Application of Nonlinear Transformations to the Evaluation of Multicenter Integrals

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(Received 20 January 1967)

The evaluation of multicenter integrals is necessary for ab initio calculations. Expansion techniques give infinite series which must be summed. We have used several nonlinear sequence-to-sequence transformations to obtain more rapidly convergent series. The best of these transformations reduces the time necessary to evaluate some four-center integrals by as much as 75%. This transformation improved the convergence of all of the twenty integrals we have treated.

INTRODUCTION

MOLECULAR systems of increasing complexity are becoming amenable to ab initio calculations. One of the major difficulties preventing the extension of these techniques to larger systems is the computer time necessary to evaluate multicenter integrals. Except in the smallest molecules, most of the computer time necessary to do a calculation is spent evaluating these integrals.

The troublesome molecular integrals are of the form

\[ I = \iiint x_{A1}^{(1)}(1) x_{A2}^{(2)}(1) F(1, 2) x_{A1}^{(3)}(2) x_{A2}^{(4)}(2) d\mathbf{r}_1 d\mathbf{r}_2 \]

where \( x_{Ai}^{(j)}(1) \) is basis function \( j \) centered on Nucleus \( A_i \), as a function of the space coordinates of Electron 1, and \( F(1, 2) \) is a function of the coordinates of both electrons. They are referred to as one-, two-, three-, or four-center integrals according to whether four, three, two, or none of the \( A_i \)'s are the same. The basis functions are usually of the Slater type

\[ \chi(j) = N(n, l, m) r_j^{n-1} \exp(-\beta r_j) P_l^m(\cos\theta_j) \exp(\imath \phi_j), \]

where \( r_j, \theta_j, \phi_j \) are the spherical coordinates of Electron \( j \) and the \( P_l^m \) are Legendre polynomials. For convenience we assume that \( n \) is less than 3. The \( \beta \)'s are usually chosen to minimize the energy. Several methods of evaluating these integrals have been proposed. The Gaussian transform method is very efficient, especially if the Aitken transformation is used to accelerate convergence. However, this method does not work well if two or more basis functions have widely different exponents. The most popular method is the zeta-function method which is based on the expansion

\[ r_A^{-n-1} \exp(-k r_A) = \sum_{\ell=0}^{\infty} \frac{(2\ell+1)}{(\ell+\rho_A)^{\ell+1/2}} P_{\ell}^0(\cos\theta_A) r_A^\ell, \]

which is a simple infinite series in the index \( \ell \). The \( \ell \)th partial sum, \( I_N \), is defined as

\[ I_N = \sum_{\ell=0}^{N} \sum_{\ell=0}^{\infty} f(i_2, i_3, 2I-i_2-i_3). \]

The forward difference operator, \( \Delta \), is defined by

\[ \Delta I_N = I_{N+1} - I_N. \]

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† Contribution No. 3472.
\(^{5}\) M. P. Barnett in Ref. 1.
where \( I_4 = 0 \). The evaluation of the functions, \( f_i \) in Eq. (5) is very time consuming and the double summation causes the evaluation of the sequence \( \{ I_N \} \), to become progressively more difficult for large \( N \). Figure 1 shows the average time required to evaluate several three- and four-center integrals from ethane as a function of the number of terms used. We can save a great deal of time by reducing the number of terms required to give the desired accuracy. The most straightforward estimate of the value of the integral is to use \( I_N \) for some large \( N \). This approach assumes that we have no knowledge of the truncation error

\[
\epsilon_N = I - I_N = \sum_{l=N+1}^{\infty} \Delta I_{l-1}.
\]

(7)

More efficient methods make use of the available knowledge of this error. In order to be useful such a method must give a reliable estimate of the truncation error for some \( N \) less than the \( N \) originally required for the desired accuracy. In Appendix A we show that the asymptotic form of the single-center zeta-function expansion series for all multicenter integrals is

\[
I_N = \sum_{i=N}^{\infty} \left\{ \sum_{j=1}^{i} a_j \cos(\theta_j + \alpha_j) \lambda_i (l - \mu i^2) \right\},
\]

(8)

where \( \lambda_i \leq 1 \) and \( n \) is finite. We use this asymptotic form to develop a method of estimating the truncation error and show that the method leads to a considerable reduction in the computer time required to evaluate these multicenter integrals.

\[\text{FIG. 1. The relative time required to calculate partial sum } I_N \text{ as a function of } N. \text{ The first curve, } a, \text{ is the average for several three-center integrals such as } \langle \chi_{A}^{(0)} \chi_{B}^{(0)} | r_{12}^{-1} | \chi_{C}^{(0)} \chi_{D}^{(0)} \rangle. \text{ The second curve, } b, \text{ is the average for several four-center integrals, } \langle \chi_{A}^{(0)} \chi_{B}^{(0)} | r_{12}^{-1} | \chi_{C}^{(0)} \chi_{D}^{(0)} \rangle, \text{ with various basis functions. These curves demonstrate that considerable time could be saved by reducing the number of terms evaluated in the series expansion.}\]

\[\text{FIG. 2. The relative change in } A, \text{ [of Eq. (9)] } \Delta A_{N}/A_{N+1}, \text{ as a function of } N \text{ for a two-center exchange integral taken from calculations on formaldehyde. Since this relative change is much less than one for small } N, \text{ the asymptotic form, Eq. (9), is a good approximation for the series expansion of this integral.}\]

The simplest multicenter integral is the two-center exchange integral, \( \langle \chi_{A}^{(0)} \chi_{B}^{(0)} | r_{12}^{-1} | \chi_{A}^{(0)} \chi_{B}^{(0)} \rangle \), for which \( \theta_i = 0, \lambda_i = 1, \) and \( m_i = 12 \) in Eq. (8). This means that asymptotically we have

\[
I \equiv I_N + \sum_{l=N+1}^{\infty} A l^{-s},
\]

(9)

where \( A \) is independent of \( N \) for large \( N \). In order to use this form to estimate the truncation error we must determine \( A \). Subtracting the analogous expression for \( I_{N-1} \) from Eq. (9) gives

\[
\Delta I_{N-1} \equiv I_N - I_{N-1} \equiv A N^{-s},
\]

(10)

which defines \( A \) as a function of the terms of the infinite series. We define a sequence of "local constants," \( \{ A_N \} \) where \( A_N \) is calculated from \( I_N \) and \( I_{N-1} \) by Eq. (10). If the sequence \( \{ I_N \} \) is nearly of the form given in Eq. (9) then the \( A_N \) should vary only slightly. In Fig. 2 we show the relative change in \( A_N, \Delta A_N/A_{N+1}, \) as a function of \( N \) for a two-center exchange integral taken from calculations on formaldehyde. The sequence \( \{ A_N \} \) is nearly constant for small \( N \) and it is reasonable to use the asymptotic form, Eq. (9), to estimate the truncation error \( \epsilon_N \) [see Eq. (7)]. We now have the estimate for the truncation error,

\[
\epsilon_N \approx N^s \delta I_{N-1} [z(6) - \sum_{l=1}^{N} l^{-s}],
\]

(11)

where \( z(6) \) is the Riemann zeta function. We use the
value of $\zeta(6)$ to define the $\xi_6$ transformation of the sequence $\{I_N\}$,

$$
\xi_6(I_N) = I_N + \sum_{n=1}^{\infty} \frac{n^6}{945} I_{N-1}
$$

(12)

which forms a new sequence $\{\xi_6(I_N)\}$ that converges to $I$ for a two-center exchange integral. For large $N$ the error in the new sequence $[I-\xi_6(I_N)]$ is much smaller than the corresponding error in the original sequence $\xi_N$ since the $\xi_6$ transformation was derived using the asymptotic form of the two-center exchange integral. This transformation is useful only if the ratio of these errors, $[I-\xi_6(I_N)]/\xi_N$, is much less than 1 for small $N$. Figure 3 shows this ratio as a function of $N$ for the integral from formaldehyde used above. The required condition is met and $\xi_6$ is a useful transformation for two-center exchange integrals.

A second interesting transformation is due to Aitken$^3$ and is based upon the assumption

$$
I = I_N + AqN^N
$$

(13)

for the truncation error, where $A$ is the "amplitude" and $q$ is the "ratio." The ratio is less than 1 for a convergent sequence. This defines the $\xi_1$ transformation,

$$
\xi_1(I_N) = I_N + \left[ (1/\Delta I_N) - (1/\Delta I_{N-1}) \right]^{-1}
$$

(14)

in the same way that Eq. (9) defines the $\xi_6$ transformation. The $\xi_1$ transformation is frequently called the Aitken $\beta^2$ process. In Appendix B we show that the application of the $\xi_1$ transformation to the Riemann zeta function gives a new sequence which converges monotonically and more rapidly than the original sequence to $\zeta(6)$. The $\xi_6$ transformation of the Riemann zeta function gives the exact limit immediately. However, Fig. 3 indicates that for small $N$ the $\xi_1$ transformation is more accurate than the $\xi_6$ transformation of a two-center exchange integral.

A generalization of the $\xi_1$ transformation is discussed in great detail by Shanks. Typical convergent sequences include both monotonic and oscillatory types. Multicenter integrals offer abundant examples of both types. If we draw a smooth curve through the discrete points of a graph of $I_N$ vs $N$, this graph looks like a stable physical transient for either of the above types of sequences. This suggests the possibility of approximating the truncation error of multicenter integrals by a mathematical transient

$$
I = I_N + \sum_{j=1}^{k} A_j q_j^N,
$$

(15)

where the transient is of "order" $k$, with "amplitudes"

| Table I. A three-center Coulomb integral from a calculation on H$_2$O. |
|---|---|---|---|
| Approximate values* for the integral $\times 10^b$ |
| Index of last term required | Sum of the first $N$ terms $I_N^b$ | Transformation of order 2, $\xi_2(I_{N-1})^e$ | Transformation of maximum order $\xi_6(I_N)^d$ |
| $N$ | | | |
| 0 | 253.7340 | 253.7340 |
| 3 | 166.1983 | -134.2630 |
| 6 | 105.1562 | 7.7023 |
| 9 | 105.1789 | 0.0677 |
| 12 | -22.6435 | 0.1474 |
| 15 | 0.1678 | 0.2007 |
| 18 | 3.4199 | 0.2184 |
| 21 | 22.6707 | 0.2027 |
| 24 | 1.2068 | 0.1907 |
| 27 | 0.0388 | 0.1866 |
| 30 | 0.8712 | 0.1904 |
| 33 | -0.1008 | 0.1875 |

* The correct value of this integral is $0.187624 \times 10^b$ which was obtained by expanding about a different center.

b See Eq. (5).

c See Eqs. (17) and (18).

d See Eq. (19).

This equation defines the \( e_k \) transformation in the same way that Eq. (9) defined the \( s_k \) transformation and Eq. (13) defined the \( e_1 \) transformation. We can solve Eq. (15) for \( I \) and for \( A_j \) and \( q_j \) \( (j=1,k) \) if we know \( I_N \) for 28+1 values of \( N \). Solution of this system of equations for \( I \) leads to the transformation

\[
I_{N-k} \quad \ldots \quad I_{N-1} \quad I_N
\]

\[
\Delta I_{N-k} \quad \ldots \quad \Delta I_{N-1} \quad \Delta I_N
\]

\[
\Delta I_{N-k+1} \quad \ldots \quad \Delta I_N \quad \Delta I_{N+1}
\]

\[
\vdots
\]

\[
\Delta I_{N-1} \quad \ldots \quad \Delta I_{N+k-1}
\]

\[ e_k(I_N) = \frac{1}{1 \cdot 1 \cdot 1 \cdot \ldots} \] (16)

which is a ratio of two determinants of dimension \( k \). This is very time consuming to evaluate. Fortunately, Wynn\(^7\) has developed an efficient algorithm for these transformations. He defines the intermediate quantities \( g_m \) as

\[ g_m(I_N) = e_m(I_N), \]

\[ g_{m+1}(I_N) = 1/e_m(\Delta I_N), \] (17)

and shows that

\[ g_{m+1}(I_N) = g_{m-1}(I_{N+1}) + [g_m(I_{N+1}) - g_m(I_N)]^{-1} \] (18)

for any \( m \) greater than zero. In particular, we choose the transformation

\[ \tilde{e}_d(I_{2N}) = e_N(I_N), \]

\[ \tilde{e}_d(I_{2N+1}) = e_N(I_{N+1}), \] (19)

which uses the highest-order transient possible for all \( N \). This transformation has been applied to the two-center exchange integral treated previously and the results are given in Fig. 3. This is the most powerful of the three transformations we have used.

Treatment of the simple Riemann zeta function by the \( e_1 \) transformation involves the approximation

\[ I^{-m/2} \approx (N+1)^{-m/2} \left[ N/(N+1) \right]^{m/2} 1^{N-1}, \quad (I>N), \] (20)

as shown in Appendix B. Applying this approximation

\[ I^{-m/2} \approx (N+1)^{-m/2} \left[ N/(N+1) \right]^{m/2} 1^{N-1}, \quad (I>N), \] (20)

Table II. A four-center integral from a calculation on \( C_6H_4 \).

<table>
<thead>
<tr>
<th>Index of last Term Required ( N )</th>
<th>Sum of the First ( N ) Terms ( I_N )</th>
<th>Transformation of Order 2 ( e_2(I_{N-2}) )</th>
<th>Transformation of Maximum Order ( e_d(I_N) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.134678</td>
<td>0.630630</td>
<td>0.632468</td>
</tr>
<tr>
<td>3</td>
<td>1.099399</td>
<td>0.630873</td>
<td>0.630630</td>
</tr>
<tr>
<td>6</td>
<td>0.664420</td>
<td>0.631958</td>
<td>0.632455</td>
</tr>
<tr>
<td>9</td>
<td>0.632337</td>
<td>0.632337</td>
<td>0.632454</td>
</tr>
<tr>
<td>12</td>
<td>0.632433</td>
<td>0.632433</td>
<td>0.632454</td>
</tr>
<tr>
<td>15</td>
<td>0.632446</td>
<td>0.632446</td>
<td>0.632454</td>
</tr>
<tr>
<td>18</td>
<td>0.632465</td>
<td>0.632465</td>
<td>0.632454</td>
</tr>
</tbody>
</table>

These results are given in Fig. 3. This is the most powerful of the three transformations we have used.

We checked the program for the Wynn algorithm\(^7\) by comparing the \( e_2 \) transformation with the algorithm developed by Aitken\(^8\) which is based on a similar asymptotic form but is completely independent. The two agreed to within 1 ppm. The Wynn algorithm is

\[ e_N = \sum \left[ \sum_{j=1}^{N} b_j \cos(\theta_j + \alpha_j) \right] \approx \sum_{j=1}^{k} A_j q_j \] (22)

where \( k \) is finite. This fits into the scheme of the \( e_k \) transformation with the \( q_j \) occurring in complex conjugate pairs. The \( \tilde{e}_d \) transformation will eventually accelerate the convergence of any multicenter integral. We have applied the Wynn algorithm to several multicenter integrals. The \( \tilde{e}_d \) transformation gives a consistently accurate estimate of the truncation error. Table I gives a dramatic example of the improvement we have achieved with this transformation. The method is most effective with the most slowly convergent series, such as the example in Table I. Table II gives the results for a typical four-center integral. Although this example is not as spectacular as the previous one, the \( \tilde{e}_d \) transformation still gives a marked improvement in the convergence. The more rapidly convergent series such as the example given in Table II show little improvement when the \( \tilde{e}_d \) transformation is substituted for the simpler \( e_2 \) transformation. The \( e_2 \) transformation is important because it is the simplest transformation based on transients which can show an oscillatory behavior for the truncation error.

\[ \tilde{e}_d = \sum_{l=1}^{N} \left[ \sum_{j=1}^{N} b_j \cos(\theta_j + \alpha_j) \mu_l \right] = \sum_{j=1}^{k} A_j q_j, \] (22)

\(^7\) P. Wynn, Math. Aids Computation 54, 91 (1956).

slightly unstable for high-order transformations because it requires finding small differences between large numbers, but the use of double-precision arithmetic eliminates this problem.

We have summarized the results of the application of the $\tilde{\alpha}_d$ transformation to 10 four-center integrals in Table III. In most cases $\tilde{\alpha}_d(I_{12})$ gives all available information about the value of the integral. The round-off error in summing $\Delta f_N$ and the error in the numerical quadrature used to calculate $\Delta f_N$ prevent accuracy greater than six significant figures. This accuracy is usually achieved with $\tilde{\alpha}_d(I_{12})$. The relative error for this transformation, $\left|I-\tilde{\alpha}_d(I_{12})\right|/\epsilon_{12}$, is listed for the 10 integrals in Table III. Our estimate for the truncation error is on the average accurate to within 1%. The third column in the table indicates that the truncation error is large enough so that this improvement is important. The final column indicates that the error in the transformed sequence after 13 terms, $I-\tilde{\alpha}_d(I_{12})$, is comparable to the error in the original sequence after 24 terms, $\epsilon_{12}$. We have reduced the number of terms required for a given accuracy by about a factor of 2. The time required to carry out the transformation is negligible compared to the time required to compute additional partial sums. From Fig. 1 we see that the time required to evaluate these four-center integrals has been reduced by about 75%. Additional three- and four-center integrals were treated and gave results similar to those reported above.

CONCLUSIONS

Expansion techniques used to evaluate multicenter integrals give rise to infinite series which must be summed. We have used the asymptotic forms of these series to develop sequence-to-sequence transformations which accelerate convergence. The Wynn algorithm provides an efficient method of obtaining rapidly convergent sequences for multicenter integrals. The application of the $\tilde{\alpha}_d$ transformation to the first 13 partial sums usually provides six significant figures accuracy for the sum of the series. This is the maximum accuracy possible if the partial sums are computed in single-precision arithmetic. This transformation reduces the time necessary to evaluate four-center integrals by as much as 75%. Although we have restricted this discussion to the zeta-function expansion of basis functions with principal quantum number less than three, the basic approach is quite general.

ACKNOWLEDGMENTS

We thank Dr. R. M. Pitzer for many helpful discussions and for providing the necessary programs and integrals. We also thank the Division of Chemistry and Chemical Engineering of the California Institute of Technology for computing time. One of the authors (G.A.P.) thanks the NSF for maintenance support.

APPENDIX A: ASYMPTOTIC FORMS OF MULTICENTER INTEGRALS

Sahni and LaBudde have derived the asymptotic forms of single-center zeta-function expansions for all integrals of interest except the four-center electron repulsion integral. We give a brief description of their method and indicate the differences which arise in the four-center case. The complexity of the four-center

\begin{table}
\centering
\caption{The $\tilde{\alpha}_d$ transformation of some four-center integrals from $C_2H_4$.}
\begin{tabular}{|c|c|c|c|}
\hline
Integral & Relative error after $\tilde{\alpha}_d$ transformation$^a$ & Relative truncation error$^b \times 10^4$ & $\left|I-\tilde{\alpha}_d(I_{12})\right|/\epsilon_{12}$ \tabularnewline \hline
$\langle 1s_1 1s_2 \mid r_{12}^{-1} \mid 1s_2 1s_2 \rangle$ & 0.046 & 17 & 3.0 \tabularnewline
$\langle 1s_1 1s_2 \mid r_{12}^{-1} \mid 1s_1 1s_2 \rangle$ & 0.050 & 340 & 1.6 \tabularnewline
$\langle 2s_1 1s_2 \mid r_{12}^{-1} \mid 1s_2 1s_2 \rangle$ & 0.0083 & 17 & 0.46 \tabularnewline
$\langle 2s_1 1s_2 \mid r_{12}^{-1} \mid 1s_1 1s_2 \rangle$ & 0.031 & 370 & 1.0 \tabularnewline
$\langle 2p_{x3} 1s_2 \mid r_{12}^{-1} \mid 1s_1 1s_2 \rangle$ & 0.0093 & 14 & 0.36 \tabularnewline
$\langle 2p_{x3} 1s_2 \mid r_{12}^{-1} \mid 1s_1 1s_2 \rangle$ & 0.00051 & 2500 & 0.071 \tabularnewline
$\langle 2p_{y3} 1s_2 \mid r_{12}^{-1} \mid 1s_1 1s_2 \rangle$ & 0.0063 & 51 & 1.0 \tabularnewline
$\langle 2p_{y3} 1s_2 \mid r_{12}^{-1} \mid 1s_1 1s_2 \rangle$ & 0.00044 & 2000 & 0.29 \tabularnewline
$\langle 2p_{z3} 1s_2 \mid r_{12}^{-1} \mid 1s_1 1s_2 \rangle$ & 0.0064 & 52 & 1.1 \tabularnewline
$\langle 2p_{z3} 1s_2 \mid r_{12}^{-1} \mid 1s_2 1s_2 \rangle$ & 0.00064 & 180 000 & 0.29 \tabularnewline
\hline
\end{tabular}
\end{table}

\begin{itemize}
\item[$^a$] Since the relative error $\left|I-\tilde{\alpha}_d(I_{12})\right|/\epsilon_{12}$ is much less than one, the $\tilde{\alpha}_d$ transformation gives considerable acceleration of convergence.
\item[$^b$] Since the relative truncation error $\epsilon_{12}/f$ is greater than $10^4$, the improved accuracy is important.
\end{itemize}
EVALUATION OF MULTICENTER INTEGRALS

Table IV. The asymptotic forms of two- and three-center integrals.

<table>
<thead>
<tr>
<th>Integral</th>
<th>Name</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>F(1, 2)</th>
<th>Asymptotic form</th>
<th>Restriction</th>
<th>λ</th>
<th>ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-center exchange integral</td>
<td>A B A B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>r₁₂⁻¹</td>
<td></td>
<td>None</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Three-center potential-energy integral</td>
<td>A B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>r₁₂⁻¹</td>
<td></td>
<td>ρB &lt; ρC (ρB/ρC)</td>
<td>2</td>
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<td></td>
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<td>ρB &gt; ρC (ρC/ρB)</td>
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<td></td>
<td></td>
<td>ρB = ρC</td>
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<td>3</td>
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<tr>
<td>Three-center exchange integral</td>
<td>A B A C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>r₁₂⁻¹</td>
<td></td>
<td>ρB &lt; ρC (ρB/ρC)</td>
<td>4</td>
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<td></td>
<td>ρB &gt; ρC (ρC/ρB)</td>
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<td></td>
<td>ρB = ρC</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Three-center Coulomb integral</td>
<td>B B A C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>r₁₂⁻¹</td>
<td></td>
<td>ρB &lt; ρC, a</td>
<td>5</td>
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<td>ρB &gt; ρC, a</td>
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<td></td>
<td>ρB = ρC, a</td>
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<td>7</td>
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<td>ρB &lt; ρC, b</td>
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<td>ρB &gt; ρC, b</td>
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<td></td>
<td></td>
<td>ρB = ρC, b</td>
<td>1</td>
<td>6</td>
</tr>
</tbody>
</table>

* χB⁰(1) = χB⁰(1) = Slater 2r orbital.  
  b Case a is not true.

The case requires the use of several questionable approximations to obtain the asymptotic form.

We first expand the potential function \( r_{ij}^{-1} \) and the Legendre polynomials at Centers A₂, A₃, and A₄ about Center A₁. Then we expand the remaining terms, \( r_{ij}^{-1} \exp(-k_{ij}r_{ij}) \), about Center A₁ using the zeta-function expansion of Coulson.⁴ The spherical harmonics are then rotated so that they are all in one coordinate system (with A₁-A₂ as the z axis) and the \( \theta \) and \( \phi \) integrations are carried out. In the four-center case we cannot carry out the \( \theta \) integration exactly, but instead we use the approximation

\[
P_\ell' (\cos \theta) \approx \left[ \Gamma(I + m + 1) / \Gamma(I + 1/2) \right] (1/2 \pi \sin \theta)^{-1/2} \times \cos \left[ (I + 1/2) \theta - 1/2 \pi + m_1 \pi \right],
\]

which reduces the \( \theta \) integrals to a simple form. The function \( \Gamma \) is just the gamma function. We obtain the asymptotic form of the radial integrals from a series of inequalities given by Sahni and LaBudde. In the four-center case we have a triply infinite series over the indices \( i_2, i_3, \) and \( i_4 \). We introduce the index \( l = i_2 + i_3 + i_4 \) and sum the resulting finite series over indices \( i_2 \) and \( i_3 \) using approximations such as

\[
\sum_{i_2 = i_2 - l}^{i_2 + l} (l + i_2)^{-1} \lambda^i_2 \cos (i_2 \theta) = 2(4l - i_2)^{-1} \sum_{i_2 = i_2 - l}^{i_2 + l} \lambda^i_2 \cos (i_2 \theta),
\]

where we have used the average value of \( i_2 \) for the slowly varying part of the expression. This approximation is quite good when \( i_2 \) is small compared to \( l \), but can be very bad for large \( i_2 \).

The resulting asymptotic form of two- and three-center integrals is

\[
I_\ell = \sum_{l=0}^{\infty} \left\{ \sum_{j=0}^{I} \lambda^j_\ell \sum_{m=0}^{I} \frac{K_j P_{4\ell}(\cos \Theta)}{L^{m/2}} \right\},
\]

which is also the approximate asymptotic form of the four-center electron repulsion integral. In the four-center case, the \( \lambda_j \) take on such values as \( (\rho < / p_p), (p_p / p_p), \) and \( (p_p / p_p) \), where \( \rho_< \) is the smallest, \( \rho_\) is the intermediate, and \( \rho_> \) is the largest of the \( \rho_{Al} \).

We now have a convenient general asymptotic form for single-center zeta-function expansions of multicenter integrals.

**APPENDIX B: THE \( \ell_1 \) TRANSFORMATION OF THE RIEMANN ZETA FUNCTION**

The transformation of this simple sequence provides valuable insight into the effect of comparable transformations on more complicated sequences. The Riemann zeta function \( \zeta(n) \) is the limit of the sequence \( \{S_N\} \) where

\[
S_N = \sum_{k=1}^{\infty} k^{-n},
\]

as \( N \) approaches infinity. Application of the \( \ell_1 \) transformation, Eq. (14), gives the new sequence

\[
el_1(S_N) = S_N + (N+1)^{-1} \left\{ 1 - \left[ N/(N+1) \right]^{1/2} \right\},
\]

where the correction term involves the sum of a
A series in the internuclear distance \( R \) is derived for the two-center overlap integral between noninteger-\( n \) Slater-type atomic orbitals. There are in general two types of terms: \( R^{n_1+n_2} \) and \( R^{n_1+n_2} \) times a power series. The series becomes an ordinary power series when both \( n_1 \) and \( n_2 \) are integers. When neither \( n_1 \) nor \( n_2 \) is an integer while \( n_1+n_2 \) is, there are logarithmic terms.

For the reader interested only in the working results, see Eqs. (7), (32), (33), (37), and (41).

**FORMULATION**

The overlap integral between a STO at the origin, characterized by the parameters \( n_1, l_1, m_1, \xi_1, \xi_2 \), and a STO at \( R \) with parameters \( n_2, l_2, m_2, \xi_3 \), is given by [Eq. (16) of I]

\[
S_{n_1l_1m_1; n_2l_2m_2}(R) = N_{n_1l_1m_1}N_{n_2l_2m_2}(2\pi)^{-1} \sum_{\ell=|l_1-l_2|}^{l_1+l_2} c^\ell(l_2, m_2; l_1, m_1) (2\ell_1+1)^{1/2}(4\pi)^{-1/2} \int_0^\infty dk k^{2\ell} f_{n_1l_1\ell_1}(k)f_{n_2l_2\ell_2}(k) j_\ell(kR). \tag{1}
\]

(A complete explanation of the symbols and conventions can be found in I.) Briefly, the \( N_{n_1} \) are normalization constants supported by a National Science Foundation Grant.