FHI-aims capabilities
for molecules, clusters, and solids

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FHI-aims

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)
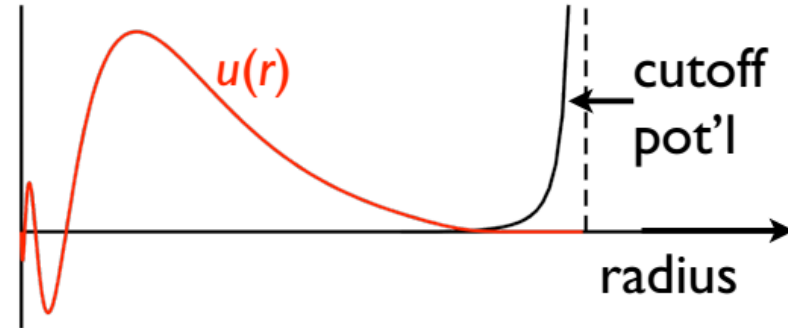
The basis set: Numeric atomic orbitals

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

Many popular implementations:
DMol³ (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.), PAOs (Siesta, Conquest, OpenMX², Fireball, ...)

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

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

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

$u(r)$

cutoff pot'l

radius

The basis set: Numeric atomic orbitals

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Many popular implementations: DMol³ (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.), PAOs (Siesta, Conquest, OpenMX², Fireball, ...)

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

→ 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

The basis set
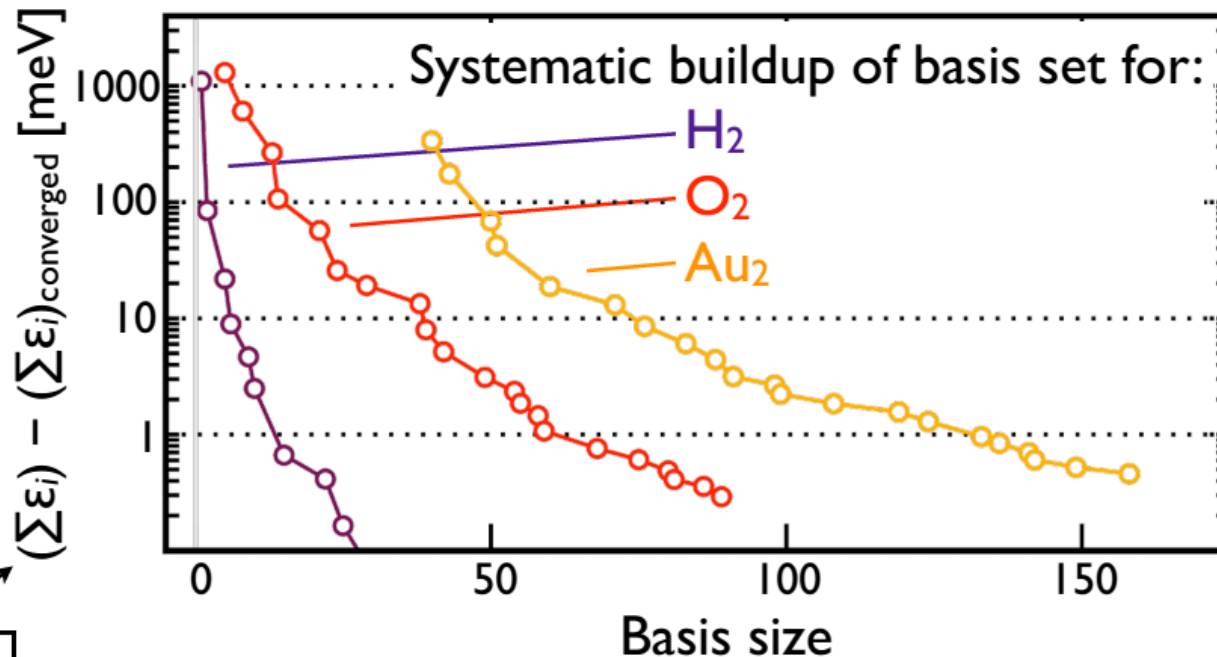
"Pool" of trial basis functions:
2+ ionic $u(r)$
Hydrogen-like $u(r)$ for z=0.1-20

Optimization target:
Non-selfconsistent symmetric
dimers, averaged for different d

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

Systematic buildup of basis set for:
H_2
O_2
Au_2

Remaining basis set error

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

The basis set

	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)
	...	...	...	...

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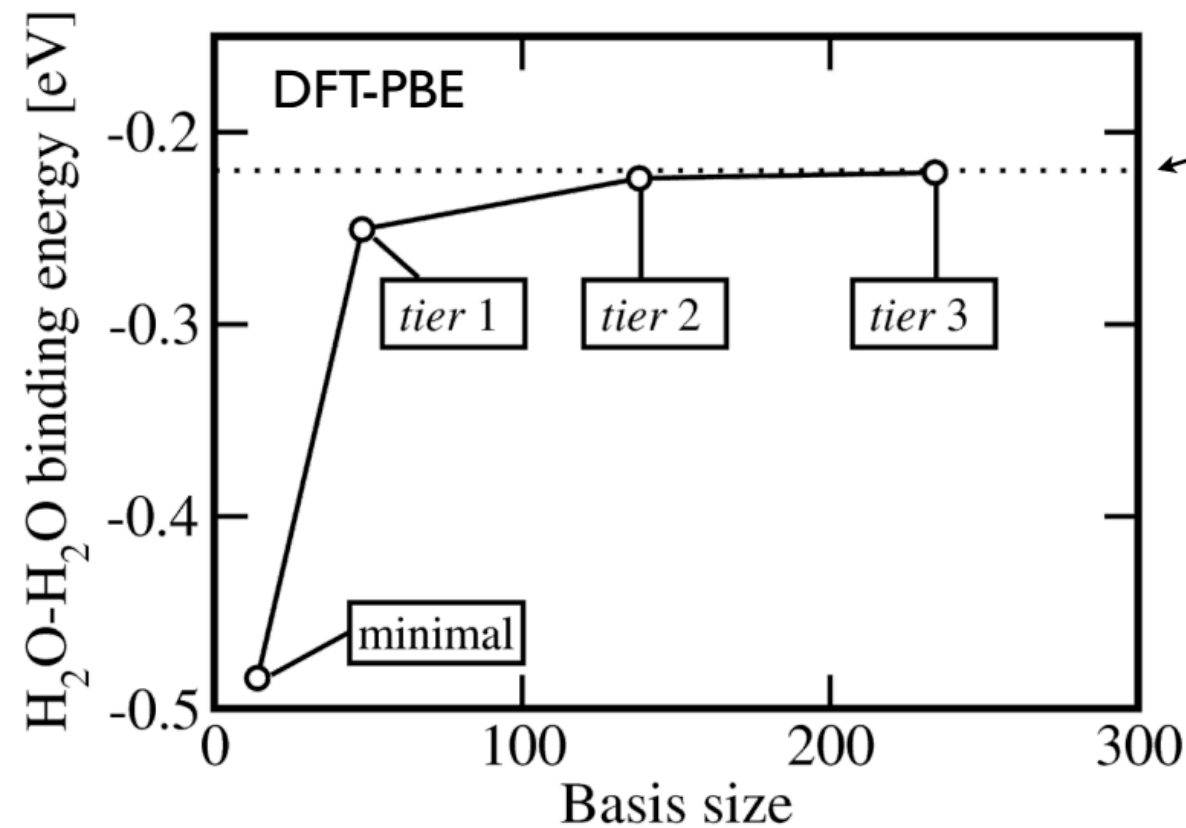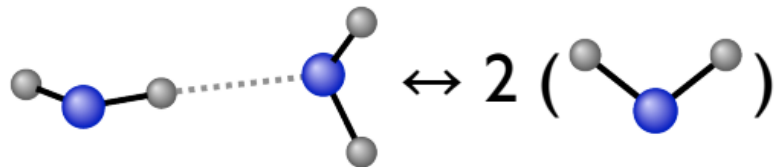
"First *tier* (level)"

"Second *tier*"

"Third *tier*"
...

The basis set

$$\leftrightarrow 2\ (\ \ )$$

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

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

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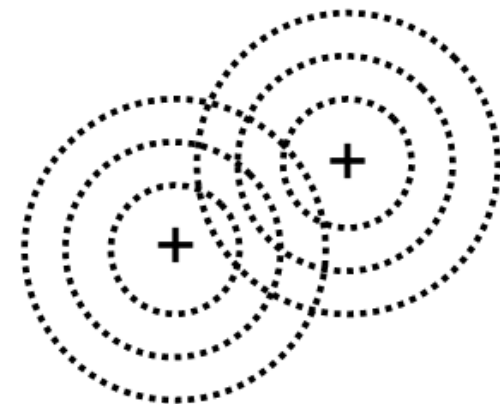
Pioneered by
Becke JCP 88, 2547 (1988), Delley, JCP 92, 508 (1990), MANY others!

Electronic structure methods

Quantum chemistry & many-body theory:

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

... successive refinement of Ψ

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

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

"Perdew's ladder" to exact solution
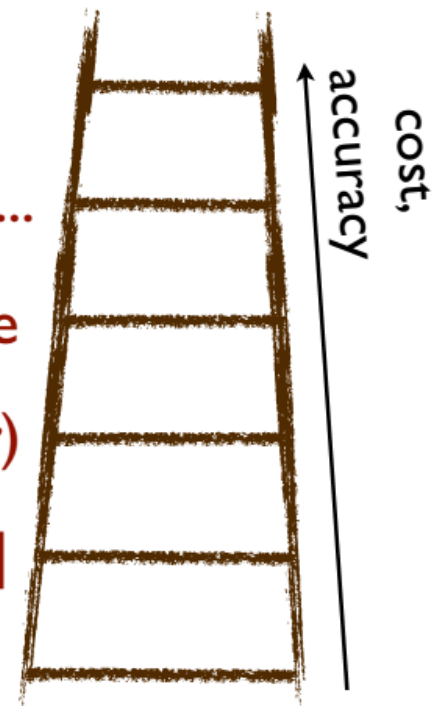
- Key practical approximation: E_{xc}

  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): $n(r)$

cost, accuracy →

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: $\quad E_{\text{XC}}[n] = E_{\text{X}}^{\text{loc}}[n] + E_{\text{C}}^{\text{loc}}[n]$

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

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

one-particle states

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

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

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."

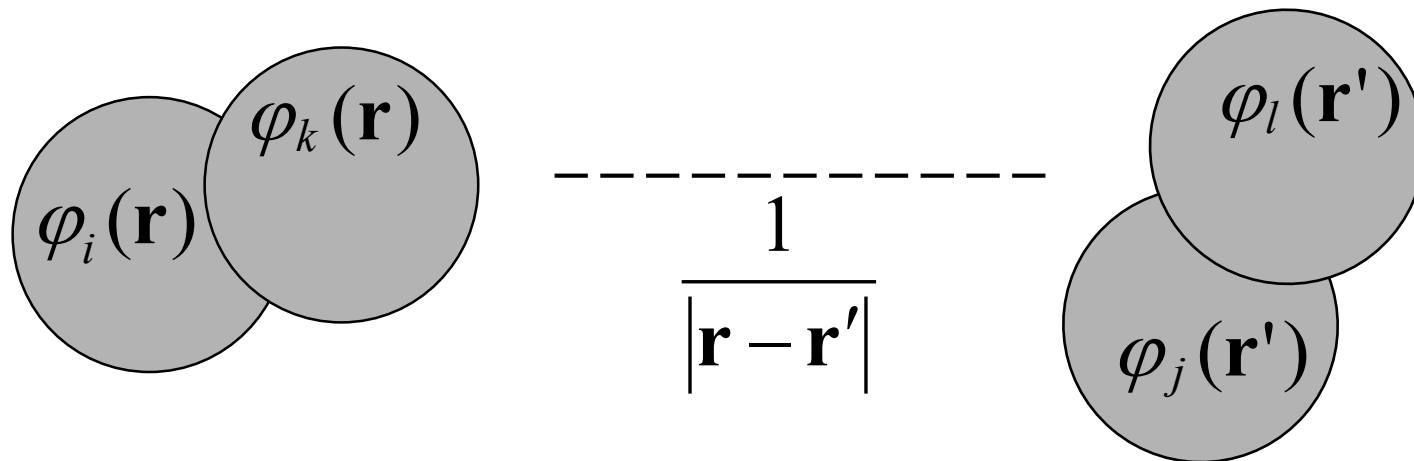**Range-separated functionals: HSE family**

$$\frac{1}{r} = \frac{1-\mathrm{erf}(\omega r)}{r} + \frac{\mathrm{erf}(\omega r)}{r}$$

short-range (SR)   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

$$E_X^{HF} = -\frac{1}{2} \sum_{i,j,k,l} D_{il} D_{jk} \int \frac{\varphi_i(\mathbf{r})\varphi_k(\mathbf{r})\varphi_j(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$

electron repulsion integrals

$$\varphi_i(\mathbf{r}) \quad \varphi_k(\mathbf{r}) \qquad ----------- \qquad \varphi_l(\mathbf{r}')$$

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} \qquad \varphi_j(\mathbf{r}')$$

Lots of integrals, naïve implementation → N^4 scaling (storage impractical for $N > 500$ basis functions)
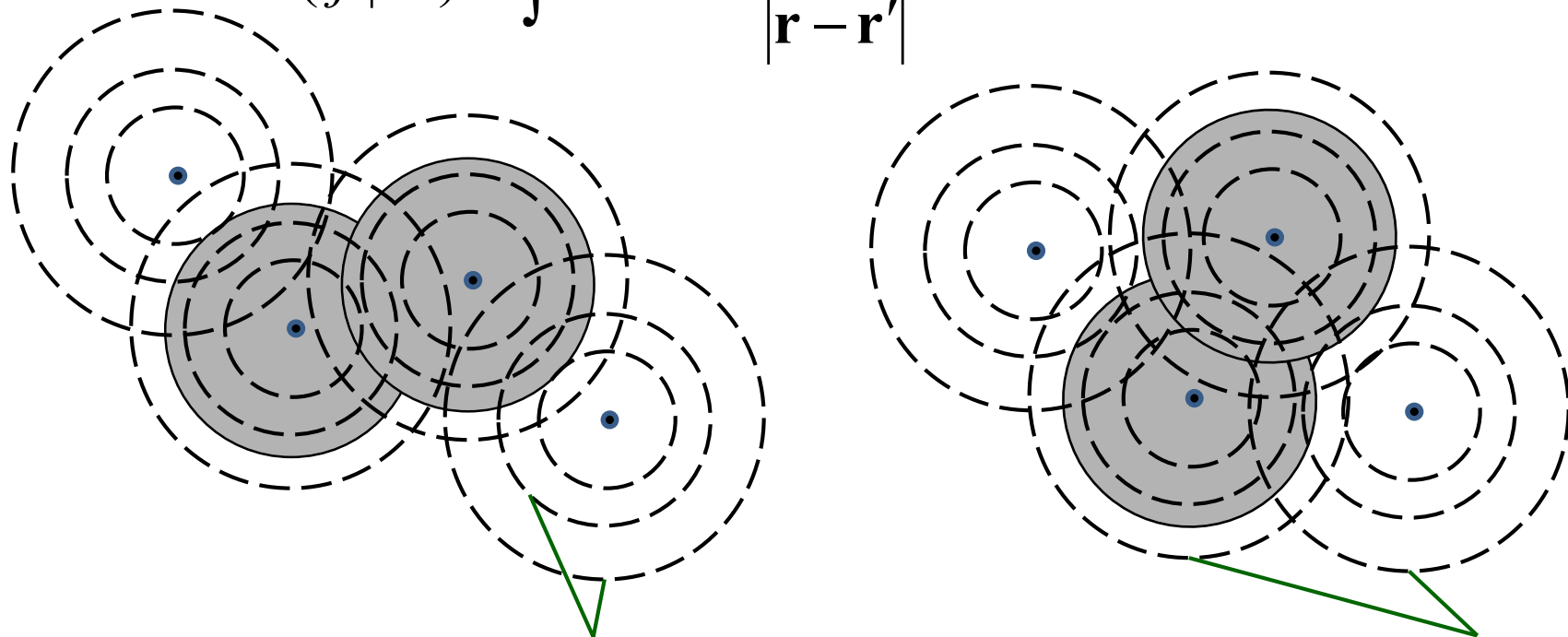
- **need fast evaluation**
- **need efficient use of sparsity (screening)**

"Resolution of identity" (RI) (density fitting)

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

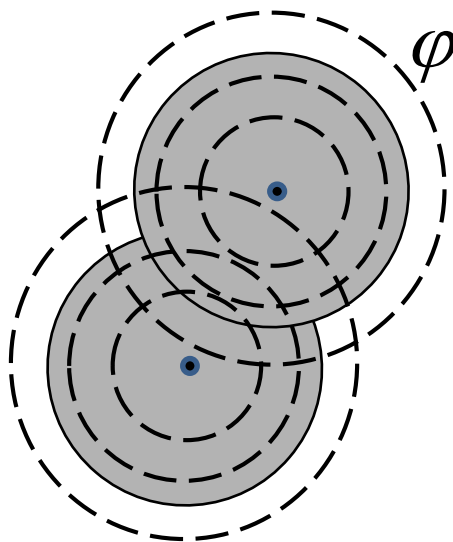$$\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) = \sum_\mu C_{ij}^\mu P_\mu(\mathbf{r}) \qquad \varphi_k(\mathbf{r})\varphi_l(\mathbf{r}) = \sum_\mu C_{kl}^\mu P_\mu(\mathbf{r})$$

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)

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

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

local inverse Coulomb matrix

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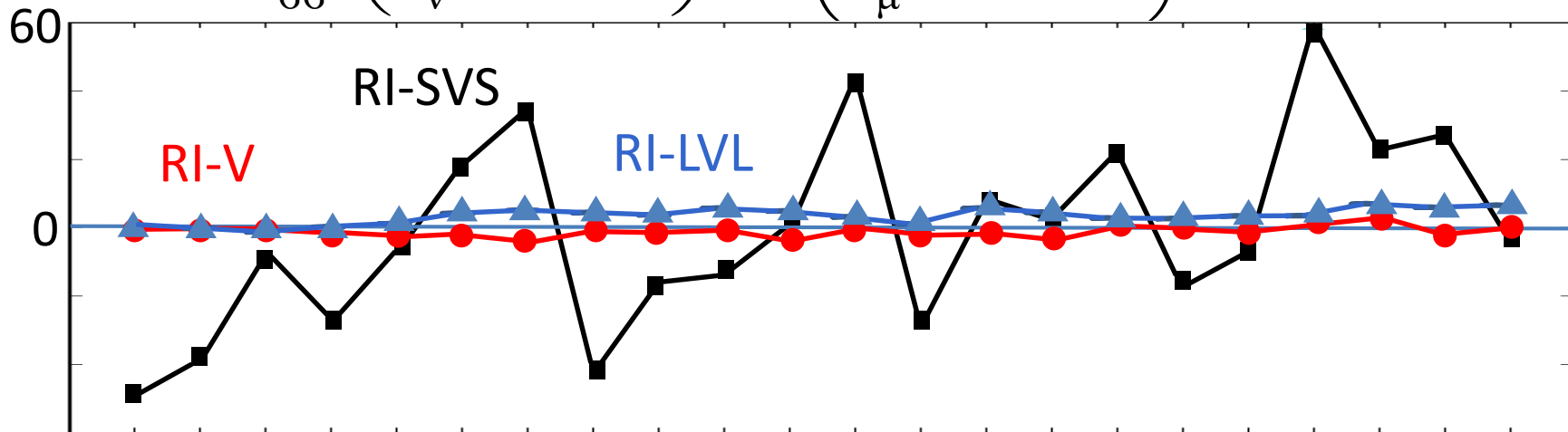
Hybrid functionals in FHI-aims

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

Zincblende GaAs

Legend:
- ●—● 128 atoms
- ■—■ 256 atoms
- ◆—◆ 512 atoms
- ▲—▲ 1024 atoms
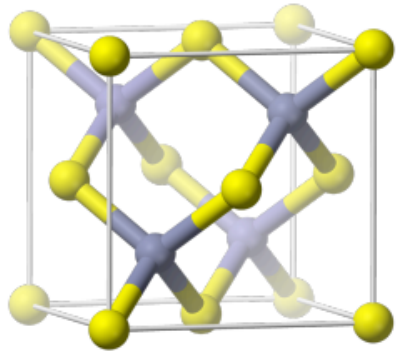
Time per iteration (seconds) vs. Number of CPUs
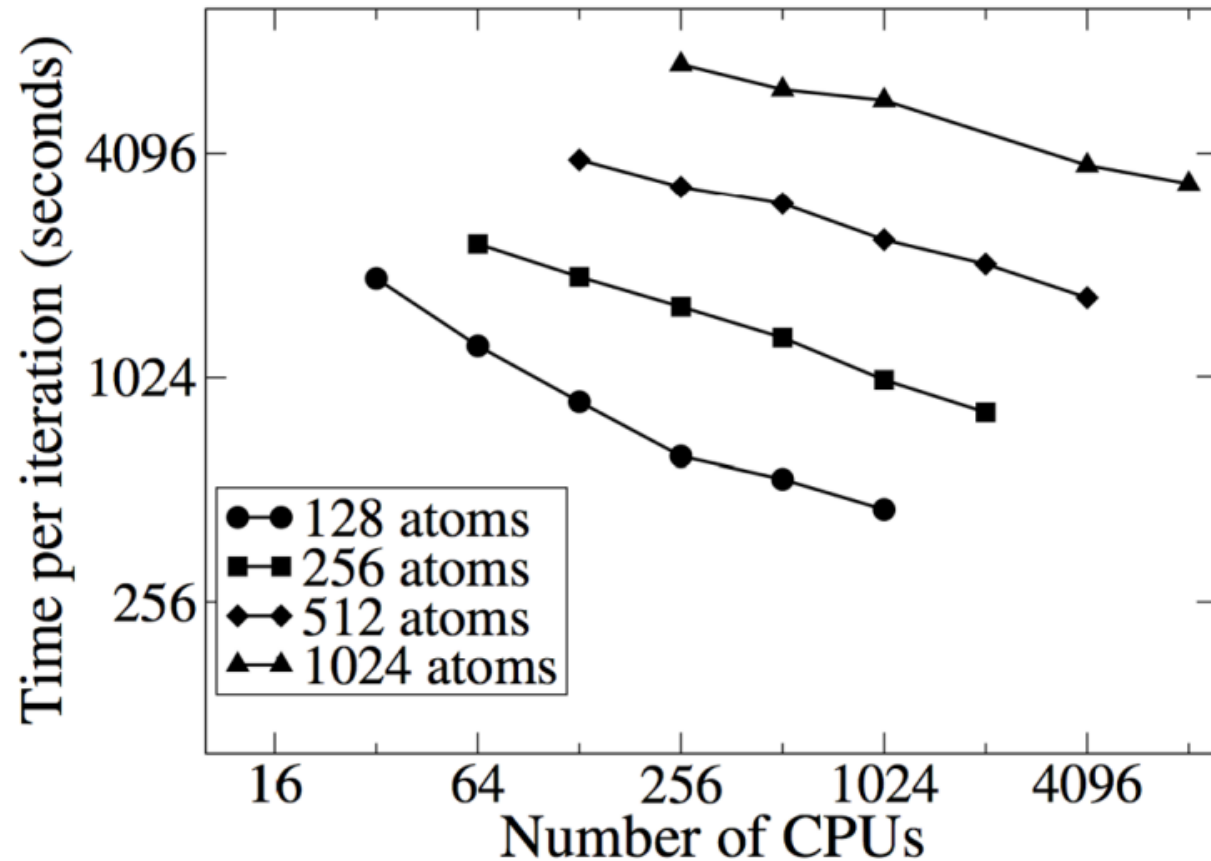
Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler,
Comp. Phys. Commun. **192**, 60-69 (2015).

Hybrid functionals in FHI-aims

Zincblende GaAs

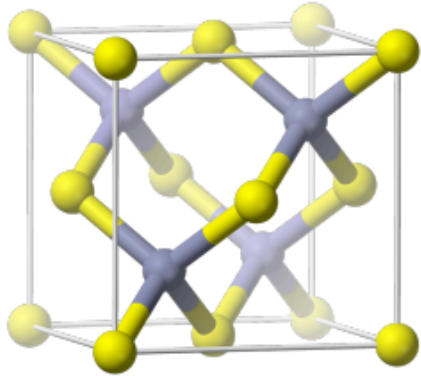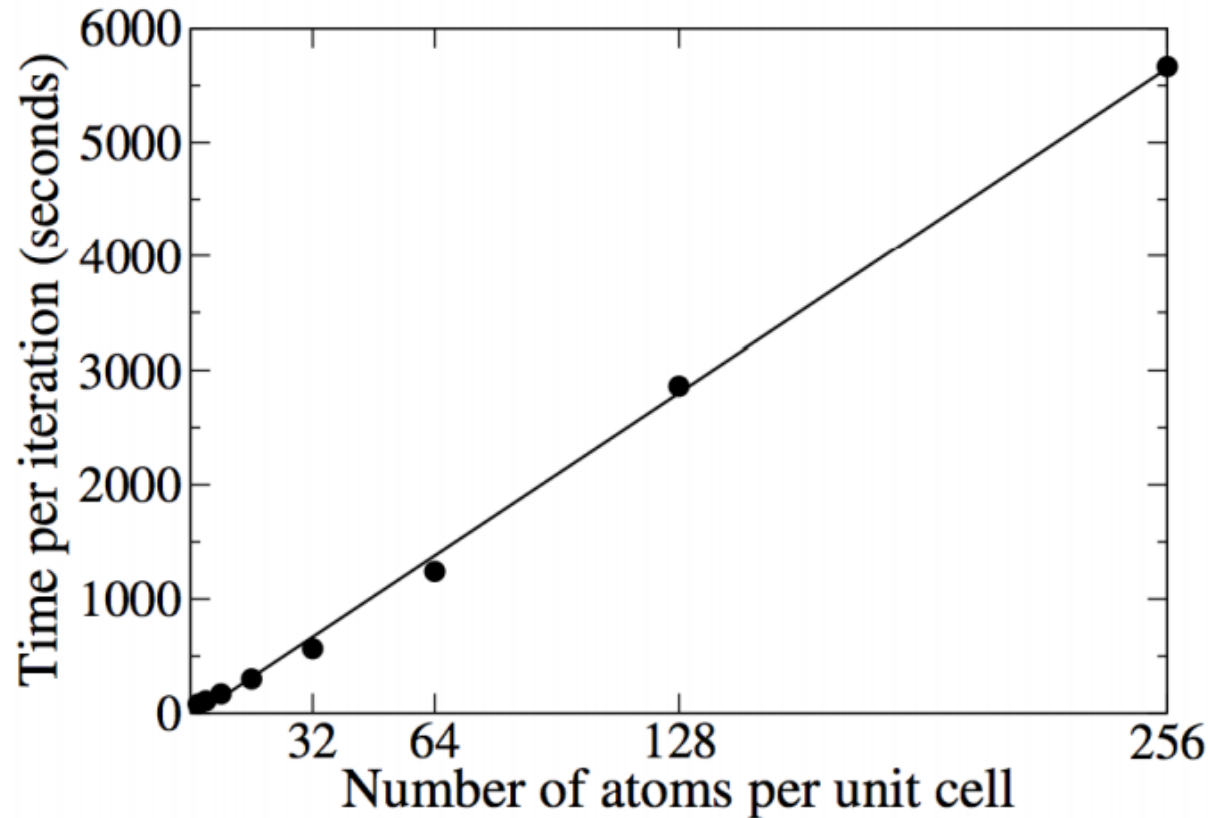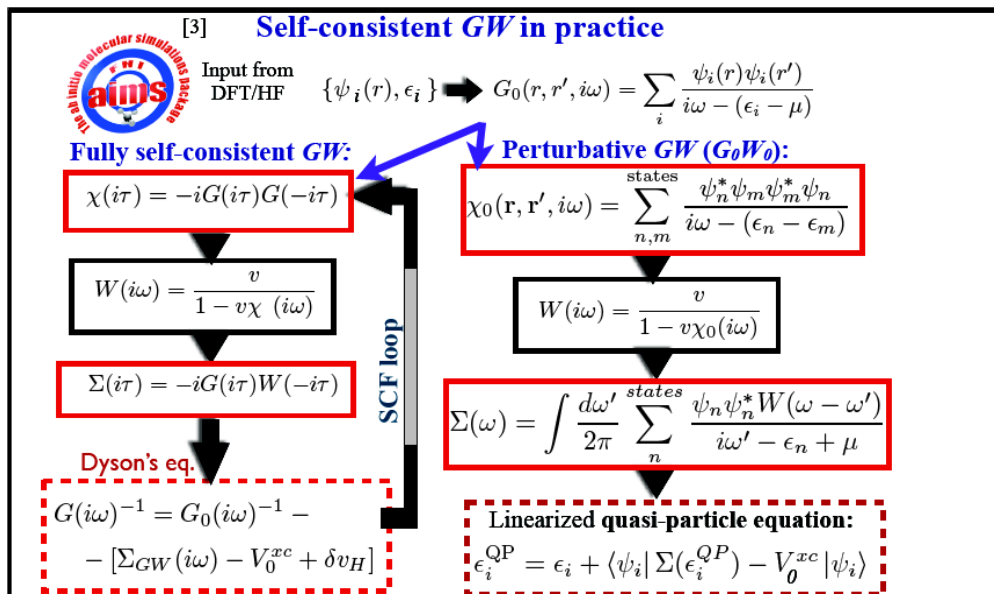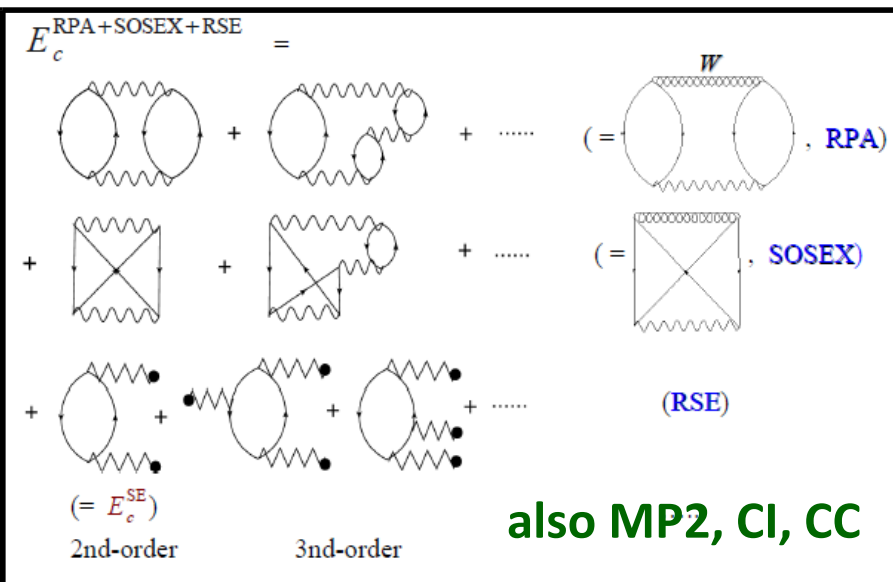Computational Scaling of Periodic GaAs,
HSE06 Hybrid Functional,
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Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler,
*Comp. Phys. Commun. **192**, 60-69 (2015).*

Advanced electronic-structure methods (active development)

$$E_c^{\text{RPA+SOSEX+RSE}} =$$

(= , RPA)

(= , SOSEX)

(RSE)

$(= E_c^{\text{SE}})$

2nd-order   3nd-order

also MP2, CI, CC

[3] **Self-consistent GW in practice**

aIMS Input from DFT/HF $\{\psi_i(r), \epsilon_i\}$ $\rightarrow$ $G_0(r, r', i\omega) = \sum_i \dfrac{\psi_i(r)\psi_i(r')}{i\omega - (\epsilon_i - \mu)}$

Fully self-consistent GW:

$\chi(i\tau) = -iG(i\tau)G(-i\tau)$

$W(i\omega) = \dfrac{v}{1 - v\chi(i\omega)}$

$\Sigma(i\tau) = -iG(i\tau)W(-i\tau)$

SCF loop

Dyson's eq.
$G(i\omega)^{-1} = G_0(i\omega)^{-1} -$
$- [\Sigma_{GW}(i\omega) - V_0^{xc} + \delta v_H]$

Perturbative GW (G_0W_0):

$\chi_0(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{n,m}^{\text{states}} \dfrac{\psi_n^* \psi_m \psi_m^* \psi_n}{i\omega - (\epsilon_n - \epsilon_m)}$

$W(i\omega) = \dfrac{v}{1 - v\chi_0(i\omega)}$

$\Sigma(\omega) = \int \dfrac{d\omega'}{2\pi} \sum_n^{\text{states}} \dfrac{\psi_n \psi_n^* W(\omega - \omega')}{i\omega' - \epsilon_n + \mu}$

Linearized quasi-particle equation:
$\epsilon_i^{QP} = \epsilon_i + \langle \psi_i | \Sigma(\epsilon_i^{QP}) - V_0^{xc} | \psi_i \rangle$

TS-vdW method

$$\alpha_A^0 = \alpha_A^0[n(\mathbf{r})]; \quad \omega_A^0 = \omega_A^0[n(\mathbf{r})]$$

Self-consistent electrostatic screening (SCS)

$$\alpha_p(i\omega) = \alpha_p^{\text{TS}}(i\omega) + \alpha_p^{\text{TS}}(i\omega) \sum_{q \neq p}^N \mathcal{T}_{pq} \alpha_q(i\omega)$$

Many-body vdW energy for a system of coupled oscillators (CFDM)

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_{\chi_i}^2 + \frac{1}{2} \sum_{i=1}^N \omega_i^2 \chi_i^2 + \sum_{i>j=1}^N \omega_i \omega_j \sqrt{\alpha_i \alpha_j} \chi_i \mathcal{T}_{ij} \chi_j.$$

A First Principles Heat Flux Definition

	Atomistic Formulation	First Principles Formulation
Total Energy	$E = \sum_i T_i + U_i$	$E = \sum_i T_i + \int d\mathbf{r}\, \varepsilon(\mathbf{r})$
Heat Flux	$\mathbf{J} = \dfrac{d}{dt} \sum_i (\mathbf{R}_i \cdot E_i)$	$\mathbf{J} = \dfrac{d}{dt} \left[\int d\mathbf{r}\, \mathbf{r} \cdot \varepsilon(\mathbf{r}) + \sum_i \mathbf{R}_i (T_i - E_i^*) \right]$

In an **atomistic** picture [7], the *heat flux J* is determined by the positions R_i and the energy contributions E_i of the **individual** atoms; the latter quantity is hard to assess in an *ab initio* framework. This fact has hitherto prevented a straightforward application of the *Green-Kubo Method* in first-principles calculations. We overcome this difficulty by computing the *heat flux J* from the *ab initio energy density ε*, which is implicitly defined by means of the *total energy functional* [8]:

$$E = \int \left(\sum_i [T_i \cdot \delta(\mathbf{r} - \mathbf{R}_i)] + \varepsilon(\mathbf{r}) \right) d\mathbf{r}$$

In our particular implementation, we use an *energy density* definition [9] that is based on the *Harris-Foulkes functional* [10]:

$$\varepsilon(\mathbf{r}) = \sum_i f_i^{\text{occ}} \epsilon_i \psi_i(\mathbf{r})^* \psi_i(\mathbf{r}) - \frac{1}{2} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \rho(\mathbf{r})(\epsilon_{xc}(\mathbf{r}) - v_{xc}(\mathbf{r}))$$
$$+ \sum_\mu \left(\frac{1}{2} \sum_\nu \frac{Z_\mu Z_\nu}{|\mathbf{R}_\mu - \mathbf{R}_\nu|} \right) \delta(\mathbf{r} - \mathbf{R}_\mu) + \sum_i [T_i \cdot \delta(\mathbf{r} - \mathbf{R}_i)]$$

Practicalities

Login to the cluster:

ssh your_user_name@10.30.99.219 -p 2222

Download the tutorial file:

scp –P 2222 your_user_name@10.30.99.219:**~/fhiaims/Tutorial.pdf**
~/path_to_your_download_folder

Set up environmental variables: source /tmp/fhiaims.sh

Read the tutorial file and follow the instructions

Download FHI-aims manual:

scp –P 2222 your_user_name@10.30.99.219:~/fhiaims/FHI-aims.pdf
~/path_to_your_download_folder

Run FHI-aims via the batch system:

1) sbatch ~/fhiaims/job.sh
2) The output is in output
3) To see the progress, type: tail   -f   output

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

Manual, chap. 2.1

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

FHI-aims/species_defaults

Predefined species
Copy-paste into control.in

Manual, chap. 2.2

- light

- tight

- really tight

Increased accuracy:

Basis
Hartree potential
Basis cutoff potential
Integration grids

Default basis sets

FHI-aims/species_defaults

Predefined species
Copy-paste into control.in

Manual, chap. 2.2

- light

- tight

- really tight

Fast, many production tasks
Fast pre-relaxation

Used to verify important results
Converged settings

Heavily converged numerical settings
Explicit convergence tests

Default basis sets

FHI-aims/species_defaults

Predefined species
Copy-paste into control.in

Manual, chap. 2.2

- 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

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

             ------------------------------------------------
```

5

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

             ------------------------------------------------
```

6

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 :    -0.1301985526094581E+02 eV
| Total energy corrected   :    -0.1301985526094581E+02 eV
| Electronic free energy   :    -0.1301985526094581E+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: O$_2$

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 III-VIII: H₃O⁺
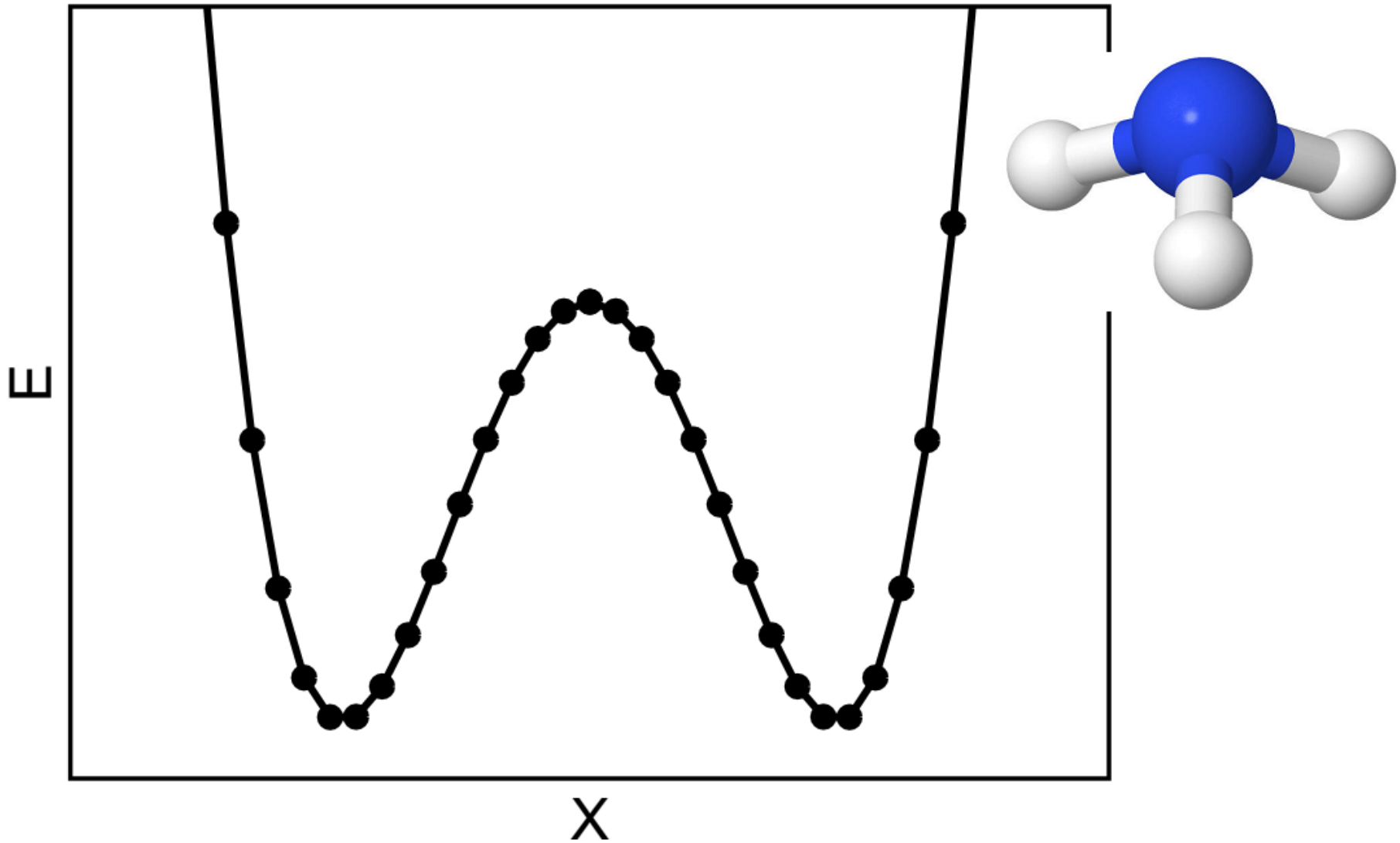
Problem III-VIII: H_3O^+

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

```
# Specify in FHI-aims
sc_accuracy_forces 1E-4
relax_geometry trm 1E-3
```
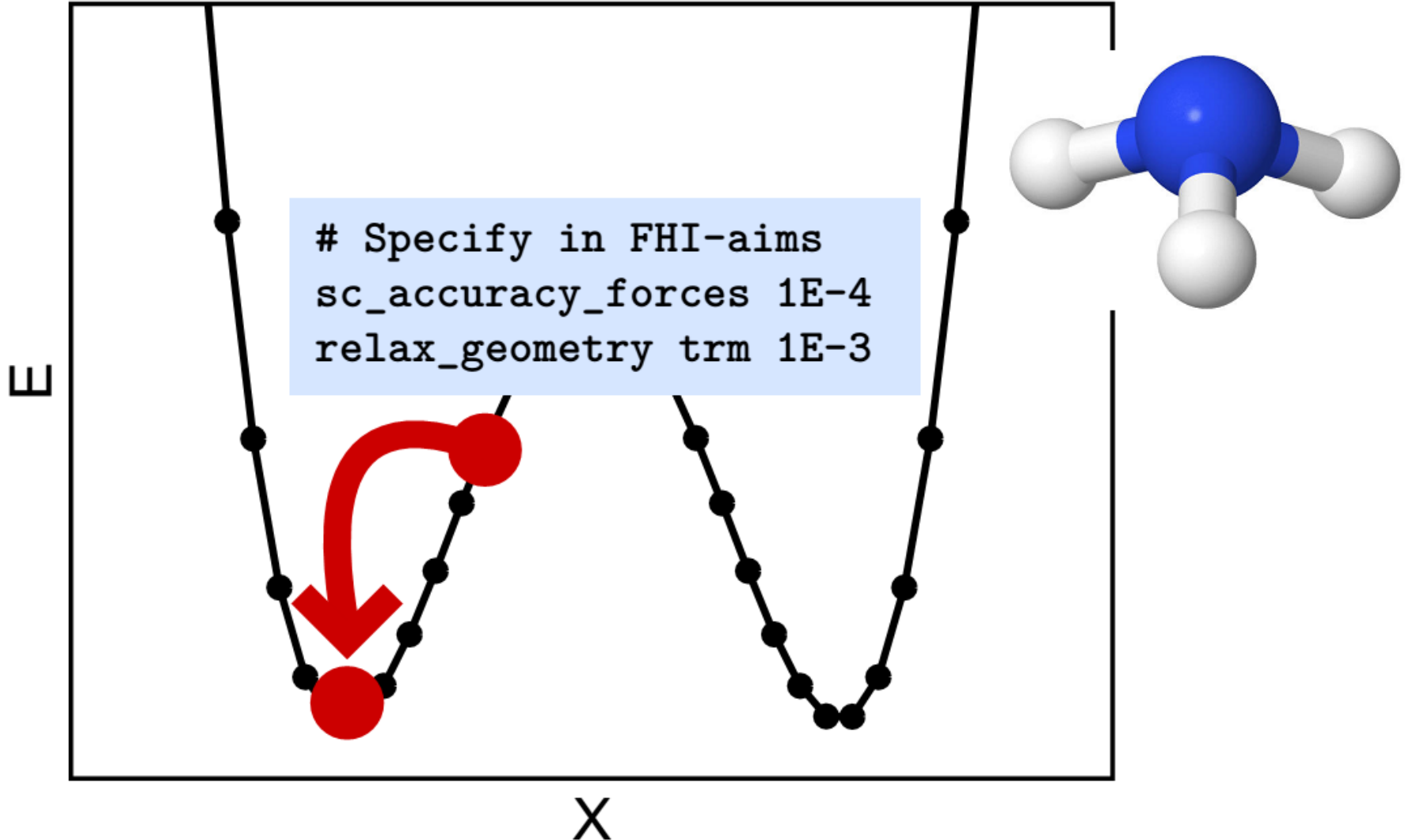
Problems III-VIII: H_3O^+

Tasks:

- Relax structure with two different starting points.
- Make a vibrational analysis.
- Explore the limits of the harmonic approximation.
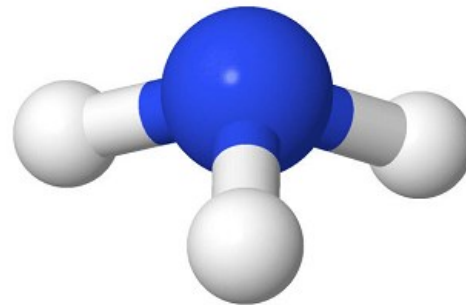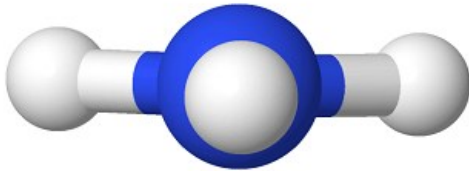
Important practical points

- Each calculation one directory, for example

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

- 2 input files (plus 1 for pseudopotential embedding)

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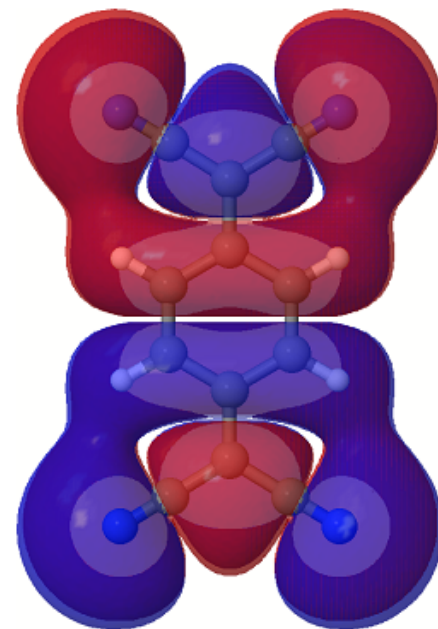
Visualization

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

$\Rightarrow$ Appendix of handout

Text editor: vi

> vi <file_name>

insert text -- i + text
esc -- exit the insert mode
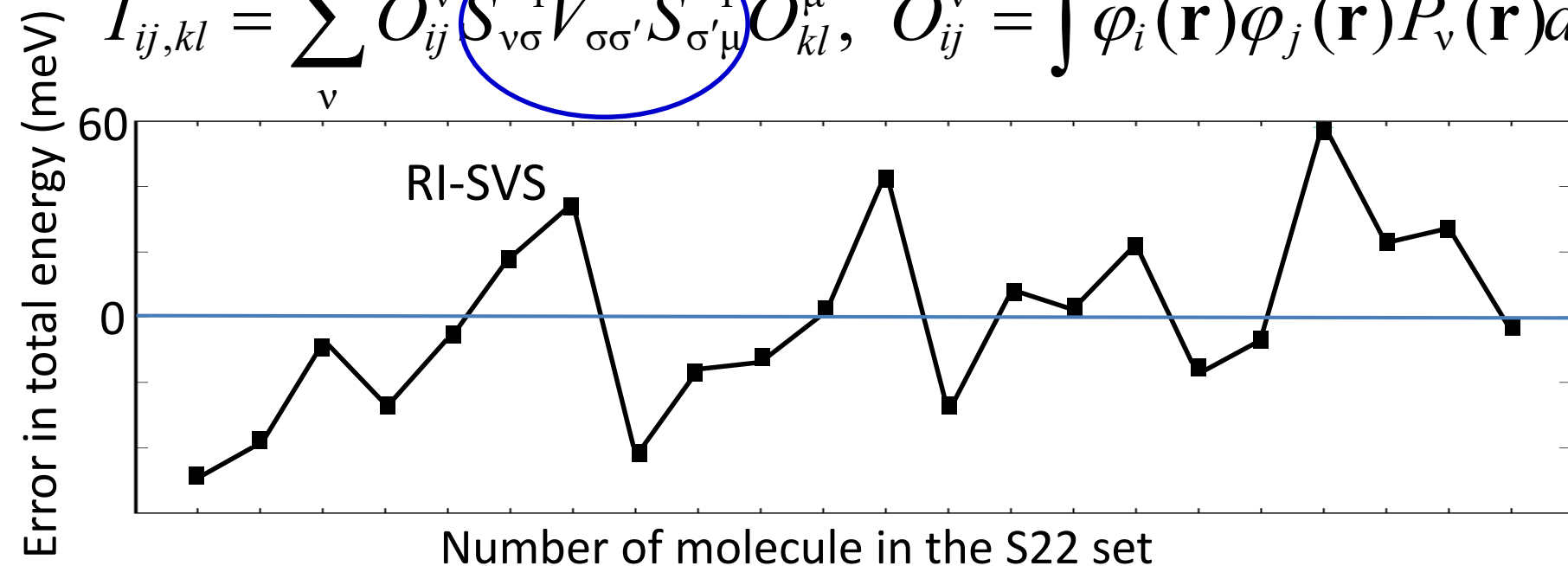:wq --   save file
dd -- delete a line

Finding the RI coefficients: RI-SVS

$$\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \approx \sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r}) \Rightarrow (ij \mid kl) \approx I_{ij,kl} = \sum_{\mu,\nu} C_{ij}^{\mu} V_{\mu\nu} C_{kl}^{\nu}$$

Minimize the error norm: $\displaystyle \min_{C} \int \left(\sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r}) - \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \right)^2 d^3r$

$$I_{ij,kl} = \sum_{\nu} O_{ij}^{\nu} S_{\nu\sigma}^{-1} V_{\sigma\sigma'} S_{\sigma'\mu}^{-1} O_{kl}^{\mu}, \quad O_{ij}^{\nu} = \int \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) P_{\nu}(\mathbf{r}) d^3r$

RI-SVS

Error in total energy (meV)

Number of molecule in the S22 set

Finding better RI coefficients

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

Let us calculate the error in ($ij|ij$) – the largest integrals:

$$\delta(ij \mid ij) = 2\int \frac{\delta\rho_{ij}(\mathbf{r})\left(\sum_v C_{ij}^v P_v(\mathbf{r}')\right)}{|\mathbf{r} - \mathbf{r}'|} d^3r \, d^3r' + \Delta(\delta\rho_{ij}^2)$$

first-order correction does not vanish in RI-SVS!

Is it possible to do better without increasing the size of the auxiliary basis?
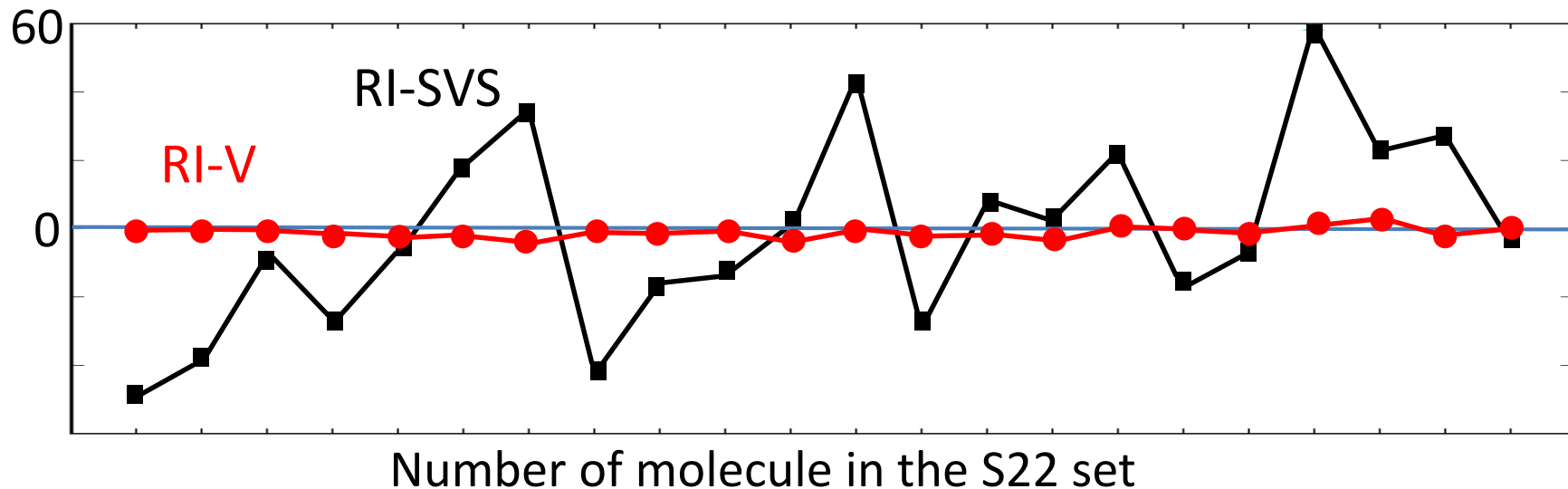
Finding better RI coefficients: RI-V

Set the first-order correction to zero, minimize second-order:

$$\Delta(\delta\rho_{ij}^2) \to \min \quad \Rightarrow \quad \Delta(\delta\rho_{ij}) \to 0$$
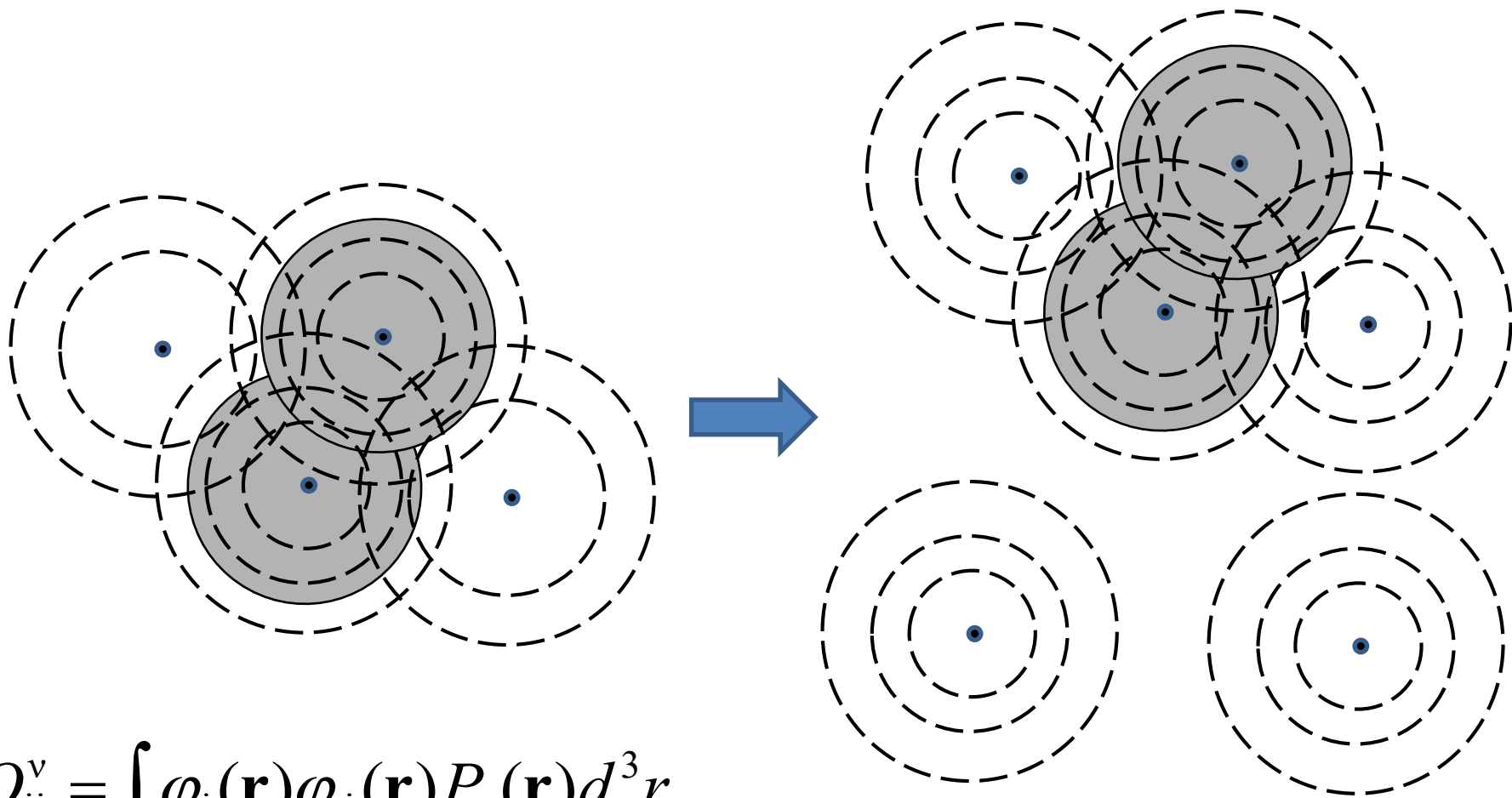
$$I_{ij,kl} = \sum_{\nu} Q_{ij}^{\nu} V_{\nu\mu}^{-1} Q_{kl}^{\mu}, \quad Q_{ij}^{\nu} = \int \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})P_{\nu}(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d^3r d^3r'$$
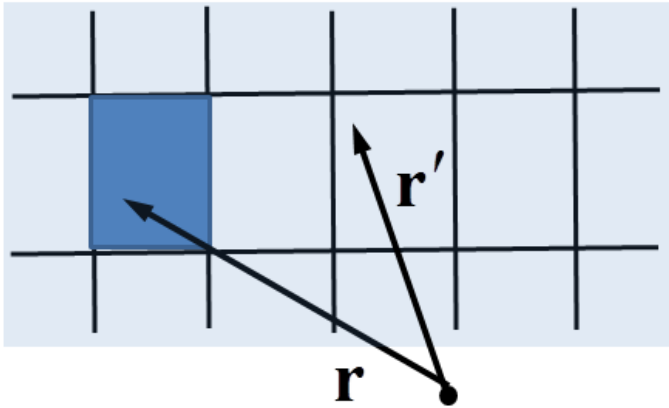
Finding better RI coefficients: RI-V

$$O_{ij}^v = \int \varphi_i(\mathbf{r})\varphi_j(\mathbf{r})P_v(\mathbf{r})d^3r$$

$$Q_{ij}^v = \int \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})P_v(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r'$$
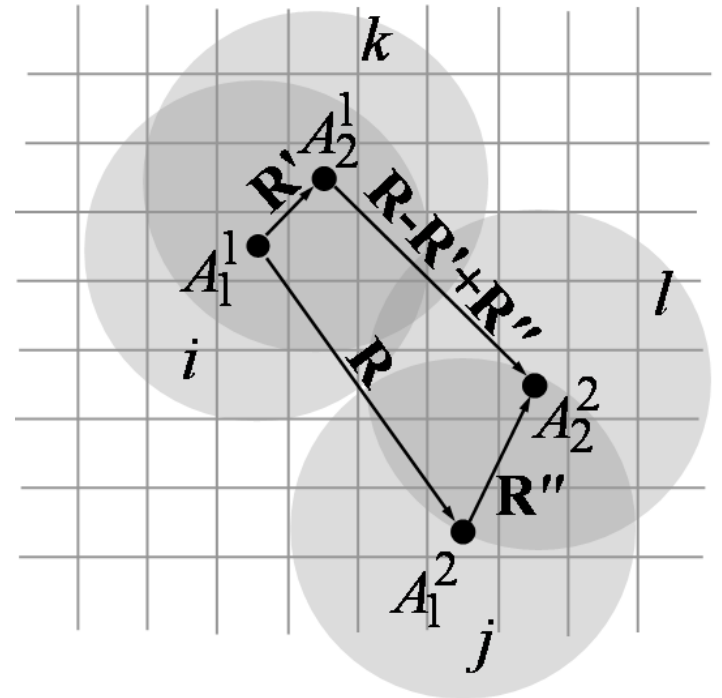
Distant aux. functions contribute to the integrals → a lot of memory and operations → scaling N^3

Hartree-Fock exchange in extended systems

$$E_{\mathrm{X}}^{\mathrm{HF}} = -\frac{1}{2} \sum_{\substack{m,n \\ \mathbf{k},\mathbf{k'}}} \int \frac{\psi_{m\mathbf{k}}^{*}(\mathbf{r},\sigma)\psi_{n\mathbf{k'}}(\mathbf{r},\sigma)\psi_{n\mathbf{k'}}^{*}(\mathbf{r'},\sigma')\psi_{m\mathbf{k}}(\mathbf{r'},\sigma')}{|\mathbf{r}-\mathbf{r'}|} d^3r \, d^3r' \, d\sigma \, d\sigma'$$

$$\psi_{m\mathbf{k}}(\mathbf{r},\sigma) = s(\sigma)\sum_{i,\mathbf{R}} c_{mi}^{\mathbf{k}\sigma} \varphi_i(\mathbf{r}-\mathbf{R})\,\mathrm{e}^{i\mathbf{kR}}$$

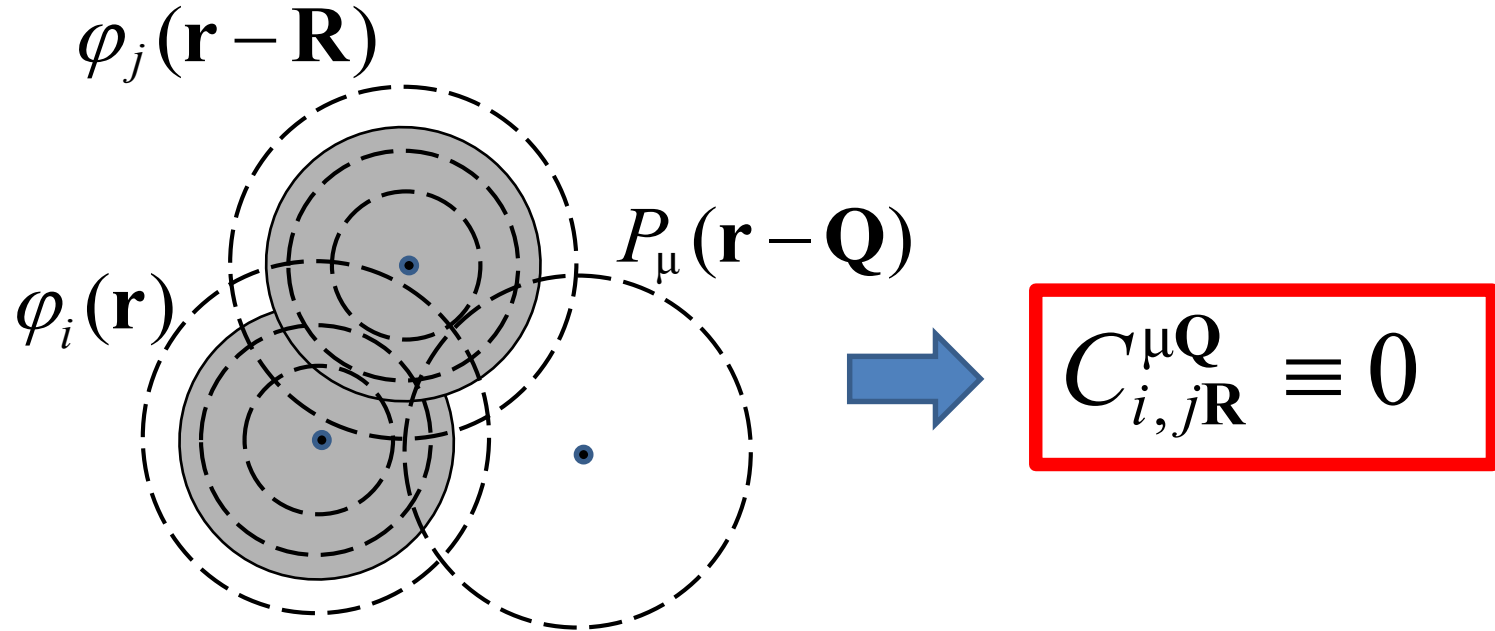$$E_{\mathrm{X}}^{\mathrm{HF}} = -\frac{1}{2} \sum_{\substack{i,j,k,l \\ \mathbf{R},\mathbf{R'},\mathbf{R''}}} D_{il}(\mathbf{R}+\mathbf{R''})D_{jk}(\mathbf{R'}-\mathbf{R}) \times$$

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

Electron repulsion integrals in periodic systems

RI-V is impractical for extended systems

$$\varphi_j(\mathbf{r} - \mathbf{R})$$

$$\varphi_i(\mathbf{r})$$

$$P_\mu(\mathbf{r} - \mathbf{Q})$$

$$C_{i,j\mathbf{R}}^{\mu\mathbf{Q}} \equiv 0$$

RI-LVL: Sparse, easier to calculate, linear scaling is possible!

$$I_{ij\mathbf{R}',k\mathbf{R}l\mathbf{R}+\mathbf{R}''} = \sum_{\mu\mathbf{Q}'}\sum_{\nu\mathbf{Q}''} C_{i,j\mathbf{R}'}^{\mu\mathbf{Q}'} V_{\mu\nu(\mathbf{R}+\mathbf{Q}''-\mathbf{Q}')} C_{k,l\mathbf{R}''}^{\nu\mathbf{Q}''}$$

Real-space dynamical mean-field embedding

Embedding surrounding (grey)

► Calculated with LDA/GGAs

Embedded region (red)

► Hybrids: PBEh and HSE

► Green's function methods: the scGW

Region described with cheaper theory

Region described with "better" theory