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A new algorithm for accurate and fast numerical evaluation of hybrid and three-centre two-electron Coulomb integrals over Slater-type functions

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Abstract

Recently we developed a new algorithm for a fast and accurate numerical evaluation of three-centre nuclear attraction integrals over Slater-type functions, the results obtained were very satisfactory. Now, it is shown that this new algorithm can also be applied to hybrid and three-centre two-electron Coulomb integrals over Slater-type functions. These integrals, which are numerous, are very difficult to evaluate to a high accuracy, because of the presence of spherical Bessel functions and hypergeometric series in the integrands. We have proved that the integrands that occur in the analytic expressions of the integrals under consideration satisfy all the conditions to apply the $S\bar{D}$ approach. The hypergeometric functions which occur in the semi-infinite integrals can be expressed as a finite expansion and the semi-infinite integrals involving the spherical Bessel functions can be transformed into semi-infinite integrals involving the simple sine function.

The numerical results obtained with linear and non-linear systems illustrate clearly a further improvement of accuracy and a substantial reduction in calculation times. Comparisons with existing codes, STOP developed by Bouferguene *et al* (1996 *Int. J. Quantum Chem.* **57** 801) and ADGGSTNGINT developed by Rico *et al* (1997 *Comp. Phys. Commun.* **105** 216), are listed.

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1. Introduction

This paper continues in the series of previous studies [1–4], concerning the development of a rapid and accurate evaluation of hybrid and three-centre two-electron Coulomb integrals over Slater-type functions (STFs) [5, 6] to a high pre-determined accuracy for molecular electronic structure calculations. The STFs can be expressed as finite linear combinations of the so-called

B functions [7–9]. These *B* functions have a much more complicated mathematical structure than STFs, but they have much more appealing properties in multicentre integrals [8–12] and their Fourier transforms are of exceptional simplicity [12, 13].

It is well known that the basis set of *B* functions is well adapted to the Fourier transform method [14–16], which allowed analytic expressions to be developed for multicentre bielectronic integrals [15, 16]. These analytic expressions are very difficult to evaluate because of the presence of two-dimensional integral representations. The inner x semi-infinite integrals are very oscillatory because of the presence of spherical Bessel functions and hypergeometric series in the integrands. We have shown [17] that these hypergeometric series can be expressed as finite expansions and that the integrands of interest satisfy fourth-order linear differential equations of the form required to apply the non-linear $\bar{D}$ transformation [18, 19]. We also showed the superiority of this transformation over the alternatives using Gauss–Laguerre quadrature, the ϵ-algorithm of Wynn [21] or Levin's u transform [22], in evaluating this kind of integrals. Unfortunately, the calculation required by these non-linear transformations presents severe numerical and computational difficulties.

In previous work [23, 24], we obtained the approximation $\bar{D}_n^{(2)}$ for the semi-infinite integrals under consideration by using a second-order differential equation satisfied by the integrands and which was obtained by Sidi [18, 20]. This led to great simplifications in the application of the $\bar{D}$ transformation.

Recently, we developed a very efficient, rapid and simple algorithm for the numerical evaluation of three-centre nuclear attraction integrals over STFs [4]. In the present work, we showed that this new algorithm can also be applied to the hybrid and three-centre two-electron Coulomb integrals, which are shown suitable to apply the $S\bar{D}$ approach [3], which consists on transforming the semi-infinite integrals involving spherical Bessel functions into semi-infinite integrals involving the simple sine function. The strong oscillations of the integrands are thus reduced and as it is well known, the numerical integration of oscillatory integrands is very difficult [25, 26]. Once the semi-infinite integral involving the spherical Bessel function is transformed into a semi-infinite integral involving the sine function, we apply the non-linear $\bar{D}$ transformation using Cramer's rule as suggested by Sidi [18].

The aim of this work is to further simplify the application of this method as well as to reduce the calculation times keeping the same high accuracy. Recurrence relations are developed and numerical and computational studies are presented and discussed.

Numerical results were obtained for H_2O and C_2H_4 molecules to show the superiority of the new algorithm for an efficient and rapid numerical evaluation of the integrand under consideration. Comparisons with the existing codes, STOP (Slater-type orbital package) developed by Bouferguene *et al* [27] and ADGGSTNGINT, using STOnG (STFs expressed as a combination of n GTFs), developed by Rico *et al* [28], are also listed.

2. General definitions and properties

Let A, B and C be arbitrary points of the Euclidian space $\mathcal{E}_3$ and let O be the origin of the fixed coordinate system. The three-centre two-electron Coulomb integral over STFs is given by

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

The hybrid integral, $\mathcal{H}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4}$, corresponds to the case where $B = A$. By performing a

translation of vector $\overrightarrow{OA}$, we can re-write $\mathcal{K}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$ as

$$\mathcal{K}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3} = \int_{\vec{r},\vec{r}'} \left[\chi^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\right]^* \left[\chi^{m_3}_{n_3,l_3}(\zeta_3,\vec{r}'-(\vec{R}_3-\vec{R}_4))\right]^* \times \frac{1}{|\vec{r}-\vec{r}'-\vec{R}_4|}\chi^{m_2}_{n_2,l_2}(\zeta_2,\vec{r})\chi^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}' \tag{2}$$

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 the hybrid integral, $\vec{R}_3 = \overrightarrow{AB} = \vec{O}$.

The following arguments are also applied to hybrid integrals.

The Slater-type functions (STFs) are defined in normalized form according to the following relationship [5, 6]:

$$\chi^m_{n,l}(\zeta,\vec{r}) = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}} r^{n-1}\,\mathrm{e}^{-\zeta r} Y^m_l(\theta_{\vec{r}},\varphi_{\vec{r}}) \tag{3}$$

where n, l, m are the quantum numbers, and $Y^m_l(\theta,\varphi)$ stands for the surface spherical harmonic [29].

The Slater-type orbitals can be expressed as finite linear combinations of B functions [8]:

$$\chi^m_{n,l}(\zeta,\vec{r}) = \sum_{p=\tilde{p}}^{n-l} \frac{(-1)^{n-l-p}\,2^{2p+2l-n}(l+p)!}{(2p-n+l)!(n-l-p)!} B^m_{p,l}(\zeta,\vec{r}) \tag{4}$$

where

$$\tilde{p} = \begin{cases} \frac{n-l}{2} & \text{if} \quad n-l \quad \text{is even} \\ \frac{n-l+1}{2} & \text{if} \quad n-l \quad \text{is odd.} \end{cases} \tag{5}$$

The B functions are defined as follows [8, 9]:

$$B^m_{n,l}(\zeta,\vec{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!}\hat{k}_{n-\frac{1}{2}}(\zeta r) Y^m_l(\theta_{\vec{r}},\varphi_{\vec{r}}) \tag{6}$$

where $\hat{k}_{n+\frac{1}{2}}(z)$ stands for the reduced Bessel function [7, 9]. This function satisfies the following recurrence relation [7]:

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

A useful property satisfied by $\hat{k}_{n+\frac{1}{2}}(z)$ is given by:

$$\left(\frac{\mathrm{d}}{z\,\mathrm{d}z}\right)^m \left[\frac{\hat{k}_{n+\frac{1}{2}}(z)}{z^{2n+1}}\right] = (-1)^m \frac{\hat{k}_{n+m+\frac{1}{2}}(z)}{z^{2(n+m)+1}}. \tag{8}$$

The Fourier transform $\bar{B}^m_{n,l}(\zeta,\vec{p})$ of $B^m_{n,l}(\zeta,\vec{r})$ is given by [12, 13]

$$\bar{B}^m_{n,l}(\zeta,\vec{p}) = \sqrt{\frac{2}{\pi}}\zeta^{2n+l-1}\frac{(-\mathrm{i}|p|)^l}{(\zeta^2+|p|^2)^{n+l+1}} Y^m_l(\theta_{\vec{p}},\varphi_{\vec{p}}). \tag{9}$$

The spherical Bessel function $j_l(x)$ of order $l \in \mathbb{N}$ is defined by [30]

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

The spherical Bessel function $j_l(x)$ satisfies the recurrence relation [30]:

$$x j_{l-1}(x) + x j_{l+1}(x) = (2l+1)\,j_l(x). \tag{11}$$

For 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 [30]

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

where $(\alpha)_n$ represents the Pochhammer symbol [30].

The infinite series (12) converge 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 $|x|>1$.

Note that if α or β in the infinite series (12) is a negative integer, then the hypergeometric function will be reduced to a finite sum.

By using equation (4), 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

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

The hybrid integral will be re-written as

$$\begin{aligned}\tilde{\mathcal{H}}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}&=\int_{\vec{r},\vec{r}'}\left[B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\right]^*\left[B^{m_3}_{n_3,l_3}(\zeta_3,\vec{r}'+\vec{R}_4)\right]^*\\&\quad\times\frac{1}{|\vec{r}-\vec{r}'-\vec{R}_4|}B^{m_2}_{n_2,l_2}(\zeta_2,\vec{r})\,B^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}'.\end{aligned} \tag{14}$$

By substituting the Fourier integral representation of the Coulomb operator [31] in equations (13), we obtain

$$\begin{aligned}\tilde{\mathcal{K}}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}&=\frac{1}{2\pi^2}\int_{\vec{x}}\frac{\mathrm{e}^{\mathrm{i}\vec{x}.\vec{R}_4}}{x^2}\left\langle B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\right|\mathrm{e}^{-\mathrm{i}\vec{x}.\vec{r}}\left|B^{m_2}_{n_2,l_2}(\zeta_2,\vec{r})\right\rangle_{\vec{r}}\\&\quad\times\left\langle B^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}')\right|\mathrm{e}^{-\mathrm{i}\vec{x}.\vec{r}'}\left|B^{m_3}_{n_3,l_3}(\zeta_3,\vec{r}'-(\vec{R}_3-\vec{R}_4))\right\rangle^*_{\vec{r}'}\mathrm{d}\vec{x}.\end{aligned} \tag{15}$$

In [3], we showed that the term $\left\langle B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\right|\mathrm{e}^{-\mathrm{i}\vec{x}.\vec{r}}\left|B^{m_2}_{n_2,l_2}(\zeta_2,\vec{r})\right\rangle_{\vec{r}}$ in the above equations, has an analytic expression involving a hypergeometric function which is given by

$$ {}_2F_1\left(\frac{l-k-l_1-l_2+1}{2},\frac{l-k-l_1-l_2}{2}+1;l+\frac{3}{2};\frac{-x^2}{(\zeta_1+\zeta_2)^2}\right) \tag{16}$$

where k and l are positive integers. We also showed that the above hypergeometric function is reduced to a finite expansion because of the fact that one of the two first arguments of the hypergeometric function is a negative integer. The Fourier transform method allowed analytic expression to be developed for the integrals over $\vec{r}'$ which occurs in equation (15) [15, 16]:

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

The above results led to an analytic expression for the three-centre two-electron Coulomb integral over B functions, which is given by [3]

$$\begin{aligned}\mathcal{K}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}&=8(4\pi)^3\sqrt{\pi}\zeta_1^{l_1}\zeta_2^{l_2}\zeta_3^{2n_3+l_3-1}\zeta_4^{2n_4+l_4-1}\\&\quad\times\frac{(2l_3+1)!!(2l_4+1)!!(n_3+l_3+n_4+l_4+1)!}{2^{l_1+l_2+1}(n_1+l_1)!(n_2+l_2)!(n_3+l_3)!(n_4+l_4)!}\\&\quad\times\sum_{l=l_{\min},2}^{l_1+l_2}\frac{(-i)^l}{2^{2n_1+2n_2+l}}\langle l_2m_2|l_1m_1|lm_2-m_1\rangle\end{aligned}$$

$$
\begin{aligned}
&\times \sum_{k=2}^{n_1+n_2} \sum_{i=k_1}^{k_2} \left[\frac{2^k (2n_1 - i - 1)!(2n_2 - k + i - 1)! \zeta_1^{i-1} \zeta_2^{k-i-1}}{(i-1)!(n_1 - i)!(k - i - 1)!(n_2 - k + i)!} \right] \\
&\times \sum_{l_4'=0}^{l_4} \sum_{m_4'=-l_4'}^{l_4'} i^{l_4+l_4'} (-1)^{l_4'} \frac{\langle l_4 m_4 | l_4 - l_4' m_4 - m_4' | l_4' m_4' \rangle}{(2l_4' + 1)!![2(l_4 - l_4') + 1]!!} \\
&\times \sum_{l_3'=0}^{l_3} \sum_{m_2'=-l_3'}^{l_3'} i^{l_3+l_3'} \frac{\langle l_3 m_3 | l_3 - l_3' m_3 - m_3' | l_3' m_3' \rangle}{(2l_3' + 1)!![2(l_3 - l_3') + 1]!!} \\
&\times \sum_{l'=l'_{\min,2}}^{l_3'+l_4'} \langle l_4' m_4' | l_3' m_3' | l' m_4' - m_3' \rangle R_{34}^{l'} Y_{l'}^{m_3'-m_4'} (\theta_{\vec{R}_{34}}, \varphi_{\vec{R}_{34}}) \\
&\times \sum_{l_{34}=l''_{\min,2}}^{l_3-l_3'+l_4-l_4'} \langle l_3 - l_3' m_3 - m_3' | l_4 - l_4' m_4 - m_4' | l_{34} m_{34} \rangle \\
&\times \sum_{\lambda=\lambda_{\min,2}}^{l+l_{34}} i^{\lambda} \langle l m_2 - m_1 | l_{34} (m_3 - m_3') - (m_4 - m_4') | \lambda \mu \rangle \\
&\times \sum_{j=0}^{\Delta l} \binom{\Delta l}{j} \frac{(-1)^j}{2^{n_3+n_4+l_3+l_4-j+1} (n_3 + n_4 + l_3 + l_4 - j + 1)!} \\
&\times \frac{\zeta_s^{n_k-l-1} \Gamma(k + l_1 + l_2 + l + 1)}{\Gamma(l + \frac{3}{2})} \sum_{r=0}^{\eta'} (-1)^r \frac{\left(\frac{\eta}{2}\right)_r \left(\frac{\eta+1}{2}\right)_r}{\left(l + \frac{3}{2}\right)_r r! \zeta_s^{2r}} \\
&\times \int_{s=0}^{1} s^{n_3+l_3+l_4-l_4'} (1-s)^{n_4+l_4+l_3-l_3'} Y_{\lambda}^{\mu} (\theta_{\vec{v}}, \varphi_{\vec{v}}) \\
&\times \left[\int_0^{+\infty} \frac{x^{n_x}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\hat{k}_v [R_{34} \gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(vx)\, \mathrm{d}x \right] \mathrm{d}s
\end{aligned}
\tag{17}
$$

where

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

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

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

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

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

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

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

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

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

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

$\langle l_1 m_1 | l_2 m_2 | l_3 m_3 \rangle$ stands for the Gaunt coefficients [34–36]

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

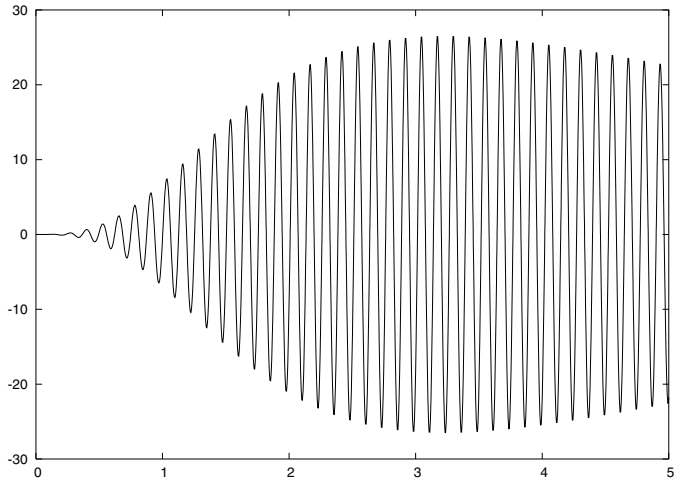

Figure 1. The integrand $\mathcal{F}_s(x)$ of $\tilde{\mathcal{K}}(s)$ (18). $s = 0.998$, $\nu = 13/2, n_\gamma = 5, n_k = 2, n_x = 4$, $\lambda = 4$, $R_{34} = 2.0$, $\zeta_s = 2.0$ and $\zeta_3 = \zeta_4 = 1.0$ ($v = 49.996$).

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

The numerical evaluation of the above analytic expression turned out to be very difficult. This is due to the presence of the two-dimensional integral representations. The inner x semi-infinite integrals, which will be referred to as $\tilde{\mathcal{K}}(s)$, are very oscillatory because of the spherical Bessel functions $j_\lambda(vx)$ in the integrands (see figure 1). Note that when the values of λ and v are large and when s is close to 0 or 1 the oscillations become very strong, thus the numerical evaluation of the two-dimensional integrals becomes very difficult.

The semi-infinite integrals which occur in the expression of hybrid integrals will be referred to as $\tilde{\mathcal{H}}(s)$.

The semi-infinite integral $\tilde{\mathcal{K}}(s)$ which occurs in equation (17) can be transformed into an infinite series of integrals as follows:

$$\tilde{\mathcal{K}}(s) = \int_0^{+\infty} \frac{x^{n_x}}{[\zeta_s^2 + x^2]^{n_k}} \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(vx)\,\mathrm{d}x \tag{18}$$

$$= \sum_{n=0}^{+\infty} \int_{j_{\lambda,v}^n}^{j_{\lambda,v}^{n+1}} \frac{x^{n_x}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(vx)\,\mathrm{d}x \tag{19}$$

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

For the following, the integrand of $\tilde{\mathcal{K}}(s)$ will be referred to as $\mathcal{F}_{\mathcal{K},s}(x)$ and the integrand of $\tilde{\mathcal{H}}(s)$ will be referred to as $\mathcal{F}_{\mathcal{H},s}(x)$.

In the case when $v \to 0$, the semi-infinite integral (18) vanishes if $\lambda \neq 0$, since $\lim_{\alpha\to 0} j_\lambda(\alpha) = 0$ and the integrand is an exponential decreasing function (converges to 0 when $x \to +\infty$), and if $\lambda = 0$, we used the fact that $j_0(\alpha) = \frac{\sin(\alpha)}{\alpha} \to 1$ when $\alpha \to 0$ and the fact that the integrand is exponentially decreasing function, to obtain the following equation:

$$\tilde{\mathcal{K}}(s) \approx \int_0^{+\infty} \frac{x^{n_x}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\hat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\,\mathrm{d}x. \tag{20}$$

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

The infinite series (19) will be used for computing values of $\tilde{\mathcal{K}}(s)$ with a certain number of correct decimals. Unfortunately, as it can be seen from tables 2, 4 and 6, the use of this approach is very time consuming when the value of v and λ are large and when s is close to 0 or 1.

It is shown [32, 33] that the use of Gauss–Laguerre quadrature even to a high order gives inaccurate results in the regions where s is close to 0 or 1 (in these regions the asymptotic behaviour of the integrand cannot be represented by a function of the form $\mathrm{e}^{-\alpha x} j_\lambda(x)$).

In [17], we demonstrated that the integrands $\mathcal{F}_{\mathcal{K},s}(x)$ and $\mathcal{F}_{\mathcal{H},s}(x)$ satisfy fourth-order linear differential equations of the form required to apply the non-linear D and $\bar{D}$ transformations [18, 19]. These two transformations are probably the most effective general approaches for increasing the rate of convergence of semi-infinite oscillatory integrals whose integrands satisfy linear differential equations with coefficients having asymptotic expansions in inverse powers of their argument x as $x \to +\infty$. The numerical results obtained for the semi-infinite integrals under consideration were very satisfactory compared with other alternatives namely the Gauss–Laguerre quadrature, the epsilon algorithm of Wynn and Levin's u transform. The calculation of the approximation $\bar{D}_n^{(4)}$, which converges very quickly to the exact value of the integral as n becomes large, is obtained by solving a set of linear equations of order $(3n + 1)$, where the computation of the successive derivatives of the integrand and its successive positive zeros are necessary. This is much time consuming.

In previous work [23, 24], we presented the approximation $\bar{D}_n^{(2)}$ that was obtained by applying $\bar{D}$ with a second-order differential equation [18, 20]. Second-order differential equations were developed for the integrands $\mathcal{F}_{\mathcal{K},s}(x)$ and $\mathcal{F}_{\mathcal{H},s}(x)$ using practical properties of spherical Bessel functions and asymptotic power series in the sense of Poincaré [37]. The approximation $\bar{D}_n^{(2)}$ is obtained by solving linear system of order $(n + 1)$ and where it is not necessary to evaluate the successive derivatives of the integrands (only the first derivative of the spherical Bessel function is required). The numerical results obtained using this approach showed the substantial gain in the calculation times keeping the high accuracy. The main difficulty of this approach is due to the fact that it is still necessary to compute the successive zeros of the spherical Bessel function. Note that it is still required to compute a method to solve the linear system for calculating the approximation $\bar{D}_n^{(2)}$.

Recently [3], we showed that $\mathcal{F}_{\mathcal{K},s}(x)$ and $\mathcal{F}_{\mathcal{H},s}(x)$ satisfy all the condition to apply the $S\bar{D}$ method, which consists in replacing the spherical Bessel in the integrands by the simple sine function and then by applying the non-linear $\bar{D}$ transformation. The semi-infinite integral $\tilde{\mathcal{K}}(s)$ can be re-written as [3]

$$\tilde{\mathcal{K}}(s) = \frac{1}{v^{\lambda+1}} \int_0^{+\infty} \left(\left(\frac{\mathrm{d}}{x\,\mathrm{d}x} \right)^{\lambda} \left[\frac{x^{n_x+\lambda-1}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\hat{k}_v[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \right] \right) \sin(vx)\,\mathrm{d}x \tag{21}$$

$$= \frac{1}{v^{\lambda+1}} \sum_{n=0}^{+\infty} \int_{\frac{n\pi}{v}}^{\frac{(n+1)\pi}{v}} \left(\left(\frac{\mathrm{d}}{x\,\mathrm{d}x} \right)^{\lambda} \left[\frac{x^{n_x+\lambda-1}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\hat{k}_v[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \right] \right) \sin(vx)\,\mathrm{d}x. \tag{22}$$

A similar formula was developed for the semi-infinite integral $\mathcal{H}(s)$ [3].

For the following, the integrand of the above semi-infinite integral will be referred to as $\tilde{\mathcal{F}}_{\mathcal{K},s}(x)$. As it can be seen from figures 1 and 2, the oscillations of the integrand $\mathcal{F}_{\mathcal{K},s}(x)$ involving spherical Bessel function are stronger than the oscillations of the integrand $\tilde{\mathcal{F}}_{\mathcal{K},s}(x)$

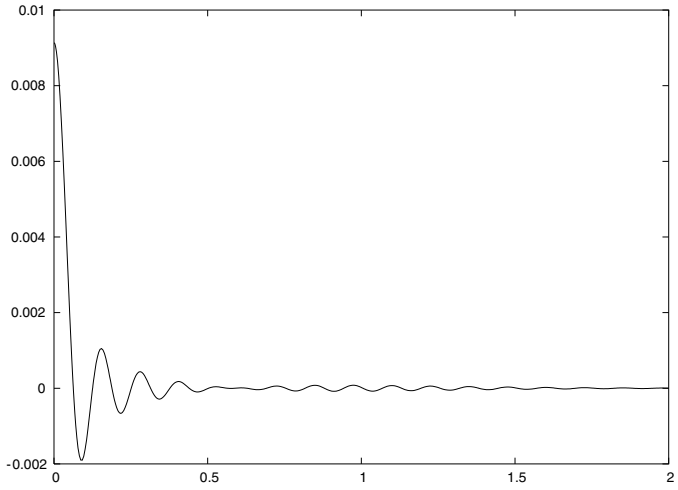

Figure 2. The integrand $\tilde{\mathcal{F}}_s(x)$ of $\tilde{\mathcal{K}}(s)$ (21). $s, \nu, n_\gamma, n_k, n_x, \lambda, R_{34}, \zeta_s, \zeta_3$ and ζ_4 are given in figure 1.

Table 1. Values with 15 correct decimals of $\tilde{\mathcal{K}}(s)$ (18) obtained using the infinite series with the sine function (22) ($s = 0.240(-2)$)[a].

ν	n_γ	n_k	n_x	λ	ζ_s	ζ_3	ζ_4	R_{34}	$n_{\max}$	$\tilde{\mathcal{K}}(s)^{n_{\max}}$	Time
5/2	1	2	0	0	4.0	1.5	0.5	2.5	1245	0.549 128 278 838(−3)	11.85
5/2	1	2	1	0	2.0	2.0	1.5	2.0	1260	0.424 640 684 563(−4)	10.96
9/2	4	3	3	3	2.0	1.5	0.5	2.5	482	0.700 836 644 746(−4)	10.89
13/2	5	2	4	4	2.0	1.0	1.0	2.0	642	0.351 661 145 091(−3)	15.29
13/2	11	2	4	4	2.0	1.0	1.0	2.0	714	0.351 661 145 092(−3)	17.14
13/2	13	2	6	6	2.0	1.0	1.0	2.0	361	0.151 074 181 930(−4)	9.15
15/2	6	2	4	4	2.0	2.0	1.5	2.0	835	0.207 548 974 232(−3)	20.23
21/2	9	2	5	5	2.0	2.0	1.5	2.0	1045	0.559 070 180 641(−1)	28.05
17/2	10	3	3	3	3.0	1.5	1.0	2.5	570	0.470 570 654 794(−1)	13.03

[a] Numbers in parentheses represent powers of 10.

involving the sine function. Note that the above infinite series converges faster than the infinite series given by equation (19) (see tables 1–6).

Practical properties of the sine function allowed the use of Cramer's rule, as suggested by Levin [22], for calculating the approximation of the above semi-infinite integrals. If we let the functions $G(x)$ and $F(x)$ be defined as

$$\begin{cases} G(x) = \left(\dfrac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda} \left[\dfrac{x^{n_x+\lambda-1}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \dfrac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\right] \\ F(x) = \displaystyle\int_0^x G(t)\sin(\nu t)\,\mathrm{d}t \end{cases} \tag{23}$$

then the approximation of $\tilde{\mathcal{K}}(s)$ is given by [3]

$$S\bar{D}_n^{(2,j)} = \frac{1}{\nu^{\lambda+1}} \frac{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i+j)^n F(x_{i+j}) \Big/ \left[x_{i+j}^2 G(x_{i+j})\right]}{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i+j)^n \Big/ \left[x_{i+j}^2 G(x_{i+j})\right]} \tag{24}$$

where $x_l = (l+1)\dfrac{\pi}{\nu}$ for $l = 0, 1, \ldots$.

Table 2. Evaluation of $\tilde{\mathcal{K}}(s)$ (18) ($s = 0.240(-2)$)[a].

$n_{\max}$	$\tilde{\mathcal{K}}(s)^a$	Error^a	Time	n	$\tilde{\mathcal{K}}(s)^b$	Error^b	Time
1245	0.549 128 2788(−3)	0.22(−18)	12.20	6	0.549 128 2788(−3)	0.13(−13)	0.09
1260	0.424 640 6846(−4)	0.18(−18)	12.14	3	0.424 640 8618(−4)	0.18(−10)	0.04
1773	0.700 836 6447(−4)	0.37(−16)	22.82	18	0.700 836 4215(−4)	0.22(−10)	0.45
4568	0.351 661 1451(−3)	0.14(−13)	58.12	20	0.351 661 1239(−3)	0.21(−10)	0.53
2632	0.351 661 1451(−3)	0.19(−13)	33.84	20	0.351 661 1380(−3)	0.71(−11)	0.54
3323	0.151 074 1808(−4)	0.11(−12)	44.17	15	0.151 074 3054(−4)	0.12(−10)	0.42
5152	0.207 548 9742(−3)	0.38(−13)	65.76	21	0.207 548 9912(−3)	0.17(−10)	0.53
6629	0.559 070 1846(−1)	0.39(−09)	89.96	23	0.559 070 1806(−1)	0.65(−11)	0.65
1256	0.470 570 6548(−1)	0.32(−13)	16.89	22	0.470 570 6548(−1)	0.41(−11)	0.51

[a] ν, n_γ, n_k, n_x, λ, ζ_s, ζ_3, ζ_4 and R_{34} are given in table 1. The values $\tilde{\mathcal{K}}(s)^a$ were obtained using the infinite series with spherical Bessel function (19). The values $\tilde{\mathcal{K}}(s)^b$ were obtained using $S\bar{D}_n^{(2,0)}$.

Table 3. Values with 15 correct decimals of $\tilde{\mathcal{K}}(s)$ (18) obtained using the infinite series with the sine function (22) ($s = 0.998$).

ν	n_γ	n_k	n_x	λ	ζ_s	ζ_3	ζ_4	R_{34}	$n_{\max}$	$\tilde{\mathcal{K}}(s)^{n_{\max}}$	Time
5/2	1	2	0	0	4.0	1.5	0.5	2.5	1301	0.496 748 720 573(−4)	12.26
5/2	1	2	1	0	2.0	2.0	1.5	2.0	1393	0.153 899 211 686(−4)	12.23
9/2	4	3	3	3	2.0	1.5	0.5	2.5	307	0.348 864 079 545(−6)	6.79
13/2	5	2	4	4	2.0	1.0	1.0	2.0	724	0.286 993 071 501(−3)	17.28
13/2	11	2	4	4	2.0	1.0	1.0	2.0	772	0.286 993 071 502(−3)	18.50
13/2	13	2	6	6	2.0	1.0	1.0	2.0	405	0.113 667 442 373(−4)	10.28
15/2	6	2	4	4	2.0	2.0	1.5	2.0	471	0.241 572 463 234(−4)	11.64
21/2	9	2	5	5	2.0	2.0	1.5	2.0	754	0.285 406 859 358(−2)	20.90
17/2	10	3	3	3	3.0	1.5	1.0	2.5	576	0.484 271 561 421(−3)	13.09

Table 4. Evaluation of $\tilde{\mathcal{K}}(s)$ (18) ($s = 0.998$)[a].

$n_{\max}$	$\tilde{\mathcal{K}}(s)^a$	Error^a	Time	n	$\tilde{\mathcal{K}}(s)^b$	Error^b	Time
1301	0.496 748 7206(−4)	0.47(−19)	12.56	5	0.496 748 6922(−4)	0.28(−11)	0.06
1393	0.153 899 2117(−4)	0.11(−18)	13.60	3	0.153 899 2578(−4)	0.46(−11)	0.06
1922	0.348 864 0795(−6)	0.41(−17)	24.59	4	0.348 864 6250(−6)	0.55(−12)	0.12
5180	0.286 993 0715(−3)	0.21(−13)	65.90	20	0.286 993 0806(−3)	0.91(−11)	0.53
2981	0.286 993 0715(−3)	0.19(−13)	38.32	20	0.286 993 0809(−3)	0.94(−11)	0.53
3792	0.113 667 4440(−4)	0.17(−12)	50.40	14	0.113 667 8632(−4)	0.42(−10)	0.40
5801	0.241 572 4632(−4)	0.70(−14)	74.40	4	0.241 572 7508(−4)	0.29(−10)	0.14
7501	0.285 406 8463(−2)	0.13(−10)	102.23	21	0.285 406 8613(−2)	0.20(−10)	0.65
1425	0.484 271 5614(−3)	0.15(−14)	19.10	20	0.484 271 5491(−3)	0.12(−10)	0.46

[a] ν, n_γ, n_k, n_x, λ, ζ_s, ζ_3, ζ_4 and R_{34} are given in table 3. The values $\tilde{\mathcal{K}}(s)^a$ were obtained using the infinite series with spherical Bessel function (19). The values $\tilde{\mathcal{K}}(s)^b$ were obtained using $S\bar{D}_n^{(2,0)}$.

3. The development of the algorithm

As it can be seen from (24), it is necessary for the calculation to compute the function $G(x)$ (23). With the help of equation (8) and the fact that $\frac{\mathrm{d}}{\mathrm{d}x} = \frac{\mathrm{d}z}{\mathrm{d}x}\frac{\mathrm{d}}{\mathrm{d}z}$, one can easily show that if $n_\gamma = 2\nu$ then for $j \in \mathbb{N}$:

$$\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^j \left[\frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{2\nu}}\right] = (-1)^j s^j (1-s)^j \frac{\hat{k}_{\nu+j}[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{2(\nu+j)}} \tag{25}$$

Table 5. Values with 15 correct decimals of the semi-infinite integral $\tilde{\mathcal{H}}(s)$, that occurs in the analytic expression of hybrid integrals ($\tilde{\mathcal{H}}(s)$ corresponds to the case where $R_3 = 0$ in equation (18)). The infinite series with the sine function was used ($s = 0.998$).

ν	n_γ	n_k	n_x	λ	ζ_s	ζ_3	ζ_4	R_4	$n_{\max}$	$\tilde{\mathcal{H}}(s)^{n_{\max}}$	Time
7/2	1	2	1	0	1.0	1.0	1.5	5.5	152	0.700 421 821 682(−1)	1.37
7/2	1	2	2	0	1.0	1.5	2.5	5.5	178	0.620 224 972 816(−3)	1.60
7/2	3	3	2	0	1.0	1.5	1.5	5.5	104	0.452 489 553 319(−3)	1.01
7/2	7	2	1	1	1.0	1.0	1.0	5.5	96	0.863 816 354 491(−1)	1.75
9/2	4	3	3	1	1.0	2.5	1.5	3.5	105	0.144 952 803 542(−2)	2.99
9/2	9	3	3	2	1.0	1.5	1.0	5.0	78	0.192 335 487 262(−2)	1.57
17/2	11	5	5	3	1.0	2.0	1.5	8.0	65	0.143 975 740 932(−2)	1.54
17/2	17	5	6	4	1.0	1.5	1.0	9.0	72	0.712 561 962 830(−2)	1.73

Table 6. Evaluation of $\tilde{\mathcal{H}}(s)$ (18) ($s = 0.998$)[a].

$n_{\max}$	$\tilde{\mathcal{H}}(s)^a$	Error^a	Time	n	$\tilde{\mathcal{H}}(s)^b$	Error^b	Time
153	0.700 421 8217(−1)	0.00(+00)	1.50	9	0.700 421 8217(−1)	0.62(−12)	0.12
179	0.620 224 9728(−3)	0.43(−18)	1.76	8	0.620 224 9719(−3)	0.93(−12)	0.10
105	0.452 489 5533(−3)	0.22(−18)	1.07	7	0.452 489 5511(−3)	0.22(−11)	0.10
110	0.863 816 3545(−1)	0.35(−15)	1.18	9	0.863 816 3545(−1)	0.47(−12)	0.18
124	0.144 952 8035(−2)	0.80(−15)	1.45	7	0.144 952 8037(−2)	0.15(−11)	0.14
104	0.192 335 4873(−2)	0.74(−15)	1.31	10	0.192 335 4870(−2)	0.28(−11)	0.21
117	0.143 975 7409(−2)	0.18(−16)	1.57	13	0.143 975 7405(−2)	0.45(−11)	0.34
128	0.712 561 9628(−2)	0.84(−15)	1.75	12	0.712 561 9625(−2)	0.34(−11)	0.31

[a] ν, n_γ, n_k, n_x, λ, ζ_s, ζ_3, ζ_4 and R_4 are given in table 5. The values $\tilde{\mathcal{H}}(s)^a$ were obtained using the infinite series with spherical Bessel function (19). The values $\tilde{\mathcal{H}}(s)^b$ were obtained using $S\bar{D}_n^{(2,0)}$.

and for $n_\gamma < 2\nu$, we obtain

$$\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^j \left[\frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\right] = \frac{s^j(1-s)^j}{[\gamma(s,x)]^{n_\gamma+2j}} \sum_{i=0}^{j} \binom{j}{i} (-1)^{j-i} \frac{(2\nu-n_\gamma)!!}{(2\nu-n_\gamma-2i)!!} \times \hat{k}_{\nu+j-i}[R_{34}\gamma(s,x)] \tag{26}$$

where the double factorial is defined by

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

Using Leibnitz formulae and the above equations, we obtain after some algebraic operations:

$$\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^\lambda \left(\frac{x^{n_x+\lambda-1}}{\left[\zeta_s^2+x^2\right]^{n_k}} \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\right) = \sum_{i=0}^{\lambda}\sum_{j=0}^{i} \binom{\lambda}{i}\binom{i}{j} \frac{(n_x+\lambda-1)!!}{(n_x+\lambda-1-2i)!!} \times (-2)^{i-j}(n_k)_{i-j} \frac{x^{n_x+\lambda-1-2i}}{\left[\zeta_s^2+x^2\right]^{n_k+i-j}} \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda-i} \left[\frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\right] \tag{27}$$

where $(n_k)_\alpha$ stands for the Pochhammer symbol.

As it can be seen from equations (25)–(27), the calculation of $G(x)$ does not present any computation difficulties.

For the computation of equation (24), we used the following procedure:

Let $A_k^{(2,j)}$ and $B_k^{(2,j)}$ be defined by

$$\begin{cases} A_k^{(2,j)} = \sum_{i=0}^{k+1} \binom{k+1}{i} (1+i+j)^k F(x_{i+j}) \Big/ \left[x_{i+j}^2 G(x_{i+j})\right] \\ B_k^{(2,j)} = \sum_{i=0}^{k+1} \binom{k+1}{i} (1+i+j)^k \Big/ \left[x_{i+j}^2 G(x_{i+j})\right]. \end{cases} \tag{28}$$

Equation (24) can now be re-written as

$$S\bar{D}_k^{(2,j)} = \frac{1}{v^{\lambda+1}} \frac{A_k^{(2,j)}}{B_k^{(2,j)}} \qquad k = 0, 1, 2, \ldots. \tag{29}$$

Let U_i^k and V_i^k be the ith terms of the finite sum $A_k^{(2,j)}$ and $B_k^{(2,j)}$, respectively. It is shown [4] that $A_k^{(2,j)}$ and $B_k^{(2,j)}$ satisfy the following recurrence relation:

$$\begin{cases} A_{k+1}^{(2,j)} = \sum_{i=0}^{k+1} \frac{(k+2)}{(k+2-i)} (1+i+j) U_i^k + U_{k+2}^{k+1} \\ B_{k+1}^{(2,j)} = \sum_{i=0}^{k+1} \frac{(k+2)}{(k+2-i)} (1+i+j) V_i^k + V_{k+2}^{k+1}. \end{cases} \tag{30}$$

In previous work, we demonstrated that from the above equations, it follows that $S\bar{D}_n^{(2,j)}$, which is given by equation (24), satisfies to the following relation [4]:

$$S\bar{D}_{k+1}^{(2,j)} = \frac{1}{v^{\lambda+1}} \frac{\sum_{i=0}^{k+1} \frac{(k+2)}{(k+2-i)} (1+i+j) U_i^k + U_{k+2}^{k+1}}{\sum_{i=0}^{k+1} \frac{(k+2)}{(k+2-i)} (1+i+j) V_i^k + V_{k+2}^{k+1}}. \tag{31}$$

Note that with the help of the relations (30) and (31), we can have a control of the degree of accuracy. In fact, we calculate the approximation $S\bar{D}_{k+1}^{(2,j)}$ only if the accuracy obtained using $S\bar{D}_k^{(2,j)}$ is not satisfactory. For this we use the following test:

$$\left| S\bar{D}_k^{(2,j)} - S\bar{D}_{k-1}^{(2,j)} \right| = \frac{1}{v^{\lambda+1}} \left| \frac{A_k^{(2,j)}}{B_k^{(2,j)}} - \frac{A_{k-1}^{(2,j)}}{B_{k-1}^{(2,j)}} \right| \leqslant \epsilon \tag{32}$$

where ϵ is defined according to the pre-determined degree of accuracy.

The use of equation (31) does not require the computation of binomial coefficients. Note also that by storing the values of U_i^k and V_i^k for $k = 0, 1, 2, 3, \ldots$ and $i = 0, 1, \ldots, k+1$, one does not need to calculate all values of $x_{i+j}^2 G(x_{i+j})$ for each order of the $S\bar{D}$. This led to a considerable gain in the calculation times.

As we explained in the previous work concerning three-centre nuclear attraction integrals [4], a numerical and computation problem occurred in the calculation of the approximations $S\bar{D}_n^{(2,j)}$. In some cases, the values of $G(x_{i+j})$ are very small ($G(x_{i+j}) \to 0$). The development presented in [4], can also be applied to three-centre two-electron Coulomb and hybrid integrals. The following formulae give a very good approximation of the semi-infinite integrals under consideration [4]:

$$S\bar{D}_n^{(2,j)} \approx \frac{1}{v^{\lambda+1}} \frac{\tilde{A}_n^{(2,j)}}{\tilde{B}_n^{(2,j)}} \tag{33}$$

where

$$\begin{cases} \tilde{A}_n^{(2,j)} = \sum_{i \in E} \binom{n+1}{i} (1+i+j)^n \frac{F(x_{i+j})}{x_{i+j}^2} \\ \tilde{B}_n^{(2,j)} = \sum_{i \in E} \binom{n+1}{i} (1+i+j)^n \frac{1}{x_{i+j}^2}. \end{cases} \tag{34}$$

Table 7. Evaluation of $S\bar{D}_{10}^{(2,0)}\ \tilde{\mathcal{K}}(s)$ using equations (31), (33) and (35) ($s = 0.500$)[a].

i	$G(x_i)$	$S\bar{D}_{10}^{(2,0)}$ (31)	$S\bar{D}_{10}^{(2,0)}$ (33)	$S\bar{D}_{10}^{(2,0)}$ (35)
0	−0.1833(−40)	0.195 235 2947(−2)		0.195 235 2947(−2)
1	−0.9395(−79)	0.195 235 2947(−2)		0.195 235 2947(−2)
2	−0.7533(−116)	0.195 235 2947(−2)		0.195 235 2947(−2)
3	−0.1819(−152)	0.195 235 2947(−2)	0.195 235 2947(−2)	0.195 235 2947(−2)
4	−0.7986(−189)	0.195 235 2947(−2)	0.195 235 2947(−2)	0.195 235 2947(−2)
5	−0.5108(−225)	0.195 235 2947(−2)	0.195 235 2947(−2)	0.195 235 2947(−2)
6	−0.4231(−261)	0.195 235 2947(−2)	0.195 235 2947(−2)	0.195 235 2947(−2)
7	−0.4233(−297)	0.195 235 2947(−2)	0.195 235 2947(−2)	0.195 235 2947(−2)
8	0.0000(00)	NaN	0.195 235 2947(−2)	0.195 235 2947(−2)
9	0.0000(00)	NaN	0.195 235 2947(−2)	0.195 235 2947(−2)

[a] $\nu = 19/2, n_\gamma = 10, n_k = 5, n_x = 3, \lambda = 3, \zeta_s = 2.00, \zeta_3 = 1.50, \zeta_4 = 1.00$ and $R_{34} = 2.50$.

and where E is a subset of $I = \{0, 1, 2, \ldots, n+1\}$ defined by

$$E = \{k \in I \quad \text{such that} \quad G(x_{k+j}) \to 0\}.$$

In the most cases where $G(x_{i+j}) \to 0$ for some values of i, the following formulae can be used for the computation of $S\bar{D}_n^{(2,j)}$ [4]:

$$S\bar{D}_n^{(2,j)} \approx \frac{1}{v^{\lambda+1}} \frac{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i+j)^n F(x_{i+j}) \big/ x_{i+j}^2}{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i+j)^n \big/ x_{i+j}^2}. \tag{35}$$

In our algorithm, the above expression is used when the following conditions are satisfied:

$$R = \left| \frac{A_n^{(2,j)}}{\tilde{A}_n^{(2,j)}} - \frac{B_n^{(2,j)}}{\tilde{B}_n^{(2,j)}} \right| \leqslant \text{tiny} \qquad \text{or} \qquad \tilde{R} = \left| \frac{\tilde{A}_n^{(2,j)}}{A_n^{(2,j)}} - \frac{\tilde{B}_n^{(2,j)}}{B_n^{(2,j)}} \right| \leqslant \text{tiny} \tag{36}$$

where 'tiny' should be set close to but not identical with the smallest floating point number that is representable on the computer.

We used equations (31), (33) and (35) for the evaluation of semi-infinite integrals, where the situation $G(x_{i+j})$ is very small for some values of i, occurred (see tables 7 and 8). From the results listed in these tables, one can easily note that the use of (33) and (35) gives accurate results.

4. Numerical discussion

The values of the semi-infinite integrals $\tilde{\mathcal{K}}(s)$ (18) and $\tilde{\mathcal{H}}(s)$ are obtained with 15 correct decimals using the infinite series involving the sine function (22), which we sum until $N = n_{\max}$ (see tables 1, 3 and 5). We also used the infinite series involving the spherical Bessel function (19) for calculating the values of the semi-infinite integrals (tables 2, 4 and 6). From these tables, we can note that the semi-infinite series with the sine function converges faster than the infinite series with the spherical Bessel function.

For the evaluation of the finite integrals involving in equations (22), (19) and (24), we separate two cases:

When $v \geqslant 1$, we used Gauss–Legendre quadrature of order 20.

Table 8. Evaluation of $S\bar{D}_{11}^{(2,0)}$ in the case of $\tilde{\mathcal{H}}(s)$ using equations (31), (33) and (35) ($s = 0.240(-02)$)[a].

i	$G(x_i)$	$S\bar{D}_{11}^{(2,0)}$ (31)	$S\bar{D}_{11}^{(2,0)}$ (33)	$S\bar{D}_{11}^{(2,0)}$ (35)
0	−0.6509(−51)	0.138 157 6998(−3)		0.138 157 6998(−3)
1	−0.3213(−82)	0.138 157 6998(−3)		0.138 157 6998(−3)
2	−0.4923(−112)	0.138 157 6998(−3)		0.138 157 6998(−3)
3	−0.2955(−141)	0.138 157 6998(−3)	0.138 157 6998(−3)	0.138 157 6998(−3)
4	−0.3709(−170)	0.138 157 6998(−3)	0.138 157 6998(−3)	0.138 157 6998(−3)
5	−0.7399(−199)	0.138 157 6998(−3)	0.138 157 6998(−3)	0.138 157 6998(−3)
6	−0.2029(−227)	0.138 157 6998(−3)	0.138 157 6998(−3)	0.138 157 6998(−3)
7	−0.7013(−256)	0.138 157 6998(−3)	0.138 157 6998(−3)	0.138 157 6998(−3)
8	−0.2892(−284)	0.138 157 6998(−3)	0.138 157 6998(−3)	0.138 157 6998(−3)
9	−0.1371(−312)	NaN	0.138 157 6998(−3)	0.138 157 6998(−3)
10	0.0000(00)	NaN	0.138 157 6998(−3)	0.138 157 6998(−3)

[a] $v = 17/2$, $n_\gamma = 14$, $n_k = 5$, $n_x = 6$, $\lambda = 3$, $\zeta_s = 3.00$, $\zeta_3 = 1.50$, $\zeta_4 = 2.00$ and $R_4 = 2.00$.

When $10^{-15} < v < 1$, we divided the finite interval $[x_{i-1}, x_i]$ into M subintervals, where $M = \min(v^{-2}, 100)$. The finite integral $\int_{x_{i-1}}^{x_i} f(t)\,\mathrm{d}t$ can be re-written as

$$\int_{x_{i-1}}^{x_i} f(t)\,\mathrm{d}t = \sum_{k=1}^{M} \int_{\tilde{x}_{k-1}}^{\tilde{x}_k} f(t)\,\mathrm{d}t$$

where $\tilde{x}_0 = x_{i-1}$, $\tilde{x}_M = x_i$ and for $k = 1, 2, \ldots, M-1$:

$$\tilde{x}_k = x_{i-1} + k\frac{x_i - x_{i-1}}{M}.$$

For the evaluation of each finite integral involving in the above finite sum, we used Gauss–Legendre quadrature of order 20.

The value of M was determined after a series of numerical tests on different values of v.

In the case of three-centre nuclear attraction integrals over B functions, it was sufficient to divide the intervals $[x_{i-1}, x_i]$ into M' subintervals, where $M' = \min(v^{-1}, 100)$. This is due to the fact that the term $\frac{1}{(\zeta_s^2+x^2)^{n_k}}$ occurs in the expression of the three-centre two-electron Coulomb and hybrid integrals and not in the three-centre nuclear attraction integrals.

For the numerical evaluation of Gaunt coefficients which occur in the complete expression of the three-centre two-electron Coulomb and hybrid integrals over B functions (17), we used the subroutine GAUNT.F developed by Weniger and Steinborn [35]. The spherical harmonics $Y_l^m(\theta, \varphi)$ are computed using the recurrence formulae presented in [35].

Tables 1 and 3 contain values with 15 correct decimals of the semi-infinite integrals $\tilde{\mathcal{K}}(s)$ (21) obtained using the infinite series with the simple sine function. These values are obtained for $s = 0.24 \times 10^{-2}$ (close to 0) and $s = 0.998$ (close to 1).

Tables 2 and 4 contain values of the semi-infinite integrals $\tilde{\mathcal{K}}(s)$ obtained using the infinite series with the spherical Bessel function ($\tilde{\mathcal{K}}(s)^a$) and values obtained using $S\bar{D}_n^{(2,0)}$ with the recurrence relations ($\tilde{\mathcal{K}}(s)^b$). The value of ϵ was set to 10^{-10}. The errors listed in these two tables are given by

$$\text{Error}^{\,a} = |\tilde{\mathcal{K}}(s)^{n_{\max}} - \tilde{\mathcal{K}}(s)^a| \qquad \text{and} \qquad \text{Error}^{\,b} = |\tilde{\mathcal{K}}(s)^{n_{\max}} - \tilde{\mathcal{K}}(s)^b|.$$

Table 5 contains values with 15 correct decimals of the semi-infinite integrals $\tilde{\mathcal{H}}(s)$ obtained using the infinite series with the simple sine function. These values are obtained for $s = 0.998$ (close to 1).

Table 9. Three-centre two-electron Coulomb and hybrid integrals over STFs. Values obtained with the H_2O.

Integral[a]	Values[a]	Values[b]	Values[c]
$\langle 1s^O 1s^O \vert 1s^{H_1} 1s^{H_2}\rangle$	0.166 733 423(0)	0.166 733 529(0)	0.166 733 320(0)
$\langle 1s^O 2s^O \vert 1s^{H_1} 1s^{H_2}\rangle$	0.336 797 277(−1)	0.336 797 499(−1)	0.336 797 078(−1)
$\langle 1s^O 2p_z^O \vert 1s^{H_1} 1s^{H_2}\rangle$	0.153 901 824(−2)	0.153 901 948(−2)	0.153 901 856(−2)
$\langle 2s^O 2s^O \vert 1s^{H_1} 1s^{H_2}\rangle$	0.145 439 173(0)	0.145 439 265(0)	0.145 439 113(0)
$\langle 2p_z^O 2p_z^O \vert 1s^{H_1} 1s^{H_2}\rangle$	0.134 763 478(0)	0.134 763 562(0)	0.134 763 449(0)
$\langle 2p_{-1}^O 2p_{-1}^O \vert 1s^{H_1} 1s^{H_2}\rangle$	0.128 387 519(0)	0.128 387 598(0)	0.128 387 564(0)
$\langle 2p_{+1}^O 2p_{-1}^O \vert 1s^{H_1} 1s^{H_2}\rangle$	−0.166 645 716(−2)	−0.166 645 661(−2)	−0.166 645 564(−2)
$\langle 1s^{H_1} 1s^{H_1} \vert 1s^{H_2} 2s^O\rangle$	0.218 488 995(0)	0.218 488 806(0)	0.218 488 712(0)
$\langle 1s^{H_1} 1s^{H_1} \vert 1s^{H_2} 2p_z^O\rangle$	0.157 272 684(0)	0.157 272 410(0)	0.157 272 721(0)
$\langle 1s^{H_1} 1s^{H_1} \vert 1s^{H_2} 2p_{+1}^O\rangle$	−0.846 278 918(−1)	−0.846 277 865(−1)	−0.846 278 181(0)
$\langle 1s^O 1s^O \vert 1s^O 1s^{H_1}\rangle$	0.175 630 427(0)	0.175 623 400(0)	0.175 622 910(0)
$\langle 2s^O 1s^O \vert 1s^O 1s^{H_1}\rangle$	0.265 463 467(−1)	0.265 463 901(−1)	0.265 463 451(−1)
$\langle 2p_z^O 1s^O \vert 2p_z^O 1s^{H_1}\rangle$	0.528 462 478(−2)	0.528 462 440(−2)	0.528 461 987(−2)
$\langle 2p_{+1}^O 1s^O \vert 2p_z^O 1s^{H_1}\rangle$	0.883 960 240(−3)	0.883 959 816(−3)	0.883 960 178(−3)
$\langle 1s^O 1s^O \vert 2p_z^O 1s^{H_1}\rangle$	0.195 970 416(0)	0.195 970 361(0)	0.195 970 464(0)
$\langle 1s^O 1s^O \vert 2p_{+1}^O 1s^{H_1}\rangle$	0.180 590 559(0)	0.180 590 518(0)	0.180 590 369(0)
$\langle 1s^{H_1} 1s^{H_1} \vert 1s^{H_1} 1s^O\rangle$	0.307 861 444(−1)	0.307 828 194(−1)	0.307 860 694(−1)
$\langle 1s^{H_1} 1s^{H_1} \vert 1s^{H_1} 2s^O\rangle$	0.323 596 407(0)	0.323 596 486(0)	0.323 596 003(0)
$\langle 1s^{H_1} 1s^{H_1} \vert 1s^{H_1} 2p_z^O\rangle$	0.258 864 903(0)	0.258 864 924(0)	0.258 864 993(0)
$\langle 1s^{H_1} 1s^{H_1} \vert 1s^{H_1} 2p_{-1}^O\rangle$	0.238 549 056(0)	0.238 549 044(0)	0.238 548 823(0)

[a] The abbreviations $2p_{+1}$ and $2p_{-1}$ refer to the Slater functions defined by the quantum numbers: $(n = 2, l = 1, m = 1)$ and $(n = 2, l = 1, m = -1)$. Results obtained with the following geometry (spherical coordinates) : O(0, 0°, 0°), H_1(1.810, 52.5°, 0°) and H_2(1.810, 52.5°, 180°). $\zeta_{1s}^O = 7.670$, $\zeta_{2s}^O = 2.09$, $\zeta_{2p_z}^O = \zeta_{2p_{\pm 1}}^O = 1.5$ and $\zeta_{1s}^H = 1.21$. Values[a]: obtained using the $S\bar{D}$ with the recurrence relations. The value of epsilon (equation (32)) was set to 10^{-15}. The finite outer s integrals and all the finite integrals which occur in the expression of $S\bar{D}$ are evaluated using Gauss–Legendre quadrature of order 48. Values[b]: obtained using Slater-type orbital package (STOP) [27]. Values[c]: obtained using the code (ADGGSTNGINT) developed by Rico *et al* [28].

Table 6 contains values of the semi-infinite integrals $\tilde{\mathcal{H}}(s)$ obtained using the infinite series with the spherical Bessel function ($\tilde{\mathcal{H}}(s)^a$) and values obtained using $S\bar{D}_n^{(2,0)}$ with the recurrence relations ($\tilde{\mathcal{H}}(s)^b$). The value of ϵ was set to 10^{-10}. The errors listed in this table are given by

$$\text{Error}^a = |\tilde{\mathcal{H}}(s)^{n_{\max}} - \tilde{\mathcal{H}}(s)^a| \qquad \text{and} \qquad \text{Error}^b = |\tilde{\mathcal{H}}(s)^{n_{\max}} - \tilde{\mathcal{H}}(s)^b|.$$

The calculation times listed in tables 1–6 are in milliseconds.

Tables 7 and 8 contain values obtained for $S\bar{D}_n^{(2,0)}$ obtained using equations (31), (33) and (35). From these two tables, we can note that when values of $G(x_{i+j})$ are very small, the use of equations (33) and (35) gives accurate results. From these tables we can note that $S\bar{D}_{10}^{(2,0)}$ and $S\bar{D}_{11}^{(2,0)}$ from equation (31) does not give any values, due to the fact that $G(x_8)$ and $G(x_9)$ in table 7 and $G(x_9)$ and $G(x_{10})$ in table 8 are considered as 0 by the machine.

Table 9 contains values of the three-centre two-electron Coulomb and hybrid integrals over STFs. These values are obtained with the planar molecule H_2O. Values[a] are obtained using the new algorithm. Values[b] were obtained with STOP developed by Bouferguene *et al* [27] and Values[c] were obtained with a code 'ADGGSTNGINT', using STOnG (STFs expressed as a combination of n GTFs), developed by Rico *et al* [28].

Table 10 contains values of the three-centre two-electron Coulomb and hybrid integrals over STFs. These values are obtained with the planar molecule C_2H_4. Values[a] are obtained

Table 10. Three-centre two-electron and hybrid integrals over STFs. Values obtained with the C_2H_4 molecule[a].

Integral	Values[a]	Values[b]	Values[c]
$\langle 1s^{C^1} 1s^{C^1} \vert 1s^H 1s^{C^2}\rangle$	0.302 190 537(−1)	0.302 168 365(−1)	0.302 189 670(−1)
$\langle 1s^{C^1} 1s^{C^1} \vert 1s^H 2s^{C^2}\rangle$	0.193 446 397(0)	0.193 452 377(0)	0.193 446 239(0)
$\langle 1s^{C^1} 1s^{C^1} \vert 1s^H 2p_z^{C^2}\rangle$	0.245 171 858(−1)	0.244 921 199(−1)	0.245 167 332(−1)
$\langle 2s^{C^1} 1s^{C^1} \vert 1s^H 1s^{C^2}\rangle$	0.495 876 724(−2)	0.495 840 359(−2)	0.495 875 301(−2)
$\langle 2s^{C^1} 2s^{C^1} \vert 1s^H 1s^{C^2}\rangle$	0.291 659 320(−1)	0.291 645 767(−1)	0.291 658 478(−1)
$\langle 2p_z^{C^1} 2p_z^{C^1} \vert 1s^H 2s^{C^2}\rangle$	0.199 079 760(0)	0.199 087 973(0)	0.199 079 574(0)
$\langle 2p_z^{C^1} 2p_z^{C^1} \vert 1s^H 2p_z^{C^2}\rangle$	0.332 481 668(−1)	0.332 174 598(−1)	0.332 476 978(−1)
$\langle 2p_z^{C^1} 2p_z^{C^1} \vert 1s^H 2p_{+1}^{C^2}\rangle$	0.900 918 656(−1)	0.901 008 177(−1)	0.900 920 232(−1)
$\langle 1s^{C^1} 1s^{C^1} \vert 1s^{C^1} 1s^{C^2}\rangle$	0.466 182 869(−4)	0.465 105 483(−4)	0.466 178 688(−4)
$\langle 1s^{C^1} 1s^{C^1} \vert 1s^{C^1} 2s^{C^2}\rangle$	0.136 049 511(0)	0.136 895 061(0)	0.136 951 019(0)
$\langle 1s^{C^1} 1s^{C^1} \vert 1s^{C^1} 2p_z^{C^2}\rangle$	−0.194 543 772(0)	−0.194 445 010(0)	−0.194 543 218(0)
$\langle 1s^{C^1} 1s^{C^1} \vert 2p_z^{C^1} 2p_z^{C^2}\rangle$	−0.235 395 380(0)	−0.235 380 213(0)	−0.235 395 379(0)
$\langle 1s^{C^1} 1s^{C^1} \vert 2p_{+1}^{C^1} 2p_{+1}^{C^2}$	0.122 440 444(0)	0.122 064 158(0)	0.122 115 515(0)
$\langle 2p_z^{C^1} 2p_z^{C^1} \vert 2p_z^{C^1} 2p_z^{C^2}\rangle$	−0.209 119 826(0)	−0.209 120 100(0)	−0.209 119 826(0)
$\langle 2p_z^{C^1} 2p_z^{C^1} \vert 2p_{+1}^{C^1} 2p_{+1}^{C^2}\rangle$	0.130 266 320(0)	0.130 211 418(0)	0.130 266 320(0)
$\langle 2p_{+1}^{C^1} 2p_{+1}^{C^1} \vert 2p_{+1}^{C^1} 2p_{+1}^{C^2}\rangle$	0.127 717 050(0)	0.127 662 095(00)	0.133 128 244(0)

[a] Results obtained with the following geometry (cartesian coordinates): $C^1(0, 0, 0)$, $C^2(0, 0, 2.551\,16)$ and H(−1.751 13, 0, 3.562 17). $\zeta_{1s}^C = 5.636\,105$, $\zeta_{2s}^C = 1.346\,562$, $\zeta_{2p_z}^C = \zeta_{2p_{\pm1}}^C = 1.581\,274$ and $\zeta_{1s}^H = 1.0$. Values[a] are obtained using the $S\bar{D}$ with the recurrence relations. The value of epsilon (equation (32)) was set to 10^{-15}. The finite outer *s* integrals and all the finite integrals which occur in the expression of $S\bar{D}$ are evaluated using Gauss–Legendre quadrature of order 48. Values[b] are obtained using Slater-type orbital package (STOP) [27]. Values[c] are obtained using the code (ADGGSTNGINT) developed by Rico *et al* [28].

using the new algorithm. Values[b] were obtained with STOP. Values[c] were obtained with ADGGSTNGINT.

For the calculation presented in tables 9 and 10, we used equation (4) to express the integrals over STFs as finite linear combinations of integrals over *B* functions.

From tables 9 and 10, one can note that the values obtained using the new algorithm are in agreement with those obtained using STOP and ADGGSTNGINT.

All the calculations were performed on a PC-Workstation Intel Xeon Processor 2.4 GHz.

5. Conclusion

Three-centre two-electron Coulomb and hybrid integrals over STFs are expressed as finite linear combination of integrals over the so-called *B* functions in order to apply the Fourier transform method, and then to develop analytic expressions for the integrals under consideration. These analytic expressions turned out very difficult to evaluate to because of the presence of highly semi-infinite integrals involving spherical Bessel functions and not a simple trigonometric function.

It was shown that these semi-infinite integrals are suitable to apply the $S\bar{D}$ method, which consists in transforming the semi-infinite integrals involving Bessel functions into semi-infinite integrals involving the simple sine function, and on applying the non-linear $\bar{D}$ with a second-order differential equation. The use of Cramer's rule was made possible with the help of practical properties of the sine function.

The algorithm developed in the present work is now shown very efficient, great simplifications are obtained with the help of the recurrence relations satisfied by the terms that occur in the expression of the approximations $S\bar{D}_n^{(2,j)}$. The numerical and computational study showed that the use of $S\bar{D}$ combined with quadrature rules can also give accurate results in certain regions corresponding to the case where the value of v is very small.

The numerical results show this approach yields values for these integrals to a predetermined high accuracy and with unprecedented rapidity.

Numerical results are obtained for three-centre two-electron Coulomb and hybrid integrals over STFs with H_2O and C_2H_4 molecules. All are precise and very rapid. These results confirm that this $S\bar{D}$ transformation represents another most significant advance on the road to routine precise and rapid evaluation of these molecular electronic integrals.

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