

Basis Sets

Basis Functions

- In standard quantum mechanical methods, the wavefunction Ψ is expressed as a Slater determinant of spin orbitals χ_a .
- Each spin orbital is represented as linear combination of basis functions ϕ_v :
 - $\chi_a = \sum_v c_{av} \phi_v$
- The basis functions used in a calculation is called the *basis set*.

Choice of Basis Set

- The choice of basis set greatly affects the accuracy and speed of a calculation.
- In general, we use basis functions that closely resemble the atomic orbitals of each atom.
- We also want functions that are easy to integrate.
- Increasing the number of basis functions in a basis set will increase the accuracy of the calculation at an often large increase in computational cost.
- Choice of basis set will depend on the system of interest, type of calculation, and desired accuracy.

Gaussian Basis Sets

- Gaussian basis sets are the most common type of basis set in quantum chemistry.
- Gaussian functions allow for relatively fast evaluation of integrals used in quantum chemistry calculations.
- These basis functions use the Linear Combination of Atomic Orbitals approximation.
- Basis functions resemble atomic orbitals (1s, 2p, etc.), and consist of a sum of multiple primitive Gaussian functions.

Gaussian Basis Sets (cont.)

- 3 parameters are used for each Gaussian primitive:
 - Type of function (1s, 2p, etc.)
 - Contraction Coefficient d
 - Contraction Exponent α
- A few examples of Gaussian primitives:
 - $d g_{1s}(\alpha, r) = d(8\alpha^3/\pi^3)^{1/4} e^{-\alpha r^2}$
 - $d g_{2p_x}(\alpha, r) = d(128\alpha^5/\pi^3)^{1/4} x e^{-\alpha r^2}$
 - $d g_{3d_{xy}}(\alpha, r) = d(2048\alpha^7/\pi^3)^{1/4} xy e^{-\alpha r^2}$

Gaussian Basis Sets (cont.)

- Each basis function is a sum of contracted Gaussian primitives of the same type with different values of d and α .
- These values are, in general *not* modified during a calculation.
- Each set of primitives are different for each atom. One cannot use basis functions from C on O, for example.

STO- n G Basis Sets

- Uses Gaussians to approximate more accurate, but slower to integrate Slater functions.
- n is the number of Gaussian primitives in each basis function. For example, STO-3G has 3 primitives for every basis function.
- More primitives increases the accuracy of the fit to the Slater functions

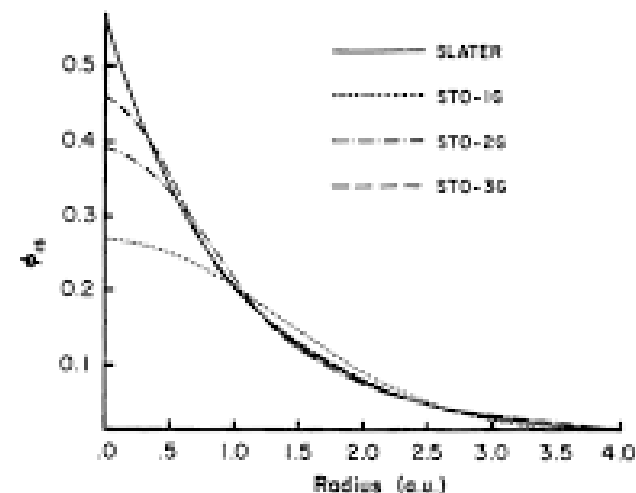


Figure 3.3 Comparison of the quality of the least-squares fit of a 1s Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.

Figure from Szabo and Ostlund, *Modern Quantum Chemistry*.

STO- n G Basis Sets (cont.)

- The STO- n G basis sets are *minimal* basis sets, meaning there is only one basis function for each atomic orbital on each atom.
- STO-3G is most common, but STO-4G and STO-5G are sometimes used.
- Provides very poor results, and is not recommended for energy or property evaluations.
- Can be useful for an initial geometry optimization, if followed by an optimization with a larger basis set.

Split-Valence Basis Sets

- Split-Valence Basis Sets add additional basis functions to valence atomic orbitals. These are commonly referred to as double zeta, triple zeta, etc. for the number of functions in each valence orbital.
- Examples include the Pople basis sets, such as 6-31G:
 - The 6 indicates the number of primitives in core electron orbitals
 - Two numbers after the dash indicates two basis functions for each valence orbital, with 3 and 1 primitives each, respectively
- Substantially more accurate than minimal basis sets.
- Provide a good starting point to which different types of functions can be added.

Polarization functions

- The shape of atomic orbitals can be distorted when exposed to an electric field, or inside a molecule.
- Can be approximated by adding basis functions of a higher angular momentum (such as *d* functions for C or *p* functions for H).
- In Pople basis sets, * indicates polarization functions added to heavy atoms (ie not H), and ** indicates polarization functions added to heavy atoms and hydrogen.
 - For example, 6-31G** adds *d* functions to second row elements and *p* functions to hydrogen

Dunning Basis Sets

- The Dunning cc-pV n Z basis sets are designed to allow extrapolation towards complete basis set limit.
 - n indicates double, triple, etc. zeta. For example, cc-pVQZ is a quadruple-zeta basis set
- Contain polarization functions in definition of basis set.
- These basis sets are particularly good for post-Hartree-Fock methods, like MP2 or CCSD(T).
- Can contain a very large number of functions for even relatively small atoms, making these basis sets potentially very expensive, particularly for large n .

Diffuse Functions

- Many systems contain diffuse orbitals that are not well described by atomic orbitals.
- Can be addressed by adding diffuse functions to basis set.
 - In Pople basis sets, + adds diffuse functions to heavy atoms, such as in 6-311+G*.
 - In Dunning basis sets, the prefix aug- adds diffuse functions, such as in aug-cc-pVDZ.
- Diffuse functions are particularly important when studying anions or systems with long range interactions, or when examining excited states.