Center for
Molecular
Modeling

Department of
Materials Science
and Engineering

the need for augmentation

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http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

BASIS SETS : RECAPITULATION

DFT	*formal*	HK1 HK2 ➔ $\rho(\vec{r})$
Kohn-Sham equations	*practical*	$\hat{H}_{KS}\phi_i = \epsilon_i\phi_i$ XC-functional
basis set	*transformation to algebra (convenient)*	$\phi_i = \sum_{j=1}^{\infty} c_{ij}\chi_j$ HC=SCE matrix diagonalization

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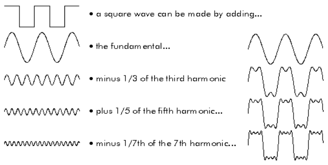
local basis set	**plane waves + pseudopotentials**	**augmented methods**
☺ small basis set	☹ not so small	☹ not so small
☺ physical insight	☹ less intuitive	☺ more intuitive
☹ not orthogonal	☺ orthogonal	☹ not orthogonal
☹ depends on atomic position	☺ position-independent	☺ position independent
☹ BSSE? completeness?	☹ effect of PP?	☺ very accurate (some)
	☺ periodic ➔ crystals	☺ periodic ➔ crystals
		☺ core information (some)

VOLUME PARTITIONING

The reason for the large size of the plane wave basis sets was the steep features in the wave functions :



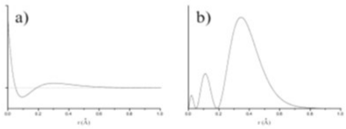


Figure 2.1: *Radial part of wave function (a) and radial probability distribution (b) of a 3s electron in Ca (Y-axis has arbitrary units).*

The steeper the feature you want to describe, the more basis functions (plane waves) are needed.

Back-of-the-envelop estimate for Ca-3s: 10^8 plane waves.
Diagonalize 10^8x10^8 matrices...?

The steepest features appear near to the nuclei:

➔ get rid of them by PP (see before)
➔ **use basis functions that have such steep features built-in** (today)

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volume partitioning

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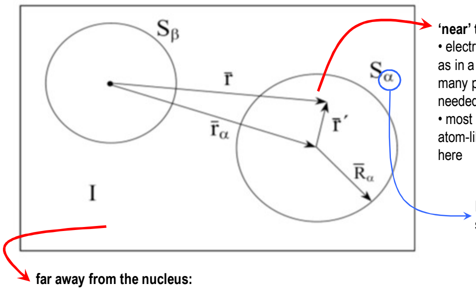
VOLUME PARTITIONING

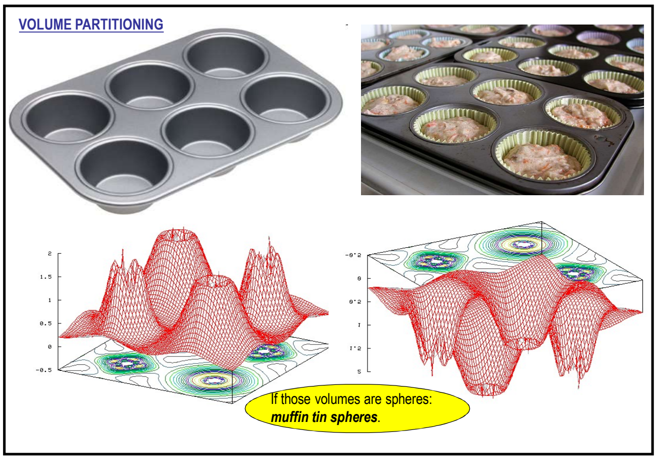


'near' to a nucleus:
- electrons behave almost as in a free atom (steep changes, many plane waves would be needed)
- most efficient to use atom-like basis functions here

Identifies which sphere/atom

far away from the nucleus:
- electron density is much smoother ('almost constant' = free electron)
- much less plane waves needed

➔ Partition space into a region of atom-like behaviour and a region of free-electron-like behaviour.



VOLUME PARTITIONING

If those volumes are spheres:
muffin tin spheres.

VOLUME PARTITIONING

We will look at a few methods that realize
in various ways this concept of volume partitioning:

augmented plane wave methods
- APW
- LAPW
- APW+lo
- LMTO

projector augmented plane wave method
- PAW

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the APW method

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THE APW METHOD

This was the final expression for a plane wave basis set:

$$\begin{aligned}\Psi_{\vec{k}}^{n}(\vec{r}) &= \sum_{\vec{K}} c_{\vec{K}}^{n,\vec{k}}\, e^{i\left(\vec{k}+\vec{K}\right)\cdot\vec{r}} \\ &= \sum_{\vec{K}} c_{\vec{K}}^{n,\vec{k}}\, \boxed{\phi_{\vec{K}}^{\vec{k}}(\vec{r})}\end{aligned}$$

plane wave basis function

THE APW METHOD

Definition of an **A**ugmented **P**lane **W**ave basis function:

$$\phi_{\vec{K}}^{\vec{k}}(\vec{r},\, E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r}\in I \\ \sum_{\ell,m} A_{\ell m}^{\alpha,\vec{k}+\vec{K}} u_{\ell}^{\alpha}(r',E) Y_{m}^{\ell}(\hat{r}') & \vec{r}\in S_{\alpha} \end{cases}$$

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plane wave basis function

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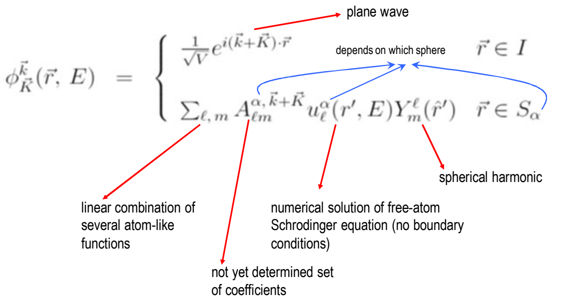

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plane wave

depends on which sphere

linear combination of several atom-like functions

not yet determined set of coefficients

numerical solution of free-atom Schrodinger equation (no boundary conditions)

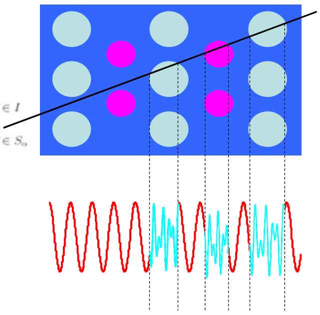
spherical harmonic

THE APW METHOD

Definition of an **A**ugmented **P**lane **W**ave basis function:

Cartoon : APW function

$$\phi_{\vec K}^{\vec k}(\vec r,\,E) \;=\; \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec k+\vec K)\cdot\vec r} & \vec r \in I \\ \sum_{\ell,m} A_{\ell m}^{\alpha,\,\vec k+\vec K} u_\ell^\alpha(r',E) Y_m^\ell(\hat r') & \vec r \in S_\alpha \end{cases}$$



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Expand the plane waves in Bessel functions around the center of the muffin tin sphere:

$$\frac{1}{\sqrt{V}} e^{i(\vec k+\vec K)\cdot\vec r} \;=\; \frac{4\pi}{\sqrt{V}} e^{i(\vec k+\vec K)\cdot\vec r_\alpha} \sum_{\ell,m} i^\ell j_\ell\left(\left|\vec k+\vec K\right|\,|\vec r'|\right) Y_m^{\ell *}\left(\widehat{\vec k+\vec K}\right) Y_m^\ell(\hat r')$$

Choose the A-coefficients such that term by term matches at the sphere boundary:

$$A_{\ell m}^{\alpha,\,\vec k+\vec K} \;=\; \frac{4\pi i^\ell e^{i(\vec k+\vec K)\cdot\vec r_\alpha}}{\sqrt{V} u_\ell^\alpha(\vec R_\alpha,\,E)} j_\ell\left(\left|\vec k+\vec K\right| R_\alpha\right) Y_m^{\ell *}(\widehat{\vec k+\vec K})$$

...and truncate the expansion at some ℓ_{max} (criterium: numerical stability).

THE APW METHOD

Definition of an **A**ugmented **P**lane **W**ave basis function:

$$\phi_{\vec{K}}^{\vec{k}}(\vec{r},\boxed{E}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r} \in I \\ \sum_{\ell,m} A_{\ell m}^{\alpha,\vec{k}+\vec{K}} u_\ell^\alpha(r',\boxed{E}) Y_m^\ell(\hat{r}') & \vec{r} \in S_\alpha \end{cases}$$

Energy-dependent...!?
What does this mean?

THE APW METHOD

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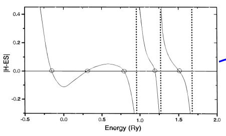
Energy-dependent...!?
What does this mean?

APW's will be an efficient basis set to describe the eigenstate $\psi_{\vec{k}}^n$ only if $E = \epsilon_{\vec{k}}^n$ $\left(\hat{H}_{KS}\,\psi_{\vec{k}}^n = \epsilon_{\vec{k}}^n\,\psi_{\vec{k}}^n\right)$

But $\epsilon_{\vec{k}}^n$ is a result of our solution, hence we cannot even write down the basis set before the problem is solved...!?

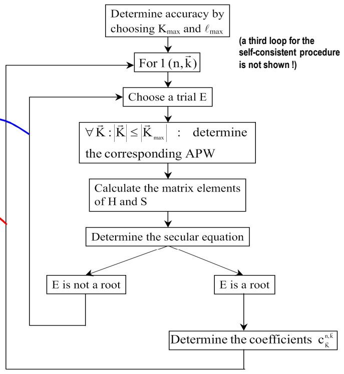
⇨ time-consuming iterative procedure needed.

THE APW METHOD



This inner loop numerically searches one by one the roots of the secular equation, the latter being possibly a nasty function with asymptotes etc.
➔ time-consuming

Every time you go through the outer loop, you obtain one eigenstate. The price: as many matrix diagonalizations as the number of times you had to go through the inner loop.



Determine accuracy by choosing K_{max} and ℓ_{max}

(a third loop for the self-consistent procedure is not shown !)

For 1 $(n,\vec{k})$

Choose a trial E

$\forall\vec{K}:|\vec{K}|\leq|\vec{K}_{max}|$: determine the corresponding APW

Calculate the matrix elements of H and S

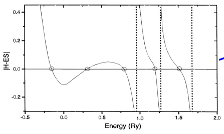
Determine the secular equation

E is not a root

E is a root

Determine the coefficients $c_{\vec{K}}^{n,\vec{k}}$

THE APW METHOD



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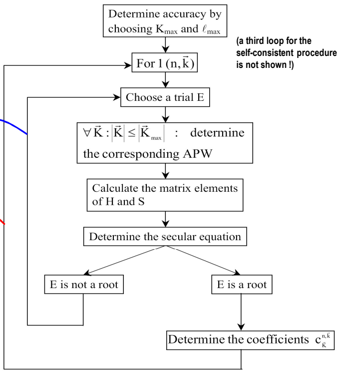

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E is a root

Determine the coefficients $c_{\vec{K}}^{n,\vec{k}}$

- Although APW is very accurate...
- ... it is extremely slow.
- Can we speed it up, without loosing too much accuracy?

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the LAPW method

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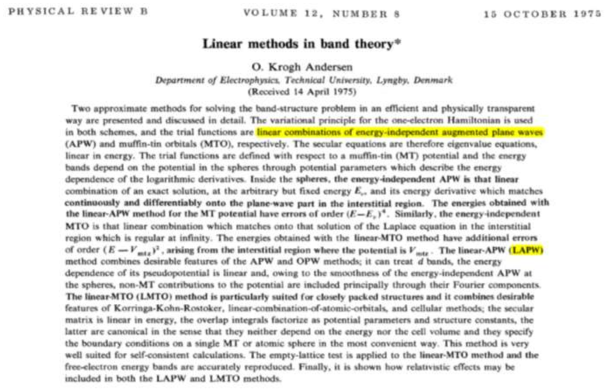
THE LAPW METHOD



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Linear methods in band theory*

O. Krogh Andersen
Department of Electrophysics, Technical University, Lyngby, Denmark

(Received 14 April 1975)

Two approximate methods for solving the band-structure problem in an efficient and physically transparent way are presented and discussed in detail. The variational principle for the one-electron Hamiltonian is used in both schemes, and the trial functions are linear combinations of energy-independent augmented plane waves (APW) and muffin-tin orbitals (MTO), respectively. The secular equations are therefore eigenvalue equations, linear in energy. The trial functions are defined with respect to a muffin-tin (MT) potential and the energy bands depend on the potential in the spheres through potential parameters which describe the energy dependence of the logarithmic derivatives. Inside the spheres, the energy-independent APW is that linear combination of an exact solution, at the arbitrary but fixed energy E_ν, and its energy derivative which matches continuously and differentiably onto the plane-wave part in the interstitial region. The energies obtained with the linear-APW method for the MT potential have errors of order $(E-E_\nu)^4$. Similarly, the energy-independent MTO is that linear combination which matches onto that solution of the Laplace equation in the interstitial region which is regular at infinity. The energies obtained with the linear-MTO method have additional errors of order $(E-V_{mtz})^2$, arising from the interstitial region where the potential is V_{mtz}. The linear-APW (LAPW) method combines desirable features of the APW and OPW methods; it can treat *d* bands, the energy dependence of its pseudopotential is linear and, owing to the smoothness of the energy-independent APW at the spheres, non-MT contributions to the potential are included principally through their Fourier components. The linear-MTO (LMTO) method is particularly suited for closely packed structures and it combines desirable features of Korringa-Kohn-Rostoker, linear-combination-of-atomic-orbitals, and cellular methods; the secular matrix is linear in energy, the overlap integrals factorize as potential parameters and structure constants, the latter are canonical in the sense that they neither depend on the energy nor the cell volume and they specify the boundary conditions on a single MT or atomic sphere in the most convenient way. This method is very well suited for self-consistent calculations. The empty-lattice test is applied to the linear-MTO method and the free-electron energy bands are accurately reproduced. Finally, it is shown how relativistic effects may be included in both the LAPW and LMTO methods.

THE LAPW METHOD

Taylor-expand the u-function around a guessed energy E_0:

$$u_\ell^\alpha(r', \epsilon_{\vec{k}}^n) = u_\ell^\alpha(r', E_0) + (E_0 - \epsilon_{\vec{k}}^n) \underbrace{\left.\frac{\partial u_\ell^\alpha(r', E)}{\partial E}\right|_{E=E_0}}_{\dot{u}_\ell^\alpha(r', E_0)} + O(E_0 - \epsilon_{\vec{k}}^n)^2$$

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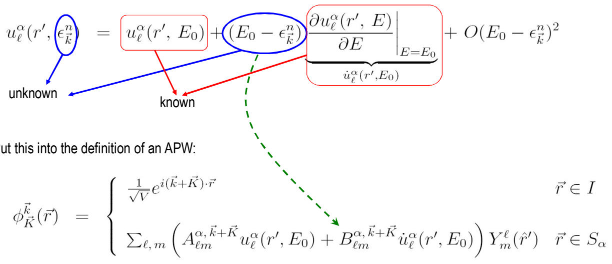

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unknown

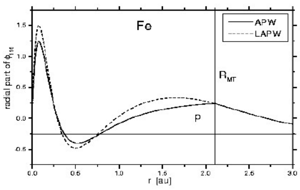
known

Put this into the definition of an APW:

$$\phi_{\vec{K}}^{\vec{k}}(\vec{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r} \in I \\ \sum_{\ell,m} \left(A_{\ell m}^{\alpha,\vec{k}+\vec{K}} u_\ell^\alpha(r', E_0) + B_{\ell m}^{\alpha,\vec{k}+\vec{K}} \dot{u}_\ell^\alpha(r', E_0) \right) Y_m^\ell(\hat{r}') & \vec{r} \in S_\alpha \end{cases}$$

Linearized **A**ugmented **P**lane **W**ave basis function (LAPW).

THE LAPW METHOD



Two sets of coefficients:
fixed by requiring that at the sphere boundary value and slope should match to the spherical expansion of plane waves.

energy-independent

$$\phi_{\vec{K}}^{\vec{k}}(\vec{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r} \in I \\ \sum_{\ell,m} \left(A_{\ell m}^{\alpha,\vec{k}+\vec{K}} u_\ell^\alpha(r', E_0) + B_{\ell m}^{\alpha,\vec{k}+\vec{K}} \dot{u}_\ell^\alpha(r', E_0) \right) Y_m^\ell(\hat{r}') & \vec{r} \in S_\alpha \end{cases}$$

Linearized **A**ugmented **P**lane **W**ave basis function (LAPW).

THE LAPW METHOD

Further details:

- E_0 should be close to the eigenvalues. Therefore, use different E-values for different atoms (α), and make them ℓ -dependent:

$$\phi^{\vec{k}}_{\vec{K}}(\vec{r}) \;=\; \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r} \in I \\ \sum_{\ell,m} \left(A^{\alpha,\vec{k}+\vec{K}}_{\ell m} u^{\alpha}_{\ell}(r', E^{\alpha}_{1,\ell}) + B^{\alpha,\vec{k}+\vec{K}}_{\ell m} \dot{u}^{\alpha}_{\ell}(r', E^{\alpha}_{1,\ell}) \right) Y^{\ell}_{m}(\hat{r}') & \vec{r} \in S_\alpha \end{cases}$$

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- For a given ℓ , several eigenvalues can appear. Example for ℓ =1 in Ga:

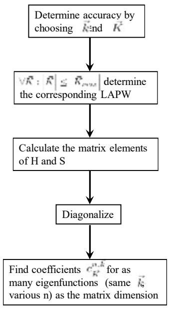
4p : a valence orbital, allow full freedom and describe by LAPW ➔ take $E^{\alpha}_{1,\ell}$ near to this (guessed) eigenvalue
3p : a 'semi-core' orbital: almost as in a free atom, but not completely. Describe by *Local Orbital* basis functions:
2p : a core orbital: as in a free atom, at most with shifted eigenvalues. Free atom calculation.

$$\phi^{\ell m}_{\alpha,LO}(\vec{r}) \;=\; \begin{cases} 0 & \vec{r} \notin S_\alpha \\ \left(A^{\alpha,LO}_{\ell m} u^{\alpha}_{\ell}(r', \underline{E^{\alpha}_{1,\ell}}) + B^{\alpha,LO}_{\ell m} \dot{u}^{\alpha}_{\ell}(r', \underline{E^{\alpha}_{1,\ell}}) + C^{\alpha,LO}_{\ell m} u^{\alpha}_{\ell}(r', \underline{E^{\alpha}_{2,\ell}}) \right) Y^{\ell}_{m}(\hat{r}') & \vec{r} \in S_\alpha \end{cases}$$

- ➢ depends on the atom (or sphere)
- ➢ no $\vec{k}$ or $\vec{K}$ dependence because not connected to plane waves
- ➢ A-B-C determined by normalization, zero value and zero slope at sphere boundary (=confined within sphere)

THE LAPW METHOD

Having now a basis set of LAPW's and LO's, we proceed with the same scheme as for PW+PP :



Determine accuracy by choosing $\vec{k}$ and $\vec{K}$

$\forall \vec{K} : |\vec{K}| \leq \vec{K}_{max}$ determine the corresponding LAPW

Calculate the matrix elements of H and S

Diagonalize

Find coefficients $c^{n,\vec{k}}_{\vec{K}}$ for as many eigenfunctions (same $\vec{k}$, various n) as the matrix dimension

(the outer loop for the self-consistent procedure is not shown !)

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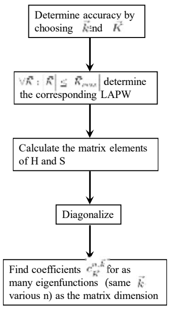
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Diagonalize

Find coefficients $c_{\vec{K}}^{n,\vec{k}}$ for as many eigenfunctions (same $\vec{k}$ various n) as the matrix dimension

(the outer loop for the self-consistent procedure is not shown !)

Instead of 1 solution per many diagonalizations (as for APW), you get many solutions for each diagonalization.

- ⇨ enormous gain in speed
- ⇨ almost no loss in accuracy (linearization error is small)

THE APW+lo METHOD (just briefly)

The present state-of-the-art in this family of methods preserves the accuracy of LAPW, but needs a smaller basis set size (10-fold speed-up).

3 types of basis functions are used (not much details here):

$$\phi_{\vec{K}}^{\vec{k}}(\vec{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r} \in I \\ \sum_{\ell,m} A_{\ell m}^{\alpha,\vec{k}+\vec{K}} u_\ell^\alpha(r', E_{1,\ell}^\alpha) Y_m^\ell(\hat{r}') & \vec{r} \in S_\alpha \end{cases}$$

APW

$$\phi_{\alpha,lo}^{\ell m}(\vec{r}) = \begin{cases} 0 & \vec{r} \notin S_\alpha \\ \left(A_{\ell m}^{\alpha,lo} u_\ell^\alpha(r', E_{1,\ell}^\alpha) + B_{\ell m}^{\alpha,lo} \dot{u}_\ell^\alpha(r', E_{1,\ell}^\alpha) \right) Y_m^\ell(\hat{r}') & \vec{r} \in S_\alpha \end{cases}$$

local orbital
(lo)

$$\phi_{\alpha,LO}^{\ell m}(\vec{r}) = \begin{cases} 0 & \vec{r} \notin S_\alpha \\ \left(A_{\ell m}^{\alpha,LO} u_\ell^\alpha(r', E_{1,\ell}^\alpha) + C_{\ell m}^{\alpha,LO} u_\ell^\alpha(r', E_{2,\ell}^\alpha) \right) Y_m^\ell(\hat{r}') & \vec{r} \in S_\alpha \end{cases}$$

Local Orbital
(LO)

PP+PW vs. LAPW

- On average, the speed of both methods is comparable
- There are good general-purpose implementations for both of them
- Why would you use PW+PP?
  - "everyone does" ➔ many benchmark cases
  - its mathematics are simple ➔ new theory developments are usually implemented first in PP codes (e.g. still no stress tensor formalism within LAPW)
- Why would you use LAPW?
  - You want to start calculating right away, without having to test PP's first
  - "the **golden standard** for accuracy" ➔ whenever there is any doubt about a subtle effect, LAPW will give the ultimate DFT answer (for that XC-functional)
  - straightforward access to effects near the nucleus (core level shifts, hyperfine interactions,...)
- Often this is the best advice:
  "Use the method that you know best."

THE LMTO METHOD (just briefly)

A method that has philosophy similar to LAPW is the Linearized Muffin Tin Orbital method (LMTO). Rather than connecting the atomic solutions inside the spheres to **plane waves**, it connects them to **Hankel functions**.

In particular for close-packed solids, LMTO can be very fast.

CONTENT OVERVIEW

- Basis sets: recapitulation
- Volume partitioning
- augmented plane wave methods
  - The APW method
  - The LAPW method
  - The APW+lo method (briefly)
  - The LMTO method (briefly)
- **The projector augmented wave method (PAW)**
- Comparisons, codes, literature

Center for
Molecular
Modeling

Department of
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the PAW method

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http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

THE PAW METHOD

What does it want to achieve ?

➔ re-write a single-particle Kohn-Sham orbital as a sum of three contributions, each of which can conveniently be expressed in a basis.

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) + \sum_a \psi_n^a(\vec{r}) - \sum_a \tilde{\psi}_n^a(\vec{r})$$

THE PAW METHOD

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$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) + \sum_a \psi_n^a(\vec{r}) - \sum_a \tilde{\psi}_n^a(\vec{r})$$

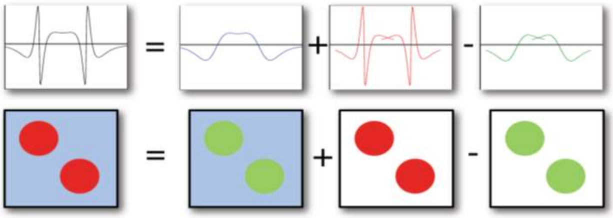
all-electron (Kohn-Sham) wave function	pseudo wave function	all-electron 1-center wave function	pseudo 1-center wave function
defined everywhere	defined everywhere	defined inside spheres	defined inside spheres
steep inside spheres smooth outside spheres	smooth everwhere	steep inside spheres	smooth inside spheres
(no suitable basis, that's the problem…)	expressed in plane wave basis	expressed in partial wave basis	expressed in pseudo partial wave basis

TU Clausthal

(slide by P. Blöchl)

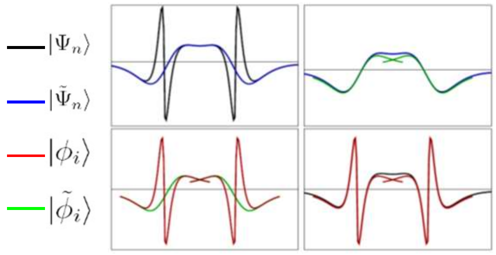
PAW augmentation

$$\underbrace{|\psi\rangle}_{\text{all-electron}} = \overbrace{|\tilde{\psi}\rangle}^{\text{pseudo}} + \overbrace{\underbrace{|\psi^1\rangle}_{\text{1-center, all-el.}}}^{\sum_a |\phi_a\rangle\langle\tilde{p}_a|\tilde{\psi}\rangle} - \overbrace{\underbrace{|\tilde{\psi}^1\rangle}_{\sum_a |\tilde{\phi}_a\rangle\langle\tilde{p}_a|\tilde{\psi}\rangle}}^{\text{1-center, pseudo}}$$



THE PAW METHOD

$$|\Psi\rangle = |\tilde\Psi\rangle + \sum_i \Big(|\phi_i\rangle - |\tilde\phi_i\rangle\Big)\langle\tilde p_i|\tilde\Psi\rangle = |\tilde\Psi\rangle + \sum_R \Big(|\Psi^1_R\rangle - |\tilde\Psi^1_R\rangle\Big)$$



p-σ orbital of a Cl_2 molecule

THE PAW METHOD

How does it achieve this ?

➔ PAW Ansatz :

$$\psi_n(\vec r) \;=\; \tilde\psi_n(\vec r) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec r)}_{1} - \underbrace{\tilde\phi_i^a(\vec r)}_{2}\right)\left\langle \underbrace{\tilde p_i^a}_{3} \middle| \tilde\psi_n \right\rangle$$

By making a choice for each of the three numbered objects,
the re-writing we are aiming for can be unambiguously defined.

a = sum over atoms in the unit cell (or 'augmentation spheres')
i = sum over basis functions

THE PAW METHOD

How does it achieve this ?

➔ PAW Ansatz :

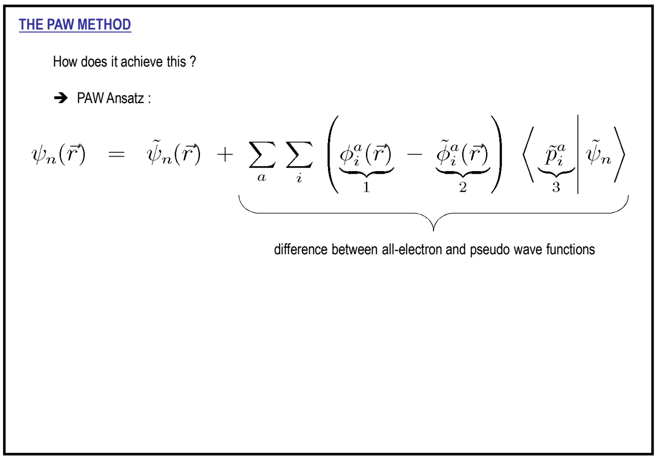
$$\psi_n(\vec r) \;=\; \boxed{\tilde\psi_n(\vec r)} + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec r)}_{1} - \underbrace{\tilde\phi_i^a(\vec r)}_{2}\right)\left\langle \underbrace{\tilde p_i^a}_{3} \middle| \tilde\psi_n \right\rangle$$

pseudo wave function

- outside the spheres:
  - identical to the all-electron wave function (which we don't know yet)
  - surely smooth, as the all-electron wave function is smooth there

- inside the spheres:
  - different from the all-electron wave function
  - smooth

➔ How the pseudo wave function will look like,
will be fully determined by the three choices we'll make.

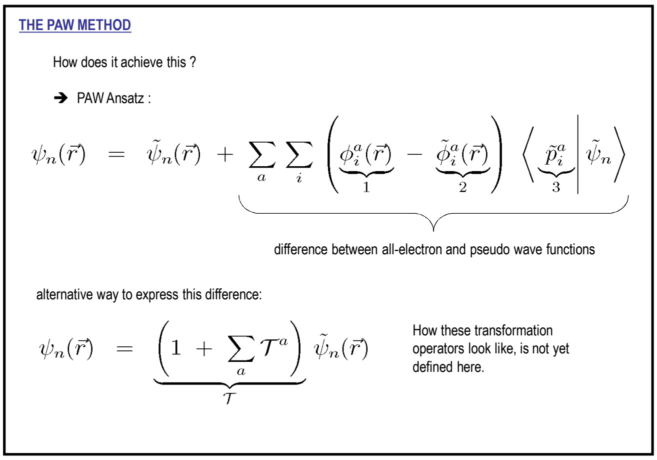


THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) + \underbrace{\sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle}_{\text{difference between all-electron and pseudo wave functions}}$$



THE PAW METHOD

How does it achieve this ?

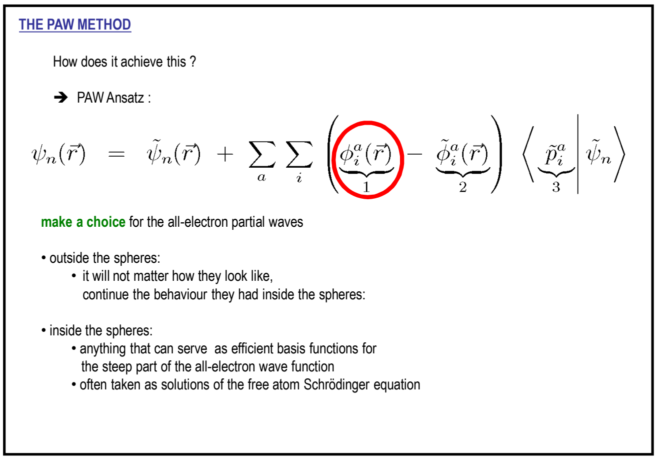
→ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) + \underbrace{\sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle}_{\text{difference between all-electron and pseudo wave functions}}$$

alternative way to express this difference:

$$\psi_n(\vec{r}) \;=\; \underbrace{\left(1 + \sum_a \mathcal{T}^a \right)}_{\mathcal{T}} \tilde{\psi}_n(\vec{r})$$

How these transformation operators look like, is not yet defined here.



THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\boxed{\underbrace{\phi_i^a(\vec{r})}_{1}} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

make a choice for the all-electron partial waves

- outside the spheres:
  - it will not matter how they look like, continue the behaviour they had inside the spheres:

- inside the spheres:
  - anything that can serve as efficient basis functions for the steep part of the all-electron wave function
  - often taken as solutions of the free atom Schrödinger equation

THE PAW METHOD

How does it achieve this ?

➔ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) \;+\; \sum_a \sum_i \left(\boxed{\underbrace{\phi_i^a(\vec{r})}_{1}} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

You can use the (as yet unspecified) transformation operators to produce smooth pseudo-versions of the all-electron partial waves:

$$\phi_i^a(\vec{r}) \;=\; (1 \;+\; \mathcal{T}^a)\; \tilde{\phi}_i^a(\vec{r})$$

Alternatively, by making a choice for these pseudo partial waves, the transformation operators are defined:

$$\mathcal{T}^a\, \tilde{\phi}_i^a \;=\; \phi_i^a \;-\; \tilde{\phi}_i^a$$

Therefore...

THE PAW METHOD

How does it achieve this ?

➔ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) \;+\; \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \boxed{\underbrace{\tilde{\phi}_i^a(\vec{r})}_{2}} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

make a choice for the pseudo partial waves

- outside the spheres:
  - choose them to be identical to the all-electron partial waves

- inside the spheres:
  - choose them such that they can serve as a basis for the pseudo wave function inside the sphere:

$$\tilde{\psi}_n(\vec{r}) \;=\; \sum_i C_{ni}^a\, \tilde{\phi}_i^a(\vec{r}) \qquad \vec{r} \in \text{sphere `a'}$$

THE PAW METHOD

How does it achieve this ?

➔ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) \;+\; \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \boxed{\left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle}$$

(omitting the proof/derivation here) the expansion coefficients are determined by applying appropriate projectors to the pseudo wave function. There is quite some freedom to **choose** these element-specific **projectors**. The choice made determines how smooth the pseudo wave function will be.

$$\tilde{\psi}_n(\vec{r}) \;=\; \sum_i \boxed{C_{ni}^a}\, \tilde{\phi}_i^a(\vec{r}) \qquad \vec{r} \in \text{sphere `a'}$$

THE PAW METHOD

How does it achieve this ?

➔ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) \;+\; \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

By defining

$$\sum_i \langle \tilde{p}_i^a \left| \tilde{\psi}_n \right\rangle \phi_i^a(\vec{r}) \;=\; \psi_n^a(\vec{r})$$

the all-electron 1-center functions (steep, inside sphere, expressed in a partial wave basis)

and

$$\sum_i \langle \tilde{p}_i^a \left| \tilde{\psi}_n \right\rangle \tilde{\phi}_i^a(\vec{r}) \;=\; \tilde{\psi}_n^a(\vec{r})$$

the pseudo 1-center functions (smooth, inside sphere, expressed in a pseudo partial wave basis)

we find that the Ansatz leads to the desired expression:

THE PAW METHOD

How does it achieve this ?

➔ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) \;+\; \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

⇓

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) \;+\; \sum_a \psi_n^a(\vec{r}) \;-\; \sum_a \tilde{\psi}_n^a(\vec{r})$$

THE PAW METHOD

Practical procedure :

After having made the required choices :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) \;+\; \sum_a \sum_i \left(\boxed{\underbrace{\phi_i^a(\vec{r})}_{1}} - \boxed{\underbrace{\tilde{\phi}_i^a(\vec{r})}_{2}} \right) \boxed{\left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle}$$

you know the transformation operator and can replace ψ_n in the Kohn-Sham equations by $\mathcal{T}\tilde{\psi}_n$. This leads to a transformed KS-equation, with $\tilde{\psi}_n$ as the unknown. Solve it for $\tilde{\psi}_n$, after which you can finally fill out all items in the right-hand side of the above expression.

THE PAW METHOD

Important issue :

$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

The choice of the element-dependent projector functions (the "P" in PAW) determines how smooth the pseudo wave function will be, and hence how small the plane wave basis (and the speed of the calculation) will be.

Generating suitable projectors is partly a kind of art, comparable to the art of generating good pseudopotentials.

Well-tested tabulations of projector functions are either a propietary part of code (e.g. for VASP), or are freely available for use across codes (e.g. http://users.wfu.edu/natalie/papers/pwpaw/newperiodictable/).

An extensive discussion on PAW generation can be found at http://arxiv.org/pdf/1309.7274.pdf .

BASIS SETS : RECAPITULATION

DFT	*formal*	HK1 HK2 ➔ $\rho(\vec{r})$
Kohn-Sham equations	*practical*	$\hat{H}_{KS}\phi_i = \epsilon_i\phi_i$ XC-functional
basis set	*transformation to algebra (convenient)*	$\phi_i = \sum_{j=1}^{\infty} c_{ij}\chi_j$ HC=SCE matrix diagonalization

PAW

local basis set	**plane waves + pseudopotentials**	**augmented methods**
☺ small basis set	☹ not so small	☹ not so small
☺ physical insight	☹ less intuitive	☺ more intuitive
☹ not orthogonal	☺ orthogonal	☹ not orthogonal
☹ depends on atomic position	☺ position-independent	☺ position independent
☹ BSSE? completeness?	☹ effect of PP?	☺ very accurate (some)
	☺ periodic ➔ crystals	☺ periodic ➔ crystals
		☺ core information (some)

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(L)APW and PAW codes, and how they compare

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LAPW codes

WIEN2k
http://www.wien2k.at

review paper
K. Schwarz, Journal of Solid State Chemistry 176 (2003) 319
http://dx.doi.org/10.1016/S0022-4596(03)00213-5

FLEUR
www.flapw.de

EXCITiNG
http://exciting-code.org/

ELK
http://elk.sourceforge.net/

PAW codes

VASP
http://cms.mpi.univie.ac.at/vasp/

review paper
Computer Physics Communications 177 (2007) 6-13

ABINIT
http://www.abinit.org/

review paper
Computer Physics Communications 180 (2009) 2582-2615

CP-PAW
https://www2.pt.tu-clausthal.de/paw/

review paper
Physical Review B 50 (1994) 17953-17979

atompw / pwpaw
http://www.wfu.edu/~natalie/papers/pwpaw/man.html

review paper
Computer Physics Communications 135 (2001) 329–347
Computer Physics Communications 135 (2001) 348–376

Further reading

Density Functional Theory and the family of (L)APW-methods: a step-by-step introduction
S. Cottenier
Instituut voor Kern- en Stralingsfysica, KU Leuven, Belgium (2002)
ISBN 90-807215-1-4
http://www.wien2k.at/reg_user/textbooks (free download)

+ references therein.

Ch. 2: PW+PP
Ch. 3-5: (L)APW(+lo)
Ch. 6: PAW

Electronic structure methods: Augmented Waves, Pseudopotentials and the Projector Augmented Wave Method
Peter E. Bloechl, Johannes Kaestner, Clemens J. Foerst
chapter in "Handbook of Materials Modeling", Sidney Yip (Ed.), Springer (2005),
ISBN 1-4020-3287-0
http://arxiv.org/abs/cond-mat/0407205 (free download)

+ references therein

Further reading

First-principles simulation: ideas, illustrations and the CASTEP code
M D Segall, Philip J D Lindan, M J Probert, C J Pickard,
P J Hasnip, S J Clark and M C Payne
J. Phys.: Condens. Matter 14 (2002) 2717–2744
http://stacks.iop.org/cm/14/2717 (available on Minerva)

+ references therein

Excellently written, without much of the usual technical slang.
Recommended reading, as a kind of text book that summarizes much of this course up to here.

Appendix: DFT-accuracy vs. experiment / accuracy of various basis sets

Source: Error Estimates for Solid-State Density-Functional Theory Predictions:
An Overview by Means of the Ground-State Elemental Crystals
K. Lejaeghere et al., Crit. Rev. Solid State Mater. Sci. 39, 1 (2014)
http://dx.doi.org/10.1080/10408436.2013.772503 (open access)

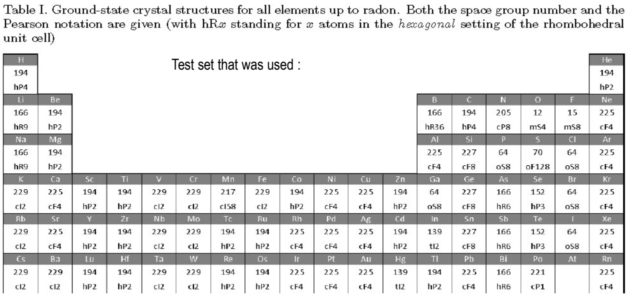
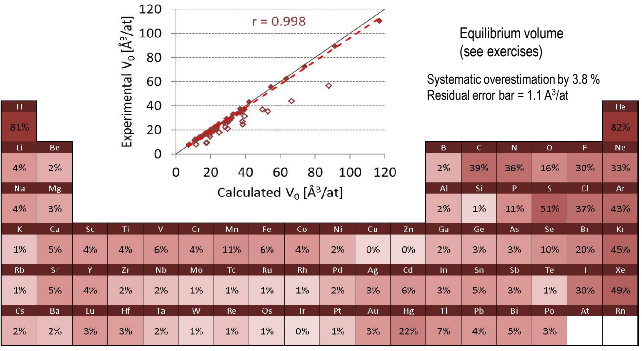


Table I. Ground-state crystal structures for all elements up to radon. Both the space group number and the Pearson notation are given (with hRx standing for x atoms in the *hexagonal* setting of the rhombohedral unit cell)

Test set that was used :

H																	He
194																	194
hP4																	hP2
Li	Be											B	C	N	O	F	Ne
166	194											166	194	205	12	15	225
hR9	hP2											hR36	hP4	cP8	mS4	mS8	cF4
Na	Mg											Al	Si	P	S	Cl	Ar
166	194											225	227	64	70	64	225
hR9	hP2											cF4	cF8	oS8	oF128	oS8	cF4
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
229	225	194	194	229	229	217	229	194	225	225	194	64	227	166	152	64	225
cI2	cF4	hP2	hP2	cI2	cI2	cI58	cI2	hP2	cF4	cF4	hP2	oS8	cF8	hR6	hP3	oS8	cF4
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
229	225	194	194	229	229	194	194	225	225	225	194	139	227	166	152	64	225
cI2	cF4	hP2	hP2	cI2	cI2	hP2	hP2	cF4	cF4	cF4	hP2	tI2	cF8	hR6	hP3	oS8	cF4
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
229	229	194	194	229	229	194	194	225	225	225	139	194	225	166	221		225
cI2	cI2	hP2	hP2	cI2	cI2	hP2	hP2	cF4	cF4	cF4	tI2	hP2	cF4	hR6	cP1		cF4

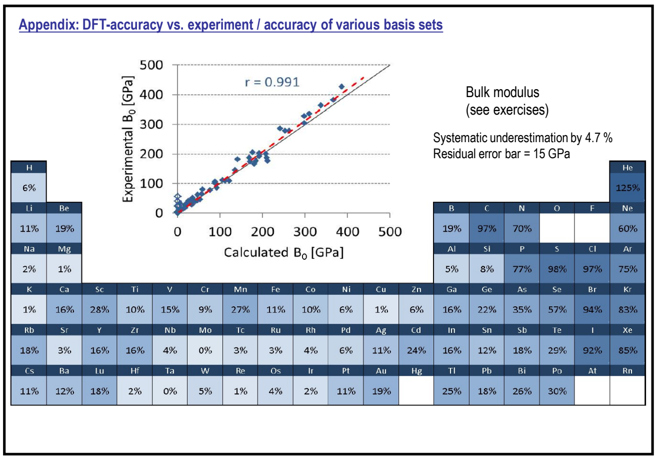
Appendix: DFT-accuracy vs. experiment / accuracy of various basis sets



Equilibrium volume
(see exercises)

Systematic overestimation by 3.8 %
Residual error bar = 1.1 A^3/at

H																	He
81%																	82%
Li	Be											B	C	N	O	F	Ne
4%	2%											2%	39%	36%	16%	30%	33%
Na	Mg											Al	Si	P	S	Cl	Ar
4%	3%											2%	1%	11%	51%	37%	43%
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
1%	5%	4%	4%	6%	4%	11%	6%	4%	2%	0%	0%	2%	3%	3%	10%	20%	45%
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
1%	5%	4%	2%	2%	1%	1%	1%	1%	2%	3%	6%	3%	5%	3%	1%	30%	49%
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
2%	2%	3%	3%	2%	1%	1%	1%	0%	1%	3%	22%	7%	4%	5%	3%		

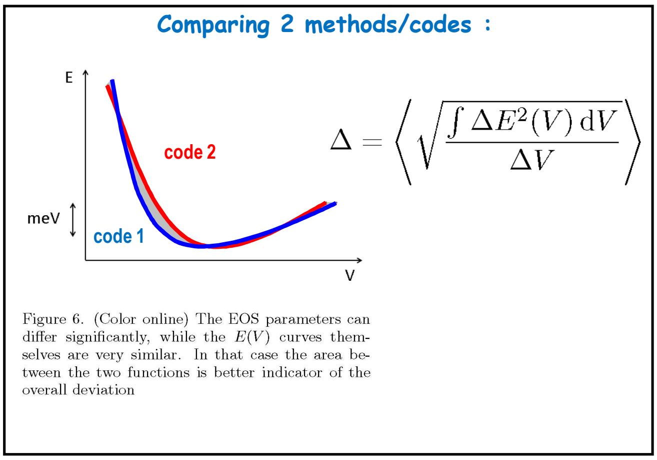


Appendix: DFT-accuracy vs. experiment / accuracy of various basis sets

Bulk modulus
(see exercises)

Systematic underestimation by 4.7 %
Residual error bar = 15 GPa

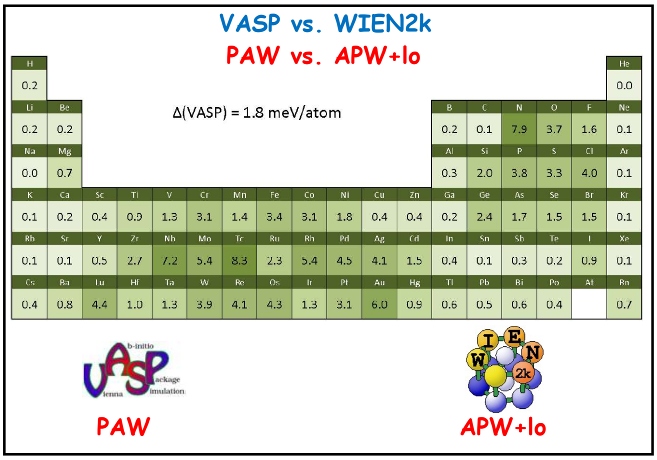
H																	He
6%																	125%
Li	Be											B	C	N	O	F	Ne
11%	19%											19%	97%	70%			60%
Na	Mg											Al	Si	P	S	Cl	Ar
2%	1%											5%	8%	77%	98%	97%	75%
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
1%	16%	28%	10%	15%	9%	27%	11%	10%	6%	1%	6%	16%	22%	35%	57%	94%	83%
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
18%	3%	16%	16%	4%	0%	3%	3%	4%	6%	11%	24%	16%	12%	18%	29%	92%	85%
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
11%	12%	18%	2%	0%	5%	1%	4%	2%	11%	19%		25%	18%	26%	30%		



Comparing 2 methods/codes :

$$\Delta = \left\langle \sqrt{\frac{\int \Delta E^2(V)\,\mathrm{d}V}{\Delta V}} \right\rangle$$

Figure 6. (Color online) The EOS parameters can differ significantly, while the $E(V)$ curves themselves are very similar. In that case the area between the two functions is better indicator of the overall deviation



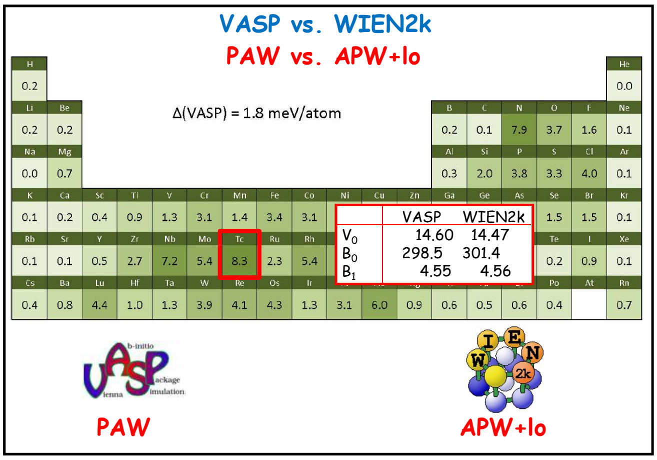
VASP vs. WIEN2k
PAW vs. APW+lo

Δ(VASP) = 1.8 meV/atom

H																	He
0.2																	0.0
Li	Be											B	C	N	O	F	Ne
0.2	0.2											0.2	0.1	7.9	3.7	1.6	0.1
Na	Mg											Al	Si	P	S	Cl	Ar
0.0	0.7											0.3	2.0	3.8	3.3	4.0	0.1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.1	0.2	0.4	0.9	1.3	3.1	1.4	3.4	3.1	1.8	0.4	0.4	0.2	2.4	1.7	1.5	1.5	0.1
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.1	0.1	0.5	2.7	7.2	5.4	8.3	2.3	5.4	4.5	4.1	1.5	0.4	0.1	0.3	0.2	0.9	0.1
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.4	0.8	4.4	1.0	1.3	3.9	4.1	4.3	1.3	3.1	6.0	0.9	0.6	0.5	0.6	0.4		0.7

PAW

APW+lo



VASP vs. WIEN2k

PAW vs. APW+lo

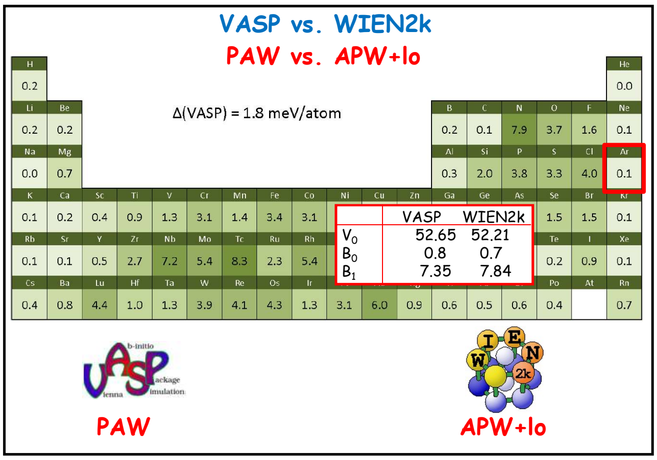
Δ(VASP) = 1.8 meV/atom

H																	He
0.2																	0.0
Li	Be											B	C	N	O	F	Ne
0.2	0.2											0.2	0.1	7.9	3.7	1.6	0.1
Na	Mg											Al	Si	P	S	Cl	Ar
0.0	0.7											0.3	2.0	3.8	3.3	4.0	0.1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.1	0.2	0.4	0.9	1.3	3.1	1.4	3.4	3.1							1.5	1.5	0.1
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh							Te	I	Xe
0.1	0.1	0.5	2.7	7.2	5.4	8.3	2.3	5.4							0.2	0.9	0.1
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir							Po	At	Rn
0.4	0.8	4.4	1.0	1.3	3.9	4.1	4.3	1.3	3.1	6.0	0.9	0.6	0.5	0.6	0.4		0.7

	VASP	WIEN2k
V_0	14.60	14.47
B_0	298.5	301.4
B_1	4.55	4.56

PAW

APW+lo



VASP vs. WIEN2k

PAW vs. APW+lo

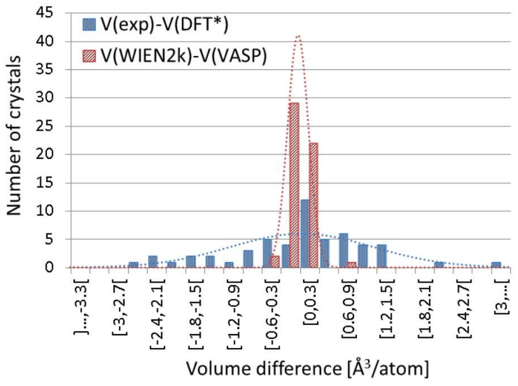
Δ(VASP) = 1.8 meV/atom

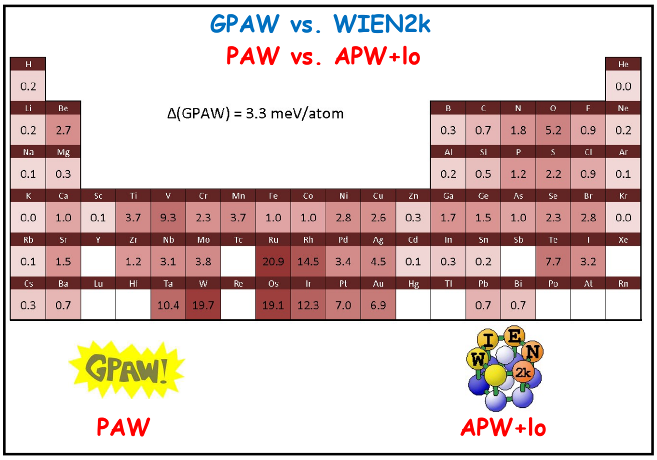
H																	He
0.2																	0.0
Li	Be											B	C	N	O	F	Ne
0.2	0.2											0.2	0.1	7.9	3.7	1.6	0.1
Na	Mg											Al	Si	P	S	Cl	Ar
0.0	0.7											0.3	2.0	3.8	3.3	4.0	0.1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.1	0.2	0.4	0.9	1.3	3.1	1.4	3.4	3.1							1.5	1.5	0.1
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh							Te	I	Xe
0.1	0.1	0.5	2.7	7.2	5.4	8.3	2.3	5.4							0.2	0.9	0.1
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir							Po	At	Rn
0.4	0.8	4.4	1.0	1.3	3.9	4.1	4.3	1.3	3.1	6.0	0.9	0.6	0.5	0.6	0.4		0.7

	VASP	WIEN2k
V_0	52.65	52.21
B_0	0.8	0.7
B_1	7.35	7.84

PAW

APW+lo





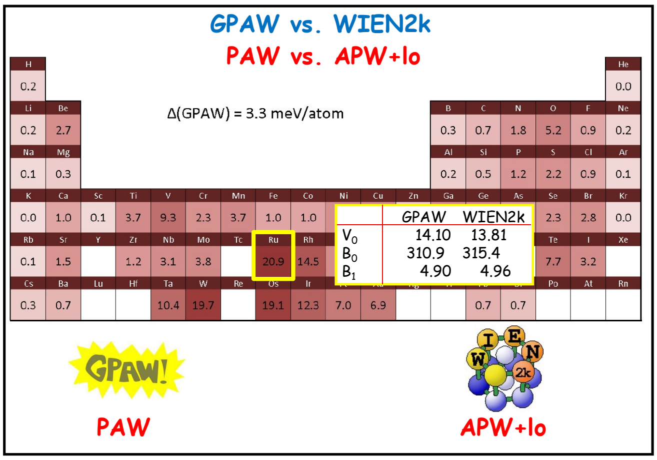
GPAW vs. WIEN2k
PAW vs. APW+lo

Δ(GPAW) = 3.3 meV/atom

H																	He
0.2																	0.0
Li	Be											B	C	N	O	F	Ne
0.2	2.7											0.3	0.7	1.8	5.2	0.9	0.2
Na	Mg											Al	Si	P	S	Cl	Ar
0.1	0.3											0.2	0.5	1.2	2.2	0.9	0.1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.0	1.0	0.1	3.7	9.3	2.3	3.7	1.0	1.0	2.8	2.6	0.3	1.7	1.5	1.0	2.3	2.8	0.0
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.1	1.5		1.2	3.1	3.8		20.9	14.5	3.4	4.5	0.1	0.3	0.2		7.7	3.2	
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.3	0.7			10.4	19.7		19.1	12.3	7.0	6.9			0.7	0.7			

PAW

APW+lo



GPAW vs. WIEN2k
PAW vs. APW+lo

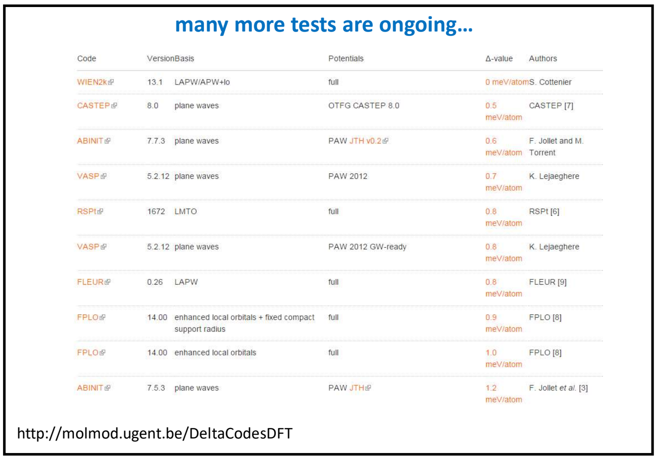
Δ(GPAW) = 3.3 meV/atom

H																	He
0.2																	0.0
Li	Be											B	C	N	O	F	Ne
0.2	2.7											0.3	0.7	1.8	5.2	0.9	0.2
Na	Mg											Al	Si	P	S	Cl	Ar
0.1	0.3											0.2	0.5	1.2	2.2	0.9	0.1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.0	1.0	0.1	3.7	9.3	2.3	3.7	1.0	1.0							2.3	2.8	0.0
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh							Te	I	Xe
0.1	1.5		1.2	3.1	3.8		20.9	14.5							7.7	3.2	
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir							Po	At	Rn
0.3	0.7			10.4	19.7		19.1	12.3	7.0	6.9			0.7	0.7			

	GPAW	WIEN2k
V_0	14.10	13.81
B_0	310.9	315.4
B_1	4.90	4.96

PAW

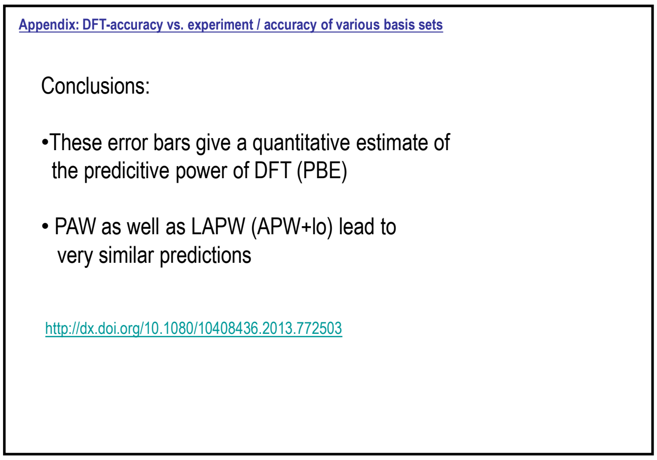
APW+lo



many more tests are ongoing…

Code	Version	Basis	Potentials	Δ-value	Authors
WIEN2k	13.1	LAPW/APW+lo	full	0 meV/atom	S. Cottenier
CASTEP	8.0	plane waves	OTFG CASTEP 8.0	0.5 meV/atom	CASTEP [7]
ABINIT	7.7.3	plane waves	PAW JTH v0.2	0.6 meV/atom	F. Jollet and M. Torrent
VASP	5.2.12	plane waves	PAW 2012	0.7 meV/atom	K. Lejaeghere
RSPt	1672	LMTO	full	0.8 meV/atom	RSPt [6]
VASP	5.2.12	plane waves	PAW 2012 GW-ready	0.8 meV/atom	K. Lejaeghere
FLEUR	0.26	LAPW	full	0.8 meV/atom	FLEUR [9]
FPLO	14.00	enhanced local orbitals + fixed compact support radius	full	0.9 meV/atom	FPLO [8]
FPLO	14.00	enhanced local orbitals	full	1.0 meV/atom	FPLO [8]
ABINIT	7.5.3	plane waves	PAW JTH	1.2 meV/atom	F. Jollet *et al.* [3]

http://molmod.ugent.be/DeltaCodesDFT



Appendix: DFT-accuracy vs. experiment / accuracy of various basis sets

Conclusions:

- These error bars give a quantitative estimate of the predicitive power of DFT (PBE)
- PAW as well as LAPW (APW+lo) lead to very similar predictions

http://dx.doi.org/10.1080/10408436.2013.772503