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Analytical Evaluation of Three-Center One-Electron Integrals of $r^N Y_L^M(\theta, \phi)$ with Slater-Type Atomic Orbitals*

HARRIS J. SILVERSTONE† AND H. DAVID TODD
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Abstract

Theoretical prediction of molecular properties, such as quadrupole coupling tensor, electron-proton hyperfine interaction, chemical shift, and spin-orbit coupling, requires computation of matrix elements of $r^N Y_L^M$, where Y_L^M is a spherical harmonic. Formulas for two- and three-center one-electron integrals of $r^N Y_L^M$ with Slater-type atomic orbitals are derived. Use is made of Fourier-transforms, generalized-function theory, and complex variable theory. The final formulas involve spherical harmonics and functions related to exp (x) and to the exponential integral, but nothing more complicated. Two alternative sets of formulas are given, but only one is valid when N–L is an even, negative integer.

1. Introduction

Matrix elements of $r^N Y_L^M(\theta, \phi)$, where Y_L^M denotes a spherical harmonic, are the crux of the theoretical calculation of such one-electron molecular properties as force on a nucleus, quadrupole coupling tensor, electron-proton hyperfine interaction, chemical shift, and spin-orbit coupling. Three methods have been outlined in some detail for calculating three-center integrals of $r^N Y_L^M$ with respect to Slater-type atomic orbitals (STO's). One is based on the Gaussian transform method [1], a second on the "Laplace-type" expansion [2, 3] of $r^N Y_L^M$, and a third on the expansion of an STO about another center [4]. All three approaches involve numerical integration. Analytical formulas seem to have been published only for the most important of the two-center "Coulomb"-type integrals [2, 5].

In this paper we derive purely analytical formulas for two- and three-center one-electron integrals of $r^N Y_L^M$ with STO's. The expansion of an STO about another center [6], the Fourier-transform technique [7], and the theory of generalized functions [7] are used extensively. The formulas obtained are valid‡ for general values of the STO parameters and for integer N and L.

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‡ Note, however, the restrictions given in Equations (3) and (5).

2. Formulation

In this section the general three-center integral is formulated in terms of Fourier transforms.

The general three-center one-electron integral with STO's is

$$I_{ab}^{NLM} = \int dV r^N Y_L^M(\theta, \phi) \psi_{n_a l_a m_a \zeta_a}(\mathbf{r} - \mathbf{R}_a) \psi^*_{n_b l_b m_b \zeta_b}(\mathbf{r} - \mathbf{R}_b) \tag{1}$$

The arrangement of the internuclear vectors is shown in Figure 1. By an STO, we mean

$$\psi_{nlm\zeta}(\mathbf{r}) \equiv r^{n-1} \exp(-\zeta r)\, Y_l^m(\theta, \phi) \tag{2}$$

where n is a positive integer, and

$$n \geqq l + 1 \tag{3}$$

It is convenient to give a symbol to the vector connecting a and b,

$$\mathscr{R} \equiv \mathbf{R}_b - \mathbf{R}_a \tag{4}$$

The N can be a negative integer. When $N \leqq -3$, the integral (1) is not absolutely convergent. It is made unambiguous and finite, however, by the restriction,

$$N + L + 2 \geqq 0 \tag{5}$$

and the convention that integration over angle be carried out before integration over radius.

There are two convenient, distinct ways by which I_{ab}^{NLM} can be recast in terms of Fourier transforms. We regard I_{ab}^{NLM} as an overlap integral:

(*1*) between $\{r^N Y_L^M\}$ and $\{\psi_a^* \psi_b\}$, and

(*2*) between $\{r^N Y_L^{M*} \psi_b\}$ and $\{\psi_a\}$.

Then with the aid of the Fourier-transform convolution theorem [7–10], we obtain,

(6)

$$I_{ab}^{NLM} = (2\pi)^{-3} \int d^3\mathbf{k}\, \mathrm{FT}^*\{\psi^*_{n_a l_a m_a \zeta_a}(\mathbf{r}) \psi_{n_b l_b m_b \zeta_b}(\mathbf{r} - \mathbf{R})\} \mathrm{FT}\{r^N Y_L^M\} \exp(-i\mathbf{k} \cdot \mathbf{R}_a)$$

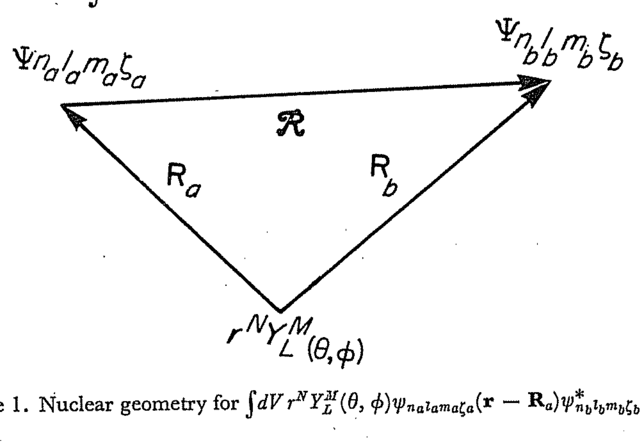

Figure 1. Nuclear geometry for $\int dV r^N Y_L^M(\theta, \phi) \psi_{n_a l_a m_a \zeta_a}(\mathbf{r} - \mathbf{R}_a) \psi^*_{n_b l_b m_b \zeta_b}(\mathbf{r} - \mathbf{R}_b)$.

and

(7)
$$I_{ab}^{NLM} = (2\pi)^{-3}\int d^3\mathbf{k}\,\text{FT}^*\{r^N Y_L^{M*}\psi_{n_b l_b m_b \zeta_b}(\mathbf{r}-\mathbf{R}_b)\}\text{FT}\{\psi_{n_a l_a m_a \zeta_a}(\mathbf{r})\}\exp(i\mathbf{k}\cdot\mathbf{R}_a)$$

Equation (6) leads naturally to an expansion in terms of $\mathscr{R}$ and $\mathbf{R}_a$. Equation (7) leads to an expansion in terms of $\mathbf{R}_a$ and $\mathbf{R}_b$. The symbol FT { } means "Fourier transform":

(8)
$$\text{FT}\{\Phi(\mathbf{r})\} \equiv \int dV \exp(i\mathbf{k}\cdot\mathbf{r})\Phi(\mathbf{r})$$

In the next section the basic Fourier transforms which enter Equations (6) and (7) are given. In Section 4, the special case of two-center integrals is treated. In Section 5 Equations (6) and (7) are evaluated for the three-center case. It should be noted in advance that the formulation of Equation (7) is very closely related to the (1-2)-type three-center two-electron integral of $1/r_{12}$ evaluated previously [10], and the resulting formulas (Equations 45–47) differ in relatively minor ways from the $1/r_{12}$ integral.

3. Basic Fourier Transforms and Special Functions

The Fourier transforms which appear in the integrands of Equations (6) and (7) are collected in this section. Various special functions appear both in these basic Fourier transforms and in the final formulas for the integrals. Definitions of the special functions are given here, but for most of their important properties the reader is referred to either a standard reference work [11] or to our previous work [10] in which the functions are used extensively.

The standard functions needed are spherical Bessel functions,

(9)
$$j_l(x) \equiv (-x)^l (x^{-1}\,d/dx)^l x^{-1} \sin(x)$$

modified spherical Bessel functions,

(10)
$$\mathscr{I}_l(x) = x^l (x^{-1}\,d/dx)^l x^{-1} \sinh(x)$$

(11)
$$\mathscr{K}_l(x) = (-x)^l (x^{-1}\,d/dx)^l x^{-1} \exp(-x)$$

the exponential-type integral,

(12)
$$E_n(x) \equiv \int_1^\infty d\,t^{-n} \exp(-xt)$$

(13)
$$= \alpha_{-n}(x)$$

(14a)
$$= \tilde{E}_n(x) - (-x)^{n-1}\{\log(x) - \psi(n)\}/(n-1)! \qquad (n \geqq 1)$$

(14b)
$$= \hat{\alpha}_{-n} + x^{n-1}(-n)! \qquad (n \leqq 0)$$

(the ψ denotes the logarithmic derivative of the gamma function), the Condon–Shortley coefficients [12],

$$[(2\lambda+1)/4\pi]^{1/2}c^{\lambda}(lm;\,l'm') \equiv \int d\Omega\, Y_l^{m*}\, Y_{l'}^{m'}\, Y_{\lambda}^{m-m'} \tag{15}$$

the double factorial function,

$$(2N)!! \equiv 2^N N! \tag{16}$$

$$(2N-1)!! \equiv (2N)!/(2N)!! \tag{17}$$

$$= (-1)^N/(-2N-1)!! \tag{18}$$

the sgn function,

$$\operatorname{sgn}(x) \equiv x/|x| \tag{19}$$

and the Dirac delta function and its derivatives [7],

$$\delta^{(N)}(x) \equiv (d/dx)^N\,\delta(x) \tag{20}$$

We also use the "plane wave expansion",

$$\exp(i\mathbf{k}\cdot\mathbf{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} 4\pi i^l j_l(kr)\, Y_l^{m*}(\theta,\phi)\, Y_l^m(\theta_k,\phi_k) \tag{21}$$

Throughout the paper, we denote the spherical polar coordinates of $\mathbf{r}$, $\mathbf{k}$, $\mathbf{R}$, etc., by (r, θ, ϕ), (k, θ_k, ϕ_k), (R, θ_R, ϕ_R), etc.

Some of the Fourier transforms needed do not exist in the ordinary sense, they are well-defined, however, as generalized functions. The Fourier transform of $r^N Y_L^M$ is such a case, which has been discussed previously [3]: the result is summarized here:

$$\mathrm{FT}\{r^N Y_L^M\} = 4\pi i^L \mathscr{F}_{NL}(k)\, Y_L^M(\theta_k,\phi_k) \tag{22}$$

$$\mathscr{F}_{NL}(k) = k^{-N-3}(N+L+1)!!/(L-N-2)!! \qquad N-L \text{ odd} \tag{23}$$

$$\begin{aligned} k^{L+1}\mathscr{F}_{NL}(k) &= k^{L+1}\,\delta^{(N+2)}(k)\,\pi(-1)^{(N+L)/2}(N+L+1)!! \\ &\quad\times (N-L)!!/(N+2)! \qquad N-L \text{ even and } \geqq 0 \end{aligned} \tag{24}$$

$$\begin{aligned} &= k^{L+1}k^{-N-3}\operatorname{sgn}(k)\tfrac{1}{2}\pi(N+L+1)!!/(L-N-2)!! \\ &\qquad\qquad N-L \text{ even and } \leqq -2 \end{aligned} \tag{25}$$

The Fourier-transform of the two-center product of two STO's, which uses implicitly the expansion of one STO about the other's center [6], is [10]

$$\begin{aligned} &\mathrm{FT}\{\psi^*_{n_a l_a m_a \zeta_a}(\mathbf{r})\,\psi_{n_b l_b m_b \zeta_b}(\mathbf{r}-\mathscr{R})\} \\ &= \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{\lambda=|l-l_b|}^{l+l_b}\sum_{\Lambda=|l-l_a|}^{l+l_a}[(2\lambda+1)(2\Lambda+1)]^{1/2}c^{\lambda}(l_b m_b;\,lm)\,c^{\Lambda}(lm,\,l_a m_a) \\ &\quad\times Y_{\lambda}^{m_b-m}(\theta_{\mathscr{R}},\phi_{\mathscr{R}})\, Y_{\Lambda}^{m-m_a}(\theta_k,\phi_k)\, G_{l\lambda l_b\Lambda}^{n_a\zeta_a n_b\zeta_b}(k,\mathscr{R}) \end{aligned} \tag{26}$$

with

$$G^{n_a\zeta_a n_b\zeta_b}_{l\lambda l_b\Lambda}(k, \mathscr{R}) = 2\pi i^{\Lambda-1}(-1)^{\Lambda+\lambda}[\cdots \mathscr{I}_\lambda(\zeta_b\mathscr{R}) \cdots]k^\Lambda(k^{-1}\, d/dk)^\Lambda k^{-1}$$
$$\times \{E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-ik)\mathscr{R}] - E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+ik)\mathscr{R}]\}$$
$$(27) \qquad + \pi i^{\Lambda-1}(-1)^\Lambda[\cdots \mathscr{K}_\lambda(\zeta_b\mathscr{R}) \cdots]k^\Lambda(k^{-1}\, d/dk)^\Lambda k^{-1}$$
$$\times \{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-ik)\mathscr{R}] - \tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+ik)\mathscr{R}]$$
$$- \tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-ik)\mathscr{R}] + \tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b+ik)\mathscr{R}]\}$$

and with

$$(28) \qquad [\cdots \mathscr{I}_\lambda(\zeta_b\mathscr{R}) \cdots] = [(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}\, d/d\zeta_b)^{l_b}\zeta_b^{l+l_b+1}\mathscr{I}_\lambda(\zeta_b\mathscr{R})(\zeta_b^{-1}d/d\zeta_b)^l\zeta_b^{-1}\mathscr{R}^{n_a-\Lambda-l}]$$

(and similarly for $[\cdots \mathscr{K}_\lambda(\zeta_b\mathscr{R}) \cdots]$). The Fourier-transform of $r^N Y_L^M$ times an STO at $\mathbf{R}_b$ is essentially a special case of the Fourier transform of the two-center STO product:

$$(29) \qquad \mathrm{FT}\{r^N Y_L^{M*}(\theta, \phi)\psi_{n_b l_b m_b \zeta_b}(\mathbf{r}-\mathbf{R}_b)\}$$
$$= \{\text{Equations (26 and (27), with } n_a, l_a, m_a, \zeta_a, \text{ and } \mathbf{R} \text{ replaced by } N+1, L, M, 0, \text{ and } \mathbf{R}_b\}$$

With the above building blocks, we can now proceed to evaluate the integrals in Equations (6) and (7).

4. Two-Center Integrals

There are two two-center cases: the (1–1)-type has both STO's on the same center, i.e.,

$$(30) \qquad \mathbf{R}_a = \mathbf{R}_b \neq 0$$

while the (1–2)-type has one STO, say ψ_a, located at the origin, i.e.,

$$(31) \qquad \mathbf{R}_a = 0$$

$$(32) \qquad \mathbf{R}_b \neq 0$$

For the (1–1)-type, we use the identity,

$$(33) \qquad \psi_{n_a l_a m_a \zeta_a}(\mathbf{r})\psi^*_{n_b l_b m_b \zeta_b}(\mathbf{r}) = \sum_{\lambda'=|l_a-l_b|}^{l_a+l_b} [(2\lambda'+1)/4\pi]^{1/2} c^{\lambda'}(l_b m_b; l_a m_a)\psi^*_{n_a+n_b-1,\lambda',m_b-m_a,\zeta_a+\zeta_b}(\mathbf{r})$$

Then note that

$$(34) \qquad I_{ab}^{NLM} = \sum_{\lambda'=|l_a-l_b|}^{l_a+l_b} [(2\lambda'+1)/4\pi]^{1/2} c^{\lambda'}(l_b m_b; l_a m_a) \times \int dV r^N Y_L^M(\theta, \phi)\psi^*_{n_a+n_b-1,\lambda',m_b-m_a,\zeta_a+\zeta_b})(\mathbf{r}-\mathbf{R}_a)$$

$$(35) \qquad = \sum_{\lambda'=|l_a-l_b|}^{l_a+l_b} [(2\lambda'+1)/4\pi]^{1/2} c^{\lambda'}(l_b m_b; l_a m_a) \times \mathrm{FT}^*_{\mathbf{k}=0}\{r^N Y_L^{M*}(\theta, \phi)\psi_{n_a+n_b-1,\lambda',m_b-m_a,\zeta_a+\zeta_b}(\mathbf{r}-\mathbf{R}_a)\}$$

which can be evaluated directly from Equations (26–29). When $\mathbf{k}$ is set equal to zero in Equation (29), only the $(\Lambda = 0)$ term does not vanish, and consequently three of the summations in Equation (26) are eliminated. With

$$\rho = (\zeta_a + \zeta_b)R_a \tag{36}$$

the result is

$$\begin{aligned}
&I_{ab}^{NLM}(\mathbf{R}_a = \mathbf{R}_b \neq 0) \\
&\quad = \sum_{\lambda'=|l_a-l_b|}^{l_a+l_b} \sum_{\lambda=|L-\lambda'|}^{L+\lambda'} [(2\lambda'+1)(2\lambda+1)]^{1/2} c^{\lambda'}(l_b m_b; l_a m_a) c^{\lambda}(LM; \lambda', m_b - m_a) \\
&\qquad \times Y_\lambda^{M+m_a-m_b}(\theta_{R_a}, \phi_{R_a}) R_a^{N+n_a+n_b+1}(-d/d\rho)^{n_a+n_b-1-\lambda'}(\rho^{-1}\, d/d\rho)^{\lambda'} \rho^{\lambda'+L+1} \\
&\qquad \times \{(-1)^\lambda \mathscr{I}_\lambda(\rho)(\rho^{-1}\, d/d\rho)^L \rho^{-1} E_{L-N-1}(\rho) \\
&\qquad + \tfrac{1}{2}\mathscr{K}_\lambda(\rho)(\rho^{-1}\, d/d\rho)^L \rho^{-1}[\bar{E}_{L-N-1}(\rho) - \bar{E}_{L-N-1}(-\rho)]\}
\end{aligned} \tag{37}$$

Note that we use implicitly the phase convention,

$$Y_l^{m*} = (-1)^m Y_l^{-m} \tag{38}$$

The (1–2)-type two-center integral can be treated in an analogous manner. First write

$$\begin{aligned}
I_{ab}^{NLM} &= \int dV r^N Y_L^M(\theta, \phi) \psi_{n_a l_a m_a \zeta_a}(\mathbf{r}) \psi^*_{n_b l_b m_b \zeta_b}(\mathbf{r} - \mathbf{R}_b) \\
&= \sum_{\lambda'=|L-l_a|}^{L+l_a} [(2L+1)/4\pi]^{1/2} c^L(\lambda', M + m_a; l_a m_a) \\
&\quad \times \int dV \psi_{n_a+N,\lambda',M+m_a,\zeta_a}(\mathbf{r}) \psi^*_{n_b l_b m_b \zeta_b}(\mathbf{r} - \mathbf{R}_b)
\end{aligned} \tag{39}$$

$$\begin{aligned}
&= \sum_{\lambda'=|L-l_a|}^{L+l_a} [(2L+1)/4\pi]^{1/2} c^L(\lambda', M + m_a; l_a m_a) \\
&\quad \times \overset{*}{\mathrm{FT}}|_{k=0}\{\overset{*}{\psi}_{n_a+N,\lambda',M+m_a,\zeta_a}(\mathbf{r}) \psi_{n_b l_b m_b \zeta_b}(\mathbf{r} - \mathbf{R}_b)\}
\end{aligned} \tag{40}$$

Then use Equations (26) and (27) to obtain

(41)

$$\begin{aligned}
&I_{ab}^{NLM}(\mathbf{R}_a = 0, \mathbf{R}_b \neq 0) \\
&= \sum_{\lambda'=|L-la|}^{L+la} \sum_{\lambda=|\lambda'-l_b|}^{\lambda'+l_b} [(2L+1)(2\lambda+1)]^{1/2} c^L(\lambda', M + m_a; l_a m_a) c^\lambda(\lambda', M + m_a; l_b m_b) \\
&\quad \times Y_\lambda^{M+m_a-m_b}(\theta_{R_b}, \phi_{R_b}) R_b^{N+n_a+n_b+1}(-d/d\rho_b)^{n_b-l_b}(\rho_b^{-1}\, d/d\rho)^{l_b} \rho_b^{l_b+\lambda'+1} \\
&\quad \times \{(-1)^\lambda \mathscr{I}_\lambda(\rho_b)(\rho_b^{-1}\, d/d\rho_b)^{\lambda'} \rho_b^{-1} E_{\lambda'-N-n_a}(\rho_a + \rho_b) \\
&\quad + \tfrac{1}{2}\mathscr{K}_\lambda(\rho_b)(\rho_b^{-1}\, d/d\rho_b)^{\lambda'} \rho_b^{-1}[\bar{E}_{\lambda'-N-n_a}(\rho_a + \rho_b) - \bar{E}_{\lambda'-N-n_a}(\rho_a - \rho_b)]\}
\end{aligned}$$

where

$$\rho_a \equiv \zeta_a R_b \tag{42}$$

$$\rho_b = \zeta_b R_b \tag{43}$$

5. Three-Center Integrals

A. *Formula based on equation* (7)

First we consider the integration of Equation (7). Except for minor differences in notation and complex conjugates, the integrand on the right hand side of Equation (7) is $(k^2/4\pi)$ times the corresponding integrand for the (1–2)-type two-electron three-center integral of $1/r_{12}$ with one of the orbital exponents set equal to zero (see Equation (5) of [10]). As a consequence

$$I_{ab}^{NLM} = -(4\pi)^{-1}\nabla^2_{\mathbf{R}_a}\{\text{corresponding (1–2)-type two-electron three-center integral of } 1/r_{12}\text{, the } r^N Y_L^M \text{ being regarded as a limit of an STO}\} \tag{44}$$

With Equation (44) and the formulas given by Equations (59) and (60) of [10], one could immediately evaluate I_{ab}^{NLM}. There is, however, one subtlety and also a slightly easier route to the answer.

The subtlety is that Equations (59) and (60) of [10] were derived for positive n_a (corresponding to $N + 1$ here). Certain equations, such as Equation (48) of [10], are invalid for sufficiently negative N (because Equation (49) of [10] would be violated). As a consequence, certain $\tilde{E}$'s in Equations (59) and (60) of [10] are really E's for negative enough N.

The modified details of the integration are as follows: (1) Follow exactly the method of [10] for the (1–2)-type three-center integral of $1/r_{12}$. (2) In the negative N cases that require certain $\tilde{E}$'s to be E's, viz., Equation (48) of [10], the E's occur in linear combinations for which their *logarithmic singularities* in the integration variable *cancel*. Consequently, the contours can be manipulated exactly as in [10], *mutatis mutandis*. (3) In the present case, there is never a pole at the origin (which in the $1/r_{12}$ integral gives rise to the $\delta_{t,\Lambda\pm l_c}$ terms). (4) The result will be (-14π) times Equations (31), (59), and (60) of [10], with proper attention given to complex conjugation differences, with care taken with E's vs. $\tilde{E}$'s, with the correspondence $(n_a l_a m_a \zeta_a n_c l_c m_c \zeta_c \mathbf{R}, \mathscr{R}$ of [10]) $\to$ $(N + 1, L, M, O, n_a l_a m_a \zeta_a \mathbf{R}_a \mathbf{R}_b$ here), with $\zeta_a^{\Lambda+l_a+1}$ replacing $\zeta_c^{\Lambda+_cl-1}$ in the appropriate places ($\leftrightarrow k^2$ difference in integrands), and with all $\delta_{t,\Lambda\pm l_c}$ terms omitted.

The integrated formulas are,

$$
\begin{aligned}
I_{ab}^{NLM} = {} & \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{\lambda=|l-l_b|}^{l+l_b} \sum_{\Lambda=|l-L|}^{l+L} \sum_{t=|\Lambda-l_a|}^{\Lambda+l_a} [(2\lambda+1)(2\Lambda+1)(2t+1)\pi]^{1/2} \\
& \times c^{\lambda}(lm;\, l_b m_b) c^{\Lambda}(lm;\, LM) c^{t}(l_a m_a;\, \Lambda,\, m-M) \\
& \times Y_{\lambda}^{m-m_b}(\theta_{R_b},\, \phi_{R_b})\, Y_{t}^{M+m_a-m}(\theta_{R_a},\, \phi_{R_a})\, I_{ab}^{NLM:tl\lambda\Lambda}
\end{aligned}
\tag{45}
$$

$$
\begin{aligned}
I_{ab}^{NLM:tl\lambda\Lambda} = {} & (-1)^{\lambda+1}(-d/d\zeta_a)^{n_a-l_a}(\zeta_a^{-1}\, d/d\zeta_a)^{l_a}\zeta_a^{l_a+\Lambda+1}\mathscr{K}_t(\zeta_a R_a)(\zeta_a^{-1}\, d/d\zeta_a)^{\Lambda}\zeta_a^{-1} \\
& \times [(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}\, d/d\zeta_b)^{l_b}\zeta_b^{l_b+l+1}\mathscr{I}_{\lambda}(\zeta_b R_b)(\zeta_b^{-1}\, d/d\zeta_b)^{l}\zeta_b^{-1}R_b^{N+1=\Lambda-l}] \\
& \times \{E_{\Lambda+l-N}[(\zeta_a+\zeta_b)R_b] - (R_b/R_a)^{\Lambda+l-N-1}E_{\Lambda+l-N}[(\zeta_a+\zeta_b)R_a] \\
& - (E_{\Lambda+l-N}[(-\zeta_a+\zeta_b)R_b] - (R_b/R_a)^{\Lambda+l-N-1}E_{\Lambda+l-N}[(-\zeta_a+\zeta_b)R_a])\} \\
& + 2(-1)^{t+\lambda}(-d/d\zeta_a)^{n_a-l_a}(\zeta_a^{-1}\, d/d\zeta_a)^{l_a+\Lambda+1}\mathscr{I}_t(\zeta_a R_a)(\zeta_a^{-1}\, d/d\zeta_a)^{\Lambda}\zeta_a^{-1} \\
& \times [(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}\, d/d\zeta_b)^{l_b}\zeta_b^{l_b+l+1}\mathscr{I}_{\lambda}(\zeta_b R_b)(\zeta_b^{-1}\, d/d\zeta_b)^{l}\zeta_b^{-1}R_b^{N+1-\Lambda-l}] \\
& \times (R_b/R_a)^{\Lambda+l-N-1}E_{\Lambda+l-N}[(\zeta_a+\zeta_b)R_a] \\
& - \tfrac{1}{2}(-d/d\zeta_a)^{n_a-l_a}(\zeta_a^{-1}\, d/d\zeta_a)^{l_a}\zeta_a^{l_a+\Lambda+1}\mathscr{K}_t(\zeta_a R_a)(\zeta_a^{-1}\, d/d\zeta_a)^{\Lambda}\zeta_a^{-1} \\
& \times [(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}\, d/d\zeta_b)^{l_b}\zeta_b^{l_b+l+1}\mathscr{K}_{\lambda}(\zeta_b R_b)(\zeta_b^{-1}\, d/d\zeta_b)^{l}\zeta_b^{-1}R_b^{N+1-\Lambda-l}] \\
& \times \{\tilde{E}_{\Lambda+l-N}[(\zeta_a+\zeta_b)R_b] - \tilde{E}_{\Lambda+l-N}[(\zeta_a-\zeta_b)R_b] \\
& - \tilde{E}_{\Lambda+l-N}[(-\zeta_a+\zeta_b)R_b] + \tilde{E}_{\Lambda+l-N}[(-\zeta_a-\zeta_b)R_b]\} \qquad (R_a > R_b)
\end{aligned}
\tag{46}
$$

$$
\begin{aligned}
I_{ab}^{NLM:tl\lambda\Lambda} = {} & 2(-1)^{t+\lambda}(-d/d\zeta_a)^{n_a-l_a}(\zeta_a^{-1}\, d/d\zeta_a)^{l_a}\zeta_a^{l_a+\Lambda+1}\mathscr{I}_t(\zeta_a R_a)(\zeta_a^{-1}\, d/d\zeta_a)^{\Lambda}\zeta_a^{-1} \\
& \times [(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}\, d/d\zeta_b)^{l_b}\zeta_b^{l_b+l+1}\mathscr{I}_{\lambda}(\zeta_b R_b)(\zeta_b^{-1}\, d/d\zeta_b)^{l}\zeta_b^{-1}R_b^{N+1-\Lambda-l}] \\
& \times E_{\Lambda+l-N}[(\zeta_a+\zeta_b)R_b] \\
& - \tfrac{1}{2}(-d/d\zeta_a)^{n_a-l_a}(\zeta_a^{-1}\, d/d\zeta_a)^{l_a}\zeta_a^{l_a+\Lambda+1}\mathscr{K}_t(\zeta_a R_a)(\zeta_a^{-1}\, d/d\zeta_a)^{\Lambda}\zeta_a^{-1} \\
& \times [(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}\, d/d\zeta_b)^{l_b}\zeta_b^{l_b+l+1}\mathscr{K}_{\lambda}(\zeta_b R_b)(\zeta_b^{-1}\, d/d\zeta_b)^{l}\zeta_b^{-1}R_b^{N+1-\Lambda-l}] \\
& \times (R_b/R_a)^{\Lambda+l-N-1}\{\tilde{E}_{\Lambda+l-N}[(\zeta_a+\zeta_b)R_a] - \tilde{E}_{\Lambda+l-N}[(\zeta_a-\zeta_b)R_a] \\
& - \tilde{E}_{\Lambda+l-N}[(-\zeta_a+\zeta_b)R_a] + \tilde{E}_{\Lambda+l-N}[(-\zeta_a-\zeta_b)R_a]\} \\
& + (-1)^{t}(-d/d\zeta_a)^{n_a-l_a}(\zeta_a^{-1}\, d/d\zeta_a)^{l_a}\zeta_a^{l_a+\Lambda+1}\mathscr{I}_t(\zeta_a R_a)(\zeta_a^{-1}\, d/d\zeta_a)^{\Lambda}\zeta_a^{-1} \\
& \times [(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}\, d/d\zeta_b)^{l_b}\zeta_b^{l_b+l+1}\mathscr{K}_{\lambda}(\zeta_b R_b)(\zeta_b^{-1}\, d/d\zeta_b)^{l}\zeta_b^{-1}R_b^{N+1-\Lambda-l}] \\
& \times \{E_{\Lambda+l-N}[(\zeta_a+\zeta_b)R_b] - (R_b/R_a)^{\Lambda+l-N-1}E_{\Lambda+l-N}[(\zeta_a+\zeta_b)R_a] \\
& - (E_{\Lambda+l-N}[(\zeta_a-\zeta_b)R_b] - (R_b/R_a)^{\Lambda+l-N-1}E_{\Lambda+l-N}[(\zeta_a-\zeta_b)R_a])\} \\
& \qquad (R_a < R_b)
\end{aligned}
\tag{47}
$$

B. *Cancellation of singularities*

That some of the arguments of $E_{\Lambda+l-N}$'s in Equations (46) and (47) can be negative requires some comment, because $E_n(x)$ has a branch cut along the negative real axis for $n \geqq 1$ and a pole at $x = 0$ for $n \leqq 0$. The E's which can have negative arguments are enclosed by boldface parentheses, $\mathbf{(\quad)}$, and in each case the troublesome terms inside the $\mathbf{(\quad)}$ can be shown to cancel.

First, when $\Lambda + l - N \leqq 0$, the E's are really α's, and the $\mathbf{(\quad)}$ term in Equation (46) takes the singularity-free form (the poles between the two α's cancel),

$$\begin{aligned}(48)\quad &\mathbf{(}E_{\Lambda+l-N}[(-\zeta_a + \zeta_b)R_b] - (R_b/R_a)^{\Lambda+l-N-1}E_{\Lambda+l-N}[(-\zeta_a + \zeta_b)R_a]\mathbf{)} \\ &\qquad = \hat{\alpha}_{N-\Lambda-l}[(-\zeta_a + \zeta_b)R_b] - (R_b/R_a)^{\Lambda+l-N-1}\hat{\alpha}_{N-\Lambda-l}[(-\zeta_a + \zeta_b)R_a]\end{aligned}$$

and similarly for Equation (47). Second, when $\Lambda + l - N > 0$, the $\mathbf{(\quad)}$ term in Equation (46) can be written in the singularity free form

$$\begin{aligned}(49)\quad &\mathbf{(}E_{\Lambda+l-N}[(-\zeta_a + \zeta_b)R_b] - (R_b/R_a)^{\Lambda+l-N-1}E_{\Lambda+l-N}[(-\zeta_a + \zeta_b)R_a]\mathbf{)} \\ &\qquad = \tilde{E}_{\Lambda+l-N}[(-\zeta_a + \zeta_b)R_b] - (R_b/R_a)^{\Lambda+l-N-1}\tilde{E}_{\Lambda+l-N}[(-\zeta_a + \zeta_b)R_a] \\ &\qquad\quad - [-(-\zeta_a + \zeta_b)R_b]^{\Lambda+l-N-1}\log(R_b/R_a)/(\Lambda + l - N - 1)!\end{aligned}$$

and similarly for Equation (47). Finally, because of $(\zeta_a^{-1}\, d/d\zeta_a)^{\Lambda}\zeta_a^{-1}(\zeta_b^{-1}\, d/d\zeta_b)^{l}\zeta_b^{-1}$ and Equation (5), *all* the $E_{\Lambda+l-N}$'s in the boldface braces, $\mathbf{\{\quad\}}$, in Equations (46) and (47) can be replaced by $\tilde{E}_{\Lambda+l-N}$'s in the following cases:

(50) $L - N - 1$ even

(51) $N \geqq L - 1$

(52) $\Lambda - l - N - 2 < 0$ [Equation (47) only]

(53) $-\Lambda + l - N - 2 < 0$ [Equation (46) only]

C. *Formula based on equation* (6)

As a first step, substitute Equations (21), (22) and (26) into Equation (6), and carry out the angular integrations to obtain,

$$\begin{aligned}(54)\quad I_{ab}^{NLM} = &\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{\lambda=|l-l_b|}^{l+l_b}\sum_{\Lambda=|l-l_a|}^{l+l_a}\sum_{t=|\Lambda-L|}^{\Lambda+L}[(2\lambda + 1)(2\Lambda + 1)(2L + 1)\pi]^{1/2} \\ &\times c^{\lambda}(lm; l_b m_b)c^{\Lambda}(l_a m_a; lm)c^{L}(t, M + m_a - m; \Lambda, m_a - m) \\ &\times Y_t^{M+m_a-m}(\theta_{R_a}, \phi_{R_a})\, Y_{\lambda}^{m-m_b}(\theta_{\mathscr{R}}, \phi_{\mathscr{R}})J_{ab}^{NL;tl\lambda\Lambda}\end{aligned}$$

where

$$(55)\quad J_{ab}^{NL;tl\lambda\Lambda} \equiv \tfrac{1}{2}\pi^{-2}(-1)^{L}i^{t+L}\int_{-\infty}^{\infty} dk\, k^2 j_t(kR_a)\mathscr{F}_{NL}(k)G_{l\lambda l_b\Lambda}^{n_a\zeta_a n_b\zeta_b}(k, \mathscr{R})$$

Note that Equations (38), (15), and the evenness of the integrand of Equation (55) have been used implicitly.

Examination of Equations (23–25) for $\mathscr{F}_{NL}$ indicates that there are three distinct cases: $N - L$ odd, $N - L$ even and $\geqq 0$, and $N - L$ even and $\leqq -2$.

The $N - L$ even and $\geqq 0$ case is very simple, because $\mathscr{F}_{NL}(k)$ involves only δ functions. This is the case that $r^N Y_L^M$ is a homogeneous polynomial in x, y, z of order N. The result for J_{ab}, which is essentially the Nth term in the power series expansion of $j_t(kR_a) G_{l\lambda l_b\Lambda}^{n_a\zeta_a n_b\zeta_b}(k, \mathscr{R})$ about $k = 0$, is

$$J_{ab} = (N + L + 1)!!\,(N - L)!!$$

$$\times \sum_{u+v=(N-t-\Lambda)/2} \frac{R_a^{t+2u}\mathscr{R}^{2\Lambda+2v+1}}{(2t + 2u + 1)!!\,(2u)!!\,(2\Lambda + 2v + 1)!!\,(2v)!!} \tag{56}$$

$$\times\ (2(-1)^{\lambda}[\cdots \mathscr{I}_\lambda(\zeta_b\mathscr{R}) \cdots]\alpha_{n_a+\Lambda-l+2v}[(\zeta_a + \zeta_b)\mathscr{R}]$$

$$+ [\cdots \mathscr{K}_\lambda(\zeta_b\mathscr{R}) \cdots]\{\hat{\alpha}_{n_a+\Lambda-l+2v}[(\zeta_a + \zeta_b)\mathscr{R}] - \hat{\alpha}_{n_a+\Lambda-l+2v}[(\zeta_a - \zeta_b)\mathscr{R}]\})$$

Note that the number of non-zero J_{ab} is finite, since J_{ab} vanishes when $t + \Lambda > N$ (when $N - L$ even and $\geqq 0$).

When $N - L$ is even and negative, J_{ab} is much more difficult to evaluate because of the sgn (k) in $\mathscr{F}_{NL}$ (Equation (25)). We have not found a closed form expression, although infinite expansions similar to those [13] which come up in the four-center two-electron integral can be obtained. We omit this case here, because the formulas obtained from Equation (7) are much simpler.

When $N - L$ is odd, substitution of Equation (23) into Equation (55) yields,

$$J_{ab}^{NL;tl\lambda\Lambda} = \tfrac{1}{2}\pi^{-2}(-1)^{L}i^{t+L}\frac{(N + L + 1)!!}{(L - N - 2)!!}\int_{-\infty}^{\infty} dk\, k^{-N-1} j_t(kR_a) G_{l\lambda l_b\Lambda}^{n_a\zeta_a n_b\zeta_b}(k, \mathscr{R}) \tag{57}$$

This formula (57) has two subtleties. If $N \geqq t + \Lambda$, then the integrand has a pole at $k = 0$. The interpretation of the integral is the principal value in the sense [10],*

$$\mathscr{P}\int_{-\infty}^{\infty} dk\, k^{-N-1} \cdots = \frac{1}{2}\left\{\int^{(-\infty,0^+,\infty)} + \int^{(-\infty,0^-,\infty)}\right\} dk\, k^{-N-1} \cdots \tag{58}$$

If $N \leqq -3$, the integrand does not vanish at $k = \pm\infty$. For this case we interpret Equation (57) via the theory of generalized functions [7] according to the rule,

$$\mathscr{P}\int_{-\infty}^{\infty} dk\, k^{-N-1} j_t(kR_a) \cdots = (-R_a)^t (R_a^{-1}\, d/dR_a)^t R_a^{-1}(-d^2/dR_a^2)^Q \;\mathscr{P}\int_{-\infty}^{\infty} dk\, k^{-N-t-2Q-2} \sin(kR_a) \cdots \tag{59}$$

where Q is *any* positive integer satisfying

$$N + t + 2Q \geqq 0 \tag{60}$$

With these two subtleties in mind, we complete the integration of Equation (57) via complex variable theory and the residue theorem.

The details of integrating Equation (57) are in part very similar to the evaluation [10] of $I_{c;ab}^{tl\lambda\Lambda}$ in the (1–2)-type three-center integral of r_{12}^{-1}. Comparison

* In the Laurent series about $k = 0$ for the integrand of Equation (57), only even powers of k occur. (Note that $L - N$ is odd, and $t + L + \Lambda$ is even.) Thus the prescription for avoiding $k = 0$ is not too critical.

of Equations (36) and (43) of [10] with Equation (57) reveals that the radial part of the Fourier transform of an STO, $f_{n_c l_c \zeta_c}(k)$, is replaced here by k^{-N-1}. Thus the present case is easier in the sense that the singularities at $k = \pm i\zeta_c$ have been eliminated. After manipulations virtually identical with those* of [10], after taking some of the derivatives implied by Equation (59), and using the function [6],

$$v_{l\lambda l_b}^{(n_b\zeta_b)}(R, \mathscr{R}) = 4\pi(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}\, d/d\zeta_b)^{l_b}\zeta_b^{l_b+1}\mathscr{K}_\lambda(\zeta_b\mathscr{R})\mathscr{I}_l(\zeta_b R) \quad (\mathscr{R} > R) \tag{61}$$

$$= 4\pi(-1)^{l_b}(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}\, d/d\zeta_b)^{l_b}\zeta_b^{l_b+1}\mathscr{I}_\lambda(\zeta_b\mathscr{R})\mathscr{K}_l(\zeta_b R) \quad (R > \mathscr{R}) \tag{62}$$

we obtain

$$J_{ab}^{NL;tl\lambda\Lambda} = J'_{ab} + J''_{ab} \tag{63}$$

$$\begin{aligned}
J'_{ab} = {} & (-1)^{(N-L+1)/2}\frac{(N+L+1)!!}{(L-N-2)!!} \\
& \times\Bigg\{\sum_{p\ge 0,\, g\ge 0,\, p+g=(N-t+\Lambda+1)/2}\frac{R_a^{2p+t}\mathscr{R}^{2g}}{(2p+2t+1)!!\,(2g)!!\,(2g-2\Lambda-1)!!\,(2p)!!} \\
& \times [H(\mathscr{R}-R_a)(2(-1)^\lambda[\cdots\mathscr{I}_\lambda(\zeta_b\mathscr{R})\cdots]E_{\Lambda+l+1-n_a-2g}[(\zeta_a+\zeta_b)\mathscr{R}] \\
& + [\cdots\mathscr{K}_\lambda(\zeta_b\mathscr{R})\cdots]\{\tilde{E}_{\Lambda+l+1-n_a-2g}[(\zeta_a+\zeta_b)\mathscr{R}] - \tilde{E}_{\Lambda+l+1-n_a-2g}[(\zeta_a-\zeta_b)\mathscr{R}] \\
& - (\mathscr{R}/R_a)^{\Lambda+l-n_a-2g}\tilde{E}_{\Lambda+l+1-n_a-2g}[(\zeta_a+\zeta_b)R_a] \\
& + (\mathscr{R}/R_a)^{\Lambda+l-n_a-2g}\tilde{E}_{\Lambda+l+1-n_a-2g}[(\zeta_a-\zeta_b)R_a]\}) + H(R_a-\mathscr{R})2(-1)^\lambda \\
& \times [\cdots\mathscr{I}_\lambda(\zeta_b\mathscr{R})\cdots](\mathscr{R}/R_a)^{\Lambda+l-n_a-2g}E_{\Lambda+l+1-n_a-2g}[(\zeta_a+\zeta_b)R_a]] \\
& + \sum_{p\ge 0,\, g\ge 0,\, p+g=(N+t-\Lambda+1)/2}\frac{R_a^{2p-t-1}\mathscr{R}^{2\Lambda+2g+1}}{(2p)!!\,(2p-2t-1)!!\,(2g)!!\,(2\Lambda+2g+1)!!} \\
& \times [H(\mathscr{R}-R_a)[\cdots\mathscr{K}_\lambda(\zeta_b\mathscr{R})\cdots](\mathscr{R}/R_a)^{l-\Lambda-n_a-2g-1} \\
& \times \{\hat{\alpha}_{n_a+\Lambda-l+2g}[(\zeta_a+\zeta_b)R_a] - \hat{\alpha}_{n_a+\Lambda-l+2g}[(\zeta_a-\zeta_b)R_a]\} \\
& + H(R_a-\mathscr{R})(2(-1)^\lambda[\cdots\mathscr{I}_\lambda(\zeta_b\mathscr{R})\cdots]\{\alpha_{n_a+\Lambda-l+2g}[(\zeta_a+\zeta_b)\mathscr{R}] \\
& - (\mathscr{R}/R_a)^{l-\Lambda-n_a-2g-1}\alpha_{n_a+\Lambda-l+2g}[(\zeta_a+\zeta_b)R_a]\} \\
& + [\cdots\mathscr{K}_\lambda(\zeta_b\mathscr{R})\cdots]\{\hat{\alpha}_{n_a+\Lambda-l+2g}[(\zeta_a+\zeta_b)\mathscr{R}] - \hat{\alpha}_{n_a+\Lambda-l+2g}[(\zeta_a-\zeta_b)\mathscr{R}]\})]\Bigg\}
\end{aligned} \tag{64}$$

$$\begin{aligned}
J''_{ab} = {} & (2\pi)^{-1}(-1)^{\Lambda+1+(N-L+1)/2}\frac{(N+L+1)!!}{(L-N-2)!!}\sum_{\substack{\mu_t\ge 0 \\ (-\mu_t-\mu-N-3\ge 0)}}\sum_{\mu\ge 0}(-1)^{\mu_t} \\
& \times\left[\frac{(t+\mu_t)!}{(t-\mu_t)!\,(2\mu_t)!!}\right]\left[\frac{(\Lambda+\mu)!}{(\Lambda-\mu)!\,(2\mu)!!}\right] \\
& \times R_a^{-\mu_t-1}(d/dR_a)^{-\mu_t-\mu-N-3}R_a^{1-\mu}R_a^{n_a-1}\exp(-\zeta_a R_a)v_{l\lambda l_b}^{(n_b\zeta_b)}(R_a, \mathscr{R})
\end{aligned} \tag{65}$$

* See especially Equations (36–50) of [10].

For convenience, we have introduced the Heaviside step function,

$$H(x) = 0 \qquad (x < 0) \tag{66}$$

$$= 1 \qquad (x > 0) \tag{67}$$

Equation (65) can be substituted back into Equation (55), and all the summations can be carried out explicitly except those over μ_t and μ. The somewhat revealing result is

$$\begin{aligned} I_{ab}^{\prime\prime NLM} \equiv & \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{\lambda=|l-l_b|}^{l+l_b} \sum_{\Lambda=|l-l_a|}^{l+l_a} \sum_{t=|\Lambda-L|}^{\Lambda+L} [(2\lambda+1)(2\Lambda+1)(2L+1)\pi]^{1/2} \\ & \times c^{\lambda}(lm; l_b m_b) c^{\Lambda}(l_a m_a; lm) c^{L}(t, M+m_a-m; \Lambda, m_a-m) \\ & \times Y_t^{M+m_a-m}(\theta_{R_a}, \varphi_{R_a}) Y_{\lambda}^{m-m_b}(\theta_R, \varphi_R) J_{ab}^{\prime\prime} \end{aligned} \tag{68}$$

$$\begin{aligned} = & 4\pi(-1)^{(N-L-1)/2+l_a+l_b} \frac{(N+L+1)!!}{(L-N-2)!!} \\ & \times \sum_{\substack{\mu_t \geqq 0 \ \mu \geqq 0 \\ (-\mu_t-\mu-N-3 \geqq 0)}} (-1)^{\mu_t} [(2\mu_t)!!\,(2\mu)!!]^{-1} R_a^{-\mu_t-1} (d/dR_a)^{-\mu-\mu_t-N-3} R_a^{1-\mu} \\ & \times \prod_{\nu_t=1}^{\mu_t} [\hat{\mathbf{l}}_{R_a}^2 - \nu_t(\nu_t-1)]\, Y_L^M(\theta_{R_a}, \varphi_{R_a}) \\ & \times \prod_{\nu=1}^{\mu} [\mathbf{l}_{R_a}^2 - \nu(\nu-1)]\, \psi_{n_a l_a m_a \zeta_a}(\mathbf{R}_a) \psi^*_{n_b l_b m_b \zeta_b}(\mathbf{R}_a + \mathscr{R}). \end{aligned} \tag{69}$$

The above formulas, (64), (65), and (69), can be obtained by a slightly easier recipe than working through Equation (59). First treat the problem as if $N \geqq -2$, and evaluate J_{ab} by the method described in [10]. One obtains J'_{ab}, Equation (64). The terms which misbehave at $k = \pm\infty$ when $N \leqq -3$ are essentially the same ones which lead to the delta-function terms [3] in the Laplace-type expansion of $r_{12}^N Y_L^M(\theta_{12}, \varphi_{12})$. Equation (69) is the result obtained by substituting those delta-function terms, $[r_{12}^N Y_L^M(\theta_{12}, \varphi_{12})]^{(\delta)}$, Equation (40) of [3], directly into Equation (1) and taking $\mathbf{r}_1 = \mathbf{r} - \mathbf{R}_a$, $\mathbf{r}_2 = -\mathbf{R}_a$. Finally, Equation (68) follows from Equation (69) by substituting the expansion of $\psi_{n_b l_b m_b \zeta_b}(\mathbf{R}_a + \mathscr{R})$ given in [6], Equation (20).

6. Comments

The formulas for two-center integrals, Equations (37) and (41), are very similar to formulas recently developed for overlap, kinetic energy, and two-center Coulomb and nuclear attraction integrals [14]. We anticipate considerable savings in computational time by calculating all these integrals simultaneously.

Of the two methods for three-center integrals, the one based on Equation (6), i.e. the expansion in terms of $\mathbf{R}_a$ and $\mathscr{R}$, seems more natural. However, for the case that $N - L$ is even and negative ($1/r^2$ is the simplest example), one must use the formula based on Equation (7).

The building blocks of the $\mathbf{R}_a\mathscr{R}$-expansion formula, Equation (64), are similar to those for the two-center integrals, Equations (37) and (41), and are considerably simpler than the $\mathbf{R}_a\mathbf{R}_b$-expansion formulas, Equations (46) and (47). The $\mathbf{R}_a\mathscr{R}$ formula for the case $N - L$ even and non-negative (Equation (56)) is essentially a sum of overlap integrals [14].

For the case of irregular solid harmonics,

$$N = -L - 1 \tag{70}$$

the $\mathbf{R}_a\mathscr{R}$-formula, Equation (64), is particularly simple. The first summation becomes the single term,

$$\sum_{p+q=(N-t+\Lambda+1)/2} = \delta_{\Lambda,t+L}\Big|_{p=q=0} \tag{71}$$

and the second,

$$\sum_{p+q=(N+t-\Lambda+1)/2} = \delta_{t,\Lambda+L}\Big|_{p=q=0} \tag{72}$$

The formula (64) for three-center nuclear attraction integrals ($N + 1 = L = 0$) is the same as that given previously [15].

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