

Localized Atomic Orbital Basis Sets in the Projector Augmented Wave Method

Ask Hjorth Larsen

Center for Atomic-scale Materials Design

2008

Outline

Density functional theory

- Quantum mechanics

- Projector augmented wave method

Basis set generation

- Overview

- Pseudo-atomic orbital generation

- Extra basis functions

Force calculations

- Evaluation of atomic force expression

- Force tests

Setup optimization

- Automatic setup optimization

Basics

What are we trying to do?

- ▶ Solve Schrödinger equation for wave functions
- ▶ Calculate useful quantities: mechanical properties, chemical properties, electrical properties ...
- ▶ But many-body wave functions with N electrons require $3N$ coordinates, having memory exponential in N

Density functional theory

- ▶ Electronic density is in fact sufficient to determine **all properties** of the system
- ▶ Density depends on only (x, y, z) , but is difficult to use without calculating wave functions

Kohn-Sham ansatz

Practical independent-particle approach to DFT

Iterative Kohn-Sham solution

Initialize wave functions, then repeat until converged:

- ▶ Calculate electron density from wave functions
- ▶ Use density to calculate effective potential from charge distribution and (approximate) interaction effects
- ▶ Use potential to find wave functions, solving

$$\hat{H}_{\text{KS}}|\psi_n\rangle = \epsilon_n|\psi_n\rangle$$

Afterwards

- ▶ Having the wave functions, we can evaluate properties such as energy, forces on atoms, band gaps, ...

Projector augmented wave method

- ▶ Nuclear potentials make wave functions oscillate swiftly. Thus, we must use high-resolution grids to represent them. The PAW method is one way to fix this problem.
- ▶ Define a transformation $\hat{\mathcal{T}}$ between inconvenient **all-electron** wave functions $|\psi_n\rangle$ and smooth **pseudo** wave functions $|\tilde{\psi}_n\rangle$.
- ▶ Quantities can then be expressed in terms of smooth and atomic parts, most operations involving the smooth parts, while atomic parts are treated on efficient radial grids.

Localized basis sets

- ▶ Each wave function $|\tilde{\psi}_n\rangle$ is a linear combination of fixed, atom-centered basis functions $|\Phi_\mu\rangle$:

$$|\tilde{\psi}_n\rangle = \sum_{\mu} c_{\mu n} |\Phi_\mu\rangle$$

- ▶ Fewer degrees of freedom $c_{\mu n}$ means less memory and less computation time, but also sacrifices accuracy
- ▶ Kohn-Sham equations become generalized eigenvalue problem:

$$\mathbf{HC} = \mathbf{SC}\mathbf{\Lambda}$$

Overview of atomic basis functions

Functional form

- ▶ Radial function times fixed spherical harmonic:

$$\Phi_{l\zeta m}(\mathbf{r}) = \varphi_{l\zeta}(r)Y_{lm}(\theta, \phi)$$

- ▶ Radial part is represented numerically and can be chosen freely

Types of basis functions

- ▶ One atomic orbital for each **valence** state, indexed by l
- ▶ Any number of **extra radial functions** for each l , indexed by ζ .
Nomenclature: single-zeta, double-zeta, ...
- ▶ **Polarization** functions: for values of l not present on atom
- ▶ Different angular parts for each $m = -l \dots l$

Pseudo-atomic orbital generation

All-electron orbital calculation

- ▶ Atomic orbitals are calculated for the isolated atom

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(r)\right] X(\mathbf{r}) = \epsilon X(\mathbf{r})$$

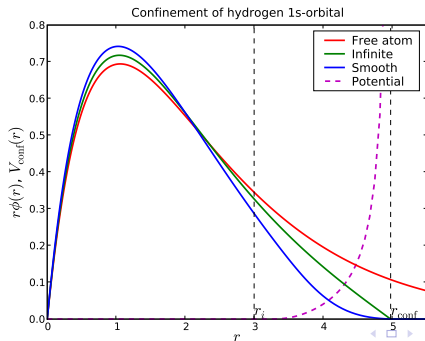
- ▶ Radial parts are found by numerical integration on radial grids

Issues to resolve

- ▶ The wave functions have long tails, and must be converted to **localized** functions, approaching zero smoothly at some cutoff.
- ▶ Wave functions oscillate swiftly near the core. They must be transformed to **smooth** pseudo wave functions.

Localization

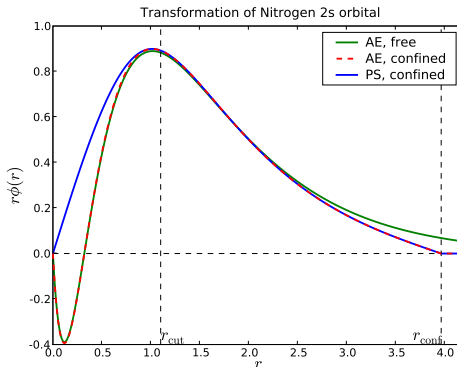
- ▶ Add smooth confinement potential v_{conf} during orbital calculation, defined to be zero inside some inner cutoff r_i , infinity at some outer cutoff r_{conf} , and smooth in between.
- ▶ Small r_{conf} means high energy. r_{conf} is chosen by requiring a particular **energy shift** (e.g. 0.1 eV) compared to free atom



Transformation to pseudo wave functions

- ▶ The PAW transformation yields all-electron wave functions from pseudo ones. This we can invert, such that (simplified)

$$|\Phi_\mu\rangle = |X_\mu\rangle + \sum_i \left(|\tilde{\phi}_i\rangle - |\phi_i\rangle \right) \langle \tilde{p}_i | \Phi_\mu \rangle$$



Multiple-zeta basis sets

Split-valence-like scheme

- ▶ Atomic orbitals alone are typically not sufficiently accurate
- ▶ To improve basis set flexibility, add extra functions for each valence state with new radial parts
- ▶ Simple method: subtract polynomial of appropriate order from each valence state, such that for some chosen radius r_{split} ,

$$\varphi_{\text{dz}}(r) = \begin{cases} \varphi_{\text{sz}}(r) - r^l(a - br^2) & r < r_{\text{split}} \\ 0 & r \geq r_{\text{split}} \end{cases},$$

- ▶ Coefficients a and b are chosen to ensure differentiability
- ▶ r_{split} can be chosen conveniently by specifying the norm of the tail of φ_{sz} beyond r_{split} (e.g. 15-20%)

Multiple-zeta basis sets

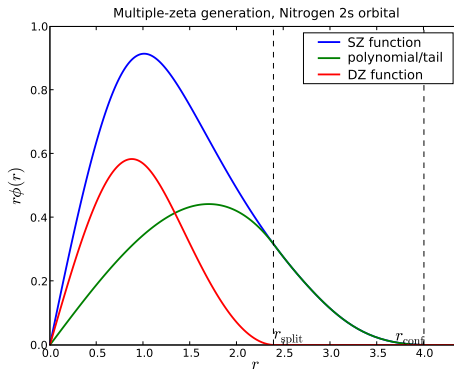


Figure: Given the pseudo-atomic orbital φ_{SZ} (blue), the second-zeta basis function φ_{DZ} (red) is obtained by subtracting a polynomial (green) joining the tail of φ_{SZ}

Polarization functions

Idea

- ▶ Calculate grid-based **reference** wave functions for some system. This could be H_2O , if we want to calculate polarization functions for O or H.
- ▶ Define polarization function as some linear combination of primitive Gaussian-like functions
- ▶ Use optimization scheme to find the coefficients with **largest projection** onto reference wave functions. This set of coefficients defines the polarization function.
- ▶ It turns out that the calculated polarization functions are pretty similar in shape – in fact we can describe them with just one Gaussian, if chosen properly.

Calculated polarization functions

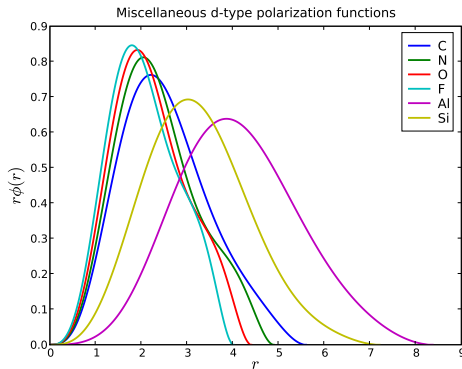


Figure: Different calculated polarization functions

Full basis set example

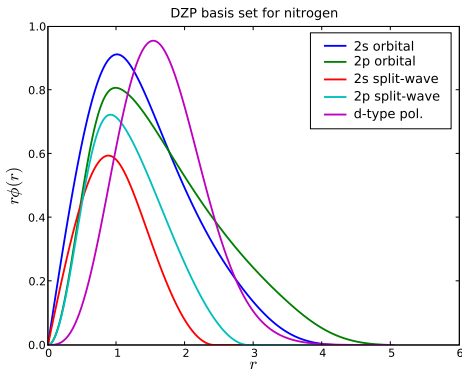


Figure: Double-zeta polarized basis set with default parameters. The five radial parts correspond to 13 basis functions in total, counting all angular parts

Atomic forces

Why?

- ▶ Structural relaxations
- ▶ Molecular-dynamics simulations

Procedure

- ▶ The force acting on an atom is the derivative of total energy with respect to nuclear coordinates: $\mathbf{F}^a = -\frac{\partial E}{\partial \mathbf{R}^a}$. This we can calculate directly from the energy expression.
- ▶ Tricky issue: must preserve wave function orthogonality
- ▶ Other tricky issue: basis functions move with atoms

Chain rule

- ▶ Choose suitable intermediate parameters
- ▶ Write:

$$\begin{aligned}
 \frac{\partial E}{\partial \mathbf{R}^a} &= \sum_{\mu\nu} \frac{\partial E}{\partial \rho_{\mu\nu}} \frac{\partial \rho_{\mu\nu}}{\partial \mathbf{R}^a} + \sum_{\mu\nu} \frac{\partial E}{\partial T_{\mu\nu}} \frac{\partial T_{\mu\nu}}{\partial \mathbf{R}^a} + \sum_L \int \frac{\delta E}{\delta \tilde{g}_L^a(\mathbf{r})} \frac{d\tilde{g}_L^a(\mathbf{r})}{d\mathbf{R}^a} d^3\mathbf{r} \\
 &\quad + \int \frac{\delta E}{\delta \tilde{n}(\mathbf{r})} \frac{\partial \tilde{n}(\mathbf{r})}{\partial \mathbf{R}^a} d^3\mathbf{r} + \int \frac{\delta E}{\delta \bar{v}^a(\mathbf{r})} \frac{d\bar{v}^a(\mathbf{r})}{d\mathbf{R}^a} d^3\mathbf{r} + \sum_{bij} \frac{\partial E}{\partial D_{ij}^b} \frac{\partial D_{ij}^b}{\partial \mathbf{R}^a} \\
 &= \sum_{\mu\nu} H_{\nu\mu} \frac{\partial \rho_{\mu\nu}}{\partial \mathbf{R}^a} + \sum_{\mu\nu} \rho_{\nu\mu} \frac{\partial T_{\mu\nu}}{\partial \mathbf{R}^a} + \sum_L Q_L^a \int \tilde{v}_{\text{Ha}}(\mathbf{r}) \frac{d\tilde{g}_L^a(\mathbf{r})}{d\mathbf{R}^a} d^3\mathbf{r} \\
 &\quad + \int \tilde{v}_{\text{eff}}(\mathbf{r}) \frac{\partial \tilde{n}(\mathbf{r})}{\partial \mathbf{R}^a} d^3\mathbf{r} + \int \tilde{n}(\mathbf{r}) \frac{d\bar{v}^a(\mathbf{r})}{d\mathbf{R}^a} d^3\mathbf{r} + \sum_{bij} \Delta H_{ij}^b \frac{\partial D_{ij}^b}{\partial \mathbf{R}^a}
 \end{aligned}$$

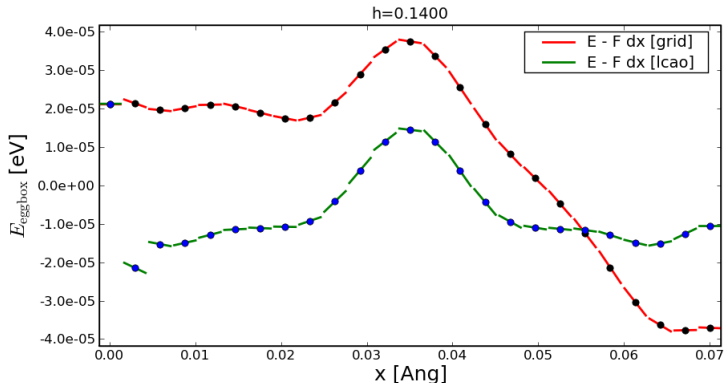
Big formula

- After some work, this can be expressed in a form where all variables can be evaluated relatively straightforwardly

$$\begin{aligned}
 \mathbf{F}^a = & -2\Re \sum_{b\mu\nu ij} \left\{ \Delta H_{ji}^b \rho_{\mu\nu} - \Delta S_{ji}^b \sum_n c_{\nu n} \epsilon_n f_n c_{\mu n}^* \right\} \frac{\partial P_{i\mu}^b}{\partial \mathbf{R}^a} P_{j\nu}^{b*} \\
 & - \sum_{\mu\nu n} c_{\nu n} \epsilon_n f_n c_{\mu n}^* \frac{\partial \Theta_{\mu\nu}}{\partial \mathbf{R}^a} - \sum_{\mu\nu} \frac{\partial T_{\mu\nu}}{\partial \mathbf{R}^a} \rho_{\nu\mu} \\
 & - 2\Re \sum_{\mu\nu} \rho_{\nu\mu} \int \frac{d\Phi_{\mu}^*(\mathbf{r})}{d\mathbf{R}^a} \tilde{v}_{\text{eff}}(\mathbf{r}) \Phi_{\nu}(\mathbf{r}) d^3\mathbf{r} - \int \tilde{v}_{\text{eff}}(\mathbf{r}) \frac{d\tilde{n}_c^a(\mathbf{r})}{d\mathbf{R}^a} d^3\mathbf{r} \\
 & - \int \tilde{v}_{\text{Ha}}(\mathbf{r}) \sum_L Q_L^a \frac{d\tilde{g}_L^a(\mathbf{r})}{d\mathbf{R}^a} d^3\mathbf{r} - \int \tilde{n}(\mathbf{r}) \frac{d\tilde{v}^a(\mathbf{r})}{d\mathbf{R}^a(\mathbf{r})} d^3\mathbf{r}.
 \end{aligned}$$

Egg-box forces

- ▶ Due to discrete grid representation, space is not homogeneous. Translation thus implies small changes in energy with the periodicity of the grid, called the **egg-box effect**.
- ▶ Do calculated forces predict egg-box effect accurately?



Structural relaxation of H₂O

Results using quasi-Newton algorithm

Method	Angle	Bond length [Å]
LCAO	101.9°	0.983
Grid	105.0°	0.975
Exp.	104.5°	0.957

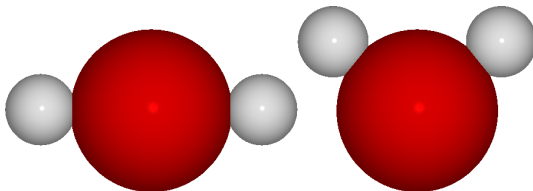


Figure: Initial (180°) and final configuration

Setups

Definition

In the PAW method, a **setup** is the collection of data which pertains to a particular type of atom

Properties of a setup

- ▶ Defines the atomic parts $\hat{\mathcal{T}}^a$ of the PAW transformation
$$\hat{\mathcal{T}} = 1 + \sum_a \hat{\mathcal{T}}^a$$
- ▶ Defines other quantities such as “compensation charge” expansion functions and “zero potential”, which are used to shift troublesome quantities between radial and regular grids
- ▶ Each quantity generally depends on a few parameters: cutoffs, decay parameters, Fourier filtering parameters

Automatic setup optimization

Idea

- ▶ Identify a handful of parameters to optimize
- ▶ Define a measure of the quality of a setup
- ▶ Use the downhill simplex method to find the best setup

Quality measure

- ▶ Atomization energy of dimer compared to all-electron value
- ▶ Bond length of dimer compared to all-electron value
- ▶ Amplitude of “egg-box” effect
- ▶ Convergence of energy with respect to grid resolution
- ▶ Quality is the sum of the squares of the above measures, times a measure of the calculation time

Results

- ▶ Some properties can be improved at the expense of others
- ▶ Algorithm frequently gets stuck in local minima too early

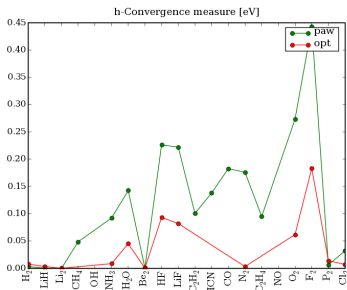


Figure: Measure of convergence with respect to grid resolution

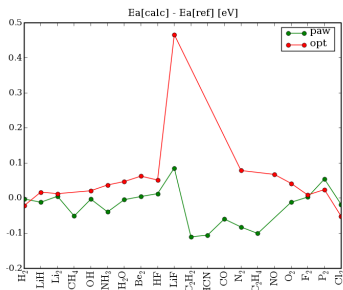


Figure: Deviation of atomization energies from reference

Summary

Basis generation

- ▶ Smooth valence basis functions are obtained by localizing and transforming atomic orbitals
- ▶ Multiple-zeta basis sets are generated by adding polynomials to valence basis functions
- ▶ Polarization functions are single Gaussians. Cutoffs must in general be estimated using the interpolation scheme

Force calculations

- ▶ Atomic forces have been implemented
- ▶ Tests confirm that forces are correct