Comparison of Different Methods and Codes: (L)APW, LMTO, PAW, Pseudo Potentials, Gaussians, etc.

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Density-Functional Theory

Kohn-Sham equations:

W. Kohn, and L. J. Sham, *Phys. Rev.* A**140** (1965) 1133.

$$\left(-\frac{1}{2}\Delta + V_{\mathrm{eff}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

single-particle Schrödinger-like equation

KS orbital $$\phi_i(\mathbf{r}) = \sum_j c_{ij}\chi_j(\mathbf{r})$$

electron density $$\rho(\mathbf{r}) = \sum_i f_i\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$$

$\phi_i(\mathbf{r})$	KS orbital
$\chi_j(\mathbf{r})$	basis function
f_i	occupation number

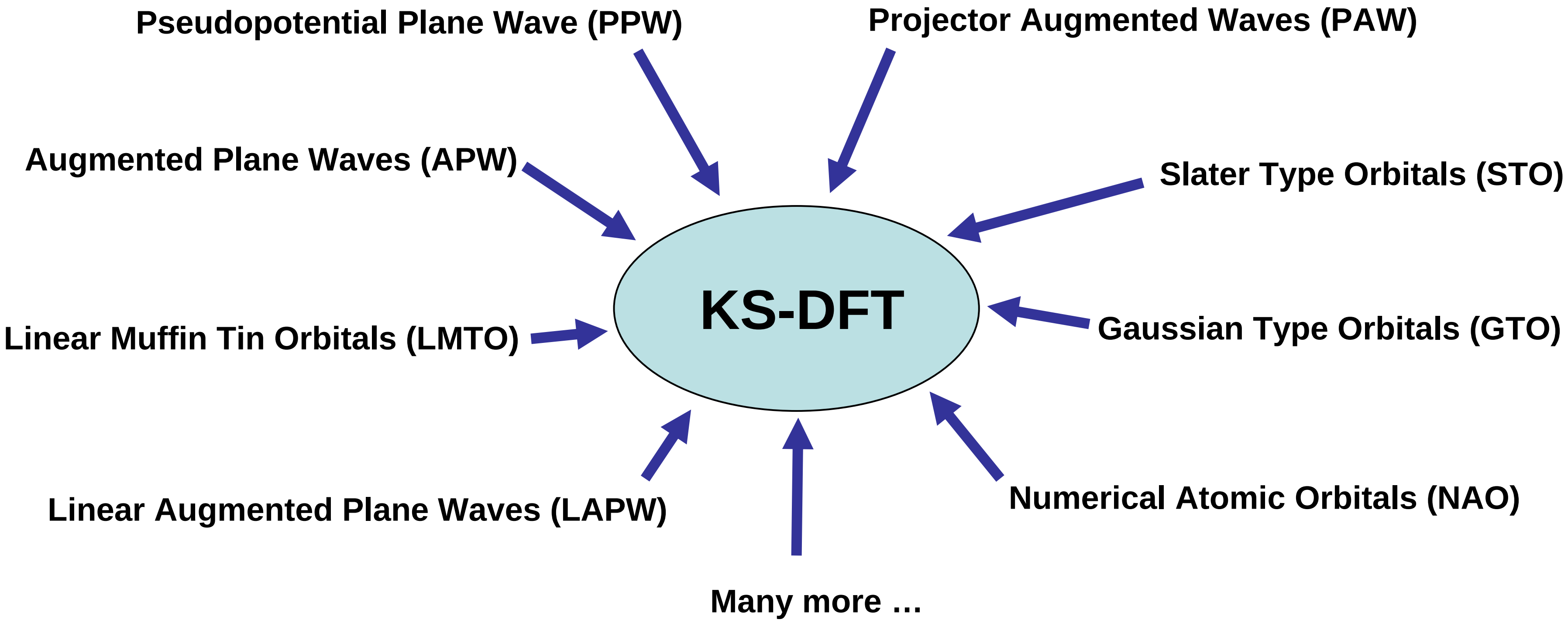
DFT-based electronic structure methods are classified according to the representation that is used for the Kohn-Sham orbitals.

$\Rightarrow$ **This is the topic of this talk**

Outline

There are many different approaches to represent the Kohn-Sham orbitals:

Basis Set Expansions



Pseudopotential Plane Wave (PPW)

Projector Augmented Waves (PAW)

Augmented Plane Waves (APW)

Slater Type Orbitals (STO)

KS-DFT

Linear Muffin Tin Orbitals (LMTO)

Gaussian Type Orbitals (GTO)

Linear Augmented Plane Waves (LAPW)

Numerical Atomic Orbitals (NAO)

Many more …

Basis Set-Free Numerical Solution of the KS Equations on a Grid

Not the topic of this talk

Outline

Atomic region:

Rapid oscillations of the wavefunctions require fine grid for accurate numerical representation, chemical environment has little effect on the shape of the wavefunction, small basis set would be sufficient if chosen properly.

Interatomic (bonding) region:

Wavefunction is smooth but very flexible and responds strongly to the environment, requires large basis sets.

Approaches:

„Atomic Point of View“

Basis functions similar to atomic orbitals:

- numerical, hard to handle but efficient
- general (Gaussians), easy to handle but larger basis

„Solid State Point of View“

Atoms are a perturbation of the free electron gas:

- plane waves + pseudopotentials
- complete but large basis, very easy to handle

Some Terms

Efficiency:

How many basis functions are needed for a given level of convergence?

Cost of the calculations

Bias:

Do the basis functions favor certain regions of space over other regions (by being more flexible in some regions)?

Accuracy of the calculations

Simplicity:

How difficult is it to calculate the matrix elements $\langle\chi_i|H|\chi_j\rangle$ and $\langle\chi_i|\chi_j\rangle$?

Effort in code development

Completeness:

Can the basis be improved arbitrarily by adding additional functions of the same type?

Accuracy of the calculations

Plane Wave Basis Sets

Why Plane Waves?

Bloch Theorem:

In a periodic solid (potential) each wavefunction can be written as a product of a lattice-periodic part $u(\mathbf{k},\mathbf{r}+\mathbf{R}) = u(\mathbf{k},\mathbf{r})$ and a plane wave $e^{i\mathbf{k}\mathbf{r}}$:

$$\psi(\mathbf{k},\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \cdot u(\mathbf{k},\mathbf{r})$$

The lattice-periodic part can be expanded in plane waves whose wave vectors $\mathbf{G}$ are reciprocal lattice vectors:

$$u(\mathbf{k},\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}}\, e^{i\mathbf{G}\mathbf{r}}$$

⇒ Kohn-Sham states $$\psi_j(\mathbf{k},\mathbf{r}) = \sum_{\mathbf{G}} c_{j,\mathbf{k},\mathbf{G}}\, e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

Note: This approach is of more general interest, also for non-periodic systems, which can be modeled by supercells.

Plane Wave Basis Sets

⇒ Each wavefunction can be expanded in plane waves!

⇒ basis functions: $\chi^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$

Problem: There are strong oscillations in the wavefunctions near the nucleus.

⇒ A very large number of plane waves is required to describe these oscillations.

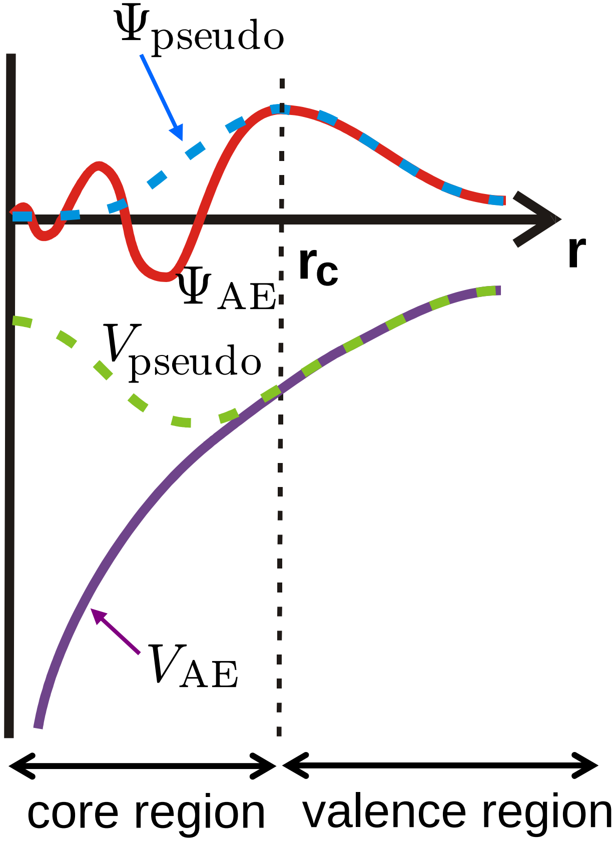
⇒ It is impossible to perform all-electron plane wave calculations for systems of practical interest.

But: Oscillations are due to core states which are less important for bonding (U. von Barth, and C. D. Gelatt, *Phys. Rev. B* **21** (1980) 2222.)

⇒ Oscillations can be removed by introducing pseudo potentials.

Norm-Conserving Pseudopotentials

Aim: Remove Oscillations in Core Region



The potential inside some core radius r_c is replaced by a pseudopotential describing the nucleus and the core electrons.

- no explicit description of the core electrons
- pseudo wavefunctions have no nodes/wiggles in the core region
- correct total charge inside core radius (norm-conservation), proper electrostatic potential for $r > r_c$
- outside r_c $\Psi_{\rm AE}$ and $\Psi_{\rm pseudo}$ are the same

$\Rightarrow$ much smaller, realistic basis sets can be used

Typically, the pseudo potential is different for each angular momentum (non-local pseudopotential).

Pseudopotentials

Transferability

The pseudopotential is generated for a given atomic environment (free atom).

But:
The pseudopotential should describe the scattering due to the ion in many different atomic environments.

Hardness

Soft pseudopotentials: few plane waves are sufficient to expand the pseudo wavefunctions

Hard pseudopotentials: many plane waves are needed to expand the pseudo wavefunctions

small r_c: hard but more transferrable pseudopotential
large r_c: soft but less transferrable pseudopotential

⇒ Compromise between efficiency and accuracy

Pseudopotentials

The Cutoff

A finite basis set of plane waves can be used, because

- there are only discrete **G** due to the lattice periodicity
- coefficients for PWs with small kinetic energy are typically most important

The size of the basis set is defined by the plane wave cutoff.

- The plane wave cutoff is the highest kinetic energy of all basis functions and determines the number of basis functions.
- The basis set convergence can systematically be controlled by increasing the plane wave cutoff.

$$E^{\mathrm{cut}} = \frac{\hbar^2}{2m}|\mathbf{G}_{\mathrm{max}}|^2$$

Construction of Pseudopotentials

All-electron DFT calculation for a spherical atom on radial grid

$\Rightarrow$ atomic potential and the all-electron partial waves $\phi_{lm}(\mathbf{r})$

There are many ways to construct the pseudo wavefunctions $\tilde{\phi}_{lm}(\mathbf{r})$:

D. R. Hamann, *Phys. Rev. Lett.* **42** (1979) 662.

G. P. Kerker, *J. Phys. C* **13** (1980) L189.

G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26** (1982) 4199.

N. Troullier, and J. L. Martins, *Phys. Rev. B* **43** (1991) 1993.

J. S. Lin, A. Qteish, M. C. Payne, and V. Heine, *Phys. Rev. B* **47** (1993) 4174.

- outside the core region: identical to the true wavefunction
- inside core region: nodeless and the same norm as the true wavefunction

From the pseudo wavefunctions a potential $u_l(\mathbf{r})$ is reconstructed by inverting the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_e}\Delta + u_l(\mathbf{r}) - \epsilon_{l,m}\right)\tilde{\phi}_{l,m}(\mathbf{r}) = 0$$

$$\Rightarrow u_l(\mathbf{r}) = \epsilon_{l,m} + \frac{1}{\tilde{\phi}_{l,m}(\mathbf{r})} \cdot \frac{\hbar^2}{2m_e}\Delta\tilde{\phi}_{l,m}(\mathbf{r})$$

Construction of Pseudopotentials

The pseudo potential can then be obtained as („unscreening“):

$$v_l^{\mathrm{ps}}(\mathbf{r}) = u_l(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0}\int d^3r\,\frac{\tilde{n}(\mathbf{r}') + \tilde{Z}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \mu_{\mathrm{xc}}([\tilde{n}(\mathbf{r})],\mathbf{r})$$

with

$$\tilde{n}(\mathbf{r}) = \sum_n f_n \tilde{\Psi}^*(\mathbf{r})\tilde{\Psi}_n(\mathbf{r})$$ pseudo density

$\tilde{Z}(\mathbf{r})$ Charge density of nucleus and core electrons (Gaussian)

Different potential for each angular momentum!

Most general form of a non-local pseudo potential (semi-local):

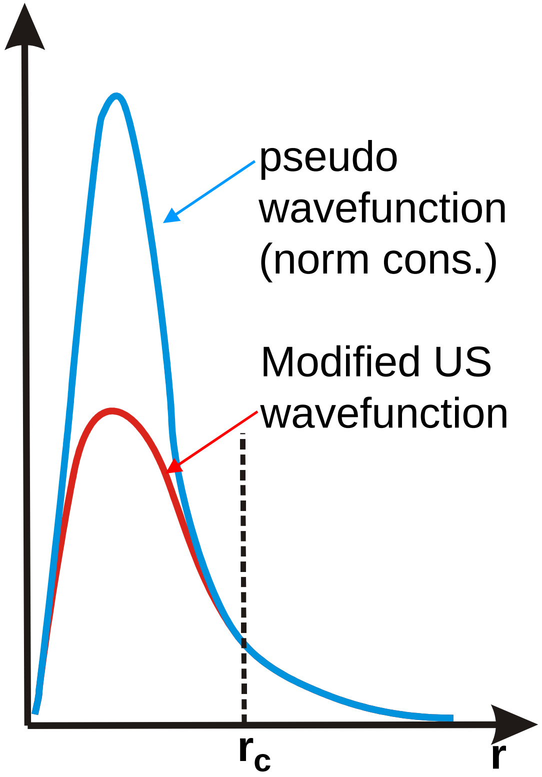
$$V_{\mathrm{PS}} = \sum_{lm} |Y_{lm}\rangle v_l \langle Y_{lm}|$$

Y_{lm} spherical harmonics

Ultrasoft Pseudo Potentials

Aim: Plane wave cutoff should be as low as possible

D. Vanderbilt, *Phys. Rev. B* **41** (1990) 7892.
K. Laasonen, R. Car, C. Lee, and D. Vanderbilt, *Phys. Rev. B* **43** (1991) 6796.



Problem:

Even for norm-conserving pseudo potentials large cutoffs might be required.

Solution:

$r > r_c$: ψ^{US} identical to the AE wavefunction
$r < r_c$: ψ^{US} as soft as possible

$\Rightarrow$ The norm-conservation rule is relaxed.

$\Rightarrow$ introduction of atom-centered augmentation charges to compensate for charge deficit

Pros and Cons of the PPW Method

Advantages:

- systematic convergence is possible by increasing the cutoff
- simple forces (no Pulay corrections required)
- basis independent of atomic positions and species (no BSSE, unbiased)
- simple coding
- no need to include core electrons (less KS orbitals to calculate)
- total energies smaller (less sensitive to numerical noise)

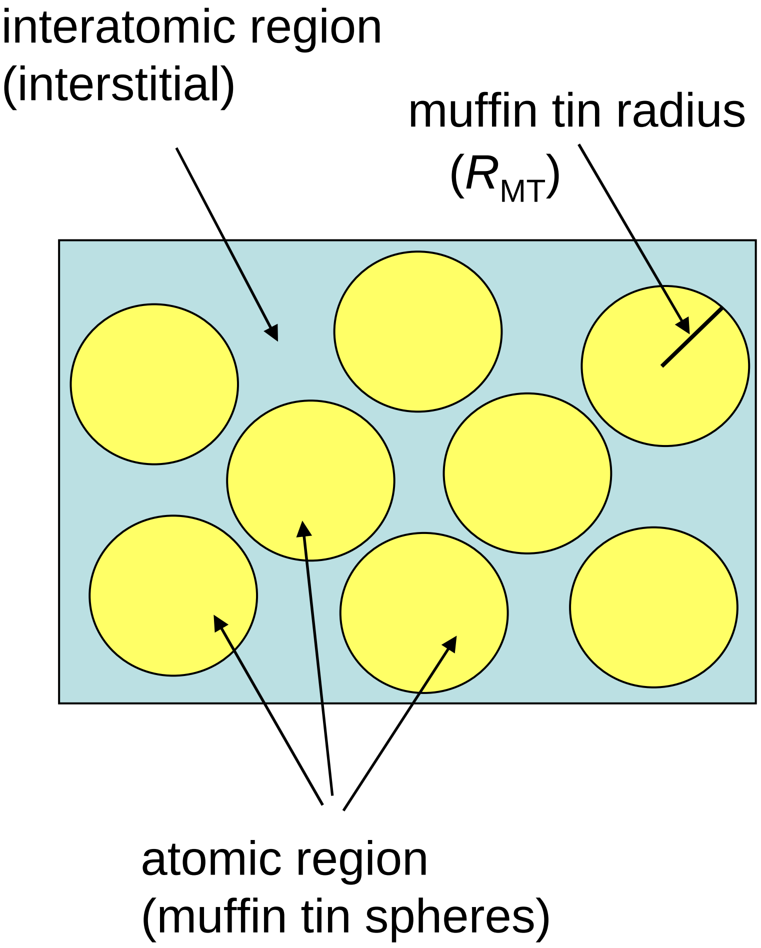
Disadvantages:

- not all-electron, pseudopotentials can introduce errors (transferability)
- large basis sets (about 100 PWs per atom)
- volume variation changes basis set size for given cutoff
- all information on the charge density and wavefunctions near the nucleus is lost (some quantities require core wavefunctions)
- bound to periodic boundary conditions (plane waves!)

References Pseudopotentials

- M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64** (1992) 1045.
- D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method,* Kluwer, 1994.
- W.E. Pickett, *Comp. Phys. Rep.* **9** (1989) 115.
- M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, *Comp. Phys. Comm.* **107** (1997) 187.
- Martin Fuchs, „Pseudopotentials for ab initio electronic structure calculations“ http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2003/Dtalks/FHI-WS2003-L04-Fuchs-Pseudopotentials_For_Ab-Initio_Calculations.pdf
- E. Pehlke, „The Plane-Wave Pseudopotential Method“ http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2003/Dtalks/FHI-WS2003-L03-Pehlke-The_Plane-Wave_Pseudopotential_Method.pdf
- G. Kresse, and J. Furthmüller, *Comp. Mat. Sci*. **6** (1996) 15.

Augmentation Methods



Motivation

Strong oscillations of the wavefunctions in the core region ⇒ PWs not sufficient

Is there an all-electron method?

Augmented Wave Methods:

⇒ all-electron method possible if suitable basis functions can be constructed

- core regions: atom-like wavefunctions
- bonding regions: „envelope functions“

J. C. Slater, *Phys. Rev.* **51** (1937) 846.
O. K. Andersen, *Phys. Rev. B* **12** (1975) 3060.

Augmentation Methods: Overview

Method	Core Region atom-centered spheres	Bonding Region Interstitial
APW	AOs	PWs
LAPW	AOs	PWs
LMTO	AOs	Hankel Functions
PAW	Projectors + PWs	PWs

Other Approaches

PPW	Pseudopotentials + PWs	PWs
Local Basis	e.g. NAOs	e.g. NAOs

Augmented Planewave Method

Muffin tin Approximation („historic“):

Muffin tin region: Solution of the radial Schrödinger equation for the spheridized effective potential.

Interstitial region: Solution of the Schrödinger equation for a constant potential.

⇒ Basis function (augmented planewave):

APWs are non-orthogonal

$$\chi^{\mathbf{k}}(\mathbf{r}, E) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} & \mathbf{r} \in I \\ \sum_{lm} A_{lm}^{\alpha,\mathbf{k}+\mathbf{G}} u_l^{\alpha}(r', E) Y_{lm}(\theta, \phi) & \mathbf{r} \in R_{\mathrm{MT}} \end{cases}$$

with $r' = \left\| \mathbf{r} - \mathbf{r}_\alpha \right\|$	radius
$u_l^{\alpha}(r, E)$	radial function
$Y_{lm}(\theta, \phi)$	spherical harmonic
$A_{lm}^{\alpha,\mathbf{k}+\mathbf{G}}$	parameter

Augmented Planewave Method

Determination of the parameter $A_{lm}^{\alpha,\mathbf{k}+\mathbf{G}}$:

The radial functions match the planewaves at the sphere boundary in value, but not in slope.

For this purpose the planewave is expanded in spherical harmonics around center α. This expansion is truncated at some l_{max}

$\Rightarrow$ number of planewaves = number of basis functions

Core states are localized within the MT sphere and are obtained by the solution of the radial Schrödinger equation in the sphere.

Valence states are given as a linear combination of APWs.

$$\phi^{\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{\mathbf{G}}\, e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} & \mathbf{r} \in I \\ \sum_{lm} A_{lm}^{\alpha,\mathbf{k}+\mathbf{G}} u_l^{\alpha}(r', E) Y_{lm}(\theta\phi) & \mathbf{r} \in R_{\mathrm{MT}} \end{cases}$$

APW

Problem:

To describe an eigenstate $\phi_n^{\mathbf{k}}(\mathbf{r})$ correctly, the parameter *E* has to be the eigenvalue $\epsilon_n^{\mathbf{k}}$ of that state.

Therefore the APWs have to be determined self-consistently for each eigenvalue. A matrix diagonalization is required for each eigenvalue $\Rightarrow$ slower than PPW

$\Rightarrow$ the original APW technique is of no practical use anymore

Linearized Augmented Planewaves

Motivation:

Energy dependence of the APWs $E = \epsilon_n^{\mathbf{k}}$

Idea: Taylor expansion

$$u_l^\alpha(r', \epsilon_n^{\mathbf{k}}) = u_l^\alpha(r', E_0) + (E_0 - \epsilon_n^{\mathbf{k}}) \frac{\partial u_l^\alpha(r', E)}{\partial E}\Big|_{E=E_0}$$

$$= u_l^\alpha(r', E_0) + (E_0 - \epsilon_n^{\mathbf{k}}) \dot{u}_l^\alpha(r', E_0)$$

But $(E_0 - \epsilon_n^{\mathbf{k}})$ is unknown ⇒ new parameter

l-dependent

Basis functions: Linearized Augmented Plane Wave:

$$\chi^{\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} & \mathbf{r} \in I \\ \sum_{lm} \left(A_{lm}^{\alpha,\mathbf{k}+\mathbf{G}} u_l^\alpha(r', E_{1,l}^\alpha) + B_{lm}^{\alpha,\mathbf{k}+\mathbf{G}} \dot{u}_l^\alpha(r', E_{1,l}^\alpha) \right) Y_{lm}(\theta, \phi) & \mathbf{r} \in R_{\mathrm{MT}} \end{cases}$$

Linearized Augmented Planewaves

We now have two parameters: $A_{lm}^{\alpha,\mathbf{k}+\mathbf{G}}$ and $B_{lm}^{\alpha,\mathbf{k}+\mathbf{G}}$

They are determined by matching the planewaves in value and slope at the sphere boundary.

With the energy $E_{1,l}^{\alpha}$ the basis functions can be determined once and for all.

⇒ one diagonalization of H sufficient to obtain all eigenvalues/eigenvectors

⇒ much faster than APW

Like in the PPW method the number of basis functions is determined by an energy cutoff $G_{\max}^2$.

$R_{\min}^{\alpha} G_{\max}$ is more commonly used.

Reason:

The larger R_{MT}, the smaller the cutoff for a given accuracy since the wavefunctions are smoother further away from the nuclei (easier to describe).

Linearized Augmented Planewaves

Core states:

- localized inside R_{MT}
- treated like in free atom, but in the potential of the valence electrons

Valence states:

- leak outside R_{MT}
- described by LAPWs

Semi-core states:

- leak outside R_{MT}, low-lying valence states, same l-value as other valence states
- described by addition of a local orbital (LO), localized in one particular R_{MT}

$$\chi^{lm}_{\alpha,\mathrm{LO}}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \in I \\ \left(A^{\alpha,\mathrm{LO}}_{lm} u^{\alpha}_{l}(r', E^{\alpha}_{1,l}) + B^{\alpha,\mathrm{LO}}_{lm} \dot{u}^{\alpha}_{l}(r', E^{\alpha}_{1,l}) + C^{\alpha,\mathrm{LO}}_{lm} u^{\alpha}_{l}(r', E^{\alpha}_{2,l})\right) Y_{lm}(\theta, \phi) & \mathbf{r} \in R_{\mathrm{MT}} \end{cases}$$

3 Parameters: LO is normalized and has zero value and slope at R_{MT}.

$$\Rightarrow \quad A^{\alpha,\mathbf{k}+\mathbf{G}}_{lm} \qquad B^{\alpha,\mathbf{k}+\mathbf{G}}_{lm} \qquad C^{\alpha,\mathbf{k}+\mathbf{G}}_{lm}$$

The APW+lo Method

Two types of basis functions:

1. APWs with fixed energy

$$\chi^{\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} & \mathbf{r} \in I \\ \sum_{lm} A_{lm}^{\alpha,\mathbf{k}+\mathbf{G}} u_l^{\alpha}(r', E_{1,l}^{\alpha}) Y_{lm}(\theta,\phi) & \mathbf{r} \in R_{\mathrm{MT}} \end{cases}$$

2. Local orbitals (different from LAPW)

$$\chi_{\alpha,\mathrm{lo}}^{lm}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \in I \\ \left(A_{lm}^{\alpha,\mathrm{lo}} u_l^{\alpha}(r', E_{1,l}^{\alpha}) + B_{lm}^{\alpha,\mathrm{lo}} \dot{u}_l^{\alpha}(r', E_{1,l}^{\alpha})\right) Y_{lm}(\theta,\phi) & \mathbf{r} \in R_{\mathrm{MT}} \end{cases}$$

$\Rightarrow$ 2 parameters $A_{lm}^{\alpha,\mathbf{k}+\mathbf{G}}$ $B_{lm}^{\alpha,\mathbf{k}+\mathbf{G}}$

Determination: normalized and zero value at R_{MT} (not zero slope)

Smaller basis set than LAPW (like APW), but basis set independent of energy (like LAPW).

Linear Muffin Tin Orbital

Linear Muffin Tin Orbital Method = LMTO

O. K. Andersen, *Phys. Rev. B* **12** (1975) 3060.

- all-electron method
- muffin-tin spheres and interstitial
- envelope functions are Hankel functions
- solutions of the radial Schrödinger equation inside MT spheres
- matching in value and slope at R_{MT}

Interstitial: $$K_{\kappa,lm}(\mathbf{r}) = -\kappa^{l+1} i^l Y_{lm}(\theta,\phi) \begin{cases} -h_l^+(\kappa r) & \kappa^2 > 0 \\ n_l(\kappa r) & \kappa^2 < 0 \end{cases}$$

MT Sphere: $$\phi_{lm}(\mathbf{r},E) = i^l Y_{lm}(\theta,\phi)\left(u_l^\alpha(E_\nu,r) + \omega(E)\dot{u}_l^\alpha(E_{\nu,r})\right)$$

$\phi_{lm}(\mathbf{r},E)$ matches tail function in value and slope at R_{MT} by normalization and choice of $\omega(E)$.

Often a muffin tin potential approximation is used:

- interstitial: constant potential
- MT sphere: spherically symmetric potential

Linear Muffin Tin Orbital

Atomic Sphere Approximation (ASA):

- potential is assumed to be spherically symmetric around each atom
- muffin tin spheres are increased up to the size of the Wigner-Seitz cell
  $\Rightarrow$ overlapping atomic spheres
- envelope (tail) functions: $\kappa = 0$

$\Rightarrow$ Interstitial: $K_{lm}(\mathbf{r}) = r^{-l-1} Y_{lm}(\theta\phi)$ (multipole potentials)

- applicable only to closed-packed systems (or introduction of empty spheres)
- energy differences due to structural changes are often qualitatively wrong
- simple and efficient method for large systems

There are much more sophisticated FP-LMTO schemes

- All materials require the same computational effort
- More complex codes than PPW
- mainly used as bandstructure method

PAW: Motivation

The Projector Augmented Wave Method

P.E. Blöchl, *Phys. Rev. B* **50** (1994) 17953. (http://www.pt.tu-clausthal.de/~paw)

We want:

- accuracy of (linear) augmented plane wave methods
- efficiency of (US) pseudo potential calculations

We need:

- smooth wavefunctions that can easily be represented in a plane wave expansion
- information of all-electron full-potential calculations

Idea:

True all-electron wave function $\Psi(\mathbf{r})$ is transformed into pseudo wavefunction $\tilde{\Psi}(\mathbf{r})$.

Caution: „Pseudo wavefunction“ has nothing to do with a pseudo potential. Better is „*auxiliary wavefunction*“.

How can we obtain well-behaved pseudo wavefunctions?

How can they be used to obtain the same information as from the all-electron wavefunctions?

Projector Augmented Wave (PAW)

Transformation operator:

$$\begin{aligned}\Psi(\mathbf{r}) &= \hat{\mathcal{T}}\tilde{\Psi}(\mathbf{r}) \\ \tilde{\Psi}(\mathbf{r}) &= \hat{\mathcal{U}}\Psi(\mathbf{r})\end{aligned} \quad \Rightarrow \quad \hat{\mathcal{T}} = \hat{\mathcal{U}}^{-1}$$

We need:

- a method to determine the pseudo wavefunctions
- the transformation operator
- other physical quantities: electron density, expectation values, …

1. Calculation of the pseudo wavefunctions:

We need to express the total energy by the pseudo wavefunctions.

$$E = E[\Psi_n(\mathbf{r})] = E[\hat{\mathcal{T}}\tilde{\Psi}_n(\mathbf{r})]$$

⇒ Schrödinger-like equation:

$$\left(\hat{\mathcal{T}}^{+}H\hat{\mathcal{T}} - \hat{\mathcal{T}}^{+}\hat{\mathcal{T}}\epsilon_n\right)\tilde{\Psi}_n(\mathbf{r}) = 0$$

(n contains **k**-point, band index, spin)

⇒ We are able to determine the $\tilde{\Psi}_n(\mathbf{r})$ of the ground state.

Projector Augmented Wave (PAW)

2. Derivation of the Transformation Operator $\hat{\mathcal{T}}$:

We have to find a transformation $\hat{\mathcal{T}}$ so that the pseudo wavefunctions are well-behaved.

What is „well-behaved“?

- $\tilde{\Psi}_n(\mathbf{r})$ should be smooth (expanded in few plane waves)
- local, linear operator $\hat{\mathcal{T}} = 1 + \sum_R \mathcal{S}_R$

(sum over atomic contributions, because $\hat{\mathcal{T}}$ has to modify $\tilde{\Psi}_n(\mathbf{r})$ in each atomic region)

For each atom, $\mathcal{S}_R$ adds the difference between $\Psi_n(\mathbf{r})$ and $\tilde{\Psi}_n(\mathbf{r})$.

This difference is expanded in partial waves for the free isolated atoms.

$$\mathcal{S}_R|\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle$$

$$i = R, l, m, \alpha$$

pseudo partial wave: $|\tilde{\phi}_i\rangle$

all-electron valence partial wave: $|\phi_i\rangle$

PAW Transformation Operator

In the augmentation region $\tilde{\Psi}_n(\mathbf{r})$ is expanded in partial waves $|\tilde{\phi}_i\rangle$.

$$\tilde{\Psi}_n(\mathbf{r}) = \sum_{i\in R} \tilde{\phi}_i(r) c_{in}$$ (times spherical harmonics)

The c_i are determined by projector functions $\langle\tilde{p}_i|$ yielding the contribution of each partial wave.

$$c_i = \langle\tilde{p}_i|\tilde{\Psi}_n\rangle \;\Rightarrow\; \boxed{|\tilde{\Psi}_n\rangle = \sum_{i\in R} |\tilde{\phi}_i\rangle\langle\tilde{p}_i|\tilde{\Psi}_n\rangle}$$

$\Rightarrow$ orthogonality $\langle\tilde{p}_i|\tilde{\phi}_j\rangle = \delta_{ij}$

Remember:

$$\mathcal{S}_R|\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle$$

$$\mathcal{S}_R|\tilde{\Psi}_n\rangle = \mathcal{S}_R \sum_{i\in R} |\tilde{\phi}_i\rangle\langle\tilde{p}_i|\tilde{\Psi}_n\rangle$$

$$= \sum_{i\in R} \Big(|\phi_i\rangle - |\tilde{\phi}_i\rangle\Big) \langle\tilde{p}_i|\tilde{\Psi}_n\rangle$$

Remember:

$$\hat{\mathcal{T}} = 1 + \sum_R \mathcal{S}_R$$

$$\hat{\mathcal{T}} = 1 + \sum_i \Big(|\phi_i\rangle - |\tilde{\phi}_i\rangle\Big) \langle\tilde{p}_i|$$

Now we have access to the true wave function $\Psi(\mathbf{r}) = \hat{\mathcal{T}}\tilde{\Psi}(\mathbf{r})$.

Projector Augmented Wave

Partial Waves:

- $|\tilde{\phi}_i\rangle$and $|\phi_i\rangle$ are pairwise identical outside some augmentation radius r_c
- solve Schrödinger equation for all-electron atomic potential
- $|\tilde{\phi}_i\rangle$ and $|\phi_i\rangle$ are represented on a radial grid (radial functions) and multiplied with spherical harmonics

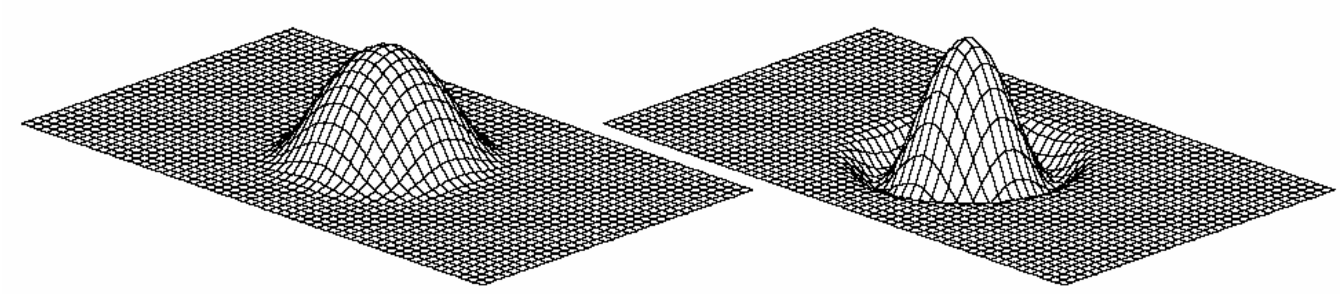
Projector Functions $|\tilde{p}_i\rangle$:

- are localized within the augmentation region of a particular atom
- obey the orthogonality condition: $\langle\tilde{p}_i|\tilde{\phi}_j\rangle = \delta_{ij}$
- probe the character of the wavefunction

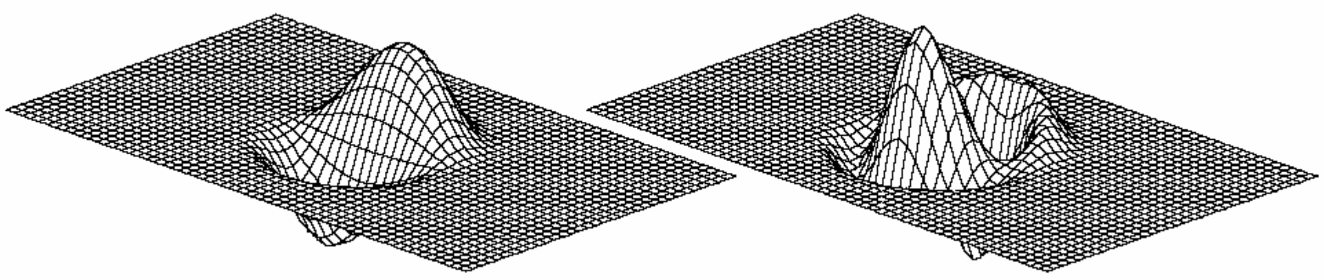
Projector Functions

$$|\tilde{p}_i\rangle$$

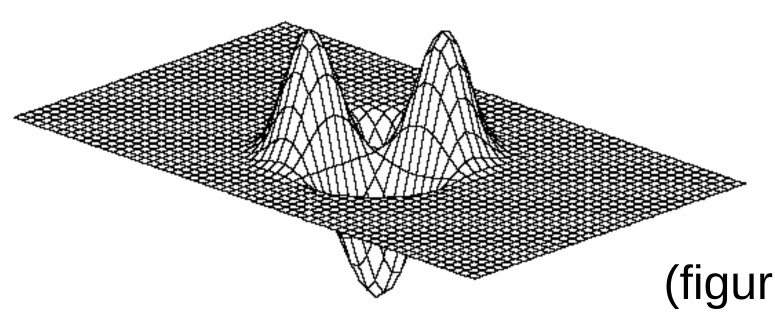
s-type projector functions



p-type projector functions



d-type projector function



(figures courtesy P. Blöchl)

PAW Expectation Values

Expectation value:

$$\langle A\rangle = \sum_n f_n \langle \Psi_n | A | \Psi_n \rangle$$

$$= \sum_n f_n \langle \tilde{\Psi}_n | A | \tilde{\Psi}_n \rangle$$

plane wave part

$$+ \sum_i \sum_j D_{ij} \langle \phi_i | A | \phi_j \rangle$$

one-center expansion of true wavefunction

$$- \sum_i \sum_j D_{ij} \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle$$

one-center expansion of pseudo wavefunction

$$+ \sum_n \langle \Psi_n^c | A | \Psi_n^c \rangle$$

core contribution

With a one-center density matrix $D_{ij} = \sum_n \langle \tilde{p}_i | \tilde{\Psi}_n \rangle f_n \langle \tilde{\Psi}_n | \tilde{p}_j \rangle$

and the core states $|\Psi_n^c\rangle$

Projector Augmented Wave

Electron density:

one-center terms, sums of atomic contributions, cancel each other outside augmentation region, but correct for $\tilde{n}(\mathbf{r})$ inside augmentation region

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \overbrace{n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r})}$$

pseudo density, PW expansion

$$\tilde{n}(\mathbf{r}) = \sum_n f_n \langle \tilde{\Psi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Psi}_n \rangle$$

$$n^1(\mathbf{r}) = \sum_{ij} \rho_{ij} \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle$$

$$\tilde{n}^1(\mathbf{r}) = \sum_{ij} \rho_{ij} \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle$$

Occupancies of augmentation channel (*ij*): $\rho_{ij} = \sum_n f_n \langle \tilde{\Psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\Psi}_n \rangle$

Total energy:

$$E([\tilde{\Psi}_n], R_i) = \tilde{E} + \underbrace{E^1 - \tilde{E}^1}$$

evaluated on regular grid

evaluated for each sphere individually on radial grid

Projector Augmented Wave

- first all-electron Car-Parrinello scheme
- core electrons explicitly included in the frozen core approximation
- works equally well for all atoms (transition metals, first row elements)
- accuracy comparable to LAPW
- PAW unifies all-electron and pseudopotential approaches
- computationally efficient
- all-electron method, full wavefunctions including their nodal structure are properly defined
- exact when converged (no transferability problem)
- periodic boundary conditions

Approximations

- frozen core approximation (ρ and E from isolated atoms, not necessary)
- truncated plane wave expansion (basis set, E^{cut} like USPP)
- truncated partial wave expansion (augmentation, 1 or 2 per (lm) and atom)

Projector Augmented Wave

References:

P.E. Blöchl, *Phys. Rev. B* **50** (1994) 17953. (http://www.pt.tu-clausthal.de/~paw)

G. Kresse, and D. Joubert, *Phys. Rev. B* **59** (1999) 1758.

P.E. Blöchl, J. Kästner, and C.J. Först, in „Handbook of Materials Modeling: Volume I: Methods and Models", p. 1-27, *ed.* S. Yip **,** Springer 2005.

N.A.W. Holzwarth, G.E. Matthews, R.B. Dunning, A.R. Tackett, and Y. Zeng, *Phys. Rev. B* **55** (1997) 2005.

Localized Basis Sets

Examples

- Numerical atomic orbitals (NAO)
- Gaussian type orbitals (GTO)
- Slater Type orbitals (STO)

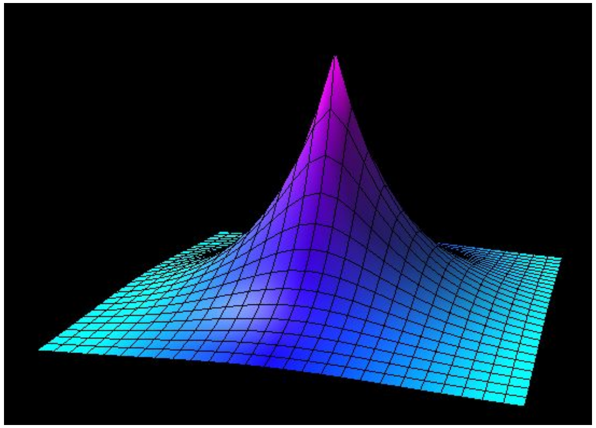
Properties

- atom-centered
- applicable to periodic and non-periodic systems
- no costs for empty space

⇒ particularly useful for molecular calculations

Slater Type Orbitals (STO)

General form of a STO: $f(r,\theta,\phi) = R(r)\cdot Y(\theta,\phi)$ (primitive STO)



Angular part: Spherical harmonics $Y(\theta,\phi)$

Radial part: $R(r) = N(n,\zeta)\cdot r^{n-1}\cdot e^{-\zeta r}$

Normalization: $N(n,\zeta) \;\Rightarrow \int_0^\infty [R(r)]^2 r^2\, dr = 1$

2 Parameters: n and ζ (n= integer quantum number)

STO Basis sets:

„single zeta“: one radial function per (*nl*) subshell (e.g. 2p_x, 2p_y, 2p_z)
„double zeta“: two radial functions per (*nl*) subshell

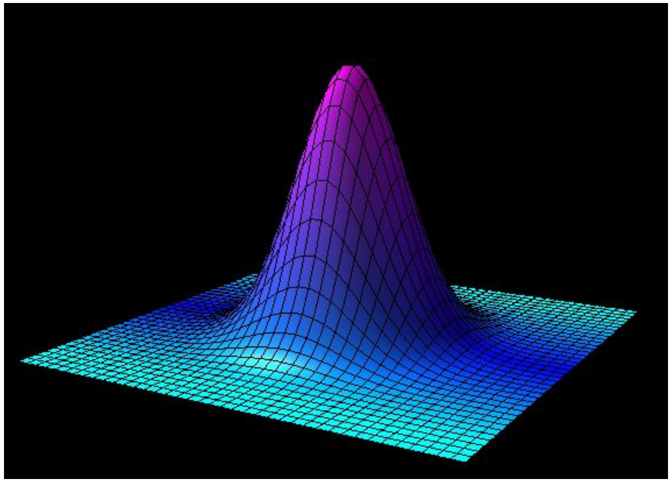
J. C. Slater, *Phys. Rev.* **36** (1930) 57.
S. Huzinaga, *Comp. Phys. Rep.* **2** (1985) 281.
A. Szabo, and N. S. Ostlund, „Modern Quantum Chemistry“, Dover Publications 1996

Gaussians Type Orbitals (GTO)

Spherical Gaussians for atomic calculations:

General form of a GTO: $f(r,\theta,\phi) = R(r)\cdot Y(\theta,\phi)$ (primitve GTO)

Angular part: Spherical harmonics $Y(\theta,\phi)$



Radial part: $R(r) = N(n,\alpha)\cdot r^{n-1}\cdot e^{-\alpha r^2}$

Normalization: $N(n,\alpha) \Rightarrow \int_0^\infty [R(r)]^2 r^2\, dr = 1$

Analytic integral evaluation possible,
in contrast to STOs ⇒ easy to handle

J. C. Slater, *Phys. Rev.* **36** (1930) 57.
S. Huzinaga, *Comp. Phys. Rep.* **2** (1985) 281.
A. Szabo, and N. S. Ostlund, „Modern Quantum Chemistry“, Dover Publications 1996

Cartesian GTOs

Cartesian Gaussians for molecular calculations:

GTO: $f_{l,m,n}(x,y,z) = N(l,\alpha)N(m,\alpha)N(n,\alpha)x^l y^m z^n e^{-\alpha r^2}$

Normalization: $N(l,\alpha), N(m,\alpha), N(n,\alpha)$

$$\Rightarrow \int_{-\infty}^{\infty} [f_{lmn}(x,y,z)]^2 \, dx\,dy\,dz = 1$$

***s*-type:** $l+m+n=0$

$e^{-\alpha r^2}$

***p*-type:** $l+m+n=1$

$(x,y,z)\cdot e^{-\alpha r^2}$

***d*-type:** $l+m+n=2$

$(x^2, y^2, z^2, xy, yz, xz)\cdot e^{-\alpha r^2}$

***f*-type:** $l+m+n=3$

$(x^3, y^3, z^3, x^2y, x^2z, y^2x, y^2z, z^2x, z^2y, xyz)\cdot e^{-\alpha r^2}$

Beyond Primitive GTOs

Contracted Gaussian Functions (CGFs):

STOs are closer to the actual physics of the system than Gaussians

$\Rightarrow$ Several primitive Gaussians can be used to mimic a STO

Linear combination of *N* primitive Gaussians $$R(\mathbf{d}, \alpha; r) = \sum_{k=1}^{N} d_k g(\alpha_k, r)$$

By using many primitive Gaussians a minimal basis set can be very accurate for atomic calculations.

Split-Valence Basis Sets:

Inner shells:
minimal basis

Valence shells:
double zeta basis

Example: 6-31G for C, N, O, and F

6 primitive Gaussians for the core orbital
3 primitive Gaussians for the valence orbitals
1 primitive Gaussian for a second set of valence orbitals

More advanced: split-valence plus polarization: STO-3G*, 3-21G*, 6-31G*, 6-31G**, …

Comparison: STOs vs. GTOs

Boundary Conditions

r → 0: cusp condition

- STOs not well,
- GTOs hopeless, since $\frac{df}{dr}|_{r\to 0} = 0$

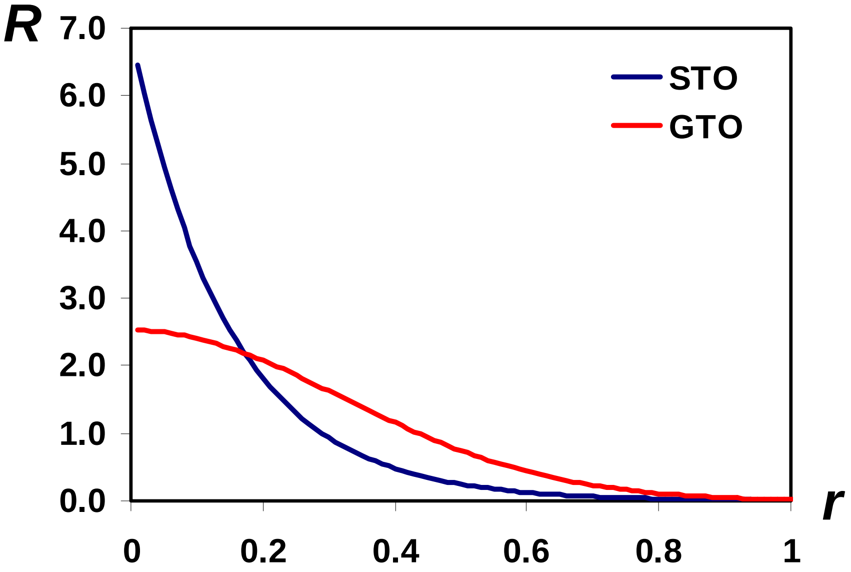
r → ∞ : $\sim e^{-\text{const}\ r}$

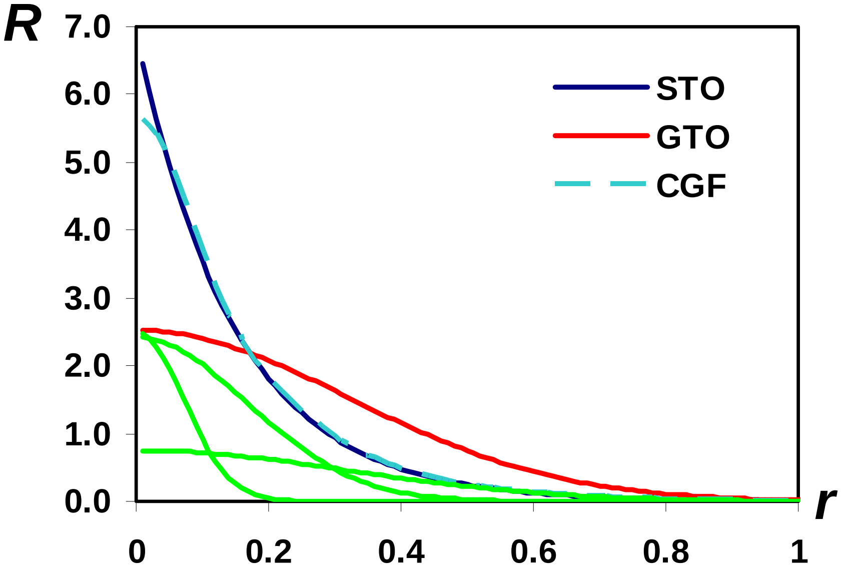
- STOs: ok
- GTOs decay too fast

Use GTOs to mimic STOs

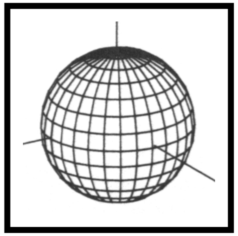
About 2 to 3 times more GTOs as STOs for the same accuracy needed

⇒ Use contracted GTOs





Numerical Atomic Orbitals (NAOs)

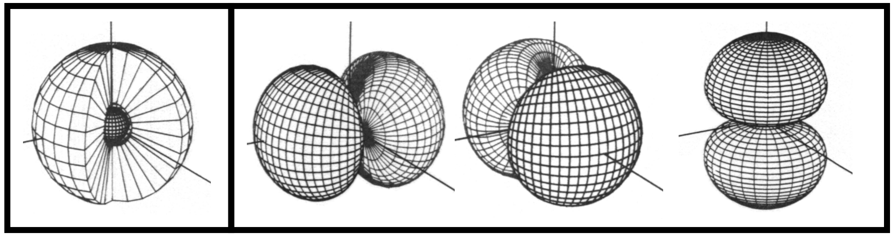


$1s$

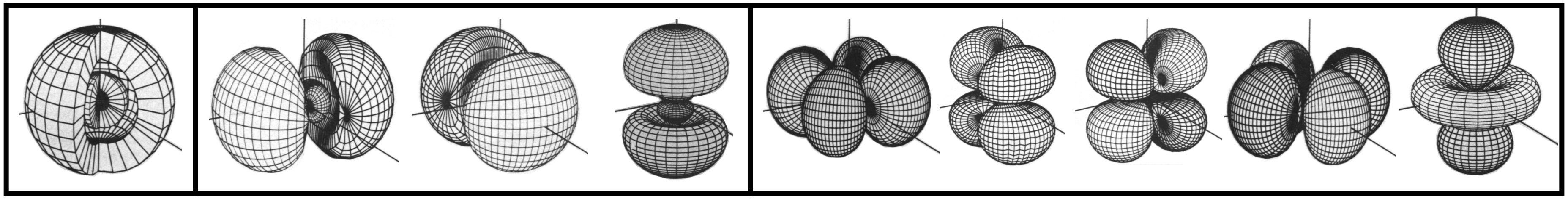
General form:

$$f(r,\theta,\phi) = R(r)\cdot Y(\theta,\phi)$$

- the exact shape depends on nuclear and atomic charges
- no general analytic form available (in contrast to STOs and GTOs)
- numerical representation on an atom-centered grid (spline interpolation)



$2s$ $2p_x$ $2p_y$ $2p_z$



$3s$ $3p_x$ $3p_y$ $3p_z$ $3d_{xy}$ $3d_{yz}$ $3d_{zx}$ $3d_{x^2-y^2}$ $3d_{z^2}$

See e.g.: B. Delley, *J. Chem. Phys.* **92** (1990) 508.

Numerical Atomic Orbitals

Determination of NAOs

- exact DFT-spherical-atomic orbitals of
    - neutral atoms
    - ions
    - hydrogenic atoms
- radial functions are calculated in the setup (free atom)
- implemented as numerically tabulated functions

Properties of NAOs

- maximum of accuracy for a given basis set size
- infinitely separated atoms limit treated *exactly*
- small basis set superposition error (BSSE)
- small number of additional functions needed for polarization
- cusp singularities at the nuclei correct

Basis Set Libraries

Minimal basis set:

One basis function per orbital in occupied subshells, not very accurate

Example: STO-3G for Carbon: 5 CGFs: 1s, 2s, $2p_x$, $2p_y$, $2p_z$, each consisting of 3 primitive GTOs

GTOs: Double zeta, triple zeta, quadruple zeta:

Several basis functions per orbital

Split-valence basis sets, e.g. 3-21G, 6-31G …

Polarization functions can be added (higher angular momentum).

NAOs: Double numeric (DN), double numeric plus polarization (DNP)…

A second set of basis functions can be obtained from an ionic calculation.

Typically, basis set libraries are provided in the DFT codes.

They are easy to use, but hard to extend/improve.

BSSE

Basis Set Superposition Error

Definition:
BSSE is a lowering of the total energy if the electrons of an atom spread into the basis functions provided by the other atoms due to an incomplete basis set for this atom (mimics binding).

Plane waves:	no BSSE
GTOs and STOs:	BSSE can be a serious problem
NAOs:	(nearly) no BSSE with respect to free atoms BSSE with respect to molecules exists

Periodic Boundary Conditions and Localized Basis Sets

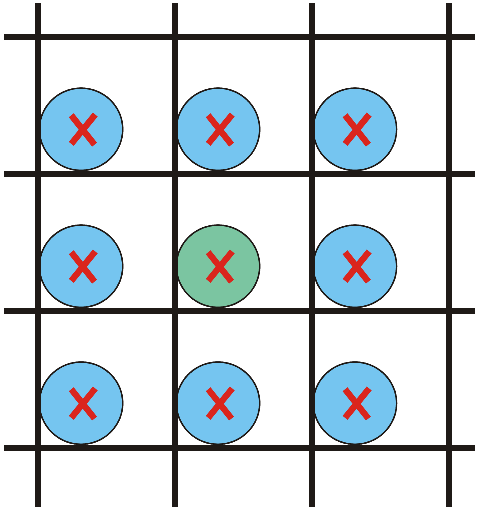
Bloch theorem:

Lattice periodic function: $\chi_i^0(\mathbf{r}) = \chi_i^{\mathbf{n}}(\mathbf{r} - \mathbf{T_n})$

with $\mathbf{T_n} = n_1 \cdot \mathbf{a}_1 + n_2 \cdot \mathbf{a}_2 + n_3 \cdot \mathbf{a}_3$

Bloch basis functions:

$$\varphi_i(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{n}=-\infty}^{\infty} e^{i\mathbf{k}\mathbf{T_n}} \chi_i^{\mathbf{n}}(\mathbf{r} - \mathbf{T_n})$$



Kohn-Sham eigenstates $\psi_j(\mathbf{k}, \mathbf{r})$ are expanded in a finite set of Bloch basis functions:

$$\psi_j(\mathbf{k}, \mathbf{r}) = \sum_i c_{ji}^{\mathbf{k}} \varphi_i(\mathbf{k}, \mathbf{r})$$

Periodic Boundary Conditions and Localized Basis Sets

The coefficients $c^{\mathbf{k}}_{ji}$ are determined self-consistently by solving coupled matrix equations for a chosen set of k-points within the reference unit cell:

Secular equation

$$\sum_{\mu} H_{\nu\mu}(\mathbf{k}) c^{\mathbf{k}}_{i\mu} = \epsilon^{\mathbf{k}}_{i} \sum_{\mu} S_{\nu\mu}(\mathbf{k}) c^{\mathbf{k}}_{i\mu}$$

Hamilton matrix

$$H_{\nu\mu}(\mathbf{k}) = \sum_{\mathbf{n}=-\infty}^{\infty} e^{i\mathbf{k}\mathbf{T}_{\mathbf{n}}} \langle \chi^{0}_{\nu} | H | \chi^{\mathbf{n}}_{\mu} \rangle$$

Overlap matrix

$$S_{\nu\mu}(\mathbf{k}) = \sum_{\mathbf{n}=-\infty}^{\infty} e^{i\mathbf{k}\mathbf{T}_{\mathbf{n}}} \langle \chi^{0}_{\nu} | \chi^{\mathbf{n}}_{\mu} \rangle$$

Comparison:
Localized vs. Periodic Basis Sets

Localized Basis Sets

- non-orthogonal
- smaller basis sets
- element specific
- all-electron and pseudopotentials

efficient, maybe biased, overcomplete, not simple

„Periodic“ Basis Sets

- systematic
- general
- userfriendly

not efficient, not biased, complete, simple

Convergence

NAOs:

quality $\Rightarrow$ basis set
extension $\Rightarrow$ r^{cut}

PWs:

quality $\Rightarrow$ E^{cut}
extension $\Rightarrow$ infinite

What is the “best” DFT Code?

The best DFT code should be

- fast (CPU time)
- economically (hardware, e.g. memory)
- accurate (within limitations of XC)
- easy to use (man-power)
- applicable to all types of systems
- maintainable (readable source code)
- available (license, price)

Benchmark Calculations

Codes:

- LAPW and APW+lo: WIEN2k
- Numerical Atomic Orbitals: DMol^3

} all-electron

- Pseudo Potential Plane Waves: Castep (USPP)

Accuracy:

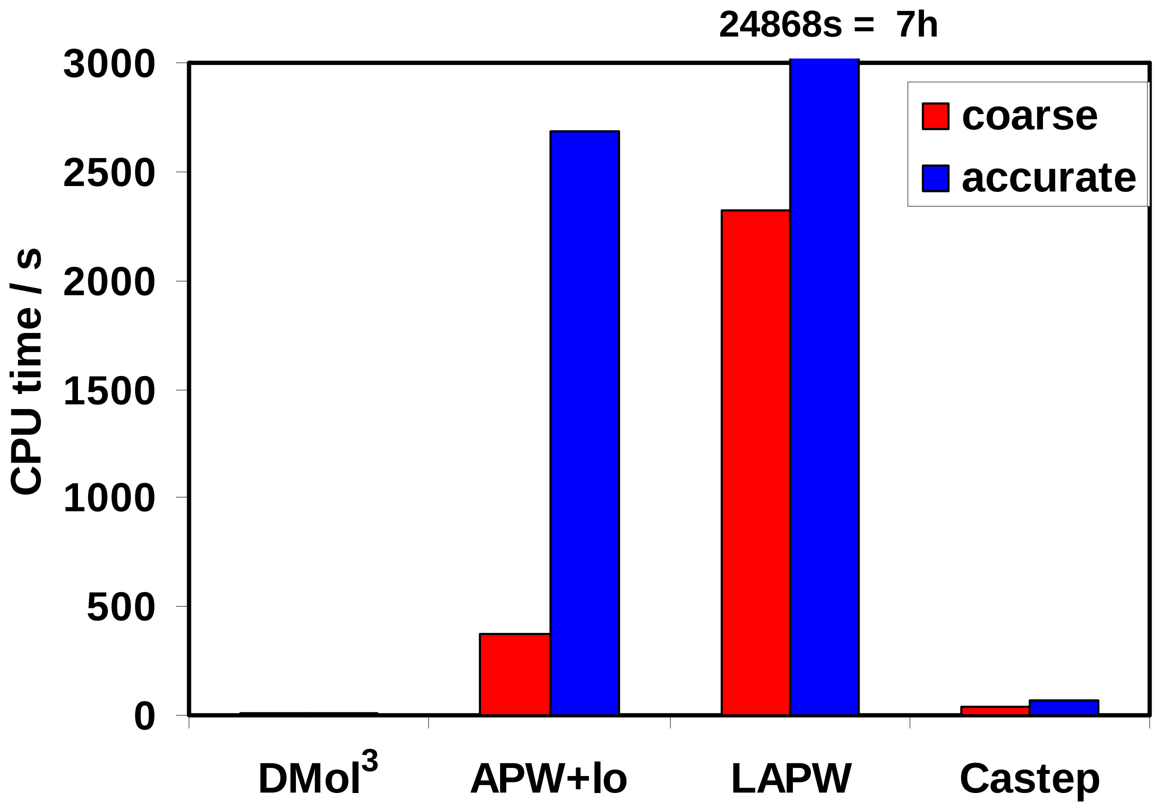
- coarse calculation: binding energy error < 0.1 eV
- accurate calculation: binding energy error < 0.02 eV
- PBE functional

Systems:

- Aluminium: atom and bulk
- 7 layer Al(111) slabs, clean and adsorbed oxygen atoms

The Free Aluminium Atom

CPU times



DMol^3 : no PBC

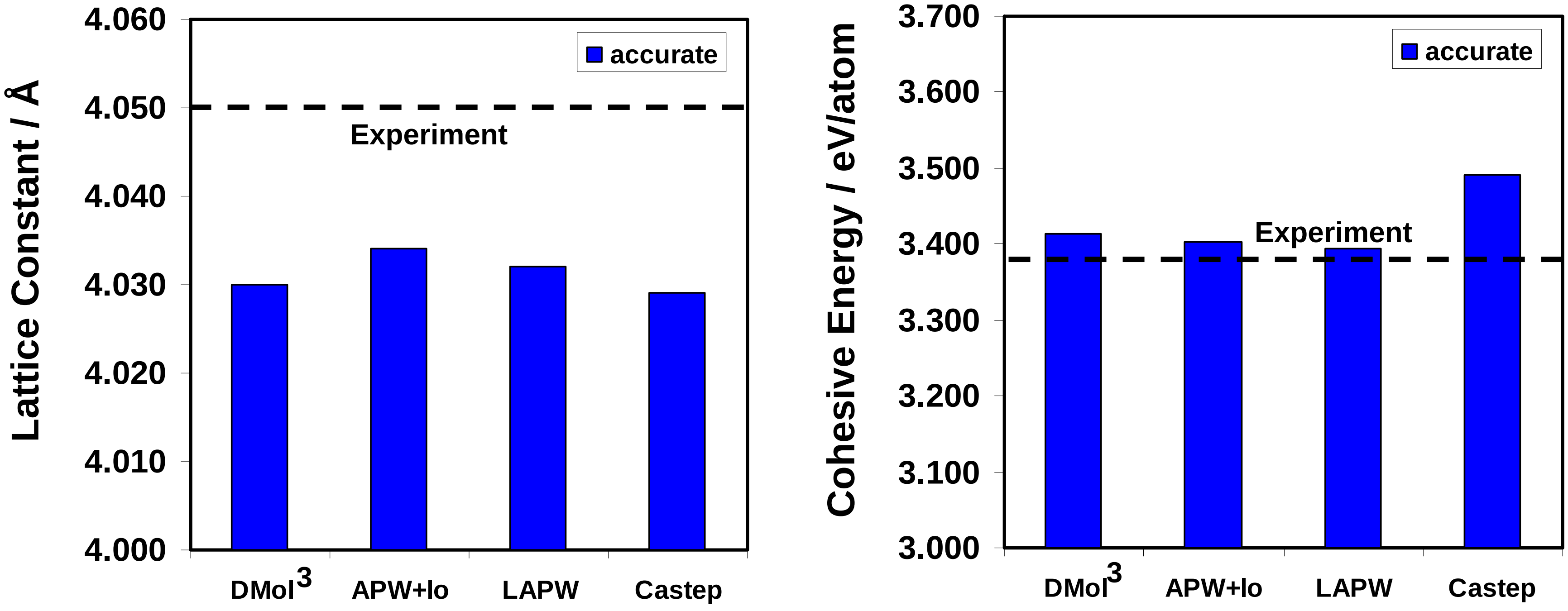
Other Codes: PBC
(box 13x14x15 Bohr^3)

The performance for small molecules is very similar.

Calculations performed by JB, Mira Todorova, Jutta Rogal, and Angelos Michaelides.

Bulk Aluminium

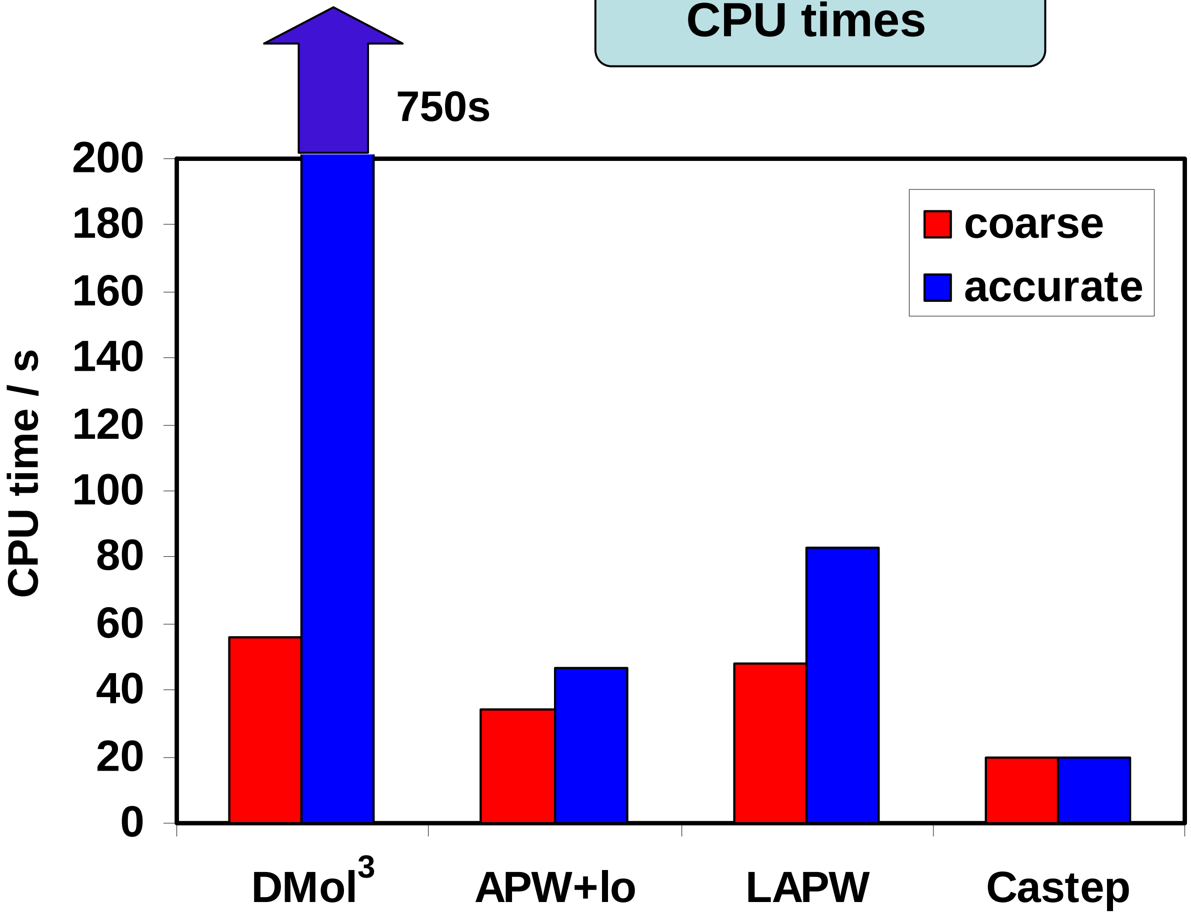
Lattice Constants and Cohesive Energy

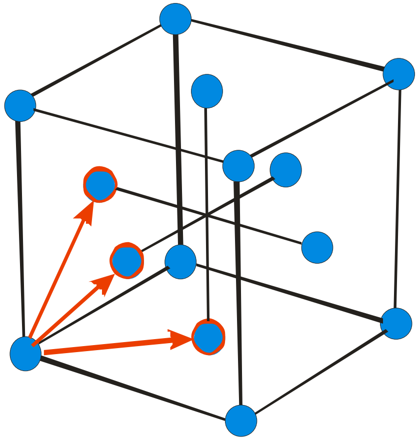


Calculations performed by JB, Mira Todorova, Jutta Rogal, and Angelos Michaelides.

Bulk Aluminium

CPU times

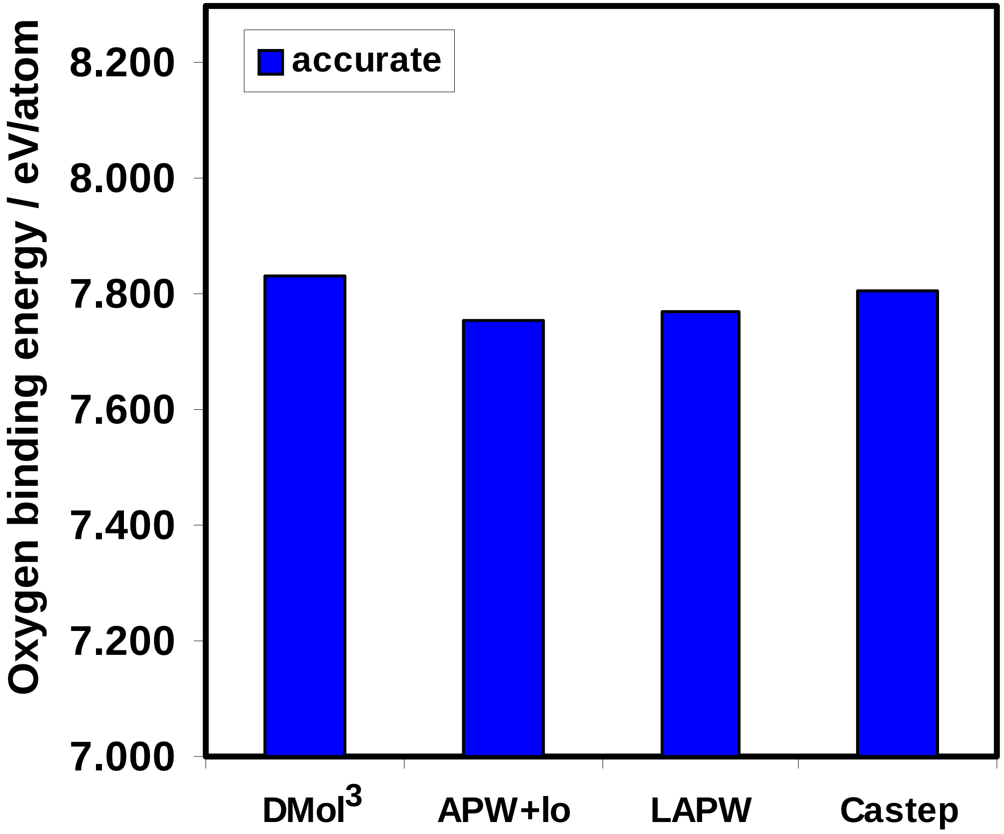




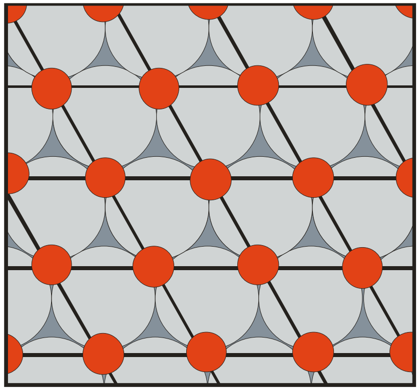
Calculations performed by JB, Mira Todorova, Jutta Rogal, and Angelos Michaelides.

Oxygen at (1x1) Al(111) Slabs

Oxygen Binding Energy



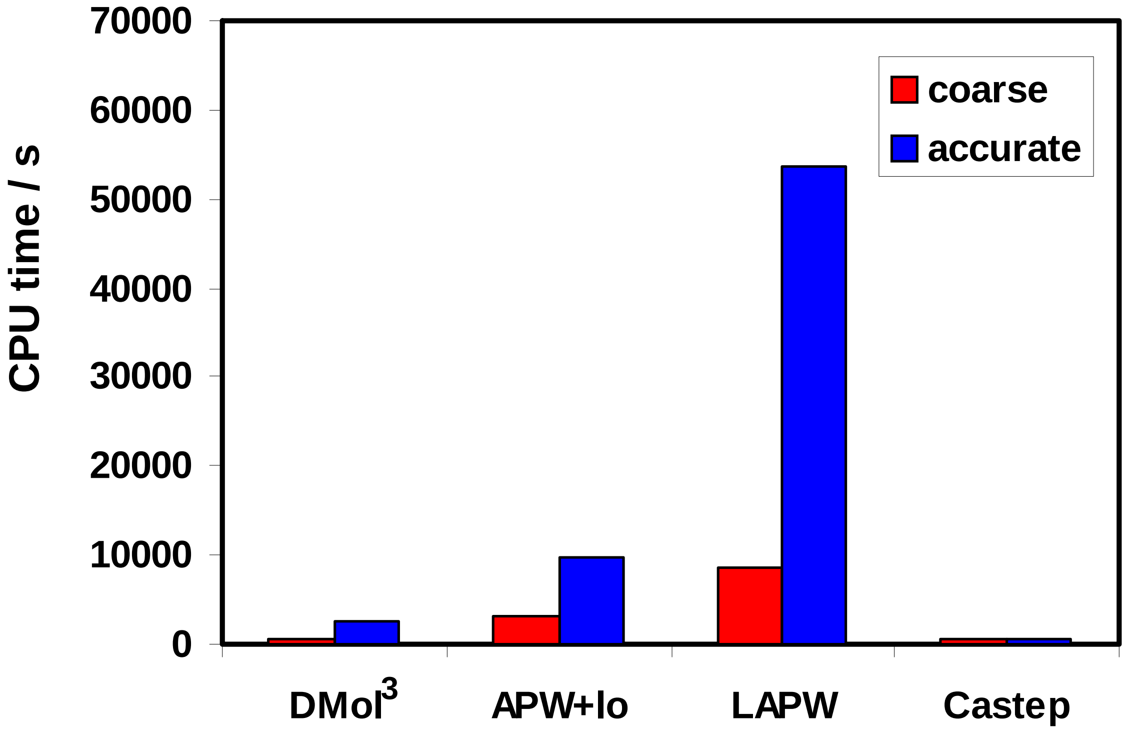
- 7 Al layers
- O adsorbed at both sides
- 15 Å vacuum



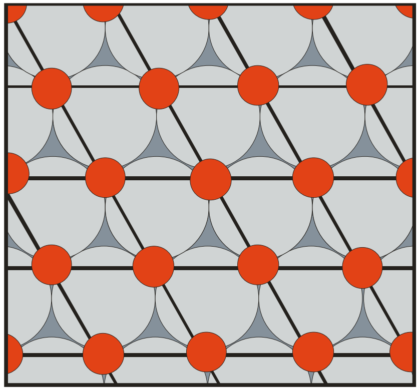
Calculations performed by JB, Mira Todorova, Jutta Rogal, and Angelos Michaelides.

Oxygen at (1x1) Al(111) Slabs

CPU Times



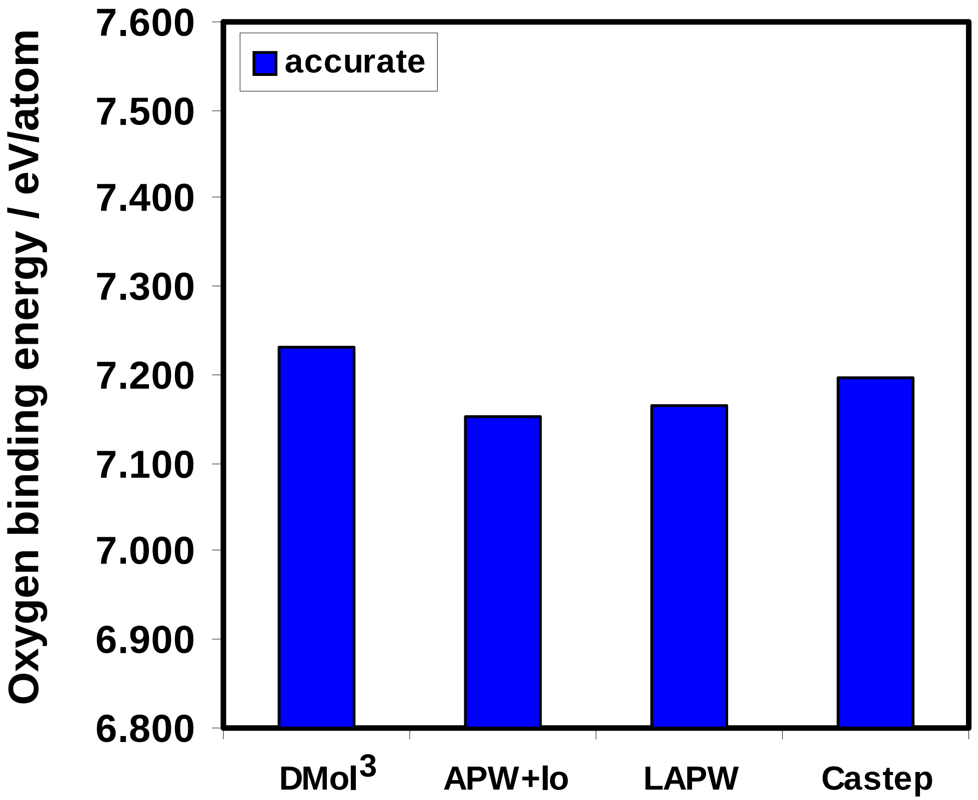
- 7 Al layers
- O adsorbed at both sides
- 15 Å vacuum



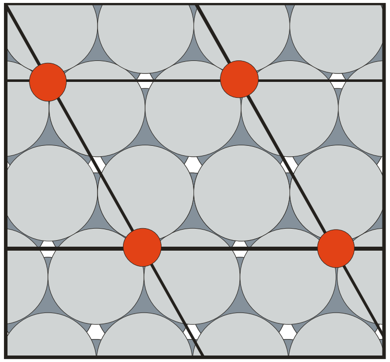
Calculations performed by JB, Mira Todorova, Jutta Rogal, and Angelos Michaelides.

Oxygen at (2x2) Al(111) Slabs

Oxygen Binding Energy



- 7 Al layers
- O adsorbed at both sides
- 15 Å vacuum



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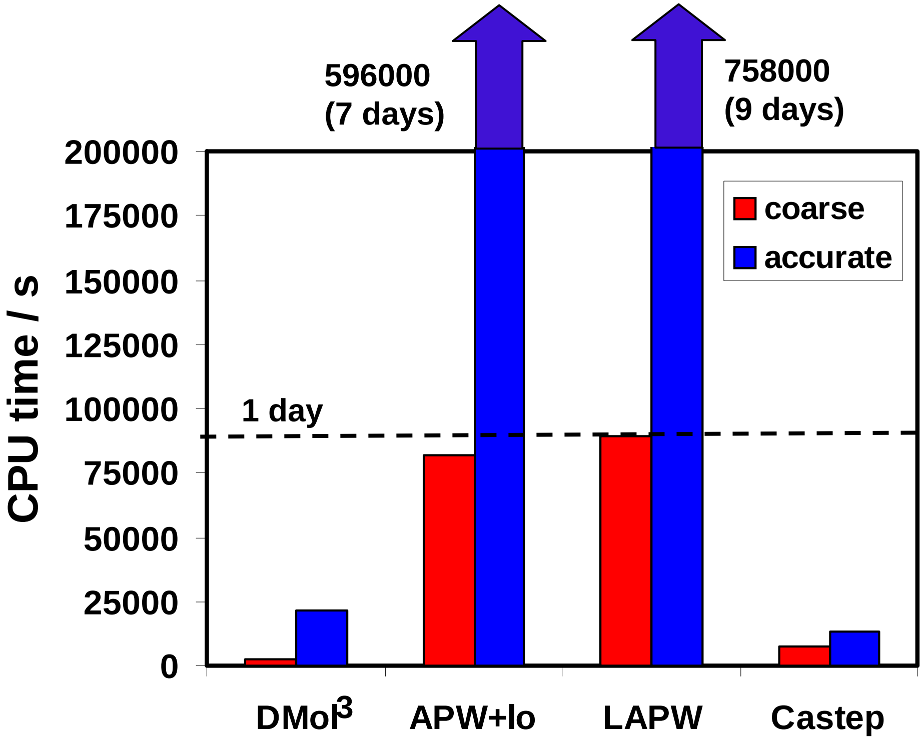
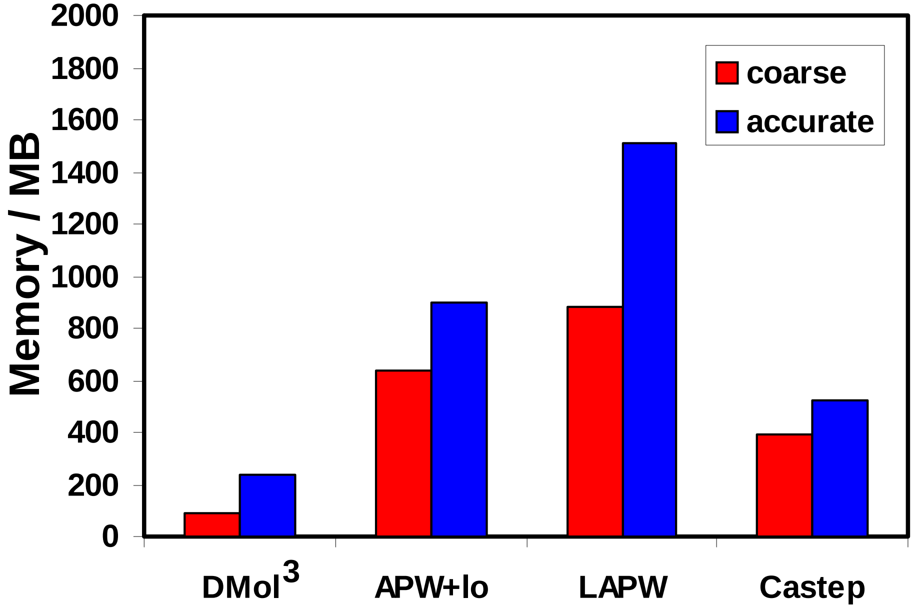
Oxygen at (2x2) Al(111) Slabs

CPU Times and Memory





Calculations performed by JB, Mira Todorova, Jutta Rogal, and Angelos Michaelides.

Conclusion

- there is no „black box“ DFT code in state-of-the-art research

- some codes hide complexity (dangerous)

- no code is the best choice for all types of questions/systems

- efficiency strongly depends on the type of basis set

- accuracy hard to check (approximations prohibit total energy comparisons), best is to use different codes on critical problems

The best code is the code the user understands!

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