Numerical properties of the convolution theorems of B functions

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For the computation of convolution integrals of B functions [Eq. (2.14) of E. Filter and E. O. Steinborn, Phys. Rev. A 18, 1 (1978)] which are a special class of exponential-type functions, different analytic representations are available. We have investigated the numerical properties of these convolution formulas and found out that results of sufficient accuracy can be obtained for molecular calculations. We have also investigated the numerical properties of the corresponding one-center integrals. Some new mathematical properties of B functions that are essential for the understanding of the numerical properties of the convolution formulas are derived.

I. INTRODUCTION

It is generally accepted that the use of Slater-type functions (STF's) or other exponential-type functions (ETF's) as basis functions in molecular *ab initio* calculations would be highly desirable. These ETF's are able to fulfill the cusp condition[1] at the origin and they decline exponentially for large distances just as the exact solutions of atomic or molecular Schrödinger equations do.[2] Accordingly, ETF's are able to approximate atomic and molecular bound-state wave functions quite accurately.

Unfortunately, the notorious problems with the evaluation of the molecular multicenter integrals which occur inevitably in the linear combination of atomic orbitals (LCAO) ansatz have so far prevented a systematic application of STF's or other ETF's. Instead, molecular *ab initio* calculations are now mainly performed by the use of a basis constructed from Gaussian-type functions (GTF's). Although GTF's are not able to describe bound-state atomic or molecular wave functions properly in the vicinity of the nucleus or for large distances they have the great advantage that molecular multicenter integrals over GTF's can be evaluated relatively easily. As a result, sophisticated program packages can be developed which allow routine calculations of small or moderately sized molecules. Nevertheless, it is felt that because of their unphysical nature, GTF's are not able to yield extremely accurate approximations which for some applications seem to be necessary, and that large-scale calculations may require too large a number of GTF's. Therefore, in spite of the undisputed success of GTF's in molecular *ab initio* calculations, the search for manageable analytical expressions of multicenter integrals over STF's and other ETF's has been continued.

In this article we are dealing with a special class of ETF's which seems to be quite promising for use in molecular calculations, namely, the reduced Bessel functions[3,4] (RBF's) and their nonscalar generalization, the so-called B functions.[5] In previous articles it could be shown that RBF's and B functions possess relatively simple addition theorems,[6,7] convolution or overlap integrals,[8,9] and Coulomb integrals.[10] The advantageous properties of B functions in multicenter problems can best be explained in terms of their extremely simple Fourier transforms.[11,12] Because of their simple Fourier transforms the four-center exchange integral over B functions could recently be evaluated with the use of numerical Fourier-transform techniques.[13]

The extremely compact analytical representations for the convolution integrals of B functions were also a very important intermediate step for the derivation of new expansions of multicenter integrals and orbitals in terms of complete biorthonormal[14] and orthonormal[15,16] sets of functions.

Recently, Antolović and Delhalle[17] investigated the numerical properties of the convolution formulas of B functions. They came to the conclusion that the numerical applicability of the convolution formulas of B functions is severely limited because they found ranges of parameters and quantum numbers where, according to their experience, no satisfactory computational method exists for the evaluation of the convolution integrals. Consequently, Antolović and Delhalle recommended that some alternative methods for the evaluation of these integrals should be sought.

There would be some very unpleasant consequences not only for multicenter integrals of B functions, but also for multicenter integrals of STF's, if the conclusions of Antolović and Delhalle concerning the numerical applicability of the convolution formulas of B functions were correct. For instance, when we investigated the analytical structures of the Fourier transforms of STF's and B functions,[12] we found that B functions should be considered as a class of basic ETF's in momentum space. Consequently, many multicenter integrals of STF's or other ETF's are best expressed as a linear combination of the corresponding multicenter integrals of B functions. One example of considerable importance would be the case of overlap integrals of STF's. These integrals do not only occur in *ab initio* calculations but are also the basis of most semiempirical approaches. If the analytical structures of the various representations of the Fourier transforms of STF's

are analyzed,[12] it becomes obvious that overlap integrals of STF's are best expressed in terms of overlap integrals of B functions. Also, in the analytical representations for the Coulomb integrals of B functions[10]—which are also much more compact than the corresponding integrals of STF's—convolution integrals occur as essential building blocks.

We therefore want to demonstrate in this article how the convolution formulas can be used for the evaluation of overlap integrals, and that the conclusions of Antolović and Delhalle are incorrect. We shall show that the representations known so far for the convolution integrals of B functions are indeed sufficient for a satisfactory evaluation of these integrals. We shall do this by analyzing the merits and limitations of the computational algorithms we use and by comparing them critically with the algorithms that were described by Antolović and Delhalle.[17] For that purpose we also have to discuss some mathematical properties of RBF's and B functions that are necessary for the understanding of the numerical properties of the convolution integrals of B functions.

II. DEFINITIONS

For the commonly occurring special functions of mathematical physics we shall use the notations and conventions of Magnus, Oberhettinger, and Soni[18] unless explicitly stated. This reference will be referred to as MOS in the following.

In this article we shall make extensive use of the Gaussian hypergeometric function ${}_2F_1$ (MOS, pp. 37–65) and the confluent hypergeometric function ${}_1F_1$ (MOS, pp. 262–295):

$$ {}_2F_1(a,b;c;z)=\sum_{n=0}^{\infty}\frac{(a)_n(b)_n}{(c)_n}\frac{z^n}{n!}\ , \tag{2.1} $$

$$ {}_1F_1(a;c;z)=\sum_{n=0}^{\infty}\frac{(a)_n}{(c)_n}\frac{z^n}{n!}\ . \tag{2.2} $$

Here, $(a)_n$ stands for the Pochhammer symbol (MOS, p. 2) which may be defined in terms of the Gamma function $\Gamma(z)$ (MOS, p. 1) according to

$$ (a)_n=\Gamma(a+n)/\Gamma(a)=a(a+1)\cdots(a+n-1)\ , $$
$$ (a)_0=1\ . \tag{2.3} $$

The binomial coefficient $\binom{\alpha}{m}$ is defined by (MOS, p. 4)

$$ \begin{bmatrix}\alpha\\ m\end{bmatrix}=(-1)^m\frac{\Gamma(m-\alpha)}{m!\Gamma(-\alpha)}=\frac{\Gamma(\alpha+1)}{m!\Gamma(\alpha-m+1)}\ . \tag{2.4} $$

The Jacobi polynomials $P_n^{(\alpha,\beta)}(x)$ (MOS, pp. 209–217) may be expressed in terms of special terminating hypergeometric functions ${}_2F_1$, for instance (MOS, p. 212),

$$ P_n^{(\alpha,\beta)}(x)=(-1)^n\begin{bmatrix}n+\beta\\ n\end{bmatrix}\times{}_2F_1\left[-n,\alpha+\beta+n-1;\beta+1;\frac{x+1}{2}\right]\ . \tag{2.5} $$

The RBF of arbitrary order ν is defined by[3,4]

$$ \hat{k}_\nu(z)=(2/\pi)^{1/2}z^\nu K_\nu(z)\ , \tag{2.6} $$

where $K_\nu(z)$ is the modified Bessel function of the second kind (MOS, p. 66).

As a nonscalar generalization of the RBF's the so-called B function was introduced[5]:

$$ B_{n,l}^m(\alpha\vec{r})=[2^{n+l}(n+l)!]^{-1}\hat{k}_{n-1/2}(\alpha r)\mathscr{Y}_l^m(\alpha\vec{r})\ , \tag{2.7a} $$

$$ n\in\mathbb{Z},\quad -l\le n<\infty\ . \tag{2.7b} $$

Here, $\mathscr{Y}_l^m(\vec{r})$ stands for the regular solid harmonic

$$ \mathscr{Y}_l^m(\vec{r})=r^lY_l^m(\theta,\phi)\ . \tag{2.8} $$

The spherical harmonics $Y_l^m(\theta,\phi)$ are defined with the use of the phase convention of Condon and Shortley,[19] i.e., they are given by the expression[20]

$$ Y_l^m(\theta,\phi)=i^{m+|m|}\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{1/2}\times P_l^{|m|}(\cos\theta)e^{im\phi}\ . \tag{2.9} $$

Here, $P_l^{|m|}(\cos\theta)$ is an associated Legendre polynomial.[21]

For the integral of three spherical harmonics, the so-called Gaunt coefficient,[22] we write

$$ \langle l_3m_3\,|\,l_2m_2\,|\,l_1m_1\rangle=\int Y_{l_3}^{m_3*}(\Omega)Y_{l_2}^{m_2}(\Omega)Y_{l_1}^{m_1}(\Omega)d\Omega\ . \tag{2.10} $$

For the overlap or convolution integral of two B functions with scaling parameters α and β we use the notation

$$ S_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\vec{R})=\int[B_{n_1,l_1}^{m_1}(\alpha\vec{r})]^*[B_{n_2,l_2}^{m_2}(\beta(\vec{r}-\vec{R}))]d\vec{r}\ . \tag{2.11} $$

III. GENERAL PROPERTIES OF RBF'S AND B FUNCTIONS

In this section we shall discuss only those mathematical properties of RBF's and B functions that are of immediate relevance for the understanding of the numerical properties of the convolution theorems of B functions. A more complete treatment of these functions was given by Weniger.[11] Most of the facts we shall present in this section are direct consequences of known properties of the modified Bessel function of the second kind, $K_\nu(z)$.

For all real orders ν and all real arguments $x>0$ the RBF's are positive and are bounded by their values at zero, i.e.,

$$ 0\le\hat{k}_\nu(x)\le\hat{k}_\nu(0)\ . \tag{3.1} $$

For positive orders ν the RBF's are finite at the origin:

$$ \hat{k}_\nu(0)=2^\nu\Gamma(\nu)/(2\pi)^{1/2}\ . \tag{3.2} $$

We conclude from the relationship

$$\hat{k}_{-\nu}(z)=z^{-2\nu}\hat{k}_{\nu}(z) \tag{3.3}$$

that in the case of negative orders ν the RBF's are singular at the origin.

It can also be proved that for all real orders ν the function $\hat{k}_{\nu}(x)$ is monotonically decreasing in the interval $0<x<\infty$ and for $\nu>\frac{1}{2}$ the function $\hat{k}_{\nu}(x)$ possesses a maximum at zero.

These monotonicity properties of RBF's can be quite helpful if one tries to prove the convergence of certain expansions in terms of RBF's. Let us assume that we want to investigate the convergence of the infinite series

$$\sum_{n=0}^{\infty} c_n(x)\hat{k}_{\nu+n}(x) . \tag{3.4}$$

If we are able to show that the series

$$\sum_{n=N}^{\infty} |c_n(x)|\,\hat{k}_{\nu+n}(0) \tag{3.5}$$

converges for sufficiently large $N\in\mathbf{N}$ we may immediately deduce from the inequality (3.1) that the infinite series (3.4) converges absolutely and uniformly.

With the help of inequality (3.1) we may also show that for all $x>0$ and $\nu>\frac{1}{2}$ the RBF's increase rapidly with increasing order ν. This can be seen quite easily from the homogeneous three-term recurrence formula satisfied by the RBF's:

$$\hat{k}_{\nu+1}(z)=2\nu\hat{k}_{\nu}(z)+z^2\hat{k}_{\nu-1}(z) . \tag{3.6}$$

As the RBF's are the dominant solution of this difference equation, the recurrence formula (3.6) may safely be used in the upward direction. Hence, as soon as two starting values $\hat{k}_{\nu-1}(z)$ and $\hat{k}_{\nu}(z)$ are known, a whole string of RBF's may safely and reliably be generated. However, it should be noted that in the case of arbitrary real or complex orders ν the computation of the starting values is apparently a nontrivial problem for which no completely satisfactory solution has been found yet. This can be concluded from the relatively large number of papers that have appeared in recent years which deal with the evaluation of the modified Bessel function of the second kind, $K_{\nu}(z)$.[23]

Fortunately, in connection with the convolution theorems, we are only interested in RBF's with half-integral orders $\nu=n+\frac{1}{2}$, $n\in\mathbf{Z}$. In that case, RBF's can be represented by an exponential multiplied by a terminating confluent hypergeometric function ${}_1F_1$[24]:

$$\hat{k}_{n+1/2}(z)=2^n(\tfrac{1}{2})_n e^{-z}\,{}_1F_1(-n;-2n;2z), \quad n\geq 0 . \tag{3.7}$$

These polynomial parts of the RBF's with half-integral orders $\nu=n+\frac{1}{2}$ have been investigated exhaustively in the mathematical literature.[25] There the following symbol is used for the polynomial part:

$$\theta_n(z)=e^z\hat{k}_{n+1/2}(z) , \tag{3.8}$$

and the polynomials $\theta_n(z)$ together with some other closely related polynomials are called Bessel polynomials. They have been applied in number theory, statistics, and the analysis of complex electrical networks.[26]

We are going to make use of known properties of the Bessel polynomials to derive new properties of RBF's. For instance, from some known asymptotic properties of other Bessel polynomials[27] we obtain the following for the asymptotic behavior ($n\to\infty$, z fixed) of the RBF's:

$$\hat{k}_{n+1/2}(z)\sim 2^n(\tfrac{1}{2})_n . \tag{3.9}$$

Comparison of Eqs. (3.2), (3.7), and (3.9) shows that in the limit of large orders $n+\frac{1}{2}$ the RBF's approach their values at the origin. Equation (3.9) is quite helpful if one wants to obtain some estimates for the rate of convergence of infinite expansions in terms of RBF's.

It can be seen from the asymptotic behavior of RBF's, Eq. (3.9), or from the recurrence formula (3.6), that RBF's increase quite rapidly with increasing order. Hence, if large orders are needed some precautions are required in order to avoid overflow. This is most easily accomplished by the introduction of another normalization. We define

$$\tilde{k}_{n-1/2}(x)=(2^n n!)^{-1}\hat{k}_{n-1/2}(x) . \tag{3.10}$$

The values of these $\tilde{k}$ functions with orders $\geq\frac{1}{2}$ lie for all arguments $x\geq 0$ between 0 and $\frac{1}{2}$. Thus overflow cannot occur.

The fact that RBF's are rapidly increasing functions of the order has some unpleasant consequences for infinite series as it will slow down the rate of convergence. This can immediately be seen if we consider the multiplication theorem of RBF's[28]

$$\hat{k}_{\nu}(\lambda z)=\lambda^{2\nu}\sum_{n=0}^{\infty}\frac{(1-\lambda^2)^n}{2^n n!}\hat{k}_{\nu+n}(z) . \tag{3.11}$$

The infinite series converges only if $|1-\lambda^2|<1$ holds. On the other hand, for the modified Bessel function of the first kind, $I_{\nu}(z)$ (MOS, p. 66), there exists also a multiplication theorem which is formally almost identical with Eq. (3.11)[28]:

$$(\lambda z)^{\nu}I_{\nu}(\lambda z)=\lambda^{2\nu}\sum_{n=0}^{\infty}\frac{(\lambda^2-1)^n}{2^n n!}z^{\nu+n}I_{\nu+n}(z) . \tag{3.12}$$

Here, the infinite series converges for all values of λ. This can be attributed to the fact that for a fixed positive argument the function $I_{\nu}(z)$ decreases monotonously with increasing order (MOS, p. 151) whereas the function $K_{\nu}(z)$ increases monotonously.

The numerical properties of the multiplication theorem (3.11)—good convergence of the infinite series if $|1-\lambda^2|$ is small and bad convergence if $|1-\lambda^2|$ approaches unity—are best understood by taking into account that Eq. (3.11) represents the Taylor-series expansion of the function $\hat{k}_{\nu}(\lambda z)$ around the expansion point $\lambda^2=1$. This is most easily proved by showing that the function $2^{-\alpha}e^{i\pi\alpha}\hat{k}_{-\alpha}(z^{1/2})$ satisfies Truesdell's functional equation[29]

$$\frac{\partial}{\partial z}F(z,\alpha)=F(z,\alpha+1) . \tag{3.13}$$

Now the Taylor-series expansion of such a function $F(kz,\alpha)$ about the point $k=1$ yields the following multiplication theorem[30]:

$$F(kz,\alpha)=\sum_{n=0}^{\infty}\frac{(k-1)^n z^n}{n!}F(z,\alpha+n)\ . \tag{3.14}$$

Hence, we only have to use Eq. (3.3) in order to obtain the multiplication theorem of RBF's, Eq. (3.11), from which the multiplication theorem of B functions can be derived quite easily[31]:

$$B^m_{n,l}(\alpha\vec{r})=(\alpha/\beta)^{2n+l-1}\times\sum_{p=0}^{\infty}\begin{pmatrix}n+l+p\\ p\end{pmatrix}[1-(\alpha/\beta)^2]^p B^m_{n+p,l}(\beta\vec{r})\ . \tag{3.15}$$

The infinite series converges if $|1-(\alpha/\beta)^2|<1$. It should be noticed that if a B function is expanded in terms of B functions which have a greater exponential parameter, all terms in the infinite series have the same sign, i.e., no catastrophic cancellation of significant digits will occur.

IV. ONE-CENTER OVERLAP INTEGRALS

In this section we want to discuss numerical and analytical problems which occur if one-center overlap integrals over B functions are to be evaluated:

$$S^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta,0)=\int B^{m_1*}_{n_1,l_1}(\alpha\vec{r})B^{m_2}_{n_2,l_2}(\beta\vec{r})d\vec{r}\ . \tag{4.1}$$

With the help of the orthonormality of the spherical harmonics the overlap integral (4.1) can be reduced to a radial integral for which a representation in terms of gamma functions and a nonterminating hypergeometric series ${}_2F_1$ is known.[32] Two different expressions for the overlap integral (4.1) can be derived:

$$S^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta,0)=\delta_{l_1l_2}\delta_{m_1m_2}\frac{(\frac{1}{2})_{n_1+n_2+l_1}(\frac{1}{2})_{l_1+1}}{(n_1+n_2+2l_1+1)!}\times\frac{\alpha^{2n_1+l_1-1}}{\beta^{2n_1+l_1+2}}{}_2F_1(n_1+n_2+l_1+\tfrac{1}{2},n_1+l_1+1;n_1+n_2+2l_1+2;1-(\alpha/\beta)^2) \tag{4.2}$$

$$=\delta_{l_1l_2}\delta_{m_1m_2}\frac{(\frac{1}{2})_{n_1+n_2+l_1}(\frac{1}{2})_{l_1+1}}{(n_1+n_2+2l_1+1)!}\times\frac{\beta^{2n_2+l_1-1}}{\alpha^{2n_2l_1+2}}{}_2F_1(n_1+n_2+l_1+\tfrac{1}{2},n_2+l_1+1;n_1+n_2+2l_1+2;1-(\beta/\alpha)^2)\ . \tag{4.3}$$

These two relationships were derived by Filter and Steinborn[33] by considering the limiting case $R\to 0$ in some representations of the two-center overlap integral which are based upon the multiplication theorem of B functions, Eq. (3.11), and which we shall discuss in Sec. VI.

The numerical applicability of Eqs. (4.2) and (4.3) depends crucially upon the rate of convergence of the two nonterminating hypergeometric series ${}_2F_1$. It is well known that the rate of convergence of a hypergeometric series ${}_2F_1(a,b;c;z)$ does not only depend upon the magnitude of the argument z, but also upon the three parameters a, b, and c. Accordingly, we may expect that the rate of convergence of the two hypergeometric series in Eqs. (4.2) and (4.3) will not only depend upon the ratio of the two exponential parameters but also upon the quantum numbers n_1, n_2, and l_1.

The dependence of the convergence upon the exponential parameters α and β can be understood quite easily. In the case of equal parameters, $\alpha=\beta$, both infinite series terminate after the first term and we obtain for the overlap integral

$$S^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\alpha,0)=\delta_{l_1l_2}\delta_{m_1m_2}\frac{(\frac{1}{2})_{n_1+n_2+l_1}(\frac{1}{2})_{l_1+1}}{\alpha^3(n_1+n_2+2l_1+1)!}\ . \tag{4.4}$$

It should be noted that we could have obtained Eqs. (4.2) and (4.3) from Eq. (4.4) by a straightforward application of the multiplication theorem (3.11). The infinite series in Eq. (4.2) converges only if $|1-(\alpha/\beta)^2|<1$ holds, whereas the infinite series in Eq. (4.3) requires $|1-(\beta/\alpha)^2|<1$. Hence, we see that the two different representations (4.2) and (4.3) may be considered to be analytic continuations. In fact, they may be transformed into each other by the use of the following linear transformation (MOS, p. 47):

$${}_2F_1(a,b;c;z)=(1-z)^{-a}{}_2F_1\left[a,c-b;c;\frac{z}{z-1}\right]\ . \tag{4.5}$$

If the two exponential parameters α and β differ only slightly we may expect a rapid convergence of the infinite series in Eqs. (4.2) or (4.3). However, in the case of larger differences of α and β a computationally very unfavorable property of the two hypergeometric series emerges. It is well known that a nonterminating hypergeometric series ${}_2F_1(a,b;c,z)$ converges on the boundary of its circle of convergence, i.e., for $|z|=1$, only if $\mathrm{Re}(a+b-c)<0$ holds (MOS, p. 37). Direct comparison shows that in the case of "physical" orbitals $B^m_{n,l}$, i.e., for $n_1,n_2\geq 1$, the two

hypergeometric series under consideration diverge if their arguments become unity. Unfortunately, this unpleasant property is not only felt on the boundary of the circle of convergence, but already in the vicinity of it. Hence, if the two parameters differ greatly we have to expect a very slow convergence.

It is much harder to estimate the influence of a variation of the quantum numbers n_1, n_2, and l_1 upon the rate of convergence of the two hypergeometric series. Accordingly, we only do an approximative analysis of the behavior of the terms of the hypergeometric series under consideration. We shall also restrict ourselves to an analysis of the behavior of terms with large summation indices because then substantial simplifications may be achieved with the help of asymptotic approximations. Inspired by the series transformation of Kummer[34] we shall construct simple hypergeometric series ${}_1F_0$ whose terms are asymptotically, i.e., in the limit of large summation indices, proportional to the terms of the two hypergeometric series ${}_2F_1$ in Eqs. (4.2) and (4.3). To do this we use the following asymptotic approximation for the quotient of two gamma functions[35]:

$$\Gamma(z+a)/\Gamma(z+b)\sim z^{a-b}\,. \tag{4.6}$$

With the help of this relationship we can show that the terms of the hypergeometric series in Eq. (4.2) are asymptotically, i.e., for large summation indices, proportional to the terms of the series

$${}_1F_0(n_1-\tfrac{1}{2};1-(\alpha/\beta)^2)=\sum_{q=0}^{\infty}\frac{(n_1-\frac{1}{2})_q}{q!}[1-(\alpha/\beta)^2]^q\,. \tag{4.7}$$

In the same way we can show that the terms of the hypergeometric series in Eq. (4.3) are asymptotically proportional to the terms of the series

$${}_1F_0(n_2-\tfrac{1}{2};1-(\beta/\alpha)^2)=\sum_{q=0}^{\infty}\frac{(n_1-\frac{1}{2})_q}{q!}[1-(\beta/\alpha)^2]^q\,. \tag{4.8}$$

If our asymptotic analysis is correct, the rate of convergence of the infinite series in Eq. (4.2) should become worse with increasing n_1 and should be relatively insensitive to variations of n_2 and l_1. Analogously, the rate of convergence of the series in Eq. (4.3) should become worse with increasing n_2 and should be relatively insensitive to variations of n_1 and l_1. Numerical tests conformed our asymptotic analysis.

Therefore, it should be emphasized that contrary to the statements by Antolović and Delhalle[17] a reliable computation of the overlap integral (4.1) using either Eq. (4.2) or (4.3) is always possible. One only has to choose that representation of the two available ones in which the argument of the hypergeometric series is positive, i.e., Eq. (4.2) for $\alpha<\beta$ and Eq. (4.3) for $\alpha>\beta$. Then all terms of the infinite series have the same sign and no appreciable rounding errors will occur. We shall show later (in Table I) that machine accuracy can be achieved even for very large differences of the exponential parameters α and β.

Unfortunately, these tests showed also that particularly for larger differences of the exponential parameters the rate of convergence of the hypergeometric series may become catastrophically slow. It is, however, a simple matter to accelerate the rate of convergence of the two infinite series in Eqs. (4.2) and (4.3) considerably. One only has to use the following linear transformation (MOS, p. 47):

$${}_2F_1(a,b;c;z)=(1-z)^{c-a-b}{}_2F_1(c-a,c-b;c;z)\,. \tag{4.9}$$

With the help of this relationship we obtain for Eqs. (4.2) and (4.3)

$$S^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta,0)=\delta_{l_1l_2}\delta_{m_1m_2}\frac{(\frac{1}{2})_{n_1+n_2+l_1}(\frac{1}{2})_{l_1+1}}{(n_1+n_2+2l_1+1)!}\frac{\alpha^{l_1}}{\beta^{l_1+3}}{}_2F_1(l_1+\tfrac{3}{2},n_2+l_1+1;n_1+n_2+2l_1+2;1-(\alpha/\beta)^2)\,, \tag{4.10}$$

$$=\delta_{l_1l_2}\delta_{m_1m_2}\frac{(\frac{1}{2})_{n_1+n_2+l_1}(\frac{1}{2})_{l_1+1}}{(n_1+n_2+2l_1+1)!}\frac{\beta^{l_1}}{\alpha^{l_1+3}}{}_2F_1(l_1+\tfrac{3}{2},n_1+l_1+1;n_1+n_2+2l_1+2;1-(\beta/\alpha)^2)\,. \tag{4.11}$$

What is gained if we use Eqs. (4.10) and (4.11) instead of Eqs. (4.2) and (4.3)? It should be noticed that the two hypergeometic series in Eqs. (4.10) and (4.11) converge in the case of physical orbitals, i.e., $n_1,n_2>0$, even on the boundary of the radius of convergence, whereas the hypergeometric series in Eqs. (4.2) and (4.3) diverge, as we already mentioned. Because of this fact we may expect an improved convergence particularly for larger differences of the exponential parameters. In addition, the infinite series in Eqs. (4.10) and (4.11) should converge faster with increasing n_1 and n_2 whereas the infinite series in Eqs. (4.2) and (4.3) converge slower as already mentioned. To demonstrate this we again use Eq. (4.6). It can be shown that the terms of the infinite series in Eq. (4.10) are asymptotically proportional to the terms of the series

$${}_1F_0(\tfrac{1}{2}-n_1;1-(\alpha/\beta)^2)=\sum_{q=0}^{\infty}\frac{(\frac{1}{2}-n_1)_q}{q!}[1-(\alpha/\beta)^2]^q\,. \tag{4.12}$$

Analogously, we can show that the terms of the series in Eq. (4.11) are asymptotically proportional to the terms of the series

TABLE I. Comparison of Eqs. (4.2) and (4.10), numbers in parentheses are powers of factors of ten.

n_1	n_2	l_1	α	β	Equation (4.2)	Number of terms	Equation (4.10)	Number of terms
1	1	0	1.25	3.30	0.530 805 989 083 974 834 488 058(−02)	349	0.530 805 989 083 974 834 488 058(−02)	321
1	1	0	1.25	6.60	0.103 362 030 939 873 531 387 042(−02)	1430	0.103362 030 939 873 531 387 043(−02)	1292
1	1	0	1.25	9.90	0.360 699 385 287 090 109 108 855(−03)	3189	0.360 699 385 287 090 109 108 859(−03)	2852
3	1	0	1.25	3.30	0.141 066 450 969 273 954 474 048(−02)	398	0.141 066 450 969 273 954 474 048(−02)	273
3	1	0	1.25	6.60	0.204 027 734 000 549 582 929 799(−03)	1647	0.204 027 734 000 549 582 929 798(−03)	1025
3	1	0	1.25	9.90	0.625 180 111 531 651 837 546 816(−04)	3689	0.625 180 111 531 651 837 546 804(−04)	2165
3	3	1	1.25	3.30	0.121 930 888 138 194 123 841 632(−03)	401	0.121 930 888 138 194 123 841 633(−03)	293
3	3	1	1.25	6.60	0.121 851 315 009 315 970 411 496(−04)	1651	0.121 851 315 009 315 970 411 496(−04)	1102
3	3	1	1.25	9.90	0.271 515 846 839 219 140 858 403(−05)	3695	0.271 515 846 839 219 140 858 402(−05)	2333
3	5	2	1.25	3.30	0.123 096 478 525 647 882 847 482(−04)	405	0.123 096 478 525 647 882 847 482(−04)	307
3	5	2	1.25	6.60	0.905 628 750 431 281 246 158 146(−06)	1658	0.905 628 750 431 281 246 158 147(−06)	1151
3	5	2	1.25	9.90	0.150 964 254 268 928 201 692 057(−06)	3703	0.150 964 254 268 928 201 692 058(−06)	2440
5	3	2	1.25	3.30	0.508 065 471 617 953 082 777 236(−05)	442	0.508 065 471 617 953 082 777 234(−05)	267
5	3	2	1.25	6.60	0.250 498 622 349 493 306 087 137(−06)	1824	0.250 498 622 349 493 306 087 137(−06)	934
5	3	2	1.25	9.90	0.366 142 552 244 832 638 534 424(−07)	4087	0.366 142 552 244 832 638 534 417(−07)	1879
5	5	5	1.25	3.30	0.101 369 663 914 979 211 683 848(−07)	449	0.101 369 663 914 979 211 683 847(−07)	297
5	5	5	1.25	6.60	0.135 509 602 882 144 576 423 248(−09)	1835	0.135 509 602 882 144 576 423 248(−09)	1046
5	5	5	1.25	9.90	0.723 129 931 823 622 212 201 820(−11)	4100	0.723 129 931 823 622 212 201 800(−11)	2121

$$ {}_1F_0\left(\tfrac{1}{2}-n_2;1-(\beta/\alpha)^2\right)=\sum_{q=0}^{\infty}\frac{\left(\frac{1}{2}-n_2\right)_q}{q!}\left[1-(\beta/\alpha)^2\right]^q . \tag{4.13} $$

On the basis of this asymptotic analysis we can expect that the rate of convergence of the hypergeometric series in Eq. (4.10) will improve with increasing n_1 and will be relatively insensitive to variations of n_2 and l_1. In Eq. (4.11) the rate of convergence will improve with increasing n_2 and variations of n_1 and l_1 will not matter much.

In Table I we compare the numerical properties of the two representations (4.2) and (4.10) for different quantum numbers. Because of systematic reasons we always try to obtain the limiting machine accuracy, which is 24 decimal digits on our machine in double precision. Two of the columns in Table I list the number of terms of the corresponding infinite series that are required to obtain this machine accuracy. The numerical results demonstrate that the new representations (4.10) and (4.11) converge significantly faster than the original representations (4.2) and (4.3), particularly for larger differences of the exponential parameters and for larger quantum numbers. We may also conclude that our asymptotic analysis leads to a quantitative understanding of the dependence of the rate of convergence upon the quantum numbers n_1, n_2, and l_1.

In the case of positive arguments of the hypergeometric functions which can always be achieved, both representations are apparently numerically stable, and reliable results can always, i.e., even for very large differences of the exponential parameters, be obtained. Unfortunately, the numerical results also demonstrate that, even for the new representation, Eq. (4.10), convergence may become quite slow. Accordingly, Antolović and Delhalle[17] tried to find computationally more attractive alternatives for the evaluation of the overlap integral (4.1). They advocated the use of a known integral representation of the hypergeometric series[36] for numerical quadratures:

$$ {}_2F_1(a,b;c;z)=\frac{\Gamma(c)}{\Gamma(a)\Gamma(c-a)}\int_0^1\frac{t^{a-1}(1-t)^{c-a-1}}{(1-zt)^b}dt . \tag{4.14} $$

As we already mentioned, the hypergeometric series in Eqs. (4.2) and (4.3) no longer converge if their arguments approach one. If the integral representation (4.14) is to be used for the evaluation of these hypergeometric series, the integrand will then become singular. Accordingly, Antolović and Delhalle required a very large number of integration points in order to obtain the required accuracy. In the close vicinity of the boundary of the circle of convergence Antolović and Delhalle[37] used a representation of the overlap integral (4.1) in terms of Jacobi polynomials which, however, becomes numerically unstable if the exponential parameters do not differ by much. They[38] also derived 15 other representations of hypergeometric series of the general type ${}_2F_1(l+\frac{1}{2},m;n;z)$ with $l,m,n\in\mathbb{N}$ in terms of Jacobi polynomials. Unfortunately, none of these representations is numerically stable for all positive values of the exponential parameters α and β. We think that if one really wants to use the integral representation (4.14) for the computation of the overlap integral (4.1), one should at least use the new representations (4.10) and (4.11) instead of Eqs. (4.2) and (4.3) because the integrand will not become singular, and a much smaller number of integration points will be required.

Nevertheless, we do not think that the numerical quadrature of the integral representation is an efficient method for the evaluation of the overlap integral (4.1). Instead we prefer to use the representation of a RBF as an exponential multiplied by a polynomial, Eq. (3.7), together with the well-known integral representation of the gamma function (MOS, p. 1)

$$ \Gamma(z)=\int_0^{\infty}e^{-t}t^{z-1}dt , \tag{4.15} $$

which leads to the following double sum for the overlap integral (4.1):

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,0)=\delta_{l_1 l_2}\delta_{m_1 m_2}\frac{(\alpha\beta)^{l_1}}{(\alpha+\beta)^{2l_1+3}}\frac{(\frac{1}{2})_{n_1-1}(\frac{1}{2})_{n_2-1}}{4^{l_1+1}(n_1+l_1)!(n_2+l_1)!}$$
$$\times\sum_{p=0}^{n_1-1}\frac{(1-n_1)_p}{(2-2n_1)_p p!}\left[\frac{2\alpha}{\alpha+\beta}\right]^p\sum_{q=0}^{n_2-1}\frac{(1-n_2)_q}{(2-2n_2)_q q!}\left[\frac{2\beta}{\alpha+\beta}\right]^q(2l_1+p+q+2)!\,. \tag{4.16}$$

Compared with Eqs. (4.2), (4.3), (4.10), and (4.11), where nonterminating hypergeometric series have to be evaluated, this representation has some remarkable advantages. The number of terms which have to be computed does not depend upon the exponential parameters α and β and is equal to $n_1 n_2$. Also, all terms are positive, i.e., we do not have to worry about significant rounding errors. One minor disadvantage of Eq. (4.16) is that unlike the previously described representations the computational complexity remains unchanged if the two exponential parameters α and β are equal.

We may therefore conclude that Eq. (4.16) is computationally much more attractive than the previously described representations, Eqs. (4.2), (4.3), (4.10), and (4.11). But it can still be improved. One of the two nested summations in Eq. (4.16) can be written as a terminating hypergeometric function:

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,0)=\delta_{l_1 l_2}\delta_{m_1 m_2}\frac{(\alpha\beta)^{l_1}}{(\alpha+\beta)^{2l_1+3}}\frac{(\frac{1}{2})_{n_1-1}(\frac{1}{2})_{n_2-1}}{4^{l_1+1}(n_1+l_1)!(n_2+l_2)!}$$
$$\times\sum_{p=0}^{n_1-1}\frac{(1-n_1)_p(2l_1+p+2)!}{(2-2n_1)_p p!}\left[\frac{2\alpha}{\alpha+\beta}\right]^p{}_2F_1\left[2l_1+p+3,1-n_2;2-2n_2;\frac{2\beta}{\alpha+\beta}\right] \tag{4.17}$$

$$=\delta_{l_1 l_2}\delta_{m_1 m_2}\frac{(\alpha\beta)^{l_1}}{(\alpha+\beta)^{2l_1+3}}\frac{(\frac{1}{2})_{n_1-1}(\frac{1}{2})_{n_2-1}}{4^{l_1+1}(n_1+l_1)!(n_2+l_2)!}$$
$$\times\sum_{q=0}^{n_2-1}\frac{(1-n_2)_q(2l_1+q+2)!}{(2-2n_2)_q q!}\left[\frac{2\beta}{\alpha+\beta}\right]^q{}_2F_1\left[2l_1+q+3,1-n_1;2-n_1;\frac{2\alpha}{\alpha+\beta}\right]. \tag{4.18}$$

What is gained if we rewrite the double sum in Eq. (4.16) as a sum of terminating hypergeometric functions? We can evaluate the hypergeometric functions recursively. In Eqs. (4.17) and (4.18) terminating hypergeometric functions of the general type ${}_2F_1(m,-n;-2n;z)$ with $m,n\in\mathbb{N}$ and $z\in\mathbb{R}$ occur. Using a known contiguous relationship of the hypergeometric series ${}_2F_1$ (MOS, p. 46) we obtain the following recurrence formula in m:

$${}_2F_1(m-1,-n;-2n;z)$$
$$=\frac{(m+1)(2-z)}{m+2n}{}_2F_1(m,-n;-2n;z)$$
$$+\frac{m(z-1)}{m+2n}{}_2F_1(m+1,-n;-2n;z)\,. \tag{4.19}$$

It is immediately obvious that this recurrence relationship is stable backwards if the argument z satisfies the inequality $1\le z\le 2$, because then only positive terms will be added. The restriction for the argument z is no obstacle as either $2\beta/(\alpha+\beta)$ in Eq. (4.17) or $2\alpha/(\alpha+\beta)$ in Eq. (4.18) will satisfy this requirement.

In our opinion the use of Eqs. (4.17) and (4.18) together with the recurrence formula (4.19) is the most accurate and most efficient method for the computation of the overlap integral (4.1) which is known so far. How does it compare with the numerical quadrature of the integral representation (4.14)? It is obvious that the numerical quadrature will be less accurate than the use of Eqs. (4.17) and (4.18) which obtain the limit of machine accuracy. In addition, our algorithm based upon Eqs. (4.17), (4.18), and (4.19) is much faster than the numerical quadrature. If the integral representation (4.14) is to be used for the evaluation of any of the hypergeometric series in Eqs. (4.2), (4.3), (4.10), and (4.11), at least one of the exponents of the integrand will be half-integral. Hence, for each integration point, at least one square-root evaluation (and also some other operations) will be required. Antolović and Delhalle needed between 50 and 200 integration points. If we now take into consideration that for one evaluation of the integral $S_{550}^{550}(\alpha,\alpha,0)$ we need a CPU (central processing unit) time which corresponds to approximately 13 calls of the FORTRAN function DSQRT, we may expect that our algorithm should be at least one order of magnitude faster than the numerical quadrature used by Antolović and Delhalle. It should be noted that the polynomial representation (4.17) and (4.18) can also be viewed as new nonlinear transformations of some special hypergeometric series.

V. TWO-CENTER OVERLAP INTEGRALS WITH EQUAL PARAMETERS

In this section we want to discuss analytical and numerical problems which occur if two-center overlap integrals over B functions with equal exponential parameters are to be evaluated:

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\alpha,\vec{R})=\int B^{m_1^*}_{n_1,l_1}(\alpha\vec{r})B^{m_2}_{n_2,l_2}(\alpha(\vec{r}-\vec{R}))d\vec{r}\ . \tag{5.1}$$

For these integrals a very compact representation is known[9]:

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\alpha,\vec{R})=(-1)^{l_2}\frac{4\pi}{\alpha^3}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2 m_2 \mid l_1 m_1 \mid l m_2-m_1\rangle \sum_{t=0}^{\Delta l}(-1)^t \begin{bmatrix}\Delta l\\ t\end{bmatrix} B^{m_2-m_1}_{n_1+n_2+l_1+l_2-l-t+1,l}(\alpha\vec{R})\ , \tag{5.2a}$$

$$\Delta l=(l_1+l_2-l)/2\ . \tag{5.2b}$$

The symbol $\sum^{(2)}$ indicates that the summation is to be performed in steps of two. The summation limits $l_{\min}$ and $l_{\max}$ of the l summation are direct consequences of the selection rules satisfied by the Gaunt coefficient. It is well known that for fixed l_1, m_1, l_2, and m_2 a Gaunt coefficient $\langle l_2 m_2 \mid l_1 m_1 \mid l m\rangle$ is different from zero only if the following conditions are satisfied[39]:

$$m=m_2-m_1\ , \tag{5.3a}$$

$$l_1+l_2+l=2n,\quad n\in\mathbb{N} \tag{5.3b}$$

$$l_{\max}=l_1+l_2\ , \tag{5.3c}$$

$$l_{\min}=\max(\,|l_1-l_2|\,,|m|\,)$$

$$\text{if } \max(\,|l_1-l_2|\,,|m|\,)+l_{\max} \text{ is even}\ , \tag{5.3d}$$

$$l_{\min}=\max(\,|l_1-l_2|\,,|m|\,)+1$$

$$\text{if } \max(\,|l_1-l_2|\,,|m|\,)+l_{\max} \text{ is odd}\ . \tag{5.3e}$$

From these selection rules it follows immediately that Δl is always an integer with $0\le\Delta l\le(l_{\max}-l_{\min})/2$.

In the convolution theorem with equal parameters, Eq. (5.2), there occur Gaunt coefficients, spherical harmonics, binomial coefficients, factorials, and RBF's. In this article we shall only discuss the computation of the binomial coefficients and RBF's. Programs which make possible a very efficient and reliable computation of Gaunt coefficients and spherical harmonics even for extremely large angular momentum quantum numbers ($l_1,l_2<200$, $l\le400$) were described elsewhere.[39]

For coding purposes we express the binomial coefficients and factorials in Eq. (5.2) in terms of Pochhammer symbols $(m)_n$ with $m,n\in\mathbb{N}$. These Pochhammer symbols are computed recursively and stored in a two-dimensional array. The B functions are expressed in terms of the $\tilde{k}$ functions which were defined in Eq. (3.10). We then obtain for Eq. (5.2)

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\alpha,\vec{R})=(-1)^{l_2}\frac{4\pi}{\alpha^3}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2 m_2 \mid l_1 m_1 \mid l m_2-m_1\rangle \left[\frac{\alpha R}{2}\right]^l Y_l^{m_2-m_1}(\vec{R}/R)$$
$$\times\sum_{t=0}^{\Delta l}\frac{(-1)^t(\Delta l-t+1)_t}{t!(n_1+n_2+l_1+l_2-l-t+2)_l}\tilde{k}_{n_1+n_2+l_1+l_2-l-t+1/2}(\alpha R)\ . \tag{5.4}$$

What accuracy can be expected if we use this expression for the overlap integrals? A comparison with tabulated values of overlap integrals of STF's which can be expressed in terms of integrals of RBF's does not help because the integral tables which are known to the authors[40] have an accuracy of, at most, five decimal digits. Also, no alternative representation which could be used for independent numerical checks is known. Hence, we have to rely on indirect evidence. In Sec. VI we shall use the multiplication theorem of B functions, Eq. (3.15), in order to express an overlap integral of B functions with different exponential parameters in terms of an infinite series of overlap integrals with equal parameters. As we can obtain very accurate results even if the two exponential parameters α and β differ greatly, which yields a very slow convergence of the corresponding infinite series, we may safely conclude that Eq. (5.4) yields very accurate results even for very large values of n_1 and n_2. This is, of course, an immediate consequence of the fact that the number of terms that occur in Eq. (5.2) or (5.4) does not depend at all on n_1 or n_2, and hence the numerical computations needed do not increase with increasing n_1 or n_2.

It is much harder to say something substantial about the accuracy of Eq. (5.4) for larger values of the angular momentum quantum numbers l_1 and l_2. It is, however, likely that Eq. (5.4) is much less accurate for larger values of l_1 and l_2 than for larger values of n_1 and n_2. This is probably a consequence of the fact that in Eq. (5.2), or equivalently in Eq. (5.4), there occurs a sum of the type

$$F_n(x)=\sum_{q=0}^{n}(-1)^q\begin{bmatrix}n\\ q\end{bmatrix}f_q^n(x)\ . \tag{5.5}$$

It is well known that such sums are severely affected by rounding errors for larger values of the summation limit n. Hence, we may expect that for larger values of

$\Delta l=(l_1+l_2-l)/2$, the inner sum in Eq. (5.4) will lose some significant digits. Fortunately, extremely large values of l do not occur and for all practical applications, Eq. (5.4) should yield a satisfactory accuracy.

VI. TWO-CENTER OVERLAP INTEGRALS WITH DIFFERENT PARAMETERS

Now we come to the central part of this paper. In this section we want to discuss analytical and numerical problems which occur if two-center overlap integrals over B functions with different exponential parameters α and β are to be evaluated:

$$S^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta,\vec{R})=\int B^{m_1*}_{n_1,l_1}(\alpha\vec{r})B^{m_2}_{n_2,l_2}(\beta(\vec{r}-\vec{R}))d\vec{r}\,. \tag{6.1}$$

For these integrals two analytical representations are known so far: one representation containing Jacobi polynomials which involves only a finite number of terms, and an infinite-series representation which is based upon the multiplication theorem of B functions, Eq. (3.15). Let us first consider the Jacobi-polynomial representation[9]:

$$S^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta,\vec{R})=(-1)^{l_2}4\pi\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2m_2\,|\,l_1m_1\,|\,lm_2-m_1\rangle$$

$$\times\left[\frac{(-1)^{n_1+l_1}(\alpha/\beta)^{l_2}}{\beta^3[1-(\alpha/\beta)^2]^{n_2+l_2+1}}\sum_{t=0}^{n_1+l_1}P^{(-n_1-\Delta l_2+t,n_2+\Delta l_1)}_{n_1+l_1-t}((\beta^2+\alpha^2)/(\beta^2-\alpha^2))B^{m_2-m_1}_{t-l,l}(\alpha\vec{R})\right.$$

$$+\frac{(-1)^{n_2+l_2}(\beta/\alpha)^{l_1}}{\alpha^3[1-(\beta/\alpha)^2]^{n_1+l_1+1}}$$

$$\left.\times\sum_{t=0}^{n_2+l_2}P^{(-n_2-\Delta l_1+t,n_1+\Delta l_2)}_{n_2+l_2-t}((\alpha^2+\beta^2)/(\alpha^2-\beta^2))B^{m_2-m_1}_{t-l,l}(\beta\vec{R})\right], \tag{6.2a}$$

$$\Delta l_1=(l-l_1+l_2)/2,\quad \Delta l_2=(l+l_1-l_2)/2\,. \tag{6.2b}$$

This expression is remarkably compact. It is easy to show that at most $[\min(l_1,l_2)+1](n_1+n_2+l_1+l_2+2)$ terms will be needed to compute one overlap integral. Accordingly, a program which is based upon Eq. (6.2) should be very fast provided it is possible to compute the Jacobi polynomials efficiently. The other functions which appear in Eq. (6.2) are already known from the convolution theorem with equal parameters, Eq. (5.2), and are computationally quite convenient.

The major disadvantage of Eq. (6.2) is the fact that for $R\to 0$ as well as for $\alpha\to\beta$ canceling singularities occur which can lead to an unacceptable loss of accuracy. For most practical applications the singularity at $R=0$ is unimportant as extremely small internuclear distances do not occur. Hence, we shall not consider it any further. More important is the singularity at $\alpha=\beta$ which is caused by the following expressions:

$$\frac{\alpha^{l_2}\beta^{2n_2+l_2-1}}{(\beta^2-\alpha^2)^{n_2+l_2+1}}\times P^{(-n_1-\Delta l_2+t,n_2+\Delta l_1)}_{n_1+l_1-t}((\beta^2+\alpha^2)/(\beta^2-\alpha^2))\,, \tag{6.3a}$$

$$\frac{\beta^{l_1}\alpha^{2n_1+l_1-1}}{(\alpha^2-\beta^2)^{n_1+l_1+1}}\times P^{(-n_2-\Delta l_1+t,n_1,+\Delta l_2)}_{n_2+l_2-t}((\alpha^2+\beta^2)/(\alpha^2-\beta^2))\,. \tag{6.3b}$$

In both cases singularities of degree $n_1+n_2+l_1+l_2-t+1$ occur. We may therefore conclude that the intrinsic numerical instability of Eq. (6.2) will be felt much more strongly in the case of larger quantum numbers. Consequently, the range of parameters α and β for which Eq. (6.2) will yield a satisfactory accuracy does not only depend on the accuracy of the computer but also upon the magnitude of the quantum numbers involved.

The central computational problem in connection with Eq. (6.2) is the efficient computation of the required Jacobi polynomials which are of the general type

$$P^{(t-m,k)}_{n-t}((x^2+y^2)/(x^2-y^2));\qquad n,m,k,t\in\mathbb{N};\quad x,y\in\mathbb{R}\,. \tag{6.4}$$

It should be noted that the arguments of these Jacobi polynomials all lie outside their orthogonality interval which is

$[-1,1]$ (MOS, p. 209). If we take into consideration that the zeros of all orthogonal polynomials are all located within their orthogonality intervals,[41] we may conclude that the Jacobi polynomials in Eq. (6.2) will never be zero. This property of these Jacobi polynomials is quite advantageous for their evaluation because it eliminates a potential source of error. It is well known that serious rounding errors may occur if one comes into the vicinity of a zero of a given function.

Now we have to develop an algorithm for the Jacobi polynomials. The use of explicit expressions like Eq. (2.5) is not recommendable as it would be quite time consuming. A recursive algorithm would be much more attractive. Unfortunately, the recurrence relationships of the Jacobi polynomials which can be found in the mathematical literature (Abramowitz and Stegun, Ref. 28, p. 782) are not suited to allow a direct computation of a string of Jacobi polynomials $P_{n-t}^{(t-m,k)}$ with $0 \le t \le n$.

Lacking a better alternative Antolović and Delhalle[42] combined known recurrence formulas to obtain a relatively complicated multidimensional recursive scheme for the evaluation of all required Jacobi polynomials. In order to demonstrate the numerical stability of their algorithm, Antolović and Delhalle presented in Table I[43] values of Jacobi polynomials obtained with their algorithm. Unfortunately, all Jacobi polynomials in Table I have the argument $x = \frac{1}{2}$ which does not occur as we mentioned earlier. Of course, the conclusion of Antolović and Delhalle, that their multidimensional recurrence scheme is numerically stable, may be correct, but nevertheless their reasoning is not conclusive.

It is usually almost impossible to control the numerical stability of the arithmetical operations involved in the multidimensional recurrence schemes. Also, such schemes usually need a relatively large storage space. We therefore feel on much safer ground if we only have to deal with one-dimensional recurrence equations. Fortunately, this can be achieved quite easily here. If we use Eq. (2.5) we obtain for the Jacobi polynomials that occur in Eq. (6.2):

$$P_{n-t}^{(t-m,k)}\left[\frac{x^2+y^2}{x^2-y^2}\right] = (-1)^{n-t}\frac{(n+k-t)!}{(n-t)!k!} \times {}_2F_1\left[t-n, n-m+k+1; k+1; \frac{x^2}{x^2-y^2}\right]. \tag{6.5}$$

The advantage of this transformation is that on the right-hand side the summation index t occurs in only one of the three parameters of the hypergeometric function ${}_2F_1$. It is now a trivial matter to use the corresponding contiguous relation of the hypergeometric function ${}_2F_1$ (MOS, p. 46) to obtain

$$P_{n-t}^{(t-m,k)}\left[\frac{x^2+y^2}{x^2-y^2}\right] = \left[\frac{2n-t+k-m}{n-t}\frac{x^2}{x^2-y^2} - \frac{2(n-t)+k-1}{n-t}\right]P_{n-t-1}^{(t-m+1,k)}\left[\frac{x^2+y^2}{x^2-y^2}\right] + \frac{n-t+k-1}{n-t}\frac{y^2}{x^2-y^2}P_{n-t-2}^{(t-m+2,k)}\left[\frac{x^2+y^2}{x^2-y^2}\right]. \tag{6.6}$$

Numerical tests confirmed that this homogeneous three-term recurrence formula is numerically stable in the direction of increasing $n-t$. The starting values are

$$P_0^{(n-m,k)}\left[\frac{x^2+y^2}{x^2-y^2}\right] = 1, \tag{6.7a}$$

$$P_1^{(n-m-1,k)}\left[\frac{x^2+y^2}{x^2-y^2}\right] = \frac{n-m-k-1}{2} + \frac{n-m+k+1}{2}\frac{x^2+y^2}{x^2-y^2}. \tag{6.7b}$$

The central computational problem in connection with Eq. (6.2) is, as we already mentioned, the efficient computation of the required Jacobi polynomials. It is therefore recommendable to invert the order of the two inner t-summations in Eq. (6.2) because then the three-term recurrence formula (6.6) in connection with the starting values (6.7) can be used most efficiently. We also express the B functions in Eq. (6.2) in terms of the $\tilde{k}$ functions just as we did it in the case of equal parameters. We then obtain

$$
\begin{aligned}
&S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\beta,\vec{\mathrm{R}}) \\
&=(-1)^{l_2} 4\pi \sum_{l=l_{\min}}^{l_{\max}} {}^{(2)}\langle l_2 m_2 \mid l_1 m_1 \mid l m_2-m_1\rangle Y_l^{m_2-m_1}(\vec{\mathrm{R}}/R) \\
&\quad\times\left\{\frac{(\alpha/\beta)^{l_2}}{\beta^3}\left[\frac{\beta^2}{\beta^2-\alpha^2}\right]^{n_2+l_2+1}\right. \\
&\quad\times\left[\left[\frac{\alpha R}{2}\right]^{l}\sum_{s=0}^{n_1+l_1-l-1}\frac{(-1)^s}{(n_1+l_1-l-s+1)_l}\tilde{k}_{n_1+l_1-l-s-1/2}(\alpha R)P_s^{(\Delta l-s,n_2+\Delta l_1)}\left[\frac{\beta^2+\alpha^2}{\beta^2-\alpha^2}\right]\right. \\
&\qquad+\sum_{t=\max(0,n_1+l_1-l)}^{n_1+l_1}(-1)^t\frac{(l-n_1-l_1+t+1)!}{(n_1+l_1-t)!}\left[\frac{\alpha R}{2}\right]^{2n_1+2l_1-2t-l-1} \\
&\qquad\left.\left.\times\tilde{k}_{l-n_1-l_1+t+1/2}(\alpha R)P_t^{(\Delta l-t,n_2+\Delta l_1)}\left[\frac{\beta^2+\alpha^2}{\beta^2-\alpha^2}\right]\right]\right. \\
&\quad+\frac{(\beta/\alpha)^{l_1}}{\alpha^3}\left[\frac{\alpha^2}{\alpha^2-\beta^2}\right]^{n_1+l_1+1} \\
&\quad\times\left[\left[\frac{\beta R}{2}\right]^{l}\sum_{s=0}^{n_2+l_2-l-1}\frac{(-1)^s}{(n_2+l_2-l-s+1)_l}\tilde{k}_{n_2+l_2-l-s-1/2}(\beta R)P_s^{(\Delta l-s,n_1+\Delta l_2)}\left[\frac{\alpha^2+\beta^2}{\alpha^2-\beta^2}\right]\right. \\
&\qquad+\sum_{t=\max(0,n_2+l_2-l)}^{n_2+l_2}(-1)^t\frac{(l-n_2-l_2+t+1)!}{(n_2+l_2-t)!}\left[\frac{\beta R}{2}\right]^{2n_2+2l_2-2t-l-1} \\
&\qquad\left.\left.\left.\times\tilde{k}_{l-n_2-l_2+t+1/2}(\beta R)P_t^{(\Delta l-t,n_2+\Delta l_2)}\left[\frac{\alpha^2+\beta^2}{\alpha^2-\beta^2}\right]\right]\right\}, \qquad (6.8a)
\end{aligned}
$$

$$
\Delta l=(l_1+l_2-l)/2,\quad \Delta l_1=(l-l_1+l_2)/2,\quad \Delta l_2=(l+l_1-l_2)/2\ . \qquad (6.8b)
$$

It is not easy to program this expression efficiently because a large number of special cases have to be distinguished. For instance, in Eq. (6.8) summation limits like n_1+l_1-l-1 or n_2+l_2-l-1 may become negative. If this happens, the corresponding sum must be set equal to zero. On the other hand, our program which is based upon Eq. (6.8) is extremely fast due to the recursive computation of the Jacobi polynomials. For instance, the evaluation of the integral $S^{555}_{555}(\alpha,\beta,\vec{\mathrm{R}})$, where 132 Jacobi polynomials have to be computed, requires a CPU time which corresponds to approximately 180 calls of the FORTRAN function DSQRT.

For which values of the exponential parameters α and β does a program based on Eq. (6.8) yield numerical results of satisfactory accuracy? Particularly important is the question how much "closeness" of the two exponential parameters can be tolerated. As we pointed out earlier, this will not only depend upon the accuracy of the computer but also upon the magnitude of the quantum numbers involved.

In order to answer this question we require an alternative representation of the overlap integral (6.1), different from that of Eq. (6.2) or (6.8), a representation that does not become singular where the two exponential parameters approach each other. To obtain such a representation we use the multiplication theorem of B functions, Eq. (3.15). We then find two different series expansions of the overlap integral with different scaling parameters in terms of overlap integrals with equal parameters[44]

$$
S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\beta,\vec{\mathrm{R}})=\left[\frac{\alpha}{\beta}\right]^{2n_1+l_1-1}\sum_{p=0}^{\infty}\binom{n_1+l_1+p}{p}\left[1-\left[\frac{\alpha}{\beta}\right]^2\right]^p S^{n_2 l_2 m_2}_{n_1+p\, l_2 m_2}(\beta,\beta,\vec{\mathrm{R}}) \qquad (6.9)
$$

$$
=\left[\frac{\beta}{\alpha}\right]^{2n_2+l_2-1}\sum_{q=0}^{\infty}\binom{n_2+l_2+q}{q}\left[1-\left[\frac{\beta}{\alpha}\right]^2\right]^q S^{n_2+q\, l_2 m_2}_{n_1 l_2 m_2}(\alpha,\alpha,\vec{\mathrm{R}})\ . \qquad (6.10)
$$

The infinite series in Eq. (6.9) converges if $|1-(\alpha/\beta)^2|<1$ holds and the infinite series in Eq. (6.10) converges if $|1-(\beta/\alpha)^2|<1$. It should be noted that all terms in the infinite-series expansion of an overlap integral with different exponential parameters will have the same sign if we expand the B function with the smaller parameter in terms of B

functions having greater parameter. In that case appreciable rounding errors are only to be expected if the terms of the infinite series—the overlap integrals with equal parameters—are affected by some appreciable inaccuracy. It should also be noted that the two infinite series (6.9) and (6.10) can be viewed as Taylor-series expansions. This is a consequence of the fact that the multiplication theorem of B functions, Eq. (3.15), can be derived as a Taylor-series expansion as we mentioned in Sec. III. Of course, this also implies that we have to expect the typical numerical properties of Taylor-series expansions for the two infinite series (6.9) and (6.10).

For coding purposes we combine Eqs. (6.9) and (6.10) with Eq. (6.4) and obtain

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\vec{\mathrm{R}}) = (-1)^{l_2} 4\pi \frac{\alpha^{2n_1+l_1-1}}{\beta^{2n_1+l_1+2}} \sum_{p=0}^{\infty} \frac{(n_1+l_1+1)_p}{p!} \left[1-\left[\frac{\alpha}{\beta}\right]^2\right]^p \sum_{l=l_{\min}}^{l_{\max}} {}^{(2)}\langle l_2 m_2 \mid l_1 m_1 \mid l m_2-m_1\rangle \left[\frac{\beta R}{2}\right]^l Y_l^{m_2-m_1}(\vec{\mathrm{R}}/R) \times \sum_{t=0}^{\Delta l} \frac{(-1)^t(\Delta l-t+1)_t}{t!(n_1+n_2+l_1+l_2+p-l-t+2)_l} \times \tilde{k}_{n_1+n_2+l_1+l_2+p-l-t+1/2}(\beta R) , \tag{6.11}$$

$$= (-1)^{l_2} 4\pi \frac{\beta^{2n_2+l_2-1}}{\alpha^{2n_2+l_2+2}} \sum_{q=0}^{\infty} \frac{(n_2+l_2-1)}{q!} \left[1-\left[\frac{\beta}{\alpha}\right]^2\right]^q \sum_{l=l_{\min}}^{l_{\max}} {}^{(2)}\langle l_2 m_2 \mid l_1 m_1 \mid l m_2-m_1\rangle \left[\frac{\alpha R}{2}\right]^l Y_l^{m_2-m_1}(\vec{\mathrm{R}}/R) \times \sum_{t=0}^{\Delta l} \frac{(-1)^t(\Delta l-t+1)_t}{t!(n_1+n_2+l_1+l_2+q-l-t+2)_l} \tilde{k}_{n_1+n_2+l_1+l_2+q-l-t+1/2}(\alpha R) . \tag{6.12}$$

The numerical applicability of these two representations depends crucially upon the rate of convergence of the corresponding infinite series. As in the case of the hypergeometric series ${}_2F_1$ that were discussed in Sec. IV and that can be obtained from Eqs. (6.11) and (6.12) by setting $R=0$ we may expect that the rate of convergence will not only depend upon the ratio of the two exponential parameters α and β but also upon the quantum numbers n_1, l_1, n_2, and l_2. We shall show later that the rate of convergence will also depend upon the magnetic quantum numbers m_1 and m_2. This is a consequence of the fact that the summation limits $l_{\min}$ and $l_{\max}$ depend, via the selection rules of the Gaunt coefficients,[39] upon m_1 and m_2.

The dependence of the rate of convergence upon the ratio of the exponential parameters α and β can be understood quite easily. In the case of equal scaling parameters, $\alpha=\beta$, both infinite series terminate after the first term and we obtain the formula for the overlap integral with equal parameters, Eq. (5.2) or (5.4). If the two exponential parameters α and β differ only slightly, we may expect a good convergence. However, in analogy with the results in Sec. IV we have to expect a very bad convergence if the two parameters α and β differ greatly.

The dependence of the rate of convergence of the infinite series in Eqs. (6.11) and (6.12) upon the quantum numbers remains to be analyzed. In order to do so we want to proceed in the same way as we did it in Sec. IV when we investigated the rate of convergence of some hypergeometric series ${}_2F_1$. However, the infinite series we have to investigate here have a much more complicated structure than those in Sec. IV. Hence, we have to introduce some further simplifications. First, we rearrange the order of summations in Eqs. (6.11) and (6.12). For Eq. (6.11) we then obtain

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\vec{\mathrm{R}}) = (-1)^{l_2} 4\pi \frac{\alpha^{2n_1+l_1-1}}{\beta^{2n_1+l_1+1}} \sum_{l=l_{\min}}^{l_{\max}} {}^{(2)}\langle l_2 m_2 \mid l_1 m_1 \mid l m_2-m_1\rangle \left[\frac{\beta R}{2}\right]^l Y_l^{m_2-m_1}(\vec{\mathrm{R}}/R) \times \sum_{t=0}^{\Delta l} \frac{(-1)^t(\Delta l-t+1)_t}{t!} \sum_{p=0}^{\infty} \frac{(n_1+l_1+1)_p[1-(\alpha/\beta)^2]^p}{p!(n_1+n_2+l_1+l_2+p-l-t+2)_l} \times \tilde{k}_{n_1+n_2+l_1+l_2+p-l-t+1/2}(\beta R) . \tag{6.13}$$

This series rearrangement is possible because for $\alpha<\beta$ both series converge absolutely. In the next step, we analyze the convergence of the infinite series in Eq. (6.13). Just as in Sec. IV we shall analyze only the behavior of the terms with large summation indices. Therefore, we can replace the RBF's in Eq. (6.13) by their asymptotic approximations, Eq. (3.9). Then we can show that the terms of the infinite series in Eq. (6.13) are proportional to the terms of the hyper-

geometric series.

$$ {}_2F_1(n_1+l_1+1,n_1+n_2+l_1+l_2-l-t+\tfrac{1}{2};n_1+n_2+l_1+l_2-t+2;1-(\alpha/\beta)^2) \; . \tag{6.14} $$

Proceeding as in Sec. IV we may conclude that in the limit of large summation indices the terms of the infinite series in Eq. (6.11) should have the same behavior as the terms of the hypergeometric series

$$ {}_1F_0(n_1+l_1-1-\tfrac{1}{2};1-(\alpha/\beta)^2) = \sum_{p=0}^{\infty} \frac{(n_1+l_1-l-\frac{1}{2})_p}{p!}[1-(\alpha/\beta)^2]^p \; . \tag{6.15} $$

In the same way we conclude that the convergence behavior of the terms of the infinite series in Eq. (6.12) is described by the hypergeometric series

$$ {}_1F_0(n_2+l_2-l-\tfrac{1}{2};1-(\beta/\alpha)^2) = \sum_{q=0}^{\infty} \frac{(n_2+l_2-l-\frac{1}{2})_q}{q!}[1-(\beta/\alpha)^2]^q \; . \tag{6.16} $$

Two critical remarks concerning the validity of Eqs. (6.15) and (6.16) for the convergence behavior of the infinite series in Eqs. (6.11) and (6.12) seem to be appropriate. (1) The starting point of our derivation was the rearrangement of the infinite series, i.e., the step from Eq. (6.11) to Eq. (6.13). Although it is clear that this rearrangement does not affect the convergence of the infinite series it may well change its rate of convergence. (2) In Eq. (6.13) we replaced the RBF's by their asymptotic approximation (3.9). However, in the case of large arguments RBF's converge quite slowly to their values at the origin and Eq. (3.9) may be a relatively bad approximation. Hence, we see that in the case of two-center overlap integrals our asymptotic analysis of the rate of convergence has, mathematically, a much more insecure foundation than the analogous analysis in Sec. IV, and the validity of Eqs. (6.15) and (6.16) should be verified experimentally.

In Table II we compare the two alternative methods for the overlap integral (6.1), the Jacobi-polynomial representation, Eq. (6.8), and the infinite-series expansion based upon the multiplication theorem of B functions, Eq. (3.15). Without loss of generality we only consider $\alpha=1.50$ and $\alpha<\beta$ in Table II. For the sake of numerical stability we always expand the B function with the smaller parameter in terms of B functions with greater parameters. Under these circumstances only Eq. (6.11) contributes to Table II. In the last column of Table II the number of terms of the infinite series (6.11) is listed that is required to obtain a relative accuracy of 10^{-24} which corresponds approximately to the machine epsilon of the computer we use.

From the numerical results presented in Table II and other, more detailed investigations, we may conclude that the numerical instabilities inherent in the Jacobi-polynomial representation, Eq. (6.2) or (6.8), are in fact felt much more strongly in the case of larger quantum numbers. We may also conclude that the rate of convergence of the infinite series (6.11) deteriorates with increasing quantum numbers n_1 and l_1 which is in agreement with our asymptotic approximation, Eq. (6.15). If the two exponential parameters α and β differ greatly, the convergence of the infinite series (6.11) becomes very bad. And yet, at least in the cases with small values of $\Delta l=(l_1+l_2-l)/2$, we get an excellent agreement between the Jacobi-polynomial representation and the infinite

TABLE II. Comparison of Eqs. (6.8) and (6.11). We always have $\alpha=1.50$, $R=2.0$, $\theta=45.0°$ and $\phi=0.0°$. Numbers in parentheses are powers of factors of ten.

n_1	l_1	m_1	n_2	l_2	m_2	β	Equation (6.8)	Equation (6.11)	Number of terms
1	0	0	1	0	0	2.20	0.241 222 730 889 277 951 797 377(−02)	0.241 222 730 889 277 951 797 377(−02)	92
1	0	0	1	0	0	5.50	0.155 947 042 412 479 991 133 595(−03)	0.155 947 042 412 479 991 135 595(−03)	716
1	0	0	1	0	0	9.90	0.260 333 516 751 266 814 197 107(−04)	0.260 333 516 751 266 814 197 104(−04)	2333
3	1	1	1	1	0	2.20	0.113 546 037 053 703 333 444 862(−03)	0.113 546 037 053 703 333 444 857(−03)	99
3	1	1	1	1	0	5.50	0.656 024 309 177 991 884 629 144(−05)	0.656 024 309 177 991 884 629 141(−05)	762
3	1	1	1	1	0	9.90	0.722 245 444 690 668 052 342 243(−06)	0.722 245 444 690 668 052 342 235(−06)	2479
1	1	0	3	1	1	2.20	0.191 855 872 151 891 881 320 153(−03)	0.191 855 872 151 891 881 319 901(−03)	90
1	1	0	3	1	1	5.50	0.229 394 207 154 352 634 698 907(−04)	0.229 394 207 154 352 634 698 906(−04)	676
1	1	0	3	1	1	9.90	0.280 729 793 721 372 842 335 670(−05)	0.280 729 793 721 372 842 335 667(−05)	2188
5	0	0	5	0	0	2.20	0.883 967 476 162 948 400 561 760(−03)	0.883 967 476 162 948 400 560 460(−03)	111
5	0	0	5	0	0	5.50	0.839 121 794 539 339 196 877 705(−04)	0.839 121 794 539 339 196 877 697(−04)	877
5	0	0	5	0	0	9.90	0.152 891 828 672 758 145 394 420(−04)	0.152 891 828 672 758 145 394 417(−04)	2867
5	5	5	5	5	5	2.20	0.301 964 649 766 618 438 755 214(−07)	0.301 964 649 719 667 481 813 599(−07)	118
5	5	5	5	5	5	5.50	0.126 343 903 632 905 072 511 485(−09)	0.126 343 903 632 905 069 516 314(−09)	909
5	5	5	5	5	5	9.90	0.106 466 616 488 298 411 777 009(−11)	0.106 466 616 488 298 810 222 856(−11)	2977
5	5	5	5	5	−5	2.20	0.158 723 132 293 731 028 497 063(−13)	0.167 342 472 707 276 739 347 582(−13)	100
5	5	5	5	5	−5	5.50	0.566 039 531 964 675 184 549 835(−14)	0.566 039 531 964 675 185 988 072(−14)	715
5	5	5	5	5	−5	9.90	0.397 085 470 133 692 722 989 423(−15)	0.397 085 470 133 692 722 989 429(−15)	2246

series. From that result we may conclude that the computation of overlap integrals with equal parameters with the use of Eq. (5.4) yields numerically reliable results even for extremely large values of n_1 and n_2.

Unfortunately, the formula for overlap integrals with equal parameters, Eq. (5.4), is much less accurate in the case of large angular momentum quantum numbers l_1 and l_2 than for large values of n_1 and n_2. This becomes immediately evident if we compare the numerical results in Table II for the integrals S_{555}^{555} and S_{555}^{55-5}. In the case of the integral S_{555}^{55-5} we have, for large differences of the parameters α and β, an excellent agreement between the Jacobi-polynomial representation and the infinite series, whereas in the case of the integral S_{555}^{555} there occur relatively larger discrepancies. This can best be explained in terms of the different angular momentum coupling. From the selection rules of the Gaunt coefficient[39] we obtain in the case of the integral S_{555}^{55-5} $l_{\min}=l_{\max}=10$, whereas for the integral S_{555}^{555} we obtain $l_{\min}=0$ and $l_{\max}=10$. Hence, in the case of S_{555}^{55-5} the two inner summations reduce to a single term, whereas in the case of S_{555}^{555} the l and t summations are relatively long and may lead to some rounding errors because of the occurrence of alternating signs.

It should also be noted that the different rate of convergence of the infinite series (6.11) for the integrals S_{555}^{555} and S_{555}^{55-5} is in perfect agreement with our asymptotic analysis, Eq. (6.15). Hence we see that the rate of convergence depends also, via the selection rules of the Gaunt coefficient,[39] upon the magnetic quantum numbers.

In their article, Antolović and Delhalle[17] investigated the numerical properties of the convolution formulas of B functions. Quite in agreement with our observations they found that the Jacobi-polynomial representation, Eq. (6.2), may lead to intolerable rounding errors for smaller differences of the two exponential parameters. However, when they analyzed the numerical properties of the infinite-series representations, Eqs. (6.9) and (6.10), they found that the rate of convergence of these infinite series is too slow to be of much practical use. Then they concluded that because of the bad convergence there exist ranges of parameters and quantum numbers for which no satisfactory computational path is available, and they recommended that some alternative procedures for the evaluation of the overlap integrals for B functions should be sought.[45]

It cannot be denied that the convergence of the infinite series (6.11) and (6.12) may become extremely slow and, accordingly, an application of these series may become quite time consuming, particularly when compared with our extremely fast program which is based upon Eq. (6.8) together with the recurrence formula of the Jacobi polynomials, Eq. (6.6). However, the results presented in Table II nevertheless demonstrate that the infinite series will yield a satisfactory accuracy even under unfavorable conditions. How can this discrepancy be resolved? In Eqs. (6.9) and (6.10) there occur binomial coefficients

$$\begin{pmatrix} n_1+l_1+p \\ p \end{pmatrix} = \frac{(n_1+l_1+1)_p}{p!}, \tag{6.17a}$$

$$\begin{pmatrix} n_2+l_2+q \\ q \end{pmatrix} = \frac{(n_2+l_2+1)_q}{q!}, \tag{6.17b}$$

where p and q are the summation indices of the infinite summations. When Antolović and Delhalle discussed the possibility of transforming the infinite series (6.9) and (6.10) into continued fractions, they wrote on p. 1822 of their paper[17]: "Also, the upper limit to the computation lies in the request that the upper index of binomial coefficients in (3.15) be smaller or equal 40." Equation (3.15) of Antolović and Delhalle is equivalent to Eq. (6.11) here.

This statement of Antolović and Delhalle suggests that they precomputed all binomial coefficients $\binom{n}{k}$ with $0 \le n \le 40$ and $0 \le k \le n$ and stored them in some array. As some of the binomial coefficients may become quite large, only relatively small values of n are admissible because, otherwise, overflow would occur. However, for the special binomial coefficients (6.17) such an approach is inappropriate, and the restriction of the magnitude of the upper index is unnecessary. In our program we use the recursive scheme:

$$\begin{aligned} \frac{(n_1+l_1+1)_{p+1}}{(p+1)!}\left[1-\left[\frac{\alpha}{\beta}\right]^2\right]^{p+1} &= \left[1-\left[\frac{\alpha}{\beta}\right]^2\right]\frac{n_1+l_1+p+1}{p+1} \\ &\times\left\{\frac{(n_1+l_1+1)_p}{p!}\left[1-\left[\frac{\alpha}{\beta}\right]^2\right]^p\right\}. \end{aligned} \tag{6.18}$$

Here, no overflow can occur for $\alpha<\beta$. Instead, the quantities which are computed with the help of Eq. (6.18) tend to zero rapidly enough to guarantee the convergence of the infinite series (6.11). Of course, all other quantities in Eqs. (6.11) and (6.12) that depend upon the summation index of the outer infinite summation have to be computed recursively as well.

Hence we conclude that the numerical problems Antolović and Delhalle encountered are not so much due to intrinsic pathological properties of the convolution formulas but are probably consequences of an unfortunate choice of computational algorithms.

The numerical properties of the convolution formulas are also of considerable importance for a project undertaken by Jones.[46–49] Starting from known analytical representations for overlap and Coulomb integrals over STF's which all have the general structure "exponentials $\times$ powers $\times$ coefficients," Jones tried to find for each individual integral an analytical representation of maximum simplicity. In order to achieve his aim, Jones used computer algebra. Only the nonzero coefficients are then stored on tape. If one wants to compute a certain integral, one only has to read in the nonvanishing coefficients and multiply them with the corresponding exponentials and powers. Jones derived computer-generated formulas for STF overlap integrals with equal scaling parameters[47] which are equivalent to the overlap integral of B functions with equal parameters, Eq. (5.4). Jones also derived formulas for STF overlap integrals with different scaling parameters which contain singular terms if the two exponential parameters approach each other[46] and which are equivalent to the Jacobi-polynomial representation, Eq.

(6.2). As this representation cannot be used if the two scaling parameters differ only slightly Jones derived an infinite series for the overlap integral via Taylor-series expansion.[49] As an example, Jones[49] gives a truncated Taylor-series expansion for the overlap integral of two $1s$ STF's. However, a $1s$ STF is, apart from an unimportant numerical factor, equal to $B^0_{1,0}$. Hence we see that because of the uniqueness of a power-series expansion the formula given by Jones[49] is proportional to the first four terms of the infinite series

$$S^{100}_{100}(\alpha,\beta,\vec{R})=\frac{\alpha}{\beta^4}\sum_{p=0}^{\infty}\frac{(2)_p}{p!}\left[1-\left[\frac{\alpha}{\beta}\right]^2\right]^p\tilde{k}_{p+5/2}(\beta R)\,, \tag{6.19}$$

which is just a special case of Eq. (6.11). In Tables I and II of his article, Jones[49] demonstrates that his two representations of the $1s$ STF overlap integral are sufficient to obtain an accuracy of 12 decimal digits. Jones also concludes on p. 1079 of his paper[49] "that the same accuracy can be achieved for all orbitals regardless of their quantum numbers, as the structure of all of our computer-generation formulas is the same." However, he overlooks that the singularities of his formula, which is equivalent to the Jacobi-polynomial representation, will be felt much more strongly in the case of larger quantum numbers, and their range of applicability becomes more and more restricted. At the same time, the rate of convergence of the Taylor-series expansions deteriorates with increasing quantum numbers. This follows immediately from the uniqueness of a Taylor-series expansion, from the fact that STF's can be expressed in terms of B functions and vice versa,[50] and from our asymptotic analysis, Eqs. (6.15) and (6.16). Therefore, we may conclude that the approach of storing the numerical coefficients on a tape will become quite inconvenient in the case of larger quantum numbers, as the convergence of the Taylor-series expansion may become relatively slow.

VII. SUMMARY

In this article the numerical properties of the convolution theorems of B functions and their applicability were analyzed.

For that purpose we first investigated some mathematical properties of RBF's that are needed for the understanding of the numerical properties of the convolution formulas, particularly monotonicity and asymptotic properties of RBF's. The connection between RBF's and Bessel polynomials which are currently investigated in the mathematical literature[25] was also emphasized.

We then analyzed the numerical properties of the hitherto known representations of the one-center overlap integrals in terms of nonterminating hypergeometric series ${}_2F_1$. We showed that machine accuracy can be achieved with these representations, although the convergence of the infinite series may be slow. However, the rate of convergence may be improved by a simple linear transformation of the hypergeometric series ${}_2F_1$. Our numerical results were supported by an approximative analysis of the dependence of the rate of convergence of the infinite series upon the quantum numbers. As the convergence of the hypergeometric series may be inconveniently slow in spite of the acceleration achieved by the linear transformation, we developed a representation by a finite number of terms which is numerically stable for all exponential parameters and allows an extremely fast computation.

Two-center overlap integrals of B functions with equal exponential parameters have the remarkable property that their computational complexity does not increase with increasing orders n_1 and n_2. Accordingly, we could show that our computational algorithm allows a reliable and fast evaluation of these integrals even for extremely high values of the orders n_1 and n_2. Unfortunately, the computational complexity of these and also of other multicenter integrals increases considerably with increasing angular momentum quantum numbers. We also found that there occurs some loss of significant digits. However, as extremely large angular momentum quantum numbers do not occur in overlap integrals, our program should be sufficiently accurate for all practical purposes.

Overlap integrals with different exponential parameters are much more complicated than overlap integrals with equal parameters. Two different representations are available, one by a finite number of terms involving Jacobi polynomials and one by infinite series which is based upon the multiplication theorem of B functions. We derived a new homogeneous three-term recurrence formula for the special Jacobi polynomials that are required for the overlap integral. Because of that recurrence formula which allows a very economical evaluation of the Jacobi-polynomial representation our program is extremely fast. Unfortunately, the Jacobi-polynomial representation contains terms which become singular if the two exponential parameters approach each other. Hence, for exponential parameters that differ only slightly we have to use an infinite-series expansion. These series can be viewed as Taylor-series expansions and are closely related to the representations of the one-center overlap integral in terms of nonterminating series ${}_2F_1$. We analyzed the numerical properties of these infinite-series representations and showed that contrary to the opinion of Antolović and Delhalle[17] they may be used even under unfavorable circumstances, i.e., if the two exponential parameters differ greatly. In addition, we extended the approximate asymptotic analysis we had done in the one-center case to two-center overlap integrals and are now able to make predictions about the dependence of the rate of convergence upon the quantum numbers involved.

The algorithms which were described in this paper are more efficient and extend further than those of Antolović and Delhalle, and should be sufficient for the practical application of the given formulas in molecular calculations.

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