

The Basis Set

-

LCAO



Atom-Centered Basis Functions

Core Concept:

Place basis functions centered on atomic nuclei

Important Features:

- Basis set overlap depends implicitly on interatomic distance
- Can be used periodic and non-periodic
- Number of basis functions depends on
 - *Number of atoms*
 - *Number of electrons*

Slater-type orbitals (STO)

Inspired by hydrogen-like solutions

Distance decay

$$\phi = Y_{l,m} \times r^{n-1} e^{-\zeta r}$$

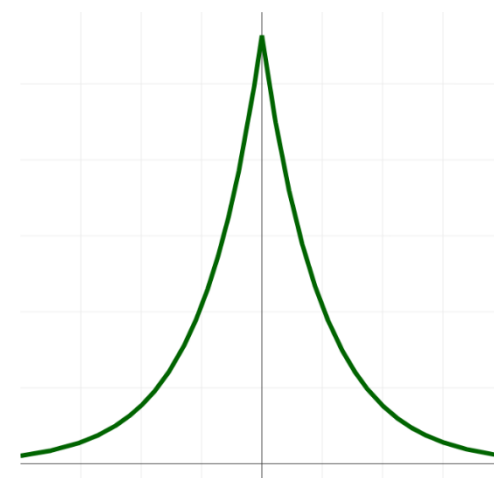
Spherical harmonics

Advantages:

- Highest accuracy / basis function

Disadvantages:

- No analytical integrals



Slater-type basis function

Gaussian-type orbitals (GTO)

$$\phi = Y_{l,m} \times r^{2n-2-l} e^{-\zeta r^2}$$

$$\phi = x^{l_x} y^{l_y} z^{l_z} \times e^{-\zeta r^2}$$

Angular Distribution

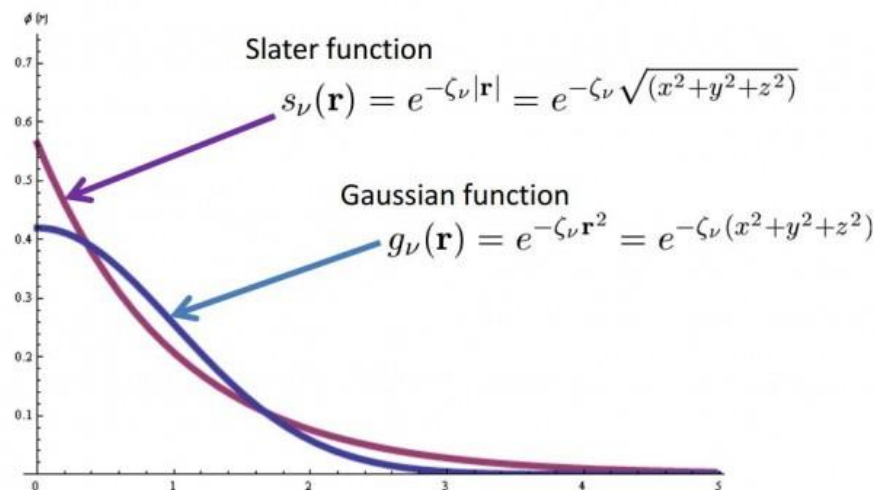
Distance decay

Advantages:

- Analytical integrals

Disadvantages:

- No „cusp“ at $r = 0$
- Falls off too quickly



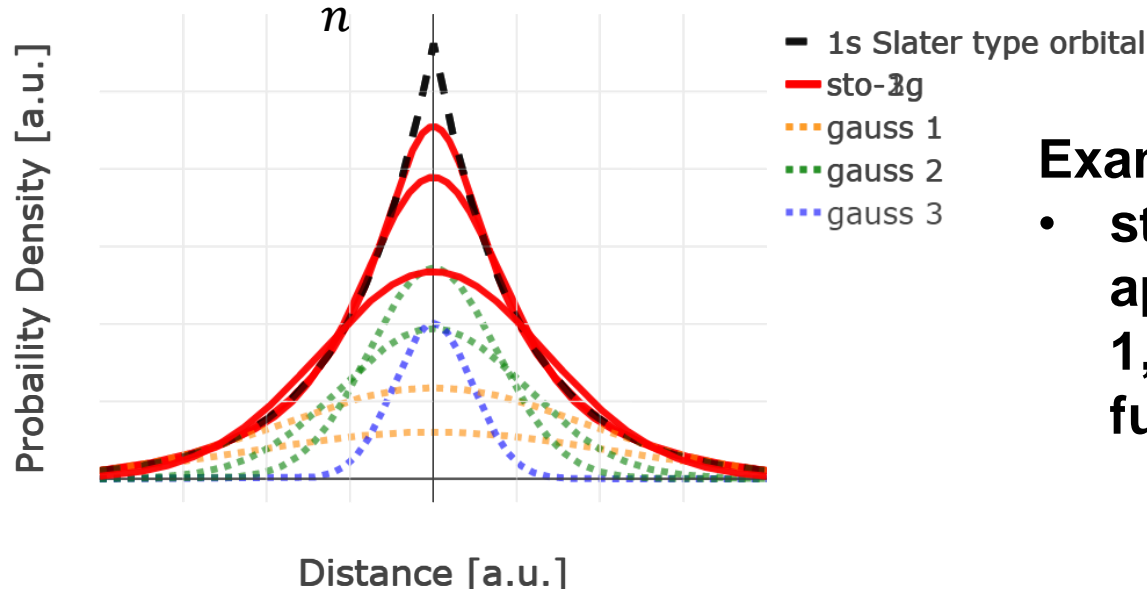
<http://blog.atoms.eu/quantenchemie-1-atomorbital/>

STO Approximation with GTOs

By using multiple Gaussian functions

$$\phi = \sum_n^N c_n GTO(\zeta_n)$$

Parameters c_n and ζ_n fitted to STO



Examples:

- sto-ng \Rightarrow STO approximated by $n = 1, 2$ and 3 gaussian functions

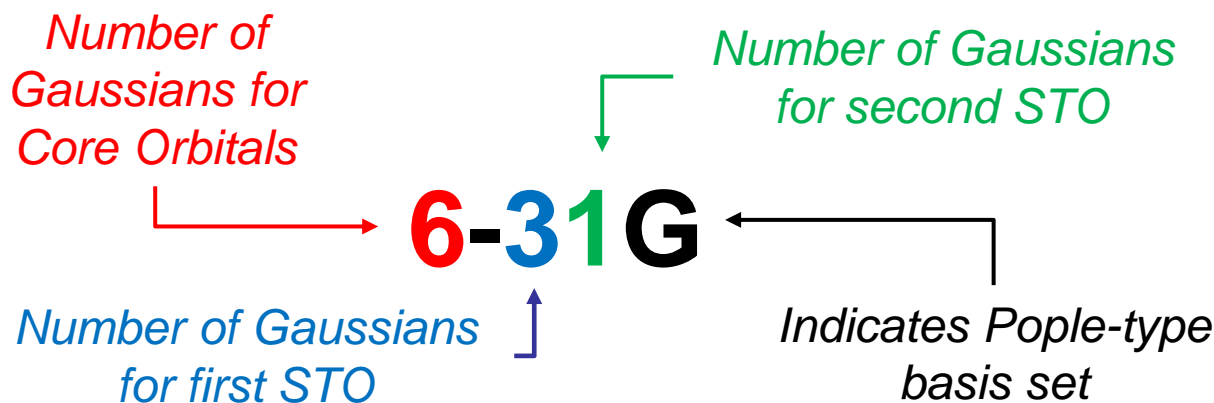
These basis functions (**contracted orbitals**), consisting of the gaussian functions (**primitive functions**), are then used, whereby the parameters c_n and ζ_n stay fixed.

Atom-Centered Basis Functions

Hierarchy:

- *Single zeta*: Only one basis function per orbital
- *Double zeta*: Two basis functions per orbital
- *Triple zeta*: Three basis functions per orbital
-

In practise, it is sufficient to multiply only the valence orbitals → Split-valence basis sets



Atom-Centered Basis Functions

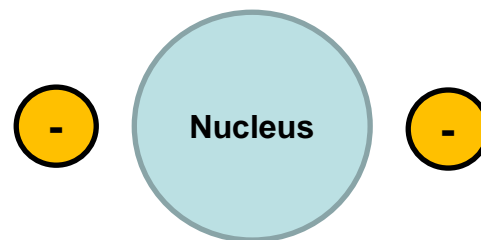
Only „natural“ orbitals are insufficient

- Add higher angular momentum („polarization functions)

6-31G*

Especially important for correlated methods

- *Angular correlation*



Angular correlation: Electrons are preferably found at opposite sides of the nucleus

Atom-Centered Basis Functions

Weakly bonded electrons require special functions with small ζ

➤ Diffuse Functions

6-31+G*

Important for anions and excited states or if properties depend primarily on least bound electrons, e.g. polarizability.

Common problem: Linear dependence of basis set

Atom-Centered Basis Functions

Pople-type Basis sets:

6-31+G*

Dunning-Type-basis sets:

aug-DZP

Karlsruhe basis sets:

aug-DVP

Different basis sets pursue different strategies. All are designed to give good **relative energies**, but **not absolute energies**.
Never compare energies across different basis sets!

Other LCAO basis set types

Correlation consistent:

Recover comparable amount of static correlation

Polarization consistent:

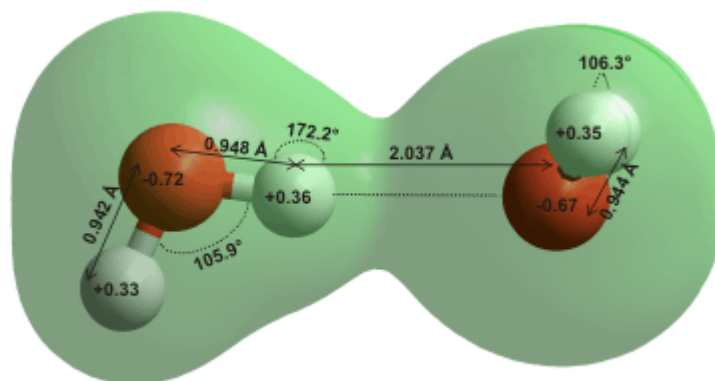
Recover comparable amount of dynamic correlation

F_{12} basis sets:

Not localized on nucleus, but depend explicitly on interatomic distance

Limitations of LCAO

- **Basis set incompleteness error:** Atom-centered are centered on atoms do not form a complete basis!
- **Basis set superposition error:** Esp. for small basis sets, functions on one moiety can „help“ describing the wave-function on another moiety
→ *Quality of basis set depends on geometry*

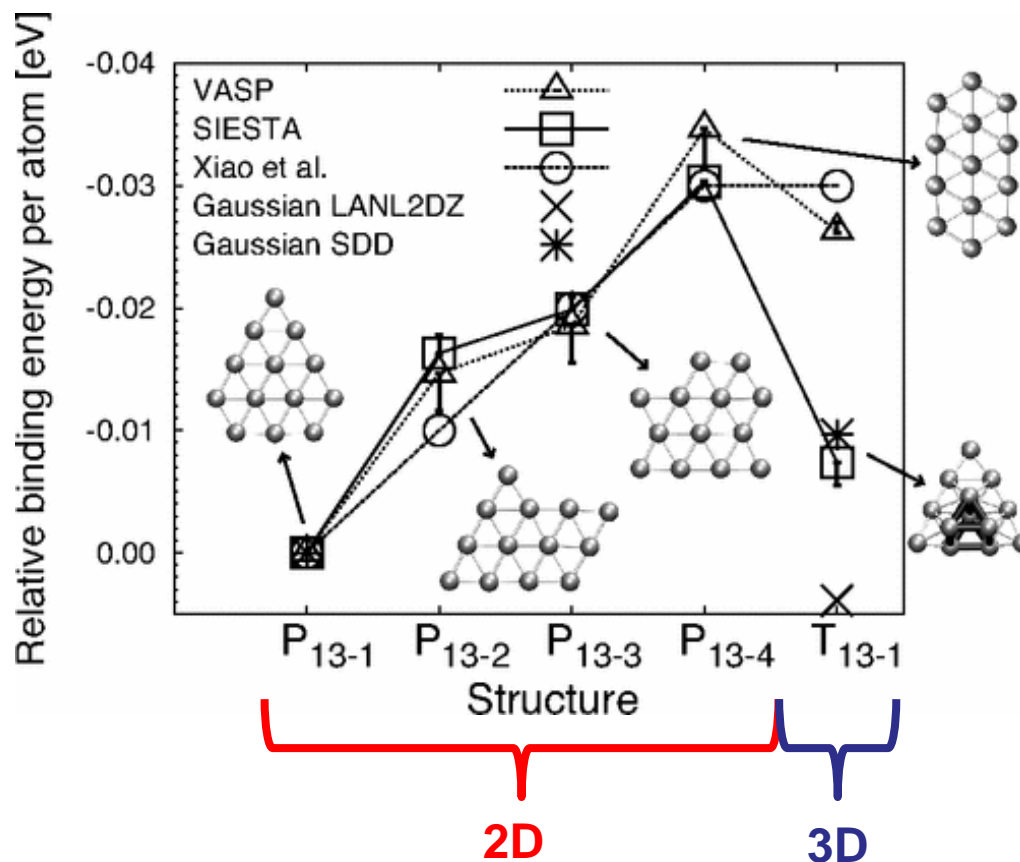


$$\Delta E_{bind} = E(AB) - (E(A) + E(B))$$

ΔE overestimated

Impact of BSSE

Spuriously favors compact structures with large wave-function overlap (e.g. 3D > 2D clusters)



Counterpoise Correction: „Ghost Atoms“

Calculate energy of monomer a and b in the presence of wave-functions both monomers (ab)

$$\Delta E^{CP} = E(A)_{ab} + E(B)_{ab} - E(A)_a - E(B)_b$$

$$\Delta E_{bind}^{CP} = \Delta E_{Bind} - \Delta E^{CP}$$

Counterpoise correction is only an **estimate**, and neither an upper nor a lower **limit**

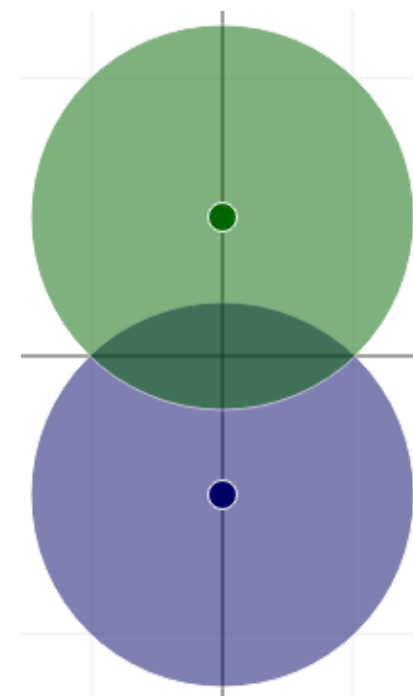
Counterpoise correction is large for

- correlated methods
- small basis sets

Integration Grids

In analogy to BSSE, numerical affects occur when the integration grid is atom-centered

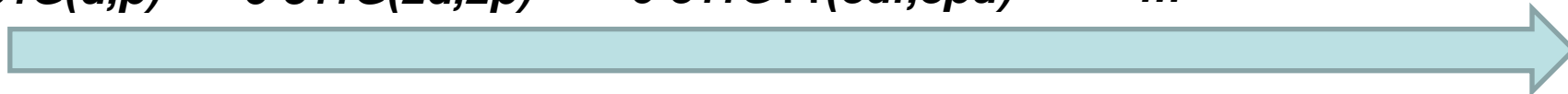
Particularly problematic when calculating vibrations („moving grid problem“)



Basis Set Extrapolation

Concept: Use ever better basis

6-31G(d,p) 6-311G(2d,2p) 6-311G++(3df,3pd) ...



Problems:

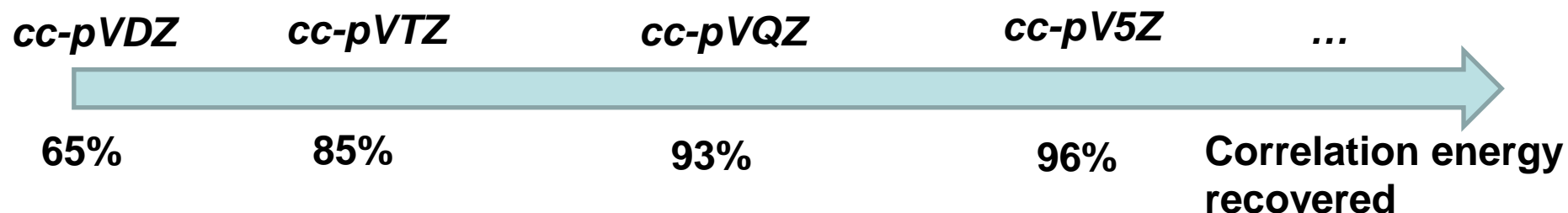
- Larger basis set guarantees better energy, but not better „property“
- Unclear which function should be added next („unbalanced“ basis sets)

Solution:

- Specifically designed, hierarchic basis sets (e.g: correlation consistent)

Basis Set Extrapolation

cc-pV N Z: correlation consistent basis set with N split valence functions



Energy convergence for HF / DFT : $E(N) \approx E(CBS) + Ae^{-B\sqrt{N}}$

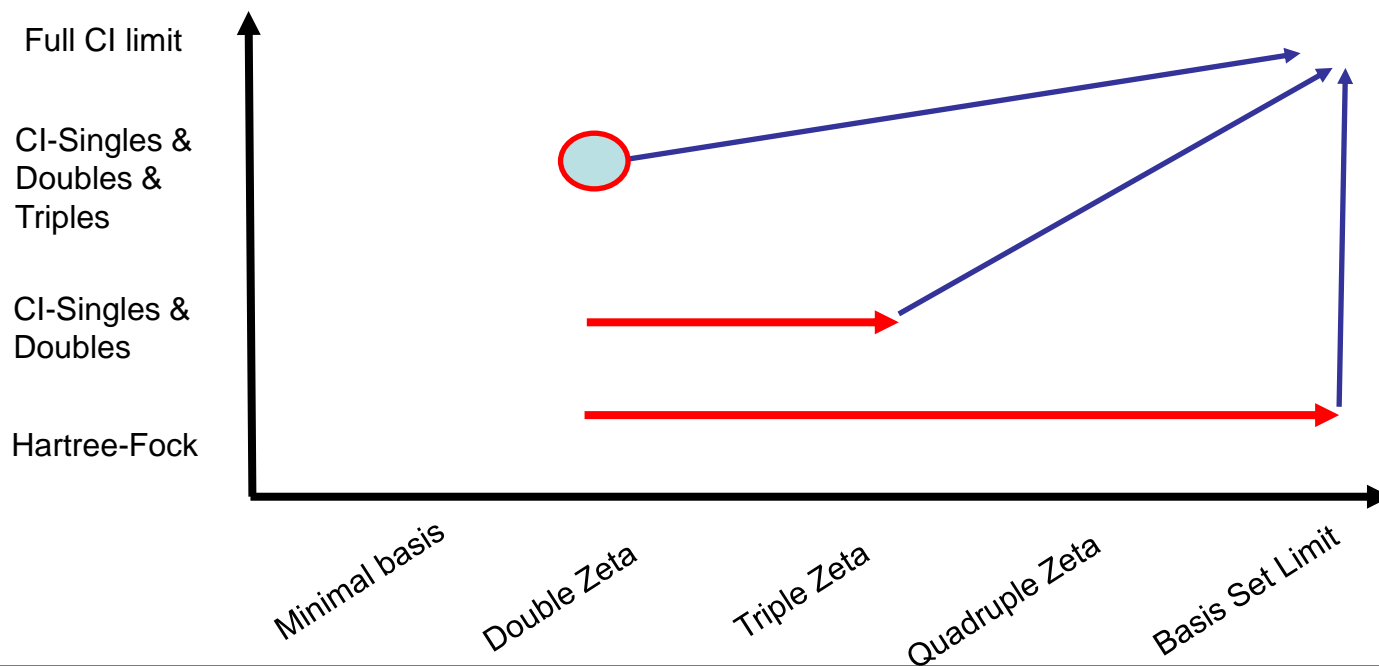
Extrapolation requires 2 or 3 points (but DZ gives poor results)
Only analysis, should always be done!

Mind the remaining errors!

(Vibrations, frozen core for correlation methods, Born-Oppenheimer, relativistic, ...)

Composite Extrapolation Schemes

- **Select geometry (fixed)**
- **Estimate Hartree-Fock limit energy**
- **Estimate electron correlation limit energy**
- **Add energy from translation/rotation/vibration**



Gaussian-n Models

Empirical Model with Pople-Type Basis sets

- **Optimize Geometry @ B3LYP / 6-31G****
- **Vibrations @ B3LYP / 6-31G**, scale with 0.9854**
- **Calculate HF limit with exponential extrapolation from aug-cc-pVQZ / aug-cc-pV5Z**
- **Calculate energy with CCSD(T)/6-31G***
- **Calculate energy for MP4/6-31G****
- **Add empirical correction**