ACKNOWLEDGMENTS

The authors are indebted to W. Garrett of Picatinny Arsenal for supplying all but one of the azides and to J. Rosen of the Naval Ordnance Laboratory for supplying the sample of monoclinic lead azide.

* This work was partially supported by the Explosives Laboratory, Picatinny Arsenal.

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THE JOURNAL OF CHEMICAL PHYSICS VOLUME 53, NUMBER 11 1 DECEMBER 1970

Analytical Evaluation of Multicenter Integrals of r_{12}^{-1} with Slater-Type Atomic Orbitals VI. Asymptotic Expansions for Large Internuclear Distances*

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(Received 15 June 1970)

Asymptotic expansions valid for large internuclear distances are derived for the four-center integral of r_{12}^{-1} with Slater-type atomic orbitals. In certain cases, the dominant part of the complete expansion is a multipole-moment-type expansion. The asymptotic formulas are simpler than the convergent formulas given previously, but some are not directly applicable when certain combinations of orbital exponents vanish.

I. INTRODUCTION

Many of the multicenter integrals of r_{12}^{-1} which occur in a quantum mechanical calculation of the electronic energy of a large molecule, or of the interaction energy of two molecules, involve large internuclear distances. The calculation of such integrals with Slater-type orbitals (STO's) is often more difficult and time consuming than when the internuclear distances are small because of the large number of terms needed in the convergent series expansions[1] or because of the large number of points necessary in some numerical integration schemes.[2,3] Also, the computational device of replacing STO's by Gaussians at the integral evaluation stage leads to inaccuracies[4] when internuclear distances are large. In this paper we develop asymptotic expansions for multicenter integrals of r_{12}^{-1} with STO's, valid for large internuclear distances.

The usefulness of the asymptotic formulas lies in their relative simplicity. For certain cases, a particularly simple part of the asymptotic formula is dominant and is a generalization of the familiar multipole-moment expansion.[5]

Some earlier asymptotic formulas have been given by Margenau,[6] Mulligan,[7] Ellison,[8] Mason and Hirschfelder,[5] and Salmon, Birss, and Ruedenberg.[9] The formulas of Margenau, Mulligan, and Ellison are intuitively obtained single terms, not full asymptotic expansions. Mason and Hirschfelder used the bipolar expansion[10] of r_{12}^{-1} to obtain the "leading terms" of the full asymptotic expansion for the case that the charge distributions are far apart. The Salmon–Birss–Ruedenberg expansion seems asymptotic for large orbital exponents, which are in some respects equivalent to large internuclear distances. The precise

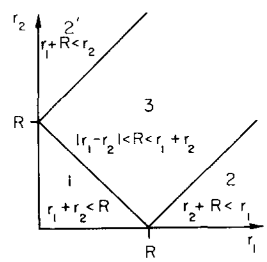

FIG. 1. The four regions of applicability for bipolar expansion formulas.

conditions for the validity of all these previously published asymptotic formulas have not been established.

In the present work, complete asymptotic expansions are given, along with their appropriate conditions on internuclear distances and orbital exponents. To the extent that the earlier work can be regarded as special cases or leading terms of the full expansions, conditions for applicability of the earlier works can be inferred.

The organization of the paper is as follows: In Secs. II and III, simple asymptotic expansions are obtained heuristically from the bipolar and Laplace expansions of $1/r_{12}$. The reader interested mainly in these simple formulas is referred to these sections. In Sec. IV, the integral is expressed in terms of auxilliary functions, and in Sec. V, asymptotic formulas are derived for the auxilliary functions. In Sec. VI, the simple asymptotic expansions given in Sec. II are justified. Some problems connected with the vanishing of sums of orbital exponents are discussed in the Appendix. Tables II and III contain some numerical illustrations.

II. SIMPLE FORMULAS BASED ON THE BIPOLAR EXPANSION OF $1/r_{12}$

Following the notation in Paper V,[1] we denote the four-center integral by

$$I_{cd;ab}(\mathfrak{R}_1,\mathfrak{R}_2,\mathbf{R})\equiv(N_aN_bN_cN_d)^{-1}\int dV_1\int dV_2 r_{12}^{-1}[\Psi_{n_cl_cm_c\zeta_c}{}^*(\mathbf{r}_2)\Psi_{n_dl_dm_d\zeta_d}(\mathbf{r}_2-\mathfrak{R}_2)]^*\times[\Psi_{n_al_am_a\zeta_a}{}^*(\mathbf{r}_1-\mathbf{R})\Psi_{n_bl_bm_b\zeta_b}(\mathbf{r}_1-\mathbf{R}-\mathfrak{R}_1)]. \quad (1)$$

The $\Psi_{nlm\zeta}$ denotes a usual Slater-type orbital (STO) with normalization constant N, and atoms a, b, c, d are located at $\mathbf{R}$, $\mathbf{R}+\mathfrak{R}_1$, the origin, and $\mathfrak{R}_2$, respectively.

A method for evaluating $I_{cd;ab}$ [Eq. (1)] could be based on the bipolar expansion[10] of $1/r_{12}$. As is well known, the bipolar expansion has different analytical forms in the four regions of the quadrant of the $\rho_1\rho_2$ plane bounded by the positive ρ_1 and ρ_2 axes and the three lines, $R=|\rho_1\pm\rho_2|$ (see Fig. 1). Here,

$$\rho_1\equiv|\mathbf{r}-\mathbf{R}|, \quad (2)$$

$$\rho_2\equiv r_2. \quad (3)$$

The existence of the four regions vastly complicates the use of the bipolar expansion.

Suppose, however, that the major contribution to the integral, in a specific case, comes from just one region in Fig. 1. Heuristically one might approximate the integral by substituting for $1/r_{12}$ in *all* regions of Fig. 1 the bipolar-expansion formula for the dominant region. One is then led to expressions primarily involving one-electron two-center integrals. The "Region 1"-dominated formula, which is the case of nonoverlapping charge distributions, corresponds to the expansion of $I_{cd;ab}$ in the interactions of multipole moments. The other three formulas are generalizations appropriate for overlapping charge distributions. The formulas so obtained are

$$I_{cd;ab}(\mathfrak{R}_1,\mathfrak{R}_2,\mathbf{R})\sim(4\pi)^{3/2}\sum_{l_1=0}^{\infty}\sum_{m_1=-l_1}^{l_1}\sum_{l_2=0}^{\infty}\sum_{m_2=-l_2}^{l_2}(-1)^{l_1}\binom{l_1+l_2}{l_1\quad l_2}R^{-l_1-l_2-1}\times(2l_1+2l_2+1)^{1/2}c^{l_1+l_2}(l_2m_2,l_1m_1)Y_{l_1+l_2}{}^{m_2-m_1}(\theta_R,\phi_R)\Omega_{ab}{}^{l_1m_1;l_1}(\mathfrak{R}_1)\Omega_{cd}{}^{l_2m_2;l_2*}(\mathfrak{R}_2) \quad \text{(Region 1 of Fig. 1)}, \quad (4)$$

$$I_{cd;ab}(\mathfrak{R}_1,\mathfrak{R}_2,\mathbf{R})\sim(4\pi)^{3/2}\sum_{l_1=0}^{\infty}\sum_{m_1=-l_1}^{l_1}\sum_{l_2=0}^{l_1}\sum_{m_2=-l_2}^{l_2}(-1)^{l_1+l_2}\binom{l_1}{l_2\quad l_1-l_2}R^{l_1-l_2}\times(2l_1-2l_2+1)^{1/2}c^{l_1-l_2}(l_2m_2;l_1m_1)Y_{l_1-l_2}{}^{m_2-m_1}(\theta_R,\phi_R)\Omega_{ab}{}^{l_1m_1;-l_1-1}(\mathfrak{R}_1)\Omega_{cd}{}^{l_2m_2;l_2*}(\mathfrak{R}_2) \quad \text{(Region 2 of Fig. 1)}, \quad (5)$$

$$I_{cd;ab}(\mathfrak{R}_1,\mathfrak{R}_2,\mathbf{R})\sim(4\pi)^{3/2}\sum_{l_2=0}^{\infty}\sum_{m_2=-l_2}^{l_2}\sum_{l_1=0}^{l_2}\sum_{m_1=-l_1}^{l_1}\binom{l_2}{l_1\quad l_2-l_1}R^{l_2-l_1}\times(2l_2-2l_1+1)^{1/2}c^{l_2-l_1}(l_2m_2;l_1m_1)Y_{l_2-l_1}{}^{m_2-m_1}(\theta_R,\phi_R)\Omega_{ab}{}^{l_1m_1;l_1}(\mathfrak{R}_1)\Omega_{cd}{}^{l_2m_2;-l_2-1*}(\mathfrak{R}_2) \quad \text{(Region 2}' \text{ of Fig. 1)}, \quad (6)$$

and

$$I_{cd;ab}(\mathfrak{R}_1,\mathfrak{R}_2,\mathbf{R})\sim2\pi^{3/2}\sum_{l_1=0}^{\infty}\sum_{m_1=-l_1}^{l_1}\sum_{l_2=0}^{\infty}\sum_{m_2=-l_2}^{l_2}\sum_{l_3=|l_1-l_2|}^{l_1+l_2}(-1)^{l_2}(2l_3+1)^{1/2}c^{l_3}(l_2m_2;l_1m_1)\times Y_{l_3}{}^{m_2-m_1}(\theta_R,\phi_R){\sum}'a_{\mu_1\mu_2\mu_3}[1-(-1)^{\mu_1}-(-1)^{\mu_2}-(-1)^{\mu_3}]R^{\mu_3-l_3-1}\times\Omega_{ab}{}^{l_1m_1;\mu_1-l_1-1}(\mathfrak{R}_1)\Omega_{cd}{}^{l_2m_2;\mu_2-l_2-1*}(\mathfrak{R}_2) \quad \text{(Region 3 of Fig. 1)}. \quad (7)$$

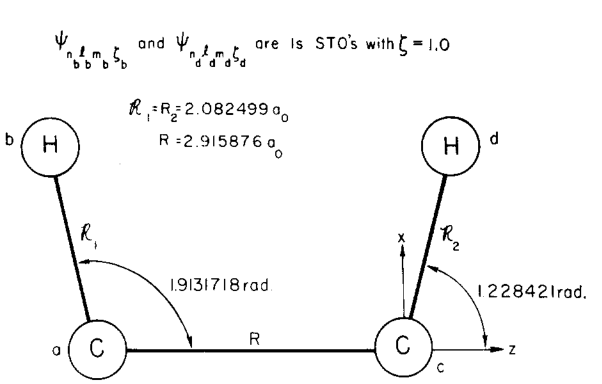

FIG. 2. Parameters for the eclipsed ethane integrals calculated in Table II.

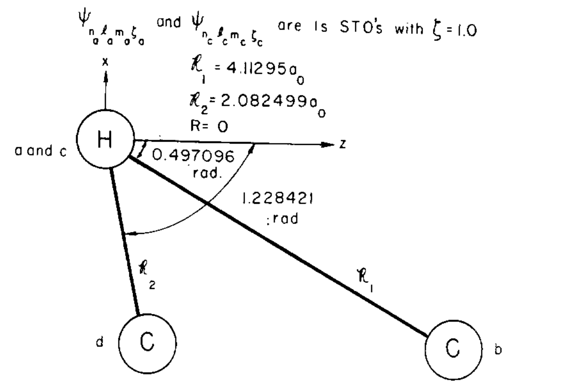

FIG. 3. Parameters for the eclipsed ethane integrals calculated in Table III.

Here, $\Omega_{nb}{}^{\Lambda\mu;M}$ denotes the two-center 1-electron integral,

$$\Omega_{ab}{}^{\Lambda\mu;M}(\mathbf{\mathcal{R}})\equiv(N_aN_b)^{-1}\int dV r^M Y_\Lambda{}^\mu(\theta,\phi)\Psi_{n_al_am_a\zeta_a}{}^*(\mathbf{r})\Psi_{n_bl_bm_b\zeta_b}(\mathbf{r}-\mathbf{\mathcal{R}}),\tag{8}$$

which is easily evaluated[5,11,12] for STO's. The remaining symbols are the Condon–Shortley coefficients,[13] the "3-Λ" symbol [Eq. (2.36) of V],

$$\begin{pmatrix} l_1 \\ l_2l_3\end{pmatrix}\equiv\frac{(2l_1-1)!!}{(2l_2+1)!!(2l_3+1)!!},\tag{9}$$

the $a_{\mu_1\mu_2\mu_3}$,

$$a_{\mu_1\mu_2\mu_3}\equiv\prod_{i=1}^{3}[\mu_i!!(\mu_i-2l_i-1)!!]^{-1},\tag{10}$$

the $\sum'$,

$$\sum{}'\equiv\underset{(\mu_1+\mu_2+\mu_3=l_1+l_2+l_3+2)}{\sum_{\mu_1\geq0}\sum_{\mu_2\geq0}\sum_{\mu_3\geq0}},\tag{11}$$

and the double factorial [see Eqs. (2.10)–(2.13) of V]. Note, in particular, that the reciprocal of an even negative double factorial is zero. In Eq. (7), note that in $\sum'$ the $(\mu_1+\mu_2+\mu_3)$ must be even, and that the sum of terms, for which two of (μ_1, μ_2, μ_3) are odd, gives exactly 1/2 times the sum of the formulas in Eqs. (4)–(6). Note, moreover, that the *form* of Eqs. (4)–(7) is independent of the nature of the atomic orbitals.

The first term in Eq. (4) was obtained by Margenau,[6] and the next few by Mason and Hirschfelder.[8] The multipole-moment approach has frequently been used for two-center Coulomb integrals.[7,8,14,15] It is shown below that Eqs. (4)–(7) are simple asymptotic expansions for $I_{cd;ab}$ under certain conditions, which are summarized in Table I. In Tables II and III, sample values of integrals appropriate for the ethane molecule, calculated with Eqs. (4) and (5), are compared with accurate values. The parameters for these ethane integrals are specified in Figs. 2 and 3. It should be noted that ethane is by no means a large molecule, and that even when the asymptotic result is poor, the first term is a good measure of the order of magnitude of the accurate value.

III. SIMPLE FORMULA BASED ON THE LAPLACE EXPANSION OF $1/r_{12}$

If the charge distribution for, say, electron 2 is dominated by, say, $\Psi_{n_cl_cm_cn_c}$, then another asymptotic expansion can be derived, the first term of which was obtained by Margenau[6] and by Ellison[8] and has the simple physical interpretation of an overlap integral times a three-center nuclear attraction integral. Heuristically, we write

$$r_{12}{}^{-1}\sim4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}r_2{}^lr_1{}^{-l-1}(2l+1)^{-1}Y_l{}^m(\theta_1,\phi_1)Y_l{}^{m*}(\theta_2,\phi_2),\tag{12}$$

where both (θ_1, ϕ_1) and (θ_2, ϕ_2) are measured from the origin (as opposed to, say, $\mathbf{R}$), and then

$$I_{cd;ab}(\mathbf{\mathcal{R}}_1,\mathbf{\mathcal{R}}_2,\mathbf{R})\sim4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(2l+1)^{-1}[\Omega_{cd}{}^{lm;l}(\mathbf{\mathcal{R}}_2)]^*I_{ab}{}^{-l-1,l,m}(\mathbf{R},\mathbf{R}+\mathbf{\mathcal{R}}_1),\tag{13}$$

where $I_{ab}{}^{-l-1,l,m}$ denotes the three-center one-electron integral of the irregular solid harmonic $r^{-l-1}Y_l{}^m$, evaluated elsewhere.[11] Values of four-center integrals estimated using just the first term[16] in Eq. (13) have also been included in Tables II and III.

TABLE I. Conditions for applicability of Eqs. (4)–(7).

Distances which are large	Other conditions on R, $\mathcal{R}_1$, $\mathcal{R}_2$	Cases	ζ Restrictions	Equation which is applicable
R	$R-\mathcal{R}_1-\mathcal{R}_2$ large	1	None	4
$\mathcal{R}_1$	$\mathcal{R}_1-R-\mathcal{R}_2$ large	2	$\zeta_b>\zeta_a$	5
R and $\mathcal{R}_1$	$\left\{\begin{matrix} R-\mathcal{R}_2 \text{ large} \\ \lvert R-\mathcal{R}_1\rvert \text{ small}\end{matrix}\right\}$	1, 2, 3	$\zeta_a>\zeta_b$	4
$\mathcal{R}_1$ and $\mathcal{R}_2$	$\left\{\begin{matrix} \mathcal{R}_1-R \text{ large} \\ \mathcal{R}_1-\mathcal{R}_2 \text{ small}\end{matrix}\right\}$	2, 3	$\zeta_b>\zeta_a$ and $\zeta_c>\zeta_d$	5
		2, 3	$\zeta_a>\zeta_b$ and $\zeta_d>\zeta_c$	6
R, $\mathcal{R}_1$, and $\mathcal{R}_2$	$R-\mathcal{R}_1-\mathcal{R}_2$ small	1	$\zeta_a>\zeta_b$ or $\zeta_c>\zeta_d$	4
	$\mathcal{R}_1-R-\mathcal{R}_2$ small	2	$\zeta_a>\zeta_b$ and $\zeta_c>\zeta_d$	4
		2	$\zeta_b>\zeta_a$ and $\zeta_c>\zeta_d$	5
	$\left\{\begin{matrix} \lvert R-\mathcal{R}_1\rvert \text{ small} \\ \lvert R-\mathcal{R}_2\rvert \text{ small}\end{matrix}\right\}$	3	$\zeta_a>\zeta_b$ and $\zeta_c>\zeta_d$	4
	$\left\{\begin{matrix} \mathcal{R}_1+\mathcal{R}_2-R \text{ large} \\ \mathcal{R}_2-R-\mathcal{R}_1 \text{ large}\end{matrix}\right\}$	3	$\zeta_b>\zeta_a$ and $\zeta_d>\zeta_c$	7

IV. COMPLETE ASYMPTOTIC EXPANSION. FORMULATION

We now begin a systematic derivation of the complete asymptotic expansions of $I_{cd;ab}$. Equations (4)–(7) will be shown to be only a part of the complete expansion. The main purpose of this section is to formulate the integral in terms of certain auxilliary functions, the asymptotic expansions of which are given in the next section (Sec. V).

We follow closely the formulation and notation of Paper V, and start with Eqs. (3.3) and Eqs. (3.7)–(3.11) of V:

$$I_{cd;ab}(\boldsymbol{\mathcal{R}}_1, \boldsymbol{\mathcal{R}}_2, \mathbf{R}) = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} \sum_{\lambda_1=|l_1-l_b|}^{l_1+l_b} \sum_{\lambda_2=|l_2-l_d|}^{l_2+l_d} \sum_{\Lambda_1=|l_1-l_a|}^{l_1+l_a} \sum_{\Lambda_2=|l_2-l_c|}^{l_2+l_c} \sum_{\Lambda_3=|\Lambda_1-\Lambda_2|}^{\Lambda_1+\Lambda_2} [(2\lambda_1+1)(2\lambda_2+1)$$
$$\times(2\Lambda_1+1)(2\Lambda_2+1)(2\Lambda_3+1)4\pi^3]^{1/2} c^{\lambda_1}(l_bm_b; l_1m_1) c^{\lambda_2}(l_dm_d; l_2m_2) c^{\Lambda_1}(l_1m_1; l_am_a) c^{\Lambda_2}(l_2m_2; l_cm_c)$$
$$\times c^{\Lambda_3}(\Lambda_1, m_1-m_a; \Lambda_2, m_2-m_c) Y_{\lambda_1}{}^{m_b-m_1}(\theta_{\mathcal{R}1}, \phi_{\mathcal{R}1}) Y_{\lambda_2}{}^{m_d-m_2*}(\theta_{\mathcal{R}2}, \phi_{\mathcal{R}2}) Y_{\Lambda_3}{}^{m_1-m_2-m_a+m_c}(\theta_R, \phi_R) I_{cd;ab}{}^{\mathrm{rad}}, \quad (14)$$

TABLE II. Simple asymptotic approximations for some four-center integrals arising from the eclipsed ethane molecule corresponding to the geometry in Fig. 2.

Carbon atom orbitals: $\Psi_{n_al_am_a\zeta_a}$ Orbital	ζ_a	$\Psi_{n_cl_cm_c\zeta_c}$ Orbital	ζ_c	Accurate value[a]	Simple asymptotic series [Eq. (4)]	Largest value of $l_1=l_2$ in series	Absolute error	Nuclear attraction $\times$overlap[b]	Overlap $\times$overlap[c]
$1s$	5.7	$1s$	5.7	0.00178916	0.00178918	5	$<2\times10^{-8}$	0.00181264	0.00183910
$2s$	1.625	$1s$	5.7	0.0120991	0.01217	6	7×10^{-5}	0.01215986	0.01416197
$2s$	1.625	$2s$	1.625	0.0863331	0.0881	4	2×10^{-3}	0.09363676	0.1090540
$2p_z$	1.625	$1s$	5.7	−0.00030097	−0.000178	11	1×10^{-4}	−0.00027229	−0.0039067
$2p_x$	1.625	$1s$	5.7	0.00887943	0.008880	11	1×10^{-6}	0.00880734	0.01096131
$2p_x$	1.625	$2p_x$	1.625	0.058611	0.0598	8	1×10^{-3}	0.05249296	0.06533099
$2p_z$	1.625	$2p_x$	1.625	−0.004079	−0.00277	9	1×10^{-3}	−0.00162289	−0.02328474

[a] R. M. Pitzer (private communication).
[b] First term in Eq. (13).
[c] First term in Eq. (4).

TABLE III. Simple asymptotic approximations for some three-center integrals arising from the eclipsed ethane molecule corresponding to the geometry in Fig. 3.

Carbon atom orbitals									
$\Psi_{n_b l_b m_b \zeta_b}$		$\Psi_{n_d l_d m_d \zeta_d}$		Accurate value[a]	Simple asymptotic series [Eq. (5)]	Largest value in series of $l_1=l_2$	Absolute error	Three-center nuclear attraction ×overlap	Two-center nuclear attraction ×overlap[d]
Orbital	ζ_b	Orbital	ζ_d						
$1s$	5.7	$1s$	5.7	0.00025535	0.0002554	10	$<5\times10^{-8}$	0.00025903[b]	0.00018228
$1s$	5.7	$2s$	1.625	0.00170408	0.001718	6	1×10^{-5}	0.00164746[c]	0.00140363
$2s$	1.625	$1s$	5.7	0.00555630	0.0076	5	2×10^{-3}	0.00560862[b]	0.00494351
$2s$	1.625	$2s$	1.625	0.0365650	0.049	4	1×10^{-2}	0.04318904[b]	0.03806743
$1s$	5.7	$2p_z$	1.625	−0.00002918	−0.0000042	12	3×10^{-5}	−0.00003689[c]	−0.00038721
$1s$	5.7	$2p_x$	1.625	0.00124042	0.00124037	14	5×10^{-8}	0.00119322[c]	0.00108640
$2p_x$	1.625	$2p_x$	1.625	0.0195540	0.0255	7	6×10^{-3}	0.01395990[b]	0.018844376
$2p_x$	1.625	$2p_z$	1.625	−0.00236167	−0.002346	10	2×10^{-5}	−0.00497547[b]	−0.00671836
$2p_z$	1.625	$2p_x$	1.625	0.0354800	0.0406	6	5×10^{-3}	0.04029213[b]	0.03473376

[a] R. M. Pitzer (private communication).
[b] First term in Eq. (13) when r_1 and r_2 in Eq. (12) are measured from center d.
[c] First term in Eq. (13) when r_1 and r_2 in Eq. (12) are measured from center b.
[d] First term in Eq. (5).

where

$$I_{cd;ab}{}^{\mathrm{rad}}=I^{(1)}+I^{(2)}+I^{(3)}+I^{(4)}, \tag{15}$$

$$\begin{aligned}I^{(1)}=(\pi i)^{-1}(1)^{\Lambda_1+\lambda_1+\lambda_2}\mathcal{P}\int_{i\infty}^{-i\infty} dx\mathcal{K}_{\Lambda_3}(xR)\{\cdots\mathcal{I}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{I}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\\ \times(x^{\Lambda_1}(x^{-1}d/dx)^{\Lambda_1}x^{-1}\{E_{2\Lambda_1+1}[(\zeta_a+\zeta_b+x)\mathcal{R}_1]-E_{2\Lambda_1+1}[(\zeta_a+\zeta_b-x)\mathcal{R}_1]\})\\ \times(x^{\Lambda_2}(x^{-1}d/dx)^{\Lambda_2}x^{-1}\{E_{2\Lambda_2+1}[(\zeta_c+\zeta_d+x)\mathcal{R}_2]-E_{2\Lambda_2+1}[(\zeta_c+\zeta_d-x)\mathcal{R}_2]\}),\end{aligned} \tag{16}$$

$$\begin{aligned}I^{(2)}=(2\pi i)^{-1}(-1)^{\Lambda_1+\lambda_1}\mathcal{P}\int_{i\infty}^{-i\infty} dx\mathcal{K}_{\Lambda_3}(xR)\{\cdots\mathcal{I}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\\ \times(x^{\Lambda_1}(x^{-1}d/dx)^{\Lambda_1}x^{-1}\{E_{2\Lambda_1+1}[(\zeta_a+\zeta_b+x)\mathcal{R}_1]-E_{2\Lambda_1+1}[(\zeta_a+\zeta_b-x)\mathcal{R}_1]\})\\ \times(x^{\Lambda_2}(x^{-1}d/dx)^{\Lambda_2}x^{-1}\{\tilde{E}_{2\Lambda_2+1}[(\zeta_c+\zeta_d+x)\mathcal{R}_2]-\tilde{E}_{2\Lambda_2+1}[(\zeta_c+\zeta_d-x)\mathcal{R}_2]-\tilde{E}_{2\Lambda_2+1}[(\zeta_c-\zeta_d+x)\mathcal{R}_2]\\ +\tilde{E}_{2\Lambda_2+1}[(\zeta_c-\zeta_d-x)\mathcal{R}_2]\}),\end{aligned} \tag{17}$$

$$\begin{aligned}I^{(3)}=(2\pi i)^{-1}(-1)^{\Lambda_1+\lambda_2}\mathcal{P}\int_{i\infty}^{-i\infty} dx\mathcal{K}_{\Lambda_3}(xR)\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{I}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\\ \times(x^{\Lambda_1}(x^{-1}d/dx)^{\Lambda_1}x^{-1}\{\tilde{E}_{2\Lambda_1+1}[(\zeta_a+\zeta_b+x)\mathcal{R}_1]-\tilde{E}_{2\Lambda_1+1}[(\zeta_a+\zeta_b-x)\mathcal{R}_1]-\tilde{E}_{2\Lambda_1+1}[(\zeta_a-\zeta_b+x)\mathcal{R}_1]\\ +\tilde{E}_{2\Lambda_1+1}[(\zeta_a-\zeta_b-x)\mathcal{R}_1]\})(x^{\Lambda_2}(x^{-1}d/dx)^{\Lambda_2}x^{-1}\{E_{2\Lambda_2+1}[(\zeta_c+\zeta_d+x)\mathcal{R}_2]-E_{2\Lambda_2+1}[(\zeta_c+\zeta_d-x)\mathcal{R}_2]\}),\end{aligned} \tag{18}$$

$$\begin{aligned}I^{(4)}=(4\pi i)^{-1}(-1)^{\Lambda_1}\mathcal{P}\int_{i\infty}^{-i\infty} dx\mathcal{K}_{\Lambda_3}(xR)\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\\ \times(x^{\Lambda_1}(x^{-1}d/dx)^{\Lambda_1}x^{-1}\{\tilde{E}_{2\Lambda_1+1}[(\zeta_a+\zeta_b+x)\mathcal{R}_1]-\tilde{E}_{2\Lambda_1+1}[(\zeta_a+\zeta_b-x)\mathcal{R}_1]-\tilde{E}_{2\Lambda_1+1}[(\zeta_a-\zeta_b+x)\mathcal{R}_1]\\ +\tilde{E}_{2\Lambda_1+1}[(\zeta_a-\zeta_b-x)\mathcal{R}_1]\})(x^{\Lambda_2}(x^{-1}d/dx)^{\Lambda_2}x^{-1}\{\tilde{E}_{2\Lambda_2+1}[(\zeta_c+\zeta_d+x)\mathcal{R}_2]-\tilde{E}_{2\Lambda_2+1}[(\zeta_c+\zeta_d-x)\mathcal{R}_2]\\ -\tilde{E}_{2\Lambda_2+1}[(\zeta_c-\zeta_d+x)\mathcal{R}_2]+\tilde{E}_{2\Lambda_2+1}[(\zeta_c-\zeta_d-x)\mathcal{R}_2]\}).\end{aligned} \tag{19}$$

The symbol $\{\cdots F_\lambda(\zeta\mathcal{R})\cdots\}$ is defined in Eq. (2.37) of V.

The further decompositions of the $I^{(i)}$ given in V, Sec. IV, are convenient for obtaining convergent infinite expansions. For asymptotic expansions, a slightly different decomposition is more suitable. Here we first decompose the integrands into terms which vanish at either $x=\infty$ or $x=-\infty$, then pull the integration contours away from the origin and deform them into the real axis in the half-plane in which the integrand vanishes at ∞. No involved manipulations of the integrands, such as those used in V, are subsequently required. The same cases defined by the relative magnitudes of R, $\mathcal{R}_1$, and $\mathcal{R}_2$ occur here as for the convergent expansions, but the special functions that occur are different.

A. Special Functions

The new special functions that arise here are denoted by variations on the letter D and are defined by

$$D^l(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2) \equiv (2\pi i)^{-1} \int_\infty^{(\zeta_2^+)} dx \mathcal{K}_{\Lambda_3}(xR) x^{\Lambda_1} \left(\frac{x^{-1}d}{dx}\right)^{\Lambda_1} x^{-1} \mathfrak{R}_1^{2\Lambda_1} (\zeta_1 + x)^{2\Lambda_1} \frac{\log(\zeta_1 + x)}{(2\Lambda_1!)} \times \left(x^{\Lambda_2} \left(\frac{x^{-1}d}{dx}\right)^{\Lambda_2} x^{-1} \mathfrak{R}_2^{2\Lambda_2} (\zeta_2 - x)^{2\Lambda_2} \frac{\log(\zeta_2 - x)}{(2\Lambda_2)!} \right), \quad (20)$$

$$D(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2) \equiv (2\pi i)^{-1} \int_\infty^{(\zeta_2^+)} dx \mathcal{K}_{\Lambda_3}(xR) \left(x^{\Lambda_1} \left(\frac{x^{-1}d}{dx}\right)^{\Lambda_1} x^{-1} E_{2\Lambda_1+1}[(\zeta_1 + x)\mathfrak{R}_1] \right) \times \left(x^{\Lambda_2} \left(\frac{x^{-1}d}{dx}\right)^{\Lambda_2} x^{-1} \mathfrak{R}_2^{2\Lambda_2} (\zeta_2 - x)^{2\Lambda_2} \frac{\log(\zeta_2 - x)}{(2\Lambda_2)!} \right), \quad (21)$$

$$\tilde{D}(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2) \equiv (2\pi i)^{-1} \int_\infty^{(\zeta_2^+)} dx \mathcal{K}_{\Lambda_3}(xR) \left(x^{\Lambda_1} \left(\frac{x^{-1}d}{dx}\right)^{\Lambda_1} x^{-1} \tilde{E}_{2\Lambda_1+1}[(\zeta_1 + x)\mathfrak{R}_1] \right) \times \left(x^{\Lambda_2} \left(\frac{x^{-1}d}{dx}\right)^{\Lambda_2} x^{-1} \mathfrak{R}_2^{2\Lambda_2} (\zeta_2 - x)^{2\Lambda_2} \frac{\log(\zeta_2 - x)}{(2\Lambda_2)!} \right). \quad (22)$$

In addition, we need

$$A(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2) \equiv \tilde{D}(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2) - \tilde{D}(\Lambda_3, R; \Lambda_1, -\zeta_1, -\mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2), \quad (23)$$

$$B(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2) \equiv \tfrac{1}{2}(-1)^{\Lambda_3+1} D(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2) - \tfrac{1}{2} D(\Lambda_3, -R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2). \quad (24)$$

The only singularity meant to be enclosed by the integration paths in Eqs. (20)–(22), regardless of the signs of ζ_1 or ζ_2, is the $\log(\zeta_2 - x)$ branch cut. The A function [in the A_2 form, see below] and the B function have already been used in Paper V.

B. "Subscript-2," "Subscript-4," and Other Aspects of Notation

The subscript-2 and subscript-4 notation introduced below enormously simplifies the final formulas. Let F denote any of the five functions defined by Eqs. (20)–(24). Then

$$F_2(\Lambda_3, R; \Lambda_1, \zeta_a \pm \zeta_b, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2) = F(\Lambda_3, R; \Lambda_1, \zeta_a + \zeta_b, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2) - F(\Lambda_3, R; \Lambda_1, \zeta_a - \zeta_b, \mathfrak{R}_1; \Lambda_2, \zeta_2, \mathfrak{R}_2), \quad (25)$$

$$F_2(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_c \pm \zeta_d, \mathfrak{R}_2) = F(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_c + \zeta_d, \mathfrak{R}_2) - F(\Lambda_3, R; \Lambda_1, \zeta_1, \mathfrak{R}_1; \Lambda_2, \zeta_c - \zeta_d, \mathfrak{R}_2), \quad (26)$$

$$F_4(\Lambda_3, R; \Lambda_1, \zeta_a \pm \zeta_b, \mathfrak{R}_1; \Lambda_2, \zeta_c \pm \zeta_d, \mathfrak{R}_2) = F(\Lambda_3, R; \Lambda_1, \zeta_a + \zeta_b, \mathfrak{R}_1; \Lambda_2, \zeta_c + \zeta_d, \mathfrak{R}_2) - F(\Lambda_3, R; \Lambda_1, \zeta_a + \zeta_b, \mathfrak{R}_1; \Lambda_2, \zeta_c - \zeta_d, \mathfrak{R}_2) - F(\Lambda_3, R; \Lambda_1, \zeta_a - \zeta_b, \mathfrak{R}_1; \Lambda_2, \zeta_c + \zeta_d, \mathfrak{R}_2) + F(\Lambda_3, R; \Lambda_1, \zeta_a - \zeta_b, \mathfrak{R}_1; \Lambda_2, \zeta_c - \zeta_d, \mathfrak{R}_2). \quad (27)$$

An additional notation used is:

$$b_{\mu_1\mu_2\mu_3} = \tfrac{1}{2}(-1)^{\Lambda_3} \mathfrak{R}_1^{\mu_1} \mathfrak{R}_2^{\mu_2} R^{\mu_3 - \Lambda_3 - 1} [1 - (-1)^{\mu_1} - (-1)^{\mu_2} - (-1)^{\mu_3}] a_{\mu_1\mu_2\mu_3}. \quad (28)$$

By the general approach sketched above [between Eqs. (19) and (20)], by using standard complex-variable theory, and by sometimes using Eqs. (2.17) and (2.6) of V relating $\tilde{E}_n$ to E_n and $\mathcal{K}$ to $\mathcal{I}$, one obtains the $I^{(i)}$ as special functions plus residues at the origin.

All terms involving Kronecker deltas or $\sum'$ in Eqs. (29)–(46) which follow, arise as residues at $x=0$, and shall be referred to as *origin terms*. Asymptotic expansions for the special functions appearing in Eqs. (29)–(46) will be obtained in Sec. V. However, the reader interested only in the derivation of the simple, multipole momentlike formulas [Eqs. (4)–(7)] that result from the origin terms alone, may skip Sec. V and proceed directly to Sec. VI.

The α_n and $\hat{\alpha}_n$ which appear in the following equations are defined in Eqs. (2.16) and (2.18) of Paper V.

C. Case 1. $R \geq \mathfrak{R}_1 + \mathfrak{R}_2$

$$I^{(1)} = 2(-1)^{\Lambda_1+\lambda_1+\lambda_2} \{\cdots \mathcal{I}_{\lambda_1}(\zeta_b \mathfrak{R}_1) \cdots\} \{\cdots \mathcal{I}_{\lambda_2}(\zeta_d \mathfrak{R}_2) \cdots\} \times \{ 2\delta_{\Lambda_3, \Lambda_1+\Lambda_2} (\Lambda_1{}^{\Lambda_3}\Lambda_2) \mathfrak{R}_1^{2\Lambda_1+1} \mathfrak{R}_2^{2\Lambda_2+1} R^{-\Lambda_3-1} \alpha_0[(\zeta_a + \zeta_b)\mathfrak{R}_1] \times \alpha_0[(\zeta_c + \zeta_d)\mathfrak{R}_2] + D(\Lambda_3, R; \Lambda_1, \zeta_a + \zeta_b, \mathfrak{R}_1; \Lambda_2, \zeta_c + \zeta_d, \mathfrak{R}_2) + D(\Lambda_3, R; \Lambda_2, \zeta_c + \zeta_d, \mathfrak{R}_2; \Lambda_1, \zeta_a + \zeta_b, \mathfrak{R}_1) - D(\Lambda_3, R; \Lambda_1, -\zeta_a - \zeta_b, -\mathfrak{R}_1; \Lambda_2, \zeta_c + \zeta_d, \mathfrak{R}_2) - D(\Lambda_3, R; \Lambda_2, -\zeta_c - \zeta_d, -\mathfrak{R}_2; \Lambda_1, \zeta_a + \zeta_b, \mathfrak{R}_1) \}, \quad (29)$$

$$I^{(2)}=(-1)^{\Lambda_1+\lambda_1}\{\cdots\mathcal{G}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\big(2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1+1}\mathcal{R}_2{}^{2\Lambda_2+1}R^{-\Lambda_3-1}\alpha_0[(\zeta_a+\zeta_b)\mathcal{R}_1]$$
$$\times\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\}+A_2(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a+\zeta_b,\mathcal{R}_1)\big),\quad(30)$$

$$I^{(3)}=(-1)^{\Lambda_1+\lambda_2}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{G}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\big(2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1+1}\mathcal{R}_2{}^{2\Lambda_2+1}R^{-\Lambda_3-1}$$
$$\times\{\hat{\alpha}_0[(\zeta_a+\zeta_b)\mathcal{R}_1]-\hat{\alpha}_0[(\zeta_a-\zeta_b)\mathcal{R}_1]\}\alpha_0[(\zeta_c+\zeta_d)\mathcal{R}_2]+A_2(\Lambda_3,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2)\big),\quad(31)$$

$$I^{(4)}=(-1)^{\Lambda_1}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1+1}\mathcal{R}_2{}^{2\Lambda_2+1}R^{-\Lambda_3-1}$$
$$\times\{\hat{\alpha}_0[(\zeta_a+\zeta_b)\mathcal{R}_1]-\hat{\alpha}_0[(\zeta_a-\zeta_b)\mathcal{R}_1]\}\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\}.\quad(32)$$

D. Case 2. $\mathcal{R}_1\geq R+\mathcal{R}_2$

$$I^{(1)}=4(-1)^{\Lambda_1+\lambda_1+\lambda_2}\{\cdots\mathcal{G}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{G}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\{\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_2}(\Lambda_2{}^{\Lambda_1}\Lambda_3)\mathcal{R}_2{}^{2\Lambda_2+1}R^{\Lambda_3}$$
$$\times E_{2\Lambda_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]\alpha_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-(-1)^{\Lambda_3}B(\Lambda_3,R;\Lambda_1,\zeta_a+\zeta_b,\mathcal{R}_1;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2)\}.\quad(33)$$

$$I^{(2)}=2(-1)^{\Lambda_1+\lambda_1}\{\cdots\mathcal{G}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_2}(\Lambda_2{}^{\Lambda_1}\Lambda_3)\mathcal{R}_2{}^{2\Lambda_2+1}R^{\Lambda_3}E_{2\Lambda_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]$$
$$\times\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\}.\quad(34)$$

$$I^{(3)}=(-1)^{\Lambda_1+\lambda_2}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{G}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}$$
$$\times\big(2\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_2}(\Lambda_2{}^{\Lambda_1}\Lambda_3)\mathcal{R}_2{}^{2\Lambda_2+1}R^{\Lambda_3}\{E_{2\Lambda_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]$$
$$-E_{2\Lambda_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}\alpha_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-2\delta_{\Lambda_3,\Lambda_2-\Lambda_1}(-1)^{\Lambda_1}$$
$$\times(\Lambda_1{}^{\Lambda_2}\Lambda_3)\mathcal{R}_1{}^{2\Lambda_1}\mathcal{R}_2{}^{2\Lambda_2}R^{\Lambda_3-2\Lambda_2}[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]$$
$$\times E_{2\Lambda_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]+2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1}\mathcal{R}_2{}^{2\Lambda_2}R^{-\Lambda_3-1}$$
$$\times[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]\{R\alpha_0[(\zeta_c+\zeta_d)R]-\mathcal{R}_2\alpha_0[(\zeta_c+\zeta_d)\mathcal{R}_2]\}$$
$$+2(-1)^{\Lambda_3+1}[B_2(\Lambda_3,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2)$$
$$-(\mathcal{R}_2/R)^{2\Lambda_2}B_2(\Lambda_3,R;\Lambda_2,\zeta_c+\zeta_d,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)]$$
$$-A_2(\Lambda_3,R;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)$$
$$+(\mathcal{R}_2/R)^{2\Lambda_2}A_2(\Lambda_3,R;\Lambda_2,\zeta_c+\zeta_d,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)\big)\quad(\text{Subcase 2a, }R>\mathcal{R}_2),\quad(35)$$

$$I^{(3)}=(-1)^{\Lambda_1+\lambda_2}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{G}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}$$
$$\times\big(2\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_2}(\Lambda_2{}^{\Lambda_1}\Lambda_3)\mathcal{R}_2{}^{2\Lambda_2+1}R^{\Lambda_3}\{E_{2\Lambda_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]$$
$$-E_{2\Lambda_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}\alpha_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-2\delta_{\Lambda_3,\Lambda_2-\Lambda_1}(-1)^{\Lambda_1}$$
$$\times(\Lambda_1{}^{\Lambda_2}\Lambda_3)\mathcal{R}_1{}^{2\Lambda_1}R^{\Lambda_3}[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]E_{2\Lambda_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]$$
$$+2(-1)^{\Lambda_3+1}[B_2(\Lambda_3,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2)$$
$$-B_2(\Lambda_3,R;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)]\big)\quad(\text{Subcase 2b, }\mathcal{R}_2\geq R).\quad(36)$$

$$I^{(4)}=\tfrac{1}{2}(-1)^{\Lambda_1}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}$$
$$\times\big(2\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_2}(\Lambda_2{}^{\Lambda_1}\Lambda_3)\mathcal{R}_2{}^{2\Lambda_2+1}R^{\Lambda_3}\{E_{2\Lambda_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]$$
$$-E_{2\Lambda_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\}$$
$$-2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1}\mathcal{R}_2{}^{2\Lambda_2+1}R^{-\Lambda_3-1}[(\zeta_a+\zeta_b)^{-1}$$
$$\zeta_a-\zeta_b)^{-1}]\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\}$$
$$-A_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)\big)\quad(\text{Subcase 2a, }R\geq\mathcal{R}_2).\quad(37)$$

$$I^{(4)}=\tfrac{1}{2}(-1)^{\Lambda_1}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}$$
$$\times[2\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_2}(\Lambda_2{}^{\Lambda_1}\Lambda_3)\mathcal{R}_2{}^{2\Lambda_2+1}R^{\Lambda_3}\{E_{2\Lambda_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]$$
$$-E_{2\Lambda_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\}$$
$$-2\delta_{\Lambda_3,\Lambda_2-\Lambda_1}(-1)^{\Lambda_1}(\Lambda_1{}^{\Lambda_2}\Lambda_3)\mathcal{R}_1{}^{2\Lambda_1}R^{\Lambda_3}[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]$$
$$\times(\tilde{E}_{2\Lambda_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]-\tilde{E}_{2\Lambda_2+1}[(\zeta_c-\zeta_d)\mathcal{R}_2]-(\mathcal{R}_2/R)^{2\Lambda_2}$$
$$\times\{\tilde{E}_{2\Lambda_2+1}[(\zeta_c+\zeta_d)R]-\tilde{E}_{2\Lambda_2+1}[(\zeta_c-\zeta_d)R]\})$$
$$-2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1}\mathcal{R}_2{}^{2\Lambda_2}R^{-\Lambda_3}[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]$$
$$\times\{\hat{\alpha}_0[(\zeta_c+\zeta_d)R]-\hat{\alpha}_0[(\zeta_c-\zeta_d)R]\}$$
$$+2(-1)^{\Lambda_3}[B_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)$$
$$-(\mathcal{R}_2/R)^{2\Lambda_2}B_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)]$$
$$-(\mathcal{R}_2/R)^{2\Lambda_2}A_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)]\quad(\text{Subcase 2b, }\mathcal{R}_2\geq R).\quad(38)$$

E. Case 3

$$I^{(1)}=2(-1)^{\Lambda_1+\lambda_1+\lambda_2}\{\cdots\mathcal{I}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{I}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}$$
$$\times\{\textstyle\sum' b_{\mu_1\mu_2\mu_3}E_{2\Lambda_1-\mu_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]E_{2\Lambda_2-\mu_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]+D(\Lambda_3,R;\Lambda_1,\zeta_a+\zeta_b,\mathcal{R}_1;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2)$$
$$+D(\Lambda_3,R;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a+\zeta_b,\mathcal{R}_1)\}.\quad(39)$$

$$I^{(2)}=(-1)^{\Lambda_1+\lambda_1}\{\cdots\mathcal{I}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}$$
$$\times(-2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1+1}\mathcal{R}_2{}^{2\Lambda_2}R^{-\Lambda_3-1}$$
$$\times\alpha_0[(\zeta_a+\zeta_b)\mathcal{R}_1][(\zeta_c+\zeta_d)^{-1}-(\zeta_c-\zeta_d)^{-1}]$$
$$+\textstyle\sum' b_{\mu_1\mu_2\mu_3}E_{2\Lambda_1-\mu_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]\{E_{2\Lambda_2-\mu_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]$$
$$-E_{2\Lambda_2-\mu_2+1}[(\zeta_c-\zeta_d)\mathcal{R}_2]\}$$
$$+\tilde{D}_2(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a+\zeta_b,\mathcal{R}_1)$$
$$+D_2(\Lambda_3,R;\Lambda_1,-\zeta_a-\zeta_b,-\mathcal{R}_1;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2)$$
$$-D_2{}^l(\Lambda_3,R;\Lambda_2,-\zeta_c\mp\zeta_d,-\mathcal{R}_2;\Lambda_1,\zeta_a+\zeta_b,\mathcal{R}_1))\quad(\text{Subcase 3a, }R\geq\mathcal{R}_1).\quad(40)$$

$$I^{(2)}=(-1)^{\Lambda_1+\lambda_1}\{\cdots\mathcal{I}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}(-2\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_2}(\Lambda_2{}^{\Lambda_1}\Lambda_3)\mathcal{R}_2{}^{2\Lambda_2}R^{\Lambda_3}$$
$$\times E_{2\Lambda_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1][(\zeta_c+\zeta_d)^{-1}-(\zeta_c-\zeta_d)^{-1}]$$
$$+\textstyle\sum' b_{\mu_1\mu_2\mu_3}E_{2\Lambda_1-\mu_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]$$
$$\times\{E_{2\Lambda_2-\mu_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]-E_{2\Lambda_2-\mu_2+1}[(\zeta_c-\zeta_d)\mathcal{R}_2]\}$$
$$+D_2(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a+\zeta_b,\mathcal{R}_1)$$
$$-(-1)^{\Lambda_3}D(\Lambda_3,-R;\Lambda_1,\zeta_a+\zeta_b,\mathcal{R}_1;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2))\quad(\text{Subcase 3b, 3c, }\mathcal{R}_1\geq R).\quad(41)$$

$$I^{(3)}=(-1)^{\Lambda_1+\lambda_2}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{I}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}(-2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1}\mathcal{R}_2{}^{2\Lambda_2+1}R^{-\Lambda_3-1}$$
$$\times[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]\alpha_0[(\zeta_c+\zeta_d)\mathcal{R}_2]$$
$$+\textstyle\sum' b_{\mu_1\mu_2\mu_3}\{E_{2\Lambda_1-\mu_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]-E_{2\Lambda_1-\mu_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}$$
$$\times E_{2\Lambda_2-\mu_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]$$
$$+\tilde{D}_2(\Lambda_3,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2)$$
$$+D_2(\Lambda_3,R;\Lambda_2,-\zeta_c-\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)$$
$$-D_2{}^l(\Lambda_3,R;\Lambda_1,-\zeta_a\mp\zeta_b,-\mathcal{R}_1;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2))\quad(\text{Subcases 3a, 3b, }R\geq\mathcal{R}_2).\quad(42)$$

$$I^{(3)}=(-1)^{\Lambda_1+\lambda_2}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{I}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\Big(-2\delta_{\Lambda_3,\Lambda_2-\Lambda_1}(-1)^{\Lambda_1}(\Lambda_1{}^{\Lambda_2}\Lambda_3)\mathcal{R}_1{}^{2\Lambda_1}R^{\Lambda_3}[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]$$
$$\times E_{2\Lambda_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]+\textstyle\sum' b_{\mu_1\mu_2\mu_3}\{E_{2\Lambda_1-\mu_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]-E_{2\Lambda_1-\mu_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}E_{2\Lambda_2-\mu_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]$$
$$+D_2(\Lambda_3,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2)-(-1)^{\Lambda_3}D(\Lambda_3,-R;\Lambda_2,\zeta_c+\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)\Big)$$
$$(\text{Subcase 3c, }\mathcal{R}_2\geq R).\quad(43)$$

$$I^{(4)}=\tfrac{1}{2}(-1)^{\Lambda_1}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\big[-2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1}\mathcal{R}_2{}^{2\Lambda_2}R^{-\Lambda_3-1}$$
$$\times\Big([(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]\mathcal{R}_2\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\}+\mathcal{R}_1\{\alpha_0[(\zeta_a+\zeta_b)\mathcal{R}_1]-\alpha_0[(\zeta_a-\zeta_b)\mathcal{R}_1\}$$
$$\times[(\zeta_c+\zeta_d)^{-1}-(\zeta_c-\zeta_d)^{-1}]\Big)+\textstyle\sum' b_{\mu_1\mu_2\mu_3}\{E_{2\Lambda_1-\mu_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]-E_{2\Lambda_1-\mu_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}$$
$$\times\{E_{2\Lambda_2-\mu_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]-E_{2\Lambda_2-\mu_2+1}[(\zeta_c-\zeta_d)\mathcal{R}_2]\}+D_4(\Lambda_3,R;\Lambda_1,-\zeta_a\mp\zeta_b,-\mathcal{R}_1;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2)$$
$$+D_4(\Lambda_3,R;\Lambda_2,-\zeta_c\mp\zeta_d,-\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)\big]\quad(\text{Subcase 3a, }R\geq\mathcal{R}_1).\quad(44)$$

$$I^{(4)}=\tfrac{1}{2}(-1)^{\Lambda_1}\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}$$
$$\times\Big(-2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1}\mathcal{R}_2{}^{2\Lambda_2}R^{-\Lambda_3-1}[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\}$$
$$-2\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_2}(\Lambda_2{}^{\Lambda_1}\Lambda_3)\mathcal{R}_2{}^{2\Lambda_2}R^{\Lambda_3}\{E_{2\Lambda_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]-E_{2\Lambda_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}$$
$$\times[(\zeta_c+\zeta_d)^{-1}-(\zeta_c-\zeta_d)^{-1}]+\textstyle\sum' b_{\mu_1\mu_2\mu_3}\{E_{2\Lambda_1-\mu_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]-E_{2\Lambda_1-\mu_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}$$
$$\times\{E_{2\Lambda_2-\mu_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]-E_{2\Lambda_2-\mu_2+1}[(\zeta_c-\zeta_d)\mathcal{R}_2]\}-A_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)$$
$$+D_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)-(-1)^{\Lambda_3}D_4(\Lambda_3,-R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2)\Big)$$
$$(\text{Subcase 2b, }\mathcal{R}_1\geq R\geq\mathcal{R}_2).\quad(45)$$

$$I^{(4)}=\tfrac{1}{2}(-1)^{\Lambda_1}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_b\mathcal{R}_1)\cdots\}\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\big[-2\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1}\mathcal{R}_2{}^{2\Lambda_2}R^{-\Lambda_3}$$
$$\times[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]\{\hat{\alpha}_0[(\zeta_c+\zeta_d)R]-\hat{\alpha}_0[(\zeta_c-\zeta_d)R]\}+2\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_2}(\Lambda_2{}^{\Lambda_1}\Lambda_3)\mathcal{R}_2{}^{2\Lambda_2+1}R^{\Lambda_3}$$
$$\times\{E_{2\Lambda_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]-E_{2\Lambda_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\}$$
$$-2\delta_{\Lambda_3,\Lambda_2-\Lambda_1}(-1)^{\Lambda_1}(\Lambda_1{}^{\Lambda_2}\Lambda_3)\mathcal{R}_1{}^{2\Lambda_1}R^{\Lambda_3}[(\zeta_a+\zeta_b)^{-1}-(\zeta_a-\zeta_b)^{-1}]\Big(\tilde{E}_{2\Lambda_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]-\tilde{E}_{2\Lambda_2+1}[(\zeta_c-\zeta_d)\mathcal{R}_2]$$
$$-(\mathcal{R}_2/R)^{2\Lambda_2}\{\tilde{E}_{2\Lambda_2+1}[(\zeta_c+\zeta_d)R]-\tilde{E}_{2\Lambda_2+1}[(\zeta_c-\zeta_d)R]\}\Big)+\textstyle\sum' a_{\mu_1\mu_2\mu_3}(-1)^{\mu_2}R^{\mu_3-\Lambda_3-1}\mathcal{R}_1{}^{\mu_1}$$
$$\times\{E_{2\Lambda_1-\mu_1+1}[(\zeta_a+\zeta_b)\mathcal{R}_1]-E_{2\Lambda_1-\mu_1+1}[(\zeta_a-\zeta_b)\mathcal{R}_1]\}$$
$$\times\Big(\mathcal{R}_2{}^{\mu_2}\{\tilde{E}_{2\Lambda_2-\mu_2+1}[(\zeta_c+\zeta_d)\mathcal{R}_2]-\tilde{E}_{2\Lambda_2-\mu_2+1}[(\zeta_c-\zeta_d)\mathcal{R}_2]\}$$
$$-\mathcal{R}_2{}^{2\Lambda_2}(\mathcal{R}_1-R)^{\mu_2-2\Lambda_2}$$
$$\times\{\tilde{E}_{2\Lambda_2-\mu_2+1}[(\zeta_c+\zeta_d)(\mathcal{R}_1-R)]-\tilde{E}_{2\Lambda_2-\mu_2+1}[(\zeta_c-\zeta_d)(\mathcal{R}_1-R)]\}\Big)$$
$$+2(-1)^{\Lambda_3}[B_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2,\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)$$
$$-(\mathcal{R}_2/R)^{2\Lambda_2}B_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)]$$
$$-(\mathcal{R}_2/R)^{2\Lambda_2}A_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)$$
$$-D_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)$$
$$+[\mathcal{R}_2/(\mathcal{R}_1-R)]^{2\Lambda_2}D_4(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_1-R;\Lambda_1,\zeta_a\pm\zeta_b,\mathcal{R}_1)\big]\quad(\text{Subcase 3c, }\mathcal{R}_2\geq R).\quad(46)$$

V. ASYMPTOTIC EXPANSIONS OF SPECIAL FUNCTIONS

A. The Singularity Problem

Before we proceed to develop asymptotic expansions for the special functions defined in Eqs. (20)–(24) we must comment on the analytic properties of Eqs. (29)–(46).

Note that some origin terms in Eqs. (29)–(46) are singular when certain combinations of ζ's vanish. Examination of Eqs. (20)–(24) reveals that the special functions are also singular for certain values of ζ_1 and ζ_2. For instance, D^l [Eq. (20)] is singular when $\zeta_2=0$, since the integration contour is squeezed between two coincident singularities in the integrand. In the formulas for $I^{(i)}$, such singularities occur in pairs so that they may be "cancelled out" if the proper terms are combined. This implies that Eqs. (29)–(46) are unsatisfactory in the neighborhood of these singularities and that asymptotic formulas should be developed for combination of terms which are analytic for all orbital exponents. However, several considerations make a systematic formulation based on "analytic special functions" impractical:

(1) Special expansions are necessary when certain combinations of ζ's vanish.

(2) The detailed recipe for cancelling singularities depends on which internuclear distances are large. This greatly complicates the development of expansions for the analytic special functions.

(3) Expansion of the special functions for the singular cases are often very complicated. In some cases, such expansions are comparable in difficulty to the formulas developed in V. Moreover, certain of these expansions are not asymptotic in the internuclear distances, in the ordinary sense.

The nature of the problem is illustrated by examination of the analytic function,

$$\hat{\alpha}_0[(\zeta_1-\zeta_2)R]\equiv\{\exp[-(\zeta_1-\zeta_2)R]-1\}/[(\zeta_1-\zeta_2)R], \tag{47}$$

for large R.

When $\zeta_1>\zeta_2$, the leading asymptotic term is $-[(\zeta_1-\zeta_2)R]^{-1}$, and when $\zeta_2>\zeta_1$, the leading term is $\exp[-(\zeta_1-\zeta_2)R]/[(\zeta_1-\zeta_2)R]$. But when $\zeta_1\approx\zeta_2$, both terms become singular, and $\hat{\alpha}_0[(\zeta_1-\zeta_2)R]$ has no asymptotic expansion in R, although it does have a Taylor series expansion in $[(\zeta_1-\zeta_2)R]$. The singularities in the $I^{(i)}$ are of a similar nature. As the relative magnitudes of certain orbital exponents are varied, the relative importance of various terms in Eqs. (29)–(46) shift. The transition region between dominance of two different terms is characterized by singularities in both terms. Asymptotic expansions for this region are unlike those for the individual terms.

We therefore take the following approach in this section: we develop asymptotic expansions for the special functions, explicitly avoiding situations where they are singular. In the Appendix we indicate how a systematic approach to the cancellation of singularities can be developed, although we do not give a complete set of formulas.

We now proceed to list the asymptotic expansions for the special functions, delaying their derivations to the end of this section, in order to preserve continuity.

B. The Asymptotic Scheme

1. Formulas for D^l

If R is large, $\zeta_1+\zeta_2\not\approx 0$, $\zeta_2\not\approx 0$,

$$D^l(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2)\sim(-1)^{\Lambda_2}\mathcal{R}_2{}^{2\Lambda_2}\sum_{\nu_2=0}^{\infty}\binom{2\Lambda_2+\nu_2}{\nu_2}R^{-2\Lambda_2-\nu_2-1}$$
$$\times(R+d/d\zeta_2)^{\nu_2}\boldsymbol{(}(\zeta_2{}^{-1}d/d\zeta_2)^{\Lambda_2}\zeta_2{}^{\Lambda_1+\Lambda_2-1}\mathcal{K}_{\Lambda_3}(\zeta_2R)(\zeta_2{}^{-1}d/d\zeta_2)^{\Lambda_1}\zeta_2{}^{-1}\boldsymbol{)}[(\zeta_1+\zeta_2)\mathcal{R}_1]^{2\Lambda_1}\log(\zeta_1+\zeta_2)/(2\Lambda_1)!. \tag{48}$$

2. Formulas for D

If $(R+\mathcal{R}_1)$ is large, $\zeta_1+\zeta_2\not\approx 0$, $\zeta_2\not\approx 0$,

$$D(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2)\sim(-1)^{\Lambda_2}\mathcal{R}_2{}^{2\Lambda_2}\sum_{\nu_2=0}^{\infty}\binom{2\Lambda_2+\nu_2}{\nu_2}(R+\mathcal{R}_1)^{-2\Lambda_2-\nu_2-1}$$
$$\times(R+\mathcal{R}_1+d/d\zeta_2)^{\nu_2}\boldsymbol{(}\cdots\mathcal{K}_{\Lambda_3}(\zeta_2R)\cdots\boldsymbol{)}E_{2\Lambda_1+1}[(\zeta_1+\zeta_2)\mathcal{R}_1], \tag{49}$$

where the $\boldsymbol{(}\cdots\mathcal{K}_{\Lambda_3}(\zeta_2R)\cdots\boldsymbol{)}$ stands for the operator enclosed by bold parentheses in Eq. (48).

If R and $\mathcal{R}_1$ are large but $(\mathcal{R}_1-R)$ is small, use

$$D(\Lambda_3, -R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2)=(-1)^{\Lambda_3}\mathcal{R}_2{}^{2\Lambda_2}(\mathcal{R}_1-R)^{-2\Lambda_2}\{D(\Lambda_3, R; \Lambda_2, \zeta_2, \mathcal{R}_1-R; \Lambda_1, \zeta_1, \mathcal{R}_1)$$
$$+\sum{}'a_{\mu_1\mu_2\mu_3}(-R)^{\mu_3-\Lambda_3-1}\mathcal{R}_1{}^{\mu_1}E_{2\Lambda_1-\mu_1+1}(\zeta_1\mathcal{R}_1)(R-\mathcal{R}_1)^{\mu_2}E_{2\Lambda_2-\mu_2+1}[\zeta_2(\mathcal{R}_1-R)]\}, \tag{50}$$

and expand the D on the rhs of Eq. (50) via Eq. (49).

If R and $\mathcal{R}_1$ are large, but $R-\mathcal{R}_1$ is small, use

$$D(\Lambda_3, R; \Lambda_1, -\zeta_1, -\mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2)=\mathcal{R}_2{}^{2\Lambda_2}(R-\mathcal{R}_1)^{-2\Lambda_2}\{-D(\Lambda_3, R; \Lambda_2, -\zeta_2, \mathcal{R}_1-R; \Lambda_1, \zeta_1, \mathcal{R}_1)$$
$$+(-1)^{\Lambda_3}\sum{}'a_{\mu_1\mu_2\mu_3}R^{\mu_3-\Lambda_3-1}(-\mathcal{R}_1)^{\mu_1}E_{2\Lambda_1-\mu_1+1}(\zeta_1\mathcal{R}_1)(\mathcal{R}_1-R)^{\mu_2}E_{2\Lambda_2-\mu_2+1}[\zeta_2(R-\mathcal{R}_1)]\}, \tag{51}$$

and expand the D on the rhs of Eq. (51) via Eq. (49).

If R is large, use

$$\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}D_2(\Lambda_3,-R;\Lambda_1,\zeta_1,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2)=\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}$$
$$\times\{(-1)^{\Lambda_3+1}D_2{}^l(\Lambda_3,R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2;\Lambda_1,\zeta_1,R)+\sum{}'a_{\mu_1\mu_2\mu_3}(-1)^{\mu_3}R^{\mu_1+\mu_3-\Lambda_3-1}$$
$$\times E_{2\Lambda_1-\mu_1+1}(\zeta_1R)\mathcal{R}_2{}^{2\Lambda_2}(d/d\zeta_c)^{\mu_2}[(\zeta_c+\zeta_d)^{2\Lambda_2}\log(\zeta_c+\zeta_d)-(\zeta_c-\zeta_d)^{2\Lambda_2}\log(\zeta_c-\zeta_d)]/(2\Lambda_2)!\},\quad(52)$$

and evaluate the D^l with Eq. (48).

If R is large, use

$$\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}D_2(\Lambda_3,R;\Lambda_1,-\zeta_1,-R;\Lambda_2,\zeta_c\pm\zeta_d,\mathcal{R}_2)=\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}$$
$$\times\{D_2{}^l(\Lambda_3,R;\Lambda_2,-\zeta_c\mp\zeta_d,-\mathcal{R}_2;\Lambda_1,\zeta_1,R)+(-1)^{\Lambda_3+1}\sum{}'a_{\mu_1\mu_2\mu_3}R^{\mu_1+\mu_3-\Lambda_3-1}(-1)^{\mu_1}$$
$$\times E_{2\Lambda_1-\mu_1+1}(\zeta_1R)\mathcal{R}_2{}^{2\Lambda_2}(d/d\zeta_c)^{\mu_2}[(\zeta_c+\zeta_d)^{2\Lambda_2}\log(\zeta_c+\zeta_d)-(\zeta_c-\zeta_d)^{2\Lambda_2}\log(\zeta_c-\zeta_d)]/(2\Lambda_2)!\},\quad(53)$$

and evaluate the D^l with Eq. (48).

3. *Formulas for* $\tilde{D}$

If R is large, $(\mathcal{R}_1/R)\ll1$, $\zeta_2\not\approx0$,

$$\tilde{D}(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)\sim(-1)^{\Lambda_2}\mathcal{R}_2{}^{2\Lambda_2}\sum_{\nu_2=0}^{\infty}\binom{2\Lambda_2+\nu_2}{\nu_2}R^{-2\Lambda_2-\nu_2}$$
$$\times(R+d/d\zeta_2)^{\nu_2}(\cdots\mathcal{K}_{\Lambda_3}(\zeta_2R)\cdots)\tilde{E}_{2\Lambda_2+1}[(\zeta_1+\zeta_2)\mathcal{R}_1].\quad(54)$$

If R and $\mathcal{R}_1$ are large, use

$$\tilde{D}(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)\sim D(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)$$
$$+D^l(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)+(-1)^{\Lambda_2}\mathcal{R}_2{}^{2\Lambda_2}\sum_{\nu_2}\binom{2\Lambda_2+\nu_2}{\nu_2}\left(R+\frac{d}{d\zeta_2}\right)^{\nu_2}(\cdots\mathcal{K}_{\Lambda_3}(\zeta_2R)\cdots)[(\zeta_1+\zeta_2)\mathcal{R}_1]^{2\Lambda_1}$$
$$\times[\log|\mathcal{R}_1|-\psi(2\Lambda_1+1)]/(2\Lambda_1)!,\quad(55)$$

and treat the D and $\tilde{D}$ by the appropriate methods [Eqs. (48)–(53)]. Note that except for the $\tilde{D}$'s arising from the A_2's [see below] in $I^{(3)}$, case 2a, the last term in Eq. (55) does not survive the differentiations from the $\{\cdots\mathcal{K}_\lambda\cdots\}$ operators, and need not be considered.

4. *Formulas for* A

If only $\mathcal{R}_2$ is large, but R and $\mathcal{R}_1$ are small, use the "exact" convergent expansions,

$$A(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)=2(-1)^{\Lambda_3+1}\zeta_2{}^{\Lambda_1+\Lambda_2-\Lambda_3-1}\mathcal{R}_1{}^{2\Lambda_1+1}\mathcal{R}_2{}^{2\Lambda_2}$$
$$\times\sum_{s=0}^{\infty}\frac{(\zeta_2\mathcal{R}_1)^s\hat{\alpha}_{2s}(\zeta_1\mathcal{R}_1)}{(2\Lambda_1+2s+1)!!(2s)!!}\sum_{\mu_2=0}^{\Lambda_2}\frac{(-1)^{\mu_2}}{(2\Lambda_2-2\mu_2)!!(2\mu_2)!!}R^{\Lambda_3}\left(\frac{R^{-1}d}{dR}\right)^{\Lambda_3}R^{-1}\alpha_{\Lambda_1+\Lambda_2-\Lambda_3+2s-2\mu_2-2}(\zeta_2R).\quad(56)$$

If R is large, use

$$A(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)=\tilde{D}(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)-\tilde{D}(\Lambda_3,R;\Lambda_1,-\zeta_1,-\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2),\quad(57)$$

and treat the $\tilde{D}$'s by either Eqs. (54) or (55).

5. *Formulas for* B

If only $\mathcal{R}_2$ is large, but R and $\mathcal{R}_1$ are small, use the convergent infinite expansion:

$$B(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)=\delta_{\Lambda_3,\Lambda_1-\Lambda_2}(-1)^{\Lambda_1}(\Lambda_2{}^{\Lambda_1}\Lambda_3)R^{\Lambda_3}\mathcal{R}_2{}^{2\Lambda_2}\zeta_2{}^{-1}E_{2\Lambda_1+1}[(\zeta_1+\zeta_2)\mathcal{R}_1]$$
$$+\delta_{\Lambda_3,\Lambda_2-\Lambda_1}(-1)^{\Lambda_2}(\Lambda_1{}^{\Lambda_2}\Lambda_3)R^{\Lambda_3}\mathcal{R}_1{}^{2\Lambda_1-2\Lambda_2}\mathcal{R}_2{}^{2\Lambda_2}\{\zeta_1{}^{-1}E_{2\Lambda_2+1}[(\zeta_1+\zeta_2)\mathcal{R}_1]-\mathcal{R}_1\alpha_0(\zeta_1\mathcal{R}_1)R_{2\Lambda_2+1}(\zeta_2\mathcal{R}_1)\}$$
$$+\mathcal{R}_1{}^{\Lambda_1-\Lambda_2+1}\mathcal{R}_2{}^{2\Lambda_2}(-1)^{\Lambda_1}\sum_{\mu_1=0}^{\Lambda_1}\sum_{\mu_2=0}^{\Lambda_2}\begin{bmatrix}\Lambda_1\\\mu_1\end{bmatrix}\begin{bmatrix}\Lambda_2\\\mu_2\end{bmatrix}(-1)^{\mu_2}\sum_{t=0}^{\infty}\binom{\Lambda_2+\mu_2+t}{t}(\zeta_2\mathcal{R}_1)^{-\mu_1-\mu_2-t-2}E_{\Lambda_1+\Lambda_2+\mu_1+\mu_2+t+2}[(\zeta_1+\zeta_2)\mathcal{R}_1]$$
$$\times\left(\sum_{\substack{s\geq0\\(\Lambda_3+2s-\mu_1-\mu_2-2\geq t)}}\frac{(\zeta_2R)^{\Lambda_3+2s}(\Lambda_3+2s-\mu_1-\mu_2-2)!}{(2\Lambda_3+2s+1)!!(2s)!!(\Lambda_3+2s-\mu_1-\mu_2-2-t)!}\right),\quad(58)$$

where the

$$\begin{bmatrix}\Lambda\\ \\ \mu\end{bmatrix}$$

symbol is defined in (2.35) of V.

If $\mathcal{R}_1$ is large, use

$$B(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2) = \tfrac{1}{2}(-1)^{\Lambda_3+1}D(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2) - \tfrac{1}{2}D(\Lambda_3, -R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2), \quad (59)$$

and treat the D's by Eqs. (49)–(53).

C. Use of the Asymptotic Scheme

Note that of the equations above, only Eqs. (48), (49), (54), and (56) give the basic asymptotic expansions, while the other formulas either manipulate functions to the form such that these expansions are valid, or else provide convergent expansions.

The use of this scheme to obtain asymptotic expansions for the $I^{(i)}$ may involve several steps, as is illustrated by the following examples. Consider $I^{(3)}$, Case 2a [Eq. (35)]. The steps required to reduce the two A and the two B functions, as well as the final asymptotic expressions depend on which internuclear distances are large. Since for Case 2a $\mathcal{R}_1 \geq R+\mathcal{R}_2$ and $R \geq \mathcal{R}_2$, there are three possibilities: (1) $\mathcal{R}_1$ large, R and $\mathcal{R}_2$ small; (2) $\mathcal{R}_1$ and R large, $\mathcal{R}_2$ small; and (3) $\mathcal{R}_1$, R, and $\mathcal{R}_2$ large. The flow charts [Figs. 4–6] describe the decomposition of the special functions in $I^{(3)}$, Case 2a [Eq. (35)], according to the recipe in Eqs. (48)–(59). We have suppressed the Λ and ζ arguments of the special functions in Figs. 4–6 for brevity. We have also used the abbreviations ***orig.*** for an origin term of the type generated by Eqs. (50)–(53), and d for the last term in Eq. (55).

The origin terms in Eqs. (29)–(46) as well as the expansions for the special functions [Eqs. (48)–(59)] often involve logarithms or E_n-exponential integrals with negative arguments. Since the imaginary parts of such functions mutually cancel in Eqs. (29)–(46), only the real parts need be retained; and the functions can always be interpreted with

$$\log x \rightarrow \log|x|, \quad (60)$$

and

$$E_n(x) \rightarrow \tilde{E}_n(x) - (-x)^{n-1}[\log|x| - \psi(n)]/(n-1)! \quad (n>0). \quad (61)$$

Indeed, many of the $\log|x|$ terms resulting from Eqs. (60) and (61) also cancel in the context of the formulas for $I^{(i)}$, but it is simpler, in general, to retain all such terms than to analyze systematically every formula for cancellations.

D. Derivations

We now describe the derivation of Eqs. (48)–(59). Asymptotic expansions (48), (49), and (54) are derived in an identical way, and we need discuss only the D function. First, integrate Eq. (21) by parts Λ_2 times:

$$\begin{aligned} D(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2) &= (-1)^{\Lambda_2}(2\pi i)^{-1}\int_{\infty}^{(\zeta_2+)} dx[(\zeta_2-x)\mathcal{R}_2]^{2\Lambda_2} \\ &\times \log(\zeta_2-x)/(2\Lambda_2)!\exp[-x(R+\mathcal{R}_1)] \\ &\times\{\exp[x(R+\mathcal{R}_1)](x^{-1}d/dx)^{\Lambda_2}x^{\Lambda_1+\Lambda_2-1} \\ &\times \mathcal{K}_{\Lambda_3}(xR)(x^{-1}d/dx)^{\Lambda_1}x^{-1}E_{2\Lambda_1+1}[(\zeta_1+x)\mathcal{R}_1]\}. \end{aligned} \quad (62)$$

Note the presence of

$$1 = \exp[-x(R+\mathcal{R}_1)]\exp[x(R+\mathcal{R}_1)]. \quad (63)$$

Since[17]

$$E_n(y) \sim \exp(-y)\sum_{\nu=0}^{\infty}\frac{(n+\nu-1)!}{(n-1)!}(-1)^{\nu}y^{-\nu-1}, \quad (y\rightarrow\infty) \quad (64)$$

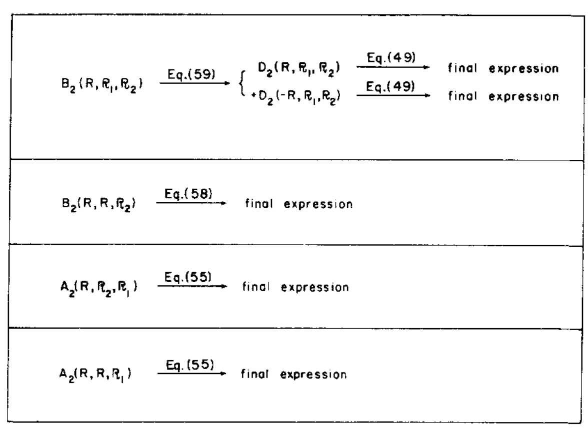

FIG. 4. Decomposition of special functions in Eq. (35) when $\mathcal{R}_1$ is large, $\mathcal{R}_2$ and R are small.

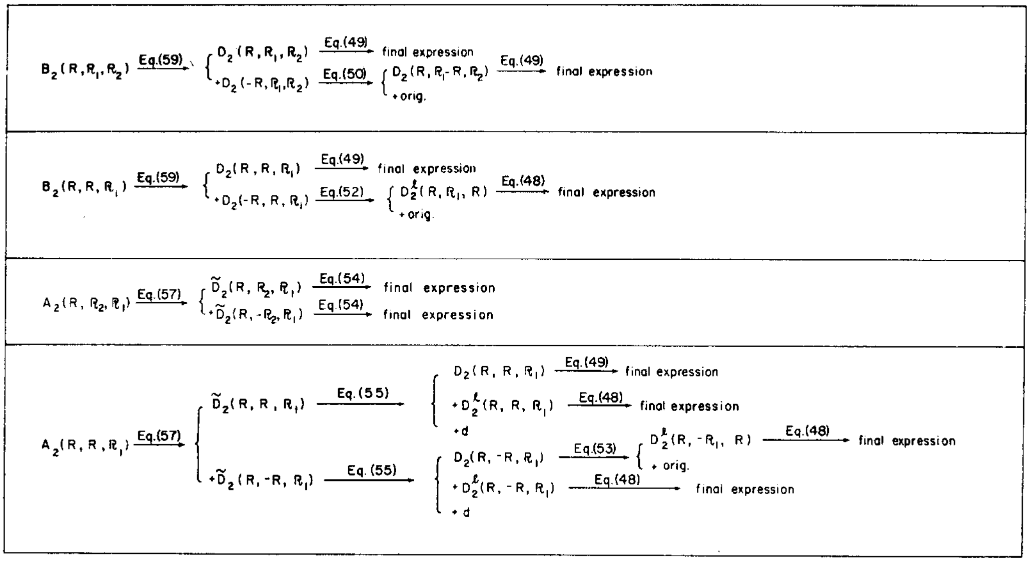

FIG. 5. Decomposition of special functions in Eq. (35) when $\mathcal{R}_1$ and R are large while $\mathcal{R}_2$ is small [$(\mathcal{R}_1-R)$ is small].

and

$$\mathcal{K}_n(y)=\exp(-y)\sum_{\mu=\nu}^{n}\begin{bmatrix}n\\ \mu\end{bmatrix}y^{-\mu-1}, \tag{65}$$

the factor in braces in Eq. (62) behaves like x^{-4} as $(\mathcal{R}_1+R)\rightarrow\infty$. An asymptotic expansion for large $(R+\mathcal{R}_1)$ can therefore be obtained by Laplace's method,[18] which here means expanding the quantity in braces as a Taylor series in $(x-\zeta_2)$, and then integrating term by term. When the identity

$$\exp(-a\zeta)(d/d\zeta)^n\exp(a\zeta)=(a+d/d\zeta)^n \tag{66}$$

is substituted, we obtain Eq. (49).

Although in this derivation, we have assumed that $\mathcal{R}_1$ and R are both large and that ζ_1 and ζ_2 are positive, Eq. (49) remains valid under much less restrictive conditions. Only one of R and $\mathcal{R}_1$ need be large for Eq. (49) to be valid, and provided that $R+\mathcal{R}_1$ is large either distance may be negative. Furthermore, Eq. (49) holds for ζ_2 negative and also for $(\zeta_1+\zeta_2)$ negative provided that $[(\zeta_1+\zeta_2)\mathcal{R}_1]$ is positive. If $[(\zeta_1+\zeta_2)\mathcal{R}_1]$ is negative, then the expansion can still be used, provided the substitution of Eq. (61) is made. The proof of this last statement depends on the context in which such D functions appear.

It is possible to derive several different asymptotic expansions for D^l, D, and $\tilde{D}$, but the expressions in

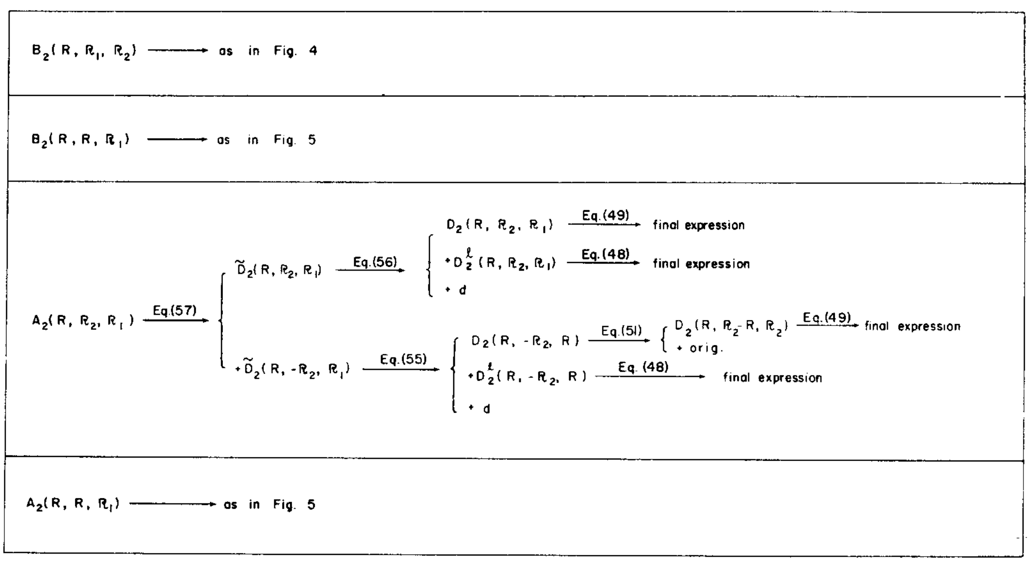

FIG. 6. Decomposition of special functions in Eq. (35) when $\mathcal{R}_1$, $\mathcal{R}_2$, and R are all large [$(R-\mathcal{R}_2)$ small].

Eqs. (48), (49), and (54) have the advantage of relative compactness. In addition, the similarity of the $(\cdots\mathcal{K}_{\Lambda_3}(\zeta R)\cdots)$ operators to the $\{\cdots\mathcal{K}_\lambda(\zeta R)\cdots\}$ operators provides a satisfying basis for comparison of the four-center asymptotic formulas with the exact three-center expressions.[19–21] For computational purposes, however, other expansions may be more useful, and we present an alternative set of formulas (which are also better adapted for singularity cancellations) in the Appendix.

We now examine those formulas of Eqs. (48)–(59) which are used to transform special functions, so that Eqs. (48), (49), and (54) are applicable. Equations (55), (57), and (59) are only restatements of the definitions for those special functions. Equations (50)–(53) can all be derived in a similar manner. As a prototype, we derive Eq. (50).

In the definition

$$\begin{aligned}D(\Lambda_3, -R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2) &= (2\pi i)^{-1}\int_\infty^{(\zeta_2+)} dx\,\mathcal{K}_{\Lambda_3}(-xR)\\ &\times\{x^{\Lambda_1}(x^{-1}d/dx)^{\Lambda_1}x^{-1}E_{2\Lambda_1+1}[(\zeta_1+x)\mathcal{R}_1]\}\\ &\times\{x^{\Lambda_2}(x^{-1}d/dx)^{\Lambda_2}x^{-1}\mathcal{R}_2^{2\Lambda_2}(\zeta_2-x)^{2\Lambda_2}\\ &\times\log(\zeta_2-x)/(2\Lambda_2)!\},\end{aligned} \tag{67}$$

we make the substitution

$$\begin{aligned}(\zeta-x)^{2\Lambda_2}\log(\zeta_2-x)/(2\Lambda_2)! &= -(\mathcal{R}_1-R)^{-2\Lambda_2}E_{2\Lambda_2+1}[(\zeta_2-x)(\mathcal{R}_1-R)]\\ &+(\mathcal{R}_1-R)^{-2\Lambda_2}\tilde{E}_{2\Lambda_2+1}[(\zeta_2-x)(\mathcal{R}_1-R)]\\ &+(\zeta_2-x)^{2\Lambda_2}[\psi(2\Lambda_2+1)-\log(\mathcal{R}_1-R)]/(2\Lambda_2)!.\end{aligned} \tag{68}$$

The integral over the last two terms in Eq. (68) vanishes since they are analytic within the contour. The integration path for the first term can be deformed to run from $(-\infty+i\epsilon, 0^+, -\infty-i\epsilon)$, since the integrand vanishes at infinity in both half-planes. When the substitution $x\to -x$ is made, this integral can be decomposed into a D function and an origin term, as in Eq. (50).

Finally, the convergent infinite expansions [Eqs. (56) and (58)] for the A and B functions are similar to formulas derived in Paper V. The formula for A [Eq. (56)] is essentially one-half of Eq. (5.4) of V for A_2, while the formula for B [Eq. (58)] is identical to Eq. (5.20) of V, where the expression for the $\aleph$ function [Eq. (5.9) of V] has been substituted and the order of summations has been interchanged.

VI. MULTIPOLE MOMENTLIKE EXPANSIONS

We now seek conditions under which the asymptotic behavior of the four-center integral is especially simple. This is the case when the origin terms dominate I^{rad} to the extent that the special functions can be neglected, and the result is Eqs. (4)–(7). The simplest example of such a situation is Case 1, when $R\gg\mathcal{R}_1+\mathcal{R}_2$. Using the expansions of the previous section to estimate the asymptotic behavior of the special functions, we conclude that although the origin terms in Eqs. (29)–(32) are $O(R^{-\Lambda_3-1})$, the special functions are

$$O\{R^{-2\Lambda_2-2}\exp[-(\zeta_c+\zeta_d)R]\}$$

and

$$O\{R^{-2\Lambda_1-2}\exp[-(\zeta_a+\zeta_b)R]\}.$$

Therefore, substituting only the origin terms into Eq. (15) we obtain

$$\begin{aligned}I_{cd;ab}{}^{\text{rad}}\sim&(-1)^{\Lambda_1}\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)\mathcal{R}_1{}^{2\Lambda_1}\mathcal{R}_2{}^{2\Lambda_2}R^{-\Lambda_3-1}\\ &\times(2(-1)^{\lambda_1}\{\cdots\mathcal{I}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\mathcal{R}_1\alpha_0[(\zeta_a+\zeta_b)\mathcal{R}_1]\\ &+\{\cdots\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\cdots\}\mathcal{R}_1\\ &\times\{\hat{\alpha}_0[(\zeta_a+\zeta_b)\mathcal{R}_1]-\hat{\alpha}_0[(\zeta_a-\zeta_b)\mathcal{R}_1]\})\\ &\times(2(-1)^{\lambda_2}\{\cdots\mathcal{I}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\mathcal{R}_2\alpha_0[(\zeta_c+\zeta_d)\mathcal{R}_2]\\ &+\{\cdots\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\cdots\}\\ &\times\mathcal{R}_2\{\hat{\alpha}_0[(\zeta_c+\zeta_d)\mathcal{R}_2]-\hat{\alpha}_0[(\zeta_c-\zeta_d)\mathcal{R}_2]\})\\ &\qquad(R\gg\mathcal{R}_1+\mathcal{R}_2).\end{aligned} \tag{69}$$

I^{rad} can now be identified as the product of the "radial parts" of two simple one-electron integrals. The moment-type integral Ω [Eq. (8)] can be written[11]:

$$\begin{aligned}\Omega_{ab}{}^{\Lambda\rho;M}(\mathcal{R})=&\sum_{l=|\Lambda-l_a|}^{\Lambda+l_a}\left(\frac{2l+1}{4\pi}\right)^{1/2}c^l(l_am_a;\Lambda\mu)\\ &\times\sum_{\lambda=|l-l_b|}^{l+l_b}\left(\frac{2\lambda+1}{4\pi}\right)^{1/2}c^\lambda(l_bm_b;l,m_a-\mu)\\ &\times Y_\lambda{}^{m_b-m_a+\mu}(\theta_{\mathcal{R}},\phi_{\mathcal{R}})J_{ab}{}^{\Lambda M,l\lambda}(\mathcal{R}),\end{aligned} \tag{70}$$

where

$$\begin{aligned}J_{ab}{}^{\Lambda M,l\lambda}=&2\pi(-1)^l\mathcal{R}^{n_a+M-l+1}\\ &\times(-d/d\zeta_b)^{n_b-l_b}[\zeta_b{}^{-1}(d/d\zeta_b)]^{l_b}\zeta_b{}^{l_a+l_b+1}\\ &\times\{2(-1)^\lambda\mathcal{I}_\lambda(\zeta_b\mathcal{R})[\zeta_b{}^{-1}(d/d\zeta_b)]^l\zeta_b{}^{-1}\\ &\times\alpha_{n_a+M-l}[(\zeta_a+\zeta_b)\mathcal{R}]\\ &+\mathcal{K}_\lambda(\zeta_b\mathcal{R})[\zeta_b{}^{-1}(d/d\zeta_b)]^l\zeta_b{}^{-1}\\ &\times(\hat{\alpha}_{n_a+M-l}[(\zeta_a+\zeta_b)\mathcal{R}]-\hat{\alpha}_{n_a+M-l}[(\zeta_a-\zeta_b)\mathcal{R}])\}.\end{aligned} \tag{71}$$

Equation (69) can therefore be written

$$\begin{aligned}I_{cd;ab}{}^{\text{rad}}\sim&(-1)^{l_a}\delta_{\Lambda_3,\Lambda_1+\Lambda_2}(\Lambda_1{}^{\Lambda_3}\Lambda_2)(2\pi)^{-1}R^{-\Lambda_3-1}\\ &\times J_{ab}{}^{\Lambda_1\Lambda_1,l_1\lambda_1}(\mathcal{R}_1)J_{cd}{}^{\Lambda_2\Lambda_2,l_2\lambda_2}(\mathcal{R}_2)\qquad(R\gg\mathcal{R}_1+\mathcal{R}_2).\end{aligned} \tag{72}$$

If we insert Eq. (72) into Eq. (14), rearrange summations, and use Eq. (70), we obtain precisely Eq. (4).

The Ω integrals in this expansion are multipole moments of the charge distributions, and Eq. (4) conforms to the expected result that when the interelectronic overlap becomes negligible (i.e., $R\to\infty$), the interaction between the two charge distributions can be represented by a multipole moment expansion.

When Eqs. (29)–(46) are systematically examined for dominance of origin terms with different choices of large internuclear distances, and when use is made of Eqs. (70) and (71), the three additional multipole momentlike formulas [Eqs. (5)–(7)] are obtained, along with the conditions on the ζ's and R's listed in Table I.

The conditions for validity given in Table I can be restated in terms of the distances $d_{a,(ab)}$ and $d_{c,(cd)}$ from expansion centers a and c to the "centers of charge" for electrons 1 and 2, respectively. (The precise definition of "center of charge" is not crucial.) Thus, Eq. (4) is applicable when

$$R \gg d_{a,(ab)}+d_{c,(cd)}, \text{ [condition for Eq. (4)].} \quad (73)$$

Applicability conditions for Eqs. (5)–(7) (which, apparently, have not previously appeared in the literature) can be summarized in a similar manner:

$$d_{a,(ab)} \gg R+d_{c,(cd)} \quad \text{[condition for Eq. (5)],} \quad (74)$$

$$d_{c,(cd)} \gg R+d_{a,(ab)} \quad \text{[condition for Eq. (6)],} \quad (75)$$

and

$$d_{a,(ab)}+d_{c,(cd)} \gg R \gg |d_{a,(ab)}-d_{c,(cd)}| \quad \text{[condition for Eq. (7)].} \quad (76)$$

Note that in every case that Eqs. (5) or (6) are valid, the four-center integral can be recast in a form such that Eq. (4) is valid by redefining **R** and relabeling centers a, b, c, and d. However, this does not detract from the possible usefulness of Eqs. (5) and (6) since in a given situation it is not clear which expansions will converge faster.

VII. SUMMARY

Asymptotic expansions are derived for the four-center integral with large internuclear distances. The simplest, and therefore probably the most useful results, are the multipole-moment-related formulas, Eqs. (4)–(7), and the generalization of the overlap-times-nuclear-attraction-integral formula, Eq. (13). Conditions for the applicability of Eqs. (4)–(7) are given in Table I. The complete asymptotic formulas are given via Eqs. (14), (15), (29)–(46), and (48)–(59). Some difficulties when certain sums of orbital exponents vanish are discussed.

ACKNOWLEDGMENT

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

APPENDIX: CANCELLATION OF SINGULARITIES

Here we discuss some methods for obtaining asymptotic expansions for I^{rad} when individual origin terms or special functions possess singularities. Since a detailed description of the cancellation of all singularities in every case would be lengthy, we will give only a brief outline of the main techniques.

We treat each singularity by one of these three procedures:

(i) using properties of the exact expansions for A and B,

(ii) directly cancelling singularities between asymptotic expansions,

and

(iii) determining asymptotic expansions for singularity-free combinations of terms.

Procedure (i) is applicable whenever the convergent expansions for A [Eq. (56)] and B [Eq. (58)] can be used in the equations for I^{rad}. Although $A(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2)$ has a singularity if $\zeta_2=0$, a singular A appearing in Eqs. (29)–(46) for I^{rad} can always be combined with an accompanying singular origin term to form a new, singularity-free, function $\hat{A}$. $\hat{A}$ appears in Paper V in the form $\hat{A}_4$ [Eq. (2.41) of V], and an expansion for $\hat{A}$ can be derived along the lines of Eq. (5.5) of V.

$B(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2)$ has singularities at $\zeta_2=0$ and at $\zeta_1+\zeta_2=0$. In the convergent expansion [Eq. (58)], the $\zeta_2=0$ singularities appear in terms preceded by Kronecker deltas, while $\zeta_1+\zeta_2=0$ singularities appear both in delta terms and in the infinite expansion. All singularities in delta terms can be algebraically cancelled with similar singularities from different B's or origin terms. Furthermore, when B functions appear in the combination

$$B(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2) - (\mathcal{R}_2/\mathcal{R}_2')^{2\Lambda_2} B(\Lambda_3, R; \Lambda_2, \zeta_2, \mathcal{R}_2'; \Lambda_1, \zeta_1, \mathcal{R}_1), \quad (A1)$$

or

$$B(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1; \Lambda_2, \zeta_2, \mathcal{R}_2) - (\mathcal{R}_1/\mathcal{R}_1')^{2\Lambda_1} \times B(\Lambda_3, R; \Lambda_1, \zeta_1, \mathcal{R}_1'; \Lambda_2, \zeta_2, \mathcal{R}_2), \quad (A2)$$

and both B's are evaluated by Eq. (58), the $\log(\zeta_1+\zeta_2)$ singularities in the infinite expansion cancel and the E_n functions which appear can be replaced by

$$E_n[(\zeta_1+\zeta_2)\mathcal{R}] \rightarrow \tilde{E}_n[(\zeta_1+\zeta_2)\mathcal{R}] - [(\zeta_1+\zeta_2)\mathcal{R}]^{n-1}[\log\mathcal{R} - \psi(n)]/(n-1)!. \quad (A3)$$

The proof of this last statement relies on a detailed examination of the terms in the expansion, and is not reproduced here.

Note that Eq. (58) is also an *asymptotic* expansion when $\mathcal{R}_1 \gg R$. This convergent expansion for B can therefore be used, rather than Eqs. (59) and (49), in such cases. Thus, the applicability of the procedure outlined above is extended to the cancellation of singularities in certain asymptotic expansions.

In a similar way, procedure (ii) involves the cancellation of singularities between two asymptotic expansions, each of which is valid for nonsingular values of the ζ's. Clearly, the derivation of these two asymptotic expansions must not rely on an assumption which is invalid when singularities arise. Since the derivation of Eq. (49) for D is based on expansion (64) for $E_n[(\zeta_1+\zeta_2)\mathcal{R}]$, and since this expansion is not valid when $\zeta_1+\zeta_2\approx 0$, the logarithmic singularity in Eq. (49) cannot legitmately be cancelled against a similar singularity in another D. We must therefore derive a new expansion for D which does not break down when $\zeta_1+\zeta_2\approx 0$.

In Eq. (21) for D, we substitute[22]

$$x^{\Lambda_1}(x^{-1}d/dx)^{\Lambda_1}x^{-1}E_{2\Lambda_1+1}[(\zeta_1+x)\mathcal{R}_1]=(-1)^{\Lambda_1}\sum_{\mu_1=0}^{\Lambda_1}\begin{bmatrix}\Lambda_1\\ \\ \mu_1\end{bmatrix}\mathcal{R}_1{}^{\Lambda_1-\mu_1}x^{-\mu_1-1}E_{\Lambda_1+\mu_1+1}[(\zeta_1+x)\mathcal{R}_1], \tag{A4}$$

and

$$(2\pi i)^{-1}\int_{\infty}^{(\zeta_2+)}dx\cdots x^{\Lambda_2}\left(x^{-1}\frac{d}{dx}\right)^{\Lambda_2}x^{-1}(\zeta_2-x)^{2\Lambda_2}\frac{\log(\zeta_2-x)}{(2\Lambda_2)!}=\int_{\zeta_2}^{\infty}dx\cdots x^{-\Lambda_2-1}\frac{(x^2-\zeta_2{}^2)^{\Lambda_2}}{(2\Lambda_2)!!}. \tag{A5}$$

If $(R+\mathcal{R}_1)$ is large, the step

$$\exp(xR)x^{-\Lambda_2-\mu_1-2}(x+\zeta_2)^{\Lambda_2}\mathcal{K}_{\Lambda_3}(xR)=2^{\Lambda_2}\sum_{\nu_2=0}^{\infty}(\nu_2!)^{-1}(x-\zeta_2)^{\nu_2}\left(\frac{d}{d\zeta_2}\right)^{\nu_2}\exp(\zeta_2R)\zeta_2{}^{-\mu_1-2}\mathcal{K}_{\Lambda_3}(\zeta_2R) \tag{A6}$$

is justified.[18] We can now use[23]

$$\int_0^{\infty}dxx^mE_n[(\zeta+x)\mathcal{R}_1]\exp(-xR)=m!R^{-m-1}\Bigg[\sum_{p=0}^{n-1}\binom{p+m}{p}\left(-\frac{\mathcal{R}_1}{R}\right)^pE_{n-p}(\zeta\mathcal{R}_1)$$
$$-\left(-\frac{\mathcal{R}_1}{R}\right)^{n-1}\exp(\zeta R)\sum_{p=0}^{m}\binom{p+n-1}{p}\left(\frac{R}{R+\mathcal{R}_1}\right)^{m-p}E_{m-p+1}[\zeta(R+\mathcal{R}_1)]\Bigg], \tag{A7}$$

to obtain

$$D(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)\sim(-1)^{\Lambda_1}\frac{\mathcal{R}_2{}^{2\Lambda_2}}{\Lambda_2!}\exp(-\zeta_2R)\sum_{\mu_1=0}^{\Lambda_1}\begin{bmatrix}\Lambda_1\\ \\ \mu_1\end{bmatrix}\mathcal{R}_1{}^{\Lambda_1-\mu_1}$$
$$\times\sum_{\mu_3=0}^{\Lambda_3}\begin{bmatrix}\Lambda_3\\ \\ \mu_3\end{bmatrix}R^{-\mu_3-1}\sum_{\nu_2=0}^{\infty}\binom{\mu_1+\mu_3+2+\nu_2}{\nu_2}(\Lambda_2+\nu_2)!(-1)^{\nu_2}\zeta_2{}^{-\mu_1-\mu_3-\nu_2-3}R^{-\Lambda_2-\nu_2-1}$$
$$\times\Bigg[\sum_{p=0}^{\Lambda_1+\mu_1}\binom{p+\Lambda_2+\nu_2}{p}\left(-\frac{\mathcal{R}_1}{R}\right)^pE_{\Lambda_1+\mu_1+1-p}[(\zeta_1+\zeta_2)\mathcal{R}_1]-\left(-\frac{\mathcal{R}_1}{R}\right)^{\Lambda_1+\mu_1}\exp[(\zeta_1+\zeta_2)R]$$
$$\times\sum_{p=0}^{\Lambda_2+\nu_2}\binom{p+\Lambda_1+\mu_1}{p}\left(\frac{R}{R+\mathcal{R}_1}\right)^{\Lambda_2+\nu_2-p}E_{\Lambda_2+\nu_2+1-p}[(\zeta_1+\zeta_2)(R+\mathcal{R}_1)]\Bigg]\quad[(R+\mathcal{R}_1)\text{ large},\ \zeta_2\not\approx 0]. \tag{A8}$$

Similarly, we can derive the following expansions for D^l and $\tilde{D}$:

$$D^l(\Lambda_3,R;\Lambda_1,\zeta_1,\mathcal{R}_1;\Lambda_2,\zeta_2,\mathcal{R}_2)$$

$\sim$Eq. (A8) with the quantity in large brackets replaced by

$$\Bigg[\sum_{p=0}^{\Lambda_1+\mu_1}\binom{p+\Lambda_2+\nu_2}{p}\left(-\frac{\mathcal{R}_1}{R}\right)^p[-(\zeta_1+\zeta_2)\mathcal{R}_1]^{\Lambda_1+\mu_2-p}\frac{\log(\zeta_1+\zeta_2)+\psi(\Lambda_1+\mu_1+1)-\psi(\Lambda_1+\mu_1+1-p)}{(\Lambda_1+\mu_1-p)!}$$
$$+\left(-\frac{\mathcal{R}_1}{R}\right)^{\Lambda_1+\mu_1}\exp[(\zeta_1+\zeta_2)R]\sum_{p=0}^{\Lambda_2+\nu_2}E_{\Lambda_2+\nu_2+1-p}[(\zeta_1+\zeta_2)R]\binom{p+\Lambda_1+\mu_1}{p}\Bigg]\quad[R\text{ large},\ \zeta_2\not\approx 0], \tag{A9}$$

$\tilde{D}\sim$Eq. (A8), with the quantity in large brackets replaced by

$$\Bigg\{\sum_{p=0}^{\Lambda_1+\mu_1}\binom{p+\Lambda_2+\nu_2}{p}\left(-\frac{\mathcal{R}_1}{R}\right)^p\tilde{E}_{\Lambda_1+\mu_1+1-p}[(\zeta_1+\zeta_2)\mathcal{R}_1]-\left(-\frac{\mathcal{R}_1}{R}\right)^{\Lambda_1+\mu_1}\exp[(\zeta_1+\zeta_2)R]$$
$$\times\sum_{p=0}^{\Lambda_2+\nu_2}\binom{p+\Lambda_1+\mu_1}{p}\Bigg[\left(\frac{R}{R+\mathcal{R}_1}\right)^{\Lambda_2+\nu_2+p}\tilde{E}_{\Lambda_2+\nu_2+1-p}[(\zeta_1+\zeta_2)(R+\mathcal{R}_1)]-\tilde{E}_{\Lambda_2+\nu_2+1-p}[(\zeta_1+\zeta_2)R]+[(\zeta_1+\zeta_2)R]^{\Lambda_2+\nu_2-p}$$
$$\times\frac{\log[R/(R+\mathcal{R}_1)]}{(\Lambda_2+\nu_2-p)!}\Bigg]\Bigg\}\quad[R\text{ large},\ (R+\mathcal{R}_1)\text{ large},\ \zeta_2\not\approx 0]. \tag{A10}$$

A typical situation in which Eqs. (A8)–(A10) can be used to eliminate singularities is $I^{(1)}$ Case 1 [Eq. (29)], $(R, \mathcal{R}_1)$ both large. Equation (51) must be applied to $D(\Lambda_3, R; \Lambda_1, -\zeta_a-\zeta_b, -\mathcal{R}_1; \Lambda_2, \zeta_c+\zeta_d, \mathcal{R}_2)$ to generate $D(\Lambda_3, R; \Lambda_2, -\zeta_c-\zeta_d, \mathcal{R}_1-R; \Lambda_1, \zeta_a+\zeta_b, \mathcal{R}_1)$. If Eq. (A8) is substituted for this function as well as for $D(\Lambda_3, R; \Lambda_2, -\zeta_c-\zeta_d, \mathcal{R}_2; \Lambda_1, \zeta_a+\zeta_b, \mathcal{R}_1)$ in Eq. (29), the logarithmic singularities at $\zeta_a+\zeta_b-\zeta_c-\zeta_d=0$ will cancel, so that the substitution in Eq. (A3) can be applied.

Procedure (iii) involves obtaining a single (contour) integral representation for the sum of two terms with cancelling singularities, and deriving an asymptotic expansion for this singularity-free function. What were singularities in the individual terms, correspond to the coincidence of two singularities in the integrand of the new function. Derivation of an asymptotic formula when these two singularities are close together requires expansion of one singularity about the other, followed by the application of Laplace's method. Thus, in $I^{(1)}$, Case 1 [Eq. (29)], when R is large, the two D functions which have logarithmic singularities at $\zeta_a+\zeta_b-\zeta_c-\zeta_d$ are combined to form

$$(2\pi i)^{-1}\int_{\infty}^{[\min(\zeta_1,\zeta_2)]+} dx\,\mathcal{K}_{\Lambda_3}(xR)\{x^{\Lambda_1}(x^{-1}d/dx)^{\Lambda_1}x^{-1}E_{2\Lambda_1+1}[(\zeta_a+\zeta_b-x)\mathcal{R}_1]\}$$
$$\times\{x^{\Lambda_2}(x^{-1}d/dx)^{\Lambda_2}x^{-1}E_{2\Lambda_2+1}[(\zeta_c+\zeta_d-x)\mathcal{R}_2]\}, \quad \text{(A11)}$$

where the integration contour encloses both branch points in the integrand. Both $E_{2\Lambda+1}$ functions are decomposed into "E" and "log" parts by Eq. (2.17) of V. Only the "log–log" term requires special treatment. The $\log(\zeta_1-x)$ is expanded in a Taylor series as powers of $[(\zeta_1-\zeta_2)/(\zeta_2-x)]$. The remainder of the integrand is expanded in *positive* powers of (ζ_2-x). The result, obtained after term-by-term integration, is rather lengthy and will not be reproduced here.

Procedure (iii) can also be used to eliminate a singularity between an origin term and a special function. For example, both the A_4 and the origin terms in $I^{(4)}$ Case 2a [Eq. (38)] are singular when $\zeta_a=\zeta_b$. This equation, however, can be recast in terms of an $\hat{A}_4$ as in Eq. (4.24) of V. The $\hat{A}_4$ is an analytic function, and is defined [Eq. (2.41) of V] as an integral whose contour encloses both a pole at the origin and a $\log(\zeta_a-\zeta_b-x)$ branch cut. If $R\gg\mathcal{R}_2$ and $\zeta_a\approx\zeta_b$, the $\log(\zeta_a-\zeta_b-x)$ can be expanded about the origin in positive powers of $[(\zeta_a-\zeta_b)/x]$, while the rest of the integrand is expanded in *positive* powers of x. Again, we do not reproduce here the result which is obtained after term-by-term integration.

* Supported in part by the U.S. Army Research Office-Durham, Durham, North Carolina.
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