1st 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 $\Psi$

$\Rightarrow$ **Complex problem**

Unsolved issues at the simplest level of approximations (multiple 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 \( \Psi(r_1...r_{N_e}) \Leftrightarrow n(r) \)

Kohn-Sham scheme

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

\[ \Rightarrow \quad n = \sum_i f_i |\psi_i|^2 \]

**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 \( s_{ij} = \langle \phi_i, \phi_j \rangle \)

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

\[ \downarrow \]

Self-consistent solution
Finding the self-consistent solution

i = 0; Initialize
Update density
Solve EV equation

i++

i > 0 converged?

no

yes

Have a nice day!

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?
Basic electronic structure with FHI-aims

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

**geometry.in**

```plaintext
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# 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**

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

**Units:**

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Manual, chap. 2.1
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# That's a comment
```

**control.in**

```plaintext
# 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**

```plaintext
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**control.in**

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# SCF convergence settings
sc_accuracy_eev 1E-2
sc_accuracy_etot 1E-5
sc_accuracy_rho 1E-4
sc_iter_limit 100

# Species specifics
```

**Units:**

- Positions in Å
- Energies in eV

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

species_default

$HANDSON/aimsfiles/species_defaults

Predefined species
Copy-paste into control.in

- light
- tight
- really tight

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

**species_default**

$\texttt{HANDSON/aimsfiles/species_defaults}$

Predefined species
Copy-paste into control.in

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

Increased accuracy:

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

Part I

Part II

Part III

Basic electronic structure with FHI-aims

species_default

$HANDSON/aimsfiles/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

Manual, chap. 2.2
species_default

$HANDSON/aimsfiles/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 ...

Introduction
**FHI-aims output**

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

Summary of control.in file
Basic electronic structure with FHI-aims

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

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

Geometry dependent preparations
Integration grid
Initialization of charge density
Begin self-consistency loop: Initialization.
Date : 20130610, Time : 162002.389

Begin self-consistency iteration # 1
Date : 20130610, Time : 162002.445

First SCF cycle
FHI-aims output

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

Begin self-consistency iteration # 1
Date : 20130610, Time : 162002.445
```

First SCF cycle

<table>
<thead>
<tr>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy    : -13.01991124 eV</td>
</tr>
<tr>
<td>Total energy, T → 0 : -13.01991124 eV</td>
</tr>
<tr>
<td>Electronic free energy : -13.01991124 eV</td>
</tr>
</tbody>
</table>

THIS TUTORIAL

Periodic metals only
FHI-aims output

---

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

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

---

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

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

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

» Energy and forces
- Total energy uncorrected : $-0.130198526094581 \times 10^{02}$ eV
- Total energy corrected : $-0.130198526094581 \times 10^{02}$ eV
- Electronic free energy : $-0.130198526094581 \times 10^{02}$ eV

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

» Timings
FHI-aims output

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Self-consistency cycle converged.

» Energy and forces

| Total energy uncorrected : $-0.130198526094581 \times 10^2$ eV |
| Total energy corrected : $-0.130198526094581 \times 10^2$ eV |
| Electronic free energy : $-0.130198526094581 \times 10^2$ eV |

» SCF info

| Number of self-consistency cycles : 6 |

» Timings

8

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.

Local structure optimisation

Problem IV to VIII: Hydronium cation (H$_3$O$^+$)

Tasks:

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

Forces
Forces

Energy gradient
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
Local structure optimization

**Forces**

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

```
# Specify in FHI-aims
sc_accuracy_forces 1E-4
relax_geometry trm 1E-3
```
Harmonic molecular motion

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: $V$
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

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

$F$: Forces
$H$: Hessian
Harmonic molecular motion

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

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

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

Eigenmodes $Q$

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

**Solve** \( \mathbb{R}^{3N} \times \mathbb{R}^{3N} \) eigenvalue equation

\[
\det(D - \omega^2 \mathbf{I}) = 0
\]

**Hessian** \( H \)

\[
H_{ij} := \frac{\partial^2 E}{\partial R_i \partial R_j}
\]

**Dynamic matrix** \( D \)

\[
D_{ij} = \frac{1}{\sqrt{M_i} \sqrt{M_j}} H_{ij}
\]

**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

\[
\det(D - \omega^2 1) = 0
\]

**Get**

- Eigenmodes \( \{Q_i, i \in 1 \ldots 3N\} \)
- Eigenfrequencies
Vibrations

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

$$\det(D - \omega^2 I) = 0$$

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

\[
\det(D - \omega^2 I) = 0
\]

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 \( \mu \))

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

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

Visualising density differences

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)

⇒ 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