

# Chemistry 137

## Basis Sets for Molecular Orbital Calculations

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## Resources

- Foresman and Frisch, *Exploring Chemistry with Electronic Structure Methods*, Chapter 5
- Cramer, Chapter 6
- Jensen, Chapter 5

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## LCAO Approximation

- numerical solutions for the Hartree-Fock orbitals only practical for atoms and diatomics
- diatomic orbitals resemble linear combinations of atomic orbitals
- e.g. sigma bond in  $H_2$   
 $\sigma \approx 1s_A + 1s_B$
- for polyatomics, approximate the molecular orbital by a linear combination of atomic orbitals (LCAO)

$$\phi = \sum_{\mu} c_{\mu} \chi_{\mu}$$

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## Basis Functions

$$\phi = \sum_{\mu} c_{\mu} \chi_{\mu}$$

- $\chi$ 's are called basis functions
- usually centered on atoms
- can be more general and more flexible than atomic orbitals
- larger number of well chosen basis functions yields more accurate approximations to the molecular orbitals

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## Slater-type Functions

$$\chi_{1s}(\vec{r}) = \left( \zeta_{1s}^3 / \pi \right)^{1/2} \exp(-\zeta_{1s} r)$$

$$\chi_{2s}(\vec{r}) = \left( \zeta_{2s}^5 / 96\pi \right)^{1/2} r \exp(-\zeta_{2s} r / 2)$$

$$\chi_{2px}(\vec{r}) = \left( \zeta_{2p}^5 / 32\pi \right)^{1/2} x \exp(-\zeta_{2p} r / 2)$$

- exact for hydrogen atom
- used for atomic calculations
- right asymptotic form
- correct nuclear cusp condition
- 3 and 4 center two electron integrals cannot be done analytically

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## Gaussian-type Functions

$$g_s(\vec{r}) = \left( 2\alpha^3 / \pi \right)^{1/4} \exp(-\alpha r^2)$$

$$g_x(\vec{r}) = \left( 128\alpha^5 / \pi^3 \right)^{1/4} x \exp(-\alpha r^2)$$

$$g_{xx}(\vec{r}) = \left( 2048\alpha^7 / 9\pi^3 \right)^{1/4} x^2 \exp(-\alpha r^2)$$

$$g_{xy}(\vec{r}) = \left( 2048\alpha^7 / \pi^3 \right)^{1/4} xy \exp(-\alpha r^2)$$

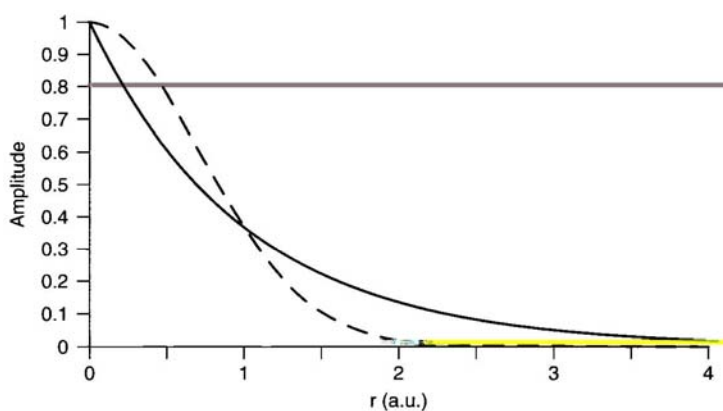
- die off too quickly for large r
- no cusp at nucleus
- all two electron integrals can be done analytically

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## Comparison of Slater and Gaussian Basis Functions



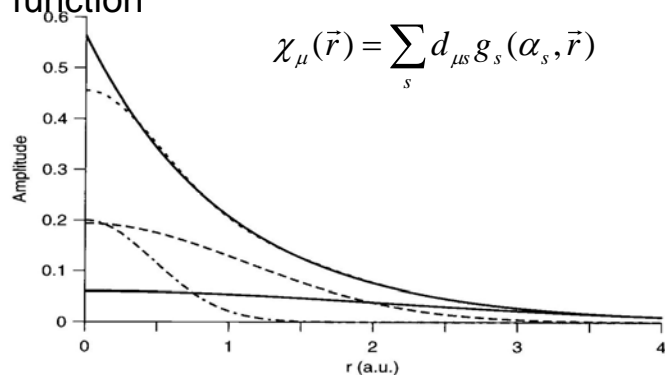
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## Contracted Gaussian Basis Functions

- Contraction: a fixed linear combination of gaussians to form a more suitable basis function



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## Basis Sets

- a basis set is set of exponents and contraction coefficients for a range of atoms
- types of basis sets
  - minimal
  - double zeta / triple zeta / etc.
  - split valence
  - polarization functions
  - diffuse functions

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## Minimal Basis Set

- only those shells of orbitals needed for a neutral atom
- e.g. 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub> for carbon
- STO-3G
  - 3 gaussians fitted to a Slater-type orbital (STO)
  - STO exponents obtained from atomic calculations, adjusted for a representative set of molecules
- also known as single zeta basis set (zeta,  $\zeta$ , is the exponent used in Slater-type orbitals)

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## Zeta concept

- Each contracted GTO has a characteristic value of 'zeta'
- One zeta value = SZ
- Two different values = DZ
- Three=TZ

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## Polarization concept

- To improve description along bond axis, add functions with higher  $l$  values than in minimal basis set
- But number grows very rapidly
- Usually need some polarization functions for decent accuracy.

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## Diffuse concept

- Sometimes need functions that stretch far from atoms
- E.g. when calculating dipole moments or polarizabilities
- Diffuse functions have zeta very small, so they stretch very wide.

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## Double Zeta Basis Set (DZ)

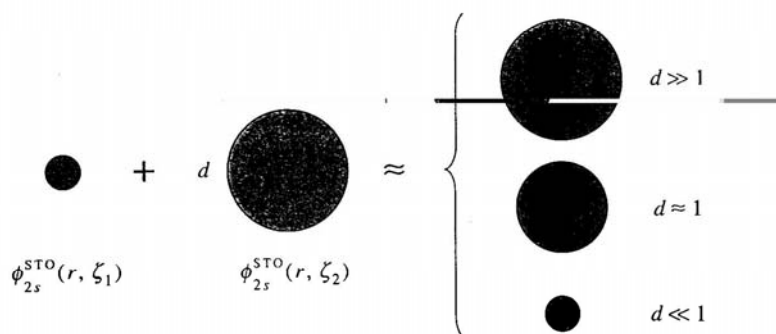
- each function in a minimal basis set is doubled
- one set is tighter (closer to the nucleus, larger exponents), the other set is looser (further from the nucleus, smaller exponents)
- allows for radial (in/out) flexibility in describing the electron cloud
- if the atom is slightly positive, the density will be somewhat contracted
- if the atom is slightly negative, the density will be somewhat expanded

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## A double zeta basis set allows for flexibility in the radial size



**FIGURE 11.3**

A linear combination of two Slater orbitals of the same type ( $\phi_{2s}^{\text{STO}}$  in the case shown) but with different orbital exponents  $\zeta_1$  and  $\zeta_2$  can generate an atomic orbital of adjustable size by varying the constant  $d$ .  
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## Split Valence Basis Set

- only the valence part of the basis set is doubled (fewer basis functions means less work and faster calculations)
- core orbitals are represented by a minimal basis, since they are nearly the same in atoms and molecules
- 3-21G (3 gaussians for 1s, 2 gaussians for the inner 2s,2p, 1 gaussian for the outer 2s,2p)
- 6-31G (6 gaussians for 1s, 3 gaussians for the inner 2s,2p, 1 gaussian for the outer 2s,2p)

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## Polarization Functions

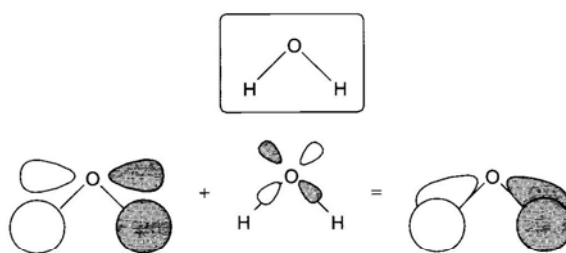
- higher angular momentum functions added to a basis set to allow for angular flexibility
- e.g. p functions on hydrogen, d functions on carbon
- large basis Hartree Fock calculations without polarization functions predict  $\text{NH}_3$  to be flat
- without polarization functions the strain energy of cyclopropane is too large
- 6-31G(d) (also known as 6-31G\*) – d functions on heavy atoms
- 6-31G(d,p) (also known as 6-31G\*\*) – p functions on hydrogen as well as d functions on heavy atoms
- DZP – DZ with polarization functions

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## Effect of Polarization Functions



**Figure 6.3** The MO formed by interaction between the antisymmetric combination of H 1s orbitals and the oxygen  $p_x$  orbital (see also Figure 6.7). Bonding interactions are enhanced by mixing a small amount of  $O d_{xz}$  character into the MO.

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## Diffuse Functions

- functions with very small exponents added to a basis set
- needed for anions, very electronegative atoms, calculating electron affinities and gas phase acidities
- 6-31+G – one set of diffuse s and p functions on heavy atoms
- 6-31++G – a diffuse s function on hydrogen as well as one set of diffuse s and p functions on heavy atoms

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## Families of basis functions

- Family has increasing number of basis functions on for each atom.
- Common families;
  - Pople Gaussian basis sets, eg 6-311++G(2df,2pd)
  - Ahlrichs sets in turbomole, eg def-DZ
  - Correlation-consistent (cc); aug=>diffuse

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## Correlation-Consistent Basis Functions

- a family of basis sets of increasing size
- can be used to extrapolate to the basis set limit
- cc-pVDZ – DZ with d's on heavy atoms, p's on H
- cc-pVTZ – triple split valence, with 2 sets of d's and one set of f's on heavy atoms, 2 sets of p's and 1 set of d's on hydrogen
- cc-pVQZ, cc-pV5Z, cc-pV6Z
- can also be augmented with diffuse functions (aug cc-pVXZ)

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## Pseudopotentials, Effective Core Potentials

- core orbitals do not change much during chemical interactions
- valence orbitals feel the electrostatic potential of the nuclei and of the core electrons
- can construct a pseudopotential to replace the electrostatic potential of the nuclei and of the core electrons
- reduces the size of the basis set needed to represent the atom (but introduces additional approximations)
- for heavy elements, pseudopotentials can also include of relativistic effects that otherwise would be costly to treat

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```

• $basis
• #
• # BASIS SET LIBRARY FOR HYDROGEN
• # ECPs, HONDO-BASIS SETS FROM basen AND
• # FULLY OPTIMIZED BASIS SETS FROM newbas (MAY 1992)
• #
• # abbreviation hondo refers to the version 7.0 of HONDO
• #
• #####
• # HF limit : E(2S) = -0.5 a.u.
• #####
• # Roothaan parameters for H(2S):
• # a = 0 b = 0
• #####
• #
• #
• # available basis sets and corresponding atomic energies H(2S):
• #
• # Basis HF(equiv) / a.u.
• # -----
• # DZ -0.49927840571
• # SV -0.49927840571
• # SV(P) -0.49927840571
• # def-SV(P) -0.49927840571
• # def2-SV(P) -0.49927840571
• # DZP -0.49927840571
• # SVP -0.49927840571
• # def-SVP -0.49927840571
• # def2-SVP -0.49927840571
• # TZ -0.49980983223

```

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```

• # Basis HF(equiv) / a.u.
• # -----
• # DZ -0.49927840571
• # SV -0.49927840571
• # SV(P) -0.49927840571
• # def-SV(P) -0.49927840571
• # def2-SV(P) -0.49927840571
• # DZP -0.49927840571
• # SVP -0.49927840571
• # def-SVP -0.49927840571
• # def2-SVP -0.49927840571
• # TZ -0.49980983223
• # TZV -0.49980983223
• # TZP -0.49980983223
• # TZVP -0.49980983223
• # def-TZVP -0.49980983223
• # def2-TZVP -0.49980983223
• # TZVPP -0.49980983223
• # def-TZVPP -0.49980983223
• # def2-TZVPP -0.49980983223
• # TZVPPP -0.49980983223
• # def-QZV -0.49998329779
• # def2-QZV -0.49998329779
• # QZV -0.49998329779
• # QZ -0.49998329779
• # def-QZVP -0.49998329779
• # def2-QZVP -0.49998329779
• # QZVP -0.49998329779
• # QZP -0.49998329779
• # def-QZVPP -0.49998329779
• # def2-QZVPP -0.49998329779
• # QZVPP -0.49998329779

```

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## Summary

- There are standard sets of basis functions
- Include more functions implies more accurate solution but also costs more.
- Types of improvements:
  - Increase number of zetas (radial)
  - Polarization functions (bond region)
  - Diffuse functions (response properties)
- Families of basis functions:
  - Pople (e.g., 6-311G\*\*)
  - Ahlrichs (e.g., SVP)
- Always converge calculation so basis-set error is smaller than other errors (method, model, etc.)

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