Non-linear transformations for rapid and efficient evaluation of multicenter bielectronic integrals over B functions

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Received 27 July 1998; revised 26 April 1999

This work presents an extremely efficient non-linear transformation based on a certain Hankel type transform, originally due to A. Sidi. The approach is applied to evaluating Coulomb integrals in the molecular context. These integrals are bielectronic one-, two-, three- and four-center terms arising from the interactions of electron distributions over a Slater type orbital basis. They occur in many millions of terms, even for small molecules, and require rapid and accurate evaluation. The present work shows how we can reduce the order of the linear differential equation required to be satisfied by the integrand considerably. Calculation times as short as 10^{-2} ms were obtained for four-center terms (the least favorable case) on an IBM RS6000-340 workstation. This method represents a considerable advance on previous work on Coulomb integrals.

1. Introduction

In many problems of applied mathematics and physics, one has often to deal with infinite series and infinite integrals to represent solutions obtained. Very often in practice these integrals and series have poor convergence: a serious drawback to their effective use. Therefore non-linear transformation methods for accelerating the convergence of infinite integrals and series have been studied for many years and applied to various situations. They form the basis of new methods for solving various problems otherwise non-tractable and also have many applications [12,13,72]. Their utility for enhancing and even inducing convergence has been amply demonstrated by Shanks [58].

Multicenter integrals are the rate limiting step in determining electronic structure for molecules, which are usually carried out using the LCAO MO approach [53]. The integrals contribute to the total energy of the molecule which is required to a precision sufficient for small fractional changes to be evaluated reliably, e.g., a chemical reaction in which a minor electronic rearrangement occurs. In practice, the precision threshold

for the total energy is of order 10^{-3} atomic units and, therefore, individual integrals must be accurate to 10^{-6}–10^{-10} au.

The choice of a basis set for the expansion of atomic orbitals is important in this approach [16,37]. A good atomic orbital basis should satisfy Kato's conditions for analytical solutions of the appropriate Schrödinger equation [1,2,36].

A good basis set for molecular orbitals should also satisfy two pragmatic requirements:

(1) A simple expansion of the atomic orbitals in terms of the basis functions should exist and yield a good accuracy.

(2) The molecular multicenter integrals should be computed efficiently.

Currently, the most popular functions used in *ab initio* calculations are the so-called Gaussian type orbitals (GTOs) [11,25,57]. This is due to the fact that with GTOs the numerous molecular integrals can be evaluated rather easily. Unfortunately, these GTO basis functions fail to satisfy the above mathematical conditions for atomic electronic distributions [16,37]. Exponential type orbitals (ETOs) are better suited than GTOs to represent electron wave functions near the nucleus and at long range, provided that multicenter integrals using such functions could be computed efficiently. The ETOs show the same behavior as exact solutions of atomic and molecular Schrödinger equations satisfying Kato's conditions [36,51,75].

Among the ETFs, Slater type functions (STFs) [10,26,34,35,48–50,64,70,75] are certainly the simplest analytical functions, hence they have a dominating position, but the use of STFs has been prevented by the fact that their multicenter integrals are extremely difficult to evaluate for polyatomic molecules, particularly bielectronic terms. Various studies have focussed on the use of B functions that have been proposed by Shavitt [59] and introduced by Filter and Steinborn [20,65]. These functions can be expressed as linear combinations of STFs [18,79]. Although B functions are more complicated than STFs, they have properties applicable to multicenter integral problems [18,20,44,65,78,79]. It is shown that B functions possess a relatively simple addition theorem [18], extremely compact convolution integrals [19,20], and they are well adapted to the Fourier transform method originally introduced by Prosser and Blanchard [47] and Bonham et al. [5,6] and which is one of the most successful methods for the evaluation of multicenter integrals [8,9,21–24,27–32,66,67,71,76,80].

In previous work, we have shown the efficiency of the non-linear transformations D due to Levin and Sidi [40], and $\overline{D}$ due to Sidi [60–63], in evaluating one- and two-electron multicenter integrals over B functions [54–56]. These transformations are efficient in the evaluation of infinite oscillatory integrals whose integrands satisfy linear differential equations with coefficients that have asymptotic expansions in inverse powers of their arguments.

By applying the Fourier transform method to the one- and two-electron multicenter integrals using a basis set of B functions, one can obtain analytical expressions involving semi-infinite oscillatory integrals [22,23,28,71], whose integrands satisfy linear differential equations of order 4 or 6, respectively, and of the form required to apply

the D and $\overline{D}$ transformations [54–56]. The number of calculations depends on the order of the linear differential equation that the integrands of interest satisfy. The approximations of $S = \int_0^\infty f(t)\,\mathrm{d}t$ using these transformations are given by $D_n^{(m)}$ and $\overline{D}_n^{(m)}$, which, as n becomes large, converge very quickly to the exact value of S and where m is the order of the differential equation that $f(x)$ satisfies [40,60–63]. These approximations are obtained by solving a set of equations of order $nm+1$ or $n(m-1)+1$, respectively, and where we need to calculate the m successive derivatives of $f(x)$ [40,60,62,63], which presents severe mathematical and computational difficulties for some complicated functions as we showed in [53–55], for the integrands involved in the one- and two-electron multicenter integrals which satisfy a fourth- or sixth-order linear differential equations, respectively, especially with large values of the quantum numbers.

Because millions of integrals are required for molecules of interest, the present work concentrates on how one can reduce the calculation time for a given high predetermined accuracy by reducing the order of the linear differential equations that the integrands of interest satisfy using some properties of the spherical Bessel functions and the reduced Bessel functions, involved in the analytical expressions of these integrands.

In this work, the symbols HD and $H\overline{D}$ specify that the D and $\overline{D}$ are used with the order of the requisite differential equation reduced to two.

2. General definitions and some properties

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

$$a(x) \sim x^\gamma \left(\alpha_0 + \frac{\alpha_1}{x} + \frac{\alpha_2}{x^2} + \cdots \right), \tag{1}$$

and their derivatives of any order have asymptotic expansions, which can be obtained by differentiating that in equation (1) formally term by term.

We define the function (ν, m) by [74]

$$(\nu, m) = (-1)^m \frac{(1/2-\nu)_m (1/2+\nu)_m}{m!} = \frac{\Gamma(\nu+m+1/2)}{m!\Gamma(\gamma-m+1/2)}, \tag{2}$$

where Γ stands for the Gamma function [12] and $(\alpha)_n$ represents the Pochhammer symbol, which is defined by [74]

$$\begin{cases} (\alpha)_0 = 1, \\ (\alpha)_n = \alpha(\alpha+1)(\alpha+2)\cdots(\alpha+n-1) = \frac{\Gamma(\alpha+n)}{\Gamma(\alpha)}. \end{cases} \tag{3}$$

The surface spherical harmonic $Y_l^m(\theta,\varphi)$ is defined explicitely using the Cordon and Shortley phase convention as follows [15]:

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

where $P_l^m(x)$ is an associated Legendre function of lth degree and mth order, which is expressed by means of the well-known Legendre polynomials [12]:

$$P_l^m(x) = \left(1-x^2\right)\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^{m/2} P_l(x) = \left(1-x^2\right)\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^{m/2}\left[\frac{(1-x^2)^l}{2^l l!}\right]. \tag{5}$$

The B functions are defined as follows [20]:

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

where the reduced Bessel function $\widehat{k}_{n-1/2}(\zeta r)$ is defined as [20,65]

$$\widehat{k}_{n-1/2}(\zeta r) = \sqrt{\frac{2}{\pi}}(\zeta r)^{n-1/2} K_{n-1/2}(\zeta r) \tag{7}$$

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

where $K_{n-1/2}$ stands for the modified Bessel function of the second kind.

The Fourier transform $\overline{B}_{n,l}^m(\zeta,\vec{p})$ of $B_{n,l}^m(\zeta\vec{r})$ is given by [18,78]

$$\overline{B}_{n,l}^m(\zeta,\vec{p}) = \frac{1}{(2\pi)^{3/2}}\int_{\vec{r}} \mathrm{e}^{-\mathrm{i}\vec{p}.\vec{r}} B_{n,l}^m(\zeta\vec{r})\,\mathrm{d}\vec{r} \tag{9}$$

$$= \sqrt{\frac{2}{\pi}}\,\zeta^{2n+l-1}\,\frac{(-\mathrm{i}|p|)^l}{(\zeta^2+|p|^2)^{n+l+1}}\,Y_l^m(\theta_{\vec{p}},\varphi_{\vec{p}}). \tag{10}$$

The analytical form of the Fourier transform of $B_{n,l}^m(\zeta\vec{r})$, equation (10), is obtained by inserting the well-known Rayleigh expansion of the plane wave function in equation (9) [43]:

$$\mathrm{e}^{\pm\mathrm{i}\vec{p}.\vec{r}} = \sum_{l=0}^{+\infty}\sum_{m=-l}^{l} 4\pi(\pm\mathrm{i})^\lambda j_l\left(|\vec{p}|\,|\vec{r}|\right) Y_l^m(\theta_{\vec{r}},\varphi_{\vec{r}})\left[Y_l^m(\theta_{\vec{p}},\varphi_{\vec{p}})\right]^*. \tag{11}$$

The spherical Bessel function $j_l(z)$ satisfies the recurrence formulae given by [4]

$$\begin{cases} z j_{l-1}(z) + z j_{l+1}(z) = (2l+1) j_l(z), \\ l j_{l-1}(z) - (l+1) j_{l+1}(z) = (2l+1) j_l'(z). \end{cases} \tag{12}$$

The Fourier integral representation of the Coulomb operator $1/|\vec{r}-\vec{R}_1|$ is given by [7]

$$\frac{1}{|\vec{r}-\vec{R}_1|}=\frac{1}{2\pi^2}\int_{\vec{k}}\frac{\mathrm{e}^{-\mathrm{i}\vec{k}.(\vec{r}-\vec{R}_1)}}{k^2}\,\mathrm{d}\vec{k}. \tag{13}$$

The three-center nuclear attraction integrals over B functions are defined as [22, 23,28,71]

$$\mathcal{I}_{n_1,l_1,m_1}^{n_2,l_2,m_2}=\int\left[B_{n_1,l_1}^{m_1}\left(\zeta_1\vec{r}\right)\right]^*\frac{1}{|\vec{r}-\vec{R}_1|}B_{n_2,l_2}^{m_2}\left[\zeta_2\left(\vec{r}-\vec{R}_2\right)\right]\mathrm{d}\vec{r}. \tag{14}$$

The two-electron multicenter integrals over B functions are defined as [22,23,28, 71]

$$\begin{aligned}\mathcal{J}_{n_1l_1m_1,n_3l_3m_3}^{n_2l_2m_2,n_4l_4m_4}=&\int\left[B_{n_1l_1}^{m_1}\left(\zeta_1\left(\vec{r}-\vec{R}_1\right)\right)\right]^*\left[B_{n_3l_3}^{m_3}\left(\zeta_3\left(\vec{r}'-\vec{R}_3\right)\right)\right]^*\frac{1}{|\vec{r}-\vec{r}'|}\\&\times B_{n_2l_2}^{m_2}\left[\zeta_2\left(\vec{r}-\vec{R}_2\right)\right]B_{n_4l_4}^{m_4}\left[\zeta_4\left(\vec{r}'-\vec{R}_4\right)\right]\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}'.\end{aligned} \tag{15}$$

3. The non-linear D and $\overline{D}$ transformations

Theorem ([40,60,62,63]). Let $f(x)$ be integrable on $[0,\infty)$ and satisfy a linear differential equation of order m of the form

$$f(x)=\sum_{k=1}^{m}p_k(x)f^{(k)}(x),\quad p_k\in A^{(i_k)},\ i_k\leqslant k. \tag{16}$$

Let also

$$\lim_{x\to+\infty}p_k^{(i-1)}(x)f^{(k-i)}(x)=0,\quad i\leqslant k\leqslant m,\ 1\leqslant i\leqslant m. \tag{17}$$

If, for every integer $l\geqslant -1$,

$$\sum_{k=1}^{m}l(l-1)\cdots(l-k+1)p_{k,0}\neq 1,\quad p_{k,0}=\lim_{x\to+\infty}x^{-k}p_k(x), \tag{18}$$

then the approximation $D_n^{(m)}$ to $S=\int_0^\infty f(t)\,\mathrm{d}t$, using the D transformation, satisfies the $N=1+mn$ equations given by [40,60,62,63]

$$D_n^{(m)}=\int_0^{x_l}f(t)\,\mathrm{d}t+\sum_{k=0}^{m-1}f^{(k)}(x_l)x_l^{\sigma_k}\sum_{i=0}^{n-1}\frac{\overline{\beta}_{i,k}}{x_l^i},\quad l=0,1,2,\ldots,mn. \tag{19}$$

$D_n^{(m)}$ and the $\overline{\beta}_{k,i}$ for $k=0,1,\ldots,m-1$, $i=0,1,\ldots,n-1$, are the N unknowns. The x_l are chosen to satisfy $0<x_0<x_1<\cdots<x_{mn}$ and $\lim_{l\to+\infty}x_l=+\infty$. σ_k is the minimum of $k+1$ and s_k, where s_k is the largest of the integers s for which $\lim_{x\to+\infty}x^sf^{(k)}(x)=0$.

Now, if we choose x_l for $l = 0, 1, 2, \ldots, mn$ to be the zeros of $f(x)$, then we can reduce the order of the above set of equations to $N = 1 + n(m-1)$, which can be re-written as [60,63]

$$\overline{D}_n^{(m)} = \int_0^{x_l} f(t)\,\mathrm{d}t + \sum_{k=1}^{m-1} f^{(k)}(x_l) x_l^{\sigma_k} \sum_{i=0}^{n-1} \frac{\overline{\beta}_{i,k}}{x_l^i}, \quad l = 0, 1, 2, \ldots, (m-1)n. \tag{20}$$

In most cases, the D and $\overline{D}$ transformations produce approximations $D_n^{(m)}$ and $\overline{D}_n^{(m)}$ which converge very quickly to the exact value of $S = \int_0^\infty f(t)\,\mathrm{d}t$ as n becomes large [40,60,63].

Now, following Sidi [60], we consider the integral $\int_0^\infty f(t)\,\mathrm{d}t$, where

$$f(x) = g(x) j_\lambda(x); \tag{21}$$

$j_\lambda(x)$ stands for the spherical Bessel function of order λ ($\lambda \in \mathbb{N}$) and $g(x)$ is of the form

$$g(x) = h(x)\,\mathrm{e}^{\phi(x)} \tag{22}$$

such that $\phi(x)$ as $x \to +\infty$ is a real polynomial in x of degree $k \geqslant 0$ for some integer k and $h(x) \in A^{(\gamma)}$ for some γ.

If $k > 0$, then for $g(x)$ to be integrable at infinity $\lim_{x\to+\infty} \phi(x) = -\infty$ is necessary. If $k = 0$, then $g(x) \in A^{(\gamma)}$, hence $\gamma < 1$ in order for $f(x)$ to be integrable at infinity.

$j_\lambda(x)$ satisfies the differential equation given by [4]

$$j_\lambda(x) = -\frac{2x}{x^2 - \lambda^2 - \lambda}\, j'_\lambda(x) - \frac{x^2}{x^2 - \lambda^2 - \lambda}\, j''_\lambda(x). \tag{23}$$

Using the fact that $f(x) = g(x) j_\lambda(x)$, we have $j_\lambda(x) = f(x)/g(x)$. Substituting this in the differential equation above, we obtain

$$f(x) = p_1(x) f'(x) + p_2(x) f''(x), \tag{24}$$

where

$$p_1(x) = \frac{2x^2(h'(x)/h(x) + \phi') - 2x}{w(x)}, \qquad p_2(x) = \frac{-x^2}{w(x)} \tag{25}$$

and

$$\begin{aligned} w(x) = -x^2 \left[\left(\frac{h'(x)}{h(x)} + \phi' \right)' - \left(\frac{h'(x)}{h(x)} + \phi' \right)^2 \right] - 2x \left(\frac{h'(x)}{h(x)} + \phi' \right) \\ + x^2 - \lambda^2 - \lambda. \end{aligned} \tag{26}$$

If $k = 0$, then $p_1(x) \in A^{(-1)}$ and $p_2(x) \in A^{(0)}$.

If $k > 0$, then $p_1(x) \in A^{(-k+1)}$ and $p_2(x) \in A^{(-2k+2)}$.

In all these cases,

$$\lim_{x\to+\infty} p_k^{(i-1)}(x) f^{(k-i)}(x) = 0 \quad \text{for } k = i, 2,\ i = 1, 2,$$

$$p_{k,0} = \lim_{x\to+\infty} x^{-k} p_k(x) = 0 \quad \text{for } k = 1, 2;$$

then, for every integer $l \geqslant -1$,

$$\sum_{k=1}^{2} l(l-1)\cdots(l-k+1)p_{k,0} = 0 \neq 1.$$

The conditions of the applicability of the D and $\overline{D}$ transformations to accelerate the convergence of $\int_0^{+\infty} f(t)\,\mathrm{d}t$ can now be shown to be satisfied. The approximation $HD_n^{(2)}$ of $S = \int_0^{+\infty} f(t)\,\mathrm{d}t$ using the D transformation is given by

$$HD_n^{(2)} = \int_0^{x_l} f(t)\,\mathrm{d}t + \sum_{k=0}^{1} \big(g(x_l) j_\lambda(x_l)\big)^{(k)} x_l^{\sigma_k} \sum_{i=0}^{n-1} \frac{\overline{\beta}_{i,k}}{x_l^i}, \quad l = 0, 1, 2, \ldots, n. \tag{27}$$

If we choose $x_l = j_\lambda^{l+1}$ for $l = 0, 1, 2, \ldots, n$, where j_λ^l is the zero of order l of the spherical Bessel function $j_\lambda(x)$, j_λ^0 is assumed to be 0. The approximation $H\overline{D}_n^{(2)}$ of $S = \int_0^{\infty} f(t)\,\mathrm{d}t$ using the $\overline{D}$ transformation is given by

$$H\overline{D}_n^{(2)} = \int_0^{x_l} f(t)\,\mathrm{d}t + g(x_l) j'_\lambda(x_l) x_l^{\sigma_1} \sum_{i=0}^{n-1} \frac{\overline{\beta}_{i,1}}{x_l^i}, \quad l = 0, 1, 2, \ldots, n. \tag{28}$$

4. One- and two-electron multicenter integrals over B functions

By applying the Fourier transform method after substituting the integral representation of the Coulomb operator, equation (13), and the analytical expression of B functions, equation (6), into equations (14) and (15) and using the Rayleigh expansion of the plane wave functions, equation (11), one can obtain expressions for these integrals, involving very oscillatory semi-infinite integrals which present severe numerical and computational difficulties [22,23,28,71]. In previous work [54–56], we demonstrated the superiority of the D and $\overline{D}$ transformations in the evaluation of these semi-infinite integrals compared with alternatives using the Gauss–Laguerre formulae, the epsilon algorithm of Wynn [81,82] and Levin's u-transform [38,39]. The purpose of the present work is to reduce the calculation time for a high predetermined accuracy.

4.1. Three-center nuclear attraction integrals

The expression for these integrals is [22,23,28,71]

$$n_\gamma = 2(n_1 + l_1 + n_2 + l_2) - \left(l'_1 + l'_2\right) - l + 1,$$

$$
\begin{aligned}
&\big[\gamma(s,x)\big]^2 = (1-s)\zeta_1^2 + s\zeta_2^2 + s(1-s)x^2,\\
&\mu_{i1} = \max\big(-l_i', m_i - l_i + l_i'\big) \quad \text{for } i = 1,2,\\
&\mu_{i2} = \min\big(l_i', m_i + l_i - l_i'\big) \quad \text{for } i = 1,2,\\
&\nu = n_1 + n_2 + l_1 + l_2 - l - j + 1/2,\\
&\lambda_1 = \big|\big(l_1 - l_1'\big) - \big(l_2 - l_2'\big)\big|, \qquad \lambda_2 = \big|\big(l_1 - l_1'\big) + \big(l_2 - l_2'\big)\big|,\\
&\mu = m_2 - m_2' - m_1 + m_1', \qquad n_x = l_1 - l_1' + l_2 - l_2',\\
&\Delta l' = \big[\big(l_1' + l_2' - l\big)/2\big], \qquad \vec{v} = (1-s)\vec{R}_2 - \vec{R}_1,
\end{aligned}
$$

$$
\begin{aligned}
\mathcal{I}_{n_1,l_1,m_1}^{n_2,l_2,m_2} = {} & 8(4\pi)^2(2l_1+1)!!(2l_2+1)!!\\
&\times \frac{(n_1+l_1+n_2+l_2+1)!}{(n_1+l_1)!}\,\zeta_1^{2n_1+l_1-1}\zeta_2^{2n_2+l_2-1}\\
&\times \sum_{l_1'=0}^{l_1}\sum_{m_1'=\mu_{11}}^{\mu_{12}} \mathrm{i}^{l_1+l_1'}(-1)^{l_1'}\,\frac{\langle l_1 m_1 | l_1' m_1' | l_1 - l_1' m_1 - m_1'\rangle}{(2l_1'+1)!![2(l_1-l_1')+1]!!}\\
&\times \sum_{l_2'=0}^{l_2}\sum_{m_2'=\mu_{21}}^{\mu_{22}} \mathrm{i}^{l_2+l_2'}(-1)^{l_2'}\,\frac{\langle l_2 m_2 | l_2' m_2' | l_2 - l_2' m_2 - m_2'\rangle}{(2l_2'+1)!![2(l_2-l_2')+1]!!}\\
&\times \sum_{l=|l_1'-l_2'|}^{|l_1'+l_2'|} \big\langle l_2' m_2' \big| l_1' m_1' \big| l m' 2 - m_1'\big\rangle R_2^l Y_l^{m_2'-m_1'}(\theta_{\vec{R}_2},\varphi_{\vec{R}_2})\\
&\times \sum_{\lambda=\lambda_1}^{\lambda_2} (-\mathrm{i})^{\lambda}\big\langle l_2 - l_2' m_2 - m_2' \big| l_1 - l_1' m_1 - m_1' \big| \lambda\mu\big\rangle\\
&\times \sum_{j=0}^{\Delta l'}(-1)^j \binom{\Delta l'}{j}\,\frac{1}{2^{n_1+n_2+l_1+l_2-j+1}(n_1+n_2+l_1+l_2-j+1)!}\\
&\times \int_{s=0}^{1} s^{n_2+l_1+l_2-l_1'}(1-s)^{n_1+l_1+l_2-l_2'} Y_\lambda^{(m_2-m_2')-(m_1-m_1')}(\theta_{\vec{v}},\varphi_{\vec{v}})\\
&\times \int_{x=0}^{+\infty} x^{n_x}\,\frac{\widehat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\,j_\lambda(vx)\,\mathrm{d}x\,\mathrm{d}s. \qquad (29)
\end{aligned}
$$

Let us consider the two-dimensional integral representation involved in the above equation, which will be referred to as $\widetilde{\mathcal{I}}$:

$$
\widetilde{\mathcal{I}} = \int_{s=0}^{1} s^{i_2}(1-s)^{i_1} Y_\lambda^{m_{12}}(\theta_{\vec{v}},\varphi_{\vec{v}}) \int_{x=0}^{+\infty} x^{n_x}\,\frac{\widehat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}}\,j_\lambda(vx)\,\mathrm{d}x\,\mathrm{d}s, \qquad (30)
$$

where i_1, i_2, m_{12}, n_x, ν, n_γ, λ, v and $\gamma(s,x)$ are defined according to equation (29).

Consider the semi-infinite x integral involved in the above equation, which will be referred to as $\widetilde{\mathcal{I}}(s)$:

$$\widetilde{\mathcal{I}}(s) = \int_0^{+\infty} x^{n_x} \frac{\widehat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(vx)\,\mathrm{d}x \tag{31}$$

$$= \sum_{n=0}^{+\infty} \int_{j_{\lambda,v}^n}^{j_{\lambda,v}^{n+1}/v} x^{n_x} \frac{\widehat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(vx)\,\mathrm{d}x, \tag{32}$$

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

The integrand is of the form

$$F_a(x) = x^{n_x} \frac{\widehat{k}_\nu[R_2\gamma(s,x)]}{\gamma(s,x)^{n_\gamma}} j_\lambda(vx) \tag{33}$$

$$= g_a(x) j_\lambda(vx), \tag{34}$$

where

$$g_a(x) = x^{n_x} \frac{\widehat{k}_\nu[R_2\gamma(s,x)]}{\gamma(s,x)^{n_\gamma}}. \tag{35}$$

In [56] we showed that the integrand $F_a(x)$ satisfies a fourth-order linear differential equation satisfying the conditions of applicability of D and $\overline{D}$ transformations. The approximations $D_n^{(4)}$ and $\overline{D}_n^{(4)}$ of $\widetilde{\mathcal{I}}(s)$ are obtained by solving sets of equations of order $4n+1$ or $3n+1$, respectively, of the form given by equations (19), (20), where the first three successive derivatives are required.

Let us consider $g_a(x)$. Assuming that

$$z = R_2\gamma(s,x) = R_2\sqrt{(1-s)\zeta_1^2 + s\zeta_2^2 + s(1-s)x^2},$$

$$z \sim R_2\sqrt{s(1-s)}\,x, \quad \text{as } x \to +\infty,$$

$\widehat{k}_\nu(z)$ has an asymptotic expansion in inverse powers of z which is given by [74]

$$\widehat{k}_\nu(z) \sim z^{\nu-1/2}\,\mathrm{e}^{-z} \sum_{m=0}^{+\infty} \frac{(\nu,m)}{(2z)^m}. \tag{36}$$

Substituting z by $R_2\sqrt{s(1-s)}\,x$ in equation (36) one can easily show that, as $x \to +\infty$,

$$g_a(x) \sim R_2^{\nu-1/2}\big(\sqrt{s(1-s)}\big)^{\nu-n_\gamma-1/2} x^{n_x+\nu-n_\gamma-1/2} \times \mathrm{e}^{-R_2\sqrt{s(1-s)}\,x} \sum_{m=0}^{+\infty} \frac{(\nu,m)}{(2R_2\sqrt{s(1-s)}\,x)^m}. \tag{37}$$

Thus, $g_a(x)$ can be written as $h(x)\,\mathrm{e}^{\phi(x)}$, where

$$\begin{cases} h(x) \in A^{(\delta)}, \quad \delta = n_x + \nu - n_\gamma - 1/2, \\ \phi(x) \sim -R_2\sqrt{s(1-s)}\,x \quad \text{as } x \to +\infty. \end{cases} \tag{38}$$

Using the previous arguments, we can show that $F_a(x)$ satisfies a second-order linear differential equation of the form

$$F_a(x) = p_1(x)F_a'(x) + p_2(x)F_a''(x), \quad p_1(x), p_2(x) \in A^{(0)}. \tag{39}$$

All the conditions of the applicability of D transformation are satisfied. The approximation $HD_n^{(2)}$ of $\int_0^{+\infty} F_a(x)\,\mathrm{d}x$ can be obtained by solving a set of equations of the form given by equation (27).

Now, if we choose

$$x_l = j_{\lambda,v}^{l+1} = j_\lambda^{l+1}/v \quad \text{for } l = 0, 1, 2, \ldots, n,$$

which are the successive zeros of $j_\lambda(vx)$, the approximation $H\overline{D}_n^{(2)}$ of $S = \int_0^{+\infty} F_a(t)\,\mathrm{d}t$ using $\overline{D}$ transformation can be obtained by solving a set of equations of the form given by equation (28).

4.2. Two-electron multicenter integrals

The expression for these integrals is [22,23,28,71]

$$\begin{aligned}
&\mu = m_2 - m_2' - (m_1 - m_1') + (m_4 - m_4') - (m_3 - m_3'),\\
&\left|(l_1 - l_1') - (l_2 - l_2')\right| \leqslant l_{12} \leqslant (l_1 - l_1') + (l_2 - l_2'),\\
&\left|(l_3 - l_3') - (l_4 - l_4')\right| \leqslant l_{34} \leqslant (l_3 - l_3') + (l_4 - l_4'),\\
&\mu_{1i} = \max(-l_i', m_i - l_i + l_i') \quad \text{for } i = 1, 2, 3, 4,\\
&\mu_{2i} = \min(l_i', m_i + l_i - l_i') \quad \text{for } i = 1, 2, 3, 4,\\
&\left[\gamma_{12}(s,x)\right]^2 = (1-s)\zeta_1^2 + s\zeta_2^2 + s(1-s)x^2,\\
&\left[\gamma_{34}(t,x)\right]^2 = (1-t)\zeta_3^2 + t\zeta_4^2 + t(1-t)x^2,\\
&n_{\gamma_{12}} = 2(n_1 + l_1 + n_2 + l_2) - (l_1' + l_2') - l + 1,\\
&n_{\gamma_{34}} = 2(n_3 + l_3 + n_4 + l_4) - (l_3' + l_4') - l' + 1,\\
&n_x = l_1 - l_1' + l_2 - l_2' + l_3 - l_3' + l_4 - l_4',\\
&v = \left|(1-s)R_{21} - (1-t)R_{43} - R_{31}\right|,\\
&\nu_1 = n_1 + n_2 + l_1 + l_2 - l - j_{12} + 1/2,\\
&\nu_2 = n_3 + n_4 + l_3 + l_4 - l' - j_{34} + 1/2,\\
&\Delta l_{12} = \frac{l_1' + l_2' - l}{2}, \qquad \Delta l_{34} = \frac{l_3' + l_4' - l'}{2},\\
&R_{ij} = R_i - R_j, \quad i, j = 1, 2, 3, 4,
\end{aligned}$$

$$\mathcal{J}^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3} = 8(4\pi)^5(2l_1+1)!!(2l_2+1)!!\,\frac{(n_1+l_1+n_2+l_2+1)!}{(n_1+l_1)!(n_2+l_2)!}$$

$$\times(-1)^{l_1+l_2}(2l_3+1)!!(2l_4+1)!!\,\frac{(n_3+l_3+n_4+l_4+1)!}{(n_3+l_3)!(n_4+l_4)!}\,\zeta_1^{2n_1+l_1-1}\zeta_2^{2n_2+l_2-1}$$

$$\times\zeta_3^{2n_3+l_3-1}\zeta_4^{2n_4+l_4-1}\sum_{l'_1=0}^{l_1}\sum_{m'_1=\mu_{11}}^{\mu_{12}}\mathrm{i}^{l_1+l'_1}\,\frac{\langle l_1m_1|l'_1m'_1|l_1-l'_1m_1-m'_1\rangle}{(2l'_1+1)!![2(l_1-l'_1)+1]!!}$$

$$\times\sum_{l'_2=0}^{l_2}\sum_{m'_2=\mu_{21}}^{\mu_{22}}\mathrm{i}^{l_2+l'_2}(-1)^{l'_2}\,\frac{\langle l_2m_2|l'_2m'_2|l_2-l'_2m_2-m'_2\rangle}{(2l'_2+1)!![2(l_2-l'_2)+1]!!}$$

$$\times\sum_{l'_3=0}^{l_3}\sum_{m'_3=\mu_{31}}^{\mu_{32}}\mathrm{i}^{l_3+l'_3}\,\frac{\langle l_3m_3|l'_3m'_3|l_3-l'_3m_3-m'_3\rangle}{(2l'_3+1)!![2(l_3-l'_3)+1]!!}$$

$$\times\sum_{l'_4=0}^{l_4}\sum_{m'_4=\mu_{41}}^{\mu_{42}}\mathrm{i}^{l_4+l'_4}(-1)^{l'_4}\,\frac{\langle l_4m_4|l'_4m'_4|l_4-l'_4m_4-m'_4\rangle}{(2l'_4+1)!![2(l_4-l'_4)+1]!!}$$

$$\times\sum_{l=|l'_1-l'_2|}^{l'_1+l'_2}\big\langle l'_2m'_2\big|l'_1m'_1\big|lm'2-m'_1\big\rangle R^l_{21}Y_l^{m'_2-m'_1}(\theta_{\vec{R}_{21}},\varphi_{\vec{R}_{21}})$$

$$\times\sum_{l_{12}}\big\langle l_2-l'_2m_2-m'_2\big|l_1-l'_1m_1-m'_1\big|l_{12}m_2-m'_2-\big(m_1-m'_1\big)\big\rangle$$

$$\times\sum_{l'=|l'_3-l'_4|}^{l'_3+l'_4}\big\langle l'_4m'_4\big|l'_3m'_3\big|l'm'4-m'_3\big\rangle R^{l'}_{43}Y_{l'}^{m'_4-m'_3}(\theta_{\vec{R}_{43}},\varphi_{\vec{R}_{43}})$$

$$\times\sum_{l_{34}}\big\langle l_4-l'_4m_4-m'_4\big|l_3-l'_3m_3-m'_3\big|l_{34}m_4-m'_4-\big(m_3-m'_3\big)\big\rangle$$

$$\times\sum_{\lambda=|l_{12}-l_{34}|}^{l_{12}+l_{34}}(-\mathrm{i})^\lambda\big\langle l_{12}m_2-m'_2-\big(m_1-m'_1\big)\big|l_{34}m_4-m'_4-\big(m_3-m'_3\big)\big|\lambda\mu\big\rangle$$

$$\times\sum_{j_{12}=0}^{\Delta l_{12}}\sum_{j_{34}=0}^{\Delta l_{34}}\binom{\Delta l_{12}}{j_{12}}\binom{\Delta l_{34}}{j_{34}}\frac{(-1)^{j_{12}+j_{34}}}{2^{\nu_1+\nu_2+l+l'+1}(\nu_1+1/2+l)!(\nu_2+1/2+l')!}$$

$$\times\int_{s=0}^1\frac{s^{n_2+l_2+l_1}(1-s)^{n_1+l_1+l_2}}{s^{l'_1}(1-s)^{l'_2}}\int_{t=0}^1\frac{t^{n_4+l_4+l_3}(1-t)^{n_3+l_3+l_4}}{t^{l'_3}(1-t)^{l'_4}}Y_\lambda^{m_2-\mu}(\theta_{\vec{v}},\varphi_{\vec{v}})$$

$$\times\int_{x=0}^{+\infty}x^{n_x}\,\frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}}\,\frac{\widehat{k}_{\nu_2}[R_{43}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}}\,j_\lambda(vx)\,\mathrm{d}x\,\mathrm{d}t\,\mathrm{d}s. \tag{40}$$

Now, consider the three-dimensional integral representation involved in the above equation, which will be referred to as $\widetilde{\mathcal{J}}$:

$$\widetilde{\mathcal{J}} = \int_{s=0}^{1} s^{i_2}(1-s)^{i_1} \int_{t=0}^{1} t^{i_4}(1-t)^{i_3} Y_{\lambda}^{m_{12}}(\theta_{\vec{v}}, \varphi_{\vec{v}}) \times \int_{x=0}^{+\infty} x^{n_x} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{43}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}} j_{\lambda}(vx)\,\mathrm{d}x\,\mathrm{d}t\,\mathrm{d}s, \tag{41}$$

where i_1, i_2, i_3, i_4, m_{12}, n_x, λ, ν_1, ν_2, $n_{\gamma_{12}}$, $n_{\gamma_{34}}$, $\gamma_{12}(s,x)$ and $\gamma_{34}(t,x)$ are defined according to equation (40).

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

$$\widetilde{\mathcal{J}}(s,t) = \int_{0}^{+\infty} x^{n_x} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{43}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}} j_{\lambda}(vx)\,\mathrm{d}x \tag{42}$$

$$= \sum_{n=0}^{+\infty} \int_{j_{\lambda,v}^{n}}^{j_{\lambda,v}^{n+1}} x^{n_x} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{43}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}} j_{\lambda}(vx)\,\mathrm{d}x. \tag{43}$$

The integrand is of the form

$$F_c(x) = x^{n_x} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{43}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}} j_{\lambda}(vx) \tag{44}$$

$$= g_c(x) j_{\lambda}(vx), \tag{45}$$

where

$$g_c(x) = x^{n_x} \frac{\widehat{k}_{\nu_1}[R_{21}\gamma_{12}(s,x)]}{[\gamma_{12}(s,x)]^{n_{\gamma_{12}}}} \frac{\widehat{k}_{\nu_2}[R_{43}\gamma_{34}(t,x)]}{[\gamma_{34}(t,x)]^{n_{\gamma_{34}}}}. \tag{46}$$

The integrand $F_c(x)$ satisfies a sixth-order linear differential equation. We demonstrated in [62] that the conditions of applicability of the D and $\overline{D}$ transformations are satisfied for the evaluation of $\widetilde{\mathcal{J}}(s,t)$. The approximations $D_n^{(6)}$ and $\overline{D}_n^{(6)}$ of $\widetilde{\mathcal{J}}(s,t)$ are obtained by solving sets of equations of order $6n+1$ or $5n+1$, respectively, of the form given by equations (19), (20) where the first five successive derivatives of the integrand are required.

Now, let us consider the functions $g_c(x)$. Assuming that

$$z_1 = R_{21}\gamma_{12}(s,x) = R_{21}\sqrt{(1-s)\zeta_1^2 + s\zeta_2^2 + s(1-s)x^2},$$

$$z_2 = R_{43}\gamma_{34}(t,x) = R_{43}\sqrt{(1-t)\zeta_3^2 + t\zeta_4^2 + t(1-t)x^2},$$

$$z_1 \sim R_{21}\sqrt{s(1-s)}\,x \quad \text{and} \quad z_2 \sim R_{43}\sqrt{t(1-t)}\,x \quad \text{as } x \to +\infty.$$

Substituting z_1 by $R_{21}\sqrt{s(1-s)}\,x$ and z_2 by $R_{43}\sqrt{t(1-t)}\,x$ in the asymptotic expansions of $\widehat{k}_{\nu_1}(z)$ and $\widehat{k}_{\nu_2}(z)$, respectively, equation (36), one can show that, as $x \to +\infty$,

$$\begin{aligned} g_c(x) \sim\ & R_{21}^{\nu_1-1/2} R_{43}^{\nu_2-1/2} \big(\sqrt{s(1-s)}\big)^{\nu_1-n_{\gamma_{12}}-1/2} \big(\sqrt{t(1-t)}\big)^{\nu_2-n_{\gamma_{34}}-1/2} \\ & \times x^{n_x+\nu_1-n_{\gamma_{12}}+\nu_2-n_{\gamma_{34}}-1}\, \mathrm{e}^{-[R_{21}\sqrt{s(1-s)}+R_{43}\sqrt{t(1-t)}]x} \\ & \times \sum_{m_1=0}^{+\infty} \frac{(\nu_1, m_1)}{(2R_{21}\sqrt{s(1-s)}\,x)^{m_1}} \sum_{m_2=0}^{+\infty} \frac{(\nu_2, m_2)}{(2R_{43}\sqrt{t(1-t)}\,x)^{m_2}}. \end{aligned} \tag{47}$$

Thus, $g_c(x)$ can be written as $h(x)\,\mathrm{e}^{\phi(x)}$, where

$$\begin{cases} h(x) \in A^{(\delta)}, \quad \delta = n_x + \nu_1 - n_{\gamma_{12}} + \nu_2 - n_{\gamma_{34}} - 1, \\ \phi(x) \sim -[R_{21}\sqrt{s(1-s)} + R_{43}\sqrt{t(1-t)}]x, \quad \text{as } x \to +\infty. \end{cases} \tag{48}$$

Using the previous arguments, we can easily show that $F_c(x)$ satisfies a second-order linear differential equation of the form

$$F_c(x) = p_1(x)F_c'(x) + p_2(x)F_c''(x), \quad p_1(x), p_2(x) \in A^{(0)}. \tag{49}$$

All the conditions of the applicability of the D transformation are satisfied. The approximation $HD_n^{(2)}$ of $\int_0^{+\infty} F_c(x)\,\mathrm{d}x$ can be obtained by solving a set of equations of the form given by equation (27).

Now, if we choose $x_l = j_{\lambda,v}^{l+1}$ for $l = 0, 1, 2, \ldots, n$, the approximation $H\overline{D}_n^{(2)}$ of $S = \int_0^{+\infty} F_c(t)\,\mathrm{d}t$ using $\overline{D}$ transformation can be obtained by solving a set of equations of the form given by equation (28).

5. Numerical results

The exact values of integrals $\widetilde{\mathcal{I}}(s)$, equation (31), $\widetilde{\mathcal{J}}(s,t)$, equation (42), $\mathcal{I}_{n_1,0,0}^{n_2,0,0}$, equation (29), and $\mathcal{J}_{n_100,n_300}^{n_200,n_400}$, equation (40), are computed to 20 correct decimals

Table 1
Exact values of $\widetilde{\mathcal{I}}(s)$, equation (31), obtained using the series expansion equation (32) which we sum to N_t. Errors obtained by using the Gauss–Laguerre quadrature of order 64 [33]. ($n_x = \lambda$, $n_\gamma = 2\nu$, $\zeta_1 = 2.0$ and $\zeta_2 = 1.0$.)

s	ν	λ	R_1	R_2	N_t	Exact values	Err(GL)
0.005	5/2	0	6.50	2.50	203	0.360140912983302D−02	0.37D−05
0.010	7/2	1	7.00	4.00	86	0.481637530646112D−03	0.20D−08
0.010	9/2	2	6.50	1.00	475	0.456117321707410D−02	0.11D−01
0.010	13/2	3	7.50	3.50	134	0.181139626222770D−01	0.20D−02
0.010	17/2	4	8.50	3.50	168	0.193274110480817D+00	0.91D+00
0.999	5/2	0	7.50	3.50	531	0.161198710040904D+00	0.69D−02
0.990	7/2	1	4.50	1.50	224	0.849175425774129D+00	0.34D−01
0.990	9/2	2	9.00	3.50	253	0.271313806558930D+00	0.30D+01

Table 2
Errors obtained in the evaluation of $\widetilde{\mathcal{I}}(s)$ using the $H\overline{D}_n^{(2)}$ and $\overline{D}_m^{(4)}$. Time T is in milliseconds. ($n_x = \lambda$, $n_\gamma = 2\nu$, $\zeta_1 = 2.0$ and $\zeta_2 = 1.0$.)

s	ν	λ	R_1	R_2	n	Err($H\overline{D}_n^{(2)}$)	T	m	Err($\overline{D}_m^{(4)}$)	T
0.005	5/2	0	6.5	2.5	7	0.59D−11	0.04	5	0.18D−11	0.18
0.010	7/2	1	7.0	4.0	7	0.50D−11	0.04	4	0.28D−11	0.11
0.010	9/2	2	6.5	1.0	9	0.27D−11	0.06	6	0.54D−11	0.30
0.010	13/2	3	7.5	3.5	7	0.50D−08	0.04	5	0.33D−08	0.19
0.010	17/2	4	8.5	3.5	8	0.96D−08	0.06	6	0.40D−07	0.30
0.999	5/2	0	7.5	3.5	5	0.51D−09	0.02	5	0.70D−09	0.18
0.990	7/2	1	4.5	1.5	9	0.74D−09	0.07	5	0.21D−09	0.18
0.990	9/2	2	9.0	3.5	8	0.81D−09	0.05	6	0.74D−09	0.30

Table 3
Errors obtained in the evaluation of $\widetilde{\mathcal{I}}(s)$ using the Levin's u-transform of order n ($u_n(S_0)$) and the ε algorithm of Wynn of order m ($\varepsilon_m^{(0)}$). Time T is in milliseconds. ($n_x = \lambda$, $\nu = n_1 + n_2 + 1/2$ and $n_\gamma = 2(n_1 + n_2) + 1$.)

s	ν	λ	R_1	R_2	n	Err($u_n(S_0)$)	T	m	Err($\varepsilon_m^{(0)}$)	T
0.005	5/2	0	6.5	2.5	10	0.23D−11	0.52	10	0.49D−10	0.47
0.010	7/2	1	7.0	4.0	10	0.23D−11	0.54	10	0.14D−10	0.51
0.010	9/2	2	6.5	1.0	10	0.83D−09	0.60	10	0.14D−08	0.54
0.010	13/2	3	7.5	3.5	9	0.81D−07	0.58	10	0.12D−07	0.61
0.010	17/2	4	8.5	3.5	8	0.92D−05	0.57	10	0.34D−06	0.67
0.999	5/2	0	7.5	3.5	7	0.55D−09	0.36	10	0.49D−09	0.47
0.990	7/2	1	4.5	1.5	10	0.30D−07	0.54	10	0.13D−07	0.50
0.990	9/2	2	9.0	3.5	10	0.56D−07	0.58	10	0.31D−07	0.55

Table 4
Exact values of $\widetilde{\mathcal{I}}_{n_1 00}^{n_2 00}$, equation (29), obtained using the series expansion for the semi-infinite integral. ($\vec{R}_1 = (R_1, 0, 0)$ and $\vec{R}_2 = (R_2, 0, 0)$.)

n_1	n_2	n_γ	n_x	λ	R_1	ζ_1	R_2	ζ_2	Exact values
1	1	5	0	0	6.00	2.50	2.50	1.50	0.9857079490760592D−01
2	1	7	1	1	4.50	1.50	2.50	1.00	0.8761720595719183D+00
2	2	9	2	2	9.00	1.00	1.50	0.50	0.4459612679987873D+00
3	2	11	3	3	3.50	1.00	2.00	1.00	0.2914294482346616D+01
3	3	13	3	3	8.50	4.50	5.00	3.00	0.9938451545759142D−06
4	3	15	4	4	4.00	1.50	1.50	1.00	0.1679864602693796D+01
4	4	17	4	4	2.50	0.50	1.00	1.00	0.1139978397585097D+00

using the series expansions given by equations (32), (43) which are alternating ones (see tables 1, 4, 7 and 13).

All the finite integrals involved in equations (20), (28), (29), (32), (40), (43) are evaluated using the Gauss–Legendre quadrature of order 16. The sets of equations (20), (28) are solved using the LU decomposition.

Table 5
Errors obtained in the evaluation of $\widetilde{\mathcal{I}}_{n_1 00}^{n_2 00}$, equation (29), using $H\overline{D}_n^{(2)}$ and $\overline{D}_m^{(4)}$ for the semi-infinite integral. Time T is in milliseconds. ($n_x = \lambda$, $n_\gamma = 2(n_1 + n_2) + 1$, $\vec{R}_1 = (R_1, 0, 0)$ and $\vec{R}_2 = (R_2, 0, 0)$.)

n_1	n_2	λ	R_1	ζ_1	R_2	ζ_2	n	Err($H\overline{D}_n^{(2)}$)	T	m	Err($\overline{D}_m^{(4)}$)	T
1	1	0	6.0	2.5	2.5	1.5	8	0.15D−11	0.87	4	0.35D−11	1.65
2	1	1	4.5	1.5	2.5	1.0	7	0.95D−11	0.65	4	0.14D−11	1.68
2	2	2	9.0	1.0	1.5	0.5	9	0.39D−11	1.10	5	0.14D−10	2.94
3	2	3	3.5	1.0	2.0	1.0	8	0.28D−12	0.83	4	0.27D−11	1.68
3	3	3	8.5	4.5	5.0	3.0	6	0.40D−12	0.48	4	0.62D−12	1.66
4	3	4	4.0	1.5	1.5	1.0	8	0.30D−12	0.84	4	0.79D−11	1.71
4	4	4	2.5	0.5	1.0	1.0	5	0.52D−12	0.37	3	0.19D−12	0.89

Table 6
Errors obtained in the evaluation of $\widetilde{\mathcal{I}}_{n_1 00}^{n_2 00}$, equation (29), using the Levin's u-transform of order n and the ε algorithm of order m for the semi-infinite integral. Time T is in milliseconds. ($n_x = \lambda$, $n_\gamma = 2(n_1 + n_2) + 1$, $\vec{R}_1 = (R_1, 0, 0)$ and $\vec{R}_2 = (R_2, 0, 0)$.)

n_1	n_2	λ	R_1	ζ_1	R_2	ζ_2	n	Err($u_n(S_0)$)	T	m	Err($\varepsilon_m^{(0)}$)	T
1	1	0	6.0	2.5	2.5	1.5	10	0.83D−11	8.24	10	0.51D−11	7.56
2	1	1	4.5	1.5	2.5	1.0	10	0.10D−10	8.67	10	0.61D−10	8.01
2	2	2	9.0	1.0	1.5	0.5	10	0.45D−10	9.35	10	0.14D−08	8.72
3	2	3	3.5	1.0	2.0	1.0	10	0.75D−11	10.0	10	0.79D−10	9.32
3	3	3	8.5	4.5	5.0	3.0	9	0.90D−12	9.40	10	0.50D−12	9.65
4	3	4	4.0	1.5	1.5	1.0	10	0.54D−11	11.0	10	0.51D−11	10.3
4	4	4	2.5	0.5	1.0	1.0	7	0.57D−12	8.18	8	0.65D−12	8.73

Table 7
Exact values of $\widetilde{\mathcal{J}}(s,t)$, equation (42), obtained using the series expansion, equation (43), which we sum to N_t. ($\nu_2 = \nu_1$, $n_{\gamma_{12}} = n_{\gamma_{34}} = 2\nu_1$, $n_x = \lambda$, $\zeta_3 = \zeta_1$ and $\zeta = \zeta_2$.)

s	t	ν_1	λ	R_1	R_2	R_3	R_4	ζ_1	ζ_2	N_t	Exact values
0.999	0.999	5/2	0	2.5	5.0	7.5	6.0	1.5	1.0	182	0.1332888362507D+01
0.999	0.005	5/2	0	1.5	4.0	5.5	6.5	2.5	1.5	211	0.4862207177866D−03
0.005	0.005	7/2	1	1.5	2.0	4.5	3.5	2.0	1.0	139	0.2241938649088D−02
0.005	0.999	9/2	2	1.0	2.0	6.0	3.5	3.5	2.0	97	0.4057636102915D−04
0.999	0.999	9/2	2	3.0	3.5	7.0	5.0	2.5	3.0	234	0.1969258557126D−05
0.999	0.005	11/2	3	5.5	6.0	8.5	7.5	5.0	1.0	233	0.1426496442764D−02
0.005	0.005	13/2	4	5.0	5.5	9.0	5.0	2.5	2.0	120	0.4625584384668D−04
0.005	0.005	17/2	5	3.5	4.0	7.0	5.0	3.0	2.5	135	0.1598600048270D−03

The calculation time using $H\overline{D}$ and $\overline{D}$ transformations computed with an IBM RS6000 340 is noted (see tables 2, 5, 8, 9 and 14). We also used the Levin's u-transform [13,38] and the epsilon algorithm of Wynn [12,13,82] to evaluate the integrals $\widetilde{\mathcal{I}}(s)$, $\widetilde{\mathcal{J}}(s,t)$, $\mathcal{I}_{n_1,0,0}^{n_2,0,0}$ and $\mathcal{J}_{n_1 00,n_3 00}^{n_2 00,n_4 00}$, by accelerating the convergence of the infinite series given by equations (32), (43). The calculation time is also computed to

Table 8
Errors obtained in the evaluation of $\widetilde{\mathcal{J}}(s,t)$ using $H\overline{D}_n^{(2)}$. Time T is in milliseconds. ($\nu_2=\nu_1$, $n_{\gamma_{12}}=n_{\gamma_{34}}=2\nu_1$, $n_x=\lambda$, $\zeta_3=\zeta_1$ and $\zeta_4=\zeta_2$.)

s	t	ν_1	λ	R_1	R_2	R_3	R_4	ζ_1	ζ_2	n	Err($H\overline{D}_n^{(2)}$)	T
0.999	0.999	5/2	0	2.5	5.0	7.5	6.0	1.5	1.0	8	0.72D−09	0.05
0.999	0.005	5/2	0	1.5	4.0	6.5	5.5	2.5	1.5	4	0.54D−11	0.02
0.005	0.005	7/2	1	1.5	2.0	4.5	3.5	2.0	1.0	7	0.90D−10	0.04
0.005	0.999	9/2	2	1.0	2.0	6.0	2.5	3.5	2.0	6	0.81D−10	0.03
0.999	0.999	9/2	2	3.0	3.5	7.0	5.0	2.5	3.0	6	0.92D−12	0.03
0.999	0.005	11/2	3	5.5	6.0	8.5	7.5	5.0	1.0	8	0.93D−10	0.05
0.005	0.005	13/2	4	5.0	5.5	9.0	5.0	2.5	2.0	7	0.32D−09	0.04
0.005	0.005	17/2	5	3.5	4.0	7.0	5.0	3.0	2.5	8	0.36D−09	0.05

Table 9
Errors obtained in the evaluation of $\widetilde{\mathcal{J}}(s,t)$ using $\overline{D}_n^{(6)}$. Time T is in milliseconds. ($\nu_2=\nu_1$, $n_{\gamma_{12}}=n_{\gamma_{34}}=2\nu_1$, $n_x=\lambda$, $\zeta_3=\zeta_1$ and $\zeta_4=\zeta_2$.)

s	t	ν_1	λ	R_1	R_2	R_3	R_4	ζ_1	ζ_2	n	Err($\overline{D}_n^{(6)}$)	T
0.999	0.999	5/2	0	2.5	5.0	7.5	6.0	1.5	1.0	5	0.27D−09	0.70
0.999	0.005	5/2	0	1.5	4.0	6.5	5.5	2.5	1.5	4	0.13D−11	0.39
0.005	0.005	7/2	1	1.5	2.0	4.5	3.5	2.0	1.0	3	0.70D−10	0.18
0.005	0.999	9/2	2	1.0	2.0	6.0	2.5	3.5	2.0	3	0.99D−09	0.19
0.999	0.999	9/2	2	3.0	3.5	7.0	5.0	2.5	3.0	5	0.58D−12	0.71
0.999	0.005	11/2	3	5.5	6.0	8.5	7.5	5.0	1.0	5	0.17D−10	0.70
0.005	0.005	13/2	4	5.0	5.5	9.0	5.0	2.5	2.0	4	0.95D−09	0.39
0.005	0.005	17/2	5	3.5	4.0	7.0	5.0	3.0	2.5	5	0.34D−09	0.71

Table 10
Errors obtained in the evaluation of $\widetilde{\mathcal{J}}(s,t)$ using $u_n(S_0)$. Time T is in milliseconds. ($\nu_2=\nu_1$, $n_{\gamma_{12}}=n_{\gamma_{34}}=2\nu_1$, $n_x=\lambda$, $\zeta_3=\zeta_1$ and $\zeta_4=\zeta_2$.)

s	t	ν_1	λ	R_1	R_2	R_3	R_4	ζ_1	ζ_2	n	Err($u_n(S_0)$)	T
0.999	0.999	5/2	0	2.5	5.0	7.5	6.0	1.5	1.0	10	0.13D−08	0.85
0.999	0.005	5/2	0	1.5	4.0	5.5	6.5	2.5	1.5	6	0.22D−10	0.55
0.005	0.005	7/2	1	1.5	2.0	4.5	3.5	2.0	1.0	10	0.29D−10	0.91
0.005	0.999	9/2	2	1.0	2.0	6.0	2.5	3.5	2.0	6	0.97D−09	0.61
0.999	0.999	9/2	2	3.0	3.5	7.0	5.0	2.5	3.0	8	0.91D−12	0.80
0.999	0.005	11/2	3	5.5	6.0	8.5	7.5	5.0	1.0	8	0.16D−07	0.85
0.005	0.005	13/2	4	5.0	5.5	9.0	5.0	2.5	2.0	8	0.19D−08	0.88
0.005	0.005	17/2	5	3.5	4.0	7.0	5.0	3.0	2.5	8	0.23D−07	0.99

show the superiority of $H\overline{D}$ transformation (see tables 3, 6, 10, 11 and 15).

In the analytical expression of $\mathcal{I}_{n_1,0,0}^{n_2,0,0}$ and $\mathcal{J}_{n_100,n_300}^{n_200,n_400}$ we let n_x and λ vary to compare the efficiency of the transformations in the evaluation of the semi-infinite integrals whose integrands are very oscillating.

(A Fortran 77 routine has been specially devised for this purpose.)

Table 11
Errors obtained in the evaluation of $\widetilde{\mathcal{J}}(s,t)$ using $\varepsilon_n^{(0)}$. Time T is in milliseconds. ($\nu_2=\nu_1$, $n_{\gamma_{12}}=n_{\gamma_{34}}=2\nu_1$, $n_x=\lambda$, $\zeta_3=\zeta_1$ and $\zeta_4=\zeta_2$.)

s	t	ν_1	λ	R_1	R_2	R_3	R_4	ζ_1	ζ_2	n	Err($\varepsilon_n^{(0)}$)	T
0.999	0.999	5/2	0	2.5	5.0	7.5	6.0	1.5	1.0	10	0.60D−08	0.84
0.999	0.005	5/2	0	1.5	4.0	6.5	5.5	2.5	1.5	8	0.18D−10	0.67
0.005	0.005	7/2	1	1.5	2.0	4.5	3.5	2.0	1.0	10	0.75D−10	0.88
0.005	0.999	9/2	2	1.0	2.0	6.0	2.5	3.5	2.0	8	0.10D−08	0.77
0.999	0.999	9/2	2	3.0	3.5	7.0	5.0	2.5	3.0	10	0.21D−12	0.94
0.999	0.005	11/2	3	5.5	6.0	8.5	7.5	5.0	1.0	8	0.41D−06	0.81
0.005	0.005	13/2	4	5.0	5.5	9.0	5.0	2.5	2.0	8	0.14D−08	0.87
0.005	0.005	17/2	5	3.5	4.0	7.0	5.0	3.0	2.5	8	0.27D−07	0.95

Table 12
Errors obtained in the evaluation of $\widetilde{\mathcal{J}}(s,t)$ using the Gauss–Laguerre quadrature of order 64. Time T is in milliseconds. ($\nu_2=\nu_1$, $n_{\gamma_{12}}=n_{\gamma_{34}}=2\nu_1$, $n_x=\lambda$, $\zeta_3=\zeta_1$ and $\zeta_4=\zeta_2$.)

s	t	ν_1	λ	R_1	R_2	R_3	R_4	ζ_1	ζ_2	Err(GL)	T
0.999	0.999	5/2	0	2.5	5.0	7.5	6.0	1.5	1.0	0.39D−03	0.30
0.999	0.005	5/2	0	1.5	4.0	5.5	6.5	2.5	1.5	0.15D−05	0.29
0.005	0.005	7/2	1	1.5	2.0	4.5	3.5	2.0	1.0	0.72D−06	0.31
0.005	0.999	9/2	2	1.0	2.0	6.0	2.5	3.5	2.0	0.65D−06	0.34
0.999	0.999	9/2	2	3.0	3.5	7.0	5.0	2.5	3.0	0.86D−04	0.21
0.999	0.005	11/2	3	5.5	6.0	8.5	7.5	5.0	1.0	0.44D−01	0.36
0.005	0.005	13/2	4	5.0	5.5	9.0	5.0	2.5	2.0	0.19D−04	0.38
0.005	0.005	17/2	5	3.5	4.0	7.0	5.0	3.0	2.5	0.25D−02	0.42

Table 13
Exact values of $\widetilde{\mathcal{J}}^{n_2 00, n_4 00}_{n_1 00, n_3 00}$, equation (40), obtained using the series expansion for the semi-infinite integral. ($n_3=n_1$, $n_4=n_2$, $n_{\gamma_{34}}=n_{\gamma_{12}}=2(n_1+n_2)+1$, $n_x=\lambda$, $\zeta_3=\zeta_1$, $\zeta_4=\zeta_2$ and $\vec{R}_i=(R_i,0,0)$, $i=1,2,3,4$.)

n_1	n_2	$n_{\gamma_{12}}$	λ	R_1	R_2	R_3	R_4	ζ_1	ζ_2	Exact values
1	1	5	0	1.5	3.5	6.5	4.5	3.0	2.5	0.1712887759698052D−01
2	1	7	1	3.0	4.5	7.5	5.0	2.0	2.5	0.1096433803364225D+00
2	2	9	2	2.5	3.0	5.5	4.0	2.0	1.5	0.5077289993314898D+01
3	2	11	2	1.5	2.5	6.0	4.0	1.0	3.0	0.2249496975806864D+01
3	3	13	3	2.5	4.0	6.0	5.0	2.0	3.5	0.1225528163777227D+00
4	3	15	3	2.5	4.5	7.5	6.5	3.5	2.0	0.2005488272296958D−03
4	4	17	4	2.5	4.5	7.0	6.0	3.0	1.5	0.3653628513846546D−02

6. Conclusion

The use of the series expansion given by equations (32), (43) is prohibitively long for sufficient accuracy, for s and t close to 0 and 1. To obtain 20 exact decimals for $\widetilde{\mathcal{I}}(s)$ for $s=0.01$, $\nu=9/2$, $n_x=\lambda=2$, we need to sum 475 terms of the series

Table 14
Errors obtained in the evaluation of $\widetilde{\mathcal{J}}^{n_2 00, n_4 00}_{n_1 00, n_3 00}$, equation (40), using $H\overline{D}^{(2)}_n$ and $\overline{D}^{(6)}_m$. Time T is in milliseconds. ($n_3 = n_1$, $n_4 = n_2$, $n_{\gamma_{34}} = n_{\gamma_{12}} = 2(n_1 + n_2) + 1$, $n_x = \lambda$, $\zeta_3 = \zeta_1$, $\zeta_4 = \zeta_2$ and $\vec{R}_i = (R_i, 0, 0)$, $i = 1, 2, 3, 4$.)

n_1	n_2	λ	R_1	R_2	R_3	R_4	ζ_1	ζ_2	n	Err($H\overline{D}^{(2)}_n$)	T	n	Err($\overline{D}^{(6)}_m$)	T
1	1	0	1.5	3.5	6.5	4.5	3.0	2.5	7	0.79D−12	9	3	0.80D−16	45
2	1	1	3.0	4.5	7.5	5.0	2.0	2.5	5	0.61D−09	5	2	0.70D−09	18
2	2	2	2.5	3.0	5.5	4.0	2.0	1.5	5	0.21D−10	7	2	0.14D−10	20
3	2	2	1.5	2.5	6.0	4.0	1.0	3.0	7	0.83D−11	9	3	0.30D−12	53
3	3	3	2.5	4.0	6.0	5.0	2.0	3.5	5	0.43D−11	6	2	0.13D−11	23
4	3	3	2.5	4.5	7.5	6.5	3.5	2.0	6	0.37D−13	4	2	0.41D−12	17
4	4	4	2.5	4.5	7.0	6.0	3.0	1.5	6	0.21D−14	8	2	0.18D−13	17

Table 15
Errors obtained in the evaluation of $\widetilde{\mathcal{J}}^{n_2 00, n_4 00}_{n_1 00, n_3 00}$ equation (40), using $u_n(S_0)$ and $\varepsilon^{(0)}_m$. Time T is in milliseconds. ($n_3 = n_1$, $n_4 = n_2$, $n_{\gamma_{34}} = n_{\gamma_{12}} = 2(n_1 + n_2) + 1$, $n_x = \lambda$, $\zeta_3 = \zeta_1$, $\zeta_4 = \zeta_2$ and $\vec{R}_i = (R_i, 0, 0)$, $i = 1, 2, 3, 4$.)

n_1	n_2	λ	R_1	R_2	R_3	R_4	ζ_1	ζ_2	n	Err($u_n(S_0)$)	T	m	Err($\varepsilon^{(0)}_m$)	T
1	1	0	1.5	3.5	6.5	4.5	3.0	2.5	6	0.20D−10	156	8	0.23D−10	171
2	1	1	3.0	4.5	7.5	5.0	2.0	2.5	5	0.72D−08	131	6	0.78D−08	143
2	2	2	2.5	3.0	5.5	4.0	2.0	1.5	6	0.26D−09	165	8	0.18D−09	202
3	2	2	1.5	2.5	6.0	4.0	1.0	3.0	9	0.42D−10	257	0	0.54D−10	249
3	3	3	2.5	4.0	6.0	5.0	2.0	3.5	7	0.13D−11	206	8	0.36D−11	213
4	3	3	2.5	4.5	7.5	6.5	3.5	2.0	7	0.28D−12	219	8	0.41D−12	232
4	4	4	2.5	4.5	7.0	6.0	3.0	1.5	6	0.57D−12	195	8	0.14D−12	241

and for $s = 0.99$, $\nu = 5/2$, $n_x = \lambda = 0$, we need to sum 531 terms of the series, equation (32) (see table 1).

From the values reported in tables 1 and 12, note that use of the Gauss–Laguerre quadrature even to high order (for instance, 64) gives inaccurate results, especially for s and t close to 0 or 1 (see $s = 0.005$, 0.01 and 0.99 in table 1, $s = 0.999$, $t = 0.999$ and $s = 0.999$, $t = 0.005$ in table 12). If we let $s, t = 0$ or 1, the integrands $F_a(x)$, equation (33), and $F_c(x)$, equation (45), will be reduced to the term $x^{n_x} j_\lambda(vx)$, because the terms $\widehat{k}_\nu[R\gamma(\alpha, x)]/[\gamma(\alpha, x)]^{n_\gamma}$ for $\alpha = s, t$ become constants and, hence, the asymptotic behaviour of the integrands $F_a(x)$ and $F_c(x)$ cannot be represented by functions of the form $\mathrm{e}^{-\alpha x} f(x)$, where $f(x)$ is not a rapidly oscillating function. We also note that the regions close to $s = t = 0$ and $s = t = 1$ carry a very small weight because of their expressions $s^{i_2}(1-s)^{i_2}$, $t^{i_4}(1-t)^{i_3}$, equations (30), (41) [27–32,66,41].

Using the epsilon algorithm and Levin's u-transform, we accelerate the convergence of the infinite oscillating series but the accuracy is still insufficient compared with the accuracy of the $H\overline{D}$ transformations (see tables 3, 6, 10, 11 and 15).

The D and $\overline{D}$ transformations are efficient in the evaluation of the integrals of interest, but their applications required the calculation of the first three successive deriv-

atives of the integrands for the three-center nuclear attraction integrals, equation (20), and the first five successive derivatives for the two-electron four-center Coulomb integrals, equation (20), entailing severe numerical and computational difficulties. Obtaining the approximations $\overline{D}_n^{(4)}$ of $\widetilde{\mathcal{I}}(s)$ and $\overline{D}_n^{(6)}$ of $\widetilde{\mathcal{J}}(s,t)$ involves solving sets of equations of order $3n+1$ and $5n+1$, respectively, equation (20), which converge very quickly to the exact values of $\widetilde{\mathcal{I}}(s)$ and $\widetilde{\mathcal{J}}(s,t)$ for large values of n.

Using the HD and $H\overline{D}$ transformations we reduce the order of the linear differential equations satisfied by the integrands of $\widetilde{\mathcal{I}}(s)$ and $\widetilde{\mathcal{J}}(s,t)$ from 4 and 6 to 2, thus the problem of computing the successive derivatives of these functions is avoided. We just need the first derivative of the spherical Bessel function j_λ, which is very easy to compute (see equations (12)). The approximations $H\overline{D}_n^{(2)}$ of $\widetilde{\mathcal{I}}(s)$ and $\widetilde{\mathcal{J}}(s,t)$ are obtained by solving sets of equations of order $n+1$ instead of $3n+1$ for the three-center nuclear attraction integrals and $5n+1$ for two-electron four-center Coulomb integrals by using D and $\overline{D}$ transformations.

From the results listed in tables 2, 5, 8, 9 and 14, note the superiority of $H\overline{D}$ over all other alternatives. To obtain 11 exact decimals using an RS6000-340 IBM workstation, for $\widetilde{\mathcal{I}}(s)$ for $s = 0.01$, $\nu = 9/2$, $n_x = \lambda = 2$ we need 0.06 ms by using $H\overline{D}$, but by using $\overline{D}$ transformation we need 0.30 ms, and for $s = 0.999$, $\nu = 5/2$, $n_x = \lambda = 0$ we obtain 9 exact decimals for $\widetilde{\mathcal{I}}(s)$ in 0.02 ms by using $H\overline{D}$ and 0.18 ms by using $\overline{D}$ (see table 2). To obtain 11 exact decimals for $\widetilde{\mathcal{J}}(s,t)$ for $s = 0.999$, $t = 0.005$, $\nu_1 = \nu_2 = 5/2$, $n_x = \lambda = 0$ we need 0.02 ms by using $H\overline{D}$ and 0.39 ms by using $\overline{D}$, and for $s = 0.999$, $t = 0.999$, $\nu_1 = \nu_2 = 9/2$, $n_x = \lambda = 2$ we obtain 12 exact decimals in 0.03 ms by using $H\overline{D}$ and 0.71 ms by using $\overline{D}$. For the evaluation of $\mathcal{I}_{n_1,0,0}^{n_2,0,0}$, equation (29), and $\mathcal{J}_{n_100,n_300}^{n_200,n_400}$, equation (40), we used the epsilon algorithm, Levin's u-transform, the D and $H\overline{D}$ transformation, to compare the calculation times for the same accuracy. For $\mathcal{I}_{n_1,0,0}^{n_2,0,0}$ for $n_1 = n_2 = 1$, $n_x = \lambda = 0$ we obtain 11 exact decimals in 0.87 ms by using $H\overline{D}$, 1.66 ms by using $\overline{D}$, 8.24 ms by using Levin's u-transform and 7.56 ms by using the epsilon algorithm, and for $n_1 = n_2 = 3$, $n_x = \lambda = 3$ we obtain 12 exact decimals in 0.48 ms by using $H\overline{D}$, 1.66 ms by using $\overline{D}$, 9.40 ms by using Levin's u-transform and 9.56 ms by using the epsilon algorithm (see tables 5 and 6). For $\mathcal{J}_{n_100,n_300}^{n_200,n_400}$ and for $n_1 = n_2 = n_3 = n_4 = 1$, $n_x = \lambda = 0$, we obtain 12 exact decimals in 10 ms by using $H\overline{D}$, 43 ms by using $\overline{D}$, 150 ms by using Levin's u-transform and more than 177 ms by using the epsilon algorithm, for $n_1 = n_2 = n_3 = n_4 = n_x = \lambda = 3$ we obtain 11 exact decimals in 5 ms by using $H\overline{D}$, 24 ms by using $\overline{D}$, 198 ms by using Levin's u-transform and 219 ms by using the epsilon algorithm (see tables 14 and 15).

These examples show that integrals which contribute to total molecular energies can be obtained to a precision of 10^{-10} atomic units, which is quite sufficient for energies of chemical processes.

The present work illustrates the substantial optimisation regarding calculation time obtained using the $H\overline{D}$ transformation over D and $\overline{D}$ transformations and its

much greater rapidity than Levin's u-transform, the ε algorithm of Wynn and series methods.

Obviously, this greatly increased rapidity of the $H\overline{D}$ transformation is a key issue. In the molecular context, many millions of such integrals are required for close range terms (long-range terms being treated by asymptotic expansions or multipole approaches), therefore rapidity is the primordial criterion when the precision has been reached.

The $H\overline{D}$ transformation methods are also able to reach precisions of 10^{-18} atomic units reliably for the first time and, certainly, some applications of this extremely high accuracy will be developed in future work.

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