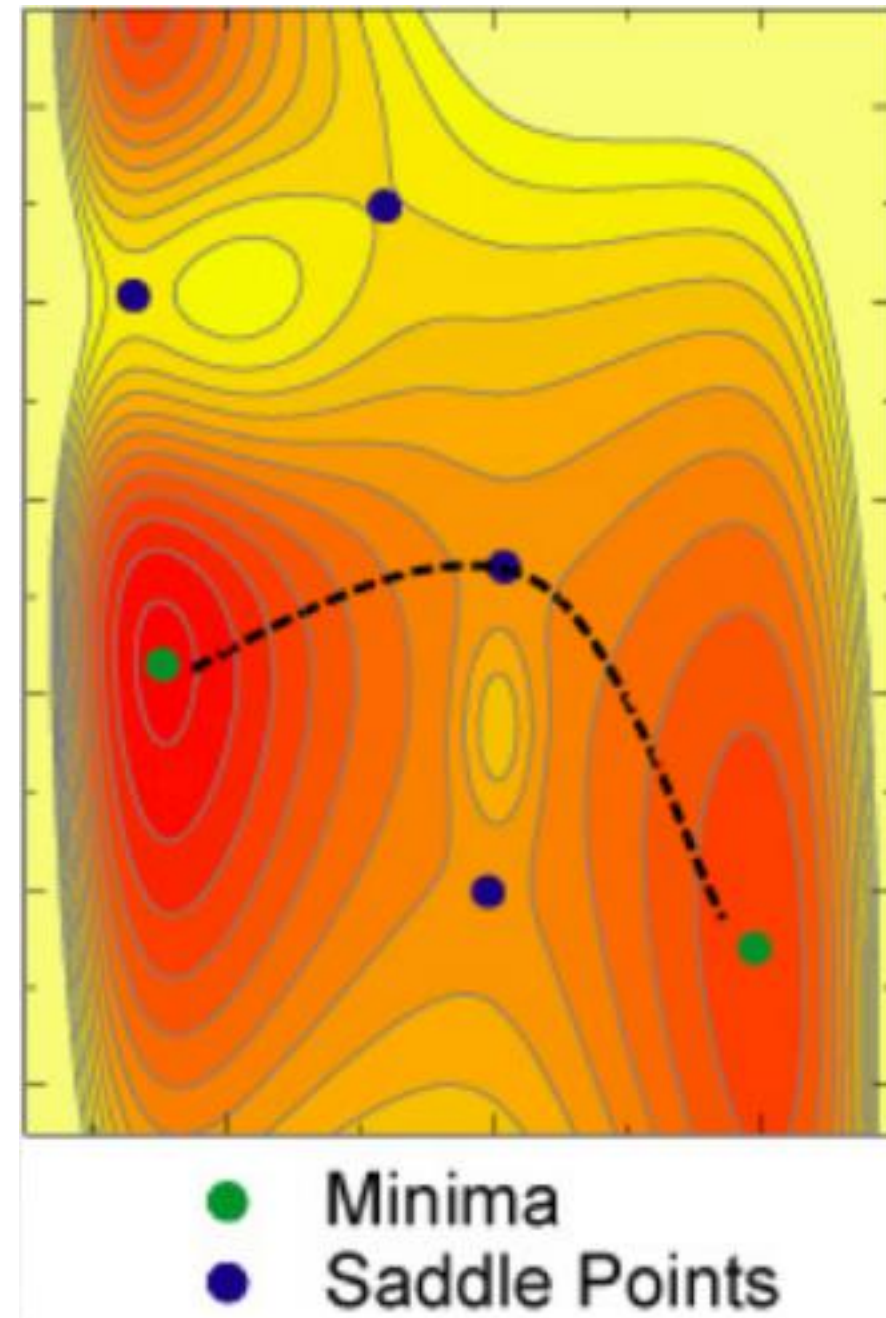
Transition state search: elastic band method

A string of **N-1** images is created between the initial **R** and final **P** configurations

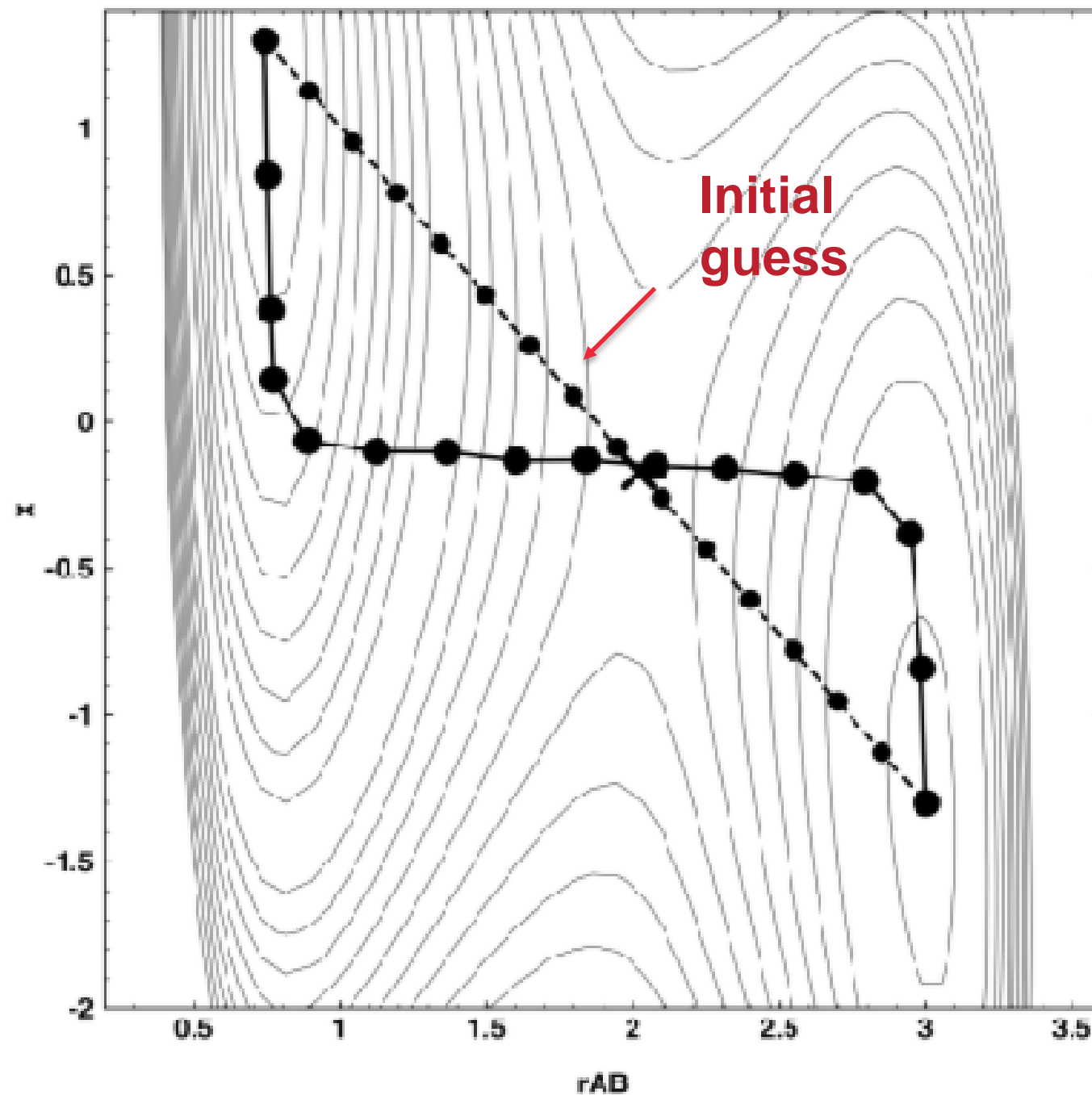Images are coupled via virtual springs with a constant **k**

Eq(1) is minimized

$$S(\mathbf{R}_1, \ldots, \mathbf{R}_N) = \sum_{i=1}^{N-1} E(\mathbf{R}_i) + \sum_{i=1}^{N} \frac{k}{2}(\mathbf{R}_i - \mathbf{R}_{i-1})^2 \quad (1)$$
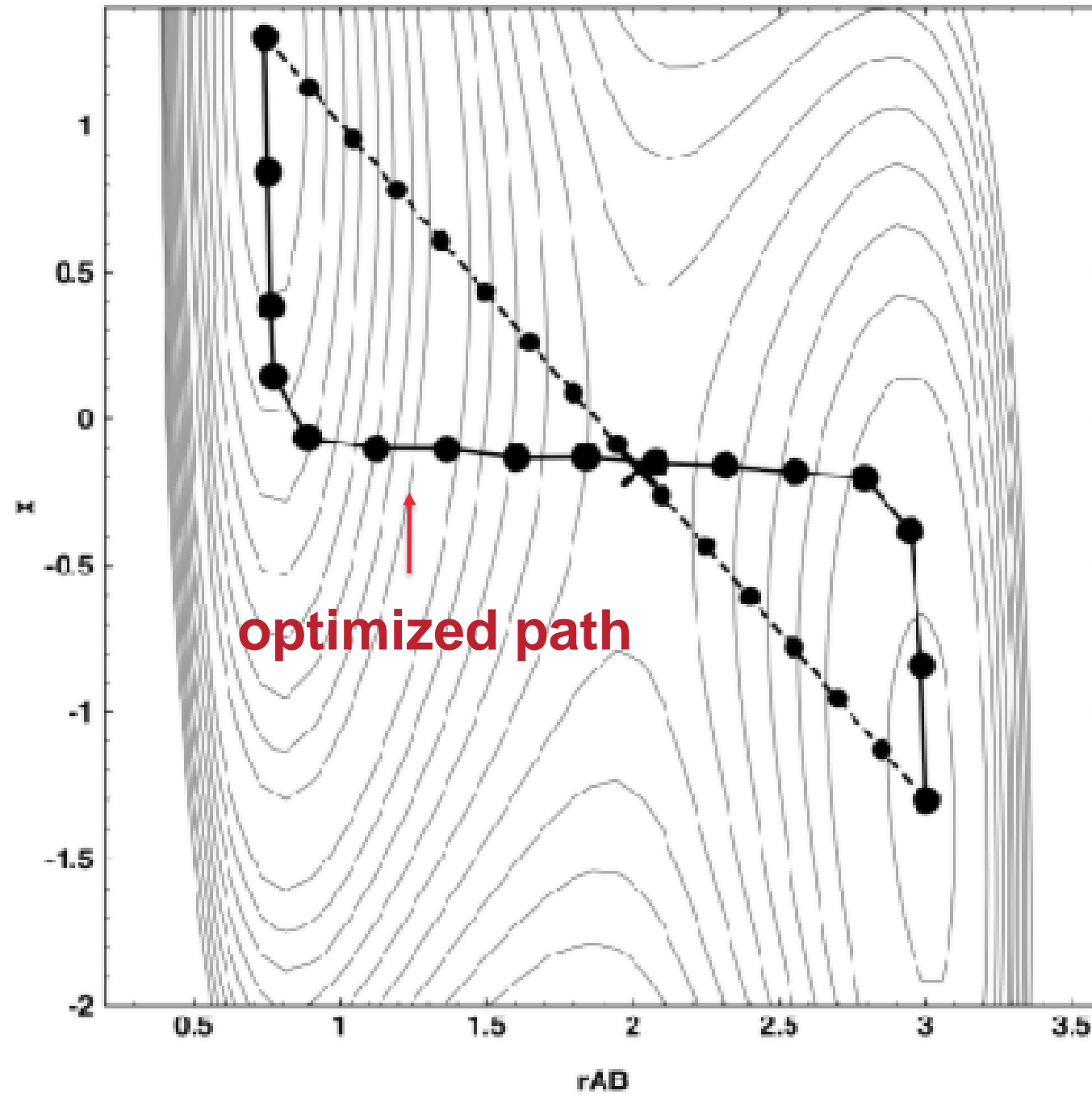
True energy   Spring potential energy

Energy path optimization
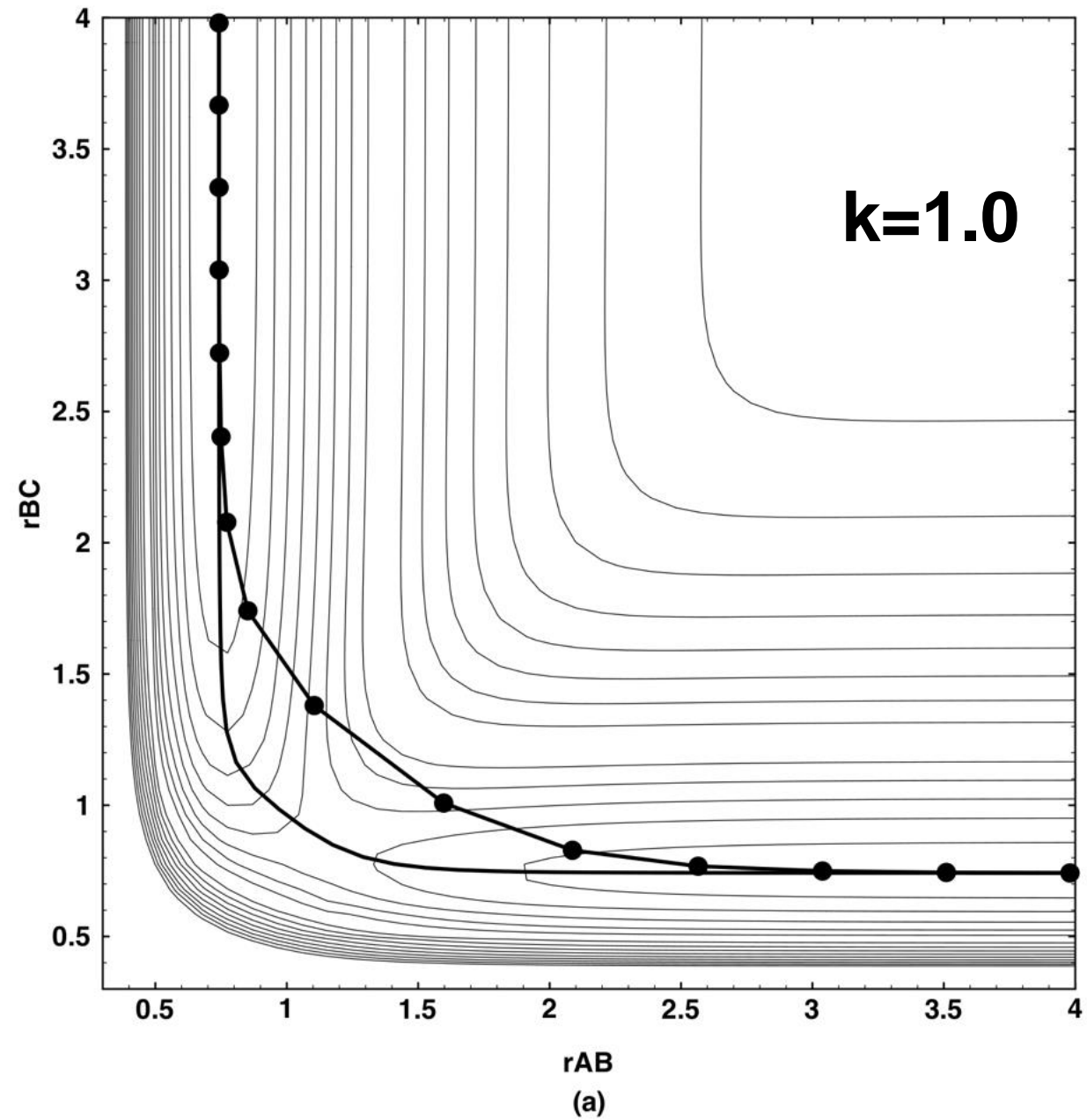

Initial guess

Energy path optimization

optimized path

Problems of elastic band

k=1.0

Too hard EB   Cutting corners

Problems of elastic band

k=0.1

Too soft EB   Sliding down

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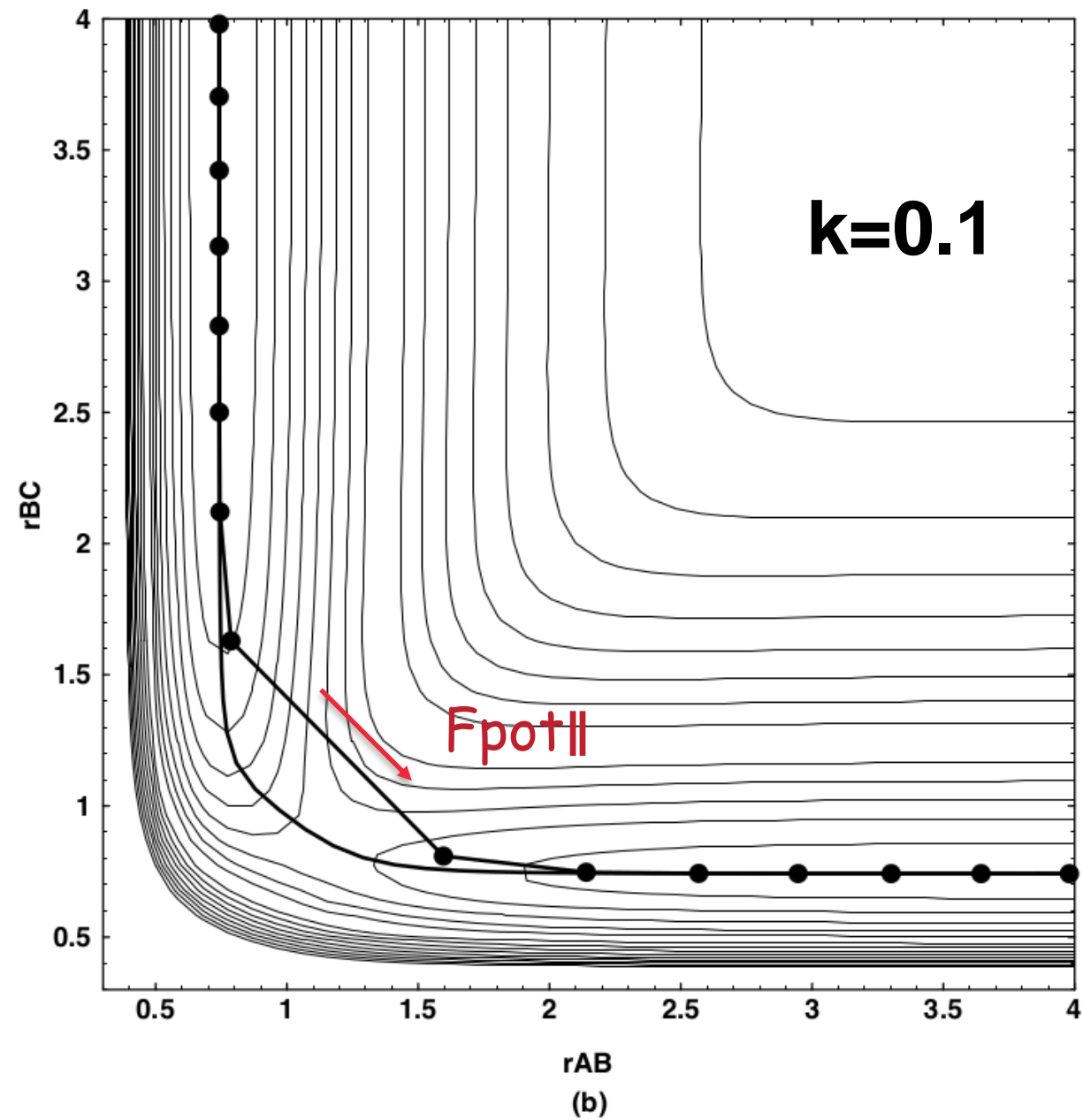School of Science

Problems of elastic band

(a)
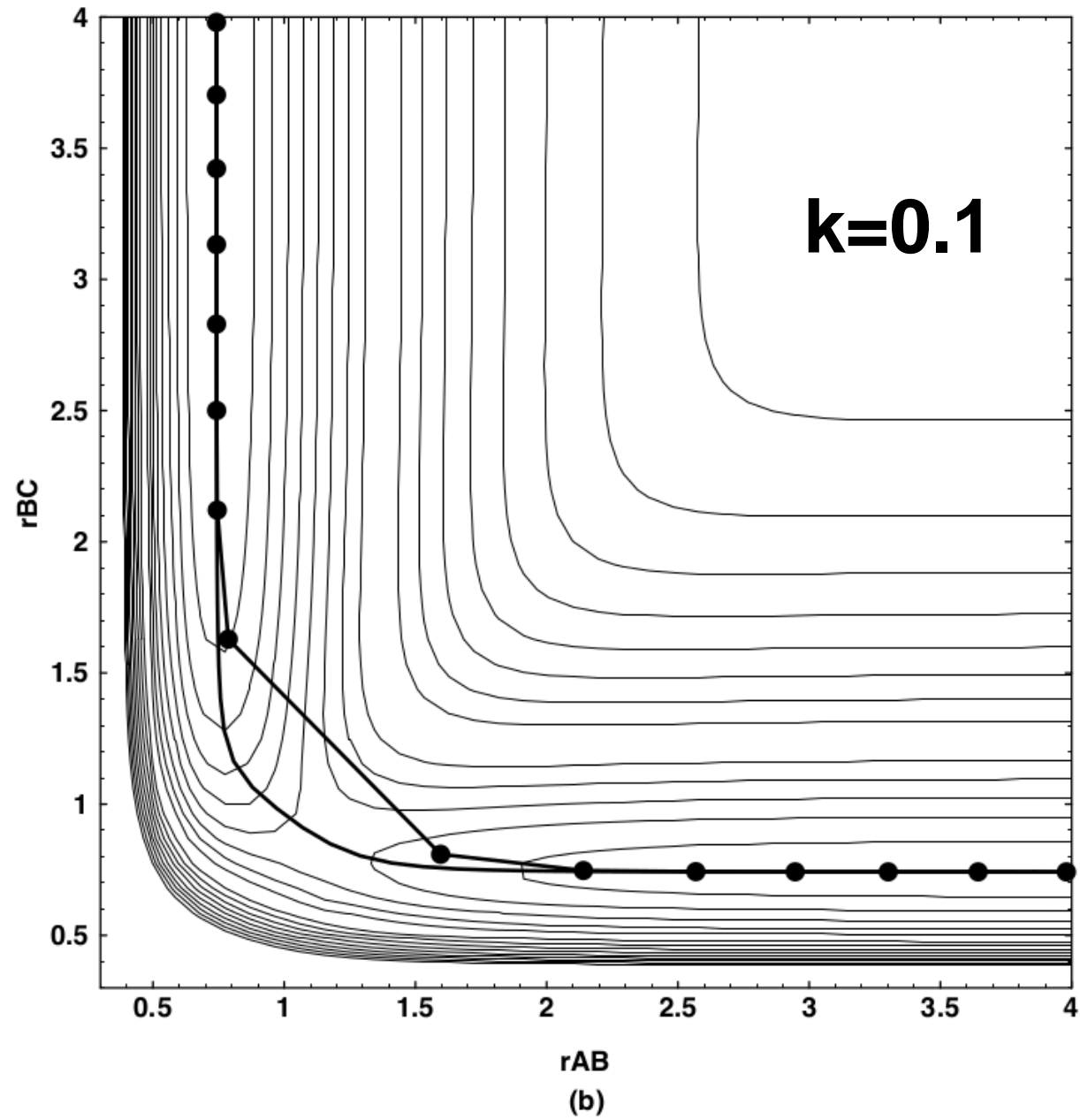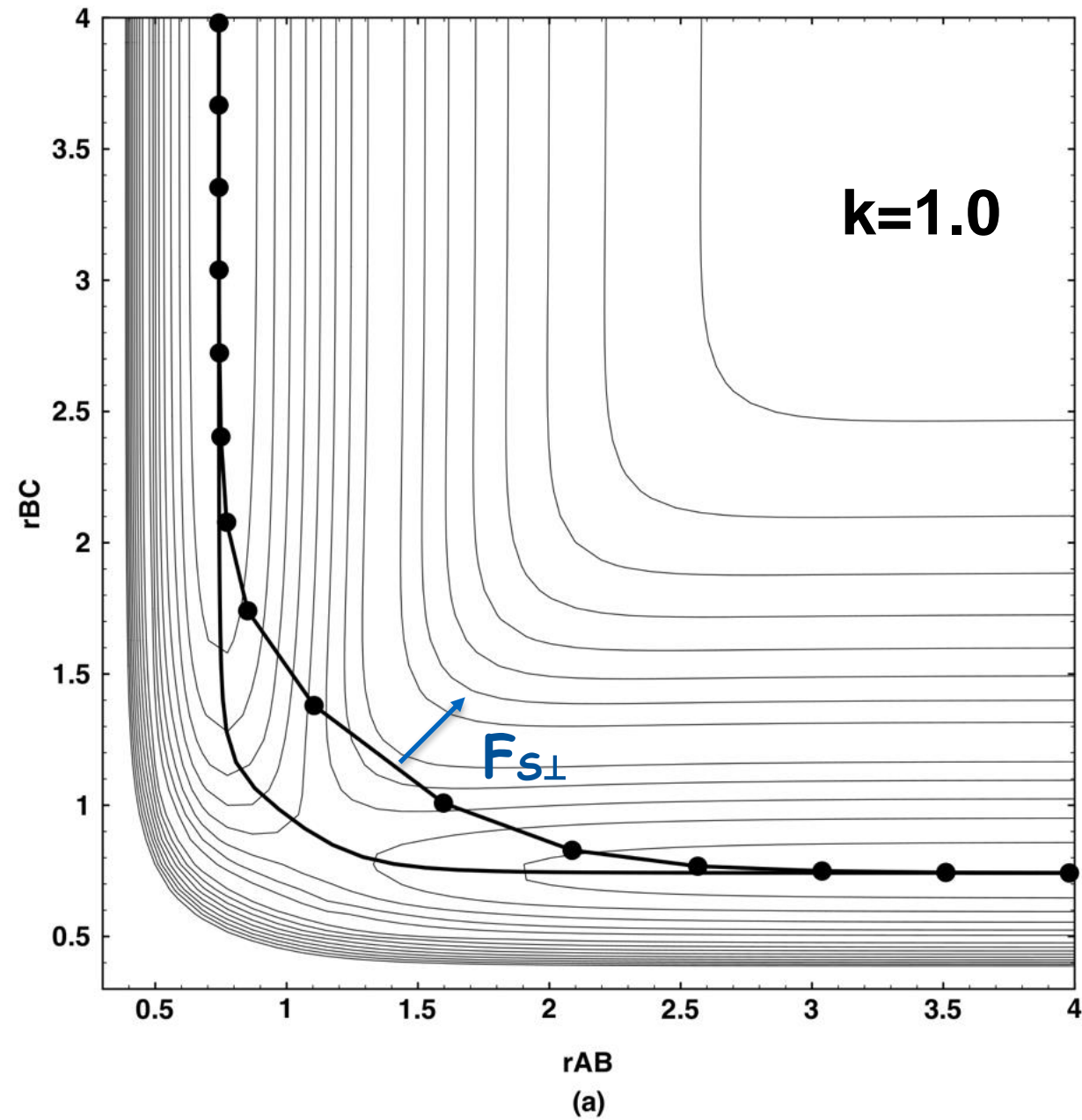
Perpendicular spring force **F$_{s\perp}$** cause corner cutting

Problems of elastic band

Parallel energy-landscape force $F_{pot\parallel}$ causes imagine sliding

Nudged Elastic Band (NEB)

A solution: "nudging " of the forces and introduce artificial force $\mathbf{F}_i^{NEB}$

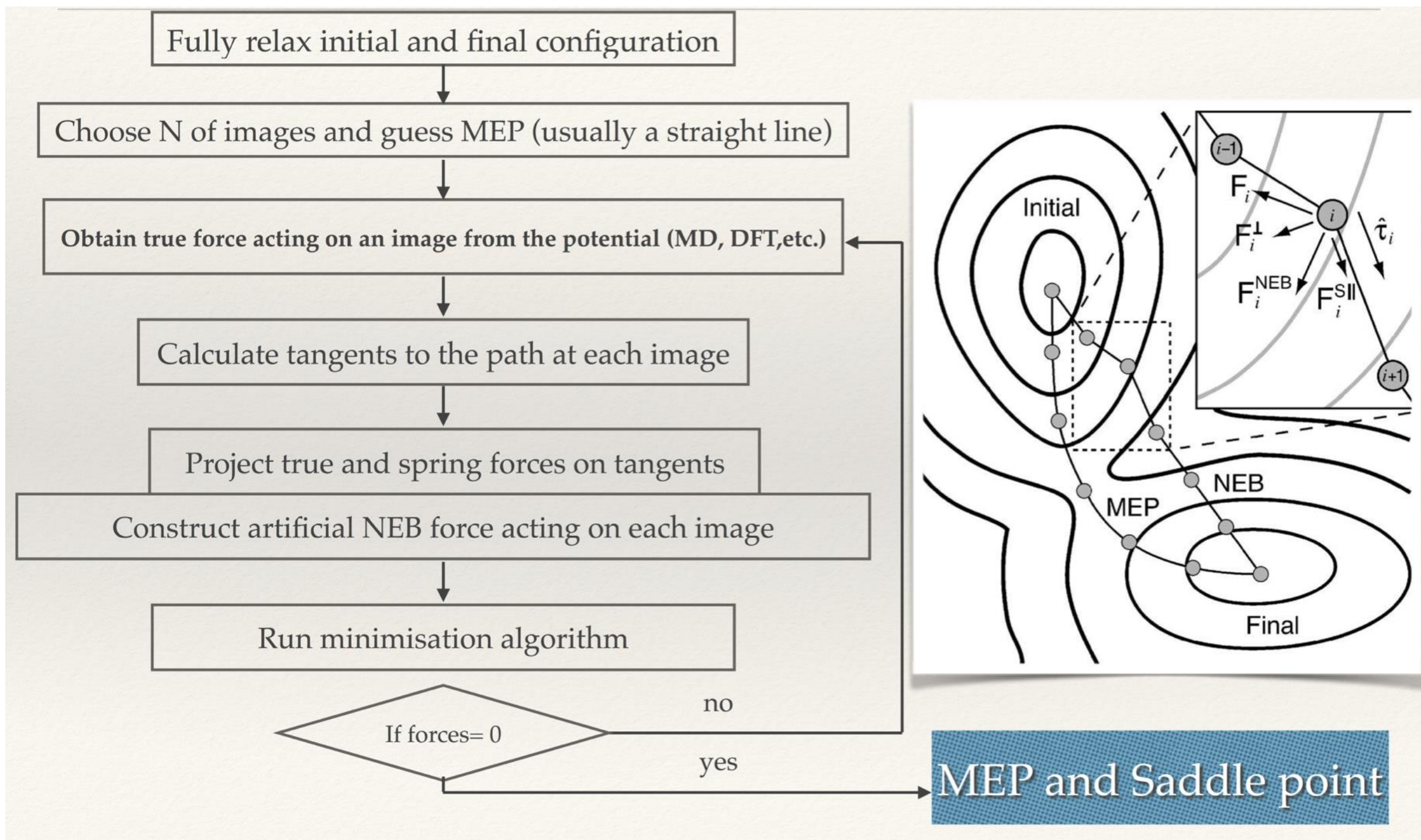Problematic components are substrated from the force:

$$F_i^{NEB} = F_i - {\color{red}F_i^{\|}} + F_i^{S} - {\color{blue}F_i^{S\perp}}$$

$$= F_i^{\perp} + F_i^{S\|}$$
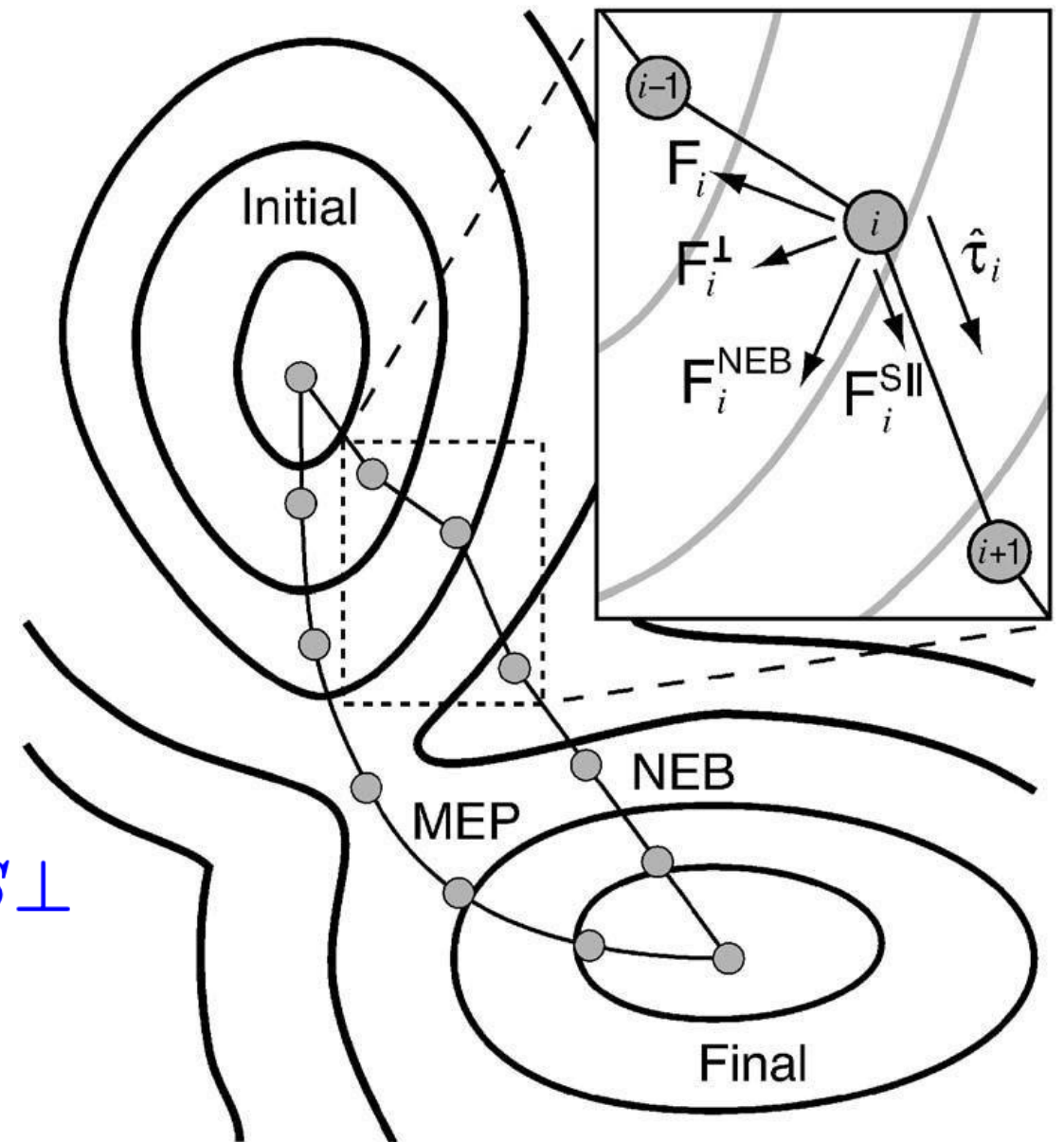
H. Jónsson, G. Mills and K. W. Jacobsen, 1998

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NEB algorithm

Fully relax initial and final configuration

Choose N of images and guess MEP (usually a straight line)

Obtain true force acting on an image from the potential (MD, DFT,etc.)

Calculate tangents to the path at each image

Project true and spring forces on tangents

Construct artificial NEB force acting on each image

Run minimisation algorithm

If forces= 0

no

yes

MEP and Saddle point

Initial

F_i

$F_i^\perp$

$\hat{\tau}_i$

F_i^{NEB}

$F_i^{S\parallel}$

$i-1$

i

$i+1$

NEB

MEP

Final
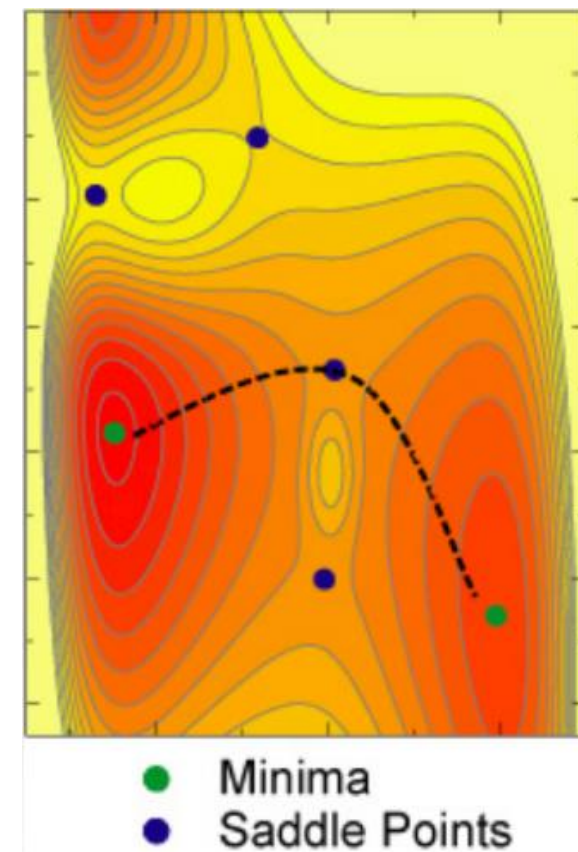
NEB Performance

+ Results always in a continuous MEP

+ Requires only the first energy derivatives

+ Parallelization is trivial

+ Preliminary tool for further exploration

- Requires known local minima

- Multiple MEP may exist

- **Many images may be needed**

- **convergence to a saddle point may not be obtained**

● Minima
● Saddle Points

Climbing Image NEB (CI-NEB)

CI-NEB change the force formula of **the highest energy image** along the band to make sure 'true' TS will be found:

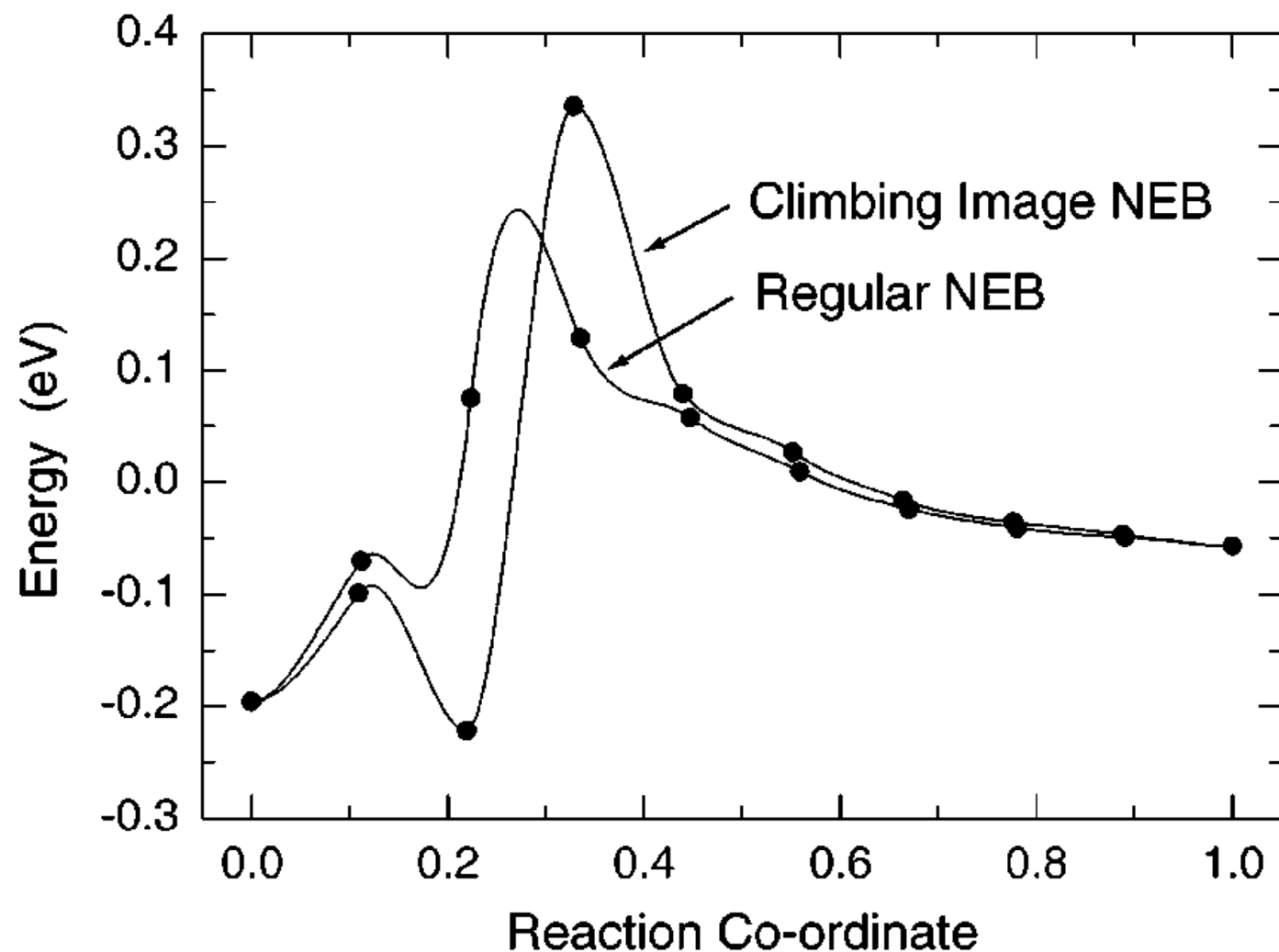$$F_i^{NEB} = F_i - F_i^{\parallel} + F_i^{S\parallel}$$

$$F_{i_{max}}^{CI-NEB} = F_{i_{max}} + 2F_{i_{max}}^{\parallel}$$

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Climbing Image NEB (CI-NEB)

Results: (1) finds the TS more accurately
(2) uses fewer images than NEB

Henkelman *et al.* J. Chem. Phys. 113, 9901 (2000)

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