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Convergence properties of the $S\overline{D}$ transformation and a fast and accurate numerical evaluation of molecular integrals

Hassan Safouhi

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

E-mail: hassan.safouhi@ualberta.ca

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Abstract

The present work concerns the study of the convergence properties of the nonlinear $S\overline{D}$ transformation. A fast and accurate numerical evaluation of highly oscillatory semi-infinite integrals involved in the analytic expressions of molecular integrals over Slater-type orbitals is obtained using the $S\overline{D}$ transformation. These semi-infinite integrals involve spherical and reduced Bessel functions. The convergence properties are analysed and they show that the approximations obtained using the $S\overline{D}$ approach converge to the exact values of the semi-infinite integrals without any constraint. The numerical tables show that the $S\overline{D}$ method gives unprecedented accuracy with speed-up by a factor 2 over the $H\overline{D}$ method and a factor 10 over the $\overline{D}$ transformation. This illustrates the superiority of this new approach.

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1. Introduction

The present work concerns the study of the convergence properties of the nonlinear $S\overline{D}$ transformation and its application for a fast and accurate numerical evaluation of semi-infinite highly oscillatory integrals. This method is based on the nonlinear D and $\overline{D}$ transformations [1–3] and on the HD and $H\overline{D}$ approaches [4, 5]. The D and $\overline{D}$ transformations are efficient in evaluating semi-infinite integrals whose integrands satisfy linear differential equations with coefficients having asymptotic expansions in inverse powers of their argument x as $x \to +\infty$. The application of D and $\overline{D}$ depends greatly on the order of the differential equation that the integrand satisfies; when this order is large the calculations become very difficult. The main idea of the HD and $H\overline{D}$ methods which are based on the Hankel transform [2], is to reduce the order of these differential equations to 2 for a certain class of integrands involving spherical

and reduced Bessel functions. This result led to a great simplification in the application of the D and $\overline{D}$ transformations.

The main idea of the $S\overline{D}$ method is to replace the spherical Bessel function in the integrands by the sine function using useful properties that relate these two functions [6]. 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 [7, 8]. Useful properties of the sine function, spherical and reduced Bessel functions and Poincaré series allowed the use of Cramer's rule in the calculations [6, 9]. The convergence properties of this new approach are now analysed and they show that the approximation $S\overline{D}_n^{(2)}$ converges without any constraint to the exact value of the semi-infinite integral.

A fast and accurate numerical evaluation of highly oscillatory semi-infinite integrals involved in the analytic expressions of three-centre molecular integrals over Slater-type orbitals is obtained using the $S\overline{D}$ transformation. These integrals are the rate determining step of *ab initio* and density functional theory (DFT) molecular structure calculations and they contribute to the total energy of the molecule. The *ab initio* calculations using the LCAO-MO approach [10], where molecular orbitals are built from a linear combination of atomic orbitals, are strongly dependent on the choice of the basis functions for the reliability of the electronic distributions they provide [11]. A good atomic orbital basis should satisfy two pragmatic conditions for analytical solutions of the appropriate Schrödinger equation, namely the cusp at the origin [12] and exponential decay at infinity [13, 14].

Various studies have focused on the use of B functions that have been proposed by Shavitt [15] and introduced by Filter and Steinborn [16, 17]. These functions have some remarkable mathematical properties applicable to multicentre integral problems. Addition theorems for B functions that have been derived in [18] have simple structures. The B functions have extremely compact convolution integrals [19, 20] and their Fourier transform is of exceptional simplicity [21, 22]. Note also that Slater-type functions [23, 24] can be expressed as finite linear combinations of B functions [17].

The B functions are well adapted to the Fourier transformation method introduced by Bonham *et al* [25] and generalized by Steinborn *et al* [26, 27]. This Fourier transformation method, which is one of the most successful approaches for the evaluation of multicentre integrals, allowed analytic expressions for molecular integrals over B functions to be developed. These analytic expressions turned out to be extremely difficult to evaluate because of the presence of two-dimensional integral representations. The integrands of the inner semi-infinite integrals are highly oscillatory functions due to the presence of spherical Bessel functions $j_\lambda(vx)$, in particular for large values of λ and v.

These semi-infinite integrals can be transformed into infinite series of integrals. These infinite series are alternating and slowly convergent and this is why their use is prohibitively long for a sufficient accuracy. In previous work [28, 29], we demonstrated that the use of Gauss–Laguerre quadrature is inefficient in evaluating this kind of oscillatory integrals since in certain regions corresponding to s close to 0 or 1, where s is one of the arguments of the integrands, the asymptotic behaviour of the integrands cannot be represented by functions of the form $\mathrm{e}^{-\alpha x} g(x)$ where $g(x)$ is not a highly oscillatory function. We also note that the regions close to $s = 0$ or 1 carry a very small weight because of their expressions $s^{n_2}(1-s)^{n_1}$ in the integrals [30–33].

The epsilon algorithm of Wynn [34] or Levin's u transform [35], accelerate the convergence of infinite series but in the case of the semi-infinite integrals involved in the analytic expressions of molecular integrals, the calculation times for a sufficient accuracy are still long especially for large values of λ and v since the zeros of $j_\lambda(vx)$ become closer [28, 29, 36]. Therefore new numerical integration techniques are required.

2. General definitions and properties

The spherical Bessel function $j_l(x)$ is defined by [37, 38]

$$j_l(x) = (-1)^l x^l \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^l j_0(x) = (-1)^l x^l \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^l \left(\frac{\sin(x)}{x}\right). \tag{1}$$

$j_l(x)$ and its first derivative $j_l'(x)$ satisfy the recurrence relations [37, 38],

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

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 reduced Bessel function $\hat{k}_{n+\frac{1}{2}}(z)$ is defined by [15, 16]

$$\hat{k}_{n+\frac{1}{2}}(z) = z^n\, \mathrm{e}^{-z} \sum_{j=0}^{n} \frac{(n+j)!}{j!(n-j)!} \frac{1}{(2z)^j}. \tag{3}$$

The reduced Bessel functions satisfy the recurrence relation [15],

$$\hat{k}_{n+\frac{1}{2}}(z) = (2n-1)\, \hat{k}_{n-\frac{1}{2}}(z) + z^2 \hat{k}_{(n-1)-\frac{1}{2}}(z). \tag{4}$$

A useful property satisfied by $\hat{k}_{n+\frac{1}{2}}(z)$ is given by [39]

$$\left(\frac{\mathrm{d}}{z\,\mathrm{d}z}\right)^m \frac{\hat{k}_{n+\frac{1}{2}}(z)}{z^{2n+1}} = \left(\frac{\mathrm{d}}{z\,\mathrm{d}z}\right)^m \left[\sqrt{\frac{\pi}{2}} \frac{K_{n+\frac{1}{2}}(z)}{z^{n+\frac{1}{2}}}\right] = (-1)^m \frac{\hat{k}_{n+m+\frac{1}{2}}(z)}{z^{2(n+m)+1}} \tag{5}$$

where $K_{n+\frac{1}{2}}$ stands for the modified Bessel function of the second kind [39].

For the following, we define $A^{(\gamma)}$ for certain γ, as the set of infinitely differentiable functions $p(x)$, which have asymptotic expansions in inverse powers of x as $x \to +\infty$, of the form

$$p(x) \sim x^\gamma \left(a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} + \cdots\right) \tag{6}$$

and their derivatives of any order have asymptotic expansions, which can be obtained by differentiating that in (6) term by term.

We denote by $\tilde{A}^{(\gamma)}$, for some γ, the set of functions $p(x)$ such that $p(x) \in A^{(\gamma)}$ and $\lim_{x\to+\infty} x^{-\gamma} p(x) \neq 0$. Thus, $p \in \tilde{A}^{(\gamma)}$ has an asymptotic expansion in inverse powers of x as $x \to +\infty$ of the form given by (6) with $a_0 \neq 0$.

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

3. The nonlinear $S\overline{D}$ transformation

Let us consider a function of the form

$$f(x) = g(x)\, j_\lambda(x) \tag{7}$$

where the function $g(x)$ is of the form $g(x) = h(x)\, \mathrm{e}^{\phi(x)}$.

The semi-infinite oscillatory integral $\int_0^{+\infty} f(x)\,\mathrm{d}x$ is difficult to evaluate because of the presence of the spherical Bessel function in the integrand. In previous work [4, 5], we showed that we can obtain an efficient and rapid numerical evaluation of the semi-infinite integrals of the form given by (7) with the help of the nonlinear $H\overline{D}$ transformation. This method requires the computation of the successive positive zeros of spherical Bessel functions and

the computation of a method to solve linear systems. This requires a considerable amount of (CPU) time in particular for large orders of spherical Bessel functions.

The principal idea of the $S\overline{D}$ transformation consists in replacing the spherical Bessel function in the integrands by the sine function using equation (1). The principal difficulty related to the strong oscillations of the spherical Bessel functions has been solved. As it is well known, the numerical integration of oscillatory integrands is very difficult when the oscillatory part is a spherical Bessel function and not a simple trigonometric function. The useful properties of the sine function, Bessel functions and Poincaré series, helped to develop the $S\overline{D}$ transformation where we can use Cramer's rule for calculating good approximations of semi-infinite highly oscillatory integrals.

Now we shall state two theorems which are fully demonstrated in [6].

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

$$f(x) = g(x)\, j_\lambda(x) \tag{8}$$

where $g(x)$ is in $\mathcal{C}^2([0, +\infty[)$, which is the set of twice continuously differentiable functions defined on the half-open interval $[0, +\infty[$. If the function $g(x)$ is of the form $g(x) = h(x)\, \mathrm{e}^{\phi(x)}$, where $h(x) \in \tilde{A}^{(\gamma)}$ for some γ and $\phi(x) \in \tilde{A}^{(k)}$ with $k > 0$ and if for all $l = 0, 1, \ldots, \lambda - 1$,

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

then $f(x)$ is integrable on $[0, +\infty[$ and

$$\int_0^{+\infty} f(x)\,\mathrm{d}x = \int_0^{+\infty} \left[\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^\lambda (x^{\lambda-1} g(x))\right] \sin(x)\,\mathrm{d}x. \tag{9}$$

Theorem 2. *If $f(x)$ is a function of the form given by (8) and satisfying all the conditions of theorem 1, then a good approximation of $\int_0^{+\infty} f(x)\,\mathrm{d}x$ is given by*

$$S\overline{D}_n^{(2)} = \int_0^{x_l} G(x)\sin(x)\,\mathrm{d}x + (-1)^{l+1} G(x_l) x_l^2 \sum_{i=0}^{n-1} \frac{\bar{\beta}_{1,i}}{x_l^i} \qquad l = 0, 1, \ldots, n \tag{10}$$

where $x_l = (l+1)\pi$ for $l = 0, 1, \ldots$. $S\overline{D}_n^{(2)}$ and the $\bar{\beta}_{1,i}$ are the $(n+1)$ unknowns of the linear system. The function $G(x)$ is given by

$$G(x) = \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^\lambda (x^{\lambda-1} g(x)). \tag{11}$$

Following Levin [35], we can use Cramer's rule for calculating the unknown $S\overline{D}_n^{(2)}$ of the above linear system, since the zeros of $\sin(x)$ *are equidistant. The approximation $S\overline{D}_n^{(2)}$ is given by*

$$S\overline{D}_n^{(2,j)} = \frac{\sum_{i=0}^n \binom{n}{i} (1+i+j)^{n-1} F(x_{i+j}) \big/ \left[x_{i+j}^2 G(x_{i+j})\right]}{\sum_{i=0}^n \binom{n}{i} (1+i+j)^{n-1} \big/ \left[x_{i+j}^2 G(x_{i+j})\right]} \tag{12}$$

where $F(x) = \int_0^x G(t)\sin(t)\,\mathrm{d}t$.

Now, let us consider the two-dimensional integral representations denoted by $\tilde{\mathcal{I}}$ and $\tilde{\mathcal{K}}$ given by [6, 42]

$$\tilde{\mathcal{I}} = \int_{s=0}^1 s^{n_2} (1-s)^{n_1} Y_\lambda^\mu(\theta_{\vec{v}}, \varphi_{\vec{v}}) \left[\int_{x=0}^{+\infty} x^{n_x} \frac{\hat{k}_v[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(vx)\,\mathrm{d}x\right] \mathrm{d}s \tag{13}$$

where n_1, n_2, λ, n_x and n_γ are positive integers, μ is an integer, ν is of the form $\nu = n + \frac{1}{2}$ where n is a positive integer, R_2 and v are positive real numbers and

$$[\gamma(s,x)]^2 = (1-s)\zeta_1^2 + s\zeta_2^2 + s(1-s)x^2$$

where ζ_1 and ζ_2 are positive real numbers. And

$$\tilde{\mathcal{K}} = \int_{s=0}^{1} s^{n_3}(1-s)^{n_4} Y_\lambda^\mu(\theta_{\vec{v}}, \varphi_{\vec{v}}) \int_{x=0}^{+\infty} \left[\zeta_s^2 + x^2\right]^{-n_k} x^{n_x} \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(vx)\,\mathrm{d}x\,\mathrm{d}s \tag{14}$$

where n_3, n_4, λ, n_x and n_γ are positive integers, μ is an integer, ν is of the form $\nu = n + \frac{1}{2}$ where n is a positive integer, R_{34} and v are positive real numbers and

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

where ζ_s, ζ_3 and ζ_4 are positive real numbers.

The above two-dimensional integrals occur in the analytic expressions of three-centre nuclear attraction integrals [6] and three-centre two-electron Coulomb and hybrid integrals [42] over B functions. These analytic expressions are obtained using the Fourier transform method [26, 27]. The numerical evaluation of the above integrals presents severe numerical and computation difficulties because of the presence of the semi-infinite integrals which will be referred to as $\tilde{\mathcal{I}}(s)$ and $\tilde{\mathcal{K}}(s)$, whose integrands are highly oscillatory functions due to the presence of the spherical Bessel function in particular for large values of λ and v since the zeros of this function become closer and then the oscillations become strong. Note also that in the regions where s is close to 0 or 1, the oscillations of the integrands become strong. Indeed, when we make the substitution $s = 0$ or 1, the term $\gamma(s,x)$ becomes a constant and hence the exponential decreasing part $\hat{k}_\nu$ of the integrands becomes a constant and the integrands will be reduced to the term $x^{n_x} j_\lambda(vx)$. Thus the rapid oscillations of $j_\lambda(vx)$ cannot be damped and suppressed by the exponential decreasing part.

In previous work [28, 36], we showed that the integrand of $\tilde{\mathcal{I}}(s)$ which will be referred to as $f_a(x)$ and the integrand of $\tilde{\mathcal{K}}(s)$ which will be referred to as $f_k(x)$, satisfy fourth-order linear differential equations and all the conditions to apply the nonlinear D and $\overline{D}$ transformations are satisfied. The approximations $\overline{D}_n^{(4)}$ of $\tilde{\mathcal{I}}(s)$ and $\tilde{\mathcal{K}}(s)$ using $\overline{D}$ are given by [28, 36]

$$\overline{D}_n^{(4)} = \int_0^{x_l} f(t)\,\mathrm{d}t + \sum_{j=1}^{3} f^{(j)}(x_l) x_l^{j+1} \sum_{i=0}^{n-1} \frac{\bar{\beta}_{j,i}}{x_l^i} \qquad l = 0, 1, \ldots, 3n \tag{15}$$

where $\overline{D}_n^{(4)}$ and $\bar{\beta}_{j,i}$ for $j = 1, 2, 3$, $i = 0, 1, \ldots, n-1$ are the $(3n+1)$ unknowns. The $x_l, l = 0, 1, \ldots$ are the leading positive zeros of $f(x)$ where $f(x)$ stands for $f_a(x)$ when evaluating $\tilde{\mathcal{I}}(s)$ and for $f_k(x)$ when evaluating $\tilde{\mathcal{K}}(s)$.

As it can be seen from (15), the application of $\overline{D}$ required the calculation of the successive derivatives and the successive positive zeros of the integrands. The accuracy obtained using this method was satisfactory but progress is still possible. By using the HD and $H\overline{D}$ methods, we obtained second-order linear differential equations satisfied by $f_a(x)$ and $f_k(x)$. This result led to great simplifications in the calculations. The numerical results obtained using $H\overline{D}$ showed the high accuracy and the substantial gain in the calculation times. The approximations $H\overline{D}_n^{(2)}$ of $\tilde{\mathcal{I}}(s)$ and $\tilde{\mathcal{K}}(s)$ are given by [4, 5]

$$H\overline{D}_n^{(2)} = \int_0^{x_l} f(t)\,\mathrm{d}t + g(x_l) j'_\lambda(vx_l) x_l^2 \sum_{i=0}^{n-1} \frac{\bar{\beta}_{1,i}}{x_l^i} \qquad l = 0, 1, \ldots, n \tag{16}$$

where $f(x)$ denotes $f_a(x)$ when dealing with $\tilde{\mathcal{I}}(s)$ and $f_k(x)$ when dealing with $\tilde{\mathcal{K}}(s)$. The function $g(x)$ is given by

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

The $H\overline{D}_n^{(2)}$ and $\bar{\beta}_{1,i}, i = 0, 1, \ldots, n-1$ are the $(n+1)$ unknowns of the above linear system. $x_l = j_{\lambda,v}^{l+1}$ for $l = 0, 1, \ldots,$ where $j_{\lambda,v}^{0}$ is assumed to be zero and $j_{\lambda,v}^{n} = j_{\lambda+\frac{1}{2}}^{n}/v, n = 1, 2, \ldots$ which are the successive zeros of $j_\lambda(vx)$.

As it can be seen from the above equation, the application of the $H\overline{D}$ method required the calculation of the successive positive zeros of spherical Bessel functions and the computation of a method to solve linear systems.

In [6, 42], we showed that the integrands $f_a(x)$ and $f_k(x)$ satisfy all the conditions of theorems 1 and 2. Good approximations of $\tilde{\mathcal{I}}(s)$ and $\tilde{\mathcal{K}}(s)$ are obtained using equation (12) where it is not necessary to calculate the successive derivatives and the successive positive zeros of the integrands and the successive positive zeros of spherical Bessel functions. The accuracy and the gain in the calculation times obtained using the $S\overline{D}$ approach are remarkable [6, 42].

4. Convergence properties

Let us consider a function $f(x)$ integrable on $[0, +\infty[$ satisfying a differential equation of order m of the form required to apply the nonlinear D transformation. The approximation $D_n^{(m)}$ of $S = \int_0^{+\infty} f(t)\,\mathrm{d}t$ satisfies the linear system of order $(mn+1)$ given by [1]

$$D_n^{(m)} = \int_0^{x_l} f(t)\,\mathrm{d}t + \sum_{k=0}^{m-1} x_l^{k+1} f^{(k)}(x_l) \sum_{i=0}^{n-1} \frac{\bar{\beta}_{k,i}}{x_l^i} \qquad l = 0, 1, \ldots, mn \tag{17}$$

where $D_n^{(m)}$ and $\bar{\beta}_{k,i}$ for $k = 0, 1, \ldots, m-1, i = 0, 1, \ldots, n-1$ are the $(nm+1)$ unknowns. The $x_l, l = 0, 1, \ldots$ are chosen to satisfy $0 < x_0 < x_1 < \cdots$ and $\lim_{l\to+\infty} x_l = +\infty$.

Let M be the matrix of the above linear system. The first column of the matrix M is the vector $(1, 1, \ldots, 1)^T$, where T denotes transpose. Let $(\gamma_0, \gamma_1, \ldots, \gamma_{mn})$ be the first row of the matrix M^{-1} which stands for the inverse of the matrix M.

Using the fact that $M^{-1}M = I$ where I stands for the matrix identity, it follows that $\sum_{l=0}^{mn} \gamma_l = 1$ and therefore

$$\sum_{l=0}^{mn} |\gamma_l| \geqslant 1.$$

Now, we shall state two corollaries fully demonstrated by Sidi [2, 43].

Corollary 1 ([2, 43])**.**

$$\left|S - D_n^{(m)}\right| \leqslant \left(\sum_{l=0}^{mn} |\gamma_l|\right) o(n^{-j}) \qquad \forall j > 0 \text{ as } n \to +\infty.$$

Corollary 2 ([2, 43])**.** *If* $\sum_{l=0}^{mn} |\gamma_l| \leqslant L < \infty$*, then*

$$\left|S - D_n^{(m)}\right| = o(n^{-j}) \qquad \forall j > 0 \text{ as } n \to +\infty.$$

Now, let us consider the linear system (10) and let K be the matrix of this system and $(\delta_0, \delta_1, \ldots, \delta_n)$ the first row of the matrix K^{-1}. It is clear that $\sum_{l=0}^{n} \delta_l = 1$ and therefore

$$\sum_{l=0}^{n} |\delta_l| \geqslant 1.$$

From the fact that $(\delta_0, \delta_1, \ldots, \delta_n)$ is the first row of the matrix K^{-1}, it follows that

$$S\overline{D}_n^{(2)} = \sum_{i=0}^{n} \delta_i F(x_i) \tag{18}$$

where $F(x_i) = \int_0^{x_i} G(x)\sin(x)\,\mathrm{d}x$.

Using equations (12) and (18), one can easily obtain an expression for δ_i for $i = 0, 1, \ldots, n$, which is given by

$$\delta_i = \frac{\binom{n}{i}(1+i)^{n-1}\big/\big[x_i^2 G(x_i)\big]}{\sum_{j=0}^{n}\binom{n}{j}(1+j)^{n-1}\big/\big[x_j^2 G(x_j)\big]}. \tag{19}$$

Now let us consider the integrand $f_a(x)$ of the semi-infinite integral $\tilde{\mathcal{I}}(s)$. The corresponding functions $g(x)$ and $G(x)$ are given by

$$g(x) = x^{n_x}\frac{\hat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \quad \text{and} \quad G(x) = \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda}(x^{\lambda-1}g(x)).$$

Using equation (5), the Leibnitz formula, and the fact that $\frac{\mathrm{d}}{\mathrm{d}x} = \frac{\mathrm{d}z}{\mathrm{d}x}\frac{\mathrm{d}}{\mathrm{d}z}$, we obtain in the case where $n_\gamma < 2\nu$

$$G(x) = \sum_{l=0}^{\lambda}\sum_{k=0}^{\lambda-l}\binom{\lambda-l}{k}\binom{\lambda}{l}\frac{(n_x+\lambda-1)!!}{(n_x+\lambda-1-2l))!!}x^{n_x+\lambda-1-2l} \times (-1)^{\lambda-l-k}\frac{(2\nu-n_\gamma)!!}{(2\nu-n_\gamma-2k)!!}s^k(1-s)^k\frac{\hat{k}_{\nu+\lambda-l-k}[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma+2k}} \tag{20}$$

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

$$G(x) = \sum_{l=0}^{\lambda}(-1)^{\lambda-l}\binom{\lambda}{l}\frac{(n_x+\lambda-1)!!}{(n_x+\lambda-1-2l))!!}x^{n_x+\lambda-1-2l}s^{\lambda-l}(1-s)^{\lambda-l}\frac{\hat{k}_{\nu+\lambda-l}[R_2\gamma(s,x)]}{[\gamma(s,x)]^{2(\nu+\lambda-l)}}. \tag{21}$$

By using the above equations with equation (3) and the fact that x_i for $i = 0, 1, \ldots$ are positive real numbers, one can easily show from equation (19) that $\frac{1}{\delta_i} > 0$ and then $\delta_i > 0$ for all i. Consequently,

$$\sum_{i=0}^{n}|\delta_i| = \sum_{i=0}^{n}\delta_i = 1.$$

Corollary 2 becomes

Corollary 3.

$$\left|\tilde{\mathcal{I}}(s) - S\overline{D}_n^{(2)}\right| = o(n^{-j}) \qquad \forall j > 0 \text{ as } n \to +\infty.$$

In the case of three-centre two-electron Coulomb and hybrid integrals, the function $g(x)$ which occurs in the integrand $f_k(x)$ of the semi-infinite integrals $\tilde{\mathcal{K}}(s)$, is given by

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

With the help of the Leibnitz formulae, one can easily show that the corresponding function $G(x)$ is given by

$$G(x) = \sum_{i=0}^{\lambda}\sum_{j=0}^{i}\binom{l}{i}\binom{i}{j}\frac{(n_x+\lambda-1)!!}{(n_x+\lambda-1-2i)!!}x^{n_x+\lambda-1-2i} \times M(n_k, i-j)\left[\zeta_s^2 + x^2\right]^{-n_k-i+j}\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^{\lambda-i}\left[\frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\right] \tag{22}$$

where

$$M(n_k, i-j) = (-2)^{i-j} n_k(n_k+1)\ldots(n_k+i-j-1).$$

With the help of equation (5) and the fact that $\frac{\mathrm{d}}{\mathrm{d}x} = \frac{\mathrm{d}z}{\mathrm{d}x}\frac{\mathrm{d}}{\mathrm{d}z}$, one can easily show that if $n_\gamma = 2\nu$ then for $j \in \mathbb{N}$

$$\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^j\left[\frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{2\nu}}\right] = (-1)^j s^j (1-s)^j \frac{\hat{k}_{\nu+j}[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{2(\nu+j)}} \tag{23}$$

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

$$\left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^j\left[\frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\right] = \sum_{i=0}^{j}\binom{j}{i}(-1)^{j-i}\frac{(2\nu-n_\gamma)!!}{(2\nu-n_\gamma-2i)!!} \times s^i(1-s)^i\frac{\hat{k}_{\nu+j-i}[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma+2i}}. \tag{24}$$

Using the above arguments, one can easily show that the $\delta_i > 0$ for all i and consequently the convergence properties of the $S\overline{D}$ method are without any constraint when evaluating semi-infinite integrals involved in three-centre molecular integrals. From the numerical point of view, the situation in which $\delta_i > 0$ corresponds to the most ideal one.

5. Numerical evaluation and discussion

The semi-infinite oscillatory integrals $\tilde{\mathcal{I}}(s)$ and $\tilde{\mathcal{K}}(s)$ are given by

$$\tilde{\mathcal{I}}(s) = \int_0^{+\infty} x^{n_x}\frac{\hat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(\upsilon x)\,\mathrm{d}x \tag{25}$$

$$= \sum_{n=0}^{+\infty}\int_{j_{\lambda,\upsilon}^n}^{j_{\lambda,\upsilon}^{n+1}/\upsilon} x^{n_x}\frac{\hat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(\upsilon x)\,\mathrm{d}x \tag{26}$$

$$\tilde{\mathcal{K}}(s) = \int_{x=0}^{+\infty}\left[\zeta_s^2 + x^2\right]^{-n_k} x^{n_x}\frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(\upsilon x)\,\mathrm{d}x \tag{27}$$

$$= \sum_{n=0}^{+\infty}\int_{j_{\lambda,\upsilon}^n}^{j_{\lambda,\upsilon}^{n+1}}\left[\zeta_s^2 + x^2\right]^{-n_k} x^{n_x}\frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(\upsilon x)\,\mathrm{d}x \tag{28}$$

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

In [6, 42], we showed by using the $S\overline{D}$ method that the semi-infinite integrals $\tilde{\mathcal{I}}(s)$ and $\tilde{\mathcal{K}}(s)$ can be rewritten as

$$\tilde{\mathcal{I}}(s) = \frac{1}{v^{\lambda+1}} \int_0^{+\infty} \left[\left(\frac{\mathrm{d}}{x\,\mathrm{d}x} \right)^{\lambda} \left(x^{n_x+\lambda-1} \frac{\hat{k}_v[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \right) \right] \sin(vx)\,\mathrm{d}x \tag{29}$$

$$= \frac{1}{v^{\lambda+1}} \sum_{n=0}^{+\infty} \int_{\frac{n\pi}{v}}^{\frac{(n+1)\pi}{v}} \left[\left(\frac{\mathrm{d}}{x\,\mathrm{d}x} \right)^{\lambda} \left(x^{n_x+\lambda-1} \frac{\hat{k}_v[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \right) \right] \sin(vx)\,\mathrm{d}x. \tag{30}$$

$$\tilde{\mathcal{K}}(s) = \frac{1}{v^{\lambda+1}} \int_{x=0}^{+\infty} \left(\left(\frac{\mathrm{d}}{x\,\mathrm{d}x} \right)^{\lambda} \left[\frac{x^{n_x+\lambda-1}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\hat{k}_v[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \right] \right) \sin(vx)\,\mathrm{d}x \tag{31}$$

$$= \frac{1}{v^{\lambda+1}} \sum_{n=0}^{+\infty} \int_{\frac{n\pi}{v}}^{\frac{(n+1)\pi}{v}} \left(\left(\frac{\mathrm{d}}{x\,\mathrm{d}x} \right)^{\lambda} \left[\frac{x^{n_x+\lambda-1}}{\left[\zeta_s^2 + x^2\right]^{n_k}} \frac{\hat{k}_v[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \right] \right) \sin(vx)\,\mathrm{d}x. \tag{32}$$

The use of equations (29) and (31) for the numerical evaluation of $\tilde{\mathcal{I}}(s)$ is more advantageous than the use of equations (25) and (27) because of the fact that the numerical integration of oscillatory integrands is very difficult when the oscillatory part is a spherical Bessel function.

The values with 15 correct decimals of the semi-infinite integrals $\tilde{\mathcal{I}}(s)$ and $\tilde{\mathcal{K}}(s)$ can be obtained by using the infinite series given by (26) or (30) and (28) or (32) which we sum until $N = \max$. It is clear that by using the infinite series involving the sine function (30) and (32), we need less terms to obtain the pre-determined accuracy. The finite integrals involved in equations (30) and (32) are evaluated using Gauss–Legendre quadrature of order 16.

The finite integrals involved in equations (12) and (16) are transformed into finite sums,

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

and each term of the above finite sum is evaluated using Gauss–Legendre quadrature of order 16.

The numerical tables contain the semi-infinite integrals $\tilde{\mathcal{I}}(s)$ and $\tilde{\mathcal{K}}(s)$, which occur in three-centre nuclear attraction, three-centre two-electron Coulomb and hybrid integrals over B functions, evaluated using the methods described below.

Tables 1, 4, 7 and 10 contain the values with 15 correct decimals of the semi-infinite integrals $\tilde{\mathcal{I}}(s)$ and $\tilde{\mathcal{K}}(s)$ obtained using the infinite series (30) and (32) which we sum until $N = \max$. These values are obtained for $s = 0.01$ and $s = 0.99$ for $\tilde{\mathcal{I}}(s)$ and for $s = 0.001$ and $s = 0.999$ for $\tilde{\mathcal{K}}(s)$. In these regions, the oscillations of the integrands become strong.

Tables 2, 5, 8 and 11, contain values of the above semi-infinite integrals obtained using the $H\overline{D}$ method (16).

Tables 3, 6, 9 and 12 contain values of the above semi-infinite integrals obtained using the $S\overline{D}$ approach (12).

Table 1. Values of $\tilde{\mathcal{I}}(s)$ obtained with 15 correct decimals by using the infinite series (30); $s = 0.01$, $v = |(1-s)R_2 - R_1|$.

v	n_γ	n_x	λ	R_1	ζ_1	R_2	ζ_2	max	$\tilde{\mathcal{I}}(s)$
5/2	5	0	0	6.31	1.0	2.0	1.0	156	0.638 243 453 884 445D+00
9/2	9	2	1	8.50	2.0	3.5	2.0	156	0.248 336 723 989 985D−03
9/2	9	2	2	9.00	2.0	3.5	1.0	206	0.183 269 571 025 634D−02
13/2	13	3	3	7.50	2.0	3.5	1.0	134	0.181 139 626 222 771D−01

Table 2. Evaluation of $\tilde{\mathcal{I}}(s)$ using $H\overline{D}_n^{(2)}$ (16); $s = 0.01$, $v = |(1-s)R_2 - R_1|$. Time T is in milliseconds.

v	n_γ	n_x	λ	R_1	ζ_1	R_2	ζ_2	n	$\tilde{\mathcal{I}}(s)$	Error	T
5/2	5	0	0	6.31	1.0	2.0	1.00	9	0.638 243 454 0D+00	0.73D−10	0.23
9/2	9	2	1	8.50	2.0	3.5	2.00	7	0.248 336 795 0D−03	0.71D−10	0.32
9/2	7	2	2	9.00	2.0	3.5	1.00	6	0.183 269 526 8D−02	0.44D−09	0.41
13/2	13	3	3	7.50	2.0	3.5	1.00	7	0.181 139 575 7D−01	0.50D−08	0.50

Table 3. Evaluation of $\tilde{\mathcal{I}}(s)$ using $S\overline{D}_n^{(2,5)}$ (12); $s = 0.01$, $v = |(1-s)R_2 - R_1|$. Time T is in milliseconds.

v	n_γ	n_x	λ	R_1	ζ_1	R_2	ζ_2	n	$\tilde{\mathcal{I}}(s)$	Error	T
5/2	5	0	0	6.31	1.0	2.0	1.00	9	0.638 243 453 8D+00	0.74D−10	0.10
9/2	9	2	1	8.50	2.0	3.5	2.00	7	0.248 336 714 9D−03	0.91D−11	0.29
9/2	7	2	2	9.00	2.0	3.5	1.00	6	0.183 269 571 6D−02	0.57D−11	0.39
13/2	13	3	3	7.50	2.0	3.5	1.00	7	0.181 139 626 1D−01	0.81D−11	0.45

Table 4. Values of $\tilde{\mathcal{I}}(s)$ obtained with 15 correct decimals by using the infinite series (30); $s = 0.99$, $v = |(1-s)R_2 - R_1|$.

v	n_γ	n_x	λ	R_1	ζ_1	R_2	ζ_2	max	$\tilde{\mathcal{I}}(s)$
5/2	5	0	0	4.50	2.0	1.5	1.0	202	0.701 581 269 512 310D+00
9/2	9	1	1	6.00	2.0	3.5	1.0	145	0.183 138 910 224 197D+01
9/2	9	2	1	6.00	2.0	3.0	1.0	195	0.476 698 176 142 352D+00
13/2	11	3	3	6.50	2.5	3.5	2.0	239	0.993 192 007 213 570D−02

Table 5. Evaluation of $\tilde{\mathcal{I}}(s)$ using $H\overline{D}_n^{(2)}$ (16); $s = 0.99$, $v = |(1-s)R_2 - R_1|$. Time T is in milliseconds.

v	n_γ	n_x	λ	R_1	ζ_1	R_2	ζ_2	n	$\tilde{\mathcal{I}}(s)$	Error	T
5/2	5	0	0	4.50	2.0	1.5	1.00	6	0.701 581 274 9D+00	0.54D−08	0.18
9/2	9	1	1	6.00	2.0	3.5	1.00	6	0.183 138 917 3D+01	0.71D−07	0.31
9/2	9	2	1	6.00	2.0	3.0	1.00	8	0.476 698 156 7D+00	0.19D−07	0.58
13/2	11	3	3	6.50	2.5	3.5	2.00	9	0.993 191 951 0D−02	0.59D−09	0.62

Table 6. Evaluation of $\tilde{\mathcal{I}}(s)$ using $S\overline{D}_n^{(2,5)}$ (12); $s = 0.99$, $v = |(1-s)R_2 - R_1|$. Time T is in milliseconds.

v	n_γ	n_x	λ	R_1	ζ_1	R_2	ζ_2	n	$\tilde{\mathcal{I}}(s)$	Error	T
5/2	5	0	0	4.50	2.0	1.5	1.00	6	0.701 581 269 5D+00	0.13D−10	0.11
9/2	9	1	1	6.00	2.0	3.5	1.00	6	0.183 138 910 2D+01	0.25D−10	0.32
9/2	9	2	1	6.00	2.0	3.0	1.00	8	0.476 698 176 1D+00	0.31D−10	0.42
13/2	11	3	3	6.50	2.5	3.5	2.00	9	0.993 192 001 2D−02	0.87D−10	0.51

Table 7. Values of the semi-infinite integral $\tilde{\mathcal{K}}(s)$ obtained with 15 correct decimals using the infinite series (32); $s = 0.001$, $n_x = \lambda$, $n_\gamma = 2\nu$, $v = |(1-s)(R_3 - R_4) - R_4|$ and $\zeta_s = \zeta_1 + \zeta_2$.

ν	n_k	λ	R_3	R_4	ζ_1	ζ_2	ζ_3	ζ_4	max	$\tilde{\mathcal{K}}(s)$
5/2	2	0	7.5	1.5	1.5	1.0	1.0	1.0	125	0.126 414 190 755 008D−02
9/2	3	2	4.5	4.0	1.0	1.0	1.0	1.0	106	0.146 157 629 412 064D+00
11/2	2	3	3.5	3.0	0.5	0.5	1.5	1.5	135	0.861 150 036 617 796D+00
15/2	3	4	3.5	3.0	1.0	1.0	1.0	1.5	81	0.204 664 014 657 073D+01

Table 8. Evaluation of the semi-infinite integral $\tilde{\mathcal{K}}(s)$ using the $H\bar{D}$ method (16) of order 7 ($H\overline{D}_7^{(2)}$); $s = 0.001$, $n_x = \lambda$, $n_\gamma = 2\nu$, $v = |(1-s)(R_3 - R_4) - R_4|$ and $\zeta_s = \zeta_1 + \zeta_2$.

ν	n_k	λ	R_3	R_4	ζ_1	ζ_2	ζ_3	ζ_4	$H\bar{D}_7^{(2)}$	Error
5/2	2	0	7.5	1.5	1.5	1.0	1.0	1.0	0.126 414 190 8D−02	0.17D−12
9/2	3	2	4.5	4.0	1.0	1.0	1.0	1.0	0.146 157 629 4D+00	0.19D−10
11/2	2	3	3.5	3.0	0.5	0.5	1.5	1.5	0.861 150 036 6D+00	0.12D−10
15/2	3	4	3.5	3.0	1.0	1.0	1.0	1.5	0.204 664 014 7D+01	0.29D−10

Table 9. Evaluation of the semi-infinite integral $\tilde{\mathcal{K}}(s)$ using the $S\bar{D}$ method (12) of order 5 ($S\bar{D}_5^{(2,5)}$); $s = 0.001$, $n_x = \lambda$, $n_\gamma = 2\nu$, $v = |(1-s)(R_3 - R_4) - R_4|$ and $\zeta_s = \zeta_1 + \zeta_2$.

ν	n_k	λ	R_3	R_4	ζ_1	ζ_2	ζ_3	ζ_4	$S\bar{D}_5^{(2,5)}$	Error
5/2	2	0	7.5	1.5	1.5	1.0	1.0	1.0	0.126 414 190 8D−02	0.26D−13
9/2	3	2	4.5	4.0	1.0	1.0	1.0	1.0	0.146 157 629 4D+00	0.46D−12
11/2	2	3	3.5	3.0	0.5	0.5	1.5	1.5	0.861 150 036 6D+00	0.33D−12
15/2	3	4	3.5	3.0	1.0	1.0	1.0	1.5	0.204 664 014 7D+01	0.89D−13

Table 10. Values of the semi-infinite integral $\tilde{\mathcal{K}}(s)$ obtained with 15 correct decimals using the infinite series (32); $s = 0.999$, $n_x = \lambda$, $n_\gamma = 2\nu$, $v = |(1-s)(R_3 - R_4) - R_4|$ and $\zeta_s = \zeta_1 + \zeta_2$.

ν	n_k	λ	R_3	R_4	ζ_1	ζ_2	ζ_3	ζ_4	max	$\tilde{\mathcal{K}}(s)$
5/2	2	0	2.5	2.0	1.5	1.5	1.0	1.0	155	0.276 599 387 190 865D−01
7/2	2	1	4.0	3.0	1.5	0.5	1.0	2.5	162	0.136 665 163 437 581D+00
13/2	3	4	3.0	2.5	1.0	1.0	2.0	1.5	103	0.826 191 642 949 067D−02
15/2	3	4	4.5	3.5	1.0	0.5	2.0	2.5	120	0.288 150 089 225 324D−01

Table 11. Evaluation of the semi-infinite integral $\tilde{\mathcal{K}}(s)$ using the $H\bar{D}$ method (16) of order 7 ($H\overline{D}_7^{(2)}$); $s = 0.999$, $n_x = \lambda$, $n_\gamma = 2\nu$, $v = |(1-s)(R_3 - R_4) - R_4|$ and $\zeta_s = \zeta_1 + \zeta_2$.

ν	n_k	λ	R_3	R_4	ζ_1	ζ_2	ζ_3	ζ_4	$H\bar{D}_7^{(2)}$	Error
5/2	2	0	2.5	2.0	1.5	1.5	1.0	1.0	0.276 599 387 2D−01	0.11D−11
7/2	2	1	4.0	3.0	1.5	0.5	1.0	2.5	0.136 665 163 5D+00	0.20D−10
13/2	3	4	3.0	2.5	1.0	1.0	2.0	1.5	0.826 191 642 9D−02	0.59D−12
15/2	3	4	4.5	3.5	1.0	0.5	2.0	2.5	0.288 150 089 2D−01	0.19D−11

We listed the calculation times in tables 2, 3, 5 and 6 to show the rapidity of the nonlinear transformations in evaluating highly oscillatory integrals. As it can be seen from these tables, the calculation times are considerably reduced by using the $S\overline{D}$ method which leads to a better accuracy.

Table 12. Evaluation of the semi-infinite integral $\tilde{\mathcal{K}}(s)$ using the $S\bar{D}$ method (12) of order 5 ($S\overline{D}_5^{(2,5)}$); $s = 0.999, n_x = \lambda, n_\gamma = 2\nu, v = |(1-s)(R_3 - R_4) - R_4|$ and $\zeta_s = \zeta_1 + \zeta_2$.

ν	n_k	λ	R_3	R_4	ζ_1	ζ_2	ζ_3	ζ_4	$S\bar{D}_5^{(2,5)}$	Error
5/2	2	0	2.5	2.0	1.5	1.5	1.0	1.0	0.276 599 387 2D−01	0.29D−13
7/2	2	1	4.0	3.0	1.5	0.5	1.0	2.5	0.136 665 163 4D+00	0.74D−12
13/2	3	4	3.0	2.5	1.0	1.0	2.0	1.5	0.826 191 642 9D−02	0.47D−14
15/2	3	4	4.5	3.5	1.0	0.5	2.0	2.5	0.288 150 089 2D−01	0.30D−13

Extensive numerical results can be found in [6, 42] where the corresponding complete three-centre nuclear attraction, three-centre two-electron Coulomb and hybrid integrals are evaluated using the above nonlinear transformations for atomic orbitals.

6. Conclusion

Analytic expressions can be obtained for molecular integrals by choosing the B functions as a basis set of atomic orbitals and applying the Fourier transform method. These analytical expressions involve two- or three-dimensional integral representations which present severe numerical and computation difficulties because of the presence of highly oscillatory semi-infinite integrals where the oscillatory part is a spherical Bessel function and not a simple trigonometric function. These integrals are shown to be suitable for the application of the nonlinear D and $\overline{D}$ transformations. The application of these two methods requires the calculation of the successive derivatives of the integrands and its successive zeros for $\overline{D}$. Great simplifications were obtained with the help of the HD and $H\overline{D}$ approaches. The calculation of the successive derivatives of the integrands is avoided and the orders of the linear systems to solve are considerably reduced for the semi-infinite integrals involved in the analytic expressions of molecular integrals. The application of the $H\overline{D}$ method requires the computation of the successive zeros of the spherical Bessel function and the computation of the method to solve linear systems.

The $S\overline{D}$ approach which is based on the above methods and on some useful properties of the sine function, spherical and reduced Bessel functions and Poincaré series led to a remarkable simplification on the numerical evaluation of highly semi-infinite integrals in particular those involved in molecular integrals over Slater-type orbitals. The gain in the calculation times and the high accuracy obtained for molecular integrals illustrate the superiority of this new approach. Obviously, this great increase in rapidity of the new method is a key issue. In the molecular context, many millions of such integrals are required for close range terms, therefore rapidity is the principal criterion when the precision has been reached. The progress represented by the $S\overline{D}$ approach is another useful step in developing software for evaluating molecular integrals over Slater-type orbitals.

The convergence properties of the $S\overline{D}$ method show that $S\overline{D}_n^{(2)}$ converges without any constraint to the exact value of the semi-infinite integrals of interest.

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