

The FHI-aims Code

Efficient, Precise, Accurate All-Electron Theory of Materials and Molecules Based on Numeric Atom-Centered Orbitals

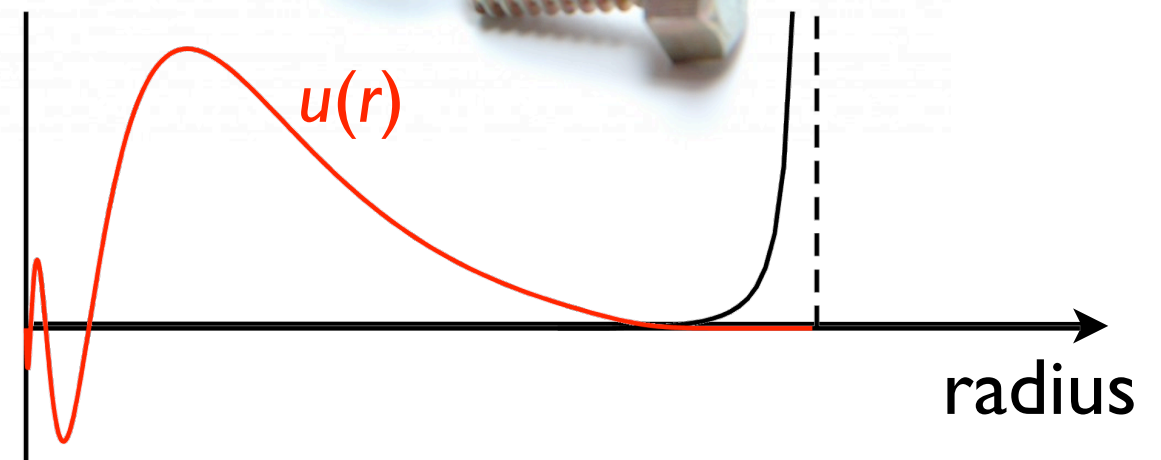
Volker Blum

Duke University
Department of Mechanical
Engineering and Materials Science
Durham, NC, USA
<http://aims.pratt.duke.edu>



<https://fhi-aims.org>

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



Who We Are

FHI-aims Code:



- **Very large community of contributors**
- Beginning: Volker Blum, Karsten Reuter, Matthias Scheffler, Fritz Haber Institute Berlin 2004
- Since then: **Hundreds of individuals, without whom FHI-aims would not exist**

Direct contributors to FHI-aims: ~150

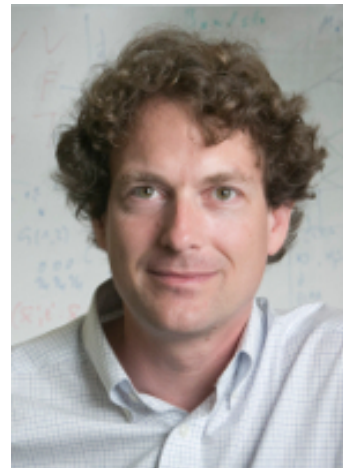
Creators of Today's Tutorial:



Sebastian Kokott
FHI / MSIP e.V.



Saeed Bohloul
FHI / MSIP e.V.



Volker Blum
Duke University

Tested by:

Jakob Filser
Mohammed Nakhaee

Amazing Community of Contributors - Thank You!



Alaa Akkoush, Heiko Appel, Victor Atalla, Kurt Baarmann, Carsten Baldauf, Alexej Bagrets, Daniel Berger, Josh Berryman, Sheng Bi, Benedikt Biedermann, Bjoern Bieniek, Volker Blum, Saeed Bohloul, Tiago Botari, Connor Box, Danilo Brambila, Daniel Bultrini, Christian Carbogno, Fabio Caruso, Marco Casadei, Michele Ceriotti, Wael Chibani, Sucismita Chutia, Fabio Della Sala, Maria Dragoumi, Andreas Dolfen, Marc Dvorak, Simon Erker, Ferdinand Evers, Eduardo Fabiano, Matt Farrow, Nicola Ferri, Karen Fidanyan, Jakob Filser, Lukas Gallandi, Ralf Gehrke, Luca Ghiringhelli, Mark Glass, Vivekanand Gobre, Dorothea Golze, Matthias Gramzow, Patrick Guetlein, Stefan Gutzeit, Volker Haigis, Felix Hanke, Paula Havu, Ville Havu, Joscha Hekele, Olle Hellman, Jan Hermann, Oliver Hofmann, Johannes Hoja, Xiaojuan Hu, William Huhn, Lukas Hörmann, Arvid Ihrig, Timo Jacob, Adam Jackson, Svenja Janke, Ran Jia, Rainer Johanni, Werner Jürgens, Matthias Kahk, Yosuke Kanai, Levi Keller, Matthias Kick, Woo Youn Kim, Jan Kloppenburg, Florian Knoop, Franz Knuth, Simone Koecher, Gabrielle Koknat, Sebastian Kokott, Raul Laasner, Lucas Lang, Bjoern Lange, Marvin Lechner, Maja-Olivia Lenz, Sergey Levchenko, Alan Lewis, Jiachen Li, Xinzheng Li, Kailai Lin, Konstantin Lion, Yair Litman, Chi Liu, Andrew Logsdaile, Andreas Marek, Thomas Markovich, Reinhard Maurer, Florian Merz, Joerg Meyer, Wenhui Mi, Evgeny Moerman, Christoph Muschielok, Mohammad Nakhaee, Lydia Nemec, Norbert Nemec, Kane O'Donnell, Harald Oberhofer, Berk Onat, Eszter Pos, Thomas Purcell, Nathaniel Raimbault, Karsten Rasim, Xinguo Ren, Karsten Reuter, Norina Richter, Stefan Ringe, Patrick Rinke, Herzain Rivera, Matti Ropo, Mariana Rossi, Tuomas Rossi, Adrienn Ruzsinszky, Nikita Rybin, Georg Michelitsch, Andrea Sanfilippo, Matthias Scheffler, Markus Schneider, Christoph Schober, Franziska Schubert, Honghui Shang, Tonghao Shen, Markus Sinstein, Justin Clifford Smith, Ari-Pekka Soikkeli, Ruyi Song, Aloysius Soon, Muhammad Tahir, Alexandre Tkatchenko, Thomas Theis, Alvaro Vazquez Mayagoitia, Suzy Wallace, Tianlin Wang, Yanyong Wang, Jürgen Wieferink, Scott Woodley, Jianhang Xu, Yong Xu, Yi Yao, Mina Yoon, Ted Yu, Victor Yu, Zhenkun Yuan, Marios Zacharias, Igor Ying Zhang, Wenxing Zhang, Rundong Zhao, Ruiyi Zhou, Yuanyuan Zhou, Tong Zhu

... and, with absolute certainty, more! Thank you!

How Are “We” Organized

FHI-aims is licensed through MSIP e.V. - registered non-profit organization, objective is support of basic science

“aimsclub” used for registration

Slack Channel - fhi-aims.slack.com, 430 users (August 24, 2021)

Community Server - <https://aims-git.rz-berlin.mpg.de>, 483 users (August 24, 2021)
Development, stable versions, issue tracker, wiki & build instructions, ...

Broad ecosystem of connected infrastructure:

ASE, i-Pi, phonopy, FHI-vibes, GIMS, MDAnalysis, GAtor/Genarris, CECAM ESL, many more.

The screenshot displays the Slack interface for the #general channel of FHI-aims. The left sidebar shows the channel list with 'FHI-aims' selected, listing members like Volker Blum and various navigation options. The main area shows a message from Tuesday, June 16th, containing a Python traceback error. The error details include file paths like '/work/07478/tg867772/stampede2/FHIaims/regression_tests/core/testparameter.py' and lines 136, 186, and 85. A discussion thread on the right, titled '#general', shows a message from Andrew Logsdail asking about the build process and executable naming, mentioning the QM/MM package and the need for users to manually define the executable name.

FHI-aims ▾
● Volker Blum

☰ All unreads
🔍 Threads
@ Mentions & reactions
📄 Drafts
🔖 Saved items
Channel browser
👤 People
📱 Apps
📁 Files
↑ Show less

#general ☆
👤 266 | 📌 1 | Main chat channel for FHI-aims users and developers. If you have issue, please note them here, too: <https://aims-g...>

Tuesday, June 16th ▾

```
Traceback (most recent call last):
  File "/work/07478/tg867772/stampede2/FHIaims/regression_tests/core/testparameter.py", line 136,
    in _diff_files
      raise StopIteration
StopIteration

The above exception was the direct cause of the following exception:

Traceback (most recent call last):
  File "./regressiontools.py", line 70, in <module>
    main()
  File "./regressiontools.py", line 49, in main
    suite.evaluate()
  File "/work/07478/tg867772/stampede2/FHIaims/regression_tests/core/regressionsuite.py", line
186, in evaluate
    statustable.add_row(suite.evaluate())
  File "/work/07478/tg867772/stampede2/FHIaims/regression_tests/core/testsuite.py", line 85, in
evaluate
```

Thread
#general

Andrew Logsdail Yesterday at 6:39 AM
Hi all. I very much like the dated stamped executables used when building FHI-aims but wonder if it would also be acceptable to include a small addition to the build process where a generically named link is created to the timestamped executable on each new build, e.g. `ln -s executable aims`? One of the problems we are finding with the QM/MM package I work on is the need for users to manually define the executable name when packages are not hard-linked, whereas just explaining the need to put the build path into `$PATH` and knowing the executable will be picked up is a little simpler. One could also see long-term benefits for other interfacing packages, e.g. ASE. Thoughts?

1 reply

Why FHI-aims?



Vision:

Quantum mechanics based simulations of real, complex molecules, materials and their properties without a priori precision and accuracy limitations.

→ Algorithmic choices and priorities:

- All-electron
- Non-periodic and periodic systems on equal footing
- Scalability to large systems (thousands of atoms) without precision limitations
- Seamless scalability from laptop to massively parallel and/or new HPC architectures
- Density functional theory and correlated methods (RPA, GW, ...)

Critical choice

- Numeric atom-centered basis functions (accurate representation of occupied orbitals and densities)

Example - Semiconductors, Hybrid DFT

Predicted
Observable

High-precision atomic structure,
energies and energy differences

Energy band structures for
large, complex systems

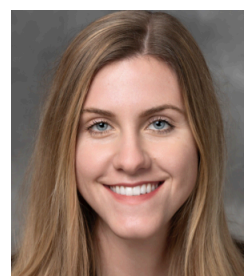
Level of
Theory

Semilocal density functional theory
with van der Waals corrections

Hybrid density functional theory
including spin-orbit coupling



Dr. Yi Yao



Gabrielle
Koknat

Example:

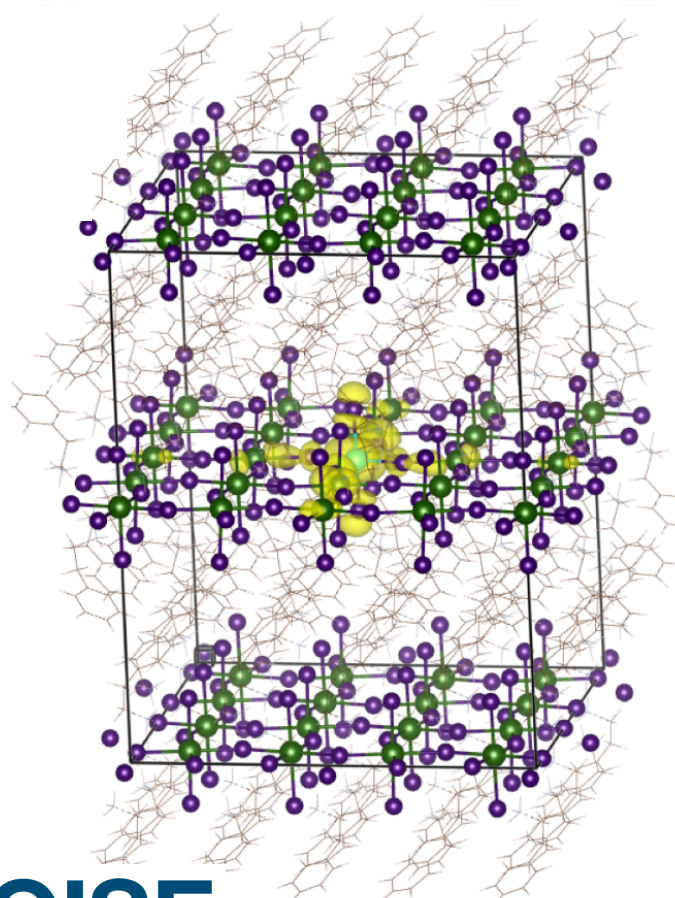
Bi-doped $(\text{PEA})_2\text{PbI}_4$

1,504 atoms

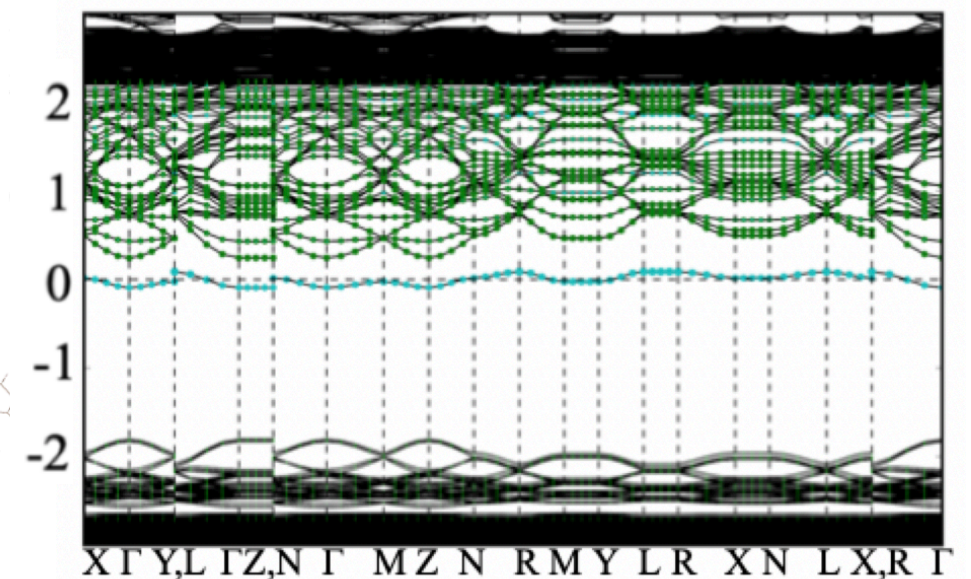
HSE06+SOC,

all-electron

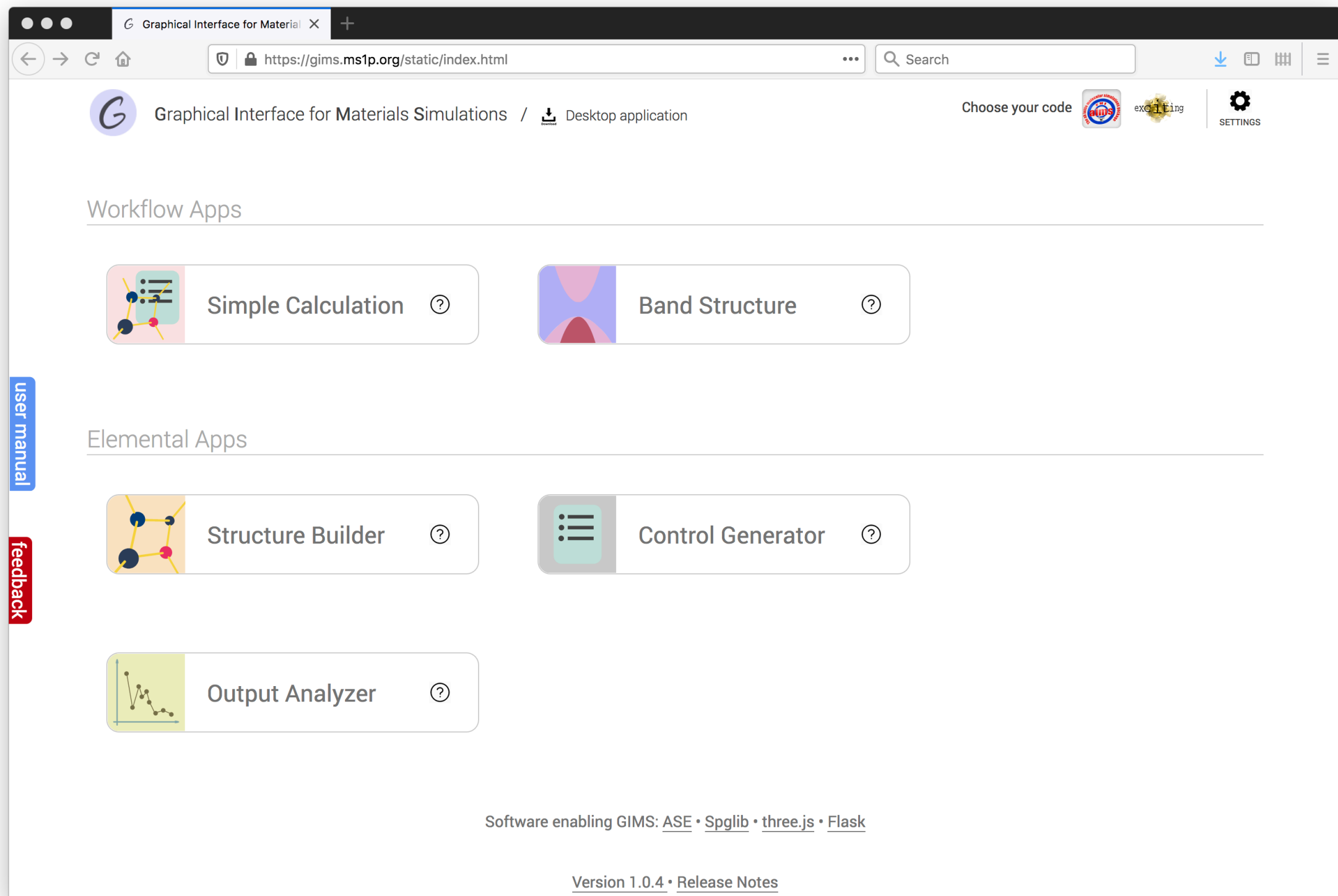
High precision -
no tricks!



DFT-HSE06+SOC Band Structure



Usability - Open, Free, Browser-Based Interface: “GIMS”



Sebastian Kokott, Iker Hurtado, Christian Vorwerk, Claudia Draxl, Volker Blum, Matthias Scheffler.
GIMS: Graphical Interface for Materials Simulations. *Journal of Open Source Software*, 6(57), 2767.
<https://doi.org/10.21105/joss.02767>

This Talk

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r})$$

Kohn-Sham Equations, 1965

Technical concepts:

- Basis sets
- Precision
- Hybrid DFT & spin-orbit coupling for large, complex materials
- Integrals and grids
- Scalability (large systems, large computers, GPU)

Standard Steps to “Practical” Electronic Structure Theory

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

P.A.M.
Dirac



1) Separate Electron and Nuclear Coordinates (Born-Oppenheimer Approximation)

2) Address the electronic problem:

$$\sum_k \frac{p_k^2}{2m_e} + \sum_{I,k} \frac{Z_I}{2|R_I - r_k|} - \sum_{k \neq k'} \frac{1}{2|r_k - r_{k'}|}$$

↘ $\hat{H}_{\text{el}}$

$$\hat{H}_{\text{el}}\Phi(\{R_I\}, \{r_k\}) = E(\{R_I\}) \cdot \Phi(\{R_I\}, \{r_k\})$$

This talk: Focus on solution of the electronic problem.

Current “workhorse” electronic structure theory

Quantum chemistry & many-body theory:

$$E_{\text{tot}} \leq \langle \psi | H | \psi \rangle \quad \dots \text{successive refinement of } \psi$$

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

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

“Perdew’s ladder”
to exact solution

- Key practical approximation: E_{xc}

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

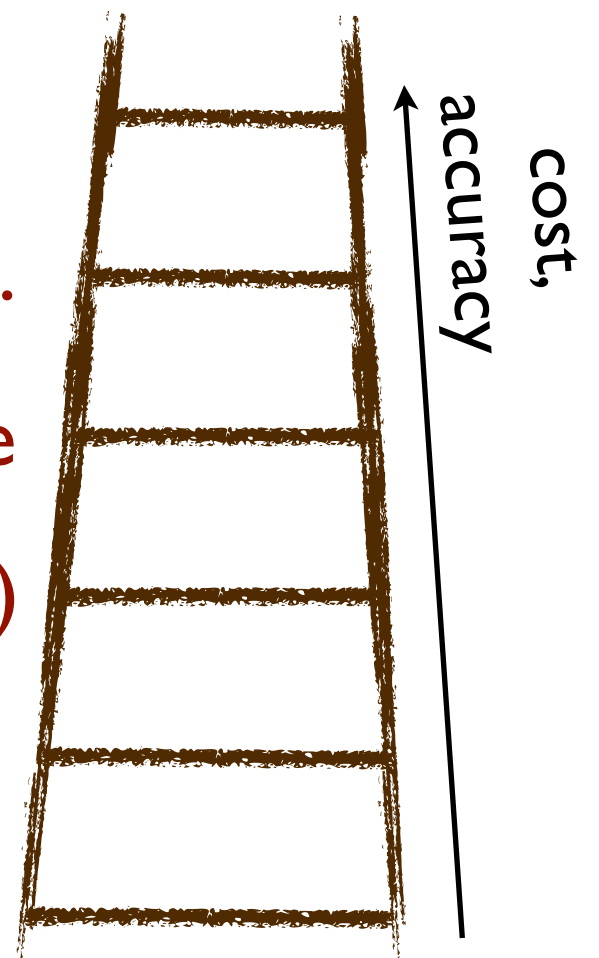
hybrid functionals: non-local exchange

+ van der Waals

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

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

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



The Kohn-Sham Equations - How to Solve Them

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r})$$

“As (almost) everyone does”:

I. Pick *basis set* $\{|\varphi_i\rangle\}$:

$$\psi_k(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r})$$

Inserting a Basis Set

$$\underbrace{\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right]}_{\hat{h}_{\text{KS}}} \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r})$$

“As (almost) everyone does”:

I. Pick *basis set* $\{|\varphi_i\rangle\}$:

$$\longrightarrow \sum_i \hat{h}_{\text{KS}} c_{ki} \varphi_i(\mathbf{r}) = \sum_i \epsilon_k c_{ki} \varphi_i(\mathbf{r})$$

$$\psi_k(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r})$$

$$\int d^3\mathbf{r} \varphi_j^*(\mathbf{r}) \dots : \quad \text{(integrate from left side)}$$

$$\sum_i c_{ki} \underbrace{\left(\int d^3\mathbf{r} \varphi_j^*(\mathbf{r}) \hat{h}_{\text{KS}} \varphi_i(\mathbf{r}) \right)}_{h_{ji}} = \sum_i \epsilon_k c_{ki} \underbrace{\left(\int d^3\mathbf{r} \varphi_j^*(\mathbf{r}) \varphi_i(\mathbf{r}) \right)}_{s_{ji}}$$

The Kohn-Sham Equations - How to Solve Them

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r})$$

“As (almost) everyone does”:

1. Pick *basis set* $\{|\varphi_i\rangle\}$:

$$\psi_k(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r})$$

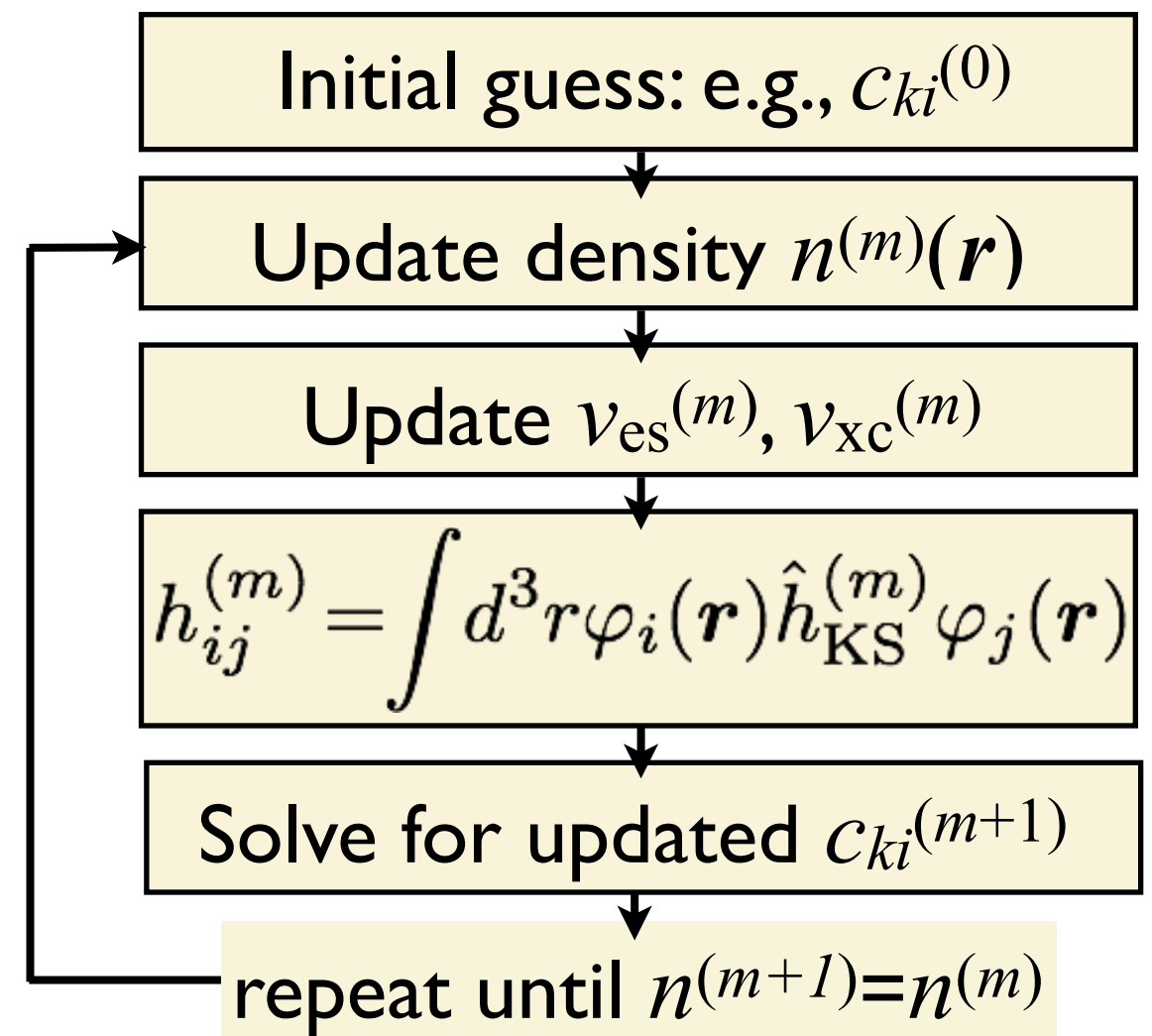
→ generalized eigenvalue problem:

$$\underline{\underline{h}} \underline{\underline{c}}_k = \epsilon_k \underline{\underline{s}} \underline{\underline{c}}_k$$

$$h_{ij} = \langle \varphi_i | \hat{h}_{\text{KS}} | \varphi_j \rangle$$

$$s_{ij} = \langle \varphi_i | \varphi_j \rangle$$

2. Self-consistency:

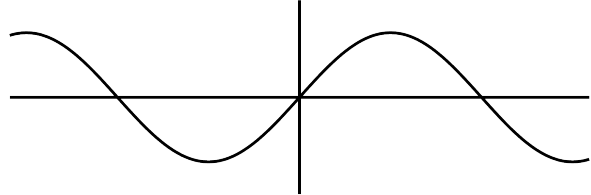
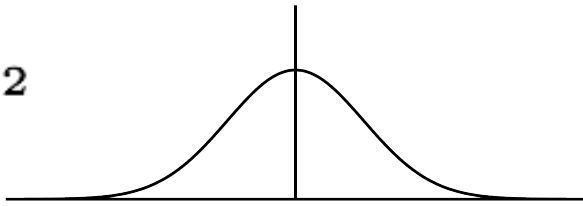


Representing the Orbitals: Basis Sets

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_i c_{\mathbf{k}i} \varphi_i(\mathbf{r})$$

... impacts all further algorithms
(efficiency, accuracy)

Many good options:

- Plane waves $\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{N} e^{i\mathbf{k}\mathbf{r}}$ 
 - efficient FFT's (density, electrostatics, XC-LDA/GGA)
 - inherently periodic
 - not all-electron (*Slater 1937*) - need “pseudoization”
- Gaussian-type orbitals $\varphi_i(\mathbf{r}) = \frac{1}{N} r^l e^{-\alpha r^2}$ 
- Augmented plane waves (*Slater 1937; Andersen 1975; etc.*)
- Many others: (L)MTO, “real-space”, wavelets, ...
- **FHI-aims (this talk)**: Numeric Atom-Centered Basis Functions

Our Choice: Numeric Atom-Centered Basis Functions

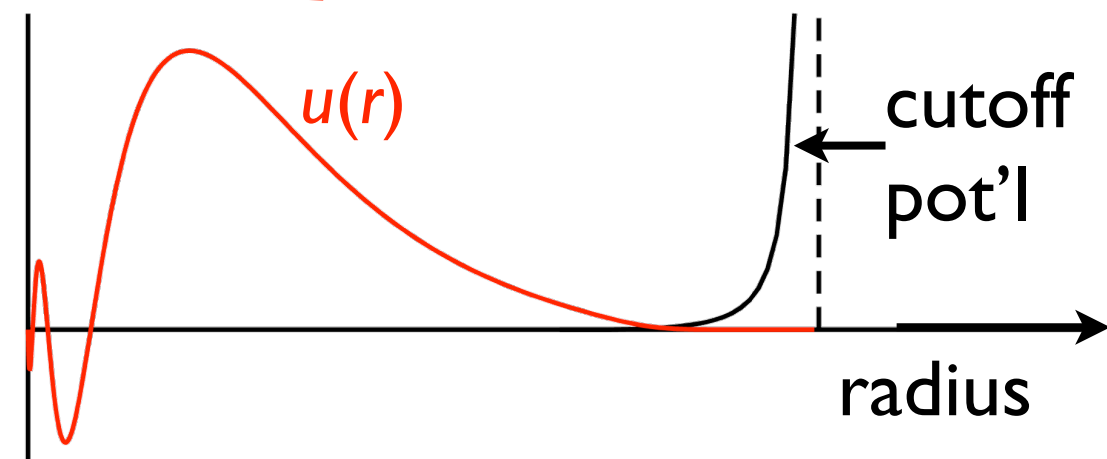
$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} \cdot Y_{lm}(\Omega)$$

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

- $u_i(r)$: 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), ...



Our Choice: Numeric Atom-Centered Basis Functions

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

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

- $u_i(r)$: Flexible choice - “Anything you like.”
 - Localized; “naturally” all-electron
 - The choice of efficient and of enough radial functions is obviously important
 - But need a “basis set library” - list of basis functions for all elements (1-102), from fast qualitative to meV-converged total energies (LDA/GGA/hybrid DF’s) - how to construct this list?

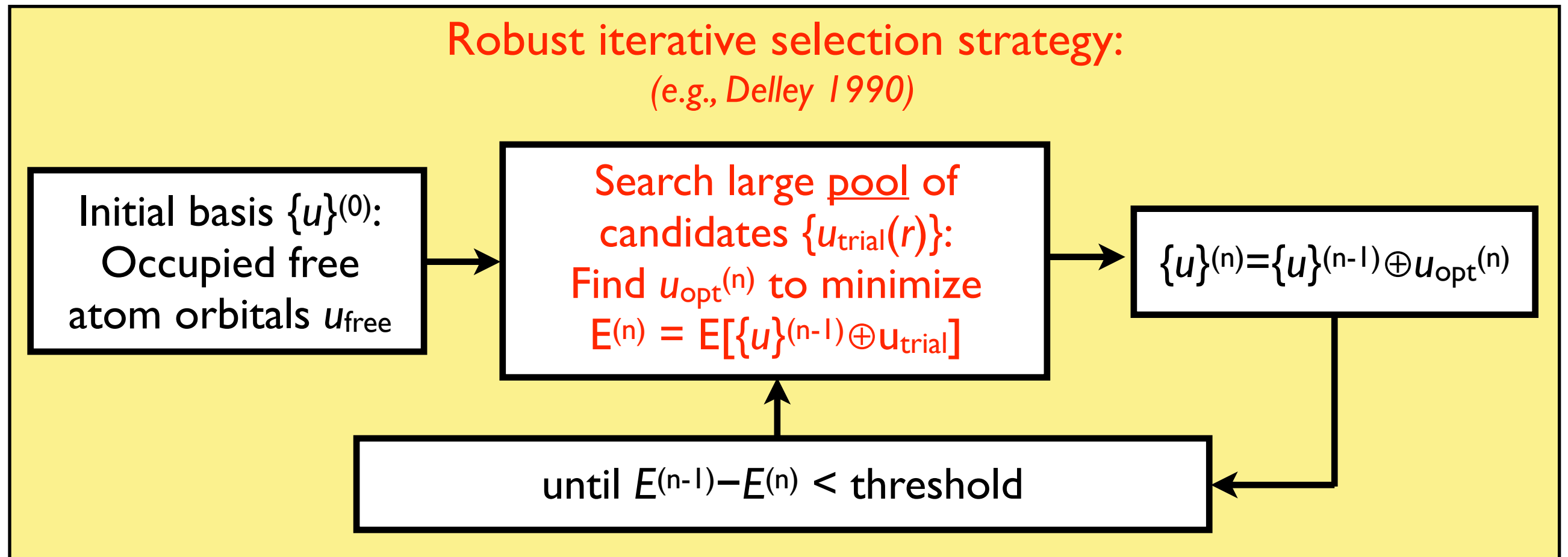
V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler,
“*Ab Initio* Molecular Simulations with Numeric Atom-Centered Orbitals”,
Computer Physics Communications **180**, 2175-2196 (2009)

Constructing a Basis Set Library for DFT

Goal: Element-dependent, *transferable* basis sets
from fast qualitative to meV-converged total energy accuracy (ground-state DFT)

Can't we have the computer pick
good basis sets for us?

Robust iterative selection strategy:
(e.g., Delley 1990)

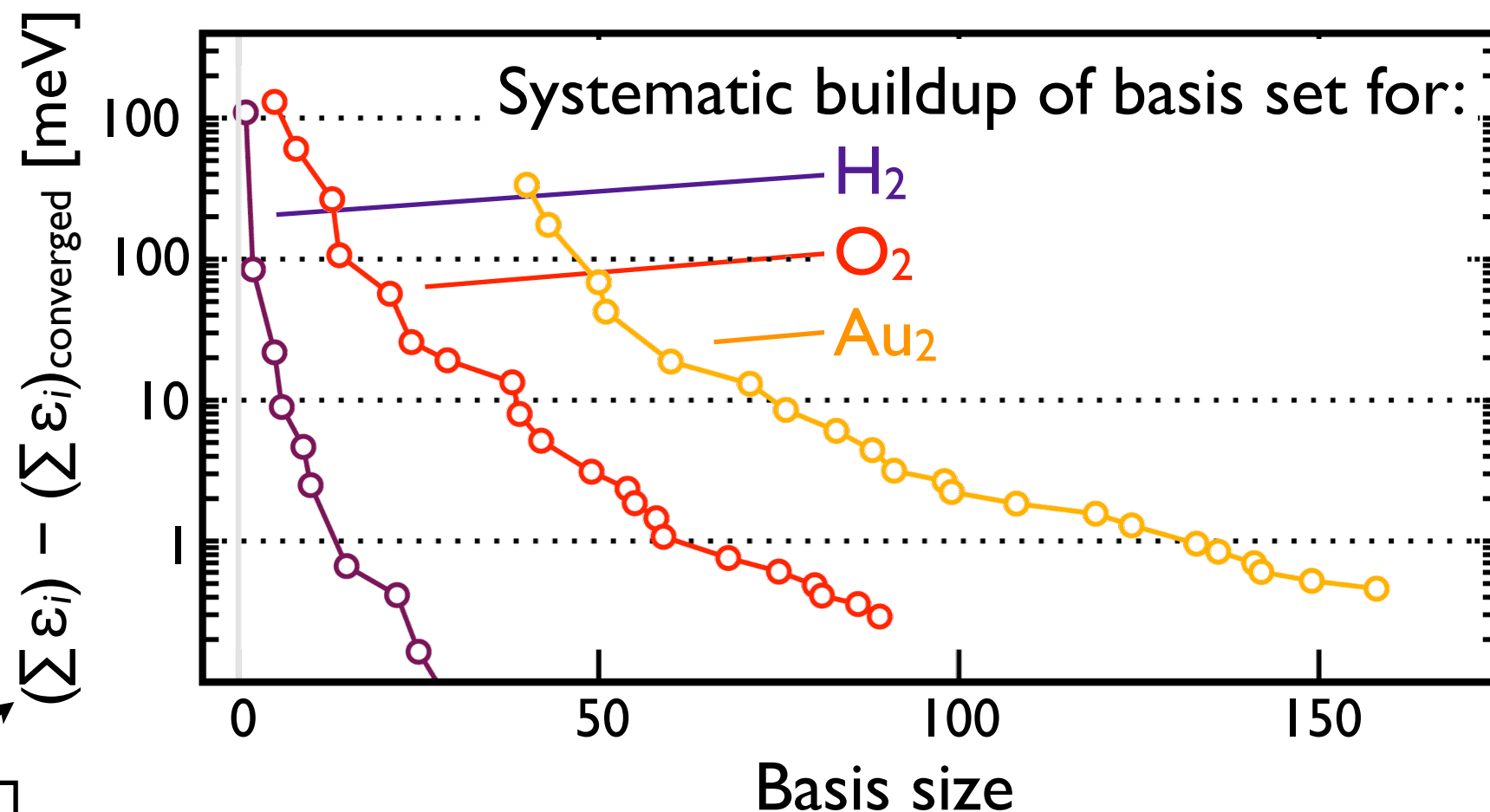


Iterative Selection of NAO Basis Functions

“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



Outcome: Hierarchical Basis Set Library for Elements 1-102

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

	H	C	O	Au
minimal	1s	[He]+2s2p	[He]+2s2p	[Xe]+6s5d4f
Tier 1	H(2s,2.1) H(2p,3.5)	H(2p,1.7) H(3d,3.5) H(2s,1.2)	H(2p,1.0) H(3d,3.5) H(2s,1.2)	H(2p,1.0) H(3d,3.5) H(2s,1.2)
Tier 2	H(1s,0.85) H(2p,3.7) H(2s,1.2) H(3d,7.0)	H(4f,11.2) H(3p,4.8) H(3s,3.2) H(5g,11.2)	H(4f,11.2) H(3p,4.8) H(3s,3.2) H(5g,11.2)	H(4f,11.2) H(3p,4.8) H(3s,3.2) H(5g,11.2)
Tier 3	H(4f,11.2) H(3p,4.8)	H(2p,1.7) H(2s,1.2)	H(2p,1.0) H(2s,1.2)	H(2p,1.0) H(2s,1.2)
...	...	...	...	...

In FHI-aims input (example: Hydrogen, tight settings):

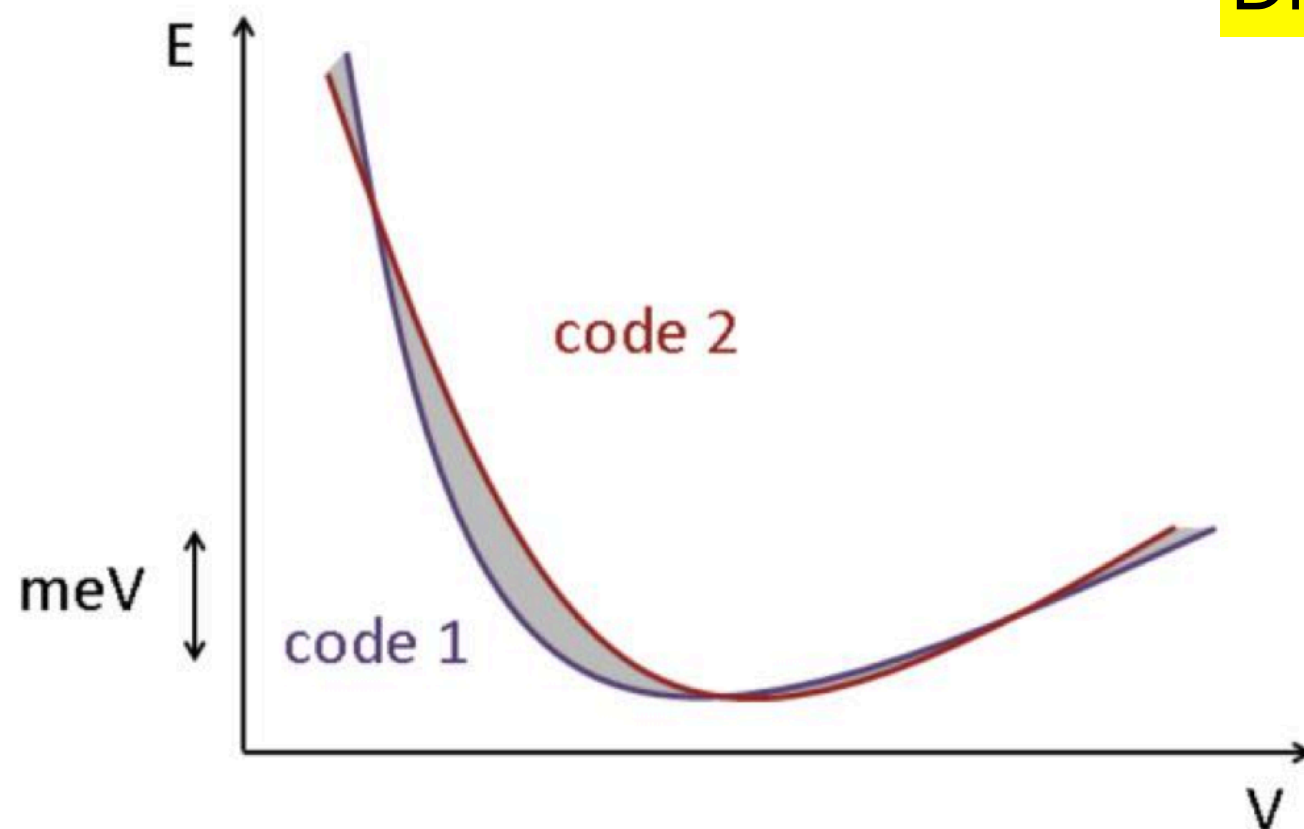
```
#####
#
# Definition of "minimal" basis
#
#####
#   valence basis states
#   valence      1 s  1.
#   ion occupancy
#   ion_occ      1 s  0.5
#####
#
# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Basis constructed for dimers: 0.5 A, 0.7 A, 1.0 A, 1.5 A, 2.5 A
#
#####
# "First tier" - improvements: -1014.90 meV to -62.69 meV
#   hydro 2 s 2.1
#   hydro 2 p 3.5
# "Second tier" - improvements: -12.89 meV to -1.83 meV
#   hydro 1 s 0.85
#   hydro 2 p 3.7
#   hydro 2 s 1.2
#   hydro 3 d 7
# "Third tier" - improvements: -0.25 meV to -0.12 meV
#   hydro 4 f 11.2
#   hydro 3 p 4.8
#   hydro 4 d 9
#   hydro 3 s 3.2
#####
```

Precision in Community Wide Benchmark - “Delta Test”

Reproducibility in Density-Functional Calculations of Solids,
K. Lejaeghere, ... **68 coauthors!** ..., S. Cottenier,
Science **351**, aad3000 (2016).
<https://molmod.ugent.be/deltacodesdft>

$E(V)$ for 71 elemental solids - 15 codes, all-electron & 40 pseudopot'l sets

FHI-aims: Test carried out independently by
Dr. Marcin Dulak, DTU (Copenhagen)



$$\rightarrow \Delta_i(a, b) = \sqrt{\int_{0.94V_{0,i}}^{1.06V_{0,i}} \frac{(E_{b,i}(V) - E_{a,i}(V))^2}{0.12V_{0,i}} dV}$$

Precision in Community Wide Benchmark - “Delta Test”

Reproducibility in Density-Functional Calculations of Solids,
K. Lejaeghere, ... 68 coauthors! ..., S. Cottenier,
Science **351**, aad3000 (2016).
<https://molmod.ugent.be/deltacodesdft>

E(V) for 71 elemental solids - 15 codes, all-electron & 40 pseudopot'l sets

Code	Basis	Electron treatment	Delta (meV)
Wien2k 13.1	LAPW/APW+lo	All-electron	0
FHI-aims 081213*	NAO, tier2	All-electron (scalar rel. atomic ZORA)	0.2
Exciting (dev.)	LAPW+xl	All-electron	0.2
Quantum Espresso 5.1	plane waves	SSSP accuracy (mixed NC/US/PAW library)	0.3
VASP 5.2.12	plane waves	PAW 2015	0.3
FHI-aims 081213*	NAO, tier2	All-electron (scalar rel., scaled ZORA)	0.3
ELK 3.1.5	APW+lo	All-electron	0.3

...

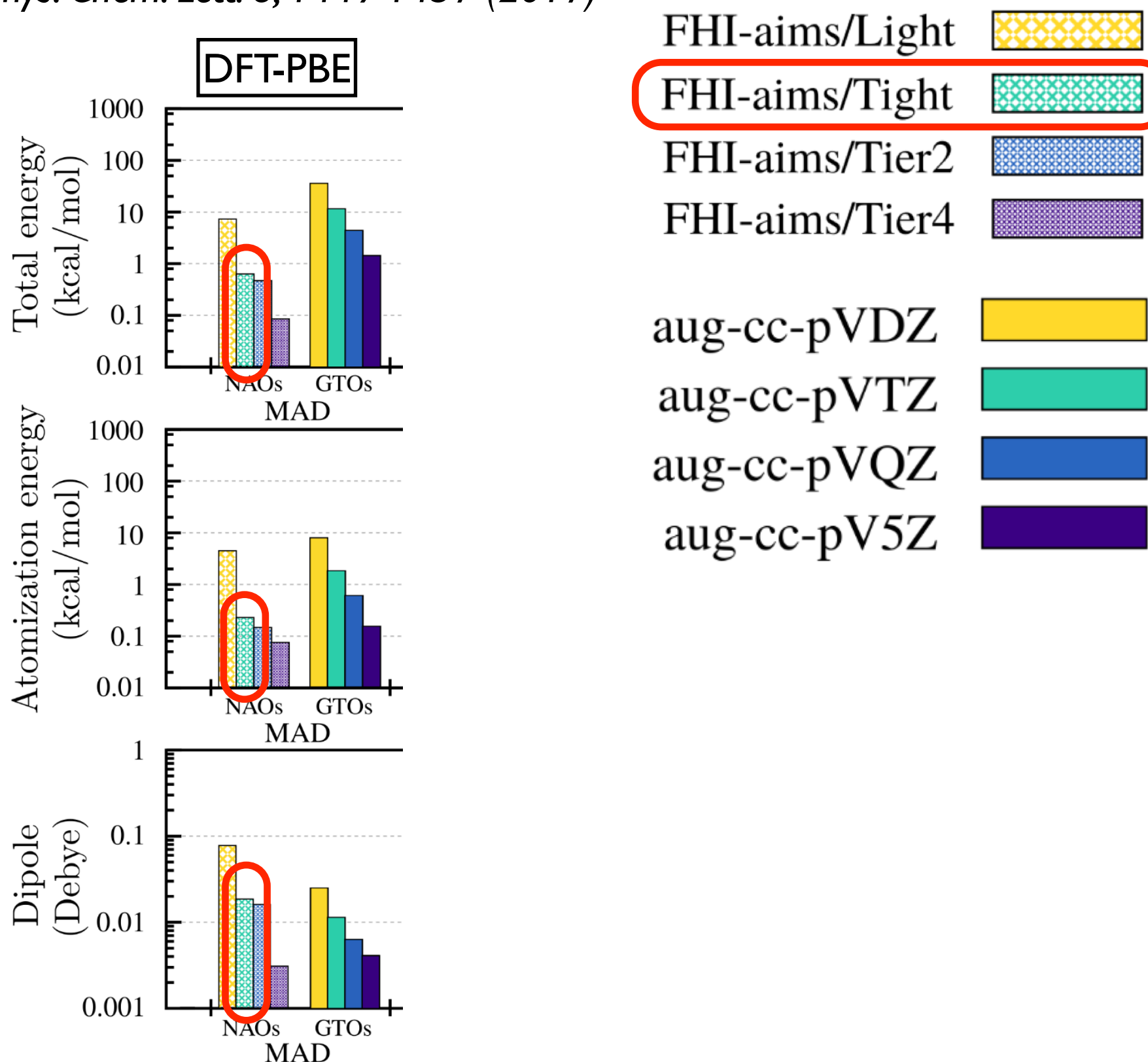
**Results: Marcin Dulak,
DTU (Copenhagen)*

Total and Atomization Energies vs. an Absolute Reference

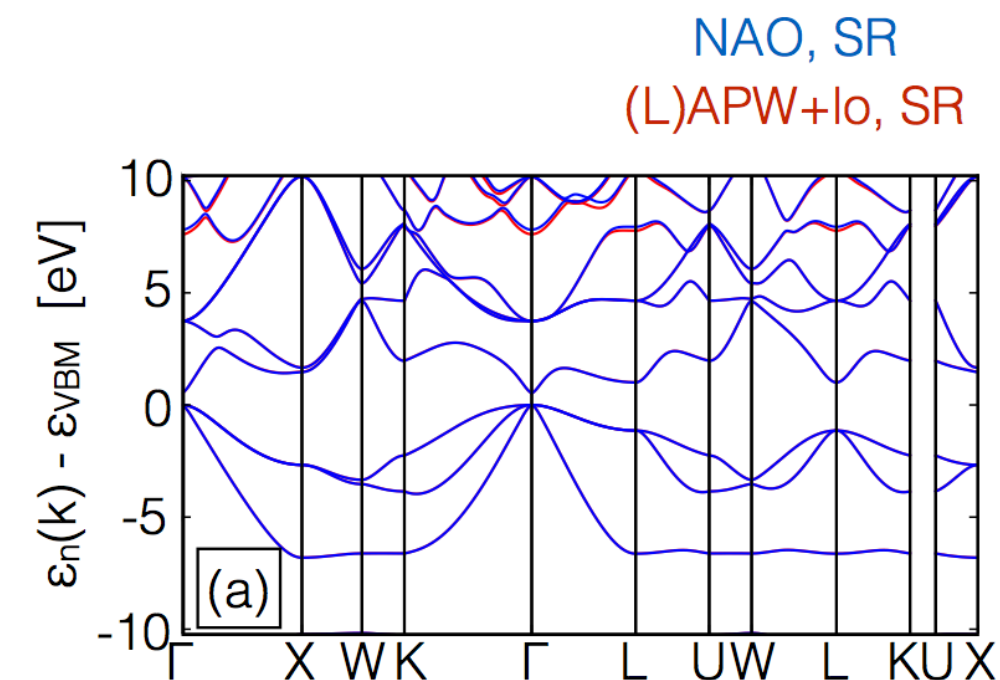
Stig Rune Jensen, Santanu Saha, Jose A. Flores-Livas, William Huhn, Volker Blum, Stefan Goedecker, Luca Frediani
J. Phys. Chem. Lett. 8, 1449-1457 (2017)

Reference: “MRChem”
Multiresolution wavelets
(μHa accuracy)

Benchmark:
211 molecules,
elements 1-18
DFT-LDA, PBE, PBE0



Benchmark: Scalar-Relativistic Band Structures for 103 Solids



45 elemental structures,
37 compound semiconductors,
21 strongly ionic compounds;
66 elements included

[VBM - 10 eV, VBM]

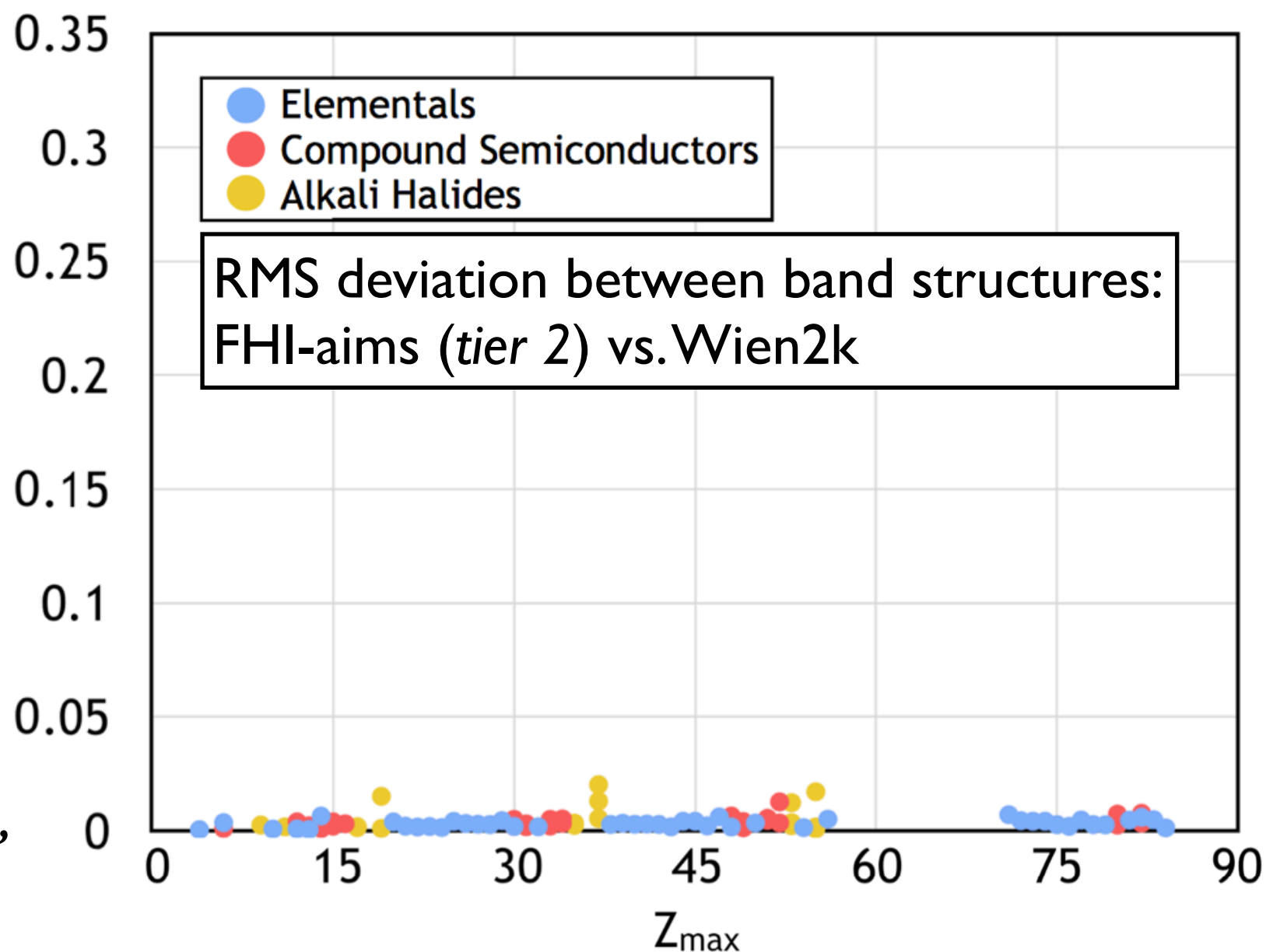
$\Delta_{\text{band}} [\text{eV}/\text{band}]$

... basically identical with Wien2k
reference set (LAPW)



Dr. William Huhn
(Duke Univ.)

Scalar-Relativistic



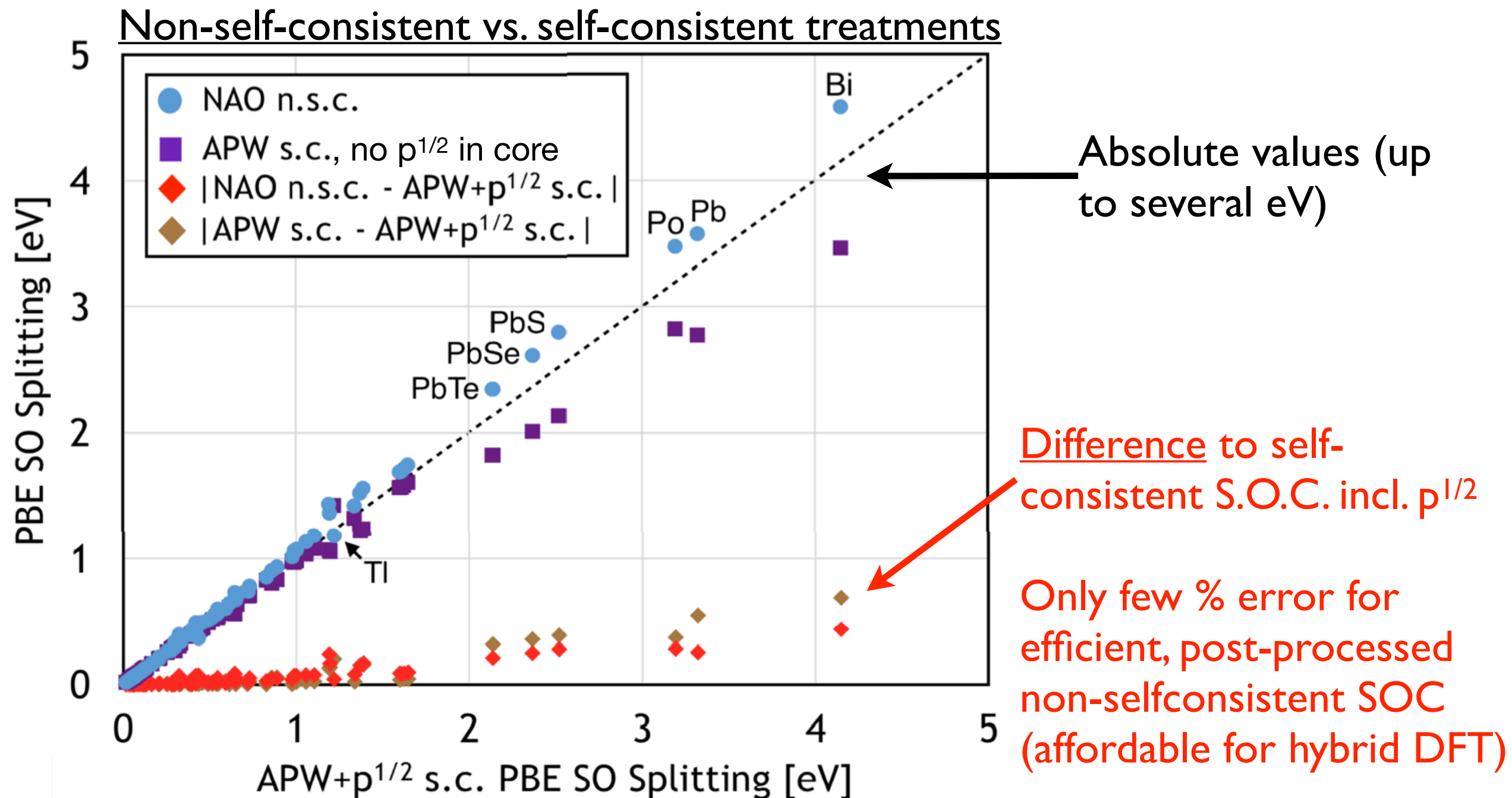
Huhn, Blum, *Phys. Rev. Materials* **1**,
033803 (2017).

Benchmark for Spin-Orbit Splittings

Huhn, Blum, Phys. Rev. Materials **1**, 033803 (2017).

Target: Largest SO Splitting in each compound band structure ($\sim$ strength of SOC)

Reference (dashed line): Wien2k, LAPW, self-consistent SOC incl. $p^{1/2}$ in core

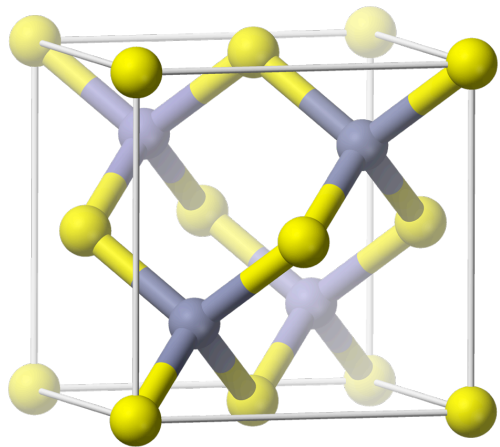


Hybrid Density Functionals: Scalable to Large Systems

*Ihrig, Wieferink, Zhang, Ropo, Ren, Rinke, Scheffler, Blum, New J. Phys. **17**, 093020 (2015)*
*Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler, Comp. Phys. Commun. **192**, 60-69 (2015).*

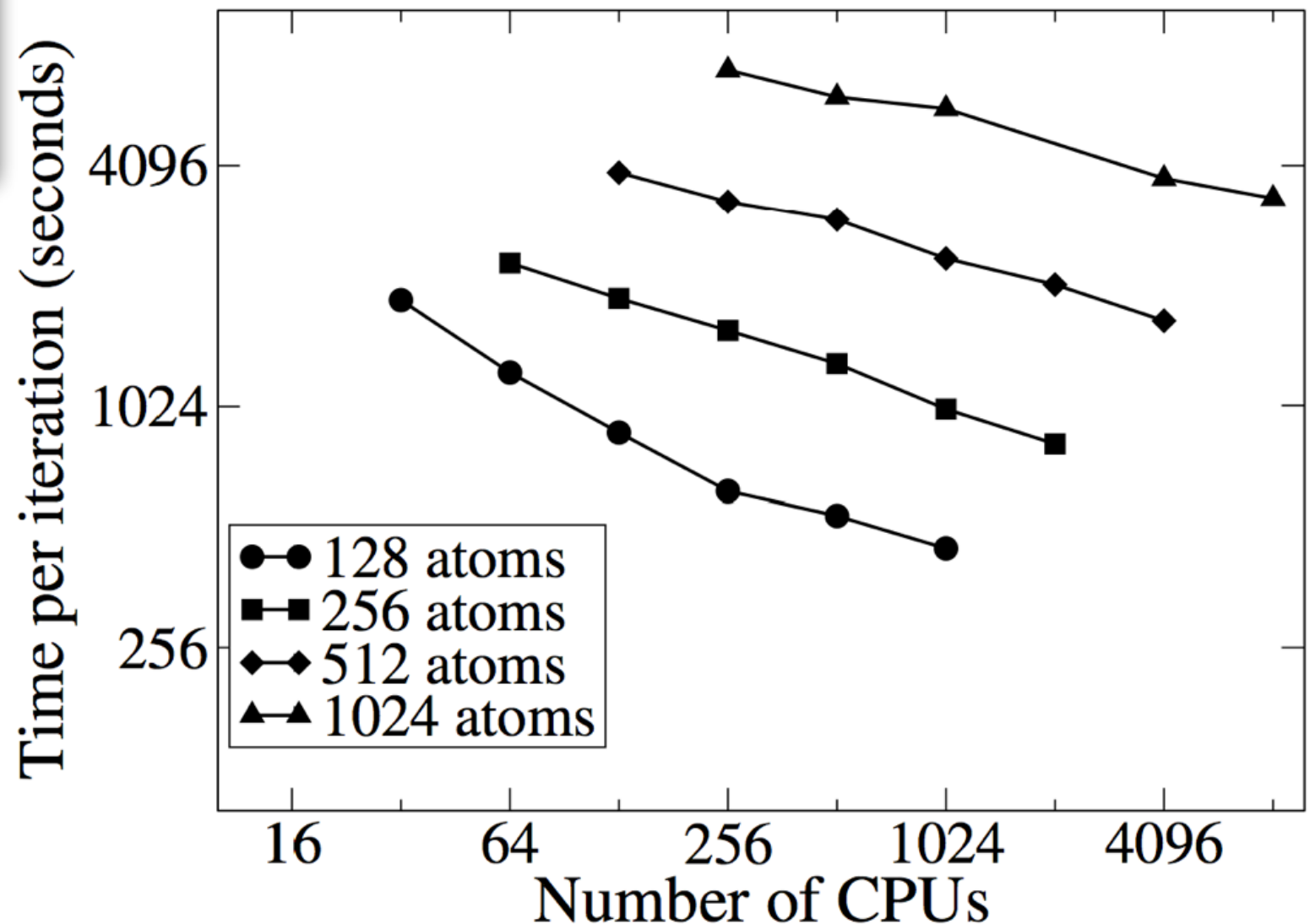
$O(N)$ scaling implementation,
localized resolution of identity.

*Note: Localized RI also works for MP2,
RPA, GW, etc. (but not $O(N)$)*



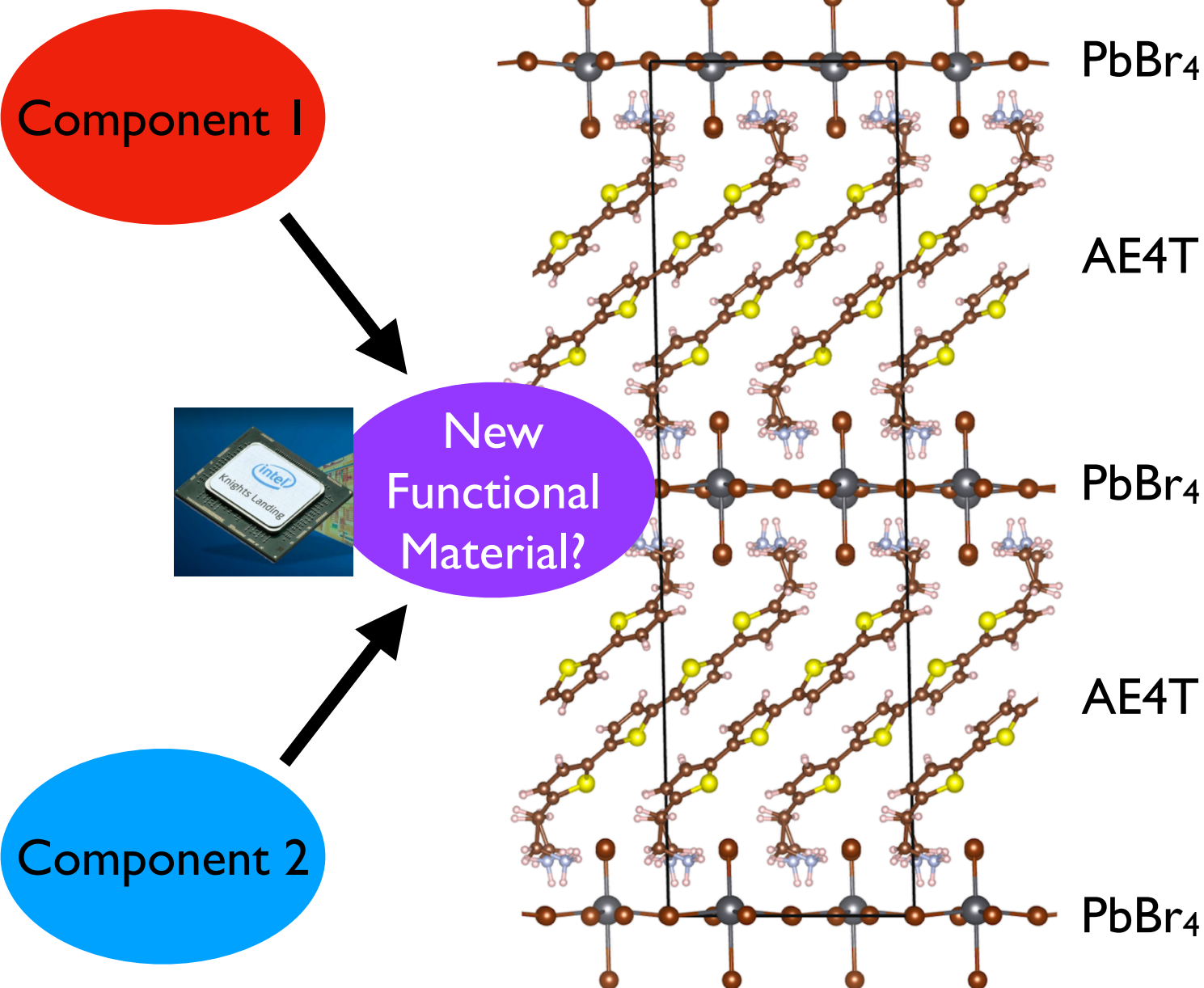
Zincblende GaAs

Computational Scaling of Periodic GaAs, “tight” HSE06 Hybrid Density-Functional Theory



SOC in Heavy-Element Containing Materials?

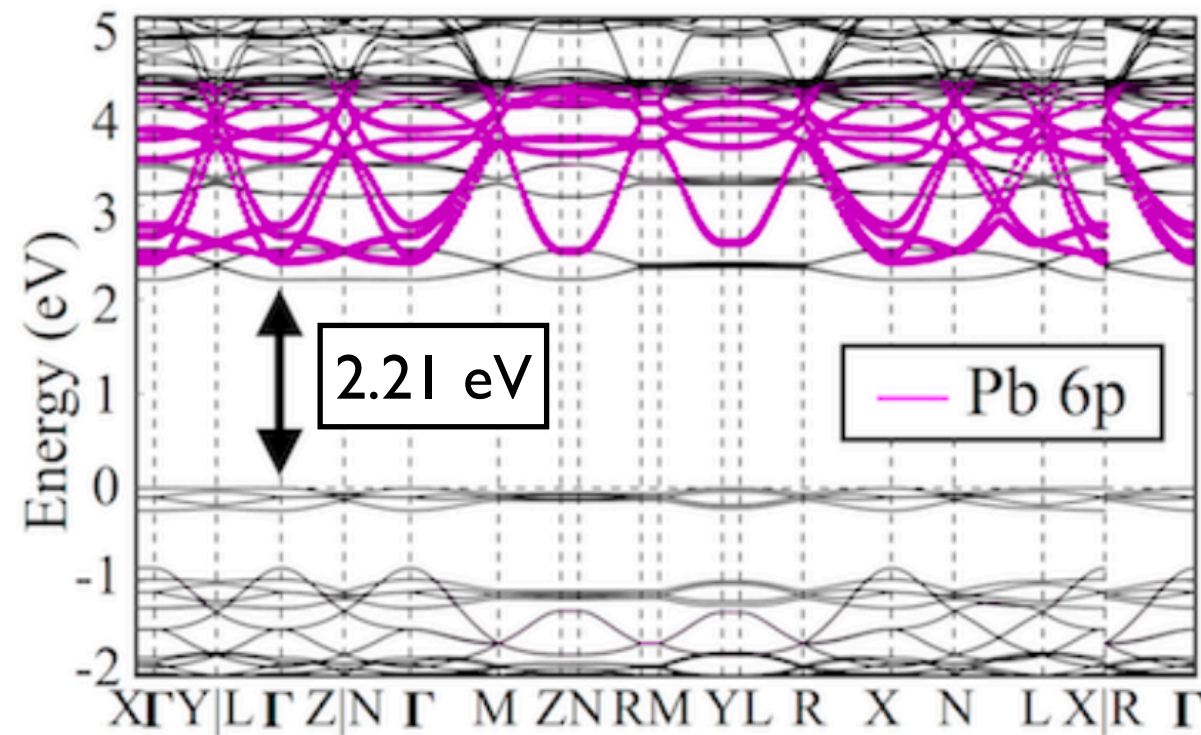
E.g., Organic-Inorganic Hybrid Semiconductors - Tailored Properties



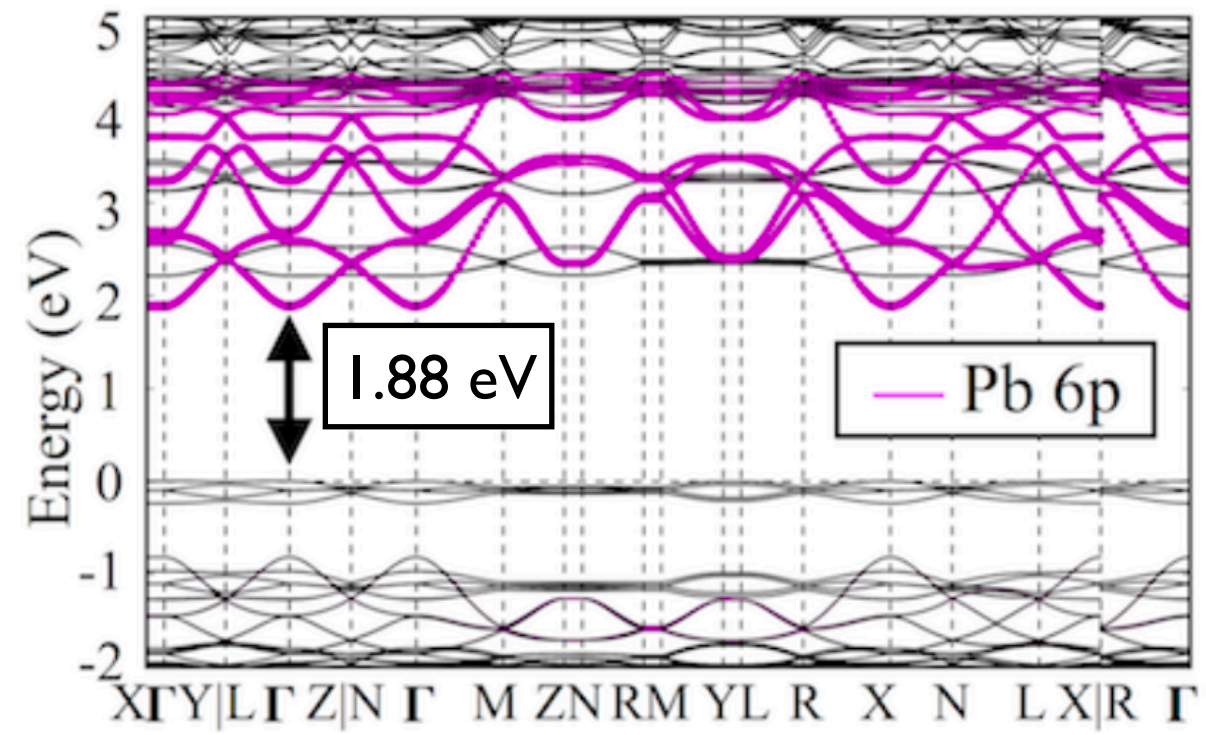
3D crystal
400+ atoms per unit cell

AE4T-PbBr₄: Energy Levels - Impact of Spin-Orbit Coupling

AE4T-PbBr₄ - HSE06, no SOC

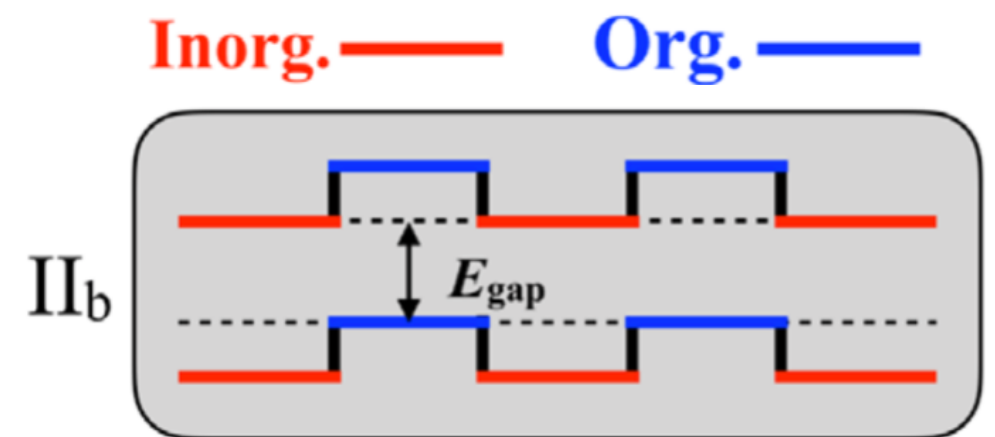


AE4T-PbBr₄ - HSE06, SOC



SOC changes the character of conduction band minimum (“electrons”)

Holes on organic component,
electrons on inorganic component:
Type IIb Quantum Well



Our Choice: Numeric Atom-Centered Basis Functions

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

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

- $u_i(r)$: 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 energies (LDA/GGA/hybrid DF's) - 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)

Using Numeric Atom-Centered Basis Functions: Pieces

- *Numerical* Integration

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

- Electron density update

$$n(\mathbf{r}) = \sum_k f_k |\psi_k(\mathbf{r})|^2$$

- All-electron electrostatics

$$v_{\text{es}}(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- Relativity

needed for heavy elements

- Eigenvalue solver

$$\underline{\underline{h}} \underline{\underline{c}}_k = \epsilon_k \underline{\underline{s}} \underline{\underline{c}}_k$$

- Periodic systems

$$\Psi_{n,\mathbf{k}} = \exp(i\mathbf{k}\mathbf{r}) \cdot u_{n,\mathbf{k}}(\mathbf{r})$$

- Coulomb operator

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

Numeric Atom-Centered Basis Functions: Integration

$$h_{ij} = \int d^3r \varphi_i(\mathbf{r}) \hat{h}_{\text{K}}$$

- Discretize to integration grid:

$$\int d^3r f$$

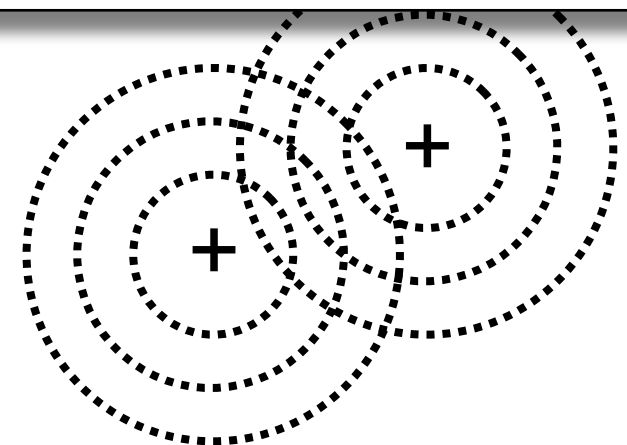
... but even-spaced integration
 $f(r)$ strongly peaked near

- 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)

In FHI-aims input (example: Hydrogen, tight settings):

```
#
radial_base      24 7.0
radial_multiplier 2
angular_grids    specified
division 0.1930 50
division 0.3175 110
division 0.4293 194
division 0.5066 302
division 0.5626 434
# division 0.5922 590
# division 0.6227 974
# division 0.6868 1202
# outer_grid 770
outer_grid 434
```



Pioneered by

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

Overlapping Atom-Centered Grids: “Partitioning of Unity”

Becke, 1988

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

- Rewrite to atom-centered integrands:

$$\int d^3r f(\mathbf{r}) = \sum_{\text{atoms}} \int d^3r p_{\text{atom}}(\mathbf{r}) f(\mathbf{r})$$

exact:

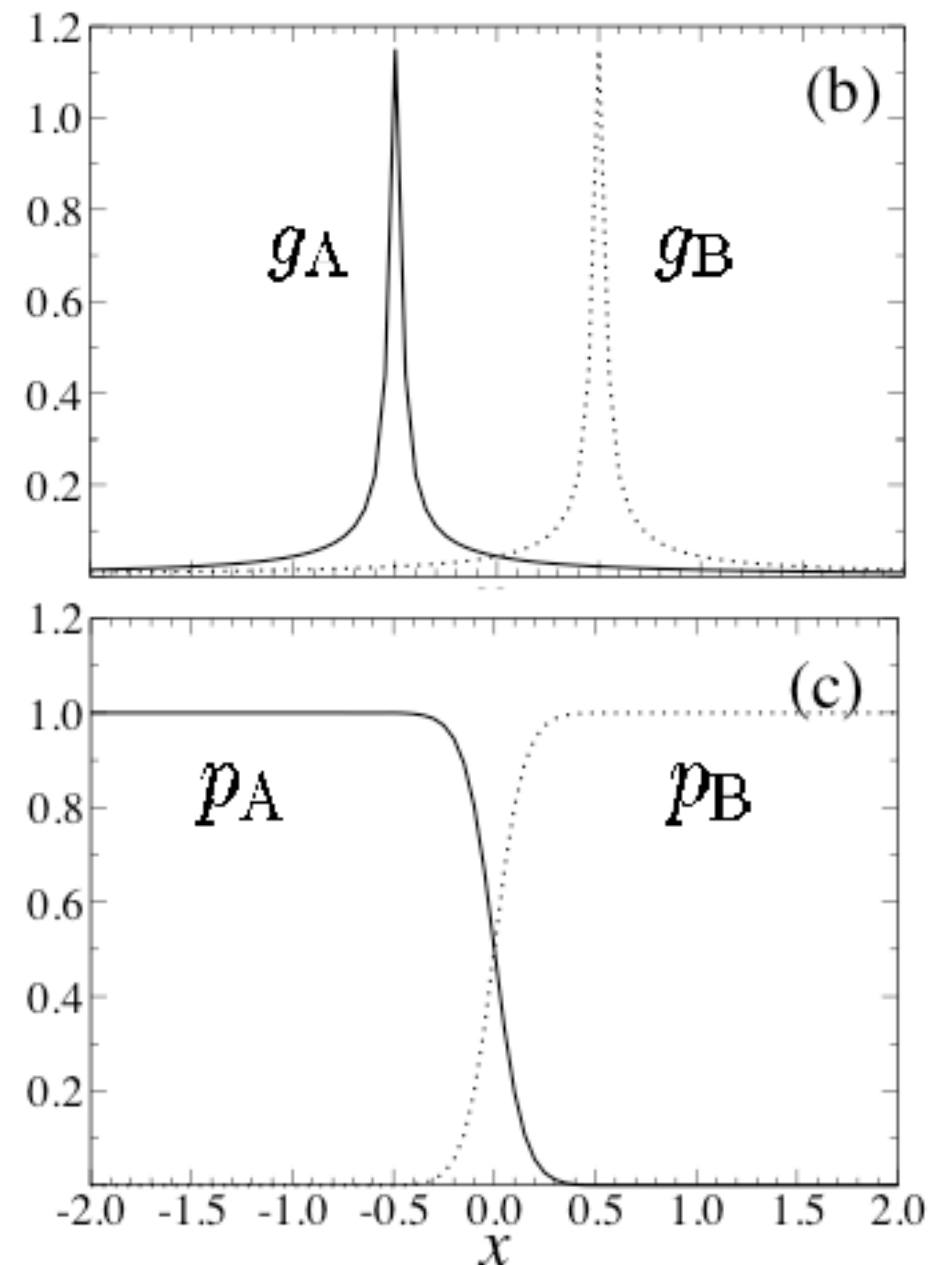
$$\sum_{\text{atoms}} p_{\text{atom}}(\mathbf{r}) = 1$$

through $p_{\text{atom}}(\mathbf{r}) = \frac{g_{\text{atom}}(\mathbf{r})}{\sum_{\text{atom}'} g_{\text{atom}'}(\mathbf{r})}$

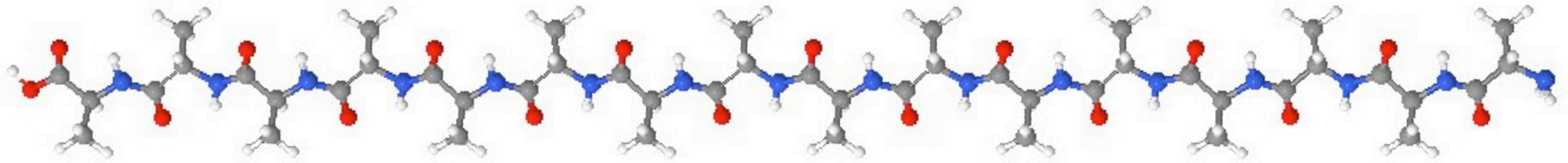
- e.g.: $g_{\text{atom}} = \frac{\rho_{\text{atom}}(r)}{r^2}$ (Delley 1990)

many alternatives:

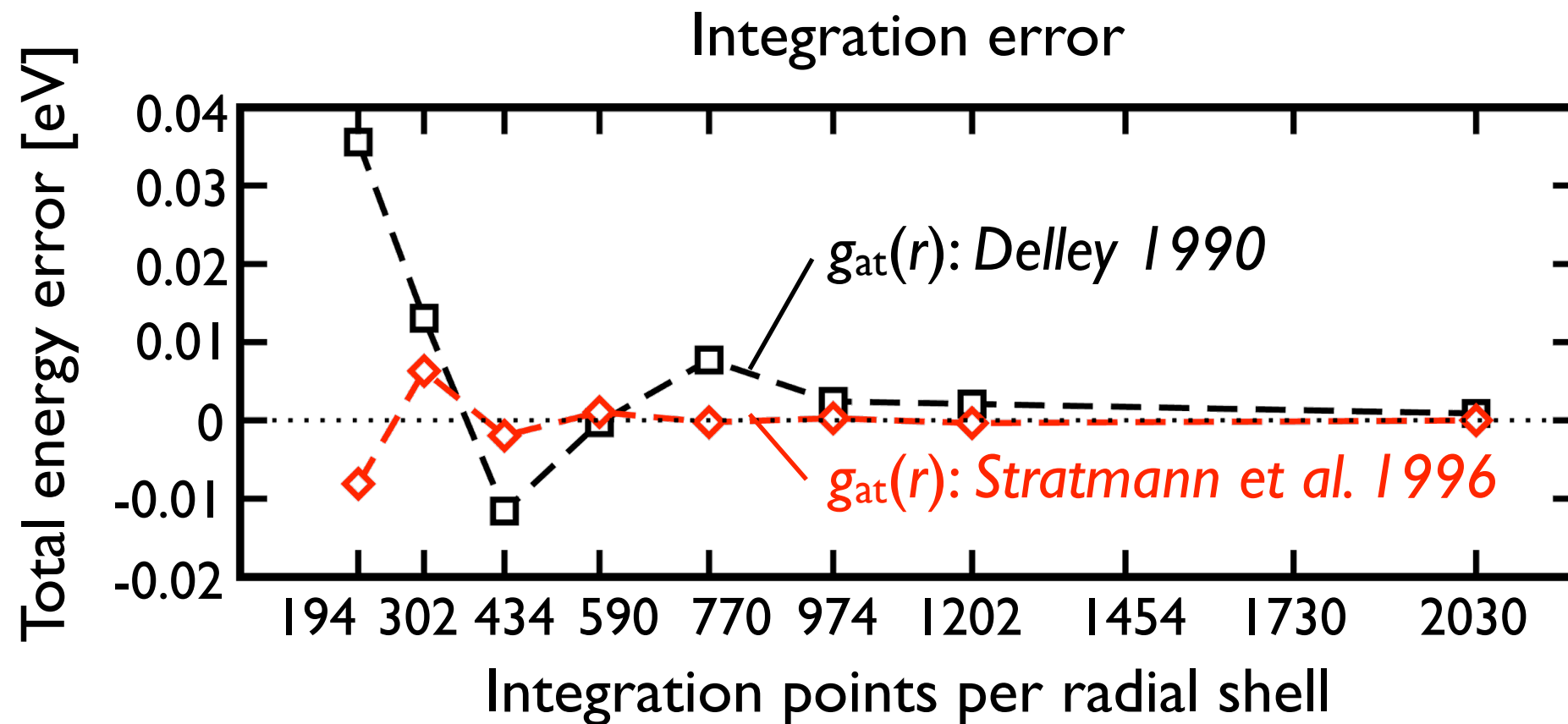
Becke 1988, Stratmann 1996, Koepernik 1999, ...



Integration in Practice: Large Systems, Small Errors!



Fully extended Polyalanine peptide molecule Ala₂₀, DFT-PBE (203 atoms)



Hartree Potential (Electrostatics): Overlapping Multipoles

$$v_{\text{es}}(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- Partitioning of Unity:
(same trick as used for integrals)

$$n(\mathbf{r}) = \sum_{\text{atoms}} p_{\text{atom}}(\mathbf{r}) n(\mathbf{r})$$

Becke 1988
Delley 1990

- Multipole expansion: $n_{\text{atom},lm}(\mathbf{r}) = \int_{s=|\mathbf{r}' - \mathbf{R}_{\text{atom}}|} p_{\text{atom}}(\mathbf{r}') n(\mathbf{r}') Y_{lm}(\Omega)$

- Classical electrostatics:

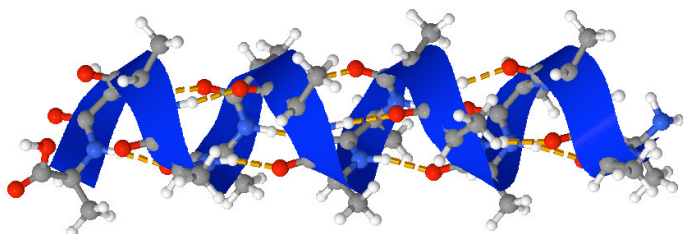
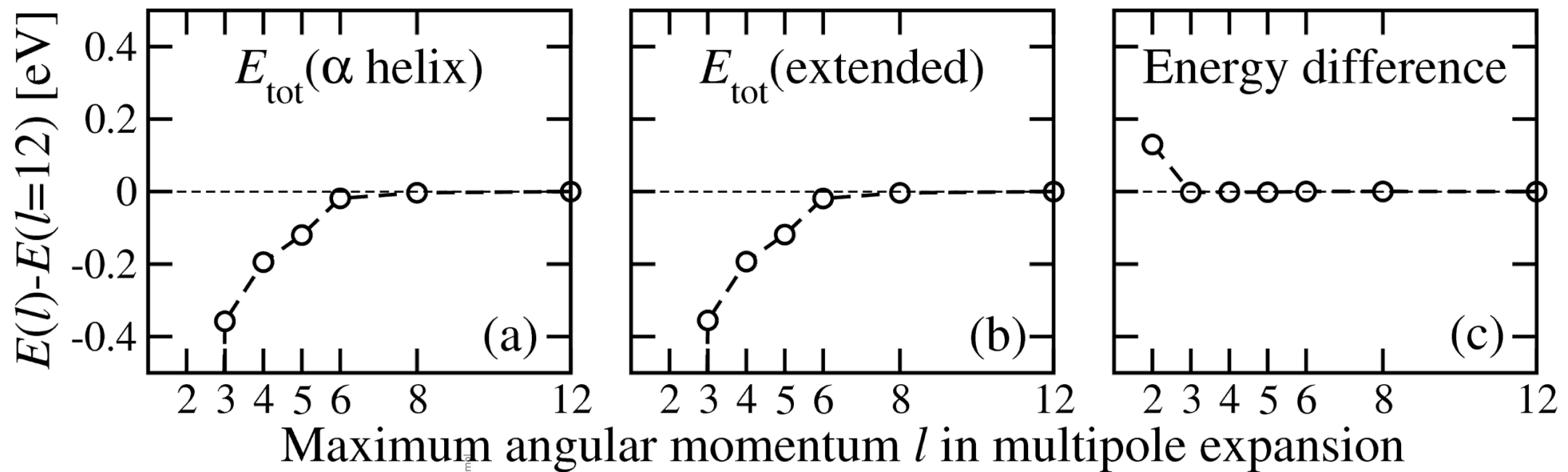
$$v_{\text{es}}(\mathbf{r}) = \sum_{\text{atoms}} \sum_{lm}^{l_{\text{max}}} v_{\text{atom},lm}(|\mathbf{r} - \mathbf{R}_{\text{atom}}|) Y_{lm}(\Omega_{\text{atom}})$$

Electrostatics: Multipole expansion

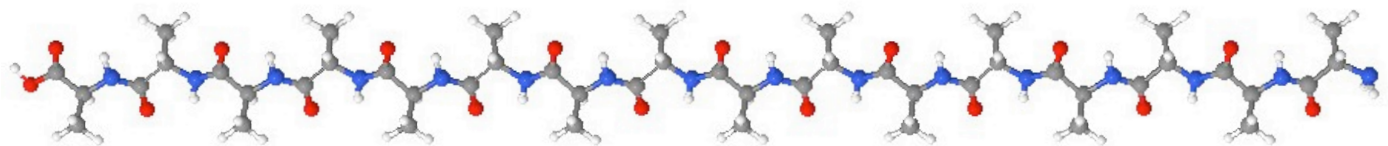
$$v_{\text{es}}(\mathbf{r}) = \sum_{\text{atoms}} \sum_{lm}^{l_{\text{max}}} v_{\text{atom},lm}(|\mathbf{r} - \mathbf{R}_{\text{atom}}|) Y_{lm}(\Omega_{\text{atom}})$$

Polyalanine Ala₂₀, DFT-PBE (203 atoms)

α -helical vs. extended: Total energy convergence with l_{max}



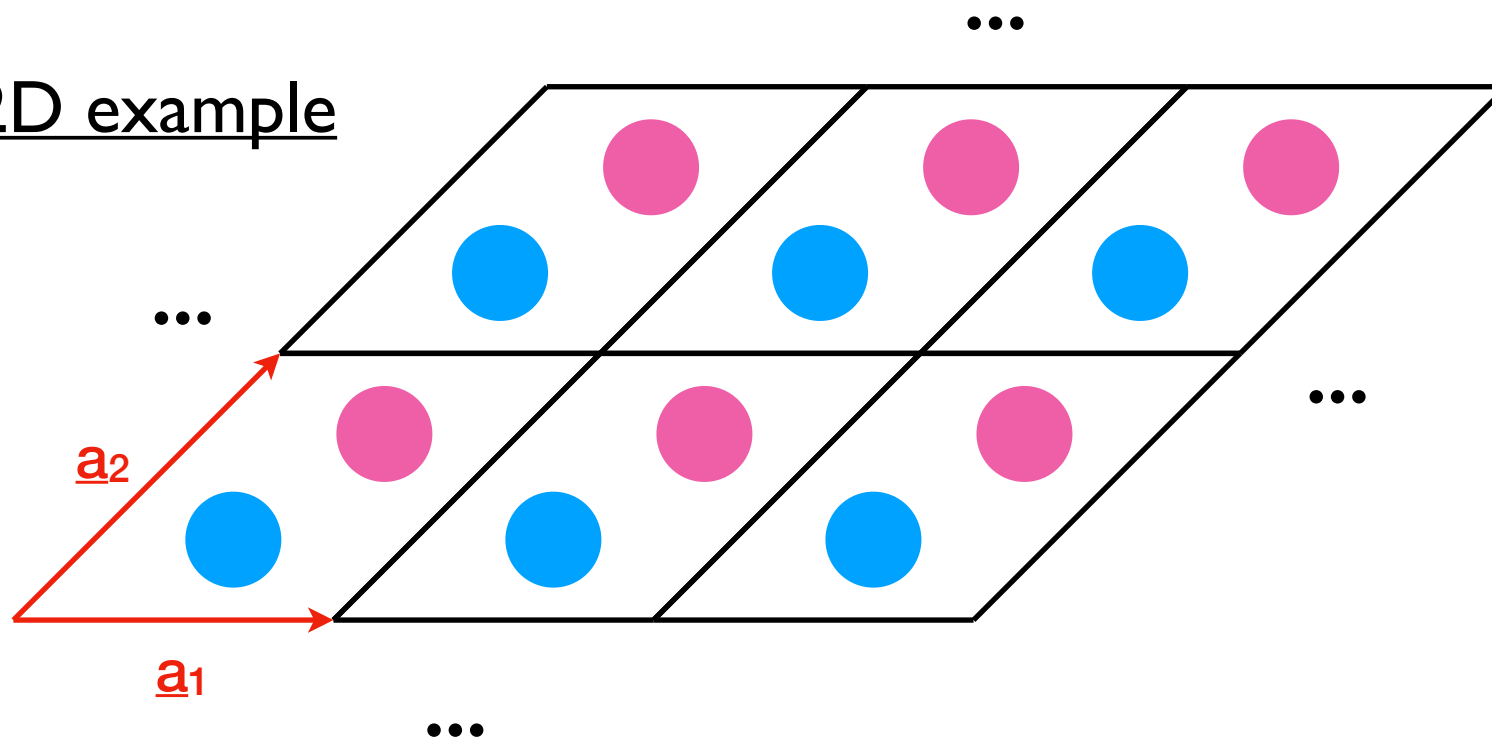
α



extended

Periodic Systems and Localized Orbitals

2D example



$$v_{\text{KS}}(\{\mathbf{R}_{\text{I}}\}) = v_{\text{KS}}(\{\mathbf{R}_{\text{I}} + \mathbf{T}_{\text{n}}\}),$$

where

$$\mathbf{T}_{\text{n}} = n_1 \cdot \underline{a}_1 + n_2 \cdot \underline{a}_2 + n_3 \cdot \underline{a}_3$$

a lattice translation vector
for any integers

$$(n_1, n_2, n_3).$$

Bloch theorem: Kohn-Sham orbitals take the form

$$\Psi_{n,\mathbf{k}} = \exp(i\mathbf{k}\mathbf{r}) \cdot u_{n,\mathbf{k}}(\mathbf{r})$$

$\mathbf{k}$: Crystal
momentum.
Real-valued
vector, unit:
 $\text{\AA}^{-1}$.

Phase factor:
Not lattice
periodic.

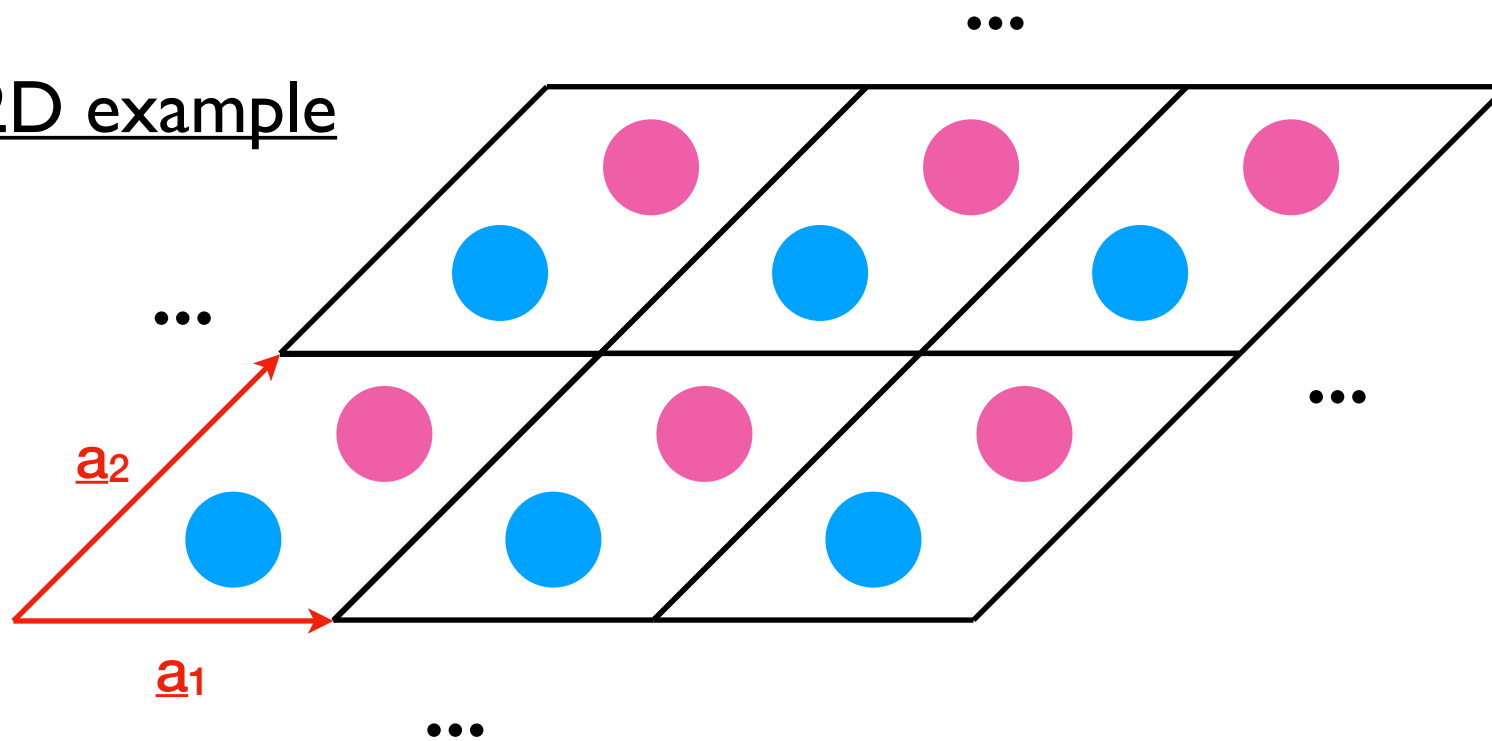
Bloch function:
Lattice periodic.

In short:

Separate solution for each $\mathbf{k}$.
Can be done for any basis set
(including localized orbitals).

Periodic Systems and Localized Orbitals

2D example



$$v_{\text{KS}}(\{\mathbf{R}_{\text{I}}\}) = v_{\text{KS}}(\{\mathbf{R}_{\text{I}} + \mathbf{T}_{\text{n}}\}),$$

where

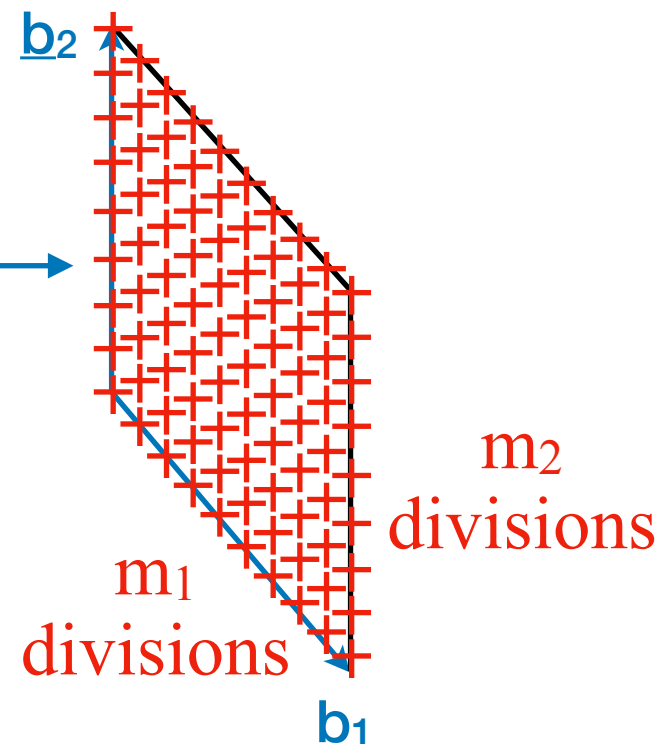
$$\mathbf{T}_{\text{n}} = n_1 \cdot \underline{a}_1 + n_2 \cdot \underline{a}_2 + n_3 \cdot \underline{a}_3$$

a lattice translation vector
for any integers

$$(n_1, n_2, n_3).$$

Practical solution:

- Only $\mathbf{k}$ vectors within finite range (“unit cell of reciprocal space”) need be considered.
- Select finite grid of $\mathbf{k}$ -points, chosen densely enough to approximate continuous range of $\mathbf{k}$ -points for practical solutions.



$\mathbf{k}_{\text{grid}}$	m_1	m_2	m_3
----------------------------	-------	-------	-------

How Strong are Relativistic Effects Across the Periodic Table?



William Huhn
(Duke Univ.)

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
Actinides			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Strength of Relativistic Effects (indicated by an orange arrow pointing from the top-left towards the bottom-right)

GaAs: Moderate (circled elements Ga and As)

Pb: Heavy (circled element Pb)

Relativity

Non-relativistic QM: Schrödinger Equation

$$V\phi + \frac{\mathbf{p}^2}{2m}\phi = \epsilon\phi$$

- ▶ one component (two with spin)
- ▶ one Hamiltonian for all states

Relativistic QM: Dirac Equation

$$\begin{pmatrix} V & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & -2c^2 + V \end{pmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix} = \epsilon \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

... simply rewrite:

$$V\phi + \boldsymbol{\sigma} \cdot \mathbf{p} \frac{c^2}{2c^2 + \epsilon - V} \boldsymbol{\sigma} \cdot \mathbf{p} \phi = \epsilon\phi$$

- ▶ ϵ -dependent Hamiltonian
- ▶ Not negligible for $\epsilon - v(\mathbf{r}) \approx 2c^2$
 $\Leftrightarrow$ affects near-nuclear part of *any* wave function

Electron-nucleus interaction: $v(r) = -Ze^2/r$ - stronger relativistic effects for higher Z .

Rewrite: Scalar Relativity plus Spin-Orbit Coupling

$$V\phi + \boldsymbol{\sigma} \cdot \mathbf{p} \frac{c^2}{2c^2 + \epsilon - V} \boldsymbol{\sigma} \cdot \mathbf{p} \phi = \epsilon \phi$$

$$\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$$

a vector of
(2x2) matrices



William Huhn
Duke Univ.

$$\sigma_1 = \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_2 = \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma_3 = \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Rewrite (exact):

$$V\phi + \left(\mathbf{p} \frac{c^2}{2c^2 + \epsilon - V} \mathbf{p} + i \mathbf{p} \frac{c^2}{2c^2 + \epsilon - V} \times \mathbf{p} \cdot \boldsymbol{\sigma} \right) \phi = \epsilon \phi$$

“Scalar relativity”
- essential for all
but lightest elements

Spin-orbit coupling - need large $\nabla V(r)$

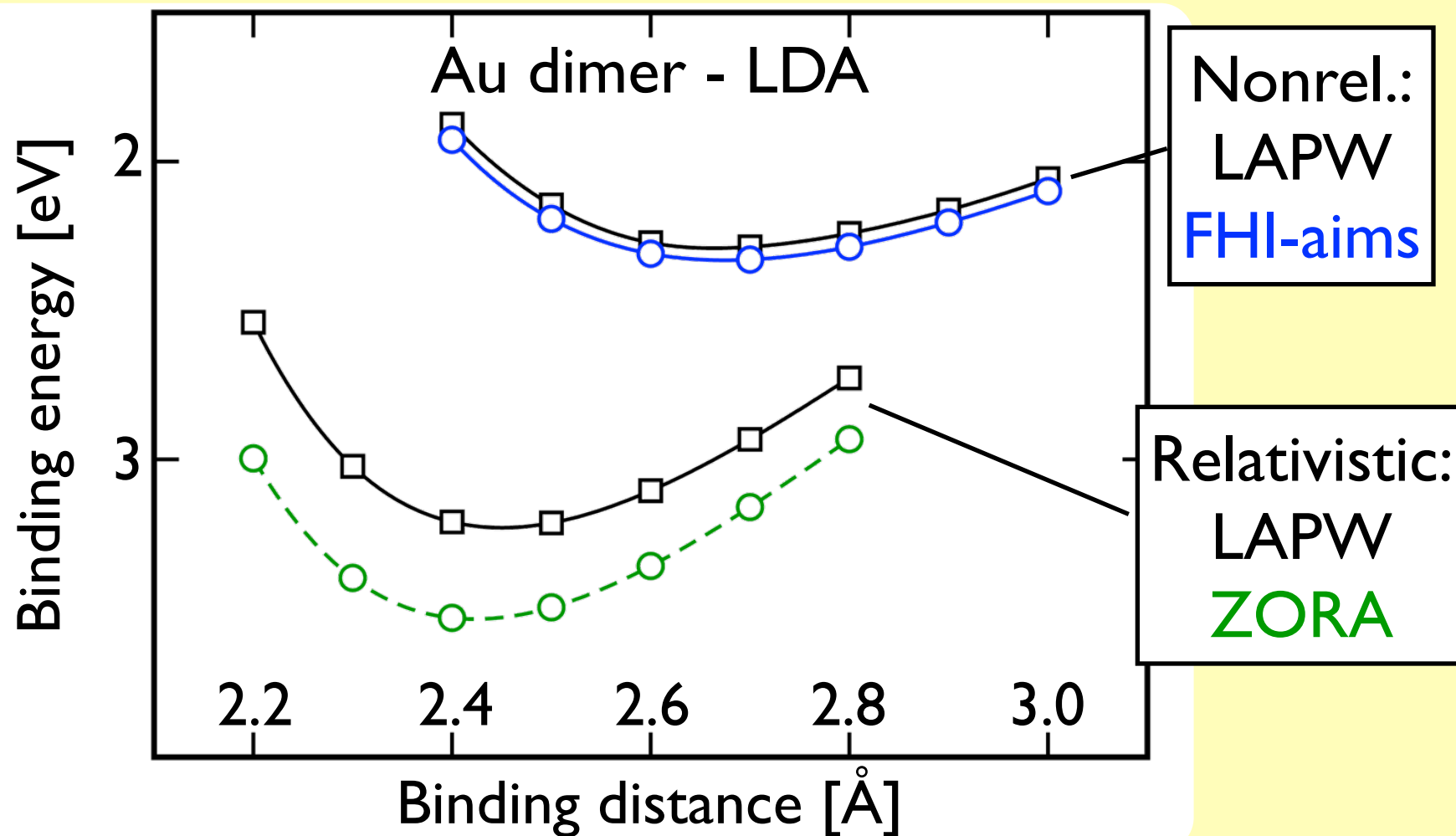
$$H_{SOC} \approx \frac{i}{4c^2} \mathbf{p} V \times \mathbf{p} \cdot \boldsymbol{\sigma}$$

[lowest order in $(\epsilon - V)/2c^2$]

Approximations to Scalar Relativity

$$V\phi + \cancel{\mathbf{p} \frac{c^2}{2c^2 + V} \mathbf{p}} \phi = \epsilon \phi$$

ZORA in practice: Harsh approximation (known)



!

Accurate, Stable Scalar Relativity: “Atomic ZORA”

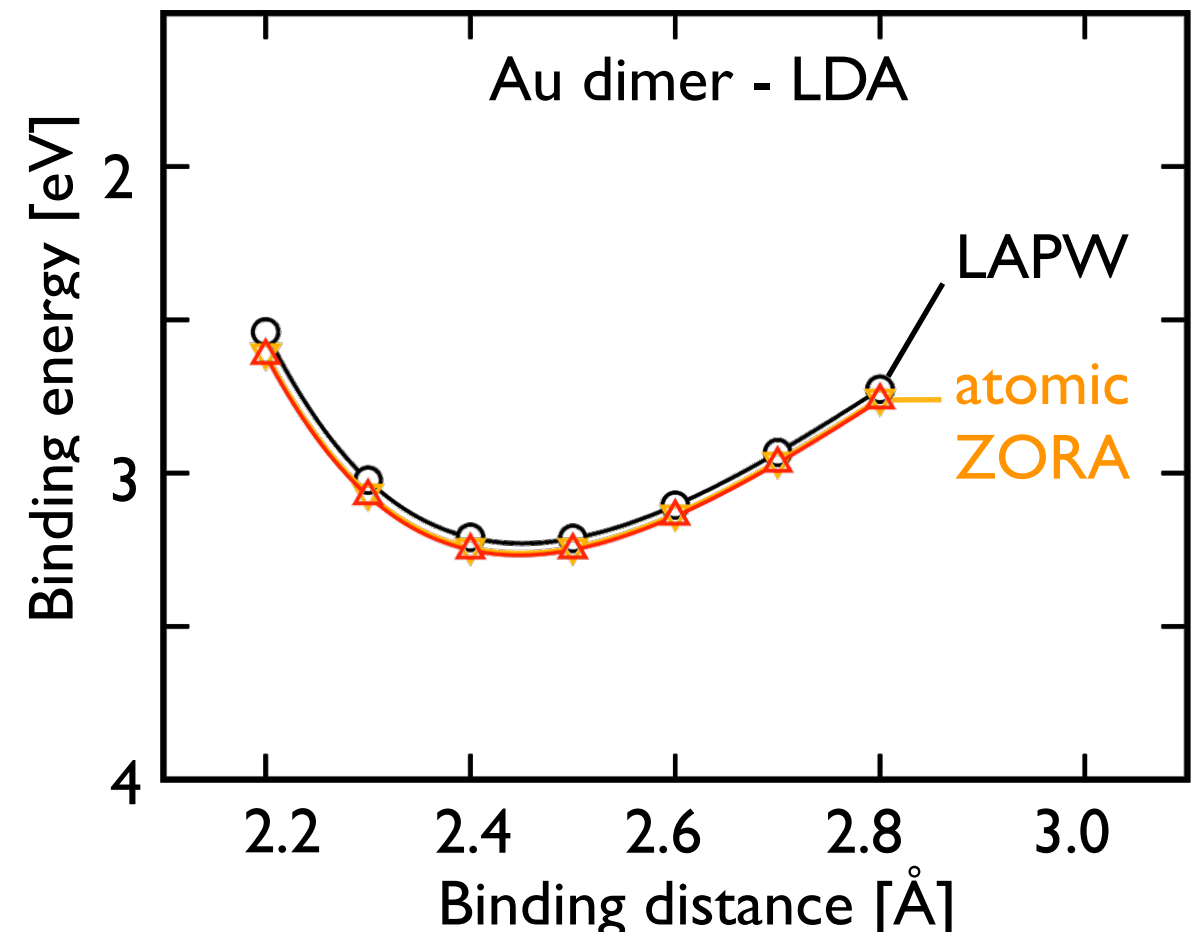
$$V\phi + \mathbf{p} \frac{c^2}{2c^2 + \cancel{\epsilon} - V} \mathbf{p} \phi = \epsilon \phi$$

ZORA

“Atomic ZORA”¹

$$V\phi + \mathbf{p} \frac{c^2}{2c^2 - V_{\text{free atom}}} \mathbf{p} \phi = \epsilon \phi$$

- No gauge-invariance problem
- Simple total-energy gradients
- Accurate energy differences²
- Accurate scalar-relativistic valence & conduction eigenvalues³



¹CPC 180, 2175 (2009); ²Science 351, aad3000 (2016); ³arXiv:1705.01804 (2017)

Spin-Orbit Coupling - Non-Selfconsistent vs. Selfconsistent

Rewrite (exact for large component):

$$V\phi + \left(\mathbf{p} \frac{c^2}{2c^2 + \epsilon - V} \mathbf{p} + i \mathbf{p} \frac{c^2}{2c^2 + \epsilon - V} \times \mathbf{p} \cdot \boldsymbol{\sigma} \right) \phi = \epsilon \phi$$

Approximate:



$$V\phi + \mathbf{p} \frac{c^2}{2c^2 - V_{\text{free atom}}} \mathbf{p} \phi = \epsilon \phi$$

e.g. (FHI-aims): atomic ZORA



$$H_{SOC} = \frac{i}{4c^2} \mathbf{p} V \times \mathbf{p} \cdot \boldsymbol{\sigma}$$

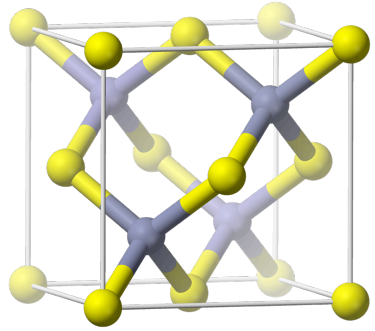
[lowest order in $(\epsilon - V)/2c^2$]



For band structures, SOC term can be included

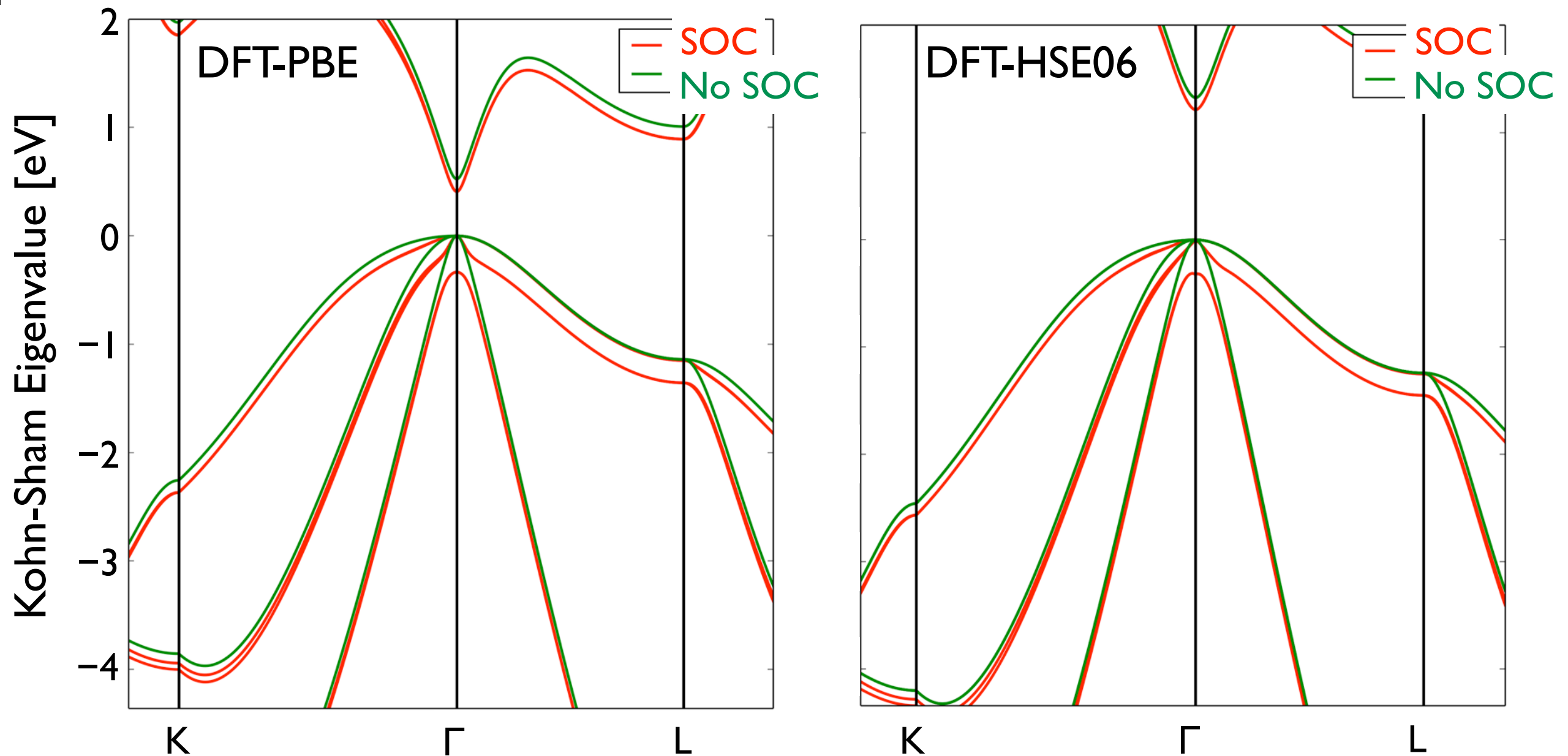
- self-consistently
 - non-selfconsistently after a self-consistent scalar relativistic band structure
- n.s.c. is computationally cheaper, simpler -
how accurate is it?

Real Materials: Impact of Relativistic Effects



$$a_{\text{exp}} = 5.6532 \text{ \AA}$$

Spin-Orbit Coupling in Zincblende GaAs
Relatively small effect - but
essential for correct carrier & excitonic properties.



Computational Scaling: Two Sub-Problems

1. Real space grid operations

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

Basis functions, Hamiltonian,
Kohn-Sham potential etc.

- Large “prefactor:” Dominant for standard problems
- Mature algorithms (Delley, others)
- $O(N)$ scalability possible in all steps
- *relatively* simple parallelization

V. Havu, V. Blum, P. Havu, M. Scheffler,
J. Comp. Phys. **228**, 8367-8379 (2009)

2. Matrix algebra (basis space)

$$\underline{\underline{h}} \underline{\underline{c}}_k = \epsilon_k \underline{\underline{s}} \underline{\underline{c}}_k$$

Kohn-Sham eigenvalue problem

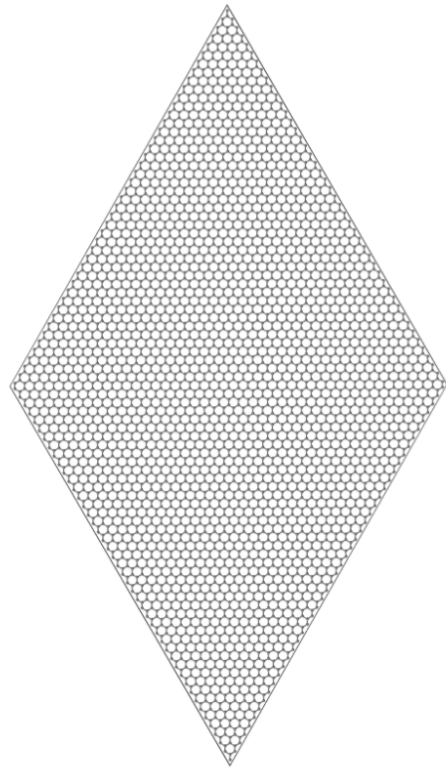
“Conventional” solvers (Lapack-like):

- Small prefactor for NAO’s: affordable up to $\geq 1,000$ atoms
- Robust, general (metals!)
- $O(\text{size}^3)$ scalability inevitable
- Massively parallel scalability not out of the box

How far can we push such solvers?

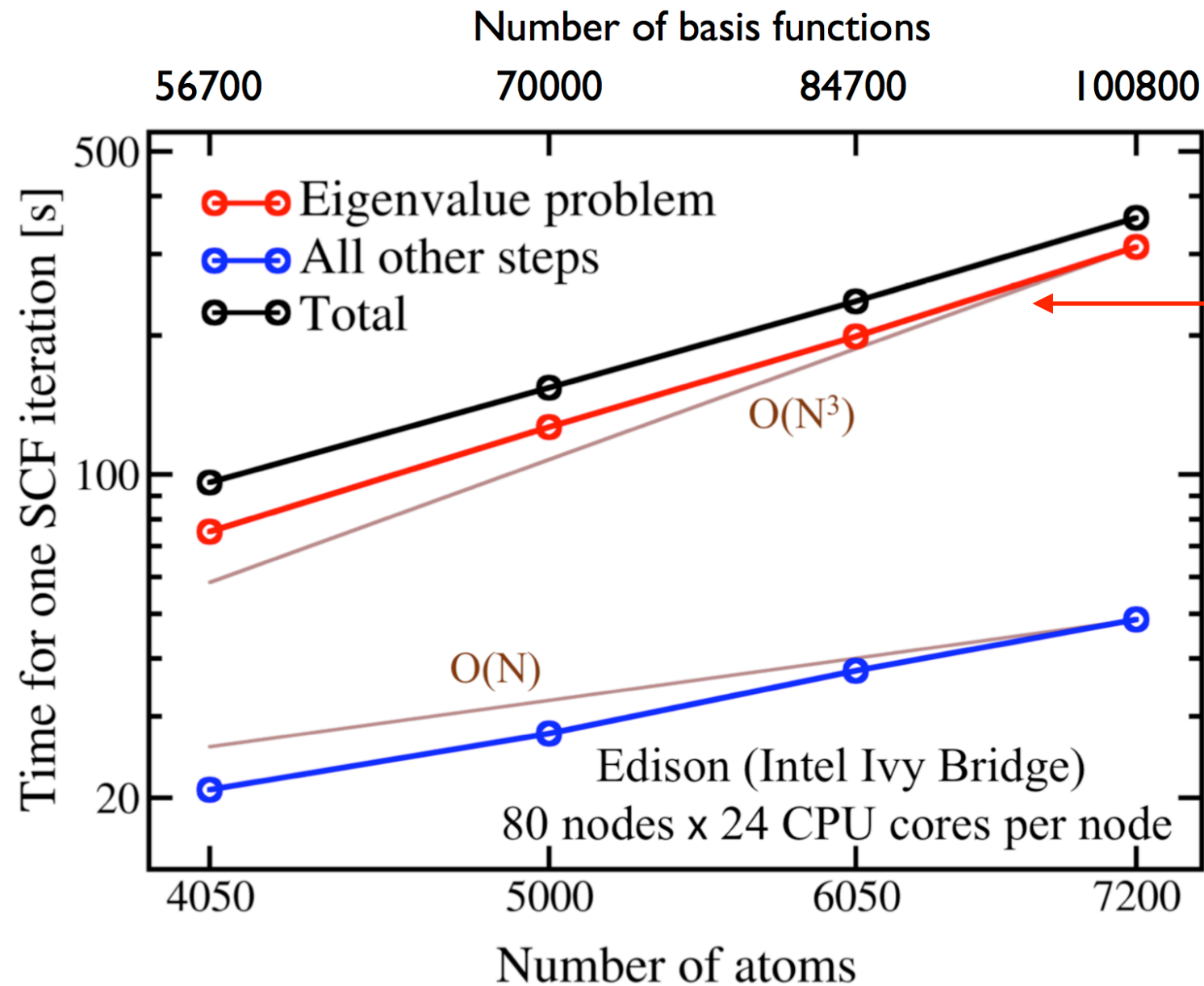
Typical Scaling - $O(N^3)$ Wall

$$H\varphi = \epsilon S\varphi$$



Graphene monolayer,
4050 atoms

FHI-aims, PBE, “light” settings



ELPA Library
<http://elpa.rzg.mpg.de>

Generic problem for any Kohn-Sham DFT code ... solution strategies?

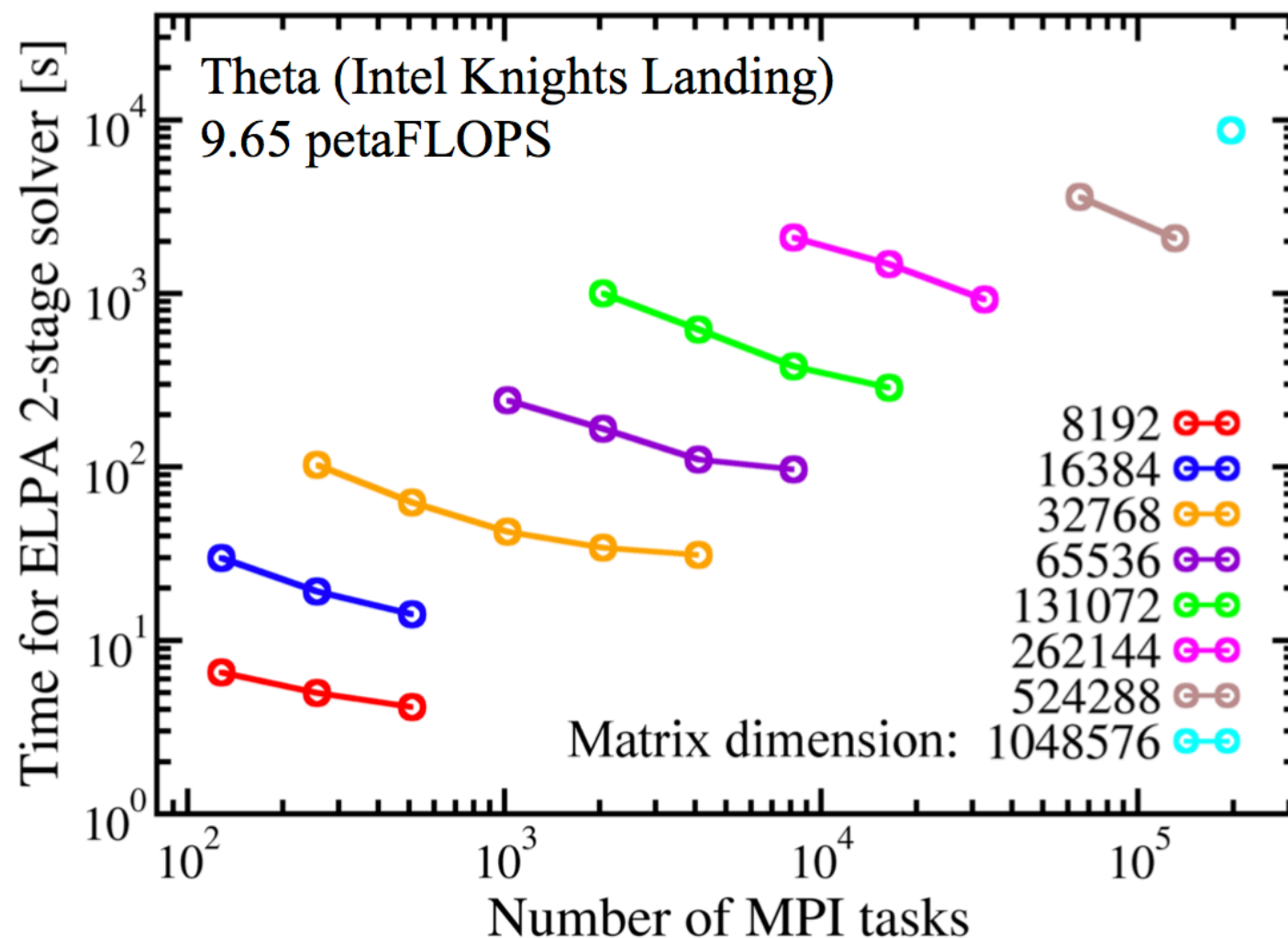
Plan A: Have Big Computer, Push the Eigensolver

ELPA Eigenvalue Solver

- Efficient full $\rightarrow$ band $\rightarrow$ tridiagonal reduction & backtransform
- Dense linear algebra up to full spectrum



Benchmark:
Alvaro Vazquez-
Mayagoitia, ANL



Auckenthaler, Blum, Bungartz, Huckle, Johanni, Krämer, Lang, Lederer, Willems, *Parallel Computing* 37, 783 (2011)

A. Marek, V. Blum, R. Johanni, V. Havu, B. Lang, T. Auckenthaler, A. Heinecke, H.-J. Bungartz, H. Lederer,
The Journal of Physics: Condensed Matter 26, 213201 (2014).

Plan B: Many Scalable Solution to Kohn-Sham Problem

$$\underline{\underline{h}} \underline{\underline{c}}_k = \epsilon_k \underline{\underline{S}} \underline{\underline{c}}_k$$

Different use cases (basis sets, physics), different “solvers”.
Solve (eigenvectors, $O(N^3)$) or circumvent (density matrix)?

Exact solvers

Lapack
Scalapack
ELPA
EigenExa
Magma
...

Robust
General

Iterative solvers

Davidson
Projected
Preconditioned
Conjugate Gradient
Chebychev Filtering
Slepc-SIPS
...

(Essentially) robust
 $N_{\text{basis}} \gg N_{\text{ev}}$

DM: $O(N)$ solvers

NTPoly
Various code-
internal and/or
proprietary
implementations

Sparse H, S
Nonmetallic systems

Other DM-based approaches

PEXSI
Orbital
Minimization
Method
FEAST
...

Sparse H, S
can depend on XC

Many Different Solvers - How to Unify Access?



Victor Yu

Electronic structure codes

?

Solvers

ELPA	NTPoly
EigenExa	PEXSI
SLEPc-SIPs	libOMM
MAGMA	More ...

?

Replicated infrastructure to implement solvers efficiently

?

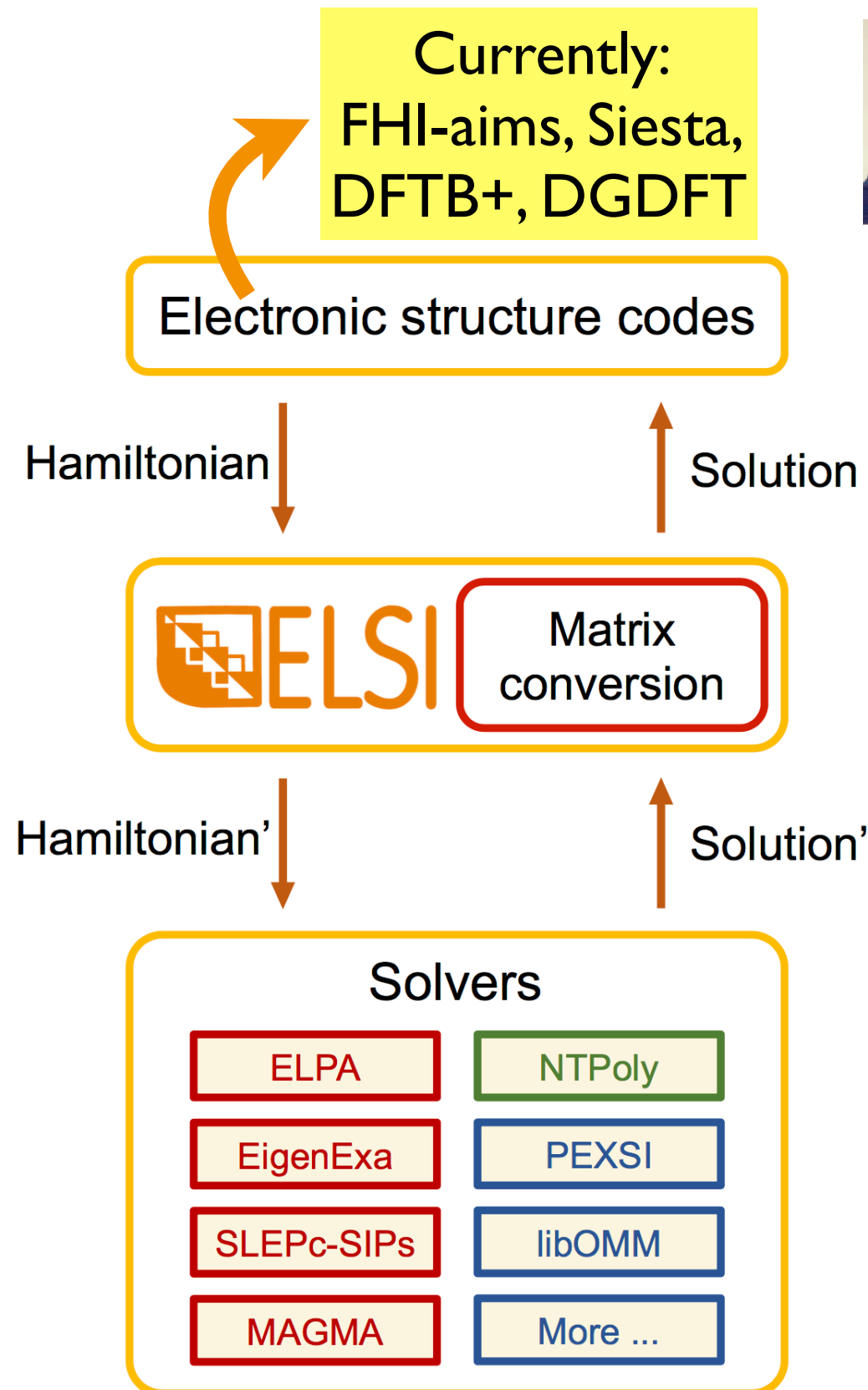
Conversion between a variety of matrix storage formats

?

Complexity in solver selection for different problems



ELSI: Connecting Electronic Structure Codes and Solvers



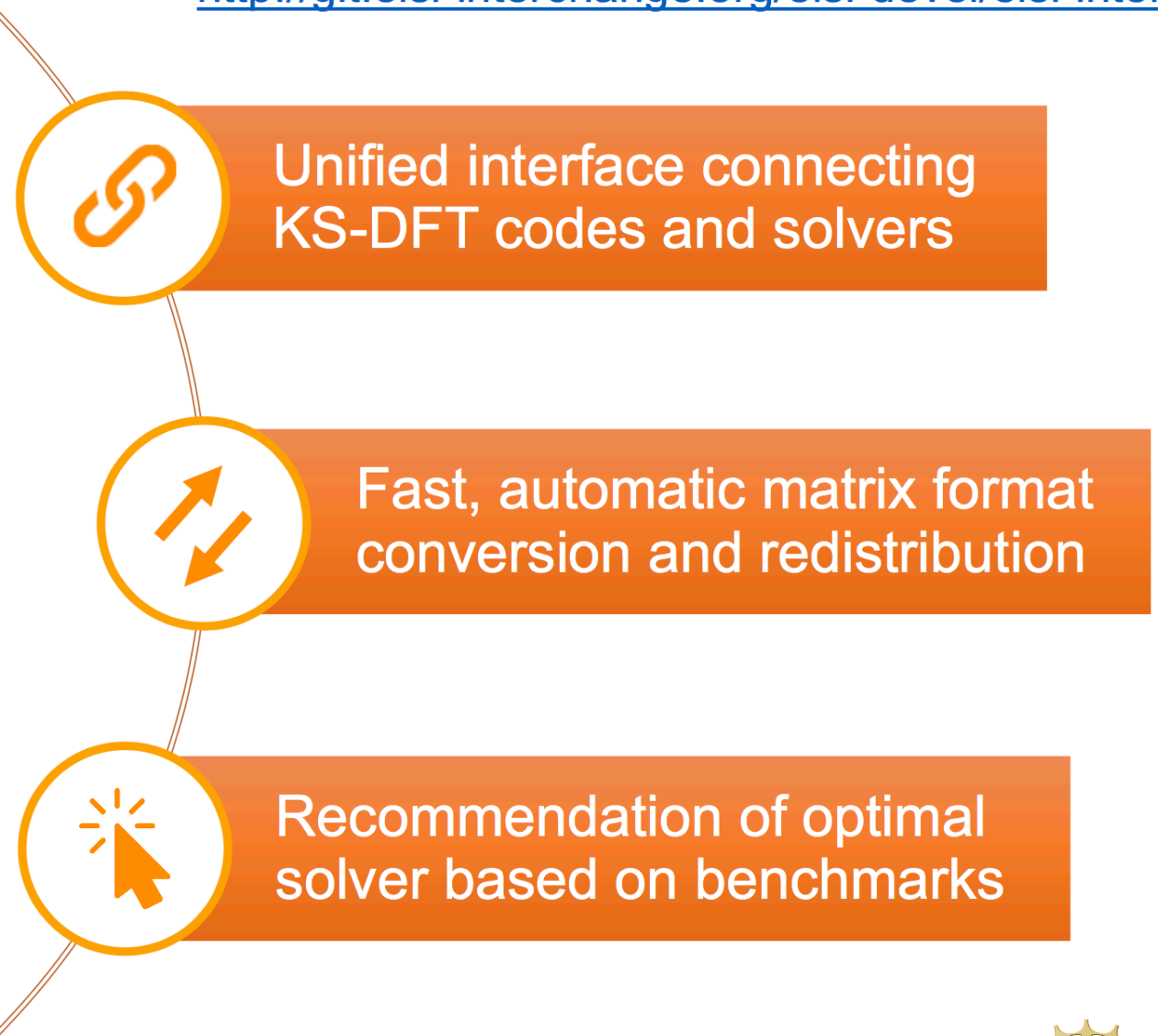
Victor Yu

Yu et al., “ELSI – An Open Infrastructure for Electronic Structure Solvers”
Comp. Phys. Commun. 256, 107459 (2019).

Yu et al., *Comput. Phys. Commun.* 2018

<http://elsi-interchange.org>

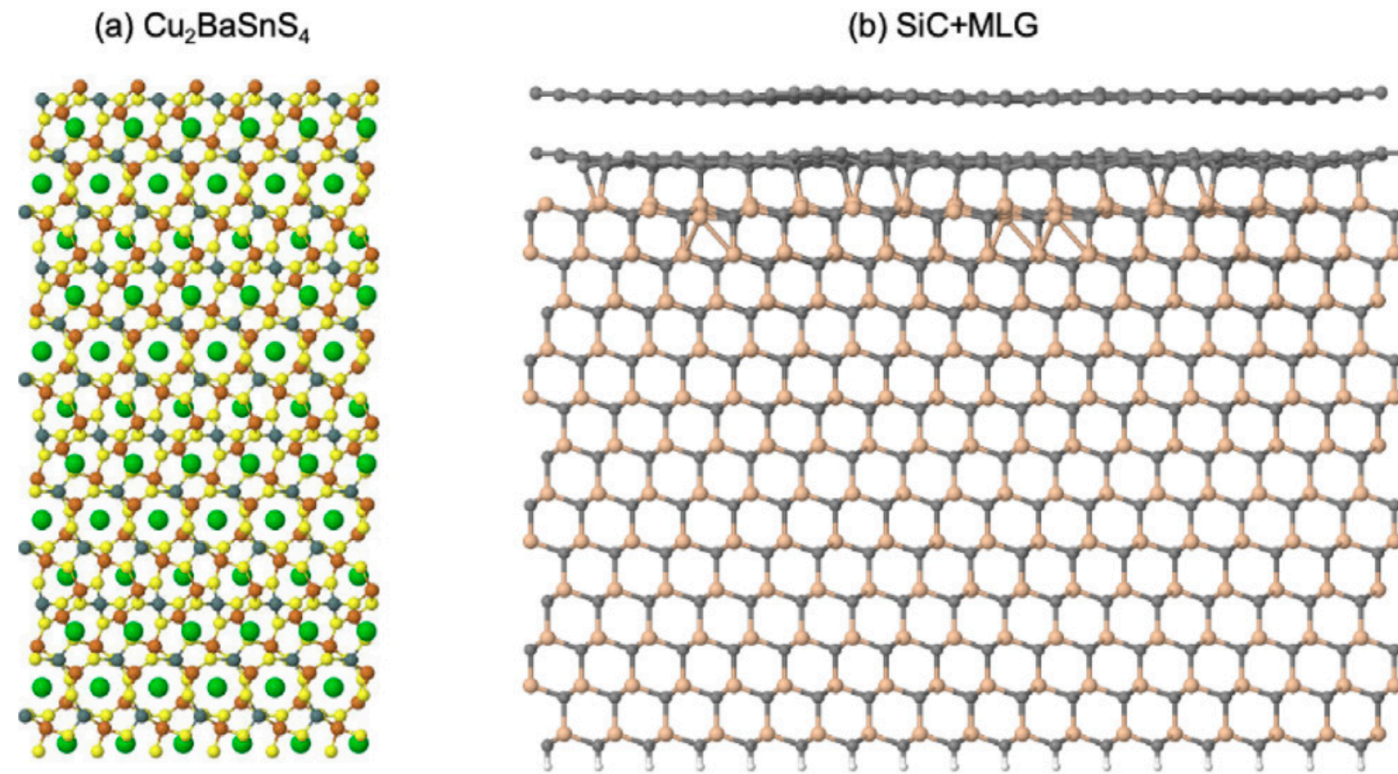
<http://git.elssi-interchange.org/elsi-devel/elsi-interface>



GPU: FHI-aims, ELSI, ELPA

Huhn, Lange, Yu, Yoon, Blum, *Comp. Phys. Commun.* 254, 107314 (2020).

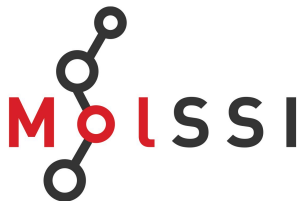
Yu, Moussa, K  s, Marek, Messmer, Yoon, Lederer, Blum, *Comp. Phys. Commun.* 262, 107808 (2021).



MAX-PLANCK-GESELLSCHAFT



ORNL



NVIDIA®



System	Computer	N _{node}	Time [s]				
			Potential	Hamiltonian	Eigenproblem	Density	Total
CBTS (3000 atoms)	Summit	2	246.1 ^a	21.3	280.7	50.8	598.9
	Summit	4	123.4 ^a	12.8	161.4	28.2	325.8
	Cori	40	15.1	3.7	277.8	23.6	320.2
	Cori	80	10.3	1.9	170.7	16.1	199.0
SiC+G (3376 atoms)	Summit	2	164.7 ^a	15.0	88.5	28.1	296.3
	Summit	4	82.6 ^a	7.5	58.4	15.7	164.2
	Cori	40	10.8	2.8	81.4	8.6	103.6
	Cori	80	6.6	1.4	60.9	6.8	75.7

^aThe electrostatic potential is computed on CPUs.

Our Electronic Structure Framework: FHI-aims



<https://fhi-aims.org>

Objectives:

Full space of materials and chemistry:

- Non-periodic & periodic models
- All elements across the periodic table

A standard periodic table of elements, color-coded by groups. It includes the main groups (1-18) and the lanthanide and actinide series at the bottom. Each element is represented by its atomic number, symbol, and name.

High numerical accuracy & reliability (all-electron)

Scalability (system size and available supercomputers)

Practical approximations to full Dirac equation:

- DFT (semilocal, hybrid, van der Waals corrections)
- Many-body perturbation theory (GW, MP2, RPA and beyond)
- Response theory (vibrations/phonons, Raman, NMR, IR, optical)
- Relativity (scalar, spin-orbit coupling, ...)
- Dynamics

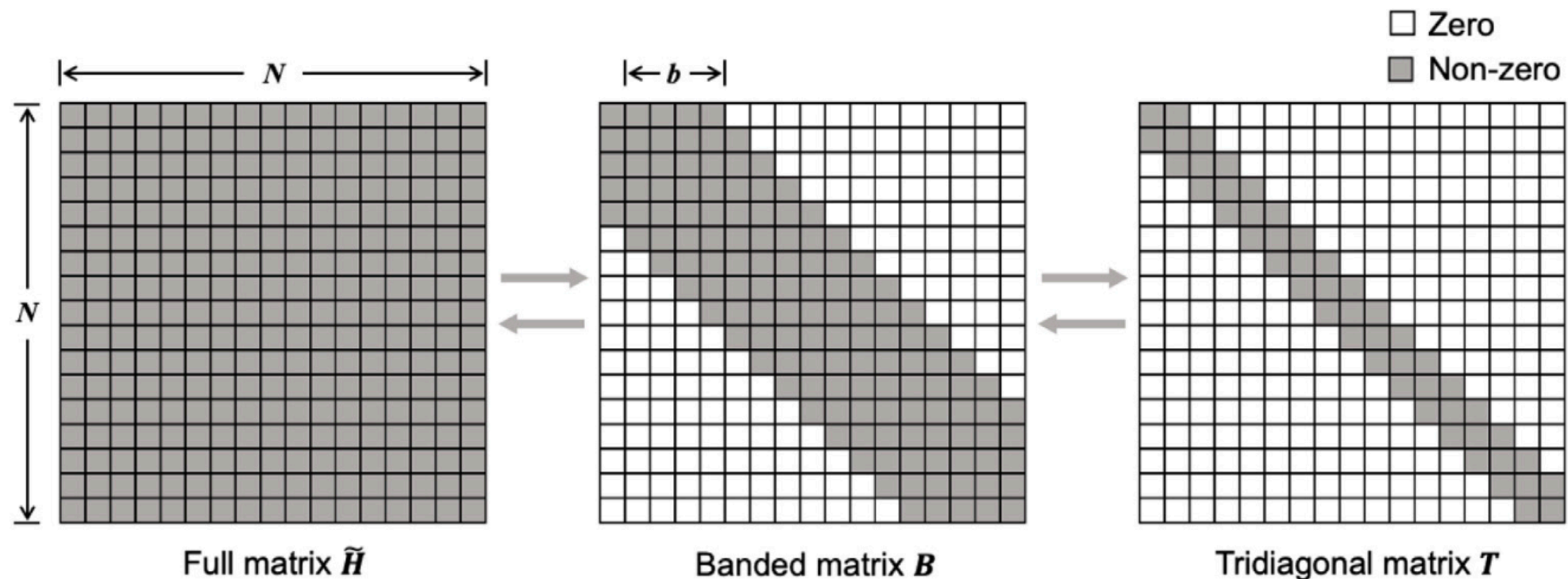
Accessibility (usable code, flexible and extendable code base)

Distributed-Parallel GPU Solver: ELPA2-GPU

V.W.-z.Yu, J. Moussa, P. Kůs, A. Marek, P. Messmer, M. Yoon, H. Lederer, V. Blum,
Comp. Phys. Commun. 262, 107808 (2021).

Kus *et al.*, 2019: GPU port of ELPA1 - however, 2-stage solver approach not efficient?

2-stage symmetric band reduction:



... in past, expected to scale to larger core / MPI rank counts than ELPA1.

... competitive advantage if M eigenpairs $< N$ (dimension) sought.

Net Result: Speedup, Extended Scaling by ELPA2-GPU

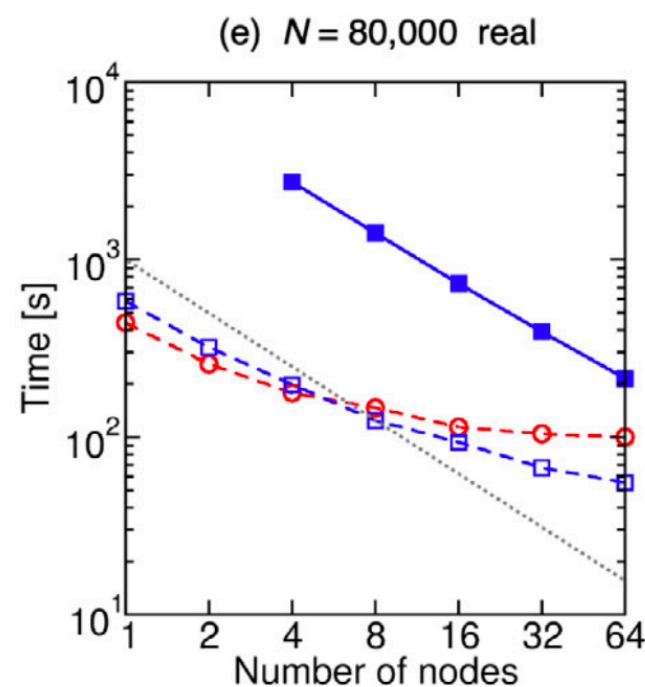
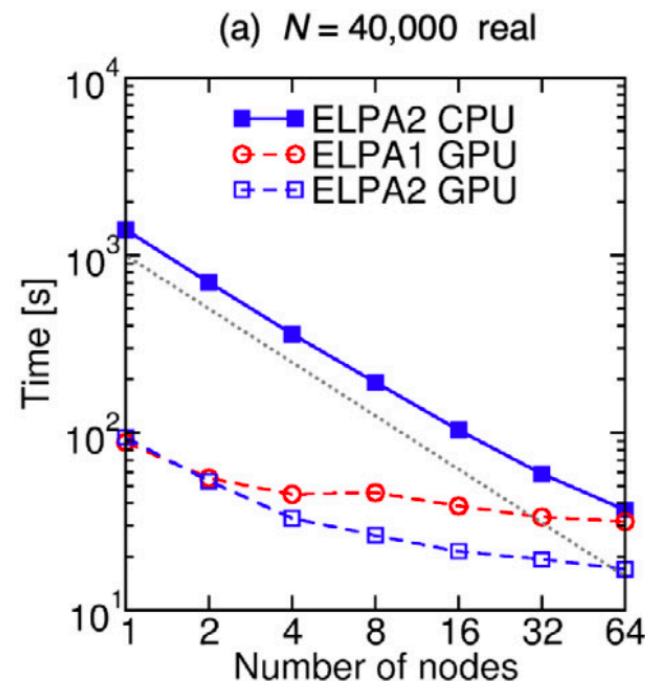
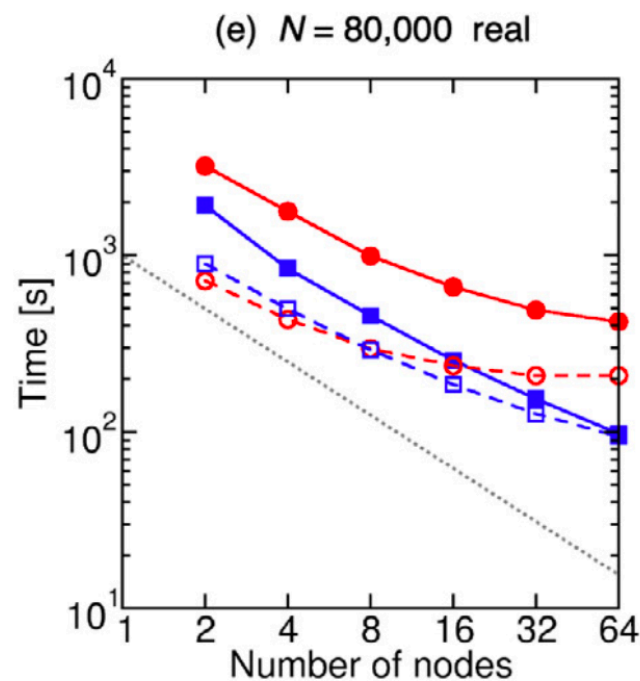
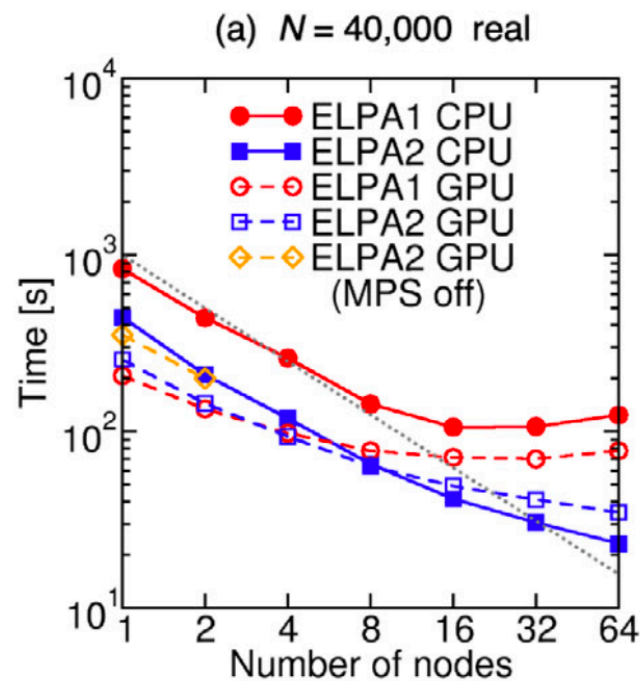
ELPA2-GPU - all M eigenpairs (worst case)

Talos Cluster (MPCDF)

40 Intel cores + 2 V100 / node

Summit (OLCF)

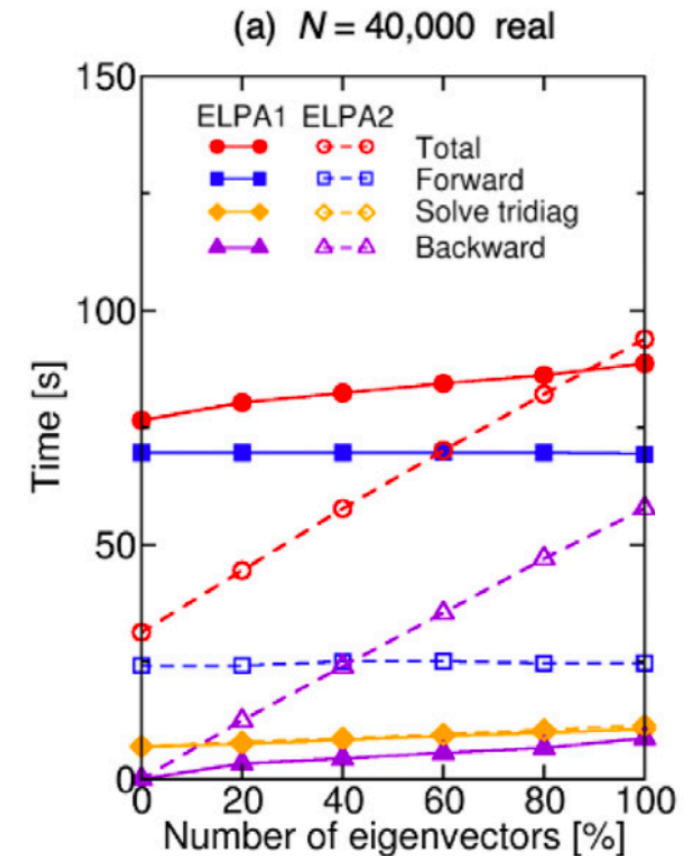
42 Power9 cores + 6 V100 / node



ELPA2-GPU

Advantage for $M < N$

Summit (OLCF), 1 node



Excursion: “Basis Set Superposition Errors”?

Traditional quantum chemistry: “Basis set superposition errors”

$$\text{e.g.: Binding energy } E_b = E(\text{●—●}) - 2E(\text{●})$$



Problem:

●—● has larger basis set than ●.
→ Distance-dependent overbinding!

Remedy: “Counterpoise correction”

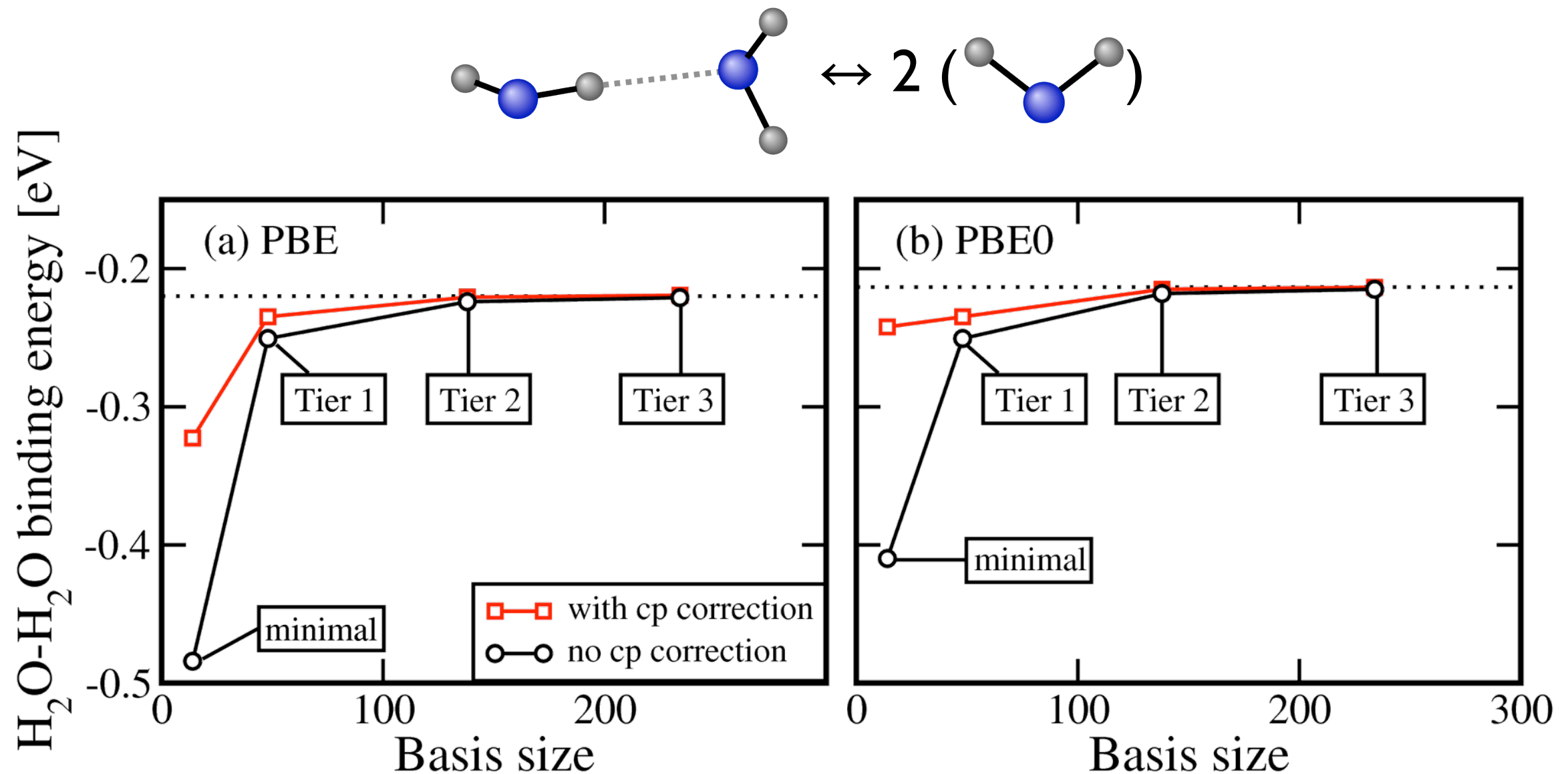
$$\Delta E_{\text{BSSE}} = E(\text{●—●}) - E(\text{●})$$



No nucleus - basis functions only

NAO basis sets: ● is already exact → no BSSE for ●—●.
But how about *molecular* BSSE?

$(\text{H}_2\text{O})_2$: “Counterpoise Correction”



Ground-State DFT, NAO's:

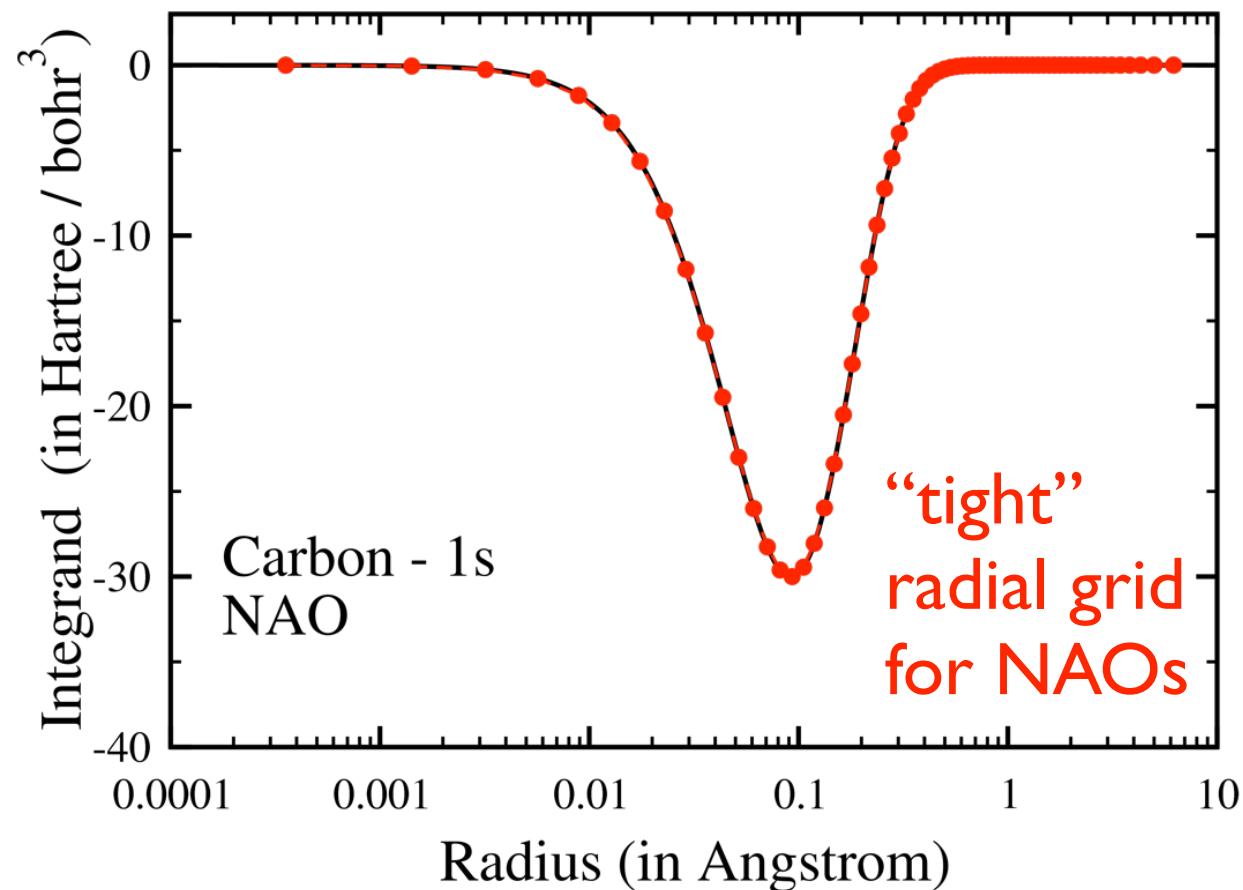
BSSE *not* the most critical basis convergence error (e.g., tier 2)*

*BUT methods that sum over infinite continuum (MP2, RPA, ...) need CP and/or basis sets that systematically approach continuum of states!

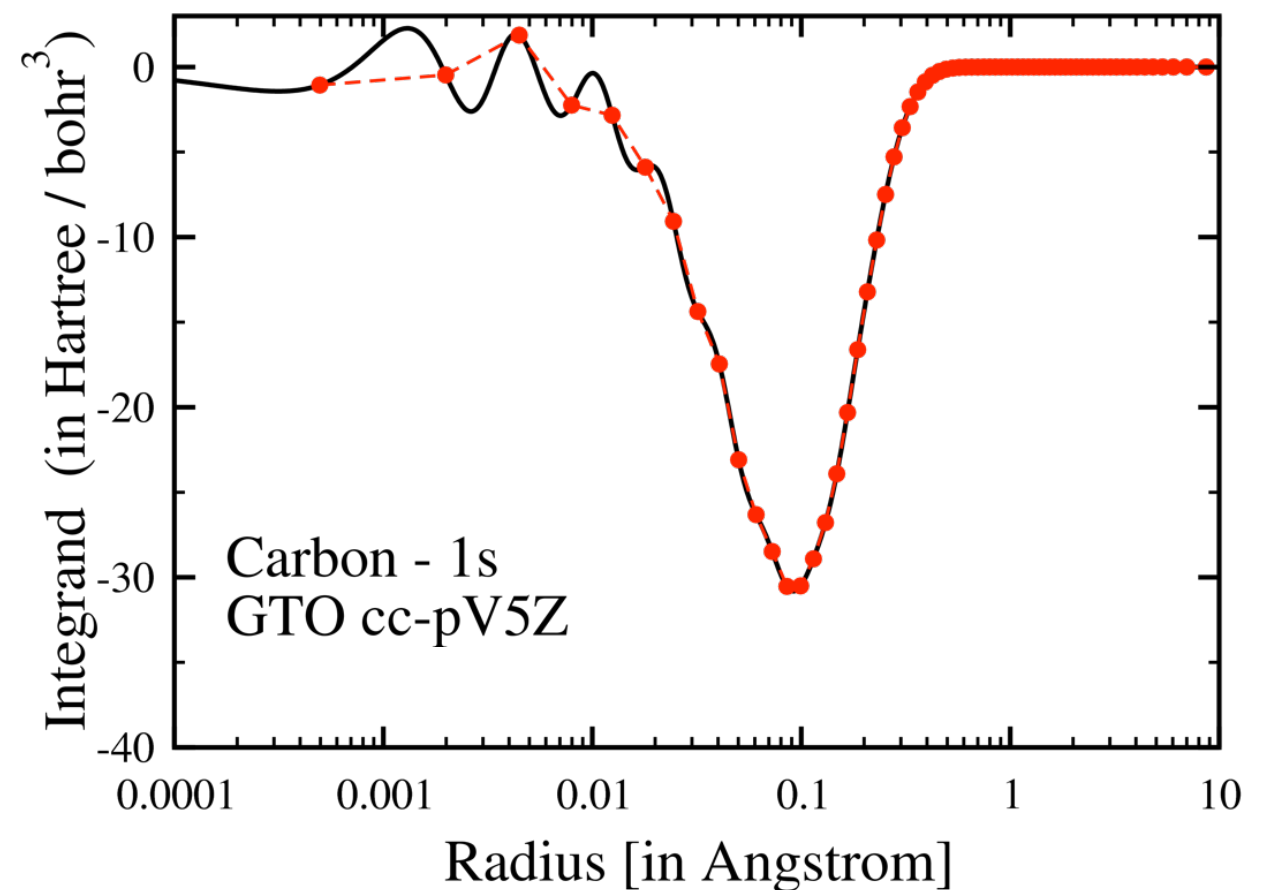
All-Electron Integrals: Rather Benign for NAOs

$$\int d^3r \phi_{1s}(\mathbf{r}) \hat{H} \phi_{1s}(\mathbf{r}) = \int dr [f(r)] \times \text{angular integral.}$$

$f(r)$ for
NAO radial function:



$f(r)$ for
contracted Gaussian
radial function:



Igor Ying Zhang, Xinguo Ren, Patrick Rinke, Volker Blum, and Matthias Scheffler,
Numeric atom-centered-orbital basis sets with valence-correlation consistency from H to Ar
New Journal of Physics 15, 123033 (2013).