The Nuts and Bolts of Electronic Structure Theory

Basis Sets, Real-Space Grids, Relativity, Scalability

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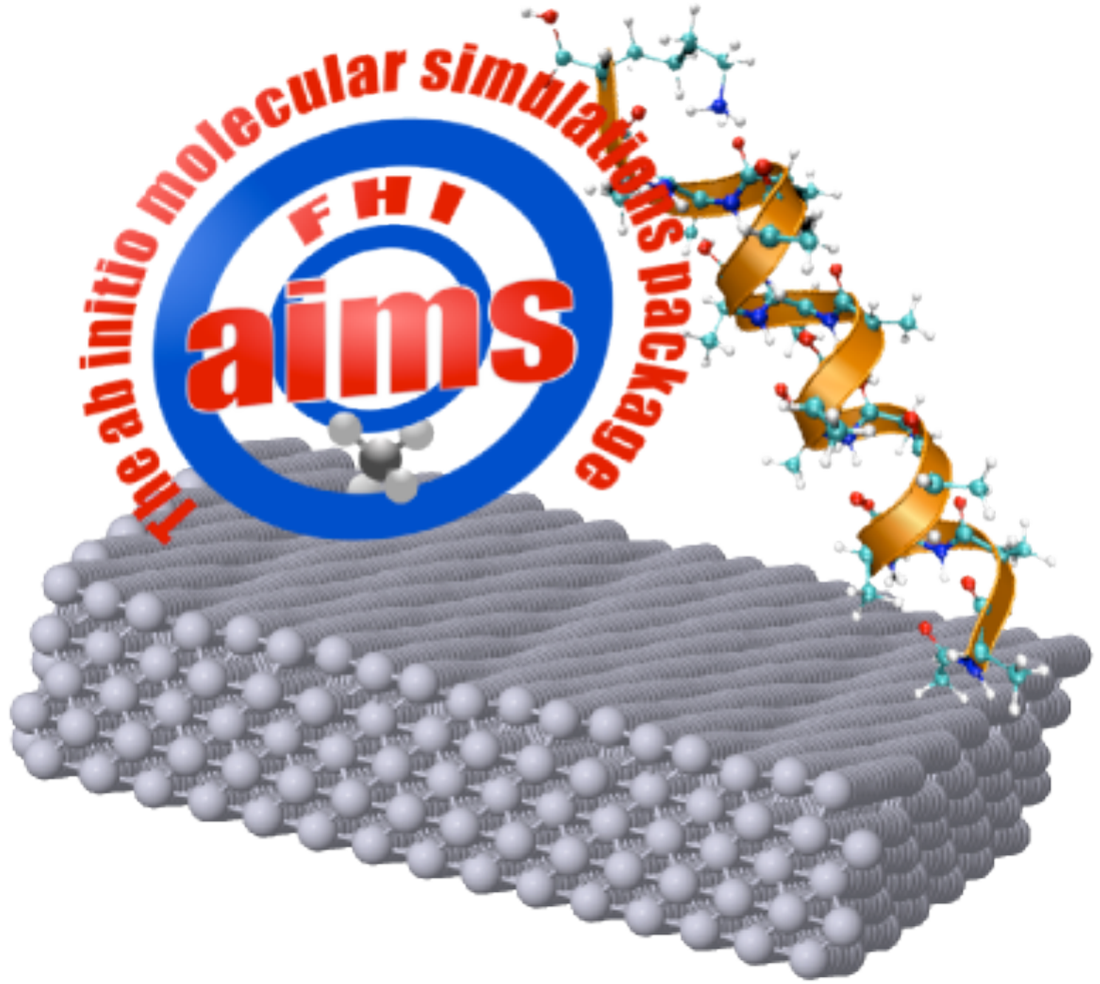

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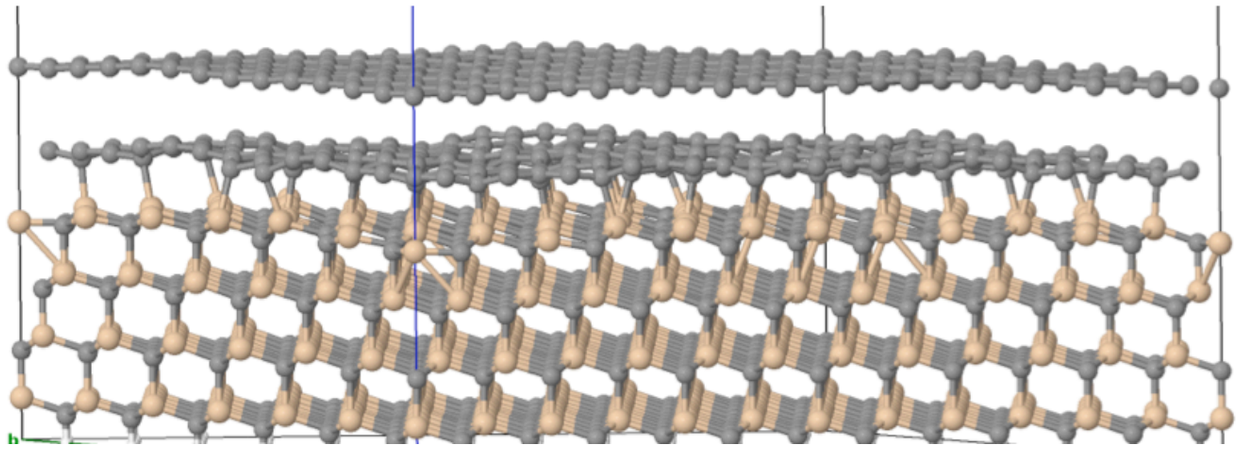
Starting September 2013 -
Duke University, Durham, NC, USA

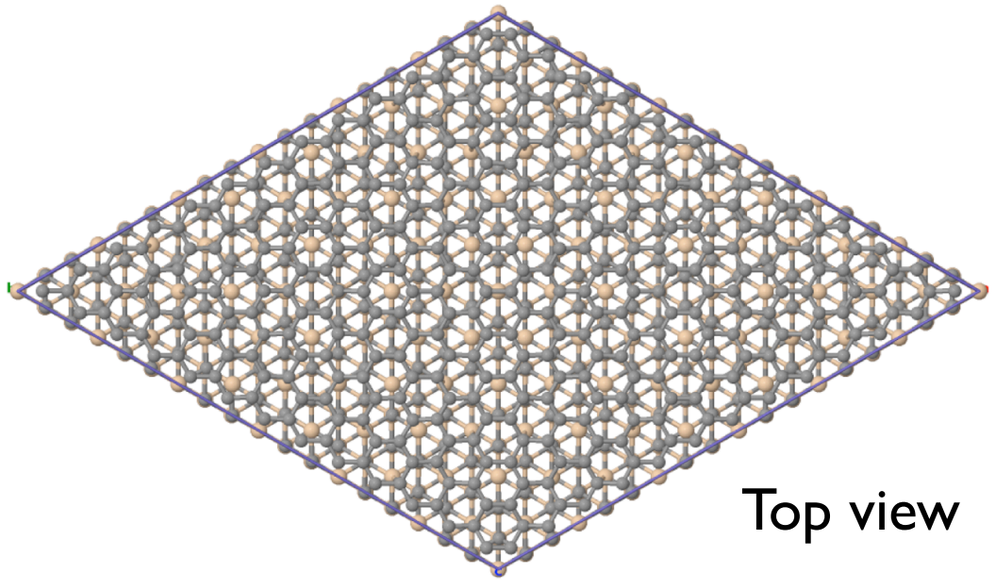
Is This a "Stable" Surface Phase?*

Graphene on SiC(0001)

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



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



Top view

338 atoms per C plane

216 atoms per SiC plane

Surface energy?

Electronic structure?

...

* under some conditions ...

Scope of this Talk

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

Kohn-Sham Equations, 1965

<u>General concepts:</u>

- Basis sets
- Integrals and grids; electrostatics; molecules vs. periodic solids
- Scalar relativity
- Eigenvalue solution, scalability (large systems, large computers)

Similar pieces for Hartree-Fock & hybrids, many-body methods etc. → S. Levchenko, Fri 09:00 h

<u>Our implementation: FHI-aims</u>

The Fritz Haber Institute ab initio molecular simulations package

→ main example for this talk (others in the next 9 days)
→ used for tutorials in the next 9 days

2004 - Wishlist for a New Electronic Structure Code

Cover the entirety of materials / chemistry:

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

"Materials and molecules" - periodic (*k*-space) and non-periodic

Hierarchy of methods: Density-Functional Theory to high level benchmarks

All-electron

Scalable (system size, number of CPUs)

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

The Kohn-Sham Equations (again)

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

"As (almost) everyone does":

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

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

→generalized eigenvalue problem:

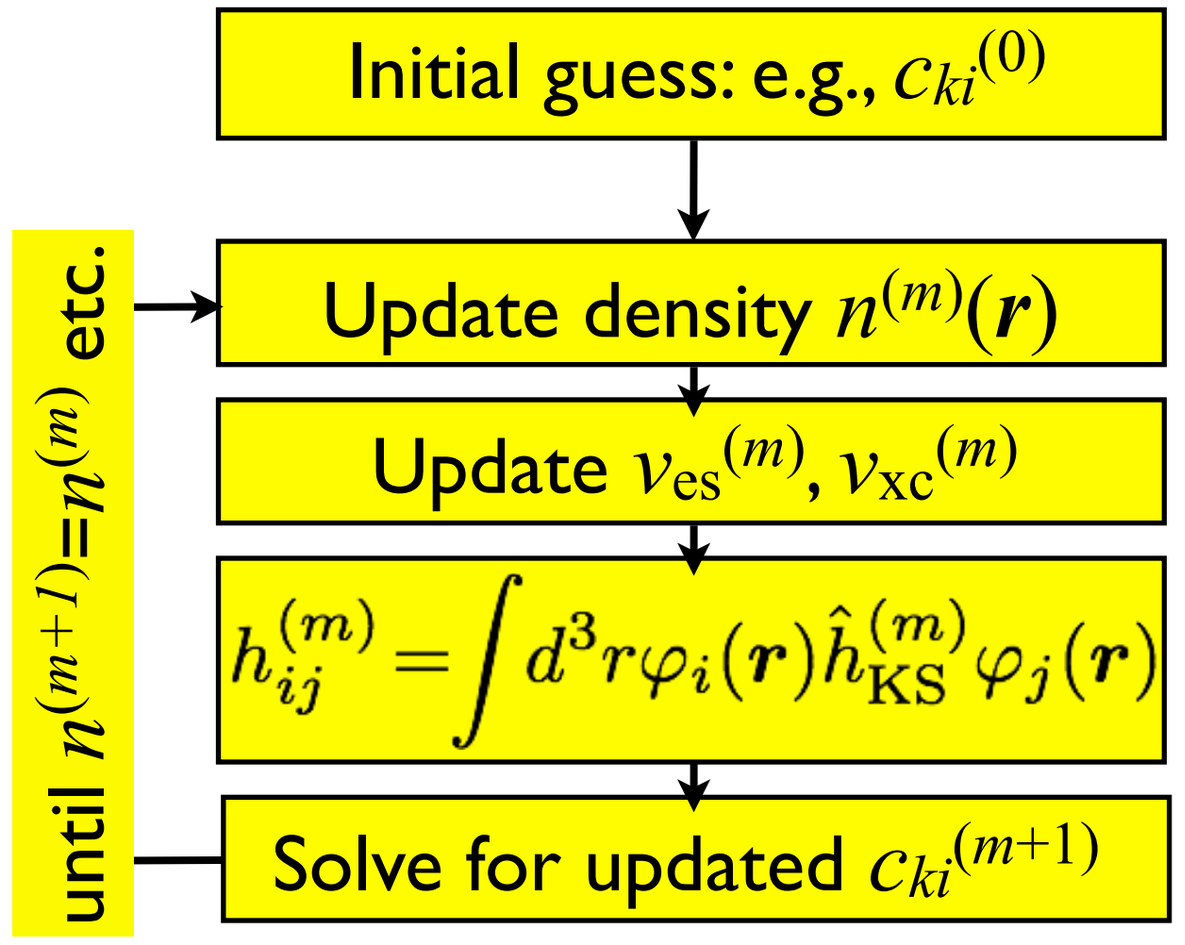
$$\underline{\underline{h}}\,\underline{c}_k = \epsilon_k\,\underline{\underline{s}}\,\underline{c}_k$$

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

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

2. Self-consistency:

O. Hofmann
Wed 11:30h



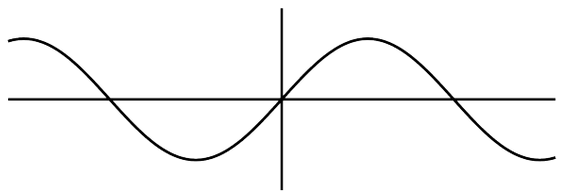
Representing the Orbitals: Basis Sets

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

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

<u>Many good options:</u>

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



R. Gebauer
Thu 10:00h

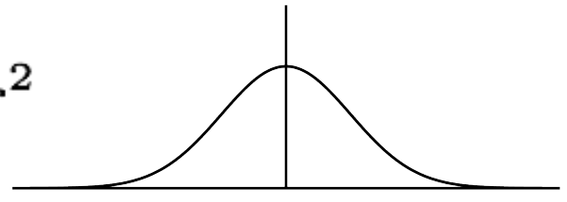
→ efficient FFT's (density, electrostatics, XC-LDA/GGA)

→ inherently periodic

→ not all-electron (*Slater 1937*) - need "pseudoization"

C. Draxl
Thu 11:30h

- *Augmented* plane waves (*Slater 1937; Andersen 1975; etc.*)
- Gaussian-type orbitals $\varphi_i(\boldsymbol{r}) = \frac{1}{N}r^l e^{-\alpha r^2}$



F. Neese
Fri 10:00h

- <u>*Many*</u> others: (L)MTO, "real-space", numeric atom-centered functions, ...

Our Choice: Numeric Atom-Centered Basis Functions

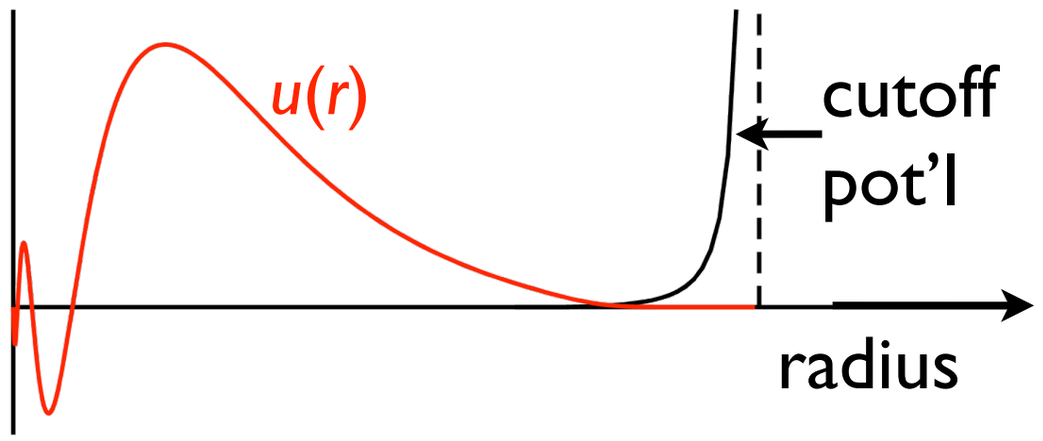
$$\varphi_{i[lm]}(\boldsymbol{r}) = \frac{u_i(r)}{r} \cdot Y_{lm}(\Omega)$$

Many popular implementations:
DMol³ (Delley), FPLO (Eschrig *et al.*), PLATO (Horsfield *et al.*), PAOs (Siesta, Conquest, OpenMX[2], 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: $v_i(r) = v^{\text{DFT}}_{\text{free atom}}(r)$
- Hydrogen-like: $v_i(r) = z/r$
- free ions, harm. osc. (Gaussians), ...



Our Choice: Numeric Atom-Centered Basis Functions

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

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

→ Localized; "naturally" all-electron

→ The choice of <u>efficient</u> and of <u>enough</u> radial functions is obviously important

→ We have a basis set library for all elements (1-102), from fast qualitative to meV-converged (total energy, LDA/GGA) calculations - <u>efficient and accurate approach</u>

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

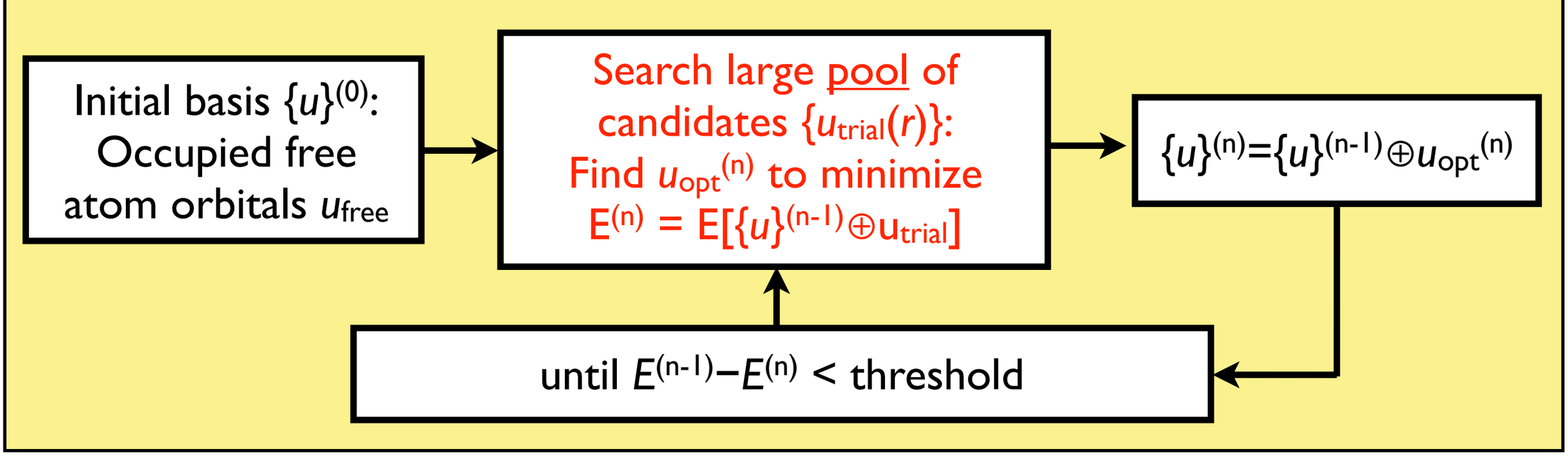
V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler,
"Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals",
Computer Physics Communications ***180****, 2175-2196 (2009)*

Constructing a Basis Set Library for DFT

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

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

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

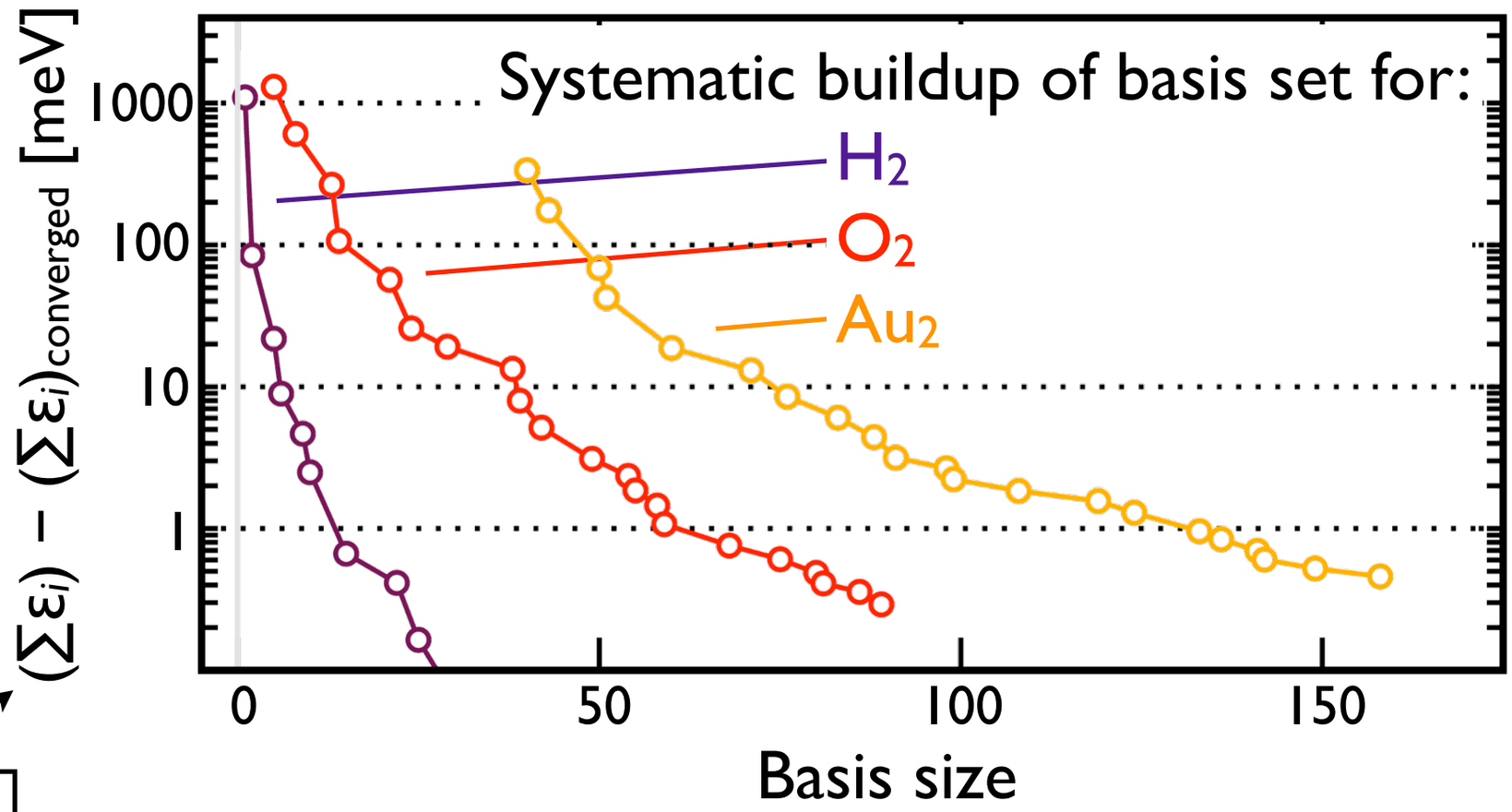


Iterative Selection of NAO Basis Functions

"Pool" of trial basis functions:
2+ ionic *u(r)*
Hydrogen-like *u(r)* for *z*=0.1-20

Optimization target:
Non-selfconsistent symmetric dimers, averaged for different *d*

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



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*

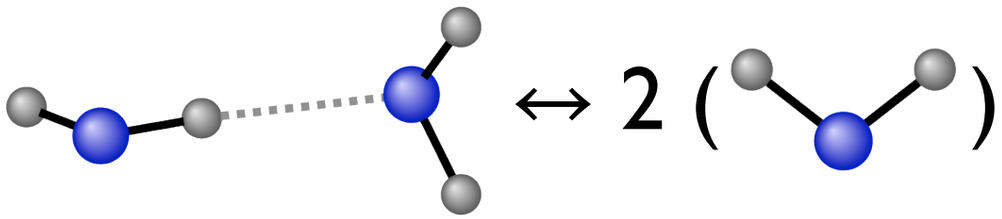
"First *tier* (level)"

"Second *tier*"

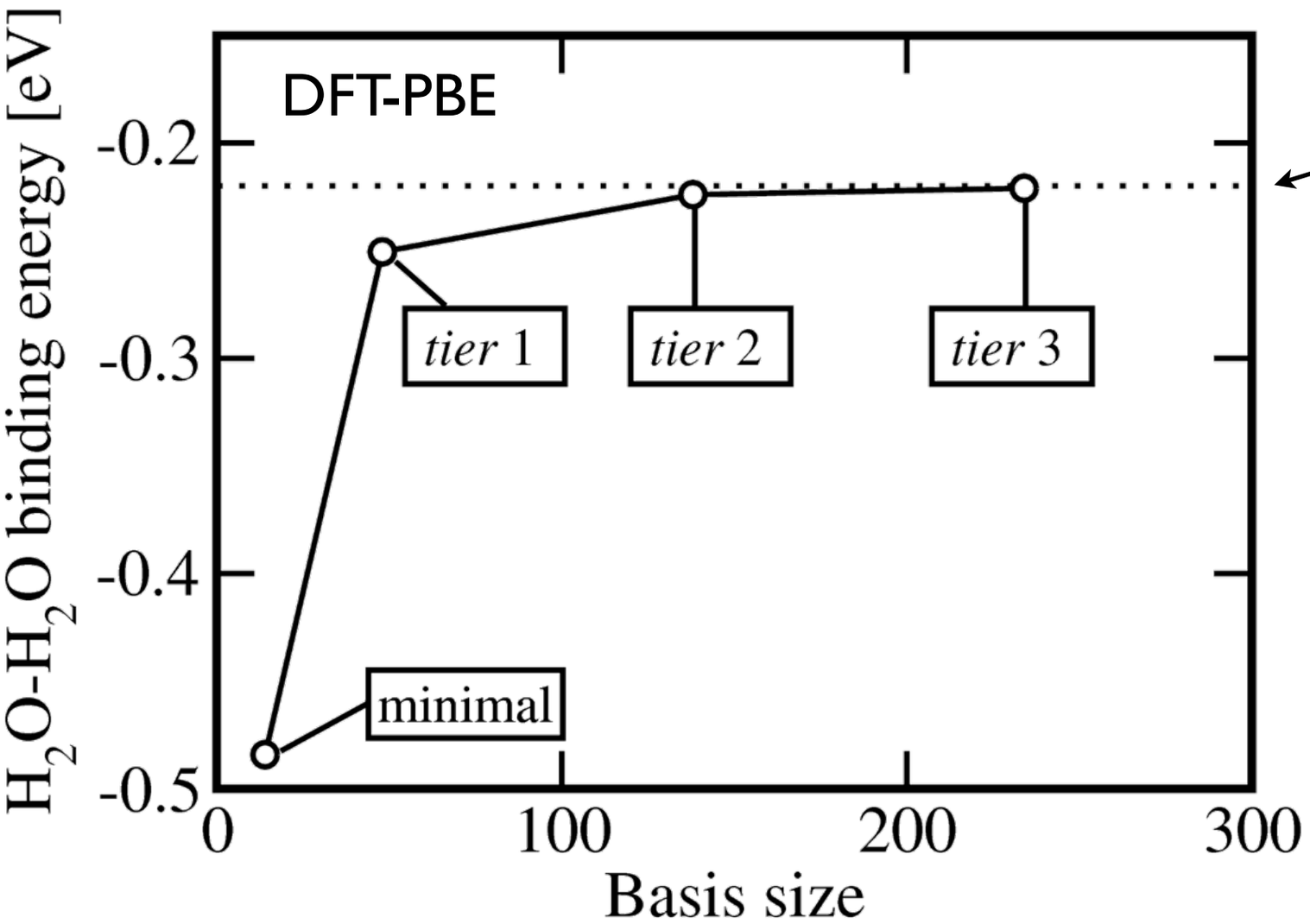
"Third *tier*"

...

Accuracy: $(H_2O)_2$ Hydrogen Bond Energy



↔ 2 ( )



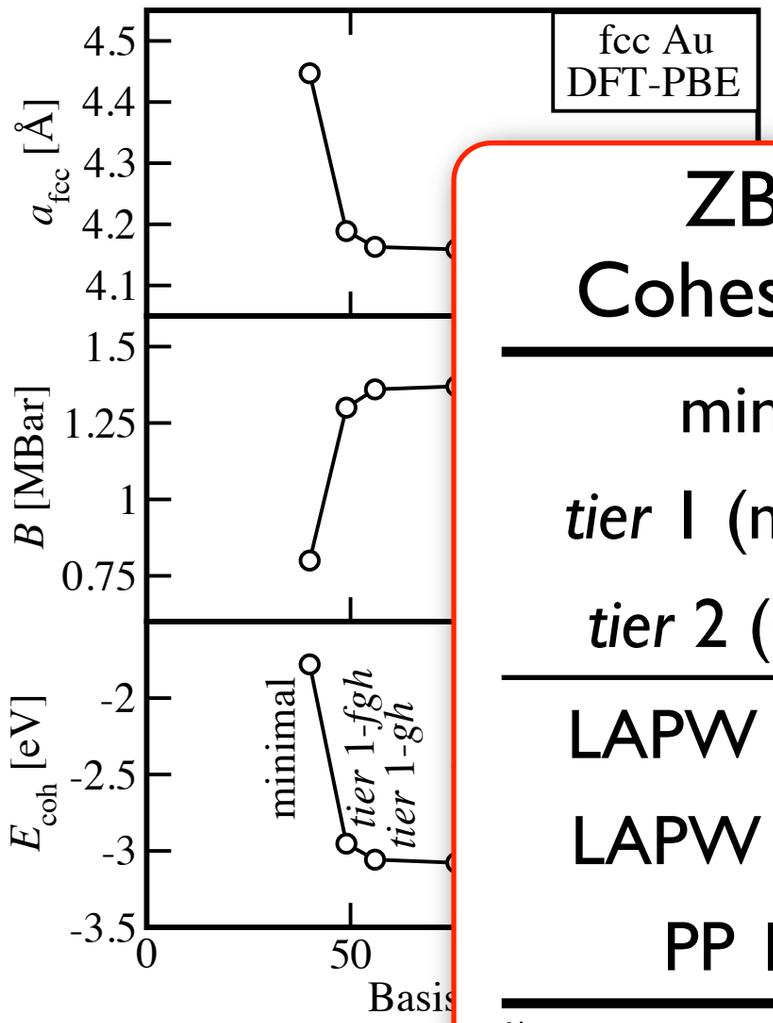
Basis set limit (independent):
E_{Hb} = −219.8 meV

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*

Transferability: Generally Not a Problem for DFT

Bulk Au: Cohesive properties



ZB GaAs, LDA: Cohesive energy [eV]

min+*spd*	7.99
tier 1 (min+spdf	
tier 2 (+*spdfgh*)	
LAPW 2009 (A	
LAPW 2009 (B	
PP 1998[1)]	

[1)] *Fuchs, Bockstedte, Pe… PRB 1998*

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

	Pt(100)	Au(100)
min+*spdf*	-65	-21
tier 1	-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( ) - 2E( )

Problem:

has larger basis set than .

→ Distance-dependent overbinding!

Remedy: "Counterpoise correction"

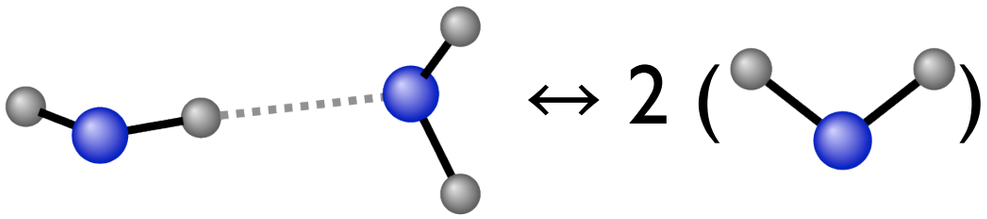
ΔE_{BSSE} = E( ) - E( )

No nucleus - basis functions only

NAO basis sets: is already exact → no BSSE for .

But how about *molecular* BSSE?

$(H_2O)_2$: "Counterpoise Correction"



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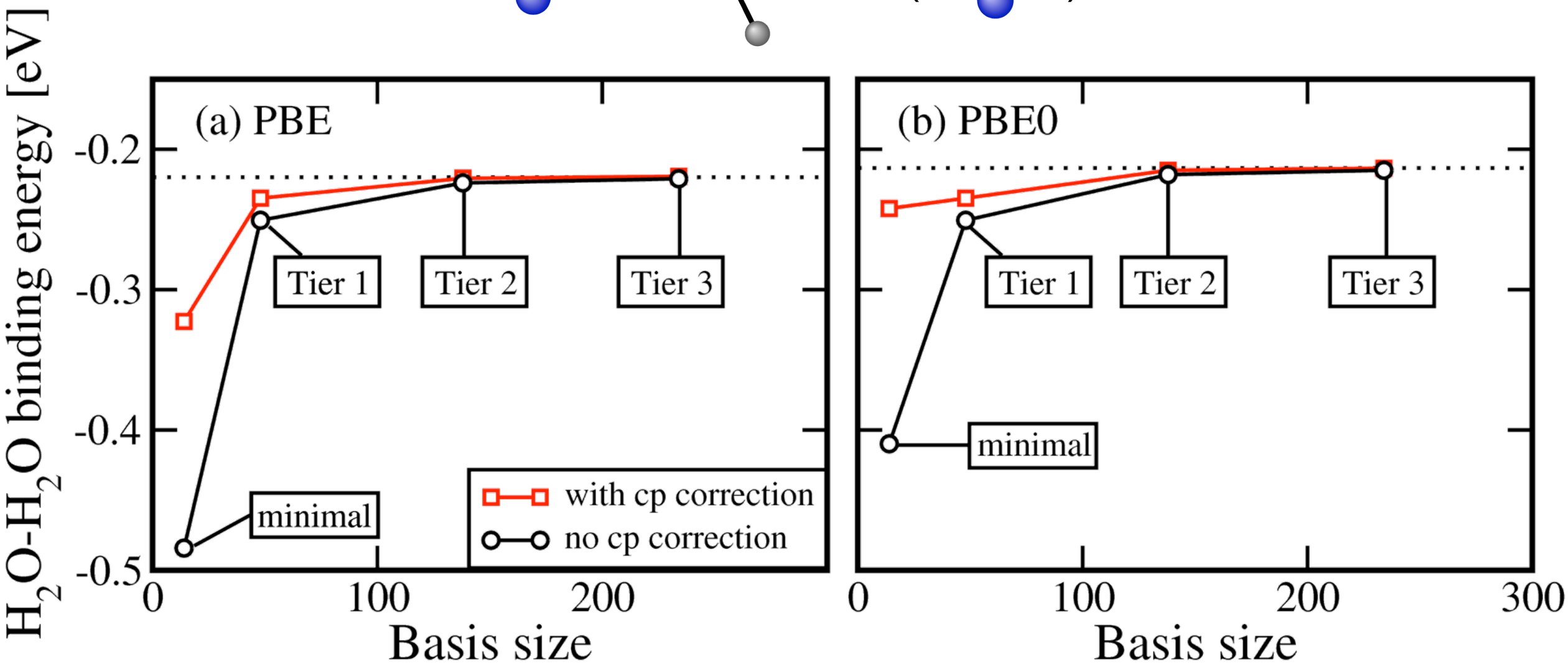


Ground-State DFT, NAO's:

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

*BUT methods that sum over infinite continuum (MP2, RPA, ...) need CP C.!

Using Numeric Atom-Centered Basis Functions: Pieces

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

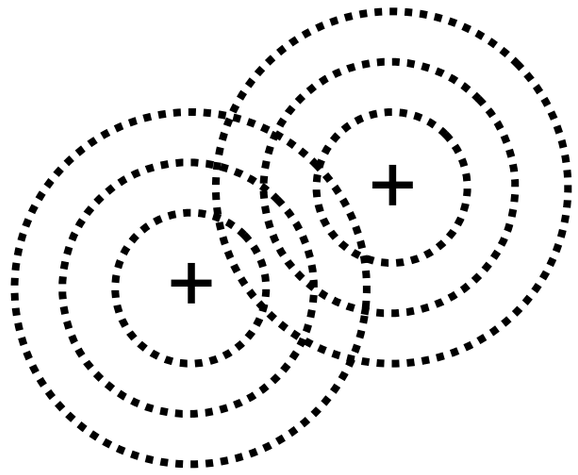
$$h_{ij} = \int d^3 r \varphi_i(\boldsymbol{r}) \hat{h}_{\mathrm{KS}} \varphi_j(\boldsymbol{r})$$

- *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!

- 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)*



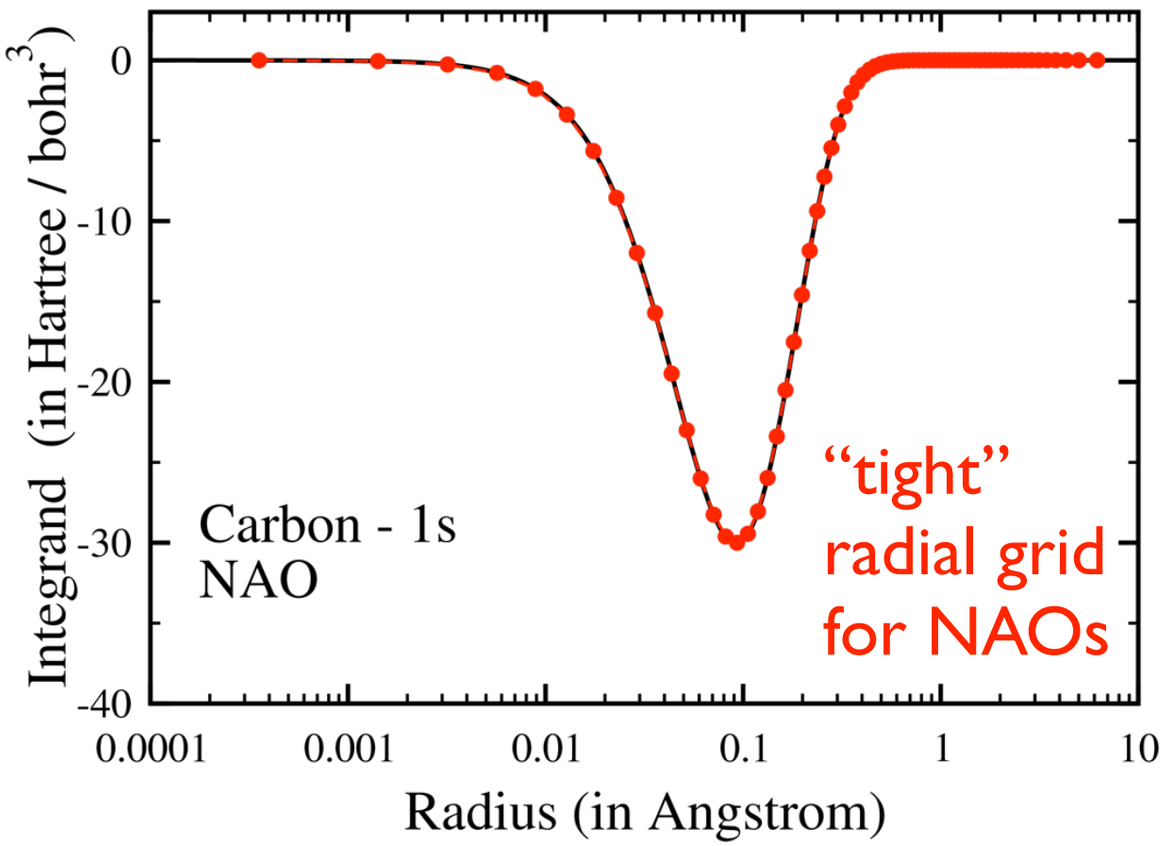
Pioneered by

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

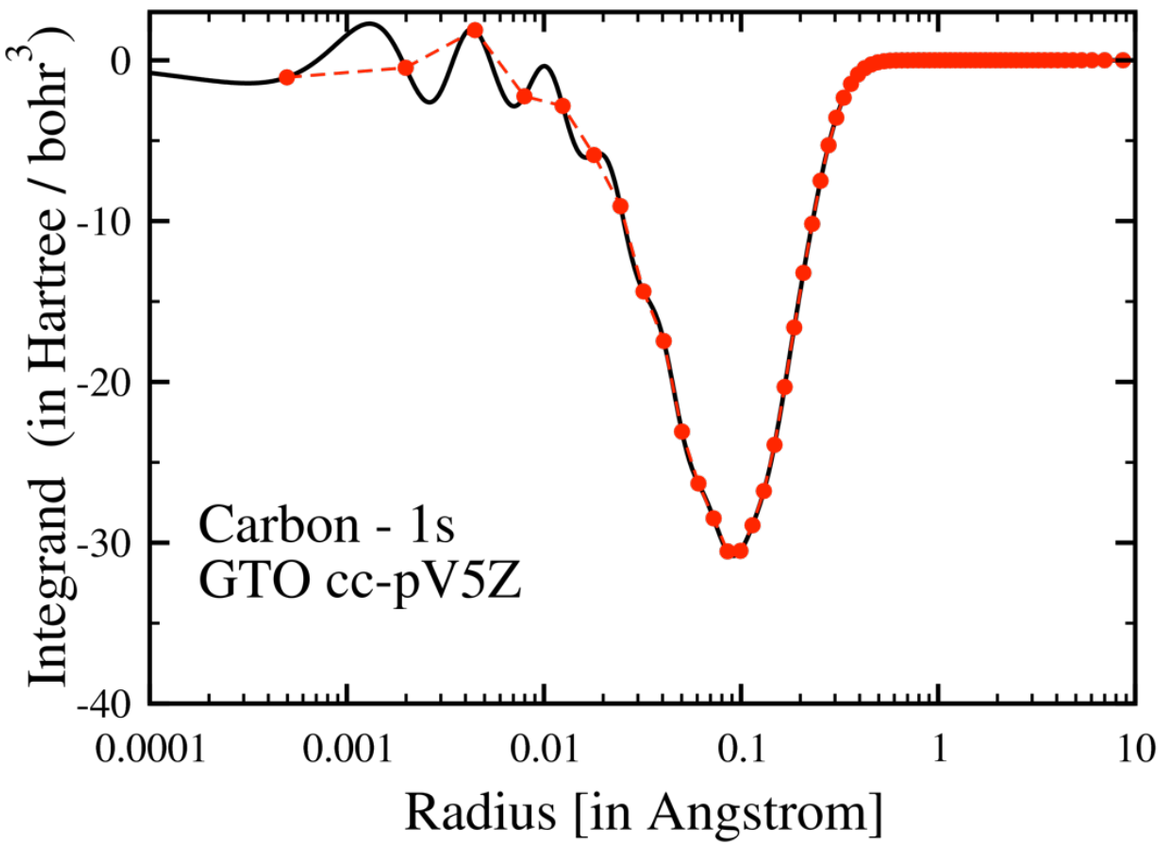
All-Electron Integrals: Rather Benign for NAOs

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

f(r) for
NAO radial function:



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:

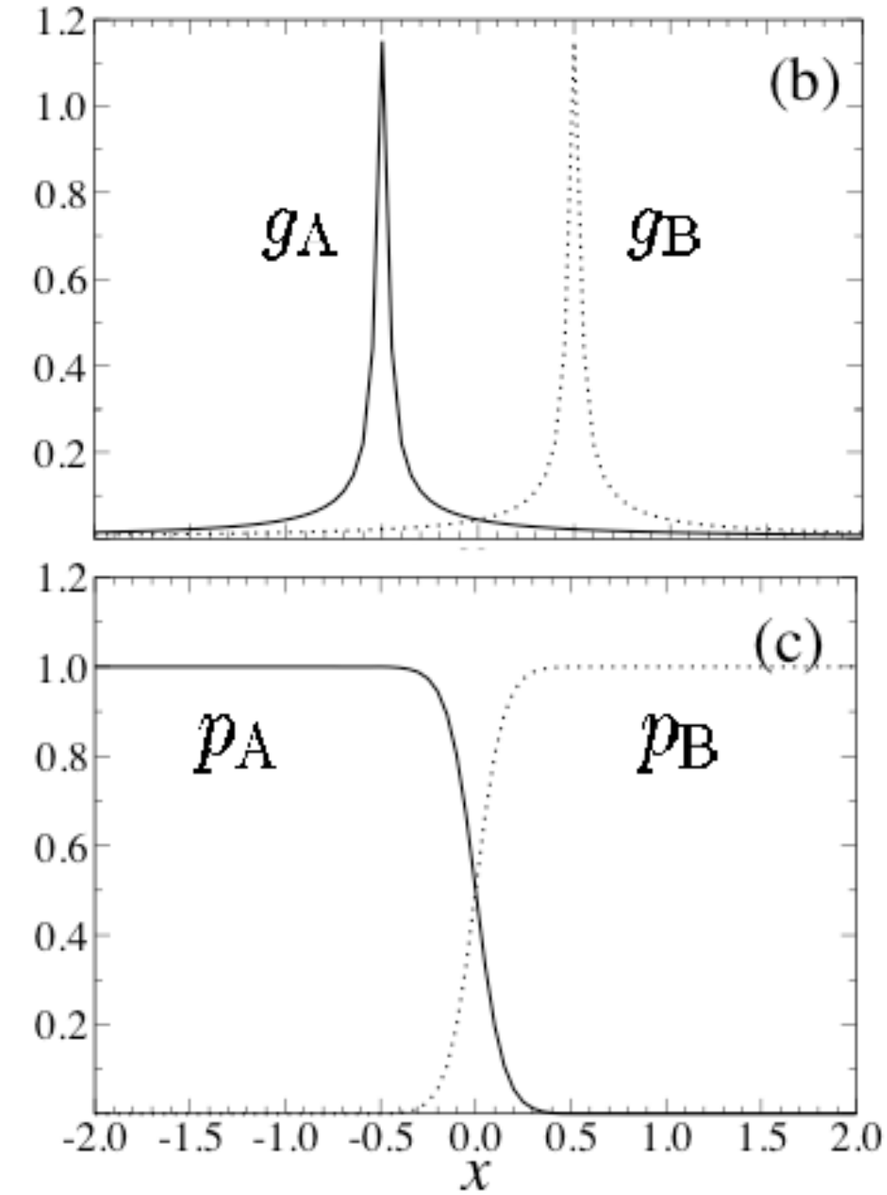
$$\int d^3r f(\boldsymbol{r}) = \sum_{\mathrm{atoms}} \int d^3r p_{\mathrm{atom}}(\boldsymbol{r}) f(\boldsymbol{r})$$

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

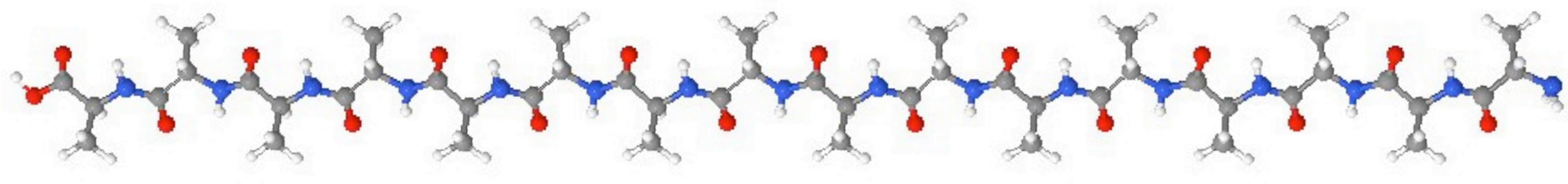
through $p_{\mathrm{atom}}(\boldsymbol{r}) = \dfrac{g_{\mathrm{atom}}(\boldsymbol{r})}{\sum_{\mathrm{atom}'} g_{\mathrm{atom}'}(\boldsymbol{r})}$

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

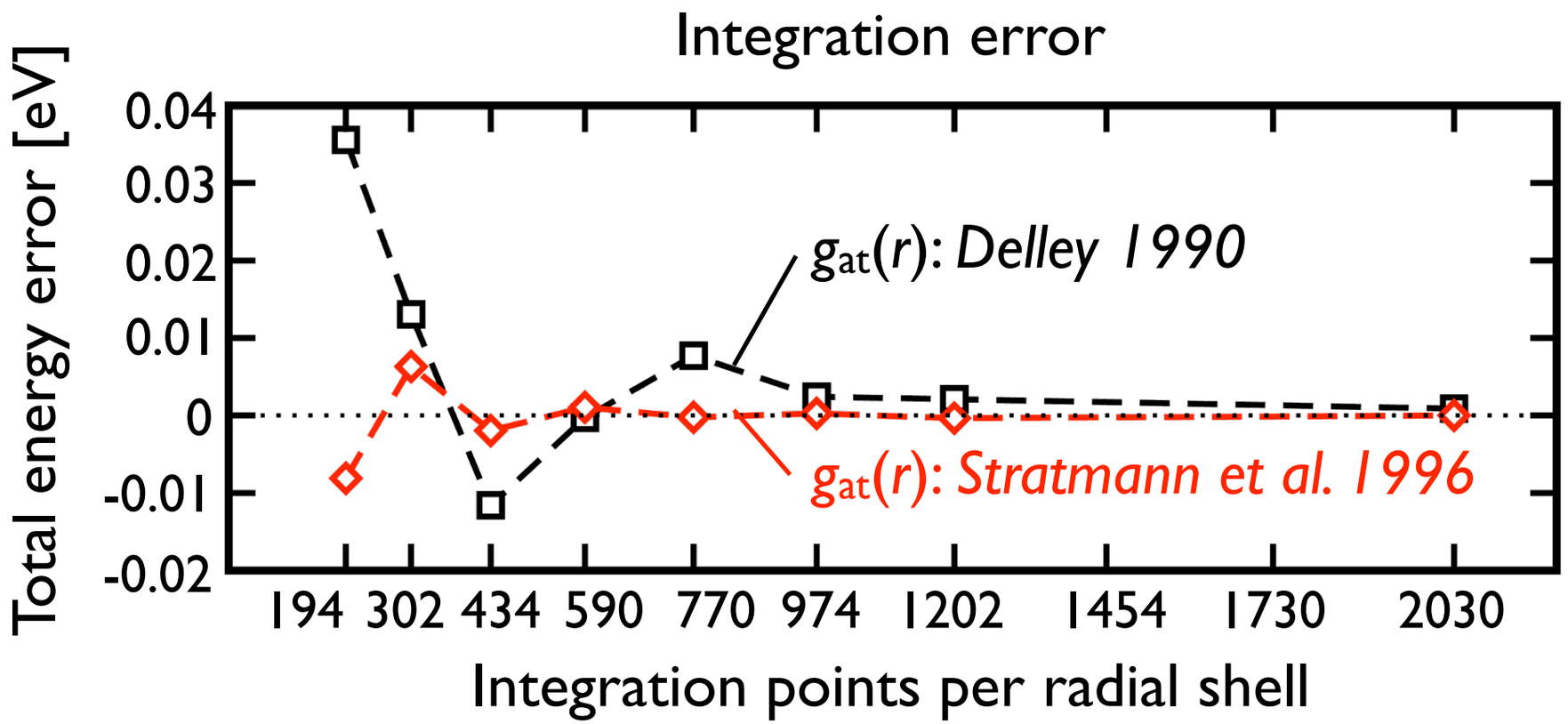
  many alternatives:
  Becke 1988, Stratmann 1996, Koepernik 1999, ...



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)

- Multipole expansion:

$$n_{\mathrm{atom},lm}(r) = \int_{s=|r'-R_{\mathrm{atom}}|} p_{\mathrm{atom}}(\boldsymbol{r}') n(\boldsymbol{r}') Y_{lm}(\Omega)$$

- Classical electrostatics:

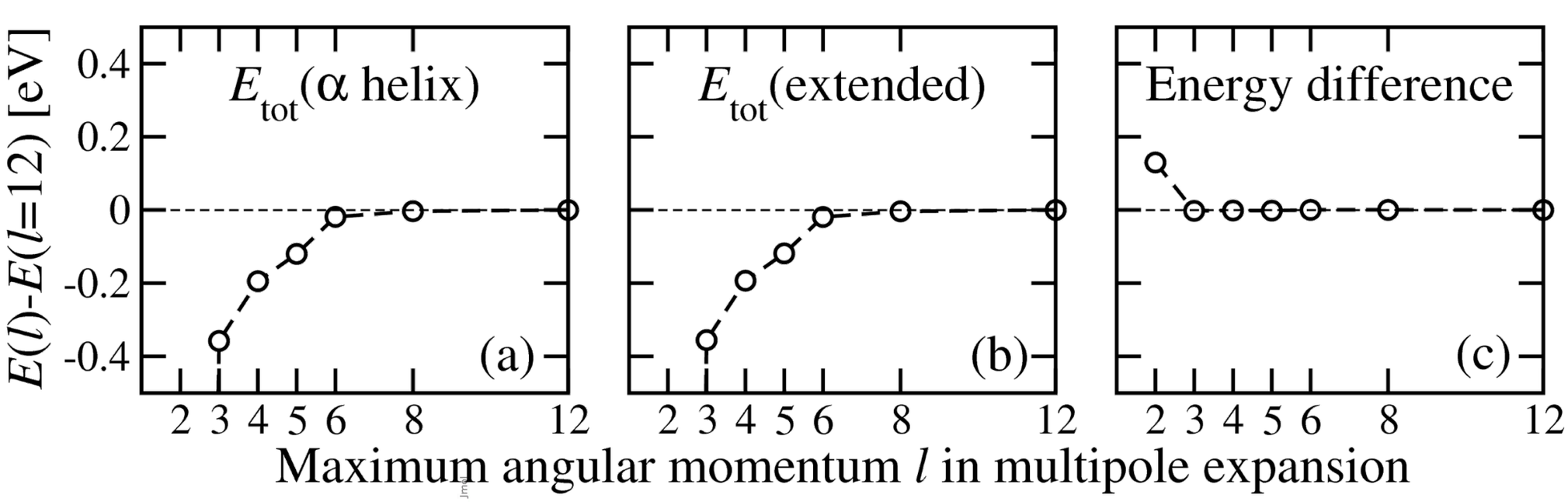
$$v_{\mathrm{es}}(\boldsymbol{r}) = \sum_{\mathrm{atoms}} \sum_{lm}^{l_{\max}} v_{\mathrm{atom},lm}(|\boldsymbol{r} - \boldsymbol{R}_{\mathrm{atom}}|) Y_{lm}(\Omega_{\mathrm{atom}})$$

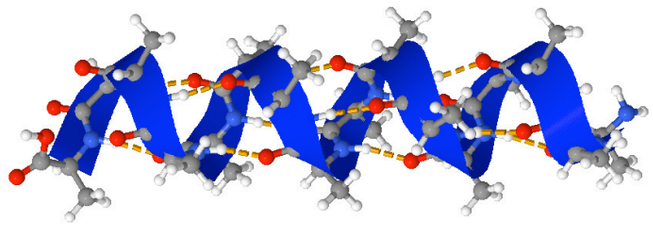
Electrostatics: Multipole expansion

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

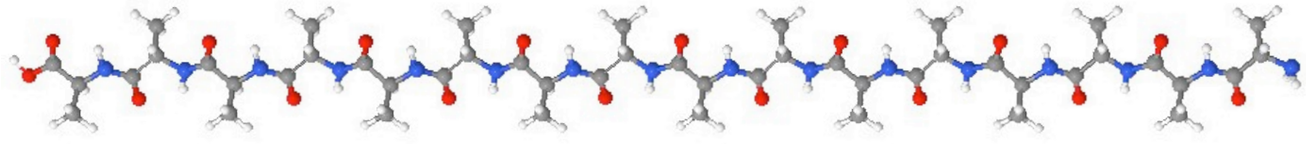
Polyalanine Ala_{20}, DFT-PBE (203 atoms)

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





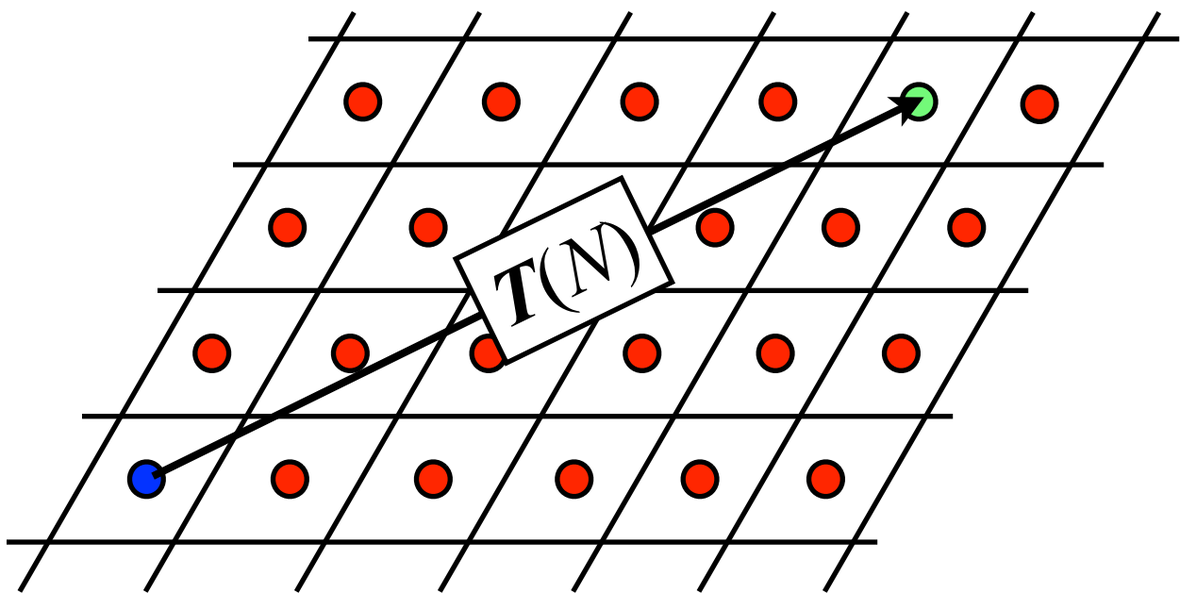
α



extended

Periodic systems

see N. Moll
Thu. 9:00



- Formally: Bloch-like basis functions

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

$\boldsymbol{k}$:"Crystal momentum" = Quantum number in per. systems

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

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

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

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

- 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:

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

- ε-dependent Hamiltonian
- Not negligible for

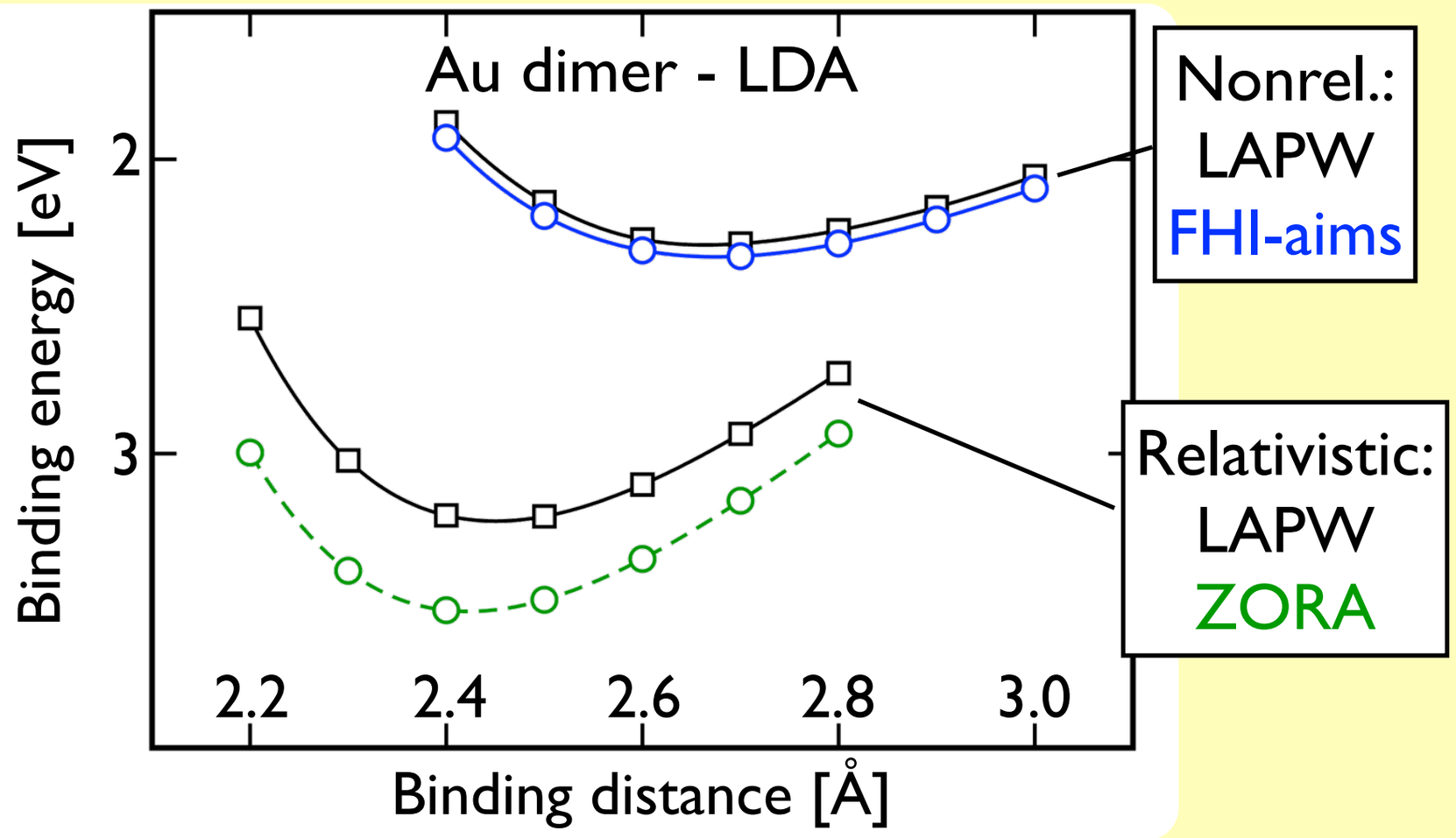
$$\epsilon - v(\boldsymbol{r}) \approx 2c^2$$

⇔ affects near-nuclear part of *any* wave function

Simple Approximation to Scalar Relativity

$$V\phi + \boldsymbol{p}\frac{c^2}{2c^2 + V}\boldsymbol{p}\,\phi = \epsilon\phi$$

ZORA in practice: Harsh approximation (known)



1. LA
→ ra
→ 3-
Trick
2. Ap
Po
...not gauge invariant!

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

Fixing ZORA

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

ZORA

1. "Atomic ZORA"

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

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

2. Scaled ZORA

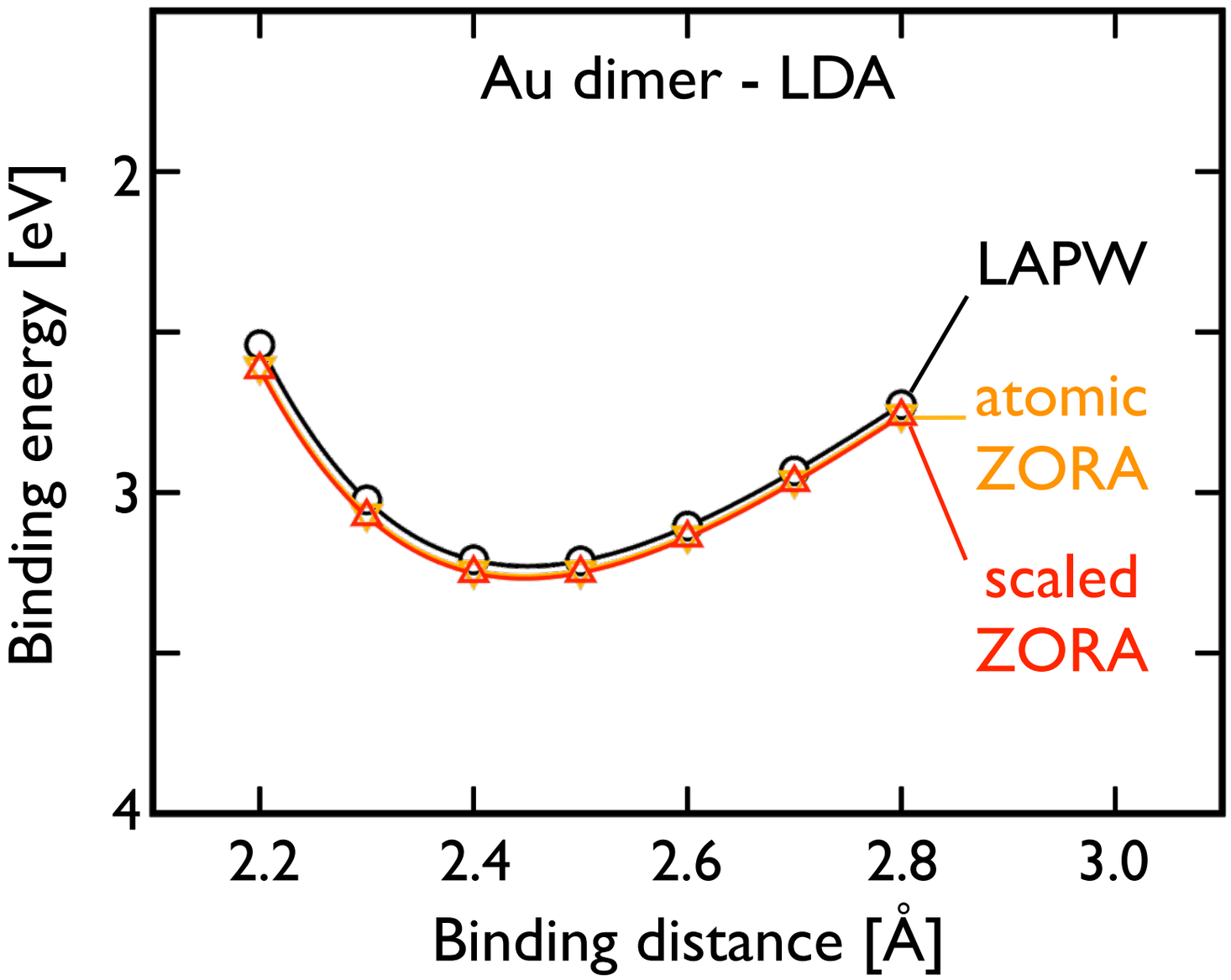
$$\epsilon_{\text{ZORA}}^{\text{scaled}} = \frac{\epsilon_{\text{ZORA}}}{1 + \langle\Phi|\boldsymbol{p}\frac{c^2}{(2c^2 - V)^2}\boldsymbol{p}|\Phi\rangle}$$

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

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

E. van Lenthe et al., JCP 101, 9783 (1994).

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
- (Final) total energies, 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

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

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)

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

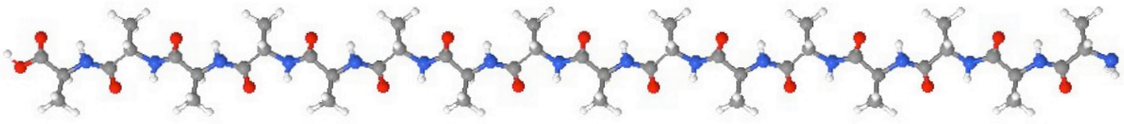
Kohn-Sham eigenvalue problem

"Conventional" solvers (Lapack-like):

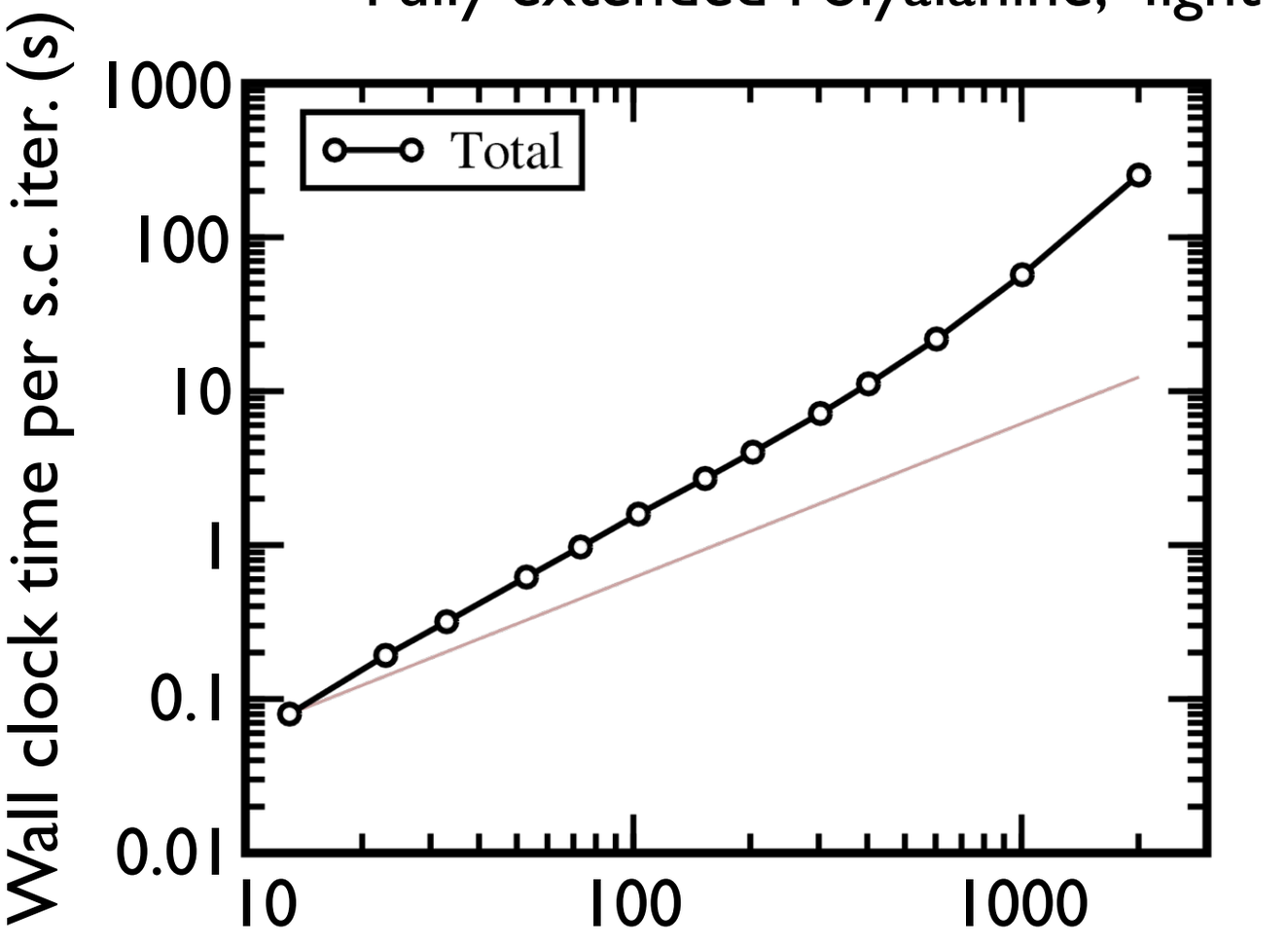
- Small prefactor for NAO's: affordable up to ≥ 1,000 atoms
- Robust, general (metals!)
- *O*(size^3) scalability inevitable
- Massively parallel scalability not out of the box

How far can we push such solvers?

Computational Scaling: CPU Time With System Size



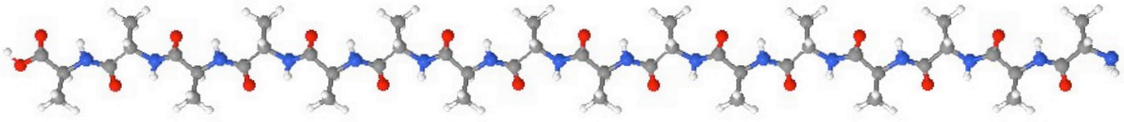
Fully extended Polyalanine, "light"



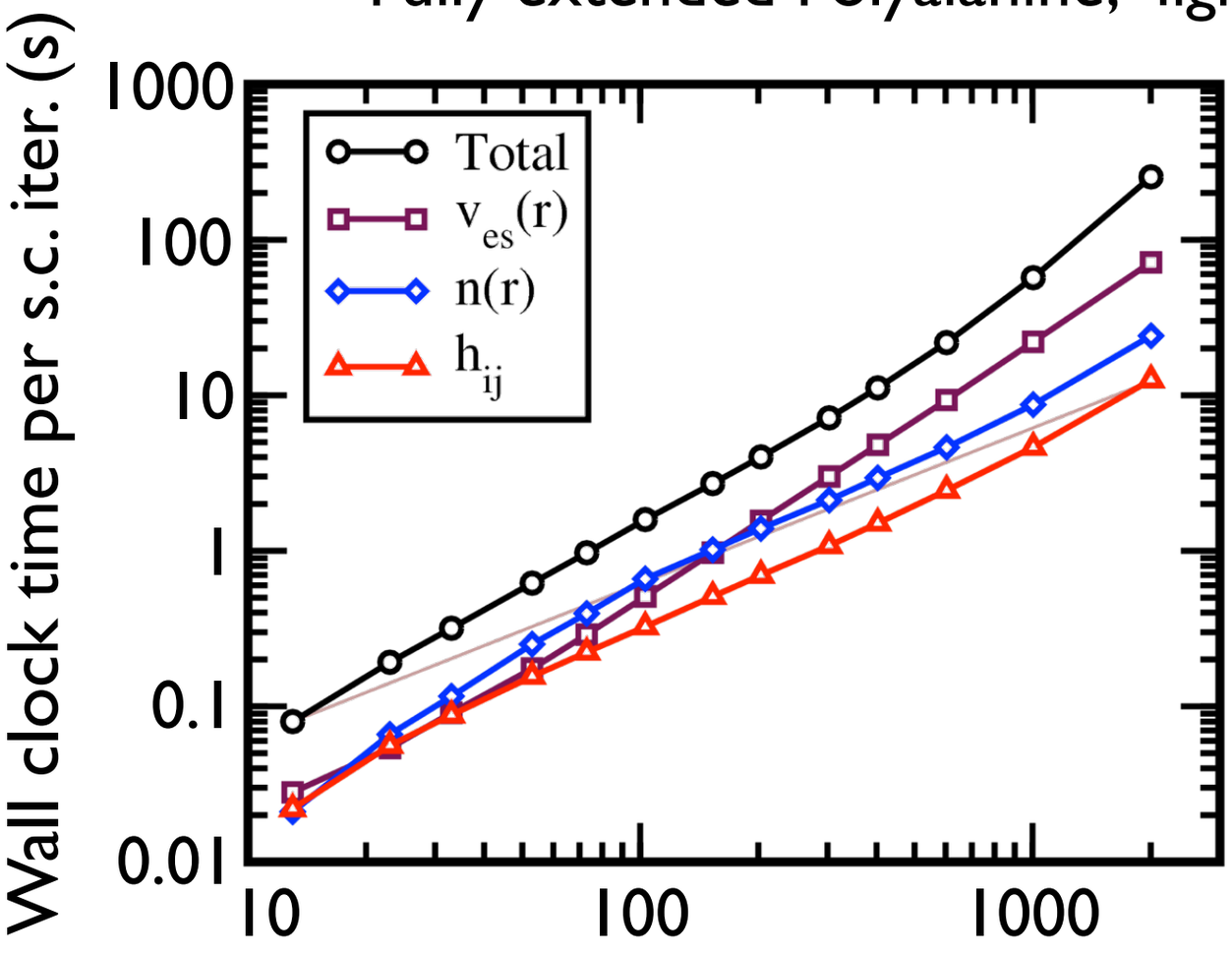
	Light:
Basis	tier 1
$l_{Hartree}$	4
radial shells	24-36
pts. per shell	302 max.
Cutoff width	5Å

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

Computational Scaling: CPU Time With System Size



Fully extended Polyalanine, "light"



	Light:
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32 CPUs
standard Infiniband/Xeon cluster
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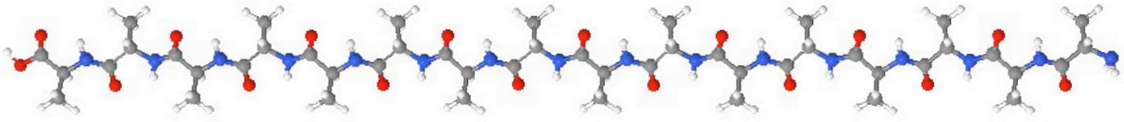
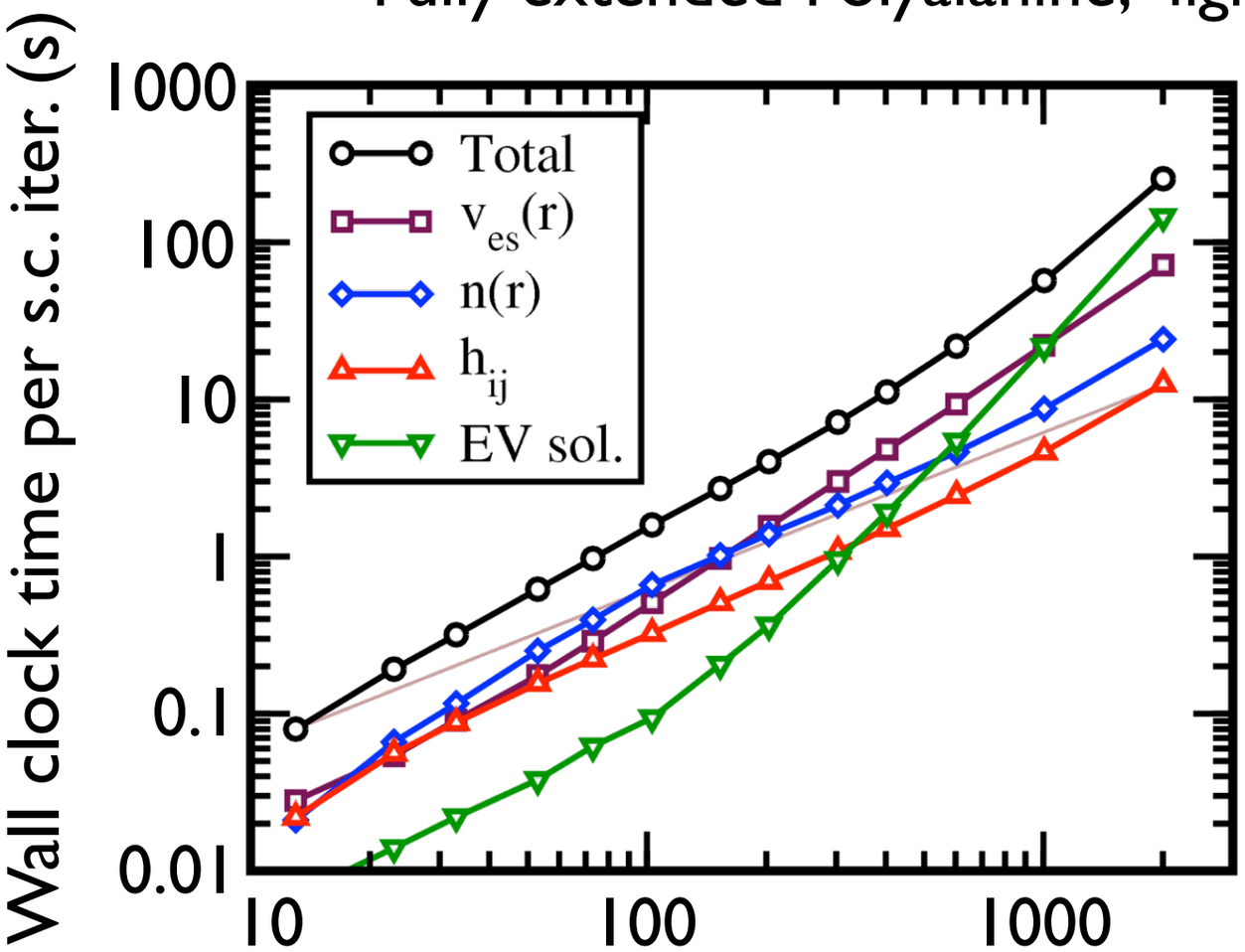
Computational Scaling: CPU Time With System Size



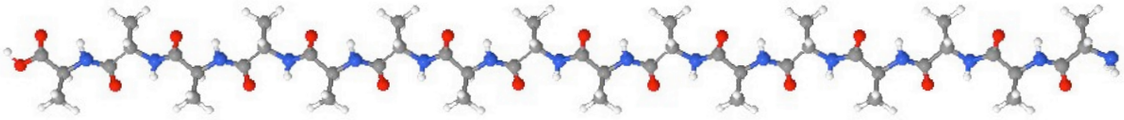
Fully extended Polyalanine, "light"



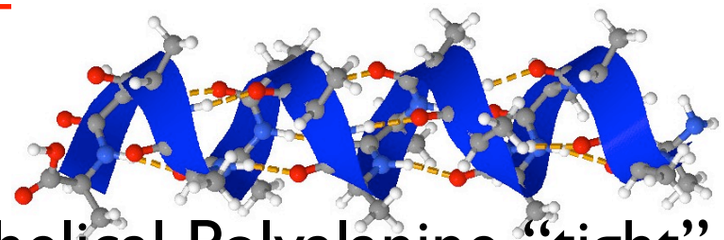
	Light:
Basis	tier 1
$l_{Hartree}$	4
radial shells	24-36
pts. per shell	302 max.
Cutoff width	5Å

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

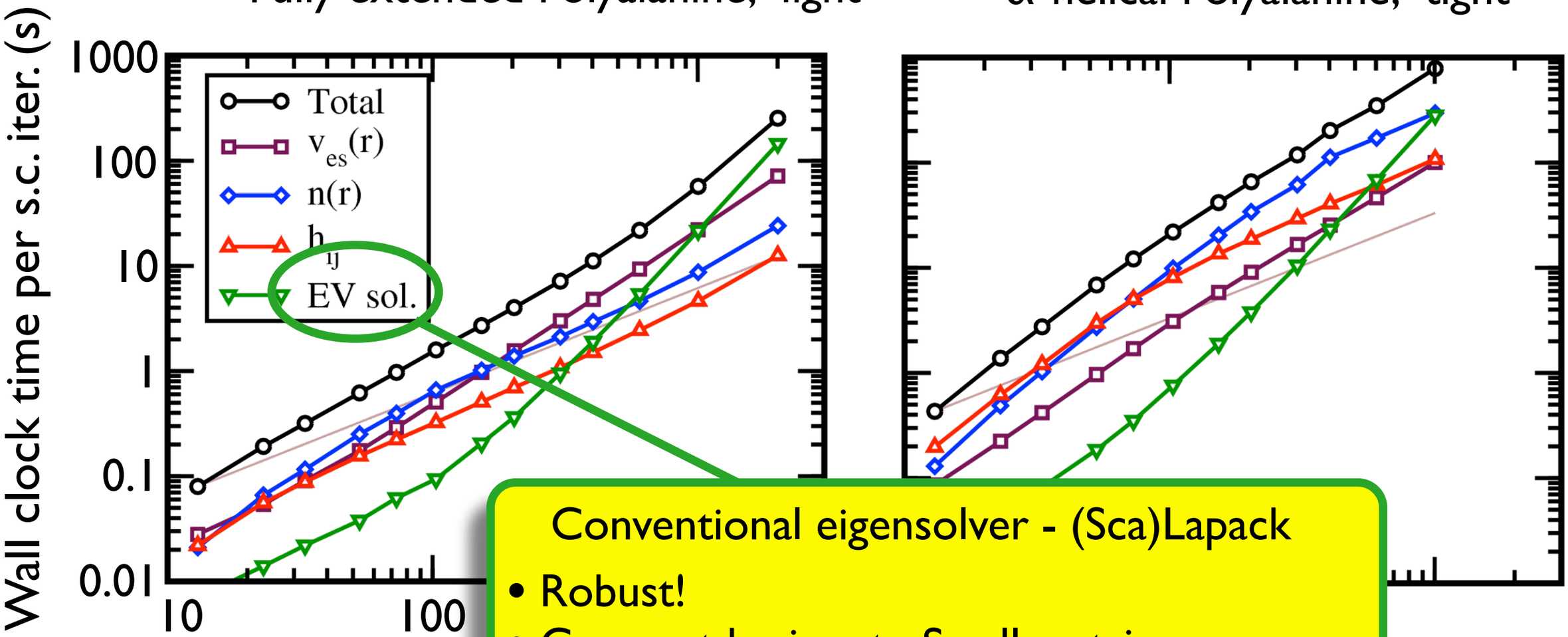
Computational Scaling: CPU Time With System Size



Fully extended Polyalanine, "light"



α-helical Polyalanine, "tight"



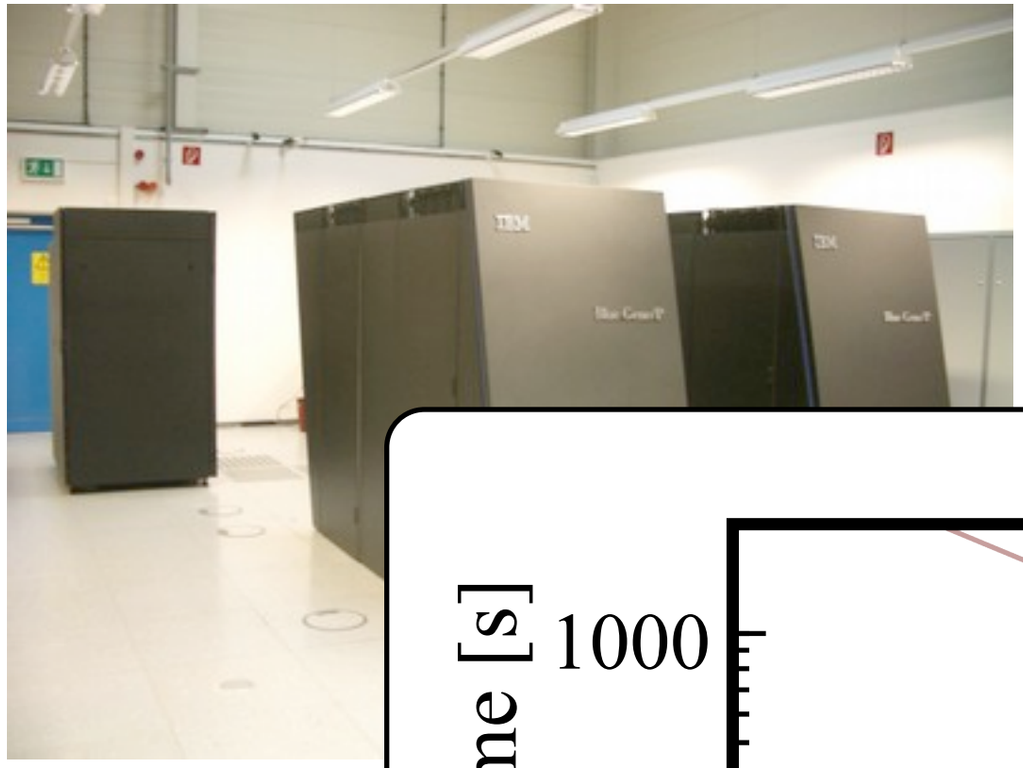
	Light:	Tigh
Basis	tier 1	tier
$l_{Hartree}$	4	6
radial shells	24-36	49-
pts. per shell	302 max.	434 max.
Cutoff width	5Å	6Å

Conventional eigensolver - (Sca)Lapack

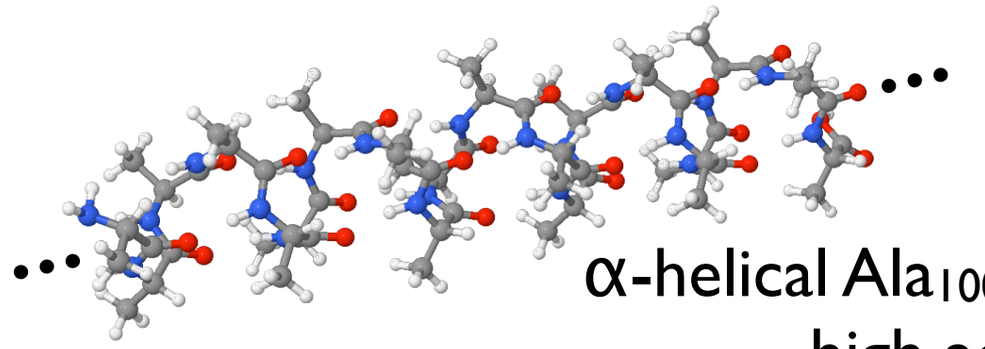
- Robust!
- Compact basis sets: Small matrices
- but $O(N^3)$ scaling - relevant ≈100s of atoms
- 1,000s of CPUs: Scaling bottleneck?

Js
standard Infiniband/Xeon cluster
Benchmarks: W. Jürgens / FHI

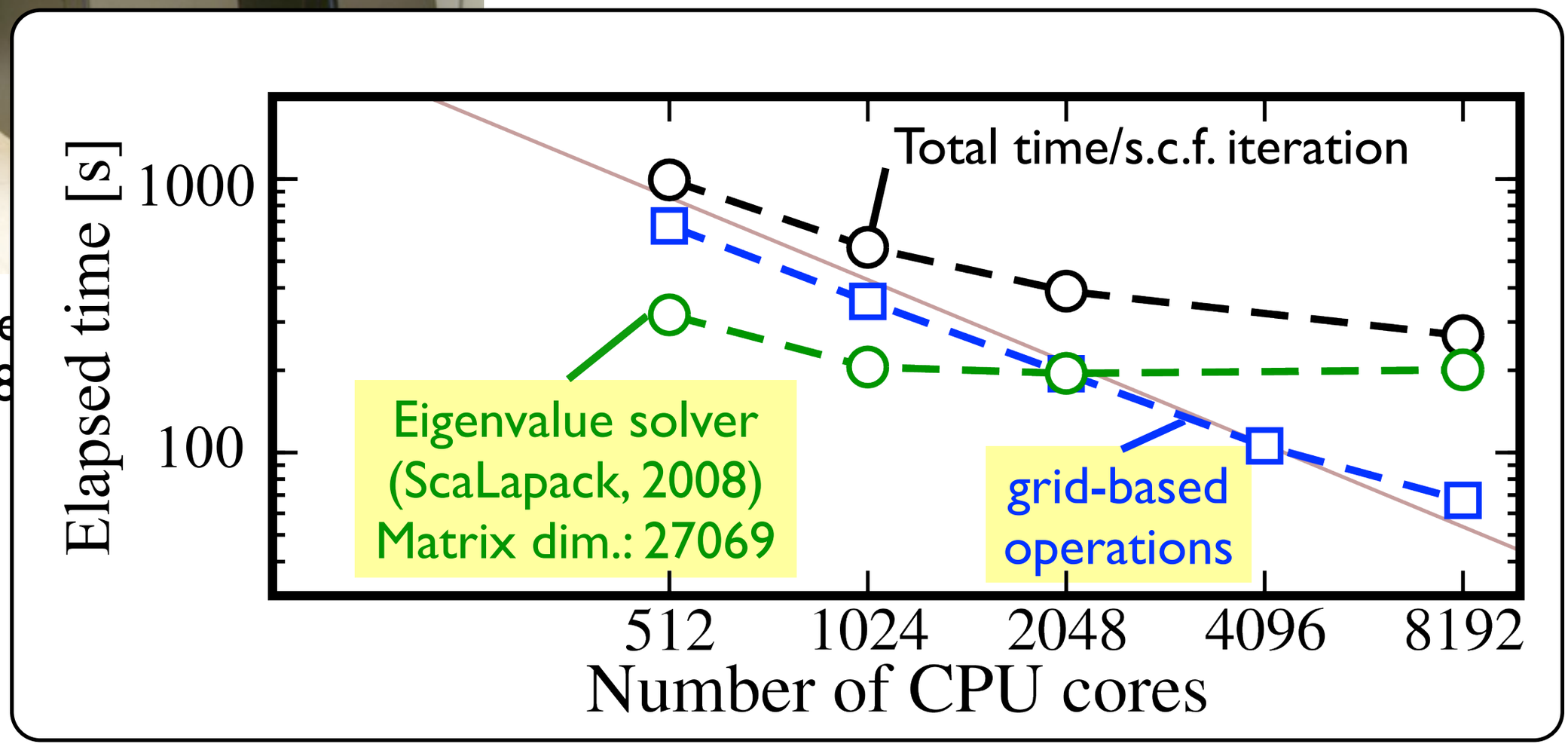
Parallel Eigenvalue Solvers - the Problem



IBM BlueGe
1638



α-helical Ala_{100} (1000 atoms), high accuracy



A Massively Parallel Dense Eigensolver: "ELPA"

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

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

<u>Goal</u>:

- scalable, Scalapack-compatible "drop-in enhancement"
- pure MPI-based implementation
- detailed rewrite based on proven robust/general algorithms

Garching Computing Center *(H. Lederer, R. Johanni)*

Wuppertal University, Mathematics *(L. Krämer, P. Willems, B. Lang)*

TU Munich, Computer Science *(Th. Auckenthaler, H.-J. Bungartz, Th. Huckle)*

FHI Berlin *(V. Blum, M. Scheffler)*

<u>Part of "Eigensolvers for Petaflop Applications" (ELPA) consortium (BMBF)</u>

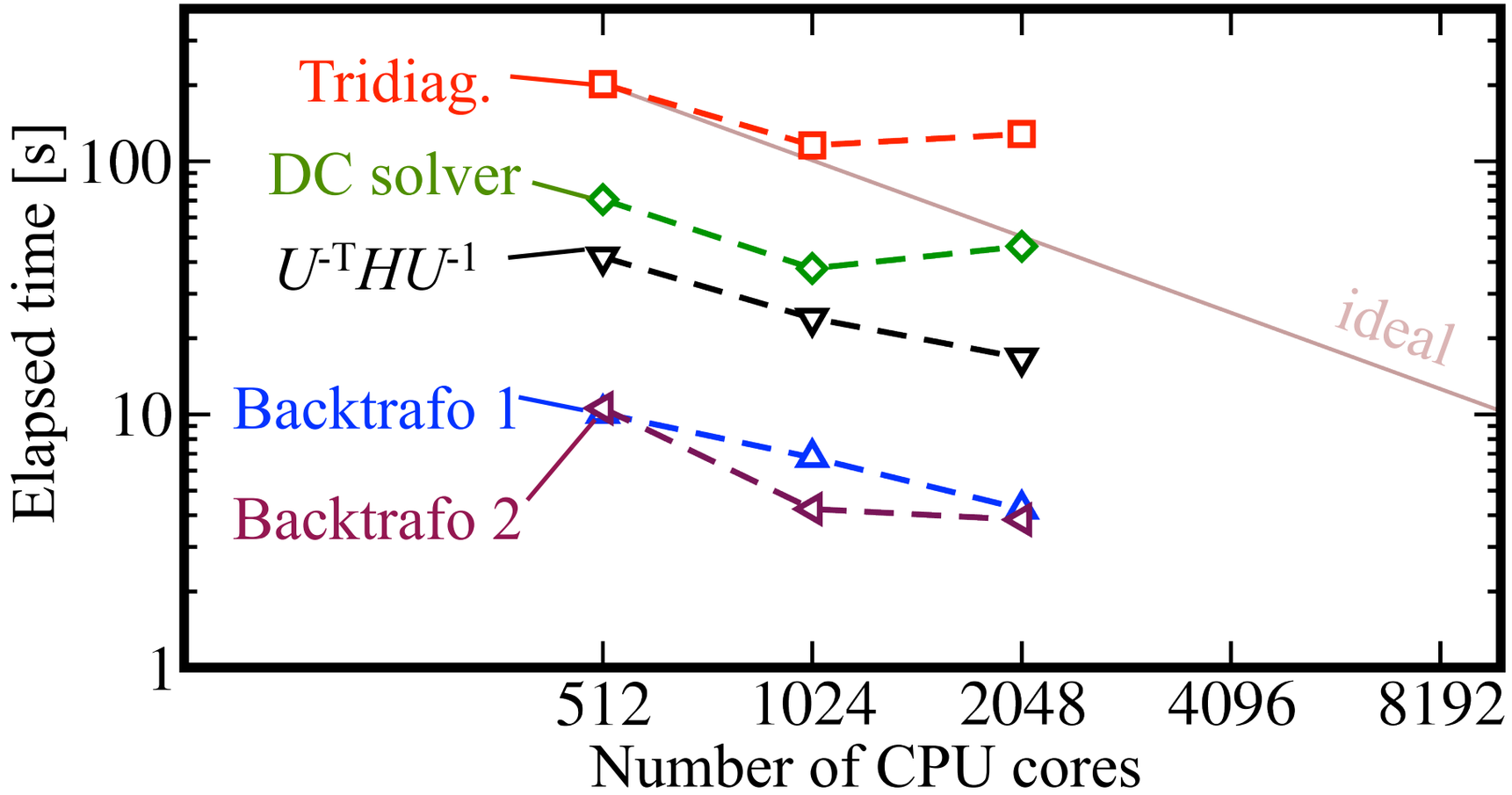
standalone open-source / LGPL library

Taking Apart the Eigenvalue Problem

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

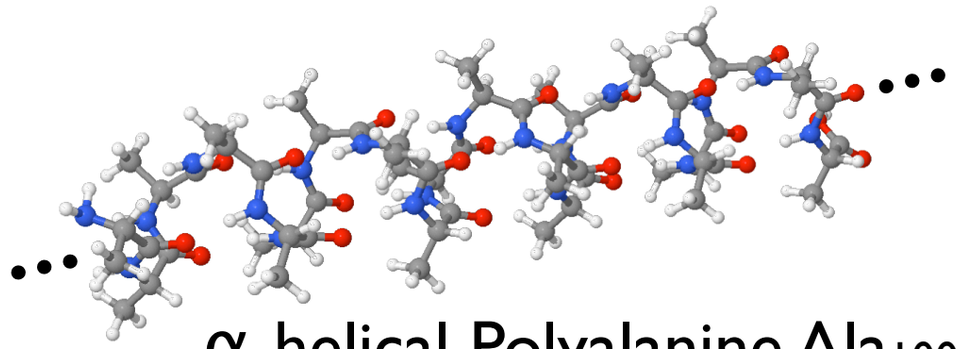
Generalized (non-orthogonal) eigenvalue problem:

- Transform to orthogonal form: $U^{-T}HU^{-1}$
- Transform orthogonal *H'* to *tridiagonal* form
- Solve *tridiagonal* eigenproblem
- Backtransform (1) solution to standard form
- Backtransform (2) standard to general form

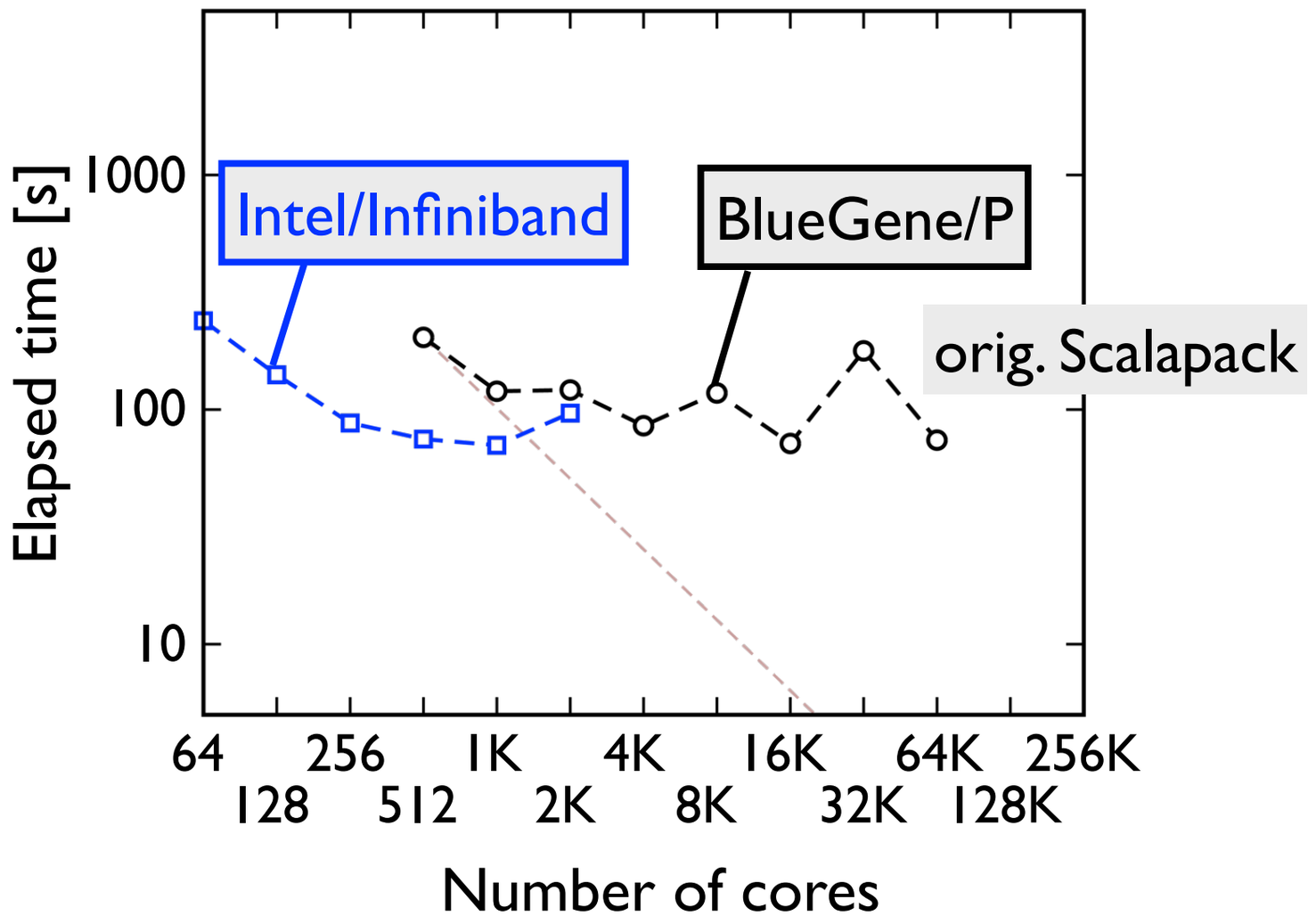


α-helical Polyalanine Ala_{100}, BlueGene/P

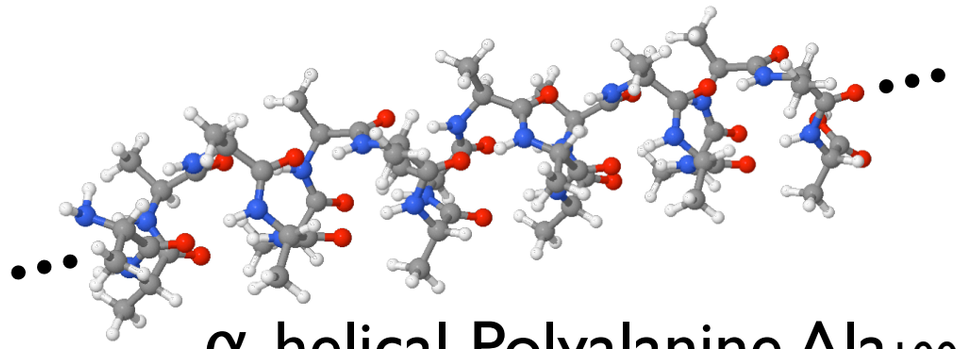
A Careful Rewrite Can Improve Scaling ("ELPA 1")



α-helical Polyalanine Ala_{100}
N=27069, *M*=3410
NAO basis set (FHI-aims)



A Careful Rewrite Can Improve Scaling ("ELPA 1")



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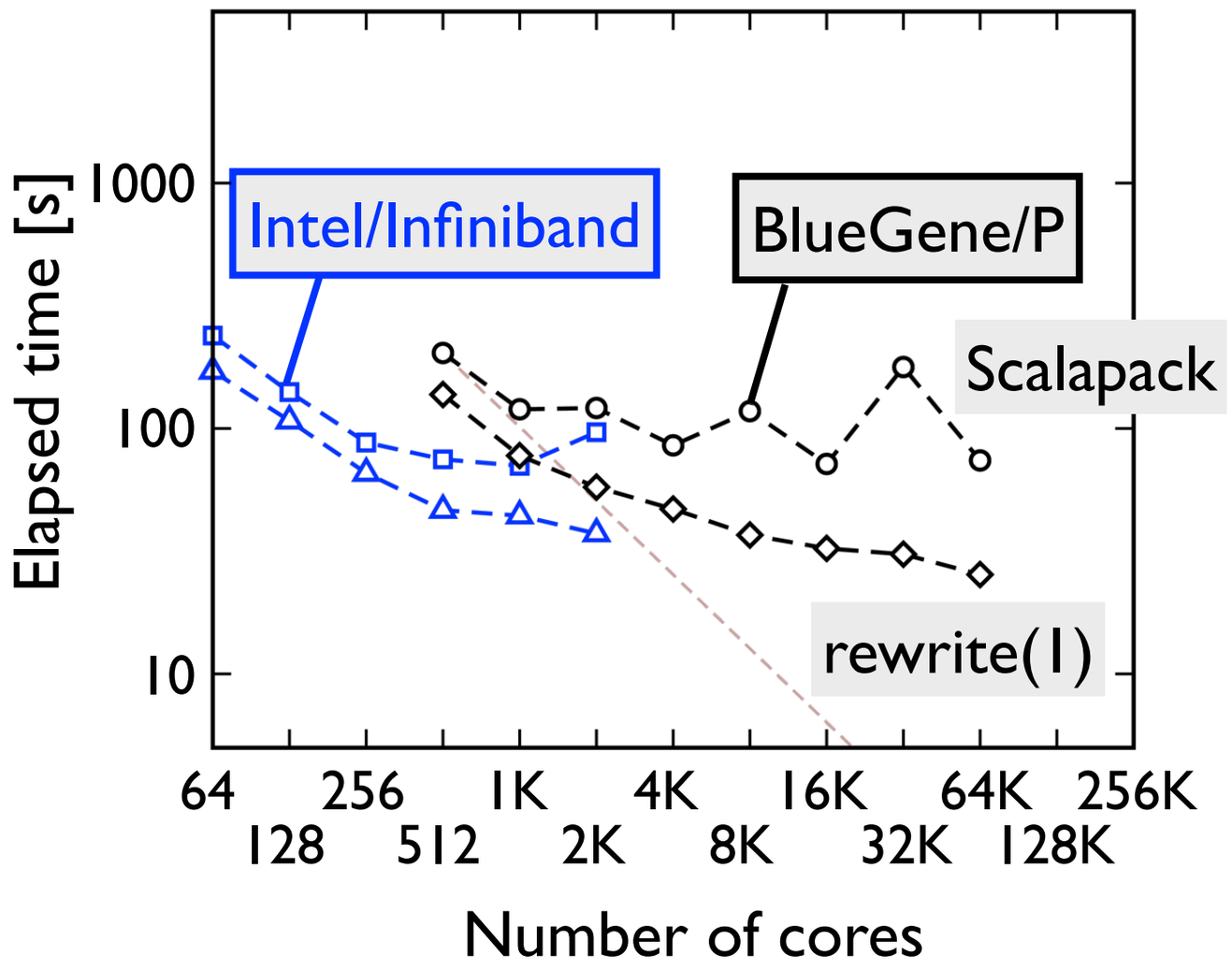
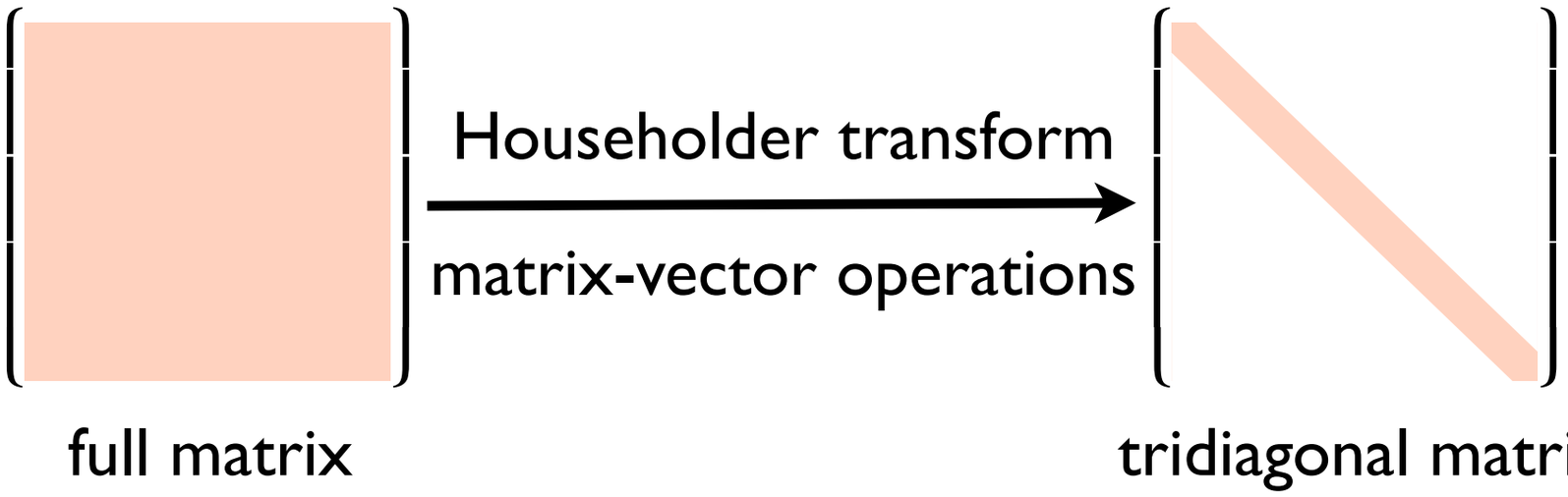
N=27069, *M*=3410
NAO basis set (FHI-aims)



Algorithmic Improvement: 2-Step Tridiagonalization

Remaining chief bottleneck: Tridiagonalization

"Conventional" reduction:

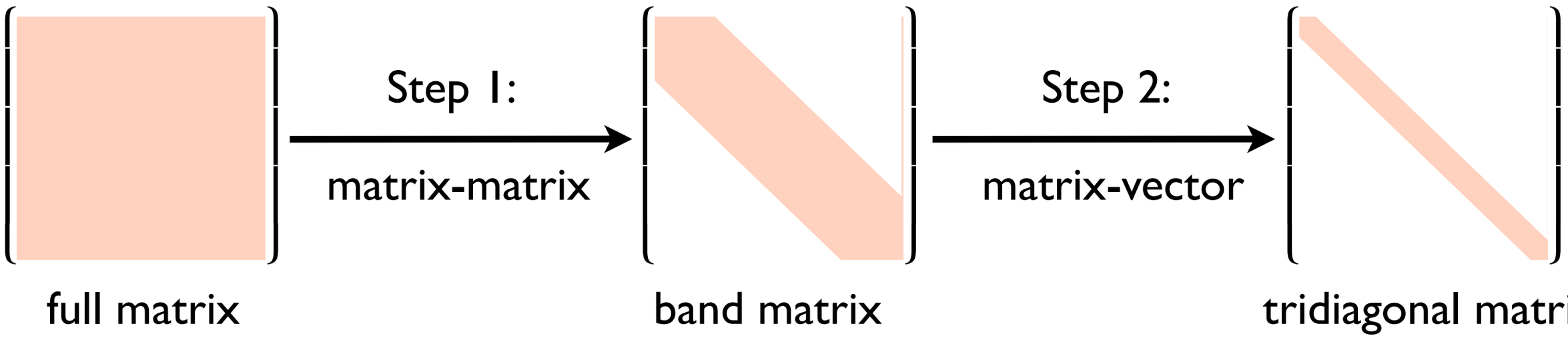


Algorithmic Improvement: 2-Step Tridiagonalization

Remaining chief bottleneck: Tridiagonalization

"Two-step" reduction:

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



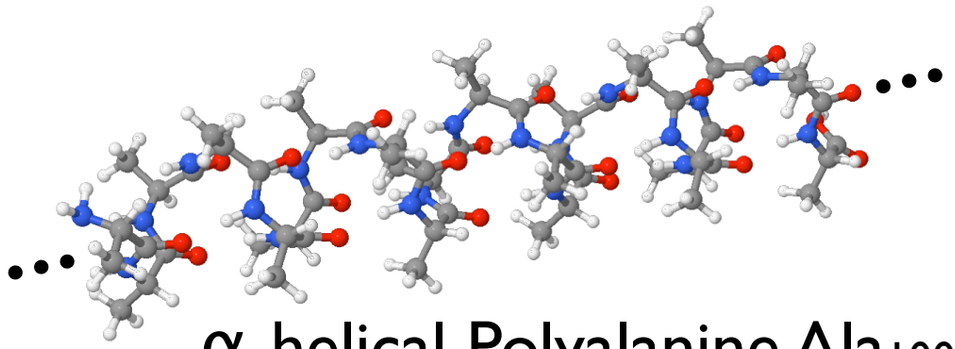
But extra back transform necessary - benefit shrinks for *M* approaching *N*

Massively parallel two-step tridiagonalization:

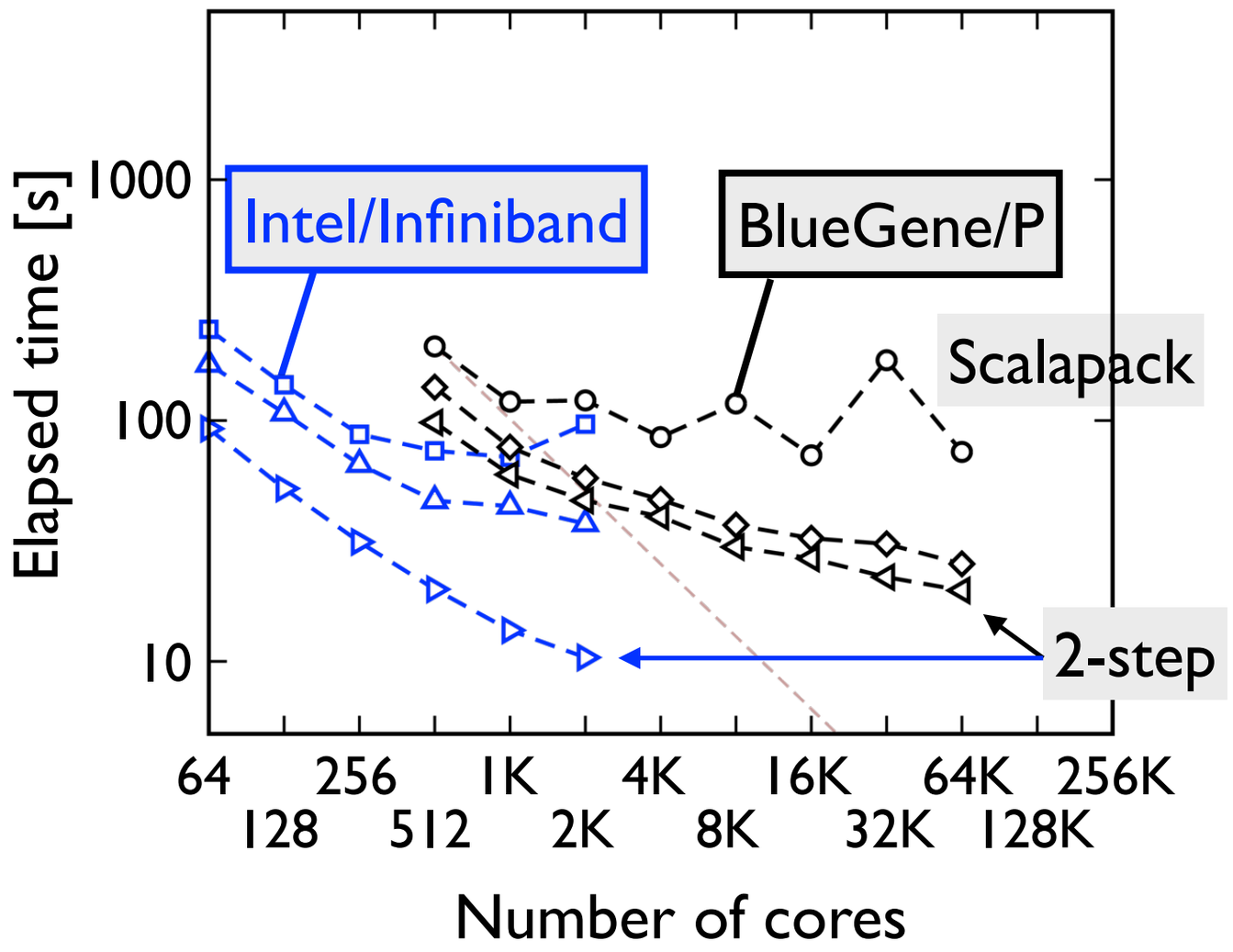
- 2-dimensional data layout for eigenvectors
- Heavily optimized backtransform steps for eigenvectors (adaptive data layout, architecture-specific linear algebra kernels - cache blocking)

Auckenthaler, Blum, Bungartz, Huckle, Johanni, Krämer, Lang, Lederer, Willems, Parallel Computing (2011)
Preprint: http://www.fhi-berlin.mpg.de/aims/aims_publications.php

ELPA, Two-Step Solver

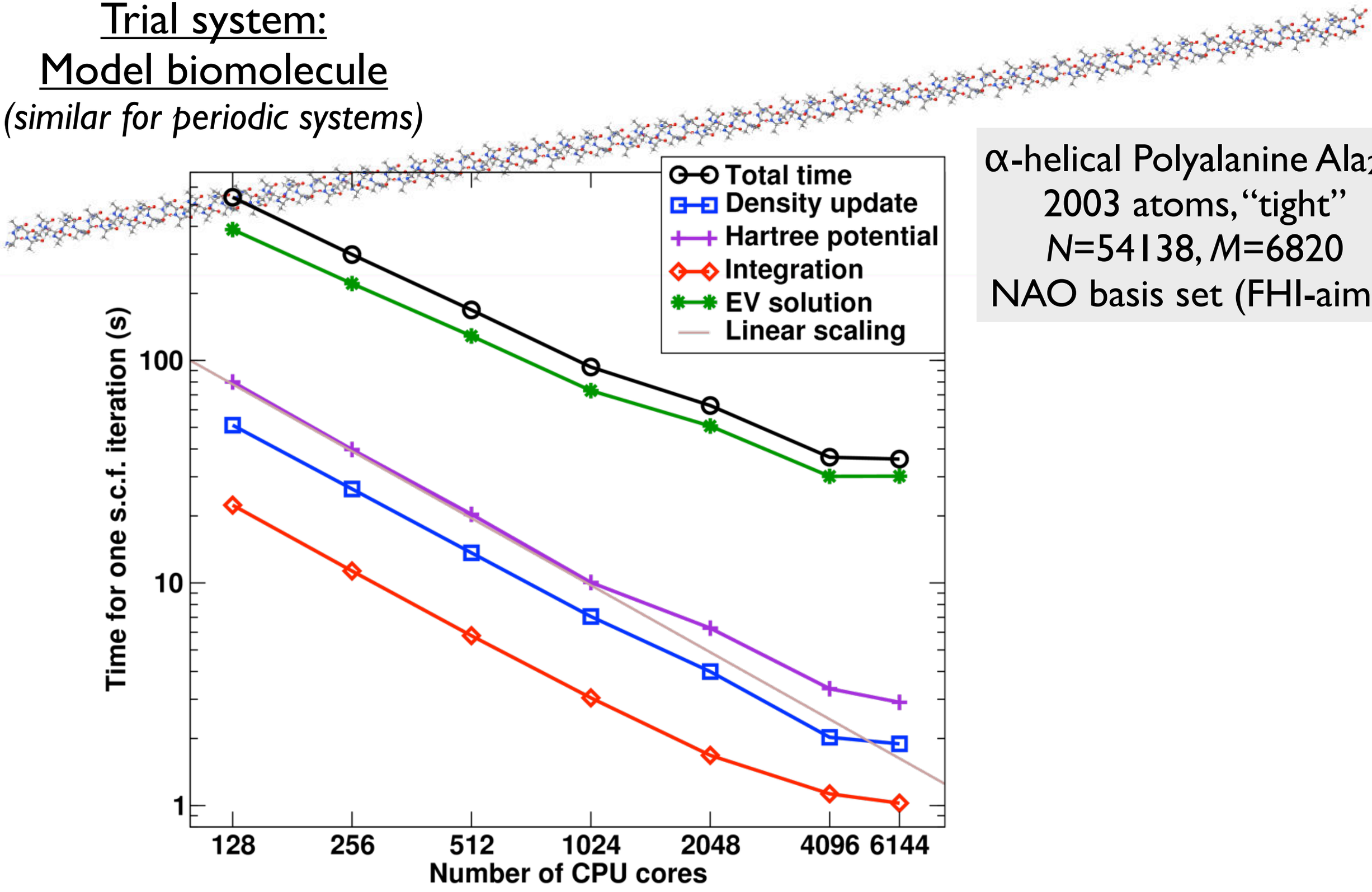


α-helical Polyalanine Ala_{100}
N=27069, M=3410
NAO basis set (FHI-aims)



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

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

LDA, GGA, mGGA etc.

Hohenberg-Kohn, Kohn-Sham, etc.

S. Levchenko
Fri 09:00h

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

Nice, clean, tractable, and sadly often insufficient

Becke, Burke, Perdew, Ernzerhoff, others

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

"Hybrid functionals" - certainly legal

Unfortunately:

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

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)

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

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

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

Basis pair product space

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

must be overcomplete if

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

itself approaches completeness

Solution (quantum chemistry):

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

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

In finite systems, "RI-V":

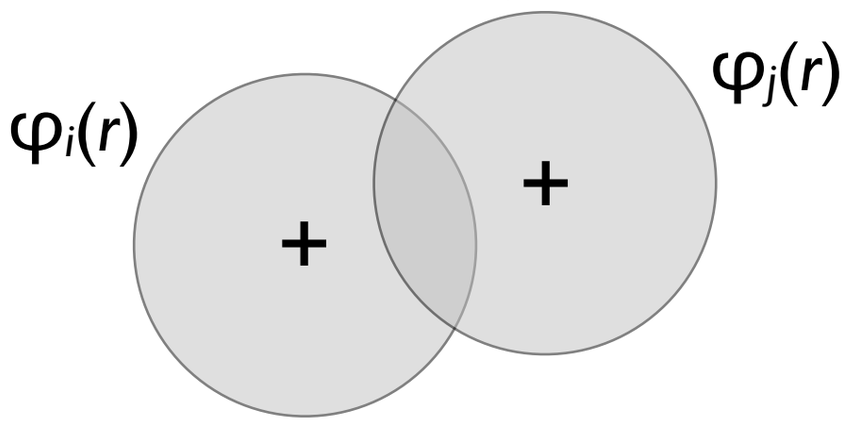
$$C_{ij}^\mu = \sum_\nu (ij|\nu) V_{\nu\mu}^{-1}$$

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

Accurate [1], but *delocalizes* C!

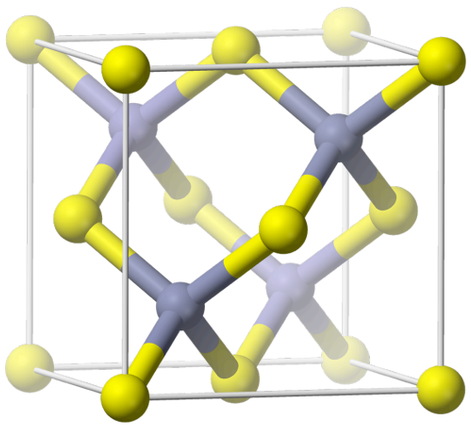
(Much) better scaling: Localized RI

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



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

Accuracy: Periodic hybrid functionals



Cohesive properties, bulk semiconductors

	Si		
PBE0	a [Å]	B_0 [Mbar]	E_{coh} [eV]
FHI-aims, *tight*	5.439	0.99	4.553
Ref. [1]	5.433	1.00	4.555
HSE06			
FHI-aims, *tight*	5.446	0.98	4.527
Ref. [2]	5.435	0.98	4.582
	GaAs		
HSE06			
FHI-aims, *tight*	5.695	0.71	3.150
Ref. [2]	5.687	0.71	3.149
	Ge		
HSE06			
FHI-aims, *tight*	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).

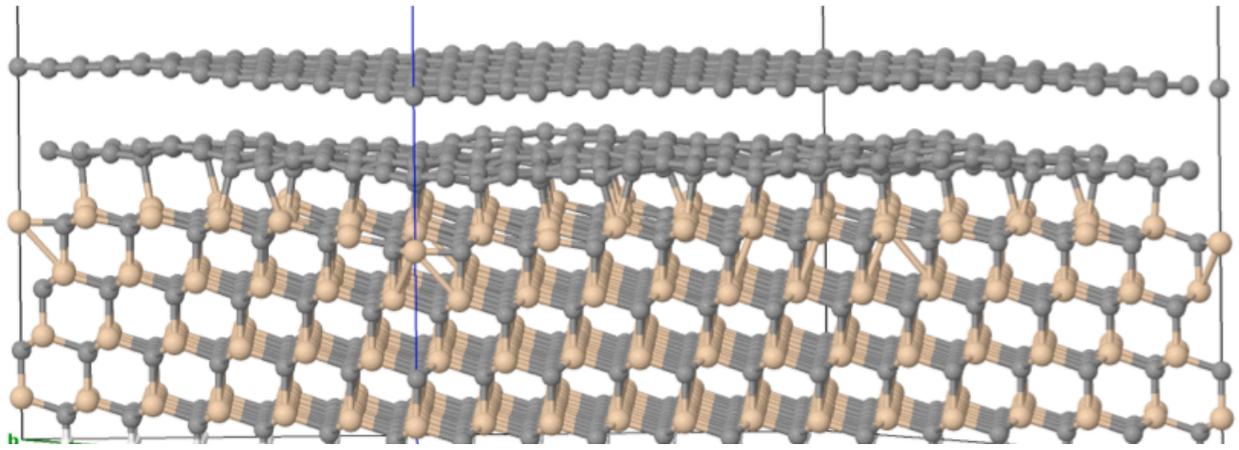
Is This a "Stable" Surface Phase?*

Lydia Nemec

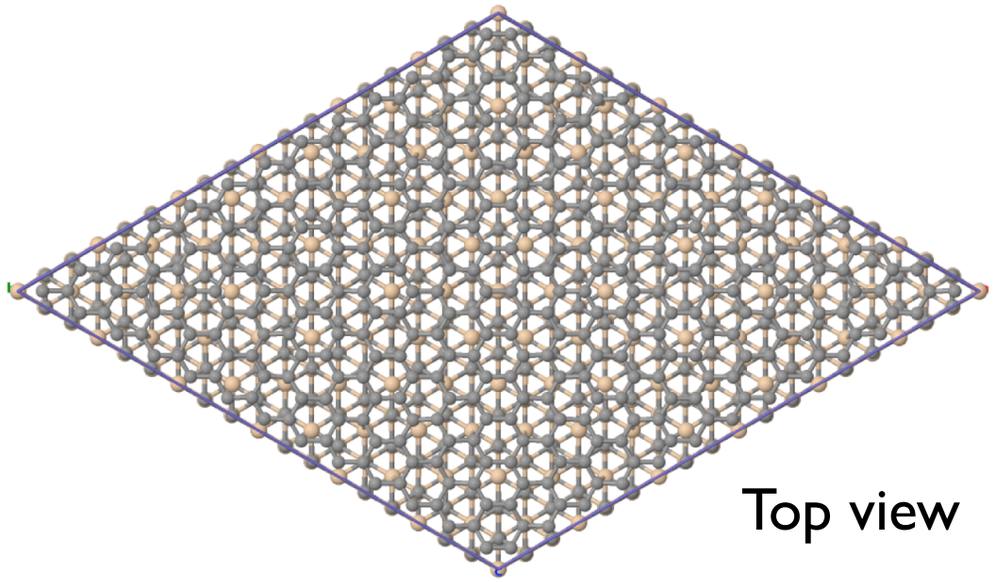
Graphene on SiC(0001)

van Bommel, Crombeen, van Tooren, Surf. Sci. 1975

many others



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



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 (2013).

Thermodynamic stability criterion for competing surface phases:

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

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

Externally (experimentally) controllable

Stability boundaries:
Bulk SiC more stable than elemental Si, C

$\mu_C \leq E_C^{bulk}$

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

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

Total energies, full relaxation from first principles:

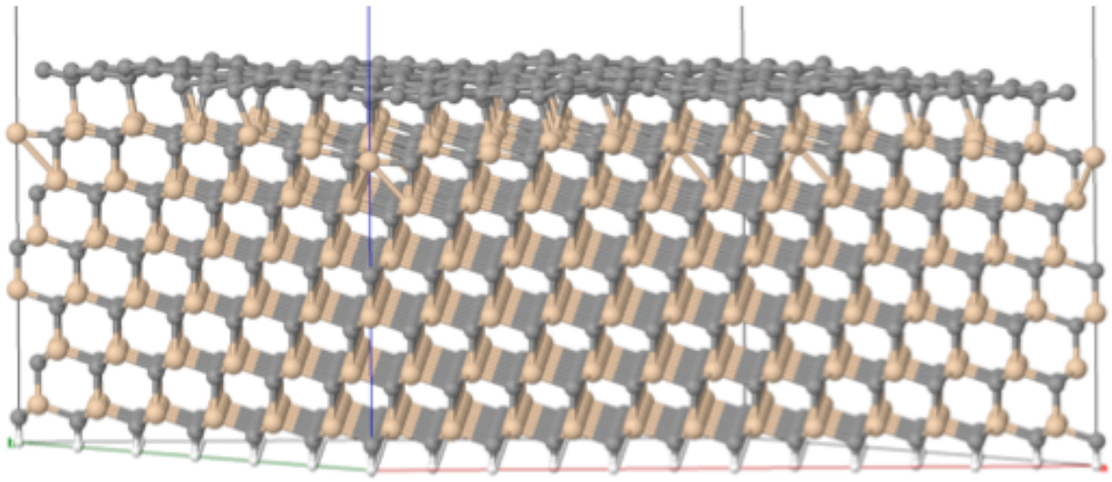
- six-bilayer SiC slabs + surface planes
- full relaxation, "tight" numerical settings (C: tier 2, Si: tier1+*gd*)
- Density functional: "GGA-PBE+vdW" [1] - straight LDA/GGA not enough.

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

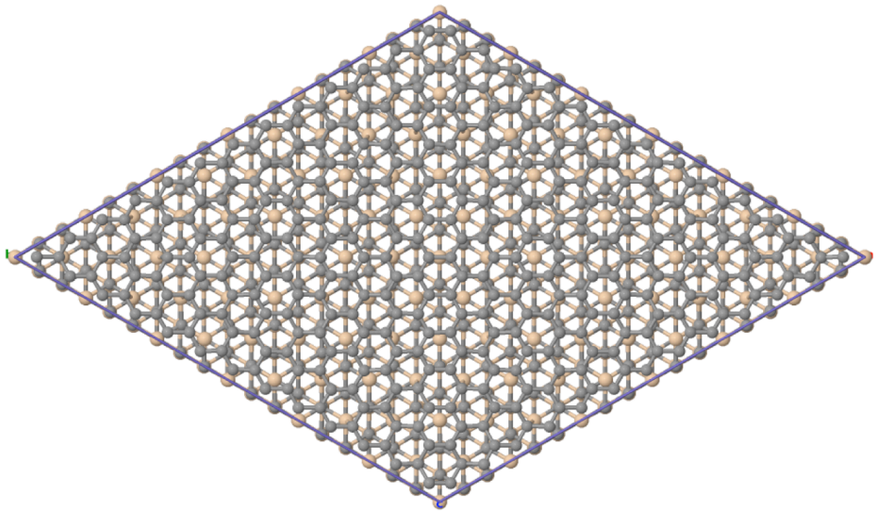
Ab Initio Thermodynamics for Si-Side Graphene/SiC

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

<u>$(6\sqrt{3}\times 6\sqrt{3})$ SiC(111) + (13x13) graphene:</u>



ZLG, side view



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

<u>Total energies, full relaxation from first principles:</u>

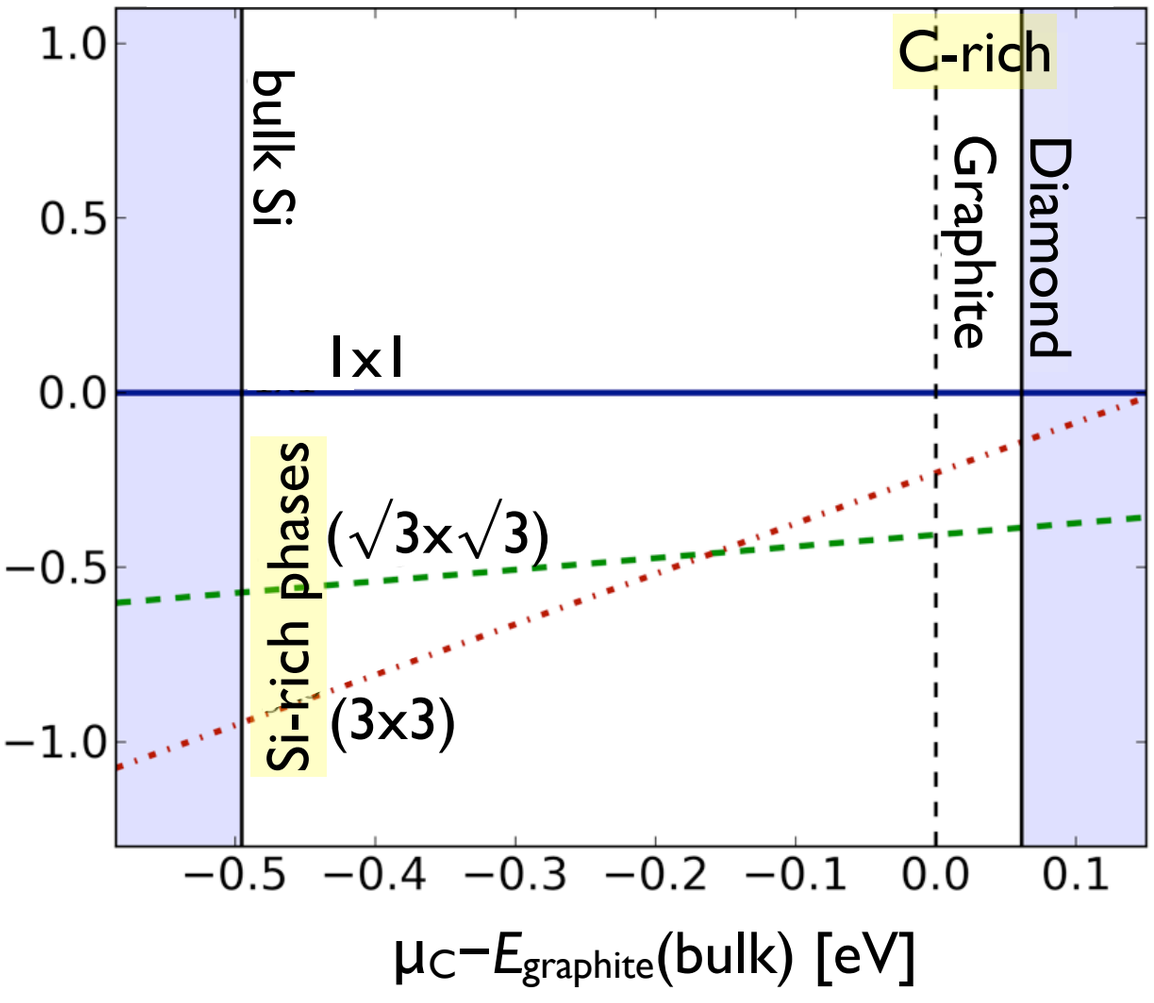
- six-bilayer SiC slabs + surface planes
- full relaxation, "tight" numerical settings (C: tier 2, Si: tier1+*gd*)
- Density functional: "GGA-PBE+vdW" [1] - straight LDA/GGA not enough.

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

Stability of Surface Phases: PBE+vdW

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

Surface energy hierarchy: 3C-SiC(111)



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

Stability of Surface Phases: PBE+vdW

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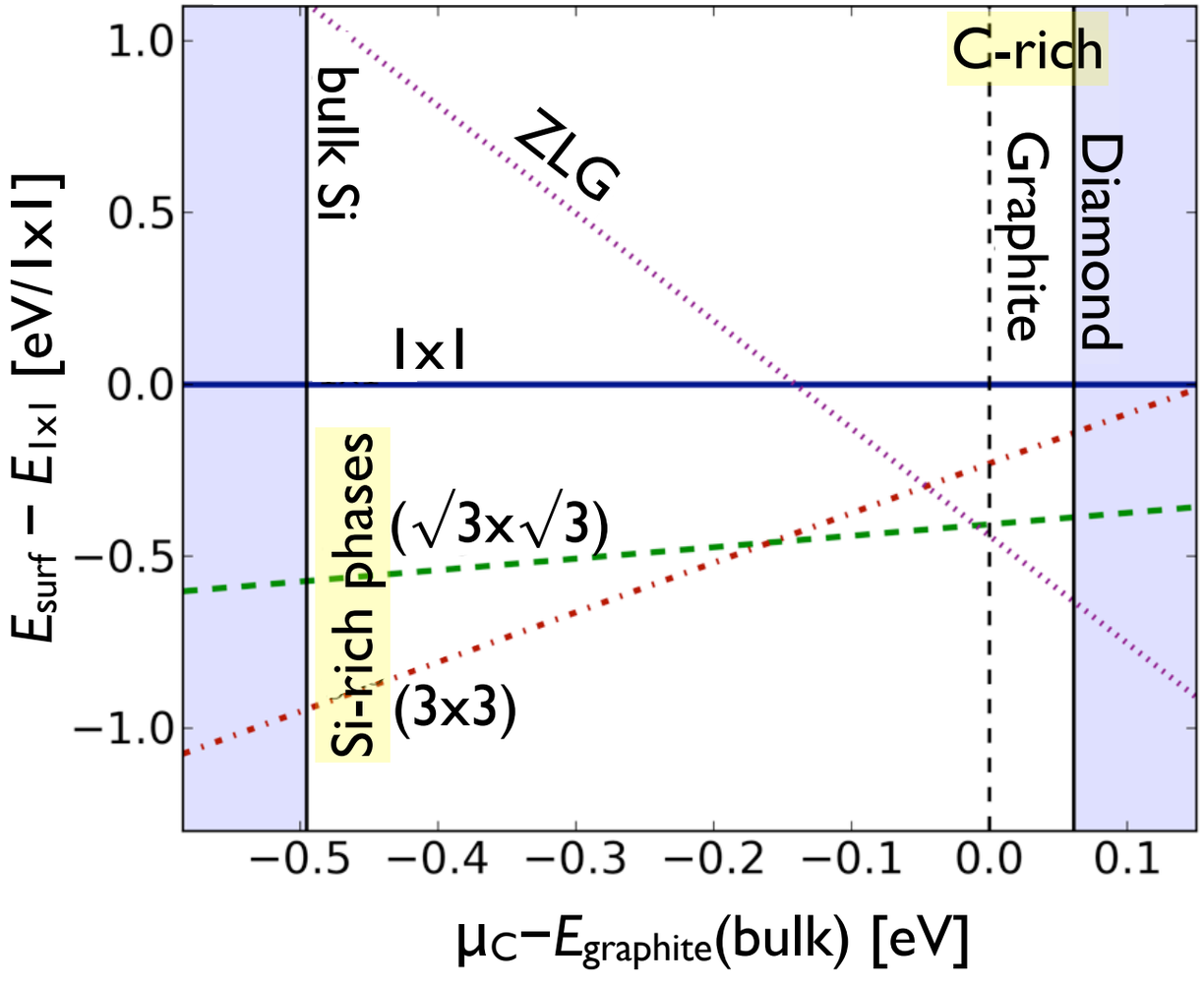

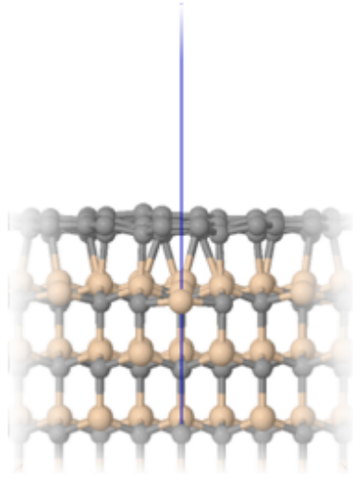

ZLG

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

Stability of Surface Phases: PBE+vdW

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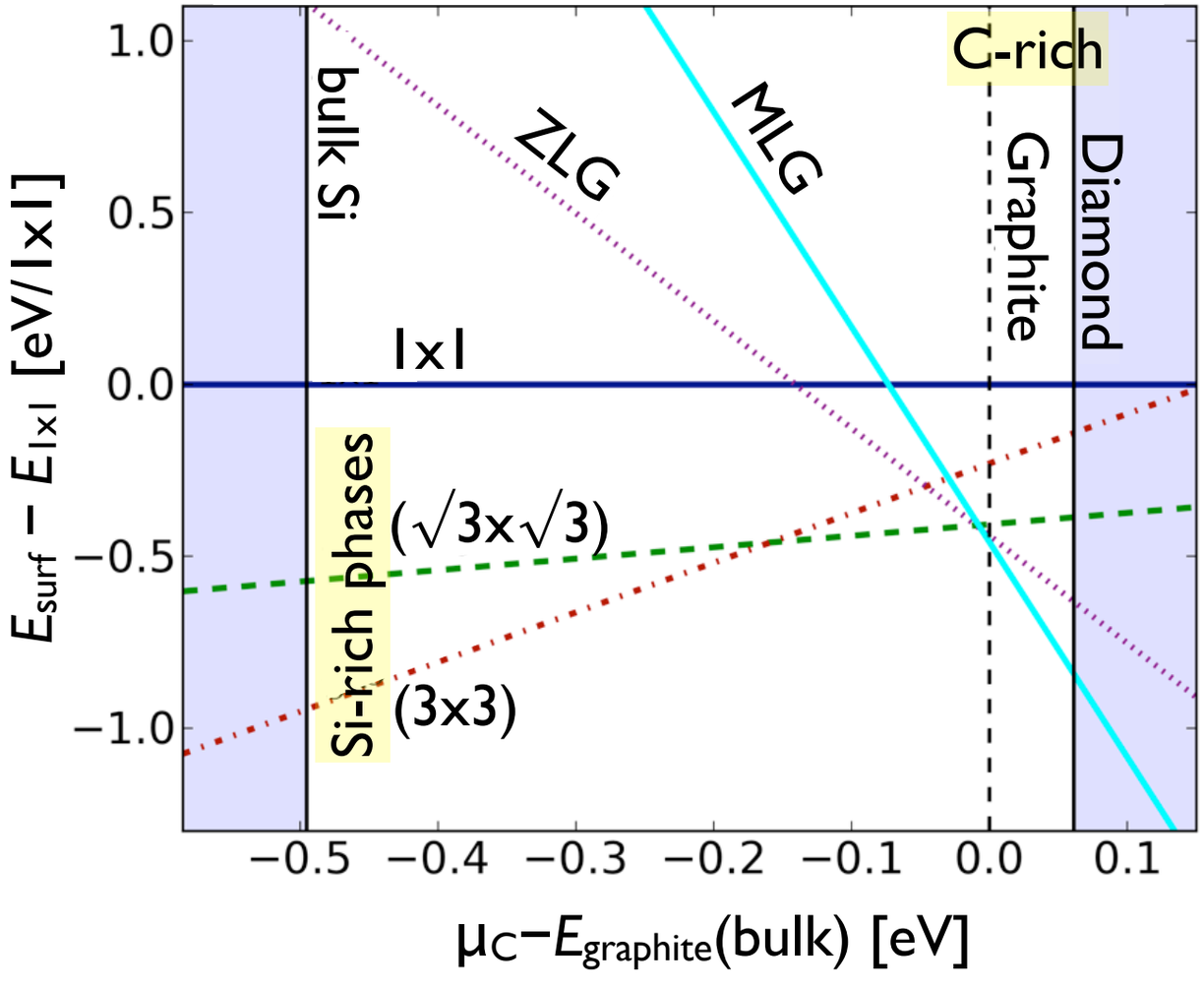

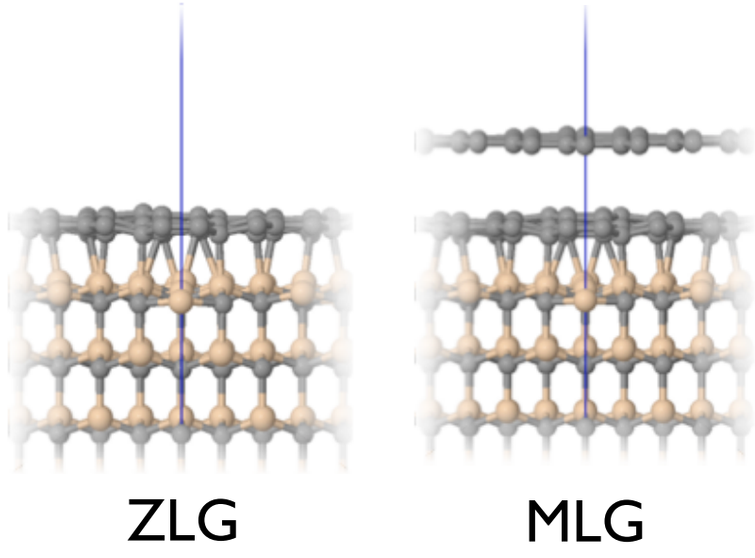

Nemec, Blum, Rinke, Scheffler, PRL (2013).

Stability of Surface Phases: PBE+vdW

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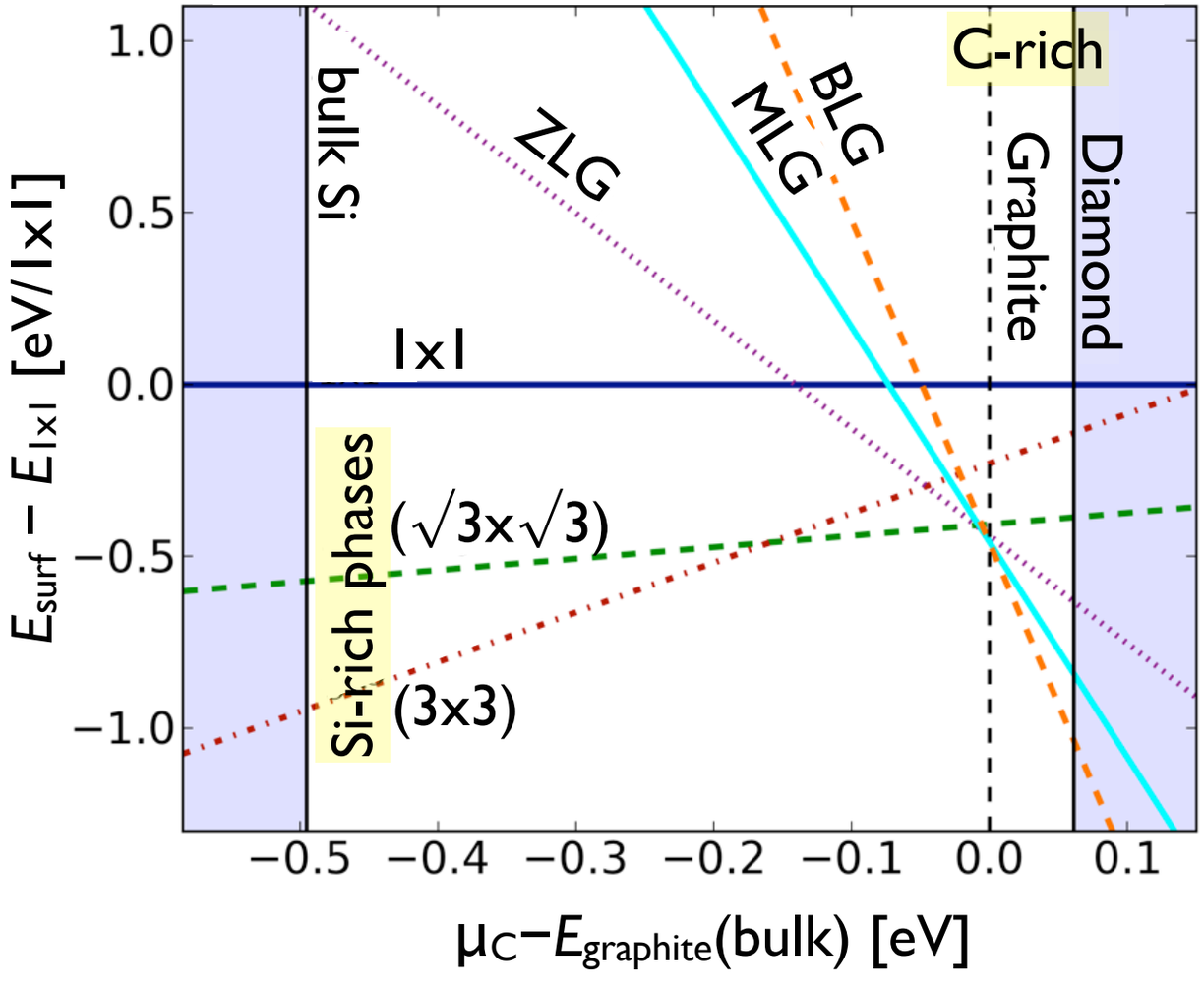

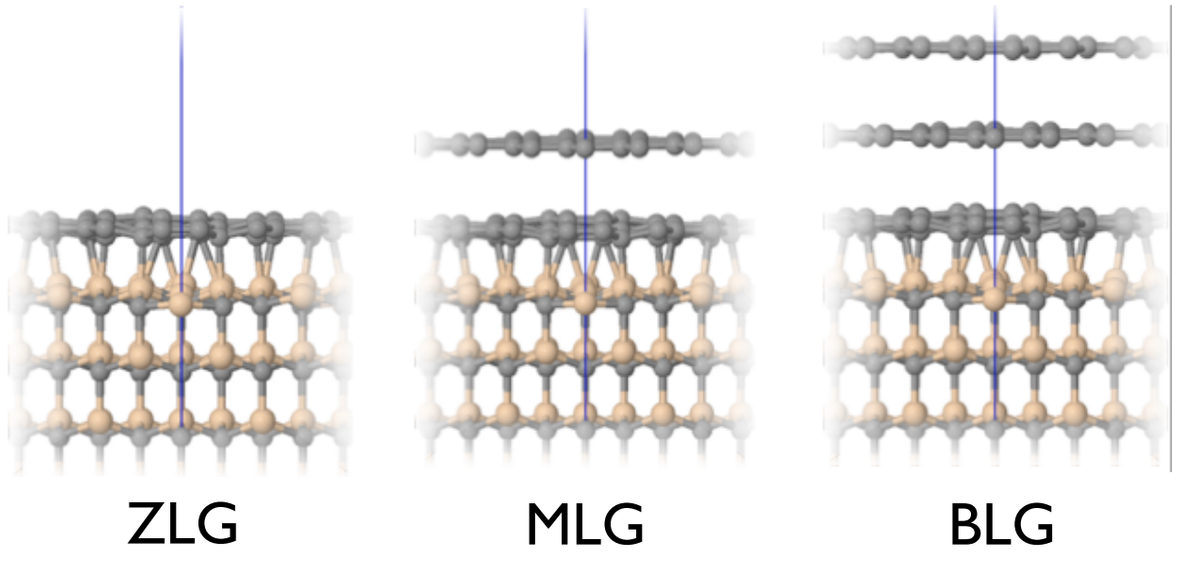

Nemec, Blum, Rinke, Scheffler, PRL (2013).

Stability of Surface Phases: PBE+vdW

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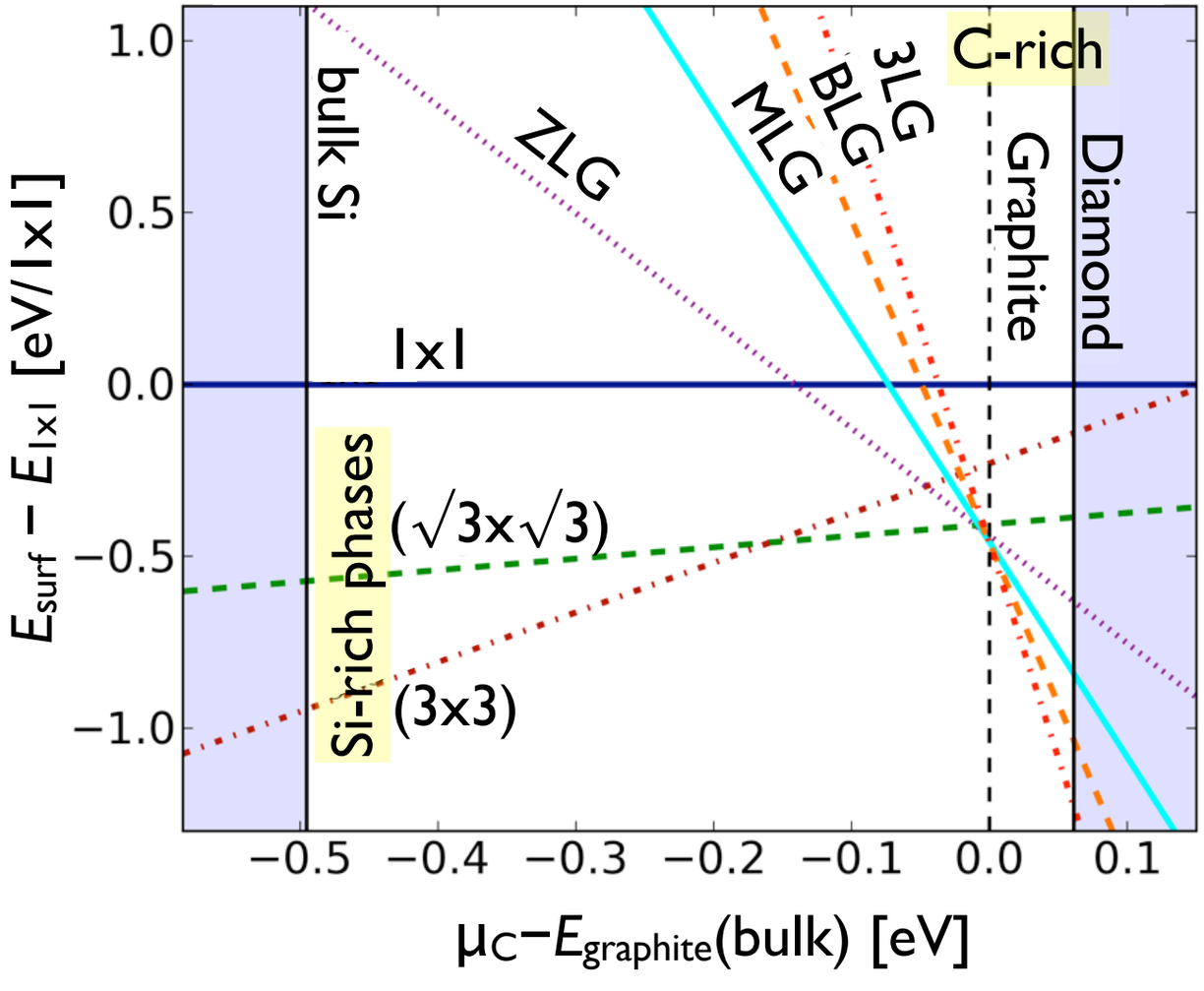

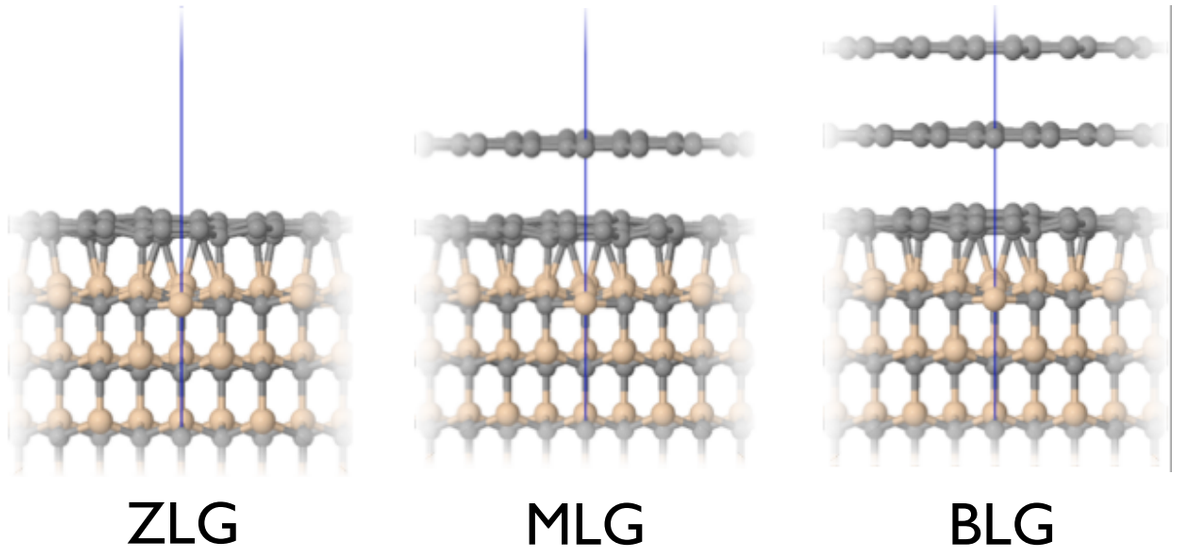

Nemec, Blum, Rinke, Scheffler, PRL (2013).

Stability of Surface Phases: PBE+vdW

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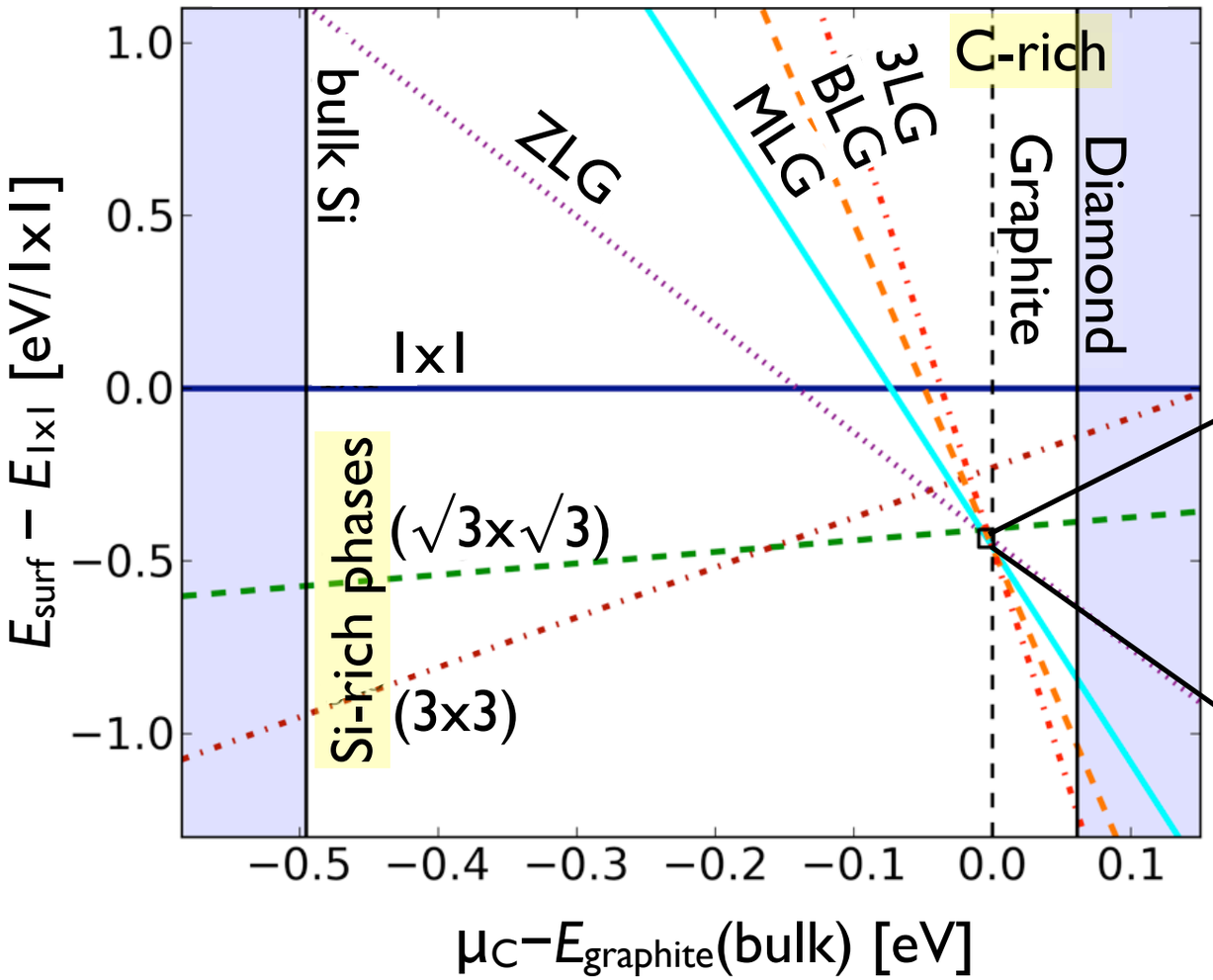
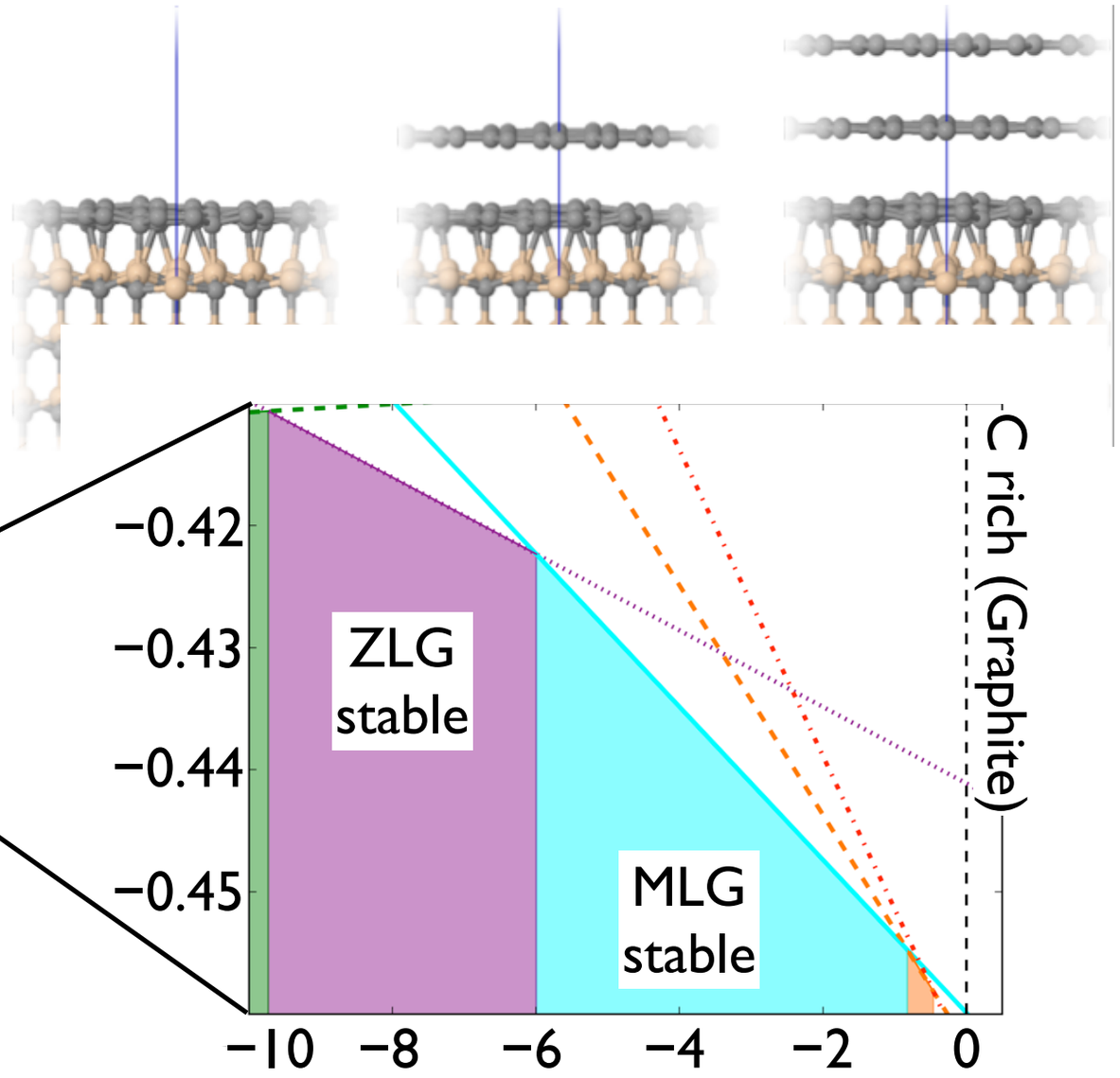




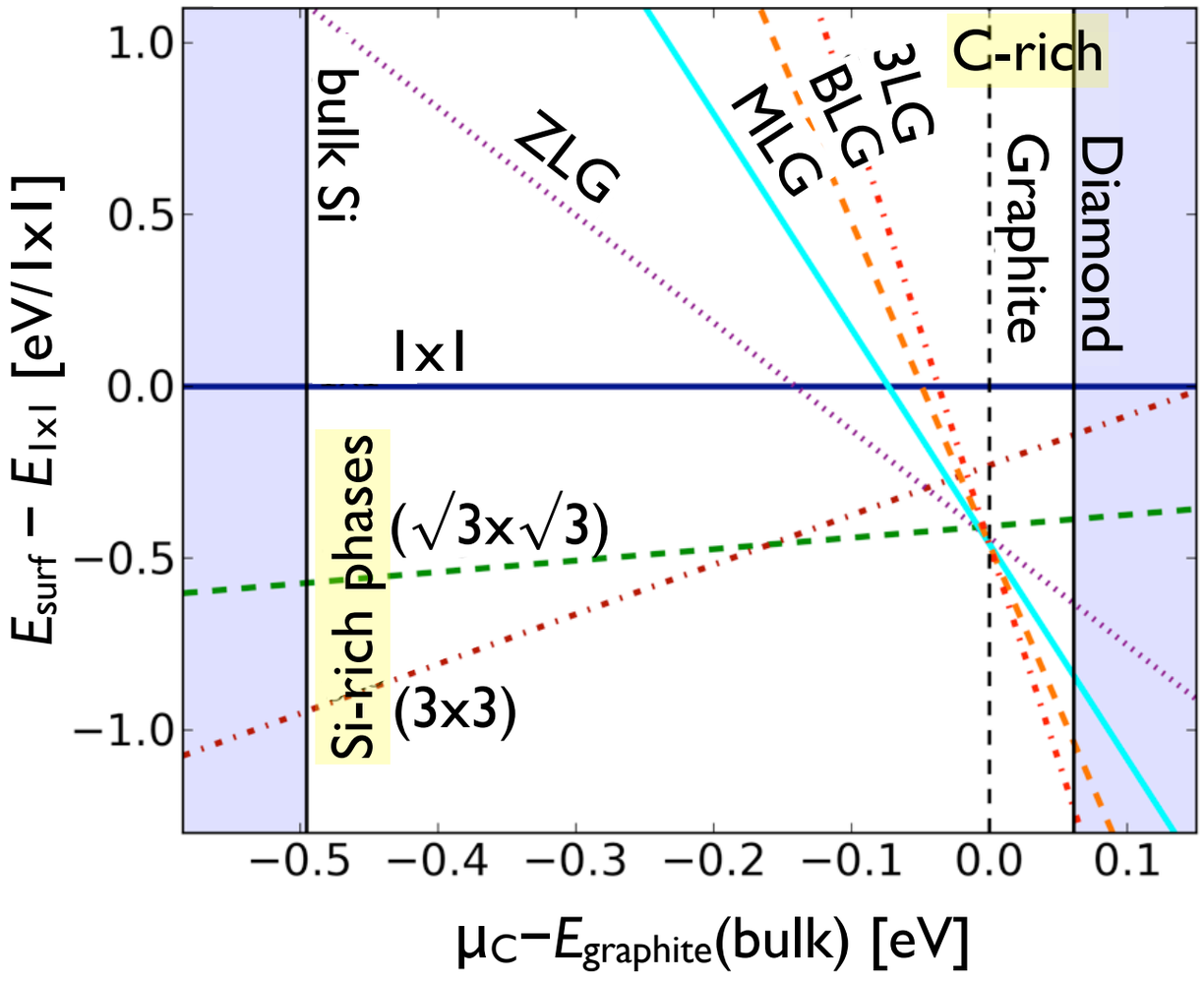
Nemec, Blum, Rinke, Scheffler, PRL (2013).

Stability of Surface Phases: Conclusion

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

PBE+vdW

Surface energy hierarchy: 3C-SiC(111)



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

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

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

2013 - Summary and Outlook

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

Key advantages:

- Reliable, affordable all-electron numbers up to large systems
- Periodic, cluster-type system on exactly equal footing
- Seamlessly from light to heavy elements
- Excellent use of (massively) parallel hardware
- Path to many-body approaches (RPA, *GW*, ...)

Much ongoing work:

QM/MM embedding into external fields
Optical properties in molecules and solids
Density functional perturbation theory (phonons, general linear response)
MANY more.

The People Behind FHI-aims