BASIS SETS

A basis set is a set of wave functions that describes the shape of atomic orbitals (AOs). The molecular orbitals (MOs) are computed using the selected theoretical model by linearly combining the AOs (LCAO).
Not all theoretical models require the user to choose a basis set to work with. For example, PMn (n=3,...,6) models use an internal basis set, while ab initio or density functional theory require a basis set specification.
The level of approximation of your calculation is directly related to the basis set used. The choice to make is a trade-off between accuracy of results and CPU time
A basis set is a set of wave functions used to create the molecular orbitals , which are expanded as a linear combination with coefficients to be determined .
The use of basis sets is equivalent to the use of an approximate resolution of the identity .
The single particle states (molecular – orbitals) are then expressed as linear combinations of the basis functions . Basis is applied to a collection of contracted Gaussian representing a atomic orbitals .
Which are optimized to reproduce the desired chemical propertied of system.
Large basis sets include more and a greater range of basis functions . Therefore larger basis set can be better refine the approximation to the true molecular wave function .
Several types atomic orbitals can be used : Gassian- type orbitals , Slater. Type orbitals (STO- GTO).

THEORY: SLATER VS GAUSSIAN

Both Slater Type Orbitals (STOs) and Gaussian Type Orbitals (GTOs) are used to describe AOs. STOs describe the shape of AOs more closely than GTOs, but GTOs have an unbeatable advantage: they are much easier to compute.
In fact, it is faster to compute several GTOs and combine them to describe an orbital than to compute one STO! This is why combinations of GTOs are commonly used to describe STOs

TYPES OF BASIS SETS

MINIMAL

These basis sets use only one function for each AO. STO-nG (n=2,...,6) means:
that n GTOs are used to describe one STO, and only one STO is used to describe an AO (single Zeta). Usually n < 3 gives too poor results, so STO-3G is called the minimal basis set.
Minimal basis sets are used for either qualitative results, very large molecules or quantitative results for very small molecules (atoms).

1-Minimum Basis Sets:

The smallest Basis sets are called minimal basis sets
A minimal basis set is one in which , on each atom in the molecule , a single basis function is used for each orbital in a Hartree – Fock calculation on the free atom .
A minimum basis set consists of one STO (Slator – Type Orbitals) for each inner shell and valence – shell AO. Of each atom .
The most common of there is STO-3G where a linear combination of (Gaussion type orbital) GTO are fitted to slater type orbital STO.
Minimal basis sets (STO-nG) contain the minimum number of atomic orbitals basis functions needed to describe each atom (n=1 for H and He)

2-Split Valence (SV)

Basis sets in which there are multiple basis functions corresponding to each valence atomic orbital are called valence double , triple , quadruple – zeta (zeta was commonly used to represent the exponent of an STO basis function).
(SV) basis set uses two or more STO for each valence AO , An(SV) basis set is minimal for inner – shell AO. Basis sets are denoted by the number of Gaussian functions used to described inner and outer shell electrons.
(6- 21G) describe an inner shell atomic orbital with a contracted Gaussian composed of six primitive Gaussian , an inner valence shell with contracted Gaussian composed of two primitive , and an outer valence shell with one primitive –other split – valence sets include 3-21G (3 the number of Gaussian functions summed to describe the inner shell orbital .

These basis sets are also called Pople basis sets and allow to specify the number of GTO's to use for core and valence electrons separately (size adjustable). These are double Zeta (2 functions per AO) or triple Zeta. The notation is as follows: K-LMG, where

- K = number of sp-type inner shell GTOs
- L = number of inner valence s- and p-type GTOs
- M = number of outer valence s- and p-type GTOs
- G = indicates that GTOs are used

POPLE basis sets are usually employed for organic molecules:

- 3-21G : 3 GTOs for inner shell, 2 GTOs for inner valence, 1 GTO for outer valence
- 4-31G
- 4-22G
- 6-21G
- 6-31G
- 6-311G : 6 GTOs for core orbital, 3 GTOs for inner valence, 2 different GTOs for outer valence (triple zeta)
- 7-41G