

Basis Set (Atomic Orbitals)

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1 Introduction

We write an normalized primitive Cartesian Gaussian function centered at \mathbf{R} as

$$g(\mathbf{r}; \zeta, \mathbf{n}, \mathbf{R}) = N(\zeta, \mathbf{n}) (x - R_x)^{n_x} (y - R_y)^{n_y} (z - R_z)^{n_z} \exp \left[-\zeta (\mathbf{r} - \mathbf{R})^2 \right], \quad (1)$$

where \mathbf{r} is the coordinate vector of the electron, ζ is the orbital exponent, and \mathbf{n} is a set of non-negative integers. The sum of n_x , n_y , and n_z will be denoted $\lambda(\mathbf{n})$ and be referred to as the angular momentum or orbital quantum number of the Gaussian function. $N(\zeta, \mathbf{n})$ is the normalization coefficient, which can be obtained through the equation

$$\int_{-\infty}^{\infty} x^n e^{-\zeta x^2} dx = \begin{cases} 2^{-(n-1)/2} \zeta^{-(n+1)/2} (n-1)!! & \text{for odd } n, \\ 2^{-n/2} \pi^{1/2} \zeta^{-(n+1)/2} (n-1)!! & \text{for even } n. \end{cases} \quad (2)$$

By virtue of the Eq.(2), we have

$$N(\zeta, \mathbf{n}) = \left(\frac{2}{\pi} \right)^{3/4} \frac{2^{\lambda(\mathbf{n})} \zeta^{(2\lambda(\mathbf{n})+3)/4}}{[(2n_x-1)!! (2n_y-1)!! (2n_z-1)!!]^{1/2}}. \quad (3)$$

A contracted Gaussian function is just a linear combination of primitive Gaussians (also termed primitives) centered at the same center \mathbf{A} and with the same momentum indices \mathbf{n} but with different exponents ζ_i :

$$g(\mathbf{r}; \zeta, \mathbf{n}, \mathbf{c}, \mathbf{R}) = (x - R_x)^{n_x} (y - R_y)^{n_y} (z - R_z)^{n_z} \sum_{i=1}^M C_i \exp \left[-\zeta_i (\mathbf{r} - \mathbf{R})^2 \right], \quad (4)$$

where $C_i = c_i N(\zeta_i, \mathbf{n})$ is the normalization-including contraction coefficient, and c_i is the corresponding contraction coefficient.

2 Product of GTOs

The GTOs have an outstanding feature (along with the square dependence in the exponent), which decides about their importance in quantum chemistry. The product of two Gaussian-type 1s orbitals (even if they have different centers) is a single Gaussian-type 1s orbital.

$$\exp \left[-\zeta_a (\mathbf{r} - \mathbf{R}_a)^2 \right] \exp \left[-\zeta_b (\mathbf{r} - \mathbf{R}_b)^2 \right] = N \exp \left[-\zeta (\mathbf{r} - \mathbf{R})^2 \right], \quad (5)$$

with parameters

$$\begin{aligned} \zeta &= \zeta_a + \zeta_b, \\ \mathbf{R} &= (\zeta_a \mathbf{R}_a + \zeta_b \mathbf{R}_b) / \zeta, \\ N &= \exp \left[\zeta \mathbf{R}^2 - (\zeta_a \mathbf{R}_a^2 + \zeta_b \mathbf{R}_b^2) \right]. \end{aligned} \quad (6)$$

And multiplying recursively, three and higher-fold products are derived:

$$\exp \left[-\zeta_a (\mathbf{r} - \mathbf{R}_a)^2 \right] \exp \left[-\zeta_b (\mathbf{r} - \mathbf{R}_b)^2 \right] \exp \left[-\zeta_c (\mathbf{r} - \mathbf{R}_c)^2 \right] = N \exp \left[-\zeta (\mathbf{r} - \mathbf{R})^2 \right], \quad (7)$$

with parameters

$$\begin{aligned} \zeta &= \zeta_a + \zeta_b + \zeta_c, \\ \mathbf{R} &= (\zeta_a \mathbf{R}_a + \zeta_b \mathbf{R}_b + \zeta_c \mathbf{R}_c) / \zeta, \\ N &= \exp \left[\zeta \mathbf{R}^2 - \left(\zeta_a \mathbf{R}_a^2 + \zeta_b \mathbf{R}_b^2 + \zeta_c \mathbf{R}_c^2 \right) \right], \end{aligned} \quad (8)$$

and so forth.

2.1 Differential Relation

$$\frac{\partial}{\partial r_i} g(\mathbf{r}; \zeta, \mathbf{n}, \mathbf{R}) = n_i g(\mathbf{r}; \zeta, \mathbf{n} - \mathbf{1}^i, \mathbf{R}) - 2\zeta g(\mathbf{r}; \zeta, \mathbf{n} + \mathbf{1}^i, \mathbf{R}) \quad (i = x, y, z), \quad (9)$$

References