The Nuts and Bolts of Electronic Structure Theory
Basis Sets, Real-Space Grids, Relativity, Scalability

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Fritz Haber Institute of the Max Planck Society
Berlin, Germany

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

Hands-On Tutorial Workshop “DFT and Beyond”- ICTP, Trieste, August 07, 2013
Is This a “Stable” Surface Phase?*

Graphene on SiC(0001)
van Bommel, Crombeen, van Tooren,
Surf. Sci. 1975
many others

(13x13) graphene on
SiC(0001)-(6√3×6√3)R30°

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

* under some conditions ...
Scope of this Talk

Kohn-Sham Equations, 1965

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

General concepts:

• Basis sets

• Integrals and grids; electrostatics; molecules vs. periodic solids

• Scalar relativity

• Eigenvalue solution, scalability (large systems, large computers)

Our implementation: FHI-aims

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

Similar pieces for Hartree-Fock & hybrids, many-body methods etc. → S. Levchenko, Fri 09:00 h
2004 - Wishlist for a New Electronic Structure Code

Cover the entirety of materials / chemistry:

“Materials and molecules” - periodic (k-space) and non-periodic

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

All-electron

Scalable (system size, number of CPUs)

Efficient (1,000s of atoms), but do not sacrifice accuracy!
The Kohn-Sham Equations (again)

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

“As (almost) everyone does”:

1. Pick basis set \{\ket{\varphi_i}\}:

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

→ generalized eigenvalue problem:

\[
\hat{h} c_k = \epsilon_k s c_k
\]

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

\[
s_{ij} = \langle \varphi_i | \varphi_j \rangle
\]

2. Self-consistency:

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

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

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

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

Solve for updated \(c_{ki}^{(m+1)}\)
Representing the Orbitals: Basis Sets

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

... 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, “real-space”, numeric atom-centered functions, ...
Our Choice: 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.”

Many popular implementations:
DMol\(^3\) (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.), PAOs (Siesta, Conquest, OpenMX\(^2\), Fireball, ...)

- 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), ...

- cutoff potent.
Our Choice: 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.”

\[ \rightarrow \text{Localized; ”naturally” all-electron} \]

\[ \rightarrow \text{The choice of efficient and of enough radial functions is obviously important} \]

\[ \rightarrow \text{We have a basis set library for all elements (1-102), from fast qualitative to meV-converged (total energy, LDA/GGA) calculations - efficient and accurate approach} \]

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

Constructing a Basis Set Library for DFT

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

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

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

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

![Graph showing systematic buildup of basis set error](image)

Remaining basis set error

Blum et al., Comp. Phys. Commun. 180, 2175-2196 (2009)
## Result: Hierarchical Basis Set Library for All Elements

<table>
<thead>
<tr>
<th>Tier</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>Au²⁺(6p)</td>
</tr>
<tr>
<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>
</tr>
<tr>
<td></td>
<td>H(2s,4.9)</td>
<td>H(3s,6.4)</td>
<td>Au²⁺(6s)</td>
<td>H(5g,10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(6h,12.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></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>
</tr>
<tr>
<td></td>
<td>H(2p,3.7)</td>
<td>H(3p,5.2)</td>
<td>H(3p,6.2)</td>
<td>H(4d,3.9)</td>
</tr>
<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>
</tr>
<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></td>
<td>H(3d,6.2)</td>
<td>H(1s,0.75)</td>
<td>H(5g,16.4)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></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>O²⁺(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>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Systematic hierarchy of basis (sub)sets, iterative **automated** construction based on dimers**

- **First tier (level)**
- **Second tier**
- **Third tier**

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

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

**Basis sets: Radial fn. character**

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C,N,O</th>
</tr>
</thead>
<tbody>
<tr>
<td>minimal</td>
<td>1s</td>
<td>[He]+2s2p</td>
</tr>
<tr>
<td>tier 1</td>
<td>s,p</td>
<td>s,p,d</td>
</tr>
<tr>
<td>tier 2</td>
<td>s,p,s,d</td>
<td>s,p,d,f,g</td>
</tr>
<tr>
<td>tier 3</td>
<td>s,p,d,f</td>
<td>s,p,d,f</td>
</tr>
</tbody>
</table>
Transferability: Generally Not a Problem for DFT

Bulk Au: Cohesive properties

ZB GaAs, LDA: Cohesive energy [eV]

<table>
<thead>
<tr>
<th>Basis size</th>
<th>minimal tier 1 (min+spdf)</th>
<th>tier 1 (min+spdf)</th>
<th>tier 2 (+spdfgh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAPW 2009 (A)</td>
<td>8.09</td>
<td>8.06</td>
<td>7.99</td>
</tr>
<tr>
<td>LAPW 2009 (B)</td>
<td>8.00</td>
<td>8.06</td>
<td>7.99</td>
</tr>
<tr>
<td>PP 1998</td>
<td>8.15</td>
<td>8.06</td>
<td>7.99</td>
</tr>
</tbody>
</table>

5d(100) surfaces: $(1\times1) \rightarrow (1\times5)$

<table>
<thead>
<tr>
<th>reconstruction energy [meV/$1\times1$]</th>
<th>Pt(100)</th>
<th>Au(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>min+spdf</td>
<td>-65</td>
<td>-21</td>
</tr>
<tr>
<td>tier 1</td>
<td>-80</td>
<td>-30</td>
</tr>
<tr>
<td>tier 2</td>
<td>-83</td>
<td>-31</td>
</tr>
<tr>
<td>FP-LAPW</td>
<td>-89</td>
<td>-24</td>
</tr>
</tbody>
</table>

\(d_{\text{fcc}}, \text{Å}\)

\(B, \text{[MBar]}\)

\(E_{\text{coh}}, \text{[eV]}\)

1) Fuchs, Bockstedte, Pehlke, Scheffler, PRB 1998
Excursion: “Basis Set Superposition Errors”? 

Traditional quantum chemistry: “Basis set superposition errors”

e.g.: Binding energy $E_b = E(\text{\ball}-\text{\ball}) - 2E(\text{\ball})$

Problem: has larger basis set than . → Distance-dependent overbinding!

Remedy: “Counterpoise correction”

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

No nucleus - basis functions only

NAO basis sets: is already exact → no BSSE for . But how about molecular BSSE?
(H₂O)₂: “Counterpoise Correction”

Ground-State DFT, NAO’s: BSSE *not* the most critical basis convergence error (e.g., tier 2)*

*BUT* methods that sum over infinite continuum (MP2, RPA, ...) need CP C.!
Using Numeric Atom-Centered Basis Functions: Pieces

• Numerical Integration

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

• Electron density update

\[ n(r) = \sum_k f_k |\psi_k(r)|^2 \]

• All-electron electrostatics

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

• Eigenvalue solver

\[ \hbar c_k = \epsilon_k s c_k \]

• Relativity?


\textit{needed for heavy elements}

• Periodic systems?

\textit{need suitable basis, electrostatics}

• Coulomb operator?

\[ (ij|kl) = \int d^3rd^3r' \frac{\varphi_i(r)\varphi_j(r')\varphi_k(r)\varphi_l(r')}{|r - r'|} \]
Numeric Atom-Centered Basis Functions: Integration

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

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

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

- **Overlapping atom-centered integration grids:**
  - Radial shells (e.g., H, light: 24; Au, tight: 147)
  - Specific angular point distribution ("Lebedev")
    exact up to given integration order \(l\)
    (50, 110, 194, 302, .... points per shell)

Pioneered by
Becke JCP 88, 2547 (1988), Delley, JCP 92, 508 (1990), MANY others!
All-Electron Integrals: Rather Benign for NAOs

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

\( f(r) \) for NAO radial function:

- Carbon - 1s NAO
- “tight” radial grid for NAOs

\( f(r) \) for contracted Gaussian radial function:

- Carbon - 1s GTO cc-pV5Z
Overlapping Atom-Centered Grids: “Partitioning of Unity”

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

- **Rewrite to atom-centered integrands:**

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

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

Integration in Practice: Large Systems, Small Errors!

Fully extended Polyalanine peptide molecule Ala$_{20}$, DFT-PBE (203 atoms)
Hartree Potential (Electrostatics): Overlapping Multipoles

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

- Partitioning of Unity: (same trick as used for integrals)
  \[ n(r) = \sum_{\text{atoms}} p_{\text{atom}}(r)n(r) \]

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

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

*Delley, JCP 92, 508 (1990)*
Electrostatics: Multipole expansion

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

Polyalanine Ala\textsubscript{20}, DFT-PBE (203 atoms)

\( \alpha \)-helical vs. extended: Total energy convergence with \( l_{\text{max}} \)

(a) \( E_{\text{tot}}(\alpha \text{ helix}) \)

(b) \( E_{\text{tot}}(\text{extended}) \)

(c) Energy difference

Maximum angular momentum \( l \) in multipole expansion

\( \alpha \)

extended
• Formally: Bloch-like basis functions

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

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

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

\[ \psi_{\text{atom},lm}(r) \rightarrow \psi_{\text{atom},lm}(r) - \psi_{\text{Gauss}}^{\text{atom},lm}(r) + \sum_{\mathcal{G}} e^{\imath \mathbf{G} \mathbf{r}} F(T)[\psi_{\text{Gauss}}_{\text{atom},lm}] \]

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

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

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

Relativistic QM: Dirac Equation

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

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

... simply rewrite:

\[ V\phi + \sigma \cdot p \frac{c^2}{2c^2 + \epsilon - V} \sigma \cdot p\phi = \epsilon\phi \]
Simple Approximation to Scalar Relativity

1. LAPW, others: Outright treatment
   \[ V\phi + \frac{p \cdot c}{2\alpha^2} + V \cdot p \phi = \epsilon \phi \]
   - 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]
   

ZORA in practice: Harsh approximation (known)

### Binding energy [eV] vs. Binding distance [Å]

- Au dimer - LDA
- Nonrel.: LAPW, FHI-aims
- Relativistic: LAPW, ZORA

In non-gauge-invariant
Fixing ZORA

1. "Atomic ZORA"

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

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

2. Scaled ZORA

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

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

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

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

E. van Lenthe et al., JCP 101, 9783 (1994).
Atomic ZORA and Scaled ZORA in Practice

Viable strategy: • Geometry optimization, energy differences: atomic ZORA
• (Final) total energies, eigenvalues: scaled ZORA

In our own benchmarks, seem to be essentially as accurate as LAPW.
Computational Scaling: Two Sub-Problems

I. Real space grid operations

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

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


II. Matrix algebra (basis space)

\[ \hat{h} c_k = \epsilon_k s c_k \]

Kohn-Sham eigenvalue problem

“Conventional” solvers (Lapack-like):

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

How far can we push such solvers?
Computational Scaling: CPU Time With System Size

Fully extended Polyalanine, “light”

Wall clock time per s.c. iter. (s)

<table>
<thead>
<tr>
<th>Atoms in structure</th>
<th>10</th>
<th>100</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>10</td>
<td>1000</td>
</tr>
</tbody>
</table>

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

32 CPUs
standard Infiniband/Xeon cluster

Benchmarks: W. Jürgens / FHI
Computational Scaling: CPU Time With System Size

Fully extended Polyalanine, “light”

Wall clock time per s.c. iter. (s)

- Total
- $v_{es}(r)$
- $n(r)$
- $h_{ij}$

Atoms in structure

- Light:
  - Basis: tier 1
  - $|\text{Hartree}|$: 4
  - Radial shells: 24-36
  - Pts. per shell: 302 max.
  - Cutoff width: 5Å

32 CPUs
standard Infiniband/Xeon cluster

Benchmarks: W. Jürgens / FHI
Light:
- Basis: tier 1
- Hartree: 4
- Radial shells: 24-36
- Points per shell: 302 max.
- Cutoff width: 5Å

32 CPUs
Standard Infiniband/Xeon cluster

Benchmarks: W. Jürgens / FHI
Light:  
- Basis: tier 1
- $l_{\text{Hartree}}$: 4
- radial shells: 24-36
- pts. per shell: 302 max.
- Cutoff width: 5Å

Tight:  
- Basis: tier 2
- $l_{\text{Hartree}}$: 6
- radial shells: 49-73
- pts. per shell: 434 max.
- Cutoff width: 6Å

Benchmarks: W. Jürgens / FHI

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

Computational Scaling: CPU Time With System Size

Fully extended Polyalanine, “light”

$\alpha$-helical Polyalanine, “tight”
Parallel Eigenvalue Solvers - the Problem

IBM BlueGene (MPG, Garching) 16384 CPU cores

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

Elapsed time [s]

- Eigenvalue solver (ScaLapack, 2008)
  - Matrix dim.: 27069
- grid-based operations

Number of CPU cores
A Massively Parallel Dense Eigensolver: “ELPA”

\[ \hbar c_k = \epsilon_k S c_k \]

Goal:
• scalable, Scalapack-compatible “drop-in enhancement”
• pure MPI-based implementation
• detailed rewrite based on proven robust/general algorithms

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

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 Eigenvalue Problem

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

\[
\hbar c_k = \epsilon_k S c_k
\]

Number of CPU cores

Elapsed time [s]

$\alpha$-helical Polyalanine Ala$_{100}$, BlueGene/P
A Careful Rewrite Can Improve Scaling (“ELPA I”)

α-helical Polyalanine Ala\textsubscript{100}

\( N=27069, \ M=3410 \)

NAO basis set (FHI-aims)

![Graph showing elapsed time vs. number of cores for different computing systems: Intel/Infiniband, BlueGene/P, and original Scalapack.](image)
A Careful Rewrite Can Improve Scaling (“ELPA 1”)
Algorithmic Improvement: 2-Step Tridiagonalization

Remaining chief bottleneck: Tridiagonalization

“Conventional” reduction:

\[
\begin{array}{c}
\text{full matrix} \\
\downarrow \text{Householder transform} \\
\downarrow \text{matrix-vector operations} \\
\end{array} \rightarrow \begin{array}{c}
\text{tridiagonal matrix} \\
\end{array}
\]
Algorithmic Improvement: 2-Step Tridiagonalization

Remaining chief bottleneck: Tridiagonalization

“Two-step” reduction:

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)
ELPA, Two-Step Solver

α-helical Polyalanine Ala\textsubscript{100}

\[ N=27069, \; M=3410 \]

NAO basis set (FHI-aims)

![Graph showing elapsed time vs. number of cores for different hardware configurations: Intel/Infiniband, BlueGene/P, and Scalapack with 2-step optimization.](image)
Trial system:
Model biomolecule
(similar for periodic systems)

α-helical Polyalanine Ala$_{200}$
2003 atoms, “tight”
$N=54138, M=6820$
NAO basis set (FHI-aims)
Beyond Kohn-Sham: Hartree-Fock and hybrid functionals


Hohenberg-Kohn, Kohn-Sham, etc.

LDA, GGA, mGGA etc.

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

Nice, clean, tractable, and sadly often insufficient

Becke, Burke, Perdew, Ernzerhoff, others

“Hybrid functionals” - certainly legal

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

Unfortunately:

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

Naively, \( O(N^4) \) - four-index Coulomb matrix, long ranged, even hard to store

OK for small molecules, impractical for solids ...
Our Preferred Route to \((ij|kl)\): Resolution of Identity (RI)

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

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

Basis pair product space \(\{\varphi_i(r) \cdot \varphi_j(r)\}\)

must be overcomplete if \(\{\varphi_i(r)\}\)

itself approaches completeness

Solution (quantum chemistry):

\[
\varphi_i(r) \varphi_j(r) = \sum_{\mu} C_{ij}^{\mu} P_\mu(r)
\]

smaller auxiliary basis set \(\{P_\mu\}\)

In finite systems, “RI-V”:

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

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

Accurate [1], but delocalizes \(C\)!

(Much) better scaling: Localized RI

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

## Accuracy: Periodic hybrid functionals

### Cohesive properties, bulk semiconductors

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Is This a “Stable” Surface Phase?*

Graphene on SiC(0001)
van Bommel, Crombeen, van Tooren,
Surf. Sci. 1975
many others

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

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

* under some conditions ...
Thermodynamic stability criterion for competing surface phases:

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

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

Stability boundaries:
- Bulk SiC more stable than elemental Si, C
- \( \mu_{\text{C}} \leq E_{\text{C}^{\text{bulk}}} \)
- \( \mu_{\text{Si}} \leq E_{\text{Si}^{\text{bulk}}} \)

Total energies, full relaxation from first principles:
- six-bilayer SiC slabs + surface planes
- full relaxation, “tight” numerical settings (C: tier 2, Si: tier 1 + gd)

Ab Initio Thermodynamics for Si-Side Graphene/SiC

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

(6\sqrt{3}\times6\sqrt{3})\text{SiC}(111) + (13\times13)\text{graphene}:

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

Total energies, full relaxation from first principles:
- six-bilayer SiC slabs + surface planes
- full relaxation, “tight” numerical settings (C: tier 2, Si: tier 1 + gd)

Stability of Surface Phases: PBE+vdW

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

Surface energy hierarchy: 3C-SiC(111)

Nemec, Blum, Rinke, Scheffler, PRL (2013).
Surface energy hierarchy: 3C-SiC(111)

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Surface energy hierarchy: 3C-SiC(111)

Nemec, Blum, Rinke, Scheffler, PRL (2013).
Stability of Surface Phases: Conclusion

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

- Thermodynamic near-stability range for ZLG, MLG possibly BLG
- Defects, dopants, electronic structure, dynamics(?) accessible without artificial strain

Nemec, Blum, Rinke, Scheffler, PRL (2013).
2013 - Summary and Outlook

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

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

Much ongoing work:
QM/MM embedding into external fields
Optical properties in molecules and solids
Density functional perturbation theory (phonons, general linear response)
MANY more.
The People Behind FHI-aims

Matthias Scheffler
(FHI/Hefei)

Xinguo Ren
(FHI/Helsinki)  (Munich)

Ville Havu
(Paula Havu)

Rainer Johanni
(Paula Havu)

Sergey Levchenko
(FHI)

Scalability

Periodic systems, relativity

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