Eq. (60), with R set equal to zero,

$$
\begin{aligned}
I_{c;a,b}{}^{tl\lambda\Lambda}(R=0)=&\,\delta_{t,0}\delta_{\Lambda,l_c}(-d/d\zeta_c)^{n_c-l_c}(-d/d\zeta_b)^{n_b-l_b}(\zeta_b{}^{-1}d/d\zeta_b)^{l_b}\zeta_b{}^{l_b+1}\mathcal{I}_\lambda(\zeta_b\mathcal{R})\zeta_b{}^{l}(\zeta_b{}^{-1}d/d\zeta_b)^{l}\zeta_b{}^{-1}\\
&\times(-8(-1)^{l+l_b+l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1+2l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1}\mathcal{R}^{n_a-l_c-l}E_{l_c+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}_{-}\\
&\quad+8(-1)^{l+l_b+l_c}\zeta_c{}^{-2l_c-2}(2l_c)!\mathcal{R}^{n_a-l_c-l}E_{l_c+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}])\\
&\quad+\delta_{t,0}\delta_{\Lambda,l_c}(-d/d\zeta_c)^{n_c-l_c}(-d/d\zeta_b)^{n_b-l_b}(\zeta_b{}^{-1}d/d\zeta_b)^{l_b}\zeta_b{}^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b{}^{l}(\zeta_b{}^{-1}d/d\zeta_b)^{l}\zeta_b{}^{-1}\\
&\times(-4(-1)^{l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1+2l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1}\mathcal{R}^{n_a-l_c-l}\\
&\times\{\tilde{E}_{l_c+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]+\tilde{E}_{l_c+l+1-n_a}[(\zeta_a-\zeta_b+\zeta_c)\mathcal{R}]\}\\
&\quad+4(-1)^{l_c}\zeta_c{}^{-2l_c-2}(2l_c)!\mathcal{R}^{n_a-l_c-l}\{\tilde{E}_{l_c+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}]-\tilde{E}_{l_c+l+1-n_a}[(\zeta_a-\zeta_b)\mathcal{R}]\}).
\end{aligned}
\tag{72}
$$

Equation (72) can be slightly simplified by use of

$$(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1+2l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1}=\zeta_c{}^{-1}(d/d\zeta_c)^{2l_c}\zeta_c{}^{-1}, \tag{73}$$

$$=(2l_c+1)^{-1}[\zeta_c{}^{-1}(d/d\zeta_c)^{2l_c+1}-(d/d\zeta_c)^{2l_c+1}\zeta_c{}^{-1}]. \tag{74}$$

Thus, Eq. (72), along with Eqs. (69), (68), (67), (31), and (1), specifies the two-center hybrid integral.

SUMMARY

An analytical formula has been derived for (1–2)-type three-center integrals of $r_{12}{}^{-1}$ with integer-n Slater-type orbitals. The main steps in the derivation were (i) use of the Fourier-transform convolution theorem to reduce the six-dimensional integral to a three-dimensional one, (ii) evaluation of the Fourier transform of a two-center charge distribution as a multipole expansion, (iii) integration over angles of products of spherical harmonics only, and (iv) extensive manipulation of integration contours and use of the residue theorem. In the end, the integral (1) is expressed as an infinite sum [(Eq. (31)] of products of spherical harmonics of the internuclear position-vector angles times a function of the internuclear distances $\mathcal{R}$ and R. The radial function has a two-part form [Eqs. (59) and (60)], depending on the sign of $\mathcal{R}-R$, and it involves functions no more complicated than spherical Bessel functions (i.e., exponentials) and the exponential-type integral. The formulas are valid for general values of the quantum numbers and orbital exponents defining the Slater-type orbitals. The two-center hybrid integral is obtained as a special case [Eq. (72)] by setting $R=0$ in the three-center formula.

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Analytical Evaluation of Multicenter Integrals of $r_{12}{}^{-1}$ with Slater-Type Atomic Orbitals. II. Three-Center Nuclear-Attraction Integrals*

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The general three-center one-electron nuclear-attraction integral with integer-n Slater-type orbitals is evaluated analytically by letting the orbital exponent of a $1s$ orbital in the analytical formula for two-electron three-center electron-repulsion integrals tend to infinity. The result is an infinite sum in which the internuclear angles appear in spherical harmonics, and the internuclear distances appear in modified spherical Bessel functions and exponential-type integrals.

INTRODUCTION

In this second paper of a series[1] on multicenter integrals, a compact analytical formula is derived for three-center nuclear-attraction integrals with integer-n Slater-type atomic orbitals (STO's). Current methods for calculating three-center nuclear-attraction integrals usually involve numerical integration (although closed-form analytical expressions are known[2] for special cases)

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[2] J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. **4,** 121 (1936).

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and are usually based on the use of elliptical coordinates,[2–5] the Gaussian transform,[6–9] or expansion[10–21] of all STO's about a single center. The analytical formulas obtained here are a by-product of the analytical evaluation of two-electron (1–2)-type three-center electron repulsion integrals given in Paper I. The result, an infinite sum in which internuclear angular coordinates appear in spherical harmonics and internuclear distances in exponential-type integrals and in modified spherical Bessel functions, is given by Eqs. (2), (6), (12), and (13). The expressions are valid for general values of the quantum numbers and orbital exponents of the STO's.

FORMULATION AS LIMIT OF (1–2)-TYPE TWO-ELECTRON THREE-CENTER INTEGRALS

By a simple device, the turning of a 1s STO into a (three-dimensional) Dirac delta function,

$$\lim_{\zeta\to\infty} \zeta^3(8\pi)^{-1}\exp(-\zeta r)=\delta(\mathbf{r}), \tag{1}$$

the general three-center nuclear attraction integral,

$$I_{n_al_am_a\zeta_a;n_bl_bm_b\zeta_b}(\mathbf{R},\boldsymbol{\mathcal{R}})$$

$$\equiv (N_aN_b)^{-1}\int dVr^{-1}\Psi^*_{n_al_am_a\zeta_a}(\mathbf{r}-\mathbf{R})\Psi_{n_bl_bm_b\zeta_b}(\mathbf{r}-\mathbf{R}-\boldsymbol{\mathcal{R}}), \tag{2}$$

$$=I_{ab}, \tag{3}$$

can be expressed as a limiting case of the two-electron three-center integral defined by Eq. (1) of I,

$$I_{ab}=\lim_{\zeta_c\to\infty}\tfrac{1}{4}\pi^{-1/2}\zeta_c^3I_{100\zeta_c;n_al_am_a\zeta_a,n_bl_bm_b\zeta_b}(\mathbf{R},\boldsymbol{\mathcal{R}}). \tag{4}$$

In Eq. (2) the Ψ's are STO's, and the N's are normalization constants [see Eq. (3) of I].

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Before making use of Eq. (4), first consider evaluating I_{ab} by the same method used for the electron-repulsion integral in I. By use of the Fourier transform convolution theorem, I_{ab} can be written

$$I_{ab}=(2\pi)^{-3}\int d^3\mathbf{k}(4\pi k^{-2})G_{n_al_am_a\zeta_a;n_bl_bm_b\zeta_b}(\mathbf{k},\boldsymbol{\mathcal{R}})\times\exp(i\mathbf{k}\cdot\mathbf{R}), \tag{5}$$

where the two-center Fourier transform G is defined by Eq. (7) of I. Expand G and $\exp(i\mathbf{k}\cdot\mathbf{R})$ in terms of spherical harmonics and radial functions [Eqs. (19) and (17) of I], and integrate over angles via Condon–Shortley coefficients [Eq. (14) of I] to obtain

$$I_{ab}=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{\lambda=|l-l_b|}^{l+l_b}\sum_{\Lambda=|l-l_a|}^{l+l_a}\tfrac{1}{4}\pi[(2\lambda+1)(2\Lambda+1)]^{1/2}\times c^\lambda(l_bm_b;lm)c^\Lambda(lm;l_am_a)Y_\lambda^{m_b-m}(\theta_{\mathcal{R}},\phi_{\mathcal{R}})\times Y_\Lambda^{m-m_a}(\theta_R,\phi_R)I_{ab}^{l\lambda\Lambda}, \tag{6}$$

where

$$I_{ab}^{l\lambda\Lambda}=8\pi^{-2}i^\Lambda\int_0^\infty dk j_\Lambda(kR)G_{l\lambda l_b\Lambda}^{n_a\zeta_an_b\zeta_b}(k,\mathcal{R}). \tag{7}$$

In Eq. (7), j_Λ denotes a spherical Bessel function [Eq. (18) of I], and $G_{l\lambda l_b\Lambda}^{n_a\zeta_an_b\zeta_b}(k,\mathcal{R})$ is given by Eq. (30) of I. The problem of evaluating I_{ab} is, by virtue of of Eq. (6), transformed into the problem of evaluating $I_{ab}^{l\lambda\Lambda}$.

If one compares Eq. (7) with the analogous quantity $I_{c;a,b}^{tl\lambda\Lambda}$, Eq. (32), of I, and notes [cf., Eq. (4)] that

$$\lim_{\zeta_c\to\infty}\zeta_c^3f_{10\zeta_c}(k)=8\pi, \tag{8}$$

where $f_{nl\zeta}(k)$ is given by Eq. (9) of I, then one sees that

$$I_{ab}^{l\lambda\Lambda}=\lim_{\zeta_c\to\infty}\zeta_c^3I_{c;a,b}^{\Lambda l\lambda\Lambda}. \tag{9}$$

Now $I_{c;a,b}^{\Lambda l\lambda\Lambda}$ is evaluated explicitly in Eqs. (59) and (60) of I, so it is necessary only to multiply those results by ζ_c^3 and take the limit.

PASSING TO THE LIMIT $\zeta_c\to\infty$

If Eq. (7) were to be evaluated by contour integration, the same manipulations used for the electron-respulsion integral in I would apply, except that there would be no singularities (and therefore no residues) in the integrand at $x=\pm\zeta_c$. No residues at $x=\pm\zeta_c$ means that in exploiting Eq. (9), only those terms in $I_{c;a,b}^{\Lambda l\lambda\Lambda}$ which arise from the residue at $x=0$ [i.e., the terms containing $\delta_{t,\Lambda\pm l_c}$ in Eqs. (59) and (60) of I] can give a nonzero limit. These terms are all proportional to $(-d/d\zeta_c)^{n_c-l_c}\zeta_c^{-2l_c-2}$, and

$$\zeta_c^3(-d/d\zeta_c)^{n_c-l_c}\zeta_c^{-2l_c-2}=2,\qquad (n_c=1,\ l_c=0), \tag{10}$$

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so that

$$\lim_{\zeta_c\to\infty} \zeta_c^3 I_{c;a,b}{}^{\Lambda l\lambda\Lambda} = \zeta_c^3 \times \{\delta_{t,\Lambda\pm l_c} \text{ terms in } I_{c;a,b}{}^{\Lambda l\lambda\Lambda}\}, \qquad (n_c=1,\ l_c=0). \tag{11}$$

The result then follows immediately from Eqs. (59) and (60) of I and Eq. (11), that

$$\begin{aligned} I_{ab}{}^{l\lambda\Lambda} = {} & \left(-\frac{d}{d\zeta_b}\right)^{n_b-l_b} \left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b} \zeta_b^{l_b+1} \mathcal{J}_\lambda(\zeta_b \mathcal{R}) \zeta_b^{l} \left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l} \zeta_b^{-1} \\ & \times 16(-1)^{\Lambda+l+l_b}(2\Lambda+1)^{-1} R^{-1-\Lambda} \{R^{n_a+\Lambda-l+1} E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)R] \\ & + \mathcal{R}^{n_a+\Lambda-l+1} \hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)\mathcal{R}] - R^{n_a+\Lambda-l+1}\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)R]\} \\ & + \left(-\frac{d}{d\zeta_b}\right)^{n_b-l_b} \left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b} \zeta_b^{l_b+1} \mathcal{K}_\lambda(\zeta_b \mathcal{R}) \zeta_b^{l} \left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l} \zeta_b^{-1} 8(-1)^{\Lambda}(2\Lambda+1)^{-1} \\ & \times R^{-1-\Lambda} \mathcal{R}^{n_a+\Lambda-l+1} \{\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)\mathcal{R}] - \hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a-\zeta_b)\mathcal{R}]\}, \qquad (\mathcal{R}<R), \end{aligned} \tag{12}$$

and

$$\begin{aligned} I_{ab}{}^{l\lambda\Lambda} = {} & \left(-\frac{d}{d\zeta_b}\right)^{n_b-l_b} \left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b} \zeta_b^{l_b+1} \mathcal{J}_\lambda(\zeta_b \mathcal{R}) \zeta_b^{l} \left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l} \zeta_b^{-1} \\ & \times 16(-1)^{\Lambda+l+l_b}(2\Lambda+1)^{-1} R^{\Lambda} \mathcal{R}^{n_a-\Lambda-l} E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}] \\ & + \left(-\frac{d}{d\zeta_b}\right)^{n_b-l_b} \left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b} \zeta_b^{l_b+1} \mathcal{K}_\lambda(\zeta_b \mathcal{R}) \zeta_b^{l} \left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l} \zeta_b^{-1} 8(-1)^{\Lambda}(2\Lambda+1)^{-1} R^{\Lambda} \\ & \times (\mathcal{R}^{n_a-\Lambda-l}\{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}] - \tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b)\mathcal{R}\} \\ & + R^{n_a-\Lambda-l}\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)R] + \tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b)R] \\ & + \hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)R] - \hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a-\zeta_b)R]\}), \qquad (\mathcal{R}>R). \end{aligned} \tag{13}$$

The functions $\mathcal{J}_\lambda$, $\mathcal{K}_\lambda$, E_n, $\tilde{E}_n$, α_n and $\hat{\alpha}_n$ are defined by Eqs. (15), (16), and (21)–(25) of I.

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Analytical Evaluation of Multicenter Integrals of r_{12}^{-1} with Slater-Type Atomic Orbitals. III. (2–2)-Type Three-Center Integrals*

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The three-center integral of r_{12}^{-1}, with each electron described by a two-center product of integer-n Slater-type orbitals, is evaluated analytically. The result, obtained via the Fourier-transform convolution theorem, is an infinite sum involving spherical harmonics for the internuclear angular coordinates and exponential integral and spherical Bessel-type functions for the internuclear distances. The two-center exchange integral is evaluated as a special case. All results given are for general values of the n, l, m, and ζ parameters of the Slater-type orbitals.

INTRODUCTION

In this third paper of a series[1] on multicenter integrals, analytical formulas are derived for the general (2–2)-type three-center two-electron integral of the Coulomb interaction r_{12}^{-1} with Slater-type atomic orbitals (STO's). The basic techniques used in evaluating the integral are the Fourier-transform convolution theorem, expansion of an STO on one center about another, evaluation of products of three spherical harmonics in terms of Condon–Shortley coefficients, contour integration, and the residue theorem. The reader is referred to paper I for a discussion of how these techniques relate to the multicenter integral problem and for appropriate references to the literature.

The most complicated functions which appear in the formulas are Condon–Shortley coefficients, $c^\lambda(l_1m_1; l_2m_2)$

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[1] The first two papers in this series, hereafter referred to as I and II, are H. J. Silverstone, J. Chem. Phys. **48**, 4098, 4106 (1968) (preceding papers).

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