Two-Center Integrals for $r_{ij}^n$ Polynomial Correlated Wave Functions

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All integrals needed to evaluate the wave function of the form

$$\Psi_{tot} = \tilde{A} \left\{ \prod_j \sum_s a_s \phi_s(j) \left[ 1 + \sum_i \sum_{j < i} w_{ij} r_{ij}^n \right] \right\}$$

for $n = 1$ and the Hamiltonian given are combined herein. For this form of the wave function, the integrals needed can be expressed as a product of integrals involving at most four electrons. An indication of how to increase or decrease exponents of $r_{ij}^n$ in steps of one or two is given. Some indication of how to proceed if the Hamiltonian contains $1/r_{ij}^3$ terms or if the wave function is of the form

$$\Psi_{tot} = \tilde{A} \left\{ \prod_j \sum_s a_s \phi_s(j) \left[ 1 + \sum_{j < l < k} \sum w_{jlk} r_{jl}^n r_{lk}^n \right] \right\}$$

is given. Consideration of all possible types of integrals involving $r_{ij}^a r_{kl}^b r_{mn}^c$ with $a < 0$, $b > 0$, $c > 0$; $|a| = |b| = |c| = 1$, is given. Integrals are given in analytical form. These can be evaluated by numerical integration routines.

INTRODUCTION

Much success in ab initio calculations has been achieved with the use of correlated wave functions (wave functions that included the distance between two electrons explicitly). For the He atom, the Li atom, and the H$_2$ molecule, these wave functions have yielded the most accurate energy levels and molecular properties. Constructing the total wave function as a Slater determinant or antisymmetrized product is tantamount to using the Pauli principle, which excludes two electrons with identical quantum numbers and spin from occupying the same volume element at the same time. It does not tell us anything about two electrons with opposite spin, which we would expect to repel each other electrostatically. By including terms dependent upon the inter-electronic separation, we cause the probability, calculated from this wave function, of finding two electrons at specified regions of space to decrease when the two electrons approach one another. A correlated wave function can be an eigenfunction of spin and angular momentum. If $\tilde{A}(F)$ is an eigenfunction of the total and $z$ component of spin and angular momentum, then $\Psi$ is an eigenfunction of the same.
the Nth-order permutation group\(^5\), all spin states\(^6\) for the N electron system can be included:

\[ \Psi = \tilde{A}(FR) \]

\[ F = F(1, 2, 3, \ldots, N) = (N!)^{-1/2}\Phi_1(1)\Phi_2(2) \cdots \Phi_N(N) \]

\[ R = 1 + \sum_j \sum_l (w_{jl}r_{jl} + x_{jl}r_{jl}^2 + y_{jl}r_{jl}^3 + \cdots) \]

and \( \tilde{A} \) is the antisymmetrization operator. \( H \) is the Hamiltonian (in the Born-Oppenheimer approximation) in atomic units, \( Z_a \) and \( Z_b \) are the nuclear charges, \( R \) is the distance between nuclei and \( b \), \( r_{i\lambda} \) is the distance between electron \( i \) and nucleus \( \lambda \), \( r_{ij} \) is the distance between electron \( i \) and electron \( j \)

\[ H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \left( \frac{Z_a}{r_{ia}} + \frac{Z_b}{r_{ib}} \right) + \sum_i \sum_j \frac{1}{r_{ij}} + \frac{Z_a Z_b}{R} \]

The coordinate system\(^7\) used is confocal elliptical. \( \phi_i \) is the out-of-plane angle and \( R \) is the distance between nuclei \( a \) and \( b \). \( d\tau_i \) is the volume element and \( r_{12} \) the interelectronic distance. We also have

\[ \xi_i = (r_{ai} + r_{bi}) / R, \quad \eta_i = (r_{ai} - r_{bi}) / R \]

\[ 1 \leq \xi_i < \infty, \quad -1 \leq \eta_i \leq 1, \]

\[ d\tau_i = \frac{1}{8} R^3 (\xi_i^2 - \eta_i^2) d\xi_i d\eta_i d\phi_i, \quad 0 \leq \phi_i < 2\pi \]

\[ r_{12}^2 = \frac{1}{4} R^2 \left\{ \xi_1^2 + \xi_2^2 + \eta_1^2 + \eta_2^2 - 2 - 2\xi_1\xi_2\eta_1\eta_2 \right\} \]

\[ -2 \left[ (\xi_1^2 - 1)(\xi_2^2 - 1)(1 - \eta_1^2)(1 - \eta_2^2) \right]^{1/2} \cos(\phi_1 - \phi_2) \] (1)

The basis functions \( \Phi_s(j) \) and the total wave function are represented in Eqs. (2) and (3):

\[ \Phi_s(j) = \xi_j^{p_s} \eta_j^{q_s} (\xi_j^2 - 1)^{\gamma_s/2} (1 - \eta_j^2)^{\nu_s/2} e^{-\alpha_s \xi_j} e^{\beta_s \eta_j} e^{im_s \phi_j}, \]

\[ s = (p_s, q_s, \gamma_s, \nu_s, \alpha_s, \beta_s, m_s), i = \sqrt{-1} \] (2)
\[ \Psi_{tot} = \tilde{A} \left\{ \prod_j \sum_s a_{s,j} \phi_s(j) \right\} \left[ 1 + \sum_j < \sum_i w_{ij} r^n_{ij} \right] \] (3)

For molecules with more than two nuclei, the spherical coordinate system and Gaussian transforms or \( \zeta \)-function expansions can be used for integral evaluation.

CLASSIFICATION OF INTEGRALS

The classification of types of integrals involving \( r_{ij}^a r_{kl}^b r_{mn}^c \) can be considered in the notation of picture writing graph theory. For the form of the wave function given in (3), the integrals needed can be expressed as a product of primitive integrals involving at most four electrons. All the integrals needed to evaluate this wave function involving \( r_{ij} \) to the first power are given.

TWO - ELECTRON INTEGRALS

We have

\[ \langle r_{12}^2 \rangle = \langle \Phi_s(2) r_{12}^2 \Phi_t(1) \rangle = \int \! d\tau \Phi_s(2) r_{12}^2 \Phi_t(1) \]

\[ = \frac{1}{64} R^8 \pi^2 \int_{-1}^{1} \int_{-1}^{1} \int_{-1}^{1} \int_{-1}^{1} (\xi_1^2 - \eta_1^2)(\xi_2^2 - \eta_2^2) d\xi_1 d\xi_2 d\eta_1 d\eta_2 \]

\[ \times \Phi_s(2) \Phi_t(1) \left\{ \left[ \xi_1^2 + \xi_2^2 + \eta_1^2 + \eta_2^2 - 2 - 2 \xi_1 \xi_2 \eta_1 \eta_2 \right] \delta(m_s; 0) \delta(m_t; 0) \right. \]

\[ - \left[ (\xi_1^2 - 1)(\xi_2^2 - 1)(1 - \eta_1^2)(1 - \eta_2^2) \right] \left[ \delta(m_s - 1; 0) \delta(m_t + 1; 0) \right. \]

\[ + \left. \delta(m_s + 1; 0) \delta(m_t - 1; 0) \right] \} \quad (4) \]

The Neumann\(^{12} \) expansion for \( 1/r_{12} \) in prolate elliptical coordinates is:

\[ \frac{1}{r_{12}} = \frac{4}{R} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-1)^m \frac{2l + 1}{2} \frac{(l - |m|)!}{(l + |m|)!} \]

\[ P_l^{|m|} \Phi_s^{|m|} (\xi_{1<2}) P_l^{|m|} (\eta_1) P_l^{|m|} (\eta_2) e^{i\phi_1 - \phi_2} \] (5)

\( P_l^{|m|} (\xi) \) and \( Q_l^{|m|} (\xi) \) are associated Legendre polynomials of the first and second kind in the complex plane. \( \xi_{1<2} \) and \( \xi_{2>1} \) mean the smaller and the larger, respectively, of \( \xi_1 \) and \( \xi_2 \). The \( P_l^{|m|} (\xi) \) and \( Q_l^{|m|} (\xi) \) have the range \([-1, 1]\). The \( P_l^{|m|} (\eta) \) have the range \([-1, 1]\). For further
details, see Refs. 13 - 23. We have

\[ P_{l}^{m}(\xi) = \frac{(\xi^2 - 1)^{m/2}}{2l!} \frac{d^{l+m}}{d\xi^{l+m}}(\xi^2 - 1)^l, \]

\[ P_{l}^{m}(\eta) = \frac{(1 - \eta^2)^{m/2}}{2l!} \frac{d^{l+m}}{d\eta^{l+m}}(\eta^2 - 1)^l, \]

\[ Q_{l}^{m}(\xi) = (\xi^2 - 1)^{m/2} \frac{d^{m}}{d\xi^{m}} Q_{l}(\xi), \]

\[ Q_{l}(\xi) = \frac{1}{2} P_{l}(\xi) \ln \left( \frac{\xi + 1}{\xi - 1} \right) \]

\[ - \sum_{j=1}^{\leq(l+1)/2} \frac{2l - 4j + 3}{(2j - 1)(l - j + 1)} P_{l-2j+1}(\xi) \] (6)

The \((1/r_{12})\), Eq. (10) can be expressed more concisely, using the definitions of Eqs. (6)-(9),

\[ a = (p_{a}, q_{a}, \gamma_{a}, \nu_{a}, \alpha_{a}, \beta_{a}, m_{a}), \quad b = (p_{b}, q_{b}, \gamma_{b}, \nu_{b}, \alpha_{b}, \beta_{b}, m_{b}), \]

\[ K_{\mu,\nu,\alpha}^{\sigma}(z) = \int_{1}^{z} \int_{-1}^{1} d\xi d\eta (\xi^2 - \eta^2)^{\nu_{\alpha}/2} \eta^{\nu_{\alpha}} (\xi^2 - 1)^{\gamma_{\alpha}/2} \]

\[ \times (1 - \eta^2)^{\nu_{\alpha}/2} e^{-\alpha_{\mu} \xi + \beta_{\mu} \eta} P_{\mu}^{\sigma}(\xi) P_{\mu^{'}}^{\sigma}(\eta) \] (7)

\[ F_{\mu}^{\sigma}(z) = -\frac{d}{dz} \left( \frac{Q_{l}^{m}(z)}{P_{l}^{m}(z)} \right) = \frac{(-1)^{\mu + \sigma}/(\mu - \sigma)!}{P_{\mu}^{\sigma}(z)}(z^2 - 1) \] (8)

\[ Z_{\mu}^{\sigma} = (-)^{\mu} \left[ \frac{(\mu + |\sigma|)!}{(\mu + |\sigma|)!} \right]^{2} \] (9)

\[ \langle 1/r_{12} \rangle = \left( \Phi_{a}(1)/r_{12} \Phi_{b}(2) \right) = \frac{1}{8} \pi^{2} R^{6} \delta(m_{a} + m_{b}; 0) \]

\[ \times \sum_{\mu = \sigma = |m_{a}|}^{\infty} (2\mu + 1) Z_{\mu}^{\sigma} \int_{1}^{\infty} F_{\mu}^{\sigma}(z) K_{\mu,\mu,a}^{\sigma}(z) K_{\mu,\mu,b}^{\sigma}(z) dz \] (10)

For \( \frac{1}{2}(\gamma_{a} + \sigma) \) and \( \frac{1}{2}(\nu_{a} + \sigma) \) integers, the one-dimensional integral \( K_{\mu,\mu',\alpha}^{\sigma}(z) \) can be evaluated analytically for each \( z \) and inserted in the
numerical integration at the appropriate mesh points.

\[
K_{\mu,\mu',\alpha}(z) = \sum_{j=0}^{[\mu-\sigma]/2} \sum_{r=0}^{[\mu'-\sigma]/2} \sum_{k=0}^{[\nu_a + \sigma]/2} \sum_{t=0}^{[\nu_a + \sigma]/2} \frac{(2\mu - 2j)! (2\mu' - 2k)!}{2^\nu j! (\mu - j)! (\mu - \sigma - 2j)! 2^\nu k!} \times \\
\frac{(-1)^{[\nu_a + \sigma]/2 - r}[\nu_a + \sigma]!}{(\mu' - k)! (\mu' - \sigma - 2k)! r! [\nu_a + \sigma]! t! [\nu_a + \sigma]!} \sum_{s=0}^{S_2} \sum_{\nu=0}^{V_0} \frac{[\alpha_a^{s+1}(S_2 - s)!]}{\beta_a^{\nu+1}(V_0 - \nu)!} \\
\times \{S_2! V_0! \sum_{s=0}^{S_2} \sum_{\nu=0}^{V_0} \frac{[\alpha_a^{s+1}(S_2 - s)!]}{\beta_a^{\nu+1}(V_0 - \nu)!} \} \\
- \{S_0! V_2! \sum_{s=0}^{S_0} \sum_{\nu=0}^{V_2} \frac{[\alpha_a^{s+1}(S_0 - s)!]}{\beta_a^{\nu+1}(V_2 - \nu)!} \} \\
\times \{S_2! V_0! \sum_{s=0}^{S_2} \sum_{\nu=0}^{V_0} \frac{[\alpha_a^{s+1}(S_2 - s)!]}{\beta_a^{\nu+1}(V_0 - \nu)!} \} \\
\times \{S_2! V_0! \sum_{s=0}^{S_2} \sum_{\nu=0}^{V_0} \frac{[\alpha_a^{s+1}(S_2 - s)!]}{\beta_a^{\nu+1}(V_0 - \nu)!} \} \\
\times \{S_0! V_2! \sum_{s=0}^{S_0} \sum_{\nu=0}^{V_2} \frac{[\alpha_a^{s+1}(S_0 - s)!]}{\beta_a^{\nu+1}(V_2 - \nu)!} \} \\
S_0 = \mu - \sigma + p_a - 2j + 2r, \quad S_2 = S_0 + 2, \quad V_0 = \mu' - \sigma + q_a - 2k + 2t, \quad V_2 = V_0 + 2 \quad (11)
\]

The upper limit of \(j\) is \(\frac{1}{2}(\mu - \sigma)\) or \(\frac{1}{2}(\mu - \sigma - 1)\), whichever is an integral. The upper limit of \(k\) is \(\frac{1}{2}(\mu' - \sigma)\) or \(\frac{1}{2}(\mu' - \sigma - 1)\), whichever is an integral. The upper limit of \(t\) is \(\frac{1}{2}(\nu_a + \sigma)\) and the upper limit of \(r\) is \(\frac{1}{2}(\gamma_a + \sigma)\); if these are not integrals, the summations are infinite ones. In practice, the \(K_{\mu,\mu',\alpha}(z)\) are evaluated recursively and numerically. If the \(\Phi_s(j)\) of Eq. (10) are Slater-type orbitals, the integrals can be reexpressed as a sum of “charge distributions”. The \(r_{12}\) expansion is needed for the evaluation of \(r_{12}\) and for raising the value of \(n\) in \(r_{12}^n\). This expansion [Eq. (12)] has been derived by Harris. The partial integration of Eq. (14) is used in the evaluation of the corresponding integral [Eq. (15)]. In Eq. (14), for \(z \to \infty\) and \(\mu \neq 0\), the first term approaches 0. For \(\mu = 0\), \(X_{\mu}^\sigma = 0\); \(O_{per}^\sigma\) denotes the interchange of
6 and charge distributions. We have

\[ r_{12} = \frac{R}{2} \sum_{\mu=0}^{\infty} \sum_{\sigma=-\mu}^{\mu} \{(U_\mu^\sigma g_\mu^\sigma + V_\mu^\sigma h_\mu^\sigma + 2W_\mu^\sigma)Q_{\mu}^{|\sigma|}(\xi_{2>1}) \]

\[ + \frac{X_{\mu}^\sigma \xi_{2>1}}{P_\mu^{|\sigma|}(\xi_{2>1})} \} P_{\mu}^{|\sigma|}(\xi_{1<2})P_{\mu}^{|\sigma|}(\eta_1)P_{\mu}^{|\sigma|}(\eta_2)e^{i\sigma(\phi_1 - \phi_2)}, \]

\[ g_\mu^\sigma = \frac{P_{\mu+2}^{|\sigma|}(\xi_1)}{P_\mu^{|\sigma|}(\xi_1)} + \frac{P_{\mu+2}^{|\sigma|}(\xi_2)}{P_\mu^{|\sigma|}(\xi_2)} + \frac{P_{\mu+2}^{|\sigma|}(\eta_1)}{P_\mu^{|\sigma|}(\eta_1)} + \frac{P_{\mu+2}^{|\sigma|}(\eta_2)}{P_\mu^{|\sigma|}(\eta_2)}, \]

\[ h_\mu^\sigma = \frac{P_{\mu-2}^{|\sigma|}(\xi_1)}{P_\mu^{|\sigma|}(\xi_1)} + \frac{P_{\mu-2}^{|\sigma|}(\xi_2)}{P_\mu^{|\sigma|}(\xi_2)} + \frac{P_{\mu-2}^{|\sigma|}(\eta_1)}{P_\mu^{|\sigma|}(\eta_1)} + \frac{P_{\mu-2}^{|\sigma|}(\eta_2)}{P_\mu^{|\sigma|}(\eta_2)}, \] (12)

\[ U_\mu^\sigma = Z_\mu^\sigma \frac{(\mu - |\sigma| + 1)(\mu - |\sigma| + 2)}{(2\mu + 3)^2}, \]

\[ V_\mu^\sigma = -Z_\mu^\sigma \frac{(\mu + |\sigma| - 1)(\mu + |\sigma|)}{(2\mu - 1)^2}, \]

\[ W_\mu^\sigma = Z_\mu^\sigma \frac{2(2\mu + 1)(4\sigma^2 - 1)}{(2\mu - 1)^2(2\mu + 3)^2}, \]

\[ X_\mu^\sigma = -\left( \frac{\mu - |\sigma|}{(\mu + |\sigma|)!(2\mu + 1)} \right) 2(2\mu + 1), \]

\[ G_\mu^\sigma = -\frac{d}{dz} \left( \frac{z}{[P_\mu^{|\sigma|}(z)]^2} \right) = \frac{-l_\mu^\sigma(z)}{[P_\mu^{|\sigma|}(z)]^2(z^2 - 1)}, \]

\[ l_\mu^\sigma(z) = (2\mu + 3)z^2 - 2(\mu - \sigma + 1)z \frac{P_{\mu+1}^{|\sigma|}(z)}{P_\mu^{|\sigma|}(z)} - 1, \] (13)

\[ X_\mu^\sigma \int_{1}^{z} \frac{x}{P_\mu^{|\sigma|}(x)}w(x)dx = \frac{X_\mu^{|\sigma|}z}{[P_\mu^{|\sigma|}(z)]^2} \int_{1}^{z} P_\mu^{|\sigma|}(x)w(x)dx \]

\[ - X_\mu^{|\sigma|} \int_{1}^{z} \frac{l_\mu^\sigma(x)dx}{[P_\mu^{|\sigma|}(x)]^2(x^2 - 1)} \int_{1}^{x} \frac{P_\mu^{|\sigma|}(\xi)w(\xi)d\xi}{P_\mu^{|\sigma|}(x)} \] (14)

\[ \langle r_{12} \rangle = \langle \Phi_{a}(1)\Phi_{b}(2) r_{12} \rangle = \frac{1}{32} \pi^2 R^7 \delta(m_a + m_b; 0) \]

\[ \times \left[ 1 + O_{per}(a \ b) \right] \sum_{\mu = |m_a|}^{\infty} \int_{1}^{\infty} dz K_{\mu, \mu, a}^{|\sigma|}(z) [ F_{\mu}^{|\sigma|}(z) \tilde{K}_{\mu, \mu, b}^{|\sigma|}(z) \]

\[ + \frac{1}{2} X_{\mu}^{|\sigma|} G_{\mu}^{|\sigma|}(z) K_{\mu, \mu, b}^{|\sigma|}(z) \] (15)
\[
\tilde{K}_{\mu,\mu,a}^\sigma(z) = U_\mu^\sigma [K_{\mu+2,\mu,a}^\sigma(z) + K_{\mu,\mu+2,a}^\sigma(z)] \\
+ V_\mu^\sigma [K_{\mu-2,\mu,a}^\sigma(z) + K_{\mu,\mu-2,a}^\sigma(z)] + W_\mu^\sigma K_{\mu,\mu,a}^\sigma(z) \quad (16)
\]

THREE-ELECTRON INTEGRALS

The three- and four- electron integrals have been formulated in a straightforward manner, using partial integration. Equation (17) illustrates a technique of partial integration useful in the derivations. Whenever the product of two or more associated Legendre polynomials occurs, these can be replaced by a sum over a single associated Legendre polynomial. The coefficients involve products of Clebsch-Gordon coefficients. Equation (22) is a Clebsch-Gordon series. For further information see Refs. 23 and 28 - 35. We have:

\[
\int_1^\infty f(y) \, dy \int_1^\infty g(t) \, dt = \int_1^\infty g(y) \, dy \int_1^y f(t) \, dt,
\]

\[u(y) = \int_1^y f(t) \, dt, \quad v(y) = \int_1^y g(s) \, ds \quad (17)\]

\[\langle r_{12}r_{13} \rangle = \langle \Phi_a(1)\Phi_b(2)\Phi_c(3)r_{12}r_{13} \rangle = \]

\[
\frac{1}{128} \pi^3 R^{11} \delta(m_a + m_b + m_c; 0) \left[ 1 + O_{per}(b/c) \right] \sum_{\mu = \sigma = |m|}^{\infty} \sum_{\mu' = \sigma' = |m'|}^{\infty} \times \{ (19) \}
\]

\[\times \left\{ \int_1^\infty dz \left[ \tilde{R}_{\mu',\mu',c}^{\sigma',\sigma,c}(z) + X_{\mu',\mu',c}^{\sigma',\sigma,c}(z) \right] \]

\[\times [F_{\mu}^\sigma(z) N_{(\mu',\mu'),a}^{(\sigma',\sigma)}(z) K_{\mu,\mu,b}^\sigma(z) + F_{\mu}^\sigma(z) N_{\mu',\mu',a}^{\sigma',\sigma}(z) \tilde{K}_{\mu,\mu,b}^\sigma(z) \\
+ X_{\mu}^\sigma G_{\mu}^\sigma(z) N_{\mu',\mu',a}^{\sigma',\sigma}(z) K_{\mu,\mu,b}^\sigma(z)] \\
+ \int_1^\infty dz \tilde{R}_{\mu',\mu',c}^{\sigma',\sigma,c}(z)[F_{\mu}^\sigma(z) N_{\mu,\mu',a}^{\sigma',\sigma}(z) K_{\mu,\mu,b}^\sigma(z) \\
+ F_{\mu}^\sigma(z) N_{(\mu',\mu),a}^{(\sigma',\sigma)}(z) \tilde{K}_{\mu,\mu,b}^\sigma(z) + X_{\mu}^\sigma G_{\mu}^\sigma(z) N_{(\mu',\mu'),a}^{(\sigma',\sigma)}(z) K_{\mu,\mu,b}^\sigma(z)] \}
\]

(18)

\[
\tilde{R}_{\mu,\mu,b}^\sigma(z) = \int_z^\infty F_{\mu}^\sigma(z) K_{\mu,\mu,b}^\sigma(z) \, dz \quad (19)
\]

\[
\tilde{R}_{\mu,\mu,b}^\sigma(z) = \int_z^\infty G_{\mu}^\sigma(z) K_{\mu,\mu,b}^\sigma(z) \, dz \quad (20)
\]

\[
\tilde{R}_{\mu,\mu,b}^\sigma(z) = \int_z^\infty F_{\mu}^\sigma(z) \tilde{K}_{\mu,\mu,b}^\sigma(z) \, dz \quad (21)
\]
\[ P_1^m(z)P_{\nu}^{m'}(z) = \sum_j \left[ \frac{l}{m} \frac{l'}{m'} \frac{j}{m+m'} \right] P_j^{(m+m')}(z) \quad (22) \]

\[
\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} = \begin{bmatrix} j_2 & j_1 & j \\ m_2 & m_1 & m \end{bmatrix} = \delta(m; m_1 + m_2) \\
\times \left[ (j-m)!(j_1+m_1)!(j_2+m_2)! \right]^{1/2} C(j_1, j_2, j; m_1, m_2, m) \\
\times C(j_1, j_2, j; 0, 0, 0) \\
= \delta(m; m_1 + m_2)(2j + 1)^{1/2}\Delta(j_1, j_2, j) \\
\times \sum_p (-1)^p \frac{p!(j_1 + j_2 - j - p)!(j_1 - m_1 - p)!}{(j + m)!(j_1 + m_1)!(j_2 + m_2)!(j_1 - m_1 - p)!(j_2 + m_2 - p)!(j - j_1 - m_2 + p)!}, \] 

\[
\Delta(a, b, c) = \left[ \frac{(a + b - c)!(b + c - a)!(c + a - b)!}{(a + b + c + 1)!} \right]^{1/2}, \]

\[
N_{\mu, \mu', a}^{\sigma, \sigma'}(z) = N_{\mu, \mu', a}^{\sigma', \sigma}(z) = \int_z^1 \int_{-1}^1 (\xi^2 - \eta^2) d\xi d\eta P_{\mu}^\sigma(\xi) P_{\mu'}^{\sigma'}(\xi) \\
\times P_{\mu}^\sigma(\eta) P_{\mu'}^{\sigma'}(\eta) \xi^{\alpha a} \eta^{\alpha a} (\xi^2 - 1)^{\nu a/2} (1 - \eta^2)^{\nu a/2} e^{-\alpha a \xi e^{2\alpha a}} \\
= \frac{1}{2} \delta(m; \sigma + \sigma') \sum_j \sum_{j'} \left[ \begin{array}{ccc} \mu & \mu' & J \\ \sigma & \sigma' & m \end{array} \right] \left[ \begin{array}{ccc} \mu & \mu' & J' \\ \sigma & \sigma' & m' \end{array} \right] \\
\times \left\{ K_J^{m, \nu, a}(z) + K_{J'}^{m, \nu, a}(z) \right\} \quad (23) \]

\[
\begin{align*}
\tilde{N}_{(\mu, \mu')}^{(\sigma, \sigma')}(z) &= \delta(m; \sigma + \sigma') \sum_j \sum_{j'} \left\{ U_{\mu}^\sigma \left[ \begin{array}{ccc} \mu + 2 & \mu' & J \\ \sigma & \sigma' & m \end{array} \right] \\
+ V_{\mu}^\sigma \left[ \begin{array}{ccc} \mu - 2 & \mu' & J \\ \sigma & \sigma' & m \end{array} \right] \left\{ K_J^{m, \nu, a}(z) + K_{J'}^{m, \nu, a}(z) \right\} \\
+ W_{\mu}^\sigma N_{(\mu, \mu')}^{(\sigma, \sigma')}(z) \right\} \quad (24)\end{align*}
\]
\[
N_{\mu,\mu',a}(z) = \sum_{J_j} \sum_{J_{j'}} \{ 
\begin{align*}
&\left( U_\mu^\sigma U_{\mu'}^{\sigma'} \left[ \mu + 2 \mu' + 2 \frac{J}{m} \right] + V_\sigma^\sigma V_{\sigma'}^{\sigma'} \left[ \mu - 2 \mu' + \frac{J}{m} \right] \right) \\
&+ U_\mu^\sigma V_{\mu'}^{\sigma'} \left[ \mu + 2 \mu' - \frac{J}{m} \right] + V_\sigma^\sigma U_{\sigma'}^{\sigma'} \left[ \mu - 2 \mu' - \frac{J}{m} \right] \right) \\
&+ \left( U_\mu^\sigma \left[ \mu + 2 \mu' \frac{J}{m} \right] + V_\sigma^\sigma \left[ \mu - 2 \mu' \frac{J}{m} \right] \right) \\
&\times \left( U_{\mu'}^{\sigma'} \left[ \mu + 2 \mu' \frac{J}{m} \right] + V_{\sigma'}^{\sigma'} \left[ \mu - 2 \mu' \frac{J}{m} \right] \right) \\
&\times \{ K_{J,j,a}^{m} + K_{J',j,a}^{m} \} + W_{\mu}^{\sigma'} \tilde{N}_{(\mu,\mu')}^{(\sigma,\sigma')} + W_{\mu}^{\sigma'} \tilde{N}_{(\mu,\mu')}^{(\sigma,\sigma')} - W_{\mu}^{\sigma'} N_{\mu,\mu',a}(z) + W_{\mu}^{\sigma'} \tilde{N}_{(\mu,\mu')}^{(\sigma,\sigma')} \} (25)
\end{align*}
\]

\[
\langle r_{12}/r_{13} \rangle = \langle \Phi_a(1) \Phi_b(2) \Phi_c(3) r_{12}/r_{13} \rangle = \frac{1}{64} R^9 \pi^2 \\
\times \delta(m_a+m_b+m_c;0) \sum_{\mu=\sigma=|m_a|} \sum_{\mu'=\sigma'=|m_c|} \int_1^\infty dz F_{\mu}^{\sigma'}(z) \\
\times R_{\mu',\mu',c}(z) \left[ \tilde{N}_{(\mu,\mu')}^{(\sigma,\sigma')} \left( z K_{\mu,\mu,b}(z) + N_{\mu,\mu',a}^{\sigma,\sigma'}(z) \tilde{K}_{\mu,\mu,b}(z) \right) \right] \\
+ \int_1^\infty dz F_{\mu}^{\sigma'}(z) K_{\mu',\mu',c}(z) \left[ \tilde{N}_{(\mu,\mu')}^{(\sigma,\sigma')} \left( z R_{\mu,\mu,b}(z) + N_{\mu,\mu',a}^{\sigma,\sigma'}(z) \tilde{R}_{\mu,\mu,b}(z) \right) \right] \\
+ X_{\mu} \int_1^\infty dz N_{\mu',\mu',a}^{\sigma,\sigma'}(z) \left[ K_{\mu,\mu,b}(z) R_{\mu',\mu',c}(z) G_{\mu}^{\sigma}(z) \\
+ \tilde{R}_{\mu,\mu,b}(z) K_{\mu',\mu',c}(z) F_{\mu'}^{\sigma'}(z) \right] \} (26)
\]
\[
\langle r_{12} r_{13} / r_{23} \rangle = \langle \Phi_a(1) \Phi_b(2) \Phi_c(3) r_{12} r_{13} / r_{23} \rangle = \frac{1}{128} R^3 \pi^3 \delta(m_a + m_b + m_c; 0) \left[ 1 + O_{\text{per}} \left( \frac{b}{c} \right) \right] \\
\times \sum_{\mu''} \sum_{\mu''} \sum_{\mu''} \sum_{\mu''} \delta(w', m_c - w'') \delta(|w'|; \sigma') \\
\times \delta(w; m_b + w''') \delta(|w|; \sigma) \delta(|w''|; \sigma'')(2\mu'' + 1) Z_{\mu''}^a \\
\times \{ \int_1^\infty dz N_{\mu', \mu'', c}(z) \left[ N_{\mu''}^{\sigma', \sigma''} N_{\mu', \mu''}(z) + N_{\mu''}^{\sigma', \sigma''} N_{\mu', \mu''}(z) F_{\mu'}(z) \right] \\
+ \tilde{N}_{(\mu, \mu''), b}(z) \tilde{N}_{(\mu, \mu''), a}(z) F_{\mu'}(z) + N_{\mu', \mu'', c}(z) F_{\mu'}(z) \left[ N_{\mu''}^{\sigma', \sigma''} N_{\mu', \mu''}(z) + N_{\mu', \mu''}(z) N_{\mu''}^{\sigma', \sigma''} F_{\mu'}(z) \right] \\
+ \int_1^\infty dz X_{\mu}^{\sigma} \tilde{N}_{(\mu, \mu''), b}(z) \left[ N_{\mu'}^{\sigma', \sigma''} N_{\mu', \mu''}(z) + N_{\mu'}^{\sigma', \sigma''} N_{\mu', \mu''}(z) F_{\mu'}(z) \right] \\
+ \frac{1}{2} \tilde{N}_{(\mu', \mu''), a}(z) + \frac{1}{2} X_{\mu'}^{\sigma'} \tilde{N}_{(\mu, \mu''), c}(z) \\
+ \int_1^\infty dz F_{\mu'}^{\sigma'}(z) N_{\mu', \mu''}^{\sigma', \sigma''}(z) F_{\mu'}^{\sigma'}(z) + \tilde{N}_{(\mu', \mu''), c}(z) \left[ N_{\mu''}^{\sigma', \sigma''} N_{\mu', \mu''}(z) + N_{\mu', \mu''}(z) N_{\mu''}^{\sigma', \sigma''} F_{\mu'}(z) \right] \\
\times \left[ \tilde{N}_{(\mu, \mu''), a}(z) + X_{\mu'}^{\sigma'} \tilde{N}_{(\mu, \mu''), a}(z) \right] \\
+ \frac{1}{2} \int_1^\infty dz F_{\mu'}^{\sigma'}(z) \tilde{N}_{(\mu, \mu''), b}(z) \tilde{N}_{(\mu', \mu''), c}(z) N_{\mu', \mu''}^{\sigma', \sigma''}(z) \tilde{N}_{(\mu, \mu''), a}(z) \right\} \quad (27)
\]

\[N_{\mu', \mu'', a}(z) = N_{\mu', \mu'', a}(z) = \int_1^\infty F_{\mu'}^{\sigma'}(x) N_{\mu', \mu''}^{\sigma', \sigma''}(x) dx, \quad (28)\]
\begin{align*}
F_{\mu,\mu'}^{\sigma,\sigma'}(x) &= -\frac{d}{dx} \left[ \frac{Q_\mu^\sigma(x) Q_{\mu'}^{\sigma'}(x)}{P_\mu^\sigma(x) P_{\mu'}^{\sigma'}(x)} \right], \\
E_{(\mu,\mu')}^{(\sigma,\sigma')}(x) &= -\frac{d}{dx} \left\{ \frac{x}{[P_\mu^\sigma(x)]^2} \frac{Q_{\mu'}^{\sigma'}(x)}{P_{\mu'}^{\sigma'}(x)} \right\}, \\
G_{\mu,\mu'}^{\sigma,\sigma'}(x) &= -\frac{d}{dx} \left\{ \frac{x}{[P_\mu^\sigma(x)]^2} \frac{x}{[P_{\mu'}^{\sigma'}(x)]^2} \right\}, \quad (29)
\end{align*}

\begin{align*}
\tilde{\mathfrak{M}}_{\mu,\mu',a}^{\sigma,\sigma'}(z) &= \tilde{\mathfrak{M}}_{\mu',\mu,a}^{\sigma',\sigma}(z) = \int_z^\infty G_{\mu,\mu'}^{\sigma,\sigma'}(x) N_{\mu,\mu',a}^{\sigma,\sigma'}(x) \, dx, \quad (30) \\
\tilde{\mathfrak{M}}_{(\mu,\mu'),a}^{(\sigma,\sigma')}(z) &= \int_z^\infty E_{(\mu,\mu')}^{(\sigma,\sigma')}(x) N_{(\mu,\mu'),a}^{(\sigma,\sigma')}(x) \, dx, \quad (31) \\
\tilde{\mathfrak{M}}_{(\mu,\mu'),a}^{(\sigma,\sigma')}(z) &= \int_z^\infty F_{\mu,\mu'}^{\sigma,\sigma'}(x) \tilde{\mathfrak{M}}_{(\mu,\mu'),a}^{(\sigma,\sigma')}(x) \, dx, \quad (32) \\
\tilde{\mathfrak{M}}_{(\mu,\mu'),a}^{(\sigma,\sigma')}(z) &= \tilde{\mathfrak{M}}_{(\mu',\mu),a}^{(\sigma,\sigma')}(z) = \int_z^\infty E_{(\mu',\mu)}^{(\sigma,\sigma')}(x) \tilde{\mathfrak{M}}_{(\mu',\mu),a}^{(\sigma,\sigma')}(x) \, dx, \quad (33) \\
\tilde{\mathfrak{M}}_{\mu,\mu',a}^{\sigma,\sigma'}(z) &= \tilde{\mathfrak{M}}_{\mu',\mu,a}^{\sigma',\sigma}(z) = \int_z^\infty F_{\mu,\mu'}^{\sigma,\sigma'}(x) \tilde{\mathfrak{M}}_{\mu,\mu',a}^{\sigma,\sigma'}(x) \, dx, \quad (34)
\end{align*}

FOUR - ELECTRON INTEGRALS
We have

\[
\langle \frac{r_{12} r_{13}}{r_{14}} \rangle = \langle \Phi_a(1) \Phi_b(2) \Phi_c(3) \Phi_d(4) \frac{r_{12} r_{13}}{r_{14}} \rangle = \frac{1}{512} R^{13}_{14} \pi^4 \delta(m_a + m_b + m_c + m_d; 0) \left[ 1 + O_{\text{per}} \left( \frac{b}{c} \right) \right] \sum_{\mu = \sigma = |m_b|}^{\infty} \sum_{\mu' = \sigma' = |m_c|}^{\infty} \times (2 \mu'' + 1) Z_{\mu''} \left\{ \int_1^\infty dz M_{(\mu, \mu', \mu''), a} (z) \mathcal{R}^{\sigma''}_{\mu', \mu'' c} (z) \\
+ \left[ F^\sigma_{\mu} (z) \mathcal{K}^{\sigma}_{\mu, \mu, b} (z) + X^\sigma G^\sigma_{\mu} (z) \mathcal{K}^{\sigma}_{\mu, \mu, b} (z) \right] \left[ X^\sigma \mathcal{R}^{\sigma}_{\mu', \mu', c} (z) + \mathcal{R}^{\sigma'}_{\mu', \mu', c} (z) \right] \\
+ \frac{1}{2} \int_1^\infty dz F^\sigma_{\mu''} (z) M^{\sigma, \sigma, \sigma''}_{(\mu', \mu'', \mu''), a} (z) \mathcal{K}^{\sigma''}_{\mu', \mu', d} (z) \\
+ \left[ X^\sigma \mathcal{R}^{\sigma'}_{\mu', \mu', b} (z) + \mathcal{R}^{\sigma'}_{\mu', \mu', b} (z) \right] \left[ X^\sigma \mathcal{R}^{\sigma'}_{\mu', \mu', c} (z) + \mathcal{R}^{\sigma'}_{\mu', \mu', c} (z) \right] \\
+ \int_1^\infty dz \mathcal{M}^{(\sigma, \sigma, \sigma'')}_{(\mu', \mu'', \mu''), a} (z) \mathcal{R}^{\sigma''}_{\mu', \mu', d} (z) \\
+ \left[ F^\sigma_{\mu} (z) \mathcal{K}^{\sigma}_{\mu, \mu, b} (z) + X^\sigma G^\sigma_{\mu} (z) \mathcal{K}^{\sigma}_{\mu, \mu, b} (z) \right] \\
+ \int_1^\infty dz \mathcal{M}^{(\sigma, \sigma, \sigma'')}_{(\mu', \mu'', \mu''), a} (z) \left[ \mathcal{R}^{\sigma'}_{\mu', \mu', c} (z) + X^\sigma \mathcal{R}^{\sigma'}_{\mu', \mu', c} (z) \right] \\
+ \left[ F^\sigma_{\mu} (z) \mathcal{K}^{\sigma}_{\mu, \mu, b} (z) \mathcal{R}^{\sigma''}_{\mu', \mu', d} (z) + F^\sigma_{\mu''} (z) K^{\sigma''}_{\mu', \mu', d} (z) \mathcal{R}^{\sigma}_{\mu, \mu, b} (z) \right] \right\} \right] 
\]

(35)

\[
M^{\sigma, \sigma', \sigma''}_{(\mu, \mu', \mu''), a} (z) = \\
= \frac{1}{2} \delta(m; \sigma + \sigma' + \sigma'') \sum_{L} \sum_{L'} \sum_{J} \sum_{J'} \left[ \begin{array}{c} \mu \\ \sigma \\ \sigma' \end{array} \right] \left[ \begin{array}{c} \mu' \\ \sigma' \end{array} \right] \left[ \begin{array}{c} J \\ \sigma + \sigma' \end{array} \right] \left[ \begin{array}{c} \mu' \\ \sigma' \end{array} \right] \left[ \begin{array}{c} J' \\ \sigma + \sigma' \end{array} \right] \\
\times \left[ \begin{array}{c} J \\ \sigma + \sigma' \\ \mu'' \end{array} \right] \left[ \begin{array}{c} \mu' \\ \sigma'' \end{array} \right] \left[ \begin{array}{c} J' \\ \sigma + \sigma' \\ \mu'' \end{array} \right] \{ K_{L, L', a}^{m} (z) + K_{L', L, a}^{m} (z) \} 
\]

(36)
\begin{align}
\tilde{M}(\sigma,\sigma';\sigma'')_{\mu,\mu'}(z) = \tilde{M}(\sigma,\sigma';\sigma'')_{\mu,\mu'}(z) = \delta(m;\sigma+\sigma'+\sigma'') \sum_{L} \sum_{L'} \sum_{J} \sum_{J'} \times \{ \mu' \begin{bmatrix} \mu + 2 & \mu' & J \\ \sigma & \sigma' & (\sigma + \sigma') \end{bmatrix} + V^{\sigma}_{\mu'} \begin{bmatrix} \mu - 2 & \mu' & J \\ \sigma & \sigma' & (\sigma + \sigma') \end{bmatrix} \} \begin{bmatrix} \mu & \mu' & J \\ \sigma & \sigma' & (\sigma + \sigma') \end{bmatrix} \\
\times \begin{bmatrix} J & \mu'' & L \\ (\sigma + \sigma') & \sigma'' & m \end{bmatrix} \begin{bmatrix} J' & \mu'' & L' \\ (\sigma + \sigma') & \sigma'' & m \end{bmatrix} \\
\times \{ K_{L,L',a}(z) + K_{L',L,a}(z) \} + W^{\sigma}_{\mu} M^{\sigma,\sigma',\sigma''}_{\mu,\mu',\mu''}(z) \}
\end{align}

\begin{align}
\approx (\sigma,\sigma';\sigma'') M(\mu,\mu',\mu'')(z) = \delta(m;\sigma+\sigma'+\sigma'') \sum_{J} \sum_{L} \sum_{L'} \sum_{J'} \times \{ \begin{bmatrix} \mu + 2 & \mu' & J \\ \sigma & \sigma' & (\sigma + \sigma') \end{bmatrix} + V^{\sigma}_{\mu'} \begin{bmatrix} \mu - 2 & \mu' & J \\ \sigma & \sigma' & (\sigma + \sigma') \end{bmatrix} \} \begin{bmatrix} \mu & \mu' & J \\ \sigma & \sigma' & (\sigma + \sigma') \end{bmatrix} \\
\times \begin{bmatrix} J & \mu'' & L \\ (\sigma + \sigma') & \sigma'' & m \end{bmatrix} \begin{bmatrix} J' & \mu'' & L' \\ (\sigma + \sigma') & \sigma'' & m \end{bmatrix} \{ K_{L,L',a}(z) + K_{L',L,a}(z) \} \\
+ W^{\sigma}_{\mu} \tilde{M}(\sigma,\sigma';\sigma'')(z) + W^{\sigma}_{\mu} \tilde{M}(\sigma,\sigma';\sigma'')(z) - W^{\sigma}_{\mu} W^{\sigma'}_{\mu'} M^{\sigma,\sigma',\sigma''}_{\mu,\mu',\mu''}(z)
\end{align}

\begin{align}
\langle r^{23} r_{14}/r_{12} \rangle = \langle \Phi_{a}(1) \Phi_{b}(2) \Phi_{c}(3) \Phi_{d}(4) r_{23} r_{14}/r_{12} \rangle = \frac{1}{512} \tilde{R}^{13} \pi^{4} \delta(\sigma';|m_{c}|) \\
\times \delta(\sigma'';|m_{d}|) \delta(\sigma;|m_{b}+m_{c}|) \delta(m_{a}+m_{b}+m_{c}+m_{d};0) \sum_{\mu=\sigma}^{\infty} \sum_{\mu'=\sigma}^{\infty} \sum_{\mu''=\sigma}^{\infty} (2\mu+1) \\
\times Z_{\mu}^{\mu} \int_{1}^{\infty} dz E^{\sigma}_{\mu}(z) \left[ N^{\sigma',\sigma}_{\mu',\mu,b}(z) \tilde{R}^{\sigma'}_{\mu',\mu',c}(z) X^{\sigma'}_{\mu} + \tilde{N}^{(\sigma',\sigma)}_{\mu',\mu,b}(z) \tilde{R}^{\sigma'}_{\mu',\mu',c}(z) \right] \\
+ N^{\sigma',\sigma}_{\mu',\mu,b}(z) \tilde{R}^{\sigma'}_{\mu',\mu',c}(z) + X^{\sigma'}_{\mu'} \tilde{J}^{(\sigma',\sigma)}_{\mu',\mu',c,b}(z) + \tilde{G}^{(\sigma',\sigma)}_{\mu',\mu',c,b}(z) \\
\times \left[ N^{\sigma'',\sigma}_{\mu',\mu,a}(z) \tilde{R}^{\sigma''}_{\mu',\mu',d}(z) X^{\sigma''}_{\mu} + \tilde{N}^{(\sigma'',\sigma)}_{\mu',\mu,a}(z) \tilde{R}^{\sigma''}_{\mu',\mu',d}(z) \right] \\
+ N^{\sigma'',\sigma}_{\mu',\mu,a}(z) \tilde{R}^{\sigma''}_{\mu',\mu',d}(z) + X^{\sigma''}_{\mu'} \tilde{J}^{(\sigma'',\sigma)}_{\mu',\mu',d,a}(z) + \tilde{G}^{(\sigma'',\sigma)}_{\mu',\mu',d,a}(z) \right] \end{align}
\[ \tilde{G}^{(\sigma''\sigma)}_{(\mu'',\mu),d,a}(z) = \int_1^z dx F_{\mu''}^{\sigma''}(x) \left[ K_{\mu'',\mu''}^{\sigma''}(x) \tilde{N}_{(\mu'',\mu),a}^{(\sigma''\sigma)}(x) \right. \\
+ \left. \bar{K}_{\mu'',\mu''}^{\sigma''}(x) N_{\mu'',\mu,a}^{\sigma''\sigma}(x) \right] \] (40)

\[ \tilde{J}^{(\sigma''\sigma)}_{(\mu',\mu')}_{d,a}(x) = \int_1^x dx G_{\mu'}^{\sigma}(x) K_{\mu',\mu'}^{\sigma}(x) N_{\mu',\mu,a}^{\sigma''\sigma}(x) \] (41)

\[ \langle r_{23} r_{12} / r_{14} \rangle = \langle \Phi_a(1) \Phi_b(2) \Phi_c(3) \Phi_d(4) r_{23} r_{12} / r_{14} \rangle = \frac{1}{512} R^{13 \mu} \pi^4 \delta(\sigma'; |m_c|) \times \delta(\sigma''; |m_d|) \delta(\sigma; |m_b+m_c|) \delta(m_a+m_b+m_c+m_d; 0) \sum_{\mu=\sigma} \sum_{\mu'=\sigma'} \sum_{\mu''=\sigma''} (2\mu''+1) \]

\[ \times Z_{\mu''}^{\sigma''} \left( \int_1^\infty dz \left\{ X_{\mu}^{\sigma'} G_{\mu}^{\sigma}(z) \left[ \tilde{J}^{(\sigma''\sigma)}_{(\mu''\mu),d,a}(z) + N_{\mu''\mu,a}^{\sigma''\sigma}(z) \tilde{N}_{\mu'',\mu'}^{\sigma''\sigma}(z) \right] \right. \\
+ \left. F_{\mu}^{\sigma}(z) \left[ \tilde{N}_{(\mu''\mu),d,a}(z) + \tilde{N}_{(\mu''\mu'),c,b}(z) \right] \right\} \right] \]

\[ \times \left\{ N_{\mu''\mu,b}(z) \tilde{N}_{\mu',\mu'}^{\sigma'}(z) + N_{\mu''\mu,b}(z) \tilde{N}_{\mu',\mu'}^{\sigma'}(z) + X_{\mu'}^{\sigma'} N_{\mu''\mu,b}(z) \tilde{N}_{\mu',\mu'}^{\sigma'}(z) \\
+ X_{\mu'}^{\sigma'} \tilde{J}^{(\sigma',\sigma)}_{(\mu',\mu'),c,b}(z) + \tilde{G}^{(\sigma',\sigma)}_{(\mu',\mu'),c,b}(z) \right\} \right] \}

\[ \times \left\{ \tilde{N}_{(\mu''\mu),b}(z) \tilde{N}_{(\mu''\mu'),c,b}(z) + N_{\mu''\mu,b}(z) \tilde{N}_{\mu',\mu'}^{\sigma'}(z) + X_{\mu'}^{\sigma'} N_{\mu''\mu,b}(z) \tilde{N}_{\mu',\mu'}^{\sigma'}(z) \\
+ X_{\mu'}^{\sigma'} \tilde{J}^{(\sigma',\sigma)}_{(\mu',\mu'),c,b}(z) + \tilde{G}^{(\sigma',\sigma)}_{(\mu',\mu'),c,b}(z) \right\} \right] \}

\[ \tilde{J}^{(\sigma''\sigma)}_{(\mu'',\mu),d,a}(z) = \int_1^z F_{\mu}^{\sigma}(x) K_{\mu',\mu'}^{\sigma}(x) \tilde{N}_{(\mu'',\mu),a}^{(\sigma''\sigma)}(x) dx, \] (43)

\[ \tilde{J}^{(\sigma''\sigma)}_{(\mu'',\mu),d,a}(z) = \int_1^z G_{\mu}^{\sigma}(x) K_{\mu',\mu'}^{\sigma}(x) \tilde{N}_{(\mu'',\mu),a}^{(\sigma''\sigma)}(x) dx, \] (44)

\[ \tilde{E}^{(\sigma',\sigma)}_{(\mu'',\mu'),c,b}(z) = \int_1^z F_{\mu'}^{\sigma'}(x) \left[ K_{\mu',\mu'}^{\sigma'}(x) N_{\mu''\mu,b}^{(\sigma',\sigma)}(x) \\
+ \bar{K}_{\mu',\mu'}^{\sigma'}(x) \tilde{N}_{(\mu''\mu),b}^{(\sigma',\sigma)}(x) \right] dx, \] (45)

\[ \tilde{J}^{(\sigma''\sigma)}_{(\mu'',\mu),d,a}(z) = \int_1^z F_{\mu''}^{\sigma''}(x) K_{\mu''\mu''}^{\sigma''}(x) N_{\mu''\mu,a}^{\sigma''\sigma}(x) dx, \] (46)

**KINETIC ENERGY INTEGRAL**
Essentially no new basic integrals are involved in the evaluation of the kinetic energy, nuclear attraction, and overlap integrals. In some cases, a modified $K_{\mu,\mu',s}(z)$ integral is used. The modified integral $H_{\mu,\mu',s}(z)$ is defined in Eq. (47); it differs in that the $\xi^2 - \eta^2$ term is not included.

$$H_{\mu,\mu',s}(z) = \int_1^z \int_{-1}^1 \xi^{p_s} \eta^{q_s} (\xi^2 - 1)^{\gamma_s/2} (1 - \eta^2)^{\nu_s/2} \times e^{-\alpha_s \xi} e^{\beta_s \eta} P^\sigma(\xi) P_{\mu'}^\sigma(\eta) d\xi d\eta, \quad (47)$$

$$- \frac{1}{2} \int d\tau \Phi_s(1) \Phi_t(2) \Phi_w(3) r_{13}^l r_{12}^{l'} \nabla_1^2 \left[ r_{12}^l \Phi_a(1) \Phi_x(2) \Phi_y(3) \right] =$$

$$- \frac{1}{2} l(l + 1) \int d\tau \Phi_e(1) \Phi_f(2) \Phi_g(3) r_{13}^l r_{12}^{l'}$$

$$- \frac{2}{R^2} \int d\tau \frac{D_a(1)}{\xi_1^2 - \eta_1^2} \Phi_f(2) \Phi_g(3) r_{13}^l r_{12}^{l'}$$

$$- l \int d\tau \frac{V_a(1,2)}{\xi_1^2 - \eta_1^2} \Phi_f(2) \Phi_g(3) r_{13}^l r_{12}^{l'}, \quad (48)$$
\[ \Phi_a(1)\Phi_a(1) = \Phi_c(1), \Phi_c(2)\Phi_c(2) = \Phi_f(2), \Phi_w(3)\Phi_y(3) = \Phi_j(3), \]
\[ D_a(1) = p_a^2 + p_a + 2p_\alpha \gamma_a + \gamma_a - \alpha_a^2 - q_a^2 - q_a - 2q_a\nu_a - \nu_a \]
\[ + \beta_a^2 - 2\alpha_a \xi_1 (p_a + \gamma_a + 1) - 2\beta_a \eta_1 (q_a + \nu_a + 1) + \frac{p_a - p_a^2}{\xi_1^2} + \frac{q_a^2 - q_a}{\eta_1^2} \]
\[ + \frac{2\alpha_a p_a}{\xi_1} + \frac{2\beta_a q_a}{\eta_1} + \gamma_a^2 \xi_1^2 + \frac{\gamma_a \xi_1}{\xi_1^2 - 1} - \beta_a \eta_1^2 + \frac{\nu_a \eta_1^2}{1 - \eta_1^2} + \frac{m_a^2 (\eta_1^2 - \xi_1^2)}{(\xi_1^2 - 1) (1 - \eta_1^2)}. \]
\[ V_a(1,2) = (1 - \eta_1^2) (q_a + \beta_a \eta_1 - \frac{q_a \xi_2 \eta_2 \xi_1}{\eta_1} - \beta_a \xi_2 \eta_2 \xi_1) \]
\[ + (\xi_1^2 - 1) (p_a - \alpha_a \xi_1 - \frac{p_a \xi_2 \eta_2 \eta_1}{\xi_1} + \alpha_a \xi_2 \eta_2 \eta_1) \]
\[ - \nu_a \eta_1^2 + (\nu_a - \gamma_a) \xi_2 \eta_2 \xi_1 + \gamma_a \xi_1^2 \]
\[ + \left( \alpha_a \xi_1 + \beta_a \eta_1 + q_a - p_a - \frac{\eta_1^2 \nu_a}{1 - \eta_1^2} - \frac{\xi_1^2 \gamma_a}{\xi_1^2 - 1} \right) \]
\[ \times \left[ \frac{[e^{i(\phi_1 - \phi_2)} + e^{-i(\phi_1 - \phi_2)}]}{2} \right] \]
\[ + m_a (\xi_1^2 - \eta_1^2) \left[ \frac{(\xi_1^2 - 1) (1 - \eta_1^2)}{(\xi_1^2 - 1)(1 - \eta_1^2)} \right]^{1/2} \]
\[ \times \left[ e^{i(\phi_1 - \phi_2)} - e^{-i(\phi_1 - \phi_2)} \right], \quad (49) \]

For \( l = l' = 0 \), the kinetic energy integral [Eq. (48)] over electron 1 is the sum of \(-\frac{1}{2} \pi R H^\sigma_{\mu,\mu',e}(\infty)\) terms. For \( l = 0 \) and \( l' = 1 \), the integral is a sum of \( \langle r_{12} \rangle \) terms [Eq. (15)], evaluated using \( H^\sigma_{\mu,\mu',e}(z) \) [Eq. (47)] for electron 1 and the usual \( K^\sigma_{\mu,\mu',f}(z) \) [Eq. (7)] for electron 2. For \( l = 0 \) and \( l' = 2 \), use [Eq. (4)] for \( \langle r_{12}^2 \rangle \) with \( H^\sigma_{\mu,\mu',e}(z) \) for electron 1. For \( l = 1 \) and \( l' = 0 \), use the usual \( \langle 1/r_{12} \rangle \) [Eq. (10)] and \( \langle r_{12} \rangle \) [Eq. (15)] with [Eq. (47)] instead of [Eq. (7)] for electron 1. For \( l = l' = 1 \), use \( \langle r_{13}/r_{12} \rangle \) [Eq. (26)] and \( \langle r_{12}r_{13} \rangle \) [Eq. (18)] with [Eq. (47)] instead of [Eq. (7)] for electron 1. For \( l = 2 \) and \( l' = 0 \), [Eq. (49)] is the sum of \[-\frac{3}{4} \pi R^3 \left( \frac{1}{4} \pi R^3 \right)^2 K^\sigma_{\mu,\mu',e}(\infty) K^\sigma_{\mu',\mu',f}(\infty) K^\sigma_{\mu,\mu',g}(\infty)\]
terms,
\[-\frac{1}{2} \pi R K^\sigma_{\mu,\mu,g}(\infty) \langle r_{12}^2 \rangle\]
terms, and
\[-\frac{1}{2} \pi R^3 \left( \frac{1}{4} \pi R^3 \right)^2 H^\sigma_{\mu,\mu,e}(\infty) K^\sigma_{\mu',\mu',f}(\infty) K^\sigma_{\mu',\mu',g}(\infty)\]
terms. The $\langle r_{12}^2 \rangle$ are evaluated using [Eq. (47)] instead of [Eq. (7)] for electron 1. The case of the kinetic energy integral in which the Laplacian operates on $r_{12}$ and this is multiplied by $r_{12}$ is represented in [Eq. (50)].

$$-\frac{1}{2} \int d\tau \Phi_s(1)\Phi_t(2)r_{12}^{l}\nabla^2[r_{12}F_a(1)\Phi_x(2)], \quad (50)$$

For $l = l' = 1$ [Eq.(50)] equals

$$\left(\frac{1}{4}\pi R^3\right)^2 \delta(m_a + m_a; 0)\delta(m_t + m_x; 0)\mathcal{K}_0^{0,0,e}(\infty)\mathcal{K}_0^{0,0,f}(\infty)$$

$$-\frac{1}{2} \int d\tau \Phi_f(1)\Phi_t(2)r_{12}^{l}[D_a(1) + D_s(1)]\Phi_g(1)$$

NUCLEAR - ELECTRON ATTRACTION AND OVERLAP INTEGRALS

We have

$$-\frac{2}{R} \int d\tau \frac{(Z_a + Z_b)\xi_1 + (Z_a - Z_b)\eta_1}{(\xi_1^2 - \eta_1^2)} \Phi_e(1)\Phi_f(2)\Phi_g(3)r_{12}^{l}\Phi_s(1), \quad (51)$$

For $l = l' = 0$, the integral over electron 1 is

$$-\frac{1}{4} R\delta(m_e; 0)\mathcal{K}_0^{0,0,e}(\infty) = (Z_a - Z_b)\mathcal{K}_0^{0,0,e}(\infty)$$

For $l' = 0$ and $l = 1$, use $\langle r_{12} \rangle$ [Eq. (15)] and [Eq. (47)] instead of [Eq. (7)] for electron 1. For $l' = 0$ and $l = 2$, use $\langle r_{12}^2 \rangle$ [Eq. (4)] without the $(\xi_1^2 - \eta_1^2)$ term. For $l' = l = 1$ use $\langle r_{12}r_{13} \rangle$ [Eq. (18)] with [Eq. (47)] instead of [Eq. (7)] for electron 1. The nuclear-nuclear repulsion integral is $Z_aZ_b/R$ times the overlap integral [Eq. (52)].

$$\langle r_{12}^{l}\Phi_s(1)\Phi_t(2)\Phi_g(3)r_{12}^{l}\Phi_s(1) \rangle \quad (52)$$

For $l = l' = 0$ the integral over electron 1 is $\frac{1}{4} R\delta(m_e; 0)\mathcal{K}_0^{0,0,e}(\infty)$. For $l' = 0$ and $l = 1$, the integral is $\langle r_{12} \rangle$. [Eq. (15)]. For $l' = 0$ and $l = 2$, the integral is $\langle r_{12}^2 \rangle$. [Eq. (4)]. For $l' = l = 1$ the overlap is $\langle r_{12}r_{13} \rangle$. [Eq. (18)].

ADDITIONAL INTEGRALS

Some integrals can be generated from previously given integrals by raising or lowering the $r_{12}$ index in even or odd steps. [Eqs. (53) and (54)] , using Eqns. (1), (5), (12), and (59). If the Hamiltonian contains the term $1/r_{ij}^3$, for the evaluation of spin-spin magnetic coupling or the relativistic effects of an external electric field, then $\langle 1/r_{ij}^3 \rangle$ [Eq. (55)] and
\( \langle 1/r_{12}^3 \rangle \) [Eq. (56)] are some of the integrals needed. These results are based on a generalization of the Neumann expansion [Eq.(59)]\( ^{23,31,36,37} \). The \( C_n^i(x) \) [Eq. (58)] are Gegenbauer polynomials. For \( l = \frac{1}{2} \), the Gegenbauer polynomials are the same as Legendre polynomials. If the wave function [Eq. (3)] is modified to be

\[
\Psi_{\text{tot}} = \mathcal{A} \left\{ \prod_j \sum_s a_s \phi_s(j) \left[ 1 + \sum_j <s< \sum_k w_{jk} r_j^n r_k^r \right] \right\},
\]

then terms \( \langle 1/r_{12} r_{13} \rangle \) [Eq. (60)] will occur in the kinetic energy integrals.

\[
\langle r_{12}^3 \rangle = \int d\tau \Phi_e(1) \Phi_f(2) r_{12}^3 = \frac{1}{4} R^2 \left\{ \langle \Phi_{(p_e, q_e)}(1) \rangle r_{12} \Phi_f(2) \right\}
+ \langle \Phi_{(p_e, q_e + 2)}(1) \rangle r_{12} \Phi_f(2) - \langle \Phi_{(p_e + 1, q_e)}(1) \rangle r_{12} \Phi_f(2)
+ \langle \Phi_{(p_e, q_e + 2)}(1) \rangle r_{12} \Phi_f(2) + \langle \Phi_{(p_e + 1, q_e + 1, \alpha, \beta)}(2) \rangle - \langle \Phi_{(p_e + 1, q_e + 1, \alpha, \beta)}(2) \rangle
- \langle \Phi_{(p_e, q_e + 1, \alpha, \beta)}(2) \rangle, \quad e_+ = (p_e, q_e, \gamma_e + 1, \nu_e + 1, \alpha_e, \beta_e, m_e + 1)
\]

\[
\langle r_{13}^2/r_{12} \rangle = \int d\tau \Phi_a(1) \Phi_b(2) r_{13}^2/r_{12} = \frac{R^2}{4} \left\{ \langle \Phi_t(3) \rangle \right\}
\times \langle \Phi_{(p_a+2, q_a+2)}(1) \rangle \langle \Phi_{(p_a+2, q_a+2)}(1) \rangle \langle \Phi_{(p_b+2, q_b+2)}(1) \rangle \langle \Phi_{(p_b+2, q_b+2)}(1) \rangle - \langle \Phi_{(p_a+2, q_a+2)}(1) \rangle \langle \Phi_{(p_b+2, q_b+2)}(1) \rangle
\times \langle \Phi_{(p_b+2, q_b+2)}(1) \rangle \langle \Phi_{(p_b+2, q_b+2)}(1) \rangle - \langle \Phi_{(p_b+2, q_b+2)}(1) \rangle \langle \Phi_{(p_b+2, q_b+2)}(1) \rangle - \langle \Phi_{(p_b+2, q_b+2)}(1) \rangle \langle \Phi_{(p_b+2, q_b+2)}(1) \rangle
- \langle \Phi_{(p_b+1, q_b+1, \alpha, \beta)}(3) \rangle \langle \Phi_{(p_b+1, q_b+1, \alpha, \beta)}(3) \rangle - \langle \Phi_{(p_b+1, q_b+1, \alpha, \beta)}(3) \rangle \langle \Phi_{(p_b+1, q_b+1, \alpha, \beta)}(3) \rangle
\]

\[
\langle 1/r_{12}^3 \rangle = \int d\tau \Phi_a(1) \Phi_b(2) (1/r_{12}^3) = \pi^2 R^2 \delta(m_a + m_b; 0)
\times \sum_{l=0}^{\infty} \sum_{m_{}\pm m_a+1} \left\{ (-1)^{m_a+1} + (-1)^m |m(2l + 1)
\times Z_l^m \int_{-1}^{+1} F^m(z) K^m_{l,l,a}(z) K^m_{l,l,b}(z) dz, \right. (55)
\]

\[
\left. \right. (55)
\]
\[
\frac{1}{r_{12}^2} = \int d\tau \Phi_a(1) \Phi_b(2)(1/r_{12}^2) = \frac{1}{2} \pi^2 R^4 \delta(m_a + m_b; 0)
\]

\[
\times \sum_{n=0}^{\infty} \sum_{l=|m_a|}^{n} \left[ \frac{1 + (-1)^{l+ma}}{2} \right] \frac{(l!)^2(n-l)!(n+1)(2l+1)}{(n+l)!}
\]

\[
\times \frac{(l-m_a)!}{[(l+ma)/2]!} \frac{(l+m_a)!}{[(l+ma)/2]!} \int_1^{\infty} \frac{dz L_{n-l,n-l,a(l)}^{l+1}(z) L_{n-l,n-l,b(l)}^{l+1}(z)}{(z^2 - 1)^{l+3/2} \left[ C_{n-l}^l(z) \right]^2},
\]

\[a(l) = (p_a, q_a, \gamma_a + l, \nu_a + l, \alpha_a, \beta_a, m_a), \]
\[b(l) = (p_b, q_b, \gamma_b + l, \nu_b + l, \alpha_b, \beta_b, m_b), \quad (56)\]

\[
L_{n,n',s}^l(z) = \int_1^{\infty} \int_{-1}^{1} d\xi d\eta \xi^p \eta^q \xi^{(\gamma^2 - 1)\gamma/2}(1 - \eta^{2\nu})^{\nu/2}
\]

\[
\times e^{-\alpha \xi}e^{\beta \eta} C_n^l(\xi) C_{n'}^{l'}(\eta), \quad (57)
\]

\[
C_{n'}^{l'} = \sum_{j=0}^{[n'/2]} \frac{2^{n-2j}(-1)^j(l+n-j-1)!x^{n-2j}}{j!(n-2j)!(l-1)!} \quad (58)
\]

The upper limit of the sum over \(j\) is \(\frac{1}{2}n\) or \(\frac{1}{2}(n - 1)\), whichever is integral. We have\(^{36,37}\)

\[
\left( \frac{2r_{12}}{R} \right)^{-2p} = \sum_{n=0}^{\infty} \sum_{l=|m_a|}^{n} d_{nl}(p) \left[ (1 - \eta_1^2)(1 - \eta_2^2)(\xi_1^2 - 1)(\xi_2^2 - 1) \right]^{1/2}
\]

\[
\times D_{n-l}(\xi_{1>2}) C_{n-l}(\eta_{1} \eta_{2}) C_{n-l}(\eta_{2}) C_{n-l}(\eta_{1}) C_{n-l}(\eta_{2}) C_{n-l}(\eta_{1}) C_{n-l}(\eta_{2}) \cos(\phi_1 - \phi_2),
\]

\[p > 0, \quad p \neq \frac{1}{2}\]

\[
d_{nl}(p) = \frac{-2^{l+1} \Gamma(2p-1)[\Gamma(p+l)]^2(n-l)!(n+p)(2p+2l-1)}{[\Gamma(p)]^2 \Gamma(2p+n+l)},
\]

\[
D_{m}^u(\xi) = -C_{m}^u(\xi) \int_{\xi}^{\infty} \frac{(x^2 - 1)^{-u-1/2} dx}{[C_{m}(x)]^2},
\]

\[
\frac{d}{d\xi} \left[ \frac{D_{m}^u(\xi)}{C_{m}^u(\xi)} \right] = \frac{(\xi^2 - 1)^{-u-1/2}}{[C_{m}(\xi)]^2}, \quad (59)
\]
\[ \frac{1}{r_{12}r_{13}} = \int d\tau \Phi_a(1)\Phi_b(2)\Phi_c(3) \frac{1}{r_{12}r_{13}} = \]

\[ \frac{1}{16} \pi^3 R^7 \delta(m_a + m_b + m_c; 0) \delta(\sigma; |m_b|) \delta(\sigma'; |m_c|) \left[ 1 + O_{perc}(\frac{b}{c}) \right] \]

\[ \times \sum_{l=\sigma}^{\infty} \sum_{j=\sigma'}^{\infty} (2l + 1)(2j + 1) Z_l^\sigma Z_j^{\sigma'} \]

\[ \times \int_1^{\infty} dz N_{l,j,a}^{\sigma,\sigma'}(z) K_{l,l,b}^{\sigma}(z) R_{j,j,c}^{\sigma'}(z) F_{l}^{\sigma}(z), \quad (60) \]

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