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

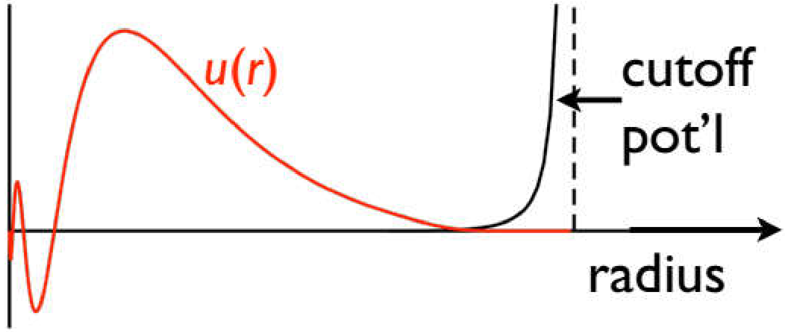
$$\boxed{\varphi_{i[lm]}(\boldsymbol{r}) = \frac{u_i(r)}{r}\cdot Y_{lm}(\Omega)}$$

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

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

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

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



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DMol^3 (Delley), FPLO (Eschrig *et al.*), PLATO (Horsfield *et al.*), PAOs (Siesta, Conquest, OpenMX^2, Fireball, ...)

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

→ Localized; "naturally" all-electron

→ The choice of <u>efficient</u> and of <u>enough</u> 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 - <u>efficient and accurate approach</u>

V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler,
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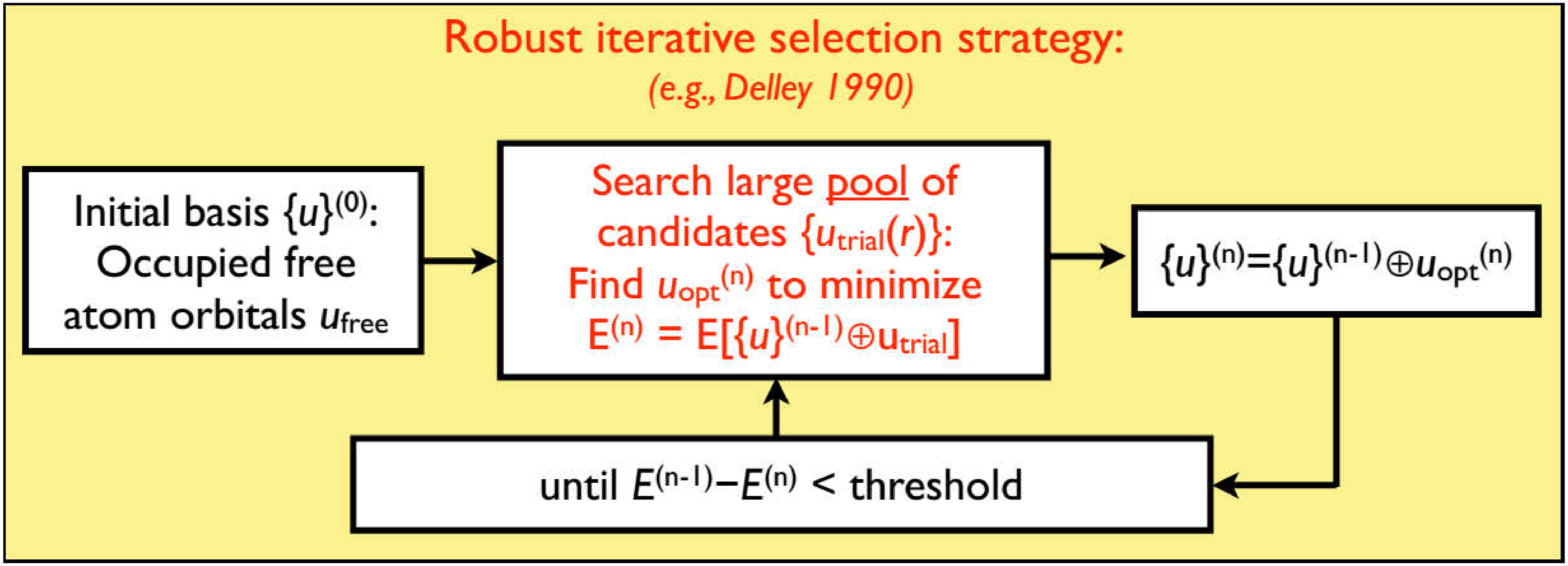
The basis set



Robust iterative selection strategy:

(e.g., Delley 1990)

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

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

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

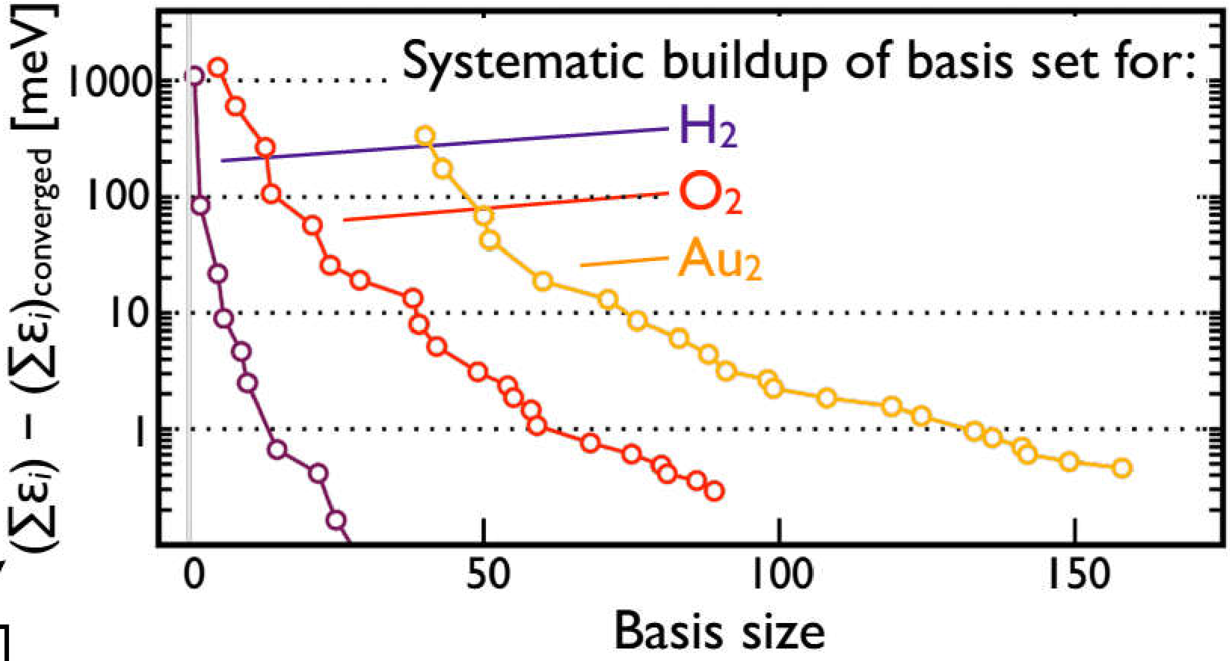
until $E^{(n-1)} - E^{(n)} <$ threshold

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

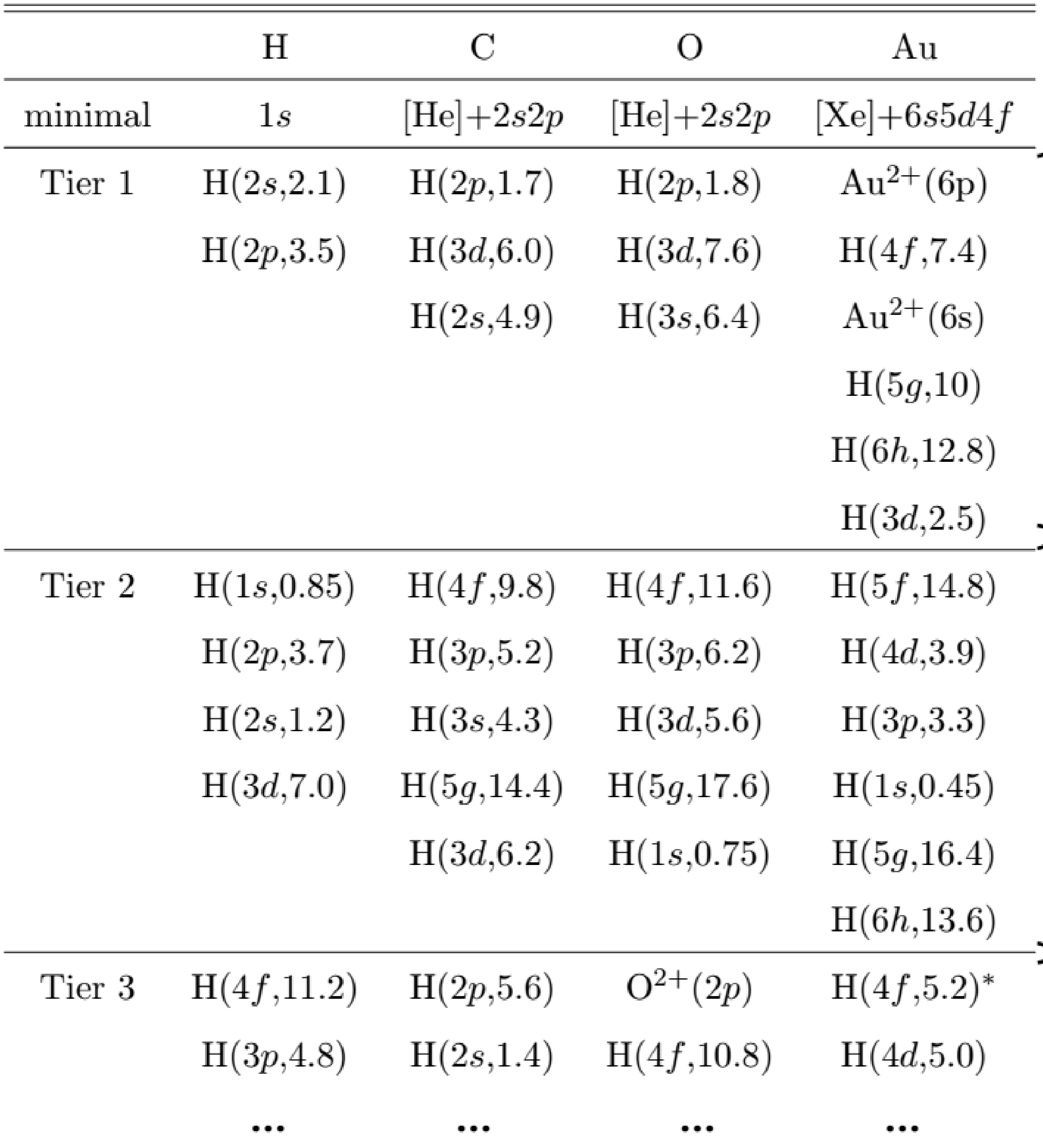


Remaining basis set error

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)
	…	…	…	…

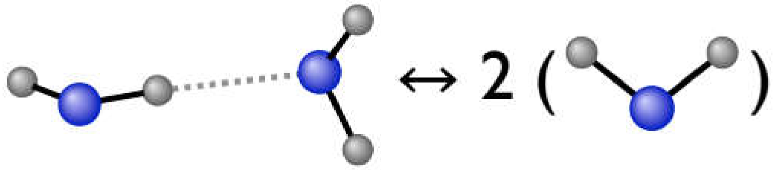
"First *tier* (level)"

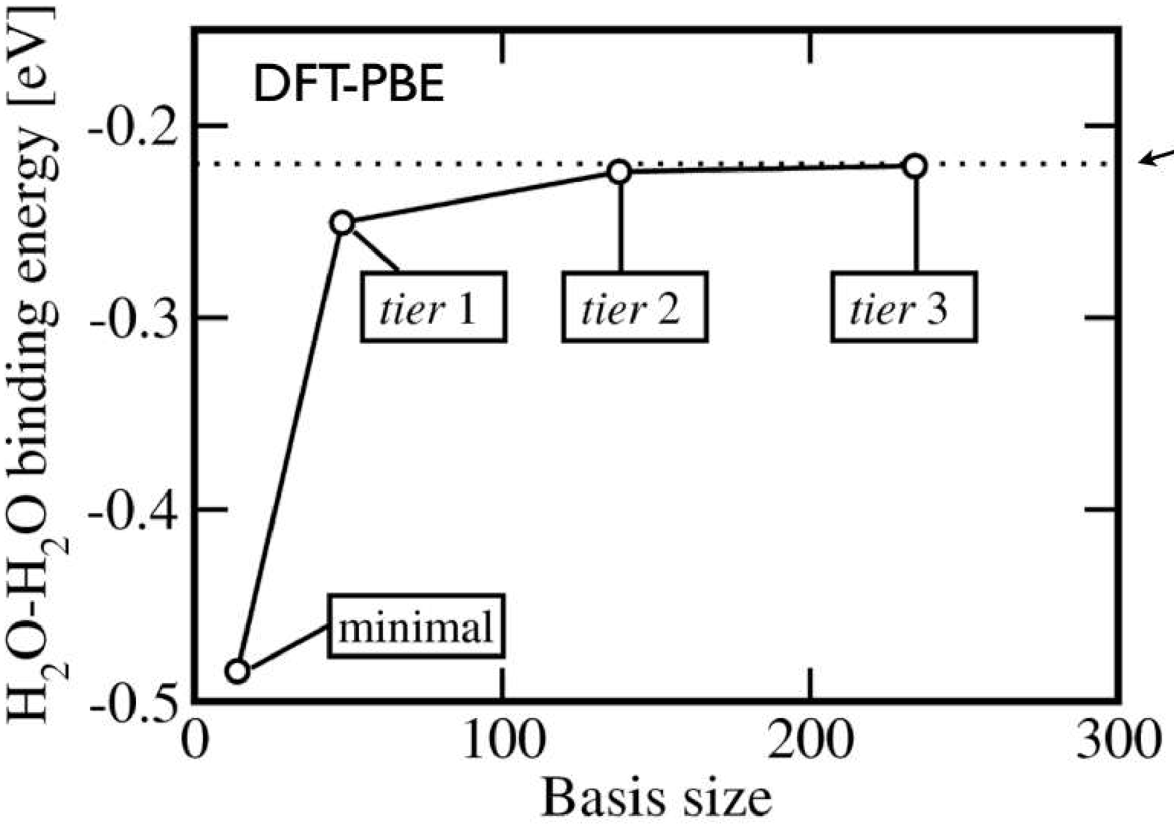
"Second *tier*"

"Third *tier*"

…

The basis set





Basis set limit (independent):
$E_{Hb} = -219.8$ 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*

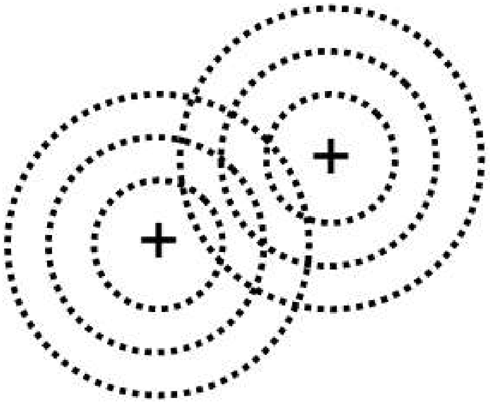
The basis set: additional parameters to converge

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

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

... 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:

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

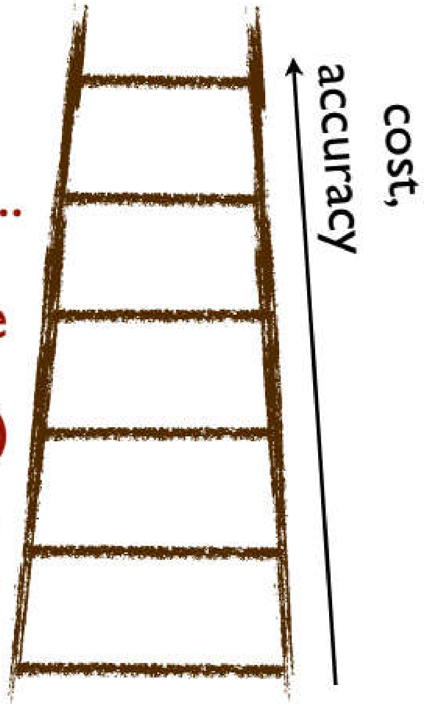
... successive refinement of ψ

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

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

"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): $n(r)$

Standard DFT and the self-interaction error

$$E_{\text{tot}} = T[n] - \sum_{I=1}^{M} Z_I \int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_I|} d^3r + \frac{1}{2}\sum_{I=1}^{M}\sum_{J=1}^{M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' + E_{\text{XC}}[n]$$

$n(\mathbf{r})$ -- electron density

(includes self-interaction)

exchange-correlation (XC) energy

LDA, GGA, meta-GGA: $E_{\text{XC}}[n] = E_{\text{X}}^{\text{loc}}[n] + E_{\text{C}}^{\text{loc}}[n]$

Standard DFT: (Semi)local XC operator → low computational cost

Removing self-interaction + preserving fundamental properties (e.g., invariance with respect to subspace rotations) is non-trivial → residual self-interaction (error) in standard DFT

Consequences of self-interaction (no cancellation of errors): localization/delocalization errors, incorrect level alignment (charge transfer, reactivity, etc.)

The Hartree-Fock (HF) approximation

$$\Psi\left(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N\right)=\frac{1}{\sqrt{N!}}\det\left|\psi_1(\mathbf{r}_1,\sigma_1),\ldots,\psi_N(\mathbf{r}_N,\sigma_N)\right|$$

one-particle states

$$E_{\text{tot}}=\sum_{n=1}^{N}\left\langle\psi_n\right|\hat{h}\left|\psi_n\right\rangle+\frac{1}{2}\sum_{I=1}^{M}\sum_{J=1}^{M}\frac{Z_IZ_J}{\left|\mathbf{R}_I-\mathbf{R}_J\right|}+\frac{1}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|}d^3r\,d^3r'-$$

$$-\frac{1}{2}\sum_{m,n=1}^{N}\int\frac{\psi_m^*(\mathbf{r},\sigma)\psi_n^*(\mathbf{r}',\sigma')\psi_n(\mathbf{r},\sigma)\psi_m(\mathbf{r}',\sigma')}{\left|\mathbf{r}-\mathbf{r}'\right|}d^3r\,d^3r'\,d\sigma\,d\sigma'$$

HF (exact) exchange energy

- No self-interaction
- Coulomb mean-field → no dynamic correlation, single determinant → no static correlation

Hybrid DFT

$$E_{\mathrm{XC}}[\{\psi\}] = \alpha E_{\mathrm{X}}^{\mathrm{HF}}[\{\psi\}] + (1-\alpha) E_{\mathrm{X}}^{\mathrm{loc}}[n] + E_{\mathrm{C}}^{\mathrm{loc}}[n]$$

-- easy in Kohn-Sham formalism ($n = \sum_n f_n |\psi_n|^2$)

Perdew, Ernzerhof, Burke (J. Chem. Phys. 105, 9982 (1996)): α = 1/*N*

MP4 → *N* = 4, but "An ideal hybrid would be sophisticated enough to optimize *N* for each system and property."

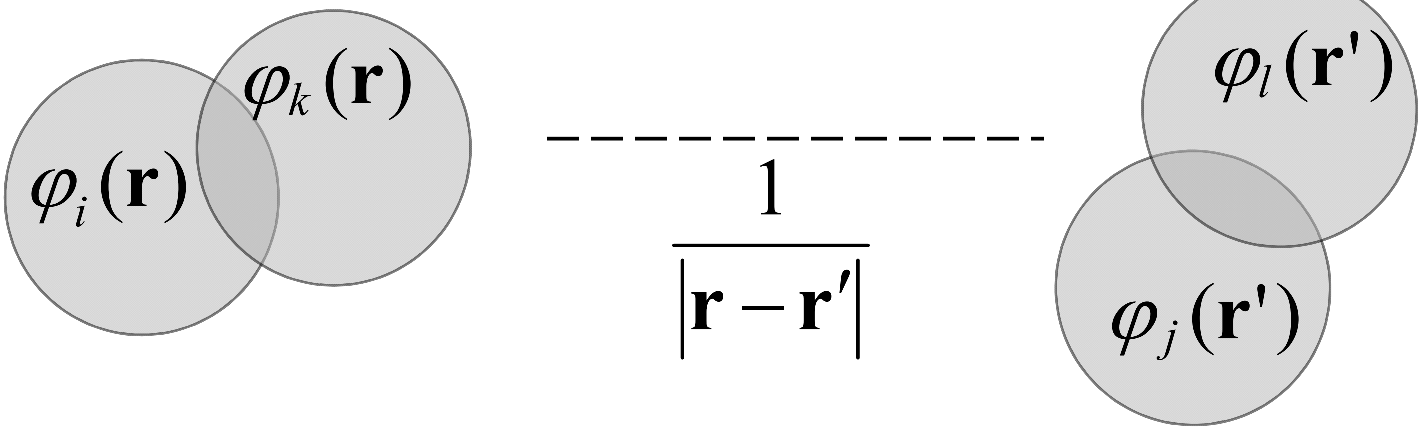
Range-separated functionals: HSE family

$$\frac{1}{r} = \underbrace{\frac{1-\mathrm{erf}(\omega r)}{r}}_{\text{short-range (SR)}} + \underbrace{\frac{\mathrm{erf}(\omega r)}{r}}_{\text{long-range (LR)}}$$

$$E_{\mathrm{XC}}^{\mathrm{HSE}} = \alpha E_{\mathrm{X}}^{\mathrm{HF,SR}}(\omega) + (1-\alpha) E_{\mathrm{X}}^{\mathrm{PBE,SR}}(\omega) + E_{\mathrm{X}}^{\mathrm{PBE,LR}}(\omega) + E_{\mathrm{C}}^{\mathrm{PBE}}$$

Hartree-Fock exchange – the problem

$$E_{\mathrm{X}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{i,j,k,l} D_{il} D_{jk} \underbrace{\int \frac{\varphi_i(\mathbf{r})\varphi_k(\mathbf{r})\varphi_j(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r\, d^3r'}_{\text{electron repulsion integrals}}$$



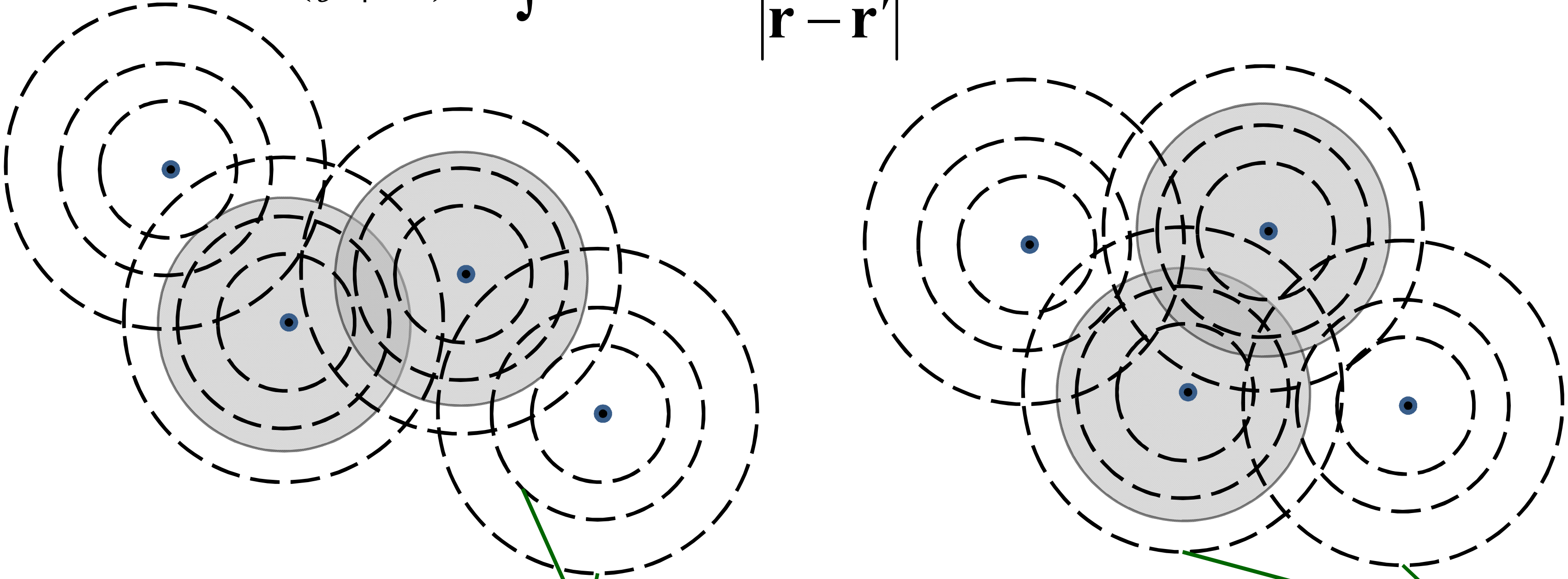
Lots of integrals, naïve implementation → N^4 scaling (storage impractical for N > 500 basis functions)

⇓

- **need fast evaluation**
- **need efficient use of sparsity (screening)**

“Resolution of identity” (RI) (density fitting)

$$(ij\,|\,kl) = \int \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})\varphi_k(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3r\,d^3r'$$

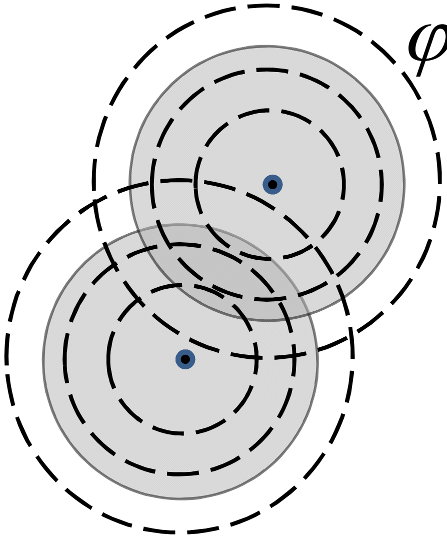


$$\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) = \sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r}) \qquad \varphi_k(\mathbf{r})\varphi_l(\mathbf{r}) = \sum_{\mu} C_{kl}^{\mu} P_{\mu}(\mathbf{r})$$

independent auxiliary basis

Basis-pair space is overcomplete, since $\{\varphi_i(\mathbf{r})\}$ approaches completeness → size of $\{P_{\mu}(\mathbf{r})\}$ ~4-5 times size of $\{\varphi_i(\mathbf{r})\}$

Localized RI-V (RI-LVL, Jürgen Wieferink)

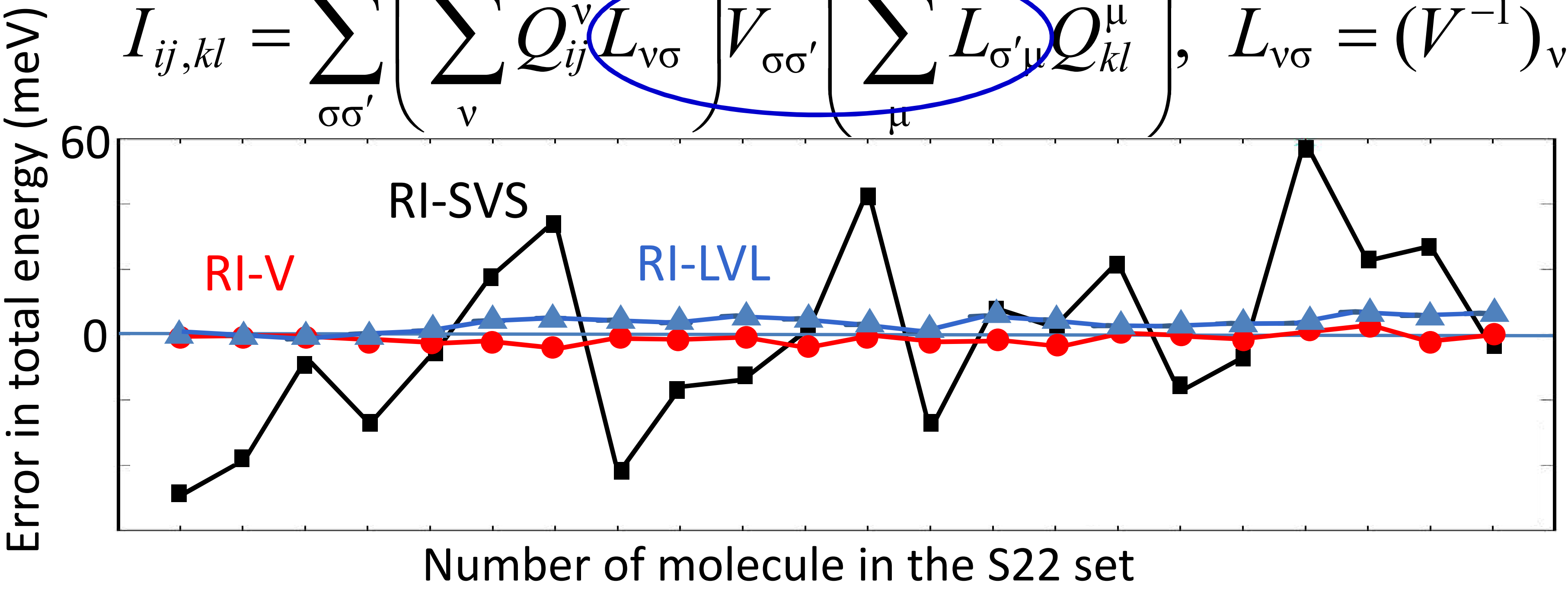


$$\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \approx \sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r}), \quad \mu \in \text{atom}(i) \text{ or atom}(j)$$

$$\Delta(\delta\rho_{ij}^2) \rightarrow \min \quad \Rightarrow \quad \Delta(\delta\rho_{ij}) \rightarrow 0$$

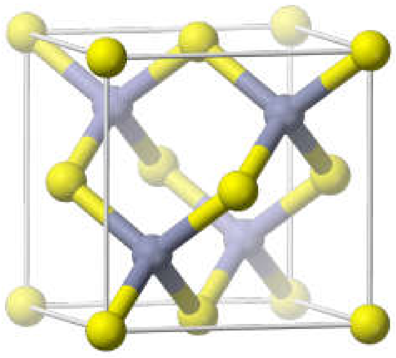
local inverse Coulomb matrix

$$I_{ij,kl} = \sum_{\sigma\sigma'} \left(\sum_{\nu} Q_{ij}^{\nu} L_{\nu\sigma} \right) V_{\sigma\sigma'} \left(\sum_{\mu} L_{\sigma'\mu} Q_{kl}^{\mu} \right), \quad L_{\nu\sigma} = (V^{-1})_{\nu\sigma}$$

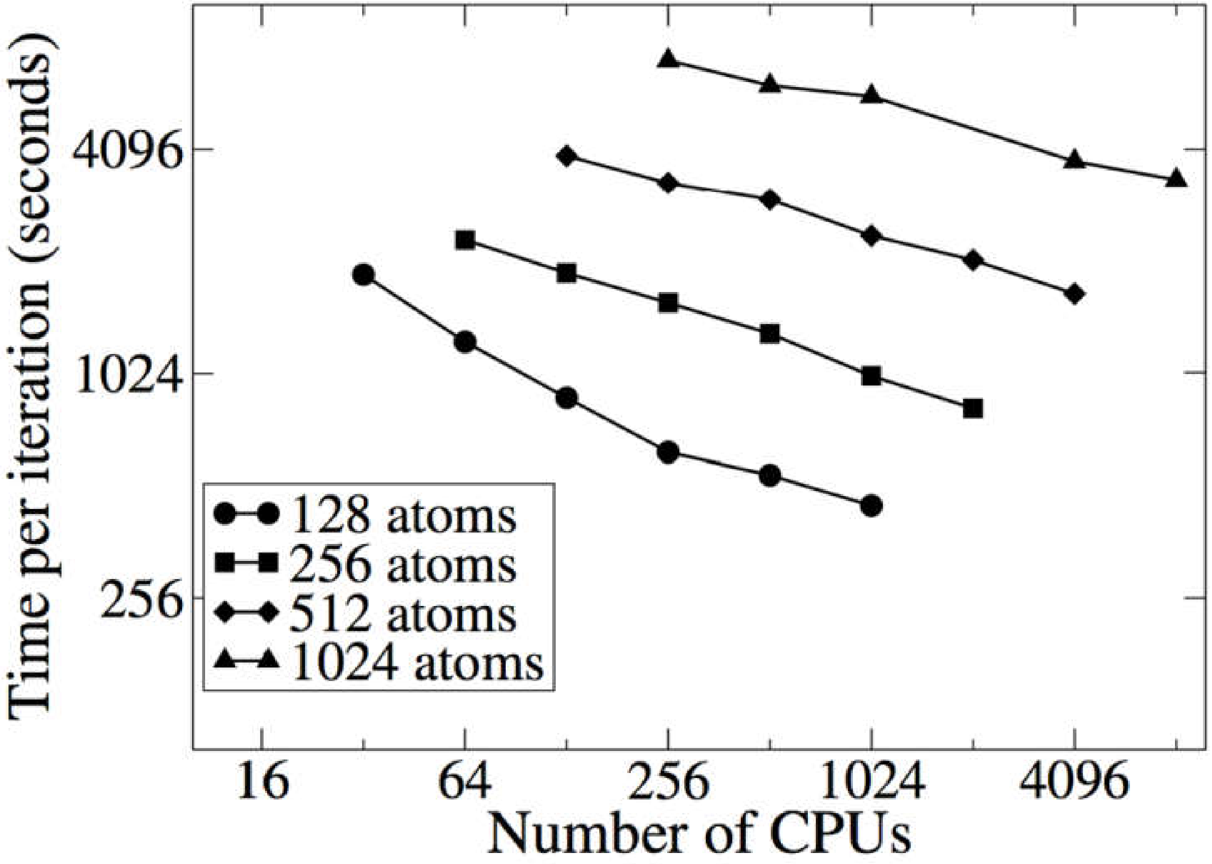


Hybrid functionals in FHI-aims

Computational Scaling of Periodic GaAs, HSE06 Hybrid Functional, with Increasing System Size

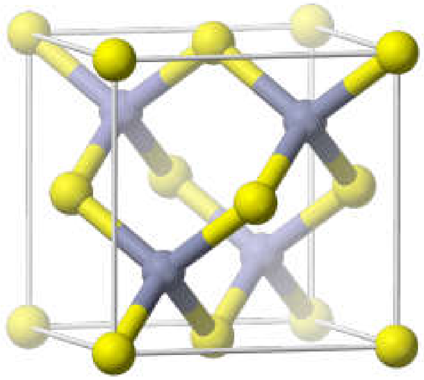


Zincblende GaAs



Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler, Comp. Phys. Commun. ***192****, 60-69 (2015).*

Hybrid functionals in FHI-aims



Zincblende GaAs

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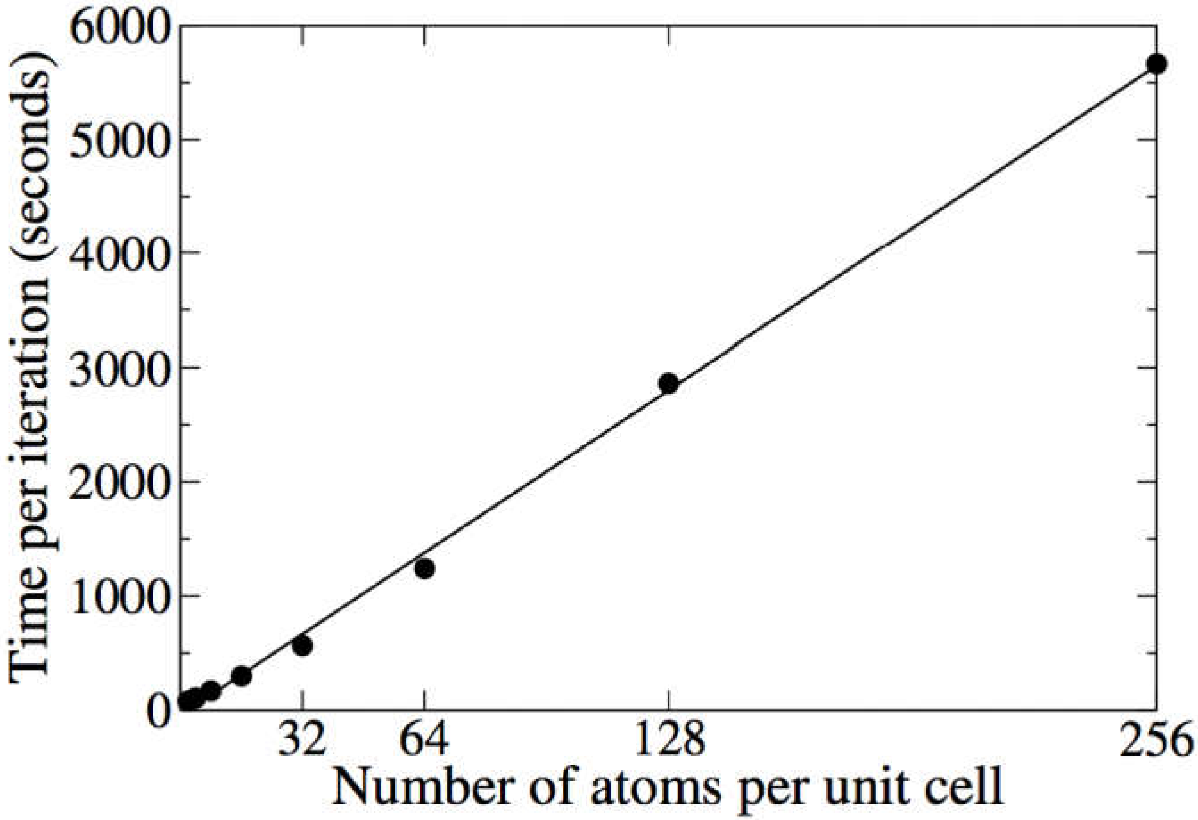


Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler,
Comp. Phys. Commun. ***192****, 60-69 (2015).*

Practicalities

```
mkdir your_name
```

Important to make different directories! Otherwise you will overwrite other’s files

```
cd your_name
```

Copy the folder tutorial_2 from $HandsOn to your working directory:

For every exercise, the sample input files and solutions can be found in $HandsOn/tutorial_2/skel/exercise_XX/templates and $HandsOn/tutorial_2/solutions, respectively.

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

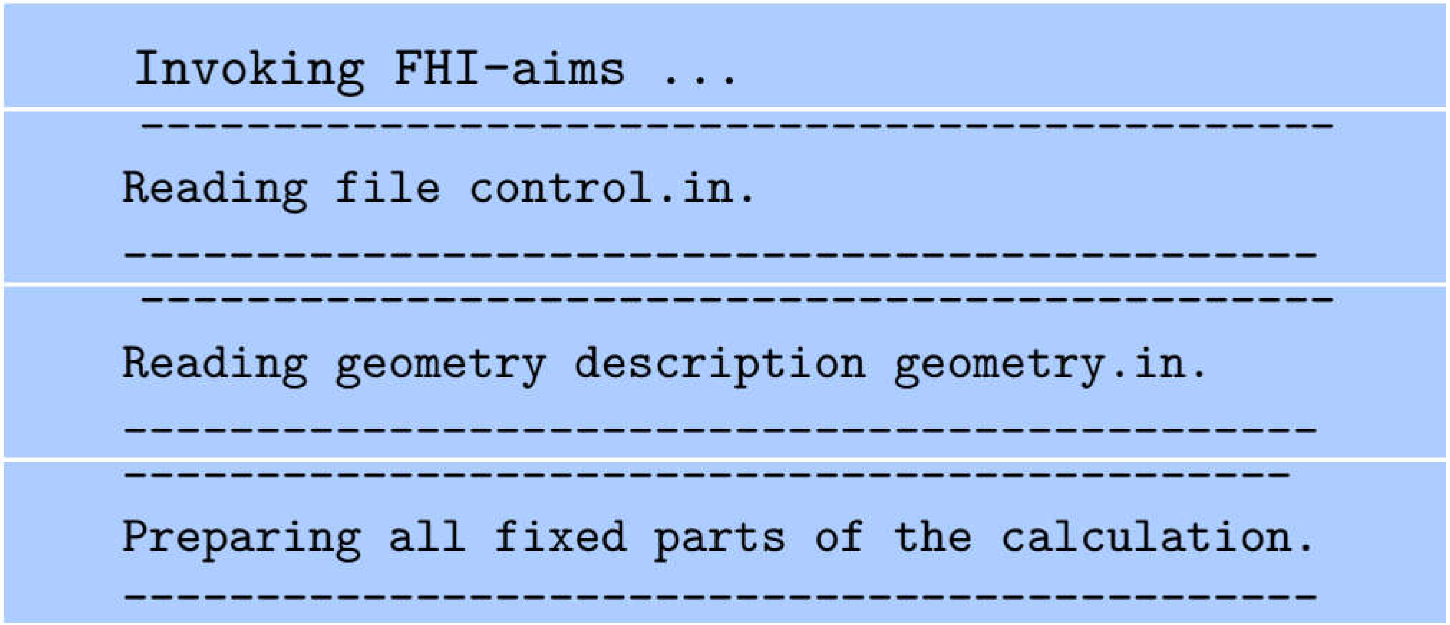
…/species_defaults

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

THIS TUTORIAL

» Energy

```
| 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:

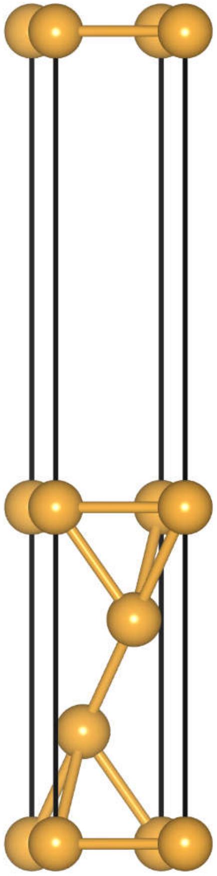
```
sbatch --ntasks=XX job.sh
```

3) To see the progress, type

```
tail   -f   output
```

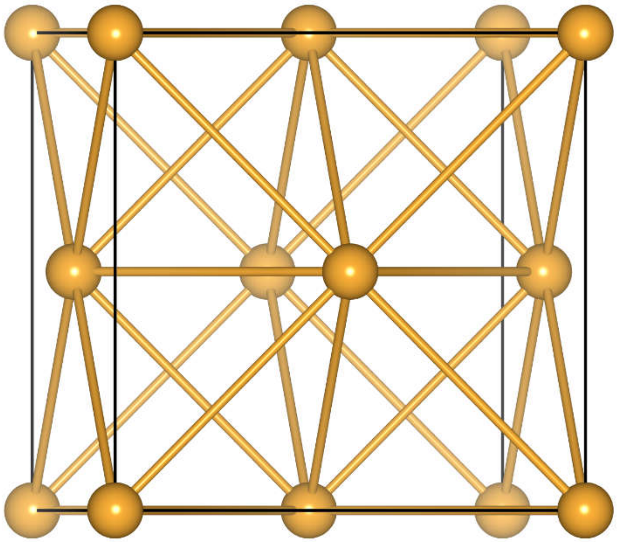
Part II: periodic system

surface



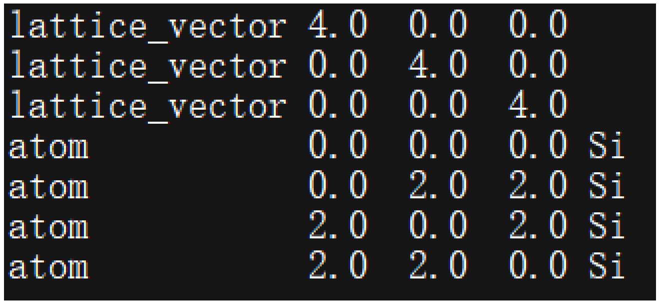
fcc(111)

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**

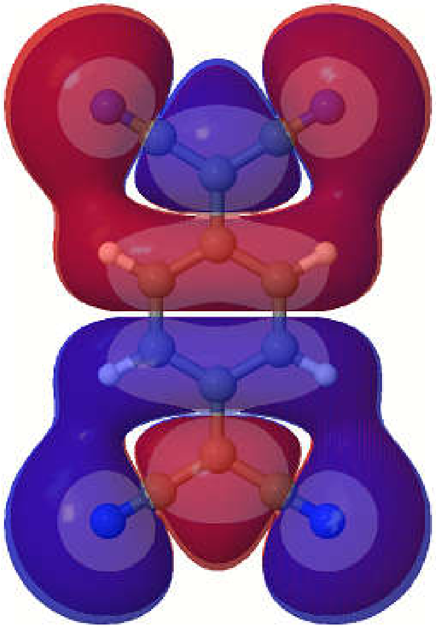
```
sbatch --ntasks=XX job.sh
```

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