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Overlap Integrals Between s-, p- and d- Gaussian Functions

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Special analytic formulae for the overlap integrals between s-, p- and d-Gaussian functions are given. In contrast to general formulae, they have a simple form useful for numerical calculations.

Приводятся специальные аналитические формулы интегралов перекрывания для гауссовых функций типа s, p и d. По сравнению с общими формулами, преимуществом этих формул является простота их формы, удобная для численных расчетов.

V práci jsou uvedeny speciální analytické vzorce pro překryvové integrály mezi Gaussovými funkcemi typu s, p a d. Ve srovnání s obecnými vzorci je výhodou těchto vzorců jejich obzvlášť jednoduchý tvar, vhodný pro numerické výpočty.

The Gaussian functions of the type

$$(x - A_x)^l (y - A_y)^m (z - A_z)^n \exp(-ar_A^2)$$

belong to the most frequently used functions in quantum chemistry.

The overlap integrals between these functions can be evaluated according to general formulae given for example in [1] or [2] where also special formulae for s- and p-functions can be found. The use of these general formulae, however, is for d-functions time consuming and complicated. Therefore, we derived special formulae for the overlap integrals between s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ functions. The use of the formulae listed below leads to the reduction of the computer time by the factor 10–100. The convention $AB_i = A_i - B_i$, $i = x, y, z$ is used throughout. We assume here that $ij = xy$, xz or yz.

$$\langle s \mid s \rangle = \left(\frac{\pi}{a + b}\right)^{3/2} \exp\left(-\frac{ab}{a + b}\,\overline{AB}^2\right)$$

$$\langle s \mid p_i \rangle = \langle s \mid s \rangle \frac{a}{a + b} AB_i$$

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$$\langle p_i | s \rangle = -\langle s | s \rangle \frac{b}{a+b} AB_i$$

$$\langle s | d_{ij} \rangle = \langle s | s \rangle \left(\frac{a}{a+b}\right)^2 AB_i \, AB_j$$

$$\langle d_{ij} | s \rangle = \langle s | s \rangle \left(\frac{b}{a+b}\right)^2 AB_i \, AB_j$$

$$\langle s | d_{x^2-y^2} \rangle = \langle s | s \rangle \left(\frac{a}{a+b}\right)^2 (AB_x^2 - AB_y^2)$$

$$\langle d_{x^2-y^2} | s \rangle = \langle s | s \rangle \left(\frac{b}{a+b}\right)^2 (AB_x^2 - AB_y^2)$$

$$\langle s | d_{3z^2-r^2} \rangle = \langle s | s \rangle \left(\frac{a}{a+b}\right)^2 (2\,AB_z^2 - AB_x^2 - AB_y^2)$$

$$\langle d_{3z^2-r^2} | s \rangle = \langle s | s \rangle \left(\frac{b}{a+b}\right)^2 (2\,AB_z^2 - AB_x^2 - AB_y^2)$$

$$\langle p_i | p_j \rangle = \langle s | s \rangle \frac{1}{a+b} \left(0.5\delta_{ij} - \frac{ab}{a+b} AB_i \, AB_j\right)$$

$$\langle p_i | d_{jk} \rangle = \langle s | s \rangle \frac{a}{(a+b)^2} \left[0.5(\delta_{ij}AB_k + \delta_{ik}AB_j) - \frac{ab}{a+b} AB_i \, AB_j \, AB_k\right]$$

$$\langle d_{jk} | p_i \rangle = -\langle s | s \rangle \frac{b}{(a+b)^2} \left[0.5(\delta_{ij}AB_k + \delta_{ik}AB_j) - \frac{ab}{a+b} AB_i \, AB_j \, AB_k\right]$$

$$\langle p_i | d_{x^2-y^2} \rangle = \langle s | s \rangle \frac{a}{(a+b)^2} \left[\delta_{ix} - \delta_{iy} - \frac{ab}{a+b} (AB_x^2 - AB_y^2)\right] AB_i$$

$$\langle d_{x^2-y^2} | p_i \rangle = -\langle s | s \rangle \frac{b}{(a+b)^2} \left[\delta_{ix} - \delta_{iy} - \frac{ab}{a+b} (AB_x^2 - AB_y^2)\right] AB_i$$

$$\langle p_i | d_{3z^2-r^2} \rangle = \langle s | s \rangle \frac{a}{(a+b)^2} \left[2\delta_{iz} - \delta_{ix} - \delta_{iy} - \frac{ab}{a+b} (2\,AB_z^2 - \right.$$

$$\left. - AB_x^2 - AB_y^2)\right] AB_i$$

$$\langle d_{3z^2-r^2} | p_i \rangle = -\langle s | s \rangle \frac{b}{(a+b)^2} \left[2\delta_{iz} - \delta_{ix} - \delta_{iy} - \right.$$

$$\left. - \frac{ab}{a+b} (2\,AB_z^2 - AB_x^2 - AB_y^2)\right] AB_i$$

$$\langle d_{ij} \mid d_{kl} \rangle = \langle s \mid s \rangle \frac{1}{(a+b)^2} \Big[0.25 \delta_{ik} \delta_{jl} -$$

$$-0.5 \frac{ab}{a+b} (\delta_{ik} AB_j AB_l + \delta_{il} AB_j AB_k + \delta_{jk} AB_i AB_l +$$

$$+ \delta_{jl} AB_i AB_k) + \left(\frac{ab}{a+b} \right)^2 AB_i AB_j AB_k AB_l \Big]$$

$$\langle d_{ij} \mid d_{x^2-y^2} \rangle = \langle d_{x^2-y^2} \mid d_{ij} \rangle = -\langle s \mid s \rangle \frac{ab}{(a+b)^3} \times$$

$$\times \left[\delta_{ix} - \delta_{iy} - \delta_{jy} - \frac{ab}{a+b} (AB_x^2 - AB_y^2) \right] AB_i AB_j$$

$$\langle d_{ij} \mid d_{3z^2-r^2} \rangle = \langle d_{3z^2-r^2} \mid d_{ij} \rangle = -\langle s \mid s \rangle \frac{ab}{(a+b)^3} \times$$

$$\times \left[3\delta_{jz} - 2 - \frac{ab}{a+b} (2\, AB_z^2 - AB_x^2 - AB_y^2) \right] AB_i AB_j$$

$$\langle d_{x^2-y^2} \mid d_{x^2-y^2} \rangle = \langle s \mid s \rangle \frac{1}{(a+b)^2} \Big[1 - 2 \frac{ab}{a+b} (AB_x^2 + AB_y^2) +$$

$$+ \left(\frac{ab}{a+b} \right)^2 (AB_x^2 - AB_y^2)^2 \Big]$$

$$\langle d_{x^2-y^2} \mid d_{3z^2-r^2} \rangle = \langle d_{3z^2-r^2} \mid d_{x^2-y^2} \rangle = \langle s \mid s \rangle \frac{ab}{(a+b)^3} \times$$

$$\times \left[2 + \frac{ab}{a+b} (2\, AB_z^2 - AB_x^2 - AB_y^2) \right] (AB_x^2 - AB_y^2)$$

$$\langle d_{3z^2-r^2} \mid d_{3z^2-r^2} \rangle = \langle s \mid s \rangle \frac{1}{(a+b)^2} \Big\{ 3 - 2 \frac{ab}{a+b} \times$$

$$\times (4\, AB_z^2 + AB_x^2 + AB_y^2) + \left(\frac{ab}{a+b} \right)^2 [4\, AB_z^2 (AB_z^2 - AB_x^2 - AB_y^2) +$$

$$+ (AB_x^2 + AB_y^2)^2] \Big\}$$

References

[1] CLEMENTI E., DAVIS D. R.: J. Comp. Phys. *1* (1967), 223.
[2] HUZINAGA S.: Prog. Theor. Phys. (Supplement) *40* (1967), 52.