

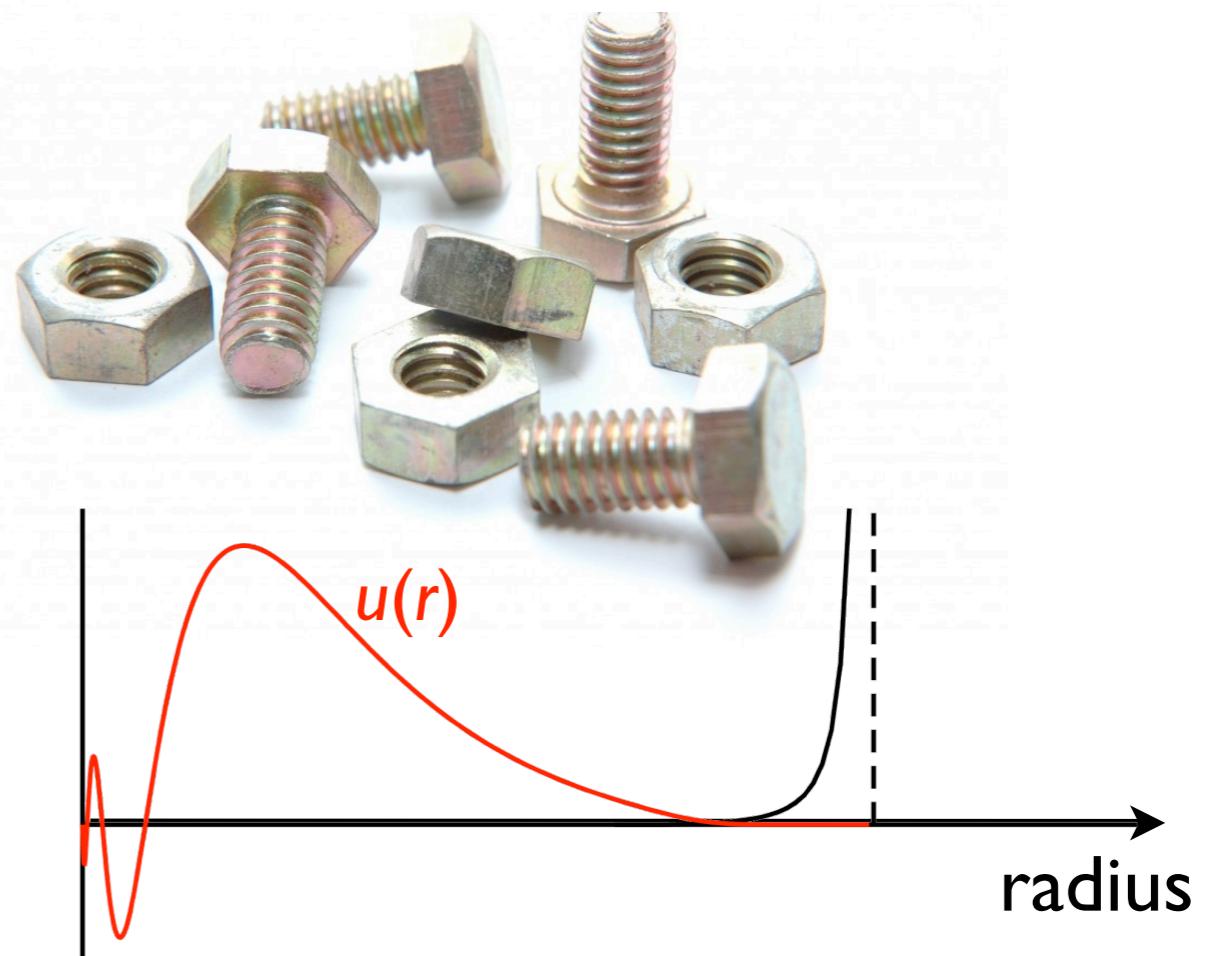
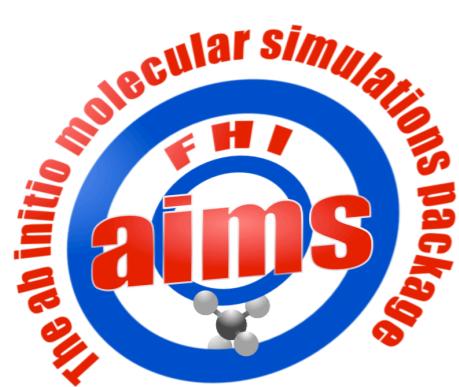
The Nuts and Bolts of Electronic Structure Theory (I)

Basis Sets, Real-Space Grids, Relativity, Scalability

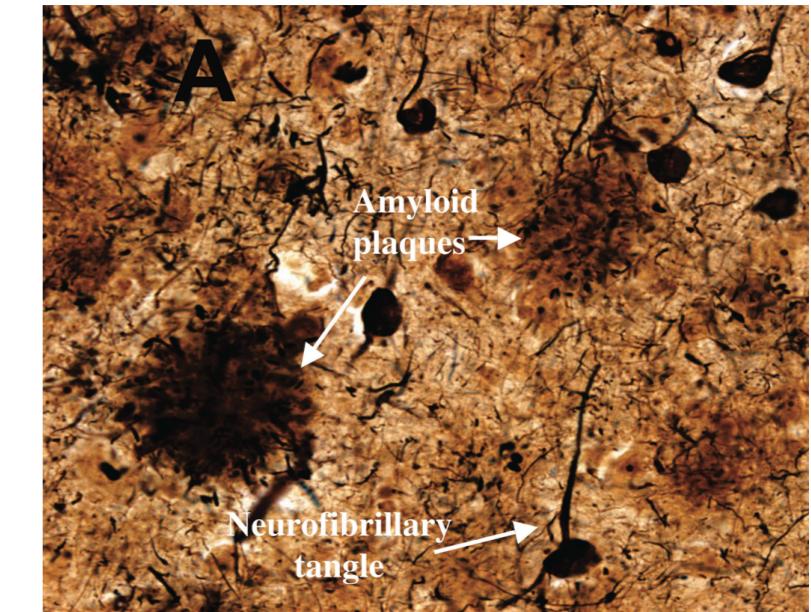
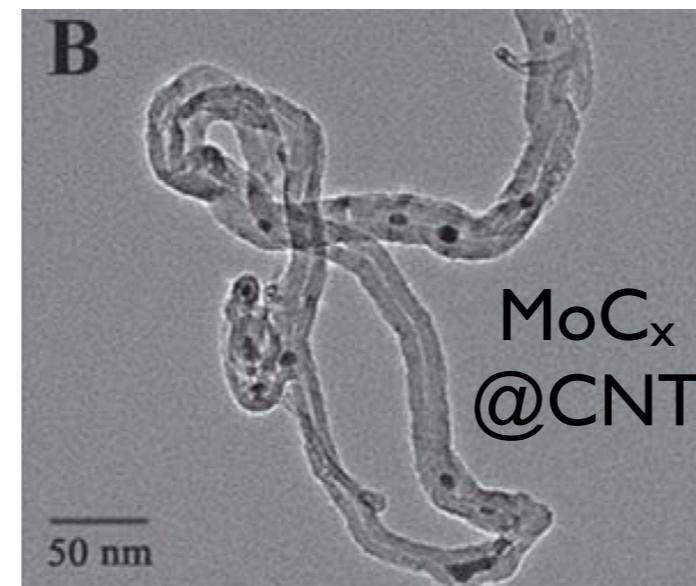
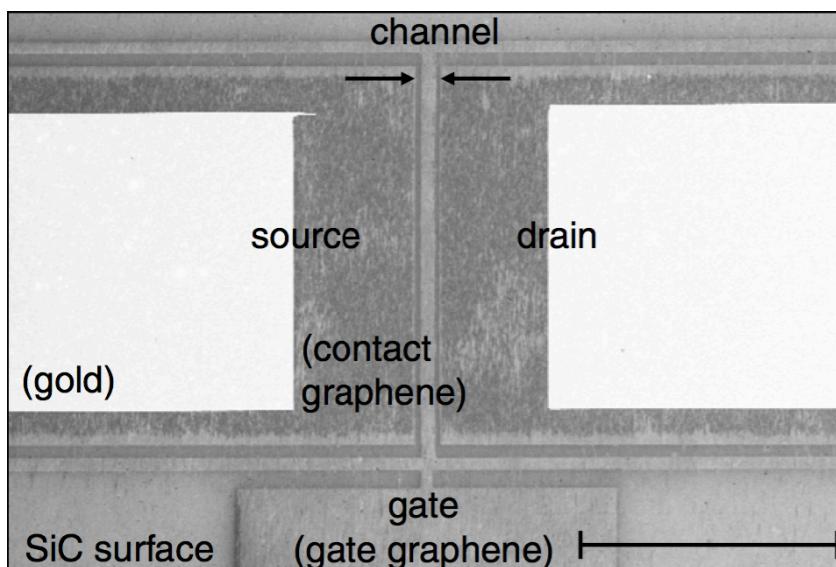
$$\hat{\mathcal{H}}\Psi = E\Psi$$

Volker Blum

Duke University
Durham, NC, USA
<http://aims.pratt.duke.edu>



Some (Nano-)Things That We Would Like to Have:



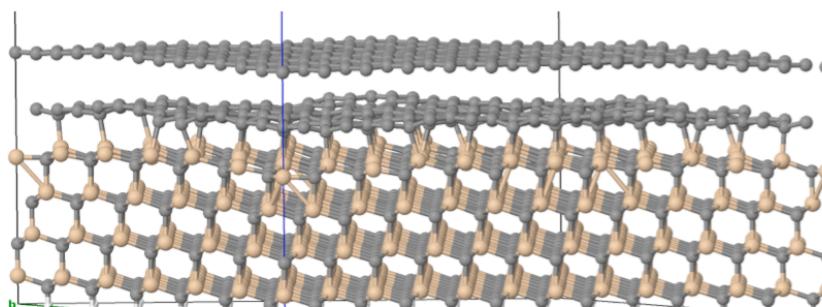
Graphene-based electronics? “Sunlight to Fuel” catalysis?

Hertel et al., *Nature Commun.* (2012)

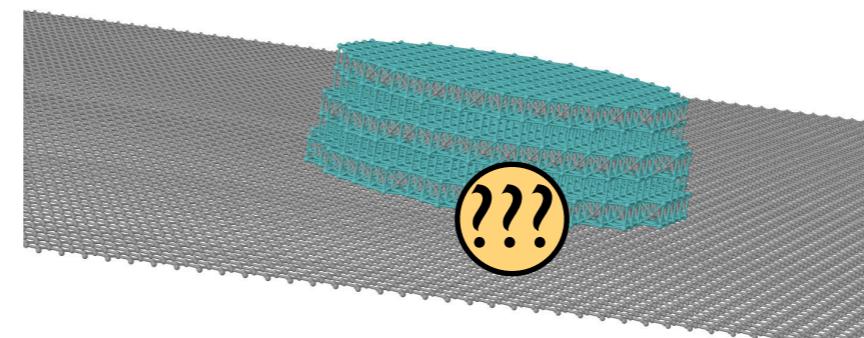
Bian et al., *Chem. Sci.* (2013)

“Fix” for
Alzheimer’s Disease?
Irvine et al., *Mol. Med.* (2008)

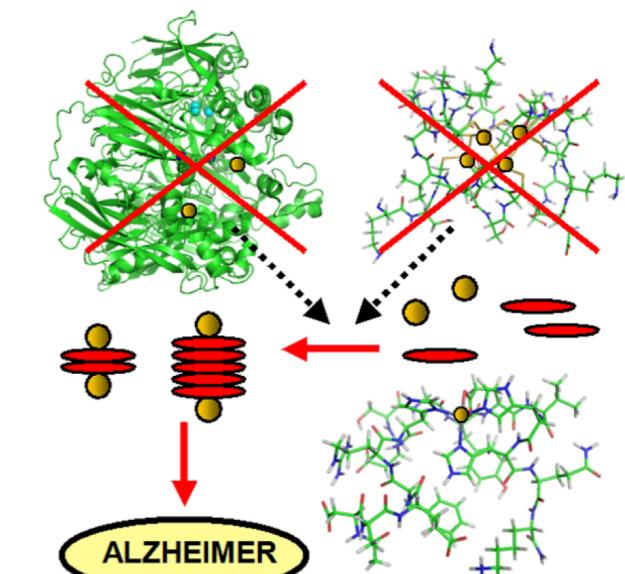
Answers? Somewhere in atomic structure!



Graphene on SiC:
Optimal Growth?



Interface?
Optimal Material?



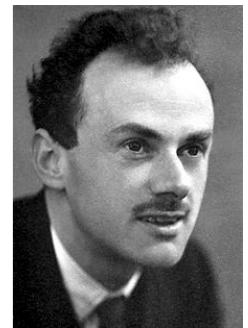
Kepp, *Chem. Rev.* (2012)

Secondary structure? Ions?

The Dualism of Quantum Mechanical Modeling

Schrödinger (Dirac) Equation

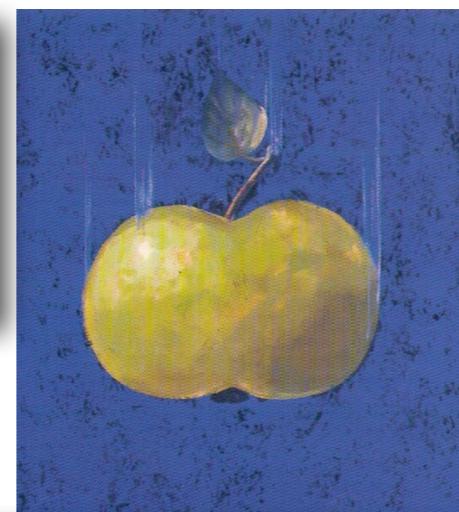
$$\hat{\mathcal{H}}\Psi = E\Psi$$



P.A.M. Dirac

Perfect recipe for parameter-free modeling ...
... but in practice, we often want a lot. Conundrum:

The approximation is accurate
but
feasible systems are too small



Feasible systems large enough
but
approximations are not great

(How?) can we work towards having both?



Scope of this Talk

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

Kohn-Sham Equations, 1965

General concepts:

- Basis sets
- Integrals and grids; electrostatics; molecules vs. periodic solids
- Scalar relativity
- Eigenvalue solution, 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

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

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		

- Universality: Cover full space of materials and chemistry
“Materials and molecules” - periodic (k -space) and non-periodic
- Accuracy: Hierarchy of methods: DFT and “beyond” (GW, MP2, RPA, rPT2, ...)
All-electron
- Efficiency: Scalable (system size, number of CPUs)
- Efficient (1,000s of atoms), but do not sacrifice accuracy!**

The Kohn-Sham Equations (again)

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

“As (almost) everyone does”:

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

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

→ generalized eigenvalue problem:

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

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

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

2. Self-consistency:

B. Lange
Tue 11:30h

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

Initial guess: e.g., $c_{ki}^{(0)}$

Update density $n^{(m)}(\mathbf{r})$

Update $v_{\text{es}}^{(m)}, v_{\text{xc}}^{(m)}$

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

Solve for updated $c_{ki}^{(m+1)}$

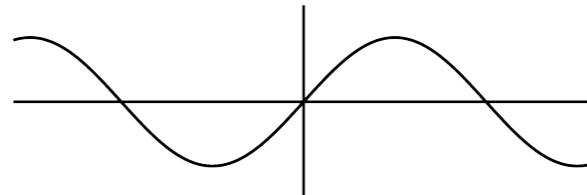
Representing the Orbitals: Basis Sets

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

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

Many good options:

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

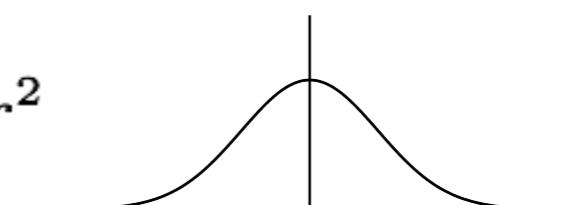


A. Janotti
Wed 10:15h

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

- Augmented plane waves (Slater 1937; Andersen 1975; etc.)

- Gaussian-type orbitals $\varphi_i(\mathbf{r}) = \frac{1}{N} r^l e^{-\alpha r^2}$



D. Singh
Wed 11:30h

- Many others: (L)MTO, “real-space”, numeric atom-centered functions, ...

Our Choice: Numeric Atom-Centered Basis Functions

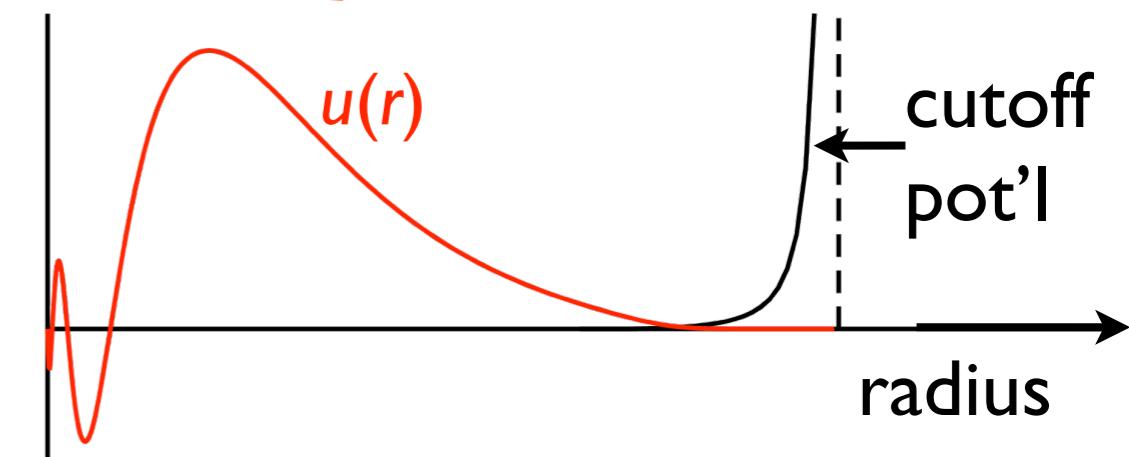
$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} \cdot Y_{lm}(\Omega)$$

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

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

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

- free-atom like: $v_i(r) = v_{\text{free atom}}^{\text{DFT}}(r)$
- Hydrogen-like: $v_i(r) = z/r$
- free ions, harm. osc. (Gaussians), ...



Our Choice: Numeric Atom-Centered Basis Functions

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

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

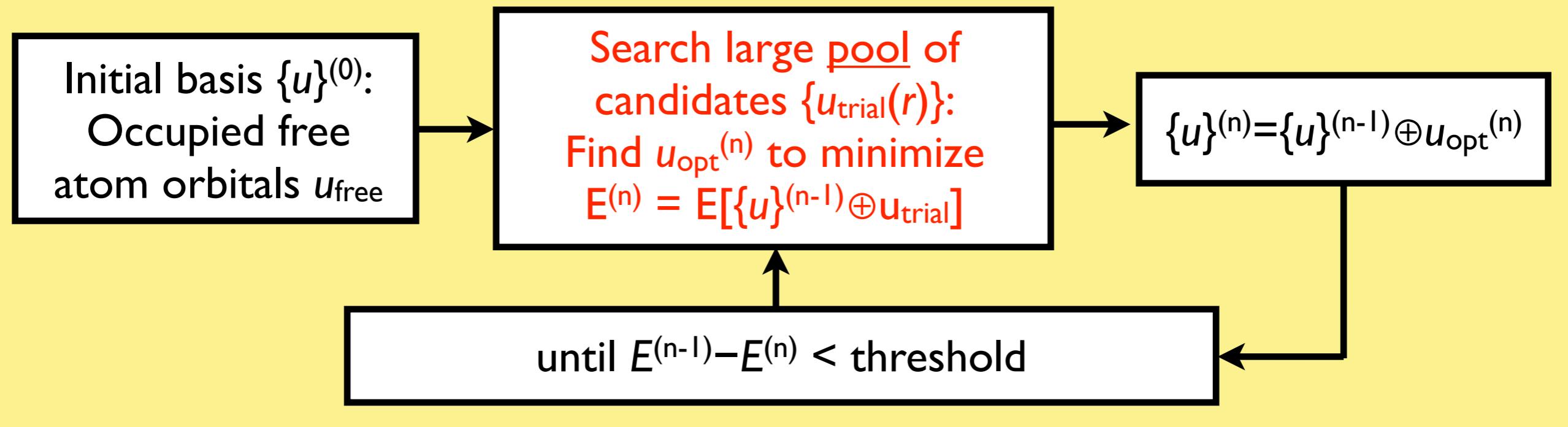
- $u_i(r)$: Flexible choice - “Anything you like.”
 - Localized; “naturally” all-electron
 - The choice of efficient and of enough radial functions is obviously important
 - We have a basis set library for all elements (I-102), from fast qualitative to meV-converged (total energy, LDA/GGA) calculations - efficient and accurate approach

Constructing a Basis Set Library for DFT

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

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

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



Iterative Selection of NAO Basis Functions

“Pool” of trial basis functions:

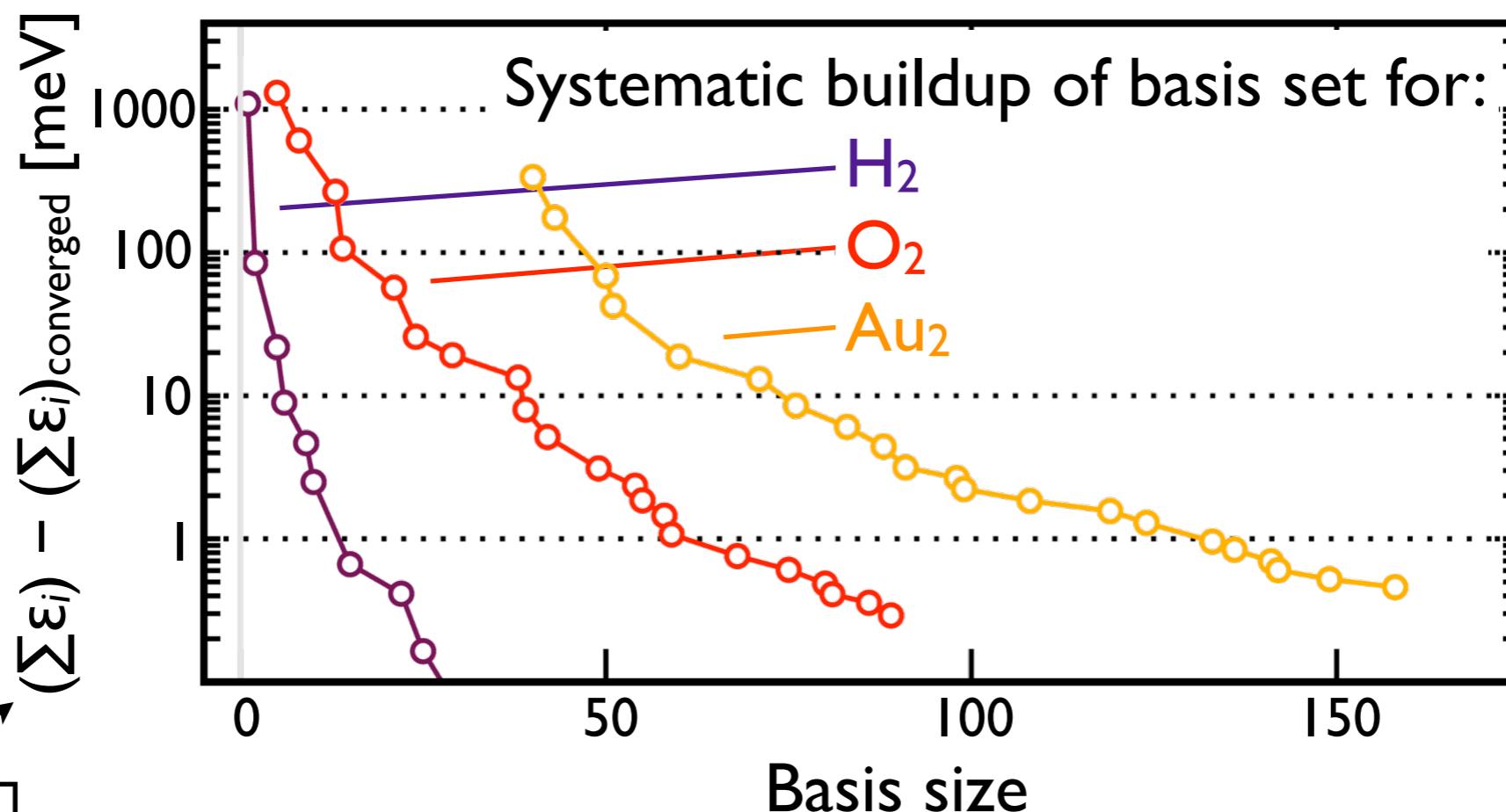
2+ ionic $u(r)$

Hydrogen-like $u(r)$ for $z=0.1-20$

Optimization target:

Non-selfconsistent symmetric dimers, averaged for different d

Pick basis functions one by one, up to complete *total* energy convergence



Remaining
basis set error

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

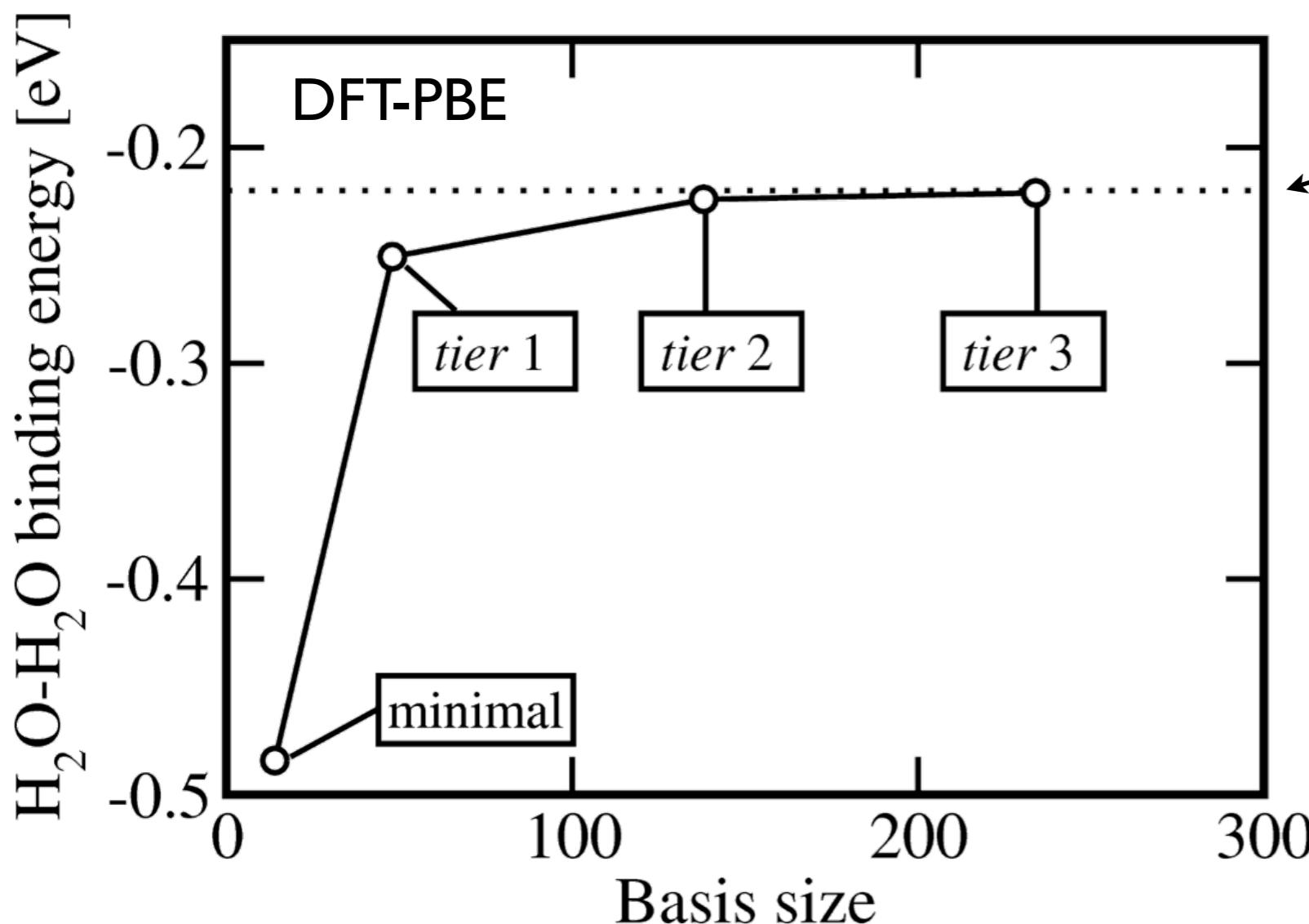
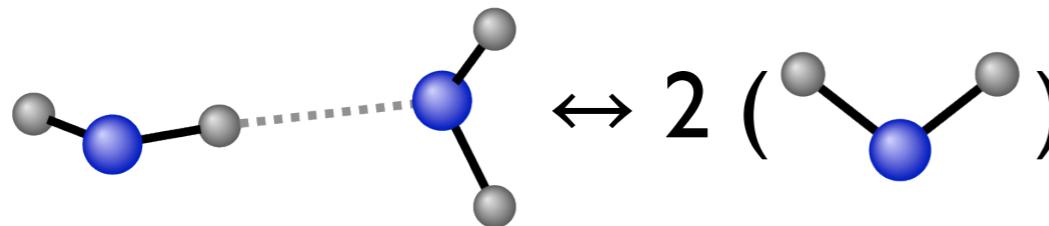
“First tier (level)”

“Second tier”

“Third tier”

...

Accuracy: $(\text{H}_2\text{O})_2$ Hydrogen Bond Energy

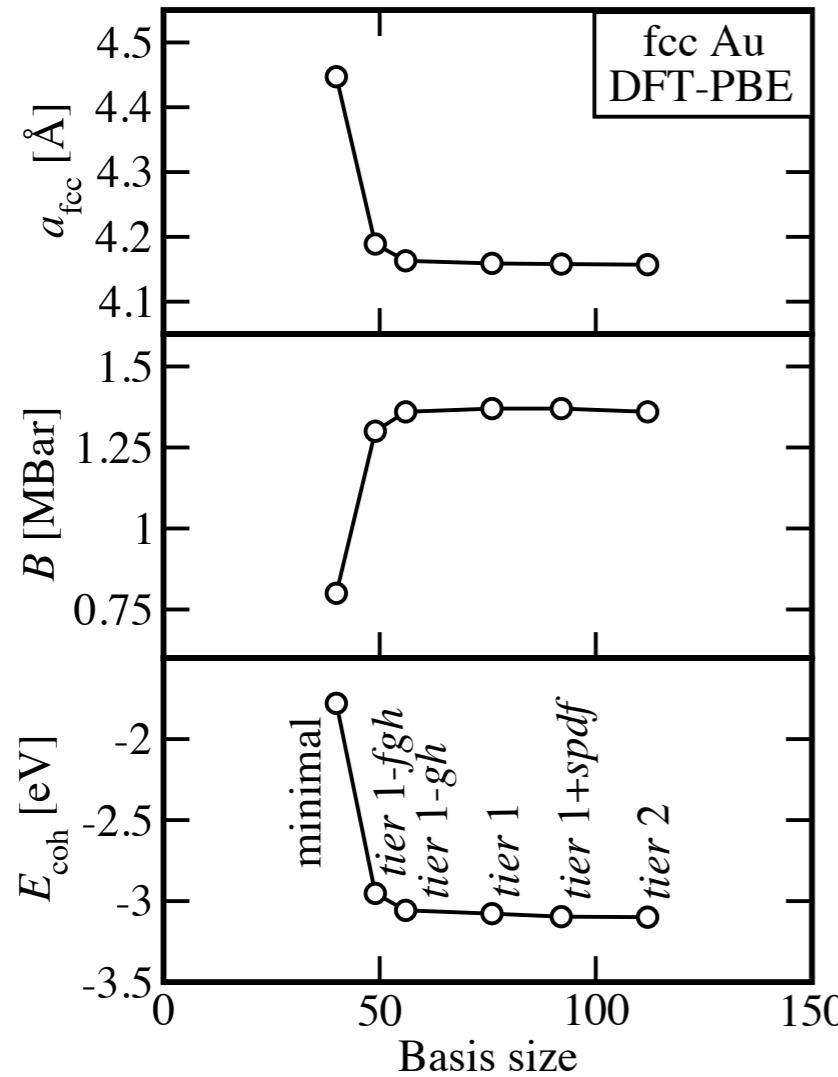


Basis set limit (independent):
 $E_{\text{Hb}} = -219.8 \text{ meV}$

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

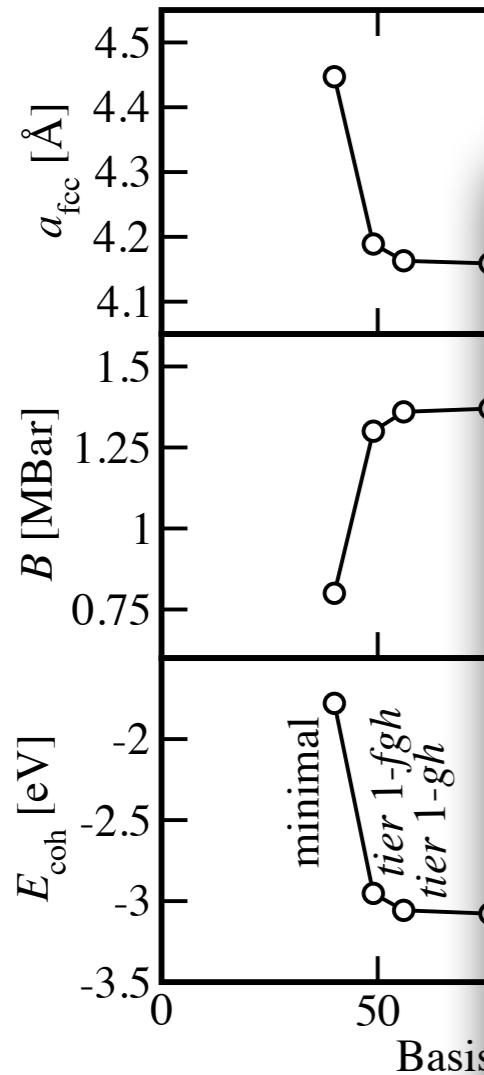
Transferability: Generally Not a Problem for DFT

Bulk Au: Cohesive properties



Transferability: Generally Not a Problem for DFT

Bulk Au: Cohesive properties



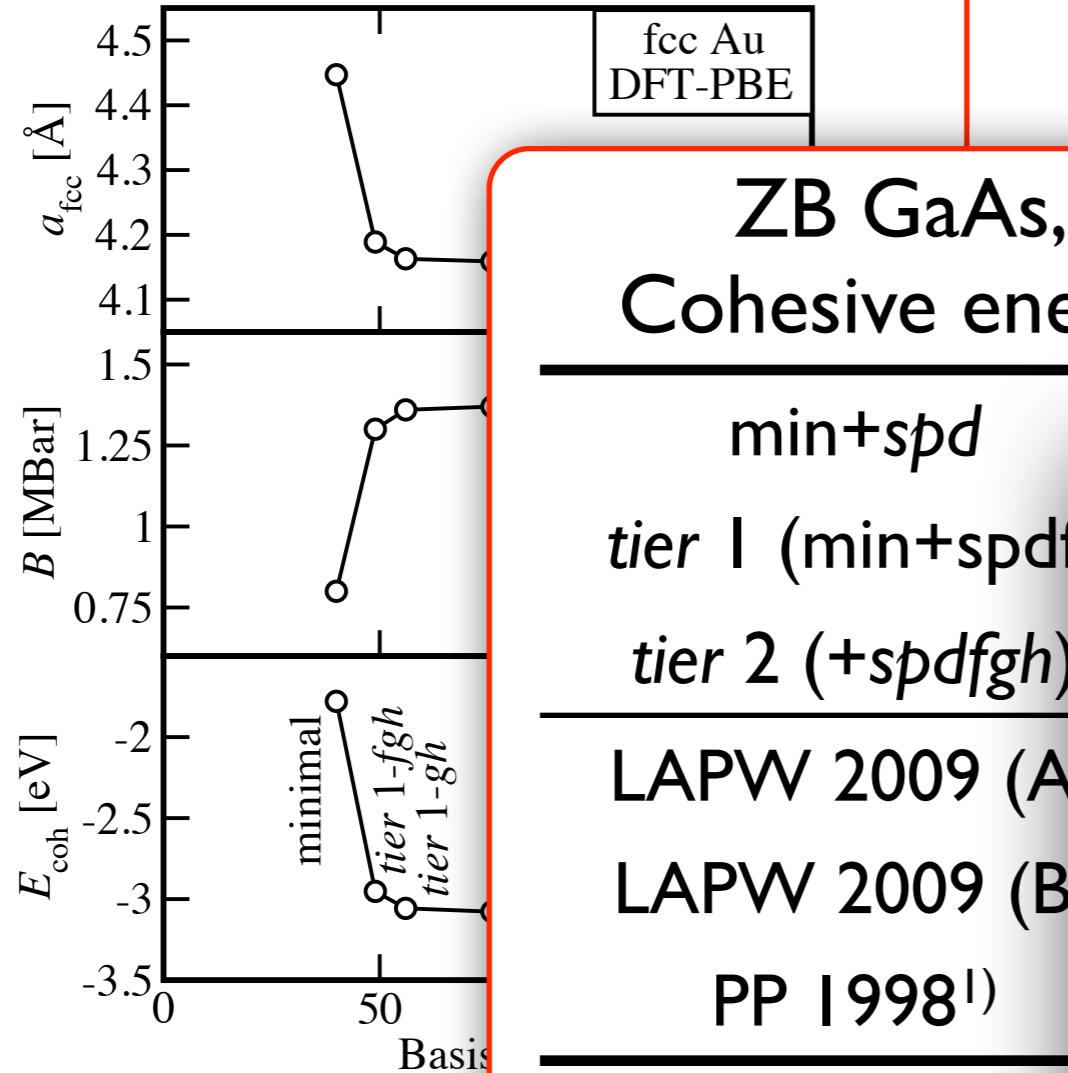
ZB GaAs, LDA: Cohesive energy [eV]

min+spd	7.99
tier I (min+spdf)	8.06
tier 2 (+spdfgh)	8.09
<hr/>	
LAPW 2009 (A)	7.80
LAPW 2009 (B)	8.00
PP 1998 ¹⁾	8.15

¹⁾ Fuchs, Bockstedte, Pehlke, Scheffler,
PRB 1998

Transferability: Generally Not a Problem for DFT

Bulk Au: Cohesive properties



ZB GaAs, LDA:
Cohesive energy [eV]

min+spd

7.99

tier I (min+spd)

tier 2 (+spd_{fgh})

LAPW 2009 (A)

LAPW 2009 (B)

PP 1998¹⁾

¹⁾ Fuchs, Bockstedte, Peierls
PRB 1998

5d(100) surfaces: (1×1)→(1×5)
reconstruction energy [meV/1×1]

Pt(100) Au(100)

min+spd_f -65 -21

tier I -80 -30

tier 2 -83 -31

FP-LAPW -89 -24

...

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!

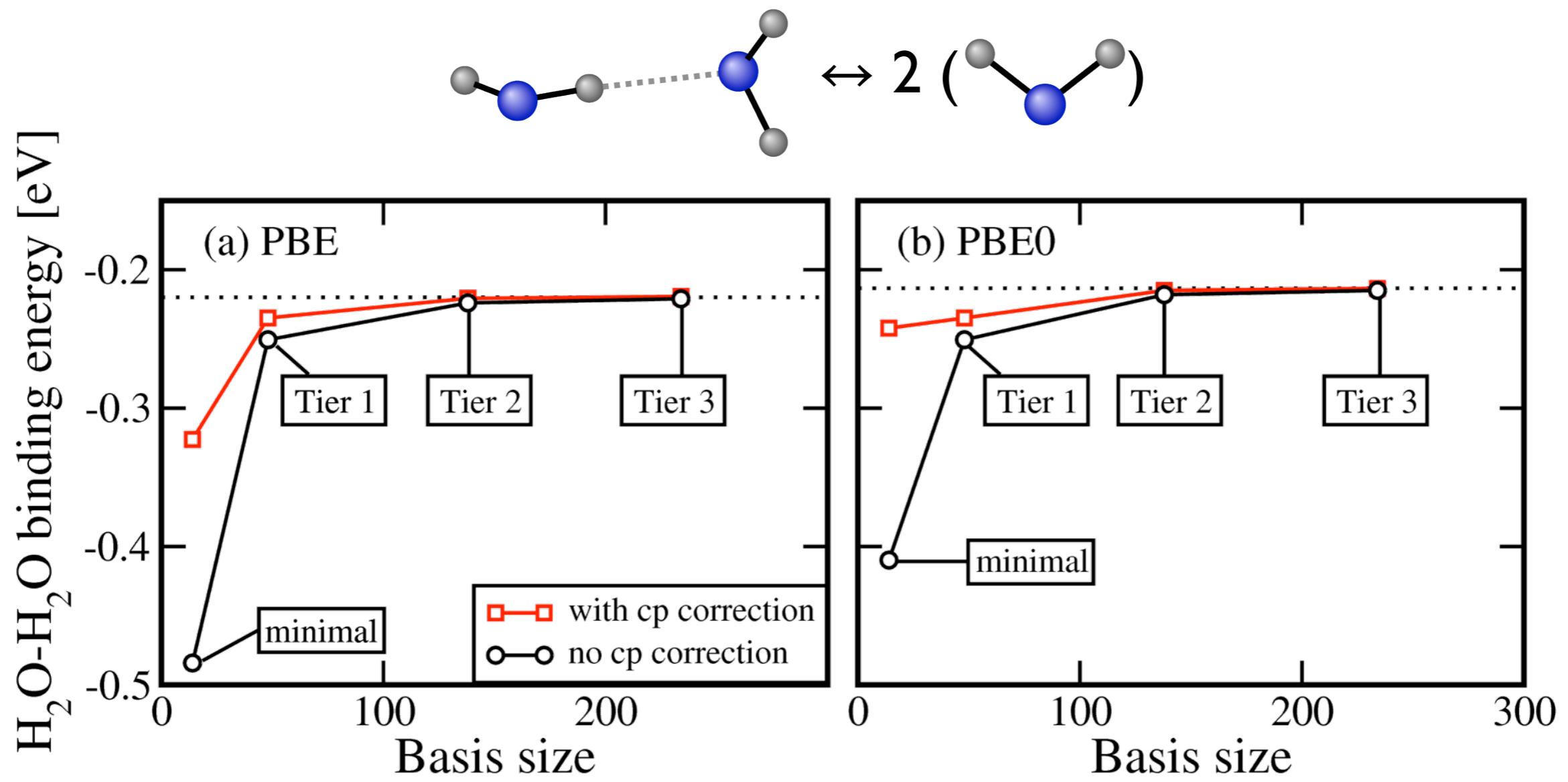
Remedy: “Counterpoise correction”

$$\Delta E_{BSSE} = E(\bullet - \bullet) - E(\bullet)$$

No nucleus - basis functions only

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)*

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

need CP and/or basis sets that systematically approach continuum of states!

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

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

- Eigenvalue solver

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

- Relativity?

needed for heavy elements

- Periodic systems?

need suitable basis, electrostatics

- Coulomb operator?

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

Numeric Atom-Centered Basis Functions: Integration

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

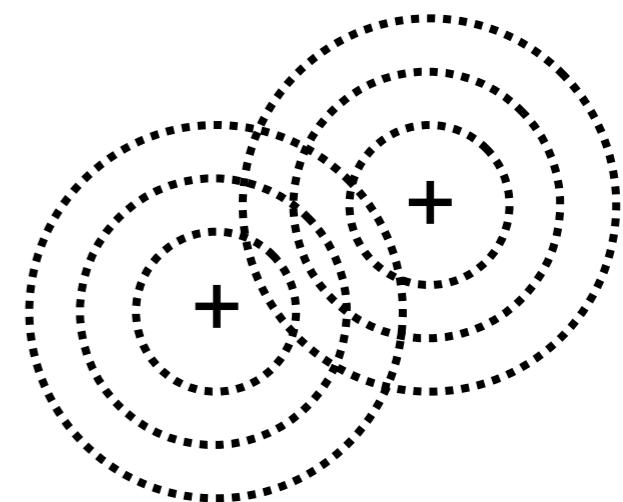
- Discretize to integration grid:

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

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

- 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!

Overlapping Atom-Centered Grids: “Partitioning of Unity”

Becke, 1988

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

- Rewrite to atom-centered integrands:

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

exact:

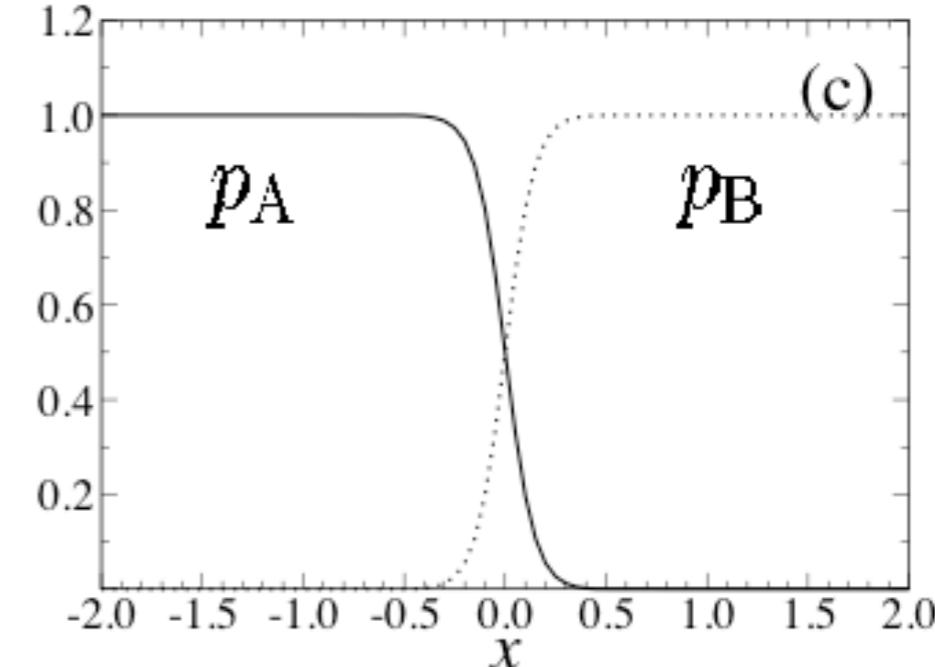
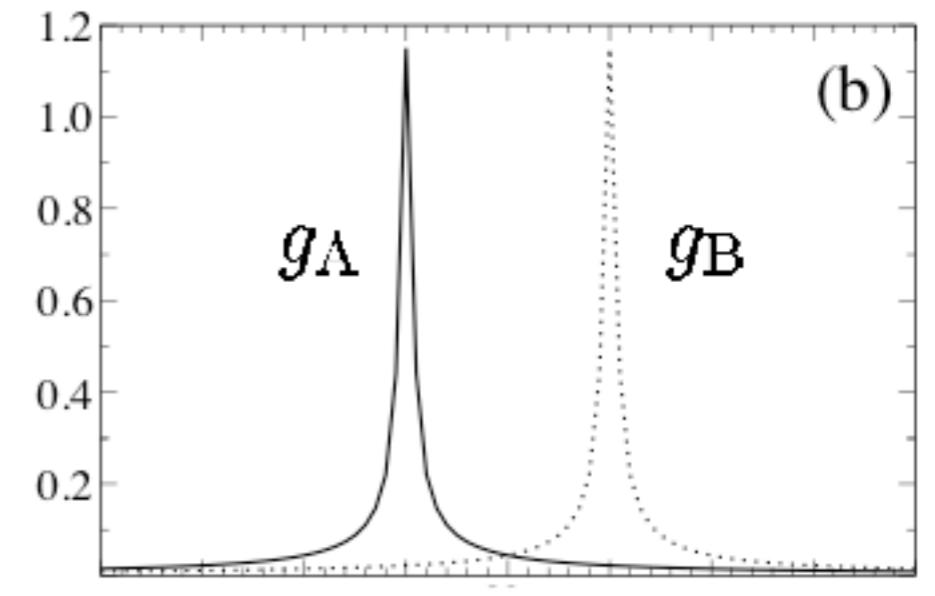
$$\sum_{\text{atoms}} p_{\text{atom}}(\mathbf{r}) = 1$$

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

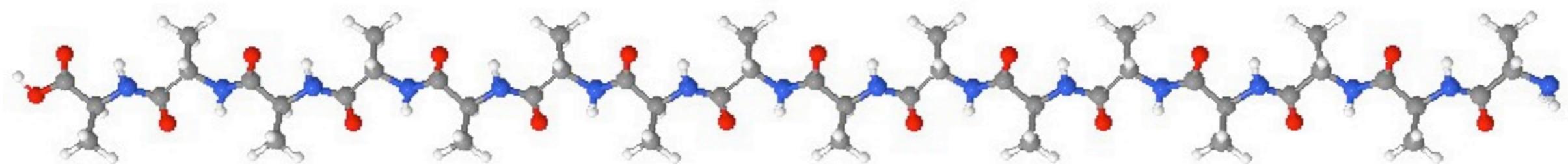
- e.g.: $g_{\text{atom}} = \frac{\rho_{\text{atom}}(r)}{r^2}$ (Delley 1990)

many alternatives:

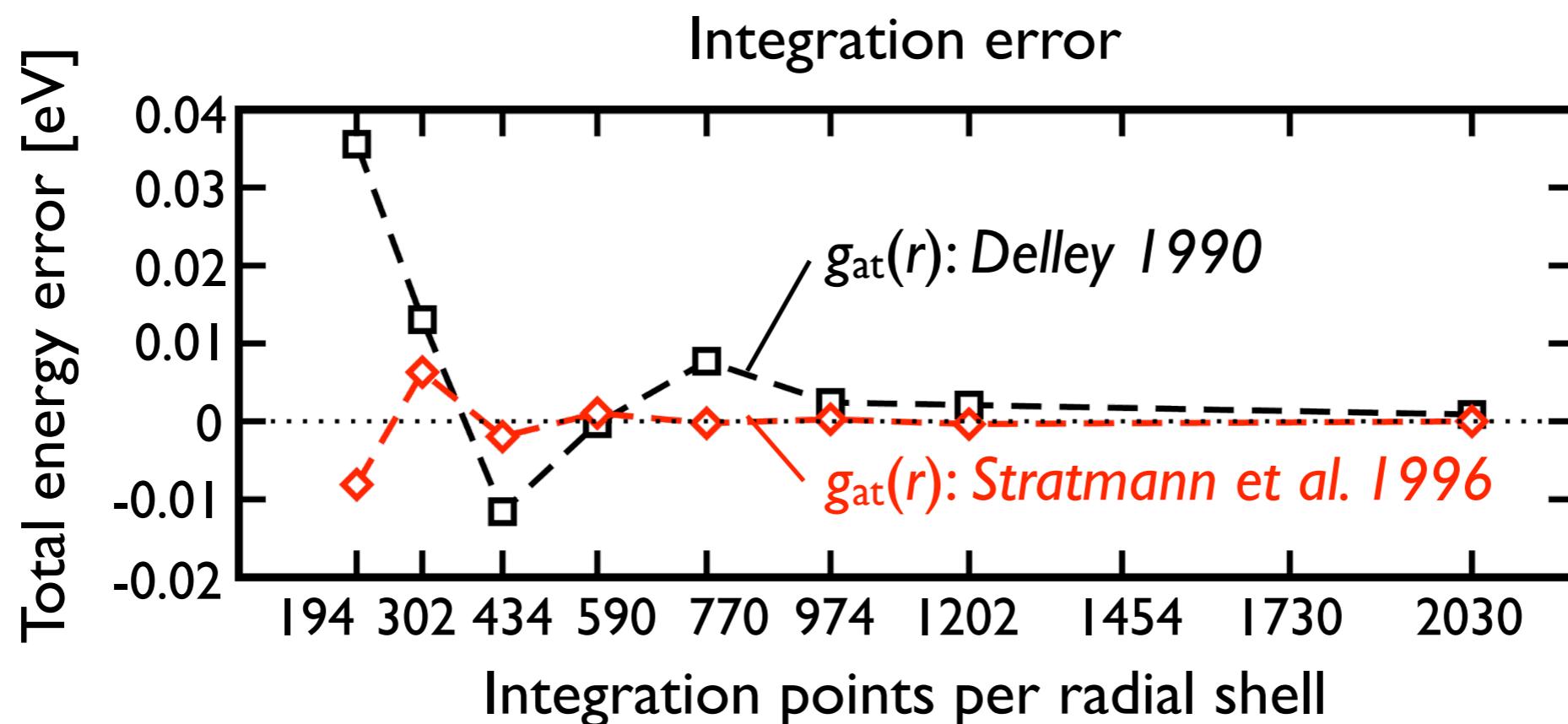
Becke 1988, Stratmann 1996, Koepernik 1999, ...



Integration in Practice: Large Systems, Small Errors!



Fully extended Polyalanine peptide molecule 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)

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

Delley
JCP 92,
508 (1990)

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

-
- Classical electrostatics:

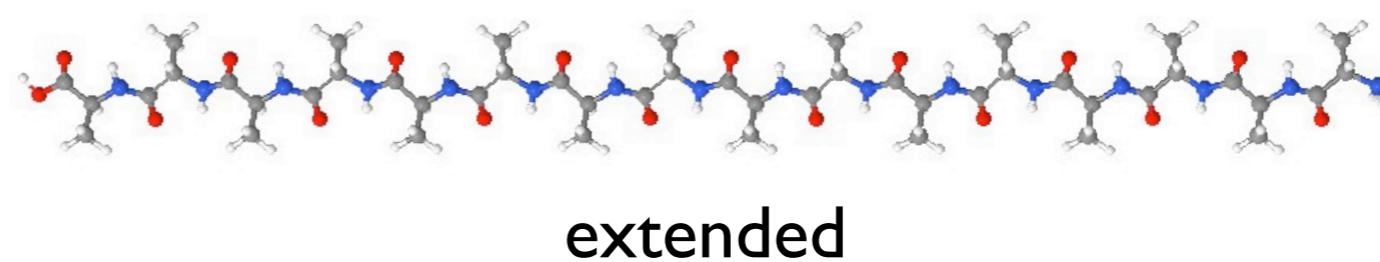
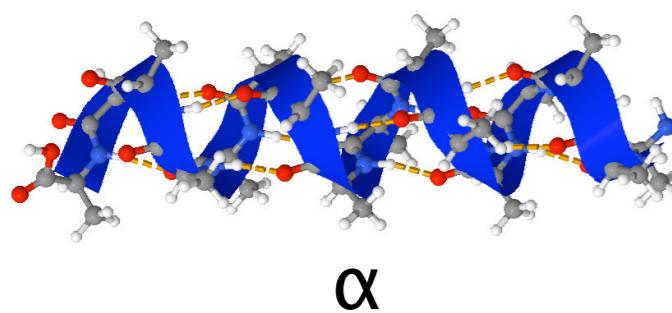
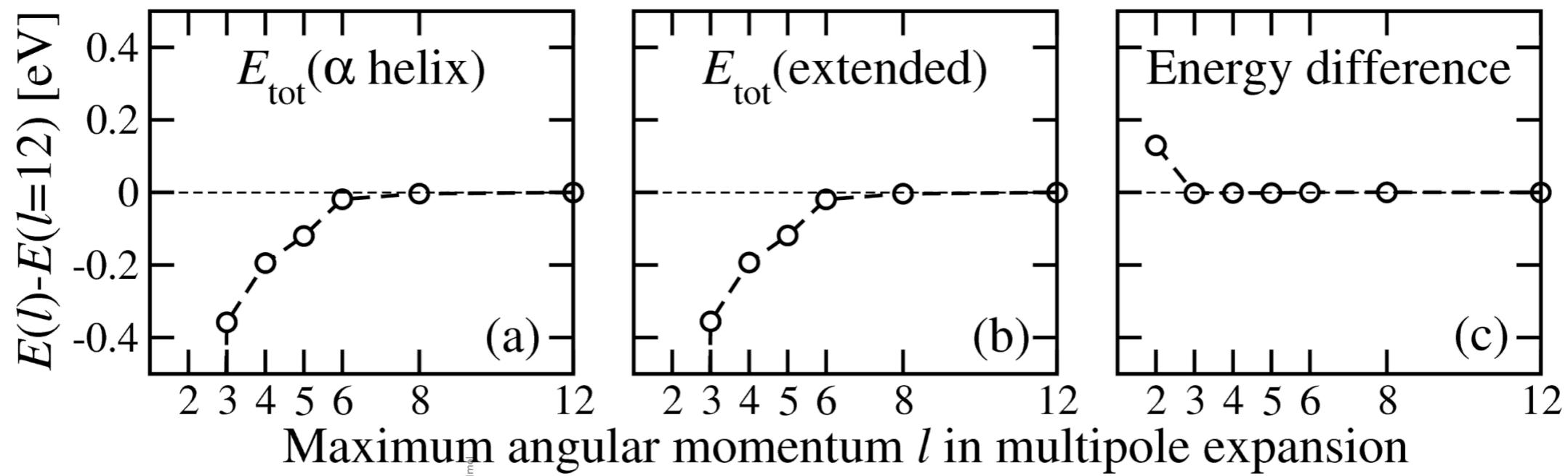
$$v_{\text{es}}(\mathbf{r}) = \sum_{\text{atoms}} \sum_{\mathbf{lm}}^{l_{\max}} v_{\text{atom},lm}(|\mathbf{r} - \mathbf{R}_{\text{atom}}|) Y_{lm}(\Omega_{\text{atom}})$$

Electrostatics: Multipole expansion

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

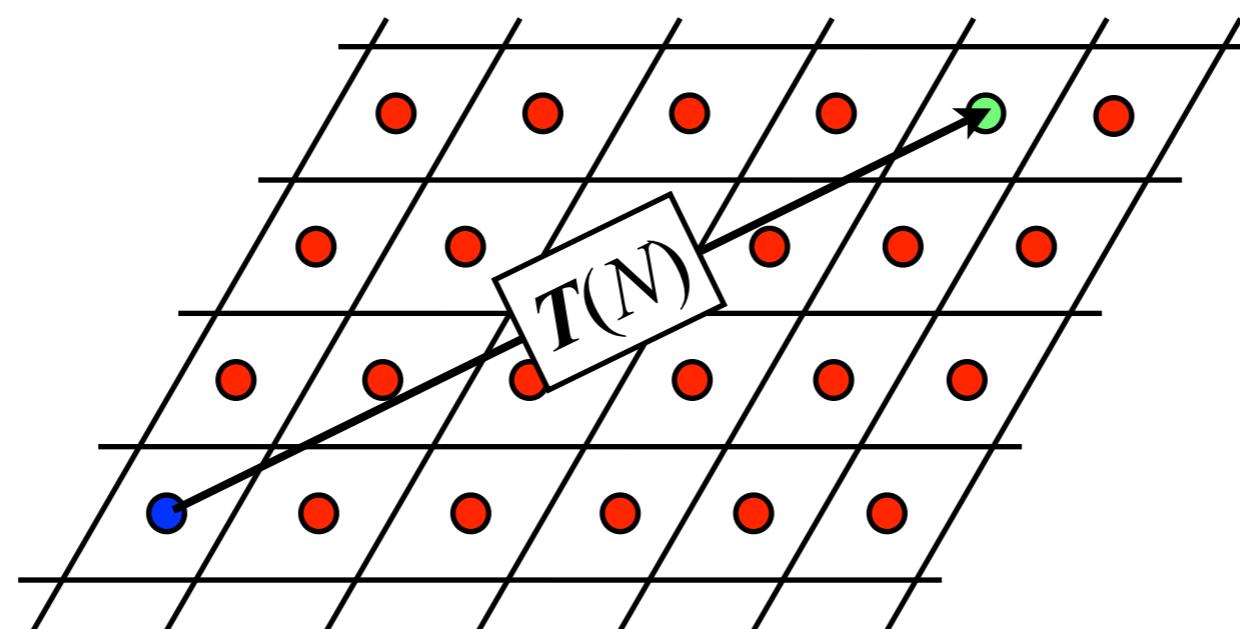
Polyalanine Ala₂₀, DFT-PBE (203 atoms)

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



Periodic systems

see C. Ratsch
Tue. 9:00



- Formally: Bloch-like basis functions

$$\chi_{i,k} = \sum_N \exp[i\mathbf{k}\cdot\mathbf{T}(N)]\varphi_i[\mathbf{r} - \mathbf{R}_{\text{atom}} + \mathbf{T}(N)]$$

\mathbf{k} : “Crystal momentum” = Quantum number in per. systems

- Long-range Hartree potential: Ewald's method (1921)

$$v_{\text{atom},lm}(r) \rightarrow v_{\text{atom},lm}(r) - \underbrace{v_{\text{atom},lm}^{\text{Gauss}}(r)}_{G} + \sum_G e^{iGr} FT[v_{\text{atom},lm}^{\text{Gauss}}]$$

short-ranged real-space part - $O(N)$

e.g., Saunders et al. 1992; Birkenheuer 1994; Delley 1996; Koepernik 1999; Trickey 2004; etc.

Relativity

Non-relativistic QM: Schrödinger Equation

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

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

Relativistic QM: Dirac Equation

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

... simply rewrite:

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

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

Simple Approximation to Scalar Relativity

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

ZORA

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

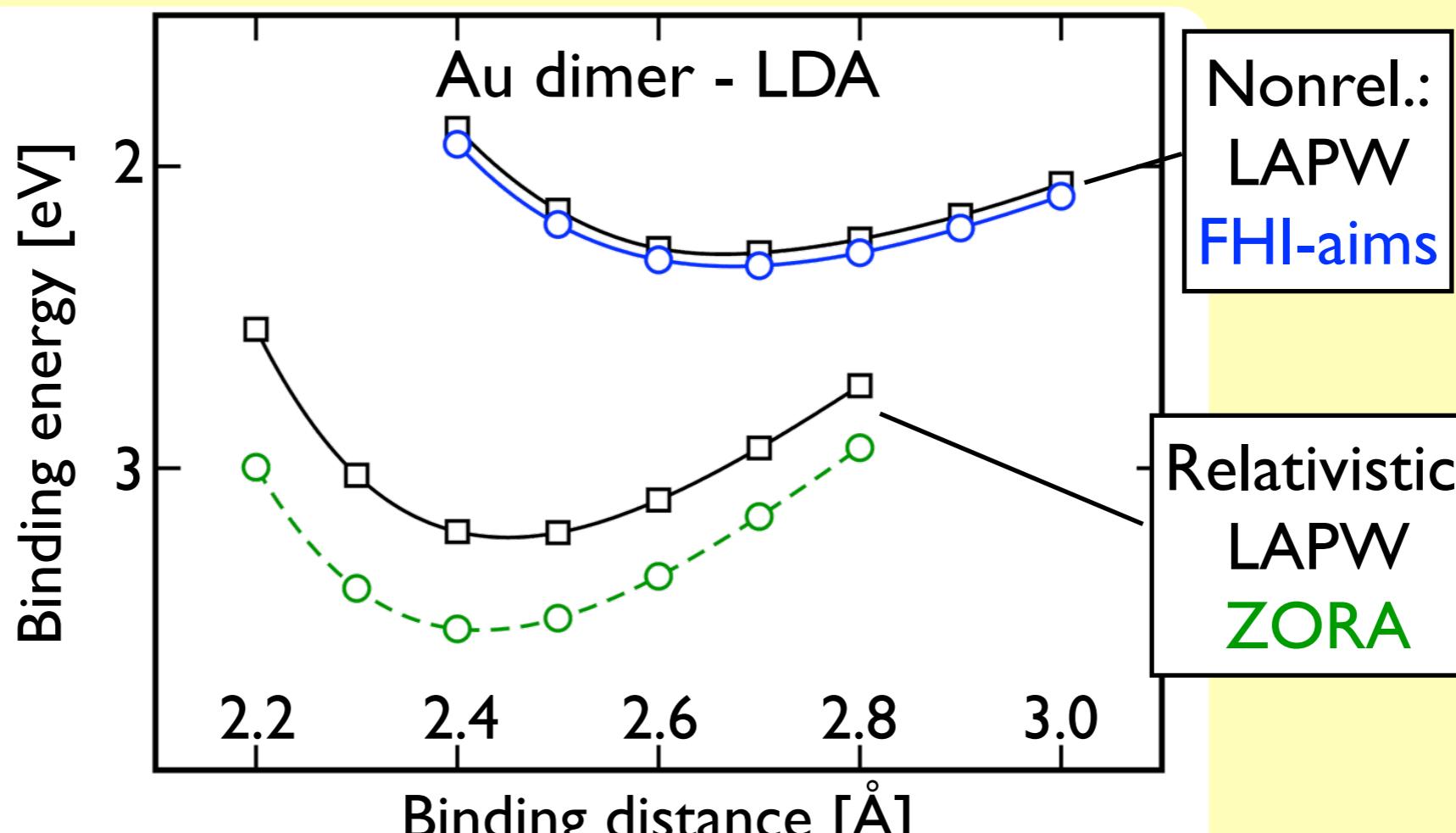
Popular: Zero-order regular approximation (ZORA) [I]
... not gauge-invariant!

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

Simple Approximation to Scalar Relativity

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

ZORA in practice: Harsh approximation (known)



Fixing ZORA

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

ZORA

I. “Atomic ZORA”

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

2. Scaled ZORA

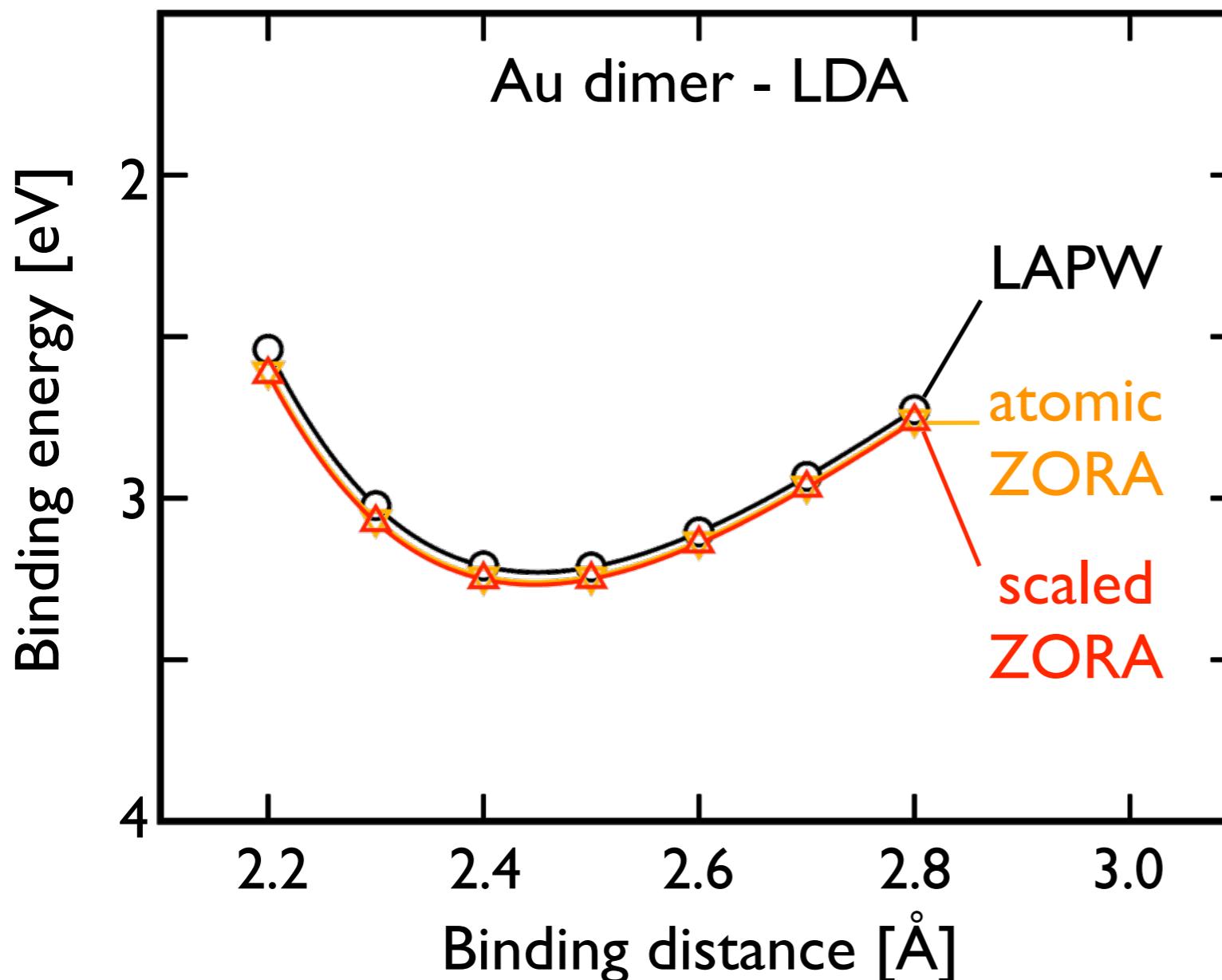
$$\epsilon_{\text{ZORA}}^{\text{scaled}} = \frac{\epsilon_{\text{ZORA}}}{1 + \langle \Phi | \mathbf{p} \frac{c^2}{(2c^2 - V)^2} \mathbf{p} | \Phi \rangle}$$

- No gauge-invariance problem
- Simple total-energy gradients

$$E_{\text{tot}}^{\text{SZ}} = E_{\text{tot}}^{\text{ZORA}} - \sum (\epsilon_{\text{ZORA}} - \epsilon_{\text{ZORA}}^{\text{scaled}})$$

- Formally exact for H-like systems
- Perturbative, based on ZORA

Atomic ZORA and Scaled ZORA in Practice



Au atom: E_{tot} [eV]	
nonrel.	-486,015.94
(at.) ZORA	-535,328.71
sc. ZORA	-517,036.15
Koelling-Harmon	-517,053.45

Viable strategy:

- Geometry optimization, energy differences: atomic ZORA
- If needed: Absolute E_{tot} , core eigenvalues: scaled ZORA

In our own benchmarks, seem to be essentially as accurate as LAPW.

Computational Scaling: Two Sub-Problems

1. Real space grid operations

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

Basis functions, Hamiltonian,
Kohn-Sham potential etc.

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

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

2. Matrix algebra (basis space)

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

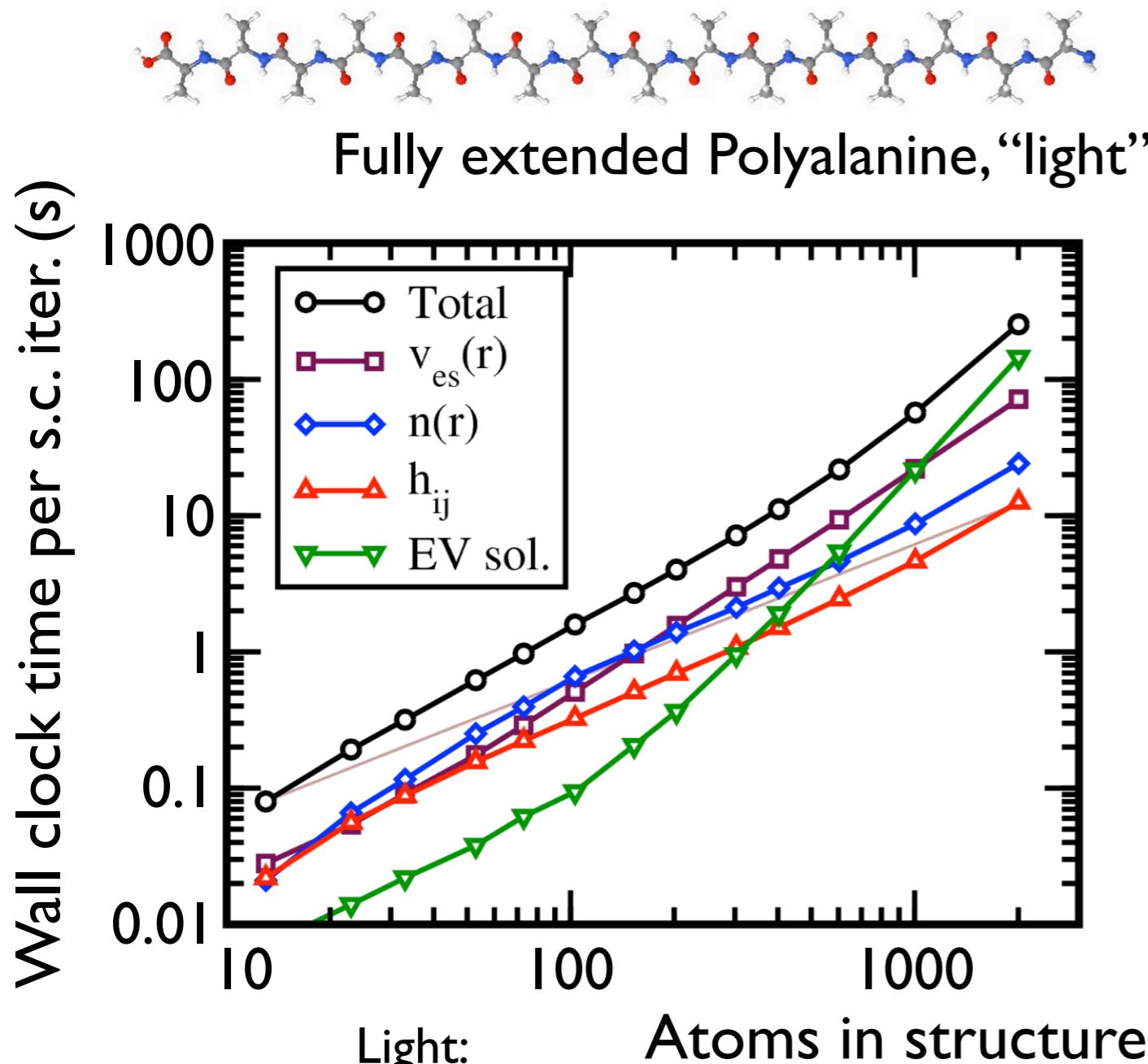
Kohn-Sham eigenvalue problem

“Conventional” solvers (Lapack-like):

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

How far can we push such solvers?

Computational Scaling: CPU Time With System Size



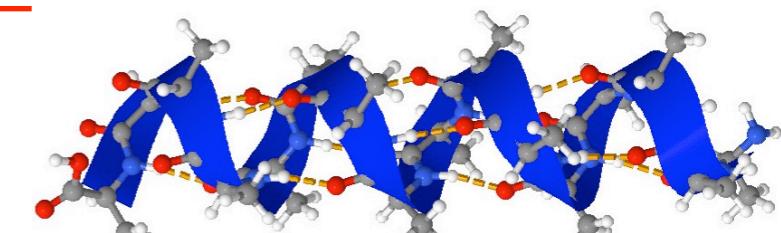
Basis	tier I
I_{Hartree}	4
radial shells	24-36
pts. per shell	302 max.
Cutoff width	5 Å

32 CPUs
standard Infiniband/Xeon cluster
Benchmarks: W. Jürgens / FHI

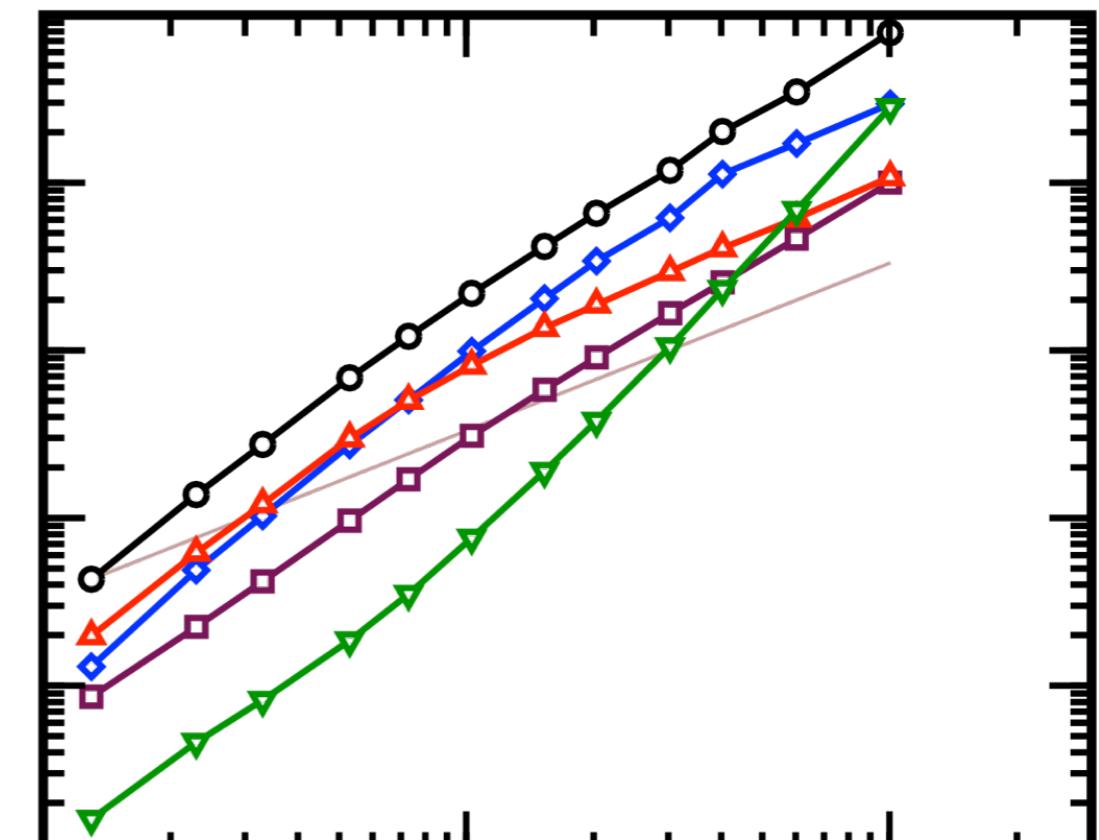
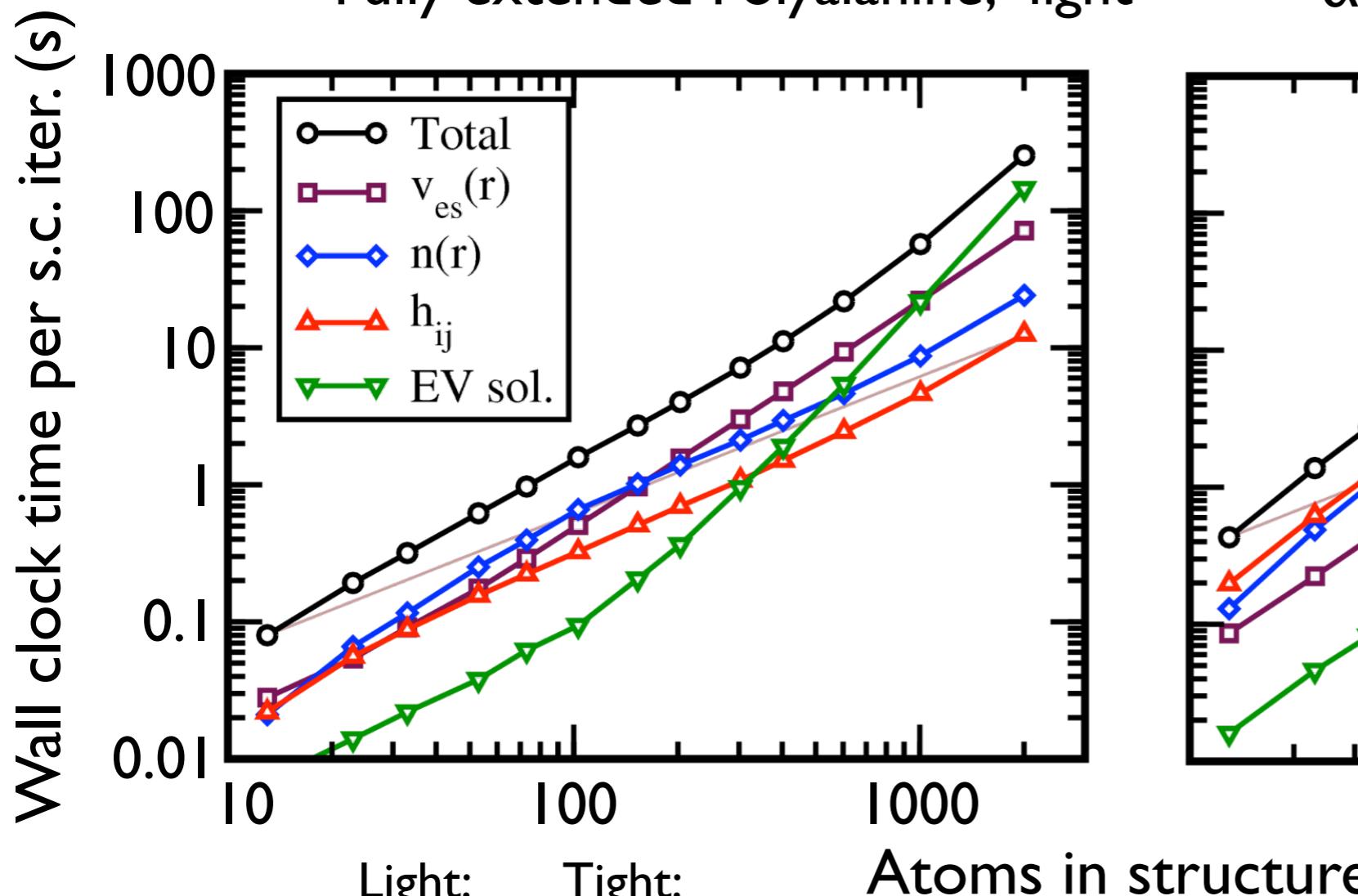
Computational Scaling: CPU Time With System Size



Fully extended Polyalanine, “light”



α -helical Polyalanine, “tight”



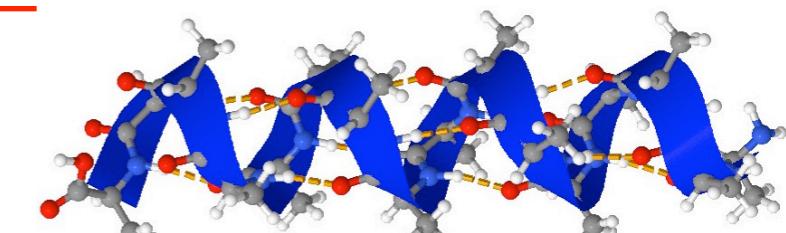
	Light:	Tight:	Atoms in structure
Basis	tier I	tier2	
I_{Hartree}	4	6	
radial shells	24-36	49-73	
pts. per shell	302 max.	434 max.	
Cutoff width	5 Å	6 Å	

32 CPUs
standard Infiniband/Xeon cluster
Benchmarks: W. Jürgens / FHI

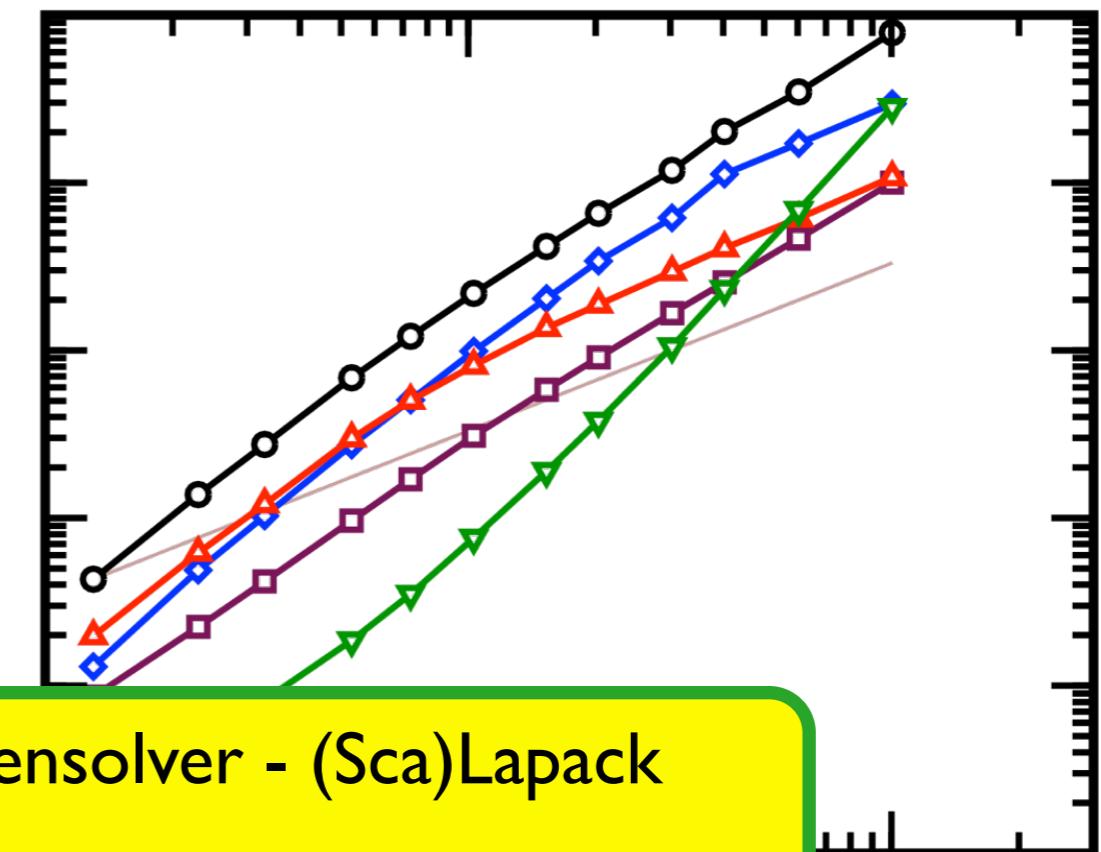
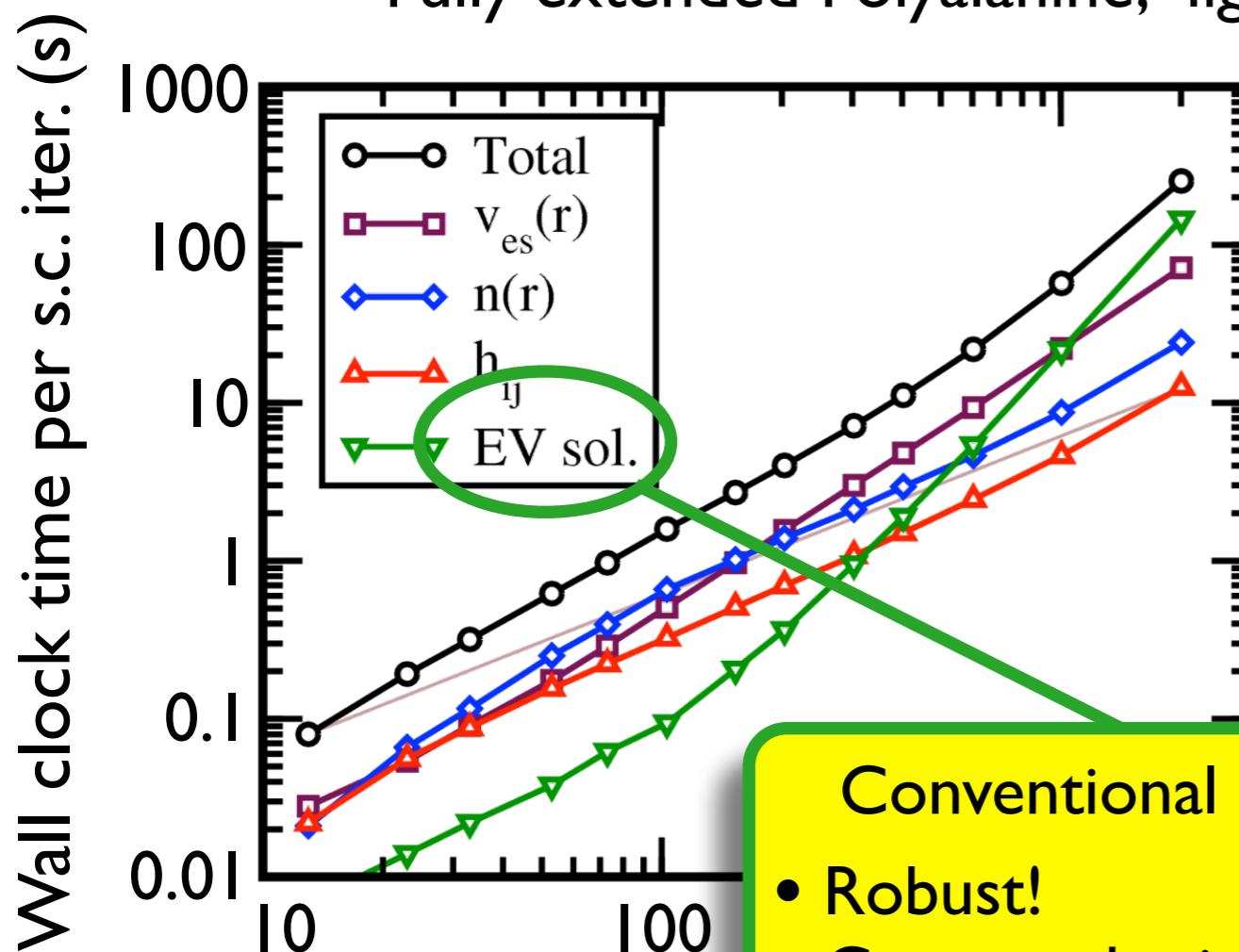
Computational Scaling: CPU Time With System Size



Fully extended Polyalanine, “light”



α -helical Polyalanine, “tight”



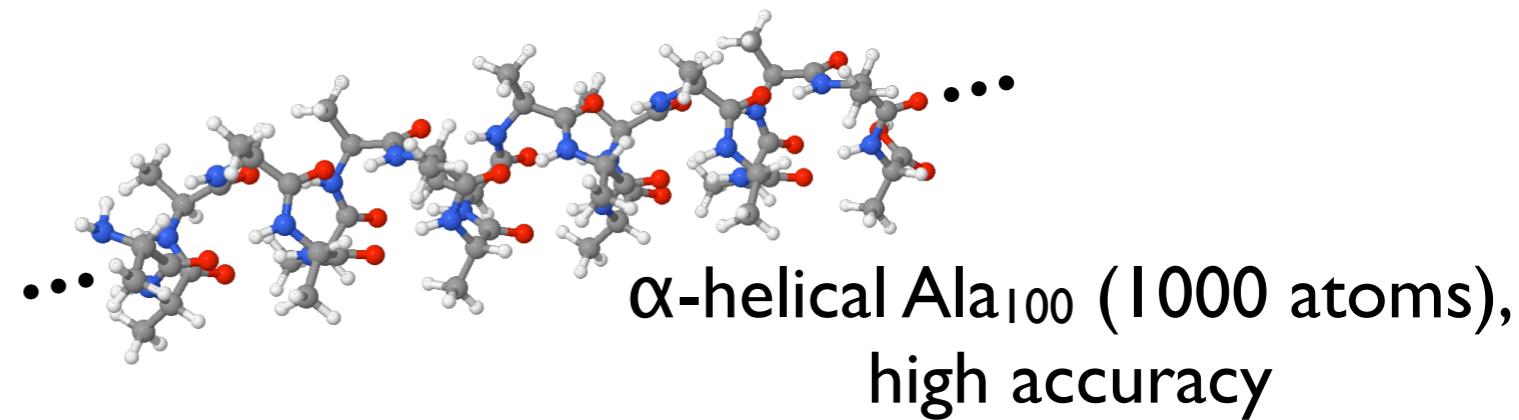
Conventional eigensolver - (Sca)Lapack

- Robust!
- Compact basis sets: Small matrices
- **but $O(N^3)$ scaling - relevant ≈ 100 s of atoms**
- **1,000s of CPUs: Scaling bottleneck?**

Basis	Light: tier I	Tight: tier II
I _{Hartree}	4	6
radial shells	24-36	49-
pts. per shell	302 max.	434 max.
Cutoff width	5Å	6Å

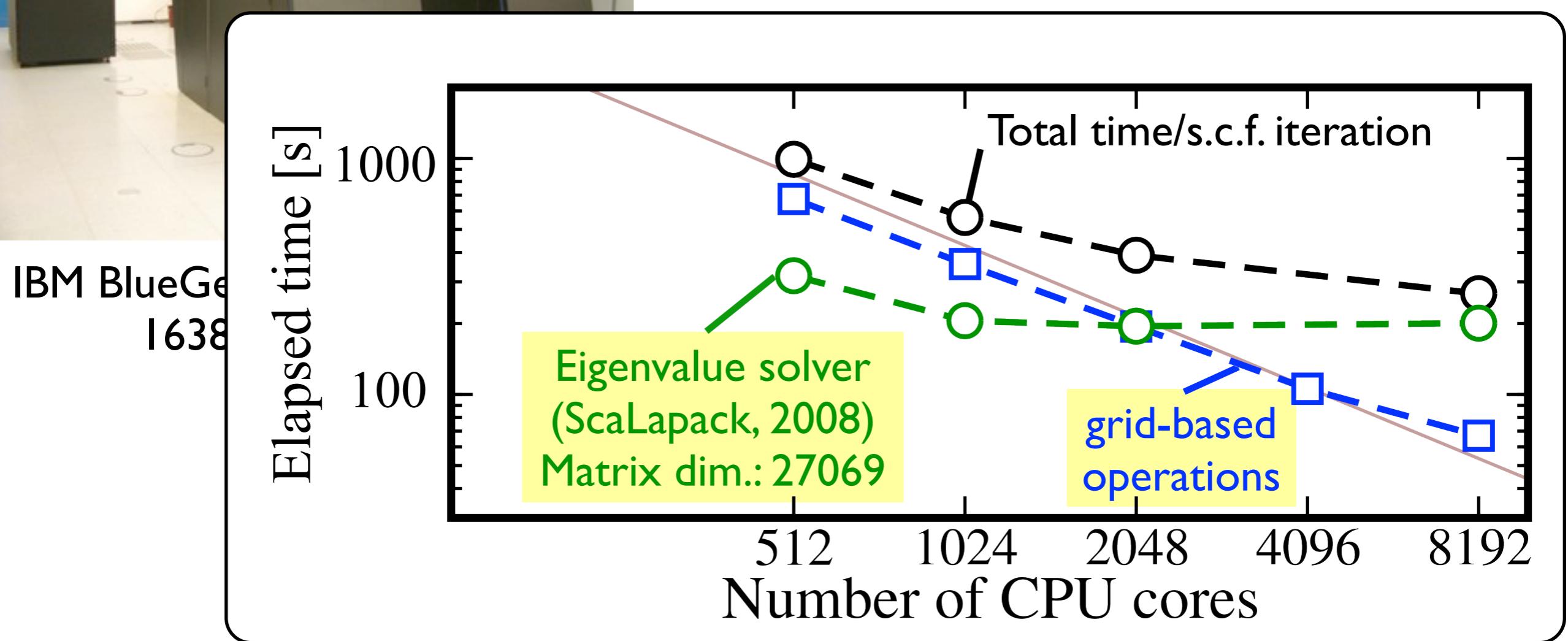
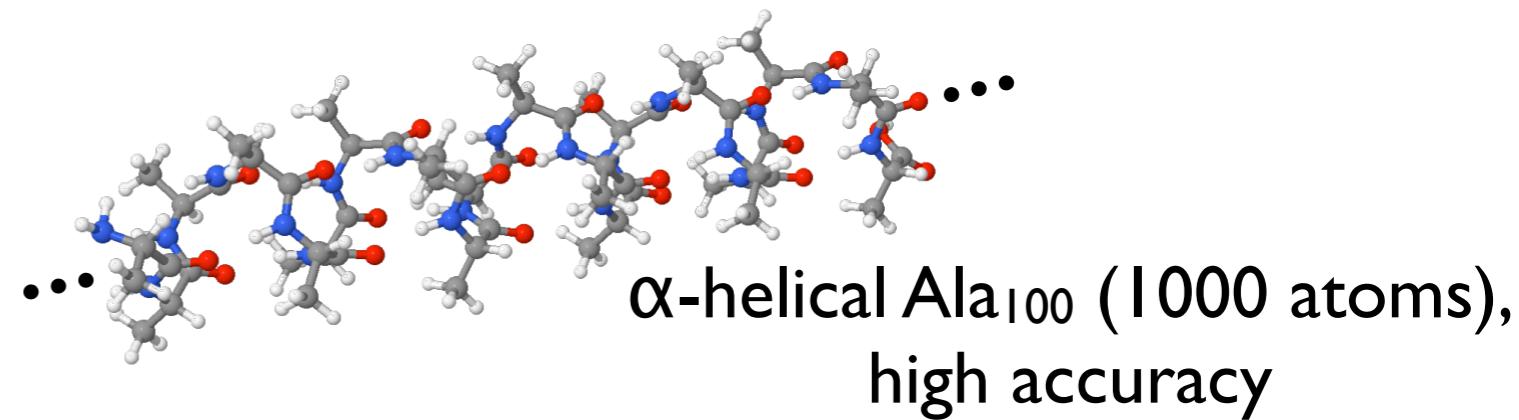
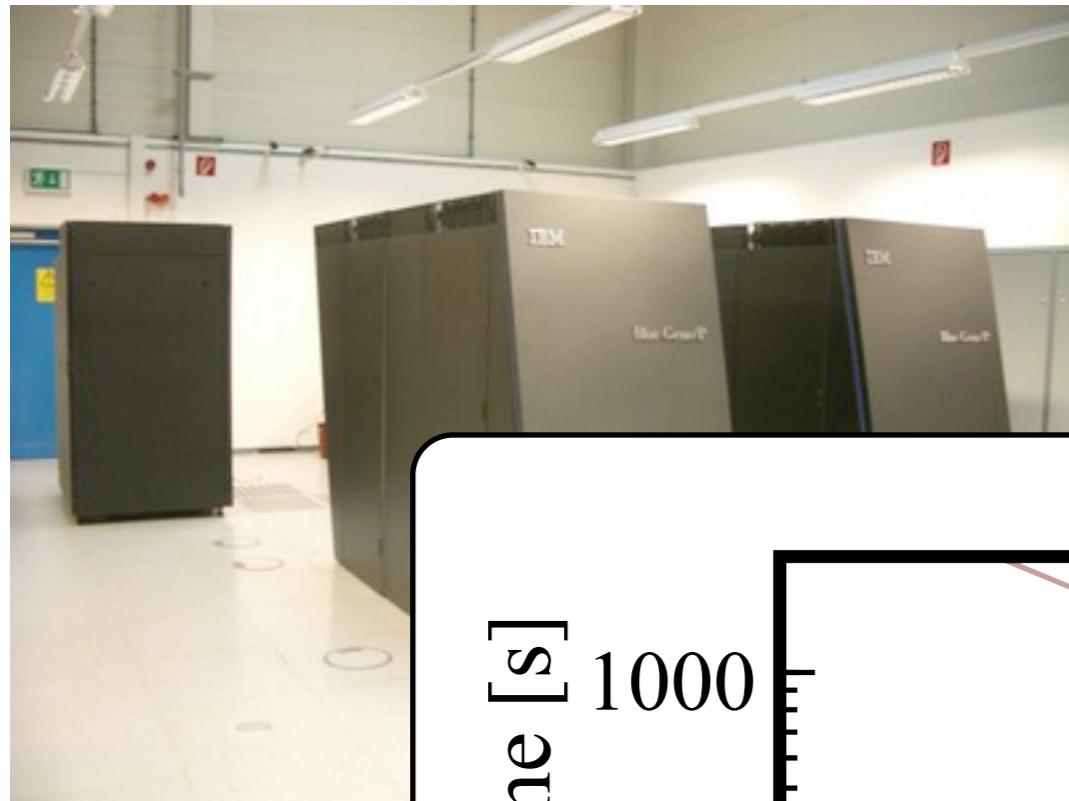
standard Intel(R)/Xeon cluster
Benchmarks: W. Jürgens / FHI

Parallel Eigenvalue Solvers - the Problem



IBM BlueGene (MPG, Garching)
16384 CPU cores

Parallel Eigenvalue Solvers - the Problem



A Massively Parallel Dense Eigensolver: “ELPA”

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

Given a matrix H and metric S (dimension N),
find M eigenvalue/eigenvector pairs ϵ_k/c_k

Original Goals:

- Scalable, Scalapack-compatible “drop-in enhancement”
- Pure MPI-based implementation
- Detailed rewrite based on proven robust/general algorithms

Today:

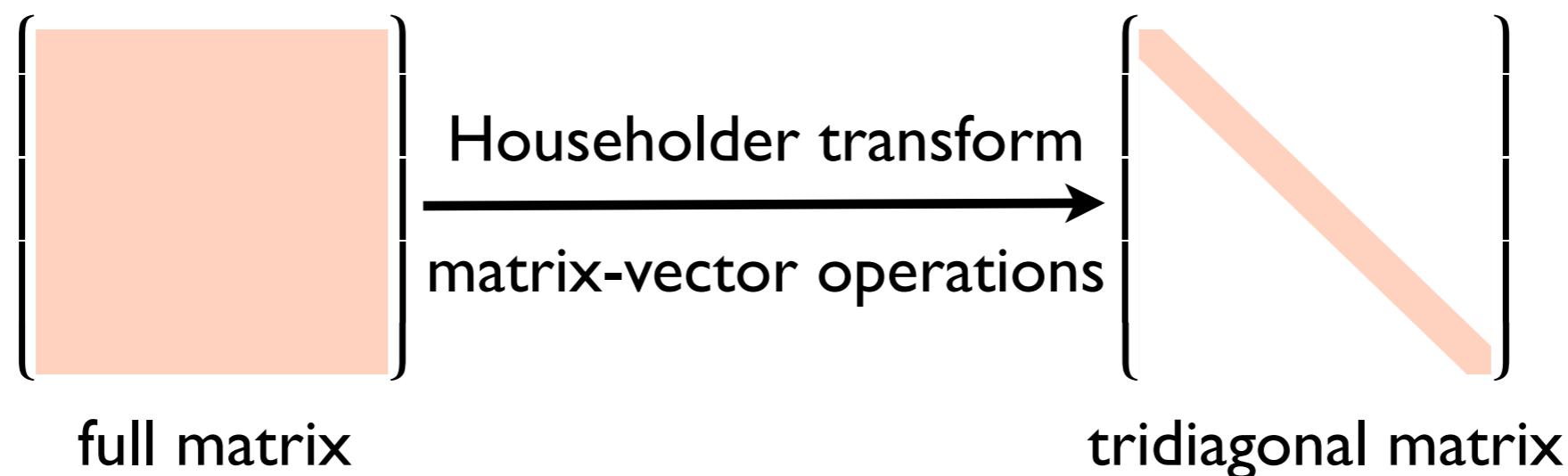
- Standalone open-source (LGPL) library,
used in other major codes (cp2k, Quantum Espresso, DMol3, ...)
- Optional support for shared-memory systems (OpenMP)
- Integration into broader infrastructure “beyond $O(N^3)$ bottleneck”

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

Algorithmic Improvement: 2-Step Tridiagonalization

Chief bottleneck before ELPA: Tridiagonalization

“Conventional” reduction:

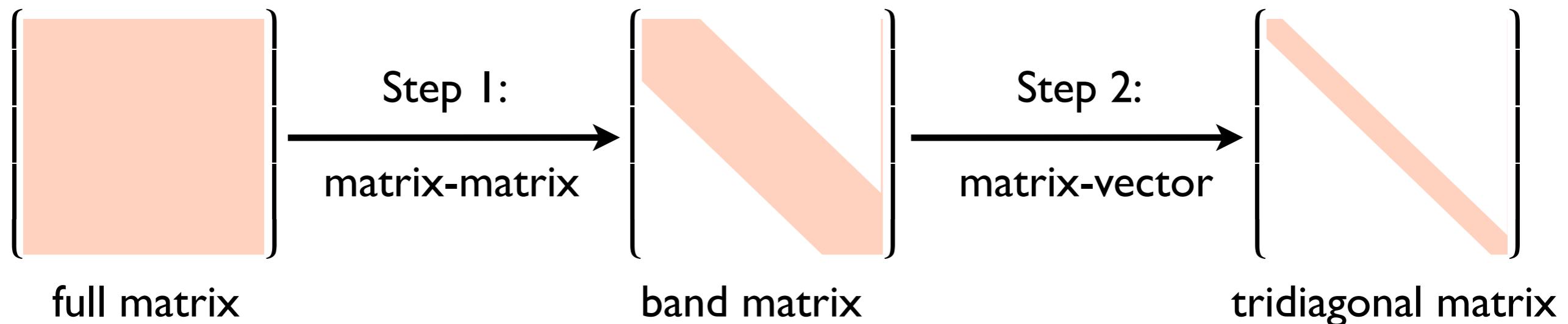


Algorithmic Improvement: 2-Step Tridiagonalization

Solution

“Two-step” reduction:

C. Bischof, B. Lang, X. Sun, ACM Trans. Math. Software **26**, 581 (2000).

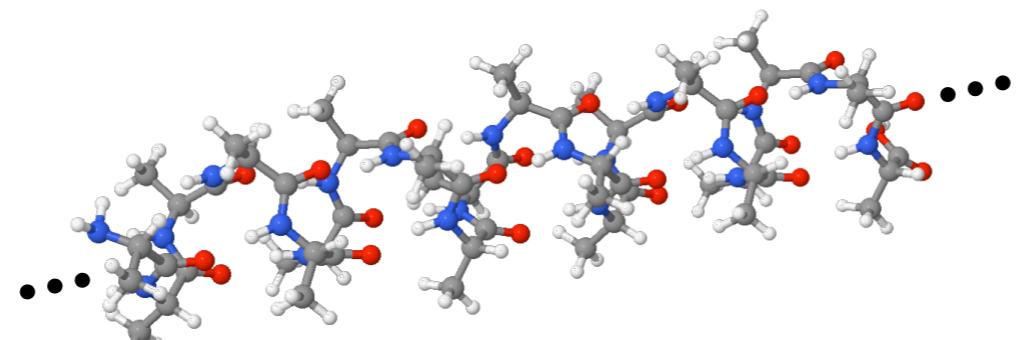


But extra back transform necessary - benefit shrinks for M approaching N

Massively parallel two-step tridiagonalization:

- 2-dimensional data layout for eigenvectors
- Heavily optimized backtransform steps for eigenvectors (adaptive data layout, architecture-specific linear algebra kernels - cache blocking)

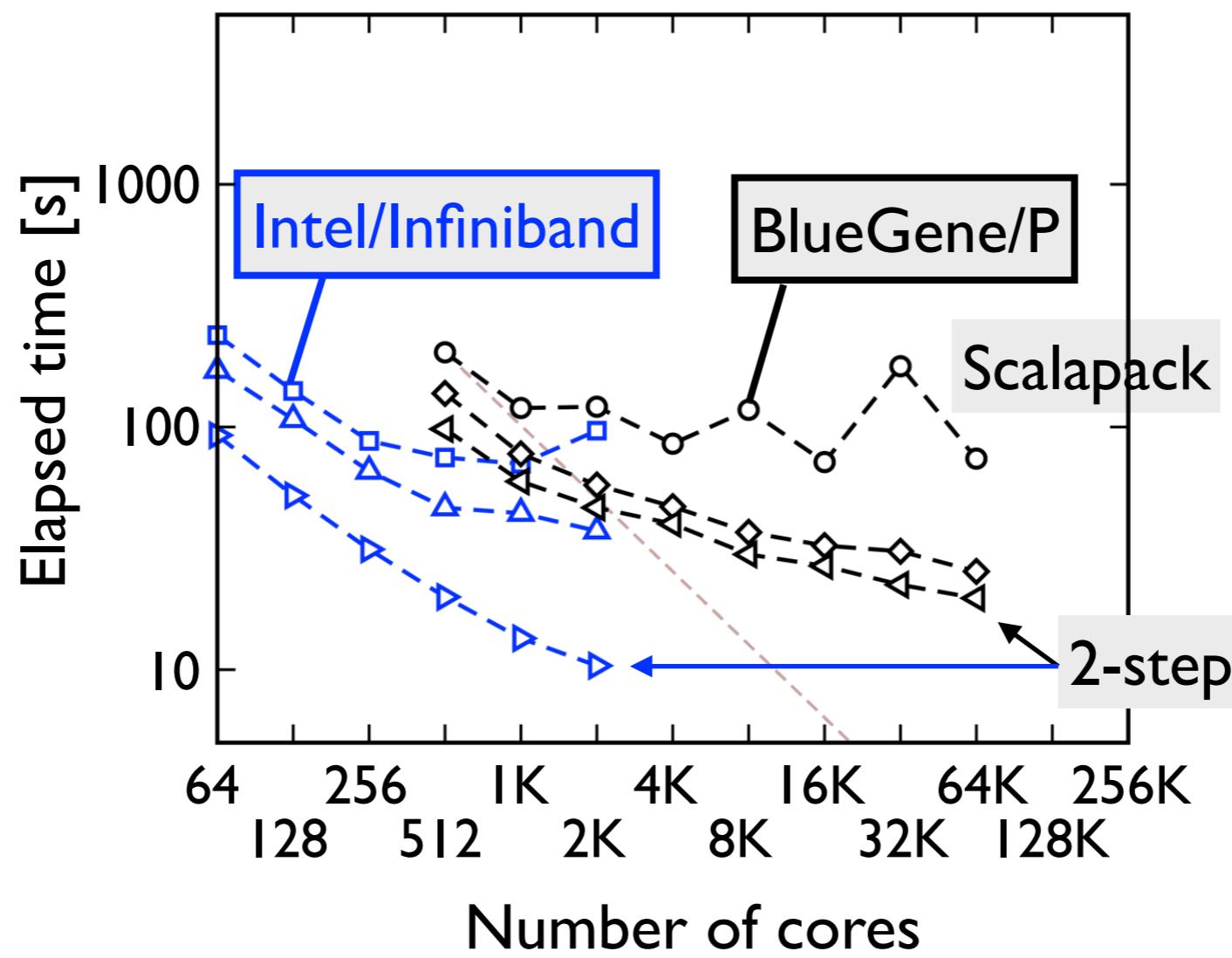
ELPA, Two-Step Solver



α -helical Polyalanine Ala₁₀₀

N=27069, M=3410

NAO basis set (FHI-aims)

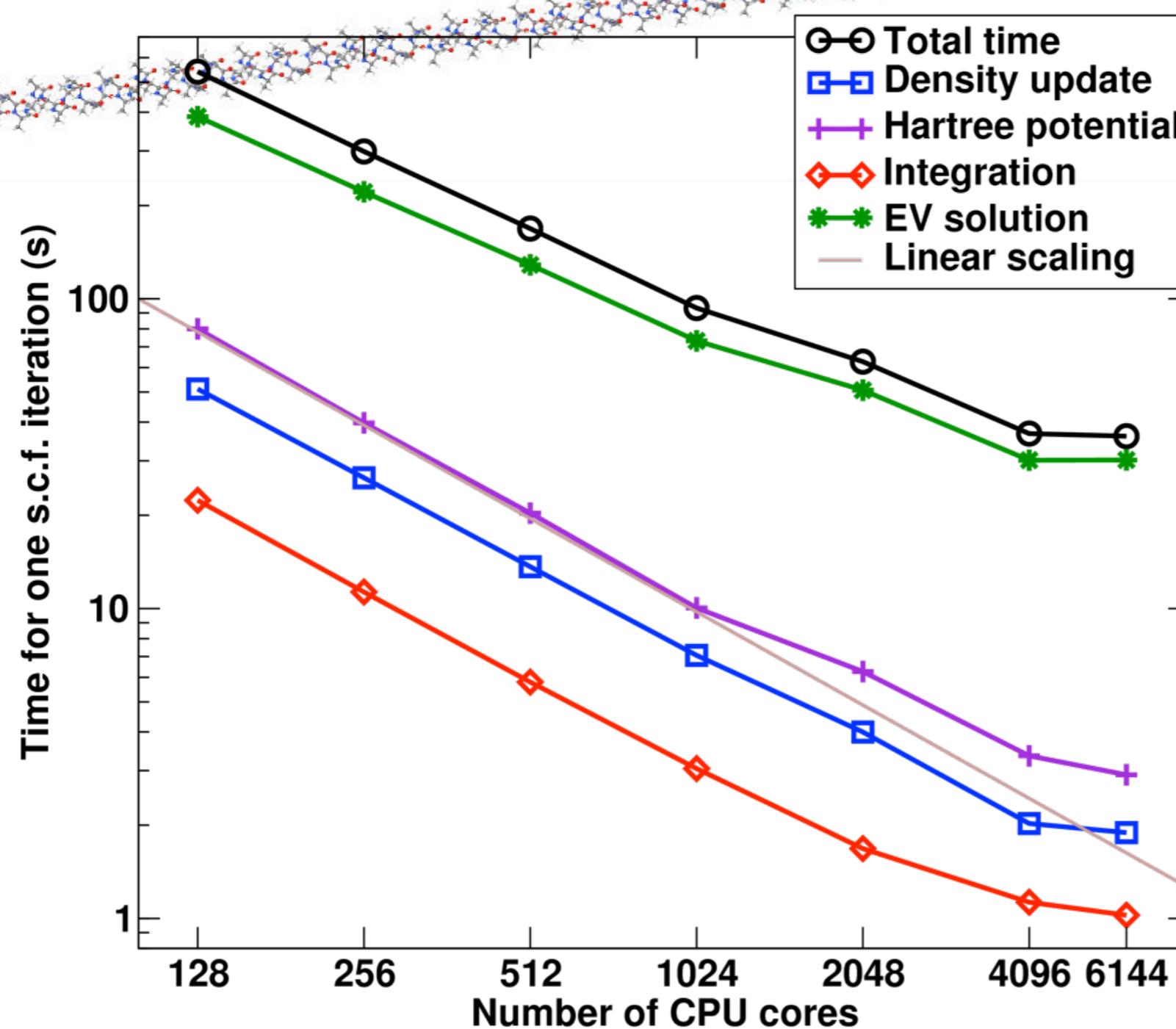


Parallel Scalability - Cray XC30, 2013 (Ville Havu, Helsinki)

Trial system:

Model biomolecule

(similar for periodic systems)



α -helical Polyalanine Ala_{200}
2003 atoms, “tight”
 $N=54138, M=6820$
NAO basis set (FHI-aims)

Beyond Kohn-Sham: Hartree-Fock and hybrid functionals

$$E = E[n] = T[n] + V[n] + E_{\text{es}}[n] + E_{\text{xc}}[n]$$

Hohenberg-Kohn,
Kohn-Sham, etc.

LDA, GGA, mGGA etc.

$$E_{\text{xc}}[n] = E_{\text{x}}^{\text{loc}}[n] + E_{\text{c}}^{\text{loc}}[n]$$

S. Levchenko
Fri 09:00h

Nice, clean, tractable, and sadly often insufficient

Becke,
Burke,
Perdew,
Ernzerhoff,
others

$$E_{\text{xc}}[n] = (1 - \alpha)E_{\text{x}}^{\text{loc}}[n] + \alpha E_{\text{x}}^{\text{HF}} + E_{\text{c}}^{\text{loc}}[n]$$

“Hybrid functionals” - certainly legal

Unfortunately:

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

Naively, $O(N^4)$ - four-index Coulomb matrix, long ranged, even hard to store
OK for small molecules, impractical for solids ...

Our Preferred Route to $(ij|kl)$: Resolution of Identity (RI)

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

Boys/Shavitt, Whitten
Dunlap, ...
many others

$(ij|kl)$ is too much work (even non-periodic) - simplify?

Basis pair product space

$$\{\varphi_i(\mathbf{r}) \cdot \varphi_j(\mathbf{r})\}$$

must be overcomplete if

$$\{\varphi_i(\mathbf{r})\}$$

itself approaches completeness

Solution (quantum chemistry):

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

↑
smaller auxiliary basis set $\{P_{\mu}\}$

In finite systems, “RI-V”:

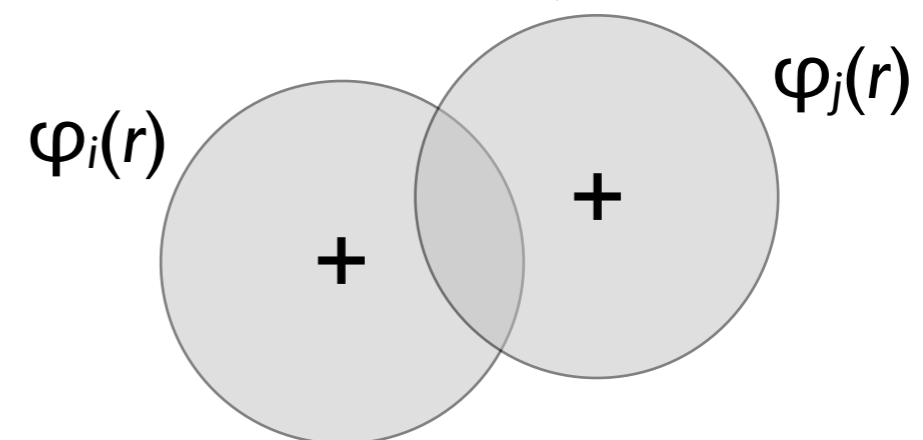
$$C_{ij}^{\mu} = \sum_{\nu} (ij|\nu) V_{\nu\mu}^{-1}$$

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

Accurate [I], but *delocalizes* C!

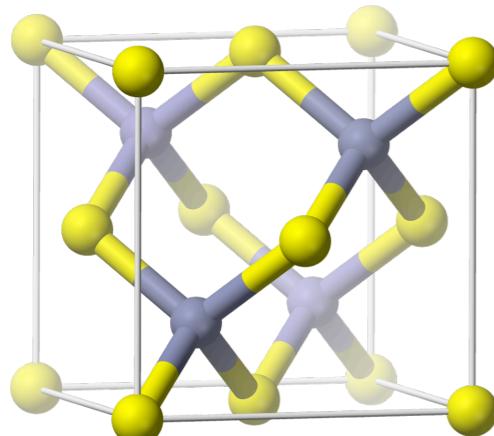
(Much) better scaling: Localized RI

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



Accuracy: Periodic hybrid functionals

Cohesive properties, bulk semiconductors



		Si		
PBE0		a [Å]	B_0 [Mbar]	E_{coh} [eV]
FHI-aims, <i>tight</i>		5.439	0.99	4.553
Ref. [1]		5.433	1.00	4.555
HSE06				
FHI-aims, <i>tight</i>		5.446	0.98	4.527
Ref. [2]		5.435	0.98	4.582
HSE06		GaAs		
FHI-aims, <i>tight</i>		5.695	0.71	3.150
Ref. [2]		5.687	0.71	3.149
HSE06		Ge		
FHI-aims, <i>tight</i>		5.700	0.71	3.761
Ref. [3]		5.703	0.73	n/a

Essentially linear scaling
exchange operator:
*Levchenko, Ren, Wieferink,
Johanni, Blum, Rinke,
Scheffler 2013*

- [1] J. Paier *et al.*, J. Chem. Phys. **124**, 154709 (2006).
- [2] J. Paier *et al.*, J. Chem. Phys. **125**, 249901 (2006).
- [3] A. Stroppa *et al.*, PRB **83**, 085201 (2011).

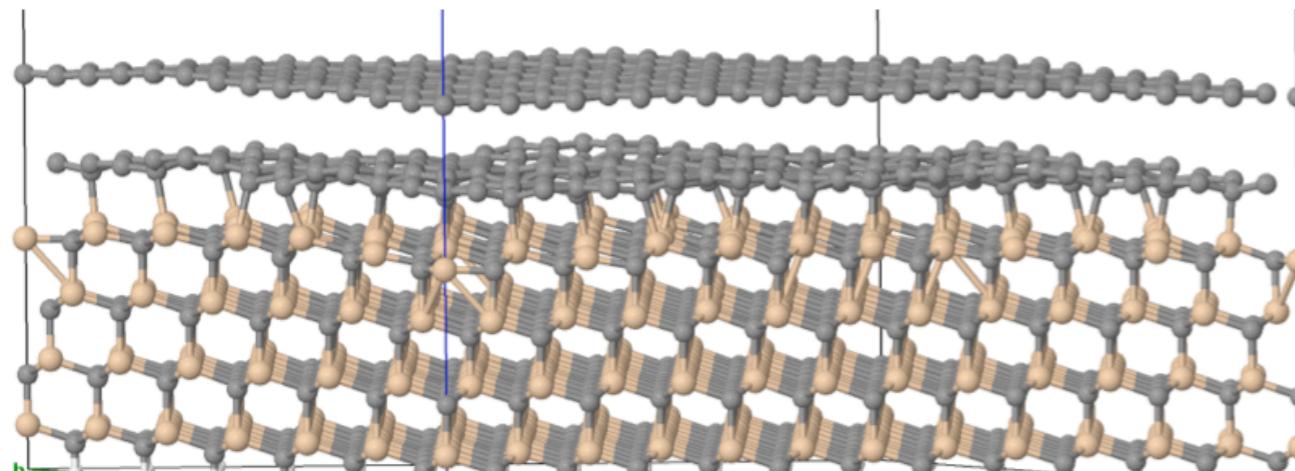
Is This a “Stable” Surface Phase?*



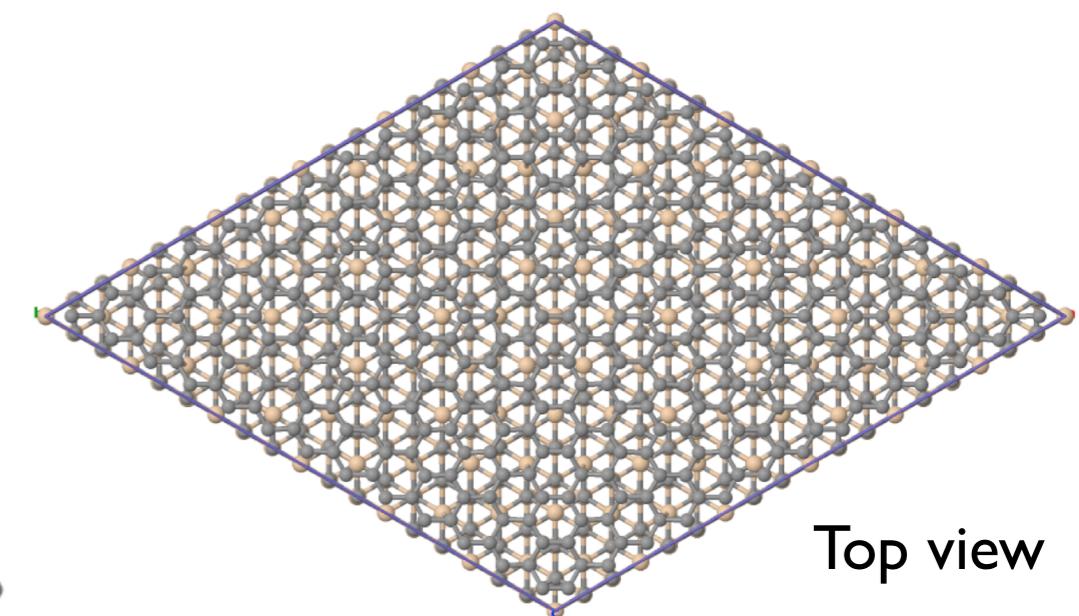
Graphene on SiC(0001)

*van Bommel, Crombeen, van Tooren,
Surf. Sci. 1975
many others*

Lydia Nemec



(13x13) graphene on
SiC(0001)-(6 $\sqrt{3}$ ×6 $\sqrt{3}$)R30°



Top view

338 atoms per C plane
216 atoms per SiC plane
Surface energy?
Electronic structure?

...

* under some conditions ...

Ab Initio Thermodynamics for Si-Side Graphene/SiC

Nemec, Blum, Rinke, Scheffler, PRL 111, 065502(2013).

Thermodynamic stability criterion for competing surface phases:

$$E_{\text{surf}} = \frac{1}{A} [E_{\text{slab}} - N_{\text{Si}}\mu_{\text{Si}} - N_{\text{C}}\mu_{\text{C}}]; \quad E_{\text{SiC}} = \mu_{\text{Si}} + \mu_{\text{C}}$$

$$\mu = \mu(T, p_{\text{C}}, p_{\text{Si}})$$

Externally (experimentally)
controllable

Stability boundaries:

Bulk SiC more stable than elemental Si, C

$$\mu_{\text{C}} \leq E_{\text{C}}^{\text{bulk}}$$

$$\mu_{\text{Si}} \leq E_{\text{Si}}^{\text{bulk}}$$

Reuter, Scheffler, PRB 65, 035406 (2001).

Total energies, full relaxation from first principles:

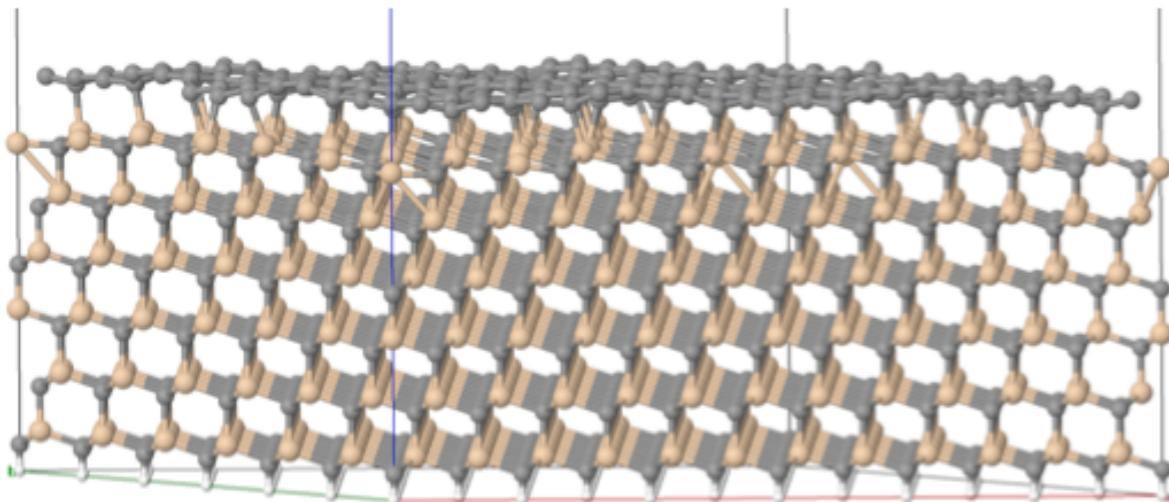
- six-bilayer SiC slabs + surface planes
- full relaxation, “tight” numerical settings (C: tier 2, Si: tier 1+gd)
- Density functional: “GGA-PBE+vdW” [I] - straight LDA/GGA not enough.

[I] Tkatchenko, Scheffler, Phys. Rev. Lett. 102, 073005 (2009)

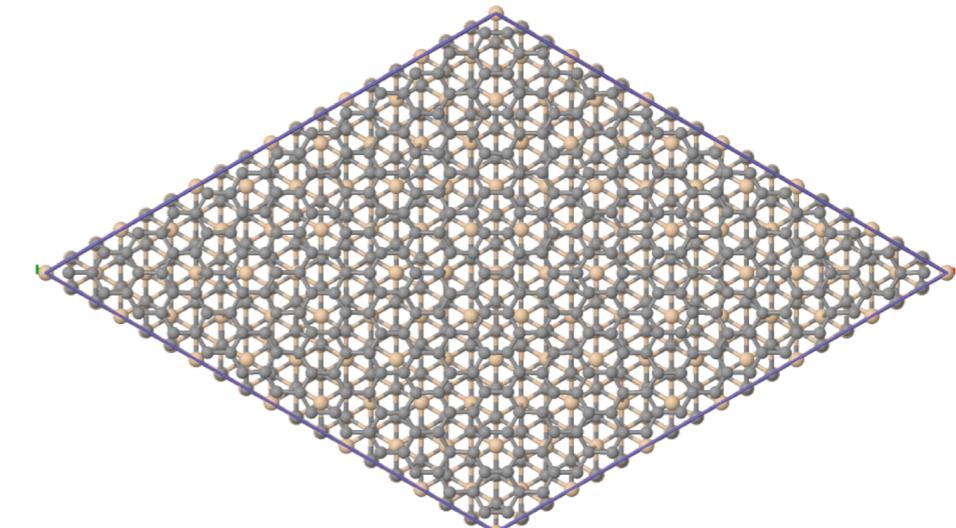
Ab Initio Thermodynamics for Si-Side Graphene/SiC

Nemec, Blum, Rinke, Scheffler, PRL 111, 065502(2013).

$(6\sqrt{3}\times 6\sqrt{3}) \text{SiC}(111) + (13\times 13) \text{graphene}$:



ZLG, side view



Commensurate growth -
nearly strain-free (0.2%), but large:
1742 atoms (ZLG) - 2756 atoms (3LG)

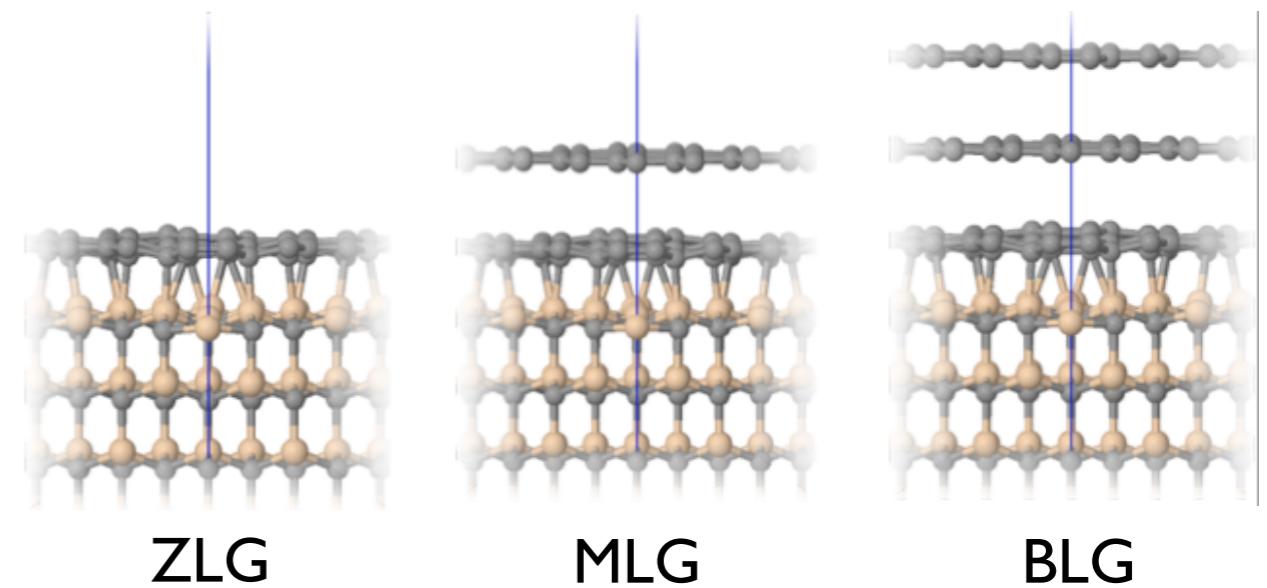
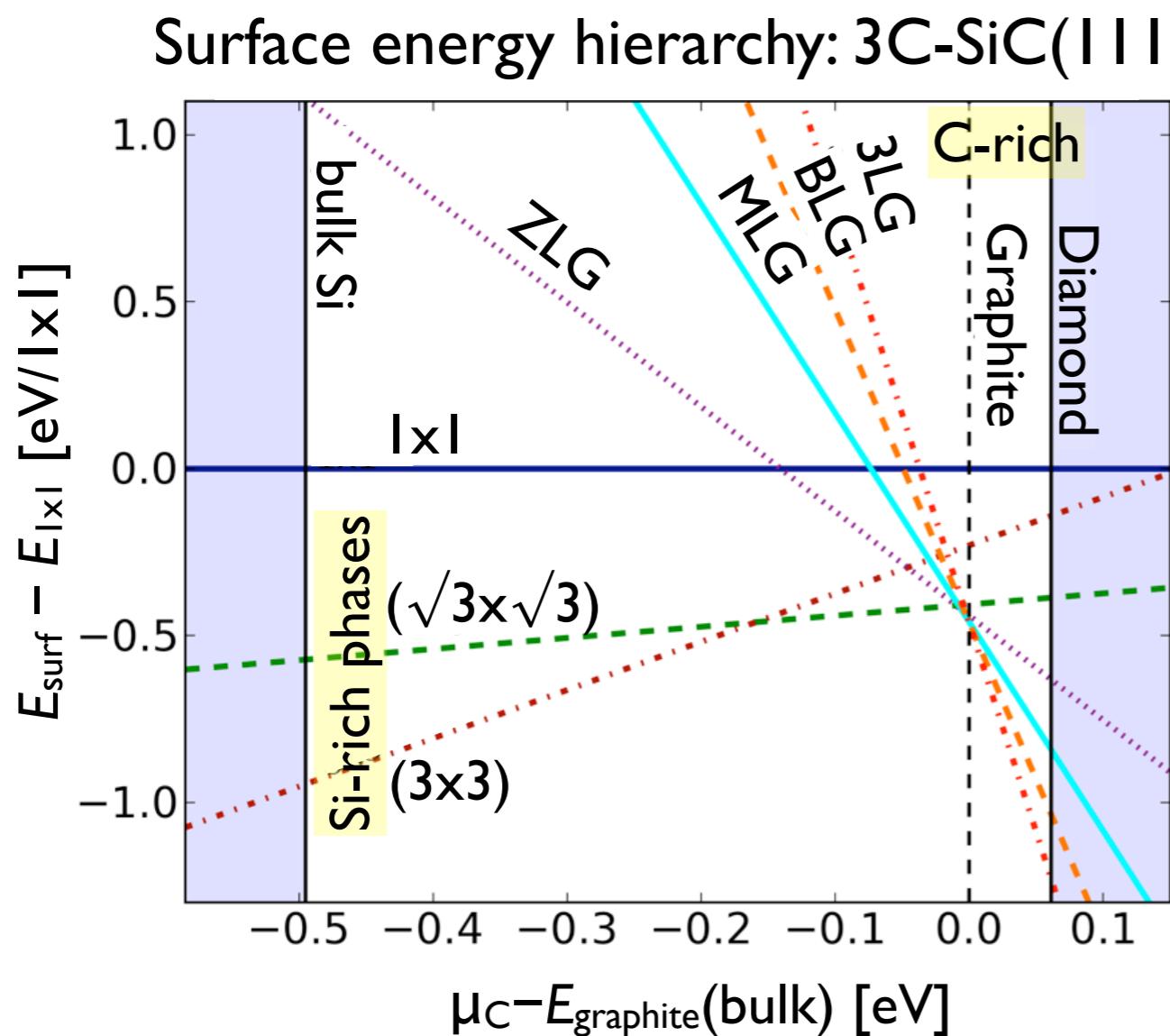
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[1] Tkatchenko, Scheffler, Phys. Rev. Lett. 102, 073005 (2009)

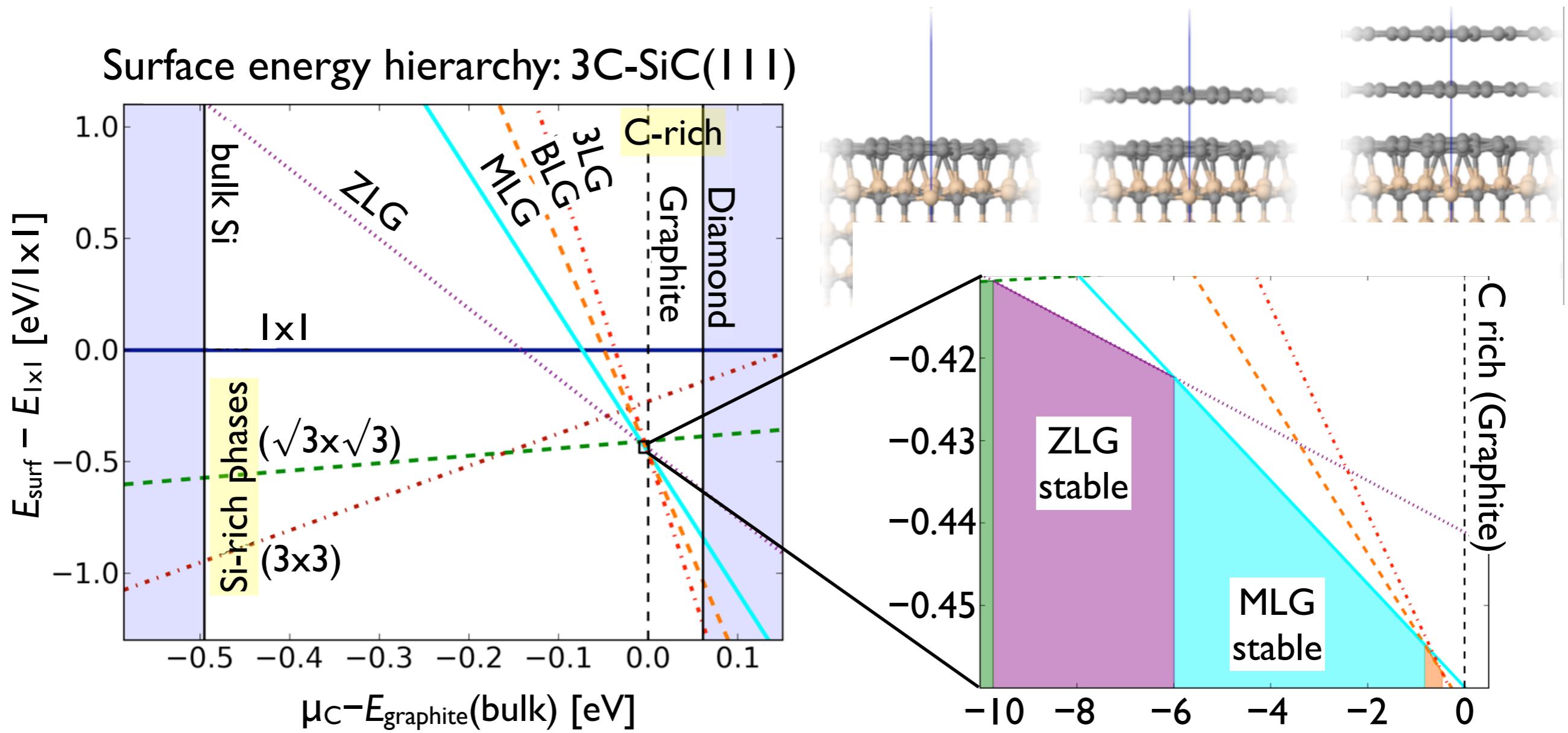
Stability of Surface Phases: PBE+vdW

$$E_{\text{surf}} = \frac{1}{A} [E_{\text{slab}} - N_{\text{Si}}\mu_{\text{Si}} - N_{\text{C}}\mu_{\text{C}}]; \quad E_{\text{SiC}} = \mu_{\text{Si}} + \mu_{\text{C}}$$



Stability of Surface Phases: PBE+vdW

$$E_{\text{surf}} = \frac{1}{A} [E_{\text{slab}} - N_{\text{Si}}\mu_{\text{Si}} - N_{\text{C}}\mu_{\text{C}}]; \quad E_{\text{SiC}} = \mu_{\text{Si}} + \mu_{\text{C}}$$

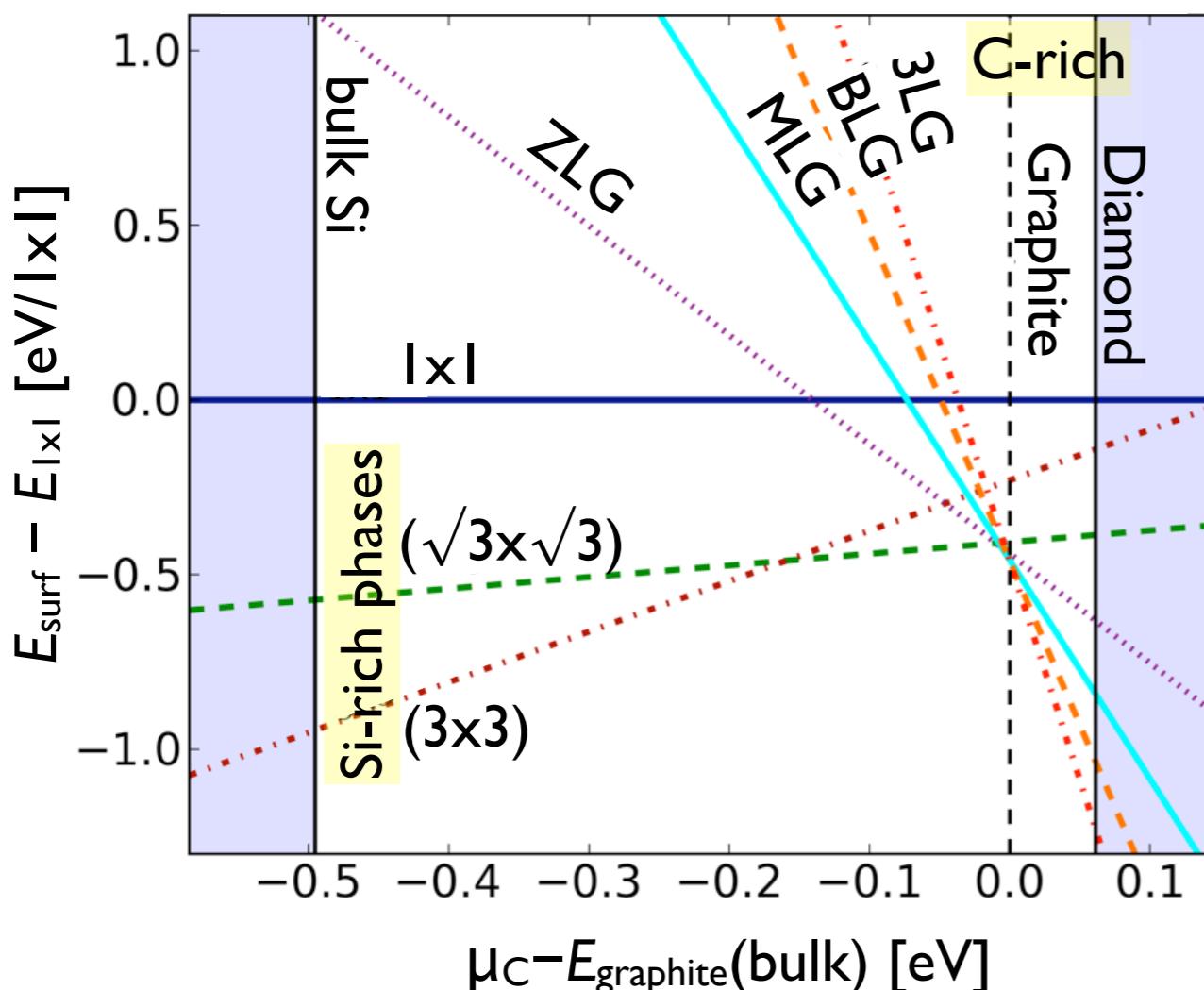


Stability of Surface Phases: Conclusion

$$E_{\text{surf}} = \frac{1}{A} [E_{\text{slab}} - N_{\text{Si}}\mu_{\text{Si}} - N_{\text{C}}\mu_{\text{C}}]; \quad E_{\text{SiC}} = \mu_{\text{Si}} + \mu_{\text{C}}$$

PBE+vdW

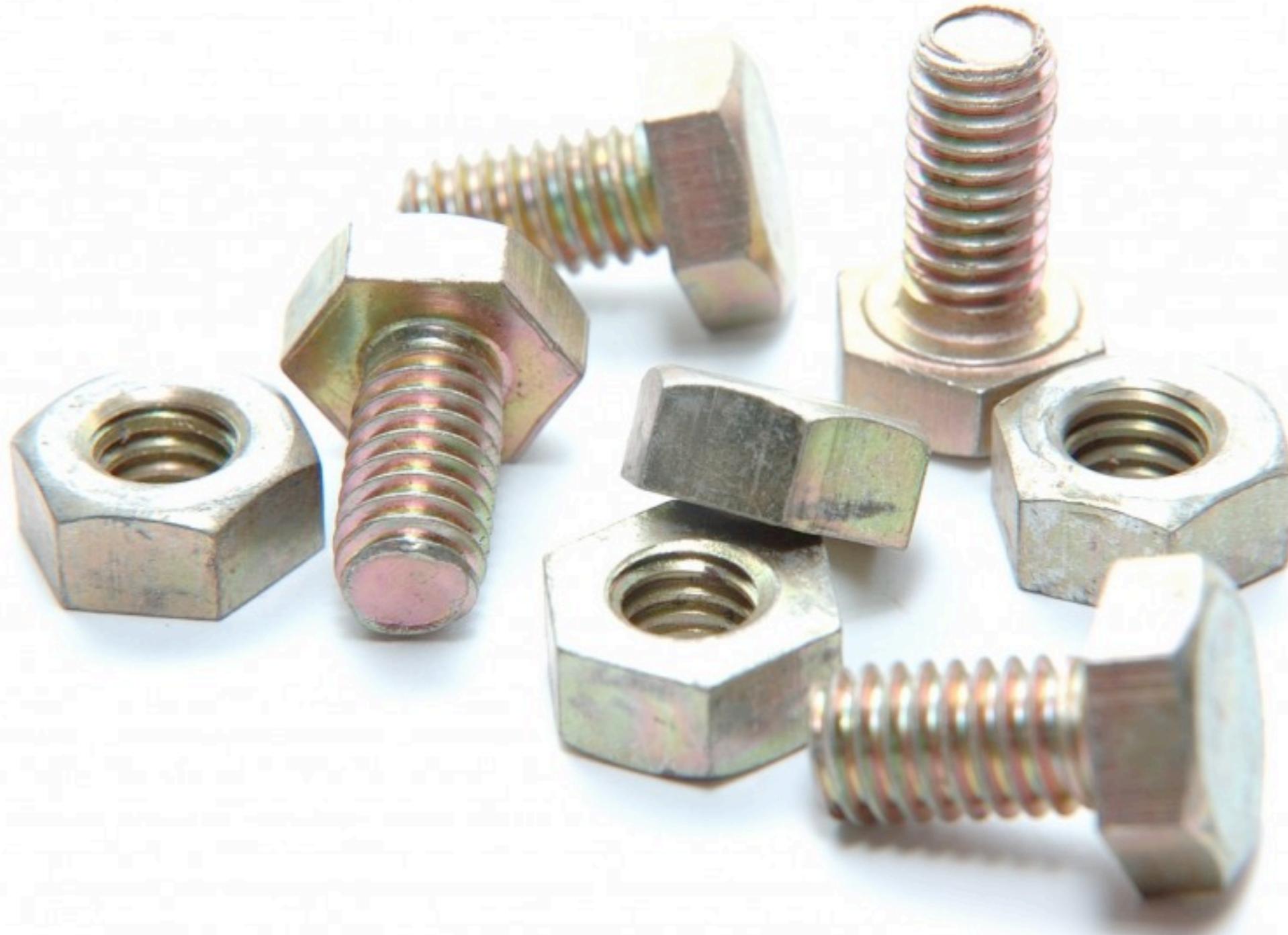
Surface energy hierarchy: 3C-SiC(111)



- Thermodynamic near-stability range for ZLG, MLG possibly BLG

- Defects, dopants, electronic structure, dynamics(?) accessible without artificial strain

Nuts and Bolts (I) - Summary and Outlook



Nuts and Bolts (I) - Summary and Outlook



Abundant application areas: (Bio)molecules, metal clusters and catalysis, thermal transport, hybrid organic-inorganic systems, oxide materials, ...

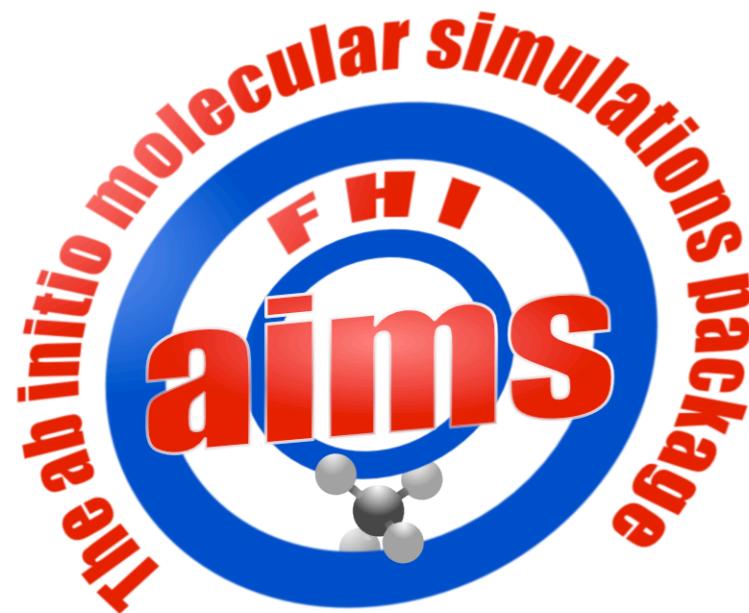
The concepts are general:

- 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 standard LDA/GGA for large systems

But how to actually get density, total energy, forces, properties?

→ Nuts and Bolts (II), Bjoern Lange - 11:30 h

Our Approach to All-Electron Simulations: FHI-aims



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



Matthias
Scheffler
(FHI Berlin)

VB
(Duke
University)

Karsten Reuter (TU Munich)

Patrick Rinke (FHI)

Xinguo Ren (USTC Hefei)

Ville Havu (Aalto Univ., Finland)

Woodley / Sokols (UCL)

...

... FHI-aims - support from **many** more:

Karsten Reuter, Ralf Gehrke, Patrick Rinke, Ville Havu, Paula Havu, Xinguo Ren, Andreas Dolfen, Felix Hanke, Stefan Gutzeit, Andrea Sanfilippo, Luca Ghiringhelli, Mariana Rossi, Rainer Johann, Alex Tkatchenko, Sergey Levchenko, Matthias Gramzow, Benedikt Biedermann, Aloysius Soon, Mina Yoon, Jörg Meyer, Christian Carbogno, Norbert Nemec, Fabio Caruso, Sucismita Chutia, Franziska Schubert, Jürgen Wieferink, Simiam Ghan, Viktor Atalla, Matti Ropo, Ferdinand Evers, Alexej Bagrets, Fabio Della Sala, Eduardo Fabiano, Heiko Appel, Daniel Berger, Oliver Hofmann, Yong Xu, Marco Casadei, Klaus Reuter, Andreas Marek, Werner Jürgens, Igor Ying Zhang, Jan Kloppenburg, Franz Knuth, Xin-Zheng Li, Lydia Nemec, Björn Bieniek, Kurt Baarman, Honghui Shang, Wael Chibani, Matt Farrow, Vivek Gobre, Andrew Logsdail, Karsten Rasim, Ran Jia, Reinhard Maurer, Markus Sinstein, Björn Lange, ...

Reliable predictions for real materials and molecules

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

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

- All-electron “Density-Functional Theory and Beyond”
- Efficient localized (*numeric atom-centered*) basis sets: One framework from fast qualitative “high throughput” to meV-level converged results
- Seamlessly from light to heavy elements
- Molecules, periodic solids, surfaces, nanostructures, etc. on equal footing
- DFT, van der Waals, many-body perturbation theory (MP2, RPA, GW, LR-TDDFT)
- Excellent scalability: System size (up to ~1,000s of atoms), CPUs (routine use on 100s to 1,000s of CPUs, demonstrated up to 262,000 CPUs)
Massively parallel eigenvalue solver library: “ELPA”
- Efficient structure optimization, stress tensor, Born-Oppenheimer *ab initio* molecular dynamics, massively parallel replica exchange, ...
- “Properties and function”:
Vibrations, phonons, harmonic and anharmonic free energies, barriers, IR spectra, work functions, electronic and thermal transport, path integral MD, many more

