(Tip-６-３）　<u>＜拡張 Hückel 法とその計算法＞ の 補足　－ 4P 軌道までの計算のために</u>

（補足の補足の１）重なり積分の一般式（σ、π　表現）

スレーター型軌道は、一般的に、ｒの最高次数のみを用い、主量子数 n、軌道ｗ（＝s,p,d）に対し以下の如く表す。

$$\chi_{nw} = K_{nw} \cdot \mu^{3/2+(n-1)} \cdot \left\{ \begin{array}{ll} r^{n-1} \cdot & 1 \\ r^{n-2} \cdot & x,y,z \\ r^{n-3} \cdot & x^2, y^2, z^2, xy, yz, zx \end{array} \right\} \cdot e^{-\mu r} \quad \begin{array}{l} \text{for s 軌道} \\ \text{for p 軌道} \\ \text{for d 軌道} \end{array}$$

または、{　} 内を $U_w$ と表すと

$$\chi_{nw} = K_{nw} \cdot \mu^{3/2+(n-1)} \cdot U_w \cdot e^{-\mu r}$$

ここに、規格化 ie $\int \chi_{nw}\chi_{nw}\, d\tau = 1$ となるために

$K_{1s} = 1/\sqrt{\pi}$

$K_{2s} = 1/\sqrt{3\pi}$　　$K_{2p} = 1/\sqrt{\pi}$

$K_{3s} = \sqrt{2/(45\pi)}$　　$K_{3p} = \sqrt{2/(15\pi)}$　　$K_{3d\triangle\triangle} = \sqrt{2/(3\pi)}$　　$K_{3d\triangle 2} = \sqrt{2/(9\pi)}$

$K_{4s} = 1/\sqrt{315\pi}$　　$K_{4p} = 1/\sqrt{105\pi}$

また、r in Å（$a_0 = 0.5292$Å）として

$$\mu = Z/a_0$$

x 座標を原子 a と原子 b を結ぶ直線で a から b へ向かう線にとるとると、楕円座標では

$x_a = r_a \cos\theta_a$　　　$x_b = r_b \cos\theta_b$

$y_a = r_a \sin\theta_a \cos\phi$　　　$y_b = r_b \sin\theta_b \cos\phi$

$z_a = r_a \sin\theta_a \sin\phi$　　　$y_b = r_b \sin\theta_b \sin\phi$

$\cos\theta_a = (\xi\eta + 1)/(\xi + \eta)$　　$\sin\theta_a = \sqrt{(\xi^2-1)(1-\eta^2)}/(\xi + \eta)$

$\cos\theta_b = (\xi\eta - 1)/(\xi - \eta)$　　$\sin\theta_b = \sqrt{(\xi^2-1)(1-\eta^2)}/(\xi - \eta)$

よって、$r_a = (R/2)\cdot(\xi+\eta)$、$r_b = (R/2)\cdot(\xi-\eta)$であるから、$m = n-1$ と表すこととして、$U_w$は、原子 a、原子 b それぞれに対し、$U_{w,a}$、$U_{w,b}$(簡単のため $U_a$、$U_b$ とも略す)として、各ｗにつき以下の通りとなる。

$U_s = U_{s,a}$ or $U_{s,b}$　　＜ $= (R/2)^{ma+mb} \cdot f(\xi, \eta, ma, mb)$　＞

$r_a^{\,n-1} = (R/2)^{n-1}(\xi+\eta)^{n-1} = (R/2)^{ma}\cdot(\xi+\eta)^{ma}$

$r_b^{\,n-1} = (R/2)^{n-1}(\xi+\eta)^{n-1} = (R/2)^{mb}\cdot(\xi+\eta)^{mb}$

$U_p = U_{p,a}$　　＜ $= (R/2)^{ma+mb} \cdot f(\xi, \eta, ma, mb)$　＞

$r_a^{\,n-2} x_a = r_a^{\,n-1}\cos\theta_a = (R/2)^{ma}\cdot(\xi+\eta)^{ma}\cdot(\xi\eta+1)/(\xi+\eta)$

$= (R/2)^{ma}\cdot(\xi+\eta)^{ma-1}\cdot(\xi\eta+1)$

$r_a^{\,n-2} y_a = r_a^{\,n-1}\sin\theta_a\cos\phi = (R/2)^{ma}\cdot(\xi+\eta)^{ma}\cdot\sqrt{(\xi^2-1)(1-\eta^2)}/(\xi+\eta)\cdot\cos\phi$

$= (R/2)^{ma}\cdot(\xi+\eta)^{ma-1}\cdot\sqrt{(\xi^2-1)(1-\eta^2)}\cdot\cos\phi$

$r_a^{\,n-2} z_a = r_a^{\,n-1}\sin\theta_a\sin\phi = (R/2)^{ma}\cdot(\xi+\eta)^{ma}\cdot\sqrt{(\xi^2-1)(1-\eta^2)}/(\xi+\eta)\cdot\sin\phi$

$= (R/2)^{ma}\cdot(\xi+\eta)^{ma-1}\cdot\sqrt{(\xi^2-1)(1-\eta^2)}\cdot\sin\phi$

$U_p = U_{p,b}$　　＜ $= (R/2)^{ma+mb} \cdot f(\xi, \eta, ma, mb)$　＞

$r_b^{\,n-2} x_b = r_b^{\,n-1}\cos\theta_b = (R/2)^{mb}\cdot(\xi-\eta)^{mb-1}\cdot(\xi\eta-1)$

$r_b^{\,n-2} y_b = r_b^{\,n-1}\sin\theta_b\cos\phi = (R/2)^{mb}\cdot(\xi-\eta)^{mb-1}\cdot\sqrt{(\xi^2-1)(1-\eta^2)}\cdot\cos\phi$

$r_b^{\,n-2} z_b = r_b^{\,n-1}\sin\theta_b\sin\phi = (R/2)^{mb}\cdot(\xi-\eta)^{mb-1}\cdot\sqrt{(\xi^2-1)(1-\eta^2)}\cdot\sin\phi$

$U_{d\triangle 2}=U_{d\triangle 2,a}$ < $=(R/2)^{ma+mb}\cdot f(\xi,\eta,ma,mb)$ >

$r_a^{\,n-3}x_a^2=r_a^{\,n-1}\cos^2\theta_a = (R/2)^{ma}\cdot(\xi+\eta)^{ma}\cdot(\xi\eta+1)^2/(\xi+\eta)^2$

$= (R/2)^{ma}\cdot(\xi+\eta)^{ma-2}\cdot(\xi\eta+1)^2$

$r_a^{\,n-3}y_a^2=r_a^{\,n-1}\sin^2\theta_a\cos^2\phi = (R/2)^{ma}\cdot(\xi+\eta)^{ma-2}\cdot(\xi^2-1)^2(1-\eta^2)^2\cdot\cos^2\phi$

$r_a^{\,n-3}z_a^2=r_a^{\,n-1}\sin^2\theta_a\sin^2\phi = (R/2)^{ma}\cdot(\xi+\eta)^{ma-2}\cdot(\xi^2-1)^2(1-\eta^2)^2\cdot\sin^2\phi$

$U_{d\triangle 2}=U_{d\triangle 2,b}$ < $=(R/2)^{ma+mb}\cdot f(\xi,\eta,ma,mb)$ >

$r_b^{\,n-3}x_b^2=r_b^{\,n-1}\cos^2\theta_b = (R/2)^{mb}\cdot(\xi-\eta)^{mb-2}\cdot(\xi\eta-1)^2$

$r_b^{\,n-3}y_b^2=r_b^{\,n-1}\sin^2\theta_b\cos^2\phi = (R/2)^{mb}\cdot(\xi-\eta)^{mb-2}\cdot(\xi^2-1)^2(1-\eta^2)^2\cdot\cos^2\phi$

$r_b^{\,n-3}z_b^2=r_b^{\,n-1}\sin^2\theta_b\sin^2\phi = (R/2)^{mb}\cdot(\xi-\eta)^{mb-2}\cdot(\xi^2-1)^2(1-\eta^2)^2\cdot\sin^2\phi$

$U_{d\triangle\triangle}=U_{d\triangle\triangle,a}$ < $=(R/2)^{ma+mb}\cdot f(\xi,\eta,ma,mb)$ >

$r_a^{\,n-3}x_a y_a = r_a^{\,n-1}\cos\theta_a\sin\theta_a\cos\phi$

$= (R/2)^{ma}\cdot(\xi+\eta)^{ma}\cdot(\xi\eta+1)\sqrt{(\xi^2-1)(1-\eta^2)}/(\xi+\eta)^2\cdot\cos\phi$

$= (R/2)^{ma}\cdot(\xi+\eta)^{ma-2}\cdot(\xi\eta+1)\sqrt{(\xi^2-1)(1-\eta^2)}\cdot\cos\phi$

$r_a^{\,n-3}y_a z_a = r_a^{\,n-1}\sin^2\theta_a\cos\phi\sin\phi$

$= (R/2)^{ma}\cdot(\xi+\eta)^{ma-2}\cdot(\xi^2-1)(1-\eta^2)\cdot\cos\phi\sin\phi$

$r_a^{\,n-3}z_a x_a = r_a^{\,n-1}\sin\theta_a\cos\theta_a\sin\phi$

$= (R/2)^{ma}\cdot(\xi+\eta)^{ma-2}\cdot\sqrt{(\xi^2-1)(1-\eta^2)}\cdot\sin\phi$

$U_{d\triangle\triangle}=U_{d\triangle\triangle,b}$ < $=(R/2)^{ma+mb}\cdot f(\xi,\eta,ma,mb)$ >

$r_b^{\,n-3}x_b y_b = r_b^{\,n-1}\cos\theta_b\sin\theta_b\cos\phi$

$= (R/2)^{mb}\cdot(\xi-\eta)^{mb-2}\cdot(\xi\eta-1)\sqrt{(\xi^2-1)(1-\eta^2)}\cdot\cos\phi$

$r_b^{\,n-3}y_b z_b = r_b^{\,n-1}\sin^2\theta_b\cos\phi\sin\phi$

$= (R/2)^{mb}\cdot(\xi-\eta)^{mb-2}\cdot(\xi^2-1)(1-\eta^2)\cdot\cos\phi\sin\phi$

$r_b^{\,n-3}z_b x_b = r_b^{\,n-1}\sin\theta_b\cos\theta_b\sin\phi$

$= (R/2)^{mb}\cdot(\xi+\eta)^{mb-2}\cdot\sqrt{(\xi^2-1)(1-\eta^2)}\cdot\sin\phi$

（σ、π　表現）の重なり積分 **$((nw_a, n'w'_b))$** は、一般式として

**$((nw_a, n'w'_b))$**

$= \int \chi_{nw,a}\,\chi_{n'w',b}\,d\tau$

$= \int K_{nw}\cdot\mu_a^{3/2+(n-1)}\cdot U_w\cdot e^{-\mu_a r_a}\cdot K_{n'w'}\cdot\mu_b^{3/2+(n'-1)}\cdot U_{w'}\cdot e^{-\mu_b r_b}\,d\tau$

$\equiv K_aK_b\int\mu_a^{3/2+(n-1)}\cdot\mu_b^{3/2+(n'-1)}\cdot U_aU_b\cdot e^{-(\mu_a r_a+\mu_b r_b)}\,d\tau$

$= K_aK_b\int\mu_a^{3/2+(n-1)}\cdot\mu_b^{3/2+(n'-1)}\cdot U_aU_b\cdot e^{-(\mu_a r_a+\mu_b r_b)}\cdot(R/2)^3(\xi^2-\eta^2)\,d\xi\,d\eta\,d\phi$

ここに、$U_a$に含まれる y の数を nya、z の数を nza、また、$U_b$に含まれる y の数を nyb、z の数を nza、さらに、ny = nya + nyb、nz = nza + nzb とし $U_aU_b=V_{ab}\cos^{ny}\phi\sin^{nz}\phi$ とすると

$= K_aK_b\int\mu_a^{3/2+(n-1)}\cdot\mu_b^{3/2+(n'-1)}\cdot V_{ab}\cdot e^{-(\mu_a r_a+\mu_b r_b)}\cdot(R/2)^3(\xi^2-\eta^2)\,d\xi\,d\eta$

$\cdot\int\cos^{ny}\phi\sin^{nz}\phi\,d\phi$

ここで、Nyz を

$Nyz\equiv\int\cos^{ny}\phi\sin^{nz}\phi\,d\phi$

| | for ny= | nz= |
|---|---|---|
| $=2\pi$ | 0 | 0 |
| $=\pi$ | 2 | 0 |
| $=(3/4)\pi$ | 4 | 0 |
| $=\pi$ | 0 | 2 |
| $=(1/4)\pi$ | 2 | 2 |
| $=(3/4)\pi$ | 0 | 4 |
| $=0$ | for　上記以外 | |

と定義すると、

$= K_aK_b\,Nyz\int\mu_a^{3/2+(n-1)}\cdot\mu_b^{3/2+(n'-1)}\cdot V_{ab}\cdot e^{-(\mu_a r_a+\mu_b r_b)}\cdot(R/2)^3(\xi^2-\eta^2)\,d\xi\,d\eta$

また、Vab は、

$$Vab = (R/2)^{ma+mb} \cdot f(\xi, \eta, ma, mb)$$

と書けるので、ma = n－1、mb = n'－１を考慮して、

$$= K_a K_b\, Nyz \int \mu_a{}^{3/2+ma} \cdot \mu_b{}^{3/2+mb} \cdot (R/2)^{ma+mb+3}$$
$$\cdot\ f(\xi, \eta, ma, mb)\,(\xi^2 - \eta^2)\ \cdot e^{-p(\xi+\eta t)}\, d\xi\, d\eta$$

さらに、g( ξ , η , ma, mb)≡ f( ξ , η , ma, mb) ( ξ ²－ η ²)とおくと

$$\equiv K_a K_b\, Nyz \cdot \mu_a{}^{3/2+ma} \cdot \mu_b{}^{3/2+mb} \cdot (R/2)^{ma+mb+3}$$
$$\cdot\ \int g(\xi, \eta, ma, mb) \cdot e^{-p(\xi+\eta t)}\, d\xi\, d\eta$$
$$\equiv K_a K_b\, Nyz \cdot \mu_a{}^{3/2+ma} \cdot \mu_b{}^{3/2+mb} \cdot (R/2)^{ma+mb+3} \cdot G(An,Bm)$$
$$= K_a K_b\, Nyz \cdot \mu_a{}^{3/2+ma} \cdot \mu_b{}^{3/2+mb} \cdot (p/2)^{ma+mb+3}\,(1-t^2)^{(ma+mb+3)/2}\,(\mu_a \mu_b)^{-(ma+mb+3)/2}$$
$$\cdot\ G(A_u, B_v)$$
$$= K_a K_b\, Nyz \cdot\ (p/2)^{ma+mb+3}\,(1-t^2)^{(ma+mb+3)/2}\,(\mu_b/\mu_a)^{(mb-ma)/2} \cdot G(A_u, B_v)$$

ここに、G(A$_n$ , B$_n$) は

$$G(A_u, B_v) = \int g(\xi, \eta, ma, mb) \cdot e^{-p(\xi+\eta t)}\, d\xi\, d\eta$$
$$= \int g'(\xi^u, \eta^u) \cdot e^{-p(\xi+\eta t)}\, d\xi\, d\eta$$
$$A_n = \int_1^{\infty} \xi^n\, e^{-p\xi}\, d\xi$$
$$B_n = \begin{cases} \int_{-1}^{1} \eta^n\, d\eta = \{(1)^{n+1} - (-1)^{n+1}\} / (n+1) & \textbf{< for t = 0 >} \\ \int_{-1}^{1} \eta^n\, e^{-p\eta t}\, d\eta = (1/(pt)^{n+1}) \cdot \int_{-pt}^{pt} v^n\, e^{-v} dv & \textbf{< for t} \neq \textbf{0 >} \end{cases}$$

結局、 $\mu_b/\mu_a = (1-t)/(1+t)$であるから

$$= \mathbf{K_{nw,,a}\, K_{n'w',b} \cdot Nyz \cdot (p/2)^{(3+ma+mb)} \cdot (1-t^2)^{(3+2ma)/2} \cdot (1-t)^{(mb-ma)} \cdot G(A_u, B_v)}$$

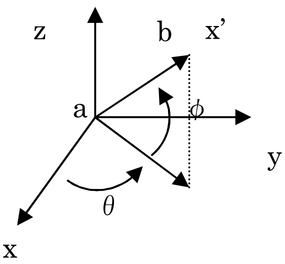
これが、**(σ、π　表現) の重なり積分**である。

## （補足の補足の２）重なり積分の一般式（一般座標 x,y,z 表現）

これまで求めた重なり積分は、原子間を結ぶ方向を x’ 軸とすると、2pσは 2px’、2pπは 2py’、2pz’ となる。従い、一般的に $\mathbf{v}\,(x, y, z)$を$\mathbf{v'}\,(x', y', z')$に変換する座標変換行列を T とすると

$$\mathbf{v'} = \mathbf{T}\,\mathbf{v}$$

$$T = \begin{pmatrix} \cos\phi\cos\theta & \cos\phi\sin\theta & \sin\phi \\ -\sin\theta & \cos\theta & 0 \\ -\sin\phi\cos\theta & -\sin\phi\sin\theta & \cos\phi \end{pmatrix}$$




逆に、

$$\mathbf{v} = \mathbf{T}^{-1}\,\mathbf{v'} = \mathbf{T}^{t}\,\mathbf{v'}$$

また

$$x_a = x - x_a\ ,\quad y_a = y - y_a\ ,\ z_a = z - z_a\ ,\quad r_a^{\,2} = x_a^{\,2} + y_a^{\,2} + z_a^{\,2}$$

$$(x_a, y_a, z_a)^t = \mathbf{T}^t\,(x', y', z')^t - \mathbf{T}^t\,(x_a', y_b', z_c')^t = \mathbf{T}^t\,(x_a', y_a', z_a')^t$$

$$r_a^2 = \mathbf{r}_a^{\,t}\,\mathbf{r}_a = (x_a, y_a, z_a)\,(x_a, y_a, z_a)^t = (x_a', y_a', z_a')\,\mathbf{T}\cdot\mathbf{T}^t\,(x_a', y_a', z_a')^t$$
$$= (x_a', y_a', z_a')\,(x_a', y_a', z_a')^t = \mathbf{r}_a'^{\,t}\,\mathbf{r}_a' = r_a'^2$$

スレーター型軌道を、 r の最高次数のみを用い、主量子数 n、軌道ｗ（＝s,p,d）に対し、

$$\chi_{Nw} = K_{Nw}\cdot\mu^{3/2+(n-1)}\cdot\left\{\begin{array}{ll} r^{n-1}\ \cdot & 1 \\ r^{n-2}\ \cdot & x,y,z \\ r^{n-3}\ \cdot & x^2, y^2, z^2, xy, yz, zx \end{array}\right\}\cdot e^{-\mu r} \qquad \begin{array}{l} \text{for s 軌道} \\ \text{for p 軌道} \\ \text{for d 軌道} \end{array}$$

ここに、規格化 ie $\int\chi_{Nw}\chi_{Nw}\,d\tau = 1$ となるために

$K_{1s} = 1/\sqrt{\pi}$

$K_{2s} = 1/\sqrt{3\pi}$　　$K_{2p} = 1/\sqrt{\pi}$

$K_{3s} = \sqrt{2/(45\pi)}$　　$K_{3p} = \sqrt{2/(15\pi)}$　　$K_{3d\triangle\triangle} = \sqrt{2/(3\pi)}$　　$K_{3d\triangle 2} = \sqrt{2/(9\pi)}$

$K_{4s} = 1/\sqrt{315\pi}$　　$K_{4p} = 1/\sqrt{105\pi}$

と表したが、更に{ } 内$U_w$を $R_{Nw}\,(r^{N-1}, r^{N-2}, r^{N-3})$、$Q_w = q^{w1}q^{w2}$ ( $q^{w1}, q^{w2}$ : 1,x,y,z）を用い

$U_w \equiv R_{Nw}\cdot Q_w$　　(ex)　$Q_s = 1\cdot 1$　ie　$q^{s1}=1,\ \ q^{s2}=1$　　for s 軌道

$Q_p = x\cdot 1$　ie　$q^{p1}=x,\ \ q^{p2}=1$　　for p 軌道

$Q_d = x\cdot y$　ie　$q^{d1}=x,\ \ q^{d2}=y$　　for d 軌道

$$C_{Nw} = K_{Nw}\cdot\mu^{3/2+(n-1)}\cdot R_{Nw}\cdot e^{-\mu r}$$

と表すと

$$\chi_{Nw} = C_{Nw}\cdot Q_w$$

であるから、行列 S ( $s_{ij}$ )を以下の如く定義すると、

$$\mathbf{S} = \begin{pmatrix} s_{11} & s_{12} & s_{13} & s_{14} \\ s_{21} & s_{22} & s_{23} & s_{24} \\ s_{31} & s_{32} & s_{33} & s_{34} \\ s_{41} & s_{42} & s_{43} & s_{44} \end{pmatrix} = \begin{pmatrix} 1 & 0 \quad 0 \quad 0 \\ \begin{matrix} 0 \\ 0 \\ 0 \end{matrix} & \boxed{\quad \mathbf{T}^t \quad} \end{pmatrix}$$

ベクトル $\mathbf{q} = (1,x,y,z)^t$、 $\mathbf{q'} = (1,x',y',z')^t$ は、

$$\mathbf{q} = \mathbf{S}\cdot\mathbf{q'} \qquad \text{ie} \qquad q^{w1} = q_i = \Sigma_i\ s_{ij}\cdot q'_j\ \ (i=1\text{-}4)$$
$$q^{w2} = q_i = \Sigma_i\ s_{ij}\cdot q'_j\ \ (i=1\text{-}4)$$

従って、

$$d\tau = d\tau'$$

を考慮すると、**重なり積分（$Nw_a$, $N'w'_b$）**は、

$$(\mathbf{Nw_a}, \mathbf{N'w'_b}) = \int\chi_{Nw,a}\ \chi_{N'w',b}\ d\tau$$
$$= \int (C_{Nw,a}\,Q_{w,a})(C_{N'w',b}\,Q_{w',b})\ d\tau$$
$$= \int (Q_{w,a}\ Q_{w',b})\,C_{Nw,a}\ C_{N'w',b}\ d\tau$$
$$= \int (\ q^{w1,a}q^{w2,a}\ q^{w1,b}q^{w2,b}\ )\,C_{nw,a}\ C_{n'w',b}\ d\tau$$

w = s なら $q_i = q_1 = 1, q_j = q_1 = 1$ 、w = px なら $q_i = q_2 = x, q_j = q_1 = 1$ 、w = dxy なら $q_i = q_2 =$

x, $q_j$＝$q_3$＝y として

$= \int (q_{i,a}\, q_{j,a}\, q_{k,a}\, q_{l,a}) C_{Nw,a}\, C_{N'w',b}\, d\tau$

$= \int (\Sigma_m s_{im} q'_{m,a} \Sigma_n s_{jn} q'_{n,a} \Sigma_p s_{kp} q'_{p,b} \Sigma_q s_{lq} q'_{q,b}) C_{Nw,a}\, C_{N'w',b}\, d\tau$

$= \int \Sigma_m \Sigma_n \Sigma_p \Sigma_q (s_{im} q'_{m,a} s_{jn} q'_{n,a} s_{kq} q'_{q,b} s_{lp} q'_{p,b}) C_{Nw,a}\, C_{N'w',b}\, d\tau$

$= \int \Sigma_m \Sigma_n \Sigma_p \Sigma_q (s_{im} s_{jn} s_{kq} s_{lp} q'_{m,a} q'_{n,a} q'_{p,b} q'_{q,b}) C_{Nw,a}\, C_{N'w',b}\, d\tau$

$= \int \Sigma_m \Sigma_n \Sigma_p \Sigma_q \{(s_{im} s_{jn} s_{kq} s_{lp})(C_{Nw,a} q'_{m,a} q'_{n,a})(C_{N'w',b} q'_{p,b} q'_{q,b})\}\, d\tau$

$= \Sigma_m \Sigma_n \Sigma_p \Sigma_q \int \{(s_{im} s_{jn} s_{kq} s_{lp})(C_{Nw,a} q'_{m,a} q'_{n,a})(C_{N'w',b} q'_{p,b} q'_{q,b})\}\, d\tau$

$= \Sigma_m \Sigma_n \Sigma_p \Sigma_q \{(s_{im} s_{jn} s_{kq} s_{lp}) \int (C_{Nw,a} q'_{m,a} q'_{n,a})(C_{N'w',b} q'_{p,b} q'_{q,b})\, d\tau\}$

ｗがｄ軌道であれば、3dx2 と 3dxy とでは、対応する$K_{Nw}$が異なるため、対応する $C_{Nw}$が異なる。従い、その補正係数αを、$K_{3d_{\triangle\triangle}} = \sqrt{2/(3\pi)}$ 、$K_{3d_{\triangle 2}} = \sqrt{2/(9\pi)}$ から

$\alpha = K_{3d_{\triangle 2}} / K_{3d_{\triangle\triangle}} = 1/3$ for (x,y,z)系 3dx2 等、(x',y',z') 系 3dx'y'等

$\alpha = K_{3d_{\triangle\triangle}} / K_{3d_{\triangle 2}} = 3$ for (x,y,z)系 3dxy 等、(x',y',z') 系 3dx'2 等

$\alpha = \qquad = 1$ for s 軌道・p 軌道、その他の d 軌道組合せ

とおくと、(x',y',z')系の重なり積分すなわちσ・π表現の重なり積分を用い、

$= \Sigma_m \Sigma_n \Sigma_p \Sigma_q \{\alpha_a \cdot \alpha_b \cdot (s_{im} s_{jn} s_{kq} s_{lp}) \int \chi'_{Nw(m,n),a}\, \chi'_{N'w'(p,q),b}\, d\tau'\}$

$= \Sigma^4_{m=1} \Sigma^4_{n=1} \Sigma^4_{p=1} \Sigma^4_{q=1} \{\alpha_a \cdot \alpha_b \cdot (s_{im} s_{jn} s_{kq} s_{lp}) \cdot \mathbf{((Nw(m,n)_a, N'w'(p,q)_b))}\}$

| (x,y,z)系 | | (x',y',z')系 | |
|---|---|---|---|
| 軌道ｗ | (i, j) or (k,l) | (m,n) or (p,q) | 軌道 w' |
| s | 1 1 | 1 1 | s |
| px | 2(x) 1 | 2(x) 1 | px |
| py | 3(y) 1 | 3(y) 1 | py |
| pz | 4(z) 1 | 4(z) 1 | pz |
| dx2 | 2(x) 2(x) | 2(x) 2(x) | dx2 |
| dy2 | 3(y) 3(y) | 3(y) 3(y) | dy2 |
| dz2 | 4(z) 4(z) | 4(z) 4(z) | dz2 |
| dxy | 2(x) 3(y) | 2(x) 3(y) | dxy |
| dyz | 3(y) 4(z) | 3(y) 4(z) | dyz |
| dzx | 4(z) 2(x) | 4(z) 2(x) | dzx |

以上で、一般座標(x,y,z)での重なり積分 Srs = **($Nw_a$, $N'w'_b$)** を、σ・π表現 ie (x',y',z')座標での重なり積分**($(Nw(m,n)_a, N'w'(p,q)_b)$)** から求めることができる。

＜重なり積分計算の具体的表現＞

$$
\begin{aligned}
(1s,1s) &= \int \chi_{1s,a}\,\chi_{1s,b}\,d\tau = \int (K_{1s}\cdot\mu_a^{3/2}\cdot 1\cdot e^{-\mu_a r_a})(K_{1s}\cdot\mu_b^{3/2}\cdot 1\cdot e^{-\mu_b r_b})d\tau \\
&= \int (K_{1s}\cdot\mu_a^{3/2}\cdot 1\cdot e^{-\mu_a r_a})(K_{1s}\cdot\mu_b^{3/2}\cdot 1\cdot e^{-\mu_b r_b})d\tau' \\
&= \int \chi'_{1s,a}\,\chi'_{1s,b}\,d\tau' \\
&= (1s,1s)
\end{aligned}
$$

$$
\begin{aligned}
(2s,2px) &= \int \chi_{2s,a}\,\chi_{2px,b}\,d\tau = \int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot x\cdot e^{-\mu_b r_b})d\tau \\
&= \int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot(s_{22}\cdot x'+s_{23}\cdot y'+s_{24}\cdot z')\cdot e^{-\mu_b r_b})d\tau \\
&= \int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot(s_{22}\cdot x'+s_{23}\cdot y'+s_{24}\cdot z')\cdot e^{-\mu_b r_b})d\tau' \\
&= \int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a})\cdot\ s_{22}\cdot(K_{2p}\cdot\mu_b^{5/2}\cdot x'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + \int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a})\ \cdot\ s_{23}\cdot(K_{2p}\cdot\mu_b^{5/2}\cdot y'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + \int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a})\ \cdot\ s_{24}\cdot(K_{2p}\cdot\mu_b^{5/2}\cdot z'\cdot e^{-\mu_b r_b})d\tau' \\
&= s_{22}\cdot\int \chi'_{2s,a}\,\chi'_{2px',b}\,d\tau' \\
&\qquad + s_{23}\cdot\int \chi'_{1s,a}\,\chi'_{2py',b}\,d\tau' \\
&\qquad + s_{24}\cdot\int \chi'_{1s,a}\,\chi'_{2pz',b}\,d\tau' \\
&= s_{22}\cdot(2s,2p\sigma)+s_{23}\cdot(2s,2p\pi)+s_{24}\cdot(2s,2p\pi)
\end{aligned}
$$

$$
\begin{aligned}
(2py,2px) &= \int \chi_{2py,a}\,\chi_{2px,b}\,d\tau = \int (K_{2p}\cdot\mu_a^{5/2}\cdot y\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot x\cdot e^{-\mu_b r_b})d\tau \\
&= \int (K_{2p}\cdot\mu_a^{5/2}\cdot(s_{32}\cdot x'+s_{33}\cdot y'+s_{34}\cdot z')\cdot e^{-\mu_a r_a}) \\
&\qquad\qquad (K_{2p}\cdot\mu_b^{5/2}\cdot(s_{22}\cdot x'+s_{23}\cdot y'+s_{24}\cdot z')\cdot e^{-\mu_b r_b})d\tau \\
&= \int (K_{2p}\cdot\mu_a^{5/2}\cdot(s_{32}\cdot x'+s_{33}\cdot y'+s_{34}\cdot z')\cdot e^{-\mu_a r_a}) \\
&\qquad\qquad (K_{2p}\cdot\mu_b^{5/2}\cdot(s_{22}\cdot x'+s_{23}\cdot y'+s_{24}\cdot z')\cdot e^{-\mu_b r_b})d\tau \\
&= s_{32}\cdot s_{22}\cdot\int (K_{2p}\cdot\mu_a^{5/2}\cdot x'\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot x'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + s_{32}\cdot s_{23}\cdot\int (K_{2p}\cdot\mu_a^{5/2}\cdot x'\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot y'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + s_{32}\cdot s_{24}\cdot\int (K_{2p}\cdot\mu_a^{5/2}\cdot x'\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot z'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + s_{33}\cdot s_{22}\cdot\int (K_{2p}\cdot\mu_a^{5/2}\cdot y'\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot x'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + s_{33}\cdot s_{23}\cdot\int (K_{2p}\cdot\mu_a^{5/2}\cdot y'\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot y'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + s_{33}\cdot s_{24}\cdot\int (K_{2p}\cdot\mu_a^{5/2}\cdot y'\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot z'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + s_{34}\cdot s_{22}\cdot\int (K_{2p}\cdot\mu_a^{5/2}\cdot z'\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot x'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + s_{34}\cdot s_{23}\cdot\int (K_{2p}\cdot\mu_a^{5/2}\cdot z'\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot y'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + s_{34}\cdot s_{24}\cdot\int (K_{2p}\cdot\mu_a^{5/2}\cdot z'\cdot e^{-\mu_a r_a})(K_{2p}\cdot\mu_b^{5/2}\cdot z'\cdot e^{-\mu_b r_b})d\tau' \\
&= s_{32}\cdot s_{22}\cdot\int \chi'_{2px',a}\,\chi'_{2px',b}\,d\tau' \\
&\qquad + s_{32}\cdot s_{23}\cdot\int \chi'_{2px',a}\,\chi'_{2py',b}\,d\tau' \\
&\qquad + s_{32}\cdot s_{24}\cdot\int \chi'_{2px',a}\,\chi'_{2pz',b}\,d\tau' \\
&\qquad + s_{33}\cdot s_{22}\cdot\int \chi'_{2py',a}\,\chi'_{2px',b}\,d\tau' \\
&\qquad + s_{33}\cdot s_{23}\cdot\int \chi'_{2py',a}\,\chi'_{2py',b}\,d\tau' \\
&\qquad + s_{33}\cdot s_{24}\cdot\int \chi'_{2py',a}\,\chi'_{2pz',b}\,d\tau' \\
&\qquad + s_{34}\cdot s_{22}\cdot\int \chi'_{2pz',a}\,\chi'_{2px',b}\,d\tau' \\
&\qquad + s_{34}\cdot s_{23}\cdot\int \chi'_{2pz',a}\,\chi'_{2py',b}\,d\tau' \\
&\qquad + s_{34}\cdot s_{24}\cdot\int \chi'_{2pz',a}\,\chi'_{2pz',b}\,d\tau' \\
&= s_{32}\cdot s_{22}\cdot(2p\sigma,2p\sigma)+s_{32}\cdot s_{23}\cdot(2p\sigma,2p\pi)+s_{32}\cdot s_{24}\cdot(2p\sigma,2p\pi) \\
&\qquad + s_{33}\cdot s_{22}\cdot(2p\pi,2p\sigma)+s_{33}\cdot s_{23}\cdot(2p\pi,2p\pi)+s_{33}\cdot s_{24}\cdot(2p\pi,2p\pi) \\
&\qquad + s_{34}\cdot s_{22}\cdot(2p\pi,2p\sigma)+s_{34}\cdot s_{23}\cdot(2p\pi,2p\pi)+s_{34}\cdot s_{24}\cdot(2p\pi,2p\pi)
\end{aligned}
$$

$$
\begin{aligned}
(2s,3dxy) &= \int \chi_{2s,a}\,\chi_{3dxy,b}\,d\tau = \int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}}\cdot\mu_b^{7/2}\cdot xy\cdot e^{-\mu_b r_b})d\tau \\
&= \int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a}) \\
&\qquad (K_{3d_{\triangle\triangle}}\cdot\mu_b^{7/2}\cdot(s_{22}\cdot x'+s_{23}\cdot y'+s_{24}\cdot z')(s_{32}\cdot x'+s_{33}\cdot y'+s_{34}\cdot z')\cdot e^{-\mu_b r_b})d\tau \\
&= s_{22}\cdot s_{32}\cdot\int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}}\cdot\mu_b^{7/2}\cdot x'x'\cdot e^{-\mu_b r_b})d\tau' \\
&\quad + s_{22}\cdot s_{33}\cdot\int (K_{2s}\cdot\mu_a^{5/2}\cdot 1\cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}}\cdot\mu_b^{7/2}\cdot x'y'\cdot e^{-\mu_b r_b})d\tau'
\end{aligned}
$$

$+ s_{22} \cdot s_{34} \cdot \int (K_{2s} \cdot \mu_a^{5/2} \cdot 1 \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot x'z' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{23} \cdot s_{32} \cdot \int (K_{2s} \cdot \mu_a^{5/2} \cdot 1 \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot y'x' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{23} \cdot s_{33} \cdot \int (K_{2s} \cdot \mu_a^{5/2} \cdot 1 \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot y'y' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{23} \cdot s_{34} \cdot \int (K_{2s} \cdot \mu_a^{5/2} \cdot 1 \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot y'z' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{24} \cdot s_{32} \cdot \int (K_{2s} \cdot \mu_a^{5/2} \cdot 1 \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot z'x' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{24} \cdot s_{33} \cdot \int (K_{2s} \cdot \mu_a^{5/2} \cdot 1 \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot z'y' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{24} \cdot s_{34} \cdot \int (K_{2s} \cdot \mu_a^{5/2} \cdot 1 \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot z'z' \cdot e^{-\mu_b r_b}) d\tau'$

$= s_{22} \cdot s_{32} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot \int \chi'_{2s,a}\ \chi'_{3dx'2,b}\, d\tau'$

$+ s_{22} \cdot s_{33} \cdot \int \chi'_{2s,a}\ \chi'_{3dx'y',b}\, d\tau'$

$+ s_{22} \cdot s_{34} \cdot \int \chi'_{2s,a}\ \chi'_{3dx'z',b}\, d\tau'$

$+ s_{23} \cdot s_{32} \cdot \int \chi'_{2s,a}\ \chi'_{3dy'x',b}\, d\tau'$

$+ s_{23} \cdot s_{33} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot \int \chi'_{2s,a}\ \chi'_{3dy'2,b}\, d\tau'$

$+ s_{23} \cdot s_{34} \cdot \int \chi'_{2s,a}\ \chi'_{3dy'z',b}\, d\tau'$

$+ s_{24} \cdot s_{32} \cdot \int \chi'_{2s,a}\ \chi'_{3dz'x',b}\, d\tau'$

$+ s_{24} \cdot s_{33} \cdot \int \chi'_{2s,a}\ \chi'_{3dz'y',b}\, d\tau'$

$+ s_{24} \cdot s_{34} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot \int \chi'_{2s,a}\ \chi'_{3dz'2,b}\, d\tau'$

$= s_{22} \cdot s_{32} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot (2s,3d\sigma\ \sigma) + s_{22} \cdot s_{33} \cdot (2s,3d\sigma\ \pi) + s_{22} \cdot s_{34} \cdot (2s,3d\sigma)$

$+ s_{23} \cdot s_{32} \cdot (2s,3d\sigma\ \pi) + s_{23} \cdot s_{33} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot (2s,3d\pi\ \pi) + s_{23} \cdot s_{34} \cdot (2s,3d\pi\ \pi)$

$+ s_{24} \cdot s_{32} \cdot (2s,3d\sigma\ \pi) + s_{24} \cdot s_{33} \cdot (2s,3d\pi\ \pi) + s_{24} \cdot s_{34} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot (2s,3d\pi\ \pi)$

$(2px,3dxy) = \int \chi_{2px,a}\ \chi_{3dxy,b}\, d\tau = \int (K_{2p} \cdot \mu_a^{5/2} \cdot x \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot xy \cdot e^{-\mu_b r_b}) d\tau$

$= \int (K_{2p} \cdot \mu_a^{5/2} \cdot (s_{22} \cdot x' + s_{23} \cdot y' + s_{24} \cdot z') \cdot e^{-\mu_a r_a})$

$(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot (s_{22} \cdot x' + s_{23} \cdot y' + s_{24} \cdot z')(s_{32} \cdot x' + s_{33} \cdot y' + s_{34} \cdot z') \cdot e^{-\mu_b r_b}) d\tau$

$= s_{22} \cdot s_{22} \cdot s_{32} \cdot \int (K_{2p} \cdot \mu_a^{5/2} \cdot x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot x'x' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{22} \cdot s_{22} \cdot s_{33} \cdot \int (K_{2p} \cdot \mu_a^{5/2} \cdot x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot x'y' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{22} \cdot s_{22} \cdot s_{34} \cdot \int (K_{2p} \cdot \mu_a^{5/2} \cdot x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot x'z' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{22} \cdot s_{23} \cdot s_{32} \cdot \int (K_{2p} \cdot \mu_a^{5/2} \cdot x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot y'x' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{22} \cdot s_{23} \cdot s_{33} \cdot \int (K_{2p} \cdot \mu_a^{5/2} \cdot x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot y'y' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{22} \cdot s_{23} \cdot s_{34} \cdot \int (K_{2p} \cdot \mu_a^{5/2} \cdot x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot y'z' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{22} \cdot s_{24} \cdot s_{32} \cdot \int (K_{2p} \cdot \mu_a^{5/2} \cdot x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot z'x' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{22} \cdot s_{24} \cdot s_{33} \cdot \int (K_{2p} \cdot \mu_a^{5/2} \cdot x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot z'y' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{22} \cdot s_{24} \cdot s_{34} \cdot \int (K_{2p} \cdot \mu_a^{5/2} \cdot x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot z'z' \cdot e^{-\mu_b r_b}) d\tau'$

$+ s_{23} \cdot \sim 2py' \sim \quad + \quad + \quad + \cdots$

$+ s_{24} \cdot \sim 2pz' \sim \quad + \quad + \quad + \cdots$

$= s_{22} \cdot s_{22} \cdot s_{32} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot \int \chi'_{2px',a}\ \chi'_{3dx'2,b}\, d\tau'$

$+ s_{22} \cdot s_{22} \cdot s_{33} \cdot \int \chi'_{2px',a}\ \chi'_{3dx'y',b}\, d\tau'$

$+ s_{22} \cdot s_{22} \cdot s_{34} \cdot \int \chi'_{2px',a}\ \chi'_{3dx'z',b}\, d\tau'$

$+ s_{22} \cdot s_{23} \cdot s_{32} \cdot \int \chi'_{2px',a}\ \chi'_{3dy'x',b}\, d\tau'$

$+ s_{22} \cdot s_{23} \cdot s_{33} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot \int \chi'_{2px',a}\ \chi'_{3dy'2,b}\, d\tau'$

$+ s_{22} \cdot s_{23} \cdot s_{34} \cdot \int \chi'_{2px',a}\ \chi'_{3dy'z',b}\, d\tau'$

$+ s_{22} \cdot s_{24} \cdot s_{32} \cdot \int \chi'_{2px',a}\ \chi'_{3dz'x',b}\, d\tau'$

$+ s_{22} \cdot s_{24} \cdot s_{33} \cdot \int \chi'_{2px',a}\ \chi'_{3dz'y',b}\, d\tau'$

$+ s_{22} \cdot s_{24} \cdot s_{34} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot \int \chi'_{2px',a}\ \chi'_{3dz'2,b}\, d\tau'$

$+ s_{23} \cdot \sim \chi'_{2py',a} \sim \quad + \quad + \quad + \cdots$

$+ s_{24} \cdot \sim \chi'_{2pz',a} \sim \quad + \quad + \quad + \cdots$

$= s_{22} \cdot s_{22} \cdot s_{32}\ (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2})\ (2p\sigma,3d\sigma\ \sigma) + s_{22} \cdot s_{22} \cdot s_{33}(2p\sigma,3d\sigma\ \pi) + s_{22} \cdot s_{22} \cdot s_{34}(2p\sigma,3d\sigma)$

$+ s_{22} \cdot s_{23} \cdot s_{32}(2p\sigma,3d\sigma\ \pi) + s_{22} \cdot s_{23} \cdot s_{33}\ (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2})\ (2p\sigma,3d\pi\ \pi) + s_{22} \cdot s_{23} \cdot s_{34}(2p\sigma,3d\pi\ \pi)$

$+ s_{22} \cdot s_{24} \cdot s_{32}(2p\sigma,3d\sigma\ \pi) + s_{22} \cdot s_{24} \cdot s_{33}(2p\sigma,3d\pi\ \pi) + s_{22} \cdot s_{24} \cdot s_{34}\ (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2})\ (2p\sigma,3d\pi\ \pi)$

$$+ s_{23} \cdot \sim(2p\pi, \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{24} \cdot \sim(2p\pi, \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$(3dx2,3dxy) = \int \chi_{3dx2,a}\chi_{3dxy,b}\, d\tau = \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot xx \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot xy \cdot e^{-\mu_b r_b})d\tau$$

$$= \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot (s_{22} \cdot x' + s_{23} \cdot y' + s_{24} \cdot z')(s_{22} \cdot x' + s_{23} \cdot y' + s_{24} \cdot z') \cdot e^{-\mu_a r_a})$$

$$(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot (s_{22} \cdot x' + s_{23} \cdot y' + s_{24} \cdot z')(s_{32} \cdot x' + s_{33} \cdot y' + s_{34} \cdot z') \cdot e^{-\mu_b r_b})d\tau$$

$$= s_{22} \cdot s_{22} \cdot s_{22} \cdot s_{32} \cdot \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot x'x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot x'x' \cdot e^{-\mu_b r_b})d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{22} \cdot s_{33} \cdot \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot x'x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot x'y' \cdot e^{-\mu_b r_b})d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{22} \cdot s_{34} \cdot \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot x'x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot x'z' \cdot e^{-\mu_b r_b})d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{23} \cdot s_{32} \cdot \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot x'x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot y'x' \cdot e^{-\mu_b r_b})d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{23} \cdot s_{33} \cdot \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot x'x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot y'y' \cdot e^{-\mu_b r_b})d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{23} \cdot s_{34} \cdot \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot x'x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot y'z' \cdot e^{-\mu_b r_b})d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{24} \cdot s_{32} \cdot \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot x'x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot z'x' \cdot e^{-\mu_b r_b})d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{24} \cdot s_{33} \cdot \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot x'x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot z'y' \cdot e^{-\mu_b r_b})d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{24} \cdot s_{34} \cdot \int (K_{3d_{\triangle}2} \cdot \mu_a^{7/2} \cdot x'x' \cdot e^{-\mu_a r_a})(K_{3d_{\triangle\triangle}} \cdot \mu_b^{7/2} \cdot z'z' \cdot e^{-\mu_b r_b})d\tau'$$

$$+ s_{22} \cdot s_{23} \cdot \sim 3dx'y' \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{22} \cdot s_{24} \cdot \sim 3dx'z' \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{23} \cdot \sim 3dy'x' \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{23} \cdot \sim 3dy'y' \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{23} \cdot \sim 3dy'z' \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{24} \cdot \sim 3dz'x' \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{24} \cdot \sim 3dz'y' \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{24} \cdot \sim 3dz'z' \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$= s_{22} \cdot s_{22} \cdot s_{22} \cdot s_{32} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot \int \chi'_{3dx'2,a}\ \chi'_{3dx'2,b}\, d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{22} \cdot s_{33} \cdot \int \chi'_{3dx'2,a}\ \chi'_{3dx'y',b}\, d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{22} \cdot s_{34} \cdot \int \chi'_{3dx'2,a}\ \chi'_{3dx'z',b}\, d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{23} \cdot s_{32} \cdot \int \chi'_{3dx'2,a}\ \chi'_{3dy'x',b}\, d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{23} \cdot s_{33} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot \int \chi'_{3dx'2,a}\ \chi'_{3dy'2,b}\, d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{23} \cdot s_{34} \cdot \int \chi'_{3dx'2,a}\ \chi'_{3dy'z',b}\, d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{24} \cdot s_{32} \cdot \int \chi'_{3dx'2,a}\ \chi'_{3dz'x',b}\, d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{24} \cdot s_{33} \cdot \int \chi'_{3dx'2,a}\ \chi'_{3dz'y',b}\, d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{24} \cdot s_{34} \cdot (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2}) \cdot \int \chi'_{3dx'2,a}\ \chi'_{3dz'2,b}\, d\tau'$$

$$+ s_{22} \cdot s_{22} \cdot s_{23} \cdot \sim \chi'_{3dx'y',a} \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{22} \cdot s_{22} \cdot s_{24} \cdot \sim \chi'_{3dx'z',a} \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{22} \cdot s_{23} \cdot \sim \chi'_{3dy'x',a} \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{22} \cdot s_{23} \cdot \sim \chi'_{3dy''2,a} \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{22} \cdot s_{23} \cdot \sim \chi'_{3dy'z',a} \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{22} \cdot s_{24} \cdot \sim \chi'_{3dz'x',a} \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{22} \cdot s_{24} \cdot \sim \chi'_{3dz'y',a} \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$+ s_{22} \cdot s_{24} \cdot \sim \chi'_{3dz'2,a} \sim \quad + \quad + \quad + \cdot\cdot\cdot$$

$$= s_{22} \cdot s_{22} \cdot s_{22} \cdot s_{32}\ (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2})\ (3d\sigma\sigma, 3d\sigma\sigma) + s_{22} \cdot s_{22} \cdot s_{22} \cdot s_{33}(3d\sigma\sigma, 3d\sigma\pi)$$

$$+ s_{22} \cdot s_{22} \cdot s_{22} \cdot s_{34}(3d\sigma\sigma, 3d\sigma)$$

$$+ s_{22} \cdot s_{22} \cdot s_{23} \cdot s_{32}(3d\sigma\sigma, 3d\sigma\pi) + s_{22} \cdot s_{22} \cdot s_{23} \cdot s_{33}\ (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2})\ (3d\sigma\sigma, 3d\pi\pi)$$

$$+ s_{22} \cdot s_{23} \cdot s_{34}(3d\sigma\sigma, 3d\pi\pi)$$

$$+ s_{22} \cdot s_{22} \cdot s_{24} \cdot s_{32}(3d\sigma\sigma, 3d\sigma\pi) + s_{22} \cdot s_{22} \cdot s_{24} \cdot s_{33}(3d\sigma\sigma, 3d\pi\pi)$$

$$+ s_{22} \cdot s_{22} \cdot s_{24} \cdot s_{34}\ (K_{3d_{\triangle\triangle}} / K_{3d_{\triangle}2})\ (3d\sigma\sigma, 3d\pi\pi)$$

$$+ \quad (K_{3d_{\triangle}2} / K_{3d_{\triangle\triangle}}) \cdot \{ s_{22} \cdot s_{23} \cdot \sim(3d\sigma\pi, \sim \quad + \quad + \cdot\cdot\cdot \sim(3d\pi\pi, \sim \quad + \cdot\cdot\cdot \}$$

$$+ \quad (K_{3d_{\triangle}2} / K_{3d_{\triangle\triangle}}) \cdot \{ s_{22} \cdot s_{24} \cdot \sim(3d\sigma\pi, \sim \quad + \quad + \sim(3d\pi\pi, \sim \quad + \cdot\cdot\cdot \}$$