

November 20th, 2025

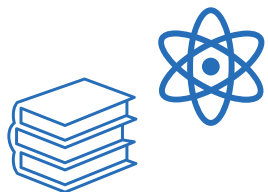
Geometry optimization and molecular dynamics using SIESTA*

Ernane de Freitas Martins

*Based on previous presentations from Emilio Artacho and Marivi Fernandez-Serra, which can be found in the SIESTA webpage

What is this presentation about?

Outline



CONCEPTS

Potential energy surface
Hellman-Feynman theorem



GO ALGORITHMS

Different options for
geometry optimization

Variable cell

Internal coordinates



MD ALGORITHMS

Different options for molecular
dynamics



EXTRA

Constraints

Continuations

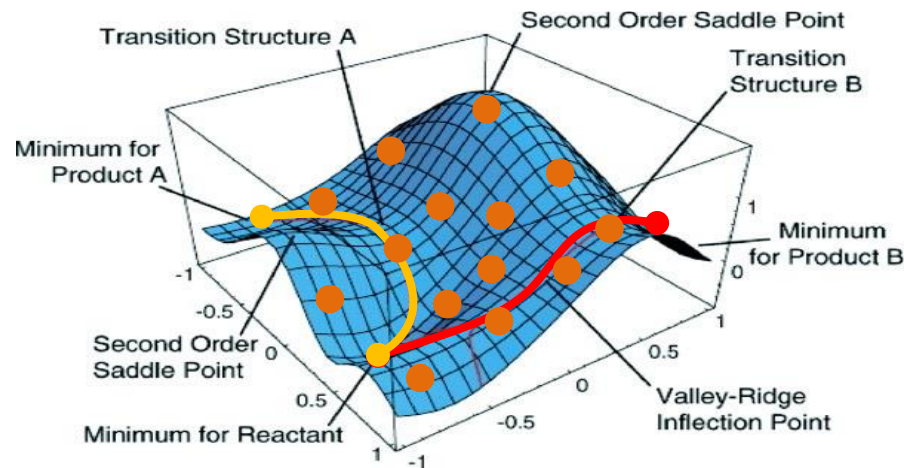
Controlling out data

Post-processing

Visualization

The potential energy surface - PES

Geometry optimization x molecular dynamics



Geometry optimizations

We move on the PES

Search for local/global minima

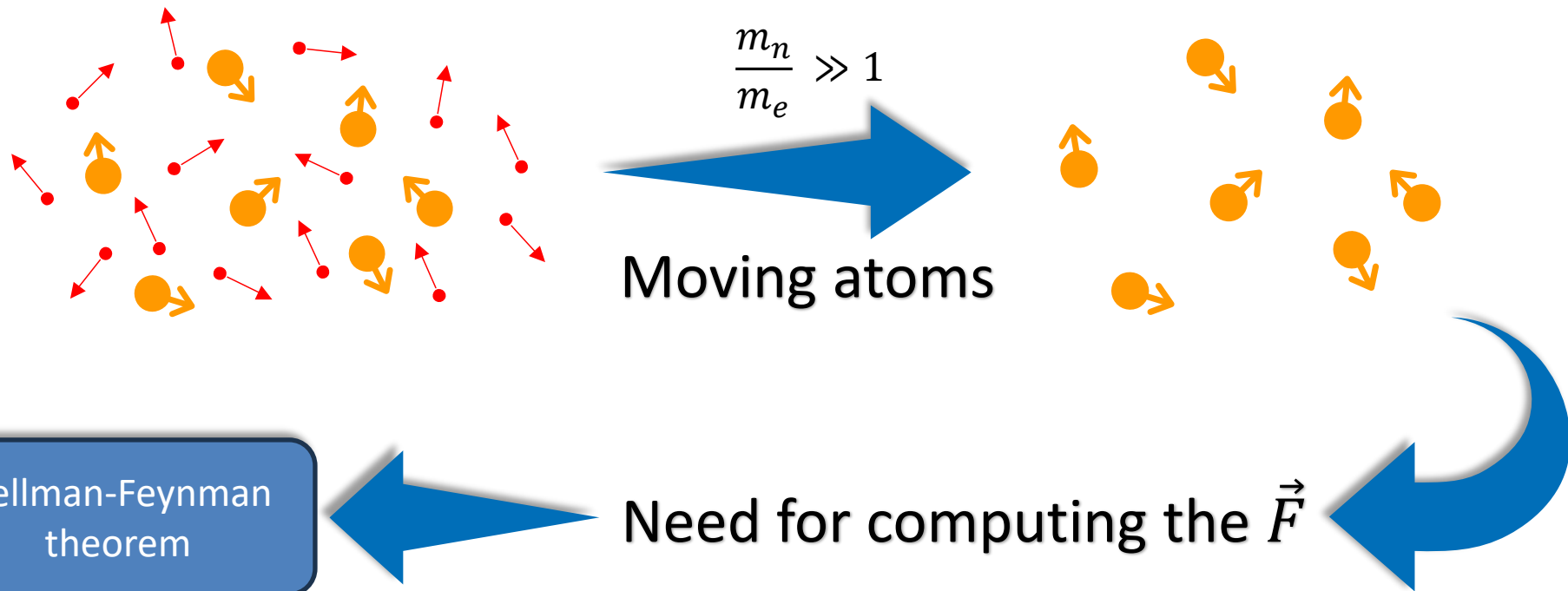
Molecular dynamics

We move over the PES

Sampling

Adiabatic decoupling

Many body problem and how to move atoms



How to compute the forces?

The Hellman-Feynman theorem

$$H(\lambda)$$

Hamiltonian as a function of a continuous parameter

$$|\psi(\lambda)\rangle$$

Eigenvector of $H(\lambda)$ with eigenvalue $E(\lambda)$

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle$$

Assuming normalized

$$\langle\psi(\lambda)|\psi(\lambda)\rangle = 1$$

$$\frac{d}{d\lambda} \langle\psi(\lambda)|\psi(\lambda)\rangle = 0$$

The Hellman-Feynman theorem

$$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle$$

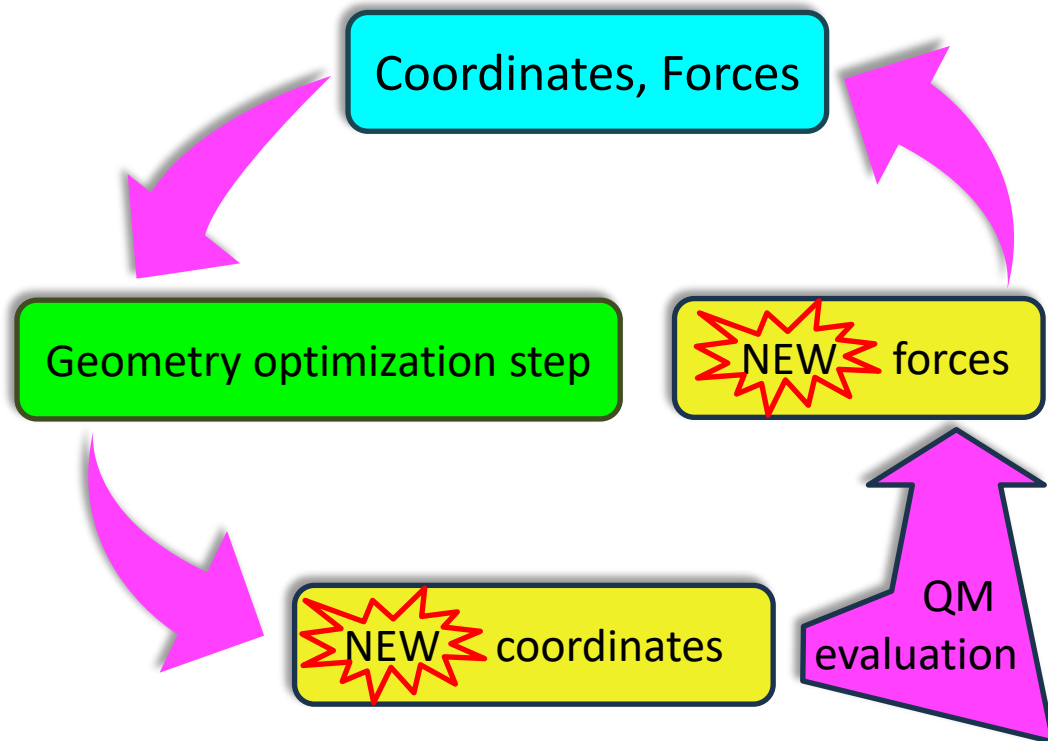
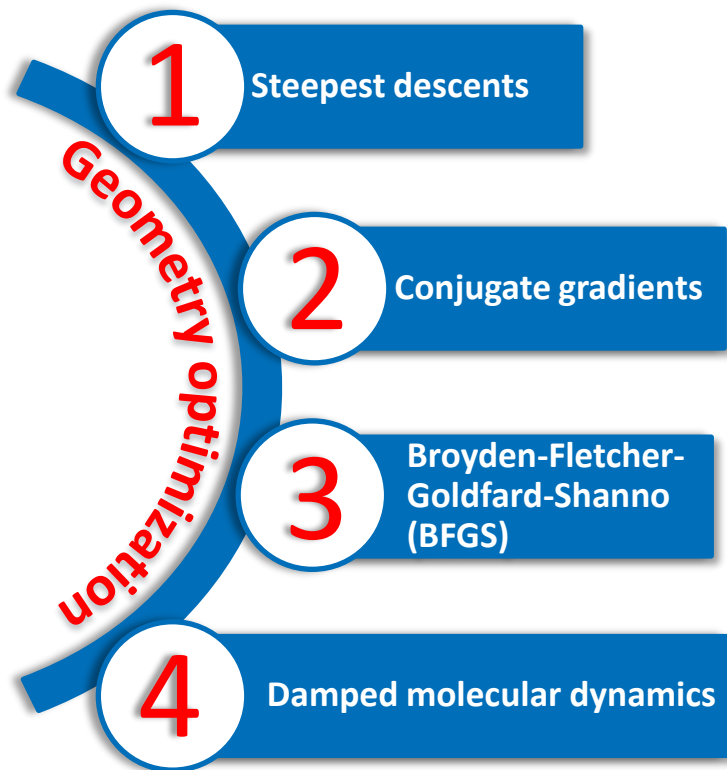
The Hellman-Feynman theorem

- ✓ A proof of concept can be done by writing the energy as $E = \langle \psi(\lambda) | H(\lambda) | \psi(\lambda) \rangle$;
- ✓ Associate parameter λ with the nuclear coordinates R ;
- ✓ The forces acting on atoms can be calculated as:
 - ✓ $F_i = \nabla_i \varepsilon(R) = \langle \psi_0 | \nabla_i H(R) | \psi_0 \rangle$

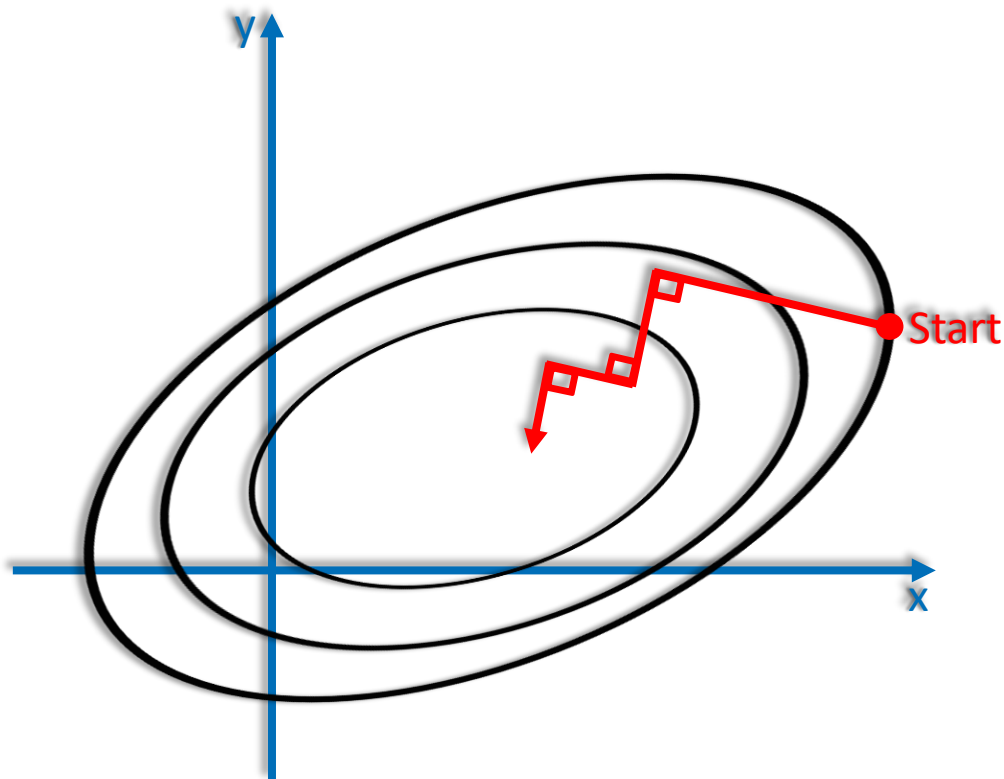


Algorithms to optimize geometries

And more in the manual...



Steepest descents



The simplest approach, taking a downhill step along the local steepest gradient

Advantages

Simple to implement

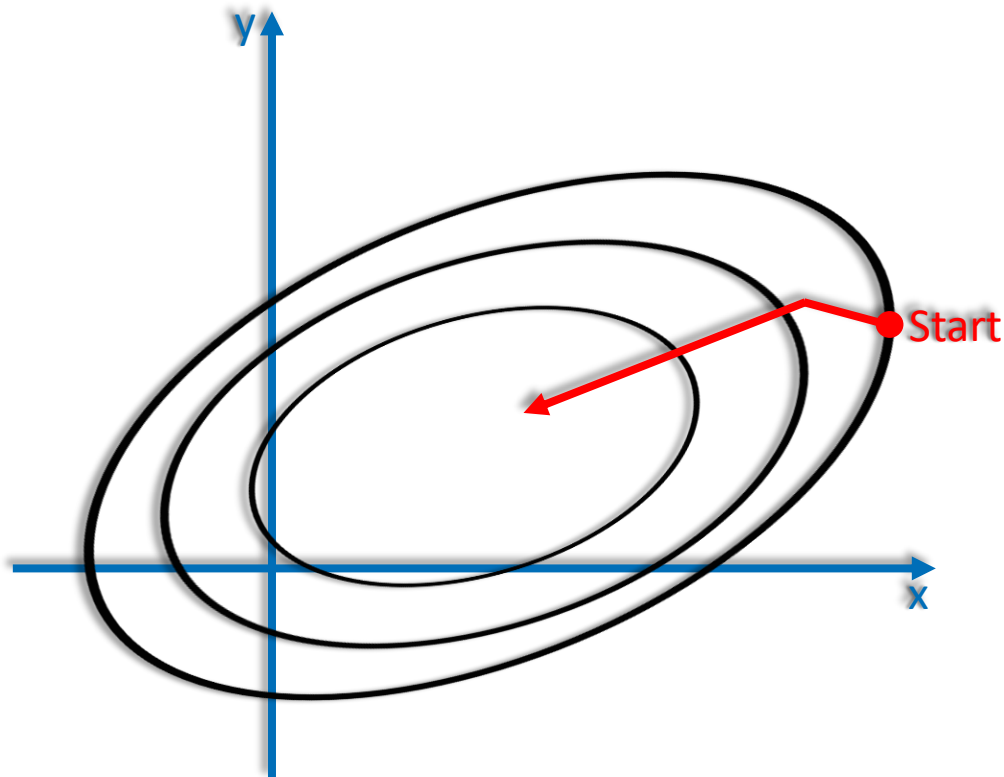
Reliable

Disadvantages

Slow to converge

Can get stuck in a local minimum

Conjugate gradients



- Improves steepest;
- Gradient constructed to be conjugate to all previous directions;
- It does not undo the previous minimization;
- It makes a line minimization.

Advantages

Rapid convergence

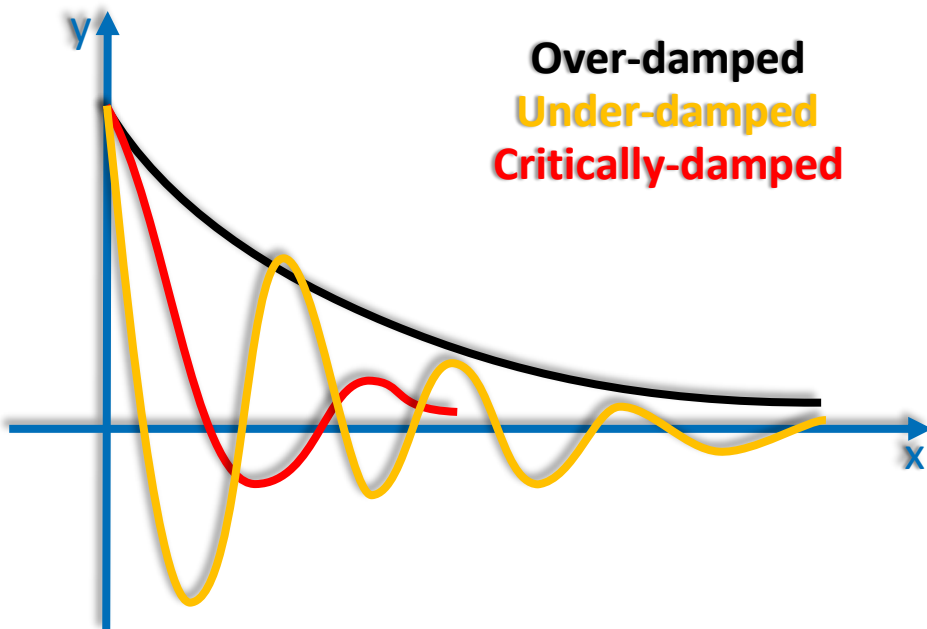
Low storage requirements

Disadvantages

More complex to implement

Can get stuck in a local minimum

Damped molecular dynamics



- Improves steepest;
- It uses velocity and forces;
- It starts with $v = 0$ and then adds damping terms to forces: $-\gamma v$;
- It adjusts γ and time step to obtain optimal convergence.

Advantages

Simple to implement

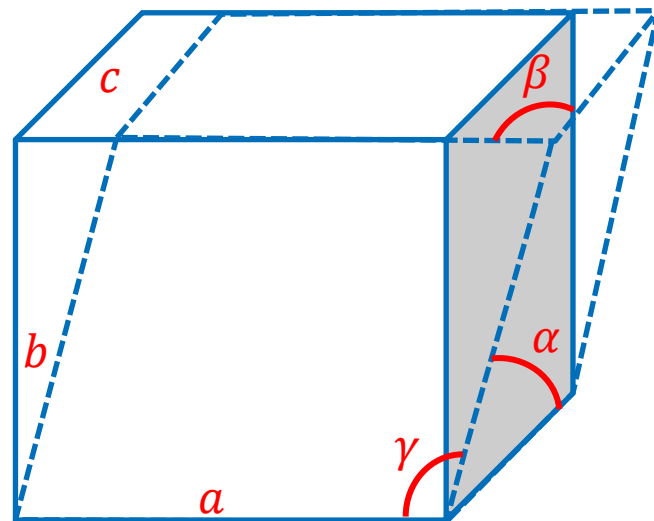
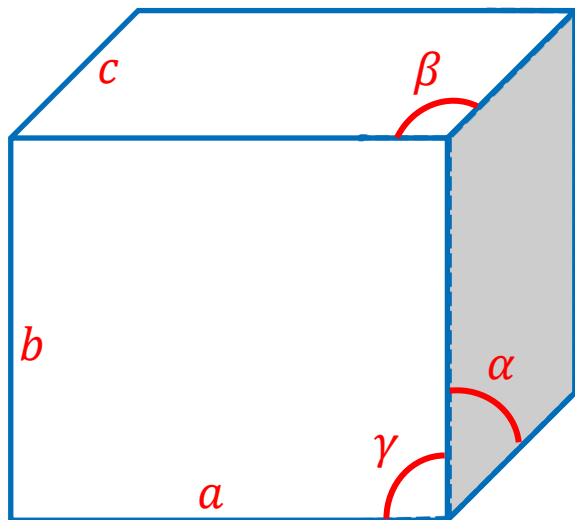
Eventually can escape a local minimum

Disadvantages

Convergence rate depends on γ

Can get stuck in a local minimum

Stress and strain: the cases where the cell is allowed to change



With and without variable cell

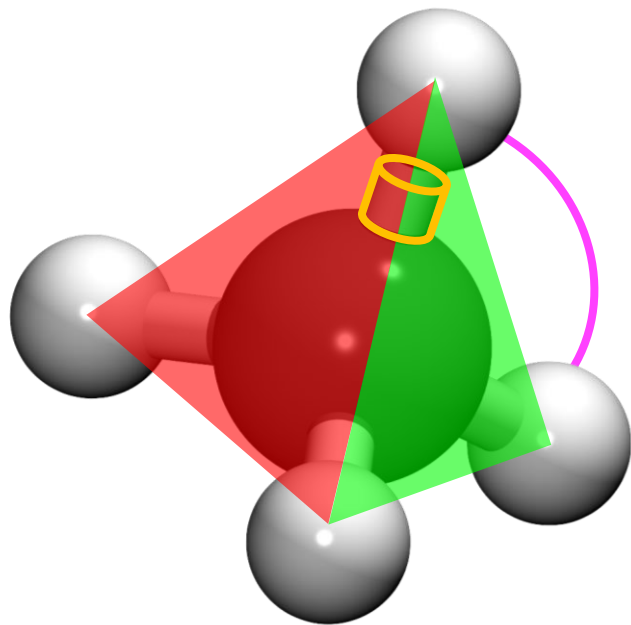
Fixed cell

- Set runtime to conjugate gradients:
 - ***MD.TypeOfRun*** CG, Broyden
- Set maximum number of iterative steps:
 - ***MD.Steps*** 100
- Optionally set force tolerance:
 - ***MD.MaxForceTol*** 0.01 eV/Ang
- Optionally set maximum displacement:
 - ***MD.MaxCGDispl*** 0.2 Bohr

Variable cell

- To allow unit cell to vary:
 - ***MD.VariableCell*** true
- Optionally set stress tolerance:
 - ***MD.MaxStressTol*** 0.1 GPa
- Set an applied pressure:
 - ***MD.TargetPressure*** 1.0 GPa

Z-matrix coordinate format



Use of internal coordinates

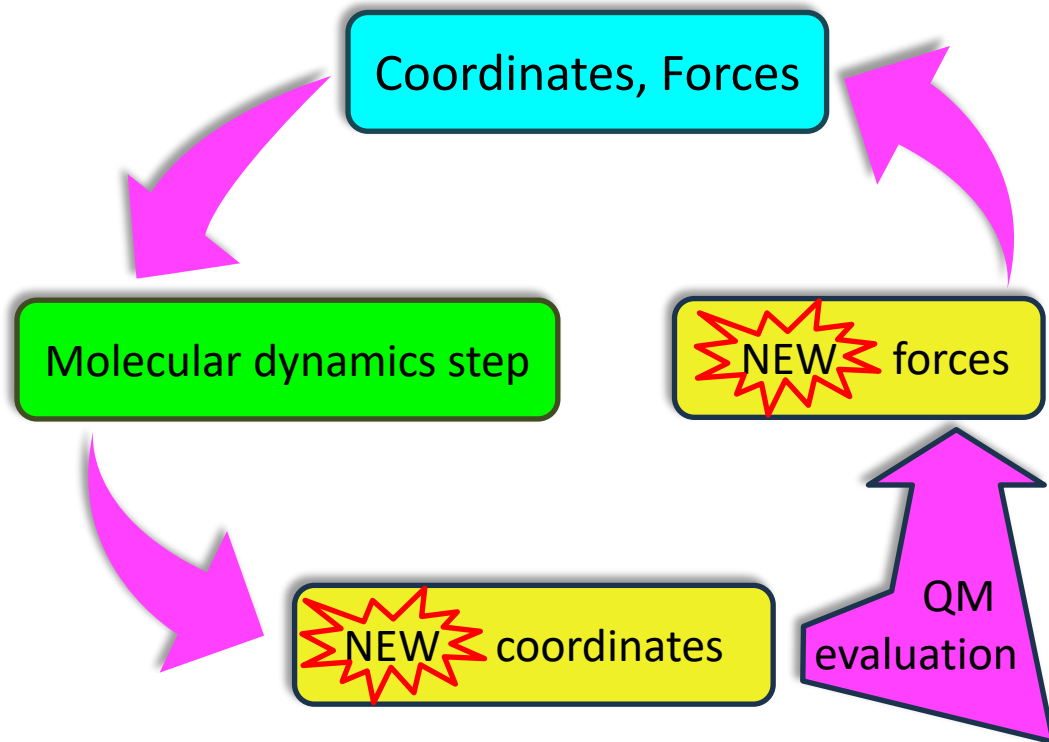
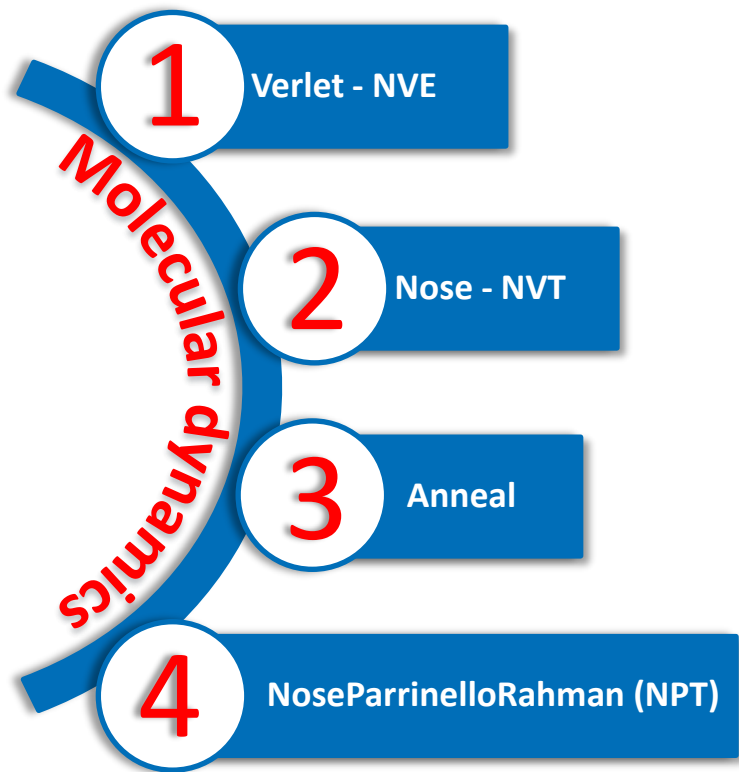
Bond lengths χ_i

Bending angles φ_i

Dihedral angles ξ_i

Algorithms for molecular dynamics

And more in the manual...

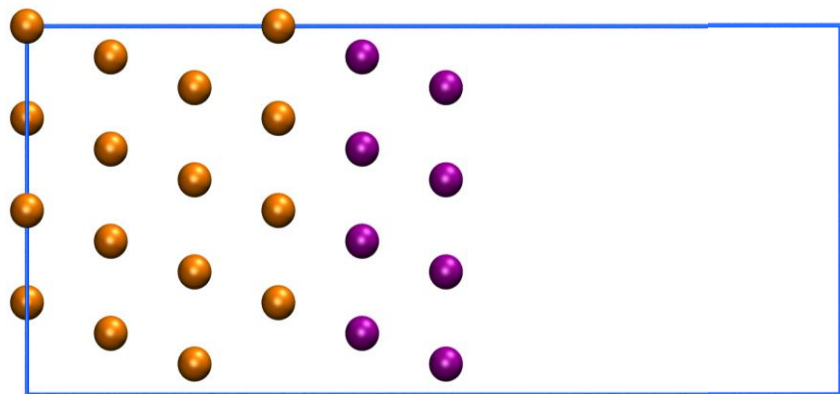


Changes in the input file

*More options in
the manual*

- Set runtime to MD:
 - ***MD.TypeOfRun*** Verlet, Nose, ...
- Set the initial time step:
 - ***MD.InitialTimeStep*** 1
- Set the final time step:
 - ***MD.FinalTimeStep*** 100
- Set the time step:
 - ***MD.LengthTimeStep*** 1 fs
- Set temperature/pressure
 - ***MD.TargetTemperature*** 300 K

When relevant, one can constrain the movement of atoms



● **Constrained**

● **Free**

```
%block GeometryConstraints  
atom Cu  
%endblock GeometryConstraints
```

or

```
%block GeometryConstraints  
position from 1 to 48  
%endblock GeometryConstraints
```

How to continue calculations not finished?

Both geometry optimization and molecular dynamics allow for that

- Files that can be read:
 - ***SystemLabel.XV*** (vel. and coord.)
 - ***SystemLabel.X_RESTART***
 - X is the type of MD
- Manually:
 - Insert the last coordinates;
 - For MD, initial velocities will be generated in this case.
- The ***SystemLabel.{ANI,MDE}*** will be updated

Make sure files will be read

- ***MD.UseSaveXV*** true

Controlling output data

Not everything is printed by default...

- Mulliken charges:
 - ***WriteMullikenPop*** 1
- Charges for MD:
 - ***PartialChargesAtEveryGeometry*** true
- Electrostatic potential:
 - ***SaveElectrostaticPotential*** true
- Total potential:
 - ***SaveTotalPotential*** true
- Coordinate steps:
 - ***WriteCoorStep*** true

How to post-process data?

Types of post-processing that can be done

- Files:
 - SystemLabel.MDE*
 - Temperature, energy...*
 - SystemLabel.out*
 - Grep command can be used to extract information to be plotted.*

To plot and generate PNG

Executable

plot_XXX.sh



To plot the data of the structural optimization tutorial:
plot_enth.sh | plot_stress.sh | plot_constr.sh

To plot the data of the molecular dynamics tutorial:
plot_temp.sh | plot_presure.sh | plot_energies.sh

How to post-process data?

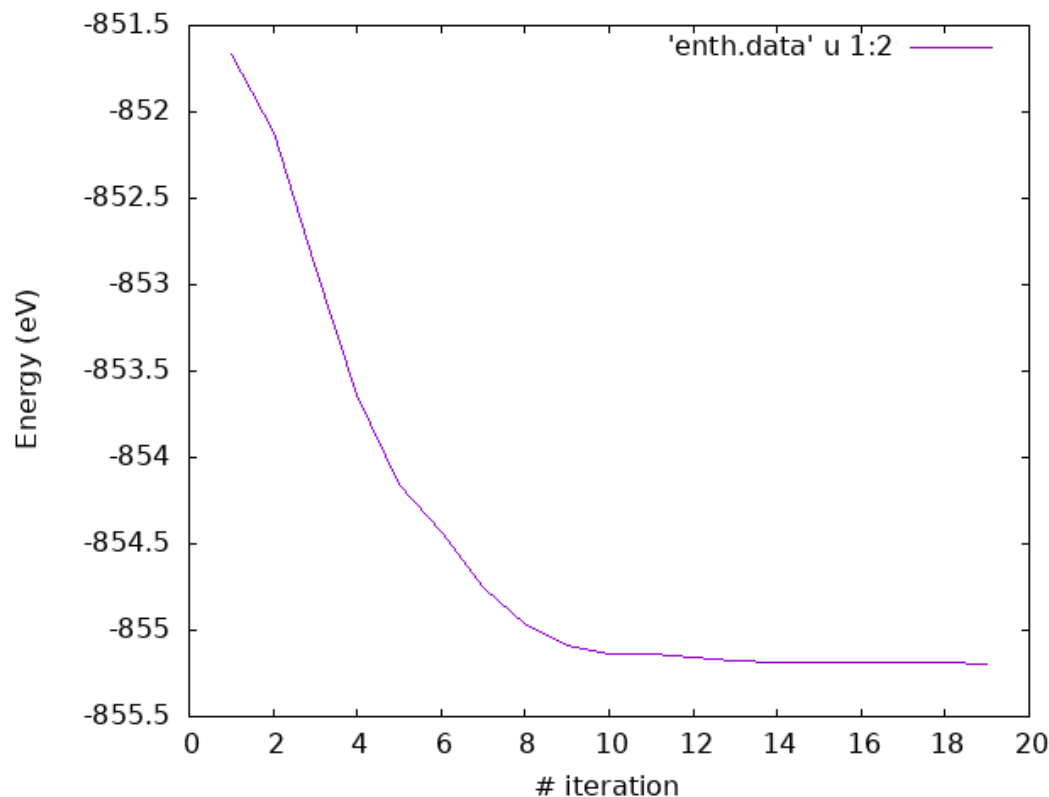
Types of post-processing that can be done

Executable

`plot_enth.sh`

Download
generated png file

Open the png file
on your local
computer



How to visualize trajectories?

Files that can be used for that

ovito SystemLabel.ANI
ovito SystemLabel.xyz
ovito SystemLabel.pdb



- Files:
 - *SystemLabel.ANI*
 - *Coordinates trajectory.*
 - *SystemLabel.STRUCT_OUT*
 - *Last coordinates;*
 - *Need to be converted into PDB:*
 - *ASE, for instance.*

<ase convert SystemLabel.STRUCT_OUT SystemLabel.pdb>



vmd -xyz SystemLabel.ANI
vmd SystemLabel.pdb

Let's try the tutorials! Questions before?

```
/gpfs/projects/nct_315/TUTORIALS/day3/01-GeometryOptimization
```

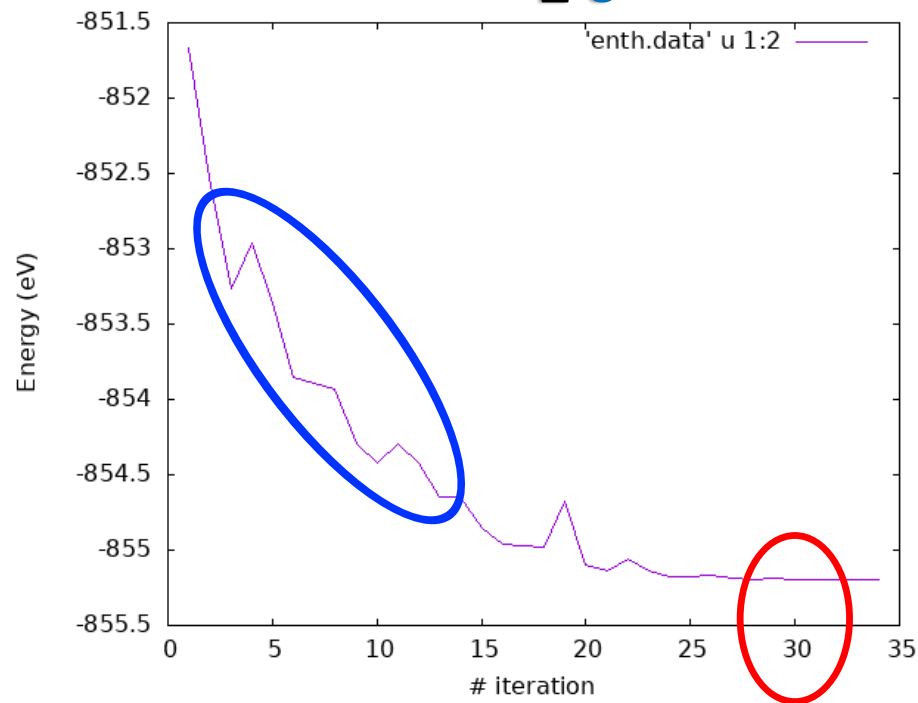
```
/gpfs/projects/nct_315/TUTORIALS/day3/02-MolecularDynamics
```

That's it!

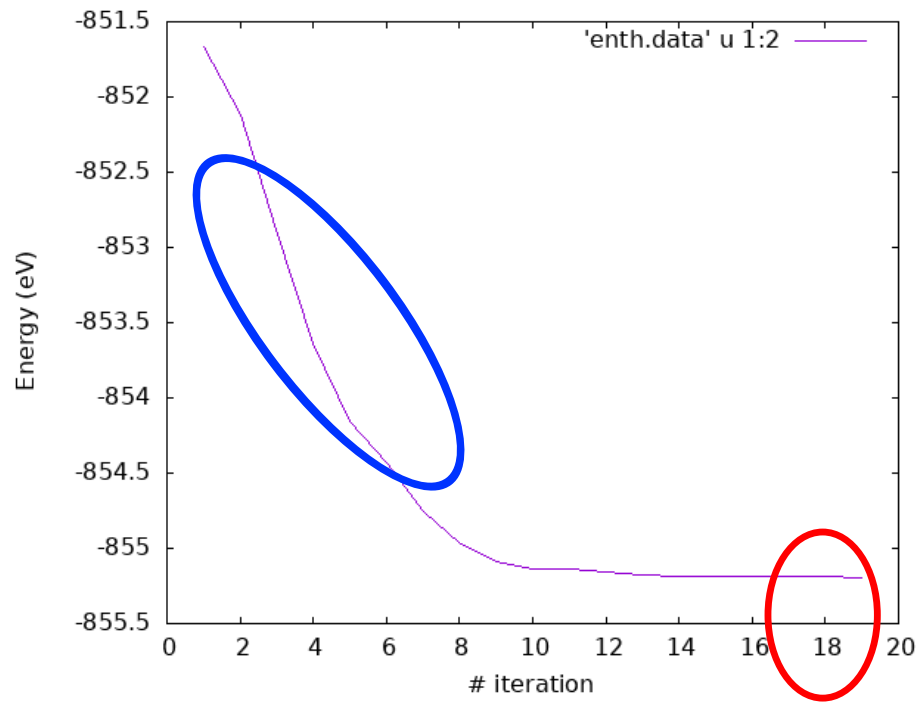
Obrigado!
¡Gracias!
Thank you!

Examples of analysis that could be done

varcell_cg

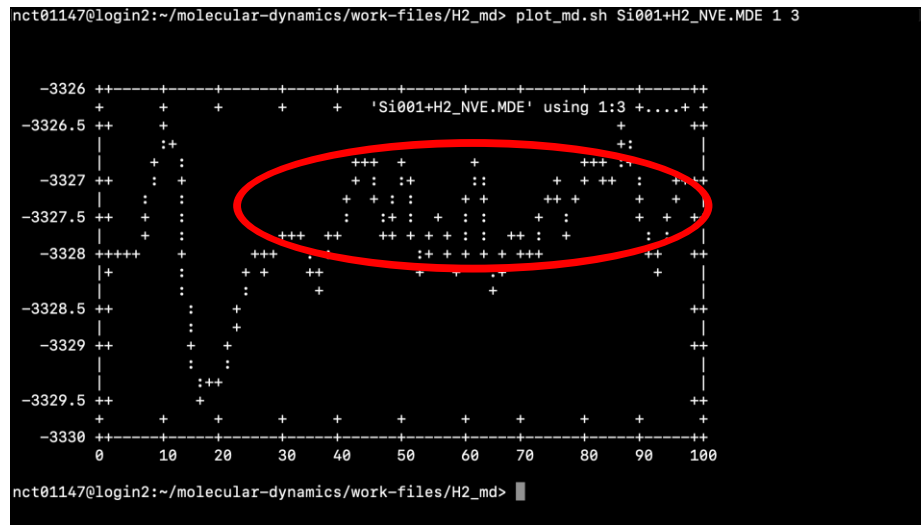
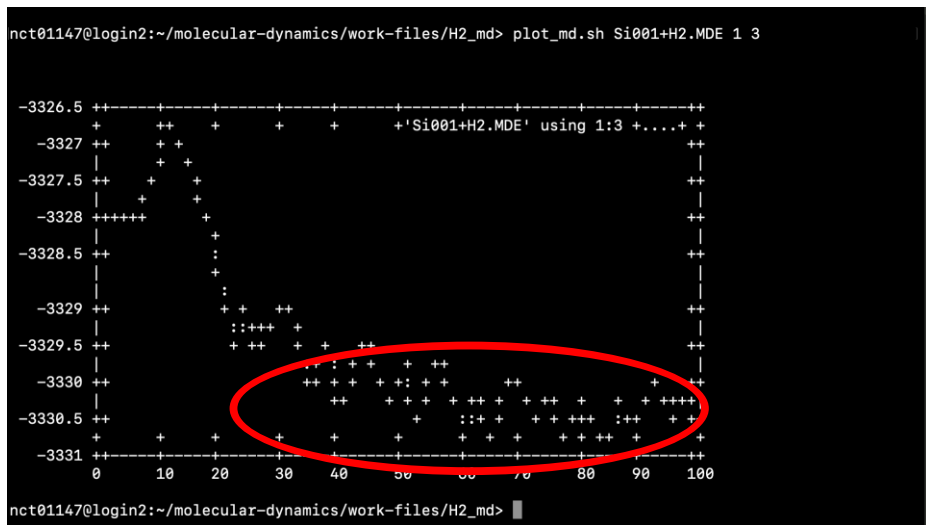


varcell_md



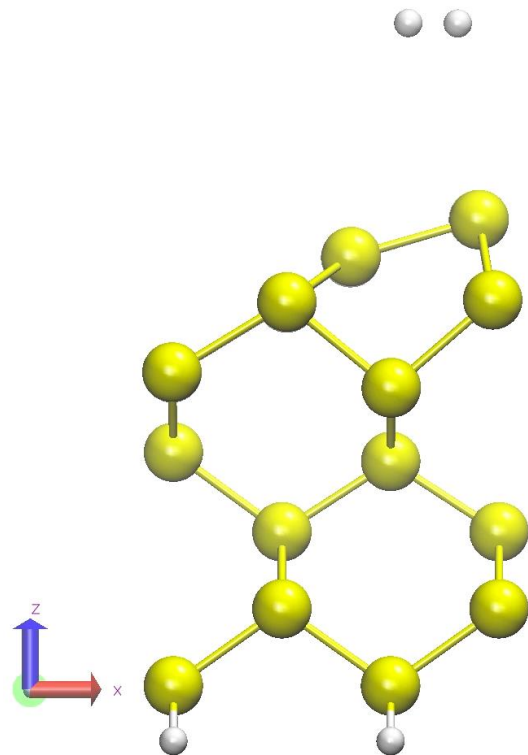
Some outcomes

Examples of analysis that could be done

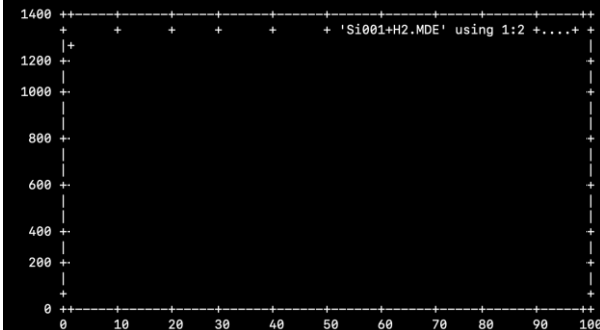


Some outcomes

Examples of analysis that could be done

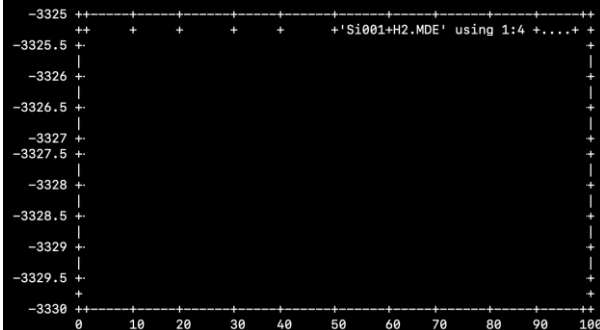


```
nct01147@login2:~/molecular-dynamics/work-files/H2_md> plot_md.sh Si001+H2.MDE 1 2
```



```
nct01147@login2:~/molecular-dynamics/work-files/H2_md>
```

```
nct01147@login2:~/molecular-dynamics/work-files/H2_md> plot_md.sh Si001+H2.MDE 1 4
```



```
nct01147@login2:~/molecular-dynamics/work-files/H2_md>
```