Gauss–Bessel Quadrature: A Tool for the Evaluation of Barnett–Coulson/Löwdin Functions

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ABSTRACT: In previous work, we analyzed the numerical efficiency of several algorithms that can be used to evaluate the so-called Barnett–Coulson/Löwdin functions (BCLFs). It was shown that series representations of these functions are generally not recommended in the neighborhood of the cusp because of their poor convergence (logarithmic convergence). In the present work, we propose to evaluate BCLFs using its symmetric integral representation combined with a tailored Gauss quadrature. The new method is shown to be capable of achieving acceptable accuracy, as illustrated by the numerical values obtained for two-center overlap integrals, which agree with previously published results. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 106: 2398–2407, 2006

Key words: Slater-type orbitals; tailored Gauss quadrature; atomic orbitals; multi-center integrals

1. Introduction

During the past few years, renewed interest in using Slater-type functions (STFs) emerged among a number of scientists and especially those working in the field ab initio methodological development. The reason for choosing STFs as the appropriate basis set to be used in quantum chemistry is supported by two very important theoretical results. On the one hand, it was shown in the early days of quantum chemistry that any exact solution of the Schrödinger equation should possess a cusp on the origin [1], that is on the nuclei. On the other hand, these solutions must also decrease exponentially at infinity. Since the most widely used approximation for building the approximate wave function of the Schrödinger equation is the well-known linear combination of atomic orbitals (LCAO), it is clear that if the AOs are carefully selected, i.e., have the right properties, the leading LCAO wave function will automatically inherit such properties. As a consequence, the pioneering work of many scientists in the field of quantum chemistry focused on developing algorithms in which STFs were used as the basis set. However, despite the efforts of these pioneers, STFs have never been used extensively in ab initio computations mainly because the procedures dealing with multi-center integrals were

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very inefficient. Of course, the Alchemy program attributable to Yoshimine et al. [2] provides proof of the concept that, at least in the case of linear systems, an efficient computer program using STFs can be developed. The Alchemy case and the challenge of solving a long-standing problem have continuously fueled the battle against multi-center integrals over STFs.

Over the past decades, several methods were proposed to tackle the difficult problem of evaluating multi-center integrals over STFs. These methods can be grouped into three major classes:

1. *Addition theorem-based methods*: In this class, we basically find the methods in which the STFs are expanded into infinite series in order to separate the electron coordinates from the molecular parameters, i.e., geometrical quantities. On closer inspection of the mathematical structure of the methods found in this class, we can distinguish two subclasses. The two-range addition theorem, which according to Weniger [3, 4] is a rearrangement of a three-dimensional (3D) Taylor expansion, provides a series expansion of a given function in terms of spherical harmonics (also known as multipole expansion). Formally, this can be written as

$$\Phi(\mathbf{r}-\mathbf{a}) = \sum_{\lambda=0}^{+\infty} \mathcal{F}_\lambda(\rho_<,\rho_>) P_\lambda\left(\frac{\mathbf{a}\cdot\mathbf{r}}{ar}\right) = \sum_{\lambda=0}^{+\infty} \mathcal{F}_\lambda(\rho_<,\rho_>) \sum_{m=-\lambda}^{\lambda} \left[Y_\lambda^m\right]^*(\theta_\mathbf{a},\phi_\mathbf{a}) Y_\lambda^m(\theta_\mathbf{r},\phi_\mathbf{r}), \quad (1)$$

where $\rho_< = \min(a,r)$ and $\rho_> = \max(a,r)$, while $P_\lambda(z)$ stands for the Legendre polynomial of degree λ. As for $Y_\lambda^m(\theta,\phi)$, it represents the spherical harmonic of degree λ and order m. The function $\mathcal{F}_\lambda(\rho_<,\rho_>)$ being nonsymmetrical with respect to its arguments $\rho_<$ and $\rho_>$, it is clear that the above expansion has two different closed analytical expressions, depending on whether $r < a$ or $r > a$.

Regarding the second subclass of addition theorem-based methods, they are known as one-range expansions since the right-hand side of Eq. (1) is expanded in terms of a complete set of functions. Formally, this is usually expressed as

$$\Phi_{n,l}^m(\mathbf{r}-\mathbf{a}) = \sum_{n',l',m'} C_{n',l'}^{m'}(\mathbf{a}) \Psi_{n',l'}^{m'}(\mathbf{r}) \qquad \text{with}$$

$$C_{n',l'}^{m'}(\mathbf{a}) = \left\langle \Psi_{n',l'}^{m'}(\mathbf{r}) \middle| \Phi_{n,l}^m(\mathbf{r}-\mathbf{a}) \right\rangle_\mathbf{r} \quad (2)$$

where the expansion coefficients depend only on the geometrical parameter **a**. In the context of multi-center integrals over STFs, this approach has been used mainly by Filter and Steinborn [5] and by Guseinov [6–10].

2. *Integral transform-based methods*: Two integral transforms were examined for the purpose of multi-center integrals over STFs: the Fourier integral transform (FIT) and the Gaussian integral transform (GIT). It is of interest to point out the mathematical similarity of the expressions of multi-center integrals as obtained in both approaches. Indeed, in both cases, multi-center integrals end up being represented by a multiple integral of the form:

$$\mathcal{I} = \int_{u=0}^{1} du f(u) \int_{v=0}^{1} dv g(u) \ldots \int_{z=0}^{+\infty} \mathcal{G}(u,v,\ldots,z)\, dz. \quad (3)$$

Proposed by Bonham et al. [11], the FIT was later thoroughly investigated by Steinborn's group [12–18], and this led to the definition of a new class of exponentially decreasing functions known as the **B** functions. More recently, using Sidi's $\overline{D}$ [19, 20] as a starting point, Safouhi [21, 22] was able to develop specialized algorithms used to evaluate efficiently the semi-infinite integral occurring in the expressions of multi-center integrals as obtained in the framework of the FIT. The GIT, which can also be regarded as a Laplace transform of an appropriately chosen function, was originally developed by Shavitt and Karplus [23–26]. The approach was used in the past few years by Rico et al. [27] to develop series expansions for multi-center integrals in terms of Gaussian-type functions (GTFs). A series of Fortran routines were published by the authors for benchmarking purposes [28]. More recently, we have proposed to evaluate the semi-infinite integral in (3) as it occurs in the framework of the GIT by means of a tailored Gauss quadrature [29] known as Gauss–Bessel. According to our preliminary results, it appears that

Gauss–Bessel quadrature used in connection with the GIT permits accurate evaluation of multi-center integrals over STFs. However, the method needs to be examined from an efficiency perspective before attempting to use it within an operational system.

3. *Hybrid methods*: In recent work, Rico et al. [30] proposed to combine GTFs and STFs within an operational system. Indeed, for some multicenter integrals, STFs were used because it was possible to develop efficient numerical procedures. However, in some other cases, including the notorious four-center two-electron integrals, the authors switch to very extended GTF basis sets in order to approximate the integral under consideration.

In the present work, we reexamine the evaluation of the Barnett–Coulson/Löwdin function (BCLF). In previous work [31], it was found that near the cusp, the convergence of the series representations of BCLFs deteriorates drastically, finally ending up as logarithmic on the cusp. In these cases, i.e., near and on the cusp, even the application of a convergence accelerating procedure (Levin u transformation [32]) was unable to achieve the required accuracy when operating on a small number of partial sums ($\leq$70). To solve this problem, we proposed to evaluate BCLFs by means of a suitable integral representation to which a combination of Gauss quadratures is applied. However, in practice the procedure was not very efficient, since high-order quadratures (as high as 80) were necessary to achieve an acceptable accuracy. In this work, we show that BCLFs can be evaluated efficiently by means of a recently developed Gauss–Bessel quadrature [29]. Compared with classical Gauss quadratures, the present method appears to be more efficient, since the weight function captures an aspect of the integrand, i.e., a moving sharp peak, which is hard to approximate accurately by a polynomial function.

2. Mathematical Preliminaries

An STF centered on some point defined by a location vector $\mathbf{a}$, is defined as

$$\chi_{n,l}^{m}(\alpha,\mathbf{r}-\mathbf{a}) = \mathcal{N}_n(\alpha)\|\mathbf{r}-\mathbf{a}\|^{n-l-1} \times \exp(-\alpha\|\mathbf{r}-\mathbf{a}\|)\mathcal{Y}_l^m(\mathbf{r}-\mathbf{a}) \qquad \text{with} \quad \mathcal{N}_n(\alpha) = \frac{(2\alpha)^{n+1/2}}{\sqrt{(2n)!}}, \tag{4}$$

where $\mathcal{Y}_l^m(\mathbf{r}) = \|\mathbf{r}\|^l Y_l^m(\theta_\mathbf{r},\varphi_\mathbf{r})$ is the solid spherical harmonic of degree l and order m. The two-range addition theorem of STF is usually derived from the Gegenbauer addition theorem given in [33 (p. 107)]. Thus, differentiation with respect to the screening parameter α yields

$$\|\mathbf{r}-\mathbf{a}\|^{n-l-1}\exp(-\alpha\|\mathbf{r}-\mathbf{a}\|) = \frac{1}{ar}\sum_{\lambda=0}^{+\infty}(2\lambda+1)\mathcal{A}_{\lambda+1/2}^{n-l}(\alpha,a,r)\mathrm{P}_\lambda\left(\frac{\mathbf{a}\cdot\mathbf{r}}{ar}\right) \qquad \text{with} \quad \begin{cases} n=0,1,\ldots \\ 0\leq l\leq n-1, \end{cases} \tag{5}$$

where the terms $\mathcal{A}_{\lambda+1/2}^{n}(\alpha,a,r)$ are known as the BCLFs. These functions are usually defined recursively as

$$\begin{cases} \mathcal{A}_{\lambda+1/2}^{0}(\alpha,a,r) = \mathbf{I}_{\lambda+1/2}(\alpha\rho_<)\mathbf{K}_{\lambda+1/2}(\alpha\rho_>) \\ \mathcal{A}_{\lambda+1/2}^{n}(\alpha,a,r) = -(\partial/\partial\alpha)\mathcal{A}_{\lambda+1/2}^{n-1}(\alpha,a,r), \end{cases} \tag{6}$$

where the $\mathbf{I}_{\lambda+1/2}(z)$ and $\mathbf{K}_{\lambda+1/2}(z)$ represent the modified Bessel functions of the first and second kind (see Ref. [34], p. 79).

2.1. NUMERICAL EVALUATION OF BCLFs

In previous work [31], two different representations were compared for the purpose of evaluating numerical values of BCLFs:

Series expansions in terms of modified Bessel functions $\mathbf{K}_{n+1/2}(\alpha\sqrt{a^2+r^2})$ (or, alternatively, $\mathbf{K}_{n+1/2}[\alpha(a+r)]$): After analysis, it was found that the convergence of both series deteriorates as r gets closer to a, finally becoming logarithmic on the cusp ($r=a$). In such a case, it was shown through several examples that even when convergence accelerators are used, the numerical procedures are still inefficient, since a fairly large number of partial sums need to be computed to ensure adequate convergence.

Integral representation of the form:

$$\mathcal{A}_{\lambda+1/2}^{n}(\alpha,a,r) = \frac{1}{2}\int_0^{+\infty}\sqrt{u^n}\mathrm{H}_n(\alpha\sqrt{u})\mathbf{I}_{\lambda+1/2}[(ar)/(2u)]\exp\left[-\alpha^2u-(a^2+r^2)/(4u)\right]\frac{du}{u}, \tag{7}$$

where $\mathrm{H}_n(z)$ stands for the Hermite polynomial of order n. After numerical experimentation, it was

found that an appropriate combination of Gauss–Legendre and Gauss–Laguerre quadratures not only permits accurate computation of BCLFs but, more importantly, does not affect the complexity of the algorithm, i.e., the number of elementary operations involved during the computational process.

In this study, we present a new procedure that could be used to evaluate BCLFs by means of a tailored Gauss quadrature, which will be referred to as the generalized Gauss–Bessel quadrature, constructed using the following weight function:

$$\mathcal{W}(\alpha, a, r; s|u) = u^{(s+1/2)-1} \exp\left[-\alpha^2 u - |a-r|^2/(4u)\right] \quad \text{with} \quad s \in \mathbb{N}. \tag{8}$$

Using the above weight function (which will be shown later to satisfy the conditions that make it an admissible weight over $[0, \infty)$), it is clear that according to the theory of Gauss quadratures, integrals of the form

$$\int_0^{+\infty} p_n(z)\mathcal{W}(\alpha, a, r; s|z)\, dz, \tag{9}$$

where $p_n(z)$ is a polynomial function, will be evaluated exactly by means of a Gauss–Bessel quadrature of order $\lfloor (n+1)/2 \rfloor$ or higher. Here the symbol $\lfloor x \rfloor$ stands for the integral part of x. At this point, it is of interest to examine the integrand of Eq. (7) to gain more insight into our expectations insofar as exact evaluation by means of Gauss–Bessel quadrature is concerned. The form of the weight function in (8) was chosen in such a way as to have the corresponding orthogonal polynomials used to interpolate the following function:

$$\mathcal{F}(u) = \underbrace{\sqrt{\left(\frac{ar}{2}z\right)^n}\, \mathrm{H}_n\left(\alpha\sqrt{(ar)/2}\sqrt{z}\right)}_{\text{Term I}} \times \underbrace{\frac{1}{\sqrt{z}} \exp(-1/z)\mathbf{I}_{\lambda+1/2}(1/z)}_{\text{Term II}}. \tag{10}$$

In the above equation, the term labeled I can easily be shown to be a polynomial of order n. Indeed, replacing the Hermite polynomial with its closed analytical form as given in Ref. [33] (p. 250), followed by some algebra yields

$$\text{Term I} = n! \sum_{p=0}^{\lfloor n/2 \rfloor} \frac{(-1)^p}{p!(n-2p)!} \frac{(\alpha a r)^{n-p}}{(2\alpha)^p} z^{n-p}. \tag{11}$$

As for the second term, its finite representation can also be easily obtained by substituting for the modified Bessel function its closed analytical form as given in Ref. [34] (p. 80). This yields

$$\text{Term II} = \frac{1}{\sqrt{2\pi}} \left\{ \sum_{p=0}^{\lambda} \frac{(-1)^p(\lambda+p)!}{p!(\lambda-p)!2^p} z^p - (-1)^\lambda \exp(-2/z) \sum_{p=0}^{\lambda} \frac{(\lambda+p)!}{p!(\lambda-p)!2^p} z^p \right\}. \tag{12}$$

Combining the above expansion with the definition of the term labeled I given in Eq. (11) yields an expression of the form $P_m(z) + \exp(-2/z)Q_m(z)$. Clearly, the first part of such a formula is a polynomial, which should not pose any problem when integrated by means of the generalized Gauss–Bessel quadrature. As for the second part, the application of the quadrature of interest can only provide an approximate value. More precisely, the occurrence of the exponential $\exp(-2/z)$ in the second part of the definition of term II prevents it from being evaluated exactly. In other words, the success of the Gauss–Bessel quadrature for the purpose of evaluating BCLFs depends mainly on how accurate the term $\exp(-2/z)Q_m(z)$ can be interpolated by the orthogonal polynomials corresponding to the weight given in Eq. (8).

2.1.1. Evaluation Using Generalized Gauss–Bessel Quadrature

According to Davis and Rabinowitz (Ref. [35] p. 21), a function $W(z)$ can be considered an admissible weight function over the semi-infinite range $[0, \infty)$, if it satisfies the following conditions:

$$\mathbf{C}_1\text{: } W(z) \geq 0 \ \forall z \in [0, \infty), \qquad \mathbf{C}_2\text{: } \int_0^{+\infty} W(z)\, dz > 0, \qquad \mathbf{C}_3\text{: } \underbrace{\int_0^{+\infty} z^n W(z)\, dz}_{n\text{th-order moment}} < \infty. \tag{13}$$

Using the function given in Eq. (8), it is clear that the first condition of the above equation holds. The second condition follows immediately, since the weight

function of interest is positive over the semi-infinite range $[0, +\infty)$. Regarding the third condition, which requires the moments to be finite, this can easily be shown to hold, since according to Ref. [36] (p. 363), we can write

$$\mathcal{M}_n^r = \int_0^{+\infty} u^{(r+1/2)+n-1} \exp\left[-\sigma/u - \tau u\right] du = 2\sqrt{(\sigma/\tau)^{(r+n+1/2)}}\mathbf{K}_{r+n+1/2}(\sqrt{\sigma\tau}) \qquad \text{with} \quad \begin{cases} \Re(\sigma) > 0 \\ \Re(\tau) > 0 \end{cases}, \tag{14}$$

where $r, n \in \mathbb{N}$. The conditions imposed on the parameters σ and τ always hold in practice, since the values of r are usually the roots of a suitably chosen classical Gauss quadrature. As a result, both parameters $\sigma = (\alpha^2 ar)/2$ and $\tau = |a - r|^2/(2ar)$ are strictly positive as required by the result in (14). Let us point out that the evaluation of the above moment can be made more efficient by using the 3-term recurrence relation satisfied by the modified Bessel function of the second kind (Ref. [34], p. 79). This yields

$$\mathcal{M}_{n+1}^r = \frac{\sigma}{\tau}\mathcal{M}_{n-1}^r + \frac{n + r + 1/2}{\tau}\mathcal{M}_n^r. \tag{15}$$

Before moving on to our next paragraph, it is of interest to note that one may argue that a weight function of the form,

$$\mathcal{W}'(\alpha, a, r) = \mathbf{I}_{\lambda+1/2}[(ar)/(2u)] \times \exp\left[-\alpha^2 u - (a^2 + r^2)/(4u)\right] \tag{16}$$

would be a better choice, since the remaining terms in the integrand of Eq. (7) may be written as a polynomial function (11), allowing BCLFs to be evaluated exactly. In fact, proceeding this way is not suitable for two main reasons. First, if the weight in Eq. (16) were used, the roots and weights of the quadrature would have to be evaluated for each value of λ. This would be very penalizing from a computational cost point of view. Second, severe numerical instabilities are to be expected during the computation of the moments. Indeed, if these are evaluated by means of their closed analytical form, easily obtainable by substituting for the modified Bessel function its closed expression, the leading formula can be written after rearranging the terms as follow,

$$\begin{aligned}\mathcal{M}'_{n,\lambda} = {} & \frac{1}{(2\alpha^2)^n\sqrt{\alpha^2 ar}} \\ & \times \left\{ \sum_{p=0}^{n+\lambda} \left\{ \sum_{q=\max(0,p-n)}^{\lambda} \frac{(-)^q(\lambda+q)![2(n+q)-p]!}{q!(\lambda-q)!p!(q+n-p)!} \frac{1}{(2\alpha^2 ar)^q} \right\} \right. \\ & \left. \times (\alpha|a-r|)^p \exp[-(\alpha/2)|a-r|] \right. \\ & - (-)^\lambda \sum_{p=0}^{n+\lambda} \left\{ \sum_{q=\max(0,p-n)}^{\lambda} \frac{(\lambda+q)![2(n+q)-p]!}{q!(\lambda-q)!p!(q+n-p)!} \frac{1}{(2\alpha^2 ar)^q} \right\} \\ & \left. \times (\alpha|a+r|)^p \exp\left[-(\alpha/2)\,|a+r|\right] \right\}. \end{aligned} \tag{17}$$

Examination of the above formula clearly shows that the coefficients generated within the summation over q grow dramatically for increasing values of λ and n. The problem met when using the above representation is similar to that encountered by Jones and Weatherford in their **C**-matrix representation of the addition theorem of STOs [37]. The numerical instabilities of the **C**-matrix formulation were investigated in Ref. [38]. The only apparent advantage of Eq. (17) and the **C**-matrix approach is their suitability for symbolic computation since the coefficients are either integers or rationals. Of course, relying on some series expansion would bring back the convergence problems described in Ref. [31], which are precisely what we are trying to avoid.

2.2. SETTING UP THE GAUSS–BESSEL QUADRATURE

It is well known that the purpose of Gauss quadratures is to allow convergent definite or improper integrals to be evaluated numerically by letting such quantities be expressed as a weighted average of the form

$$\int_a^b f(x)w(x)\,dx = \sum_{k=1}^{n_G} w_k f(x_k), \tag{18}$$

where w_k and x_k are the so-called weights and roots corresponding to the Gauss quadrature currently in use, and n_G is its order. Because the values of the weights w_k and roots x_k are at the heart of any Gauss quadrature, it is very important to have a procedure that allows their efficient calculation. In the context of the Gauss–Bessel approach, the orthogonal polynomials are not known analytically;

i.e., their coefficients are not explicitly defined. As a consequence, to generate the weights and roots needed for our calculations, we use a numerical approach in combination with some fundamental results on orthogonal polynomials. Practically, the process is carried out as a two-step task. First, the orthogonal polynomials up to a predefined order are generated, usually by means of the so-call Gram–Schmidt orthogonalization algorithm. In the theory of orthogonal polynomials, it was shown that such mathematical constructs satisfy a 3-term recurrence relationship as stated in the following theorem [39 (theorem 1.29)]:

Theorem 2.1. Let $\pi_k(t)$, $k = 0, 1, 2, \ldots$, be the orthogonal polynomials with respect to the measure $d\lambda$. Then,

$$\pi_{k+1}(t) = (t - \alpha_k)\pi_k(t) - \beta_k\pi_{k-1}(t), \qquad k = 0, 1, 2, \ldots$$
$$\pi_{-1}(t) = 0, \qquad \text{and} \qquad \pi_0(t) = 1. \tag{19}$$

To generate the coefficients α_k and β_k we use the Gram–Schmidt procedure allowing one to write the following for the unnormalized orthogonal polynomials (monic polynomials):

$$\alpha_k = \frac{\langle t\pi_k(t), \pi(t)\rangle}{\langle \pi_k(t), \pi_k(t)\rangle} \qquad \text{and} \qquad \beta_k = \frac{\langle x\pi_k(t), \pi_{k-1}(t)\rangle}{\langle \pi_{k-1}(t), \pi_{k-1}(t)\rangle} \tag{20}$$

where the symbol $\langle \cdot, \cdot \rangle$ stands for the inner product with respect to an appropriate measure. After obtaining the coefficients $\{(\alpha_p, \beta_p)\}_{p=0,1,\ldots}$, the second step required for the setup of the Gauss–Bessel quadrature is the computation of the corresponding nodes and roots. Numerous routes can be used to complete such a task but, from a practical point of view, the most effective is probably that relying on the diagonalization of the Jacobi tridiagonal matrix,

$$\mathbf{J}_n(\mathcal{W}) = \begin{bmatrix} \alpha_0 & \sqrt{\beta_1} & & & & & 0 \\ \sqrt{\beta_1} & \alpha_1 & \sqrt{\beta_2} & & & & \\ 0 & \sqrt{\beta_2} & \alpha_2 & \sqrt{\beta_3} & & & \\ 0 & 0 & \sqrt{\beta_3} & \alpha_3 & \sqrt{\beta_4} & & \\ & & & \ddots & \ddots & \ddots & \\ & & & & & \ddots & \ddots & \sqrt{\beta_{n-1}} \\ 0 & & & & & \sqrt{\beta_{n-1}} & \alpha_n \end{bmatrix} \tag{21}$$

It turns out that the eigenvalues of the above defined matrix are in fact the nodes of the Gauss quadrature (for which the orthogonal polynomials satisfy Eq. (20) (cf. Ref. [39]). As regards the weights they are proportional to the first component $v_{k,1}$ of the kth normalized eigenvector,

$$w_k = \beta_0 v_{k,1}^2 \qquad k = 1, 2, \ldots n. \tag{22}$$

3. Numerical Analysis and Applications

As mentioned briefly in Section 2.1.1, the evaluation of BCLFs can be quite cumbersome since the corresponding closed analytical form are numerically unstable while their series representation can be very slowly convergent. In fact, in previous work [31], it was shown that infinite expansions of BCLFs in terms of Bessel functions $K_{n+1/2}(\zeta\sqrt{a^2 + r^2})$ and $K_{n+1/2}(\zeta\sqrt{|a - r|})$ become logarithmically convergent in the neighborhood of the cusp. Obviously, this makes the numerical procedure based on such expansions time consuming which hinders their use for practical purposes. An alternative to the series representation is to use a suitable numerical integration techniques which in the present case is the Gauss–Bessel.

In practice, it is important to point out that when the order λ of the modified Bessel function occurring in the integrand of (7) is small, the closed analytical form of BCLFs, or equivalently their **C** matrix representation, is numerically stable. In this context, there is little argument in favoring the Gauss–Bessel quadrature method over the closed form. Based on the above remarks, we have generated a 3-D figure, which was afterward projected on the XY-plane (cf. Fig. 1). In the projected figure, dark areas correspond to combinations of λ and r that make the closed analytical form of BCLF numerically unstable. Clearly, Figure 1 shows that the most unfavorable situation correspond to small values of r, in which case the closed form breaks down for relatively small values of λ ($\sim$5). At the root of this problem we find the expression of the closed form of BCLFs, represented as a difference of two large positive numbers that happen to be very close in magnitude.

As r increases, a numerically stable region, i.e., with $\geq$10 exact figures, appears and clearly visible in the neighborhood of the lower right corner of Figure 1(a) and beyond the cusp shown as Figure 1(b). This stability holds for values of λ ranging from 0 to 8. One particular feature of the region

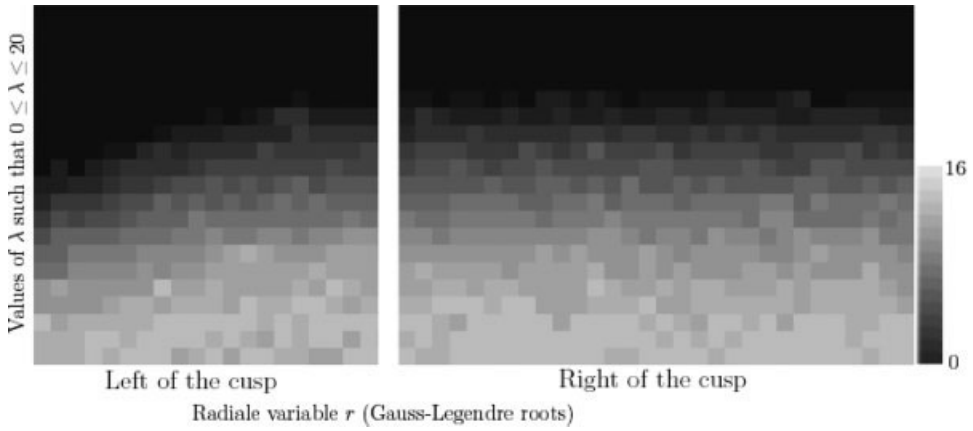

FIGURE 1. Number of exact figures in the closed analytical form of BCLFs as a function of λ and r. The figure was obtained using the parameters $\zeta = 1.5$, $a = 3.0$ and $1.002197 \leq r \leq 8.991792$.

below the cusp [Fig. 1(a)] is the visible linear trend, which suggests the existence of an empirical relationship of the form $\lambda = ar + b$ that defines a line below which it may be numerically safe to use the closed form of BCLFs. Outside this area (which includes areas in which λ is large), it is necessary to rely on another numerically stable scheme albeit approximate. One such schemes is the Gauss–Bessel approach as described in Section 2.1, which uses only one weight function (8) to compute an approximation of BCLFs. To assess the quality of the present algorithm as applied in the context of multi-center integrals, we address the case of overlap integrals. It must be pointed out that overlap integrals, which may be considered as a classroom example, were essentially chosen because of the simplicity of the corresponding computer code. Thus, starting from the most general form of such integrals, which can be written as

$$\mathcal{S}^{n_2,l_2,m_2}_{n_1,l_1,m_1}(\zeta_1,\zeta_2,\mathbf{a}) = \left\langle \chi^{m_1}_{n_1,l_1}(\zeta_1,\mathbf{r}) \middle| \chi^{m_2}_{n_2,l_2}(\zeta_1,\mathbf{r}-\mathbf{a}) \right\rangle, \tag{23}$$

we can derive a working formula for overlap integrals in the context of the one-center two-range expansion by combining the result in Eq. (5) with the addition theorem of solid spherical harmonics [40]:

$$\mathcal{Y}^m_l(\mathbf{r}+\mathbf{a}) = 4\pi(2l+1)!! \times \sum_{l'=0}^{l}\sum_{m'=-l'}^{l'} \frac{\langle lm|l'm'|l-l'm-m'\rangle}{(2l'+1)!![2(l-l')+1]!!} \mathcal{Y}^{m'}_{l'}(\mathbf{r})\mathcal{Y}^{m-m'}_{l-l'}(\mathbf{a}) \tag{24}$$

In addition, to simplify the final result, we also make use of the following expansion:

$$\mathrm{P}_l\left(\frac{\mathbf{a}\cdot\mathbf{r}}{ar}\right) = 4\pi \sum_{m=-l}^{l} \left[\mathcal{Y}^m_l(\mathbf{a}/a)\right]^* \mathcal{Y}^m_l(\mathbf{r}/r). \tag{25}$$

Based on the above results, we are now in a position to derive a working formula for overlap integrals over STFs in the framework of the single center two-range addition theorem,

$$\begin{aligned}\mathcal{S}^{n_2,l_2,m_2}_{n_1,l_1,m_1}(\zeta_1,\zeta_2,\mathbf{a}) &= \left\langle \chi^{m_1}_{n_1,l_1}(\zeta_1,\mathbf{r}) \middle| \chi^{m_2}_{n_2,l_2}(\zeta_1,\mathbf{r}-\mathbf{a}) \right\rangle \\ &= \mathcal{N}_1(\zeta_1)\mathcal{N}_2(\zeta_2)(4\pi)^2(2l_2+1)!! \\ &\times \sum_{l'_2=0}^{l_2}\sum_{m'_2=-l'_2}^{l'_2} \frac{\langle l_2m_2|l'_2m'_2|l_2-l'_2m_2-m'_2\rangle}{(2l'_2+1)!![2(l_2-l'_2)+1]!!} \mathcal{Y}^{m_2-m'_2}_{l_2-l'_2}(-\mathbf{a}) \\ &\times \sum_{\lambda=|l_1-l'_2|}^{l_2+l'_2} (2\lambda+1)\langle l_1m_1|\lambda m_1-m'_2|l'_2m'_2\rangle \\ &\times \left\langle r^{n_1-1}\exp(-\zeta_1 r) \middle| r^{l'_2} \frac{\mathcal{A}^{n_2-l_2}_{\lambda+1/2}(\zeta_2,a,r)}{\sqrt{ar}} \right\rangle. \end{aligned} \tag{26}$$

For practical purposes, the Gaunt coefficients occurring in the above expression are evaluated using the code developed by Weniger and Steinborn [41]. As for the radial integral, it was found after inspecting several BCLFs cf. Fig. 2, that such functions reach their maximum on the cusp, suggesting the use of a Gauss–Legendre quadrature centered on that very point and covering the interval $[a - w_a, a + w_a]$. For the case considered in this work, we have empirically

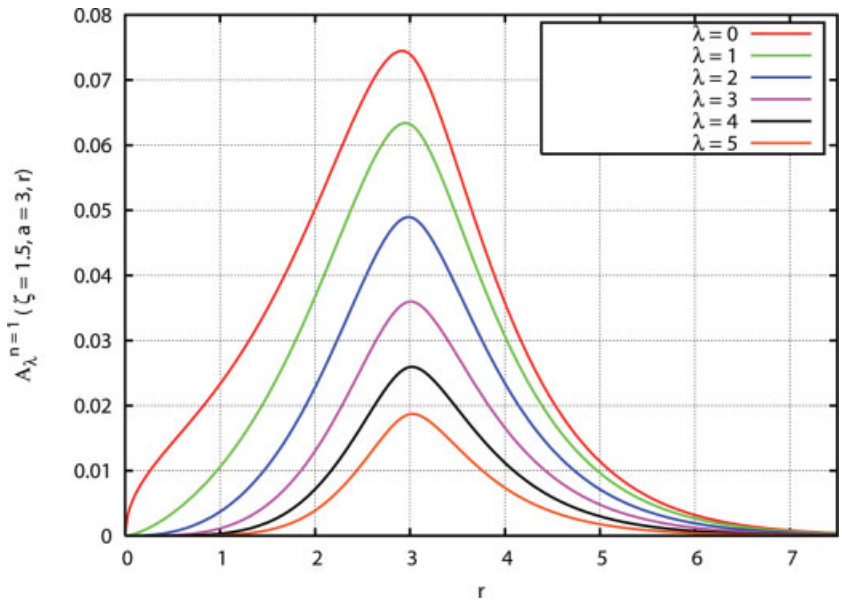

FIGURE 2. Graphical representation of BCLF for increasing values of λ. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

selected $w_a = 1$. In the two remaining subintervals, i.e., $[0, a - w_a)$ and $(a + w_a, +\infty)$, we use two low-order Gauss–Legendre (16 points) and Gauss–Laguerre (24 points) quadratures. According to Table I, it appears that our values are generally in agreement with previously published results. For the cases we have examined, it can clearly be seen that our values (generated by the method developed above) are in agreement with those published by Safouhi [42]. However, to broaden the spectrum of comparisons, we also present selected values of overlap integrals published by other investigators, i.e., Talman [43] and Guseinov and colleagues [44–46]. Based on the reference from which the data were extracted, we have divided the entries in Table I into four classes. In the first group, the rightmost column holds the values published by Talman [43], where we can clearly see a good agreement between the author's values, Safouhi's, and ours. The last three groups of results were extracted from the work of Guseinov and coworkers, which appeared in Refs. [44–46]. While our values still agree with Safouhi's [42], we can note some disagreement when comparing those of Guseinov and coworkers. In fact, after investigating this matter, we came to believe that possible inaccuracies might have been overlooked by these investigators. Indeed, in the tables provided by Guseinov and coworkers [44–46], two calculations referred to as left-hand side and right-hand side are given. These values are supposed to be very close if not equal, since they represent two different routes for the computation of the same integral. However, after careful inspection of the tables provided by Guseinov and coworkers, we have noted in several instances that the two values (left-hand side and right-hand side) do not agree (e.g., Table I in Ref. [46]). In addition, in the discussion section of Ref. [44], the authors admit that, for large quantum numbers, it was necessary to use quadruple precision in order to accurately represent some of the coefficients needed by their computational procedure. In other words, this implicitly means that their working formula requires manipulating very large intermediate quantities before generating the final result, which, in the case of interest, is an overlap integral such that $0 \leq |S| \leq 1$. Generally this is not an ideal situation for numerical stability.

4. Conclusion

We have presented a new procedure that can be used for the evaluation of BCLFs, which appear in the framework of multi-center integrals over STFs as treated within the one-center two-range expansion. Indeed, for those integrals, which can be represented by finite expansion, this method should be comparable in terms of efficiency with other available techniques such as those based on integral transforms. In fact, for problems in which efficiency is not

TABLE I

Overlap integrals computed by means of Eq. (26).*

(n_1, l_1, m_1, ζ_1)	(n_2, l_2, m_2, ζ_2)	a	This work	Ref. [42]	Refs. [43–46][a]
(5, 4, 0, 1.0)	(5, 4, 0, 1.0)	1.0	7.68617011 (−1)	7.68617011 (−1)	7.68617016 (−1)
(5, 4, 4, 1.0)	(5, 4, 4, 1.0)	1.0	9.55778747 (−1)	9.55778746 (−1)	9.55778746 (−1)
(5, 4, 0, 5.0)	(5, 4, 0, 1.0)	1.0	9.00262306 (−3)	9.00262308 (−3)	9.00262309 (−3)
(5, 4, 4, 5.0)	(5, 4, 4, 1.0)	1.0	3.18003745 (−2)	3.18003745 (−2)	3.18003745 (−2)
(5, 4, 0, 5.0)	(5, 4, 0, 5.0)	1.0	−1.38257012 (−1)	−1.38257012 (−1)	−1.38257012 (−1)
(5, 4, 4, 5.0)	(5, 4, 4, 5.0)	1.0	3.56825987 (−1)	3.56825987 (−1)	3.56825987 (−1)
(8, 0, 0, 1.0)	(8, 0, 0, 1.0)	1.0	9.89015721 (−1)	9.89015721 (−1)	9.89015721 (−1)
(8, 0, 0, 5.0)	(8, 0, 0, 1.0)	1.0	1.07437342 (−2)	1.07437341 (−2)	1.07437341 (−2)
(8, 0, 0, 5.0)	(8, 0, 0, 5.0)	1.0	7.85230850 (−1)	7.85230850 (−1)	7.85230850 (−1)
(3, 2, 1, 8.0)	(3, 2, 1, 2.0)	5.0	−4.42287767 (−4)	−4.42287767 (−4)	−4.42287766 (−4)
(10, 7, 1, 2.5)	(8, 1, 1, 10.0)	2.5	1.52138456 (−2)	1.52138456 (−2)	1.52138456 (−2)
(18, 12, 6, 1.5)	(18, 12, 6, 30.0)	1.5	9.48615868 (−3)	9.48615868 (−3)	9.48615878 (−3)
(21, 10, 5, 6.0)	(9, 6, 5, 10.0)	6.0	−2.93153656 (−8)	−2.93153644 (−8)	−2.93153644 (−8)
(30, 10, 8, 1.5)	(14, 8, 8, 10.0)	1.5	1.22364599 (−1)	1.22364599 (−1)	1.22376276 (−1)
(4, 3, 0, 1.9)	(6, 5, 0, 0.1)	100.0	−5.34413560 (−6)	−5.34413558 (−6)	−5.34413558 (−6)
(6, 3, 2, 1.4)	(8, 5, 2, 0.6)	40.0	−3.21391600 (−5)	−3.21391598 (−5)	−3.21391598 (−5)
(9, 5, 3, 6.0)	(8, 4, 3, 4.0)	9.0	−5.46608470 (−8)	−5.46608468 (−8)	−5.46510243 (−8)
(10, 7, 1, 14.4)	(8, 2, 1, 9.6)	5.0	−1.84096844 (−10)	−1.84096844 (−10)	−1.84189026 (−10)
(10, 9, 9, 4.8)	(10, 9, 9, 1.2)	5.0	6.23122318 (−4)	6.23122318 (−4)	6.23122318 (−4)
(12, 7, 3, 1.3)	(12, 7, 3, 0.7)	15.0	2.29354179 (−2)	2.29354179 (−2)	2.29354178 (−2)
(17, 8, 4, 1.8)	(14, 6, 4, 0.2)	30.0	9.13913987 (−7)	9.13913987 (−7)	9.13905849 (−7)
(17, 8, 4, 11.0)	(8, 7, 4, 9.0)	5.0	−1.00636030 (−6)	−1.00636030 (−6)	−1.00623367 (−6)[b]
(21, 10, 6, 9.0)	(9, 8, 6, 9.0)	5.0	5.38979431 (−5)	5.38979476 (−5)	5.38980685 (−5)
(30, 10, 8, 7.0)	(14, 10, 8, 7.0)	5.0	1.35074705 (−2)	1.35074705 (−2)	1.35074709 (−2)
(40, 4, 3, 4.8)	(12, 4, 3, 1.2)	5.0	9.48246700 (−2)	9.48246700 (−2)	9.48379265 (−2)
(43, 10, 6, 7.2)	(18, 8, 6, 16.8)	5.0	−1.15808749 (−4)	−1.15808750 (−4)	−1.15907687 (−4)[c]

*To illustrate the stability of the approach described in this work, we have computed a variety of overlap integrals (small and large quantum numbers). BCLFs were evaluated by means of a Gauss–Bessel quadrature of order 32.

[a]Values grouped according to the reference from which they were taken: [43], [44], [45], and [46].

[b]There is a discrepancy between the left-hand side ($-1.00640061\ 10^{-6}$) and right-hand side ($-1.00623367\ 10^{-6}$) [46]. Note that other similar cases have are listed in Table 1 of Guseinov and Mamedov [46].

[c]We suspect that this value should read: $-1.15807687\ 10^{-4}$.

an issue, the present approach is an ideal tool, since it can easily be applied to the problem at hand and also straightforwardly implemented. However, even in such a case, one may need a large number of terms to be summed up to ensure an acceptable convergence. It is in that very context that the use of a tailored Gauss quadrature may prove helpful, as it permits accurate generation of the required coefficients.

References

1. Kato, T. Commun Pure Appl Math 1957, 10, 151.
2. Yoshimine, M.; Lengsfield, B. H.; Bagus, P. S.; McLean, T.; Liu, B. Alchemy II; MOTECC-90; International Business Machines: Kingston, New York, 1990.
3. Weniger, E. J. Int J Quantum Chem 2000, 76, 280.
4. Weniger, E. J. Int J Quantum Chem 2002, 90, 92.
5. Filter, E.; Steinborn, E. O. J Math Phys 1980, 21, 2725.
6. Guseinov, I. J Chem Phys 1976, 65, 4718.
7. Guseinov, I. J Chem Phys 1978, 69, 4990.
8. Guseinov, I. Phys Rev A 1980, 22, 369.
9. Guseinov, I. Phys Rev A 1985, 32, 1864.
10. Guseinov, I. Phys Rev A 1988, 37, 2314.
11. Bonham, R. A.; Peacher, J. L.; Cox, H. L. J Chem Phys 1964, 40, 3083.
12. Filter, E.; Steinborn, E. O. J Math Phys 1978, 19, 79.
13. Weniger, E. J.; Steinborn, E. O. J Chem Phys 1983, 78, 6121.
14. Trivedi, H. P.; Steinborn, E. O. Phys Rev A 1983, 27, 670.
15. Weniger, E. J.; Steinborn, E. O. Phys Rev A 1983, 28, 2026.
16. Grotendorst, J.; Steinborn, E. O. J Comput Phys 1985, 61, 195.
17. Weniger, E. J.; Grotendorst, J.; Steinborn, E. O. Phys Rev A 1986, 33, 3688.

18. Weniger, E. J.; Steinborn, E. O. Theor Chim Acta 1988, 73, 323.
19. Sidi, A. J Inst Math Appl 1980, 26, 1.
20. Levin, D.; Sidi, A. Appl Math Comput 1981, 9, 175.
21. Safouhi, H. J Phys A Math Gen 2001, 34, 2801.
22. Safouhi, H. J Phys A Math Gen 2001, 34, 881.
23. Shavitt, I.; Karplus, M. J Chem Phys 1962, 36, 550.
24. Karplus, M.; Shavitt, I. J Chem Phys 1963, 38, 1256.
25. Shavitt, I. Methods in Computational Physics; Vol 2; Academic Press: New York, 1963; p 45.
26. Shavitt, I.; Karplus, M. J Chem Phys 1965, 43, 398.
27. Rico, J. F.; Lopez, R.; Ema, I.; Ramirez, G. J Comp Chem 2004, 25, 1987.
28. Rico, J. F.; López, R.; Aguado, A.; Ema, I.; Ramírez, G. J Comput Chem 1998, 19, 1284.
29. Bouferguene, A. J Phys A Math Gen 2005, 38, 3923.
30. Rico, J. F.; Fernandez, J. J.; Ema, I.; Lopez, R.; Ramirez, G. Int J Quantum Chem 2000, 78, 83.
31. Bouferguene, A. J Phys A Math Gen 2005, 38, 2899.
32. Levin, D. Int J Comput Math 1973, B3, 371.
33. Magnus, W.; Oberhettinger, F.; Soni, R. P. Formulas and Theorems for the Special Functions of Mathematical Physics; Springer-Verlag: New York, 1966.
34. Watson, G. N. A Treatise on the Theory of Bessel Functions; 2nd ed.; Cambridge University Press: Cambridge, UK, 1944.
35. Davis, P. J.; Rabinowitz, P. Methods of Numerical Integration; 2nd ed.; Academic Press: New York, 1984.
36. Gradshteyn, I. S.; Ryzhik, I. M. Table of Integrals; Series and Products; Academic Press: Orlando, FL, 1980.
37. Jones, H. W.; Weatherford, C. A. Int J Quantum Chem Symp 1978, 12, 483.
38. Bouferguene, A.; Rinaldi, D. Int J Quantum Chem 1994, 50, 21.
39. Gautchi, W. Orthogonal Polynomials; 1st ed.; Oxford Science Publications: Oxford, UK, 2004.
40. Steinborn, E. O.; Ruedenberg, K. Adv Quantum Chem 1973, 7, 1.
41. Weniger, E. J.; Steinborn, E. O. Comput Phys Commun 1982, 25, 149.
42. Safouhi, H. J Mol Mod 2006, 12, 213.
43. Talman, J. D. Phys Rev A 1993, 48, 243.
44. Guseinov, I.; Özmen, A.; Atav, Ü.; Yüksel, H. Int J Quantum Chem 1998, 67, 199.
45. Guseinov, I. I.; Öztekin, E.; Hüseyin, S. J Mol Struct (Theochem) 2001, 536, 59.
46. Guseinov, I. I.; Mamedov, B. A. J Mol Struct (Theochem) 2001, 538, 295.