Molecular Integrals over Cartesian Gaussian Functions

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1 Cartesian Gaussian Functions

We write an unnormalized primitive Cartesian Gaussian function centered at $mathbfR$ as

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

where $\mathbf{r}$ is the coordinate vector of the electron, ζ is the orbital exponent, and 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. The functions with $\lambda(\mathbf{n})$ equal to $0, 1, 2, \ldots,$ are referred to as $s, p, d, \ldots,$ respectively. A set of $(\lambda+1)(\lambda+2)/2$ functions at $\mathbf{R}$ associated with the same angular momentum λ and orbital exponent ζ constitute a shell, and the functions in the shell are components of the shell. Some examples are listed in the Table 1.

Table 1: Some shells and their components

$\lambda(\mathbf{n})$	Shell	Components $(i, j = x, y, z)$
0	s	$\mathbf{0} = (0,0,0)$
1	p	$\mathbf{1}^i = (\delta_{ix}, \delta_{iy}, \delta_{iz})$
2	d	$\mathbf{1}^i + \mathbf{1}^j$

And the normalization coefficient $N(\zeta,\mathbf{n})$ of $g'(\mathbf{r};\zeta,\mathbf{n},\mathbf{R})$ can be obtained through the equation

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

by virtue of which, we have

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

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:

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

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

2 Features of Gaussian Functions

2.1 Product of GFs

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.

$$\exp\left[-\zeta_a(\mathbf{r}-\mathbf{R}_a)^2\right]\exp\left[-\zeta_b(\mathbf{r}-\mathbf{R}_b)^2\right] = N_{ab}\exp\left[-\zeta_{ab}(\mathbf{r}-\mathbf{R}_{ab})^2\right], \tag{5}$$

with parameters

$$\begin{aligned}\zeta_{ab} &= \zeta_a + \zeta_b,\\ \mathbf{R}_{ab} &= (\zeta_a\mathbf{R}_a + \zeta_b\mathbf{R}_b)/\zeta_{ab},\\ N_{ab} &= \exp\left[\zeta_{ab}\mathbf{R}_{ab}^2 - \left(\zeta_a\mathbf{R}_a^2 + \zeta_b\mathbf{R}_b^2\right)\right].\end{aligned} \tag{6}$$

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

$$\exp\left[-\zeta_a(\mathbf{r}-\mathbf{R}_a)^2\right]\exp\left[-\zeta_b(\mathbf{r}-\mathbf{R}_b)^2\right]\exp\left[-\zeta_c(\mathbf{r}-\mathbf{R}_c)^2\right] = N_{abc}\exp\left[-\zeta_{abc}(\mathbf{r}-\mathbf{R}_{abc})^2\right], \tag{7}$$

with parameters

$$\begin{aligned}\zeta_{abc} &= \zeta_a + \zeta_b + \zeta_c,\\ \mathbf{R}_{abc} &= (\zeta_a\mathbf{R}_a + \zeta_b\mathbf{R}_b + \zeta_c\mathbf{R}_c)/\zeta_{abc},\\ N_{abc} &= \exp\left[\zeta_{abc}\mathbf{R}_{abc}^2 - \left(\zeta_a\mathbf{R}_a^2 + \zeta_b\mathbf{R}_b^2 + \zeta_c\mathbf{R}_c^2\right)\right],\end{aligned} \tag{8}$$

and so forth.

2.2 Differential Relation

The Cartesian Gaussian functions satisfy the differential relation

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

In the Cartesian Gaussian function the nuclear coordinate R_i always appears in the form of $r_i - R_i$. Therefore, differentiation with respect to R_i can be replaced by that with respect to r_i:

$$\frac{\partial}{\partial r_i} g'(\mathbf{r};\zeta,\mathbf{n},\mathbf{R}) = n_i g'(\mathbf{r};\zeta,\mathbf{n}-\mathbf{1}^i,\mathbf{R}) - 2\zeta g'(\mathbf{r};\zeta,\mathbf{n}+\mathbf{1}^i,\mathbf{R}) \qquad (i = x, y, z). \tag{10}$$

3 Three-Center Overlap Integrals

Three-center overlap integrals over unnormalized Cartesian Gaussian functions are of the form:

$$(\mathbf{a}|\mathbf{c}|\mathbf{b}) = \int d\mathbf{r}\, g'(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{R}_a) g'(\mathbf{r};\zeta_c,\mathbf{c},\mathbf{R}_c) g'(\mathbf{r};\zeta_b,\mathbf{b},\mathbf{R}_b). \tag{11}$$

According to Eq.(9), the integral $(\mathbf{a}+\mathbf{1}^i|\mathbf{c}|\mathbf{b})$ can be decomposed as

$$(\mathbf{a}+\mathbf{1}^i|\mathbf{c}|\mathbf{b}) = \frac{1}{2\zeta_a}\frac{\partial}{\partial R_{a,i}}(\mathbf{a}|\mathbf{c}|\mathbf{b}) - \frac{1}{2\zeta_a} a_i (\mathbf{a}-\mathbf{1}^i|\mathbf{c}|\mathbf{b}). \tag{12}$$

Here the integral $(\mathbf{a}|\mathbf{c}|\mathbf{b})$ can be factored as

$$(\mathbf{a}|\mathbf{c}|\mathbf{b}) = N_{abc} I_x(a_x, b_x, c_x) I_y(a_y, b_y, c_y) I_z(a_z, b_z, c_z), \tag{13}$$

where

$$I_i(a_i,b_i,c_i) = \left(\frac{\pi}{\zeta_{abc}}\right)^{1/2} \underbrace{\sum_{\alpha_i=0}^{a_i}\sum_{\beta_i=0}^{b_i}\sum_{\gamma_i=0}^{c_i}}_{\alpha_i+\beta_i+\gamma_i=\text{even}} \binom{a_i}{\alpha_i}\binom{b_i}{\beta_i}\binom{c_i}{\gamma_i}$$
$$\times(R_{abc,i}-R_{a,i})^{a_i-\alpha_i}(R_{abc,i}-R_{b,i})^{b_i-\beta_i}(R_{abc,i}-R_{c,i})^{c_i-\gamma_i}\frac{(\alpha_i+\beta_i+\gamma_i-1)!!}{(2\zeta_{abc})^{\alpha_i+\beta_i+\gamma_i}} \quad (14)$$

Differentiating N_{abc} and $I_i(a_i,b_i,c_i)$ with respect to $R_{a,i}$, we have

$$\frac{1}{2\zeta_a}\frac{\partial}{\partial R_{a,i}}N_{abc} = (R_{abc,i}-R_{a,i})N_{abc}, \quad (15)$$

and

$$\frac{1}{2\zeta_a}\frac{\partial}{\partial R_{a,i}}I_i(a_i,b_i,c_i) = a_i\left[\frac{1}{2\zeta_{abc}}-\frac{1}{2\zeta_a}\right]I_i(a_i-1,b_i,c_i)$$
$$+\,b_i\frac{1}{2\zeta_{abc}}I_i(a_i,b_i-1,c_i)+c_i\frac{1}{2\zeta_{abc}}I_i(a_i,b_i,c_i-1). \quad (16)$$

Substitution of Eqs. (15) and (16) into Eq.(12) gives finally

$$(\mathbf{a}+\mathbf{1}^i|\mathbf{c}|\mathbf{b}) = (R_{abc,i}-R_{a,i})(\mathbf{a}|\mathbf{c}|\mathbf{b}) + \frac{1}{2\zeta_{abc}}\left[a_i(\mathbf{a}-\mathbf{1}^i|\mathbf{c}|\mathbf{b})+b_i(\mathbf{a}|\mathbf{c}|\mathbf{b}-\mathbf{1}^i)+c_i(\mathbf{a}|\mathbf{c}-\mathbf{1}^i|\mathbf{b})\right]. \quad (17)$$

The integral over s-functions is given by

$$(\mathbf{0}^a|\mathbf{0}^c|\mathbf{0}^b) = \left(\frac{\pi}{\zeta_{abc}}\right)^{3/2}N_{abc} = \left(\frac{\zeta_{ab}}{\zeta_{abc}}\right)^{3/2}(\mathbf{0}^a|\mathbf{0}^b)\exp\left[-\frac{\zeta_{ab}\zeta_c}{\zeta_{abc}}(\mathbf{R}_{ab}-\mathbf{R}_c)^2\right], \quad (18)$$

where $(\mathbf{0}^a|\mathbf{0}^b)$ is the overlap integral between two s-functions centered at $\mathbf{R}_a$ and $\mathbf{R}_b$:

$$(\mathbf{0}^a|\mathbf{0}^b) = (\pi/\zeta)^{3/2}\exp\left[-\frac{\zeta_a\zeta_b}{\zeta_{ab}}(\mathbf{R}_a-\mathbf{R}_b)^2\right]. \quad (19)$$

4 Electron Repulsion Integrals

For the electron repulsion integrals (ERI's) over unnormalized Cartesian Gatissian functions

$$(\mathbf{ab}|\mathbf{cd}) = \int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\, g'(\mathbf{r}_1;\zeta_a,\mathbf{a},\mathbf{R}_a)g'(\mathbf{r}_1;\zeta_b,\mathbf{b},\mathbf{R}_b)\,|\mathbf{r}_1-\mathbf{r}_2|^{-1}\,g'(\mathbf{r}_2;\zeta_c,\mathbf{c},\mathbf{R}_c)g'(\mathbf{r}_2;\zeta_d,\mathbf{d},\mathbf{R}_d), \quad (20)$$

we may substitute the identity

$$|\mathbf{r}_1-\mathbf{r}_2|^{-1} = \frac{2}{\pi^{1/2}}\int_0^\infty \mathrm{d}u\,\exp\left[-(\mathbf{r}_1-\mathbf{r}_2)^2u^2\right], \quad (21)$$

to obtain

$$(\mathbf{ab}|\mathbf{cd}) = \frac{2}{\pi^{1/2}}\int_0^\infty \mathrm{d}u\,(\mathbf{ab}|u|\mathbf{cd}), \quad (22)$$

where

$$(\mathbf{ab}|u|\mathbf{cd}) = \int \mathrm{d}\mathbf{r}_2 g'(\mathbf{r}_2;\zeta_c,\mathbf{c},\mathbf{R}_c)g'(\mathbf{r}_2;\zeta_d,\mathbf{d},\mathbf{R}_d)(\mathbf{a}|\mathbf{0}^{r_2}|\mathbf{b}) \quad (23)$$

and

$$(\mathbf{a}|\mathbf{0}^{r_2}|\mathbf{b}) = \int \mathrm{d}\mathbf{r}_1 g'(\mathbf{r}_1;\zeta_a,\mathbf{a},\mathbf{R}_a)g'(\mathbf{r}_1;\zeta_b,\mathbf{b},\mathbf{R}_b)\exp\left[-u^2(\mathbf{r}_1-\mathbf{r}_2)^2\right]. \quad (24)$$

Since the exponential function in Eq.(24) corresponds to an s-type Cartesian Gaussian function with the orbital exponent u^2 centered at $\mathbf{r}_2$, $(\mathbf{a}|\mathbf{0}^{r_2}|\mathbf{b})$ is just a three-center overlap integral. Using Eq.(18), we obtain

$$(\mathbf{a}+\mathbf{1}^i|\mathbf{0}^{r_2}|\mathbf{b}) = (R_{ab,i}-R_{a,i})(\mathbf{a}|\mathbf{0}^{r_2}|\mathbf{b}) + \frac{1}{2\zeta_{ab}}\left(1-\frac{\rho}{\zeta_{ab}}\frac{u^2}{\rho+u^2}\right)\left[a_i(\mathbf{a}-\mathbf{1}^i|\mathbf{0}^{r_2}|\mathbf{b}) + b_i(\mathbf{a}|\mathbf{0}^{r_2}|\mathbf{b}-\mathbf{1}^i)\right]$$
$$+\frac{1}{\zeta_{ab}+\zeta_{cd}}\frac{u^2}{\rho+u^2}\left[\zeta_{cd}(r_{2i}-R_{ab,i})(\mathbf{a}|\mathbf{0}^{r_2}|\mathbf{b}) - u^2(\mathbf{a}|\mathbf{1}^{1,r_2}|\mathbf{b})\right], \tag{25}$$

where we have made use of the relations

$$(\mathbf{a}|\mathbf{1}^{i,r_2}|\mathbf{b}) = -\frac{\zeta_{ab}}{\zeta_{ab}+u^2}(r_{2i}-R_{ab,i})(\mathbf{a}|\mathbf{0}^{r_2}|\mathbf{b}) + \frac{1}{2(\zeta_{ab}+u^2)}\left[a_i(\mathbf{a}-\mathbf{1}^i|\mathbf{0}^{r_2}|\mathbf{b}) + b_i(\mathbf{a}|\mathbf{0}^{r_2}|\mathbf{b}-\mathbf{1}^i)\right], \tag{26}$$

and

$$\frac{1}{\zeta_{ab}+u^2} = \frac{1}{\zeta_{ab}}\left(1-\frac{\zeta_{ab}\rho}{\zeta_a\zeta_b}\frac{u^2}{\rho+u^2}\right) - \frac{1}{\zeta_{ab}+\eta}\frac{u^2}{\zeta_{ab}+u^2}\frac{u^2}{\rho+u^2} \tag{27}$$

with the parameters ζ_{cd} and ρ defined by

$$\zeta_{cd} = \zeta_c + \zeta_d \qquad \text{and} \qquad \rho = \frac{\zeta_{ab}\zeta_{cd}}{\zeta_{ab}+\zeta_{cd}}. \tag{28}$$

The integration over $\mathbf{r}_2$ of the last term of Eq.(25) multiplied by $g'(\mathbf{r}_2;\zeta_c,\mathbf{c},\mathbf{R}_c)$ and $g'(\mathbf{r}_2;\zeta_d,\mathbf{d},\mathbf{R}_d)$ can be rewritten as

$$-\frac{1}{\zeta_{ab}+\zeta_{cd}}\frac{u^2}{\rho+u^2}\int d\mathbf{r}_2\, g'(\mathbf{r}_2;\zeta_c,\mathbf{c},\mathbf{R}_c)g'(\mathbf{r}_2;\zeta_d,\mathbf{d},\mathbf{R}_d)u^2(\mathbf{a}|\mathbf{1}^{1,r_2}|\mathbf{b})$$
$$= \frac{1}{\zeta_{ab}+\zeta_{cd}}\frac{u^2}{\rho+u^2}\int d\mathbf{r}_2\, g'(\mathbf{r}_2;\zeta_a,\mathbf{a},\mathbf{R}_a)g'(\mathbf{r}_2;\zeta_b,\mathbf{b},\mathbf{R}_b)u^2(\mathbf{c}|\mathbf{1}^{1,r_1}|\mathbf{d}). \tag{29}$$

Multiplying the recurrence formula for $(\mathbf{c}|\mathbf{i}^{1,r_1}|\mathbf{d})$ by $\zeta_{cd}+u^2$ we find

$$u^2(\mathbf{c}|\mathbf{1}^{1,r_1}|\mathbf{d}) = -\zeta_{cd}(r_{1i}-\mathbf{R}_{cd})(\mathbf{c}|\mathbf{0}^{r_1}|\mathbf{d})$$
$$+\frac{1}{2}\left[(\mathbf{c}-\mathbf{1}^i|\mathbf{1}^{1,r_1}|\mathbf{d}) + (\mathbf{c}|\mathbf{1}^{1,r_1}|\mathbf{d}-\mathbf{1}^i)\right] - \zeta_{cd}(\mathbf{c}|\mathbf{1}^{1,r_1}|\mathbf{d}), \tag{30}$$

where

$$\mathbf{R}_{cd} = (\zeta_c\mathbf{R}_c + \zeta_d\mathbf{R}_d)/\zeta_{cd}. \tag{31}$$

Referring to Eq.(23), and using Eqs. (25), (29), and (30), we arrive at

$$((\mathbf{a}+\mathbf{1}^i)\mathbf{b}|u|\mathbf{cd}) = (R_{ab,i}-R_{a,i})(\mathbf{ab}|u|\mathbf{cd}) + (R_{abcd,i}-R_{a,i})\frac{u^2}{\rho+u^2}(\mathbf{ab}|u|\mathbf{cd})$$
$$+\frac{1}{2\zeta_{ab}}\left(1-\frac{\rho}{\zeta_{ab}}\frac{u^2}{\rho+u^2}\right)\left[a_i((\mathbf{a}-\mathbf{1}^i)\mathbf{b}|u|\mathbf{cd}) + b_i(\mathbf{a}(\mathbf{b}-\mathbf{1}^i)|u|\mathbf{cd})\right]$$
$$+\frac{1}{2(\zeta_{ab}+\zeta_{cd})}\frac{u^2}{\rho+u^2}\left[c_i(\mathbf{ab}|u|(\mathbf{c}-\mathbf{1}^i)\mathbf{d}) + d_i\left(\mathbf{ab}|u|\mathbf{c}\left(\mathbf{d}-\mathbf{1}^i\right)\right)\right], \tag{32}$$

where

$$\mathbf{R}_{abcd} = \frac{\zeta_{ab}\mathbf{R}_{ab}+\zeta_{cd}\mathbf{R}_{cd}}{\zeta_{ab}+\zeta_{cd}}. \tag{33}$$

References