Evaluation of some integrals for the atomic three-electron problem using convergence accelerators

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An analysis is presented for the evaluation of atomic integrals of the form $\int r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_3} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$. General formulas are worked out for the two cases (i) $l=-2$, $m \geq -1$, $n \geq -1$, and (ii) $l=-2$, $m=-2$. A series solution for both cases is obtained. The Levin u transformation and the Richardson extrapolation techniques are employed to obtain a reasonable number of digits of precision for the integral with minimum CPU requirements.

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I. INTRODUCTION

The purpose of this paper is to present an evaluation scheme for the integrals

$$I \equiv I(i,j,k,l,m,n,\alpha,\beta,\gamma) = \int r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_3} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \ . \quad (1)$$

For the situation where $l \geq -1$, $m \geq -1$, and $n \geq -1$ a considerable literature exists describing effective evaluation approaches [1–8]. These integrals arise in the determination of various properties for three-electron atomic systems when a Hylleraas-type basis set is employed [9–12]. The focus of this paper is to consider the cases (i) $l=-2$, $m \geq -1$, and $n \geq -1$; and (ii) $l=-2$, $m=-2$, and $n \geq -1$. These integrals are required for the calculation of certain relativistic corrections and also in the evaluation of particular lower-bound formulas, when a Hylleraas wave function is used to describe a three-electron system. Much less attention has been directed towards the aforementioned two cases [13–15].

Previous work on integrals with $l=-2$ has employed the Sack [16] expansion for the interelectronic coordinate. Employing this expansion leads to a simple angular integration with the complexity of the integral evaluation tied up in the radial integral. In this investigation, a different approach is taken. The factors r_{ij}^{-2} are expanded in such a way that the resulting radial integrals are simpler to evaluate, while this is at the expense of a more complicated angular-integration problem. The next two sections give the analysis for the two cases mentioned above, and Sec. IV deals with the numerical evaluation of the formulas obtained in Secs. II and III.

II. THE CASE $l=-2$, $m \geq -1$, $n \geq -1$

The analysis presented below is general and applies for integrals with $i \geq -2$, $j \geq -2$, $k \geq -2$, $l=-2$, $m \geq -1$, and $n \geq -1$. The most difficult subcase arises for m and n both odd. For integrals with one or both of m and n even, more effective evaluation procedures have been presented elsewhere [13,14].

To evaluate Eq. (1) the following two expansions are employed [16,17]:

$$r_{23}^{-2} = \sum_{w_1=0}^{\infty} \frac{r_{23<}^{w_1}}{r_{23>}^{w_1+2}} C_{w_1}^1(\cos\theta_{23}) \ , \quad (2)$$

$$r_{13}^m = \sum_{w_2=0}^{\infty} R_{mw_2}(r_1,r_3) P_{w_2}(\cos\theta_{13}) \ . \quad (3)$$

Equation (3) is the Sack expansion for the interelectronic coordinate. $R_{mw_2}(r_1,r_3)$ denotes a radial function and $P_{w_2}(\cos\theta_{13})$ is a Legendre polynominal. In Eq. (2) $r_{23<}$ denotes the lesser of (r_2,r_3) and $r_{23>}$ designates the larger of (r_2,r_3). $C_{w_1}^1(\cos\theta_{23})$ represents a Gegenbauer polynominal. If Eqs. (2) and (3) and an analogous expression for r_{12}^n are inserted into Eq. (1), then

$$I = \sum_{w_1=0}^{\infty} \sum_{w_2=0}^{\infty} \sum_{w_3=0}^{\infty} I_R(w_1,w_2,w_3) I_A(w_1,w_2,w_3) \ , \quad (4)$$

where the angular integral is

$$I_A(w_1,w_2,w_3) = \int C_{w_1}^1(\cos\theta_{23}) P_{w_2}(\cos\theta_{13}) P_{w_3}(\cos\theta_{12}) \times d\Omega_1 d\Omega_2 d\Omega_3 \quad (5)$$

and the radial integral is

$$I_R(w_1,w_2,w_3) \equiv I_R(w_1,w_2,w_3,i,j,k,m,n,\alpha,\beta,\gamma) = \int r_1^{i+2} r_2^{j+2} r_3^{k+2} r_{23<}^{w_1} r_{23>}^{-w_1-2} \times R_{mw_2}(r_1,r_3) R_{nw_3}(r_1,r_2) \times e^{-\alpha r_1 - \beta r_2 - \gamma r_3} dr_1 dr_2 dr_3 \ . \quad (6)$$

The evaluation of I_A is now considered. Expressing $P_{w_2}(\cos\theta_{13})$ and $P_{w_3}(\cos\theta_{12})$ as $C_{w_2}^{1/2}(\cos\theta_{13})$ and $C_{w_3}^{1/2}(\cos\theta_{12})$, respectively, and employing the addition

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theorem for the Gegenbauer polynominals [18] allows I_A to be separated into a product of integrals in the variables $\{\theta_i,\phi_i\}$, $i=1$ to 3. The resulting integrals can be readily evaluated, but the final expression is rather complex. The key observation to obtaining a simple formula for I_A is to employ the following expansion for the Gegenbauer polynomials:

$$C^1_{w_1}(x)=\sum_{k=0}^{w_1} b_{w_1k}P_k(x) \; . \tag{7}$$

The expansion coefficients b_{w_1k} are given by

$$b_{w_1k}=\frac{2k+1}{2}\int_{-1}^{1}P_k(x)C^1_{w_1}(x)dx \; , \tag{8}$$

a result obtained by multiplying both sides of Eq. (7) by $P_j(x)$ (for $0\le j\le w_1$) and integrating over $[-1,1]$. Equation (8) can be written as

$$\begin{aligned} b_{w_1k}&=\frac{2k+1}{2}\int_0^{\pi}\sin\theta C^1_{w_1}(\cos\theta)C^{1/2}_k(\cos\theta)d\theta \\ &=\frac{2k+1}{2}A(1;w_1,1;k,\tfrac{1}{2}) \; , \end{aligned} \tag{9}$$

where the A integral is discussed in the Appendix. Inserting Eq. (7) (with $x=\cos\theta_{23}$) into Eq. (5) leads to

$$\begin{aligned} I_A(w_1,w_2,w_3)&=\sum_{k=0}^{w_1} b_{w_1k}\int P_k(\cos\theta_{23})P_{w_2}(\cos\theta_{13})P_{w_3}(\cos\theta_{12}) \\ &\quad\times d\Omega_1 d\Omega_2 d\Omega_3 \; . \end{aligned} \tag{10}$$

On expanding each Legendre polynominal in terms of spherical harmonics, the following result is obtained:

$$I_A(w_1,w_2,w_3)=\frac{(4\pi)^3}{(2w_2+1)^2}\sum_{k=0}^{w_1} b_{w_1k}\delta_{kw_2}\delta_{w_2w_3} \; , \tag{11}$$

where δ_{jk} denotes a Kronecker delta. Since

$$w_2>w_1 \Longrightarrow I_A=0 \; , \tag{12}$$

Eq. (4) can be simplified to

$$I=\sum_{w_1=0}^{\infty}\sum_{w_2=0}^{w_1} I_R(w_1,w_2)I_A(w_1,w_2) \; , \tag{13}$$

with

$$I_A(w_1,w_2)=\frac{(4\pi)^3}{(2w_2+1)^2}b_{w_1w_2} =\begin{cases} \dfrac{2^{1/2(w_1+w_2+12)}\pi^3}{(2w_2+1)}\displaystyle\sum_{\tau=0}^{\tau_{\max}}\frac{(w_1-\tau)!}{(-2)^{\tau}\left[\dfrac{w_1-w_2}{2}-\tau\right]!(w_1+w_2+1-2\tau)!!} & \text{for } w_1+w_2 \text{ even and } w_1\ge w_2 \; , \\ 0 \quad \text{for } w_1+w_2 \text{ odd or } w_2>w_1 \; , \end{cases} \tag{14}$$

and Eqs. (9) and (A11) have been employed in Eq. (11). In Eq. (14)

$$\tau_{\max}=\min\left\{\left[\frac{w_1}{2}\right],\frac{w_1-w_2}{2}\right\} \; ,$$

where the standard convention $[x/2]=x/2$ if x is even and $(x-1)/2$ if x is odd, has been employed.

To evaluate the radial integral in Eq. (6) (with $w_2=w_3$) the Sack formulas for the R functions are employed. These take the form

$$R_{mw_2}(r_1,r_3)=\sum_{p=0}^{\infty} a_{w_2mp}r_{13<}^{w_2+2p}r_{13>}^{m-w_2-2p} \tag{15}$$

$$R_{nw_2}(r_1,r_2)=\sum_{q=0}^{\infty} a_{w_2nq}r_{12<}^{w_2+2q}r_{12>}^{n-w_2-2q} \; , \tag{16}$$

with

$$a_{tuv}=\frac{\left[-\dfrac{u}{2}\right]_t\left[t-\dfrac{u}{2}\right]_v\left[-\dfrac{1}{2}-\dfrac{u}{2}\right]_v}{(\frac{1}{2})_t v!(t+\frac{3}{2})_v} \tag{17}$$

and $(k)_l$ denotes a Pochhammer symbol. If Eqs. (15) and (16) are inserted into Eq. (6), then

$$\begin{aligned} I_R(w_1,w_2)=\sum_{p=0}^{\infty}\sum_{q=0}^{\infty} a_{w_2mp}a_{w_2nq}\int & r_1^{i+2}r_2^{j+2}r_3^{k+2}r_{23<}^{w_1}r_{23>}^{-w_1-2}r_{13<}^{w_2+2p}r_{13>}^{m-w_2-2p} \\ &\times r_{12<}^{w_2+2q}r_{12>}^{n-w_2-2q}e^{-\alpha r_1-\beta r_2-\gamma r_3}dr_1dr_2dr_3 \; . \end{aligned} \tag{18}$$

If the integration range in Eq. (18) is broken up according to $0\le r_i\le r_j\le r_k$, then Eq. (18) simplifies to

$$I_R(w_1,w_2)=\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}a_{w_2mp}a_{w_2nq}$$
$$\times\{W(w_1+w_2+2p+k+2,w_2-w_1+2q+j,n+m+i+2-2w_2-2p-2q,\gamma,\beta,\alpha)$$
$$+W(w_1+w_2+2p+k+2,2q-2p+m+i+2,n+j-w_1-w_2-2q,\gamma,\alpha,\beta)$$
$$+W(2w_2+2p+2q+i+2,w_1-w_2-2p+m+k+2,n+j-w_1-w_2-2q,\alpha,\gamma,\beta)$$
$$+W(2w_2+2p+2q+i+2,w_1-w_2-2q+n+j+2,m+k-w_1-w_2-2p,\alpha,\beta,\gamma)$$
$$+W(w_1+w_2+2q+j+2,2p-2q+n+i+2,m+k-w_1-w_2-2p,\beta,\alpha,\gamma)$$
$$+W(w_1+w_2+2q+j+2,w_2-w_1+2p+k,n+m+i+2-2w_2-2p-2q,\beta,\gamma,\alpha)\}\ , \tag{19}$$

where

$$W(L,M,N,a,b,c)=\int_0^{\infty}x^Le^{-ax}dx\int_x^{\infty}y^Me^{-by}dy\int_y^{\infty}z^Ne^{-cz}dz\ . \tag{20}$$

The W integrals in Eq. (20) have been discussed extensively in the literature and efficient algorithms are available for their evaluation [1,2,19,20].

Eqs. (13), (14), and (19) thus represent the required solution of the integral. Our attention is now turned to the summation limits occurring in Eqs. (13) and (19). Because of the following result for the Pochhammer symbol

$$(-k)_l=0\ ,\quad l>k \text{ for integer } k\ , \tag{21}$$

the p summation terminates at $(m+1)/2$ if m is odd and $m/2-w_2$ if m is even. Similarly the q summation terminates at $(n+1)/2$ for odd n and $n/2-w_2$ for even n. These conditions follow from the definition of a_{tuv} given in Eq. (17). The w_2 summation in Eq. (13) terminates at one of the following values:

w_1, m and n *both* odd ,

$\min\left\{w_1,\frac{m}{2}\right\}$, m even ,

$\min\left\{w_1,\frac{n}{2}\right\}$, n even ,

$\min\left\{w_1,\frac{m}{2},\frac{n}{2}\right\}$, m and n both even .

The last three conditions follow from the definition of a_{tuv} given in Eq. (17). The w_1 summation is nonterminating.

III. THE CASE $l=-2$, $m=-2$

Inserting Eq. (2) and the analogous expression for r_{13}^{-2} into Eq. (1), as well as the Sack expansion for r_{12}^n, leads to the result

$$I=\sum_{w_1=0}^{\infty}\sum_{w_2=0}^{\infty}\sum_{w_3=0}^{\infty}I_R(w_1,w_2,w_3)I_A(w_1,w_2,w_3)\ , \tag{22}$$

where

$$I_A(w_1,w_2,w_3)=\int C_{w_1}^1(\cos\theta_{23})C_{w_2}^1(\cos\theta_{31})P_{w_3}(\cos\theta_{12})\times d\Omega_1d\Omega_2d\Omega_3 \tag{23}$$

and

$$I_R(w_1,w_2,w_3)=\int r_1^{i+2}r_2^{j+2}r_3^{k+2}r_{23<}^{w_1}r_{23>}^{-w_1-2}r_{13<}^{w_2}r_{31>}^{-w_2-2}R_{nw_3}(r_1,r_2)e^{-\alpha r_1-\beta r_2-\gamma r_3}dr_1dr_2dr_3\ . \tag{24}$$

To simplify Eq. (23), Eq. (7) is employed for each Gegenbauer polynomial; the result is

$$I_A(w_1,w_2,w_3)=\sum_{j=0}^{w_1}\sum_{k=0}^{w_2}b_{w_1j}b_{w_2k}\int P_j(\cos\theta_{23})P_k(\cos\theta_{31})P_{w_3}(\cos\theta_{12})d\Omega_1d\Omega_2d\Omega_3$$

$$=\frac{(4\pi)^3}{(2w_3+1)^2}\sum_{j=0}^{w_1}\sum_{k=0}^{w_2}b_{w_1j}b_{w_2k}\delta_{kw_3}\delta_{jw_3} \tag{25a}$$

$$=\frac{(4\pi)^3}{(2w_3+1)^2}b_{w_1w_3}b_{w_2w_3}\ , \tag{25b}$$

and the b coefficient is given in Eq. (9). The radial integral in Eq. (24) can be evaluated by employing the expansion for the Sack R function; the result is

$$
\begin{aligned}
I_R(w_1,w_2,w_3)= \sum_{q=0}^{\infty} a_{w_3nq}\{ & W(w_1+w_2+k+2,w_3-w_1+2q+j,n+i-w_2-w_3-2q,\gamma,\beta,\alpha)\\
&+W(w_1+w_2+k+2,w_3-w_2+2q+i,n+j-w_1-w_3-2q,\gamma,\alpha,\beta)\\
&+W(w_2+w_3+2q+i+2,w_1-w_3-2q+n+j+2,k-2-w_1-w_2,\alpha,\beta,\gamma)\\
&+W(w_2+w_3+2q+i+2,w_1-w_2+k,n+j-w_1-w_3-2q,\alpha,\gamma,\beta)\\
&+W(w_1+w_3+2q+j+2,w_2-w_3-2q+n+i+2,k-2-w_1-w_2,\beta,\alpha,\gamma)\\
&+W(w_1+w_3+2q+j+2,w_2-w_1+k,n+i-w_2-w_3-2q,\beta,\gamma,\alpha)\}\ ,
\end{aligned}
\tag{26}
$$

where the W integral is defined in Eq. (20).

Equations (22), (25), and (26) constitute the solution of the $l=-2$, $m=-2$ case. The q summation terminates at $(n+1)/2$ if n is odd or $n/2-w_3$ if n is even [see Eqs. (17) and (21)]. The w_3 summation in Eq. (22) terminates at $\min\{w_1,w_2\}$ if n is odd and $\min\{w_1,w_2,n/2\}$ if n is even. The first part of each condition comes from the result

$$I_A=0 \quad \text{if } w_3>w_1 \text{ or } w_3>w_2\ , \tag{27}$$

which follows directly from Eq. (25a). The second constraint involving $n/2$ follows from the coefficient a_{w_3nq} in Eq. (26). The w_1 and w_2 summations are both nonterminating. Equation (26) is valid for $n\geq -1$. Additional constraints are required on i, j, and k. These may be found from the conditions required for the convergence of the W integral in Eq. (20), that is, $L\geq 0$, $L+M\geq -1$, and $L+M+N\geq -2$. This leads to the requirement that $i+j+k+3\geq 0$.

IV. NUMERICAL EVALUATION STRATEGIES

The evaluation of Eqs. (13), (14), and (19) is considered first. The function $I_A(w_1,w_2)$ [Eq. (14)] is independent of any of the arguments $\{i,j,k,m,n,\alpha,\beta,\gamma\}$, so this function need only be evaluated once. In the present work Eq. (14) was calculated analytically using the symbolic package MATHEMATICA [21], and the final expressions evaluated numerically. In a similar fashion, an array for the a coefficients appearing in Eq. (19) was constructed in MATHEMATICA. The constraint given in Eq. (14) that w_1+w_2 must be even simplifies the calculations considerably. For the case when m and n are both odd, which is the one of principle interest in this work, the summation limit of the w_2 sum in Eq. (13) is w_1. However, in practical calculations, this limit can be replaced by a cutoff of the summation as the terms $I_R(w_1,w_2)$ become increasingly small. This particular simplification was not needed in the approach employed in this study.

Equation (13) is not suitable for direct numerical evaluation, particularly if a large number of digits of precision are required. The key expansion employed for r_{23}^{-2} [Eq. (2)] is deceptive in one sense. An alternative expansion in terms of Legendre polynomials can be written, but the radial factor now involves a logarithmic function of r_2 and r_3 [13,14,22]. This logarithmic behavior must be imbedded in the series expansion of Eq. (13), so a slow convergence of the series is to be expected.

To get an idea of the behavior of the series in Eq. (13), the asymptotic forms for two cases, (i) large w_2 (which must also have w_1 large) and (ii) large w_1 with w_2 small, are examined. For the first case, $w_1=w_2$ is employed to simplify the analysis. From Eq. (33) of Ref. [2], the asymptotic behavior of the W integrals can be evaluated. From Eq. (19) two different cases arise,

$$W\sim\frac{1}{(w_1+w_2)^2}\sim\frac{1}{w_2^2}\ , \tag{28}$$

$$W\sim\frac{1}{w_2(w_1+w_2)}\sim\frac{1}{w_2^2}\ . \tag{29}$$

The a coefficients in Eq. (19) lead to

$$\frac{\left(\dfrac{-m}{2}\right)_{w_2}\left(-\dfrac{n}{2}\right)_{w_2}}{[(\frac{1}{2})_{w_2}]^2}\sim\frac{1}{w_2^{(m+n+2)/2}}\ . \tag{30}$$

So $I_R(w_1,w_2)$ behaves like

$$I_R\sim\frac{1}{w_2^{(m+n+6)/2}}\ . \tag{31}$$

For the case $w_1=w_2$ only one term remains in Eq. (14), with the result that

$$I_A\sim w_2^{-3/2}\ . \tag{32}$$

Combining Eqs. (31) and (32) leads to the result

$$I\sim\frac{1}{w_2^{(m+n+9)/2}}\ . \tag{33}$$

The worst case involves $m=-1$ and $n=-1$, where $I\sim w_2{}^{-3.5}$. So it is clear that a rather large number of terms are needed to obtain an accurate result for I. The second situation, where w_2 is small (we set $w_2=0$ to simplify the analysis) is now examined. When $\tau=\tau_{\max}$

$$I_A\sim 1 \tag{34}$$

[see Eq. (A11) with $k=0$]. Using Eq. (29) for the asymptotic behavior of the W integral (worst-case convergence) leads to

$$I\sim\frac{1}{w_1}\ . \tag{35}$$

It should therefore be clear from the combination of results, Eq. (33) and in particular Eq. (35), that a direct summation strategy is not feasible.

In place of a direct summation approach, two convergence acceleration techniques were applied to Eq. (13). The first acceleration method employed was Levin's u transformation [23,24]. This is widely regarded as a very effective procedure to accelerate a series with logarithmic convergence characteristics [25,26]. This transformation has been applied in other atomic and two-center integration problems [15,27].

A sequence of partial sums are defined,

$$S_n = \sum_{w=0}^{n} A_w \ , \tag{36}$$

and these converge to some limit S. Then an improved approximation to the sum is given by

$$u_k = \frac{\sum_{j=0}^{k} (-1)^j \binom{k}{j} (j+1)^{k-2} S_j A_j^{-1}}{\sum_{j=0}^{k} (-1)^j \binom{k}{j} (j+1)^{k-2} A_j^{-1}} \tag{37}$$

where $\binom{k}{j}$ denotes a binomial coefficient. A well-known difficulty associated with the application of Eq. (37) is that serious cancellation errors occur when k becomes large [27,28].

The series expansion of Eq. (13) shows it to be composed of two monotonically decreasing series, one for w_1 even, the other for w_1 odd. Since the A_n values for the separate series are significantly different in size, a direct application of Eq. (37) is not expected to be very satisfactory, and that turns out to be true for the test cases examined. However, if Eq. (13) is split as

$$I = \sum_{\substack{w_1=0 \\ (w_1 \text{ even})}}^{\infty} A_{w_1} + \sum_{\substack{w_1=1 \\ (w_1 \text{ odd})}}^{\infty} A_{w_1} \tag{38}$$

and the u transformation applied separately to each series in Eq. (38), then a fairly significant improvement in convergence is obtained. The other important factor is that this improvement is obtained for only a modest number of terms in each series in Eq. (38). Some representative test cases are presented in Table I. The principal drawback of the application of the u transformation is that the number of digits of precision obtained for the sum is critically tied to the computer precision available. All the results reported in this work were carried out on a Cray YMP in double precision.

The Richardson extrapolation technique [29] was also tested on Eq. (13). As for the previous technique, this was also applied to Eq. (13) in the form of Eq. (38). The Richardson extrapolation is given by

$$S_0 = \sum_{k=0}^{N} \frac{S_{n+k}(n+k)^N(-1)^{k+N}}{k!(N-k)!} \ , \tag{39}$$

where S_0 is an approximation to the total sum in Eq. (13). The results of a representative test case are shown in Table II, where S_0 is presented as a function of N and n. The Richardson technique is also subject to the loss of numerical precision (for higher N,n values) similar to that found for Levin's u transformation.

Evaluation of the I integral for the case $l=-2$, $m=-2$ by direct summation of the series in Eq. (22) is not viable. Because of the presence of two factors r_{ij}^{-2} and r_{jk}^{-2} there is a product logarithmic dependence (in the variables r_i+r_j and r_j+r_k) imbedded in the series given by Eq. (22). For this reason, a direct summation of the series will not be feasible.

The Levin u transformation was applied to evaluate Eq. (22). Suppose the cutoff for the w_1 and w_2 summations in Eq. (22) is denoted by N. Then it proves to be most useful to restructure Eq. (22) in the form

$$\begin{aligned} \sum_{w_1=0}^{\infty} \sum_{w_2=0}^{\infty} f(w_1,w_2) &\Longrightarrow \sum_{w_1=0}^{N} \sum_{w_2=0}^{N} f(w_1,w_2) \\ &\Longrightarrow \sum_{\substack{w=0 \\ (\text{even } w)}}^{N} \sum_{w_2=0}^{w} f(w-w_2,w_2) \ , \end{aligned} \tag{40}$$

where $f(w_1,w_2)$ can be identified as the sum over w_3 in Eq. (22). The even condition on w in Eq. (40) follows directly from the product of the b coefficients given in Eq. (25b) and from Eq. (14). The Levin u transformation was applied to the sum over w in Eq. (40). Table III presents a couple of representative test cases showing the nature of the convergence obtained using Levin's transformation. Table IV collects some additional test values. The first four entries included in Table IV have been reported by Luchow and Kleindienst [15], though to a smaller number of digits of precision. Generally 13 to 14 digits of precision are obtained from the application of the Levin u transformation to Eq. (40). The level of precision starts to fall significantly for values of k higher than those reported in Table III. This was found for all the entries reported in Table IV as well.

V. DISCUSSION

The results from the application of the Levin u transformation shown in Table I indicate that approximately 16 to 17 digits of precision have been obtained. The optimum value of k appears to be around $k=22$. The possibility of convergence to an incorrect value was excluded by computing several of the test cases by an independent method and also by employing the Richardson extrapolation technique.

The precision starts to drop off after the optimal k value is reached. The precision of the results reported in Table I is limited by the substantial round off that occurs in the use of Eq. (37). This problem could be avoided in part by the use of a multiprecision arithmetic package.

Particularly noteworthy is the convergence of the case $m=-1$, $n=-1$. It is extremely difficult to evaluate integrals of this form to even a modest number of digits of precision by any other available procedure.

The Richardson extrapolation also performs fairly well. The test case reported in Table II agrees with the value found using the Levin u transformation to approxi-

TABLE I. Convergence of some integrals as a function of k for the Levin u transformation defined in Eq. (37) and applied to Eq. (38). $[n]$ denotes $\times 10^n$.

k	$I(1,1,1,-2,1,1,2.7,2.7,2.7)$	$I(0,0,0,-2,1,3,2.7,2.9,0.65)$	$I(0,0,0,-2,-1,1,2.7,2.9,0.65)$	$I(0,0,0,-2,-1,-1,2.7,2.9,0.65)$	$I(2,1,1,-2,3,3,7.384,4.338,4.338)$
0	5.245	330.997	13.366	11.603	3.538[−3]
1	6.555	377.963	15.649	14.071	4.541[−3]
2	7.100	400.736	16.779	15.056	4.943[−3]
3	7.172	406.342	16.979 174	15.277	4.983[−3]
4	7.187	406.059	16.992 682	15.275 007	4.991 054[−3]
5	7.188 316	405.737 494	16.986 468	15.270 495	4.994 532[−3]
6	7.187 717	405.792 447	16.986 666	15.270 980	4.993 635[−3]
7	7.187 639	405.800 842	16.986 790 873	15.271 080	4.993 696[−3]
8	7.187 642	405.798 804	16.986 784 951	15.271 060 216	4.993 652[−3]
9	7.187 646 100	405.798 525	16.986 781 246	15.271 058 976	4.993 662 031[−3]
10	7.187 646 345	405.798 620 758	16.986 781 530	15.271 059 483	4.993 661 712[−3]
11	7.187 646 261	405.798 621 678	16.986 781 611 324	15.271 059 481 844	4.993 661 878[−3]
12	7.187 646 244	405.798 619 380	16.986 781 604 910	15.271 059 471 963	4.993 661 828[−3]
13	7.187 646 244 562	405.798 619 354	16.986 781 603 167	15.271 059 472 439	4.993 661 825 963[−3]
14	7.187 646 245 053	405.798 619 420 332	16.986 781 603 287	15.271 059 472 598	4.993 661 826 090[−3]
15	7.187 646 245 100	405.798 619 420 692	16.986 781 603 322 158	15.271 059 472 582 828	4.993 661 826 319[−3]
16	7.187 646 245 093 897	405.798 619 419 004	16.986 781 603 320 156	15.271 059 472 580 598	4.993 661 826 331 664[−3]
17	7.187 646 245 091 881	405.798 619 418 971	16.986 781 603 319 481	15.271 059 472 580 964	4.993 661 826 327 339[−3]
18	7.187 646 245 091 791 038	405.798 619 419 015 728	16.986 781 603 319 515	15.271 059 472 580 991	4.993 661 826 326 234 609[−3]
19	7.187 646 245 091 830 619	405.798 619 419 017 040	16.986 781 603 319 527 89	15.271 059 472 580 983 43	4.993 661 826 326 231 182[−3]
20	7.187 646 245 091 838 043	405.798 619 419 015 854 7	16.986 781 603 319 527 24	15.271 059 472 580 983 14	4.993 661 826 326 263 763[−3]
21	7.187 646 245 091 837 974	405.798 619 419 015 810 9	16.986 781 603 319 526 98	15.271 059 472 580 983 30	4.993 661 826 326 268 186[−3]
22	7.187 646 245 091 837 780	405.798 619 419 015 841 4	16.986 781 603 319 527 00	15.271 059 472 580 983 22	4.993 661 826 326 267 817[−3]
23	7.187 646 245 091 837 826	405.798 619 419 015 8485	16.986 781 603 319 526 97	15.271 059 472 580 983 44	4.993 661 826 326 267 624[−3]
24	7.187 646 245 091 837 635	405.798 619 419 015 842 3	16.986 781 603 319 526 63	15.271 059 472 580 983 47	4.993 661 826 326 267 929[−3]
25	7.187 646 245 091 838 249	405.798 619 419 015 784 8	16.986 781 603 319 526 76	15.271 059 472 580 982 30	4.993 661 826 326 267 807[−3]

TABLE II. Results for the Richardson extrapolation [Eq. (39)] applied to the integral $I(0,0,0,-2,-1,-1,2.7,2.9,0.65)$.

n	$N=2$	$N=4$	$N=6$	$N=8$	$N=10$
1	15.070	15.263	15.270 89	15.271 057 07	15.271 059 450
5	15.255	15.270 85	15.271 057 53	15.271 059 459	15.271 059 472 519
9	15.267 07	15.271 033	15.271 059 333	15.271 059 472 016	15.271 059 472 579 63
13	15.269 48	15.271 053 19	15.271 059 452	15.271 059 472 525	15.271 059 472 580 907
17	15.270 28	15.271 057 41	15.271 059 467 84	15.271 059 472 572 13	15.271 059 472 580 976

TABLE III. Convergence of some integrals as a function of k for the Levin u transformation applied to Eq. (40).

k	$I(0,0,0,-2,-2,4,2.7,2.9,0.65)$	$I(0,0,0,-2,-2,6,2.7,2.9,0.65)$
0	59.19	41.54
1	63.78	42.20
2	57.39	41.81
3	65.67	42.56
4	49.79	42.04
5	68.70	43.34
6	79.60	41.40
7	72.58	45.26
8	74.08	75.68
9	73.62	47.90
10	73.727 5	49.72
11	73.703 5	48.96
12	73.708 227	49.169
13	73.707 395	49.110 22
14	73.707 537	49.125 49
15	73.707 514 84	49.121 78
16	73.707 517 55	49.122 62
17	73.707 517 108	49.122 442
18	73.707 517 170 98	49.122 476 9
19	73.707 517 172 34	49.122 470 5
20	73.707 517 174 187	49.122 471 65
21	73.707 517 174 106	49.122 471 467
22	73.707 517 174 113 9	49.122 471 495 6
23	73.707 517 174 160 3	49.122 471 491 33
24	73.707 517 174 197 1	49.122 471 491 95
25	73.707 517 174 217 5	49.122 471 491 866
26	73.707 517 174 228 6	49.122 471 491 875 5
27	73.707 517 174 234 9	49.122 471 491 874 1

TABLE IV. Some I integrals evaluated from Eq. (40).

i	j	k	l	m	n	α	β	γ	I
0	5	5	-2	-2	4	1.42	6.52	6.52	$2.648\,011\,637\,084\times10^{-2}$
3	7	1	-2	-2	4	6.52	6.52	1.42	$1.775\,862\,983\,358\times10^{-2}$
0	0	0	-2	-2	4	3.97	3.97	6.52	$1.239\,128\,937\,797\times10^{-2}$
1	3	2	-2	-2	4	3.97	3.97	6.52	$2.417\,774\,258\,610\times10^{-2}$
2	1	3	-2	-2	4	2.7	2.9	0.65	$3.696\,961\,214\,545\times10^{3}$
2	2	2	-2	-2	4	2.7	2.9	0.65	$2.076\,347\,965\,559\times10^{3}$
3	7	2	-2	-2	4	2.7	2.9	0.65	$9.284\,583\,074\,892\times10^{5}$
1	3	2	-2	-2	6	2.7	2.9	0.65	$3.875\,442\,706\,644\times10^{4}$
5	5	5	-2	-2	2	2.7	2.9	0.65	$2.340\,828\,566\,559\times10^{6}$
1	1	1	-2	-2	5	2.7	2.9	0.65	$7.604\,960\,853\,6948\times10^{2}$

mately 16 digits of precision. The other integrals evaluated by the Richardson approach yielded a similar level of precision.

For the more difficult case of $l=-2$, $m=-2$, the Levin u transformation also does a particularly satisfactory job at producing a converged value for the integrals. The optimum value of k for these cases appears to be around $k=26$.

A particularly significant feature of the present work is that both techniques employed to evaluate Eq. (38) are computationally fast. The acceleration techniques avoid the problem of having to deal with some rather difficult integration problems. These procedures are feasible for application to large scale *ab initio* calculations.

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APPENDIX

In the appendix we consider the evaluation of the integral

$$A(\alpha;m,\mu;n,\nu)=\int_0^\pi \sin^\alpha\theta C_m^\mu(\cos\theta)C_n^\nu(\cos\theta)d\theta$$
$$=\int_{-1}^{1}(1-x^2)^{(\alpha-1)/2}C_m^\mu(x)C_n^\nu(x)dx \ . \quad \text{(A1)}$$

The case $\mu=\gamma=\alpha/2$ is the standard orthogonality condition for the Gegenbauer polynominals.

If $m+n$ is odd then $A=0$. Equation (A1) is recast as

$$A=\int_{-1}^{1}(1-x^2)^{\mu-1/2}C_m^\mu(x)q(x)dx \ , \quad \text{(A2)}$$

with

$$q(x)=(1-x^2)^{\alpha/2-\mu}C_n^\nu(x) \ . \quad \text{(A3)}$$

If $\alpha-2\mu$ is even and ≥ 0, then $q(x)$ is a polynomial of degree $x-2\mu+n$. For the case $\alpha-2\mu+n<m$, $A=0$. This follows from the well-known result in the theory of orthogonal polynomials that

$$\int_a^b w(x)p_n(x)q(x)=0 \ , \quad \text{(A4)}$$

where $p_n(x)$ is an orthogonal polynomial on the interval $[a,b]$ with weight function $w(x)$ and $q(x)$ is a polynomial of degree less than n.

If $\alpha-2\mu+n\geq m$, then substituting the Rodrigues formula for $C_m^\mu(x)$ [30],

$$C_m^\mu(x)=\frac{1}{a_m^\mu}(1-x^2)^{-\mu+1/2}\frac{d^m}{dx^m}[(1-x^2)^{\mu+m-1/2}] \ , \quad \text{(A5)}$$

with

$$a_m^\mu=(-2)^m\frac{m!\Gamma(2\mu)\Gamma(m+\mu+\frac{1}{2})}{\Gamma(\mu+\frac{1}{2})\Gamma(m+2\mu)} \ , \quad \text{(A6)}$$

into Eq. (A2), yields, on integration by parts,

$$A=\frac{(-1)^m}{a_m^\mu}\int_{-1}^{1}(1-x^2)^{\mu+m-1/2}\frac{d^m q(x)}{dx^m}dx \ . \quad \text{(A7)}$$

From Eq. (A3) $q(x)$ is evaluated to be

$$q(x)=\sum_{\sigma=0}^{\frac{\alpha-2\mu}{2}}(-1)^\sigma\begin{pmatrix}\frac{\alpha-2\mu}{2}\\ \sigma\end{pmatrix}\sum_{\tau=0}^{[\frac{n}{2}]}\frac{(-1)^\tau\Gamma(\nu+n-\tau)}{\Gamma(\nu)2^{2\tau-n}\tau!(n-2\tau)!}x^{n+2\sigma-2\tau} \ . \quad \text{(A8)}$$

Inserting this expression for $q(x)$ into Eq. (A7) leads to a sum of β functions. The final result is

$$A(\alpha;m,\mu,n,\nu)=\frac{[1+(-1)^{m+n}]\pi\Gamma(m+2\mu)}{4^\mu m!\Gamma(\mu)\Gamma(\nu)}\sum_{\sigma=\sigma_{\min}}^{\frac{\alpha-2\mu}{2}}\begin{pmatrix}\frac{\alpha-2\mu}{2}\\ \sigma\end{pmatrix}\frac{1}{(-4)^\sigma}$$
$$\times\sum_{\tau=0}^{\tau_{\max}}\frac{(-1)^\tau\Gamma(\nu+n-\tau)(n+2\sigma-2\tau)!}{\tau!(n-2\tau)!\left[\frac{n-m}{2}+\sigma-\tau\right]!\Gamma\left[\frac{n+m}{2}+\mu+\sigma-\tau+1\right]} \ , \quad \text{(A9)}$$

with

$$\sigma_{\min}=\max\left\{0,\frac{m-n}{2}\right\} \ ,$$

$$\tau_{\max}=\min\left\{\left[\frac{n}{2}\right],\frac{n-m}{2}+\sigma\right\} \ . \quad \text{(A10)}$$

The duplication formula for the Γ function has been employed to obtain the final result given in Eq. (A9).

If $\alpha-2\mu$ is odd or less than 0, then the above procedure could be repeated if $\alpha-2\nu$ is even and ≥ 0, because of the symmetric nature of A with respect to the interchange $m\leftrightarrow n$ and $\mu\leftrightarrow\nu$. If neither condition on $\alpha-2\mu$ or $\alpha-2\nu$ is satisfied, a formula involving a double sum can be obtained by employing explicit expansions for both Gegenbauer polynomials $C_m^\mu(x)$ and $C_n^\nu(x)$.

The special case of A required in Eq. (9) is $A(1;\, w_1,\, 1;\, k,\frac{1}{2})$. The condition w_1+k even must hold; otherwise $A=0$. Because of the factor δ_{kw_1} in Eq. (11), the condition w_1+w_2 even emerges in Eq. (14). With the substitutions $\alpha=1$, $m=k$, $\mu=\frac{1}{2}$, $n=w_1$, $\nu=1$ in Eq. (A9), the following result is obtained:

$$A(1;w_1,1;k,\tfrac{1}{2})=\sqrt{\pi}\sum_{\tau=0}^{\tau_{\max}}\frac{(-1)^{\tau}(w_1-\tau)!}{\tau!\left[\dfrac{w_1-k}{2}-\tau\right]!\Gamma\left[\dfrac{w_1+k}{2}-\tau+\frac{3}{2}\right]}, \tag{A11}$$

with

$$\tau_{\max}=\min\left\{\left[\frac{w_1}{2}\right],\frac{w_1-k}{2}\right\}.$$

For the cases $\alpha-2\mu\geq 0$ and even, or $\alpha-2\nu\geq 0$ and even, the procedure employed above leads to a more efficient formula than the use of explicit expansions for both Gegenbauer polynomials. For the particular case of interest just discussed, the number of terms required for expansion of both Gegenbauer polynomials is

$$\left[\frac{m}{2}\right]\left[\frac{n}{2}\right]=\left[\frac{w_1}{2}\right]\left[\frac{k}{2}\right],$$

while from Eq. (A11) the number of terms is governed by

$$\tau_{\max}=\min\left\{\left[\frac{w_1}{2}\right],\frac{w_1-k}{2}\right\}.$$

There will be considerable reduction in computational effort for the latter case when w_1 and k are both large.

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