
Computational Materials Science From Scratch

The Nuts and Bolts of Electronic Structure Theory

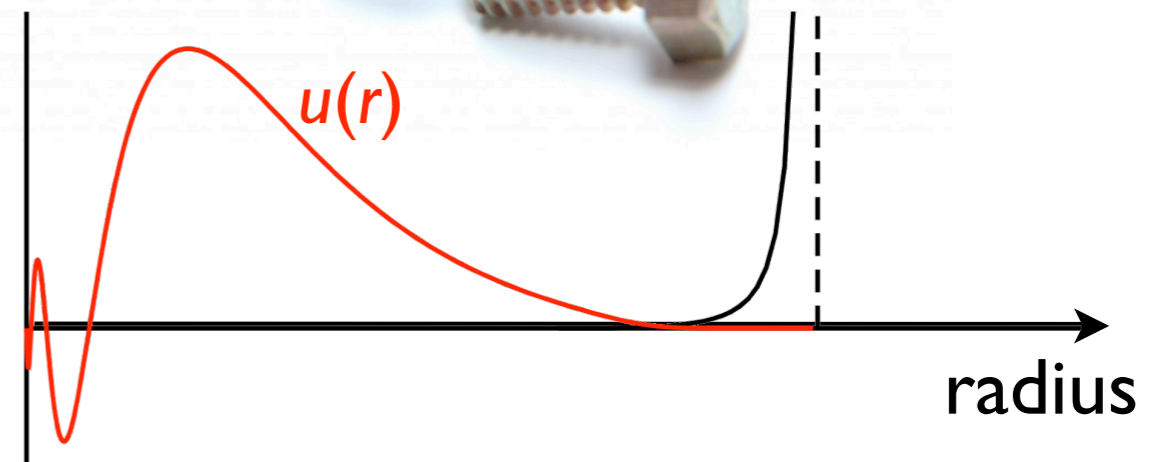
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<https://aimsclub.fhi-berlin.mpg.de>

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



Who Did the Work?

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Fritz Haber Institute, Berlin

[Richard-Willstätter-Haus]

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FHI-aims team and collaborators: Matthias Scheffler (Berlin), Xinguo Ren (Hefei), Karsten Reuter (Munich), well over 100 individuals with contributions to the project. Development in Berlin, Duke, Hefei, Munich, Helsinki, Cardiff, Argonne, etc.



Dr. William Huhn
Spin-Orbit Coupling,
ELSI, GPU



Dr. Svenja Janke
O-I Hybrids



Victor Yu
ELSI / ESL

Ab Initio Materials Simulations Group
Hudson Hall, Duke University



Dr. Rundong Zhao, Ruyi Song, Xixi Qin, Fan Zhang, Tianlin Wang
Xiaochen Du, Connor Clayton, Tianlin Wang, Tommy Lin,
Kimberly Zhang, Douglas Heine, Xinyi Lin, Xin Han



Dr. Raul Laasner
NMR
ELSI



Tong Zhu
PV Materials



Garnett Liu
Perovskites
Bethe-Salpeter

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National Science Foundation



U.S. DEPARTMENT OF
ENERGY

Office of
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Research Fund



MAX-PLANCK-GESELLSCHAFT



ORNL
LLNL



TRIANGLE
MRSEC

Materials Research Science
and Engineering Center

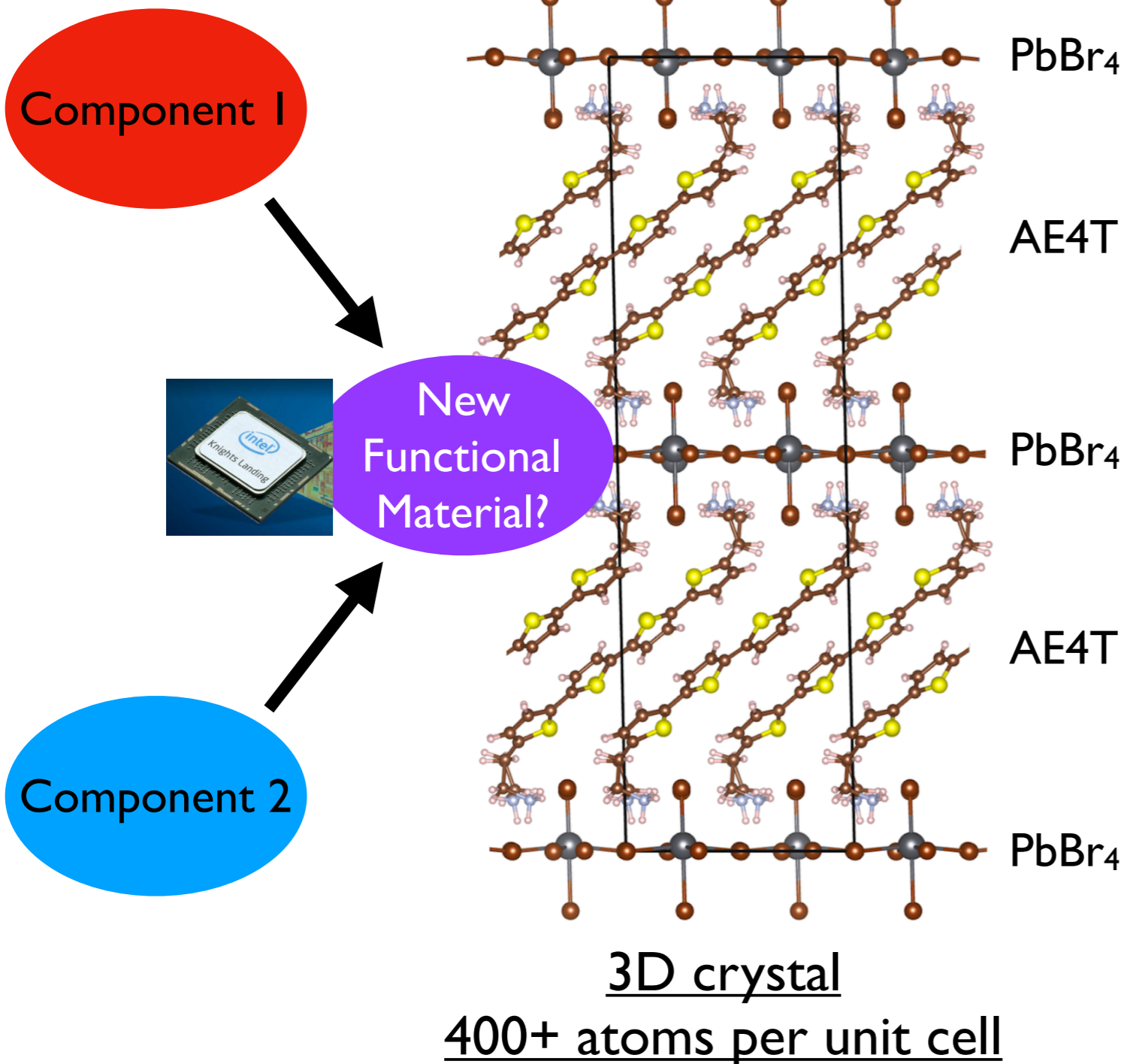


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Materials Properties from Theory?

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



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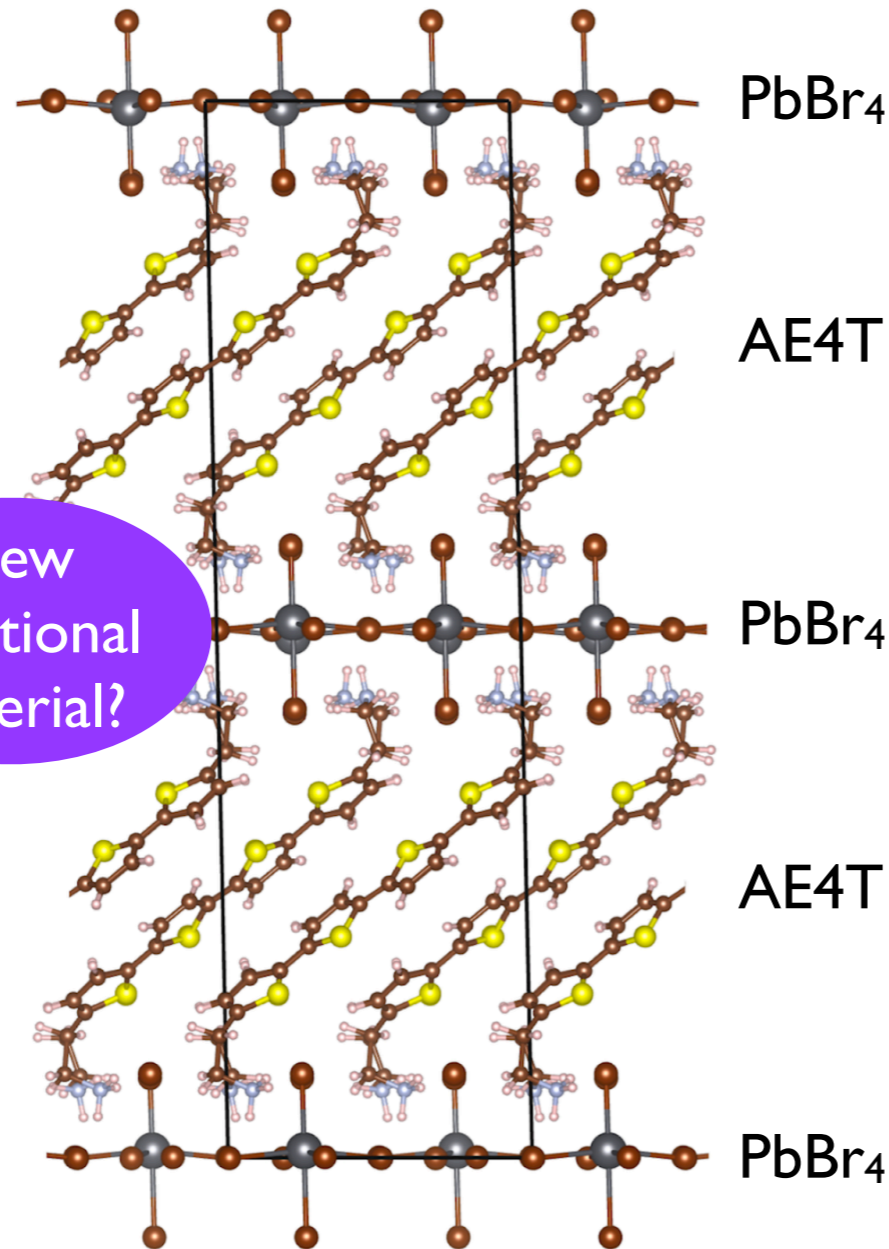
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Component 1



Component 2

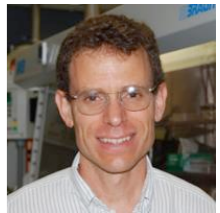
New Functional Material?



3D crystal

400+ atoms per unit cell

Pathway I: Make material, find out its properties.
Mitzi, Chondroudis, Kagan, Inorg. Chem. 38, 6246 (1999)



David Mitzi

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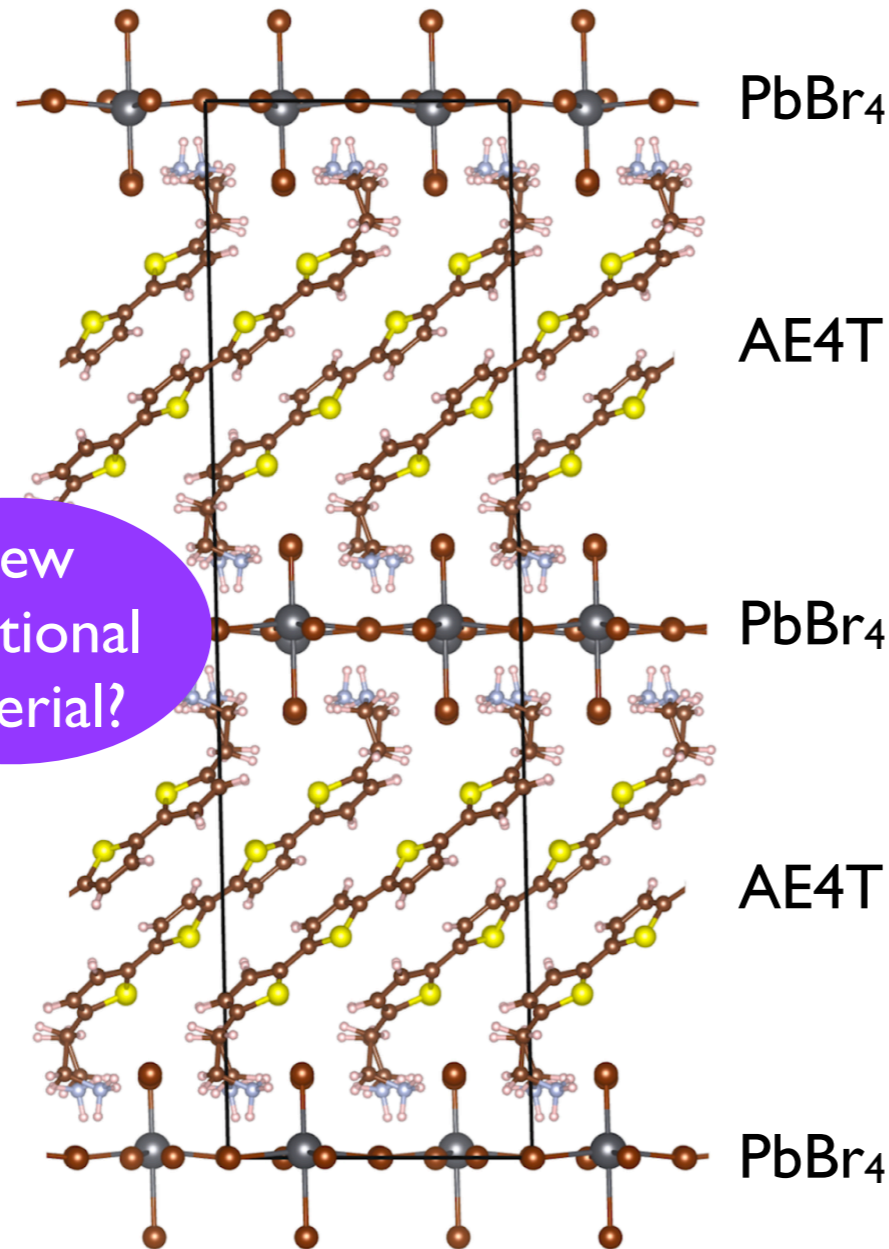
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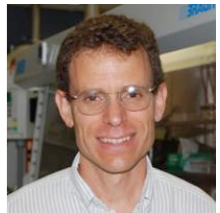
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Pathway 2: Accurate computational prediction?

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

The theory we have is accurate enough.

But need to implement sufficiently good approximations on a real computer.

Scope of this Lecture

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

Kohn-Sham Equations, 1965

Technical concepts (I):

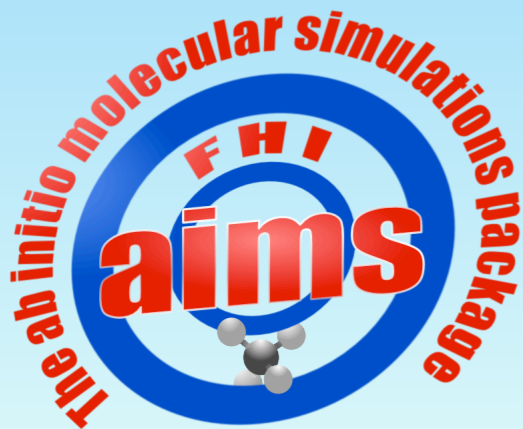
- Basis sets
- Integrals and grids; electrostatics; molecules vs. periodic solids
- How to deal with relativity
- Scalability (large systems, large computers)

Our implementation: FHI-aims

All-electron, molecules and periodic systems

Main example for this talk (others in the next 10+ days)

Used for tutorials in the next 10+ days



Standard Steps to “Practical” Electronic Structure Theory

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

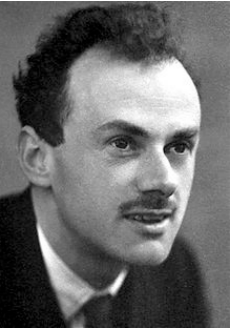
P.A.M.
Dirac



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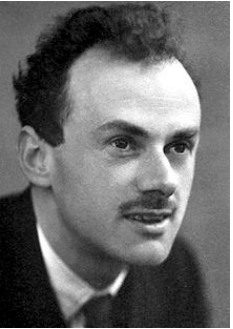


I) Separate Electron and Nuclear Coordinates (Born-Oppenheimer Approximation)

Standard Steps to “Practical” Electronic Structure Theory

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

P.A.M.
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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}_{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:

$$E_{\text{tot}} \leq \langle \psi | H | \psi \rangle$$

... successive refinement of ψ

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

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

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

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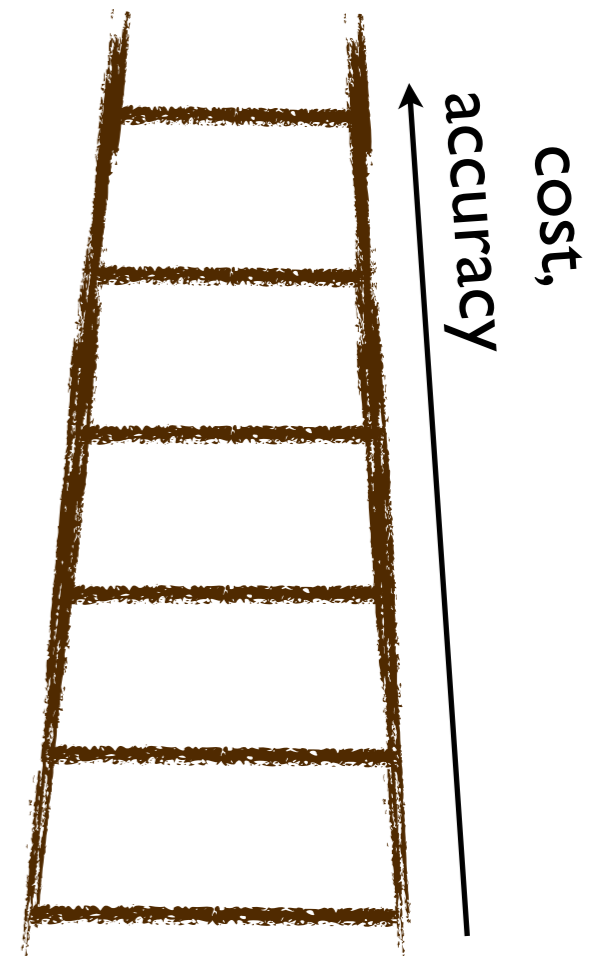
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“Perdew’s ladder”
to exact solution



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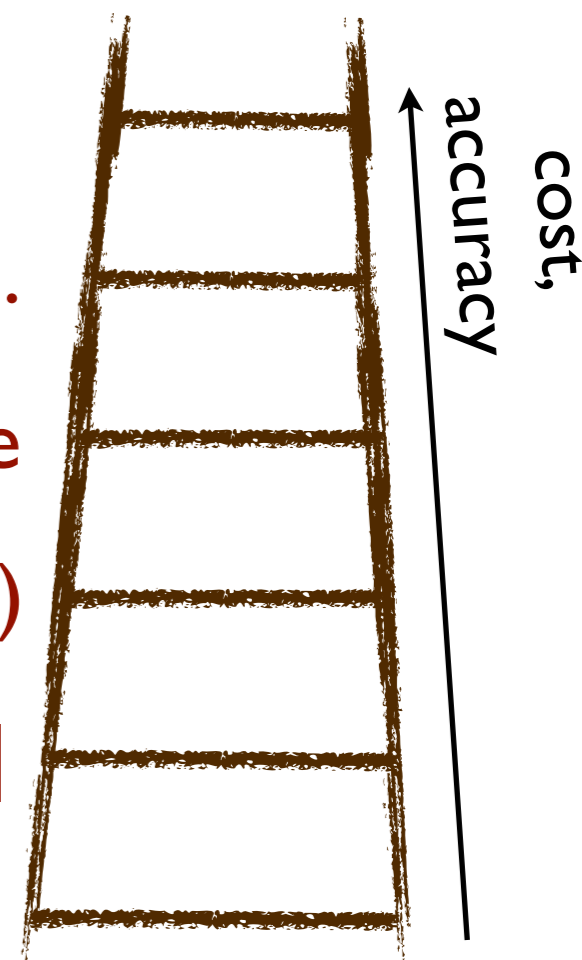
response / many-body terms: GW, RPA, SOSEX, ...

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): $n(r)$



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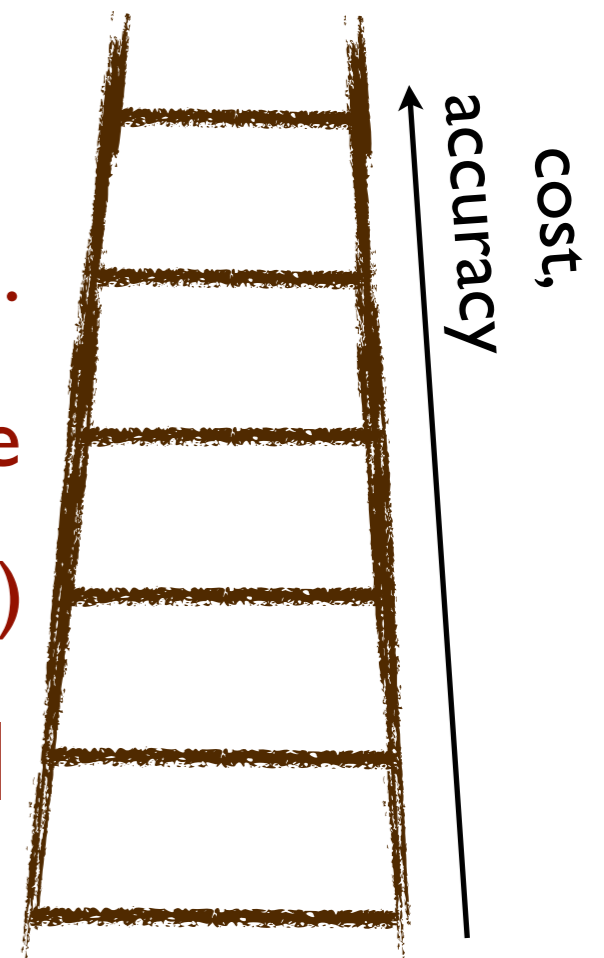
hybrid functionals: non-local exchange

+ van der Waals

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The Kohn-Sham Equations - How to Solve Them

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

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“As (almost) everyone does”:

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

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→ generalized eigenvalue problem:

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

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

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

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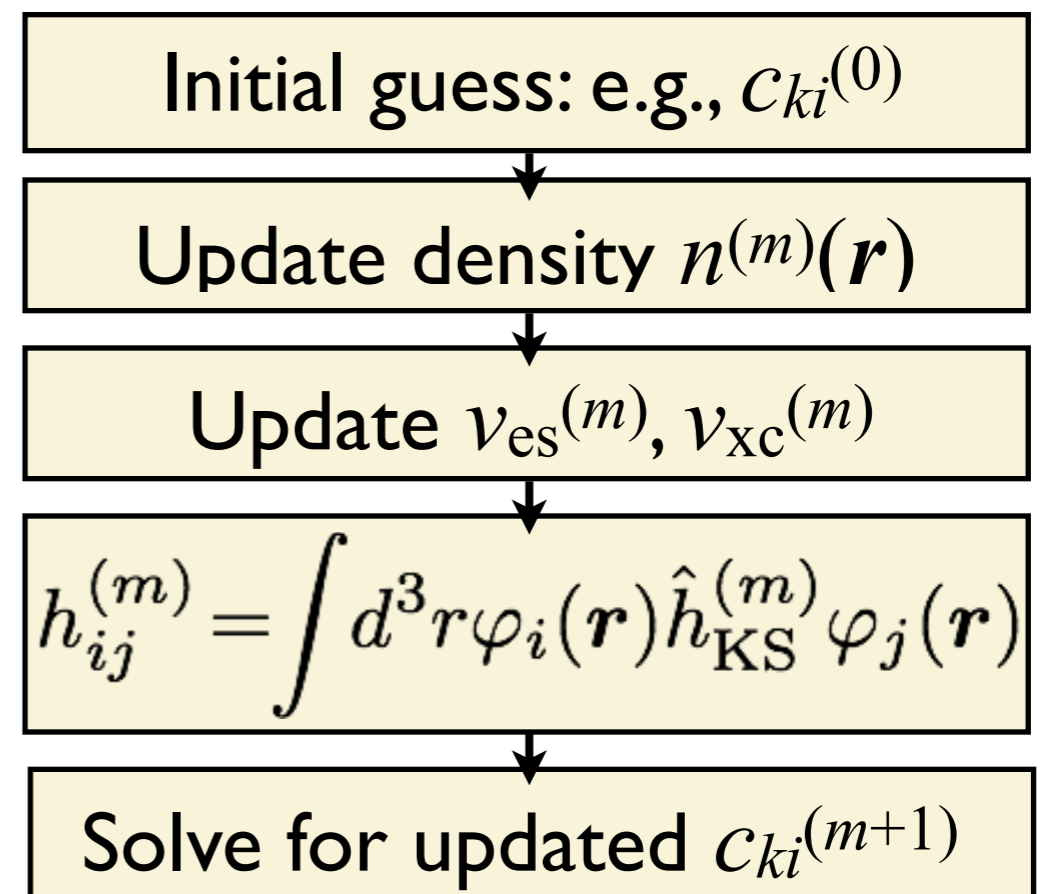
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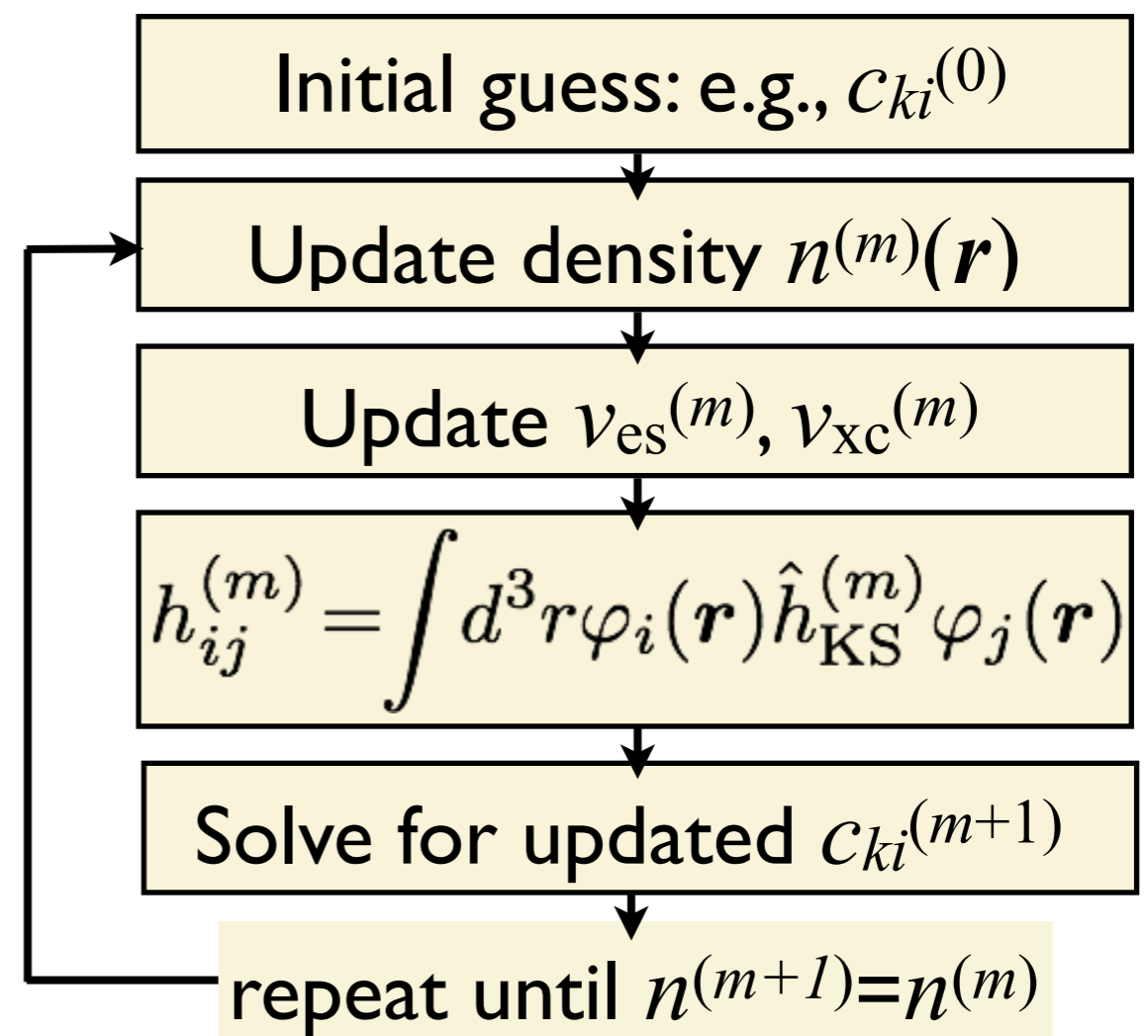
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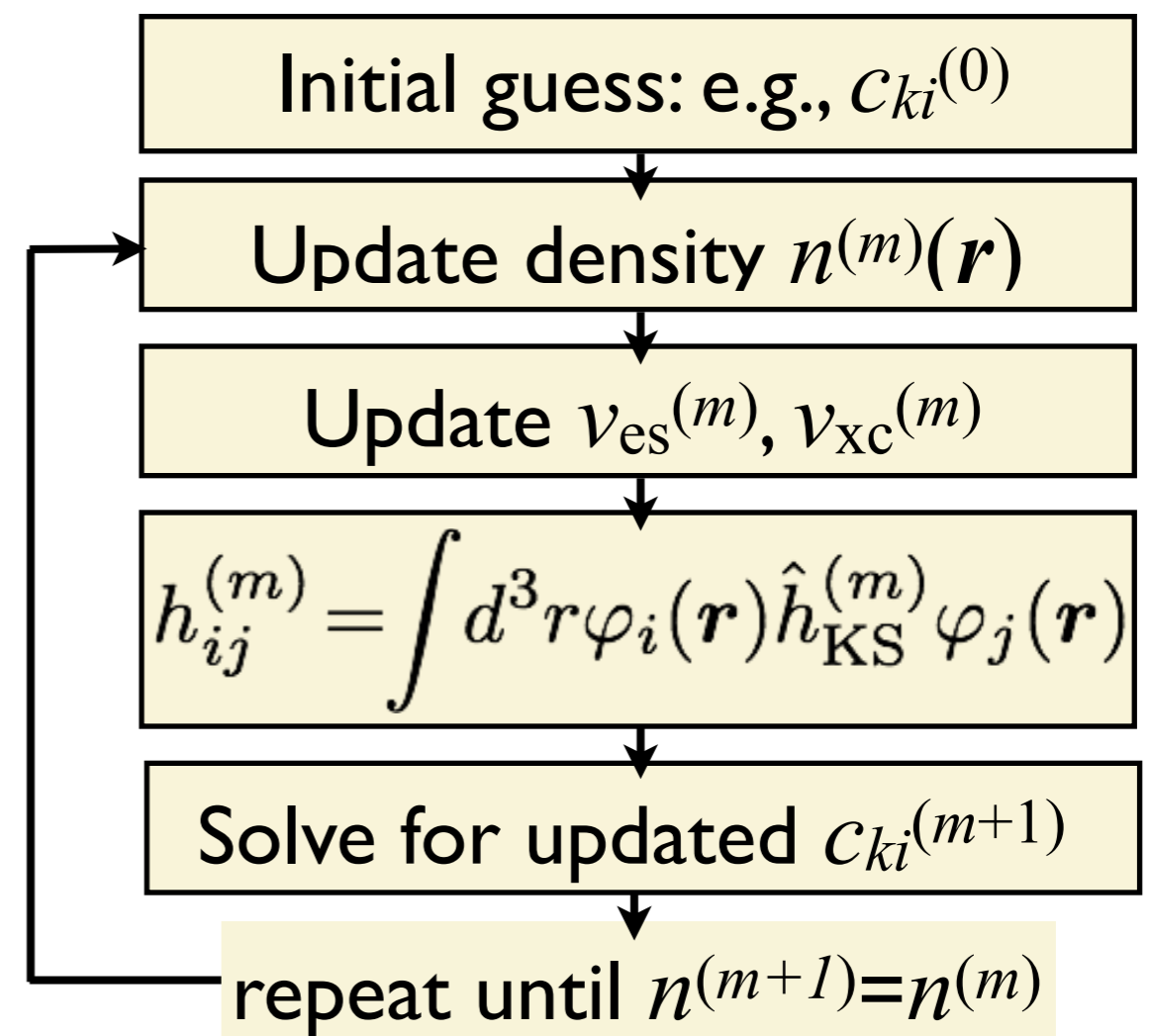
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Florian Knoop
Tue 10:00h



Representing the Orbitals: Basis Sets

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

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

Many good options:

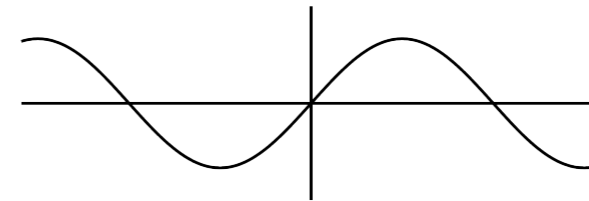
Representing the Orbitals: Basis Sets

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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"

Nicola Marzari
Tue 11:30h

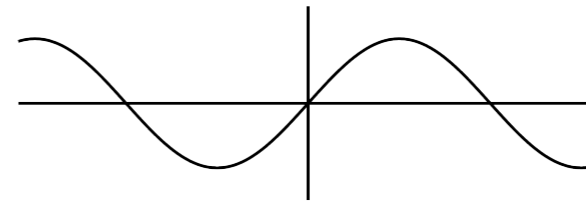
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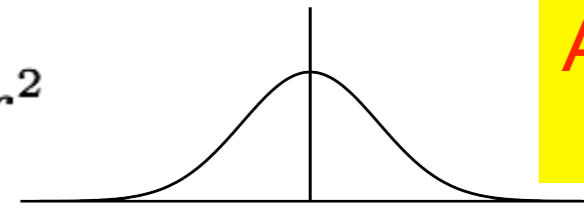
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Andreas Grüneis
Wed 10:00h

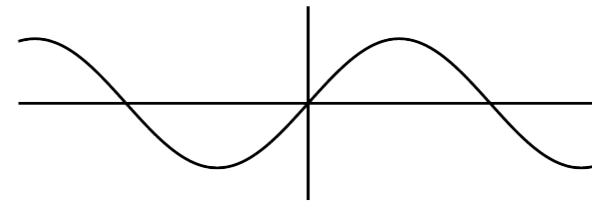
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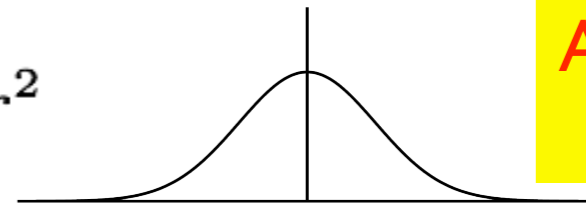
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(Claudia Draxl
Mon 10:00h)

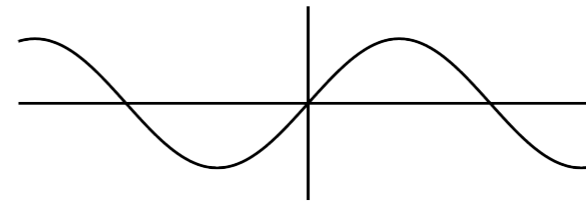
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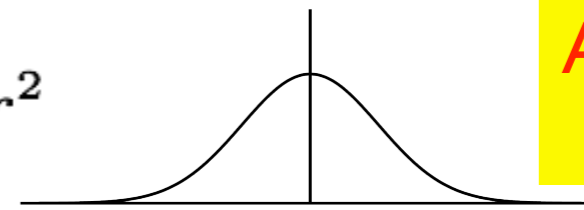
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- Augmented plane waves (*Slater 1937; Andersen 1975; etc.*)
- Many others: (L)MTO, "real-space", wavelets, ...



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(Claudia Draxl
Mon 10:00h)

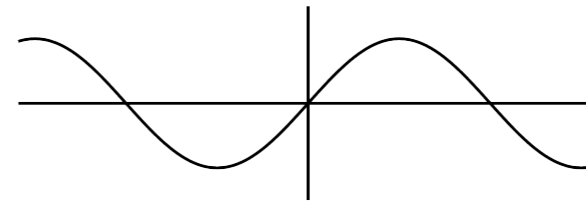
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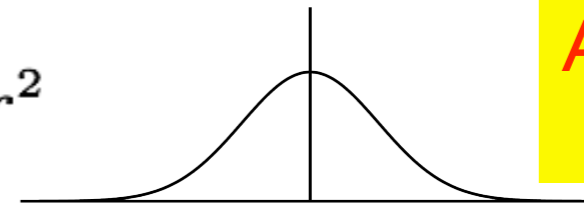
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- **FHI-aims (this talk)**: Numeric Atom-Centered Basis Functions

Our Choice: Numeric Atom-Centered Basis Functions

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

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

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

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

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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.”

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- free-atom like: $v_i(r) = v_{\text{free atom}}^{\text{DFT}}(r)$
- Hydrogen-like: $v_i(r) = z/r$
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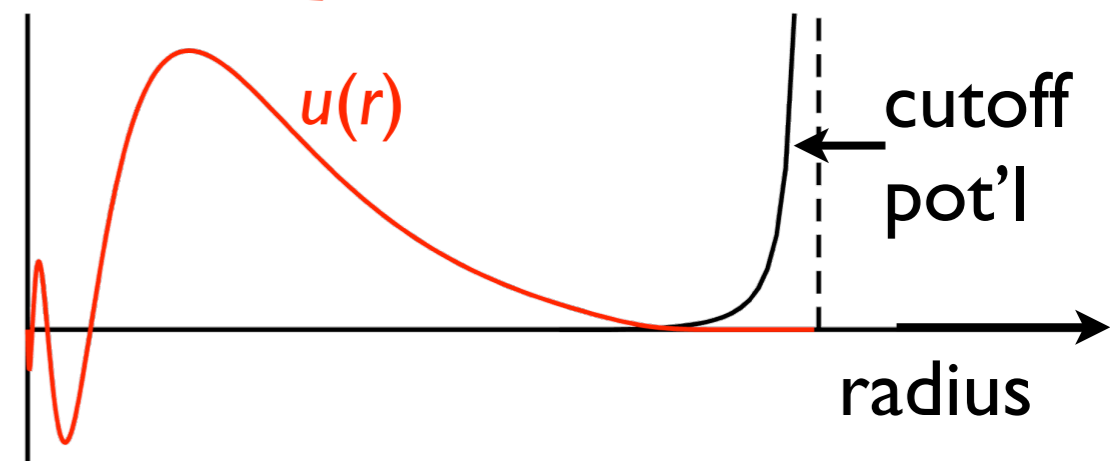
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 - Localized; “naturally” all-electron
 - The choice of efficient and of enough radial functions is obviously important
 - But need a “basis set library” - list of basis functions for all elements (1-102), from fast qualitative to meV-converged total 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,
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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
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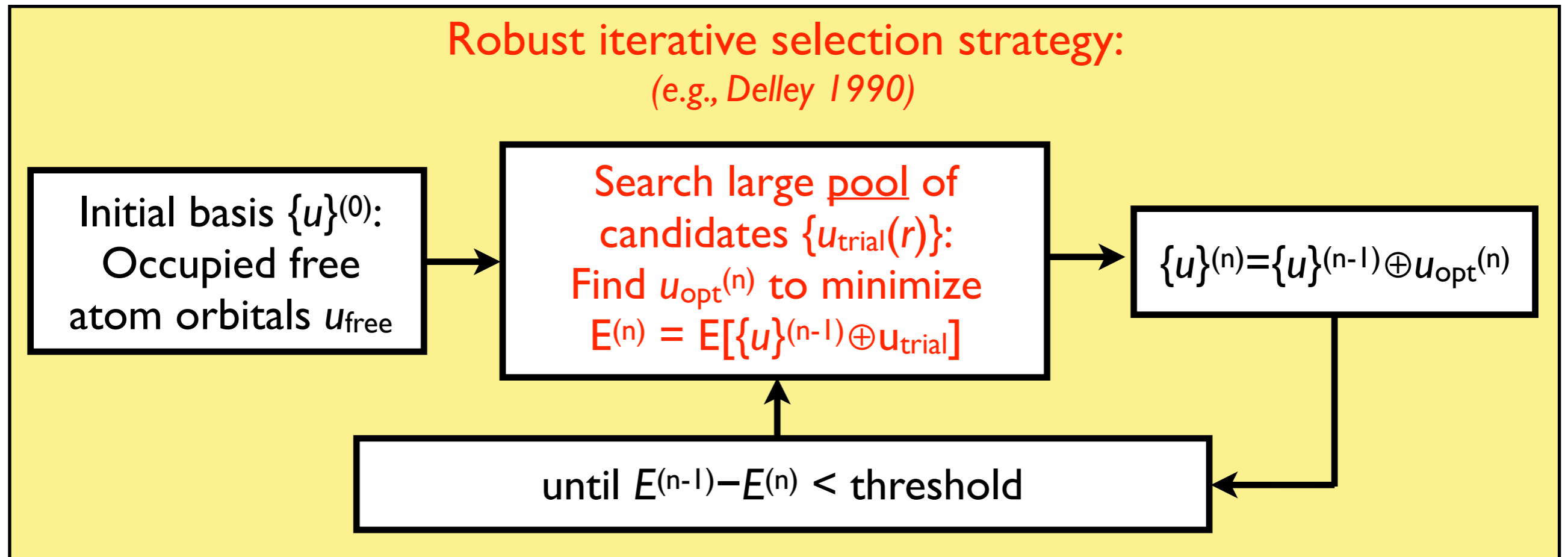
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Iterative Selection of NAO Basis Functions

“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

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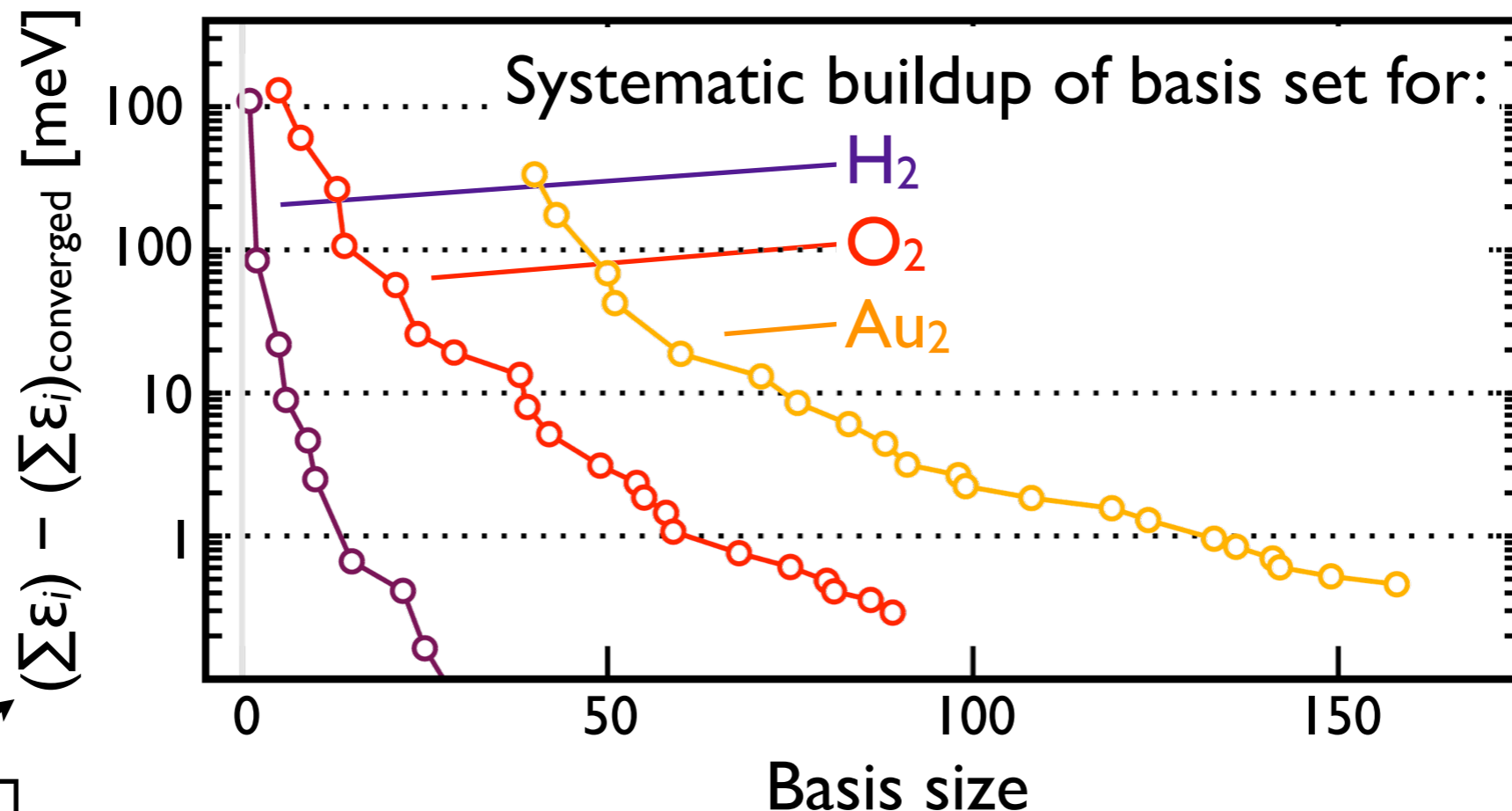
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Remaining
basis set error

Outcome: Hierarchical Basis Set Library for Elements 1-102

	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”

...

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

	H	C	O	Au
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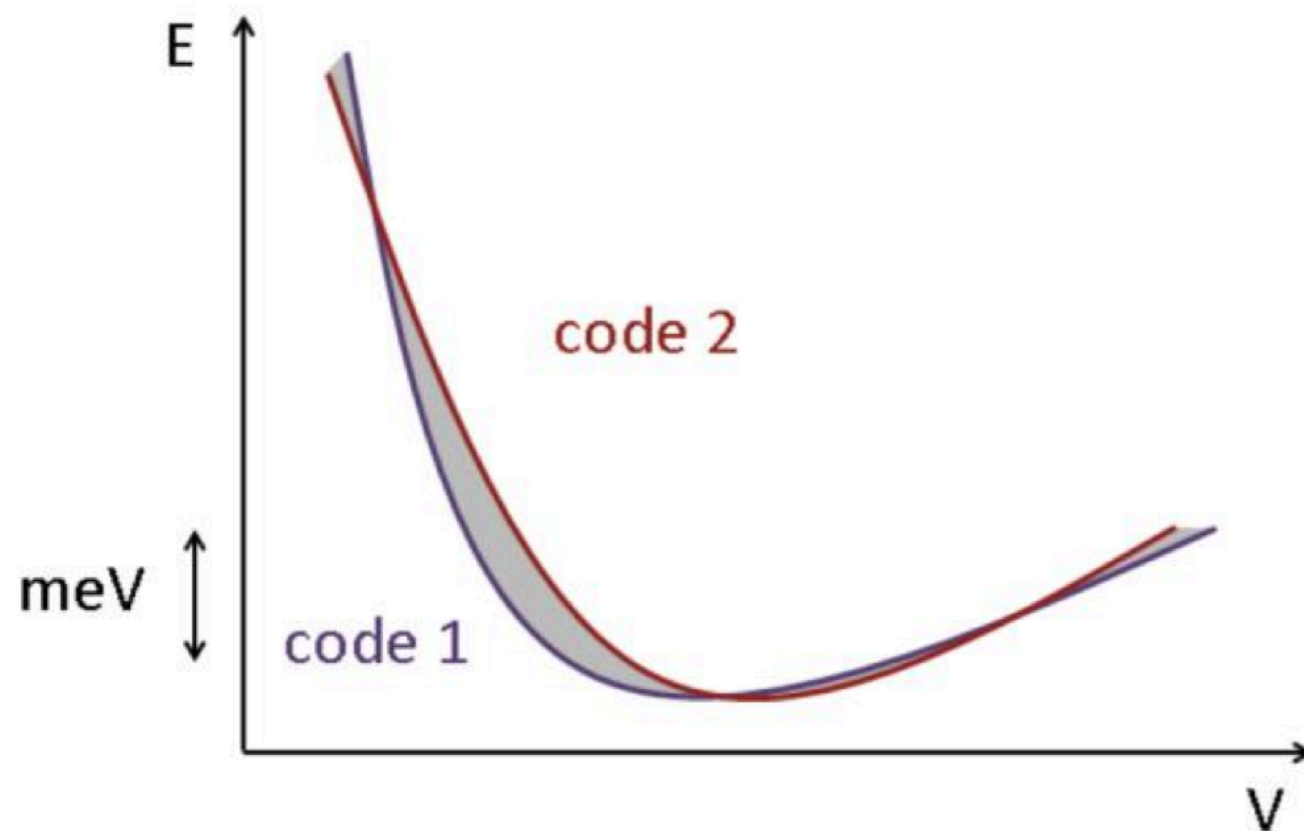
In FHI-aims input (example: Hydrogen, tight settings):

```
#####
#
# 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
#####
```

Accuracy 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



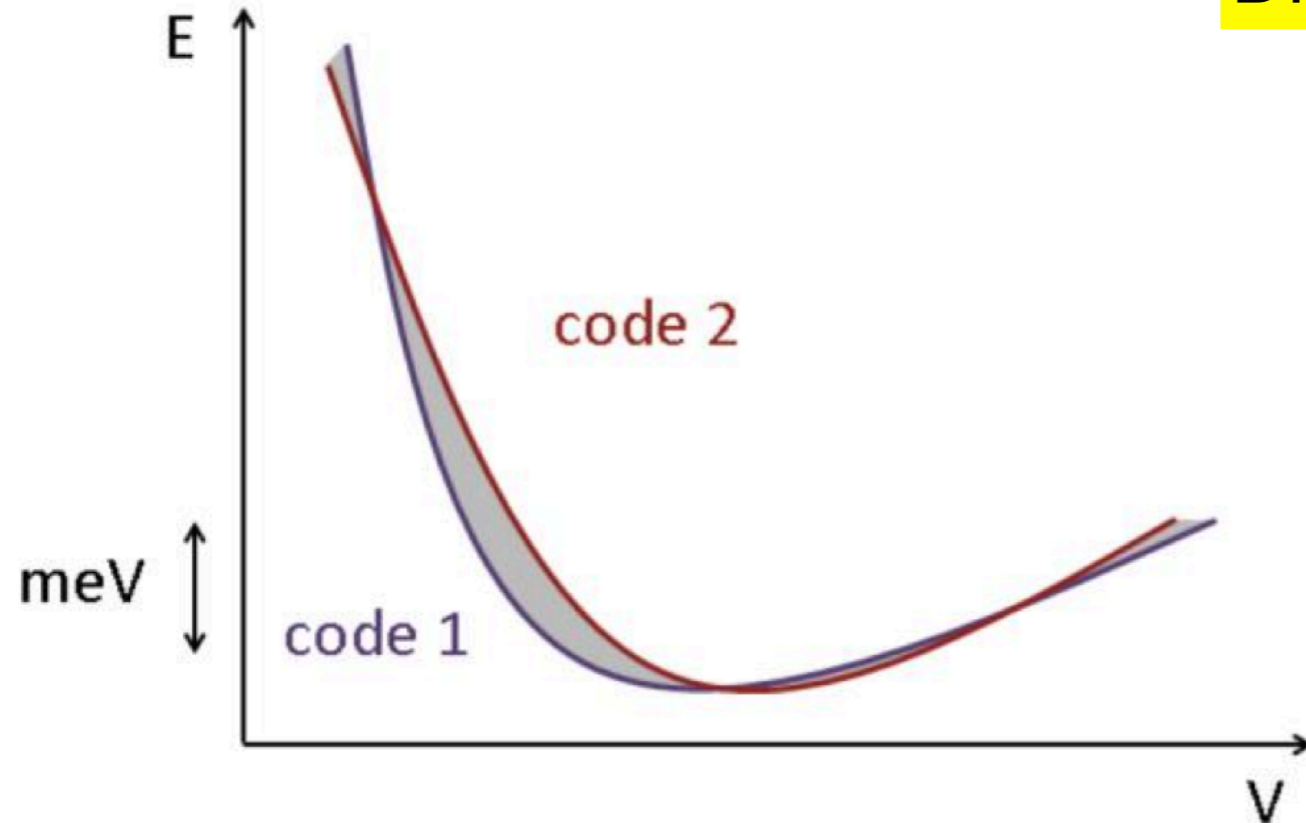
$$\rightarrow \Delta_i(a, b) = \sqrt{\int_{0.94V_{0,i}}^{1.06V_{0,i}} \frac{(E_{b,i}(V) - E_{a,i}(V))^2}{0.12V_{0,i}} dV}$$

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



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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+xlo	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
(μ Ha accuracy)

DFT-PBE

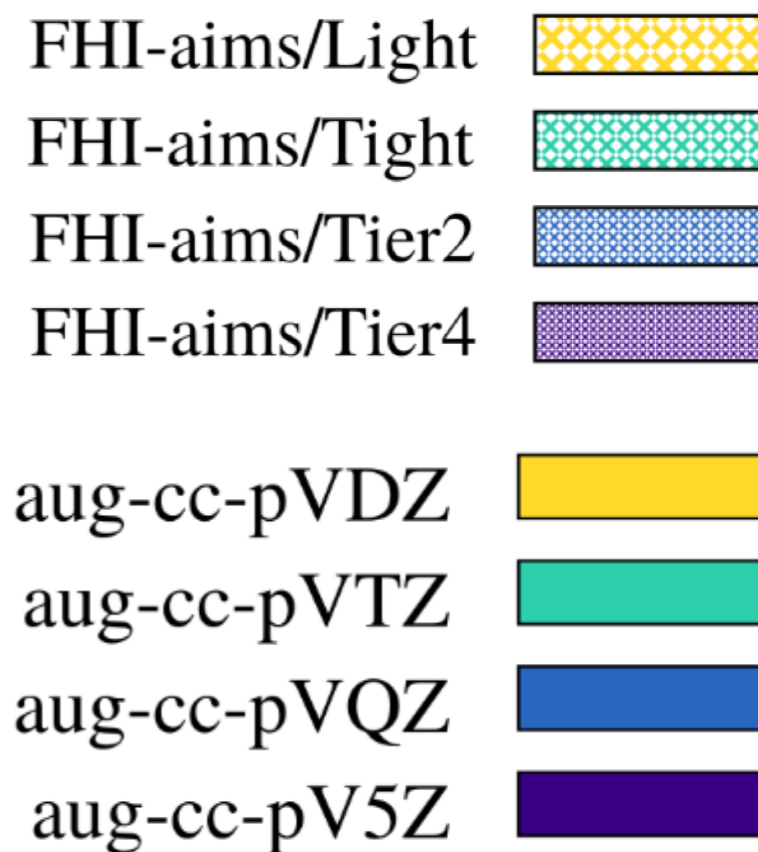
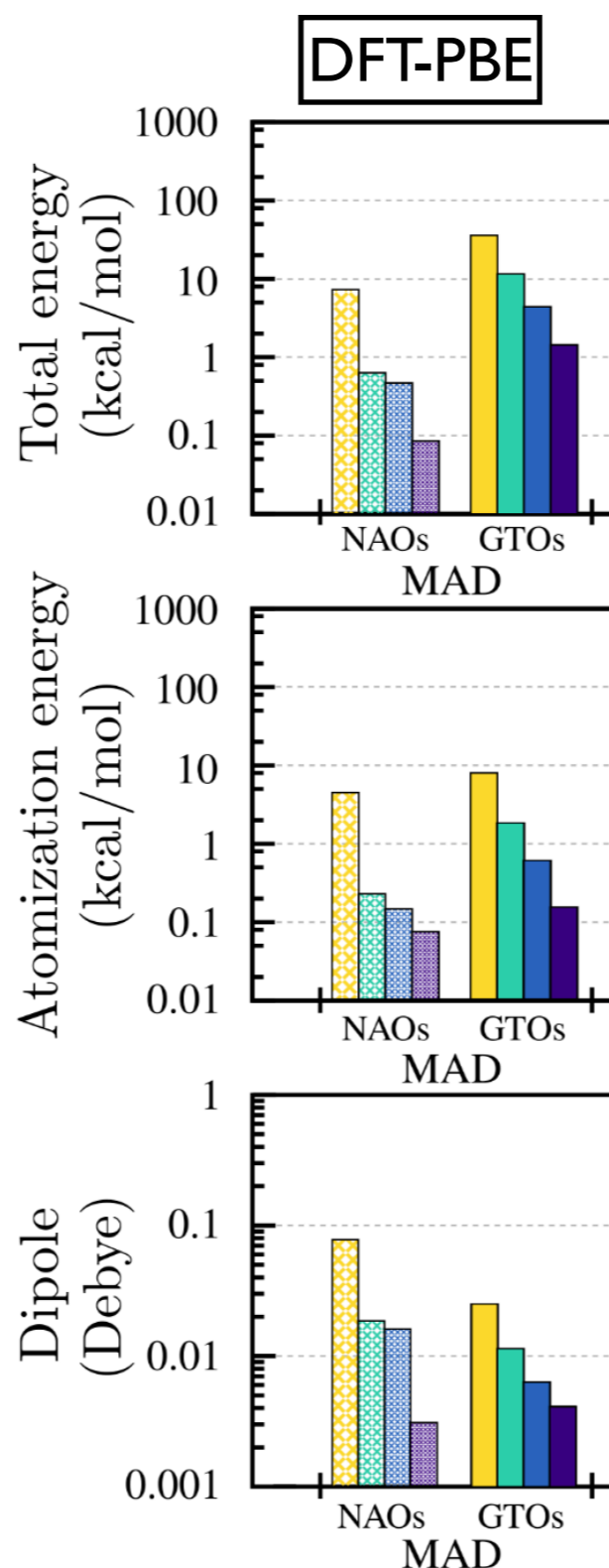
Benchmark:
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DFT-LDA, PBE, PBE0

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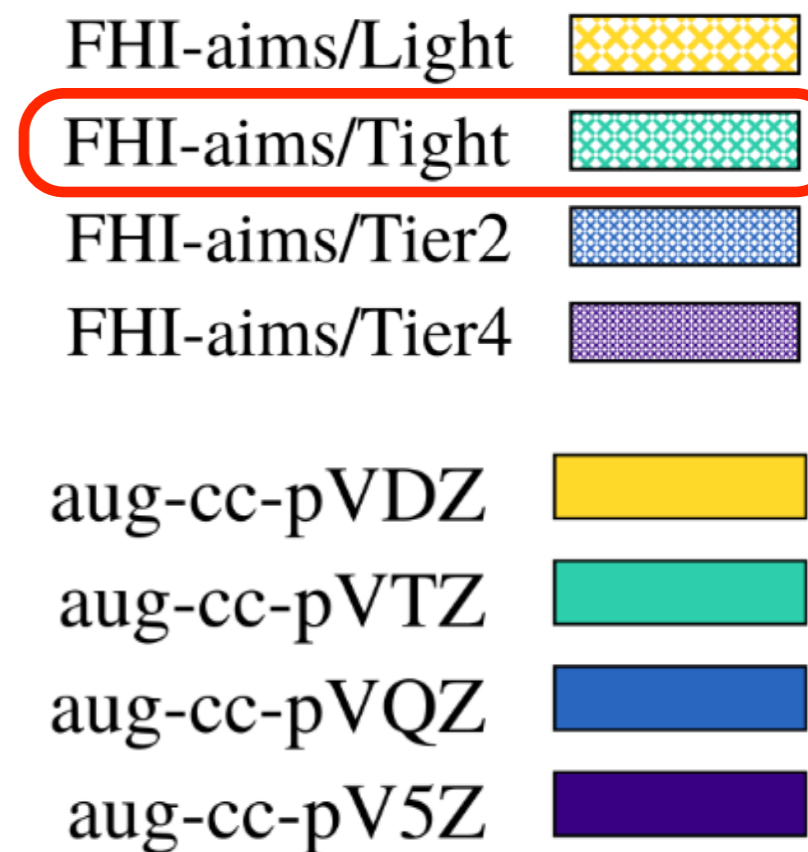
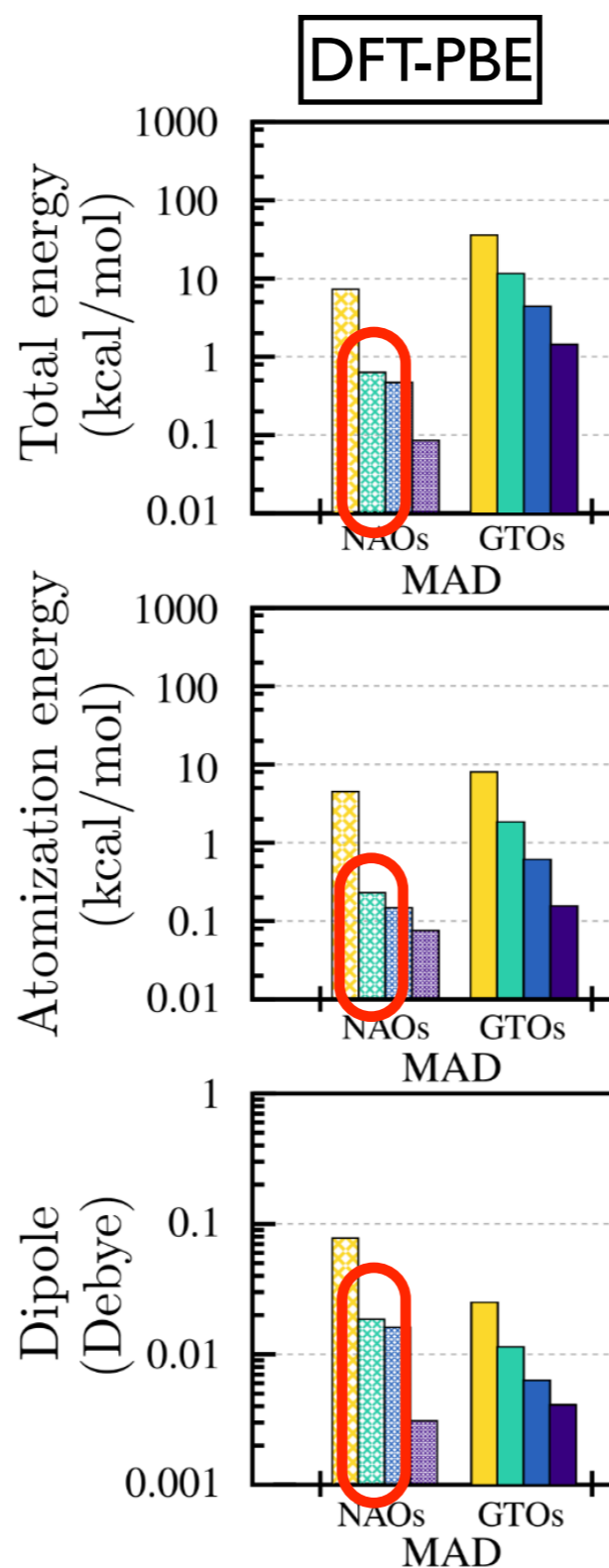


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Using Numeric Atom-Centered Basis Functions: Pieces

- *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

- Coulomb operator

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

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S. Levchenko
Wed 09:00h

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Numeric Atom-Centered Basis Functions: Integration

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

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

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

Numeric Atom-Centered Basis Functions: Integration

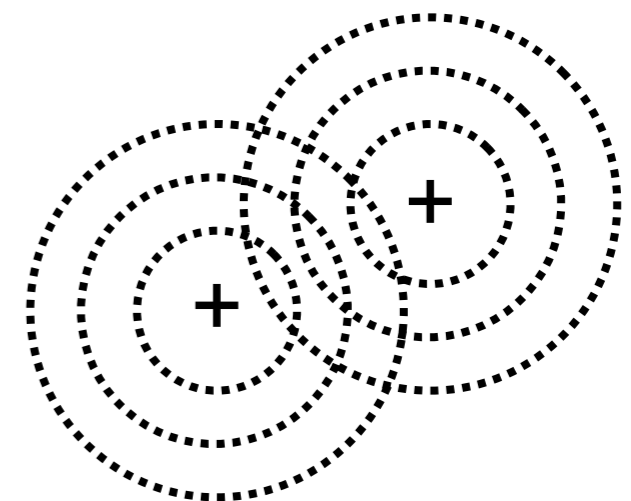
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- Overlapping atom-centered integration grids:

- 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!

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

- Discretize to integration grid:

$$\int d^3r f$$

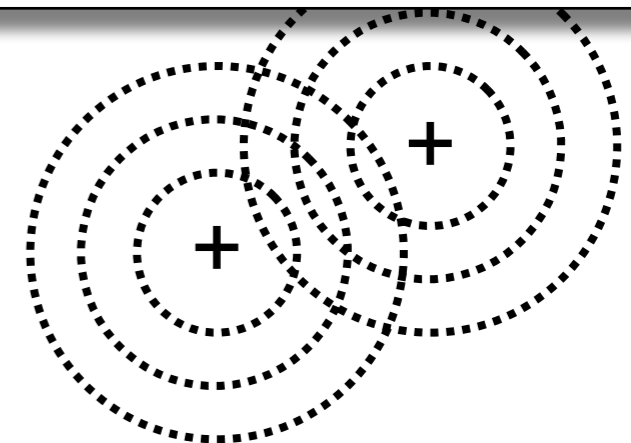
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In FHI-aims input (example: Hydrogen, tight settings):

```
#  
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

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

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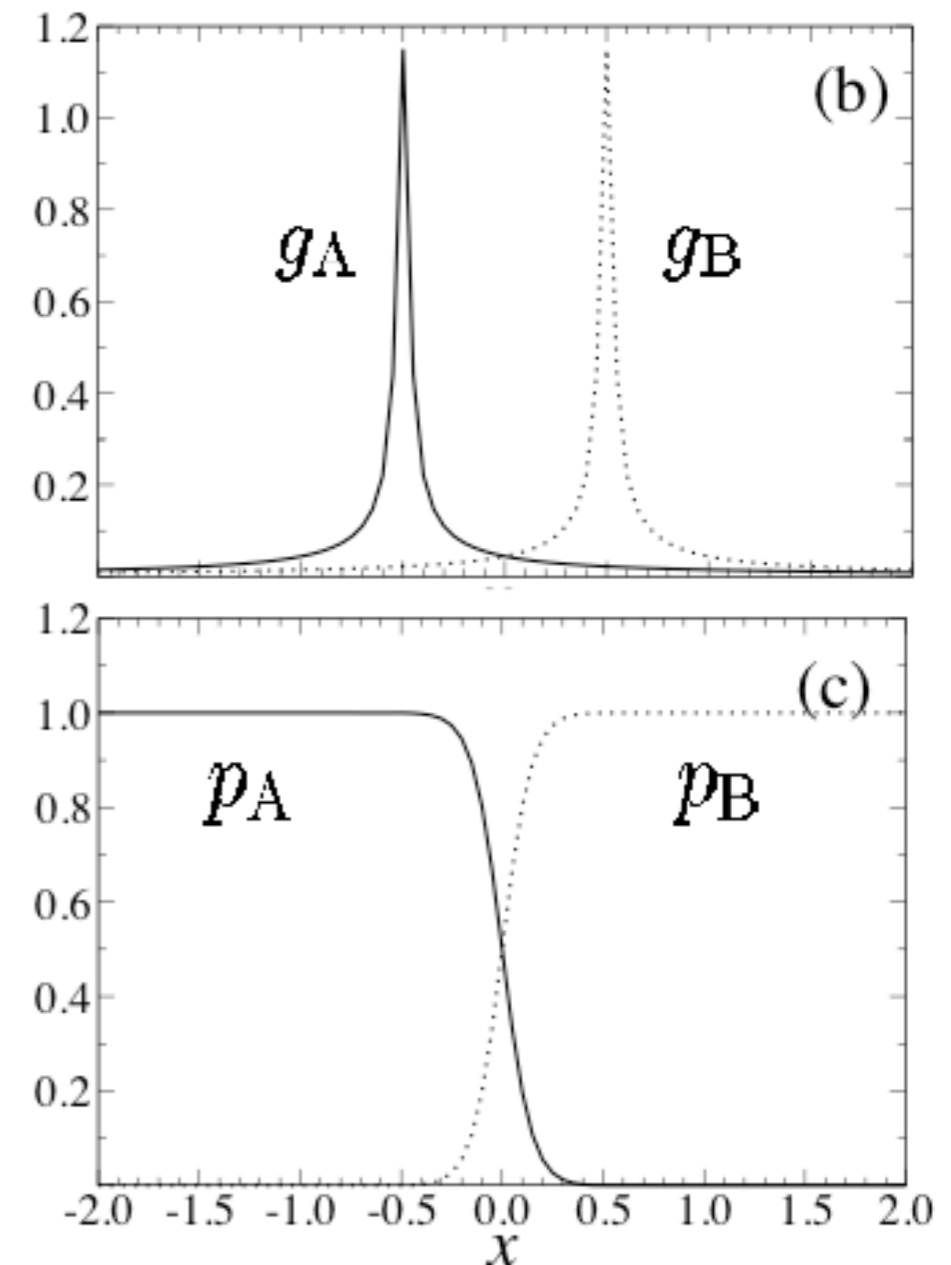
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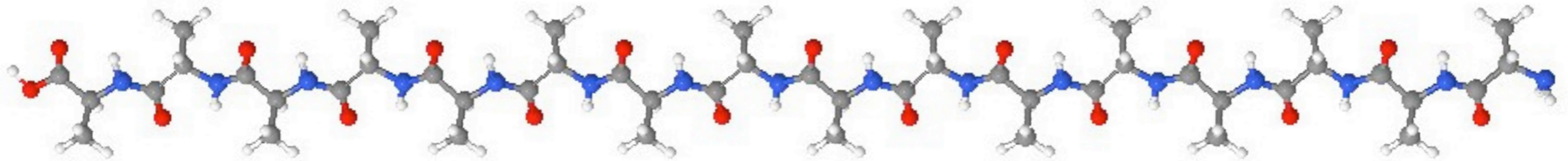
- e.g.:
$$g_{\text{atom}} = \frac{\rho_{\text{atom}}(r)}{r^2} \quad (\text{Delley 1990})$$

many alternatives:

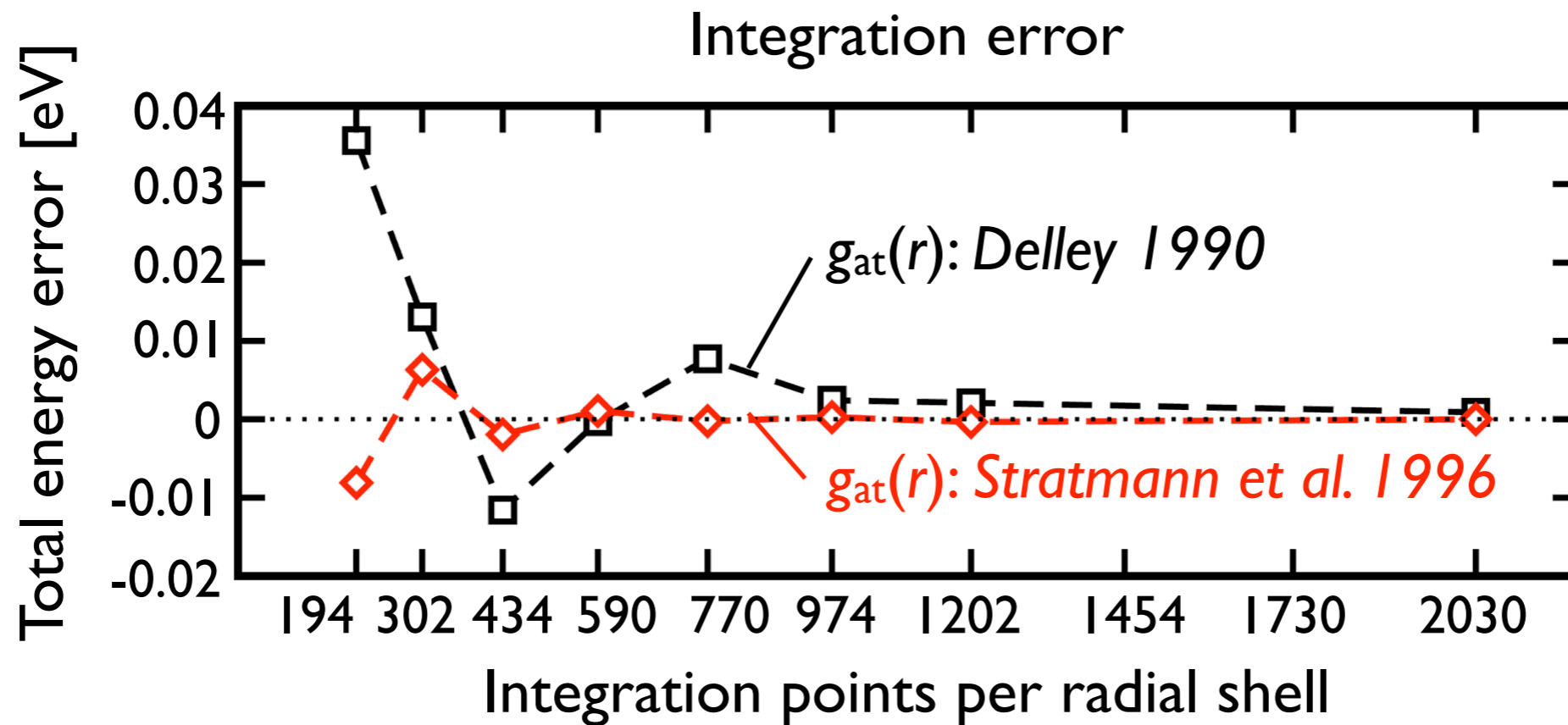
Becke 1988, Stratmann 1996, Koepernik 1999, ...



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

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

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- Classical electrostatics:

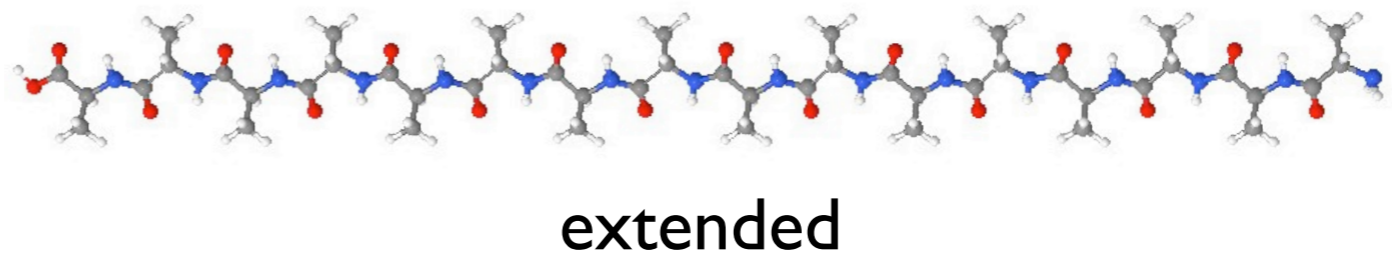
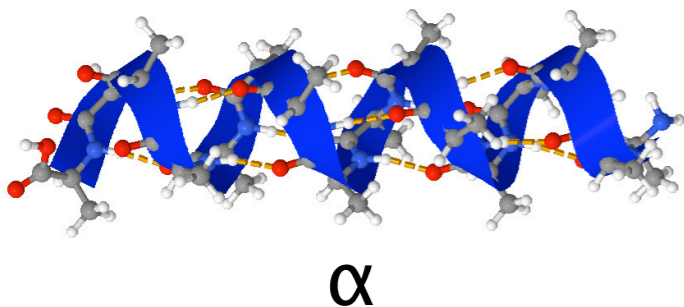
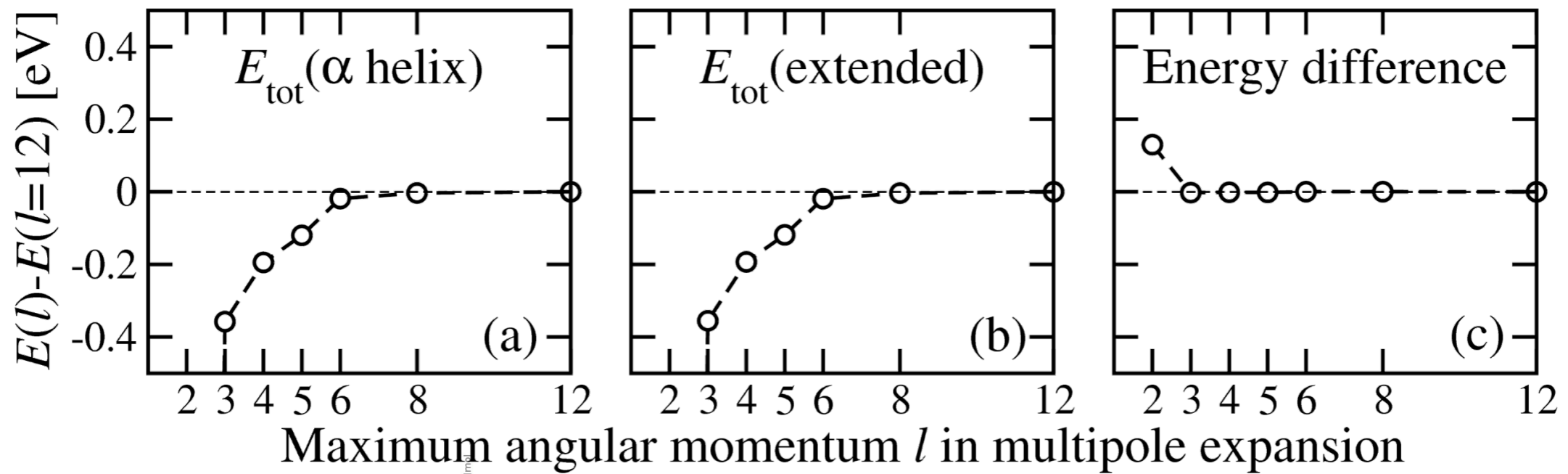
$$v_{\text{es}}(\mathbf{r}) = \sum_{\text{atoms}} \sum_{lm}^{l_{\text{max}}} v_{\text{atom},lm}(|\mathbf{r} - \mathbf{R}_{\text{atom}}|) Y_{lm}(\Omega_{\text{atom}})$$

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}



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

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

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- Coulomb operator

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S. Levchenko
Wed 09:00h

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How Strong are Relativistic Effects Across the Periodic Table?

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	



William Huhn
(Duke Univ.)

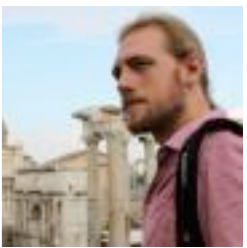
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Strength of Relativistic Effects

GaAs: Moderate

Pb: Heavy



William Huhn
(Duke Univ.)

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

Relativity

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Relativistic QM: Dirac Equation

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

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... 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.

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“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

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

1. LAPW, others: Outright treatment

- radial functions in atomic sphere (core, valence): Per-state relativistic
- 3-dimensional non-relativistic treatment of interstitial regions

Tricky with NAO's: Basis functions from different atomic centers overlap!

2. Approximate one-Hamiltonian treatment

Popular: Zero-order regular approximation (ZORA) [1]

[1] E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.* **99**, 4597 (1993)

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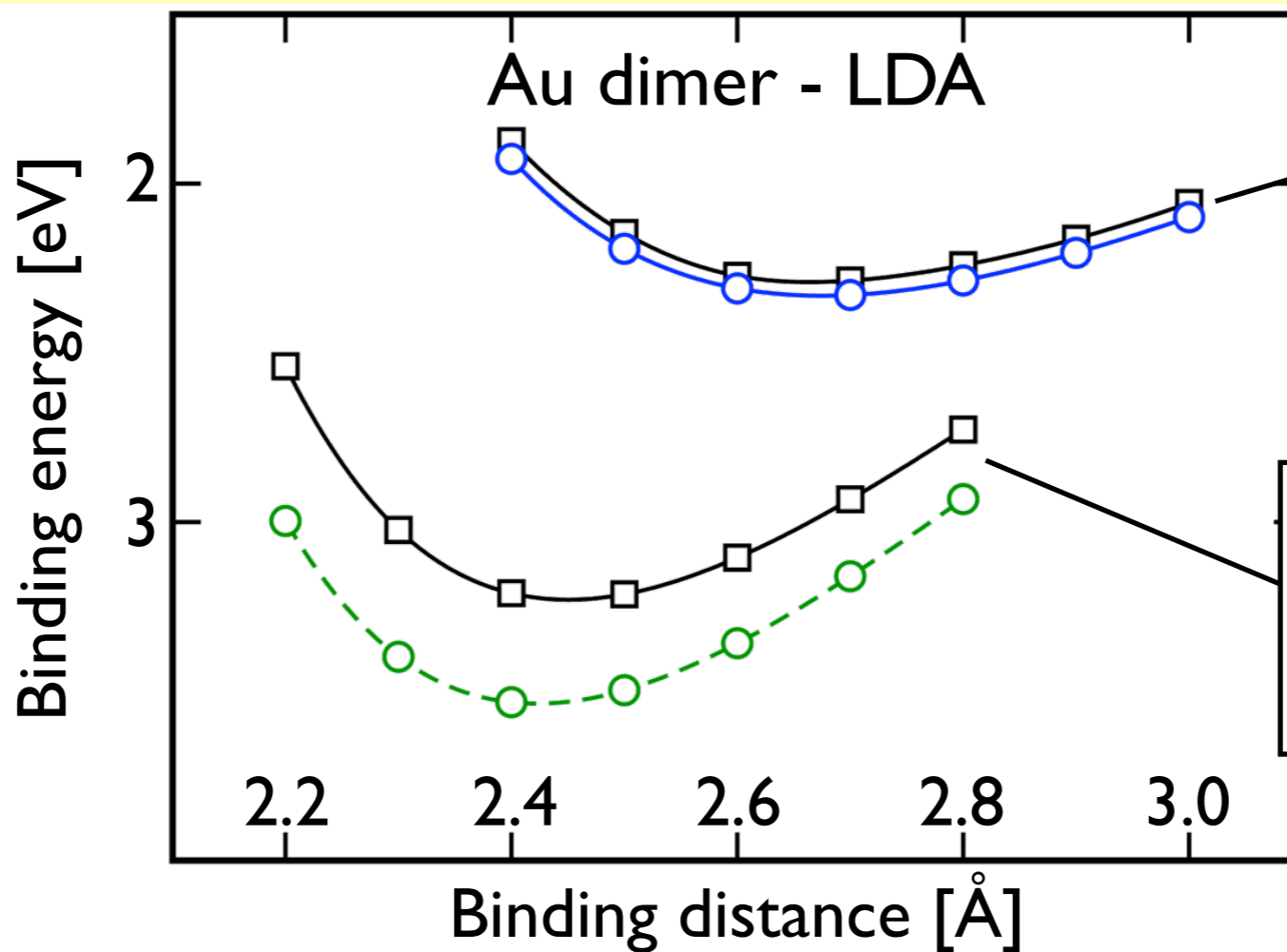
... not gauge-invariant!

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ZORA in practice: Harsh approximation (known)



Nonrel.:
LAPW
FHI-aims

Relativistic:
LAPW
ZORA

I. LA
→ ra
→ 3-
Trick
2. Ap
Po

...no gauge invariance!

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Accurate, Stable Scalar Relativity: “Atomic ZORA”

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ZORA

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“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**

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

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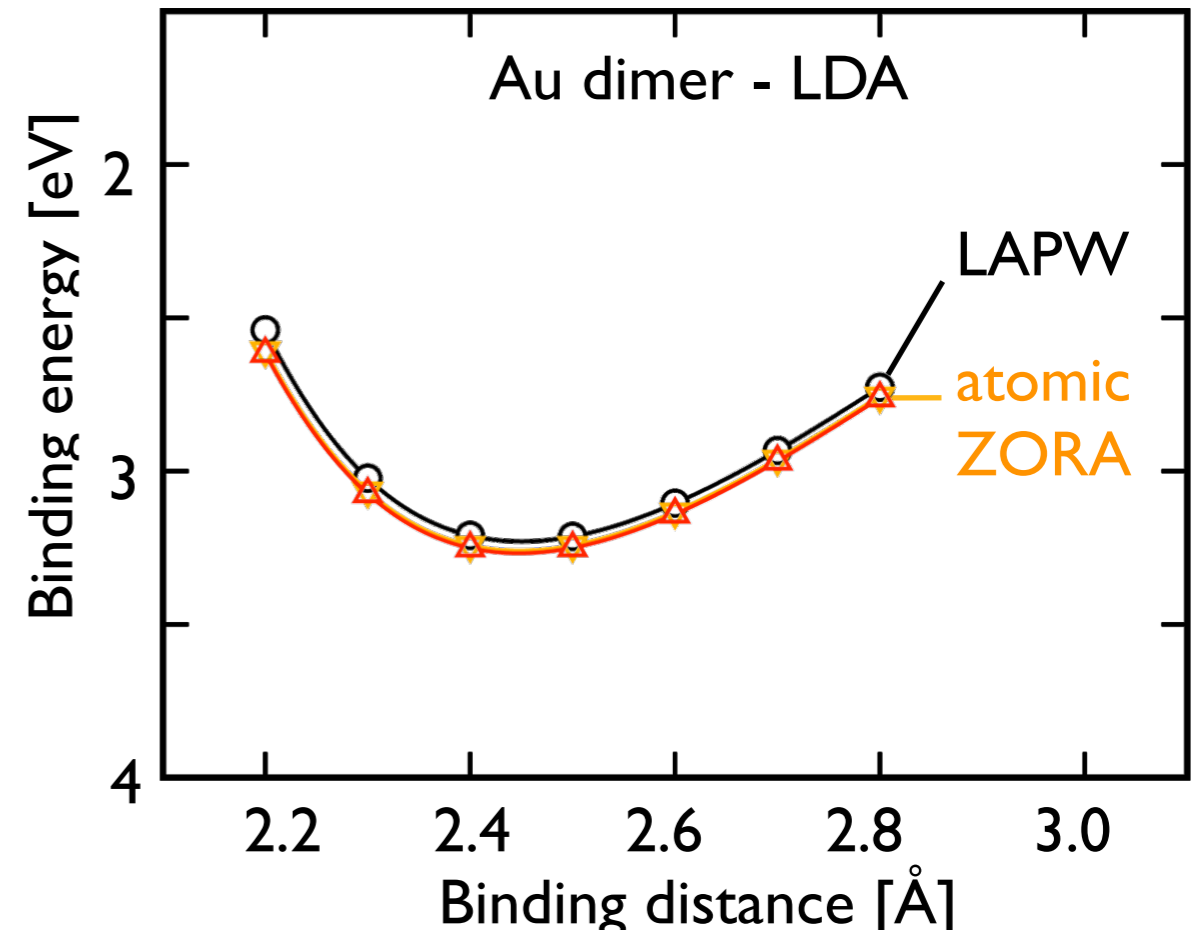
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ZORA

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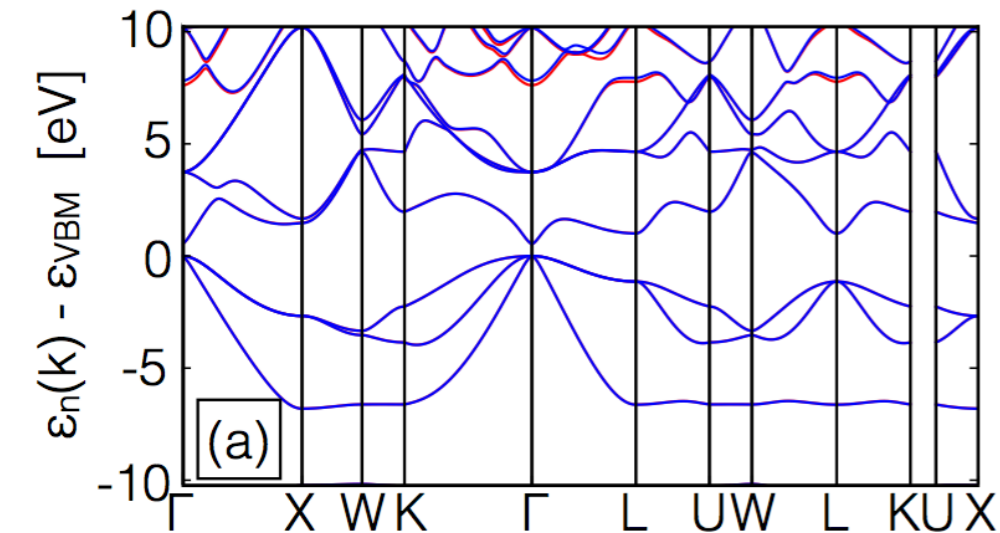
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Benchmark: Scalar-Relativistic Band Structures for 103 Solids

NAO, SR
(L)APW+lo, SR



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



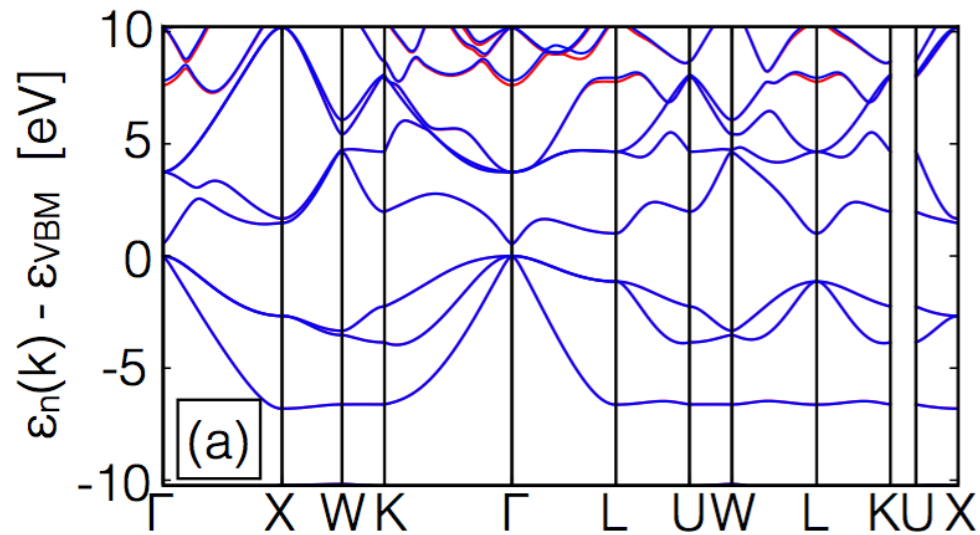
Dr. William Huhn
(Duke Univ.)

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

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

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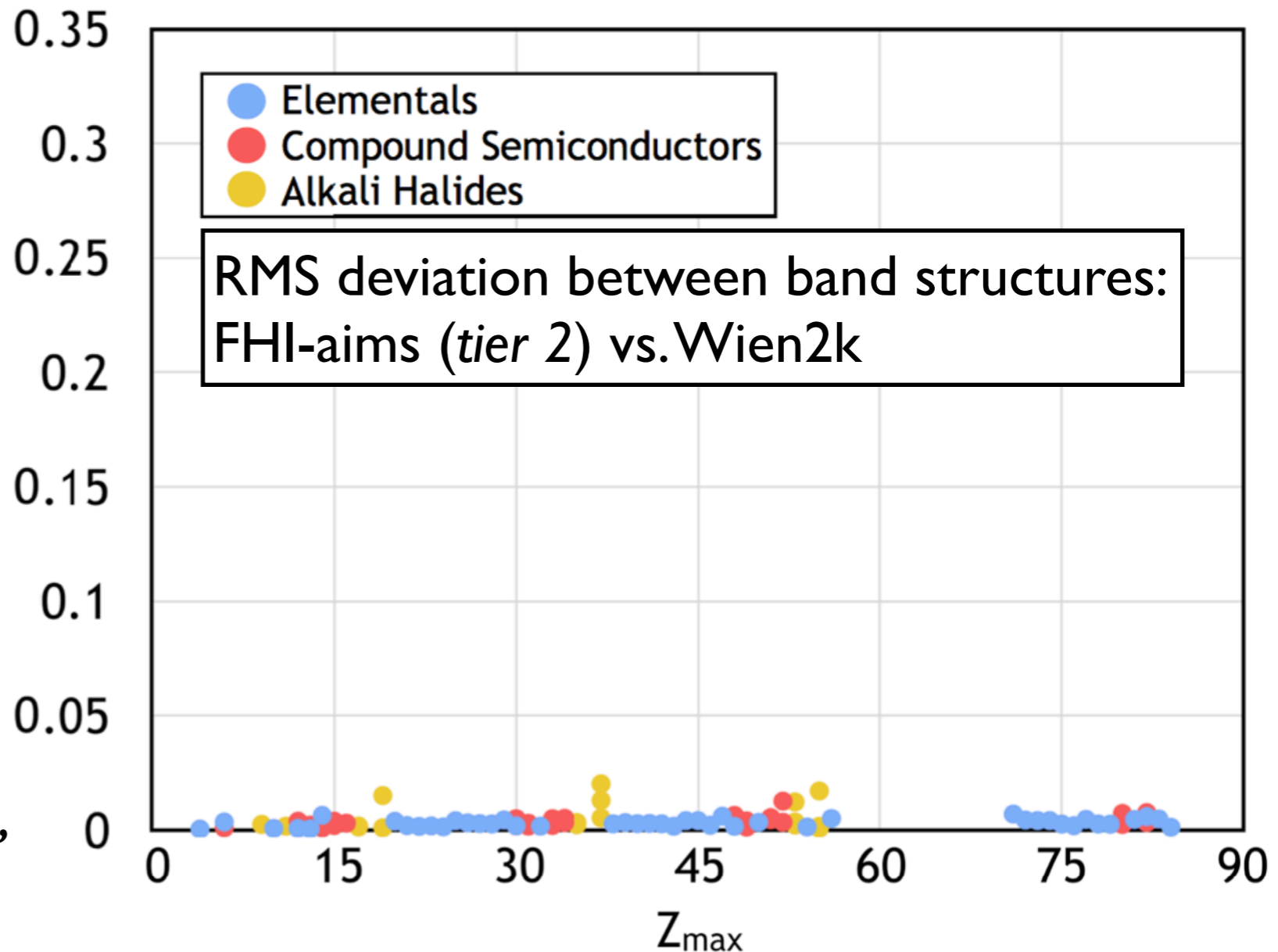
Dr. William Huhn
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Scalar-Relativistic

45 elemental structures,
37 compound semiconductors,
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[VBM - 10 eV, VBM]

Δ_{band} [eV/band]



RMS deviation between band structures:
FHI-aims (*tier 2*) vs. Wien2k

Huhn, Blum, *Phys. Rev. Materials* **1**,
033803 (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:



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



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

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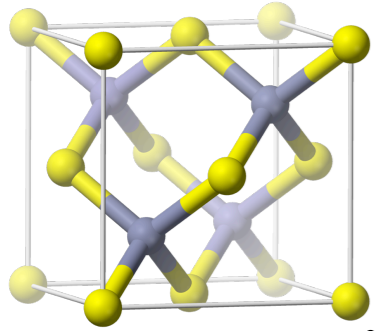
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For band structures, SOC term can be included

- self-consistently
- non-selfconsistently after a self-consistent scalar relativistic band structure

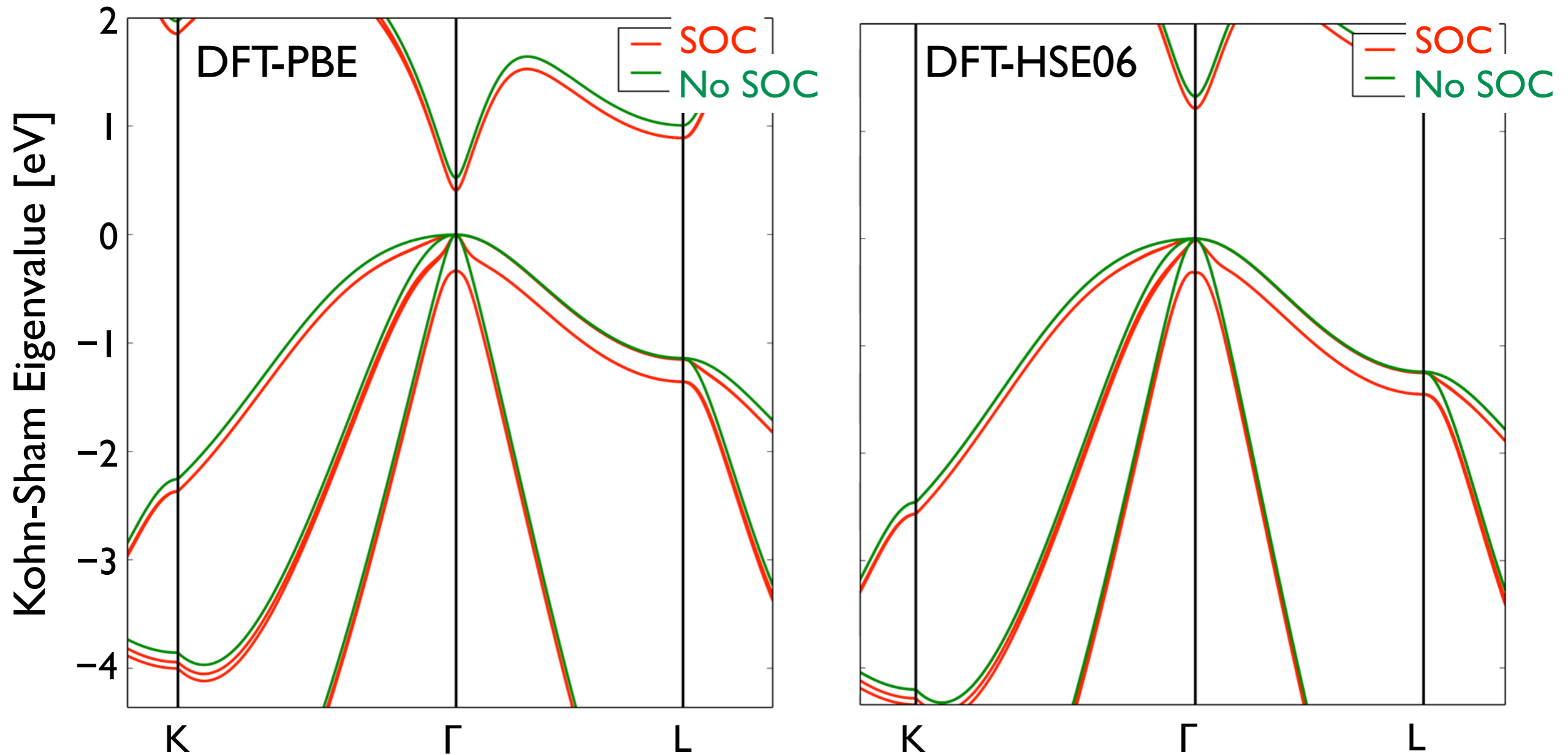
n.s.c. is computationally cheaper, simpler -
how accurate is it?

Real Materials: Impact of Relativistic Effects



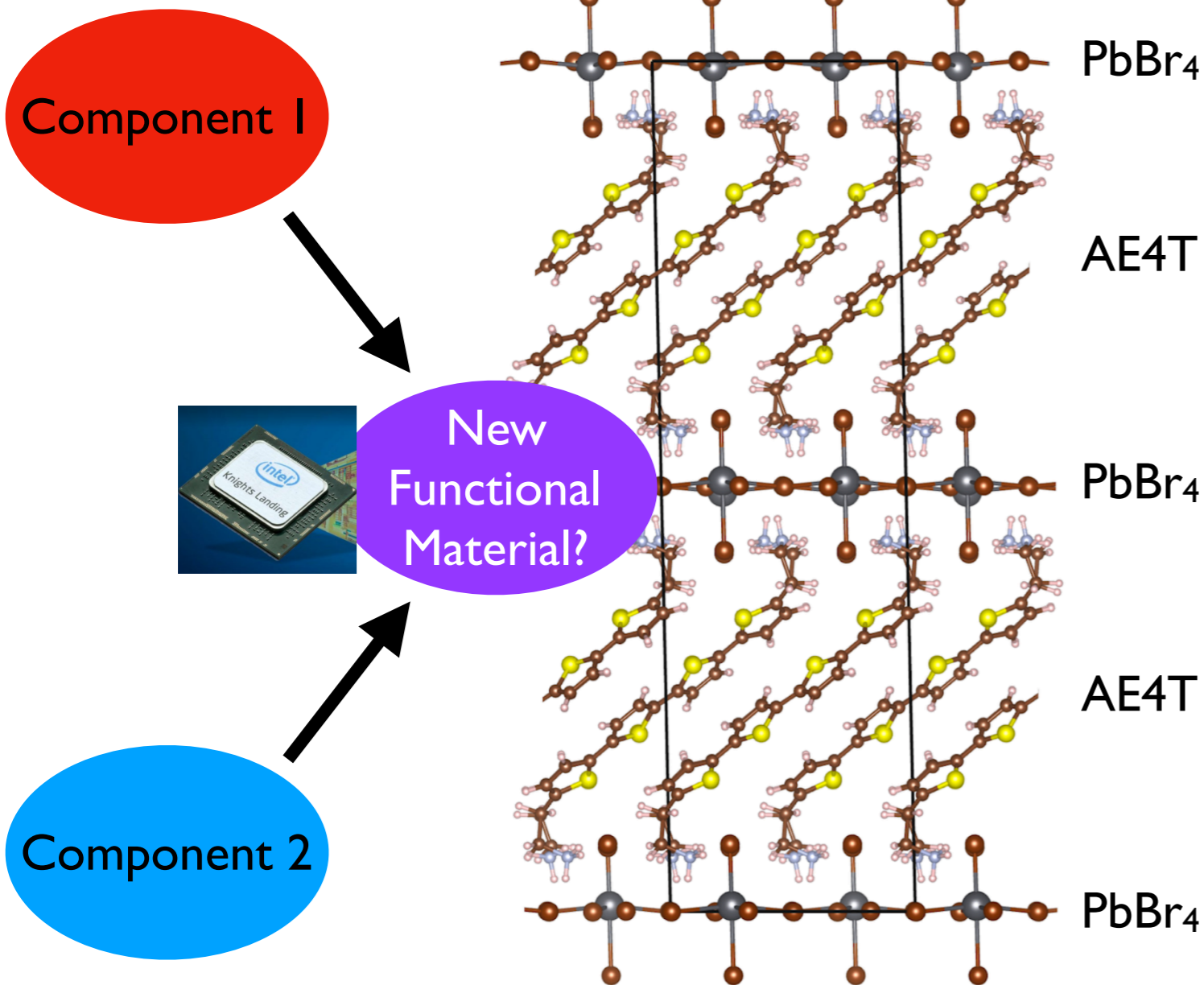
$$a_{\text{exp}} = 5.6532 \text{ \AA}$$

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



SOC in Heavy-Element Containing Materials?

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

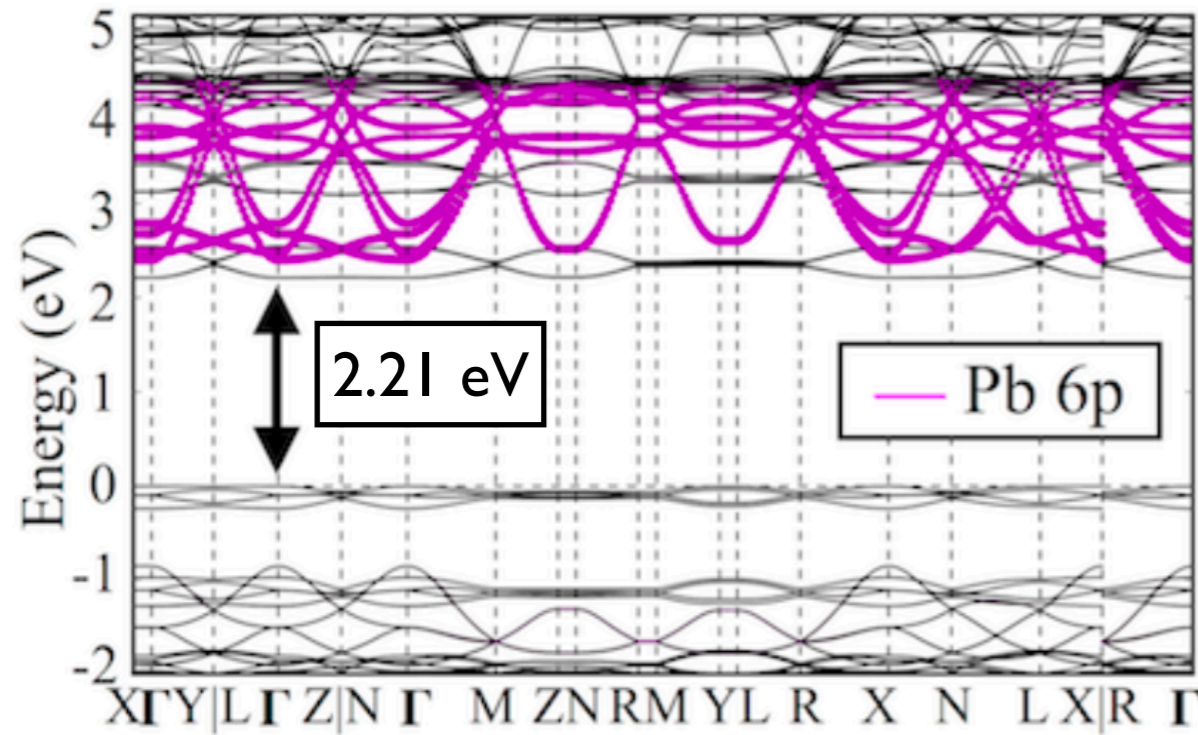


3D crystal

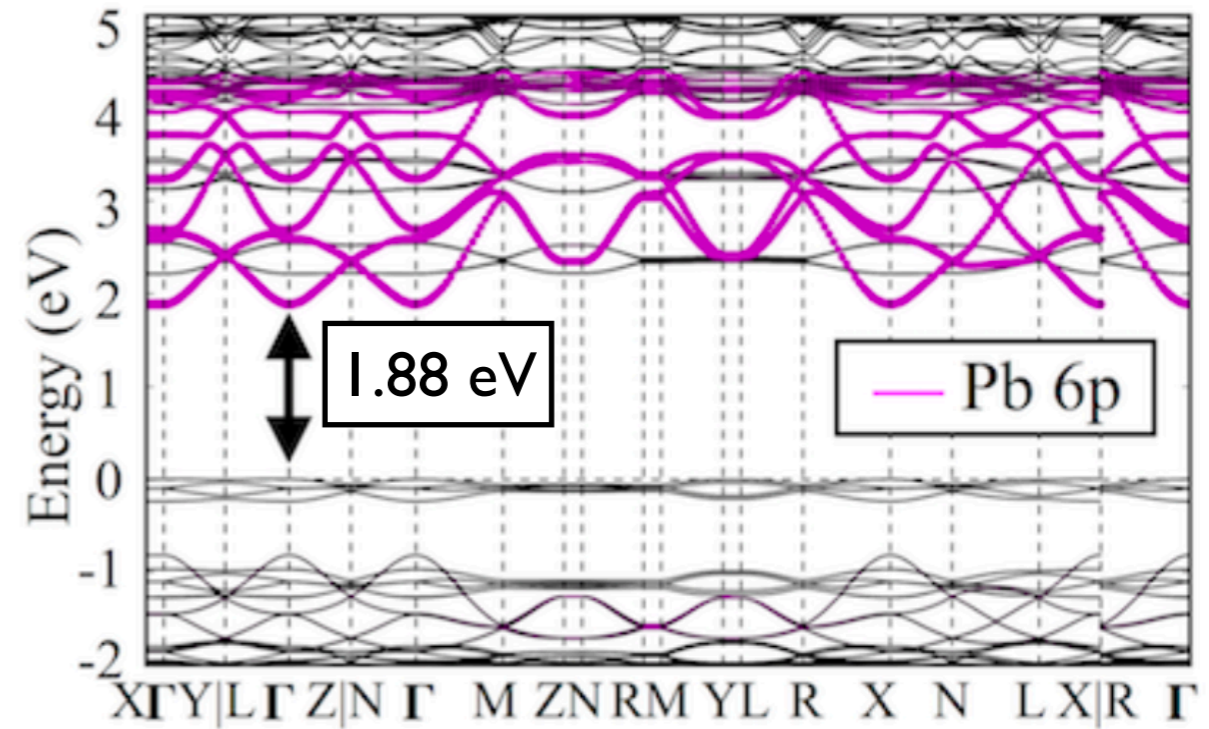
400+ atoms per unit cell

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

AE4T-PbBr₄ - HSE06, no SOC

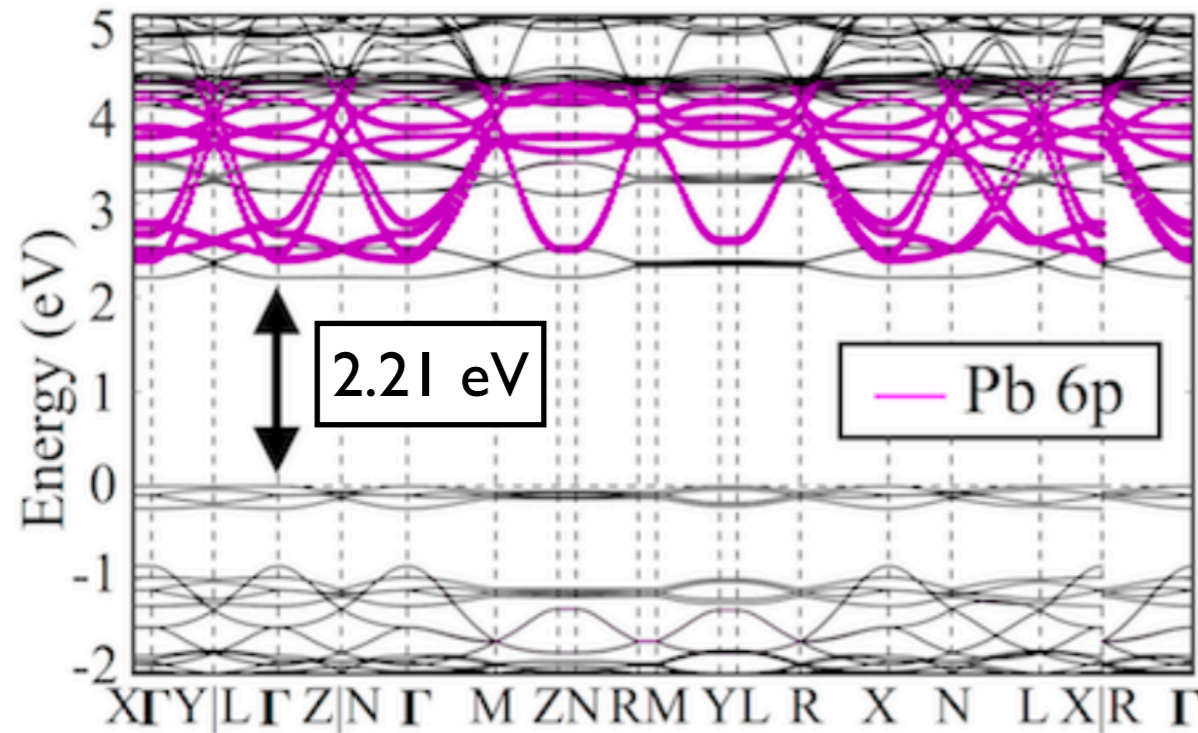


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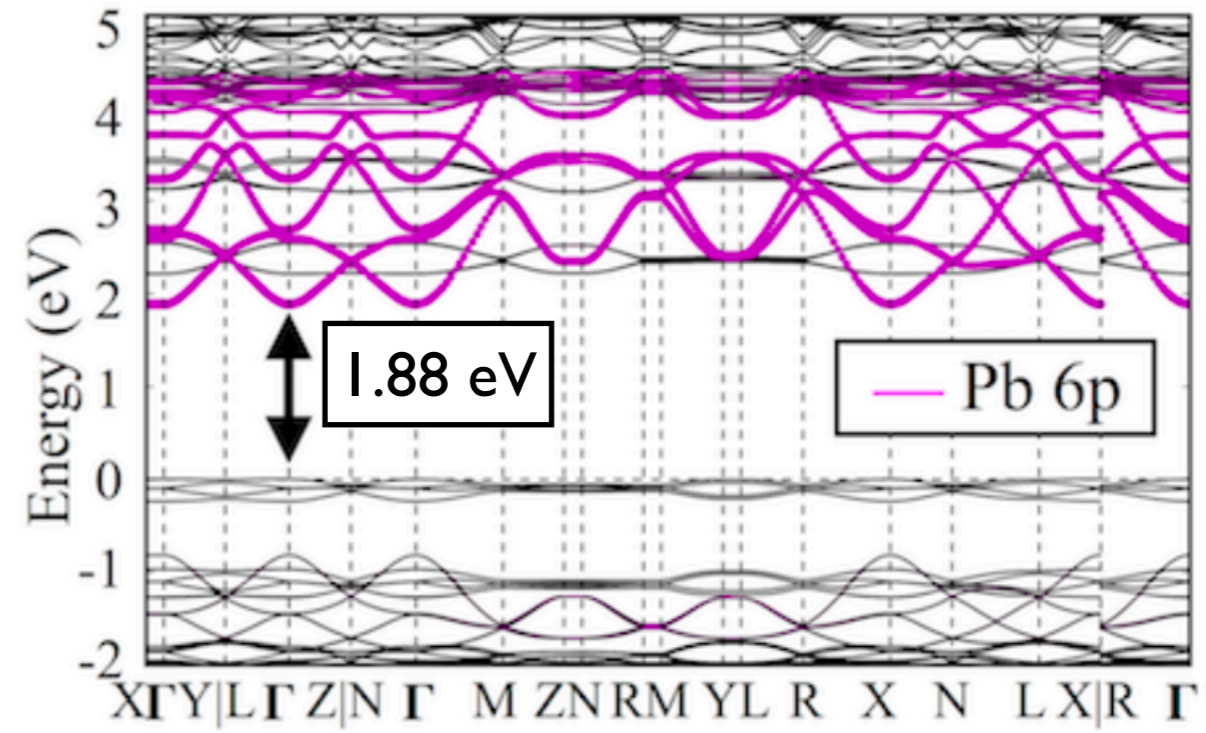


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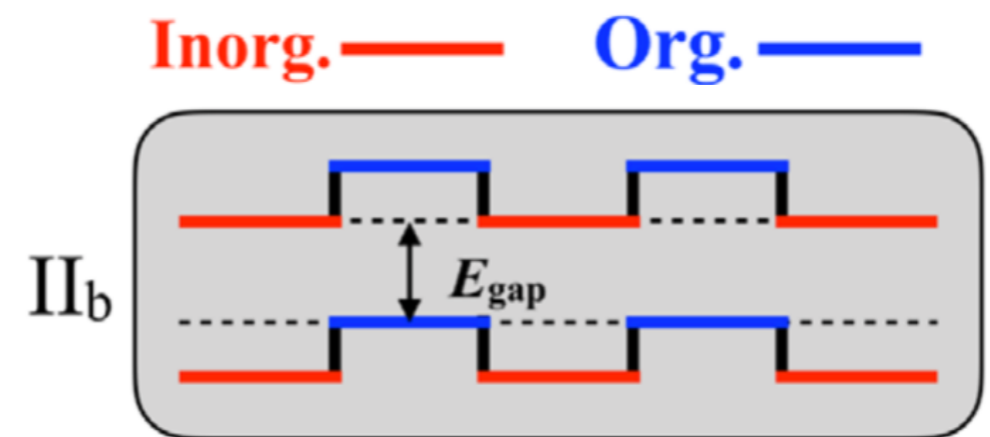


AE4T-PbBr₄ - HSE06, SOC



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

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

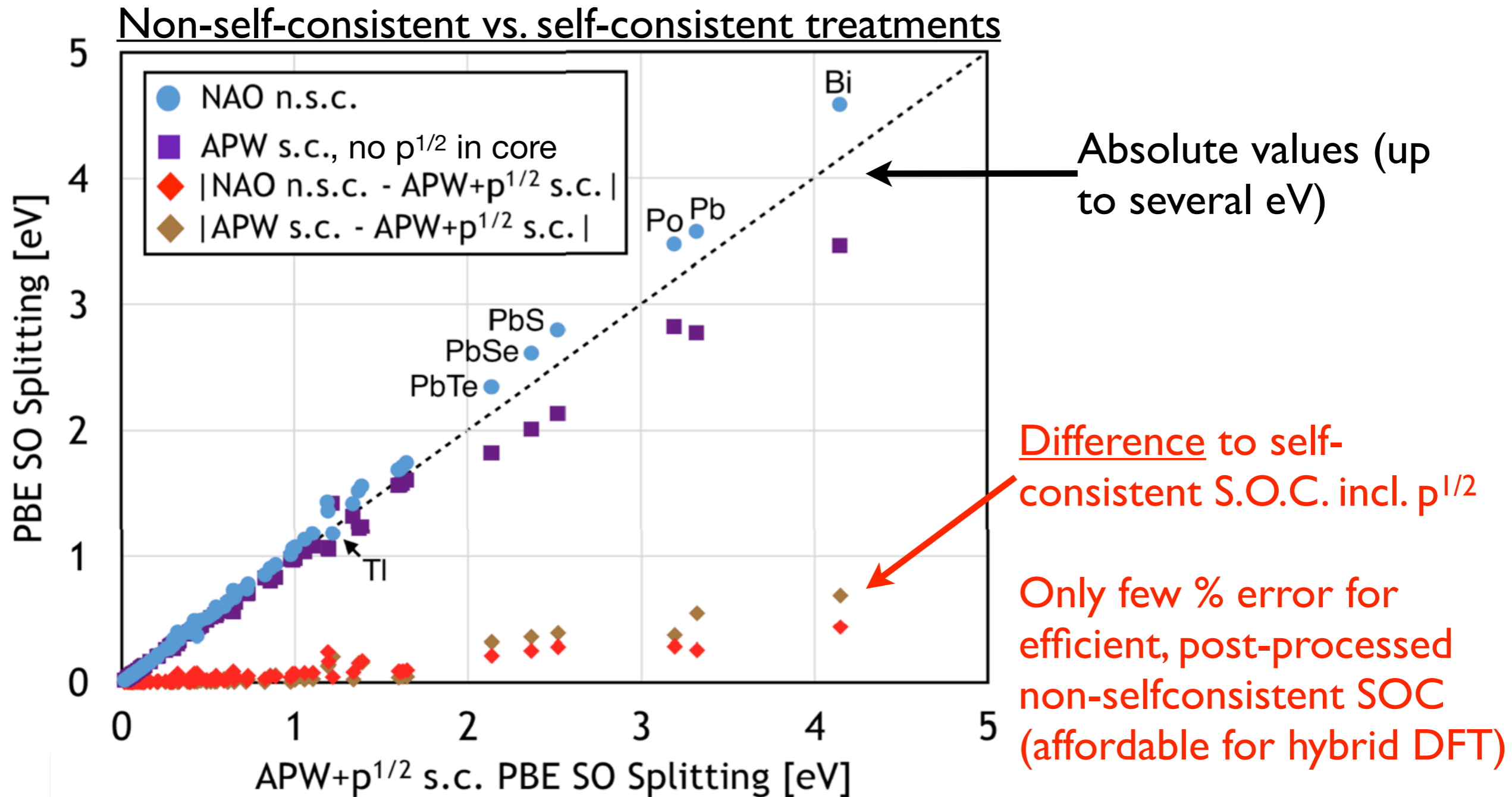


Benchmark for Spin-Orbit Splittings

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



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needed for heavy elements

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*need suitable basis,
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S. Levchenko
Wed 09:00h

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Computational Scaling: Two Sub-Problems

I. 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.

2. Matrix algebra (basis space)

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Kohn-Sham eigenvalue problem

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- 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)

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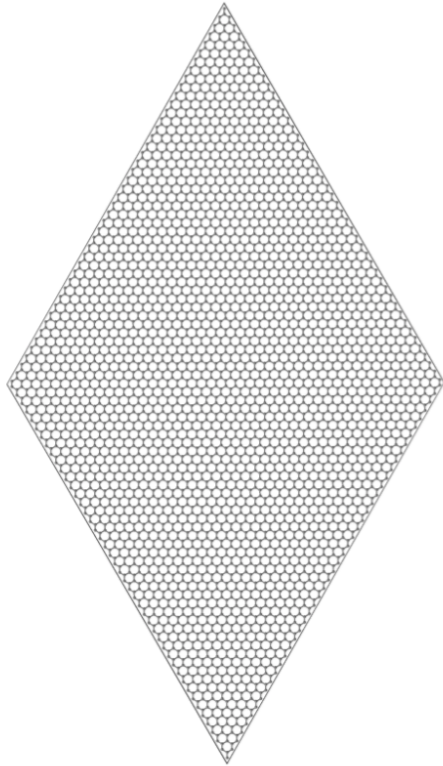
“Conventional” solvers (Lapack-like):

- 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?

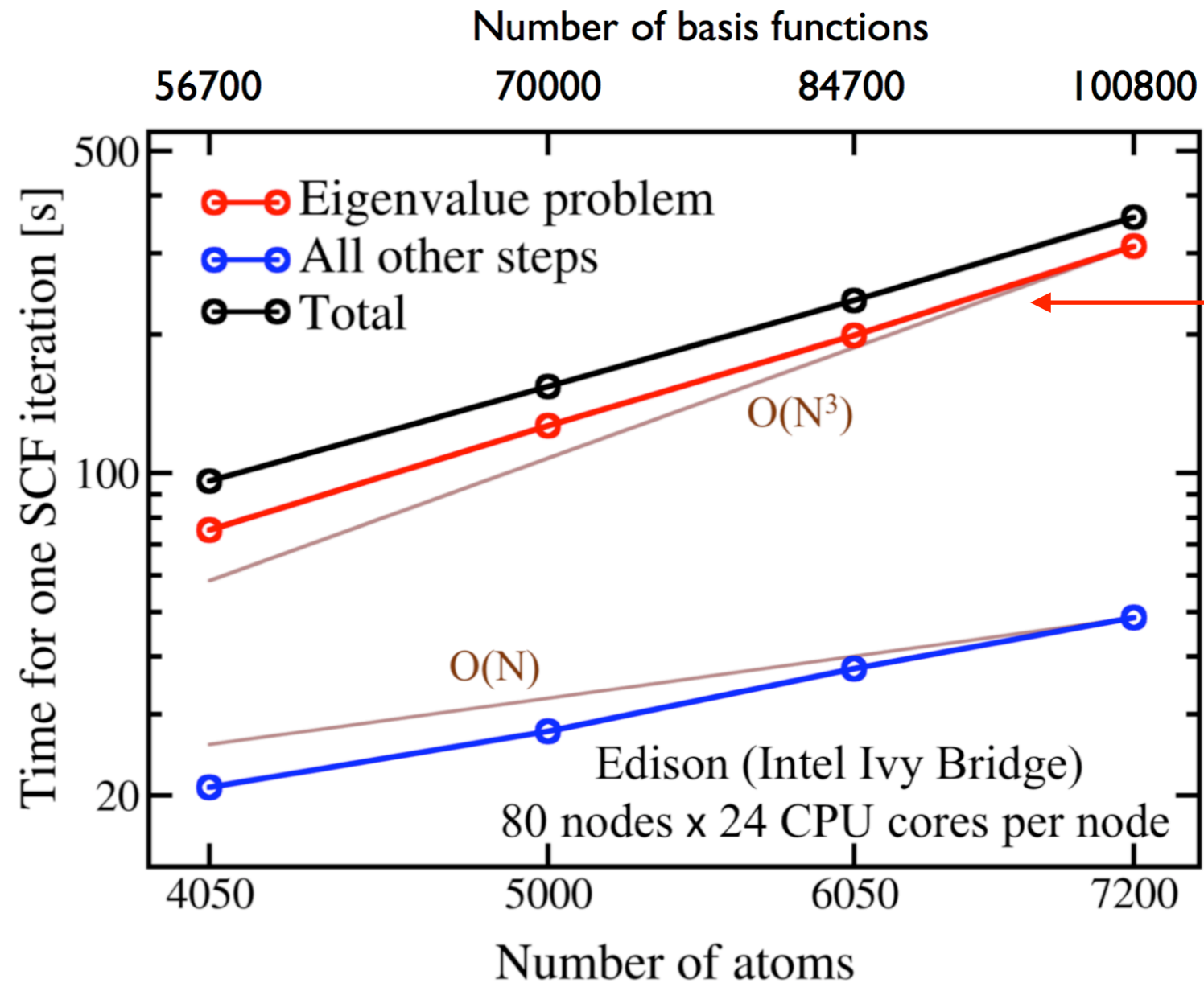
Typical Scaling - $O(N^3)$ Wall

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



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?

VB
Thu 10:00h

Our Electronic Structure Framework: FHI-aims



<http://aims.fhi-berlin.mpg.de>

Objectives:

Full space of materials and chemistry:

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

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)

Summary

<https://aimsclub.fhi-berlin.mpg.de>

<http://aims.pratt.duke.edu>



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



National Science Foundation



ACS Petroleum Research Fund

Materials Research Science and Engineering Center



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The concepts are general:

- Basis sets (Key decision upon which everything else relies!)
- Integration, density, potential update
- Seamlessly from light to heavy elements
- Excellent use of (massively) parallel hardware
- Beyond semilocal DFT for large systems



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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!

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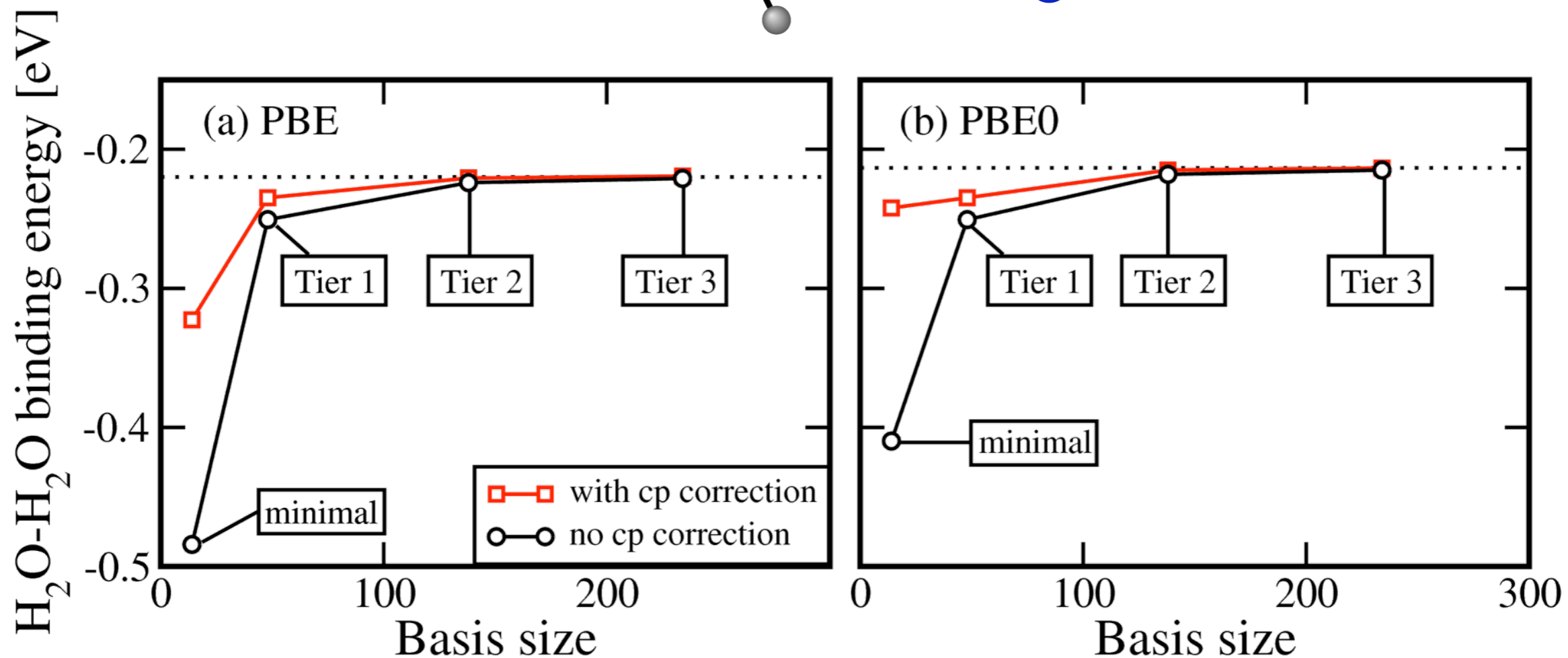
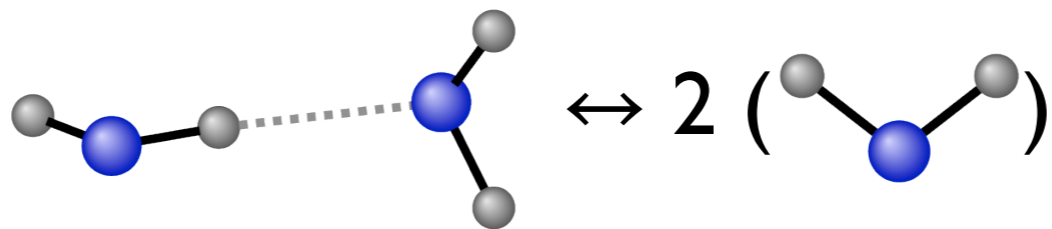
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NAO basis sets: ● is already exact → no BSSE for ●—●.
But how about *molecular* BSSE?

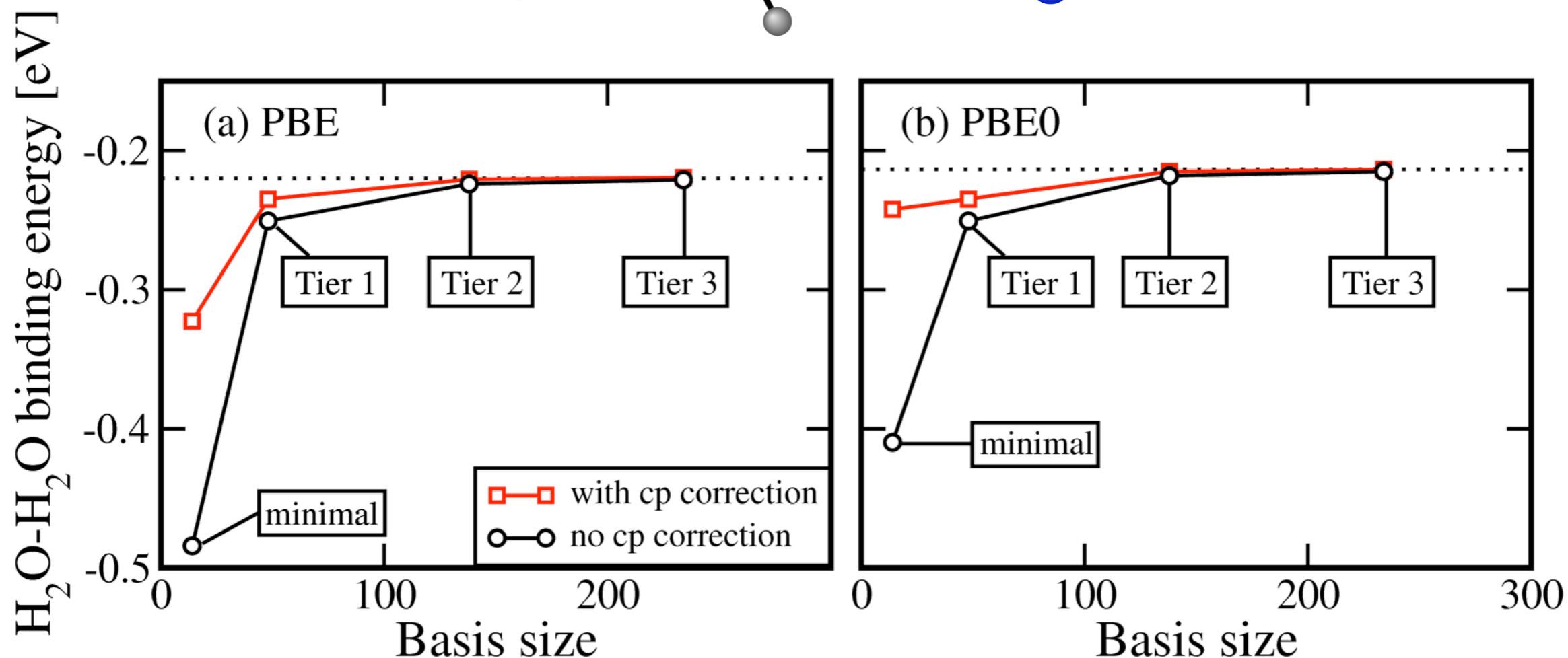
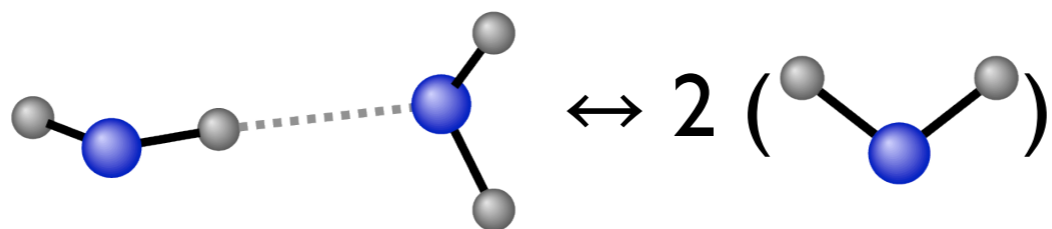
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Ground-State DFT, NAO's:

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

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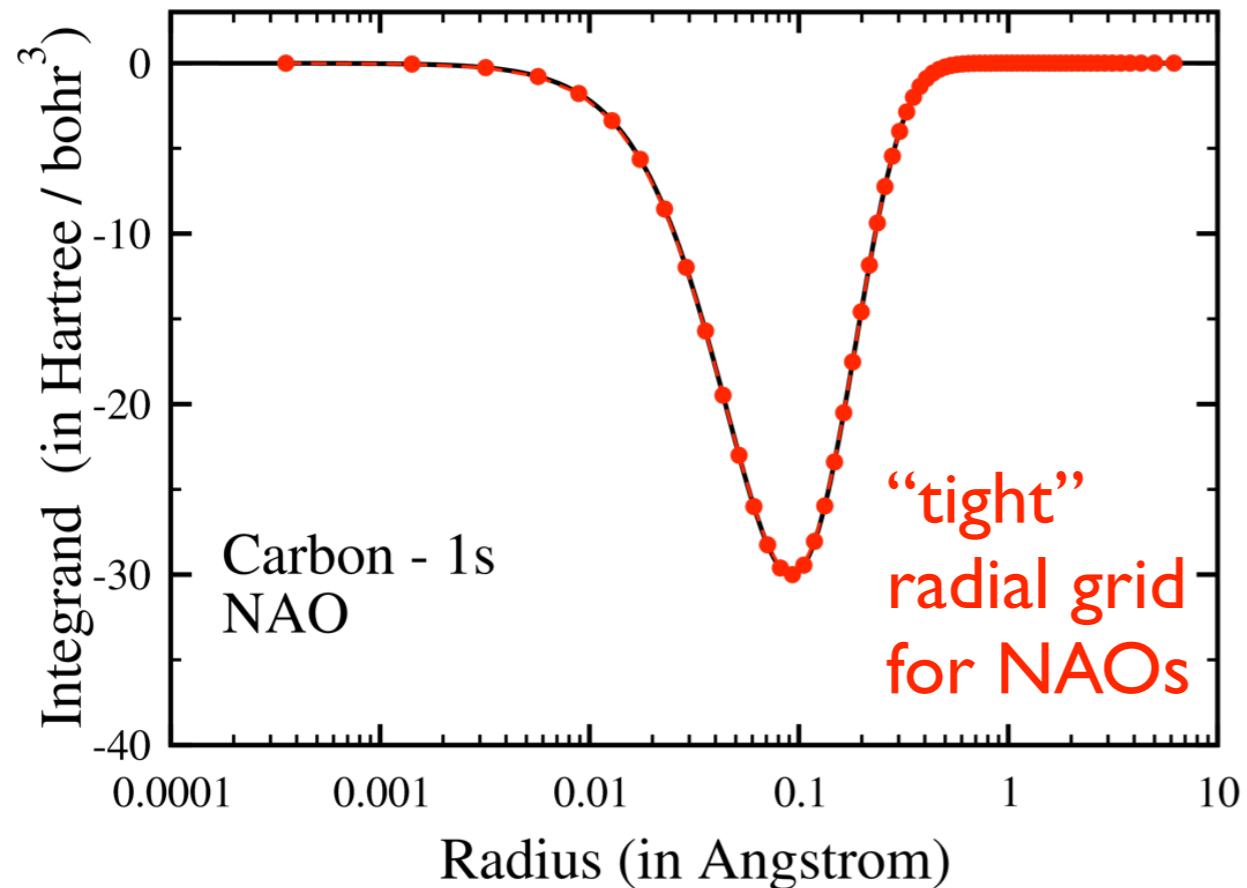
BSSE *not* the most critical basis convergence error (e.g., tier 2)*

*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:

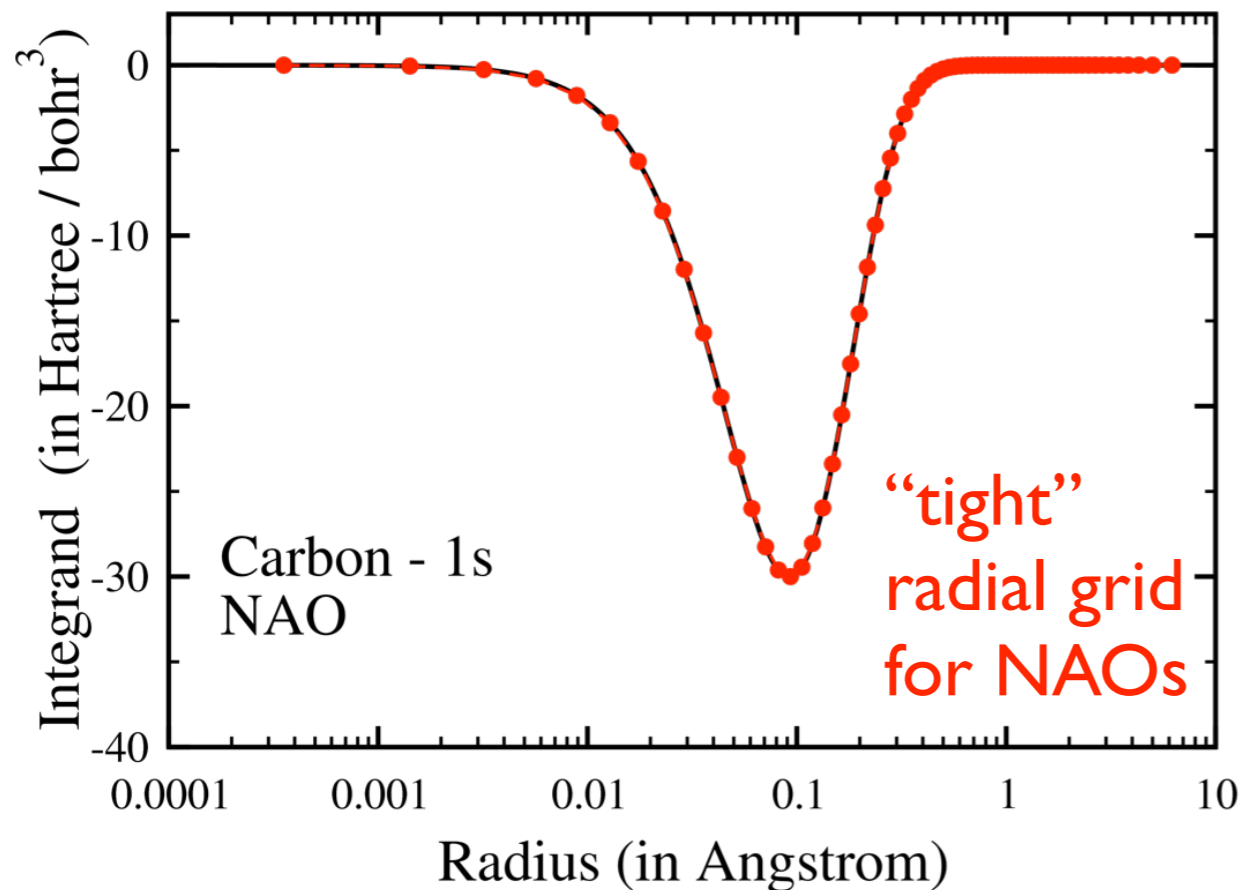


Igor Ying Zhang, Xinguo Ren, Patrick Rinke, Volker Blum, and Matthias Scheffler,
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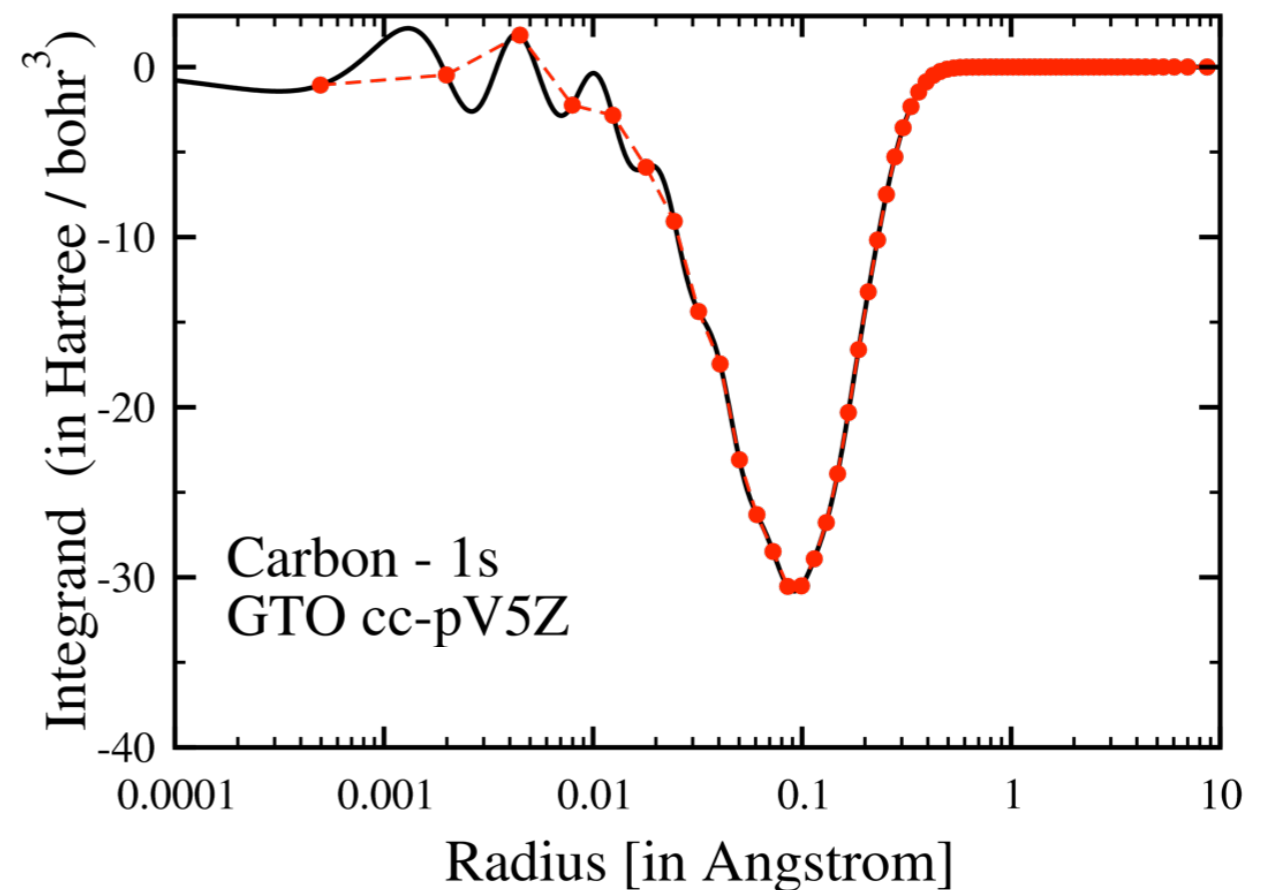
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$f(r)$ for
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$f(r)$ for
contracted Gaussian
radial function:



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