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Double-Exponential Quadrature and the S Transformation for Three-Centre Two-Electron Coulomb and Hybrid Integrals

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Abstract. Hybrid and three-centre two-electron Coulomb integrals over Slater-type functions (STFs) contain semi-infinite oscillatory kernels involving spherical Bessel functions. We investigate two double-exponential (DE) formulations for their numerical evaluation. The first applies DE quadrature directly to the spherical Bessel kernel, whereas the second combines Fourier-type DE quadrature with the S transformation introduced by the author, which reduces the spherical Bessel kernel to a sine integral. Both formulations lead to highly accurate values for the complete molecular integrals and agree with the corresponding benchmarks to the precision reported in the literature. The numerical results demonstrate, in particular, the high efficiency of $S + \text{DE}$ for strongly oscillatory integrals.

Keywords. Molecular integrals; Exponential type functions; Double-exponential transformations; S transformation; oscillatory integrals; spherical Bessel functions.

1 Introduction

Three-centre two-electron Coulomb and hybrid integrals over Slater-type functions (STFs) admit Fourier- B representations in which the remaining numerical problem contains an outer Feynman-parameter integral and an inner semi-infinite spherical-Bessel integral [1,2]. The S transformation converts the latter to a sine integral and has previously been combined with Sidi’s $\bar{D}$ transformation in [2,3]. The present work develops the complementary S +DE formulation for the complete hybrid and three-centre two-electron Coulomb problem. In contrast with $S + \bar{D}$, which accelerates the transformed tail through its asymptotic expansion, S +DE exploits the arithmetic sequence of zeros of the sine factor through Fourier-type DE quadrature.

Recent developments confirm a continuing interest in the accurate and efficient evaluation of molecular integrals over exponential-type functions (ETFs). General representations for multicentre integrals over STFs have recently been investigated [8], while new numerical approaches have been developed for Slater-basis Coulomb and nuclear-attraction integrals in polyatomic calculations and for two-electron four-centre Coulomb integrals on modern GPU architectures [9,10]. These developments emphasize the importance of accurate and efficient methods for the evaluation of molecular integrals over ETFs.

The combination of the S transformation with DE quadrature was previously applied to three-centre nuclear-attraction integrals [4]. The two-electron Coulomb integrals considered here lead to a substantially richer radial structure than the previously treated three-centre nuclear-attraction integrals. In particular, the interaction between oscillation and molecular damping changes with the Feynman parameter and becomes especially important near its endpoints. We therefore examine the transformed radial integral, its complex singularities, and the resulting behaviour of the DE quadrature. The obtained formulation is then developed and tested for complete hybrid and three-centre two-electron Coulomb integrals, with particular attention to strongly oscillatory cases, near-endpoint behaviour, and higher angular momenta.

The complete molecular expression is first reduced to the semi-infinite radial integrals containing the spherical Bessel functions, and then to their transformation by the S method into semi-infinite sine integrals. This transformation replaces the more complicated oscillatory structure of the spherical Bessel functions by a sine kernel whose regularly spaced zeros can be exploited directly by Fourier-type DE quadrature. These semi-infinite sine integrals are then treated by DE quadrature, together with an analysis of their asymptotic structure, analyticity, and convergence. For comparison, DE quadrature is also applied directly to the original spherical-Bessel integrals.

The numerical analysis examines the accuracy and efficiency of the proposed methods for the semi-infinite integrals and subsequently carries the calculation through the complete H_2O and C_2H_4 molecular integrals.

2 Three-centre two-electron Coulomb and hybrid integrals

The B -function framework used below follows the established derivation [1, 2]. The three-centre two-electron Coulomb integral considered in this work contains four basis functions distributed over the three spatial centres A , B , and C . With a and b centred at A , c at B , and d at C , it is defined by:

$$^{(3)}E_{ab,cd}[AA|BC] = \iint_{\mathbb{R}^3 \times \mathbb{R}^3} a^*(\vec{r}_1 - \vec{A})b(\vec{r}_1 - \vec{A}) \frac{1}{|\vec{r}_1 - \vec{r}_2|} c^*(\vec{r}_2 - \vec{B})d(\vec{r}_2 - \vec{C}) d\vec{r}_1 d\vec{r}_2. \quad (1)$$

Here the lowercase letters a , b , c , and d label B functions, whereas the uppercase letters A , B , and C label spatial centres. The left superscript gives the number of distinct centres and the bracketed descriptor gives their distribution. The notation $^{(3)}E_{ab,cd}[AA|BC]$ displays directly that four basis functions are distributed over three centres.

A normalized STF is represented by a finite linear combination of B functions. The corresponding complete three-centre STF integral is therefore assembled from the B -function integrals in (1):

$$^{(3)}E_{\text{STFs}}[AA|BC] = \sum_{a=1}^{N_a} \sum_{b=1}^{N_b} \sum_{c=1}^{N_c} \sum_{d=1}^{N_d} C_a C_b C_c C_d ^{(3)}E_{ab,cd}[AA|BC]. \quad (2)$$

Since the Coulomb integral is invariant under a common translation of the electronic coordinates and all spatial centres, one centre may be placed at the origin without loss of generality. We choose A as the origin and introduce the translated centre vectors:

$$\vec{A} = \mathbf{0}, \quad \vec{R}_3 = \vec{B} - \vec{A} = \vec{B}, \quad \vec{R}_4 = \vec{C} - \vec{A} = \vec{C}, \quad \vec{R}_{34} = \vec{R}_3 - \vec{R}_4 = \vec{B} - \vec{C} \quad \text{and} \quad r_{12} = |\vec{r}_1 - \vec{r}_2|. \quad (3)$$

In these translated coordinates, the same integral is:

$$^{(3)}E_{ab,cd}[AA|BC] = \iint_{\mathbb{R}^3 \times \mathbb{R}^3} a^*(\vec{r}_1)b(\vec{r}_1) \frac{1}{r_{12}} c^*(\vec{r}_2 - \vec{R}_3)d(\vec{r}_2 - \vec{R}_4) d\vec{r}_1 d\vec{r}_2. \quad (4)$$

The Fourier-transform formalism provides an analytic representation of molecular integrals in a basis of B functions. For the integrals under consideration, the complete analytic expression is given by:

$$\begin{aligned} ^{(3)}E_{ab,cd}[AA|BC] = & \mathcal{C} \sum_{l=|l_1-l_2|}^{l_1+l_2} \frac{(-i)^l \mathcal{G}(l_2 m_2; l_1 m_1; l, m_2 - m_1)}{2^{2n_1+2n_2+l}} \sum_{k=2}^{n_1+n_2} \sum_{i=k_1}^{k_2} \frac{2^k (2n_1 - i - 1)! (2n_2 - k + i - 1)! \zeta_1^{i-1} \zeta_2^{k-i-1}}{(i-1)!(n_1-i)!(k-i-1)!(n_2-k+i)!} \\ & \times \sum_{l'_4=0}^{l_4} \sum_{m'_4=-l'_4}^{l'_4} \frac{i^{l_4+l'_4} (-1)^{l'_4} \mathcal{G}(l_4 m_4; l_4 - l'_4, m_4 - m'_4; l'_4 m'_4)}{(2l'_4 + 1)!! [2(l_4 - l'_4) + 1]!!} \\ & \times \sum_{l'_3=0}^{l_3} \sum_{m'_3=-l'_3}^{l'_3} \frac{i^{l_3+l'_3} \mathcal{G}(l_3 m_3; l_3 - l'_3, m_3 - m'_3; l'_3 m'_3)}{(2l'_3 + 1)!! [2(l_3 - l'_3) + 1]!!} \\ & \times \sum_{l'=0}^{l'_3+l'_4} \mathcal{G}(l'_4 m'_4; l'_3 m'_3; l', m'_4 - m'_3) R_{34}^{l'} Y_{l'}^{m'_3-m'_4}(\hat{R}_{34}) \\ & \times \sum_{l_{34}=0}^{(l_3-l'_3)+(l_4-l'_4)} \mathcal{G}(l_3 - l'_3, m_3 - m'_3; l_4 - l'_4, m_4 - m'_4; l_{34} m_{34}) \\ & \times \sum_{\lambda=0}^{l+l_{34}} i^\lambda \mathcal{G}(l, m_2 - m_1; l_{34}, m_{34}; \lambda \mu) \sum_{j=0}^{\Delta l} \binom{\Delta l}{j} \frac{(-1)^{(l'_4+l'_3+l')/2+j}}{2^{n_3+n_4+l_3+l_4-j+1} (n_3 + n_4 + l_3 + l_4 - j + 1)!} \\ & \times \frac{\zeta_s^{n_k-l-1} \Gamma(k + l_1 + l_2 + l + 1)}{\Gamma(l + 3/2)} \sum_{r=0}^{\eta'} (-1)^r \frac{(\eta/2)_r ((\eta+1)/2)_r}{(l + 3/2)_r r! \zeta_s^{2r}} \end{aligned}$$

$$\times \int_0^1 s^{n_3+l_3+l_4-l'_4} (1-s)^{n_4+l_4+l_3-l'_3} Y_\lambda^\mu(\widehat{v}(s)) \widetilde{K}(s) ds. \quad (5)$$

The semi-infinite integral appearing in (5) is:

$$\widetilde{K}(s) = \int_0^\infty \frac{x^{n_x}}{(\zeta_s^2 + x^2)^{n_k}} \frac{\widehat{k}_\nu(R_{34}\gamma(s, x))}{\gamma(s, x)^{n_\gamma}} j_\lambda(vx) dx. \quad (6)$$

The reduced modified Bessel function appearing in (6) is defined by:

$$\widehat{k}_\nu(z) = \sqrt{\frac{2}{\pi}} z^\nu K_\nu(z), \quad (7)$$

where K_ν denotes the modified Bessel function of the second kind.

For simplicity, in the radial kernel and in the S -transformed representation below, we write v for the s -dependent magnitude $v(s)$. The quantities involved in the complete molecular expression and its semi-infinite integral are:

$$\begin{aligned} \mathcal{C} &= 8(4\pi)^3 \sqrt{\pi} \zeta_1^{l_1} \zeta_2^{l_2} \zeta_3^{2n_3+l_3-1} \zeta_4^{2n_4+l_4-1} \frac{(2l_3+1)!!(2l_4+1)!!(n_3+l_3+n_4+l_4+1)!}{2^{l_1+l_2+1} \prod_{q=1}^4 (n_q+l_q)!}, \\ \zeta_s &= \zeta_1 + \zeta_2, \quad k_1 = \max(1, k - n_2) \quad \text{and} \quad k_2 = \min(n_1, k - 1), \\ n_x &= l_3 - l'_3 + l_4 - l'_4 + 2r + l \quad \text{and} \quad n_k = k + l_1 + l_2, \\ n_\gamma &= 2(n_3 + l_3 + n_4 + l_4) - (l'_3 + l'_4) - l' + 1, \\ \Delta l &= \frac{l_3 + l_4 - l'}{2} \quad \text{with} \quad \eta = l - k - l_1 - l_2 + 1, \\ \eta' &= \begin{cases} -\eta/2 & \text{if } \eta \text{ is even,} \\ -(\eta+1)/2 & \text{if } \eta \text{ is odd,} \end{cases} \\ m_{34} &= (m_3 - m'_3) - (m_4 - m'_4) \quad \text{with} \quad \mu = (m_2 - m_1) - m_{34}, \\ \nu &= n_3 + n_4 + l_3 + l_4 - l' - j + \frac{1}{2}, \\ \vec{v}(s) &= (1-s)\vec{R}_{34} + \vec{R}_4 \quad \text{with} \quad v(s) = |\vec{v}(s)|, \\ \gamma(s, x)^2 &= (1-s)\zeta_4^2 + s\zeta_3^2 + s(1-s)x^2. \end{aligned} \quad (8)$$

The angular factors involved in (5) are expressed in terms of the Gaunt coefficient, which is defined by:

$$\mathcal{G}(l_1 m_1; l_2 m_2; LM) = \int_{S^2} [Y_{l_1}^{m_1}(\Omega)]^* Y_{l_2}^{m_2}(\Omega) Y_L^M(\Omega) d\Omega. \quad (9)$$

The hybrid integral is obtained from the same molecular expression by imposing the coalesced-centre geometry $\vec{R}_3 = \vec{0}$. The three-centre topology $[AA|BC]$ then reduces, after relabelling the remaining distinct centre, to the hybrid topology $[AA|AB]$.

The endpoint hypotheses of the S transformation established in [2, 3] are satisfied by the present molecular kernel. The radial amplitude multiplying the spherical Bessel function in (6) is:

$$g_s(x) = \frac{x^{n_x}}{(\zeta_s^2 + x^2)^{n_k}} \frac{\widehat{k}_\nu(R_{34}\gamma(s, x))}{\gamma(s, x)^{n_\gamma}}. \quad (10)$$

Its behavior at the origin therefore gives:

$$\left(\frac{1}{x} \frac{d}{dx}\right)^\ell \left[x^{\lambda-1} g_s(x)\right] = O\left(x^{n_x+\lambda-1-2\ell}\right) \quad \text{as } x \rightarrow 0^+ \quad \text{for } 0 \leq \ell \leq \lambda-1. \quad (11)$$

The Gaunt selection rules in (5) give $l_{34} \leq (l_3 - l'_3) + (l_4 - l'_4)$ and $\lambda \leq l + l_{34}$. Since $r \geq 0$, the radial index therefore satisfies:

$$\lambda \leq l + l_{34} \leq l + (l_3 - l'_3) + (l_4 - l'_4) \leq n_x = l + (l_3 - l'_3) + (l_4 - l'_4) + 2r. \quad (12)$$

The worst exponent in (11) is consequently $n_x - \lambda + 1 \geq 1$, so the origin boundary terms required by the S transformation vanish.

For fixed $0 < s < 1$, the Macdonald factor gives:

$$\left(\frac{1}{x} \frac{d}{dx}\right)^\ell \left[x^{\lambda-1} g_s(x)\right] = O\left(x^{\eta_\ell} e^{-R_{34}\sqrt{s(1-s)}x}\right) \quad \text{as } x \rightarrow \infty, \quad (13)$$

for finite algebraic exponents η_ℓ , so the corresponding boundary terms at infinity vanish.

The S transformation therefore applies directly and gives:

$$\tilde{K}(s) = \frac{1}{v^{\lambda+1}} \int_0^\infty \left(\frac{1}{x} \frac{d}{dx}\right)^\lambda \left[\frac{x^{n_x+\lambda-1} \hat{k}_\nu(R_{34}\gamma(s, x))}{(\zeta_s^2 + x^2)^{n_k} \gamma(s, x)^{n_\gamma}} \right] \sin(vx) dx. \quad (14)$$

For numerical reference, the same transformed integral can also be accumulated over successive half-periods of the sine factor. Defining $G_{\lambda,s}(x)$ as the differentiated amplitude in (14), the corresponding S -series decomposition is:

$$\tilde{K}(s) = \frac{1}{v^{\lambda+1}} \sum_{n=0}^\infty \int_{n\pi/v}^{(n+1)\pi/v} G_{\lambda,s}(x) \sin(vx) dx. \quad (15)$$

The complete S -series reference follows by carrying (15) through the same outer integration and finite molecular assembly.

For fixed $0 < s < 1$, we set:

$$\alpha_s = R_{34}\sqrt{s(1-s)}. \quad (16)$$

The Macdonald factor gives exponential radial decay with rate α_s , and the spherical-Bessel expansion:

$$j_\lambda(z) = \sum_{q=0}^\infty \frac{(-1)^q z^{\lambda+2q}}{2^q q! (2\lambda + 2q + 1)!!}, \quad (17)$$

has an absolute sum satisfying, for fixed λ :

$$\sum_{q=0}^\infty \frac{|v|^{\lambda+2q} x^{\lambda+2q}}{2^q q! (2\lambda + 2q + 1)!!} \leq C_\lambda (|v|x)^\lambda e^{|v|x}, \quad (18)$$

with a constant $C_\lambda > 0$ depending only on λ .

Since the reduced Macdonald factor contributes the large- x decay $e^{-\alpha_s x}$, the termwise absolute majorant therefore has the form:

$$\sum_{q=0}^\infty \left| \frac{v^{\lambda+2q} x^{\lambda+2q}}{2^q q! (2\lambda + 2q + 1)!!} \frac{\hat{k}_\nu(R_{34}\gamma(s, x))}{(\zeta_s^2 + x^2)^{n_k} \gamma(s, x)^{n_\gamma}} \right| = O\left(x^\lambda e^{-(\alpha_s - |v|)x}\right), \quad (19)$$

for a finite algebraic exponent χ . From this, it follows that $|v| < \alpha_s$ is a sufficient condition for dominated termwise integration. The resulting moment representation is:

$$\tilde{K}(s) = \sum_{q=0}^{\infty} \frac{(-1)^q v^{\lambda+2q}}{2^q q! (2\lambda + 2q + 1)!!} \mathcal{M}_q(s) \quad \text{with} \quad \mathcal{M}_q(s) = \int_0^{\infty} \frac{x^{n_x + \lambda + 2q}}{(\zeta_s^2 + x^2)^{n_k}} \frac{\widehat{k}_\nu(R_{34}\gamma(s, x))}{\gamma(s, x)^{n_\gamma}} dx. \quad (20)$$

As $s \rightarrow 0^+$ or $s \rightarrow 1^-$, however, $\alpha_s \rightarrow 0$, so the moment representation does not provide a uniform expansion at the Feynman endpoints.

The endpoint and large- x structure follows directly from (8). For fixed x :

$$\gamma(s, x) = \zeta_4 + \frac{s}{2\zeta_4} (\zeta_3^2 - \zeta_4^2 + x^2) + O(s^2) \quad \text{as} \quad s \rightarrow 0^+, \quad (21)$$

and, with $\varepsilon = 1 - s$:

$$\gamma(1 - \varepsilon, x) = \zeta_3 + \frac{\varepsilon}{2\zeta_3} (\zeta_4^2 - \zeta_3^2 + x^2) + O(\varepsilon^2). \quad (22)$$

For fixed $0 < s < 1$ and $x \rightarrow \infty$:

$$\gamma(s, x) = \sqrt{s(1-s)} x \left[1 + \frac{(1-s)\zeta_4^2 + s\zeta_3^2}{2s(1-s)x^2} + O(x^{-4}) \right]. \quad (23)$$

Using the standard large-argument Macdonald-function expansion [14]:

$$K_\nu(z) \sim \sqrt{\frac{\pi}{2z}} e^{-z} \left[1 + \frac{4\nu^2 - 1}{8z} + O(z^{-2}) \right], \quad (24)$$

this gives the dominant molecular damping scale:

$$\exp[-R_{34}\sqrt{s(1-s)}x]. \quad (25)$$

Its decay rate collapses at the Feynman endpoints. The dimensionless ratio:

$$\rho(s) = \frac{v}{R_{34}\sqrt{s(1-s)}}, \quad (26)$$

measures the oscillation accumulated over the characteristic exponential decay length.

Since the characteristic exponential decay length is $[R_{34}\sqrt{s(1-s)}]^{-1}$ and the sine period is $2\pi/v(s)$, their ratio is $\rho(s)/(2\pi)$. From this, it follows that $\rho(s)/(2\pi)$ is the characteristic number of sine periods contained in one exponential decay length.

The sufficient condition derived above for the moment expansion corresponds to $\rho(s) < 1$.

3 Double-exponential quadrature and the two numerical formulations

The two quadrature routes differ only in the oscillatory factor:

$$\mathcal{O}(vx) = \begin{cases} j_\lambda(vx) & \text{for direct DE,} \\ \sin(vx) & \text{for } S + \text{DE.} \end{cases} \quad (27)$$

The DE transformation and trapezoidal discretization follow [15–20]. We consider:

$$I = \int_0^\infty F(x) \mathcal{O}(vx) dx, \quad (28)$$

and set $x = M\phi(t)$:

$$I = M \int_{-\infty}^\infty F(M\phi(t)) \mathcal{O}(vM\phi(t)) \phi'(t) dt. \quad (29)$$

The infinite and truncated trapezoidal approximations are:

$$I_h = Mh \sum_{k=-\infty}^\infty F(M\phi(kh)) \mathcal{O}(vM\phi(kh)) \phi'(kh), \quad (30)$$

and:

$$I_{h,N_-,N_+} = Mh \sum_{k=-N_-}^{N_+} F(M\phi(kh)) \mathcal{O}(vM\phi(kh)) \phi'(kh). \quad (31)$$

The separate indices N_- and N_+ allow asymmetric transformed tails. The error decomposition is:

$$I - I_{h,N_-,N_+} = (I - I_h) + (I_h - I_{h,N_-,N_+}), \quad (32)$$

with $I - I_h$ controlled by the analytic strip and $I_h - I_{h,N_-,N_+}$ by the transformed tails. Their asymptotic balance is derived below.

For the transformed sine integral, the zeros of the oscillatory factor occur exactly at:

$$x_n = \frac{n\pi}{v} \quad \text{for } n = 0, 1, 2, \dots \quad (33)$$

The Fourier-type DE construction exploits these regularly spaced zeros by choosing:

$$Mh = \frac{\pi}{v}. \quad (34)$$

Two Fourier-type mappings are considered for the S -transformed sine integral. The first is:

$$\phi_1(t) = \frac{t}{1 - \exp[-K \sinh t]} \quad \text{with } K = 6, \quad (35)$$

and the second is:

$$\phi_2(t) = \frac{t}{1 - \exp[-Q_2(t)]} \quad \text{with } Q_2(t) = 2t + \alpha(1 - e^{-t}) + \beta(e^t - 1), \quad (36)$$

with:

$$\beta = \frac{1}{4} \quad \text{and} \quad \alpha = \frac{\beta}{\sqrt{1 + M \log(1 + M)/(4\pi)}}. \quad (37)$$

Both mappings satisfy $\phi_j(t) \rightarrow 0$ double exponentially as $t \rightarrow -\infty$ and $\phi_j(t) - t \rightarrow 0$ double exponentially as $t \rightarrow +\infty$. Consequently, (34) gives for $j = 1, 2$:

$$vM\phi_j(kh) = k\pi + vM[\phi_j(kh) - kh] \rightarrow k\pi, \quad (38)$$

so the positive DE nodes approach the zeros of the sine function for both mappings.

For $j_\lambda(vx)$ the zeros are not equally spaced at finite index. Since its asymptotic period is $2\pi/v$, direct DE is supplemented by the conservative phase-resolution criterion:

$$vMh \leq \frac{\pi}{2}, \quad (39)$$

which gives asymptotically at least four nodes per oscillation and is used to ensure adequate resolution of the oscillations. Equations (34) and (39) therefore reflect the different numerical mechanisms of asymptotic alignment with the sine zeros and direct phase resolution.

4 Asymptotic Analysis and Convergence

We begin the convergence analysis with the inner radial kernel, for which the relative importance of molecular damping and oscillation is characterized by the parameter $\rho(s)$ defined in (26).

Figure 1 presents the results as a function of $\rho(s)$ (26) for $R_{34} = 2$ and $\lambda = 2$ and 4, using the nine combinations of $s \in \{0.0024, 0.5, 0.998\}$ and $v \in \{10, 25, 50\}$. The quadrature parameters are $M = 4$ and $h = \frac{\pi}{2vM}$ for direct DE, and $M = 8, 4, 2$ with $h = \frac{\pi}{vM}$ for $S + \text{DE}$. In both cases, the quadrature is truncated when the absolute value of its terms falls below 2×10^{-15} .

Figure 1 compares direct DE with both $S + \text{DE}$ mappings under these fixed quadrature parameters. The separation between direct DE and the two $S + \text{DE}$ routes increases strongly with $\rho(s)$ and λ . For the near-endpoint, strongly oscillatory grid case $(s, v, \lambda) = (0.998, 50, 4)$, the direct DE and $S + \text{DE}$ calculations require, respectively:

$$N_{\text{direct DE}} = 10194, \quad N_{S+\text{DE}(\phi_1)} = 174 \quad \text{and} \quad N_{S+\text{DE}(\phi_2)} = 303. \quad (40)$$

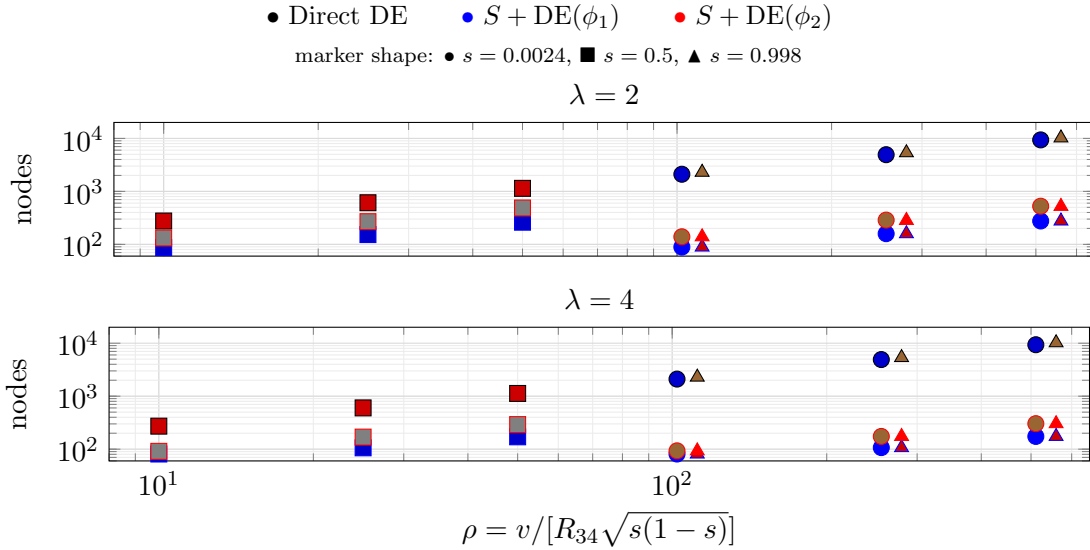


Figure 1: Quadrature-node counts for direct DE, $S + \text{DE}(\phi_1)$, and $S + \text{DE}(\phi_2)$ over the complete nine-point (s, v) grid for each $\lambda = 2, 4$.

The large- x behavior explains the short truncation after S . On the positive side, the hyperbolic sine and the exponential factor satisfy:

$$\sinh t \sim \frac{e^t}{2} \quad \text{and} \quad \epsilon(t) = \exp[-K \sinh t] \sim \exp\left(-\frac{K}{2}e^t\right) \quad \text{as} \quad t \rightarrow +\infty. \quad (41)$$

Using $\phi_1(t) = t/[1 - \epsilon(t)]$, subtraction of the identity map gives:

$$\phi_1(t) - t = t \frac{\epsilon(t)}{1 - \epsilon(t)} = O\left(te^{-Ke^t/2}\right) \quad \text{as} \quad t \rightarrow +\infty. \quad (42)$$

On the negative side, the corresponding asymptotic scale is:

$$\sinh t \sim -\frac{e^{-t}}{2} \quad \text{and} \quad \phi_1(t) \sim (-t) \exp\left(-\frac{K}{2}e^{-t}\right) = O\left((-t)e^{-Ke^{-t}/2}\right) \quad \text{as} \quad t \rightarrow -\infty. \quad (43)$$

The negative nodes collapse double exponentially toward $x = 0$, whereas on the positive side the map approaches the identity with a double-exponentially small difference. With $vMh = \pi$:

$$vM\phi_1(kh) = k\pi + \delta_k \quad \text{and} \quad \delta_k = O\left(ke^{-Ke^{kh}/2}\right), \quad (44)$$

which gives:

$$\sin[vM\phi_1(kh)] \sim (-1)^k \delta_k. \quad (45)$$

The sampled sine factor therefore decays double exponentially as the Fourier-DE nodes converge asymptotically to its equally spaced zeros. This property follows directly from the sine representation obtained by the S transformation.

For ϕ_2 , the positive-side exponent satisfies:

$$Q_2(t) = \beta e^t + 2t + \alpha - \beta + o(1) \quad \text{as} \quad t \rightarrow +\infty, \quad (46)$$

so:

$$\phi_2(t) - t = O\left(te^{-2t}e^{-\beta e^t}\right) \quad \text{as} \quad t \rightarrow +\infty. \quad (47)$$

On the negative side, $Q_2(t) \sim -\alpha e^{-t}$ and therefore:

$$\phi_2(t) = O\left((-t)e^{-\alpha e^{-t}}\right) \quad \text{as} \quad t \rightarrow -\infty. \quad (48)$$

Both maps generate double-exponential endpoint compression and double-exponential asymptotic alignment with the zeros of the sine function, but with different complex analytic structures.

Figure 2 shows the change in oscillatory geometry. For $\lambda > 0$ the finite-index zeros of j_λ are nonuniform, while the transformed sine factor has the equally spaced zeros in (33), precisely the structure used in (34).

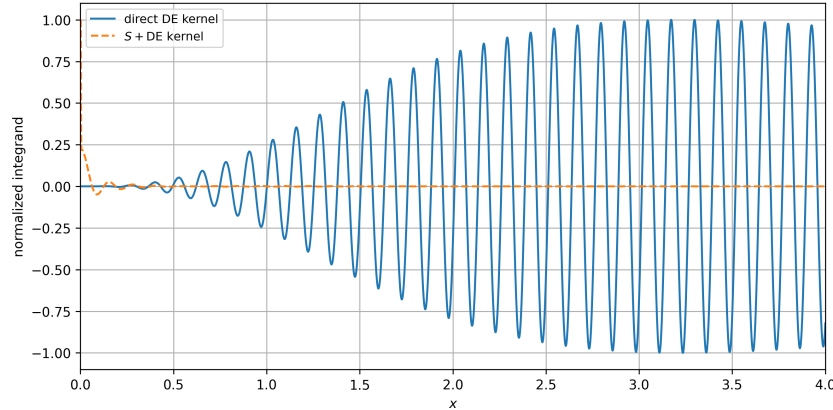


Figure 2: Normalized oscillatory kernels before and after the S transformation for the severe test case.

For fixed $0 < s < 1$, define:

$$a_s^2 = \frac{(1-s)\zeta_4^2 + s\zeta_3^2}{s(1-s)} \quad \text{and} \quad \gamma(s, x)^2 = s(1-s)(x^2 + a_s^2). \quad (49)$$

After the removable origin behavior established in (11), the factor $(\zeta_s^2 + x^2)^{-n_k}$ gives the candidate locations $x = \pm i\zeta_s$. Moreover, (49) gives $\gamma(s, x) = 0$ at $x = \pm ia_s$. Since ν is half-integer, the reduced

Macdonald function in (7) is an exponential multiplied by a finite polynomial and introduces no additional finite locations beyond those generated through $\gamma(s, x)$. The operator $(x^{-1}d/dx)^\lambda$ can change the orders of the nonremovable singularities but introduces no additional finite locations.

The set for the finite molecular singularities is:

$$\Sigma_x(s) = \{\pm i\zeta_s, \pm ia_s\}. \quad (50)$$

For ϕ_1 , the denominator vanishes when $K \sinh t = 2\pi im$. The point $t = 0$ is removable, but the other solutions on the $m = 0$ branch, $t = n\pi i$ with $n \neq 0$, are not. The set of nonremovable singularities of ϕ_1 , denoted by Σ_{ϕ_1} , is:

$$\Sigma_{\phi_1} = \{t \in \mathbb{C} : K \sinh t = 2\pi im, m \in \mathbb{Z}\} \setminus \{0\}. \quad (51)$$

For $K = 6$, writing $t = u + iy$ shows that the $m = \pm 1$ solutions nearest the real axis satisfy $|y| = \pi/2$ and $\cosh |u| = \pi/3$, whereas the nearest nonzero $m = 0$ points have $|y| = \pi$. Thus:

$$\text{dist}(\mathbb{R}, \Sigma_{\phi_1}) = \frac{\pi}{2}. \quad (52)$$

For ϕ_2 , the corresponding nonremovable map singularities are contained in:

$$\Sigma_{\phi_2} = \{t \in \mathbb{C} : Q_2(t) = 2\pi im, m \in \mathbb{Z}\} \setminus \{0\}, \quad (53)$$

where the individual solutions depend on M through α .

The locations of the molecular singularities in the t -plane depend on the transformation ϕ_j . We define their distance from the real axis by:

$$d_{\text{mol},j}(s, M) = \text{dist}(\mathbb{R}, \{t : M\phi_j(t) \in \Sigma_x(s)\}) \quad \text{for } j = 1, 2. \quad (54)$$

An admissible strip for either transformed sine integral satisfies:

$$0 < d_j < \min\{\text{dist}(\mathbb{R}, \Sigma_{\phi_j}), d_{\text{mol},j}(s, M)\} \quad \text{for } j = 1, 2. \quad (55)$$

The same molecular singularities are therefore present for both mappings, but the corresponding singularities in the t -plane can lie at different distances from the real axis. This dependence on the map and on the molecular parameters makes the convergence estimate below parameter dependent rather than uniform. The DE asymptotics determine the decay of the transformed trapezoidal tails. For the finite DE rule in (31), classical DE theory separates the trapezoidal discretization error from the two tail-truncation errors [15, 19, 21]. The transformed integrand is assumed to be analytic in the strip:

$$F(M\phi(t))\mathcal{O}(vM\phi(t))\phi'(t) \quad \text{is analytic for } |\Im t| < d. \quad (56)$$

Its decay along the real axis satisfies:

$$|F(M\phi(t))\mathcal{O}(vM\phi(t))\phi'(t)| \leq A \exp[-\beta e^{\gamma|t|}]. \quad (57)$$

The first condition gives a discretization contribution of scale $\exp(-2\pi d/h)$, while the second gives two truncation contributions that decay double exponentially with N_-h and N_+h . For a symmetric model with $N_- = N_+ = N$, balancing the discretization and truncation exponents gives:

$$\frac{2\pi d}{h} \approx \beta e^{\gamma Nh}. \quad (58)$$

Introducing $y = \gamma Nh$ reduces (58) to $ye^y \approx cN$ for $c > 0$ independent of N . Using the definition of the Lambert W function, we obtain:

$$\gamma Nh \approx W(cN) \quad \text{and} \quad h \asymp \frac{W(cN)}{\gamma N}. \quad (59)$$

Consequently, the characteristic near-exponential DE rate is:

$$\begin{aligned} |I - I_{h,N,N}| &= O\left(\exp\left[-C \frac{N}{W(cN)}\right]\right) \\ &= O\left(\exp\left[-C \frac{N}{\log N}\right]\right) \quad \text{as } N \rightarrow \infty, \end{aligned} \quad (60)$$

where $C > 0$ is also independent of N .

For each fixed molecular parameter set for which the strip described above has positive width, (60) gives the characteristic DE convergence scale. Since the constants, including the strip width d , depend on the molecular parameters, this estimate is not uniform over the complete molecular parameter domain.

The numerical results in the following section illustrate the performance of direct DE and S +DE for representative molecular parameters.

5 Numerical Analysis and Discussion

The numerical results below were generated in double-precision floating-point arithmetic. The ϕ_1 calculations use $K = 6$, while ϕ_2 uses (37). Both quadrature sums are truncated when their terms become smaller than 2×10^{-15} in absolute value, except where a different tolerance is stated explicitly. The complete H_2O calculations use a molecular tolerance of 10^{-10} . The outer Feynman-parameter integration uses a 48-point Gauss–Legendre quadrature for both the three-centre and hybrid calculations.

A direct comparison of the two Fourier-type maps is first made for the near-endpoint, strongly oscillatory kernel with $s = 0.998$, $\lambda = 4$, and $v = 49.996$. Both maps use the condition $vMh = \pi$ and the same termwise truncation threshold of 2×10^{-15} . A segmented numerical evaluation of the S -transformed representation gives the reference value $\tilde{K}_{\text{ref}} = 2.869930715021202 \times 10^{-4}$. The absolute error is defined by:

$$|E| = |\tilde{K} - \tilde{K}_{\text{ref}}|. \quad (61)$$

Table 1 shows that both maps reach approximately the same accuracy, but ϕ_1 requires substantially fewer quadrature nodes throughout the displayed refinement. We therefore use ϕ_1 for the remaining S +DE calculations.

Table 1: Comparison of the two Fourier-type DE maps for the near-endpoint, strongly oscillatory kernel with $s = 0.998$, $\lambda = 4$, $v = 49.996$, $R_{34} = 2$, $\zeta_s = 2$, and $\zeta_3 = \zeta_4 = 1$. Both maps use $vMh = \pi$.

Method	M	Nodes	Absolute error $ E $
S +DE(ϕ_1)	1	106	4.35×10^{-16}
S +DE(ϕ_1)	2	174	5.93×10^{-16}
S +DE(ϕ_1)	4	304	9.51×10^{-16}
S +DE(ϕ_2)	1	171	1.68×10^{-15}
S +DE(ϕ_2)	2	303	8.22×10^{-16}
S +DE(ϕ_2)	4	559	1.09×10^{-15}

Table 2 gives the corresponding refinement comparison. In this table h or M is varied to show the convergence of direct DE and $S+\text{DE}(\phi_1)$ for the same kernel. The severe case reported in [2] clearly illustrates the effectiveness of the S transformation. The direct-DE mesh with $h = 0.04$ does not adequately resolve the oscillations, leading to an inaccurate evaluation of the integral. Reducing the spacing to $h = 0.018$ requires 4591 nodes to reach an absolute error of 3.49×10^{-15} . By contrast, $S+\text{DE}(\phi_1)$ reaches an absolute error of 4.35×10^{-16} with 106 nodes at $M = 1$.

Table 2: Comparison for the severe inner-kernel benchmark of [2], with $s = 0.998$, $\lambda = 4$, $v = 49.996$, $R_{34} = 2$, $\zeta_s = 2$, and $\zeta_3 = \zeta_4 = 1$.

Method	Control	Nodes	Absolute error $ E $
Direct DE	$M = 4, h = 0.040$	2137	1.21
Direct DE	$M = 4, h = 0.020$	4150	1.36×10^{-13}
Direct DE	$M = 4, h = 0.018$	4591	3.49×10^{-15}
$S+\text{DE}(\phi_1)$	$M = 1$	106	4.35×10^{-16}
$S+\text{DE}(\phi_1)$	$M = 2$	174	5.93×10^{-16}
$S+\text{DE}(\phi_1)$	$M = 4$	304	9.51×10^{-16}

Table 3 shows the convergence with increasing M for near-endpoint weak-damping and interior strong-damping cases. The interior case reaches essentially full retained accuracy at moderate M , while the near-endpoint cases require additional refinement as the molecular damping becomes weaker. For each calculation, the mesh spacing h is determined from (34).

Table 3: Refinement of the $S+\text{DE}(\phi_1)$ quadrature for representative inner radial kernels.

(s, v, λ)	M	Nodes	Absolute error $ E $
$(0.0024, 10, 0)$	4	202	1.23×10^{-11}
$(0.0024, 10, 0)$	8	213	5.09×10^{-13}
$(0.5, 25, 2)$	2	97	2.29×10^{-15}
$(0.5, 25, 2)$	4	153	2.83×10^{-17}
$(0.998, 49.996, 4)$	1	106	4.35×10^{-16}
$(0.998, 49.996, 4)$	2	174	5.93×10^{-16}

Tables 4 and 5 present the twenty H_2O three-centre and hybrid integrals reported in Table 9 of [2]. The results obtained with direct DE and $S+\text{DE}(\phi_1)$ are compared with the complete S -series and agree with the corresponding values in [2]. The complete molecular integrals were evaluated using a 48-point Gauss–Legendre quadrature for the outer Feynman-parameter integration.

Table 4: Three-centre H_2O two-electron Coulomb benchmarks from Table 9 of [2].

Orbital descriptor	$S+\text{DE}(\phi_1)$	Direct DE	Complete S series
$1s_{\text{O}} 1s_{\text{O}} 1s_{\text{H}_1} 1s_{\text{H}_2}$	0.16673342273688249	0.16673342273647890	0.16673342273689856
$1s_{\text{O}} 2s_{\text{O}} 1s_{\text{H}_1} 1s_{\text{H}_2}$	0.033679727712775510	0.033679727712567269	0.033679727712788571
$1s_{\text{O}} 2p_{z,\text{O}} 1s_{\text{H}_1} 1s_{\text{H}_2}$	0.0015390182431065718	0.0015390182431966198	0.0015390182431086203
$2s_{\text{O}} 2s_{\text{O}} 1s_{\text{H}_1} 1s_{\text{H}_2}$	0.14543917348030505	0.14543917348020158	0.14543917348032670
$2p_{z,\text{O}} 2p_{z,\text{O}} 1s_{\text{H}_1} 1s_{\text{H}_2}$	0.13476347768925548	0.13476347768924848	0.13476347768928781
$2p_{-,\text{O}} 2p_{-,\text{O}} 1s_{\text{H}_1} 1s_{\text{H}_2}$	0.12838751944282475	0.12838751944282689	0.12838751944283502
$2p_{+,\text{O}} 2p_{+,\text{O}} 1s_{\text{H}_1} 1s_{\text{H}_2}$	-0.0016664571554343812	-0.0016664571554302627	-0.0016664571554373835
$1s_{\text{H}_1} 1s_{\text{H}_1} 1s_{\text{H}_2} 2s_{\text{O}}$	0.21848899525172549	0.21848899525171317	0.21848899525175847
$1s_{\text{H}_1} 1s_{\text{H}_1} 1s_{\text{H}_2} 2p_{z,\text{O}}$	0.15727268356179613	0.15727268356180352	0.15727268356182164
$1s_{\text{H}_1} 1s_{\text{H}_1} 1s_{\text{H}_2} 2p_{+,\text{O}}$	-0.084627891776168016	-0.084627891776158273	-0.084627891776177605

Table 5: Hybrid H₂O two-electron Coulomb benchmarks from Table 9 of [2].

Orbital descriptor	$S+DE(\phi_1)$	Direct DE	Complete S series
$1s_O 1s_O 1s_O 1s_{H_1}$	0.17563042735309245	0.17563042735117018	0.17563042735296155
$2s_O 1s_O 1s_O 1s_{H_1}$	0.026546346614613053	0.026546346765768211	0.026546346649179514
$2p_{z,O} 1s_O 2p_{z,O} 1s_{H_1}$	0.0052846247813397749	0.0052846247811819515	0.0052846247813461205
$2p_{+,O} 1s_O 2p_{z,O} 1s_{H_1}$	0.00088396023993295538	0.00088396024003546214	0.00088396023993574005
$1s_O 1s_O 2p_{z,O} 1s_{H_1}$	0.19597041600236950	0.19597041600376816	0.19597041600246379
$1s_O 1s_O 2p_{+,O} 1s_{H_1}$	0.18059055948521360	0.18059055948650241	0.18059055948530048
$1s_{H_1} 1s_{H_1} 1s_{H_1} 1s_O$	0.030786144383451900	0.030786144383331007	0.030786144383432128
$1s_{H_1} 1s_{H_1} 1s_{H_1} 2s_O$	0.32359640715248900	0.32359640715245541	0.32359640717367238
$1s_{H_1} 1s_{H_1} 1s_{H_1} 2p_{z,O}$	0.25886490309498722	0.25886490309498117	0.25886490313585997
$1s_{H_1} 1s_{H_1} 1s_{H_1} 2p_{+,O}$	0.23854905569238616	0.23854905569238075	0.23854905573005128

Tables 6 and 7 show the molecular content of the selected C₂H₄ benchmarks explicitly. The three-centre rows test the $2s$ and $2p_z$ sectors on the second carbon centre, while the hybrid rows include the more demanding high-angular-momentum cases. The values obtained with $S+DE(\phi_1)$ and direct DE are in complete agreement with those reported in [2], and agree with the S -series values to approximately 10^{-12} or better for the selected rows.

 Table 6: Selected complete three-centre two-electron Coulomb integrals for C₂H₄.

orbital descriptor	$S+DE(\phi_1)$	direct DE	complete S series
$1s_{C_1} 1s_{C_1} 1s_H 2s_{C_2}$	0.1934463965892313786	0.1934463965891601855	0.1934463965892695980
$1s_{C_1} 1s_{C_1} 1s_H 2p_{z,C_2}$	0.0245171857594094628	0.0245171857609684310	0.0245171857594243016

 Table 7: Complete hybrid two-electron Coulomb integrals for C₂H₄.

hybrid orbital descriptor	$S+DE(\phi_1)$	direct DE	complete S series
$1s_{C_1} 1s_{C_1} 1s_{C_1} 2s_{C_2}$	0.1360495110353241444	0.1360495110396955920	0.1360495110346501280
$2p_{z,C_1} 2p_{z,C_1} 2p_{z,C_1} 2p_{z,C_2}$	-0.2091198262132444308	-0.2091198262092846538	-0.2091198262088796722
$2p_{+,C_1} 2p_{+,C_1} 2p_{+,C_1} 2p_{+,C_2}$	0.1277170504840919318	0.1277170504851455890	0.1277170504851271871

6 Conclusions

A double-exponential formulation has been developed for the semi-infinite radial integrals arising in three-centre two-electron Coulomb and hybrid integrals over exponential-type functions. The S transformation plays a central role by converting the spherical-Bessel kernel into a sine integral whose regular zero structure is particularly well suited to Fourier-type DE quadrature. The analysis of the oscillatory and damping behaviour, the complex singularities, and the analyticity of the transformed integrands provides the mathematical basis for the resulting quadrature.

The numerical results demonstrate the accuracy and efficiency of both direct DE and $S+DE$ for the complete molecular integrals. The advantage of $S+DE$ becomes particularly significant for strongly oscillatory and weakly damped integrals, where the S transformation reorganizes the oscillatory structure before numerical quadrature. The calculations for complete molecular systems confirm that this advantage is retained in the evaluation of the molecular integrals and that the results reproduce the available reference values.

The $S+DE$ formulation thus provides an efficient computational approach for molecular-structure calculations involving strongly oscillatory integrals over exponential-type basis functions.

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