Density-Functional Theory for Practitioners - Tutorial 6

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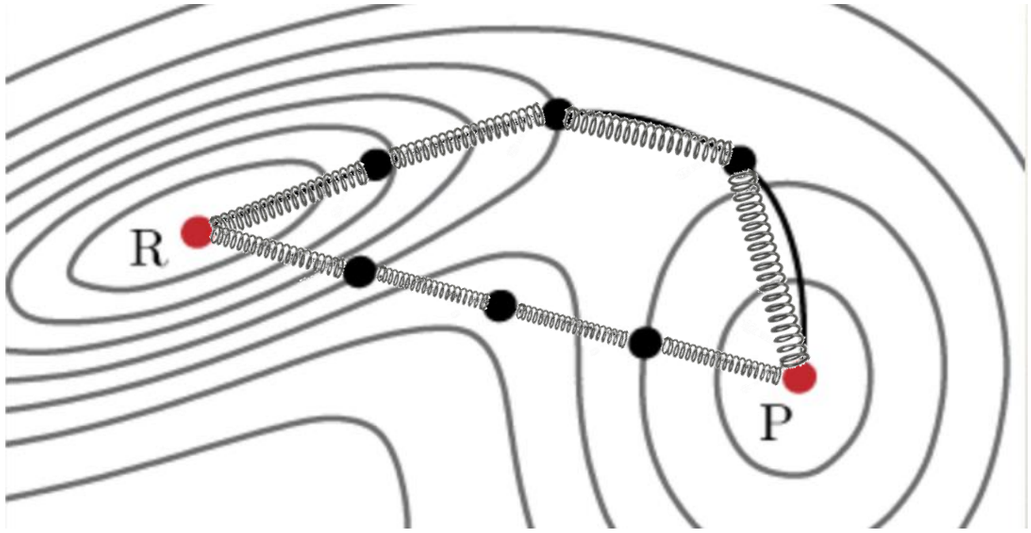
Transition state search: elastic band method

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

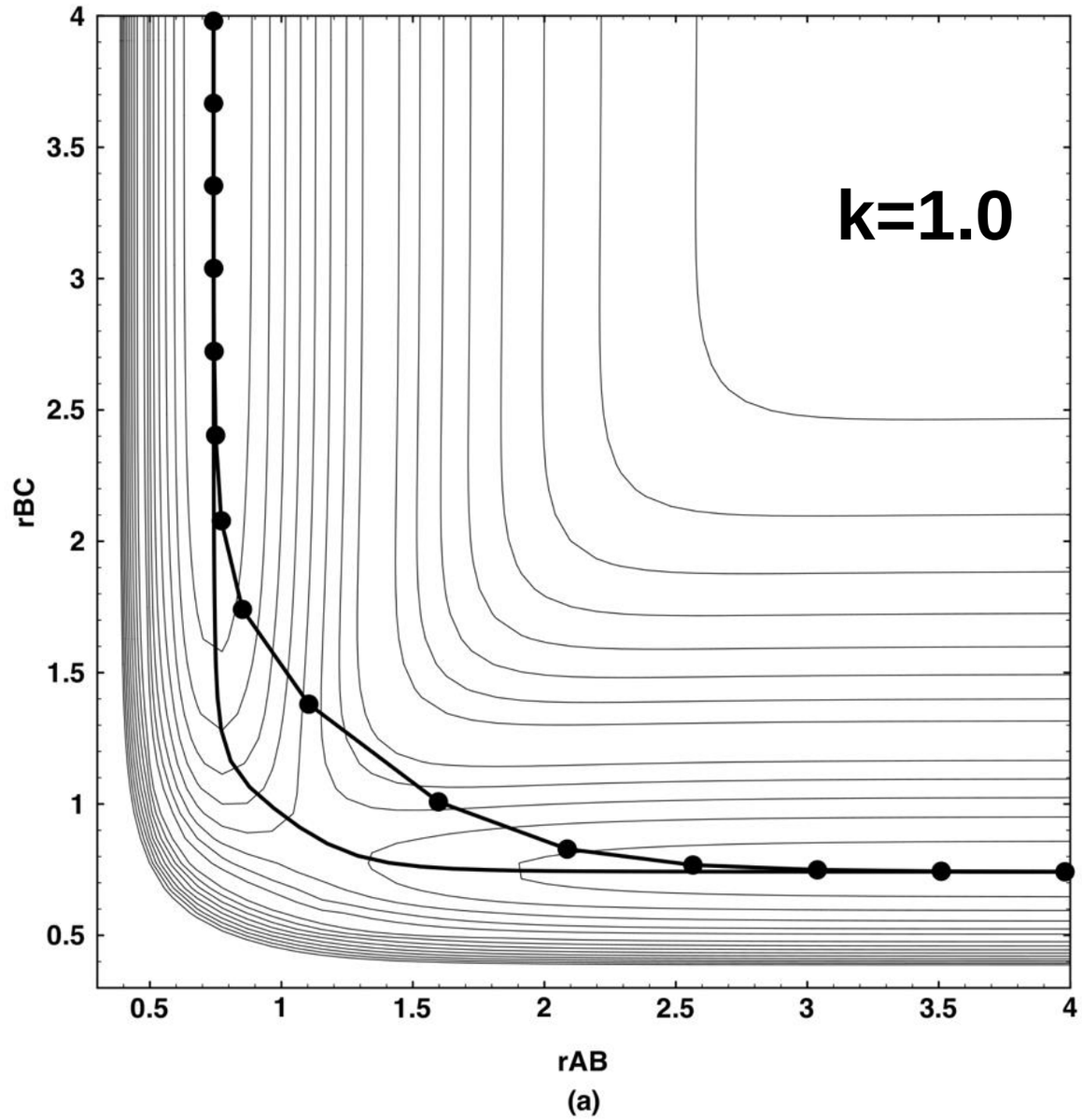


$$S(\mathbf{R}_1,\ldots,\mathbf{R}_N) = \sum_{i=1}^{N-1} E(\mathbf{R}_i) + \sum_{i=1}^{N} \frac{k}{2}(\mathbf{R}_i - \mathbf{R}_{i-1})^2 \quad (1)$$

True energy

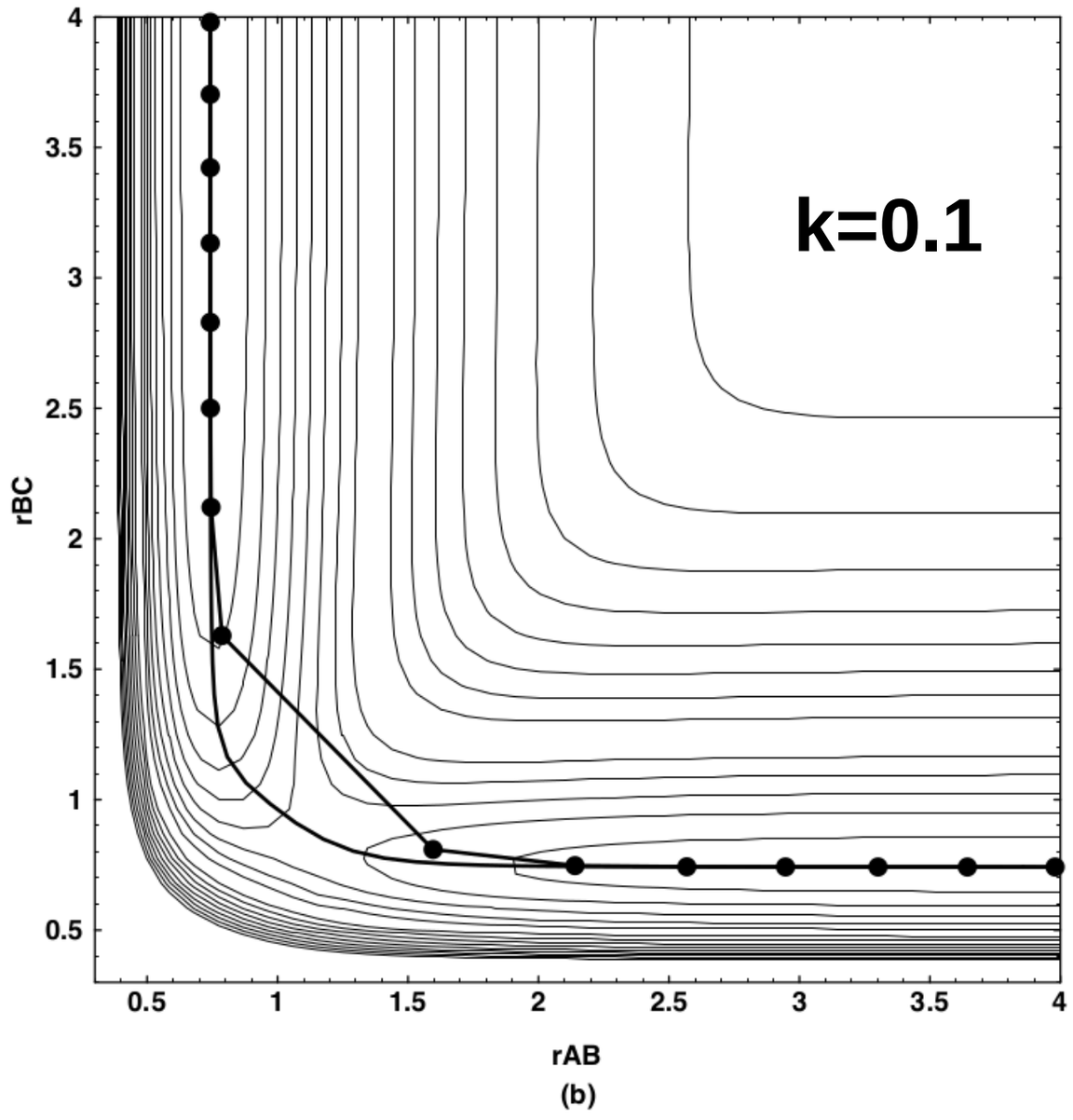
Spring potential energy

Problems of elastic band



Too hard EB Cutting corners

Problems of elastic band



Too soft EB **Sliding down**

Nudged Elastic Band (NEB)

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

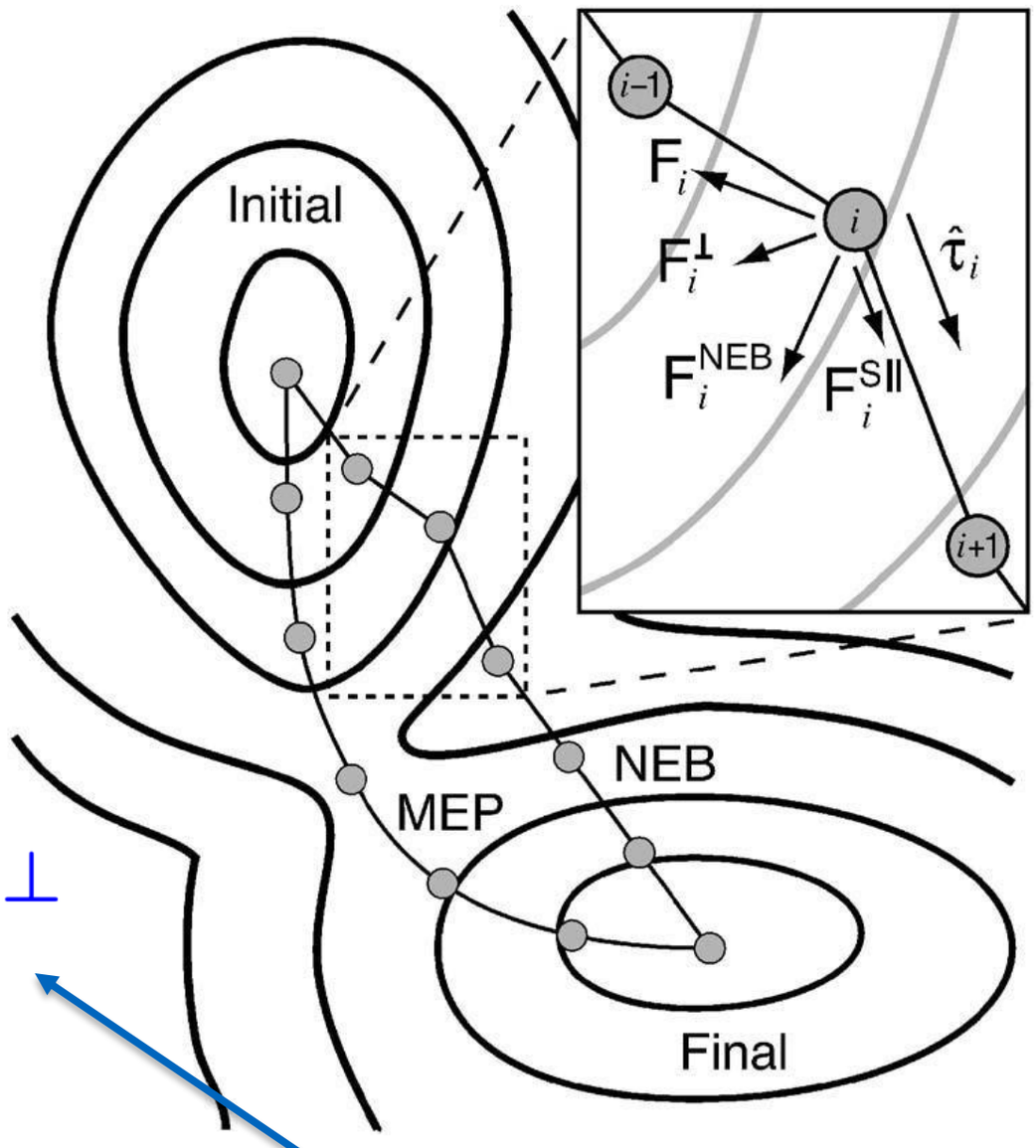
Problematic components are substrated from the force:

Forces parallel to the tangent in between images

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

$$= F_i^{\perp} + F_i^{S\parallel}$$

Spring forces perpendicular to the tangent in between images



H. Jónsson, G. Mills and K. W. Jacobsen, 1998

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

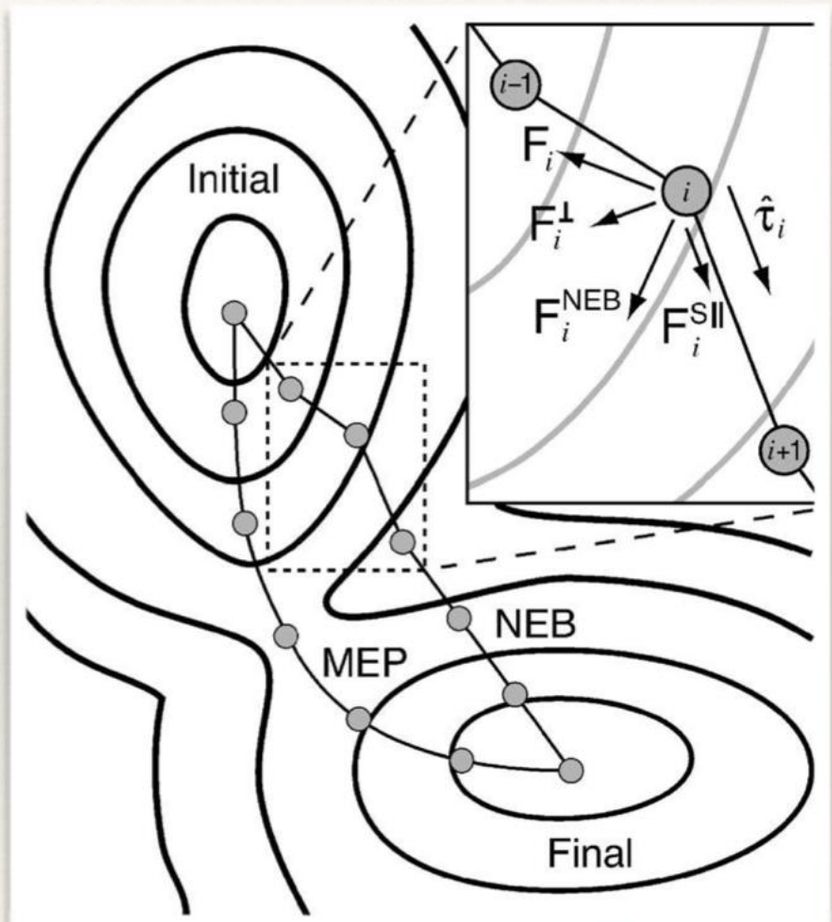
Run minimisation algorithm

If forces= 0

no

yes

MEP and Saddle point



NEB Performance

+ Results always in a continuous MEP

+ Requires only the first energy derivatives

+ Parallelization is trivial

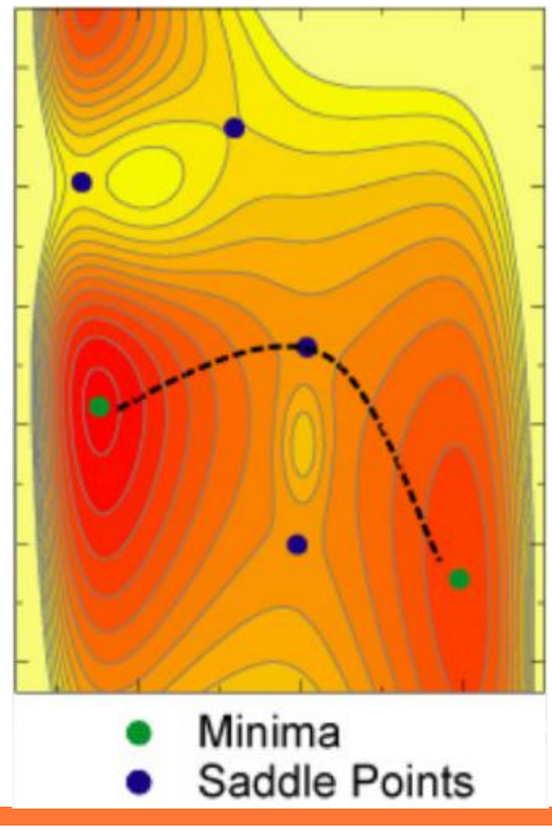
+ Preliminary tool for further exploration

- Requires known local minima

- Multiple MEP may exist

- Many images may be needed

- convergence to a saddle point may not be obtained



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:

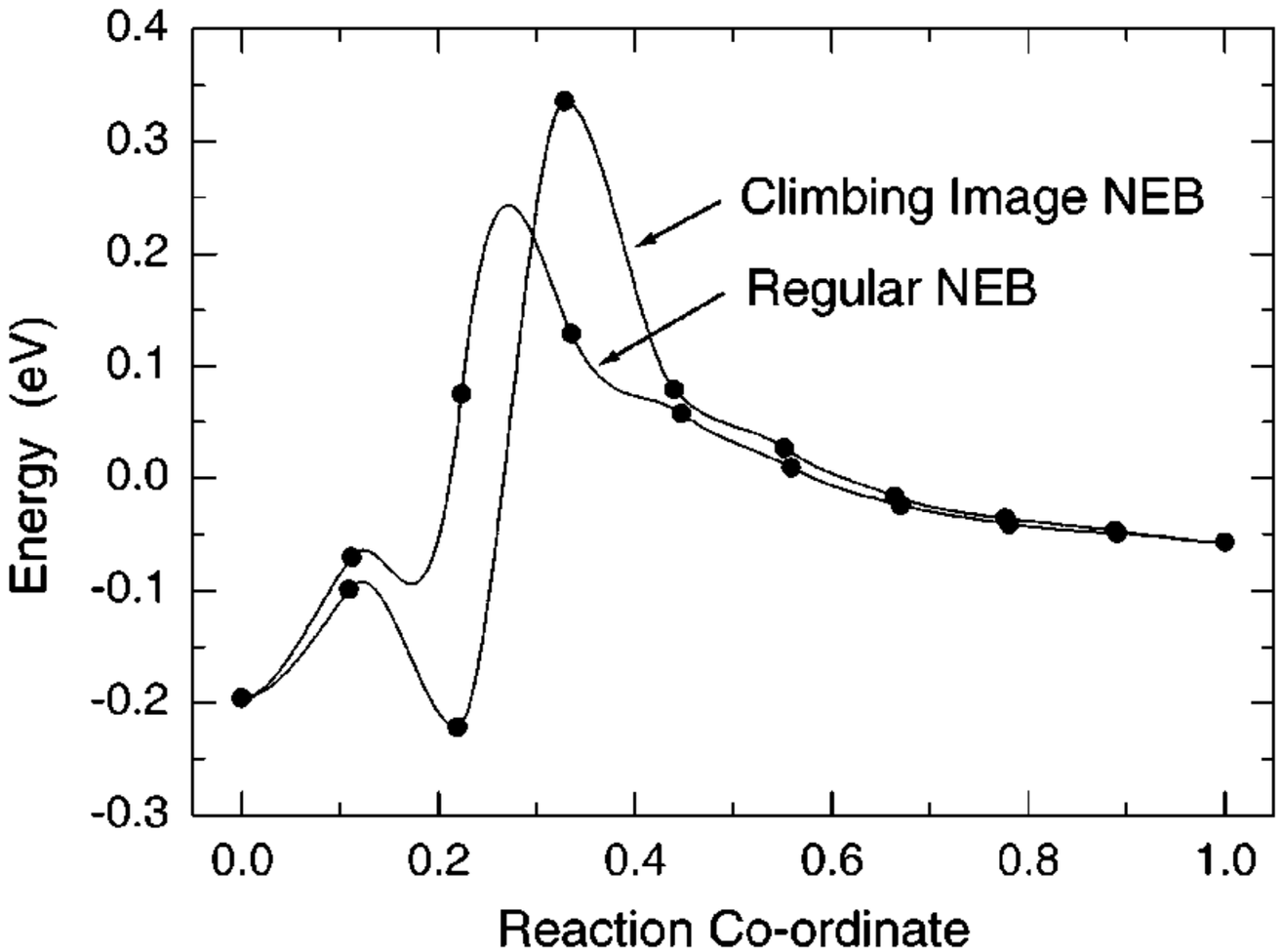
$$F_i^{NEB} = F_i - F_i^{\parallel} + F_i^{S\parallel}$$

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

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

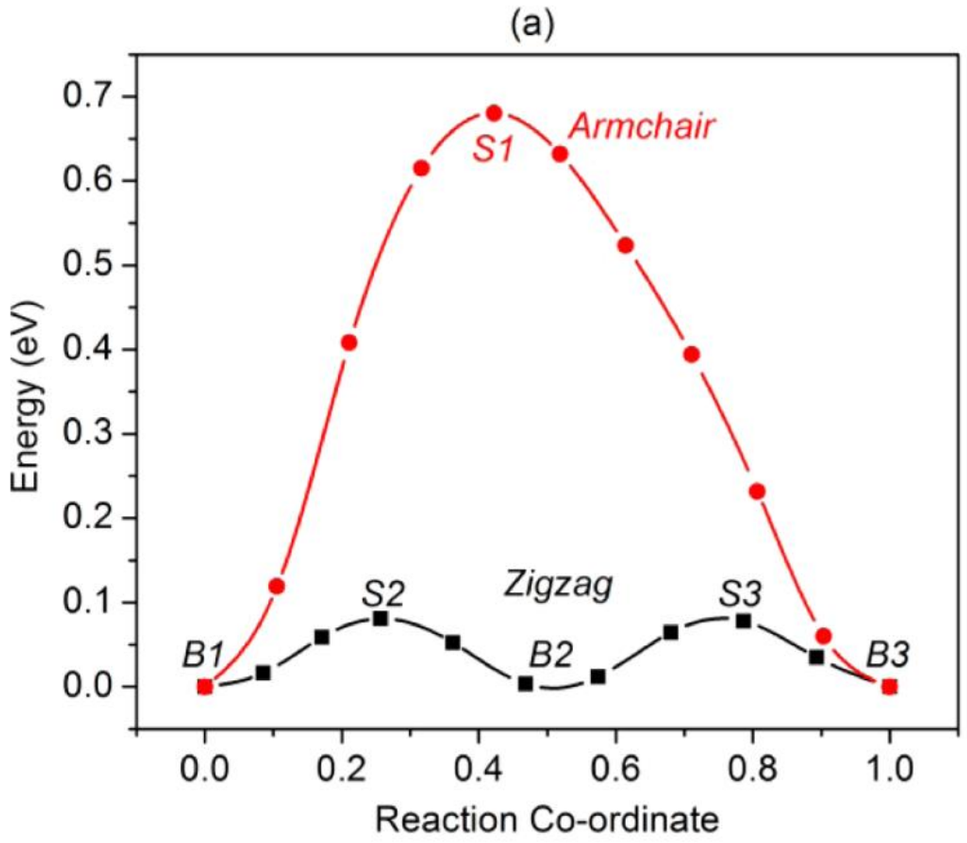
Climbing Image NEB (CI-NEB)

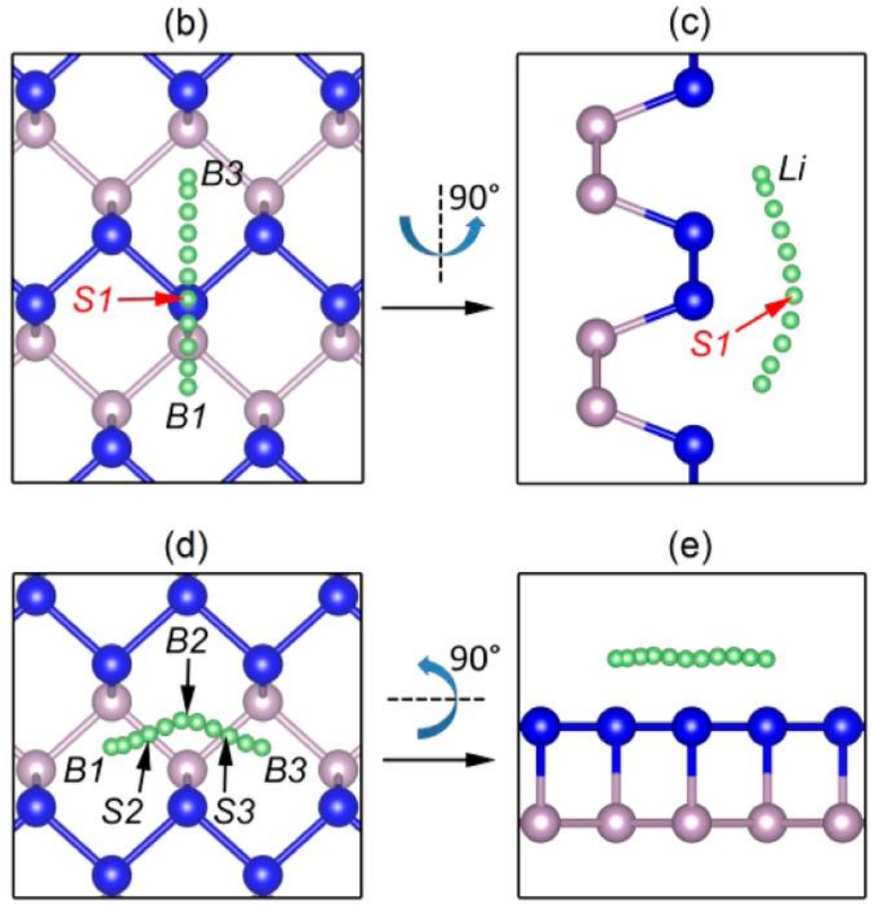
Results: (1) finds the TS more accurately
(2) uses fewer images than NEB



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

Li diffusion on phosphorene suface





Armchair

Zigzag

$\Gamma \sim e^{-E_{diff}/k_B T}$

Li diffusion along ziagzag direction is about $\mathbf{10^{10}}$ faster than that along armchair direction at room temperature, $\mathbf{10^2 \sim 10^4}$ times faster than that on MoS_2 (graphene).

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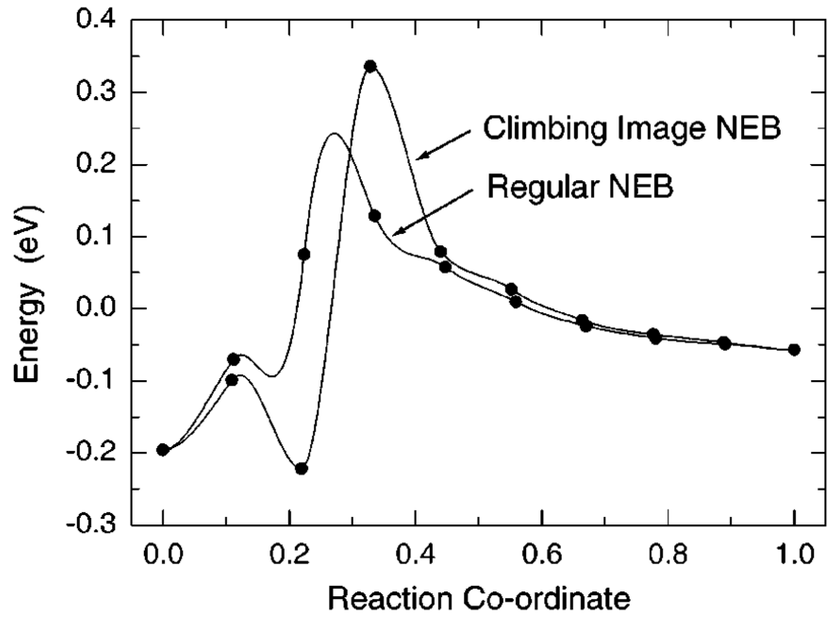
Questions on (Climbing Image) NEB ?

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



Sometimes you can run CI-NEB immediately, sometimes you need to optimize classical NEB and then run the CI version. (Depending on the system and code)

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

Time line

Period 1 (5.9. - 14.10.)

Period 2 (24.10. - 2.12.)

02. 2013

Virtual Winter School on Computational Chemistry

NEXT edition February 2023

More info at:

https://winterschool.cc/home/news/winterschool

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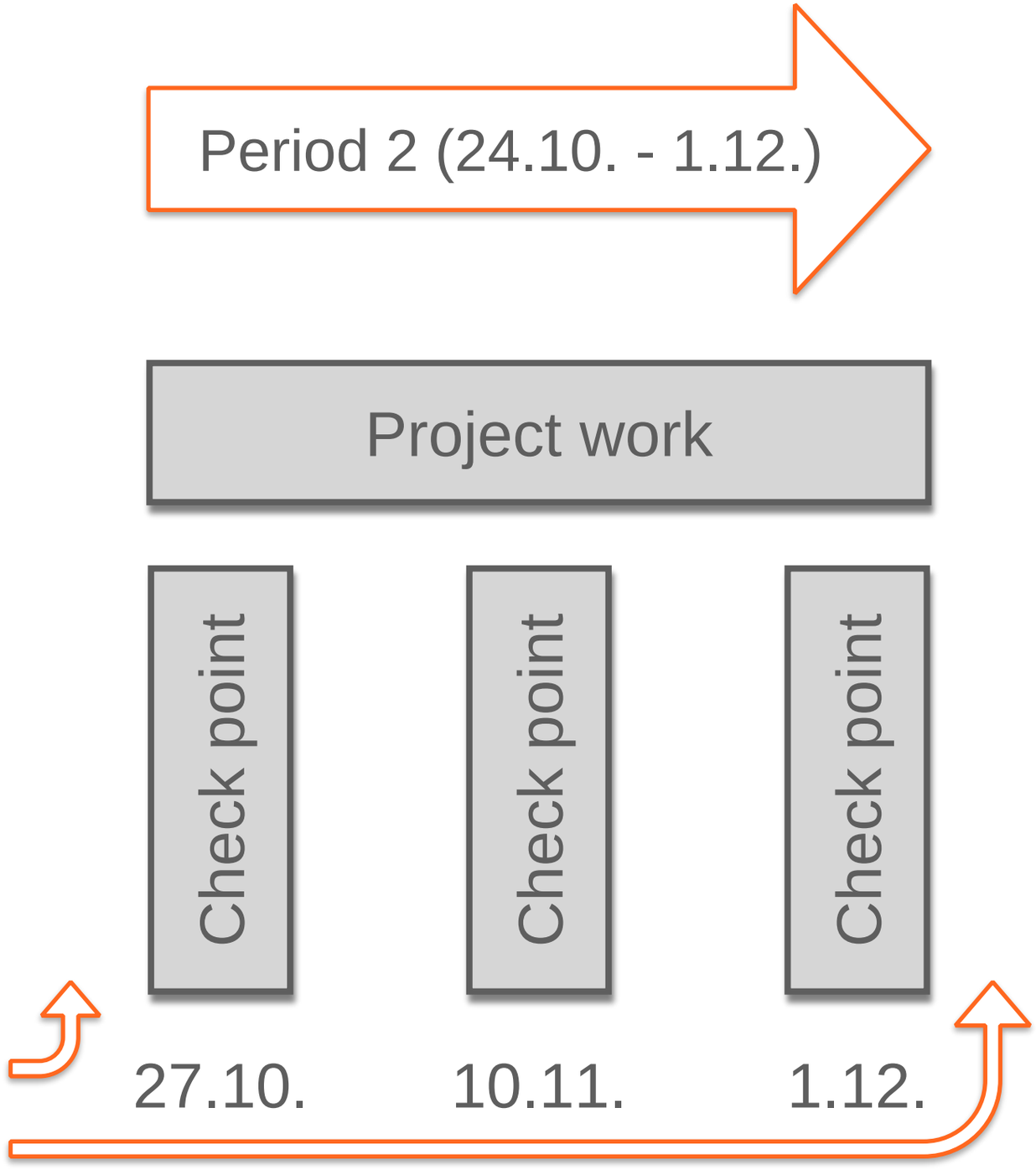
Project work

Project:

Propose and solve an original problem with DFT.

The problem can be:
- from your own research.
- something you are interested in.
- something you discover in this course and would like to pursue further.

Must be doable in 6 weeks!



Project timeline

24.10. (end of week 7):	Submit project plan

Project plan - on MyCourses → Project Work

PHYS-E0546 Density-Functional Theory for Practitioners

Project Proposal

No more than 2 pages

Project title:

Your name:

Department:

1. Project description

Context and background

Briefly describe the problem you would like to solve and its context. (Delete this text, when you fill out the box.)

DFT contribution

Describe how the problem can be broken down into steps that can be tackled with DFT. (Delete this text, when you fill out the box.)

Expected outcome

Briefly describe the results you expect and how they could contribute to the solution of your problem (and to your field in general). (Delete this text, when you fill out the box.)

Project plan - on MyCourses → Project Work

2. Computational methodology

Calculations

Please name the DFT code you are planning to use and describe the types of DFT calculations for your project (e.g. total energies (e.g. for conformer search), total energy differences (e.g. for cohesive energies), geometry optimization, molecular dynamics, etc.). Also think which scripts (if any) you might need, whether you have to modify them or even write new scripts. (Delete this text, when you fill out the box.)

Computational budget

Please estimate roughly how feasible your project is based on the computational scaling laws that were shown in the lecture. You can estimate base times for small systems or take them from the tutorial exercises. (Delete this text, when you fill out the box.)

3. Work plan

Please sketch out the tasks for each week of the project (e.g. prepare atomic geometries, run calculation for structure xyz, analyze data, write report).

	Task
Week 1	
Week 2	

Project timeline

24.10. (end of week 7):	Submit project plan
27.10. contact session:	Project presentations
10.11. contact session:	Progress report presentations
01.12. contact session:	Final results presentations
05.12. dead line	Submit final report

We will want your presentation after each of the contact session!

Triton :

the Triton computational cluster (overview here) with different architectures, but which allows you to run your calculations up-to 192 cores. For getting the access (if you do not have already), please contact us. We can provide you a temporary acccess to the cluster - for the time of the course.
You can login to the cluster through *ssh -X YOUR_USERNAME@triton.aalto.fi*, (don't forget to add your username) from any computer at Aalto. Otherwise use double ssh through *kosh* or *taltta* (see the remote accesss).
You can start to create your input files in your *scratch* directory:
/scratch/work/YOUR_USERNAME
Navigate there, create new folder and you can start to create your files. Beware that not all the visualization software is on triton, and not all the pop-up windows can tunnel through ssh -X.

DO NOT RUN YOUR CALCULATIONS ON THE LOGIN NODE!!! - You should put your calculations into a queue via slurm command. The example of slurm script for running the FHI-aims code on Triton is provided here. You will submit it into the queue via:
sbatch YOUR_SCRIPT

You can check the status of your calculations through:

squeue -u YOUR_USERNAME
If there are no running jobs, check the output of your calculations - either they are already done, or there was a mistake somewhere in the inputs.
The species for your calculations can be found in:
/scratch/scip/PHYS-E0546/CODE/species_defaults/

Triton submitting code examples:

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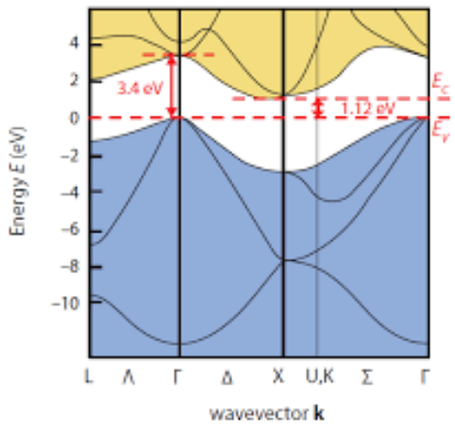
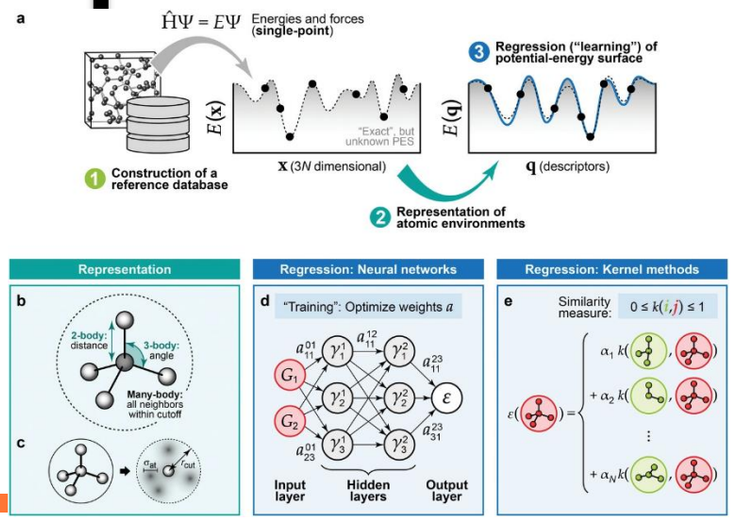
```
!/bin/bash
#SBATCH -p short # debug - for testing max 15 minutes ; short - up to 4 hours ; batch - up to 5 days #
#SBATCH -t 00-04:00:00 # dd-hh:mm:ss ; maximum of 15-30 minutes on the test queue #
#SBATCH -J NAME  # name of the job #
#SBATCH --mem-per-cpu=2000 #amount of memory per CPU in MB:4800 max for skl/csl and 12000 is maximum for hsw (only 10 nodes) #
#SBATCH -o sbatch-%j.out # output file with errors and so on #
#SBATCH -n 80 # amount of cores you want to use,  if full nodes: 40xN for skl or csl, Nx24 for hsw; max 48 for testing ; ~192 max for batch #
#SBATCH --constraint=skl # skl or csl # in case of long waiting time, you can also use old hsw #
##SBATCH -N 2  # remove the first '#' and adjust the number cores and nodes in case you want to use full nodes - better numerical stability if
you run into problems, but much longer queueing time #

export OMP_NUM_THREADS=1
AIMSBIN='/scratch/scip/PHYS-E0546/CODE/bin/aims.x'
module intel-parallel-studio/cluster.2020.0-intelmpi
ulimit -s unlimited

srun $AIMSBIN > output.txt

echo "finished"
```

Is DFT dead?

Not yet – but its usage will decline in some types of modelling



- We have seen that DFT is able to calculate many ground-state properties, but it is hard to get many information about dynamics and kinetics of processes.
- Classical MD is much better at these, but do not have enough precision, especially to capture reactivity of atoms
- The MD potentials are based on DFT/experiment fitting some “human intuition”
- What if we omit biased human, and choose **ML based method** to create better potentials to study geometries and dynamics with high precision, but lower costs*:



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*Volker L. Deringer, Miguel A. Caro, Gábor Csányi: **Machine Learning Interatomic Potentials as Emerging Tools for Materials Science**
https://doi.org/10.1002/adma.201902765

Questions?

Enjoy our “diffusion/reaction simulating” tutorial:

- **Download from Mycourses**
- **/work/courses/unix/PHYS/E0546/TUTORIALS**
- **Ask for printouts**

Project proposal template:
https://mycourses.aalto.fi/mod/folder/view.php?id=914400

Interesting materials modellings:

Creating surfaces with VESTA
https://youtu.be/OzO_zZi7g0I

Creating surfaces with ASE:
https://wiki.fysik.dtu.dk/ase/ase/build/surface.html

Something about vdW:
https://libvdwxc.gitlab.io/libvdwxc/

And check the FHI-aims manual for further methods…

Don’t forget to put your name in the list of attendance!