FHI-aims capabilities for molecules, clusters, and solids

FHI-aims

V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, "*Ab Initio* Molecular Simulations with Numeric Atom-Centered Orbitals", *Computer Physics Communications* **180**, 2175-2196 (2009)

Main focus:

- **Accurate all-electron electronic-structure calculations (DFT and beyond) for both periodic and cluster/ molecular systems**
- **Massively parallel**

Robust interface: atomic simulation environment (ASE)

Approximations to the electronic problem: Basis set

Idea: represent all unknown functions ($\rho(\mathbf{r}),\psi_i(\mathbf{r})$) as a linear combination of known functions with well-defined properties: $\psi_i(\mathbf{r}) = \sum_p C_{ip}\varphi_p(\mathbf{r})$

Widely used basis sets:

gaussians $x^i y^j z^k \exp(-\alpha r^2)$ **(localized, analytic integrals)**

plane waves $\exp(i\mathbf{k}\cdot\mathbf{r})$ **(delocalized, analytic integrals)**

Slater-type $x^i y^j z^k \exp(-\alpha r)$ **(localized, nuclear cusp)**

grid-based $\delta(\mathbf{r}-\mathbf{r}_i)$ **(localized, analytic integrals)**

Core electrons are often treated separately (pseudopotentials, plane-wave + localized basis)

The basis set: Numeric atomic orbitals

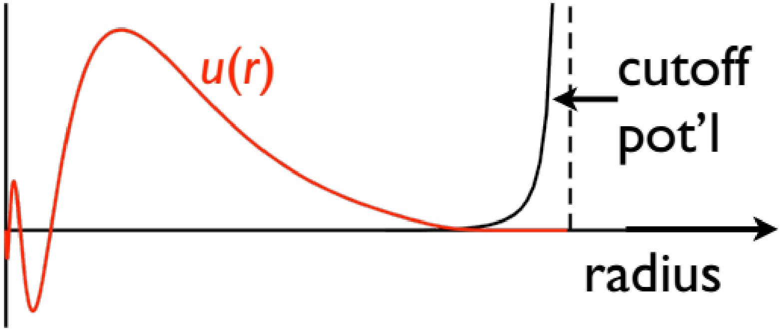
$$\boxed{\varphi_{i[lm]}(\boldsymbol{r}) = \frac{u_i(r)}{r} \cdot Y_{lm}(\Omega)}$$

- $u_i(r)$: Flexible choice - “Anything you like.”

<u>Many popular implementations:</u>
DMol^3 (Delley), FPLO (Eschrig *et al.*), PLATO (Horsfield *et al.*), PAOs (Siesta, Conquest, OpenMX^2, Fireball, ...)

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

- free-atom like: $v_i(r) = v^{\mathrm{DFT}}_{\mathrm{free\ atom}}(r)$
- Hydrogen-like: $v_i(r) = z/r$
- free ions, harm. osc. (Gaussians), ...



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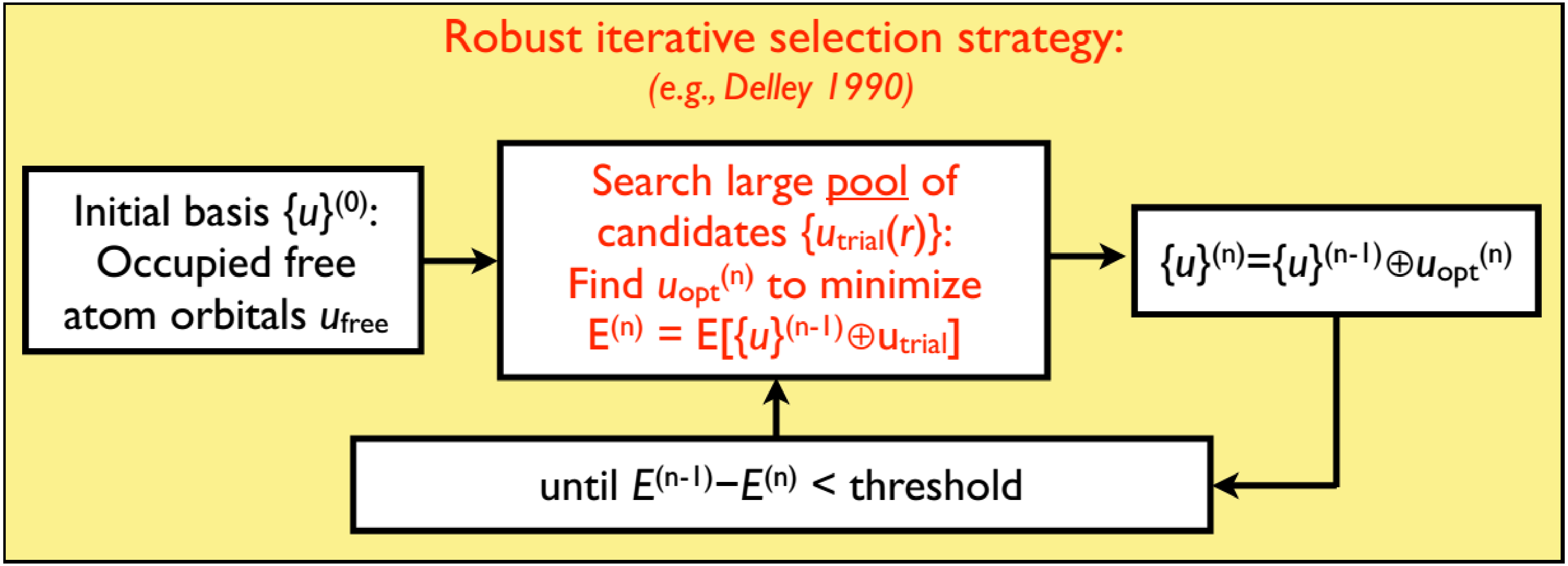
→ Localized; ”naturally” all-electron

→ The choice of efficient and of enough radial functions is obviously important

→ We have a basis set library for all elements (1-102), from fast qualitative to meV-converged (total energy, LDA/GGA) calculations - efficient and accurate approach

V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler,
“*Ab Initio* Molecular Simulations with Numeric Atom-Centered Orbitals”,
Computer Physics Communications ***180****, 2175-2196 (2009)*

The basis set



Robust iterative selection strategy:

(e.g., Delley 1990)

Initial basis $\{u\}^{(0)}$: Occupied free atom orbitals u_{free}

Search large pool of candidates $\{u_{\mathrm{trial}}(r)\}$: Find $u_{\mathrm{opt}}^{(n)}$ to minimize $E^{(n)} = E[\{u\}^{(n-1)} \oplus u_{\mathrm{trial}}]$

$\{u\}^{(n)}=\{u\}^{(n-1)}\oplus u_{\mathrm{opt}}^{(n)}$

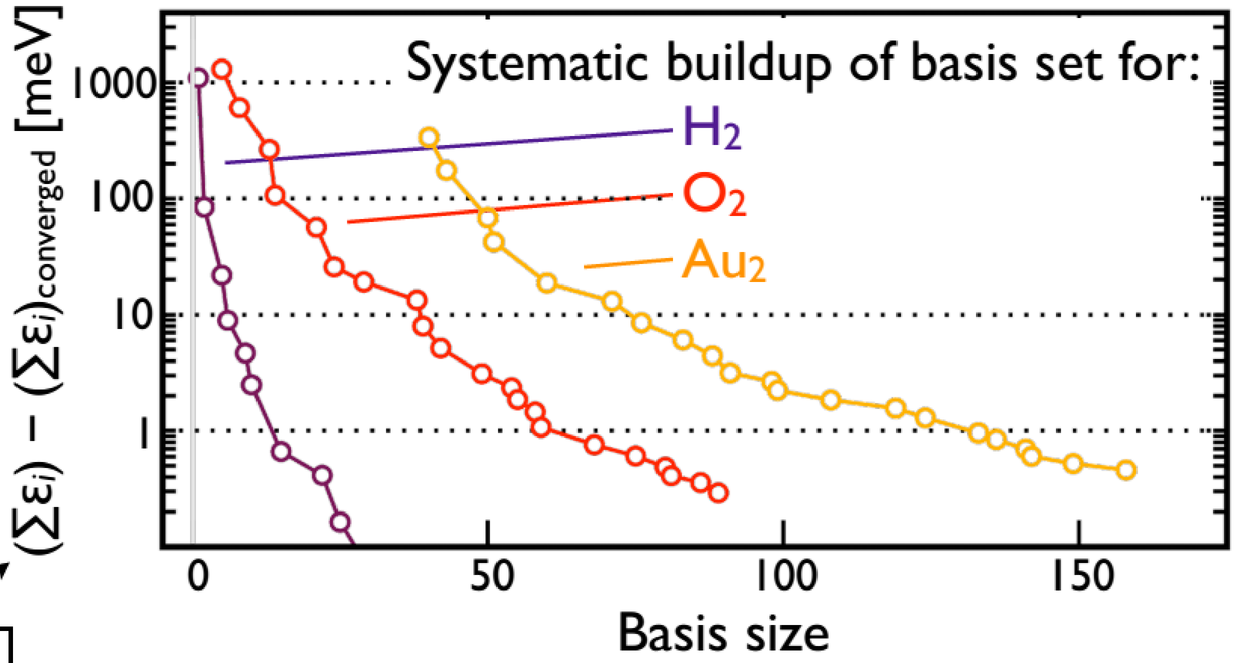
until $E^{(n-1)} - E^{(n)} <$ threshold

The basis set

<u>"Pool" of trial basis functions:</u>
2+ ionic *u(r)*
Hydrogen-like *u(r)* for *z*=0.1-20

<u>Optimization target:</u>
Non-selfconsistent symmetric dimers, averaged for different *d*

Pick basis functions one by one, up to complete *total energy* convergence



Remaining basis set error

Blum et al., Comp. Phys. Commun. ***180****, 2175-2196 (2009)*

The basis set

Systematic hierarchy of basis (sub)sets, iterative *automated* construction based on *dimers*

	H	C	O	Au
minimal	1s	[He]+2s2p	[He]+2s2p	[Xe]+6s5d4f
Tier 1	H(2s,2.1)	H(2p,1.7)	H(2p,1.8)	Au^{2+}(6p)
	H(2p,3.5)	H(3d,6.0)	H(3d,7.6)	H(4f,7.4)
		H(2s,4.9)	H(3s,6.4)	Au^{2+}(6s)
				H(5g,10)
				H(6h,12.8)
				H(3d,2.5)
Tier 2	H(1s,0.85)	H(4f,9.8)	H(4f,11.6)	H(5f,14.8)
	H(2p,3.7)	H(3p,5.2)	H(3p,6.2)	H(4d,3.9)
	H(2s,1.2)	H(3s,4.3)	H(3d,5.6)	H(3p,3.3)
	H(3d,7.0)	H(5g,14.4)	H(5g,17.6)	H(1s,0.45)
		H(3d,6.2)	H(1s,0.75)	H(5g,16.4)
				H(6h,13.6)
Tier 3	H(4f,11.2)	H(2p,5.6)	O^{2+}(2p)	H(4f,5.2)*
	H(3p,4.8)	H(2s,1.4)	H(4f,10.8)	H(4d,5.0)
	…	…	…	…

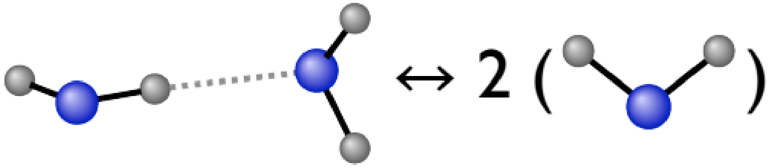
"First *tier* (level)"

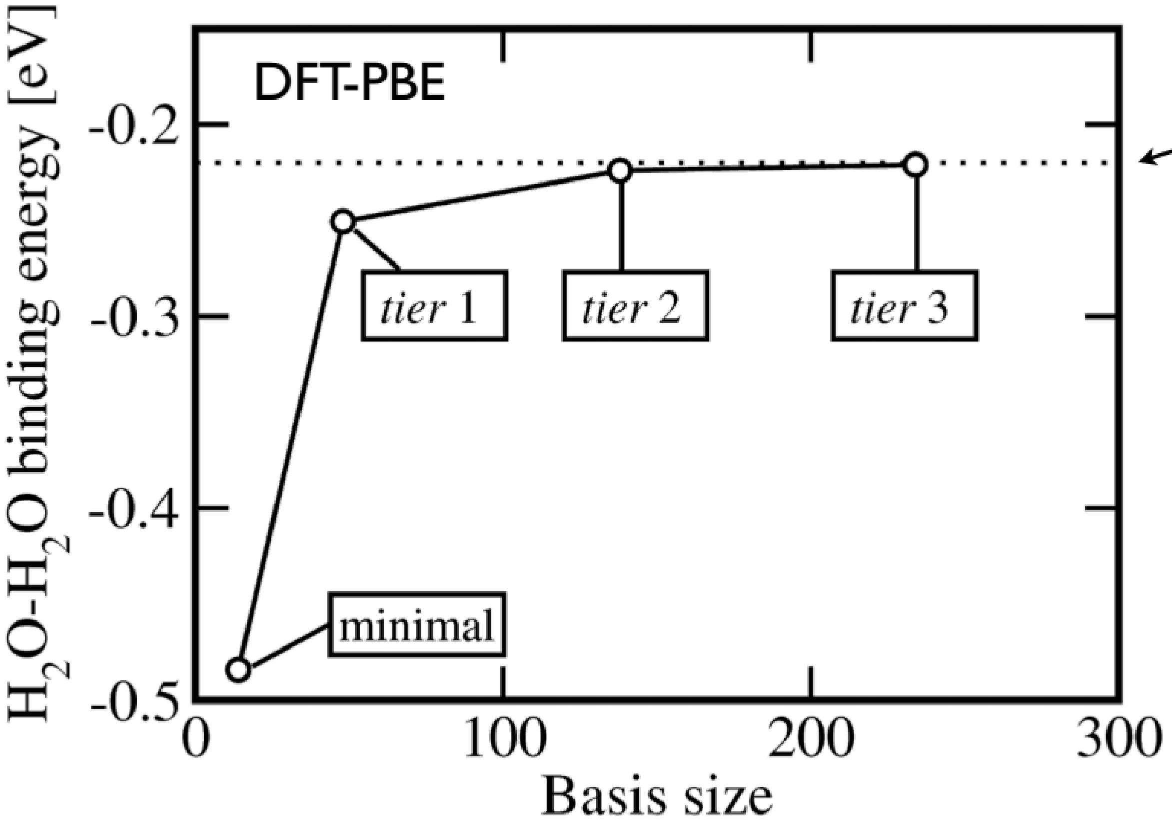
"Second *tier*"

"Third *tier*"

…

The basis set





Basis set limit (independent):
$E_{\mathrm{Hb}} = -219.8$ meV

Basis sets: Radial fn. character

	H	C,N,O
minimal	1s	[He]+2s2p
tier 1	*s,p*	*s,p,d*
tier 2	*s,p,s,d*	*s,p,d,f,g*
tier 3	*s,p,d,f*	*s,p,d,f*

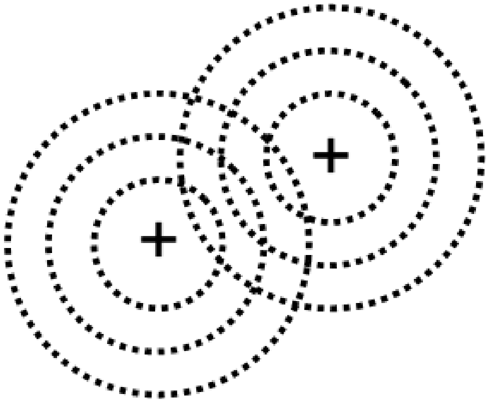
The basis set: additional parameters to converge

$$\boxed{h_{ij} = \int d^3r \varphi_i(\boldsymbol{r}) \hat{h}_{\mathrm{KS}} \varphi_j(\boldsymbol{r})}$$

- *Discretize* to integration grid: $\int d^3r f(\boldsymbol{r}) \rightarrow \sum_{\boldsymbol{r}} w(\boldsymbol{r}) f(\boldsymbol{r})$

... but even-spaced integration grids are *out*:
f(*r*) strongly peaked near all nuclei!

- Overlapping atom-centered integration grids:
  - Radial *shells (e.g., H, light: 24; Au, tight: 147)*
  - *Specific* angular point distribution ("Lebedev") exact up to given integration order l *(50, 110, 194, 302, ... points per shell)*



Pioneered by
Becke JCP 88, 2547 (1988), Delley, JCP 92, 508 (1990), MANY others!

Electronic structure methods

Quantum chemistry & many-body theory:

$$\boxed{\hat{\mathcal{H}}\Psi = E\Psi}$$

... successive refinement of ψ

Density functional theory: *(Hohenberg-Kohn 1964, Kohn-Sham 1965)*

$$\boxed{E_{\mathrm{tot}} = E[n(r)] = T_s[n] + V[n] + V_{\mathrm{es}}[n] + E_{\mathrm{xc}}[n]}$$

"Perdew's ladder" to exact solution

- Key practical approximation: E_{xc}

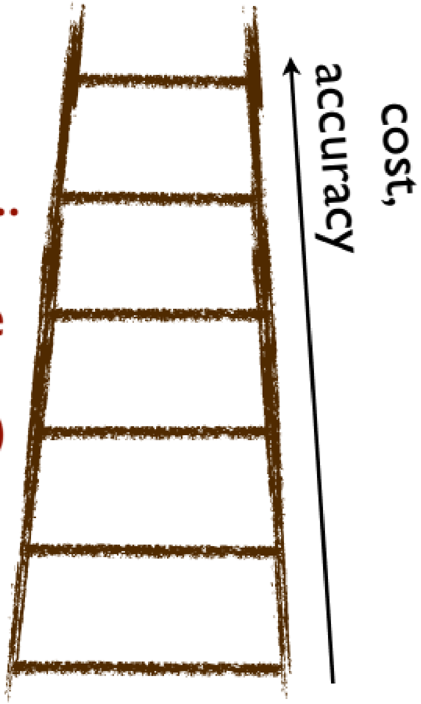
response / many-body terms: RPA, SOSEX, ...

hybrid functionals: non-local exchange

meta-GGAs: $\nabla^2 n(r), \nabla^2 \varphi(r)$

Generalized gradient approximations (GGAs): $|\nabla n(r)|$

Local-density approximation (LDA): $n(r)$



Part I: atom and molecule

Problem I: 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

```
# 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

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
...
```

Default basis sets

.../species_defaults

Predefined species
Copy-paste into control.in

- light
- tight
- really tight

Increased accuracy:

Basis
Hartree potential
Basis cutoff potential
Integration grids

Default basis sets

…/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

Default basis sets

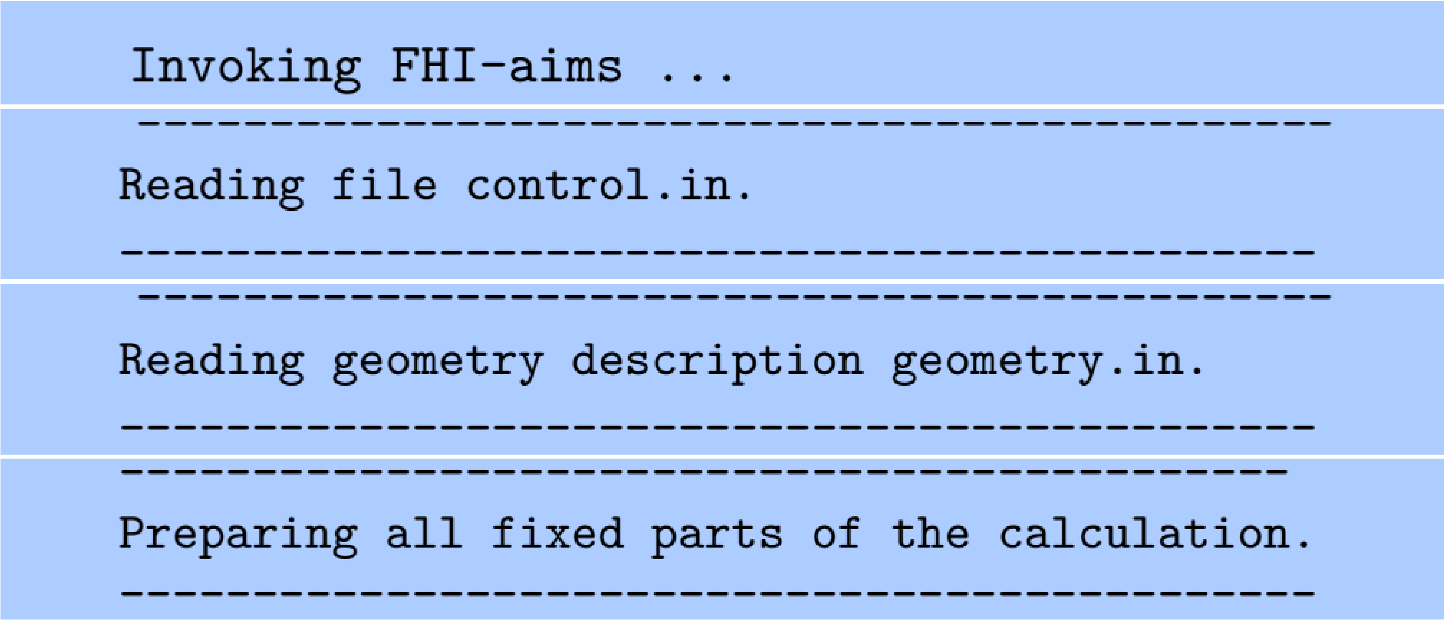
…/species_defaults

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 “tiers”

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

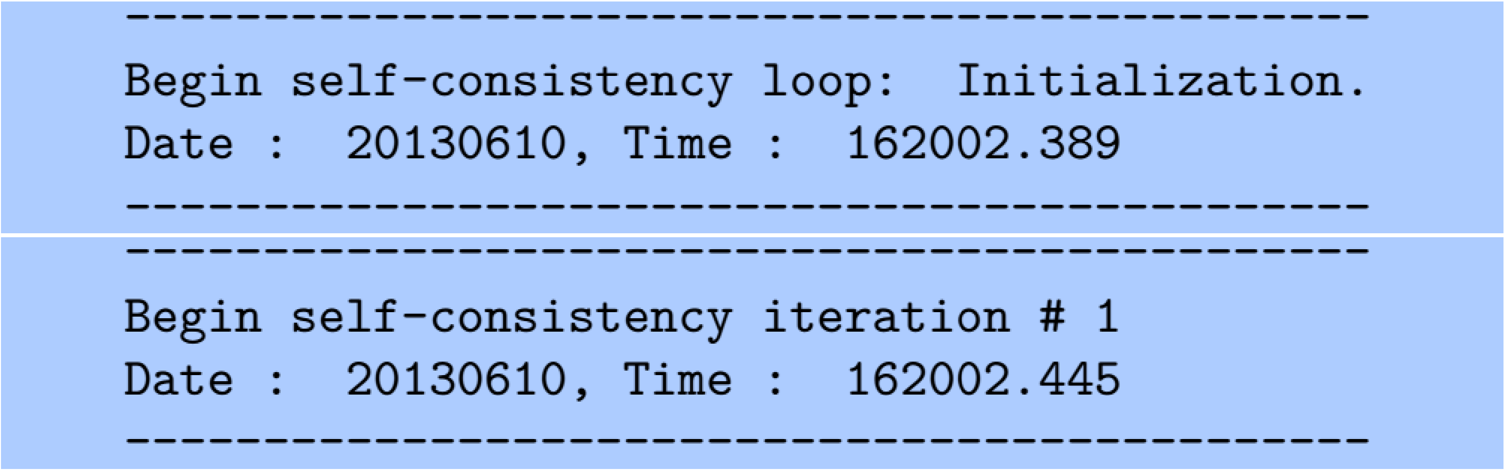
» Energy

THIS TUTORIAL →

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

Periodic metals only

FHI-aims output

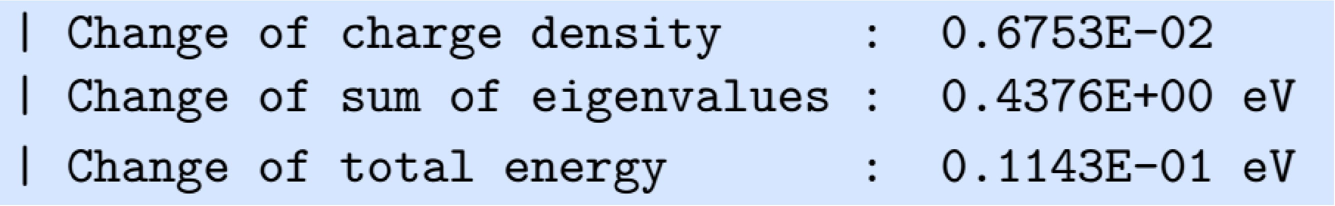


5
```
  ------------------------------------------------------------
  Begin self-consistency loop:  Initialization.
  Date :  20130610, Time :  162002.389
  ------------------------------------------------------------
```

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 # 1
  Date :  20130610, Time :  162002.445
  ------------------------------------------------------------
```

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.
```

» 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

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-III: H_2

Tasks:

- Learn how to optimize geometry with FHI-aims.
- Calculate relative energies of different spin states.
- Calculate the atomization energy (ΔH_{at}).
- See how geometry and atomization energy depend on the exchange-correlation functional.

Problem II-III: H_2

From now on, run FHI-aims via the batch system:

1) copy the file job.sh from the tutorial folder to your working directory

2) submit a job:

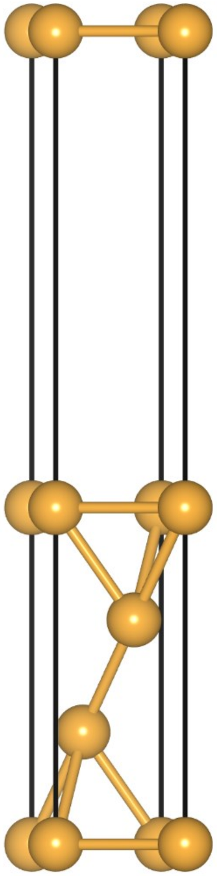
```
sbatch --ntasks=XX job.sh
```

3) To see the progress, type

```
tail   -f   output
```

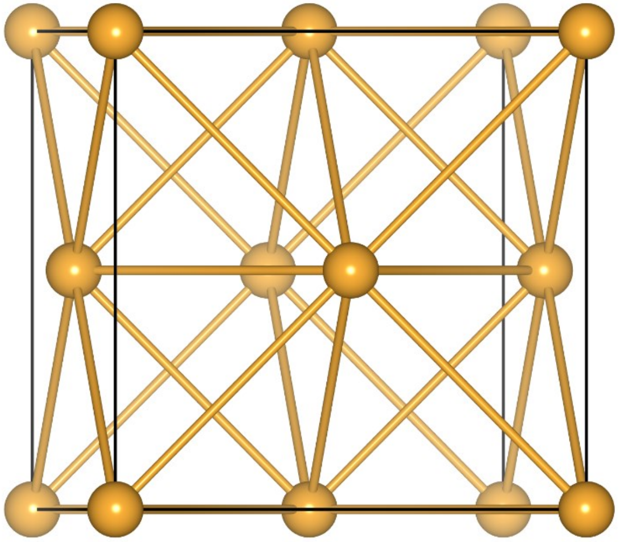
Part II: periodic system

surface



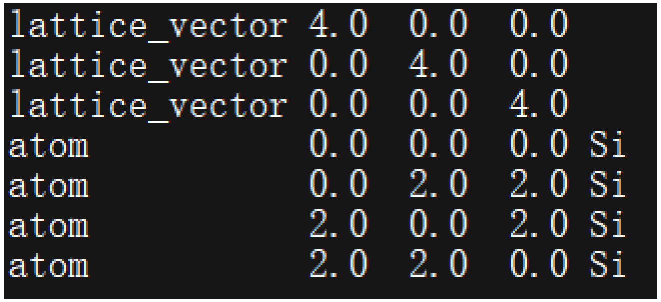
fcc(111)

bulk



fcc

geometry.in



```
lattice_vector 4.0  0.0  0.0
lattice_vector 0.0  4.0  0.0
lattice_vector 0.0  0.0  4.0
atom           0.0  0.0  0.0 Si
atom           0.0  2.0  2.0 Si
atom           2.0  0.0  2.0 Si
atom           2.0  2.0  0.0 Si
```

Important practical points

- Each calculation one directory, for example

```
> mkdir tutorial1
> cd tutorial1
> mkdir O2
```

- 2 input files (plus 1 for pseudopotential embedding)

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

- Launching FHI-aims calculation

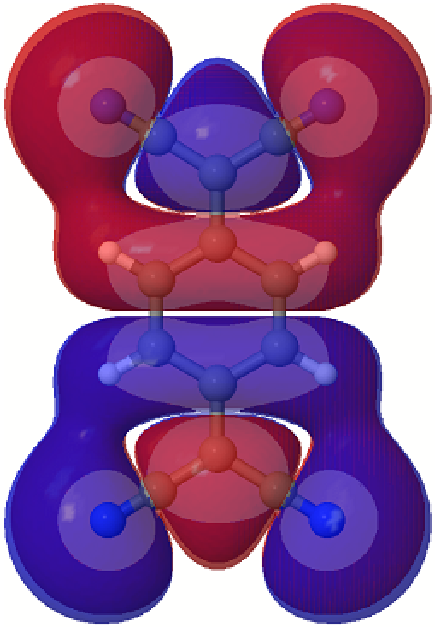
```
sbatch --ntasks=XX job.sh
```

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
```

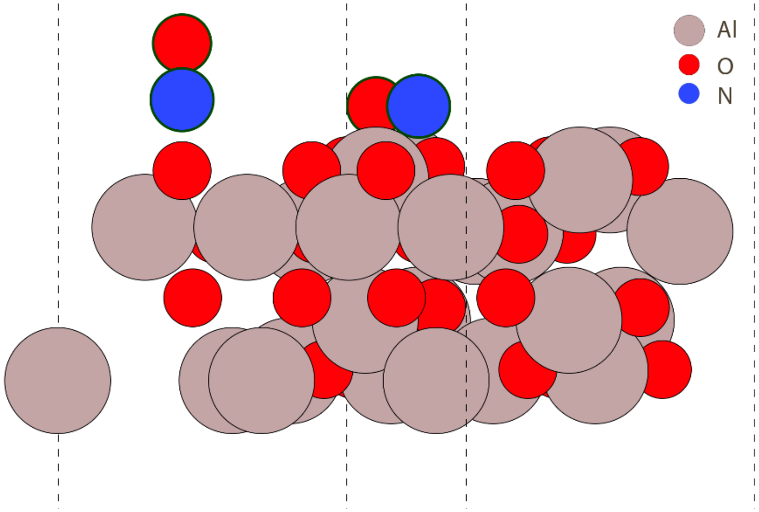


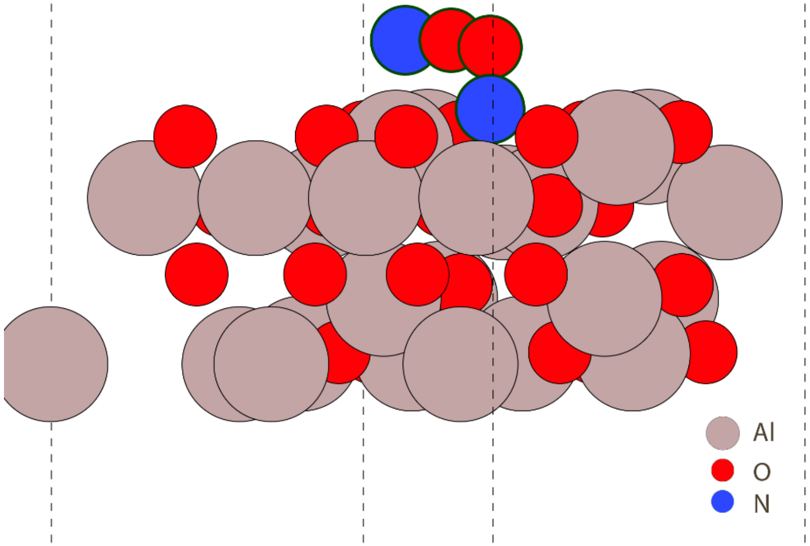
Get: *.cube file - values on a regular 3D grid.

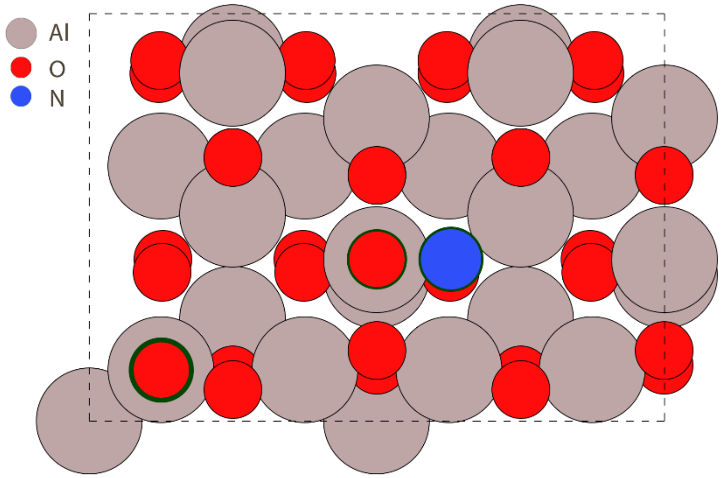
Software: jmol

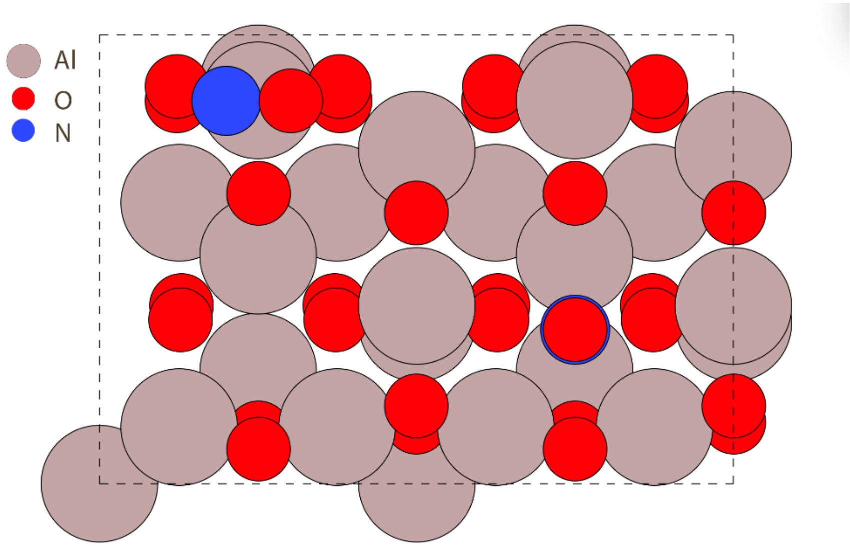
⇒ Appendix of handout

Lab 2: Calculate phase diagram of γ-Al_2O_3 (110) surface in NO atmosphere









Lab 2: Calculate phase diagram of γ-Al_2O_3 (110) surface in NO atmosphere

Both team and individual work

1) Relax NO molecule (team)
2) Construct surface slab model from bulk (team)
3) Place NO at the surface in three different configurations and *different* coverages for each student (overall 27 structures) (team)
4) Distribute the structures among students evenly (3 each) (team)
5) Test convergence of NO adsorption energy as a function of the number of relaxed bottom layers for one structure (individual)
6) Choose the optimal number of relaxed layers (team)
7) Relax the structures, report the energy, discuss the difference between starting and final geometries, calculate, report, and discuss work function (individual)
8) Build a surface phase diagram in NO atmosphere combining all obtained energies (team)