On the Computation of (2-2) Three-Center Slater-Type Orbital Integrals of $1/r_{12}$ Using Fourier-Transform-Based Analytical Formulas

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ABSTRACT: We describe a computational scheme devised for using Fourier-transform-based analytic formulas for three-center integrals of r_{12}^{-1}, wherein each electron is described by a two-center product of Slater-type orbitals. The asymptotic behavior of the auxiliary functions, which are related to modified spherical Bessel functions and to exponential integrals, is investigated, and recursive computational schemes are derived that are shown to be numerically stable for high summation indices and large internuclear distances. Int J Quantum Chem 100: 146–154, 2004

Key words: Slater-type orbital integrals; exponential orbital integrals; multicenter integrals; three-center integrals

Introduction

There has been recent renewed interest in molecular integrals with exponential-type orbitals [1–7], including the use of techniques to accelerate convergence. Accordingly, we present an analysis of a class of Slater-type orbital (STO) molecular integrals, the (2-2) three-center electron–electron repulsion integrals that contain two bicentric electron distributions that share one center in common. The (2-2) three-center integral is defined in the notation of Ref. [8] as

$$I_{n_cl_cm_c\zeta_c,n_dl_dm_d\zeta_d;n_al_am_a\zeta_a,n_bl_bm_b\zeta_b}(\mathbf{R}_1, \mathbf{R}_2)$$

$$= (N_aN_bN_cN_d)^{-1} \int dV_1 dV_2 r_{12}^{-1} \times [\Psi^*_{n_cl_cm_c\zeta_c}(\mathbf{r}_2)\Psi_{n_dl_dm_d\zeta_d}$$

$$\times (\mathbf{r}_2 - \mathbf{R}_2)]^* \times [\Psi^*_{n_al_am_a\zeta_a}(\mathbf{r}_1)\Psi_{n_bl_bm_b\zeta_b}(\mathbf{r}_1 - \mathbf{R}_1)] \quad (1)$$

$$= I_{cd;ab}(\mathbf{R}_1, \mathbf{R}_2) \quad (2)$$

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where the Slater orbital is defined by

$$\Psi_{nlm\zeta}(r) = Nr^{n-1}\exp(-\zeta r)Y_l^m(\theta, \phi). \quad (3)$$

The N is a normalization constant factored out of Eq. (1); $Y_l^m(\theta, \phi)$ is a spherical harmonic, and $n \geq l + 1$. $\mathbf{R}_1$ and $\mathbf{R}_2$ are internuclear-distance vectors characterizing the two bicentric electron distributions. The STOs a and c share a common center—the origin.

This work builds upon the methodology developed in Refs. [8–26], which we summarize here:

1. The six-dimensional integral is converted into a three-dimensional integral in Fourier transform space by using the convolution theorem.
2. To evaluate the Fourier transform of the two-center STO product that is required for Step (1), expand the orbital at the displaced center in an infinite series around the origin. The terms of this series involve spherical Bessel functions, spherical harmonics, and vector-coupling coefficients. Carry out the angular integration, and obtain a series of one-dimensional Fourier transforms. The final one-dimensional Fourier integration can be carried out by means of the calculus of residues and can be expressed in terms of exponential-type integrals.
3. The convolution integral is resolved first by carrying out the angular integrations, which are easy, because each Fourier-transformed two-center STO product is a sum over spherical harmonics, and second by evaluating the radial integration using contour integration techniques and the residue theorem.

In this way, the molecular integrals are expressed as infinite series over angular momentum numbers {Eq. (7) of Ref. [8]}:

$$I_{cd;ab}(R_1, R_2) = \sum_{l_1=0}^{\infty} \sum_{\lambda_1=|l_1-l_b|}^{l_1+l_b} \sum_{l_2=0}^{l_1+l_a+l_c} \sum_{\lambda_2=|l_2-l_d|}^{l_2+l_d} \sum_{m_1=-l_1}^{l_1} \sum_{\Lambda=\max\{|l_1-l_a|,|l_2-l_c|\}}^{\min\{l_1+l_a,l_2+l_c\}} \pi[(2\lambda_1+1)(2\lambda_2+1)]^{1/2} c^{\lambda_1}(l_b m_b; l_1 m_1)$$
$$\times\, c^{\lambda_2}(l_d m_d; l_2, m_1+m_c-m_a) c^{\Lambda}(l_1 m_1; l_a m_a) c^{\Lambda}(l_2, m_1+m_c-m_a; l_c m_c)$$
$$\times\, Y_{\lambda_1}^{m_b-m_1}(\theta_{R_1}, \phi_{R_1}) Y_{\lambda_2}^{m_d-m_c+m_a-m_1^*}(\theta_{R_2}, \phi_{R_2}) I_{cd;ab}^{l_1\lambda_1;l_2\lambda_2;\Lambda}(R_1, R_2). \quad (4)$$

Each term of the series contains vector coupling coefficients, spherical harmonics of the two internuclear distance vectors, and a "radial" term. The series is a fivefold sum over angular-momentum indices l_1, l_2, λ_1, λ_2, and Λ that go to infinity "together": the difference between any two summation indices is bounded by $l_a + l_b + l_c + l_d$, because the vector-coupling coefficients otherwise vanish. The radial term consists of modified spherical Bessel functions and exponential-type integrals with internuclear distances times STO exponents (ζ's) as arguments, and it decomposes into four terms {Eqs. (17)–(20) of Ref. [8]}:

$$I_{cd;ab}^{l_1\lambda_1;l_2\lambda_2}(\mathbf{R}_1, \mathbf{R}_2) = I^{(1)} + I^{(2)} + I^{(3)} + I^{(4)}. \quad (5)$$

Our main task is to compute the radial term.

The Radial Term

The simplest of the four parts of the radial term is

$$I^{(2)} = 2(-1)^{l_1+l_b}[(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}d/d\zeta_b)^{l_b}$$
$$\times\, \zeta_b^{l_b+1}\mathrm{I}_{\lambda_1}(\zeta_b R_1)\zeta_b^{l_1}(\zeta_b^{-1}d/d\zeta_b)^{l_1}\zeta_b^{-1}R_1^{n_a-\Lambda-l_1}]$$
$$\times[(-d/d\zeta_d)^{n_d-l_d}(\zeta_d^{-1}d/d\zeta_d)^{l_d}\zeta_d^{l_d+1}\mathrm{K}_{\lambda_2}(\zeta_d R_2)$$
$$\times\zeta_d^{l_2}(\zeta_d^{-1}d/d\zeta_d)^{l_2}\zeta_d^{-1}R_2^{n_c-\Lambda-l_2}]$$
$$\times\, R_2^{2\Lambda+1}E_{\Lambda+l_1+1-n_a}[(\zeta_a+\zeta_b)R_1]\{\hat{\alpha}_{n_c+\Lambda-l_2}[(\zeta_c+\zeta_d)R_2]$$
$$-\, \hat{\alpha}_{n_c+\Lambda-l_2}[(\zeta_c-\zeta_d)R_2]\},(R_1 \geq R_2) \quad (6)$$

where the modified spherical Bessel functions are given by

$$\mathrm{I}_l(x) = x^l(x^{-1}d/dx)^l x^{-1}\sinh(x) \quad (7)$$

$$\mathrm{K}_l(x) = (-x)^l(x^{-1}d/dx)^l x^{-1}\exp(-x). \quad (8)$$

The (relative) transparency of the formula (6) is due to the use of derivative operators with respect to STO exponents, which commute with all of the Fourier-transform operations. As was the case for the (1-2) three-center integral [25], before the formulas can be programmed for a computer, the derivatives appearing in them must be dealt with explicitly. We give the results here and sketch the use of stable recursion formulas for the calculation of the $I^{(k)}$. The reader is referred to [24] for a more complete account of the details.

The derivative operators in Eq. (6) for $I^{(2)}$ and in the companion formulas for the other $I^{(k)}$ appear in a common, four-element structure: first, $(-d/d\zeta_e)^{n_e-l_e}(\zeta_e^{-1}d/d\zeta_e)^{l_e}\zeta_e^{l_e}+1$, where e specifies a STO; next, a modified spherical Bessel function with argument $\zeta_e R_i$, where i is 1 or 2; then, $\zeta_e^{l_i}(\zeta_e^{-1}d/d\zeta_e)^{l_i}\zeta_e^{-1}$; then at the far right, a function of exponential-integral class. Our strategy [20] is to express $(-d/d\zeta_e)^{n_e-l_e}$ in powers of $(\zeta_e^{-1}d/d\zeta_e)$, then absorb the latter either into the spherical Bessel functions or into auxiliary functions based on the exponential-integral functions. In such a manner we obtain for the $I^{(k)}$:

$$I^{(1)} = 4R_1^{n_a+n_b+n_c+2}R_2^{n_d-1}(-1)^{n_b-n_d}\sum_{u_b=0}^{n_b}\sum_{u_d=0}^{n_d}(-1)^{u_b+u_d}(R_1/R_2)^{u_d}\sum_{j_b}\begin{bmatrix} n_b-l_b-j_b \\ j_b\end{bmatrix}\sum_{s_b}\binom{n_b-j_b}{s_b t_b u_b}$$
$$\times\frac{(l_b+\lambda_1+l_1+1)!!}{(l_b+\lambda_1+l_1+1-2s_b)!!}\rho_{1b}^{1-j_b-s_b}\mathrm{I}_{\lambda_1+t_b}(\rho_{1b})\sum_{j_d}\begin{bmatrix} n_d-l_d-j_d \\ j_d\end{bmatrix}\sum_{s_d}\binom{n_d-j_d}{s_d t_d u_d}$$
$$\times\frac{(l_d+\lambda_2+l_2+1)!!}{(l_d+\lambda_2+l_2+1-2s_d)!!}\rho_{2d}^{1-j_d-s_d}\mathrm{I}_{\lambda_2+t_d}(\rho_{2d})\,[A^{l_1+u_b}_{n_a+\Lambda-l_1}(\rho_{1b},\rho_{1a})\,E^{l_2+u_d}_{\Lambda+l_2+1-n_c}(\rho_{1d},\rho_{1c}) - E^{l_1+u_b,l_2+u_d,n_a+\Lambda-l_1}_{\Lambda+l_2+1-n_c}(\rho_{1b},\rho_{1d},\rho_{1a},\rho_{1c})$$
$$+(R_2/R_1)^{n_c+u_d+\Lambda+2}A^{l_2+u_d}_{n_c+\Lambda-l_2}(\rho_{2d},\rho_{2c})\,E^{l_1+u_b}_{\Lambda+l_1+1-n_a}(\rho_{1b},\rho_{1a}) - E^{l_2+u_d,l_1+u_b,n_c+\Lambda-l_2}_{\Lambda+l_1+1-n_a}(\rho_{1d},\rho_{1b},\rho_{1c},\rho_{1a})] \quad (9)$$

$$I^{(2)} = 4R_1^{n_a+n_b-\Lambda}R_2^{n_c+n_d+\Lambda+1}(-1)^{n_b+n_d-l_d}\sum_{u_b=0}^{n_b}\sum_{u_d=0}^{n_d}(-1)^{u_b}\sum_{j_b}\begin{bmatrix} n_b-l_b-j_b \\ j_b\end{bmatrix}\sum_{s_b}\binom{n_b-j_b}{s_b t_b u_b}\frac{(l_b+\lambda_1+l_1+1)!!}{(l_b+\lambda_1+l_1+1-2s_b)!!}$$
$$\times\rho_{1b}^{1-j_b-s_b}\mathrm{I}_{\lambda_1+t_b}(\rho_{1b})\sum_{j_d}\begin{bmatrix} n_d-l_d-j_d \\ j_d\end{bmatrix}\sum_{s_d}\binom{n_d-j_d}{s_d t_d u_d}\frac{(l_d+\lambda_2+l_2+1)!!}{(l_d+\lambda_2+l_2+1-2s_d)!!}\rho_{2d}^{1-j_d-s_d}\mathrm{K}_{\lambda_2+t_d}(\rho_{2d})$$
$$\times E^{l_1+u_b}_{\Lambda+l_1+1-n_a}(\rho_{1b},\rho_{1a})\hat{A}^{l_2+u_d}_{n_c+\Lambda-l_2}(\rho_{2d},\rho_{2c}) \quad (10)$$

$$I^{(3)} = 4R_1^{n_a+n_b+n_c+2}R_2^{n_d-1}(-1)^{n_b+n_d-l_b}\sum_{u_b=0}^{n_b}\sum_{u_d=0}^{n_d}(-1)^{u_d}(R_1/R_2)^{u_d}(\cdots\mathrm{K}_{\lambda_1+t_b}(\rho_{1b}))(\cdots\mathrm{I}_{\lambda_2+t_d}(\rho_{2d}))$$
$$\times(E^{l_2+u_d}_{\Lambda+l_2+1-n_c}(\rho_{1d},\rho_{1c})\hat{A}^{l_1+u_b}_{n_a+\Lambda-l_1}(\rho_{1b},\rho_{1a}) - (R_2/R_1)^{n_a+n_c+u_b+u_d+3}A^{l_2+u_d}_{n_c+\Lambda-l_2}(\rho_{2d},\rho_{2c})\times[\tilde{E}^{l_1+u_b}_{\Lambda+l_1+1-n_a}(\rho_{2b},\rho_{2a})$$
$$-(R_1/R_2)^{n_a+u_b-\Lambda+1}\tilde{E}^{l_1+u_b}_{\Lambda+l_1+1-n_a}(\rho_{1b},\rho_{1a})] - [\tilde{E}^{l_2+u_d,l_1+u_b,n_c+\Lambda-l_2}_{\Lambda+l_1+1-n_a}(\rho_{1d},\rho_{1b},\rho_{1c},\rho_{1a})$$
$$-(R_2/R_1)^{n_a+n_c+u_b+u_d+3}\tilde{E}^{l_2+u_d,l_1+u_b,n_c+\Lambda-l_2}_{\Lambda+l_1+1-n_a}(\rho_{2d},\rho_{2b},\rho_{2c},\rho_{2a})] - [\varepsilon^{l_1+u_b,l_2+u_d,n_a+\Lambda-l_1}_{\Lambda+l_2+1-n_c}(\rho_{1b},\rho_{1d},\rho_{1a},\rho_{1c})$$
$$-(R_2/R_1)^{n_a+n_c+u_b+u_d+3}\varepsilon^{l_1+u_b,l_2+u_d,n_a+\Lambda-l_1}_{\Lambda+l_2+1-n_c}(\rho_{2b},\rho_{2d},\rho_{2a},\rho_{2c})]) \quad (11)$$

$$I^{(4)} = 4R_1^{n_b-1}R_2^{n_a+n_b+n_c+n_d+2}(-1)^{n_b+n_d-l_b-l_d}\sum_{u_b=0}^{n_b}\sum_{u_d=0}^{n_d}$$
$$\times(R_1/R_2)^{u_b}(\cdots\mathrm{K}_{\lambda_1+t_b}(\rho_{1b}))(\cdots\mathrm{K}_{\lambda_2+t_d}(\rho_{2d}))$$
$$\times(-\hat{A}^{l_2+u_d}_{n_c+\Lambda-l_2}(\rho_{2d},\rho_{2c})\times[\tilde{E}^{l_1+u_b}_{\Lambda+l_1+1-n_a}(\rho_{2b},\rho_{2a})$$
$$-(R_1/R_2)^{n_a+u_b-\Lambda+1}\tilde{E}^{l_1+u_b}_{\Lambda+l_1+1-n_a}(\rho_{1b},\rho_{1a})]$$
$$+\tilde{\varepsilon}^{l_1+u_b,l_2+u_d,n_a+\Lambda-l_1}_{\Lambda+l_2+1-n_c}(\rho_{2b},\rho_{2d},\rho_{2a},\rho_{2c})$$
$$+\tilde{\varepsilon}^{l_2+u_d,l_1+u_b,n_c+\Lambda-l_2}_{\Lambda+l_1+1-n_a}(\rho_{2d},\rho_{2b},\rho_{2c},\rho_{2a})). \quad (12)$$

We have introduced the notation:

$$\rho_{1a}=R_1\zeta_a \quad \rho_{2a}=R_2\zeta_a$$
$$\rho_{1b}=R_1\zeta_b \quad \rho_{2b}=R_2\zeta_b$$
$$\rho_{2c}=R_2\zeta_c \quad \rho_{1c}=R_1\zeta_c$$
$$\rho_{2d}=R_2\zeta_d \quad \rho_{1d}=R_1\zeta_d \quad (13)$$

$$n!! = n(n-2)(n-4)\cdots 5\cdot 3\cdot 1 \quad \text{or} \quad 6\cdot 4\cdot 2 \quad (14)$$

$$\begin{bmatrix}\Lambda \\ \mu\end{bmatrix} = \frac{(\Lambda+\mu)!}{(\Lambda-\mu)!(2\mu)!!} \quad (15)$$

and a number of auxiliary functions, the analysis of which follows in the next section.

Auxiliary Functions

In Eqs. (9)–(12) for the $I^{(k)}$, there are three sets of functions: the modified spherical Bessel functions I_l and K_l, whose properties are well known; and auxiliary functions that we shall call 1-l (one upper index) and 3-l (three upper indices) functions, which are based on exponential-type integrals. The 1-l functions have an integral representation involving the spherical Bessel functions, and the 3-l functions have an integral representation involving both the 1-l and spherical Bessel functions. These integral representations are useful for deriving recursion relations and asymptotics.

1-*L* FUNCTIONS

The four 1-l functions are the descendants of α, $\hat{\alpha}$, E, and $\tilde{E}$, which were used in Refs. [8, 12–25] (see also Ref. [26]):

$$E_n(x) = \int_1^\infty t^{-n} e^{-xt} dt \tag{16}$$

$$= \alpha_{-n}(x) \tag{17}$$

$$\tilde{E}_n(x) = E_n(x) + (-x)^{n-1}[\log(x) - \psi(n)] / (n-1)!, \quad (n-1 \geq 0) \tag{18}$$

$$= E_n(x) - x^{n-1}(-n)!, \quad (n \leq 0) \tag{19}$$

$$= \hat{\alpha}_{-n}(x) \tag{20}$$

$$\psi(n) = (d/dn)\ln\Gamma(n) \tag{21}$$

$$A_n^l(x, y) = (-x)^l (x^{-1} d/dx)^l x^{-1} \alpha_n(x+y) \tag{22}$$

$$= \int_1^\infty dt t^{n+l+1} \mathrm{K}_l(xt) \exp(-yt) \tag{23}$$

$$\hat{A}_n^l(x, y) = x^l (x^{-1} d/dx)^l x^{-1} [\hat{\alpha}_n(y \pm x)]^{(2)} / 2 \tag{24}$$

$$= \int_0^1 dt t^{n+l+1} \mathrm{I}_l(xt) \exp(-yt) \tag{25}$$

$$E_n^l(x, y) = (-x)^l (x^{-1} d/dx)^l x^{-1} E_n(x+y) \tag{26}$$

$$= A_{-n}^l(x, y) \tag{27}$$

$$\tilde{E}_n^l(x, y) = x^l (x^{-1} d/dx)^l x^{-1} [\tilde{E}_n(y \pm x)]^{(2)} / 2 \tag{28}$$

$$= (2\pi i)^{-1} \oint_1^{(0+)} dt \ln(e^{-i\pi} t) t^{-n+l+1} \mathrm{I}_l(xt) \exp(-yt) \tag{29}$$

where

$$[\hat{\alpha}_n(y \pm x)]^{(2)} = [\hat{\alpha}_n(y+x) - \hat{\alpha}_n(y-x)]. \tag{30}$$

3-*L* FUNCTIONS

The four 3-l functions are similarly defined.

$$E_n^{l_1 l_2 l_3}(x, y, z, w) = (-x)^{l_1} (x^{-1} d/dx)^{l_1} x^{-1} (-y)^{l_2} (y^{-1} d/dy)^{l_2} y^{-1} \times (-d/dz)^{l_3} (x+z)^{-1} E_n(x+y+z+w) \tag{31}$$

$$= \int_1^\infty dt t^{-n+l_1+l_2+l_3+3} A_{l_3}^{l_1}(xt, zt) \mathrm{K}_{l_2}(yt) \exp(-wt) \tag{32}$$

$$\tilde{E}_n^{l_1 l_2 l_3}(x, y, z, w) = (-x)^{l_1} (x^{-1} d/dx)^{l_1} x^{-1} y^{l_2} (y^{-1} d/dy)^{l_2} y^{-1} \times (-d/dz)^{l_3} (x+z)^{-1} \cdot 2^{-1} [\tilde{E}_n(x \pm y + z + w)]^{(2)} \tag{33}$$

$$= \int_0^1 dt t^{-n+l_1+l_2+l_3+3} A_{l_3}^{l_1}(xt, zt) \mathrm{I}_{l_2}(yt) \exp(-wt) \tag{34}$$

$$\varepsilon_n^{l_1 l_2 l_3}(x, y, z, w) = x^{l_1} (x^{-1} d/dx)^{l_1} x^{-1} (-y)^{l_2} (y^{-1} d/dy)^{l_2} y^{-1} \times (-d/dz)^{l_3} \{2^{-1} (z \pm x)^{-1} [\tilde{E}_n(\pm x + y + z + w) - \tilde{E}_n(y+w)]\}^{(2)} \tag{35}$$

$$= -\int_0^1 dt t^{-n+l_1+l_2+l_3+3} \hat{A}_{l_3}^{l_1}(xt, zt) K_{l_2}(yt) \exp(-wt) \quad (36)$$

$$\tilde{\varepsilon}_n^{l_1 l_2 l_3}(x, y, z, w) = x^{l_1}(x^{-1}d/dx)^{l_1} x^{-1} y^{l_2}(y^{-1}d/dy)^{l_2} y^{-1} \times (-d/dz)^{l_3} \cdot 4^{-1}\{(z \pm x)^{-1}[\tilde{E}_n(z \pm x \pm y + w) - \tilde{E}_n(w \pm y)]\}^{(4)} \quad (37)$$

$$= \int_0^1 dt t^{-n+l_1+l_2+l_3+3} \hat{A}_{l_3}^{l_1}(xt, zt) I_{l_2}(yt) \exp(-wt) \quad (38)$$

In Eq. (38), we use the notation,

$$\{(z \pm x)^{-1}[\tilde{E}_n(z \pm x \pm y + w) - \tilde{E}_n(w \pm y)]\}^{(4)} = (z + x)^{-1}\{[\tilde{E}_n(z + x \pm y + w)]^{(2)} - [\tilde{E}_n(w \pm y)]^{(2)}\} - (z - x)^{-1} \times \{[\tilde{E}_n(z - x \pm y + w)]^{(2)} - [\tilde{E}_n(w \pm y)]^{(2)}\}. \quad (39)$$

ASYMPTOTIC BEHAVIOR OF THE AUXILIARY FUNCTIONS

There are two asymptotic cases of interest: large indices (for the summation of the infinite series) and large R_i (the physical case of large internuclear distances). In both cases, the asymptotic forms for the 1-l and 3-l functions follow from the formulas for the modified spherical Bessel functions:

$$\left.\begin{aligned} I_l(x) &\sim x^l[(2l+1)!!]^{-1} \\ K_l(x) &\sim x^{-l-1}(2l-1)!! \end{aligned}\right\}, \quad \text{as} \quad l \to \infty, \quad (40)$$

$$\left.\begin{aligned} I_l(x) &\sim e^x/2x \\ K_l(x) &\sim e^{-x}/x \end{aligned}\right\}, \quad \text{as} \quad x \to \infty. \quad (41)$$

For instance,

$$A_n^l(x, y) \sim \frac{(2l-1)!!}{x^{l+1}} \alpha_n(y), \quad \text{as} \quad l \to \infty, \quad (42)$$

$$A_n^l(x, y) \sim \frac{e^{-x-y}}{x(x+y)}, \quad \text{as} \quad x \to \infty. \quad (43)$$

Asymptotic formulas for all the 1-l and 3-l auxiliary functions can similarly be found [24]. In short, A_n^l, E_n^l, and $E_n^{l_1 l_2 l_3}$ have K-like asymptotics; $\hat{A}_n^l$, $\tilde{E}_n^l$, and $\tilde{\varepsilon}_n^{l_1 l_2 l_3}$ are I-like; $\tilde{E}_n^{l_1 l_2 l_3}$ and $\varepsilon_n^{l_1 l_2 l_3}$ have opposite asymptotics for large indices l_1 and l_2. Because the integral terms $I^{(1)} \cdots I^{(4)}$ contain products of I-like and K-like functions, which have opposite asymptotic behavior, it is convenient to use a set of "reduced" functions in the numerical implementation, where the factors $x^l[(2l + 1)!!]^{-1}$ and $x^{-l-1}(2l - 1)!!$ have been extracted and explicitly canceled out.

Recursion Relations

There are a large number of recursion relations for the auxiliary functions. On the whole, they follow a few simple patterns. For each 1-l function, there is a pair of three-term recursions in the nl plane—one homogeneous, the other inhomogeneous. Each 3-l function has two analogous pairs of recursions, one pair in the nl_2 plane, and the other in the $l_1 l_3$ plane. Within each plane, new recursions can be derived as linear combinations of the basic pair.

To illustrate the use of recursion formulas, and especially the question of numerical stability, we take as an example the function A_n^l. The basic pair can be derived from the integral representation (23) by applying a recursion formula for the modified spherical Bessel functions, or by integration by parts:

$$A_n^l(x, y) = (2l - 1)x^{-1}A_n^{l-1}(x, y) + A_{n+2}^{l-2}(x, y) \quad (44)$$

$$A_n^l(x, y) = [xA_{n+2}^{l-1}(x, y) + yA_{n+1}^l(x, y) - e^{-y}K_l(x)]/(n + 1). \quad (45)$$

These recursions can be represented by diagrams show in Figures 1 and 2, in which we note the relative power of l by which the term in the recursion follows as $l \to \infty$.

One can see from the diagrams that recursive computation of low-l terms from high-l terms would necessarily involve numerical cancellation, but that upwards recursion should be "safe."

In the limit of large R_i (x and y), we have also annotated the diagrams with the relative powers of x and y that the term follows as $x \to \infty$ and $y \to \infty$. Because of numerical cancellation, it would be unsafe to calculate the middle term in Figure 1 or the

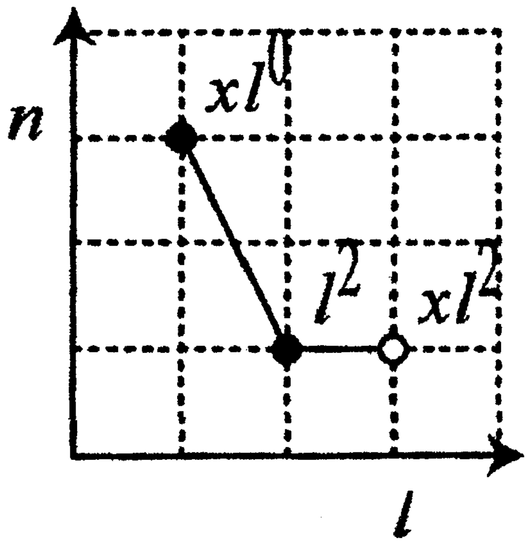

FIGURE 1. Diagram for the homogeneous $A_n^l(x, y)$ recursion formula (44) that shows relative l dependence for large l and relative x dependence for large x. The term marked by an open circle can be safely computed (with the least numerical cancellation).

bottom term in Figure 2 when x and y are large. In both Figures 1 and 2, the safe term is indicated by an open circle.

The following simple rules describe how to generate new recursions from the existing ones:

- diagrams can be translated relative to one another in the index plane
- a diagram does not change if the relative l-, x-, or y-dependency is increased uniformly for every term
- if two diagrams overlap, one and only one pair of overlapping points may be eliminated, provided that the same l-, x-, and y-dependencies are assigned to both points
- if the overlapping points are not eliminated, the resulting point acquires the higher l-, x-, and y-dependencies of the two points

By following these rules, we construct the (inhomogeneous) recursion

$$xA_n^{l+1}(x, y) = (2l - n)A_n^l(x, y) + yA_{n+1}^l(x, y) - e^{-y}K_l(x) \quad (46)$$

with diagram shown in Figure 3 and predict that only the term marked by an open circle may be safely computed.

The same principles apply to diagrams for the other auxiliary functions: the basic pairs of recursions always lead to the same shape diagrams within each class (1-l and 3-l), but with different

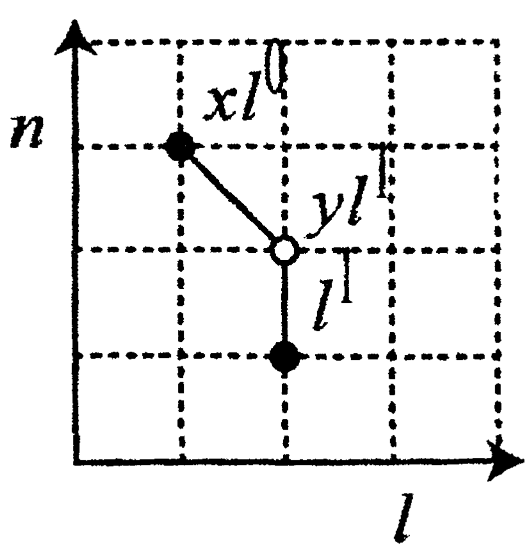

FIGURE 2. Diagram for the inhomogeneous $A_n^l(x, y)$ recursion formula (45) that shows relative l dependence for large l and relative x dependence for large x and y. The term marked by an open circle can be safely computed (with the least numerical cancellation).

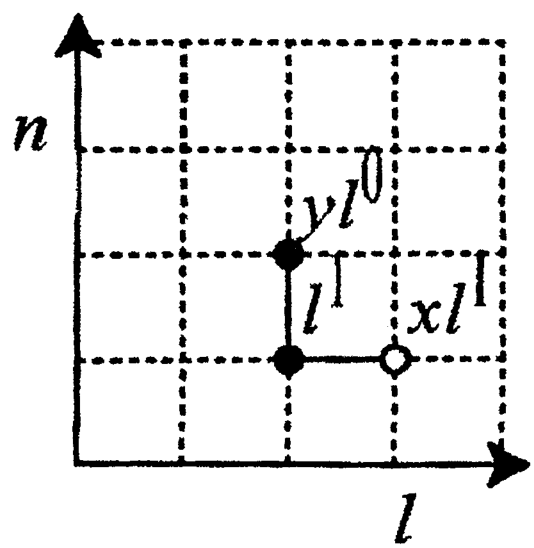

FIGURE 3. Diagram for $A_n^l(x, y)$ recursion formula (46) that shows relative x- and y-dependence for large x and relative l-dependence for large l. The term marked by an open circle may be safely computed (with the least numerical cancellation).

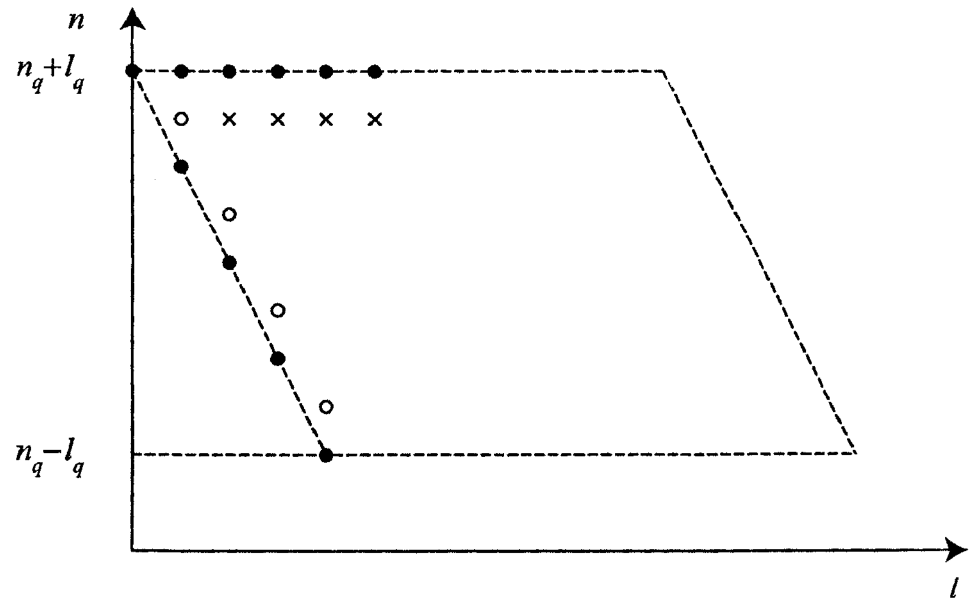

FIGURE 4. Domain of indices of the $A_n^l(x, y)$ functions.

relative asymptotics, because of the different asymptotics of the various auxiliary functions.

Computation of Auxiliary Functions

We illustrate the strategy of calculating auxiliary functions with $A_n^l(x, y)$. The ranges of the indices n and l are determined by the STO indices, how many terms are to be calculated in the series (4), and the fact that the vector-coupling coefficients vanish unless the three l quantum numbers have even sum and satisfy the triangular inequality. For the function $A_n^l(x, y)$, the domain in the nl plane is a parallelogram, as shown in Figure 4.

Before any recursion relation can be used, initial values must be calculated. We use the formula

$$A_n^l(x, y) = \sum_{m=0}^{l} \begin{bmatrix} l \\ m \end{bmatrix} x^{-m-1} \alpha_{n+l-m}(x + y) \quad (47)$$

to seed the top row and the leftmost edge, as indicated by solid dots $(\cdot)$ in Figure 4.

All the remaining positions are filled by recursion. First, the inhomogeneous recursion (45) is used to compute the slanting line adjacent to the left edge and marked by open circles, and in the direction indicated by the open circle in Figure 2, for which it is asymptotically stable for large l and $R_i(x$ and $y)$. Second, the second row of Figure 4, marked by $\times$'s, is completed using the recursion (46) with diagram Figure 3. Third, the rest of Figure 4 is filled in using recursion (44) in its asymptotically stable direction as indicated in Figure 1.

We remark that it is possible to construct seemingly stable recursions, such as to connect $A_n^l(x, y)$, $A_n^{l+1}(x, y)$, and $A_n^{l+2}(x, y)$, but which contain the factor $x^2 - y^2$ in the inhomogeneous term, and which are unstable for close values of the two arguments. For this reason we have avoided the use of such recursions.

Computational schemes for the other 1-l auxiliary functions follow along the lines similar to the above example, except that the nl domain of E-functions is somewhat different. The ranges for the 3-l auxiliary functions fill a four-dimensional direct-product of two two-dimensional ranges, one in the nl_2 plane, the other in $l_1 l_3$. The reader is referred to Chapter 3 of Ref. [24] for the details.

Cancellations in $I^{(3)}$ and in $I^{(4)}$ When the Internuclear Distances Are Equal: *G* Functions

There are terms in Eqs. (11) and (12) for $I^{(3)}$ and $I^{(4)}$ that contain differences of 1-l $\tilde{E}$ functions and powers of the ratio of radii, $r = R_1/R_2 \geq 1$, and similarly for 3-l $\tilde{E}$ functions. These differences vanish linearly as $r \to 1$. For small R_1 and R_2 there are no significant numerical problems, but for large R_1 and R_2 the two $\tilde{E}$ functions can be exponentially larger than their difference, with a significant loss of accuracy.

To illustrate the point, we abstract the simplest of the difference terms in $I^{(4)}$, which can be shown to have the integral representation,

$$\tilde{E}_n^l(x, y) - r^{-n+l+2}\tilde{E}_n^l(rx, ry) = -\int_1^r dt\, t^{-n+l+1} \mathrm{I}_l(xt)e^{-yt} \quad (48)$$

$$\sim -\mathrm{I}_l(x)e^{-y}(r-1), \quad \text{as} \quad r \to 1. \quad (49)$$

The first-order cancellation for sufficiently small r is obvious. Note that the integrand in Eq. (48) is strictly positive.

Now consider the value of the difference for large x and y:

$$\tilde{E}_n^l(x, y) - r^{-n+l+2}\tilde{E}_n^l(rx, ry) \sim -\frac{e^{x-y}}{2x}(r-1), \quad (r \to 1,\ x \text{ and } y \to \infty). \quad (50)$$

If $x > y$, the factor multiplying $(r - 1)$ is exponentially large; if $x < y$, it is exponentially small. On the other hand, the asymptotic behavior of $\tilde{E}_n^l(x, y)$ is quite different when $x < y$. Take, for instance,

$$\tilde{E}_2^1(x, y) \sim -\frac{1}{x} + \frac{y}{2x^2}\ln\frac{y+x}{y-x}, \quad y > x \to \infty, \quad (51)$$

$$\sim \frac{c}{R_1}, \quad (52)$$

where c is a constant (note that x/y is a ratio of orbital exponents). The exponentially small asymptotics of Eq. (50) is therefore the result of cancellation of the dominant nonexponential terms exemplified by Eq. (52).

Such a cancellation can be avoided computationally by introducing a new auxiliary function $\tilde{G}_n^l(x, y)$ to use instead of $\tilde{E}_n^l(x, y)$:

$$\tilde{G}_n^l(x, y) = -\int_1^\infty dt\, t^{-n+l+1}\mathrm{I}_l(xt)e^{-yt} \quad (53)$$

$$= \frac{(-1)^l E_n^l(x, y) + E_n^l(-x, y)}{2}. \quad (54)$$

We use $\tilde{G}_n^l(x, y)$ only when $x - y < 0$. $\tilde{G}_n^l(x, y)$ has the asymptotic formula,

$$\tilde{G}_n^l(x, y) \sim \frac{e^{x-y}}{2x(x-y)} \quad (55)$$

and recasts Eq. (50) as a difference of auxiliary functions which have the same asymptotic form as their difference itself:

$$\tilde{E}_n^l(x, y) - r^{-n+l+2}\tilde{E}_n^l(rx, ry) = \tilde{G}_n^l(x, y) - r^{-n+l+2}\tilde{G}_n^l(rx, ry) \quad (56)$$

$$\sim \frac{e^{x-y}}{2x(x-y)} - r^{-n+l}\frac{e^{r(x-y)}}{2x(x-y)} \quad (57)$$

$$\sim -\frac{e^{x-y}}{2x}(r-1)[1 + \mathrm{O}(r-1) + \mathrm{O}(1/(x-y))]. \quad (58)$$

Analogous considerations apply to the other "difference terms." Recursion formulas for the $\tilde{G}$ functions are identical to their $\tilde{E}$ counterparts, and the numerical stability patterns of the recursions are identical as well.

Vector-Coupling Coefficients

The same vector-coupling coefficients recur in all the STO integrals, but their number is large, and a standard array on the indices would be sparse. One strategy to avoid such a large array would be to calculate the coefficients efficiently as needed, and not to store and reuse them. We have opted for an alternative strategy, tabulation in a packed array: the coefficients were computed once by means of Racah's formula, then stored via a packing scheme that leaves no empty spaces in the storage array.

Summary

We have shown how to cast Fourier-transform-based analytic formulas for (2-2)-type STO three-center integrals of r_{12}^{-1} in a computationally convenient form. The explicit derivatives are replaced by summations over auxiliary functions, for which, in the light of the asymptotics of the auxiliary functions for large l indices and for large R_i, stable recursion schemes have been derived.

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