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The Fourier transform method and the $S\overline{D}$ approach for the analytical and numerical treatment of multicenter overlap-like quantum similarity integrals

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Abstract

Molecular overlap-like quantum similarity measurements imply the evaluation of overlap integrals of two molecular electronic densities related by Dirac delta function. When the electronic densities are expanded over atomic orbitals using the usual LCAO-MO approach (linear combination of atomic orbitals), overlap-like quantum similarity integrals could be expressed in terms of four-center overlap integrals.

It is shown that by introducing the Fourier transform of delta Dirac function in the integrals and using the Fourier transform approach combined with the so-called B functions, one can obtain analytic expressions of the integrals under consideration. These analytic expressions involve highly oscillatory semi-infinite spherical Bessel functions, which are the principal source of severe numerical and computational difficulties.

In this work, we present a highly efficient algorithm for a fast and accurate numerical evaluation of these multicenter overlap-like quantum similarity integrals over Slater type functions. This algorithm is based on the $S\overline{D}$ approach due to Safouhi. Recurrence formulae are used for a better control of the degree of accuracy and for a better stability of the algorithm. The numerical result section shows the efficiency of our algorithm, compared with the alternatives using the one-center two-range expansion method, which led to very complicated analytic expressions, the epsilon algorithm and the nonlinear $\overline{D}$ transformation.

Keywords: The $S\overline{D}$ approach; Multicenter overlap-like quantum similarity integrals; Fourier transform; Nonlinear transformations; Extrapolation methods

1. Introduction

Previous work [1,2] on the accurate and fast numerical evaluation of multicenter overlap-like quantum similarity integrals over Slater type functions continues with the present contribution. These integrals are required accurately in molecular similarity measurements, where molecules are compared with each other to explain

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changes in their chemical reactivity in a series. The chemical activity of a molecule is completely described by its electronic density, from this it follows that molecules with similar electronic structures have similar chemical properties [3,4].

The quantum similarity measurements (QSM) are based on a quantitative comparison of electronic densities of two molecules superposed and aligned to optimize a well-defined similarity function [5–9]. This procedure leads to nuclear distances smaller than usually encounter in molecular bonds. This is why one should choose basis functions which describe as well as possible the electronic density near the nucleus. Therefore, the choice of the basis set of atomic orbitals is of a great importance.

A good atomic orbital basis should also satisfy Kato's conditions for analytical solutions of the appropriate Schrödinger equation [10] and should decay exponentially for large distances [11,12]. The most popular functions are the Gaussian type functions (GTFs) [13]. Unfortunately, these GTF basis functions fail to satisfy the above mathematical conditions for atomic electronic distributions. Slater type functions (STFs) [14,15] are better suited than GTFs to represent electron wave functions near the nucleus and at long range [16]. Unfortunately, the use of STFs has been prevented by the fact that their multicenter integrals are extremely difficult to evaluate.

In [2], we presented an analytic development of multicenter overlap-like quantum similarity integrals over STFs. These STFs were expressed in terms of the so-called B functions [17,18]. The use of the so-called B functions was proposed by Shavitt [19], since reduced Bessel functions possess a representation in terms of a remarkably simple Gauss transform [19]. This Gauss transform was also the reason why reduced Bessel functions were used as basis functions in electronic structure calculations of simple systems [20–23]. Detailed discussions of the mathematical properties of reduced Bessel functions and of their anisotropic generalizations can be found in the Ph.D. theses of Weniger [24] and Homeier [25].

These B functions have much more appealing properties applicable to multicenter integral problems, compared to other exponentially decaying functions. They possess a relatively simple addition theorem [18] and remarkably simple convolution theorems as well as Coulomb integrals [17,26–28]. The addition theorem of reduced Bessel functions was applied for the computation over overlap and related multicenter integrals [29,30]. The convolution formulas for overlap integrals of B functions derived by Filter [26] were applied in [31].

The multicenter molecular integrals of B functions can be computed (much) more easily than the corresponding integrals of other exponentially decaying functions. This can be explained in terms of the Fourier transform of B functions, which is of exceptional simplicity among exponentially decaying functions. This Fourier transform was derived in the Ph.D. thesis of Weniger [24] and later published in [32]. Independently and almost simultaneously, the expression for the Fourier transform of a B function was also derived by Niukkanen [33]. Moreover, the Fourier transforms of STFs, of hydrogen eigenfunctions, or of other functions based on the generalized Laguerre polynomials can all be expressed as finite linear combinations of Fourier transforms of B functions [32,34]. The basis set of B functions is well adapted to the Fourier transform method [35–42], which allowed analytic expressions to be developed for molecular multicenter integrals [41,42].

Detailed discussions on B functions and their Fourier transform and the application to multicenter molecular integral problems can be found in a recent paper by Weniger [43].

The Dirac delta Fourier representation was also introduced and a convolution theorem was used to obtain analytic expressions for the overlap-like quantum similarity integrals.

The obtained analytic expressions for the integrals under consideration turned out to be almost identical to the analytic expressions obtained for the four-center two-electron Coulomb integrals. Many approaches were developed for a fast and accurate numerical evaluation of these Coulomb integrals [41,42,44–59]. In [60], we used the nonlinear $\overline{D}$ transformation of Sidi [61–63] for a numerical evaluation of the analytic expressions obtained for the overlap-like quantum similarity integrals. The numerical results that we obtained demonstrated the high accuracy of the $\overline{D}$ transformation.

In the present work, we focus on the application of the $S\overline{D}$ approach due to Safouhi [64,65], which was shown to be highly efficient and rapid [58,66,67], compared with alternatives using Gauss–Laguerre quadrature, the epsilon algorithm of Wynn [68] and Levin's u transform [69], in the numerical evaluation of two-, three- and four-center one and two-electron Coulomb integrals over STFs or related functions. This $S\overline{D}$ approach consists on transforming the semi-infinite spherical Bessel integral, into a semi-infinite integral involving the simple sine function. This transformation will be referred to as the S transformation. The oscillatory part of the integrand, the spherical Bessel function, is replaced by the simple trigonometric sine

function, using a relation between these two functions and a series of integration by part with respect to $x\,\mathrm{d}x$. The strong oscillations of the integrand were considerably reduced and this helps the extrapolation methods. The obtained integrand was shown to be suitable to apply the nonlinear $\overline{D}$ transformation of Sidi. This nonlinear transformation improves the convergence of highly oscillatory semi-infinite integrals, whose integrands satisfy linear differential equations with coefficients having asymptotic expansions in the sense of Poincaré [70]. Cramer's rule is used to compute approximations of the semi-infinite integrals, which is shown to be faster than solving the linear systems generated by the $\overline{D}$ transformation. Recurrence relations were also developed for a better control of the degree of accuracy and for better stability of the algorithm [67,58]. Extensive numerical results with linear and nonlinear molecules, and comparisons with results from the literature and results obtained using existing codes such as Alchemy package [71], STOP (Slater type orbital package) developed by Bouferguene et al. [72] and ADGGSTNGINT, using STOnG (STFs expressed as a combination of n GTFs), developed by Rico et al. [46], can be found in [58,66,67]. The numerical results section also prove the ability to reproduce values of the two-center integrals, obtained in previous works [1,73,74].

2. General definitions and properties

Unnormalized STFs are defined by [14,15]:

$$\widetilde{\chi}^m_{n,l}(\zeta,\vec{r}) = r^{n-1}\,\mathrm{e}^{-\zeta r}\,Y^m_l(\theta_{\vec{r}},\varphi_{\vec{r}}), \tag{1}$$

where n, l, m are the quantum numbers and they are such that $n = 1,2,\ldots,l = 0,1,\ldots,n-1$ and $m = -l,-l+1,\ldots,l-1,l$, and where $Y^m_l(\theta,\varphi)$ stands for the surface spherical harmonic and is defined explicitly using the Condon–Shortley phase convention as follows [75]:

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

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

The Slater type functions (STFs) are defined in normalized form according to the following relationship:

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

STFs can be expressed as finite linear combinations of B functions [17]:

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

where

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

The B functions are defined as follows [17]:

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

where the reduced Bessel function $\hat{k}_{n-\frac{1}{2}}(z)$ is given by [18,76]:

$$\hat{k}_{n-\frac{1}{2}}(z) = \sum_{j=1}^{n}\frac{(2n-j-1)!}{(j-1)!(n-j)!}\frac{z^{j-1}\mathrm{e}^{-z}}{2^{n-1}}. \tag{7}$$

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

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

The Fourier transform $\overline{B}^m_{n,l}(\zeta,\vec{p})$ of $B^m_{n,l}(\zeta,\vec{r})$ is given by [32]:

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

Let the function γ be defined by:

$$\gamma(\kappa,x) = \sqrt{\tau+\kappa x^2}.$$

Now, 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 $n_\gamma = 2v = 2n+1$ then for $j \in \mathbb{N}$:

$$\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^j\left[\frac{\hat{k}_v[\gamma(\kappa,x)]}{[\gamma(\kappa,x)]^{n_\gamma}}\right] = (-1)^j\kappa^j\frac{\hat{k}_{v+j}[\gamma(\kappa,x)]}{[\gamma(\kappa,x)]^{2(v+j)}}, \tag{10}$$

and for $n_\gamma < 2v$, we obtain:

$$\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^j\left[\frac{\hat{k}_v[\gamma(\kappa,x)]}{[\gamma(\kappa,x)]^{n_\gamma}}\right] = \frac{\kappa^j}{[\gamma(\kappa,x)]^{n_\gamma+2j}}\sum_{i=0}^{j}\binom{j}{i}\frac{(-1)^{j-i}(2v-n_\gamma)!!}{(2v-n_\gamma-2i)!!}\hat{k}_{v+j-i}[\gamma(\kappa,x)], \tag{11}$$

Gaunt coefficients are defined by [77–80]:

$$\langle l_1m_1|l_2m_2|l_3m_3\rangle = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}[Y^{m_1}_{l_1}(\theta,\varphi)]^*Y^{m_2}_{l_2}(\theta,\varphi)Y^{m_3}_{l_3}(\theta,\varphi)\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\varphi. \tag{12}$$

The Gaunt coefficients linearize the product of two spherical harmonics:

$$\begin{aligned}\left[Y^{m_1}_{l_1}(\theta,\varphi)\right]^*Y^{m_2}_{l_2}(\theta,\varphi) &= \sum_{l=l_{\min},2}^{l_{\max}}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle Y^{m_2-m_1}_l(\theta,\varphi)\\ &= \sum_{l=l_{\min},2}^{l_{\max}}\langle l_1,m_1|l_2,m_2|l,m_1-m_2\rangle[Y^{m_1-m_2}_l(\theta,\varphi)]^*,\end{aligned} \tag{13}$$

where the subscript $l = l_{\min},2$ in the summation symbol implies that the summation index l runs in steps of 2 from $l_{\min}$ to $l_{\max}$. The summation limits are given in [79].

The spherical Bessel function $j_n(z)$ is defined by [81]:

$$j_n(z) = (-1)^n z^n\left(\frac{\mathrm{d}}{z\,\mathrm{d}z}\right)^n\left[\frac{\sin(z)}{z}\right]. \tag{14}$$

In the following all the integration over physical variables extend over the whole $\mathbb{R}^3$.

The Fourier representation of the Dirac delta function [81]:

$$\delta(\vec{r}_1-\vec{r}_2) = \frac{1}{(2\pi)^3}\int \mathrm{e}^{-\vec{x}\cdot(\vec{r}_1-\vec{r}_2)}\,\mathrm{d}\vec{x}. \tag{15}$$

3. Multicenter overlap-like quantum similarity integral

The molecular quantum similarity measurement is defined as an integral involving two molecular electronic density functions, $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$, related by an hermitian bielectronic operator, $\Omega(\vec{r}_1,\vec{r}_2)$ [3,82]:

$$Z_{AB} = \int\int \rho_A(\vec{r}_1)\Omega(\vec{r}_1,\vec{r}_2)\rho_B(\vec{r}_2)\,\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2. \tag{16}$$

In the case where $\Omega(\vec{r}_1,\vec{r}_2)$ is the Dirac delta function, $\delta(\vec{r}_1-\vec{r}_2)$, we obtain the expression of the overlap-like quantum similarity measurement, which gives an index of the similarity of the electronic densities of molecules A and B:

$$Z_{AB} = \int\int \rho_A(\vec{r}_1)\delta(\vec{r}_1 - \vec{r}_2)\rho_B(\vec{r}_2)\,\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2. \tag{17}$$

To provide a general normalized index which allows comparison of molecules in a series, Carbò et al. introduced the normalized quantum similarity index [83]:

$$C_{AB} = \frac{Z_{AB}}{\sqrt{Z_{AA}Z_{BB}}}, \tag{18}$$

where Z_{AA} and Z_{BB} stand for the self-similarity measures. The index C_{AB} is close to the unity when molecular electronic structures are similar.

Using the linear combination of atomic orbitals (LCAO) approach, with STFs as a basis set of atomic orbitals, one can express the overlap-like quantum similarity measurement (17) as follows:

$$Z_{AB} = \sum_{i,j}\sum_{k,l} C_{iA}C_{jA}C_{kB}C_{lB}Z_{1234}, \tag{19}$$

where Z_{1234} stand for the overlap-like quantum similarity integrals over STFs:

$$Z_{1234} = \int\int \chi^{m_1}_{n_1,l_1}(\zeta_1,\vec{r}_1 - \overrightarrow{OA})^*\chi^{m_2}_{n_2,l_2}(\zeta_2,\vec{r}_1 - \overrightarrow{OB})\delta(\vec{r}_1 - \vec{r}_2) \times \chi^{m_3}_{n_3,l_3}(\zeta_3,\vec{r}_2 - \overrightarrow{OC})^*\chi^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}_2 - \overrightarrow{OD})\,\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2. \tag{20}$$

After a translation of vectors $\overrightarrow{OA}$ and $\overrightarrow{OD}$, the above integral will be re-written as follows:

$$Z_{1234} = \int\int \chi^{m_1}_{n_1,l_1}(\zeta_1,\vec{r}_1)^*\chi^{m_2}_{n_2,l_2}(\zeta_2,\vec{r}_1 - \vec{R}_{21})\delta(\vec{r}_1 - \vec{r}_2 - \vec{R}_{41}) \times \chi^{m_3}_{n_3,l_3}(\zeta_3,\vec{r}_2 - \vec{R}_{34})^*\chi^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}_2)\,\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2, \tag{21}$$

where $\vec{R}_{21} = \overrightarrow{AB}$ and $\vec{R}_{34} = \overrightarrow{DC}$.

By using expression (4), we can express Eq. (21) as a finite linear combination of overlap-like quantum similarity integrals over B functions as follows:

$$\begin{aligned} Z_{1234} = &\sqrt{\frac{2^{2n_1+2n_2+2n_3+2n_4+4}\zeta_1^{2n_1+1}\zeta_2^{2n_2+1}\zeta_3^{2n_3+1}\zeta_4^{2n_4+1}}{(2n_1)!(2n_2)!(2n_3)!(2n_4)!}}\sum_{p_1=\tilde{p}_1}^{n_1-l_1}\frac{(-1)^{n_1-l_1-p_1}2^{2p_1+2l_1-n_1}(l_1+p_1)!}{\zeta_1^{n_1-1}(2p_1-n_1+l_1)!(n_1-l_1-p_1)!} \\ &\times\sum_{p_2=\tilde{p}_2}^{n_2-l_2}\frac{(-1)^{n_2-l_2-p_2}2^{2p_2+2l_2-n_2}(l_2+p_2)!}{\zeta_2^{n_2-1}(2p_2-n_2+l_2)!(n_2-l_2-p_2)!}\sum_{p_3=\tilde{p}_3}^{n_3-l_3}\frac{(-1)^{n_3-l_3-p_3}2^{2p_3+2l_3-n_3}(l_3+p_3)!}{\zeta_1^{n_3-1}(2p_3-n_3+l_3)!(n_3-l_3-p_3)!} \\ &\times\sum_{p_4=\tilde{p}_4}^{n_4-l_4}\frac{(-1)^{n_4-l_4-p_4}2^{2p_4+2l_4-n_4}(l_4+p_4)!}{\zeta_2^{n_4-1}(2p_4-n_4+l_4)!(n_4-l_4-p_4)!}\widetilde{Z}_{1234}, \end{aligned} \tag{22}$$

where $\widetilde{Z}_{1234}$ stands for overlap-like quantum similarity integrals over B functions:

$$\begin{aligned} \widetilde{Z}_{1234} = &\int\int\left[B^{m_1}_{p_1,l_1}(\zeta_1,\vec{r}_1)\right]^*B^{m_2}_{p_2,l_2}(\zeta_2,\vec{r}_1 - \vec{R}_{21})\delta(\vec{r}_1 - \vec{r}_2 - \vec{R}_{41}) \\ &\times\left[B^{m_3}_{p_3,l_3}(\zeta_3,\vec{r}_2 - \vec{R}_{34})\right]^*B^{m_4}_{p_4,l_4}(\zeta_4,\vec{r}_2)\,\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2, \end{aligned} \tag{23}$$

where $\tilde{p}_i$ with $i = 1,2,3,4$ are given by (5).

Now, introducing the Fourier representation of the Dirac delta function (15) in the above integral over B functions, we obtain:

$$\begin{aligned} \widetilde{Z}_{1234} = &\frac{1}{(2\pi)^3}\int \mathrm{e}^{\mathrm{i}\vec{x}\cdot\vec{R}_{41}}\left[\int\left[B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r}_1)\right]^*\mathrm{e}^{-\mathrm{i}\vec{x}\cdot\vec{r}_1}B^{m_2}_{n_2,l_2}\left(\zeta_2,\vec{r}_1 - \vec{R}_{21}\right)\mathrm{d}\vec{r}_1\right] \\ &\times\left[\int\left[B^{m_3}_{n_3,l_3}\left(\zeta_3,\vec{r}_2 - \vec{R}_{34}\right)\right]^*\mathrm{e}^{\mathrm{i}\vec{x}\cdot\vec{r}_2}B^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}_2)\,\mathrm{d}\vec{r}_2\right]\mathrm{d}\vec{x}. \end{aligned} \tag{24}$$

With the help of the Fourier transform method [41,42], analytic expressions are developed for the terms [41,42]:

$$\int \left[B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r}_1)\right]^* \mathrm{e}^{-\mathrm{i}\vec{\kappa}\cdot\vec{r}_1} B^{m_2}_{n_2,l_2}\left(\zeta_2,\vec{r}_1-\vec{R}_{21}\right)\mathrm{d}\vec{r}_1$$

and

$$\int \left[B^{m_3}_{n_3,l_3}\left(\zeta_3,\vec{r}_2-\vec{R}_{34}\right)\right]^* \mathrm{e}^{\mathrm{i}\vec{\kappa}\cdot\vec{r}_2} B^{m_4}_{n_4,l_4}(\zeta_4,\vec{r}_2)\,\mathrm{d}\vec{r}_2.$$

By using the analytic expressions obtained for the above terms occurring in Eq. (24), we obtained analytic expressions for multicenter overlap-like quantum similarity integrals over B functions. These analytic expressions are given by:

$$\begin{aligned}
\widetilde{Z}_{1234} = {} & 8(4\pi)^4(2l_1+1)!!(2l_2+1)!!(2l_3+1)!!(2l_4+1)!! \\
& \times \frac{(n_1+n_2+l_1+l_2+1)!}{(n_1+l_1)!(n_2+l_2)!}\,\frac{(n_3+n_4+l_3+l_4+1)!}{(n_3+l_3)!(n_4+l_4)!} \\
& \times \sum_{l'_1=0}^{l_1}\sum_{m'_1=\mu_{1\min}}^{\mu_{1\max}} (-i)^{l_1+l'_1}\frac{\langle l_1,m_1|l'_1,m'_1|l_1-l'_1,m_1-m'_1\rangle}{(2l'_1+1)!![2(l_1-l'_1)+1]!!} \\
& \times \sum_{l'_2=0}^{l_2}\sum_{m'_2=\mu_{2\min}}^{\mu_{2\max}} (-i)^{l_2+l'_2}\frac{\langle l_2,m_2|l'_2,m'_2|l_2-l'_2,m_2-m'_2\rangle}{(2l'_2+1)!![2(l_2-l'_2)+1]!!} \\
& \times \sum_{l'_3=0}^{l_3}\sum_{m'_3=\mu_{3\min}}^{\mu_{3\max}} (i)^{l_3+l'_3}\frac{\langle l_3,m_3|l'_3,m'_3|l_3-l'_3,m_3-m'_3\rangle}{(2l'_3+1)!![2(l_3-l'_3)+1]!!} \\
& \times \sum_{l'_4=0}^{l_4}\sum_{m'_4=\mu_{4\min}}^{\mu_{4\max}} (i)^{l_4+l'_4}\frac{\langle l_4,m_4|l'_4,m'_4|l_4-l'_4,m_4-m'_4\rangle}{(2l'_4+1)!![2(l_4-l'_4)+1]!!} \\
& \times \sum_{l'_{21}=l'_{21\,\min},2}^{l'_1+l'_2} (-1)^{l'_1}\langle l'_2,m'_2|l'_1,m'_1|l'_{21},m'_{21}\rangle R^{l'_{21}}_{21}\,Y^{m'_{21}}_{l'_{21}}(\theta_{\vec{R}_{21}},\varphi_{\vec{R}_{21}}) \\
& \times \sum_{l'_{34}=l'_{34\,\min},2}^{l'_3+l'_4} (-1)^{l'_4}\langle l'_4,m'_4|l'_3,m'_3|l'_{34},m'_{34}\rangle R^{l'_{34}}_{34}\,Y^{m'_{34}}_{l'_{34}}(\theta_{\vec{R}_{34}},\varphi_{\vec{R}_{34}}) \\
& \times \sum_{l_{21}=l_{21\,\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_{21},m_{21}\rangle \\
& \times \sum_{l_{34}=l_{34\,\min},2}^{l_4-l'_4+l_3-l'_3} \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_{21}+l_{34}} (-i)^{\lambda}\langle l_{21},m_{21}|l_{34},m_{34}|\lambda,\mu\rangle \sum_{j_{21}=0}^{\Delta l_{21}}\binom{\Delta l_{21}}{j_{21}}\frac{(-1)^{j_{21}}\zeta_1^{2n_1+l_1-1}\zeta_2^{2n_2+l_2-1}}{2^{n_1+n_2+l_1+l_2-j_{21}+1}(n_1+n_2+l_1+l_2-j_{21}+1)!} \\
& \times \sum_{j_{34}=0}^{\Delta l_{34}}\binom{\Delta l_{34}}{j_{34}}\frac{(-1)^{j_{34}}\zeta_3^{2n_3+l_3-1}\zeta_4^{2n_4+l_4-1}}{2^{n_3+n_4+l_3+l_4-j_{34}+1}(n_3+n_4+l_3+l_4-j_{34}+1)!} \\
& \times \int_0^1 \alpha^{n_2+l_2+l_1-l'_1}(1-\alpha)^{n_1+l_1+l_2-l'_2}\int_0^1 \beta^{n_3+l_3+l_4-l'_4}(1-\beta)^{n_4+l_4+l_3-l'_3}\,Y^{\mu}_{\lambda}(\theta_{\vec{v}},\varphi_{\vec{v}}) \\
& \times \int_0^{+\infty} x^{n_x}\frac{\hat{k}_{v_{21}}[\gamma_{21}(\alpha,x)R_{21}]}{[\gamma_{21}(\alpha,x)]^{n_{\gamma_{21}}}}\,\frac{\hat{k}_{v_{34}}[\gamma_{34}(\beta,x)R_{34}]}{[\gamma_{34}(\beta,x)]^{n_{\gamma_{34}}}}\,j_{\lambda}(vx)\,\mathrm{d}x\,\mathrm{d}\beta\,\mathrm{d}\alpha,
\end{aligned} \tag{25}$$

where

$$\mu_{i_{\min}} = \max\left(-l'_i, m_i - l_i + l'_i\right),$$
$$\mu_{i_{\max}} = \min\left(l'_i, m_i + l_i - l'_i\right) \quad \text{for } i = 1,2,3,4,$$
$l'_{21\,\min}$, $l'_{34\,\min}$, $l_{21\,\min}$, $l_{34\,\min}$ and $\lambda_{\min}$ given by (13)
$$m_{21} = (m_2 - m'_2) - (m_1 - m'_1),$$
$$m_{34} = (m_3 - m'_3) - (m_4 - m'_4) \text{ and } \mu = m_{21} - m_{34},$$
$$\Delta l_{21} = (l'_1 + l'_2 - l'_{21})/2 \text{ and } \Delta l_{34} = (l'_3 + l'_4 - l'_{34})/2,$$
$$n_x = l_1 - l'_1 + l_2 - l'_2 + l_3 - l'_3 + l_4 - l'_4 + 2,$$
$$v_{21} = n_1 + n_2 + l_1 + l_2 - l'_{21} - j_{21} + \frac{1}{2},$$
$$n_{\gamma_{21}} = 2(n_1 + n_2 + l_1 + l_2) - (l'_1 + l'_2 + l'_{21}) + 1,$$
$$v_{34} = n_3 + n_4 + l_3 + l_4 - l'_{34} - j_{34} + \frac{1}{2},$$
$$n_{\gamma_{34}} = 2(n_3 + n_4 + l_3 + l_4) - (l'_3 + l'_4 + l'_{34}) + 1,$$
$$\gamma_{21}(\alpha, x) = \left[(1-\alpha)\zeta_1^2 + \alpha\zeta_2^2 + \alpha(1-\alpha)x^2\right]^{\frac{1}{2}},$$
$$\gamma_{34}(\beta, x) = \left[(1-\beta)\zeta_4^2 + \beta\zeta_3^2 + \beta(1-\beta)x^2\right]^{\frac{1}{2}},$$
$$\vec{v} = (1-\alpha)\vec{R}_{21} - (1-\beta)\vec{R}_{34} - \vec{R}_{41},$$
$$R_{21} = |\vec{R}_{21}|,\ R_{34} = |\vec{R}_{34}| \text{ and } v = |\vec{v}|.$$

4. The $S\overline{D}$ approach and the development of the algorithm

It is well known that in applied mathematics, in the numerical treatment of scientific problems and in engineering, oscillatory integrals, slowly convergent or divergent sequences and series occur abundantly. They are produced by approximation procedures depending on a parameter, iterative methods and perturbation techniques. Very often, the use of these oscillatory integrals and slowly convergent or divergent series presents

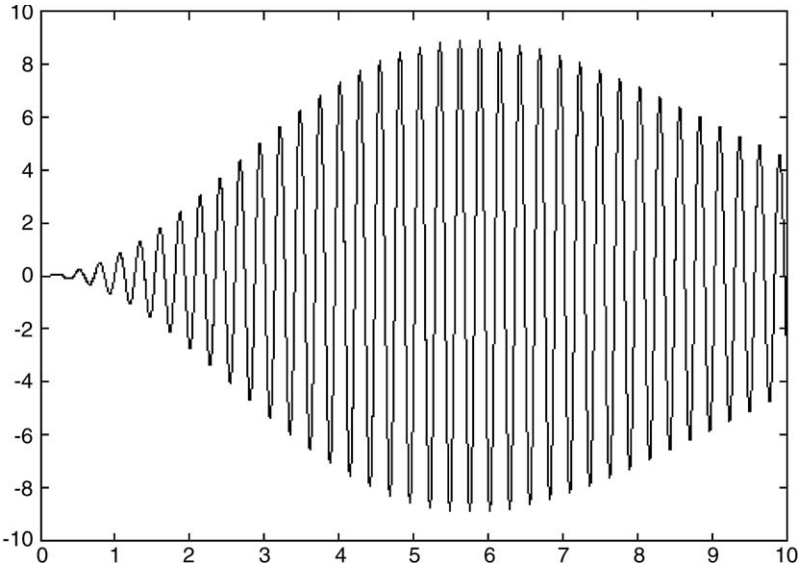

Fig. 1. The integrand of the semi-infinite integral with the spherical Bessel function (26) ($\alpha = .999$, $\beta = .005$, $v_{12} = v_{34} = 5/2$, $n_{\gamma_{12}} = n_{\gamma_{34}} = 1$, $n_x = \lambda = 1$, $\zeta_1 = \zeta_4 = 1.0$, $\zeta_2 = 1.5$, $\zeta_3 = 2.0$, $R_{12} = 2.0$, $R_{34} = 1.0$ and $v = 45.993$).

severe numerical and computation difficulties. This is the reason why nonlinear transformation methods for accelerating the convergence of oscillatory integrals or infinite series have been studied for many years and applied to various situations. These methods are based on the idea of extrapolation [84–86]. Their utility for enhancing and even inducing convergence has been amply demonstrated by Shanks [87]. With the help of nonlinear transformations or convergence accelerators, oscillatory integrals, slowly convergent and divergent sequences and series can be transformed into sequences and series with hopefully numerical properties. In the case of nonlinear transformations the improvement of convergence can be remarkable. These methods form the basis of new methods for solving various problems which were unsolvable otherwise and have many applications as well [84].

In the present work, we focus on the application of nonlinear $\overline{D}$ transformation of Sidi for improving convergence of highly oscillatory integrals and on some extrapolation techniques developed by Safouhi for accurate and fast numerical evaluation of complicated multicenter integrals as they occur in electronic structure calculations.

Let $\widetilde{\mathscr{Z}}(\alpha,\beta)$ be the semi-infinite integrals which occurs in the above analytic expression. It is given by:

$$\widetilde{\mathscr{Z}}(\alpha,\beta)=\int_0^{+\infty} x^{n_x}\frac{\hat{k}_{v_{21}}[\gamma_{21}(\alpha,x)R_{21}]}{[\gamma_{21}(\alpha,x)]^{n_{\gamma_{21}}}}\frac{\hat{k}_{v_{34}}[\gamma_{34}(\beta,x)R_{34}]}{[\gamma_{34}(\beta,x)]^{n_{\gamma_{34}}}}j_\lambda(vx)\,\mathrm{d}x. \tag{26}$$

The above semi-infinite integral is identical to the semi-infinite integral occurring in the analytic expression of four-center two-electron Coulomb integral [53,58,59]. The semi-infinite integral can be transformed into an infinite series as follows:

$$\widetilde{\mathscr{Z}}(\alpha,\beta)=\sum_{n=0}^{+\infty}\int_{j_{\lambda,v}^n}^{j_{\lambda,v}^{n+1}} x^{n_x}\frac{\hat{k}_{v_{21}}[\gamma_{21}(\alpha,x)R_{21}]}{[\gamma_{21}(\alpha,x)]^{n_{\gamma_{21}}}}\frac{\hat{k}_{v_{34}}[\gamma_{34}(\beta,x)R_{34}]}{[\gamma_{34}(\beta,x)]^{n_{\gamma_{34}}}}j_\lambda(vx)\,\mathrm{d}x, \tag{27}$$

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

The numerical evaluation of the three-dimensional integral representation, which occurs in Eq. (25) turned out to be extremely difficult when the values of α and β are close to *0* or *1*. In these regions the asymptotic behavior of the integrand of $\widetilde{\mathscr{Z}}(\alpha,\beta)$, which will be referred to as $\mathscr{F}_{\alpha,\beta}(x)$, cannot be represented by a function of the form $\mathrm{e}^{-\varrho x}g(x)$ where $g(x)$ is not a rapidly oscillating function. This is due to the fact that when α and β are close to 0 or 1, the arguments $\gamma_{21}(\alpha,x)$ and $\gamma_{34}(\beta,x)$ of $\hat{k}_{v_{21}}$ and $\hat{k}_{v_{34}}$ become constants and therefore the rapid oscillations of $j_\lambda(vx)$ cannot be damped by the exponential decreasing functions $\hat{k}_{v_{21}}$ and $\hat{k}_{v_{34}}$ (see Fig. 1). Note that when the value of v is very large, the zeros of $\mathscr{F}_{\alpha,\beta}(x)$ become closer and therefore the oscillations become strong and then the numerical evaluation of $\widetilde{\mathscr{Z}}(\alpha,\beta)$ become very difficult in particular for large values of λ (see Fig. 1).

In [60], we demonstrated the applicability of the nonlinear $\overline{D}$ transformation for improving convergence of the semi-infinite integrals $\widetilde{\mathscr{Z}}(\alpha,\beta)$ (26). The approximation $\overline{D}_n^{(2)}$ of the semi-infinite integral is obtained by solving the following linear set of equations:

$$\overline{D}_n^{(2)}=\int_0^{x_l}\mathscr{F}(t)\,\mathrm{d}t+x_l^2 g_{\alpha,\beta}(x_l)j'_\lambda(vx_l)\sum_{i=0}^{n-1}\frac{\bar{\beta}_{1,i}}{x_l^i},\quad l=0,1,\ldots,n, \tag{28}$$

where

$$\begin{aligned} g_{\alpha,\beta}(x)&=x^{n_x}\frac{\hat{k}_{v_{21}}[\gamma_{21}(\alpha,x)R_{21}]}{[\gamma_{21}(\alpha,x)]^{n_{\gamma_{21}}}}\frac{\hat{k}_{v_{34}}[\gamma_{34}(\beta,x)R_{34}]}{[\gamma_{34}(\beta,x)]^{n_{\gamma_{34}}}},\\ F(x)&=\int_0^x g_{\alpha,\beta}(t)j'_\lambda(v\ t)\,\mathrm{d}t, \end{aligned} \tag{29}$$

and where $x_l=\frac{j_{\lambda+\frac{1}{2}}^{l+1}}{v}$ for $l=0,1,2,\ldots$ are the leading positive zeros of $j_\lambda(vx)$.

It is clear that the calculation of the approximations $\overline{D}_n^{(2)}$ requires a large amount of CPU time, since it requires the computation of the successive leading zeros of the spherical Bessel functions (except in the case where $\lambda=0$) and it also requires the computation of a method to solve linear systems. This is due to the presence of the spherical Bessel functions. In the present contribution, we used another approach, which will

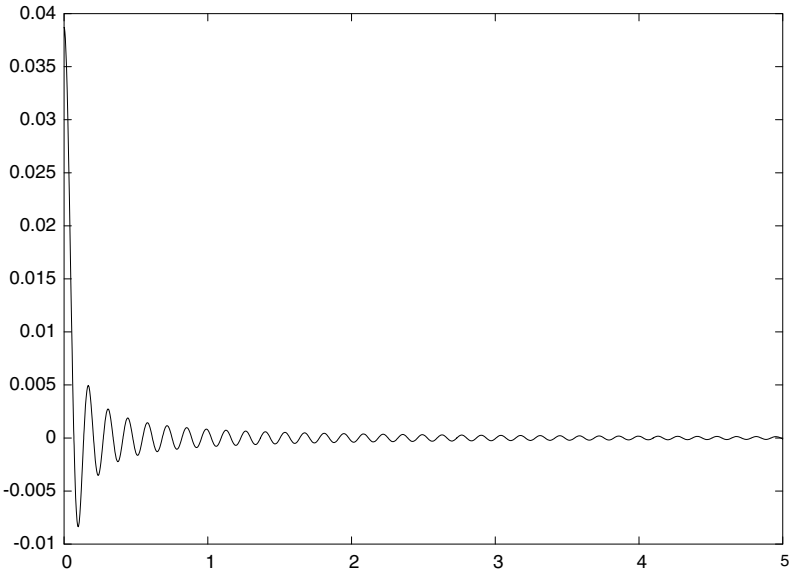

Fig. 2. The integrand of the semi-infinite integral with the sine function (30) ($\alpha = .999$, $\beta = .005$, $v_{12} = v_{34} = 5/2$, $n_{\gamma_{12}} = n_{\gamma_{34}} = 1$, $n_x = \lambda = 1$, $\zeta_1 = \zeta_4 = 1.0$, $\zeta_2 = 1.5$, $\zeta_3 = 2.0$, $R_{12} = 2.0$, $R_{34} = 1.0$ and $v = 45.993$).

further reduce the calculation times and further improve the accuracy in the numerical evaluation of the semi-infinite integrals under consideration. This algorithm is based on the so-called $S\overline{D}$ approach [53,64]. This method consists on applying the S and $\overline{D}$ transformations. The S transforms the semi-infinite spherical Bessel integral $\widetilde{\mathscr{Z}}(\alpha,\beta)$ into a semi-infinite integral involving the simple sine function. The obtained semi-infinite integral is given by [53,64]:

$$\widetilde{\mathscr{Z}}(\alpha,\beta) = \frac{1}{v^{\lambda+1}} \int_0^{+\infty} G_{\alpha,\beta} \sin(vx)\, \mathrm{d}x, \tag{30}$$

$$= \frac{1}{v^{\lambda+1}} \sum_{n=0}^{+\infty} \int_{n\pi/v}^{(n+1)\pi/v} G_{\alpha,\beta}(x) \sin(vx)\, \mathrm{d}x, \tag{31}$$

where the function $G_{\alpha,\beta}(x)$ is given by:

$$G_{\alpha,\beta}(x) = \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda} \left(x^{n_x+\lambda-1} \frac{\hat{k}_{v_{21}}[\gamma_{21}(\alpha,x)R_{21}]}{[\gamma_{21}(\alpha,x)]^{n_{\gamma_{21}}}} \frac{\hat{k}_{v_{34}}[\gamma_{34}(\beta,x)R_{34}]}{[\gamma_{34}(\beta,x)]^{n_{\gamma_{34}}}} \right). \tag{32}$$

From Fig. 2 it follows that the new integrand with the simple sine function is not a highly oscillatory function compared with the integrand $\mathscr{F}_{\alpha,\beta}(x)$ with the spherical Bessel function. The fact that the strong oscillations were considerably reduced helps the extrapolation method. Note also that the new integrand converges faster to 0 than the integrand $\mathscr{F}_{\alpha,\beta}(x)$ with the spherical Bessel function.

It is shown [53,64] that the integrand of the above semi-infinite integral, which will be referred to as $\widetilde{\mathscr{F}}_{\alpha,\beta}(x)$ satisfy all the conditions to apply the nonlinear $\overline{D}$ transformation. The fact that the zeros of the sine function are equidistant allowed the use of Cramer's rules as demonstrated by Sidi [62] for calculating the approximation of the semi-infinite integral $\widetilde{\mathscr{Z}}(\alpha,\beta)$, which is given by [64]:

$$S\overline{D}_n^{(2,j)} = \frac{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i+j)^n \widetilde{F}(x_{i+j}) \Big/ \left[x_{i+j}^2 G_{\alpha,\beta}(x_{i+j})\right]}{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i+j)^n \Big/ \left[x_{i+j}^2 G_{\alpha,\beta}(x_{i+j})\right]}, \tag{33}$$

where $\widetilde{F}(x) = \int_0^x G_{\alpha,\beta}(t) \sin(vt)\, \mathrm{d}t$ and $x_l = (l+1)\frac{\pi}{v}$ for $l = 0, 1, \ldots$, which are the successive positive zeros of $\sin(vx)$.

As it can be seen from Eq. (33), the computation of the successive zeros of the spherical Bessel function and the computation of a method to solve linear systems were avoided and this led to a great simplifications in the calculation and to a considerable reduction in the calculation times. The accuracy was also improved using this approach, since the oscillation of the integrand $\widetilde{\mathscr{F}}_{\alpha,\beta}(x)$ with the sine function was considerably reduced compared to the oscillations of the integrand $\mathscr{F}_{\alpha,\beta}(x)$ with the spherical Bessel function, and this helped the extrapolation method.

The computation of the approximation $S\overline{D}_n^{(2,j)}$ using Eq. (33) is not advantageous, because of the absence of the control of the degree of accuracy. Note also that Eq. (33) cannot be computed recursively. In [66], we developed recurrence relations satisfied by both numerator $A_n^{(2,j)}$ and denominator $B_n^{(2,j)}$ of the term in the right-hand side of Eq. (33).

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 [66], we showed that $A_n^{(2,j)}$ and $B_n^{(2,j)}$ satisfy the following relations:

$$\begin{aligned} A_n^{(2,j)} &= \sum_{i=0}^{n+1} U_i^n = \sum_{i=0}^{n} \frac{(n+1)}{(n+1-i)}(1+i+j)U_i^{n-1} + U_{n+1}^n, \\ B_n^{(2,j)} &= \sum_{i=0}^{n+1} V_i^n = \sum_{i=0}^{n} \frac{(n+1)}{(n+1-i)}(1+i+j)V_i^{n-1} + V_{n+1}^n. \end{aligned} \tag{34}$$

From the above equations, it follows that $S\overline{D}_n^{(2,j)}$ can be re-written as [66]:

$$S\overline{D}_n^{(2,j)} = \frac{1}{v^{+1}} \frac{\sum_{i=0}^{n} \frac{(n+1)}{(n+1-i)}(1+i+j)U_i^{n-1} + U_{n+1}^n}{\sum_{i=0}^{n} \frac{(n+1)}{(n+1-i)}(1+i+j)V_i^{n-1} + V_{n+1}^n}. \tag{35}$$

The values of U_i^k and V_i^k, $k = 0,1,2,\ldots$ and $i = 0,1,\ldots,k+1$, are stored at each iteration. This led to a substantial gain in the calculation times, since the calculation of all values of $x_{i+j}^2 G_{\alpha,\beta}(x_{i+j})$ for each order of the $S\overline{D}$ is avoided. By storing the values of U_i^k and V_i^k, one can perform the following test allowing the control of the degree of accuracy:

$$\left| S\overline{D}_n^{(2,j)} - S\overline{D}_{n-1}^{(2,j)} \right| = \frac{1}{v^{\lambda+1}} \left| \frac{A_n^{(2,j)}}{B_n^{(2,j)}} - \frac{A_{n-1}^{(2,j)}}{B_{n-1}^{(2,j)}} \right| \leqslant \epsilon, \tag{36}$$

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

In some cases $G_{\alpha,\beta}(x_{i+j}) \to 0$ or $+\infty$. We demonstrated [66,58] that in these cases we can obtain a very good approximation of the semi-infinite integral under consideration using the following formulae:

$$S\overline{D}_n^{(2,j)} \approx \frac{1}{v^{+1}} \frac{\sum_{i\in E} \binom{n+1}{i} (1+i+j)^n \frac{F(x_{i+j})}{x_{i+j}^2}}{\sum_{i\in E} \binom{n+1}{i} (1+i+j)^n \frac{1}{x_{i+j}^2}}, \tag{37}$$

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

$$E = \{k \in I \text{ such that } G_{\alpha,\beta}(x_{k+j}) \to 0 \text{ or } +\infty\}.$$

Note that the recurrence relations given by Eq. (34) are still applicable for the computation of to the approximation $S\overline{D}_n^{(2,j)}$ given by Eq. (37).

The following test was included in the algorithm:

$$R = \left| \frac{A_n^{(2,j)}}{\widetilde{A}_n^{(2,j)}} - \frac{B_n^{(2,j)}}{\widetilde{B}_n^{(2,j)}} \right| \leqslant \text{tiny} \quad \text{or} \quad \widetilde{R} = \left| \frac{\widetilde{A}_n^{(2,j)}}{A_n^{(2,j)}} - \frac{\widetilde{B}_n^{(2,j)}}{B_n^{(2,j)}} \right| \leqslant \text{tiny}, \tag{38}$$

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 Eq. (37) 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 Eq. (37) with the recurrence relations (34).

As it can be seen from Eq. (33), the computation of the function $G_{\alpha,\beta}(x)$ is necessary for the calculations. With the help of Eqs. (8), (10) and (11) and by using the Leibnitz formula, one can easily obtain in the case where $n_{\gamma_{12}} = 2v_{12}$ and $n_{\gamma_{34}} = 2v_{34}$:

$$\begin{aligned}
&\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda}\left[x^{n_x+\lambda-1}\frac{\hat{k}_{v_{21}}[\gamma_{21}(\alpha,x)R_{21}]}{[\gamma_{21}(\alpha,x)]^{n_{\gamma_{21}}}}\frac{\hat{k}_{v_{34}}[\gamma_{34}(\beta,x)R_{34}]}{[\gamma_{34}(\beta,x)]^{n_{\gamma_{34}}}}\right]\\
&\quad=\sum_{l_1=0}^{\lambda}\binom{\lambda}{l_1}\sum_{l_2=0}^{\lambda-l_1}\binom{\lambda-l_1}{l_2}\sum_{l_3=0}^{\lambda-l_1-l_2}\binom{\lambda-l_1-l_2}{l_3}\frac{(n_x+\lambda-1)!!}{(n_x+\lambda-1-2l_1)!!}x^{n_x+\lambda-1-2l_1}\\
&\qquad\times(-1)^{l_2}\alpha^{\lambda-l_1}(1-\alpha)^{\lambda-l_1}\frac{\hat{k}_{v_{21}+\lambda-l_1}[\gamma_{21}(\alpha,x)R_{21}]}{[\gamma_{21}(\alpha,x)]^{2(v_{21}+\lambda-l_1)}}\beta^{\lambda-l_1-l_2}(1-\beta)^{\lambda-l_1-l_2}\frac{\hat{k}_{v_{34}+\lambda-l_1-l_2}[\gamma_{34}(\beta,x)R_{34}]}{[\gamma_{34}(\beta,x)]^{2(v_{34}+\lambda-l_1-l_2)}},
\end{aligned}\tag{39}$$

and for $n_{\gamma_{12}} < 2v_{12}$ and $n_{\gamma_{34}} < 2v_{34}$, one can obtain:

$$\begin{aligned}
&\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda}\left[x^{n_x+\lambda-1}\frac{\hat{k}_{v_{21}}[\gamma_{21}(\alpha,x)R_{21}]}{[\gamma_{21}(\alpha,x)]^{n_{\gamma_{21}}}}\frac{\hat{k}_{v_{34}}[\gamma_{34}(\beta,x)R_{34}]}{[\gamma_{34}(\beta,x)]^{n_{\gamma_{34}}}}\right]\\
&\quad=\sum_{l_1=0}^{\lambda}\binom{\lambda}{l_1}\sum_{l_2=0}^{\lambda-l_1}\binom{\lambda-l_1}{l_2}\sum_{l_3=0}^{\lambda-l_1-l_2}\binom{\lambda-l_1-l_2}{l_3}\frac{(n_x+\lambda-1)!!}{(n_x+\lambda-1-2l_1)!!}x^{n_x+\lambda-1-2l_1}\\
&\qquad\times\frac{\alpha^{\lambda-l_1}(1-\alpha)^{\lambda-l_1}}{[\gamma_{21}(\alpha,x)]^{n_{\gamma_{21}}+2\lambda-2l_1}}\sum_{i=0}^{\lambda-l_1}\binom{\lambda-l_1}{i}\frac{(-1)^i(2v_{21}-n_{\gamma_{21}})!!}{(2v_{21}-n_{\gamma_{21}}-2i)!!}\hat{k}_{v_{21}+\lambda-l_1-i}[\gamma_{21}(\alpha,x)R_{21}]\\
&\qquad\times\frac{\beta^{\lambda-l_1-l_2}(1-\beta)^{\lambda-l_1-l_2}}{[\gamma_{34}(\beta,x)]^{n_{\gamma_{34}}+2\lambda-2l_1-2l_2}}\sum_{j=0}^{\lambda-l_1-l_2}\binom{\lambda-l_1-l_2}{j}\frac{(-1)^{l_2+j}(2v_{34}-n_{\gamma_{34}})!!}{(2v_{34}-n_{\gamma_{34}}-2j)!!}\hat{k}_{v_{34}+\lambda-l_1-j}[\gamma_{34}(\beta,x)R_{34}].
\end{aligned}\tag{40}$$

From Eqs. (40), (10) and (11), it follows that the computation of the function $G_{\alpha,\beta}(x)$ does not present any difficulty.

5. Numerical results and discussion

In the case when $v \to 0$, the semi-infinite integral $\widetilde{\mathscr{Z}}(\alpha,\beta)$ (26) vanishes if $\lambda \neq 0$, since $\lim_{x\to 0} j_\lambda(x) = 0$ and the integrand is an exponentially decreasing function (converges to *0* when $x \to +\infty$), and if $\lambda = 0$, we used the fact that $j_0(x) = \frac{\sin(x)}{x} \to 1$ when $x \to 0$ and the fact that the integrand is exponentially decreasing function, to obtain a good approximation of the semi-infinite integral which is given by:

$$\widetilde{\mathscr{Z}}(\alpha,\beta) \approx \int_0^{+\infty} x^{n_x}\frac{\hat{k}_{v_{21}}[\gamma_{21}(\alpha,x)R_{21}]}{[\gamma_{21}(\alpha,x)]^{n_{\gamma_{21}}}}\frac{\hat{k}_{v_{34}}[\gamma_{34}(\beta,x)R_{34}]}{[\gamma_{34}(\beta,x)]^{n_{\gamma_{34}}}}\,\mathrm{d}x.\tag{41}$$

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

The finite integrals $\widetilde{F}(x)$ occurring in Eq. (33) are transformed into a finite sum as follows:

$$\widetilde{F}(x) = \sum_{i=0}^{n+1}\int_{x_i}^{x_{i+1}}\widetilde{\mathscr{F}}_{\alpha,\beta}(t)\,\mathrm{d}t,\tag{42}$$

where $x_0 = 0$ and $x_i = i\frac{\pi}{v}$ for $i = 1,2,\ldots,n+1$.

The evaluation of each term of the finite sum is evaluated using the following procedure:

- When $v \geqslant 1$, we used Gauss–Legendre quadrature of order 24.
- When $10^{-15} < v < 1$, we divided the finite interval $[x_i, x_{i+1}]$ into M subintervals, where $M = \min(v^{-1}, 100)$. The finite integral $\int_{x_i}^{x_{i+1}}\widetilde{\mathscr{F}}_{\alpha,\beta}(t)\,\mathrm{d}t$ can be re-written as:

$$\int_{x_i}^{x_{i+1}} \widetilde{\mathscr{F}}_{\alpha,\beta}(t)\,\mathrm{d}t = \sum_{k=0}^{M-1} \int_{\tilde{x}_k}^{\tilde{x}_{k+1}} \widetilde{\mathscr{F}}_{\alpha,\beta}(t)\,\mathrm{d}t, \tag{43}$$

where $\tilde{x}_0 = x_0$, $\tilde{x}_M = x_{n+1}$ and for $k = 1,\ 2, \ldots, M-1$, $\tilde{x}_k = x_i + k\frac{x_{i+1}-x_i}{M}$.

For the evaluation of each finite integral involving in the above finite sum, we used Gauss–Legendre quadrature of order 24.

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

For the numerical evaluation of the outer finite α and β integrals occurring in Eq. (25), we used Gauss–Legendre quadrature of order 48. The value of epsilon ϵ in Eq. (36) was set to 10^{-15}. We notice that one can increase the accuracy by decreasing the value of epsilon. For the numerical evaluation of Gaunt coeffi-

Table 1
Values of the semi-infinite integral $\widetilde{\mathscr{I}}(\alpha,\beta)$ (26) obtained using the infinite series with the sine function (31)

α	β	v_{12}	$n_{\gamma_{12}}$	v_{34}	$n_{\gamma_{34}}$	n_x	λ	ζ_1	ζ_2	ζ_3	ζ_4	v	$n_{\max}^{\sin}$	$\tilde{\mathscr{J}}(s,t)^{n_{\max}^{\sin}}$
.999	.999	5/2	5	5/2	5	1	1	1.5	1.0	1.0	1.5	24.501	950	.477544764867146(−02)
.999	.001	5/2	1	5/2	1	1	1	1.0	1.7	2.0	1.0	27.495	1675	.105272707975582(−02)
.999	.001	5/2	3	5/2	3	1	1	1.0	1.2	1.2	1.0	27.495	1316	.181953669767981(−02)
.999	.001	5/2	5	5/2	5	1	1	1.0	1.3	1.3	1.0	27.495	1040	.762343846671344(−03)
.001	.001	7/2	5	7/2	5	1	1	1.5	1.5	1.5	1.5	25.499	1165	.964223000847461(−03)
.001	.001	7/2	7	7/2	7	1	1	1.4	5.0	5.0	1.4	25.499	939	.581682312428543(−03)
.001	.999	9/2	5	9/2	5	2	2	1.9	6.5	1.9	6.5	22.505	1250	.452480351741839(−03)
.999	.999	9/2	9	9/2	9	2	2	2.0	1.5	1.5	2.0	24.501	893	.392989948554829(−03)
.999	.999	9/2	7	9/2	7	3	3	6.0	1.4	1.4	5.0	24.501	1103	.117483365648093(−02)
.999	.999	9/2	9	9/2	9	3	3	2.0	1.4	1.4	5.0	24.501	898	.322043911410257(−03)
.999	.001	11/2	10	11/2	10	3	3	8.0	1.7	3.5	1.5	27.495	1070	.556027981384833(−03)
.999	.001	11/2	11	11/2	11	3	3	8.0	1.4	8.0	1.6	27.495	982	.791379364173145(−03)
.001	.001	13/2	11	13/2	11	4	4	2.0	5.0	2.5	1.7	25.499	1075	.393944366125535(−03)
.001	.001	13/2	13	13/2	13	4	4	1.6	2.5	2.5	1.6	25.499	902	.219334200082080(−03)
.001	.001	17/2	11	17/2	11	4	4	2.7	2.0	9.0	2.7	25.499	1474	.110480172181313(−02)
.001	.001	17/2	17	17/2	17	4	4	2.0	6.0	3.0	2.0	25.499	904	.662354870374030(−03)

$R_1 = 2.5$, $R_2 = 4.5$, $R_3 = 30.0$ and $R_4 = 27.0$.

Table 2
Evaluation of the semi-infinite integral $\widetilde{\mathscr{I}}(\alpha,\beta)$ (26), using the infinite series with the spherical Bessel function (27), the $\bar{D}$ transformation (28) and the $S\bar{D}$ approach (35)

$n_{\max}^{J_\lambda}$	$\tilde{\mathscr{J}}(s,t)^{n_{\max}^{J_\lambda}}$	Error	$\bar{D}_{10}^{(2)}$	Error	$S\bar{D}_{10}^{(2,0)}$	Error
1138	.477544764867258(−02)	.11(−14)	.477544764862978(−02)	.42(−13)	.477544764867217(−02)	.71(−15)
1987	.105272707975487(−02)	.94(−15)	.105272707975473(−02)	.11(−14)	.105272707975536(−02)	.46(−15)
1582	.181953669768073(−02)	.92(−15)	.181953669767635(−02)	.35(−14)	.181953669768036(−02)	.55(−15)
1258	.762343846672292(−03)	.95(−15)	.762343846668867(−03)	.25(−14)	.762343846671861(−03)	.52(−15)
1389	.964223000846548(−03)	.91(−15)	.964223000845251(−03)	.22(−14)	.964223000847002(−03)	.46(−15)
1122	.581682312428577(−03)	.33(−16)	.581682312425974(−03)	.26(−14)	.581682312428073(−03)	.47(−15)
1694	.452480351737068(−03)	.48(−14)	.452480351737322(−03)	.45(−14)	.452480351741370(−03)	.47(−15)
1231	.392989948556617(−03)	.18(−14)	.392989948542320(−03)	.13(−13)	.392989948555340(−03)	.51(−15)
1745	.117483365647546(−02)	.55(−14)	.117483365632605(−02)	.15(−12)	.117483365648060(−02)	.33(−15)
1432	.322043911392475(−03)	.18(−13)	.322043911348076(−03)	.62(−13)	.322043911410818(−03)	.56(−15)
1689	.556027981624919(−03)	.24(−12)	.556027981336169(−03)	.49(−13)	.556027981385363(−03)	.53(−15)
1542	.791379364304491(−03)	.13(−12)	.791379364074091(−03)	.99(−13)	.791379364173737(−03)	.59(−15)
1883	.393944353305154(−03)	.13(−10)	.393944366010891(−03)	.11(−12)	.393944366126083(−03)	.55(−15)
1578	.219334194340248(−03)	.57(−11)	.219334199969961(−03)	.11(−12)	.219334200081674(−03)	.41(−15)
2438	.110480173781362(−02)	.16(−10)	.110480172173683(−02)	.76(−13)	.110480172181269(−02)	.44(−15)
1487	.662354850714832(−03)	.20(−10)	.662354870104294(−03)	.27(−12)	.662354870373728(−03)	.30(−15)

α, β, v_{12}, $n_{\gamma_{12}}$, v_{34}, $n_{\gamma_{34}}$, n_x, λ, ζ_1, ζ_2, ζ_3, ζ_4, R_1, R_2, R_3, R_4 and v are given in Table 1.

cients which occur in the complete expressions of the integrals under consideration, we used the subroutine GAUNT.F developed by Weniger [79]. The spherical harmonics $Y_l^m(\theta,\varphi)$ are computed using the recurrence formulae presented in [79].

Table 1 contains values of the semi-infinite integral $\widetilde{\mathscr{Z}}(\alpha,\beta)$ (26) obtained using the infinite series with the sine function (31). In Table 2, we evaluated the semi-infinite integral $\widetilde{\mathscr{Z}}(\alpha,\beta)$ (26) using the infinite series with the spherical Bessel function (27), the $\overline{D}$ transformation (28) and the $S\overline{D}$ approach (35). In these tables, the errors stand for the absolute errors.

Table 3
Slater exponents

Orbitals	Carbon	Nitrogen	Oxygen
STO 1s	5.6727	6.6651	7.6579
STO 2s	1.6083	1.9237	2.2458
STO $2p_z(2z)$	1.5679	1.9170	2.2266

Table 4
Values of multicenter overlap-like quantum similarity integrals over STFs Z_{1234} (25)

Z_{ABCD}[a]	$A^{(b)}$	$B^{(b)}$	$C^{(b)}$	$D^{(b)}$	$\bar{D}_8^{(2)}$	$S\bar{D}_n^{(2)}$
Tricenter Coulomb-like (aligned)						
$Z_{1s1s1s1s}$	(0,0,0)	(0,0,0)	(0,0,1)	(0,0,−1)	.116 377 193 119(−3)	.116 377 190 222(−3)
$Z_{1s2s1s2s}$	(0,0,0)	(0,0,0)	(0,0,1)	(0,0,−1)	.222 636 464 988(−2)	.222 636 464 987(−2)
Z_{2s2p_z1s2s}	(0,0,0)	(0,0,0)	(0,0,1)	(0,0,−1)	.454 480 662 531(−2)	.454 480 662 531(−2)
$Z_{2p_z2p_z1s2p_z}$	(0,0,0)	(0,0,0)	(0,0,1)	(0,0,−1)	.119 583 679 103(−1)	.119 583 679 103(−1)
$Z_{2p_z2p_z2p_z2p_z}$	(0,0,0)	(0,0,0)	(0,0,1)	(0,0,−1)	−.164 009 565 733(−1)	−.164 009 565 708(−1)
Tricenter exchange-like (aligned)						
$Z_{1s1s1s1s}$	(0,0,0)	(0,0,1)	(0,0,0)	(0,0,−1)	.507 698 321 030(−4)	.507 698 333 634(−4)
$Z_{1s2s1s2s}$	(0,0,0)	(0,0,1)	(0,0,0)	(0,0,−1)	.581 546 572 656(−1)	.581 546 572 656(−1)
Z_{2s2p_z1s2s}	(0,0,0)	(0,0,1)	(0,0,0)	(0,0,−1)	−.159 105 821 383(−1)	−.159 105 821 383(−1)
$Z_{2p_z2p_z1s2p_z}$	(0,0,0)	(0,0,1)	(0,0,0)	(0,0,−1)	.176 868 161 248(−2)	.176 868 161 247(−2)
$Z_{2p_z2p_z2p_z2p_z}$	(0,0,0)	(0,0,1)	(0,0,0)	(0,0,−1)	−.134 167 397 640(−1)	−.134 167 397 640(−1)
Tricenter Coulomb-like (equilateral triangle)						
$Z_{1s2s2s2s}$	(1,0,0)	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.305 435 816 795(−2)	.305 435 816 843(−2)
$Z_{2s2s2s2s}$	(1,0,0)	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.874 706 538 478(−2)	.874 706 538 477(−2)
$Z_{2p_z2s2s2p_z}$	(1,0,0)	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.496 481 028 442(−2)	.496 481 028 441(−2)
$Z_{2p_z2p_z2s2s}$	(1,0,0)	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.586 324 108 548(−2)	.586 324 108 549(−2)
$Z_{2p_z2p_z2p_z2p_z}$	(1,0,0)	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.446 819 460 293(−2)	.446 819 460 293(−2)
Tricenter exchange-like (equilateral triangle)						
$Z_{1s2s2s2s}$	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	(1,0,0)	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.218 873 297 824(−2)	.218 873 297 836(−2)
$Z_{2s2s2s2s}$	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	(1,0,0)	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.821 484 459 122(−2)	.821 484 459 121(−2)
$Z_{2p_z2s2s2p_z}$	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	(1,0,0)	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.410 767 865 180(−2)	.410 767 865 180(−2)
$Z_{2p_z2p_z2s2s}$	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	(1,0,0)	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.410 767 865 179(−2)	.410 767 865 179(−2)
$Z_{2p_z2p_z2p_z2p_z}$	(1,0,0)	$(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$	(1,0,0)	$(-\frac{1}{2},-\frac{\sqrt{3}}{2},0)$	.409 199 451 345(−2)	.409 199 451 345(−2)
Tetracenter integrals (regular tetrahedron)						
$Z_{2s2s2s2s}$	(1,1,1)	(−1,1,−1)	(−1,−1,1)	(1,−1,−1)	.549 964 345 914(−3)	.549 964 345 904(−3)
Z_{1s2s2p_z2s}	(1,1,1)	(−1,1,−1)	(−1,−1,1)	(1,−1,−1)	−.347 848 333 360(−5)	−.347 848 341 005(−5)
Z_{2s2p_z1s2s}	(1,1,1)	(−1,1,−1)	(−1,−1,1)	(1,−1,−1)	.180 963 998 996(−4)	.180 963 999 020(−4)
$Z_{2p_z2p_z1s2p_z}$	(1,1,1)	(−1,1,−1)	(−1,−1,1)	(1,−1,−1)	−.368 161 920 446(−5)	−.368 161 918 533(−5)
$Z_{2p_z2p_z2p_z2p_z}$	(1,1,1)	(−1,1,−1)	(−1,−1,1)	(1,−1,−1)	.287 234 575 143(−3)	.287 234 575 143(−3)

[a] Z_{ABCD}: A and C are carbon atoms, B is a nitrogen and D is an oxygen.

In Tables 1 and 2, the parameters $n_{\max}^{\sin}$ and $n_{\max}^{j_\lambda}$ stand for the numbers of terms of the infinite series with the sine function (31) and the infinite series with the spherical Bessel function (27), needed to obtain values of the semi-infinite integrals computed in double precision (15 correct digits). From these two parameters, one can easily notice that the infinite series with the sine function has better convergence properties than the one with the spherical Bessel function.

Note that the numerical evaluation of the semi-infinite integrals was performed in the regions where the oscillations of the integrand are strong (α and β are close to 0 or 1). In these regions, the functions $\gamma_{21}(\alpha, x)$ and $\gamma_{34}(\beta, x)$ become constants and the strong oscillations of the spherical Bessel function cannot be damped by the exponential decreasing functions $\hat{k}_v$. Note also that the values of v (see Table 1) are large. Numerical tables and more details on the stability of the algorithm and the control of the degree of accuracy in the numerical evaluation of this kind of semi-infinite integrals are presented in [58].

Table 3 contains orbital screening parameters used for the calculations.

Table 4 contains values for multicenter overlap-like quantum similarity integrals.

Tables 5 and 6 contain values of the two kinds of two-center overlap-like quantum similarity integrals. These values are in a complete agreement with those obtained using different approaches, namely the one-center two-range expansion method [73], the epsilon algorithm of Wynn [74] and the nonlinear $\overline{D}$ transforma-

Table 5
Two-center overlap-like quantum similarity integrals of the first kind over STFs[a]

Integrals	AB (a.u.)	$\bar{D}_8^{(2)}$	$S\bar{D}_n^{(2)}$
Z_{1S1S1S_1S}	0.500	.858 425 852 923(0)	.858 425 852 924(0)
	1.000	.347 537 772 524(−1)	.347 537 772 530(−1)
	1.500	.129 121 270 397(−2)	.129 121 270 361(−2)
	2.000	.469 995 445 766(−4)	.469 995 449 874(−4)
Z_{1S1S2S_2S}	0.500	.501 673 492 454(−1)	.501 673 492 454(−1)
	1.000	.390 192 927 181(−1)	.390 192 927 166(−1)
	1.500	.230 003 633 004(−1)	.230 003 632 973(−1)
	2.000	.119 325 313 955(−1)	.119 325 313 974(−1)
Z_{1S1S2S_2Z}	0.500	−.737 342 853 412(−1)	−.737 342 853 102(−1)
	1.000	−.646 915 685 904(−1)	−.646 915 685 910(−1)
	1.500	−.391 549 466 792(−1)	−.391 549 466 819(−1)
	2.000	−.205 463 625 957(−1)	−.205 463 625 987(−1)

[a] Z_{AAA_B}: A is a carbon atom and B is a nitrogen.

Table 6
Two-center overlap-like quantum similarity integrals of the second kind over STFs[a]

Integrals	AB (a.u.)	$\bar{D}_8^{(2)}$	$S\bar{D}_n^{(2)}$
Z_{1S1S_1S1S}	0.500	.392 518 041 090(0)	.392 518 041 226(0)
	1.000	.287 290 954 878(−2)	.287 291 437 606(−2)
	1.500	.141 995 989 999(−4)	.142 141 727 540(−4)
	2.000	.623 967 358 452(−7)	.598 047 418 124(−7)
Z_{1S2S_1S2S}	0.500	.185 319 048 860(−1)	.185 319 048 857(−1)
	1.000	.266 806 719 558(−2)	.266 806 719 069(−2)
	1.500	.206 888 522 479(−3)	.206 888 508 304(−3)
	2.000	.115 770 030 096(−4)	.115 769 693 510(−4)
Z_{1S2S_1S2Z}	0.500	−.159 539 764 712(−1)	−.159 539 764 712(−1)
	1.000	−.324 008 017 562(−2)	−.324 008 017 676(−2)
	1.500	−.280 545 794 472(−3)	−.280 545 795 515(−3)
	2.000	−.165 259 598 173(−4)	−.165 259 528 941(−4)

[a] Z_{AA_BB}: A is a carbon atom and B is a nitrogen.

tion [60]. From these tables, one can notice that the analytic expression (25) is general and able to produce values for two- or three-center integrals. In these tables, nuclei are placed along the (oz) axis.

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 and all entries are in atomic units. Calculations were performed on a Workstation with an Intel Xeon Processor with 2.4 GHz.

6. Conclusion

Quantum similarity measurements are expressed in terms of four-center overlap-like quantum similarity integrals, using the LCAO approach with STFs as basis set of atomic orbitals. These STFs are expressed in terms of the so-called B functions, better suited to apply the Fourier transform method. The use of the Fourier representation of delta Dirac function and the Fourier transform method, analytic expressions were developed for the integrals under consideration. The obtained analytic expressions turned out to be very difficult to evaluate accurately and rapidly, because of the presence of highly oscillatory spherical Bessel integrals.

The nonlinear $\overline{D}$ transformation led to an accurate algorithm for the numerical evaluation of these spherical Bessel integral functions. Unfortunately, this transformation, which is one of the most powerful tool for improving convergence of oscillatory integrals, requires the computation of the successive zeros of the spherical Bessel functions and a computation of a method to solve linear systems. This requires a large amount of CPU time.

In the present contribution, we showed that these spherical Bessel integrals can be transformed into semi-infinite integrals involving the simple sine function, using the $S\overline{D}$ approach. The strong oscillations of the integrand are considerably reduced. The obtained sine integral function is shown to be suitable to apply the $\overline{D}$ transformation. The successive zeros of the spherical Bessel function and the computation of a method to solve linear systems are not required anymore for the calculations. The calculation times were considerably reduced.

The recurrence relations developed for the computation of the approximations $S\overline{D}_n^{(2,j)}$ allowed the control of the degree of accuracy and the algorithm developed from this method is stable.

A series of numerical tests showed that some cases have to be treated separately; $v \to 0$, $G_{\alpha,\beta}(x_{i+j}) \to 0$ or $+\infty$. Formulae were developed for each case.

The introduction of the $S\overline{D}$ approach in the numerical evaluation of overlap-like quantum similarity integrals will definitely lead to the development of a complete package for the numerical evaluation of quantum molecular measurements using STFs as basis set of atomic orbitals.

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