

AUGMENTED PLANE WAVES



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Kohn-Sham equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\rm KS}(\mathbf{r})\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

$$v_{\rm KS}(\mathbf{r}) = v_{\rm n}(\mathbf{r}) + v_{\rm h}(\mathbf{r}) + v_{\rm xc}(\mathbf{r})$$

Potential due to nuclei

Exchange-correlation potential

Potential due to electron repulsuion, or simply Hartree potential



Mapping onto a linear algebra problem

$$\begin{pmatrix} -\frac{1}{2}\nabla^2 + v_{\rm KS}(\mathbf{r}) \end{pmatrix} \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$$

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i(\mathbf{G}+\mathbf{k})} \phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r})$$

Basis functions

Hamiltonian matrix elements $H^{\mathbf{k}}_{\mathbf{GG'}} = \langle \phi_{\mathbf{G}+\mathbf{k}} | \hat{H} | \phi_{\mathbf{G'}+\mathbf{k}} \rangle$

Overlap matrix elements $S^{\bf k}_{{\bf G}{\bf G}'} = \langle \phi_{{\bf G}+{\bf k}} | \phi_{{\bf G}'+{\bf k}} \rangle$

Linear generalized eigenvalue problem

 $Hc = \varepsilon Sc$



Mapping onto a linear algebra problem

$$\begin{pmatrix} -\frac{1}{2}\nabla^2 + v_{\rm KS}(\mathbf{r}) \end{pmatrix} \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$$

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i(\mathbf{G}+\mathbf{k})} \phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r})$$

Basis functions

Hamiltonian matrix elements $H^{\mathbf{k}}_{\mathbf{GG'}} = \langle \phi_{\mathbf{G+k}} | \hat{H} | \phi_{\mathbf{G'+k}} \rangle$

Overlap matrix elements $S^{\bf k}_{{\bf G}{\bf G}'} = \langle \phi_{{\bf G}+{\bf k}} | \phi_{{\bf G}'+{\bf k}} \rangle$

Linear generalized eigenvalue problem

 $Hc = \varepsilon Sc$

But the potential depends on the electron density, which depends on the wavefunctions...



Workflow





(L)APW basis

• LAPW stands for (linearized) augmented plane waves.

•We have some *a priori* knowledge what to expect from wavefunctions close to nuclei and far away from them.



MT = Muffin tin, augmentation spheres

• Close to nucleus → atom-like WFs. Use "atomic orbitals"!

• Away from nucleus → smooth, slowly varying WFs. Use plane waves!

APW basis

$$\phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{lm} A_{lm}^{\mathbf{G}+\mathbf{k}} u_l(r;\epsilon) Y_{lm}(\theta,\varphi), & \text{if } r \in \mathrm{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}, & \text{otherwise} \end{cases}$$





MT = Muffin tin, augmentation spheres





Kohn-Sham equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\rm KS}(\mathbf{r})\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

• If the potential is spherically symmetric, we could solve just the radial equation

$$\left[-\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{l(l+1)}{2r^2} + v_{\rm KS}(r)\right]u_l(r) = \epsilon u_l(r)$$



Example: Helium atom

• 1s state can be solved for using just the radial equation

$$\left[-\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{l(l+1)}{2r^2} + v_{\rm KS}(r)\right]u_l(r) = \varepsilon u_l(r)$$





Example: Helium atom with APW

 $\psi(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}} \phi_{\mathbf{G}}(\mathbf{r})$



Example: Helium atom with APW

$$\psi(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \sum_{lm} C_{\mathbf{G}} A_{lm}^{\mathbf{G}} u_l(r; \epsilon) Y_{lm}(\theta, \varphi), & \text{if } r \in \mathrm{MT} \\ \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{Gr}}, & \text{otherwise} \end{cases}$$



• 1s state is spherically symmetric, and only the *l*=0 component should be non-zero.

But how do we know the energy in advance?



Which energy would you take?

 $\phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{lm} A_{lm}^{\mathbf{G}+\mathbf{k}} u_l(r; \boldsymbol{\epsilon}) Y_{lm}(\theta, \varphi), & \text{if } r \in \mathrm{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}, & \text{otherwise} \end{cases}$



The energy parameter should match eigenenergies of a studied system.

The original APW method finds the energy parameters *automatically* by considering energy-dependent Hamiltonian. It is too complicated!



What if we just guess the energy?



Linearization

• Problem: we know how to compute $u(r, \epsilon)$, but we do not know which specific ϵ to take.

• A step towards solution: linearize *u*.

$$u_l(r,\epsilon) = u_l(r,\varepsilon_l) + (\epsilon - \varepsilon_l)\dot{u}_l(r,\varepsilon_l) + O((\epsilon - \varepsilon_l)^2)$$

Still depends on energy, but now we know the direction for the improvement





LAPW basis





Example: Helium atom with LAPW

 $\psi(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \sum_{lm} C_{\mathbf{G}} \left[A_{lm}^{\mathbf{G}} u_l(r; \epsilon) + B_{lm}^{\mathbf{G}} \dot{u}_l(r; \epsilon) \right] Y_{lm}(\theta, \varphi), & \text{if } r \in \mathrm{MT} \\ \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{Gr}}, & \text{otherwise} \end{cases}$





Features of LAPW

• Improves upon APW with frozen energy parameters.

• Preserves the number of basis functions compared to APW.

• Is limited to description of valence electrons, since there can be only one energy parameter per *l*. Core states are treated differently than valence states.



APW+lo basis

• APW

$$\phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{lm} A_{lm}^{\mathbf{G}+\mathbf{k}} u_l(r;\varepsilon_l) Y_{lm}(\theta,\varphi), & \text{if } r \in \mathrm{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}, & \text{otherwise} \end{cases}$$

• Local orbital $\phi_{\mu}(\mathbf{r}) = [a_{\mu}u_{l}(r;\varepsilon_{l}) + b_{\mu}\dot{u}_{l}(r;\varepsilon_{l})]Y_{lm}(\hat{\mathbf{r}})\delta_{ll_{\mu}}\delta_{mm_{\mu}}$

Local orbital is normalized and turns to zero on the augmentation sphere

Size of the basis and Hamiltonian is defined by the number of plane-waves and local orbitals.



Linearization, quadratization etc.

$$u_l(r,\epsilon) = u_l(r,\varepsilon_l) + (\epsilon - \varepsilon_l)\dot{u}_l(r,\varepsilon_l) + \frac{(\epsilon - \varepsilon_l)^2}{2}\ddot{u}_l(r,\varepsilon_l) + \frac{(\epsilon - \varepsilon_l)^3}{6}\ddot{u}_l(r,\varepsilon_l) + \cdots$$

• APW

$$\phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{lm} A_{lm}^{\mathbf{G}+\mathbf{k}} u_l(r;\varepsilon_l) Y_{lm}(\theta,\varphi), & \text{if } r \in \mathrm{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}, & \text{otherwise} \end{cases}$$

Local orbitals

$$\phi_{\mu}(\mathbf{r}) = [a_{\mu}u_{l}(r;\varepsilon_{l}) + b_{\mu}\dot{u}_{l}(r;\varepsilon_{l})]Y_{lm}(\hat{\mathbf{r}})\delta_{ll_{\mu}}\delta_{mm_{\mu}}$$
$$\phi_{\nu}(\mathbf{r}) = [a_{\nu}u_{l}(r;\varepsilon_{l}) + b_{\nu}\ddot{u}_{l}(r;\varepsilon_{l})]Y_{lm}(\hat{\mathbf{r}})\delta_{ll_{\nu}}\delta_{mm_{\nu}}$$
$$\phi_{\xi}(\mathbf{r}) = [a_{\xi}u_{l}(r;\varepsilon_{l}) + b_{\xi}\ddot{u}_{l}(r;\varepsilon_{l})]Y_{lm}(\hat{\mathbf{r}})\delta_{ll_{\nu}}\delta_{mm_{\xi}}$$

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Example: diamond

• Consider l=1 $\varepsilon_{2p} = 0.15$

method	Etot, Ha
APW	-75.576230
LAPW	-75.590045
APW+lo	-75.590101
APW+2lo	-75.590103
APW+3lo	-75.590103

rgkmax=8



Core electrons are considered separately using the 4-component Dirac equation



Example: diamond

• Consider l=1 $\varepsilon_{2p} = 0.15$

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APW	-75.576230
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•rgkmax=8

Core electrons are considered

Diamond: band dispersion

Radial degrees of freedom for I=1

 $\begin{aligned} \hline u_1(r, \varepsilon_{2p}) & \text{APW} \\ a_1 u_1(r, \varepsilon_{2p}) + b_1 \dot{u}_1(r, \varepsilon_{2p}) & \text{APW+lo} \\ a_2 u_1(r, \varepsilon_{2p}) + b_2 \ddot{u}_1(r, \varepsilon_{2p}) & \text{APW+2lo} \\ a_3 u_1(r, \varepsilon_{2p}) + b_3 \dddot{u}_1(r, \varepsilon_{2p}) \end{aligned}$

APW+3lo



```
<wf matchingOrder="3" trialEnergy="0.15" searchE="false"/>
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```
</lo>
```



Semicore states

• $u_l(r; \varepsilon_l), \dot{u}_l(r; \varepsilon_l), \cdots$ have nodal structures that are not compatible with the semicore. We need a basis function that recovers the correct nodal structure.

- A choice that brings you to the "APW level": $\phi_{\mu}(\mathbf{r}) = [a_{\mu}u_{l}(r;\varepsilon_{l}) + b_{\mu}u_{l}(r;\varepsilon_{l}^{c})]Y_{lm}(\hat{\mathbf{r}})\delta_{ll_{\mu}}\delta_{mm_{\mu}}$
- Use expansion in series to go beyond it! $\phi_{\mu}(\mathbf{r}) = [a_{\mu}u_{l}(r;\varepsilon_{l}^{c}) + b_{\mu}\dot{u}_{l}(r;\varepsilon_{l}^{c})]Y_{lm}(\hat{\mathbf{r}})\delta_{ll_{\mu}}\delta_{mm_{\mu}}$ $\phi_{\nu}(\mathbf{r}) = [a_{\nu}u_{l}(r;\varepsilon_{l}^{c}) + b_{\nu}\ddot{u}_{l}(r;\varepsilon_{l}^{c})]Y_{lm}(\hat{\mathbf{r}})\delta_{ll_{\nu}}\delta_{mm_{\nu}}$ $\phi_{\xi}(\mathbf{r}) = [a_{\xi}u_{l}(r;\varepsilon_{l}^{c}) + b_{\xi}\ddot{u}_{l}(r;\varepsilon_{l}^{c})]Y_{lm}(\hat{\mathbf{r}})\delta_{ll_{\nu}}\delta_{mm_{\xi}}$



Example: diamond

• Consider *l*=0 with 1s and 2s both considered as valence electrons

 $\varepsilon_{1s} = -9.20$ $\varepsilon_{2s} = 0.15$

method	Etot, Ha
APW	-29.678023
LAPW	-29.745748
APW+lo	-75.526692
APW+2lo	-75.589507
APW+3lo	-75.590142
APW+4lo	-75.590143







Example: diamond

• Consider *l*=0 wit as valence electron $\varepsilon_{1s} = -9.20$ $\varepsilon_{2s} = 0.15$

method	Etot, Ha
APW	-29.678023
LAPW	-29.745748
APW+lo	-75.526692
APW+2lo	-75.589507
APW+3lo	-75.590142
APW+4lo	-75.590143

rgkmax=8



Features of APW+lo

• Improves upon APW with frozen energy parameters.

• Slightly increases the number of basis functions compared to APW.

• Can describe valence states, semicore states and even core states. But normally core states are treated differently than valence states.

• Can be easily adjusted to yield any accuracy you like.



What about plane waves?

• Accuracy of the plane-wave part of the basis is controlled by their cut-off. However, the required cut-off strongly depends on the size of muffin tins. Hence the LAPW community uses $R_{\rm MT}G_{\rm max}$ as the dimensionless cut-off parameter.

• Larger is $R_{MT}G_{max}$, more accurate is your calculation. But do not abuse it! By the value of ~12 you get ~1 µHa at a high expense. Beyond it, the basis becomes almost linearly dependent.



Example: diamond



A. Gulans et al., J. Phys.: Condens. Matter 26, 363202 (2014)



Summary

• "FP-LAPW" refers to a whole family of methods and APW+lo is among them.

• "FP-LAPW" is the gold-standard method for DFT calculations of solids.

• Local orbitals can be used for implementing a simple and efficient strategy how to arrive at the essentially exact solutions of the Kohn-Sham equation.