J Mol Model (2006) 12: 213–220
DOI 10.1007/s00894-005-0020-z

ORIGINAL PAPER

Hassan Safouhi

Numerical treatment of two-center overlap integrals

Received: 20 April 2005 / Accepted: 11 July 2005 / Published online: 27 August 2005

Abstract Among the two-center integrals occurring in the molecular context, the two-center overlap integrals are numerous and difficult to evaluate to a level of high accuracy. The analytical and numerical difficulties arise mainly from the presence of the spherical Bessel integrals in the analytic expressions of these molecular integrals. Different approaches have been used to develop efficient algorithms for the numerical evaluation of the molecular integrals under consideration. These approaches are based on quadrature rules, Levin's u transform, or the epsilon-algorithm of Wynn. In the present work, we use the nonlinear $\bar{D}$ transformation of Sidi. This transformation is shown to be highly efficient in improving the convergence of highly oscillatory integrals, and it has been applied to molecular multicenter integrals, namely three-center attraction, hybrid, two-, three-, and four-center two-electron Coulomb and exchange integrals over B functions and over Slater-type functions. It is also been shown that when evaluating these molecular multicenter integrals the $\bar{D}$ transformation is more efficient compared with the methods cited above. It is now proven that the integrand occurring in the analytic expression of the two-center overlap integrals satisfies all the conditions required to apply the $\bar{D}$ transformation. A highly accurate algorithm based on this transformation is now developed. Special cases are presented and discussed for a better optimization of the algorithm. The numerical results section illustrates clearly the high efficiency of our algorithm.

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

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

Introduction

The numerical evaluation of two-center overlap integrals over exponential-type functions is of great importance for any accurate molecular structure calculations. Different approaches have been used for the analytical development of these two-center integrals and for their accurate numerical evaluation [1–20]. Note that multicenter molecular integrals can be expressed in terms of the two-center overlap integrals. Therefore, the accurate and rapid numerical evaluation of these integrals becomes more important in quantum-mechanical calculations of the electronic structures of molecules.

A basis set of the so-called B functions [21, 22] is used. These functions are analytically more complicated than Slater-type functions (STFs) [23, 24], but they have much more appealing properties applicable to multicenter integral problems [2, 22, 25]. Note that STFs can be expressed as finite linear combinations in terms of B functions [8]. The most important advantage of using these B functions is for the fact that their Fourier transforms are exceptionally simple [1], and they are well adapted to the Fourier transform method [10, 11, 26, 27].

In the present work, we used the analytic expressions obtained by Weniger and Steinborn [1] for the molecular integrals under consideration, using the Fourier transform method. These analytical expressions turned out to be extremely difficult to be evaluated accurately and rapidly, due to the presence of semi-infinite highly oscillatory integrals, involving spherical Bessel functions $j_\lambda(Rx)$.

Different approaches have been used for the numerical evaluation of these spherical Bessel integrals. Gauss–Laguerre quadrature is not efficient when the values of R and λ are large. Note that when these values are large, the oscillation of the integrand becomes strong (see Fig. 1). Therefore, the numerical evaluation of the semi-infinite integrals presents severe numerical difficulties. The semi-infinite oscillatory integrals can be

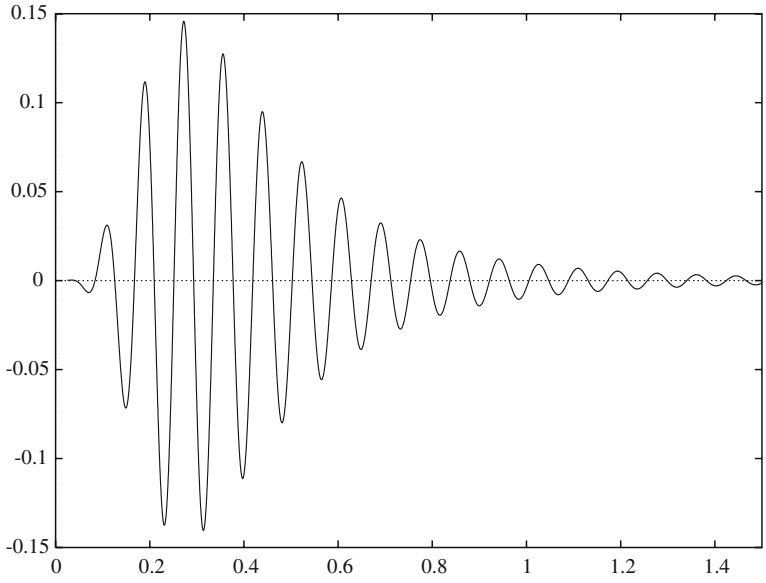

Fig. 1 The integrand Fx) of the semi-infinite integral (16); $n_x = 5$, $k_1 = 2$, $k_2 = 2$, $n_x = 5$, $\lambda = 5$, $\xi_1 = 0.25$, $\xi_2 = 0.3$, and $v = 75.0$

transformed into infinite series. These series are slowly convergent and this is why their use is prohibitively long for sufficient accuracy. The epsilon algorithm of Wynn [28] or Levin's u transform [29] accelerate the convergence of infinite series, but in the case of the semi-infinite integrals involved in the analytical expressions of overlap integrals, the calculation times for sufficient accuracy are still long, especially for large values of R and λ, since the zeros of $j_\lambda(Rx)$. become closer.

The nonlinear D [30] and $\bar{D}$ [31, 32] transformations have been shown to be highly efficient when evaluating oscillatory integrals, whose integrands satisfy linear differential equations with coefficients having asymptotic expansions in inverse powers of their arguments x as $x \to \infty$. In previous work [33–40], we demonstrated that the semi-infinite integrals occurring in the analytic expressions of three- and four-center molecular electronic integrals satisfy all the conditions required to apply the D and $\bar{D}$ transformations. In this work, we demonstrated that the semi-infinite Bessel integrals occurring in the analytic expressions of two-center overlap integrals over B functions also satisfy all the conditions required to apply D and $\bar{D}$. This led to the development of a highly accurate algorithm for the numerical evaluation of the molecular integrals under consideration.

The numerical results section contains tables with values of the semi-infinite integrals in question. These semi-infinite integrals were transformed into infinite series. These infinite series were used to compute values of these integrals with a certain number of correct digits. Tables with values of the semi-infinite integrals obtained using the $\bar{D}$ transformation are listed. The values of the complete expression of two-center overlap integrals obtained using the algorithm described in this work are in complete accordance with those obtained by Grotendorst et al. [3] and Weniger and Steinborn [2] (see Table 1). The numerical results obtained using the algorithm described in the present work are in complete agreement with those obtained using the ACJU program developed by Homeier et al. [41] (see Table 2).

Note that the algorithm presented in this work can also be applied to the molecular integrals under consideration over STFs, by expressing them in terms of integrals over B functions (see Table 3). The numerical results that we obtained using the algorithm described in the present contribution are in an excellent agreement with those obtained by Talman [13], Guseinov et al. [14, 15], and Guseinov and Mamedov [16].

General definitions and properties

The B functions are defined as follows [8, 22]:

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

where n,l and m are the quantum numbers and $Y^m_l(\theta_r,\varphi_r)$ stands for the surface spherical harmonic [42]

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

$P^m_l(z)$ is the associated Legendre polynomial [43].

The function $\hat{k}_{n+(1/2)}(\zeta r)$ stands for the reduced Bessel function [21, 22]. The reduced Bessel functions satisfy the following relations [21, 43]

$$\hat{k}_{n+\frac{1}{2}}(z) = (2n-1)\hat{k}_{n-\frac{1}{2}}(z) + z^2\hat{k}_{(n-1)+\frac{1}{2}}(z) \tag{3}$$

The Fourier transform of a B function is given by [1]

$$\bar{B}^m_{n,l}(\zeta,\vec{P}) = \sqrt{\frac{2}{\pi}}\zeta^{2n+l-1}\frac{(-i|p|)^l}{(\zeta^2+|p|^2)^{n+l+1}}Y^m_l(\theta_{\vec{p}},\varphi_{\vec{p}}) \tag{4}$$

Table 1 Evaluation of two-center overlap integrals given by Eq. (13); $\xi_1 = 1.5$ and $\vec{R} = (10.0, 40°, 0°)$

N_1	l_1	m_1	n_2	l_2	M_2	ξ_2	Values †[a]	Values $\bar{D}$[b]
1	0	0	1	0	0	2.2	0.241222730889(−2)	0.241222730889(−2)
1	0	0	1	0	0	5.5	0.155947042412(−3)	0.155947042412(−3)
1	0	0	1	0	0	9.9	0.260333516751(−4)	0.260333516752(−4)
3	1	1	1	1	0	2.2	0.113546037054(−3)	0.113546037054(−3)
3	1	1	1	1	0	5.5	0.656024309138(−5)	0.656024309178(−5)
1	1	0	3	1	1	2.2	0.191855872152(−3)	0.191855872152(−3)
1	1	0	3	1	1	5.5	0.229394206519(−4)	0.229394207154(−4)
5	0	0	5	0	0	2.2	0.883967476163(−3)	0.883967476163(−3)
5	0	0	5	0	0	5.5	0.839121793485(−4)	0.839121794539(−4)
5	5	5	1	0	0	2	−0.508703856143(−7)	−0.508703856032(−7)
4	4	4	3	3	3	2	−0.156368843565(−5)	−0.156368843560(−5)
3	3	3	4	4	4	2	0.167067525483(−5)	0.167067525481(−5)
1	0	0	5	5	5	2	0.131799235096(−6)	0.131799234943(−6)

[a] Values † were obtained using the infinite series given by Eq. 17. These values are computed with 15 correct digits.
[b] Values $\bar{D}$ were obtained using the nonlinear $\bar{D}$ transformation of order n (41).These values are in complete accordance with those listed in Table 3 in Ref. [2] and in Table 3 in Ref. [3].

Table 2 Evaluation of two-center overlap integrals given by Eq. 13;$n_2 = n_1$, $\xi_1 = 1.5$, $\xi_2 = 1.0$ and $\vec{R} = (10.0, 40°, 0°)$

n_1	l_1	m_1	l_2	m_2	Values †[a]	Values $\bar{D}$[b]	Values †[c]
1	0	0	0	0	0.149634124134(−04)	0.149634124086(−4)	0.149634251158(−4)
2	1	0	1	0	−0.429351058233(−04)	−0.429351058233(−4)	−0.429350754943(−4)
2	1	1	1	1	−0.738355546788(−05)	−0.738355546777(−5)	−0.738358522963(−5)
3	2	1	1	1	−0.573632030119(−05)	−0.573632030122(−5)	−0.573634375218(−5)
3	2	2	2	2	−0.256606777006(−05)	−0.256606777007(−5)	−0.256607268877(−5)
4	3	2	2	1	0.166443014555(−05)	0.166443014553(−5)	0.166442517055(−5)
4	3	3	2	2	−0.151260133537(−06)	−0.151260133540(−6)	−0.151258163223(−6)
4	3	3	3	2	0.162220578863(−06)	0.162220578877(−6)	0.162218711653(−6)
5	2	1	3	2	−0.181938285907(−05)	−0.181938285910(−5)	−0.181937858166(−5)
5	3	3	3	3	−0.330662288558(−06)	−0.330662288559(−6)	−0.330662733751(−6)

[a] Values † were obtained using the infinite series given by Eq. 17. These values are computed with 15 correct digits.
[b] Values $\bar{D}$ were obtained using the nonlinear $\bar{D}$ transformation of order n (41).
[c] Values † were obtained using the ACJU program developed by Homeier et al. [41].

Table 3 Evaluation of two-center overlap integrals over STFs given by Eq. 15; $\theta = \phi = 0°$

n_1	L_1	m_1	ξ_1	n_2	l_2	m_2	ξ_2	R	Values $\bar{D}$	Values [13–16]
5	4	0	1	5	4	0	1	1	0.768617011(0)	0.768617016(0)
5	4	4	1	5	4	4	1	1	0.955778746(0)	0.955778746(0)
5	4	0	5	5	4	0	1	1	0.900262308(−2)	0.900262309(−2)
5	4	4	5	5	4	4	1	1	0.318003745(−1)	0.318003745(−1)
5	4	0	5	5	4	0	5	1	−0.138257012	−0.138257012
5	4	4	5	5	4	4	5	1	0.356825987(0)	0.356825987(0)
8	0	0	1	8	0	0	1	1	0.989015∼721(0)	0.989015721(0)
8	0	0	5	8	0	0	1	1	0.107437341(−1)	0.107437341(−1)
8	0	0	5	8	0	0	5	1	0.785230850(0)	0.785230850(0)
4	3	0	1.9	6	5	0	0.1	100	−0.534413558(−5)	−0.534413558(−5)
6	3	2	1.4	8	5	2	0.6	40	−0.321391598(−4)	−0.321391598(−4)
12	7	3	1.3	12	7	3	0.7	15	0.229354179(−1)	0.229354178(−1)
17	8	4	1.8	14	6	4	0.2	30	0.913913987(−6)	0.913905849(−6)
10	7	1	2.5	8	1	1	10	2.5	0.152138456(−1)	0.152138456(−1)
18	12	6	1.5	18	12	6	30	1.5	0.948615868(−2)	0.948615878(−2)
21	10	5	6	9	6	5	10	6	−0.293153644(−7)	−0.293153644(−7)
30	10	8	1.5	14	8	8	10	1.5	0.122364599(0)	∼0.122376276(0)
3	2	1	8	3	2	1	2	5	−0.442287767(−3)	−0.442287766(−3)
9	5	3	6	8	4	3	4	9	−0.546608468(−7)	−0.546510243(−7)
10	7	1	14.4	8	2	1	9.6	5	−0.184096844(−9)	−0.184189026(−9)
10	9	9	4.8	10	9	9	1.2	5	0.623122318(−3)	0.623122318(−3)
17	8	4	11	8	7	4	9	5	−0.100636030(−5)	−0.100623367(−5)
21	10	6	9	9	8	6	9	5	0.538979476(−4)	0.538980685(−4)
30	10	8	7	14	10	8	7	5	0.135074705(−1)	0.135074709(−1)
40	4	3	4.8	12	4	3	1.2	5	0.948246700(−1)	0.948379265(−1)
43	10	6	7.2	18	8	6	16.8	5	−0.115808750(−3)	−0.115907687(−3)

The spherical Bessel function is defined by [43]

$$j\lambda(x) = (-1)^{\lambda} x^{\lambda} \left(\frac{\mathrm{d}}{x\mathrm{d}x}\right)^{\lambda} \left(\frac{\sin(x)}{x}\right) \tag{5}$$

The spherical Bessel function satisfies the following recurrence relations [43]:

$$\begin{cases} x j_{l-1}(x) + x j_{l+1}(x) & = (2l+1)\mathrm{jl}\ (\mathrm{x}) \\ l j_{l-1}(x) - (l+1) j_{l+1}(x) & = (2l+1)\mathrm{jl'}\ (\mathrm{x}). \\ x j_{l-1}(x) - (l+1) j_l(x) & = \mathrm{xj'l(x)} \end{cases} \tag{6}$$

For the following, we use $j^n_{\lambda+(1/2)}$ with $n = 1,2,3, \ldots$ for the successive positive zeros $j_\lambda(x)$. $j_{\lambda+(1/2)}{}^0$ are assumed to be 0.

The STFs are defined in normalized form according to the following relationship [23, 24]:

$$\chi^m_{n,l}(\zeta, \vec{r}) = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}} r^{n-1} \mathrm{e}^{-\zeta r} Y^m_l(\theta_{\vec{r}}, \varphi_{\vec{r}}) \tag{7}$$

STFs can be expressed as finite linear combinations of B functions [8]:

$$\chi^m_{n,l}(\zeta, \vec{r}) = \frac{1}{\zeta^{n-1}} \sum_{p=\tilde{p}}^{n-1} \frac{(-1)^{n-l-p} 2^{2p+2l-n} (l+p)!}{(2p-n+l)!(n-l-p)!} B^m_{p,l}(\zeta, \vec{r}) \tag{8}$$

where

$$\tilde{p} = \begin{cases} \frac{n-l}{2} & \text{if n - 1 is even} \\ \frac{n-l+1}{2} & \text{if n - 1 is odd} \end{cases} \tag{9}$$

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

$$p(x) \sim x^{\gamma}(a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} + \ldots) \tag{10}$$

Gaunt coefficients are defined by [44–47]

$$\left\langle l^1, m_1 | l_2, m_2 | l_3, m_3 \right\rangle = \int_0^{\pi} \int_0^{2\pi} \left[Y^{m_1}_{l_1}(\theta, \varphi) \right] \times Y^{m_2}_{l_2}(\theta, \varphi) Y^{m_3}_{l_3}(\theta, \varphi) \sin(\theta) \mathrm{d}\theta \mathrm{d}\varphi \tag{11}$$

Two-center overlap integrals over B functions are defined by

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1} = \int_{\vec{r}} \left[B^{m_1}_{n_1 l_1}(\zeta_1, \vec{r}) \right] * B^{m_2}_{n_2, l_2}(\zeta_2, \vec{r} - \vec{R}) \mathrm{d}\vec{r} \tag{12}$$

By using the Fourier transform method, one can obtain analytical expressions for the two-center overlap and Coulomb integrals over B functions. These analytical expressions are given by [1]

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1} = 8(-1)^{l_2} i^{l_1+l_2} \zeta_1^{2n_1+l_1-1} \zeta_2^{2n_2+l_2-1} \times \sum_{\lambda=\lambda_{\min},2}^{l_1+l_2} (-i)^{\lambda} \left\langle l_2 m_2 | l_1 m_1 | \lambda m_2 - m_1 \right\rangle \ Y^{m_2-m_1}_{\lambda}(\theta_{\vec{v}}, \varphi_{\vec{v}}) \times \int_0^{+\infty} \frac{x^{n_x}}{\left(\zeta_1^2 + x^2\right)^{k_1} \left(\zeta_2^2 + x^2\right)^{k_2}} j_\lambda(Rx) \mathrm{d}x \tag{13}$$

where

$$\begin{cases} R = ||\overrightarrow{R}|| \text{ the modulus of } \vec{R} \\ k_1 = n_1 + l_1 + 1 \\ k_2 = n_2 + l_2 + 1 \\ n_x = l_1 + l_2 + 2 \end{cases} \tag{14}$$

By using Eq. 8, one can easily express two-center overlap integrals over STFs in terms of two-center overlap integrals over B functions. If we let $\tilde{S}^{n_2 l_2 m_2}_{n_1 l_1 m_1}$ be the two-center overlap integrals over STFs, then we obtain

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1} = \sum_{p_1=\tilde{p}_1}^{n_1-l_1} \frac{(-1)^{n_1-l_1-p_1} 2^{2p_1+2l_1-n_1} (l_1+p_1)!}{(2p_1-n_1+l_1)!(n_1-l_1-p_1)!} \times \sum_{p_2=\tilde{p}_2}^{n_2-l_2} \frac{(-1)^{n_2-l_2-p_2} 2^{2p_2+2l_1-n_1} (l_1+p_1)!}{(2p_1-n_1+l_1)!(n_1-l_1-p_1)!} S^{p2,l2,m2}_{p1,l1,m1} \tag{15}$$

where $S^{p_2 l_2 m_2}_{p_1 l_1 m_1}$ is given by Eq. 12.

The nonlinear $\bar{D}$ transformation and the development of the algorithm

The numerical evaluation of the analytical expression (13) turned out to be extremely difficult due to the presence of the semi-infinite integrals. The integrands of these semi-infinite integrals are highly oscillatory because of the presence of the spherical Bessel functions, in particular for large values of λ. Note that when the value of R is large, the zeros of the integrands become closer and consequently the oscillations become sharp. In this situation, the evaluation of the semi-infinite integrals presents severe computational and numerical difficulties.

Let us consider the semi-infinite integrals occurring in Eq. 13, which is given by

$$I = \int_0^{+\infty} \frac{x^{n_x}}{\left(\zeta_1^2 + x^2\right)^{k_1} \left(\zeta_2^2 + x^2\right)^{k_2}} j_\lambda(Rx) \mathrm{d}x \tag{16}$$

$$I = \sum_{n=0}^{+\infty} \int_{j^n_{X,R}}^{j^{n+1}_{X,R}} \frac{x^{n_x}}{\left(\zeta_1^2 + x^2\right)^{k_1} \left(\zeta_2^2 + x^2\right)^{k_2}} j_\lambda(Rx) \mathrm{d}x \tag{17}$$

where $j^0_{\lambda,R} = 0$ and for $n = 1,2,3, \ldots$ $j^n_{\lambda,R}$ are the leading positive zeros $j_\lambda(Rx)$, and they are given by

$$j^n_\lambda, R = \frac{j^n_{\lambda+(1/2)}}{R} \tag{18}$$

where $j^n_{\lambda+(1/2)}$ for $n = 1,2,3, \ldots$ are the successive positive zeros $j_\lambda(x)$.

As it can be seen from Table 4, one needs to sum a large number of terms of the infinite series to obtain an accurate evaluation of the semi-infinite integral (16). This slow-convergence problem prevented the use of the infinite series (17) for the numerical evaluation of overlap integrals.

By using the fact that the integrand $F(x)$ converges to 0 when $x \rightarrow \infty$ and if $\lambda \neq 0$ then

$$\lim_{\alpha \to 0} j_\lambda(\alpha) = 1$$

one can easily show that when $R \rightarrow 0$ and $\lambda \neq 0$ the semi-infinite integral (16) vanishes.

In the case where $\lambda = 0$ and $R \rightarrow 0$, we replaced $j_\lambda(Rx)$ by its Taylor development and obtained the following equation:

$$I \approx \int_0^{+\infty} \frac{x^{n_x}}{(\zeta_1^2 + x^2)^{k_1}(\zeta_2^2 + x^2)^{k_2}} \left(1 - \frac{R^2x^2}{3!} + \frac{R^4x^4}{5!} - \cdots\right) \mathrm{d}x \tag{19}$$

Note that in the case where $\zeta_1 = \zeta_2$, Weniger and Steinborn [1] developed an expression of the semi-infinite integral (16), which is given by

$$I = (-1)^{\Delta t} \frac{\pi}{2^{n_1+n_2+l_1+l_2+2}\zeta^{2n_1+2n_2+l_1+l_2+1}} \times \sum_{n=0}^{\Delta t} \frac{(-2)^\alpha \binom{}{i} (\zeta_1 v)^l}{(n_1 + n_2 + l_1 + l_2 - \alpha + 1)!} \hat{k}_v(\zeta_1 R) \tag{20}$$

$$\begin{cases} \Delta l = (l_1 + l_2 - \lambda)/2 \\ v = n_1 + n_2 + l_1 + l_2 - \lambda - \alpha + \frac{1}{2} \end{cases} \tag{21}$$

In the case where the scaling parameters ζ_1 and ζ_2 are not equal, Weniger and Steinborn [1] developed an expression of the semi-infinite integral (16) in terms of reduced Bessel functions, from which one can obtain, as explained in Ref. [1], the well-known representation of overlap integrals in terms of Jacobi polynomials [8].

In the present work, we present an approach based on nonlinear transformations for a highly accurate numerical evaluation of the semi-infinite integrals of the form given above.

Theorem 1 [30] Let $f(x)$ be integrable on $[0,\infty]$ and satisfy a linear differential equation of order m of the form

$$f(x) = \sum_{k=1}^{m} p_k(x) f^{(k)}(x), \quad \text{with } p_k \in A^{(i_k)}, i_k \leq k \tag{22}$$

If for all $k = i, i+1, \ldots, m$; $i = 1,2,3, \ldots, m$

$$\lim_{x \to +\infty} p_k^{(i-1)}(x) f^{(k-i)}(x) = 0 \tag{23}$$

and for all $l \geq 1$

$$\sum_{k=1}^{m} l(l-1)\cdots(l-k+1)p_{k,0} \neq 1 \tag{24}$$

where

$$p_{k,0} = \lim_{x \to +\infty} x^{-k} p_k(x), \quad 1 \leq k \leq m \tag{25}$$

then as $x \rightarrow \infty$

$$\int_x^{+\infty} f(t)\,\mathrm{d}t \sim \sum_{k=0}^{m-1} f^{(k)}(x) x^{jk} \left(\beta_{0,k} + \frac{\beta_{1,k}}{x} + \frac{\beta_{2,k}}{x^2} + \cdots\right) \tag{26}$$

where

$$j_k \leq \max(i_{k+1}, i_{k+2} - 1, \ldots, i_m - m + k + 1), \quad k = 0, 1, \ldots, m-1$$

The approximation $\bar{D}_n^{(m)}$ of $\int_0^{+\infty} f(x)\mathrm{d}x$, using the nonlinear $\bar{D}$ transformation, satisfies the $n(m-1)+1$ equations given by [31]

Table 4 Evaluation of the semi-infinite integral (16);$\xi_1 = 0.25$ and $\xi_2 = 0.3$

n_x	M_1	m_2	λ	R	$n_{\max}$	Values†[a]	n	Values $\bar{D}$[b]
3	1	2	2	5	4,759	0.4724113899(0)	5	0.4724113900(0)
3	1	2	3	5	4,758	0.2465110056(0)	5	0.2465110055(0)
5	1	3	3	5	4,758	0.1938959416(0)	5	0.1938959415(0)
5	1	3	4	5	4,758	0.1111094118(0)	5	0.1111094118(0)
7	1	4	5	5	4,757	0.5867845838(−1)	5	0.5867845838(−1)
3	1	2	2	25	10,642	0.5259869539(−1)	8	0.5259869544(−1)
3	1	2	3	25	10,642	0.8348898819(−1)	8	0.8348898821(−1)
5	1	3	3	25	10,642	0.1566408549(−1)	6	0.1566408553(−1)
5	1	3	4	25	10,641	0.2948688697(−1)	8	0.2948688698(−1)
7	1	4	5	25	10,641	0.1501930094(−1)	7	0.1501930089(−1)
3	2	1	2	55	15,786	0.2783143897(−2)	8	0.2783143956(−2)
3	2	1	3	55	15,785	0.7294018766(−2)	9	0.7294018727(−2)
5	2	2	5	55	15,784	0.1631535222(−2)	8	0.1631535283(−2)
7	3	2	7	55	15,783	0.1038418325(−2)	7	0.1038418377(−2)
9	3	3	8	55	15,783	0.3201457351(−3)	8	0.3201457519(−3)

[a] Values † were obtained using the infinite series given by Eq. 17. These values are computed with 15 correct digits.
[b] Values $\bar{D}$ were obtained using the nonlinear $\bar{D}$ transformation of order n(41).

$$\bar{D}_n^{(m)} = \int_0^{x_l} f(t)\mathrm{d}t + \sum_{h=1}^{m-1} f^{(k)}(x_l)x_l^{k+1}\sum_{i=0}^{n-1}\frac{\bar{\beta}_{k,i}}{x_l^i},\ l=0,1,\ldots,nm \quad (27)$$

where $\bar{D}_n^{(m)}$ and $\bar{\beta}_{k,i}$ are the unknowns of the above system. The x_l for $l=0,1,2,\ldots$ are the leading positive zeros of $f(x)$.

Now let us consider the integrand $F(x)$ of the semi-infinite integral (17)

$$F(x) = g(x)j_\lambda(Rx) \quad (28)$$

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

$$g(x) = \frac{x^{n_x}}{(\zeta_1^2+x^2)^{k_1}(\zeta_2^2+x^2)^{k_2}} \quad (29)$$

The spherical Bessel function satisfies a second-order linear differential equation given by [43]

$$\begin{aligned} j_\lambda(Bx) &= -\frac{2x}{(Rx)^2-\lambda^2-\lambda}j'_\lambda(Rx) \\ &\quad -\frac{x^2}{(Rx)^2-\lambda^2-\lambda}j''_\lambda(Rx) \\ &= q_1(x)j''_\lambda(Rx)+q_2(x)j''_\lambda(Rx) \end{aligned} \quad (30)$$

Note that the coefficients $q_1(x)$ and $q_2(x)$ of the linear differential equation (30) are, respectively, in $A^{(-1)}$ and $A^{(0)}$.

Corollary [30] If the function f is integrable on $[0,+\infty[$ and satisfies a linear mth order differential equation of the form

$$f(x) = \sum_{k=1}^{m} p_k(x)f^{(k)}(x) \quad (31)$$

where p_k are in $A(k)$ for $k=1,2,\ldots,m$ and $g \in A^{(\gamma)}$, then fg satisfies a linear differential equation of order m or less with coefficients that have asymptotic expansions in inverse powers of x.

From Eq. 29, one can easily show that $g \in A^{(n_x+2(k_1+k_2))}$. From this and the corollary it follows that $g(x)j_\lambda(vx)$ satisfies a linear differential equation of order 2 or less with coefficients that have asymptotic expansions in inverse powers of x. This differential equation can be obtained explicitly by $j_\lambda(vx)$ by $F(x)/g(x)$ in Eq. 30:

$$F(x) = p_1(x)F'(x)+p_2(x)F''(x) \quad (32)$$

where

$$p_1(x) = \frac{g(x)q_1(x)-2q_2(x)g'(x)}{g(x)H(x)} \text{ and } p_2(x) = \frac{q_2(x)}{H(x)} \quad (33)$$

and where $H(x)$ is given by

$$H(x) = 1+\frac{q_2(x)g'(x)}{g(x)}-\frac{2q_2(x)(g'(x))^2}{g^2(x)}+\frac{q_2(x)g''(x)}{g(x)} \quad (34)$$

The above second-order linear differential equation was obtained by Sidi for a function $F(x)=g(x)J_\lambda(x)$ [31].

Using the properties of asymptotic expansions in inverse powers of x, one can easily show that $H(x) \in A^{(0)}$. From this it follows that

$$p_1(x) \in A^{(-1)} \text{ and } p_2(x) \in A^{(0)} \quad (35)$$

Using the analytic expression of $F(x)$ with the fact that $n_x \le 2(k_1+k_2)$ and with the help of Eq. 35, one can easily show that for all $k=i,2$; $i=1,2$:

$$\begin{cases} \lim_{x\to+\infty} p_1^{(i-1)}(x)f^{(k-i)}(x) = 0 \\ \lim_{x\to+\infty} p_2^{(i-1)}(x)f^{(k-i)}(x) = 0 \end{cases} \quad (36)$$

and for all $l \ge 1$

$$\sum_{k=1}^{2} l(l-1)\cdots(l-k+1)p_{k,0} = 0 \ne 1 \quad (37)$$

It is now shown that all conditions of Theorem 1 are satisfied by the integrand $Fx)$. From this it follows that $\int_x^{+\infty} f(t)\mathrm{d}t$ has an asymptotic expansion in inverse powers of x of the form given by Eq. 26 when $x \to \infty$. The approximation of using the nonlinear $\bar{D}$ transformation can be obtained by solving the following linear system:

$$\bar{D}_n^{(2)} = \int_0^{x_l} f(t)dt + x_l^2 g(x_l)j'_l(Rx_l)\sum_{i=0}^{n-1}\frac{\bar{\beta}_{1,i}}{x_l^i},\ l=0,1,\ldots,n \quad (38)$$

where x_l are the leading positive zeros of $j_\lambda(Rx)$.

Note that if x_l is a zero of $j_\lambda(Rx)$ then from Eq. 6 it follows

$$\begin{aligned} j'_\lambda(Rx_1) &= \frac{\lambda}{x_1}j_\lambda(Rx_1) - Rj_{\lambda+1}(Rx_1) = -Rj_{\lambda+}(Rx_1) \\ &= -Rj_{\lambda+1}(Rx_1) \end{aligned} \quad (39)$$

$$j'_\lambda(Rx_l) = Rj_{\lambda-1}(Rx_l) - \frac{\lambda+1}{x_1}j_\lambda(Rx_l) = Rj_{\lambda-1}(Rx_l) \quad (40)$$

From the above equations, it follows that one does not have to compute the first derivative of the spherical Bessel function for calculating the approximation $\bar{D}_n^{(2)}$. Note that the use of Eq. 40 is faster than the use of Eq. 39, and in this case we obtain for $\lambda \ge 1$:

$$\bar{D}_n^{(2)} = \int_0^{x_l} f(t)\,\mathrm{d}t + x_l^2 g(x_l)j_{\lambda-1}(Rx_l) \sum_{i=0}^{n-1}\frac{\bar{\beta}_{1,i}}{x_l^i},\ l=0,1,\ldots,n \quad (41)$$

and for $\lambda=1$, we use Cramer's rule [31] for calculating the approximation $\bar{D}_n^{(2)}$, since the zeros of $j_0(Rx)$ are equidistant. In this case, the expression of $\bar{D}_n^{(2)}$ is given by

$$\overline{D}_n^{(2)} = \frac{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i)^n A(x_i)/[x_i^2 g(x_i)]}{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+i)^n /[x_i^2 g(x_i)]} \tag{42}$$

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

The convergence properties of the nonlinear $\bar{D}$ transformation were analyzed by Sidi [31], who showed that the approximation $\bar{D}_n^{(2)}$ converges to the exact values of the semi-infinite integrals.

Numerical results and discussion

In Table. 4 and 5, we listed values of the semi-infinite integral (16), which are obtained using the infinite series (17) for $R = 5.0$, 25.0, and 50.0 These values which are referred to as values "†", were obtained by performing the following test: If:

$$\int_{j_{\lambda,R}^n}^{j_{\lambda,R}^{n+1}} \frac{x^{n_x}}{(\zeta_1^2 + x^2)^{k_1} (\zeta_2^2 + x^2)^{k_2}} j_\lambda(Rx) dx > \varepsilon \tag{43}$$

then $n_{\max} = n$ and the value I^S of the semi-infinite integral is given by

$$I^S = \sum_{n=0}^{n_{\max}-1} \int_{j_{\lambda,R}^n}^{j_{\lambda,R}^{n+1}} \frac{x^{n_x}}{(\zeta_1^2 + x^2)^{k_1} (\zeta_2^2 + x^2)^{k_2}} j_\lambda(Rx)\, \mathrm{d}x \tag{44}$$

The value of ϵ was set to10^{-15}.

Each term of the finite sum (44) is computed using the Gauss–Legendre quadrature of order 96.

As can be seen from Table 4, the infinite series is slowly convergent, especially when the value of R is large. The value of $n_{\max}$ increases considerably when the value of R gets larger, and the oscillations of the integrand become stronger due to the fact that the zeros of the integrand become closer.

The linear system (38) is solved using the LU decomposition method. The finite integrals, $A(x) = \int_0^{x_l} F(t)\mathrm{d}t$, occurring in Eqs. 38 and 42 are transformed into a finite sum as follows:

$$A = \int_0^{x_l} F(t)\, \mathrm{d}t = \sum_{i=0}^{l-1} \int_{x_i}^{x_{i+1}} F(t)\, \mathrm{d}t \tag{45}$$

and each term of the above finite sum is evaluated using Gauss–Legendre quadrature of order 48.

In Table 5, values "†" are obtained using the analytic expression (20) developed by Weniger and Steinborn [1] in the case where the scaling parameters are equal.

In Table. 4 and 5, values $\bar{D}$ are obtained using the nonlinear $\bar{D}$ transformation of order n (38).

Table. 1 and 2 contain values of the two-center overlap integrals over B functions. In these tables, values "†" are obtained using the infinite series and values $\bar{D}$ are obtained using the $\bar{D}$ transformation of order $n = 10$, to evaluate the semi-infinite integrals occurring in the analytic expressions of the molecular integrals under consideration.

In Table 2, values "†" are obtained using the ACJU program developed by Homeier et al. [41]. As can be seen from this table, our numerical results are in complete accordance with those obtained using the ACJU program.

Table 1 contains values of overlap integrals over B functions, which are in complete accordance with values obtained by Weniger and Steinborn [2] and Grotendorst et al. [3].

Table 3 contains values of two-center overlap integrals over STFs. These overlap integrals over STFs were expressed in terms of overlap over B functions. Values obtained using the algorithm described in the present work are in excellent agreement with those obtained by Talman [13], Guseinov et al. [14, 15], and Guseinov and Mamedov [16].

For the numerical evaluation of Gaunt coefficients, which occur in the complete analytical expressions of two-center overlap integrals, we used the subroutine GAUNT.F developed by Weniger and Steinborn [47].

Table 5 Evaluation of the semi-infinite integral (16); $n_2 = n_1$, $l_2 = l_1$, $n_x = 5$, $\xi_1 = \xi_2 = 1.0$, and $R = 10.0$

n_1	l_1	λ	$n_{\max}$	Values[a]	N	Values $\bar{D}$[b]	Values †[c]
1	1	0	96	−0.1486637795(−3)	12	−0.148663779(−3)	−0.1486637795(−3)
1	1	2	95	0.2469991590(−3)	11	0.2469991590(−3)	0.2469991590(−3)
2	2	2	23	0.1098778914(−4)	8	0.1098778914(−4)	0.1098778914(−4)
2	2	4	22	0.9847230030(−4)	8	0.9847230030(−4)	0.9847230030(−4)
3	2	4	14	0.6147295734(−4)	7	0.6147295734(−4)	0.6147295734(−4)
3	3	4	11	0.1050100332(−4)	6	0.1050100332(−4)	0.1050100332(−4)
4	3	6	7	0.4476757274(−5)	4	0.4476757274(−5)	0.4476757274(−5)
4	4	6	6	0.9414467934(−6)	4	0.9414467934(−6)	0.9414467933(−6)

[a] Values were obtained using the infinite series given by Eq. 17. These values are computed with 15 correct digits.
[b] Values $\bar{D}$ were obtained using the nonlinear $\bar{D}$ transformation of order n (41).
[c] Values ‡ were obtained using the analytic expression given by Eq. 20.

The spherical harmonics are computed using the recurrence formulae given in Ref. [47].

From the numerical tables, one can notice that the nonlinear $\bar{D}$ is able to reach high accuracy in the numerical evaluation of the molecular integrals under consideration.

In all tables, the numbers in parentheses represent powers of 10 and all entries are in atomic units.

Conclusion

Analytic expressions for the two-center overlap integrals over the so-called B functions are obtained with the help of the Fourier transform method. These analytic expressions turned out to be very difficult to evaluate because of the presence of highly semi-infinite integrals involving spherical Bessel functions and not a simple trigonometric function.

It was shown that these semi-infinite integrals are suitable to apply $\bar{D}$, which consists of transforming the semi-infinite integrals involving Bessel functions into asymptotic expansions in inverse powers of x as $x \rightarrow \infty$. These asymptotic expansions are transformed into sets of linear equations. The approximations of semi-infinite integrals are obtained by solving these linear systems and it is shown that the approximations obtained using the $\bar{D}$ transformation converge to the exact values of the semi-infinite integrals.

The algorithm developed in the present work is now shown to be very efficient. The numerical results show that the approach described in this work yields values for these integrals to a high predetermined accuracy. This algorithm can be optimized and will definitely lead to a fast numerical evaluation of the molecular integrals under consideration.

Numerical results are obtained for the complete expressions of two-center overlap and Coulomb integrals over B functions. All are precise and very rapid. These results confirm that this $\bar{D}$ transformation represents another most significant advance on the road to routine, precise and rapid evaluation of these molecular electronic integrals.

Acknowledgments The author acknowledges the financial support, for this research, by the Natural Sciences and Engineering Research Council of Canada.

References

1. Weniger EJ, Steinborn EO (1983) J Chem Phys 78:6121–6132
2. Weniger EJ, Steinborn EO (1983) Phys Rev A 28:2026–2041
3. Grotendorst J, Weniger EJ, Steinborn EO (1986) Phys Rev A 33:3706–3726
4. Weniger EJ, Steinborn EO (1988) Theor Chim Acta 73:323–336
5. Homeier HHH, Steinborn EO (1992) Int J Quantum Chem 42:761–778
6. Homeier HHH, Weniger EJ, Steinborn EO (1992) Comput Phys Commun 72:269–287
7. Steinborn EO (1983) In: Dierckesen HH, Wilson S (eds) Methods in computational molecular physics. D Reidel, Dordrecht
8. Filter E, Steinborn EO (1978) Phys Rev A 18:1–11
9. Prosser FP, Blanchard CH (1962) J Chem Phys 36:1112
10. Trivedi HP, Steinborn EO (1983) Phys Rev A 27:670–679
11. Grotendorst J, Steinborn EO (1988) Phys Rev A 38:3857–3876
12. Harris FE (2002) Int J Quantum Chem 88:701–734
13. JD Talman (1993) Phys Rev A 48:243–249
14. Guseinov II, Özmen A, Atav Ü, Yüksel H (1998) Int J Quantum Chem 67:199–204
15. Guseinov II, Öztekin E, Hüseyin S (2001) J Mol Struct (THEOCHEM) 536:59–63
16. Guseinov II, Mamedov BA (2001) J Mol Struct (THEOCHEM) 538:295–296
17. Guseinov II, Mamedov BA, Öner F, Hüseyin S (2001) J Mol Struct (THEOCHEM) 545:265–270
18. Guseinov II, Mamedov BA (1999) J Mol Struct (THEOCHEM) 465:1–6
19. Mekelleche SM, Baba-Ahmed A (2000) Theor Chem Acc 103:463–468
20. Mekelleche SM, Baba-Ahmed A (1997) Int J Quantum Chem 63:843–852
21. Shavitt I (1963) The Gaussian function in calculation of statistical mechanics, quantum mechanics. Methods in computational physics 2. In: Alder B, Fernbach S, Rotenberg M (eds) Quantum mechanics. Academic, New York
22. Steinborn EO, Filter E (1975) Theor Chim Acta 38:273–281
23. Slater JC (1930) Phys Rev 36:57–64
24. Slater JC (1932) Phys Rev 42:33
25. Weniger EJ, Steinborn EO (1989) J Math Phys 30:774–784
26. Bonham RA, Peacher JL, Cox HL (1964) J Chem Phys 40:3083–3086
27. Homeier HHH, Steinborn EO (1992) Int J Quantum Chem 41:399–411
28. Wynn P (1956) Math Tables Aids Comput 10:91–96
29. Levin D (1973) Int J Comput Math B 3:371–388
30. Levin D, Sidi A (1981) Appl Math Comput 9:175–215
31. Sidi A (1980) J Inst Math Appl 26:1–20
32. Sidi A (1997) J Comput Appl Math 78:125–130
33. Safouhi H, Pinchon D, Hoggan PE (1998) Int J Quantum Chem 70:181–188
34. Safouhi H, Hoggan PE (1998) J Phys A: Math Gen 31:8941–4951
35. Safouhi H, Hoggan PE (1999) J Math Chem 25:259–280
36. Safouhi H, Hoggan PE (1999) J Phys A: Math Gen 32:6203–6217
37. Safouhi H, Hoggan PE (1999) J Comp Phys 155:331–347
38. Safouhi H (2000) J Comput Phys 165:473–495
39. Safouhi H (2000) J Math Chem 29:213–232
40. Safouhi H, Hoggan PE (2001) Int J Quantum Chem 84:580–591
41. Homeier HHH, Weniger EJ, Steinborn EO (1992) Comput Phys Commun 72:269–287
42. Condon EU, Shortley GH (1970) The theory of atomic spectra. Cambridge University Press, Cambridge
43. Arfken GB, Weber HJ (1995) Mathematical methods for physicists, 4th edn. Academic, New York
44. Gaunt JA (1929) Phil Trans R Soc A 228:151–196
45. Homeier HHH, Steinborn EO (1996) J Mol Struct (THEOCEM) 368:31–37
46. Xu Y-L (1997) J Comput Appl Math 85:53–65
47. Weniger EJ, Steinborn EO (1982) Comput Phys Commun 25:149–157