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The evaluation of some four-electron correlated integrals with a Slater basis arising in linear and nonlinear r12 theories

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Abstract

This study considers the analytic evaluation of correlated integrals involving explicit inter-electron separation distances using a basis of standard Slater-type functions. These basis functions are employed in Hylleraas-CI calculations, Hylleraas calculations on atomic four-electron systems, and in non-Born–Oppenheimer calculations on small molecular systems. A Fourier transform approach allows a principal auxiliary integral to be evaluated analytically, permitting a number of four-electron integrals to be reduced to various one-dimensional Cauchy–Frullani integrals, which can be evaluated in closed form. The stability of some of the formulas with respect to numerical evaluation, particularly for the high-order derivative cases, is discussed in detail. Numerical values for a selection of test integrals are provided.

Keywords: correlated integrals, Hylleraas calculations, Hylleraas-CI calculations

(Some figures may appear in colour only in the online journal)

1. Introduction

This work examines the closed form evaluation of some one-center four-electron integrals involving explicit inter-electron separation factors, r_{ij}. Two integrals that will form the focus of the present study are:

$$I_4(i, j, k, l, m, n, p, a, b, c, d, w_1, w_2, w_3) = \int r_1^i\ r_2^j\ r_3^k\ r_4^l\ r_{12}^m\ r_{23}^n\ r_{24}^p\ \mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_2r_{23}-w_3r_{24}} \times \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4 \tag{1}$$

and

$$J_4(i, j, k, l, m, n, p, a, b, c, d, w_1, w_2, w_3) = \int r_1^i\ r_2^j\ r_3^k\ r_4^l\ r_{12}^m\ r_{23}^n\ r_{34}^p \mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_2r_{23}-w_3r_{34}} \times \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4, \tag{2}$$

where the members of the set of indices $\{i, j, k, l, m, n, p\}$ are each $\geqslant -1$, $a > 0$, $b > 0$, $c > 0$, and $d > 0$, and the set $\{w_1, w_2, w_3\}$ are defined such that the integrals in equations (1) and (2) are convergent. The particular cases in many practical applications will be $w_1 = 0$, $w_2 = 0$, $w_3 = 0$, but the more general case of non-zero values for these parameters allows a large number of additional integral cases to be obtained by partial differentiation with respect to these parameters. The integrals appearing in equations (1) and (2) are special cases of the more general and very complex four-electron integral

$$\mathscr{I}_4(i, j, k, l, m, n, p, q, s, t, a, b, c, d, w_{12}, w_{13}, w_{14}, w_{23}, w_{24}, w_{34}) = \int r_1^i\ r_2^j\ r_3^k\ r_4^l\ r_{12}^m\ r_{13}^n r_{14}^p r_{23}^q\ r_{24}^s r_{34}^t \times \mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_{12}r_{12}-w_{13}r_{13}-w_{14}r_{14}-w_{23}r_{23}-w_{24}r_{24}-w_{34}r_{34}} \times \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4. \tag{3}$$

The only fairly general cases of this integral that have been studied have $w_{ij} = 0$ for $i = 1, 2, 3$ and $j = 2, 3, 4$ with $j > i$ [1–3]. The three-electron analogue of this integral has been studied [4–6].

A principal integral of interest is $J_4(0, 0, 0, 0, 1, 1, -1, a, b, c, d, 0, 0, 0)$:

$$J_4(0, 0, 0, 0, 1, 1, -1, a, b, c, d, 0, 0, 0) = \int \frac{r_{12} r_{23}}{r_{34}} \mathrm{e}^{-ar_1 - br_2 - cr_3 - dr_4} \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\mathbf{r}_2 \,\mathrm{d}\mathbf{r}_3 \,\mathrm{d}\mathbf{r}_4. \quad (4)$$

This integral arises in linear r12 theories for systems with at least four electrons when Slater-type basis functions incorporating a linear r_{ij} term are employed. In particular, it occurs in the Hylleraas-configuration interaction investigation of the S states of the beryllium I isoelectronic series. This integral also arises in the standard Hylleraas treatment of atomic four-electron S states, and also of small molecular systems treated in the non-Born–Oppenheimer approach.

The integral in equation (4) is a particular example of the more general integral

$$J_4(i, j, k, l, m, n, -1, a, b, c, d, 0, 0, 0) = \int r_1^i r_2^j r_3^k r_4^l \frac{r_{12}^m r_{23}^n}{r_{34}} \mathrm{e}^{-ar_1 - br_2 - cr_3 - dr_4} \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\mathbf{r}_2 \,\mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4, \quad (5)$$

where the members of the set of indices $\{i, j, k, l, m, n\}$ are each $\geqslant -1$, and $a > 0, b > 0, c > 0$, and $d > 0$. This integral arises in Hylleraas calculations that use Slater-type basis functions multiplied by nonlinear powers of r_{ij}, e.g. r_{ij}^m. An approach to the evaluation of this more general case is also discussed. There has been some discussion of equation (5) and some of its generalizations in the literature [1–17]. In particular, [14] considers some of the four-electron correlated integrals by an approach different than that presented in the present work. I note parenthetically that there are two typographical sign errors in equation (44) of [14]: the fourth and fifth terms inside the curly brackets should have positive and negative signs, respectively.

For the evaluation of the energy of various states, no exponent on an r_{ij} factor is less than -1. However, for the evaluation of certain relativistic corrections, and for calculations of lower bounds to the energy, integrals arise with factors r_{ij}^{-2} present. For the four-electron case very little published work is available, although the corresponding problem for the three-electron case has received attention [18–26].

After the present manuscript was substantially completed, Bholanath Padhy informed the author that he had treated some exponentially correlated two-electron, three-electron, and four-electron integrals [27], as well as some restrictive cases of the five-electron exponentially correlated integrals [28]. A key component of the present work is a consideration of the stability of the formulas as far as numerical evaluation is concerned. This is a critical issue if the analytic formulas are to be used for practical calculations. This topic is not considered in Padhy's work. The present study also gives a generalization of one of the two key results in [27].

2. A preliminary three-electron correlated integral

The approach to be employed to evaluate equation (4) in closed form is to reduce the four-electron integral to a three-electron problem. To deal with the resulting three-electron integrals, the following preliminary integral is considered first. Let $I_3(i, j, k, l, m, a, b, c, w_1, w_2)$ denote the following integral:

$$I_3(i, j, k, l, m, a, b, c, w_1, w_2) = \int r_1^i r_2^j r_3^k r_{12}^l r_{23}^m \mathrm{e}^{-ar_1 - br_2 - cr_3 - w_1 r_{12} - w_2 r_{23}} \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\mathbf{r}_2 \,\mathrm{d}\mathbf{r}_3, \quad (6)$$

for the indices $\{i, j, k, l, m\}$ each $\geqslant -1$, and with the exponential constants positive and chosen such that the integral converges. More complicated cases of this integral arise: those having l or $m = -2$, but they are not germane to the present analysis, and they do not arise in an evaluation of the energy or a number of other properties. Particular cases of I_3 will be required in the following sections. The following special case of equation (6) is useful in what follows:

$$I_3(-1, -1, -1, -1, -1, a, b, c, w_1, w_2) = \int \frac{\mathrm{e}^{-ar_1 - br_2 - cr_3 - w_1 r_{12} - w_2 r_{23}}}{r_1 r_2 r_3 r_{12} r_{23}} \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\mathbf{r}_2 \,\mathrm{d}\mathbf{r}_3. \quad (7)$$

This is a simpler case of a much more complicated correlated integral considered by Fromm and Hill [4], Harris [5], and related work is given in Remiddi [6]; see also [29–32]. This integral serves as an auxiliary function for the evaluation of a collection of other three-electron integrals, and in particular, to all those occurring in equation (6).

Equation (7) can be expressed as

$$I_3(-1, -1, -1, -1, -1, a, b, c, w_1, w_2) = \int \frac{\mathrm{e}^{-br_2}}{r_2} g(a, w_1, r_2)\, g(c, w_2, r_2)\, \mathrm{d}\mathbf{r}_2, \quad (8)$$

with

$$g(a, w_1, r_2) = \int \frac{\mathrm{e}^{-ar_1 - w_1 r_{12}}}{r_1 r_{12}} \mathrm{d}\mathbf{r}_1. \quad (9)$$

One approach to resolving the preceding integral in an expedient fashion is to employ the Fourier integral representation:

$$\frac{\mathrm{e}^{-wr}}{r} = \frac{1}{2\pi^2} \int \frac{\mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{r}}}{p^2 + w^2} \mathrm{d}\mathbf{p}. \quad (10)$$

Using equation (10) for each of the exponential factors appearing in equation (9) leads to

$$g(a, w_1, r_2) = \frac{1}{4\pi^4}\int\int\frac{\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_1}}{q^2+a^2}\mathrm{d}\mathbf{q}\int\frac{\mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{r}_{12}}}{p^2+w_1^2}\mathrm{d}\mathbf{p}\,\mathrm{d}\mathbf{r}_1$$
$$= \frac{1}{4\pi^4}\int\frac{\mathrm{d}\mathbf{p}}{p^2+w_1^2}\int\frac{\mathrm{d}\mathbf{q}}{q^2+a^2}\int\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_1+\mathrm{i}\mathbf{p}\cdot\mathbf{r}_{12}}\mathrm{d}\mathbf{r}_1. \tag{11}$$

Employing the three-dimensional Dirac delta distribution representation:

$$\delta(\mathbf{k}) = \frac{1}{(2\pi)^3}\int\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\,\mathrm{d}\mathbf{r}, \tag{12}$$

allows equation (11) to be simplified to

$$g(a, w_1, r_2) = \frac{2}{\pi}\int\frac{\mathrm{e}^{-\mathrm{i}\mathbf{p}\cdot\mathbf{r}_2}\mathrm{d}\mathbf{p}}{p^2+w_1^2}\int\frac{\delta(\mathbf{p}+\mathbf{q})\mathrm{d}\mathbf{q}}{q^2+a^2}$$
$$= \frac{2}{\pi}\int\frac{\mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{r}_2}\mathrm{d}\mathbf{p}}{(p^2+w_1^2)(p^2+a^2)}$$
$$= \frac{2}{\pi(w_1^2-a^2)}\int\left\{\frac{1}{p^2+a^2}-\frac{1}{p^2+w_1^2}\right\}$$
$$\times\,\mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{r}_2}\mathrm{d}\mathbf{p} = \frac{4\pi}{(w_1^2-a^2)r_2}(\mathrm{e}^{-ar_2}-\mathrm{e}^{-w_1r_2}), \tag{13}$$

where equation (10) has been employed to obtain the final result. The case of principal interest in the following analysis is $a \neq w_1$ in the preceding equation. Employing equation (13) for $g(a, w_1, r_2)$ allows equation (8) to be written as a Cauchy–Frullani integral:

$$I_3(-1, -1, -1, -1, -1, a, b, c, w_1, w_2)$$
$$= \int\frac{\mathrm{e}^{-br_2}}{r_2}g(a, w_1, r_2)\,g(c, w_2, r_2)\,\mathrm{d}\mathbf{r}_2$$
$$= \frac{64\pi^3}{(w_1^2-a^2)(w_2^2-c^2)}$$
$$\times\int_0^\infty\frac{\mathrm{e}^{-br_2}}{r_2}(\mathrm{e}^{-ar_2}-\mathrm{e}^{-w_1r_2})(\mathrm{e}^{-cr_2}-\mathrm{e}^{-w_2r_2})\mathrm{d}r_2$$
$$= \frac{64\pi^3}{(w_1^2-a^2)(w_2^2-c^2)}$$
$$\times\ln\left[\frac{(a+b+w_2)(b+c+w_1)}{(a+b+c)(b+w_1+w_2)}\right]. \tag{14}$$

The result in equation (14) can be used to generate a sequence of integrals of the form given in equation (6) for $\{i, j, k, l, m\}$ each $\geqslant -1$, by partial differentiation of equation (14) with respect to the parameters $\{a, b, c, w_1, w_2\}$. For example:

$$I_3(-1, 0, -1, -1, -1, a, b, c, w_1, w_2)$$
$$= -\frac{\partial}{\partial b}I_3(-1, -1, -1, -1, -1, a, b, c, w_1, w_2)$$
$$= \frac{64\pi^3}{(w_1^2-a^2)(w_2^2-c^2)}\left\{\frac{1}{a+b+c}+\frac{1}{b+w_1+w_2}\right.$$
$$\left.-\frac{1}{a+b+w_2}-\frac{1}{b+c+w_1}\right\} \tag{15}$$

and

$$I_3(0, 0, 0, -1, -1, a, b, c, w_1, w_2)$$
$$= \frac{\partial^2}{\partial a\partial c}I_3(-1, 0, -1, -1, -1, a, b, c, w_1, w_2)$$
$$= \frac{128\pi^3}{(w_1^2-a^2)^2(w_2^2-c^2)^2}$$
$$\times\left(\frac{(a^2c^2-c^2w_1^2-a^2w_2^2+w_1^2w_2^2)}{(a+b+c)^3}\right.$$
$$+\frac{(a^2c+ac^2-cw_1^2-aw_2^2)}{(a+b+c)^2}+\frac{2ac}{(a+b+c)}$$
$$+\frac{c(w_1^2-a^2)}{(a+b+w_2)^2}+\frac{a(w_2^2-c^2)}{(b+c+w_1)^2}$$
$$\left.+2ac\left(\frac{1}{b+w_1+w_2}-\frac{1}{a+b+w_2}-\frac{1}{b+c+w_1}\right)\right). \tag{16}$$

3. Four-electron integrals involving the factor $r_{12}r_{23}r_{34}^{-1}$

Our focus in this section is the integral having a factor $r_{12}r_{23}r_{34}^{-1}$ in the integrand, which is a special case of equation (2):

$$J_4(-1, -1, 0, 0, 1, 1, -1, a, b, c, d, 0, 0, 0)$$
$$= \int\frac{r_{12}r_{23}}{r_1r_2r_{34}}\mathrm{e}^{-ar_1-br_2-cr_3-dr_4}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4. \tag{17}$$

The first step is to reduce the four-electron to a three-electron by integrating over the coordinate of one electron. The most convenient choice here is to integrate over electron four: a straightforward calculation yields

$$\int\frac{\mathrm{e}^{-dr_4}}{r_{34}}\mathrm{d}\mathbf{r}_4 = \frac{4\pi}{d^3}\left(\frac{2}{r_3}-d\,\mathrm{e}^{-dr_3}-\frac{2}{r_3}\mathrm{e}^{-dr_3}\right). \tag{18}$$

Inserting equation (18) into equation (17) leads to the result

$$J_4(-1, -1, 0, 0, 1, 1, -1, a, b, c, d, 0, 0, 0)$$
$$= \frac{4\pi}{d^3}\{2A(a, b, c) - d\,B(a, b, c+d)$$
$$-2A(a, b, c+d)\}. \tag{19}$$

The auxiliary functions $A(a, b, c)$ and $B(a, b, c)$ in equation (19) can be evaluated from equations (7) and (14) as:

$$A(a, b, c) = \int \frac{r_{12}r_{23}}{r_1 r_2 r_3} e^{-ar_1 - br_2 - cr_3} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3$$
$$= \left. \frac{\partial^4 I_3(-1, -1, -1, -1, -1, a, b, c, w_1, w_2)}{\partial w_1^2 \partial w_2^2} \right|_{\substack{w_1 \to 0 \\ w_2 \to 0}}$$
$$= \frac{128\pi^3}{(abc)^4}\Bigg(a^2b^2 + 3a^2c^2 + b^2c^2 + b^4\left\{2\ln\left[\frac{\lambda_2\lambda_3}{b\lambda_1}\right] - \frac{a^2}{\lambda_3^2} - \frac{c^2}{\lambda_2^2}\right\}\Bigg), \tag{20}$$

where

$$\lambda_1 = a + b + c, \quad \lambda_2 = a + b, \quad \lambda_3 = b + c, \tag{21}$$

and

$$B(a, b, c + d) = \int \frac{r_{12}r_{23}}{r_1 r_2} e^{-ar_1 - br_2 - (c+d)r_3} d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3$$
$$= -\left. \frac{\partial^5 I_3(-1, -1, -1, -1, -1, a, b, \gamma, w_1, w_2)}{\partial w_1^2 \partial w_1^2 \partial \gamma} \right|_{\substack{w_1 \to 0 \\ w_2 \to 0 \\ \gamma \to c+d}}$$
$$= -\left. \frac{\partial A(a, b, \gamma)}{\partial \gamma} \right|_{\gamma \to c+d}$$
$$= \frac{256\pi^3}{a^4\lambda_6^5}\Bigg(b^{-4}(2a^2b^2 + \lambda_6^2(3a^2 + b^2)) - \frac{\lambda_6^2}{\lambda_2^2} - \frac{2a^2}{\lambda_5^2} - \frac{a\lambda_6}{\lambda_5}\left(\frac{1}{\lambda_4} + \frac{a}{\lambda_5^2}\right) + 4\ln\left[\frac{\lambda_2\lambda_5}{b\lambda_4}\right]\Bigg), \tag{22}$$

where

$$\lambda_4 = a + b + c + d, \quad \lambda_5 = b + c + d, \quad \lambda_6 = c + d. \tag{23}$$

From equations (19)–(23) the special case of equation (17) for $a = b = c = d$ yields:

$$J_4(-1, -1, 0, 0, 1, 1, -1, a, a, a, a, 0, 0, 0) = \frac{16\pi^4}{27a^{11}}\{5167 + 7344\ln(2) - 3888\ln(3)\}. \tag{24}$$

The second integral case considered having an integrand contribution of $r_{12}r_{23}r_{34}^{-1}$ is

$$J_4(0, 0, 0, 0, 1, 1, -1, a, b, c, d, 0, 0, 0) = \int \frac{r_{12}r_{23}}{r_{34}} e^{-ar_1 - br_2 - cr_3 - dr_4} d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 d\mathbf{r}_4. \tag{25}$$

This integral follows directly from $J_4(-1, -1, 0, 0, 1, 1, -1, a, b, c, d, 0, 0, 0)$ by partial differentiation with respect to the parameters a and b:

$$J_4(0, 0, 0, 0, 1, 1, -1, a, b, c, d, 0, 0, 0) = \frac{\partial^2 J_4(-1, -1, 0, 0, 1, 1, -1, a, b, c, d, 0, 0, 0)}{\partial a \partial b}. \tag{26}$$

The auxiliary functions $C(a, b, c)$ and $D(a, b, c)$ are introduced using the following definitions:

$$C(a, b, c) = \frac{\partial^2 A(a, b, c)}{\partial a \partial b}$$
$$= \frac{256\pi^3}{a^5b^5c^4}(12a^2c^2 + 2b^2(a^2 + 2b^2 + 2c^2) + b^5\{4(\lambda_1^{-1} - \lambda_2^{-1} - \lambda_3^{-1}) + a(\lambda_1^{-2} - \lambda_2^{-2}) - c^2\lambda_2^{-3}(4 + 3a\lambda_2^{-1}) - 2a^2\lambda_3^{-3}\}) \tag{27}$$

and

$$D(a, b, c) = \frac{\partial^2 B(a, b, c)}{\partial a \partial b}$$
$$= \frac{256\pi^3}{(ab\lambda_6)^5}(24a^2\lambda_6^2 + 8b^2(a^2 + 2b^2 + \lambda_6^2) + b^5\{16(\lambda_4^{-1} - \lambda_2^{-1} - \lambda_5^{-1}) + 4a(\lambda_4^{-2} - \lambda_2^{-2}) - 3a\lambda_6\lambda_4^{-1}\lambda_5^{-1}(\lambda_5^{-1} + \lambda_4^{-1}) - 8a^2\lambda_5^{-3} - 8\lambda_6^2\lambda_2^{-3} - a^2\lambda_6(6\lambda_5^{-4} + \lambda_4^{-2}\lambda_5^{-2} + 2\lambda_4^{-3}\lambda_5^{-1}) - 6a\lambda_6^2\lambda_2^{-4}\}). \tag{28}$$

Hence

$$J_4(0, 0, 0, 0, 1, 1, -1, a, b, c, d, 0, 0, 0) = \frac{4\pi}{d^3}\{2C(a, b, c) - dD(a, b, c + d) - 2C(a, b, c + d)\}. \tag{29}$$

From equations (26)–(29) the special case of equation (25) for $a = b = c = d$ yields:

$$J_4(0, 0, 0, 0, 1, 1, -1, a, a, a, a, 0, 0, 0) = \frac{668890\pi^4}{27a^{13}}. \tag{30}$$

4. Four-electron integrals involving the factor $(r_{12}r_{23}r_{24})^{-1}$

In this section the following integral is considered:

$$I_4(-1, 0, -1, -1, -1, -1, -1, a, b, c, d, w_1, w_2, w_3) = \int \frac{e^{-ar_1 - br_2 - cr_3 - dr_4 - w_1r_{12} - w_2r_{23} - w_3r_{24}}}{r_1 \, r_3 \, r_4 \, r_{12}r_{23}r_{24}} d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 d\mathbf{r}_4 \tag{31}$$

and a further generalization of this integral will also be considered. To solve equation (31) employ equations (7) and (14) and integrate over $\mathbf{r}_4$ to obtain

$$I_4(-1{,}0,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3)\,\frac{4\pi}{(w_3^2-d^2)}\{I_3(-1,-1,-1,-1,-1,a,b+d,c,w_1,w_2) - I_3(-1,-1,-1,-1,-1,a,b+w_3,c,w_1,w_2)\}$$
$$= \frac{256\pi^4}{(w_1^2-a^2)(w_2^2-c^2)(w_3^2-d^2)} \times \ln\left[\frac{(a+b+d+w_2)(b+c+d+w_1)(a+b+c+w_3)(b+w_1+w_2+w_3)}{(a+b+c+d)(b+d+w_1+w_2)(a+b+w_2+w_3)(b+c+w_1+w_3)}\right]. \quad (32)$$

This result will be useful as a check on the following integral.

A generalization of equation (31) is:

$$I_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3) = \int \frac{\mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_2r_{23}-w_3r_{24}}}{r_1\,r_2\,r_3\,r_4\,r_{12}r_{23}r_{24}}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4. \quad (33)$$

To evaluate this integral in closed form, it will be assumed that $a \neq w_1$, $c \neq w_2$, and $d \neq w_3$, then integrate over $\mathbf{r}_4$ followed by integration over $\mathbf{r}_3$ and $\mathbf{r}_1$ to obtain

$$\begin{aligned} &I_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3)\\ &= \frac{4\pi}{(w_3^2-d^2)}\int_0^\infty \frac{(\mathrm{e}^{-dr_2}-\mathrm{e}^{-w_3r_2})}{r_2}\,\frac{\mathrm{e}^{-br_2}}{r_2}\mathrm{d}r_2\\ &\times \int_0^\infty \frac{\mathrm{e}^{-ar_1-w_1r_{12}}}{r_1\,r_{12}}\mathrm{d}\mathbf{r}_1\int_0^\infty \frac{\mathrm{e}^{-cr_3-w_2r_{23}}}{r_3\,r_{23}}\mathrm{d}\mathbf{r}_3\\ &= \frac{256\pi^4}{(w_1^2-a^2)(w_2^2-c^2)(w_3^2-d^2)}\\ &\times \int_0^\infty \frac{(\mathrm{e}^{-(a+b)r_2}-\mathrm{e}^{-(b+w_1)r_2})(\mathrm{e}^{-cr_2}-\mathrm{e}^{-w_2r_2})(\mathrm{e}^{-dr_2}-\mathrm{e}^{-w_3r_2})}{r_2^2}\mathrm{d}r_2. \end{aligned} \quad (34)$$

The resulting Cauchy–Frullani integral can be evaluated by integration by parts with the result that

$$\begin{aligned} &I_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3)\\ &= \frac{256\pi^4}{(w_1^2-a^2)(w_2^2-c^2)(w_3^2-d^2)}\\ &\times\{(a+b+c+d)\ln(a+b+c+d)\\ &-(b+c+d+w_1)\ln(b+c+d+w_1)\\ &-(a+b+d+w_2)\ln(a+b+d+w_2)\\ &-(a+b+c+w_3)\ln(a+b+c+w_3)\\ &+(b+d+w_1+w_2)\ln(b+d+w_1+w_2)\\ &+(b+c+w_1+w_3)\ln(b+c+w_1+w_3)\\ &+(a+b+w_2+w_3)\ln(a+b+w_2+w_3)\\ &-(b+w_1+w_2+w_3)\ln(b+w_1+w_2+w_3)\}. \end{aligned} \quad (35)$$

This result serves as the auxiliary function for generating additional analytic results by taking partial derivatives with respect to the parameter sets (a, b, c, d) and (w_1, w_2, w_3). The final form given makes it immediately apparent what the analytic structure of the partial derivative terms will be, and renders obvious the simplifications that result on taking a partial derivative with respect to any of the parameters. This integral has been considered in [27], but the final form given in that work makes it a bit less obvious as to the structure of the partial derivatives, without making further algebraic manipulations. As an immediate check on equation (35), it follows that

$$I_4(-1{,}0,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3) - \frac{\partial I_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3)}{\partial b}. \quad (36)$$

Essentially by inspection it can be observed that equation (32) is recovered from the preceding result. Equation (35) represents a generalization of a result given by Roberts [7].

5. Four-electron integrals involving the factor $(r_{12}r_{23}r_{34})^{-1}$

In this section the following integral is considered:

$$J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3) = \int \frac{\mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_2r_{23}-w_3r_{34}}}{r_1\,r_2\,r_3\,r_4\,r_{12}r_{23}r_{34}}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4. \quad (37)$$

This integral is not connected to the integral considered in the previous section by a simple change of integration variables. A simpler case of equation (37) is considered first. The result obtained will provide a check on the more general result to be considered, and will also provide an avenue for generating other results in a more straightforward fashion. Consider

$$J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,0,w_3) = \int \frac{\mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_3r_{34}}}{r_1\,r_2\,r_3\,r_4\,r_{12}r_{23}r_{34}}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4. \quad (38)$$

Making use of equations (9) and (13) and assuming that $a \neq w_1$ and $d \neq w_3$, the preceding integral can be simplified by integrating over $\mathbf{r}_1$ and $\mathbf{r}_4$ to obtain

$$J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,0,w_3) = \frac{16\pi^2}{(w_1^2-a^2)(w_3^2-d^2)} \int \frac{\mathrm{e}^{-br_2-cr_3}}{r_2\,r_3\,r_{23}} \left(\frac{\mathrm{e}^{-ar_2}-\mathrm{e}^{-w_1r_2}}{r_2}\right) \times \left(\frac{\mathrm{e}^{-dr_3}-\mathrm{e}^{-w_3r_3}}{r_3}\right) \mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3. \tag{39}$$

The preceding integral can be evaluated in a number of ways: for example working directly in the $\{r_2, r_3, r_{23}\}$ coordinates, working in perimetric coordinates, or by a standard Legendre expansion of the r_{23}^{-1} factor. Using the latter approach leads to

$$\begin{aligned} J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,0,w_3) &= \frac{256\pi^4}{(w_1^2-a^2)(w_3^2-d^2)} \int_0^\infty [\mathrm{e}^{-(a+b)r_2}-\mathrm{e}^{-(b+w_1)r_2}]\mathrm{d}r_2 \\ &\times \left\{ r_2^{-1}\int_0^{r_2} [\mathrm{e}^{-(c+d)r_3}-\mathrm{e}^{-(c+w_3)r_3}]dr_3 \right. \\ &\left. + \int_{r_2}^\infty [\mathrm{e}^{-(c+d)r_3}-\mathrm{e}^{-(c+w_3)r_3}]r_3^{-1}\mathrm{d}r_3 \right\}. \end{aligned} \tag{40}$$

Using a change of integration order leads to a simple Cauchy–Frullani integral, and hence

$$\begin{aligned} J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,0,w_3) &= \frac{256\pi^4}{(w_1^2-a^2)(w_3^2-d^2)} \\ &\times \left\{ \frac{1}{a+b} \ln\left[\frac{(c+w_3)(a+b+c+d)}{(c+d)(a+b+c+w_3)}\right] \right. \\ &+ \frac{1}{c+d} \ln\left[\frac{(b+w_1)(a+b+c+d)}{(a+b)(b+c+d+w_1)}\right] \\ &+ \frac{1}{b+w_1} \ln\left[\frac{(c+d)(b+c+w_1+w_3)}{(c+w_3)(b+c+d+w_1)}\right] \\ &\left. + \frac{1}{c+w_3} \ln\left[\frac{(a+b)(b+c+w_1+w_3)}{(b+w_1)(a+b+c+w_3)}\right] \right\}. \end{aligned} \tag{41}$$

Two special cases of the preceding result are:

$$\begin{aligned} J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,0,0,0) &= \frac{256\pi^4}{a^2d^2} \left\{ \frac{1}{a+b} \ln\left[\frac{c(a+b+c+d)}{(c+d)(a+b+c)}\right] \right. \\ &+ \frac{1}{c+d} \ln\left[\frac{b(a+b+c+d)}{(a+b)(b+c+d)}\right] \\ &+ \frac{1}{b} \ln\left[\frac{(c+d)(b+c)}{c(b+c+d)}\right] \\ &\left. + \frac{1}{c} \ln\left[\frac{(a+b)(b+c)}{b(a+b+c)}\right] \right\} \end{aligned} \tag{42}$$

and

$$J_4(-1,-1,-1,-1,-1,-1,-1,a,a,a,a,0,0,0) = \frac{128\pi^4}{a^5}\{9\ln 2 - 5\ln 3\}. \tag{43}$$

To evaluate the more general auxiliary integral case, equation (37), the integrations over $\mathbf{r}_1$ and $\mathbf{r}_4$ are carried out to obtain:

$$J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3) = \frac{16\pi^2}{(w_1^2-a^2)(w_3^2-d^2)} \int \frac{\mathrm{e}^{-br_2-cr_3-w_2r_{23}}}{r_2\,r_3\,r_{23}} \times \left(\frac{\mathrm{e}^{-ar_2}-\mathrm{e}^{-w_1r_2}}{r_2}\right)\left(\frac{\mathrm{e}^{-dr_3}-\mathrm{e}^{-w_3r_3}}{r_3}\right)\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3. \tag{44}$$

To handle this integral, perimetric coordinates are employed. These coordinates are often defined by

$$x = r_2 + r_3 - r_{23}, \quad y = r_3 + r_{23} - r_2, \quad z = r_{23} + r_2 - r_3 \tag{45}$$

and

$$\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3 = \frac{1}{32}(x+y)(x+z)(y+z) \times \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\sin\theta_2\,\mathrm{d}\theta_2\,\mathrm{d}\phi_2\,\mathrm{d}\chi, \tag{46}$$

where $\{\theta_2, \phi_2\}$ are the polar angles and χ ranges over the interval $[0, 2\pi]$. After integration over the angular variables equation (44) simplifies to

$$\begin{aligned} J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3) &= \frac{256\pi^4}{(w_1^2-a^2)(w_3^2-d^2)} \int_0^\infty\int_0^\infty\int_0^\infty \mathrm{e}^{-w_2(y+z)} \\ &\times \left(\frac{\mathrm{e}^{-(a+b)(x+z)}-\mathrm{e}^{-(b+w_1)(x+z)}}{x+z}\right) \\ &\times \left(\frac{\mathrm{e}^{-(c+d)(x+y)}-\mathrm{e}^{-(c+w_3)(x+y)}}{x+y}\right)\mathrm{d}x\mathrm{d}y\mathrm{d}z. \end{aligned} \tag{47}$$

Employing the change of variables $y = xu$ and $z = xv$ followed by integration over the x variable and then the v variable leads to

$$\begin{aligned} J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3) &= \frac{256\pi^4}{(w_1^2-a^2)(w_3^2-d^2)} \int_0^\infty \frac{\mathrm{d}u}{(1+u)} \\ &\times \left\{ \frac{1}{c+d-w_2+(c+d+w_2)u} \right. \end{aligned}$$

$$\times\{\ln(b+w_1+w_2)-\ln(a+b+w_2) + \ln[a+b+c+d+(c+d+w_2)u] - \ln[b+c+d+w_1+(c+d+w_2)u]\} + \frac{1}{c+w_3-w_2+(c+w_3+w_2)u} \times\{\ln(a+b+w_2)-\ln(b+w_1+w_2) + \ln[a+b+c+w_3+(c+w_3+w_2)u] - \ln[b+c+w_3+w_1+(c+w_3+w_2)u]\}\}. \quad (48)$$

To simplify equation (48) the following result is required:

$$\int_0^\infty \frac{\ln(1+\alpha u)\,\mathrm{d}u}{(1+u)(\beta+u)} = \frac{1}{\beta-1}\{\mathrm{Li}_2(1-\alpha) - \mathrm{Li}_2(1-\alpha\beta)\} \quad \text{for } 0<\alpha<1 \text{ and } 0<\beta\leqslant 1. \quad (49)$$

In equation (49), $\mathrm{Li}_2(x)$ is the dilogarithm function defined by [33]

$$\mathrm{Li}_2(x) = -\int_0^x \frac{\ln(1-t)\,\mathrm{d}t}{t}, \quad (50)$$

and a series representation is

$$\mathrm{Li}_2(x) = \sum_{n=1}^\infty \frac{x^n}{n^2}, \quad \text{for } |x|\leqslant 1. \quad (51)$$

Evaluating the integral in equation (48) leads to the result:

$$J_4(-1,-1,-1,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3) = \frac{128\pi^4}{(w_1^2-a^2)(w_3^2-d^2)w_2} \times\left\{\ln\left[\frac{(c+d-w_2)(c+w_2+w_3)}{(c+d+w_2)(c-w_2+w_3)}\right] \times\{\ln(a+b+w_2)-\ln(b+w_1+w_2)\} + \ln\left[\frac{b+c+d+w_1}{a+b+c+d}\right]\ln\left[\frac{c+d-w_2}{c+d+w_2}\right] + \ln\left[\frac{a+b+c+w_3}{b+c+w_1+w_3}\right]\ln\left[\frac{c+w_3-w_2}{c+w_3+w_2}\right] - \mathrm{Li}_2\left[\frac{a+b-w_2}{a+b+c+d}\right] + \mathrm{Li}_2\left[\frac{a+b+w_2}{a+b+c+d}\right] - \mathrm{Li}_2\left[\frac{b+w_1-w_2}{b+c+w_1+w_3}\right] + \mathrm{Li}_2\left[\frac{b+w_1+w_2}{b+c+w_1+w_3}\right] + \mathrm{Li}_2\left[\frac{b+w_1-w_2}{b+c+d+w_1}\right] - \mathrm{Li}_2\left[\frac{b+w_1+w_2}{b+c+d+w_1}\right] + \mathrm{Li}_2\left[\frac{a+b-w_2}{a+b+c+w_3}\right] - \mathrm{Li}_2\left[\frac{a+b+w_2}{a+b+c+w_3}\right]\right\}. \quad (52)$$

This result serves as a master auxiliary function for generating additional analytic results. One check on equation (52) is to establish that the special case given in equation (41) can be recovered. This can be accomplished by noticing that the dilogarithm functions in equation (52) appear in pairs, and then employ the following result

$$\lim_{w_2\to 0}\{\mathrm{Li}_2[\alpha-\beta w_2] - \mathrm{Li}_2[\alpha+\beta w_2]\} = \frac{2\beta\, w_2}{\alpha}\ln(1-\alpha) + O(w_2^3). \quad (53)$$

It is a now straightforward calculation to check that equation (52) simplifies to give equation (41). Padhy [27] has given a formula for the integral $J_4(-1,-1,0,-1,-1,-1,-1,a,b,c,d,w_1,w_2,w_3)$, which is a special case of equation (52). Padhy's result is obtained by taking $-\partial/\partial c$ of equation (52) followed by some algebraic simplification.

Equation (52) would not be stable for numerical evaluation for very small values of w_2, in this case it is necessary to develop a series expansion for each of the terms involving w_2. Equation (52) represents a generalization of a result given by Bonham [8].

6. Computational results

The values reported in table 1 were evaluated using equation (24) for the first two entries in table 1, equations (19)–(23) for entry 3, equation (30) for entries 4 and 5, and equations (27)–(29) for entry 6. The calculations were carried out using *Mathematica*. Table 2 reports values for integrals given in equation (32) for the first three entries, and from equation (35) for entries four through six. Approximately the first 30 digits of the values given in each table were checked by evaluating the integrals in Fortran quadruple precision using the numerical method detailed in [1].

7. Stability issues

Understanding the stability issues associated with the analytic formulas generated in the previous sections is of paramount importance in obtaining correct numerical results in a computer code. Two stability issues that can arise when numerical evaluation of the analytical formulas are considered are discussed in this section. Since the formulas derived involve terms with opposite signs, a programmer needs to be alert for the possibility of serious loss of significant digits when numerical evaluation of the formulas is carried out.

The first stability issue occurs when there is a major spread in the range of exponent parameters. For example, consider the particular case of equation (32) when $w_1 = w_2 = w_3 = 0$, then

$$I_4(-1,0,-1,-1,-1,-1,-1,a,b,c,d,0,0,0) = \frac{256\pi^4}{a^2c^2d^2}\left\{\ln\left[\frac{(a+b+c+d)(a+b)}{(b+c+d)b}\right] - \ln\left[\frac{(a+b+d)(a+b+c)}{(b+d)(b+c)}\right]\right\}. \quad (54)$$

Table 1. Numerical values for some selected integrals defined in equation (2) with $k = 0$, $l = 0$, $m = 1$, $n = 1$, $p = 1$, $w_1 = 0$, $w_2 = 0$, and $w_3 = 0$.

i	j	a	b	c	d	Value of integral $J_4(i, j, k, l, m, n, p, a, b, c, d, w_1, w_2, w_3)$
−1	−1	1.0	1.0	1.0	1.0	$3.45539\ 24355\ 48835\ 61747\ 60578\ 38500\ 94785\ 47888 \times 10^5$
−1	−1	1.1	1.1	1.1	1.1	$1.21109\ 39689\ 74017\ 59523\ 00900\ 73653\ 52335\ 73747 \times 10^5$
−1	−1	1.10	1.85	2.37	2.91	$2.23992\ 51764\ 52198\ 18876\ 32798\ 24447\ 81943\ 42854 \times 10^2$
0	0	1.0	1.0	1.0	1.0	$2.41318\ 39593\ 23477\ 41641\ 04657\ 08598\ 07266\ 16233 \times 10^6$
0	0	1.1	1.1	1.1	1.1	$6.99013\ 43476\ 79600\ 45679\ 99755\ 49780\ 96695\ 60957 \times 10^5$
0	0	1.10	1.85	2.37	2.91	$8.03931\ 01779\ 69560\ 20612\ 05053\ 72530\ 43664\ 96571 \times 10^2$

Table 2. Numerical values for some selected integrals defined in equation (1) with $k = -1$, $l = -1$, $m = -1$, $n = -1$, $p = -1$, $w_1 = 0$, $w_2 = 0$, and $w_3 = 0$.

i	j	a	b	c	d	Value of integral $I_4(i, j, k, l, m, n, p, a, b, c, d, w_1, w_2, w_3)$
−1	0	1.0	1.0	1.0	1.0	$4.23672\ 59498\ 98803\ 75144\ 82411\ 34017\ 15341\ 98603 \times 10^3$
−1	0	1.1	1.1	1.1	1.1	$2.39152\ 13475\ 00201\ 09465\ 50760\ 22794\ 10837\ 10131 \times 10^3$
−1	0	1.10	1.85	2.37	2.91	$7.38981\ 96016\ 67390\ 39639\ 62882\ 67469\ 50894\ 45730 \times 10^1$
−1	−1	1.0	1.0	1.0	1.0	$4.57464\ 43739\ 51803\ 04393\ 40441\ 54551\ 14758\ 64139 \times 10^3$
−1	−1	1.1	1.1	1.1	1.1	$2.84049\ 42371\ 99274\ 17025\ 29286\ 71384\ 31154\ 50472 \times 10^3$
−1	−1	1.10	1.85	2.37	2.91	$1.54222\ 62030\ 58219\ 36368\ 88385\ 66887\ 49225\ 79271 \times 10^2$

Numerical evaluation of the preceding formula for the set of exponents $a = 0.01$, $b = 15$, $c = 0.1$, $d = 0.1$ leads to a positive contribution (the first logarithm term) of

$$2.70814\ 33576\ 98039\ 26364\ 94617\ 82973 \times 10^{13},$$

and a negative contribution (the second logarithm term)

$$-\ 2.70814\ 33432\ 26111\ 26685\ 54214\ 33563 \times 10^{13},$$

and the value of the integral is $1.44719\ 27996\ 79404\ 03494\ 10 \times 10^6$, leading to the loss of eight digits of precision when the positive and negative contributions are combined. The loss of precision in this example can be avoided by doing a series expansion of the logarithm factors treating the exponent a as small with respect to the exponent b. The exponent spread in this example would be atypical, but a carefully constructed computer integral evaluation algorithm would need to be prepared to handle this type of situation.

A more complicated situation arises when high-order partial derivatives are taken, and the possibility for serious loss of precision can occur when powers of the radial coordinates (or the electron–electron coordinates) are large. This issue is addressed by considering some specific examples. The basic strategy is to write a particular integral in the following form:

$$I_4(i, j, k, l, m, n, p, a, b, c, d, \ w_1, w_2, w_3) = \sum_{\mu=1}^{N_\mathrm{p}} \{\mathrm{pos}\}_\mu + \sum_{\mu=1}^{N_\mathrm{n}} \{\mathrm{neg}\}_\mu, \tag{55}$$

where N_p and N_n denote the number of positive and negative terms, respectively, and $\{\mathrm{pos}\}_\mu$ and $\{\mathrm{neg}\}_\mu$ denote the individual algebraic terms that are >0 and <0, respectively. Once the two summations are calculated the precision loss when the final value is obtained can be directly evaluated from equation (55).

The specific examples considered are the following:

case 1: $a = 1.2$, $b = 1.5$, $c = 1.9$, $d = 2.7$ and $w_1 = w_2 = w_3 = 0$;

$$I_4(-1, m-1, -1, -1, -1, -1, -1, a, b, c, d, w_1, w_2, w_3) = \int r_1^{-1} r_2^{m-1} r_3^{-1} r_4^{-1} r_{12}^{-1} r_{23}^{-1} r_{24}^{-1} \times \mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_2r_{23}-w_3r_{24}}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4, \tag{56}$$

case 2: $a = 1.2$, $b = 1.5$, $c = 1.9$, $d = 2.7$ and $w_1 = w_2 = w_3 = 0$;

$$I_4(m-1, -1, -1, -1, -1, -1, -1, a, b, c, d, w_1, w_2, w_3) = \int r_1^{m-1} r_2^{-1} r_3^{-1} r_4^{-1} r_{12}^{-1} r_{23}^{-1} r_{24}^{-1} \times \mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_2r_{23}-w_3r_{24}}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4, \tag{57}$$

case 3: $a = 1.2$, $b = 1.5$, $c = 1.9$, $d = 2.7$ and $w_1 = w_2 = w_3 = 0$;

$$I_4(-1, -1, -1, m-1, -1, -1, -1, a, b, c, d, w_1, w_2, w_3) = \int r_1^{-1} r_2^{-1} r_3^{-1} r_4^{m-1} r_{12}^{-1} r_{23}^{-1} r_{24}^{-1} \times \mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_2r_{23}-w_3r_{24}}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4, \tag{58}$$

case 4: $a = 1.2$, $b = 1.5$, $c = 1.9$, $d = 2.7$ and $w_1 = w_2 = w_3 = 0$;

$$I_4(-1, -1, -1, -1, m-1, -1, -1, a, b, c, d, w_1, w_2, w_3) = \int r_1^{-1} r_2^{-1} r_3^{-1} r_4^{-1} r_{12}^{m-1} r_{23}^{-1} r_{24}^{-1} \times \mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_2r_{23}-w_3r_{24}}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4, \tag{59}$$

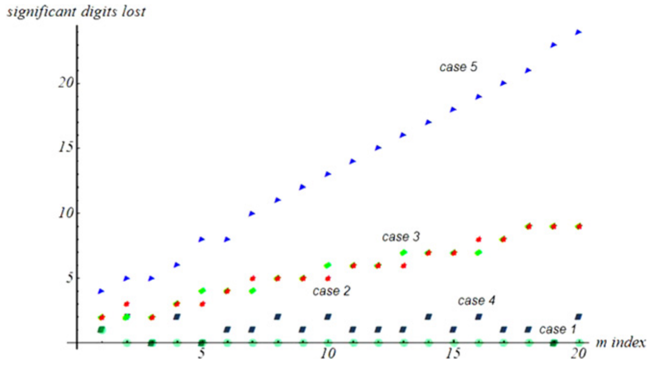

Figure 1. A plot of the significant digit loss as a function of the index m for the correlated integral cases given in cases 1 to 5 (equations (56)–(60)). The online colors are indicated in parentheses. Case 1, solid circle (off-green); case 2, six-pointed star (red); case 3, solid diamond (green); case 4, solid rhombus (dark blue); and case 5, solid triangles (blue).

$$\begin{aligned}&\text{case 5: } a = 1.2,\ b = 1.5,\ c = 1.9,\ d = 2.7\\ &\quad \text{and } w_1 = 1,\ w_2 = w_3 = 0;\\ &I_4(-1, -1, -1, -1, m-1, -1,\\ &\qquad -1, a, b, c, d, w_1, w_2, w_3)\\ &\quad = \int r_1^{-1} r_2^{-1} r_3^{-1} r_4^{-1} r_{12}^{m-1} r_{23}^{-1} r_{24}^{-1}\\ &\qquad \times \mathrm{e}^{-ar_1-br_2-cr_3-dr_4-w_1r_{12}-w_2r_{23}-w_3r_{24}}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4.\end{aligned} \tag{60}$$

Evaluation of equation (55) for each of the preceding five test cases was carried out by calculating the required derivatives symbolically, splitting the resulting expressions apart term by term, and then numerically determining each positive and negative contribution separately, and finally calculating the separate sums of positive and negative terms. The final expressions for the separate algebraic sums in equation (55) become extremely complicated as the index m is increased, and are too lengthy to reproduce in the present paper. These calculations were performed in *Mathematica*. The results for these five test cases are summarized in figure 1.

8. Discussion

For case 1, there is no loss of precision for a wide range of values of the index m. For cases 2 and 3 the loss in precision as a function of increasing values of the index m is similar. At $m = 20$ the loss in precision is sufficiently large that standard double precision arithmetic in a Fortran code would not be sufficient for an effective evaluation of cases 2 and 3. Integrals with large values of the index m would occur in particular for excited states, or for ground state and low-lying excited states when very large basis sets are employed. It would be useful for the reader to recall that a basis function with a radial electron-nuclear coordinate raised to the power $m/2$ will lead to correlated integrals with an exponent with an index of m on a radial coordinate.

For case 4 there is loss of precision of 0, 1, or 2 digits for values of the index m up to 20. For an energy evaluation using an r12 approach, the values of the index m are small, typically $m = 2$ or smaller. However, if expectation values of the inter-electronic coordinates are evaluated, then the values of the index m can be much larger. Note that the same integrals arise in other computational approaches, for example, a standard Hylleraas approach on atomic systems with four or more electrons or on molecular systems treated within the non-Born–Oppenheimer model. For this situation, higher powers on the inter-electronic coordinate arise naturally.

Case 5, which employs a non-zero value for one of the parameter set $\{w_1, w_2, w_3\}$, shows a major loss in digits of precision as the index m is increased. Exponentially correlated Slater-type basis functions are not commonly employed in the construction of wave functions. The loss of significant digits for this particular example indicates that particular care would be needed in the evaluation of this type of integral, particularly when the exponent index m becomes large.

When the power indices on the r_{ij} terms take on small values such as -1, the rate of convergence of the series expansion formulas of the integrals decreases [1]. In these cases in particular, access to the analytic formulas can be particularly advantageous. The reason for the slow convergence rate of the series expansion approach arises from the attempt to represent a logarithm term by a series, which is slowly converging. Inspection of several of the analytic formulas for these types of cases show the presence of logarithm factors in the final answers.

For correlated integrals with r_{ij} terms to higher powers than the first in equation (5), these cases can be obtained by direct partial differentiation of equation (52) with respect to the parameters w_1 and w_2 and then taking the limits $w_i \to 0$, for $i = 1, 2, 3$. For example, from equation (52)

$$\begin{aligned}&J_4(-1, -1, -1, -1, 3, 3, -1, a, b, c, d, 0, 0, 0)\\ &= \int \frac{r_{12}^3 r_{23}^3}{r_1 r_2 r_3 r_4 r_{34}} \mathrm{e}^{-ar_1-br_2-cr_3-dr_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4\\ &= \lim_{w_1\to 0} \lim_{w_2\to 0} \lim_{w_3\to 0} \frac{\partial^4}{\partial w_1^4} \frac{\partial^4}{\partial w_2^4} J_4\\ &\quad \times (-1, -1, -1, -1, -1, -1, -1, a, b, c, d, w_1, w_2, w_3).\end{aligned} \tag{61}$$

The powers on the r_i terms can be increased by taking the appropriate partial derivatives with respect to the parameters a, b, c, and d. A similar approach can be applied to the I_4 integrals starting from equation (35).

9. Conclusion

In this study, a number of the four-electron correlated integrals that can arise in Hylleraas-CI calculations, Hylleraas calculations on atomic four-electron systems, and in non-Born–Oppenheimer calculations on small molecular systems, have been evaluated analytically. A further class of integrals can be evaluated by taking partial derivatives with respect to the parameters which appear in the key auxiliary integrals. The numerical stability of the analytic formulas is investigated for several of the key analytic formulas.

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