**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:

$$|\Omega> = \sum c_i |\Psi_i>$$

$$\vec{v} = \sum c_i \vec{e}_i$$

**Analogy with ordinary vector analysis**

One refers to a vector in \( \mathbb{R}^3 \) using its projections on a given basis set

One speaks about:

Vector analysis: QM:

| COORDINATES | \( \leftrightarrow \) | COEFFICIENTS | \( \leftrightarrow \) | BASIS FUNCTIONS |

**Basis Sets: example**

Atomic basis function \( \chi^{AO} : p_z \) orbital on every carbon atom

$$\chi^{AO}(r) = N z e^{-\xi r}$$

| MO's | $\Psi_1^{MO}(r) = [\phi_1^{MO} \phi_2^{MO} \phi_3^{MO}]$ |

LCAO

$$\phi^{MO}(r) = N^+ \sum_n^\infty \chi^{MO}(r-R_n)$$

$\rightarrow$
Basis Sets: AO vs MO

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

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

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

- 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)

\[
\phi^{STO}_{abc}(x, y, z) = N x^a y^b z^c e^{-cr}
\]

- \( N \) is a normalization constant
- \( a, b, c \) control angular momentum, \( L = a + b + c \)
- \( \zeta \) (zeta) controls the width of the orbital (large \( \zeta \) gives tight function, small \( \zeta \) 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, \( \zeta \) 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

---

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...

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

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Basis Sets: functional forms

![Graph showing basis sets comparison](image)

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.

Basis Sets: Gaussian product theorem

![Graph showing Gaussian product theorem](image)

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

Ex. unnormalized 1s GTO's:

$$g_x(\vec{r} - \vec{R}_x)g_y(\vec{r} - \vec{R}_y)$$

$$= \exp\left[-\alpha(\vec{r} - \vec{R}_x)\right]\exp\left[-\beta(\vec{r} - \vec{R}_y)\right]$$

$$= \exp\left[-\frac{\alpha + \beta}{\alpha \beta} (\vec{R}_x - \vec{R}_y)^2\right]$$

$$R_S = \frac{\alpha R_x + \beta R_y}{\alpha + \beta}$$

→ 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

---

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?)
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 \( \zeta \) 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 ($\zeta_i$‘s) and the contraction coefficients ($c_i$‘s). These are given below in the format used by the Gaussian program (exponents first)

\[
\phi_{\alpha \beta}^{i \nu} (x, y, z) = N \sum_{\nu} \sum_{\alpha} \sum_{\beta} c_{\alpha \beta} \left( x^\alpha y^\beta e^{-\zeta_i r} \right)
\]

Slide adapted from lecture of David Sherill

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Basis Sets: types

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

\[
\phi_{\alpha \beta}^ {i \nu} (x, y, z) = N \sum_{\nu} \sum_{\alpha} \sum_{\beta} c_{\alpha \beta} \left( x^\alpha y^\beta e^{-\zeta_i r} \right)
\]

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

Slide adapted from lecture of David Sherill

Basis Sets: types

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

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Slide adapted from lecture of David Sherill
**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

*Slide adapted from lecture of David Sherill*

---

**Basis Sets: accuracy**

Convergence of Bond Lengths for BH, CH\(^+\), and NH

*Figure 1. Convergence of CCSD(T) \( r_r \) and \( \alpha_r \) toward the CBS limit derived for valence-only (cc-pVXZ) basis sets.*

Basis Set Superposition Error (BSSE)

Calculation of binding energies:

\[ E_{\text{bind}} = E_{AB} - E_A - E_B \]

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 \( \rightarrow \) artificially better basis set for molecule AB than for isolated A, B \( \rightarrow \) lower \( E_{AB} \)
\( \rightarrow \) too high binding energy

Especially severe for the case weak interactions:

\[ E_{\text{bind}} \gg E_{AB}, E_A, E_B \]

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.

Slide adapted from lecture of Stefan Grimme
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: \[ E^{\text{CP}} = E(A^*)_a - E(A^*)_{ab} + E(B^*)_b - E(B^*)_{ab} \]

<table>
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<th>Standard complex calculation</th>
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Basis sets without nuclei are called “ghost basis”.

---

Counter-Poise correction II

- Because it adds too much variational freedom (basis functions “correctly occupied” in \( E(A^*B^*)_{ab} \) become available in \( E(A^*)_a \)), 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.

---

Slide adapted from lecture of Stefan Grimme
2. Example: A weak hydrogen bond/small complex

\[
\text{(NH}_2)_2
\]

Hartree-Fock

\[
\begin{array}{c|c|c|c|c|c|c}
\text{SVP} & \text{TZVP} & \text{TZVP} & \text{QZVP} & \text{cc-pV} & \text{aug-cc-pV} \\
\hline
\text{D}_1 [\text{kcal/mol}] & \text{uncorrected} & \text{CP corrected} & \text{CP corrected} & \text{CP corrected} & \text{CP corrected} \\
\end{array}
\]

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)