*ANALYTICAL EVALUATION OF THREE- AND FOUR-CENTER INTEGRALS OF r_{12}^{-1} WITH SLATER-TYPE ORBITALS**

By Harris J. Silverstone

DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY, BALTIMORE

Communicated by Paul H. Emmett, May 11, 1967

Three- and four-center integrals of r_{12}^{-1} with Slater-type orbitals (STO) have long been the "bottlenecks of molecular quantum mechanics." Evaluation of multicenter integrals is usually carried out, after some analytical manipulations, by numerical integrations,[1–4] except in the special case of linear triatomic molecules.[5] In this communication, a technique is sketched for the *analytical* evaluation of arbitrary three- and four-center integrals, and a particular three-center integral is evaluated as an example.

The method is beguilingly simple. The first key ingredient is the Fourier transform convolution theorem,[6–8] which automatically reduces the six-dimensional integration to a three-dimensional one. The second key ingredient is the expansion[2, 3, 9] of an STO on one center about another center, which reduces the Fourier transform of a two-center charge distribution to the sum of Fourier transforms of one-center distributions. The technique is successful because (1) the angular integration in the convolution integral is over spherical harmonics—therefore easy—and (2) the radial integration can be carried out by contour integration and the residue theorem.[10]

For an illustration, first consider the Fourier transform of the two-center product of two $1s$ orbitals,

$$G(\mathbf{k}) \equiv (N_bN_c)^{-1}\int dv \exp(i\mathbf{k}\cdot\mathbf{r})\ 1s_b(\mathbf{r})\ 1s_c(\mathbf{r} - \mathcal{R}), \tag{1}$$

$$= (4\pi)^{-1}\int dv \exp(i\mathbf{k}\cdot\mathbf{r} - \zeta_b r - \zeta_c|\mathbf{r} - \mathcal{R}|). \tag{2}$$

Evaluate (2) after expanding $\exp(-\zeta_c|\mathbf{r} - \mathcal{R}|)$ about the origin to obtain

$$\begin{aligned} G(\mathbf{k}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} & 4\pi i^l Y_l^{m*}(\theta_{\mathcal{R}},\phi_{\mathcal{R}}) Y_l^m(\theta_k,\phi_k) \\ & \times \left[-\frac{d}{d\zeta_c}\zeta_c\right]\left\{\mathcal{K}_l(\zeta_c\mathcal{R})(4i)^{-1}(-k)^l\left(\frac{1}{k}\frac{d}{dk}\right)^l k^{-1}\right. \\ & \times \zeta_c^l\left(\frac{1}{\zeta_c}\frac{d}{d\zeta_c}\right)^l \zeta_c^{-1}\mathcal{R}^{1-2l}(\hat{E}_{2l}[(\zeta_b - \zeta_c + ik)\mathcal{R}] \\ -\hat{E}_{2l}[(\zeta_b - \zeta_c - ik)\mathcal{R}] & - \hat{E}_{2l}[(\zeta_b + \zeta_c + ik)\mathcal{R}] + \hat{E}_{2l}[(\zeta_b + \zeta_c - ik)\mathcal{R}]) \\ & + \mathcal{I}_l(\zeta_c\mathcal{R})(2i)^{-1}k^l\left(\frac{1}{k}\frac{d}{dk}\right)^l k^{-1}\zeta_c^l\left(\frac{1}{\zeta_c}\frac{d}{d\zeta_c}\right)^l\zeta_c^{-1}\mathcal{R}^{1-2l} \\ & \left.\times (E_{2l}[(\zeta_b + \zeta_c - ik)\mathcal{R}] - E_{2l}[(\zeta_b + \zeta_c + ik)\mathcal{R}])\right\}. \end{aligned} \tag{3}$$

In equations (2) and (3), $N_x = 2\zeta_x^{3/2}$, (k,θ_k,ϕ_k) and $(\mathcal{R},\theta_{\mathcal{R}},\phi_{\mathcal{R}})$ denote the spherical coordinates of $\mathbf{k}$ and $\mathcal{R}$, E_n is an exponential-type integral,[11] $E_n(x) = \int_1^\infty t^{-n} \exp(-xt)dt$, and $\hat{E}_n$ is the "entire" part of E_n, $\hat{E}_n(x) = E_n(x) + (-x)^{n-1}\ln x/(n - 1)!$.

The $\mathcal{I}_l$ and $\mathcal{K}_l$ are essentially[12] modified spherical Bessel functions: $\mathcal{I}_l(x) = x(x^{-1}d/dx)^l x^{-1}\sinh x;$ $\mathcal{K}_l(x) = (-x)^l(x^{-1}d/dx)^l x^{-1}\exp(-x)$.

Note particularly that the only singularities of $G(\mathbf{k})$ are poles and logarithmic branch points at $k = \pm i(\zeta_b + \zeta_c)$.

Next, we use $G(\mathbf{k})$ in the simplest example of a three-(noncolinear)-center integral,

$$I \equiv \int dv_1 \int dv_2\, 1s_a(\mathbf{r}_1)\, 1s_a(\mathbf{r}_1)\, r_{12}^{-1}\, 1s_b(\mathbf{r}_2 - \mathbf{R})\, 1s_c(\mathbf{r}_2 - \mathbf{R} - \mathcal{R}). \tag{4}$$

Expressed as a convolution integral,[6–8, 10] we obtain

$$I = {}^1/_4\pi^{-5/2}N_a{}^2N_bN_c\int d^3\mathbf{k}F(\mathbf{k})G(\mathbf{k})k^{-2}\exp(i\mathbf{k}\cdot\mathbf{R}), \tag{5}$$

where $F(\mathbf{k}) \equiv (4\pi)^{-1/2}\int dv\, \exp(i\mathbf{k}\cdot\mathbf{r} - 2\zeta_a r) = (4\pi)^{-1/2}\, 2\pi(ik)^{-1}[(Z - ik)^{-2} - (Z + ik)^{-2}]$ (see eq. (13) of ref. 8), and where $Z \equiv 2\zeta_a$. Denote the spherical coordinates of $\mathbf{R}$ by (R,θ_R,ϕ_R), let $\cos\Theta = \mathbf{R}\cdot\mathcal{R}/(R\mathcal{R})$, and let P_l denote the Legendre polynomial of order l. Carrying out the integration of equation (5) for the case $R > \mathcal{R}$, we obtain

$$I = N_a{}^2N_bN_c\sum_{l=0}^{\infty}(2l+1)(-1)^lP_l(\cos\Theta) \times R^l\left(\frac{1}{R}\frac{d}{dR}\right)^l R^{-1}(-d/d\zeta_c)\zeta_c\{\mathcal{I}_l(\zeta_c\mathcal{R})I_1{}^{(l)} + \mathcal{K}_l(\zeta_c\mathcal{R})I_2{}^{(l)}\}, \tag{6}$$

$$\begin{aligned}
I_1{}^{(l)} \equiv{}& \frac{2^{l+1}l!}{(2l+1)!}Z^{-3}\zeta_c{}^l\left(\frac{1}{\zeta_c}\frac{d}{d\zeta_c}\right)^l\zeta_c{}^{-1}(\zeta_b+\zeta_c)^{-2}[1+(\zeta_b+\zeta_c)\mathcal{R}] \\
&\times\exp[-(\zeta_b+\zeta_c)\mathcal{R}] + {}^1/_2(-1)^l\zeta_c{}^{-1}(\zeta_b+\zeta_c)^{-3-l}[(Z+\zeta_b+\zeta_c)^{-2} \\
&-(Z-\zeta_b-\zeta_c)^{-2}]\exp[-(\zeta_b+\zeta_c)R] - {}^1/_2\frac{d}{dZ}\exp(-ZR)Z^{-2}\left(\frac{1}{Z}\frac{d}{dZ}\right)^l Z^{-1} \\
&\times\zeta_c{}^l\left(\frac{1}{\zeta_c}\frac{d}{d\zeta_c}\right)^l\zeta_c{}^{-1}\mathcal{R}^{1-2l}\left(E_{2l}[(\zeta_b+\zeta_c+Z)\mathcal{R}] - E_{2l}[(\zeta_b+\zeta_c-Z)\mathcal{R}]\right) \\
&-{}^1/_2[(2l-1)!]^{-1}\exp(ZR)\left(-(\zeta_b+\zeta_c+Z)^{-1}E_2[(\zeta_b+\zeta_c+Z)R]\right. \\
&\left.+E_1[(\zeta_b+\zeta_c+Z)R]\frac{d}{dZ}\right)Z^{-2}\left(\frac{1}{Z}\frac{d}{dZ}\right)^l Z^{-1}\zeta_c{}^l\left(\frac{1}{\zeta_c}\frac{d}{d\zeta_c}\right)^l\zeta_c{}^{-1} \\
&\times(\zeta_b+\zeta_c+Z)^{2l-1} + {}^1/_2[(2l-1)!]^{-1}\exp(-ZR)\left((\zeta_b+\zeta_c-Z)^{-1}E_2\right. \\
&\times\left.[(\zeta_b+\zeta_c-Z)R] + E_1[(\zeta_b+\zeta_c-Z)R]\frac{d}{dZ}\right)Z^{-2}\left(\frac{1}{Z}\frac{d}{dZ}\right)^l Z^{-1}\zeta_c{}^l\left(\frac{1}{\zeta_c}\frac{d}{d\zeta_c}\right)^l \\
&\times\zeta_c{}^{-1}(\zeta_b+\zeta_c-Z)^{2l-1} - {}^1/_2\sum_{M=0}^{l-1}\sum_{N=0}^{M+1}\frac{(-)^M(N+1)}{2^{l-3}M!(l-M-1)!}Z^{-3-2N} \\
&\times(\zeta_b+\zeta_c)^{2N-2M-3}E_{2M-2N+4}[(\zeta_b+\zeta_c)R]\,\zeta_c{}^l\left(\frac{1}{\zeta_c}\frac{d}{d\zeta_c}\right)^l\zeta_c{}^{-1}(\zeta_b+\zeta_c)^{2M+1},
\end{aligned} \tag{7}$$

$$
\begin{aligned}
I_2^{(l)} = {} & \frac{2^l l!}{(2l+1)!}\,(-1)^l Z^{-3}\,\zeta_c^{\,l}\left(\frac{1}{\zeta_c}\frac{d}{d\zeta_c}\right)^l \zeta_c^{-1}\,((\zeta_b-\zeta_c)^{-2}\{1-[1+(\zeta_b-\zeta_c)\mathcal{R}] \\
& \times \exp[-(\zeta_b-\zeta_c)\mathcal{R}]\} - (\zeta_b+\zeta_c)^{-2}\{1-[1+(\zeta_b+\zeta_c)\mathcal{R}]\exp[-(\zeta_b+\zeta_c)\mathcal{R}]\}) \\
& + {}^1\!/_4(-1)^l\,\frac{d}{dZ}\exp(-ZR)Z^{-2}\left(\frac{1}{Z}\frac{d}{dZ}\right)^l Z^{-1}\,\zeta_c^{\,l}\left(\frac{1}{\zeta_c}\frac{d}{d\zeta_c}\right)^l \zeta_c^{-1}\mathcal{R}^{1-2l} \\
& \times (\hat{E}_{2l}[(\zeta_b-\zeta_c+Z)\mathcal{R}] - \hat{E}_{2l}[(\zeta_b-\zeta_c-Z)\mathcal{R}] - \hat{E}_{2l}[(\zeta_b+\zeta_c+Z)\mathcal{R}] \\
& + \hat{E}_{2l}[(\zeta_b+\zeta_c-Z)\mathcal{R}]). \qquad (8)
\end{aligned}
$$

Horrendous as it may be, the analytical formula (eqs. (6)–(8)) has much to recommend it: (1) Computational accuracy with analytical formulas is easier to assess than with numerical integrations. (2) The internuclear angular coordinates enter in a transparent manner. (3) The functions $\mathcal{I}_l$ and $\mathcal{K}_l$ are characteristic of the two-center charge distribution and are independent of the integral in which they appear. (4) Convenient numerical methods exist[11] for evaluating the classical functions $\mathcal{I}_l$, $\mathcal{K}_l$, and E_{2l}, for all ranges of their arguments and parameters. (5) Behavior for large R is easy to estimate.

More complicated three- and four-center integrals work out similarly, but with considerably more bookkeeping. In a subsequent paper, detailed derivations and computationally convenient formulas will be given for the general r_{12}^{-1} integrals involving arbitrary STO's.

* Supported by a National Science Foundation grant.

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[11] *Handbook of Mathematical Functions*, ed. M. Abramowitz and I. A. Stegun (National Bureau of Standards (U.S.), Applied Mathematics Series, no. 55, 1964).

[12] The author has been unable to find a standard notation for these two functions. Throughout this paper, all "derivatives" differentiate everything to their right.