All electron *ab initio* molecular simulations
Status, successes, and some computational challenges

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Berlin

100 YEARS OF PHYSICAL CHEMISTRY IN BERLIN—DAHLEM
100 YEARS

The ab initio molecular simulations package
FHI aims

IPAM Workshop "Challenges in Warm Dense Matter" - IPAM, May 24, 2012

Electronic structure theory for real materials

Enormous successes:

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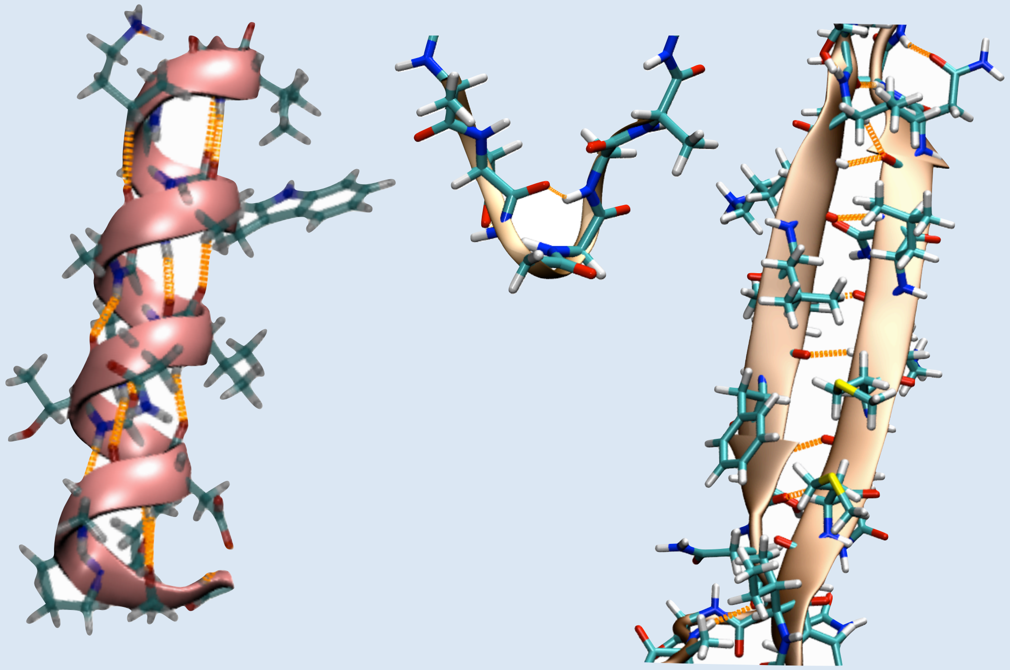

(Bio)molecular matter

- Structural complexity
- statistical averages & dynamics
- “weak” interactions critical

Electronic structure theory for real materials

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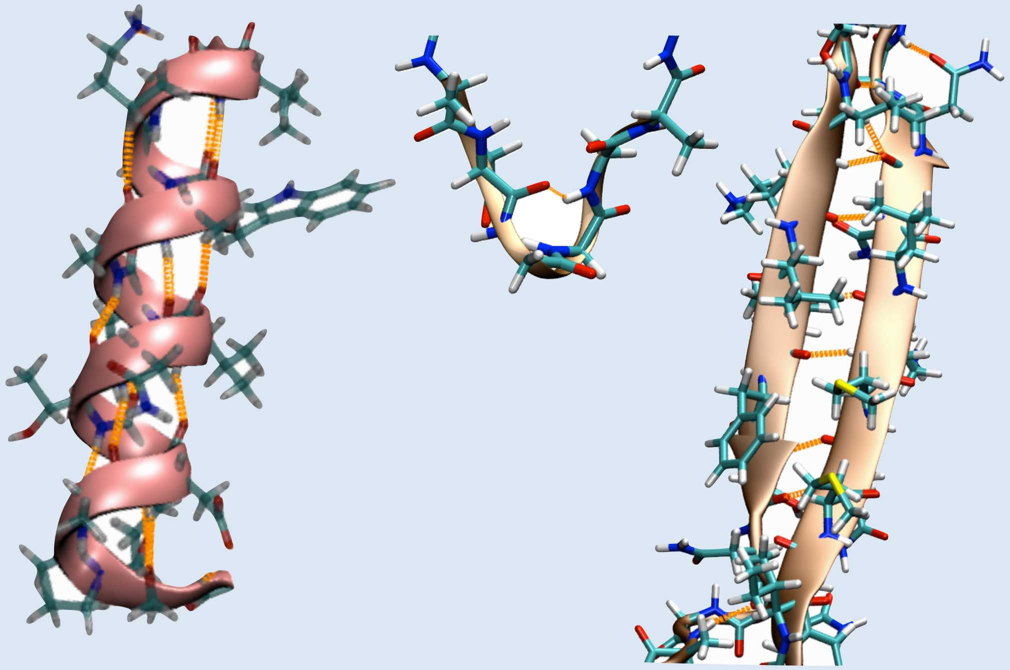

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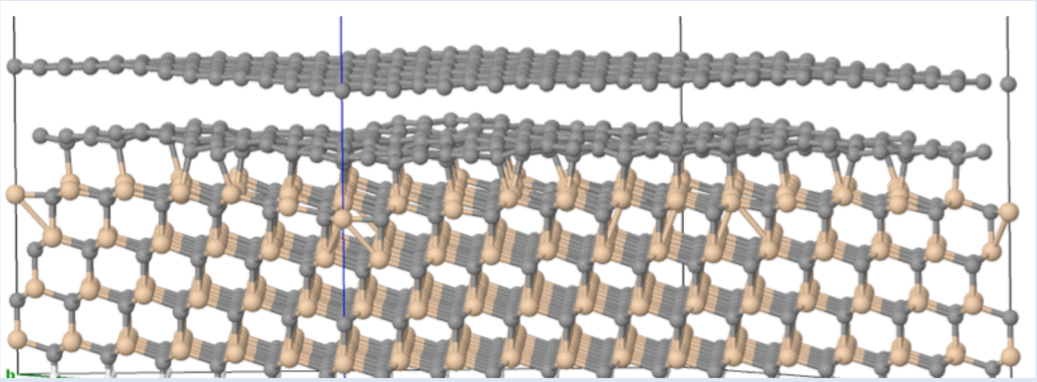
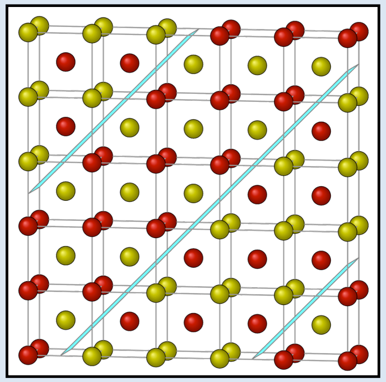


Graphene / SiC



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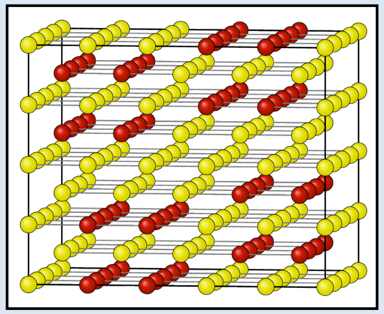

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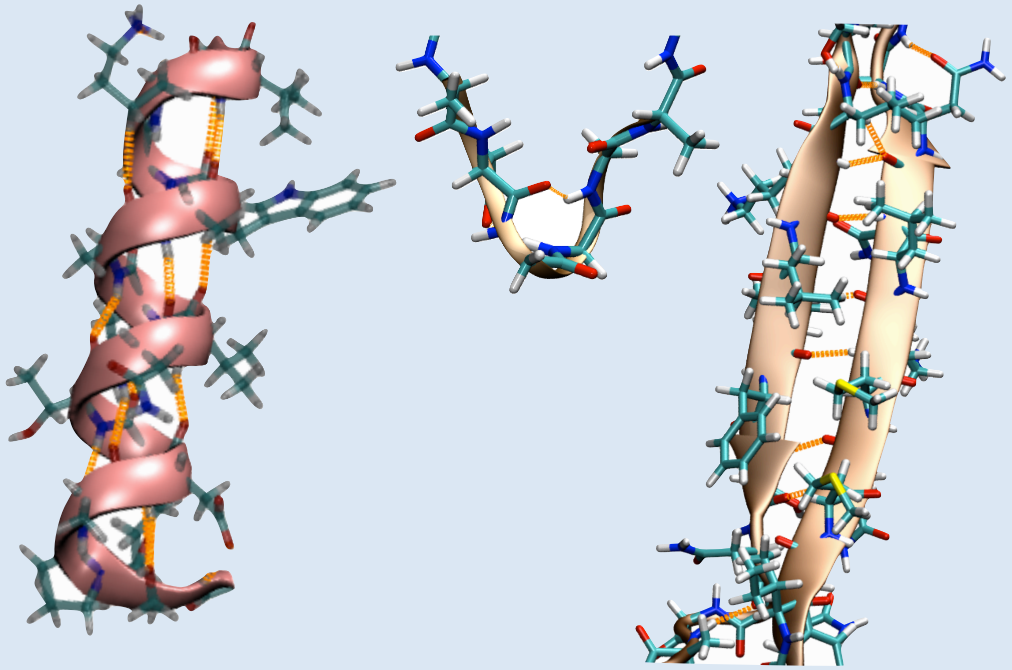
Condensed phases

(solids, surfaces, ...)

- Structure!
- Stability, free energies
- electronic, mechanical, optical, ... properties

Electronic structure theory for real materials



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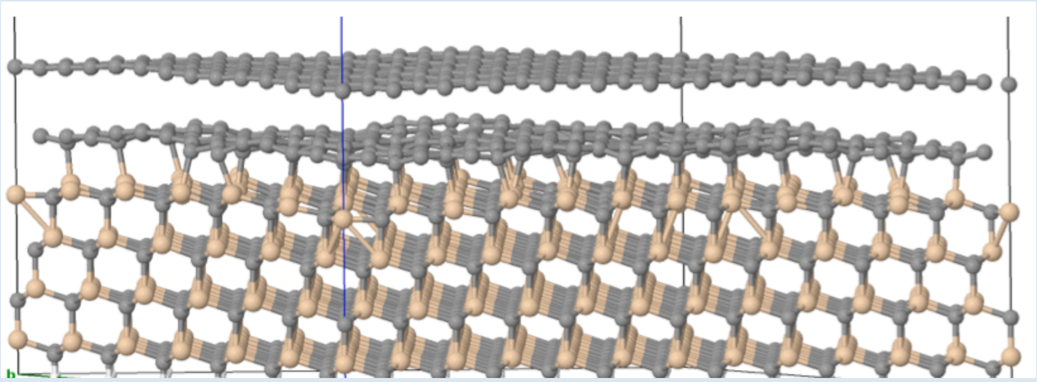

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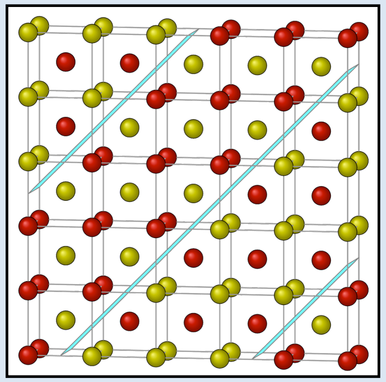

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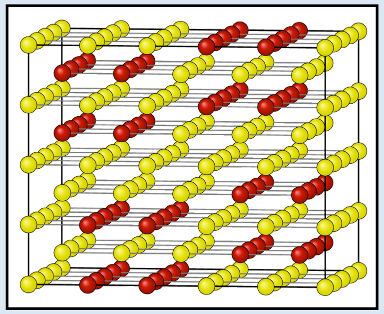

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- “electron gas + protons”; high-pressure compounds, transitions
- (Born-Oppenheimer) molecular dynamics, classical nuclei
- Quantum nuclei? (PIMD)

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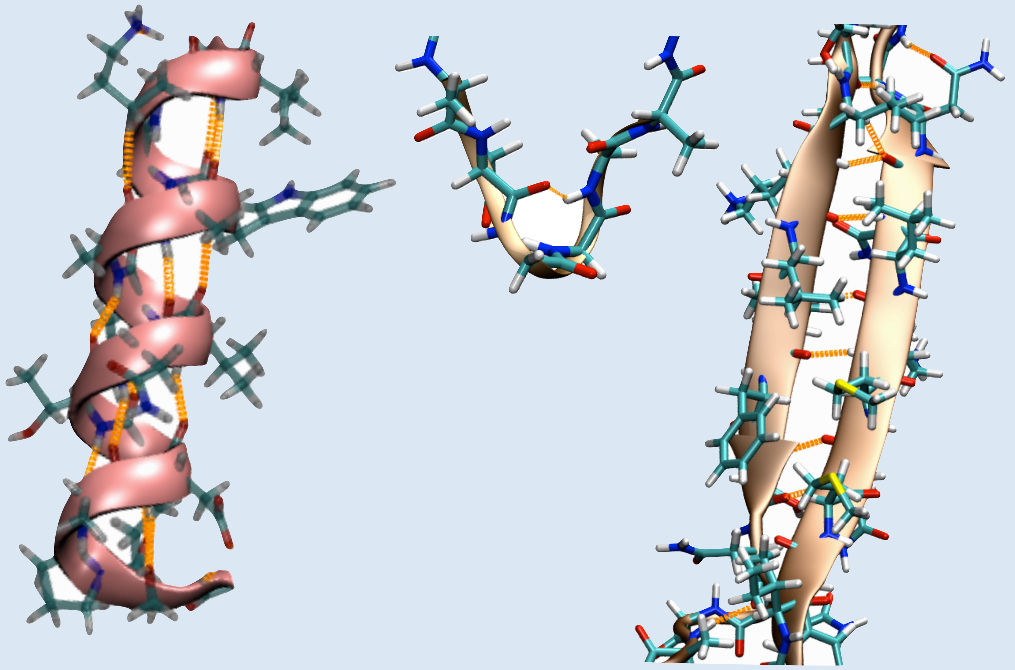

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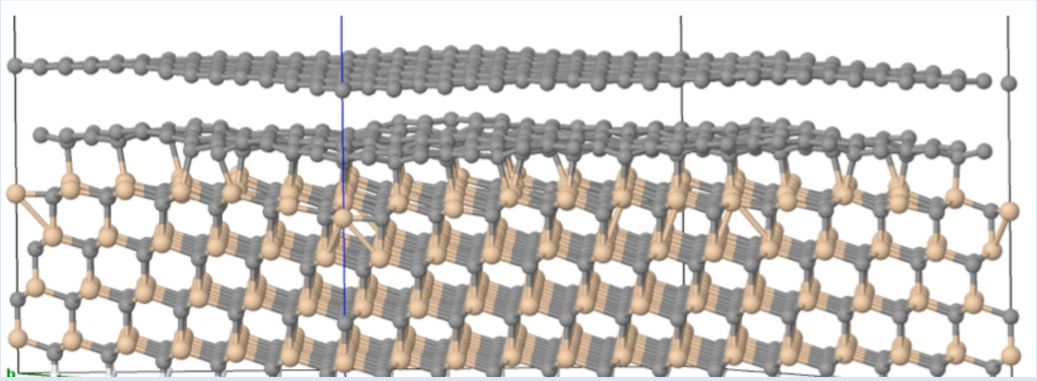

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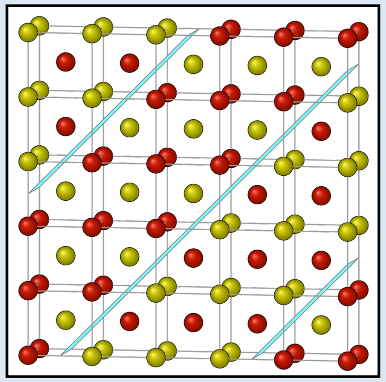

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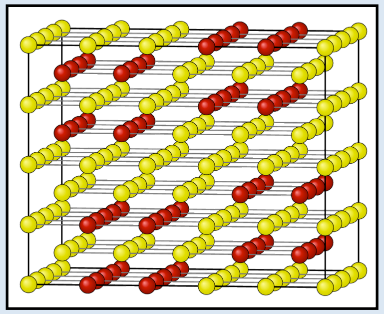

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Today: “Mostly density-functional theory”, plenty of flavors

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- Algorithms. Can we compute the right thing?
  - Realistically sized systems to capture "reality"
  - Statistical averages, dynamics, combinatorial complexity of "structure"?
  - Simply, hardware vs. software - utilize *available* hardware effectively

Outline

An approach to all-electron "density functional theory and beyond": FHI-aims [1]

- Numeric atom-centered (localized) basis sets
- Scalability (1,000s of atoms, 1(0),000s of CPUs)
- Pushing towards "better" functionals (→P. Rinke)

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[1] The Fritz Haber Institute ab initio molecular simulations suite (FHI-aims)
V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler,
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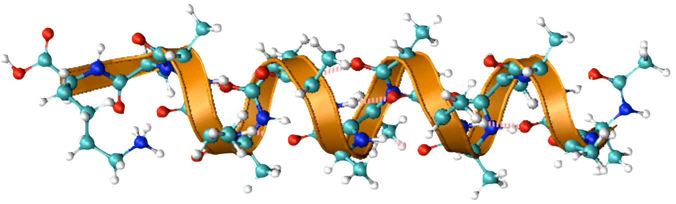

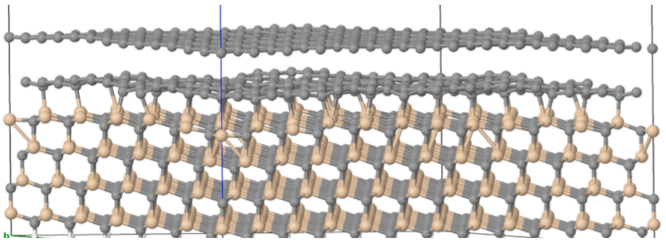

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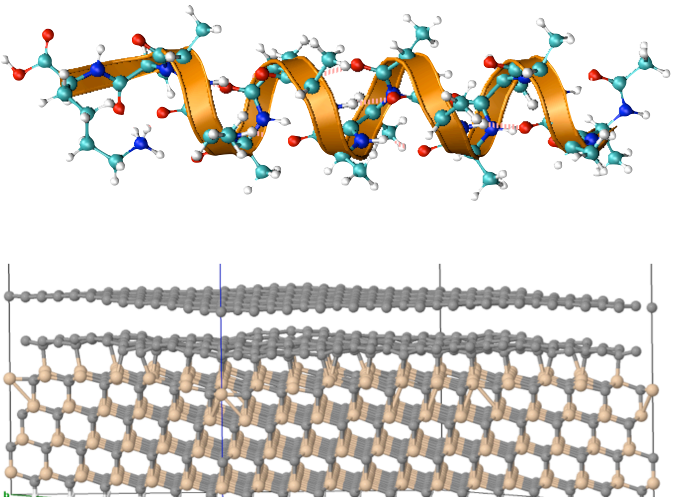

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... and some challenges (towards WDM)

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Fritz Haber Institute, Berlin

[Richard-Willstätter-Haus]

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

Karsten Reuter, Patrick Rinke, Ralf Gehrke, Paula Havu, Andreas Dolfen, Felix Hanke, Stefan Gutzeit, Andrea Sanfilippo, Luca Ghiringhelli, Sergey Levchenko, Matthias Gramzow, Mina Yoon, Christian Carbogno, Norbert Nemec, Jörg Meyer, Fabio Caruso, Sucismita Chutia, Jürgen Wieferink, Simiam Ghan, Viktor Atalla, Matti Ropo, Ferdinand Evers, Alex Bagrets, Heiko Appel, Daniel Berger, Oliver Hofmann, ...

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Our goal: *Efficient* method, but do not sacrifice accuracy

Numerical approximations (including all electrons) should be reliably convergable for the *actual* problem of interest!

Central decision: the basis set

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

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

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

<u>Many popular implementations:</u>
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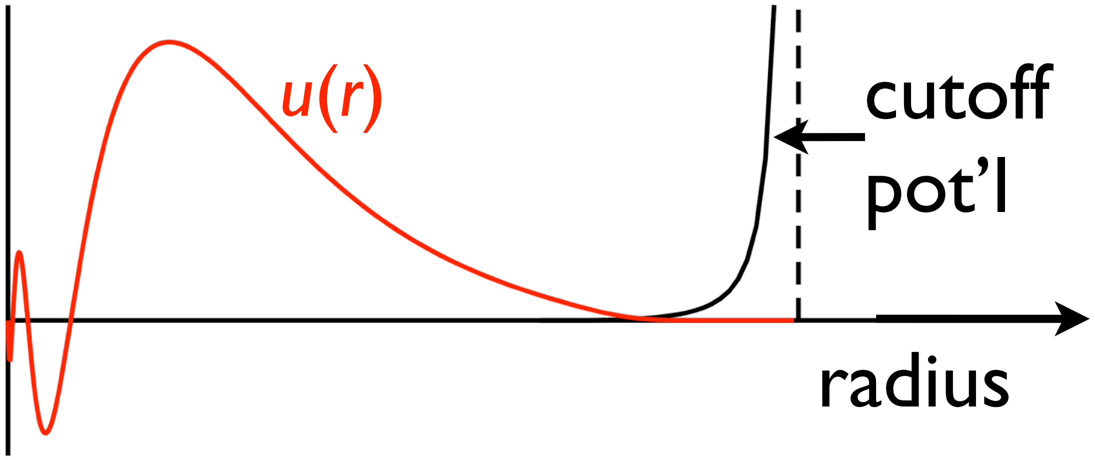

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→ The choice of <u>efficient</u> and of <u>enough</u> radial functions is obviously important

→ 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>

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)*

How to find good basis sets - and how far do they carry?

Lots of shapes $u(r)$ available:
Confined free atoms, hydrogen-like, free ions, ...

Simple robust selection strategy:

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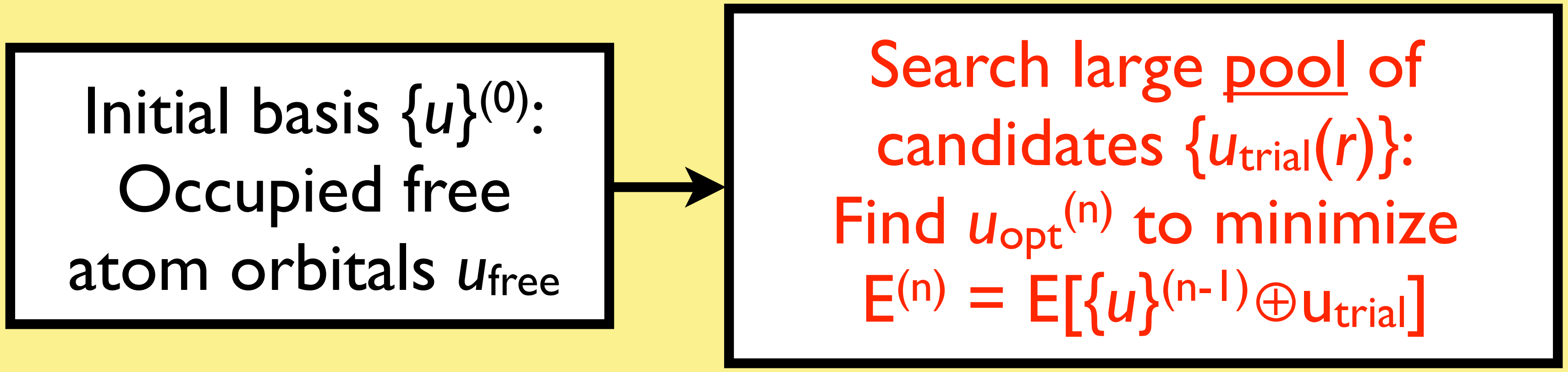

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Find $u_{\text{opt}}^{(n)}$ to minimize
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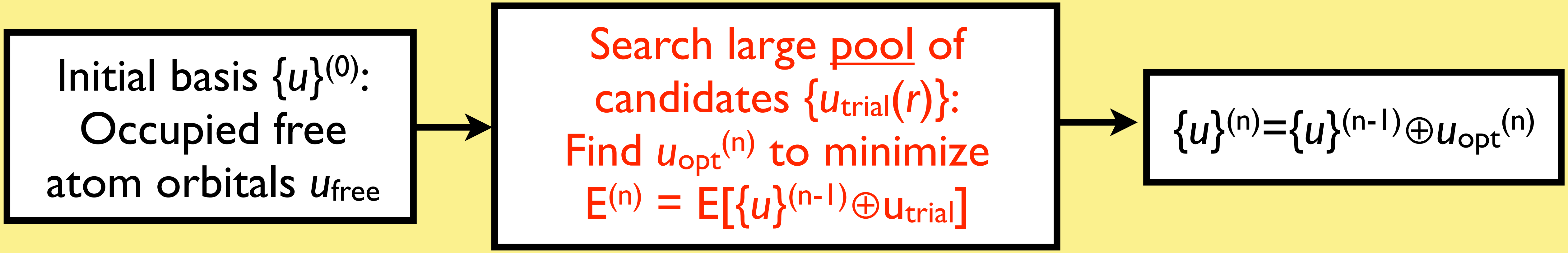

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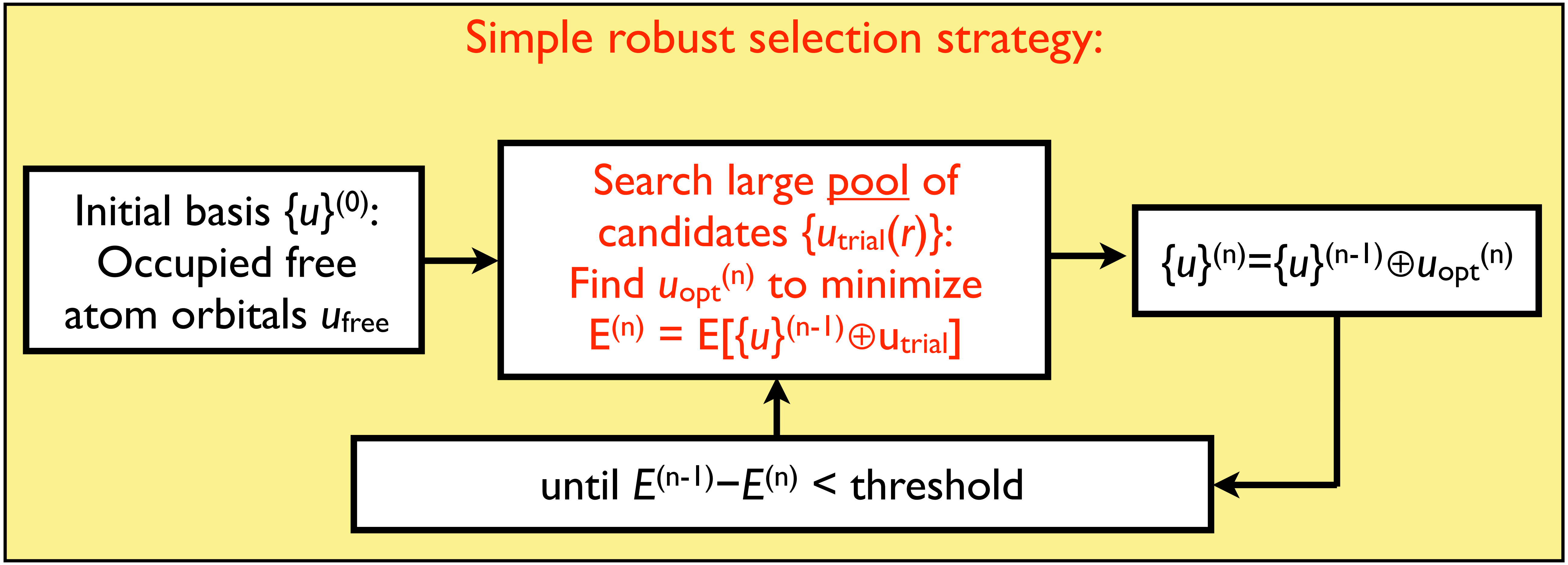

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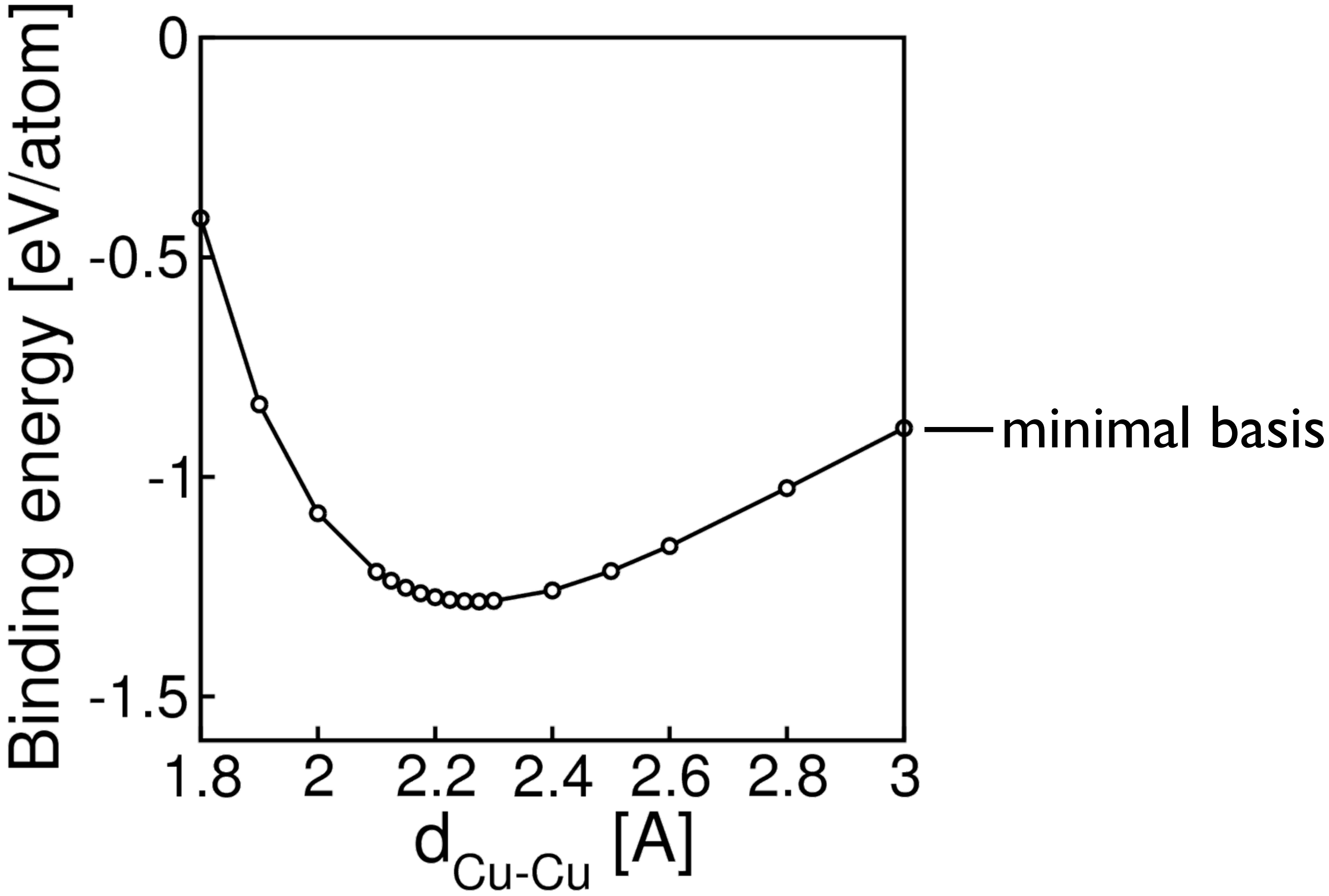
$\{u\}^{(n)} = \{u\}^{(n-1)} \oplus u_{\text{opt}}^{(n)}$

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

Dimer binding curves to optimize the basis

Example: Cu_2 binding curve for different basis sets



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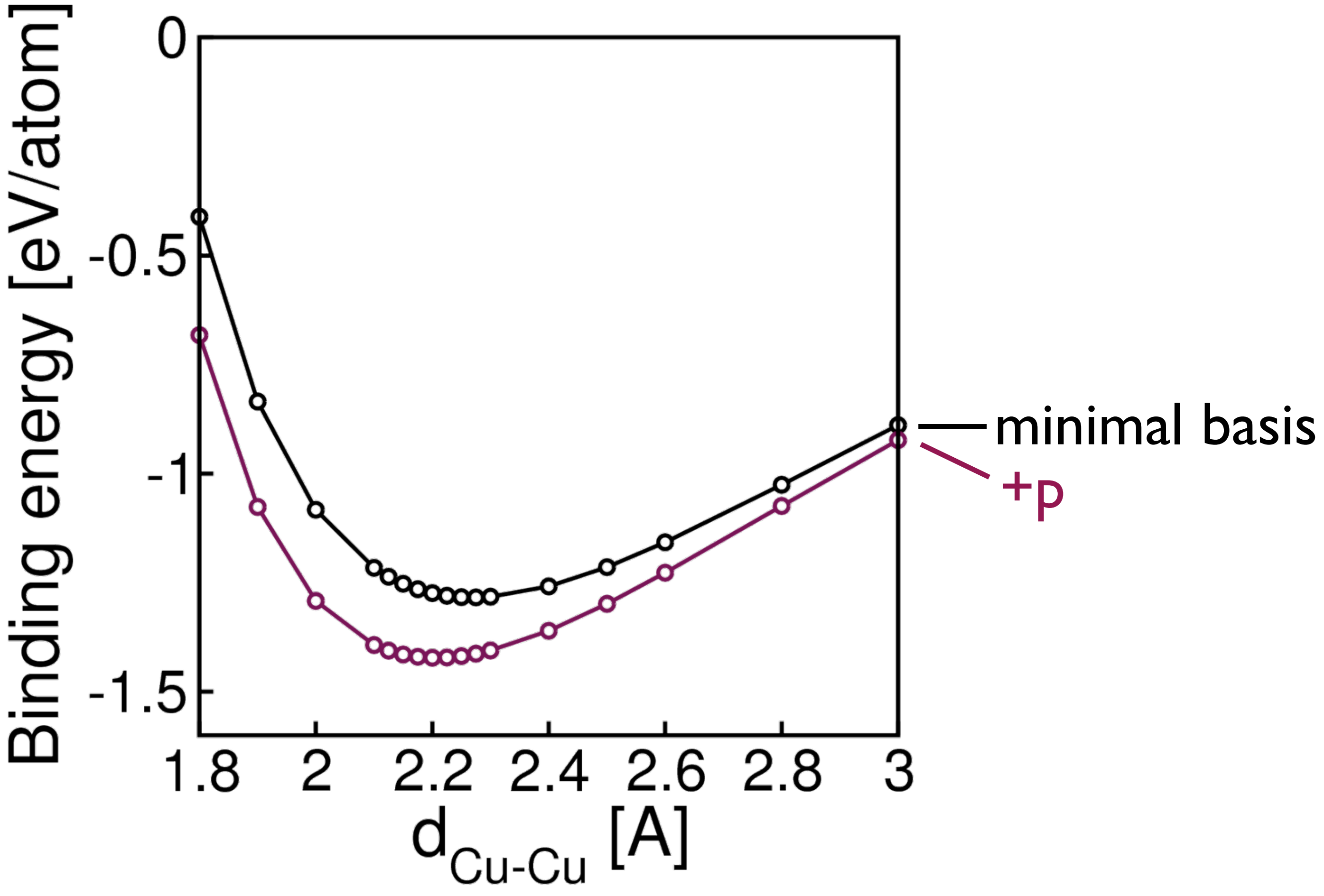

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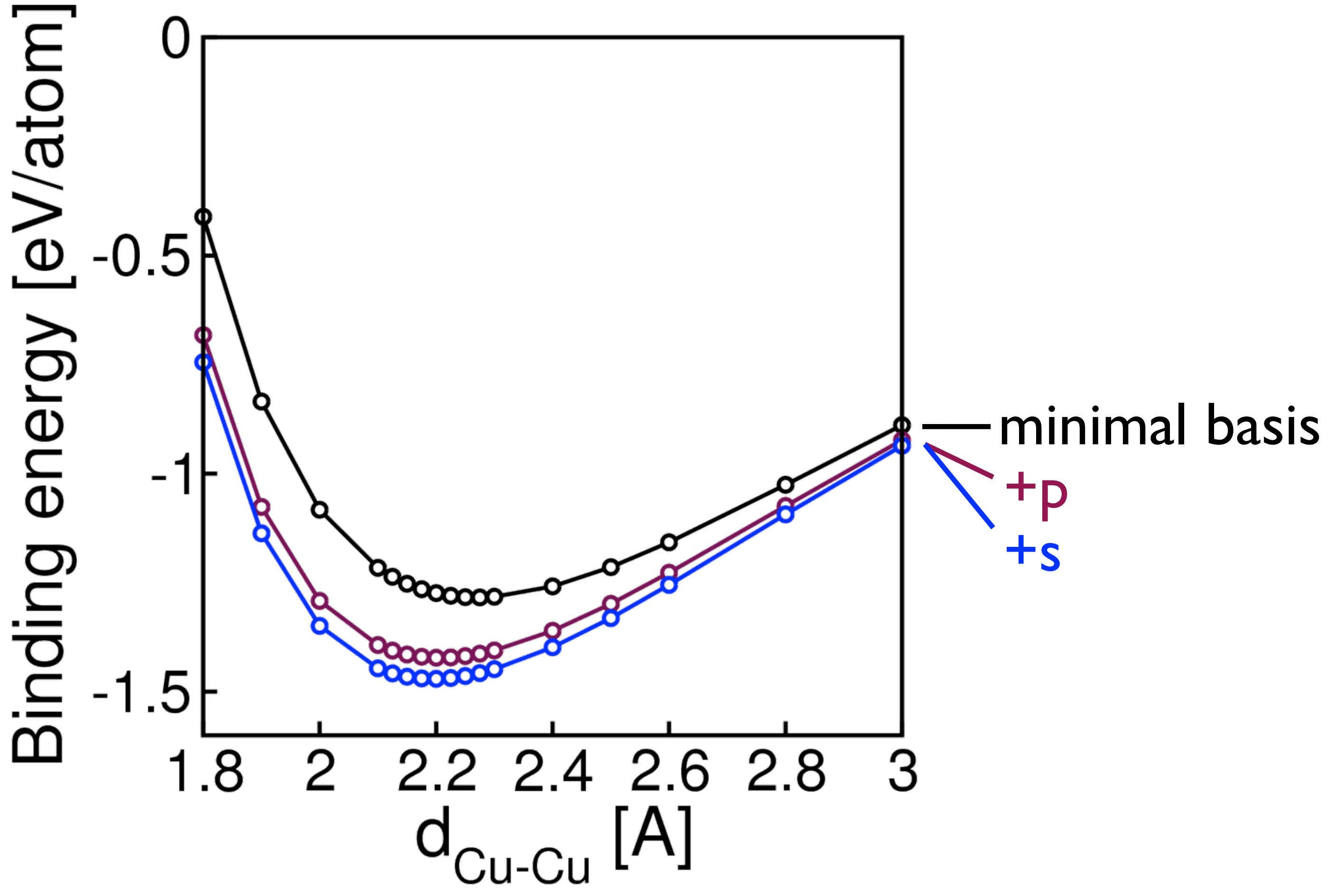

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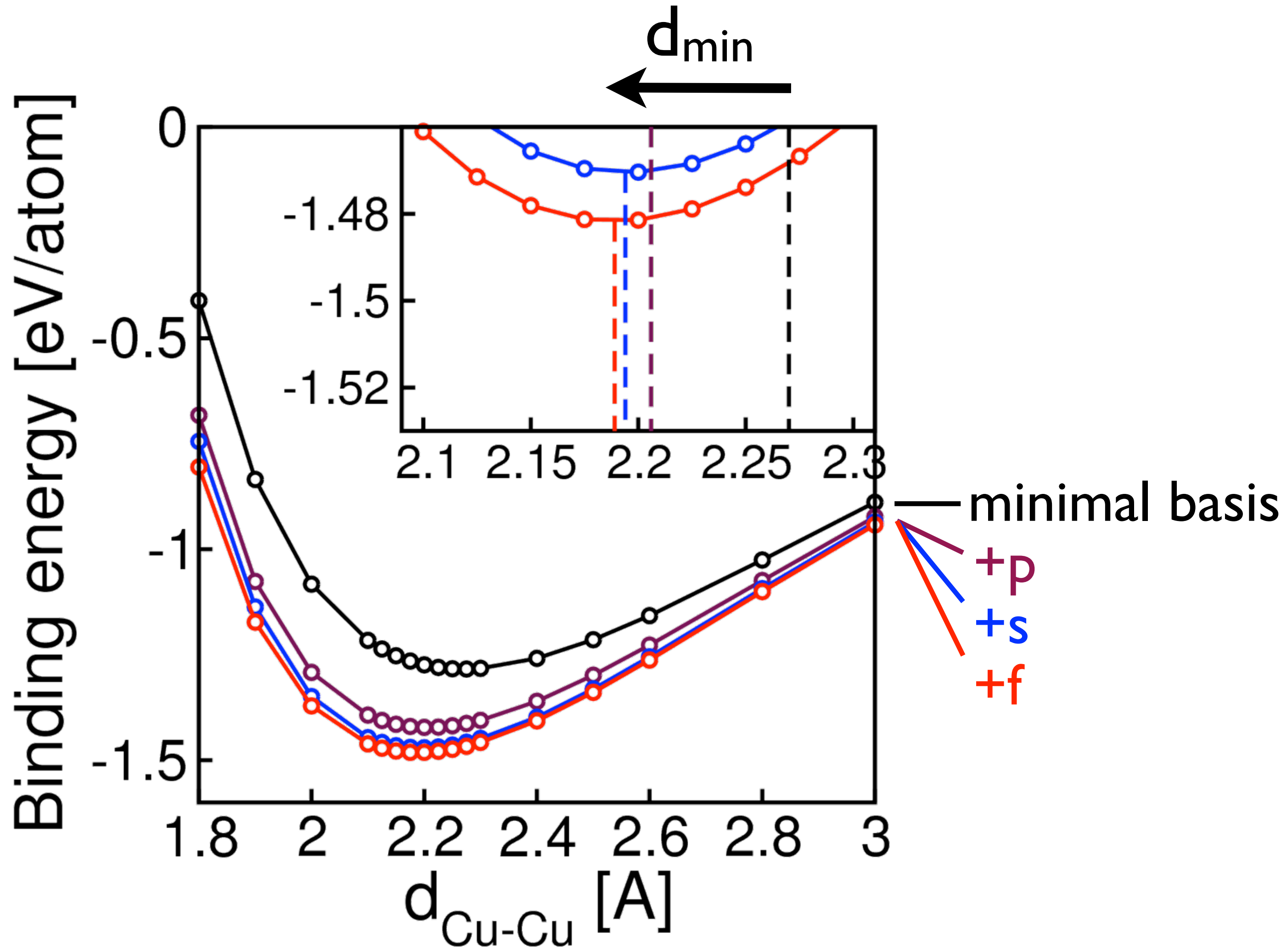

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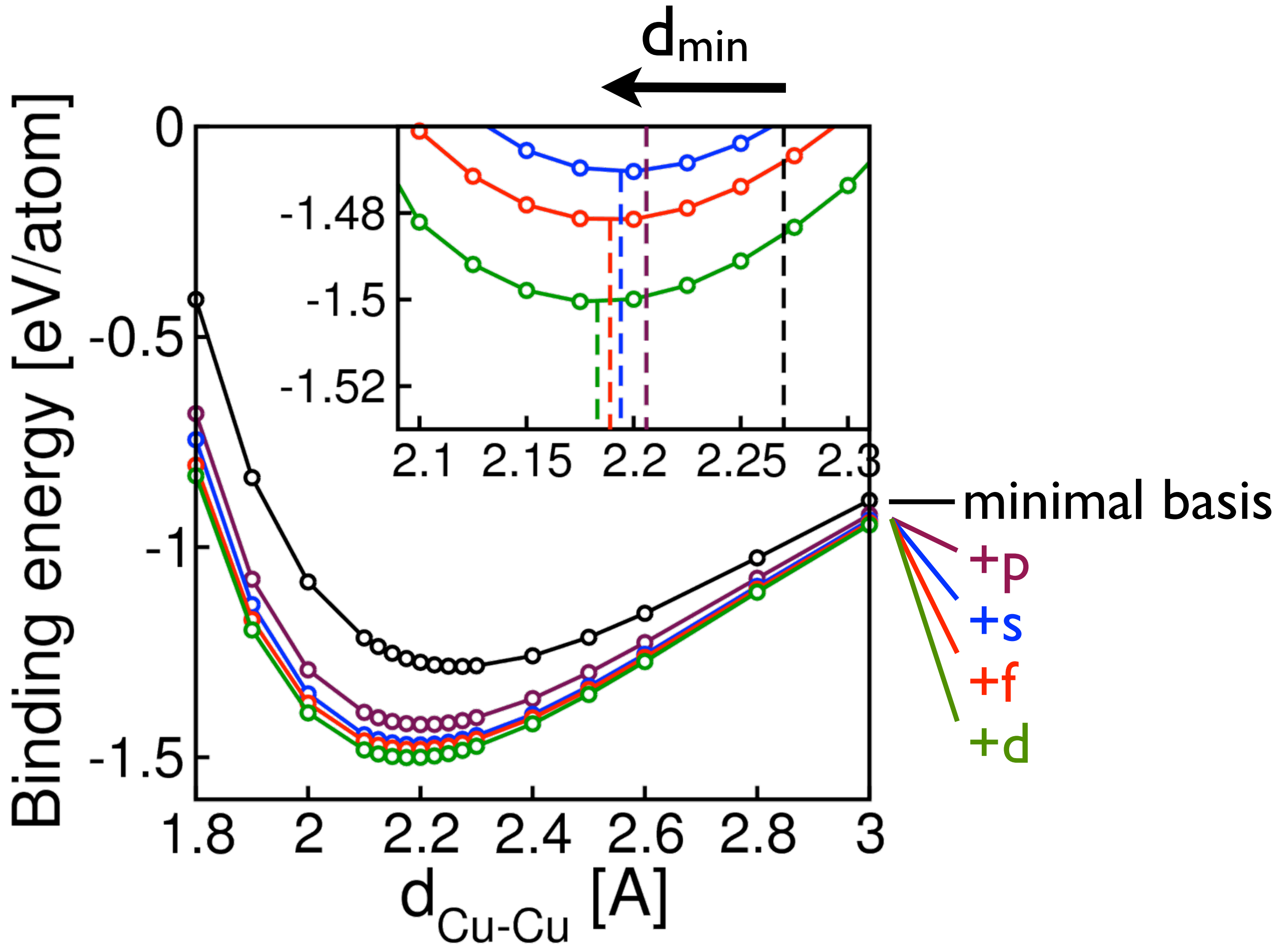

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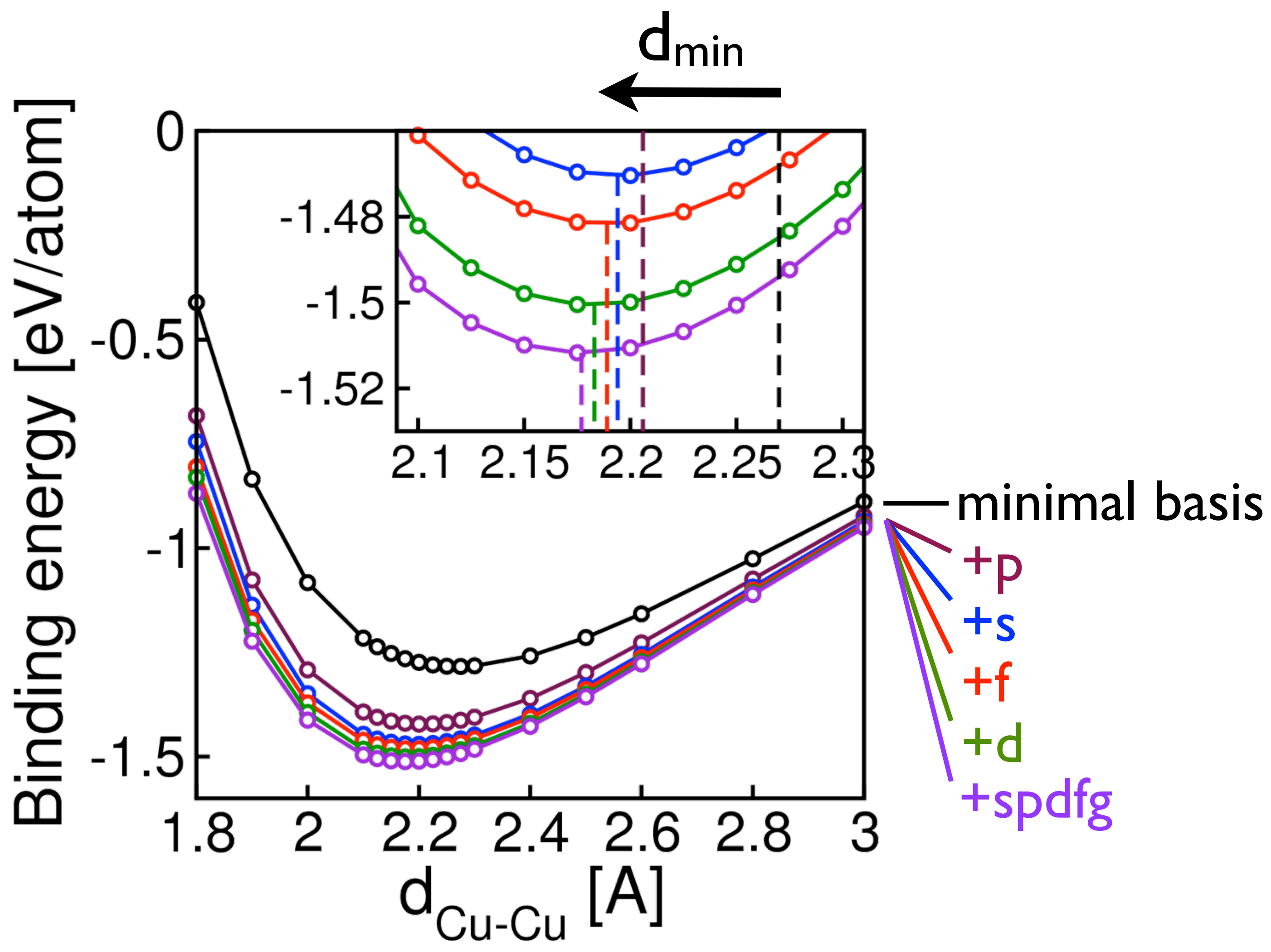

- Increasing basis set: clear drift of d$_{min}$ towards smaller values

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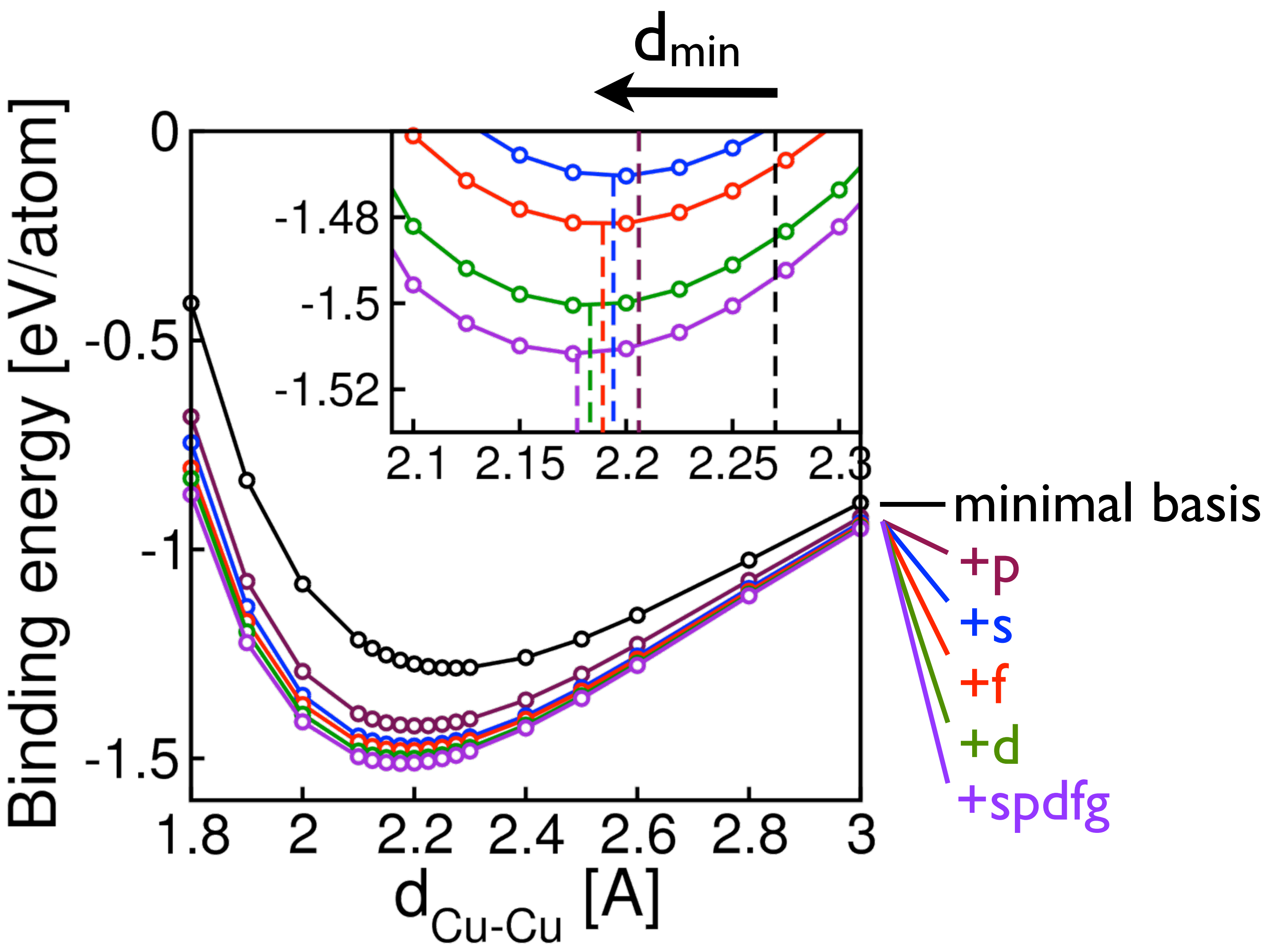

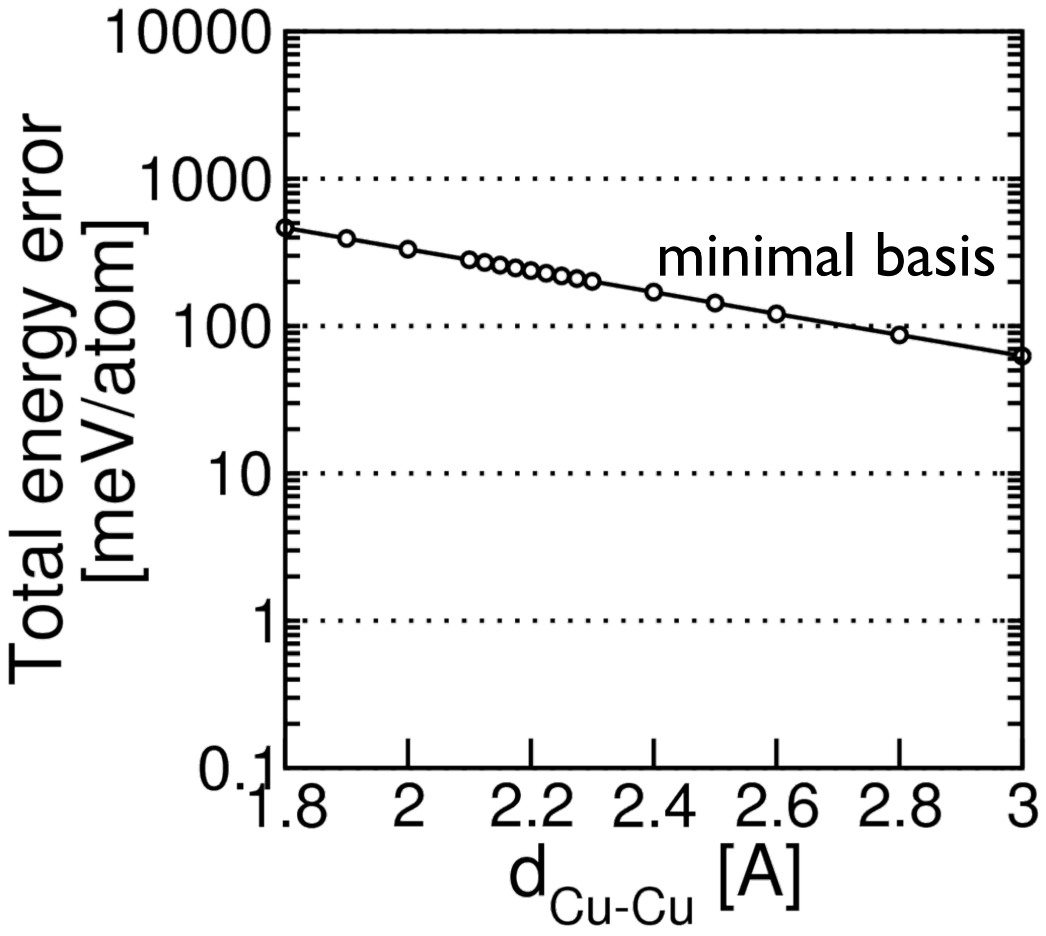

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- Reason: Minimal basis → exponential basis set error as function of d

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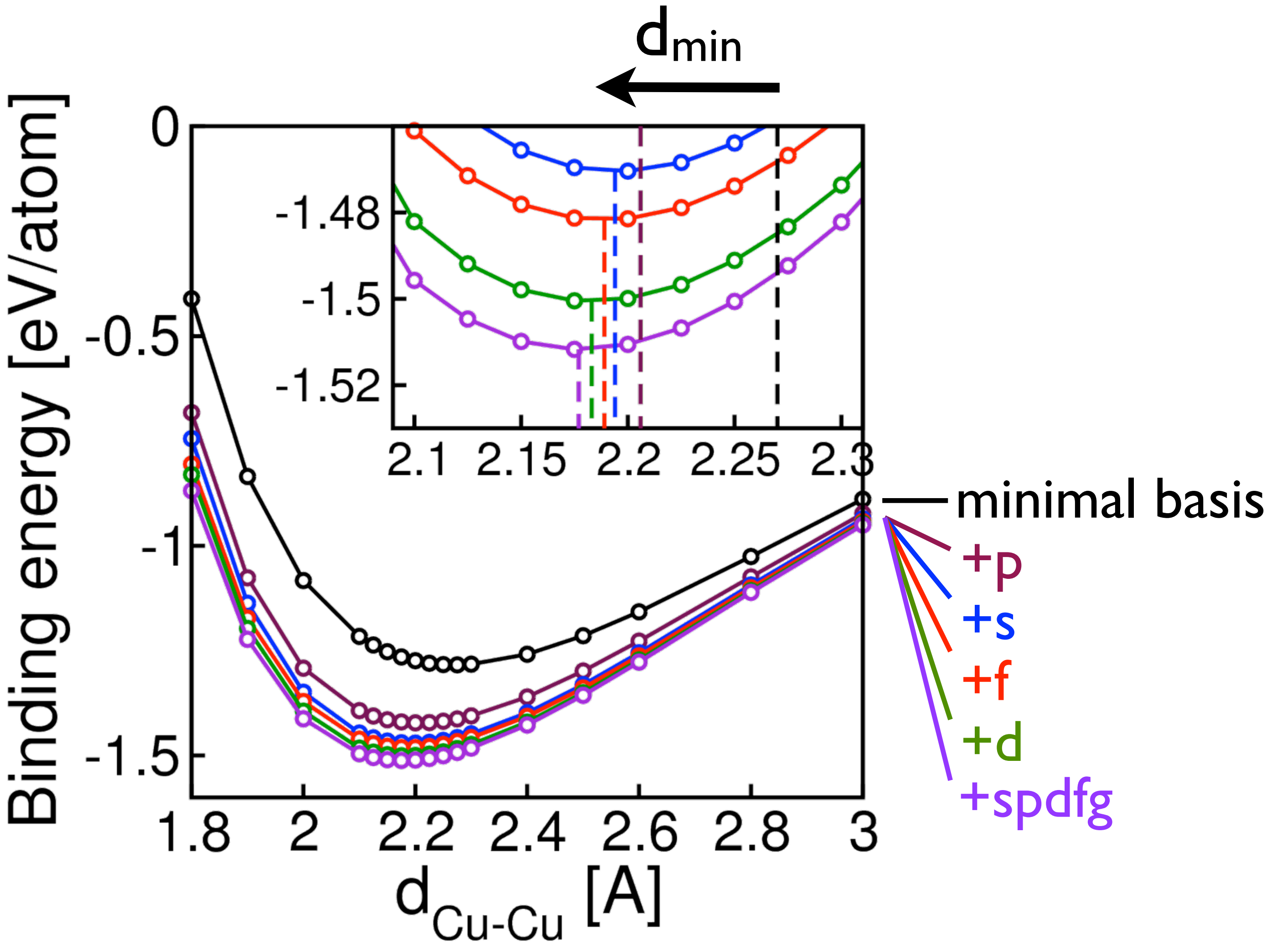
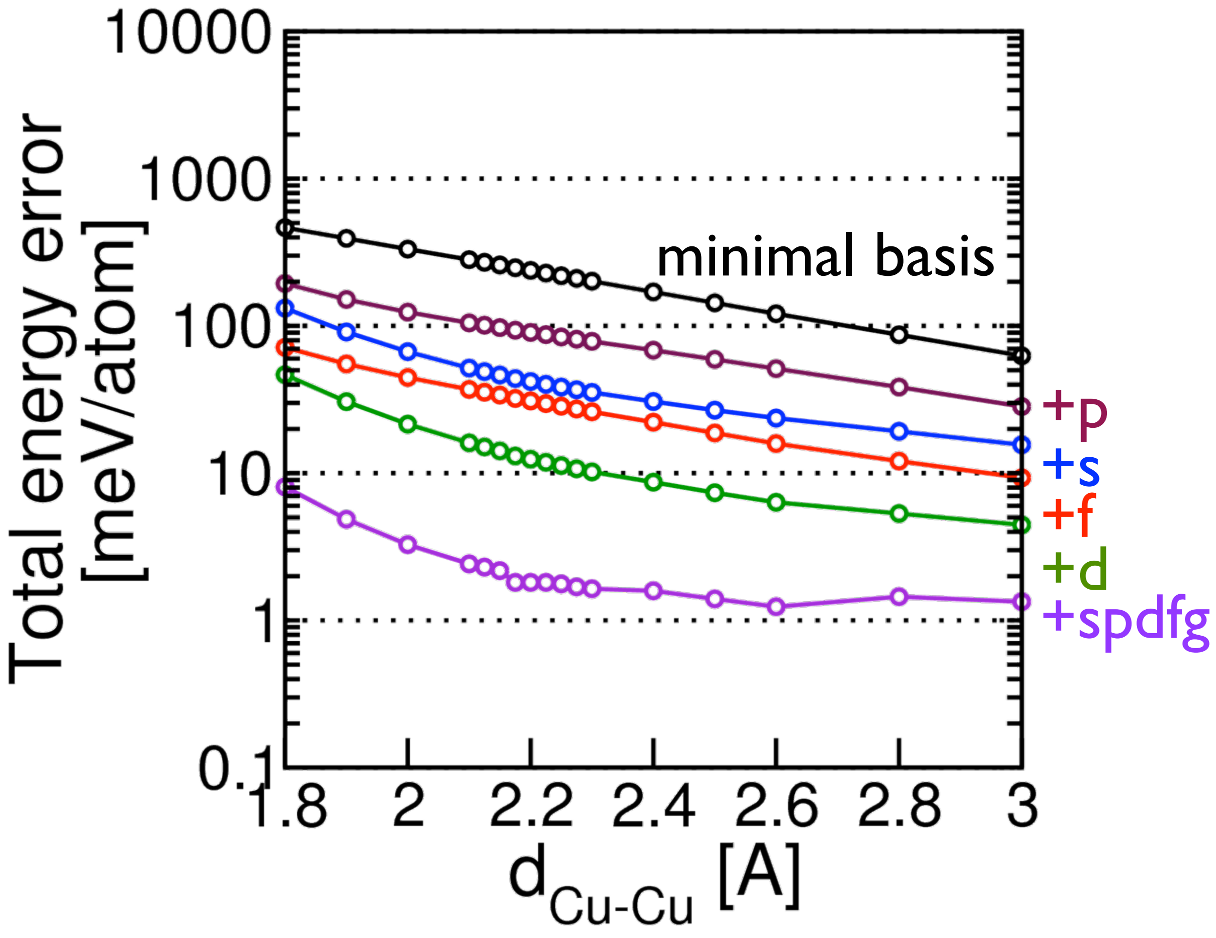
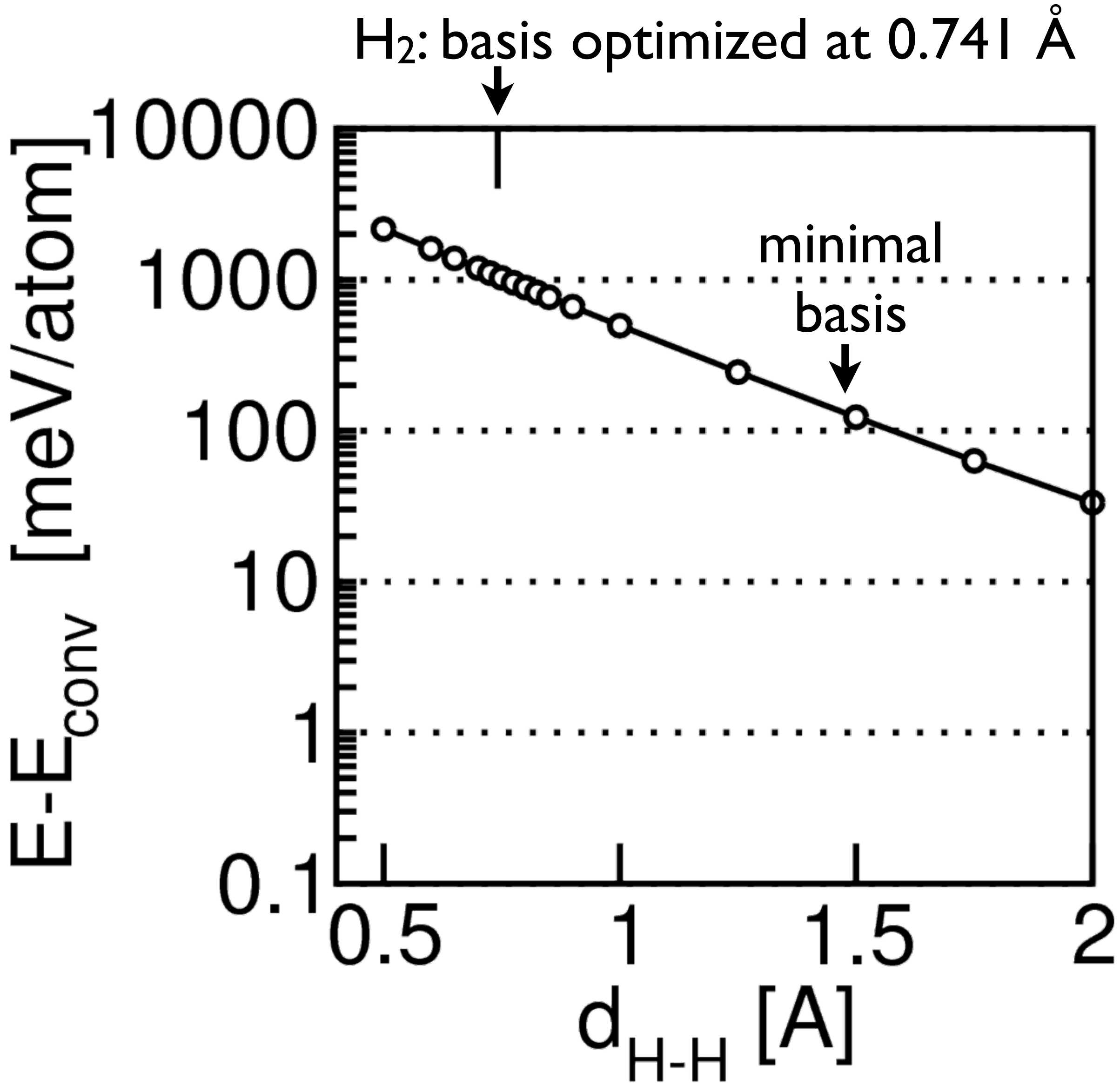




- Increasing basis set: clear drift of d_{min} towards smaller values
- Minimal basis → exponential basis set error as function of d
- meV-level accuracy for practical basis sets; small d require larger basis

Dimer binding curves to optimize the basis

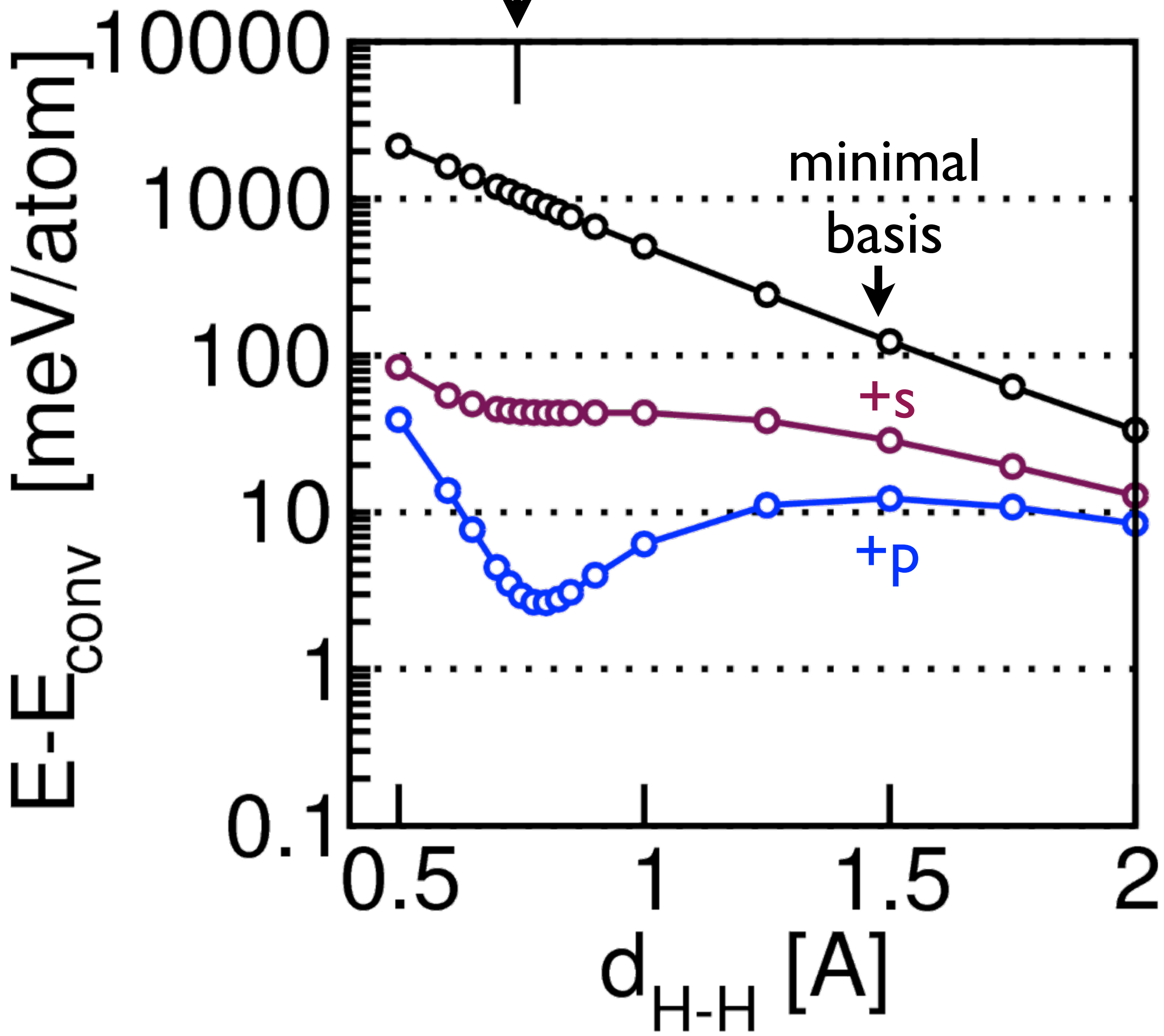
Extreme example: H_2 (only one occupied orbital)



Dimer binding curves to optimize the basis

Extreme example: H_2 (only one occupied orbital)

H_2: basis optimized at 0.741 Å



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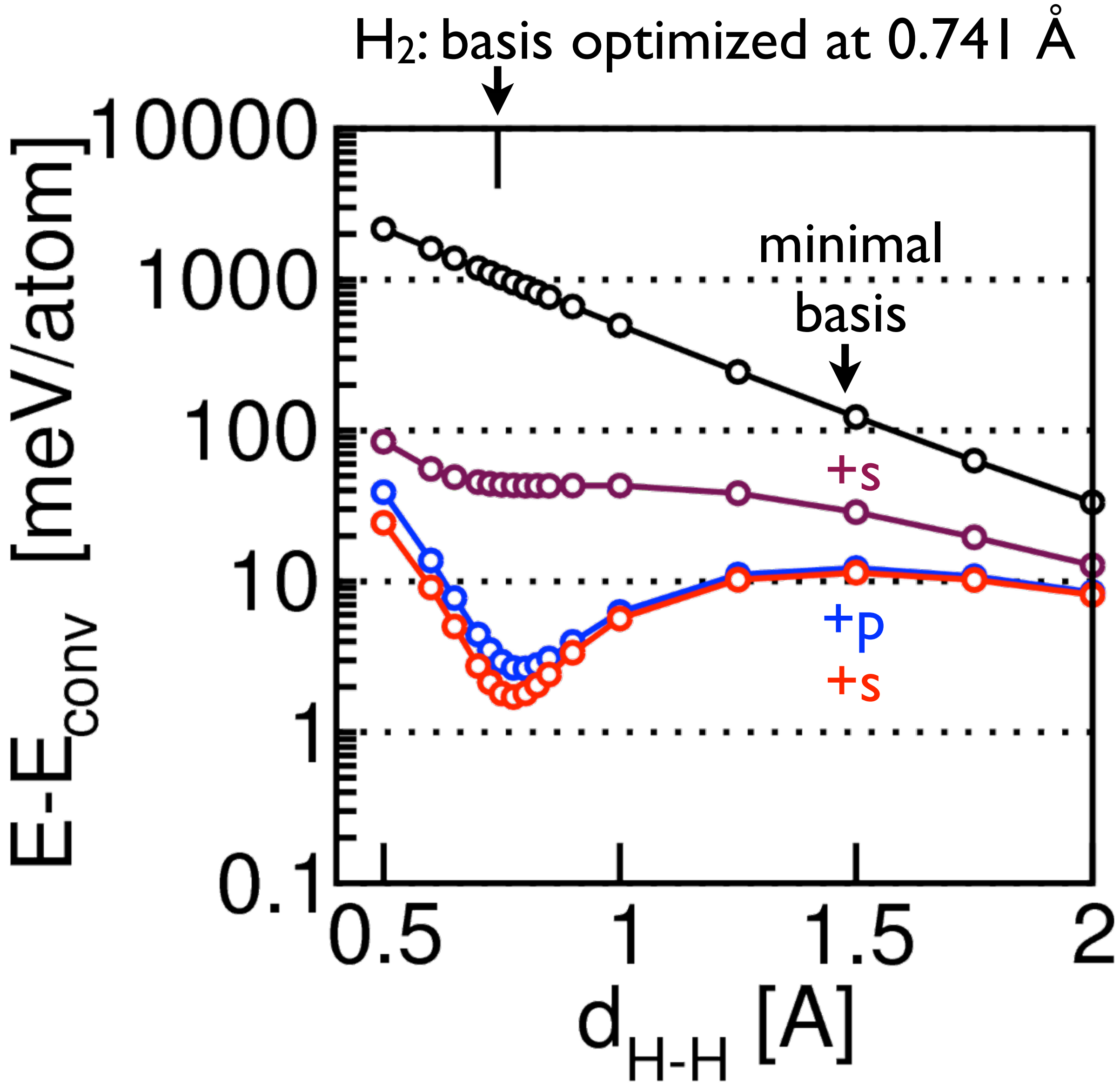

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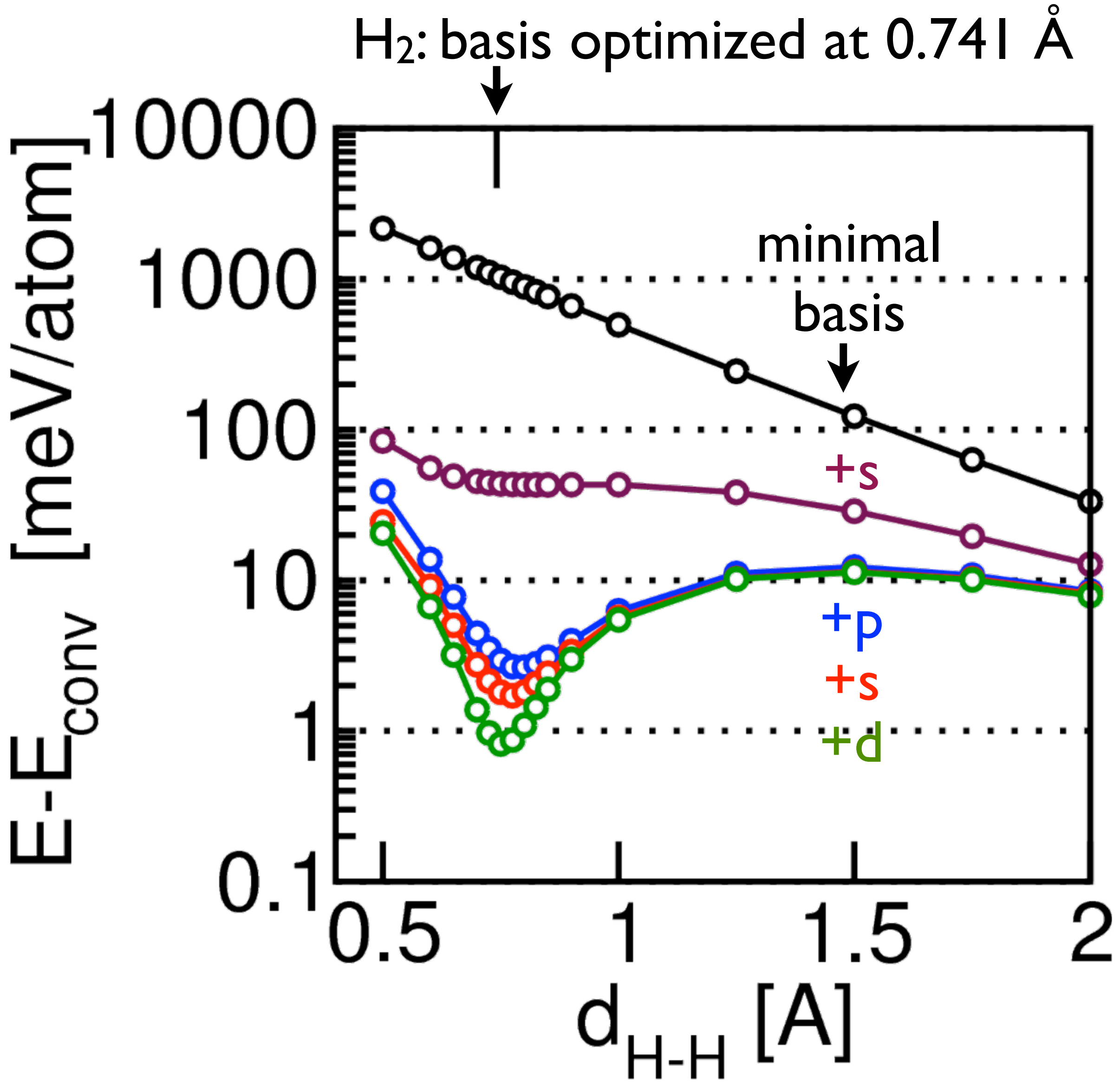

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Basis optimization for single geometry not enough!

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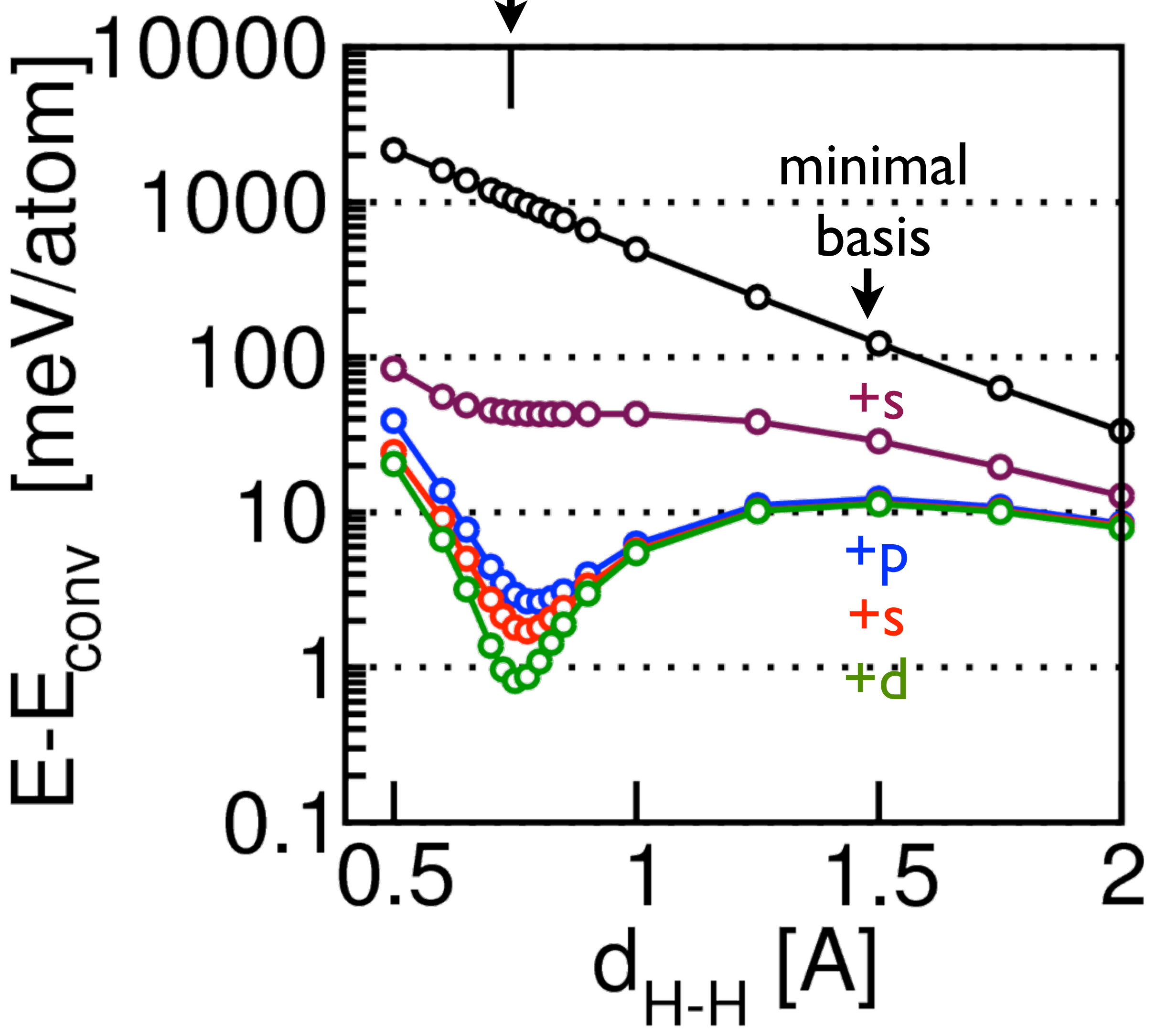
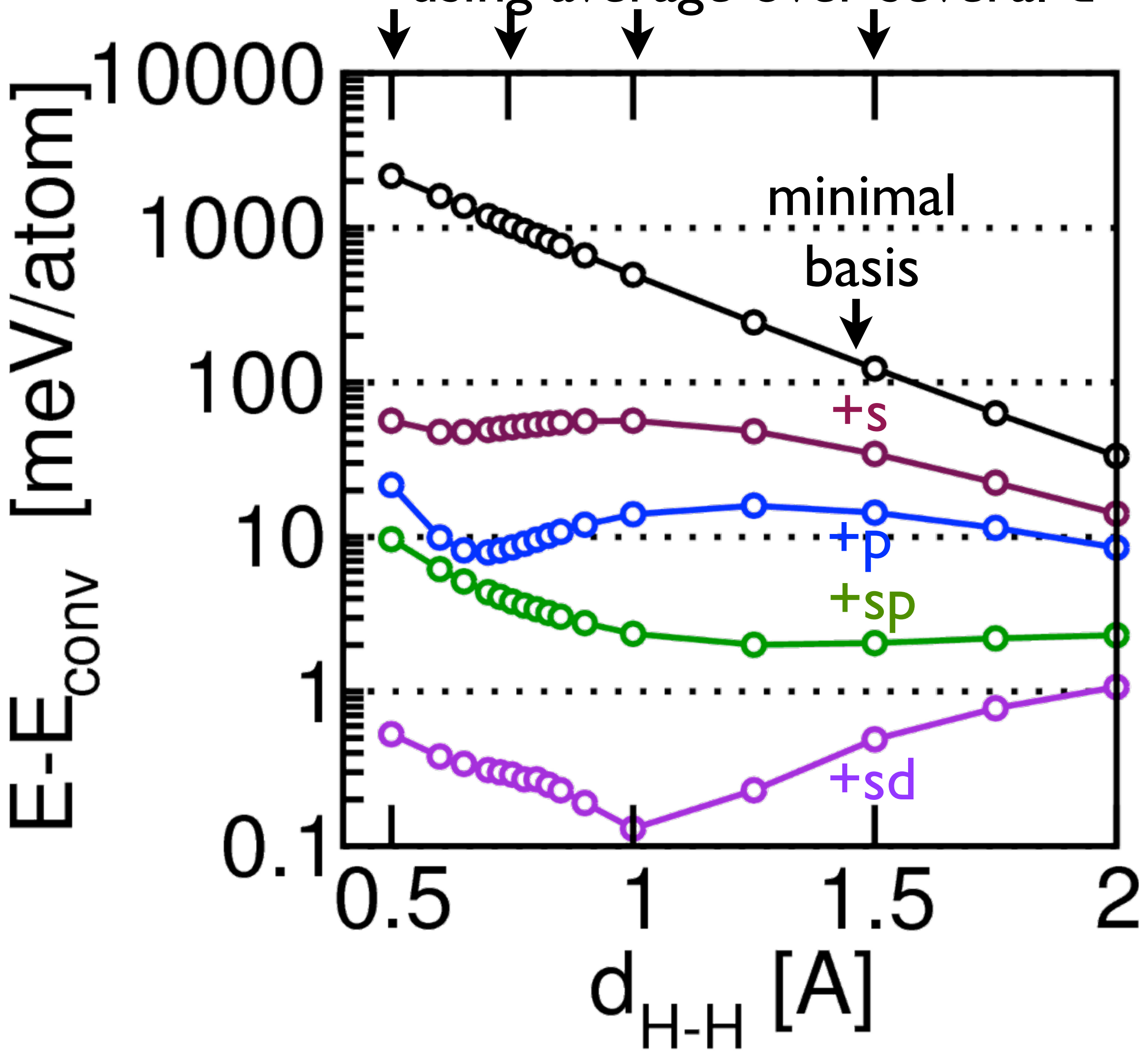


H_2: basis optimized using average over several d



Light elements (particularly H):

Basis optimization for single geometry not enough!

Robust basis construction:

Optimize average of several dimer bond distances

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: T*otal energy* convergence

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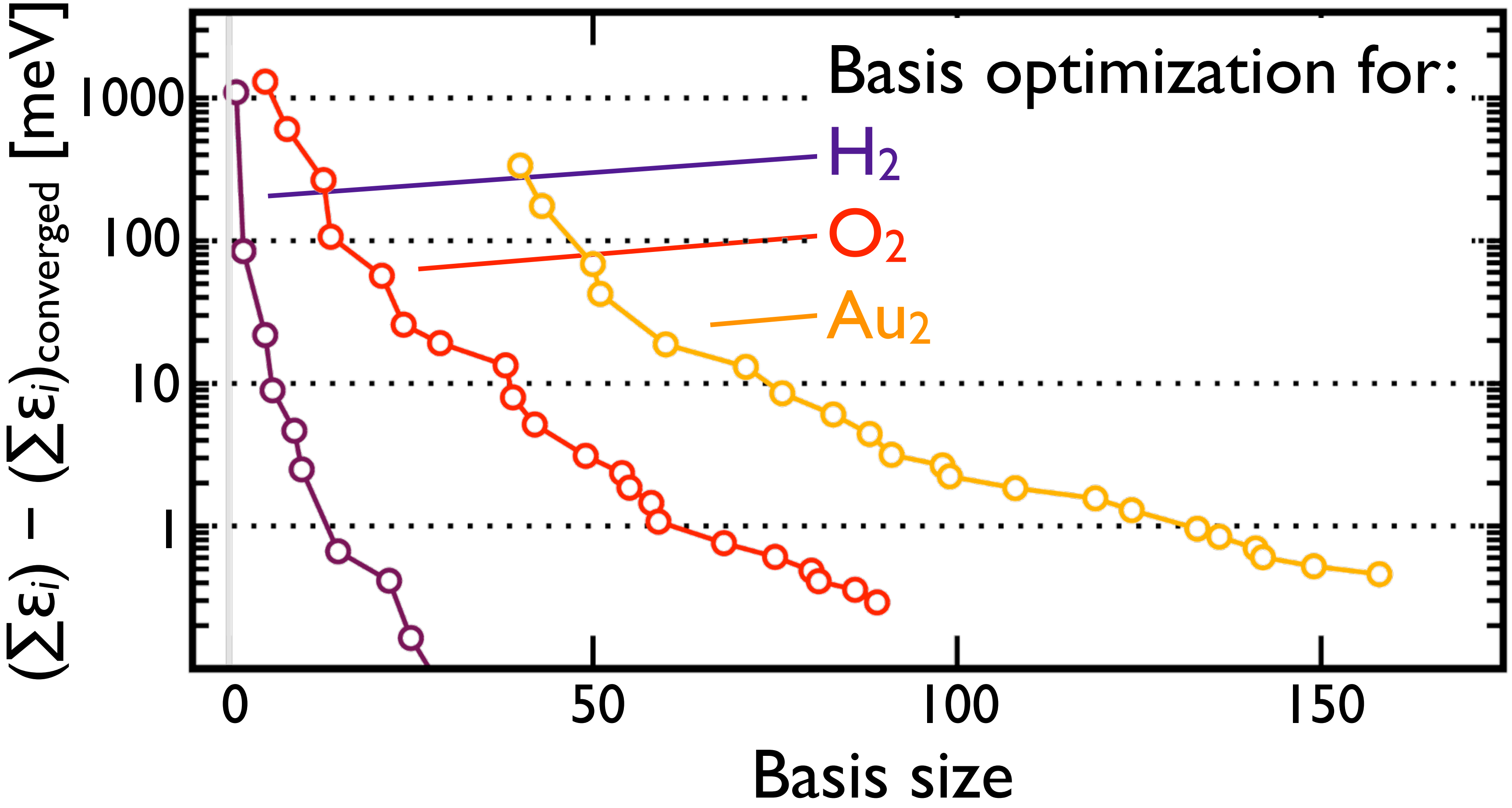


In practice: Hierarchical basis set library for all elements

	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*

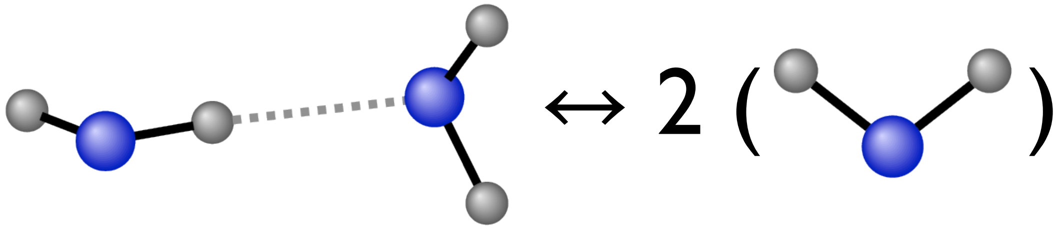
"First tier"

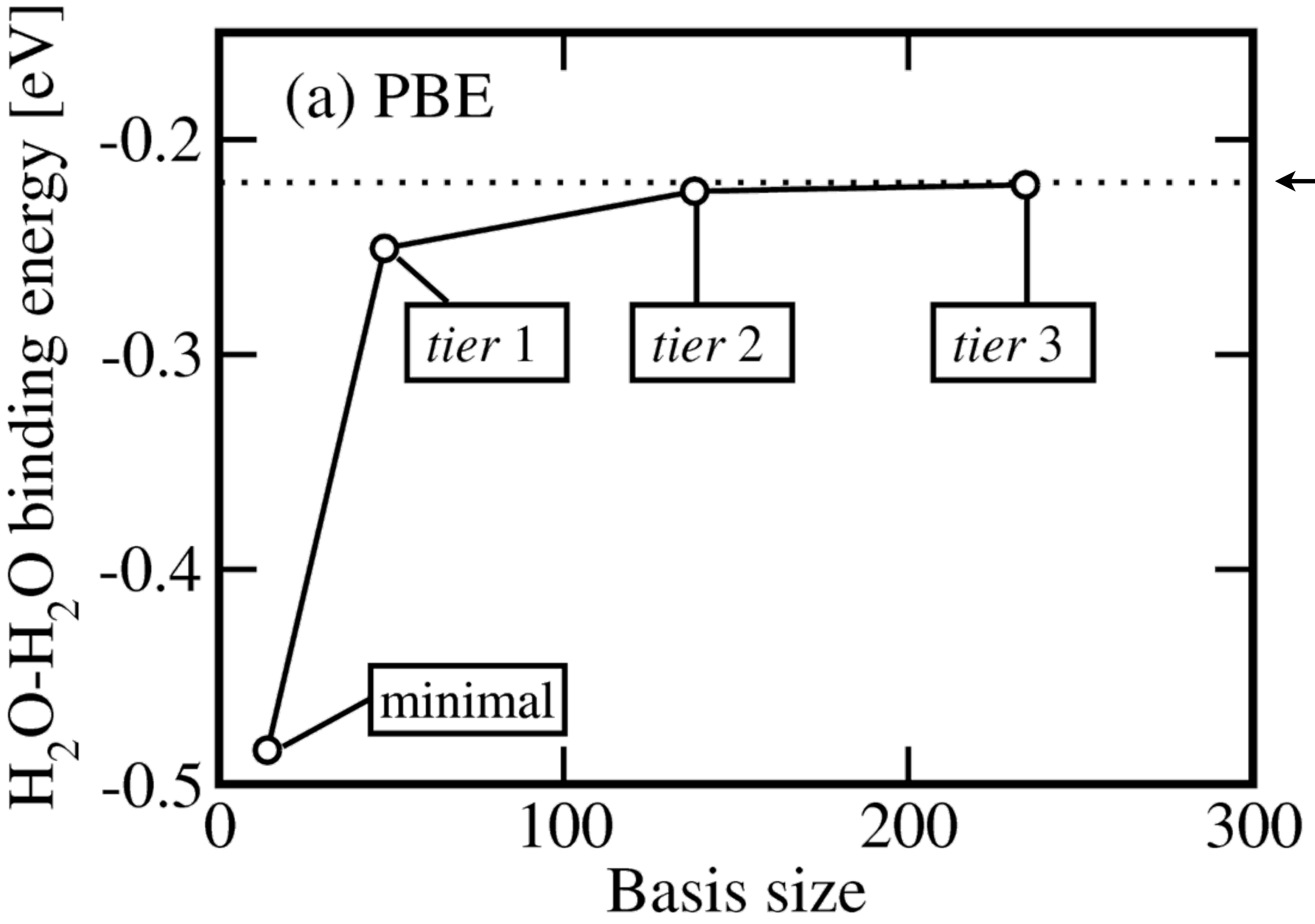
"Second tier"

"Third tier"

...

Transferability: $(H_2O)_2$ hydrogen bond energy ...





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

... conformational energy hierarchy, large molecules ...

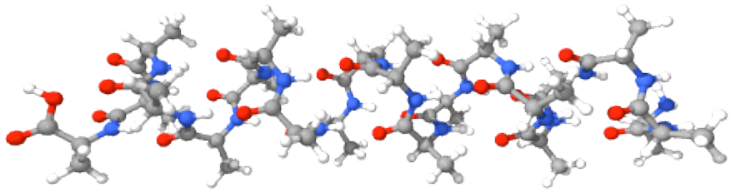
Ala$_{20}$ - fully extended structure

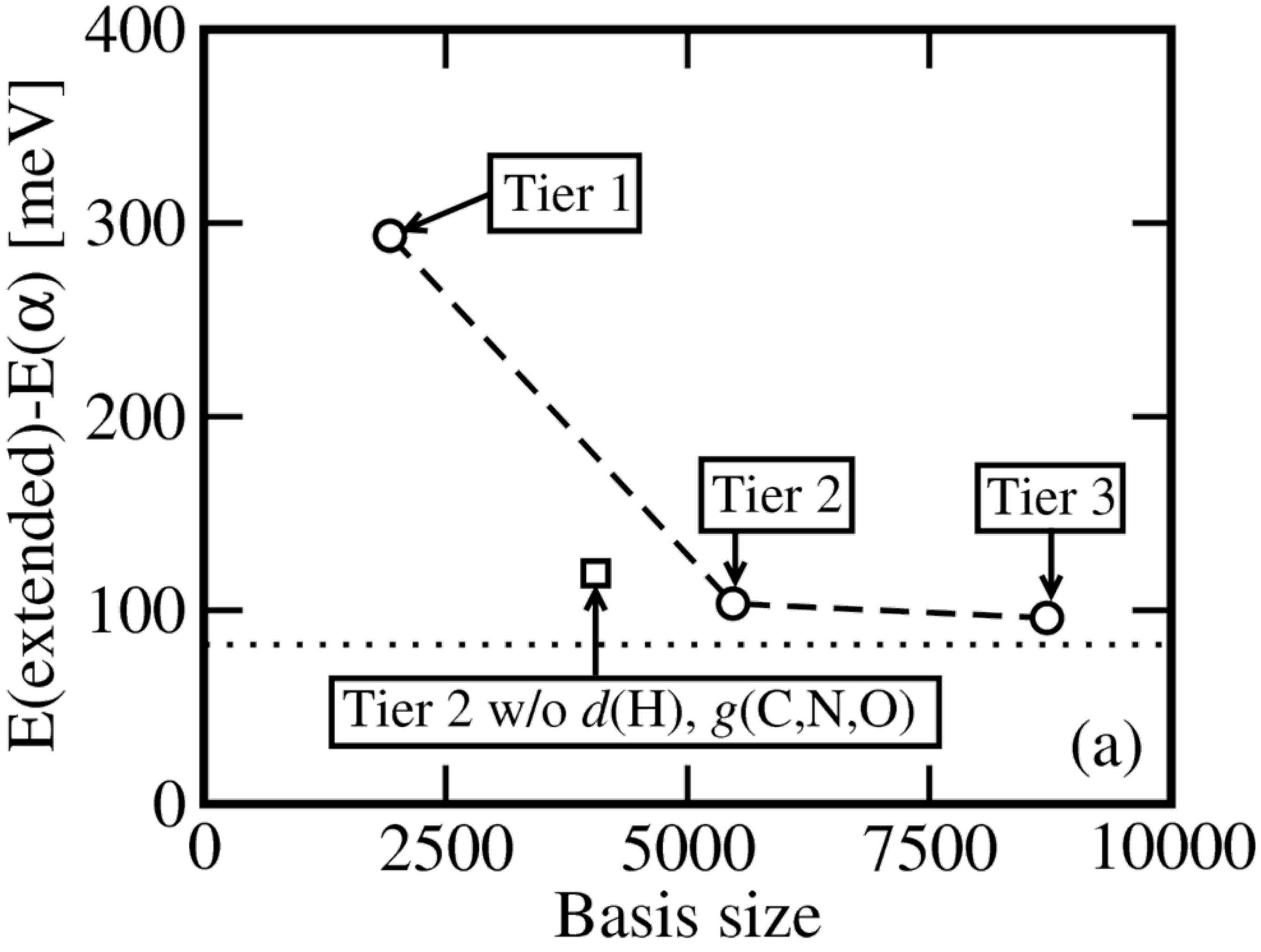
203 atoms

⟷

ΔE=0.08 eV

Ala$_{20}$ - α helix





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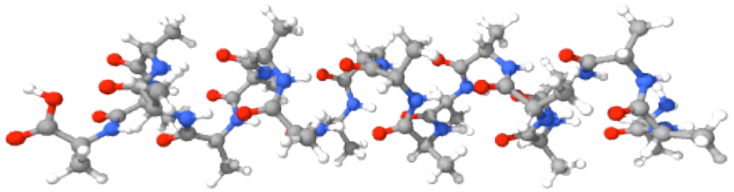
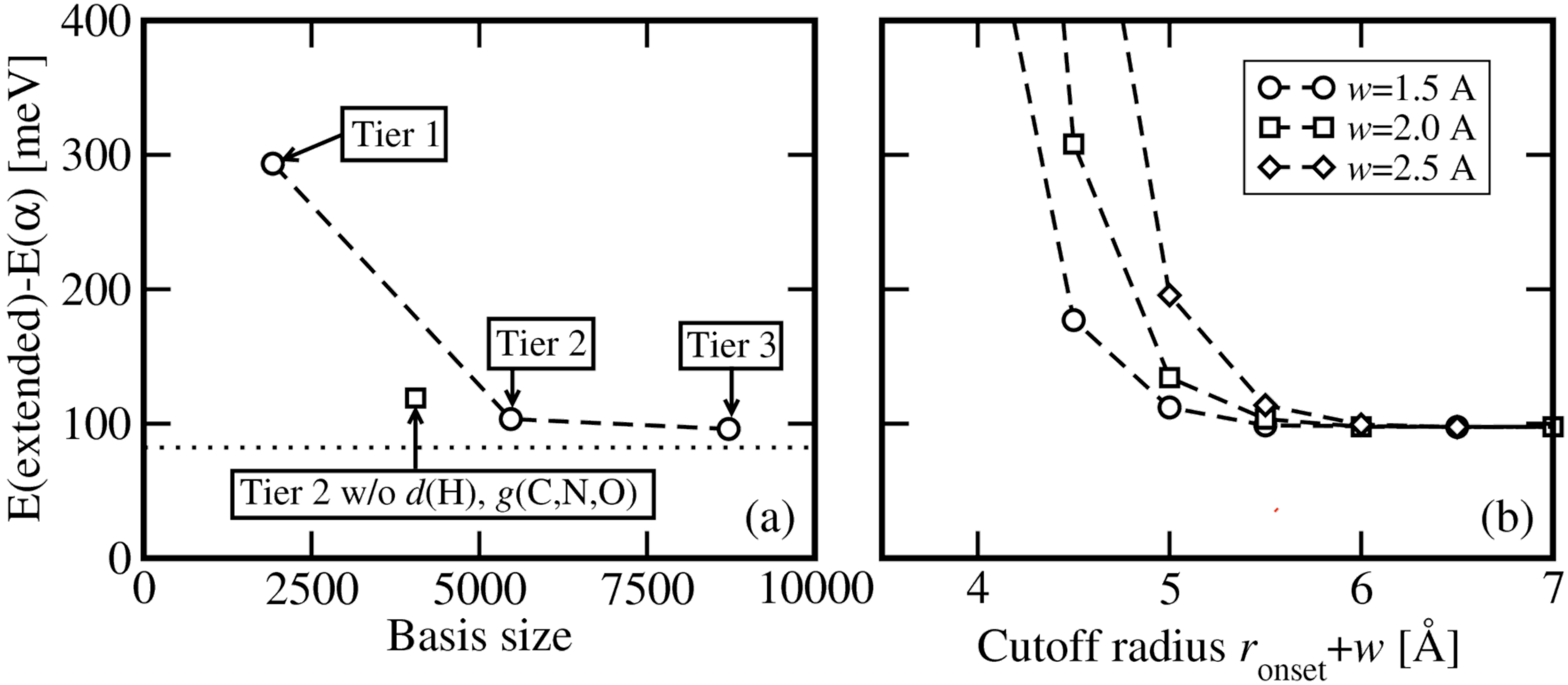




... periodic hybrid functionals ...

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

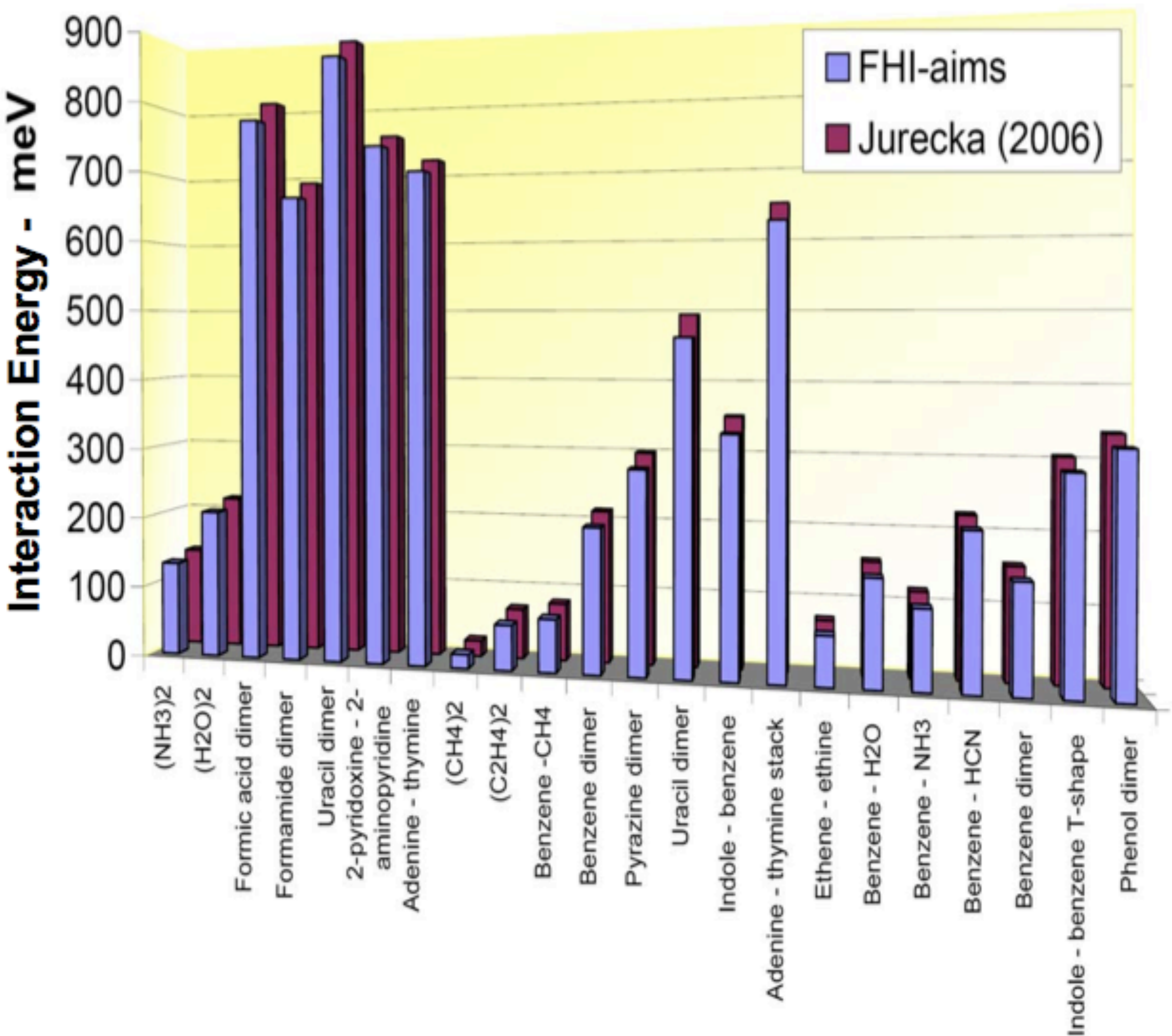
[1] J. Paier *et al.*, J. Chem. Phys. **124**, 154709 (2006).

[2] J. Paier *et al.*, J. Chem. Phys. **125**, 249901 (2006).

[3] A. Stroppa *et al.*, PRB **83**, 085201 (2011).

... and many-body perturbation theory - MP2, RPA, *GW*

*Ren, Rinke, Blum, Wieferink, Tkatchenko, Sanfilippo, Reuter, Scheffler, NJP **14**, 053020 (2012)*



NAO basis set:
CNO: min.+3*s*3*p*3*d*1*f*
H: min.+4*s*3*p*2*d*

Resolution of identity
for Coulomb operator

→ recover CBS limit
within 5%!

Perturbation theory:
Counterpoise correction
ESSENTIAL
for MP2, RPA

MP2: Complete basis set limit benchmark set "S22":
Jurecka et al., Phys. Chem. Chem. Phys 8, 1985 (2006)

So where are we at?

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- Sound, accurate basis sets, elements 1-102

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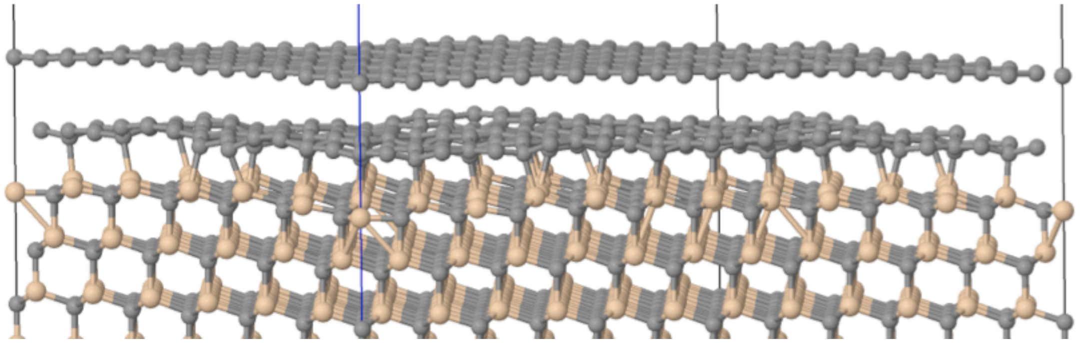
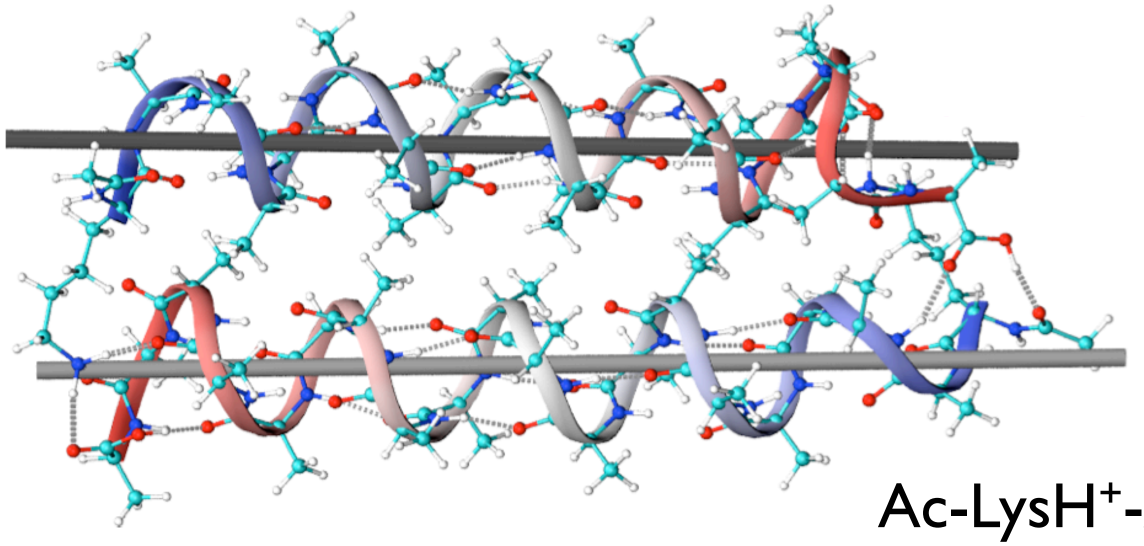
Scalability: Real systems (Kohn-Sham DFT)



SiC(111)-(6√3x6√3) graphene-like monolayer
(216-338 atoms/layer ... want >2000 atoms total)



Ac-LysH$^+$-Ala$_{19}$
dimerized peptide

<u>What we would like to do routinely:</u>

- 1,000s of atoms, light or heavy
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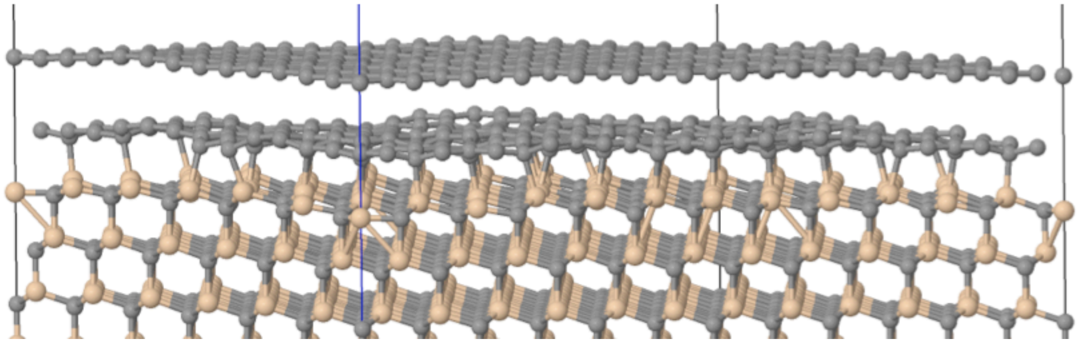

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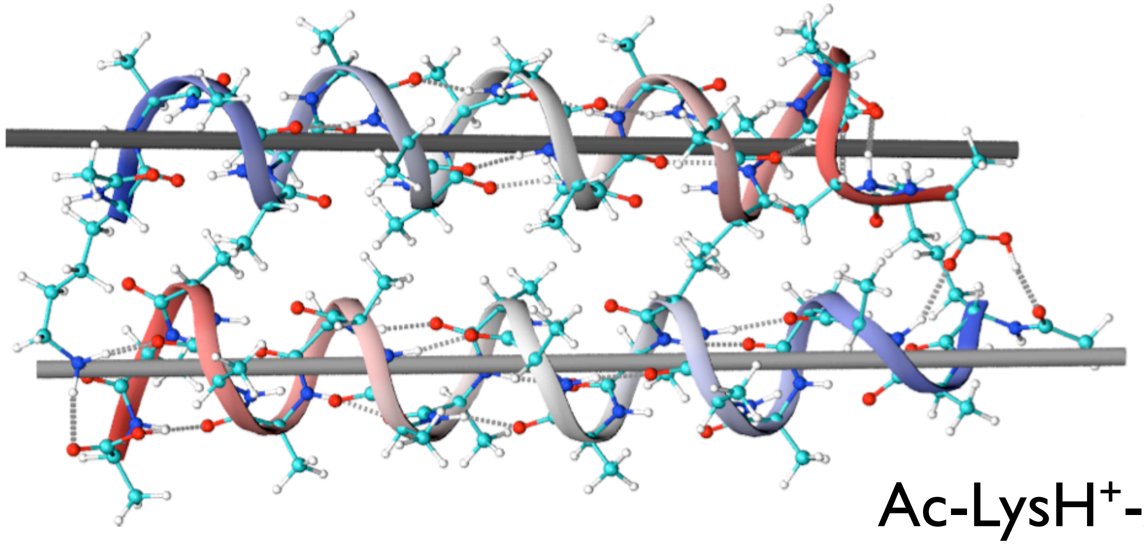

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... and we have (now!) large computers:

IBM BlueGene (MPG, Garching)
16384 CPU cores

Where does the time go? (Kohn-Sham DFT)

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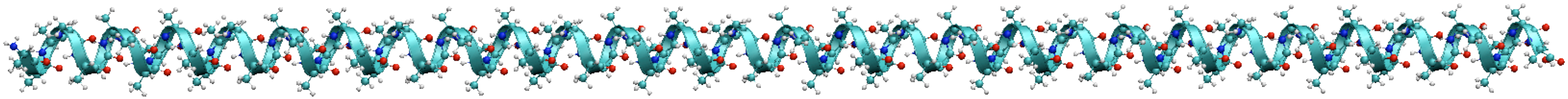

α-helical Ala$_{100}$ (1000 atoms),
high accuracy, DFT-PBE

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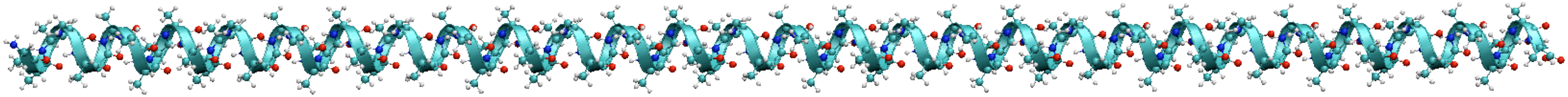

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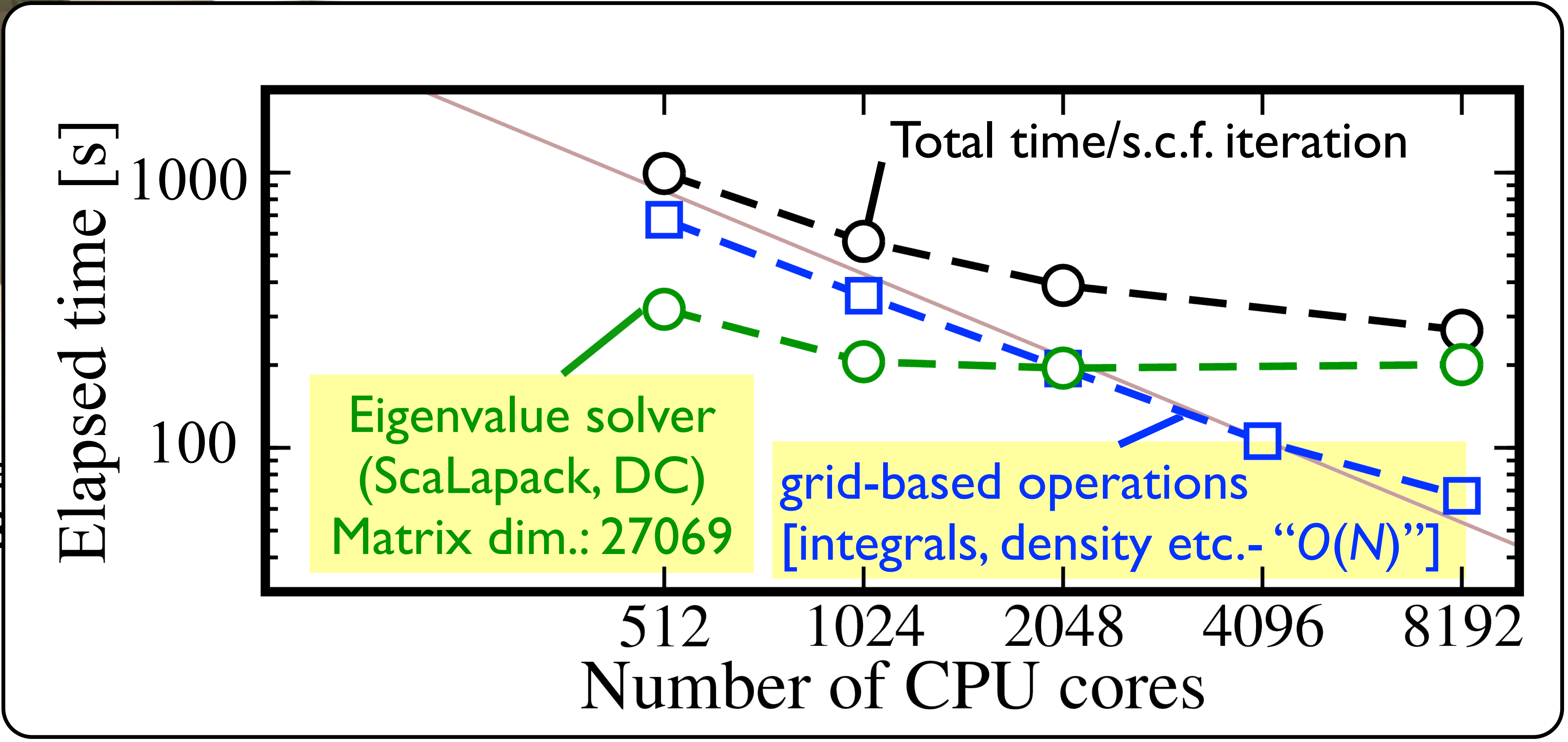
IBM BlueGe
1638



Taking apart the eigenproblem

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

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

Data: (2008)

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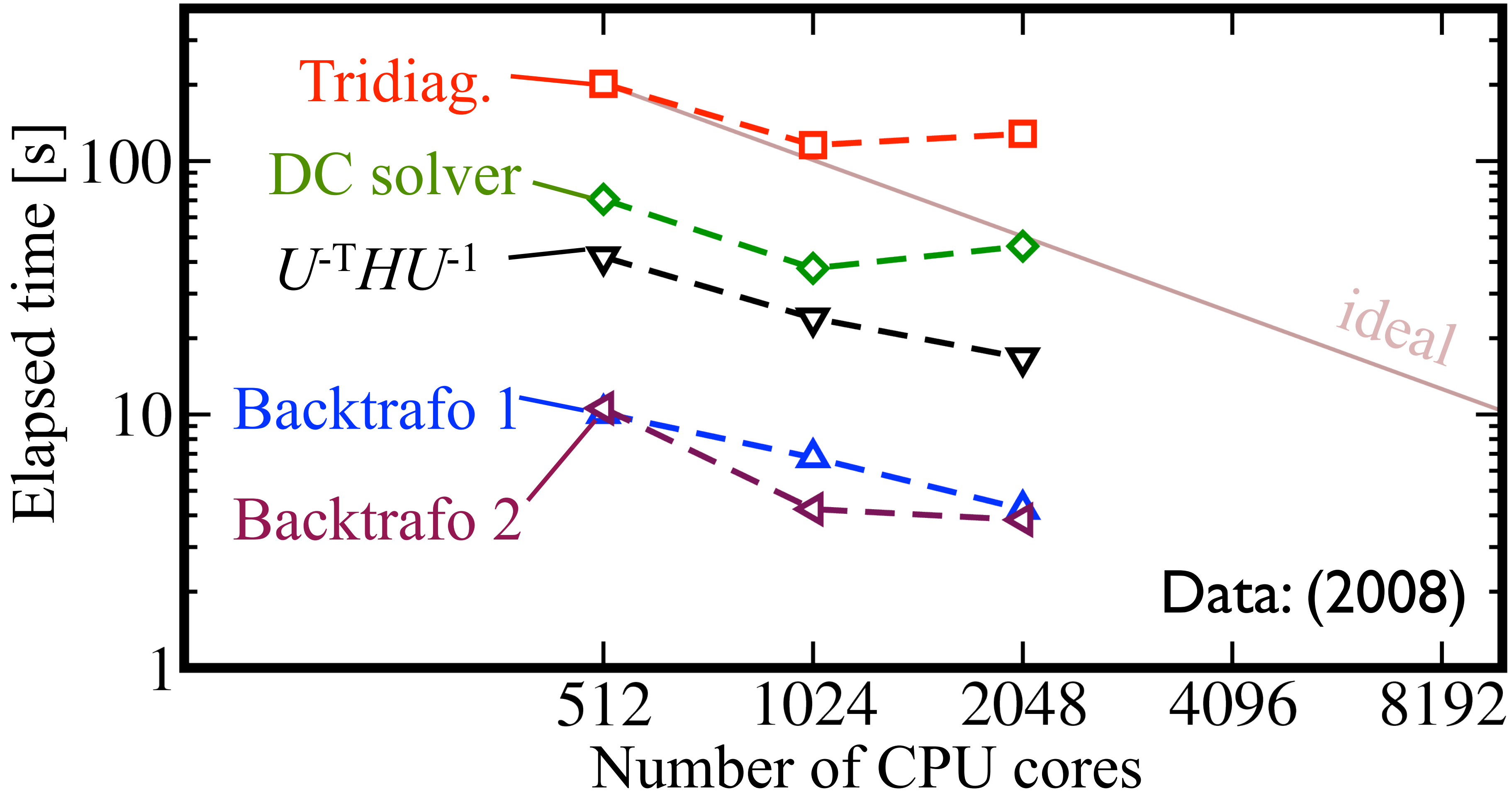


α-helical Polyalanine Ala_{100}, BlueGene/P

Significant improvement: “ELPA” library

http://elpa.rzg.mpg.de
http://elpa-lib.fhi-berlin.mpg.de

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

“EigensoLver for Petaflop Applications”

- “Drop-in enhancement” for ScaLapack solution (same layout)
- Rewrite of all communication, data handling etc. from scratch (retain only serial BLAS, Lapack)
- LGPL license - free to use with open or closed codes as long as modifications to ELPA library itself are open

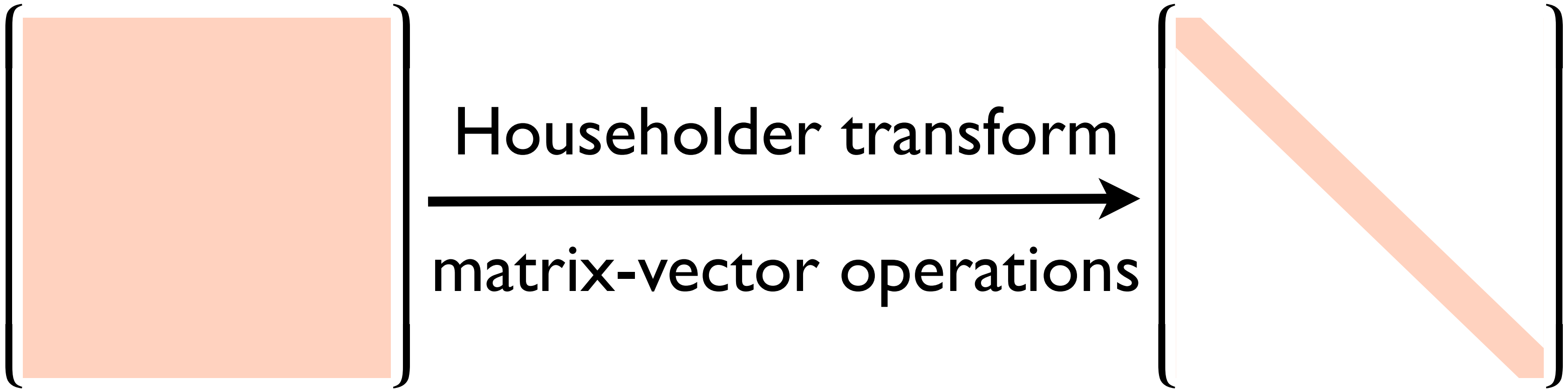
ELPA

German Ministry for Research and Education (BMBF) funded consortium, 2008-2011:
Garching Computing Center (Max Planck Society); Fritz Haber Institute;
Wuppertal University; Technical University Munich; MPI Mathematics in Science; IBM

Example: Reduction to tridiagonal form (just linear algebra)

Chief bottleneck: Tridiagonalization

“Conventional” reduction:



Householder transform

matrix-vector operations

full matrix

tridiagonal matrix

Example: Reduction to tridiagonal form (just linear algebra)

Chief bottleneck: Tridiagonalization

"Two-step" reduction:
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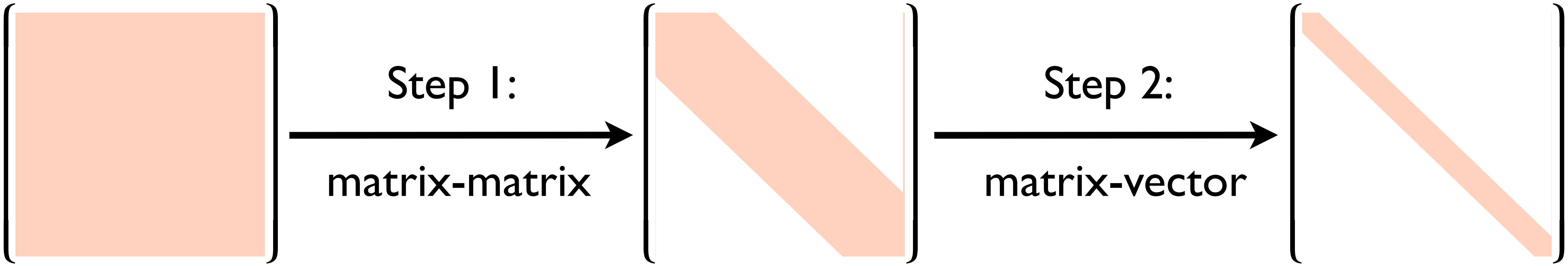

Step 1:

matrix-matrix

Step 2:

matrix-vector

full matrix

band matrix

tridiagonal matrix

Auckenthaler, Blum, Bungartz, Huckle, Johanni, Krämer, Lang, Lederer, Willems,
Parallel Computing ***37****, 783-794 (2011).*

Example: Reduction to tridiagonal form (just linear algebra)

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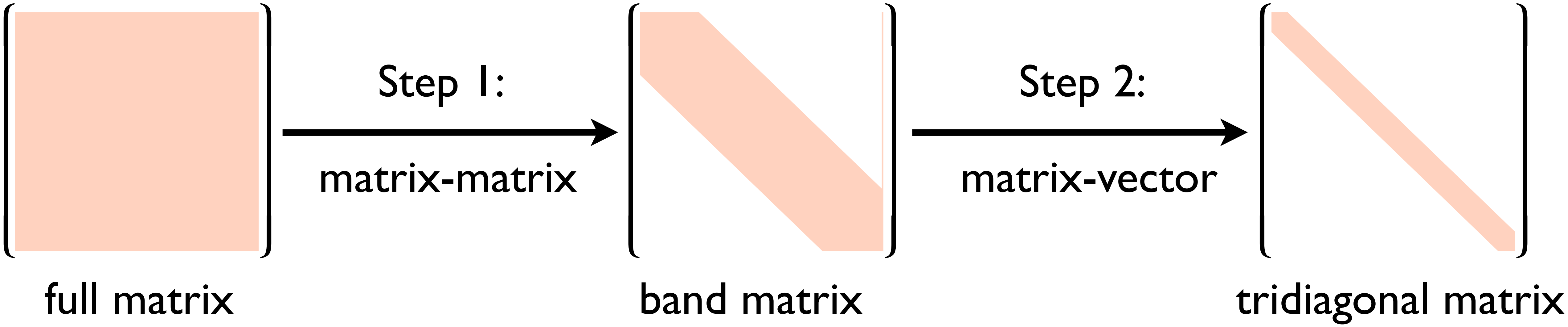


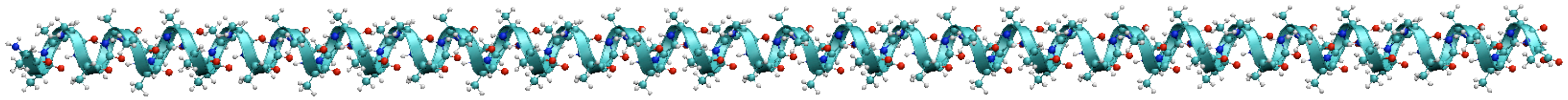
Need two eigenvector backtransformation steps instead of one

- Heavily optimized backtransform for eigenvectors (adaptive data layout, architecture-specific linear algebra kernels) to offset overhead

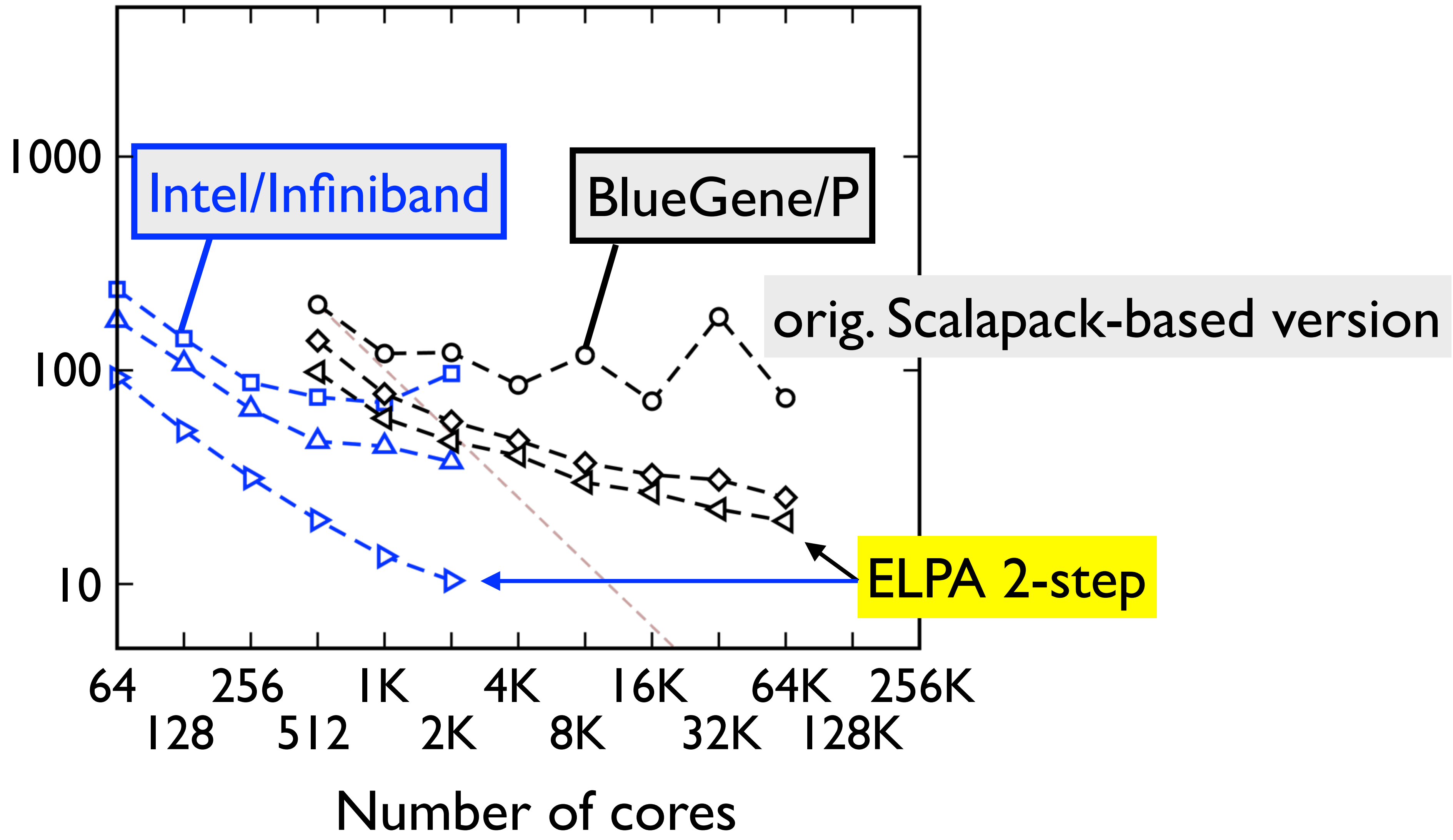
Auckenthaler, Blum, Bungartz, Huckle, Johanni, Krämer, Lang, Lederer, Willems,
Parallel Computing ***37****, 783-794 (2011).*

Our experience: Significant improvement

Open source (LGPL): http://elpa.rzg.mpg.de



α-helical Polyalanine Ala$_{100}$
Matrix: 27069, *States:* 3410



Intel/Infiniband

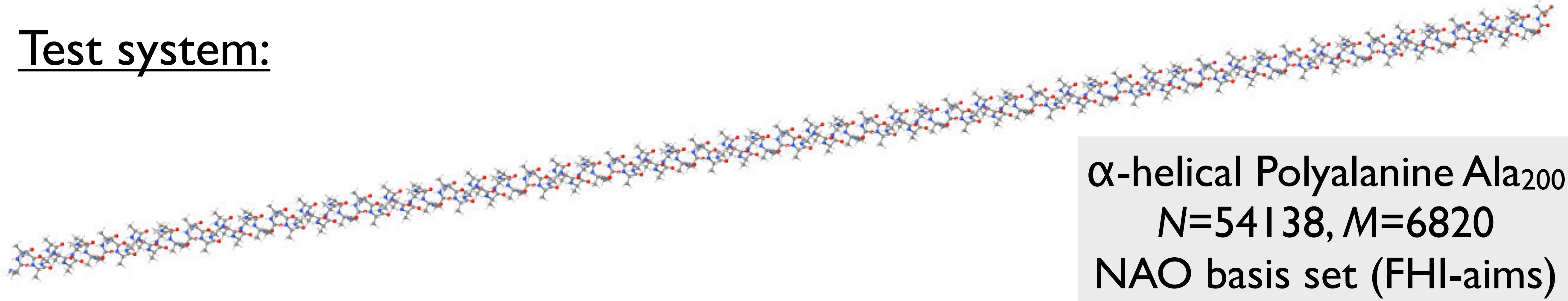
BlueGene/P

orig. Scalapack-based version

ELPA 2-step

... so what about that "petascale"?

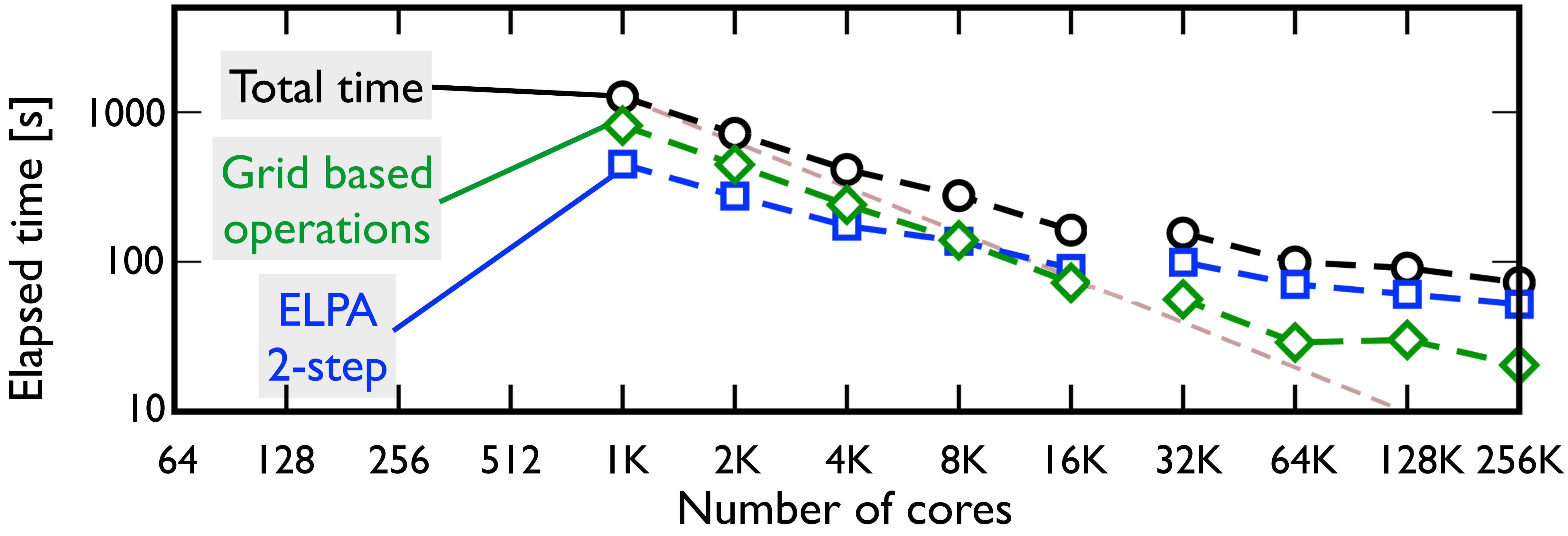
Test system:



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

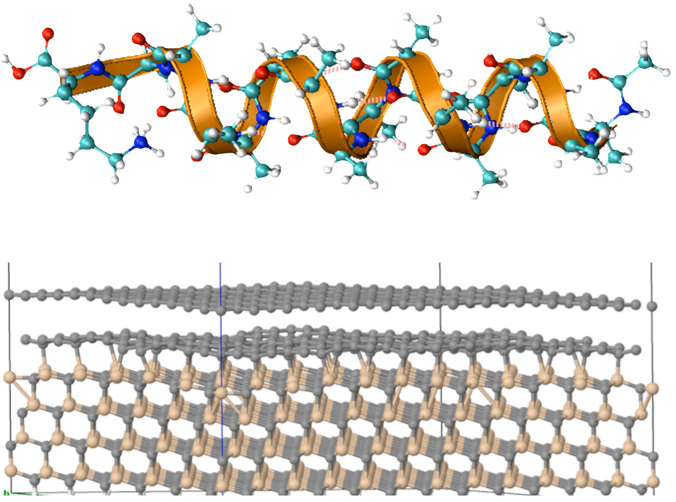
Timings: A. Marek, R. Johanni, Rechenzentrum Garching



Outline

An approach to all-electron "density functional theory and beyond": FHI-aims [1]

- Numeric atom-centered (localized) basis sets
- Scalability (1,000s of atoms, 1(0),000s of CPUs)
- Pushing towards "better" functionals (→P. Rinke)



Where do "we" come from?

- (Bio)molecular structure and spectroscopy
- Nanostructured inorganic surfaces

... and some challenges (towards WDM)

[1] The Fritz Haber Institute ab initio molecular simulations suite (FHI-aims)
V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler,
Computer Physics Communications ***180****, 2175-2196 (2009) - http://www.fhi-berlin.mpg.de/aims/*

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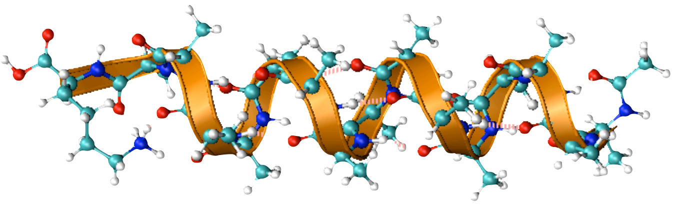

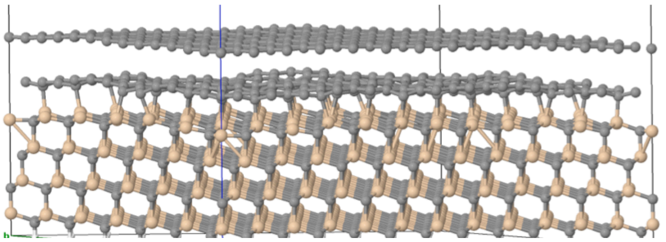

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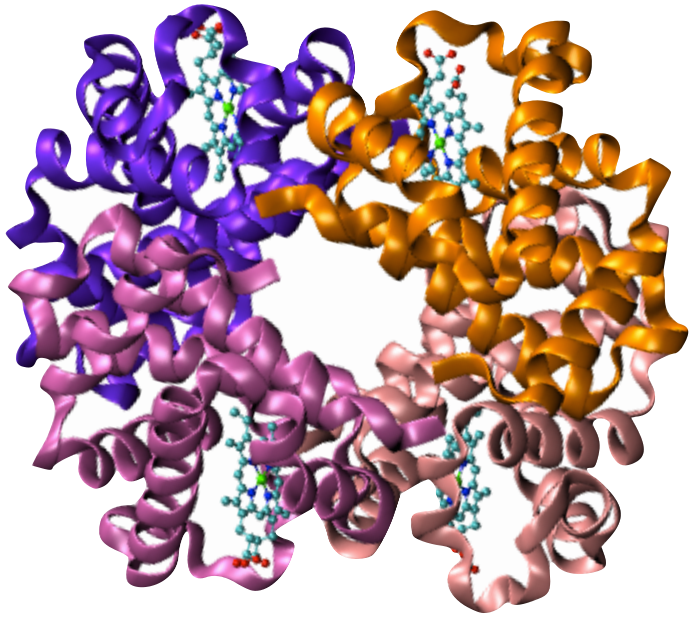
Cold, not so dense world: Biomolecules

- Proteins: macromolecules that perform essential tasks inside living organisms
- ~60.000 different proteins in human organism, several billion per cell.
- *<u>The structure of a protein determines its function!</u>*

  This structure is not random, but tuned by the amino acid sequence.

Hemoglobin



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Typical "building blocks:"
Secondary structure

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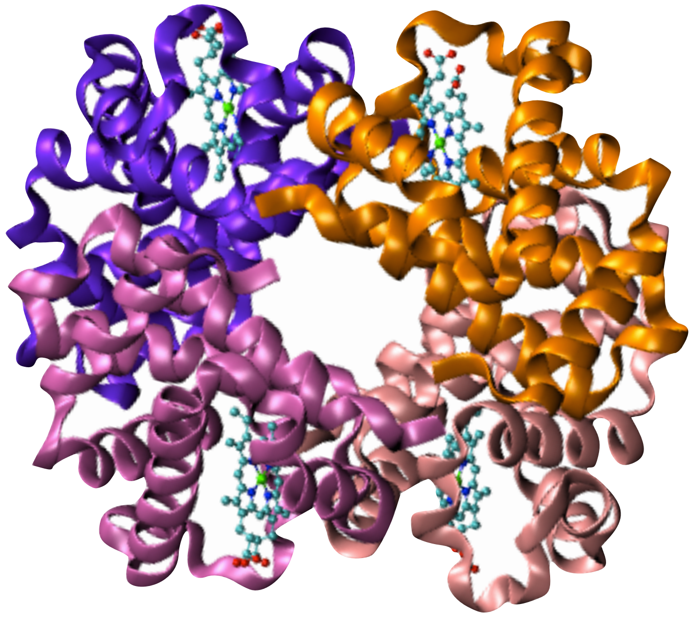

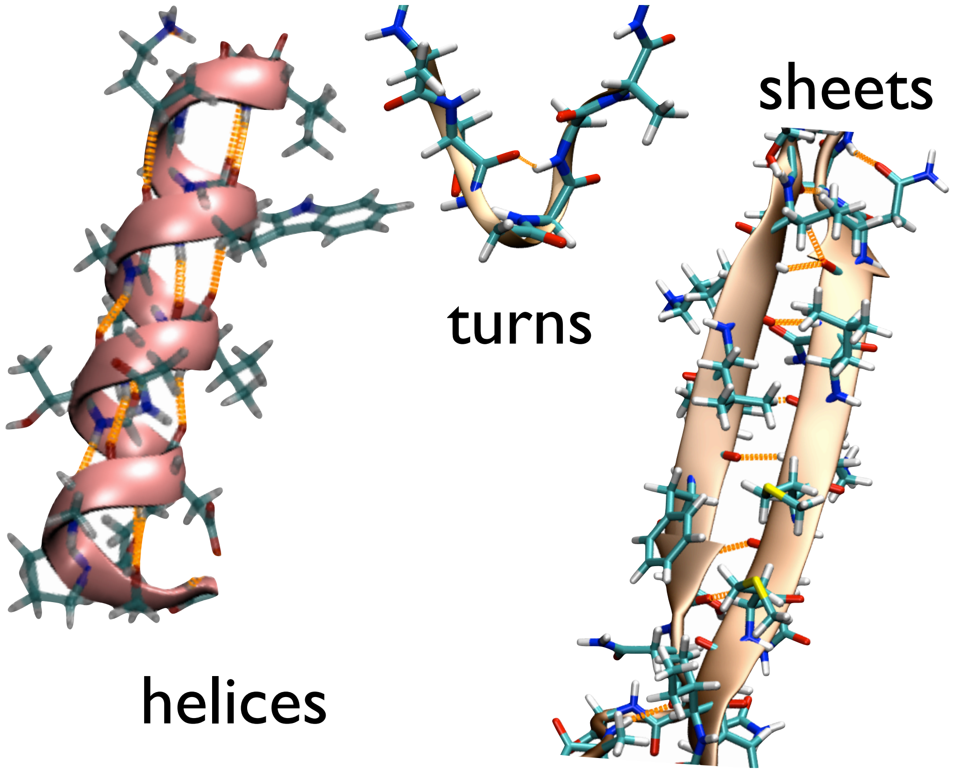

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- *The structure of a p*

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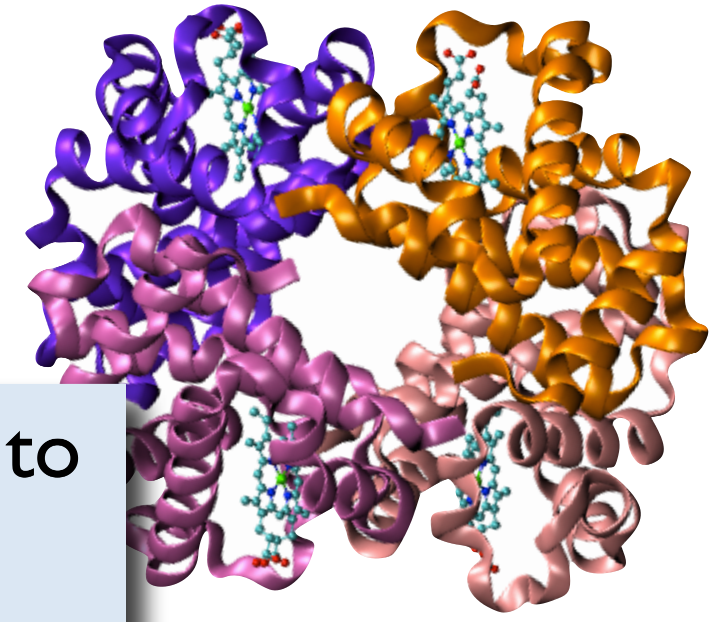
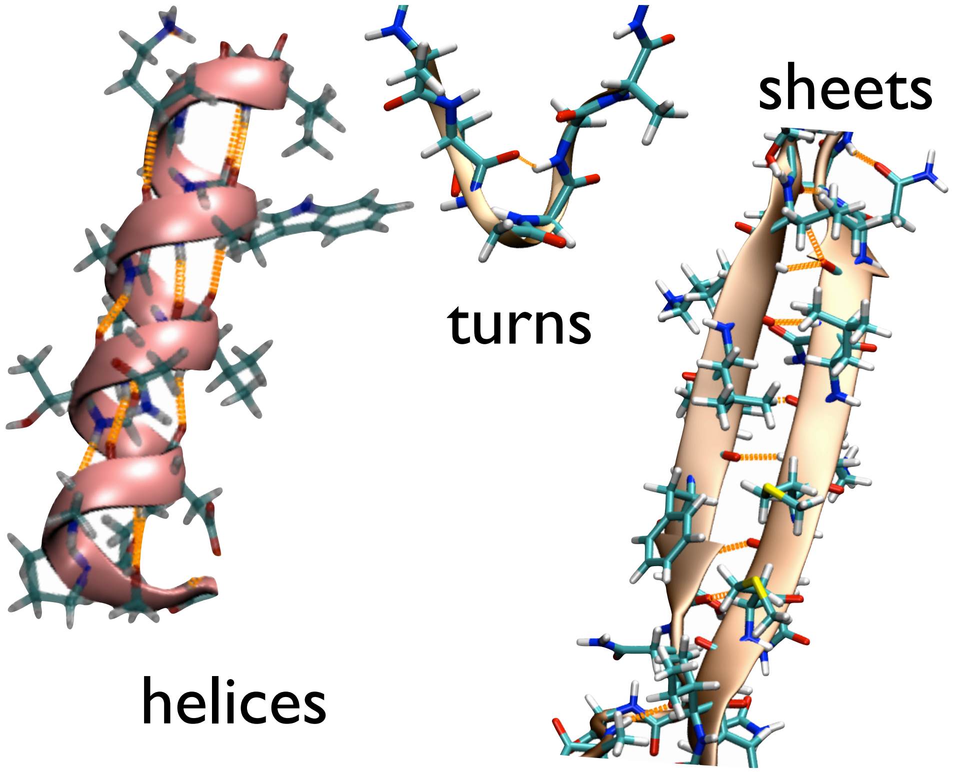
  Secondary structure

Can we push "first principles" to predict secondary structure? (~100s of atoms)

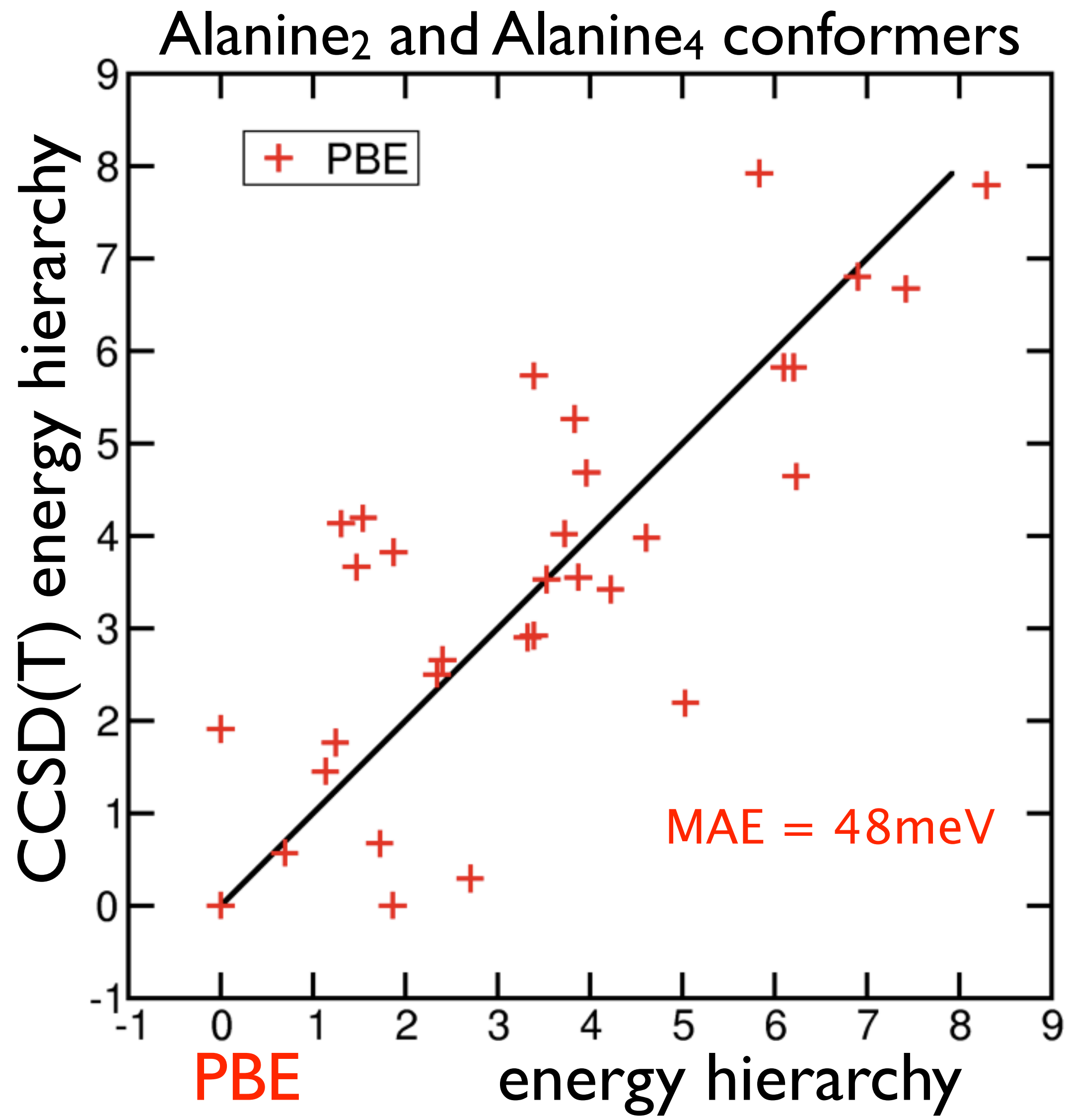
Hemoglobin





The first ingredient is weak: van der Waals

- DFT in the Perdew-Burke-Ernzerhof (1996) generalized gradient approximation
- Non-empirical, widely used, but *any* GGA lacks van der Waals tails



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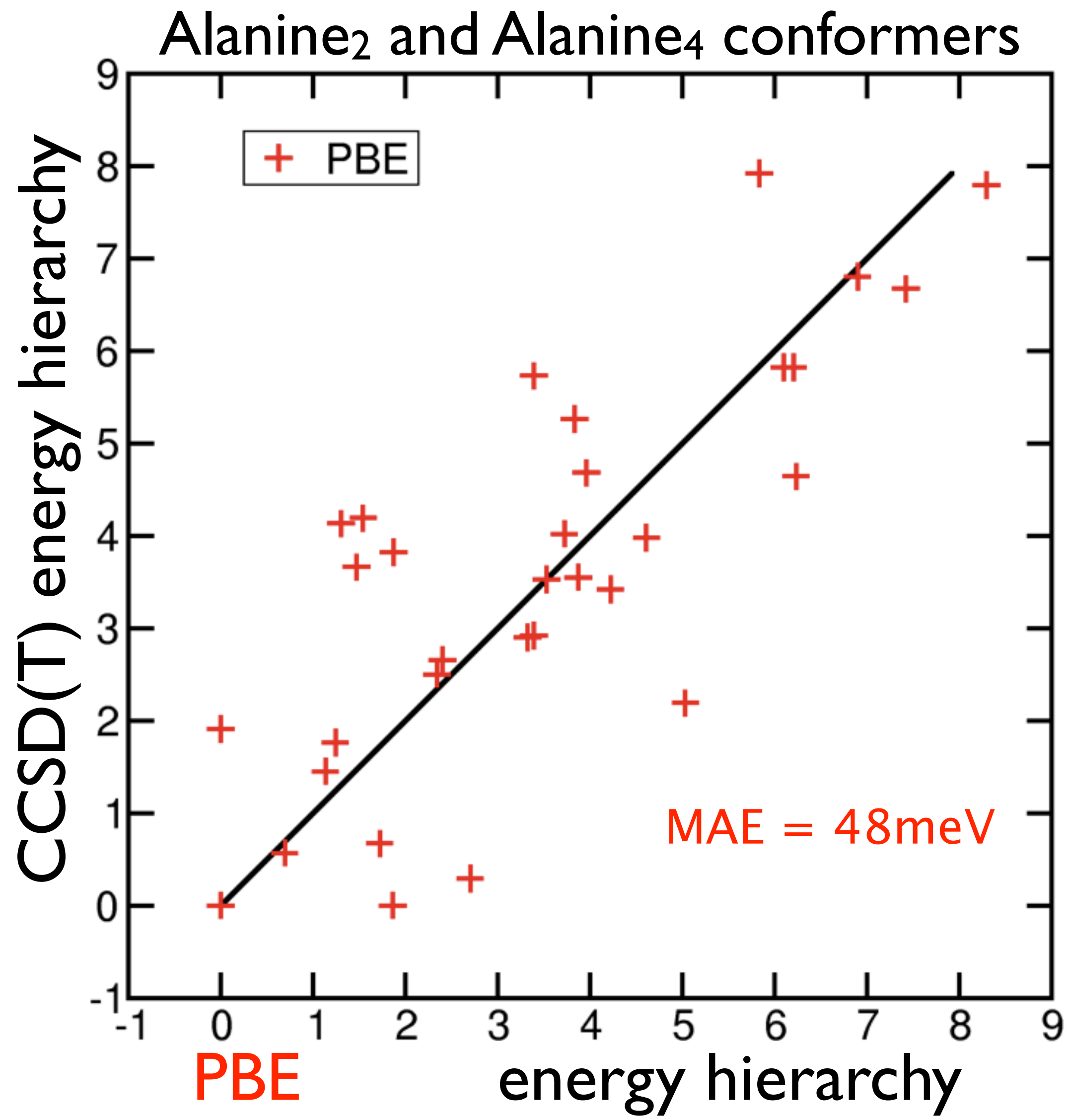
$$E_{\mathrm{DFT}} + \sum_{\mathrm{atoms}\ ij} \frac{C_6^{ij}}{R_{ij}^6} \cdot f_{\mathrm{damp}}(R_{ij})$$



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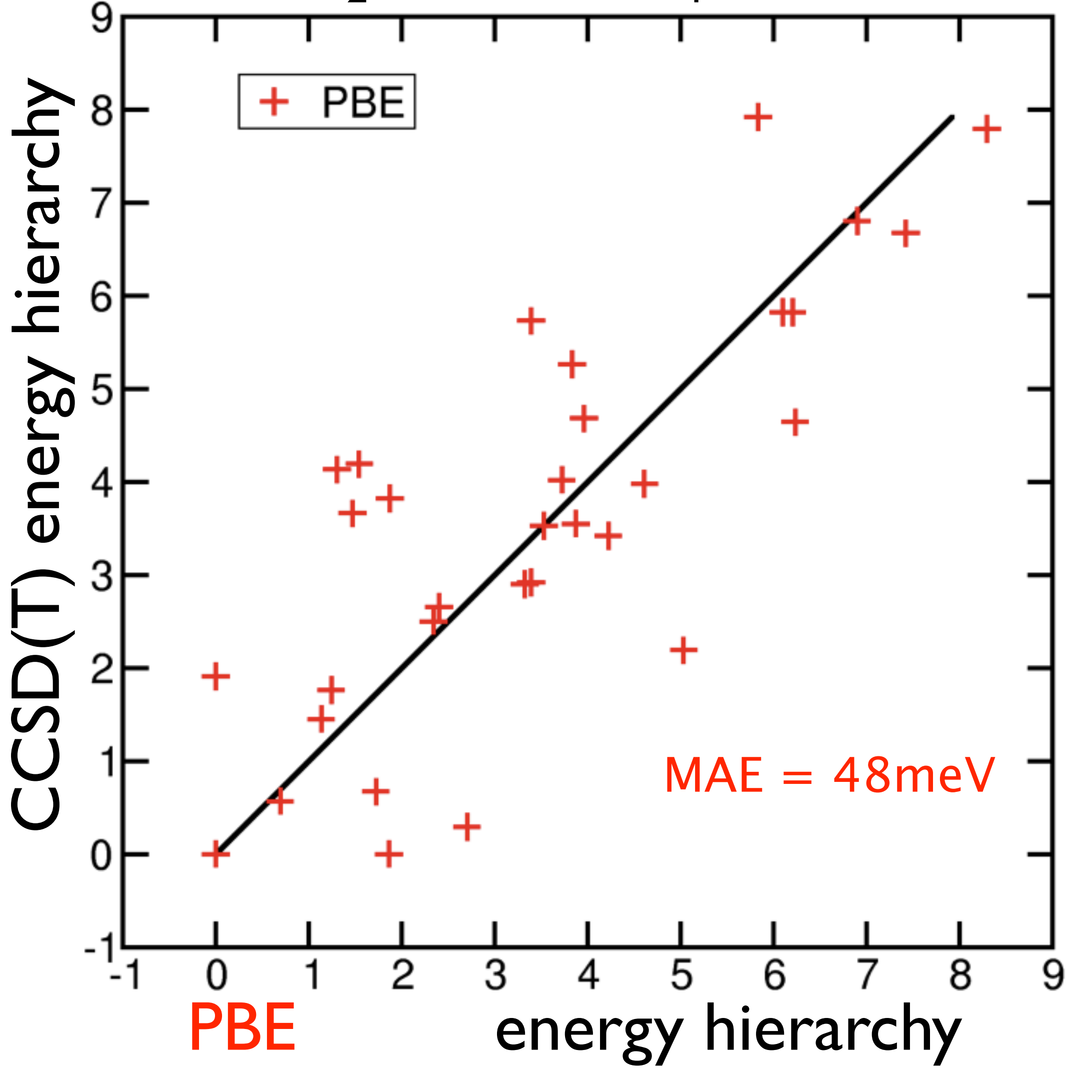
Alanine$_2$ and Alanine$_4$ conformers



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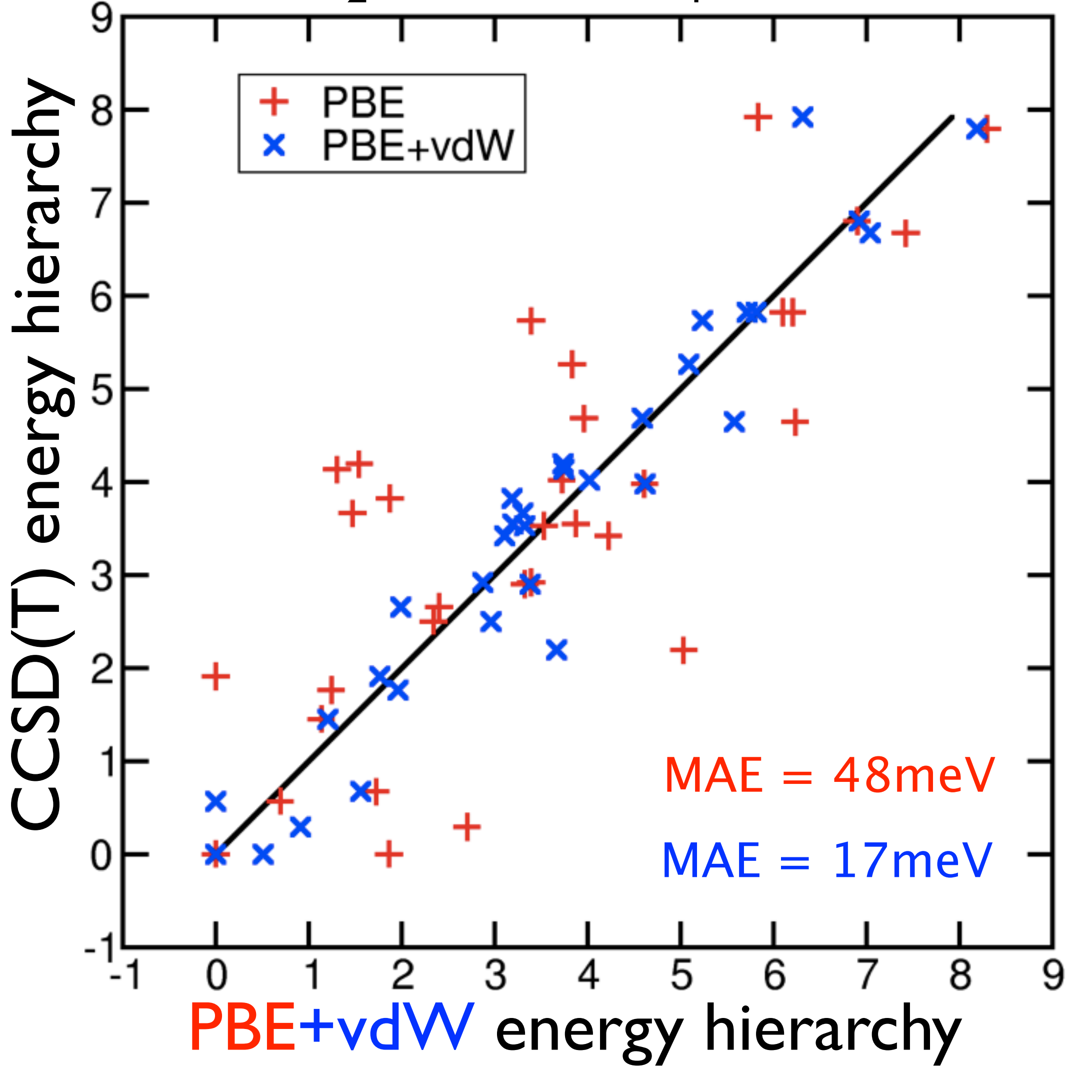

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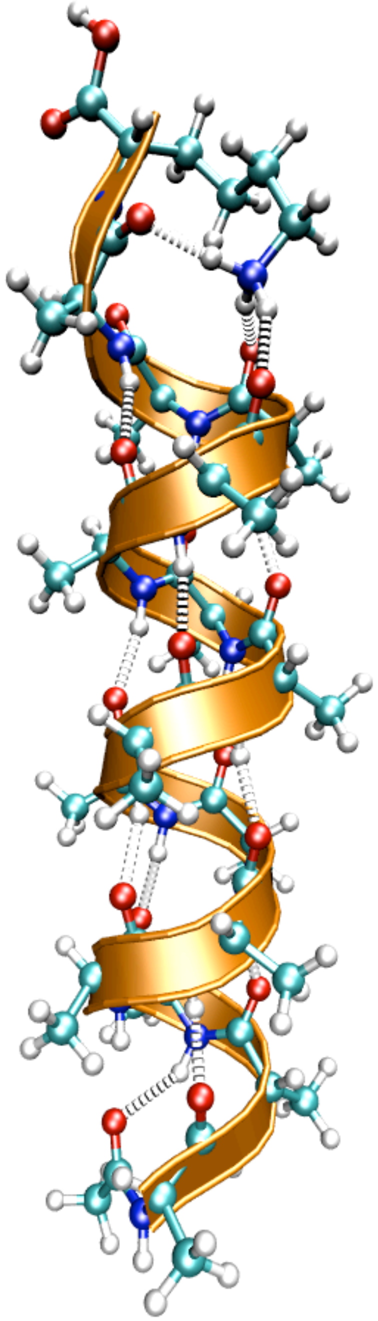
A known helix in the gas phase: Ac-Ala$_{15}$-LysH$^+$

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



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

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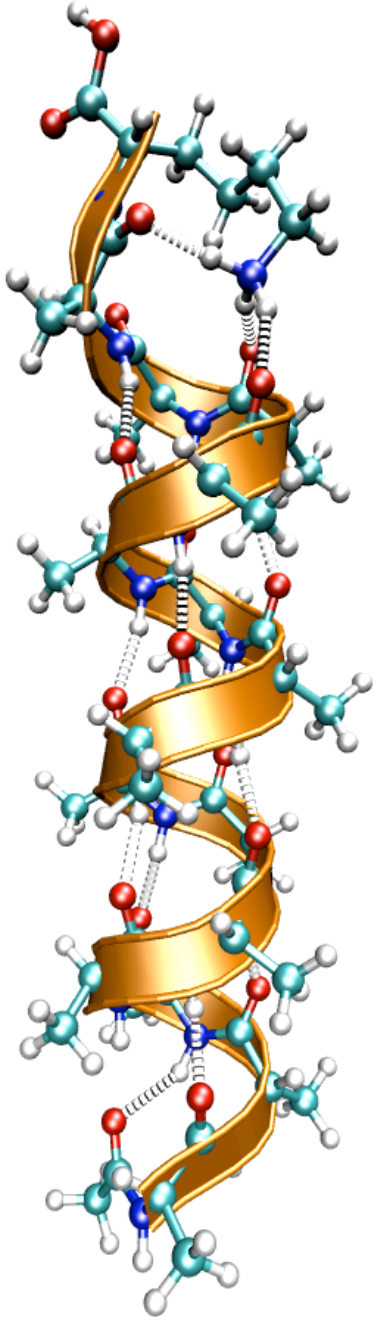

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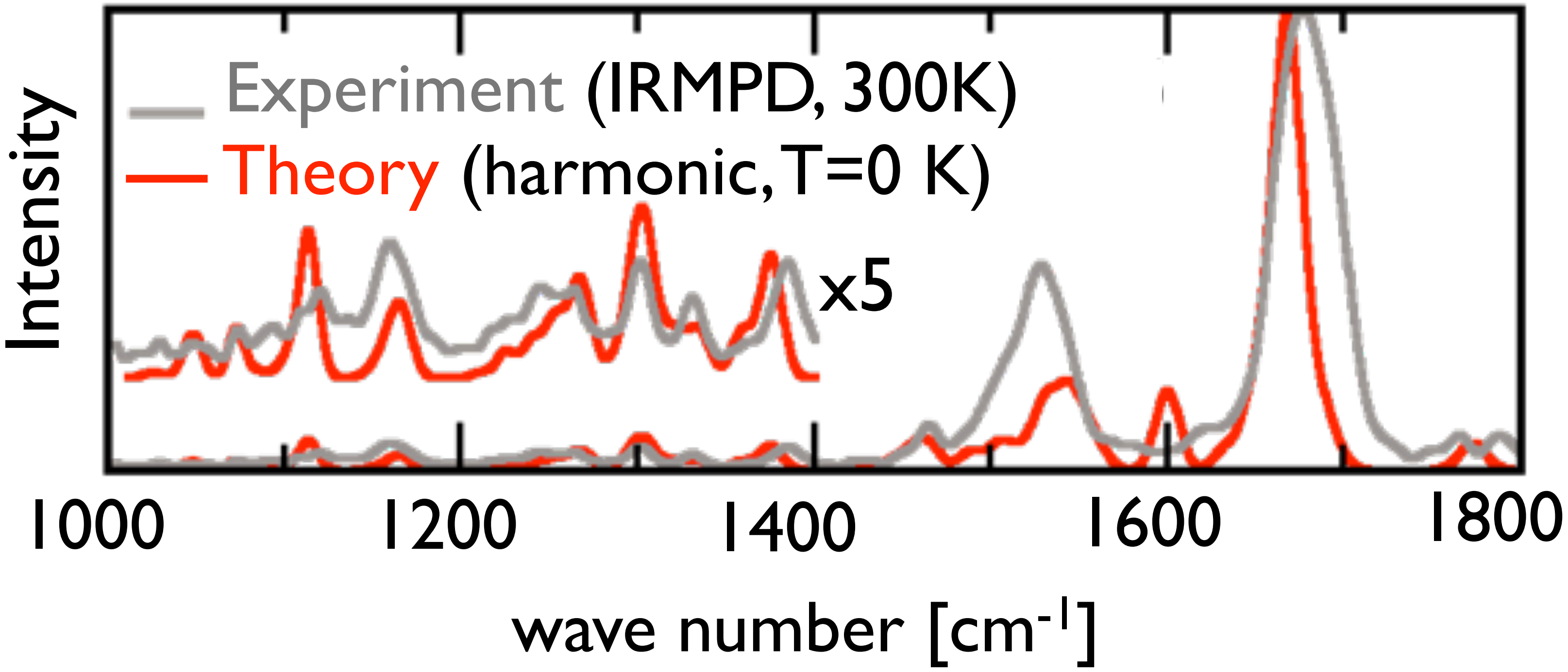

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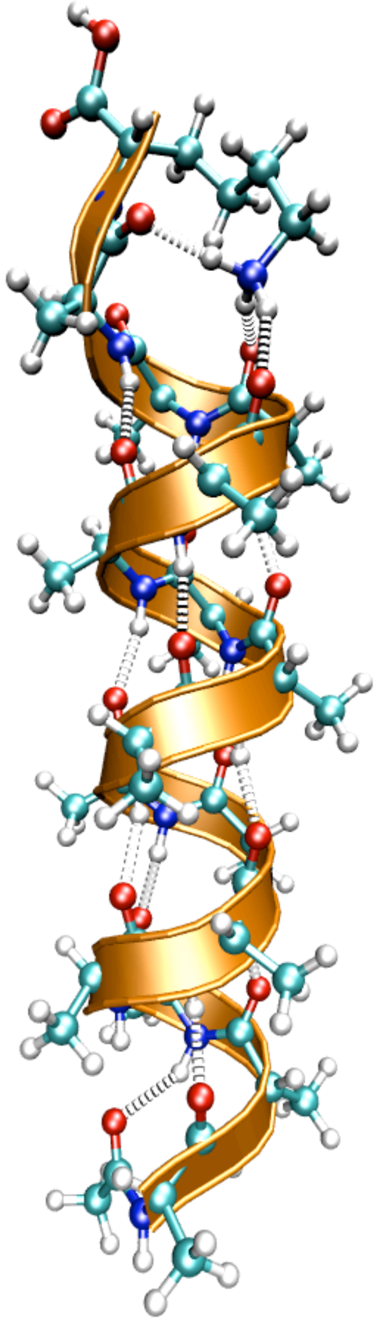

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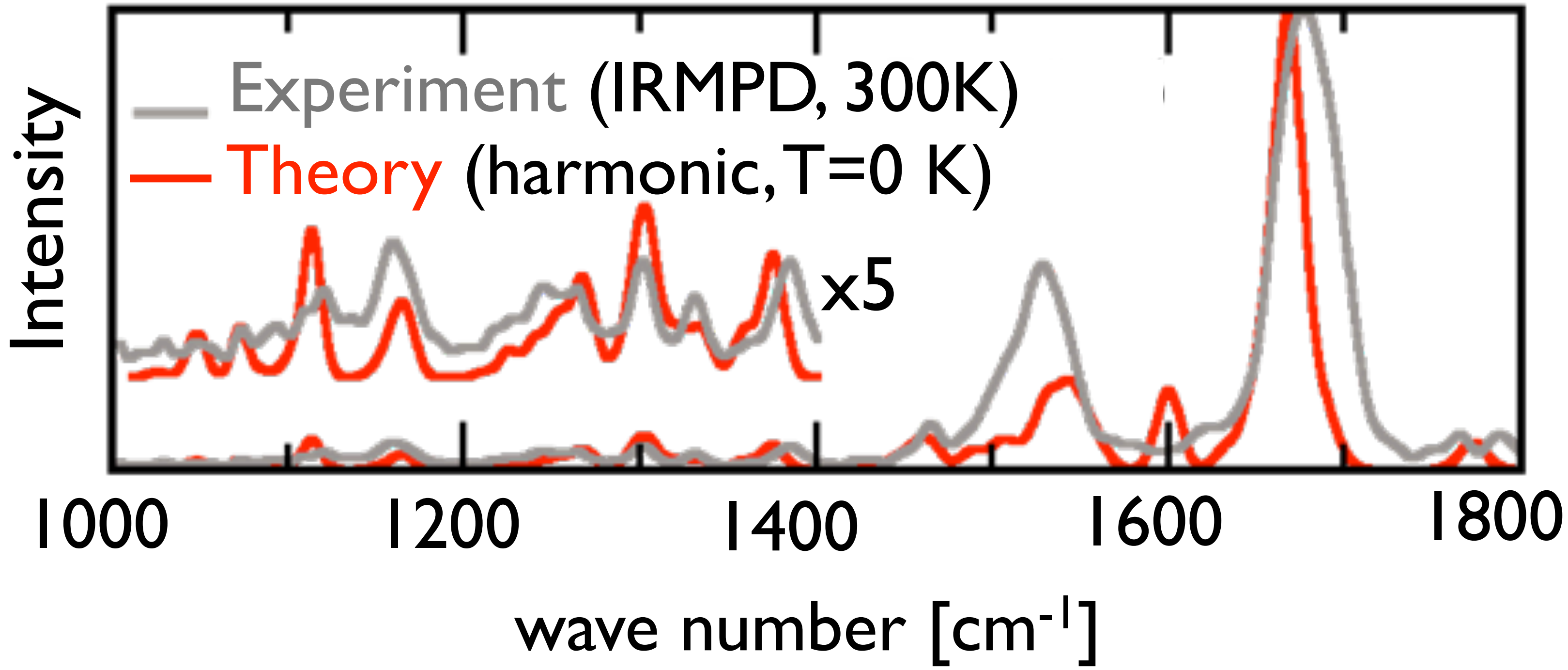

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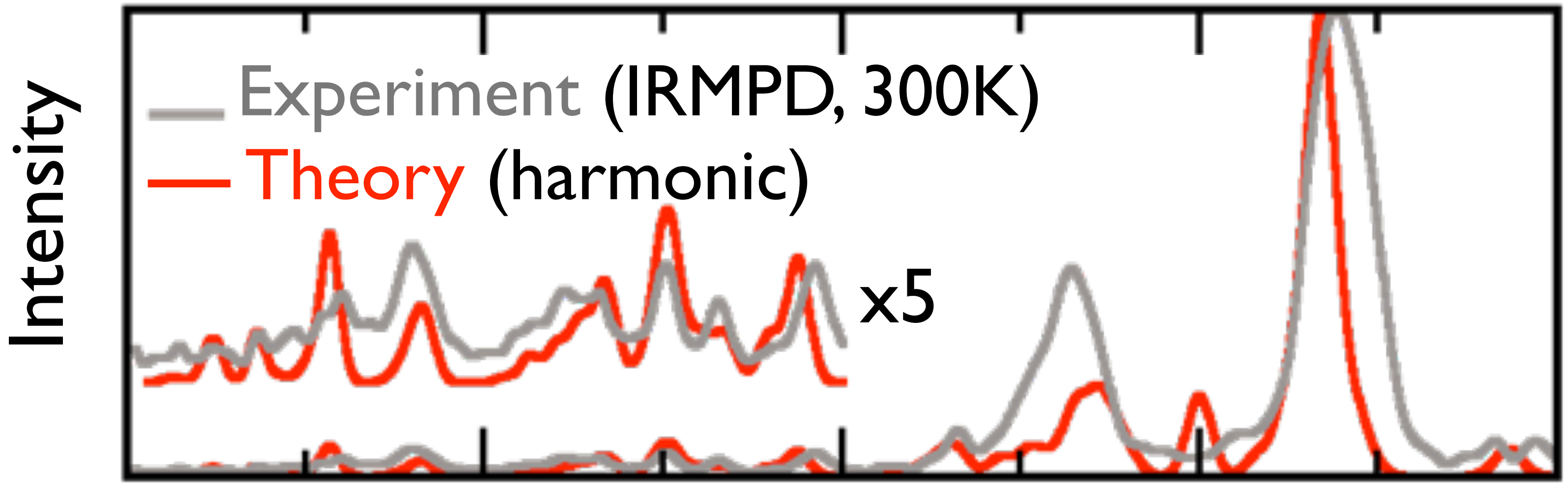

$$I(\omega) \propto \omega^2 \int_{-\infty}^{\infty} dt \, \underbrace{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}_{\text{dipole-dipole time correlation function}} e^{iwt}$$

dipole-dipole time correlation function

see, e.g., *M.-P. Gaigeot, others*

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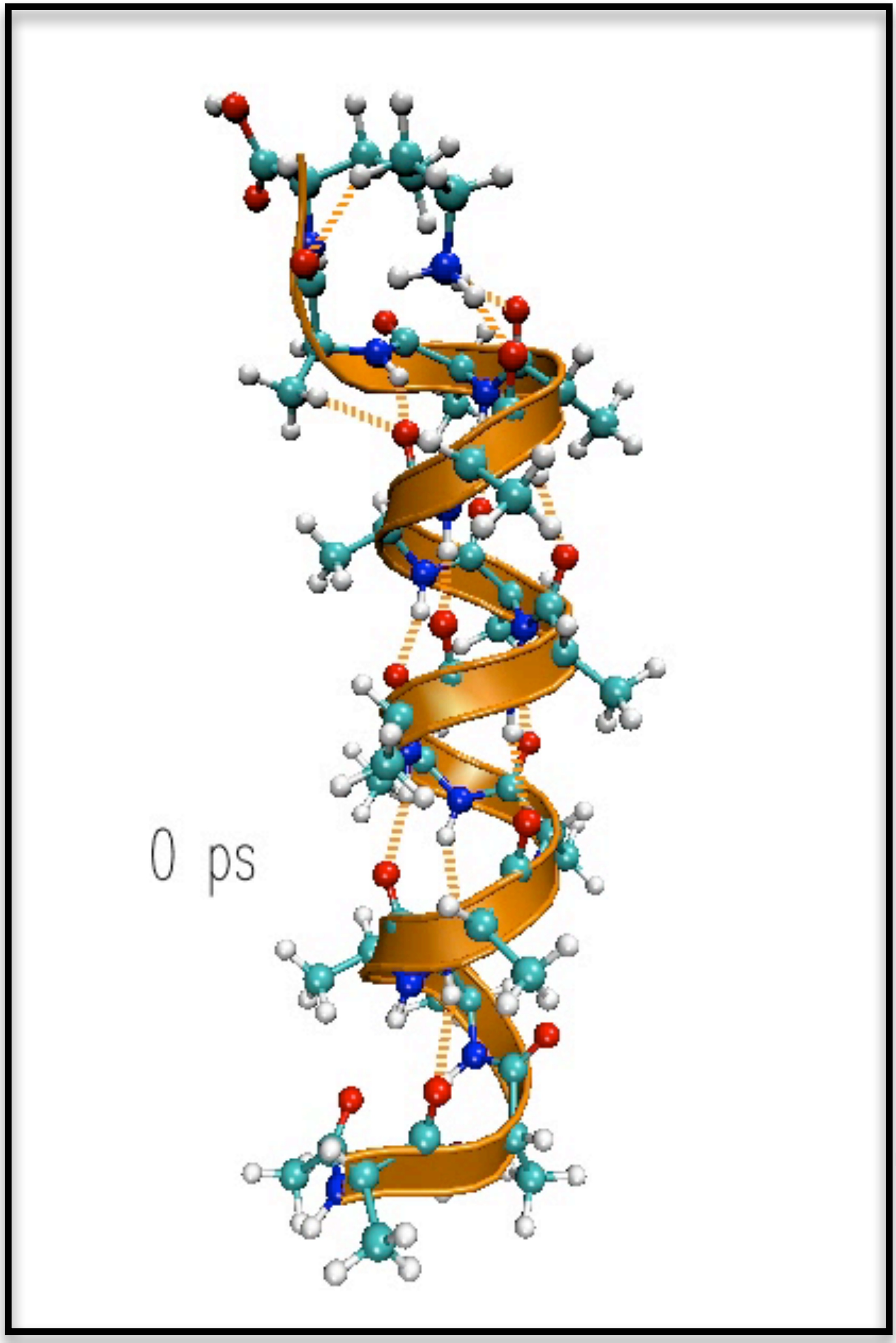

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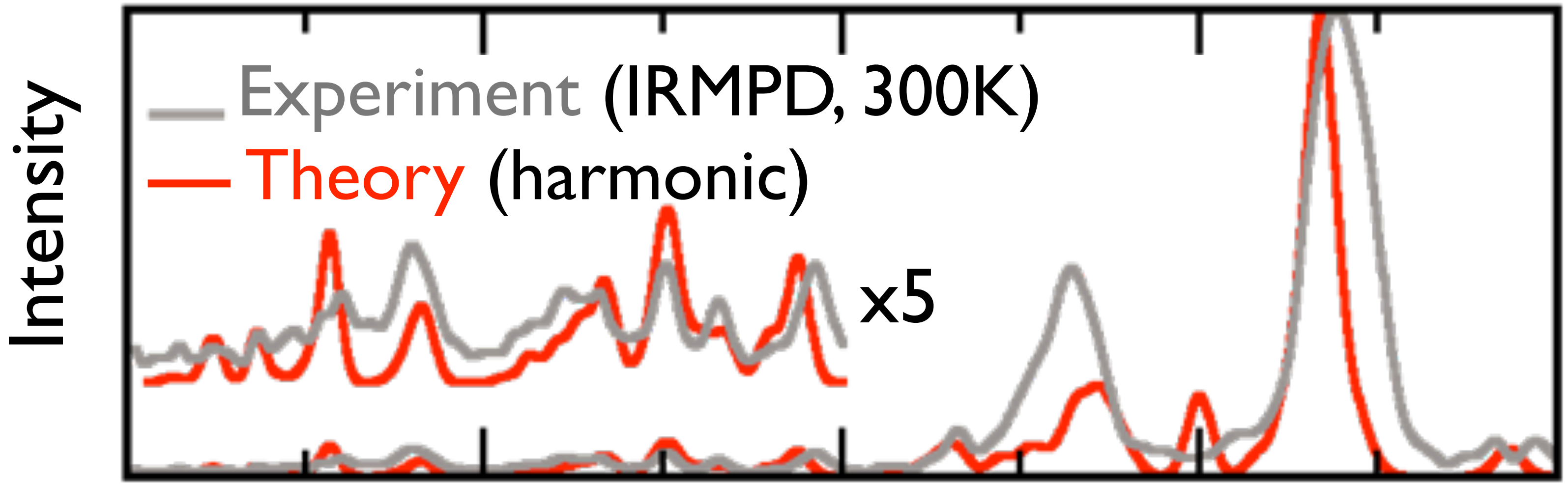

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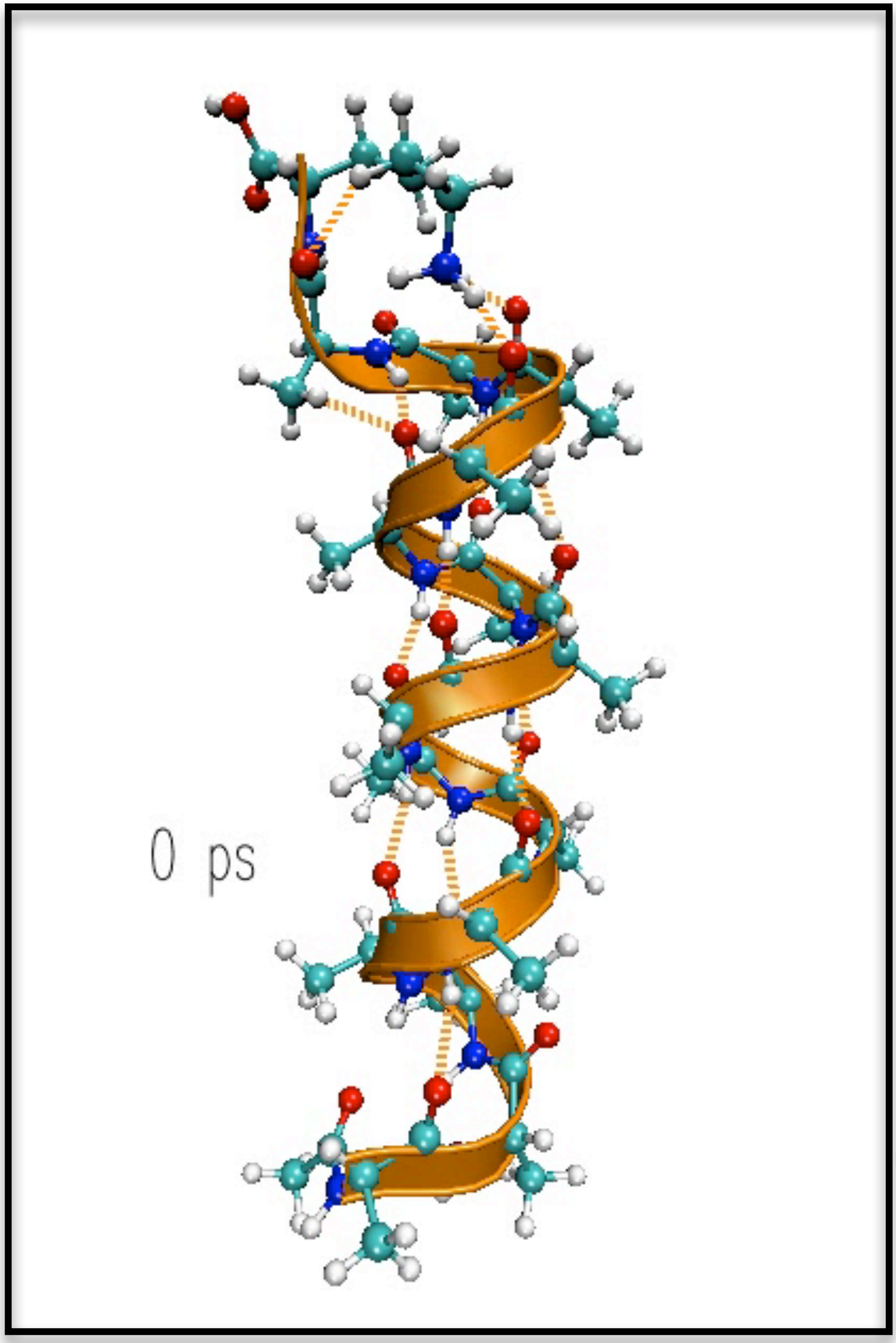

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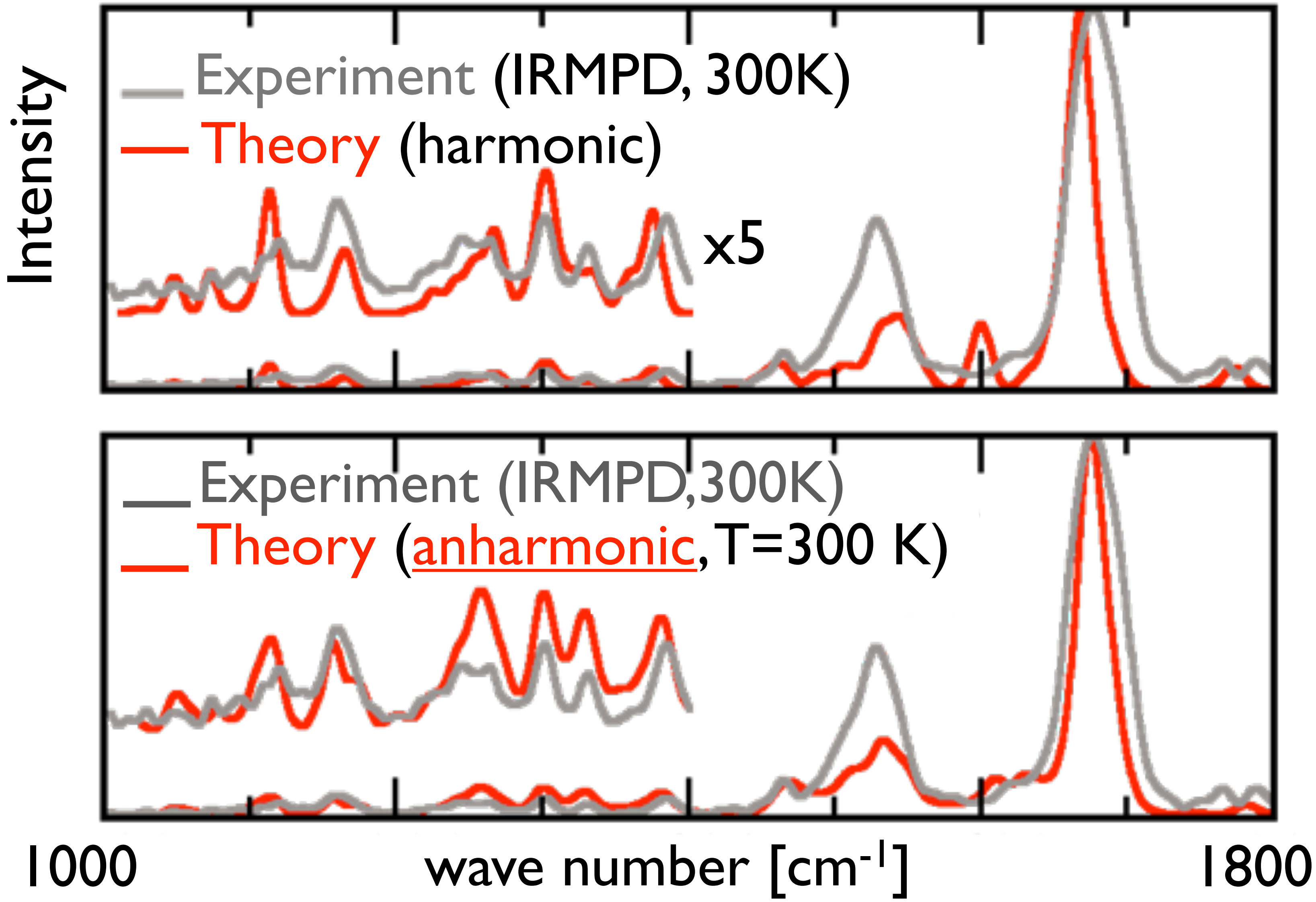

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Now what happens without van der Waals?

Kohtani et al., JACS ***126****, 7420 (2004)*: "Extreme stability of an unsolvated helix"
Ac-Ala$_{15}$-LysH$^+$ **α-helix** is stable up to ≈ 650 K

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PBE

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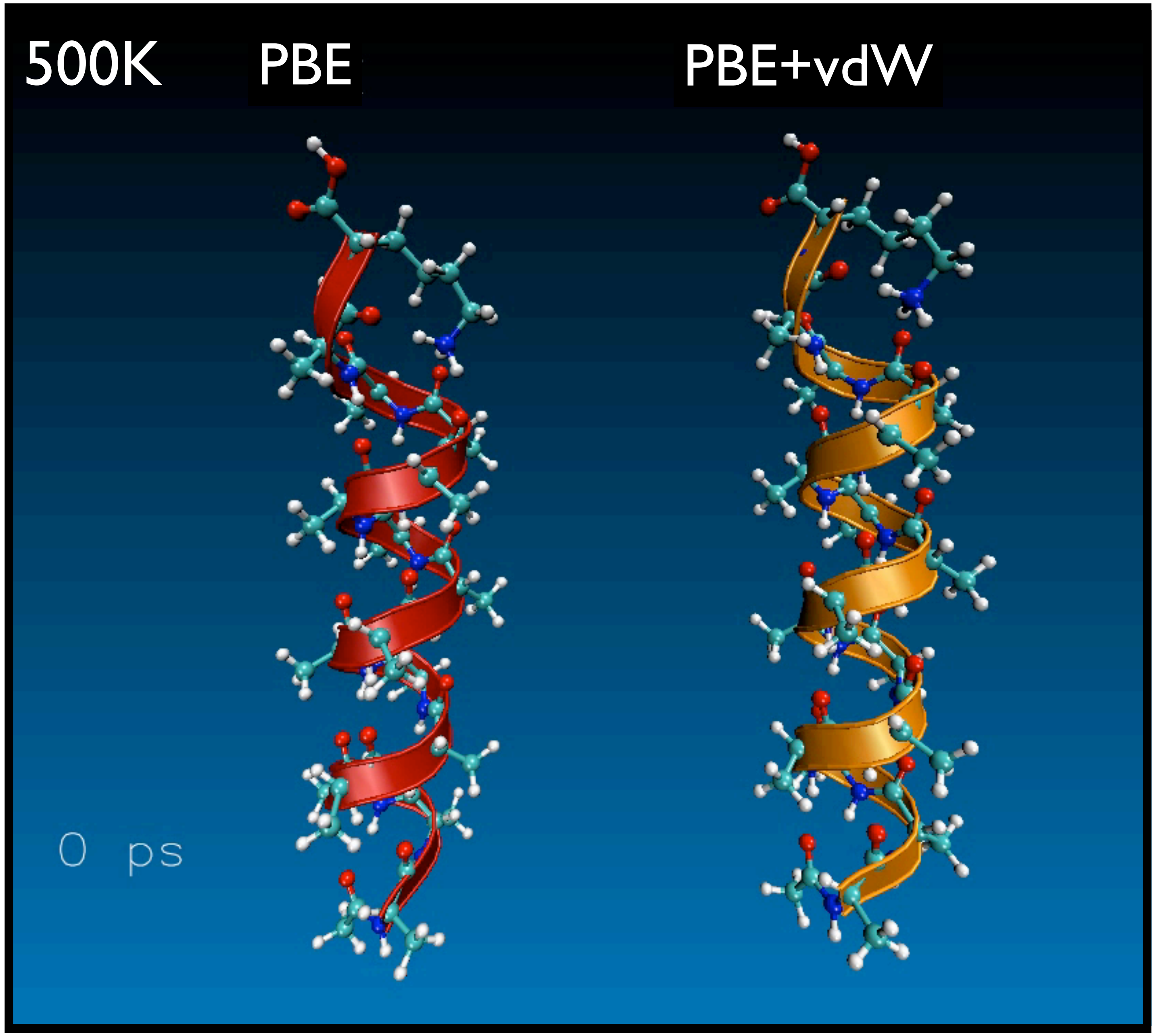

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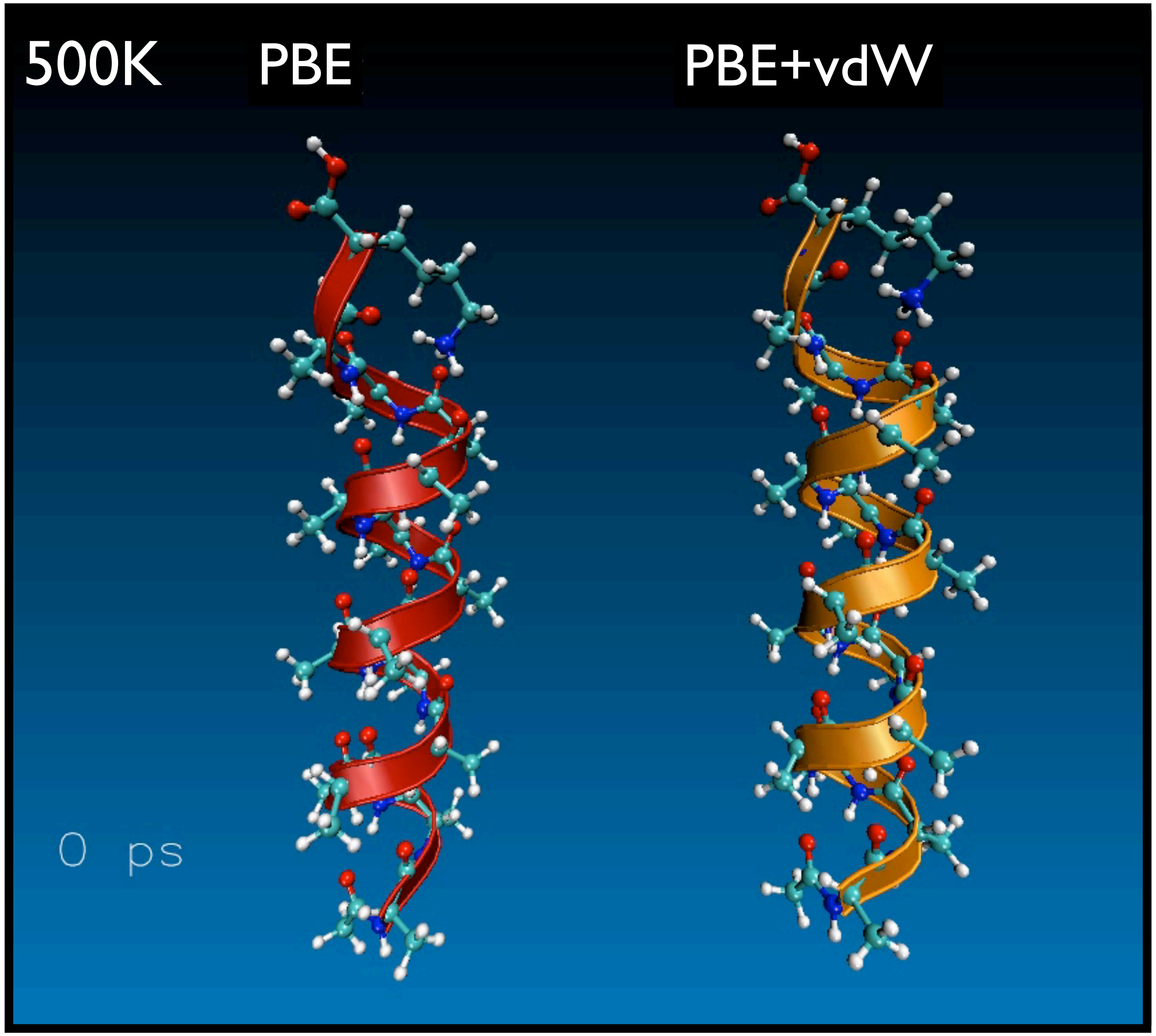
Mostly 3$_{10}$ helical!



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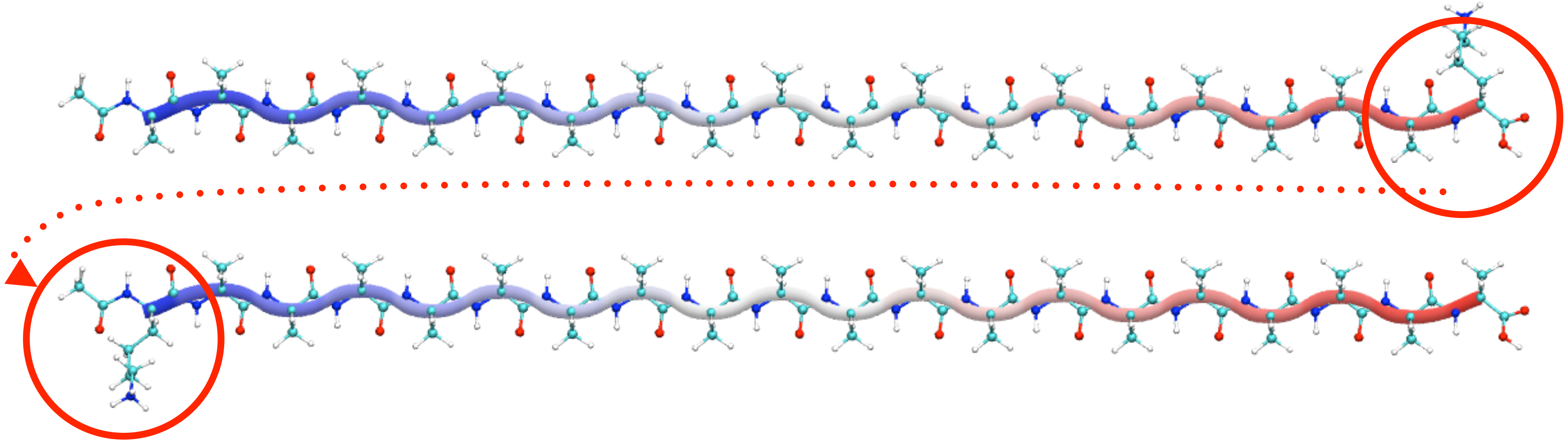
... and what if we "structurally destroy" the helix?



Ac-Ala$_{19}$-LysH$^+$

Ac-LysH$^+$-Ala$_{19}$

Can we tackle the conformational space of a 220-atom system?
Combinatorial explosion!

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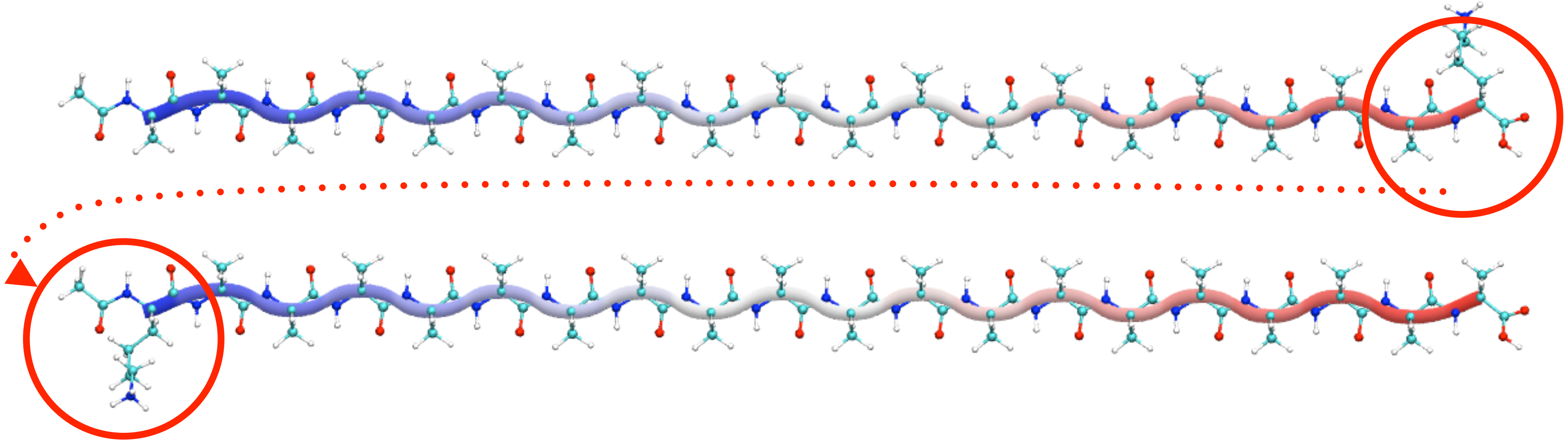

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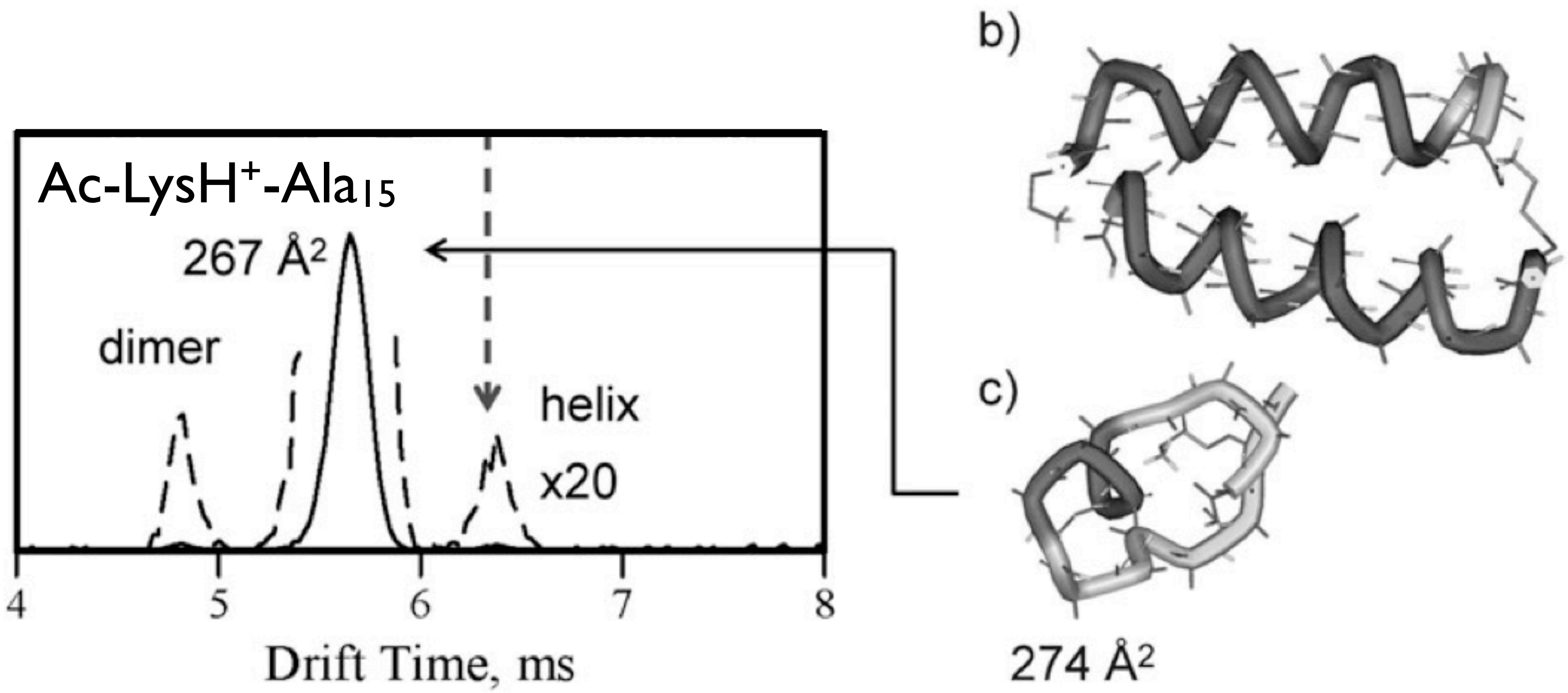

[2] Jarrold, PCCP 9, 1659, 2007

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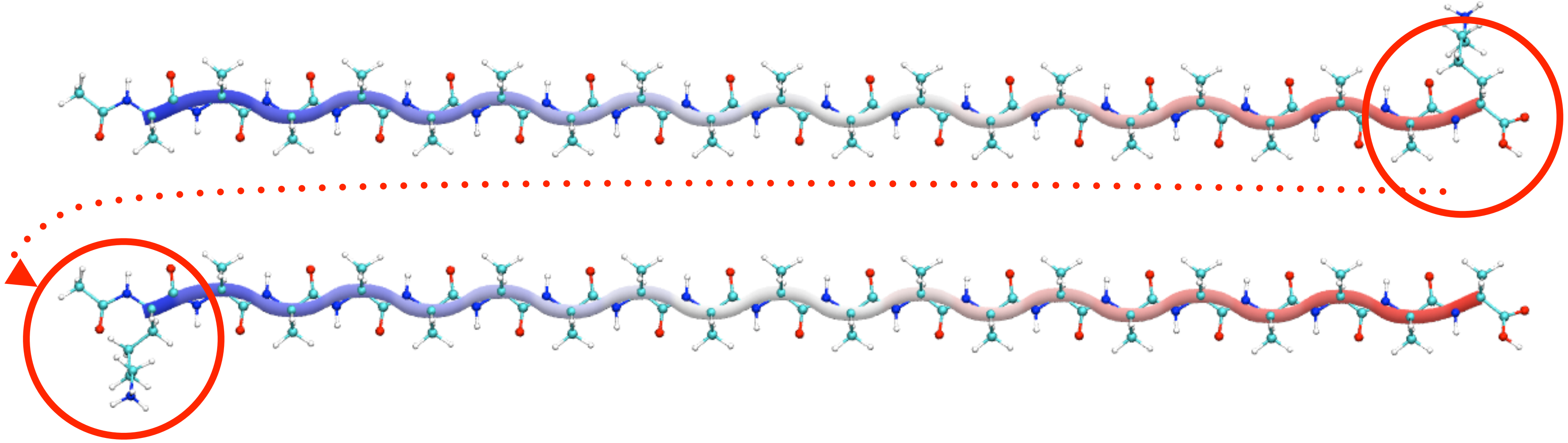

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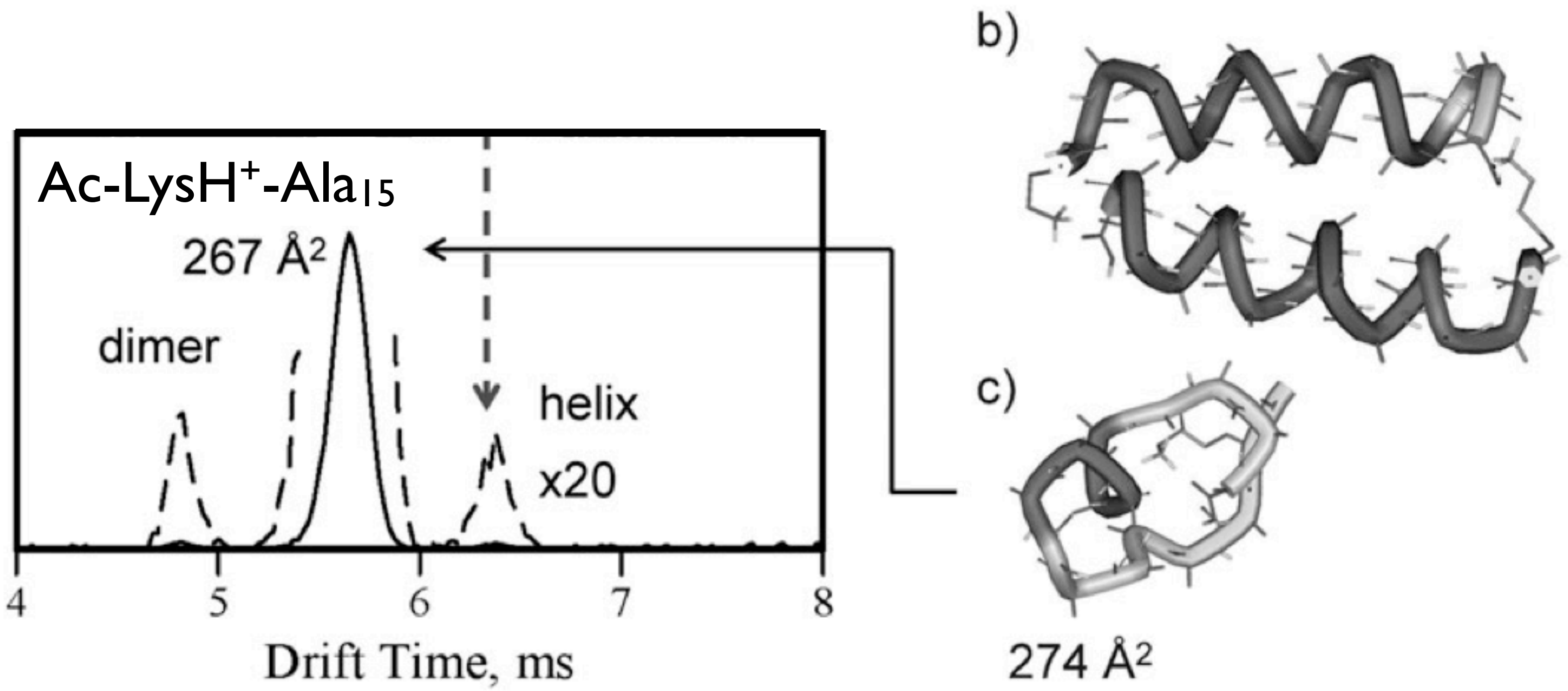

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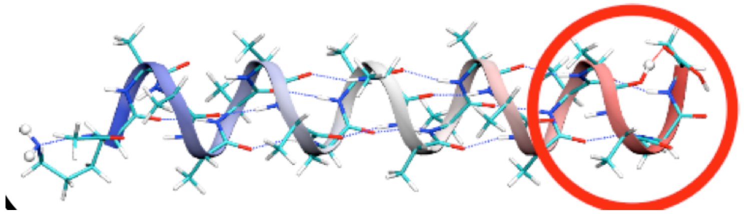

Helix, protonated C-terminus?

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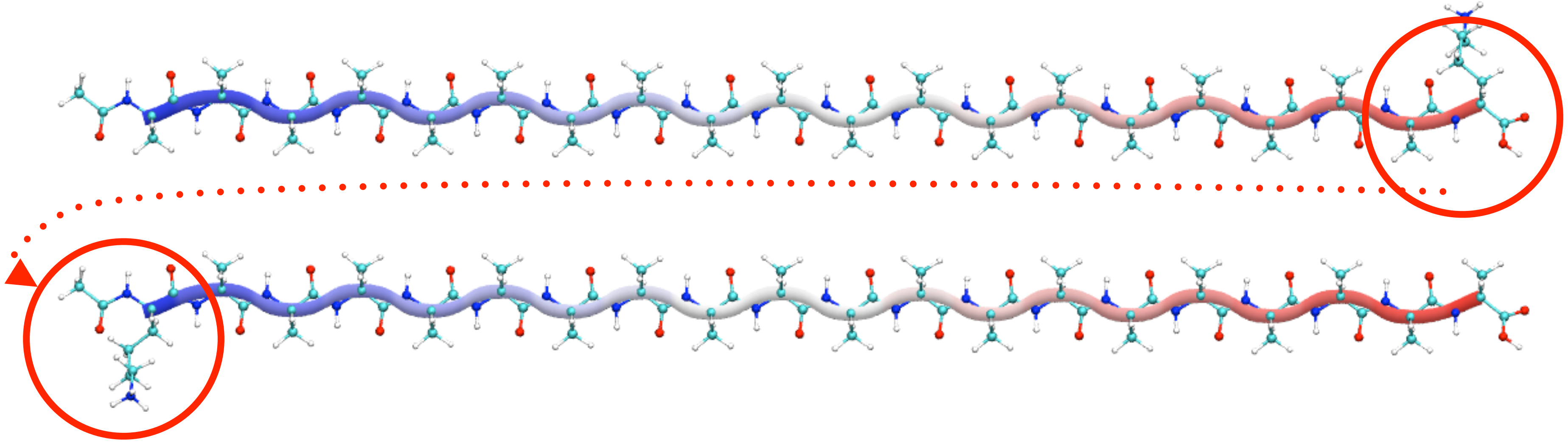
$\text{Ac-LysH}^+\text{-Ala}_{19}$



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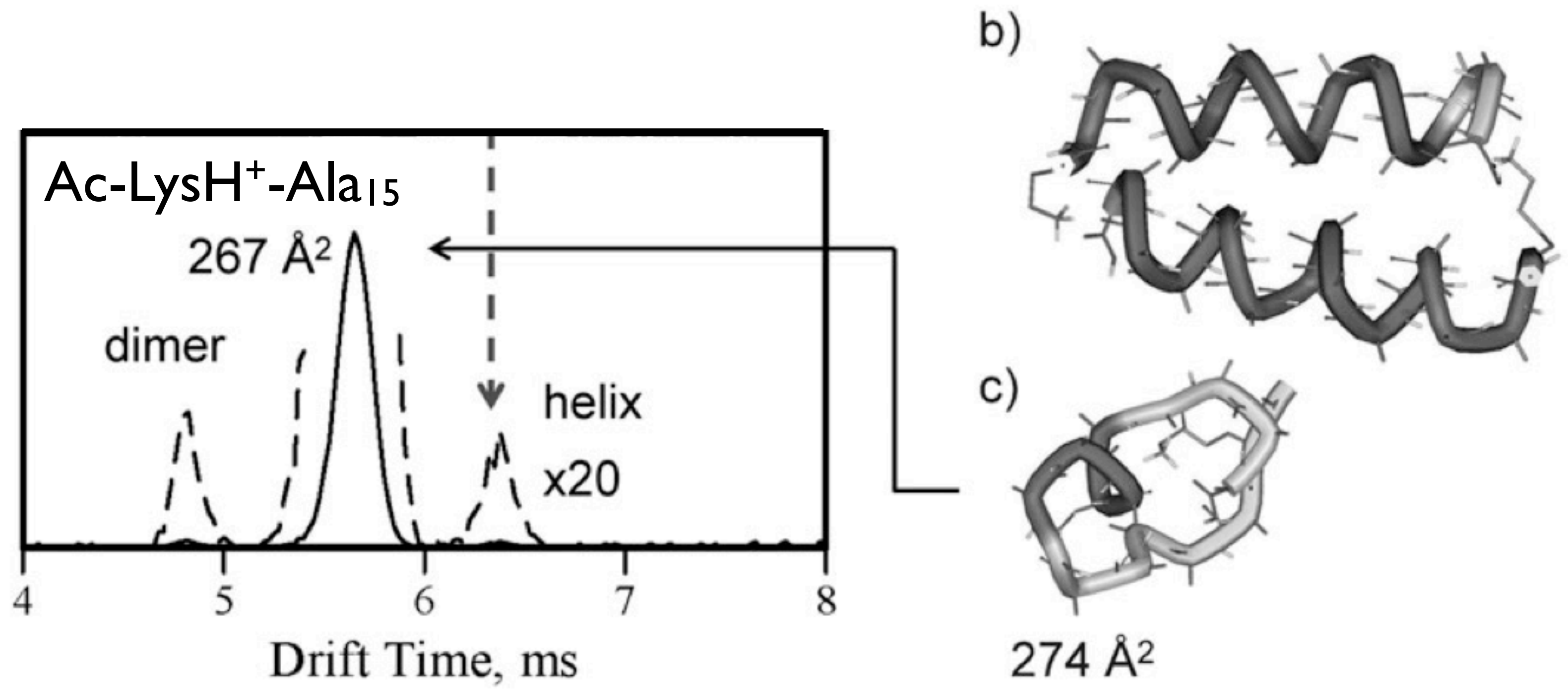

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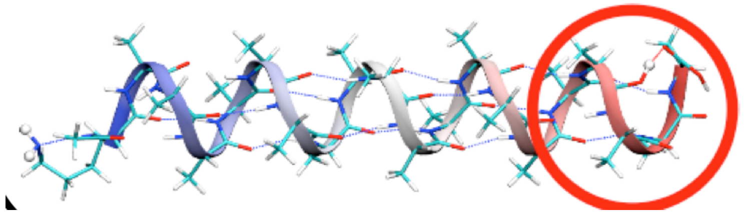

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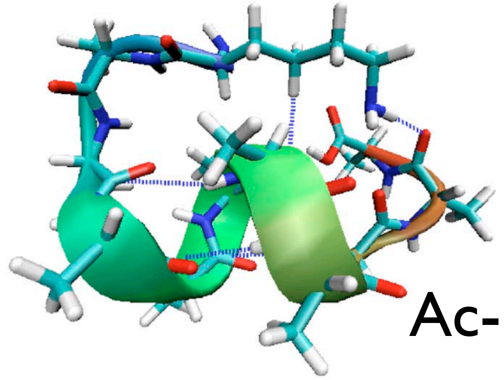


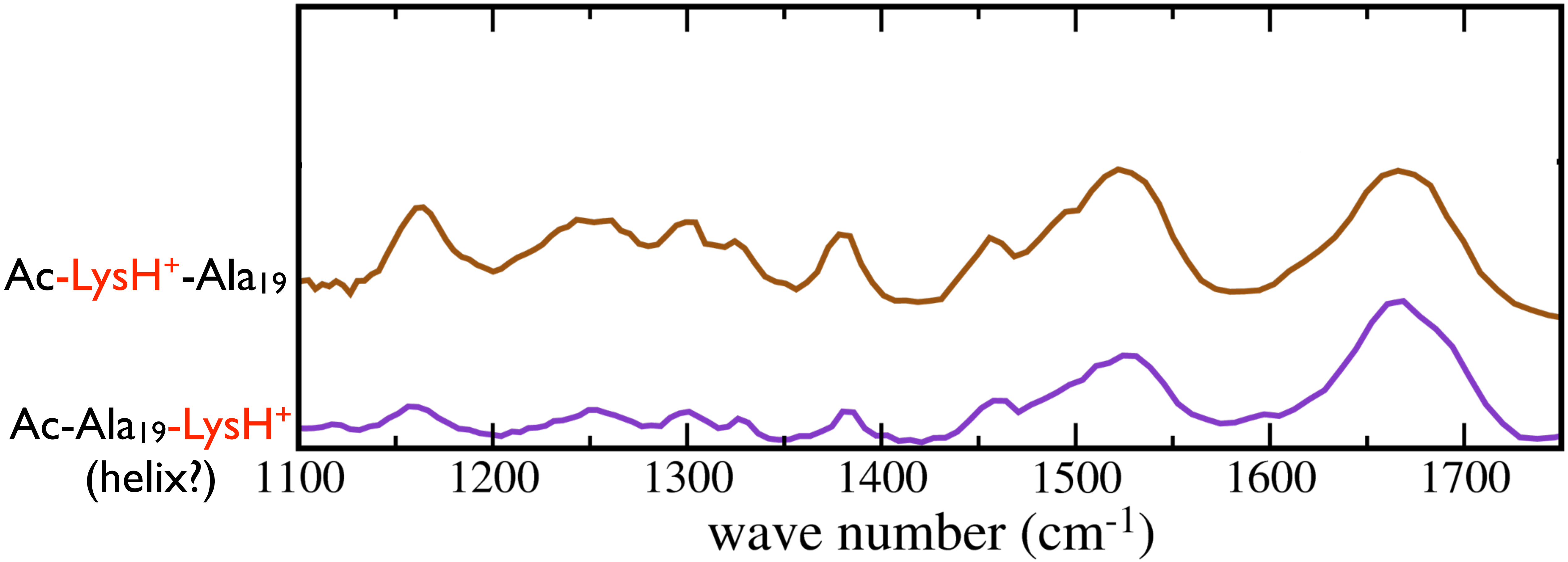
$\text{Ac-Lys}^+\text{-Ala}_{10}$

Wei et al., JCP 126, 204307 (2007)
Replica Exchange / Force Field

Turn again to vibrational spectroscopy: Helical?

Peter Kupser, Gert von Helden, Frank Filsinger, Kevin Pagel, Gerard Meijer,
Molecular Physics, FHI Berlin

Infrared multiphoton dissociation spectroscopy, FELIX, room temperature



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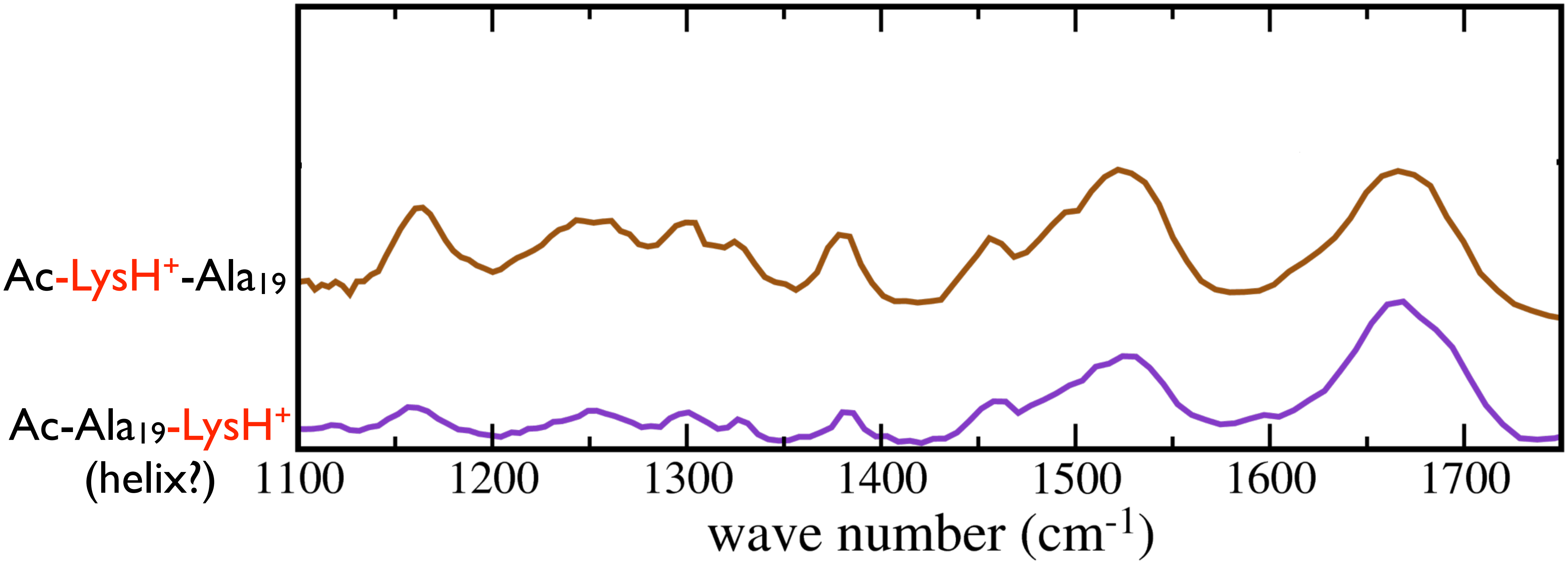
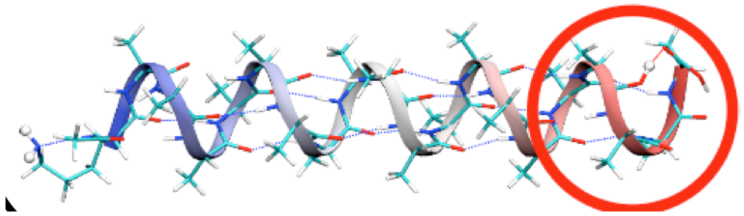
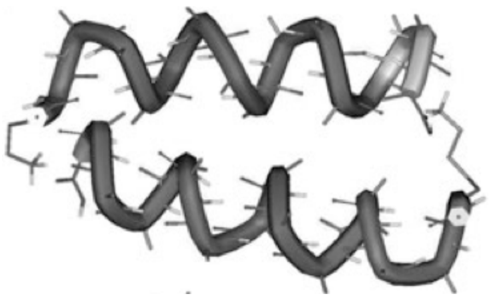
Molecular Physics, FHI Berlin

Infrared multiphoton dissociation spectroscopy, FELIX, room temperature





helix after all?



helix dimer?

Turn again to vibrational spectroscopy: Helical?

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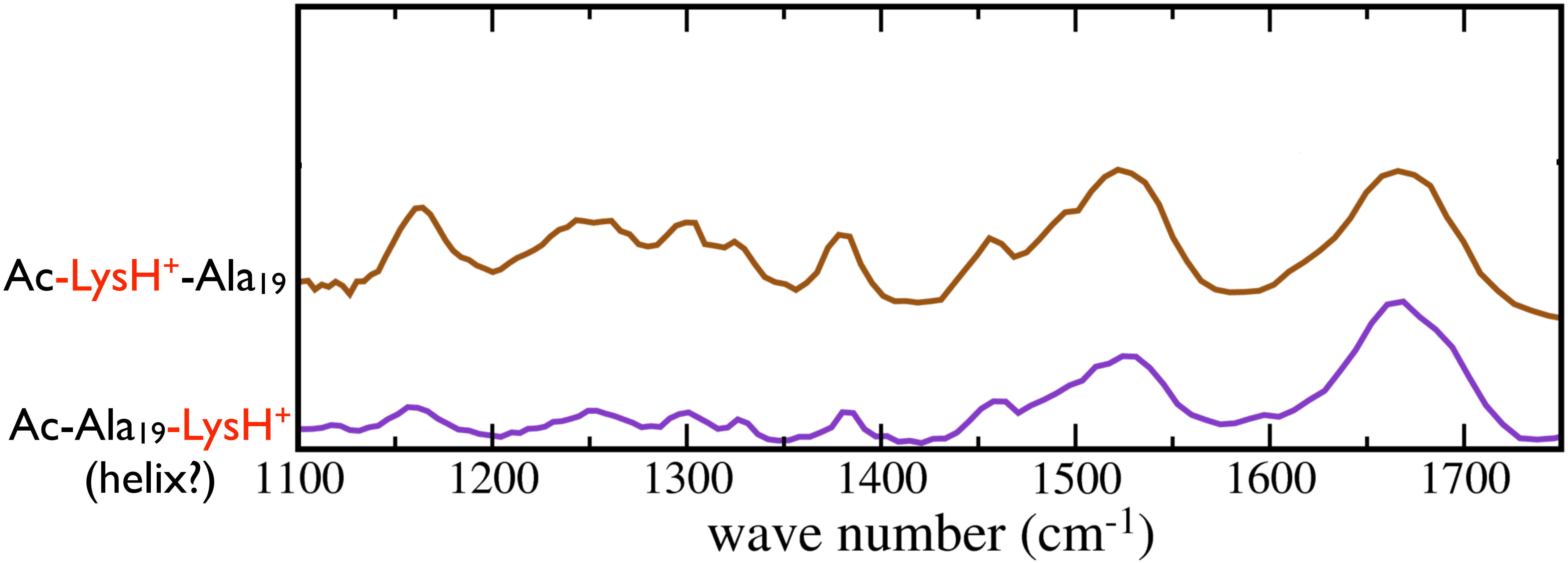

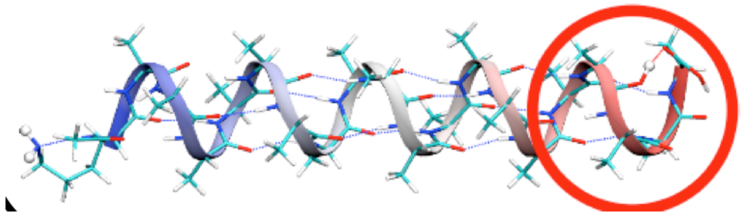
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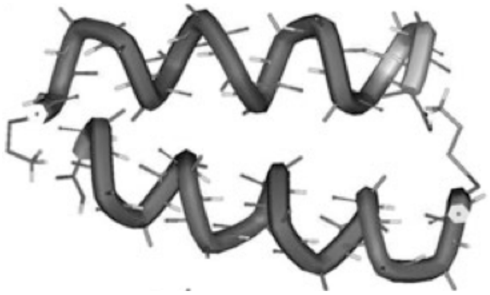
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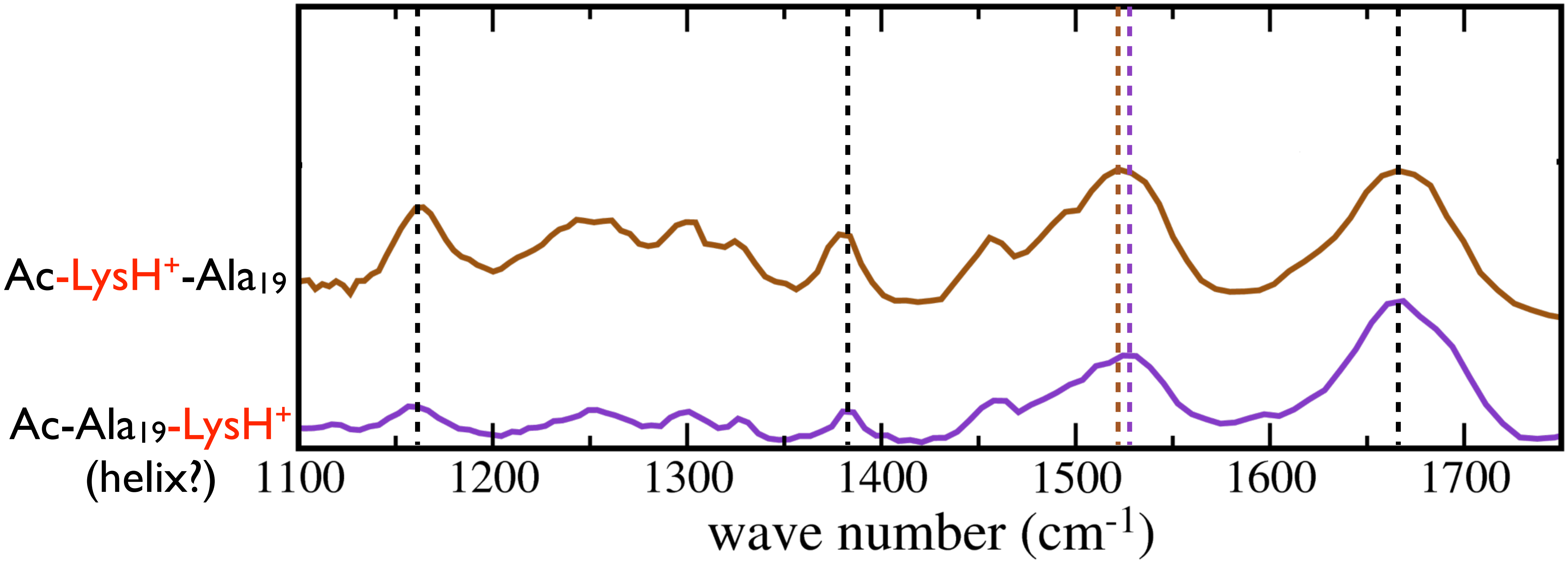

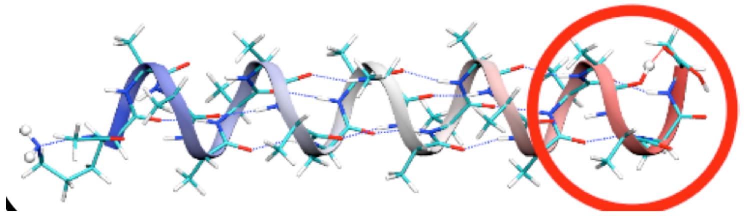

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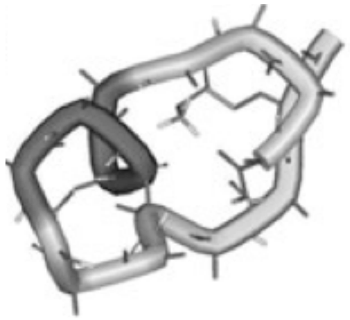

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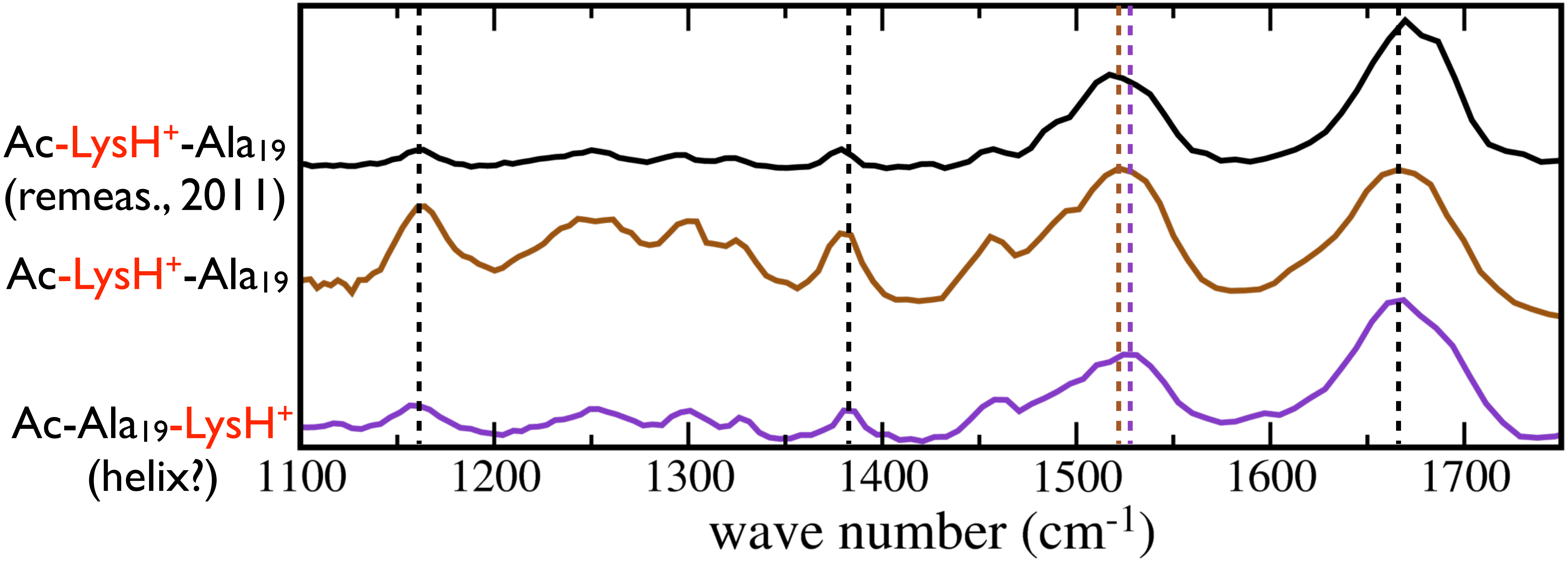

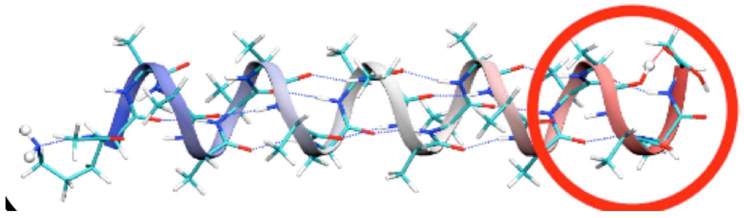

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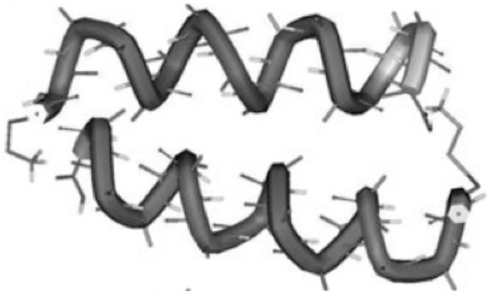

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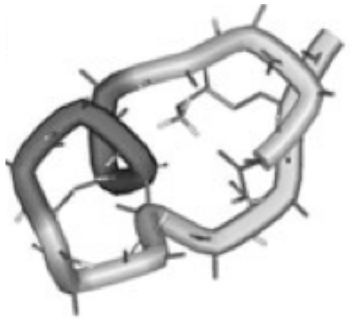

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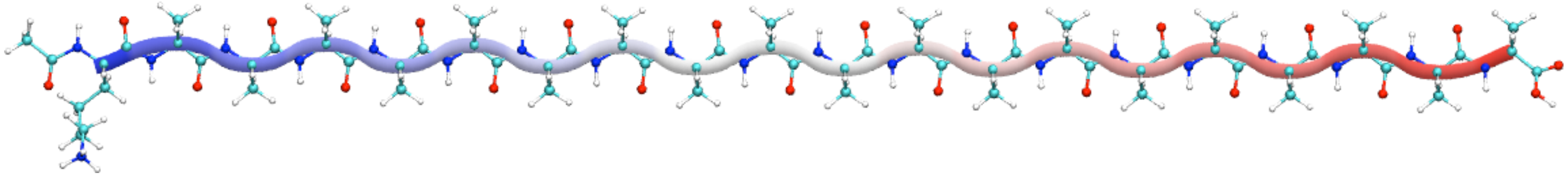
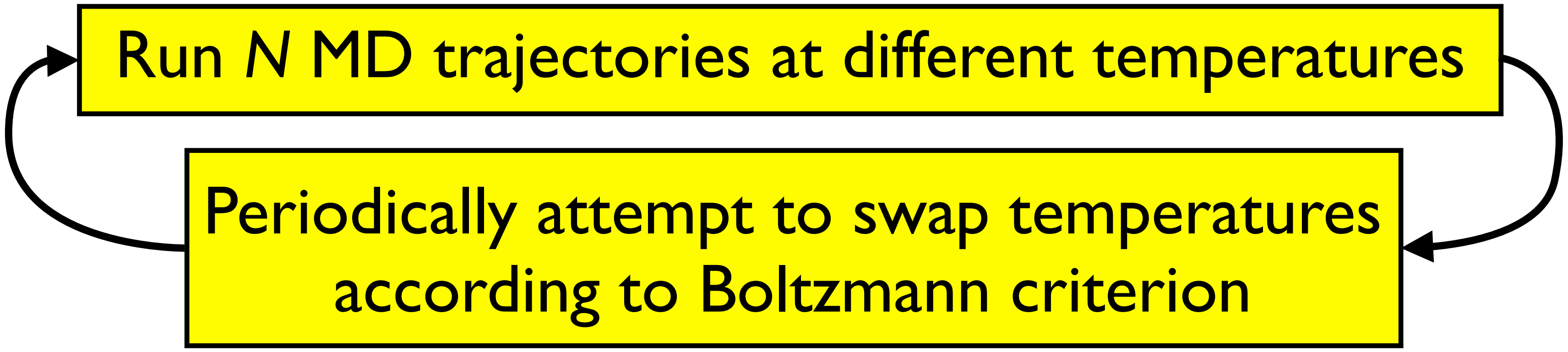
Ac-LysH$^+$-Ala$_{19}$: Searching a huge conformational space

Franziska Schubert, Carsten Baldauf, Mariana Rossi, VB - FHI



220 atoms - well beyond brute force “enumeration”.

One alternative:
Replica Exchange Molecular Dynamics (REMD)



Run *N* MD trajectories at different temperatures

Periodically attempt to swap temperatures according to Boltzmann criterion

Marinari, Parisi, Europhys. Lett ***19****, 451 (1992); U.H.E. Hansmann, Chem. Phys. Lett.* ***281****, 140 (1997); Y. Sugita, Y. Okamoto, Chem. Phys. Lett.* ***314****, 14 (1999); many others*

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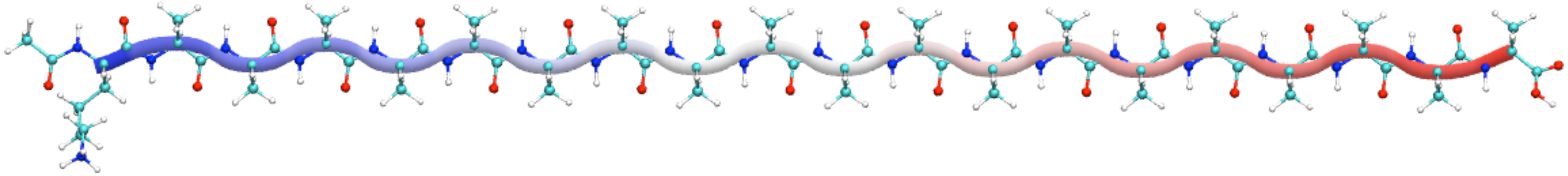

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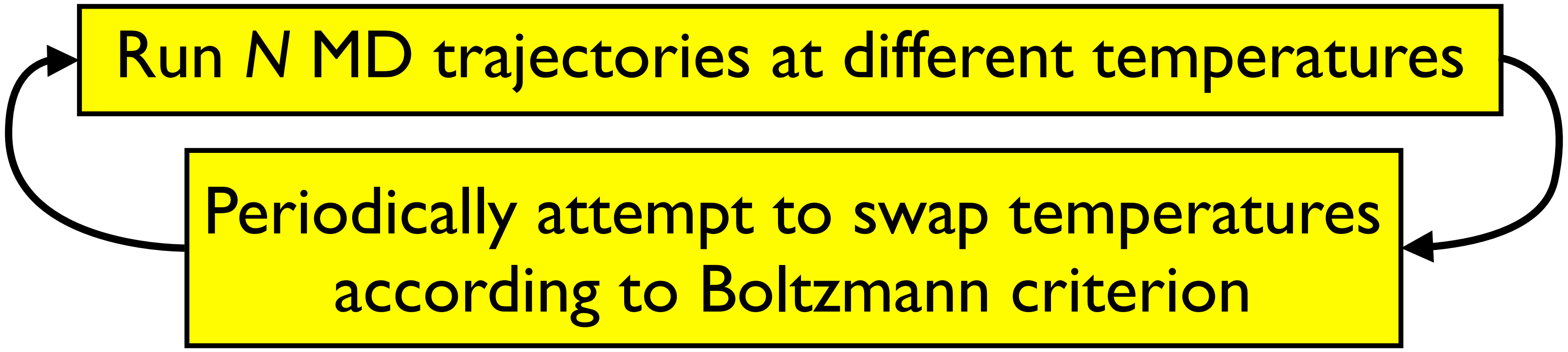

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But typical (even just to scan for structures):
100s of nanoseconds, O(10) trajectories
→ first principles??

Marinari, Parisi, Europhys. Lett ***19****, 451 (1992); U.H.E. Hansmann, Chem. Phys. Lett.* ***281****, 140 (1997); Y. Sugita, Y. Okamoto, Chem. Phys. Lett.* ***314****, 14 (1999); many others*

Coupling REMD & first principles:

<u>Strategy:</u>

"Global" FF REMD (e.g., 500 ns × 16 trajectories)

(Gromacs OPLS-AA)

Postrelax, reweight $O(10^3)$ midpoint structures by DFT-PBE+vdW

"Local" *ab initio* REMD for few "best" conformers DFT-PBE+vdW, 10-20 ps × 16 trajectories

ai-REMD in FHI-aims: Luca Ghiringhelli, FHI

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For:

Monomers
Dimers
Helices with "mobile proton"
"Unlikely α-helix" with proton at LysH^+

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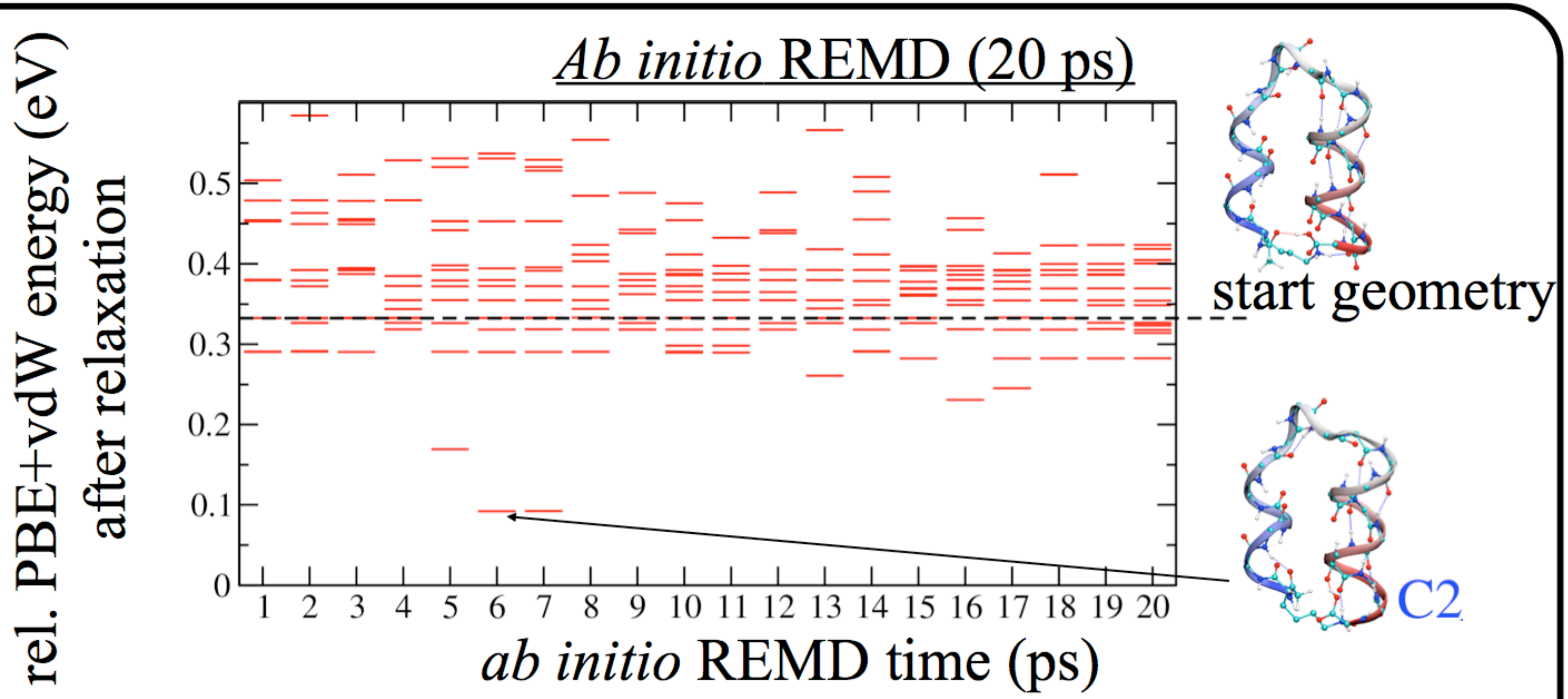

Ab initio REMD (20 ps)

→ rearrange local bond networks (termination!) successfully

Conformation prototypes vs. IRMPD: (1) Helical monomers

Theory-theory comparison, harmonic:

$\underline{\text{Ac-LysH}^+\text{-Ala}_{19} \leftrightarrow \text{Ac-Ala}_{19}\text{-LysH}^+}$

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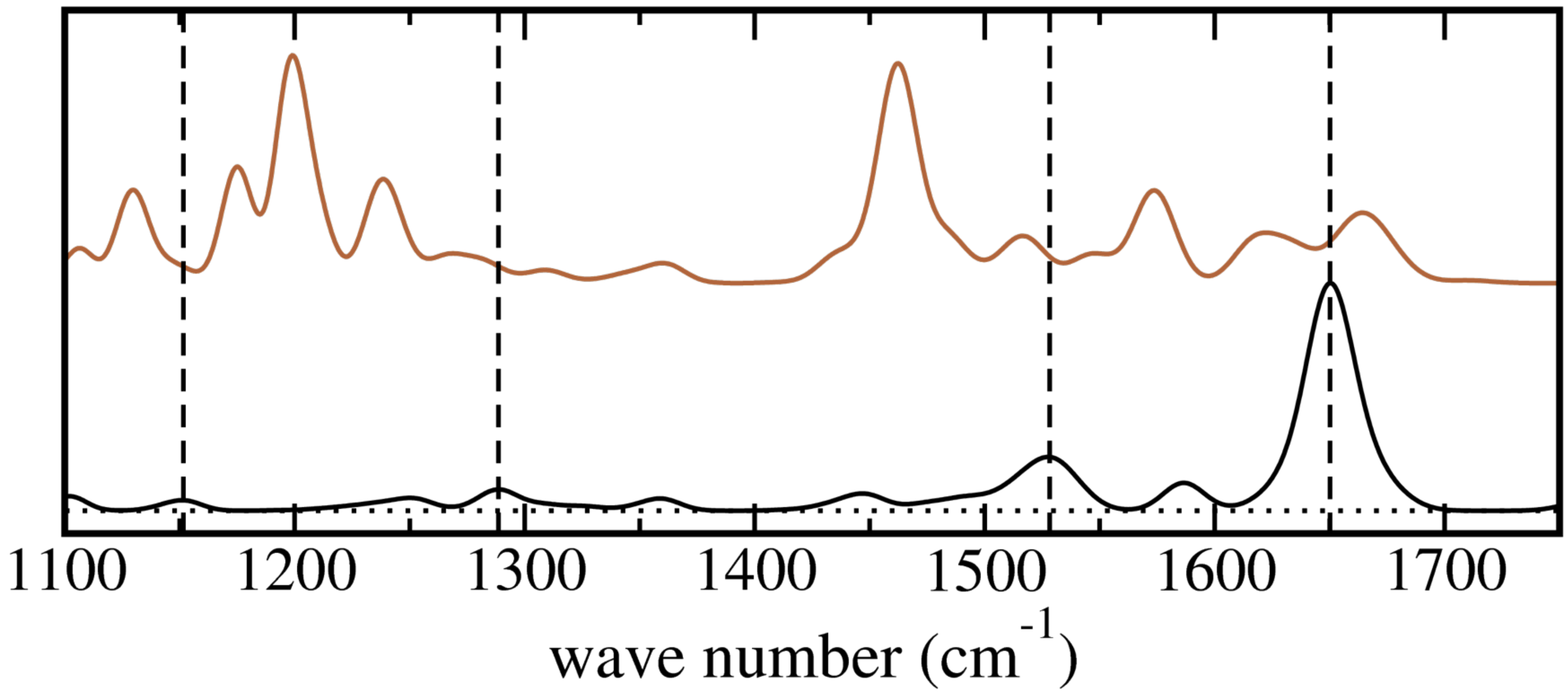
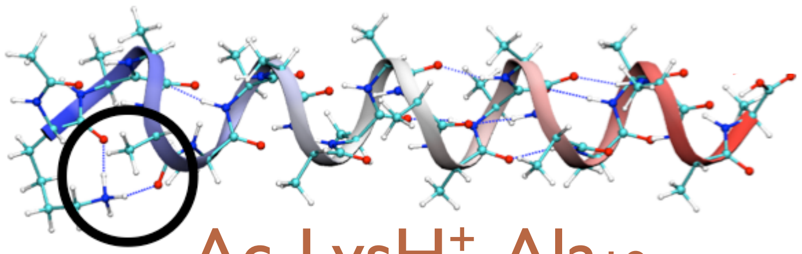
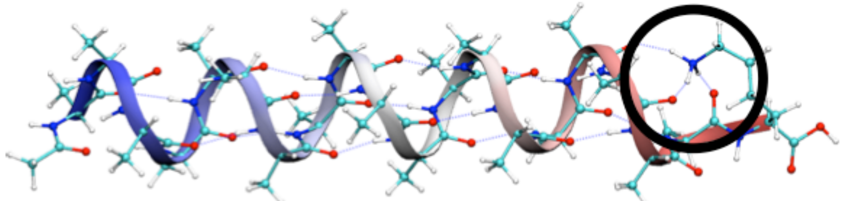




Ac-LysH$^+$-Ala$_{19}$
proton at N terminus



Ac-Ala$_{19}$-LysH$^+$
helix

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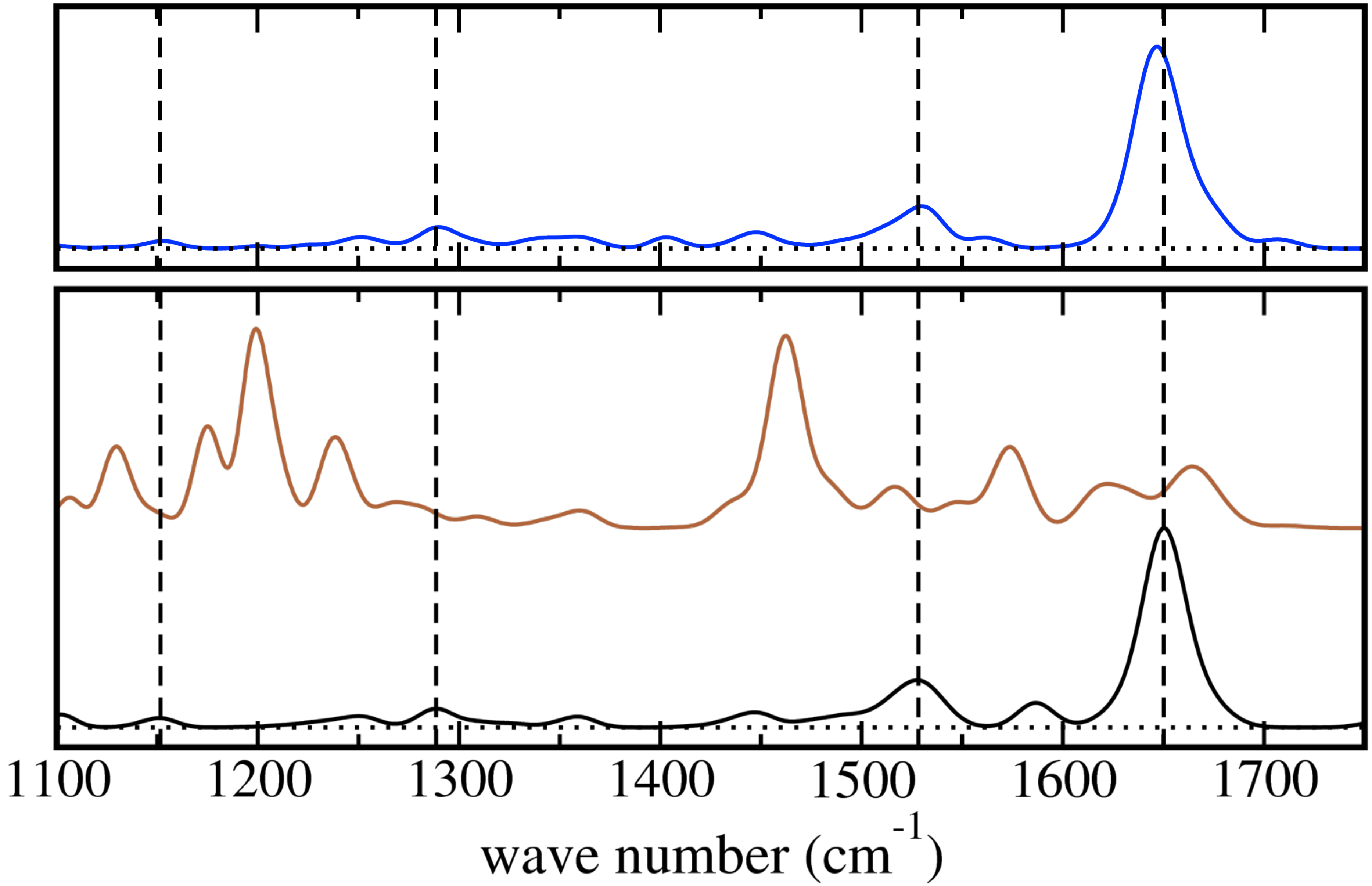
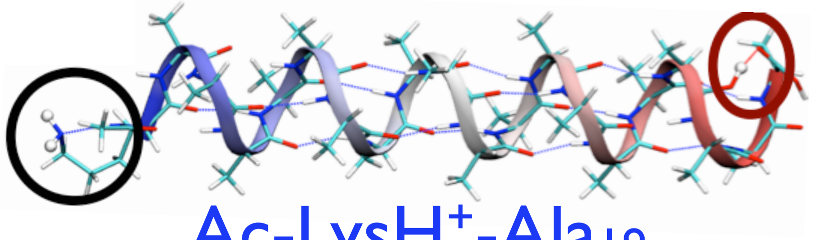
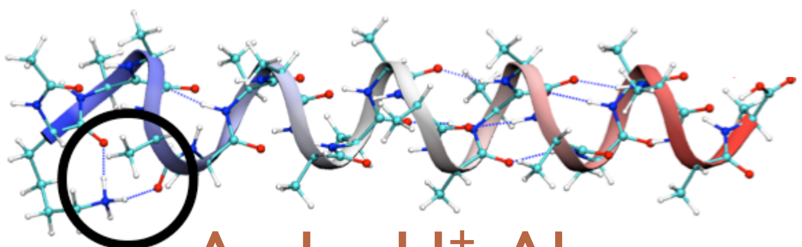




Ac-LysH$^+$-Ala$_{19}$
proton at C terminus



Ac-LysH$^+$-Ala$_{19}$
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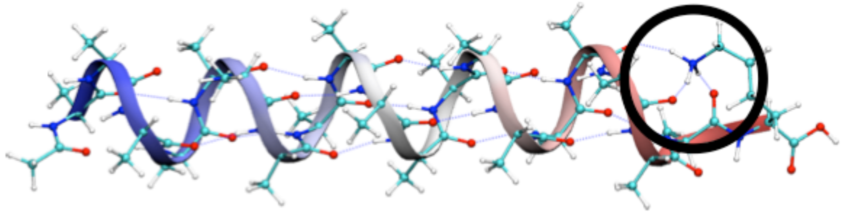


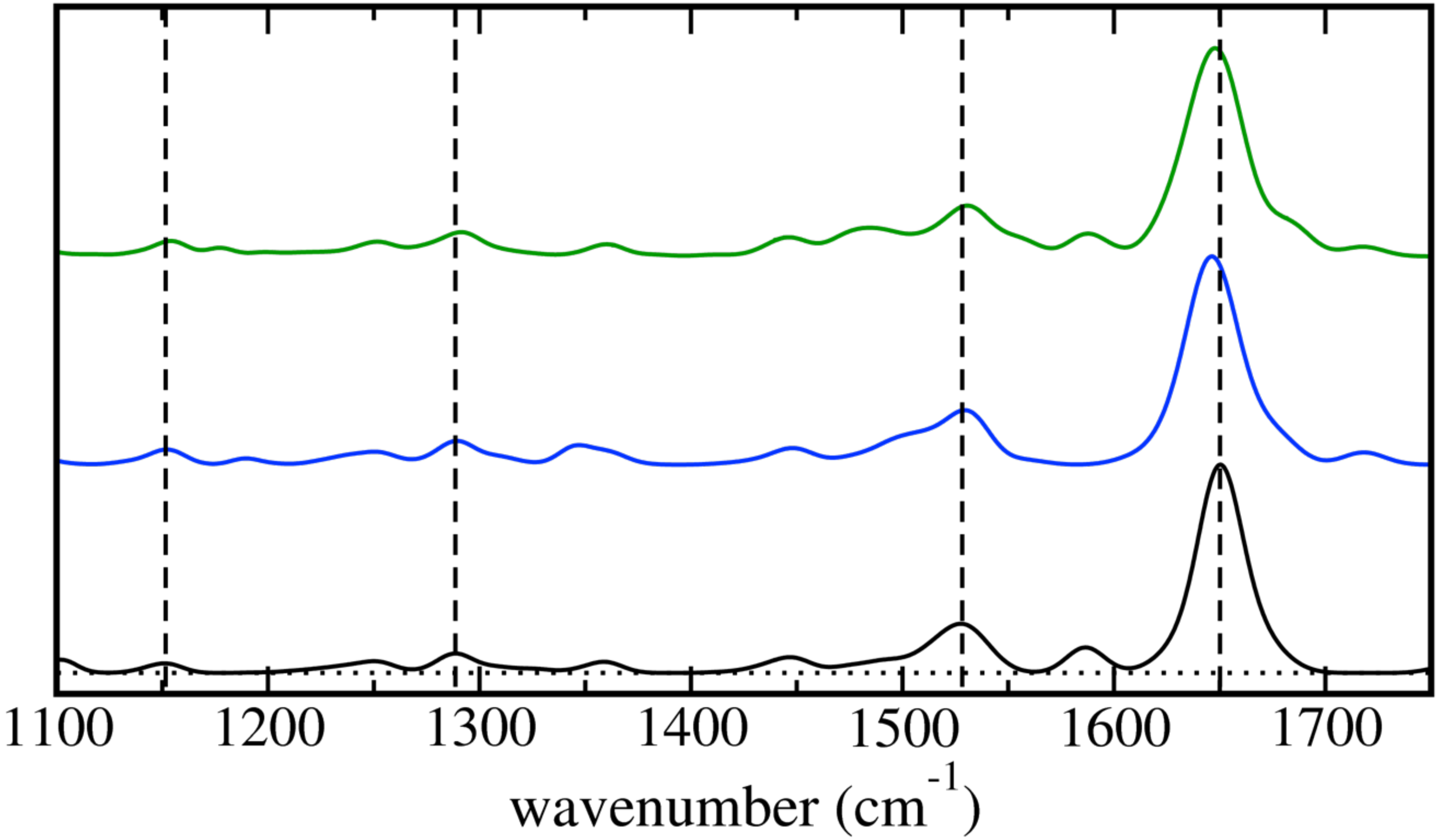
Ac-Ala$_{19}$-LysH$^+$
helix

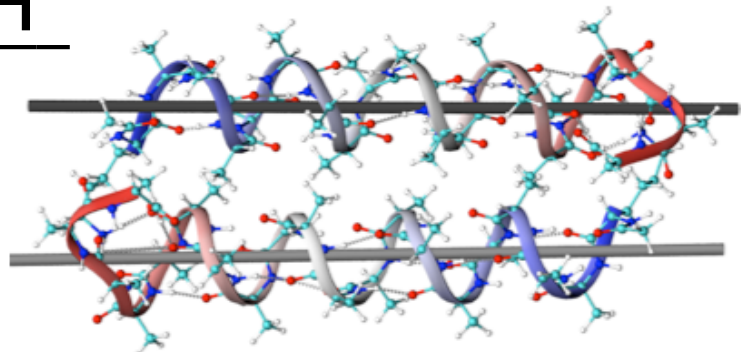
1) "Just helical" models: Need C-terminus proton. No Amide-II shift.

Conformation prototypes vs. IRMPD: (2) Helical dimers

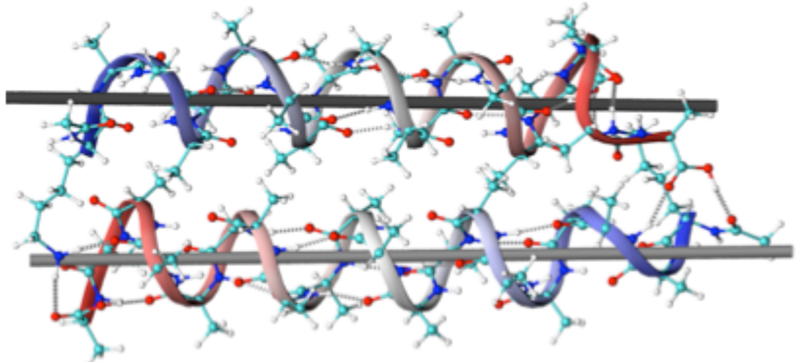
Theory-theory comparison, harmonic:

Ac-LysH$^+$-Ala$_{19}$ ↔ Ac-Ala$_{19}$-LysH$^+$

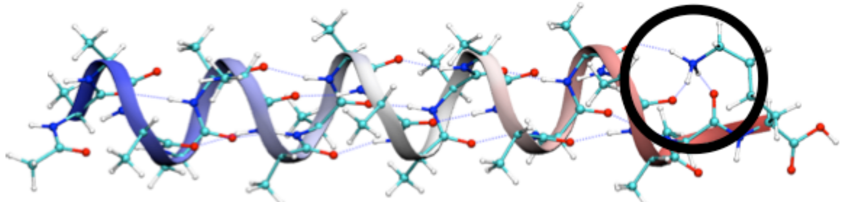




Ac-Ala$_{19}$-LysH$^+$, dimer 2



Ac-Ala$_{19}$-LysH$^+$, dimer 1

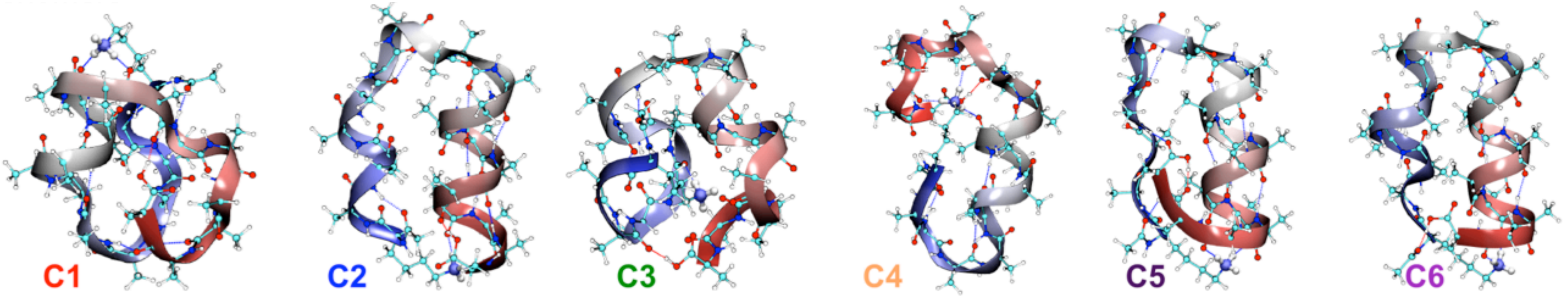


Ac-Ala$_{19}$-LysH$^+$
helix

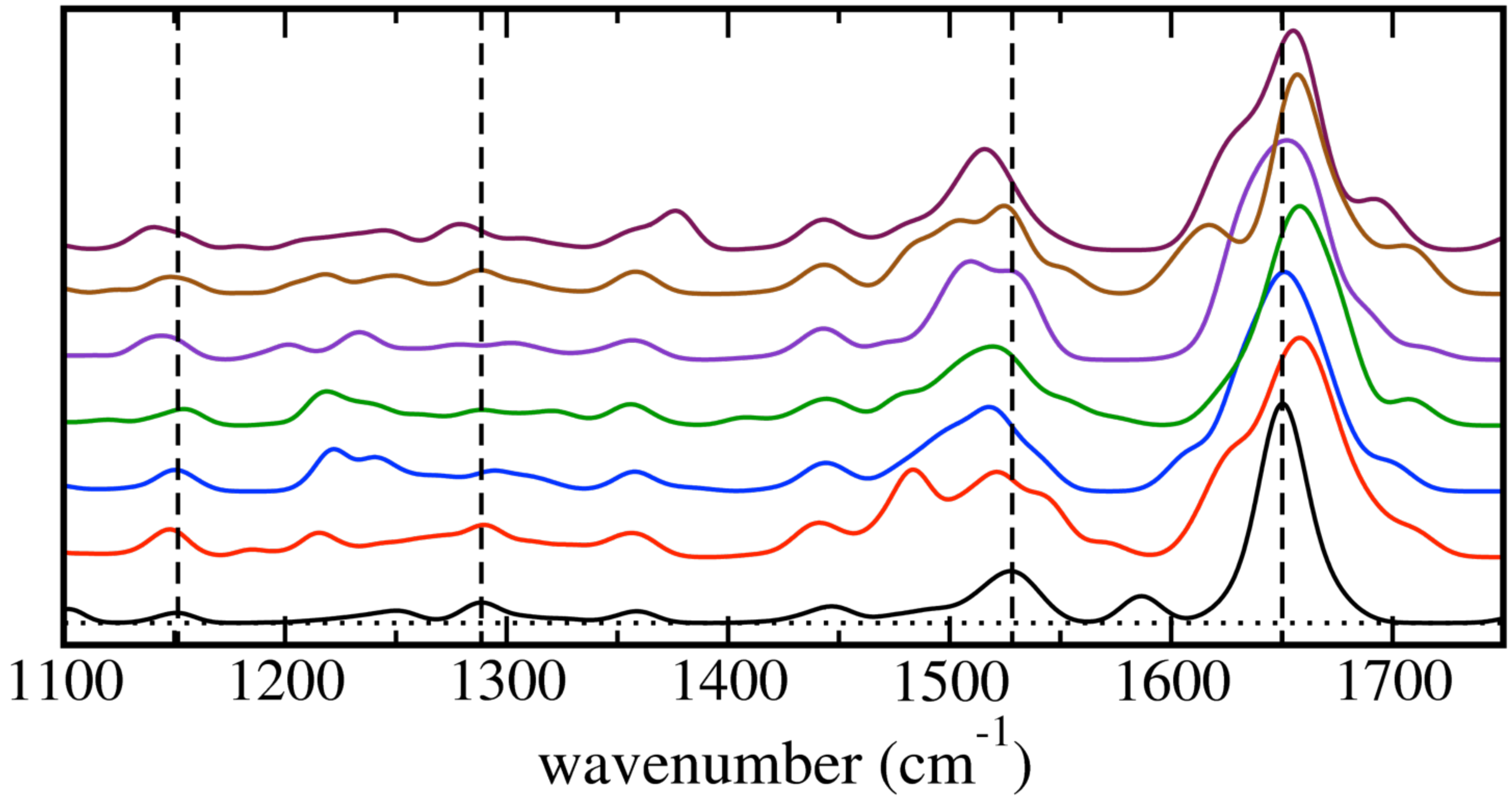
2) “Best dimer” models: Plausible, but no Amide-II shift.

Conformation prototypes vs. IRMPD: (3) *Any* monomers

Plenty of options close in (harmonic) free energy:

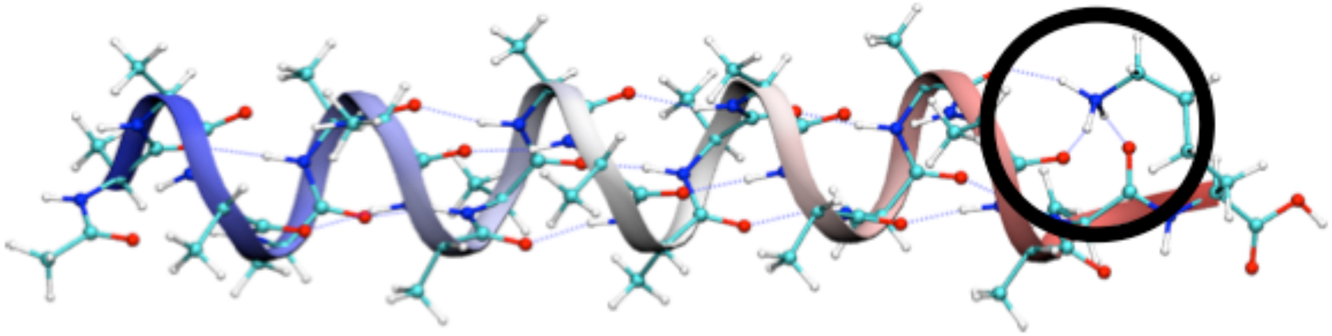


ΔF (300K) 0.0 0.06 eV 0.09 eV 0.15 eV 0.09 eV 0.12 eV



3) *Many* possible monomers.
Amide-II shift.

Upshot: Ac-Ala$_{19}$-LysH$^+$ vs. Ac-LysH$^+$-Ala$_{19}$



Ac-Ala$_{19}$-LysH$^+$:

“Helix seeker” - Alanine likes helices, and proton at electrostatically favorable end

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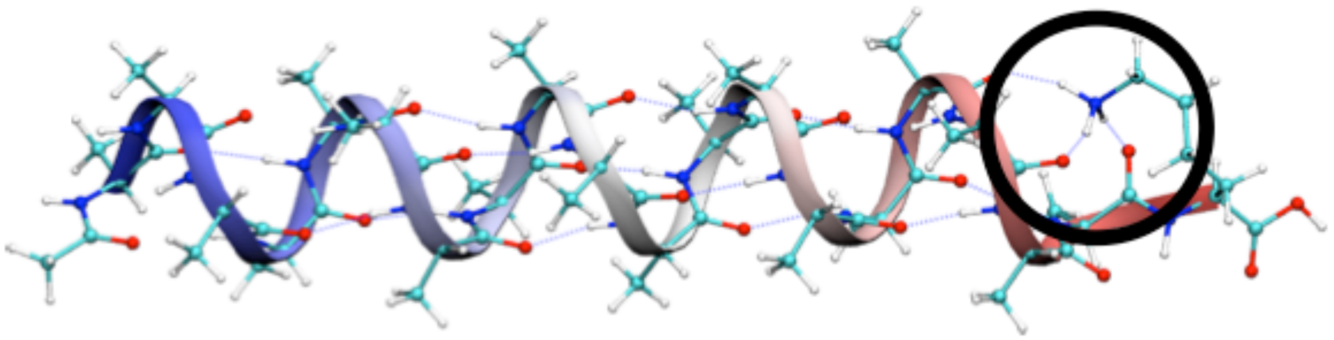

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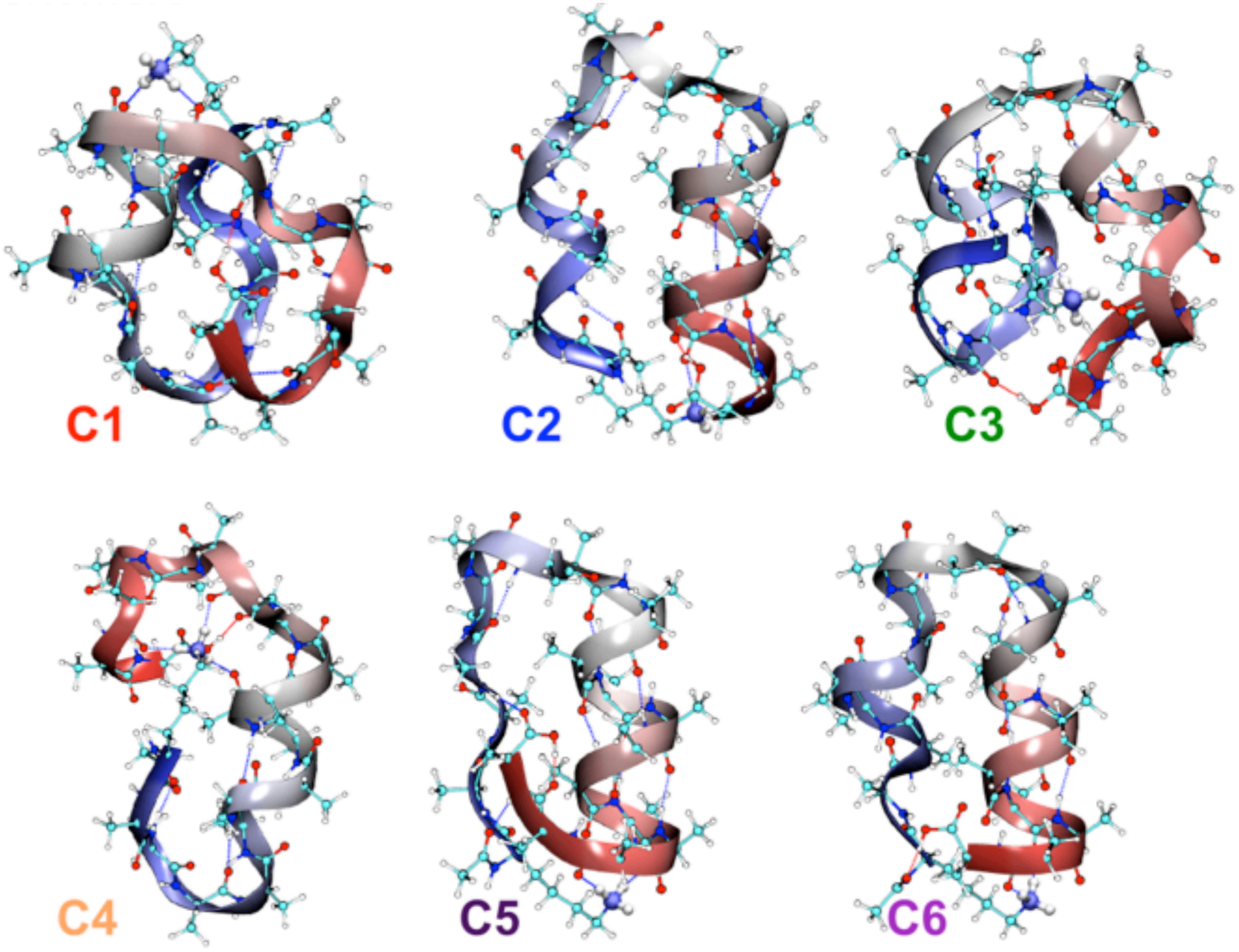


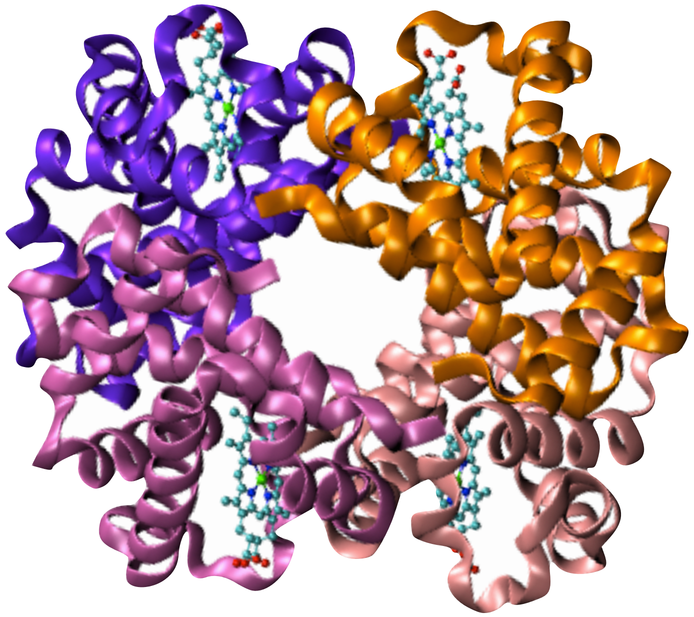
Ac-LysH$^+$-Ala$_{19}$

“Frustrated helix seeker” - Alanine likes helices, but proton at “wrong” end

→Mix of energetically similar “bent” helix segments that twist proton to “right” end of helix explains spectra!

Cold, not so dense world: Challenges

Hemoglobin
("Real" protein)



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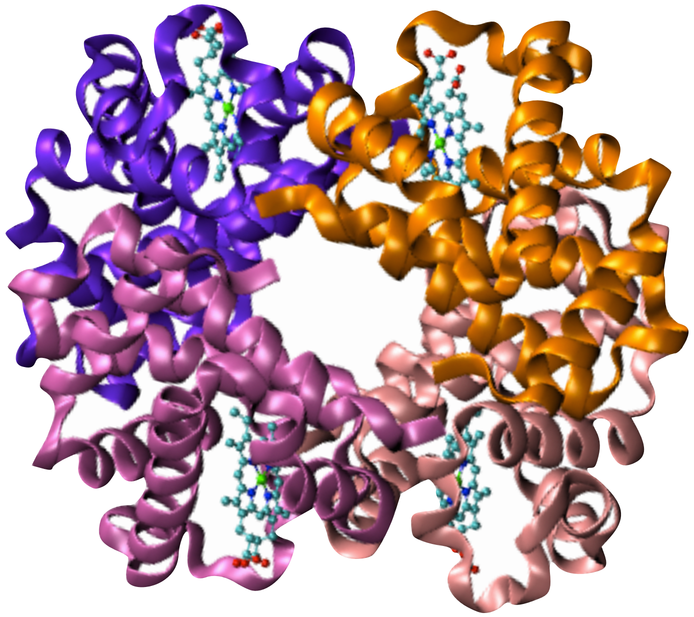

"Trivial": System sizes, simulation times -
~100 picoseconds, ~1000 atoms is still low end

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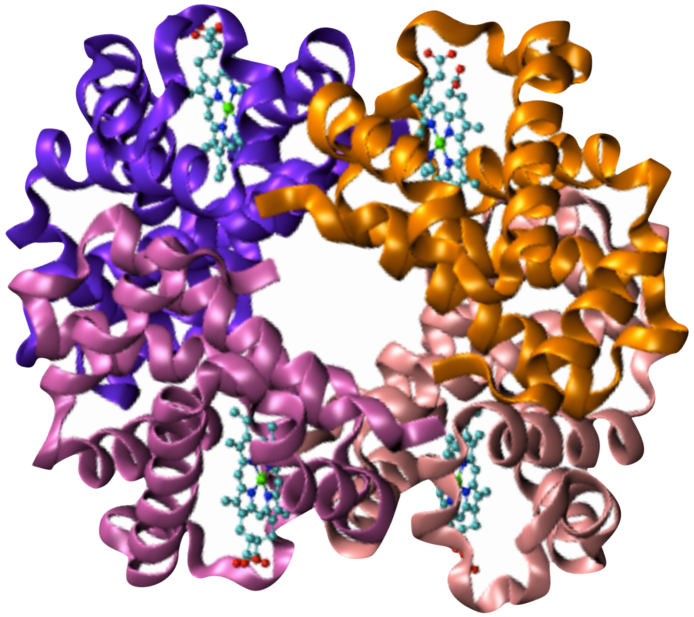

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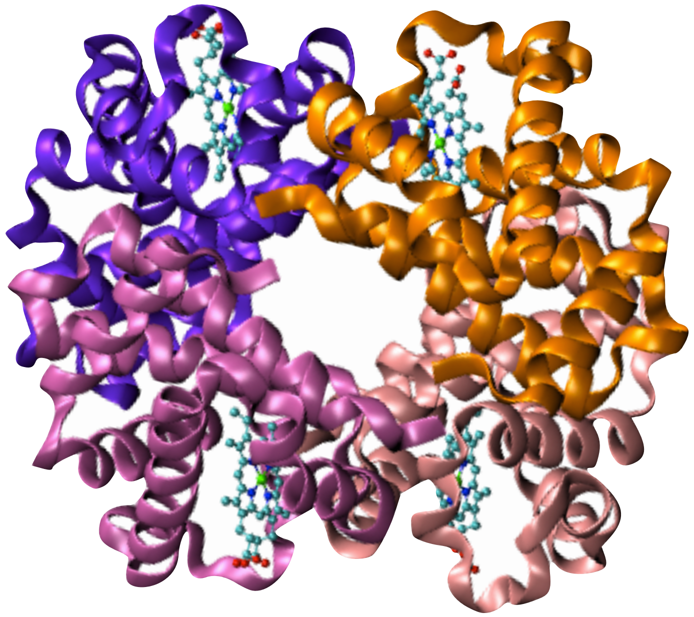

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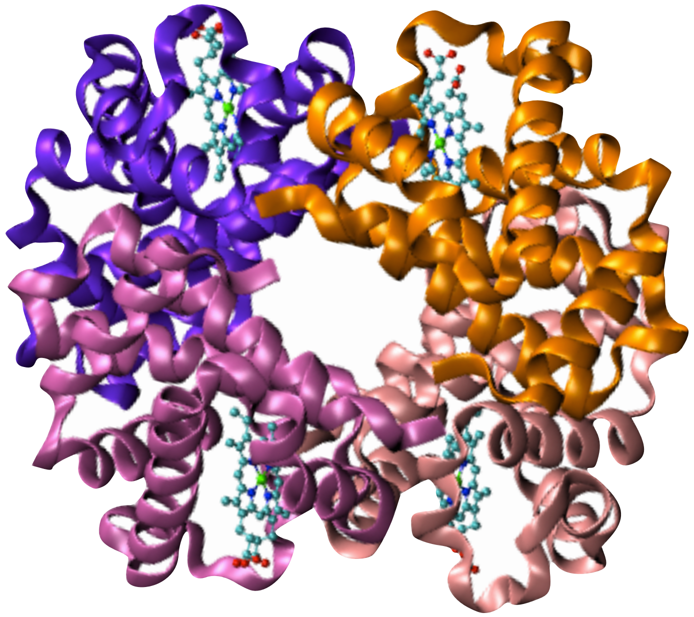

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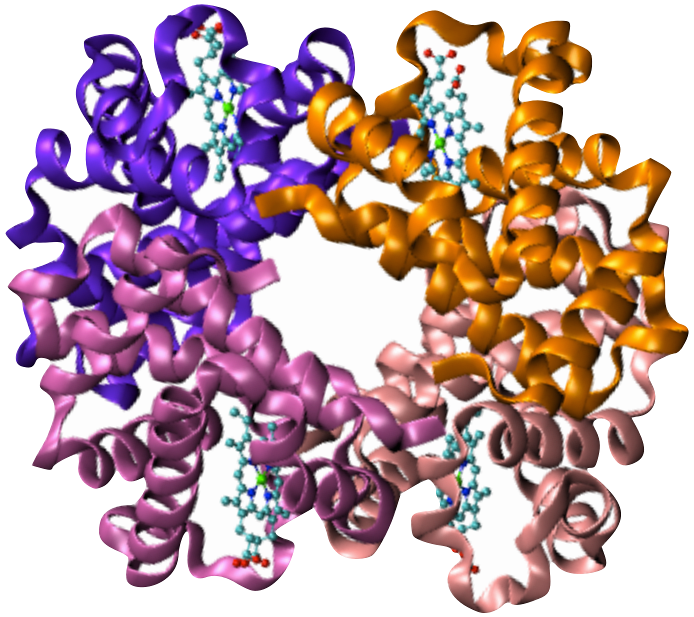

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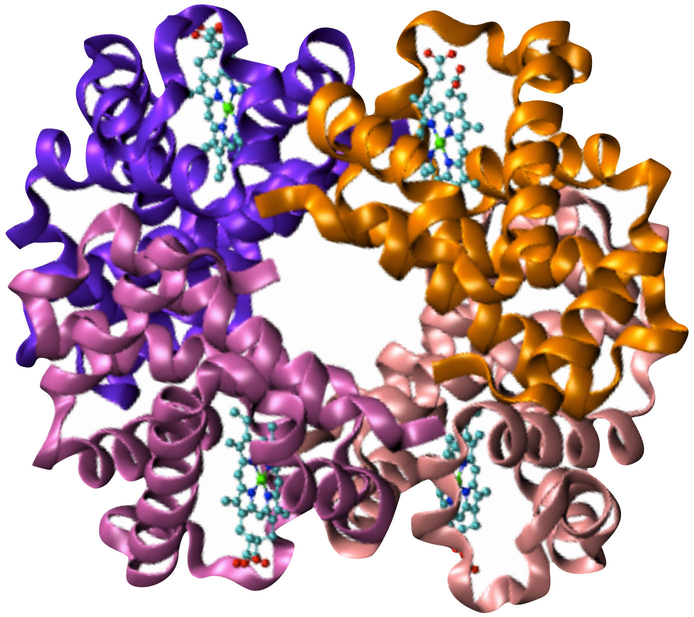

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Most of these sound suspiciously like "warm, (somewhat) dense" as well!

Warm, dense: “Hopes” and challenges

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- Sound, accurate basis sets, elements 1-102

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S.B. Carroll, Science 316, 1427 (2007)

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S.B. Carroll, Science 316, 1427 (2007)

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- For *very dense* conditions, add basis functions for low-distance limit?
- Are sums over high-lying states really the way?

So where are we at?

- Sound, accurate basis sets, elements 1-102
- Basic numerical techniques for DFT
  Real-space integrals, Poisson equation, scalar relativity etc. *(Becke, Delley, Baerends, many others)*
- Non-periodic, periodic boundary conditions on exactly equal footing
- "Properties": Structure optimization, *ab initio* molecular dynamics, vibrations/phonons, spectroscopy, etc.
- LDA, GGA, van der Waals corrections, hybrid functionals, Hartree-Fock+MP2, RPA, *GW*, ...
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Thank you!