1st Tutorial:

Basics of Electronic-Structure Theory

Hagen-Henrik Kowalski, Igor Y. Zhang, Tonghao Shen, Björn Bieniek, Lydia Nemec, Oliver Hoffman and many others

Fritz Haber Institute of the Max Planck Society

1st of August 2017

Hands-on Workshop:
Density-functional theory and beyond - accuracy, efficiency and reproducibility in computational materials science
Solving the Kohn-Sham equations

**Hohenberg-Kohn Theorem**  \( \psi(r_1, \ldots, r_{N_e}) \leftrightarrow n(r) \)

**Kohn-Sham scheme**

\[
\left( -\frac{1}{2} \nabla^2 + \int \frac{n(r')}{|r - r'|} dr' + v_{xc} + v \right) \psi_i = \epsilon_i \psi_i
\]

\[ \rightarrow n = \sum_i f_i |\psi_i|^2 \]

- **KS Orbitals** \( \psi_i \)
  \[ \langle \psi_i, \psi_j \rangle = \delta_{ij} \]
- **XC Potential** \( v_{xc} \)
  unknown, but many approximations exist LDA, PBE, etc.
- **External potential** \( v \)
  contains ionic contributions
Solving the Kohn-Sham equations

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

Kohn-Sham scheme

\[
\left( -\frac{1}{2} \nabla^2 + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc} + v \right) \psi_i = \epsilon_i \psi_i \\
\Rightarrow n = \sum_i f_i |\psi_i|^2
\]

- KS Orbitals \( \psi_i \)
  \[ \langle \psi_i, \psi_j \rangle = \delta_{ij} \]
- XC Potential \( v_{xc} \)
  unknown, but many approximations exist LDA, PBE, etc.
- External potential \( v \)
  contains ionic contributions

Needs to be solved self-consistently!
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)
Getting started

First things first:

- Copy folder tutorial_1 from $HandsOn (/public/hands-on-2017-tutorials) to your working directory.
- tutorial_1/skel contains folders and templates for all exercises.
- Scripts and tools are prepared in python
  ```
  >python run.py
  ```
- Visualization: Jmol, Molden, VMD, Xcrysden, ...
- Ploting: Matplotlib (see provided scripts), xmgrace, ...
- Most importantly: the terminal can be opened by clicking on this icon
Basic electronic structure with FHI-aims

Problem I: The hydrogen atom

Tasks:
- Learn how to generate 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
Basic electronic structure with FHI-aims

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

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

**Units:**
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**Manual, chap. 2.1**
FHI-aims: input files

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**control.in**

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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
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control.in

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Units:
Positions in Å
Energies in eV

Manual, chap. 2.1
# Basic electronic structure with FHI-aims

## FHI-aims: input files

<table>
<thead>
<tr>
<th>geometry.in</th>
<th>control.in</th>
</tr>
</thead>
<tbody>
<tr>
<td># Atomic structure</td>
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# Units:
- Positions in Å
- Energies in eV

Manual, chap. 2.1
species_default

$SPECIES_DEFAULTS

Predefined species
Copy-paste into control.in

- light
- tight
- really tight
Basic electronic structure with FHI-aims

species_default

$SPECIES_DEFAULTS

Predefined species
Copy-paste into control.in

- light

- tight

- really tight

Increased accuracy:

- Basis
- Hartree potential
- Basis cutoff potential
- Integration grids

Manual, chap. 2.2
Basic electronic structure with FHI-aims

**species_default**

Predefined species

Copy-paste into control.in

- **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

Specify:

$SPECIES_DEFAULTS

Predefined species
Copy-paste into control.in

- 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

Additionally converge basis ("tiers")!
FHI-aims output

1 Invoking FHI-aims ...
Basic electronic structure with FHI-aims

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
Basic electronic structure with FHI-aims

FHI-aims output

---

Begin self-consistency loop: Initialization.
Date: 20170727, Time: 162002.389
---

Geometry dependent preparations
Integration grid
Initialization of charge density
FHI-aims output

---
Begin self-consistency loop: Initialization.
Date: 20170727, Time: 162002.389
---

---
Begin self-consistency iteration # 1
Date: 20170727, Time: 162002.445
---

First SCF cycle
FHI-aims output

---

Begin self-consistency loop: Initialization.
Date: 20170727, Time: 162002.389
---

---

Begin self-consistency iteration # 1
Date: 20170727, Time: 162002.445
---

First SCF cycle

» Energy
| Total energy: -13.01991124 eV
| Total energy, $T \to 0$: -13.01991124 eV
| Electronic free energy: -13.01991124 eV

---

THIS TUTORIAL

Periodic metals only
FHI-aims output

Begin self-consistency loop: Initialization.
Date: 20170727, Time: 162002.389

Begin self-consistency iteration # 1
Date: 20170727, 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

Begin self-consistency loop: Initialization.
Date: 20170727, Time: 162002.389

Begin self-consistency iteration # 6
Date: 20170727, Time: 162002.560

Sixth SCF cycle

» Self-consistency convergence accuracy
| Change of charge density            : 0.3163E-05
| Change of sum of eigenvalues       : -0.9415E-05 eV
| Change of total energy             : 0.2388E-10 eV
Self-consistency cycle converged.
Basic electronic structure with FHI-aims

FHI-aims output

7

Self-consistency cycle converged.

» Energy and forces
| Total energy uncorrected : \(-0.130198526094581E+02\) eV
| Total energy corrected : \(-0.130198526094581E+02\) eV
| Electronic free energy : \(-0.130198526094581E+02\) eV

» SCF info
| Number of self-consistency cycles : 6

» Timings
FHI-aims output

Self-consistency cycle converged.

» Energy and forces

| Total energy uncorrected :  -0.130198526094581E+02 eV |
| Total energy corrected :  -0.130198526094581E+02 eV |
| Electronic free energy :  -0.130198526094581E+02 eV |

» SCF info

| Number of self-consistency cycles :  6 |

» Timings

Have a nice day.
FHI-aims output

Self-consistency cycle converged.

Postprocessing

Structure optimization

» Get next relaxation step
» Redo SCF for new geometry

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 ($\Delta H_{at}$).
- Compute the dipole moment for different methods and bond lengths.

Problem III: Molecular oxygen - a critical look

It is important to always have a critical look at your calculations to ensure that the results are reasonable. Default settings might not be adequate or common assumptions might fail for the system at hand.

Tasks:

- Find the equilibrium bond distance of $O_2$.
- Compare the $O_2$ bond length for different spin treatments.
- Calculate the atomization energy ($\Delta H_{at}$).
Problem IV to VIII: Hydronium cation (H$_3$O$^+$)

Tasks:
- Relax structure with two different starting points.
- Make a vibrational analysis.
Harmonic Vibrations

Expand potential in a Taylor series up to second order!

\[ V(R_1, \ldots, R_N) = V(R_0) + \sum_I \frac{\partial V}{\partial R_I} R_I + \frac{1}{2} \sum_{IJ} \frac{\partial^2 V}{\partial R_I \partial R_J} R_I R_J + O(R^3) \]
Expand potential in a Taylor series up to second order!

\[ V(R_1, \ldots, R_N) = V(R_0) + \sum_I \frac{\partial V}{\partial R_I} R_I + \frac{1}{2} \sum_{IJ} \frac{\partial^2 V}{\partial R_I \partial R_J} R_I R_J + \mathcal{O}(R^3) \]

Hessian determined via finite difference approach!

\[ \Phi_{IJ} = \frac{\partial F_I}{\partial R_J} \approx \frac{F_I(R_0 + \delta R_J)}{\delta R_J} \]
Expand potential in a Taylor series up to second order!

\[
\rightarrow V(R_1, \ldots, R_N) = V(R_0) + \sum I \frac{\partial V}{\partial R_I} R_I + \frac{1}{2} \sum_{IJ} \frac{\partial^2 V}{\partial R_I \partial R_J} R_I R_J + O(R^3)
\]

Hessian determined via finite difference approach!

\[
\Phi_{IJ} = \frac{\partial F_I}{\partial R_J} \approx \frac{F_I(R_0 + \delta R_J)}{\delta R_J}
\]

Finding eigenfrequencies:
Define Dynamical matrix \( D_{IJ} = \frac{1}{\sqrt{M_I M_J}} \Phi_{IJ} \)
Obtain eigenfrequencies \( \omega \) via eigenvalue equation

\[
D Q = \omega^2 Q
\]
Local structure optimisation

Harmonic Vibrations

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 \( \mu \))

\[ I_i \sim \left| \frac{d\mu}{dQ_i} \right|^2 \]
Harmonic Vibrations

Get

» Eigenmodes \( \{ Q_i, i \in 1 \ldots 3N \} \)

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» Infrared intensities (derivative of dipole moment \( \mu \))

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

Based on harmonic approximation!

Beyond: Tutorial 4 (MD) on Friday
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:** jmol (gdis, xcrysden)

⇒ See tutorial video
Practical issues

- Each calculation one directory
  ```
  > cd tutorial_1
  > 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)