

Structural Optimizations & Molecular Dynamics in ABINIT

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1 – Introduction

2 – The keyword ionmov

- Structural Optimizations

- Molecular Dynamics

3 – The keyword imgmov

- Minimum Energy Paths

- Path Integral Molecular Dynamics

4 – Conclusion



1 - Introduction

General framework :

DFT is formulated in the **Born-Oppenheimer (BO) Approximation**

Atoms move on a given potential energy surface

Hamiltonian of the system of atoms :

$$H(\{\vec{R}_n\}, \{\vec{P}_n\}) = \sum_{n=1}^N \frac{\vec{P}_n^2}{2M_n} + \sum_{n < n'} \frac{Z_n Z_{n'} e^2}{4\pi\epsilon_0 \|\vec{R}_n - \vec{R}_{n'}\|} + E_e(\{\vec{R}_n\})$$

 Kinetic energy of the nuclei

 Ion-ion (repulsive) electrostatic energy

Energy of the **electron gas** at FIXED positions of the nuclei $\{\vec{R}_n\}$

 Potential energy of the nuclei $V(\{\vec{R}_n\})$



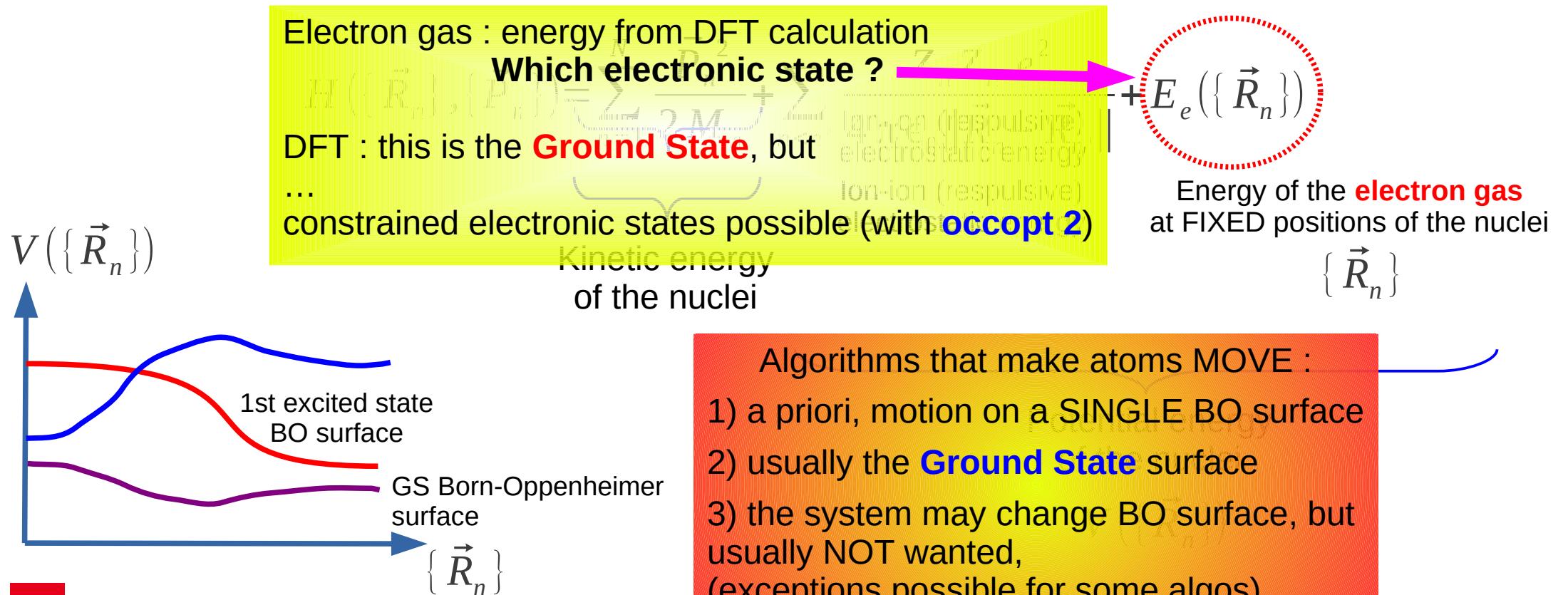
1 - Introduction

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DFT is formulated in the **Born-Oppenheimer (BO) Approximation**

Atoms move on a given potential energy surface

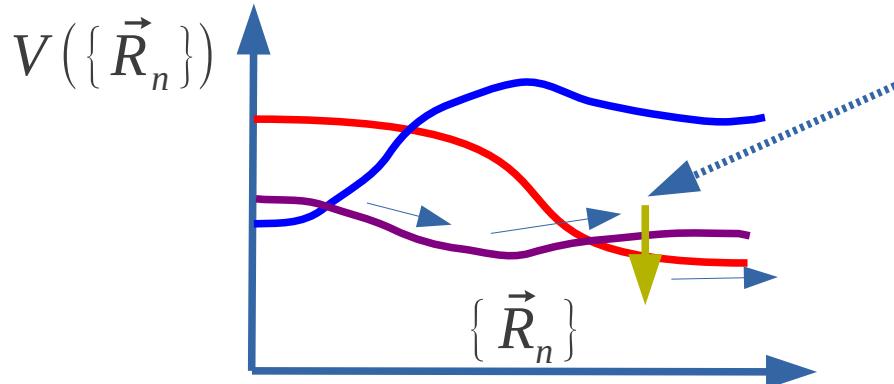
Hamiltonian of the system of atoms :



1 - Introduction

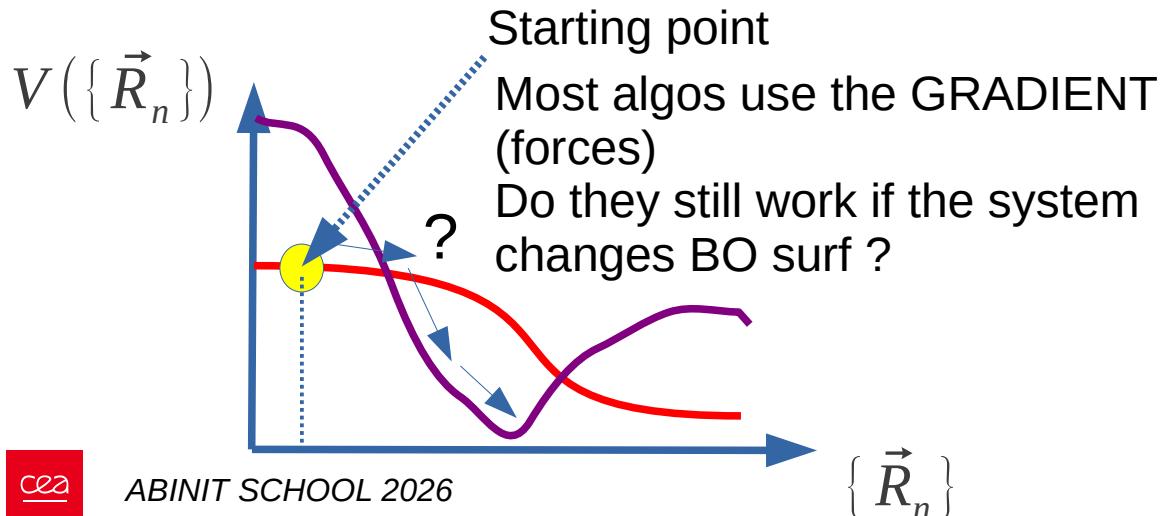
Example 1 : Molecular dynamics

=> MD always performed in a *STATISTICAL ENSEMBLE* (NVE, NVT, NPT, etc)



At that point, imagine the system is changing BO surface
 Energy not conserved, forces discontinuous !
 => The statistical ensemble is (temporarily) LOST !
 => necessity for MD to remain on the same BO surface

Example 2 : Structural optimization



Non spin-polarized system :
 => no problem for staying
 on the GS BO surface, a priori...

Spin-polarized system :
 You can constrain the
 electronic state using **occpt 2** (& **occ**)

Rq : in DFT+U, this constraint
 can be achieved on the occupation
 matrices of correlated orbitals
(usedmatpu, dmatpawu)



1 - Introduction

Calculation of the FORCES : the HELLMAN-FEYNMAN theorem

We suppose that $|\Psi(x)\rangle$ is an eigenvector of $H(x)$, both functions of a parameter x
The corresponding eigenvalue is

$$E(x) = \langle \Psi(x) | H(x) | \Psi(x) \rangle$$

Then we have :

$$\frac{dE}{dx} = \langle \Psi(x) | \frac{dH}{dx} | \Psi(x) \rangle$$

Force $F_{n\alpha}$: take x = displacement of atom n along the direction α

=> the force can be evaluated directly from the electronic calculation of $|\Psi(x)\rangle$,

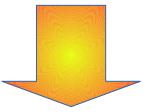
No need to know the derivative of $|\Psi(x)\rangle$



1 - Introduction

ABINIT : many algorithms allowing ions to move
=> controlled by one among **TWO keywords** :

ionmov



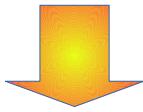
The algorithm **need not replicas** of the system

=> **Structural Optimizations**

=> **Molecular Dynamics**

=> ...

imgmov

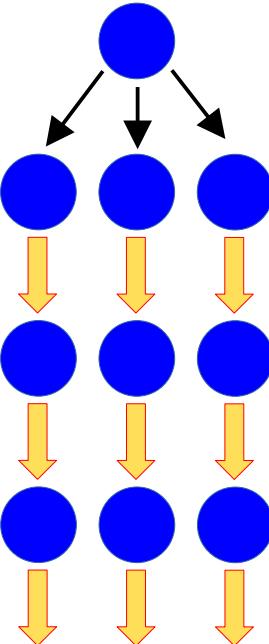
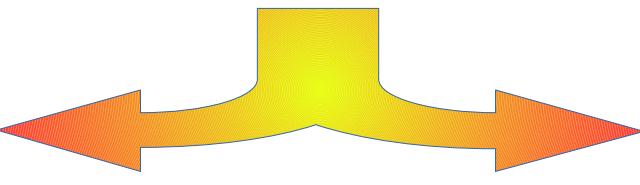
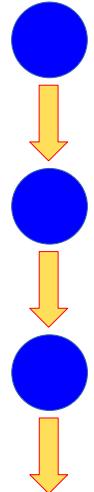


The algorithm **involves replicas** of the system

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

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

=> ...





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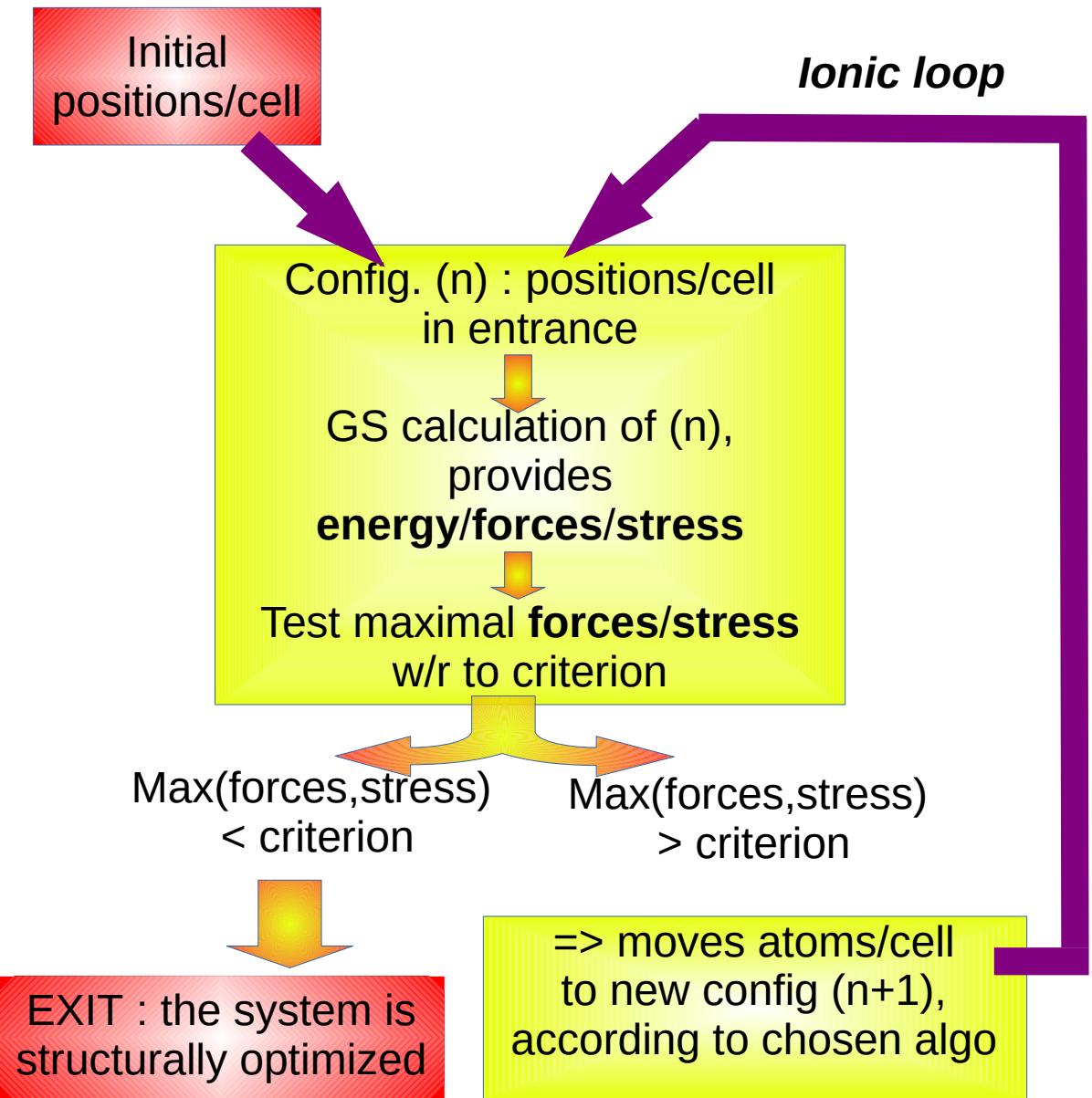
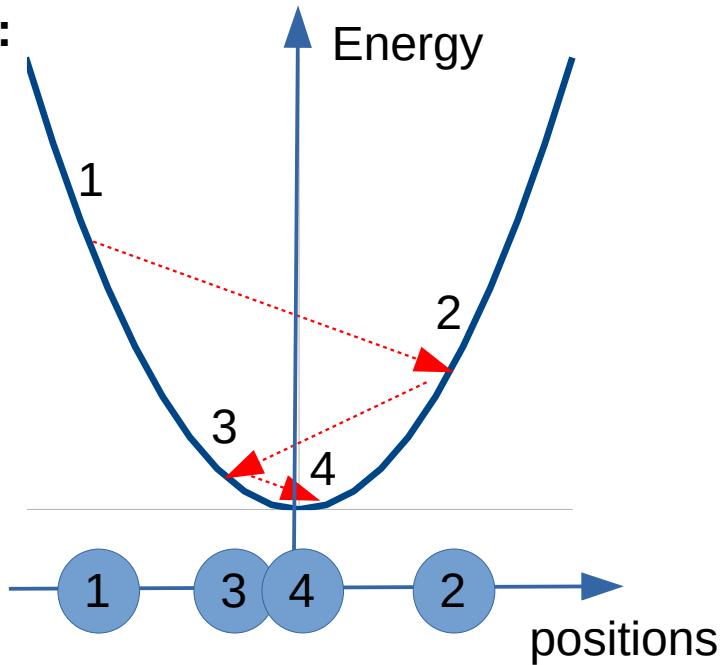
4 – Conclusion

2 - The keyword IONMOV : structural optimizations

Principle :

Starting from an initial set of atomic positions, modifies these positions (**possibly also the cell**) to minimize the energy (**enthalpy**).

Example :



2 - The keyword IONMOV : structural optimizations

Principle :

Starting from an initial set of atomic positions, modify

these positions (possibly) to minimize

Numerical parameters needed :

- initial positions/cell of the system : try to make it as close as possible to the solution !

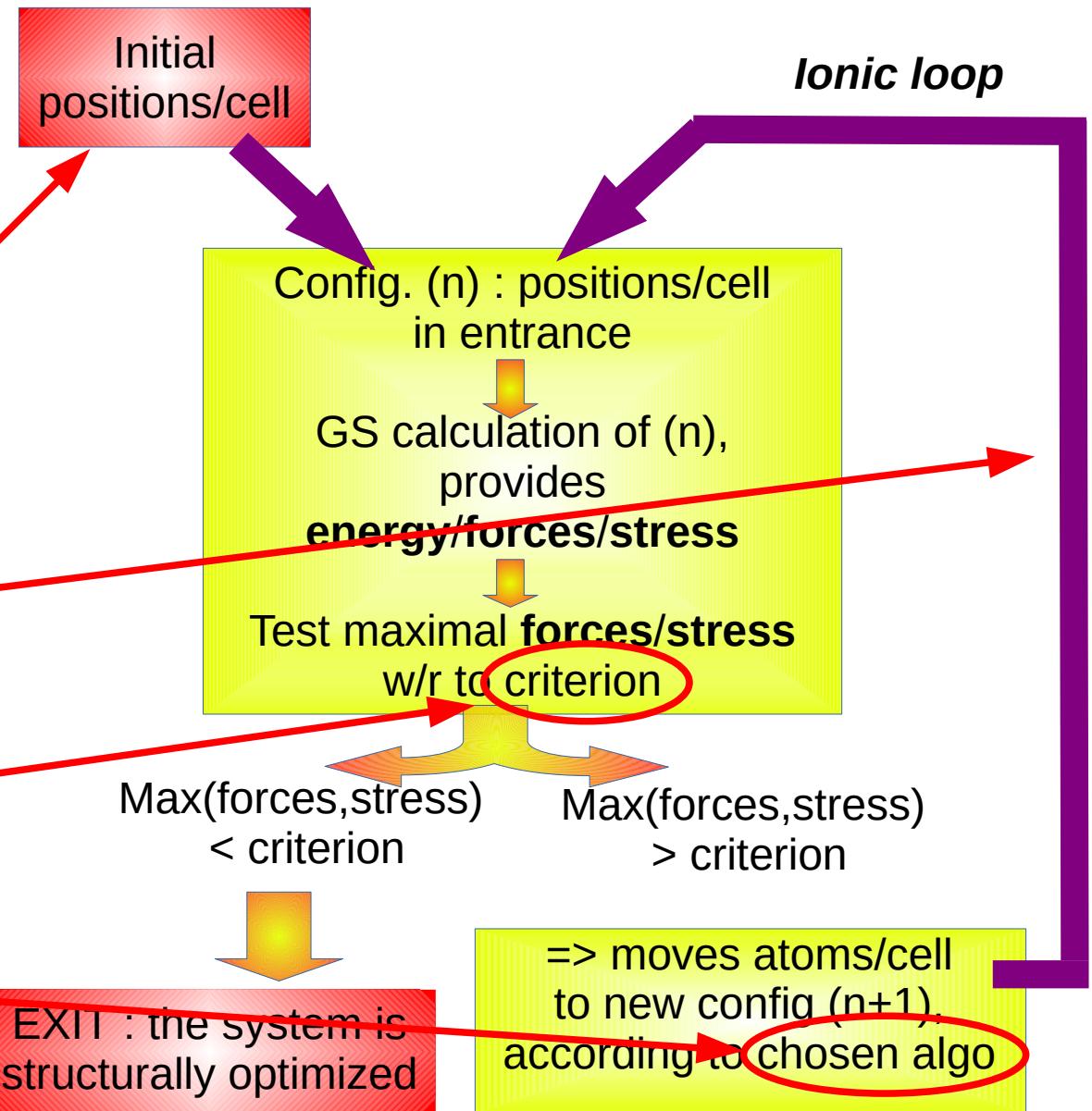
- maximal number of steps (it may never converge!) :

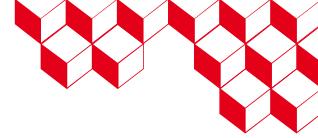
ntime

- Stopping criterion on Maximal forces/stress :
tolmxf, tolmxf/strfact

- choose an algorithm : value of **ionmov**

Example





2 - The keyword IONMOV : structural optimizations

Algorithms :

Many algorithms do exist : **Speepest-Descent, Conjugate Gradient, Newton, quasi-Newton etc**

In ABINIT : **Broyden-Fletcher-Goldfarb-Shanno minimization (BFGS) algorithm**

Belongs to the family of **QUASI-NEWTON** methods

Very efficient minimization algorithm :

Uses not only the GRADIENT (forces) but also (approximations of) the HESSIAN to predict the direction to follow.

Principle of NEWTON methods :

- the function to minimize is replaced by its 2nd-order Taylor expansion (at current position) :

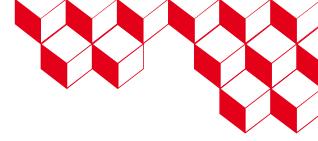
$$V(R_k + dR_k) \approx V(R_k) + \nabla V(R_k) \cdot dR_k + \frac{1}{2} dR_k \cdot [H_k \cdot dR_k] + \dots$$

- $X_k \Rightarrow X_{k+1}$ to be placed at the minimum of this function : $\nabla V(R_k) + H_k \cdot (R_{k+1} - R_k) = 0$

- we obtain :

$$R_{k+1} = R_k - [H_k^{-1}] \cdot \nabla V(R_k)$$

Inverse of Hessian



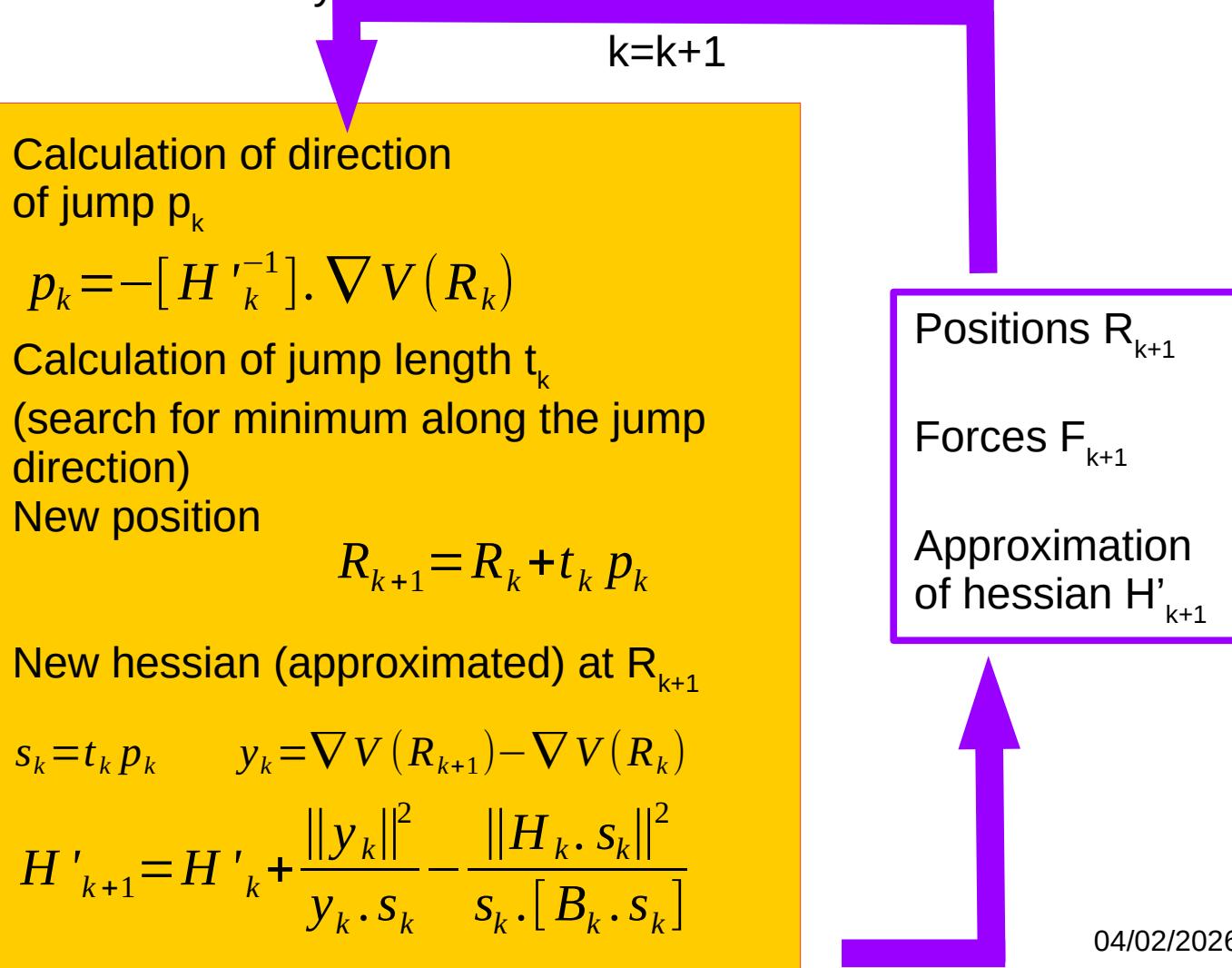
2 - The keyword IONMOV : structural optimizations

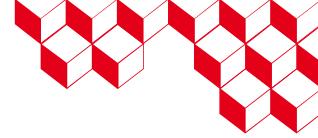
- Newton methods not applicable to DFT because requires knowledge of Hessian at each step !

⇒ « Quasi-Newton method » : replace the Hessian by successive approximations

BFGS algo :

initialize algo
with
 $H'_{00} = I$
+
Knowledge of X_0
(initial config)
+ initial forces
(DFT calculation)





2 - The keyword IONMOV : structural optimizations

ABINIT Keywords :

Broyden-Fletcher-Goldfarb-Shanno minimization (BFGS) algorithm : **ionmov 2 or 3 or 22**

Number of optimization steps (ionic loop) : **ntime**

Stopping criterion – on maximal forces : **tolmxf** (in Ha/bohr : default = 5.0×10^{-5})

Optimize the atomic positions ONLY (**optcell 0**) or also the cell (**optcell $\neq 0$**)

optcell 1: homothetic dilatation of the cell to optimize volume only

optcell 2 : all degrees of freedom optimized

optcell 3 : optimize under constant volume

optcell 4 ... 9 : optimize one or two lattice vectors

You can continue a previous run using **restartxf**

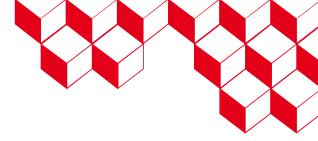
If **optcell $\neq 0$** , criterion on stresses : **strfact** (default=100) stress_max = **tolmxf/strfact** (in Ha/bohr³)

Target stress : **strttarget** (Voigt notations)

Other keywords : **ecutsm**, **dilatmx**

Rq : **initial SYMMETRIES are constrained along the optimizations**

(one can release this constraint by setting **nsym 1**)



2 - The keyword IONMOV : structural optimizations

Performing properly a structural optimization :

Structural optimization AND electronic ground state calculation are in relation:

At each step, Max of forces/stress is compared to stopping criterion



To make sense, the numerical precision on forces/stress must be << criterion = **tolmxr**

Numerical precision on forces/stress : depends on convergence of the GS calculation
ABINIT possesses a GS convergence criterion related to forces : **toldff** (or **tolrff**)

Typically you may use,
(very safe value)

$$\text{toldff} = \text{tolmxr}/50$$

(or **tolrff** = $1/50 = 0.02$)

Ex : tolmxr 5.0d-05 (default, in Ha/bohr)
toldff 1.0d-06 (in Ha/bohr)

GS criterion for structural optimization (and MD) :

Preferred : **toldff**, **tolrff**

Also possible : **tolvrs**

In some cases, forces are always zero by symmetry => **tolvrs** or **toldfe**

NOW CORRECTED !
toldff/tolrff also work



2 - The keyword IONMOV : structural optimizations

Example of **input file for structural optimization (ATOMIC POSITIONS ONLY)**

```

## CaZrO3: structural optimization at fixed lattice vectors ##

##### The system #####
acell 5.583 8.007 5.759 Angstrom #expt latt con
natom 20
znuc 20 40 8
ntypat 3
typat 4*1 4*2 12*3

xred
..... # here follows the 20 atomic positions in reduced coord.

##### parameters for GS calculations #####
ixc 11 #GGA-PBE
ecut 18.0 #plane-wave cut-off
pawecutdg 30.0 #cut-off double grid
kptopt 1
ngkpt 4 3 4 #k-point mesh sampling the Brillouin Zone
toldff 4.0d-06 ## tolmxsf/50
nstep 100 # maximal number of iterations for GS convergence
occpt 1 #default: insulator
nband 100

##### structural optimization #####
ionmov 2 #Broyden algo
optcell 0 #lattice vectors kept fixed (this is the default value)
ntime 200
tolmxsf 2.0d-04 #stopping criterion for struct. opt. in Ha/bohr

```

**toldff =
tolmxsf/50**

Rq : here **tolmxsf=2.0d-04** Ha/bohr ~ 0.01 eV/Å

**tolmxsf and toldff should
be chosen in coherence
with each other**

2 - The keyword IONMOV : structural optimizations

Example of output :
Structural optimization
of H_2 molecule

iter	Etot(hartree)	deltaE(h)	residm	nres2	diffor	maxfor
ETOT 1	-1.1626798387780	-1.163E+00	3.879E-13	2.503E-04	1.160E-03	1.973E-04
ETOT 2	-1.1626810426665	-1.204E-06	1.070E-14	2.829E-05	1.446E-04	5.263E-05
ETOT 3	-1.1626809824101	6.026E-08	2.566E-11	4.586E-07	6.917E-05	1.653E-05
ETOT 4	-1.1626809602542	2.216E-08	9.907E-14	4.447E-08	3.945E-07	1.614E-05
ETOT 5	-1.1626809603685	-1.143E-10	1.098E-13	1.132E-08	9.116E-07	1.523E-05
ETOT 6	-1.1626809672017	-6.833E-09	6.748E-14	3.727E-09	5.323E-07	1.470E-05
ETOT 7	-1.1626809772975	-1.010E-08	8.807E-15	1.216E-09	4.866E-07	1.421E-05
ETOT 8	-1.1626809845912	-7.294E-09	4.658E-15	4.987E-10	2.656E-07	1.394E-05
ETOT 9	-1.1626809876569	-3.066E-09	1.527E-15	2.564E-10	1.694E-07	1.377E-05
ETOT 10	-1.1626809902953	-2.638E-09	1.839E-14	1.009E-10	1.393E-07	1.363E-05

At SCF step 10, forces are converged :
 for the second time, max diff in force= 1.393E-07 < toldff = 2.000E-07

Final maximal force = 1.36d-05 Ha/bohr : this is a **VERY LOW** value !
 Does it make sense ?

Yes because the GS is converged using **toldff** = 2.0d-07 !

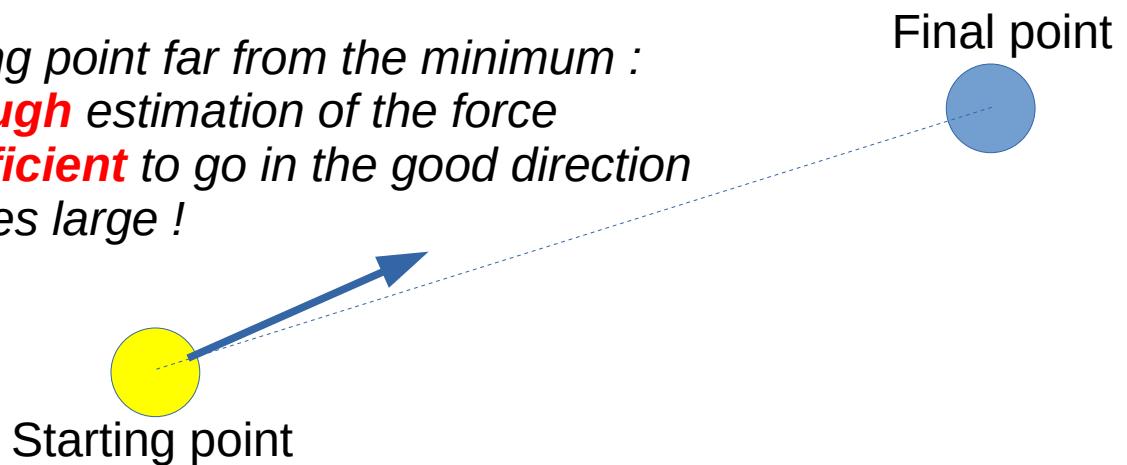
=> the numerical precision on forces at the end of the SCF loop is $\sim 2.0d-07$ Ha/bohr

2 - The keyword IONMOV : structural optimizations

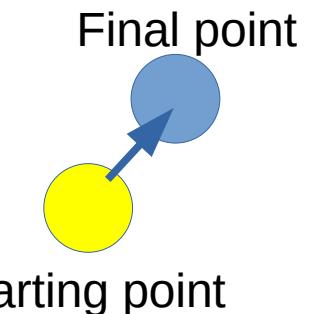
The keyword **tolrff** for GS convergence

The idea : if the initial geometry is FAR from the minimum, you need not converge the first SCF cycles with a high precision, but you need to refine convergence when you approach the minimum !

Starting point far from the minimum :
 => **rough** estimation of the force
 is **sufficient** to go in the good direction
 + forces large !



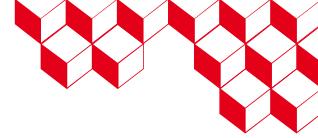
Solution : **tolrff**



Starting point close to the minimum :
 => **precise** estimation of the force
 is **necessary** to go in the good direction
 + forces small !

Stops the electronic loop when : diffor/maxfor < **tolrff** (twice consecutively)

Suggested value for tolrff = 0.02 (=1/50)



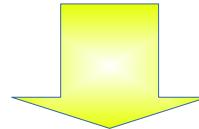
2 - The keyword IONMOV : structural optimizations

Example :

Initial config :

iter	Etot(hartree)	deltaE(h)	residm	nres2	diffor	maxfor
ETOT 1	-660.31969297315	-6.603E+02	4.540E-01	1.799E+02	6.460E-01	6.460E-01
ETOT 2	-662.93461378251	-2.615E+00	1.436E-02	1.068E+02	4.883E-01	8.833E-01
ETOT 3	-662.84457843461	9.004E-02	3.872E-03	2.298E+01	2.150E-01	6.695E-01
ETOT 4	-662.85676465636	-1.219E-02	4.155E-03	1.258E+02	2.835E-01	5.390E-01
ETOT 5	-662.80945102193	4.731E-02	1.940E-03	1.907E+01	1.625E-01	6.201E-01
ETOT 6	-662.79564881801	1.380E-02	6.608E-04	2.164E+00	1.021E-01	5.902E-01
ETOT 7	-662.79164620269	4.003E-03	1.519E-04	2.598E-01	2.972E-02	5.725E-01
ETOT 8	-662.79180014724	-1.539E-04	8.317E-06	1.035E-01	9.571E-03	5.644E-01
ETOT 9	-662.79189607734	-9.593E-05	3.928E-06	1.063E-01	7.093E-03	5.601E-01

At SCF step 9, forces are sufficiently converged :
for the second time, max diff in force= **7.093E-03** is less than < tolrf= 2.000E-02 times max force

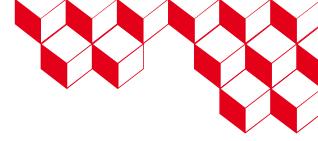


Last config :

iter	Etot(hartree)	deltaE(h)	residm	nres2	diffor	maxfor
ETOT 1	-664.27218782796	-6.643E+02	2.233E-06	2.186E-04	4.815E-04	5.324E-04
ETOT 2	-664.27218776245	6.551E-08	2.412E-10	2.710E-05	5.763E-04	3.568E-04
ETOT 3	-664.27218770753	5.492E-08	3.384E-09	3.335E-06	3.378E-04	6.656E-05
ETOT 4	-664.27218770225	5.283E-09	4.361E-10	4.611E-07	3.349E-05	4.602E-05
ETOT 5	-664.27218770055	1.703E-09	4.847E-11	1.388E-07	1.558E-05	5.053E-05
ETOT 6	-664.27218769856	1.986E-09	1.680E-11	3.846E-08	6.561E-06	5.031E-05
ETOT 7	-664.27218769719	1.374E-09	1.210E-11	1.657E-08	6.143E-06	4.844E-05
ETOT 8	-664.27218769715	3.956E-11	9.212E-13	1.090E-08	1.853E-06	4.800E-05
ETOT 9	-664.27218769731	-1.612E-10	9.455E-13	6.016E-09	1.609E-06	4.709E-05
ETOT 10	-664.27218769833	-1.020E-09	6.241E-12	2.022E-09	2.365E-06	4.604E-05
ETOT 11	-664.27218769952	-1.191E-09	8.622E-12	1.466E-09	4.689E-07	4.587E-05
ETOT 12	-664.27218770090	-1.378E-09	7.484E-12	8.249E-10	4.205E-07	4.565E-05

At SCF step 12, forces are sufficiently converged :
for the second time, max diff in force= **4.205E-07** is less than < tolrf= 2.000E-02 times max force

Here :
tolmx 5.0d-05
tolrff 0.02



2 - The keyword IONMOV : structural optimizations

CONSTRAINTS :

1) Fixing atoms or coordinates

All coordinates : **natfix** (number of fixed atoms), **iatfix** (indices of the fixed atoms)

Or just one coordinate :

natfixx, iatfixx

natfixy, iatfixy

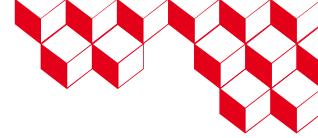
natfixz, iatfixz

2) Fixing linear relations between atomic coordinates

Number of such relations : **nconeq**

Atoms involved : **iatcon**

Coefficients of the linear combination : **wtatcon**



2 - The keyword IONMOV : structural optimizations

Fixed pressure structural optimizations : optcell=2

= all degrees of freedom relaxed under symmetry constraints (those of the initial configuration)

Ex : T=0 K equation of state of a solid

In conjunction with **ionmov=2**

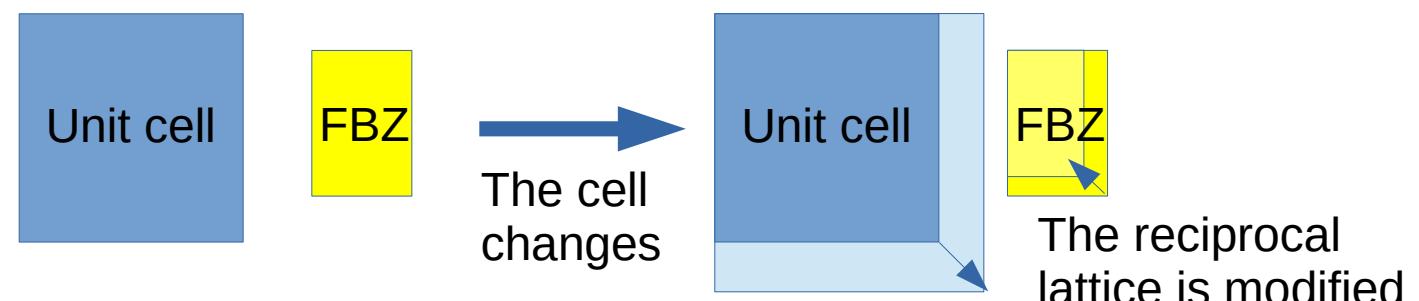
Stopping criterion on stresses : ABINIT uses **tolmxf/strfact**

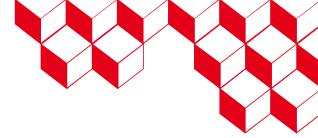
Default : **strfact**=100 bohr²

For **tolmxf**=5.0d-05 Ha/bohr => max stress = 5.0d-07 Ha/bohr³

optcell=2 performs the optimization under SYMMETRY constraints, i.e. the space group of the starting configuration is maintained.

A few additional keywords have to be specified when **optcell** ≠ 0 :





2 - The keyword IONMOV : structural optimizations

⇒ **G-vectors of the Reciprocal Lattice can get in or out the plane-wave sphere :**

1) may cause discontinuities of the energy :

These discontinuities are **SMOOTHED** by using **ecutsm** ≠ 0

Recommended value : **ecutsm** = 0.5 (Ha)

Rq : **ecutsm** ≠ 0 is compulsory to perform cell optimization

2) A maximal permitted dilatation of the lattice vectors has to be defined, thanks to **dilatmx**

NB : if **dilatmx** ≥ 1.15, you have to set : **chkdilatmx** 0

Rq : a too large value of dilatmx causes waste of memory and CPU time !

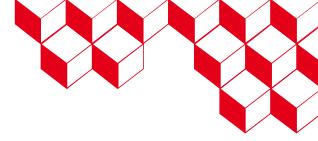
3) the final stress tensor can be specified using **strtarget** (Voigt notations)

Ex : suppose you want to optimize a crystal under an hydrostatic pressure of 15 GPa

This corresponds to a stress tensor of

$$\sigma = \begin{bmatrix} -0.000509839 & 0.0 & 0.0 \\ 0.0 & -0.000509839 & 0.0 \\ 0.0 & 0.0 & -0.000509839 \end{bmatrix}$$

strtarget -0.000509839 -0.000509839 -0.000509839 0.0 0.0 0.0 (in Ha/bohr³)



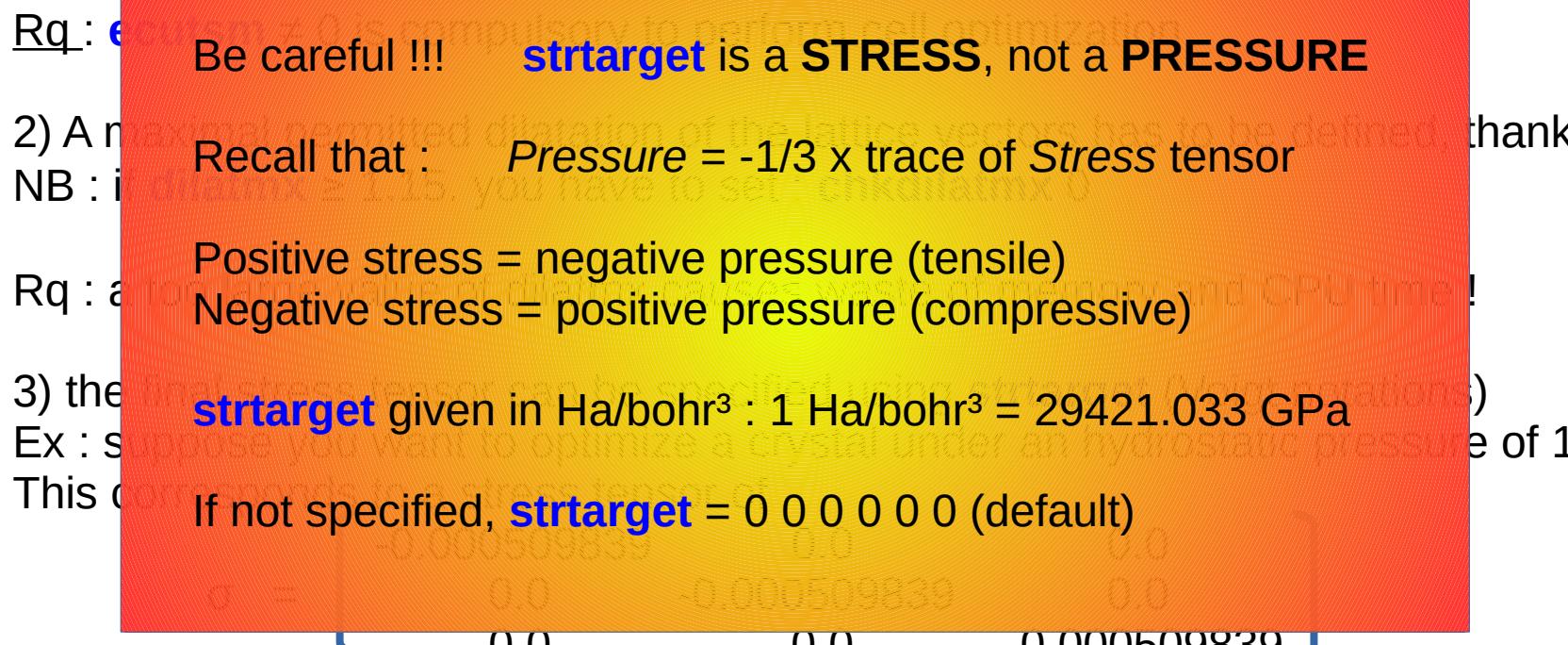
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⇒ **G-vectors of the Reciprocal Lattice can get in or out the plane-wave sphere :**

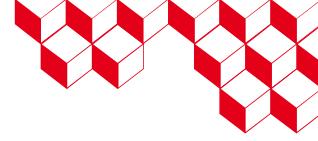
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Recommended value : **ecutsm** = 0.5 (Ha)



strttarget -0.000509839 -0.000509839 -0.000509839 0.0 0.0 0.0 (in Ha/bohr³)



2 - The keyword IONMOV : structural optimizations

1st example : optimize the lattice constants of CaZrO₃ in GGA-PBE

```
### CaZrO3: structural optimization at zero pressure ###  
##### The system #####  
acell 5.583 8.007 5.759 Angstrom #expt latt con  
natom 20  
znucl 20 40 8  
ntypat 3  
typat 4*1 4*2 12*3  
  
xred  
..... # here follows the 20 atomic positions in reduced coord.  
  
##### parameters for GS calculations #####  
ixc 11 #GGA-PBE  
ecut 18.0 #plane-wave cut-off  
pawecutdg 30.0 #cut-off double grid  
kptopt 1  
ngkpt 4 3 4 #k-point mesh sampling the Brillouin Zone  
toldff 4.0d-06 ## tolmx/50 ←  
nstep 100 # maximal number of iterations for GS convergence  
occpt 1 #default: insulator  
nband 100  
  
##### structural optimization #####  
ionmov 2 #Broyden algo  
optcell 2 #lattice vectors kept fixed (this is the default value)  
ntime 200  
tolmx 2.0d-04 #stopping criterion for struct. opt. in Ha/bohr  
ecutsm 0.5  
dilatmx 1.1  
strttarget 0.0 0.0 0.0 0.0 0.0 0.0 ## optional because 0 = default value
```

Take previous input
Change **optcell** from 0 to 2
Add :
ecutsm 0.5
dilatmx 1.1 (allows max dilatation of 10%)
If dilatmx exceeds 1.15, add
chkdilatmx 0
Add optionnally :
strttarget (default= 0 0 0 0 0 0)

toldff =
tolmx/50

2 - The keyword IONMOV : structural optimizations

2nd example : T=0 K EOS of FeH₃

```
#####
# T=0K equation of state of FeH3 #####
chksymbreak 0

#####
# The system #####
acell 3*4.69
natom 4
ntypat 2
znucl 26 1
typat 1 2 2 2
xred
0.0 0.0 0.0
0.5 0.5 0.0
0.5 0.0 0.5
0.0 0.5 0.5

#####
parameters for GS calculations #####
ixc 11 #GGA-PBE
ecut 30.0 pawecutdg 40.0
kptopt 1 ngkpt 24 24 24
nstep 100
toldfe 1.0d-12
occpt 3 #metallic occupation
tsmear 0.001
nband 60

#####
structural optimization #####
ionmov 2
optcell 2
ntime 200
tolmx 1.0d-05
ecutsm 0.5
dilatmx 1.3 chkdilatmx 0
```

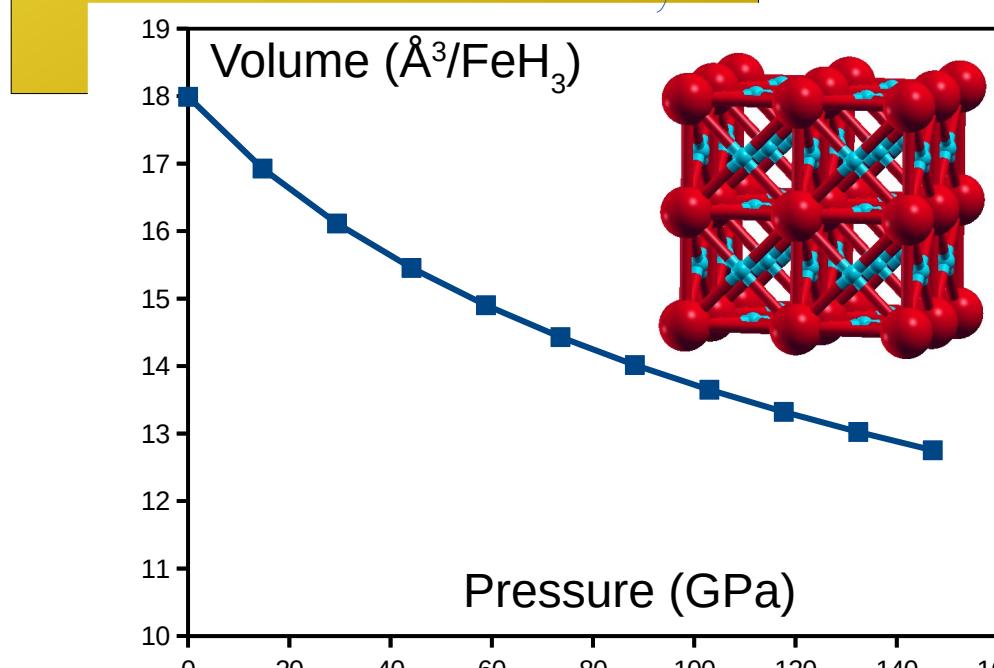
FeH₃=cubic crystal,
space group *Pm-3m*
Forces are ZERO
by symmetry !
Here **toldfe** used, but
now you can use
toldff or **tolrff**

=> use alternative
GS criterion
toldfe or **tolvrs**

```
getcell -1 getxred -1
Takes final positions/cell of dataset n
to initialize dataset n+1
```

ndset 11
strtarget1 -0.0050 -0.0050 -0.0050 0.0 0.0 0.0
strtarget2 -0.0045 -0.0045 -0.0045 0.0 0.0 0.0
strtarget3 -0.0040 -0.0040 -0.0040 0.0 0.0 0.0
strtarget4 -0.0035 -0.0035 -0.0035 0.0 0.0 0.0
strtarget5 -0.0030 -0.0030 -0.0030 0.0 0.0 0.0
strtarget6 -0.0025 -0.0025 -0.0025 0.0 0.0 0.0
strtarget7 -0.0020 -0.0020 -0.0020 0.0 0.0 0.0
strtarget8 -0.0015 -0.0015 -0.0015 0.0 0.0 0.0
strtarget9 -0.0010 -0.0010 -0.0010 0.0 0.0 0.0
strtarget10 -0.0005 -0.0005 -0.0005 0.0 0.0 0.0
strtarget11 0.0000 0.0000 0.0000 0.0 0.0 0.0

Multidataset mode to compute several pressures





CONTENT

1 – Introduction

2 – The keyword ionmov

- Structural Optimizations

- Molecular Dynamics

3 – The keyword imgmov

- Minimum Energy Paths

- Path Integral Molecular Dynamics

4 – Conclusion

2 - The keyword IONMOV : Molecular Dynamics

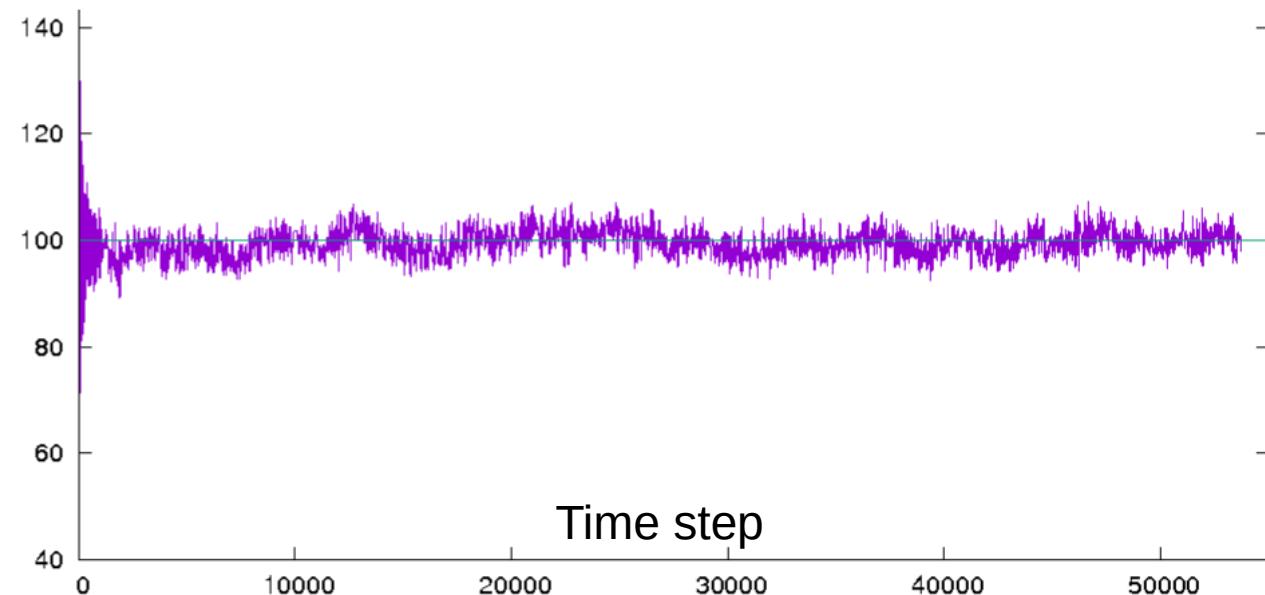
Molecular Dynamics : numerical technique in **Classical Statistical Physics**

Allows **exploring Phase Space**, produces a trajectory characteristic of a **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





2 - The keyword IONMOV : Molecular Dynamics

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

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

usually : GS BO surface
(+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**

KEYWORDS for AIMD :

To start a MD simulation, you **ABSOLUTELY** need to specify : **nsym 1** (suppress symmetries)

- initial positions and cell (**xred/acell/rprim**)
- initial velocities (**vel**), usually 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**, one for each atom type



2 - The keyword IONMOV : Molecular Dynamics

Molecular Dynamics at Thermodynamic Equilibrium (atoms are **classical**) : TWO goals

THERMODYNAMICS

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 ...

KINETICS

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

2 - The keyword IONMOV : Molecular Dynamics

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

=> We need a **time step**, specified in ABINIT by the keyword **dtion** (number of time steps = **ntime**)
 (expressed in atomic times units, i.e. 1 a.u. of time $\sim 2.4 \times 10^{-17}$ s)
 Typical value of dtion : 100 or below (determined by maximal phonon frequency) default=100

VERLET algorithm :

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

At time step 1 : **Taylor** algorithm

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

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**.

2 – The keyword IONMOV : Molecular Dynamics

MD can be performed with ABINIT in several ways :

- **NVE ensemble (microcanonical)** :

the total energy is fixed

The volume (and more generally the supercell) is 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 value).

The rate of exchange is controlled by a parameter (« mass » or friction coeff) :

- **Nose-Hoover** thermostat

Nose « mass » : **noseinert**

ionmov 8

- **Langevin** thermostat :

stochastic thermostat, uses random numbers

ionmov 9

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

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)

mdtemp(2) = final temperature (at time step *ntime*)

Thermostat temperature evolves linearly inbetween

- **Isokinetic ensemble** (rescaling of velocities) : **ionmov 12**

Temperature maintained strictly constant

2 - The keyword IONMOV : Molecular Dynamics

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

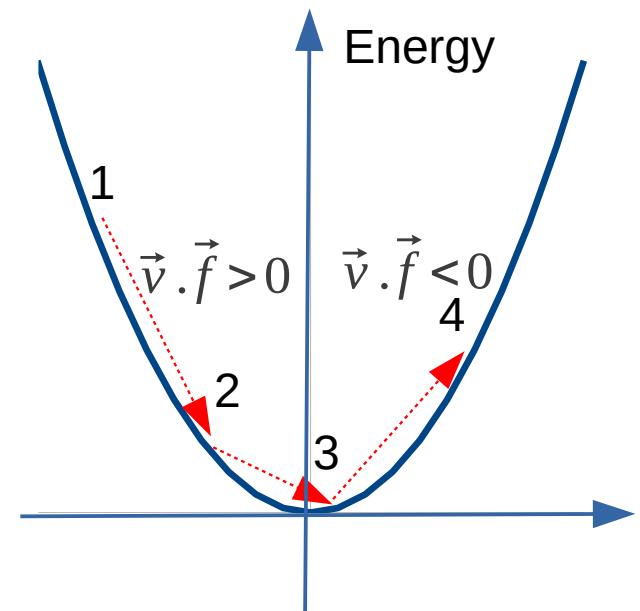
- « Quenched » molecular dynamics **ionmov 7**

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**).



2 - The keyword IONMOV : alternative formulation

Structural optimizations : « geoopt » + keyword

geoopt bfgs : structural optimization based on BFGS algo

geoopt viscous = **ionmov 1**

geoopt quenched = **ionmov 7**

Molecular Dynamics : « moldyn » + keyword

moldyn nve_verlet = **ionmov 6**

Moldyn nvt_isokin = **ionmov 12**

Moldyn nvt_nose = **ionmov 8**

Moldyn nvt_langevin = **ionmov 9**

...



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1 – Introduction

2 – The keyword ionmov

- Structural Optimizations

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4 – Conclusion



CONTENT

1 – Introduction

2 – The keyword ionmov

- Structural Optimizations

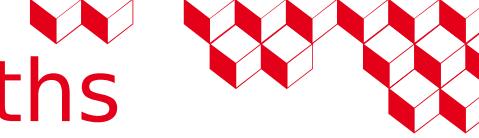
- Molecular Dynamics

3 – The keyword imgmov

- Minimum Energy Paths

- Path Integral Molecular Dynamics

4 – Conclusion



3 - The keyword **IMGMOV** : 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)



3 - The keyword **IMGMOV** : 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 (default)

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



3 - The keyword IMGMOV : 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:

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

with

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

(present implementation = steepest-descent)

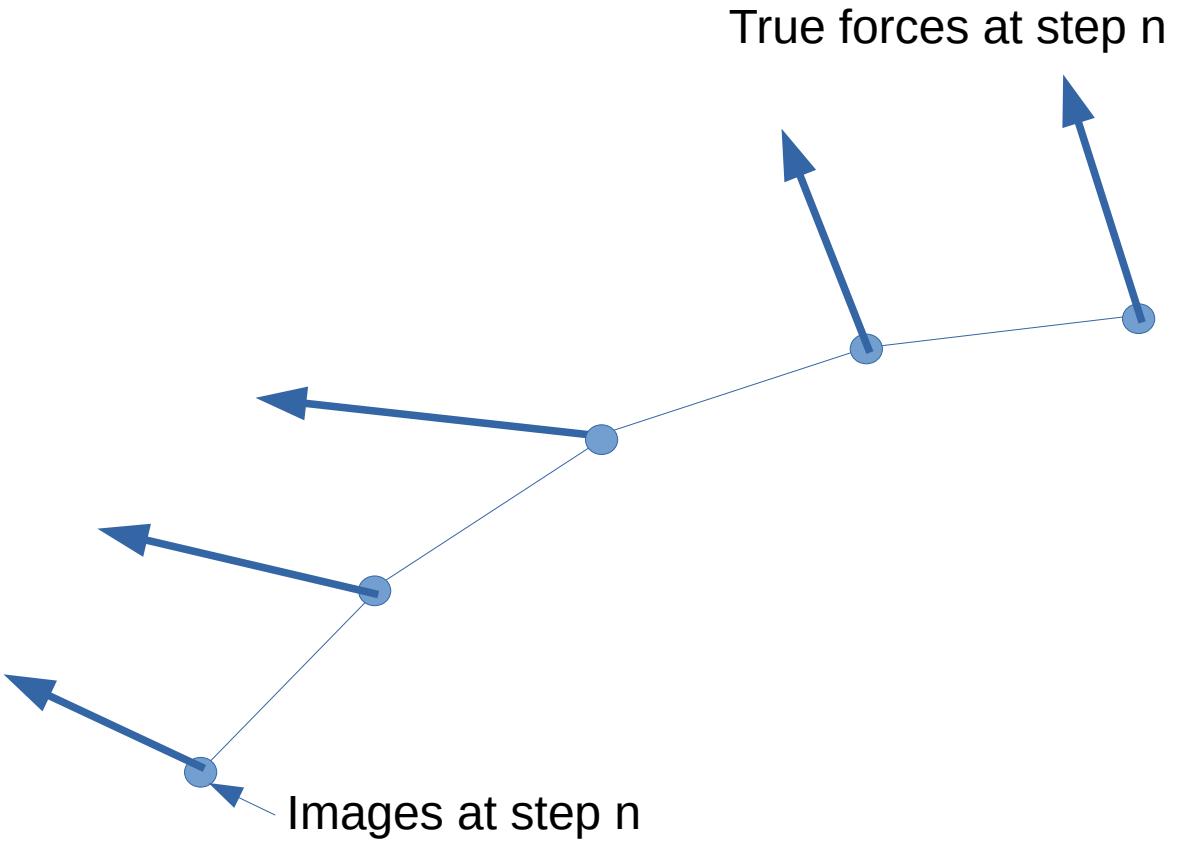
Step 2: reparametrization

The images are equally redistributed along the string

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

3 - The keyword **IMGMOV** : Minimum Energy Paths The String Method

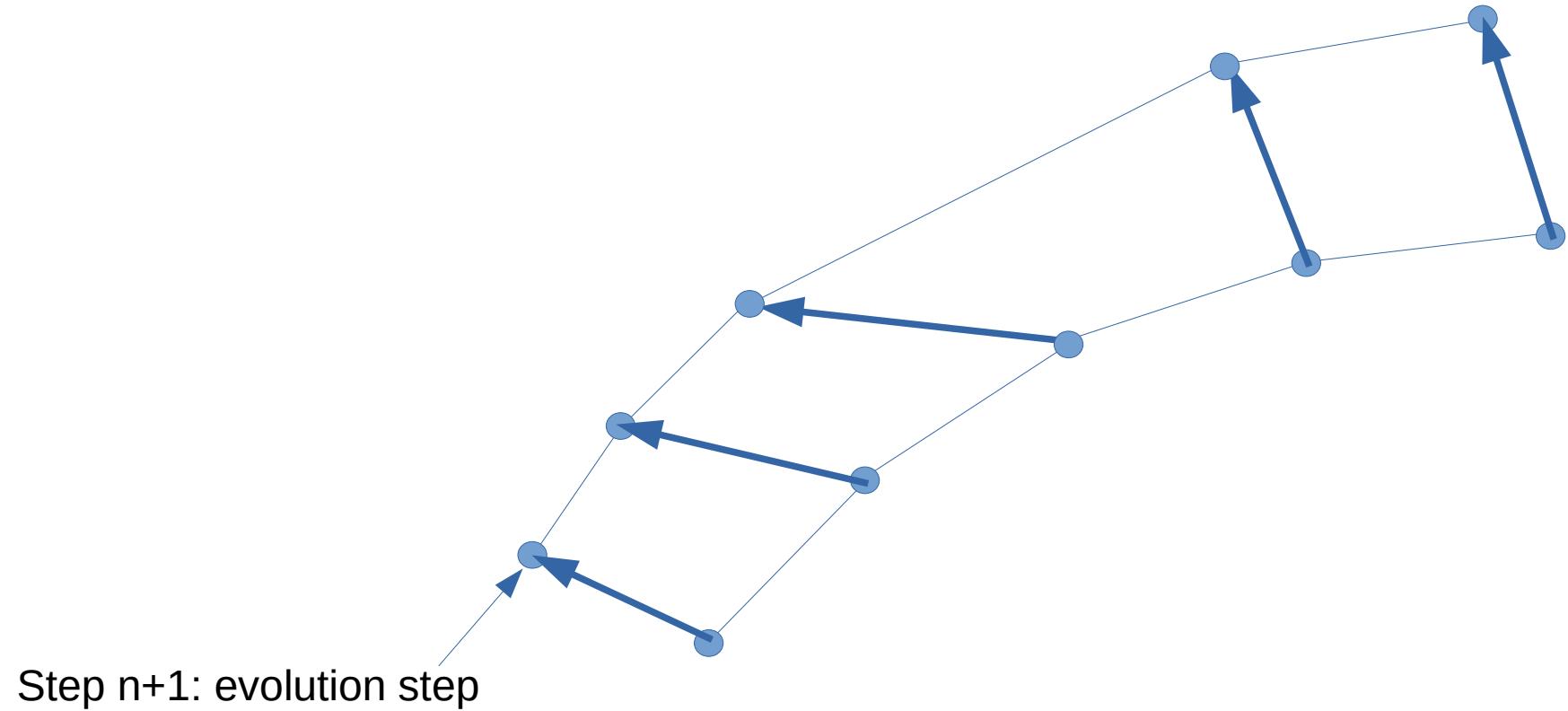
Example (2D):



3 - The keyword IMGMOV : Minimum Energy Paths

The String Method

Example (2D):

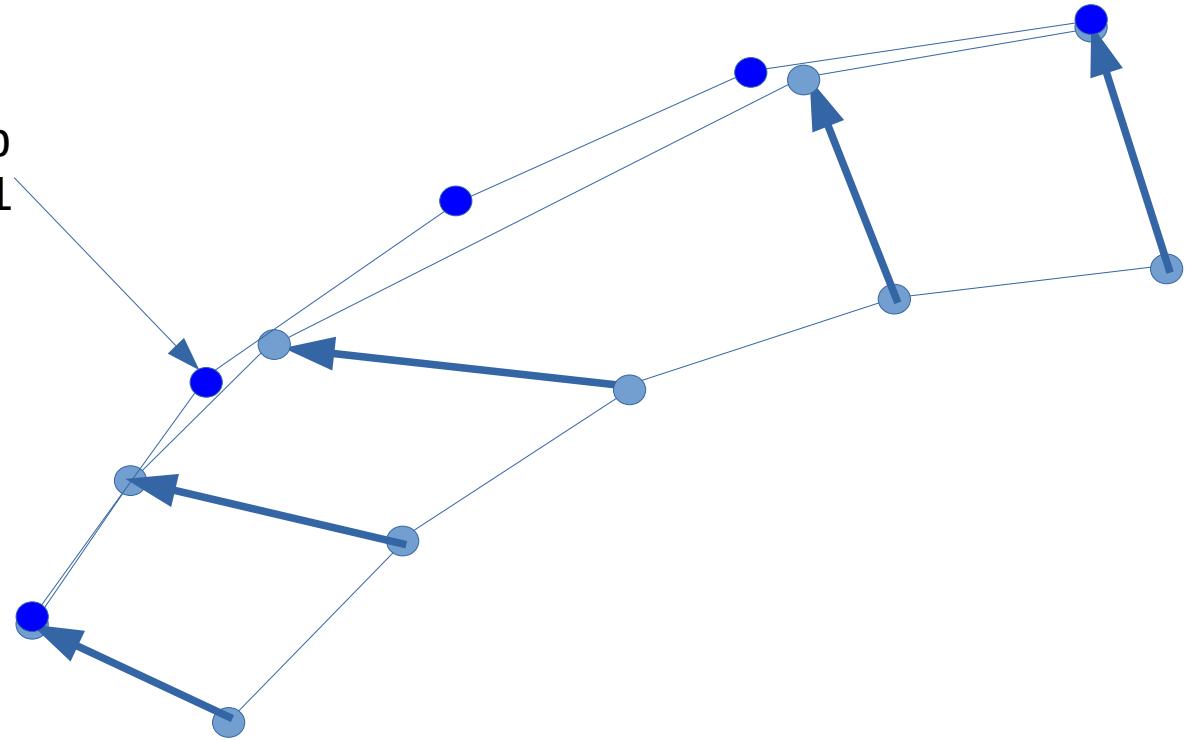


3 - The keyword IMGMOV : Minimum Energy Paths

The String Method

Example (2D):

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



3 - The keyword **IMGMOV** : Minimum Energy Paths The String Method

Example (the one of the Tutorial) : 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 # 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
prt_wf 0          # Option for WF printing
prt_den 0         # Option for density printing
prt_eig 0         # Option for eigvalues printing

#ground state
ecut 20 pawecutdg 40
tolddf 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)
dynamimage 0 10*1 0 # Keep first and last images fixed
fxcartfactor 1.0 # Time step for evolution step of string method
prtvolimg 0 # Printing volume (0=full, 1=intermediate, 2=minimal)
```



3 - The keyword **IMGMOV** : Minimum Energy Paths The String Method

See the tutorial about Minimum Energy Paths :
https://docs.abinit.org/tutorial/paral_images/



3 - The keyword **IMGMOV** : Minimum Energy Paths The String Method

If no particular assumption about symmetries along the MEP :

=> set **nsym 1**

Keywords for atomic positions :

First image : **xred_1img** or simply **xred**

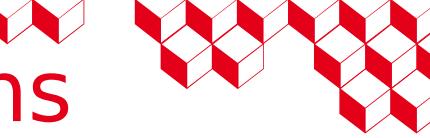
Last image : **xred_lastimg** or **xred_9img** (if nimage=9)

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

You can specify intermediate configurations

SM performed under **FIXED** lattice vectors !

(no relaxation of the cell along the MEP, the cell is fixed ; it is the same for all the images)



3 - The keyword **IMGMOV** : 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 :

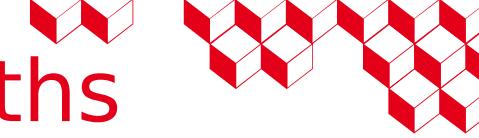
dynimage 0 1 1 1 1 0

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 !



3 - The keyword **IMGMOV** : 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 !

Rq : this si also the case for the NEB using **neb_algo 1**

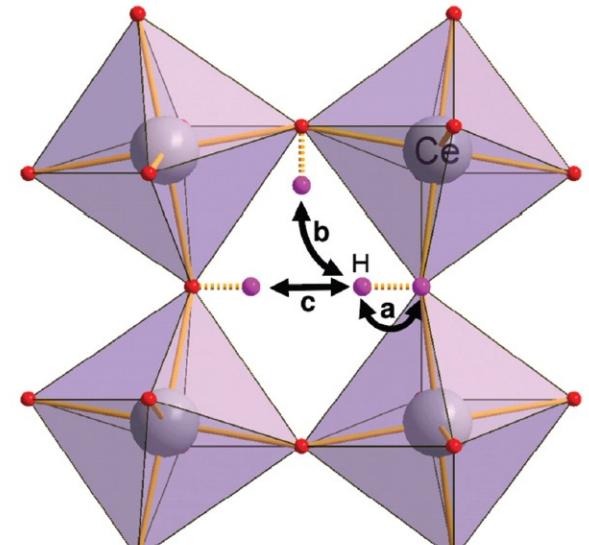
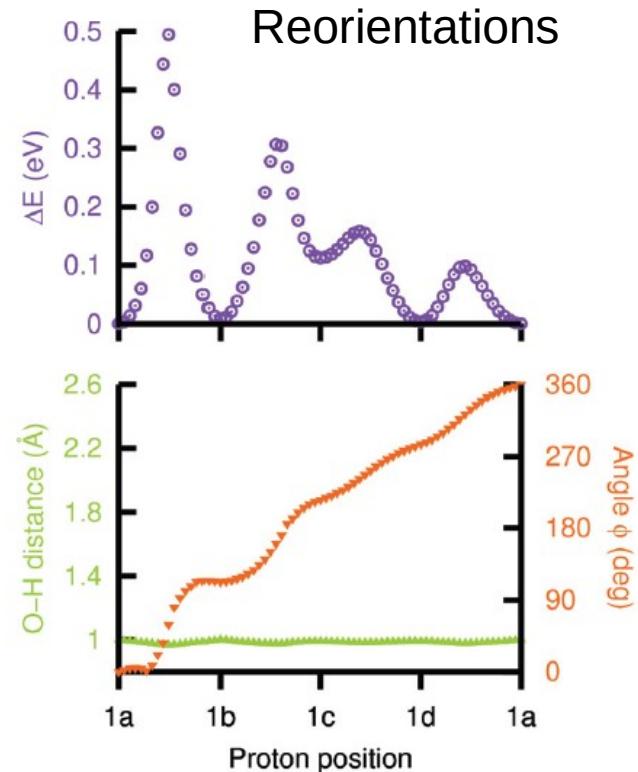
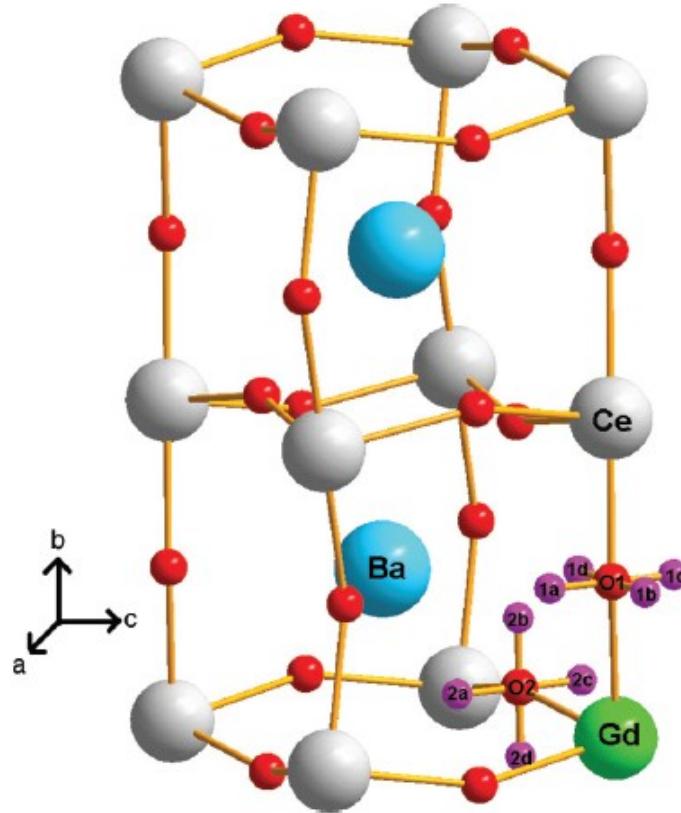
There is physical information not only at the saddle point !
(see below polaron and proton transfers)

NB : **in some 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...

3 - The keyword **IMGMOV** : Minimum Energy Paths Examples published

Hoppings and reorientations of protons in $\text{Gd}:\text{BaCeO}_3$: PhD of Jessica Hermet (2013)

String Method



3 - The keyword IMGMOV : Minimum Energy Paths Examples published

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.

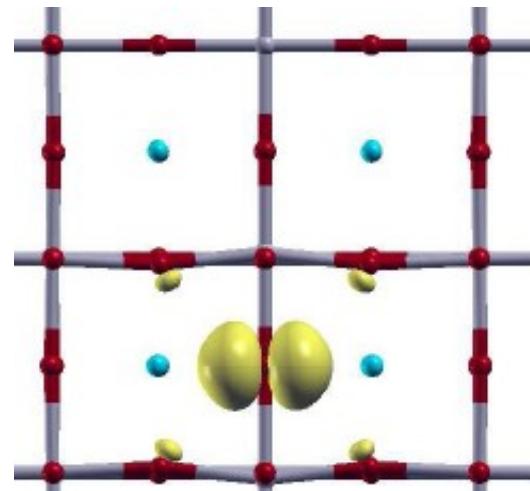
=> the crystal around is distorted (polarized), which in return creates a potential favorable to the localization of the electron (or hole)

= SELF-TRAPPING

Energy of the relaxed polaronic configuration minus energy of the configuration with perfect crystal and delocalized electron/hole = **self-trapping energy**

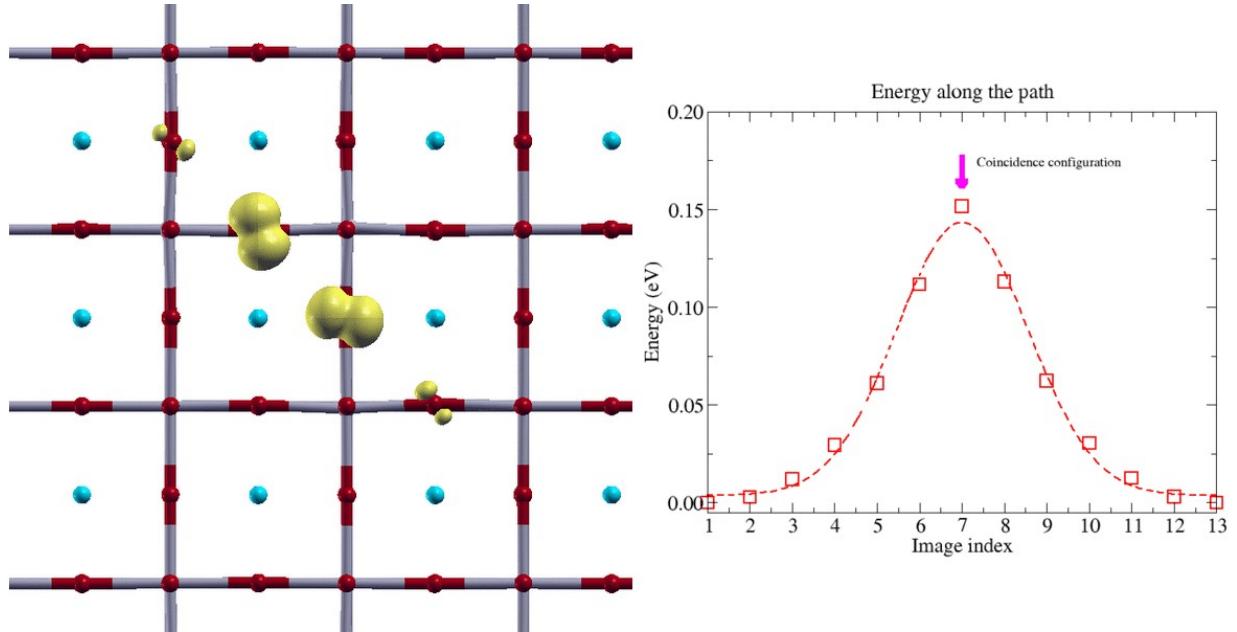
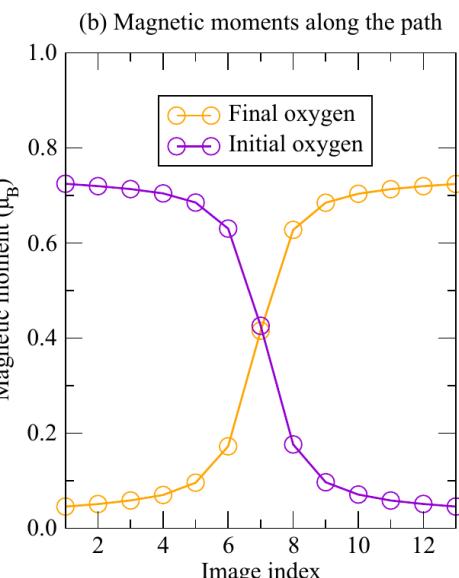
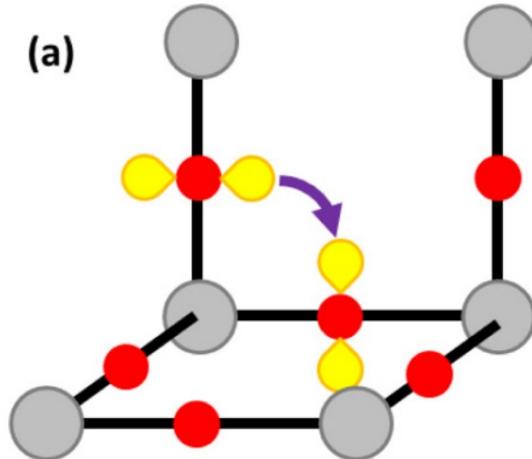
The small polaron is stable if the self-trapping energy is negative.

Ex : oxygen-type hole polaron in BaSnO₃
(DFT+U with U on oxygen p)



3 - The keyword **IMGMOV** : Minimum Energy Paths Examples published

Hopping of the oxygen-type hole polaron in BaSnO₃



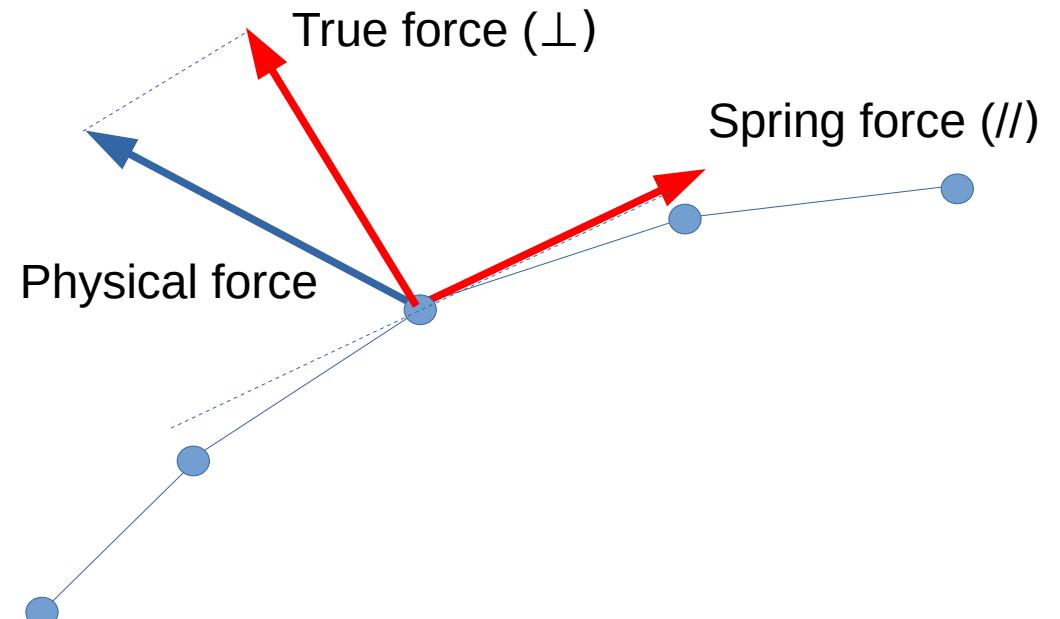
Warning :

- 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 at the saddle point can be long (if electronic coupling is weak)

3 - The keyword **IMGMOV** : Minimum Energy Paths The Nudged Elastic Band (NEB)

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
 - projection of **spring** forces **parallel** to the tangent
 - +
 - projection of **physical** forces **perpendicular** to the tangent



neb_algo 1 : the spring constant is the same for all images and ensures equal spacing of the images along the MEP.



3 - The keyword **IMGMOV** : Minimum Energy Paths The Nudged Elastic Band (NEB)

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 **neb_algo** 1, it is constant along the path

- For **neb_algo** 2, it can vary and become stronger close to the saddle point.

Default=[0.05-0.05] if **neb_algo** = 0 or 1, [0.02-0.15] Ha/Bohr² if **neb_algo** = 2.

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)

* 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).

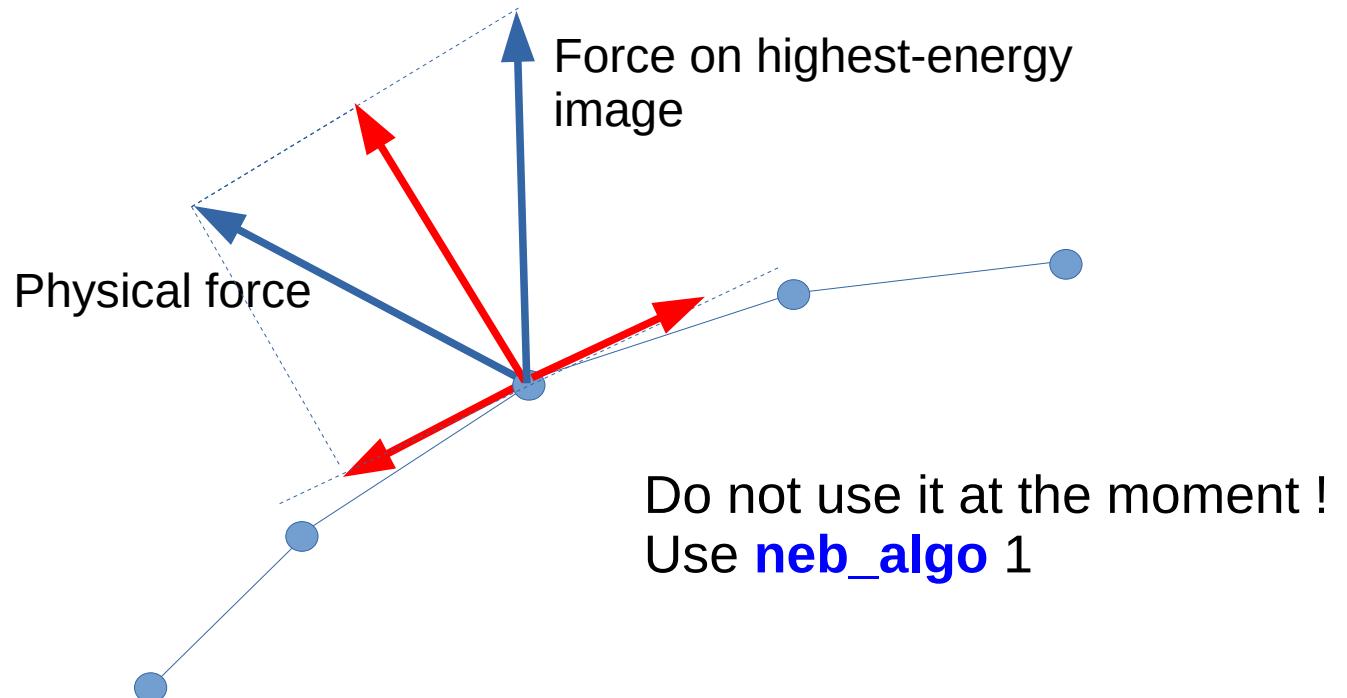
3 - The keyword **IMGMOV** : Minimum Energy Paths The Nudged Elastic Band (NEB)

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.





3 - The keyword **IMGMOV** : Minimum Energy Paths The Nudged Elastic Band (NEB)

NEB with variable cell

Possibility to perform a NEB calculation with evolution of the cell/primitive vectors along the Minimum Energy Path

Keyword **neb_cell_algo** (default=0, no variation of the cell)

Two methods implemented :

- Generalized Solid-State NEB (**neb_cell_algo** 1)

Sheppard *et al*, J. Chem. Phys. **136**, 074103 (2012)

- Variable-Cell NEB (**neb_cell_algo** 2) (not yet usable)

Qian *et al*, J. Comput. Phys. Comm. **184**, 2111 (2013)



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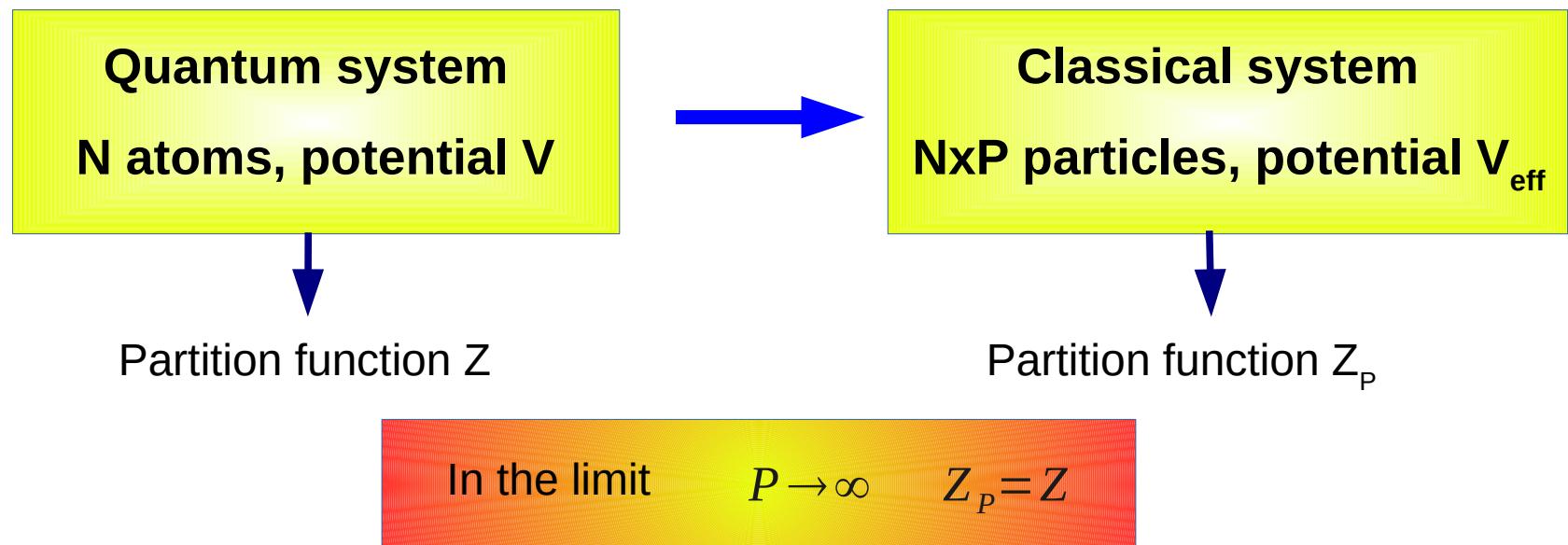
3 - The keyword **IMGMOV** : PIMD

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** :





3 - The keyword **IMGMOV** : PIMD

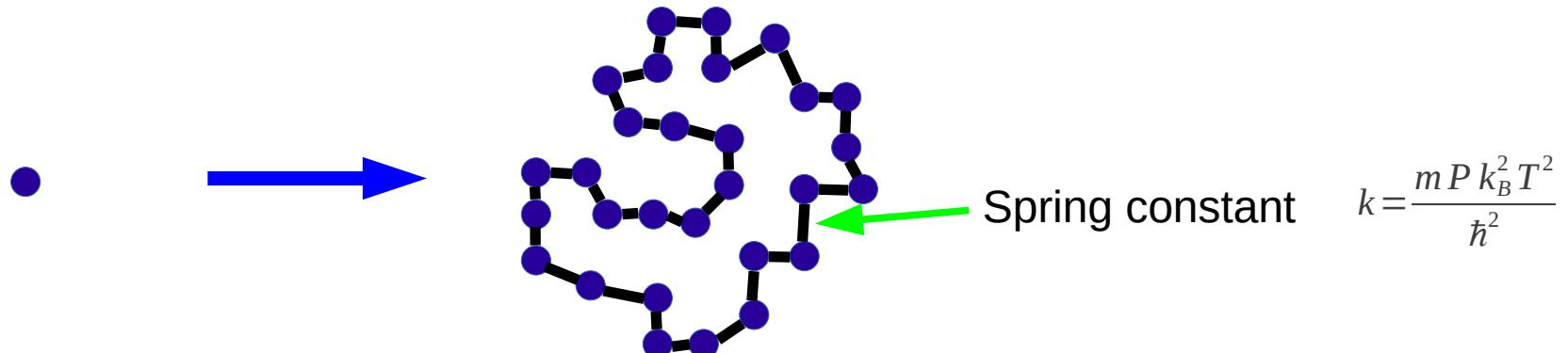
$$Z = \lim_{P \rightarrow \infty} \left[\frac{2\pi m P k_B T}{h^2} \right]^{3NP/2} \int_{\vec{R}_1} \dots \int_{\vec{R}_P} e^{-\beta V_{eff}(\vec{R}_1 \dots \vec{R}_P)} d\vec{R}_1 \dots d\vec{R}_P$$

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

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

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

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



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**



3 - The keyword **IMGMOV** : PIMD

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 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)



3 - The keyword **IMGMOV** : PIMD

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 $\sim 2.4 \times 10^{-17}$ 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)

dynamimage(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)



3 - The keyword **IMGMOV** : PIMD

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

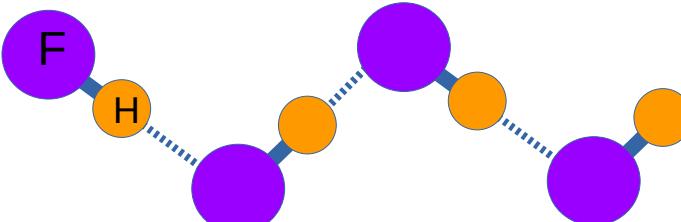
restartxf -1 #restart from _HIST file written on disk (see below)

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

3 - The keyword IMGMOV : PIMD

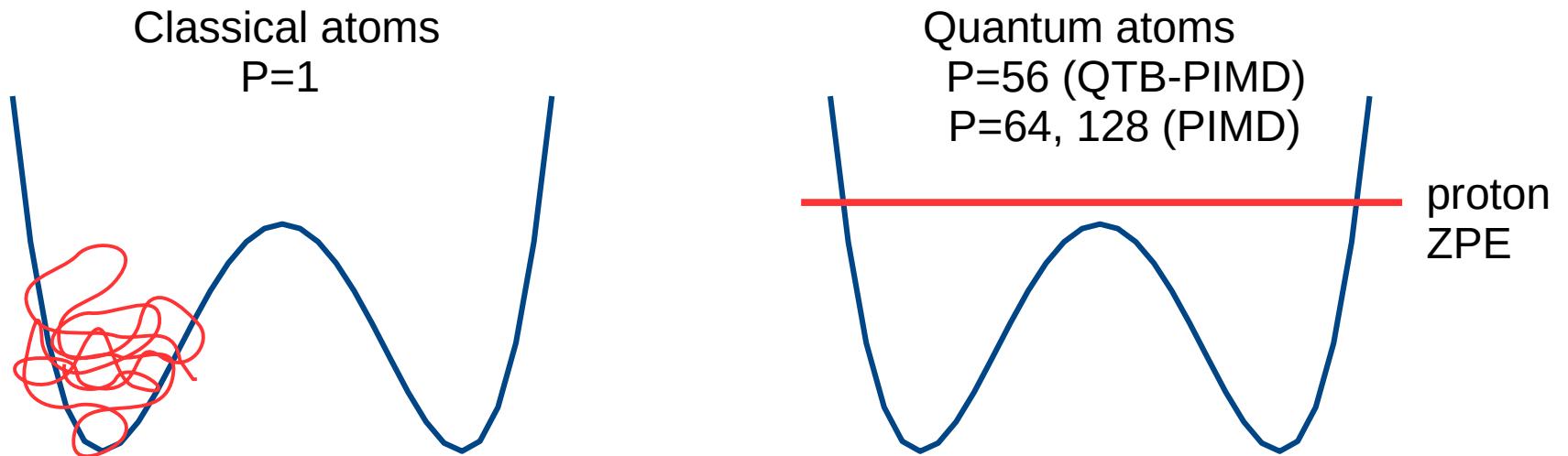
Example : symmetrization of hydrogen bond in HF at low temperature (T=100 K)
(H. Dammak, F. Brieuc, G. Geneste, M. Torrent, M. Hayoun, PCCP 2019)

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 above the proton barrier
 \Rightarrow H-bond symmetrization !



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



3 - The keyword **IMGMOV** : PIMD

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/Bohr³):
 -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 0.00000000000 0.00000000000

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



3 - The keyword **IMGMOV** : PIMD

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
 -0.000014616 -0.000000000
 -0.000005422 0.000000000
 0.000003090 0.000000000

Pressure (primitive estimator)

Center of mass:
 0.7086472998 0.000000000

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

Atomic positions and velocities for all beads
 (here P=4 and natom=m=2)

About energies in PIMD :

Two values are given, using two estimators :

$$E^{(prim)} = \frac{3}{2} N P k_B T - \left\langle \sum_{s=1}^P \sum_{i=1}^N \frac{1}{2} m_i \omega_P^2 (\vec{r}_i^{(s+1)} - \vec{r}_i^{(s)})^2 \right\rangle + \frac{1}{P} \left\langle \sum_{s=1}^P V(\vec{r}_1^{(s)} \dots \vec{r}_N^{(s)}) \right\rangle$$

$$E^{(vir)} = \frac{3}{2} N k_B T + \frac{1}{P} \left\langle \sum_{s=1}^P \sum_{i=1}^N \frac{1}{2} (\vec{r}_i^{(s)} - \vec{r}_i^c) \cdot (-\vec{F}_i^{(s)}) \right\rangle + \frac{1}{P} \left\langle \sum_{s=1}^P V(\vec{r}_1^{(s)} \dots \vec{r}_N^{(s)}) \right\rangle$$

$$\vec{r}_i^c = \frac{1}{P} \sum_{s=1}^P \vec{r}_i^{(s)}$$

Important point : the kinetic part is computed using the **thermostat temperature**, not the instantaneous one ; thus do not be surprised if, using NVE (**vis**=0), the energy does not seem to be conserved...



3 - The keyword **IMGMOV** : PIMD

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 velocities of previous run.

Warning : internal energy computed using thermostat temperature, not instantaneous one

Alternatively, restarts can be made by using last positions and velocities :

xred_1img ... xred_lastimg, vel_1img ... vel_lastimg

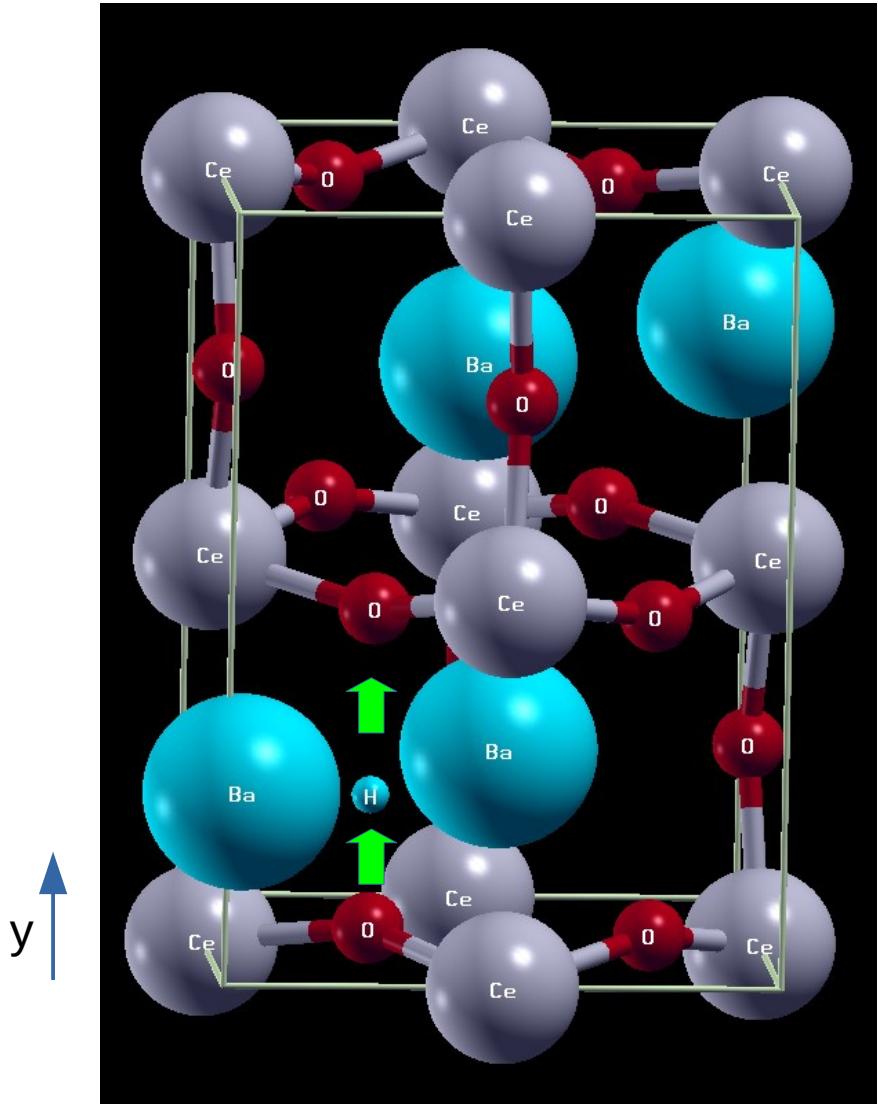
NPT ensemble: coming soon !

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**)

3 - The keyword **IMGMOV** : PIMD

Example of input file of constrained PIMD



BaCeO_3 : orthorhombic perovskite
 $Pnma$ space group

Excellent protonic conductor

Inter-octahedral transfer of H^+

Cell = 20 atoms

Reaction coordinate : $(\text{O}_1\text{H})_y - (\text{O}_2\text{H})_y$
 $= y(\text{H}) - y(\text{O}_1) - [y(\text{O}_2) - y(\text{H})]$

PIMD, T=200 K
P=32 beads

3 - The keyword **IMGMOV** : PIMD

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


```

```

# 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

# 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

```



CONTENT

1 – Introduction

2 – The keyword ionmov

- Structural Optimizations

- Molecular Dynamics

3 – The keyword imgmov

- Minimum Energy Paths

- Path Integral Molecular Dynamics

4 – Conclusion

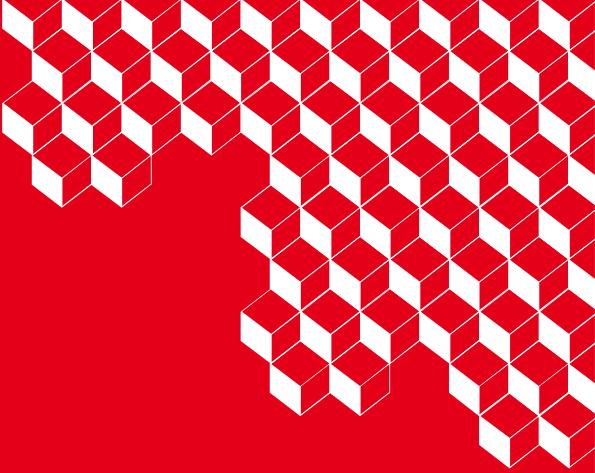


4 - Conclusion

With ABINIT, you can

- **structurally optimize** a system,
 - * atomic positions only (cell fixed)
 - * atomic positions + cell
 - * atomic positions + cell under non zero pressure/stress
- perform **Molecular Dynamics** in various statistical ensembles
- compute the **Minimum Energy Path** between two optimized configurations
(useful to study, e.g. diffusion of defects in solids)
- perform **Path-Integral Molecular Dynamics** to simulate the quantum effects associated to nuclear motions.
- many other things ! See the website at **input variables ionmov, imgmov**.





Thanks for your attention !



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