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On the evaluation of four-electron correlated integrals with a Slater basis: some simplifications and some closed form examples

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Abstract

Four-electron correlated integrals with explicit r_{ij} dependence and derived from a Slater-type basis set are discussed. Attention is directed to the more complex cases where the powers on the r_{ij} factors are odd. Particular effort is focused on the case where there are five factors of r_{ij} raised to odd powers, a case that has considerable practical significance. Several integral cases involving three and four r_{ij} factors raised to odd powers are evaluated in closed form.

Keywords: correlated integrals, Hylleraas calculations, four-electron systems

1. Introduction

Standard Hylleraas-type calculations on four-electron atomic systems and non-Born–Oppenheimer studies on few-electron molecular systems using a basis set of Slater-type functions have been limited by the rather recalcitrant nature of the integral problem that underlies the calculations. The Hylleraas trial wave function for an S state of a four-electron atomic system takes the following form:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \mathscr{A} \sum_{\mu=1}^{N} C_\mu r_1^{i_\mu} r_2^{j_\mu} r_3^{k_\mu} r_4^{l_\mu} r_{12}^{m_\mu} r_{13}^{n_\mu} r_{14}^{p_\mu} r_{23}^{q_\mu} r_{24}^{s_\mu} r_{34}^{t_\mu} \times \mathrm{e}^{-a_\mu r_1 - b_\mu r_2 - c_\mu r_3 - d_\mu r_4} \chi_\mu, \quad (1)$$

where r_i is the electron–nucleus separation distance for electron i, r_{ij} is an electron–electron separation distance for electrons i and j, $\mathscr{A}$ is the four-electron antisymmetrizer, C_μ denotes the expansion coefficients, χ_μ is a spin eigenfunction, and N represents the number of basis terms in the expansion. The constants a_μ, b_μ, c_μ, and d_μ are > 0, and the integer indices $\{i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu, p_\mu, q_\mu, s_\mu, t_\mu\}$ are each $\geqslant 0$. The explicit appearance of r_{ij} factors in the expansion leads to an integration problem of considerable complexity. In the past few years, considerable progress on high-precision calculations on three-, four- and five-electron systems has been achieved by avoiding the use of a Slater-type basis, and working in terms of explicitly correlated Gaussian functions [1–7]. The major advantage of the latter choice is that the integration problem is now significantly simplified. Two limitations of using explicitly correlated Gaussian functions are they do not have the appropriate asymptotic behaviour, and they do not describe the necessary cusp conditions. These latter drawbacks can be overcome if one is willing to use a rather large number of basis functions.

The nonrelativistic Hamiltonian in either the finite nuclear mass form or in the infinite nuclear mass model, can be written in terms of derivatives with respect to the variables r_i and r_{ij}. It is a straightforward calculation to show that the evaluation of the energy and a number of other expectation values for the S states of four-electron atomic systems can be reduced to the evaluation of four-electron integrals that take the following form:

$$I_4(i, j, k, l, m, n, p, q, s, t, \alpha, \beta, \gamma, \delta) = \int r_1^i r_2^j r_3^k r_4^l r_{12}^m r_{13}^n r_{14}^p r_{23}^q r_{24}^s r_{34}^t \times \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\mathbf{r}_3 \, \mathrm{d}\mathbf{r}_4. \quad (2)$$

In equation (2), the exponents satisfy $\alpha > 0$, $\beta > 0$, $\gamma > 0$, and $\delta > 0$. In order for the integral to converge the individual

integer indices i through t must be $\geqslant -2$. An energy evaluation requires integrals that have the integer parameters m, n, p, q, s, t each $\geqslant -1$, and various cases of the integral satisfying these constraints have been discussed in the literature [8–21]. More complicated expectation values, such as those arising for some of the relativistic corrections to the energy, require integrals where some of the integer indices $\{m, n, p, q, s, t\}$ are equal to -2. These cases are significantly more difficult to evaluate; they will not be discussed further in the present work.

The present work has two principal objectives. The first is to consider some major simplifications of a complex general formula of the author, which allows numerical values to be obtained for four-electron integrals containing five odd powers of the inter-electronic coordinates r_{ij} in equation (2). The second objective is to obtain some closed form expressions for some particular cases of the four-electron integrals, which cannot be obtained by simple separation of the four-electron cases into products of integrals of lower dimensionality.

The complexity of the integral in equation (2) is governed in large part by the number of odd values of the parameter set $\{m, n, p, q, s, t\}$. In previous work [15] the general integral was worked out, but the effectiveness of the algorithm presented restricts integrals to a maximum of four odd values of the parameter set $\{m, n, p, q, s, t\}$. In the present work our focus will be on the five odd case—that is, five members of the parameter set $\{m, n, p, q, s, t\}$ are odd integers. This integral case does merit special attention for the following reason. If a basis set member is selected for example with a core–core correlation factor and either a core–valence or valence–valence correlation factor, then the simplest such term would have two odd entries for the parameter set $\{m, n, p, q, s, t\}$. Allowing for the four-electron antisymmetrizer in equation (1), then matrix elements of the electron–electron potential operator in the Hamiltonian immediately lead to a four-electron integral with five odd entries for the parameter set $\{m, n, p, q, s, t\}$. Basis set terms with the aforementioned correlation contributions are expected to be important for energy considerations. One can of course argue that these terms could be offset by using a number of similar correlated basis functions, but with even powers. The cost however, is that larger basis set sizes are required, and also the general convergence of the calculations of both the energy and other expectation values is now slower.

2. Theory

The electron–electron separation distance r_{ij} is commonly expanded using a Sack expansion [22], which takes the form:

$$r_{12}^{m} = \sum_{m_1=0}^{\infty} R_{mm_1}(r_1, r_2) P_{m_1}(\cos\theta_{12}), \tag{3}$$

where $R_{mm_1}(r_1, r_2)$ is a Sack radial function. The Sack radial function [22] can be written as

$$R_{mm_1}(r_1, r_2) = \frac{(-m/2)_{m_1}}{(1/2)_{m_1}} r_{12<}^{m_1} r_{12>}^{m-m_1} \sum_{u=0}^{\infty} a_{m_1 mu} \left(\frac{r_{12<}}{r_{12>}}\right)^{2u}, \tag{4}$$

where $r_{12<} = \min(r_1, r_2)$ and $r_{12>} = \max(r_1, r_2)$, and the coefficients a_{wmu} are given by

$$a_{m_1 mu} = \frac{\left(m_1 - \frac{m}{2}\right)_u \left(-\frac{1}{2} - \frac{m}{2}\right)_u}{u! \left(m_1 + \frac{3}{2}\right)_u}, \tag{5}$$

and $(\alpha)_n$ denotes a Pochhammer symbol, defined in terms of the gamma function $\Gamma(p)$ as [23]

$$(p)_q = p(p+1)(p+2)\cdots(p+q-1) = \frac{\Gamma(p+q)}{\Gamma(p)}. \tag{6}$$

The expansion in equation (3) has been recast in a different form by Perkins [24]:

$$r_{12}^{v} = \sum_{q=0}^{\infty} P_q(\cos\theta_{12}) \sum_{k=0}^{\infty} C_{vqk} r_{12<}^{q+2k} r_{12>}^{v-q-2k}, \tag{7}$$

where the coefficients C_{vqk} are given by:

$$C_{v0k} = \frac{(1+v)!}{(2k+1)!(v+1-2k)!}, \tag{8}$$

and for $q \geqslant 1$,

$$\begin{aligned} C_{vqk} &= \frac{(3/2)_q}{(1/2)_q} \frac{\left(k - \frac{v}{2}\right)_q}{\left(k + \frac{3}{2}\right)_q} C_{v0k} \\ &= (2q+1)\, C_{v0k} \prod_{t=0}^{q-1} \frac{(2k - v + 2t)}{(2k + 3 + 2t)}. \end{aligned} \tag{9}$$

The factor after the product symbol can be written in more than one equivalent form. Equation (7) simplifies to

$$r_{12}^{v} = \sum_{q=0}^{v/2} P_q(\cos\theta_{12}) \sum_{k=0}^{\frac{v}{2}-q} C_{vqk} r_{12<}^{q+2k} r_{12>}^{v-q-2k},$$
$$\text{for } v \text{ even and} \quad v \geqslant 0, \tag{10}$$

and

$$r_{12}^{v} = \sum_{q=0}^{\infty} P_q(\cos\theta_{12}) \sum_{k=0}^{(v+1)/2} C_{vqk} r_{12<}^{q+2k} r_{12>}^{v-q-2k},$$
$$\text{for } v \text{ odd and} \quad v \geqslant -1. \tag{11}$$

Equation (11) follows directly from the property of the Pochhammer symbol:

$$(-p)_q = 0 \quad \text{for integer } p \text{ and} \quad q > p. \tag{12}$$

The preceding condition also implies that the summation in equation (4) will terminate at finite values because of the definition of the a_{wmu} coefficient in equation (5). The summation in equation (3) will also be terminating if m is even, because of the Pochhammer condition $(-m/2)_{m_1}$ appearing in equation (4). When m is an odd integer, then the series in equation (3) is nonterminating, unless there is a constraint imposed by the angular integration.

If each inter-electronic distance factor appearing in equation (2) is expanded using a separate Sack expansion, then the following result is obtained [15, 17, 21]:

$$\begin{aligned} &I_4(i, j, k, l, m, n, p, q, s, t, \alpha, \beta, \gamma, \delta) \\ &= \sum_{m_1=0}^{\infty} \sum_{n_1=0}^{\infty} \sum_{p_1=0}^{\infty} \sum_{q_1=0}^{\infty} \sum_{s_1=0}^{\infty} \sum_{t_1=0}^{\infty} I_R(m_1, n_1, p_1, q_1, s_1, t_1) \\ &\quad \times I_\Omega(m_1, n_1, p_1, q_1, s_1, t_1), \end{aligned} \tag{13}$$

where

$$I_\Omega(m_1,n_1,p_1,q_1,s_1,t_1) = 256\pi^4(-1)^{m_1+t_1}\begin{pmatrix} m_1 & n_1 & p_1 \\ 0 & 0 & 0\end{pmatrix} \times \begin{pmatrix} m_1 & q_1 & s_1 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} n_1 & q_1 & t_1 \\ 0 & 0 & 0\end{pmatrix} \times \begin{pmatrix} p_1 & s_1 & t_1 \\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} m_1 & n_1 & p_1 \\ t_1 & s_1 & q_1\end{Bmatrix}, \tag{14}$$

and

$$\begin{aligned} I_R(m_1,n_1,p_1,q_1,s_1,t_1) &\equiv \int r_1^{i+2}r_2^{j+2}r_3^{k+2}r_4^{l+2} \\ &\quad\times \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}R_{mm_1}(r_1,r_2)\,R_{nn_1}(r_1,r_3)\,R_{pp_1}(r_1,r_4) \\ &\quad\times R_{qq_1}(r_2,r_3)\,R_{ss_1}(r_2,r_4)\,R_{tt_1}(r_3,r_4)\,\mathrm{d}r_1\,\mathrm{d}r_2\,\mathrm{d}r_3\,\mathrm{d}r_4 \\ &= \sum_{m_2=0}^{\infty}\sum_{n_2=0}^{\infty}\sum_{p_2=0}^{\infty}\sum_{q_2=0}^{\infty}\sum_{s_2=0}^{\infty}\sum_{t_2=0}^{\infty} h(m_1,n_1,p_1,q_1,s_1, \\ &\quad t_1,m_2,n_2,p_2,q_2,s_2,t_2). \end{aligned} \tag{15}$$

In equation (14), $\begin{pmatrix} a & b & c \\ d & e & f\end{pmatrix}$ denotes a $3j$ symbol and $\begin{Bmatrix} a & b & c \\ d & e & f\end{Bmatrix}$ designates a $6j$ symbol. To simplify the notation in equations (13) and (15), the $\{i,j,k,l,m,n,p,q,s,t,\alpha,\beta,\gamma,\delta\}$ dependence of I_R and the h function have been suppressed. The h function appearing in equation (15) can be obtained by reference to equations (38)–(42) of [15]: the final expression is lengthy and is not repeated here. The radial integral $I_R(m_1,n_1,p_1,q_1,s_1,t_1)$ involves a six-fold summation of a set of 24 auxiliary integrals that take the form [15]:

$$W_4(i,j,k,l,a,b,c,d) = \int_0^\infty x^i\,\mathrm{e}^{-ax}\,\mathrm{d}x\int_x^\infty y^j\,\mathrm{e}^{-by}\,\mathrm{d}y \times \int_y^\infty z^k\,\mathrm{e}^{-cz}\,\mathrm{d}z\int_z^\infty w^l\,\mathrm{e}^{-dw}\,\mathrm{d}w. \tag{16}$$

In order that $W_4(i,j,k,l,a,b,c,d)$ converge, requires the conditions $a>0, b>0, c>0, d>0$, and

$$i\geqslant 0,\quad i+j\geqslant -1,\quad i+j+k\geqslant -2,\quad i+j+k+l\geqslant -3. \tag{17}$$

The W_4 integrals have been discussed extensively in the literature [13–15, 25–28]. The final formula for $I_R(m_1,n_1,p_1,q_1,s_1,t_1)$ is fairly involved: the details of the derivation can be found in [15, 17, 18] (see equation (42) of [15] for the final result).

As previously indicated, the most difficult cases of equation (2) to evaluate arise when the integer indices $\{m,n,p,q,s,t\}$ take on odd values. For the case of even values of these indices, both summations in equations (3) and (4) terminate at finite values of the summation index; for odd values of the indices the summation in equation (4) terminates at finite values, but equation (3) does not. So it should be evident that an increasing number of odd powers leads to a considerable increase in the complexity of the integral evaluation.

By imposing some constraints, a number of special cases of equation (13) can be obtained which lead to substantial simplifications. A huge simplification results if the index $t=0$ in equation (2). Note that there is an intrinsic symmetry for the I_4 integral:

$$\begin{aligned} I_4(i,j,k,l,m,n,p,q,s,t,\alpha,\beta,\gamma,\delta) &= I_4(j,i,k,l,m,q,s,n,p,t,\beta,\alpha,\gamma,\delta) \\ &= I_4(k,j,i,l,q,n,t,m,s,p,\gamma,\beta,\alpha,\delta) \\ &= I_4(l,j,k,i,s,t,p,q,m,n,\delta,\beta,\gamma,\alpha), \quad \text{etc}, \end{aligned} \tag{18}$$

and hence the condition $t=0$ can equally well be replaced by a condition where any single one of the indices $\{m,n,p,q,s,t\}$ is taken to be zero. This represents a fairly useful case to consider, for the following reason. If the choice of basis functions in equation (1) include terms with no more than two nonzero powers, which could both be odd, then the most complicated integral required in an energy evaluation has a maximum of five odd indices with the sixth index being zero. This can be seen directly by evaluating the expectation value of the electron–electron repulsion energy and keeping in mind the presence of the antisymmetrizer operator.

Equation (14) can be simplified by noting the following property of the $6j$ symbol [29]

$$\begin{Bmatrix} m_1 & n_1 & p_1 \\ 0 & s_1 & q_1\end{Bmatrix} = \frac{(-1)^{m_1+p_1+q_1}}{\sqrt{(2p_1+1)(2q_1+1)}}\delta_{p_1s_1}\delta_{q_1n_1}, \tag{19}$$

where δ_{xy} denotes a Kronecker delta. A direct consequence of equation (19) and the requirement that the triangle condition must be satisfied by the $3j$ symbols, it follows that the third and fourth $3j$ symbols in equation (14) lead to the Kronecker deltas $\delta_{q_1n_1}$ and $\delta_{p_1s_1}$, respectively. Hence equation (14) simplifies for the case $t=0$ to yield

$$\begin{aligned} I_\Omega(m_1,n_1,p_1,q_1,s_1,0) &= 256\pi^4\frac{(-1)^{p_1+q_1}}{\sqrt{(2n_1+1)(2p_1+1)}} \\ &\quad\times\delta_{p_1s_1}\delta_{q_1n_1}\begin{pmatrix} m_1 & n_1 & p_1 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} m_1 & q_1 & s_1 \\ 0 & 0 & 0\end{pmatrix} \\ &\quad\times\begin{pmatrix} n_1 & q_1 & 0 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} p_1 & s_1 & 0 \\ 0 & 0 & 0\end{pmatrix} \\ &= \frac{256\pi^4(-1)^{p_1+q_1}\delta_{p_1s_1}\delta_{q_1n_1}}{\sqrt{(2n_1+1)(2p_1+1)}}\begin{pmatrix} m_1 & n_1 & p_1 \\ 0 & 0 & 0\end{pmatrix}^2 \\ &\quad\times\begin{pmatrix} n_1 & n_1 & 0 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} p_1 & p_1 & 0 \\ 0 & 0 & 0\end{pmatrix}. \end{aligned} \tag{20}$$

Note that the $3j$ symbol $\begin{pmatrix} m_1 & n_1 & p_1 \\ 0 & 0 & 0\end{pmatrix}$ vanishes unless $m_1+n_1+p_1$ is an even integer [29, 30]. Inserting the expression

$$\begin{pmatrix} n_1 & n_1 & 0 \\ 0 & 0 & 0\end{pmatrix} = \frac{(-1)^{n_1}}{\sqrt{2n_1+1}}, \tag{21}$$

and the corresponding result for $\begin{pmatrix} p_1 & p_1 & 0 \\ 0 & 0 & 0\end{pmatrix}$ into equation (20), leads to

$$I_\Omega(m_1,n_1,p_1,q_1,s_1,0) = \frac{256\pi^4\delta_{p_1s_1}\delta_{q_1n_1}}{(2n_1+1)(2p_1+1)}\begin{pmatrix} m_1 & n_1 & p_1 \\ 0 & 0 & 0\end{pmatrix}^2. \tag{22}$$

Set

$$2p = m_1 + n_1 + p_1, \tag{23}$$

then the square of the $3j$ symbol appearing in equation (22) simplifies to

$$\begin{pmatrix} m_1 & n_1 & p_1 \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{f(p-m_1)f(p-n_1)f(p-p_1)}{(2p+1)f(p)}, \tag{24}$$

where $f(p)$ is defined by

$$f(p) = \frac{(2p)!}{(p!)^2}. \tag{25}$$

The function f can be readily evaluated and stored as an array outside of any of the loop structure, so that the square of the required $3j$ symbol can be efficiently evaluated. The angular integral for the case $t = 0$ simplifies to

$$I_\Omega(m_1, n_1, p_1, q_1, s_1, 0) = \frac{256\pi^4 \delta_{p_1 s_1} \delta_{q_1 n_1}}{(2p_1+1)(2q_1+1)} \times \frac{f(p-m_1)f(p-n_1)f(p-p_1)}{(2p+1)f(p)}, \tag{26}$$

with p defined in equation (23).

Because of the requirement that the triangle condition must be satisfied by the $3j$ symbols in equation (14), it immediately follows using the result for I_Ω in equation (26) that the six-fold summations in equation (13) simplify to

$$I_4(i, j, k, l, m, n, p, q, s, 0, \alpha, \beta, \gamma, \delta) = \sum_{m_1=0}^{\infty} \sum_{n_1=0}^{\infty} \sum_{p_1=|m_1-n_1|}^{m_1+n_1} I_R(m_1, n_1, p_1, n_1, p_1, 0) \times I_\Omega(m_1, n_1, p_1, n_1, p_1, 0), \tag{27}$$

which is now in a much more manageable form for computational evaluation. Recall that the explicit dependence of I_R on $\{i, j, k, l, m, n, p, q, s, t, \alpha, \beta, \gamma, \delta\}$ has been suppressed. Equation (27) is the key result of section 2.

3. Special cases

In this section some specialized cases where various four-electron integrals can be evaluated in closed form are discussed. These closed form results serve two purposes. The analytical results are particularly valuable for testing purposes: in particular, for testing code performance and precision loss. A couple of the cases considered converge somewhat more slowly than the integrals required for an energy evaluation, so these examples become rather useful for optimizing code performance. Integrals with multiple r_{ij} factors raised to the power -1 do arise in the calculation of certain expectation values, for example, certain relativistic corrections to the energy require these integrals. The latter expectation values also require more singular integrals involving powers of -2 on the r_{ij} factors, but these recalcitrant cases are not considered in the present work. In a practical Hylleraas calculation some of the low-order integrals, that is, integrals with the powers on the r_{ij} factors restricted to the range -1 to 1, occur fairly frequently. Having relatively simple formulas available for some of these cases can speed up calculations of the energy and other expectation values. Our principal interest here is on the more difficult correlated integrals cases involving odd values for some of the indices $\{m, n, p, q, s, t\}$.

A strategy for the evaluation of some of the special cases considered will be to integrate out one of the coordinates, thereby reducing the problem to a simpler three-electron integral problem. This type of approach has been used in a number of correlated integral cases of varying complexity: see for example [15, 20, 31].

The simplest integral involving each of the four-electron coordinates, but with only two inter-electronic factors is

$$I_4(i, j, k, l, m, 0, 0, 0, 0, t, \alpha, \beta, \gamma, \delta) = \int r_1^i r_2^j r_3^k r_4^l r_{12}^m r_{34}^t \times \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4. \tag{28}$$

This case reduces in an immediately obviously fashion to a product of two-electron integrals:

$$I_4(i, j, k, l, m, 0, 0, 0, 0, t, \alpha, \beta, \gamma, \delta) = I_2(i, j, m, \alpha, \beta) I_2(k, l, t, \gamma, \delta), \tag{29}$$

where

$$I_2(i, j, k, \alpha, \beta) = \iint r_1^i r_2^j r_{12}^k \, \mathrm{e}^{-\alpha r_1 - \beta r_2}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2. \tag{30}$$

The two-electron correlated integrals with Slater-type functions have been studied extensively in the literature and formulas are available for a number of cases [32–36].

The next special case considered is

$$I_4(-1, 0, 0, -1, -1, 0, 0, -1, 0, -1, \alpha, \beta, \gamma, \delta) = \int r_1^{-1} r_4^{-1} r_{12}^{-1} r_{23}^{-1} r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4. \tag{31}$$

Making a standard expansion of the r_{ij}^{-1} factors in terms of Legendre polynomials leads to the integral

$$\int r_1^{-1} r_4^{-1} r_{12}^{-1} r_{23}^{-1} r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4 = \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \int r_1\, r_2^2\, r_3^2\, r_4 \times r_{12<}^{l} r_{12>}^{-l-1} r_{23<}^{m} r_{23>}^{-m-1} r_{34<}^{n} r_{34>}^{-n-1} \times \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}\, \mathrm{d}r_1\, \mathrm{d}r_2\, \mathrm{d}r_3\, \mathrm{d}r_4 \int P_l(\cos\theta_{12}) \times P_m(\cos\theta_{23}) P_n(\cos\theta_{34})\, \mathrm{d}\Omega_1\, \mathrm{d}\Omega_2\, \mathrm{d}\Omega_3\, \mathrm{d}\Omega_4. \tag{32}$$

Expressing the Legendre polynomials in terms of spherical harmonics allows the angular integral to be readily evaluated as:

$$\int P_l(\cos\theta_{12}) P_m(\cos\theta_{23}) P_n(\cos\theta_{34})\, \mathrm{d}\Omega_1\, \mathrm{d}\Omega_2\, \mathrm{d}\Omega_3\, \mathrm{d}\Omega_4 = 256\pi^4 \delta_{l0} \delta_{m0} \delta_{n0}, \tag{33}$$

and hence

$$\int r_1^{-1} r_4^{-1} r_{12}^{-1}\, r_{23}^{-1}\, r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4 = 256\pi^4 \int r_1\, r_2^2\, r_3^2\, r_4 \times r_{12>}^{-1}\, r_{23>}^{-1}\, r_{34>}^{-1} \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}\, \mathrm{d}r_1\, \mathrm{d}r_2\, \mathrm{d}r_3\, \mathrm{d}r_4. \tag{34}$$

On writing $r_i r_j r_{ij>}^{-1}$ in the form

$$r_i r_j r_{ij>}^{-1} = r_j H(r_i - r_j) + r_i H(r_j - r_i), \tag{35}$$

where $H(x)$ denotes a Heaviside step function, then equation (34) can be expressed as

$$\int r_1^{-1} r_4^{-1} r_{12}^{-1}\, r_{23}^{-1}\, r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}\, \mathrm{d}r_1\, \mathrm{d}r_2\, \mathrm{d}r_3\, \mathrm{d}r_4$$
$$= 256\,\pi^4 \int \{r_2 H(r_1-r_2)+r_1 H(r_2-r_1)\}$$
$$\times \{r_3 H(r_2-r_3)+r_2 H(r_3-r_2)\}$$
$$\times \{r_4 H(r_3-r_4)+r_3 H(r_4-r_3)\}$$
$$\times \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}\, \mathrm{d}r_1 \mathrm{d}r_2\, \mathrm{d}r_3\, \mathrm{d}r_4. \tag{36}$$

Evaluation of equation (36) leads to

$$\int r_1^{-1} r_4^{-1} r_{12}^{-1}\, r_{23}^{-1}\, r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4$$
$$= 256\pi^4\{\alpha\beta\gamma\delta(\alpha+\beta)(\beta+\gamma)(\gamma+\delta)(\alpha+\beta+\gamma)$$
$$\times (\beta+\gamma+\delta)(\alpha+\beta+\gamma+\delta)\}^{-1}$$
$$\times \{2\beta^3+4\beta^2(2\gamma+\delta)+2\beta(2\gamma+\delta)^2+\alpha^2(\beta+2\gamma+\delta)$$
$$+\gamma(2\gamma^2+3\gamma\delta+\delta^2)+\alpha(3\beta^2+4\beta(2\gamma+\delta)+(2\gamma+\delta)^2)\}. \tag{37}$$

Integrals with higher powers of r_i in the preceding integral can be obtained directly by differentiation of equation (37) with respect to the appropriate parameter α, β, γ, or δ.

For the situation that $\alpha=\beta=\gamma=\delta$, then equation (37) simplifies to give

$$\int r_1^{-1}\, r_4^{-1} r_{12}^{-1}\, r_{23}^{-1}\, r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1-\alpha r_2-\alpha r_3-\alpha r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4$$
$$= \frac{176\pi^4}{3\alpha^7}. \tag{38}$$

Special cases such as equation (38) can be useful for validating and improving software performance.

A slightly more basic auxiliary integral is the following:

$$I_4(-1,-1,-1,-1,-1,0,0,-1,0,-1,\alpha,\beta,\gamma,\delta)$$
$$= \int \frac{\mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}}{r_1 r_2 r_3 r_4 r_{12} r_{23} r_{34}} \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4. \tag{39}$$

Making a standard expansion of the r_{ij}^{-1} factors in terms of Legendre polynomials, evaluation of the resulting angular integration, and calculation of the resulting radial integrals, leads to the result

$$I_4(-1,-1,-1,-1,-1,0,0,-1,0,-1,\alpha,\beta,\gamma,\delta)$$
$$= \frac{256\pi^4}{\alpha^2\delta^2}\left\{\frac{1}{(\alpha+\beta)}\ln\left[\frac{(\alpha+\beta+\gamma+\delta)\gamma}{(\alpha+\beta+\gamma)(\gamma+\delta)}\right]\right.$$
$$+\frac{1}{(\gamma+\delta)}\ln\left[\frac{(\alpha+\beta+\gamma+\delta)\beta}{(\alpha+\beta)(\beta+\gamma+\delta)}\right]$$
$$+\frac{1}{\beta}\ln\left[\frac{(\beta+\gamma)(\gamma+\delta)}{(\beta+\gamma+\delta)\gamma}\right]$$
$$\left.+\frac{1}{\gamma}\ln\left[\frac{(\alpha+\beta)(\beta+\gamma)}{(\alpha+\beta+\gamma)\beta}\right]\right\}. \tag{40}$$

The particular case of this integral with equal exponent parameters yields

$$I_4(-1,-1,-1,-1,-1,0,0,-1,0,-1,\alpha,\alpha,\alpha,\alpha)$$
$$= \frac{256\pi^4}{\alpha^5}\ln\left(\frac{32}{27}\right). \tag{41}$$

Differentiation of equation (40) with respect to the parameters α, β, γ, and δ can be used to increase the powers on the factors r_1, r_2, r_3, and r_4, respectively.

An integral related to equation (39), but not by a simple permutation of integration variables, is the following auxiliary integral:

$$I_4(-1,-1,-1,-1,-1,0,0,-1,-1,0,\alpha,\beta,\gamma,\delta)$$
$$= \int \frac{\mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}}{r_1 r_2 r_3 r_4 r_{12} r_{23} r_{24}}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4. \tag{42}$$

Employing a standard expansion of the r_{ij}^{-1} factors in terms of Legendre polynomials, evaluation of the resulting angular integral, followed by integration over three of the radial coordinates leads to the following Cauchy–Frullani-type integral

$$I_4(-1,-1,-1,-1,-1,0,0,-1,-1,0,\alpha,\beta,\gamma,\delta)$$
$$= \frac{256\pi^4}{(\alpha\gamma\delta)^2}\int_0^\infty \frac{(\mathrm{e}^{-\beta r_2}-\mathrm{e}^{-(\beta+\delta)r_2})(1-\mathrm{e}^{-\gamma r_2})(1-\mathrm{e}^{-\delta r_2})}{r_2^2}\mathrm{d}r_2. \tag{43}$$

Evaluation of the preceding integral leads to

$$I_4(-1,-1,-1,-1,-1,0,0,-1,-1,0,\alpha,\beta,\gamma,\delta)$$
$$= \frac{256\pi^4}{(\alpha\gamma\delta)^2}\left\{\gamma\ln\left[\frac{(\alpha+\beta+\gamma)(\beta+\gamma+\delta)}{(\beta+\gamma)(\alpha+\beta+\gamma+\delta)}\right]\right.$$
$$-\beta\ln\left(\frac{\beta+\gamma}{\beta}\right)+(\alpha+\beta)\ln\left(\frac{\alpha+\beta+\gamma}{\alpha+\beta}\right)$$
$$-(\beta+\delta)\ln\left(\frac{\beta+\gamma+\delta}{\beta+\delta}\right)$$
$$\left.+(\alpha+\beta+\delta)\ln\left(\frac{\alpha+\beta+\gamma+\delta}{\alpha+\beta+\delta}\right)\right\}. \tag{44}$$

The special case of equation (44) with equal exponent parameters simplifies to

$$I_4(-1,-1,-1,-1,-1,0,0,-1,-1,0,\alpha,\alpha,\alpha,\alpha)$$
$$= \frac{256\pi^4}{\alpha^5}\ln\left(\frac{19\,683}{16\,384}\right). \tag{45}$$

Differentiation of equation (44) with respect to the parameters α, β, γ, and δ can be used to increase the powers on the factors r_1, r_2, r_3, and r_4, respectively. A particular example, which leads to a fairly compact symmetric formula, is obtained by differentiation of equation (44) with respect to the parameter β,

$$I_4(-1,0,-1,-1,-1,0,0,-1,-1,0,\alpha,\beta,\gamma,\delta)$$
$$= \frac{256\pi^4}{(\alpha\gamma\delta)^2}\ln\left(\frac{(\alpha+\beta)(\beta+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)}{\beta(\alpha+\beta+\gamma)(\alpha+\beta+\delta)(\beta+\gamma+\delta)}\right), \tag{46}$$

and the special case of equation (46) with equal exponent parameters is

$$I_4(-1,0,-1,-1,-1,0,0,-1,-1,0,\alpha,\alpha,\alpha,\alpha)$$
$$= \frac{256\pi^4}{\alpha^6}\ln\left(\frac{32}{27}\right). \tag{47}$$

The particular special case of equation (44) given in equation (46) was also reported by Roberts [8].

For an integral with a positive power on one of the r_{ij} factors consider:

$$I_4(-1,0,0,-1,-1,0,0,1,0,-1,\alpha,\beta,\gamma,\delta) = \int r_1^{-1} r_4^{-1} r_{12}^{-1} r_{23} r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4. \tag{48}$$

This case can be evaluated by employing an expansion of the two r_{ij}^{-1} factors in terms of Legendre polynomials and using a Sack expansion for r_{23}. The angular integration is given by equation (33) and hence the integral simplifies to yield

$$\int r_1^{-1} r_4^{-1} r_{12}^{-1} r_{23} r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4 = 256\,\pi^4 \int r_1^2 r_2^2 r_3^2 r_4^2 r_{12>}^{-1} R_{10}(r_2,r_3)\, r_{34>}^{-1} \times \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}\, \mathrm{d}r_1\, \mathrm{d}r_2\, \mathrm{d}r_3\, \mathrm{d}r_4. \tag{49}$$

A short calculation using equation (4) leads to

$$R_{10}(r_2,r_3) = r_{23>}\left(1+\frac{r_{23<}^2}{3r_{23>}^2}\right) = \left(r_3+\frac{r_2^2}{3r_3}\right)H(r_3-r_2) + \left(r_2+\frac{r_3^2}{3r_2}\right)H(r_2-r_3). \tag{50}$$

Inserting equation (50) into equation (49) and evaluating the resulting integrals leads to

$$\begin{aligned}\int r_1^{-1} r_4^{-1} r_{12}^{-1} r_{23} r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4 &= \frac{512\pi^4}{(\alpha+\beta)^4\delta^2}\left\{\frac{1}{\gamma^3}\left(5+\frac{\alpha^2}{\beta^2}+\frac{4\alpha}{\beta}+\frac{2\beta}{\alpha}\right)\right.\\ &+\frac{(\alpha^2+4\alpha\beta)}{\beta^4}\left(\frac{1}{\gamma}+\mu-\varsigma-\eta\right)\\ &+\mu\varsigma\eta\delta\left(\frac{8}{\alpha}+\frac{12}{\beta}+\frac{6}{\gamma}+\frac{4\beta}{\alpha\gamma}+\frac{4\delta}{\alpha\gamma}+\frac{6\delta}{\beta\gamma}\right)\\ &-\delta\kappa\lambda\mu\varsigma\left(1+\frac{2\beta}{\alpha}+\frac{2\gamma}{\alpha}+\frac{\delta}{\alpha}\right)\\ &\left.-\eta^3\left(5+\frac{\alpha^2}{\beta^2}+\frac{4\alpha}{\beta}+\frac{2\beta}{\alpha}\right)\right\},\end{aligned} \tag{51}$$

where

$$\kappa=(\alpha+\beta+\gamma+\delta)^{-1},\quad \lambda=(\alpha+\beta+\gamma)^{-1},\quad \mu=(\beta+\gamma+\delta)^{-1},\quad \varsigma=(\beta+\gamma)^{-1},\quad \eta=(\gamma+\delta)^{-1}. \tag{52}$$

Differentiation of equation (51) with respect to the appropriate parameter α, β, γ, or δ will generate closed form expressions for integrals with higher powers of r_i. For the case where $\alpha=\beta=\gamma=\delta$, then

$$\int r_1^{-1} r_4^{-1} r_{12}^{-1} r_{23} r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1-\alpha r_2-\alpha r_3-\alpha r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4 = \frac{1480\pi^4}{3\alpha^9}. \tag{53}$$

Additional examples of four-electron integrals that arise in the linear r_{12} computational approach will be discussed elsewhere including generalizations of results given by Bonham [9] and of Roberts [8].

A considerably more complicated example is the following integral containing four odd powers of the inter-electronic coordinates:

$$I_4(-1,-1,0,0,-1,-1,0,-1,0,-1,\alpha,\beta,\gamma,\delta) = \int r_1^{-1} r_2^{-1} r_{12}^{-1} r_{23}^{-1} r_{13}^{-1} r_{34}^{-1} \times \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4. \tag{54}$$

To evaluate this integral in closed form, the following strategy is employed. On integrating over the coordinates of electron 4, the preceding integral is reduced to a set of three-electron integrals. Of the three-electron integrals encountered, two have been worked out in closed form in an important paper by Remiddi [37], and the third integral can be readily obtained using one of Remiddi's final formulas. Some key misprints to the complex formulas in Remiddi's work have been reported [38–40] and some extensions discussed [41].

A short calculation employing equations (3) and (4) leads to the result:

$$\int r_{34}^{-1}\, \mathrm{e}^{-\delta r_4}\mathrm{d}\mathbf{r}_4 = 4\pi\left(2\delta^{-3}r_3^{-1}-\delta^{-2}\,\mathrm{e}^{-\delta r_3}-2\delta^{-3}r_3^{-1}\,\mathrm{e}^{-\delta r_3}\right). \tag{55}$$

Hence, equation (54) simplifies to

$$\begin{aligned}\int r_1^{-1} r_2^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} r_{34}^{-1}\, \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3-\delta r_4}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4 &= \frac{8\pi}{\delta^3}\int r_1^{-1} r_2^{-1} r_3^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1}\, \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\\ &-\frac{8\pi}{\delta^3}\int r_1^{-1} r_2^{-1} r_3^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} \times \mathrm{e}^{-\alpha r_1-\beta r_2-(\gamma+\delta) r_3}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\\ &-\frac{4\pi}{\delta^2}\int r_1^{-1} r_2^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} \times \mathrm{e}^{-\alpha r_1-\beta r_2-(\gamma+\delta) r_3}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3.\end{aligned} \tag{56}$$

Remiddi [37] has given the result

$$\int r_1^{-1} r_2^{-1} r_3^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1}\, \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3 = \frac{32\pi^3}{\alpha\beta\gamma}D(\alpha,\beta,\gamma), \tag{57}$$

where the function D, which is symmetric in its dependent variables, α, β, and γ,is given by

$$\begin{aligned}D(\alpha,\beta,\gamma) &= \ln\left(\frac{w_{12}}{\gamma}\right)\ln\left(\frac{w_s}{w_{12}}\right)-\mathrm{Li}_2\left(-\frac{\gamma}{w_{12}}\right)\\ &-\mathrm{Li}_2\left(1-\frac{\gamma}{w_{12}}\right)+\ln\left(\frac{w_{13}}{\beta}\right)\ln\left(\frac{w_s}{w_{13}}\right)-\mathrm{Li}_2\left(-\frac{\beta}{w_{13}}\right)\\ &-\mathrm{Li}_2\left(1-\frac{\beta}{w_{13}}\right)+\ln\left(\frac{w_{23}}{\alpha}\right)\ln\left(\frac{w_s}{w_{23}}\right)\\ &-\mathrm{Li}_2\left(-\frac{\alpha}{w_{23}}\right)-\mathrm{Li}_2\left(1-\frac{\alpha}{w_{23}}\right),\end{aligned} \tag{58}$$

with

$$w_s=\alpha+\beta+\gamma,\quad w_{12}=\alpha+\beta,\quad w_{13}=\alpha+\gamma,\quad \text{and}\quad w_{23}=\beta+\gamma. \tag{59}$$

In equation (58), $\mathrm{Li}_2(x)$ is the dilogarithm function, which can be defined by the series representation [42]

$$\mathrm{Li}_2(x) = \sum_{n=1}^{\infty} \frac{x^n}{n^2}, \quad \text{for} \quad |x| \leqslant 1. \tag{60}$$

For some ranges of the arguments the evaluation of the auxiliary function $D(\alpha, \beta, \gamma)$in equation (58) leads to dilogarithm functions with arguments outside the stated limits given in equation (60). From Landen's transformation [42], which follows from the integral representation of the dilogarithm function, the following result can be given:

$$\mathrm{Li}_2(1-y) = -\tfrac{1}{2}\{\ln(y)\}^2 - \mathrm{Li}_2(1-y^{-1}). \tag{61}$$

This result is useful when $y > 2$, and this case arises in equation (58) when $\alpha > 2w_{23}$, $\beta > 2w_{13}$, or $\gamma > 2w_{12}$. Two other results for the dilogarithm function that are advantageous for the evaluation of particular cases of the auxiliary function $D(\alpha, \beta, \gamma)$ are:

$$\mathrm{Li}_2(1-y) = \mathrm{Li}_2(y^{-1}) - \frac{\pi^2}{6} + \ln(y^{-1}) \ln\left(\frac{y-1}{y}\right) - \frac{1}{2}\{\ln(y)\}^2 \quad \text{for} \quad y > 1. \tag{62}$$

and

$$\mathrm{Li}_2(-y) = -\mathrm{Li}_2\left(\frac{y}{y+1}\right) - \frac{1}{2}\{\ln(1+y)\}^2 \quad \text{for} \quad y > 1. \tag{63}$$

Equation (62) would be the preferred choice for computation when $y > 2$ and equation (61) the better choice when $1 < y \leqslant 2$.

To evaluate equation (56), the derivative of equation (57) with respect to the parameter γ is required, so that

$$\int r_1^{-1} r_2^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} \, \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\mathbf{r}_3 = \frac{32\pi^3}{\alpha\beta\gamma}\{\gamma^{-1} D(\alpha, \beta, \gamma) - D_\gamma(\alpha, \beta, \gamma)\}, \tag{64}$$

and it follows from equation (58) that

$$D_\gamma(\alpha, \beta, \gamma) \equiv \frac{\partial D(\alpha, \beta, \gamma)}{\partial \gamma} = \frac{\ln\left(\frac{w_{12} w_{23} w_{13}}{\alpha\beta\gamma}\right)}{w_s} + \frac{\ln\left(\frac{w_{12}}{\gamma}\right)}{w_s - 2\gamma} - \frac{\ln\left(\frac{w_{23}}{\alpha}\right)}{w_s - 2\alpha} - \frac{\ln\left(\frac{w_{13}}{\beta}\right)}{w_s - 2\beta}. \tag{65}$$

Hence,

$$\int r_1^{-1} r_2^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} r_{34}^{-1} \, \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\mathbf{r}_3 \, \mathrm{d}\mathbf{r}_4 = \frac{128\pi^4}{\alpha\beta\delta^2}\left\{\frac{2}{\gamma\delta} D(\alpha, \beta, \gamma) - \frac{2}{\delta(\gamma+\delta)} D(\alpha, \beta, \gamma+\delta) - \frac{1}{(\gamma+\delta)^2} D(\alpha, \beta, \gamma+\delta) + \frac{1}{(\gamma+\delta)} D_{\gamma+\delta}(\alpha, \beta, \gamma+\delta)\right\}. \tag{66}$$

A further set of integrals in closed form can be generated by differentiating equation (66) with respect to the parameters α, β, γ, or δ.

For the case where $\alpha = \beta = \gamma = \delta$, a short calculation leads to

$$\int r_1^{-1} r_2^{-1} r_3^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} \, \mathrm{e}^{-\alpha r_1 - \alpha r_2 - \alpha r_3} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\mathbf{r}_3 = \frac{96\pi^3}{\alpha^3}\left\{-\frac{\pi^2}{12} + \ln 2 \ln(3/2) + \frac{1}{2}(\ln 2)^2 - \mathrm{Li}_2\left(-\frac{1}{2}\right)\right\}, \tag{67}$$

$$\int r_1^{-1} r_2^{-1} r_3^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} \, \mathrm{e}^{-\alpha r_1 - \alpha r_2 - 2\alpha r_3} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\mathbf{r}_3 = \frac{16\pi^3}{\alpha^3}\left\{\frac{\pi^2}{12} + 2\ln 3 \ln(4/3) - 2\mathrm{Li}_2\left(-\frac{1}{3}\right) - 2\mathrm{Li}_2\left(\frac{2}{3}\right)\right\}, \tag{68}$$

and to evaluate $\int r_1^{-1} r_2^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} \, \mathrm{e}^{-\alpha r_1 - \alpha r_2 - 2\alpha r_3} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\mathbf{r}_3$ a factor of $\mathrm{e}^{-\varepsilon r_3}$ is inserted in the integrand, the derivative with respect to ε is taken, and then the $\lim_{\varepsilon \to 0}$ is evaluated, leading to the result

$$\int r_1^{-1} r_2^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} \, \mathrm{e}^{-\alpha r_1 - \alpha r_2 - 2\alpha r_3} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\mathbf{r}_3 = \frac{8\pi^3}{\alpha^4}\left\{\ln 3 - 1 + \frac{\pi^2}{12} + 2\ln 3 \ln(4/3) - 2\mathrm{Li}_2\left(-\frac{1}{3}\right) - 2\mathrm{Li}_2\left(\frac{2}{3}\right)\right\}. \tag{69}$$

Inserting the preceding three results into equation (56), with $\alpha = \beta = \gamma = \delta$, leads to

$$\int r_1^{-1} r_2^{-1} r_{12}^{-1} r_{13}^{-1} r_{23}^{-1} r_{34}^{-1} \, \mathrm{e}^{-\alpha r_1 - \alpha r_2 - \alpha r_3 - \alpha r_4} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\mathbf{r}_3 \, \mathrm{d}\mathbf{r}_4 = \frac{32\pi^4}{\alpha^6}\left\{1 - \ln 3 - \frac{29}{12}\pi^2 + 4\ln 2 \ln 3 + 10(\ln 3)^2 - 12(\ln 2)^2 + 10\mathrm{Li}_2\left(-\frac{1}{3}\right) + 10\mathrm{Li}_2\left(\frac{2}{3}\right) - 24\mathrm{Li}_2\left(-\frac{1}{2}\right)\right\}. \tag{70}$$

4. Results

Values for the three-electron integrals appearing in equation (56) for specific values of α, β, and $(\gamma + \delta)$ are given as the first three entries in table 1. These are evaluated using equations (57), (58), (64), and (65). Entries four through six in table 1 employ equations (67)–(69). These three-electron integrals are used to evaluate the four-electron integrals appearing in equation (56).

Some results for the evaluation of the closed form expressions are collected in table 2. The first six entries are evaluated using equations (47), (41), (45), (38), (53), and (70), respectively. Results 7 to 12 in table 2 are evaluated using equations (46), (40), (44), (37), (51), and (66), respectively. The results in both tables 1 and 2 were evaluated using

Table 1. $I_3(i, j, k, l, m, n, \alpha, \beta, \gamma)$ integrals employed in equations (56) and (67)–(69).

i	j	k	l	m	n	α	β	γ	$I_3(i, j, k, l, m, n, \alpha, \beta, \gamma)$
−1	−1	−1	−1	−1	−1	1.1	1.85	2.37	84.142 223 494 536 808 793 007 290 429 325 435 789 364 103 6
−1	−1	−1	−1	−1	−1	1.1	1.85	5.28	29.494 790 252 590 869 105 114 449 366 732 144 065 264 850 1
−1	−1	0	−1	−1	−1	1.1	1.85	5.28	8.043 435 542 936 109 705 630 471 463 456 177 831 623 519 81
−1	−1	−1	−1	−1	−1	1.1	1.1	1.1	329.239 251 776 476 653 367 111 635 160 066 681 059 119 415
−1	−1	−1	−1	−1	−1	1.1	1.1	2.2	151.361 557 273 647 716 057 430 249 815 886 826 900 212 933
−1	−1	0	−1	−1	−1	1.1	1.1	2.2	85.507 762 869 872 676 004 155 244 273 032 499 845 350 578 1

Table 2. Values for the I_4 integrals for $\alpha = \beta = \gamma = \delta = 1.1$, first six entries, and for $\alpha = 1.1$, $\beta = 1.85$, $\gamma = 2.37$, $\delta = 2.91$, last six entries.

i	j	k	l	m	n	p	q	s	t	$I_4(i, j, k, l, m, n, p, q, s, t, 1.1, 1.1, 1.1, 1.1)$
−1	0	−1	−1	−1	0	0	−1	−1	0	2 391.521 347 500 201 094 655 076 022 794 108 371 013
−1	−1	−1	−1	−1	0	0	−1	0	−1	2 630.673 482 250 221 204 120 583 625 073 519 208 114
−1	−1	−1	−1	−1	0	0	−1	−1	0	2 840.494 237 199 274 170 252 928 671 384 311 545 047
−1	0	0	−1	−1	0	0	−1	0	−1	2 932.527 596 742 908 270 884 726 940 476 566 109 391
−1	0	0	−1	−1	0	0	1	0	−1	20 380.075 334 238 844 106 449 079 037 872 454 178 71
−1	−1	0	0	−1	−1	0	−1	0	−1	2 470.758 530 285 724 338 168 192 474 582 383 772 588
										$I_4(i, j, k, l, m, n, p, q, s, t, 1.1, 1.85, 2.37, 2.91)$
−1	0	−1	−1	−1	0	0	−1	−1	0	73.898 196 016 673 903 963 962 882 674 695 089 445 73
−1	−1	−1	−1	−1	0	0	−1	0	−1	155.278 822 917 276 203 044 870 506 199 256 204 270 9
−1	−1	−1	−1	−1	0	0	−1	−1	0	154.222 620 305 821 936 368 883 856 688 749 225 792 7
−1	0	0	−1	−1	0	0	−1	0	−1	50.142 925 226 281 738 237 522 146 645 123 308 771 94
−1	0	0	−1	−1	0	0	1	0	−1	104.726 046 405 803 694 763 305 480 511 512 405 488 1
−1	−1	0	0	−1	−1	0	−1	0	−1	43.799 157 697 259 175 395 120 802 046 187 742 284 23

Table 3. Values for the I_4 integrals for $\alpha = 1.1$, $\beta = 1.85$, $\gamma = 2.37$, $\delta = 2.91$.

i	j	k	l	m	n	p	q	s	t	$I_4(i, j, k, l, m, n, p, q, s, t, \alpha, \beta, \gamma, \delta)$
1	2	3	4	−1	−1	1	1	1	0	$1.319\,718\,095\,949\,78 \times 10^{5}$
1	2	3	4	−1	1	−1	1	1	0	$1.399\,083\,943\,972\,054 \times 10^{5}$
1	2	3	4	1	−1	−1	1	1	0	$1.838\,425\,409\,057\,485\,925\,1 \times 10^{5}$
1	2	3	4	1	1	1	−1	−1	0	$4.792\,191\,362\,637\,498\,947\,0 \times 10^{5}$
1	2	3	4	1	1	1	1	1	0	$5.818\,716\,984\,115\,258\,991\,422\,97 \times 10^{7}$
1	2	3	4	7	−1	3	1	5	0	$8.348\,193\,021\,485\,396\,011\,639\,935\,64 \times 10^{16}$

Mathematica. All the digits reported in tables 1 and 2 are expected to be accurate. The first 30 digits of the tabulated results were checked by an independent Fortran program running in quadruple precision. The results reported in table 3 were evaluated in Fortran using quadruple precision arithmetic.

In table 3 some results for more complicated cases involving five-odd indices are given. These have been evaluated using equation (27). The number of significant digits reported is based on the convergence pattern for the individual integrals. The uncertainty for the numerical value of each integral is expected to reside in the last one to two digits reported. To the best of the author's knowledge, reference values are not available in the literature for the correlated four-electron integral case with five factors of r_{ij} each raised to an odd power.

Two modifications have been made to equation (27) to improve the numerical evaluation. The first change employs a summation rearrangement, so that equation (27) is written as

$$I_4 = \sum_{m_1=0}^{\infty} a_{m_1} \sum_{n_1=0}^{\infty} b_{m_1,n_1}, \tag{71}$$

where the coefficients a_{m_1} denotes the m_1 dependent part of I_R and I_Ω, and similarly, the coefficients b_{m_1,n_1} includes the m_1 and n_1 dependent part of both I_R and I_Ω, then equation (71) can be expressed as

$$I_4 = \sum_{u=0}^{\infty} \sum_{v=0}^{u} a_v b_{v,u-v}. \tag{72}$$

This rearrangement has the effect of regrouping terms of approximately the same size together, which leads to a more efficient numerical evaluation. For the entries reported in table 3, the convergence behaviour of equation (72) is governed by the sum of the odd powers on the r_{ij} terms. The lower this sum the slower the convergence. This connects directly with the number of significant digits reported for the entries in table 3. Judicious application of convergence acceleration techniques will probably be an important approach to speed up the numerical evaluation of these cases. In a practical application, double precision calculations will suffice to around the one micro-Hartree level of accuracy for the ground state energy. Substantial progress beyond this accuracy level will only be obtained working in quadruple precision arithmetic. To perform the evaluation of these five odd power

cases to machine precision working in quadruple precision will require effective use of OpenMP strategies.

A detailed comparison of the computational speed of evaluating the correlated integral with five odd powers on the r_{ij} terms using an OpenMP approach versus a graphical processing unit (gpu) evaluation strategy is currently in progress. One major limitation of current generation gpus is the inability to directly perform calculations in quadruple precision. Overcoming this limitation will allow significant computational speed up for the evaluation of the difficult cases of the correlated integrals considered in this work.

5. Discussion

The approach outlined in section 2 for the evaluation of a four-electron integral with five non-zero integer indices $\{m, n, p, q, s, t\}$ has the effect of entirely bypassing the numerical evaluation of any $6j$ symbol in the calculations. In addition, only the square of a $3j$ symbol requires evaluation, and that can be done efficiently in terms of the f function defined in equation (25). The f function can be tabled once outside the integral evaluation module, allowing for the efficient evaluation of the square of the required $3j$ symbol in equation (22).

The appearance of logarithm functions in the answers for some of the closed form results reported in section 3, gives an immediate indication that the series representation of these results, equation (72), is expected to have a fairly slow rate of convergence. This follows directly from the requirement to represent the logarithmic terms as a series representation, which inevitably will be a slowly converging series. Increasing the powers on the r_{ij} terms removes the logarithm terms, and consequently, the rate of convergence for equation (72) improves. See for example, the result in equation (51). The final example reported in table 3 converges much more quickly than the other entries reported in the same table, and consequently, the number of significant digits obtained is increased.

It would be particularly valuable to obtain in closed form, some of the four-electron integrals with five odd values for the powers on the r_{ij} terms. The particular integrals of most interest have relatively low values for the powers, e.g. -1 and 1, as these represent the integral cases arising frequently in practical calculations of the energy and other expectation values. Work is in progress on this topic, but so far, progress has been rather limited.

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