## (Tip-４-３） CGTO における重なり積分・分子コア積分・交換積分の具体的表現

すべての積分の計算の基本的ルールがわかる範囲を以下の表に示す。

$p=(\alpha+\beta)$　　　$q=(\gamma+\delta)$　　　$w=pq/(p+q)$

$s=\alpha\beta/(\alpha+\beta)=\alpha\beta/p$　　　$t=\gamma\delta/(\gamma+\delta)$

$x_p=\alpha/(\alpha+\beta)x_a+\beta/(\alpha+\beta)x_b$　　　$x_q=\gamma/(\gamma+\delta)x_c+\delta/(\gamma+\delta)x_d$　　　$x_s$ ; 原子 s（全原子）x 座標

＜$\triangle x_a = x_p - x_a = \beta/(\alpha+\beta)(x_b - x_a)$＞　　　＜$\nabla x_{pq} = x_p - x_q$＞　　　＜$\nabla x_p = x_p - x_s$＞

| 積分名 | 式 | | | 補助式 |
|---|---|---|---|---|
| | | 共通項 | 変化項 | |
| 重なり | $(S_aS_b)$ = | $(\pi/p)^{3/2}\cdot\exp(-sR_{ab}^2)$ | | |
| | $(x_a S_b)$ = | | $\triangle x_a$ | $\triangle x_a = x_p - x_a$ |
| | $(x_a x_b)$ = | | $\triangle x_a \triangle x_b + 1/(2p)$ | $\triangle x_b = x_p - x_b$ |
| | $(x_a y_b)$ = | | $\triangle x_a \triangle y_b$ | $\triangle y_b = y_p - y_b$ |
| ﾗﾌﾟﾗｽ | $[S_aS_b]$ | $(\pi/p)^{3/2}\cdot s\cdot\exp(-sR_{ab}^2)$ | $(3-2sR_{ab}^2)$ | |
| | $[x_a S_b]$ = | | $\triangle x_a(3-2sR_{ab}^2)+2\triangle x_a$ | |
| | $[x_a x_b]$ = | | $\triangle x_a \triangle x_b(3-2sR_{ab}^2)$<br>$+2\triangle x_a \triangle x_b$<br>$+\triangle x_a 2\triangle x_b$<br>$+1/(2p)(3-2sR_{ab}^2)$<br>$+2/(2p)$ | |
| | $[x_a y_b]$ = | | $\triangle x_a \triangle y_b(3-2sR_{ab}^2)$<br>$+2\triangle x_a y_b$<br>$+\triangle x_a 2\triangle y_b$ | |
| ｸｰﾛﾝ | ＜$S_aS_b$＞= | $Z_s\cdot 2\pi/p\cdot\exp(-sR_{ab}^2)$ | $F0(X)$ | $X = p^{1/2}R_s$<br>$F0(X)=\ \mathrm{erf}(X)/X = (1/X)\int^{\infty} e^{-u^2}du$ |
| | ＜$x_a S_b$＞= | | $\triangle x_a$ $\cdot F0$<br>$+(1/2p)\nabla x_p$ $\cdot p\cdot F0X/X$ | $\nabla x_p = x_p - x_s$<br>$F0X=(\exp(-X^2)-F0(X))/X$ |
| | ＜$x_a\ x_b$＞= | | $\triangle x_a \cdot \triangle x_b$ $\cdot F0$<br>$+\triangle x \cdot (1/2p)\nabla x_p$ $\cdot p\cdot F0X/X$<br>$+(1/2p)\nabla x_p\cdot\triangle x_b$ $\cdot p\cdot F0X/X$<br>$+(1/2p)\nabla x_p\cdot(1/2p)\nabla x_p$ $\cdot p^2\cdot F0X3/X^2$<br>$+(1/2p)\cdot(1/2p)$ $\cdot p\cdot F0X/X$<br>$+(1/2p)$ $\cdot F0$ | $F0X3=-(2X\exp(-X^2)-3F0X)/X$ |
| | ＜$x_a y_a$＞= | | $\triangle x_a\cdot\triangle y_b$ $\cdot F0$<br>$+\triangle x_a\cdot(1/2p)\nabla y_p$ $\cdot p\cdot F0X/X$<br>$+(1/2p)\nabla x_p\cdot\triangle y_p$ $\cdot p\cdot F0X/X$<br>$+(1/2p)\nabla x_p\cdot(1/2p)\nabla y_p$ $\cdot p^2\cdot F0X3/X^2$ | $\nabla y_p = y_p - y_s$ |

| | | | | |
|---|---|---|---|---|
| **交換** | $(S_aS_b \mid S_cS_d)=$ | $= 2(\pi)^{5/2}\cdot(1/(pq(p+q)^{1/2}))\cdot\exp(-sR_{ab}^2)\exp(-tR_{cd}^2)$ | $F0(X)$ | $X=((pq/(p+q))^{1/2}R_{pq}$<br>$F0(X)=erf(X)/X$ |
| | $(x_aS_b \mid S_cS_d)=$ | | $\triangle x_a \cdot F0$<br>$+(1/2p)\nabla x_{pq} \cdot w \cdot F0X/X$ | $\nabla x_{pq}=x_p-x_q$ |
| | $(x_ax_b \mid S_cS_d)=$ | | $\triangle x_a \cdot \triangle x_b \cdot F0$<br>$+\triangle x_a \cdot (1/2p)\nabla x_{pq} \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_b \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla x_{pq} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2p) \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot F0$ | $F0X3=(-2X\exp(-X^2)-3F0(X))/X$ |
| | $(x_aS_b \mid x_cS_d)=$ | | $\triangle x_a \cdot \triangle x_c \cdot F0$<br>$+\triangle x_a \cdot (1/2q)\nabla x_{qp} \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_c \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (-1/2q) \cdot w \cdot F0X/X$ | $\nabla x_{qp}=x_q-x_p$ |
| | $(x_ay_b \mid S_cS_d)=$ | | $\triangle x_a \cdot \triangle y_b \cdot F0$<br>$+\triangle x_a \cdot (1/2p)\nabla y_{pq} \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle y_b \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla y_{pq} \cdot w^2 \cdot F0X3/X^2$ | $\nabla y_{pq}=y_p-y_q$ |
| | $(x_aS_b \mid y_cS_d)=$ | | $\triangle x_a \cdot \triangle y_c \cdot F0$<br>$+\triangle x_a \cdot (1/2p)\nabla y_{qp} \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle y_c \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla y_{qp} \cdot w^2 \cdot F0X3/X^2$ | $\nabla y_{qp}=y_q-y_p$ |
| | $(x_ax_b \mid x_cS_d)=$ | | $\triangle x_a \cdot \triangle x_b \cdot \triangle x_c \cdot F0$<br>$+\triangle x_a \cdot (1/2p)\nabla x_{pq} \cdot \triangle x_c \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_b \cdot \triangle x_c \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla x_{pq} \cdot \triangle x_c \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2p) \cdot \triangle x_c \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot \triangle x_c \cdot F0$<br>$+\triangle x_a \cdot \triangle x_b \cdot (1/2q)\nabla x_{qp} \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_b \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot (1/2p)\nabla x_{pq} \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla x_{pq} \cdot (1/2q)\nabla x_{qp} \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p) \cdot (1/2p) \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2q)\nabla x_{qp} \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot \triangle x_b \cdot (-1/2q) \cdot w \cdot F0X/X$<br>$+\triangle x_a \cdot (1/2p) \cdot (-1/2q) \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot (1/2p)\nabla x_{pq} \cdot (-1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p) \cdot (-1/2q) \cdot w^2 \cdot F0X3/X^2$ | $F0X5=(4X^2\exp(-X^2)-5F0(X))/X$ |
| | $(x_ay_b \mid x_cS_d)=$ | | $\triangle x_a \cdot \triangle y_b \cdot \triangle x_c \cdot F0$<br>$+\triangle x_a \cdot (1/2p)\nabla y_{pq} \cdot \triangle x_c \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle y_b \cdot \triangle x_c \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla y_{pq} \cdot \triangle x_c \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot \triangle y_b \cdot (1/2q)\nabla x_{qp} \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle y_b \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot (1/2p)\nabla y_{pq} \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla y_{pq} \cdot (1/2q)\nabla x_{qp} \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p) \cdot \triangle y_b \cdot (-1/2q) \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot (1/2p)\nabla y_{pq} \cdot (-1/2q) \cdot w^2 \cdot F0X3/X^2$ | |

| | | | | |
|---|---|---|---|---|
| | $(x_a x_b \mid x_c x_d) =$ | | $\triangle x_a \cdot \triangle x_b \cdot \triangle x_c \cdot \triangle x_d \cdot F0$<br>$+\triangle x_a \cdot (1/2p)\nabla x_{pq} \cdot \triangle x_c \cdot \triangle x_d \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_b \cdot \triangle x_c \cdot \triangle x_d \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla x_{pq} \cdot \triangle x_c \cdot \triangle x_d \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2p) \cdot \triangle x_c \cdot \triangle x_d \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot \triangle x_c \cdot \triangle x_d \cdot F0$<br>$+\triangle x_a \cdot \triangle x_b \cdot (1/2q)\nabla x_{qp} \cdot \triangle x_d \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_b \cdot (1/2q)\nabla x_{qp} \cdot \triangle x_d \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot (1/2p)\nabla x_{pq} \cdot (1/2q)\nabla x_{qp} \cdot \triangle x_d \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla x_{pq} \cdot (1/2q)\nabla x_{qp} \cdot \triangle x_d \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p) \cdot (1/2p) \cdot (1/2q)\nabla x_{qp} \cdot \triangle x_d \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2q)\nabla x_{qp} \cdot \triangle x_d \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot \triangle x_b \cdot (-1/2q) \cdot \triangle x_d \cdot w \cdot F0X/X$<br>$+\triangle x_a \cdot (1/2p) \cdot (-1/2q) \cdot \triangle x_d \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot (1/2p)\nabla x_{pq} \cdot (-1/2q) \cdot \triangle x_d \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p) \cdot (-1/2q) \cdot \triangle x_d \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot \triangle x_b \cdot \triangle x_c \cdot (1/2q)\nabla x_{qp} \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_b \cdot \triangle x_c \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot (1/2p)\nabla x_{pq} \cdot \triangle x_c \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla x_{pq} \cdot \triangle x_c \cdot (1/2q)\nabla x_{qp} \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p) \cdot (1/2p) \cdot \triangle x_c \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot \triangle x_c \cdot (1/2q)\nabla x_{qp} \cdot w \cdot F0X/X$<br>$+\triangle x_a \cdot \triangle x_b \cdot (1/2q)\nabla x_{qp} \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_b \cdot (1/2q)\nabla x_{qp} \cdot (1/2q)\nabla x_{qp} \cdot w^3 \cdot F0X5/X^3$<br>$+\triangle x_a \cdot (1/2p)\nabla x_{pq} \cdot (1/2q)\nabla x_{qp} \cdot (1/2q)\nabla x_{qp} \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla x_{pq} \cdot (1/2q)\nabla x_{qp} \cdot (1/2q)\nabla x_{qp} \cdot w^4 \cdot F0X7/X^4$<br>$+(1/2p) \cdot (1/2p) \cdot (1/2q)\nabla x_{qp} \cdot (1/2q)\nabla x_{qp} \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p) \cdot (1/2q)\nabla x_{qp} \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot \triangle x_b \cdot (-1/2q) \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot (1/2p) \cdot (-1/2q) \cdot (1/2q)\nabla x_{qp} \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2p)\nabla x_{pq} \cdot (-1/2q) \cdot (1/2q)\nabla x_{qp} \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p) \cdot (-1/2q) \cdot (1/2q)\nabla x_{qp} \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p) \cdot \triangle x_b \cdot \triangle x_c \cdot (-1/2q) \cdot w \cdot F0X/X$<br>$+\triangle x_a \cdot (1/2p) \cdot \triangle x_c \cdot (-1/2q) \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot (1/2p)\nabla x_{pq} \cdot \triangle x_c \cdot (-1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p)\ \nabla x_{pq} \cdot (1/2p) \cdot \triangle x_c \cdot (-1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot \triangle x_b \cdot (1/2q) \cdot (1/2q) \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot \triangle x_b \cdot (1/2q)\nabla x_{qp} \cdot (-1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_b \cdot (1/2q) \cdot (1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot (1/2p) \cdot (1/2q)\nabla x_{qp} \cdot (-1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot (1/2p)\nabla x_{pq} \cdot (1/2q) \cdot (1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2p)\nabla x_{pq} \cdot (1/2q)\nabla x_{qp} \cdot (-1/2q) \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p) \cdot (1/2q)\nabla x_{qp} \cdot (-1/2q) \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla x_{pq} \cdot (1/2q) \cdot (1/2q) \cdot w^3 \cdot F0X5/X^3$<br>$+(1/2p) \cdot (1/2p) \cdot (1/2q) \cdot (1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2q) \cdot (1/2q) \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot (1/2p) \cdot (-1/2q) \cdot (-1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2p) \cdot (-1/2q) \cdot (-1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+\triangle x_a \cdot \triangle x_b \cdot (1/2q) \cdot F0$<br>$+(1/2p)\nabla x_{pq} \cdot \triangle x_b \cdot (1/2q) \cdot w \cdot F0X/X$<br>$+\triangle x_a \cdot (1/2p)\nabla x_{pq} \cdot (1/2q) \cdot w \cdot F0X/X$<br>$+(1/2p)\nabla x_{pq} \cdot (1/2p)\nabla x_{pq} \cdot (1/2q) \cdot w^2 \cdot F0X3/X^2$<br>$+(1/2p) \cdot (1/2p) \cdot (1/2q) \cdot w \cdot F0X/X$<br>$+(1/2p) \cdot (1/2q) \cdot F0$ | $F0X7 = (-8X^3 \exp(-X^2)$<br>$-7F0(X)) / X$ |

上表に出てくる誤差関数を含む関数系は微小なXに対し以下の如く展開できる

$\exp(-x^2) = \Sigma_{n=0}(-1)^n \frac{1}{n!} x^{2n} = 1-x^2+1/2x^4-1/6x^6+1/24x^8 \cdots$

$F0(x) = \int \exp(-x^2)dx/x$

$= \Sigma_{n=0}(-1)^n \frac{1}{n!} \frac{1}{2n+1} x^{2n} = 1-1/3x^2+1/10x^4-1/42x^6+\cdots$

$F0X(x)/x = (-F0+\exp(-x^2))/x^2$

$= \Sigma_{n=0}(-1)^n \frac{1}{n!} \frac{-2}{2n+3} x^{2n} = -2/3+2/5x^2-1/7x^4+\cdots$

$F0X3(x)/x^2 = (-3F0X-2x\cdot\exp(-x^2))/x^3$

$= \Sigma_{n=0}(-1)^n \frac{1}{n!} \frac{4}{2n+5} x^{2n} = 4/5-4/7x^2+2/9x^4-\cdots$

$F0X5(x)/x^3 = (-5F0X3+4x^2\cdot\exp(-x^2))/x^4$

$= \Sigma_{n=0}(-1)^n \frac{1}{n!} \frac{-8}{2n+7} x^{2n} = -8/7+8/9x^2-8/22x^4+\cdots$

$F0X7(x)/x^4 = (-7F0X5-8x^3\cdot\exp(-x^2))/x^5$

$= \Sigma_{n=0}(-1)^n \frac{1}{n!} \frac{16}{2n+9} x^{2n} = 16/9-16/11x^2+8/13x^4-\cdots$

$F0X9(x)/x^5 = (-9F0X7+16x^4\cdot\exp(-x^2))/x^6$

$= \Sigma_{n=0}(-1)^n \frac{1}{n!} \frac{-32}{2n+11} x^{2n} = -32/11+32/13x^2-16/15x^4+\cdots$

<u>誤差関数</u>計算プログラムが内臓されていない場合は、下記の方法で求めることができる。

(1) 近似式１ （ 誤差：0.00000028、 ６桁 ）

$erf(x) = \sqrt{\pi}/2 \{ 1-1/(1+\Sigma a_i x^i)^{16} \}$

$a_1$=0.0705230784
$a_2$=0.0422820123
$a_3$=0.0092705272
$a_4$=0.0001520143
$a_5$=0.0002765672
$a_6$=0.0000430638

(2) 近似式２ （erf=0 at x<10^(-6)）

$erf(x) = \sqrt{\pi}/2 \{ 1-\exp(-x2)\Sigma [a_i/(1+px)^i] \}$

p =0.3275911
$a_1$=0.254829592
$a_2$=−0.284496736
$a_3$=1.421413741
$a_4$=−1.453152027
$a_5$=1.061405429