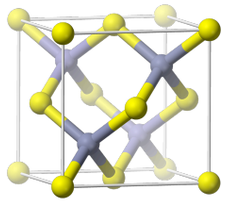
The FHI-aims All-Electron Framework for Molecular and Materials Simulations

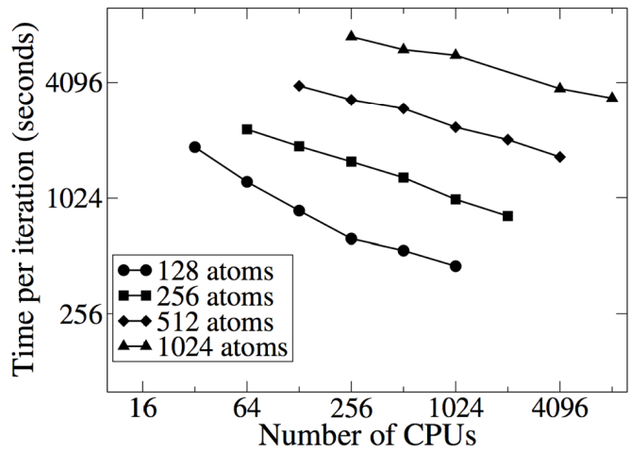
Volker Blum

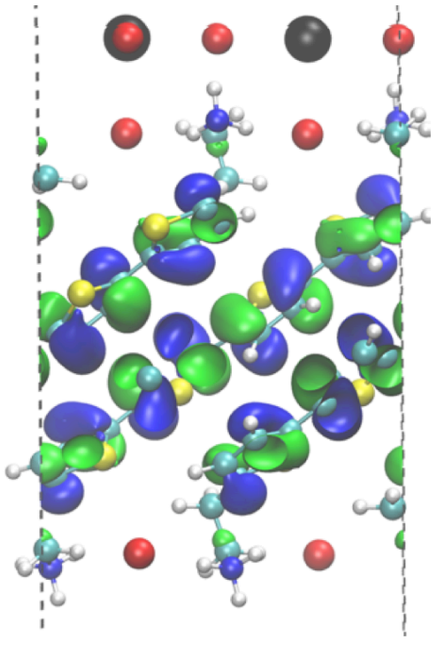
Department of Mechanical Engineering & Materials Science - Duke University, Durham, NC

http://aims.pratt.duke.edu



HSE06, GaAs





$PbBr_4$

AEQT

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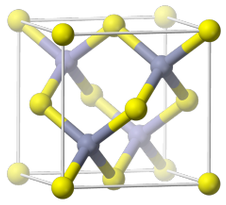
All-Electron Theory for Large Systems: FHI-aims

Extending the Reach of DFT & Many-Body Theory



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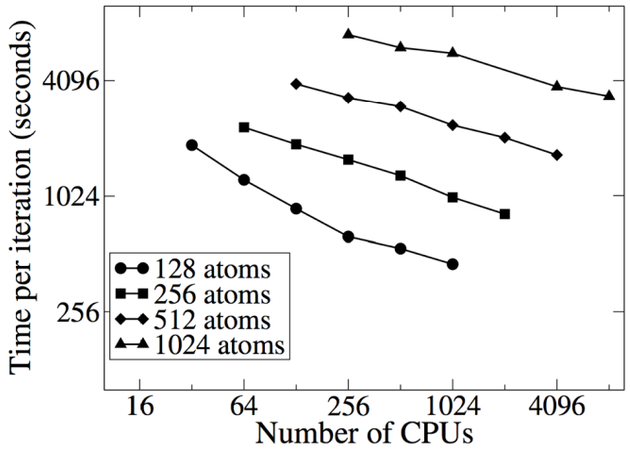
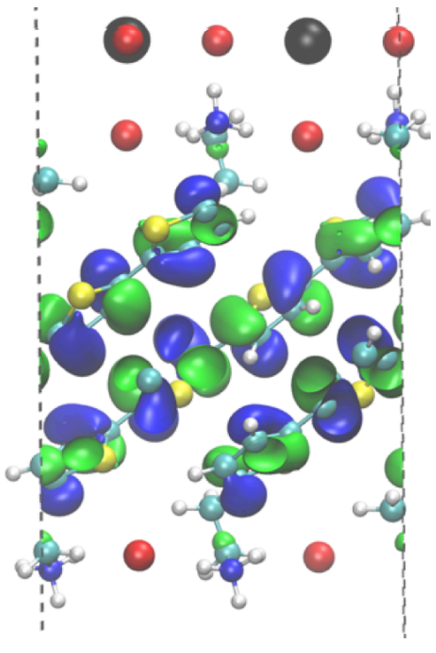


Tunable Electronic Structure in Organic-Inorganic Hybrids



Many Individuals Contributed to This Work - Thanks!

Fritz Haber Institute, Berlin [Richard-Willstätter-Haus]

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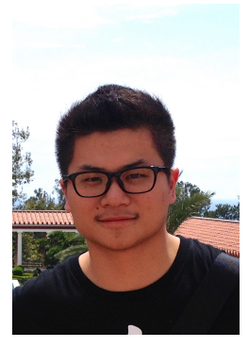
Dr. William Huhn
Spin-Orbit Coupling
"Energy Materials"

Victor Yu
Electronic Structure
Infrastructure (NSF)

Björn Lange
Jan Kloppenburg
Tiago Botari

Dr. Raul Laasner
Nuclear Spin States
& NMR



Tong Zhu
PV Materials
GW & RPA

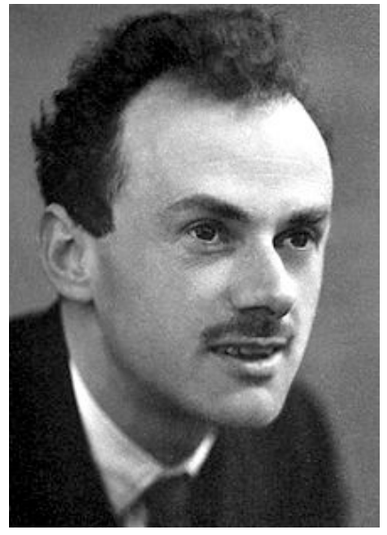
Garnett Liu
Perovskites
Excitonic Effects

FHI-aims team and collaborators: Matthias Scheffler (Berlin), Xinguo Ren (Hefei), over 100 individuals with contributions to the project. Development continues in Berlin, Hefei, Munich, Helsinki, London, Duke, Argonne, and many more.

So, We Have a Theory to Model "Everything"

Schrödinger (Dirac) Equation

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



P.A.M. Dirac

Perfect recipe for parameter-free modeling ...

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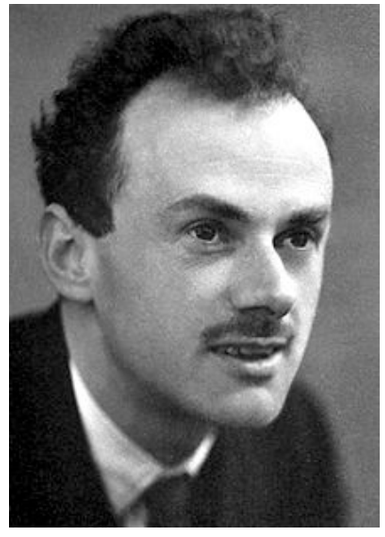
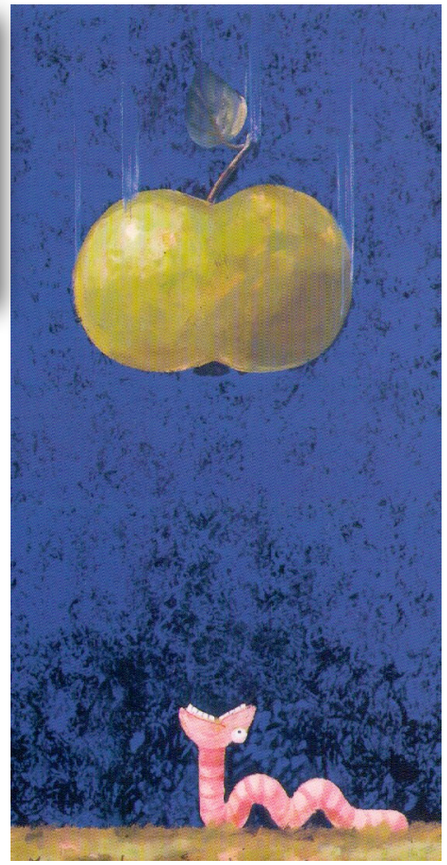


P.A.M. Dirac

Perfect recipe for parameter-free modeling ...

... but how do we make it practical?

The approximation is accurate
but
feasible systems are too small



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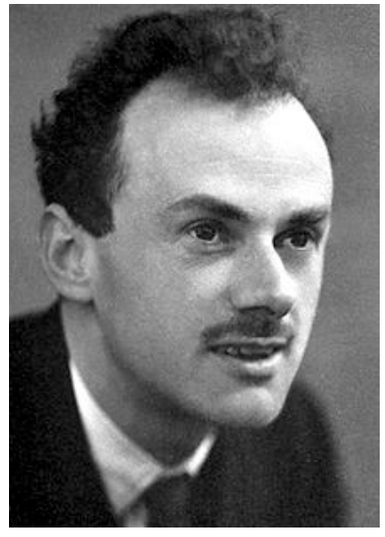

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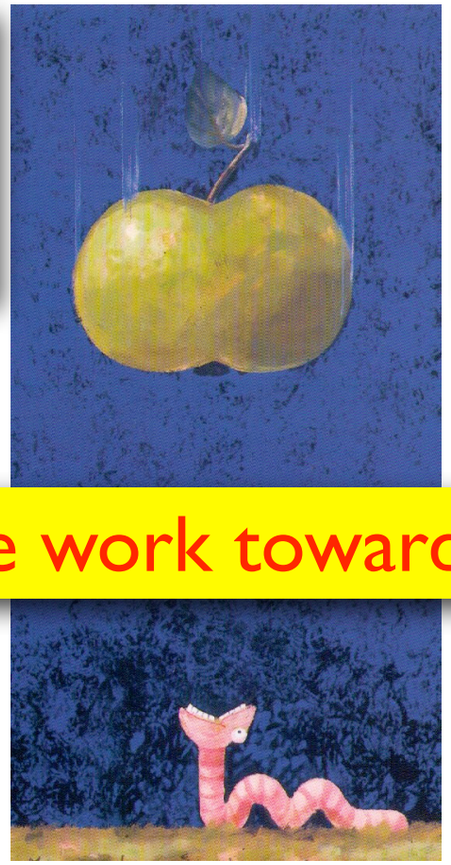

Feasible systems large enough
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(How?) can we work towards having both?

Current "Workhorse" Electronic Structure Theory

Quantum chemistry & many-body theory:

$E_{tot} \leq \langle \psi | H | \psi \rangle$ ... successive refinement of ψ

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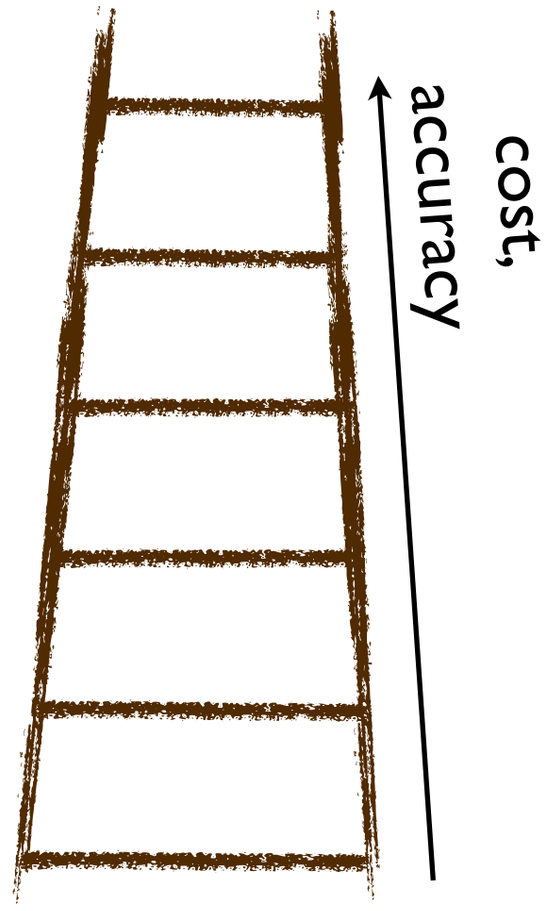
"Perdew's ladder" to exact solution



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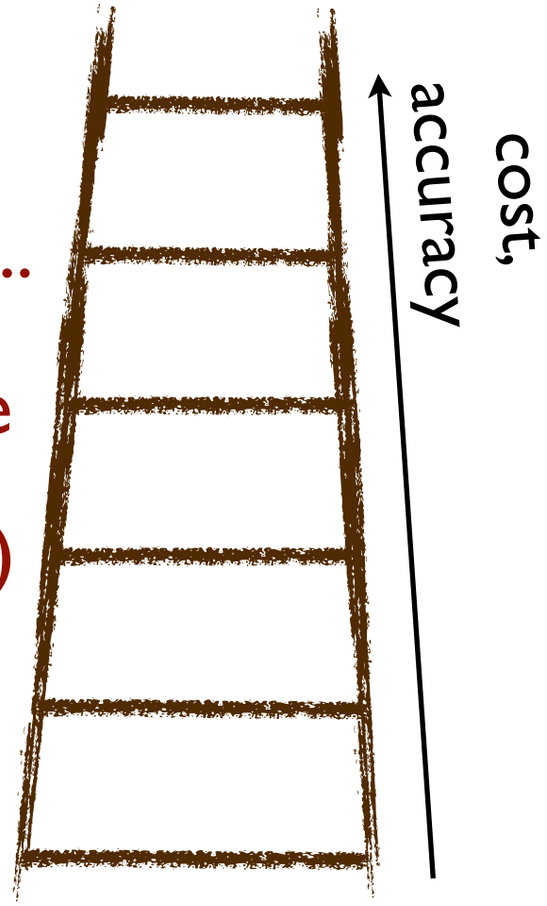
response / many-body terms: RPA, SOSEX, ...

hybrid functionals: non-local exchange

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

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

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



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+ van der Waals

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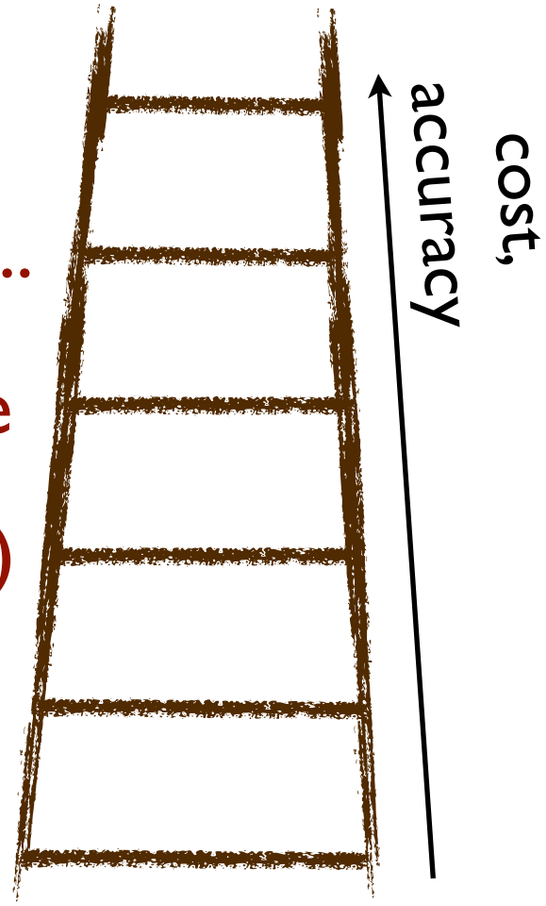
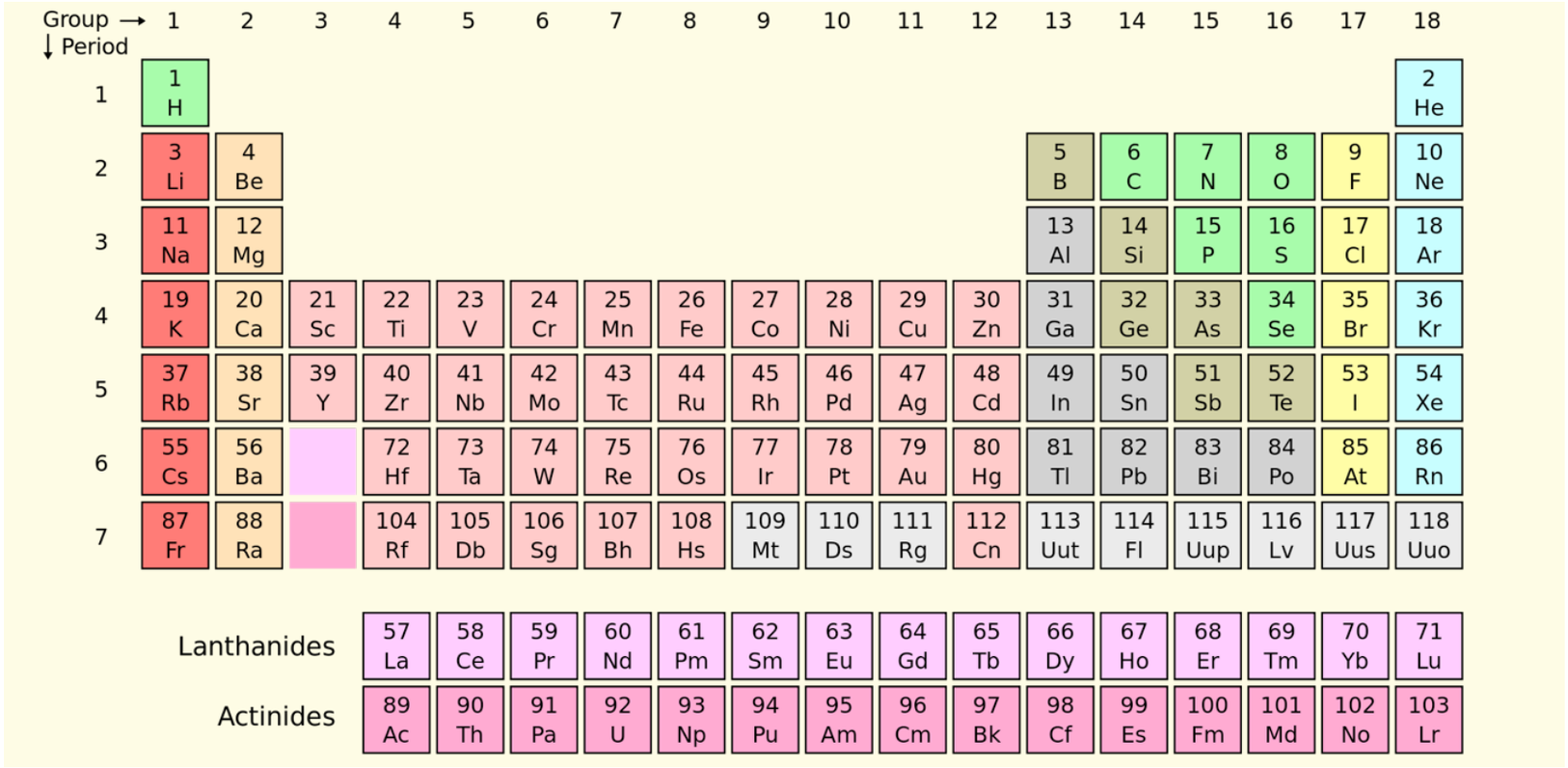


In 2004, We Began a New Electronic Structure Code ...



<u>Universality:</u> Cover full space of materials and chemistry

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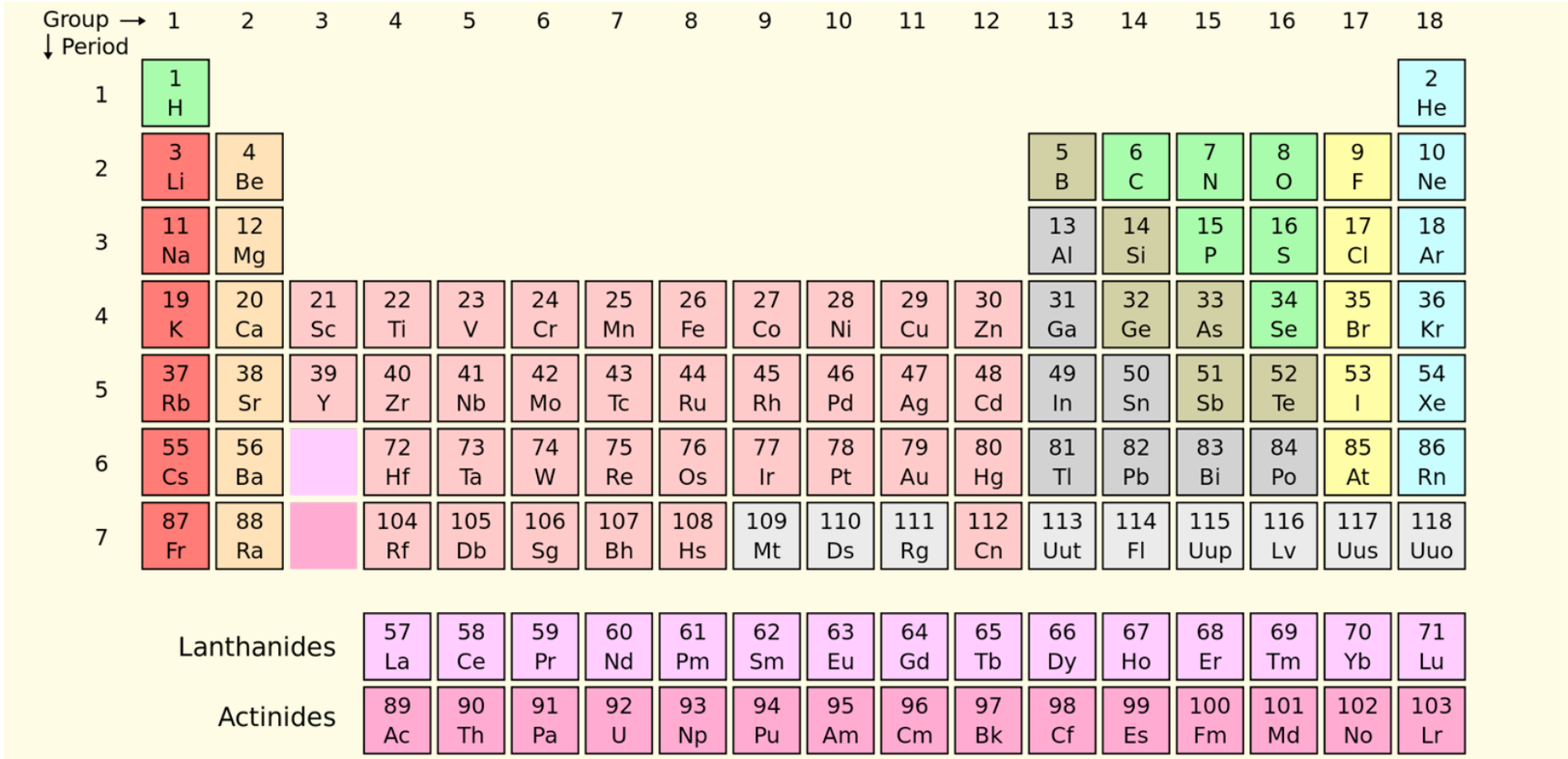

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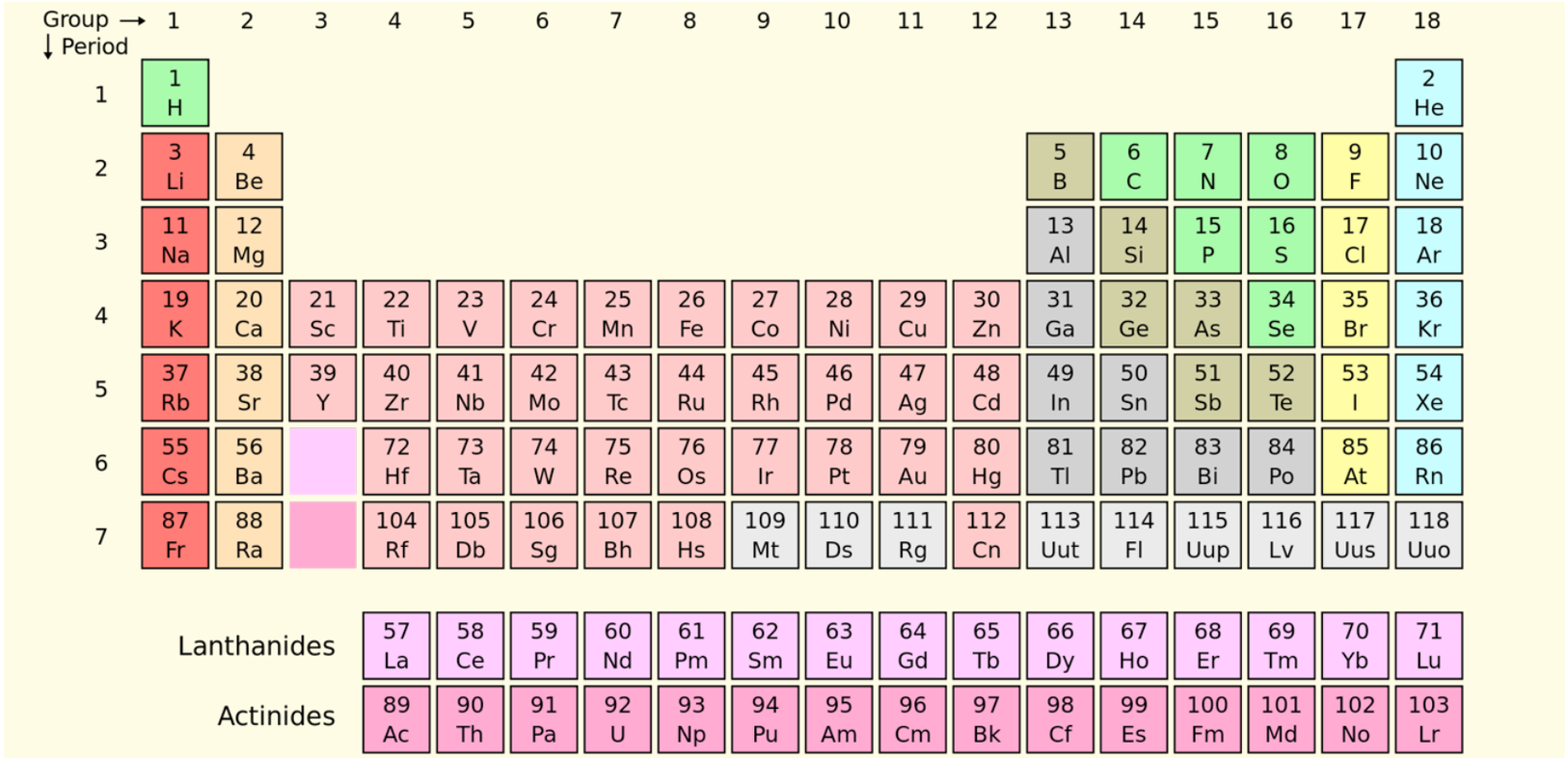

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All-electron

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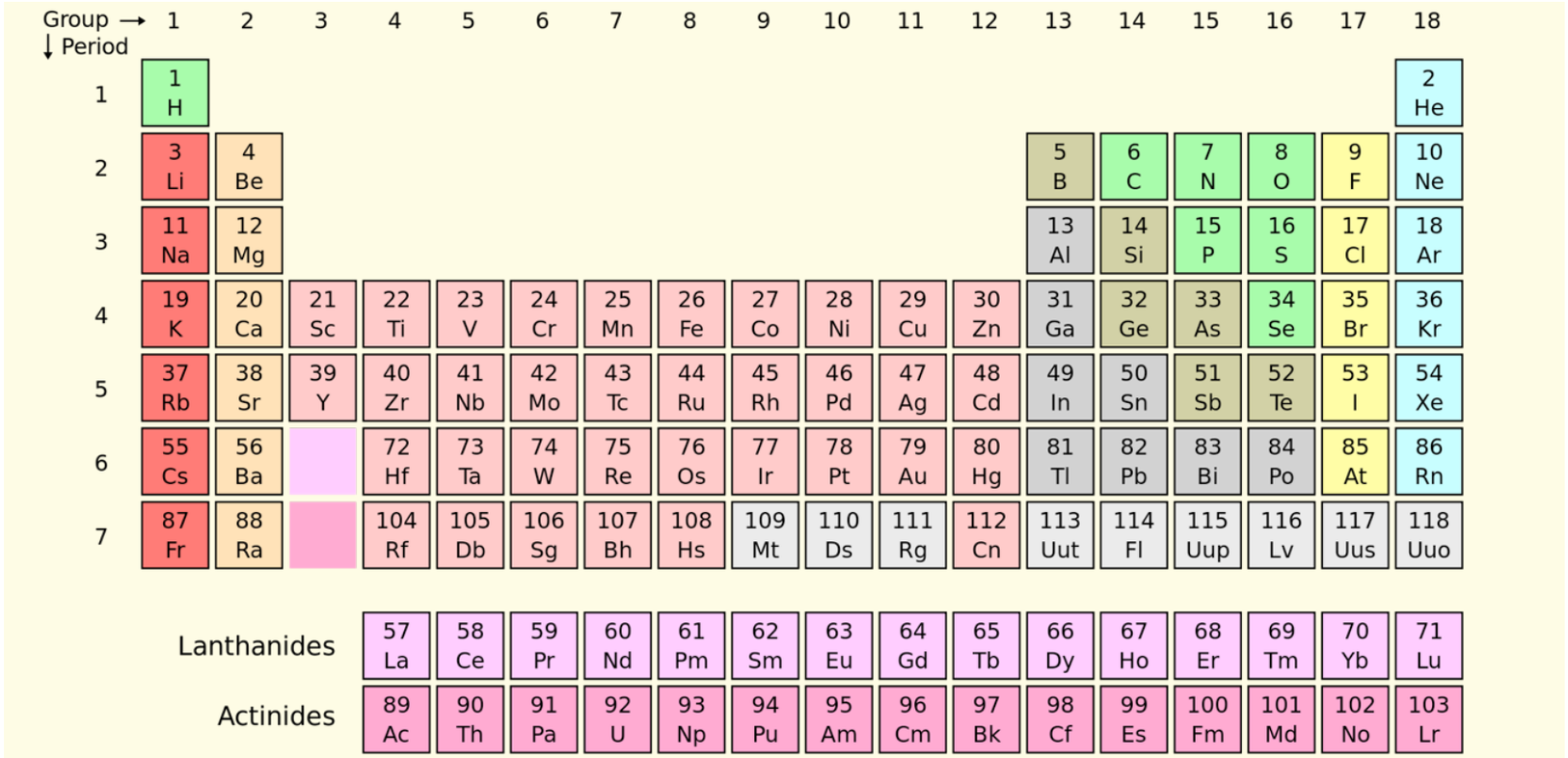

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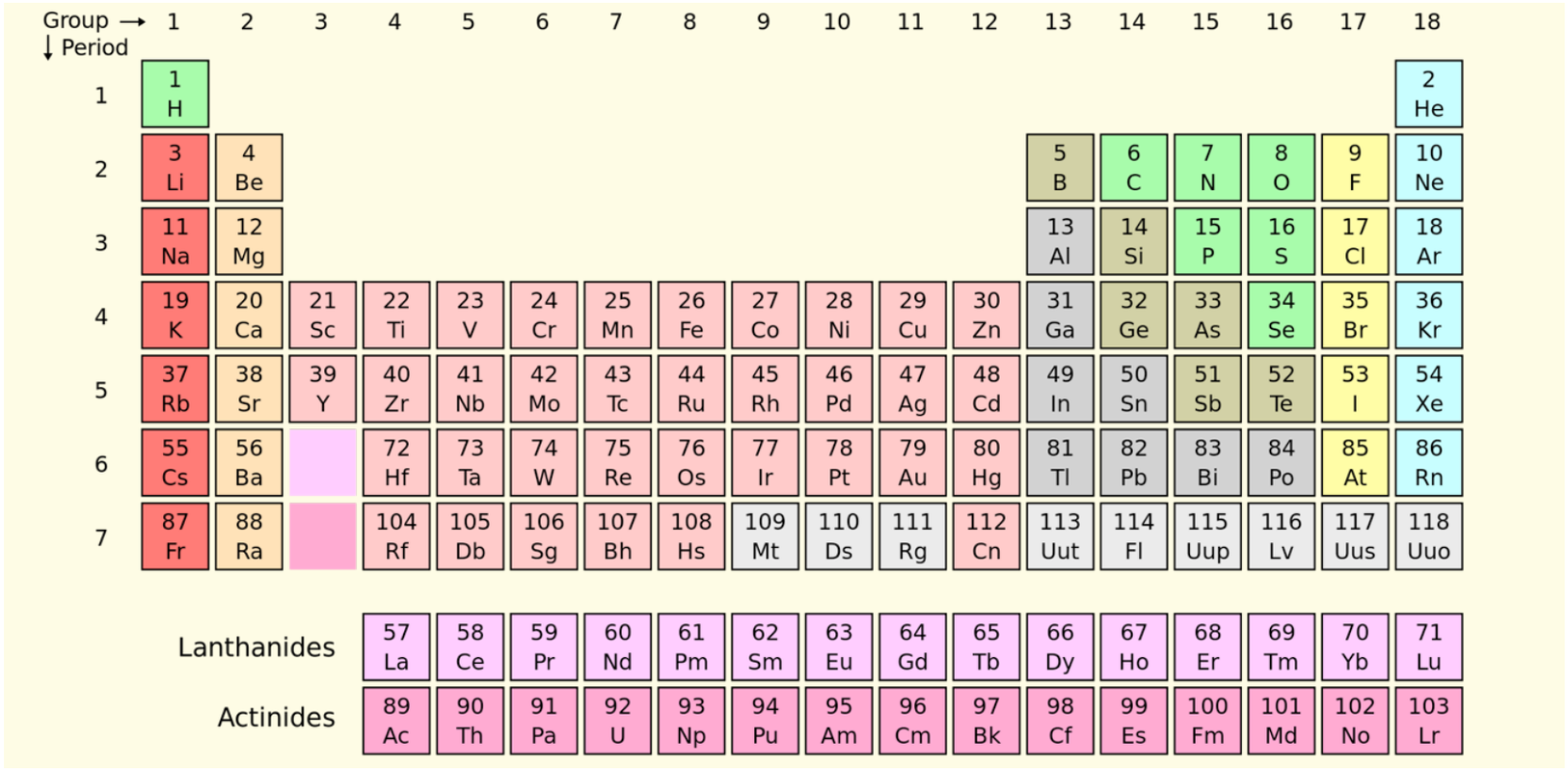

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All-electron

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Efficient (1,000s of atoms), but do not sacrifice accuracy!

Central Decision: How to Discretize the Problem?

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

Kohn, Sham 1965

"Basis set expansion":

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

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

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

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Many good options:

- Plane waves (*VASP*, *abinit*, ...)

$$\varphi_{\underline{k}}(\boldsymbol{r}) = \frac{1}{N}e^{i\underline{k}r}$$

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$$\varphi_{lmn}(\boldsymbol{r}) = \frac{1}{N}x^l y^m z^n e^{-\alpha r^2}$$

- *Many* others: "Augmented plane waves", wavelets, finite elements, numeric atom-centered functions, ...

Our choice!

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

Numeric Atom-Centered Basis Functions: Some Advantages

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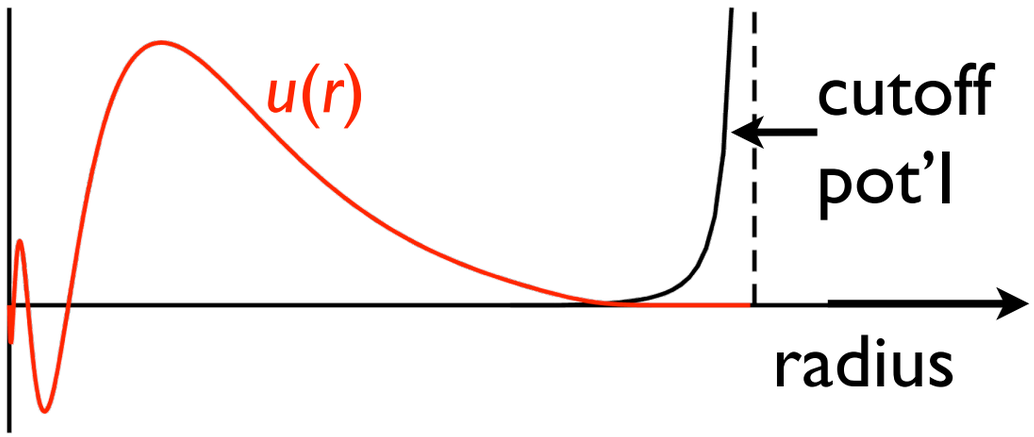

Many popular implementations:
DMol[3] (Delley), FPLO (Eschrig *et al.*)
PLATO (Horsfield *et al.*), ADF, BDF,
PAOs (Siesta, Conquest, OpenMX[2],
Fireball, ...)

Blum, Gehrke, Hanke, Havu, Havu, Ren, Reuter, Scheffler, Computer Physics Communications ***180****, 2175 (2009)*

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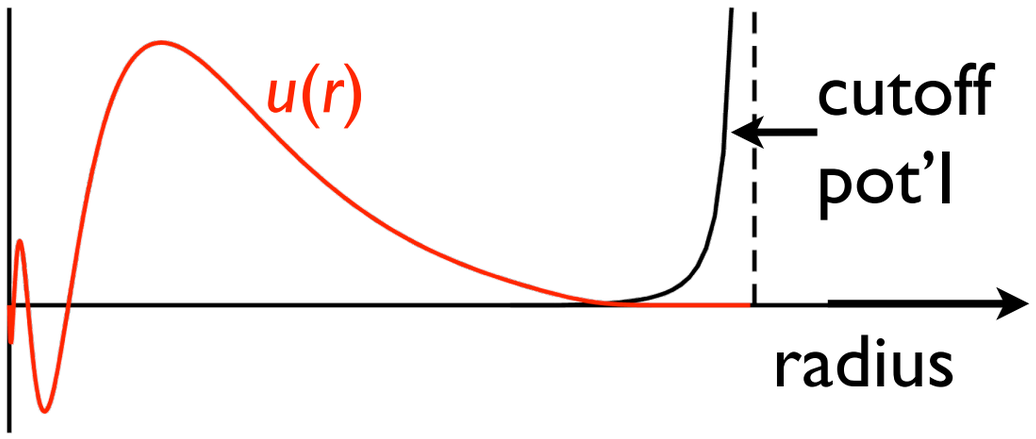

- Flexible shape
- "Naturally" all-electron
- Strictly localizable - *O*(*N*) computational scaling for most expensive steps
- Rather compact basis sets for converged results

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DMol[3] (Delley), FPLO (Eschrig *et al.*)
PLATO (Horsfield *et al.*), ADF, BDF,
PAOs (Siesta, Conquest, OpenMX[2],
Fireball, ...)

We have a basis set library for all elements (1-102), from fast qualitative to meV-converged calculations. (total energy, DFT).

Blum, Gehrke, Hanke, Havu, Havu, Ren, Reuter, Scheffler, Computer Physics Communications ***180****, 2175 (2009)*

Accuracy in Community Wide Benchmark - "Delta Test"

S. Cottenier and coworkers (Ghent University):
https://molmod.ugent.be/deltacodesdft

E(V) for 71 elemental solids - Reference: Full-Potential LAPW (*Wien2k*).

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Comparing Solid State DFT Codes, Basis Sets and Potentials | Center for Molecular Modeling

https molmod.ugent.be/deltacodesdft Reader

Comparing Solid State DFT Codes, Basis Sets and Potentials | Center for Molecular Modeling

Code	Version	Basis	Electron treatment	Δ-value	Authors
WIEN2k	13.1			0 meV/atom	S. Cottenier
FHI-aims	081213	tier2 numerical orbitals	all-electron (relativistic atomic_zora scalar)	0.2 meV/atom	ASE [2]
Exciting	develop version			0.2 meV/atom	Exciting [10]
FHI-aims	081213		2)	0.4 meV/atom	ASE [2]
CASTEP	8.0	plane waves	QTEG CASTEP 8.0	0.5 meV/atom	CASTEP [7]
ABINIT	7.7.3			0.6 meV/atom	F. Jollet and M. Torrent
FHI-aims	081213	tight numerical orbitals	all-electron (relativistic atomic_zora scalar)	0.6 meV/atom	ASE [2]
VASP	5.2.12	plane waves	PAW 2012	0.7 meV/atom	K. Lejaeghere

FHI-aims, standard "tight" defaults:
Δ=0.6 meV

FHI-aims, really tight / *tier* 2 basis sets:
Δ=0.2 meV (!)
Dr. Marcin Dulak, DTU

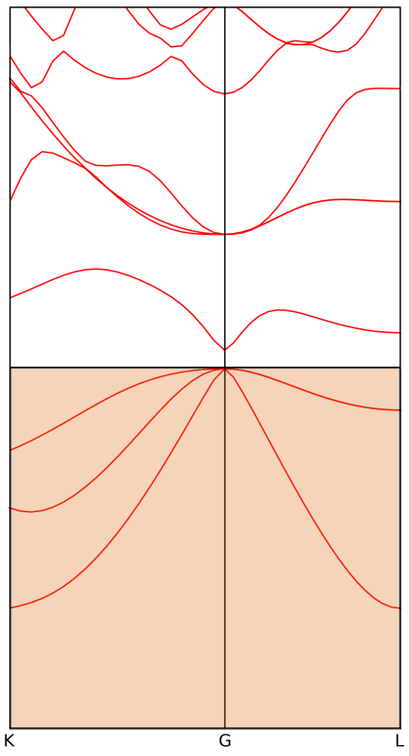
Reproducibility in Density-Functional Calculations of Solids,
K. Lejaeghere, ... 68 coauthors! ..., S. Cottenier,
Science **351**, aad3000 (2016).

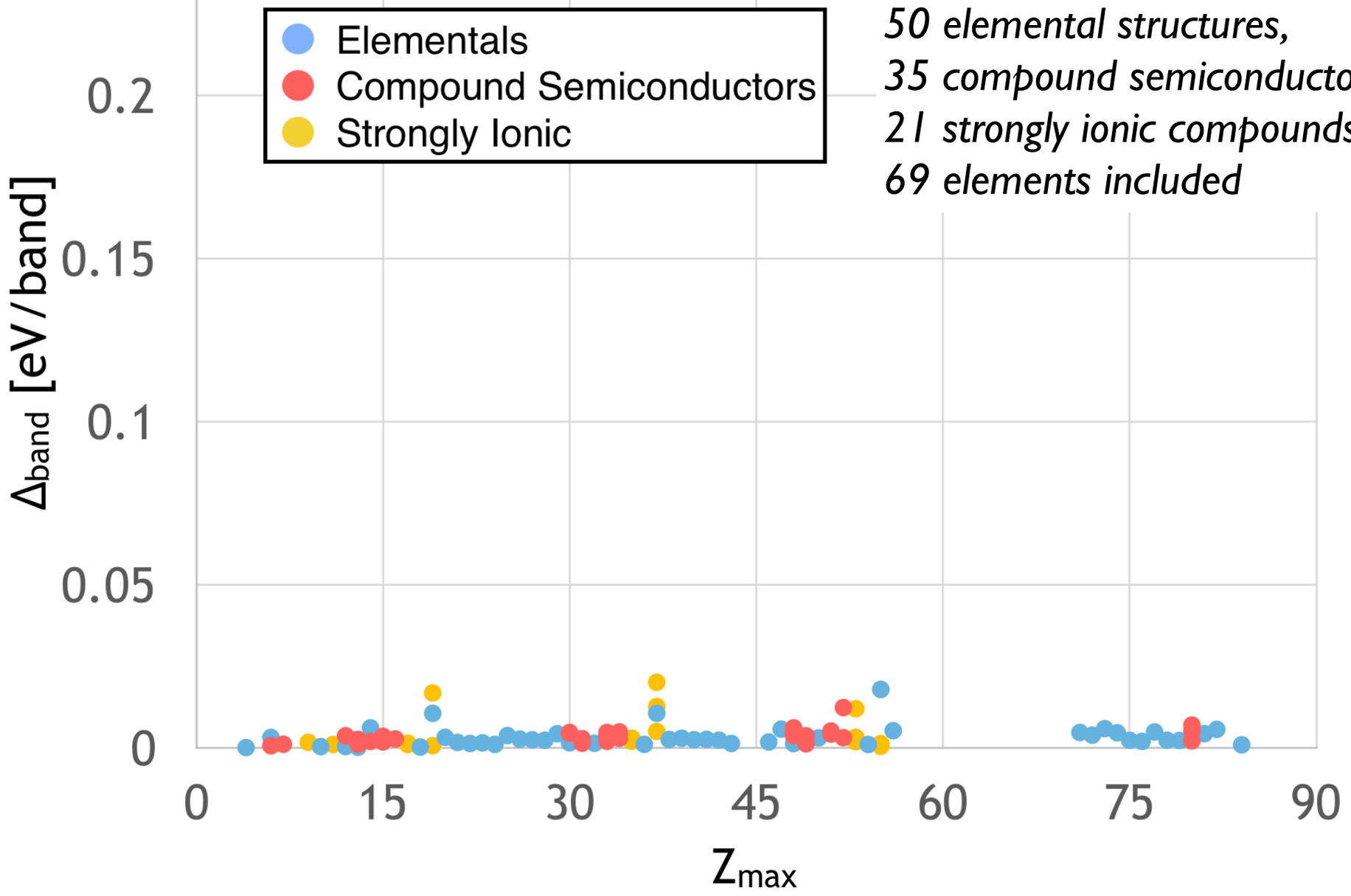
Similar High Precision Achievable for Band Structures

Root-mean-square deviation between calculated band structures:

FHI-aims (*tier 2*) vs. Wien2k, scalar relativistic, valence bands, DFT-PBE

Dr. William Huhn
(Duke Univ.)





50 elemental structures,
35 compound semiconductors,
21 strongly ionic compounds;
69 elements included

All-Electron Accuracy for Large Systems: FHI-aims

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

- Accurate, efficient quantum mechanics for molecules, materials
- Numerical Foundation: Numeric atom-centered basis functions
  Seamless from "light" to basis-converged results,
  from light to heavy elements
- Non-periodic and periodic structure models, same framework
- Density Functional Theory (semilocal, global and range-separated hybrid functionals, van der Waals corrections)
- Beyond DFT (non-periodic): RPA, *GW*, MP2, TD-LDA, ...
- Scalable (1,000s of atoms on 1(00),000s of CPU cores)
- Properties (charged and neutral excitations, IR spectra, transport, dielectric functions, dynamics & transition states, ...)

~100 contributors to date, over 100 licensing groups.
Active development in Berlin, Duke, Munich, Hefei,
Helsinki, London, Argonne, ...
New stable release "160328"

Blum, Gehrke, Hanke, Havu, Havu, Ren, Reuter, Scheffler, Computer Physics Communications ***180****, 2175(2009)*
Ren, Rinke, Blum, Wieferink, Tkatchenko, Sanfilippo, Reuter, Scheffler, New J. Phys. ***14****, 053020 (2012)*

... But How to Push an All-Electron Approach to Large Systems?

1. Kohn-Sham DFT Eigenvalue Problem ($O(N^3)$)

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

2. Exact Exchange & Hybrid Functionals

$$E_{\mathrm{x}}^{\mathrm{HF}} = \frac{1}{2}\sum_{ij\sigma} D_{ij}^{\sigma} K_{ij}^{\sigma} = \frac{1}{2}\sum_{ijkl} D_{ij}^{\sigma} D_{kl}^{\sigma} (ik|lj)$$

3. Many-Body Perturbation Theory "Beyond DFT"

$$\Sigma_{\sigma}^{GW}(\mathbf{r},\mathbf{r}',\epsilon) = \frac{i}{2\pi}\int d\epsilon' \left[G_{\sigma}(\mathbf{r},\mathbf{r}',\epsilon+\epsilon') W(\mathbf{r},\mathbf{r}',\epsilon') e^{i\eta\epsilon'} \right]$$

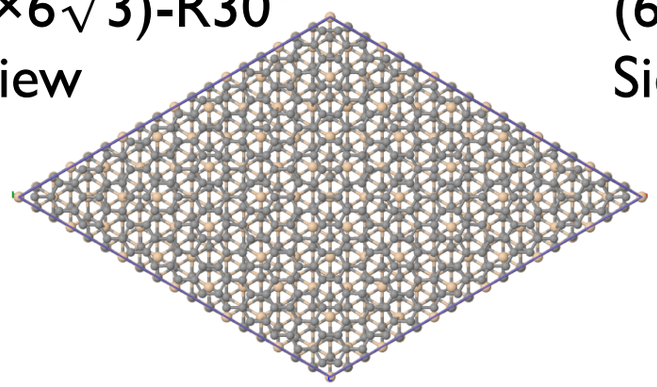
Cost

Accuracy?

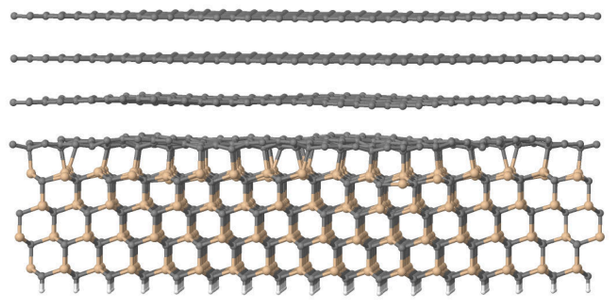
Difficulty!

Scalability: 3-Layer Graphene on 3C-SiC(0001)

$(6\sqrt{3}\times6\sqrt{3})$-R30°
Top View



$(6\sqrt{3}\times6\sqrt{3})$-R30°, 3-layer graphene
Side View



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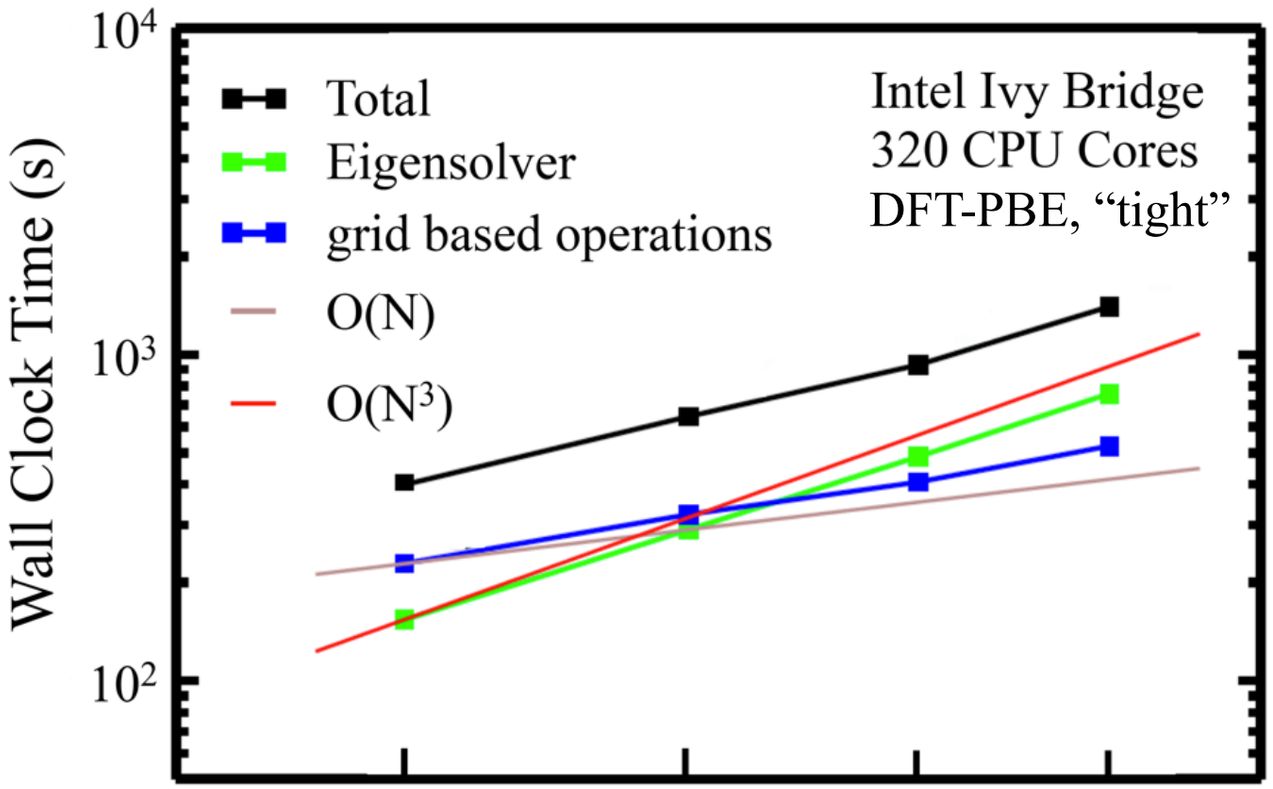

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N_{at}	1310	1648	1986	2324

*Structure: Nemec et al., PRL **111**, 065502 (2013).*

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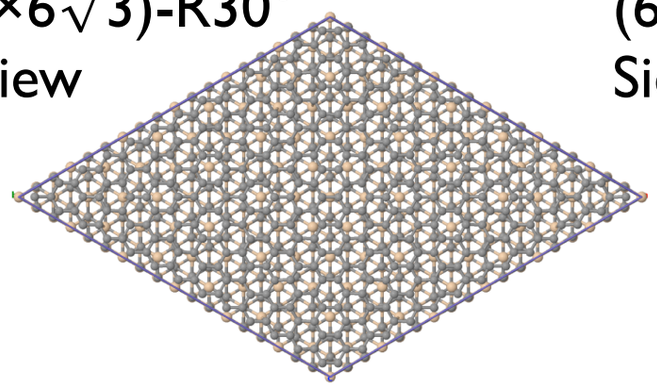

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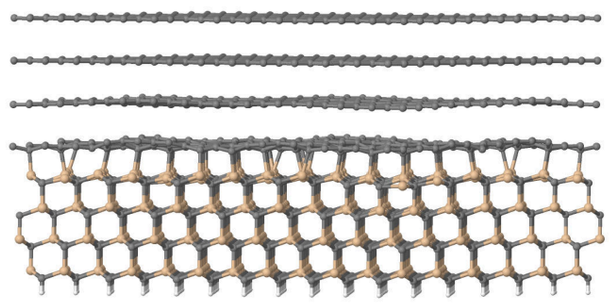

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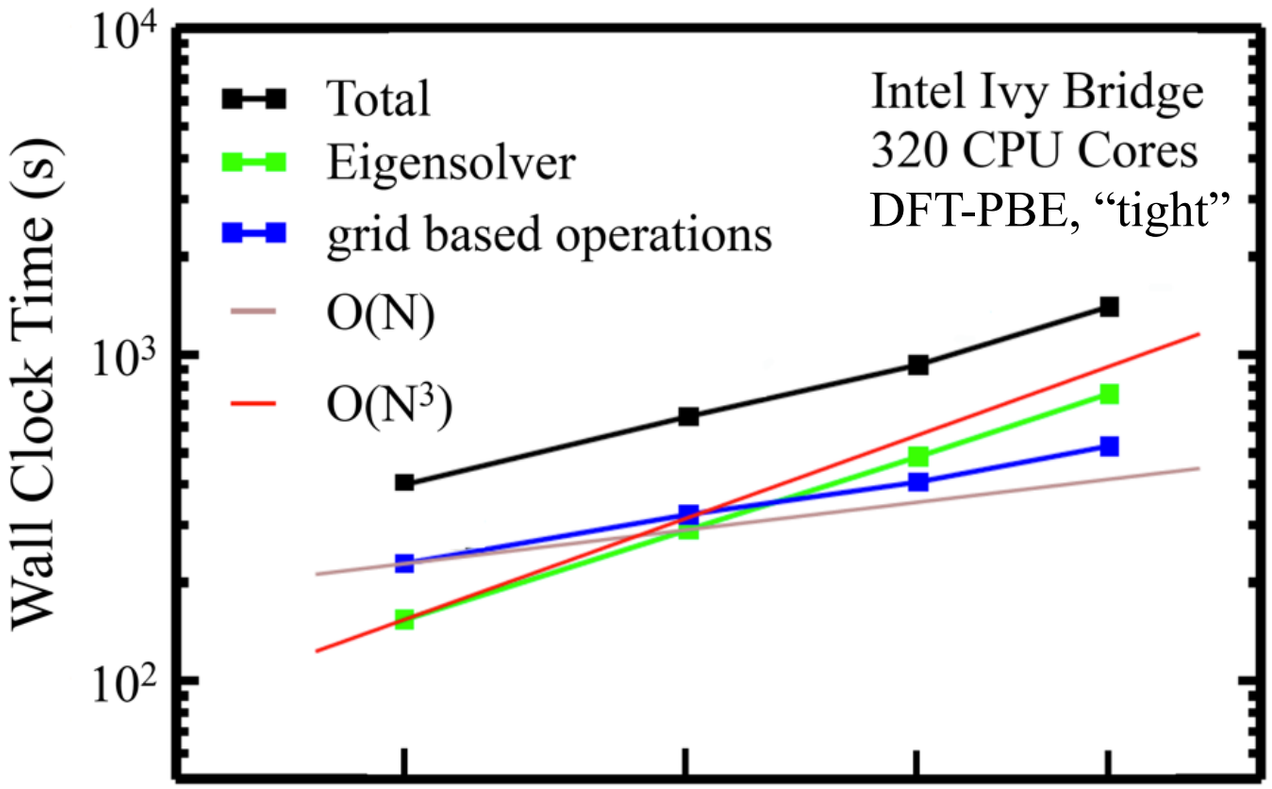

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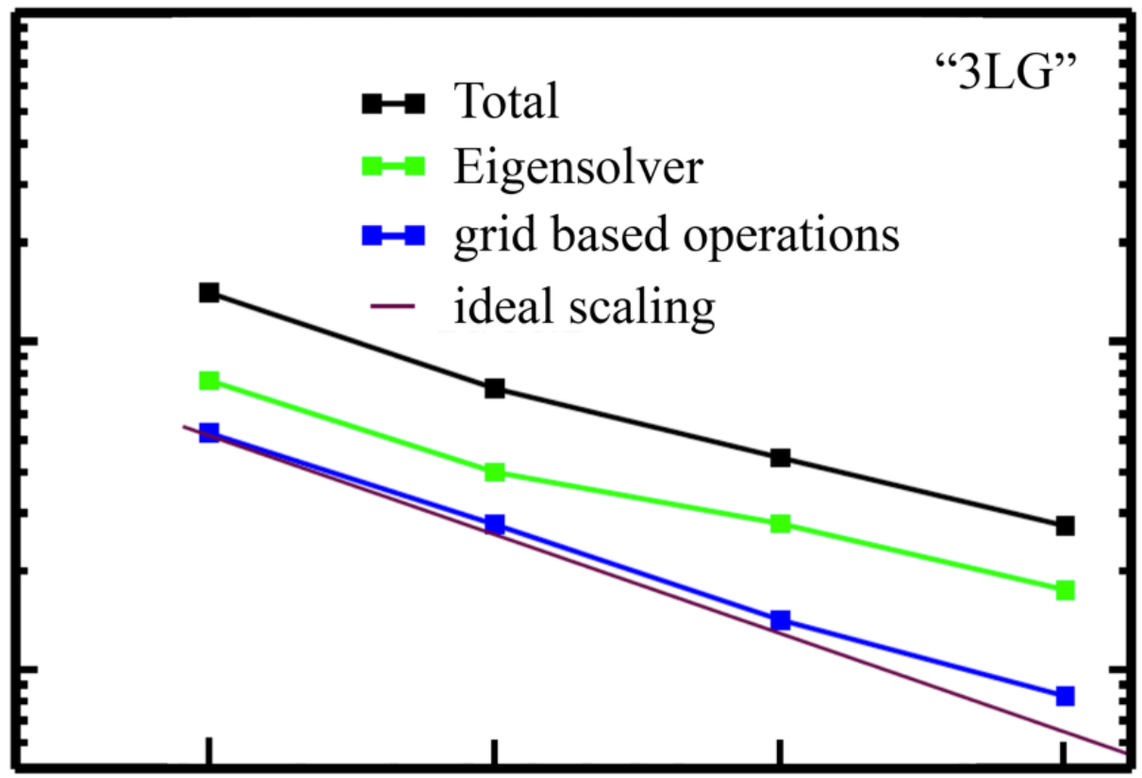

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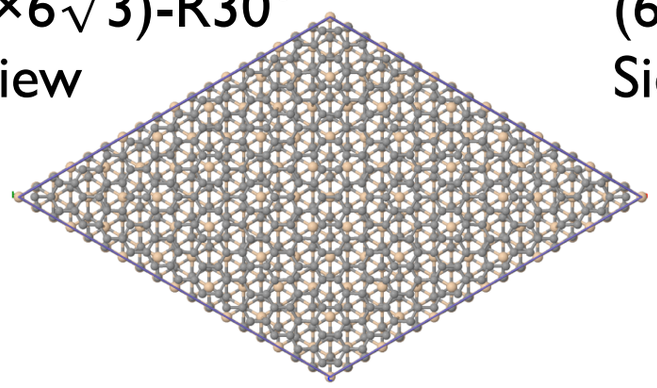

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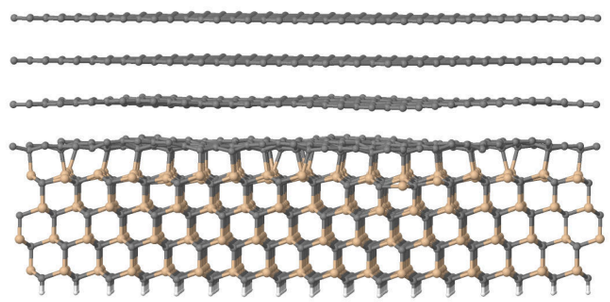
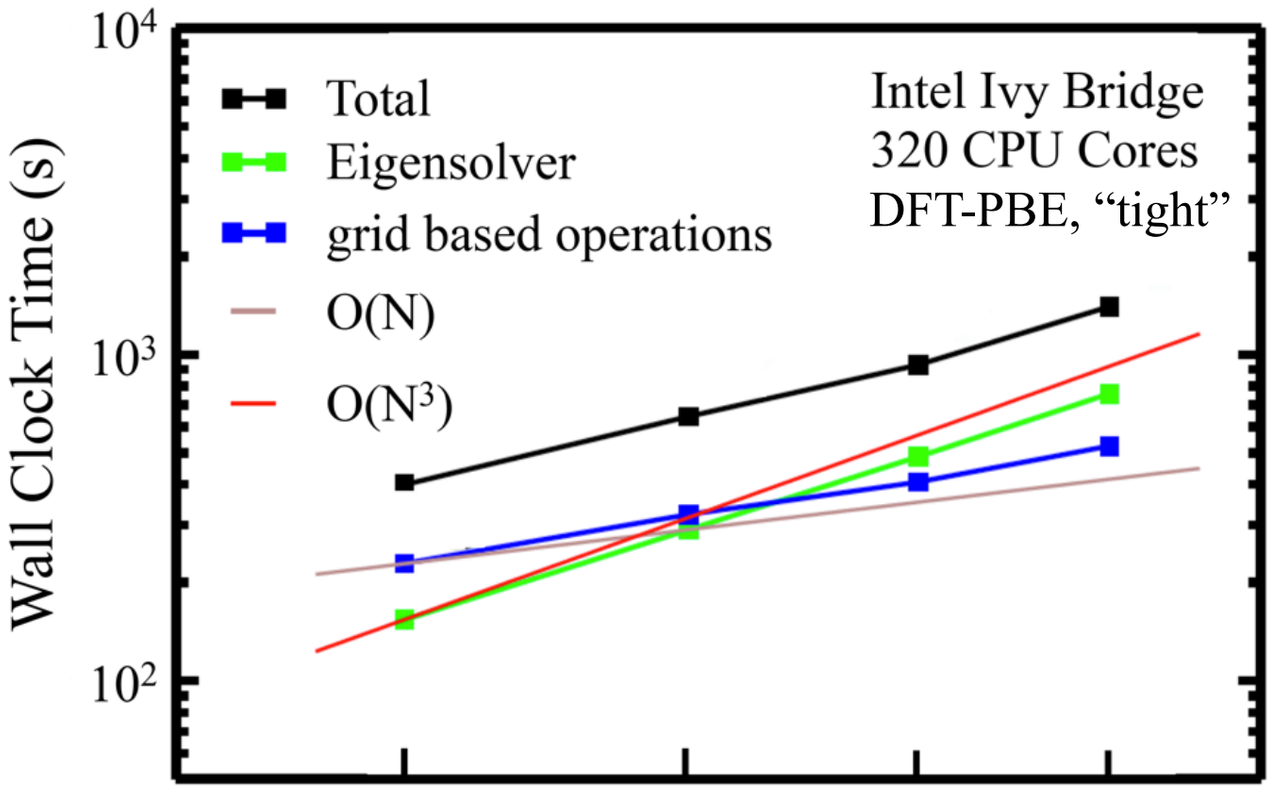


...

Open Source
Scalable Eigensolver:
ELPA
http://elpa.rzg.mpg.de



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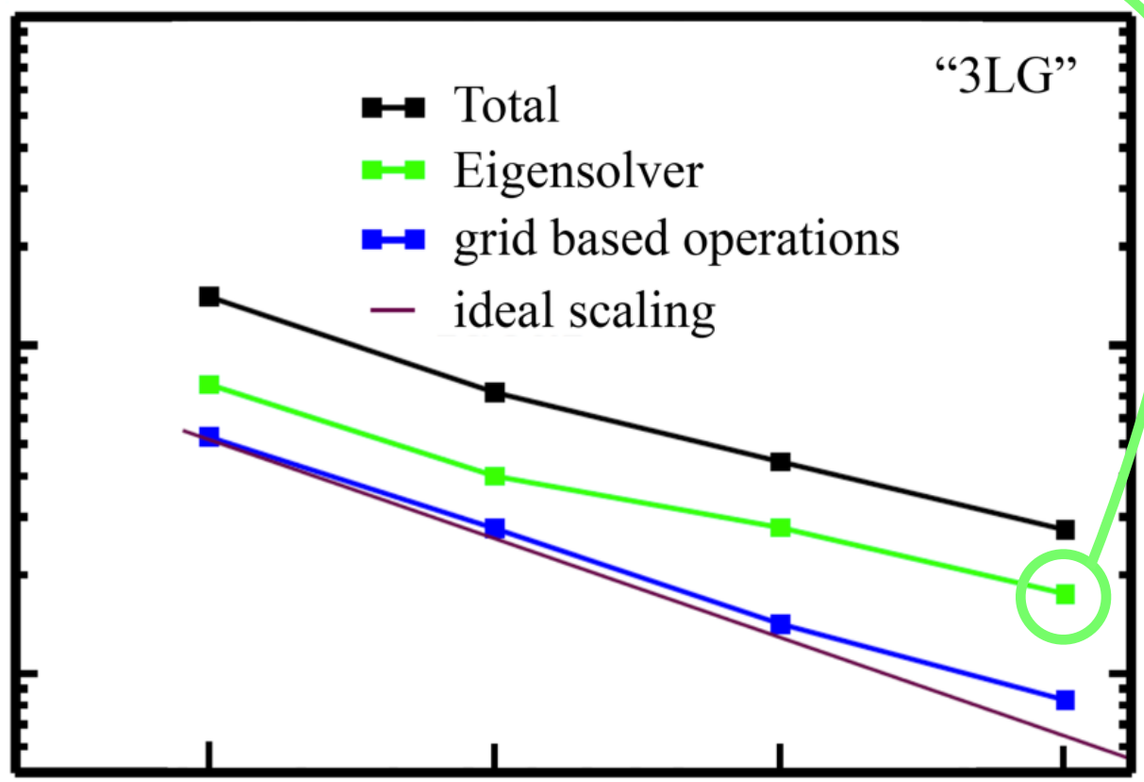

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Parallel Eigenvalue Solvers - the Problem

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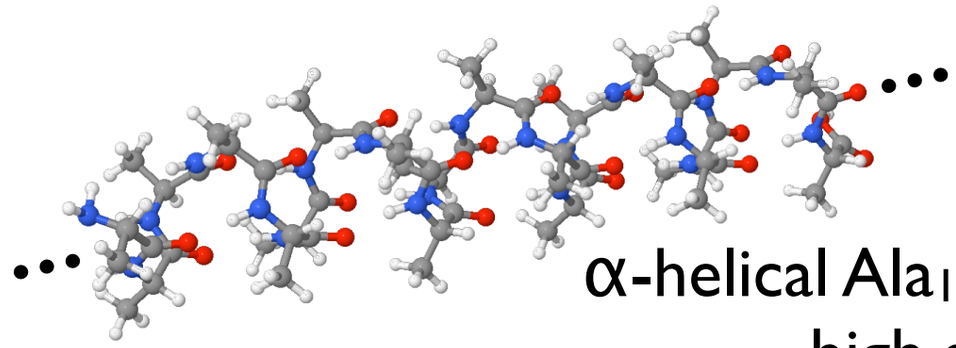

α-helical Ala_{100} (1000 atoms),
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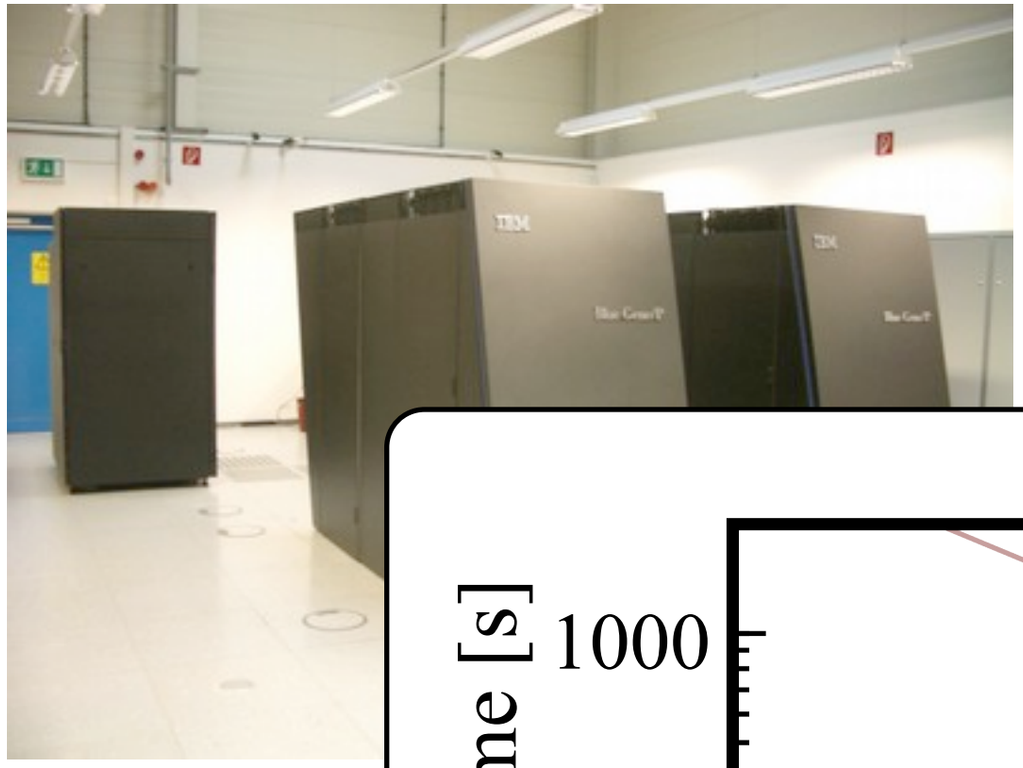

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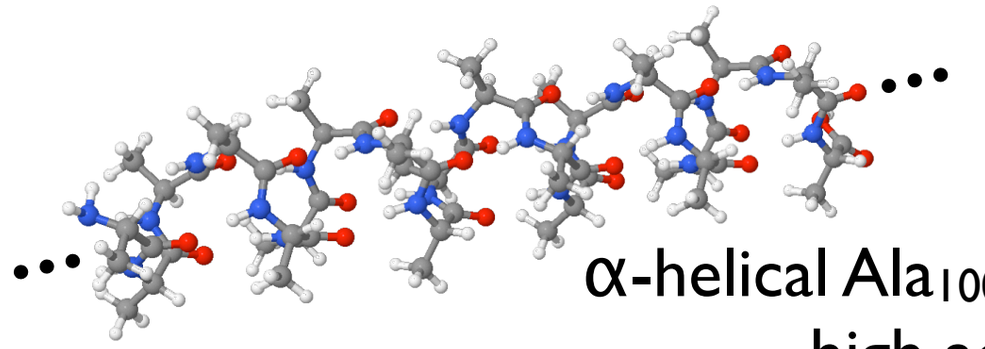

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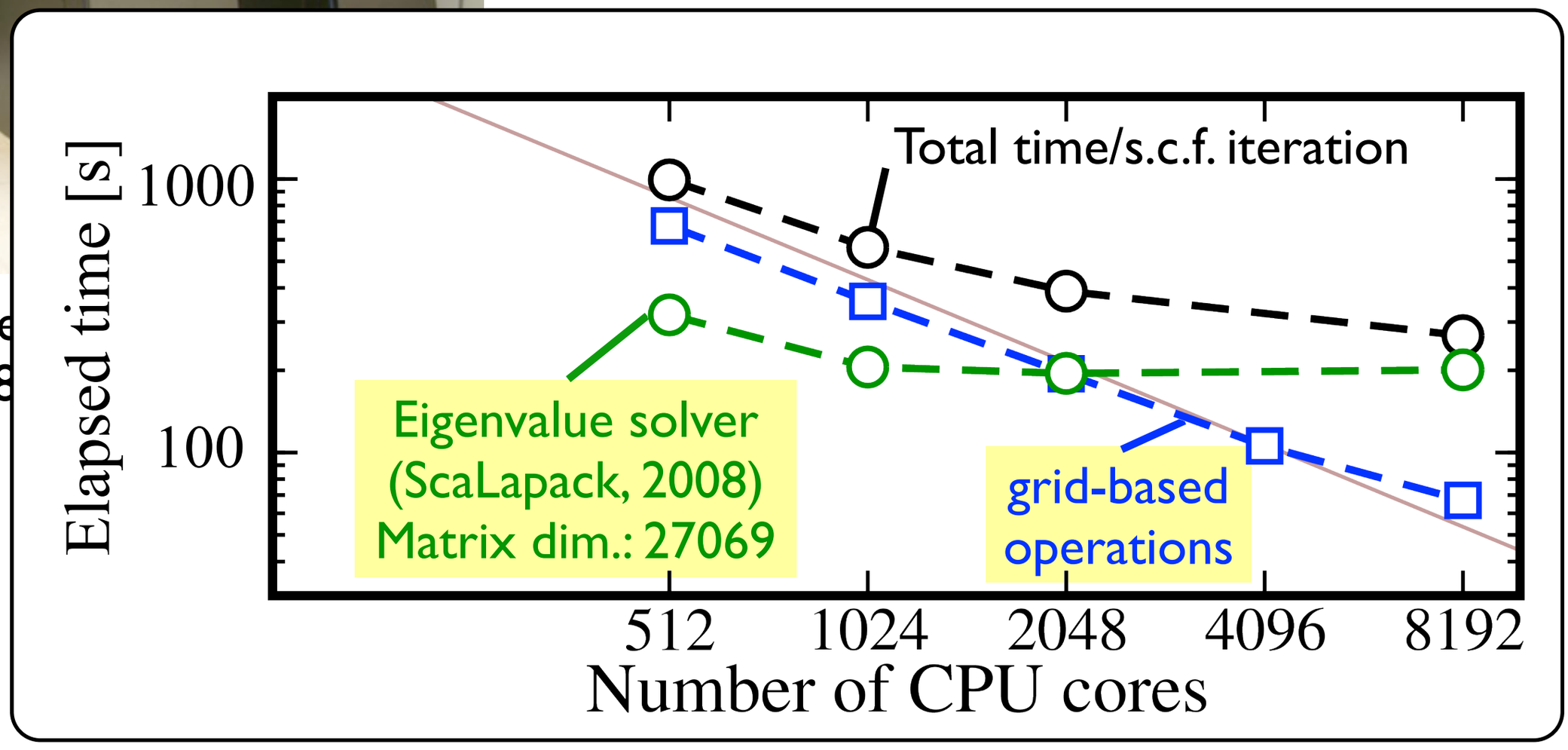
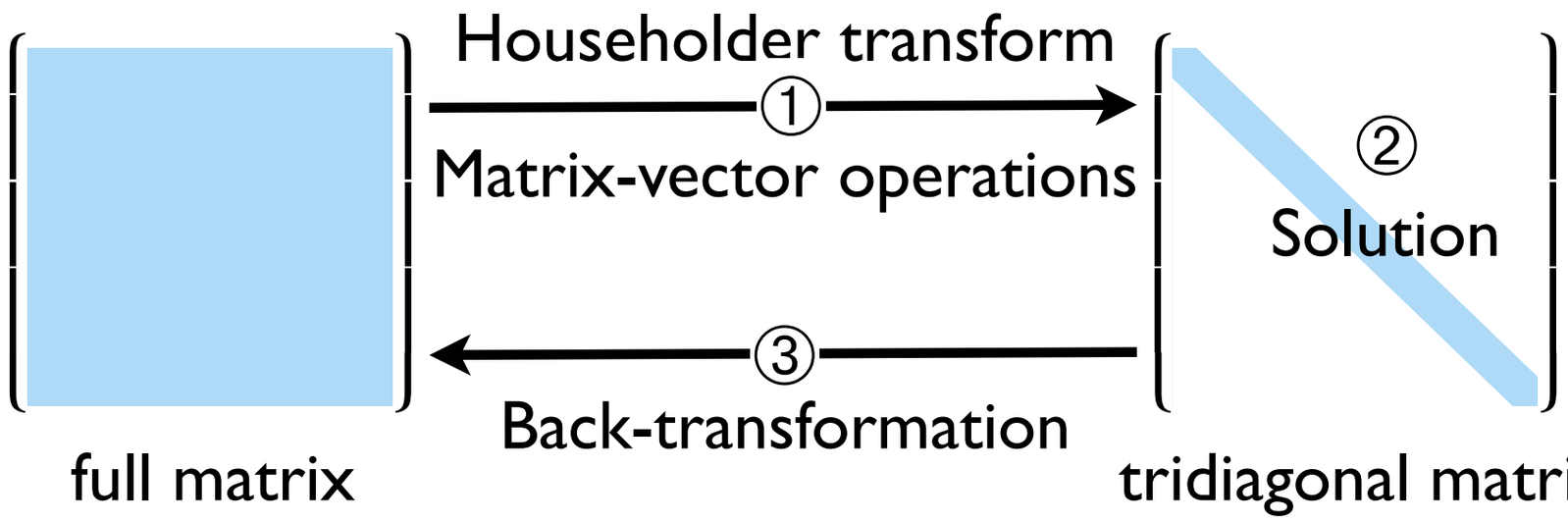


Bottleneck: Tridiagonalization

"Conventional" reduction:



Key Step in ELPA: Two-Step MPI-Parallel Tridiagonalization

Two-stage reduction algorithm, ELPA:

Larger fraction of efficient matrix-matrix operations

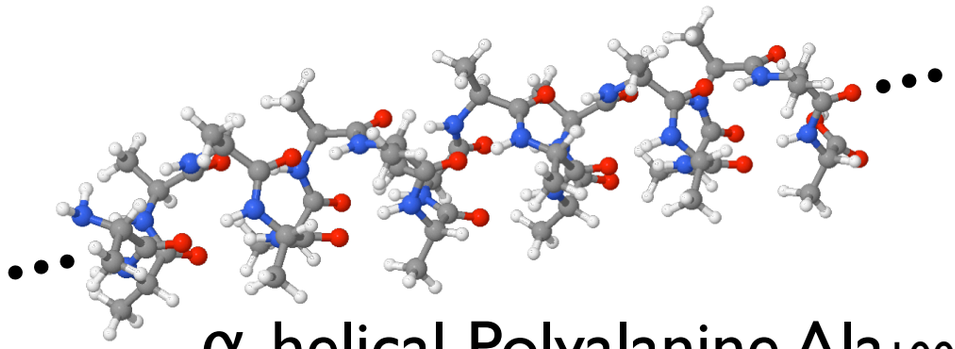
Efficient compute kernels for added backtransform step ④

Note: Hard to beat dense linear algebra for small to midsized problems, many EVs

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).

ELPA, Two-Step Solver



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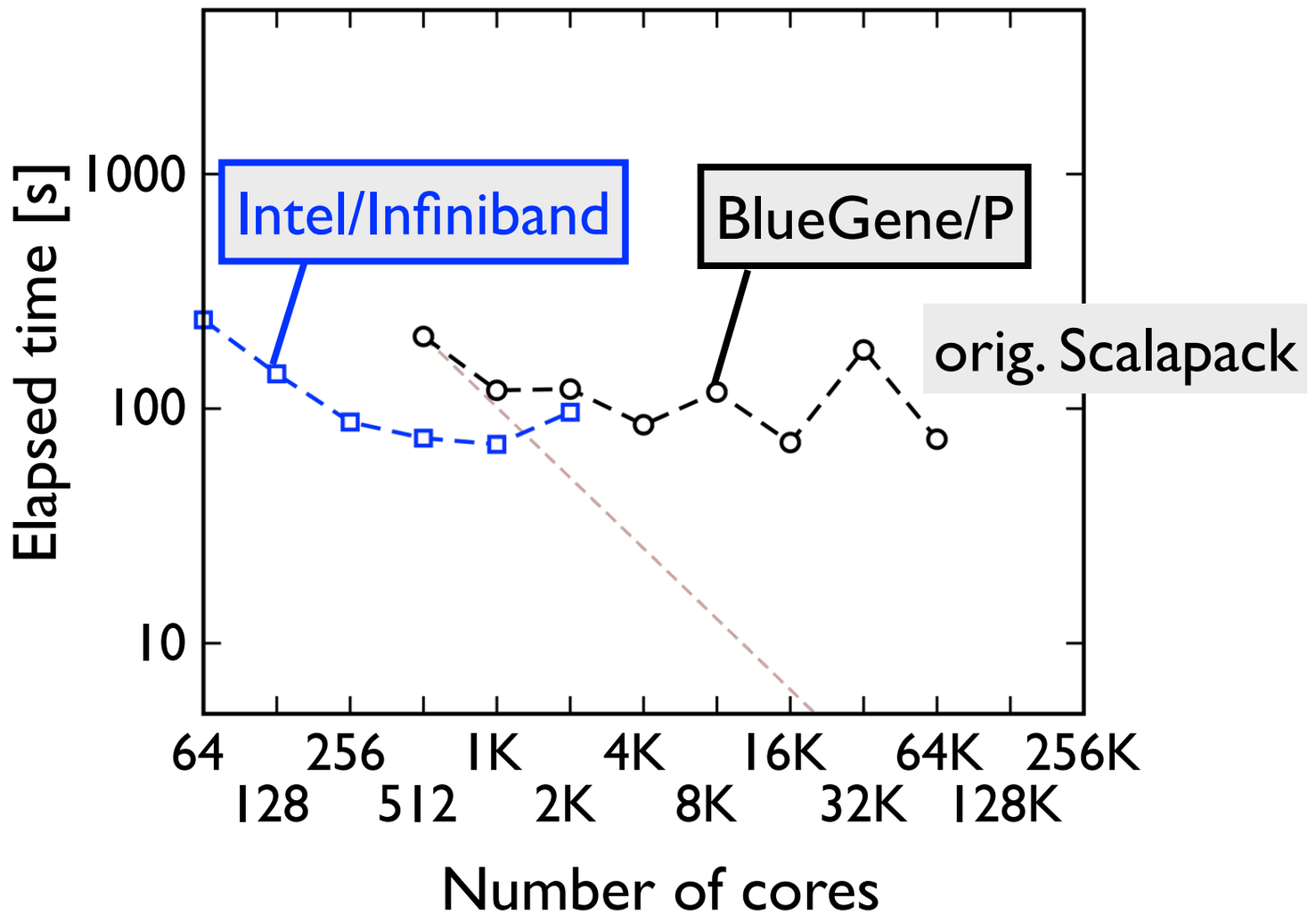

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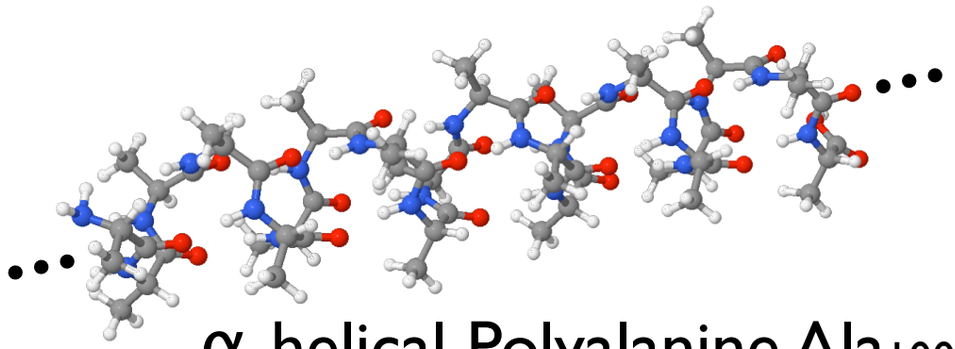

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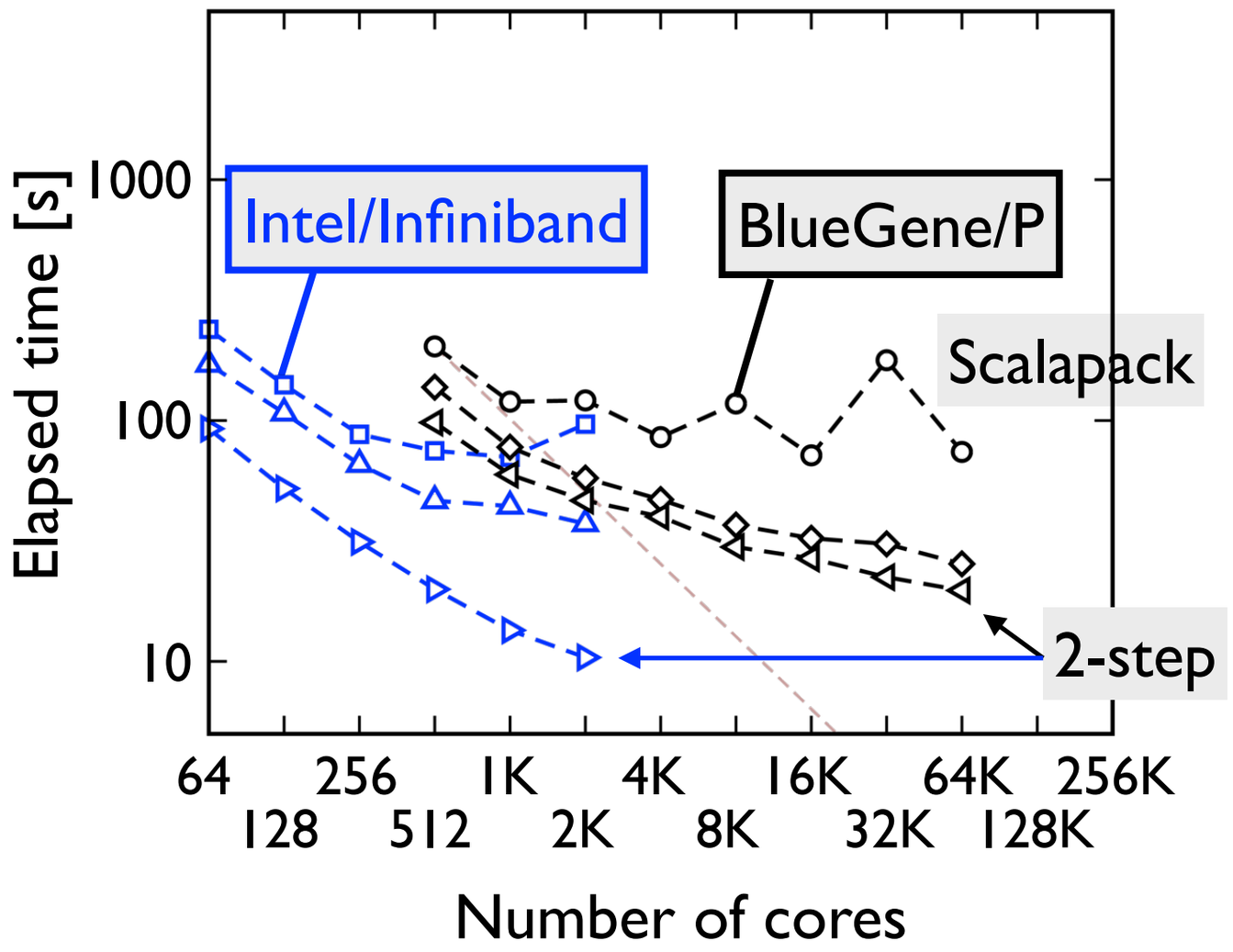

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   → *new hardware? (GPU, MIC)*

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ELSI: Solving *or Circumventing* the Eigenvalue Problem

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& for "any" code?

... and many other "stakeholders" from the community

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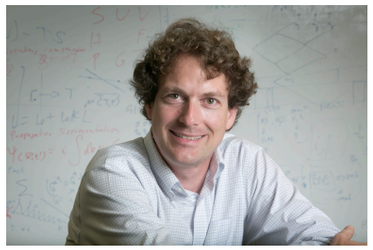
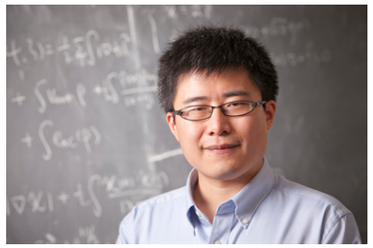
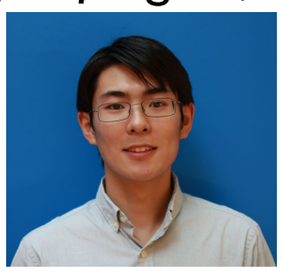


VB, Duke

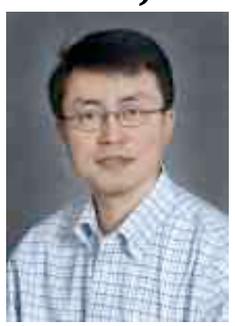


Jianfeng Lu, Duke

Fabiano Corsetti, London



Lin Lin, Berkeley

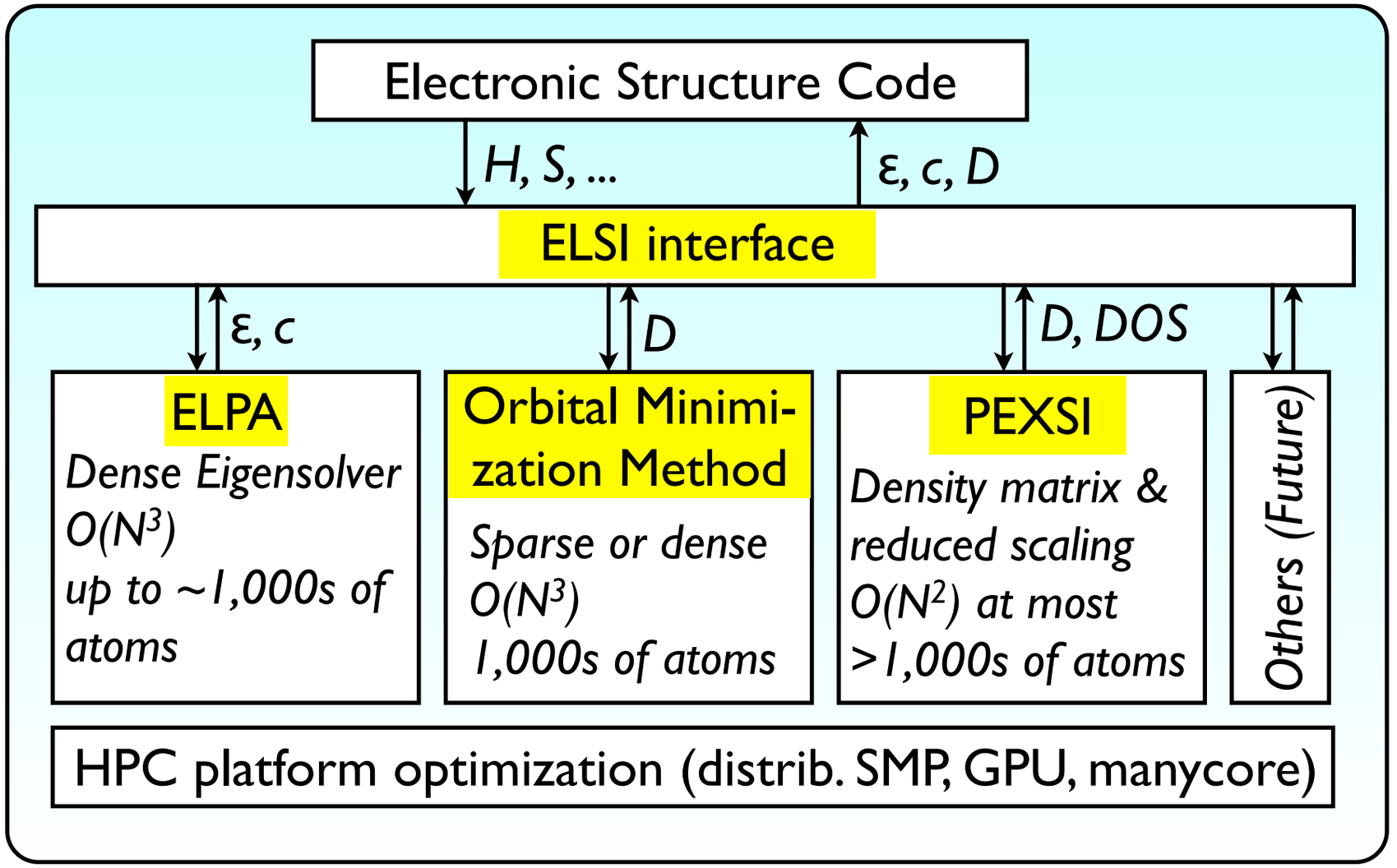


Chao Yang, LBL

Alvaro Vazquez-Mayagoitia, ANL

... and many other "stakeholders" from the community

Work in Progress:
"ELSI" - Electronic Structure Infrastructure (NSF-SI2)



http://elsi-interchange.org

... But How to Push an All-Electron Approach to Large Systems?

1. Kohn-Sham DFT Eigenvalue Problem ($O(N^3)$)

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

2. Exact Exchange & Hybrid Functionals

$$E_{\mathrm{x}}^{\mathrm{HF}} = \frac{1}{2}\sum_{ij\sigma} D_{ij}^{\sigma} K_{ij}^{\sigma} = \frac{1}{2}\sum_{ijkl} D_{ij}^{\sigma} D_{kl}^{\sigma} (ik|lj)$$

3. Many-Body Perturbation Theory "Beyond DFT"

$$\Sigma_{\sigma}^{GW}(\mathbf{r},\mathbf{r}',\epsilon) = \frac{i}{2\pi}\int d\epsilon' \left[G_{\sigma}(\mathbf{r},\mathbf{r}',\epsilon+\epsilon') W(\mathbf{r},\mathbf{r}',\epsilon') e^{i\eta\epsilon'} \right]$$

Cost

Accuracy?

Difficulty!

Beyond DFT-LDA/GGA: Two-Electron Integrals

Common bottleneck: Two-electron interactions, e.g.:

$$\int d^3r d^3r' \phi_i(r)\phi_j(r') \frac{1}{|r-r'|} \phi_k(r')\phi_l(r)$$

Ren, Rinke, Blum, Wieferink, Tkatchenko, Sanfilippo, Reuter, Scheffler, New J. Phys. ***14****, 053020 (2012)*

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Early Solution: "Resolution of the identity"

[Boys and Shavitt (1950s), Whitten (1974), Dunlap et al. (1979), Vahtras et al. (1993), many others]

1. Expand pair products in smaller auxiliary basis set $\{P_\mu\}$

$$\varphi_i(\boldsymbol{r})\varphi_j(\boldsymbol{r}) = \sum_\mu C_{ij}^\mu P_\mu(\boldsymbol{r})$$

2. Use "Coulomb metric" *V* to cancel linear error terms

$$C_{ij}^\mu = \sum_\nu (ij|\nu)V_{\nu\mu}^{-1}$$

$$(ij|\nu) = \int d^3r d^3r' \frac{\varphi_i(\boldsymbol{r})\varphi_j(\boldsymbol{r})P_\nu(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

→ The rest is matrix algebra - works with NAO basis sets!
Hartree-Fock, hybrid functionals, MP2, *GW*, RPA, LR-TDLDA, ...

Ren, Rinke, Blum, Wieferink, Tkatchenko, Sanfilippo, Reuter, Scheffler, New J. Phys. ***14****, 053020 (2012)*

Localized "Resolution of Identity" (RI) for Two-Electron Terms

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Ihrig, Wieferink, Zhang, Ropo, Ren, Rinke, Scheffler, Blum, New J. Phys. ***17****, 093020 (2015)*

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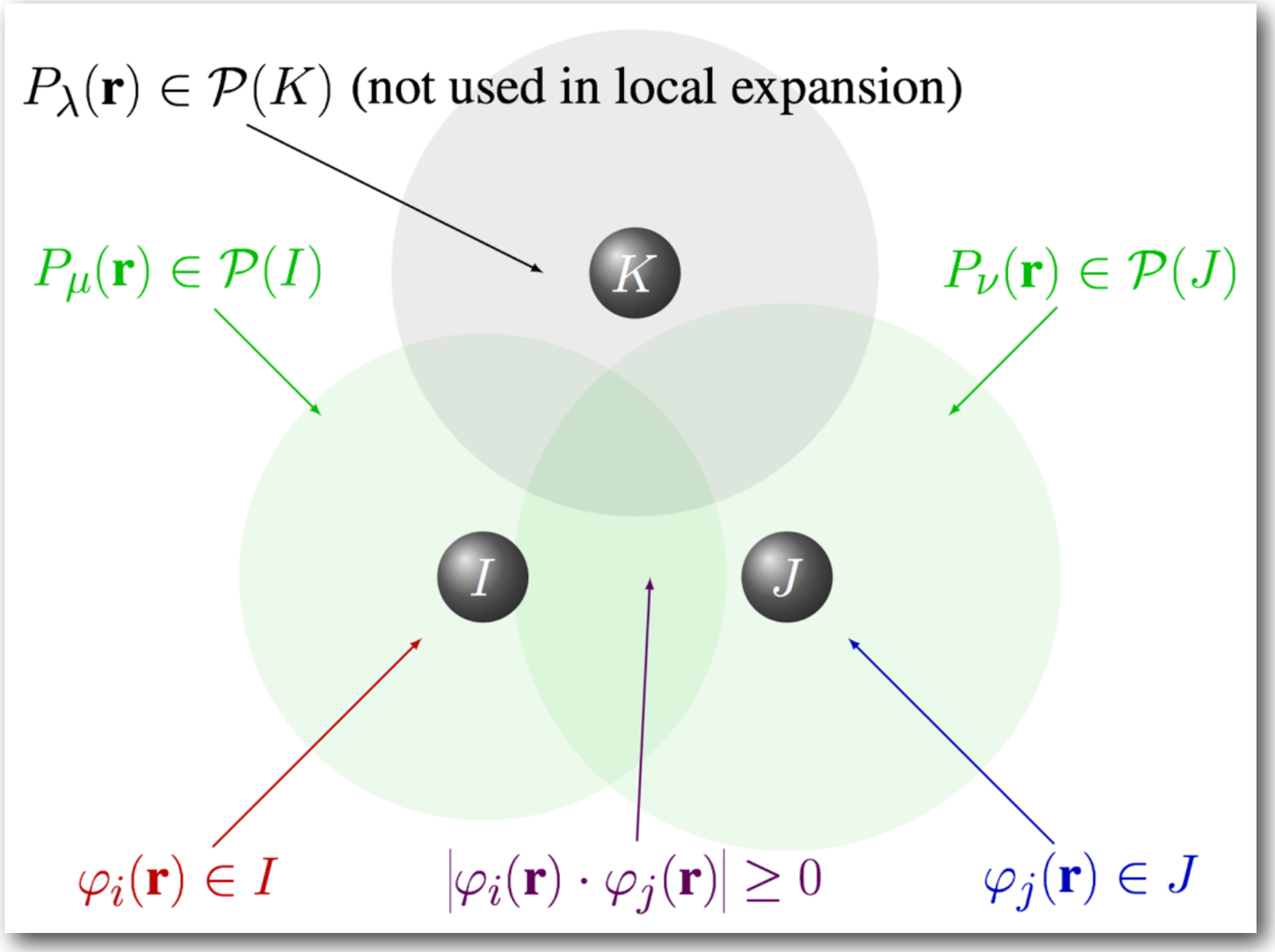
Solution: For each C_{ij}^{μ}, restrict μ only to atoms I and J at which i and j are centered!



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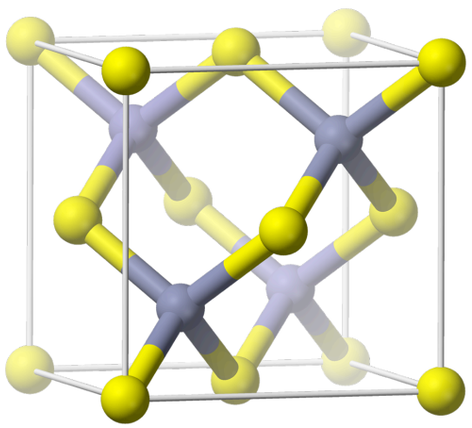
Hybrid Functionals: Scalability, Large Systems

Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler, Comp. Phys. Commun. ***192****, 60-69 (2015).*

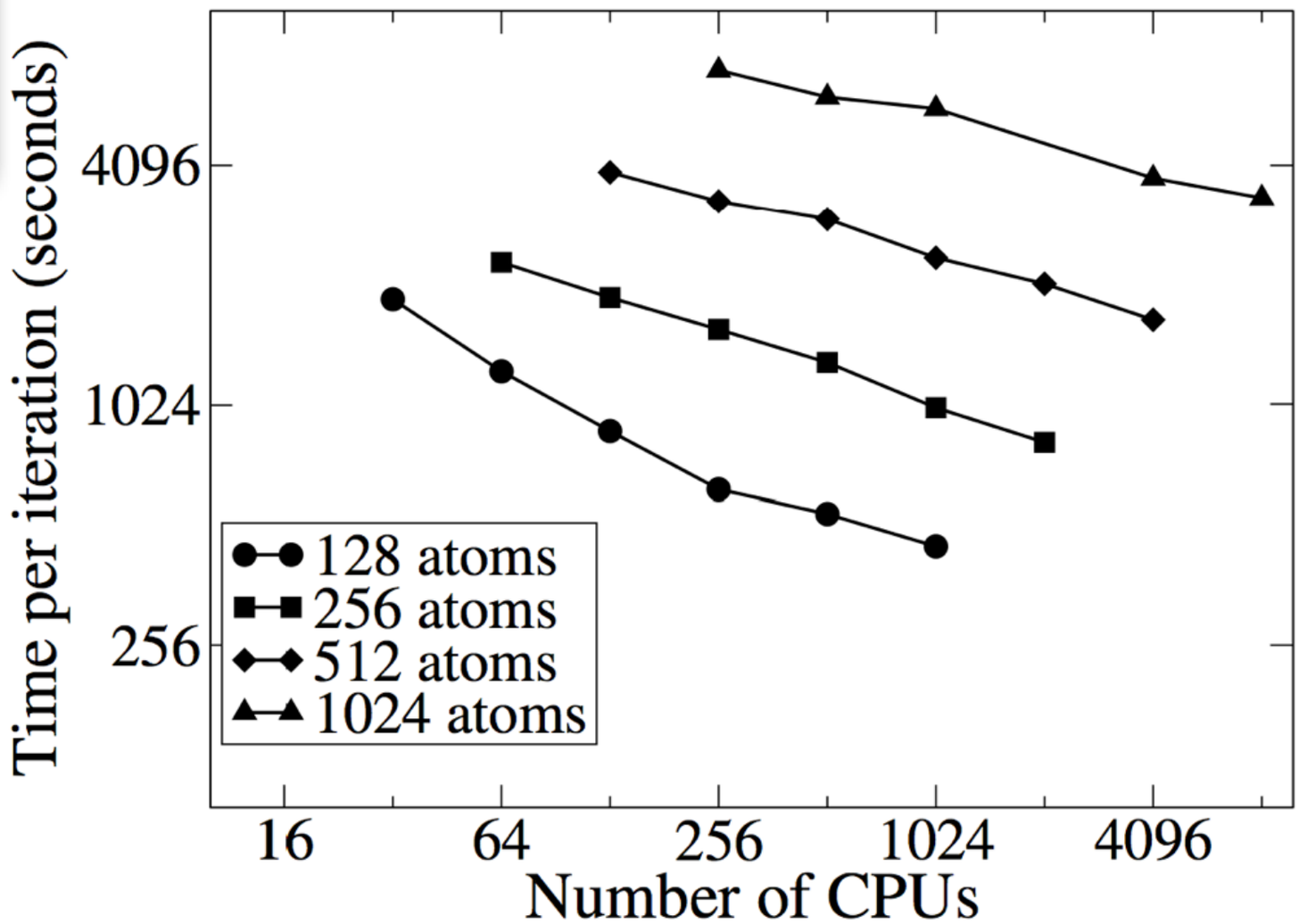
O(N) scaling implementation, localized resolution of identity.

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



Zincblende GaAs

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



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Scaling Limitations for Many-Body Theory: *GW*

G_0W_0: Widely used to obtain accurate quasiparticle energies (molecules and materials)

Central: Self-Energy

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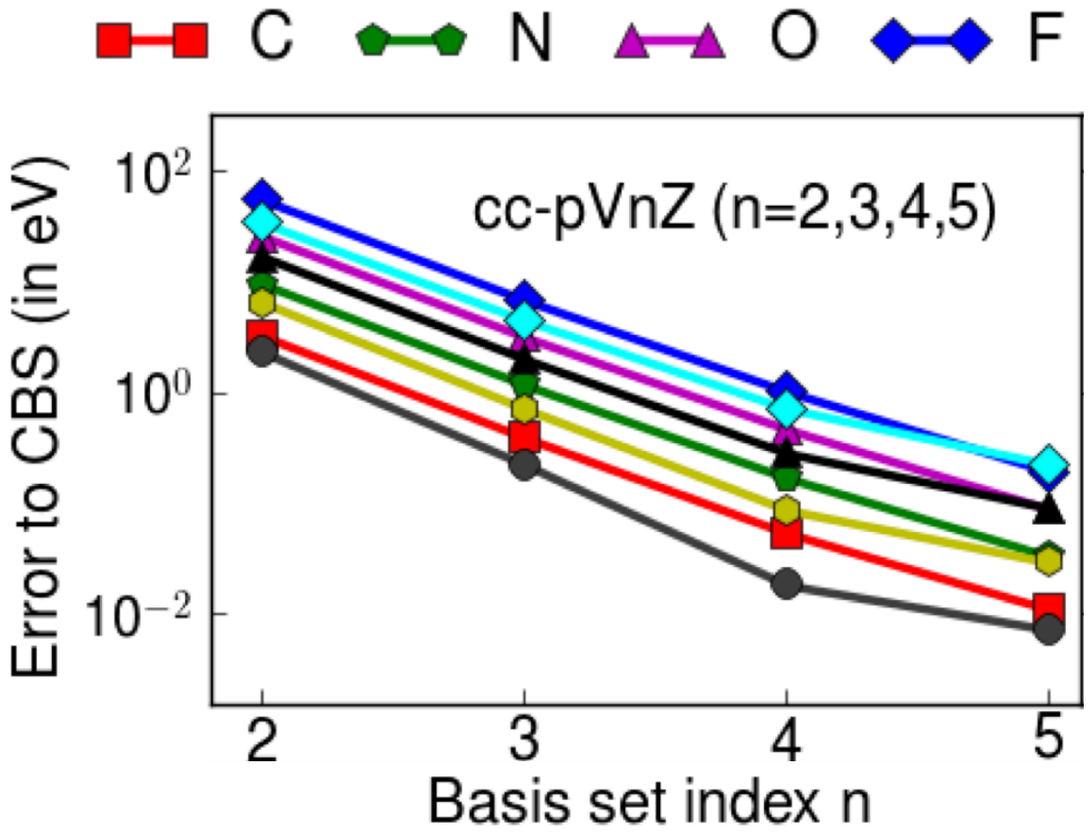
However, G_0, W_0 not easy to converge -
known by different terminologies in different communities:

- "Slow-converging sums over states"
- "Slow convergence with basis set size"
- "Slow convergence of the electron-electron cusp" (Quantum Chemistry)

↔ Large basis set requirement *and* formal $O(N^4)$ scaling: Doubly challenging.

Result: Notoriously Tedious Convergence (Any Basis Set!)

RPA@PBE Total Energy Convergence of Free Atoms:

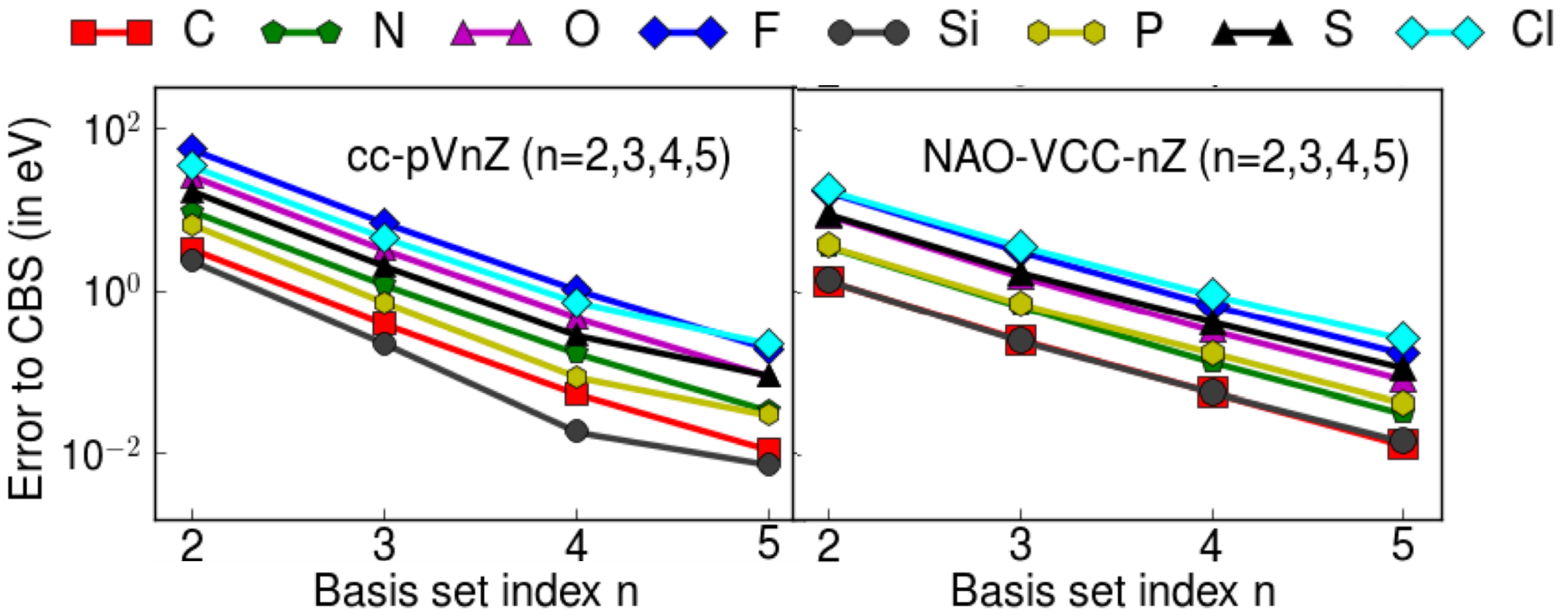


Known issue in quantum chemistry.
Light elements: Correlation consistent Gaussian basis sets (Dunning) + "complete basis set" (CBS) extrapolation

Igor Ying Zhang, Xinguo Ren, Patrick Rinke, Volker Blum, and Matthias Scheffler, New Journal of Physics ***15****, 123033 (2013).*

Result: Notoriously Tedious Convergence (Any Basis Set!)

RPA@PBE Total Energy Convergence of Free Atoms:

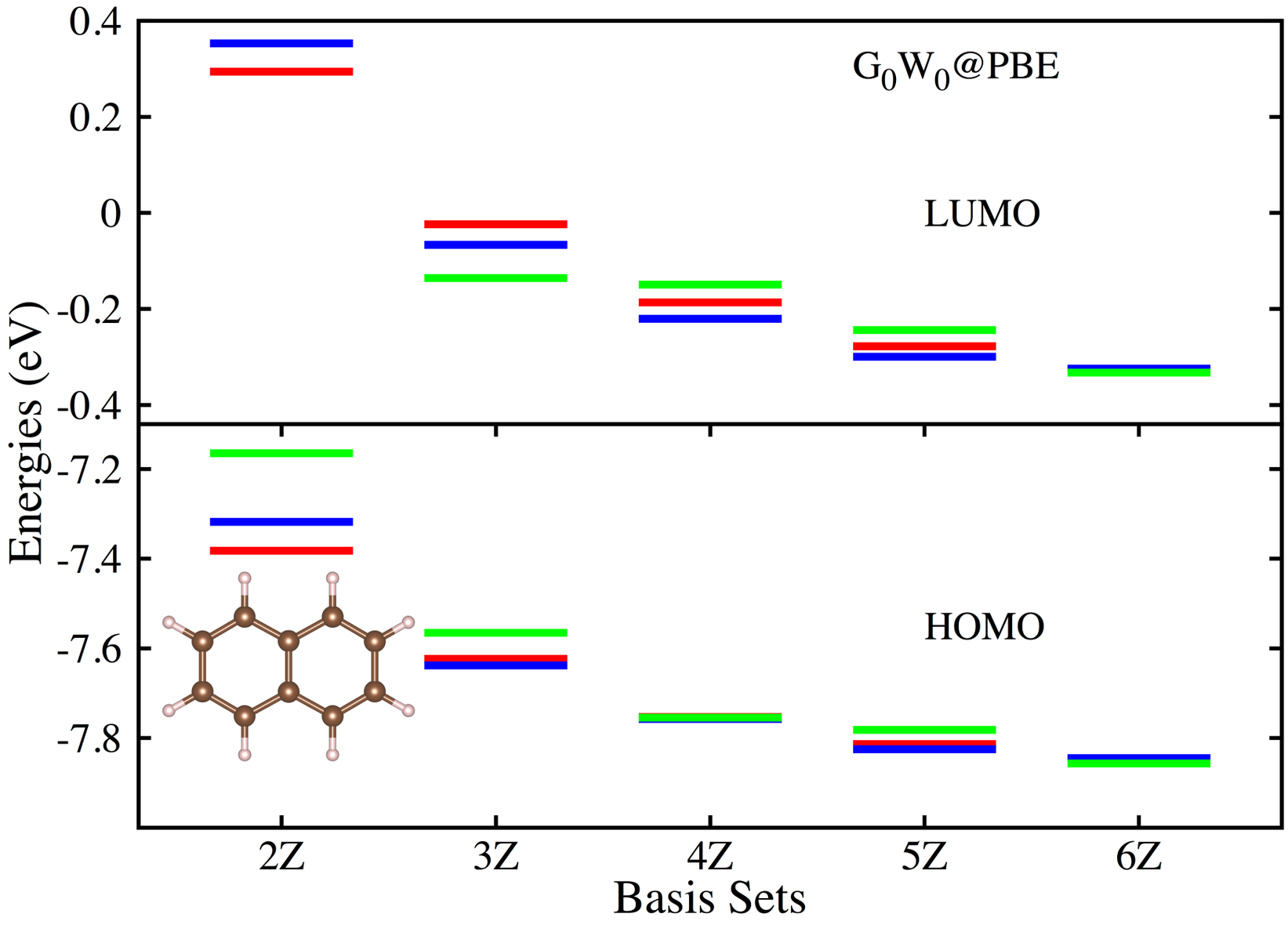


New NAO-VCC-nZ basis sets (H-Ar):
More systematic convergence of unoccupied state sums*
**not a problem in occupied-state based DFT*

Igor Ying Zhang, Xinguo Ren, Patrick Rinke, Volker Blum, and Matthias Scheffler, New Journal of Physics ***15****, 123033 (2013).*

Basis Set Extrapolation for G_0W_0?

Example: Naphthalene, G_0W_0@PBE HOMO / LUMO



NAO-VCC-nZ (NAO) aug-CC-pVnZ (AUG) CC-pVnZ (CC)

Tong Zhu

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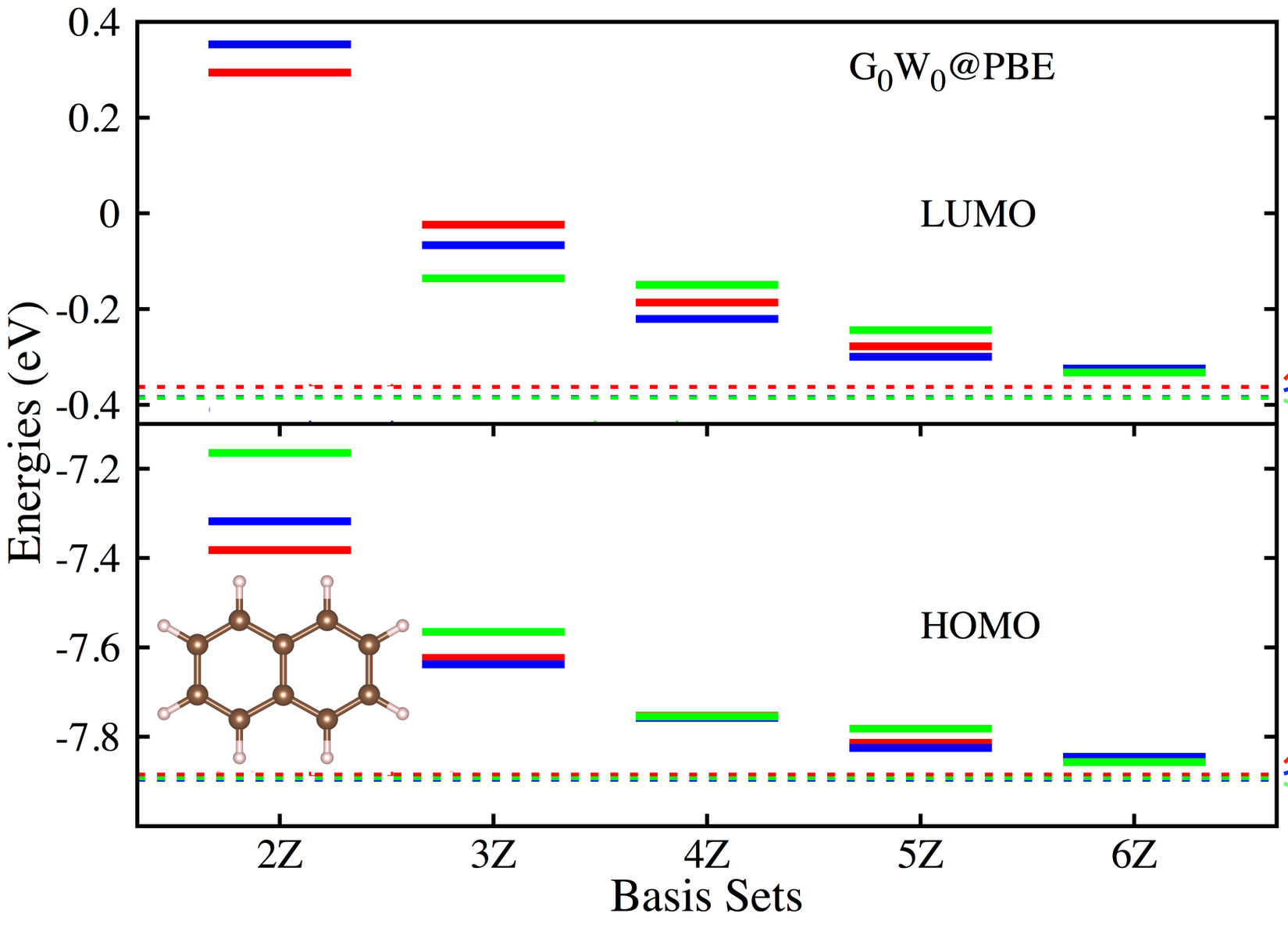

CBS extrapolation:

Halkier et al., Chem. Phys. Lett. 302, 437 (1999); Helgaker et al., J. Chem. Phys. 106, 9639 (1997)

[4Z-5Z] NAO
[4Z-5Z] AUG
[4Z-6Z] CC

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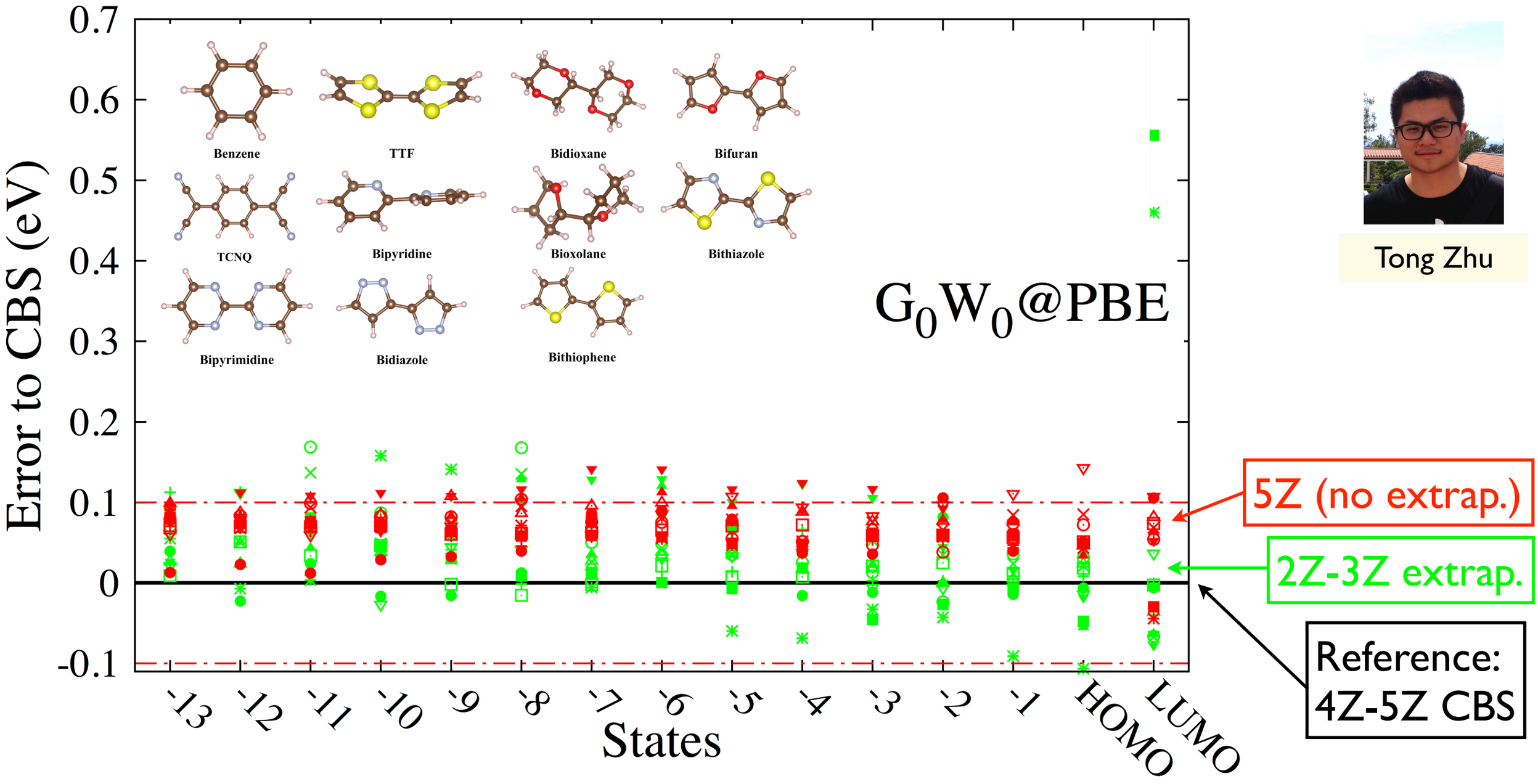
Can We Extrapolate Smaller (Cheaper) Basis Sets?



Tong Zhu

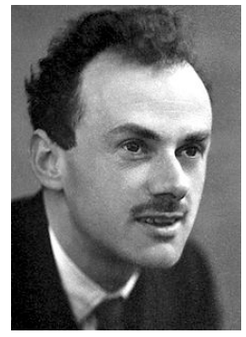
2Z-3Z Extrapolation *(T. Zhu)*: 5Z quality, but at the price of 3Z.

Works for valence and low-lying conduction levels, light-element molecules.

However, not for core states, unbound states; restricted to H-Ar.

Summary

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

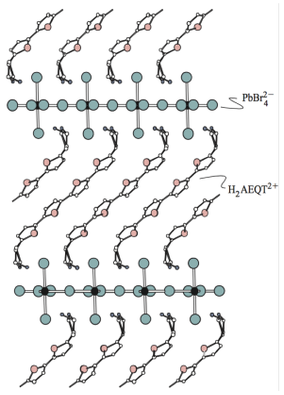


P.A.M. Dirac

High-accuracy platform for predictive molecular, materials simulations

Scalable to large systems, advanced electronic structure approximations

Ongoing frontier: Accurate, affordable many-body perturbation theory towards excited states for real materials



Crystalline tunable organic-inorganic hybrid materials - predictive approach to truly "new" materials, close integration with experiment

Argonne NATIONAL LABORATORY ALCF

National Science Foundation

TRIANGLE MRSEC | Materials Research Science and Engineering Center

NVIDIA

MAX-PLANCK-GESELLSCHAFT

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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Initial basis $\{u\}^{(0)}$:
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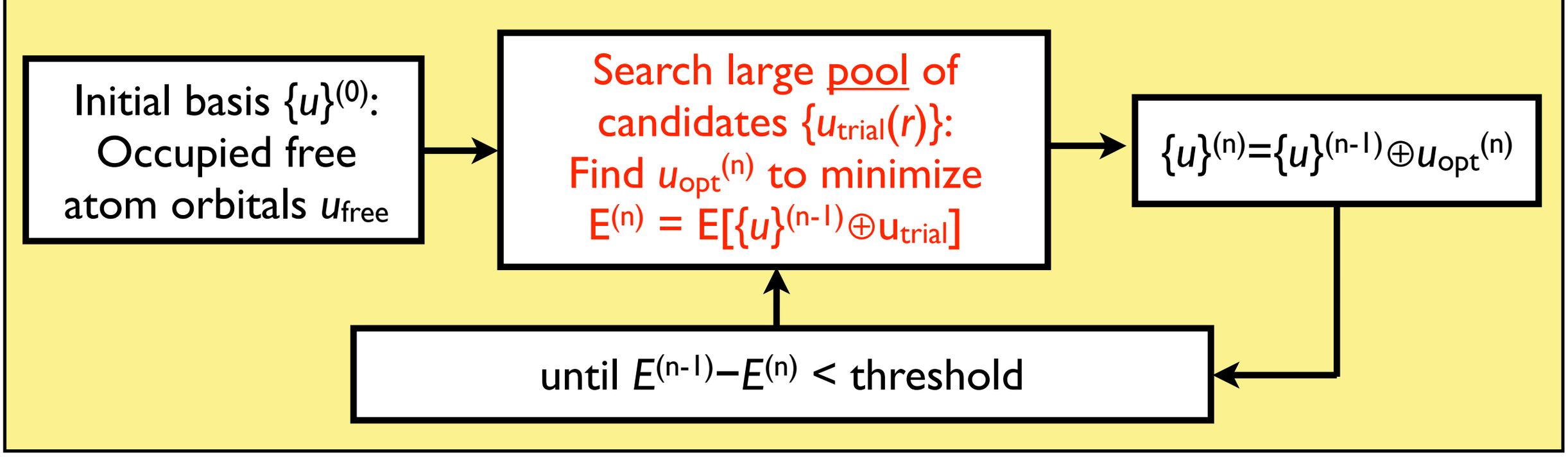

Iterative Selection of NAO Basis Functions

"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

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

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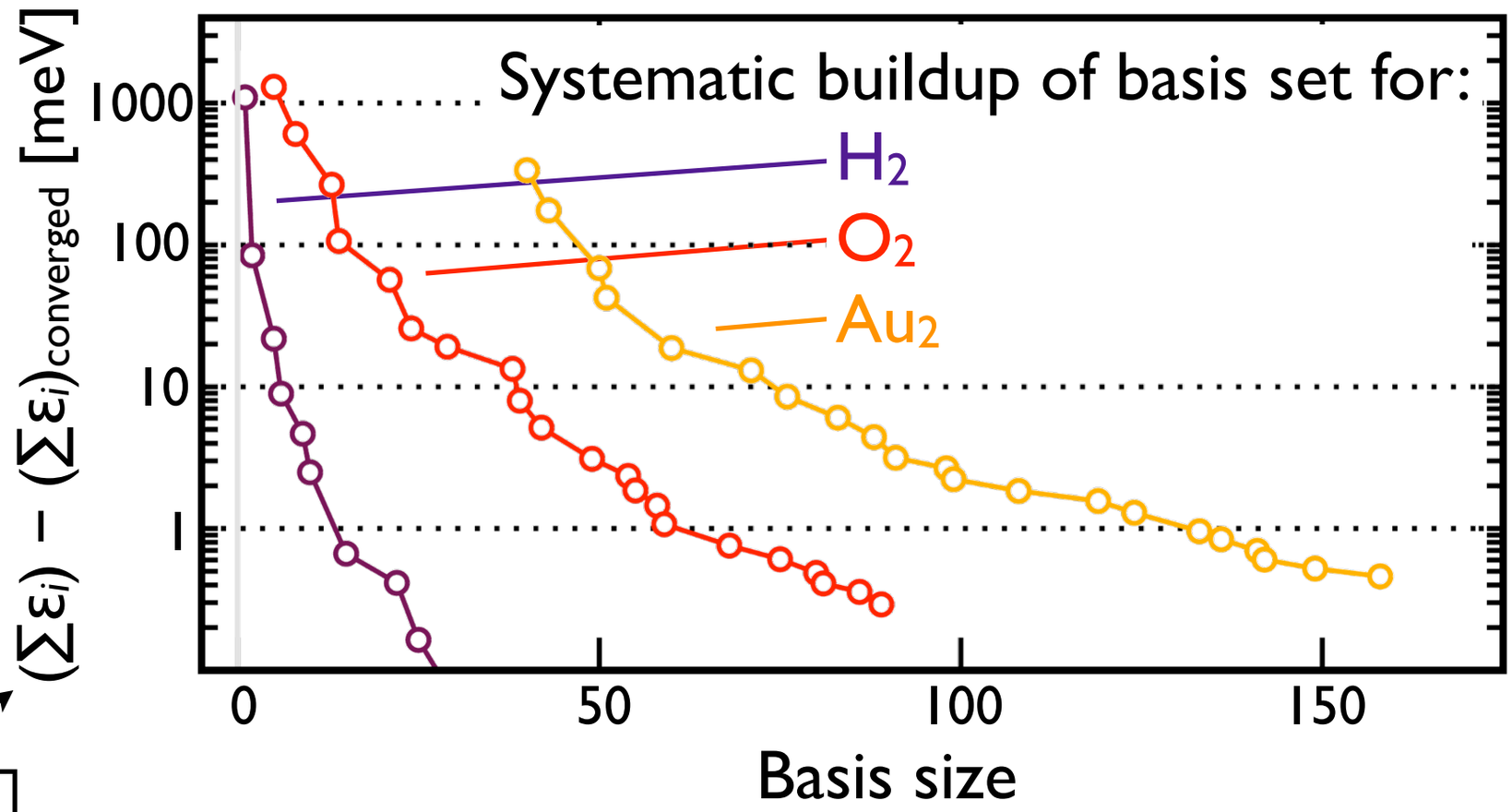


Remaining basis set error

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

Result: Hierarchical Basis Set Library for All Elements

	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*

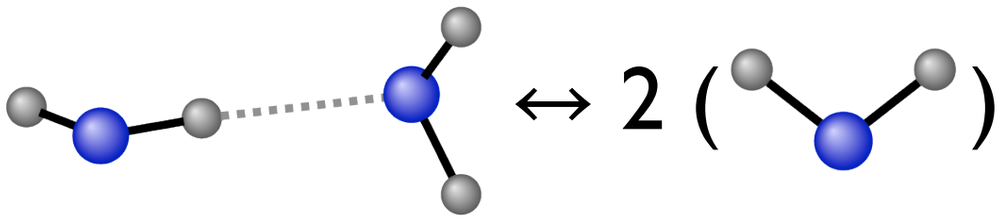
"First *tier* (level)"

"Second *tier*"

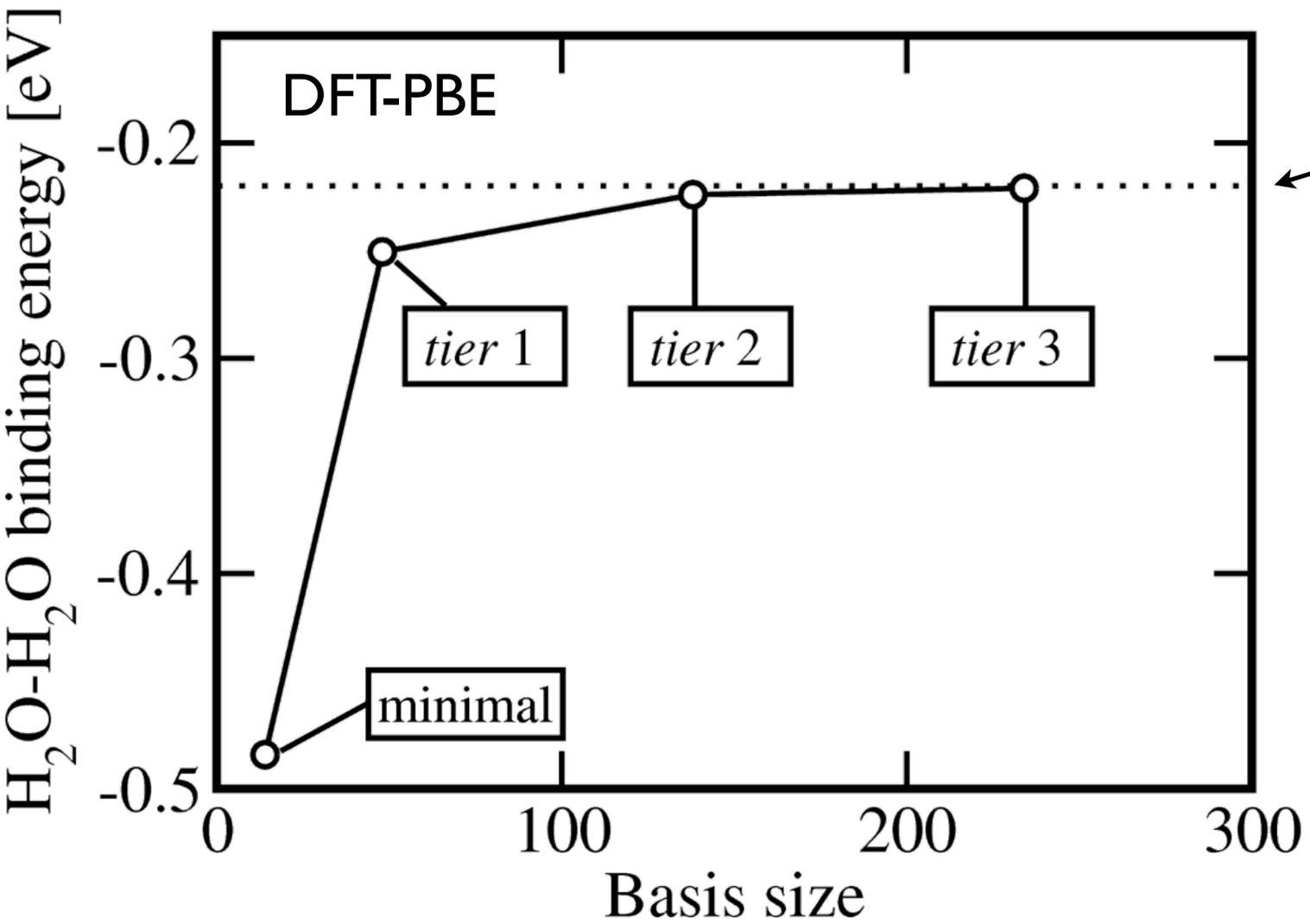
"Third *tier*"

...

Accuracy: $(H_2O)_2$ Hydrogen Bond Energy



↔ 2 ( )



Basis set limit (independent):
E_{Hb} = −219.8 meV

Basis sets: Radial fn. character

	H	C,N,O
minimal	1s	[He]+2s2p
tier 1	*s,p*	*s,p,d*
tier 2	*s,p,s,d*	*s,p,d,f,g*
tier 3	*s,p,d,f*	*s,p,d,f*

Using Numeric Atom-Centered Basis Functions: Pieces

- *Numerical* Integration $$h_{ij} = \int d^3r \varphi_i(\boldsymbol{r}) \hat{h}_{\mathrm{KS}} \varphi_j(\boldsymbol{r})$$
- Electron density update $$n(\boldsymbol{r}) = \sum_k f_k |\psi_k(\boldsymbol{r})|^2$$
- All-electron electrostatics $$v_{\mathrm{es}}(\boldsymbol{r}) = \int d^3r' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$
- Eigenvalue solver $$\underline{\underline{h}}\, \underline{c}_k = \epsilon_k\, \underline{\underline{s}}\, \underline{c}_k$$

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- Relativity? *needed for heavy elements*
- Periodic systems? *need suitable basis, electrostatics*
- Coulomb operator? $$(ij|kl) = \int d^3 r d^3 r' \frac{\varphi_i(\boldsymbol{r}) \varphi_j(\boldsymbol{r}') \varphi_k(\boldsymbol{r}) \varphi_l(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

Numeric Atom-Centered Basis Functions: Integration

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

- *Discretize* to integration grid:

$$\int d^3 r f(\boldsymbol{r}) \rightarrow \sum_{\boldsymbol{r}} w(\boldsymbol{r}) f(\boldsymbol{r})$$

... but even-spaced integration grids are *out*:

$f(r)$ strongly peaked near all nuclei!

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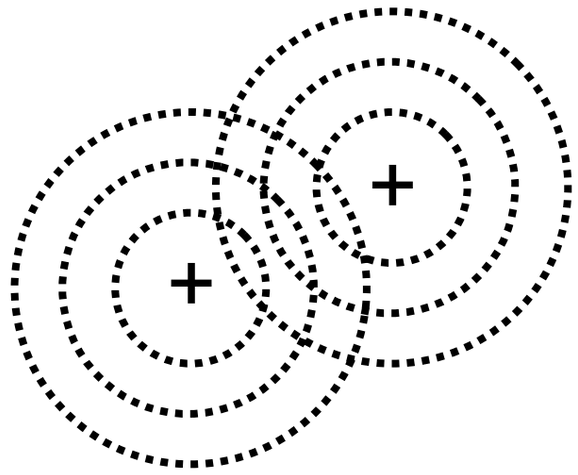
- Overlapping atom-centered integration grids:
  - Radial *shells (e.g., H, light: 24; Au, tight: 147)*
  - *Specific* angular point distribution ("Lebedev") exact up to given integration order *l* *(50, 110, 194, 302, ... points per shell)*



Pioneered by

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

All-Electron Integrals: Rather Benign for NAOs

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

f(r) for
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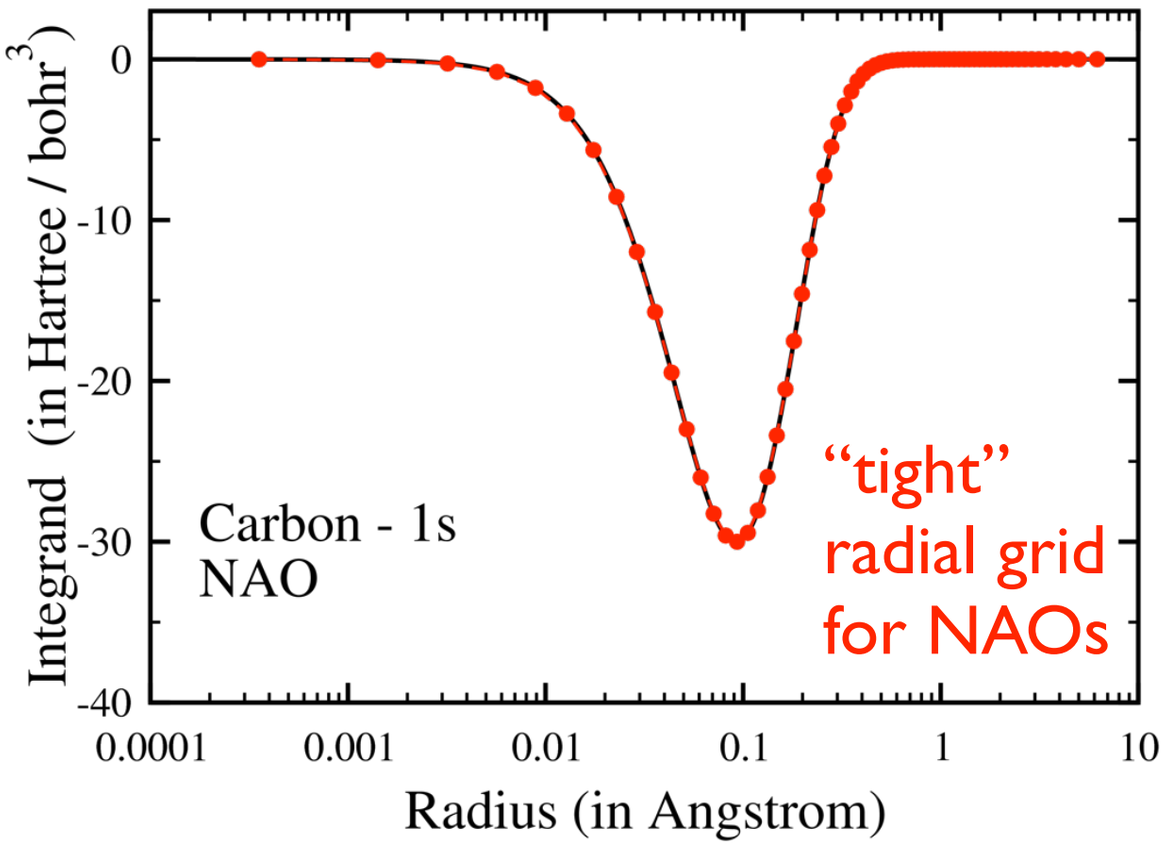

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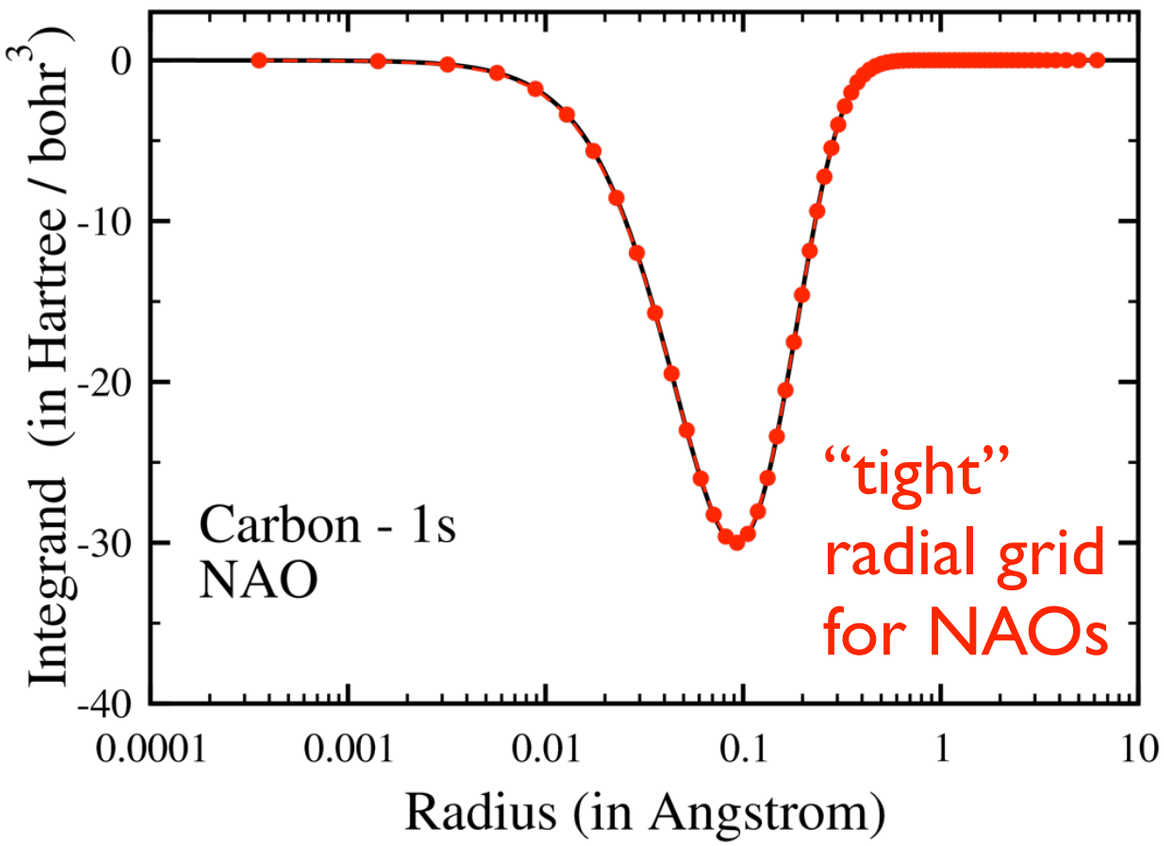
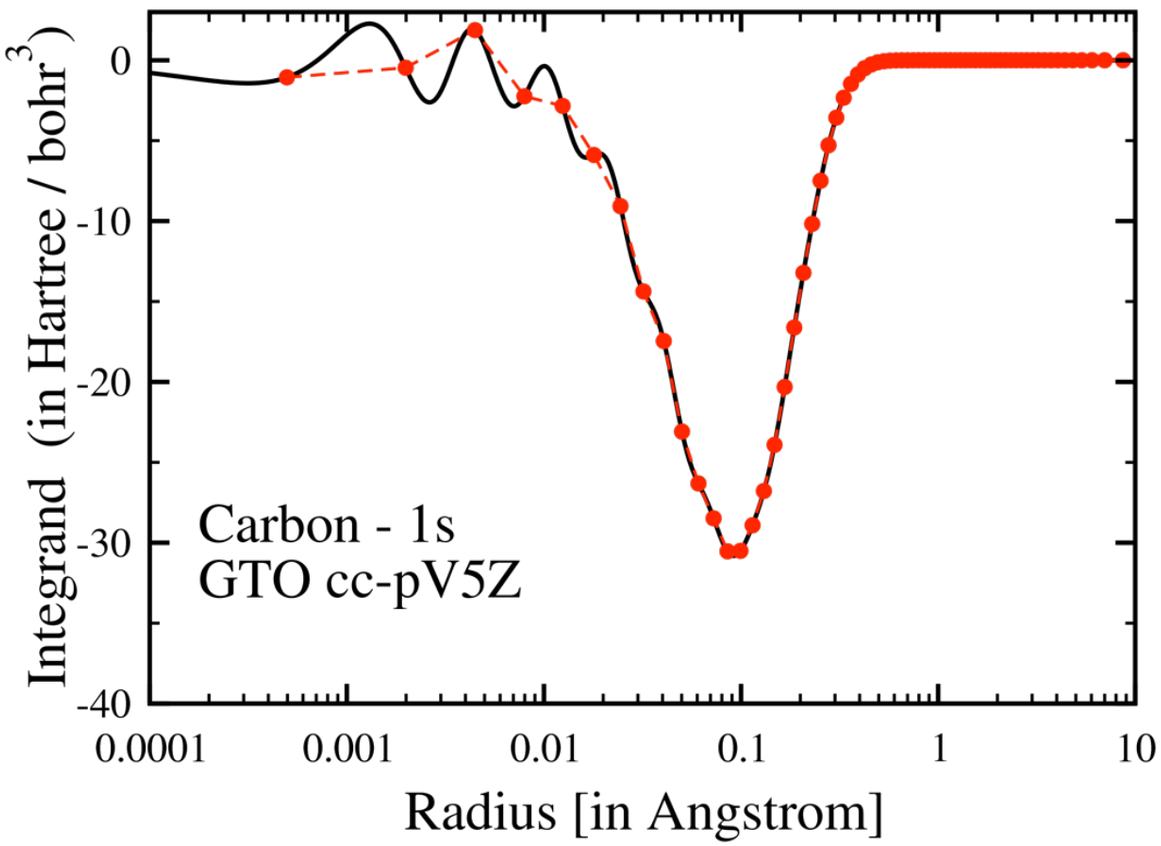


f(r) for
contracted Gaussian
radial function:



Overlapping Atom-Centered Grids: "Partitioning of Unity"

Becke, 1988

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

- Rewrite to atom-centered integrands:

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

exact: $\sum_{\mathrm{atoms}} p_{\mathrm{atom}}(\boldsymbol{r}) = 1$

through $p_{\mathrm{atom}}(\boldsymbol{r}) = \dfrac{g_{\mathrm{atom}}(\boldsymbol{r})}{\sum_{\mathrm{atom}'} g_{\mathrm{atom}'}(\boldsymbol{r})}$

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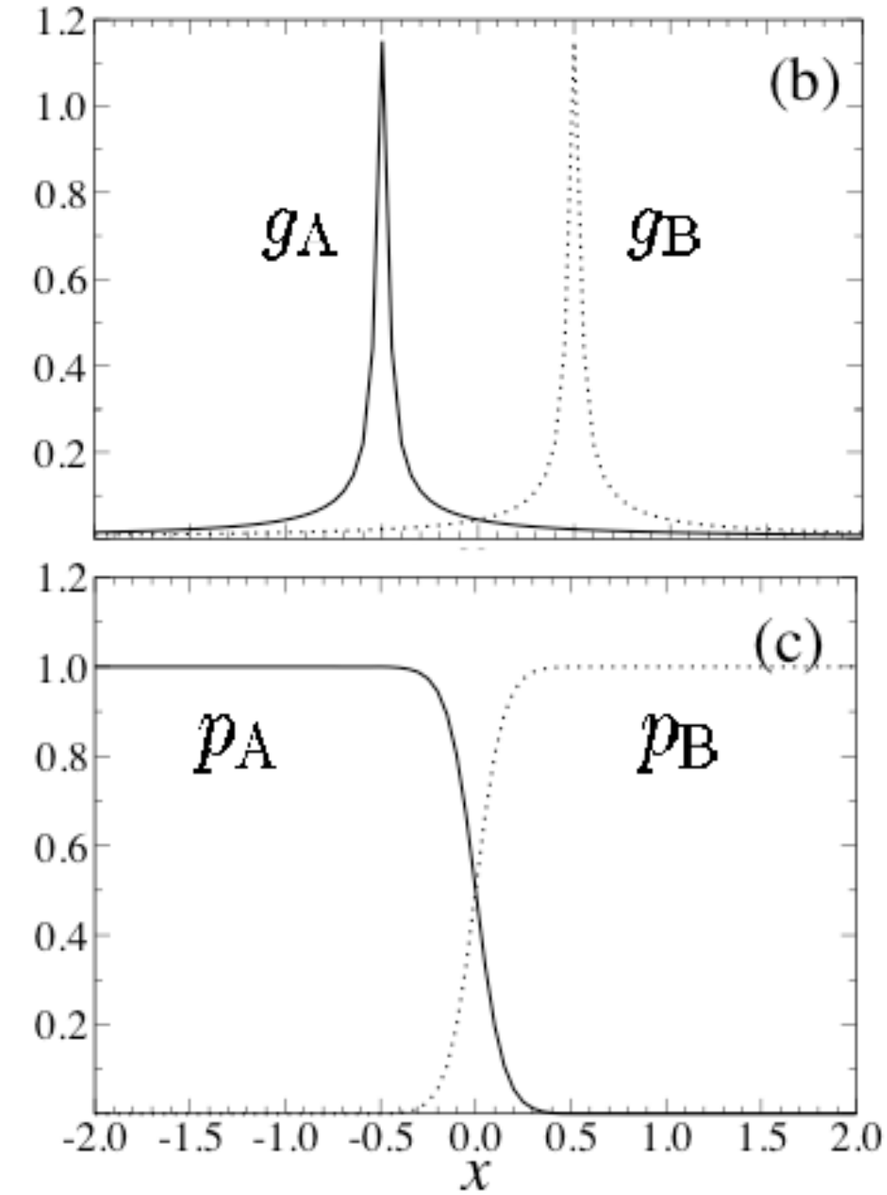
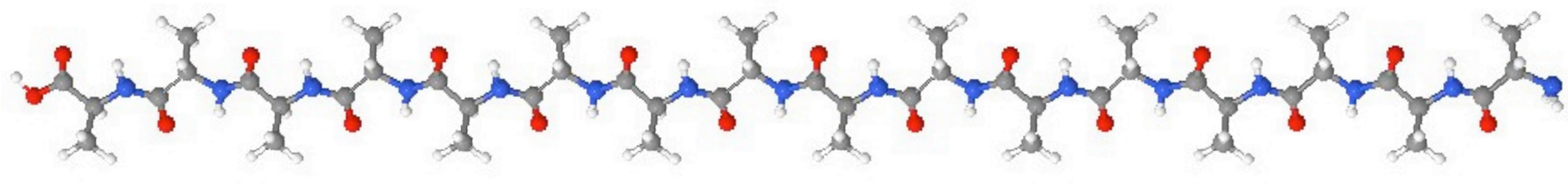
- e.g.: $g_{\mathrm{atom}} = \dfrac{\rho_{\mathrm{atom}}(r)}{r^2}$ *(Delley 1990)*

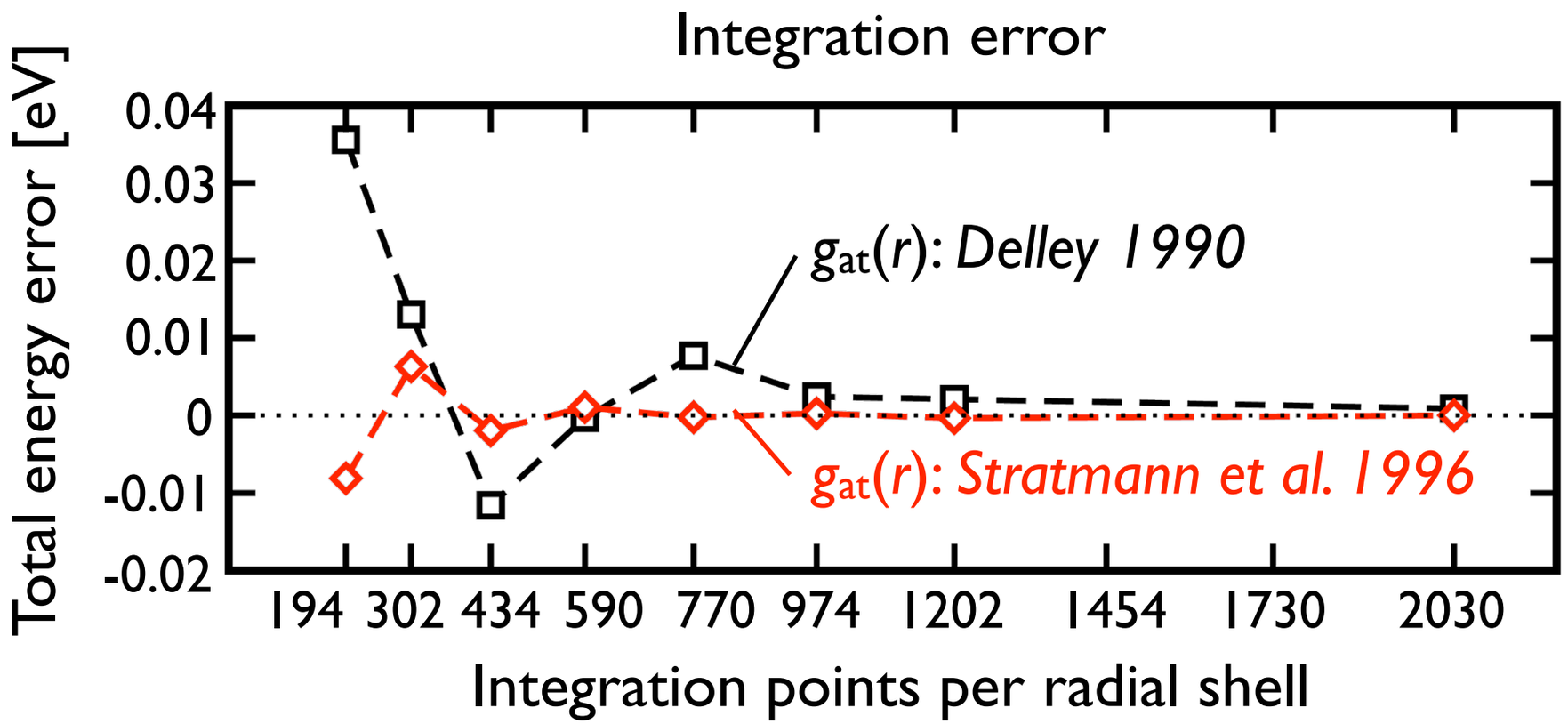
  many alternatives:
  Becke 1988, Stratmann 1996, Koepernik 1999, ...



Integration in Practice: Large Systems, Small Errors!



Fully extended Polyalanine peptide molecule Ala_{20}, DFT-PBE (203 atoms)



Hartree Potential (Electrostatics): Overlapping Multipoles

$$v_{\mathrm{es}}(\boldsymbol{r}) = \int d^3r' \, \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

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

$$n(\boldsymbol{r}) = \sum_{\mathrm{atoms}} p_{\mathrm{atom}}(\boldsymbol{r}) n(\boldsymbol{r})$$

Delley
JCP 92, 508 (1990)

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- Classical electrostatics:

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

Electrostatics: Multipole expansion

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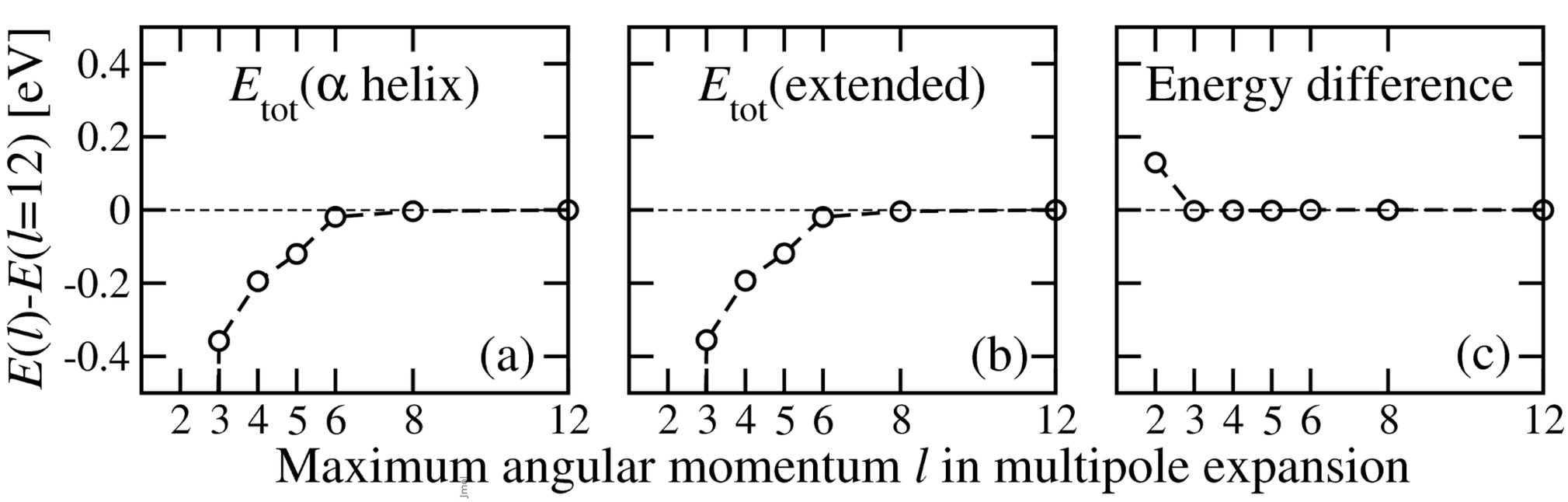
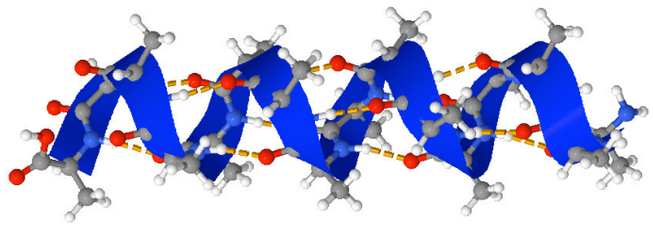
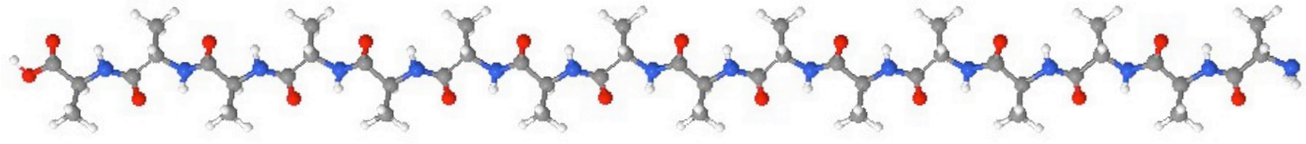
Polyalanine Ala_{20}, DFT-PBE (203 atoms)

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





α



extended