DE LA RECHERCHE À L’INDUSTRIE

Molecular Dynamics, Path-Integral Molecular Dynamics, Minimum Energy Paths

Grégory Geneste, Marc Torrent

Introduction

ABINIT : many algorithms allowing ions to move

=> controlled by one among **TWO keywords :**

ionmov

The algorithm **need not replicas** of the system

=> **Structural Optimizations**

=> **Molecular Dynamics**

=> ...

imgmov

The algorithm **involves replicas** of the system

=> **Minimum Energy Paths** (MEPs)

=> **Path Integral Molecular Dynamics** (PIMD)

=> ...

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=> **Minimum Energy Paths** (MEPs)

=> **Path Integral Molecular Dynamics** (PIMD)

=> ...

Part 1: Molecular Dynamics

Molecular Dynamics

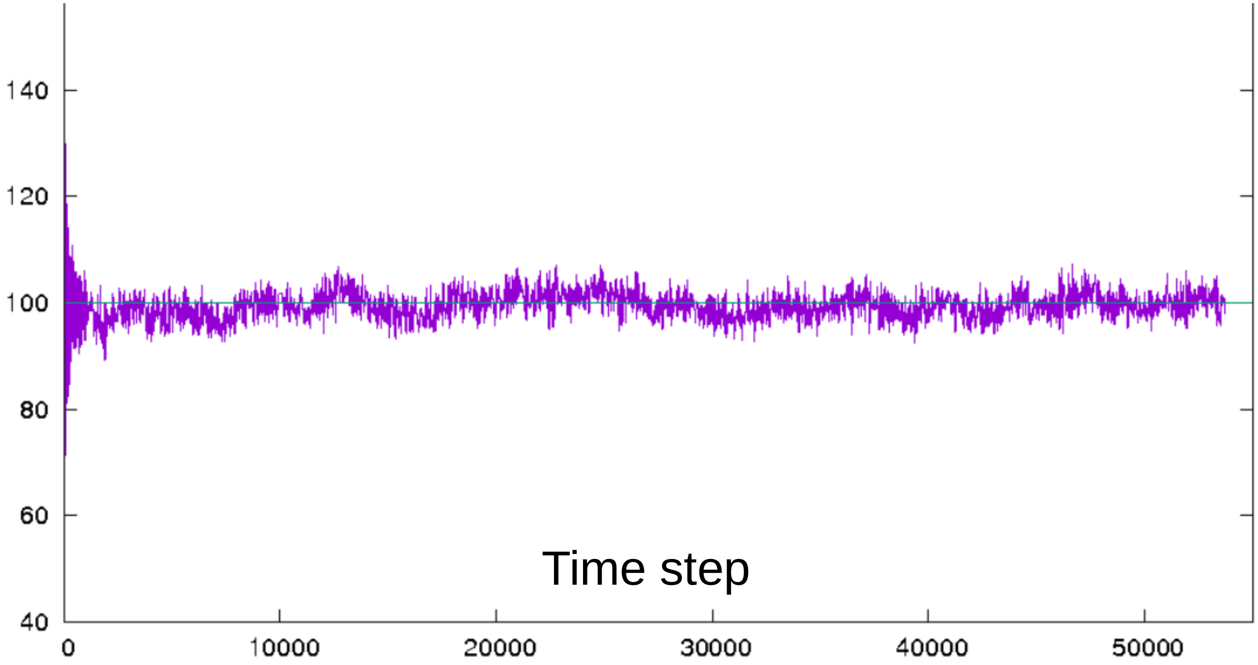
Molecular Dynamics : numerical technique in **Classical Statistical Physics**

Allows **exploring Phase Space**, produces a trajectory characteristic of a chosen **Statistical Ensemble**.

After an **equilibration period**, the observables ***fluctuate around a mean value***
= that of thermodynamic equilibrium

Hypothesis : the system must be **ERGODIC**, i.e. the time-averages quantities are equal to the ensemble-average ones.

Example :
instantaneous temperature



Molecular Dynamics

Molecular dynamics : the ions move according to the **Newton equations of motion**

usually : GS BO surface

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{f}_i = -\frac{\partial V}{\partial \vec{r}_i}$$

(+additional forces if thermostat/barostat)

Force : computed by Hellman-Feynman theorem, from DFT ground state calculation

= AB INITIO Molecular Dynamics
("Quantum Molecular Dynamics")

Rq : the nuclei remain **CLASSICAL particles**

To start a MD simulation, you **ABSOLUTELY** need to specify :

nsym 1

- initial positions and cell (**xred**/**acell**/**rprim**)
- initial velocities (**vel**), or controlled by an initial temperature => **mdtemp(1)**
- the kind of MD (see below), controlled by the value of **ionmov**
- number of time steps **ntime**
- atomic masses **amu**

Molecular Dynamics at Thermodynamic Equilibrium (atoms are classical)

TWO goals :

THERMODYNAMICS	***KINETICS***
Compute **static thermodynamic quantities** = ensemble averages of some microscopic quantities Ex : energy, enthalpie, g(r), density of proba of atomic positions, volume ... ***TIME does not need to have physical meaning*** You can use **any mass you want !**[1] MD here does same job as MC = Explore configuration space according to the probability density of the chosen statistical ensemble : NVE, NVT, NPT ...	Compute **Time-correlation functions** Ex : diffusion coefficient, susceptibility as a function of frequency ... ***TIME must have correct physical meaning*** You must use **the true mass !** NVE preferred

[1] see e.g. Hopkins et al, JCTC **11**, 1864 (2015) and references therein

Molecular Dynamics

	CLASSICAL ATOMS	**QUANTUM ATOMS**
Static thermodynamic quantities	DO **NOT** DEPEND ON THE MASS	DEPEND ON THE MASS
Time-correlation functions	DEPEND ON THE MASS	DEPEND ON THE MASS

Classical Statistical Physics

Quantum Statistical Physics

Molecular Dynamics

To be integrated, the Newton equations of motion are **DISCRETIZED**

=> We need a **time step**, specified in ABINIT by the keyword **dtion**
(expressed in atomic times units, i.e. 1 a.u. of time ~ 2.4x10^{-17} s)
Typical value of dtion : 100 or below (determined by maximal phonon frequency)

VERLET algorithm :

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{f}_i = -\frac{\partial E_0}{\partial \vec{r}_i} \quad \longrightarrow \quad \vec{r}_i(t+dtion) = 2\vec{r}_i(t) - \vec{r}_i(t-dtion) + \frac{dtion^2}{m_i}\vec{f}_i(t)$$

At time step 1 : **Taylor** algorithm

$$\vec{r}_i(dtion) = \vec{r}_i(0) + \vec{v}_i(0) \times dtion + \frac{1}{2}\frac{dtion^2}{m_i}\vec{f}_i(0)$$

Initial velocities (**vel** or **mdtemp(1)**)

At each time step : electronic GS recalculated ! => provides **FORCES** & **ENERGY**
Electronic loops : convergence using **toldff** preferred (also possible : **tolvrs**)

An alternative = « velocity Verlet »
Many other algorithms implemented, see the website at input variable **ionmov**.

Molecular Dynamics

MD can be performed with ABINIT in several ways :

- **NVE ensemble (microcanonical)** : $m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{f}_i$ **ionmov 6**
the total energy is fixed
The volume (more generally the cell vectors) are fixed

- **NVT ensemble (canonical)** : one uses a **THERMOSTAT**
(=additional degrees of freedom that exchange energy with the system to maintain the temperature fluctuating around a fixed, chosen, value).
The rate of exchange is controlled by a parameter (« mass » or friction coeff) :

  - **Nose-Hoover** thermostat
    Nose « mass » : **noseinert** **ionmov 8**
  - **Langevin** thermostat : **ionmov 9**
    stochastic thermostat, uses random numbers

$$m \frac{d^2 \vec{r}_i}{dt^2} = \vec{f}_i - \gamma m \frac{d \vec{r}_i}{dt} + \vec{R}_i$$

friction

Langevin force, drawn in a gaussian with variance $\sqrt{\frac{2 \gamma m k_B T}{\delta t}}$

mdtemp(1) = initial temperature (a random distribution of velocities is generated)
available for ionmov 8 and 9
mdtemp(2) = final temperature (at time step *ntime*):
thermostat temperature evolves linearly inbetween

- **Isokinetic ensemble** (rescaling of velocities) : **ionmov 12**
Temperature maintained strictly constant

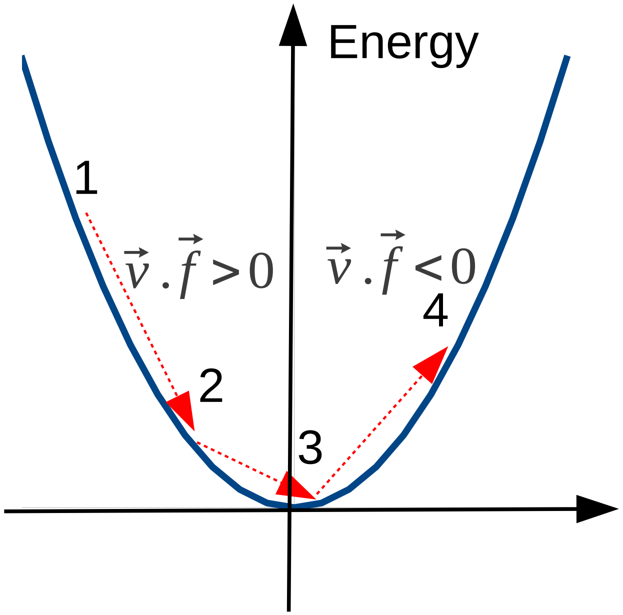
Molecular Dynamics

MD can be used also to perform **STRUCTURAL optimizations** :

- **« Quenched » molecular dynamics** **ionmov 7**

The velocities are set to zero as soon as the force and the velocity have opposite direction (because it means that you have gone too far and are beyond the minimum...)

Very efficient way to pump kinetic energy and go to the minimum, but can be long if your starting point is far from the minimum.



- **« Damped » molecular dynamics** **ionmov 1**

Molecular Dynamics with a viscous damping (**vis**).

Part 2: Path-Integral Molecular Dynamics (PIMD)

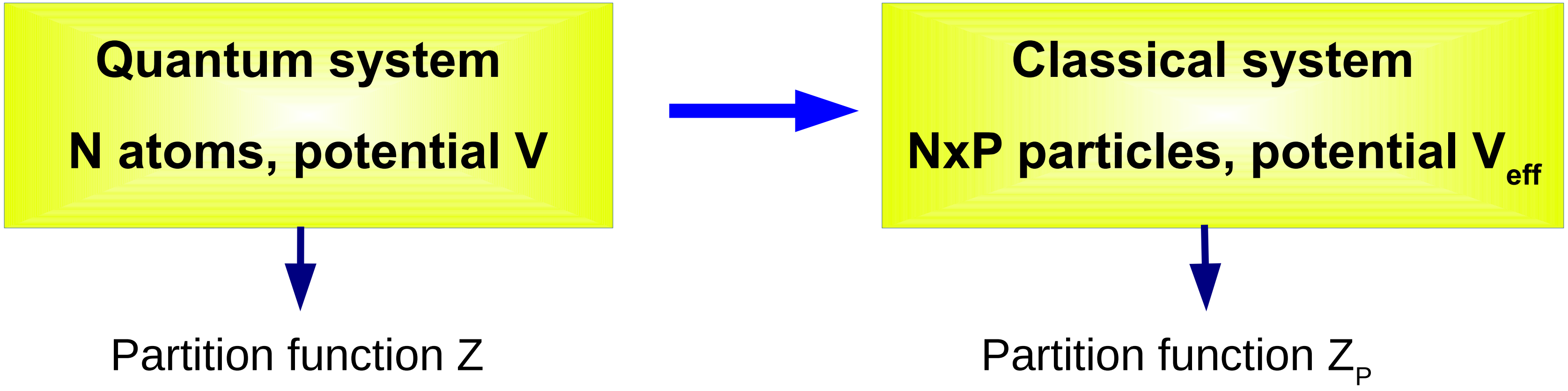
Path-Integral Molecular Dynamics

Describes the **quantum effects** associated with the **nuclei motions**

With following assumptions :

- **thermal equilibrium** (described a statistical mixing – quantum canonical ensemble)
- **discernible** nuclei (*Boltzmann* statistics)
- no information on **time correlation functions**

Based on an analogy between a quantum system of nuclei and a fictitious system of classical particles in which **each nucleus is replicated P times** :



Quantum system

N atoms, potential V

Partition function Z

Classical system

NxP particles, potential V_{eff}

Partition function Z_P

In the limit $P \rightarrow \infty$ $Z_P = Z$

D. Marx, M. Parrinello, J. Chem. Phys. **104**, 4077 (1996)

Path-Integral Molecular Dynamics

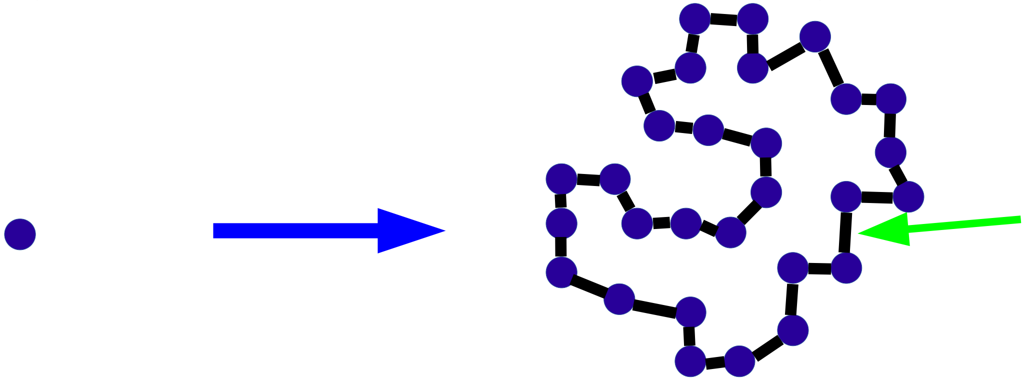
$$Z=\lim_{P\to\infty}\left[\frac{2\pi m P k_B T}{h^2}\right]^{3NP/2}\int_{\vec{R}_1}\dots\int_{\vec{R}_P} e^{-\beta V_{eff}(\vec{R}_1\dots\vec{R}_P)}\,d\vec{R}_1\dots d\vec{R}_P$$

$$\vec{R}_s=(\vec{r}_1^{\,(s)}\dots\vec{r}_N^{\,(s)})\quad 3\mathrm{N}-vector$$

$$V_{eff}(\vec{R}_1\dots\vec{R}_P)=V_{eff}(\vec{r}_1^{\,(1)}\dots\vec{r}_N^{\,(1)}\dots\vec{r}_1^{\,(P)}\dots\vec{r}_N^{\,(P)})$$

$$V_{eff}(\vec{R}_1\dots\vec{R}_P)=\sum_{s=1}^{P}\left[\sum_{i=1}^{N}\frac{1}{2}k(P,\beta)(\vec{r}_i^{\,(s)}-\vec{r}_i^{\,(s+1)})^2+\frac{1}{P}V(\vec{r}_1^{\,(s)}\dots\vec{r}_N^{\,(s)})\right]$$

1 – replace each (quantum) nucleus by a closed ring of P replicas (beads, imaginary time slices) bonded to each other by a harmonic attraction :



Spring constant

$$k=\frac{m P k_B^2 T^2}{\hbar^2}$$

2 – In each slice, the images interact through the physical potential (divided by P)

3 – The system of the NxP replicas is treated **classically**, by MD = **PIMD**

Path-Integral Molecular Dynamics

Time has no physical meaning in standard PIMD !
It just allows to system to explore phase space and sample it according to the probability distribution of the desired statistical ensemble (here canonical).

*=> Time-correlation functions are **not accessible !!!!!***

In ABINIT, PIMD equations are integrated using the Verlet algorithm.

Warning: temperature is in PIMD controlled by the keyword **mdtemp:**
mdtemp(1) = initial temperature
mdtemp(2) = thermostat temperature

There is no linear evolution between the two (in contrast to ionmov 9)

To perform PIMD, do not forget to set **nsym** 1 (like in MD)

Path-Integral Molecular Dynamics

Main keywords for PIMD in ABINIT :

imgmov=9 (PIMD with Langevin thermostat), 13 (Nose-Hoover chains)
nimage : Trotter number = number of slices
ntimimage : number of time steps
dtion : time steps in atomic units (1 a.u. of time ~ 2.4×10^{-17} s)
npimage : keyword to parallelize over images
pitransform : controls the coordinate transformation
(0 : primitive ; 1 : normal mode ; 2 : staging)
amu(ntypat) : real masses in atomic mass units (proton =1)
pimass(ntypat) : fictitious masses (same unit as amu)
dynimage(nimage) : 1 if the image is free to move, 0 if it is fixed
(for PIMD, use nimage x 1, or let to the default value)
prtvolimg : controls the volume of printed information
mdtemp(2) : array of two values to control the temperature
mdtemp(1) = initial temperature ; mdtemp(2) = thermostat temperature
restartxf : -1 to restart automatically from _HIST file written on disk

Langevin thermostat :

vis (friction coeff for Langevin thermostat in a.u.) : 5.0d-05 is usually OK
irandom : choice of the random number generator (use 3 for non-deterministic Random number generator)

Path-Integral Molecular Dynamics

Performing PIMD in the canonical ensemble :
Preferred way at the moment : ***USE LANGEVIN THERMOSTAT (imgmov 9)***

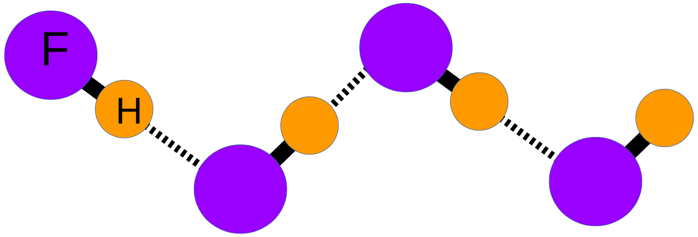
Example of input file : H2 molecule at 200 K, canonical ensemble

```
##### H2 molecule in a box : example of PIMD input  ######

################## The system ####################
acell 20.0 20.0 20.0 Angstrom
natom 2  znucl 1  ntypat 1  typat 1 1

xangst_1img
0.0 0.0 0.0
0.75 0.0 0.0

xangst_lastimg #all images at the same position initially
0.0 0.0 0.0
0.75 0.0 0.0

######### electronic GS parameters ###########
ixc 11  #GGA-PBE
ecut 20.0 #plane-wave cut-off
pawecutdg 30.0 #cut-off double grid
kptopt 1
ngkpt 1 1 1  nshiftk 1  shiftk 0 0 0 # Gamma point only
toldff 1.0d-06
nstep 100  # maximal number of iterations for GS convergence
occopt 1  #default: insulator
nband 1

nsym 1 #### VERY IMPORTANT
```

```
################## PIMD ######################
imgmov 9   #Langevin thermostat
nimage 64  #nb of beads
dynimage 64*1  #this is the default value for PIMD
vis 5.0d-05   #friction Langevin : recommended value
dtion 20  #time step
ntimimage 10000
mdtemp 400 200 #initial T=400K, thermostat T=200 K
amu 1.0 #physical mass (here hydrogen, e.g. use 2 for deuterium)
irandom 3 #non-deterministic random number generator, advised
optcell 0 #no cell evolution, this is the default

pitransform 0 #no coord transformation
                  #1 for normal mode ; 2 for staging
pimass 1.0 #fictitious mass
             #automatically fixed to the correct value if pitransform=1 or 2

restartxf -1  #restart from _HIST file written on disk (see below)

######## parallelization (if any), here over 64 cores, one per bead
paral_kgb 1
npkpt 1
npband 1
npfft 1
bandpp 1
npimage 64
```

Path-Integral Molecular Dynamics

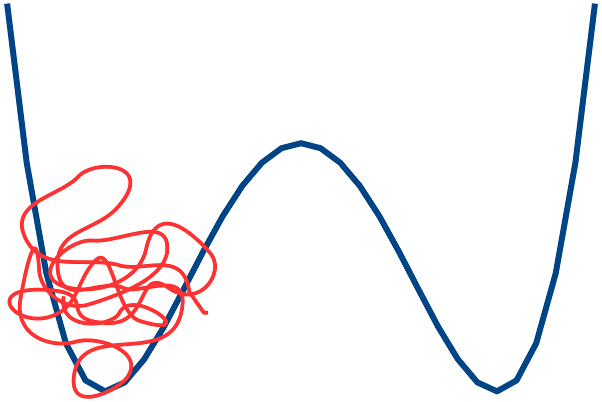
Example : symmetrization of hydrogen bond in HF at low temperature (T=100 K)
*H. Dammak, F. Brieuc, G. Geneste, M. Torrent, M. Hayoun, PCCP **21**, 3211 (2019)*



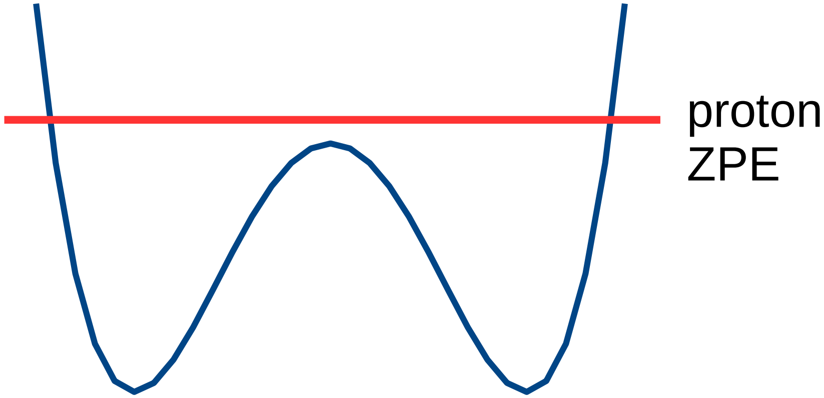
Barrier for hopping ~ 30 meV.

Langevin thermostat (**imgmov** 9)
- Classical simulation T=100 K : no proton jump
- QTB-PIMD/PIMD simulation T=100 K : the ZPE lies aboe the proton barrier
  => H-bond symmetrization !

Classical atoms
P=1



Quantum atoms
P=56 (QTB-PIMD)
P=64, 128 (PIMD)



Rq : QTB-PIMD **imgmov** 10 (coming soon)

Path-Integral Molecular Dynamics

imgmov 9 can be used also to perform **CLASSICAL MD** by simply setting **nimage** to 1
=> Advised way to make Classical MD with Langevin thermostat

At each PIMD time step, ABINIT prints (after GS calculation of all images) :

```
PATH-INTEGRAL MOLECULAR DYNAMICS (LANGEVIN):
Moving images of the cell...

At PIMD time step    10, the temperature is   387.66856 K

Energy:
  Internal energy (PRIMITIVE estimator) =      -1.156702170 Ha
  Internal energy (VIRIAL    estimator) =      -1.158625897 Ha


Stress tensor from PRIMITIVE estimator (Ha/Bohr^3):
       -0.000014616      -0.000005422       0.000003090
       -0.000005422       0.000025695       0.000003793
        0.000003090       0.000003793       0.000005807
Pressure (primitive estimator) =      -0.165607799 GPa

Center of mass:
    0.7086472998      0.0000000000      0.0000000000
```

```
Atomic positions:
xred
   -0.0009056794    -0.0021311176     0.0010474810
    0.1830400967     0.0026994680     0.0107059589
xred_2img
    0.0123610044     0.0097888890    -0.0009567539
    0.1755687527     0.0236438047    -0.0045914081
xred_3img
    0.0001715794    -0.0473470595    -0.0041760251
    0.1701962959    -0.0434734851    -0.0232401971
xred_4img
   -0.0033910323     0.0572334113     0.0092800439
    0.1716062825    -0.0004139108     0.0119309005

Velocities:
vel
    0.0001563291     0.0001049462     0.0000971409
    0.0000297633     0.0001299715     0.0003940452
vel_2img
   -0.0001516894     0.0002730760    -0.0000649509
    0.0005404062     0.0008878152    -0.0002122851
vel_3img
   -0.0002223423    -0.0018146927    -0.0001225370
   -0.0001028884    -0.0016686690    -0.0009454436
vel_4img
    0.0000179793     0.0022523886     0.0003877888
   -0.0002675578    -0.0001648357     0.0004662416
```

Atomic positions and velocities for all beads

(here P=4 and natom=2)

Can be used to restart the dynamics by putting xred_1img, xred_2img… vel_1img, vel_2img … in input file

Path-Integral Molecular Dynamics

Energy in PIMD:

$$E^{(prim)} = \frac{3}{2}NPk_BT - < \sum_{s=1}^{P}\sum_{i=1}^{N}\frac{1}{2}m_i\omega_P^2(\vec{r}_i^{(s+1)} - \vec{r}_i^{(s)})^2 > + \frac{1}{P} < \sum_{s=1}^{P} V(\vec{r}_1^{(s)}...\vec{r}_N^{(s)}) >$$

$$E^{(vir)} = \frac{3}{2}Nk_BT + \frac{1}{P} < \sum_{s=1}^{P}\sum_{i=1}^{N}\frac{1}{2}(\vec{r}_i^{(s)} - \vec{r}_i^{c}).(-\vec{F}_i^{(s)}) > + \frac{1}{P} < \sum_{s=1}^{P} V(\vec{r}_1^{(s)}...\vec{r}_N^{(s)}) >$$

Energy printed at each step for the two estimators
Example: primitive estimator
At each time step, ABINIT prints the quantity:

$$\frac{3}{2}NPk_BT_{therm} - \sum_{s=1}^{P}\sum_{i=1}^{N}\frac{1}{2}m_i\omega_P^2(\vec{r}_i^{(s+1)} - \vec{r}_i^{(s)})^2 + \frac{1}{P}\sum_{s=1}^{P} V(\vec{r}_1^{(s)}...\vec{r}_N^{(s)})$$

Path-Integral Molecular Dynamics

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Energy printed at each step for the two estimators
Example: primitive estimator
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$$\frac{3}{2}NPk_B\boxed{T_{therm}} - \sum_{s=1}^{P}\sum_{i=1}^{N}\frac{1}{2}m_i\omega_P^2(\vec{r}_i^{(s+1)} - \vec{r}_i^{(s)})^2 + \frac{1}{P}\sum_{s=1}^{P} V(\vec{r}_1^{(s)}...\vec{r}_N^{(s)})$$

Important point : it has been chosen to print the kinetic part calculated using the **thermostat temperature**, not the instantaneous one.

Thus if you do NVE (**vis**=0), the energy printed does not seem to be conserved (although it is correctly conserved in the calculation)
=> the time-averaged energy is correct.

Path-Integral Molecular Dynamics

restartxf -1 : the next run automatically starts from the last configuration of the previous one, and continues Verlet integration, by reading the _HIST file

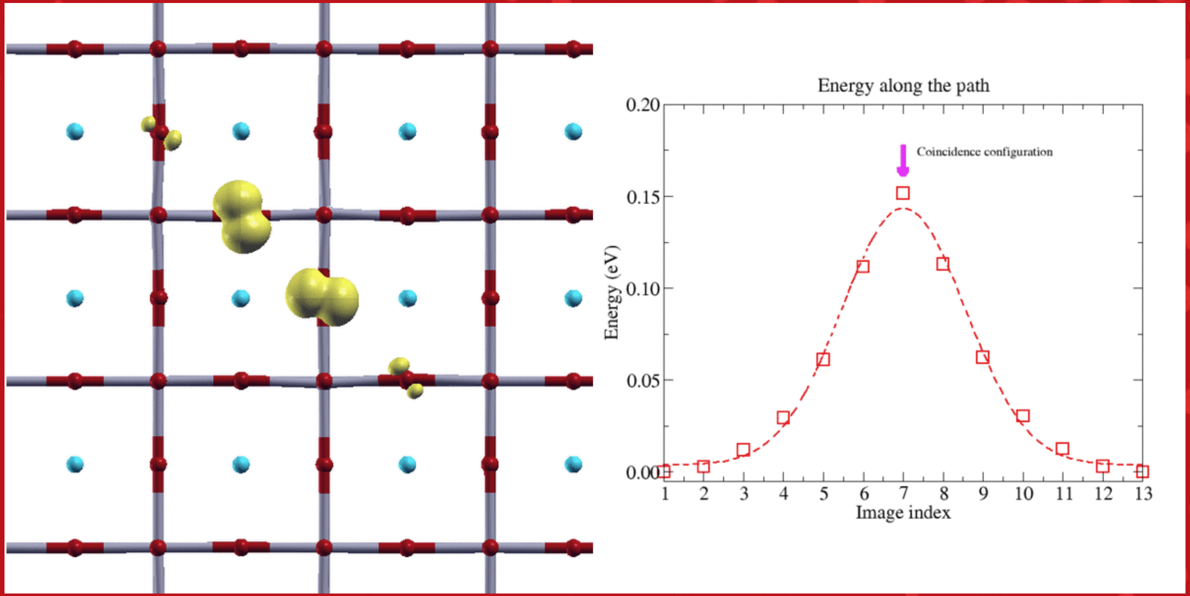
One known (minor) problem : with **restartxf** -1 and **irandom** 3, ABINIT rewrites at each restart incorrect velocities (and thus incorrect temperature), but the trajectory is correct. Positions, forces, stress in _HIST are OK. If you use this option, rather takes instantaneous temperature in ABINIT output files (as written when calculated at the first time).
Alternatively for restart : take manually positions and velocitites of previous run.

Warning : internal energy printed using thermostat temperature, not instantaneous one (time-averaged is correct)

Alternatively, restarts can be made by using last positions and velocities :
xred_1img … **xred_lastimg**, **vel_1img** … **vel_lastimg**

NPT ensemble: coming soon !

Constraints :
PIMD has been made compatible with constraints, using the keyword **pimd_constraint**
For the moment, only one constraint which is a linear combination of atomic positions is possible (using **natcon**, **iatcon**, **wtatcon**, **nconeq**)



Part 3: Minimum Energy Paths (MEPs)

Minimum Energy Paths

This week, you have learnt how to perform
STRUCTURAL OPTIMIZATIONS with ABINIT
= how to obtain ***(local) minima*** of the ***energy landscape*** in configuration space.

What happens inbetween ?

There are specific physical problems in which the energy landscape between the minima is important and plays a role.

Example : *Transition between two local minima* of the energy landscape
According to **Transition State Theory (TST)**, the transition **rate**,
if the mechanism if **THERMALLY ACTIVATED**
(thermal overbarrier motion),
is controlled by an ENERGY BARRIER

$$k = k_0 e^{-E_a / k_B T}$$

Minimum Energy Paths

TST : activation energy ~ free energy barrier

=> approximated by a static (« T=0K ») barrier ΔE

ΔE can be obtained by **computing the MEP**

$$\Delta E = E(\text{saddle point}) - E(\text{Min})$$

Prefactor ?

Harmonic Transition State Theory :

Classical framework:

« attempt frequency »

$$k_0 = \frac{\prod_{i}^{3N-3} \nu_i^{Min}}{\prod_{i}^{3N-4} \nu_i^{Saddle}}$$

Phonon frequencies in the stable (initial) configuration of the 3N-3 modes (acoustic modes excluded)

Phonon frequencies in the Saddle point configuration of the 3N-4 modes (acoustic modes + imaginary mode excluded)

See e.g. Sundell, Björketun, Wahnstrom, PRB 76, 094301 (2007)

Minimum Energy Paths

Quantum corrections :

$$\Delta E^{qm} = E(saddle) - E(min) + \frac{1}{2}\sum_{i}^{3N-4} h\nu_i^{Saddle} - \frac{1}{2}\sum_{i}^{3N-3} h\nu_i^{Min}$$

$$k_0^{qm} = \frac{k_B T}{h} \frac{\prod_i^{3N-3} \left[1 - e^{-h\nu_i^{Saddle}/k_B T}\right]}{\prod_i^{3N-4} \left[1 - e^{-h\nu_i^{Min}/k_B T}\right]}$$

Thermal overbarrier regime but quantization of vibration modes taken into account.

See e.g. Sundell, Björketun, Wahnstrom, PRB 76, 094301 (2007)

Minimum Energy Paths

High-temperature limit ($k_B T >> h\nu_i$) :

$$k_0^{qm} \rightarrow k_0$$

Low-temperature limit ($k_B T << h\nu_i$) :

$$k_0^{qm} \rightarrow \frac{k_B T}{h} \qquad k \rightarrow \frac{k_B T}{h} e^{-\Delta E^{qm}/k_B T}$$

NB1 : the regime remains thermal overbarrier (no tunneling)

NB2 : at very low temperature, one might have a quantum tunneling regime (requires specific modeling ! e.g. Flynn-Stoneham formula)
Ex : diffusion of H atoms in metals (e.g. in Nb or Ta below ~ 200 K)

See e.g. Sundell, Björketun, Wahnstrom, PRB 76, 094301 (2007)

Minimum Energy Paths

Path between two local minima (stable or metastable configurations) in configuration space, that involves the smallest possible energy barrier.

There are **two main algorithms** allowing computation of MEPs :
String Method (SM) & **Nudged Elastic Band** (NEB)

Computing a MEP requires to sample the path between the two minima => the path is **discretized** : it is approximated by **a finite number of intermediate configurations**

Needs replicas of the system => performed using keyword **imgmov**

String Method : **imgmov** 2 NEB : **imgmov** 5

Number of replicas (intermediate configurations) along the path : **nimage**
Maximal number of steps for SM/NEB : **ntimimage**
Tolerance criterion for convergence : **tolimg**
(energy difference with previous step, per image)

Minimum Energy Paths

String Method & NEB :

Path computed between two local minima =
Two optimized configurations (that have been obtained before, e.g. by a structural optimization !) => **xred_1img** & **xred_lastimg**

Allows determination of **energy barriers**
(fundamental to evaluate rate of thermally-activated mechanisms)

Other keywords :
dynimage(nimage): 0 if fixed image, 1 if evolving
=> 0 for first and last image, 1 for intermediate images
Parallelization over images : **npimage** (recommended = **nimage**)

Precise optionnally
fxcartfactor: « time step »
string_algo : 1 by default, Simplified String Method, 2 (energy-weighted arc length)
neb_algo : 0, 1 (NEB + improved tangent, default), 2 : CI-NEB

The MEP should be CONVERGED with the number of images

Minimum Energy Paths: The String Method

SM : Iterative procedure in which each iteration consists of two steps:

Step 1: evolution

Positions are modified following the forces:

For image (s): $x_{i,\alpha}^{(s)}(n+1) = x_{i,\alpha}^{(s)}(n) + fxcartfactor \times f_{i,\alpha}^{(s)}(n)$

with $$f_{i,\alpha}^{(s)}(n) = -\frac{\partial E_{tot}^{(s)}(n)}{\partial x_{i\alpha}^{(s)}}$$

(present implementation = steepest-descent)

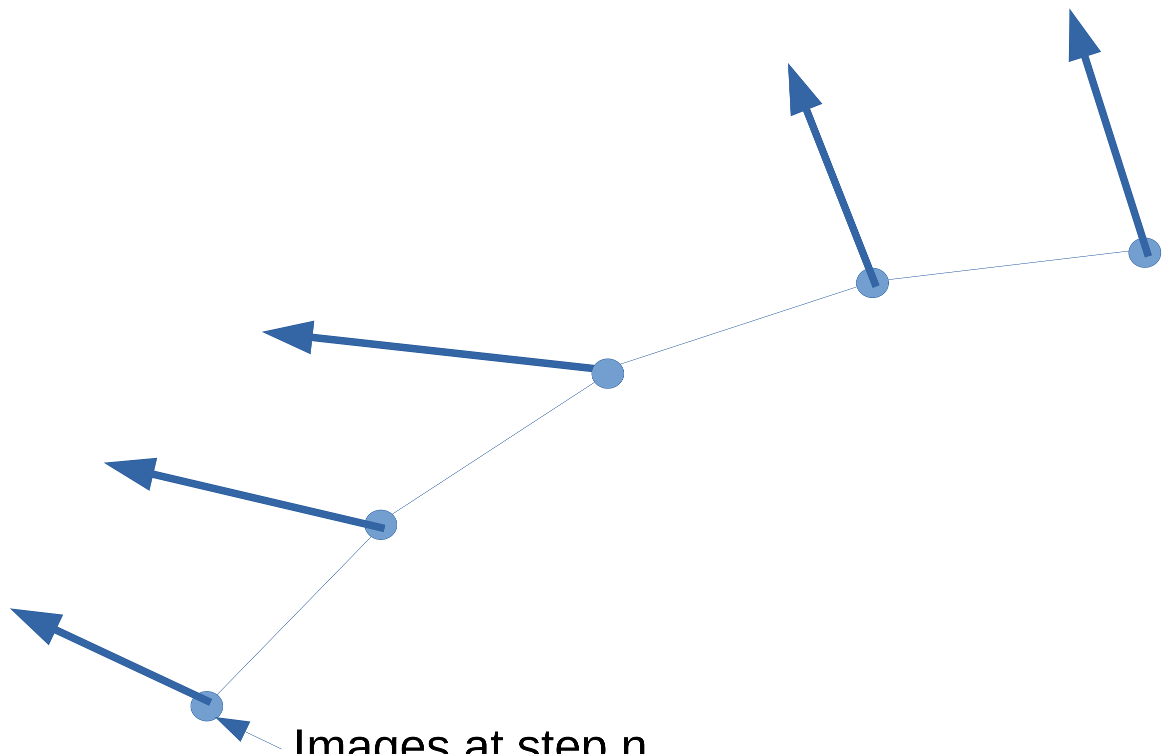
Step 2: reparametrization

The images are equally redistributed along the string

E, Ren, Vanden-Eijnden, The Journal of Chemical Physics 126, 164103 (2007).

Minimum Energy Paths: The String Method

Example (2D):

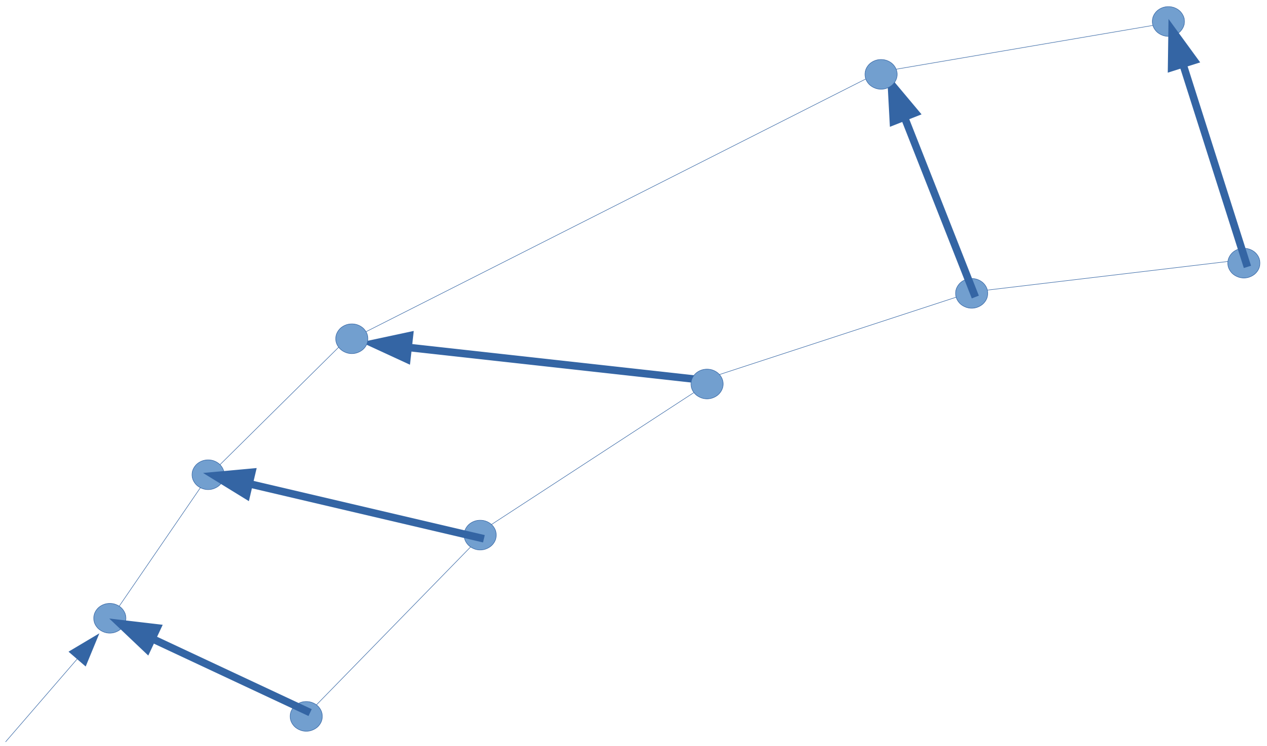


True forces at step n

Images at step n

Minimum Energy Paths: The String Method

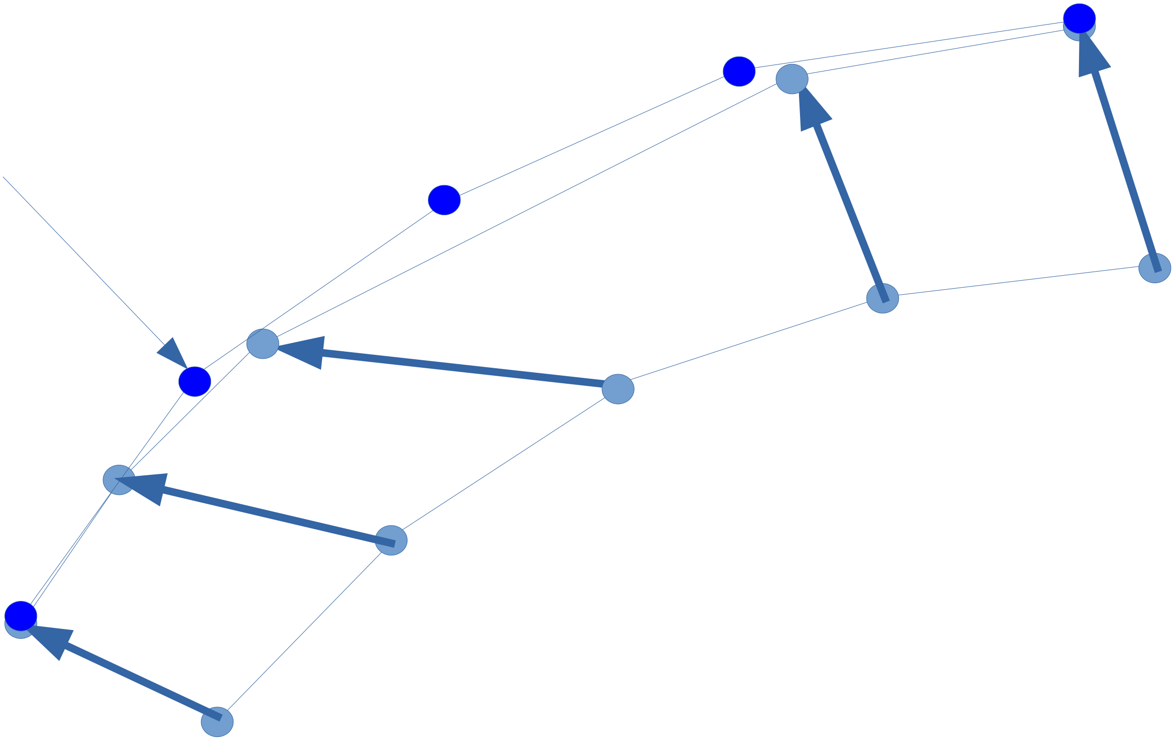
Example (2D):



Step n+1: evolution step

Example (2D):

Step n+1:
reparametrization step
=> Images at step n+1



Example (Tutorial website ABINIT) : Hopping of a proton between a H2O and a NH3 molecules, supposed at fixed (arbitrary) distance.

```
#Cell and atoms
acell  10.0 5.0 5.0 Angstrom
natom  8                       # Number of atoms
ntypat 3  typat 1 3 3 2 3 3 3 3 # Type of atoms (H2O + NH3 + H)
znucl 8.0 7.0 1.0              # Z of atoms
natfix 2  iatfix 1 4           # Keep O and N atoms fixed

#parallelization
#paral_kgb 1   npimage 10   npband 10 npfft 2  bandpp 1

#options for printing
 prtwf 0                     # Option for WF printing
 prtden 0                    # Option for density printing
 prteig 0                    # Option for eigvalues printing

#ground state
ecut 20    pawecutdg 40
toldff 5.0d-7                # Stopping criterion of SCF cycle
nstep 50
nband  10                    # Number of bands to compute
occopt 1                     # Occupations scheme
kptopt 0                     # Scheme for k-points generation
nkpt 1  kpt 0.0 0.0 0.0  # Explicit k-point (gamma point)

#XC
ixc -001009   # Select LDA XC functional (LDA PZ from LibXC)

nsym 1        # No symmetry
charge 1.0   # Charge of the simulation cell
```

```
#String Method
xangst          0.0000000000E+00  0.0000000000E+00  0.0000000000E+00
               -3.7593832509E-01 -2.8581911534E-01  8.7109635973E-01
               -3.8439081179E-01  8.6764073738E-01 -2.8530130333E-01
                4.0000000000E+00  0.0000000000E+00  0.0000000000E+00
                4.3461703447E+00 -9.9808458269E-02 -9.5466143436E-01
                4.3190273240E+00 -7.8675247603E-01  5.6699786920E-01
                4.3411410402E+00  8.7383785043E-01  4.0224838603E-01
                1.0280313162E+00  2.2598784215E-02  1.5561763093E-02

xangst_lastimg      0.0000000000E+00  0.0000000000E+00  0.0000000000E+00
               -3.0400286349E-01 -1.9039526061E-01  9.0873550186E-01
               -3.2251946581E-01  9.0284480687E-01 -1.8824324581E-01
                4.0000000000E+00  0.0000000000E+00  0.0000000000E+00
                4.4876385468E+00 -1.4925704575E-01 -8.9716581956E-01
                4.2142401901E+00 -7.8694929117E-01  6.3097154506E-01
                4.3498225718E+00  8.7106686509E-01  4.2709343135E-01
                2.9570301511E+00  5.5992672027E-02 -1.3560839453E-01

 nimage 12      # Number of images along the string
 imgmov 2       #String Method
 ntimimage 100      # Max. number of relaxation steps of the string
 tolimg 0.0001   # Tol. criterion (will stop when average energy of cells < tolimg)
 dynimage 0 10*1 0     # Keep first and last images fixed
 fxcartfactor 1.0       # Time step for evolution  step of string metho
 prtvolimg 0       # Printing volume (0=full, 1=intermediate, 2=minimal)
```

Minimum Energy Paths: The String Method

If no particular assumption about symmetries along the MEP :
=> set **nsym** 1

Keywords to atomic positions :
First image : **xred_1img** or simply **xred**
Last image : **xred_lastimg** of **xred_9image** (if nimage=9)

xred can be replaced by **xangst** or **xcart**

You can specify intermediate points

SM performed under FIXED lattice vectors !
(no relaxation fo the cell along the MEP, the cell is fixed ;
It is the same for all the images)

Minimum Energy Paths: The String Method

First step of SM : ABINIT interpolates linearly between the images specified in the input file

Fixed images :
The first and last images are fixed (do not evolve) and must correspond to optimized configurations previously obtained.
By default :
dynimage 0 1 1 …. 1 1 0

string_algo
1 : default, Simplified String Method,
2 : « energy-weighted arc length », must give a finer distribution of the images near the saddle point

Symmetric path : it's better using an **odd** number of images !

Minimum Energy Paths: The String Method

Strong point :

string_algo = 1
Images equidistant along the MEP => the index of the image is proportional to the distance along the MEP

=> index of the image = ideal reaction coordinate !

There is physical information not only at the saddle point !
(see below polaron and proton transfers)

NB : **in somes favorable cases**, you need not compute the MEP to have the Barrier ! i.e. if you can constrain the saddle point, e.g. with symmetries !
(structural opt with symmetry constraints can give you directly the saddle point)
Unfortunately, this is rarely the case...

Minimum Energy Paths: The Nudged Elastic Band

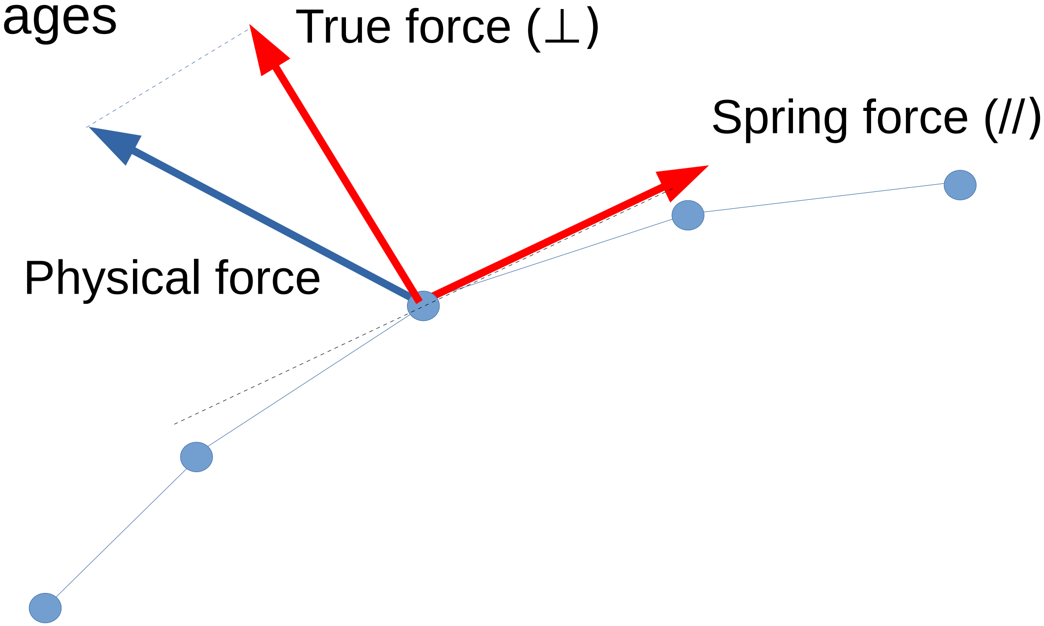
Nudged Elastic Band method (NEB):

- construct **nimage** images intermediate between the initial and the final configuration (*previously optimized*)

- add spring forces between the images

- evolve images according to

a) projection of spring forces
parallel to the tangent
+
b) projection of physical forces
perpendicular to the tangent



neb_algo 1 : the spring constant is the same for all images.

Minimum Energy Paths: The Nudged Elastic Band

Keywords for NEB :

imgmov 5

neb_algo 0 :original method

1 : NEB + improved tangent* (default value)

(improved calculation of tangent direction, modifies the spring force acting on the images)

2 : CI-NEB : Climbing-image NEB (algo seems to be broken...)

neb_spring : minimal and maximal values of the spring constant connecting images for the NEB method. For **neb_algo** 1, it is constant, for **neb_algo** 2 it can vary.

Related to CI-NEB :

cineb_start : 1st iteration at which the CI-NEB begins (default=7) (several iterations of standard NEB first performed to find the highest-energy image)

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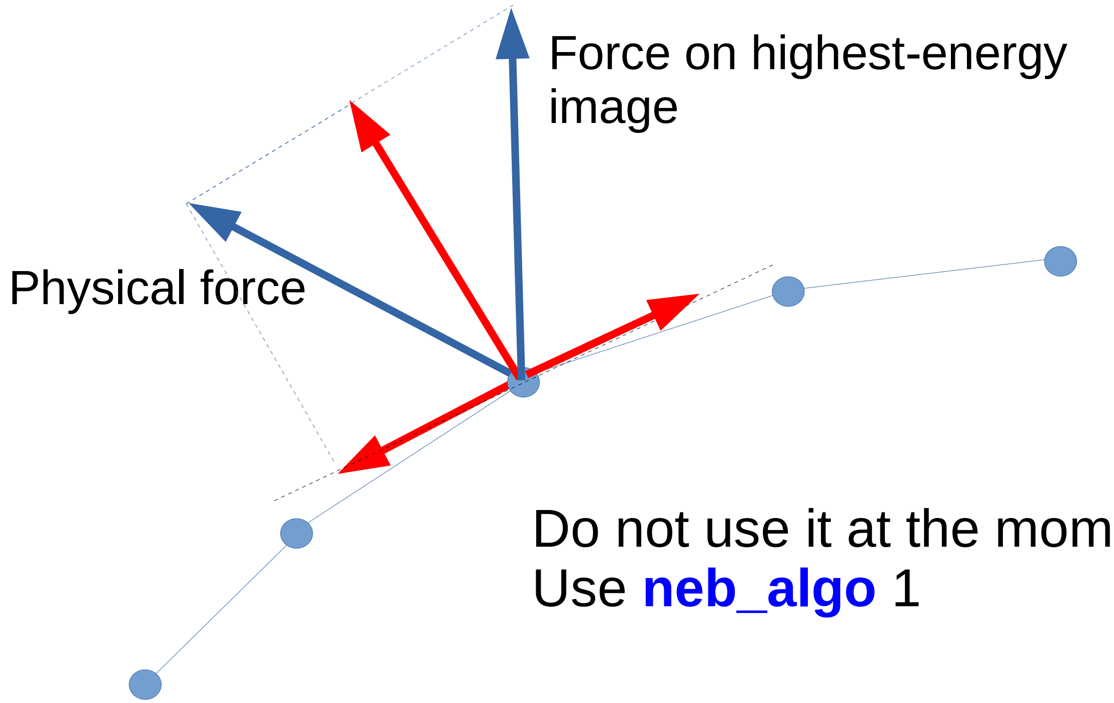
* G. Henkelman and H. Jónsson, "Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points", The Journal of chemical physics 113, 9978–9985 (2000).

Principle of the CI-NEB :
The highest-energy image is forced to come at the saddle point by inverting the // component of the physical force on it.
To identify this image, a number of iterations (**cineb_start**) of standard NEB is first performed. No spring force on this highest-energy image.
Spring constants are variable.

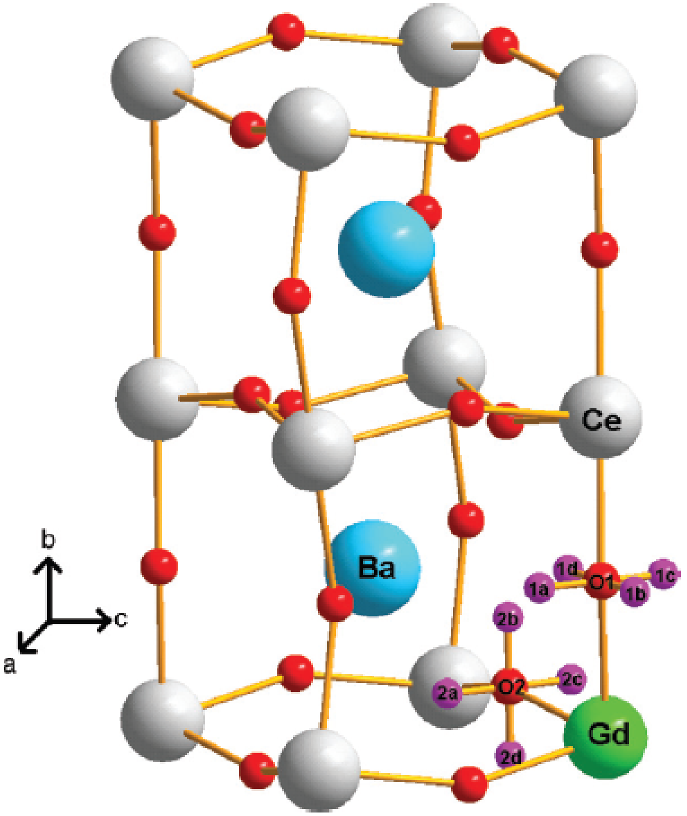


Do not use it at the moment !
Use **neb_algo** 1

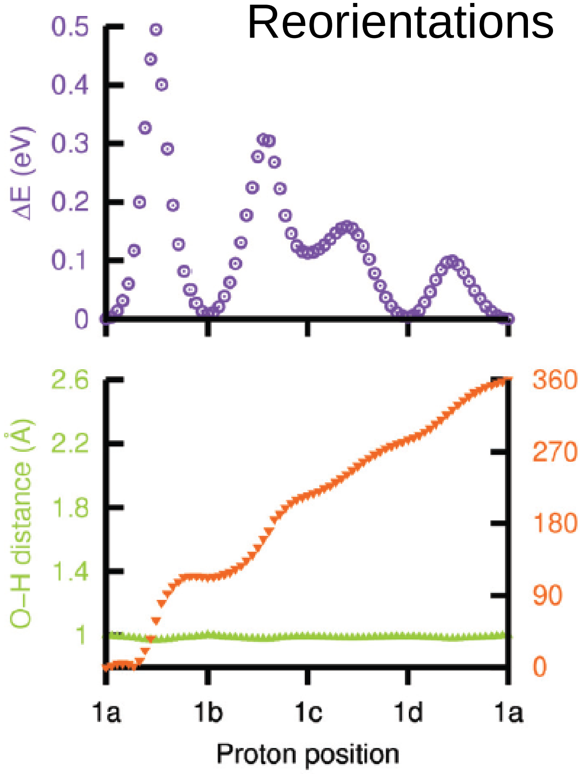
* G. Henkelman, B. P. Uberuaga, H. Jonsson The Journal of chemical physics 113, 9901 (2000).

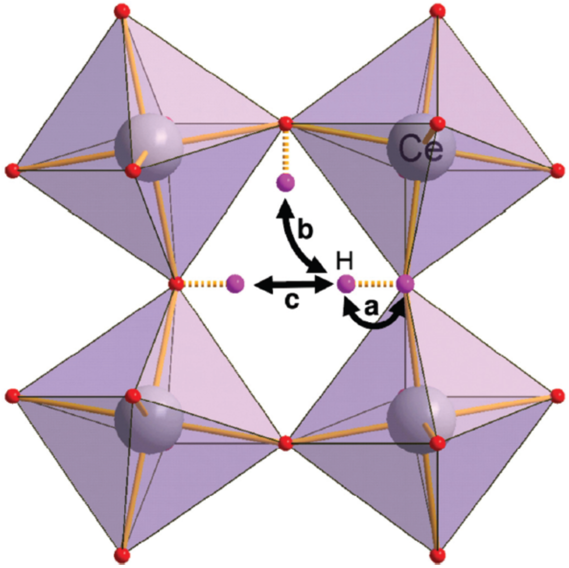
Minimum Energy Paths: Examples

Hoppings and reorientations of protons in Gd:BaCeO_3



Reorientations



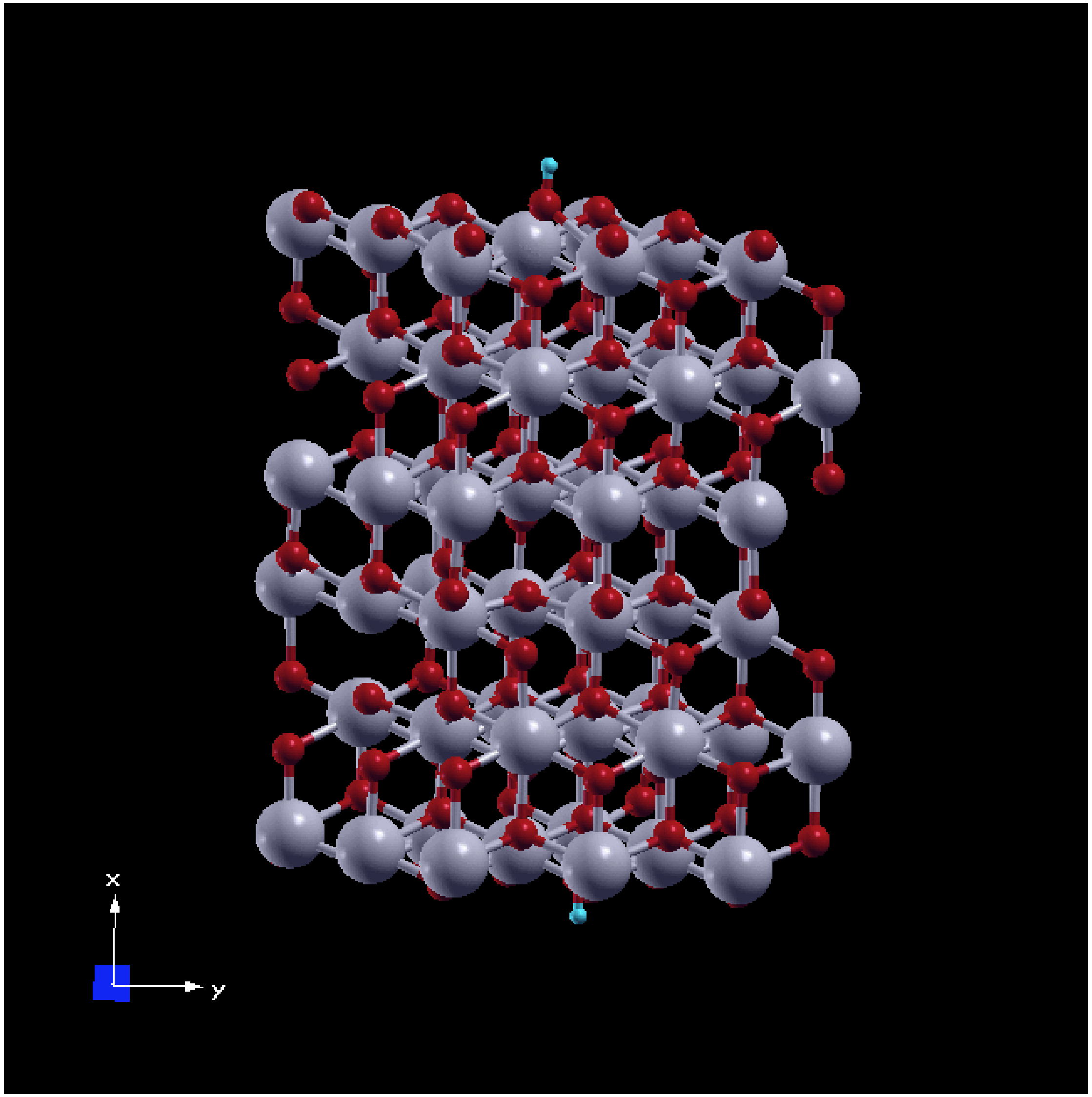


PhD J. Hermet

J. Hermet, M. Torrent, F. Bottin, G. Dezanneau, G. Geneste, PRB **87**, 104303 (2013)

Minimum Energy Paths: Examples

Proton transfer on the O-ZrO2(111) surface



nimage 11
(9 evolving)

motions of the two oxygens

Proton transfer made possible by « cooperative » motion of the two oxygens

Minimum Energy Paths: Small Polaron Hopping

When an electron or a hole is released in the lattice of an insulator (e.g. by a point defect), it may localize on a single atom, instead of staying in a Bloch like delocalized band state = small polaron.

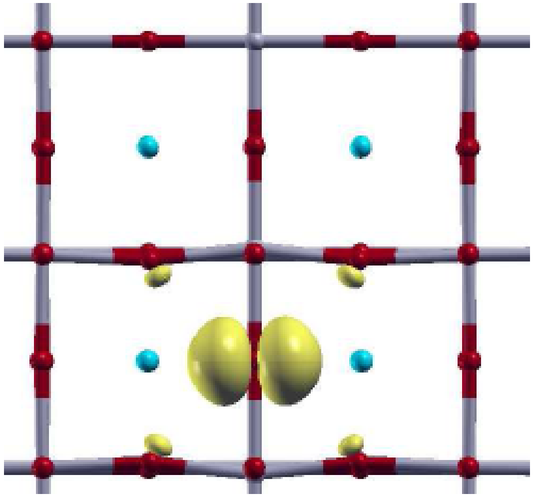
=> the crystal around is distorted (polarized), which in return creates a potential favorable to the localization of the electron(or hole)

= **SELF-TRAPPING**

Energy of the relaxed polaronic configuration minus energy of the configuration with perfet crystal and delocalized electron/hole = **self-trapping energy**
The small polaron is stable if the self-trapping energy is negative.

Ex : oxygen-type hole polaron in $BaSnO_3$

(DFT+U with
U on oxygen p)



G. Geneste, B. Amadon,
M. Torrent, G. Dezanneau,
PRB 96, 134124 (2017)

Minimum Energy Paths: Small Polaron Hopping

Small polarons may diffuse in the lattice, by hopping from an atom onto another ; their hopping rate is usually **thermally activated**.

$$r = r_0 e^{-E_a/k_B T}$$

=> Hopping requires to overcome an energy barrier ; which one ?

It is not the electron/hole that overcomes an energy barrier (the electron gas is supposed to stay in its ground state, thus no thermal agitation for the electron gas) => tunneling ?

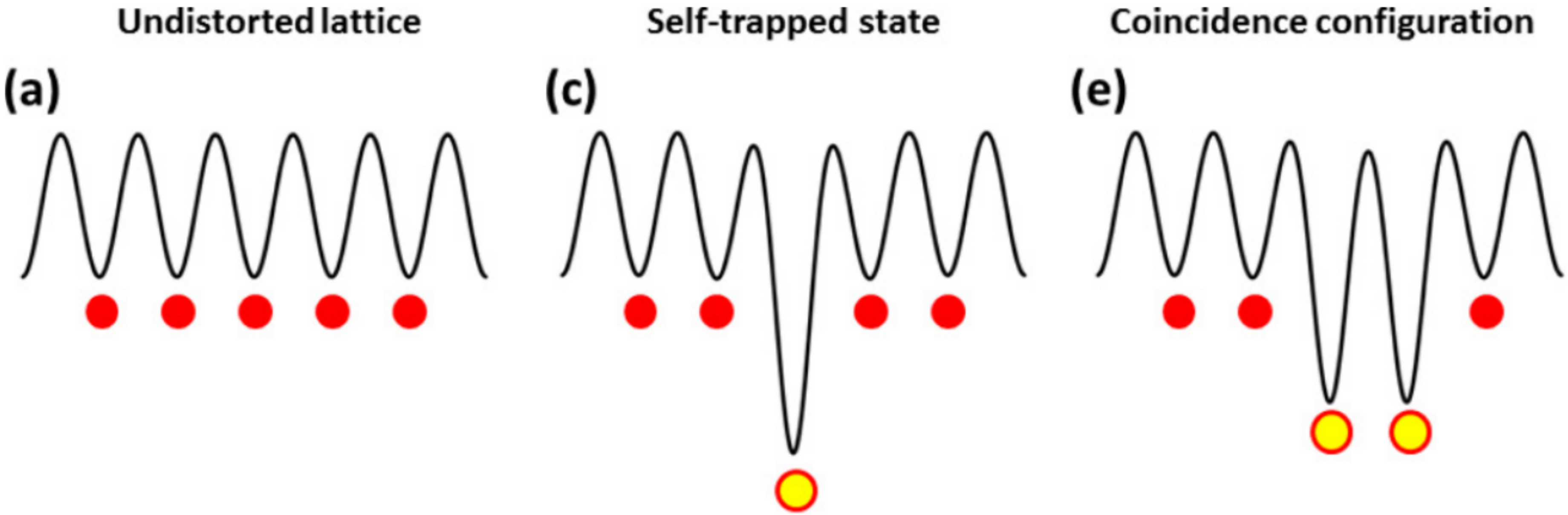
Self-trapped configuration : tunneling impossible !

Resonant tunneling possible in specific configurations
in which the levels on either side of the electronic barrier are in coincidence
= coincidence configurations (CC).

These configurations have energy ~ **Ec** and occur by the thermal fluctuations of the lattice atoms

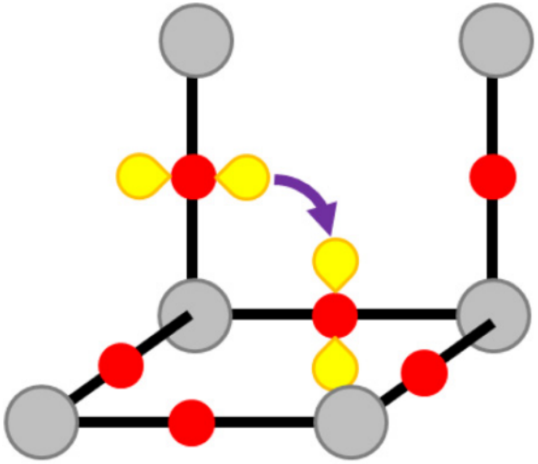
$$r \sim r_0 e^{-E_c/k_B T}$$

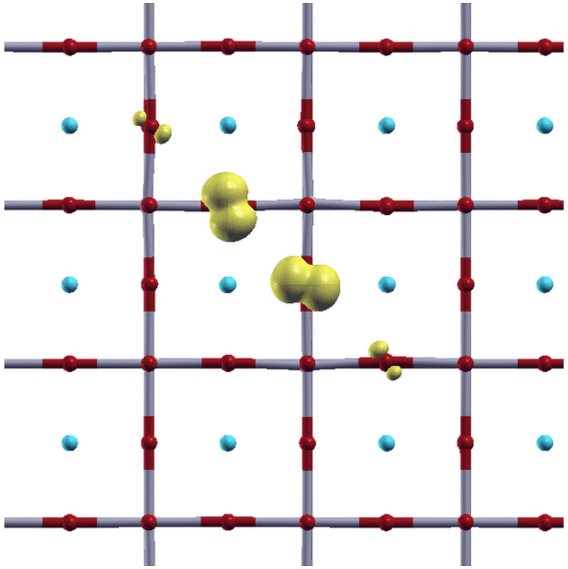
Minimum Energy Paths: Small Polaron Hopping

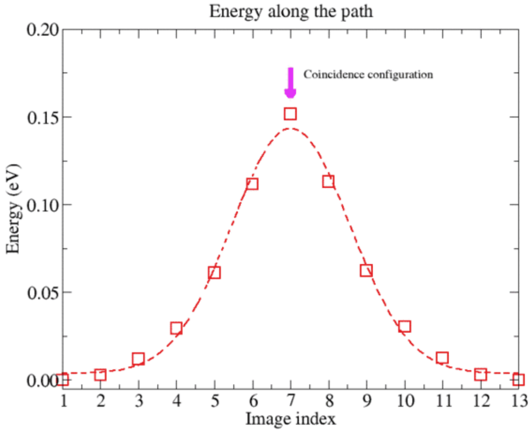


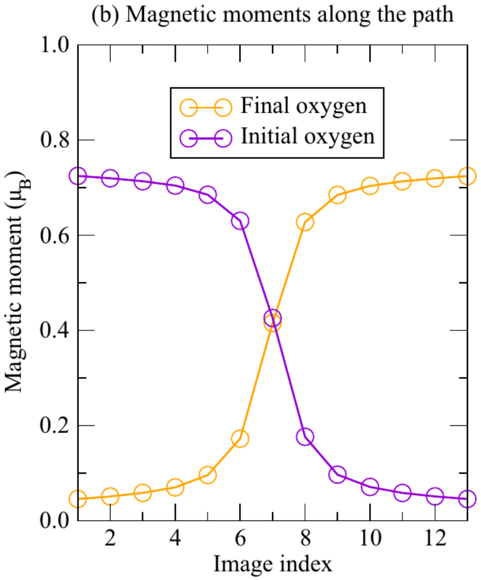
Minimum Energy Paths: Small Polaron Hopping

Case of the oxygen-type hole polaron in BaSnO3









Warning :

- DFT calculation assumes the polaron in its ground state all along the path
- this may not be the case in reality
- because the tunneling transfer in the CC can be long (if electronic coupling is weak)

G. Geneste, B. Amadon, M. Torrent, G. Dezanneau, PRB 96, 134124 (2017)

Minimum Energy Paths: Small Polaron Hopping

If the polaron **has the time to adjust** to the lattice configuration (i.e. adiabatic approximation OK along the MEP)

=> adiabatic transfer

$$r \sim r_0 e^{-E_c/k_B T}$$

Controlled by lattice vibrations

If the polaron **has the NOT time** to adjust to the lattice configuration (i.e. adiabatic approximation not valid anymore near the CC)

=> non-adiabatic transfer :

- the polaron may not have the time to cross, and remains on the starting site
- many occurrences of the CC are necessary before transfer occurs
- at CC, the polaron is not in an (adiabatic) eigenstate
- prefactor controlled by tunneling of the hole at CC

(usually << that of lattice vibrations)

Requires to know the electronic coupling at CC (not provided by NEB)
= [E(1st excited state) – E(GS)]/2 at CC

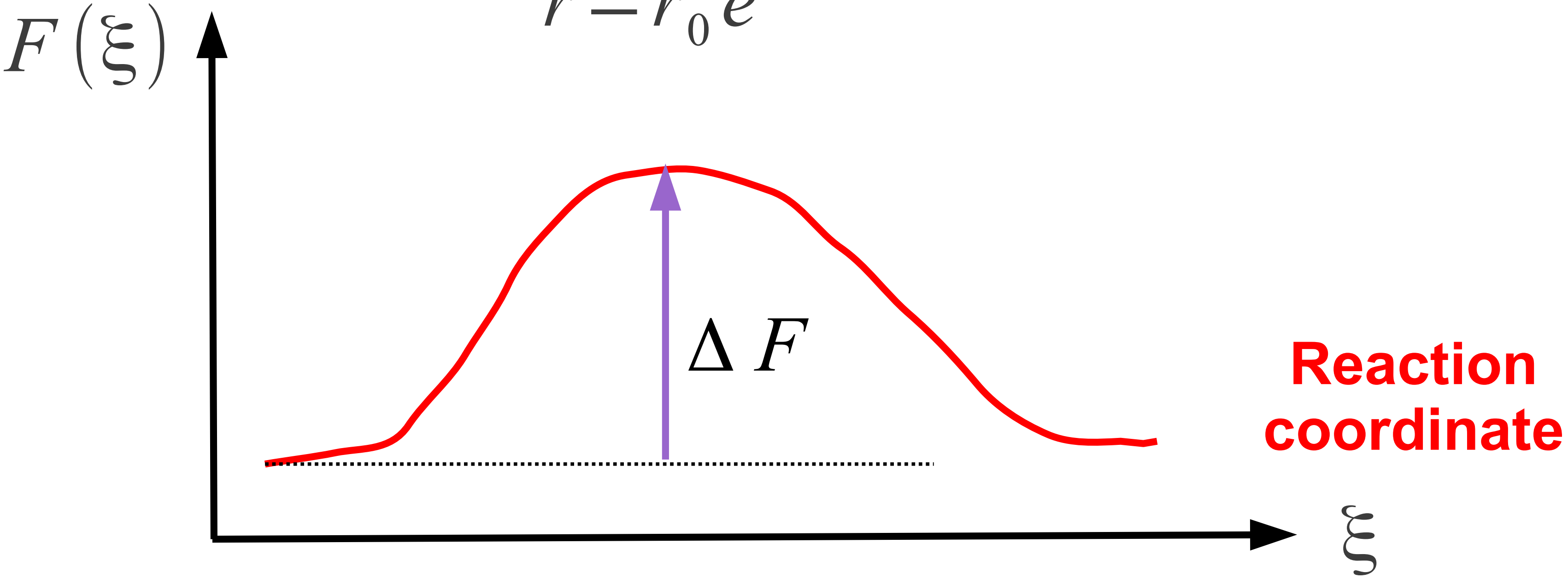
Thermal effects: free energy landscape

MEPs (String Method, NEB) provide a **« static » barrier.**

This static barrier is free of thermal and/or quantum effects.

=> TST normally involves a « free energy » barrier in the expression of the **transition rate** :

$$r = r_0 e^{-\Delta F / k_B T}$$



Thermal effects: free energy landscape

How to obtain this free energy barrier ?

Remember that the free energy as a function a reaction coordinate ξ is related to the density of probability of this reaction coordinate ξ, as

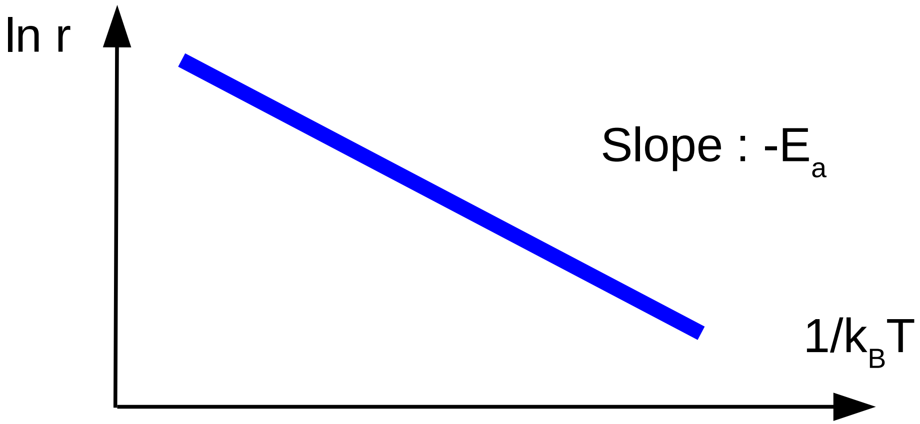
$$F(\xi)-F(\xi_0)=-k_B T \ln\frac{P(\xi)}{P(\xi_0)}$$

With P(ξ) the density of probability of ξ at thermodynamic equilibrium :

$$P(\xi)\propto C\int\dots\int_{\{x_{i\alpha}\}}\delta(\xi(\{x_{i\alpha}\})-\xi)\,e^{-V(\{x_{i\alpha}\})/k_B T}\,dX$$

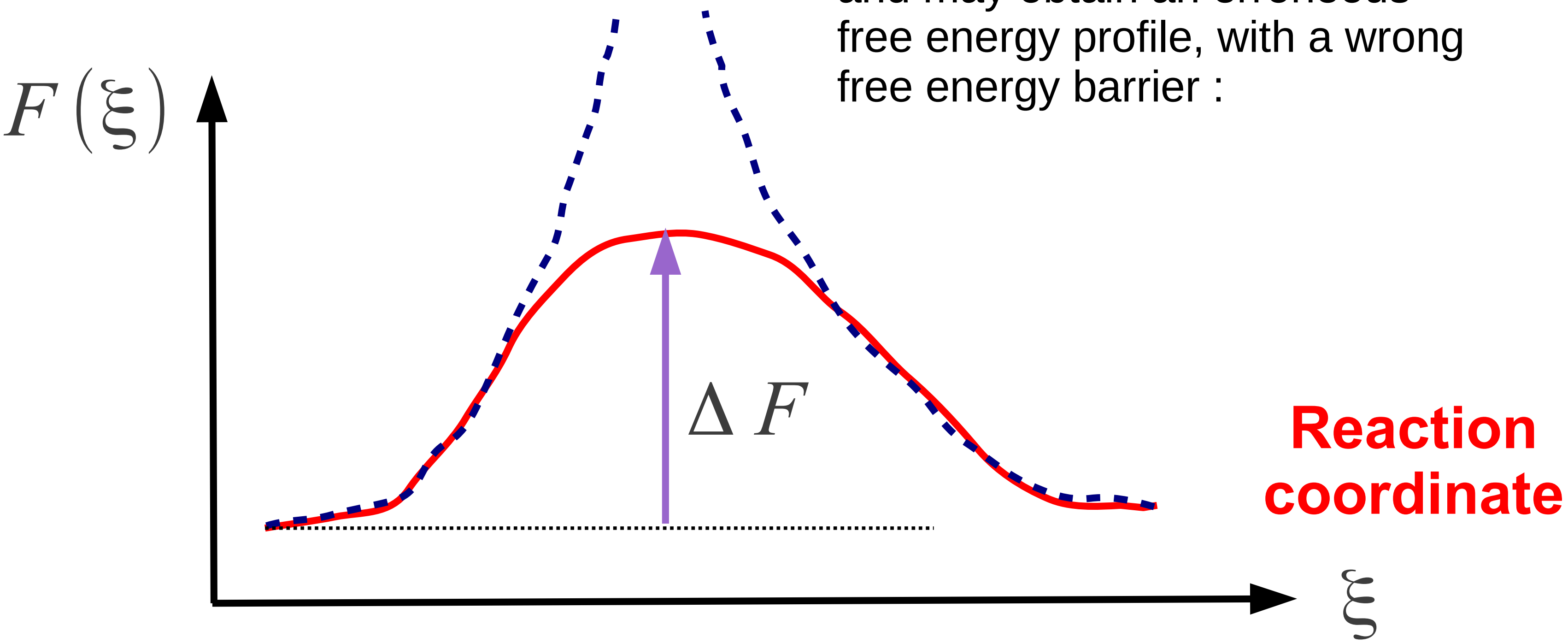
1st possibility : make very long MD runs, at various temperatures, and count the events ! Then plot the log of the rate as a function of 1/T : The slope should be minus the activation energy !

Thermal effects: free energy landscape



Unfortunately, this is rarely POSSIBLE because the statistics will be too bad, especially if the barrier is large w/r to kT !

You will not sample correctly the high free energy (=low proba) regions and may obtain an erroneous free energy profile, with a wrong free energy barrier :



Thermal effects: free energy landscape

Chemists have treated and solved this problem since a long time !
« Blue-Moon » ensemble : Method to simulate the **occurrence of RARE events** within Molecular Dynamics (MD)

- simulate each step of the event by **« forcing » ξ to take a chosen value :**

=> MD under (<u>holonomic) constraint</u> of FIXED ξ

Method of Lagrange multipliers

- Obtain for each value of ξ the derivative of the free energy

« mean force » on the constraint : $-\frac{dF}{d\xi}$

- recover the (free) energy profile by (thermodynamic) integration :

$$\Delta F = F(\xi) - F(\xi_0) = \int_{\xi_0}^{\xi} \frac{dF}{d\xi}(\xi')\, d\xi'$$

Sprik, Cicotti, J. Chem. Phys. ***109****, 7737, (1998)*

Thermal effects: free energy landscape

General case :

$$\xi(\{x_{i\alpha}\})$$

$$\boxed{\frac{dF}{d\xi} = \frac{\langle Z^{-1/2}(-\lambda + k_B T G)\rangle_\xi}{\langle Z^{-1/2}\rangle_\xi}}$$

with :

$$Z = \sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial \xi}{\partial \vec{r}_i}\right)^2$$

$$G = \frac{1}{Z^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{m_i m_j} \frac{\partial \xi}{\partial \vec{r}_i} \frac{\partial^2 \xi}{\partial \vec{r}_i \partial \vec{r}_j} \frac{\partial \xi}{\partial \vec{r}_j}$$

Time average under fixed ξ (constrained MD)

= « blue-moon » ensemble average

$$\boxed{F(\xi_2) - F(\xi_1) = \int_{\xi_1}^{\xi_2} \frac{dF}{d\xi}(\xi')\, d\xi'}$$

Sprik, Cicotti, J. Chem. Phys. ***109****, 7737, (1998)*

Thermal effects: free energy landscape

Implementation **in ABINIT of the LINEAR constraint**
i.e. linear combination between atomic positions

$$\xi(\{x_{i\alpha}\}) = \sum_{i\alpha} a_{i\alpha} x_{i\alpha}$$

Real coefficients

1) *Lagrangian* with *constraints*

$$L = [T(\{\dot{x}_{i\alpha}\}) - V(\{x_{i\alpha}\})] - \lambda\left[\sum_{i\alpha} a_{i\alpha} x_{i\alpha} - \xi\right]$$

2) Apply *Euler-Lagrange equations* :

$$m_i \frac{d^2 x_{i\alpha}}{dt^2} = f_{i\alpha} - \lambda a_{i\alpha}$$

Lagrange multiplier computed at each step as

$$\lambda(t) = \frac{\sum_{i\alpha} a_{i\alpha} \frac{f_{i\alpha}(t)}{m_i}}{\sum_{i\alpha} \frac{a_{i\alpha}^2}{m_i}}$$

3) *Derivative of the free energy* :

$$\frac{dF}{d\xi} = -\langle\lambda\rangle_{\xi} = -\frac{\sum_{i\alpha} \frac{a_{i\alpha}}{m_i} \langle f_{i\alpha}\rangle_{\xi}}{\sum_{i\alpha} \frac{a_{i\alpha}^2}{m_i}}$$

Thermal effects: free energy landscape

- **Physically acceptable** linear constraints satisfy : $\sum_{i\alpha} a_{i\alpha}=0$

- However, even if $\sum_{i\alpha} a_{i\alpha}\neq 0$, a supplemental constraint has been added to ensure that center of mass does not move.

- Value of the constraint ξ : **FIXED** by **INITIAL** set of positions.

- Initialization of the velocities :
The initial velocities must be modified to ensure that the constraint is obeyed, i.e.

$$\sum_{i\alpha} a_{i\alpha}\frac{dx_{i\alpha}}{dt}=0$$

- Implemented in the routine **pimd_apply_constraint** (m_pimd.F90).

- PIMD : the constraint is applied on the centroid.

Thermal effects: free energy landscape

- The constraint is STRICTLY obeyed all along the MD trajectory (at EACH step, NOT on average)

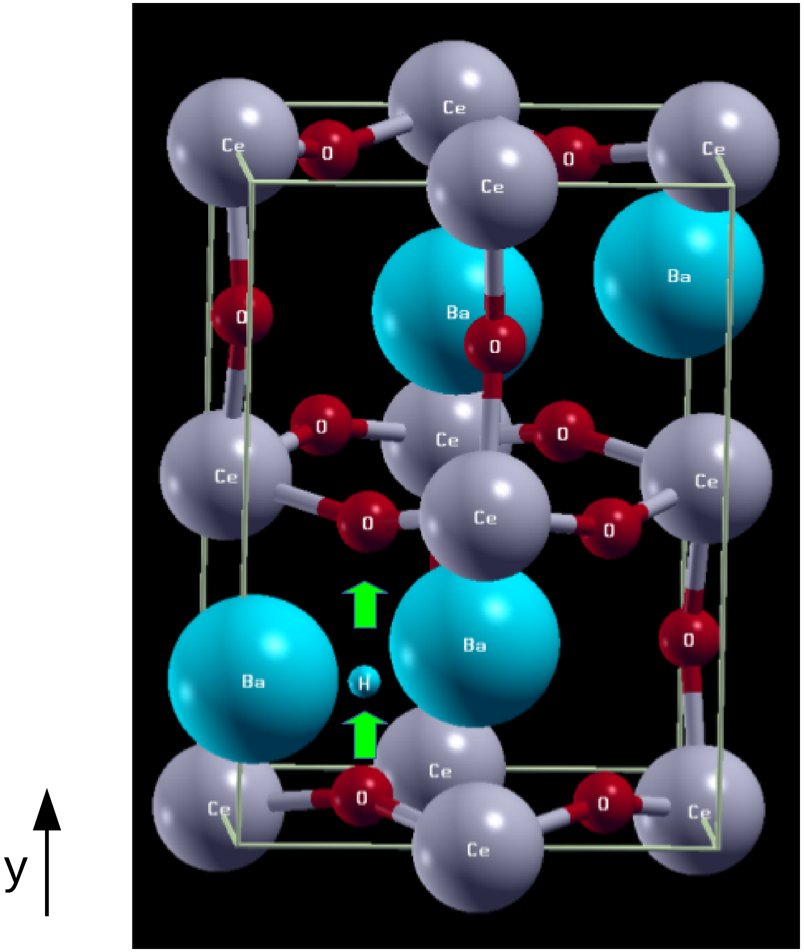
Ex :

```
 - Reaction coordinate =    -36.5852098477
 - Reaction coordinate =    -36.5852098477
 - Reaction coordinate =    -36.5852098477
 - Reaction coordinate =    -36.5852098477
 - Reaction coordinate =    -36.5852098477
 - Reaction coordinate =    -36.5852098477
 - Reaction coordinate =    -36.5852098477
```

- the Center of mass is also strictly FIXED

```
 Center of mass:
     4.6876358799     6.5991695708     4.6808066009
Center of mass:
     4.6876358799     6.5991695708     4.6808066009
Center of mass:
     4.6876358799     6.5991695708     4.6808066009
```

Thermal effects: free energy landscape



Example :

$BaCeO_3$: orthorhombic perovskite
Pnma space group

Excellent protonic conductor

Inter-octahedral transfer of H^+

Cell = 20 atoms
Reaction coordinate : $(O_1H)_y$ - $(O_2H)_y$
$= y(H)-y(O_1) – [y(O_2) – y(H)]$

PIMD, T=200 K
P=32 beads

Thermal effects: free energy landscape

Example of input file of constrained PIMD

```
# PARALLELIZATION
              # => 864 procs
paral_kgb 1
npkpt 9
npband 3
npfft 1
npimage 32

# PIMD/MD
optcell 0
irandom 3
restartxf -1
imgmov 9   # langevin PIMD
ntimimage 10000
nimage 32
mdtemp 400 200
vis 5d-05
dynimage 32*1
nsym 1
pitransform 0
amu      140 16 138 1 # ce o ba h
pimass  140 16 138 1
dtion 10
```

```
# CONSTRAINTS
pimd_constraint 1
nconeq 1
natcon 3
iatcon 5 20 1 #ox1 ox2 hydrogen
wtatcon
0.0 -1.0 0.0 0.0 -1.0 0.0 0.0 2.0 0.0

# ground state
nband 111
occopt 3
tsmear 0.001
pawovlp -1
ixc 11
ecut 18.0
pawecutdg 25.0
kptopt 1
ngkpt 3 2 3
nstep 100
toldff 1.0d-05
prtden 0
prtwf 0

charge 1.0
```

```
# atoms
znucl  58 8 56 1
ntypat 4
natom 21
typat
4 3 1 2 2 3 2 2 3 3 1 1 1 2 2 2 2 2 2 2 2

# cell and atomic positions
acell 11.941471  16.813056  11.913748

xred
  0.279                    0.216                   0.723  #yH to be varied
  2.5108646807E-02  2.5000000000E-01 -8.0469316958E-03
 -1.3877787808E-17 -9.7144514655E-17  5.0000000000E-01
  4.8011508619E-01  2.5000000000E-01  7.9658009587E-02
  2.7974388262E-01  4.3160947462E-02  7.2102708776E-01 #ox1
  9.7489135319E-01  7.5000000000E-01  1.0080469317E+00
  5.1988491381E-01  7.5000000000E-01  9.2034199041E-01
  7.2025611738E-01  9.5683905254E-01  2.7897291224E-01
  5.2510864681E-01  2.5000000000E-01  5.0804693170E-01
  4.7489135319E-01  7.5000000000E-01  4.9195306830E-01
  5.0000000000E-01  5.0000000000E-01 -6.9388939039E-17
 -1.3877787808E-17  5.0000000000E-01  5.0000000000E-01
  5.0000000000E-01 -9.7144514655E-17 -6.9388939039E-17
  9.8011508619E-01  2.5000000000E-01  4.2034199041E-01
  1.9884913809E-02  7.5000000000E-01  5.7965800959E-01
  7.7974388262E-01  4.5683905254E-01  7.7897291224E-01
  7.2025611738E-01  5.4316094746E-01  2.7897291224E-01
  2.2025611738E-01  9.5683905254E-01  2.2102708776E-01
  2.2025611738E-01  5.4316094746E-01  2.2102708776E-01
  2.7974388262E-01  4.5683905254E-01  7.2102708776E-01 #ox2
  7.7974388262E-01  4.3160947462E-02  7.7897291224E-01
```

Thanks for your attention !

DE LA RECHERCHE À L’INDUSTRIE