Polyalanine: Infinite periodic structure prototypes

Textbook (bio-)chemistry (Corey/Pauling 1951, others) 
... will accompany us as benchmark systems in this talk
All-electron electronic structure theory - scope

Wishlist for electronic structure theory:

- First- / second-row elements
- 3d transition metals (magnetism)
- 4d / 5d transition metals (incl. relativity)
- f-electron chemistry
- periodic and cluster systems on equal footing
- all-electron

... and all this in an accurate, efficient computational framework!

The Kohn-Sham Equations

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

“As (almost) everyone does”:

1. Pick basis set \( \{ |\varphi_i\rangle \} \):
   \[ \psi_k(r) = \sum_i c_{ki} |\varphi_i\rangle \]
   \( \rightarrow \) generalized eigenvalue problem:
   \[ \hbar^2 c_k = \epsilon_k \sum_i c_{ki} \]
   \[ h_{ij} = \langle \varphi_i | \hat{h}_{\text{KS}} | \varphi_j \rangle \]
   \[ s_{ij} = \langle \varphi_i | \varphi_j \rangle \]

2. Self-consistency:
   Initial guess: e.g., \( c_{ki}^{(0)} \)
   Update density \( n^{(m)}(r) \)
   Update \( v_{\text{es}}^{(m)}, v_{\text{xc}}^{(m)} \)
   \[ h_{ij}^{(m)} = \int d^3r \varphi_i(r) \hat{h}_{\text{KS}}^{(m)} \varphi_j(r) \]
   Solve for updated \( c_{ki}^{(m+1)} \)

R. Gehrke
Tue 11:30h
Electronic Structure Basis Sets

\[ \psi_k(r) = \sum_i c_{ki} \varphi_i(r) \]

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

Many good options:

- **Plane waves**
  \[ \varphi_k(r) = \frac{1}{N} e^{ikr} \]
  
  → efficient FFT’s (density, electrostatics, XC-LDA/GGA)
  
  → inherently periodic
  
  → not all-electron (*Slater 1937*) - need “pseudoization”

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

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

- **Many others**: (L)MTO, grid-based, numeric atom-centered functions, ...

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Our choice [FHI-aims\(^1\)]: Numeric atom-centered basis functions

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

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

- **Free-atom like**: \( v_i(r) = v_{\text{free atom}}^{\text{DFT}}(r) \)

- **Hydrogen-like**: \( v_i(r) = z/r \)

- **Free ions, harm. osc. (Gaussians)**, ...

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\(^1\)The Fritz-Haber-Institute *ab initio molecular simulations* package

V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler,

Computer Physics Communications (2009) accepted

http://www.fhi-berlin.mpg.de/aims/
Our choice [FHI-aims1]: Numeric atom-centered basis functions

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

“LAPW-like accuracy and reliability - plane wave pseudopotential-like speed”

- All-electron
- Periodic, cluster systems on equal footing
- good scaling (system size & CPUs)
- Hybrid functionals, Hartree-Fock, MP2, RPA
- Quasiparticle self-energies: GW, MP2, ...

... but which particular basis functions should we use?

1) The Fritz-Haber-Institute ab initio molecular simulations package
V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler,
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Find 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
find basis sets for us?

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

Initial basis \{u\}^{(0)}:
Occupied free atom orbitals \(u_{\text{free}}\)

Search large pool of candidates \{u_{\text{trial}}(r)\}:
Find \(u_{\text{opt}}^{(n)}\) to minimize
\[ E^{(n)} = E[\{u\}^{(n-1)} \oplus u_{\text{trial}}] \]

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

until \(E^{(n-1)} - E^{(n)} < \text{threshold}\)
Iterative selection of NAO basis functions

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

Optimization target:
- Non-selfconsistent symmetric dimers, averaged for different \(d\)

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

Results: Hierarchical Basis Sets for All Elements

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>O</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>minimal</td>
<td>(1s)</td>
<td>[He](+2s2p)</td>
<td>[He](+2s2p)</td>
<td>[Xe](+6s5d4f)</td>
</tr>
<tr>
<td>Tier 1</td>
<td>H(2s,2.1)</td>
<td>H(2p,1.7)</td>
<td>H(2p,1.8)</td>
<td>Au(^{2+}) (6p)</td>
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<td></td>
<td>H(2p,3.5)</td>
<td>H(3d,6.0)</td>
<td>H(3d,7.6)</td>
<td>H(4f,7.4)</td>
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<tr>
<td></td>
<td>H(2s,4.9)</td>
<td>H(3s,6.4)</td>
<td>H(4f(^{2+}) (6s)</td>
<td>H(5g,10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H(6h,12.8)</td>
<td>H(3d,2.5)</td>
</tr>
<tr>
<td>Tier 2</td>
<td>H(1s,0.85)</td>
<td>H(4f,9.8)</td>
<td>H(4f,11.6)</td>
<td>H(5f,14.8)</td>
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<td>H(2p,3.7)</td>
<td>H(3p,5.2)</td>
<td>H(3p,6.2)</td>
<td>H(4d,3.9)</td>
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<tr>
<td></td>
<td>H(2s,1.2)</td>
<td>H(3s,4.3)</td>
<td>H(3d,5.6)</td>
<td>H(3p,3.3)</td>
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<tr>
<td></td>
<td>H(3d,7.0)</td>
<td>H(5g,14.4)</td>
<td>H(5g,17.6)</td>
<td>H(1s,0.45)</td>
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<tr>
<td></td>
<td>H(3d,6.2)</td>
<td>H(1s,0.75)</td>
<td>H(5g,16.4)</td>
<td>H(6h,13.6)</td>
</tr>
<tr>
<td>Tier 3</td>
<td>H(4f,11.2)</td>
<td>H(2p,5.6)</td>
<td>O(^{2+}) (2p)</td>
<td>H(4f,5.2)*</td>
</tr>
<tr>
<td></td>
<td>H(3p,4.8)</td>
<td>H(2s,1.4)</td>
<td>H(4f,10.8)</td>
<td>H(4d,5.0)</td>
</tr>
</tbody>
</table>

Systematic hierarchy of basis (sub)sets

- "First tier"
- "Second tier"
- "Third tier"
Transferability: \((\text{H}_2\text{O})_2\) hydrogen bond energy

\[ \leftrightarrow 2 \quad (\quad) \]

(a) PBE

\[
\text{H}_2\text{O}-\text{H}_2\text{O} \text{ binding energy [eV]}
\]

\[
\begin{array}{c|c|c|c|c|c|c}
\text{H}_2\text{O}-\text{H}_2\text{O} & \text{binding energy} & \text{Basis size} \\
\hline
\text{minimal} & -0.5 & 0 \\
\text{tier 1} & -0.4 & 100 \\
\text{tier 2} & -0.3 & 200 \\
\text{tier 3} & -0.2 & 300 \\
\end{array}
\]

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

But how about “Basis Set Superposition Errors”? 

Traditional quantum chemistry: “Basis set superposition errors”

- e.g.: Binding energy \( E_b = E(\quad) - 2E(\quad) \)

Problem:
- \( \bullet \) has larger basis set than \( \bullet \).
- Distance-dependent overbinding!

Remedy: “Counterpoise correction”

\[ \Delta E_{\text{BSSE}} = E(\quad) - E(\quad) \]

No nucleus - basis functions only

NAO basis sets: \( \bullet \) is already exact \( \Rightarrow \) no BSSE for \( \bullet \).
But how about molecular BSSE?
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**
  \[ h_{ij} = \int d^3r \varphi_i(r) \hat{h}_{\text{KS}} \varphi_j(r) \]

- **Electron density update**
  \[ n(r) = \sum_k f_k |\psi_k(r)|^2 \]

- **All-electron electrostatics**
  \[ v_{\text{es}}(r) = \int d^3r' \frac{n(r')}{|r - r'|} \]

- **Eigenvalue solver**
  \[ \hbar c_k = \epsilon_k s c_k \]

- **Relativity?**
  *needed for heavy elements*

- **Periodic systems?**
  *need suitable basis, electrostatics*
**Numeric Atom-Centered Basis Functions: Integration**

\[ h_{ij} = \int d^3 r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

- **Discretize to integration grid:** \[ \int d^3 r f(r) \rightarrow \sum_r w(r) f(r) \]

... 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”**

\[ h_{ij} = \int d^3 r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

- **Rewrite to atom-centered integrands:**
  \[ \int d^3 r f(r) = \sum_{\text{atoms}} \int d^3 r p_{\text{atom}}(r) f(r) \]
  
  **exact:** \[ \sum_{\text{atoms}} p_{\text{atom}}(r) = 1 \]
  
  **through** \[ p_{\text{atom}}(r) = \frac{g_{\text{atom}}(r)}{\sum_{\text{atom}} g_{\text{atom}}(r)} \]

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

**many alternatives:**
Becke 1988, Stratmann 1996, Koepernik 1999, ...
Integrals in practice: Any problem?

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

Integration error

Integration points per radial shell

Hartree potential (electrostatics): Same trick

\[ v_{es}(\vec{r}) = \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \]

- Partitioning of Unity:
  \[ n(\vec{r}) = \sum_{\text{atoms}} p_{\text{atom}}(\vec{r}) n(\vec{r}) \]

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

- Classical electrostatics:
  \[ v_{es}(\vec{r}) = \sum_{\text{atoms}} \sum_{lm} v_{\text{atom},lm}(|\vec{r} - \vec{R}_{\text{atom}}|) Y_{lm}(\Omega_{\text{atom}}) \]

  e.g., Delley, JCP 92, 508 (1990)
Electrostatics: Multipole expansion

\[ v_{es}(\mathbf{r}) = \sum_{\text{atoms}} \sum_{lm} v_{\text{atom},lm}(|\mathbf{r} - \mathbf{R}_{\text{atom}}|) Y_{lm}(\Omega_{\text{atom}}) \]

Polyalanine Ala\textsubscript{20}, DFT-PBE (203 atoms!)
\[ \alpha \text{-helical vs. extended: Total energy convergence with } l_{\text{max}} \]

Periodic systems

- Formally: Bloch-like basis functions
  \[ \chi_{i,k} = \sum_{N} \exp[ikT(N)]\varphi_{i}[\mathbf{r} - \mathbf{R}_{\text{atom}} + T(N)] \]
  \( k \): “Crystal momentum” = Quantum number in per. systems

- Long-range Hartree potential: Ewald’s method (1921)
  \[ v_{\text{atom},lm}(\mathbf{r}) \rightarrow v_{\text{atom},lm}(\mathbf{r}) - v_{\text{Gauss}}^{\text{atom},lm}(\mathbf{r}) + \sum_{G} e^{iGr} \text{FT}[v_{\text{Gauss}}^{\text{G}}] \]
  short-ranged real-space part - \( O(N) \)

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

see P. Kratzer
Wed. 9:00
... but how does it all scale?

Fully extended Polyalanine, “light”

![Graph showing time per S.C.F. iteration vs. Atoms in structure.](image)

<table>
<thead>
<tr>
<th>Basis</th>
<th>tier 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>h_{Hartree}</td>
<td>4</td>
</tr>
<tr>
<td>radial shells</td>
<td>24-36</td>
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<tr>
<td>pts. per shell</td>
<td>194 max.</td>
</tr>
<tr>
<td>Cutoff width</td>
<td>5Å</td>
</tr>
</tbody>
</table>

see V. Havu
Tue 9:00
... but how does it all scale?

**Fully extended Polyalanine, “light”**

![Graph showing time per s.c.f. iteration vs. atoms in structure.](image)

- **Basis**: tier 1
- **\( \hbar \text{hartree} \)**: 4
- **Radial shells**: 24-36
- **Pts. per shell**: 194 max.
- **Cutoff width**: 5Å

see V. Havu
Tue 9:00

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**\( \alpha \)-helical Polyalanine, “tight”**

- **Basis**: tier 1, tier 2
- **\( \hbar \text{hartree} \)**: 4, 6
- **Radial shells**: 24-36, 49-73
- **Pts. per shell**: 194 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
- 1000s of CPUs: Scaling bottleneck?

see V. Havu
Tue 9:00
Towards the “petaflop”: Tackling the eigenvalue solver

IBM BlueGene (MPG, Garching)
16384 CPU cores, #9 on Green500

Total time/s.c.f. iteration
(ScaLapack-based)

Eigenvalue solver
(ScaLapack, DC)
Matrix dim.: 27000

Going (massively) parallel: Towards the “petaflop”

DC eigenvalue solver, 1st step: straight, optimized rewrite!
There is some life left in “conventional” solvers yet!

Ongoing work: with R. Johanni (RZG), Ville Havu (Helsinki), BMBF project "ELPA"
Relativity

Non-relativistic QM: Schrödinger Equation

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

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

Relativistic QM: Dirac Equation

\[
\begin{pmatrix}
V \\
\sigma \cdot \mathbf{p} + c^2 - 2c^2 + V
\end{pmatrix}
\begin{pmatrix}
\phi \\
\chi
\end{pmatrix}
= \epsilon
\begin{pmatrix}
\phi \\
\chi
\end{pmatrix}
\]

- \(\epsilon\)-dependent Hamiltonian
- Not negligible for \(\epsilon - V(r) \approx 2c^2\)
- \(\epsilon\) affects near-nuclear part of any wave function

Implementing scalar relativity

\[ V\phi + \frac{\mathbf{p}^2}{2c^2} \phi = \epsilon \phi \]

ZORA in practice: Harsh approximation (known)

1. LAPW, others: Outright treatment
   \(\rightarrow\) radial functions in atomic sphere (core, valence): Per-state relativistic
   \(\rightarrow\) 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]

Fixing ZORA

1. “Atomic ZORA”
   - No gauge-invariance problem
   - Simple total-energy gradients

2. Scaled ZORA
   - 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

Viable strategy:
- Geometry optimization: atomic ZORA (simple gradients)
- (Final) total energies, eigenvalues: scaled ZORA
Outlook: Beyond scaled ZORA with NAO’s

\[ V\phi + \frac{\mathbf{p}^2 c^2}{2} + V\mathbf{p} \phi = \epsilon \phi \]

Koelling-Harmon relativistic energies for NAO’s:

1. Deep core states (non-overlapping): **On-site basis functions only** (no shape restriction!)
2. Numerically stable per-state core kinetic energy:
3. Remaining states: **scaled ZORA**

<table>
<thead>
<tr>
<th>Au atom, LDA: ( E_{\text{tot}} ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>sc. ZORA.</td>
</tr>
<tr>
<td>- 517,036.15</td>
</tr>
<tr>
<td>+ KH (1s)</td>
</tr>
<tr>
<td>- 517,048.70</td>
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<tr>
<td>+ KH (2s,2p)</td>
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<td>- 517,052.81</td>
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<td>+ KH (3s,3p,3d)</td>
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<td>- 517,053.42</td>
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<tr>
<td>+KH (4s,4p,4d)</td>
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<td>- 517,053.44</td>
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<tr>
<td>full KH</td>
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<tr>
<td>- 517,053.45</td>
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</tbody>
</table>

Koelling-Harmon scalar relativity with NAOs: \( \text{Au}_2 \)

Stable physical results for increasingly “correct” core - yet now
- correct (KH) total energies
- correct (KH) core eigenvalues, Kohn-Sham wave fns., densities
- path to further improvements (small component; Dirac core; ...)

Au dimer - LDA

<table>
<thead>
<tr>
<th>Binding energy [eV]</th>
<th>Binding distance [Å]</th>
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<tbody>
<tr>
<td>2</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>2.4</td>
</tr>
<tr>
<td>4</td>
<td>2.6</td>
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<tr>
<td>4.5</td>
<td>2.8</td>
</tr>
<tr>
<td>4.5</td>
<td>3.0</td>
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</table>

LAPW

scaled ZORA

Koelling-Harmon: 1s

Koelling-Harmon: 4s,4p,4d
Summary

Density functional theory and beyond with FHI-aims:
Versatile all-electron framework across the periodic table

Compact, hierarchical, transferable basis sets
“fast qualitative” up to meV accuracy (ground-state DFT)

Proven real-space algorithms
efficient, but always verifiable accuracy

Ongoing - “DFT and beyond” with FHI-aims

Large (bio)molecules & clusters
Forces, scf stability:
R. Gehrke (K. Reuter)
Vibrations, MD, IR spectra:
F. Hanke, M. Rossi, L. Ghiringhelli

Numerical efficiency
Localization & parallelization: V. Havu
Eigenvalue solvers:
V. Havu, R. Johanni

Periodic systems & heavy elements
Energy and forces, relativity:
P. Havu

“Computational spectroscopy”:
GW & MP2 self-energies:
X. Ren (P. Rinke)
STM: S. Levchenko
Core levels (XAS):
M. Gramzow (K. Reuter)

FHI-aims
Core concepts and strategy
V. Blum & M. Scheffler

“Beyond DFT”:
Resolution of Identity:
X. Ren (P. Rinke)
MP2: A. Sanfilippo (K. Reuter)
RPA: X. Ren (P. Rinke)
Hybrid XC: S. Gutzeit, M. Rossi
van der Waals: A. Tkatchenko, M. Yoon