Institut Català
de Nanociència
i Nanotecnologia

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Geometry optimization and molecular dynamics using SIESTA*

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

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What is this presentation about?

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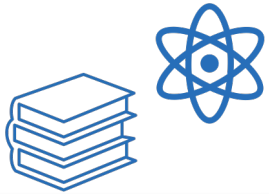
Outline



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

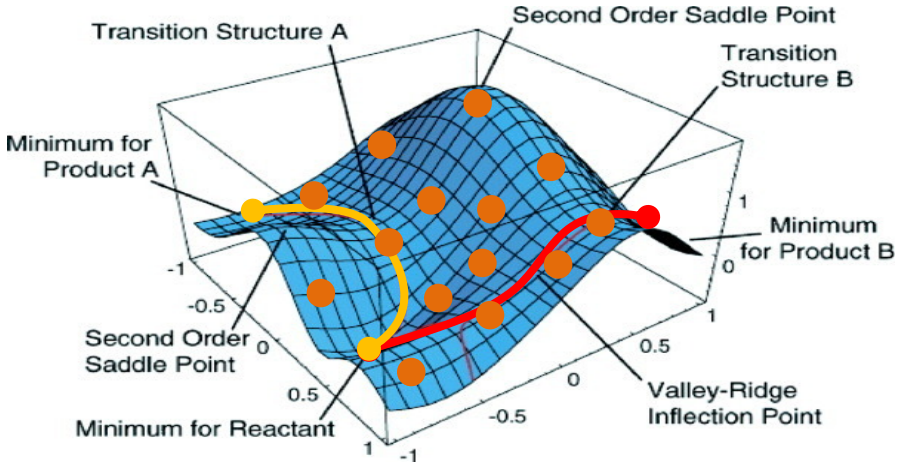
Controlling out data

Post-processing

Visualization

The potential energy surface - PES

Geometry optimization x molecular dynamics



$$\text{Reactants} \xrightarrow{TS_A} A$$

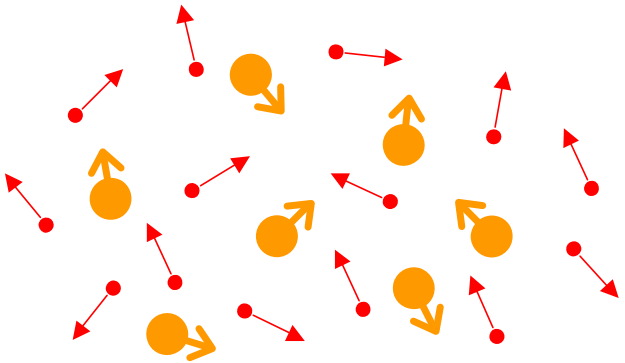
$$\text{Reactants} \xrightarrow{TS_B} B$$

Geometry optimizations	Molecular dynamics
We move on the PES	We move over the PES
Search for local/global minima	Sampling

Schlegel, H. B. J. Comput. Chem. (2003)

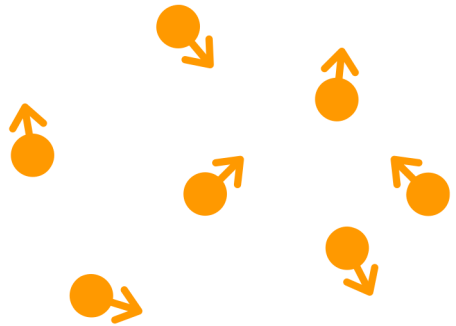
Adiabatic decoupling

Many body problem and how to move atoms



$$\frac{m_n}{m_e} \gg 1$$

Moving atoms



Need for computing the $\vec{F}$

Hellman-Feynman theorem

How to compute the forces?

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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

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

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

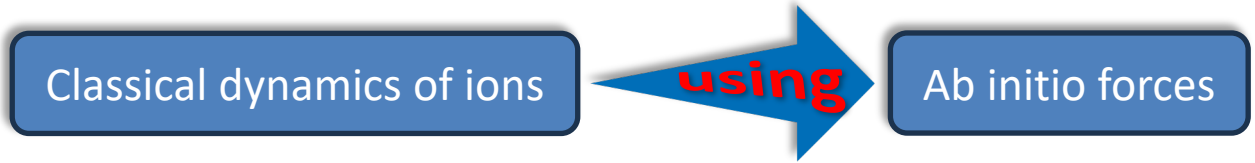
The Hellman-Feynman theorem

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

How to compute the forces?

The Hellman-Feynman theorem

- ✓ A proof of concept can be done by writing the energy as $\mathrm{E} = \langle\psi(\lambda)|H(\lambda)|\psi(\lambda)\rangle$;
- ✓ 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

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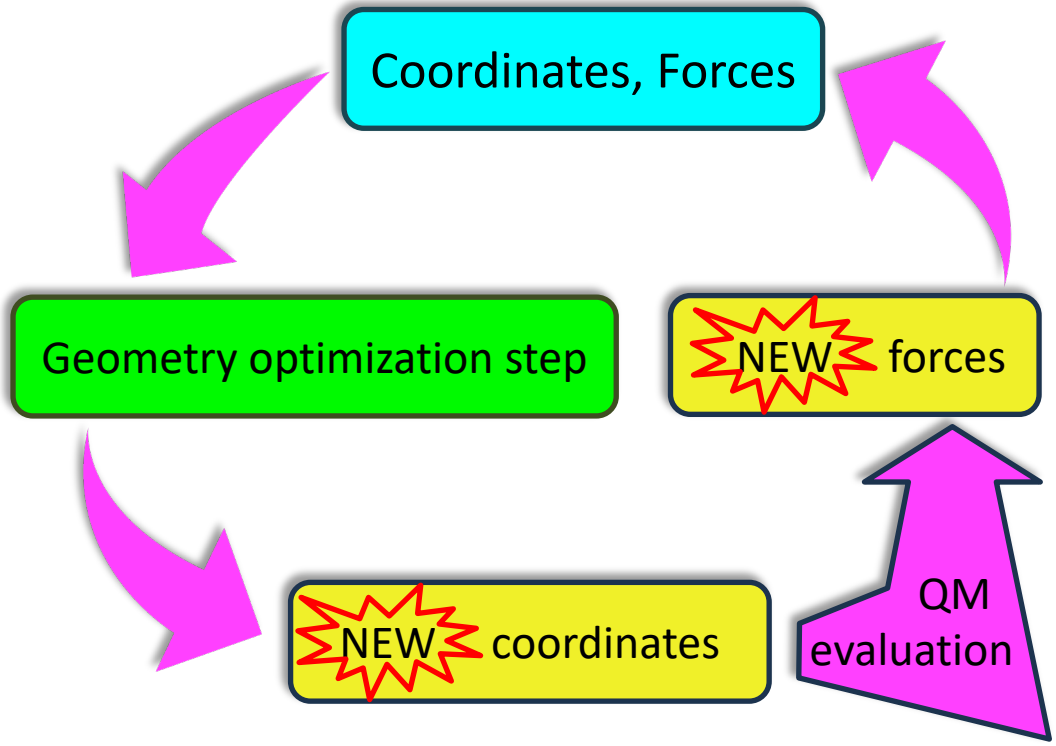
And more in the manual...

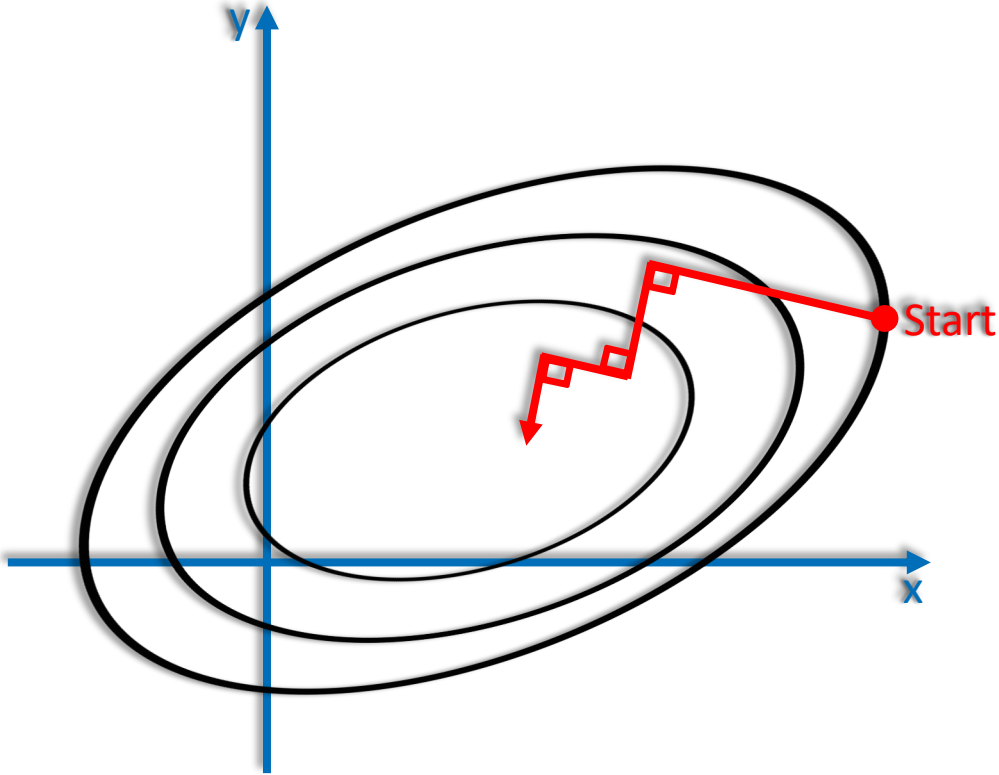
Geometry optimization

1. Steepest descents
2. Conjugate gradients
3. Broyden-Fletcher-Goldfard-Shanno (BFGS)
4. Damped molecular dynamics



Structural optimization

Steepest descents

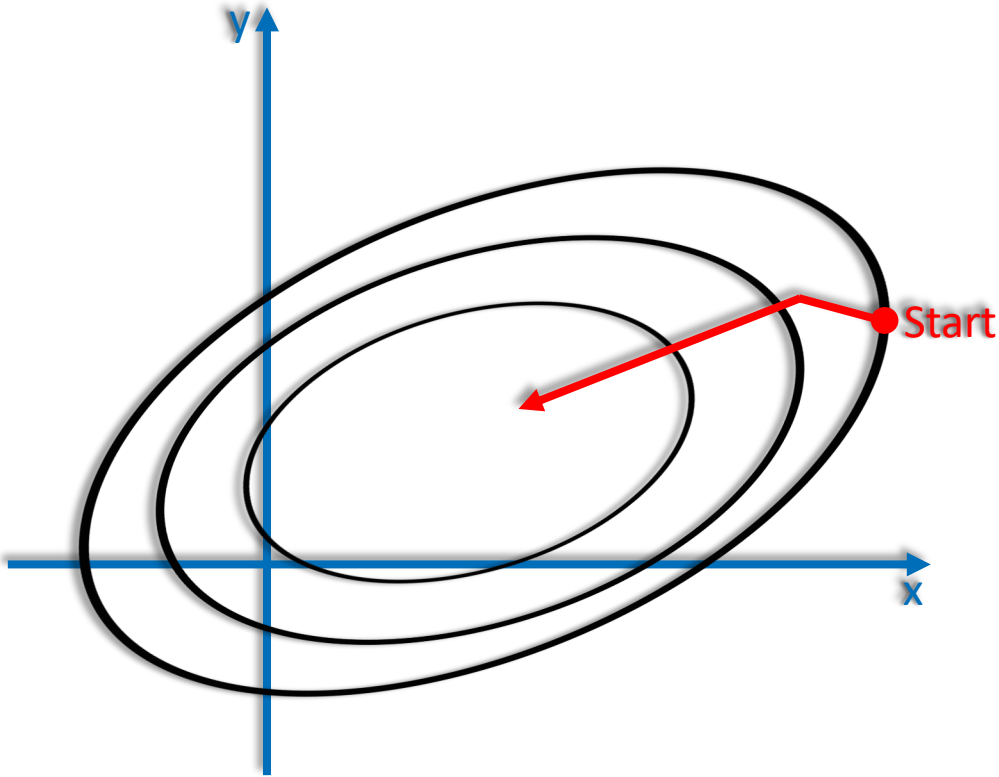


The simplest approach, taking a downhill step along the local steepest gradient

Advantages	Disadvantages
Simple to implement	Slow to converge
Reliable	Can get stuck in a local minimum

Structural optimization

Conjugate gradients

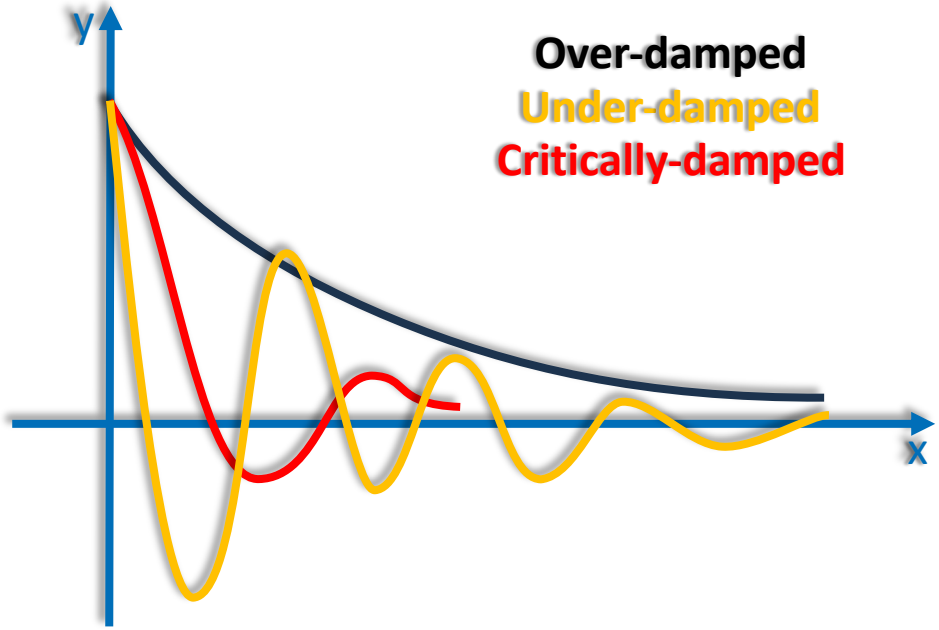


- Improves steepest;
- Gradient constructed to be conjugate to all previous directions;
- It does not undo the previous minimization;
- It makes a line minimization.

Advantages	Disadvantages
Rapid convergence	More complex to implement
Low storage requirements	Hessian not explicitly calcualted
	Can get stuck in a local minimum

Structural optimization

Damped molecular dynamics

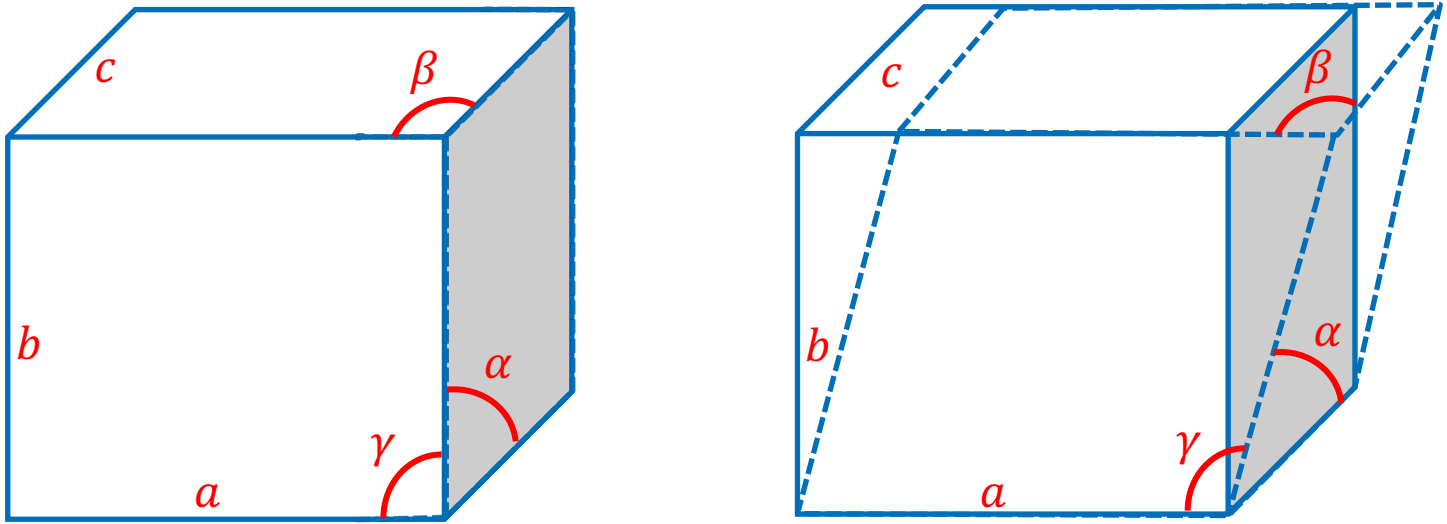


- Improves steepest;
- It uses velocity and forces;
- It starts with $v = o$ and then adds damping terms to forces: $-\gamma v$;
- It adjusts γ and time step to obtain optimal convergence.

Advantages	Disadvantages
Simple to implement	Convergence rate depends on γ
Eventually can escape a local minimum	Can get stuck in a local minimum

Structural optimization

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



Structural optimization

With and without variable cell

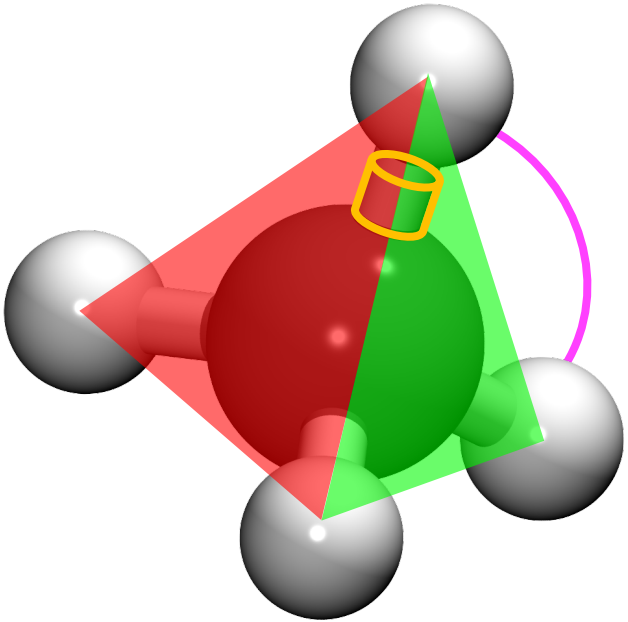
Fixed cell

- Set runtype 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

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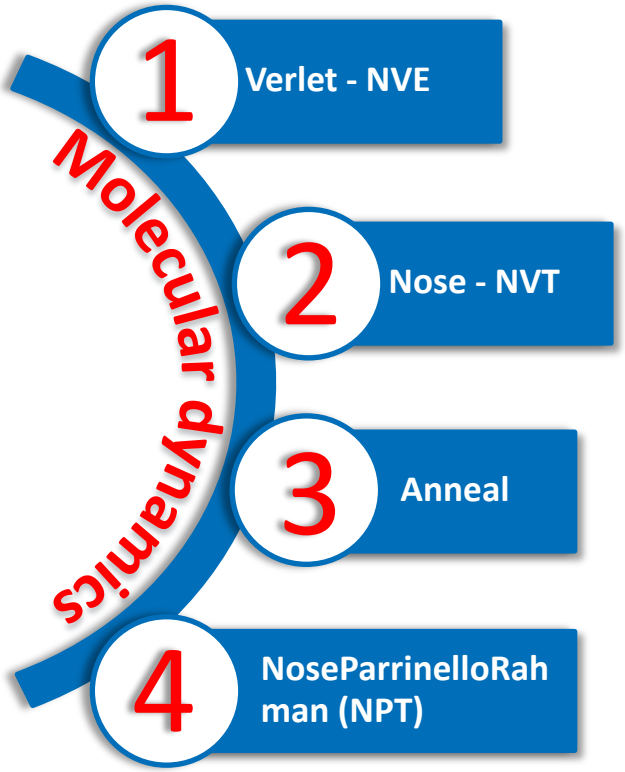
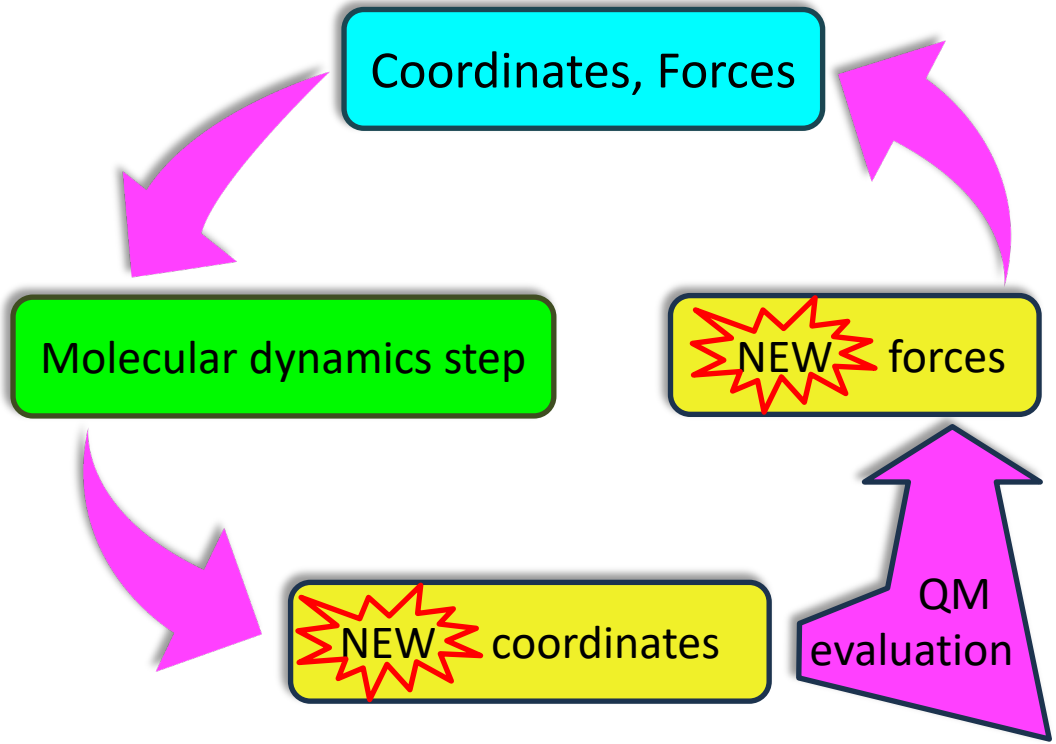
And more in the manual...





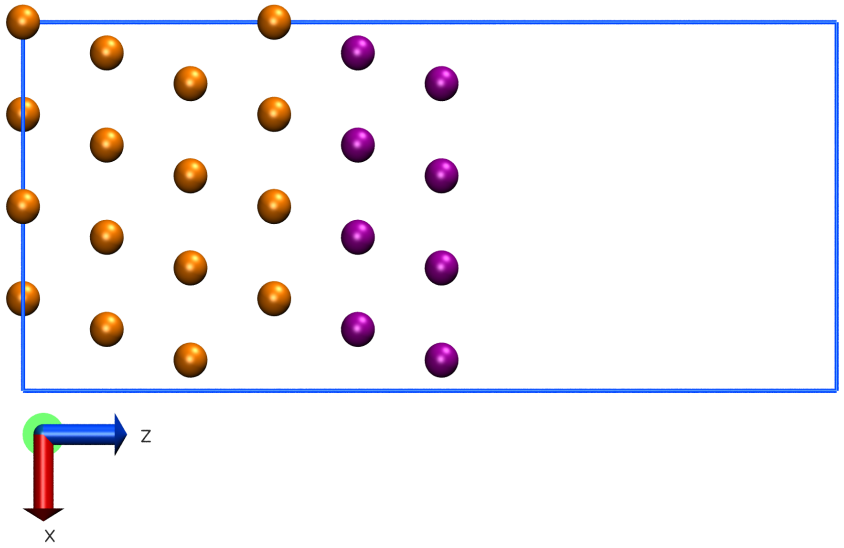
Changes in the input file

More options in the manual

- Set runtype 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

Use of constraints

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?

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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 direct on the terminal

To plot the energies:
plot SystemLabel.MDE 1 2 #will plot the first and second columns of the MDE file
To plot the energies from a grep command:
grep enth | plot '<cat' 0 4 #will plot the first and second columns of the grep outcome
If you want to define ranges:
plot SystemLabel.MDE 1 2 5 10 #from step 5 to 10

How to visualize trajectories?

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Files that can be used for that

- 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 Visual Molecular Dynamics

<vmd -xyz SystemLabel.ANI>
<vmd SystemLabel.pdb>

Hands-on now

Let's try the tutorials! Questions before?