



**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.

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

single-particle Schrödinger-like equation

KS orbital	$\phi_i(\mathbf{r}) = \sum_j c_{ij} \chi_j(\mathbf{r})$	$\phi_i(\mathbf{r})$ KS orbital
		$\chi_j(\mathbf{r})$ basis function
electron density	$\rho(\mathbf{r}) = \sum_i f_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})$	f_i occupation number

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

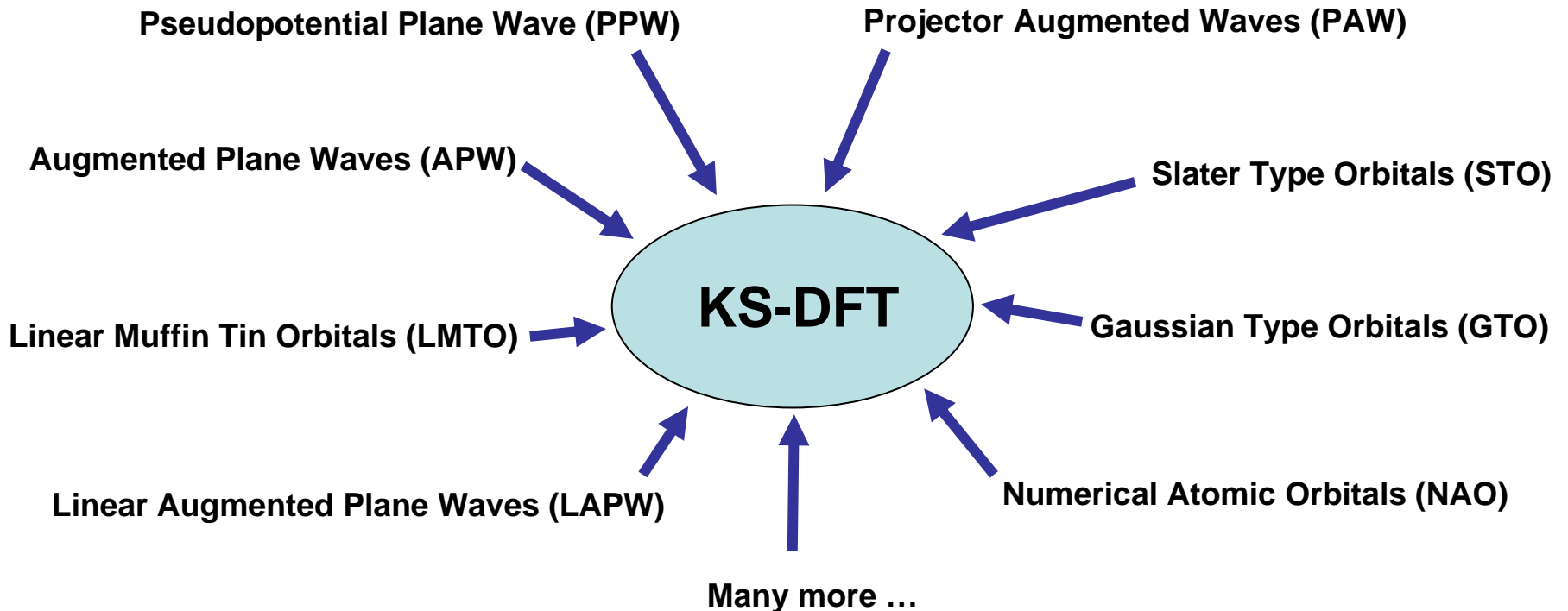
⇒ This is the topic of this talk

Outline



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

Basis Set Expansions



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:

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

\Rightarrow 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.

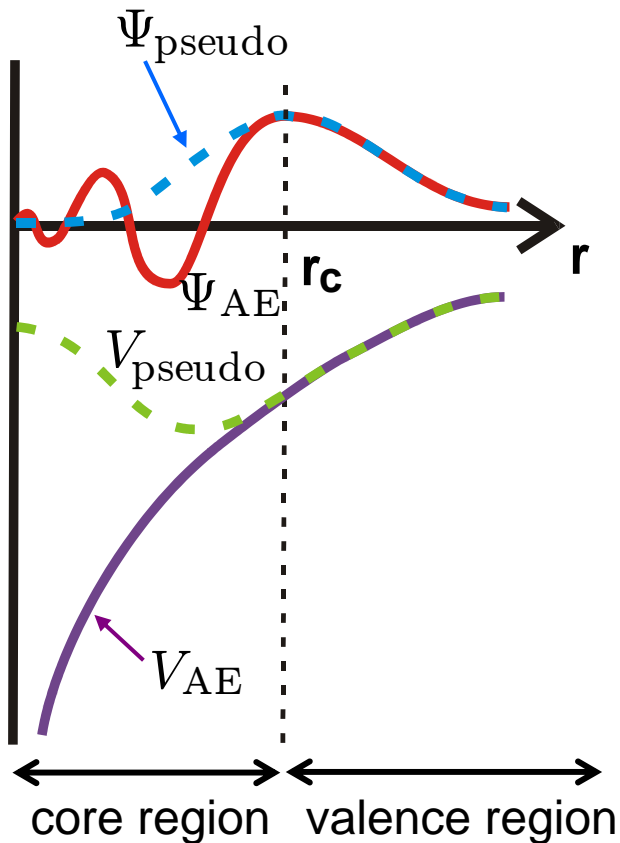
But: Oscillations are due to core states which are less important for bonding (U. von Barth, and C. D. Gelatt, *Phys. Rev. B* **21** (1980) 2222.)

⇒ 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 Ψ_{AE} and Ψ_{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 \mathbf{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.

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

Construction of Pseudopotentials



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

⇒ 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“):

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

with

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

$\tilde{Z}(\mathbf{r})$ 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):

$$V_{\text{PS}} = \sum_{lm} |Y_{lm}\rangle v_l \langle Y_{lm}| \quad Y_{lm} \text{ spherical harmonics}$$

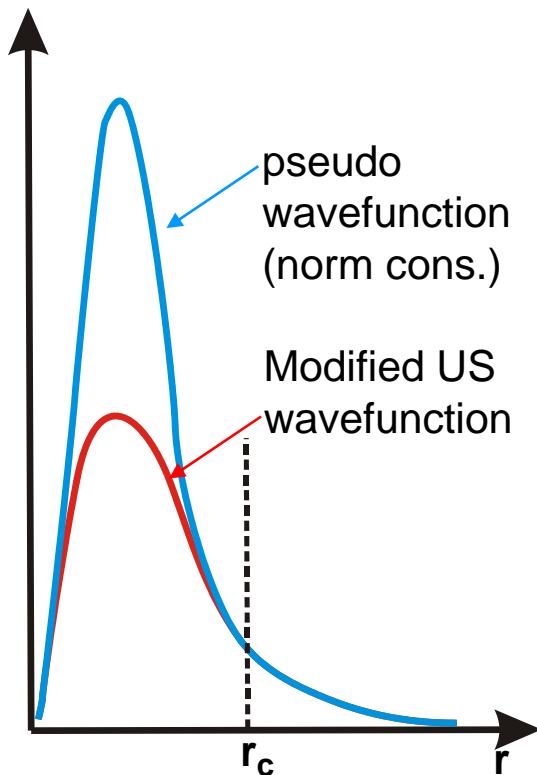
Ultrasoft Pseudo Potentials



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

⇒ The norm-conservation rule is relaxed.

⇒ 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



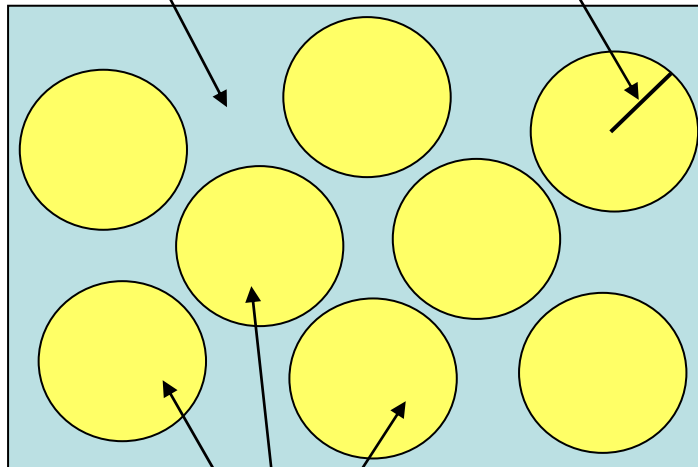
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- W.E. Pickett, *Comp. Phys. Rep.* **9** (1989) 115.
- M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, *Comp. Phys. Comm.* **107** (1997) 187.
- Martin Fuchs, „Pseudopotentials for ab initio electronic structure calculations“
http://www.fhi-berlin.mpg.de/th/Meetings/FHIImd2003/Dtalks/FHI-WS2003-L04-Fuchs-Pseudopotentials_For_Ab-Initio_Calculations.pdf
- E. Pehlke, „The Plane-Wave Pseudopotential Method“
http://www.fhi-berlin.mpg.de/th/Meetings/FHIImd2003/Dtalks/FHI-WS2003-L03-Pehlke-The_Plane-Wave_Pseudopotential_Method.pdf
- G. Kresse, and J. Furthmüller, *Comp. Mat. Sci.* **6** (1996) 15.

Augmentation Methods



interatomic region
(interstitial)

muffin tin radius
(R_{MT})



atomic region
(muffin tin spheres)

Motivation

Strong oscillations of the wavefunctions
in the core region \Rightarrow PWs not sufficient

Is there an all-electron method?

Augmented Wave Methods:

\Rightarrow 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

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

with $r' = |\mathbf{r} - \mathbf{r}_{\alpha}|$ 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.

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

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

$$\begin{aligned}
 u_l^\alpha(r', \epsilon_n^{\mathbf{k}}) &= u_l^\alpha(r', E_0) + (E_0 - \epsilon_n^{\mathbf{k}}) \left. \frac{\partial u_l^\alpha(r', E)}{\partial E} \right|_{E=E_0} \\
 &= u_l^\alpha(r', E_0) + (E_0 - \epsilon_n^{\mathbf{k}}) \dot{u}_l^\alpha(r', E_0)
 \end{aligned}$$

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

Basis functions: **L**inearized **A**ugmented **P**lane **W**ave:

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

\swarrow l -dependent

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}

$$\chi_{\alpha, \text{LO}}^{lm}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \in I \\ \left(A_{lm}^{\alpha, \text{LO}} u_l^{\alpha}(r', E_{1,l}^{\alpha}) + B_{lm}^{\alpha, \text{LO}} \dot{u}_l^{\alpha}(r', E_{1,l}^{\alpha}) + C_{lm}^{\alpha, \text{LO}} u_l^{\alpha}(r', E_{2,l}^{\alpha}) \right) Y_{lm}(\theta, \phi) & \mathbf{r} \in R_{\text{MT}} \end{cases}$$

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

$$\Rightarrow A_{lm}^{\alpha, \mathbf{k}+\mathbf{G}} \quad B_{lm}^{\alpha, \mathbf{k}+\mathbf{G}} \quad C_{lm}^{\alpha, \mathbf{k}+\mathbf{G}}$$

The APW+lo Method



Two types of basis functions:

1. APWs with fixed energy

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

2. Local orbitals (different from LAPW)

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

\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}

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

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

$\phi_{lm}(\mathbf{r}, E)$ 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
⇒ overlapping atomic spheres
- envelope (tail) functions: $\kappa = 0$

⇒ 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 **P**rojector **A**ugmented **W**ave 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:

$$\left(\hat{\mathcal{T}}^\dagger H \hat{\mathcal{T}} - \hat{\mathcal{T}}^\dagger \hat{\mathcal{T}} \epsilon_n\right) \tilde{\Psi}_n(\mathbf{r}) = 0 \quad (n \text{ contains } \mathbf{k}\text{-point, band index, spin})$$

⇒ 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{T} :

We have to find a transformation \hat{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 $\hat{T} = 1 + \sum_R \mathcal{S}_R$

(sum over atomic contributions, because \hat{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.

$$\mathcal{S}_R |\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle \quad \begin{array}{l} \text{pseudo partial wave:} \quad |\tilde{\phi}_i\rangle \\ \text{all-electron valence partial wave:} \quad |\phi_i\rangle \end{array}$$

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

PAW Transformation Operator



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

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

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

$$c_i = \langle \tilde{p}_i | \tilde{\Psi}_n \rangle \Rightarrow |\tilde{\Psi}_n\rangle = \sum_{i \in R} |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\Psi}_n \rangle \Rightarrow \text{orthogonality } \langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}$$

Remember:

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

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

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

Remember:

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

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

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

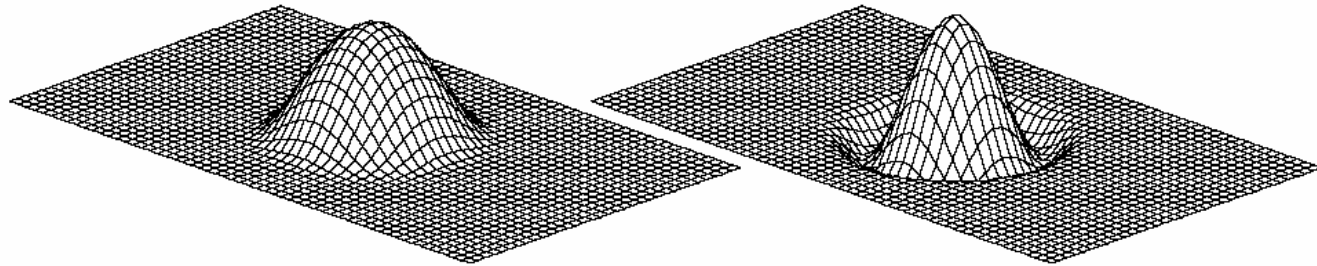
Projector Functions $|\tilde{p}_i\rangle$:

- 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

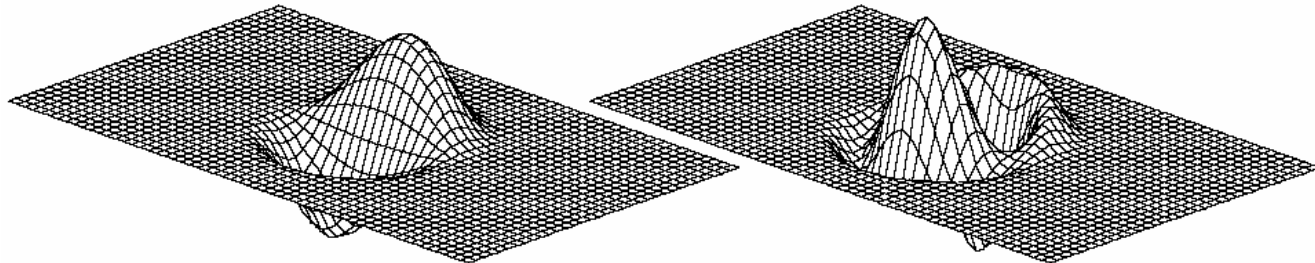
Projector Functions



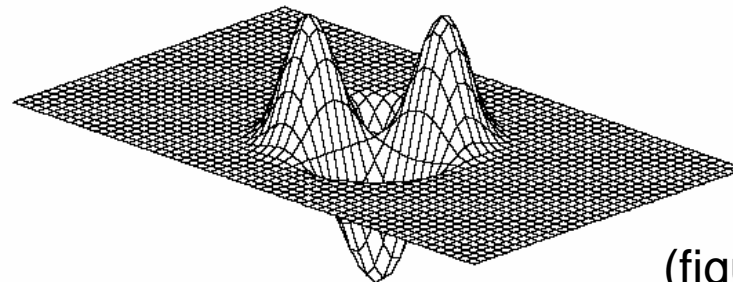
s-type projector functions



p-type projector functions



d-type projector function



(figures courtesy P. Blöchl)

$|\tilde{p}_i\rangle$

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:

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

pseudo density, PW expansion

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

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

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

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

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)



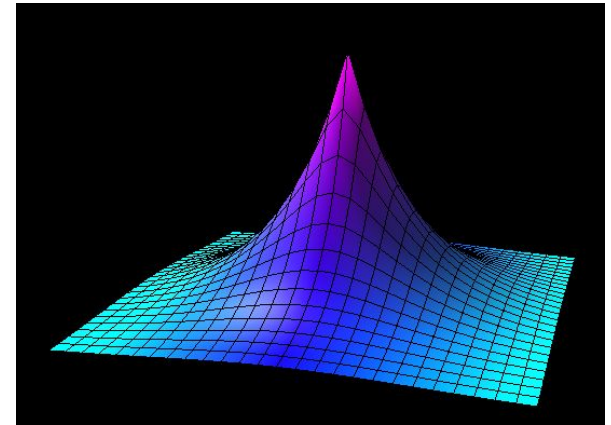
General form of a STO: $f(r, \theta, \phi) = R(r) \cdot Y(\theta, \phi)$ (primitive STO)

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 (n l) subshell (e.g. $2p_x, 2p_y, 2p_z$)

„double zeta“: two radial functions per (n l) 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:

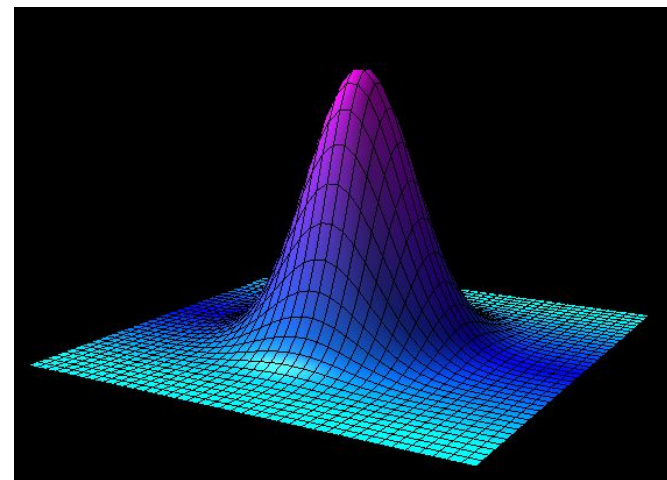
General form of a GTO: $f(r, \theta, \phi) = R(r) \cdot Y(\theta, \phi)$ (primitive GTO)

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 \Rightarrow 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:

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

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: $l + m + n = 3$
 $(x^3, y^3, z^3, x^2 y, x^2 z, y^2 x, y^2 z, z^2 x, z^2 y, xyz) \cdot e^{-\alpha r^2}$

Beyond Primitive GTOs



Contracted Gaussian Functions (CGFs):

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

⇒ 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

$r \rightarrow 0$: cusp condition

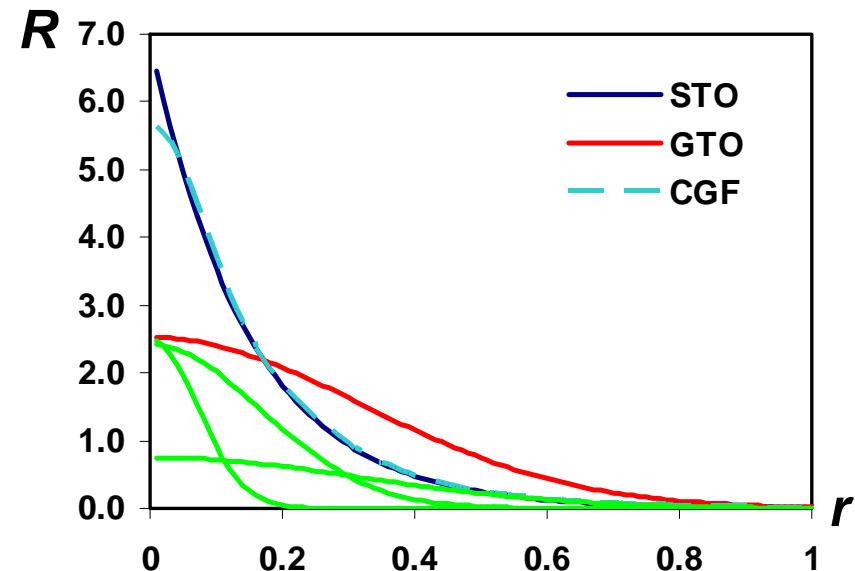
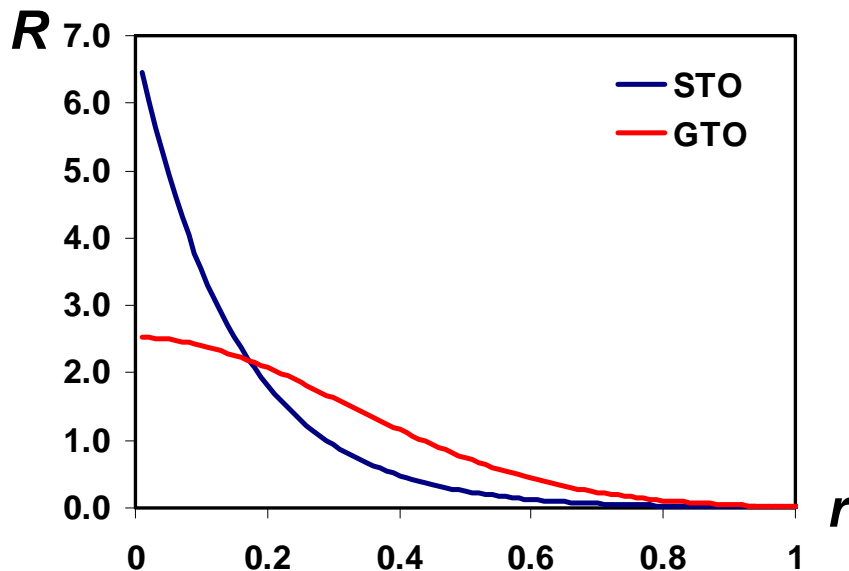
- STOs not well,
- GTOs hopeless, since $\left. \frac{df}{dr} \right|_{r \rightarrow 0} = 0$

$r \rightarrow \infty$: $\sim e^{-\text{const } r}$

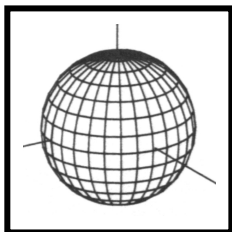
- STOs: ok
- GTOs decay too fast

Use GTOs to mimic STOs

About 2 to 3 times more GTOs as STOs for the same accuracy needed
 \Rightarrow Use contracted GTOs



Numerical Atomic Orbitals (NAOs)

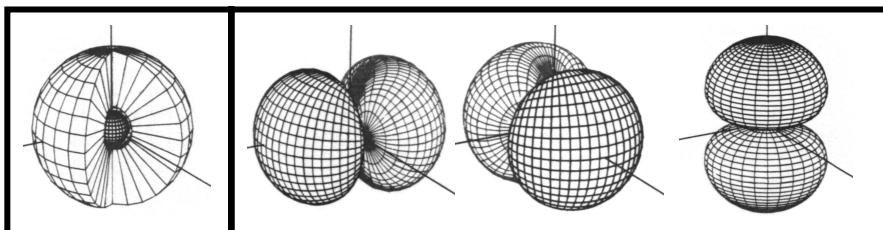


1s

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)

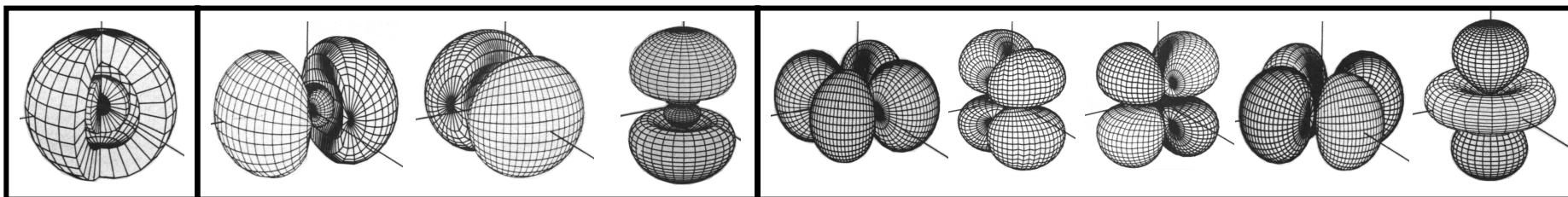


2s

2p_x

2p_y

2p_z



3s

3p_x

3p_y

3p_z

3d_{xy}

3d_{yz}

3d_{zx}

3d_{x²-y²}

3d_{z²}

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

