

Computational Materials Science From Scratch

The Nuts and Bolts of Electronic Structure Theory

Volker Blum

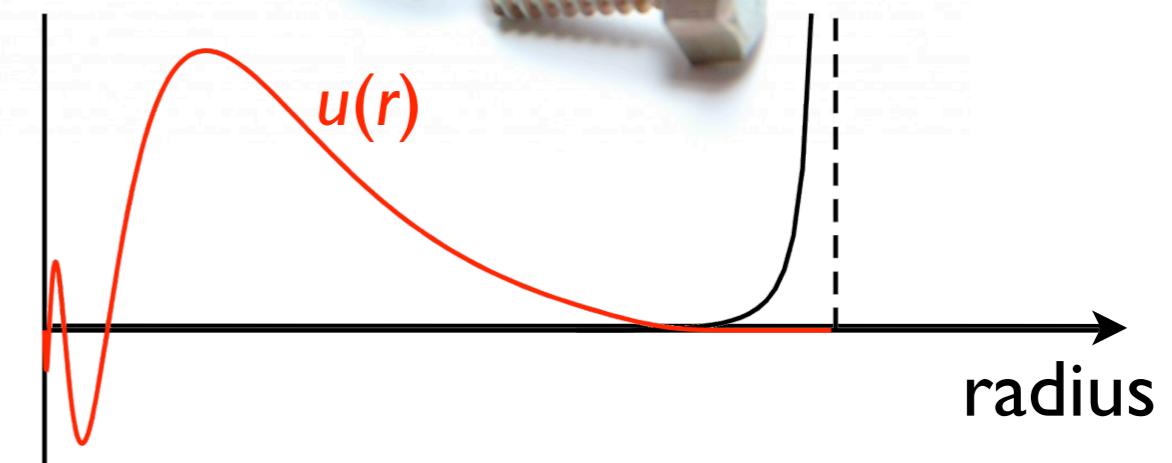
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Department of Mechanical
Engineering and Materials Science
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<https://aimsclub.fhi-berlin.mpg.de>

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



HybriD³ Theory Training Workshop - Duke University, UNC, NCSU and Online, January 20, 2021



National Science Foundation, DMR-1728921, -1729297, -1729383

Who Did the Work?

Duke Univ. / Ab Initio Molecular Simulations Group



Dr.Yi Yao



Ruyi
Song



Xixi
Qin



Gabrielle
Koknat



Tianlin Wang



Dr. Rundong
Zhao

now Beihang Univ.



Dr. William
Huhn

now Argonne



Dr. Victor Yu



Dr. Raul
Laasner

now SRON

Becca Lau, Xiaochen Du, Tommy Lin, Douglas Heine,
Kimberly Zhang, Connor Clayton

Dr. Svenja Janke (now Warwick), Dr. Chi Liu (now TSMC),
Dr. Tong Zhu (now Univ.Toronto), ...

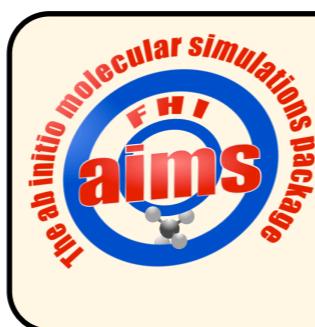
UNC



Prof.Yosuke
Kanai



Sampreeti
Bhattacharya



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



NSF SI²-SSI:
ACI-1450280

William Dawson, Alberto Garcia, Ville Havu, Ben Hourahine, Mathias Jacquelin, Weile Jia, Murat Keceli, Raul Laasner, Björn Lange, Yingzhou Li, Lin Lin, Jianfeng Lu, Wenhui Mi, Jonathan Moussa, Jose E. Roman, Ali Seifitokaldani, Alvaro Vazquez-Mayagoitia, Haizhao Yang, Victor Yu; ELPA, PEXSI, NTPoly, Slepce, ...

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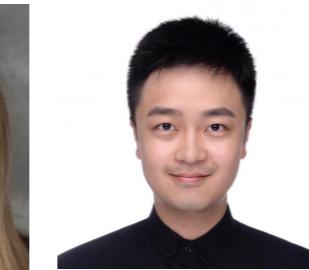
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National Science Foundation
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U.S. DEPARTMENT OF
ENERGY

Argonne
NATIONAL LABORATORY
ALCF

ORNL
LLNL



TRIANGLE
MRSEC

MolSSI

Office of
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tc.

Materials Research Science
and Engineering Center

NVIDIA

NERSC

U.S. DEPARTMENT OF ENERGY
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LEADERSHIP COMPUTING



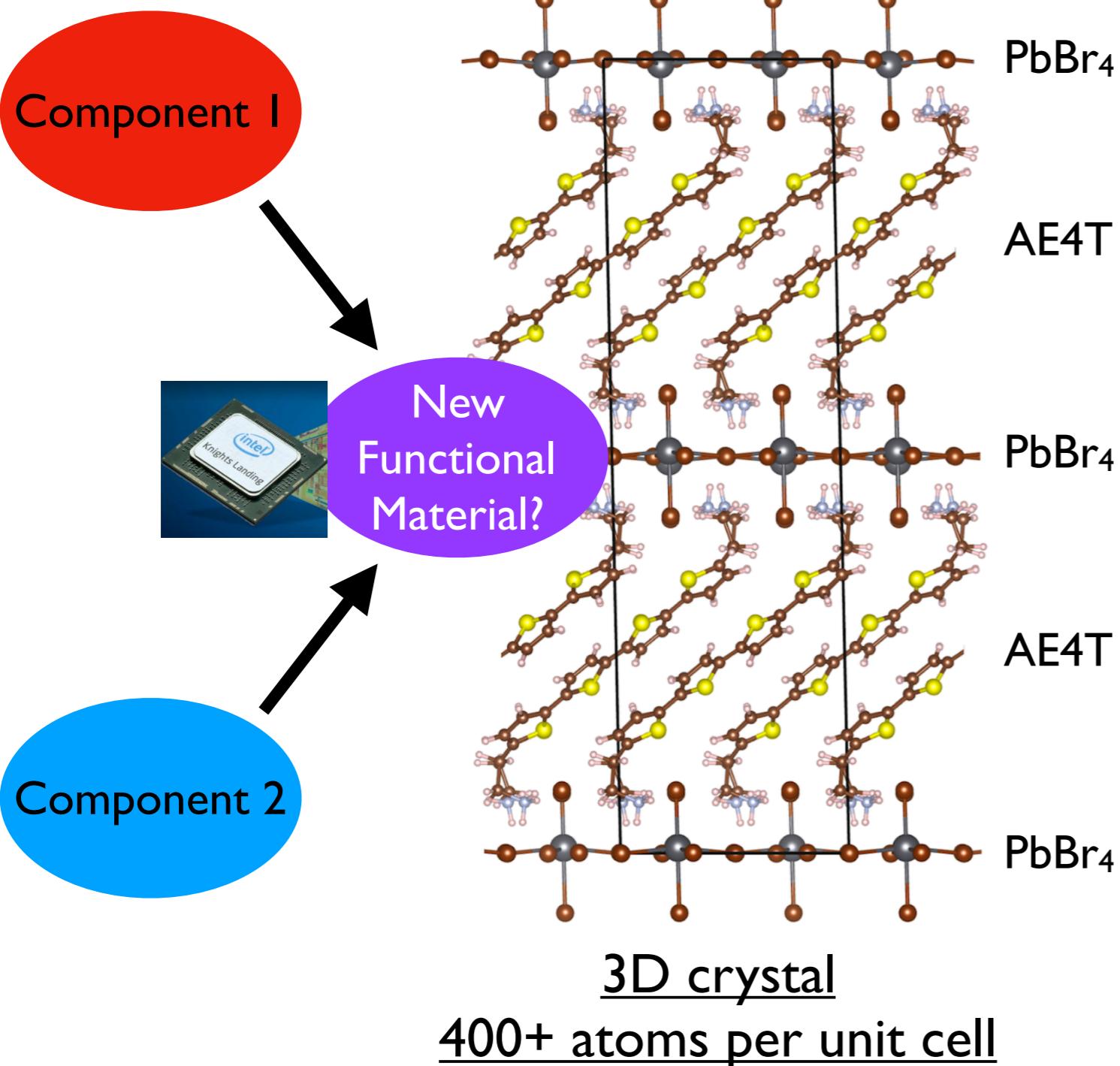
NSF SI²-SSI:
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CHOISE
Center for Hybrid Organic Inorganic
Semiconductors for Energy

Moussa, Jose E. Roman, Ali Seifitokaldani, Alvaro Vazquez-
Mayagoitia, Haizhao Yang, Victor Yu; ELPA, PEXSI, NTPoly, Slepce, ...

Materials Properties from Theory?

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



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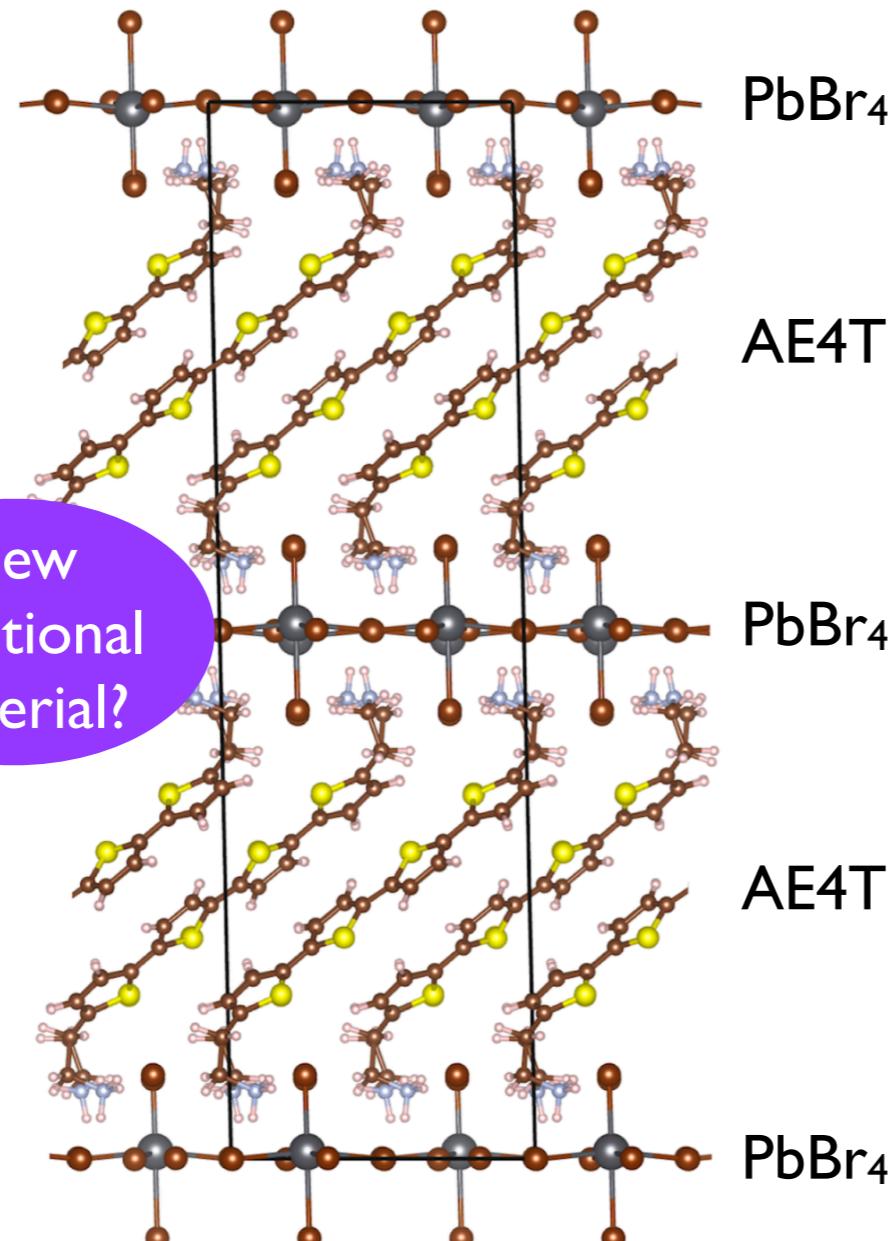
E.g., Organic-Inorganic Hybrid Semiconductors - Tailored Properties?

Component 1



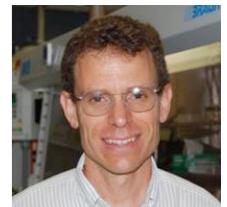
New Functional Material?

Component 2



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

Materials Properties from Theory?

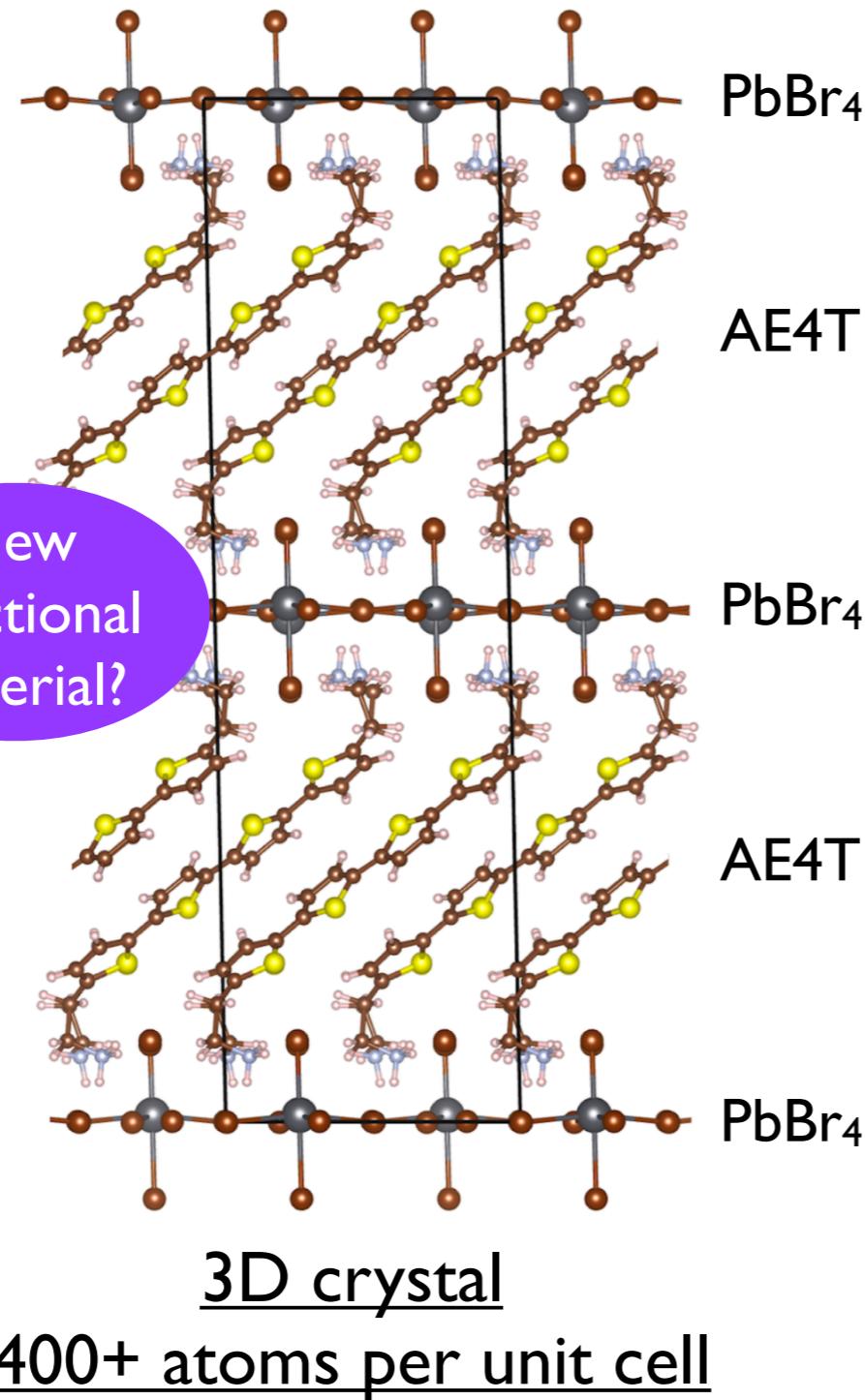
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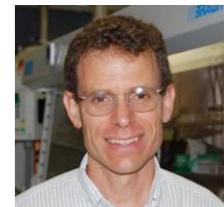
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Liu, Huhn, Du, Vazquez-Mayagoitia, Dirkes, You, Kanai, Mitzi, Blum, Phys. Rev. Lett. **121**, 146401 (2018)

Pathway 1: Make material, find out its properties.
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David
Mitzi

Pathway 2: Accurate computational prediction?

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

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

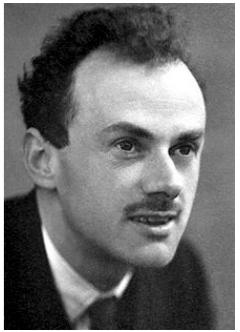
All-electron, molecules and periodic systems

Main example for this talk
Used for tutorials in the next 2 days

Standard Steps to “Practical” Electronic Structure Theory

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

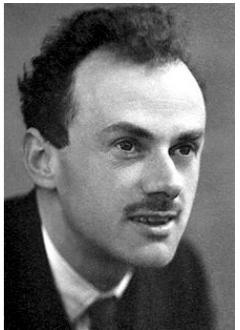
P.A.M.
Dirac



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

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I) 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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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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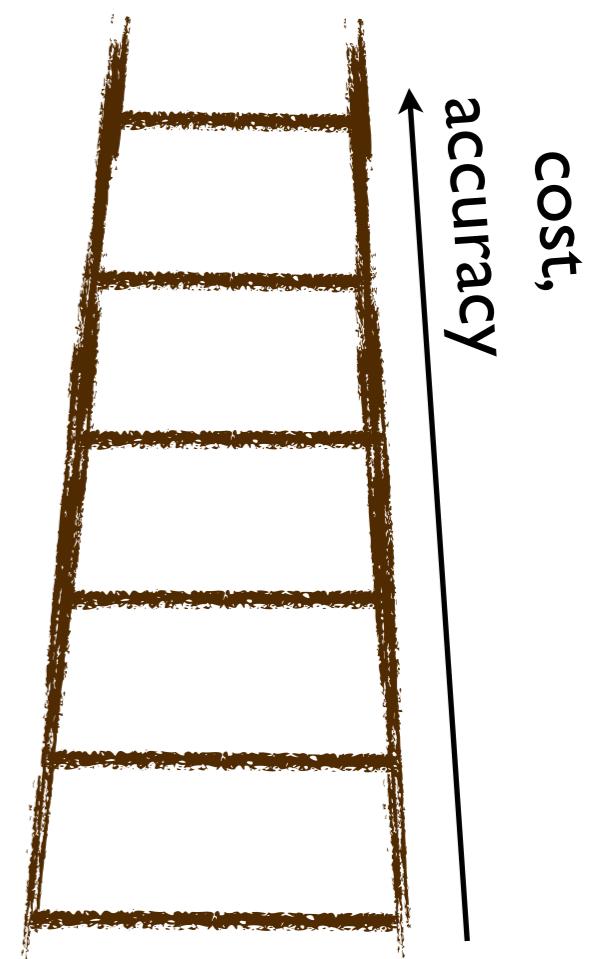
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“Perdew’s ladder”
to exact solution

- Key practical approximation: E_{xc}



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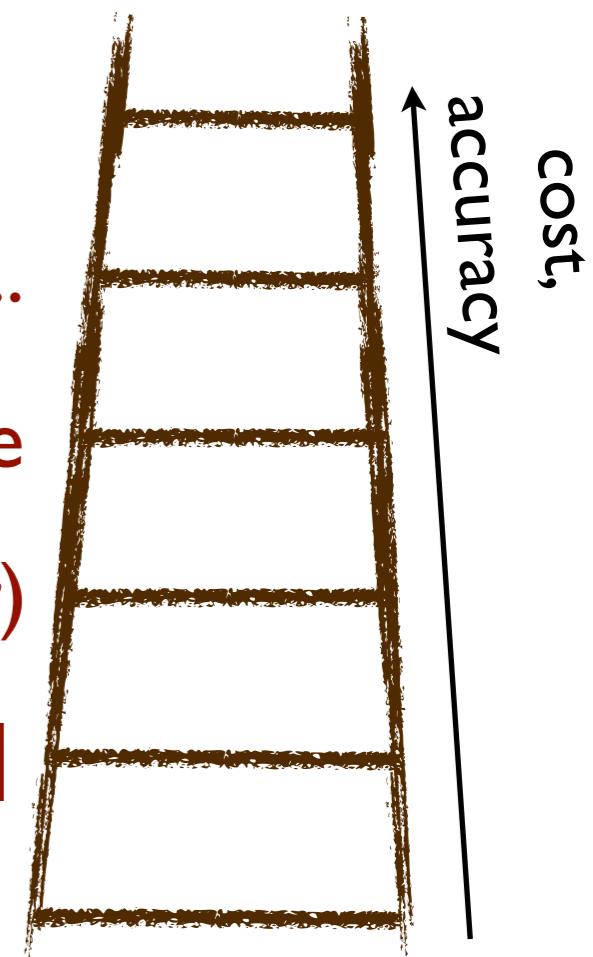
- Key practical approximation: E_{xc}
response / many-body terms: GW, RPA, SOSEX, ...

hybrid functionals: non-local exchange

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

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

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



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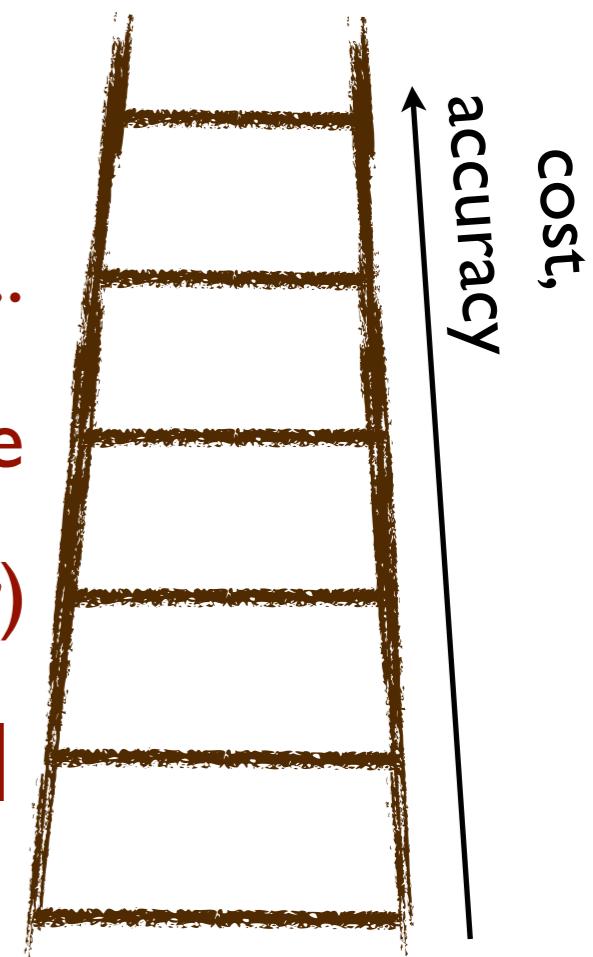
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+ van der Waals → hybrid functionals: non-local exchange

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

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



The Kohn-Sham Equations - How to Solve Them

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

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“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

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h_{ji} s_{ji}

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repeat until $n^{(m+1)}=n^{(m)}$

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:

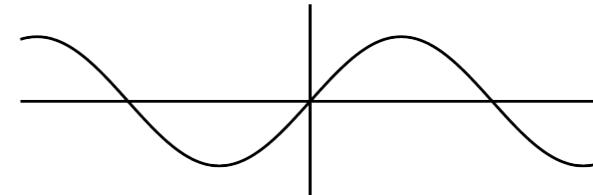
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Many good options:

- Plane waves $\varphi_k(\mathbf{r}) = \frac{1}{N} e^{i\mathbf{k}\cdot\mathbf{r}}$



- efficient FFT's (density, electrostatics, XC-LDA/GGA)
- inherently periodic
- not all-electron (Slater 1937) - need “pseudoization”

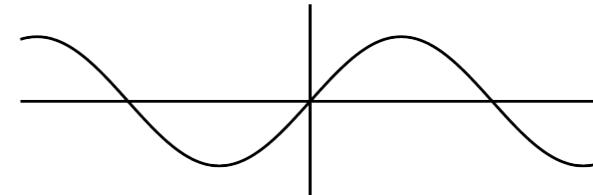
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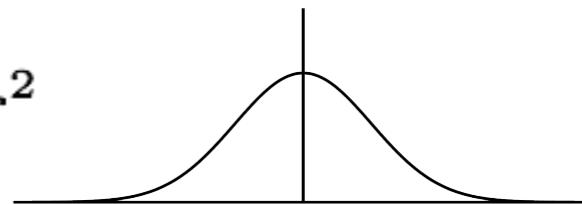
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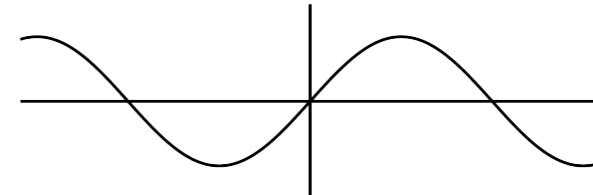
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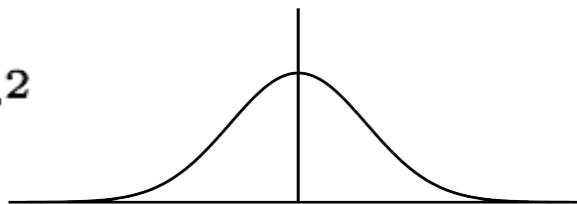
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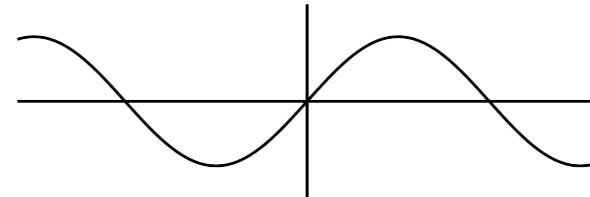
Representing the Orbitals: Basis Sets

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

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

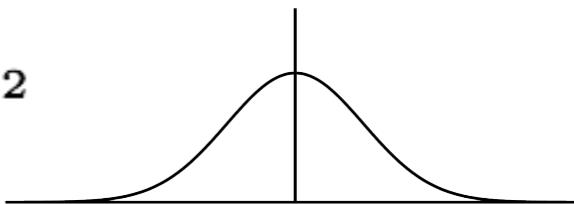
Many good options:

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- efficient FFT's (density, electrostatics, XC-LDA/GGA)
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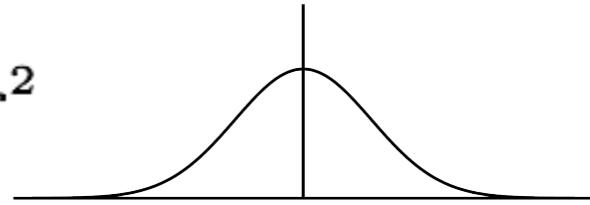
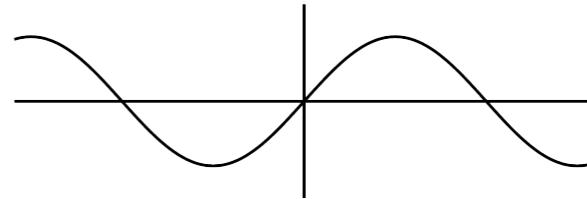
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- **FHI-aims (this talk):** Numeric Atom-Centered Basis Functions



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.”

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

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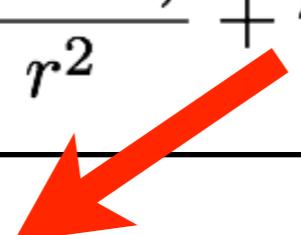
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- free ions, harm. osc. (Gaussians), ...

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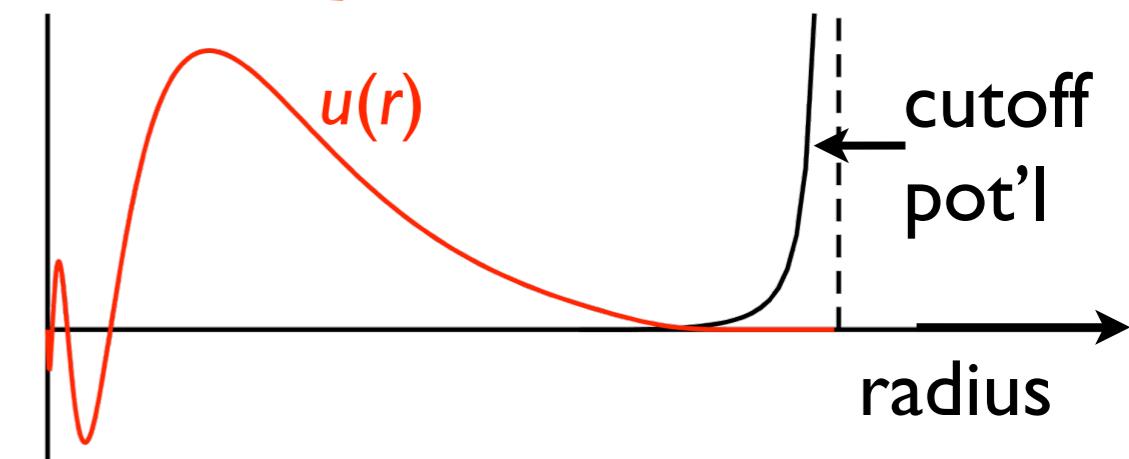
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- Localized; “naturally” all-electron
- The choice of efficient and of enough radial functions is obviously important
- But need a “basis set library” - list of basis functions for all elements (I-I02), from fast qualitative to meV-converged total energies (LDA/GGA/hybrid DF’s) - how to construct this list?

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?

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

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

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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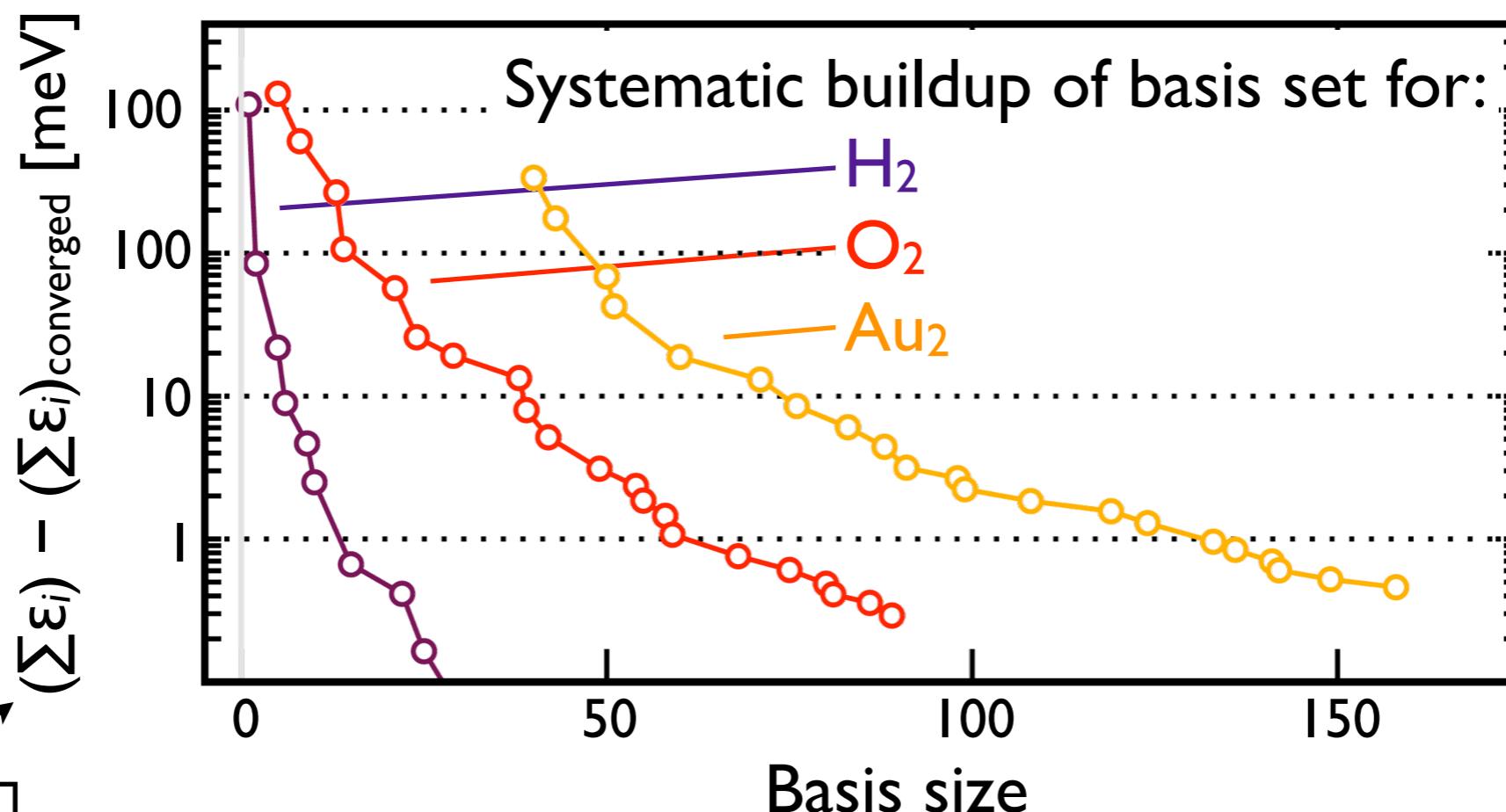
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Remaining
basis set error

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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	H	C	O	Au
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...		...		

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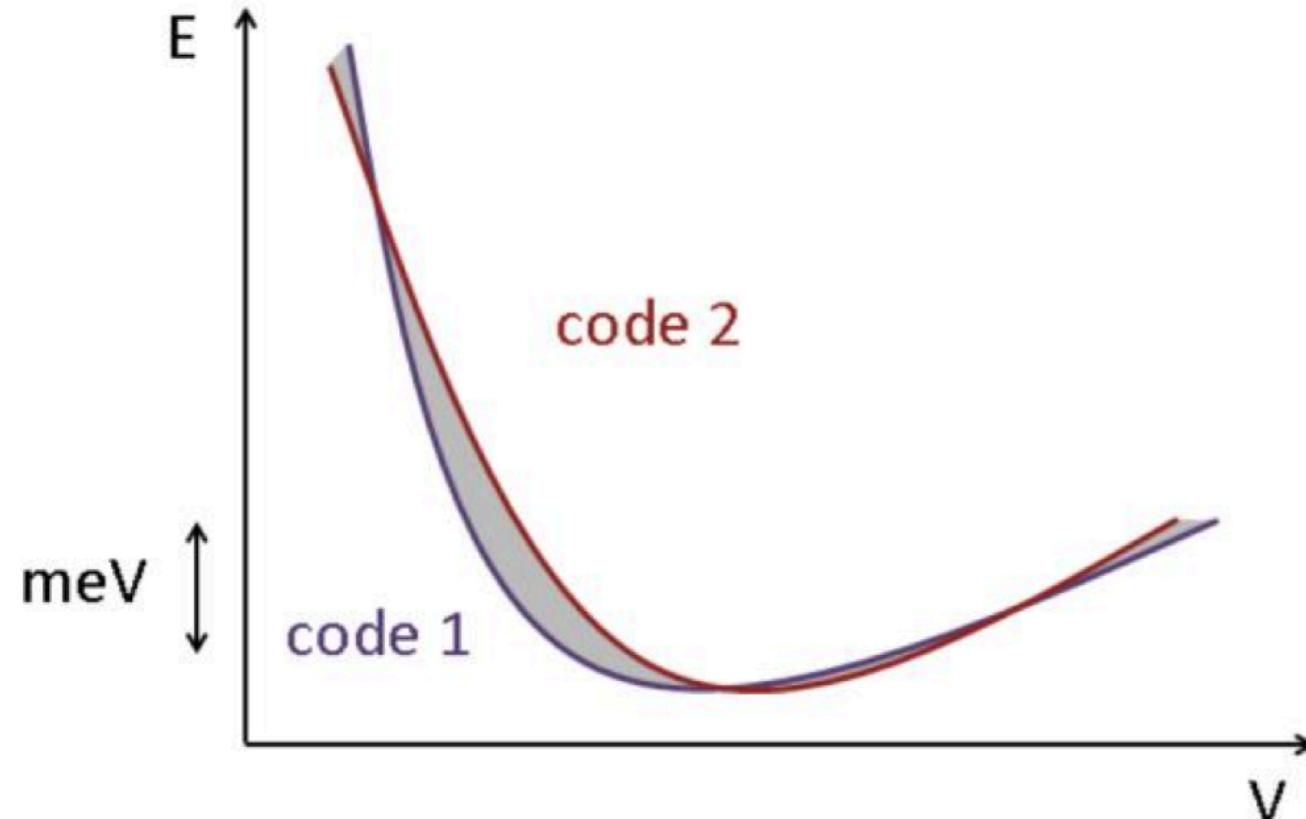
In FHI-aims input (example: Hydrogen, tight settings):

```
#####
# 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 Å, 0.7 Å, 1.0 Å, 1.5 Å, 2.5 Å
#
#####
# "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,
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$E(V)$ for 71 elemental solids - 15 codes, all-electron & 40 pseudopot'l sets

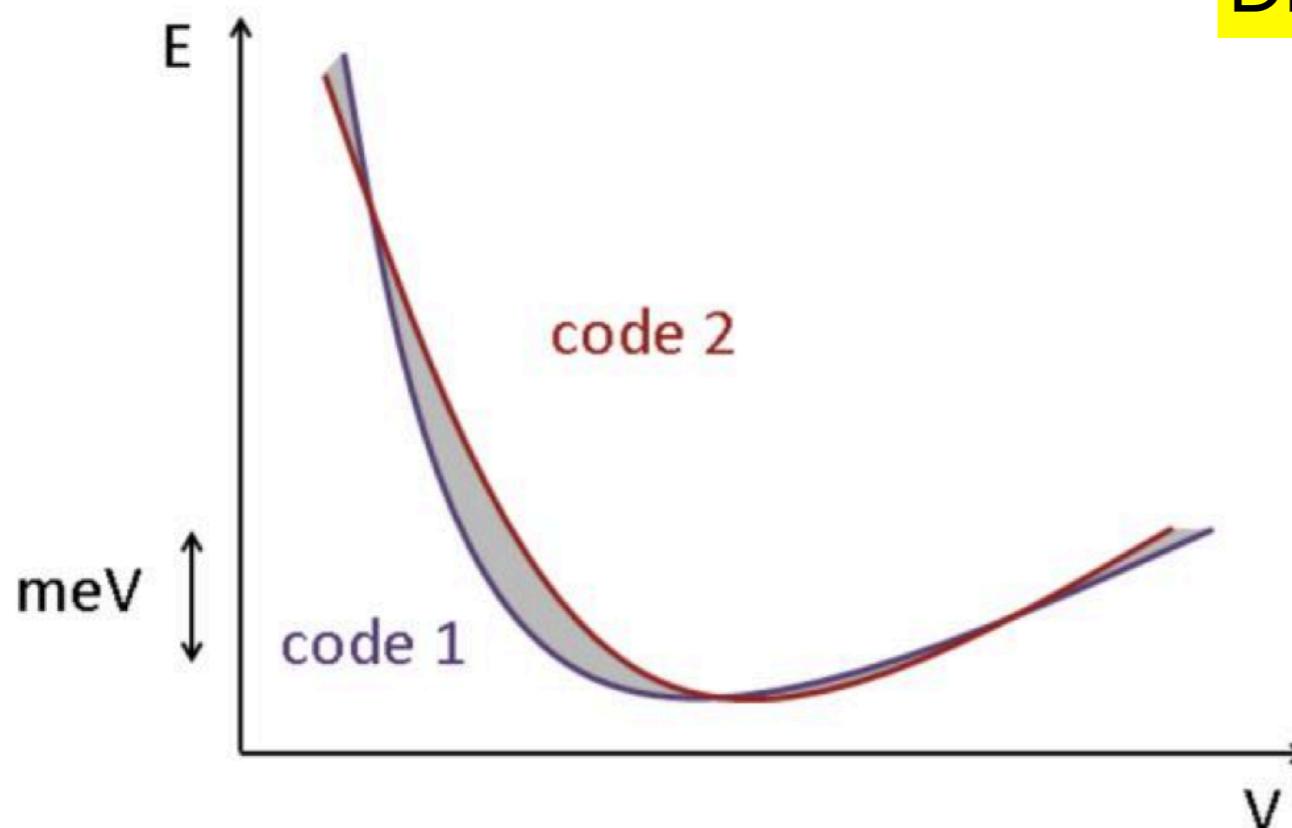


$$\rightarrow \Delta_i(a, b) = \sqrt{\int_{0.94V_{0,i}}^{1.06V_{0,i}} \frac{(E_{b,i}(V) - E_{a,i}(V))^2}{0.12V_{0,i}} dV}$$

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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 , 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:

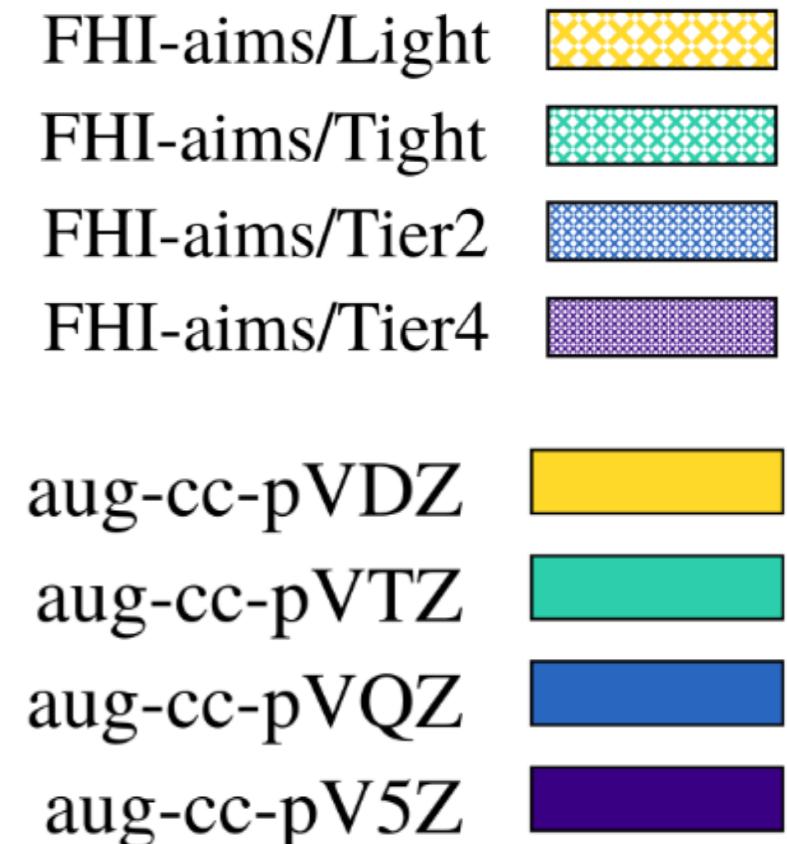
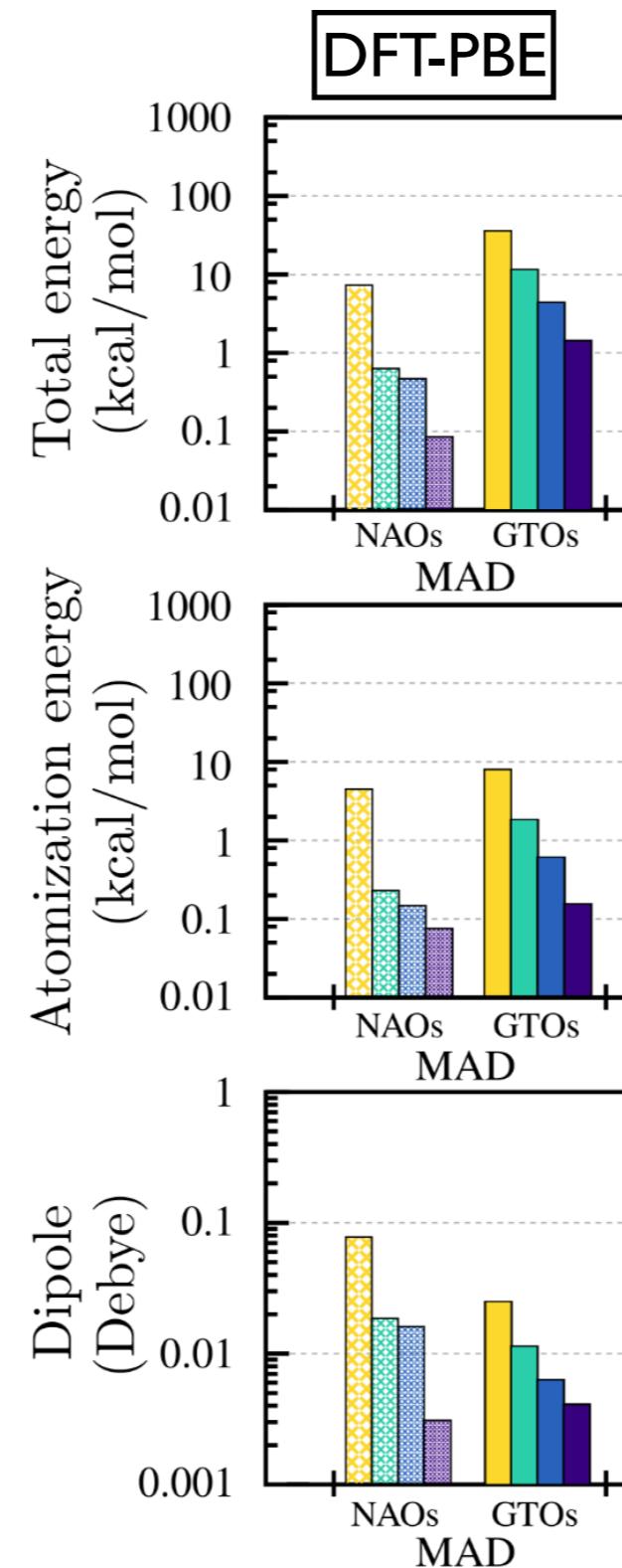
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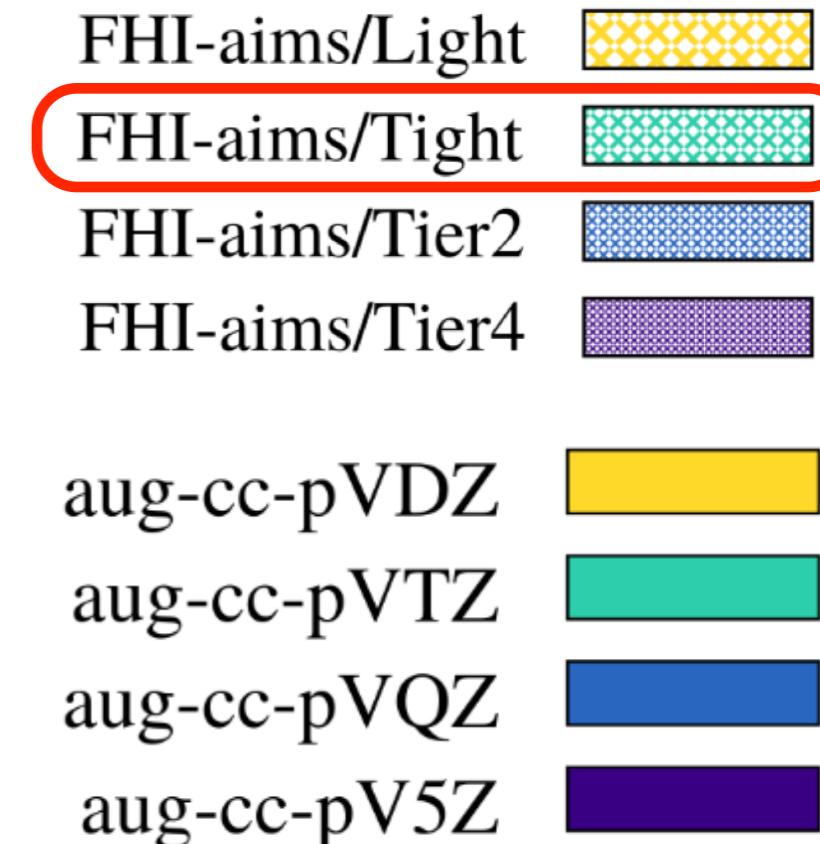
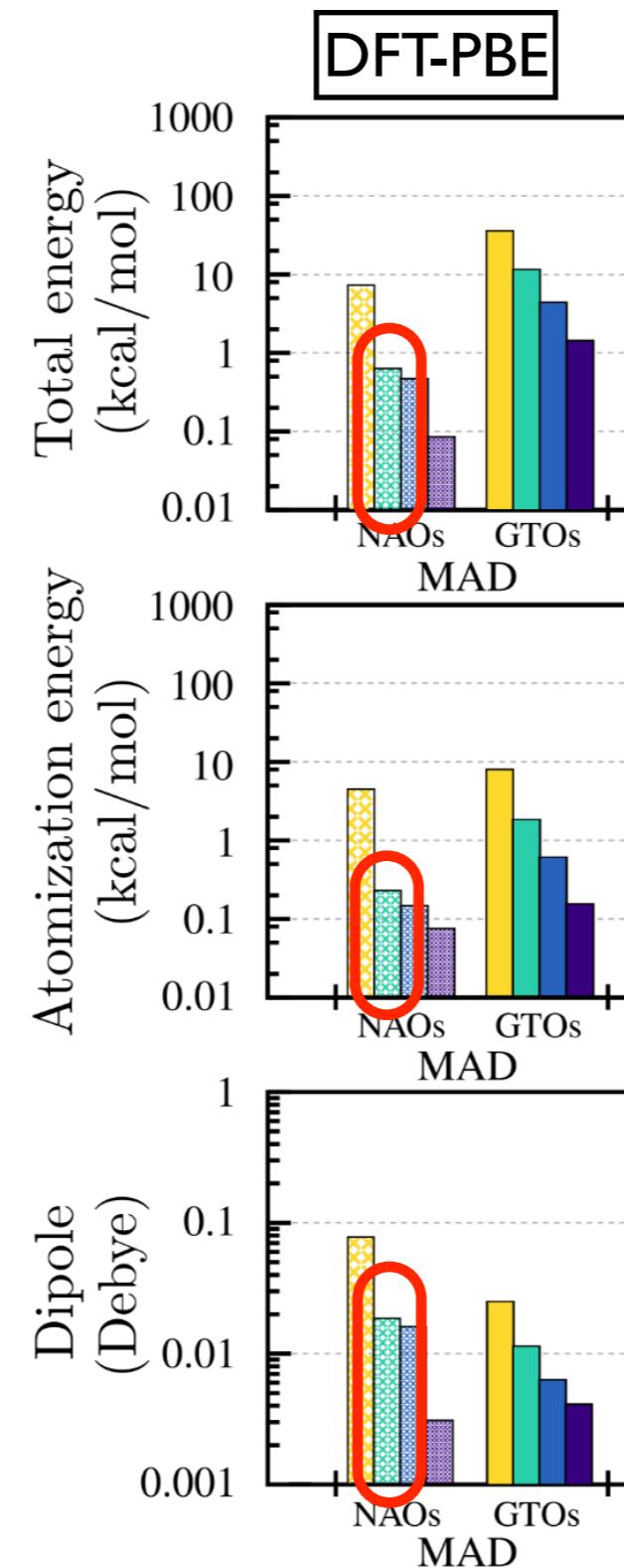


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Using Numeric Atom-Centered Basis Functions: Pieces

- 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

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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!

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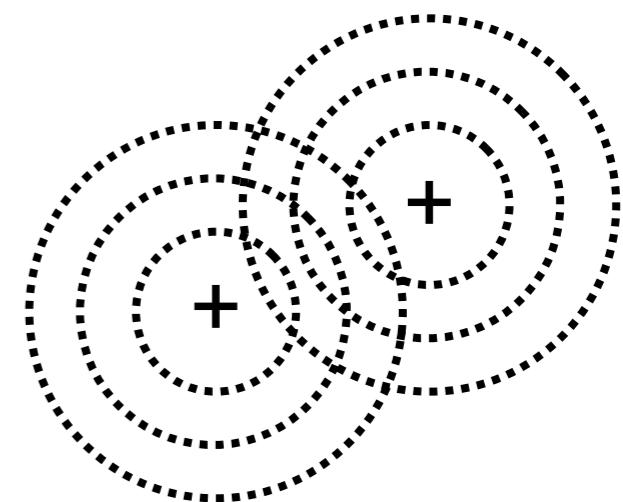
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- Overlapping atom-centered integration grids:

- 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!

Numeric Atom-Centered Basis Functions: Integration

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

- Discretize to integration grid:

$$\int d^3r f$$

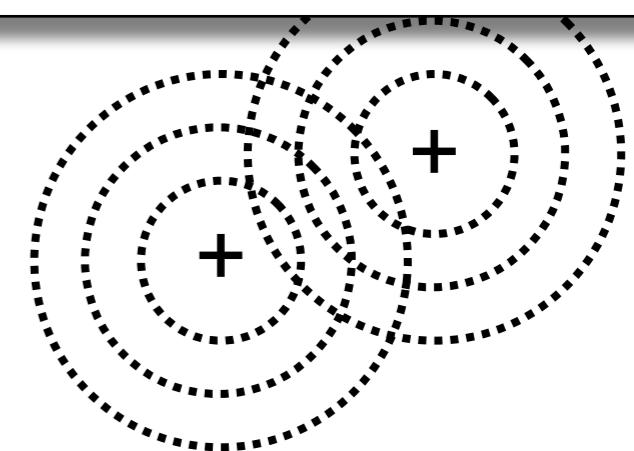
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In FHI-aims input (example:
Hydrogen, tight settings):

```
#          - - -
#      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
```



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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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exact:

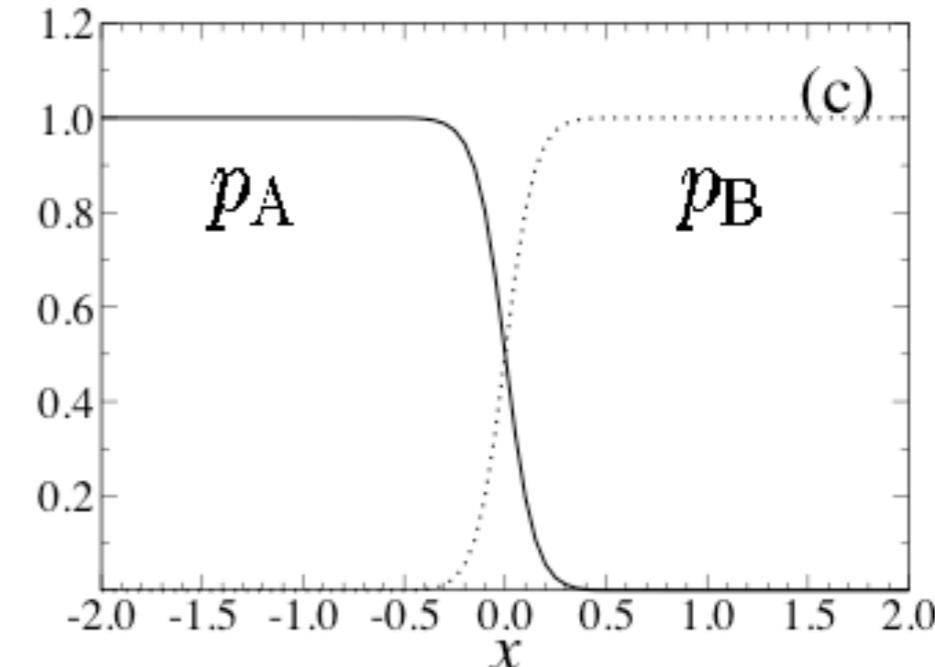
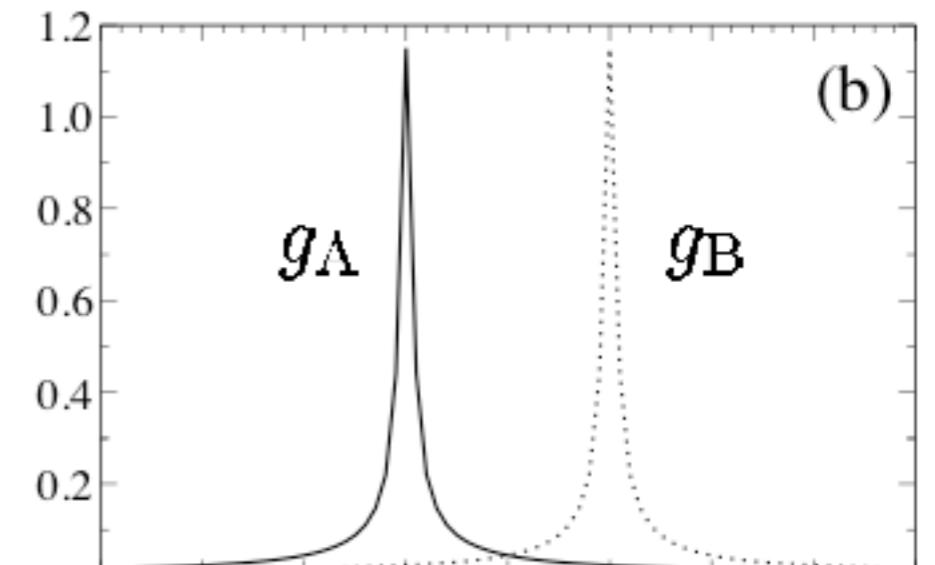
$$\sum_{\text{atoms}} p_{\text{atom}}(\mathbf{r}) = 1$$

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

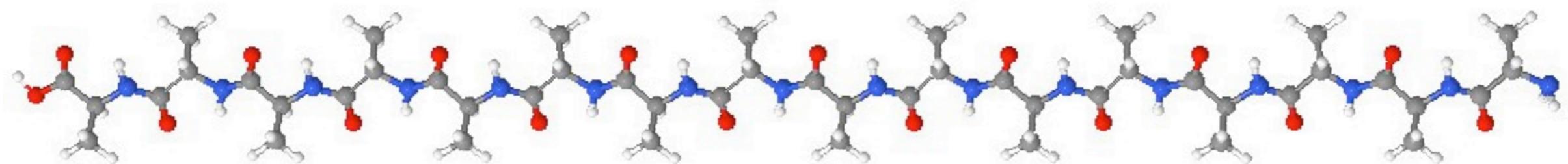
- e.g.: $g_{\text{atom}} = \frac{\rho_{\text{atom}}(r)}{r^2}$ (Delley 1990)

many alternatives:

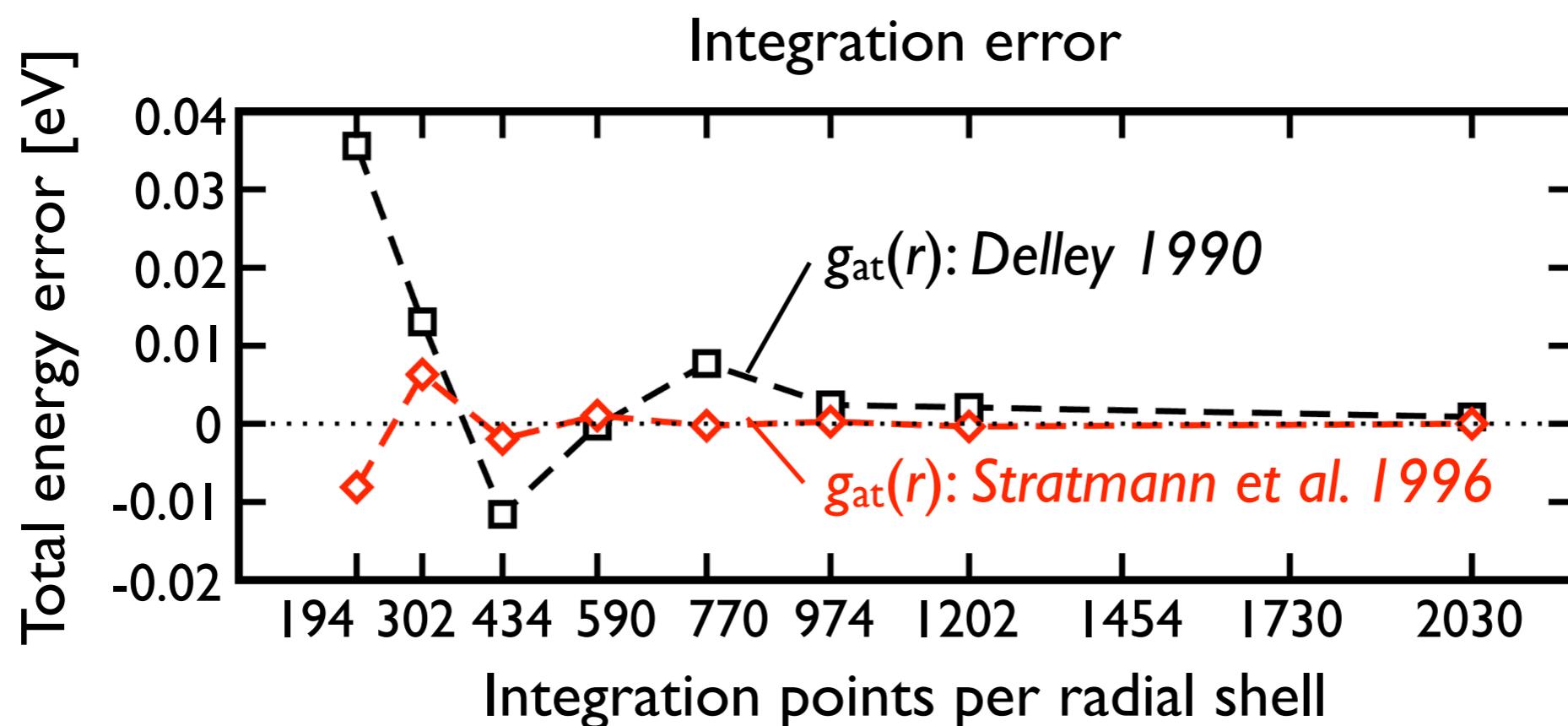
Becke 1988, Stratmann 1996, Koepernik 1999, ...



Integration in Practice: Large Systems, Small Errors!



Fully extended Polyalanine peptide molecule Ala_{20} , 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: $n_{\text{atom},lm}(r) = \int_{s=|\mathbf{r}' - \mathbf{R}_{\text{atom}}|} p_{\text{atom}}(\mathbf{r}') n(\mathbf{r}') Y_{lm}(\Omega)$

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-
- Classical electrostatics:

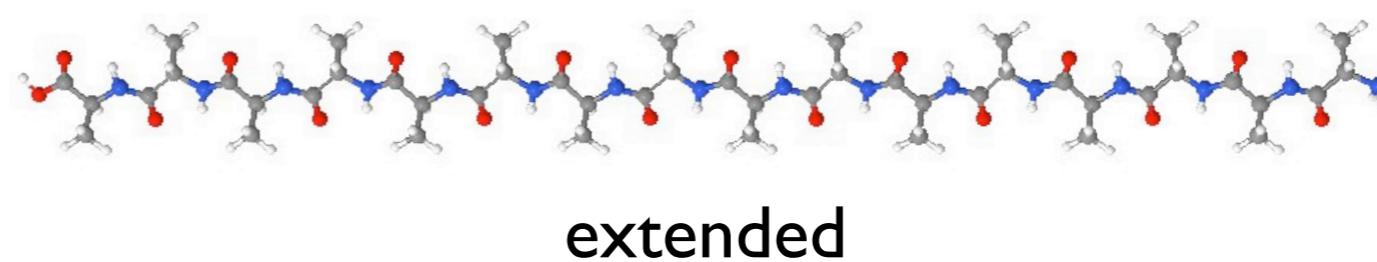
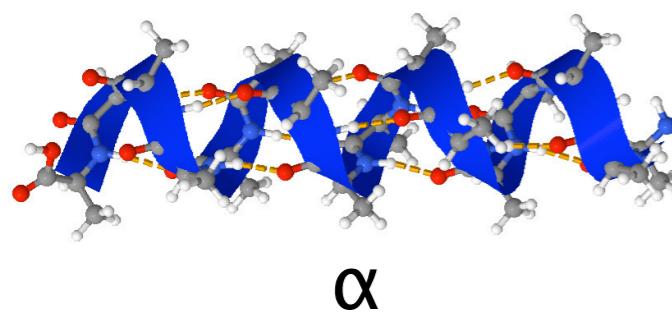
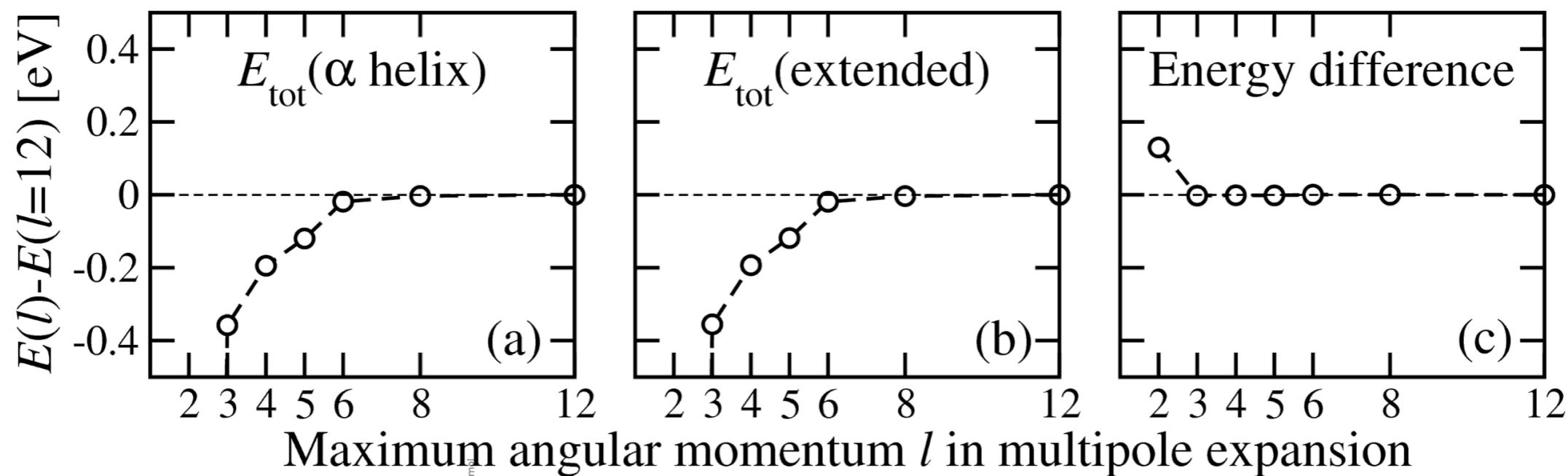
$$v_{\text{es}}(\mathbf{r}) = \sum_{\text{atoms}} \sum_{\mathbf{lm}}^{l_{\max}} v_{\text{atom},lm}(|\mathbf{r} - \mathbf{R}_{\text{atom}}|) Y_{lm}(\Omega_{\text{atom}})$$

Electrostatics: Multipole expansion

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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

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

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

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needed for heavy elements

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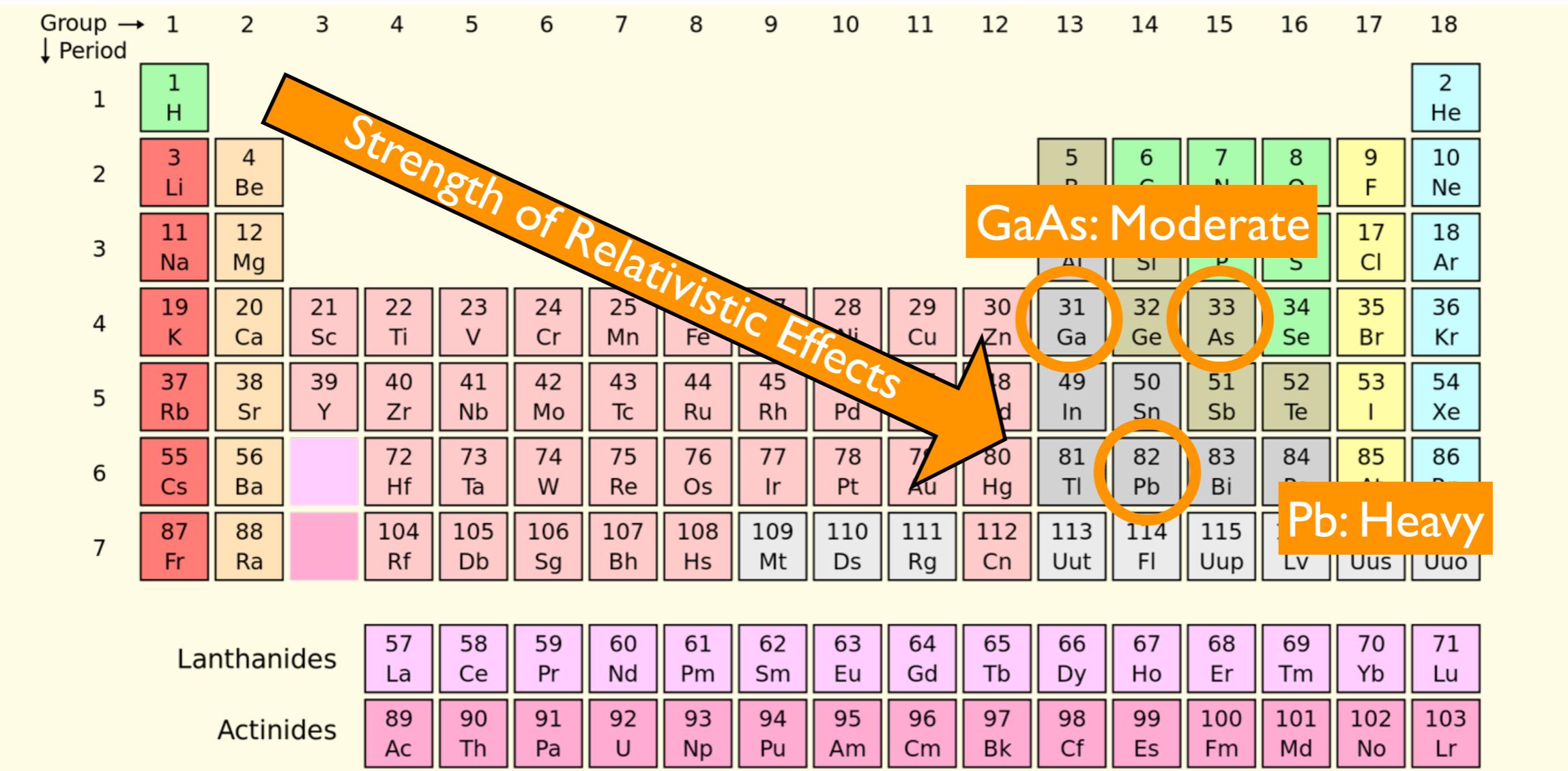
How Strong are Relativistic Effects Across the Periodic Table?



William Huhn
(Duke Univ.)

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period	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		

How Strong are Relativistic Effects Across the Periodic Table?



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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

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Relativistic QM: Dirac Equation

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

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... simply rewrite:

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

- ▶ 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



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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

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

I. 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) [I]

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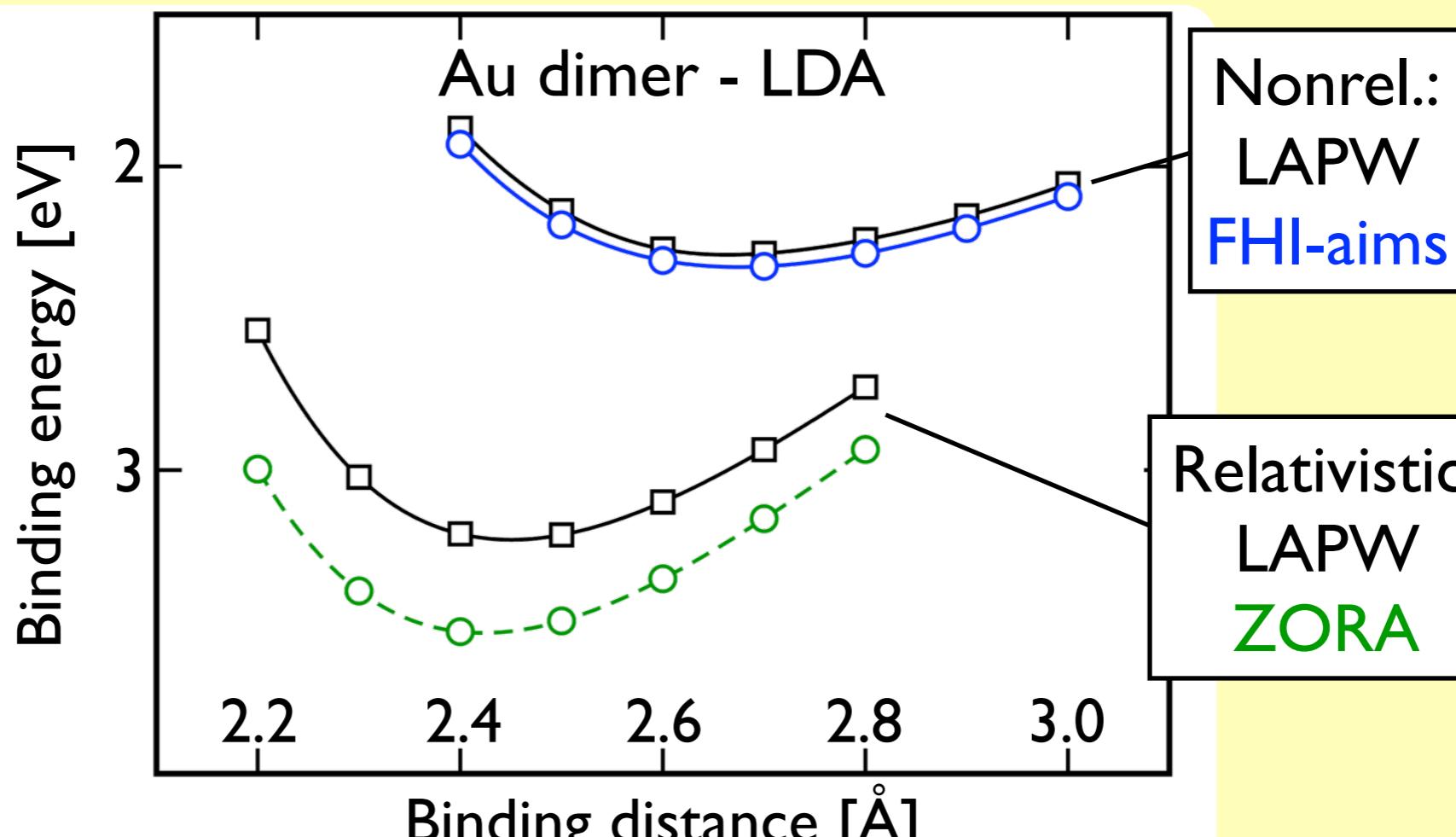
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... not gauge-invariant!

Approximations to Scalar Relativity

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

ZORA in practice: Harsh approximation (known)



Accurate, Stable Scalar Relativity:“Atomic ZORA”

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ZORA

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ZORA

“Atomic ZORA”!

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

- 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)

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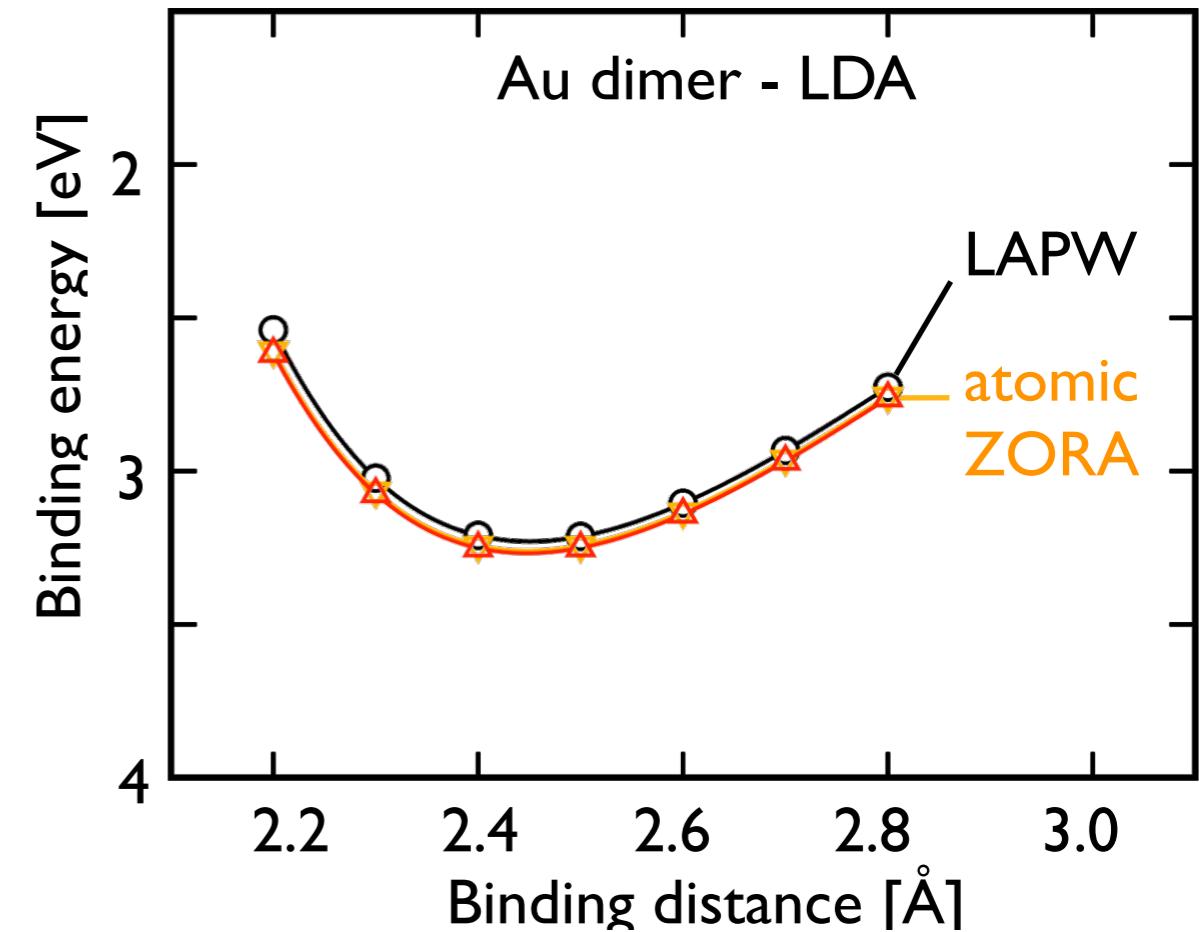
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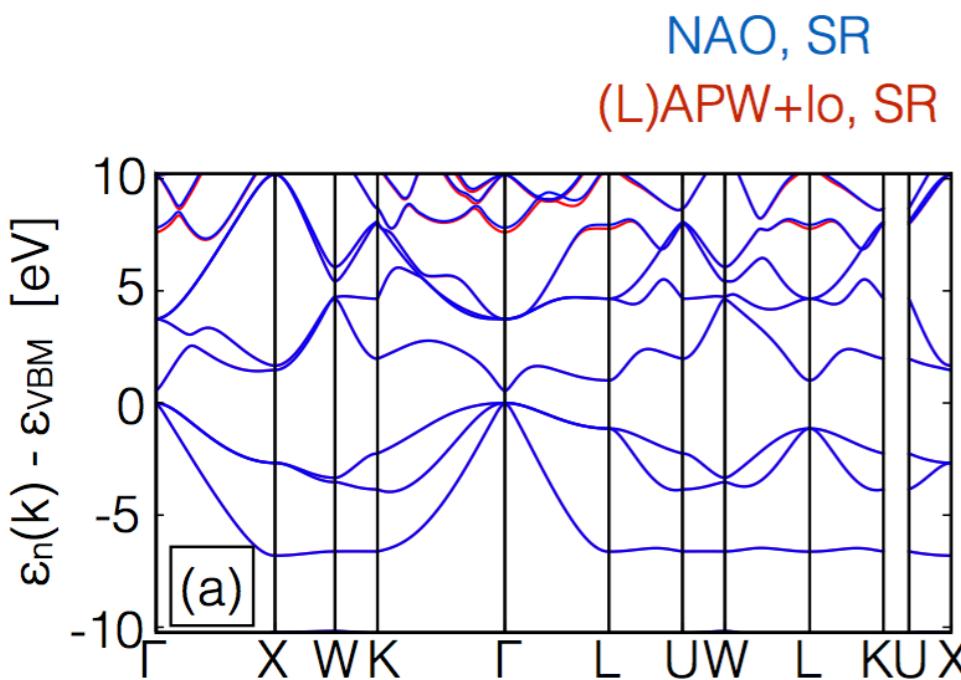
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Benchmark: Scalar-Relativistic Band Structures for 103 Solids



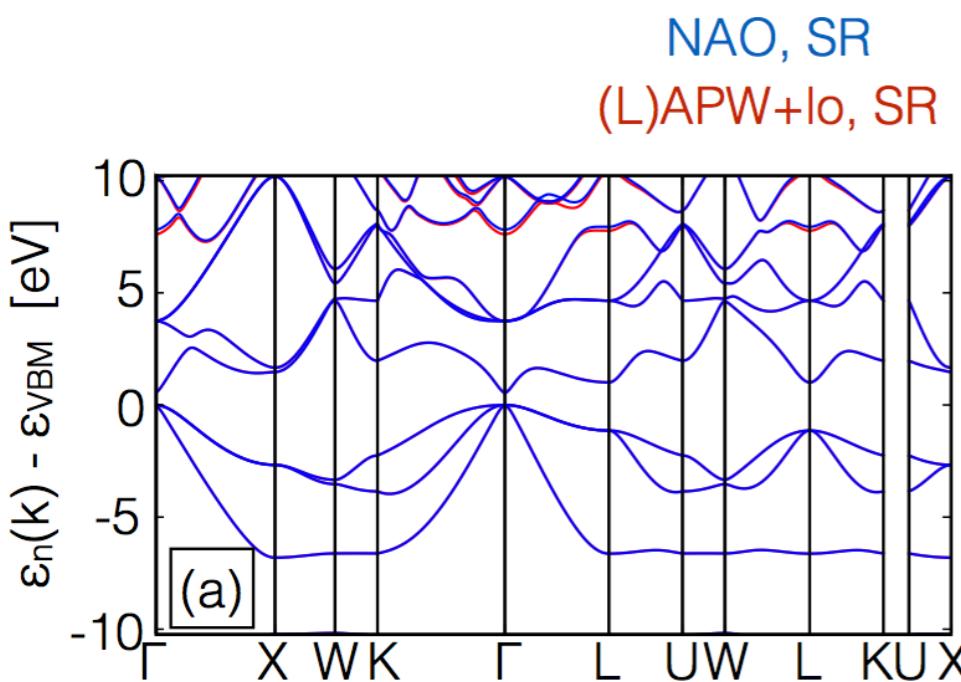
... basically identical with Wien2k
reference set (LAPW)



Dr. William Huhn
(Duke Univ.)

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

Δ_{band} [eV/band]

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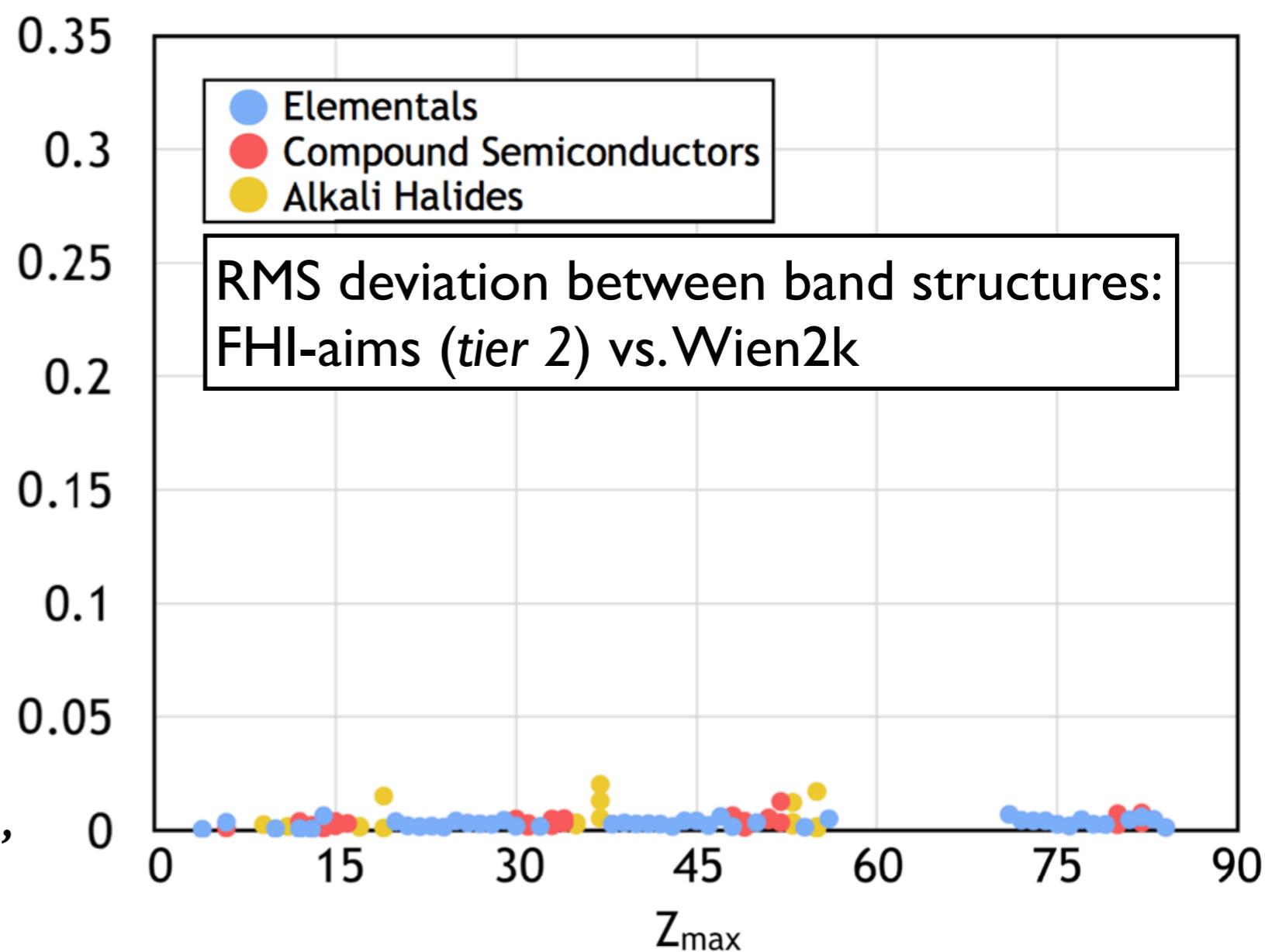


Dr. William Huhn
(Duke Univ.)

Scalar-Relativistic

● Elementals
● Compound Semiconductors
● Alkali Halides

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



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

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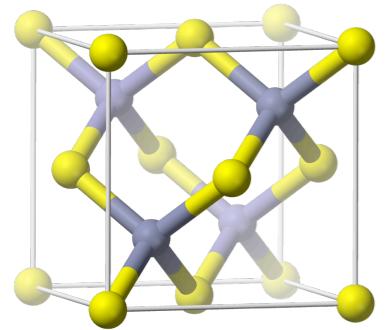
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For band structures, SOC term can be included

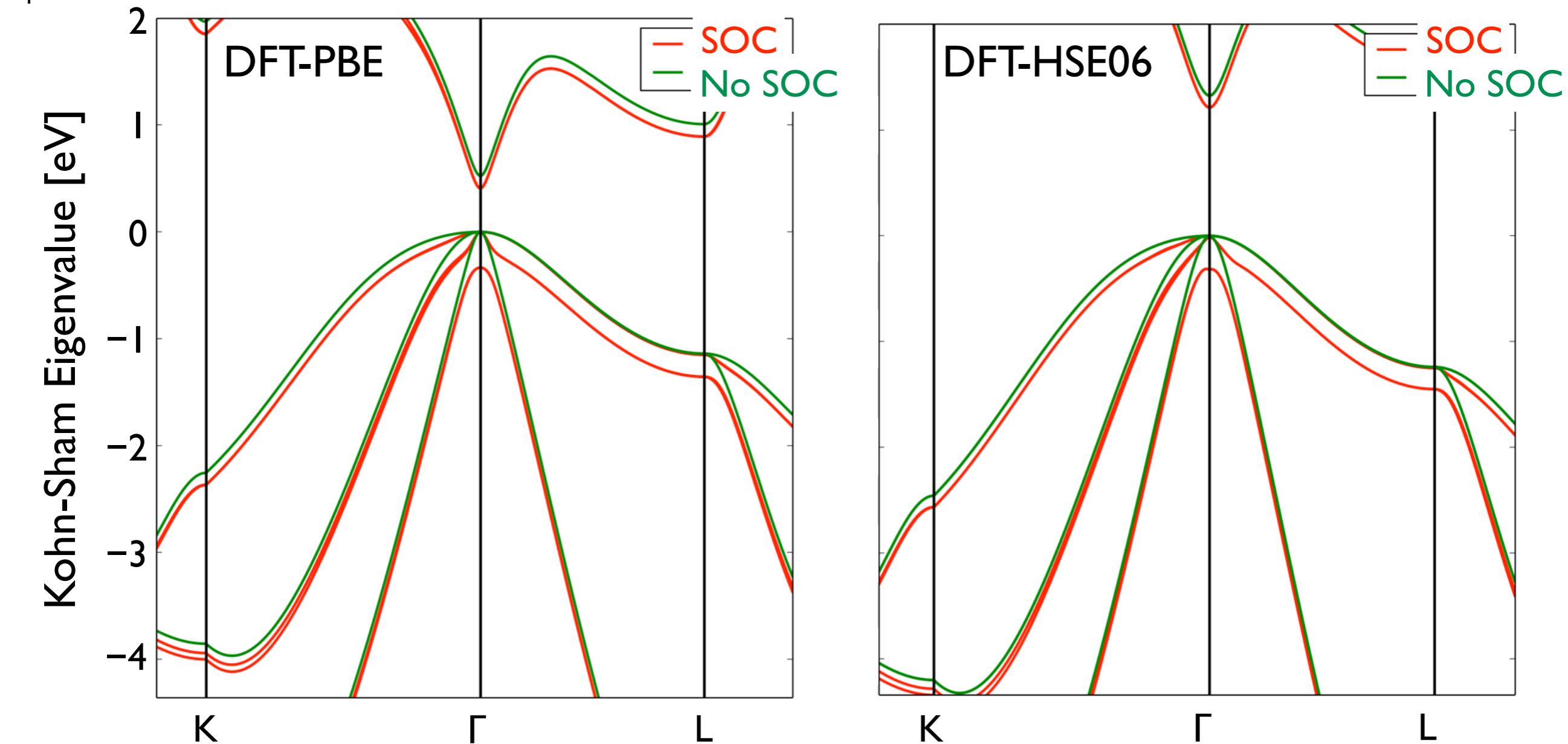
- self-consistently
- non-selfconsistently after a self-consistent scalar relativistic band structure

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

Real Materials: Impact of Relativistic Effects

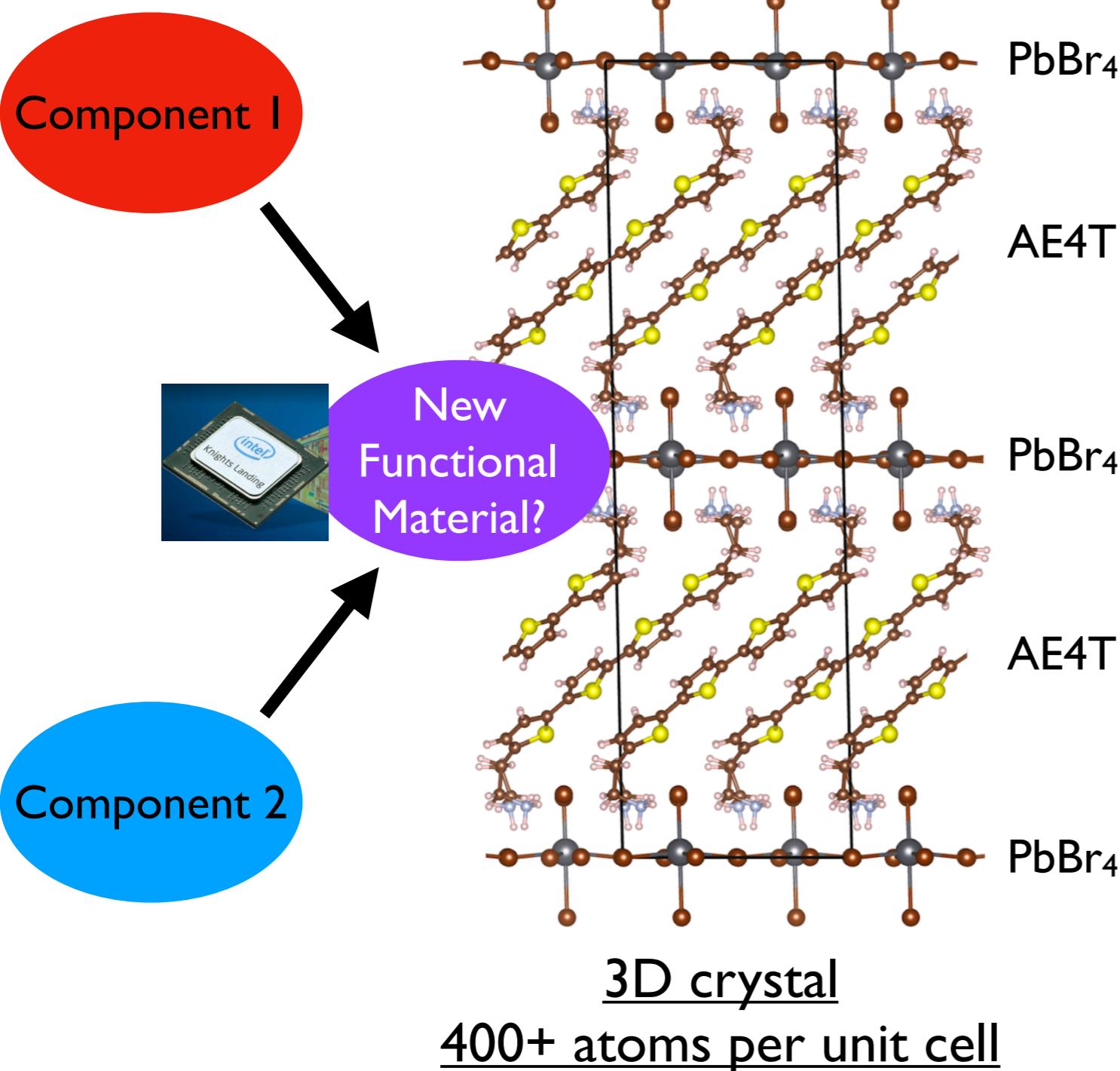


$$a_{\text{exp}} = 5.6532 \text{ \AA}$$



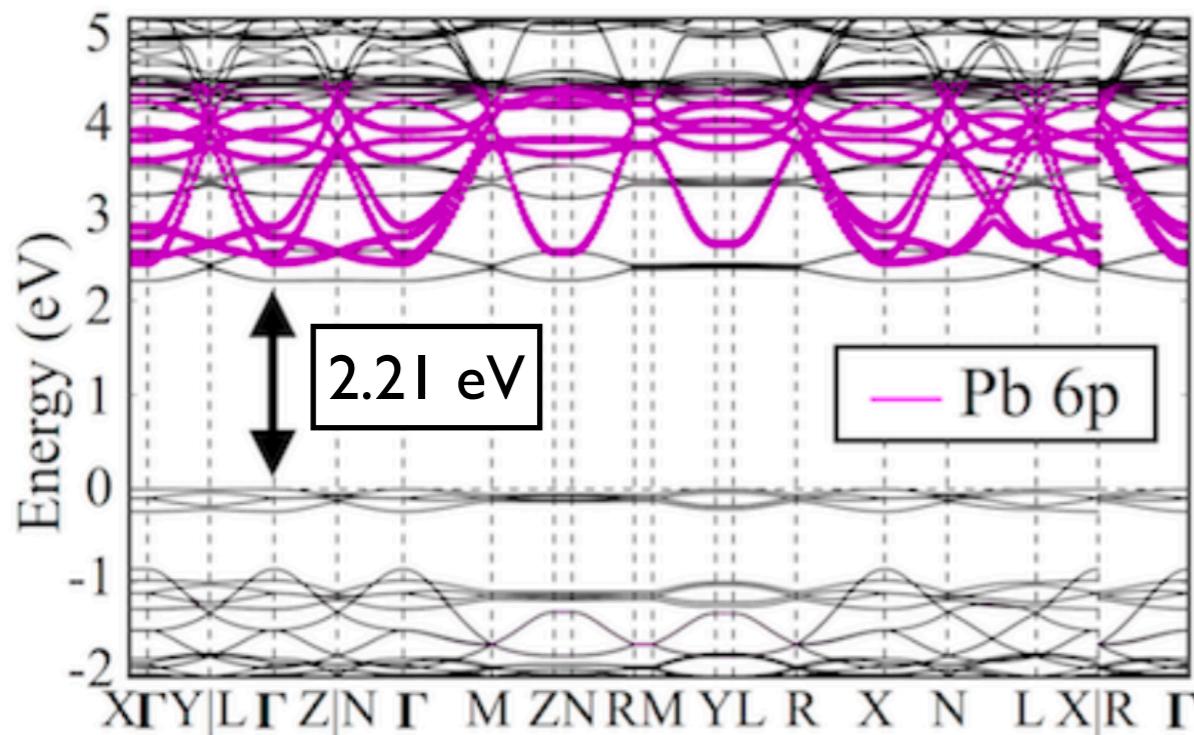
SOC in Heavy-Element Containing Materials?

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

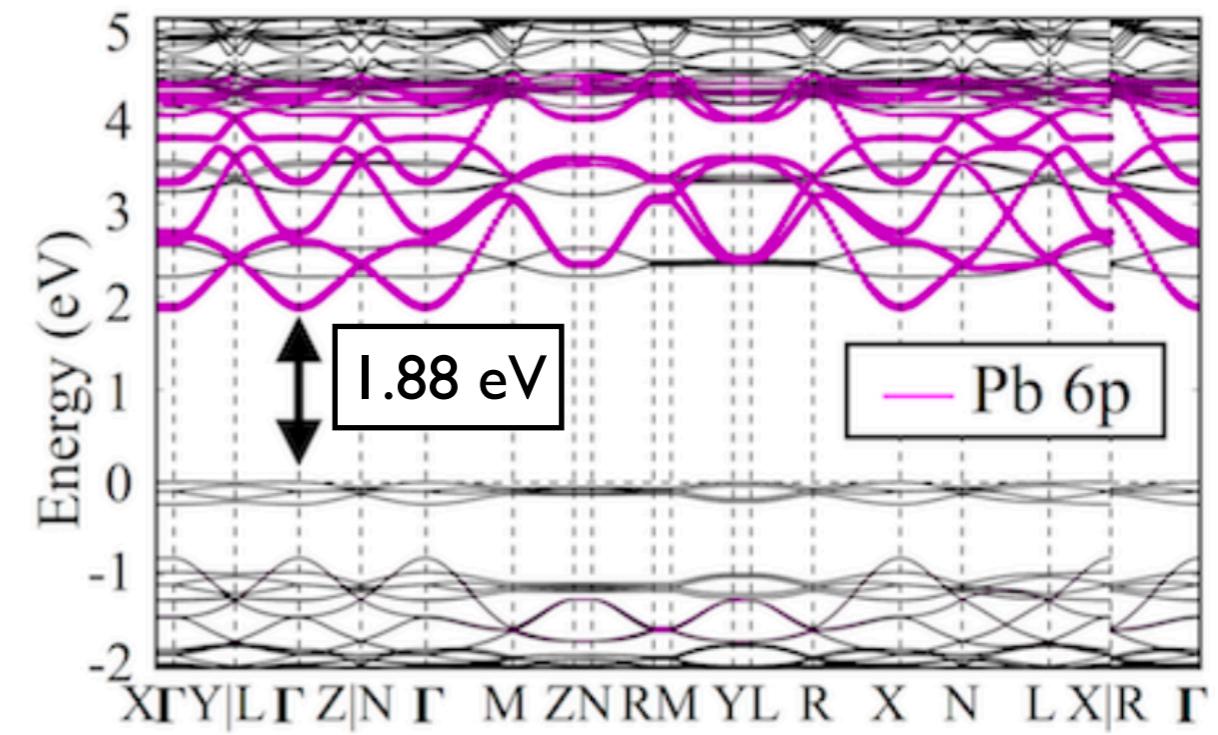


AE4T-PbBr₄: Energy Levels - Impact of Spin-Orbit Coupling

AE4T-PbBr₄ - HSE06, no SOC

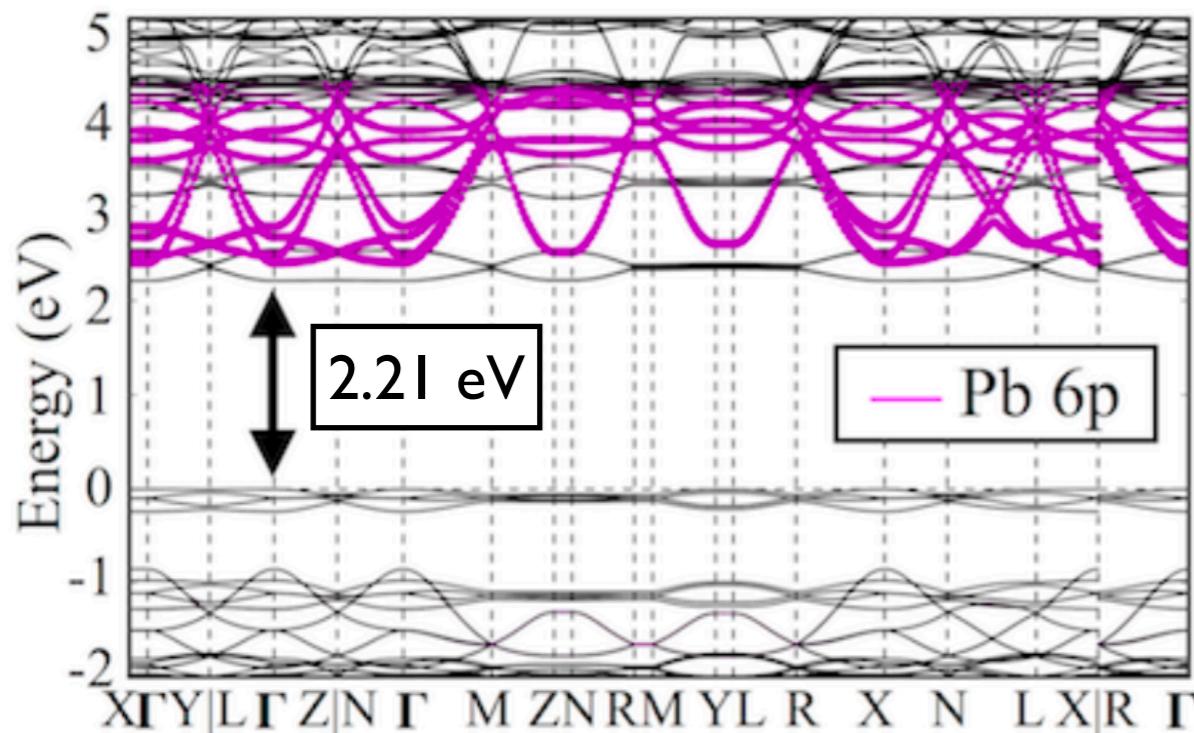


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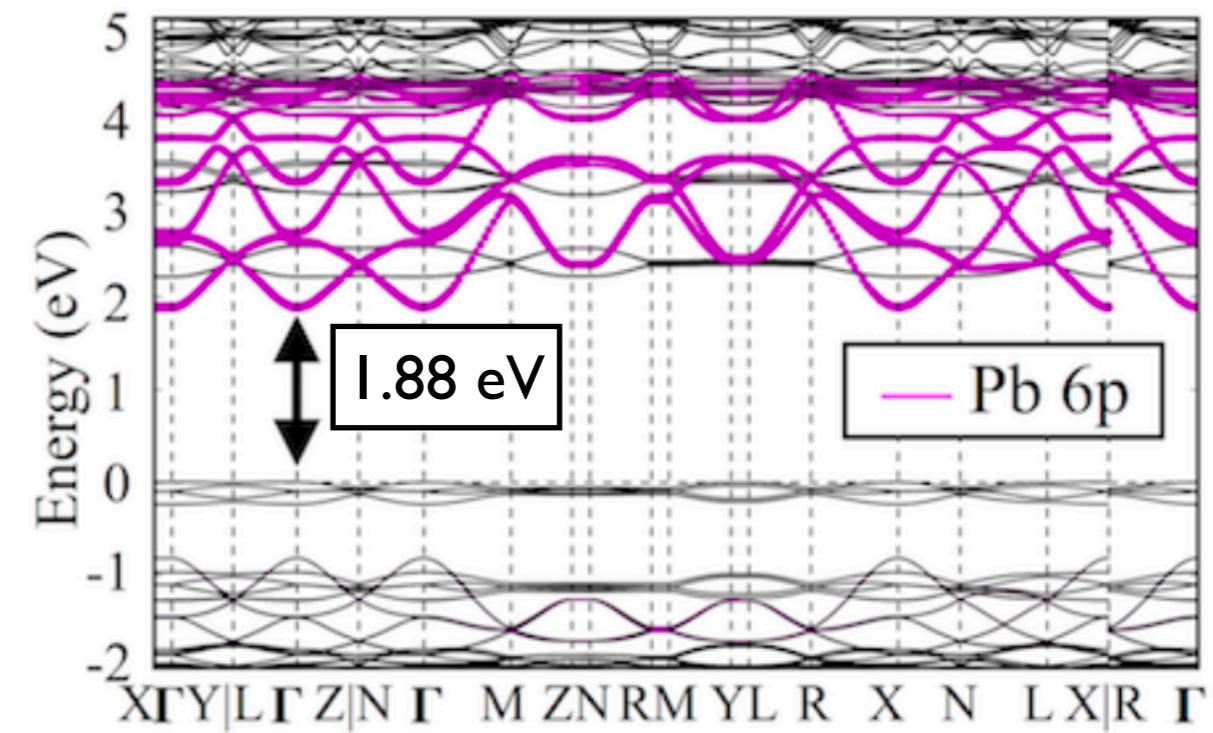


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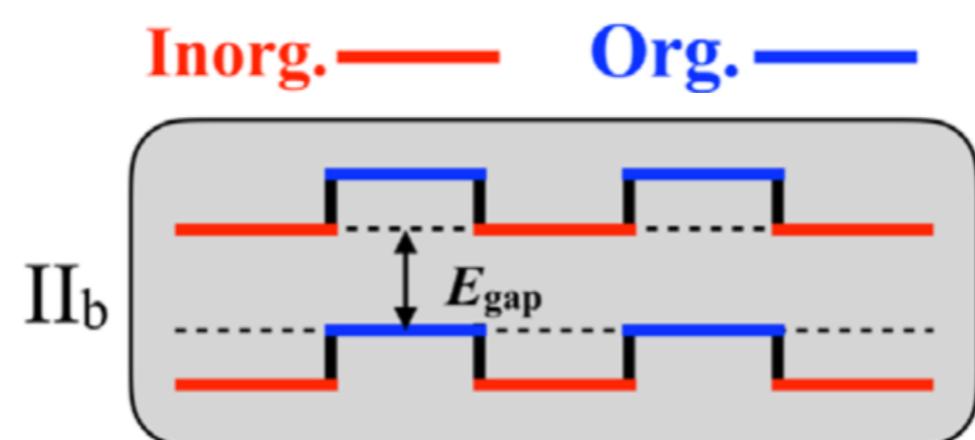


AE4T-PbBr₄ - HSE06, SOC



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

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

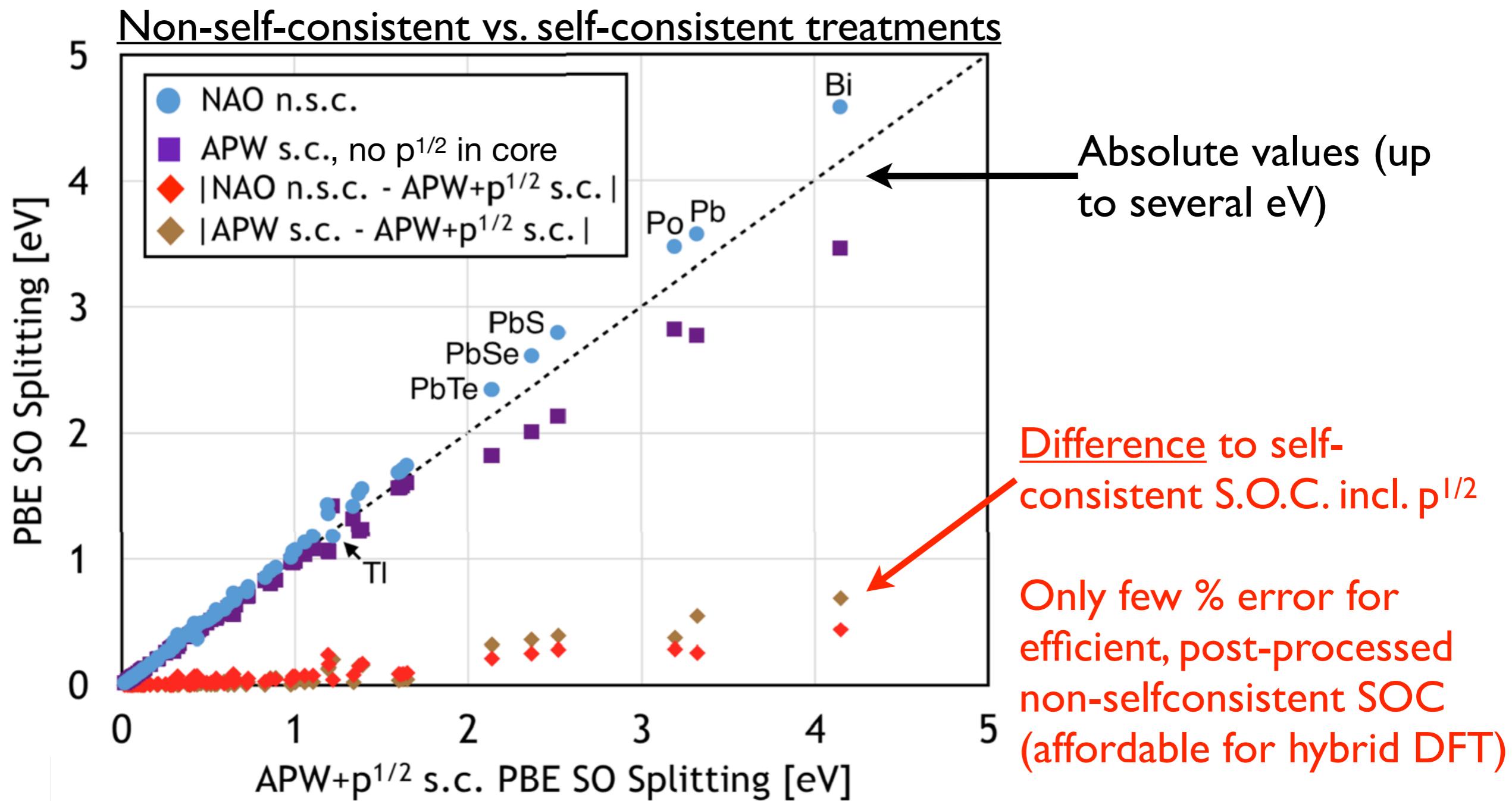


Benchmark for Spin-Orbit Splittings

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

Target: Largest SO Splitting in each compound band structure (~strength of SOC)

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



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*need suitable basis,
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Computational Scaling: Two Sub-Problems

1. Real space grid operations

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Basis functions, Hamiltonian,
Kohn-Sham potential etc.

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

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Basis functions, Hamiltonian,
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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)

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

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

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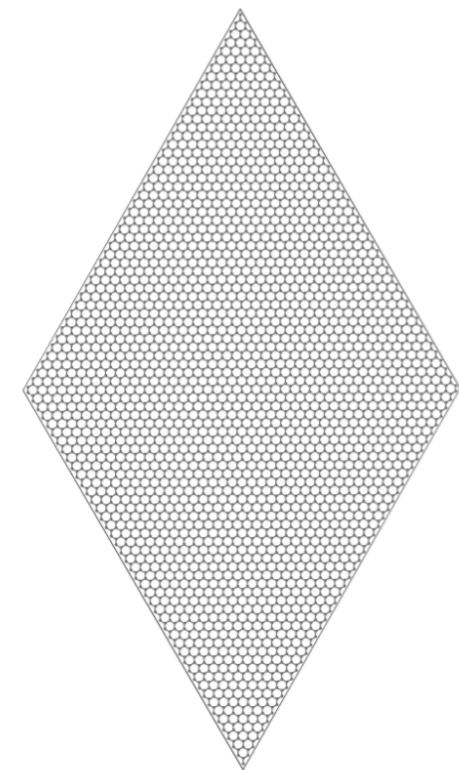
“Conventional” solvers (Lapack-like):

- 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?

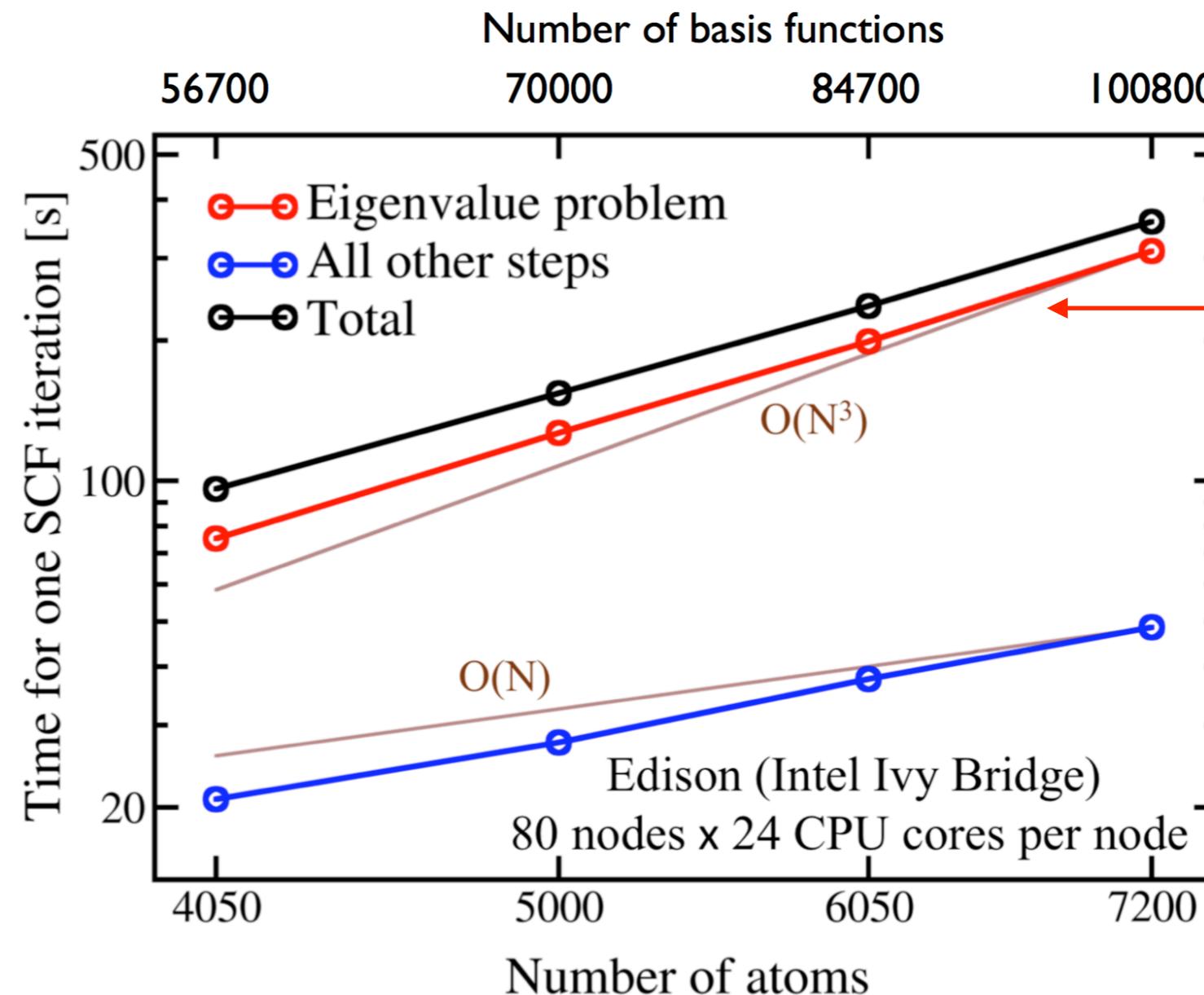
Typical Scaling - $O(N^3)$ Wall

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



Graphene monolayer,
4050 atoms

FHI-aims, PBE, “light” settings



ELPA Library
[http://elpa.
rzg.mpg.de](http://elpa.rzg.mpg.de)

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

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

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18						
↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18						
	1 H																	2 He						
1		3 Li	4 Be															10 Ne						
2				11 Na	12 Mg													18 Ar						
3						19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn							
4								37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag						
5									55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au					
6													87 Fr	88 Ra	104 Rf	105 Db	106 Sg	107 Bh	108 Hs					
7															109 Mt	110 Ds	111 Rg	112 Cn	113 Uut					
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

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)

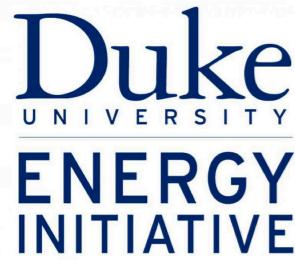
Summary

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



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

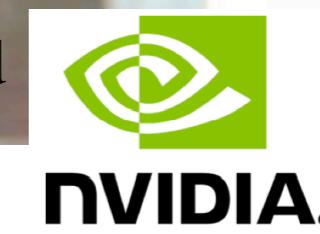
<http://aims.pratt.duke.edu>



National Science Foundation



Materials Research Science
and Engineering Center



ORNL



MAX-PLANCK-GESELLSCHAFT

ACS Petroleum Research Fund

Summary

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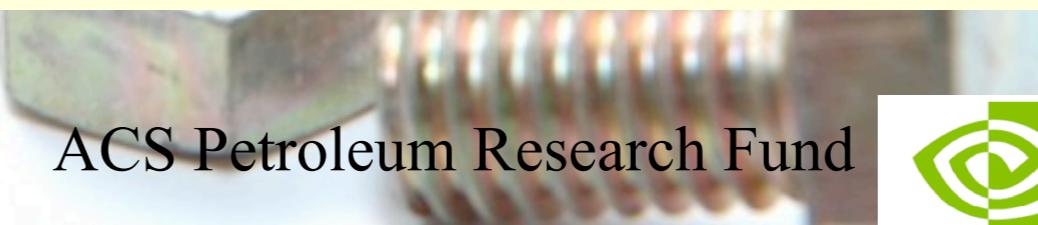
$$\hat{\mathcal{H}}\Psi = E\Psi$$

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



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



Excursion:“Basis Set Superposition Errors”?

Traditional quantum chemistry:“Basis set superposition errors”

e.g.: Binding energy $E_b = E(\bullet - \bullet) - 2E(\bullet)$



Problem:

$\bullet - \bullet$ has larger basis set than \bullet .
→ Distance-dependent overbinding!

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No nucleus - basis functions only

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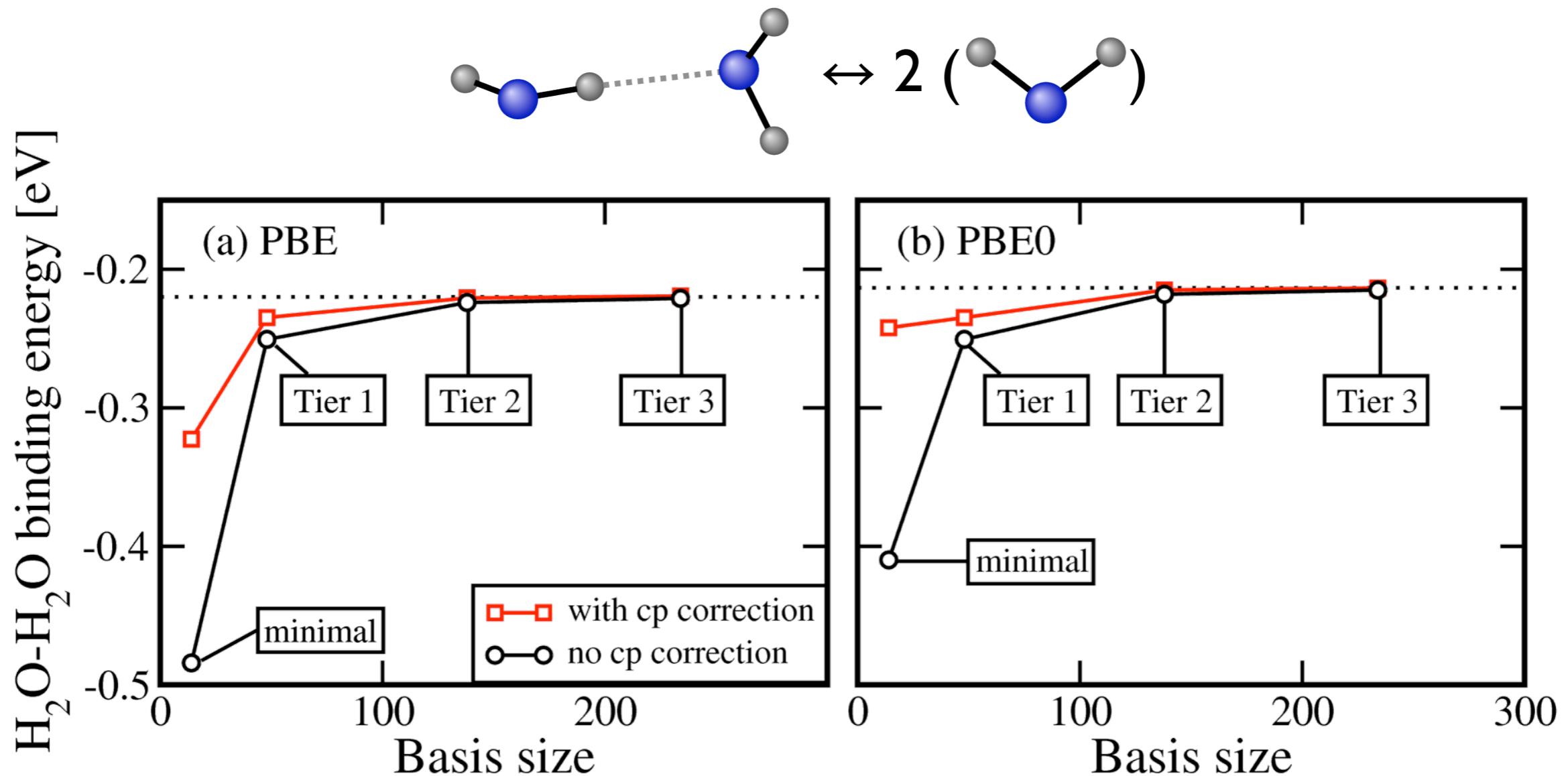
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NAO basis sets: \bullet is already exact → no BSSE for $\bullet - \bullet$.
But how about *molecular* BSSE?

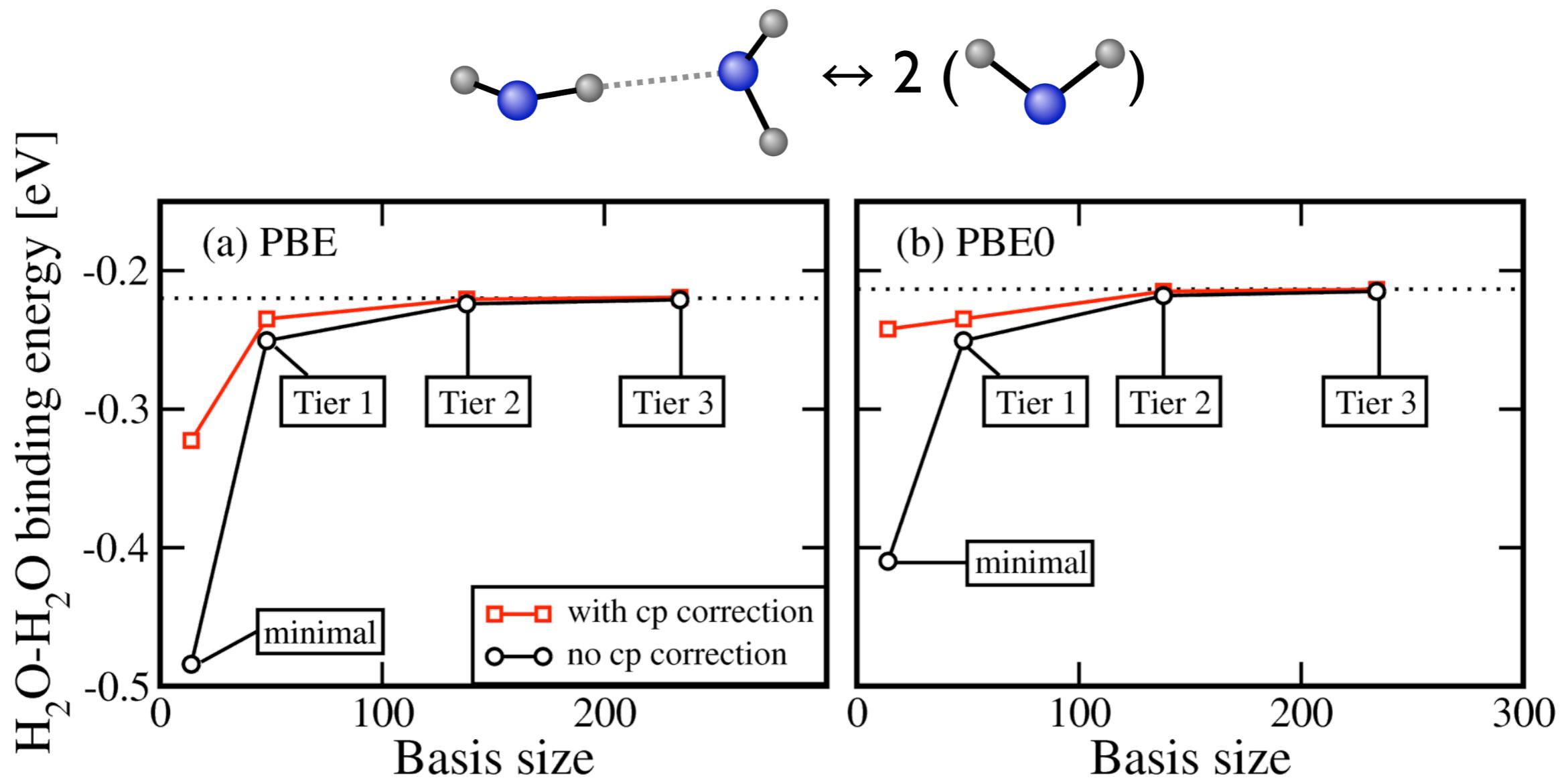
$(\text{H}_2\text{O})_2$: “Counterpoise Correction”



Ground-State DFT, NAO's:

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

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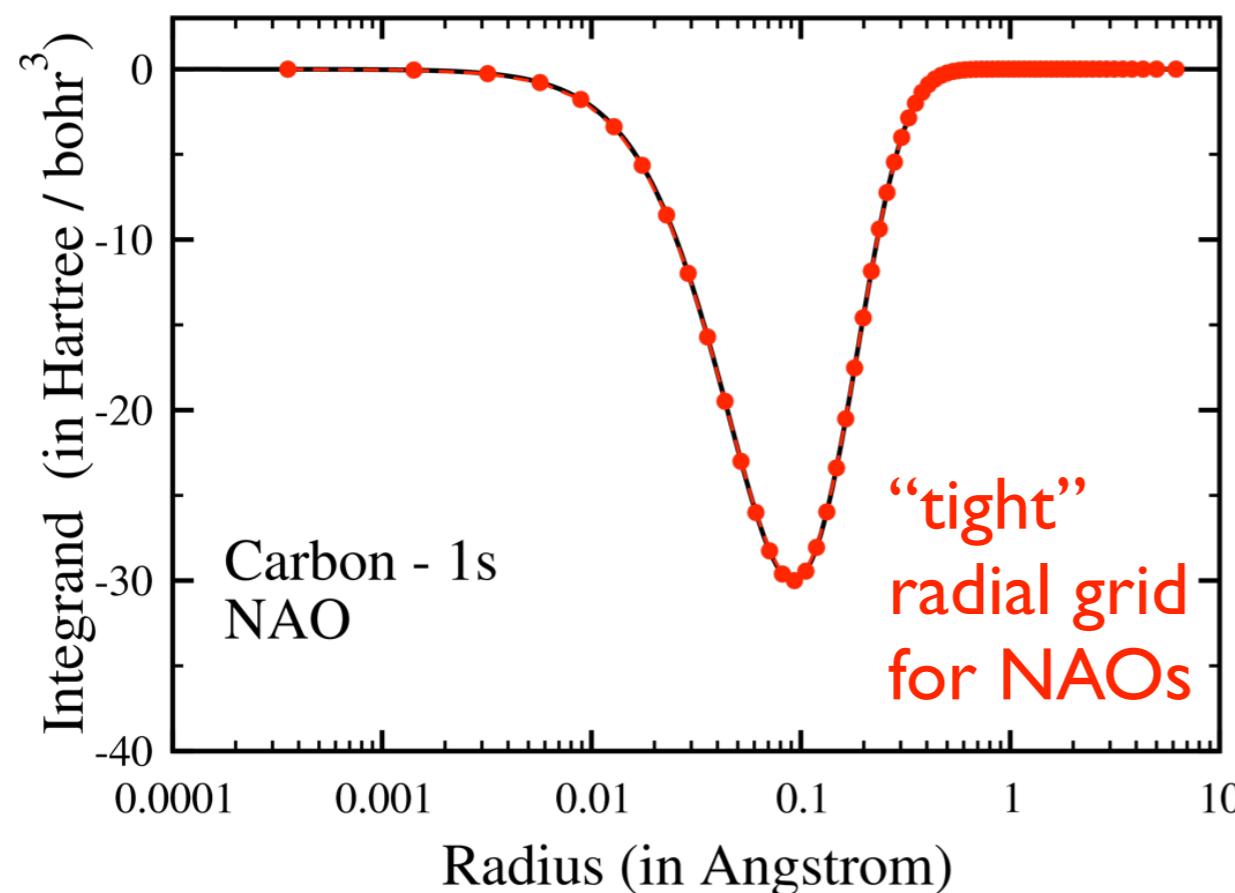
*BUT methods that sum over infinite continuum (MP2, RPA, ...)

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:

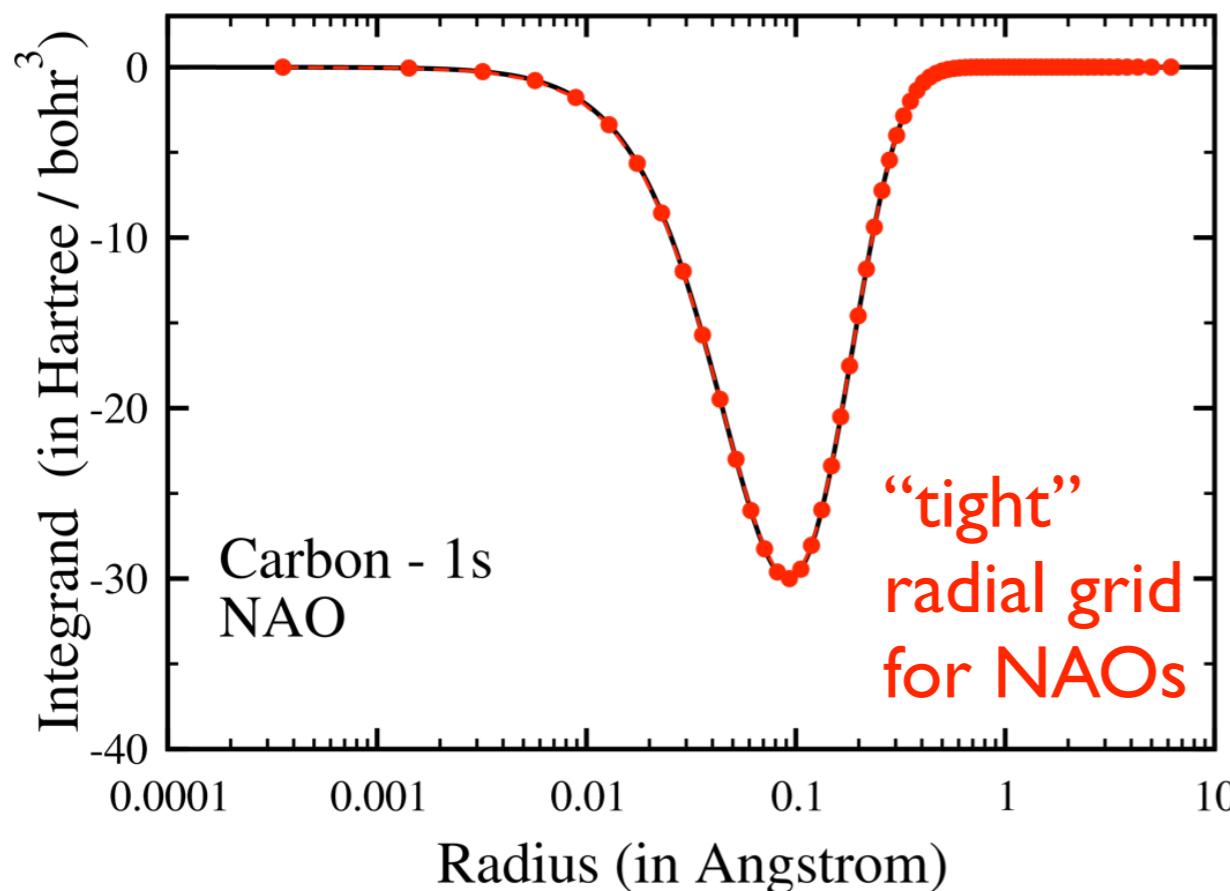


Igor Ying Zhang, Xinguo Ren, Patrick Rinke, Volker Blum, and Matthias Scheffler,
Numeric atom-centered-orbital basis sets with valence-correlation consistency from H to Ar
New Journal of Physics 15, 123033 (2013).

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$f(r)$ for
NAO radial function:



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

