Theor Chem Acc (2007) 117:213–222
DOI 10.1007/s00214-006-0179-0

REGULAR ARTICLE

Nonlinear transformation methods for accelerating the convergence of Coulomb integrals over exponential type functions

Hassan Safouhi · Ahmed Bouferguene

Received: 1 June 2006 / Accepted: 27 September 2006 / Published online: 3 November 2006

Abstract It is well known that in any ab initio molecular orbital (MO) calculation, the major task involves the computation of molecular integrals, among which the computation of Coulomb integrals are the most frequently encountered. As the molecular system gets larger, computation of these integrals becomes one of the most laborious and time consuming steps in molecular systems calculation. Improvement of the computational methods of molecular integrals would be indispensable to a further development in computational studies of large molecular systems. The atomic orbital basis functions chosen in the present work are Slater type functions. These functions can be expressed as finite linear combinations of B functions which are suitable to apply the Fourier transform method. The difficulties of the numerical evaluation of the analytic expressions of the integrals of interest arise mainly from the presence of highly oscillatory semi-infinite integrals. In this work, we present a generalized algorithm based on the nonlinear $\overline{D}$ transformation of Sidi, for a precise and fast numerical evaluation of molecular integrals over Slater type functions and over B functions. Numerical results obtained for the three-center two-electron Coulomb and hybrid integrals over B functions and over Slater type functions. Comparisons with numerical results obtained using alternatives approaches and an existing code are listed.

H. Safouhi (✉) · A. Bouferguene
Campus Saint-Jean, University of Alberta, 8406,
91 Street, Edmonton, AB T6C 4G9, Canada
e-mail: hassan.safouhi@ualberta.ca

A. Bouferguene
e-mail: ahmed.bouferguene@ualberta.ca

Keywords Nonlinear transformations · Extrapolation methods · Numerical integration · Molecular integrals · Slater type functions · B functions

1 Introduction

In the numerical treatment of scientific problems, slowly convergent or divergent sequences and series and oscillatory integrals occur abundantly. Therefore, convergence accelerators and nonlinear transformation methods for accelerating the convergence of infinite series and integrals have been invented and applied to various situations. Those techniques have been applied to molecular multicenter integrals over exponential type functions [1] and over B functions [2–4].

It is well known that in any ab initio molecular orbital (MO) calculation, the major task involves the computation of molecular integrals, among which the computation of two-electron Coulomb integrals are the most frequently encountered. As the molecular system gets larger, computation of these integrals becomes one of the most laborious and time consuming steps in molecular systems calculation. Improvement of the computational methods of molecular integrals would be indispensable to a further development in computational studies of large molecular systems.

In ab initio calculations using the LCAO-MO approximation, molecular orbitals are built from a linear combination of atomic orbitals. Thus, the choice of a reliable basis functions is of prime importance in accurate molecular integral calculations. A good atomic orbital basis should decay exponentially for large distances [5] and should also satisfy Kato's conditions for

analytical solutions of the appropriate Schrödinger equation [6].

Exponential type functions (ETFs) satisfy the aforementioned mathematical requirements, this is why they are better suited than gaussian type functions (GTFs) to represent electron wave functions near the nucleus and at long range. From this it follows implies that a smaller number of ETFs than GTFs is needed for comparable accuracy.

Previous work [7–11] on the accurate and fast numerical evaluation of molecular multicenter Coulomb integrals over B functions [14–16] and over Slater type functions (STFs) [12,13] using nonlinear transformations continues with the present contribution.

Among the integrals required to develop electronic structure theory over STFs, hybrid and three-center two-electron Coulomb integrals are the most difficult to evaluate rapidly and accurately. These integrals are given by:

$$\begin{aligned}\mathcal{K}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4} = & \int \left[\chi_{n_1,l_1}^{m_1}\left(\zeta_1,\vec{R}-\overrightarrow{OA}\right)\right]^* \\ & \times\left[\chi_{n_3,l_3}^{m_3}\left(\zeta_3,\vec{R}'-\overrightarrow{OB}\right)\right]^* \\ & \times\frac{1}{\left|\vec{R}-\vec{R}'\right|}\,\chi_{n_2,l_2}^{m_2}\left(\zeta_2,\vec{R}-\overrightarrow{OA}\right) \\ & \times\chi_{n_4,l_4}^{m_4}\left(\zeta_4,\vec{R}'-\overrightarrow{OC}\right)\,\mathrm{d}\vec{R}\,\mathrm{d}\vec{R}', \end{aligned} \tag{1}$$

where $\chi_{n,l}^{m}\left(\zeta,\vec{r}\right)$ is a Slater function, n, l and m are the quantum numbers, A, C and D are arbitrary points of the euclidian space, while O stands for the origin of the fixed coordinate system.

Hybrid integrals, $\mathcal{H}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4}$, correspond to the case where $B = A$.

The above integrals can be expressed in terms of integrals over the so-called B functions [14–16]. The advantage of using B functions is the fact that their Fourier transforms are exceptionally simple [17] and this is why they are suitable to apply the Fourier transform method [18,19]. Analytic expressions are obtained for the integrals under consideration and they involve two-dimensional integral representations. The semi-infinite inner x integrals are highly oscillatory due to the presence of hypergeometric series and spherical Bessel functions. The accurate and rapid numerical evaluation of the molecular integrals under consideration depend strongly on how fast and accurate one can evaluate these semi-infinite inner x integrals.

It is shown [7,8] that these hypergeometric series can be reduced to a finite sum and that the obtained integrands satisfy all the conditions to apply the nonlinear $\overline{D}$ transformation of Sidi [20,21]. With the help of practical properties of the sine and Bessel functions, a highly efficient algorithm for the numerical evaluation of the semi-infinite spherical Bessel integral functions occurring in the analytic expressions of the molecular integrals over B functions or over STFs is now developed.

The purpose of the present work is the development of algorithms for accurate and rapid numerical evaluation of the Coulomb and hybrid integrals. In these algorithms, we used the nonlinear $\overline{D}$ transformation, which is shown to be highly efficient for improving convergence of the semi-infinite spherical Bessel integrals occurring in the analytic expressions of the molecular integrals under consideration [7–9]. Special cases are presented and discussed.

Note that the algorithm described in the present work has been applied to three-center nuclear attraction integrals and to the notorious four-center two-electron Coulomb and exchange integrals [22]. Extensive numerical results for the molecular integrals mentioned above with linear and nonlinear molecules, and comparisons with results from the literature and results obtained using existing codes such as Alchemy package [23] and ADGGSTNGINT, using STOnG code developed by Rico et al. [24], can be found in [22].

Comparisons with alternatives using the epsilon algorithm of Wynn [25] and Levin's u transform [26] are presented. Numerical results that we obtained for the molecular integrals with different values of quantum numbers are in a complete accordance with those obtained using ADGGSTNGINT code developed by Rico et al. [24].

2 General definitions and properties

The Slater type functions (STFs) are defined in normalized form according to the following relationship [12, 13]:

$$\chi_{n,l}^{m}(\zeta,\vec{r}) \;=\; \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}}\,r^{n-1}\,\mathrm{e}^{-\zeta r}\,Y_l^m(\theta_{\vec{r}},\varphi_{\vec{r}}), \tag{2}$$

where n, l, m are the quantum numbers, $Y_l^m(\theta,\varphi)$ stands for the surface spherical harmonic [27].

STFs can be expressed as finite linear combinations of B functions [16]:

$$\begin{aligned}\chi_{n,l}^{m}(\zeta,\vec{r}) \;=\; & \frac{1}{\zeta^{n-1}}\sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}} \\ & \times\sum_{p=\tilde{p}}^{n-l}\frac{(-1)^{n-l-p}\;2^{2p+2l-n}\;(l+p)!}{(2p-n+l)!(n-l-p)!}\,B_{p,l}^{m}(\zeta,\vec{r}),\end{aligned} \tag{3}$$

where

$$\tilde{p} = \begin{cases} \dfrac{n-l}{2} & \text{if } n-l \quad \text{is even} \\ \dfrac{n-l+1}{2} & \text{if } n-l \quad \text{is odd.} \end{cases} \tag{4}$$

The B functions are defined as follows [15,16] :

$$B^m_{n,l}(\zeta,\vec{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!}\, \widehat{k}_{n-\frac{1}{2}}(\zeta r)\; Y^m_l(\theta_{\vec{r}},\varphi_{\vec{r}}), \tag{5}$$

where $\widehat{k}_{n+\frac{1}{2}}(z)$ stands for the reduced Bessel function [14,15] :

$$\hat{k}_{n+\frac{1}{2}}(z) \;=\; z^n\, \mathrm{e}^{-z} \sum_{j=0}^{n} \frac{(n+j)!}{j!\,(n-j)!}\frac{1}{(2\,z)^j}. \tag{6}$$

This function satisfies the following recurrence relation [14]:

$$\widehat{k}_{n+\frac{1}{2}}(z) \;=\; (2n-1)\,\widehat{k}_{n-\frac{1}{2}}(z) + z^2\,\widehat{k}_{(n-1)-\frac{1}{2}}(z). \tag{7}$$

The Fourier transform $\overline{B}^m_{n,l}(\zeta,\vec{p})$ of $B^m_{n,l}(\zeta,\vec{r})$ is given by [17]:

$$\overline{B}^m_{n,l}(\zeta,\vec{p}) \;=\sqrt{\frac{2}{\pi}}\,\zeta^{2n+l-1}\,\frac{(-i|p|)^l}{(\zeta^2+|p|^2)^{n+l+1}}\; Y^m_l(\theta_{\vec{p}},\varphi_{\vec{p}}). \tag{8}$$

The spherical Bessel function $j_\lambda(x)$ is related to the Bessel function of the first kind $J_{\lambda+\frac{1}{2}}(x)$ by the following relation:

$$j_\lambda(x) \;=\; [\pi/(2\,x)]^{\frac{1}{2}}\; J_{\lambda+\frac{1}{2}}(x), \tag{9}$$

where the Bessel function of the first kind $J_{\lambda+\frac{1}{2}}(x)$ is given by:

$$J_{\lambda+\frac{1}{2}}(x) \;=\; \left(\frac{x}{2}\right)^{\lambda+\frac{1}{2}} \sum_{k=0}^{+\infty} \frac{\left(-x^2/4\right)^k}{k!\,\Gamma(\lambda+k+1)}. \tag{10}$$

The spherical Bessel function $j_l(x)$ and its first derivative $j'_l(x)$ satisfy the following recurrence relations [28]:

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

In the following, we write $j^n_{l+\frac{1}{2}}$ with $n = 1,2,\ldots$ for the successive positive zeros of $j_l(x)$. $j^0_{l+\frac{1}{2}}$ are assumed to be 0.

The hypergeometric function is given by [28]:

$${}_2F_1(\alpha,\beta;\gamma;x) \;=\; \sum_{r=0}^{+\infty} \frac{(\alpha)_r\;(\beta)_r\;x^r}{(\gamma)_r\;r!}, \tag{12}$$

where $(\alpha)_n$ represents the Pochhammer symbol [28].

The infinite series (12) converges only for $|x| < 1$, and they converge quite slowly if $|x|$ is slightly less than one. The corresponding functions nevertheless are defined in a much larger subset of the complex plane, including the case $|x| > 1$. Convergence problems of this kind can often be overcome by using nonlinear sequence transformations [29].

Note that if α or β in the infinite series (12) is a negative integer, then $(\alpha)_{-\alpha}$ or $(\beta)_{-\beta}$ vanishes and consequently the hypergeometric function (12) will be reduced to a finite sum.

By using Eq. (3), we can express $\mathcal{K}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$ and $\mathcal{H}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$ as finite linear combinations of integrals involving B functions. These integrals over B functions are given by:

$$\begin{aligned} {}_B\mathcal{K}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3} &= \int_{\vec{r},\vec{r}'} \left[B^{m_1}_{n_1,l_1}\left(\zeta_1,\vec{r}\right)\right]^* \left[B^{m_3}_{n_3,l_3}\left(\zeta_3,\vec{r}\,'-\left(\vec{R}_3-\vec{R}_4\right)\right)\right]^* \\ &\quad\times\frac{1}{|\vec{r}-\vec{r}\,'-\vec{R}_4|}\; B^{m_2}_{n_2,l_2}\left(\zeta_2,\vec{r}\right)\; B^{m_4}_{n_4,l_4}\left(\zeta_4,\vec{r}\,'\right)\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' \qquad (13) \\ &= \frac{1}{2\pi^2}\int_{\vec{x}} \frac{\mathrm{e}^{i\vec{x}.\vec{R}_4}}{x^2}\left\langle B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\left|\mathrm{e}^{-i\vec{x}.\vec{r}}\right|B^{m_2}_{n_2,l_2}(\zeta_2,\vec{r})\right\rangle_{\vec{r}} \\ &\quad\times\left\langle B^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}\,')\left|\mathrm{e}^{-i\vec{x}.\vec{r}\,'}\right|\right. \\ &\quad\times\left. B^{m_3}_{n_3,l_3}\left(\zeta_3,\vec{r}\,'-(\vec{R}_3-\vec{R}_4)\right)\right\rangle^*_{\vec{r}\,'}\mathrm{d}\vec{x}, \qquad (14) \end{aligned}$$

where $\vec{r} = \vec{R} - \overrightarrow{OA}$, $\vec{r}\,' = \vec{R}' - \overrightarrow{OC}$, $\vec{R}_3 = \overrightarrow{AB}$ and $\vec{R}_4 = \overrightarrow{AC}$.

In the case of hybrid integrals, $\vec{R}_3 = \overrightarrow{AB} = \overrightarrow{O}$.

It is shown that the term $\left\langle B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\left|\mathrm{e}^{-i\vec{x}.\vec{r}}\right|B^{m_2}_{n_2,l_2}(\zeta_2,\vec{r})\right\rangle_{\vec{r}}$ in the above equation, has an analytic expression involving a hypergeometric function which is given by [7]:

$$\begin{aligned} {}_2F_1\left(\frac{l-k-l_1-l_2+1}{2},\frac{l-k-l_1-l_2}{2}+1;\right. \\ \left. l+\frac{3}{2};\frac{-x^2}{(\zeta_1+\zeta_2)^2}\right), \end{aligned} \tag{15}$$

where k and l are positive integers. We showed that the above hypergeometric function reduces to a finite expansion since one of the two first arguments of the hypergeometric function is a negative integer [7,8].

The Fourier transform method allowed analytic expression to be developed for the integrals over $\vec{r}\,'$ occurring in Eq. (14) [18,19]:

$$\left\langle B^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}\,')\left|\mathrm{e}^{-i\vec{x}.\vec{r}''}\right|B^{m_3}_{n_3,l_3}\left(\zeta_3,\vec{r}\,'-(\vec{R}_3-\vec{R}_4)\right)\right\rangle^*_{\vec{r}\,'}.$$

The above results led to an analytic expressions for the three-center two-electron Coulomb and hybrid integrals over B functions, which are given by [10]:

$$
\begin{aligned}
&\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} \\
&= 8(4\pi)^3 \sqrt{\pi}\, \zeta_1^{l_1}\, \zeta_2^{l_2}\, \zeta_3^{2n_3+l_3-1}\, \zeta_4^{2n_4+l_4-1} \\
&\quad \times \frac{(2l_3+1)!!\,(2l_4+1)!!\,(n_3+l_3+n_4+l_4+1)!}{2^{l_1+l_2+1}\,(n_1+l_1)!\,(n_2+l_2)!\,(n_3+l_3)!\,(n_4+l_4)!} \\
&\quad \times \sum_{l=l_{\min},2}^{l_1+l_2} \frac{(-i)^l}{2^{2n_1+2n_2+l}}\, \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \\
&\quad \times \sum_{k=2}^{n_1+n_2} \sum_{i=k_1}^{k_2} \left[\frac{2^k\,(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)!} \right] \\
&\quad \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_4 m_4 | l_4 - l'_4 m_4 - m'_4 | l'_4 m'_4 \rangle}{(2l'_4+1)!![2(l_4-l'_4)+1]!!} \\
&\quad \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]!!} \\
&\quad \times \sum_{l'=l'_{min},2}^{l'_3+l'_4} \langle l'_4 m'_4 | l'_3 m'_3 | l' m'_4 - m'_3 \rangle R^{l'}_{34}\, Y_{l'}^{m'_3-m'_4}(\theta_{\overrightarrow{R}_{34}}, \varphi_{\overrightarrow{R}_{34}}) \\
&\quad \times \sum_{l_{34}=l''_{min},2}^{l_3-l'_3+l_4-l'_4} \langle l_3 - l'_3 m_3 - m'_3 | l_4 - l'_4 m_4 - m'_4 | l_{34} m_{34} \rangle \\
&\quad \times \sum_{\lambda=\lambda_{min},2}^{l+l_{34}} i^{\lambda} \langle l m_2 - m_1 | l_{34} (m_3 - m'_3) - (m_4 - m'_4) | \lambda \mu \rangle \\
&\quad \times \sum_{j=0}^{\Delta l} \binom{\Delta l}{j} \frac{(-1)^j}{2^{n_3+n_4+l_3+l_4-j+1}(n_3+n_4+l_3+l_4-j+1)!} \\
&\quad \times \frac{\zeta_s^{n_k-l-1}\,\Gamma(k+l_1+l_2+l+1)}{\Gamma(l+\frac{3}{2})} \sum_{r=0}^{\eta'} (-1)^r \frac{(\frac{\eta}{2})_r\,(\frac{\eta+1}{2})_r}{(l+\frac{3}{2})_r\, r!\, \zeta_s^{2r}} \\
&\quad \times \int_{s=0}^{1} s^{n_3+l_3+l_4-l'_4}\,(1-s)^{n_4+l_4+l_3-l'_3}\, Y_{\lambda}^{\mu}(\theta_{\vec{v}}, \varphi_{\vec{v}}) \\
&\quad \times \left[\int_0^{+\infty} \frac{x^{n_x}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\widehat{k}_v[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\, j_\lambda(v\,x)\,\mathrm{d}x \right] \mathrm{d}s,
\end{aligned}
\tag{16}
$$

where

$$
\begin{aligned}
&k_1 = \max(1, k-n_2),\ k_2 = \min(n_1, k-1),\ \zeta_s = \zeta_1 + \zeta_2 \\
&n_x = l_3 - l'_3 + l_4 - l'_4 + 2r + l,\ n_k = k + l_1 + l_2 \\
&n_\gamma = 2(n_3 + l_3 + n_4 + l_4) - (l'_3 + l'_4) - l' + 1 \\
&\eta = l - k - l_1 - l_2 + 1, \quad \Delta l = \frac{l_3 + l_4 - l'}{2}
\end{aligned}
$$

$\eta' = -\frac{\eta}{2}$ if η is even, otherwise $\eta' = -\frac{\eta+1}{2}$

$\vec{v} = (1-s)\left(\overrightarrow{R}_3 - \overrightarrow{R}_4\right) + \overrightarrow{R}_4 = (1-s)\,\overrightarrow{R}_{34} + \overrightarrow{R}_4$

$\mu = (m_2 - m_1) - (m_3 - m'_3) + (m_4 - m'_4)$

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

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

$m_{34} = (m_3 - m'_3) - (m_4 - m'_4)$

$\langle l_1 m_1 | l_2 m_2 | l_3 m_3 \rangle$ stands for the Gaunt coefficients [30].

v and R_{34} stand for the modulus of $\vec{v}$ and $\overrightarrow{R}_{34}$, respectively.

The analytic expression of hybrid integrals over B functions can be obtained by replacing R_3 by 0 in the above equation.

Note that with the help of Eq. (3), one can develop analytic expressions for the molecular integrals under consideration using the above analytic development.

Let us consider the two-dimensional integral representations occurring in the above equation, which will be refereed to as $\mathcal{K}$, and which is given by [7,8]:

$$
\begin{aligned}
\mathcal{K} = &\int_{s=0}^{1} s^{n_3+l_3+l_4-l'_4}\,(1-s)^{n_4+l_4+l_3-l'_3}\, Y_{\lambda}^{\mu}(\theta_{\vec{v}}, \varphi_{\vec{v}}) \\
&\times \left[\int_0^{+\infty} \frac{x^{n_x}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\widehat{k}_v[R\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\, j_\lambda(v\,x)\,\mathrm{d}x \right] \mathrm{d}s.
\end{aligned}
\tag{17}
$$

3 The development of the algorithm

Let us consider the semi-infinite spherical Bessel integral, which will be referred to as $\mathcal{K}(s)$ and whose integrand will be referred to as $\mathcal{F}(x)$, occurring in Eq. (17). It is well known that numerical integration is very difficult when the oscillatory part of the integrand is a spherical Bessel function $j_\lambda(v\,x)$, in particular for large values of λ and v since the zeros of the function become closer and thus the oscillations become sharp.

First, we will separate the case where v is very close to 0 ($v \to 0$). In this case, the semi-infinite integral $\mathcal{K}(s)$ vanishes if $\lambda \neq 0$ and when $\lambda = 0$, we replaced $j_0(v\,x)$ by its Taylor development and we obtained:

$$
\begin{aligned}
\mathcal{K}(s) \approx &\int_0^{+\infty} \frac{x^{n_x}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\hat{k}_v[R\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \\
&\times \left(1 - \frac{v^2 x^2}{3!} + \frac{v^4 x^4}{5!} - \cdots\right) \mathrm{d}x.
\end{aligned}
\tag{18}
$$

For the evaluation of the above semi-infinite integral, we used Gauss–Laguerre quadrature of order 64.

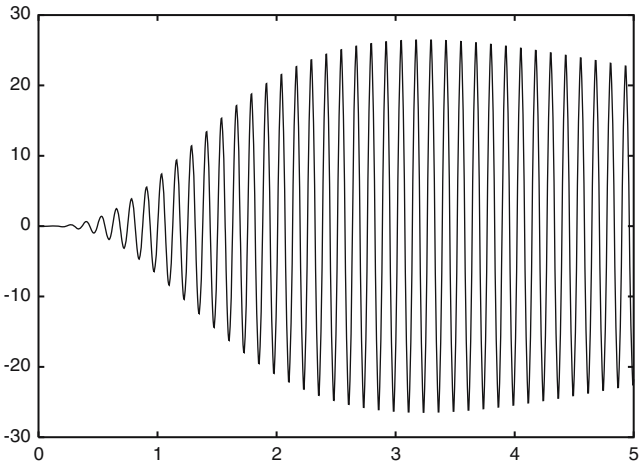

Fig. 1 The integrand $\mathcal{F}(x)$ of the semi-infinite integral $\mathcal{K}(s)$ (17). $s = 0.998$, $\nu = 13/2$, $n_\gamma = 5$, $n_k = 2$, $n_x = 4$, $\lambda = 4$, $R = 2.0$, $\zeta_s = 2.0$ and $\zeta_3 = \zeta_4 = 1.0$. ($v = 49.996$)

The semi-infinite integral $\mathcal{K}(s)$ can be transformed into an infinite series:

$$\mathcal{K}(s) = \sum_{n=0}^{+\infty} \int_{j_{\lambda,\nu}^n}^{j_{\lambda,\nu}^{n+1}} \frac{x^{n_x}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\hat{k}_\nu[R\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(\nu x)\,\mathrm{d}x, \qquad (19)$$

where $j_{\lambda,\nu}^0$ is assumed to be 0 and $j_{\lambda,\nu}^n = j_{\lambda+\frac{1}{2}}^n/\nu$, $n = 1, 2, \ldots$ which are the successive positive zeros of $j_\lambda(\nu x)$.

Let us consider the function $\gamma(s,x)$. If $s = 0$ or 1 then $\gamma(s,x)$ becomes a constant:

$$\gamma(0,x) = \zeta_4 \quad \text{and} \quad \gamma(1,x) = \zeta_3.$$

From this it follows that when $s = 0$ or 1 the exponentially decreasing part of the integrand $\hat{k}_\nu[R\gamma(s,x)]$ becomes also a constant and thus the strong oscillation of the spherical Bessel function cannot be damped and suppressed. Note also that when $s = 0$ or 1, the asymptotic behavior of the integrand cannot be represented by a function of the form $\mathrm{e}^{-\alpha x} j_\lambda(x)$. This is why, in these regions, Gauss–Laguerre quadrature even to high order gives inaccurate results and presents severe numerical difficulties for these kinds of highly oscillatory integrals, especially for large values of ν and λ since the integrands oscillations become very rapid because of the spherical Bessel functions (see Fig. 1). It should be mentioned that the regions where s is close to 0 or 1 carry a very small weight due to factors $s^{i_2}(1-s)^{i_1}$ in the integrand (17) [31].

The infinite series (19) is slowly convergent as it can be seen from the numerical Tables (1). Note that for large values of ν and λ, one needs to sum more than 10,000 terms to obtains values with 10–15 correct digits. This slow convergence problem, prevented the use of this infinite series for the evaluation of $\mathcal{K}(s)$. Note that the use of the infinite series requires the computation of the successive positive zeros of spherical Bessel functions and this presents a severe computational difficulty when the value of λ is large. The convergence of the infinite series could be improved by the use of the epsilon algorithm of Wynn [25] or Levin's u transform [26]. It has been proved that these two convergence accelerators, are the best suited for the infinite series (19). Let I_k be the kth term of the infinite series and S_k be the kth partial sum of the infinite series. The approximation of the infinite series using the epsilon algorithm of Wynn is given by [32]:

$$\begin{aligned} &\epsilon_{-1}^{(n)} = 0 \quad \text{and} \quad \epsilon_0^{(n)} = S_n, \quad n = 0, 1, \ldots \\ &\epsilon_{k+1}^{(n)} = \epsilon_{k-1}^{(n+1)} + \frac{1}{\epsilon_k^{(n+1)} - \epsilon_k^{(n)}}, \; n = 0, 1, \ldots. \end{aligned} \qquad (20)$$

The approximation of the infinite series using Levin's u transform, can be obtained by using the following rules [26]:

$$u_k(S_n) = \frac{\sum_{i=0}^k (-1)^i \binom{k}{i} (n+i+1)^{k-1} S_{n+i}/I_{n+i}}{\sum_{i=0}^k (-1)^i \binom{k}{i} (n+i+1)^{k-1}/I_{n+i}}, \quad n = 0, 1, \ldots. \qquad (21)$$

The convergence of the infinite series was improved using the above convergence accelerators (see Table 1). Unfortunately, the calculation times are still prohibitively long for a high pre-determined accuracy. Note that, even for small molecules, millions of integrals are required for the calculations. Rapidity is a primordial criterion when a high accuracy needs to be reached.

In previous work [7], we presented an approach based on the nonlinear $\overline{D}$ transformation of Sidi [20,21]. To apply this nonlinear transformation, the integrand should satisfy a linear differential equation with coefficients having asymptotic expansions in a sense of Poincaré series [33]. It is shown that the integrand $\mathcal{F}(x)$ of $\mathcal{K}(s)$ satisfies a fourth order linear differential equation of the form required to apply $\overline{D}$ [7,34]. The symbolic programming language Maple was used to obtain this differential equation [34] and to demonstrate that all the condition required by $\overline{D}$ are satisfied.

The approximation of the semi-infinite integral $\mathcal{K}(s)$ using the nonlinear $\overline{D}$ transformation can be obtained by solving the following set of linear equations [20]:

Table 1 Evaluation of $\mathcal{K}(s)$ (17) obtained using the infinite series (19), Levin's u transform of order n_u, the ϵ algorithm of Wynn of order n_ϵ and the $\overline{D}$ transformation of order $n_{\overline{D}}$. $n_k = 2$, $\lambda = n_x$, $R = 48.0$ and $R_4 = 2.0$. $\nu = 48.002$ when $s = 0.001$ and 49.998 when $s = 0.999$. (Calculation times is in milliseconds)

s	ν	n_γ	n_x	ζ_s	ζ_3	ζ_4	$n_{\max}$	$\widetilde{\mathcal{K}}(s)^{n_{\max}}$	n_u	Error^u	T_u	n_ϵ	Error$^\epsilon$	T_ϵ	$n_{\overline{D}}$	Error$^{\overline{D}}$	$T_{\overline{D}}$
0.001	5/2	1	1	3	1.5	1.0	2,479	0.147893400 (−4)	8	0.56 (−12)	0.25	10	0.90 (−13)	0.29	6	0.59 (−12)	0.12
0.999	5/2	1	1	3	1.5	1.0	2,523	0.541130081 (−5)	7	0.72 (−12)	0.17	8	0.90 (−12)	0.21	4	0.97 (−12)	0.06
0.001	7/2	1	1	4	1.5	0.5	3,024	0.721505467 (−4)	8	0.89 (−12)	0.18	10	0.34 (−12)	0.28	7	0.36 (−12)	0.14
0.999	7/2	1	1	4	1.5	0.5	3,073	0.114992869 (−4)	7	0.93 (−12)	0.17	10	0.53 (−13)	0.26	4	0.79 (−12)	0.07
0.001	9/2	2	2	2	2.0	1.5	4,353	0.692093254 (−4)	13	0.22 (−03)	0.34	12	0.11 (−12)	0.34	9	0.34 (−12)	0.18
0.999	9/2	2	2	2	2.0	1.5	4,474	0.231205890 (−4)	13	0.73 (−04)	0.40	12	0.37 (−13)	0.39	9	0.17 (−12)	0.20
0.001	11/2	2	3	2	2.0	1.5	6,536	0.726654028 (−4)	13	0.13 (−02)	0.40	12	0.51 (−12)	0.40	11	0.90 (−12)	0.28
0.999	11/2	2	3	2	2.0	1.5	6,757	0.248684748 (−4)	13	0.47 (−03)	0.46	12	0.17 (−12)	0.43	9	0.82 (−12)	0.21
0.001	13/2	3	5	3	1.5	1.0	9,952	0.130005096 (−4)	13	0.48 (−02)	0.53	12	0.44 (−12)	0.46	11	0.33 (−12)	0.32
0.999	13/2	3	5	3	1.5	1.0	10,329	0.244210601 (−5)	13	0.90 (−03)	0.48	12	0.74 (−13)	0.42	10	0.33 (−12)	0.25
0.001	15/2	3	5	2	1.5	0.5	10,980	0.779406740 (−2)	13	0.26 (01)	0.46	14	0.15 (−09)	0.46	14	0.36 (−10)	0.40
0.999	15/2	3	5	2	1.5	0.5	11,392	0.170175743 (−3)	13	0.57 (−01)	0.46	14	0.66 (−11)	0.46	14	0.48 (−12)	0.40
0.001	17/2	3	7	4	1.5	0.5	15,669	0.454082090 (−3)	13	0.18 (01)	0.48	14	0.30 (−10)	0.48	14	0.11 (−11)	0.40
0.999	17/2	3	7	4	1.5	0.5	16,282	0.100760454 (−4)	13	0.38 (−01)	0.50	14	0.63 (−12)	0.48	12	0.64 (−12)	0.34
0.001	19/2	3	7	4	2.0	2.0	16,812	0.736936828 (−4)	13	0.32 (00)	0.54	14	0.53 (−11)	0.54	14	0.56 (−13)	0.46
0.999	19/2	3	7	4	2.0	2.0	17,488	0.655692512 (−4)	13	0.23 (00)	0.53	14	0.38 (−11)	0.54	13	0.91 (−12)	0.42

Numbers in parentheses represent powers of 10

$$\overline{D}_n^{(4)} = \int_0^{x_l} \mathcal{F}(t)\mathrm{d}t + \sum_{k=1}^{3} \mathcal{F}^{(k)}(x_l)\, x_l^2 \sum_{i=0}^{n-1} \frac{\bar{\beta}_{k,i}}{x_l^i}, \quad l = 0, 1, \ldots, 3n, \tag{22}$$

where $\overline{D}_n^{(4)}$ and $\bar{\beta}_{k,i}$ for $k = 1, 2, 3$ and $i = 0, 1, \ldots, n-1$ are the $3n+1$ unknowns of the linear system. The $x_l = j_{\lambda,\nu}^{l+1}$ for $l = 0, 1, \ldots$, which are the successive positive zeros of $j_\lambda(\nu x)$.

In [7], we demonstrated the superiority of the nonlinear $\overline{D}$ transformation in the numerical evaluation of the semi-infinite integrals under consideration compared to the approaches using the epsilon algorithm of Wynn [25] or Levin's u transform [26]. In the present work, we performed calculations for the integrals under consideration over B functions and also over STFs and with different values of quantum numbers to show that the approach using nonlinear transformations is highly efficient when evaluating molecular integrals for linear and nonlinear systems.

As it can be seen from Eq. (22), the computation of the successive derivatives of the integrands is necessary. By using Leibnitz formulae, one can easily obtain for $1 \le k \le 3$:

$$\mathcal{F}^{(k)}(x) = \sum_{i=0}^{k} \binom{k}{i} \frac{n_x}{(n_x - i - 1)!}\, x^{n_x - i} \times \sum_{l=0}^{k-i} \binom{k-i}{l} \frac{(2\nu - n_\gamma)!!\, s^l\, (1-s)^l}{(2\nu - n_\gamma - 2l)!!} \gamma(s,x)^{2\nu - n_\gamma - 2l} \times \sum_{n=0}^{k-i-l} \binom{k-i-l}{n} \left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^n \frac{1}{\left[\zeta_s^2 + x^2\right]^{n_k}} \times \sum_{m=0}^{k-i-l-n} \binom{k-i-l-n}{m} \left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^m j_\lambda(\nu x) \times \left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^{k-i-l-n-m} \left[\frac{\widehat{k}_\nu[R\,\gamma(s,x)]}{[\gamma(s,x)]^{2\nu}}\right], \tag{23}$$

where the double factorial is defined by:

$$\begin{aligned} (2k)!! &= 2 \times 4 \times 6 \times \cdots \times (2k) = 2^k\, k! \\ (2k+1)!! &= 1 \times 3 \times 5 \times \cdots \times (2k+1) = \frac{(2k+1)!}{2^k\, k!} \\ 0!! &= 1. \end{aligned}$$

The three successive derivatives of $\dfrac{1}{\left[\zeta_s^2 + x^2\right]^{n_k}}$ with respect to x can be easily computed. The successive derivatives of the spherical Bessel function $j_\lambda(\nu x)$ can be computed recursively using the relations given by (11).

The successive derivatives of the term $\dfrac{\widehat{k}_\nu[R\,\gamma(s,x)]}{[\gamma(s,x)]^{2\nu}}$ can be easily computed by using the Leibnitz formulae with the help of the following properties:

$$\frac{\mathrm{d}}{\mathrm{d}x} = \frac{\mathrm{d}\gamma}{\mathrm{d}x}\frac{\mathrm{d}}{\mathrm{d}\gamma} = s(1-s)\,x\frac{\mathrm{d}}{\gamma\,\mathrm{d}\gamma} \quad \text{and} \quad \left(\frac{\mathrm{d}}{\gamma\,\mathrm{d}\gamma}\right)^i \frac{\widehat{k}_\nu(\gamma)}{\gamma^{2\nu}} = (-1)^i \frac{\widehat{k}_{\nu+i}(\gamma)}{\gamma^{2\nu+i}}. \tag{24}$$

It is clear that the calculations required by the linear system (22) are difficult in particular for large values of

n. Note that as n becomes large, $\overline{D}_n^{(4)}$ converges to the exact value of the semi-infinite integral.

In [8], we showed that $\mathcal{F}(x)$ satisfied a second order differential equation. This second order differential equation can be obtained by substituting $j_\lambda(vx)$ by $\dfrac{\mathcal{F}(x)}{g(x)}$ in the second-order linear differential equation satisfied by $j_\lambda(vx)$, and which is given by [28]:

$$\begin{aligned} j_\lambda(v\,x) &= -\frac{2x}{(v\,x)^2-\lambda^2-\lambda}\,j'_\lambda(v\,x) - \frac{x^2}{(v\,x)^2-\lambda^2-\lambda}\,j''_\lambda(v\,x) \\ &= q_{2,1}(x)\,j'_\lambda(v\,x) \;+\; q_{2,2}(x)\,j''_\lambda(v\,x), \end{aligned} \tag{25}$$

where the function $g(x)$ is given by:

$$g(x) \;=\; \frac{\mathcal{F}(x)}{j_\lambda(vx)} \;=\; \frac{x^{n_x}}{\left[\zeta_s^2+x^2\right]^{n_k}}\,\frac{\widehat{k}_v[R\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}. \tag{26}$$

Note that this technique was first used by Sidi [20,21] for functions of the form $g(x)\,J_{l+\frac{1}{2}}(x)$.

In this work, we used Maple to obtain explicitly this second order differential equation. Let α and β be defined by:

$$\alpha = s\,\zeta_3^2 + (1-s)\,\zeta_4^2 \quad \text{and} \quad \beta = s\,(1-s). \tag{27}$$

For simplicity and without loss of generality we assume $n_x = 1, n_k = 2, \nu = \dfrac{5}{2}, \zeta_s = 1$ and $\alpha = \nu = 1$. The second order linear differential equation is given by :

$$\mathcal{F}(x) \;=\; \frac{q_1(x)}{q_0(x)}\,\mathcal{F}'(x) + \frac{q_2(x)}{q_0(x)}\,\mathcal{F}''(x), \tag{28}$$

where

$$\begin{aligned} q_0(x) = -&\frac{1}{\left(x^2+1\right)^2\left(\beta+x^2\right)\left(\sqrt{\beta+x^2}+\beta+x^2\right)^2} \\ &\times\Bigg[-2\,x^{12}+\Bigg(\lambda-9\,n_\gamma-2\sqrt{\beta+x^2}n_\gamma \\ &-26+\lambda^2-{n_\gamma}^2-10\sqrt{\beta+x^2}-5\,\beta\Bigg)x^{10} \\ &+\Bigg(2\,\lambda\sqrt{\beta+x^2}-21\sqrt{\beta+x^2}\beta-66\,\beta+3\,\beta\,\lambda \\ &-17\,n_\gamma-18\,\beta\,n_\gamma-36\sqrt{\beta+x^2}-30 \\ &+2\,\lambda^2\sqrt{\beta+x^2}-18\sqrt{\beta+x^2}n_\gamma \\ &-\beta\,{n_\gamma}^2+3\,\lambda^2-4\,\beta^2-2\,\beta\,n_\gamma\sqrt{\beta+x^2} \\ &+3\,\lambda+3\,\beta\,\lambda^2-3\,{n_\gamma}^2-2\,{n_\gamma}^2\sqrt{\beta+x^2}\Bigg)x^8 \\ &+\Bigg(-6+3\,\lambda^2+3\,\lambda-7\,n_\gamma-14\sqrt{\beta+x^2}n_\gamma \\ &+4\,\lambda\sqrt{\beta+x^2}-54\,\beta^2-\beta^3-2\,\beta\,{n_\gamma}^2 \\ &-9\,\beta^2 n_\gamma-29\,\beta\,n_\gamma+8\,\beta\,\lambda+8\,\beta\,\lambda^2 \\ &-4\,{n_\gamma}^2\sqrt{\beta+x^2}+4\,\lambda^2\sqrt{\beta+x^2} \\ &-74\sqrt{\beta+x^2}\beta-65\,\beta-11\,\beta^2\sqrt{\beta+x^2} \\ &+3\,\beta^2\lambda 3\,\beta^2\lambda^2+4\,\beta\,\lambda\sqrt{\beta+x^2} \\ &+4\,\beta\,\lambda^2\sqrt{\beta+x^2}-22\,\beta\,n_\gamma\sqrt{\beta+x^2} \\ &-10\sqrt{\beta+x^2}-3\,{n_\gamma}^2\Bigg)x^6 \\ &+\Bigg(\lambda^2+\lambda+n_\gamma+2\sqrt{\beta+x^2}n_\gamma+2\,\lambda\sqrt{\beta+x^2} \\ &-40\,\beta^2-14\,\beta^3-\beta\,{n_\gamma}^2-10\,\beta^2 n_\gamma-12\,\beta\,n_\gamma \\ &+7\,\beta\,\lambda+7\,\beta\,\lambda^2-2\,{n_\gamma}^2\sqrt{\beta+x^2} \\ &+2\,\lambda^2\sqrt{\beta+x^2}-21\sqrt{\beta+x^2}\beta-12\,\beta \\ &-38\,\beta^2\sqrt{\beta+x^2}+2\,\beta^2\lambda^2\sqrt{\beta+x^2}+\beta^3\lambda^2 \\ &+\beta^3\lambda+7\,\beta^2\lambda+7\,\beta^2\lambda^2+2\,\beta^2\lambda\sqrt{\beta+x^2} \\ &+8\,\beta\,\lambda\sqrt{\beta+x^2}+8\,\beta\,\lambda^2\sqrt{\beta+x^2} \\ &-22\,\beta\,n_\gamma\sqrt{\beta+x^2}-{n_\gamma}^2\Bigg)x^4 \\ &+\Bigg(4\,\beta\,\lambda^2\sqrt{\beta+x^2}+4\,\beta\,\lambda\sqrt{\beta+x^2}+2\,\beta^3\lambda \\ &-2\,\beta\,n_\gamma\sqrt{\beta+x^2}-5\,\beta^3+2\,\beta\,\lambda^2-6\,\beta^2-\beta\,n_\gamma \\ &+5\,\beta^2\lambda^2+2\,\beta^3\lambda^2-\beta^2 n_\gamma-11\,\beta^2\sqrt{\beta+x^2} \\ &+4\,\beta^2\lambda^2\sqrt{\beta+x^2}+5\,\beta^2\lambda+2\,\beta\,\lambda \\ &+4\,\beta^2\lambda\sqrt{\beta+x^2}\Bigg)x^2+\beta^3\lambda^2+\beta^2\lambda+\beta^2\lambda^2 \\ &+2\,\beta^2\lambda\sqrt{\beta+x^2}+2\,\beta^2\lambda^2\sqrt{\beta+x^2}+\beta^3\lambda\Bigg] \end{aligned} \tag{29}$$

$$\begin{aligned} q_1(x) = &\frac{-2x^3}{\left(x^2+1\right)\left(\sqrt{\beta+x^2}+\beta+x^2\right)\left(\beta+x^2\right)} \\ &\times\Bigg[\left(\sqrt{\beta+x^2}+4+n_\gamma\right)x^4 \\ &+\Bigg(8\,\beta+\sqrt{\beta+x^2}n_\gamma+n_\gamma+\beta\,n_\gamma+5\sqrt{\beta+x^2} \\ &+\sqrt{\beta+x^2}\beta\Bigg)x^2+4\,\beta^2+\beta\,n_\gamma \\ &+5\sqrt{\beta+x^2}\beta+\sqrt{\beta+x^2}n_\gamma\Bigg] \end{aligned} \tag{30}$$

$$q_2(x) = -x^2. \tag{31}$$

Once the differential equation is obtained explicitly, it becomes easy to show that all conditions required to apply $\overline{D}$ are satisfied. From this it follows that the approximation of the semi-infinite integral $\mathcal{K}(s)$ can be obtained using $\overline{D}_n^{(2)}$, which can be computed by solving a set of linear equations, which is given by:

$$\overline{D}_n^{(2)} = \int_0^{x_l} \mathcal{F}(t)\mathrm{d}t + g(x_l)\, j'_\lambda(vx)\, x_l^2 \sum_{i=0}^{n-1} \frac{\bar{\beta}_{1,i}}{x_l^i}, \quad l = 0,1,\ldots,n, \tag{32}$$

where $\overline{D}_n^{(2)}$ and $\bar{\beta}_{1,i}$ for $i = 0,1,\ldots,n-1$ are the $(n+1)$ unknowns of the linear system. The $x_l = \frac{j_{\lambda+\frac{1}{2}}^{l+1}}{v}$ for $l = 0,1,\ldots$ (the leading positive zeros of $j_\lambda(vx)$).

As it can be seen from the above equation, the order of the linear system is reduced to $(n+1)$. The calculation of the successive derivatives of the integrands is avoided, only the first derivative of spherical Bessel functions is required. Note that if x_l is a zero of $j_\lambda(v\,x)$ then from Eq. (11) and for $\lambda \neq 0$ it follows:

$$j'_\lambda(v\,x_l) = v\, j_{\lambda-1}(v\,x_l) - \frac{\lambda+1}{x_l}\, j_\lambda(v\,x_l) = v\, j_{\lambda-1}(v\,x_l), \tag{33}$$

and when $\lambda = 0$, one can use the Cramer's rule for calculating the approximation $\overline{D}_n^{(2)}$, since the zeros of $j_0(x) = \dfrac{\sin(x)}{x}$ are equidistant. In this case, the expression of $\overline{D}_n^{(2)}$ is given by:

$$\overline{D}_n^{(2)} = \frac{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i)^n F(x_i) \Big/ \left[x_i^2\, g(x_i)\right]}{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i)^n \Big/ \left[x_i^2\, g(x_i)\right]}, \tag{34}$$

where $x_l = \dfrac{(l+1)\,\pi}{v}$ for $l = 0,1,\ldots$ and where $F(x) = \displaystyle\int_0^x \mathcal{F}(t)\,\mathrm{d}t$.

The convergence properties of the nonlinear $\overline{D}$ transformations were analyzed [20,35] and they showed that under certain conditions the approximations $\overline{D}_n^{(m)}$ (m stands for the order of the differential equation that the integrand satisfies) converge to the exact value of the semi-infinite integrals without any constraint. It is demonstrated [9,36], that the integrands of the semi-infinite integrals which occur in the analytic expressions of three-center two-electron Coulomb and hybrid integrals over B functions satisfy all the conditions developed by Sidi for the convergence of the $\overline{D}$ transformation. The approximations $\overline{D}_n^{(2)}$ converge to the exact values of the semi-infinite integrals $\widetilde{\mathcal{K}}(s)$ without any constraint.

4 Numerical discussion

Values of the semi-infinite integral $\mathcal{K}(s)$ are computed with 15 correct decimals using the infinite series (19). Each term of the infinite series is computed using Gauss–Legendre quadrature of order 92.

The finite integrals which occur in Eqs. (20), (21), (22), (32) and (34) are transformed into finite sums as follows:

$$\int_0^{x_n} f(x)\mathrm{d}x = \sum_{l=0}^{n-1} \int_{x_l}^{x_{l+1}} f(x)\mathrm{d}x, \tag{35}$$

and each term of the above finite sum is evaluated using Gauss–Legendre quadrature of order 20 in the case of the $\overline{D}$ transformation and of order 48 in the case of Levin's u transform and the ϵ algorithm of Wynn. When using Gauss–Legendre quadrature of order less than 48, the numerical results obtained using both Levin's u transform and the ϵ algorithm are inaccurate.

The linear systems (22) and (32) were solved using the LU decomposition method.

For the evaluation of the outer s finite integral, which occur in Eq. (17), Gauss–Legendre quadrature of order 48 was used.

For the Gaunt coefficients which occur in the analytic expressions of the molecular integrals, we used the code GAUNT.F developed by Weniger [30]. The spherical harmonics $Y_l^m(\theta,\varphi)$ are computed using the recurrence relations presented in [30].

All the entries are in atomic unit. The calculation times are in milliseconds. All the calculations were performed on a PC Workstation with Intel Xeon Processor with 2.4 GHz.

Table 1 contains values with 15 correct digits of the semi-infinite integral $\mathcal{K}(s)$ (17) obtained using the infinite series (19) ($\widetilde{\mathcal{K}}(s)^{n_{\max}}$), which we sum until $n_{\max}$. In this table we also listed the accuracy and calculation times obtained using Levin's u transform of order n_u, the ϵ algorithm of Wynn of order n_ϵ and the $\overline{D}$ transformation of order $n_{\overline{D}}$.

Table 2 contains values of ${}_B\mathcal{K}_{n_1 l_1 m_1, n_3 l_3 m_3}^{n_2 l_2 m_2, n_4 l_4 m_4}$ (14) with 15 correct digits obtained using the infinite series to evaluate the semi-infinite integrals (Values). It also contains the accuracy obtained using Levin's u transform (21) of order 8, the ϵ algorithm of Wynn (20) of order 8 and the $\overline{D}$ transformation (32) of order 8.

Table 3 contains values of $\mathcal{K}_{n_1 l_1 m_1, n_3 l_3 m_3}^{n_2 l_2 m_2, n_4 l_4 m_4}$ over STFs with 15 correct digits obtained using the infinite series to evaluate the semi-infinite integrals. It also contains the accuracy obtained using Levin's u transform (21) of order 8, the ϵ algorithm of Wynn (20) of order 8 and the $\overline{D}$ transformation (32) of order 8. STOnG are obtained

Table 2 Evaluation of ${}_B\mathcal{K}^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3}$ (14)

n_1	l_1	m_1	n_3	l_3	m_3	n_4	l_4	m_4	Values	Error^u	Error$^\epsilon$	Error$^{\overline{D}}$
1	0	0	1	0	0	1	0	0	0.1177149301 (−4)	0.12 (−12)	0.65 (−12)	0.25 (−12)
2	1	0	2	1	0	1	0	0	0.3381846260 (−5)	0.92 (−12)	0.73 (−11)	0.10 (−11)
2	1	−1	2	1	1	1	0	0	−0.4137845598 (−6)	0.12 (−11)	0.26 (−11)	0.13 (−11)
3	1	0	3	1	0	1	0	0	0.1083637846 (−3)	0.31 (−10)	0.26 (−08)	0.33 (−10)
4	1	0	4	1	0	1	0	0	0.5449603913 (−2)	0.16 (−08)	0.12 (−08)	0.15 (−08)
1	0	0	1	0	0	1	0	0	0.1177149301 (−4)	0.12 (−12)	0.65 (−12)	0.25 (−12)
1	0	0	2	1	0	2	1	0	0.4000009841 (−5)	0.47 (−13)	0.27 (−12)	0.77 (−13)
1	0	0	2	1	−1	2	1	−1	0.4431133378 (−5)	0.11 (−14)	0.17 (−13)	0.22 (−13)
1	0	0	3	1	0	3	1	0	0.2988141332 (−4)	0.28 (−12)	0.28 (−11)	0.41 (−12)
1	0	0	3	2	0	3	2	0	0.7383559276 (−6)	0.48 (−15)	0.69 (−13)	0.31 (−14)
1	0	0	3	2	1	3	2	1	0.7485973540 (−6)	0.55 (−14)	0.24 (−13)	0.55 (−16)
1	0	0	4	1	0	4	1	0	0.2598732211 (−3)	0.15 (−11)	0.53 (−11)	0.23 (−11)

Values are obtained with 15 correct digits obtained using the infinite series to evaluate the semi-infinite integrals. Levin's u transform (21) of order 8, the ϵ algorithm of Wynn (20) of order 8 and the $\overline{D}$ transformation (32) of order 8 were used to evaluate the semi-infinite integrals. Results obtained with the following geometry (spherical coordinates): $A = (0, 0°, 0°)$, $B = (48, 180°, 0°)$ and $C = (50, 180°, 0°)$. $n_2 = 1, l_2 = 0, m_2 = 0, \zeta_1 = \zeta_2 = \zeta_3 = \zeta_4 = 0.5$

Table 3 Evaluation of $\mathcal{K}^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3}$ over STFs

n_1	l_1	m_1	n_3	l_3	m_3	n_4	l_4	m_4	Values	STOnG†	Error^u	Error$^\epsilon$	Error$^{\overline{D}}$
1	0	0	1	0	0	1	0	0	0.1751952812(−1)	0.1751952811(−1)	0.20(−10)	0.54(−10)	0.79(−11)
2	1	0	2	1	0	1	0	0	0.2929548049(−3)	0.2929548048(−3)	0.56(−11)	0.18(−11)	0.54(−11)
2	1	−1	2	1	1	1	0	0	−0.3086333132(−4)	−0.3086333132(−4)	0.13(−10)	0.12(−11)	0.48(−11)
3	1	0	3	1	0	1	0	0	0.2019440007(−3)	0.2019440006(−3)	0.34(−11)	0.11(−11)	0.39(−11)
4	1	0	4	1	0	1	0	0	0.1073990314(−3)	0.1073990313(−3)	0.12(−11)	0.16(−12)	0.17(−11)
1	0	0	1	0	0	1	0	0	0.1751952812(−1)	0.1751952811(−1)	0.20(−10)	0.54(−10)	0.79(−11)
1	0	0	2	1	0	2	1	0	0.1511587450(−1)	0.1511587450(−1)	0.22(−10)	0.32(−10)	0.17(−11)
1	0	0	2	1	−1	2	1	−1	0.1847266070(−1)	0.1847266069(−1)	0.19(−12)	0.32(−10)	0.14(−11)
1	0	0	3	1	0	3	1	0	0.1786642358(−1)	0.1786642357(−1)	0.19(−10)	0.11(−10)	0.18(−11)
1	0	0	3	2	0	3	2	0	0.1579665402(−1)	0.1579665373(−1)	0.19(−10)	0.11(−10)	0.30(−11)
1	0	0	3	2	1	3	2	1	0.1644641185(−1)	0.1644641155(−1)	0.48(−11)	0.22(−10)	0.21(−11)
1	0	0	4	1	0	4	1	0	0.1900808590(−1)	0.1900808589(−1)	0.84(−11)	0.74(−09)	0.56(−11)

Values are obtained with 15 correct digits obtained using the infinite series to evaluate the semi-infinite integrals. Levin's u transform (21) of order 8, the ϵ algorithm of Wynn (20) of order 8 and the $\overline{D}$ transformation (32) of order 8 were used to evaluate the semi-infinite integrals. Results obtained with the following geometry (spherical coordinates): $A = (0, 0°, 0°)$, $B = (48, 180°, 0°)$ and $C = (50, 180°, 0°)$. $n_2 = 1, l_2 = 0, m_2 = 0, \zeta_1 = \zeta_2 = \zeta_3 = \zeta_4 = 0.5$
Values obtained using the ADGGSTNGINT code developed by Rico et al. [24]

using the ADGGSTNGINT code developed by Rico et al. [24]. From this numerical table, one can notice that the algorithm described in this work leads to values which are in a complete agreement with those obtained using ADGGSTNGINT.

5 Conclusion

This work presents the nonlinear $\overline{D}$ transformation approach for a highly efficient numerical evaluation of three-center two electron Coulomb and hybrid integrals over Slater type functions. These integrals appear in molecular calculations and they are very difficult to evaluate rapidly and accurately. STFs are used as a basis of atomic orbitals. These STFs can be expressed as a finite linear combination of B functions in order to apply the Fourier transform method, which allowed analytic expressions to be developed for the molecular integrals under consideration. The main difficulty in the numerical evaluation of the obtained analytic expressions arises from the presence of semi-infinite highly oscillatory integrals involving hypergeometric and Bessel functions. The approach presented in this work relies on the nonlinear $\overline{D}$ transformation and on practical 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 fourth order linear differential equation of the form required to apply the nonlinear $\overline{D}$ transformation and that the order of the equation satisfied by the integrands can be reduced to two simplifying the linear system required to estimate

the integrand. This led to a substantial gain in the calculation times keeping the same high accuracy. Obviously this greatly increased rapidity of the $\overline{D}$ method with a second order linear differential equation is a key issue. In the molecular context, many millions of such integrals are required, therefore rapidity is the primordial criterion when the precision has been reached.

The numerical results obtained with the algorithms described in the present work for three-center two electron Coulomb and hybrid integrals over *B* functions and over STFs show that it does not seem impossible to envisage that STFs or related functions may compete with GTFs in accurate and rapid molecular calculations in the near future.

References

1. Petersson GA, McKoy V (1967) Application of nonlinear transformations to the evaluation of multicenter integrals. J Chem Phys 46:4362
2. Grotendorst J, Weniger EJ, Steinborn EO (1986) Efficient evaluation of infinite-series representations for overlap, two-center nuclear attraction, and Coulomb integrals using nonlinear convergence accelerators. Phys Rev A 33:3706
3. Weniger EJ, Steinborn EO (1988) Overlap integrals of B functions. A numerical study of infinite series representations and integrals representation. Theor Chim Acta 73:323
4. Bouferguene A, Fares M (1994) Convergence accelerators in the computation of molecular integrals over Slater-type basis functions in the two-range one-center expansion method. Phys Rev E 49:3462
5. Agmon S (1985) Bounds on exponential decay of eigenfunctions of Schrödinger operators. In: Graffi S (ed) Schrödinger operators. Springer, Berlin Heidelberg New York
6. Kato T (1957) On the eigenfunctions of many-particle systems in quantum mechanics. Commun Pure Appl Math 10:151
7. Safouhi H, Hoggan PE (1999) Three-centre two-electron Coulomb and hybrid integrals evaluated using nonlinear *D*- and $\overline{D}$-transformations. J Phys A Math Gen 32:6203
8. Safouhi H, Hoggan PE (1999) Efficient and rapid evaluation of three-center two electron Coulomb and hybrid integrals using nonlinear transformations. J Comp Phys 155:331
9. Safouhi H (2000) Numerical evaluation of three-center two-electron Coulomb and hybrid integrals over *B* functions using the *HD* and $H\bar{D}$ methods and convergence properties. J Math Chem 29:213–232
10. Safouhi H (2001) An extremely efficient approach for accurate and rapid evaluation of three- center two-electron Coulomb and hybrid integral over *B* functions. J Phys A Math Gen 34:881
11. Berlu L, Safouhi H (2003) A new algorithm for accurate and fast numerical evaluation of hybrid and three-center two-electron Coulomb integrals over Slater type functions. J Phys A Math Gen 36:11267
12. Slater JC (1930) Atomic shielding constants. Phys Rev 36:57
13. Slater JC (1932) Analytic atomic wave functions. Phys Rev 42:33
14. Shavitt I (1963) The Gaussian function in calculation of statistical mechanics and quantum mechanics, methods. In: Alder B, Fernbach S, Rotenberg M (eds) Computational Physics. 2. Quantum mechanics. Academic, New York
15. Steinborn EO, Filter E (1975) Translations of fields represented by spherical-harmonics expansions for molecular calculations. III. Translations of reduced Bessel functions, Slater-type s-orbitals, and other functions. Theor Chim Acta 38:273
16. Filter E, Steinborn EO (1978) Extremely compact formulas for molecular one-electron integrals and Coulomb integrals over Slater-type orbitals. Phys Rev A 18:1
17. Weniger EJ, Steinborn EO (1983) The Fourier transforms of some exponential-type functions and their relevance to multicenter problems. J Chem Phys 78:6121
18. Trivedi HP, Steinborn EO (1983) Fourier transform of a two-center product of exponential-type orbitals. Application to one- and two-electron multicenter integrals. Phys Rev A 27:670
19. Grotendorst J, Steinborn EO (1988) Numerical evaluation of molecular one- and tow-electron multicenter integrals with exponential-type orbitals via the Fourier-transform method. Phys Rev A 38:3857
20. Sidi A (1980) Extrapolation methods for oscillating infinite integrals. J Inst Math Appl 26:1
21. Sidi A (1997) Computation of infinite integrals involving Bessel functions of arbitrary order by the $\overline{D}$-transformation. J Comp Appl Math 78:125
22. Safouhi H (2004) Highly accurate numerical results for three-center nuclear attraction and two-electron Coulomb and exchange integrals over Slater type functions. Int J Quantum Chem 100:172
23. Bagus McLean PS, Yoshimine M, Lengsfield BH, Liu B (1990) Alchemy II. In: International Business Machines, from MOTECC-90, San Jose
24. J. Fernàndez Rico, R. Ema LI, Ramìrez G (1997) Calculation of many centre two-electron molecular integrals with STO. Comp Phys Commun 105:216
25. Wynn P (1956) On a device for computing the $e_m(S_n)$ transformation. Math Tables Aids Comput 10:91
26. Levin D (1973) Developement of non-linear transformations for improving convergence of sequences. Int J Comput Math B 3:371
27. Condon EU, Shortley GH (1970) The theory of atomic spectra. Cambridge University Press, Cambridge
28. Arfken GB, Weber HJ (1995) Mathematical methods for Physicists, 4th edn. Academic, New York
29. Weniger EJ (1989) Nonlinear sequence transformations for the acceleration of convergence and the summation of divergent series. Comput Phys Rep 10:189
30. Weniger EJ, Steinborn EO (1982) Programs for the coupling of spherical harmonics. Comput Phys Commun 25:149
31. Homeier HHH, Steinborn EO (1992) Improved quadrature methods for the Fourier transform of a two-center product of exponential-type basis functions. Int J Quantum Chem 41:399
32. Brezinski C, Zaglia MR (1991) Extrapolation methods: theory and practice. North-Holland, Amsterdam
33. Bromwich TJI'A (1959) An introduction to the theory of infinite series. Macmillan, London
34. Safouhi H, Bouferguene A (2005) The symbolic programming language in molecular multicenter integral problem. Int J Quantum Chem (in press)
35. Sidi A (1979) Some properties of a generalization of the Richardson extrapolation process. J Inst Math Appl 24:327
36. Safouhi H (2002) Convergence properties of the $S\overline{D}$ transformation and a fast and accurate numerical evaluation of molecular integrals. J Phys A Math Gen 35:1
37. Bouferguene A, Fares M, Hoggan PE (1996) STOP: A Slater type orbitals package for molecular electronic structure determination. Int J Quantum Chem 57:801