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Overlap integrals of *B* functions*

A numerical study of infinite series representations and integral representations

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Two different methods for the evaluation of overlap integrals of *B* functions with different scaling parameters are analyzed critically. The first method consists of an infinite series expansion in terms of overlap integrals with equal scaling parameters [14]. The second method consists of an integral representation for the overlap integral which has to be evaluated numerically. Bhattacharya and Dhabal [13] recommend the use of Gauss-Legendre quadrature for this purpose. However, we show that Gauss-Jacobi quadrature gives better results, in particular for larger quantum number. We also show that the convergence of the infinite series can be improved if suitable convergence accelerators are applied. Since an internal error analysis can be done quite easily in the case of an infinite series even if it is accelerated, whereas it is very costly in the case of Gauss quadratures, the infinite series is probably more efficient than the integral representation. Overlap integrals of all commonly occurring exponentially declining basis functions such as Slater-type functions, can be expressed by finite sums of overlap integrals of *B* functions, because these basis functions can be represented by linear combinations of *B* functions.

Key words: Overlap integrals — Exponentially declining atomic orbitals — Numerical quadrature — Convergence acceleration

1. Introduction

The problem of evaluating overlap integrals of exponentially declining functions such as Slater-type functions both accurately and efficiently occurs not only in

* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

ab initio calculations but also in semiempirical calculations and in solid-state theory. Consequently, overlap integrals of Slater-type functions and of other exponentially declining functions have already been investigated by numerous authors and yet, it seems, that no definite conclusion about the optimal approach has been reached so far.

In this article we shall consider a special class of exponentially declining functions, the so-called B functions, which are defined by [1]:

$$B^m_{n,l}(\alpha, \boldsymbol{r}) = (2/\pi)^{1/2}[2^{n+l}(n+l)!]^{-1}(\alpha r)^{n+l-1/2}K_{n-1/2}(\alpha r)\, Y^m_l(\theta, \phi),$$
$$\alpha \in \mathbb{R}_+, \qquad n \in \mathbb{Z}, \qquad n \geq -l. \tag{1.1}$$

Here, Y^m_l stands for a spherical harmonic using Condon–Shortley phases and $K_{n-1/2}$ denotes a modified Bessel function of the second kind [2]. $\mathbb{R}_+$ denotes the set of positive real numbers and $\mathbb{Z}$ the set of positive and negative integers. Scalar B functions are essentially reduced Bessel functions as introduced by Shavitt [28].

At first sight, this choice may appear to be somewhat surprising since B functions are relatively complicated mathematical objects. However, the currently most promising approach for the evaluation of molecular multicenter integrals is based upon the Fourier transform convolution theorem which was introduced into quantum chemistry by Prosser and Blanchard [3]. Hence, if one looks at the momentum space properties of B functions it turns out that their Fourier transforms $\bar{B}$ are of exceptional simplicity [4]:

$$\bar{B}^m_{n,l}(\alpha, \boldsymbol{p}) = (2\pi)^{-3/2} \int e^{-i\boldsymbol{p}\cdot\boldsymbol{r}} B^m_{n,l}(\alpha, \boldsymbol{r})\, d^3\boldsymbol{r}$$
$$= (2/\pi)^{1/2}\alpha^{2n+l-1} \frac{(-ip)^l}{(\alpha^2+p^2)^{n+l+1}}\, Y^m_l(\boldsymbol{p}/p). \tag{1.2}$$

The Fourier transforms of other exponentially declining functions such as Slater-type functions or bound-state hydrogen eigenfunctions are significantly more complicated. In articles by Niukkanen [5] and ourselves [4, 6, 7] it was shown that the Fourier transforms of all commonly occurring atomic orbitals can be expressed as linear combinations of Fourier transforms of B functions. In view of the Fourier transform convolution theorem [3] this also implies that overlap integrals of all the other commonly occurring atomic orbitals can be expressed as finite sums of overlap integrals of B functions. Hence, it is sufficient to study overlap integrals of B functions for which we use the following notation:

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \boldsymbol{R}) = \int B^{m_1 *}_{n_1,l_1}(\alpha, \boldsymbol{r}) B^{m_2}_{n_2,l_2}(\beta, \boldsymbol{r}-\boldsymbol{R})\, d^3\boldsymbol{r}. \tag{1.3}$$

Overlap integrals of B functions were already studied by several authors [1, 4, 5, 8–15]. Computationally particularly troublesome are those cases in which the two scaling parameters α and β are different. In this article, we shall compare two different approaches to overcome these computational problems. Recently, Bhattacharya and Dhabal [13] proposed to use a one-dimensional integral

representation for overlap integrals which, however, they had to evaluate numerically using Gauss-Legendre quadrature. On the other hand, we were recently able to derive some new infinite series expansions for overlap integrals [14] which converge quite rapidly if suitable convergence accelerators are applied. In the following, we want to compare critically the relative merits of these two approaches.

As overlap integrals are basic entities occurring also in formulas for more complicated molecular integrals, it is of considerable interest also for the purpose of evaluating other molecular integrals to investigate which would be the most efficient way of evaluating overlap integrals of B functions.

2. Different expressions for overlap integrals

The Fourier transform convolution theorem [3] makes it possible to express an overlap integral as an inverse Fourier integral:

$$\int f^*(\boldsymbol{r}) g(\boldsymbol{r}-\boldsymbol{R})\, d^3\boldsymbol{r} = \int e^{-i\boldsymbol{R}\cdot\boldsymbol{p}} \bar{f}^*(\boldsymbol{p}) \bar{g}(\boldsymbol{p})\, d^3\boldsymbol{p}. \tag{2.1}$$

Here, $\bar{f}$ and $\bar{g}$ are the Fourier transforms of f and g, respectively. If we combine this relationship with the Fourier transform of a B function, Eq. (1.2), and if we linearize the product of the two spherical harmonics by introducing Gaunt coefficients [16],

$$\langle l_3 m_3 | l_2 m_2 | l_1 m_1 \rangle = \int Y_{l_3}^{m_3 *}(\Omega)\, Y_{l_2}^{m_2}(\Omega)\, Y_{l_1}^{m_1}(\Omega)\, d\Omega, \tag{2.2}$$

we then obtain for the overlap integral of two B functions [4, 14]:

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \boldsymbol{R}) = \frac{2}{\pi}\, \alpha^{2n_1+l_1-1} \beta^{2n_2+l_2-1} \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle$$
$$\times \int e^{-i\boldsymbol{R}\cdot\boldsymbol{p}} \frac{p^{l_1+l_2} Y_l^{m_2-m_1}(\boldsymbol{p}/p)}{(\alpha^2+p^2)^{n_1+l_1+1} (\beta^2+p^2)^{n_2+l_2+1}}\, d^3\boldsymbol{p}. \tag{2.3}$$

The limits of the l summation in Eq. (2.3) follow from some selection rules satisfied by the Gaunt coefficients [16], and the symbol $\Sigma^{(2)}$ indicates that the summation proceeds in steps of two.

In the case of equal scaling parameters, $\alpha = \beta$, the remaining Fourier integrals in Eq. (2.3) pose no problems since they can be expressed by finite sums of Fourier integral representations of B functions [14]:

$$B_{n,l}^m(\alpha, \boldsymbol{r}) = \frac{\alpha^{2n+l-1}}{2\pi} \int e^{i\boldsymbol{r}\cdot\boldsymbol{p}} \frac{(-ip)^l Y_l^m(\boldsymbol{p}/p)}{(\alpha^2+p^2)^{n+l+1}}\, d^3\boldsymbol{p}. \tag{2.4}$$

Thus, the overlap integral of two B functions with equal scaling parameters is given by the following simple sum of B functions [1]:

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \alpha, \boldsymbol{R}) = (-1)^{l_2} \frac{4\pi}{\alpha^3} \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle$$
$$\times \sum_{t=0}^{\Delta l} (-1)^t \binom{\Delta l}{t} B_{n_1+n_2+l_1+l_2-l-t+1,\, l}^{m_2-m_1}(\alpha, \boldsymbol{R}), \tag{2.5a}$$

$$\Delta l = (l_1 + l_2 - l)/2. \tag{2.5b}$$

In the case of different scaling parameters α and β it is much harder to do the remaining integrations in Eq. (2.3) since a straightforward application of Eq. (2.4) is not possible. Hence, first the denominators in Eq. (2.3) have to be transformed in such a way that Eq. (2.4) becomes applicable. So far, three different techniques, which accomplish this transformation, were described in the literature: Partial fraction decompositions, Taylor expansions, and integral representations.

If we use a partial fraction decomposition for $(\alpha^2+p^2)^{-n_1-l_1-1}\cdot(\beta^2+p^2)^{-n_2-l_2-1}$ [4] in Eq. (2.3), we can derive the so-called Jacobi polynomial representation for the overlap integral with different scaling parameters [1]:

$$
\begin{aligned}
S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\beta,\boldsymbol{R}) = (-1)^{l_2} 4\pi \sum_{l=l_{\min}}^{l_{\max}{}^{(2)}} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1\rangle \\
\times \Bigg\{ \frac{(-1)^{n_1+l_1}(\alpha/\beta)^{l_2}}{\beta^3[1-(\alpha/\beta)^2]^{n_2+l_2+1}} \\
\times \sum_{s=0}^{n_1+l_1} (-1)^s P^{(s-n_1-\Delta l_2,\, n_2+\Delta l_1)}_{n_1+l_1-s}\left(\frac{\beta^2+\alpha^2}{\beta^2-\alpha^2}\right) B^{m_2-m_1}_{s-l,l}(\alpha,\boldsymbol{R}) \\
+ \frac{(-1)^{n_2+l_2}(\beta/\alpha)^{l_1}}{\alpha^3[1-(\beta/\alpha)^2]^{n_1+l_1+1}} \\
\times \sum_{s=0}^{n_2+l_2} (-1)^s P^{(s-n_2-\Delta l_1,\, n_1+\Delta l_2)}_{n_2+l_2-s}\left(\frac{\alpha^2+\beta^2}{\alpha^2-\beta^2}\right) B^{m_2-m_1}_{s-l,l}(\beta,\boldsymbol{R}) \Bigg\},
\end{aligned}
\tag{2.6a}
$$

$$
\Delta l_1 = (l-l_1+l_2)/2, \qquad \Delta l_2 = (l+l_1-l_2)/2. \tag{2.6b}
$$

Here. $P_n^{(\alpha,\beta)}$ is a Jacobi polynomial. The original derivation of Eq. (2.6) was relatively complicated since it involved some nontrivial manipulations of special functions [8]. However, this derivation could later be simplified considerably, and the contribution of three-dimensional delta functions, which occur quite naturally in the theory of B functions [17], was also analyzed [14]. An algorithm for the partial fraction decomposition of more general rational functions than the ones occurring in Eq. (2.3) was discussed by Niukkanen in an article on convolution integrals [12].

The Jacobi polynomial representation for overlap integrals, Eq. (2.6), allows a very economical evaluation of overlap integrals [9, 11, 13]. However, in Eq. (2.6) there are terms which become singular for $\alpha \to \beta$ and for $R \to 0$. This implies that Eq. (2.6) will yield reliable results only if the two scaling parameters α and β differ by a sufficient amount, and if R is large enough. Outside these regions alternative representations have to be used.

The first attempt to overcome the stability problems of the otherwise very efficient Jacobi polynomial representation, Eq. (2.6), was to use one of the following two

Taylor expansions of an overlap integral with different scaling parameters in terms of overlap integrals with equal scaling parameters [11].

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \boldsymbol{R}) = (\alpha/\beta)^{2n_1+l_1-1} \sum_{\nu=0}^{\infty} \frac{(n_1+l_1+1)_\nu}{\nu!} \times \left(\frac{\beta^2-\alpha^2}{\beta^2}\right)^\nu S^{n_2 l_2 m_2}_{n_1+\nu l_1 m_1}(\beta, \beta, \boldsymbol{R}) \tag{2.7}$$

$$= (\beta/\alpha)^{2n_2+l_2-1} \sum_{\nu=0}^{\infty} \frac{(n_2+l_2+1)_\nu}{\nu!} \left(\frac{\alpha^2-\beta^2}{\alpha^2}\right)^\nu \times S^{n_2+\nu l_2 m_2}_{n_1 l_1 m_1}(\alpha, \alpha, \boldsymbol{R}). \tag{2.8}$$

The infinite series in Eq. (2.7) converges for $|1-(\alpha/\beta)^2|<1$, whereas the infinite series in Eq. (2.8) requires $|1-(\beta/\alpha)|^2<1$. The easiest way to derive these infinite series is to use the Taylor expansion

$$(\xi^2+p^2)^{-n-l-1} = (\eta^2+p^2)^{-n-l-1} \sum_{\nu=0}^{\infty} \frac{(n+l+1)_\nu}{\nu!} \left(\frac{\eta^2-\xi^2}{\eta^2+p^2}\right)^\nu \tag{2.9}$$

in Eq. (2.3). The computational problems associated with the two infinite series expansions (2.7) and (2.8) were already discussed quite extensively in the literature [9, 11, 13, 15], and it was found that for larger differences of the scaling parameters α and β convergence could become quite slow. However, it should be emphasized that even in the case of slow convergence the infinite series (2.7) and (2.8) are able to produce reliable numbers.

The not entirely satisfactory convergence properties of the infinite series (2.7) and (2.8) motivated us to look for alternative, more rapidly convergent series expansions for overlap integrals. We found that this aim can be accomplished with the help of the following generating function for terminating hypergeometric series ${}_2F_1$ [14]:

$$(\alpha^2+p^2)^{-n_1-l_1-1}(\beta^2+p^2)^{-n_2-l_2-1} = [(\alpha^2+\beta^2)/2+p^2]^{-n_1-n_2-l_1-l_2-2} \times \sum_{\nu=0}^{\infty} {}_2F_1(-\nu, n_1+l_1+1; n_1+n_2+l_1+l_2+2; 2) \times \frac{(n_1+n_2+l_1+l_2+2)_\nu}{\nu!} \left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2+2p^2}\right]^\nu. \tag{2.10}$$

Inserting this into Eq. (2.3) yields [14]:

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \boldsymbol{R}) = \frac{\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}}{[(\alpha^2+\beta^2)/2]^{n_1+n_2+(l_1+l_2)/2-1}} \times \sum_{\nu=0}^{\infty} {}_2F_1(-\nu, n_1+l_1+1; n_1+n_2+l_1+l_2+2; 2) \times \frac{(n_1+n_2+l_1+l_2+2)_\nu}{\nu!} \left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2}\right]^\nu \times S^{n_2 l_2 m_2}_{n_1+\nu l_1 m_1}([(\alpha^2+\beta^2)/2]^{1/2}, [(\alpha^2+\beta^2)/2]^{1/2}, \boldsymbol{R}). \tag{2.11}$$

Since the terminating hypergeometric series ${}_2F_1$ in Eq. (2.11) can be computed with the help of a stable three-term recurrence formula [14], the terms of the series in Eq. (2.11) can be computed just as easily as the terms in Eqs. (2.7) and (2.8), respectively. However, we found that in all practically relevant cases the infinite series in Eq. (2.11) converges faster than the infinite series in Eqs. (2.7) and (2.8).

Finally, the well-known Feynman identity can be generalized to give [18]

$$a^{-m}b^{-n}=\frac{(m+n-1)!}{(m-1)!(n-1)!}\int_0^1\frac{t^{m-1}(1-t)^{n-1}}{[at-b(1-t)]^{m+n}}\,dt. \tag{2.12}$$

With the help of this relationship one obtains for the numerator in Eq. (2.3):

$$(\alpha^2+p^2)^{-n_1-l_1-1}(\beta^2+p^2)^{-n_2-l_2-1}=\frac{(n_1+n_2+l_1+l_2+1)!}{(n_1+l_1)!(n_2+l_2)!}\times\int_0^1\frac{x^{n_1+l_1}(1-x)^{n_2+l_2}\,dx}{[p^2+\alpha^2x+\beta^2(1-x)]^{n_1+n_2+l_1+l_2+2}}. \tag{2.13}$$

If this integral representation is used in Eq. (2.3), and if the order of integrations is interchanged one obtains an integral representation for the overlap integral with different scaling parameters [10, 13]:

$$S^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta,\boldsymbol{R})=\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}\frac{(n_1+n_2+l_1+l_2+1)!}{(n_1+l_1)!(n_2+l_2)!}\times\int_0^1\frac{x^{n_1+l_1}(1-x)^{n_2+l_2}}{[\gamma(\alpha,\beta;x)]^{2n_1+2n_2+l_1+l_2-2}}\times S^{n_2l_2m_2}_{n_1l_1m_2}(\gamma(\alpha,\beta;x),\gamma(\alpha,\beta;x),\boldsymbol{R})\,dx \tag{2.14a}$$

$$\gamma(\alpha,\beta;x)=[\alpha^2x+\beta^2(1-x)]^{1/2}. \tag{2.14b}$$

No simple closed form expression is known for the remaining integral in Eq. (2.14). Consequently, it has to be evaluated by numerical quadrature.

3. Numerical properties of different representations for overlap integrals

In this section we want to compare how the new infinite series expansion (2.11) does in comparison with the integral representation (2.14) which has been recommended strongly by Bhattacharya and Dhabal [13].

It was mentioned earlier that the infinite series (2.11) normally converges more rapidly than the older series expansions (2.7) and (2.8), respectively. A further improvement of the rate of convergence can be achieved if suitable convergence accelerators are applied. We tried several nonlinear accelerators, for instance Levin's u transformation [19] and Brezinski's θ algorithm [20], but we found that in the case of Eq. (2.11) Wynn's ε algorithm [21] gives the best results since the number of terms, which is required to reach a certain accuracy, is reduced drastically. Also no numerical instabilities induced by the nonlinear transformation were observed [15].

Since the use of such extrapolation methods is not yet very well known among theoretical chemists we want to sketch briefly how we apply Wynn's ε algorithm for the acceleration of convergence. Let $\{s_n\}$ be a sequence of partial sums of an infinite series,

$$s_n = \sum_{\nu=0}^{n} a_\nu, \qquad n \geq 0. \tag{3.1}$$

Then, Wynn's ε algorithm is given by the following two-dimensional nonlinear recursive scheme [21]:

$$\varepsilon_{-1}^{(n)} = 0, \qquad \varepsilon_0^{(n)} = s_n, \tag{3.2a}$$

$$\varepsilon_{m+1}^{(n)} = \varepsilon_{m-1}^{(n+1)} + [\varepsilon_m^{(n+1)} - \varepsilon_m^{(n)}]^{-1}, \qquad m, n \geq 0. \tag{3.2b}$$

Only those elements of the ε table with even lower index can be used as approximations to the limit of the series. The elements of the type $\varepsilon_{2m+1}^{(n)}$ are only intermediate quantities. Hence, if we know the partial sums $s_0, \ldots, s_{2k}$, we use $\varepsilon_{2k}^{(0)}$ as an approximation to the limit, and if we know the partial sums $s_1, \ldots, s_{2k+1}$, we use $\varepsilon_{2k}^{(1)}$ as an approximation to the limit. This can also be expressed in the language of Padé approximants. Let $f(z)$ be a function which is analytic in a neighborhood of zero,

$$f(z) = \sum_{k=0}^{\infty} a_k z^k, \tag{3.3}$$

and let $[L/M]_f(z)$ be the Padé approximant which agrees with the power series (3.3) up to terms of order $0(z^{L+M+1})$. Then, it can be shown [22] that the ε algorithm yields the upper half of the Padé table,

$$\varepsilon_{2k}^{(n)} = [k+n/k]_f(z). \tag{3.4}$$

Hence, in our case we always use the following staircase sequence in the Padé table as approximants to the limit:

$$[0/0], [1/0], [1/1], \ldots, [\nu/\nu], [\nu+1/\nu], [\nu+1/\nu+1], \ldots \tag{3.5}$$

Finally, we would like to mention that there is not only practical but also strong theoretical evidence that the ε algorithm is able to accelerate the convergence of the infinite series in Eq. (2.11). For instance, assume that in the limit of large summation indices a sequence of partial sums $\{s_n\}$ satisfies

$$s_n \sim s + \lambda^n n^\theta \sum_{r=0}^{\infty} c_r n^{-r}, \qquad c_0 \neq 0, \; n \to \infty. \tag{3.6}$$

Now, if $|\lambda| < 1$ and $\theta \neq 0, 1, \ldots, k-1$, the application of the ε algorithm to this sequence gives [23]

$$\varepsilon_{2k}^{(n)} = s + \frac{c_0 \lambda^{n+2k} n^{\theta-2k} k! (-\theta)_k}{(\lambda-1)^{2k}} (1 + 0(n^{-1})). \tag{3.7}$$

Obviously, this represents a considerable improvement of the rate of convergence. The above analysis can be applied to the infinite series in Eq. (2.11) since in the

limit of large summation indices the partial sums of Eq. (2.11) are of the form of Eq. (3.6) [15].

If one tries to use the integral representation (2.14) for the evaluation of overlap integrals one first has to choose a quadrature method. If only a relatively small number of overlap integrals is to be evaluated, and if the values obtained in this way should have a certain guaranteed accuracy, then it is a good idea to use an adaptive quadrature routine such as the IMSL [24] subroutine DCADRE which was used by Trivedi and Steinborn [10] when they first investigated the numerical properties of the integral representation (2.14). The underlying philosophy and the performance of DCADRE is described in a book by Rice [25]. However, an adaptive algorithm will quite often require more integrand evaluations than other quadrature methods. The reason is that a good adaptive algorithm is rather cautious about accepting a result as being correct up to a certain accuracy. It usually does some extra integrand evaluations in order to confirm its preliminary conclusions.

Hence, if efficiency rather than reliability becomes the decisive issue, adaptive quadrature methods are not particularly attractive. In such cases, Gauss formulas which not only optimize the weights but also the abscissae, are very popular since they are known to produce high accuracy at low cost for reasonably well-behaved integrands. Accordingly, Bhattacharya and Dhabal [13] used Gauss-Legendre quadrature for the evaluation of the integral representation (2.14). However, from the general theory of Gauss quadrature [26] one may immediately conclude that Gauss-Legendre formulas, which are derived for the weight function $w(x) = 1$, are not the optimal choice for evaluating the integral in Eq. (2.14). The reason is that the integrand in Eq. (2.14) contains the factor $x^{n_1+l_1}(1-x)^{n_2+l_2}$ which is also the weight function for some special Jacobi polynomials. Consequently, we may expect that appropriate Gauss-Jacobi formulas will do better than Gauss-Legendre, in particular for larger quantum numbers.

In Tables 1-3 we compare the performance of the infinite series (2.11) with the infinite series accelerated by Wynn's ε algorithm, Eq. (3.2), and with Gauss-Jacobi and Gauss-Legendre quadratures of Eq. (2.14). The number N in the first column of the tables corresponds either to the number of terms of the partial sums of the series (2.11) or to the number of integration points used in the quadratures. Hence, in all cases it indicates how many overlap integrals with equal scaling parameters, Eq. (2.5), had been evaluated. The computational complexity of an overlap integral with equal scaling parameters depends only upon the angular momentum quantum numbers l_1, m_1, l_2, and m_2, and not upon the orders n_1 and n_2 of the two B functions in the integral. Consequently, N is a relatively good measure of the numerical costs of the different computational methods. The "exact" values given in the last row of the tables were obtained from Table IV of [15]. The weights and abscissae for both Gauss-Jacobi and Gauss-Legendre quadratures were computed with the help of the subroutine D01BCF from the NAG library [27]. The computer which we use now has in Fortran Double Precision an accuracy of 15 to 16 decimal digits.

Table 1. Comparison of the performance of the infinite series with the infinite series accelerated by Wynn's ε algorithm, with Gauss-Jacobi and with Gauss-Legendre quadratures. $n_1 = 4$; $l_1 = 4$; $m_1 = 4$; $\alpha = 1.5$; $n_2 = 3$; $l_2 = 3$; $m_2 = 3$; $\beta = 2.0$; $R = 2.0$; $\theta = 45.0$ degrees; $\phi = 0.0$ degrees

N	Partial sum	Epsilon	Gauss-Jacobi	Gauss-Legendre
5	$-0.15460763492315D-05$	$-0.15712964427862D-05$	$-0.15636876582270D-05$	$-0.15520577545084D-05$
7	$-0.15573604161767D-05$	$-0.15622486122998D-05$	$-0.15636884002629D-05$	$-0.15670824840364D-05$
8	$-0.15611651429669D-05$	$-0.15637634537367D-05$	$-0.15636884341497D-05$	$-0.15640852440093D-05$
9	$-0.15628175187150D-05$	$-0.15636431866121D-05$	$-0.15636884355896D-05$	$-0.15636203839913D-05$
10	$-0.15633616669332D-05$	$-0.15636726480964D-05$	$-0.15636884356473D-05$	$-0.15636682793424D-05$
11	$-0.15635788805913D-05$	$-0.15636892425731D-05$	$-0.15636884356494D-05$	$-0.15636858215336D-05$
12	$-0.15636491111896D-05$	$-0.15636884200971D-05$	$-0.15636884356495D-05$	$-0.15636881985466D-05$
13	$-0.15636755384284D-05$	$-0.15636884618534D-05$	$-0.15636884356495D-05$	$-0.15636884184640D-05$
14	$-0.15636839586559D-05$	$-0.15636884465889D-05$	$-0.15636884356495D-05$	$-0.15636884345877D-05$
15	$-0.15636869924529D-05$	$-0.15636884355341D-05$	$-0.15636884356495D-05$	$-0.15636884355914D-05$
16	$-0.15636879475730D-05$	$-0.15636884356451D-05$	$-0.15636884356495D-05$	$-0.15636884356466D-05$
17	$-0.15636882804847D-05$	$-0.15636884356466D-05$	$-0.15636884356495D-05$	$-0.15636884356494D-05$
18	$-0.15636883842554D-05$	$-0.15636884356434D-05$	$-0.15636884356495D-05$	$-0.15636884356495D-05$
19	$-0.15636884194964D-05$	$-0.15636884356495D-05$	$-0.15636884356495D-05$	$-0.15636884356496D-05$
20	$-0.15636884303892D-05$	$-0.15636884356495D-05$	$-0.15636884356495D-05$	$-0.15636884356495D-05$
Exact	$-0.15636884356495D-05$	$-0.15636884356495D-05$	$-0.15636884356495D-05$	$-0.15636884356495D-05$

Table 2. Comparison of the performance of the infinite series with the infinite series accelerated by Wynn's ε algorithm, with Gauss-Jacobi and with Gauss-Legendre quadratures. $n_1 = 4$; $l_1 = 4$; $m_1 = 4$; $\alpha = 1.5$; $n_2 = 3$; $l_2 = 3$; $m_2 = 3$; $\beta = 3.5$; $R = 2.0$; $\theta = 45.0$ degrees; $\phi = 0.0$ degrees

N	Partial sum	Epsilon	Gauss-Jacobi	Gauss-Legendre
12	$-0.16516146252281D-06$	$-0.23412042564559D-06$	$-0.22974463811083D-06$	$-0.22982380205739D-06$
14	$-0.18658539325609D-06$	$-0.23588169323298D-06$	$-0.22975342088396D-06$	$-0.22976882051512D-06$
16	$-0.20185959519790D-06$	$-0.22966288566845D-06$	$-0.22975405043781D-06$	$-0.22975350807137D-06$
18	$-0.21223244739113D-06$	$-0.22966287314793D-06$	$-0.22975409098149D-06$	$-0.22975366946911D-06$
20	$-0.21900888500384D-06$	$-0.22975433557144D-06$	$-0.22975409337724D-06$	$-0.22975402353666D-06$
22	$-0.22329829850723D-06$	$-0.22975490051367D-06$	$-0.22975409350913D-06$	$-0.22975408581565D-06$
24	$-0.22594338159433D-06$	$-0.22975409143502D-06$	$-0.22975409351598D-06$	$-0.22975409284380D-06$
26	$-0.22753901994028D-06$	$-0.22975409324917D-06$	$-0.22975409351631D-06$	$-0.22975409346619D-06$
28	$-0.22848373810144D-06$	$-0.22975409356653D-06$	$-0.22975409351633D-06$	$-0.22975409351301D-06$
30	$-0.22903413345807D-06$	$-0.22975409353956D-06$	$-0.22975409351633D-06$	$-0.22975409351614D-06$
32	$-0.22935033828898D-06$	$-0.22975409351179D-06$	$-0.22975409351633D-06$	$-0.22975409351633D-06$
34	$-0.22952978486920D-06$	$-0.22975409352020D-06$	$-0.22975409351633D-06$	$-0.22975409351634D-06$
36	$-0.22963052404869D-06$	$-0.22975409351718D-06$	$-0.22975409351633D-06$	$-0.22975409351634D-06$
38	$-0.22968653600992D-06$	$-0.22975409351706D-06$	$-0.22975409351633D-06$	$-0.22975409351634D-06$
Exact	$-0.22975409351633D-06$	$-0.22975409351633D-06$	$-0.22975409351633D-06$	$-0.22975409351633D-06$

Table 3. Comparison of the performance of the infinite series with the infinite series accelerated by Wynn's ε algorithm, with Gauss-Jacobi and with Gauss-Legendre quadratures. $n_1 = 4$; $l_1 = 4$; $m_1 = 4$; $\alpha = 1.5$; $n_2 = 3$; $l_2 = 3$; $m_2 = 3$; $\beta = 5.0$; $R = 2.0$; $\theta = 45.0$ degrees; $\phi = 0.0$ degrees

N	Partial sum	Epsilon	Gauss-Jacobi	Gauss-Legendre
20	$-0.20685007475276D-07$	$-0.44734581270397D-07$	$-0.44374378509102D-07$	$-0.44377421222281D-07$
23	$-0.25608319816122D-07$	$-0.44370447818941D-07$	$-0.44375486537697D-07$	$-0.44375530913880D-07$
26	$-0.29874982742828D-07$	$-0.44375372795681D-07$	$-0.44375564420388D-07$	$-0.44375526085718D-07$
29	$-0.33460425993095D-07$	$-0.44375544576686D-07$	$-0.44375569324841D-07$	$-0.44375562508078D-07$
32	$-0.36310106004687D-07$	$-0.44375572178584D-07$	$-0.44375569607452D-07$	$-0.44375568866327D-07$
35	$-0.38532934712532D-07$	$-0.44375572587860D-07$	$-0.44375569622587D-07$	$-0.44375569559936D-07$
38	$-0.40201806600007D-07$	$-0.44375572520589D-07$	$-0.44375569623349D-07$	$-0.44375569618865D-07$
41	$-0.41439437689173D-07$	$-0.44375574192951D-07$	$-0.44375569623386D-07$	$-0.44375569623104D-07$
44	$-0.42332160186910D-07$	$-0.44375571204261D-07$	$-0.44375569623388D-07$	$-0.44375569623374D-07$
47	$-0.42970608061250D-07$	$-0.44375570040410D-07$	$-0.44375569623388D-07$	$-0.44375569623390D-07$
50	$-0.43417719773618D-07$	$-0.44375569099852D-07$	$-0.44375569623388D-07$	$-0.44375569623390D-07$
53	$-0.43728898879494D-07$	$-0.44375569461419D-07$	$-0.44375569623387D-07$	$-0.44375569623391D-07$
56	$-0.43941944087401D-07$	$-0.44375569583153D-07$	$-0.44375569623388D-07$	$-0.44375569623391D-07$
59	$-0.44087124707235D-07$	$-0.44375569611662D-07$	$-0.44375569623388D-07$	$-0.44375569623392D-07$
Exact	$-0.44375569623388D-07$	$-0.44375569623388D-07$	$-0.44375569623388D-07$	$-0.44375569623388D-07$

On the basis of the results presented in Tables 1-3, which according to our experience are quite typical, one is tempted to conclude that Gauss-Jacobi clearly does best and that Gauss-Legendre is slightly better than the accelerated series (2.11). However, the situation is not as simple as it looks. The above conclusion is certainly correct if one only has to calculate a single overlap integral and if one knows in advance how many integration points will be needed to produce some given relative accuracy. But such circumstances are certainly the exception. Normally, one has to calculate a large number of integrals with various different sets of quantum numbers and with a wide range of possible scaling parameters. Then a very serious defect of the otherwise "superaccurate" Gauss formulas comes into play. Let $E_N(f)$ be the quadrature error of an N point Gauss rule associated with some weight function $w(x)$ and $a \leq x \leq b$,

$$E_N(f) = \int_a^b w(x) f(x)\, dx - \sum_{k=1}^{N} w_k f(x_k). \tag{3.8}$$

Here, w_k and x_k are the appropriate Gaussian weights and abscissae, respectively. Then, it is well known that the quadrature error $E_N(f)$ can be estimated by the $2N$th derivative of f [26],

$$E_N(f) \leq C_N f^{(2N)}(\xi), \qquad a < \xi < b. \tag{3.9}$$

The constant C_N depends only upon N and the weight function w but not upon f.

Thus, if we would want to apply this theoretical error estimate we would have to know a bound on the $2N$th derivative of the integrand in the integral representation (2.14). Clearly, this is very unpractical and the error analysis has to be done numerically.

In practice, this means that if one wants to find out whether an N point quadrature rule has already produced the required accuracy one has to compare it with another, say $(N+K)$ point rule. Unfortunately, Gaussian abscissae are in general different for different orders N. This implies that this simple convergence check requires already $2N+K$ integrand evaluations. If such convergence checks have to be done repeatedly Gauss quadrature soon becomes hopelessly uneconomical.

Consequently, if one would have to calculate a somewhat broader class of overlap integrals and if one would want to use the integral representation (2.14) in connection with Gauss quadrature, it would be advisable to avoid any internal error analysis at all. Instead, one would first determine experimentally how many abscissae are needed to produce the required accuracy even for those integrals which are believed to represent the most unfavorable cases. Then, all integrals would be evaluated with this fixed number of abscissae.

Apart from the fact that such a "worst case design" is not entirely satisfactory from a theoretical point of view - one can never be sure that one really found the worst case - it also reduces the efficiency of Gauss quadratures considerably since many overlap integrals would then be computed with an accuracy which is higher than actually needed. Such problems cannot occur in the case of the

infinite series (2.11) even if it is accelerated, because an internal error analysis is quite simple.

Consequently, we feel that it is by no means clear whether the infinite series (2.11), if it is accelerated by Wynn's ε algorithm, Eq. (3.2), is really inferior to the integral representation (2.14), if it is evaluated by means of Gauss-Jacobi or Gauss-Legendre quadrature rules. In our opinion, the answer to this question will not only depend upon the number and types of overlap integrals, which are to be calculated, but also very much upon the computer implementation. But we feel that an efficient implementation can be accomplished much more easily in the case of the infinite series (2.11) which allows a simple and economical internal error analysis even if it is accelerated.

Finally, we would like to remark that if one has access to a good adaptive quadrature program such as the IMSL [24] subroutine DCADRE and if efficiency is not of particular importance, then the simplest way to compute overlap integrals of B functions would be to use the integral representation (2.14) in connection with this adaptive quadrature routine. One would only need a program for overlap integrals with equal scaling parameters according to Eq. (2.5) which would be relatively simple. All the error analysis of the quadrature would then be done by the computer.

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References

1. Filter E, Steinborn EO (1978) Phys Rev A 18:1-11, p 2, Eq (2.14)
2. Magnus W, Oberhettinger F, Soni RP (1966) Formulas and theorems for the special functions of mathematical physics. Springer, Berlin Heidelberg New York, p 66
3. Prosser FP, Blanchard CH (1962) J Chem Phys 36:1112
4. Weniger EJ, Steinborn EO (1983) J Chem Phys 78:6121-6132, p 6123, Eq (3.7)
5. Niukkanen AW (1984) Int J Quantum Chem 25:941-955
6. Weniger EJ, Steinborn EO (1984) Phys Rev A 29:2268-2271
7. Weniger EJ (1985) J Math Phys 26:276-291
8. Filter E, Steinborn EO (1978) J Math Phys 19:79-84
9. Antolović D, Delhalle J (1980) Phys Rev A 21:1815-1828
10. Trivedi HP, Steinborn EO (1983) Phys Rev A 27:670-679
11. Weniger EJ, Steinborn EO (1983) Phys Rev A 28:2026-2041
12. Niukkanen AW (1984) Int J Quantum Chem 25:957-964
13. Bhattacharya AK, Dhabal SC (1986) J Chem Phys 84:1598-1605
14. Weniger EJ, Grotendorst J, Steinborn EO (1986) Phys Rev A 33:3688-3705
15. Grotendorst J, Weniger EJ, Steinborn EO (1986) Phys Rev A 33:3706-3726
16. Weniger EJ, Steinborn EO (1982) Comput Phys Commun 25:149-157
17. Weniger EJ, Steinborn EO (1983) J Math Phys 24:2553-2563
18. Joachain CJ (1975) Quantum collision theory. North Holland, Amsterdam, p 678, Eq (D.3)
19. Levin D (1973) Int J Comput Math B 3:371-388
20. Brezinski C (1978) Algorithmes d'accélération de la convergence. Éditions Technip, Paris
21. Wynn P (1956) Math Tables Aids Comput 10:91-96

22. Baker Jr GA, Graves-Morris P (1981) Padé approximants, part I: Basic theory. Addison-Wesley, Reading, Mass
23. Wimp J (1981) Sequence transformations and their applications. Academic Press, New York
24. International Mathematical and Statistical Library, Inc, Houston, Texas
25. Rice JR (1983) Numerical methods, software, and analysis. McGraw-Hill, New York
26. Davis PJ, Rabinowitz P (1984) Methods of numerical integration. Academic Press, New York
27. The NAG FORTRAN Library (1981) Mark 8, Numerical Analysis Group, NAG Central Office, Oxford
28. Shavitt I (1963) The gaussian function in calculations of statistical mechanics and quantum mechanics. In: Alder B, Fernbach S, Rotenberg M (eds) Methods in computational physics, vol. 2 Academic Press, New York, pp 1–45