

About basis sets

From chapter 7.2 in
the book by
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(Wiley 2001)

The Cartesian *Gaussian-type-orbitals*, GTO of the general form

$$\eta^{\text{GTO}} = N x^l y^m z^n \exp[-\alpha r^2]. \quad (7-19)$$

N is a normalization factor which ensures that $\langle \eta_\mu | \eta_\mu \rangle = 1$ (but note that the η_μ are not orthogonal, i. e., $\langle \eta_\mu | \eta_\nu \rangle \neq 0$ for $\mu \neq \nu$). α represents the orbital exponent which determines how compact (large α) or diffuse (small α) the resulting function is. $L = l + m + n$ is used to classify the GTO as s-functions ($L = 0$), p-functions ($L = 1$), d-functions ($L = 2$), etc. Note, however, that for $L > 1$ the number of cartesian GTO functions exceeds the number of $(2l+1)$ physical functions of angular momentum l . For example, among the six cartesian functions with $L = 2$, one is spherically symmetric and is therefore not a d-type, but an s-function. Similarly the ten cartesian $L = 3$ functions include an unwanted set of three p-type functions.

The preference for GTO basis functions in HF and related methods is motivated by the computational advantages these functions offer, because very efficient algorithms exist for analytically calculating the huge number of four-center-two-electron integrals occurring in the Coulomb and HF-exchange terms. On the other hand, from a physical point of view, *Slater-type-orbitals* (STO) seem to be the natural choice for basis functions. They are simple exponentials that mimic the exact eigenfunctions of the hydrogen atom. Unlike the GTO functions, Slater-type-orbitals exhibit the correct cusp behavior at $r \rightarrow 0$ with a discontinuous derivative (while a GTO has a slope of zero at $r \rightarrow 0$) and the desired exponential decay in the tail regions as $r \rightarrow \infty$ (GTO fall off too rapidly). A typical STO is expressed as

$$\eta^{\text{STO}} = N r^{n-1} \exp[-\zeta r] Y_{lm}(\Theta, \Phi). \quad (7-20)$$

Here, n corresponds to the principal quantum number, the orbital exponent is termed ζ and Y_{lm} are the usual spherical harmonics that describe the angular part of the function. In fact as a rule of thumb one usually needs about three times as many GTO than STO func-

tions to achieve a certain accuracy. Unfortunately, many-center integrals such as described in equations (7-16) and (7-18) are notoriously difficult to compute with STO basis sets since no analytical techniques are available and one has to resort to numerical methods. This explains why these functions, which were used in the early days of computational quantum chemistry, do not play any role in modern wave function based quantum chemical programs. Rather, in an attempt to have the cake and eat it too, one usually employs the so-called contracted GTO basis sets, in which several primitive Gaussian functions (typically between three and six and only seldom more than ten) as in equation (7-19) are combined in a fixed linear combination to give one *contracted Gaussian function* (CGF),

$$\eta_{\tau}^{\text{CGF}} = \sum_a^A d_{a\tau} \eta_a^{\text{GTO}} . \quad (7-21)$$

The original motivation for contracting was that the contraction coefficients $d_{s\tau}$ can be chosen in a way that the CGF resembles as much as possible a single STO function. In addition, contracting the primitives is also another trick to reduce the computational burden.

Irrespective of whether we use Gaussian functions, Slater type exponentials or numerical sets, certain categories of functions that can help to characterize the quality of a basis set have become customary in quantum chemistry. The simplest and least accurate expansion of the molecular orbitals utilizes only one basis function (or one contracted function in the case of CGF sets) for each atomic orbital up to and including the valence orbitals. These basis sets are for obvious reasons called *minimal* sets. A typical representative is the STO-3G basis set, in which three primitive GTO functions are combined into one CGF. For

carbon, this basis set consists of five functions, one each describing the 1s and 2s atomic orbitals and three functions for the 2p shell (p_x , p_y , and p_z). One should expect no more than only qualitative results from minimal sets and nowadays they are hardly used anymore. The next level of sophistication are the *double-zeta* basis sets. Here, the set of functions is doubled, i. e., there are two functions for each orbital (the generic name ‘double-zeta’ for such basis sets still points to the beginnings of computational quantum chemistry, when STO functions were in use, where the orbital exponent is called ζ). If we take into account that it is in the valence space where changes in the electronic wave function occur during chemical processes, we can limit the doubled set of functions to the valence orbitals, while the chemically mostly inert core electrons are still treated in a minimal set. This defines the *split-valence* type sets. Typical examples are the 3-21G or 6-31G Gaussian basis sets developed by Pople and coworkers. In most applications, such basis sets are augmented by *polarization functions*, i. e., functions of higher angular momentum than those occupied in the atom, e. g., p-functions for hydrogen or d-functions for the first-row elements. Polarization functions have by definition more angular nodal planes than the occupied atomic orbitals and thus ensure that the orbitals can distort from their original atomic symmetry and better adapt to the molecular environment. Polarized double-zeta or split valence basis sets are the mainstay of routine quantum chemical applications since usually they offer a balanced compromise between accuracy and efficiency. In terms of CGF type basis sets, typical examples are the standard 6-31G(d,p) sets of Hehre, Ditchfield, and Pople, 1972, and Hariharan and Pople, 1973, or the more recent SVP (split-valence polarization) sets of

Schäfer, Horn, and Ahlrichs, 1992. Equivalents consisting of two STO functions per atomic orbital or two numerical functions are of comparable importance in their respective domains. In the latter case the doubling of the numerical functions can be achieved, for example, by adding numerically generated atomic orbitals from calculations on doubly or even higher positively charged ions.

It is obvious how these schemes can be extended by increasing the number of functions in the various categories. This results in triple- or quadruple-zeta basis sets which are augmented by several sets of polarization functions including functions of even higher angular momentum. The cc-pVQZ (for *correlation-consistent polarized valence quadruple zeta*) and cc-pV5Z (the 5 stands for quintuple) basis sets mentioned earlier are typical, modern representatives of this approach in terms of Gaussian functions (Dunning, 1989). For example, the large cc-pV5Z contraction consists for the first-row atoms boron to neon of 14s-, 8p-, 4d-, 3f-, 2g-, and 1h-type primitive GTO. These are contracted to 6s- and 5p-type contracted Gaussian functions while the polarization functions are left uncontracted, leading to a final basis set of size 6s, 5p, 4d, 3f, 2g, 1h. This is a valence quintuple set because there is 1 CGF for the 1s core electrons and 5 sets of s- and p-functions representing the corresponding 2s and 2p orbitals of the valence shell. If the so-called spherical harmonic functions are used, where the contaminants in the d- and higher sets are deleted and only the true angular momentum functions are retained, this basis set contains 91 CGF per first-row atom as compared to only 15 in a 6-31G(d,p) basis (by definition the 6-31G(d,p) basis set employs six cartesian d-functions).

If the molecules of interest contain elements heavier than, say, krypton, one usually employs a *(relativistic) effective core potential* ((R)ECP), also called *pseudopotential*, to model the energetically deep-lying and chemically mostly inert core electrons, as reviewed recently by Frenking et al., 1996, and Cundari et al., 1996. The potentials are called 'relativistic' if they have been fitted to atomic calculations that explicitly incorporate relativistic effects.