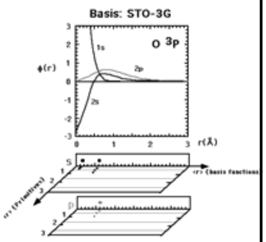
Session 2: Basis Sets

- Two of the major methods (*ab initio* and DFT) require some understanding of basis sets and basis functions
- This session describes the essentials of basis sets:
  - What they are
  - How they are constructed
  - How they are used
  - Significance in choice



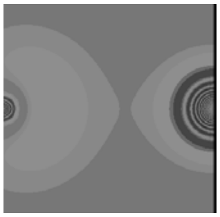
The <r> for each basis function is indicated by the position of a colored dot along a horizontal axis. Basis functions may consist of individual Gaussian primitives or a linear combination of Gaussians. In the latter case, the <r> for the underlying Gaussians will be indicated by a row of dots which appear to come out of the page.

Running a Calculation

- In performing a computational chemistry calculation, the chemist has to make several decisions of input to the code:
  - The molecular geometry (and spin state)
  - The basis set used to determine the wavefunction
  - The properties to be calculated
  - The type(s) of calculations and any accompanying assumptions

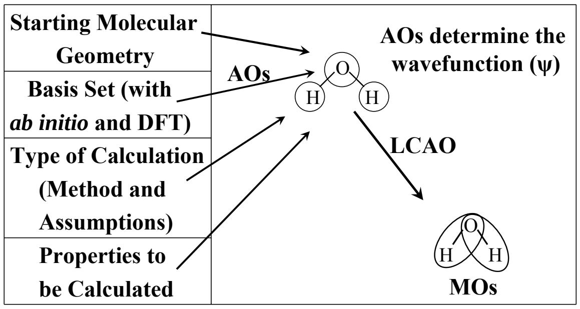
Running a calculation

- For *ab initio* or DFT calculations, many programs require a basis set choice to be made
  - The basis set is an approximate representation of the atomic orbitals (AOs)
  - The program then calculates molecular orbitals (MOs) using the Linear Combination of Atomic Orbitals (LCAO) approximation



Computational Chemistry Map

Chemist Decides: Computer calculates:



Starting Molecular Geometry

Basis Set (with *ab initio* and DFT)

Type of Calculation (Method and Assumptions)

Properties to be Calculated

AOs

AOs determine the wavefunction (ψ)

LCAO

MOs

Critical Choices

- Choice of the method (and basis set) used is critical
  - Which method?
    - Molecular Mechanics, *Ab initio*, Semiempirical, or DFT
  - Which approximation?
    - MM2, MM3, HF, AM1, PM3, or B3LYP, etc.
  - Which basis set (if applicable)?
    - Minimal basis set
    - Split-valence
    - Polarized, Diffuse, High Angular Momentum, ...

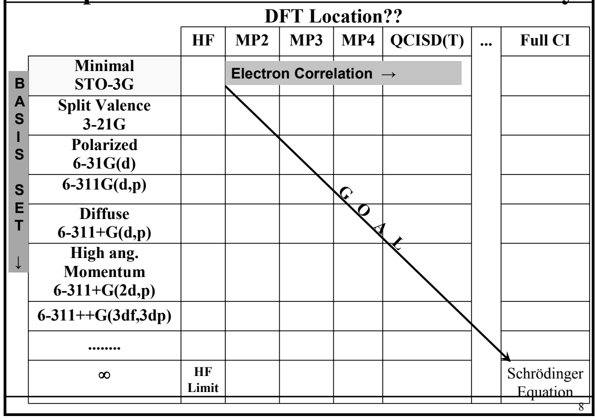
Why is Basis Set Choice Critical?

- The basis set needs to be able to approximate the actual wave function sufficiently well to give chemically meaningful results
  - Also needs a reasonable computational “cost”
    - Integrals should be evaluated quickly and accurately
- Trade-offs
  - Choice always involves a balance between accuracy and computational cost
  - More accurate methods using larger basis sets will take more computer time

Theoretical Models

- Goal of computational chemistry is to mathematically represent chemical reality
  - Improving the basis set and the degree of electron correlation improves the ability of the computational model to approach reality
- Ultimate goal is an exact solution of the Schrödinger equation

Comparison of Some Methods for Accuracy



DFT Location??

BASIS SET ↓

	HF	MP2	MP3	MP4	QCISD(T)	...	Full CI
Minimal STO-3G		**Electron Correlation →**					
Split Valence 3-21G							
Polarized 6-31G(d)							
6-311G(d,p)							
Diffuse 6-311+G(d,p)							
High ang. Momentum 6-311+G(2d,p)							
6-311++G(3df,3dp)							
....							
∞	**HF Limit**						Schrödinger Equation

Possible Basis Functions

1. Hydrogen-like Orbitals
   - Derived for a *one-electron* atom
     - Not truly accurate for a *many-electron* atom
   - Form: $\Psi(r,\theta,\phi) = R(r)Y_l^m(\theta,\phi)$

     $R(r) =$ radial function

     $Y_l^m =$ spherical harmonic
   - \+ Advantages: Mutually orthogonal
   - – Disadvantages: Complex form is awkward for calculations; Most atoms of interest > one electron

Possible Basis Functions

- True wavefunction should be antisymmetric to electron interchange – use spin orbitals
  - Antisymmetric linear combination of products of spin orbitals used in an SCF calculation
  - → **HF-SCF calculation**
  - Numerical methods were originally used to solve and find the Hartree-Fock orbitals
- Roothaan: Represent the HF orbitals as linear combinations of a set of known (basis) functions
  - Commonly used set of basis functions for atomic HF calculations is the set of Slater-type orbitals (STOs)

Possible Basis Functions

2. Slater Type Orbitals (STOs)
   - Normalized form:

$$\mu(r,\theta,\phi) = \frac{(2\zeta/a_0)^{n+0.5}}{[(2n)!]^{0.5}} r^{(n-1)} e^{(-\zeta r/a_0)} Y_l^m(\theta,\phi)$$

where n, m, and l are integers and ζ (orbital exponent) is a variational parameter

   - Improve results by using a linear combination of several STOs to represent each HF orbital
   - HF-SCF atomic calculations require lots of computation
     - Hartree did this numerically in the 1930's

Slater Type Orbitals

+ Advantages: Have a complete set
  - Radial behavior closely matches hydrogenic orbitals

– Disadvantages:
  - No nodes, as with H-like orbitals
  - Not mutually orthogonal
  - For larger molecules, computer evaluation of the many integrals involved is <u>quite</u> time consuming

→ Need to reduce the computational cost

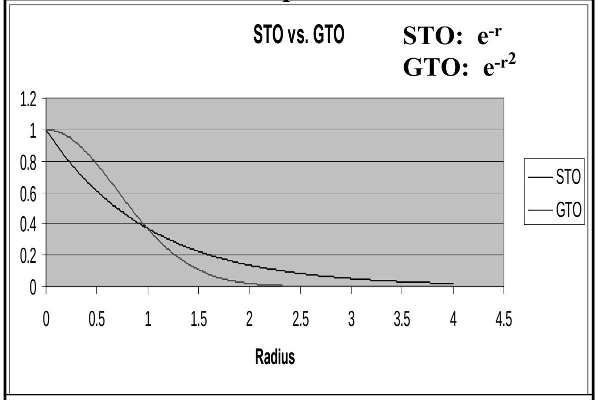
Possible Basis Functions

3. Gaussian Type Orbitals (GTOs)
   - Proposed by S.F. Boys in 1950
   - GTO form:

$$g(r,\theta,\phi)=\left[\frac{2^{(2n+1.5)}}{(2n-1)!\sqrt{\pi}}\right]^{0.5}\varsigma^{(2n+1)/4}r^{(n-1)}e^{(-\alpha r^2)}Y_l^m(\theta,\phi)$$

   + Advantages: Have a complete set
     - Computer evaluation of integrals <u>much faster</u>
       - → Closed integrals; Integrated GTO gives a GTO
   - Disadvantages: Not mutually orthogonal
     - Representation of e- probability is poor near and far away from the nucleus

Comparison

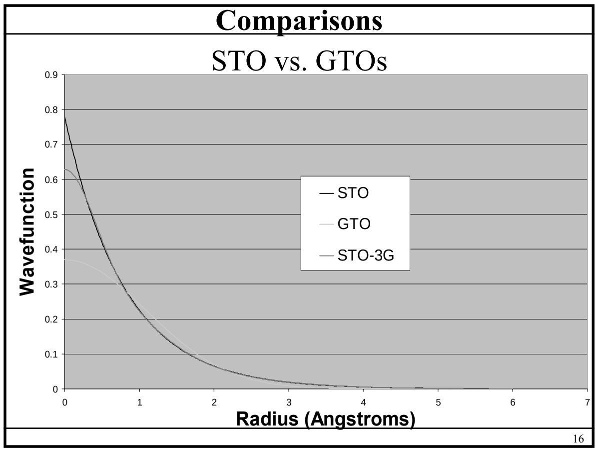


STO: e^{-r}
GTO: e^{-r^2}

GTOs

- Linear combinations of GTO's are used to approximate STOs (which are themselves approximations)
  - A single GTO basis function has significant errors when compared to a STO, especially near the nucleus
  - If several GTOs are combined in a linear combination, the basis function is greatly improved
    - → See next slide

Comparisons



Use of GTOs

- Individual GTOs not used as basis functions:
  - Use a normalized linear combination of a few GTOs (called *primitives*), each with different α values to give a "contracted" Gaussian function

$$g_c = \sum c_i g_p$$

where g_c is a contracted gaussian,

g_p is a primitive gaussian, and c_i is

a *contraction coefficient*

    - A linear combination of these primitives (typically 1-7) is used to approximate the STO

Use of GTOs

- Using contracted GTOs instead of primitive GTOs as the basis set has advantages:
  - Number of variational coefficients to be determined is reduced, which saves a lot of computational time
  - Accuracy is NOT reduced significantly, as long as the contraction coefficients (c_i's) are well chosen
- Increasing the number of primitive GTOs used in each contracted Gaussian improves the accuracy
- Different types of basis sets use different numbers and types of GTOs

Minimal Basis Sets

- Jargon Used → STO-NG (Single ζ)
  - N is the number of primitive GTOs used
  - Example: STO-3G
  - Used as default basis set in semiempirical MO calculations (AM1, PM3, etc.)
    - Three primitive GTOs used per AO
    - Popular starting point for calculations
    - STO-3G basis functions have been developed for most of the elements in the Periodic table
  - →Minimal basis sets do not adequately describe non-spherical (anisotropic) electron distribution in molecules

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Minimal Basis Sets

- GTO representation of a STO for *1s* AO:

$$\Phi_{STO}^{1s}(r) = \pi^{-0.5}\zeta^{1.5}e^{(-\zeta r)} \quad \text{where } \zeta = 1$$

$$\Phi_{\text{STO-3G}}^{1s}(r) = c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{(-\alpha_1 r^2)} + c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{(-\alpha_2 r^2)} + c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4} e^{(-\alpha_3 r^2)}$$

$$\text{where } c_1 = 0.444615, c_2 = 0.535336, c_3 = 0.154340$$

$$\text{and } \alpha_1 = 0.109818, \alpha_2 = 0.405771, \alpha_3 = 0.2.22766$$

  - "*c*" values are called the ***contraction coefficients***
  - The exponents are the alpha (*α*) values

Split Valence Basis Sets

- Jargon Used → K-LMG (Double ζ)
  - Differentiate between core and valence electrons
    - Developed to overcome problems of inadequate description of anisotropic electron distributions using minimal basis sets

K = number of sp-type inner shell primitive GTOs

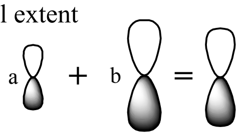
L = number of inner valence s- and p-type primitive GTOs

M = number of outer valence s- and p-type primitive GTOs

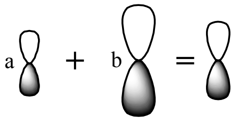
Split Valence Basis Sets

– Each split valence atomic orbital is composed of a variable proportion of two (or more) functions of different size or radial extent

For a larger e^- cloud
(longer bond)
a < b



For a smaller e^- cloud
(shorter bond)
a > b



→ **a** and **b** are normalized and sum to 1

Split Valence Basis Sets

- Examples:

3-21G

Three primitives for the inner shell (STO-**3**G); each valence orbital is constructed with **two** sizes of basis function (*Two* GTOs for contracted valence orbitals; *One* GTO for extended valence orbitals)

6-311G

STO-**6**G for inner shell; **Three** sizes of basis function for each valence orbital (*Three* GTOs for contracted valence orbitals, and *two different sizes* of GTO for extended valence orbitals)

Polarized Basis Sets

- Jargon Used → 6-31G(d) or 6-31G*
- Also have 6-31G(d,p) or 6-31G**

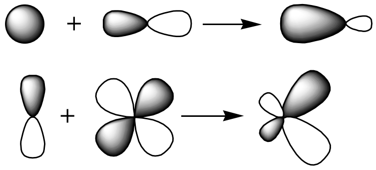
→ (d) or * type
- d-type functions added to atoms with Z > 2
- f-type functions added to transition metals

→ (d,p) or ** type
- p-type functions added to H atoms
- d-type functions added to atoms with Z > 2
- f-type functions added to transition metals

6-31G(d) is another popular basis set choice

Polarized Basis Sets

- In molecule formation, AOs become distorted in shape (polarization)
  - Orbitals are influenced by other nuclei
  - Polarization accounts for these influences which distort the orbital shape



Diffuse Basis Sets

- Jargon Used → 6-31+G(d) or 6-31++G(d)

  6-31+G(d)
  - 6-31G(d) basis set with an additional larger p-function for atoms with $Z > 2$

  6-31++G(d)
  - 6-31+G(d) basis set with an additional larger s-function for H atoms
- Diffuse basis sets are useful for describing anions, molecules with lone pairs, excited states, and transition states (loosely held e^-)

Basis Set Progression

- Increasing number of GTOs Used:

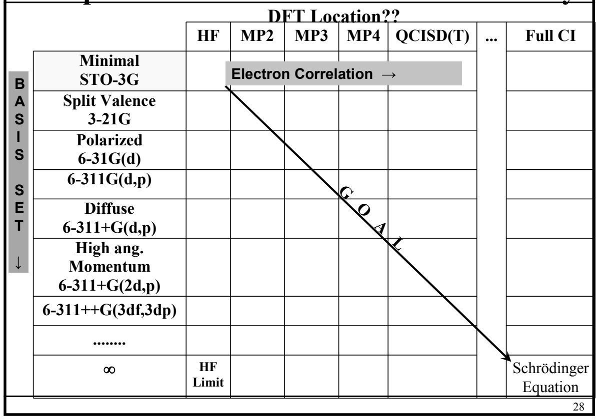
Minimal< Split Valence < Double Zeta < Polarized < Diffuse

Get an increasingly good approximation to the actual wave function

- The number of integrals increases as N^4 where N is the number of basis functions
- During the minimization process, the orbital exponents are adjusted to define a new basis set to start another iteration

→Computational cost has to be considered

Comparison of Some Methods for Accuracy



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Diffuse 6-311+G(d,p)							
High ang. Momentum 6-311+G(2d,p)							
6-311++G(3df,3dp)							
....							
∞	HF Limit						Schrödinger Equation

Basis Set Choice and Expense

axial-methylcyclohexane on SGI Indigo2
(*Spartan* cpu time in sec.)

Method/Basis Set	s.p.	opt.
AM1/STO-3G	~1	10
HF/STO-3G	72	983
HF/ 3-21G(d)	193	2214
HF/ 6-31G(d,p)	2632	34655 (9.6 h)

- As larger basis sets are used, the energy decreases (Variational Principle)

Common Basis Sets

Brief Description of Standard Basis Sets

Basis Set	Description
STO-3G	Minimal basis; qualitative results - large systems
3-21G	Double ζ; more accurate results on large systems
6-31G(d)	Moderate set; Common use for medium systems
6-31G(d,p)	Used where H is site of interest; More accurate
6-31+G(d)	Used with anions, excited states, lone pairs, etc.
6-31+G(d,p)	Used with anions, etc., where H is site of interest
6-311++G(d,p)	Good for final, accurate energies, but expensive

- Many other sets are in use. Existing sets can be modified

Optimization of a Basis Set

- Variational Principle: Energy values are bounded from below
  - The lower the calculated energy, the better
  - Procedure:
    - Vary the constants and exponents that describe the Gaussian functions *sequentially* until the lowest energy is obtained
    - → Such a basis set may only apply to that individual molecule, however

Lab: Gaussian Orbitals

- **Question:** How are Gaussian orbitals used to approximate a Slater Type Orbital?
- **Importance:** Basis sets are approximations based on mathematical use of two or more gaussian functions
- **Goal:** Visualize an “STO-3G” basis set - what does the resultant function look like?
- **Computational Tool:** Spreadsheet
- Refer to Basis Set Case Study handout for detailed instructions