Augmented Planewave Methods

Claudia Draxl
Kohn-Sham equation

\[ [-\nabla^2 + V_{\text{eff}}(r)] \psi(r) = \varepsilon \psi(r) \]

Ritz variational principle

\[ \psi(r) = \sum_n c_n \phi_n(r) \]

Matrix form

\[ \sum_{n'} \left( H_{n,n'} - \varepsilon_n S_{n,n'} \right) c_{n'} = 0 \]
Kohn-Sham equation

\[ \sum_{n'} \left( H_{n,n'} - \varepsilon_n S_{n,n'} \right) c_{n'} = 0 \]

Hamiltonian matrix

\[ H_{n,n'} \equiv \langle \phi_n | - \nabla^2 + V_{\text{eff}} | \phi_{n'} \rangle \]

Overlap matrix

\[ S_{n,n'} \equiv \langle \phi_n | \phi_{n'} \rangle \]
Augmented-planewave methods …

\[ \sum_{n'} \left( H_{n,n'} - \varepsilon_n S_{n,n'} \right) c_{n'} = 0 \]
The best of two worlds ...
The best of two worlds

Dual basis
- **Atomic spheres** $\alpha, \beta$
  - Atomic-like basis functions
- **Interstitial**
  - Planewave basis
- **All-electron method**
  - Can handle strong variations
  - Can explore the core region
What determines the size of the basis?

Each planewave living in the interstitial is augmented by atomic-like functions inside each sphere.

- **Large muffin-tin sphere**: few planewaves
- **Small sphere size**: many planewaves

The product $R_{MT}\text{G}_{\text{max}}$ is a good measure for a converged basis.
Potential and density: dual basis

Potential

\[ V_{\text{eff}}(r) = \sum_K V_K e^{iKr} \]

\[ V_{\text{eff}}(S_\alpha + r) = \sum_{LM} V_{LM}^\alpha(r) Y_{LM}(\hat{r}) \]

Density

\[ \rho(r) = \sum_K \rho_K e^{iKr} \]

\[ \rho(S_\alpha + r) = \sum_{LM} \rho_{LM}^\alpha(r) Y_{LM}(\hat{r}) \]
All-electron description

- **valence**
  - delocalized

- **semi-core**
  - localized, but not confined in MT sphere

- **core**
  - confined in the sphere

- **atom-like**

- **scalar-relativistic SO in second variation**

- **Dirac equation**

[Image of a graph with energy levels and labels for valence, semi-core, core, and atom-like regions]
A bit of history …
The APW basis set

### Augmented Plane Waves

\[ \phi_{k+G}(r) = \frac{1}{\sqrt{\Omega}} e^{i(k+G)r} \]

basis continuous at sphere boundary \( R_{MT} \)

\[ \phi_{k+G}(S_{\alpha} + r) = \sum_{lm} A_{lm}^{\alpha}(k + G) u_{j}^{\alpha}(r, E) Y_{lm}(\hat{r}) \]

solutions of the radial Schrödinger equation

\[
\left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{\alpha}(r) - E \right\} r u_{j}^{\alpha}(r, E) = 0
\]

**APW: advantages & drawbacks**

- \( E \) has to be the exact KS eigenvalue
  - \( E \) is a variational parameter
- Energy-dependent basis set
- Non-linear eigenvalue problem
- Search for zeros of the determinant
  - No single diagonalization
  - Time-consuming
- No full-potential method

**BUT** a true all-electron method!
The LAPW basis set

Linearized Augmented Plane Waves

\[ \phi_{k+G}(r) = \frac{1}{\sqrt{\Omega}} e^{i(k+G)r} \]

basis continuous in value and slope at \( R_{MT} \)

\[ \phi_{k+G}(S_\alpha + r) = \sum_{lm} [A_{lm}^\alpha(k+G)u_{l}^\alpha(r, E_l) Y_{lm}(\hat{r})] \]

energy derivative

energy parameter

LAPW: advantages & drawbacks

$E_i$ is a fixed parameter
Energy-independent basis set
Linear eigenvalue problem

$$\sum_{G'} (H_{k+G,k+G'} - \varepsilon_{nk} S_{k+G,k+G'}) c_{nk}(G') = 0$$

No true all-electron method!
Only one principle quantum number per $l$
The problem …

Example: Cu: $3p^63d^{10}4s^1$

- 3p states not confined in the muffin-tin sphere
- 4p states needed to have a flexible basis set

Ways out

- Two-window calculation
  - Orthogonality problems
- A better basis set
  - Super-LAPW (SLAPW)
  - or better …
The Super LAPW method


\[ \phi_{\alpha G}(S_{\alpha} + r) = \sum_{l,m} [A_{lm}^{\alpha}(k+G)u^{\alpha}_l(r, E_l) + B_{lm}^{\alpha}(k+G)\dot{u}^{\alpha}_l(r, E_l) + C_{lm}^{\alpha}(k+G)u^{\alpha}_l(r, E_{lo})] Y_{lm}(\hat{r}) \]

basis continuous up to 2\textsuperscript{nd} derivative

different energy parameters
SLAPW: Advantages & drawbacks

All-electron method
 Kinetic energy continuos
   No surface terms needed

Costly: more basis functions needed
   Roughly 50% larger basis set

Why?
Radial functions in APW & LAPW

They get distorted by boundary conditions
More basis functions needed in LAPW to describe the same behavior as in APW

Same effect in SLAPW
Even more pronounced
The concept of local orbitals

LAPW+LO

 augmentation to PWs

\[ \phi_{k+G}(s_\alpha + r) = \sum_{lm} [A_{lm}^\alpha(k + G)u_{l_i}^\alpha(r, E_l) + B_{lm}^\alpha(k + G)\tilde{u}_{l_i}^\alpha(r, E_l)] \]

valence state

\[ \phi_{LO}^{lm}(s_\alpha + r) = [\tilde{A}_{lm}^\alpha u_{l_i}^\alpha(r, E_l) + \tilde{B}_{lm}^\alpha \tilde{u}_{l_i}^\alpha(r, E_l) + \tilde{C}_{lm}^\alpha \tilde{u}_{l_i}^\alpha(r, E_{lo})] Y_{lm}(\hat{r}) \]

live in spheres only

semicore state

Nearly no extra cost!

Can we do better?


... Is it possible to combine the advantages of the LAPW and the APW methods, i.e., to find an energy-independent basis that does not demand a noticeable higher planewave cutoff than the original APW functions? ...

YES !!
The APW+lo basis set

Forget *classic* LAPW

Use APW & *local orbital* at the same energy

Alternative way of linearization
APW+$\sigma$: only advantages - **NO** drawbacks

- All-electron method
- As accurate as LAPW
- Can be supplemented by LOs
- Very efficient
  - 50% less basis functions compared to LAPW
  - Saves a factor of ~5 for large cells

**Different augmentations can be combined**
- APW+lo for *relevant* valence states only
- LAPW-like augmentation for all other /states

G. Madsen et al., PRB 64, 195134 (2001)
Our LAPW flavor of choice

- **atom-like**
  - localized, but not confined
  - confined in the sphere

- **core**
  - localized, but not confined

- **valence**
  - delocalized

- **semi-core**
  - localized, but not confined

- **unoccupied**

- **LAPW**

- **APW+lo**

- **LO**
The most exciting code


**exciting** is a full-potential all-electron density-functional-theory package implementing the families of linearized augmented planewave methods. It can be applied to all kinds of materials, irrespective of the atomic species involved, and also allows for exploring the physics of core electrons. A particular focus are excited states within many-body perturbation theory.
A few examples ...
Reproducibility in density functional theory calculations of solids

Delta test

Compute $E(V)$ using PBE
Fit to the Birch-Murnaghan equation of state
Compare with other code (method)

Quality factor

$$\Delta = \sqrt{\frac{\int \Delta E^2 (V) dV}{\Delta V}}$$

K. Lejaeghere et al., Science 351, aad3000 (2016).
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<tr>
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Data quality

Excellent overall agreement between codes – great!

... but just the beginning

What about

Other systems?
  Surfaces, defects, molecules, ...

Other quantities?
  Band gaps, barriers, spectra, ...

Larger discrepancies for certain elements

![Data quality chart](image-url)
Can we reach ultimate precision?

Total energies of atoms compared to MADNESS
Multiresolution analysis
Same precision for molecules
**G2-1 test set**

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A. Gulans, A. Kozhevnikov, and CD, preprint.
Can we reach ultimate precision for solids?

Linearized augmented planewave method

"Self-validation"

Make use of dual basis

Atomic spheres $\alpha, \beta$

Atomic-like basis functions

Interstitial

Planewave basis

A. Gulans, A. Kozhevnikov, and CD, preprint.

http://exciting-code.org
Can we reach ultimate precision for solids?

Results independent of sphere radius \( R_{MT} \)

LAPW can serve as benchmark

A. Gulans, A. Kozhevnikov, and CD, preprint.

\[ \begin{array}{cccccc}
R_{MT} & R_{MT}G_{max} & V_0 & B_0 & B' & \Delta E^{tot} \\
1.4 & 14 & 71.3298 & 236.296 & 4.5992 & 0.0 \\
1.5 & 14 & 71.3299 & 236.297 & 4.5996 & 0.1 \\
1.6 & 14 & 71.3299 & 236.295 & 4.5998 & 0.2 \\
1.7 & 14 & 71.3299 & 236.294 & 4.5994 & 0.3 \\
1.8 & 14 & 71.3299 & 236.295 & 4.5994 & 0.4 \\
1.9 & 14 & 71.3300 & 236.295 & 4.5989 & 0.5 \\
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2.1 & 11 & 71.3285 & 236.311 & 4.5965 & 18.1 \\
2.1 & 10 & 71.3243 & 236.337 & 4.5968 & 95.0 \\
\end{array} \]
Getting excited …
**G₀W₀ approach**

**Role of empty states**

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**ZnO**
$G_0W_0$ approach

Eigenvalues at $\Gamma$
Role of empty states

Role of empty states

Is ZnO special?

0.30 eV
wz-ZnO

0.01 eV
Si

0.17 eV
GaAs

0.40 eV
LiF
Is Si special?
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* Γ-X gap

Klimeš, et al., PRB 90, 075125 (2014)
Shishkin and Kresse, PRB 75, 235102 (2007)

D. Nabok, A. Gulans & CD, PRB 94, 035418 (2016)
We are precise. Can we be efficient?

Yes, currently implemented …

**SIRIUS**

LAPW-specific library with optimized performance using CPUs and GPUs

A. Kozhevnikov, T. Schulthess (CSCS)
A. Gulans, and CD (HU Berlin)
SIRIUS: Example SrTi\textsubscript{1-x}Cr\textsubscript{x}O\textsubscript{3} (CPU)

- 1080 atoms
- 66261 basis functions

Courtesey A. Kozhevnikov

Graph showing:
- Time [s] vs. Efficiency
- Number of nodes: 64, 100, 144, 196
- Setup and Diagonalization
THANKS !!

exciting