Before we start: Important setup of your Computer

change directory:
cd /afs/ictp/public/shared/smr2475
./setup-config.sh
logout
login again
1st Tutorial:

The Basics of DFT

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Density functional theory and beyond: Computational materials science for real materials, 2013
The ultimate goal!

\[ H\psi = E\psi \]

Second order differential equation for a $3N_e$-variable function $\psi$  
\[ \Rightarrow \text{Complex problem} \]

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 \( \{\psi_i\} \quad \langle \psi_i, \psi_j \rangle = \delta_{ij} \)

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 \( \{ \phi_i \} \): \( \psi_j = \sum_{i=1}^{N} c_{ij} \phi_i \)

\[ \Rightarrow \]

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

\[ \Rightarrow \]

Self-consistent solution
Finding the self-consistent solution

i = 0; Initialize

Update density

i++

Solve EV equation

i > 0 converged?

no

yes

Have a nice day!

Mixing (Pulay)

(SCa)Lapack

ELPA

Criteria

Energy

Charge density

Sum of eigenvalues

Force
Introduction

Part I

Basic electronic structure with FHI-aims

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

# 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

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

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
```

**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

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
...

Units:
Positions in Å
Energies in eV

Manual, chap. 2.1
species_default

/usr/local/aimsfiles/species_default

Predefined species
Copy-paste into control.in

- light
- tight
- really tight
species_default

/usr/local/aimsfiles/species_default

Predefined species
Copy-paste into control.in

- light
- tight
- really tight

Increased accuracy:

- Basis
- Hartree potential
- Basis cutoff potential
- Integration grids
Basic electronic structure with FHI-aims

**species_default**

```
/usr/local/aimsfiles/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
Basic electronic structure with FHI-aims

species_default

/usr/local/aimsfiles/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

Additionally converge basis ("tiers")!
1

Invoking FHI-aims ...

Introduction
Basic electronic structure with FHI-aims

FHI-aims output

1
Invoking FHI-aims ...
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

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
Basic electronic structure with FHI-aims

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

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

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  

---
Basic electronic structure with FHI-aims

FHI-aims output

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Self-consistency cycle converged.
FHI-aims output

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
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.
Basic electronic structure with FHI-aims

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.

Basic electronic structure with FHI-aims

Forces

![Diagram of a potential energy curve with a molecule model.](image)
Basic electronic structure with FHI-aims

**Forces**

**Energy gradient**

[Diagram showing energy gradient with a molecule structure]
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)

# Specify in FHI-aims
sc_accuracy_forces 1E-4
relax_geometry trm 1E-3
Problem IV to VIII: Hydronium cation (H$_3$O$^+$)

Tasks:

- Relax structure with two different starting points.
- Make a vibrational analysis.
- Explore the limits of the harmonic approximation.
Harmonic molecular motion

How do atoms move in a potential $V$?
⇒ Solve equations of motion!

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

Kinetic energy: $T$
Potential energy: $V$
Harmonic molecular motion

How do atoms move in a potential $V$?
⇒ 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: $V$

⇒ **Taylor expansion of $V$**
around equilibrium position $R_0$ + harmonic approximation

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

$F$: Forces
$H$: Hessian

$= 0$ equilibrium
$= 0$ harmonic approximation
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

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

**Hessian** \( H \)  
**Dynamic matrix** \( D \)

\[
H_{ij} := \frac{\partial^2 E}{\partial R_i \partial R_j} \quad D_{ij} = \frac{1}{\sqrt{M_i} \sqrt{M_j}} H_{ij}
\]

**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

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

Get

» Eigenmodes $\{Q_i, i \in 1 \ldots 3N\}$
» Eigenfrequencies
Local structure optimisation

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 $\mu$)

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

Based on harmonic approximation!
Limitation: Problem IX
Beyond: Tutorial 3 (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 \( \mu \))

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

Keyword in control.in

- output cube eigenstate homo
- output cube total_density
- cube filename HOMO.cube
- 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
  
  ```
  mpirun -np 4 aims.hands-on-2013.scalapack.mpi.x
  | tee aims.out
  ```

- ... scripting helps!
  
  (Sample scripts in appendix of handout)
Before we start: Important setup of your Computer

change directory:
   cd /afs/ictp/public/shared/smr2475
   ./setup-config.sh
logout from your KDE session
login again

Access the info-lab machine from outside via ssh:
Access the ICTP gateway
   ssh your_user_name@ssh.ictp.it
From the gateway you can reach your workstation:
   ssh hp83-inf-XX
replace XX by the number of your machine (XX=1,..51)
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