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Multicentre two-electron Coulomb and exchange integrals over Slater functions evaluated using a generalized algorithm based on nonlinear transformations

Lilian Berlu and Hassan Safouhi

Faculté Saint-Jean/University of Alberta, 8406, 91 Street, Edmonton, Alberta T6C 4G9, Canada

E-mail: hassan.safouhi@ualberta.ca and lilian.berlu@chimsrv1.univ-bpclermont.fr

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Abstract
When calculating molecular electronic energies, the contributions involving the Coulomb operator for bielectronic terms are required rapidly and to high chemically significant accuracy. The atomic orbital basis functions chosen in the present work are Slater-type functions (STFs). 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 two- or three-dimensional integral representations. In this work, we present a generalized algorithm for a precise and fast numerical evaluation of molecular integrals over STFs. Numerical results obtained with C_2H_2, C_2H_4 and CH_4 molecules show the efficiency of the approach presented in this work. Comparisons with the existing codes are also listed.

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1. Introduction

Previous work [1–5] on the accurate and fast numerical evaluation of multicentre one- and two-electron integrals over Slater-type functions (STFs) [6, 7] continues with the present contribution. Among the integrals required to develop electronic structure theory over STFs are the four-centre two-electron Coulomb integrals (the most difficult type of integrals which occur in molecular structure calculations). These integrals are given by

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

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

In the case where $A = C$, we obtain the expression of three-centre exchange integrals. Two-centre exchange integrals correspond to the case where $A = C$ and $B = D$. If $A = B$, then we obtain the expression of three-centre two-electron Coulomb integrals denoted by $\mathcal{K}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$. Hybrid integrals, $\mathcal{H}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$, are obtained in the case where $A = B = C$.

STFs constitute an important basis set for all calculations of physical properties of molecules and solids, which use the linear combination of atomic orbitals (LCAO) approach [8]. However, the systematic use of STFs has been prevented by the fact that their multicentre integrals turned out to be extremely complicated. We note that many researchers hope that the next generation of *ab initio* programs will be based on the usage of STFs [9–12]. Recently [12], Handy and co-workers reported extensions to their Slater code for density functional theory (DFT) to include exact exchange. They used a resolution of the identity approach to simplify the integrals.

Various studies have focused on the use of B functions, proposed by Shavitt [13] and introduced by Filter and Steinborn [14, 15]. These functions are analytically more complicated than STFs but they have much more appealing properties applicable to multicentre integral problems [15–19]. Note that the Fourier transform of a B function is of exceptional simplicity [19, 20] and that STFs can be expressed as finite linear combinations of STFs [14, 16]. The molecular integrals over STFs can be expressed as finite linear combinations of integrals over B functions.

The B functions are well adapted to the Fourier-transform method [21–23], which led to analytic expressions for molecular multicentre integrals. These analytic expressions present severe numerical and computational difficulties due to the presence of two- or three-dimensional integral representations, whose integrands are highly oscillatory functions because of the presence of spherical Bessel functions.

It is well known that numerical integration of oscillatory integrands is difficult, especially when the oscillatory part is a spherical Bessel function and not a simple trigonometric function [24, 25].

Nonlinear-transformation methods for accelerating the convergence of oscillatory integrals or infinite series have been studied for many years and applied to various situations [26]. These methods are based on the idea of extrapolation. Their utility for enhancing convergence has been amply demonstrated by Shanks [27]. With the help of nonlinear transformations, the improvement of convergence can be remarkable. Note that different techniques based on nonlinear transformations for improving convergence of highly oscillatory integrals including Bessel function integrals and algorithms for their efficient computation are presented in [28–32].

In the present work, we used the $S\overline{D}$ approach [1–3]. With the help of this method, the semi-infinite integrals involving spherical Bessel functions are transformed into semi-infinite integrals involving the sine function, and the nonlinear $\overline{D}$ transformation of Sidi [28, 29] is applied with a second-order differential equation.

Recently, we developed an extremely efficient algorithm, based on the $S\overline{D}$ method, for a fast numerical evaluation for three-centre nuclear attraction [4], three-centre two-electron

Coulomb and hybrid integrals [5] over STFs. It is now shown that this algorithm can be generalized to be applied to all multicentre two-electron Coulomb and exchange integrals, which are the most difficult integrals occurring in any accurate molecular structure calculations using the LCAO-MO approach. Recurrence relations are developed to further simplify the calculation and to further reduce the calculation times for a high pre-determined accuracy.

The numerical results that we obtained for the integrals under consideration over B functions are in complete agreement with those obtained by Grotendorst and Steinborn [23]. Values of the Coulomb integrals over STFs are obtained with C_2H_2, C_2H_4 and CH_4 molecules. We performed the same calculations using the code ADGGSTNGINT developed by Rico *et al* [33] using STOnG (STFs expressed as a combination of n GTFs).

Numerical tables for the three-centre nuclear attraction integrals over B functions and over STFs with linear and nonlinear systems can be found in [4] where we listed values obtained with the Alchemy package [34] and with STOP (Slater-type orbital package) [35]. Numerical tables for the three-centre two-electron Coulomb and hybrid integrals could be found in [5], where comparisons with values obtained using STOP and ADGGSTNGINT are listed.

2. General definitions and properties

The Slater-type functions are defined in normalized form according to the following relationship [6, 7]:

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

where n, l, m are the quantum numbers and $Y_l^m(\theta,\varphi)$ stands for the surface spherical harmonic and is defined explicitly using the Condon–Shortley phase convention as follows [36]:

$$Y_l^m(\theta,\varphi) = \mathrm{i}^{m+|m|}\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{\frac{1}{2}} P_l^{|m|}(\cos\theta)\,\mathrm{e}^{\mathrm{i}m\varphi} \tag{3}$$

$P_l^m(x)$ is the associated Legendre polynomial of lth degree and mth order.

STFs can be expressed as finite linear combinations of B functions [14]:

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

where

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

The B functions are defined as follows [14, 15]:

$$B_{n,l}^{m}(\zeta,\vec{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!}\widehat{k}_{n-\frac{1}{2}}(\zeta r) Y_l^m(\theta_{\vec{r}},\varphi_{\vec{r}}). \tag{6}$$

The reduced Bessel function $\hat{k}_{n+\frac{1}{2}}(z)$ is defined by [13, 15]:

$$\hat{k}_{n+\frac{1}{2}}(z) = \sqrt{\frac{2}{\pi}}(z)^{n+\frac{1}{2}} K_{n+\frac{1}{2}}(z) \tag{7}$$

$$= z^n\,\mathrm{e}^{-z}\sum_{j=0}^{n}\frac{(n+j)!}{j!(n-j)!}\frac{1}{(2z)^j} \tag{8}$$

where $K_{n+\frac{1}{2}}$ stands for the modified Bessel function of the second kind [37].

The reduced Bessel functions satisfy the following relations [13, 37]:

$$\widehat{k}_{n+\frac{1}{2}}(z) = (2n-1)\,\widehat{k}_{n-\frac{1}{2}}(z) + z^2\,\widehat{k}_{(n-1)-\frac{1}{2}}(z) \tag{9}$$

$$\left(\frac{\mathrm{d}}{z\,\mathrm{d}z}\right)^m \frac{\widehat{k}_{n+\frac{1}{2}}(z)}{z^{2n+1}} = (-1)^m \frac{\widehat{k}_{n+m+\frac{1}{2}}(z)}{z^{2(n+m)+1}}. \tag{10}$$

The spherical Bessel function $j_l(x)$ is defined by [37]

$$j_l(x) = (-1)^l x^l \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^l \left(\frac{\sin(x)}{x}\right). \tag{11}$$

The spherical Bessel function satisfies the following recurrence relation [37]:

$$x j_{l-1}(x) + x j_{l+1}(x) = (2l+1)\,j_l(x). \tag{12}$$

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 Fourier-transform $\bar{f}$ of a function f is given by

$$\bar{f}(\vec{k}) = (2\pi)^{-3/2} \int_{\vec{r}} \mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}} f(\vec{r})\,\mathrm{d}\vec{r}. \tag{13}$$

The Fourier-transform $\overline{B}^m_{n,l}(\zeta, \vec{p})$ of $B^m_{n,l}(\zeta, \vec{r})$ is given by [19, 20]

$$\overline{B}^m_{n,l}(\zeta, \vec{p}) = \sqrt{\frac{2}{\pi}}\,\zeta^{2n+l-1} \frac{(-\mathrm{i}|p|)^l}{(\zeta^2 + |p|^2)^{n+l+1}} Y^m_l(\theta_{\vec{p}}, \varphi_{\vec{p}}). \tag{14}$$

The Fourier-integral representation of the Coulomb operator is given by [38]

$$\frac{1}{|\vec{r} - \overrightarrow{R}_1|} = \frac{1}{2\pi^2} \int_{\vec{k}} \frac{\mathrm{e}^{-\mathrm{i}\vec{k}\cdot(\vec{r} - \overrightarrow{R}_1)}}{k^2}\,\mathrm{d}\vec{k}. \tag{15}$$

By using equation (4), one can express the four-centre two-electron Coulomb integrals ${}_S\mathcal{J}^{\tilde{n}_2 l_2 m_2, \tilde{n}_4 l_4 m_4}_{\tilde{n}_1 l_1 m_1, \tilde{n}_3 l_3 m_3}$ over STFs (1) as finite linear combinations of integrals over B functions:

$$\begin{aligned}
{}_S\mathcal{J}^{\tilde{n}_2 l_2 m_2, \tilde{n}_4 l_4 m_4}_{\tilde{n}_1 l_1 m_1, \tilde{n}_3 l_3 m_3} = {} & \sum_{n_1=\tilde{p}_1}^{\tilde{n}_1 - l_1} \frac{(-1)^{\tilde{n}_1 - l_1 - n_1} 2^{2n_1 + 2l_1 - \tilde{n}_1} (l_1 + n_1)!}{(2n_1 - \tilde{n}_1 + l_1)!(\tilde{n}_1 - l_1 - n_1)!} \\
& \times \sum_{n_2=\tilde{p}_2}^{\tilde{n}_2 - l_2} \frac{(-1)^{\tilde{n}_2 - l_2 - n_2} 2^{2n_2 + 2l_2 - \tilde{n}_2} (l_2 + n_2)!}{(2n_2 - \tilde{n}_2 + l_2)!(\tilde{n}_2 - l_2 - n_2)!} \\
& \times \sum_{n_3=\tilde{p}_3}^{\tilde{n}_3 - l_3} \frac{(-1)^{\tilde{n}_3 - l_3 - n_3} 2^{2n_3 + 2l_3 - \tilde{n}_3} (l_3 + n_3)!}{(2n_3 - \tilde{n}_3 + l_3)!(\tilde{n}_3 - l_3 - n_3)!} \\
& \times \sum_{n_4=\tilde{p}_4}^{\tilde{n}_4 - l_4} \frac{(-1)^{\tilde{n}_4 - l_4 - n_4} 2^{2n_4 + 2l_4 - \tilde{n}_4} (l_4 + n_4)!}{(2n_4 - \tilde{n}_4 + l_4)!(\tilde{n}_4 - l_4 - n_4)!} \\
& \times {}_B\mathcal{J}^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3}
\end{aligned} \tag{16}$$

where $\tilde{p}_1$, $\tilde{p}_2$, $\tilde{p}_3$ and $\tilde{p}_4$ are given by equation (5) and ${}_B\mathcal{J}^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3}$ is given by

$$\begin{aligned}
{}_B\mathcal{J}^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3} = {} & \int_{\overrightarrow{R}, \overrightarrow{R}'} \left[B^{m_1}_{n_1, l_1}(\zeta_1, \overrightarrow{R} - \overrightarrow{OA})\right]^* \left[B^{m_3}_{n_3, l_3}(\zeta_3, \overrightarrow{R}' - \overrightarrow{OC})\right]^* \\
& \times \frac{1}{|\overrightarrow{R} - \overrightarrow{R}'|} B^{m_2}_{n_2, l_2}(\zeta_2, \overrightarrow{R} - \overrightarrow{OB}) B^{m_4}_{n_4, l_4}(\zeta_4, \overrightarrow{R}' - \overrightarrow{OD})\,\mathrm{d}\overrightarrow{R}\,\mathrm{d}\overrightarrow{R}'.
\end{aligned} \tag{17}$$

By substituting the integral representation of the Coulomb operator (15) in the above expression after performing a translation of vector $\overrightarrow{OA}$ and $\overrightarrow{OD}$, we obtain

$$\begin{aligned}{}_{B}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3} &= \frac{1}{2\pi^2}\int \frac{\mathrm{e}^{\mathrm{i}\vec{x}.\overrightarrow{R}_{41}}}{x^2}\big\langle B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\big|\,\mathrm{e}^{-\mathrm{i}\vec{x}.\vec{r}}\,\big|B^{m_2}_{n_2,l_2}(\zeta_2,\vec{r}-\overrightarrow{R}_{21})\big\rangle_{\vec{r}} \\ &\quad\times\big\langle B^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}\,')\big|\,\mathrm{e}^{-\mathrm{i}\vec{x}.\vec{r}\,'}\,\big|B^{m_3}_{n_3,l_3}(\zeta_3,\vec{r}\,'-\overrightarrow{R}_{34})\big\rangle^{*}_{\vec{r}\,'}\,\mathrm{d}\vec{x} \qquad (18)\end{aligned}$$

where $\overrightarrow{R}_1 = \overrightarrow{OA}, \overrightarrow{R}_2 = \overrightarrow{OB}, \overrightarrow{R}_3 = \overrightarrow{OC}, \overrightarrow{R}_4 = \overrightarrow{OD}, \vec{r} = \overrightarrow{R} - \overrightarrow{R}_1$, $\vec{r}\,' = \overrightarrow{R}' - \overrightarrow{R}_4$ and $\overrightarrow{R}_{ij} = \overrightarrow{R}_i - \overrightarrow{R}_j$.

In the case of three-centre two-electron exchange integrals, $\overrightarrow{R}_1 = \overrightarrow{R}_3$ and in the case of two-centre two-electron exchange integrals, $\overrightarrow{R}_1 = \overrightarrow{R}_3$ and $\overrightarrow{R}_2 = \overrightarrow{R}_4$.

The Fourier-transform method allowed analytic expressions to be developed for the terms $\big\langle B^{m_i}_{n_i,l_i}(\zeta_i,\vec{r})\big|\,\mathrm{e}^{-\mathrm{i}\vec{x}.\vec{r}}\,\big|B^{m_j}_{n_j,l_j}(\zeta_j,\vec{r}-\overrightarrow{R})\big\rangle_{\vec{r}}$ [22, 23]. This result led to analytic expressions for two-electron multicentre integrals over B functions, which are given by [23]

$$\begin{aligned}{}_{B}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3} &= 8(4\pi)^5(2l_1+1)!!(2l_2+1)!!\frac{(n_1+l_1+n_2+l_2+1)!}{(n_1+l_1)!(n_2+l_2)!} \\ &\quad\times(-1)^{l_1+l_2}(2l_3+1)!!(2l_4+1)!!\frac{(n_3+l_3+n_4+l_4+1)!}{(n_3+l_3)!(n_4+l_4)!}\zeta_1^{2n_1+l_1-1}\zeta_2^{2n_2+l_2-1} \\ &\quad\times\zeta_3^{2n_3+l_3-1}\zeta_4^{2n_4+l_4-1}\sum_{l_1'=0}^{l_1}\sum_{m_1'=\mu_{11}}^{\mu_{12}}\mathrm{i}^{l_1+l_1'}\frac{\langle l_1m_1|l_1'm_1'|l_1-l_1'm_1-m_1'\rangle}{(2l_1'+1)!![2(l_1-l_1')+1]!!} \\ &\quad\times\sum_{l_2'=0}^{l_2}\sum_{m_2'=\mu_{21}}^{\mu_{22}}\mathrm{i}^{l_2+l_2'}(-1)^{l_2'}\frac{\langle l_2m_2|l_2'm_2'|l_2-l_2'm_2-m_2'\rangle}{(2l_2'+1)!![2(l_2-l_2')+1]!!} \\ &\quad\times\sum_{l_3'=0}^{l_3}\sum_{m_1'=\mu_{31}}^{\mu_{32}}\mathrm{i}^{l_3+l_3'}\frac{\langle l_3m_3|l_3'm_3'|l_3-l_3'm_3-m_3'\rangle}{(2l_3'+1)!![2(l_3-l_3')+1]!!} \\ &\quad\times\sum_{l_4'=0}^{l_4}\sum_{m_4'=\mu_{41}}^{\mu_{42}}\mathrm{i}^{l_4+l_4'}(-1)^{l_4'}\frac{\langle l_4m_4|l_4'm_4'|l_4-l_4'm_4-m_4'\rangle}{(2l_4'+1)!![2(l_4-l_4')+1]!!} \\ &\quad\times\sum_{l=l_{1,\min},2}^{l_1'+l_2'}\langle l_2'm_2'|l_1'm_1'|l\,m_2'-m_1'\rangle R_{21}^{l}Y_l^{m_2'-m_1'}\big(\theta_{\overrightarrow{R}_{21}},\varphi_{\overrightarrow{R}_{21}}\big) \\ &\quad\times\sum_{l_{12}=l'_{1,\min},2}^{l_1-l_1'+l_2-l_2'}\langle l_2-l_2'm_2-m_2'|l_1-l_1'm_1-m_1'|l_{12}m_{21}\rangle \\ &\quad\times\sum_{l'=l_{2,\min},2}^{l_3'+l_4'}\langle l_4'm_4'|l_3'm_3'|l'\,m_4'-m_3'\rangle R_{34}^{l'}Y_{l'}^{m_4'-m_3'}\big(\theta_{\overrightarrow{R}_{34}},\varphi_{\overrightarrow{R}_{34}}\big) \\ &\quad\times\sum_{l_{34}=l'_{2,\min},2}^{l_3-l_3'+l_4-l_4'}\langle l_4-l_4'm_4-m_4'|l_3-l_3'm_3-m_3'|l_{34}m_{43}\rangle \\ &\quad\times\sum_{\lambda=l''_{\min},2}^{l_{12}+l_{34}}(-\mathrm{i})^{\lambda}\langle l_{12}m_{21}|l_{34}m_{43}|\lambda\mu\rangle\end{aligned}$$

$$\times \sum_{j_{12}=0}^{\Delta l_{12}} \sum_{j_{34}=0}^{\Delta l_{34}} \binom{\Delta l_{12}}{j_{12}} \binom{\Delta l_{34}}{j_{34}} \frac{(-1)^{j_{12}+j_{34}}}{2^{\nu_1+\nu_2+l+l'+1}\left(\nu_1+\frac{1}{2}+l\right)!\left(\nu_2+\frac{1}{2}+l'\right)!}$$
$$\times \int_{s=0}^{1} \frac{s^{n_2+l_2+l_1}(1-s)^{n_1+l_1+l_2}}{s^{l'_1}(1-s)^{l'_2}} \int_{t=0}^{1} \frac{t^{n_4+l_4+l_3}(1-t)^{n_3+l_3+l_4}}{t^{l'_3}(1-t)^{l'_4}} Y_{\lambda}^{m_2-\mu}(\theta_{\vec{v}}, \varphi_{\vec{v}})$$
$$\times \left[\int_{x=0}^{+\infty} x^{n_x} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{34}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}} j_{\lambda}(vx)\,\mathrm{d}x\right] \mathrm{d}t\,\mathrm{d}s \qquad (19)$$

where $\langle l_1m_1|l_2m_2|l_3m_3\rangle$ stands for the Gaunt coefficients [42–44], and

$$\begin{aligned}
&\mu = (m_2-m'_2)-(m_1-m'_1)+(m_4-m'_4)-(m_3-m'_3)\\
&n_{\gamma_{12}} = 2(n_1+l_1+n_2+l_2)-(l'_1+l'_2)-l+1\\
&n_{\gamma_{34}} = 2(n_3+l_3+n_4+l_4)-(l'_3+l'_4)-l'+1\\
&\mu_{1i} = \max(-l'_i, m_i-l_i+l'_i) \qquad \text{for} \quad i=1,2,3,4\\
&\mu_{2i} = \min(l_i, m_i+l_i-l'_i) \qquad \text{for} \quad i=1,2,3,4\\
&[\gamma_{12}(s,x)]^2 = (1-s)\zeta_1^2+s\zeta_2^2+s(1-s)x^2\\
&[\gamma_{34}(t,x)]^2 = (1-t)\zeta_3^2+t\zeta_4^2+t(1-t)x^2\\
&n_x = l_1-l'_1+l_2-l'_2+l_3-l'_3+l_4-l'_4\\
&\nu_1 = n_1+n_2+l_1+l_2-l-j_{12}+\frac{1}{2}\\
&\nu_2 = n_3+n_4+l_3+l_4-l'-j_{34}+\frac{1}{2}\\
&\vec{v} = (1-s)\overrightarrow{R}_{21}+(1-t)\overrightarrow{R}_{43}-\overrightarrow{R}_{41}\\
&\Delta l_{12} = \frac{l'_1+l'_2-l}{2} \qquad \Delta l_{34} = \frac{l'_3+l'_4-l'}{2}\\
&m_{ij} = m_i-m'_i-(m_j-m'_j).
\end{aligned}$$

Let $\widetilde{\mathcal{J}}(s,t)$ be the semi-infinite integral which occurs in the above analytic expression. It is given by

$$\widetilde{\mathcal{J}}(s,t) = \int_0^{+\infty} x^{n_x} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{34}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}} j_{\lambda}(vx)\,\mathrm{d}x. \qquad (20)$$

The numerical evaluation of the three-dimensional integral representation, which occurs in equation (19), turned out to be extremely difficult when the values of s and t are close to 0 or 1. In these regions the asymptotic behaviour of the integrand of $\widetilde{\mathcal{J}}(s,t)$, which will be referred to as $\mathcal{F}_{s,t}(x)$, cannot be represented by a function of the form $\mathrm{e}^{-\alpha x}g(x)$ where $g(x)$ is not a rapidly oscillating function. This is due to the fact that when s and t are close to 0 or 1, the arguments $\gamma_{12}(s,x)$ and $\gamma_{34}(t,x)$ of $\widehat{k}_{\nu_1}$ and $\widehat{k}_{\nu_2}$ become constants and therefore the rapid oscillations of $j_\lambda(vx)$ cannot be damped by the exponential decreasing functions $\widehat{k}_{\nu_1}$ and $\widehat{k}_{\nu_2}$. Note that when the value of v is very large, the zeros of $\mathcal{F}_{s,t}(x)$ become closer and therefore the oscillations become strong (see figure 1) and then the numerical evaluation of $\widetilde{\mathcal{J}}(s,t)$ become very difficult in particular for large values of λ.

We note that in the case when $v \to 0$, the semi-infinite integral $\widetilde{\mathcal{J}}(s,t)$ (20) 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 an exponentially decreasing function, to obtain a good

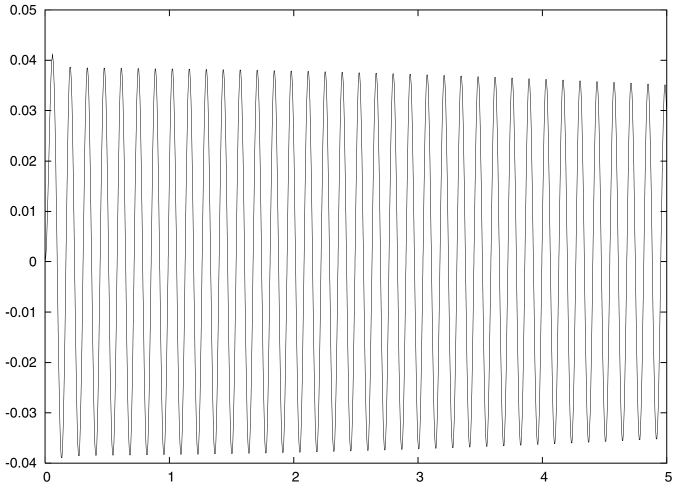

Figure 1. The integrand $\mathcal{F}_{s,t}(x)$ of $\widetilde{\mathcal{J}}(s,t)$ (20). $s = 0.999$, $t = 0.005$, $\nu_{12} = \nu_{34} = 5/2$, $n_{\gamma_{12}} = n_{\gamma_{34}} = 1$, $n_x = \lambda = 1$, $\zeta_1 = \zeta_4 = 1.0$, $\zeta_2 = 1.5$, $\zeta_3 = 2.0$, $R_{12} = 2.0$ and $R_{34} = 1.0$.

approximation of the semi-infinite integral which is given by

$$\widetilde{\mathcal{J}}(s,t) \approx \int_0^{+\infty} x^{n_x} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{34}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}}\,\mathrm{d}x. \qquad (21)$$

For the evaluation of the above semi-infinite integral, we used the Gauss–Laguerre quadrature of order 64. Note that the accuracy in the evaluation of the above semi-infinite integral can be further improved by including higher terms of the power series expansion of $j_0(\alpha)$ around $\alpha = 0$.

The semi-infinite integral $\widetilde{\mathcal{J}}(s,t)$ can be transformed into an infinite series of integrals as follows:

$$\widetilde{\mathcal{J}}(s,t) = \sum_{n=0}^{+\infty} \int_{j^n_{\lambda,v}}^{j^{n+1}_{\lambda,v}} x^{n_x} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{34}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}} j_\lambda(vx)\,\mathrm{d}x \qquad (22)$$

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

The above infinite series is convergent and alternating, therefore the sum of N first terms, for N sufficiently large, gives a good approximation of the semi-infinite integral. Unfortunately, the use of this approach requires a large amount of (CPU) time in particular for large values of v as can be seen from table 1.

In previous work [39], we demonstrated that $\widetilde{\mathcal{J}}(s,t)$ is suitable to apply the nonlinear $\overline{D}$ transformation [28, 29]. The integrand $\mathcal{F}_{s,t}(x)$ satisfies a sixth-order linear differential equation with coefficients having asymptotic expansions in inverse powers of their argument x as $x \to +\infty$. The approximation $\overline{D}^{(6)}_n$ of $\widetilde{\mathcal{J}}(s,t)$ is obtained by solving a linear set of equations of order $(5n+1)$ where the computation of the fifth successive derivatives of $\mathcal{F}_{s,t}(x)$ and the computation of the $(5n+1)$ successive positive zeros of spherical Bessel functions are required for the calculations. This requires a considerable amount of (CPU) time especially when the values of the quantum numbers are large.

With the help of previous work of Sidi [29, 30], a second-order linear differential equation satisfied by the integrand $\mathcal{F}_{s,t}(x)$ was obtained. This differential equation is suitable to apply

Table 1. Evaluation of $\widetilde{\mathcal{J}}(s,t)$ (20). $s, t, \nu_{12}, n_{\gamma_{12}}, \nu_{34}, n_{\gamma_{34}}, n_x, \lambda, \zeta_1, \zeta_2, \zeta_3, \zeta_4, R_{12}$ and R_{34} are given in table 2. $\widetilde{\mathcal{J}}(s,t)^{(a)}$ were obtained using the infinite series with spherical Bessel function (22). $\widetilde{\mathcal{J}}(s,t)^{(b)}$ were obtained using $S\overline{D}_n^{(2,0)}$ (31). Calculation times are in milliseconds.

$m_{\max}$	$\widetilde{\mathcal{J}}(s,t)^{(a)}$	Error$^{(a)}$	Time	n	$\widetilde{\mathcal{J}}(s,t)^{(b)}$	Error$^{(b)}$	Time
1424	0.444 524 8692(0)	0.33(−15)	22.81	7	0.444 524 8693(0)	0.77(−10)	0.15
2172	0.288 524 0417(−2)	0.11(−14)	38.45	7	0.288 524 0418(−2)	0.50(−12)	0.20
1252	0.845 400 1547(−2)	0.28(−15)	22.59	7	0.845 400 1548(−2)	0.14(−11)	0.20
912	0.352 713 8436(−2)	0.11(−14)	16.36	7	0.352 713 8437(−2)	0.55(−12)	0.17
2168	0.923 138 8415(−2)	0.11(−14)	39.92	7	0.923 138 8417(−2)	0.16(−11)	0.21
1084	0.433 358 1086(−2)	0.96(−15)	20.21	7	0.433 358 1086(−2)	0.68(−12)	0.19
1873	0.177 355 4024(−2)	0.33(−14)	37.66	7	0.177 355 4025(−2)	0.30(−12)	0.26
1543	0.128 293 3783(−2)	0.11(−13)	30.74	6	0.128 293 3783(−2)	0.25(−13)	0.20
2395	0.358 146 1352(−2)	0.26(−12)	49.35	7	0.358 146 1353(−2)	0.60(−12)	0.33
1845	0.981 745 6422(−3)	0.46(−13)	37.06	6	0.981 745 6422(−3)	0.18(−13)	0.26
1796	0.201 074 7195(−2)	0.12(−12)	37.98	7	0.201 074 7195(−2)	0.30(−12)	0.35
1439	0.242 745 1639(−2)	0.78(−13)	29.99	7	0.242 745 1639(−2)	0.34(−12)	0.29
942	0.186 622 9608(−2)	0.25(−12)	21.57	7	0.186 622 9608(−2)	0.69(−12)	0.47
1145	0.339 934 5708(−2)	0.31(−11)	25.41	7	0.339 934 5704(−2)	0.69(−12)	0.39
1630	0.250 394 2519(−2)	0.26(−10)	39.29	7	0.250 394 2546(−2)	0.40(−12)	0.49
840	0.172 215 3979(−2)	0.41(−11)	19.15	6	0.172 215 3984(−2)	0.98(−12)	0.36

the nonlinear $\overline{D}$. This led to the approximation $\overline{D}_n^{(2)}$, which is obtained by solving a set of linear equations of order $(n+1)$ and where it is not necessary to compute the successive derivatives of the integrand, only the first derivative of the spherical Bessel function is required for the calculations [40]. Great simplifications and a substantial gain in the calculation times were realized using this approach. However, it is still necessary for the calculation of the approximation $\overline{D}_n^{(2)}$ to compute the successive zeros of the spherical Bessel functions and a method to solve linear systems. This requires a considerable amount of (CPU) time, especially when dealing with spherical Bessel functions with large order.

Now, we will state a theorem which is fully demonstrated in [1].

Let $\tilde{A}^{(\gamma)}$ for some γ be the set of infinitely differentiable functions $p(x)$, which have asymptotic expansions in inverse powers of x as $x \to +\infty$, of the form

$$p(x) \sim x^{\gamma}\left(a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} + \cdots\right) \tag{23}$$

such that $a_0 = \lim_{x\to+\infty} x^{-\gamma} p(x) \neq 0$.

We define the functional $\alpha_0(p)$ by $\alpha_0(p) = a_0 = \lim_{x\to+\infty} x^{-\gamma} p(x)$.

Theorem 1 [1]. *Let $f(x)$ be a function of the form*

$$f(x) = g(x) j_{\lambda}(x)$$

where $g(x)$ is in $\mathcal{C}^2([0,+\infty[)$, which is the set of functions that are twice continuously differentiable on $[0,+\infty[$, and of the form

$$g(x) = h(x)\,\mathrm{e}^{\phi(x)}$$

and where $h(x) \in \tilde{A}^{(\gamma)}$ and $\phi(x) \in \tilde{A}^{(k)}$ for some γ and k.

If $k > 0, \alpha_0(\phi) < 0$ and for all $l = 0, \ldots, \lambda - 1$:

$$\lim_{x\to 0} x^{l-\lambda+1}\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{l}(x^{\lambda-1}g(x))\,j_{\lambda-1-l}(x) = 0$$

then $f(x)$ *is integrable on* $[0, +\infty[$ *(i.e.* $\int_0^{+\infty} f(t)\,\mathrm{d}t$ *exists) and*

$$\int_0^{+\infty} f(x)\,\mathrm{d}x = \int_0^{+\infty} \left[\left(\frac{\mathrm{d}}{x\,\mathrm{d}x} \right)^{\lambda} (x^{\lambda-1} g(x)) \right] \sin(x)\,\mathrm{d}x. \tag{24}$$

As can be seen from equation (24), the semi-infinite integral involving spherical Bessel functions is transformed into a semi-infinite integral involving the simple sine function. It is well known that the numerical integration of oscillatory integrands is very difficult when the oscillatory part is a spherical Bessel function and not a simple trigonometric function [24, 25].

It is shown [2], that the integrand of the semi-infinite integral in the right-hand side of equation (24) satisfies a second-order linear differential equation of the form required to apply the nonlinear $\overline{D}$ transformation. The approximation of the semi-infinite integral was then obtained by solving a linear set of equations of order $(n + 1)$. Practical properties of the sine function allowed, as demonstrated by Levin [41], the use of Cramer's rule for calculating the approximation of the semi-infinite integral under consideration. This approximation is given by [2]

$$S\overline{D}_n^{(2,j)} = \frac{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i+j)^n F(x_{i+j}) \big/ \big[x_{i+j}^2 G(x_{i+j})\big]}{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i+j)^n \big/ \big[x_{i+j}^2 G(x_{i+j})\big]} \tag{25}$$

where $x_l = (l+1)\pi$ for $l = 0, 1, \ldots,$ $G(x) = \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda} (x^{\lambda-1} g(x))$ and where $F(x) = \int_0^x G(t) \sin(t)\,\mathrm{d}t$.

It is shown that $\mathcal{F}_{s,t}(x)$ satisfies all the conditions of theorem 1 [2]. The semi-infinite integral $\tilde{\mathcal{J}}(s,t)$ can be re-written as

$$\tilde{\mathcal{J}}(s,t) = \frac{1}{v^{\lambda+1}} \int_0^{+\infty} G_{s,t}(x) \sin(vx)\,\mathrm{d}x \tag{26}$$

$$= \frac{1}{v^{\lambda+1}} \sum_{n=0}^{+\infty} \int_{n\pi/v}^{(n+1)\pi/v} G_{s,t}(x) \sin(vx)\,\mathrm{d}x. \tag{27}$$

where the function $G_{s,t}(x)$ is given by

$$G_{s,t}(x) = \left(\frac{\mathrm{d}}{x\,\mathrm{d}x} \right)^{\lambda} \left(x^{n_x+\lambda-1} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{34}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}} \right). \tag{28}$$

As can be seen from figures 1 and 2, the oscillations of the integrand which occurs in the integral (26), which will be referred to as $\tilde{\mathcal{F}}_{s,t}(x)$, are slower than the oscillations of the integrand $\mathcal{F}_{s,t}(x)$. From tables 2 and 1, it follows that the above infinite series converges faster than the series involving the spherical Bessel function (22).

The approximation of the above semi-infinite integral can be obtained by using equation (25). Unfortunately, the computation of the approximation $S\overline{D}_n^{(2,j)}$ using equation (25) is not advantageous, because of the absence of the control of the degree of accuracy. Note also that equation (25) cannot be computed recursively. In [4], we developed a recurrence relation satisfied by both numerator $A_n^{(2,j)}$ and denominator $B_n^{(2,j)}$ of the term in the right-hand side of equation (25).

The approximation $S\overline{D}_n^{(2,j)}$, can be re-written as

$$S\overline{D}_n^{(2,j)} = \frac{1}{v^{\lambda+1}} \frac{A_n^{(2,j)}}{B_n^{(2,j)}} \qquad n, j = 0, 1, 2, \ldots. \tag{29}$$

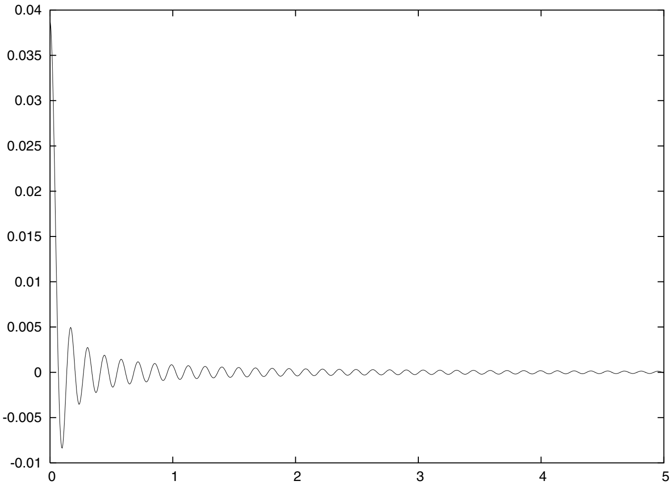

Figure 2. The integrand $\widetilde{\mathcal{F}}_{s,t}(x)$ of $\widetilde{\mathcal{J}}(s,t)$ given by equation (26). $s = 0.999, t = 0.005, \nu_{12} = \nu_{34} = 5/2, n_{\gamma_{12}} = n_{\gamma_{34}} = 1, n_x = \lambda = 1, \zeta_1 = \zeta_4 = 1.0, \zeta_2 = 1.5, \zeta_3 = 2.0, R_{12} = 2.0$ and $R_{34} = 1.0$.

Let U_i^n and V_i^n be the ith term of the finite sum $A_n^{(2,j)}$ and $B_n^{(2,j)}$, respectively. In [4], we showed that $\left(A_n^{(2,j)}\right)_n$ and $\left(B_n^{(2,j)}\right)_n$ satisfy the following relations:

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

From the above equations, it follows that $S\overline{D}_{n+1}^{(2,j)}$ can be re-written as [4]

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

As we explained in [4, 5], the most important advantage of using the above equation is the control of the degree of accuracy. In fact, we do not calculate the approximation $S\overline{D}_{k+1}^{(2,j)}$, unless the accuracy obtained using $S\overline{D}_{k}^{(2,j)}$ is not satisfactory. For this we use the following test:

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

where ϵ is defined according to the pre-determined degree of accuracy. In table 3, we listed values obtained for the semi-infinite integral $\widetilde{\mathcal{J}}(s,t)$ with ϵ varying from 10^{-8} to 10^{-16}, to show the efficiency of the above test.

The storage of the values of U_i^k and V_i^k, $k = 0, 1, 2, \ldots$ and $i = 0, 1, \ldots, k+1$, led to a substantial gain in the calculation times. The calculation of all values of $x_{i+j}^2 G(x_{i+j})$ for each order of the $S\overline{D}$ is avoided.

Table 2. Values with 15 correct decimals of $\widetilde{\mathcal{J}}(s,t)$ (20) obtained using the infinite series with the sine function (27). Calculation times are in milliseconds.

s	t	ν_{12}	$n_{\gamma_{12}}$	ν_{34}	$n_{\gamma_{34}}$	n_x	λ	ζ_1	ζ_2	ζ_3	ζ_4	R_{12}	R_{34}	$n_{\max}$	$\widetilde{\mathcal{J}}(s,t)^{n_{\max}}$	Time
0.999	0.999	5/2	5	5/2	5	0	0	1.5	1.0	1.0	1.5	0.5	1.5	1424	0.444 524 869 234 410(0)	21.84
0.999	0.005	5/2	1	5/2	1	1	1	1.0	1.7	2.0	1.0	2.0	1.0	1818	0.288 524 041 734 135(−2)	37.98
0.999	0.005	5/2	3	5/2	3	1	1	1.0	1.2	1.2	1.0	2.0	1.0	1035	0.845 400 154 683 400(−2)	22.00
0.999	0.005	5/2	5	5/2	5	1	1	1.0	1.3	1.3	1.0	2.0	1.0	744	0.352 713 843 625 665(−2)	14.15
0.005	0.005	7/2	5	7/2	5	1	1	1.5	1.5	1.5	1.5	0.2	0.4	1484	0.923 138 841 518 954(−2)	32.25
0.005	0.005	7/2	7	7/2	7	1	1	1.4	5.0	5.0	1.4	0.2	0.2	764	0.433 358 108 553 502(−2)	14.94
0.005	0.999	9/2	5	9/2	5	2	2	1.9	6.5	1.9	6.5	0.5	2.5	1288	0.177 355 402 426 657(−2)	35.64
0.999	0.999	9/2	9	9/2	9	2	2	2.0	1.5	1.5	2.0	2.0	1.0	1047	0.128 293 378 253 670(−2)	25.40
0.999	0.999	9/2	7	9/2	7	3	3	6.0	1.4	1.4	5.0	2.0	1.0	1359	0.358 146 135 268 246(−2)	48.21
0.999	0.999	9/2	9	9/2	9	3	3	2.0	1.4	1.4	5.0	2.0	1.0	1043	0.981 745 642 221 362(−3)	32.04
0.999	0.005	11/2	10	11/2	10	3	3	8.0	1.7	3.5	1.5	0.5	1.0	946	0.201 074 719 471 237(−2)	34.43
0.999	0.005	11/2	11	11/2	11	3	3	8.0	1.4	8.0	1.6	0.5	1.0	794	0.242 745 163 858 075(−2)	25.06
0.005	0.005	13/2	11	13/2	11	4	4	2.0	5.0	2.5	1.7	1.0	2.0	533	0.186 622 960 871 429(−2)	26.60
0.005	0.005	13/2	13	13/2	13	4	4	1.6	2.5	2.5	1.6	0.7	1.0	571	0.339 934 570 445 075(−2)	23.36
0.005	0.005	17/2	11	17/2	11	4	4	2.7	2.0	9.0	2.7	1.0	2.0	935	0.250 394 254 557 966(−2)	48.56
0.005	0.005	17/2	17	17/2	17	4	4	2.0	6.0	3.0	2.0	1.0	1.0	489	0.172 215 398 336 898(−2)	20.74

In [4, 5], we discussed the situation where $G(x_{i+j}) \to 0$ or $+\infty$. We demonstrated that in this situation we can obtain a very good approximation of the semi-infinite integral under consideration using the following formulae:

$$S\overline{D}_n^{(2,j)} \approx \frac{1}{v^{\lambda+1}} \frac{\sum_{i\in E} \binom{n+1}{i}(1+i+j)^n \frac{F(x_{i+j})}{x_{i+j}^2}}{\sum_{i\in E} \binom{n+1}{i}(1+i+j)^n \frac{1}{x_{i+j}^2}} \tag{33}$$

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

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

Note that the relations given by equation (30) are still applicable to the approximation $S\overline{D}_n^{(2,j)}$ given by equation (33). The following test was included in the algorithm:

$$R = \left| \frac{A_n^{(2,j)}}{\widetilde{A}_n^{(2,j)}} - \frac{B_n^{(2,j)}}{\widetilde{B}_n^{(2,j)}} \right| \leqslant \text{tiny} \qquad \text{or} \qquad \widetilde{R} = \left| \frac{\widetilde{A}_n^{(2,j)}}{A_n^{(2,j)}} - \frac{\widetilde{B}_n^{(2,j)}}{B_n^{(2,j)}} \right| \leqslant \text{tiny} \tag{34}$$

where $\widetilde{A}_n^{(2,j)}$ stands for the numerator and $\widetilde{B}_n^{(2,j)}$ for the denominator of the term in the right-hand side of equation (33) and where tiny should be set close to but not identical with the smallest floating point number that is representable on the computer. If the test is realized then the subroutine returns the approximation $S\overline{D}_n^{(2,j)}$ using equation (33) with the recurrence relations (30).

As can be seen from equation (25), the computation of the function $G_{s,t}(x)$ is necessary for the calculations. By using the Leibnitz formula, one can easily obtain

$$\begin{aligned}
&\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda} \left[x^{n_x+\lambda-1} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{34}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}}\right] \\
&\quad = \sum_{l_1=0}^{\lambda} \binom{\lambda}{l_1} \sum_{l_2=0}^{\lambda-l_1} \binom{\lambda-l_1}{l_2} \sum_{l_3=0}^{\lambda-l_1-l_2} \binom{\lambda-l_1-l_2}{l_3} \frac{(n_x+\lambda-1)!!}{(n_x+\lambda-1-2l_1)!!} x^{n_x+\lambda-1-2l_1} \\
&\quad \times \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda-l_1} \left[\frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}}\right] \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda-l_1-l_2} \left[\frac{\widehat{k}_{\nu_2}[R_{34}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}}\right].
\end{aligned} \tag{35}$$

By using equation (10) and with the help of the Leibnitz formula 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 $j \in \mathrm{N}$:

$$\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{j} \left[\frac{\widehat{k}_{\nu}[R\gamma_{ij}(s,x)]}{[\gamma_{ij}(s,x)]^{2\nu}}\right] = (-1)^j s^j (1-s)^j \frac{\widehat{k}_{\nu+j}[R\gamma_{ij}(s,x)]}{[\gamma_{ij}(s,x)]^{2(\nu+j)}} \tag{36}$$

and for $n_{\gamma_{ij}} < 2\nu$, we obtain

$$\begin{aligned}
&\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{j} \left[\frac{\widehat{k}_{\nu}[R\gamma_{ij}(s,x)]}{[\gamma_{ij}(s,x)]^{n_{\gamma_{ij}}}}\right] \\
&\quad = \frac{s^j(1-s)^j}{[\gamma_{ij}(s,x)]^{n_{\gamma_{ij}}+2j}} \sum_{i=0}^{j} \binom{j}{i} \frac{(2\nu-n_\gamma)!!}{(2\nu-n_\gamma-2i)!!} (-1)^{j-i} \widehat{k}_{\nu+j-i}[R\gamma_{ij}(s,x)].
\end{aligned} \tag{37}$$

From equations (35)–(37), it follows that the computation of the function $G_{s,t}(x)$ (28) does not present any difficulty.

3. Numerical discussion

The values of the semi-infinite integrals $\widetilde{\mathcal{J}}(s,t)$ (20) are obtained with 15 correct decimals using the infinite series involving the sine function (27), which we sum until $N = n_{\max}$ (see table 2). We also used the infinite series involving the spherical Bessel function (22) for calculating the values of the semi-infinite integrals (see table 1). The parameter $m_{\max}$ in table 1, stands for the number of terms of the infinite series that we sum.

From tables 2 and 1, 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 involved in equations (22), (27) and (31), we separate two cases:

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

When $10^{-15} < v < 1$, we divided the finite interval $[x_{i-1}, x_i]$ into M subintervals, where $M = \min(v^{-1}, 100)$. 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 involved in the above finite sum, we used the Gauss–Legendre quadrature of order 20.

For the numerical evaluation of Gaunt coefficients which occur in the expression of the four-centre two-electron Coulomb integrals over B functions (19), we used the subroutine GAUNT.F developed by Weniger and Steinborn [43]. The spherical harmonics $Y_l^m(\theta, \varphi)$ are computed using the recurrence formulae in [43].

Table 2 contains values with 15 correct decimals of the semi-infinite integral ($\widetilde{\mathcal{J}}(s,t)^{n_{\max}}$) obtained using the infinite series with the simple sine function. These values are obtained for s and t close to 0 or 1.

Table 1 contains values of $\widetilde{\mathcal{J}}(s,t)$ obtained using the infinite series with the spherical Bessel function ($\widetilde{\mathcal{J}}(s,t)^{(a)}$) and values obtained using $S\overline{D}_n^{(2,0)}$ with the recurrence relations ($\widetilde{\mathcal{J}}(s,t)^{(b)}$). The value of ϵ was set to 10^{-10}. The errors listed in these two tables are given by

$$\begin{cases} \mathrm{Error}^{(a)} = |\widetilde{\mathcal{J}}(s,t)^{n_{\max}} - \widetilde{\mathcal{J}}(s,t)^{(a)}| \\ \mathrm{Error}^{(b)} = |\widetilde{\mathcal{J}}(s,t)^{n_{\max}} - \widetilde{\mathcal{J}}(s,t)^{(b)}|. \end{cases}$$

The calculation times listed in tables 2 and 1 are in milliseconds.

Table 3 contains values obtained for $\widetilde{\mathcal{J}}(s,t)$ using $S\overline{D}_n^{(2,0)}$ for different values of ϵ which occur in the test given by (32).

Tables 4 and 5 contain values of Coulomb integrals over B functions (19). ${}_B\mathcal{J}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4(a)}$ are obtained using the algorithm described in the present work. ${}_B\mathcal{J}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4(b)}$ were obtained by Grotendorst *et al* [23].

Tables 6–8 contain values of Coulomb integrals over STFs (1), obtained with the C_2H_2, C_2H_4 and CH_4 molecules. ${}_S\mathcal{J}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4(a)}$ are obtained using the algorithm described in the present work. ${}_S\mathcal{J}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4(b)}$ are obtained with ADGGSTNGINT, using STOnG (STFs expressed as a combination of n GTFs), developed by Rico *et al* [33].

The finite s and t integrals that occur in equation (19) are evaluated using Gauss–Legendre quadrature of order 48. In the calculation of Coulomb integrals, the value of ϵ was set to 10^{-15}.

Table 3. Values of $\widetilde{\mathcal{J}}(s,t)$ obtained using $S\overline{D}_n^{(2,0)}$ with recurrence relations. The test (32) was performed to control the degree of accuracy. $\nu_{34} = \nu_{12}$, $n_{\gamma_{34}} = n_{\gamma_{12}}$, $\zeta_3 = \zeta_1$ and $\zeta_4 = \zeta_2$.

ϵ	s	t	ν_{12}	$n_{\gamma_{12}}$	n_x	λ	R_{12}	R_{34}	ζ_1	ζ_2	n	Error
10^{-8}	0.999	0.999	5/2	5	0	0	1.5	1.0	1.5	1.0	6	0.20(−08)
10^{-12}	0.999	0.999	5/2	5	0	0	1.5	1.0	1.5	1.0	14	0.24(−13)
10^{-16}	0.999	0.999	5/2	5	0	0	1.5	1.0	1.5	1.0	18	0.44(−15)
10^{-8}	0.005	0.005	7/2	7	1	1	0.2	0.2	1.5	1.0	15	0.11(−09)
10^{-12}	0.005	0.005	7/2	7	1	1	0.2	0.2	1.5	1.0	18	0.48(−13)
10^{-16}	0.005	0.005	7/2	7	1	1	0.2	0.2	1.5	1.0	22	0.44(−15)
10^{-8}	0.005	0.999	9/2	9	2	2	0.5	0.5	1.5	1.0	20	0.11(−08)
10^{-12}	0.005	0.999	9/2	9	2	2	0.5	0.5	1.5	1.0	58	0.12(−12)
10^{-16}	0.005	0.999	9/2	9	2	2	0.5	0.5	1.5	1.0	64	0.58(−15)
10^{-8}	0.005	0.005	13/2	13	3	3	1.0	1.5	2.0	2.5	4	0.54(−09)
10^{-12}	0.005	0.005	13/2	13	3	3	1.0	1.5	2.0	2.5	23	0.92(−13)
10^{-16}	0.005	0.005	13/2	13	3	3	1.0	1.5	2.0	2.5	92	0.48(−15)
10^{-8}	0.005	0.005	17/2	17	4	4	1.0	2.0	3.0	2.5	10	0.10(−08)
10^{-12}	0.005	0.005	17/2	17	4	4	1.0	2.0	3.0	2.5	58	0.49(−12)
10^{-16}	0.005	0.005	17/2	17	4	4	1.0	2.0	3.0	2.5	67	0.28(−15)

Table 4. Evaluation of ${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$ (19). $n_i = 1, l_i = m_i = 0$ and $\zeta_i = 1.0$ for $i = 1, 2, 3, 4$. ${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$ obtained using the $S\overline{D}$ method. ${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$ were obtained by Grotendorst *et al* [23].

$\overrightarrow{R}_1$	$\overrightarrow{R}_2$	$\overrightarrow{R}_3$	$\overrightarrow{R}_4$	${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$	${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$
(0, 0, 0)	(0, 0, 0)	(1.5, 0, 0)	(1.5, 0, 0)	0.191 538 0727(−2)	0.191 538 0724(−2)
(0, 0, 0)	(1, 0, 0)	(1.5, 0, 0)	(1.5, 0, 0)	0.182 915 8060(−2)	0.182 915 8056(−2)
(−5, 0, 0)	(5, 0, 0)	(0, 5, 0)	(0, −5, 0)	0.419 964 3636(−8)	0.419 964 1217(−8)

Table 5. Evaluation of ${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$ (19). $\overrightarrow{R}_1 = (1.0, 0, 0)$, $\overrightarrow{R}_2 = (0, 0, 1.0)$, $\overrightarrow{R}_3 = (0, 0, 0)$ and $\overrightarrow{R}_4 = (0, 0, -1.0)$. $\zeta_1 = \zeta_3 = 1.2$. ${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$ obtained using the $S\overline{D}$ method. ${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$ were obtained by Grotendorst *et al* [23].

n_1	l_1	m_1	n_2	l_2	m_2	n_3	l_3	m_3	n_4	l_4	m_4	ζ_2	ζ_4	${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$	${}_B\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$
1	0	0	1	0	0	1	0	0	1	0	0	1.2	1.2	0.409 904 2951(−03)	0.409 903 0795(−03)
2	0	0	2	0	0	2	0	0	2	0	0	1.2	5.0	0.145 395 6058(−06)	0.145 396 7814(−06)
3	0	0	1	0	0	2	0	0	2	0	0	1.2	6.0	0.740 386 0779(−06)	0.740 384 7726(−06)
4	0	0	4	0	0	4	0	0	4	0	0	1.2	3.0	0.376 977 6274(−06)	0.376 976 9739(−06)
2	0	0	2	0	0	2	0	0	2	0	0	1.2	1.2	0.906 328 3306(−06)	0.906 318 0318(−06)
1	1	0	1	1	0	1	0	0	1	0	0	1.2	1.2	0.499 202 0456(−04)	0.499 200 6019(−04)
2	2	2	2	1	0	2	1	0	2	0	0	1.2	5.0	0.360 177 1334(−09)	0.360 181 1116(−09)
3	0	0	1	1	−1	2	2	−2	2	0	0	1.2	6.0	0.341 298 6063(−10)	0.341 297 8738(−10)
4	4	4	4	0	0	4	4	4	4	0	0	1.2	3.0	0.452 572 6037(−19)	0.452 591 3008(−19)
2	2	2	2	2	2	2	2	2	2	2	2	1.2	1.2	0.534 870 0825(−10)	0.534 869 3608(−10)

Table 6. Four-centre two-electron Coulomb integrals over STFs ${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$ (1). Values obtained with C_2H_2. The calculation are obtained with the following geometry in Cartesian coordinates: $C_1(0; 0; 1.1405)$, $C_2(0; 0; -1.1405)$, $H_1(0; 0; 3.1425)$ and $H_2(0; 0; -3.1425)$. $\zeta^{C}_{1s} = 5.700$ and $\zeta^{C}_{2p_z} = \zeta^{C}_{2p_{+1}} = 1.625$. $\zeta^{H}_{1s} = 1.200$ and $\zeta^{H}_{2p_z} = \zeta^{H}_{2p_{+1}} = 2.220$. ${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$ obtained using the $S\overline{D}$ method. ${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$ obtained using ADGGSTNGINT code developed by Rico *et al* [33].

${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$	${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$	${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$
$\langle 1s^{C_1}\,1s^{H_1}\,\vert\,1s^{C_2}\,1s^{H_2}\rangle$	0.195 966 315 243(−2)	0.195 966 312 886(−2)
$\left\langle 1s^{C_1}\,1s^{H_1}\,\middle\vert\,1s^{C_2}\,2p_z^{H_2}\right\rangle$	0.283 669 225 792(−2)	0.283 669 224 706(−2)
$\left\langle 1s^{C_1}\,2p_z^{H_1}\,\middle\vert\,1s^{C_2}\,2p_z^{H_2}\right\rangle$	−0.410 711 928 328(−2)	−0.410 711 931 655(−2)
$\left\langle 2p_z^{C_1}\,1s^{H_1}\,\middle\vert\,2p_z^{C_2}\,1s^{H_2}\right\rangle$	−0.384 782 080 613(−1)	−0.384 782 080 602(−1)
$\left\langle 2p_z^{C_1}\,2p_z^{H_1}\,\middle\vert\,2p_z^{C_2}\,2p_z^{H_2}\right\rangle$	0.178 337 206 024(−1)	0.178 337 206 021(−1)
$\left\langle 2p_{+1}^{C_1}\,1s^{H_1}\,\middle\vert\,2p_{+1}^{C_2}\,1s^{H_2}\right\rangle$	0.279 688 126 236(−2)	0.279 688 126 236(−2)

Table 7. Four-centre two-electron Coulomb integrals over STFs ${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$ (1). Values obtained with C_2H_4. The calculation are obtained with the following geometry in Cartesian coordinates: $C_1(0; 0; 1.2755)$, $C_2(0; 0; -1.2755)$, $H_1(1.7528; 0; 2.2875)$, $H_2(1.7528; 0; -2.2875)$, $H_3(-1.7528; 0; 2.2875)$ and $H_4(-1.7528; 0; -2.2875)$. $\zeta^{C}_{1s} = 5.700$, $\zeta^{C}_{2p_z} = 1.625$ and $\zeta^{C}_{3d_z} = 1.250$. $\zeta^{H}_{1s} = 1.200$ and $\zeta^{H}_{2p_z} = 2.220$. ${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$ obtained using the $S\overline{D}$ method. ${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$ obtained using ADGGSTNGINT code developed by Rico *et al* [33].

${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$	${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$	${}_{S}\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$
$\langle 1s^{H_1}\,1s^{H_2}\,\vert\,1s^{H_3}\,1s^{H_4}\rangle$	0.121 073 2512(−2)	0.121 073 2512(−2)
$\langle 1s^{C_1}\,1s^{C_2}\,\vert\,1s^{H_1}\,1s^{H_2}\rangle$	0.126 220 3273(−5)	0.126 220 0016(−5)
$\langle 1s^{C_1}\,1s^{H_2}\,\vert\,1s^{C_2}\,1s^{H_3}\rangle$	0.210 918 8680(−4)	0.210 876 1322(−4)
$\left\langle 1s^{C_1}\,2p_z^{C_2}\,\middle\vert\,1s^{H_1}\,1s^{H_2}\right\rangle$	0.230 206 4620(−2)	0.230 206 4005(−2)
$\left\langle 2p_z^{C_1}\,2p_z^{C_2}\,\middle\vert\,1s^{H_1}\,1s^{H_2}\right\rangle$	−0.102 656 8856(−1)	−0.102 656 8856(−1)
$\left\langle 2p_z^{C_1}\,1s^{H_2}\,\middle\vert\,2p_z^{C_2}\,1s^{H_3}\right\rangle$	−0.749 068 3546(−2)	−0.749 068 3544(−2)
$\left\langle 3d_z^{C_1}\,2p_z^{H_2}\,\middle\vert\,3d_z^{C_2}\,1s^{H_3}\right\rangle$	0.555 282 9776(−2)	0.555 282 9771(−2)
$\left\langle 3d_z^{C_1}\,2p_z^{H_2}\,\middle\vert\,3d_z^{C_2}\,2p_z^{H_3}\right\rangle$	−0.248 064 4501(−2)	−0.248 064 4499(−2)

For the evaluation of the Coulomb integrals over STFs, we used equation (4) to express these integrals as finite linear combinations of integrals over B functions, as can be seen from equation (16). A single-zeta basis was used in all calculations performed in the present work.

All the computations were done in FORTRAN DOUBLE PRECISION. We used Lahey ED compiler (15 significant decimals in DOUBLE PRECISION).

In all tables, the numbers in parentheses represent powers of 10. Calculations were performed on a Workstation with an Intel Xeon Processor with 2.4 GHz.

Table 8. Four-centre two-electron Coulomb integrals over STFs ${}_S\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$ (1). Values obtained with CH$_4$. The calculation are obtained with the following geometry in Cartesian coordinates: C(0; 0; 0), H$_1$(1.0; 1.0; 1.0), H$_2$(−1.0; −1.0; 1.0), H$_3$(1.0; −1.0; −1.0) and H$_4$(−1.0; 1.0; −1.0). $\zeta^{\mathrm{C}}_{1\mathrm{s}} = 5.700$, $\zeta^{\mathrm{C}}_{2\mathrm{p}_z} = 1.625$ and $\zeta^{\mathrm{C}}_{3\mathrm{d}_z} = 1.250$. $\zeta^{\mathrm{H}}_{1\mathrm{s}} = 1.200$ and $\zeta^{\mathrm{H}}_{2\mathrm{p}_z} = 2.220$. ${}_S\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$ obtained using the $S\overline{D}$ method. ${}_S\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$ obtained using ADGGSTNGINT code developed by Rico *et al* [33].

${}_S\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}$	${}_S\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(a)}_{n_1l_1m_1,n_3l_3m_3}$	${}_S\mathcal{J}^{n_2l_2m_2,n_4l_4m_4(b)}_{n_1l_1m_1,n_3l_3m_3}$
$\langle 1\mathrm{s}^{\mathrm{C}}1\mathrm{s}^{\mathrm{H}_1}\vert 1\mathrm{s}^{\mathrm{H}_2}1\mathrm{s}^{\mathrm{H}_3}\rangle$	0.165 817 4001(−1)	0.165 817 3997(−1)
$\langle 2\mathrm{p}_z^{\mathrm{C}}1\mathrm{s}^{\mathrm{H}_1}\vert 1\mathrm{s}^{\mathrm{H}_2}1\mathrm{s}^{\mathrm{H}_3}\rangle$	0.357 202 3202(−1)	0.357 202 3202(−1)
$\left\langle 2\mathrm{p}_z^{\mathrm{C}}2\mathrm{p}_z^{\mathrm{H}_1}\middle\vert 1\mathrm{s}^{\mathrm{H}_2}1\mathrm{s}^{\mathrm{H}_3}\right\rangle$	0.197 447 0693(−1)	0.197 447 0693(−1)
$\langle 1\mathrm{s}^{\mathrm{H}_1}1\mathrm{s}^{\mathrm{H}_2}\vert 1\mathrm{s}^{\mathrm{H}_3}1\mathrm{s}^{\mathrm{H}_4}\rangle$	0.307 539 6000(−1)	0.307 539 6000(−1)
$\langle 2\mathrm{p}_z^{\mathrm{H}_1}1\mathrm{s}^{\mathrm{H}_2}\Big\vert 1\mathrm{s}^{\mathrm{H}_3}1\mathrm{s}^{\mathrm{H}_4}\rangle$	−0.451 723 6685(−2)	−0.451 723 6685(−2)
$\left\langle 2\mathrm{p}_z^{\mathrm{H}_1}2\mathrm{p}_z^{\mathrm{H}_2}\middle\vert 1\mathrm{s}^{\mathrm{H}_3}1\mathrm{s}^{\mathrm{H}_4}\right\rangle$	0.933 787 6689(−2)	0.933 787 6702(−2)
$\left\langle 2\mathrm{p}_z^{\mathrm{H}_1}2\mathrm{p}_z^{\mathrm{H}_2}\middle\vert 2\mathrm{p}_z^{\mathrm{H}_3}1\mathrm{s}^{\mathrm{H}_4}\right\rangle$	0.134 523 0205(−2)	0.134 523 0222(−2)
$\left\langle 2\mathrm{p}_z^{\mathrm{H}_1}2\mathrm{p}_z^{\mathrm{H}_2}\middle\vert 2\mathrm{p}_z^{\mathrm{H}_3}2\mathrm{p}_z^{\mathrm{H}_4}\right\rangle$	0.282 422 7596(−2)	0.282 422 7654(−2)

4. Conclusion

The basis set of B functions was used in order to apply the Fourier-transform method which led to analytical expressions for all Coulomb integrals. The Coulomb integrals over STFs are expressed as finite linear combinations of integrals over B functions.

The $S\overline{D}$ approach is used to improve the convergence of the semi-infinite highly oscillatory integrals which occur in the analytic expressions that were obtained for the molecular integrals under consideration. Recurrence relations are developed to further reduce the calculation time keeping a high pre-determined accuracy. These recurrence relations allowed a better control of the degree of accuracy and led to a very efficient and fast algorithm for all multicentre one- and two-electron integrals over the preferable STFs. Obviously this greatly increased rapidity of the $S\overline{D}$ method 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 algorithm described in the present contribution for all Coulomb and exchange 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. Note that the $S\overline{D}$ approach is able to reach precisions of 10^{-16} atomic units reliably for the first time and certainly some applications of this extremely high accuracy will be developed in future work.

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