Basis Sets: advantages

Why a basis set?

Possibilities for a numerical solution of the Schrödinger-Eqs:

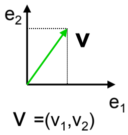
- Fully numerical on a 3D grid (basis set free)
  - advantages:
    - no basis set truncation error
    - no basis set superposition error
  - disadvantages:
    - large memory requirements, expensive
    - numerical difficulties
- expansion in a chosen basis
  - advantages:
    - all or most terms (integrals, derivatives..) in analytic form
  - disadvantages:
    - effects of finite basis
    - BSSE

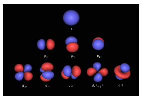
→most modern quantum chemistry methods use a basis set expansion:

$$|\Omega> = \sum_i c_i|\Phi_i> \qquad \vec{v} = \sum_{i=1}^{3} c_i \vec{e}_i$$

Analogy with ordinary vector analysis

One refers to a vector in R^3 using its projections on a given basis set





One speaks about:

Vector analysis:		QM:
COORDINATES	⇔	COEFFICIENTS
COORD. SYSTEM	⇔	BASIS FUNCTIONS

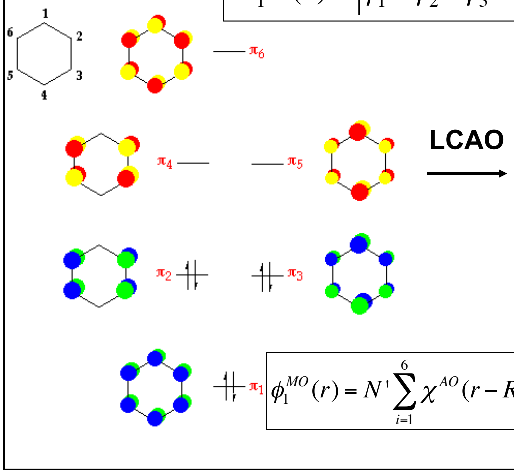
Basis Sets: example

Atomic basis function χ^{AO} : p_z orbital on every carbon atom

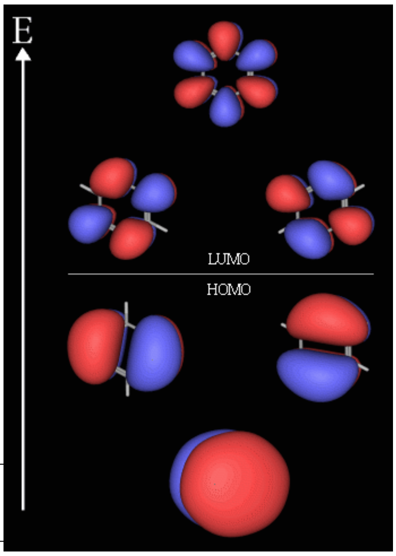
MO’s

$$\boxed{\chi^{AO}(r) = Nze^{-\xi r}}$$

$$\boxed{\Psi_1^{MO}(r) = \left|\phi_1^{MO}\phi_2^{MO}\phi_3^{MO}\right|}$$



$$\boxed{\phi_1^{MO}(r) = N'\sum_{i=1}^{6}\chi^{AO}(r-R_I)}$$



Basis Sets: AO vs MO

- LCAO (linear combination of atomic orbitals) approximation: MO's can be constructed from AO's

$$\chi_n^{AO}(r,R_n) = \sum_{i=1} c_i\, \phi_i^{basis}(r,R_n), \quad c_i : fix\ coefficients$$

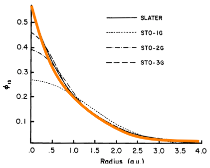
$$\Phi_m^{MO}(r) = \sum_n D_{mn}\, \chi_n^{AO}(r,R_n) \quad , \quad D_{nm} : computed$$

- An "orbital" is a one-electron quantity
- Basis functions, $\phi^{basis}(r,R_n)$, are represented by atom-centered ***Gaussians*** in most quantum chemistry programs (why?)
- Some older programs used ***Slater*** functions
- Physicists like ***plane wave*** basis sets

Basis Sets: functional forms

Slater-Type Orbitals (STO's)

$$\phi_{abc}^{STO}(x,y,z) = N x^a y^b z^c e^{-\zeta r}$$



- N is a normalization constant
- a, b, c control angular momentum, $L = a + b + c$
- ζ (zeta) controls the width of the orbital (large ζ gives tight function, small ζ gives diffuse function)
- These are H-atom-like, at least for 1s; however, they lack radial nodes and are not pure spherical harmonics (how to get 2s or 2p, then?)
- Correct short-range and long-range behavior

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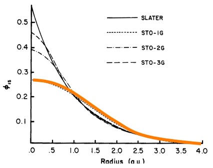
Basis Sets: functional forms



Gaussian-Type Orbitals (GTO's)

$$\phi_{abc}^{GTO}(x,y,z) = N x^a y^b z^c e^{-\zeta r^2}$$

- Again, a, b, c control angular momentum, $L = a + b + c$
- Again, ζ controls width of orbital
- No longer H-atom-like, even for 1s
- Much easier to compute (Gaussian product theorem)
- Almost universally used by quantum chemists

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Basis Sets: functional forms

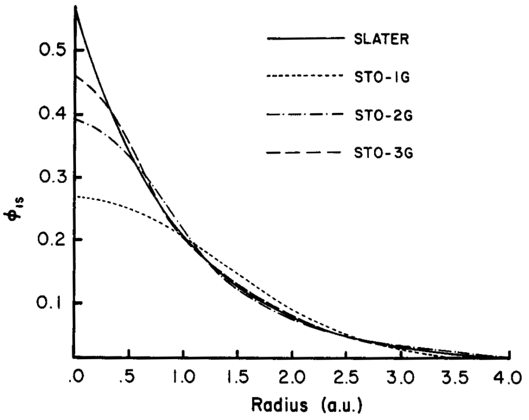

Figure 3.3 Comparison of the quality of the least-squares fit of a 1*s* Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.

Figure from Szabo and Ostlund, Modern Quantum Chemistry.

Basis Sets: functional forms

Contracted Gaussian-Type Orbitals (CGTO's)

- *Problem:* STO's are more accurate, but it takes longer to compute integrals using them
- *Solution:* Use a linear combination of enough GTO's to mimic an STO
- *Unfortunate:* A combination of n Gaussians to mimic an STO is often called an "STO-nG" basis, even though it is made of CGTO's...

n: length of contraction
c_i,ζ_i fixed (determined once)

$$\phi_{abc}^{CGTO}(x,y,z) = N \sum_{i=1}^{n} c_i x^a y^b z^c e^{-\zeta_i r^2} \qquad (1)$$

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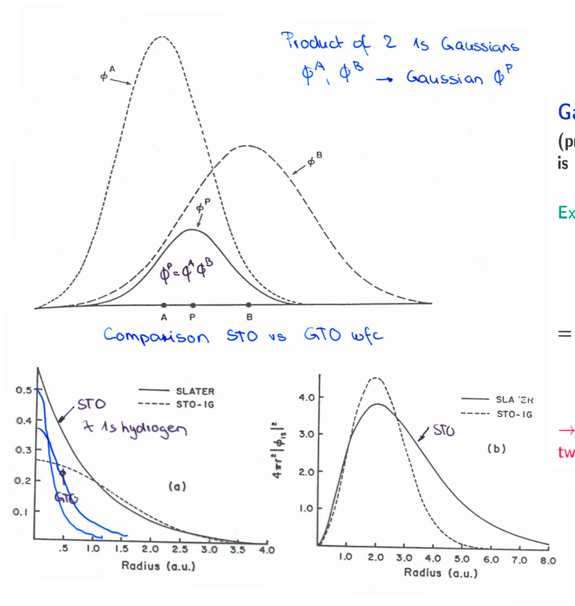
Basis Sets: Gaussian product theorem



Gaussian Product Theorem:

(product of 2 Gaussian on two different centers is 1 Gaussian at a third center)

Ex. unormalized 1s GTO's:

$$g_{1s}(\vec{r}-\vec{R}_A)g_{1s}(\vec{r}-\vec{R}_B)$$

$$= exp[-\alpha(\vec{r}-\vec{R}_A)^2]exp[-\beta(\vec{r}-\vec{R}_B)^2]$$

$$= exp[-\frac{\alpha\beta}{\alpha+\beta}(\vec{R}_A-\vec{R}_B)^2]exp[-(\alpha+\beta)(\vec{r}-\vec{R}_p)^2]$$

$$R_p = \frac{\alpha R_A + \beta R_B}{\alpha+\beta}$$

→4-center integrals (for 1s Gaussians) reduce to two-center integrals

Basis Sets: types

Types of Basis Sets

Minimal: One basis function (STO, GTO, or CGTO) for each atomic orbital in the atom

Double-zeta: Two basis functions for each AO

Triple-zeta: Three basis functions for each AO

... and etc. for quadruple-zeta (QZ), 5Z, 6Z, ... Having different-sized functions allows the orbital to get bigger or smaller when other atoms approach it

A split-valence basis uses only one basis function for each core AO, and a larger basis for the valence AO's

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Basis Sets: types

Examples

H atom, minimal basis: One 1s AO, one (STO, GTO, or CGTO) basis function

C atom, minimal basis: 1s, 2s, $2p_x$, $2p_y$, $2p_z$ AO's (5), so 5 basis functions

C atom, double-zeta basis: Two basis functions per AO, so 10 basis functions

C atom, split-valence double-zeta basis: 9 basis functions (why?)

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Basis Sets: types - polarization

Polarization Functions

- As other atoms approach, an atom's orbitals might want to shift to one side or the other (polarization). An s orbital can polarize in one direction if it's mixed with a p orbital.
- p orbitals can polarize if mixed with d orbitals
- In general, to polarize a basis function with angular momentum l, mix it with basis functions of angular momentum $l + 1$
- This gives "polarized double-zeta", or "double-zeta plus polarization" basis sets, etc

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Basis Sets: types – diffuse functions

Diffuse Functions

- Diffuse functions have small ζ exponents; this means the electron is held far away from the nucleus
- Necessary for anions, Rydberg states, very electronegative atoms (fluorine) with a lot of electron density
- Necessary for accurate polarizabilities or binding energies of van der Waals complexes (bound by dispersion)
- It is very bad to do computations on anions without using diffuse functions; your results could change completely!

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Basis Sets: types

Anatomy of a Basis Set: H atom, STO-3G

A basis set of Contracted Gaussian-Type Orbitals (CGTO's) needs to specify the exponents (ζ_i's) and the contraction coefficients (c_i's). These are given below in the format used by the Gaussian program (exponents first)

```
H    0
S    3   1.00
       3.42525091          0.154328970
       0.623913730         0.535328140
       0.168855400         0.444634540
****
```

(3s)->[1s]

3 primitive GTOs
1 contracted basis function

$$\phi^{1S}_{a,b,c}(x,y,z) = N\sum_{i=1}^{3} c_i\left(x^a y^b z^c e^{-\zeta_i r^2}\right)$$

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Basis Sets: types

Anatomy of a Basis Set: C atom, STO-3G

(3s/3s3p)->[1s/1s1p]

```
C    0
S    3   1.00
       71.6168370          0.154328970
       13.0450960          0.535328140
       3.53051220          0.444634540
SP   3   1.00
       2.94124940         -0.999672300E-01      0.155916270
      0.683483100          0.399512830          0.607683720
      0.222289900          0.700115470          0.391957390
****
```

STO-3G and other basis sets by John Pople use "SP" shells, which share exponents for s and p functions

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Basis Sets: types

Pople Basis Sets

- Developed by the late Nobel Laureate, John Pople, and popularized by the Gaussian set of programs
- STO-3G is a minimal basis set in which each AO is represented by 3 Gaussians (3G), chosen to mimic the behavior of a STO
- Pople's split-valence double-zeta basis set is called 6-31G; the core orbital is a CGTO made of 6 Gaussians, and the valence is described by two orbitals — one CGTO made of 3 Gaussians, and one single Gaussian

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Basis Sets: types

Anatomy of a Basis Set: C atom, 6-31G

(6s/4s4p)->[1s/2s2p]

22 primitive GTOs
9 contracted basis functions

```
C    0
S    6   1.00
        3047.52490         0.183470000E-02
        457.369510         0.140373000E-01
        103.948690         0.688426000E-01
        29.2101550         0.232184400
        9.28666300         0.467941300
        3.16392700         0.362312000
SP   3   1.00
        7.86827240        -0.119332400         0.689991000E-01
        1.88128850        -0.160854200         0.316424000
       0.544249300          1.14345640         0.744308300
SP   1   1.00
       0.168714400          1.00000000          1.00000000
```

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Basis Sets: types

More on Pople Basis Sets

- 6-31G* [or 6-31G(d)] is 6-31G with added d polarization functions on non-hydrogen atoms; 6-31G** [or 6-31G(d,p)] is 6-31G* plus p polarization functions for hydrogen
- 6-311G is a split-valence triple-zeta basis; it adds one GTO to 6-31G
- 6-31+G is 6-31G plus diffuse s and p functions for non-hydrogen atoms; 6-31++G has diffuse functions for hydrogen also

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Basis Sets: accuracy

Convergence of Bond Lengths for BH, CH$^+$, and NH

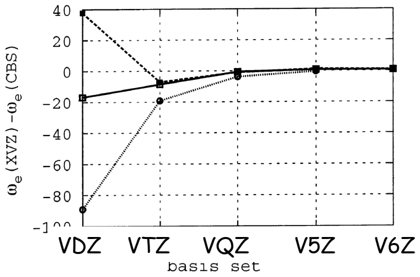
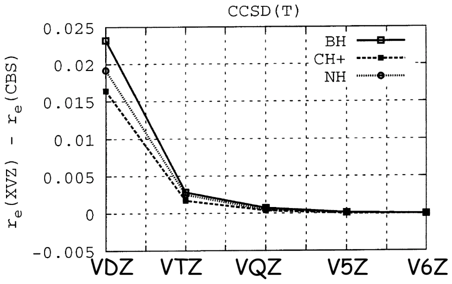


Figure 1. Convergence of CCSD(T) r_e and ω_e toward the CBS limit derived for valence-only (cc-pVNZ) basis sets.



Temelso, Valeev, and Sherrill, *J. Phys. Chem. A* **108**, 3068 (2004).

Temelso, Valeev, and Sherrill, *J. Phys. Chem. A* **108**, 3068 (2004).

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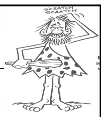
Basis Sets: drawbacks



Basis-Set Superposition Error (BSSE)

Calculation of binding energies:
$E_{bind} = E_{AB} - E_A - E_B$
To be consistent E_{AB}, E_A and E_B have to be calculated with the same basis set

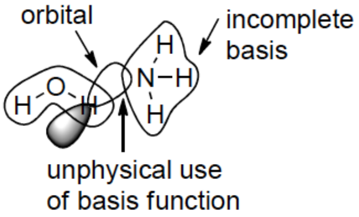
Problem:

If basis at A is incomplete, Basis at B will improve wf at A →artificially better basis set for molecule AB than for isolated A,B →lower E_{AB} →too high binding energy

Especially severe for the case weak interactions:

$$\boldsymbol{E_{bind} >> E_{AB}, E_A, E_B}$$

Basis set superposition error (BSSE) II



Note that diffuse (containing low exponent functions) basis sets can be more susceptible to BSSE because the functions extend further into space.

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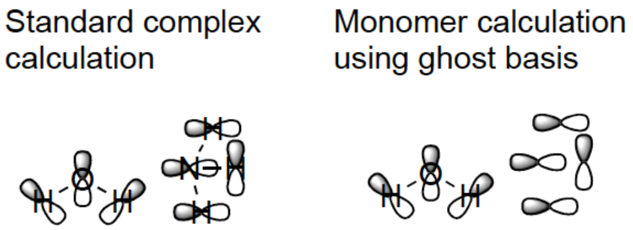
Counter-Poise correction I

The CP correction is an attempt to estimate the BSSE.
Notation: A,B indicate relaxed monomer geometries, * indicates monomer geometries as in the complex, a,b indicate the monomer basis sets.

Standard complexation: $\Delta E_{\text{complex}} = E(A^*B^*)_{ab} - E(A)_a - E(B)_b$

Additive CP correction: $E^{\text{CP}} = E(A^*)_a - E(A^*)_{ab} + E(B^*)_b - E(B^*)_{ab}$



Basis sets without nuclei are called "ghost basis".

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Counter-Poise correction II

- Because it adds too much variational freedom (basis functions "correctly occupied" in $E(A^*B^*)_{ab}$ become available in $E(A^*)_{ab}$), it should overestimate the BSSE
- It must be used for double-zeta basis sets and should be investigated for triple-zeta
- There are no well-tested concepts for the intramolecular case. For these problems, only a larger basis can lower the BSSE
- BSSE affects primarily post-HF; HF and DFT calculations suffer less from basis set incompleteness
- Plane wave calculations are BSSE-free given equal cell size

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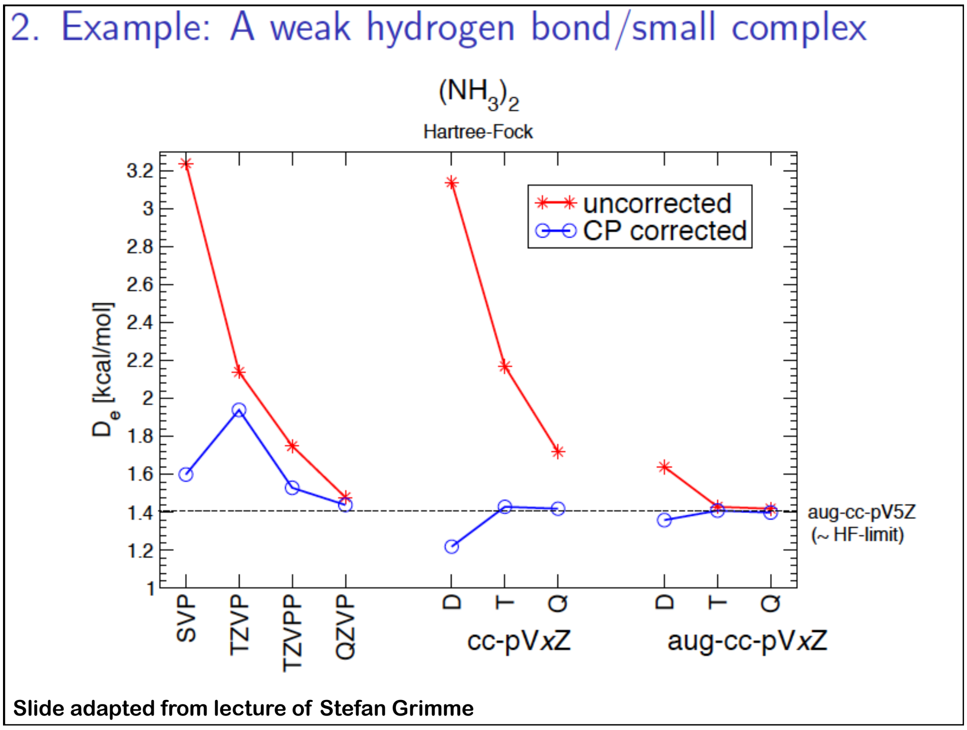

2. Example: A weak hydrogen bond/small complex

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The Ten Basis Set Commandments

- The possible accuracy is largely determined by the choice of basis set
- Any good QC paper/thesis must investigate basis set effects (or give appropriate references)
- Use a balanced basis
- SCF and correlated calculations have different basis set convergence
- Some molecular properties pose different demands to the basis set than others
- Basis set effects concerning energies are strongest for fragmentations
- Use double-zeta basis sets for exploratory calculations only
- Use at least triple-zeta basis sets for calculations in publications
- Quantitative SCF/DFT calculations need at least two sets of valence polarization functions for heavy atoms
- Adding diffuse functions is expensive and can lead to near linear dependence of the basis (needs special consideration for large molecules)

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