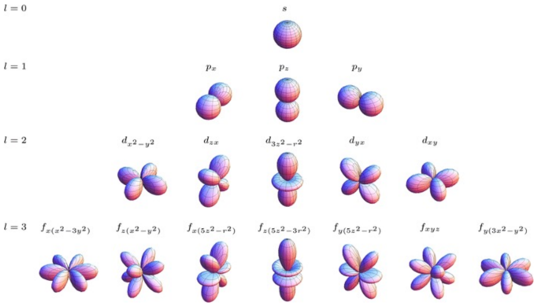
Basis Sets

Motivation

Need to describe orbitals φ_i or densities ρ or wave functions Ψ easily, but they are all similar. Idea: basis expasion:

$$f(\mathbf{r}) = \sum_i \underbrace{C_i}_{\text{Coefficients}} \underbrace{\phi_i}_{\text{Basis functions}} \qquad (74)$$

Quality depends on completeness of basis functions.



Overview

Properties

- Finite
- Either fitted (STO/GTO) or systematic (plane wave, wavelet, real space)
- Typically defined per element
- Connection locality and cost

Key terms

- Minimal basis set: one basis function for each orbital
- Polarization functions: asymmetry close to the nucleus: bonds
- Diffuse functions: asymmetry away from the nuclei: hydrogen bond, dipoles
- Complete basis set limit: can express any density

Database (GTO)

- basissetexchange.org

Basis set families

Families

- atom-centered
  - Slater-type orbitals (STO): expensive integrals
  - Gaussian-type orbitals (GTO): Primitive gaussian functions build up orbitals
- Plane waves
- Wavelets
- Real space

Plane waves

Properties

- Path to complete basis set (CBS limit)
- Easy and elegant implementation except HF
- Easy derivatives
- Requires “fake” boundary conditions
- Empty space is not free
- Pseudopotentials required as cutoff too high
- Commonly used for materials

Atom-centered basis functions

Properties

- Localised, so empty space is free
- Scales linearly with number of atoms
- Numerical issues if atoms close together
- Any boundary conditions possible
- No path to complete basis set limit: empirical schemes necessary
- Commonly used for molecules / mixed settings
- Popular: Gaussian-Type orbitals, since cheaper

Real-Space and Wavelets

Properties

- Multi-dimensional grid
- Easiest to approach CBS
- Hard to implement
- Slow in evaluation
- Mostly used for technical demonstrations / settling one-off questions

Wavelets

- Finite Support: easy to subdivide
- Niche implementations
- Unclear whether “best of both worlds” or “worst of both worlds”

Example for missing features

Electron density cusp

- Slater-type orbital (radial part): $\exp(-\alpha r)$
- Gaussian-type orbital (radial part): $\exp(-\alpha r^2)$
- Plane wave: $\sum \sin(kx)$

GTO construction

For given angular momentum quantum numbers l, m:

$$\underbrace{\Phi}_{\text{Orbital}}(\mathbf{r}) = R_l(\overbrace{r}^{\text{Radial distance}})\underbrace{Y_{lm}}_{\text{Spherical harmonic}}(\overbrace{\theta, \phi}^{\text{Angles}}) \tag{75}$$

Primitive:

$$R_l(r) = r^l N(l, \alpha) \exp(-\underbrace{\alpha}_{\text{Width of the basis function}} r^2) \tag{76}$$

Contraction

- sum of weighted primitives
- weights normalized

GTO nomenclature: Pople

Gaussian-type orbitals

- Minimal basis set: “single zeta” (Zeta commonly used for the exponent in STO-nG)
- Twice/three times the basis functions for valence atomic orbitals: double-zeta, triple-zeta, …
- Split valence (single zeta for core, multiple for valence)

6-31++G**

- 6: One core basis function with 6 contracted Gaussians
- 31: Two valence basis functions with 3 and 1 contracted Gaussian respectively
- *: Polarization on heavy atoms
- **: Polarization also on hydrogen atoms
- +: Diffuse functions on heavy atoms
- ++: Diffuse function also on hydrogen atoms

GTO nomenclature: Dunning

aug-cc-pCVDZ

- aug Diffuse functions
- p Polarization functions
- DZ Double zeta
- C core basis functions

Contraction

- (6s,3p) → [2s,1p]
- (primitives) -> [basis functions]
- (not main quantum numbers)

Question: [3s2p1d] is how many basis functions?