

10.3: 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*. This set of functions is called the *basis set*. The fact that one function can be represented by a linear combination of other functions is a general property. All that is necessary is that the basis functions *span-the-space*, which means that the functions must form a complete set and must be describing the same thing. For example, spherical harmonics cannot be used to describe a hydrogen atom radial function because they do not involve the distance r , but they can be used to describe the angular properties of anything in three-dimensional space.

This span-the-space property of functions is just like the corresponding property of vectors. The unit vectors [\[Math Processing Error\]](#) describe points in space and form a complete set since any position in space can be specified by a linear combination of these three unit vectors. These unit vectors also could be called **basis vectors**.

Exercise [\[Math Processing Error\]](#)

Explain why the unit vectors [\[Math Processing Error\]](#) do not form a complete set to describe your classroom.

Just as we discussed for atoms, parameters in the basis functions and the coefficients in the linear combination can be optimized in accord with the Variational Principle to produce a self-consistent field (SCF) for the electrons. This optimization means that the ground state energy calculated with the wavefunction is minimized with respect to variation of the parameters and coefficients defining the function. As a result, that ground state energy is larger than the exact energy, but is the best value that can be obtained with that wavefunction.

Slater-type atomic orbitals (STOs)

Intuitively one might select hydrogenic atomic orbitals as the basis set for molecular orbitals. After all, molecules are composed of atoms, and hydrogenic orbitals describe atoms exactly if the electron-electron interactions are neglected. At a better level of approximation, the nuclear charge that appears in these functions can be used as a variational parameter to account for the shielding effects due to the electron-electron interactions. Also, the use of atomic orbitals allows us to interpret molecular properties and charge distributions in terms of atomic properties and charges, which is very appealing since we picture molecules as composed of atoms. As described in the previous chapter, calculations with hydrogenic functions were not very efficient so other basis functions, **Slater-type atomic orbitals (STOs)**, were invented.

A minimal basis set of STOs for a molecule includes only those STOs that would be occupied by electrons in the atoms forming the molecule. A larger basis set, however, improves the accuracy of the calculations by providing more variable parameters to produce a better approximate wavefunction, but at the expense of increased computational time.

For example, one can use more than one STO to represent one atomic orbital, as shown in Equation [\[Math Processing Error\]](#), and rather than doing a nonlinear variational calculation to optimize each zeta, use two STOs with different values for zeta. The linear variation calculation then will produce the coefficients ([\[Math Processing Error\]](#) and [\[Math Processing Error\]](#)) for these two functions in the linear combination that best describes the charge distribution in the molecule. The function with the large zeta accounts for charge near the nucleus, while the function with the smaller zeta accounts for the charge distribution at larger values of the distance from the nucleus. This expanded basis set is called a **double-zeta basis set**.

[\[Math Processing Error\]](#)

Example [\[Math Processing Error\]](#)

- Plot the normalized radial probability density for a 2s hydrogenic orbital for lithium using an effective nuclear charge of 1.30.
- Fit that radial probability density with the radial probability density for 1 STO by varying the zeta parameter in the STO.
- Also fit the radial probability density for the hydrogenic orbital with that for the sum of 2 STOs, as in Equation ([\[Math Processing Error\]](#)), by varying the zeta parameters for each and their coefficients in the sum.
- Report your values for the zeta parameters and the coefficients and provide graphs of these functions and the corresponding radial probability densities. What are your conclusions regarding the utility of using STOs with single or double zeta values to describe the charge distributions in atoms and molecules?

The use of double zeta functions in basis sets is especially important because without them orbitals of the same type are constrained to be identical even though in the molecule they may be chemically inequivalent. For example, in acetylene the p_z orbital along the internuclear axis is in a quite different chemical environment and is being used to account for quite different bonding than the p_x and p_y orbitals. With a double zeta basis set the p_z orbital is not constrained to be the same size as the p_x and p_y orbitals.

Example [Math Processing Error]

Explain why the [Math Processing Error], [Math Processing Error], and [Math Processing Error] orbitals in a molecule might be constrained to be the same in a single-zeta basis set calculation, and how the use of a double-zeta basis set would allow the [Math Processing Error], [Math Processing Error], and [Math Processing Error] orbitals to differ.

The use of a minimal basis set with fixed zeta parameters severely limits how much the electronic charge can be changed from the atomic charge distribution in order to describe molecules and chemical bonds. This limitation is removed if STOs with larger n values and different spherical harmonic functions, the [Math Processing Error] in the definition of STO's in Chapter 9, are included. Adding such functions is another way to expand the basis set and obtain more accurate results. Such functions are called polarization functions because they allow for charge polarization away from the atomic distribution to occur.

Gaussian Basis Function

While the STO basis set was an improvement over hydrogenic orbitals in terms of computational efficiency, representing the STOs with Gaussian functions produced further improvements that were needed to accurately describe molecules. A **Gaussian basis function** has the form shown in Equation [Math Processing Error]. Note that in all the basis sets, only the radial part of the orbital changes, and the spherical harmonic functions are used in all of them to describe the angular part of the orbital.

[Math Processing Error]

Unfortunately Gaussian functions do not match the shape of an atomic orbital very well. In particular, they are flat rather than steep near the atomic nucleus at $r = 0$, and they fall off more rapidly at large values of r .

Example [Math Processing Error]

Make plots of the following two functions

- [Math Processing Error]
- [Math Processing Error]

to illustrate how Gaussian functions differ from hydrogenic orbitals and Slater-type orbitals. The constants multiplying the exponentials normalize these functions. Describe the differences you observe between a Gaussian and a Slater-type function.

To compensate for this problem, each STO is replaced with a number of Gaussian functions with different values for the exponential parameter [Math Processing Error]. These Gaussian functions form a *primitive Gaussian basis set*. Linear combinations of the primitive Gaussians are formed to approximate the radial part of an STO. This linear combination is not optimized further in the energy variational calculation but rather is frozen and treated as a single function. The linear combination of *primitive Gaussian functions* is called a *contracted Gaussian function*. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials so there is a net gain in the efficiency of the calculation.

Gaussian basis sets are identified by abbreviations such as N-MPG*. N is the number of Gaussian primitives used for each inner-shell orbital. The hyphen indicates a split-basis set where the valence orbitals are double zeta. The M indicates the number of primitives that form the large zeta function (for the inner valence region), and P indicates the number that form the small zeta function (for the outer valence region). G identifies the set as being Gaussian. The addition of an asterisk to this notation means that a single set of Gaussian 3d polarization functions is included. A double asterisk means that a single set of Gaussian 2p functions is included for each hydrogen atom.

For example, 3G means each STO is represented by a linear combination of three primitive Gaussian functions. 6-31G means each inner shell (1s orbital) STO is a linear combination of 6 primitives and each valence shell STO is split into an inner and outer part (double zeta) using 3 and 1 primitive Gaussians, respectively.

Example *[Math Processing Error]*

The 1s Slater-type orbital *[Math Processing Error]* with *[Math Processing Error]* is represented as a sum of three primitive Gaussian functions,

$$\text{[Math Processing Error]}$$

This sum is the contracted Gaussian function for the STO.

- a. Make plots of the STO and the contracted Gaussian function on the same graph so they can be compared easily. All distances should be in units of the Bohr radius. Use the following values for the coefficients, C, and the exponential parameters, *[Math Processing Error]*.

b.

index j	<i>[Math Processing Error]</i>	C _j
1	0.1688	0.4
2	0.6239	0.7
3	3.425	1.3

- c. Change the values of the coefficients and exponential parameters to see if a better fit can be obtained.
 d. Comment on the ability of a linear combination of Gaussian functions to accurately describe a STO.

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