1^{st} Tutorial:

The Basics of DFT

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Hands-on Summer School: Electronic Structure Theory for Materials and (Bio)molecules

The ultimate goal!

$$H\Psi = E\Psi$$

Second order differential equation for a $3N_e$-variable function Ψ
$\Rightarrow$ **Complex problem**
Unsolved issues at the simplest level of approximations (mulitiple solutions, ...)

Goals of this tutorial

- Familiarise with practical aspects of electronic structure theory in general and density functional theory (DFT) in particular
- Hartree-Fock (HF) method and Kohn-Sham DFT (non-periodic)
- Numerical solution of the approximate equations (tool: FHI-aims)
- Exploring potential energy surfaces (total energies at fixed nuclei, local minima, vibrational spectra)
- Electronic structure analysis (visualisation tools, electron density, Kohn-Sham orbitals and spectrum)

Solving the Kohn-Sham equations

Hohenberg-Kohn Theorem $\Psi(\mathbf{r}_1 \ldots \mathbf{r}_{N_e}) \Leftrightarrow n(\mathbf{r})$

Kohn-Sham scheme

$$\left(-\frac{1}{2}\nabla^2 + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc} + v\right)\psi_i = \epsilon_i \psi_i$$

$$\Rightarrow \quad n = \sum_i f_i |\psi_i|^2$$

KS Orbitals $\{\psi_i\}$ $\langle \psi_i, \psi_j \rangle = \delta_{ij}$

XC Potential v_{xc} unknown,but many approximations exist

LDA, PBE, ... $\rightarrow$ `control.in`

External potential contains ionic contributions $\rightarrow$ `geometry.in`

Basis set

Expand in a finite basis $\{\phi_i\}$: $\psi_j = \sum_{i=1}^{N} c_{ij}\phi_i$

Finite Basis

Numeric atom centered

Gaussians

Plane waves + pseudoisation

Slater type

Grid based

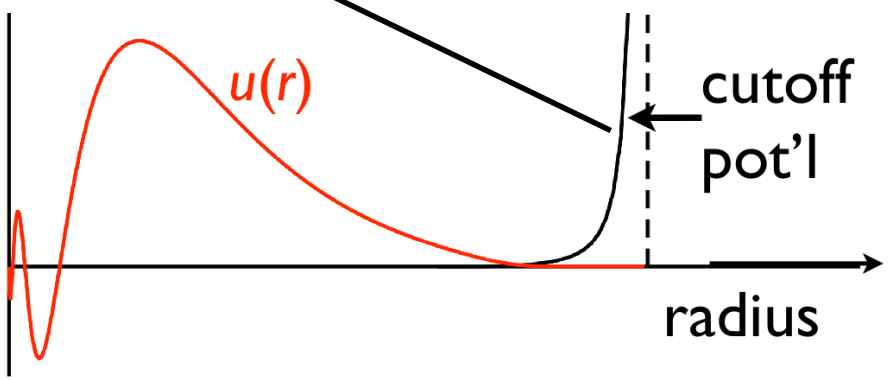
... many more

Basis set

Expand in a finite basis $\{\phi_i\}$: $\psi_j = \sum_{i=1}^{N} c_{ij}\phi_i$

Numeric atom centered (FHI-aims)

$$\phi_i(r) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$



Flexible:

- Free-atom like
- Hydrogen like
- Free Ions
- and many more ...

Courtesy V. Blum

Basis set

Expand in a finite basis $\{\phi_i\}$: $\psi_j = \sum_{i=1}^{N} c_{ij}\phi_i$

$$\Downarrow$$

Generalized matrix eigenvalue equation in c_{ij}

$$\hat{h}^{KS}\psi = E\psi \quad \Rightarrow \quad \sum_j h_{ij}(c)c_{jl} = \epsilon_l \sum_j s_{ij}c_{jl}$$

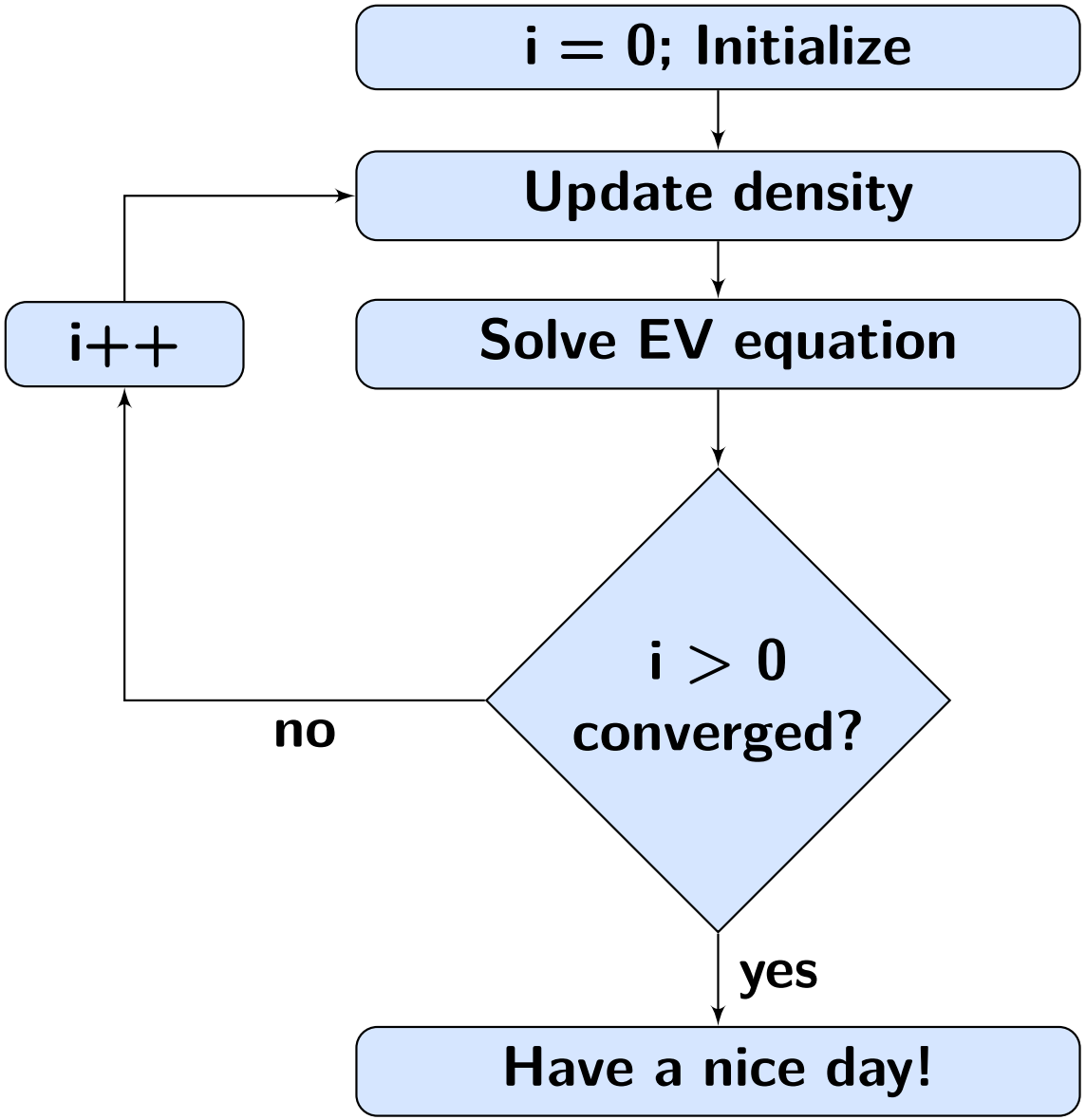
Overlap matrix $\quad s_{ij} = \langle \phi_i, \phi_j \rangle$

Hamilton matrix $\quad h_{ij} = \langle \phi_i, \hat{h}^{KS}\phi_j \rangle$

$$\Downarrow$$

Self-consistent solution

Finding the self-consistent solution



Mixing (Pulay)

(Sca)Lapack
ELPA

Criteria

- Energy
- Charge density
- Sum of eigenvalues
- Force

Problem I: The hydrogen atom

Tasks:

- Input files needed to run FHI-aims.
- Test the convergence of the total energy with basis size.
- Compare the total energy of the hydrogen atom computed with different methods implemented in FHI-aims. Do all methods converge to the same result?

FHI-aims: input files

`geometry.in`

`control.in`

FHI-aims: input files

geometry.in

```
# Atomic structure
#     x    y    z

atom 0.0 0.0 0.0 H
atom 1.0 0.0 0.0 H
initial_moment 1.0

# That's a comment
```

control.in

Units:

Positions in Å

Energies in eV

Manual, chap. 2.1

FHI-aims: input files

geometry.in

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control.in

```
# Physical model settings
  xc pw-lda
  charge 0.
  spin collinear
```

Units:

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FHI-aims: input files

geometry.in

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atom 1.0 0.0 0.0 H
initial_moment 1.0

# That's a comment
```

control.in

```
# Physical model settings
  xc pw-lda
  charge 0.
  spin collinear
# SCF convergence settings
  sc_accuracy_eev  1E-2
  sc_accuracy_etot 1E-5
  sc_accuracy_rho  1E-4
  sc_iter_limit 100
```

Units:

Positions in Å

Energies in eV

Manual, chap. 2.1

FHI-aims: input files

geometry.in

```
# Atomic structure
#     x    y    z

atom 0.0 0.0 0.0 H
atom 1.0 0.0 0.0 H
initial_moment 1.0

# That's a comment
```

Units:

Positions in Å

Energies in eV

Manual, chap. 2.1

control.in

```
# Physical model settings
  xc pw-lda
  charge 0.
  spin collinear
# SCF convergence settings
  sc_accuracy_eev  1E-2
  sc_accuracy_etot 1E-5
  sc_accuracy_rho  1E-4
  sc_iter_limit 100
# Species specifics
...
```

species_default

```
$HANDSON/aimsfiles/species_defaults
```

Predefined species
Copy-paste into control.in

Manual, chap. 2.2

- **light**
- **tight**
- **really tight**

species_default

```
$HANDSON/aimsfiles/species_defaults
```

Predefined species
Copy-paste into control.in

Manual, chap. 2.2

- **light**
- **tight**
- **really tight**

Increased accuracy:

Basis
Hartree potential
Basis cutoff potential
Integration grids

species_default

```
$HANDSON/aimsfiles/species_defaults
```

Predefined species
Copy-paste into control.in

Manual, chap. 2.2

- **light**
- **tight**
- **really tight**

Fast, many production tasks
Fast pre-relaxation

Used to verify important results
Converged settings

Heavily converged numerical settings
Explicit convergence tests

species_default

```
$HANDSON/aimsfiles/species_defaults
```

Predefined species
Copy-paste into control.in

Manual, chap. 2.2

- **light**
- **tight**
- **really tight**

Fast, many production tasks
Fast pre-relaxation

Used to verify important results
Converged settings

Heavily converged numerical settings
Explicit convergence tests

Additionally converge basis ("tiers")!

FHI-aims output

1

```
Invoking FHI-aims ...
```

Introduction

FHI-aims output

```
1  Invoking FHI-aims ...
   ------------------------------------
2  Reading file control.in.
   ------------------------------------
```

Summary of control.in file

FHI-aims output

```
1  Invoking FHI-aims ...
   ------------------------------------------
2  Reading file control.in.
   ------------------------------------------
   ------------------------------------------
3  Reading geometry description geometry.in.
   ------------------------------------------
```

Summary of geometry.in file

FHI-aims output

```
1  Invoking FHI-aims ...
   ------------------------------------------
2  Reading file control.in.
   ------------------------------------------
   ------------------------------------------
3  Reading geometry description geometry.in.
   ------------------------------------------
   ------------------------------------------
4  Preparing all fixed parts of the calculation.
   ------------------------------------------
```

Geometry independent preparations

Basis set generation

FHI-aims output

5

```
------------------------------------------
Begin self-consistency loop:  Initialization.
Date :  20130610, Time :  162002.389
------------------------------------------
```

Geometry dependent preparations
Integration grid
Initialization of charge density

FHI-aims output

```
5  ------------------------------------------
   Begin self-consistency loop:  Initialization.
   Date :  20130610, Time :  162002.389
   ------------------------------------------
   ------------------------------------------
6  Begin self-consistency iteration # 1
   Date :  20130610, Time :  162002.445
   ------------------------------------------
```

First SCF cycle

FHI-aims output

```
5  ------------------------------------------
   Begin self-consistency loop:  Initialization.
   Date :  20130610, Time :  162002.389
   ------------------------------------------
6  ------------------------------------------
   Begin self-consistency iteration # 1
   Date :  20130610, Time :  162002.445
   ------------------------------------------
```

First SCF cycle

» Energy

```
| Total energy                  :   -13.01991124 eV
| Total energy, T -> 0          :   -13.01991124 eV
| Electronic free energy        :   -13.01991124 eV
```

THIS TUTORIAL

Periodic metals only

FHI-aims output

```
5  ------------------------------------------
   Begin self-consistency loop:  Initialization.
   Date :  20130610, Time :  162002.389
   ------------------------------------------
6  ------------------------------------------
   Begin self-consistency iteration # 1
   Date :  20130610, Time :  162002.445
   ------------------------------------------
```

First SCF cycle

» Self-consistency convergence accuracy

```
| Change of charge density     :  0.6753E-02
| Change of sum of eigenvalues :  0.4376E+00 eV
| Change of total energy       :  0.1143E-01 eV
```

FHI-aims output

```
5   ------------------------------------------
    Begin self-consistency loop:  Initialization.
    Date :  20130610, Time :  162002.389
    ------------------------------------------
6   ------------------------------------------
    Begin self-consistency iteration # 6
    Date :  20130610, Time :  162002.560
    ------------------------------------------
```

Sixth SCF cycle

» Self-consistency convergence accuracy

```
| Change of charge density      :  0.3163E-05
| Change of sum of eigenvalues :  -.9415E-05 eV
| Change of total energy        :  0.2388E-10 eV
```

FHI-aims output

```
7          Self-consistency cycle converged.
```

FHI-aims output

```
 7      Self-consistency cycle converged.
```

» **Energy and forces**

```
| Total energy uncorrected :   -0.13019852609458 1E+02 eV
| Total energy corrected   :   -0.13019852609458 1E+02 eV
| Electronic free energy   :   -0.13019852609458 1E+02 eV
```

» **SCF info**

```
| Number of self-consistency cycles :  6
```

» **Timings**

FHI-aims output

```
7      Self-consistency cycle converged.
```

» **Energy and forces**

```
| Total energy uncorrected :   -0.13019852609458 1E+02 eV
| Total energy corrected   :   -0.13019852609458 1E+02 eV
| Electronic free energy   :   -0.13019852609458 1E+02 eV
```

» **SCF info**

```
| Number of self-consistency cycles :  6
```

» **Timings**

```
8      Have a nice day.
```

FHI-aims output

7 `Self-consistency cycle converged.`

Postprocessing

Structure optimization

- Get next relaxation step
- Redo SCF for new geometry

8 `Have a nice day.`

Problem II: Hydrofluoric acid (HF)

One of the first papers which systematically investigated the performance of DFT was published by John A. Pople and coworker in 1993.

Tasks:

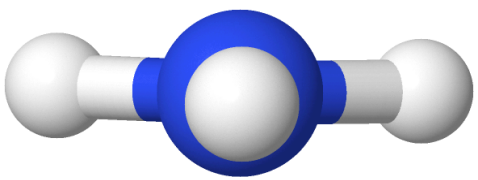
- Find the equilibrium bond distance of HF.
- Compare the HF bond length for different methods.
- Calculate the atomization energy (ΔH_{at}).
- Compute the dipole moment for different methods and bond lengths.

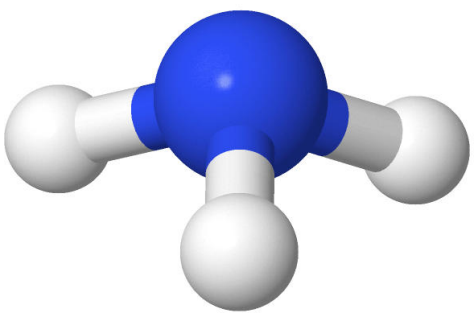
B. G. Johnson, P. M. W. Gill and J. A. Pople, *The performance of a family of density functional methods*, The Journal of Chemical Physics **98**, 5612 (1993).

Problem IV to VIII: Hydronium cation (H_3O^+)

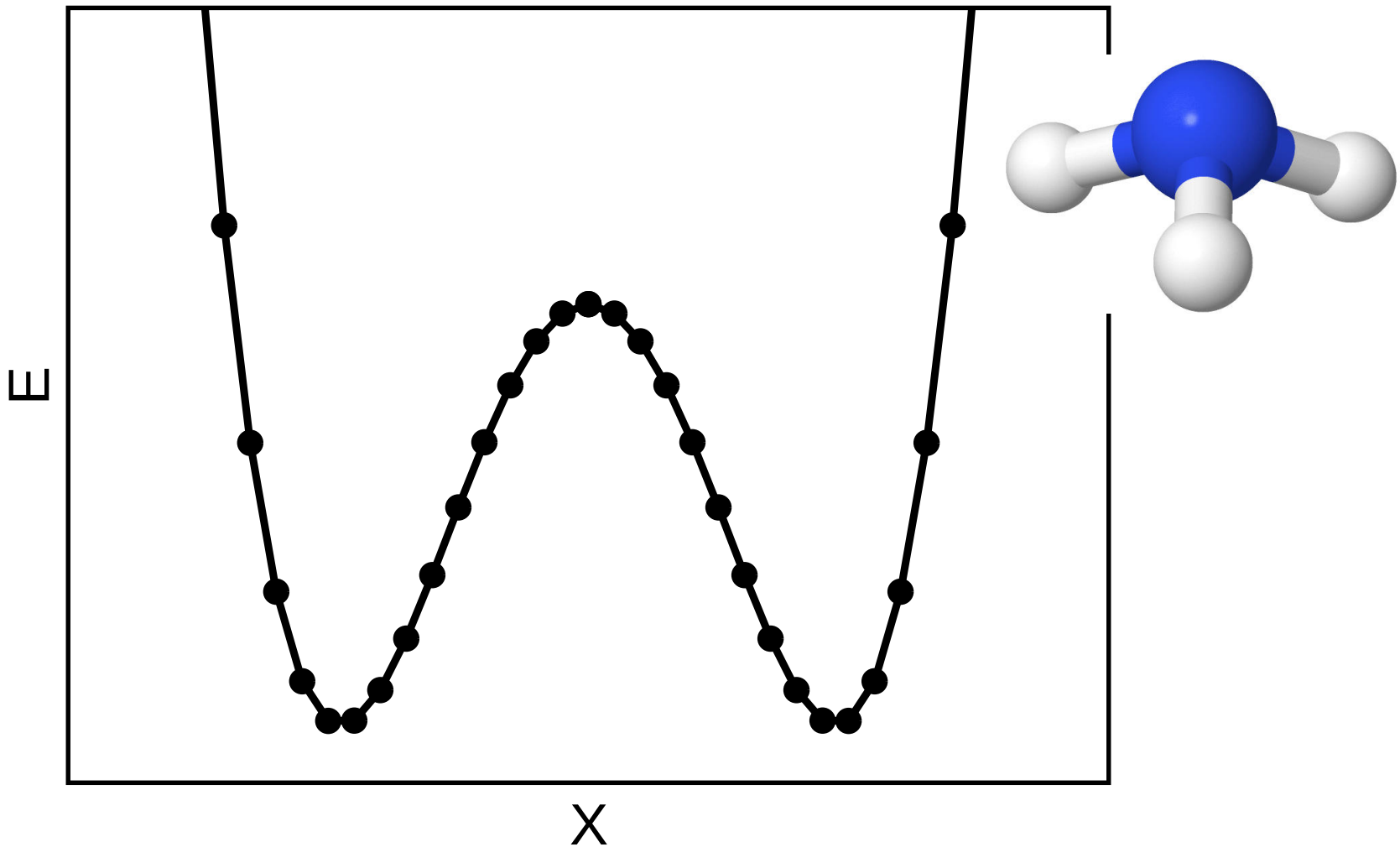
Tasks:

- Relax structure with two different starting points.
- Make a vibrational analysis.

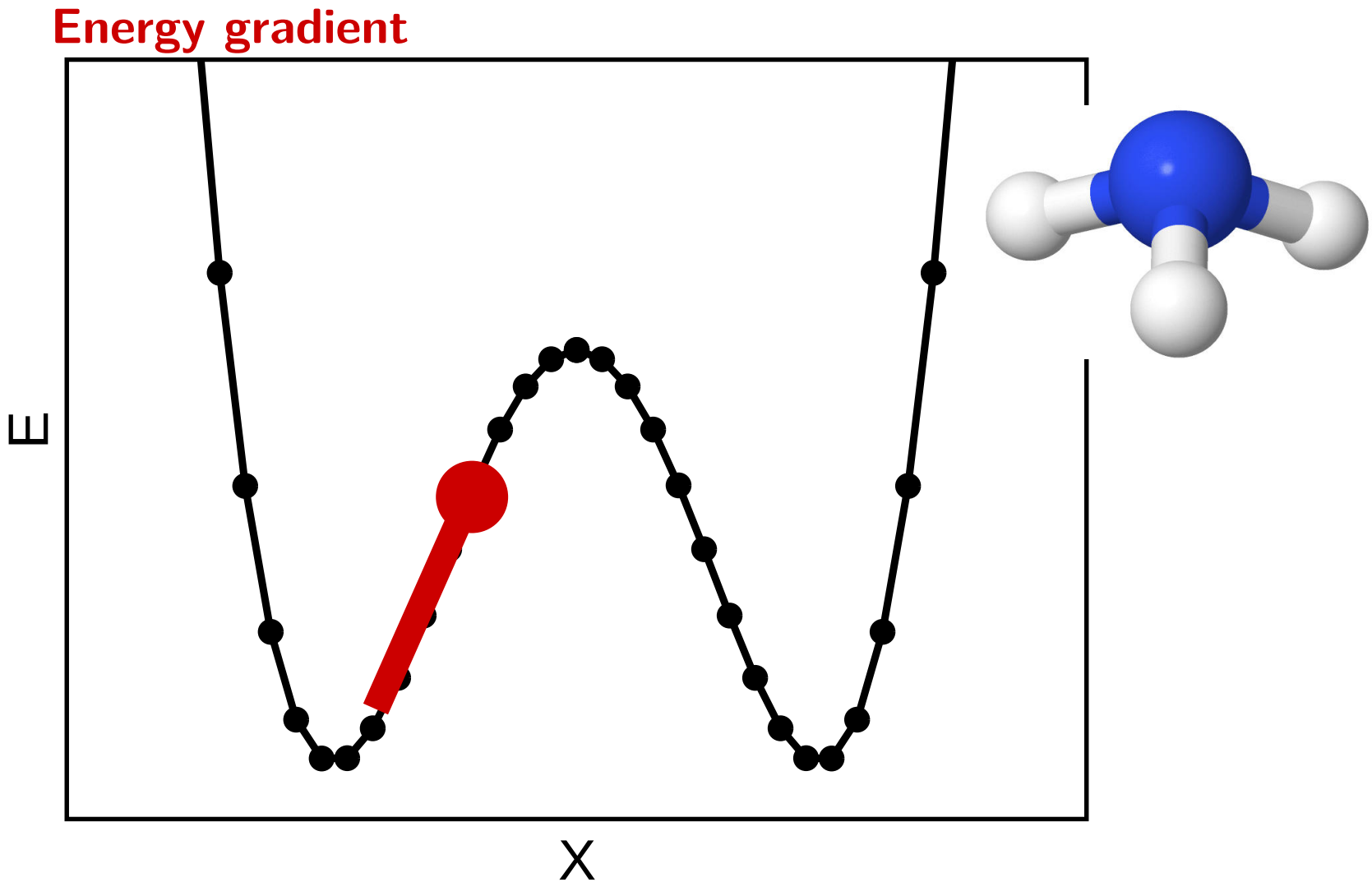




Forces

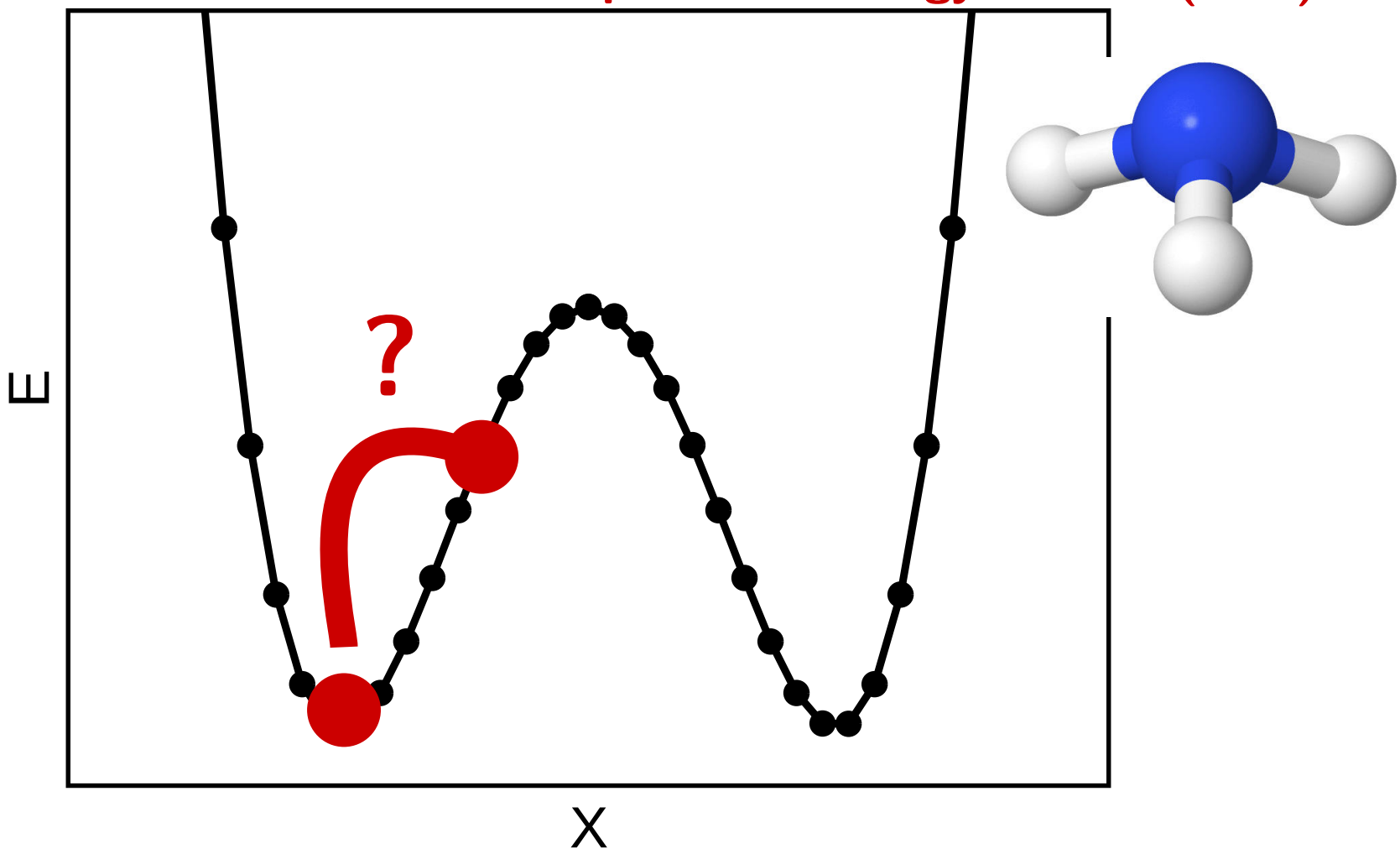


Forces



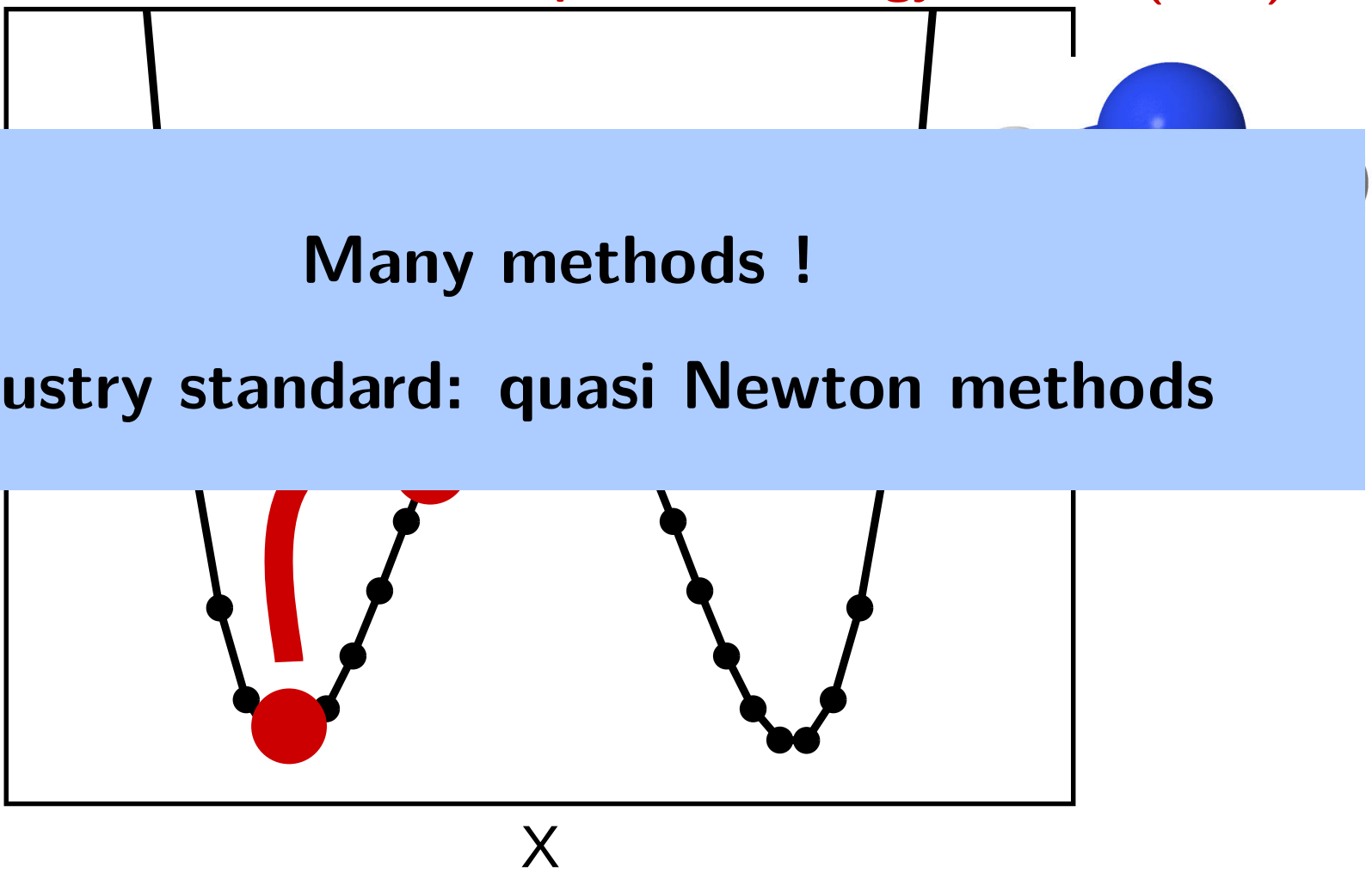
Forces

Structure optimization:
Find local minimum on potential energy surface (PES)



Forces

Structure optimization:
Find local minimum on potential energy surface (PES)

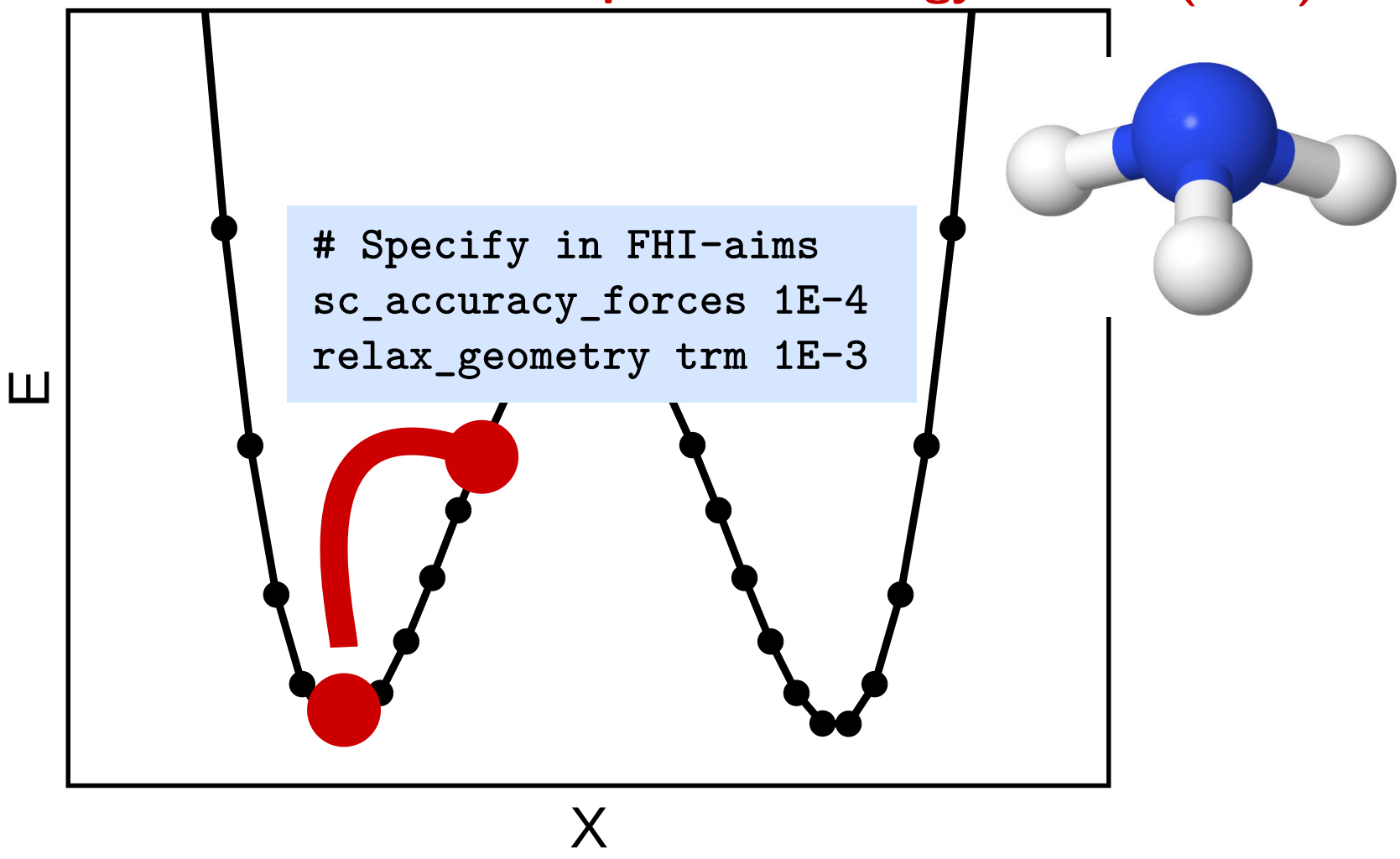


Many methods !

Industry standard: quasi Newton methods

Forces

Structure optimization:
Find local minimum on potential energy surface (PES)



Harmonic molecular motion

How do atoms move in a potential V?

$\Rightarrow$ **Solve equations of motion!**

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{R}_i} + \frac{\partial V}{\partial R_i} = 0$$

Kinetic energy: T

Potential energy: V

Harmonic molecular motion

How do atoms move in a potential V?

$\Rightarrow$ **Solve equations of motion!**

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{R}_i} + \frac{\partial V}{\partial R_i} = 0$$

Kinetic energy: T

Potential energy: V

$\Rightarrow$ **Taylor expansion of V**

around equilibrium position R_0 + harmonic approximation

$$V = V_0 \underbrace{-F(R_0)R}_{\text{=0 equilibrium}} + \frac{1}{2}R^T H(R_0)R \underbrace{+\ldots higher\ terms}_{\text{=0 harmonic approximation}}$$

F: Forces

H: Hessian

Harmonic molecular motion

How do atoms move in a potential V?

$\Rightarrow$ **Solve equations of motion!**

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{R}_i} + \frac{\partial V}{\partial R_i} = 0$$

Kinetic energy: T

Potential energy: V

$\Rightarrow$ **Solution**

The Dynamic Matrix D_{ij}: $D_{ij} = \frac{1}{\sqrt{M_i}\sqrt{M_j}} H_{ij}$

$$R \sim Qe^{i\omega t}, \quad \text{with} \qquad DQ - \omega^2 Q = 0$$

Eigenmodes Q

If (1) Harmonic approximation is valid
(2) Equilibrium geometry

Vibrations

Solve $\mathbb{R}^{3N} \times \mathbb{R}^{3N}$ eigenvalue equation

$$\det(D - \omega^2 \mathbf{1}) = 0$$

Hessian H $\quad$ **Dynamic matrix** D

$$H^{ij} := \frac{\partial^2 E}{\partial R_i \partial R_j} \qquad D_{ij} = \frac{1}{\sqrt{M_i}\sqrt{M_j}} H_{ij}$$

In practice: finite central numerical differences (of forces)

Wrapper

```
> aims_vibrations.mpi.pl
```

Manual, chap 4.6

Vibrations

Solve $\mathbb{R}^{3N} \times \mathbb{R}^{3N}$ eigenvalue equation

$$\det(D - \omega^2 \mathbf{1}) = 0$$

Get

- **Eigenmodes** $\{Q_i, i \in 1 \ldots 3N\}$
- **Eigenfrequencies**

Vibrations

Solve $\mathbb{R}^{3N} \times \mathbb{R}^{3N}$ eigenvalue equation

$$\det(D - \omega^2 \mathbf{1}) = 0$$

Get

- **Eigenmodes** $\{Q_i, i \in 1 \ldots 3N\}$
- **Eigenfrequencies**
- **6 (almost) zero frequency modes** (if molecule non-linear) **translations + rotations**
- **Imaginary frequency** $\Rightarrow$ Saddle point

Vibrations

Solve $\mathbb{R}^{3N} \times \mathbb{R}^{3N}$ eigenvalue equation

$$\det(D - \omega^2 \mathbf{1}) = 0$$

Get

- **Eigenmodes** $\{Q_i, i \in 1 \ldots 3N\}$
- **Eigenfrequencies**
- **6 (almost) zero frequency modes** (if molecule non-linear) **translations + rotations**
- **Imaginary frequency** $\Rightarrow$ Saddle point
- **Infrared intensities** (derivative of dipole moment μ)

$$I_i \sim \left| \frac{d\mu}{dQ_i} \right|^2$$

Vibrations

Based on harmonic approximation !
Beyond: Tutorial 4 (MD) on Friday

Get

- **Eigenmodes** $\{Q_i, i \in 1 \ldots 3N\}$
- **Eigenfrequencies**
- **6 (almost) zero frequency modes** (if molecule non-linear)
  translations + rotations
- **Imaginary frequency** $\Rightarrow$ Saddle point
- **Infrared intensities** (derivative of dipole moment μ)

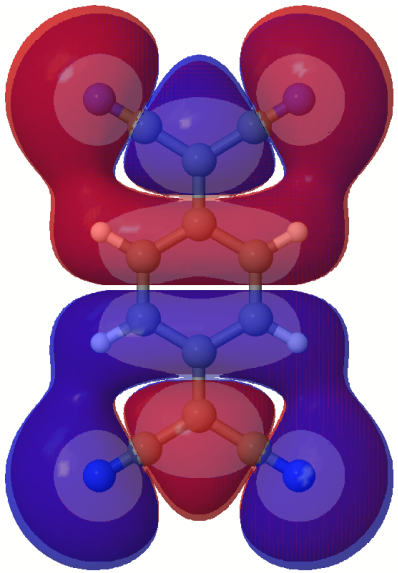
$$I_i \sim \left| \frac{d\mu}{dQ_i} \right|^2$$

Visualization

Orbitals and densities

Keyword in `control.in`

```
output cube eigenstate homo
cube filename HOMO.cube
output cube total_density
cube filename tot_dens_uc.cube
```



Get: *.cube file - values on a regular 3D grid.

Software: molden (jmol, gdis, xcrysden)

$\Rightarrow$ Appendix of handout

Practical issues

- **Each calculation one directory**

```
> mkdir tutorial1
> cd tutorial1
> mkdir HF
```

- **2 input files**

```
geometry.in
control.in
```

- **Launching FHI-aims calculation**

```
aims.x | tee aims.out
```

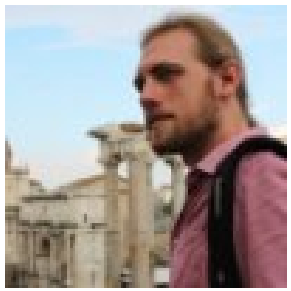
- **... scripting helps !**
  (Sample scripts in appendix of handout)

Your Tutors for the afternoon

Oliver T. Hofmann

Lydia Nemec

Christian Carbogno



William P. Huhn

Volker Blum

Markus Schneider