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Efficient and Rapid Evaluation of Three-Center Two Electron Coulomb and Hybrid Integrals Using Nonlinear Transformations

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Among the two electron integrals occurring in the molecular context, the three-center Coulomb and hybrid integrals are numerous and difficult to evaluate to high accuracy. The analytical and numerical difficulties arise mainly from the presence of the spherical Bessel function and hypergeometric series in these integrals. The present work pursues the acceleration of convergence for three-center two electron Coulomb and hybrid integrals. We have proven that the hypergeometric function can be expressed as a finite expansion and that the integrand involving this series and a product of Bessel functions satisfies a linear differential equation with coefficients having a power series expansion in the reciprocal of the variable suitable for application of the nonlinear D- and $\bar{D}$-transformations. These transformations depend strongly on the order of the differential equation that the integrand of interest satisfies. This work concentrates on reduction of this order to two, exploiting properties of spherical and reduced Bessel functions, leading to greatly simplified calculations to evaluate the integrals precisely by reducing the order of linear systems to be solved. It also avoids the long and difficult implementations of successive derivatives of the integrands. The numerical results section illustrates clearly the reduction of the calculation time we obtained for a high predetermined accuracy.

Key Words: nonlinear transformations; three-center two electron Coulomb integrals; hybrid integrals; rapid evaluation of infinite oscillatory integrals.

1. INTRODUCTION

Previous work on the rapid and efficient evaluation of two electron integrals to predetermined accuracy [1–4] continues with the present contribution. Among the integrals required to develop electronic structure theory over Slater type orbitals are three-center Coulomb and hybrid integrals.

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The advantage of using a basis set of B functions [5–7] which can be expressed as linear combinations of Slater type functions (STF) and vice versa [6, 8], can be explained by the fact that their Fourier transforms are of exceptional simplicity among the exponentially declining functions [9, 10]. The B functions are well adapted to the Fourier transform method [11–35] that allowed analytical expressions for the integrals of interest to be developed [22, 35]. These expressions involve semi-infinite integrals whose integrands oscillate rapidly due to the spherical Bessel functions $j_l(\alpha x)$, especially for large values of α.

Recently [3], we showed that these integrands satisfy all the conditions of applicability of the nonlinear D- (due to Levin and Sidi) and $\bar{D}$- (due to Sidi) transformations [36–39]. It is shown that these transformations are efficient in convergence acceleration of infinite oscillatory integrals whose integrands satisfy linear differential equations with coefficients having asymptotic expansions in inverse powers of their arguments [1–4, 36].

The efficiency of such transformations depends strongly on the order of the differential equation that the integrand satisfies. The approximations $D_n^{(m)}$ and $\bar{D}_n^{(m)}$, which as n becomes large converge very quickly to the exact value of the integral and where m is the order of the differential equation that the integrand satisfies, are obtained by solving sets of equations of order $mn + 1$ and $(m - 1)n + 1$, respectively, where the calculation of the $(m - 1)$ successive derivatives of the integrand is necessary.

The order of differential equations satisfied by the integrands involved in the analytical expressions developed for the three-center two electron Coulomb and hybrid integrals is 4 [3]; thus the approximations are obtained by solving sets of linear equations of order $4n + 1$ and $3n + 1$, respectively, where the calculation of the three successive derivatives of the integrands is necessary. The present work concentrates on exploiting some properties of the spherical and reduced Bessel functions to decrease the order of these differential equations to two. This avoids calculating successive derivatives of the integrands which present severe computational and numerical difficulties.

In this work, the symbols HD and $H\bar{D}$ specify that the D and $\bar{D}$ are used with the order of requisite differential equation reduced to two.

The numerical results section compares the $H\bar{D}$ evaluations with those previously made using the $\bar{D}$ for the same integrands with the usual demands for predetermined high accuracy required for molecule calculations.

2. GENERAL DEFINITIONS AND BASIC FORMULAE

We define $A^{(\gamma)}$ to be the set of infinitely differentiable functions $a(x)$, which have asymptotic expansions in inverse powers of x as $x \to +\infty$, of the form

$$a(x) \sim x^{\gamma}\left(\alpha_0 + \frac{\alpha_1}{x} + \frac{\alpha_2}{x^2} + \cdots\right) \tag{1}$$

and their derivatives of any order have asymptotic expansions, which can be obtained by differentiating that in Eq. (1) formally term by term.

From this definition it follows that $A^{(\gamma)} \supset A^{(\gamma-1)} \supset \cdots$.

The gamma function Γ is defined by [40]

$$\Gamma(z) = \int_0^{+\infty} t^{z-1} e^{-t}\, dt. \tag{2}$$

For $n \in \mathbb{N}$,

$$\begin{cases} \Gamma(n+1) = n! = 1 \times 2 \times 3 \times \cdots \times n \\ \Gamma\left(n+\frac{1}{2}\right) = \frac{(2n)!}{2^{2n}\, n!}\sqrt{\pi}. \end{cases} \tag{3}$$

The Pochhammer symbol $(\alpha)_n$ is defined by [40]

$$\begin{cases} (\alpha)_0 = 1 \\ (\alpha)_n = \alpha(\alpha+1)(\alpha+2)\cdots(\alpha+n-1) = \frac{\Gamma(\alpha+n)}{\Gamma(\alpha)}. \end{cases} \tag{4}$$

We define the Hankel symbol (ν, m) by [41]

$$(\nu, m) = (-1)^m \frac{(1/2-\nu)_m (1/2+\nu)_m}{m!} = \frac{\Gamma(\nu+m+1/2)}{m!\,\Gamma(\nu-m+1/2)}. \tag{5}$$

We define the general hypergeometric function by [41]

$${}_mF_n(\alpha_1, \alpha_2, \ldots, \alpha_m; \beta_1, \beta_2, \ldots, \beta_n; x) = \sum_{r=0}^{+\infty} \frac{(\alpha_1)_r(\alpha_2)_r \cdots (\alpha_m)_r x^r}{(\beta_1)_r(\beta_2)_r \cdots (\beta_n)_r r!}. \tag{6}$$

For $m=2$, $n=1$, the hypergeometric function becomes

$${}_2F_1(\alpha, \beta; \gamma; x) = \sum_{r=0}^{+\infty} \frac{(\alpha)_r(\beta)_r x^r}{(\gamma)_r r!}. \tag{7}$$

We define the reduced Bessel function $\hat{k}_{n-1/2}(\zeta r)$ by [5, 6]

$$\hat{k}_{n-\frac{1}{2}}(\zeta r) = \sqrt{\frac{2}{\pi}}(\zeta r)^{n-\frac{1}{2}} K_{n-\frac{1}{2}}(\zeta r) \tag{8}$$

$$= \frac{e^{-\zeta r}}{\zeta r} \sum_{j=1}^{n} \frac{(2n-j-1)!}{(j-1)!(n-j)!} 2^{j-n} (\zeta r)^j, \tag{9}$$

where $K_{n-1/2}$ stands for the modified Bessel function of the second kind [42].

The spherical Bessel function $j_l(x)$ of order $l \in \mathbb{N}$ is defined by [41]

$$j_l(x) = (-1)^l x^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \left(\frac{\sin(x)}{x}\right). \tag{10}$$

$j_l(x)$ satifies the recurrence relations [41]

$$\begin{cases} x j_{l-1}(x) + x j_{l+1}(x) = 2l j_l(x) \\ j_{l-1}(x) - j_{l+1}(x) = 2 j_l'(x). \end{cases} \tag{11}$$

The surface spherical harmonic $Y_l^m(\theta, \varphi)$ is defined explicitly using the Condon and Shortley phase convention as [43]

$$Y_l^m(\theta, \varphi) = i^{m+|m|} \left[\frac{(2l+1)(l-|m|)!)}{4\pi(l+|m|)!)}\right]^{\frac{1}{2}} P_l^{|m|}(\cos\theta) e^{im\varphi}. \tag{12}$$

$P_l^m(x)$ stands for the associated Legendre function of lth degree and mth order, which is expressed by means of the well-known Legendre polynomials [41]

$$P_l^m(x) = (1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_l(x) = (1-x^2)^{m/2}\left(\frac{d}{dx}\right)^{l+m}\left[\frac{(x^2-1)^l}{2^l l!}\right]. \tag{13}$$

The well-known Rayleigh expansion of the plane wave functions is defined by [44]

$$e^{\pm i\mathbf{p}\cdot\mathbf{r}} = \sum_{l=0}^{+\infty}\sum_{m=-l}^{l} 4\pi(\pm i)^\lambda j_l(|\mathbf{p}||\mathbf{r}|)Y_l^m(\theta_\mathbf{r},\varphi_\mathbf{r})\left[Y_l^m(\theta_\mathbf{p},\varphi_\mathbf{p})\right]^*. \tag{14}$$

The Slater type orbitals are defined in normalized form according to the relationship [45, 46]

$$\chi_{n,l}^m(\zeta\mathbf{r}) = N(n,\zeta)r^{n-1}e^{-\zeta r}Y_l^m(\theta_\mathbf{r},\varphi_\mathbf{r}), \begin{cases} n = 1, 2, 3, \ldots \\ l = 0, 1, 2, \ldots, (n-1) \\ m = -l, -l+1, \ldots, l, \end{cases} \tag{15}$$

where $N(n,\zeta)$ stands for the normalisation factor defined by

$$N(n,\zeta) = \zeta^{-n+1}\left[(2\zeta)^{2n+1}/(2n)!\right]^{\frac{1}{2}}. \tag{16}$$

The STFs (and their Fourier transforms) can be expressed as finite linear combinations of B functions (or their Fourier transforms) [6],

$$\chi_{n,l}^m(\zeta\mathbf{r}) = \sum_{p=\tilde{p}}^{n-l}\frac{(-1)^{n-l-p}(n-l)!2^{l+p}(l+p)!}{(2p-n-l)!(2n-2l-2p)!!}B_{p,l}^m(\zeta,\mathbf{r}), \tag{17}$$

where

$$\tilde{p} = \begin{cases} (n-l)/2 & \text{if } n-l \text{ is even,} \\ (n-l+1)/2 & \text{if } n-l \text{ is odd.} \end{cases} \tag{18}$$

The double factorial is defined by

$$(2k)!! = 2\times 4\times 6\times\cdots\times(2k) = 2^k k! \tag{19}$$

$$(2k+1)!! = 1\times 3\times 5\times\cdots\times(2k+1) = \frac{(2k+1)!}{2^k k!} \tag{20}$$

$$0!! = 1. \tag{21}$$

The B functions are defined as [6, 7]

$$B_{n,l}^m(\zeta,\mathbf{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!}\hat{k}_{n-\frac{1}{2}}(\zeta r)Y_l^m(\theta_\mathbf{r},\varphi_\mathbf{r}). \tag{22}$$

The Fourier transform $\bar{B}_{n,l}^m(\zeta,\mathbf{p})$ of $B_{n,l}^m(\zeta,\mathbf{r})$ is given by

$$\bar{B}_{n,l}^m(\zeta,\mathbf{p}) = \frac{1}{(2\pi)^{3/2}}\int_\mathbf{r} e^{-i\mathbf{p}\cdot\mathbf{r}}B_{n,l}^m(\zeta,\mathbf{r})\,d\mathbf{r}. \tag{23}$$

By inserting the Rayleigh expansion Eq. (14) and the analytical expression of the B function Eq. (22) in the above equation, one can obtain an expression for $\bar{B}^m_{n,l}(\zeta, \mathbf{p})$ which is given by [9, 10]

$$\bar{B}^m_{n,l}(\zeta, \mathbf{p}) = \sqrt{\frac{2}{\pi}}\zeta^{2n+l-1}\frac{(-i|p|)^l}{(\zeta^2+|p|^2)^{n+l+1}}Y_l^m(\theta_{\mathbf{p}}, \varphi_{\mathbf{p}}). \tag{24}$$

The Fourier integral representation of the Coulomb operator $1/|\mathbf{r}-\mathbf{R}_1|$ is given by [12, 24]

$$\frac{1}{|\mathbf{r}-\mathbf{R}_1|} = \frac{1}{2\pi^2}\int_{\mathbf{k}}\frac{e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_1)}}{k^2}\,d\mathbf{k}. \tag{25}$$

The Gaunt coefficients are defined as [47–53]

$$\langle l_1 m_1|l_2 m_2|l_3 m_3\rangle = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\left[Y_{l_1}^{m_1}(\theta,\varphi)\right]^* Y_{l_2}^{m_2}(\theta,\varphi)Y_{l_3}^{m_3}(\theta,\varphi)\sin\theta\,d\theta\,d\varphi. \tag{26}$$

3. THREE-CENTER TWO ELECTRON COULOMB INTEGRALS OVER *B* FUNCTIONS

The three-center two electron Coulomb integrals over B functions are defined by [3, 22, 35]

$$\mathcal{K}^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3}$$

$$= \left\langle B^{m_1}_{n_1 l_1}(\zeta_1, \mathbf{r}) B^{m_3}_{n_3 l_3}[\zeta_3, (\mathbf{r}'-\mathbf{R}_3)]\left|\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right| B^{m_2}_{n_2 l_2}(\zeta_2, \mathbf{r}) B^{m_4}_{n_4 l_4}[\zeta_4, (\mathbf{r}'-\mathbf{R}_4)]\right\rangle_{\mathbf{r},\mathbf{r}'} \tag{27}$$

$$= \frac{1}{2\pi^2}\int_{\mathbf{x}} e^{i\mathbf{x}\cdot\mathbf{R}_4}\left\langle B^{m_1}_{n_1 l_1}(\zeta_1,\mathbf{r})|e^{-i\mathbf{x}\cdot\mathbf{r}}|B^{m_2}_{n_2 l_2}(\zeta_2,\mathbf{r})\right\rangle_{\mathbf{r}}$$

$$\times\left\langle B^{m_4}_{n_4 l_4}(\zeta_4,\mathbf{r}'')|e^{-i\mathbf{x}\cdot\mathbf{r}''}|B^{m_3}_{n_3 l_3}[\zeta_3, (\mathbf{r}''-(\mathbf{R}_3-\mathbf{R}_4))\right\rangle^*_{\mathbf{r}''}\frac{d\mathbf{x}}{x^2}. \tag{28}$$

The expression (28) is obtained by inserting the integral representation of the Coulomb operator Eq. (25) in Eq. (27).

Let ${}_kI_1$ denote the term in $\mathbf{r}$,

$${}_kI_1 = \left\langle B^{m_1}_{n_1 l_1}(\zeta_1,\mathbf{r})|e^{-i\mathbf{x}\cdot\mathbf{r}}|B^{m_2}_{n_2 l_2}(\zeta_2,\mathbf{r})\right\rangle_{\mathbf{r}}.$$

The two B functions are centered on the same point. By inserting the analytical expression of the B function Eq. (14) and using the Rayleigh expansion of plane wave functions Eq. (22), one can readily express ${}_kI_1$ using a semi infinite integral as

$$\tilde{I}(x) = \int_0^{+\infty} r^{(k+l_1+l_2+\frac{1}{2})-1} J_{l+\frac{1}{2}}(xr)e^{-\zeta_s r}\,dr$$

which is known analytically [42]. The expression of ${}_kI_1$ is given by [3]

$$
\begin{aligned}
{}_kI_1 = {} & \left[2^{n_1+l_1+n_2+l_2}(n_1+l_1)!(n_2+l_2)!\right]^{-1}\zeta_1^{l_1}\zeta_2^{l_2}\sqrt{\frac{\pi}{2x}} \\
& \times \sum_{l=l_{min},2}^{l_{max}}(-i)^l\langle l_1m_1|lm_1-m_2|l_2m_2\rangle\left[Y_l^{m_1-m_2}(\theta_{\mathbf{x}},\varphi_{\mathbf{x}})\right]^* \\
& \times \sum_{k=2}^{n_1+n_2}\sum_{i=k_1}^{k_2}\left[\frac{(2n_1-i-1)!\,(2n_2-k+i-1)!\,\zeta_1^{i-1}\,\zeta_2^{k-i-1}}{(i-1)!\,(n_1-i)!(k-i-1)!(n_2-k+i)!\,2^{n_1+n_2-k}}\right] \\
& \times \frac{[x/2\zeta_s]^{l+\frac{1}{2}}\Gamma(k+l_1+l_2+l+1)}{\zeta_s^{k+l_1+l_2+\frac{1}{2}}\Gamma(l+3/2)}\left[1+\frac{x^2}{\zeta_s^2}\right]^{-k-l_1-l_2} \\
& \times {}_2F_1\left(\frac{l-k-l_1-l_2+1}{2},\frac{l-k-l_1-l_2}{2}+1;l+\frac{3}{2};-\frac{x^2}{\zeta_s^2}\right), \qquad (29)
\end{aligned}
$$

where

$$k_1=\max(1,k-n_2), \qquad k_2=\min(n_1,k-1), \qquad \zeta_s=\zeta_1+\zeta_2,$$

and where [50]

$$
\begin{aligned}
l_{max} &= l_1+l_2 \\
l_{min} &= \begin{cases}\max(|l_1-l_2|,|m_2-m_1|), & \text{if } l_{max}+\max(|l_1-l_2|,|m_2-m_1|) \text{ is even} \\ \max(|l_1-l_2|,|m_2-m_1|)+1, & \text{if } l_{max}+\max(|l_1-l_2|,|m_2-m_1|) \text{ is odd.}\end{cases}
\end{aligned}
$$

The subscript $l=l_{min},2$ in the first summation symbol in Eq. (29) implies that the summation index l runs in steps of 2 from l_{min} to l_{max}.

One of the arguments of the hypergeometric function $(l-k-l_1-l_2+1)/2$ or $(l-k-l_1-l_2)/2+1$ is a negative integer; thus the hypergeometric series is reduced to a finite expansion.

Now if we apply the Fourier transform method to the term in $\mathbf{r}''$ from Eq. (28) after substituting the Rayleigh expansion (14) of a plane wave, we obtain an expression for $\mathcal{K}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4}$, involving a semi-infinite oscillatory integral, which is given by [3, 22, 35]

$$
\begin{aligned}
\mathcal{K}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4} = {} & 8(4\pi)^3(2l_3+1)!!(2l_4+1)!!\zeta_1^{l_1}\zeta_2^{l_2}\zeta_3^{2n_3+l_3-1}\zeta_4^{2n_4+l_4-1} \\
& \times \frac{(n_3+l_3+n_4+l_4+1)!}{(n_3+l_3)!(n_4+l_4)!}\sum_{l=l_{min},2}^{l_{max}}(-i)^l\langle l_1m_1|l_2m_2|lm_1-m_2\rangle \\
& \times \sum_{k=2}^{n_1+n_2}\sum_{i=k_1}^{k_2}\left[\frac{(2n_1-i-1)!\,(2n_2-i-1)!\,\zeta_1^{i-1}\,\zeta_2^{k-i-1}}{(i-1)!\,(n_1-i)!\,(k-i-1)!\,(n_2-k+i)!\,2^{n_1+n_2-k}}\right] \\
& \times \sum_{l_4'=0}^{l_4}\sum_{m_4'=-l_4'}^{l_4'}(i)^{l_4+l_4'}(-1)^{l_4'}\frac{\langle l_4m_4|l_4-l_4'm_4-m_4'|l_4'm_4'\rangle}{(2l_4'+1)!![2(l_4-l_4')+1]!!}
\end{aligned}
$$

$$\times \sum_{l_3'=0}^{l_3} \sum_{m_2'=-l_3'}^{l_3'} (i)^{l_3+l_3'} \frac{\langle l_3 m_3 | l_3 - l_3' m_3 - m_3' | l_3' m_3' \rangle}{(2l_3'+1)!![2(l_3 - l_3')+1]!!}$$

$$\times \sum_{l'=|l_3'-l_4'|}^{l_3'+l_4'} \langle l_4' m_4' | l_3' m_3' | l' m_4' - m_3' \rangle R_{34}^{l'} Y_{l'}^{m_4'-m_3'}(\theta_{\mathbf{R}_{34}}, \varphi_{\mathbf{R}_{34}})$$

$$\times \sum_{l_{34}} \langle l_3 - l_3' m_3 - m_3' | l_4 - l_4' m_4 - m_4' | l_{34} m_{34} \rangle$$

$$\times \sum_{\lambda=|l-l_{34}|}^{l+l_{34}} i^{\lambda} \langle l m_1 - m_2 | l_{34}(m_4 - m_4') - (m_3 - m_3') | \lambda \mu \rangle$$

$$\times \sum_{j=0}^{\Delta l} \binom{\Delta l}{j} \frac{(-1)^j \, \Gamma(k + l_1 + l_2 + l + 1)}{2^{n_3+n_4+l_3+l_4-j+1+l+\frac{1}{2}} \, (n_3 + n_4 + l_3 + l_4 - j + 1)!}$$

$$\times \frac{\zeta_s^{n_k-l-1}}{\Gamma\left(l+\frac{3}{2}\right)} \sum_{r=0}^{\eta'} (-1)^r \frac{(\eta/2)_r \, ((\eta+1)/2)_r}{(l+3/2)_r \, r! \, \zeta_s^{2r}} \int_{s=0}^{1} s^{n_{33}} (1-s)^{n_{44}} Y_{\lambda}^{-\mu}(\theta_{\mathbf{v}}, \varphi_{\mathbf{v}})$$

$$\times \int_{x=0}^{+\infty} \left[\zeta_s^2 + x^2\right]^{-n_k} x^{n_x+\frac{1}{2}} j_{\lambda}(vx) \frac{\hat{k}_{\nu}[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_{\gamma}}} \, dx \, ds, \tag{30}$$

where

$$k_1 = \max(1, k - n_2), \qquad k_2 = \min(n_1, k - 1), \qquad \zeta_s = \zeta_1 + \zeta_2$$

$$|(l_3 - l_3') - (l_4 - l_4')| \le l_{34} \le (l_3 - l_3') + (l_4 - l_4')$$

$$n_x = l_3 - l_3' + l_4 - l_4' + 2r + l, \qquad n_k = k + l_1 + l_2$$

$$n_{33} = n_3 + l_3 + l_4 - l_4', \qquad n_{44} = n_4 + l_4 + l_3 - l_3'$$

$$n_{\gamma} = 2(n_3 + l_3 + n_4 + l_4) - (l_3' + l_4') - l' + 1$$

$$\mu = (m_1 - m_2) - (m_4 - m_4') + (m_3 - m_3')$$

$$[\gamma(s,x)]^2 = (1-s)\zeta_4^2 + s\zeta_3^2 + s(1-s)x^2$$

$$\eta = l - k - l_1 - l_2 + 1, \qquad \Delta l = \frac{l_3 + l_4 - l'}{2}$$

$$\eta' = -\frac{\eta}{2} \qquad \text{if } \eta \text{ is even, if not } \eta' = -\frac{\eta+1}{2}$$

$$\mathbf{v} = s(\mathbf{R}_3 - \mathbf{R}_4) - \mathbf{R}_3 = s\mathbf{R}_{34} - \mathbf{R}_3$$

$$\nu = n_3 + n_4 + l_3 + l_4 - l' - j + \frac{1}{2}$$

$$m_{34} = (m_3 - m_3') - (m_4 - m_4').$$

Let $\tilde{\mathcal{K}}$ be the two-dimensional integral involved in the above equation:

$$\tilde{\mathcal{K}} = \int_{s=0}^{1} s^{n_{33}} (1-s)^{n_{44}} Y_{\lambda}^{-\mu}(\theta_{\mathbf{v}}, \varphi_{\mathbf{v}}) \int_{x=0}^{+\infty} \left[\zeta_s^2 + x^2\right]^{-n_k}$$
$$\times x^{n_x+\frac{1}{2}} j_{\lambda}(vx) \frac{\hat{k}_{\nu}[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_{\gamma}}} \, dx \, ds. \tag{31}$$

Its inner semi-infinite x integral $\tilde{\mathcal{K}}(s)$ is given by

$$\tilde{\mathcal{K}}(s) = \int_{x=0}^{+\infty} \left[\zeta_s^2 + x^2\right]^{-n_k} x^{n_x+\frac{1}{2}} j_\lambda(vx) \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\, dx \tag{32}$$

$$= \sum_{n=0}^{+\infty} \int_{j_{\lambda,v}^{n}}^{j_{\lambda,v}^{n+1}} \left[\zeta_s^2 + x^2\right]^{-n_k} x^{n_x+\frac{1}{2}} j_\lambda(vx) \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\, dx. \tag{33}$$

$j_{\lambda,v}^0$ is assumed to be 0 and for $n \neq 0$, $j_{\lambda,v}^n = j_{\lambda+1/2}^n / v$, where $j_{\lambda+1/2}^n$ is the zero of order n of the spherical Bessel function of the first kind $J_{\lambda+1/2}(x)$ [54].

4. THE NONLINEAR *D*- AND $\bar{D}$-TRANSFORMATIONS

THEOREM 1 [36]. *Let $f(x)$ be integrable on $[0,\infty)$ and satisfy a linear differential equation of order m of the form*

$$f(x) = \sum_{k=1}^{m} p_k(x)\, f^{(k)}(x), \tag{34}$$

where

$$p_k \in A^{(i_k)}, \qquad i_k \leq k,\ 1 \leq k \leq m.$$

Let also

$$\lim_{x\to+\infty} p_k^{(i-1)}(x)\, f^{(k-i)}(x) = 0, \qquad i \leq k \leq m,\ 1 \leq i \leq m. \tag{35}$$

If for every integer $l \geq -1$,

$$\sum_{k=1}^{m} l(l-1)\cdots(l-k+1)\, p_{k,0} \neq 1, \tag{36}$$

where

$$p_{k,0} = \lim_{x\to+\infty} x^{-k} p_k(x), \qquad 1 \leq k \leq m,$$

then the approximation $D_n^{(m)}$ to $S = \int_0^\infty f(t)\, dt$, using the D-transformation, satisfies the $N = 1 + mn$ equations given by [36],

$$D_n^{(m)} = \int_0^{x_l} f(t)\, dt + \sum_{k=0}^{m-1} f^{(k)}(x_l) x_l^{\sigma_k} \sum_{i=0}^{n-1} \frac{\bar{\beta}_{i,k}}{x_l^i}, \qquad l = 0, 1, 2, \ldots, mn. \tag{37}$$

σ_k, $k = 0, 1, \ldots, m-1$, are the minima of $k+1$ and s_k where s_k is the largest of the integers s for which $\lim_{x\to+\infty} x^s f^{(k)}(x) = 0$.

$D_n^{(m)}$ and the $\bar{\beta}_{k,i}$ for $k = 0, 1, \ldots, m-1$, $i = 0, 1, \ldots, n-1$ are the N unknowns.

The x_l, $l = 0, 1, \ldots$ are chosen to satisfy $0 < x_0 < x_1 < \cdots$ and $\lim_{l\to+\infty} x_l = +\infty$.

The order of the above set of equations can be reduced by choosing x_l, $l = 0, 1, 2, \ldots$ to be the successive zeros of $f(x)$. In this case Eq. (37) can be rewritten as [39]

$$\bar{D}_n^{(m)} = \int_0^{x_l} f(t)\,dt + \sum_{k=1}^{m-1} f^{(k)}(x_l)x_l^{\sigma_k} \sum_{i=0}^{n-1} \frac{\bar{\beta}_{i,k}}{x_l^i}, \qquad l = 0, 1, 2, \ldots, (m-1)n. \quad (38)$$

Now, we consider the integral $\int_0^{\infty} f(t)\,dt$, where [4]

$$f(x) = g(x)\, j_\lambda(x), \quad (39)$$

where $g(x)$ is of the form

$$g(x) = h(x)e^{\phi(x)} \quad (40)$$

such that $\phi(x)$ as $x \to +\infty$ is a real polynomial in x of degree $k \geq 0$ for some integer k and $h(x) \in A^{(\gamma)}$ for some γ.

If $k > 0$, then for $f(x)$ to be integrable at infinity $\lim_{x\to+\infty} \phi(x) = -\infty$ is necessary. If $k = 0$, then $g(x) \in A^{(\gamma)}$, hence $\gamma < 1$ in order for $f(x)$ to be integrable at infinity.

$j_\lambda(x)$ satisfies the differential equation given by

$$j_\lambda(x) = -\frac{2x}{x^2 - \lambda^2 - \lambda} j_\lambda'(x) - \frac{x^2}{x^2 - \lambda^2 - \lambda} j_\lambda''(x). \quad (41)$$

Using the fact that $f(x) = g(x)\, j_\lambda(x)$, we have $j_\lambda(x) = \frac{f(x)}{g(x)}$. Substituting this in the differential equation above, we obtain

$$f(x) = p_1(x)\, f'(x) + p_2(x)\, f''(x). \quad (42)$$

where

$$p_1(x) = \frac{2x^2(h'(x)/h(x) + \phi') - 2x}{w(x)}, \qquad p_2(x) = \frac{-x^2}{w(x)} \quad (43)$$

and

$$w(x) = -x^2\left[\left(\frac{h'(x)}{h(x)} + \phi'\right)' - \left(\frac{h'(x)}{h(x)} + \phi'\right)^2\right] - 2x\left(\frac{h'(x)}{h(x)} + \phi'\right) + x^2 - \lambda^2 - \lambda. \quad (44)$$

If $k = 0$ then $p_1(x) \in A^{(-1)}$ and $p_2(x) \in A^{(0)}$.
If $k > 0$ then $p_1(x) \in A^{(-k+1)}$ and $p_2(x) \in A^{(-2k+2)}$.
In all these above cases

$$\lim_{x\to+\infty} p_k^{(i-1)}(x)\, f^{(k-i)}(x) = 0, \qquad k = i, 2,\; i = 1, 2.$$

We can easily note that

$$\forall l \geq -1, \qquad \sum_{k=1}^{2} l(l-1)\cdots(l-k+1)\, p_{k,0} = 0 \neq 1 \;(p_{k,0} = 0, \quad k = 1, 2).$$

The conditions of the applicability of the D- and $\bar{D}$-transformations to accelerate the convergence of $\int_0^{+\infty} f(t)\,dt$ can now be shown to be satisfied.

The approximation $HD_n^{(2)}$ of $S = \int_0^{+\infty} f(t)\,dt$ using the D-transformation is given by

$$HD_n^{(2)} = \int_0^{x_l} f(t)\,dt + \sum_{k=0}^{1} (g(x_l) j_\lambda(x_l))^{(k)} x_l^{\sigma_k} \sum_{i=0}^{n-1} \frac{\bar{\beta}_{i,k}}{x_l^i}, \qquad l = 0, 1, 2, \ldots, 2n. \quad (45)$$

If we choose $x_l = j_{\lambda+1/2}^{l+1}$ for $l = 0, 1, 2, \ldots, n$ where $j_{\lambda+1/2}^{l+1}$ is the zero of order $l+1$ of the spherical Bessel function of the first kind $J_{\lambda+1/2}(x)$ ($j_{\lambda+1/2}^{0}$ is assumed to be 0), then the approximation $H\bar{D}_n^{(2)}$ of $S = \int_0^{+\infty} f(t)\,dt$ using the $\bar{D}$-transformation is given by

$$H\bar{D}_n^{(2)} = \int_0^{x_l} f(t)\,dt + g(x_l) j_\lambda'(x_l) x_l^{\sigma_1} \sum_{i=0}^{n-1} \frac{\bar{\beta}_{i,1}}{x_l^i}, \qquad l = 0, 1, 2, \ldots, n. \quad (46)$$

$H\bar{D}_n^{(2)}$ and the $\bar{\beta}_{i,1}$, $i = 0, 1, \ldots, n-1$ are the $n+1$ unknowns of the above set of equations.

Let us consider the semi-infinite x integral $\tilde{\mathcal{K}}(s)$ Eq. (32). Its integrand which will be referred to as $F_k(x)$ is of the form

$$F_k(x) = g_k(x) j_\lambda(vx),$$

where

$$g_k(x) = x^{n_x + \frac{1}{2}} \left[\zeta_s^2 + x^2\right]^{-n_k} \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}.$$

In previous work [3], we showed that $F_k(x)$ satisfies a 4th order linear differential equation of the form required to apply the nonlinear D- and $\bar{D}$-transformations. The approximation of $\tilde{\mathcal{K}}(s)$ was given by $\bar{D}_n^{(4)}$. The implementation of the three successive derivatives of $F_k(x)$ which presents severe computational difficulties, especially for large values of n_3, n_4, l_3, l_4, and λ, was necessary for the calculations. We also demonstrated the superiority of these transformations in the evaluation of this kind of semi-infinite oscillatory integral [1–4], compared with other alternatives using the Gauss–Laguerre formulae, the epsilon algorithm of Wynn [55, 56] and Levin's u transform [57, 58].

Consider the integrand $F_k(x)$ of $\tilde{\mathcal{K}}(s)$. The reduced Bessel function $\hat{k}_\nu(z)$ has an asymptotic expansion in inverse powers of z which is given by [42]

$$\hat{k}_\nu(z) \sim z^{\nu-\frac{1}{2}} e^{-z} \sum_{m=0}^{+\infty} \frac{(\nu, m)}{(2z)^m} \quad (47)$$

and

$$R_{34}\gamma(s,x) \sim R_{34}\sqrt{s(1-s)x}, \qquad x \to +\infty. \quad (48)$$

By expressing the Hankel symbol (ν, m) in terms of the Pochhammer symbol and using the fact $\nu = n + \frac{1}{2}$ where n is an integer, one can show that the asymptotic series for the reduced Bessel function $\hat{k}_\nu(z)$ given above terminates after a finite number of terms,

$$\hat{k}_\nu(z) = z^n e^{-z} \sum_{j=0}^{n} \frac{(n+j)!}{j!(n-j)!(2z)^j}. \tag{49}$$

Substituting z by $R_{34}\sqrt{s(1-s)}x$ in Eq. (49), one can easily show that

$$g_k(x) \sim R_{34}^n(\sqrt{s(1-s)})^{n-n_\gamma} x^{n_x+n-n_\gamma-2n_k+\frac{1}{2}} \left(1+\frac{\zeta_s^2}{x^2}\right)^{-n_k} \times e^{-R_{34}\sqrt{s(1-s)x}} \sum_{j=0}^{n} \frac{(n+j)!}{j!(n-j)!(2R_{34}\sqrt{s(1-s)}x)^j}. \tag{50}$$

Thus, $g_k(x)$ can be written as $h(x)e^{\phi(x)}$ where

$$\begin{cases} h(x) \in A^{(\delta)}, & \delta = n_x + n - n_\gamma - 2n_k + \frac{1}{2} \\ \phi(x) \sim -R_{34}\sqrt{s(1-s)x} & \text{as } x \to +\infty. \end{cases} \tag{51}$$

Using the previous arguments, we can show that $F_k(x)$ satisfies a 2nd order linear differential equation of the form

$$F_k(x) = p_1(x)F_k'(x) + p_2(x)F_k''(x); \qquad p_1(x),\ p_2(x) \in A^{(0)}. \tag{52}$$

All the conditions of the applicability of D- and $\bar{D}$-transformations are satisfied.

$F_k(x)$ is exponentially decreasing, thus $\sigma_i = i+1$ for $i = 1, 2$, thus the approximation $H\bar{D}_n^{(2)}$ of $\int_0^{+\infty} F_k(x)\,dx$ using the $\bar{D}$-transformation is given by

$$H\bar{D}_n^{(2)} = \int_0^{x_l} F_k(t)\,dt + g_k(x_l)\,j_\lambda'(vx_l)x_l^2 \sum_{i=0}^{n-1} \frac{\bar{\beta}_{i,1}}{x_l^i}, \qquad l = 0, 1, 2, \ldots, n, \tag{53}$$

where the $x_l = j_{\lambda,v}^{l+1} = j_{\lambda+1/2}^{l+1}/v, l = 0, 1, \ldots, n$ which are the successive zeros of $j_\lambda(vx)$. $j_{\lambda,v}^0$ is assumed to be zero.

5. HYBRID INTEGRAL OVER *B* FUNCTIONS

The hybrid integral over B functions is defined by [3, 22, 35]

$$\mathcal{H}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4} = \left\langle B_{n_1l_1}^{m_1}(\zeta_1, \mathbf{r})B_{n_3l_3}^{m_3}(\zeta_3, \mathbf{r}') \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| B_{n_2l_2}^{m_2}(\zeta_2, \mathbf{r})B_{n_4l_4}^{m_4}[\zeta_4, (\mathbf{r}'-\mathbf{R})] \right\rangle. \tag{54}$$

The analytical expression of this integral is obtained using the same calculations as for the three-center two electron Coulomb integral. It involves a semi-infinite oscillatory integral and will be referred to as $\tilde{\mathcal{H}}(s)$ given by [3, 22, 35]

$$\mathcal{H}(s) = \int_{x=0}^{+\infty} \left[\zeta_s^2 + x^2\right]^{-n_k} x^{n_x+\frac{1}{2}}\, j_\lambda(vx) \frac{\hat{k}_\nu[R_1\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\, dx \tag{55}$$

$$= \sum_{n=0}^{+\infty} \int_{j_{\lambda,v}^n}^{j_{\lambda,v}^{n+1}} \left[\zeta_s^2 + x^2\right]^{-n_k} x^{n_x+\frac{1}{2}}\, j_\lambda(vx) \frac{\hat{k}_\nu[R_1\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\, dx, \tag{56}$$

TABLE I
Values of $\tilde{\mathcal{K}}(s)$ with 20 Correct Decimals

s	n_3	n_4	n_k	λ	R_3	ζ_3	R_4	ζ_4	max	$\tilde{\mathcal{K}}(s)$
0.005	1	1	2	0	2.5	1.5	1.5	0.5	81	0.1711045433135376D+01
0.005	2	1	3	1	4.5	2.5	4.0	1.5	225	0.8773983875160202D−05
0.999	2	2	3	2	3.0	2.0	2.5	2.5	292	0.6582270298028570D−05
0.999	3	2	2	3	3.5	1.5	2.5	0.5	304	0.2602612255845514D+00
0.999	3	3	3	4	2.0	2.0	1.5	1.5	186	0.7482795290391810D−02
0.010	4	3	3	4	3.5	2.0	3.0	1.5	112	0.1167202585151612D+00
0.999	4	3	5	5	6.5	1.0	5.5	0.5	145	0.3900383635977973D+02
0.005	4	4	5	5	4.5	1.5	3.0	1.0	67	0.2412209745299977D+02

Note. $n_x = \lambda$, $\nu = n_3 + n_4 + \frac{1}{2}$, $n_\gamma = 2(n_3 + n_4) + 1$, $\zeta_1 = \zeta_3$, and $\zeta_2 = \zeta_4$.

where $\mathbf{v} = s\mathbf{R}_1$ and $\mathbf{R}_1 = -\mathbf{R}$. $n_{33}, n_{44}, \mu, \lambda, \zeta_s, n_k, n_x, \nu, n_\gamma$, and $\gamma(s, x)$ are defined according to Eq. (30).

The integrand of $\tilde{\mathcal{H}}(s)$ is exactly of the same form as $F_k(x)$, thus it satisfies a second order differential equation of the form given by Eq. (52).

The approximation $H\bar{D}_n^{(2)}$ of $\tilde{\mathcal{H}}(s)$ using the $\bar{D}$-transformation is obtained by solving a set of equations of the form given by Eq. (53).

6. DISCUSSION

In this section the accuracy and efficiency of the present approach to three-center Coulomb and hybrid integrals is demonstrated numerically. The numerical tables are presented and their content discussed with a view to explaining the objectives they illustrate.

Exact values were computed (see Tables I, IV, VII) using the infinite series Eqs. (33), (56) which we sum to $n =$ max to obtain 20 correct decimals for comparison. These tables are intended to establish the accuracy of the transformation methods.

All finite integrals involved in Eqs. (30), (31), (38), (53) used to obtain numerical values of tables were evaluated using Gauss–Legendre quadrature of order 16.

The sets of equations Eqs. (38), (53) used in the $\bar{D}$- and $H\bar{D}$-transformations are solved using the LU decomposition.

TABLE II
Evaluation of $\tilde{\mathcal{K}}(s)$ Eq. (32) Using the $H\bar{D}$-Transformation of Order $n(H\bar{D}_n^{(2)})$ Eq. (53)

s	n_3	n_4	n_k	λ	R_3	ζ_3	R_4	ζ_4	n	$H\bar{D}_n^{(2)}$	Error	Time
0.005	1	1	2	0	2.5	1.5	1.5	0.5	5	0.17110454D+01	0.82D−10	0.02
0.005	2	1	3	1	4.5	2.5	4.0	1.5	5	0.87739833D−05	0.49D−12	0.03
0.999	2	2	3	2	3.0	2.0	2.5	2.5	5	0.65822625D−05	0.78D−11	0.03
0.999	3	2	2	3	3.5	1.5	2.5	0.5	8	0.26026122D+00	0.12D−12	0.06
0.999	3	3	3	4	2.0	2.0	1.5	1.5	5	0.74827953D−02	0.15D−10	0.02
0.010	4	3	3	4	3.5	2.0	3.0	1.5	9	0.11672025D+00	0.53D−10	0.07
0.999	4	3	5	5	6.5	1.0	5.5	0.5	8	0.39003836D+02	0.12D−10	0.05
0.005	4	4	5	5	4.5	1.5	3.0	1.0	9	0.24122097D+02	0.20D−09	0.07

Note. Time is in milliseconds. $n_x = \lambda$, $\nu = n_3 + n_4 + \frac{1}{2}$, $n_\gamma = 2(n_3 + n_4) + 1$, $\zeta_1 = \zeta_3$, and $\zeta_2 = \zeta_4$.

TABLE III
Evaluation of $\tilde{\mathcal{K}}(s)$ Eq. (32) Using the $\bar{D}$-Transformation of Order $n(\bar{D}_n^{(4)})$ Eq. (38)

s	n_3	n_4	n_k	λ	R_3	ζ_3	R_4	ζ_4	n	$\bar{D}_n^{(4)}$	Error	Time
0.005	1	1	2	0	2.5	1.5	1.5	0.5	3	0.17110454D+01	0.14D−10	0.05
0.005	2	1	3	1	4.5	2.5	4.0	1.5	3	0.87739848D−05	0.93D−12	0.05
0.999	2	2	3	2	3.0	2.0	2.5	2.5	3	0.65822714D−05	0.11D−11	0.05
0.999	3	2	2	3	3.5	1.5	2.5	0.5	4	0.26026122D+00	0.41D−11	0.10
0.999	3	3	3	4	2.0	2.0	1.5	1.5	3	0.74827952D−02	0.17D−10	0.05
0.010	4	3	3	4	3.5	2.0	3.0	1.5	4	0.11672025D+00	0.12D−10	0.10
0.999	4	3	5	5	6.5	1.0	5.5	0.5	4	0.39003836D+02	0.10D−09	0.10
0.005	4	4	5	5	4.5	1.5	3.0	1.0	4	0.24122097D+02	0.19D−09	0.10

Note. Time is in milliseconds. $n_x = \lambda$, $\nu = n_3 + n_4 + \frac{1}{2}$, $n_\gamma = 2(n_3 + n_4) + 1$, $\zeta_1 = \zeta_3$, and $\zeta_2 = \zeta_4$.

TABLE IV
Values of $\tilde{\mathcal{H}}(s)$ with 20 Correct Decimals

s	n_3	n_4	n_k	λ	R_1	ζ_3	ζ_4	max	$\tilde{\mathcal{H}}(s)$
0.999	1	1	2	0	2.0	1.5	1.0	106	0.4389694801769310D−01
0.999	2	1	2	1	2.5	1.0	1.0	128	0.8381930355747709D+00
0.999	2	2	2	2	4.5	1.5	0.5	225	0.6591267611907475D−02
0.999	2	2	3	2	3.0	1.5	0.5	155	0.2416349159698181D−01
0.999	3	2	3	2	5.0	2.0	1.0	218	0.8345089126157430D−04
0.999	3	3	3	3	4.5	1.5	0.5	168	0.1444960392938570D+00
0.999	4	3	3	3	2.0	2.0	1.0	133	0.1337354257788697D+00
0.999	4	4	4	4	4.0	2.0	1.0	139	0.2113558111341813D−01

Note. $n_x = \lambda$, $\nu = n_3 + n_4 + \frac{1}{2}$, $n_\gamma = 2(n_3 + n_4) + 1$, and $\zeta_1 = \zeta_2 = 0.50$.

TABLE V
Evaluation of $\tilde{\mathcal{H}}(s)$ Eq. (55) Using the $H\bar{D}$-Transformation of Order $n(H\bar{D}_n^{(2)})$ Eq. (53)

s	n_3	n_4	n_k	λ	R_1	ζ_3	ζ_4	n	$H\bar{D}_n^{(2)}$	Error	Time
0.999	1	1	2	0	2.0	1.5	1.0	6	0.4389694802D−01	0.52D−12	0.03
0.999	2	1	2	1	2.5	1.0	1.0	5	0.8381930363D+00	0.70D−09	0.02
0.999	2	2	2	2	4.5	1.5	0.5	6	0.6591267605D−02	0.66D−11	0.03
0.999	2	2	3	2	3.0	1.5	0.5	6	0.2416349160D−01	0.99D−12	0.04
0.999	3	2	3	2	5.0	2.0	1.0	6	0.8345089101D−04	0.25D−12	0.03
0.999	3	3	3	3	4.5	1.5	0.5	5	0.1444960399D+00	0.57D−09	0.03
0.999	4	3	3	3	2.0	2.0	1.0	6	0.1337354259D+00	0.87D−10	0.03
0.999	4	4	4	4	4.0	2.0	1.0	6	0.2113558111D−01	0.35D−12	0.03

Note. Time is in milliseconds. $n_x = \lambda$, $\nu = n_3 + n_4 + \frac{1}{2}$, $n_\gamma = 2(n_3 + n_4) + 1$, and $\zeta_1 = \zeta_2 = 0.50$.

TABLE VI

Evaluation of $\tilde{\mathcal{H}}(s)$ Eq. (55) Using the $\bar{D}$-Transformation of Order $n(\bar{D}_n^{(4)})$ Eq. (38)

s	n_3	n_4	n_k	λ	R_1	ζ_3	ζ_4	n	$\bar{D}_m^{(4)}$	Error	Time
0.999	1	1	2	0	2.0	1.5	1.0	3	0.4389694802D−01	0.37D−12	0.06
0.999	2	1	2	1	2.5	1.0	1.0	3	0.8381930359D+00	0.34D−09	0.05
0.999	2	2	2	2	4.5	1.5	0.5	3	0.6591267646D−02	0.34D−10	0.06
0.999	2	2	3	3	3.0	1.5	0.5	3	0.2416349160D−01	0.31D−11	0.06
0.999	3	2	3	3	5.0	2.0	1.0	3	0.8345089215D−04	0.89D−12	0.05
0.999	3	3	3	3	4.5	1.5	0.5	3	0.1444960394D+00	0.15D−09	0.05
0.999	4	3	3	4	2.0	2.0	1.0	3	0.1337354258D+00	0.54D−10	0.05
0.999	4	4	4	4	4.0	2.0	1.0	3	0.2113558111D−01	0.16D−11	0.05

Note. Time is in milliseconds. $n_x = \lambda$, $\nu = n_3 + n_4 + \frac{1}{2}$, $n_\gamma = 2(n_3 + n_4) + 1$, and $\zeta_1 = \zeta_2 = 0.50$.

TABLE VII

Values of $\mathcal{K}_{n_1 00, n_3 00}^{n_2 00, n_4 00}$ Eq. (30) with 20 Correct Decimals

n_1	n_2	n_3	n_4	R_3	ζ_3	R_4	ζ_4	$\tilde{\mathcal{K}}_{n_1 00, n_2 00}^{n_3 00, n_4 00}$
1	1	1	1	6.50	2.50	2.00	1.00	0.1499696884201018D−01
2	1	2	1	6.50	4.00	4.00	3.00	0.1131392221111710D+00
2	2	2	2	8.00	3.50	2.00	3.00	0.4605249321948066D+01
2	2	3	2	9.50	3.50	3.00	3.00	0.1849981520442438D+01
2	2	3	3	7.00	2.50	3.00	3.00	0.1069300805307034D+04
2	2	4	3	9.50	3.50	4.00	3.00	0.1097122311454484D+02
2	2	4	4	8.00	3.00	3.50	3.50	0.1356218523398202D+02

Note. $\mathbf{R}_3 = (R_3, 0, 0)$, $\mathbf{R}_4 = (R_4, 0, 0)$, $\zeta_1 = \zeta_3$, and $\zeta_2 = \zeta_4$.

TABLE VIII

Evaluation of $\mathcal{K}_{n_1 00, n_3 00}^{n_2 00, n_4 00}$, Eq. (30) Using the $H\bar{D}$-Transformation of Order $n(H\bar{D}_n^{(2)})$ Eq. (53)

n_1	n_2	n_3	n_4	R_3	ζ_3	R_4	ζ_4	n	$\tilde{\mathcal{K}}_{n_1 00, n_2 00}^{n_3 00, n_4 00}$	Error	Time
1	1	1	1	6.5	2.5	2.0	1.0	9	0.1499696884D−01	0.38D−12	1.10
2	1	2	1	6.5	4.0	4.0	3.0	9	0.1131392222D+00	0.43D−10	3.23
2	2	2	2	8.0	3.5	2.0	3.0	10	0.4605249322D+01	0.17D−09	6.81
2	2	3	2	9.5	3.5	3.0	3.0	9	0.1849981521D+01	0.59D−09	5.47
2	2	3	3	7.0	2.5	3.0	3.0	9	0.1069300805D+04	0.12D−08	5.42
2	2	4	3	9.5	3.5	4.0	3.0	10	0.1097122311D+02	0.57D−09	6.86
2	2	4	4	8.0	3.0	3.5	3.5	10	0.1356218523D+02	0.29D−10	6.87

Note. Time is in milliseconds. $\mathbf{R}_3 = (R_3, 0, 0)$, $\mathbf{R}_4 = (R_4, 0, 0)$, $\zeta_1 = \zeta_3$, and $\zeta_2 = \zeta_4$.

TABLE IX

Evaluation of $\mathcal{K}_{n_1 00, n_3 00}^{n_2 00, n_4 00}$ Eq. (30) Using the $\bar{D}$-Transformation of Order $n(\bar{D}_m^{(4)})$ Eq. (39)

n_1	n_2	n_3	n_4	R_3	ζ_3	R_4	ζ_4	n	$\tilde{\mathcal{K}}_{n_1 00, n_2 00}^{n_3 00, n_4 00}$	Error	Time
1	1	1	1	6.5	2.5	2.0	1.0	4	0.1499696884D−01	0.11D−12	1.65
2	1	2	1	6.5	4.0	4.0	3.0	4	0.1131392221D+00	0.13D−10	5.01
2	2	2	2	8.0	3.5	2.0	3.0	4	0.4605249322D+01	0.37D−09	8.38
2	2	3	2	9.5	3.5	3.0	3.0	4	0.1849981521D+01	0.10D−09	8.42
2	2	3	3	7.0	2.5	3.0	3.0	4	0.1069300805D+04	0.11D−08	8.40
2	2	4	3	9.5	3.5	4.0	3.0	4	0.1097122312D+02	0.92D−09	8.41
2	2	4	3	9.5	3.5	4.0	3.0	4	0.1097122312D+02	0.92D−09	8.41
2	2	4	4	8.0	3.0	3.5	3.5	4	0.1356218523D+02	0.76D−10	8.38

The calculation times are evaluated on an IBM RS 6000 340.

A comparative study is tabulated for $H\bar{D}$- and $\bar{D}$-transformation methods (inner semi-infinite integrals: Tables I and II for the three-center Coulomb integrals, Tables III–VI for the hybrid integrals, followed by Tables VIII and IX of the complete expression of the three-center Coulomb integrals).

7. CONCLUSION

This work presents the nonlinear $H\bar{D}$-transformation approach to efficient evaluation of three-center Coulomb and two electron hybrid integrals over Slater type orbitals in the molecular context.

The approach relies on properties of the Bessel functions and a finite series expansion of the hypergeometric function appearing in the integrands.

It is shown that the integrand satisfies a linear differential equation suitable for application of the nonlinear D- and $\bar{D}$-transformations and the order of this equation can be reduced simplifying the linear system required to estimate the integrand in the $H\bar{D}$ method.

The aim of this study is to show that the $H\bar{D}$ is more efficient. For a given high accuracy it is 2 times faster than the $\bar{D}$ approach. The factor gained is reflected in the evaluation of complete integrals (see Tables VIII and IX).

The resulting algorithm has been written in Fortran 77 and tested in comparison with the $\bar{D}$ program previously written. Precise evaluation required for chemically significant values remains readily accessible and the calculation times are reduced by a factor of 2 for the $H\bar{D}$, compared with the $\bar{D}$ approach.

The progress represented by the $H\bar{D}$ approach is another useful step in developing software for evaluating molecular integrals over Slater type orbitals.

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