J. Phys. A: Math. Gen. **32** (1999) 6203–6217. Printed in the UK PII: S0305-4470(99)99738-X

Three-centre two-electron Coulomb and hybrid integrals evaluated using nonlinear D- and $\bar{D}$-transformations

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Received 30 November 1998, in final form 30 April 1999

Abstract. Of the two-electron integrals occuring in the molecular context, the three-centre Coulomb and hybrid integrals are numerous and difficult to evaluate to high accuracy. The analytical and numerical difficulties arise mainly from the presence of the spherical Bessel function and hypergeometric series in these integrals.

The present work accelerates the convergence of these integrals by first manipulating the indices of the hypergeometric function and exploiting relationships to express this function as a finite expansion and exploiting the properties of Bessel functions which satisfy second-order linear differential equations. This is a suitable form of the integrand to apply the nonlinear D (due to D Levin and A Sidi) and $\bar{D}$ (due to A Sidi) transformations.

The extensive numerical results section illustrates the accuracy and unprecedented efficiency of evaluation of these integrals.

1. Introduction

This paper continues the series of previous studies [1–3] concerning the rapid and efficient evaluation of two-electron integrals to pre-determined accuracy for the development of molecular electronic structure calculations over Slater-type orbitals (STO) [4–10].

The present work considers the method of applying the nonlinear D- and $\bar{D}$-transformations to accelerate the convergence of the semi-infinite oscillatory integrals involved in analytical expressions of three-centre, two-electron Coulomb and hybrid integrals [11–16].

Of the exponential-type functions (ETFs), Slater-type functions (STFs) are the simplest analytical functions but their use was limited because their multicentre integrals are extremely difficult to evaluate for polyatomic molecules, particularly integrals involving two electrons. Various studies have focussed on the use of B functions proposed by Shavitt [17] and introduced by Filter and Steinborn [18, 19]. These functions have a much more complicated mathematical structure than STFs, but they have much more appealing properties in multicentre integrals [18, 19] and their Fourier transforms are exceptionally simple [20, 22].

As in previous work [1–3], we apply the Fourier transform method which takes advantage of the properties of B functions [10, 23, 34]. These functions are linear combinations of Slater-type orbitals [21, 36] and they are well adapted to the Fourier transform method as shown by the Steinborn group [10, 18–33].

Initial attempts to analyse the integrand all indicate that the principal source of difficulties regarding accuracy and speed up of evaluation arises from the presence of the spherical Bessel function and a hypergeometric series in the integrands. Bessel functions lead to rapid

0305-4470/99/346203+15$30.00

oscillations of the integrands, whereas the non-terminating hypergeometric series ${}_{p+1}F_p$ with $p = 0, 1, \ldots$ converges as long as its argument z satisfies $|z| < 1$. If $|z|$ is sufficiently small, convergence is usually good and the series can be used for the evaluation of the hypergeometric function. If, however, $|z|$ is slightly smaller than 1, convergence can become so slow that the infinite series is computationally useless. Finally, for $|z| > 1$, the hypergeometric series diverges. However, it is often possible to find an analytic continuation—for instance, with the help of sequence transformations—which makes it possible to associate a finite value to a divergent hypergeometric series even outside its circle of convergence. These distinct properties can cause difficulty in the evaluation of the integrals. It is in fact not obvious that the nonlinear transformations can be applied to such integrals.

After a re-arrangement of the combined indices appearing as arguments in the hypergeometric functions, it is shown here that they can be expressed in the form of a finite sum. This key analytical passage shows the hypergeometric function to result in the type of integrand suitable for application of the nonlinear D- and $\bar{D}$-transformations [37–40] which have proved to be highly efficient in previous work [1–3].

In order for these nonlinear transformations to be applicable, it is required that the integrand can be shown to satisfy a differential equation with coefficients having a power series expansion in the reciprocal of the variable.

The symbolic computation system *Axiom* [41] was used to derive the required linear differential equation that the integrand of interest satisfies explicitly [1].

The integrals are evaluated numerically to unprecedented accuracy and with much reduced calculation times compared with other techniques.

2. Some definitions

The complete set of definitions and properties will be found in [2]. The present definitions are the minimum required.

The B functions are defined as follows [18, 19]:

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

where the reduced Bessel function $\hat{k}_{n-\frac{1}{2}}(\zeta r)$ is defined [19] as

$$\hat{k}_{n-\frac{1}{2}}(\zeta r) = \sqrt{\frac{2}{\pi}}(\zeta r)^{n-\frac{1}{2}} K_{n-\frac{1}{2}}(\zeta r) \tag{2}$$

$$= \frac{e^{-\zeta r}}{\zeta r} \sum_{j=1}^{n} \frac{(2n-j-1)!}{(j-1)!(n-j)!} 2^{j-n} (\zeta r)^j \tag{3}$$

where $K_{n-\frac{1}{2}}$ stands for the modified Bessel function of the second kind [42].

The Fourier transform $\bar{B}_{n,l}^{m}(\zeta, \vec{p})$ of $B_{n,l}^{m}(\zeta, \vec{r})$ is given [20, 22] by

$$\bar{B}_{n,l}^{m}(\zeta, \vec{p}) = \frac{1}{(2\pi)^{3/2}} \int_{\vec{r}} \mathrm{e}^{-i\vec{p}\cdot\vec{r}}\, B_{n,l}^{m}(\zeta, \vec{r})\, \mathrm{d}\vec{r} \tag{4}$$

$$= \sqrt{\frac{2}{\pi}}\, \zeta^{2n+l-1} \frac{(-i|p|)^l}{(\zeta^2 + |p|^2)^{n+l+1}}\, Y_l^m(\theta_{\vec{p}}, \varphi_{\vec{p}}). \tag{5}$$

The well known Rayleigh expansion of the plane wavefunctions is defined by

$$\mathrm{e}^{\pm i\vec{p}\cdot\vec{r}} = \sum_{l=0}^{+\infty} \sum_{m=-l}^{l} 4\pi\, (\pm i)^{\lambda}\, j_l(|\vec{p}||\vec{r}|)\, Y_l^m(\theta_{\vec{r}}, \varphi_{\vec{r}})\, [Y_l^m(\theta_{\vec{p}}, \varphi_{\vec{p}})]^{*}. \tag{6}$$

The Fourier integral representation of the Coulomb operator $1/|\vec{r} - \vec{R}_1|$ is given [30, 45] by

$$\frac{1}{|\vec{r} - \vec{R}_1|} = \frac{1}{2\pi^2} \int_{\vec{k}} \frac{e^{-i\vec{k}.(\vec{r}-\vec{R}_1)}}{k^2} \, d\vec{k}. \tag{7}$$

The Gaunt coefficients are defined [47–53] as

$$\langle l_1 m_1 | l_2 m_2 | l_3 m_3 \rangle = \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} [Y_{l_1}^{m_1}(\theta, \varphi)]^* Y_{l_2}^{m_2}(\theta, \varphi) Y_{l_3}^{m_3}(\theta, \varphi) \sin\theta \, d\theta \, d\varphi. \tag{8}$$

We define the generalized hypergeometric function [42, 43] by

$${}_mF_n(\alpha_1, \alpha_2, \ldots, \alpha_m; \beta_1, \beta_2, \ldots, \beta_n; x) = \sum_{r=0}^{+\infty} \frac{(\alpha_1)_r (\alpha_2)_r \cdots (\alpha_m)_r x^r}{(\beta_1)_r (\beta_2)_r \cdots (\beta_n)_r r!} \tag{9}$$

where $(\alpha)_n$ represents the Pochhammer symbol, which is defined [42, 43] by

$$\begin{aligned} &(\alpha)_0 = 1 \\ &(\alpha)_n = \alpha(\alpha+1)(\alpha+2)\cdots(\alpha+n-1) = \frac{\Gamma(\alpha+n)}{\Gamma(\alpha)} \end{aligned} \tag{10}$$

where Γ stands for the Gamma function which is defined [42, 43] by

$$\Gamma(z) = \int_0^{+\infty} t^{z-1} e^{-t} \, dt. \tag{11}$$

For $n \in \mathbb{N}$

$$\begin{aligned} &\Gamma(n+1) = n! = 1 \times 2 \times 3 \times \cdots \times n \\ &\Gamma(n + \tfrac{1}{2}) = \frac{(2n)!}{2^{2n}\, n!} \sqrt{\pi}. \end{aligned} \tag{12}$$

For $m = 2$, $n = 1$, the hypergeometric function [42, 43] becomes

$${}_2F_1(\alpha, \beta; \gamma; x) = \sum_{r=0}^{+\infty} \frac{(\alpha)_r (\beta)_r x^r}{(\gamma)_r r!}. \tag{13}$$

The infinite series (9), (13) converge only for $|x| < 1$, and they converge quite slowly if $|x|$ is slightly less than one. The corresponding functions nevertheless are defined in a much larger subset of the complex plane, including the case $|x| > 1$. Convergence problems of this kind can often be overcome by using nonlinear sequence transformations [54].

We define $A^{(\gamma)}$ to be the set of infinitely differentiable functions $a(x)$, which have asymptotic expansions in inverse powers of x as $x \to +\infty$, of the form

$$a(x) \sim x^\gamma \left(\alpha_0 + \frac{\alpha_1}{x} + \frac{\alpha_2}{x^2} + \cdots \right). \tag{14}$$

Their derivatives of any order therefore have asymptotic expansions, which can be obtained by differentiating that in (14) formally term by term.

3. Three-centre, two-electron Coulomb integrals over the B functions

The three-centre two-electron Coulomb integrals over the B functions are defined [9, 23, 44, 46] by

$$\mathcal{K}_{n_1 l_1 m_1, n_3 l_3 m_3}^{n_2 l_2 m_2, n_4 l_4 m_4} = \left\langle B_{n_1 l_1}^{m_1}(\zeta_1, \vec{r}) \, B_{n_3 l_3}^{m_3}[\zeta_3, (\vec{r'} - \vec{R}_3)] \right| \frac{1}{|\vec{r} - \vec{r'}|} \times$$

$$\times \left| B_{n_2 l_2}^{m_2}(\zeta_2, \vec{r})\, B_{n_4 l_4}^{m_4}[\zeta_4, (\vec{r'} - \vec{R}_4)] \right\rangle_{\vec{r},\vec{r'}} \tag{15}$$

$$= \int_{\vec{r}} \int_{\vec{r'}} \left[B_{n_1 l_1}^{m_1}(\zeta_1, \vec{r})\right]^* \left[B_{n_3 l_3}^{m_3}(\zeta_3, (\vec{r'} - \vec{R}_3))\right]^* \frac{1}{|\vec{r} - \vec{r'}|}$$
$$\times B_{n_2 l_2}^{m_2}(\zeta_2, \vec{r}) B_{n_4 l_4}^{m_4}\left[\zeta_4, (\vec{r'} - \vec{R}_4)\right] \mathrm{d}\vec{r}\, \mathrm{d}\vec{r'}. \tag{16}$$

By inserting the integral representation of the Coulomb operator, equation (7), in the above equation, one can obtain

$$\mathcal{K}_{n_1 l_1 m_1, n_3 l_3 m_3}^{n_2 l_2 m_2, n_4 l_4 m_4} = \frac{1}{2\pi^2} \int_{\vec{x}} \mathrm{e}^{i\vec{x}\cdot\vec{R}_4} \left\langle B_{n_1 l_1}^{m_1}(\zeta_1, \vec{r}) \right| \mathrm{e}^{-i\vec{x}\cdot\vec{r}} \left| B_{n_2 l_2}^{m_2}(\zeta_2, \vec{r}) \right\rangle_{\vec{r}}$$
$$\times \left\langle B_{n_4 l_4}^{m_4}(\zeta_4, \vec{r''}) \right| \mathrm{e}^{-i\vec{x}\cdot\vec{r''}} \left| B_{n_3 l_3}^{m_3}[\zeta_3, (\vec{r''} - (\vec{R}_3 - \vec{R}_4))] \right\rangle_{\vec{r''}}^* \frac{\mathrm{d}\vec{x}}{x^2}. \tag{17}$$

Let us consider the term in $\vec{r}$:

$${}_k I_1 = \left\langle B_{n_1 l_1}^{m_1}(\zeta_1, \vec{r}) \right| \mathrm{e}^{-i\vec{x}\cdot\vec{r}} \left| B_{n_2 l_2}^{m_2}(\zeta_2, \vec{r}) \right\rangle_{\vec{r}}. \tag{18}$$

In this expression, it is clear that the two B functions are centred on the same point. By using equations (1), (3), one can easily find an expression for the radial part of the product of the two B functions, which is given by

$$\mathrm{Rad}\left\{B_{n_1 l_1}^{m_1}(\zeta_1, \vec{r}) B_{n_2 l_2}^{m_2}(\zeta_2, \vec{r})\right\} = \left[2^{n_1+l_1+n_2+l_2}(n_1+l_1)!(n_2+l_2)!\right]^{-1} \zeta_1^{l_1} \zeta_2^{l_2}$$
$$\times \sum_{k=2}^{n_1+n_2} \sum_{i=k_1}^{k_2} \frac{(2n_1-i-1)!\,(2n_2-i-1)!\,\zeta_1^{i-1}\,\zeta_2^{k-i-1}\, r^{k+l_1+l_2-2}\, \mathrm{e}^{-\zeta_s r}}{(i-1)!\,(n_1-i)!\,(k-i-1)!\,(n_2-k+i)!\,2^{n_1+n_2-k}} \tag{19}$$

where

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

By using the above equation and introducing the expansion of $\mathrm{e}^{-i\vec{x}\cdot\vec{r}}$ in terms of the Bessel functions of the first kind (6), in (18) we can obtain an analytical expression of ${}_k I_1$ given by

$${}_k I_1 = \left[2^{n_1+l_1+n_2+l_2}(n_1+l_1)!(n_2+l_2)!\right]^{-1} \zeta_1^{l_1} \zeta_2^{l_2} \sqrt{\frac{\pi}{2x}}$$
$$\times \sum_{l=l_{\min},2}^{l_{\max}} (-i)^l \langle l_1 m_1 | l m_1 - m_2 | l_2 m_2 \rangle [Y_l^{m_1-m_2}(\theta_{\vec{x}}, \varphi_{\vec{x}})]^*$$
$$\times \sum_{k=2}^{n_1+n_2} \sum_{i=k_1}^{k_2} \left[\frac{(2n_1-i-1)!\,(2n_2-k+i-1)!\,\zeta_1^{i-1}\,\zeta_2^{k-i-1}}{(i-1)!\,(n_1-i)!\,(k-i-1)!\,(n_2-k+i)!\,2^{n_1+n_2-k}}\right]$$
$$\times \int_0^{+\infty} r^{k+l_1+l_2-\frac{1}{2}} J_{l+\frac{1}{2}}(xr)\, \mathrm{e}^{-\zeta_s r}\, \mathrm{d}r \tag{20}$$

where [50]

$$l_{\max} = l_1 + l_2$$

$$l_{\min} = \begin{cases} \max(|l_1-l_2|, |m_2-m_1|) & \text{if } l_{\max} + \max(|l_1-l_2|, |m_2-m_1|) \text{ is even} \\ \max(|l_1-l_2|, |m_2-m_1|) + 1 & \text{if } l_{\max} + \max(|l_1-l_2|, |m_2-m_1|) \text{ is odd.} \end{cases}$$

The subscript $l = l_{\min}, 2$ in the first summation symbol in (20) indicates that the summation index l runs in steps of 2 from $l_{\min}$ to $l_{\max}$.

The semi-infinite r integral involved in the above equation, which we denote $\tilde{I}(x)$, has an analytical expression given [42, 43] by

$$\tilde{I}(x) = \int_0^{+\infty} r^{k+l_1+l_2-\frac{1}{2}} J_{l+\frac{1}{2}}(xr)\, \mathrm{e}^{-\zeta_s r}\, \mathrm{d}r$$
$$= \frac{\left[x/2\zeta_s\right]^{l+\frac{1}{2}} \Gamma(k+l_1+l_2+l+1)}{\zeta_s^{k+l_1+l_2+\frac{1}{2}} \Gamma(l+\frac{3}{2})} \left[1+\frac{x^2}{\zeta_s^2}\right]^{-k-l_1-l_2}$$
$$\times {}_2F_1\left(\frac{l-k-l_1-l_2+1}{2}, \frac{l-k-l_1-l_2}{2}+1; l+\frac{3}{2}; -\frac{x^2}{\zeta_s^2}\right). \tag{21}$$

One can easily show that one of the arguments $\frac{1}{2}(l-k-l_1-l_2+1)$, $\frac{1}{2}(l-k-l_1-l_2)+1$ of the hypergeometric function is a negative integer. Thus, the hypergeometric series is reduced to a finite expansion. The analytical expression involved in the above equation becomes

$$\tilde{I}(x) = \frac{\Gamma(k+l_1+l_2+l+1)}{2^{l+\frac{1}{2}} \Gamma(l+\frac{3}{2})} \zeta_s^{n_k-l-1} [\zeta_s^2 + x^2]^{-k-l_1-l_2} \sum_{r=0}^{\eta'} (-1)^r \frac{(\frac{\eta}{2})_r\, (\frac{\eta+1}{2})_r}{(l+\frac{3}{2})_r\, r!\, \zeta_s^{2r}} x^{2r+l+\frac{1}{2}} \tag{22}$$

where

$$\eta = l-k-l_1-l_2+1 \qquad \eta' = \begin{cases} -\frac{1}{2}\eta & \text{if } \eta \text{ is even} \\ \eta' = -\frac{1}{2}(\eta+1) & \text{otherwise.} \end{cases}$$

Special case

If $l = l_1 + l_2$ and $k = 2$, an expression for $\tilde{I}(x)$ is given [42] by

$$\int_0^{+\infty} r^{(l+\frac{1}{2})+1} J_{l+\frac{1}{2}}(xr)\, \mathrm{e}^{-\zeta_s r}\, \mathrm{d}r = \frac{2(l+1)!\zeta_s}{\sqrt{\pi}} \frac{(2x)^{l+\frac{1}{2}}}{(\zeta_s^2+x^2)^{l+\frac{1}{2}}}. \tag{23}$$

Now, by applying the Fourier-transform method [10, 23–32], to the term

$$\left\langle B_{n_4 l_4}^{m_4}(\zeta_4, \vec{r''}) \middle| \mathrm{e}^{-i\vec{x}\cdot\vec{r''}} \middle| B_{n_3 l_3}^{m_3}[\zeta_3, (\vec{r''} - (\vec{R}_3 - \vec{R}_4)]\right\rangle_{\vec{r''}}^{*}$$

involved in (17), substituting the Rayleigh expansion of the plane wavefunctions (6), we obtain an expression for these integrals involving a two-dimensional integral representation, which is given [23, 44] by

$$\mathcal{K}_{n_1 l_1 m_1, n_3 l_3 m_3}^{n_2 l_2 m_2, n_4 l_4 m_4} = 8(4\pi)^3 (2l_3+1)!!(2l_4+1)!!\zeta_1^{l_1}\zeta_2^{l_2}\zeta_3^{2n_3+l_3-1}\zeta_4^{2n_4+l_4-1}$$
$$\times \frac{(n_3+l_3+n_4+l_4+1)!}{(n_3+l_3)!(n_4+l_4)!} \sum_{l=l_{\min},2}^{l_{\max}} (-i)^l \langle l_1 m_1 | l_2 m_2 | l m_1 - m_2\rangle$$
$$\times \sum_{k=2}^{n_1+n_2} \sum_{i=k_1}^{k_2} \left[\frac{(2n_1-i-1)!\,(2n_2-i-1)!\,\zeta_1^{i-1}\,\zeta_2^{k-i-1}}{(i-1)!\,(n_1-i)!\,(k-i-1)!\,(n_2-k+i)!\,2^{n_1+n_2-k}}\right]$$
$$\times \sum_{l_4'=0}^{l_4} \sum_{m_4'=-l_4'}^{l_4'} (i)^{l_4+l_4'}(-1)^{l_4'} \frac{\langle l_4 m_4 | l_4 - l_4' m_4 - m_4' | l_4' m_4'\rangle}{(2l_4'+1)!![2(l_4-l_4')+1]!!}$$
$$\times \sum_{l_3'=0}^{l_3} \sum_{m_2'=-l_3'}^{l_3'} (i)^{l_3+l_3'} \frac{\langle l_3 m_3 | l_3 - l_3' m_3 - m_3' | l_3' m_3'\rangle}{(2l_3'+1)!![2(l_3-l_3')+1]!!}$$

$$\times \sum_{l'=|l'_3-l'_4|}^{l'_3+l'_4} \langle l'_4 m'_4 | l'_3 m'_3 | l' m'_4 - m'_3 \rangle R_{34}^{l'} Y_{l'}^{m'_4-m'_3}(\theta_{\vec{R}_{34}}, \varphi_{\vec{R}_{34}})$$
$$\times \sum_{l_{34}} \langle l_3 - l'_3 m_3 - m'_3 | l_4 - l'_4 m_4 - m'_4 | l_{34} m_{34} \rangle$$
$$\times \sum_{\lambda=|l-l_{34}|}^{l+l_{34}} i^{\lambda} \langle l m_1 - m_2 | l_{34} (m_4 - m'_4) - (m_3 - m'_3) | \lambda \mu \rangle$$
$$\times \sum_{j=0}^{\Delta l} \binom{\Delta l}{j} \frac{(-1)^j}{2^{n_3+n_4+l_3+l_4-j+1}\,(n_3+n_4+l_3+l_4-j+1)!}$$
$$\times \frac{\Gamma(k+l_1+l_2+l+1)}{2^{l+\frac{1}{2}}\Gamma(l+\frac{3}{2})} \zeta_s^{n_k-l-1} \sum_{r=0}^{\eta'} (-1)^r \frac{(\frac{\eta}{2})_r\,(\frac{\eta+1}{2})_r}{(l+\frac{3}{2})_r\, r!\, \zeta_s^{2r}}$$
$$\times \int_{s=0}^{1} s^{n_{33}}\,(1-s)^{n_{44}}\, Y_{\lambda}^{-\mu}(\theta_{\vec{v}}, \varphi_{\vec{v}})$$
$$\times \int_{x=0}^{+\infty} [\zeta_s^2 + x^2]^{-n_k} x^{n_x+\frac{1}{2}}\, j_{\lambda}(vx)\, \frac{\hat{k}_{\nu}[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_{\gamma}}}\, \mathrm{d}x\, \mathrm{d}s \tag{24}$$

where

$$k_1 = \max(1, k-n_2) \qquad k_2 = \min(n_1, k-1) \qquad \zeta_s = \zeta_1 + \zeta_2$$
$$|(l_3 - l'_3) - (l_4 - l'_4)| \leqslant l_{34} \leqslant (l_3 - l'_3) + (l_4 - l'_4)$$
$$n_x = l_3 - l'_3 + l_4 - l'_4 + 2r + l \qquad n_k = k + l_1 + l_2$$
$$n_{33} = n_3 + l_3 + l_4 - l'_4 \qquad n_{44} = n_4 + l_4 + l_3 - l'_3$$
$$n_{\gamma} = 2(n_3 + l_3 + n_4 + l_4) - (l'_3 + l'_4) - l' + 1$$
$$\mu = (m_1 - m_2) - (m_4 - m'_4) + (m_3 - m'_3)$$
$$[\gamma(s,x)]^2 = (1-s)\zeta_4^2 + s\zeta_3^2 + s(1-s)x^2$$
$$\eta = l - k - l_1 - l_2 + 1 \qquad \Delta l = \tfrac{1}{2}(l_3 + l_4 - l')$$
$$\eta' = \begin{cases} -\frac{1}{2}\eta & \text{if } \eta \text{ is even} \\ -\frac{1}{2}(\eta+1) & \text{otherwise} \end{cases}$$
$$\vec{v} = s(\vec{R}_3 - \vec{R}_4) - \vec{R}_3 = s\vec{R}_{34} - \vec{R}_3$$
$$\nu = n_3 + n_4 + l_3 + l_4 - l' - j + \tfrac{1}{2}$$
$$m_{34} = (m_3 - m'_3) - (m_4 - m'_4).$$

The two-dimensional integral in the above equation, which will be referred to as $\mathcal{T}$, is given by

$$\mathcal{T} = \int_{s=0}^{1} s^{n_{33}}\,(1-s)^{n_{44}}\, Y_{\lambda}^{-\mu}(\theta_{\vec{v}}, \varphi_{\vec{v}}) \int_{x=0}^{+\infty} [\zeta_s^2 + x^2]^{-n_k}$$
$$\times x^{n_x+\frac{1}{2}}\, j_{\lambda}(vx)\, \frac{\hat{k}_{\nu}[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_{\gamma}}}\, \mathrm{d}x\, \mathrm{d}s. \tag{25}$$

The inner semi-infinite x integral involved in the above equation, which will be referred to as $\tilde{\mathcal{T}}(s)$ is defined as

$$\tilde{\mathcal{T}}(s) = \int_{x=0}^{+\infty} [\zeta_s^2 + x^2]^{-n_k} x^{n_x+\frac{1}{2}} \, j_\lambda(vx) \, \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \, \mathrm{d}x. \tag{26}$$

The zeros of the integrand of $\tilde{\mathcal{T}}(s)$ are the zeros of the Bessel function of the first kind $J_{\lambda+\frac{1}{2}}(vx)$:

$$J_{\lambda+\frac{1}{2}}(z) = \left(\frac{z}{2}\right)^{\lambda+\frac{1}{2}} \sum_{k=0}^{+\infty} \frac{\left(-x^2/4\right)^k}{k!\,\Gamma(\lambda+k+1)} \tag{27}$$

which because of the relation $j_\lambda(z) = [\pi/(2z)]^{\frac{1}{2}} \, J_{\lambda+\frac{1}{2}}(z)$ are for $\lambda \geqslant 1$ are identical with the zeros of the spherical Bessel function j_λ.

We set $j^n_{\lambda,v} = j^n_{\lambda+\frac{1}{2}}/v$, where $j^n_{\lambda+\frac{1}{2}}$ is the nth real zero of of the Bessel function of the first kind $J_{\lambda+\frac{1}{2}}(x)$. $j^0_{\lambda+\frac{1}{2}}$ is assumed to be 0. Then we can write the integral $\tilde{\mathcal{T}}(s)$ (26) as follows:

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

The semi-infinite x integral $\tilde{\mathcal{T}}(s)$ was evaluated using Gauss–Laguerre quadrature [23,33], or using the infinite series, equation (28). Unfortunately, as we showed in previous work [1–3], the use of Gauss-Laguerre quadrature even to high order gives inaccurate results and presents severe numerical difficulties for this kind of oscillating integrand, especially for large values of v since the integrand oscillations become very rapid due to the spherical Bessel function [42,43] and for s close to 0 or 1. If we let $s = 0$ or 1, the integrand will be reduced to the term $[\zeta_s^2 + x^2]^{-n_k} x^{n_x+\frac{1}{2}} \, j_\lambda(vx)$ because the term $\hat{k}_\nu[R_{34}\gamma(s,x)]/[\gamma(s,x)]^{n_\gamma}$ becomes a constant and therefore the asymptotic behaviour of the integrand cannot be represented by a function of the form $\mathrm{e}^{-\lambda x} \, g(x)$ where $g(x)$ is not a rapidly oscillating function. We also note that the region close to $s = 0$ and $s = 1$ carry a very small weight because of the expression $s^{n_{33}}(1-s)^{n_{44}}$.

The use of the infinite series (28) is prohibitively long for sufficient accuracy. The epsilon algorithm of Wynn [56, 58] or Levin's u transform [57, 59, 60], accelerate the convergence of the infinite series but the accuracy is still insufficient, especially for s close to 0 or 1. Therefore new numerical integration techniques are required. The present work concentrates on the use of the nonlinear D- and $\bar{D}$-transformations [37–40]. They are efficient in evaluating semi-infinite integrals of rapidly oscillating functions which satisfy linear differential equations of the form $f(t) = \sum_{k=1}^{m} p_k(t) \, f^{(k)}(t)$.

The coefficients p_k should satisfy the following conditions [42, 43]:

1. p_k are in $A^{(i_k)}$ where $i_k \leqslant k$ for $k = 1, 2, \ldots, m$;
2. $\lim_{x\to+\infty} p_k^{(i-1)}(x) f^{(k-i)}(x) = 0$, for $k = i, i+1, \ldots, m$; $i = 1, \ldots, m$;
3. $\forall l \geqslant -1$, $\sum_{k=1}^{m} l(l-1)\cdots(l-k+1) p_{k,0} \neq 1$; $p_{k,0} = \lim_{x\to+\infty} x^{-k} p_k(x)$.

To apply these transformations successfully, there is no need to know explicitly the differential equation that the integrand satisfies; knowledge of its existence and its order is sufficient.

Let us consider the integrand $F(x)$ of the integral (26). It has the form

$$F(x) = w_1(x) w_2(x) f(x) j_\lambda(vx)$$

where

$$f(x) = \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} \qquad w_1(x) = x^{n_x+\frac{1}{2}} \qquad w_2(x) = \left[\zeta_s^2 + x^2\right]^{-k-l_1-l_2}.$$

$j_\lambda(vx)$ satisfies a linear second-order differential equation given [42, 43] by

$$j_\lambda(vx) = -\frac{2x}{(vx)^2 - \lambda^2 - \lambda} j_\lambda^{(1)}(vx) - \frac{x^2}{(vx)^2 - \lambda^2 - \lambda} j_\lambda^{(2)}(vx) \tag{29}$$

$$= q_{1,1}(x) j_\lambda^{(1)}(vx) + q_{2,1}(x) j_\lambda^{(2)}(vx). \tag{30}$$

Assuming that

$$R_{34}\gamma(s,x) = R_{34}\sqrt{(1-s)\zeta_4^2 + s\zeta_3^2 + s(1-s)x^2} = \sqrt{\beta + \alpha x^2}$$

the function $f(x)$ satisfies the linear second-order differential equations given [42, 43] by

$$f(x) = x^{-1}\left[(2\nu+1)\tau + \frac{\delta\tau}{x^2}\right] f^{(1)}(x) + \left[\tau - \frac{\delta\tau}{x^2}\right] f^{(2)}(x) \tag{31}$$

$$= q_{2,1}(x) f^{(1)}(x) + q_{2,2}(x) f^{(2)}(x) \tag{32}$$

where

$$\delta = -\frac{\beta}{\alpha} \qquad \tau = \frac{1}{\alpha}.$$

The coefficients $q_{i,1}$, equation (30) are in $A^{(-1)}$, and the coefficients $q_{i,2}$, equation (32) are in $A^{(0)}$, for $i = 1, 2$.

The function $w_1(x)w_2(x) = x^{n_x+\frac{1}{2}}[\zeta_s^2 + x^2]^{-k-l_1-l_2}$, can be written as

$$w_1(x)w_2(x) = x^{n_x-2(k+l_1+l_2)+\frac{1}{2}}\left[1 + \frac{\zeta_s^2}{x^2}\right]^{-k-l_1-l_2} \qquad \in A^{(n_x-2(k+l_1+l_2)+\frac{1}{2})}.$$

To prove the existence of the linear differential equation which the function $F(x)$ satisfies and to determine its order, we state a lemma and corollaries which are proven in [37].

Lemma. *If the functions f and g satisfy linear differential equations of order m and n respectively, then their product fg satisfies a linear differential equation of order less than or equal to mn.*

Corollary 1. *If the coefficients of the linear differential equations that f and g satisfy have asymptotic expansions in inverse powers of x as $x \to +\infty$, then so do the coefficients of the linear differential equation that fg satisfies.*

Corollary 2. *If the function f satisfies a linear differential equation of order m with coefficients that have asymptotic expansions in inverse powers of x as $x \to +\infty$ and if $g \in A^{(\gamma)}$, then fg satisfies a linear differential equation of order less than or equal to m with coefficients that have asymptotic expansions in inverse powers of x as $x \to +\infty$.*

Now, it is clear that the function $f(x)j_\lambda(vx)$ satisfies a linear differential equation of order 4 or less, with coefficients q_k that have asymptotic expansions of the inverse powers of x as $x \to +\infty$. In previous work [1], we used the symbolic computation system *Axiom* [41] to determine this linear differential equation explicitly, to confirm that it is of the form required to apply the D- and $\bar{D}$-transformations and its order is exactly 4.

The coefficients q_k for $k = 1, 2, 3, 4$; of the linear differential equation that $f(x)j_\lambda(vx)$ satisfies are linear combinations of $q_{1,i}$, $q_{2,i}$, $i = 1, 2$ and their successive derivatives, thus $q_k \in A^{(i_k)}$ where $i_k \leqslant 0$ for $k = 1, 2, 3, 4$.

Corollary 2 shows that $F(x) = w_1(x)w_2(x)f(x)j_\lambda(vx)$ satisfies a linear differential equation of order 4, with coefficients p_k that have asymptotic expansions in inverse powers of x as $x \to +\infty$.

Now, by substituting $f(x)j_\lambda(vx)$ by $F(x)/w_1(x)w_2(x)$ in its linear differential equation, one can easily find expressions for p_k, $k = 1, 2, 3, 4$; depending on q_k, $k = 1, 2, 3, 4$; $w(x) = w_1(x)w_2(x)$ and the first three successive derivatives of $1/w(x)$. The p_k are in $A^{(i_k)}$, where $i_k \leqslant 0$, thus $p_{k,0} = 0$, $k = 1, 2, 3, 4$; then

$$\forall l \geqslant -1 \qquad \sum_{k=1}^{4} l(l-1)\cdots(l-k+1)p_{k,0} = 0 \neq 1.$$

The behaviour of $F(x)$ and its successive derivatives is dominated by the exponentially decreasing $\hat{k}_\nu$, thus

$$\lim_{x\to+\infty} p_k^{(i-1)}(x)\, F^{(k-i)}(x) = 0 \quad k = i, i+1, \ldots, 4 \qquad i = 1, 2, 3, 4.$$

The conditions required to apply the nonlinear D- and $\bar{D}$-transformations are satisfied. The approximations $D_m^{(4)}$ to $\tilde{\mathcal{T}}$, using the D-transformation, satisfy $M = 4m + 1$ equations given [37] by

$$D_m^{(4)} = \int_0^{x_n} F(t)\,\mathrm{d}t + \sum_{k=0}^{3} F^{(k)}(x_n)\, x_n^{k+1} \sum_{i=0}^{m-1} \frac{\bar{\beta}_{k,i}}{x_n^i} \qquad n = 0, 1, 2, \ldots, 4m. \tag{33}$$

The x_n are chosen to satisfy $0 < x_0 < x_1 < \cdots < x_{4m}$. The choice of the x_n is important and this point has been investigated by Sidi [37, 38]. It turns out that a suitable choice of the x_n can make the D-transformation more efficient for rapidly oscillating functions. The above set of equations form a linear set of M unknowns, namely, $D_m^{(4)}$ and the $\bar{\beta}_{k,i}$ for $k = 0, 1, 2, 3$; $i = 0, 1, \ldots, m-1$.

By choosing $x_n = j_{\lambda,v}^{n+1}$, for $n = 0, 1, 2, \ldots$, which are the zeros of $F(x)$, we reduce the order of the above set of equations to $M = 3m + 1$ which can be re-written [37] as

$$\bar{D}_m^{(4)} = \int_0^{x_n} F(t)\,\mathrm{d}t + \sum_{k=1}^{3} F^{(k)}(x_n)\, x_n^{k+1} \sum_{i=0}^{m-1} \frac{\bar{\beta}_{k,i}}{x_n^i} \qquad n = 0, 1, 2, \ldots, 3m. \tag{34}$$

The above sets of equations (33) and (34) can, in general, be solved for the M unknowns [37]. The convergence analysis of the D- and $\bar{D}$-transformations has been taken up by Sidi [38].

4. Hybrid integrals over the B functions

The hybrid integrals over B functions are defined [9, 23, 44, 46] by

$$\mathcal{H}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4} = \left\langle B_{n_1l_1}^{m_1}(\zeta_1,\vec{r})\, B_{n_3l_3}^{m_3}(\zeta_3,\vec{r'}) \right| \frac{1}{|\vec{r}-\vec{r'}|} \left| B_{n_2l_2}^{m_2}(\zeta_2,\vec{r}) B_{n_4l_4}^{m_4}[\zeta_4,(\vec{r'}-\vec{R})] \right\rangle_{\vec{r},\vec{r'}}. \tag{35}$$

By inserting the integral representation of the Coulomb operator, equation (7), in the above equation, we obtain

$$\begin{aligned}\mathcal{H}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4} = \frac{1}{2\pi^2}\int_{\vec{x}} \mathrm{e}^{-i\vec{x}\cdot\vec{R}_1} \left\langle B_{n_1l_1}^{m_1}(\zeta_1\vec{r}) \right| \mathrm{e}^{-i\vec{x}\cdot\vec{r}} \left| B_{n_2l_2}^{m_2}(\zeta_2\vec{r}) \right\rangle_{\vec{r}} \\ \times \left\langle B_{n_4l_4}^{m_4}(\zeta_4\vec{r''}) \right| \mathrm{e}^{-i\vec{x}\cdot\vec{r''}} \left| B_{n_3l_3}^{m_3}[\zeta_3(\vec{r''}-\vec{R}_1)] \right\rangle_{\vec{r''}}^{*} \frac{\mathrm{d}\vec{x}}{x^2}.\end{aligned} \tag{36}$$

Using the same calculations as for the three-centre, two-electron Coulomb integrals, we obtain an expression for $\mathcal{H}_{n_1 l_1 m_1, n_3 l_3 m_3}^{n_2 l_2 m_2, n_4 l_4 m_4}$ involving a semi-infinite integral which will be referred to as $\tilde{\mathcal{H}}(s)$ given [23, 44] by

$$\tilde{\mathcal{H}}(s) = \int_{x=0}^{+\infty} [\zeta_s^2 + x^2]^{-n_k} x^{n_x+\frac{1}{2}}\, j_\lambda(vx)\, \frac{\hat{k}_\nu[R_1\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\, \mathrm{d}x \tag{37}$$

$$= \sum_{n=0}^{+\infty} \int_{j_{\lambda,v}^{n}}^{j_{\lambda,v}^{n+1}} [\zeta_s^2 + x^2]^{-n_k} x^{n_x+\frac{1}{2}}\, j_\lambda(vx)\, \frac{\hat{k}_\nu[R_{34}\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\, \mathrm{d}x \tag{38}$$

where $\vec{v} = s\vec{R}_1$; $\lambda, \zeta_s, n_k, n_x, \nu, n_\gamma$ and $\gamma(s,x)$ are defined according to equation (25).

Using the previous arguments, one can easily show that the integrand of the semi-infinite x integral involved in the above equation, (25), which will be referred to as $\tilde{\mathcal{H}}(s)$, satisfies a linear differential equation of order 4 of the form required to apply the D and $\bar{D}$ transformations. The order of the set of equations which gives the approximation $D_m^{(4)}$ is $M = 4m + 1$, but it can be reduced to $3m + 1$ by choosing the $x_n = j_{\lambda,v}^{n+1}$ for $n = 0, 1, 2, \ldots, 3m$.

5. Numerical results and discussion

Our numerical results are given in tables 1–12.

All the expressions are implemented in an original set of Fortran 77 subroutines.

The zeros of the spherical Bessel function $j_\lambda(x)$ are computed to 20 correct decimals using the symbolic programing language *Axiom*.

Exact values were computed to 20 correct decimals using the infinite series (equation (28)) (for comparison and in order to establish the accuracy of the transformations methods).

Table 1. Evaluation of $\tilde{\mathcal{T}}(s)$, equation (26), using the $\bar{D}$-transformation of order m ($\bar{D}_m^{(4)}$), equation (34). Time is in milliseconds. ($\nu = n_\gamma/2$, $\zeta_1 = \zeta_3$ and $\zeta_2 = \zeta_4$.)

s	m	n_k	n_x	n_γ	λ	ζ_3	ζ_4	R_3	R_4	Error	Time
0.01	3	2	0	5	0	4.50	0.75	7.75	3.25	0.84D−10	0.15
0.25	3	2	0	5	0	1.50	1.75	5.75	3.25	0.54D−13	0.15
0.50	2	2	0	5	0	0.75	1.50	2.75	1.45	0.14D−11	0.07
0.75	2	2	0	5	0	0.75	1.50	2.75	1.45	0.35D−12	0.07
0.99	2	2	0	5	0	3.25	2.50	6.75	2.45	0.28D−13	0.07
0.25	2	6	2	11	3	0.50	1.25	8.75	4.50	0.17D−10	0.07
0.01	2	6	4	13	4	0.25	1.50	3.75	1.50	0.84D−10	0.06
0.99	2	7	5	15	5	1.25	1.75	1.25	4.75	0.24D−12	0.07

Table 2. Evaluation of $\tilde{\mathcal{T}}(s)$, equation (26), using Levin's u-transform of order m ($u_m(S_0)$). Time is in milliseconds. ($\nu = n_\gamma/2$, $\zeta_1 = \zeta_3$ and $\zeta_2 = \zeta_4$.)

s	m	n_k	n_x	n_γ	λ	ζ_3	ζ_4	R_3	R_4	Error	Time
0.01	7	2	0	5	0	4.50	0.75	7.75	3.25	0.57D−10	0.97
0.25	8	2	0	5	0	1.50	1.75	5.75	3.25	0.48D−13	1.08
0.50	5	2	0	5	0	0.75	1.50	2.75	1.45	0.37D−11	0.71
0.75	5	2	0	5	0	0.75	1.50	2.75	1.45	0.25D−11	0.74
0.99	3	2	0	5	0	3.25	2.50	6.75	2.45	0.18D−12	0.47
0.25	4	6	2	11	3	0.50	1.25	8.75	4.50	0.43D−09	1.53
0.01	5	6	4	13	4	0.25	1.50	3.75	1.50	0.64D−10	2.32
0.99	4	7	5	15	5	1.25	1.75	1.25	4.75	0.28D−11	2.40

Table 3. Evaluation of $\tilde{\mathcal{T}}(s)$, equation (26), using the epsilon-algorithm of Wynn of order m (ϵ_m^0). Time is in milliseconds. ($\nu = n_\gamma/2$, $\zeta_1 = \zeta_3$ and $\zeta_2 = \zeta_4$.)

s	m	n_k	n_x	n_γ	λ	ζ_3	ζ_4	R_3	R_4	Error	Time
0.01	6	2	0	5	0	4.50	0.75	7.75	3.25	0.91D−09	0.83
0.25	8	2	0	5	0	1.50	1.75	5.75	3.25	0.38D−10	1.09
0.50	4	2	0	5	0	0.75	1.50	2.75	1.45	0.26D−09	0.59
0.75	4	2	0	5	0	0.75	1.50	2.75	1.45	0.35D−09	0.60
0.99	4	2	0	5	0	3.25	2.50	6.75	2.45	0.21D−13	0.59
0.25	4	6	2	11	3	0.50	1.25	8.75	4.50	0.11D−08	1.53
0.01	6	6	4	13	4	0.25	1.50	3.75	1.50	0.22D−10	2.64
0.99	4	7	5	15	5	1.25	1.75	1.25	4.75	0.17D−10	2.38

Table 4. Evaluation of $\tilde{\mathcal{H}}(s)$, equation (37), using the $\bar{D}$-transformation of order m ($\bar{D}_m^{(4)}$), equation (34). Time is in milliseconds. ($\nu = n_\gamma/2$ and $s = 0.99$.)

m	n_k	n_x	n_γ	λ	ζ_1	ζ_2	ζ_3	ζ_4	R_1	Error	Time
3	2	0	5	0	1.00	1.00	1.00	1.00	6.50	0.441D−11	0.15
3	2	0	5	0	0.75	1.50	0.75	1.50	7.75	0.599D−10	0.15
3	3	1	7	1	1.25	2.50	1.25	2.50	2.00	0.200D−12	0.15
3	4	2	9	2	0.75	0.25	0.75	0.25	5.00	0.346D−10	0.15
4	4	2	9	2	0.75	0.25	0.75	0.25	5.00	0.533D−14	0.28
2	6	2	11	3	1.50	1.75	1.50	1.75	2.05	0.236D−15	0.07
2	6	4	13	4	0.25	2.50	0.25	2.50	2.25	0.541D−10	0.07
3	7	5	15	5	0.50	1.75	0.50	1.75	1.75	0.568D−13	0.15

Table 5. Evaluation of $\tilde{\mathcal{H}}(s)$, equation (37), using Levin's u-transform of order m ($u_m(S_0)$). Time is in milliseconds. ($\nu = n_\gamma/2$ and $s = 0.99$.)

m	n_k	n_x	n_γ	λ	ζ_1	ζ_2	ζ_3	ζ_4	R_1	Error	Time
7	2	0	5	0	1.00	1.00	1.00	1.00	6.50	0.239D−11	0.91
8	2	0	5	0	0.75	1.50	0.75	1.50	7.75	0.184D−10	1.05
6	3	1	7	1	1.25	2.50	1.25	2.50	2.00	0.621D−12	1.17
8	4	2	9	2	0.75	0.25	0.75	0.25	5.00	0.242D−10	2.06
8	4	2	9	2	0.75	0.25	0.75	0.25	5.00	0.242D−10	2.06
5	6	2	11	3	1.50	1.75	1.50	1.75	2.05	0.571D−15	1.78
6	6	4	13	4	0.25	2.50	0.25	2.50	2.25	0.327D−10	2.67
5	7	5	15	5	0.50	1.75	0.50	1.75	1.75	0.568D−13	2.85

Table 6. Evaluation of $\tilde{\mathcal{H}}(s)$, equation (37), using the epsilon-algorithm of Wynn of order m (ϵ_m^0). Time is in milliseconds. ($\nu = n_\gamma/2$ and $s = 0.99$.)

m	n_k	n_x	n_γ	λ	ζ_1	ζ_2	ζ_3	ζ_4	R_1	Error	Time
8	2	0	5	0	1.00	1.00	1.00	1.00	6.50	0.963D−11	1.08
8	2	0	5	0	0.75	1.50	0.75	1.50	7.75	0.444D−10	1.06
8	3	1	7	1	1.25	2.50	1.25	2.50	2.00	0.541D−12	1.54
8	4	2	9	2	0.75	0.25	0.75	0.25	5.00	0.428D−09	2.07
8	4	2	9	2	0.75	0.25	0.75	0.25	5.00	0.428D−09	2.06
6	6	2	11	3	1.50	1.75	1.50	1.75	2.05	0.375D−15	2.06
6	6	4	13	4	0.25	2.50	0.25	2.50	2.25	0.730D−09	2.67
8	7	5	15	5	0.50	1.75	0.50	1.75	1.75	0.568D−13	4.28

Table 7. Evaluation of $\mathcal{T}$, equation (25), using the $\bar{D}$-transformation of order m ($\bar{D}_m^{(4)}$), equation (34). Time is in milliseconds. ($\nu = n_\gamma/2$, $\mu = 0$, $\zeta_1 = \zeta_3$ and $\zeta_2 = \zeta_4$.)

m	n_{33}	n_{44}	n_k	n_x	n_γ	λ	ζ_3	ζ_4	R_3	R_4	Error	Time
3	1	1	2	0	5	0	4.50	0.75	7.75	3.25	0.66D−14	2.38
3	1	1	2	0	5	0	1.50	1.75	5.75	3.25	0.30D−14	2.40
4	2	1	3	1	7	1	3.25	2.50	6.75	2.45	0.75D−14	4.55
4	2	2	4	2	9	2	1.25	2.45	8.75	4.45	0.34D−15	4.54
2	3	2	6	2	11	3	0.50	1.25	8.75	4.50	0.15D−11	1.03
2	4	3	6	4	15	4	0.25	1.50	5.75	1.50	0.00D + 00	0.99
3	4	4	6	5	17	5	2.25	2.00	6.00	5.75	0.11D−11	2.38

Table 8. Evaluation of $\mathcal{T}$, equation (25), using Levin's u-transform of order m ($u_m(S_0)$). Time is in milliseconds. ($\nu = n_\gamma/2$, $\mu = 0$, $\zeta_1 = \zeta_3$ and $\zeta_2 = \zeta_4$.)

m	n_{33}	n_{44}	n_k	n_x	n_γ	λ	ζ_3	ζ_4	R_3	R_4	Error	Time
6	1	1	2	0	5	0	4.50	0.75	7.75	3.25	0.34D−13	13.10
7	1	1	2	0	5	0	1.50	1.75	5.75	3.25	0.31D−13	14.97
8	2	1	3	1	7	1	3.25	2.50	6.75	2.45	0.75D−14	24.82
8	2	2	4	2	9	2	1.25	2.45	8.75	4.45	0.35D−15	33.52
4	3	2	6	2	11	3	0.50	1.25	8.75	4.50	0.22D−11	24.13
5	4	3	6	4	15	4	0.25	1.50	5.75	1.50	0.11D−15	42.00
5	4	4	6	5	17	5	2.25	2.00	6.00	5.75	0.11D−11	51.62

Table 9. Evaluation of $\mathcal{T}$, equation (25), using the epsilon-algorithm of Wynn of order m (ϵ_m^0). Time is in milliseconds. ($\nu = n_\gamma/2$, $\mu = 0$, $\zeta_1 = \zeta_3$ and $\zeta_2 = \zeta_4$.)

m	n_{33}	n_{44}	n_k	n_x	n_γ	λ	ζ_3	ζ_4	R_3	R_4	Error	Time
6	1	1	2	0	5	0	4.50	0.75	7.75	3.25	0.93D−13	13.72
8	1	1	2	0	5	0	1.50	1.75	5.75	3.25	0.20D−13	17.64
8	2	1	3	1	7	1	3.25	2.50	6.75	2.45	0.75D−14	25.25
8	2	2	4	2	9	2	1.25	2.45	8.75	4.45	0.31D−15	33.94
6	3	2	6	2	11	3	0.50	1.25	8.75	4.50	0.14D−11	34.29
4	4	3	6	4	15	4	0.25	1.50	5.75	1.50	0.67D−13	35.32
6	4	4	6	5	17	5	2.25	2.00	6.00	5.75	0.11D−11	60.56

Table 10. Evaluation of $\mathcal{K}_{n_1 00, n_3 00}^{n_2 00, n_4 00}$, equation (24) using the $\bar{D}$-transformation of order m ($\bar{D}_m^{(4)}$), equation (34). Time is in milliseconds. ($\vec{R}_3 = (R_3, 0, 0)$ and $\vec{R}_4 = (R_4, 0, 0)$.)

m	n_1	n_2	n_3	n_4	ζ_1	ζ_2	ζ_3	ζ_4	R_3	R_4	Error	Time
3	1	1	1	1	2.50	1.25	4.50	0.75	7.50	2.00	0.79D−10	2.35
3	2	1	2	1	1.50	0.25	4.25	3.75	2.50	1.25	0.14D−13	2.37
3	2	2	2	2	3.45	0.25	1.50	0.50	3.50	1.50	0.15D−10	2.35
3	3	2	3	2	5.00	2.75	0.75	3.50	4.50	2.50	0.34D−10	2.32
4	3	3	3	3	1.95	3.45	1.50	1.50	5.00	3.25	0.34D−12	4.50
3	4	3	4	3	3.50	4.00	3.45	2.75	3.50	2.00	0.90D−09	2.33

All the finite integrals involved in (24), (25), (28), (34), (38) were evaluated using Gauss–Legendre quadrature of order 16.

The set of equations (34) used in the $\bar{D}$-transformation is solved using Gaussian elimination with maximal column pivoting.

Table 11. Evaluation of $\mathcal{K}^{n_2 00, n_4 00}_{n_1 00, n_3 00}$, equation (24), using Levin's u-transform of order m ($u_m(S_0)$). Time is in milliseconds. ($\vec{R}_3 = (R_3, 0, 0)$, $\vec{R}_4 = (R_4, 0, 0)$.)

m	n_1	n_2	n_3	n_4	ζ_1	ζ_2	ζ_3	ζ_4	R_3	R_4	Error	Time
6	1	1	1	1	2.50	1.25	4.50	0.75	7.5	2.00	0.45D−09	13.00
6	2	1	2	1	1.50	0.25	4.25	3.75	2.5	1.25	0.31D−11	16.50
8	2	2	2	2	3.45	0.25	1.50	0.50	3.5	1.50	0.36D−10	26.46
8	3	2	3	2	5.00	2.75	0.75	3.50	4.5	2.50	0.25D−09	32.52
7	3	3	3	3	1.95	3.45	1.50	1.50	5.0	3.25	0.74D−08	34.94
7	4	3	4	3	3.50	4.00	3.45	2.75	3.5	2.00	0.10D−08	41.70

Table 12. Evaluation of $\mathcal{K}^{n_2 00, n_4 00}_{n_1 00, n_3 00}$, equation (24), using the epsilon-algorithm of Wynn of order m (ϵ^0_m). Time is in milliseconds. ($\vec{R}_3 = (R_3, 0, 0)$, $\vec{R}_4 = (R_4, 0, 0)$.)

m	n_1	n_2	n_3	n_4	ζ_1	ζ_2	ζ_3	ζ_4	R_3	R_4	Error	Time
6	1	1	1	1	2.50	1.25	4.50	0.75	7.5	2.00	0.13D−08	14.53
6	2	1	2	1	1.50	0.25	4.25	3.75	2.5	1.25	0.12D−10	18.01
8	2	2	2	2	3.45	0.25	1.50	0.50	3.5	1.50	0.37D−09	28.36
8	3	2	3	2	5.00	2.75	0.75	3.50	4.5	2.50	0.32D−08	34.36
8	3	3	3	3	1.95	3.45	1.50	1.50	5.0	3.25	0.14D−06	41.19
8	4	3	4	3	3.50	4.00	3.45	2.75	3.5	2.00	0.24D−08	48.81

The calculation time using the $\bar{D}$-transformation and the other alternatives are computed using an IBM RS 6000 340.

The tabulated numerical results clearly illustrate the speed up obtained with the $\bar{D}$-transformation as compared with its counterparts (Levin's u-transform and the epsilon algorithm of Wynn). This is seen both for the three-centre Coulomb ($\mathcal{K}$) and hybrid ($\mathcal{H}$) two-electron integrals. These results confirm the advantages of the strategy involving $\bar{D}$-transformation as already noted in previous work. The tables compare evaluations to a highly adequate pre-determined accuracy and in general the $\bar{D}^{(4)}_m$ values are more accurate than those obtained with Levin's u-transform and epsilon algorithm of Wynn, whereas the calculation times for the $\bar{D}$ approach are at least 10 times quicker.

Note also that the evaluation of such integrals using the Gauss–Laguerre formulae even to high order leads to limited and insufficient accuracy and prohibitive calculation times.

6. Conclusion

The three-centre Coulomb and hybrid two-electron integrals appear in molecular calculations. An atomic orbitals basis of Slater type functions can be expressed as B functions in order to apply the Fourier transform method.

The analytic expressions of the B functions and their Fourier transforms involved a product of Bessel functions which satisfy linear differential equations are of the form required to apply the D- and $\bar{D}$-transformations used in our previous integral work.

The numerical results show this approach yields values for these integrals to a pre-determined high accuracy and with unprecedented speed.

Acknowledgments

The first author wishes to thank Madame T Chevreau and Monsieur J Lamotte of Laboratoire de Spectrochimie et Catalyse, Caen, for showing interest in this work and for their practical assistance.

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