DFT and beyond: Hands-on Tutorial Workshop 2011

Tutorial 1: Basics of Electronic Structure Theory

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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, generalized Hartree-Fock method, ...)

Goals of this tutorial

- Familiarize 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, transition states, vibrational spectra)
- Electronic structure analysis (visualization 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

$$\left(-\frac{1}{2}\nabla^2 + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc} + v\right)\phi_i = \varepsilon_i \phi_i \quad \Rightarrow n = \sum_i f_i |\phi_i|^2$$

KS Orbitals $\{\phi_i\}$ $\langle \phi_i, \phi_j \rangle = \delta_{ij}$

XC Potential v_{xc} unknown,but $\exists$ many approximations

LDA, PBE, ...

External potential v contains ionic contributions

Hartree-Fock method

$$\Psi = \text{det}\ |(\phi_1(r_1)...\phi_{N_e}(r_{Ne})|$$

$$\left(-\frac{1}{2}\nabla^2 + \sum_j \int d^3r' \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \underbrace{-\sum_j \int d^3r' \frac{\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\text{exact (HF) exchange}} + v \right) \phi_i = \varepsilon_i \phi_i$$

(1) Single Slater determinant
(2) Mean-field approximation

No self-interaction error
But also: no correlation

Hybrid functionals: DFT + fraction of exact exchange
B3LYP, PBE0, HSE06, ...

Basis sets

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

Finite Basis

Numeric atom centered

Gaussians

Plane waves + Pseudopotenials

Slater type

Grid based

Projector augmented waves (PAW)

... many more

Basis sets

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

Numeric atom centered (FHI-aims)

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

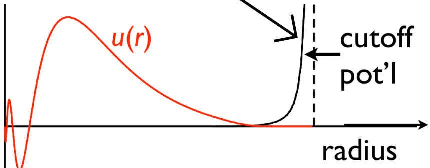
$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\text{cut}}\right] u_i(r) = \varepsilon_i u_i(r)$$

Flexible:

» Free-atom like

» Hydrogen like

» Free Ions, harmonic osc...



Courtesy V. Blum

Basis sets

Expand in a finite basis $\{\varphi_i\}$**:** $\phi_j = \sum_{i=1}^{N} c_{ij}\varphi_i$

$$\Downarrow$$

Generalized matrix eigenvalue equation in c_{ij}

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

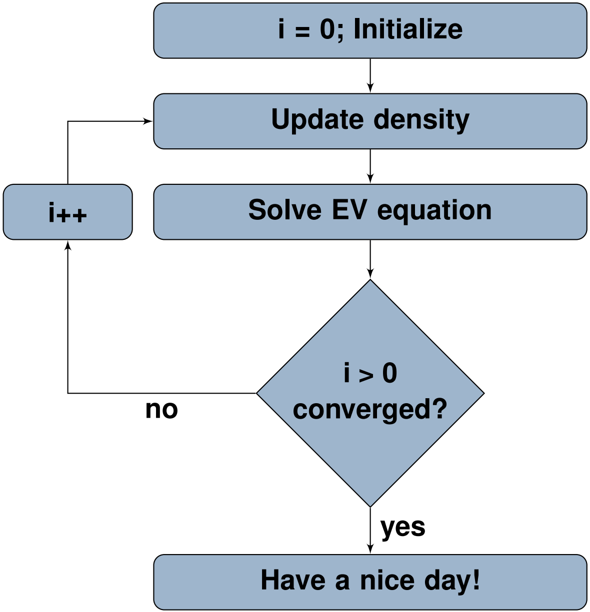
Overlap matrix $\quad s_{ij} = \langle \varphi_i, \varphi_j \rangle$

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

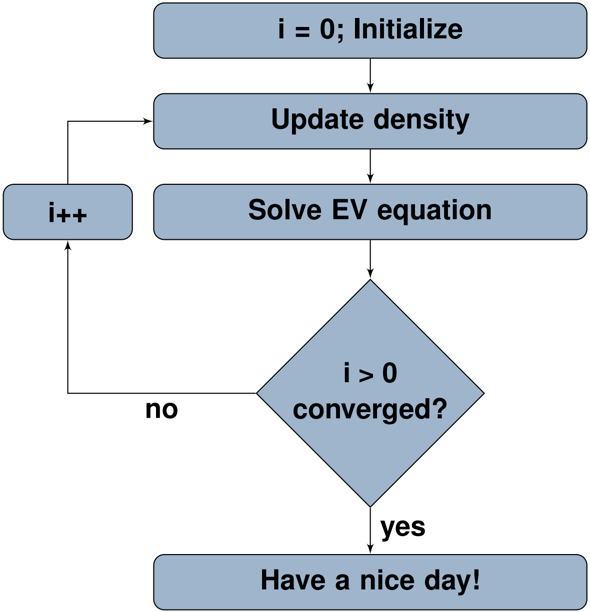
$$\Downarrow$$

Self-consistent solution

Finding the self-consistent solution



Finding the self-consistent solution



Mixing (Pulay)

(Sca)Lapack
ELPA

Criteria

- Energy
- Charge density
- Sum of eigenvalues
- Force

FHI-aims: 2 input files

geometry.in **control.in**

FHI-aims: 2 input files

geometry.in

control.in

 # Atomic structure

```
#    x   y   z

atom 0.0 0.0 0.0 N
atom 1.1 0.0 0.0 N

# That's a comment
```

Units:

Positions in Å

Energies in eV

Manual, chap. 2.1

FHI-aims: 2 input files

geometry.in

 # Atomic structure

```
#    x   y   z

atom 0.0 0.0 0.0 N
atom 1.1 0.0 0.0 N

# That's a comment
```

control.in

 # Physical model settings

```
xc pw-lda
charge 0.
spin none
relativistic none
```

Units:

Positions in Å

Energies in eV

Manual, chap. 2.1

FHI-aims: 2 input files

geometry.in

Atomic structure

```
#    x   y   z

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atom 1.1 0.0 0.0 N

# 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 none
relativistic none
```

SCF convergence settings

```
occupation_type gaussian 0.01
mixer pulay
n_max_pulay 10
charge_mix_param 0.2
sc_accuracy_rho  1E-4
sc_accuracy_eev  1E-2
sc_accuracy_etot 1E-5
sc_iter_limit 100
```

FHI-aims: 2 input files

geometry.in

Atomic structure

```
#    x   y   z

atom 0.0 0.0 0.0 N
atom 1.1 0.0 0.0 N

# That's a comment
```

Units:

Positions in Å

Energies in eV

Manual, chap. 2.1

control.in

Physical model settings

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sc_accuracy_rho  1E-4
sc_accuracy_eev  1E-2
sc_accuracy_etot 1E-5
sc_iter_limit 100
```

Species specifics

```
...
```

species_default

```
/usr/local/aimsfiles/species_default
```

Predefined species **Manual, chap. 2.2**

Copy-paste into control.in

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

species_default

```
/usr/local/aimsfiles/species_default
```

Predefined species
Copy-paste into control.in

Manual, chap. 2.2

- **light** — **Fast, many production tasks**
  Fast pre-relaxation
- **tight** — **Used to verify important results**
  Converged settings
- **really tight** — **Heavily converged numerical settings**
  Explicit convergence tests

species_default

```
/usr/local/aimsfiles/species_default
```

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

```
/usr/local/aimsfiles/species_default
```

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

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 :  20110615, Time :  003756.746
----------------------------------------------
```

Geometry dependent preparations
Integration grid
Initialization of charge density

FHI-aims output

5
```
------------------------------------------------------------
Begin self-consistency loop:  Initialization.
Date :  20110615, Time :  003756.746
------------------------------------------------------------
```

6
```
------------------------------------------------------------
Begin self-consistency iteration # 1
Date :  20110615, Time :  003756.810
------------------------------------------------------------
```

First SCF cycle

FHI-aims output

5
```
  ------------------------------------------------------------
  Begin self-consistency loop:  Initialization.
  Date  :  20110615, Time  :  003756.746
  ------------------------------------------------------------
```

6
```
  ------------------------------------------------------------
  Begin self-consistency iteration # 1
  Date  :  20110615, Time  :  003756.810
  ------------------------------------------------------------
```

First SCF cycle

THIS TUTORIAL →

» **Energy**

```
| Total energy                :  -2920.4718774 eV
| Total energy, T -> 0        :  -2920.4718774 eV
| Electronic free energy      :  -2920.4718774 eV
```

Periodic metals only

FHI-aims output

5

```
  ------------------------------------------------------------
  Begin self-consistency loop:  Initialization.
  Date :  20110615, Time :  003756.746
  ------------------------------------------------------------
```

6

```
  ------------------------------------------------------------
  Begin self-consistency iteration # 1
  Date :  20110615, Time :  003756.810
  ------------------------------------------------------------
```

First SCF cycle

» Self-consistency convergence accuracy

```
| Change of charge density      :  0.4491E-04
| Change of sum of eigenvalues  :  -.7874E-02 eV
| Change of total energy        :  0.2591E-07 eV
```

FHI-aims output

5
```
------------------------------------------------------------
Begin self-consistency loop:  Initialization.
Date :  20110615, Time :  003756.746
------------------------------------------------------------
```

6
```
------------------------------------------------------------
Begin self-consistency iteration # 2
Date :  20110615, Time :  003756.810
------------------------------------------------------------
```

Second SCF cycle

» Self-consistency convergence accuracy

```
| Change of charge density      :  0.4491E-04
| Change of sum of eigenvalues  :  -.7874E-02 eV
| Change of total energy        :  0.2591E-07 eV
```

FHI-aims output

7

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

FHI-aims output

7

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

» **Energy and forces**

```
| Total energy uncorrected :  -0.290332172209443E+04 eV
| Total energy corrected   :  -0.290332172209443E+04 eV
| Electronic free energy   :  -0.290332172209443E+04 eV
```

» **SCF info**

```
 | Number of self-consistency cycles :  7
```

» **Timings**

FHI-aims output

7

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

» **Energy and forces**

```
| Total energy uncorrected :   -0.290332172209443E+04 eV
| Total energy corrected   :   -0.290332172209443E+04 eV
| Electronic free energy   :   -0.290332172209443E+04 eV
```

» **SCF info**

```
 | Number of self-consistency cycles :   7
```

» **Timings**

8

```
    Have a nice day.
```

FHI-aims output

7

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

Postprocessing

Structure optimization

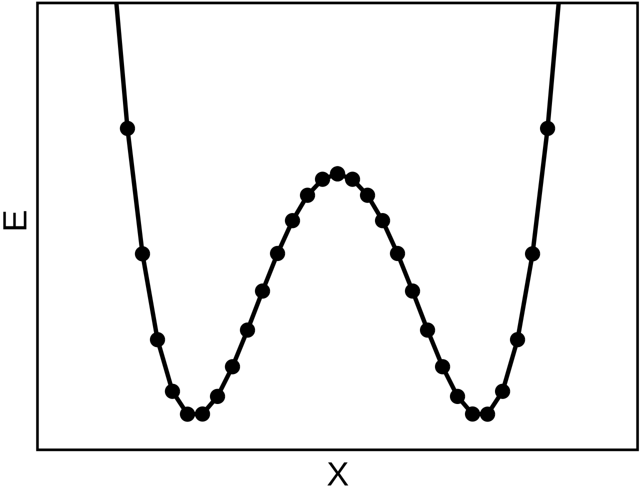
» Get next relaxation step

» Redo SCF for new geometry

8

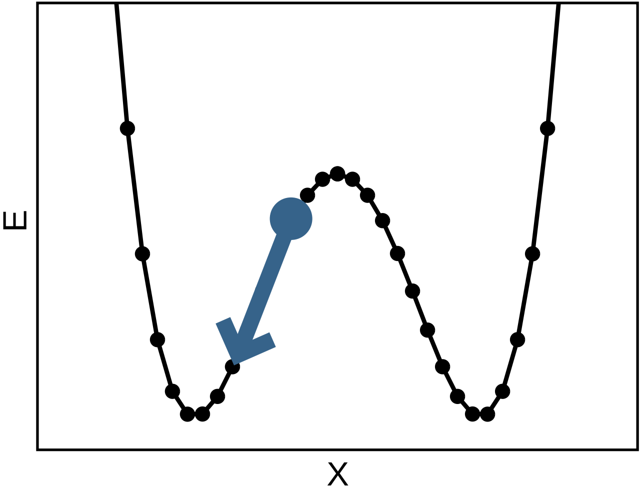
```
    Have a nice day.
```

Forces



Forces

Energy gradient



Forces

Force component α on atom I

$$E^{tot} = E^{tot}(R_I, c_j)$$
$$F^I_\alpha = \frac{dE^{tot}}{dR^\alpha_I} = \frac{\partial E^{tot}}{\partial R^\alpha_I} + \sum_j \underbrace{\frac{\partial E^{tot}}{\partial c_j}}_{=0} \frac{dc_j}{dR^\alpha_I}$$

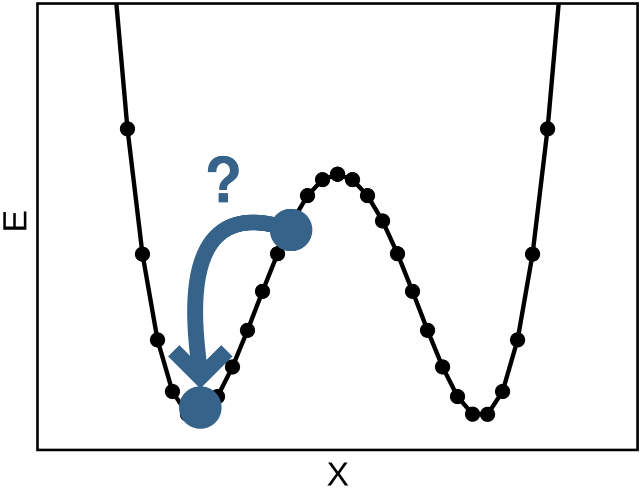
E^{tot} is minimized with respect to c_j
In FHI-aims basis functions depend on atomic postitions.

Keyword in control.in

```
sc_accuracy_forces 1E-4
```

Structure optimization

Aim: Find local minimum on potential energy surface (PES)

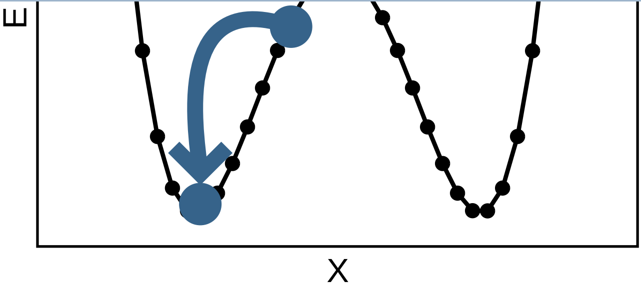


Structure optimization

Aim: Find local minimum on potential energy surface (PES)

Many methods !

Industry standard: quasi Newton methods



Structure optimization in FHI-aims

Basic idea: local harmonic model of PES

$$\tilde{E}(X_0 + X) = E(X_0) - F^T(X_0)X + \frac{1}{2}X^T B(X_0)X$$

Next relaxation step

Trust radius method (TRM) recommended
BFGS + simple line search also implemented

Keyword in control.in

```
relax_geometry trm 1E-3
```

↑ Force convergence criterion eV/Å

Manual, chap. 3.10

Vibrations

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

Vibrations

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

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

F: Forces

B: Hessian

Vibrations

How do atoms move in a potential V?

⇒ **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

⇒ **Solution**

$$R \sim u e^{i\omega t}, \quad \text{with} \qquad Bu - \omega^2 M u = 0$$

Eigenmodes u
Mass-weighted diagonal matrix M

If (1) Harmonc approximation valid
(2) Equilibrium geometry

Vibrations

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

$$\det(B - \omega^2 M) = 0$$

Hessian B

$$B^{ij} := \frac{\partial^2 E}{\partial R_i \partial R_j}$$

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

$$\det(B - \omega^2 M) = 0$$

Get

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

Vibrations

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

$$\det(B - \omega^2 M) = 0$$

Get

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

$$\det(B - \omega^2 M) = 0$$

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 !
Limitation: Exercise 2.6
Beyond: Tutorial 5 (MD)

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

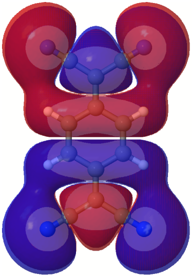
Keyword in control.in

```
output cube eigenstate 52
output cube total_density
```

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 N2
```

- **2 input files**

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

- **Launching FHI-aims calculation**

```
mpirun -np 4 aims.hands-on-2011.scalapack.mpi.x
| tee calculation.out
```

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

Timeline

PART 1: Basic electronic structure	**90 mins**
PART 2: Born-Oppenheimer surface	**90 mins**
PART 3: Visualization	**30 mins**

Next: exercises

PART 1
Basic electronic structure

90 (CPU 20) mins

PART 2
Born Oppenheimer Surface

90 (CPU $<$ 20) mins

Exercise 4: Planar NH_3 (!) 10 min

geometry.in

```
atom   0.0   0.0   0.0   N
atom   0.8  -0.5   0.0   H
atom  -0.8  -0.5   0.0   H
atom   0.0   1.0   0.0   H
```

control.in

```
xc            pw-lda
charge        0
spin          none
relax_geometry trm 1E-3
sc_accuracy_eev    1E-2
sc_accuracy_rho    1E-4
sc_accuracy_etot   1E-5
sc_iter_limit      300
```

+ copy/paste **light species**

How can I do a geometry optimization ?

Relax the NH_3 molecule starting from a planar initial guess.

Exercise 4: Planar NH_3 (!) 10 min

geometry.in

```
atom  0.0  0.0  0.0  N
atom  0.8 -0.5  0.0  H
atom -0.8 -0.5  0.0  H
atom  0.0  1.0  0.0  H
```

control.in

```
xc           pw-lda
charge       0
spin         none
relax_geometry trm 1E-3
sc_accuracy_eev    1E-2
sc_accuracy_rho    1E-4
sc_accuracy_etot   1E-5
sc_iter_limit      300
```

Visualization: Molden ⇒ Appendix of handout

How does the fully relaxed structure look like?

Exercise 4: Planar NH_3 (!) 10 min

geometry.in

```
atom   0.0  0.0  0.0  N
atom   0.8 -0.5  0.0  H
atom  -0.8 -0.5  0.0  H
atom   0.0  1.0  0.0  H
```

control.in

```
xc              pw-lda
charge          0
spin            none
relax_geometry trm 1E-3
sc_accuracy_eev    1E-2
sc_accuracy_rho    1E-4
sc_accuracy_etot   1E-5
sc_iter_limit      300
```

Visualization: (/pub/tutorial1/utilities)

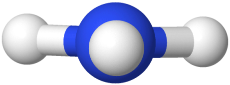
```
> create_relax_movie.pl aims.NH3.out > NH3.molden
> molden NH3.molden
```

How does the fully relaxed structure look like?

Exercise 4: Planar NH_3 (!) 10 min

Solution

Stays planar



Exercise 5: Planar NH_3 (!) 15 min

Is this geometry stable ?

⇒ perform a vibrational analysis

```
> aims.vibrations.hands-on-2011.mpi.pl  NH3_planar
```

control.in + geometry.in in same folder!

From Exercise 4:

- **control.in**
- **geometry.in** from output file
  grep `Final atomic structure`

Exercise 5: Planar NH_3 (!) 15 min

Do you find negative frequencies?
How do they look like?

```
> aims.vibrations.hands-on-2011.mpi.pl  NH3_planar
```

control.in + geometry.in in same folder!

From Exercise 4:

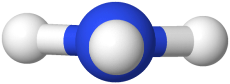
- **control.in**
- **geometry.in** from output file
  grep `Final atomic structure`

Visualization: `/pub/tutorial1/utilities`

```
> troublemaker -xyz2molden NH3_planar.xyz > NH3.molden
> molden NH3.molden
```

Exercise 5: Planar NH_3 (!) 15 min

Solution



Unstable

Imaginary frequency: out of plane mode

Exercise 6: Getting NH_3 right 10 min

Can I find a stable geometry?

(1) Distort the geometry of the planar NH_3 molecule along the imaginary mode ← `*xyz` **from Exercise 5** (`/pub/tutorial1/utilities`).

```
> ./troublemaker.pl NH3_planar.xyz | tail -4
```

(2) Relax the geometry again.
Same control.in as before

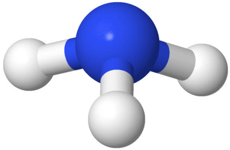
How does the structure look like?
What is the difference in energy with respect to the planar geometry?

Exercise 6: Getting NH_3 right 10 min

Solution

3D geometry

0.2 eV lower in energy



Exercise 7: 3D NH_3 15 min

Now stable?
For 3D geometry, perform a vibrational analysis for the 3D optimized NH_3 molecule.

Is the structure stable?
What does the mode lowest in energy that is not a rotation or translation look like?

Exercise 7: 3D NH_3 15 min

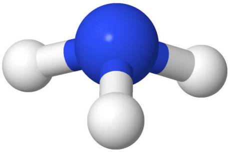
Now stable?

For 3D geometry, perform a vibrational analysis for the 3D optimized NH_3 molecule.

Is the structure stable?
What does the mode lowest in energy that is not a rotation or translation look like?

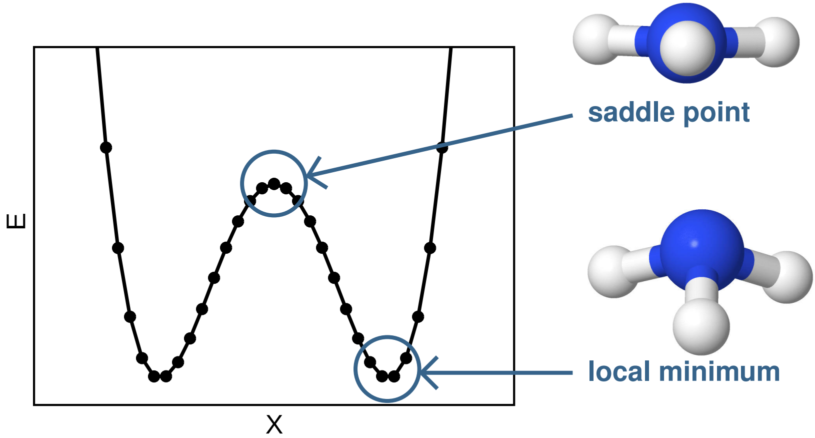
Solution

Stable
Umbrella mode (lowest non-trivial mode)



Summary

A: Saddle point or local minimum ?



B: Do a vibrational analysis!

Exercise 8: Infrared (IR) intensities 20 min

Are (numerical) settings sensitive?

$\Rightarrow$ Compare IR spectra!

(1) Optimize geometry

(2) Perform vibrational analysis

Exercise 8: Infrared (IR) intensities 20 min

Are (numerical) settings sensitive?

⇒ Compare IR spectra!

~~(1) Optimize geometry~~

(2) Perform vibrational analysis

Vibration script does that for you!

```
relax_geometry trm 1E-3
```

control.in

Exercise 8: Infrared (IR) intensities 20 min

Important! `relax_geometry trm 1E-3`

- Perform a convergence tests with respect to light, tight and really tight settings of the IR spectrum (`xc pw-lda`).
- For light setting compute the PBE IR spectrum and compare it with the LDA spectrum.
- Compare to experiment.
- **(Bonus)** For light settings compare the IR spectrum of the planar and 3D NH_3 molecule (`xc pw-lda`).

```
> aims.vibrations.hands-on-2011.mpi.pl  NH3_foo
```

Visualization: 2 column *dat file (gnuplot/xmgrace) (`/pub/tutorial1/utilities`)

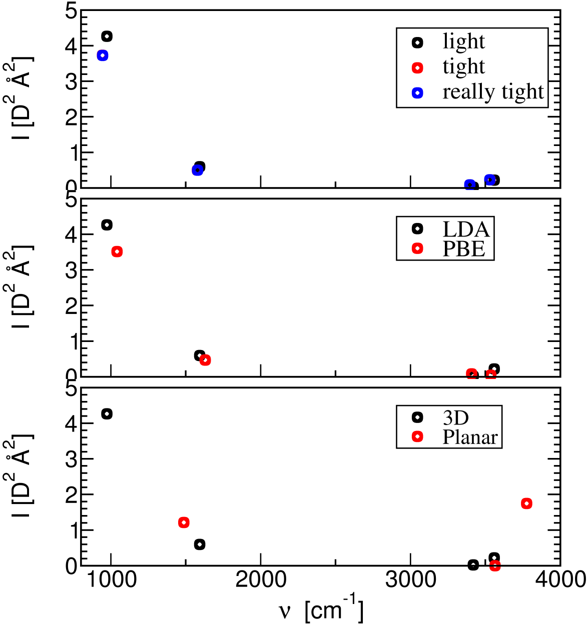
```
extract_harmivb.sh NH3_foo.vib.out > NH3_foo.dat
```

Solution

Numerical settings

Light settings

Light settings

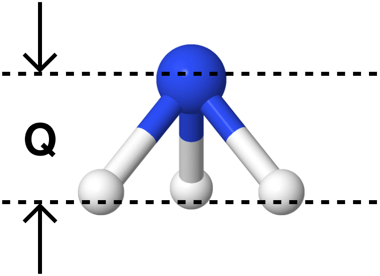


Exercise 9: Limits of the harmonic approximation (!)

Where does it break down?

Consider a cut through the Born Oppenheimer surface where the N atom is distorted perpendicular to the plane spaned by the H atoms.

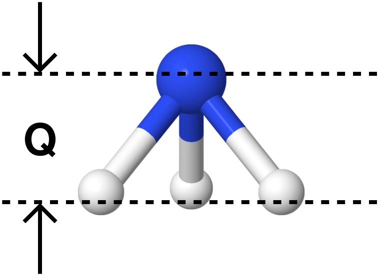
Define coordinate Q



Exercise 9: Limits of the harmonic approximation (!)

Compute total energies as a function of Q:

- **Define 1D PES**
  Constrained relaxation
  H atoms in one plane
- **Out-of-plane mode**
  relative to planar geometry
- **Umbrella mode**
  relative to 3D geometry



In which range is the process described by one mode only ?

Exercise 9 - Part I 15 min

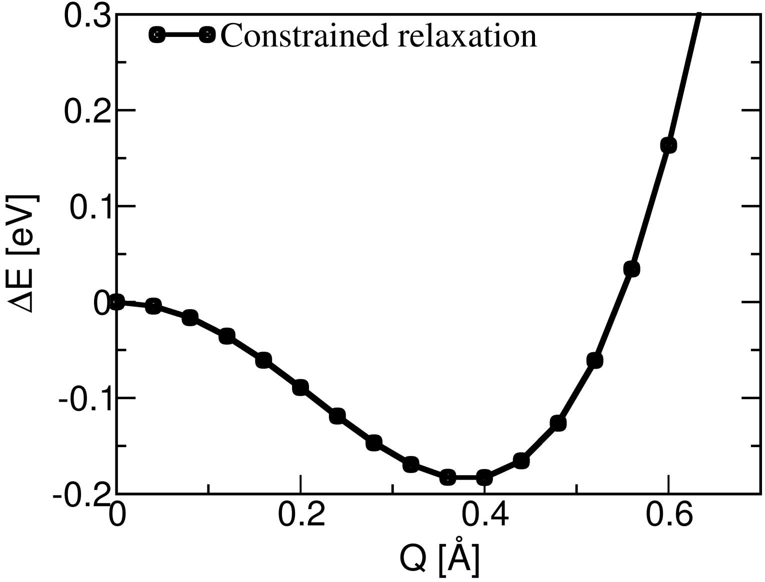
Constrained relaxation `relax_geometry trm 1E-3`
Q within [0,1.2] Å, stepwidth 0.04 Å.

geometry.in

```
atom   0.000   0.000   <Q>     N
constrain_relaxation .true.
atom   0.873  -0.504   0.000   H
constrain_relaxation z
atom  -0.873  -0.504   0.000   H
constrain_relaxation z
atom   0.000   1.008   0.000   H
constrain_relaxation z
```

Reference energy with respect to saddle point (Q = 0)
Sample script? → Appendix A of handout

Solution



Exercise 9 - Part II 30 min

Approximate PES along planar out-of-plane mode

(1) get `*xyz` file from planar vibrational analysis

(2) For Q within [0,1.2] Å, stepwidth 0.04 Å generate the corresponding geometry.in files

```
./troublemaker -norm N -mode 1 NH3_planar.xyz
```

Important: $Q \neq N$
N describes the extension of the whole mode. Can you find the relation $Q \leftrightarrow N$ by inspecting the `*xyz` file ?

(3) Calculate the energy for this geometry.
Refernce it to the saddle point energy (Q=0)

Do NOT perform a structure relaxation!

... similar for umbrella mode of 3D geometry

Exercise 9 - Part II 30 min

Approximate PES along planar out-of-plane mode

(1) get `*xyz` file from planar vibrational analysis

(2) For Q within [0,1.2] Å, stepwidth 0.04 Å generate the corresponding geometry.in files

```
./troublemaker -norm N -mode 1 NH3_planar.xyz
```

Important: $Q \neq N$

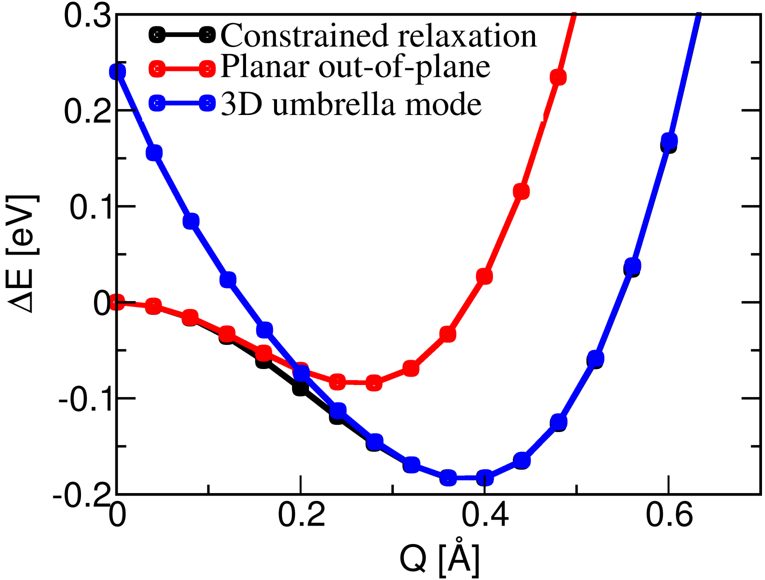
$$N = Q/0.6966$$

(3) Calculate the energy for this geometry.
Refernce it to the saddle point energy (Q=0)

Do NOT perform a structure relaxation!

... similar for umbrella mode of 3D geometry

Solution



Constrained relaxation
Planar out-of-plane
3D umbrella mode
ΔE [eV]
Q [Å]
0.3
0.2
0.1
0
-0.1
-0.2
0
0.2
0.4
0.6

Exercise 10: Mode mixing (!) (Bonus)

Consider the 'reaction coordinate' Q of the previous exercise. For every geometry step project the 'real PES' (i.e. Part I of exercise 9) on the modes of the planar NH_3 molecule.

$$\mathbf{X} = \mathbf{X_0} + \sum_{i=1}^{3N} \lambda_i \mathbf{M_i}, \qquad \mathbf{M_i}, \mathbf{X}, \mathbf{X_0} \in \mathbb{R}^{3N} \qquad \lambda_i \in \mathbb{R}$$

Was our assumption that the system can by described by the out-of-pane mode only appropriate?

Exercise 10: Mode mixing (!) (Bonus)

(1) Get the *xyz file from the planar vibrational analysis.

(2) Get the constrained relaxed geometries from EX 9 (`/pub/tutorial1/utilities`).

```
./FinalAtomicStructure.sh aims.NH3_PES_Q.out >
geo_Q.in
```

(3) For every Q: get projection coefficients

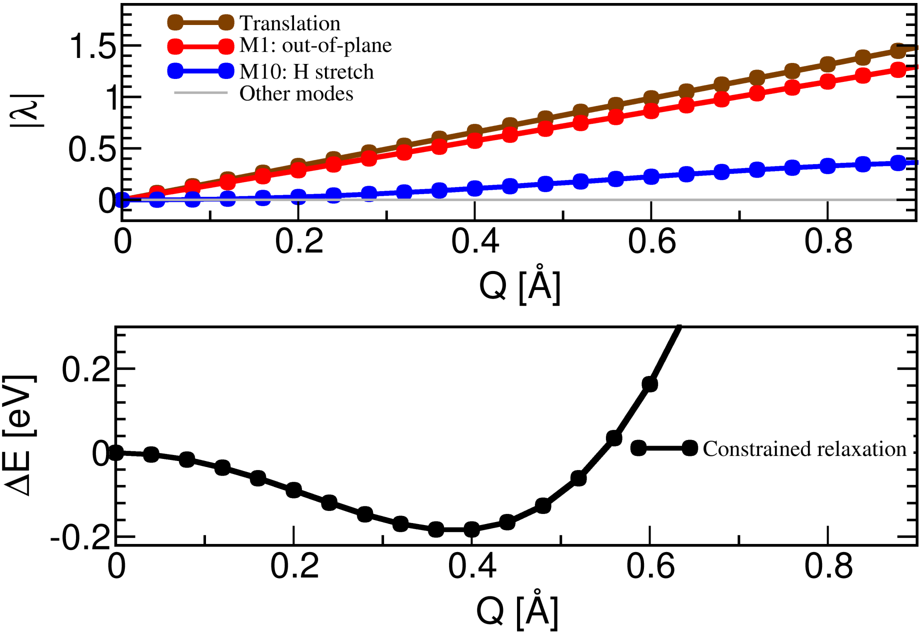
$\Rightarrow$ Plot λ as a function of Q. Which modes contribute ?

```
> troublemaker.pl -project geo_Q.in NH3_planar.xyz
```

(4) For contributing modes compute the energetic contribution as a function of Q

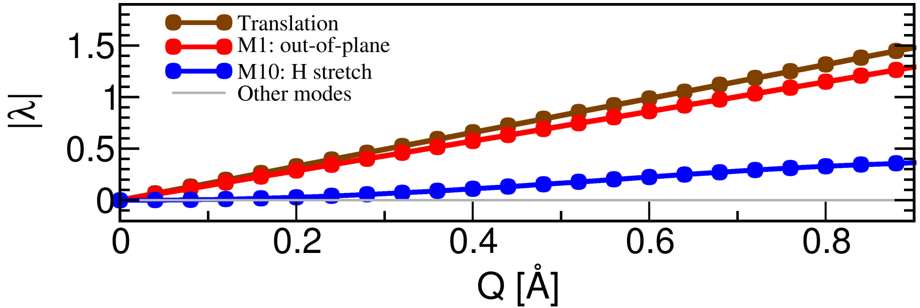
> ./troublemaker.pl -mode N -norm λ
> NH3_planar.xyz

Solution

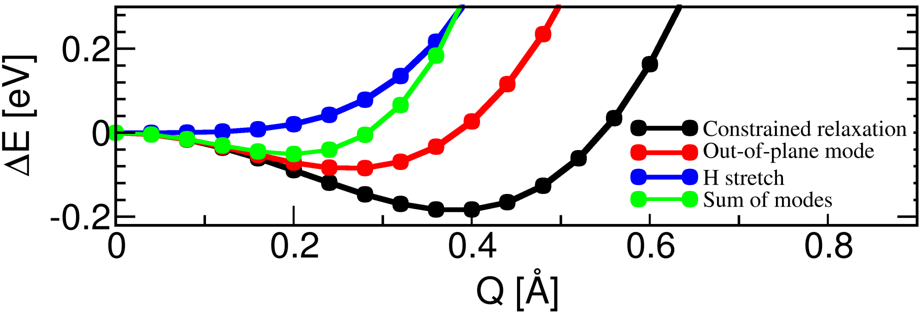


Translation
M1: out-of-plane
M10: H stretch
Other modes
|λ|
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
Q [Å]
ΔE [eV]
0.2
0
-0.2
Constrained relaxation
0
0.2
0.4
0.6
0.8
Q [Å]

Solution



Translation
M1: out-of-plane
M10: H stretch
Other modes
|λ|
1.5
1
0.5
0
0.2
0.4
0.6
0.8
Q [Å]



ΔE [eV]
0.2
0
-0.2
0
0.2
0.4
0.6
0.8
Q [Å]
Constrained relaxation
Out-of-plane mode
H stretch
Sum of modes

PART 3
Visualization

30 (CPU $<$ 5) mins

That’s it!