


COMPUTATIONAL CHEMISTRY
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BASIS SETS

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BASIS SET

- ▶ The atom-centred functions used to describe the atomic orbitals are known as basis functions and collectively form a basis set
- ▶ The basis set is an approximate representation of the atomic orbitals (AOs) – They help us to calculate molecular orbitals (MOs) using the Linear Combination of Atomic Orbitals (LCAO) approximation
- ▶ They are a Set of One-particle Functions Used To Build Molecular Orbitals
- ▶ They are intended to convert the partial differential equations of the model into algebraic equations suitable for efficient implementation on a computer.

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- ▶ Larger basis sets give a better approximation to the atomic orbitals as they place fewer restrictions on the wavefunction
 - ▶ Larger basis sets attract a higher computational cost
 - ▶ Basis sets are carefully designed to give the best description for the lowest cost

Basis Sets in Quantum Chemistry

- ▶ LCAO-MO approximation: MO's built from AO's
- ▶ An “orbital” is a one-electron function
- ▶ AO's represented by atom- centred Gaussians in most quantum chemistry programs
- ▶ Some older programs used “Slater functions” (STO's)

Basis Sets and Basis Functions

- ▶ The molecular spin-orbitals that are used in the Slater determinant usually are expressed as a linear combination of some chosen functions, which are called basis functions.
- ▶ A set of functions is called the basis set
- ▶ The basis function should describe something
- ▶ Consider spherical harmonics as an example- It is a function which can describe the angular properties of hydrogen atom
- ▶ But it fails to describe hydrogen atom without the radial function.
- ▶ By considering both radial function and spherical harmonics, H atom can be solved.

SLATER TYPE ORBITAL

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

- ▶ 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 functions, at least for 1s; however, they lack radial nodes and are not pure spherical harmonics, but they possess correct short-range and long-range behaviour.

GAUSSIAN TYPE ORBITAL

- ▶ $\phi_{abc}^{GTO}[\mathbf{x}, \mathbf{y}, \mathbf{z}] = N x^a y^b z^c e^{-\zeta r^2}$
- ▶ 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
- ▶ Almost universally used by quantum chemists

STO & GTO

- ▶ STOs require more calculating, which takes tremendous amounts of time, however their calculations have been found to be more accurate than GTOs. On the other hand, GTOs, although less accurate, are much faster to calculate than STOs.
- ▶ By adding several GTOs, we can mimic the STOs accuracy. As the number of GTOs used increased, the better they were able to model the STO equation.
- ▶ When using GTOs to model STOs, the new equations are given a new name. They are identified as STO-nG equations where n is a constant that represents the number of GTOs used. For instance, two common equations are the STO-3G and the STO-6G in which 3 and 6 GTOs are used respectively.

CONTRACTED GAUSSIAN-TYPE ORBITALS (CGTO'S)

- ▶ STO's are more accurate, but it takes longer to compute integrals using them.
- ▶ So we use a linear combination of enough GTO's to mimic an STO
- ▶ A combination of GTO's used to mimic an STO is called an STO-nG even though it is made of contracted GTO's
- ▶ $\phi_{abc}^{CGTO}[\mathbf{x}, \mathbf{y}, \mathbf{z}] = N \sum C_i x^a y^b z^c e^{-\zeta r^2}$

TYPES OF BASIS SETS

- ▶ Minimal basis sets contain the minimum number of basis functions to accommodate all of the electrons in the atom
- ▶ For example:
 - H a single function (1s)
 - C has 5 functions, (1s, 2s, 2p_x, 2p_y, 2p_z)
 - Al has 9 functions, (1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z)
- ▶ Functions are always added in shells

TYPES OF BASIS SETS

- ▶ 1) Minimal basis set: One basis function (STO, GTO, or CGTO) for each atomic orbital in the atom
- ▶ 2) Double-zeta basis set: Two basis functions for each AO. It allows treatment of spatially different bonds at the same atom.
 - ▶ Zeta ζ value accounts for the size of the AO
- ▶ 3) Triple-zeta basis sets: Three basis functions for each AO and etc.
- ▶ Having different-sized functions allows the orbital to get bigger or smaller when other atoms approach it

SPLIT VALENCE

- ▶ “Split-Valence” basis uses only one basis function for each core AO, and a larger basis for the valence AO's .
- ▶ In Split-valence basis set each valence orbital are modelled by two or more basis functions that have different exponents

Examples

- ▶ H atom, minimal basis: One 1s AO So 1 basis Function
- ▶ C atom, minimal basis: 1s, 2s, 2px, 2py, 2pz 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: 6 basis functions

Eg- 3-21G

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

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.
- ▶ It is very bad to do computations on anions without using diffuse functions; results could change completely.

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, chosen to mimic the behaviour of an 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.

- ▶ **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** added with diffuse functions for non-hydrogen atoms;
- ▶ **6-31++G** has diffuse functions for hydrogen also

| Basis Set | Description | No: of functions for | | | |
|--------------|------------------------------------------------------------------------------------------------|----------------------|-------|---------|--|
| | | H | Water | benzene | |
| STO-3G | Minimal | 1 | 7 | 36 | |
| 6-31G | Double zeta split valance | 2 | 13 | 66 | |
| 6-31G(d) | Double zeta split valance with d polarisation | 2 | 9 | 102 | |
| 6-31G(d,p) | Double zeta split valance with d & p polarisation | 5 | 25 | 120 | |
| 6-311+G(d,p) | Triple zeta split valance with d & p polarisation and diffuse functions for non hydrogen atoms | 6 | 34 | 168 | |