The Nuts and Bolts of Electronic Structure Theory

Basis sets, Real-Space Grids, Relativity, Scalability

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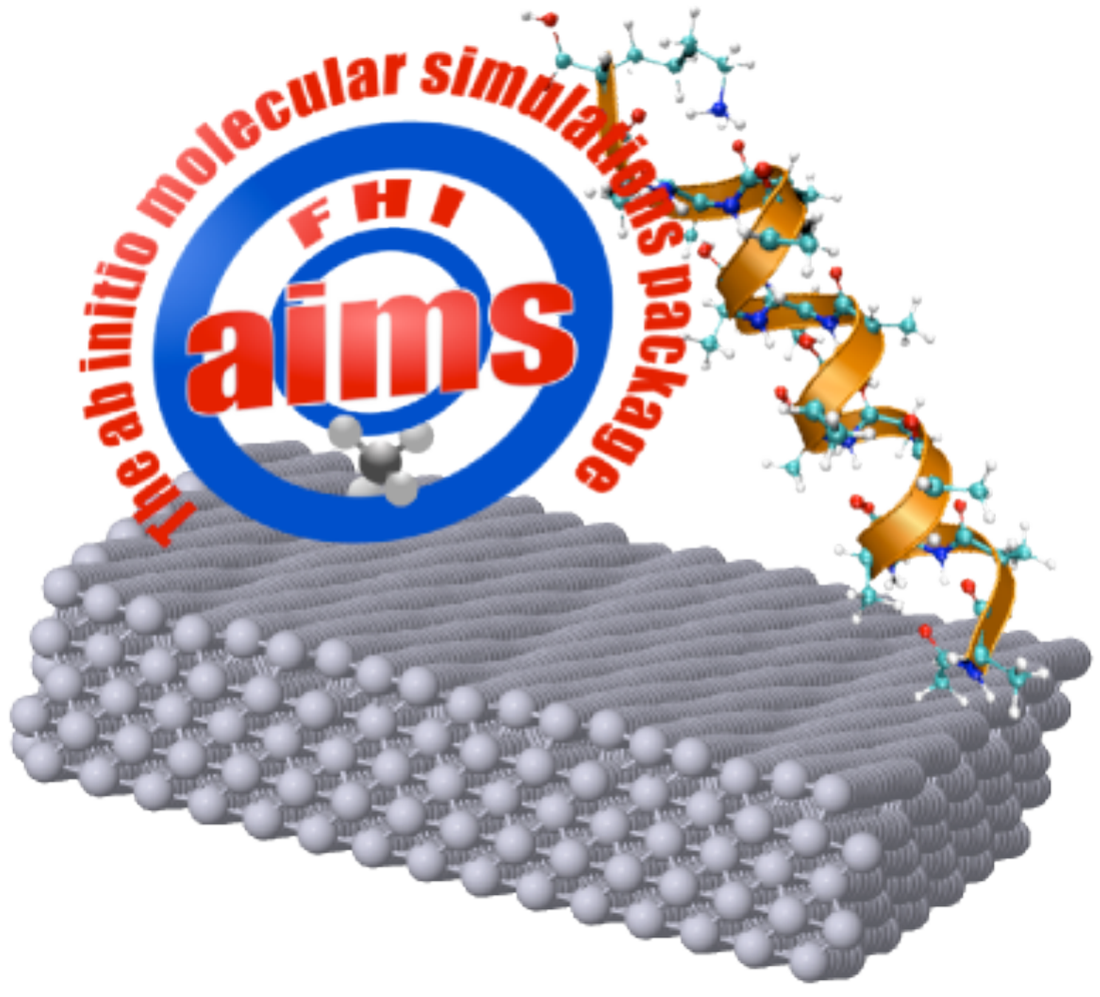


Hands-On Tutorial, Berlin - July 13, 2011

Scope

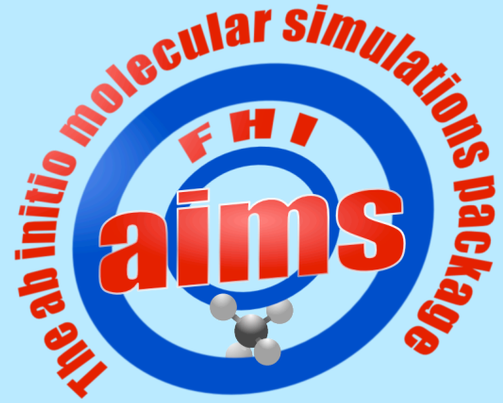
$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\boldsymbol{r}) + v_{\text{es}}(\boldsymbol{r}) + v_{\text{xc}}(\boldsymbol{r})\right]\psi_k(\boldsymbol{r}) = \epsilon_k \psi_k(\boldsymbol{r})$$

Kohn-Sham 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. → X. Ren, Fri 11:30h



<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

Wishlist for Electronic Structure Theory

- Cover (essentially) the entirety of chemistry / materials:
  - first/second row elements
  - 3*d* transition metals (magnetism)
  - 4*d*/5*d* elements (relativity)
  - *f*-electron systems
  - ...
- Periodic, cluster systems on equal footing
- all-electron
- Path "beyond" DFT-LDA/GGA (HF, hybrids, RPA, MP2, *GW*, ...)
- (Massively) parallel scalability

And, efficiency, but under a constraint: Accuracy

Accurate numerical convergence must be affordable for real systems

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:

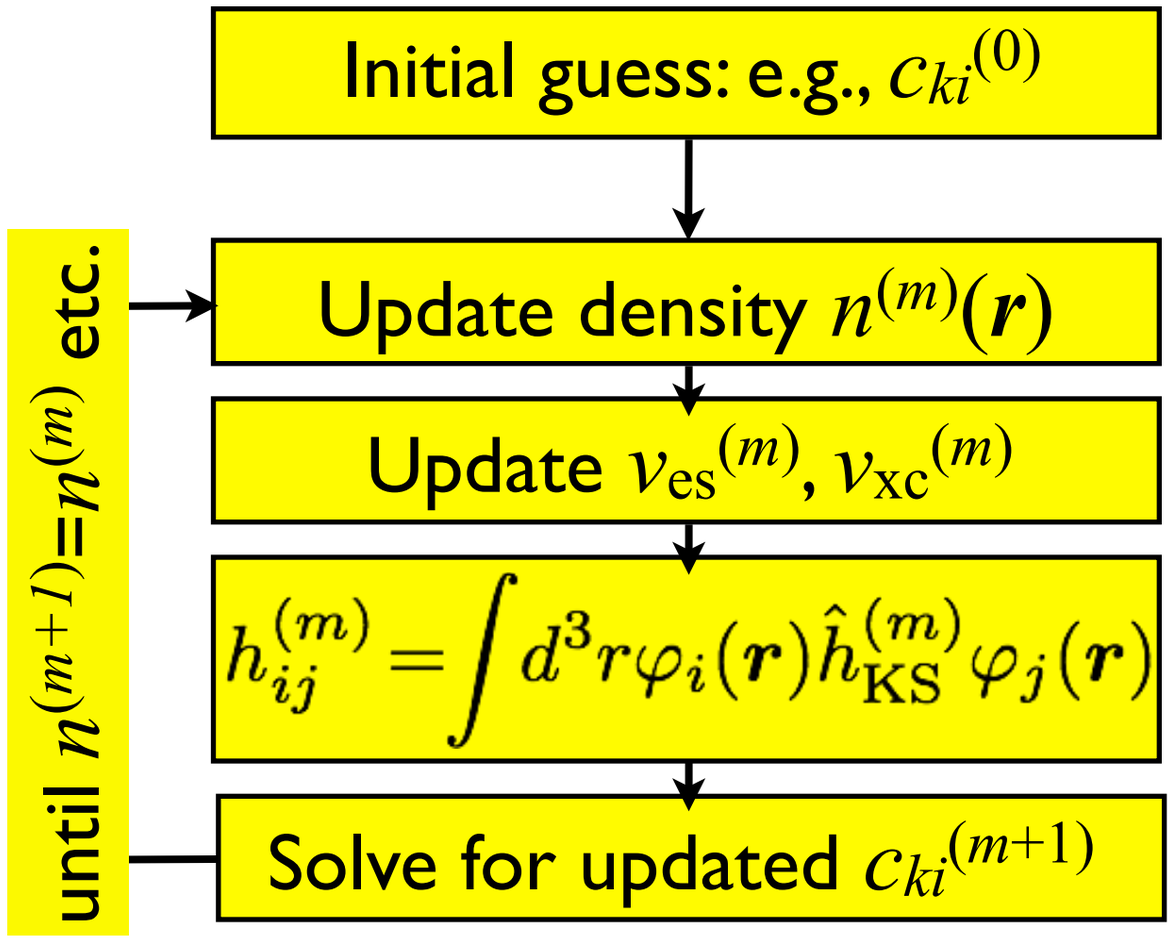
$$\underline{\underline{h}}\,\underline{c}_k = \epsilon_k\,\underline{\underline{s}}\,\underline{c}_k$$

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

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

2. Self-consistency:

J. Wieferink
Wed 11:30h



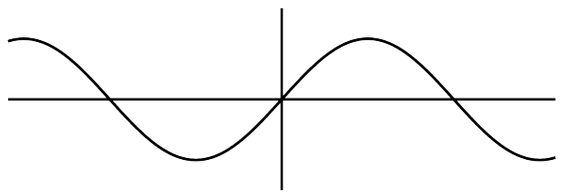
Electronic Structure Basis Sets

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

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

Many good options:

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



M. Marsman Thu 11:30h

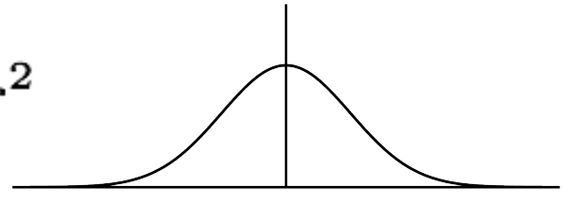
→ efficient FFT's (density, electrostatics, XC-LDA/GGA)

→ inherently periodic

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

C. Ambrosch-Draxl Thu 10:00h

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



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

H. Appel Tue 11:30h

FHI-aims: Numeric atom-centered basis functions

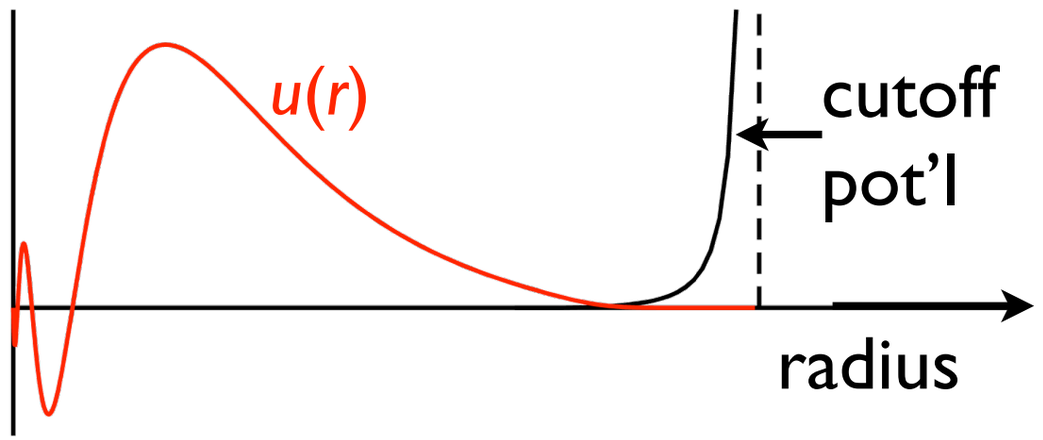
$$\varphi_{i[lm]}(\boldsymbol{r}) = \frac{u_i(r)}{r} \cdot Y_{lm}(\Omega)$$

Many popular implementations:
DMol³ (Delley), FPLO (Koepernik *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), ...



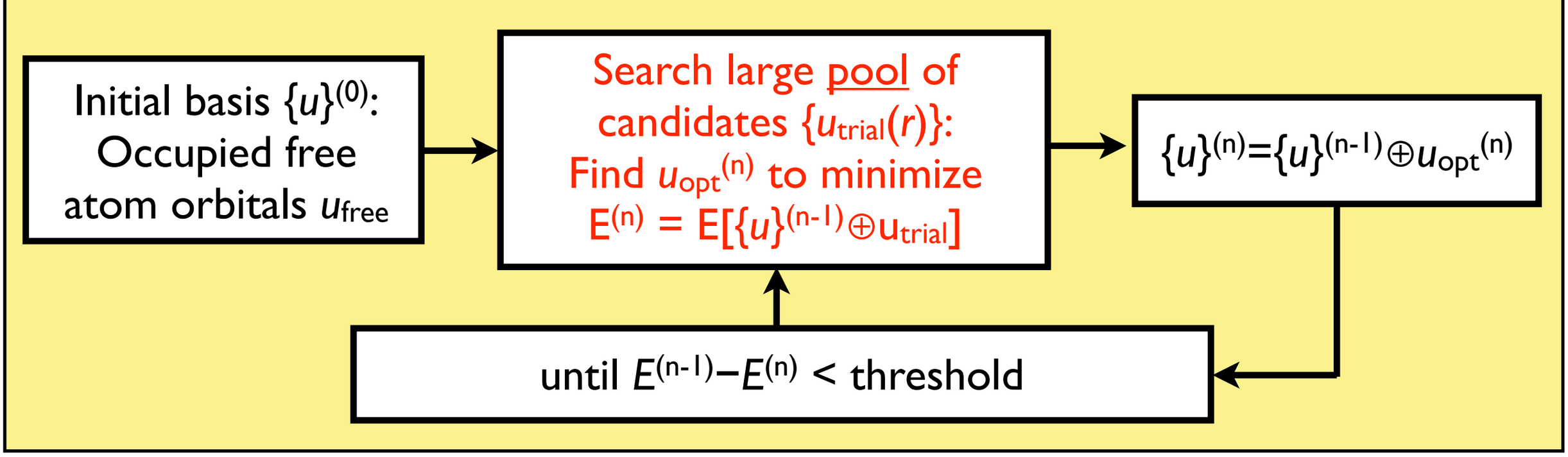
... but how do we find good radial functions for practical calculations?
(efficient yet systematically convergeable!)

Finding accurate, transferable NAO basis sets

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)

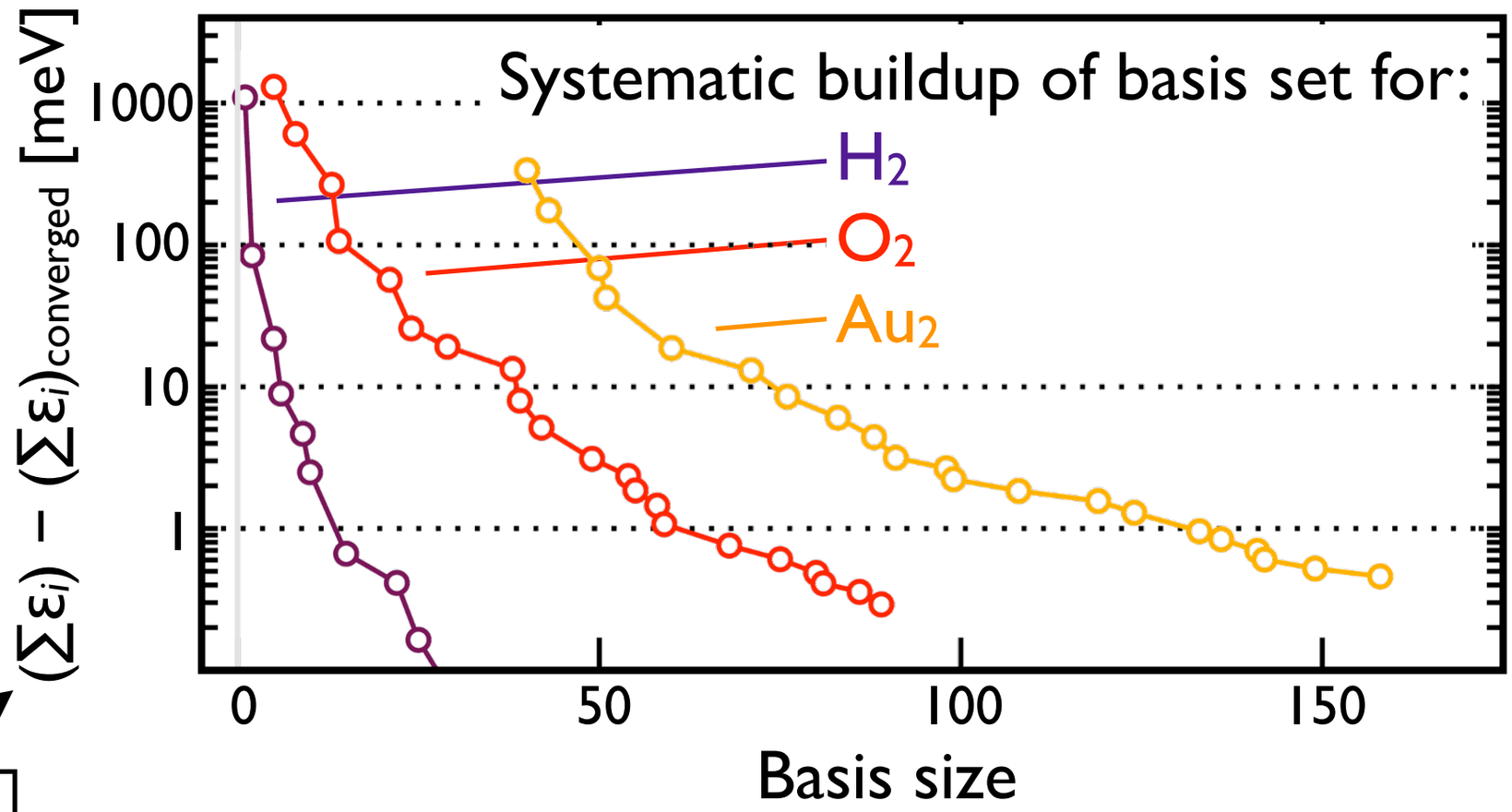


Iterative selection of NAO basis functions

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

<u>Optimization target:</u>
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*

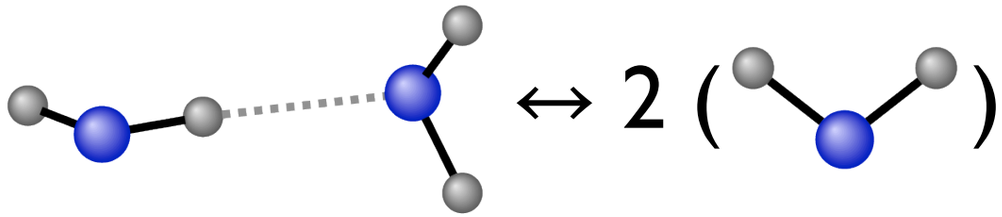
"First *tier* (level)"

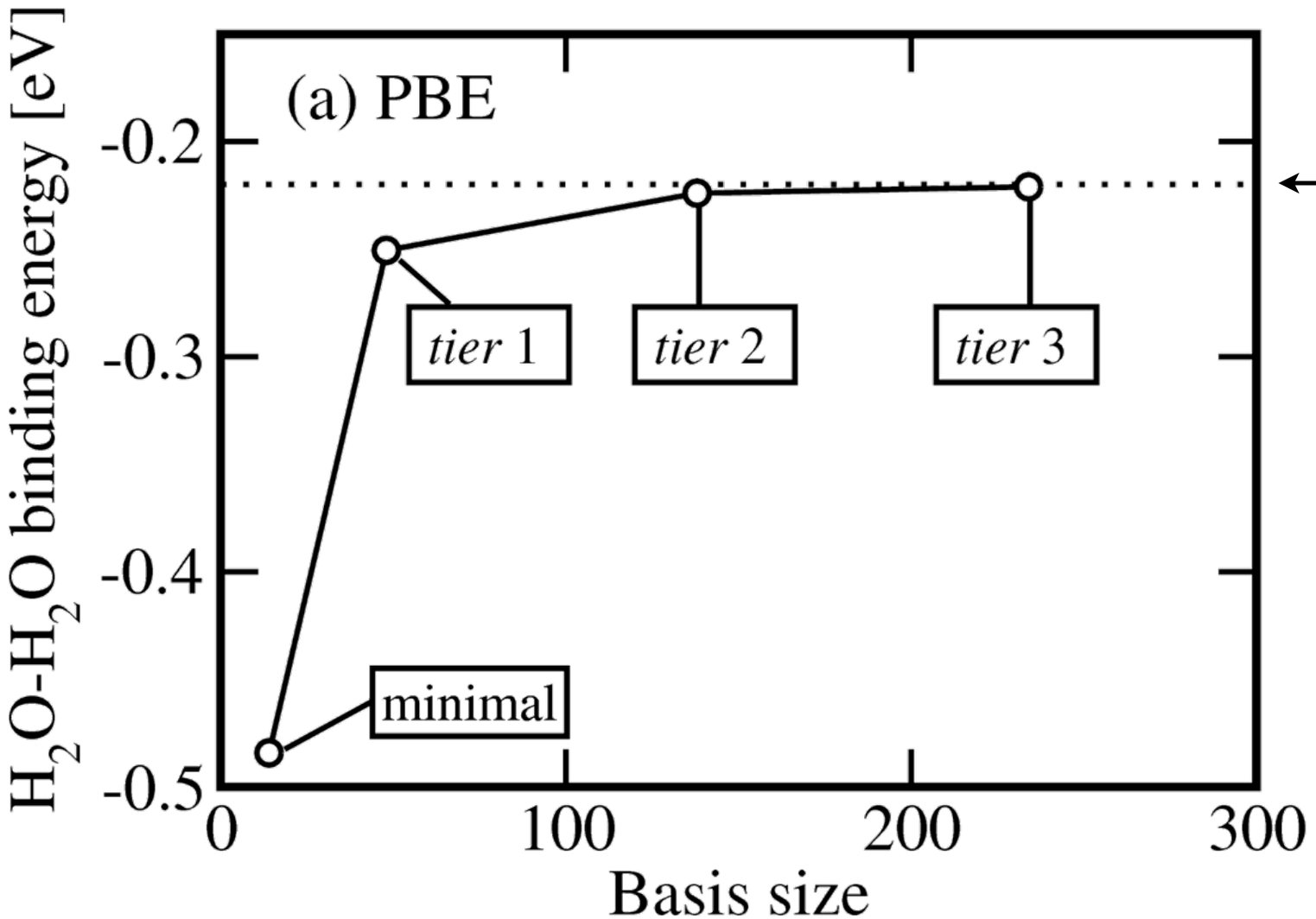
"Second *tier*"

"Third *tier*"

...

Transferability: $(H_2O)_2$ hydrogen bond energy

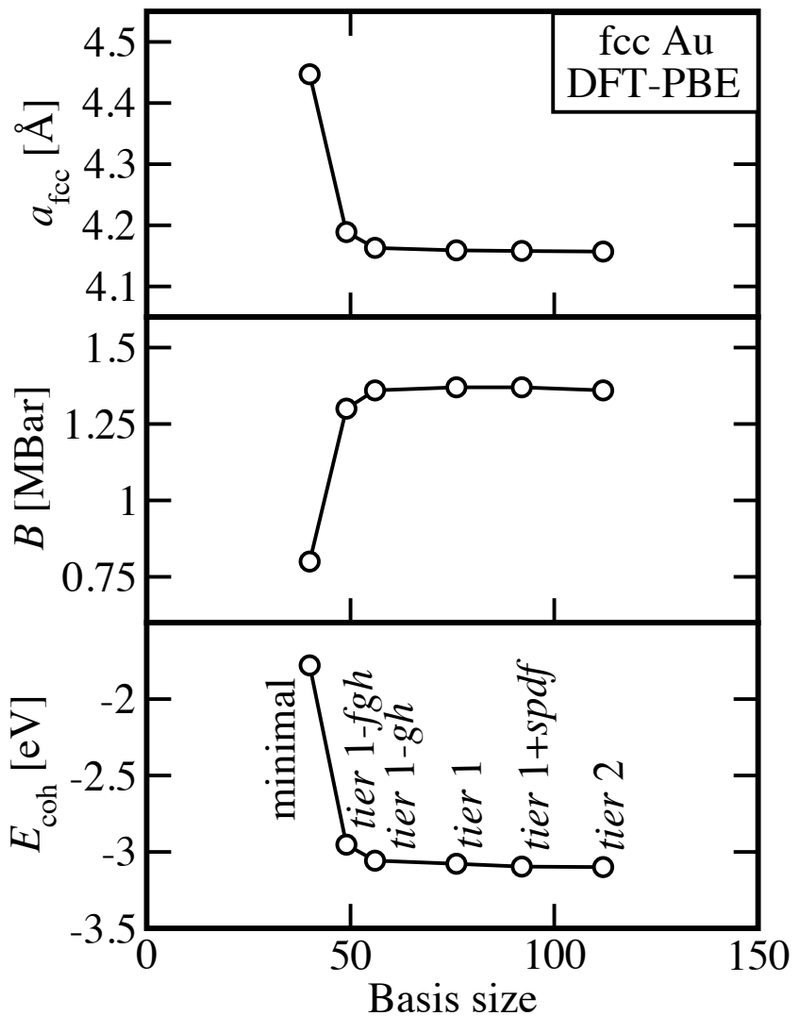




Basis set limit (independent):
E_{Hb} = −219.8 meV

Transferability: generally not a problem for DFT

Bulk Au: Cohesive properties



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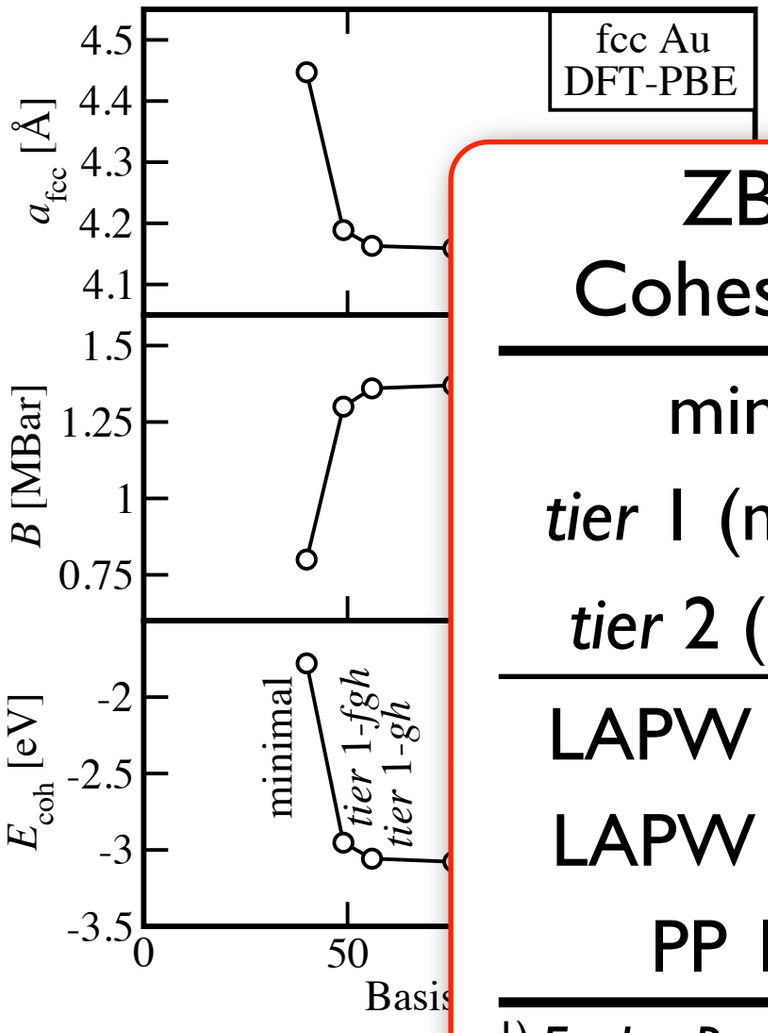


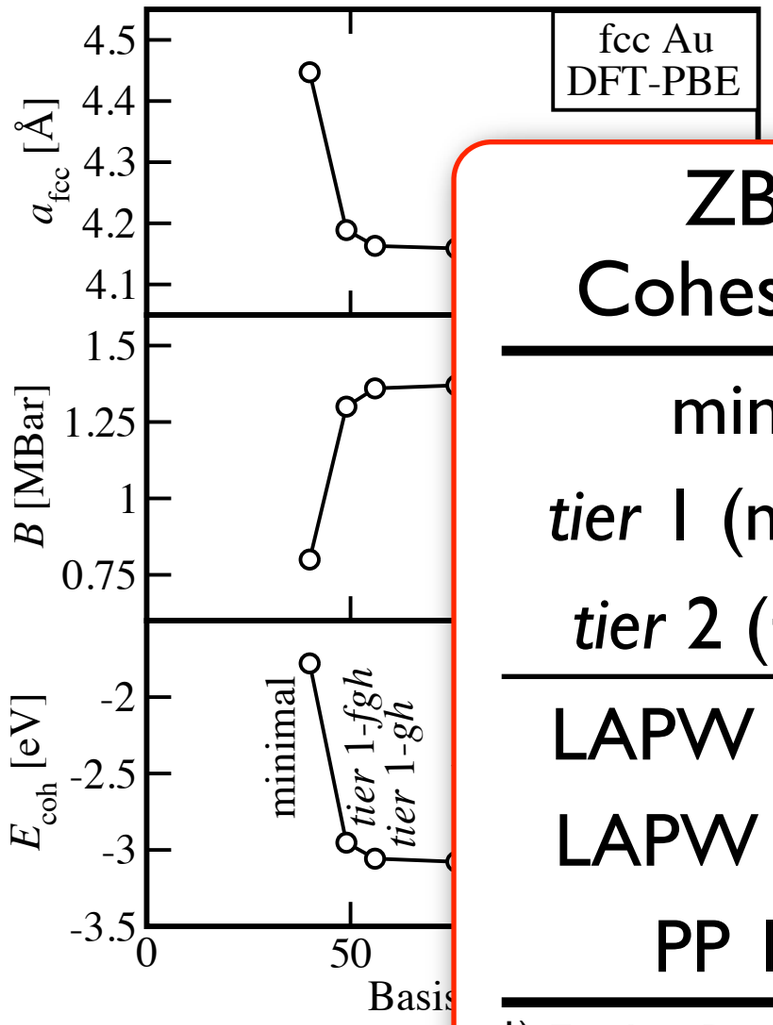
ZB GaAs, LDA: Cohesive energy [eV]

min+*spd*	7.99
tier 1 (min+spdf)	8.06
tier 2 (+*spdfgh*)	8.09
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



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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]

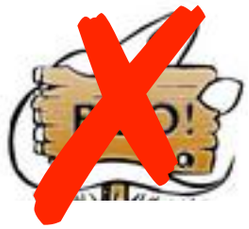
	Pt(100)	Au(100)
min+*spdf*	-65	-21
tier 1	-80	-30
tier 2	-83	-31
FP-LAPW	-89	-24

…

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"

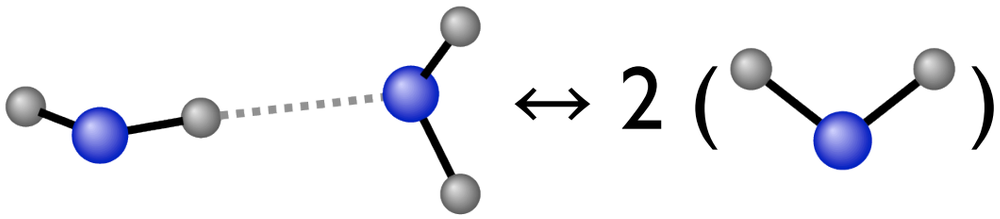
ΔE_{BSSE} = E( ) - E( )

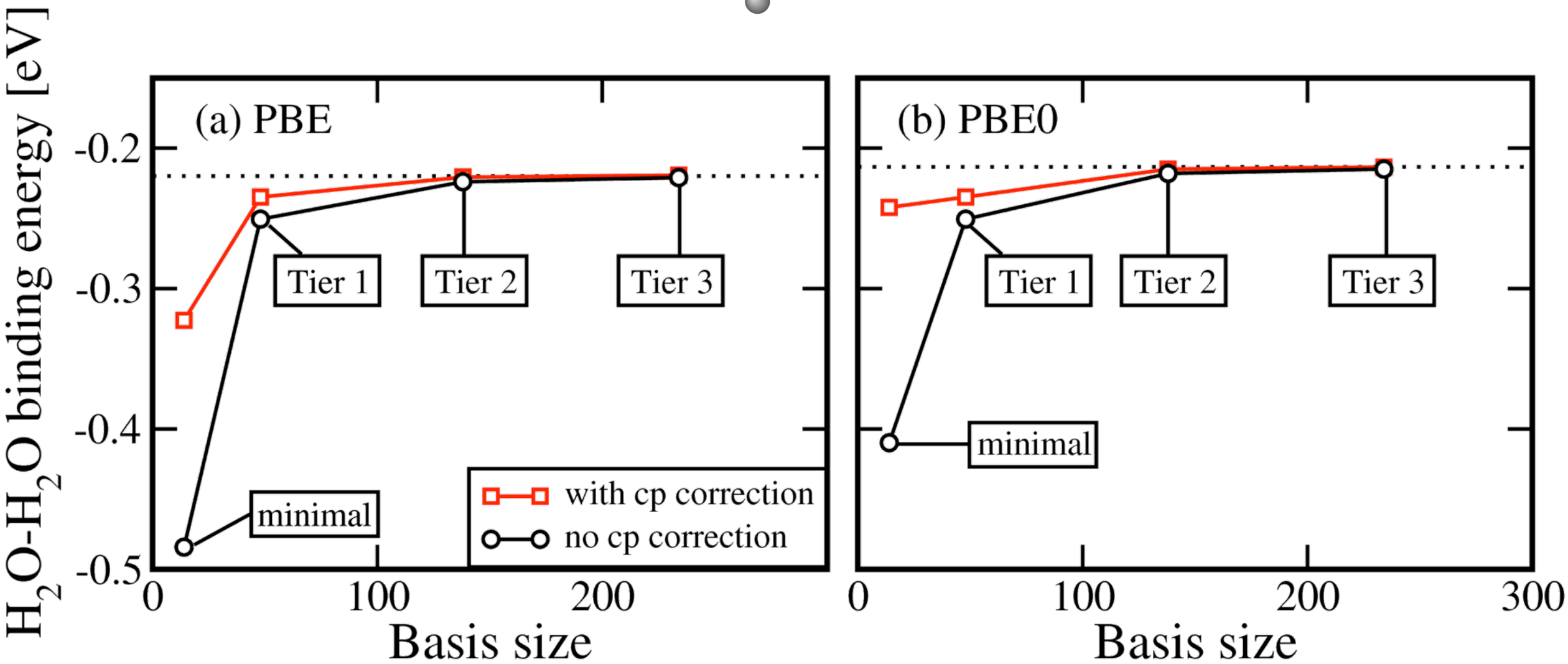
No nucleus - basis functions only

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

But how about *molecular* BSSE?

$(H_2O)_2$: "Counterpoise correction"





Ground-state energetics, NAO's:

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

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 $$\underline{\underline{h}}\, \underline{c}_k = \epsilon_k \underline{\underline{s}}\, \underline{c}_k$$
- Relativity? *needed for heavy elements*
- Periodic systems? *need suitable basis, electrostatics*

Numeric Atom-Centered Basis Functions: Integration

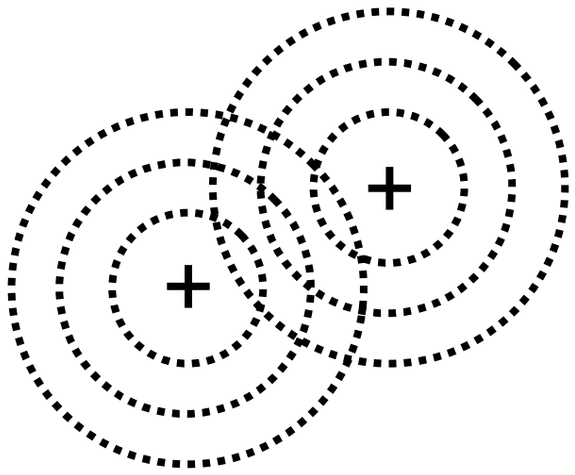
$$h_{ij} = \int d^3r \varphi_i(\boldsymbol{r}) \hat{h}_{\mathrm{KS}} \varphi_j(\boldsymbol{r})$$

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

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

f(*r*) has peaks, wiggles 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!

Integrals: "Partitioning of Unity"

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

- Rewrite to atom-centered integrands:

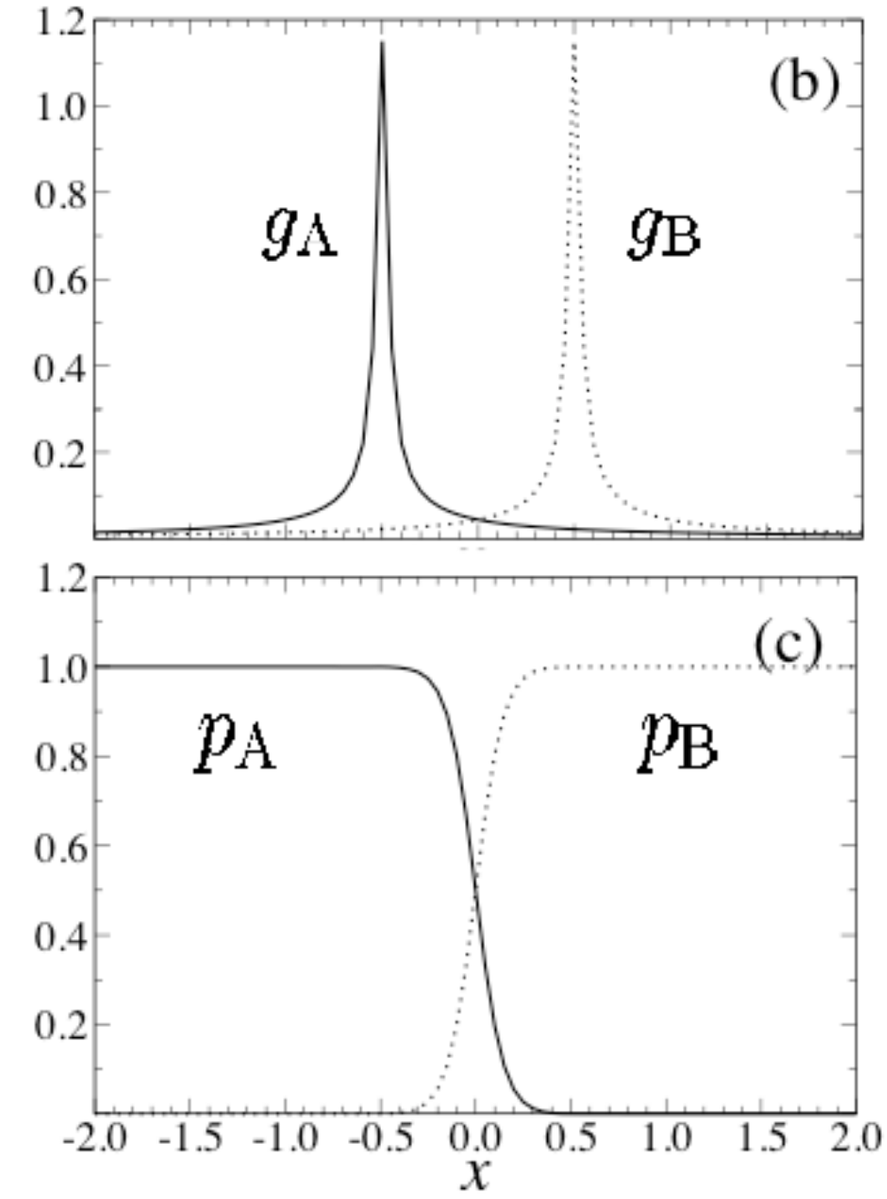
$$\int d^3r f(\boldsymbol{r}) = \sum_{\mathrm{atoms}} \int d^3r p_{\mathrm{atom}}(\boldsymbol{r}) f(\boldsymbol{r})$$

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

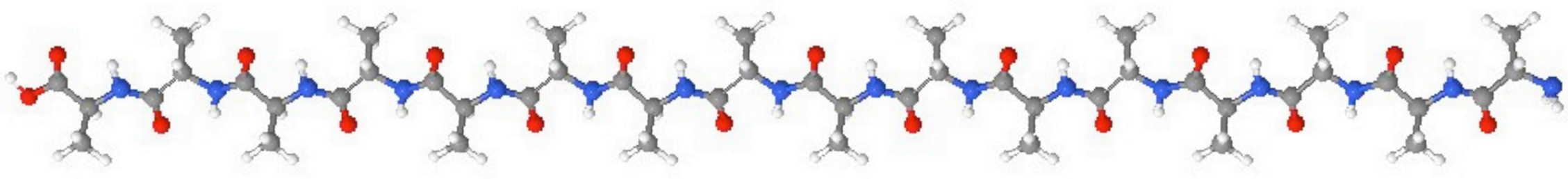
through $p_{\mathrm{atom}}(\boldsymbol{r}) = \dfrac{g_{\mathrm{atom}}(\boldsymbol{r})}{\sum_{\mathrm{atom}'} g_{\mathrm{atom}'}(\boldsymbol{r})}$

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

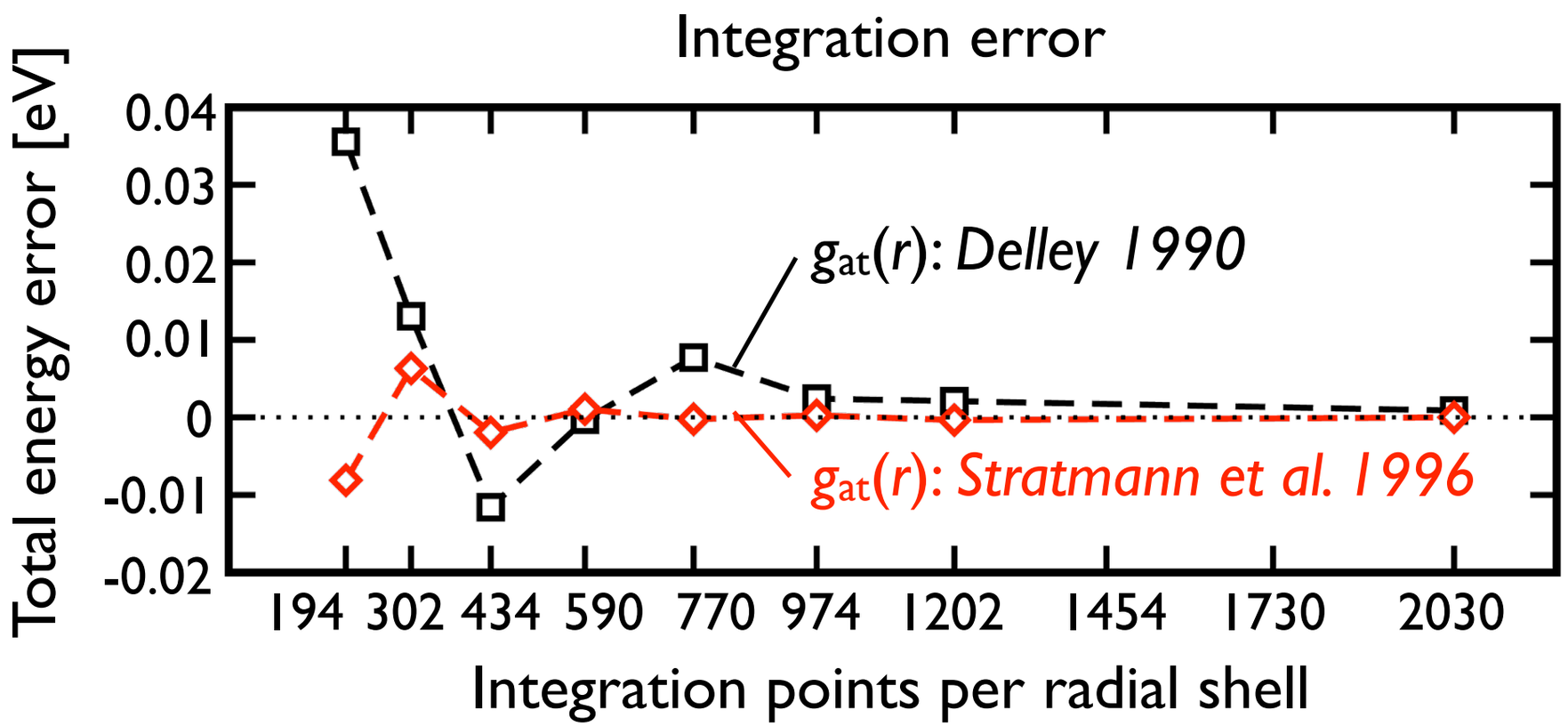
  many alternatives:
  Becke 1988, Stratmann 1996, Koepernik 1999, ...



Integrals in practice: Any problem?



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



Hartree potential (electrostatics): Same trick

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

- Partitioning of Unity:

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

- 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:

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

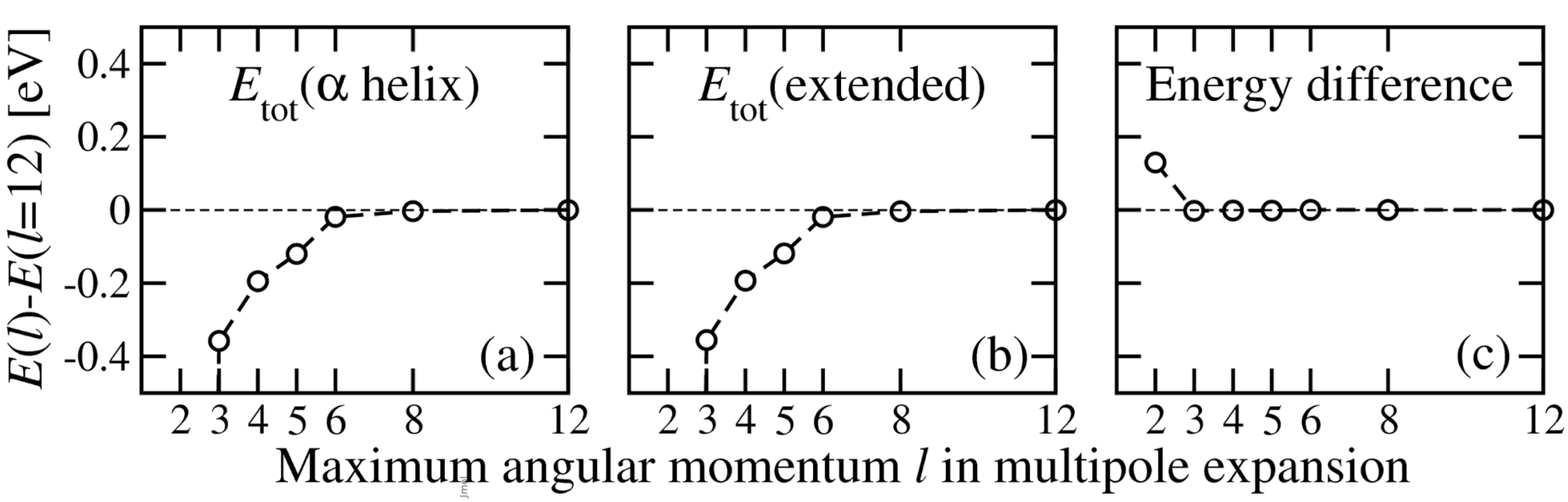
e.g., Delley, JCP 92, 508 (1990)

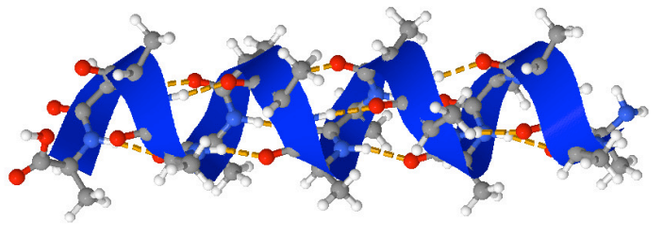
Electrostatics: Multipole expansion

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

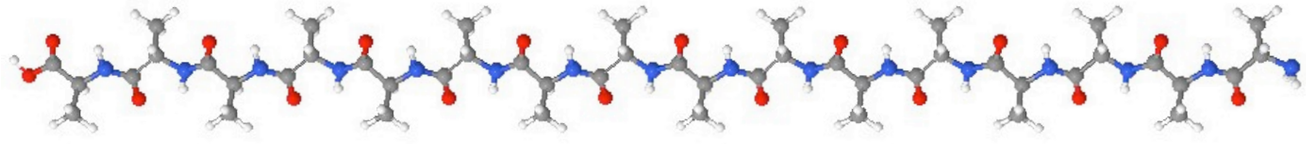
Polyalanine Ala_{20}, DFT-PBE (203 atoms)

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





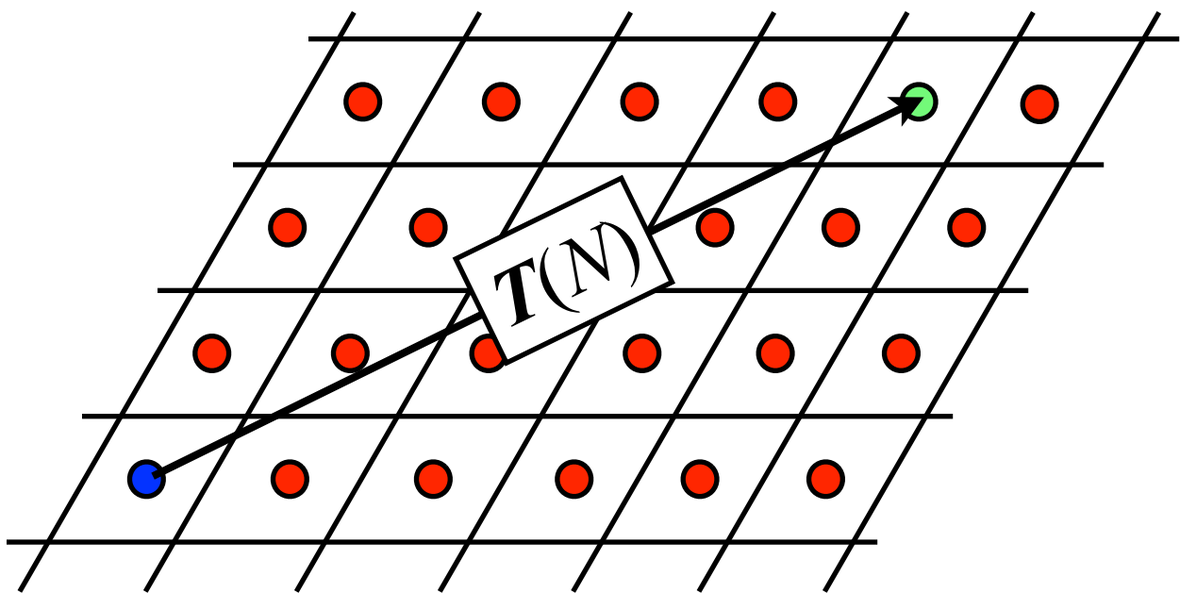
α



extended

Periodic systems

see S. Levchenko
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

Implementing scalar relativity

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

1. LAPW, others: Outright treatment

→ radial functions in atomic sphere (core, valence): Per-state relativistic

→ 3-dimensional non-relativistic treatment of interstitial regions

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

2. Approximate one-Hamiltonian treatment

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

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

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ZORA

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... not gauge-invariant!

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Implementing scalar relativity

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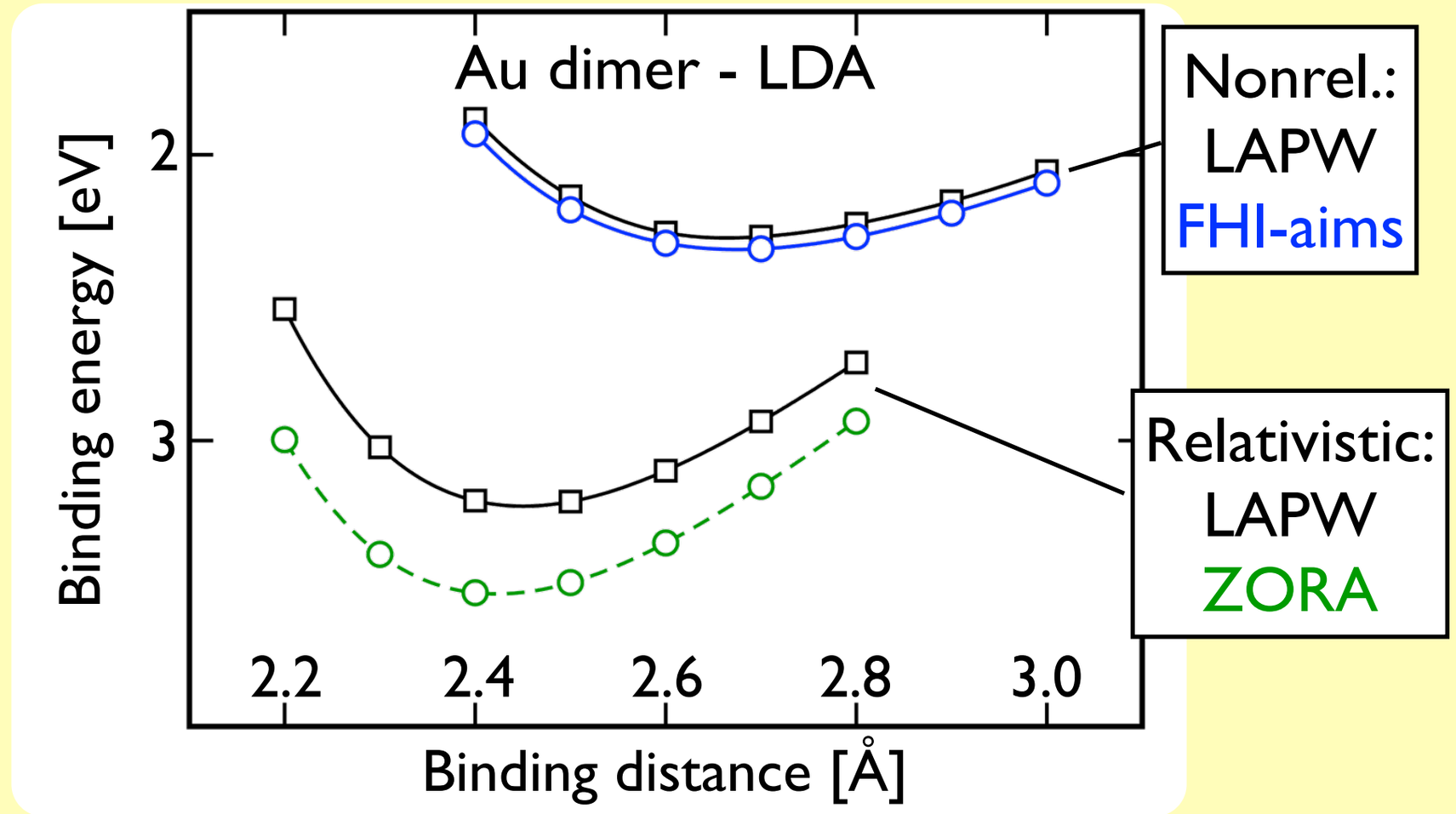
ZORA in practice: Harsh approximation (known)



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

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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

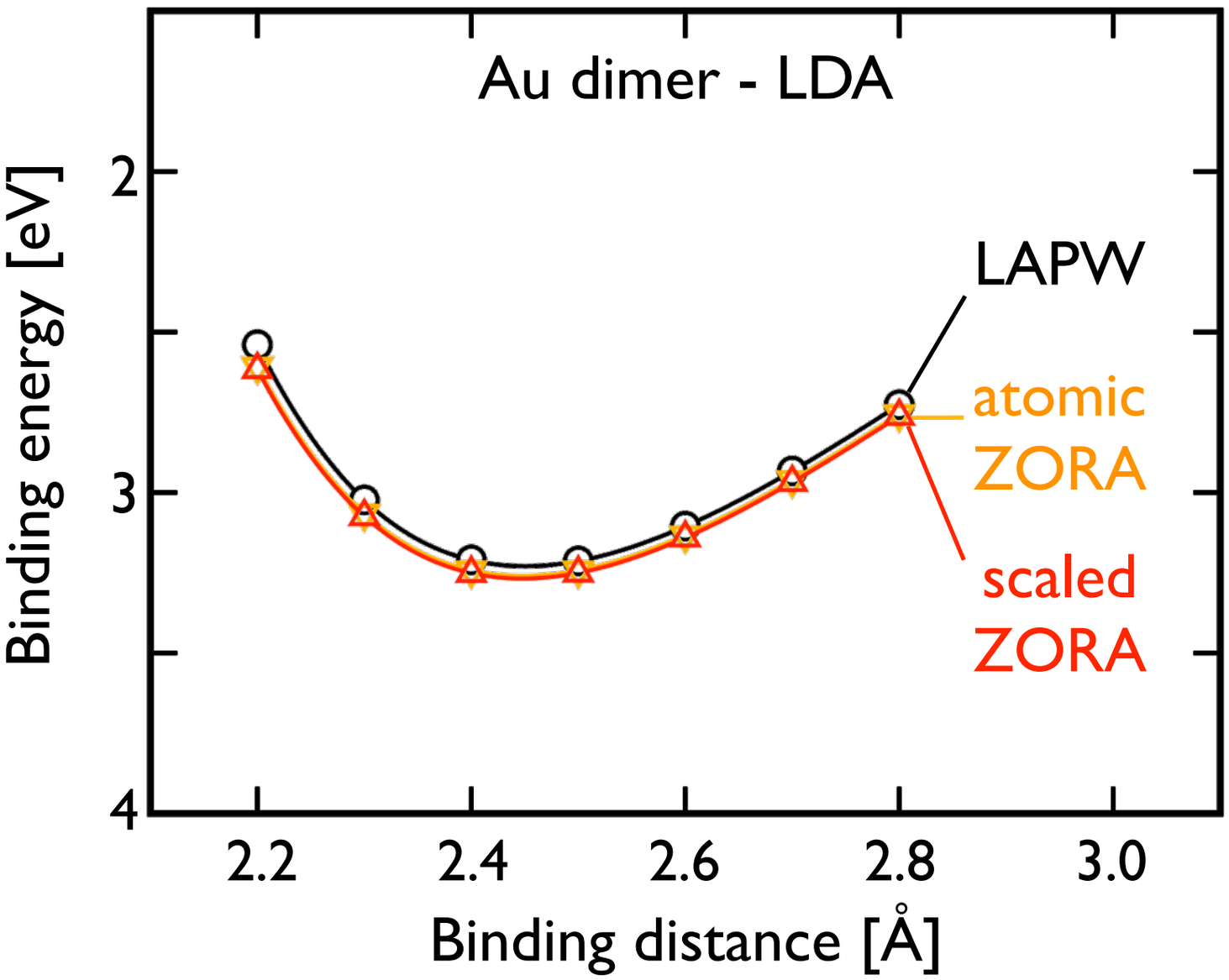
$$\epsilon_{\text{ZORA}}^{\text{scaled}} = \frac{\epsilon_{\text{ZORA}}}{1 + \langle\Phi|\boldsymbol{p}\frac{c^2}{(2c^2 - V)^2}\boldsymbol{p}|\Phi\rangle}$$

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

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

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

Atomic ZORA + scaled ZORA: A viable strategy



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: atomic ZORA (simple gradients)
- (Final) total energies, eigenvalues: scaled ZORA

In all our benchmarks so far, we seem to be essentially as accurate as LAPW.

How does this scale? 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)

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

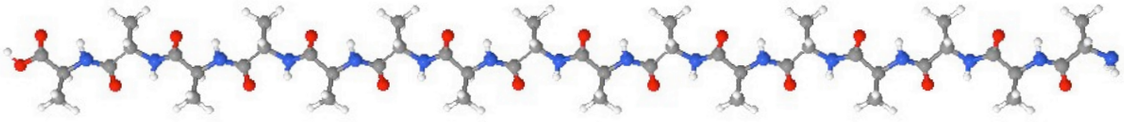
Kohn-Sham eigenvalue problem

"Conventional" solvers (Lapack-like):

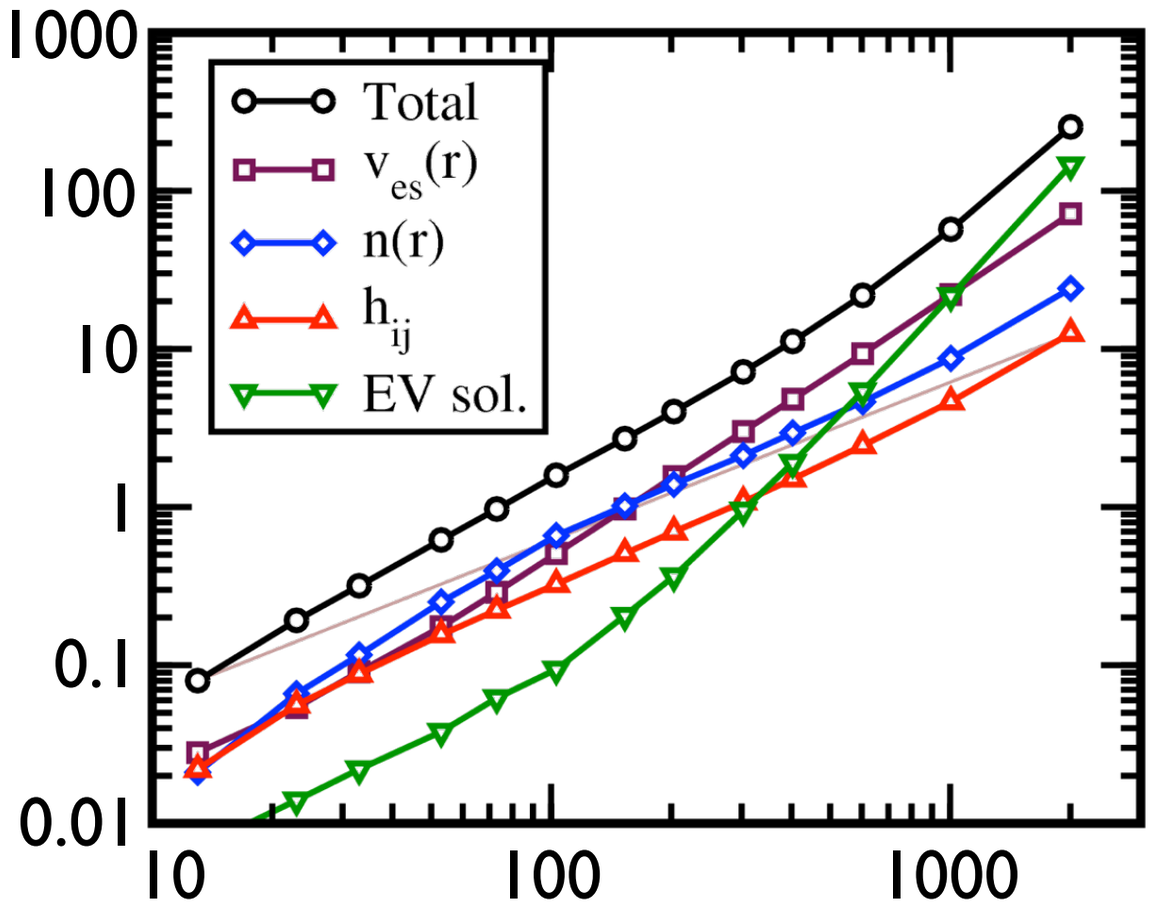
- Small prefactor for NAO's: affordable up to ≥ 1,000 atoms
- Robust, general (metals!)
- *O*(size^3) scalability inevitable
- Massively parallel scalability not out of the box

How far can we push such solvers?

... but how does it all scale?



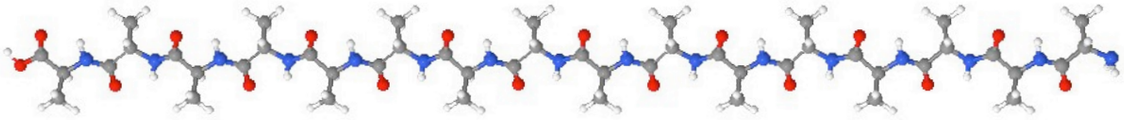
Fully extended Polyalanine, "light"



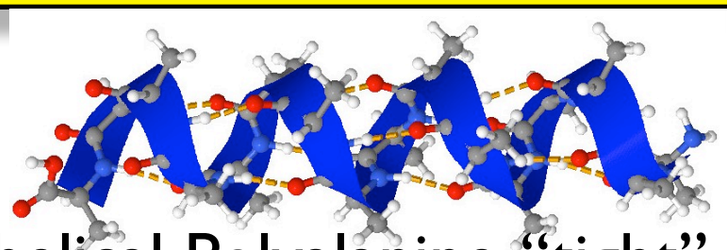
	Light:
Basis	tier 1
$l_{Hartree}$	4
radial shells	24-36
pts. per shell	302 max.
Cutoff width	5Å

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

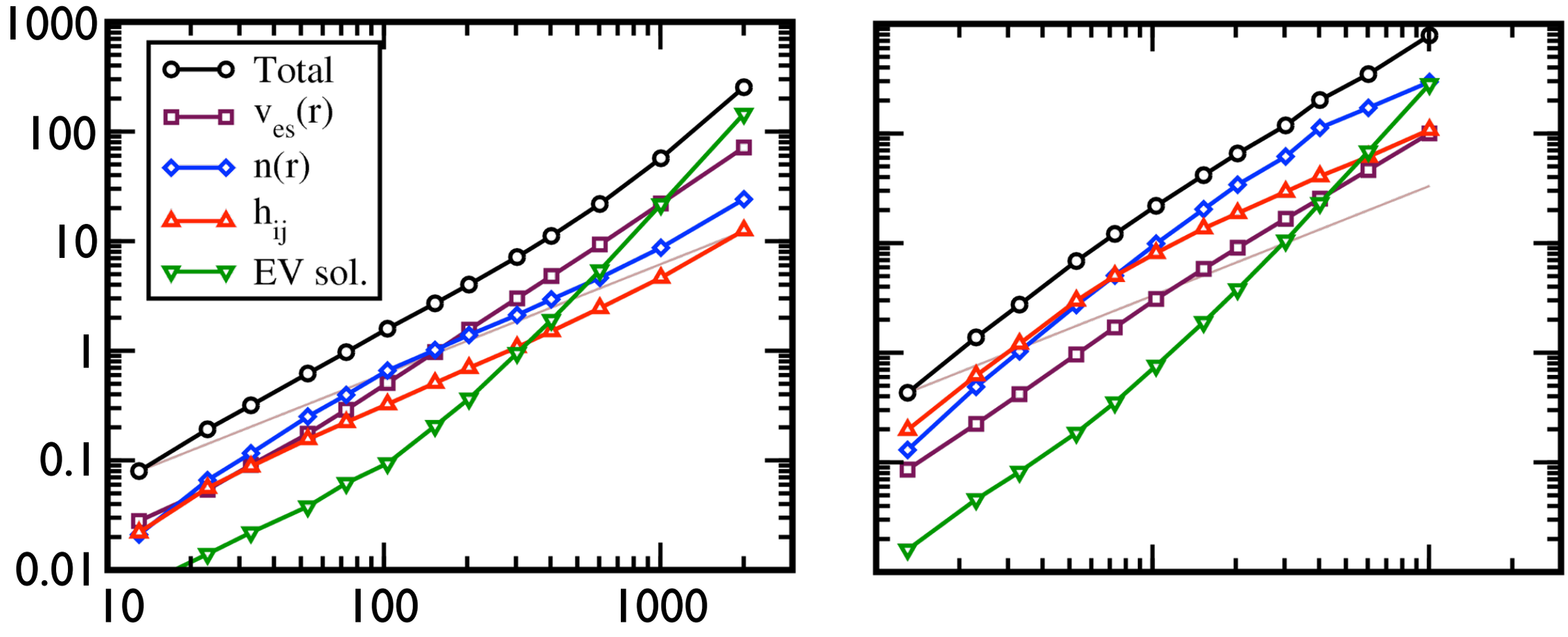
... but how does it all scale?



Fully extended Polyalanine, "light"



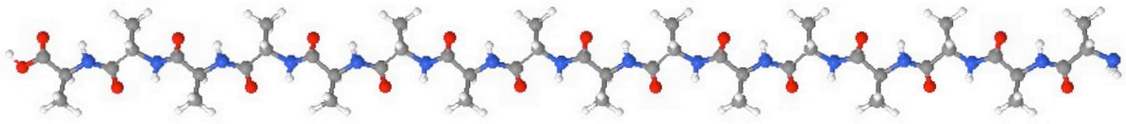
α-helical Polyalanine, "tight"



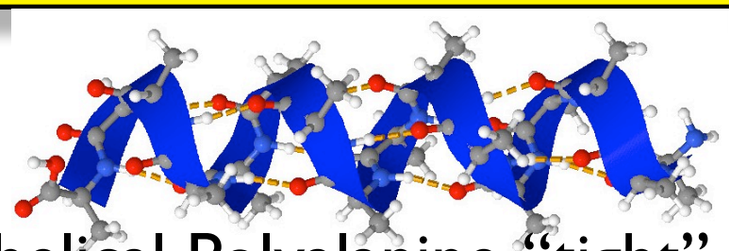
	Light:	Tight:
Basis	tier 1	tier2
$l_{Hartree}$	4	6
radial shells	24-36	49-73
pts. per shell	302 max.	434 max.
Cutoff width	5Å	6Å

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

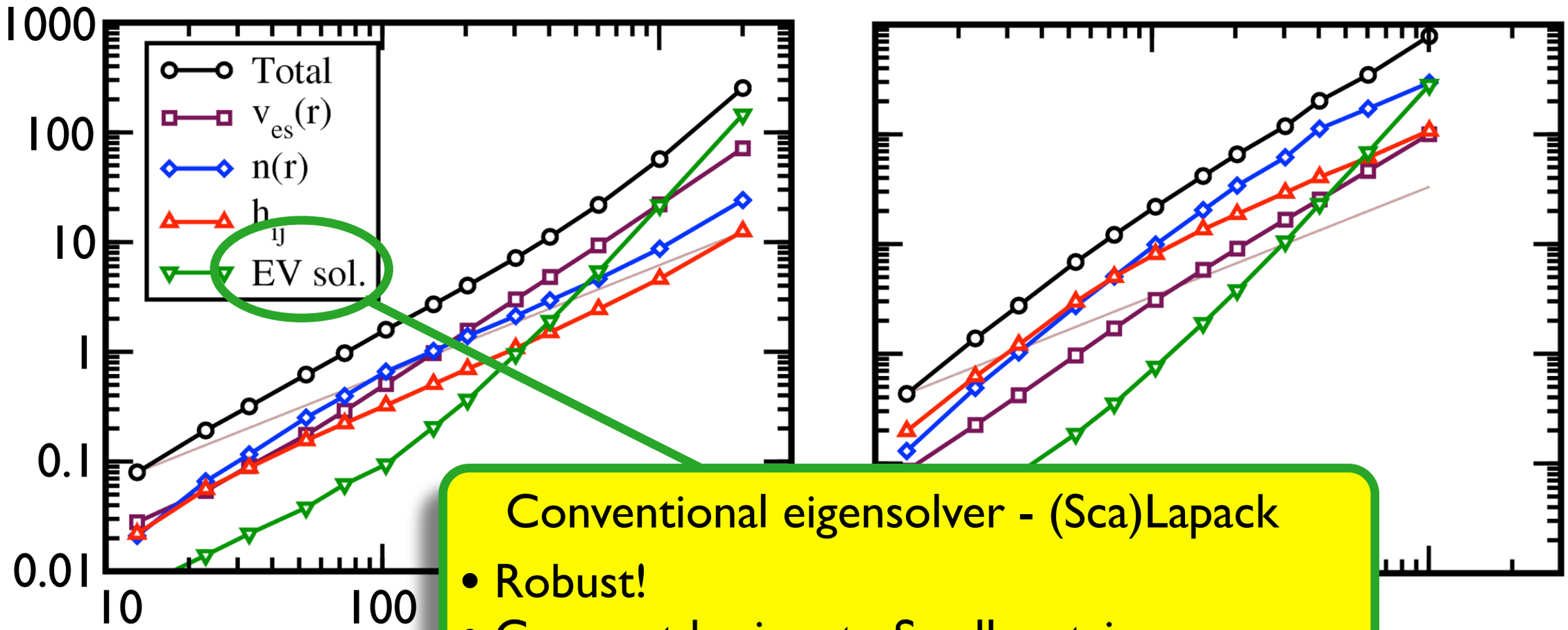
... but how does it all scale?



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

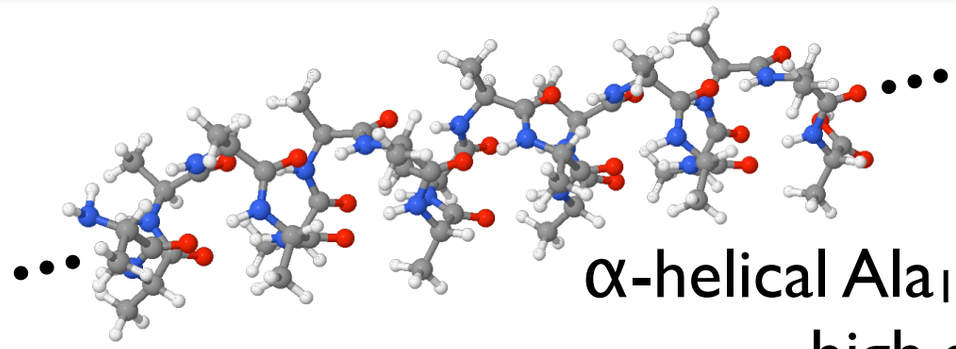
- Robust!
- Compact basis sets: Small matrices
- but $O(N^3)$ scaling - relevant ≈100s of atoms
- 1,000s of CPUs: Scaling bottleneck?

Js
/Xeon cluster

Benchmarks: W. Jürgens / FHI

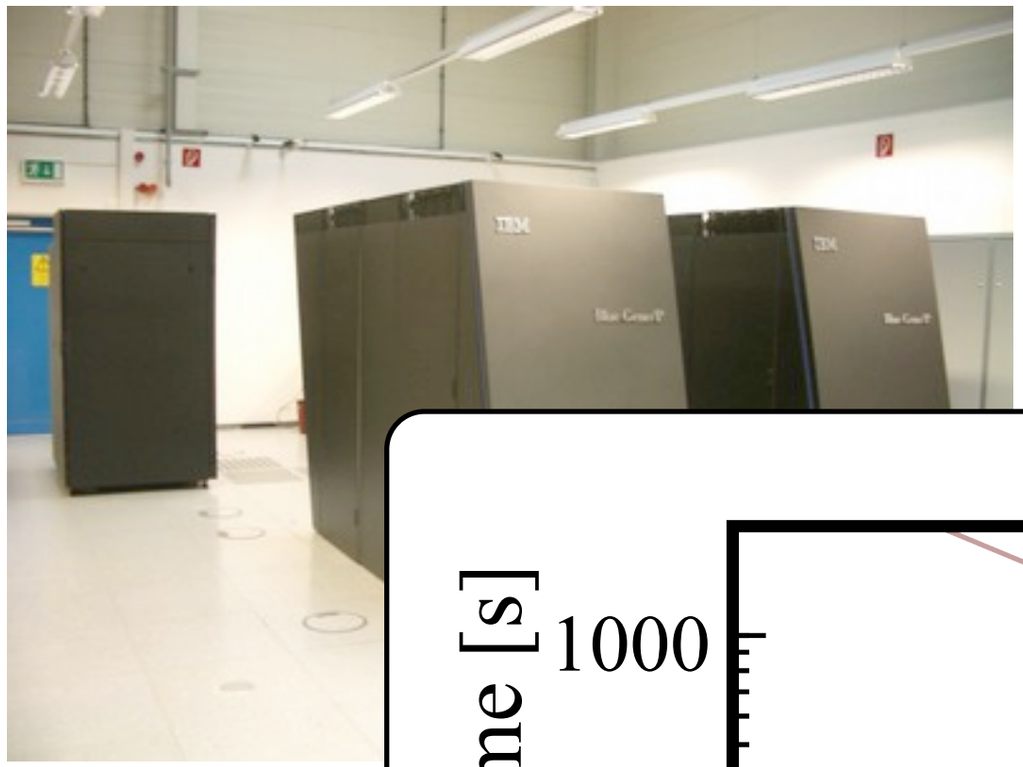
Towards the "petaflop": Tackling the eigenvalue solver

IBM BlueGene (MPG, Garching)
16384 CPU cores

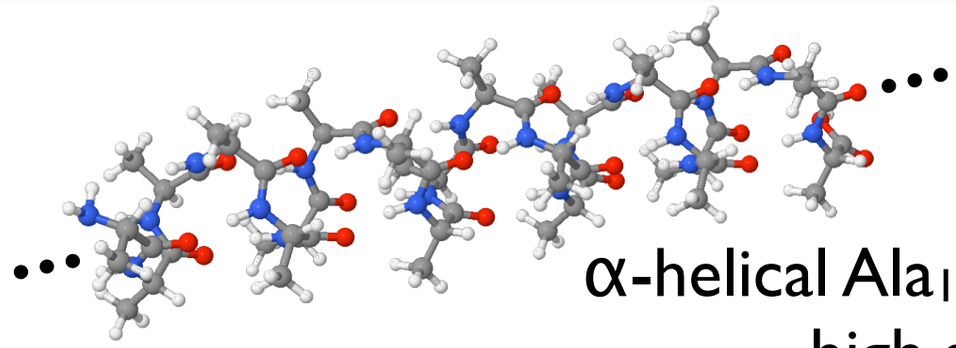


α-helical Ala_{100} (1000 atoms),
high accuracy

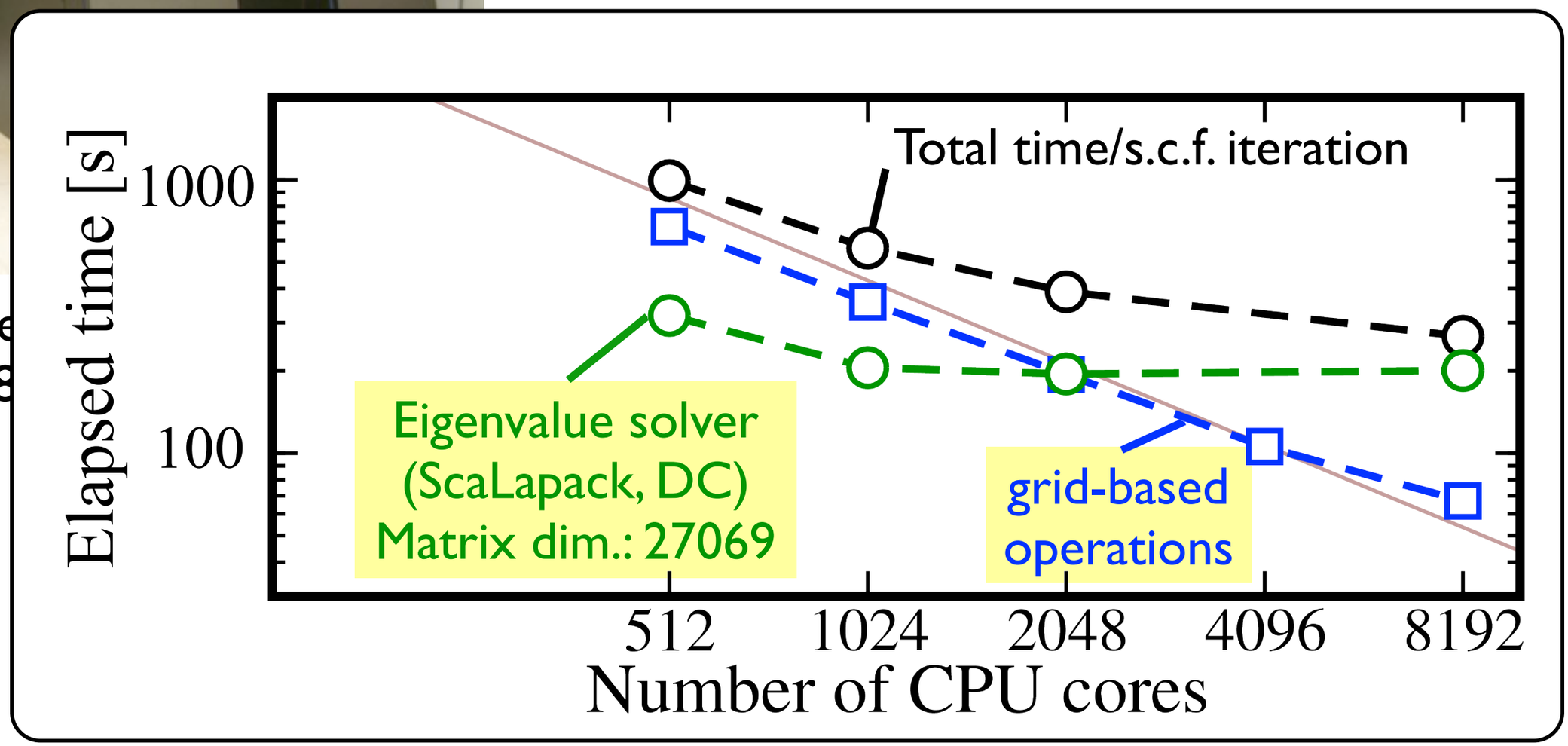
Towards the "petaflop": Tackling the eigenvalue solver



IBM BlueGe
1638



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



A conventional, massively parallel 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

Goal:

- 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)*

part of "Eigensolvers for Petaflop Applications" (ELPA) consortium (BMBF)

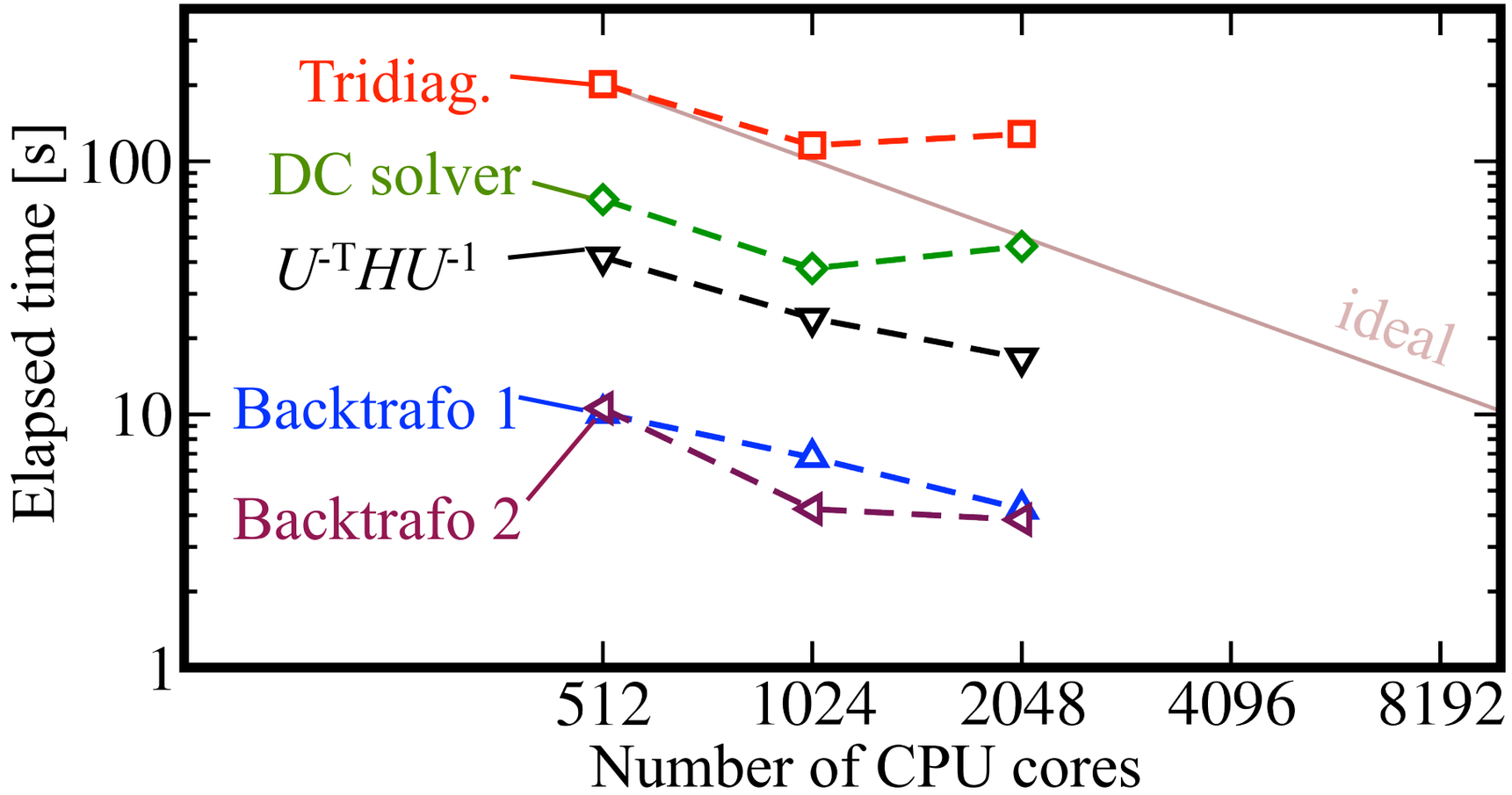
standalone open-source / LGPL library

Taking apart the eigenproblem

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

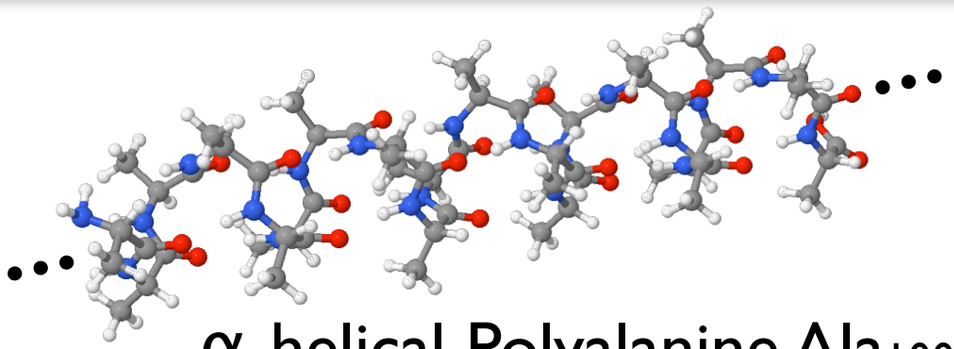
Generalized (non-orthogonal) eigenvalue problem:

- 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

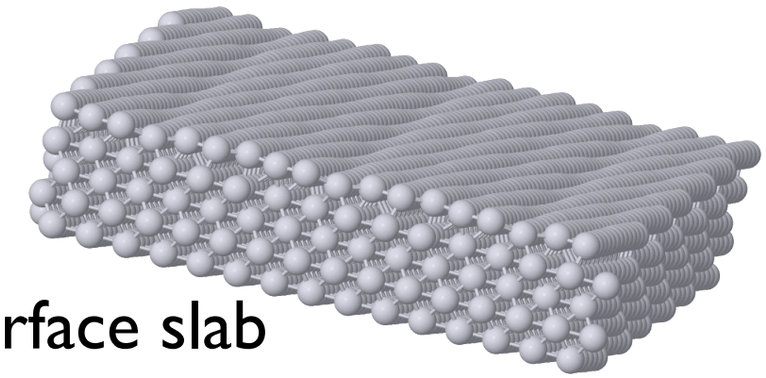


α-helical Polyalanine Ala_{100}, BlueGene/P

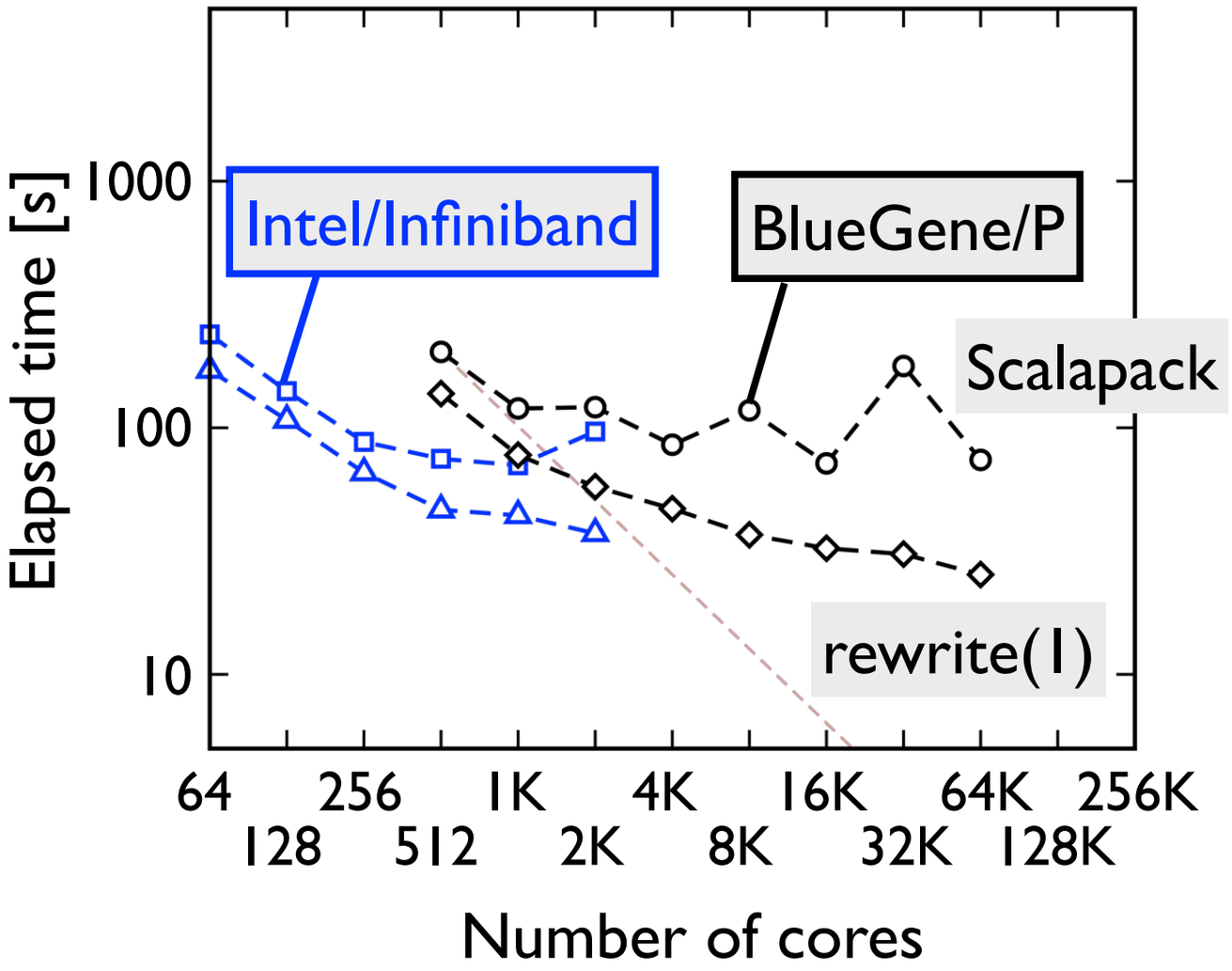
Rewritten eigensolver (ELPA1)

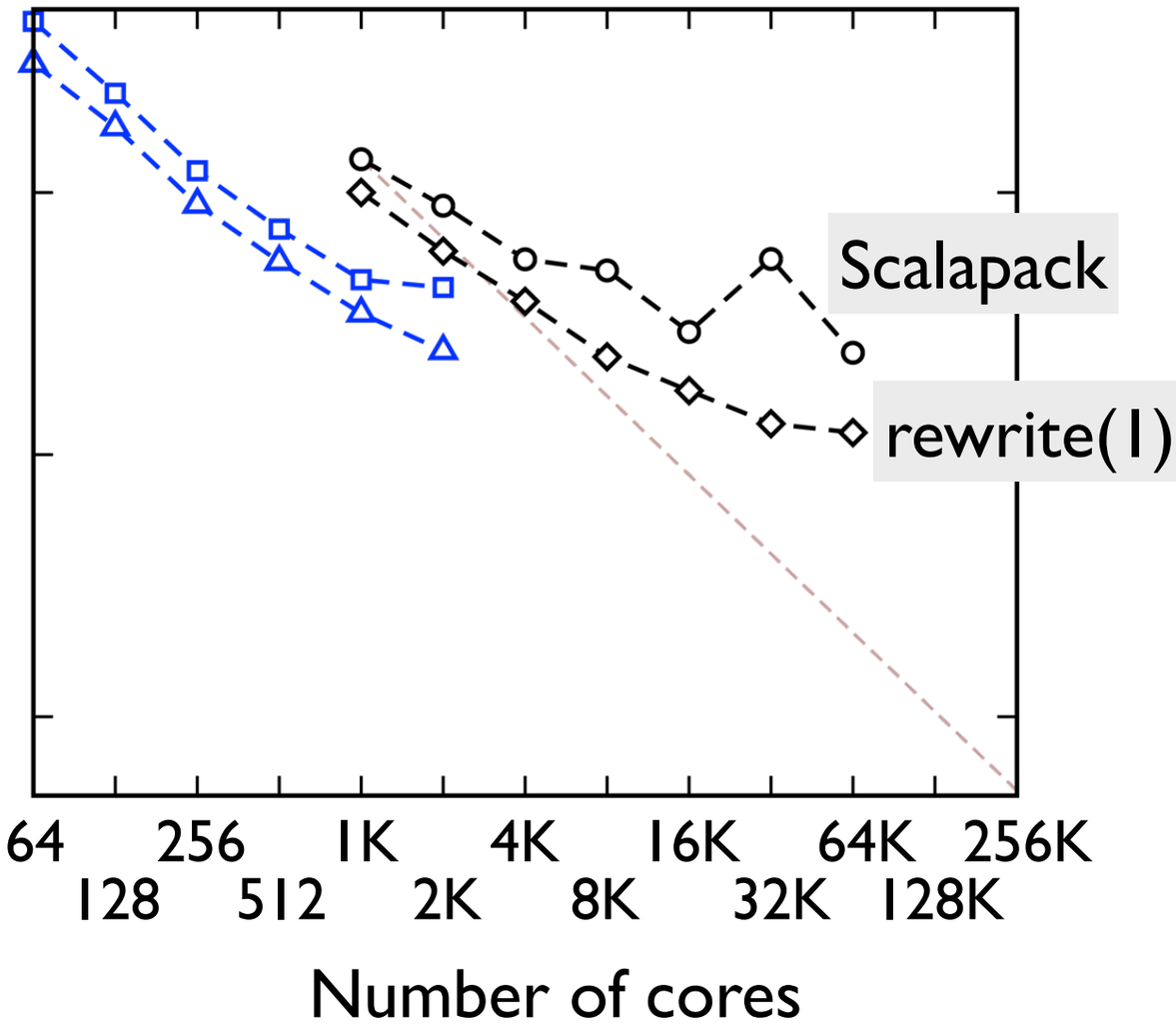


α-helical Polyalanine Ala_{100}
N=27069, *M*=3410
NAO basis set (FHI-aims)



Pt(100)-5x40 surface slab
N=67990, *M*=43409
NAO basis set (FHI-aims)

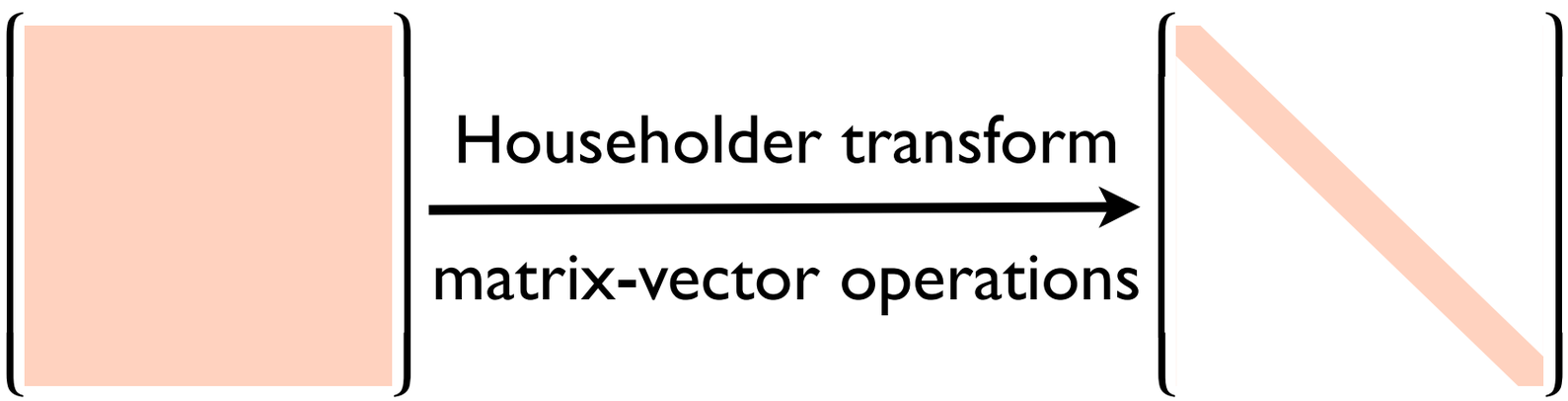




Optional improvement: 2-step tridiagonalization

Remaining chief bottleneck: Tridiagonalization

"Conventional" reduction:



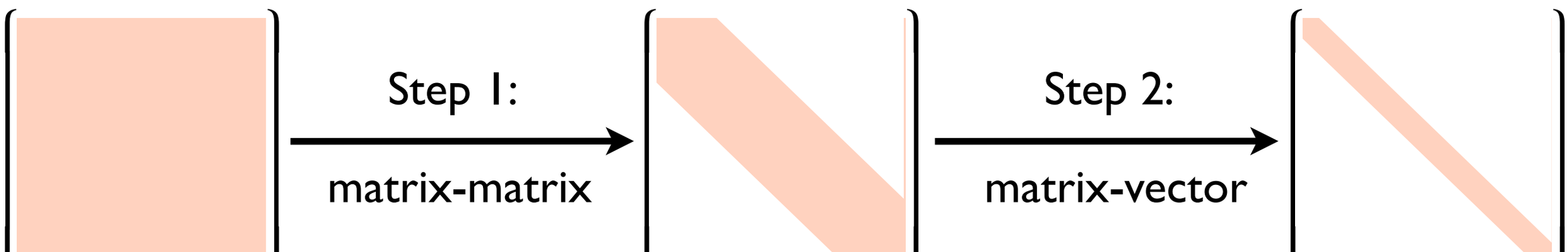
full matrix

tridiagonal matrix

Optional improvement: 2-step tridiagonalization

Remaining chief bottleneck: Tridiagonalization

"Two-step" reduction:
C. *Bischof, B. Lang, X. Sun, ACM Trans. Math. Software* ***26****, 581 (2000).*



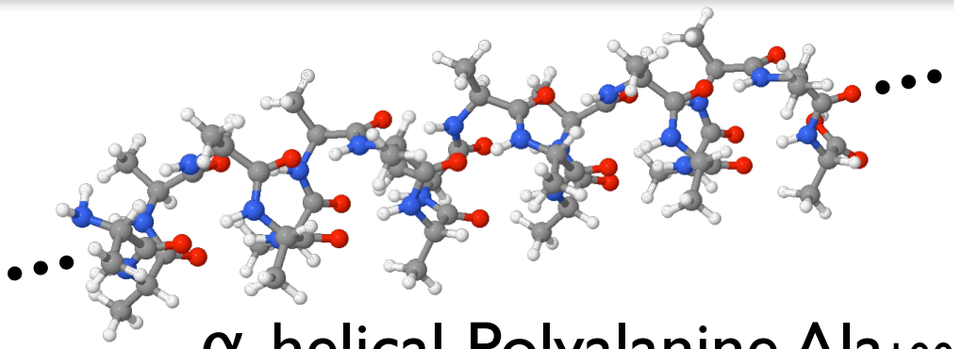
But extra back transform necessary - benefit shrinks for *M* approaching *N*

Massively parallel two-step tridiagonalization:

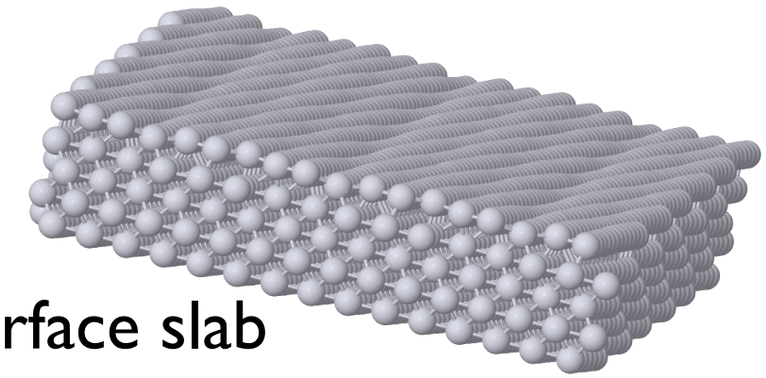
- 2-dimensional data layout for eigenvectors
- Heavily optimized backtransform steps for eigenvectors (adaptive data layout, architecture-specific linear algebra kernels - cache blocking)

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)



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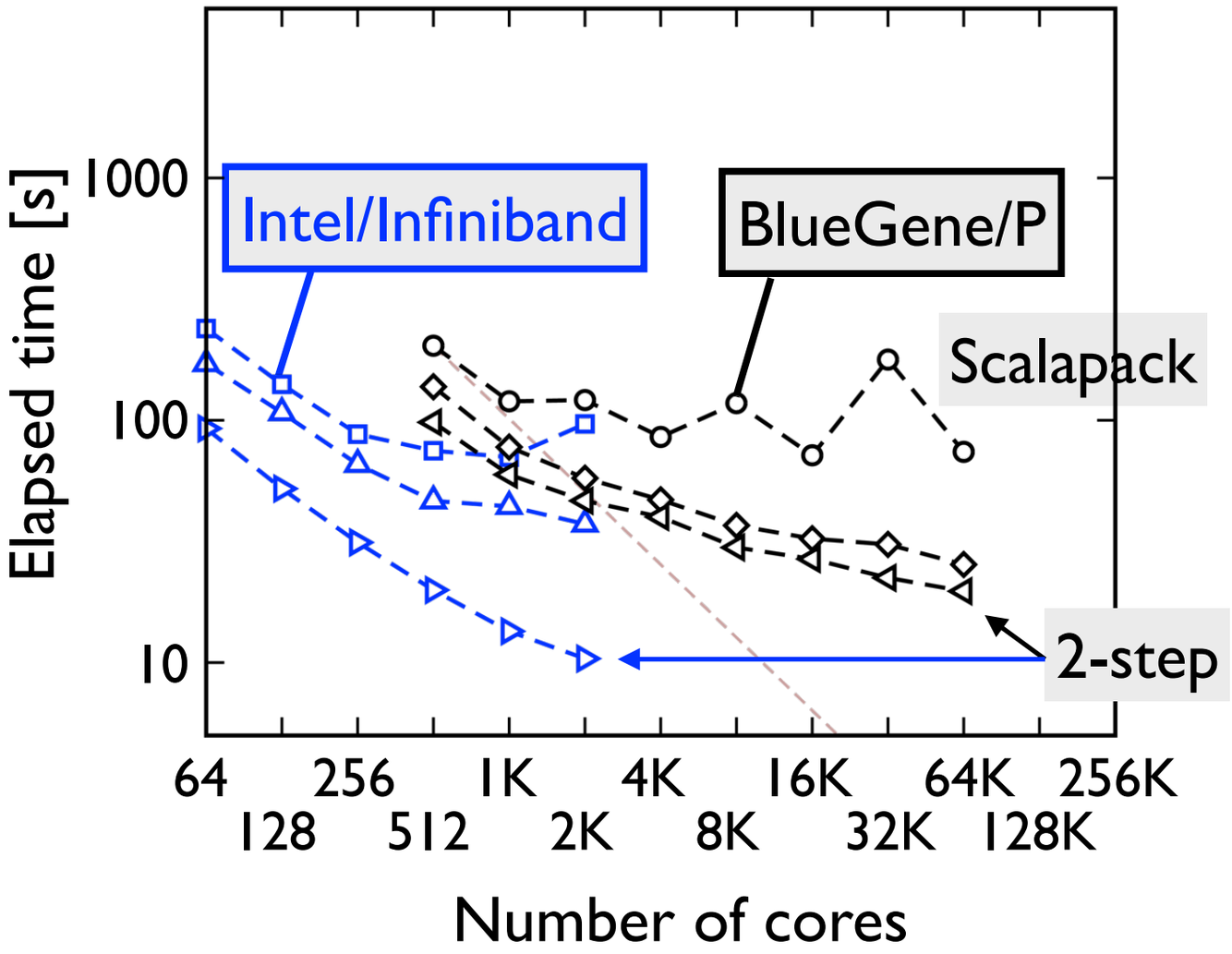
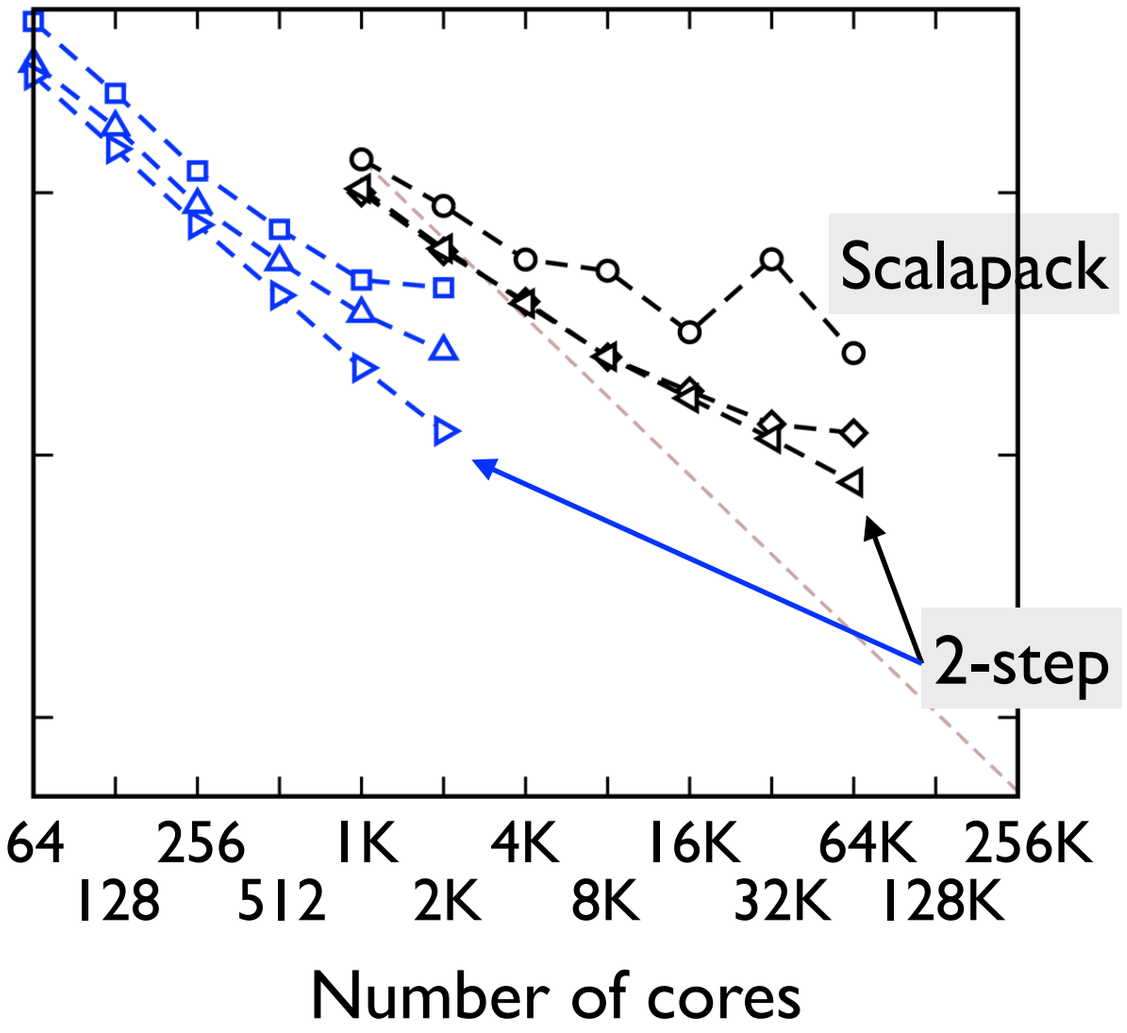
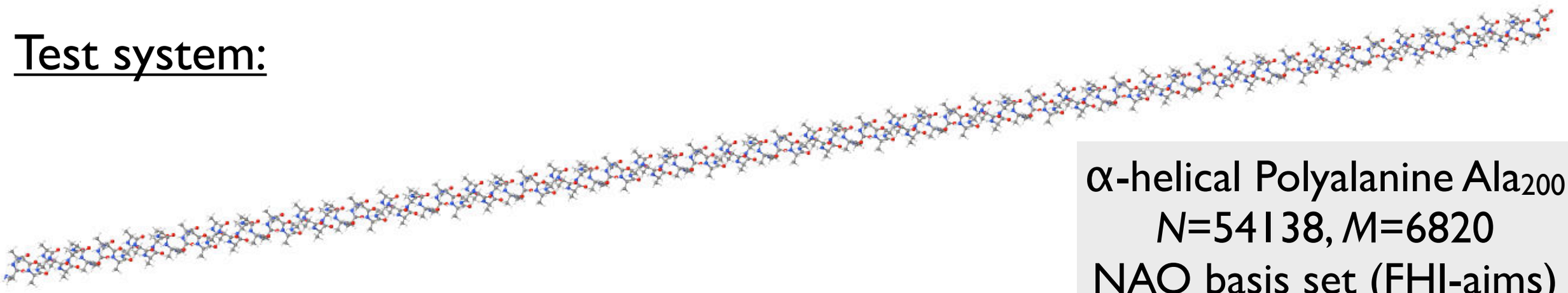




So what about the "Petascale"?

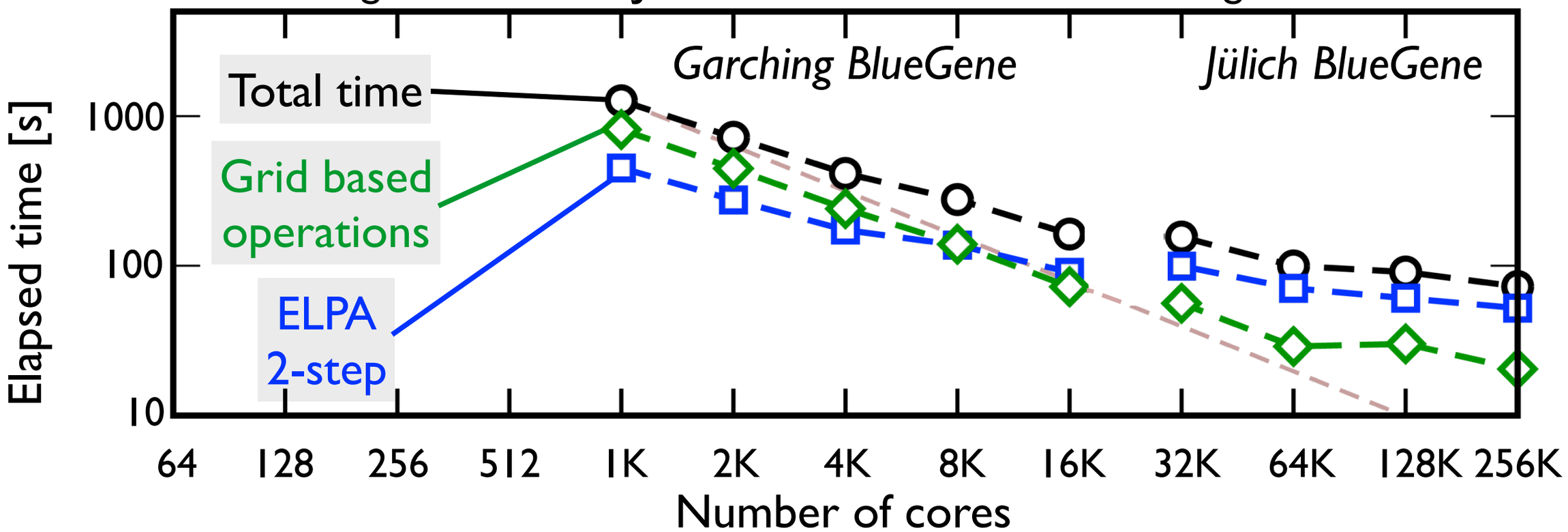
Test system:



α-helical Polyalanine Ala_{200}
N=54138, *M*=6820
NAO basis set (FHI-aims)

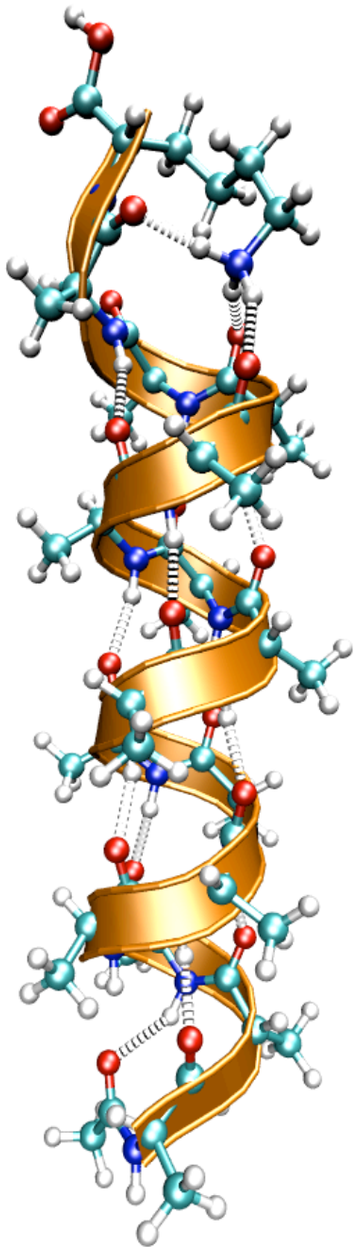
Time per FULL DFT-PBE s.c.f. iteration: BlueGene/P

Timings: A. Marek, R. Johanni, Rechenzentrum Garching, Feb. 2011



FHI-aims - what is it good for?

Pushing the limits of all-electron molecular dynamics



α-helical Ac-Ala$_{15}$-LysH$^+$
(180 atoms): Helical?

Experiment:
von Helden, Kupser, Bierau, Meijer,
Molecular Physics, FHI Berlin

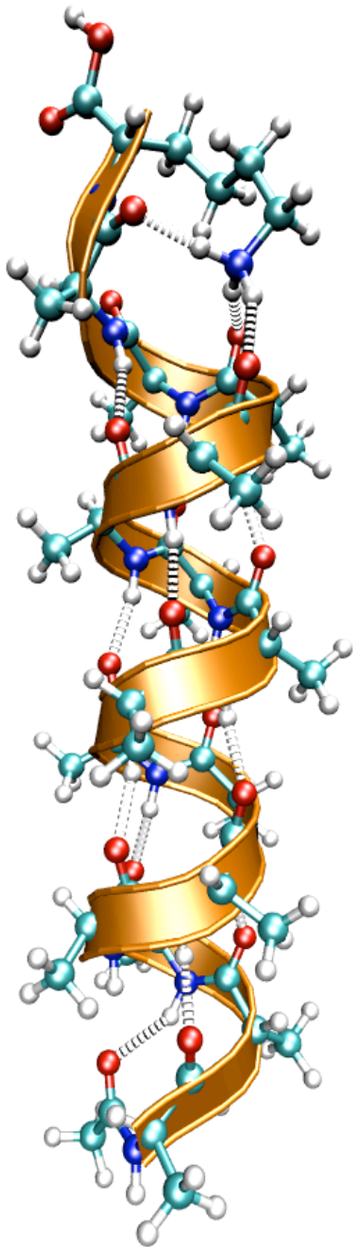
Infrared multiphoton dissociation spectroscopy, FELIX free electron laser

Room temperature

Rossi, Blum, Kupser, von Helden, Bierau,
Pagel, Meijer, Scheffler, J. Phys. Chem. Lett. ***1****, 3465 (2010)*

(Bio)molecular vibrational spectroscopy *in vacuo*

Rossi, Blum, Kupser, von Helden, Bierau, Pagel, Meijer, Scheffler, J. Phys. Chem. Lett. ***1****, 3465 (2010)*



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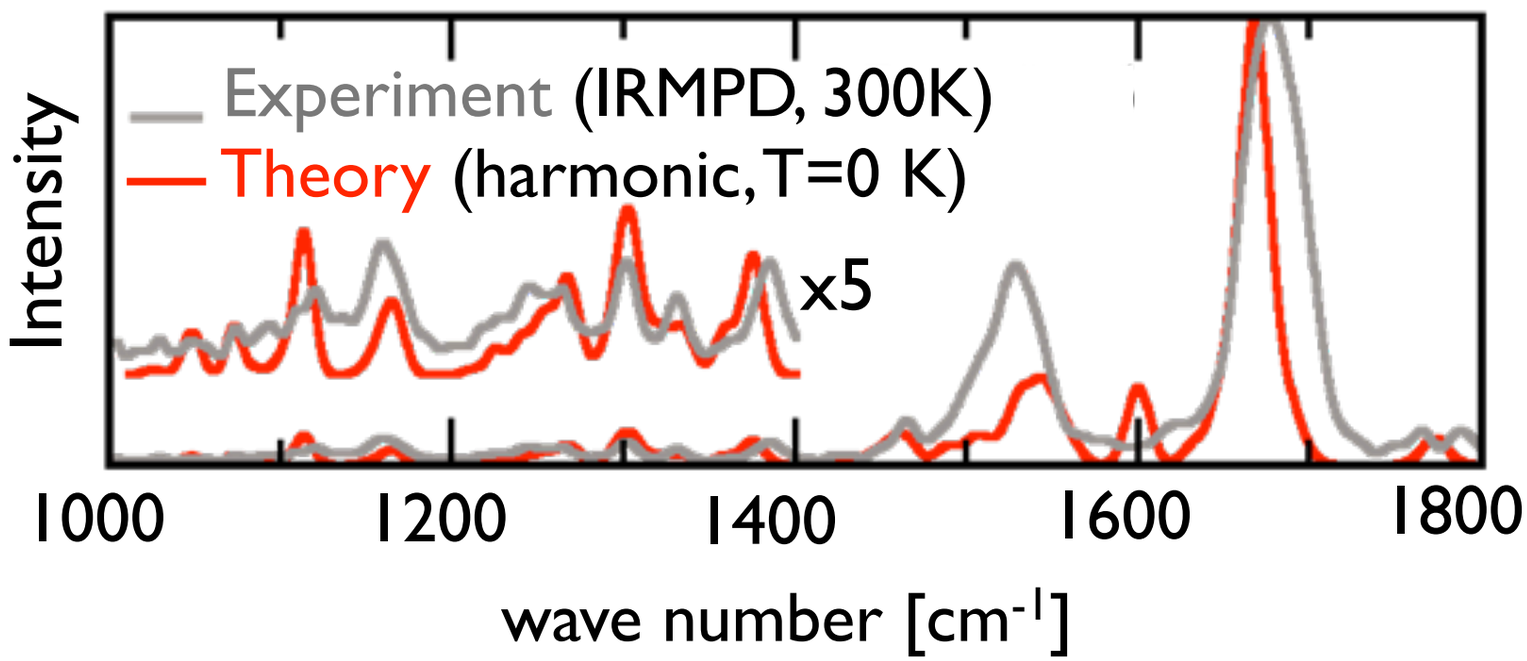
Room temperature

Theory: DFT-PBE+vdW; shifted, not scaled



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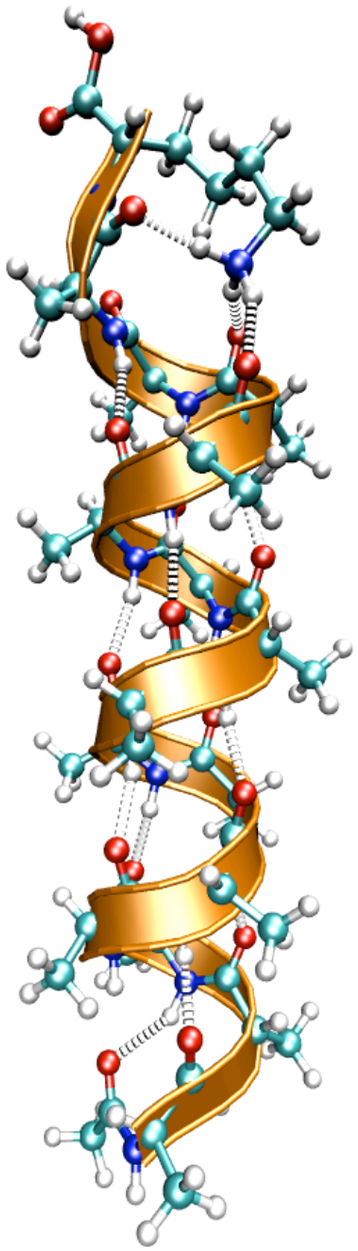

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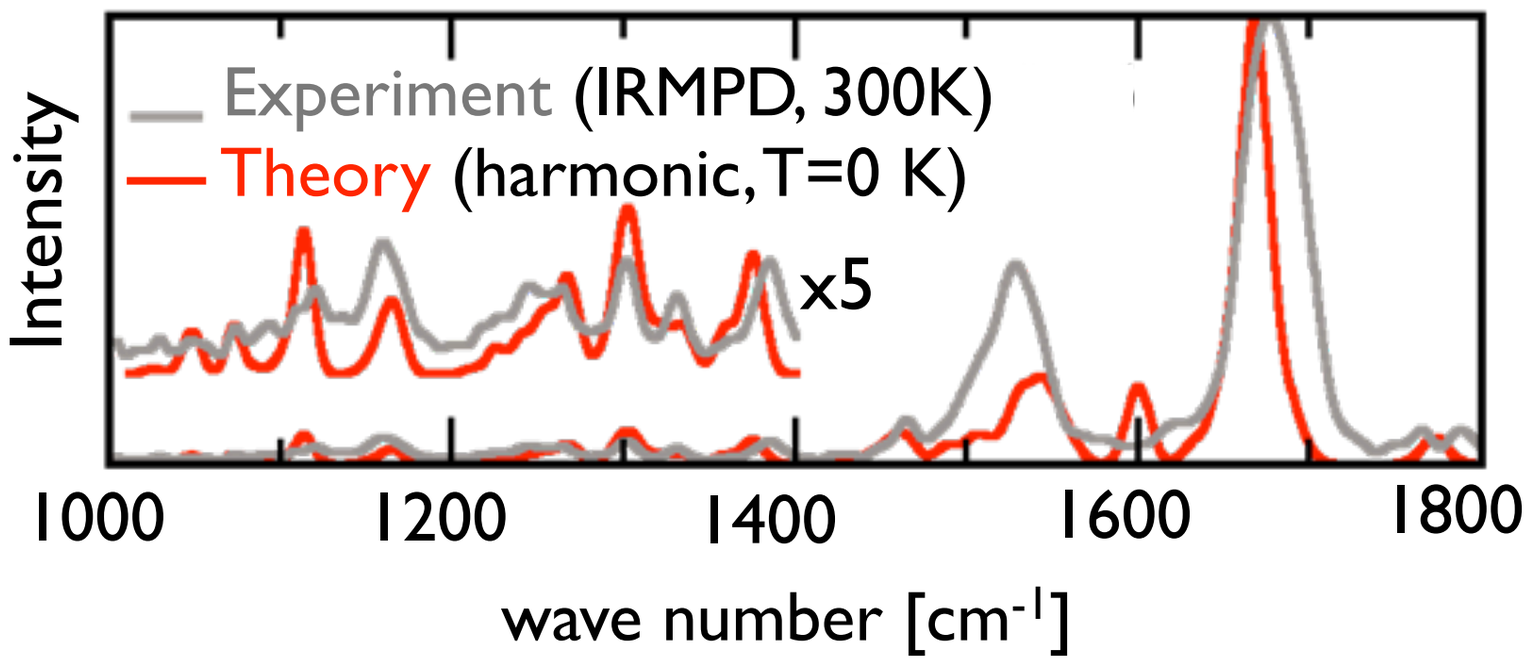

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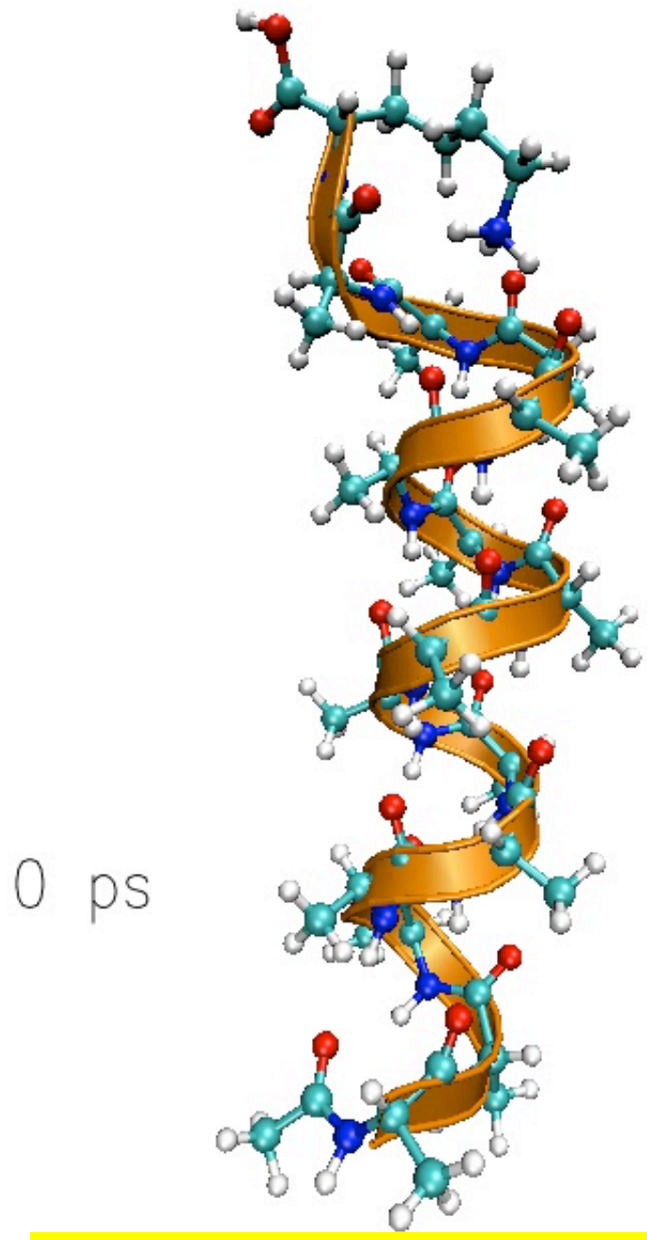
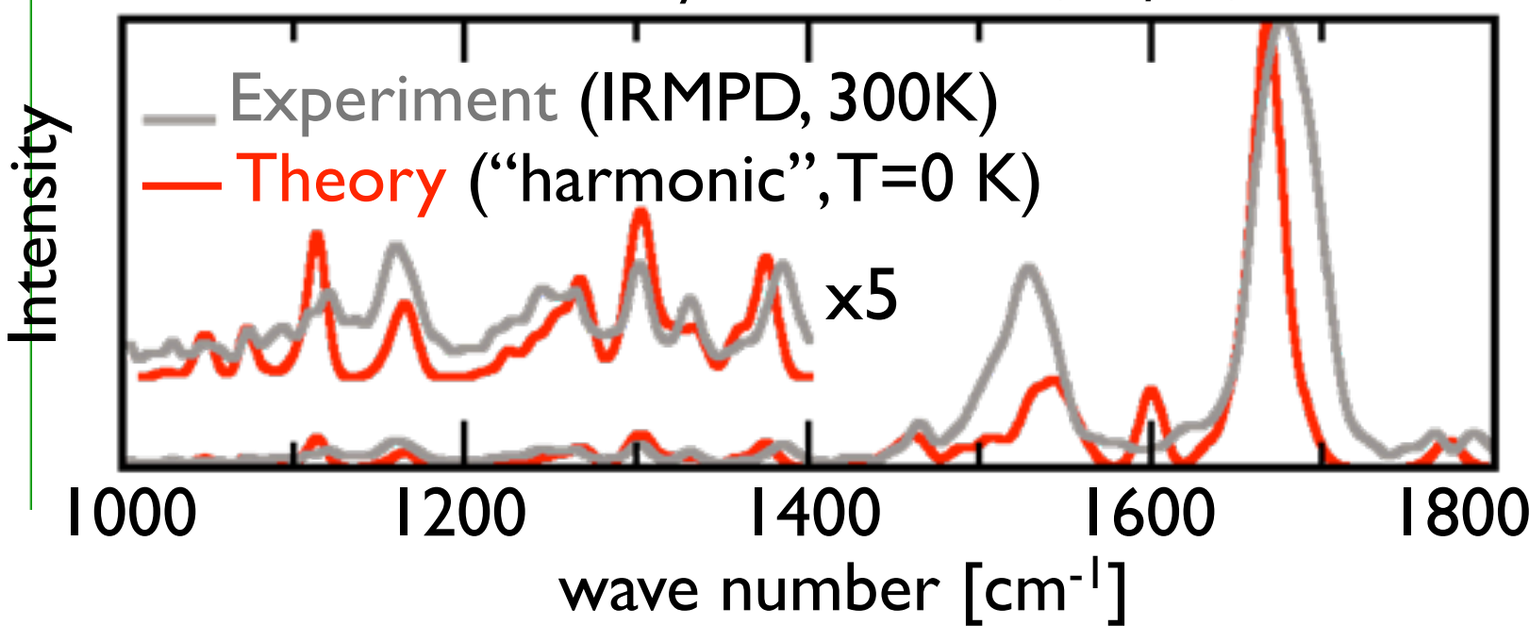


Theory: DFT-PBE+vdW; shifted, not scaled



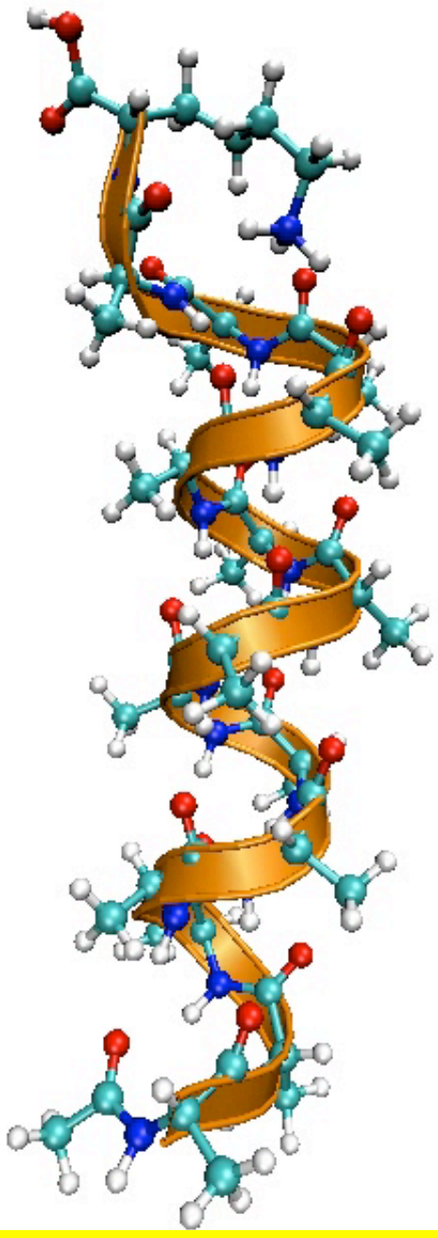
18 ps Born-Oppenheimer molecular dynamics, DFT-PBE+vdW,"tight"/tier 2!

$$I(\omega) \propto \omega^2 \int_{\infty}^{\infty} dt \, \underbrace{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}_{} \, e^{iwt}$$

dipole-dipole time correlation function

(Bio)molecular vibrational spectroscopy *in vacuo*

Rossi, Blum, Kupser, von Helden, Bierau, Pagel, Meijer, Scheffler, J. Phys. Chem. Lett. ***1****, 3465 (2010)*



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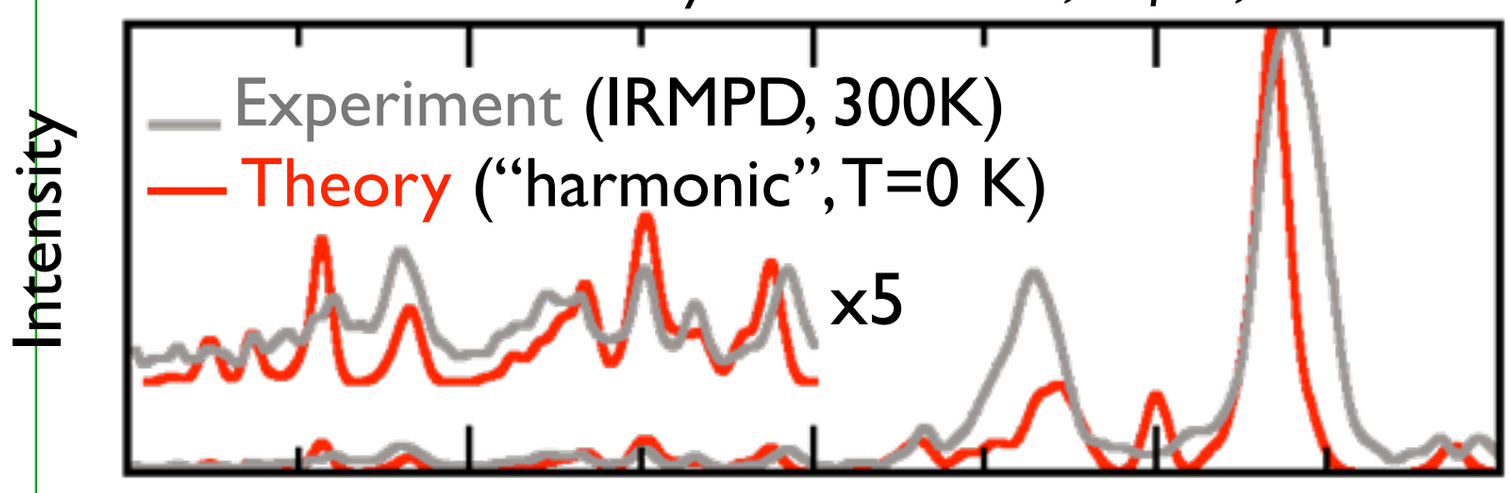

$$I(\omega) \propto \omega^2 \int_{\infty}^{\infty} dt \, \underbrace{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}_{} \, e^{iwt}$$

dipole-dipole time correlation function

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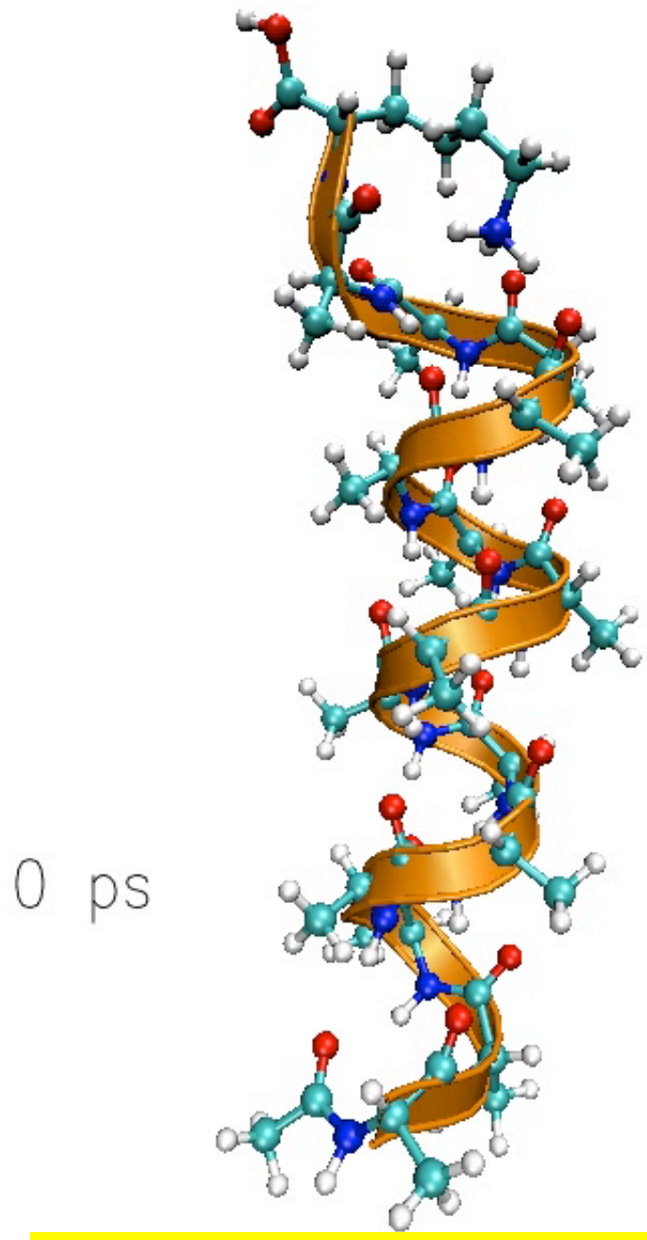
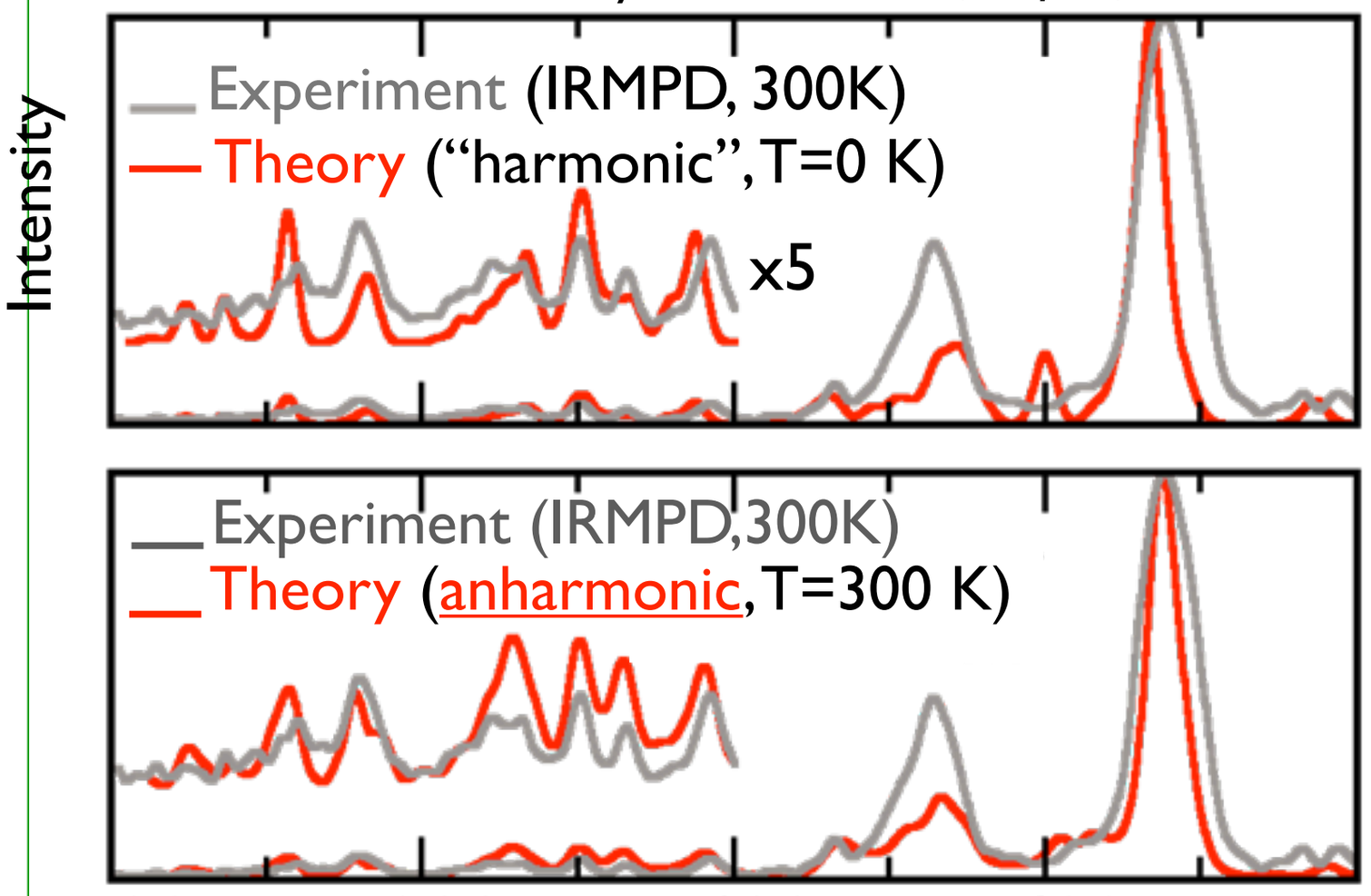


Theory: DFT-PBE+vdW; shifted, not scaled



18 ps Born-Oppenheimer molecular dynamics, DFT-PBE+vdW, "tight"/tier 2!

$$I(\omega) \propto \omega^2 \int_{\infty}^{\infty} dt \underbrace{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}_{\text{dipole-dipole time correlation function}} e^{iwt}$$

(Bio)molecular vibrational spectroscopy *in vacuo*

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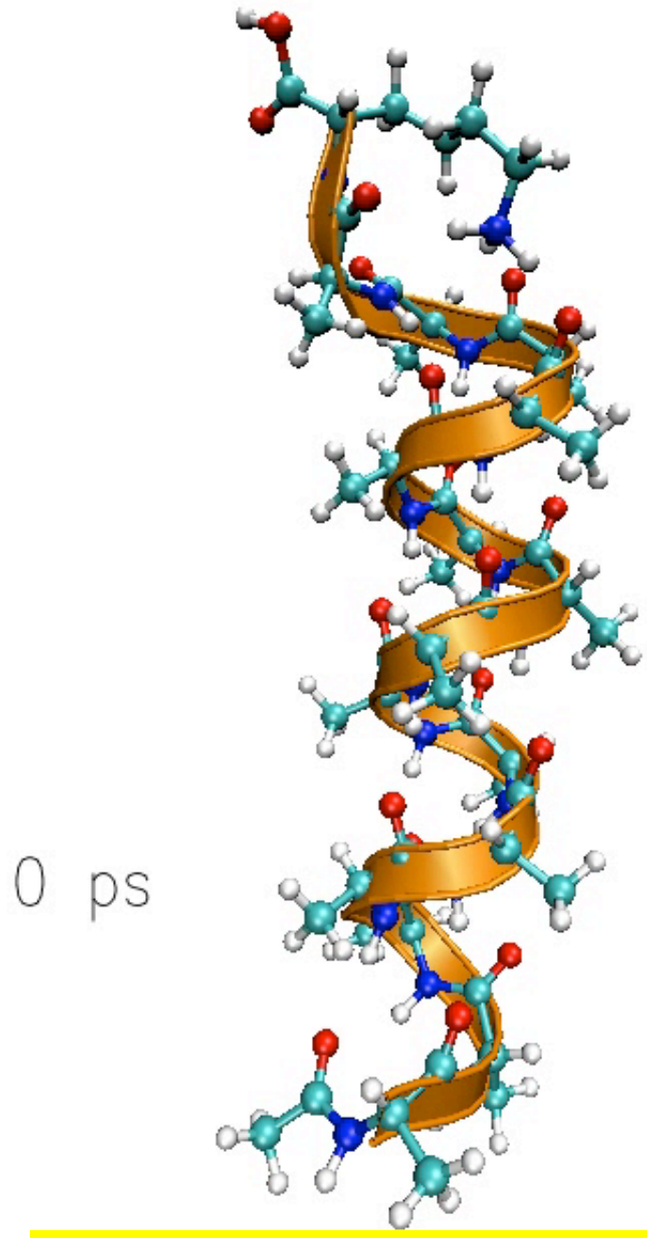
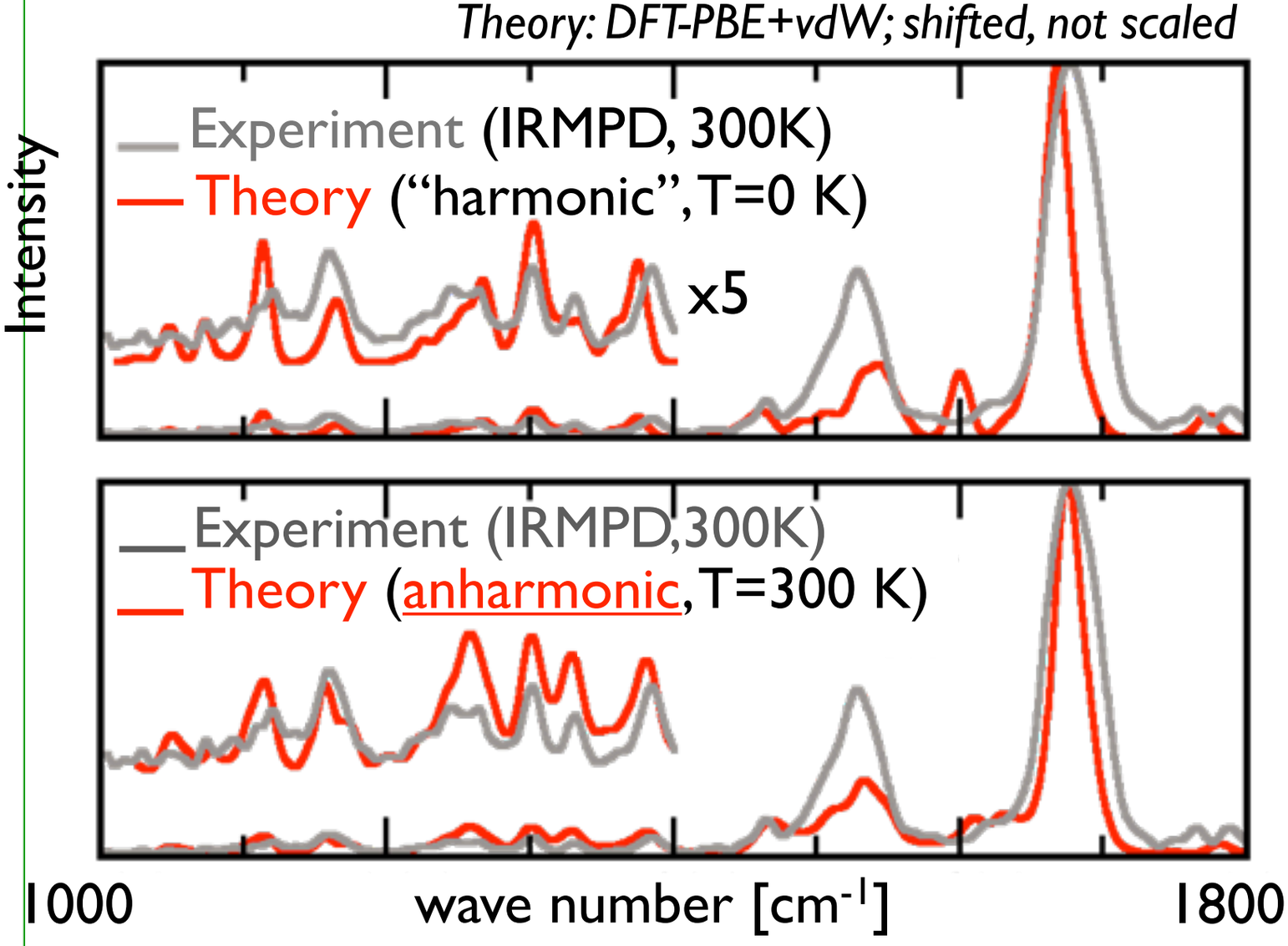


R_P=0.46

R_P=0.32

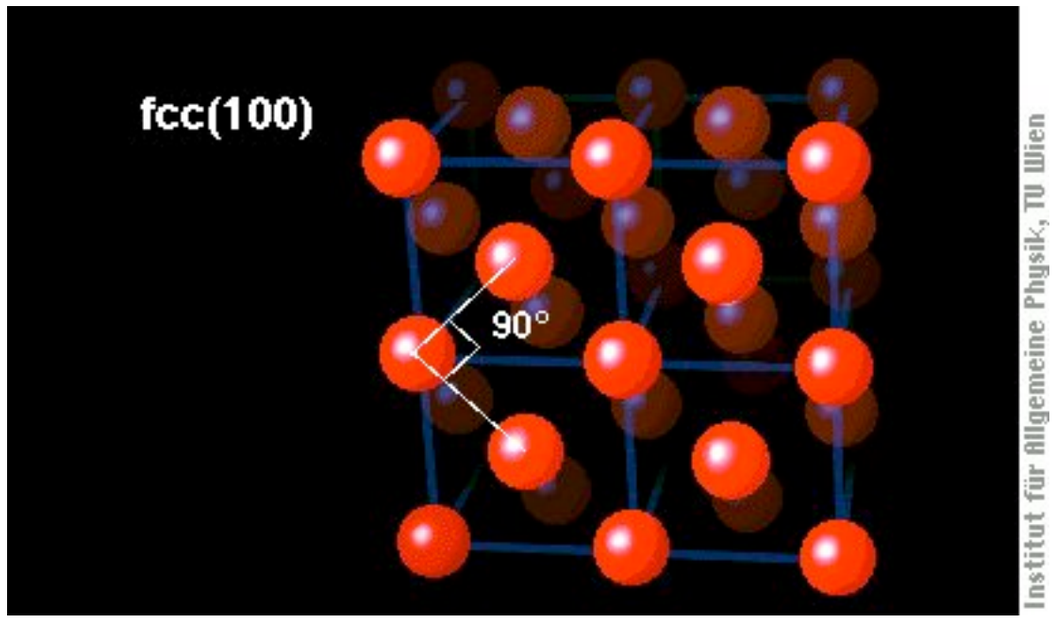
18 ps Born-Oppenheimer molecular dynamics, DFT-PBE+vdW,"tight"/tier 2!

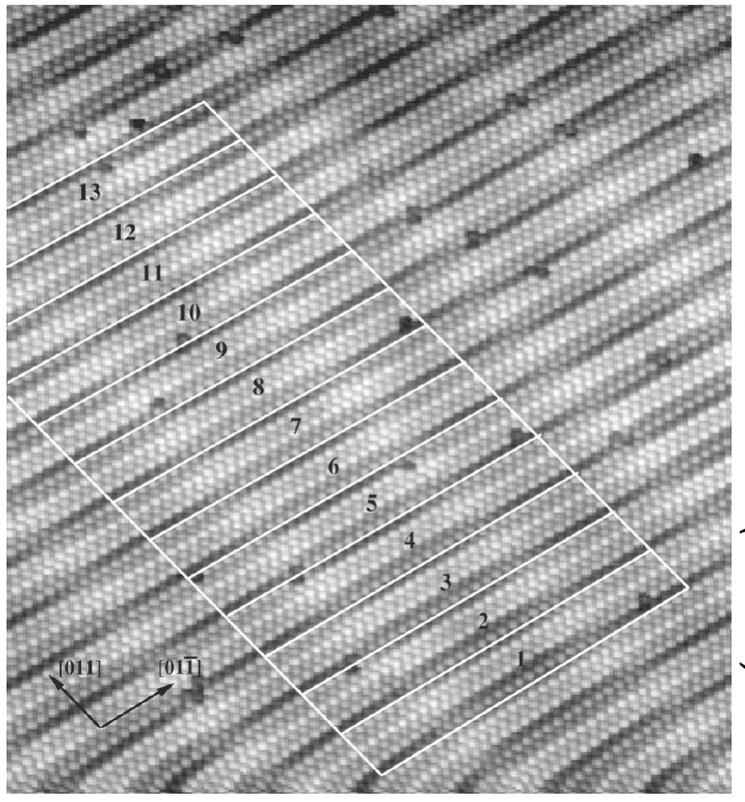


$$I(\omega) \propto \omega^2 \int_{\infty}^{\infty} dt \, \underbrace{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}_{\text{dipole-dipole time correlation function}} e^{iwt}$$

FHI-aims - what is it good for?

(100)-(1x1) ⟶ ("hex")





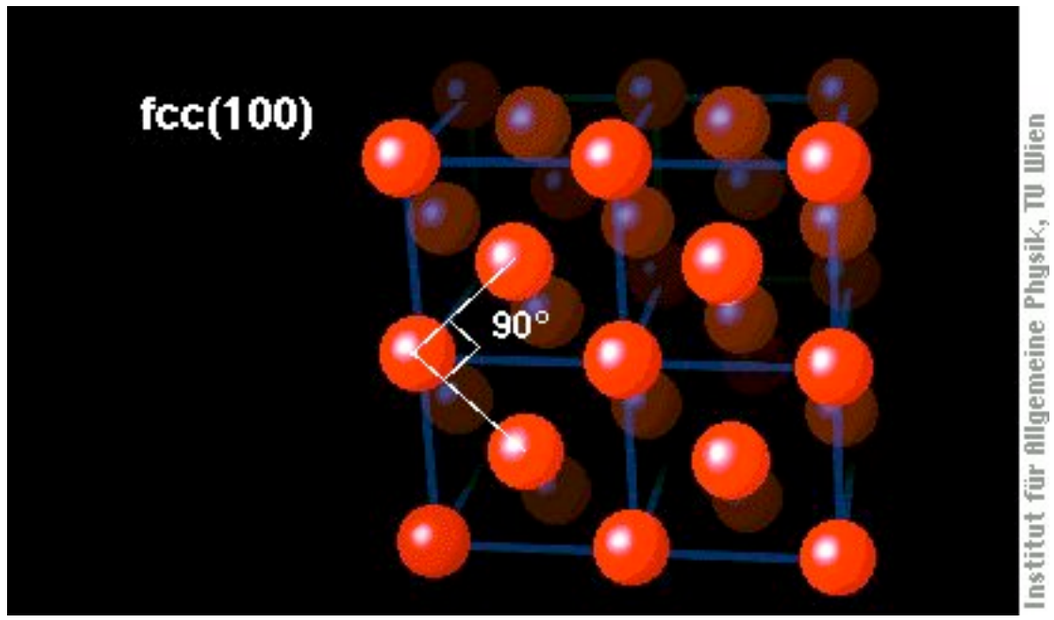
Pt(100), Ritz et al, PRB 56, 10518 (1997).

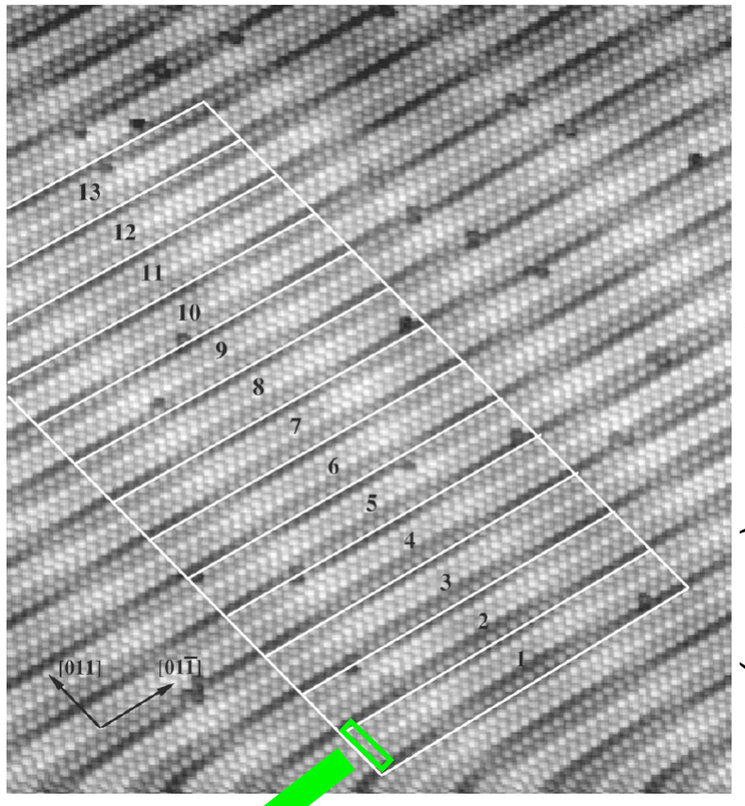
Large-scale surface reconstructions: Au(100), Pt(100)

P. Havu, V. Blum, V. Havu, P. Rinke, M. Scheffler, PRB ***82****, 161418(R) (2010)*

Large-scale surface reconstructions: Au,Pt(100)

(100)-(1x1) ⟶ ("hex")





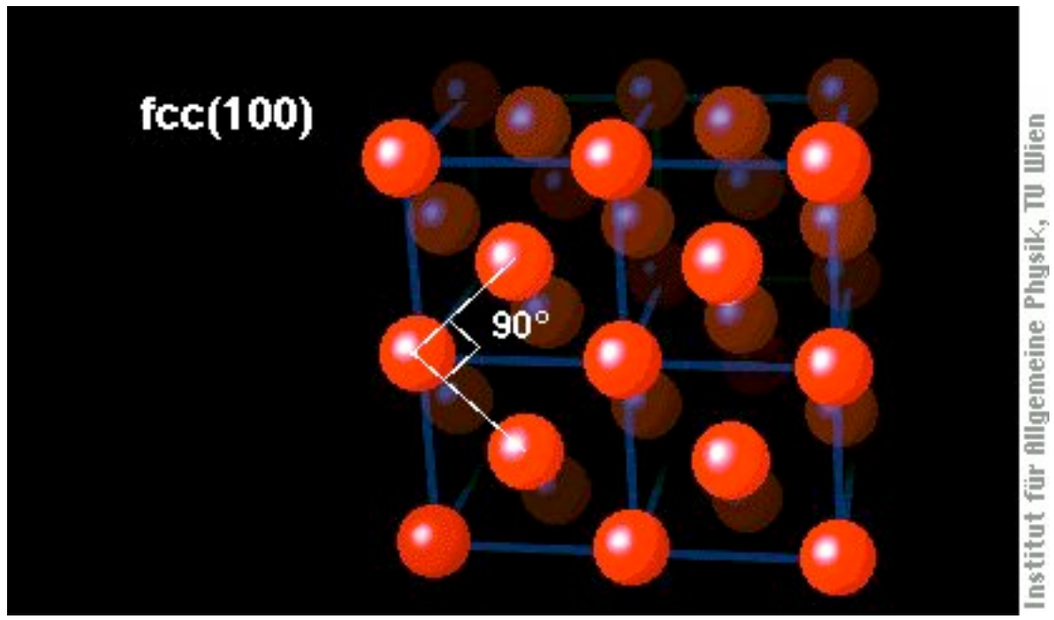
Pt(100), Ritz et al, PRB 56, 10518 (1997).

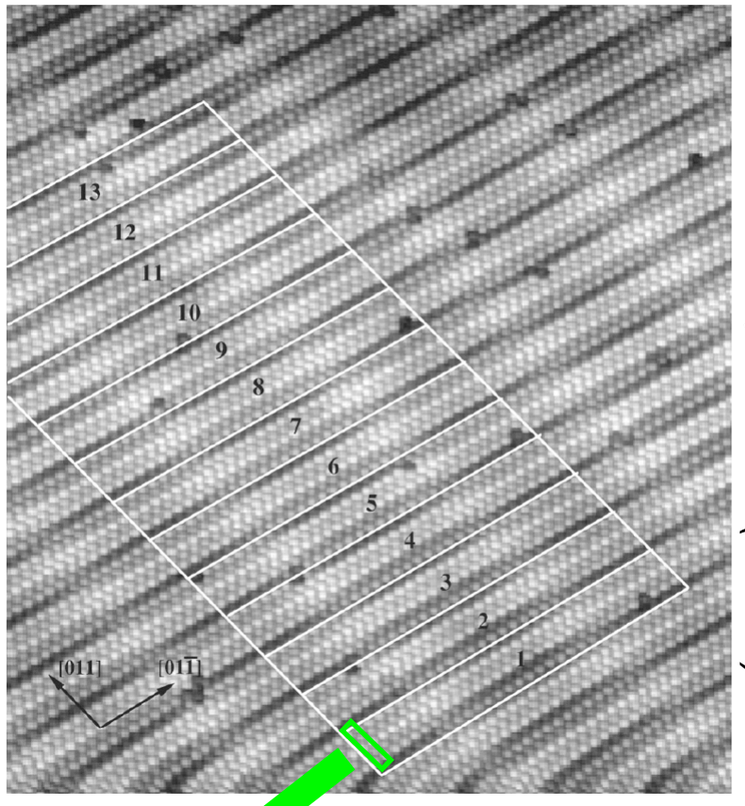
Reconstruction energetics (stability!) challenges experiment and theory:

	Experiment	Theory (DFT), "5x1"
Au(100)		
Pt(100)		

Large-scale surface reconstructions: Au,Pt(100)

(100)-(1x1) ⟶ ("hex")





Pt(100), Ritz et al, PRB 56, 10518 (1997).

Reconstruction energetics (stability!) challenges experiment and theory:

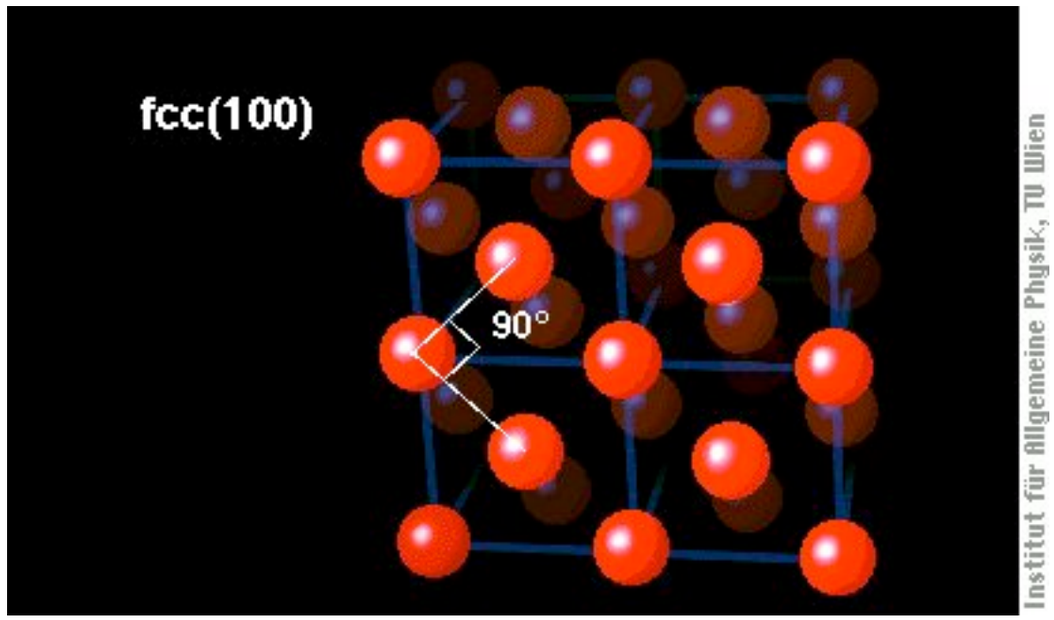
	Experiment	Theory (DFT), "5x1"
Au(100)		
Pt(100)	−0.12 eV/1x1 *(vacuum, CO titration[1])*	−0.05-0.07 eV/1x1

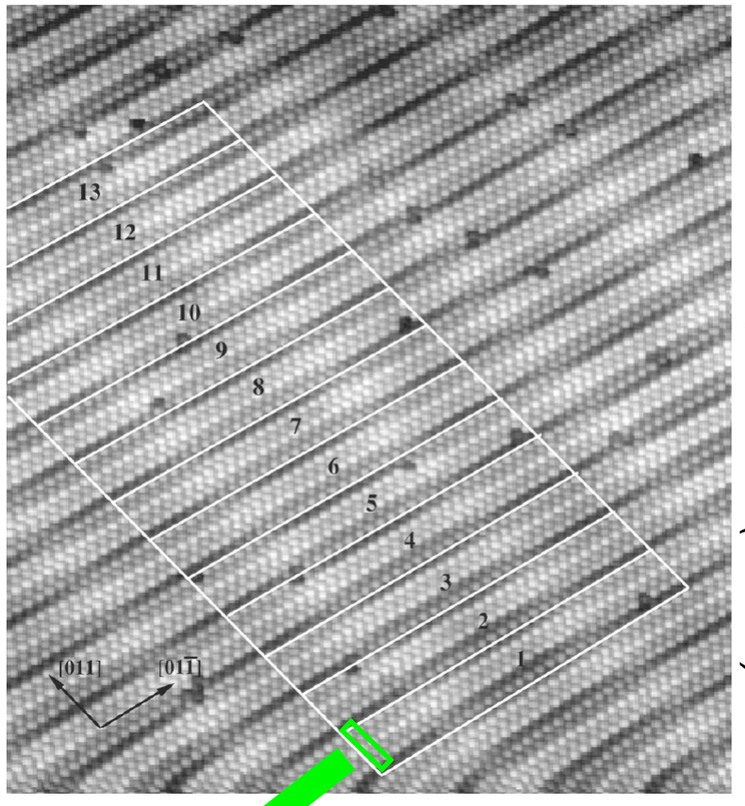
?

[1] Brown, Kose, King, Chem Rev. ***98****, 797 (1998).*

Large-scale surface reconstructions: Au,Pt(100)

(100)-(1x1) ⟶ ("hex")





Pt(100), Ritz et al, PRB 56, 10518 (1997).

Reconstruction energetics (stability!) challenges experiment and theory:

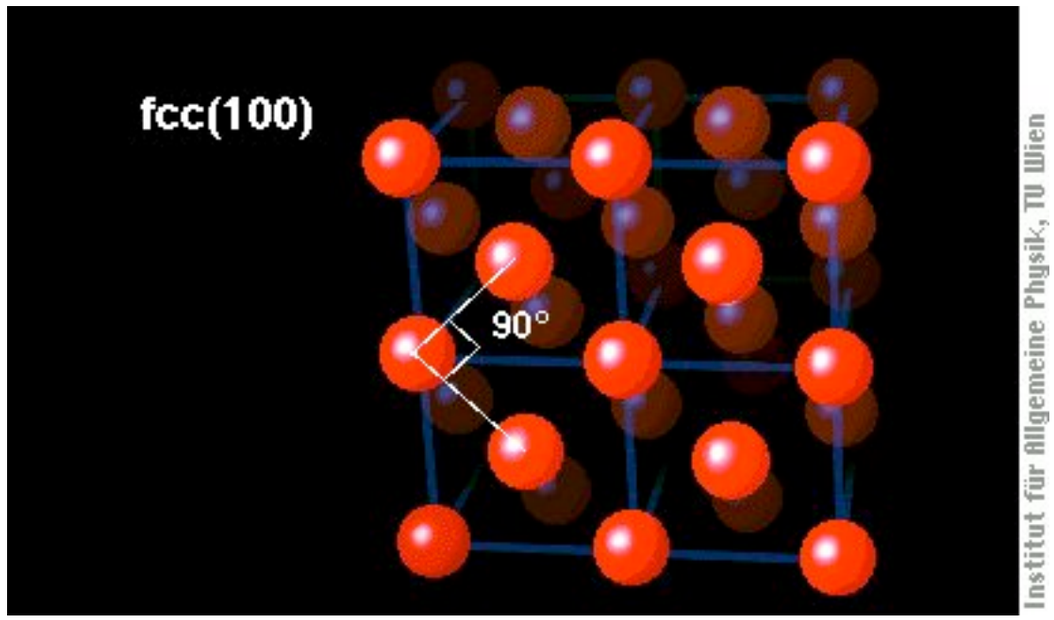
	Experiment	Theory (DFT), "5x1"
Au(100)	−0.02 eV/1x1 *(but in solution [2])*	−0.02-0.03 eV/1x1
Pt(100)	−0.12 eV/1x1 *(vacuum, CO titration[1])*	−0.05-0.07 eV/1x1

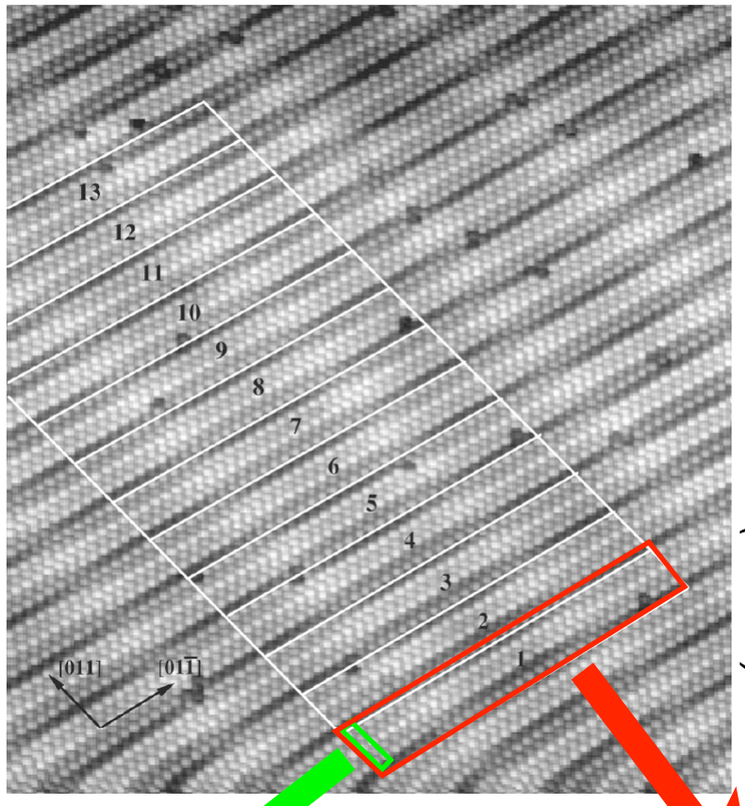
? ?

[1] Brown, Kose, King, Chem Rev. ***98****, 797 (1998).* *[2] Santos, Schmickler, Chem. Phys. Lett. 400,* ***26*** *(2004).*

Large-scale surface reconstructions: Au,Pt(100)

(100)-(1x1) ⟶ ("hex")





Pt(100), Ritz et al, PRB 56, 10518 (1997).

Reconstruction energetics (stability!) challenges experiment and theory:

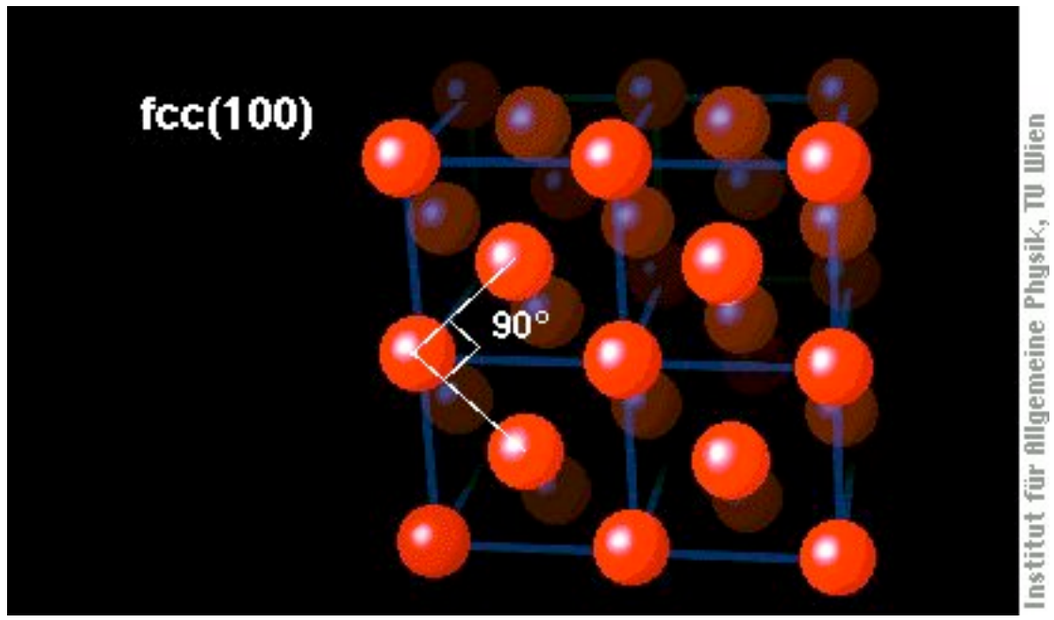
	Experiment	Theory (DFT), "5x1"	Theory (DFT), "5x*N*"
Au(100)	−0.02 eV/1x1 *(but in solution [2])*	−0.02-0.03 eV/1x1	??
Pt(100)	−0.12 eV/1x1 *(vacuum, CO titration[1])*	−0.05-0.07 eV/1x1	??

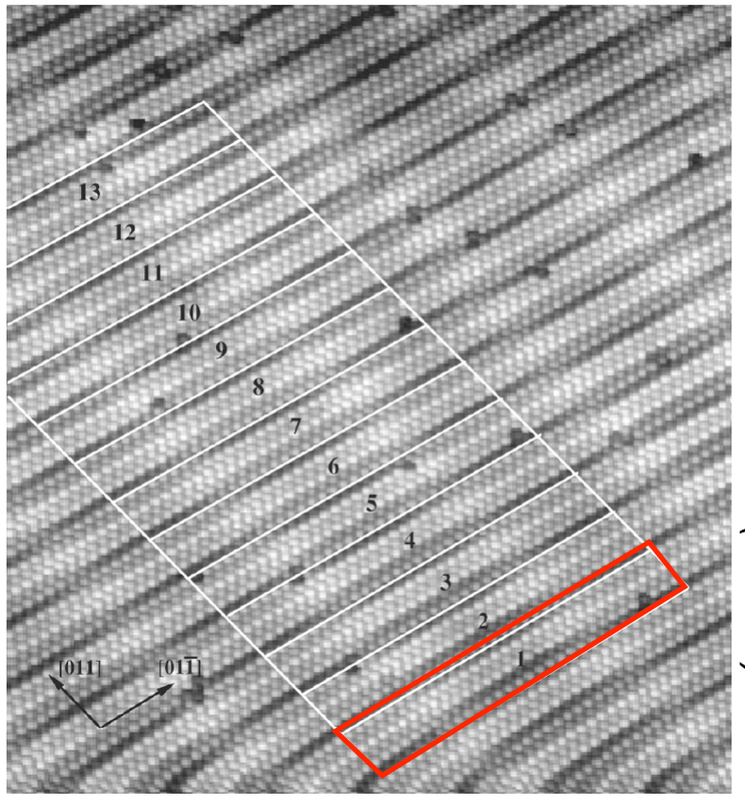
? ?

[1] Brown, Kose, King, Chem Rev. ***98****, 797 (1998). [2] Santos, Schmickler, Chem. Phys. Lett. 400,* ***26*** *(2004).*

Large-scale surface reconstructions: Au,Pt(100)

(100)-(1x1) ⟶ ("hex")





Pt(100), Ritz et al, PRB 56, 10518 (1997).

Reconstruction energetics (stability!) challenges experiment and theory:

	Experiment	Theory (DFT), "1x5"	Theory (DFT), "*N*x5"
Au(100)	−0.02 eV/1x1 *(but in solution[2])*	−0.02-0.03 eV/1x1	−0.07-0.08 eV/1x1
Pt(100)	−0.12 eV/1x1 *(vacuum, CO titration[1])*	−0.05-0.07 eV/1x1	−0.10-0.11 eV/1x1

? ?

up to 1046 atom slab, tight!

[1] Brown, Kose, King, Chem Rev. ***98****, 797 (1998).* *[2] Santos, Schmickler, Chem. Phys. Lett. 400,* ***26*** *(2004).*

FHI-aims - what is it good for?

- ... when you need reliable, affordable all-electron numbers
- no problem comparing molecules, periodic systems (DFT-LDA/GGA)
- seamlessly from light to heavy elements
- *Beyond* DFT-LDA/GGA for cluster-type geometries (Hartree-Fock, hybrids, MP2, RPA, GW)
- Good scaling towards large systems (1,000s of atoms), parallel computers (10,000s of cores)

X. Ren,
Fri 11:30h

Many ongoing efforts:

Periodic "beyond DFT" · Much work around molecular dynamics, vibrations, phonons · Spin-orbit & core level spectroscopy · Transport frameworks · ...

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)*
http://www.fhi-berlin.mpg.de/aims/

People

Scalability

Periodic systems, relativity

Matthias Scheffler

Ville Havu (FHI/Helsinki)

Rainer Johanni (Munich)

Paula Havu (FHI/Helsinki)

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

Karsten Reuter, Patrick Rinke, Xinguo Ren, Ralf Gehrke, Felix Hanke, Mariana Rossi, Alex Tkatchenko, Jürgen Wieferink, Luca Ghiringhelli, Mina Yoon, Christian Carbogno, Norbert Nemec, Jörg Meyer, Andreas Dolfen, Stefan Gutzeit, Andrea Sanfilippo, Sucismita Chutia, Matti Ropo, Fabio Caruso, Matthias Gramzow, Viktor Atalla, Oliver Hofmann, Werner Jürgens, Sergey Levchenko, ...

Fritz Haber Institute, Berlin

[Richard-Willstätter-Haus]

People

Matthias Scheffler

Ville Havu (FHI/Helsinki)

Scalability

Rainer Johanni (Munich)

Periodic systems, relativity

Paula Havu (FHI/Helsinki)

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