بسم الله الرحمن الرحيم

Introduction to Basis Sets and the SCF Method

Lecture # 03

Instructor: Dr. Muhammad Ali Hashmi

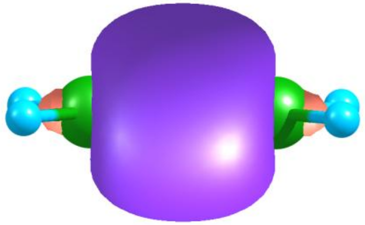
January 08, 2021

Key Concepts

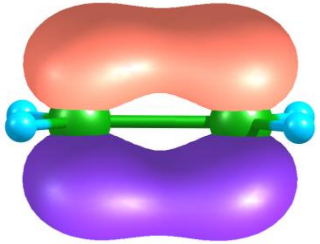
- In this lecture we ‘ll learn:
- Molecular Orbitals
- Basis Functions and Basis Sets
- Minimal Basis Set

Molecular Orbitals

- We represent our electronic structure with a set of orbitals.



C-C σ-bond in ethene



C-C π-bond in ethene

- We represent molecular orbitals as a linear combination of ***basis functions***.

$$\chi_i\left(\mathbf{x}\right) = g\left(\omega\right)\sum_{\nu=1}^{K} c_{\nu i}\phi_\nu\left(\mathbf{r}\right)$$

artificial spin function

coefficient in linear expansion (called molecular orbital coefficients)

basis function with a fixed form

Basis Functions & Basis Set

- The atom-centred functions used to describe the *atomic orbitals* are known as ***basis functions*** and collectively form a ***basis set***.

✓ Electron density is large in core orbitals, bonds, lone pairs, etc.

✓ Electron density is small far away from nuclei.

❖ *A basis set is a set of basis functions that are centered on a specific atom.*

❖ Larger basis sets give a *better approximation* to the atomic orbitals as the place fewer restrictions on the wavefunction.

❖ Larger basis sets attract a *higher computational cost.*

Basis Set

- Basis sets usually include at least 1 basis function for each type of occupied orbital on the atom.
- *Each contracted Gaussian function represents 1 atomic orbital.*
- The simplest possible atomic orbital representation is called a ***minimal basis set***.
- Minimal basis sets contain the minimum number of basis functions to accommodate all of the electrons in the atom.
- For example:
  - **H & He** a single function (1*s*)
  - **1st row** 5 functions, (1*s*, 2*s*, 2p_x, 2p_y, 2p_z)
  - **2nd row** 9 functions, (1*s*, 2*s*, 2p_x, 2p_y, 2p_z, 3*s*, 3p_x, 3p_y, 3p_z)

Minimal Basis Sets

- The **STO-3G** basis set is a minimal basis set where each atomic orbital is made up of 3 Gaussians. STO-*n*G also exist.
- Minimal basis sets are not well suited to model the anisotropic effects of bonding
- Because the exponents do not vary, the orbitals have a fixed size and therefore *cannot expand or contract*

Basis Set

- Example:
- **Carbon = $1s^2\ 2s^2\ 2p^2$**
- 1 contracted Gaussian for the 1*s* orbital
- 1 contracted Gaussian for the 2*s* orbital
- 1 contracted Gaussian for the 2*p* orbital
- the 2*p* contracted Gaussian would be multiplied by a '*p*' angular function to give 3 different basis functions

Note that 3 p functions are included even though there are only 2 p electrons on Carbon

These are the minimum number of basis functions that must be included for each atom

Single and Multiple Zeta Basis Set

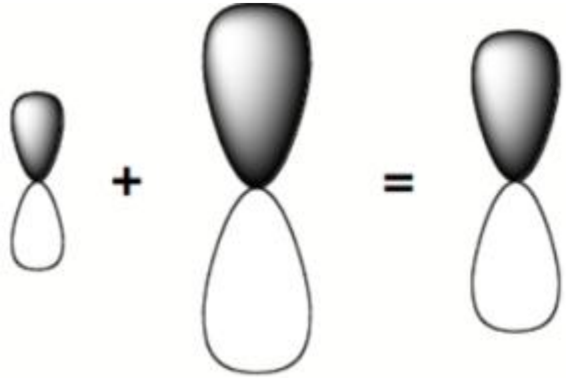
- Single-zeta (ζ) basis set include one contracted Gaussian basis function for each occupied type of orbital on the atom.
- These are also called minimal basis sets.
- Multiple-zeta basis set include multiple contracted Gaussian basis functions for each occupied type of orbital on the atom.

Benefits of Multiple Zeta Basis Sets:

- Each contracted Gaussian function gets a variational coefficient in the definition of molecular orbitals
- More coefficients means more variational flexibility to get a lower energy wavefunction
- More basis functions gives more flexibility in describing bonding

Split Valence Functions

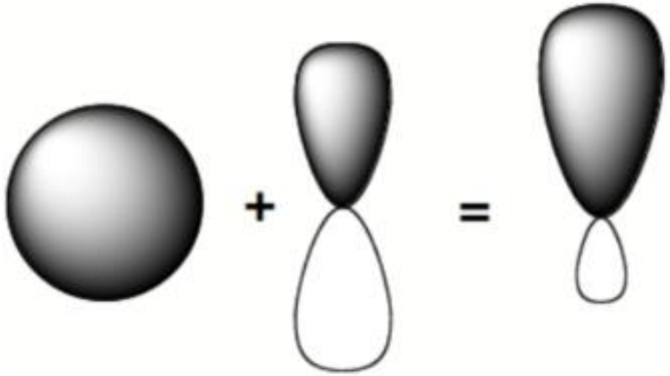
- Split-valence basis sets model each valence orbital by two or more basis functions that have different exponents
- They allow for size variations that occur in bonding



- Examples include the double split valence basis sets, 3-21G and 6-31G, and triple split valence basis sets such as 6-311G

Polarization Functions

- Polarization functions have higher angular momentum
- They allow for anisotropic variations that occur in bonding and help model the inter-electronic cusp.

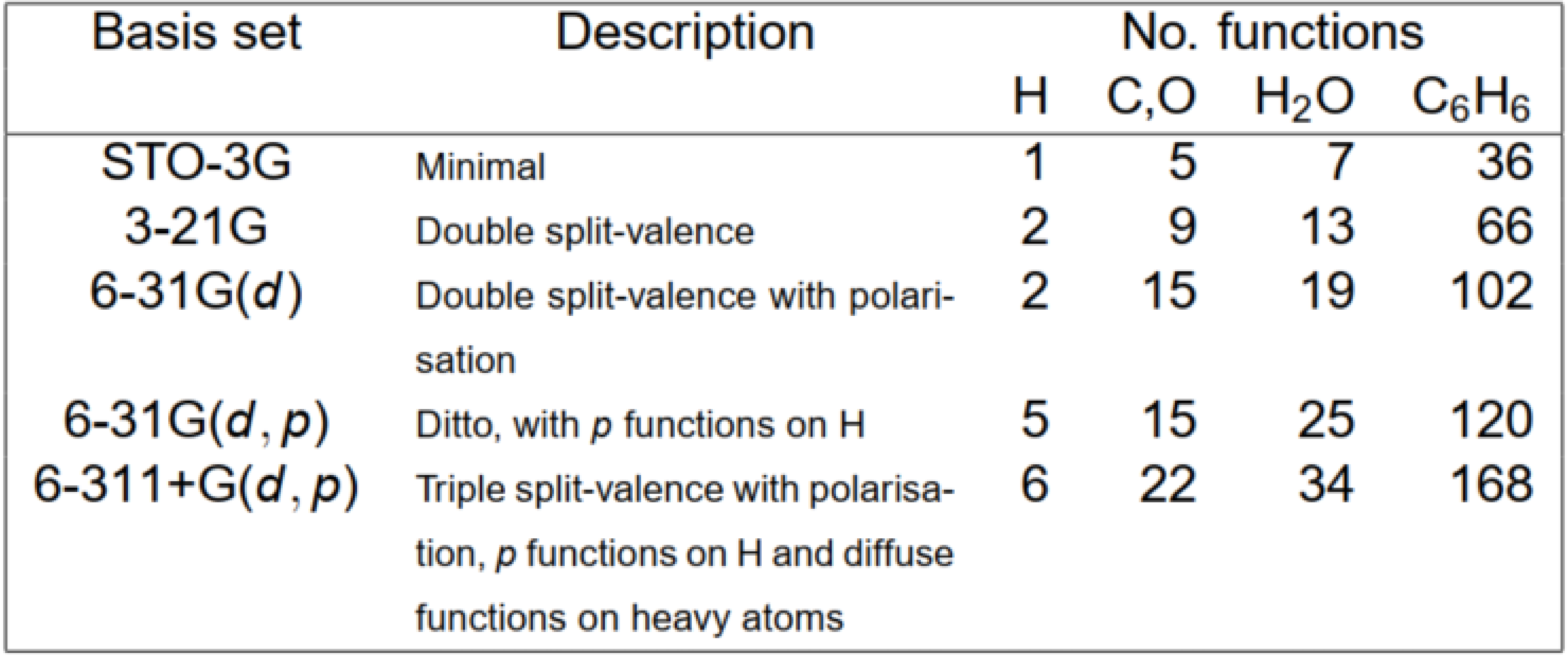


- Examples include **6-31G(*d*)** or **6-31G*** which include *d* functions on the *heavy* atoms and **6-31G(*d,p*)** or **6-31G**** which include *d* functions on heavy atoms and *p* functions on hydrogen atoms.

Diffuse Functions

- Diffuse basis functions are additional functions with small exponents, and are therefore large
- They allow for accurate modelling of systems with weakly bound electrons, such as
  - ✓ Anions
  - ✓ Excited states
- A set of diffuse functions usually includes a diffuse *s* orbital and a set of diffuse *p* orbitals with the same exponent
- Examples in include 6-31+G which has diffuse functions on the heavy atoms and 6-31++G which has diffuse functions on hydrogen atoms as well.

Examples



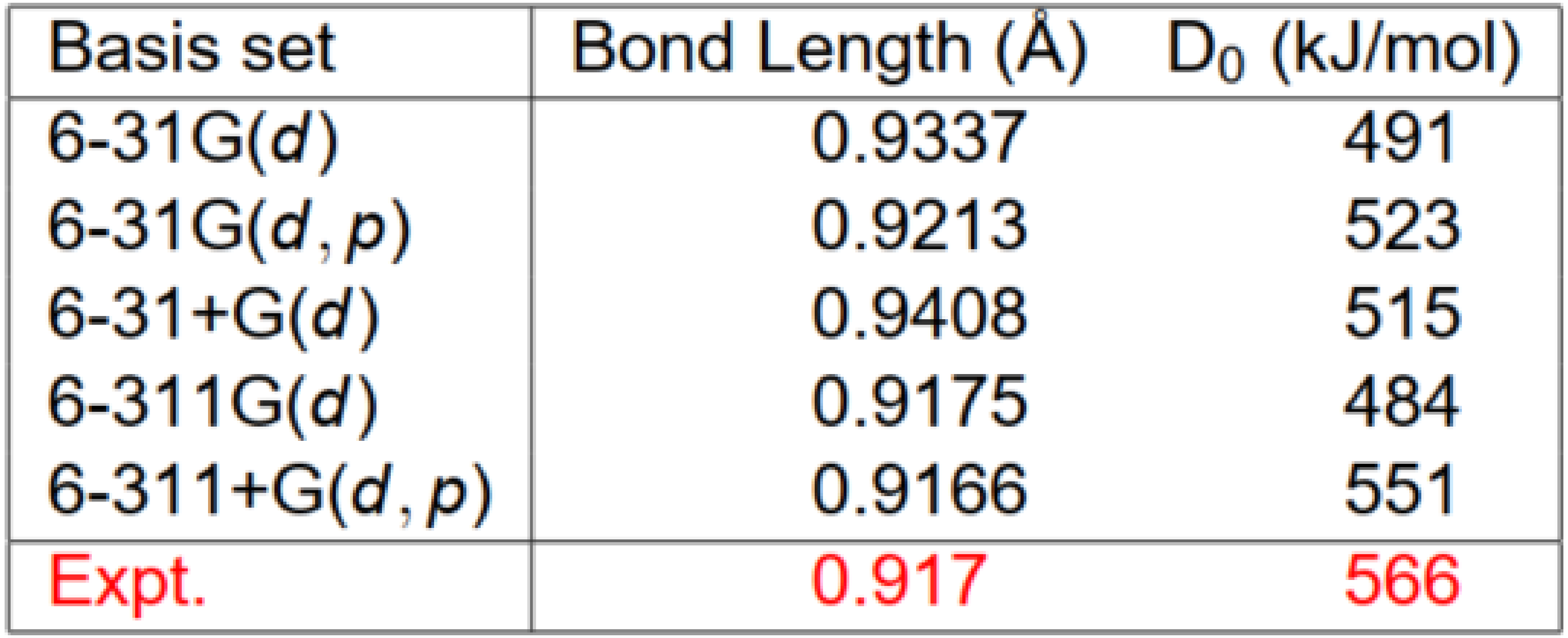
Basis set	Description	No. functions			
		H	C,O	H_2O	C_6H_6
STO-3G	Minimal	1	5	7	36
3-21G	Double split-valence	2	9	13	66
6-31G(*d*)	Double split-valence with polarisation	2	15	19	102
6-31G(*d*, *p*)	Ditto, with *p* functions on H	5	15	25	120
6-311+G(*d*, *p*)	Triple split-valence with polarisation, *p* functions on H and diffuse functions on heavy atoms	6	22	34	168

Different Basis Sets

Basis Set Type	People Basis Sets	Ahlrichs Basis Sets	Duning Huzinga Basis Sets	Misc.
Double ζ	6-31G	Def2-SVP	cc-pVDZ	LANL2DZ
Triple ζ	6-311G	def2-TZVP	cc-pVTZ	LANL2TZ
Quadruple ζ		Def2-QZVP	cc-pVQZ	

Accuracy and Basis Set

- The accuracy of the computed properties is sensitive to the quality of the basis set.
- Consider the bond length and dissociation energy of the hydrogen fluoride molecule:



Basis set	Bond Length (Å)	D_0 (kJ/mol)
6-31G(*d*)	0.9337	491
6-31G(*d*, *p*)	0.9213	523
6-31+G(*d*)	0.9408	515
6-311G(*d*)	0.9175	484
6-311+G(*d*, *p*)	0.9166	551
Expt.	0.917	566

The Self-Consistent Field (SCF) Method

- Simply, to calculate a potential energy surface, we must solve the electronic Schrödinger equation for a system of *n* electrons and *N* nuclei, over a range of nuclear coordinates.
- This is termed an *ab intio* method, since it is derived from ‘first principles.
- Generally, the real wavefunction of a system is too complex to be found directly but can be approximated by a simpler wavefunction.
- This then enables the electronic Schrödinger equation to be solved numerically.

The Self-Consistent Field (SCF) Method

- The self-consistent field method is an iterative method that involves selecting an approximate Hamiltonian, solving the Schrödinger equation to obtain a more accurate set of orbitals, and then solving the Schrödinger equation again with theses until the results converge.

The SCF Process

1) Guess a set of MOs
2) Use MOs to compute one-electron terms arising from the kinetic energy of the electrons and the nuclear attraction energy, two-electron terms associated with the coulomb repulsion between the electrons, two-electron terms associated with the exchange of electronic coordinates
3) Solve the equations for energy and the new MOs
4) Are the new MOs different? Yes→ (2), No → (5)
5) Self-consistent field (SCF) converged

Important Software

- MS Word (Word Processor)
- Endnote (Referencing Software)
- ChemDraw (To Draw Chemical Structures)
- Dropbox
- GaussView
- Gaussian