Hybrid DFT
with numeric atomic orbitals

Monday Meeting, 22 April 2024

Florian Knoop (florian.knoop@liu.se)

DFT in a nutshell
Hohenberg-Kohn [1]

Walter Kohn
(1923-2016)

Ground state properties of matter determined by density

$$\Psi_{\text{el}}\left(r_1, r_2, \ldots, r_{3N}\right) \Longleftrightarrow \rho(x, y, z)$$

→ **Reduce degrees of freedom** by a factor N (~10^{23})

→ **Electron ground state properties**: total energy, forces, dipole moments, …

[1] P. Hohenberg, W. Kohn, *Phys Rev.* **136**, B864 (1964)
[2] W. Kohn, L.J. Sham, *Phys. Rev.* **140**, A1133 (1965)

DFT in a nutshell
Kohn-Sham [2]

Walter Kohn
(1923-2016)

Map electron density on effective one-particle orbitals

$$\rho(r) \Longrightarrow \sum_i f_i \left| \psi_i^{\text{KS}} \right|^2$$

→ can be solved **self-consistently** via **Schrödinger-like equation**

→ Kohn-Sham orbitals are **not electrons!**

[1] P. Hohenberg, W. Kohn, *Phys Rev.* **136**, B864 (1964)

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DFT in a nutshell
Kohn-Sham [2]

Map electron density on effective one-particle or

KS equations:

$$\left(-\frac{1}{2}\nabla^2 + V^{\mathrm{KS}}\left[\{\psi_i^{\mathrm{KS}}\}\right]\right)\psi_i^{\mathrm{KS}} = \epsilon_i\psi_i^{\mathrm{KS}}$$

$$\rho(r) \Longrightarrow \sum_i f_i \left|\psi_i^{\mathrm{KS}}\right|^2$$

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$$\rho(r) \Longrightarrow \sum_i f_i \left|\psi_i^{\mathrm{KS}}\right|^2$$

DFT energy → DF**A**(pproximation)   dinger-like equation

$$E_{\mathrm{total}} = T_0 + \int \rho V_{\mathrm{nuc}} d^3\mathbf{r}$$

$$+ \frac{1}{2}\iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d^3\mathbf{r}_1 d^3\mathbf{r}_2 + E_{\mathrm{XC}}, \qquad (3)$$

[1] P. Hohenberg, W. Kohn, *Phys Rev.* **136**, B864 (1964)
[2] W. Kohn, L.J. Sham, *Phys. Rev.* **140**, A1133 (1965)

DFT: Basissets
used to represent KS states

Basisset: Complete set of functions to represent KS states

$$\psi_i^{\mathrm{KS}}(\boldsymbol{r}) = \lim_{K \to \infty} \sum_{k=1}^{K} c_k \phi_k(\boldsymbol{r})$$

Problem

Complete basis set = infinite size ($K = \infty$)

Solution

Find *good enough* basis ($K < \infty$)

Popular basissets
1) Plane waves (VASP, Quantum Espresso, …)

basically a Fourier transform, K corresponds to highest energy: $|\mathbf{k}| \leq K = E_{\text{cut}}/\hbar$

$$\phi_k(\boldsymbol{r}) \propto \exp(i\boldsymbol{k} \cdot \boldsymbol{r})$$

<u>Advantages</u> 👍

easy integrals, natural choice for periodic systems, single cutoff

<u>Disadvantages</u> 👎

huge basis needed, cores need extra treatment (pseudopotentials, PAW, …)

non-periodic systems

Popular basissets
2) Gaussian type orbitals (Gaussian, ORCA, …)

$$\phi_{k \equiv lmn;\alpha}(\boldsymbol{r}) \propto x^l y^m z^n \exp\left(-\alpha r^2\right)$$

Advantages 👍

analytic integrals

local → good for molecules

Disadvantages 👎

more cutoff parameters

Popular basissets
3) Numeric atom-centered orbitals (FHI-aims, DFTB+, …)

$$\phi_{k\equiv ilm}(\boldsymbol{r}) \propto \frac{u_i(r)}{r}Y_{lm}(\varphi, \vartheta)$$

Advantages 👍

local → good for molecules, **treat molecules and solids on same footing**

small amount of basis functions needed → **linear scaling**

all electrons can be treated with little extra cost (no pseudos or PAW)

Disadvantages 👎

movable grids → complicated Pulay terms

more difficult to handle analytically than plane waves or Gaussians

Popular basissets
3) Numeric ato... TB+, ...)

Advanta...

local

small a...

all electron...

Disadvantages 👇

movable grid... ...plicated Pulay te...

more diff... ...t to handle analytically than plane waves or Gaussians

Question:
Can I treat periodic systems with a local basisset?

Answer:
Yes.

NAOs in FHI-aims
What should we know?

`light`

   Get to know a system, geometry optimization, molecular dynamics, ...

`intermediate`

   tighter grids, often converged

`tight`

   Converged geometries and energies for checking

`really_tight`

   Overcomplete Benchmark basisset for double checking

NAOs in FHI-aim

What should we know?

light

Get to know a system, geomet... ...lar dynamics, ...

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Overcomplete Benchmark basi... ...g

NAOs in FHI-aims
Example: Silicon

$$\phi_{k \equiv ilm}(\boldsymbol{r}) \propto \frac{u_i(r)}{r} Y_{lm}(\varphi, \vartheta)$$

Si, fcc diamond	light	intermediate	tight	really_tight
r_{cut} [Å]	5	6	6	6
# Integration points	11,208	35,840	35,840	56,860
Multipole l_{max}	4	6	6	8
Max. # basis functions	36	68	78	78
Error [meV per atom]	28.1	11.6	0.6	0.0
Time per scf step [s]*	0.4	3.4	4.7	9.8

OK fine — why bother?

FHI-aims
The ab initio materials simulation package

Efficient All-electron Hybrid Density Functionals for Atomistic Simulations Beyond 10,000 Atoms

Sebastian Kokott,[1] Florian Merz,[2] Yi Yao,[3] Christian Carbogno,[1] Mariana Rossi,[4] Ville Havu,[5] Markus Rampp,[5] Matthias Scheffler,[1] and Volker Blum[3,7]

[1] The NOMAD Laboratory at the Fritz Haber Institute of the Max-Planck-Gesellschaft and IRIS Adlershof of the Humboldt-Universität zu Berlin, Germany
[2] Lenovo HPC Innovation Center, Stuttgart, Germany
[3] Thomas Lord Department of Mechanical Engineering and Material Science, Duke University, Durham, North Carolina 27708, USA
[4] MPI for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22761 Hamburg, Germany
[5] Department of Applied Physics, School of Science, Aalto University, Espoo, Finland
[6] Max Planck Computing and Data Facility, 85748 Garching, Germany
[7] Department of Chemistry, Duke University, Durham, North Carolina 27708, USA

(Dated: 18 March 2024)

Hybrid density functional approximations (DFAs) offer compelling accuracy for *ab initio* electronic-structure simulations of molecules, nanosystems, and bulk materials, addressing some deficiencies of computationally cheaper, frequently used semilocal DFAs. However, the computational bottleneck of hybrid DFAs is the evaluation of the non-local exact exchange contribution, which is the limiting factor for the application of the method for large-scale simulations. In this work, we present a drastically optimized resolution-of-identity-based real-space implementation of the exact exchange evaluation for both non-periodic and periodic boundary conditions in the all-electron code FHI-aims, targeting high-performance CPU compute clusters. The introduction of several new refined Message Passing Interface (MPI) parallelization layers and shared memory arrays according to the MPI-3 standard were the key components of the optimization. We demonstrate significant improvements of memory and performance efficiency, scalability, and workload distribution, extending the reach of hybrid DFAs to simulation sizes beyond ten thousand atoms. As a necessary byproduct of this work, other code parts in FHI-aims have been optimized as well, e.g., the computation of the Hartree potential and the evaluation of the force and stress components. We benchmark the performance and scaling of the hybrid DFA based simulations for a broad range of chemical systems, including hybrid organic-inorganic perovskites, organic crystals and ice crystals with up to 30,576 atoms (101,920 electrons described by 244,608 basis functions).
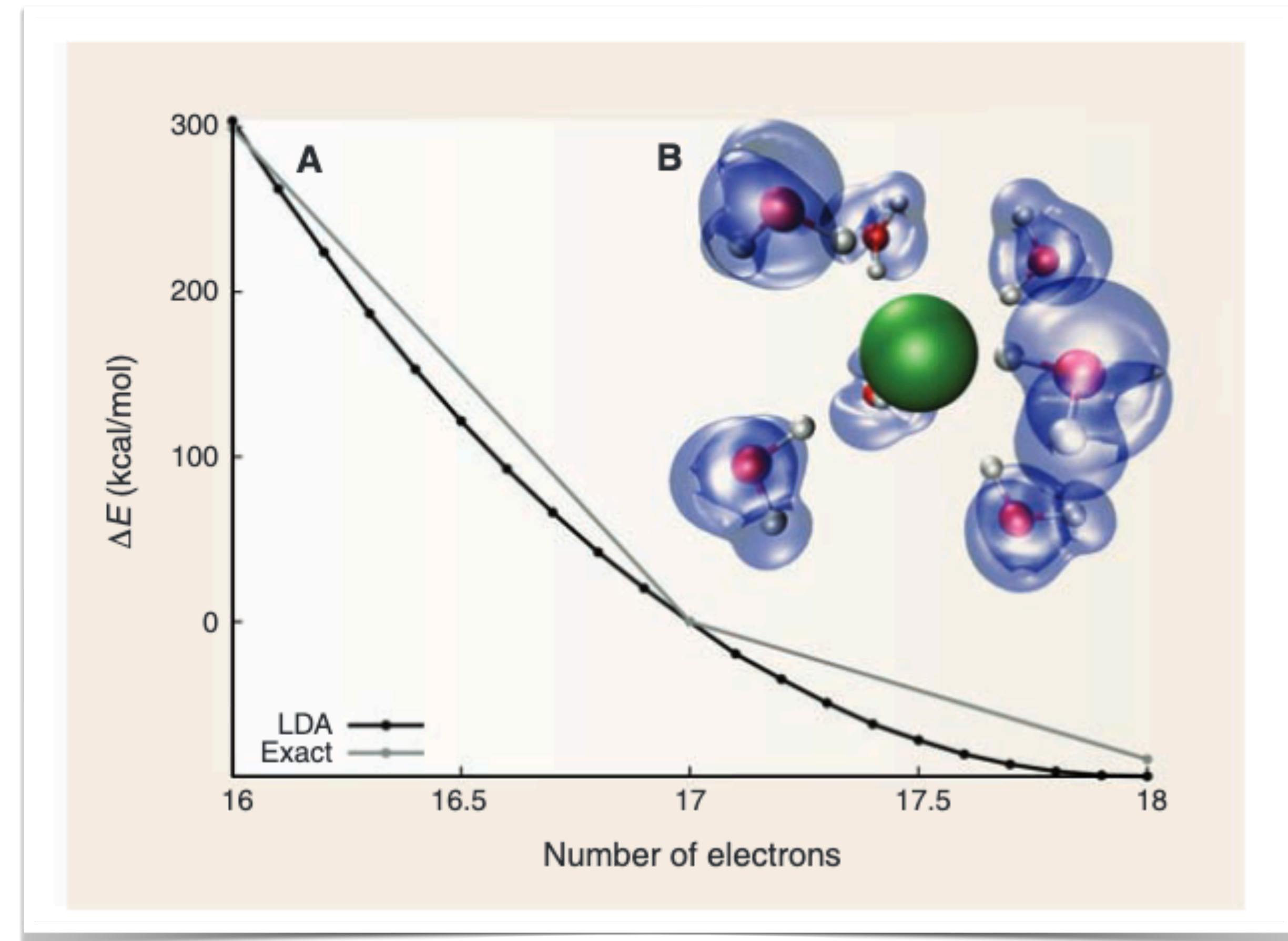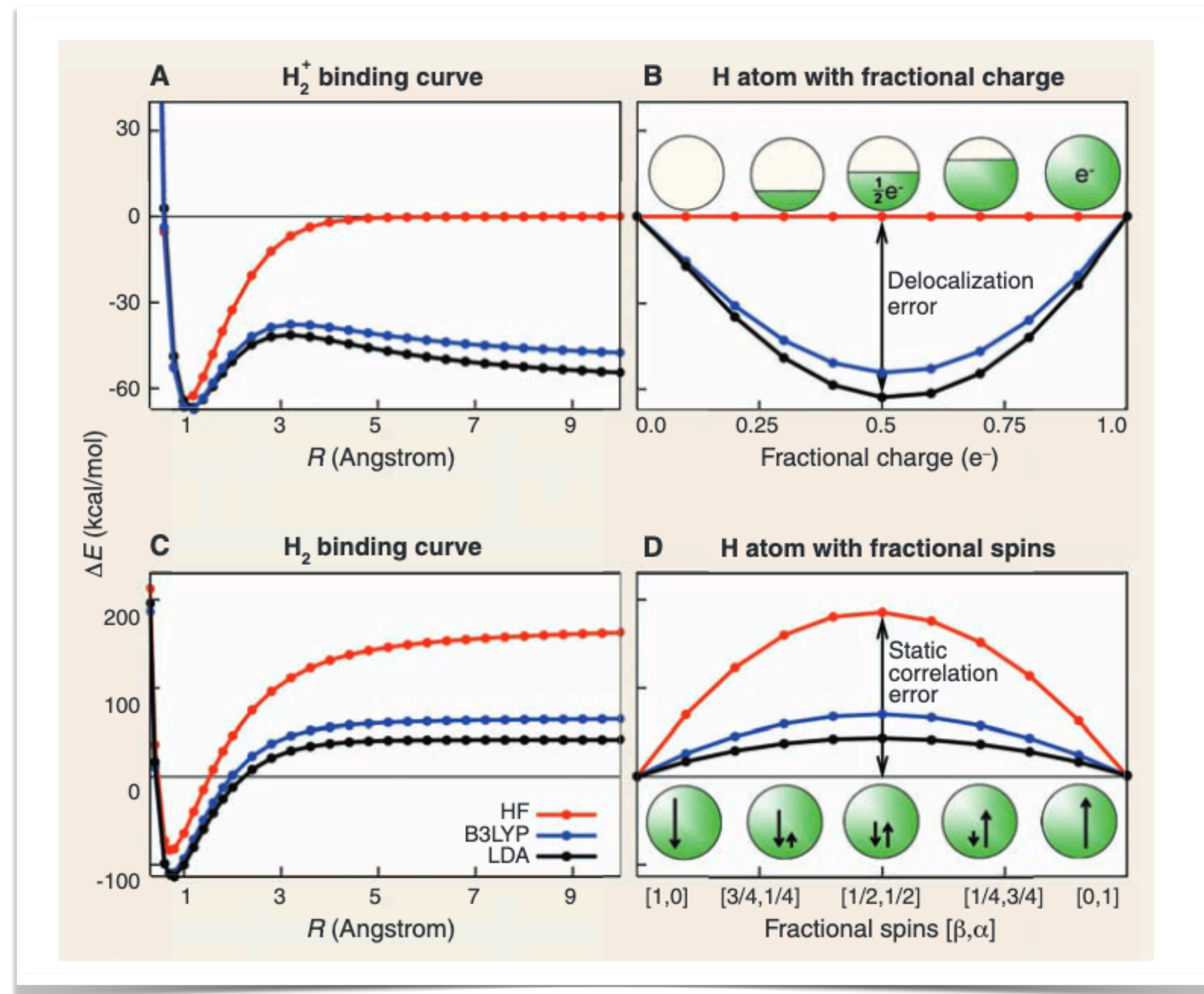
Interlude: **Hybrid functionals**

Why hybrid functionals?
(semi-local) DFT can fail dramatically, e.g., delocalization error [1]

[1] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Science **321**, 792 (2008).

Why hybrid functionals?

exchange can be computed exactly → **exact exchange (EXX *or HF*) [1]**

$$E_{\text{total}} = T_0 + \int \rho V_{\text{nuc}} d^3\mathbf{r}$$

$$+ \frac{1}{2} \int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d^3\mathbf{r}_1 d^3\mathbf{r}_2 + E_{\text{XC}}, \qquad (3)$$

Naïve:

$$E_{\text{XC}} = E_X + E_C^{\text{LSDA}}, \qquad (8)$$

Becke: Use adiabatic connection from noninteracting (λ=0) to interacting (λ=1)

$$E_{\text{XC}} = \int_0^1 U_{\text{XC}}^\lambda d\lambda, \qquad (9)$$

some approximations →

$$E_{\text{XC}} \simeq \frac{1}{2}E_X + \frac{1}{2}U_{\text{XC}}^{\text{LSDA}}, \qquad (12)$$

[1] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).

How to get a good hybrid?
About 25% exact exchange is good [1]

$$E_{xc}^{hyb} = E_{xc}^{DFA} + a_0(E_x - E_x^{DFA}), \qquad (5)$$

Perdew, Ernzerhof, Burke **(PBE0)** [1]:

"We will show that
$a_0 \approx 0.25$ is to be expected for the atomization energies of most molecules,
but also that
larger values of a_0 may be more appropriate for the total energies of atoms and molecules,
and
smaller values for atomization energies of molecules with nearly degenerate ground states
for the unperturbed ($\lambda = 0$) problem."

[1] J. P. Perdew, M. Ernzerhof, and K. Burke, *J. Chem. Phys.* **105**, 9982 (1996).

Problems with exact exchange (EXX, HF)

$$E_{\mathrm{x}} = \sum_{\mu\nu,\lambda\sigma} c_{\mu\nu,\lambda\sigma} \langle \mu\nu \,|\, \lambda\sigma \rangle$$

$$\langle \mu\nu \,|\, \lambda\sigma \rangle = \iint \mathrm{d}r_1 \mathrm{d}r_2 \; \psi_\mu(\mathbf{r}_1)\psi_\nu(\mathbf{r}_1) \frac{1}{r_{12}} \psi_\lambda(\mathbf{r}_2)\psi_\sigma(\mathbf{r}_2)$$
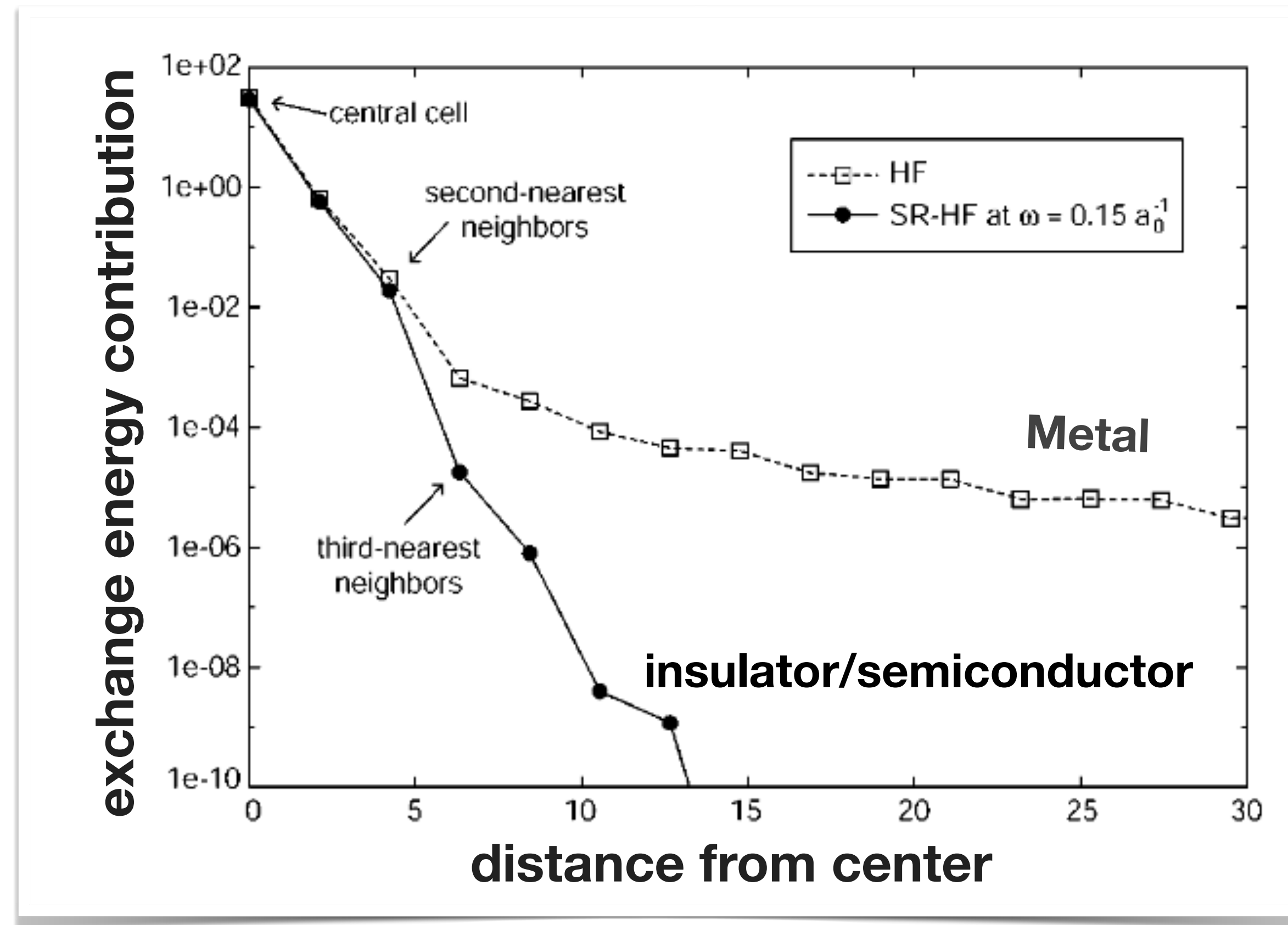
two-electron Coulomb integrals   **Coulomb interaction**

Problem 1: Coulomb interaction is long-ranged (**= expensive**)

Problem 2: (unscreened) Coulomb interactions **diverges for metals**

[1] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J Chem Phys **118**, 8207 (2003).

Solve problem 1: Nearsightedness
Range of exchange decays exponentially for systems with gap [2, 3]

[1] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J Chem Phys **118**, 8207 (2003).
[2] E. Prodan and W. Kohn, Proc. Natl. Acad. Sci. **102**, 11635 (2005).
[3] W. Kohn, Int. J. Quantum Chem. **56**, 229 (1995).

Introduce range separation in HF compuation
→ HSE06 [1, 2]

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

short-range part

neglect long-range part

$$\langle \mu\nu \,|\, \lambda\sigma \rangle^{\mathrm{SR}} = \iint dr_1 dr_2 \; \psi_\mu(\mathbf{r}_1)\psi_\nu(\mathbf{r}_1) \frac{\mathrm{erfc}(\omega r_{12})}{r_{12}} \psi_\lambda(\mathbf{r}_2)\psi_\sigma(\mathbf{r}_2)$$

$$\langle \mu\nu \,|\, \lambda\sigma \rangle^{\mathrm{LR}} \approx 0$$

$$E_{\mathrm{xc}}^{\mathrm{HSE}} = aE_x^{\mathrm{HF,SR}}(\omega) + (1-a)E_x^{\mathrm{PBE,SR}}(\omega) + E_x^{\mathrm{PBE,LR}}(\omega) + E_c^{\mathrm{PBE}}$$

[1] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J Chem Phys **118**, 8207 (2003).
[2] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J Chem Phys **124**, 219906 (2006).

Introduce ra   ompuation

→ **HSE06 [1**

Bottom line 1:

Hybrid functionals [1, 2] solve *some* errors [3]

of (semi-)local DFAs.

Bottom line 2:

Range-separated hybrid functionals

can do the same but *faster* and *for metals.*

e part

$\langle \mu\nu \,|\, \lambda\sigma \rangle^{\mathrm{SR}}$ $\rangle^{\mathrm{LR}} \approx 0$

[1] S. Kümmel and L. Kronik, Rev Mod Phys **80**, 3 (2008
[2] A. M. Teale *et al.*, Phys Chem Chem Phys (2022)
[3] P. Borlido et al., J. Chem. Theory Comput. **15**, 5069 (2019)

$) + E_{\mathrm{c}}^{\mathrm{PBE}}$

[1] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J Chem Phys **118**, 8207 (2003).
[2] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J Chem Phys **124**, 219906 (2006).

Back to FHI-aims

Efficient All-electron Hybrid Density Functionals for Atomistic Simulations Beyond 10,000 Atoms

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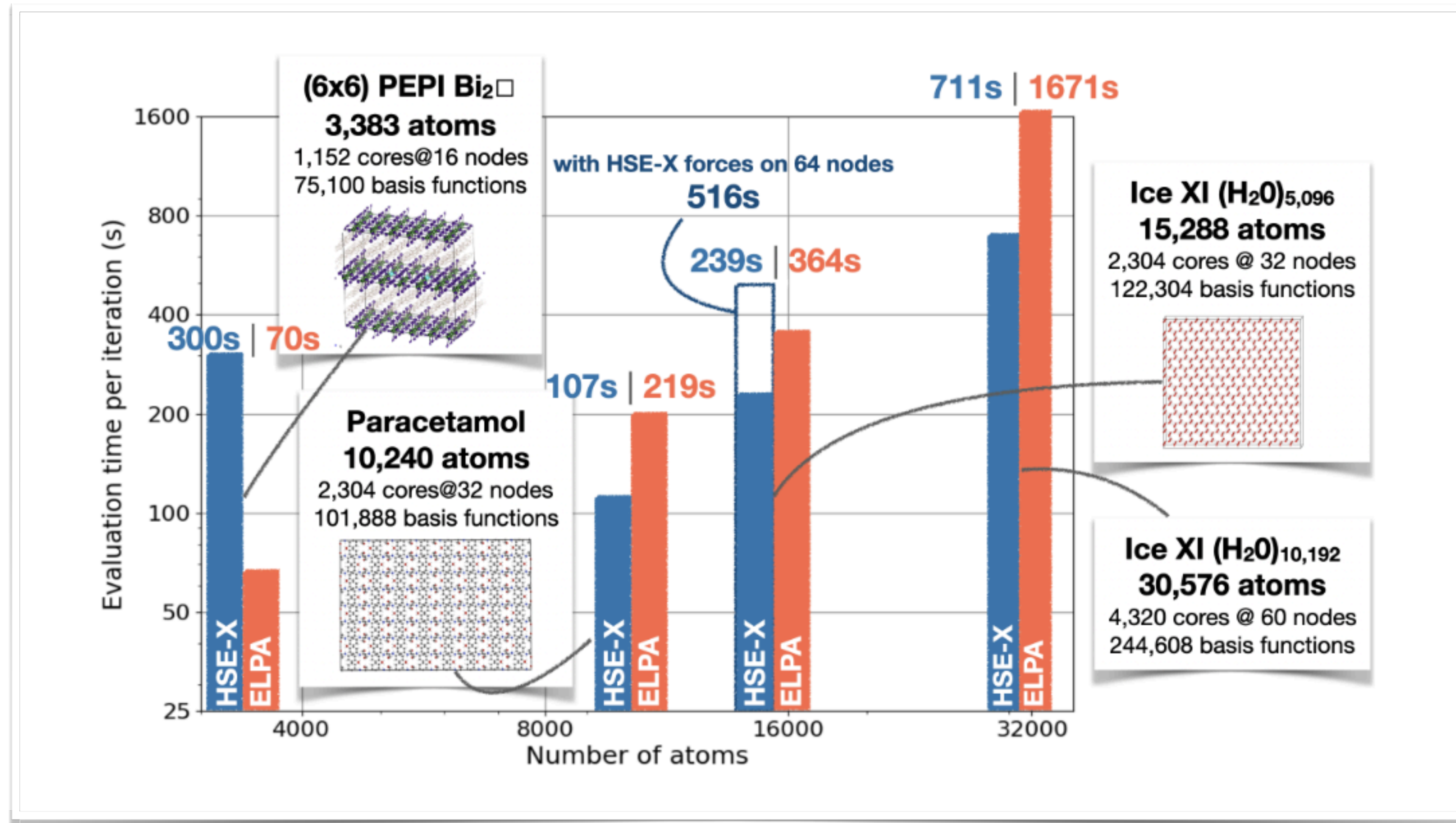[7] Department of Chemistry, Duke University, Durham, North Carolina 27708, USA

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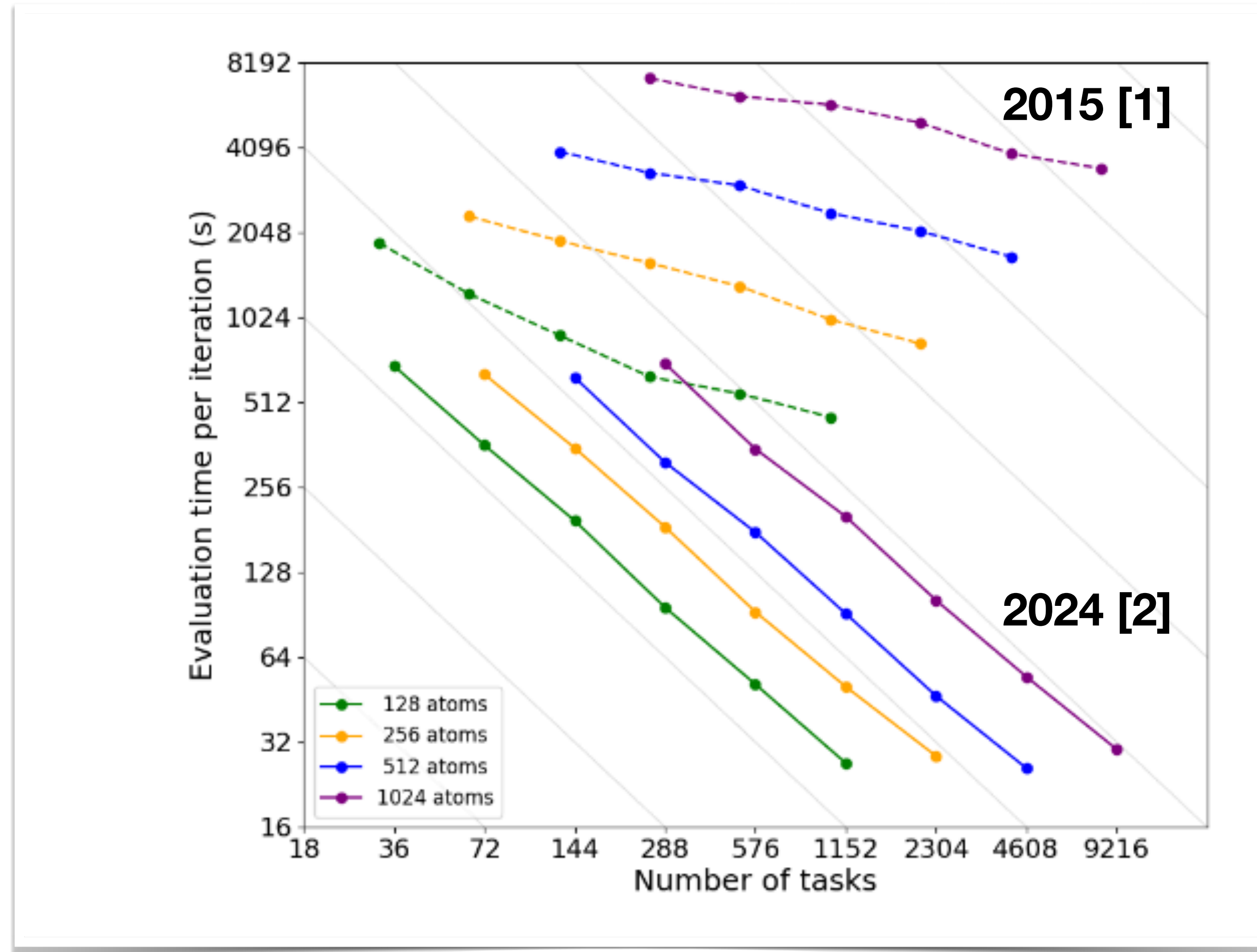
HSE06 for *many* atoms

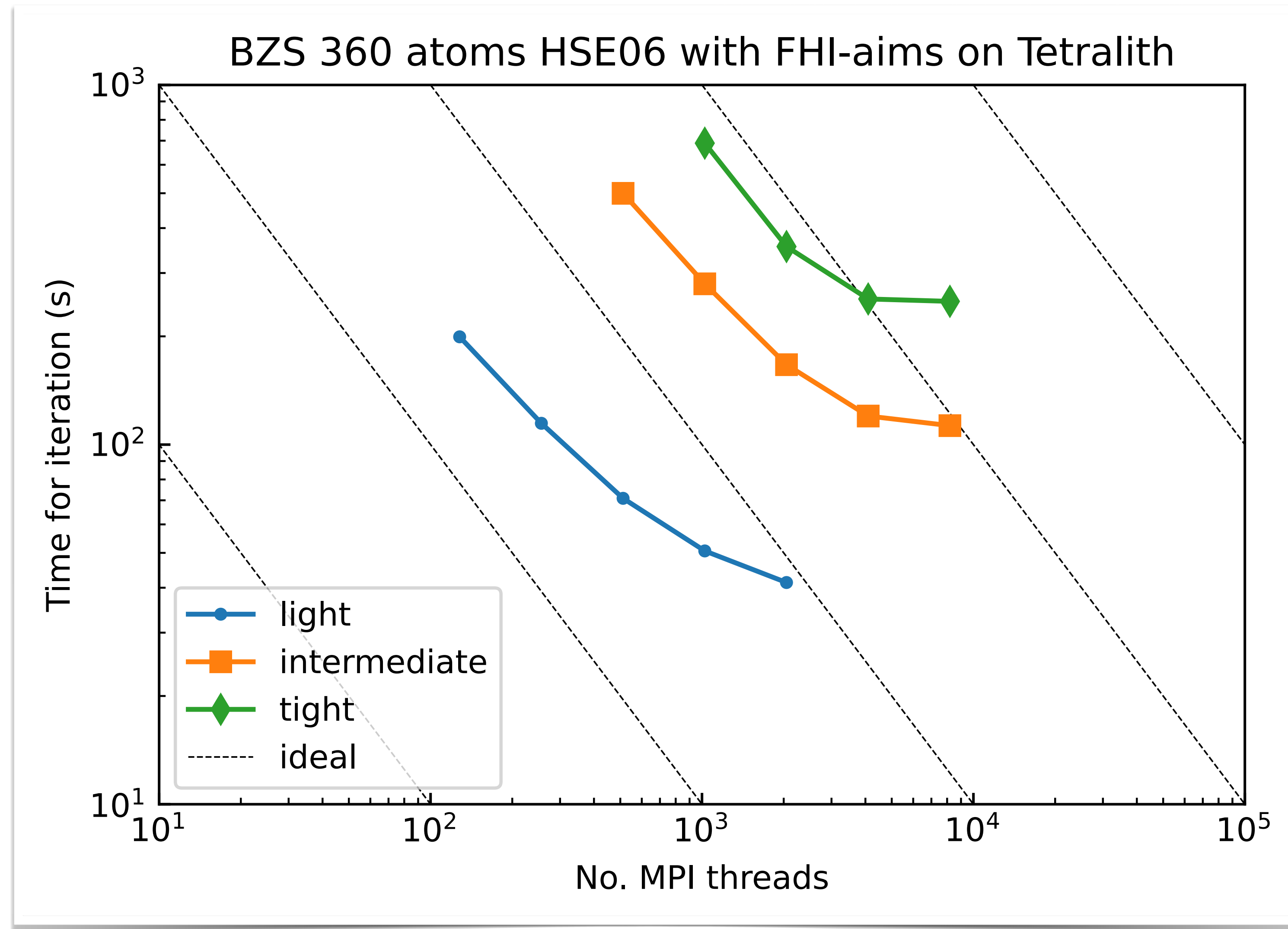[1] S. Kokott *et al.*, *arXiv* 2403.10343 (2024)

Strong scaling

[1] S. V. Levchenko *et al*., Comput Phys Commun **192**, 60 (2015)
[2] S. Kokott *et al*., *arXiv* 2403.10343 (2024)

Strong scaling on NSC's tetralith

BZS 360 atoms HSE06 with FHI-aims on Tetralith

Strong scaling on NSC's tetralith

Dardel?

Unfortunately no. Cray MPI libraries are too buggy 👀.

PDC is aware.

No. MPI threads

Bandstructures in reasonable time
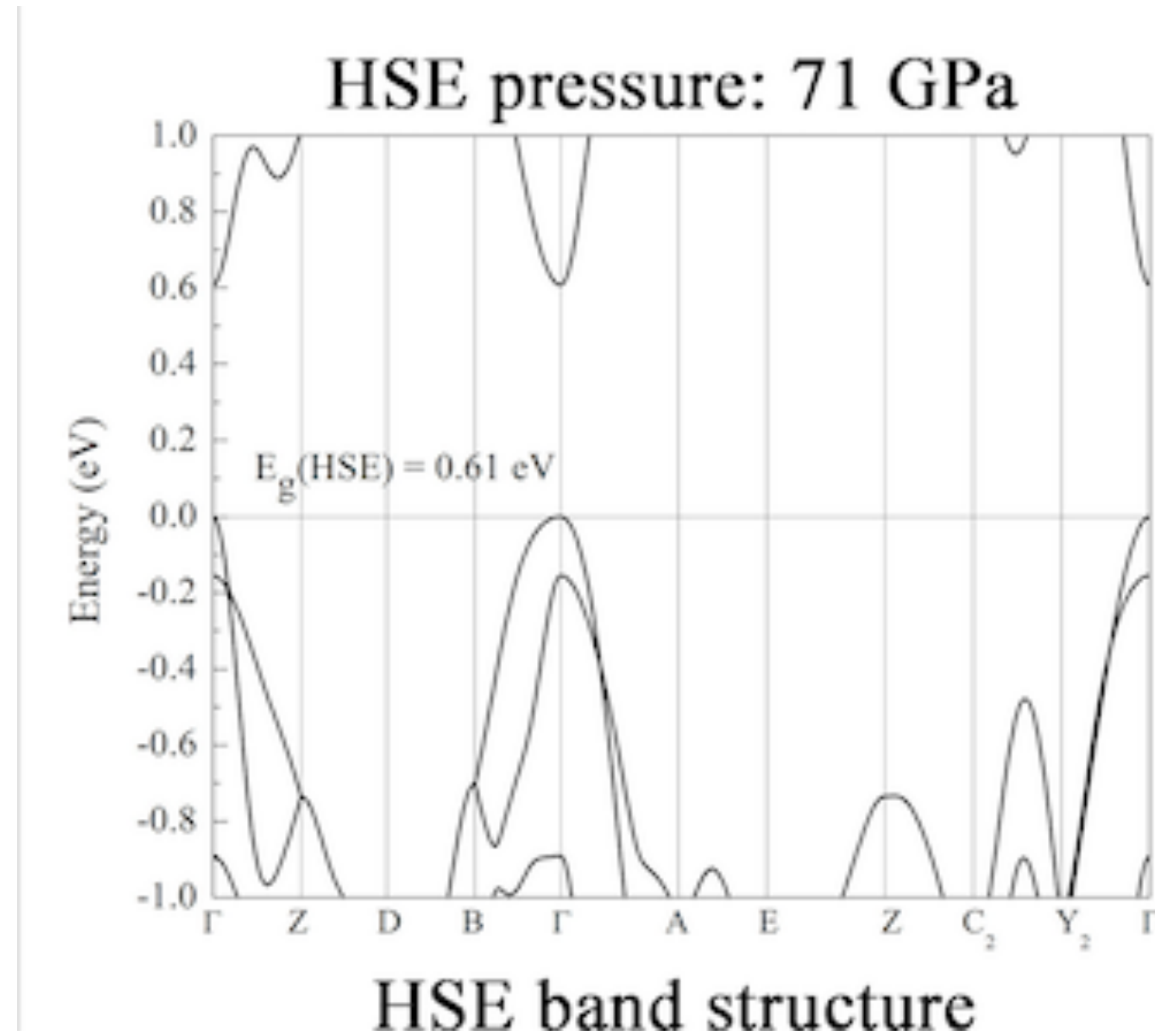
VASP:
4 nodes, 16 cores per node, 72h walltime
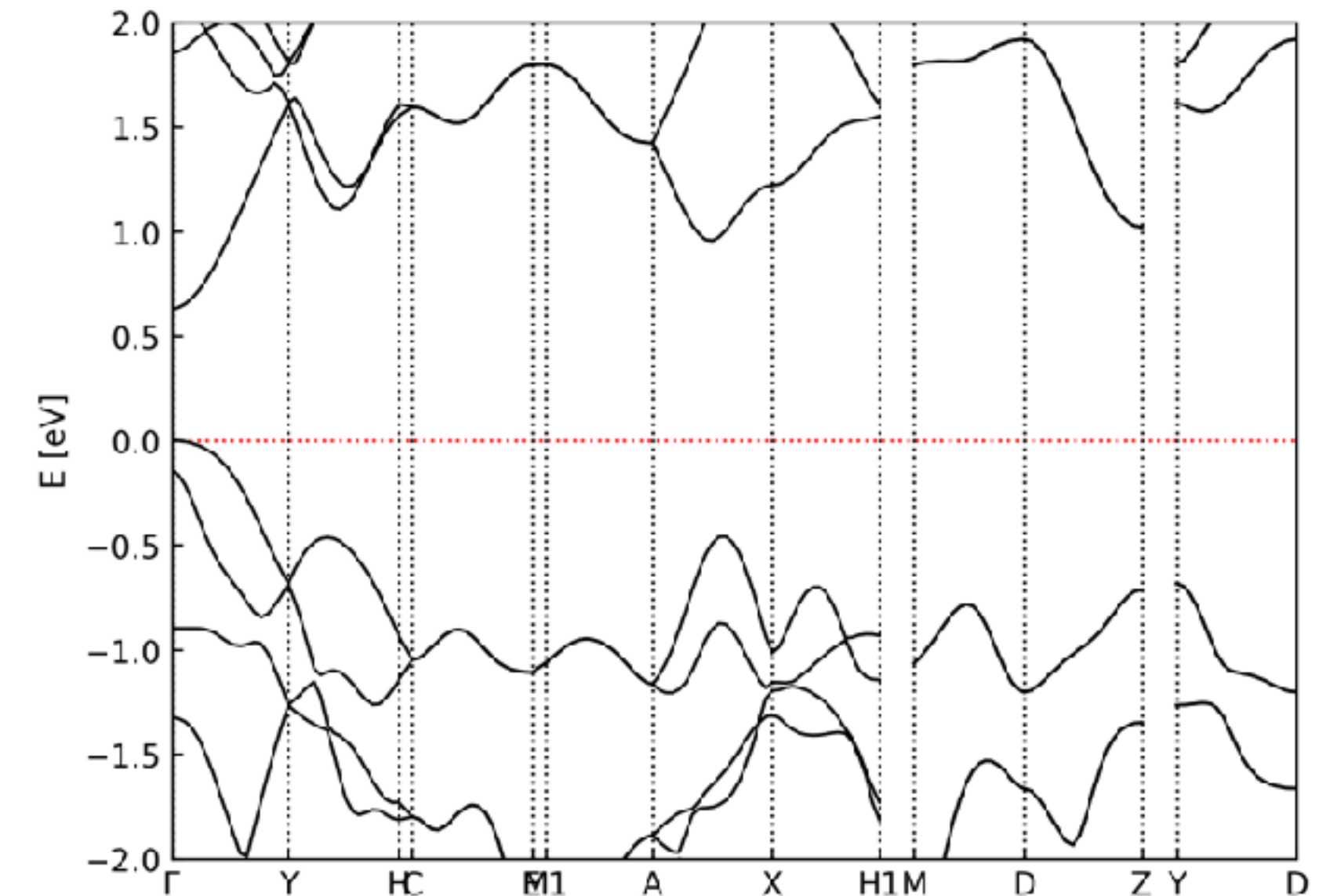
FHI-aims:
2 nodes, 32 cores per node, 1.5h walltime

How does it work?

Structures: `geometry.in`

```
>>> ase convert POSCAR geometry.in
```

How does it work?
CLI: CLIMS uses ASE

```
>>> pip install clims

>>> clims-configure --species-path \

    ~/local/FHIaims/species_defaults/defaults_2020/


>>> clims-prepare-run --species light --relax
```

How does it work?
Calculation parameters: `control.in`

```
xc                         pbe
relativistic               atomic_zora scalar
k_grid                     8 8 8
relax_geometry             trm 5e-3
relax_unit_cell            full

# plus more input for the basissets
…
```

How does i[...]
Calculation param[...]

```
xc
relativistic
k_grid
relax_geometry
relax_unit_cell

# plus more inp[...]
…
```



```
#==========================================================================
# FHI-aims file: control.in
# Created using the Atomic Simulation Environment (ASE)
# Fri Apr 19 16:55:22 2024
#==========================================================================
xc                          pbe
relativistic                atomic_zora scalar
k_grid                      8 8 8
relax_geometry              trm 5e-3
relax_unit_cell             full
#==========================================================================

################################################################################
#
#  FHI-aims code project
#  VB, Fritz-Haber Institut, 2009
#
#  Suggested "light" defaults for Pt atom (to be pasted into control.in file)
#  Be sure to double-check any results obtained with these settings for post-processing,
#  e.g., with the "tight" defaults and larger basis sets.
#
################################################################################
  species        Pt
#     global species definitions
    nucleus             78
    mass                195.084
#
    l_hartree           4
#
    cut_pot             3.5  1.5  1.0
    basis_dep_cutoff    1e-4
#
    radial_base         72 5.0
    radial_multiplier   1
    angular_grids specified
      division   0.4222   50
      division   0.9557  110
      division   1.2477  194
      division   1.5393  302
#     division   1.9382  434
#     division   2.0887  590
#     division   2.1534  770
#     division   2.2208  974
#     division   2.6985 1202
#     outer_grid    974
      outer_grid    302
################################################################################
#
#  Definition of "minimal" basis
#
################################################################################
```

How does it work?
CLI: CLIMS

```
>>> clims-prepare-run --species light --bands --dos —hse06
```

How does it work?
Calculation parameters: `control.in`

```
xc                              hse06 0.11
hse_unit                        bohr
hybrid_xc_coeff                 0.25
relativistic                    atomic_zora scalar
k_grid                          9 9 9
exx_band_structure_version      1
output             band   0.00000   0.00000   0.00000    0.00000   0.00000   0.50000   18 G  Y
output             band   0.00000   0.00000   0.50000   -0.46222   0.00000   0.54058   18 Y  H
output             band  -0.46222   0.00000   0.54058   -0.50000   0.00000   0.50000    2 H  C
output             band  -0.50000   0.00000   0.50000   -0.50000   0.50000   0.50000   19 C  E
output             band  -0.50000   0.50000   0.50000   -0.53778   0.50000   0.45942    2 E  M1
output             band  -0.53778   0.50000   0.45942   -0.50000   0.50000   0.00000   17 M1 A
output             band  -0.50000   0.50000   0.00000   -0.50000   0.00000   0.00000   19 A  X
output             band  -0.50000   0.00000   0.00000   -0.53778   0.00000   0.45942   17 X  H1
output             band  -0.46222   0.50000   0.54058    0.00000   0.50000   0.50000   18 M  D
output             band   0.00000   0.50000   0.50000    0.00000   0.50000   0.00000   18 D  Z
output             band   0.00000   0.00000   0.50000    0.00000   0.50000   0.50000   19 Y  D


# plus more input for the basissets
```

How does it work?
Run the job

```
#!/bin/bash -l


ulimit -s unlimited
export OMP_NUM_THREADS=1


srun /path/to/aims/build/aims.231208.scalapack.mpi.x
```

Final words

✔ **FHI-aims is easy to install** on tetralith/dardel → contact me

✔ **we have an FHI-aims license** → Florian Trybel

⚙ we could do a **small code tutorial?** → contact me

References

[1] V. Blum *et al*., Comput Phys Commun **180**, 2175 (2009).

[2] S. V. Levchenko *et al*., Comput Phys Commun **192**, 60 (2015).

[3] A. C. Ihrig *et al*., New J Phys **17**, 093020 (2015).
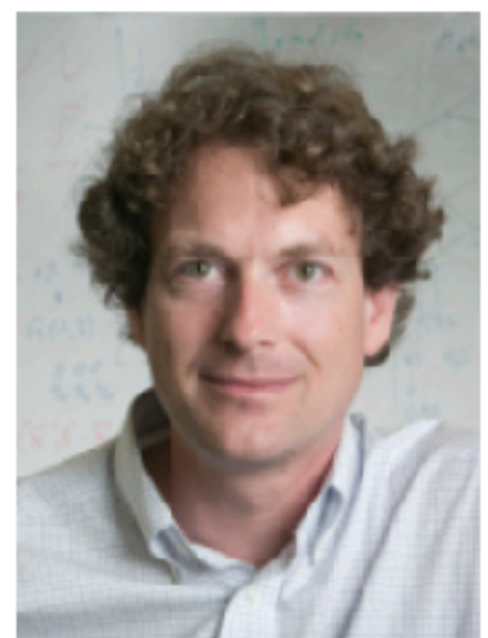
[4] S. Kokott *et al*., *arXiv* 2403.10343 (2024)

Thanks!

More info, code tutorials, etc:

fhi-aims.org

Sebastian Kokott
FHI / MSIP e.V.

Volker Blum
Duke University