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Addition theorem of Slater type orbitals: a numerical evaluation of Barnett–Coulson/Löwdin functions*

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Abstract

When using the one-centre two-range expansion method to evaluate multicentre integrals over Slater type orbitals (STOs), it may become necessary to compute numerical values of the corresponding Fourier coefficients, also known as Barnett–Coulson/Löwdin Functions (BCLFs) (Bouferguene and Jones 1998 *J. Chem. Phys.* **109** 5718). To carry out this task, it is crucial to not only have a stable numerical procedure but also a fast algorithm. In previous work (Bouferguene and Rinaldi 1994 *Int. J. Quantum Chem.* **50** 21), BCLFs were represented by a double integral which led to a numerically stable algorithm but this turned out to be disappointingly time consuming. The present work aims at exploring another path in which BCLFs are represented either by an infinite series involving modified Bessel functions $\mathbf{K}_\nu(\sqrt{a^2+r^2})$ or by an integral whose integrand is a smooth function. Both of these representations have the advantage of being symmetrical with respect to the cusp parameter a and the radial variable r. As a consequence, it is no longer necessary to split the integrals over $r \in [0, +\infty)$ into several components with a different analytical form in each of these. A numerical study is also carried out to help select the most appropriate method to be used in practice.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is a well-known fact that in order to determine the electronic structure of any molecular system, one needs to solve the Schrödinger equation. Unfortunately, except for a few small systems of little interest such an equation cannot be fully solved. For practical purposes,

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various approximations are introduced in the Schrödinger equation so as to simplify the mathematics. This pragmatic approach has led to efficient and reliable numerical procedures with various degrees of sophistication and these proved to give trustworthy descriptions of most common physical and chemical phenomena.

In setting up quantum chemical methods, the variational approach is probably the most popular scheme used to find approximate solutions of the exact Schrödinger equation. Accordingly, the choice of the trial function is of great importance for convergence purposes. Fortunately, among the legion of such trial functions there exists a special class which may be considered as the most appropriate. Indeed, much work about the Schrödinger equation has revealed that its solutions must possess two fundamental mathematical properties, namely a cusp at the origin [1] and an exponential tail at infinity [2]. STOs [3] satisfy these criteria and as such they constitute an adequate family of trial functions for the variational scheme. Unfortunately, their extensive use in quantum chemistry packages was impeded by inextricable mathematical and numerical difficulties arising from multicentre integrals.

With the progress in computer technology, a number of scientists have renewed their interest in a possible use of STOs for the determination of molecular structures and chemical properties. As a result, several methods aimed at an efficient evaluation of multicentre integrals over STOs were proposed. These methods are usually based on two main mathematical approaches, namely addition theorems and integral transforms.

In practice two types of addition theorems are generally used. One range addition theorems [4–9] which in principle can be derived by considering an expansion over a complete orthonormal set of functions $\left\{\Psi^m_{n,l}(\mathbf{r})\right\}$ with respect to the scalar product of Hilbert space $L^2(\mathbb{R}^3)$ of square summable functions. Indeed given a function: $\Phi(\mathbf{r}-\mathbf{r}') \in L^2(\mathbb{R}^3)$, one can write the following expansion:

$$\Phi^m_{n,l}(\mathbf{r}-\mathbf{r}') = \sum_{n',l',m'} C_{n',l',m'}(\mathbf{r}')\Psi^{m'}_{n',l'}(\mathbf{r}) \qquad \text{with} \qquad C_{n',l',m'}(\mathbf{r}') = \left\langle \Psi^{m'}_{n',l'}(\mathbf{r}) | \Phi(\mathbf{r}-\mathbf{r}') \right\rangle. \tag{1}$$

Clearly, the expansion coefficients $C^m_{n,l}(\mathbf{r}')$ occurring in the above equation depend only on $\mathbf{r}'$ which makes the corresponding addition theorem to be referred to as one range. Perhaps the most obvious choice falling in the above described category, i.e. completeness in $L^2(\mathbb{R}^3)$, is the set of functions defined as

$$\Lambda^m_{n,l}(\zeta,\mathbf{r}) = \mathcal{N}_{n,l}(\zeta)\exp(-\zeta r)L^{2l+2}_{n-l-1}(2\zeta r)\mathcal{Y}^m_l(2\zeta\mathbf{r}) \quad \text{with}$$
$$\mathcal{N}_{n,l}(\zeta) = (2\zeta)^{3/2}\sqrt{\frac{(n-l-1)!}{(n+l+1)!}} \tag{2}$$

in which $\mathcal{Y}^m_l(\mathbf{k})$ stands for the regular solid spherical harmonic defined in (7) and $L^\alpha_n(\zeta)$ for the generalized Laguerre polynomials [10, p 239]. Such functions which were used in the field of atomic/molecular physics by Hylleras as early as 1929 [11] were also used by Shull and Löwdin [12, 13] and later by Filter and Steinborn [5] for the derivation of one-range addition theorem. To achieve a similar purpose, Guseinov [14–18] has used the following form:

$$\Psi^m_{m,l}(\zeta,\mathbf{r}) = \mathcal{N}_{n,l}(\zeta)\exp(-\zeta r)L^{2l+2}_{n+l+1}(2\zeta r)\mathcal{Y}^m_l(2\zeta\mathbf{r}) \qquad \text{with}$$
$$\mathcal{N}_{n,l}(\zeta) = (2\zeta)^{3/2}\sqrt{\frac{(n-l-1)!}{[(n+l+1)!]^3}}. \tag{3}$$

Note that the apparent difference between equations (3) and (2) is probably due to the fact that Guseinov used a non-standard convention for the generalized Laguerre polynomials. In fact, the convention normally used in special function theory leads to the generalized

Laguerre polynomials $L_{n-l-1}^{2l+2}(z)$ as they occur in equation (2). Non-standard conventions were discussed in a paper by Kaijser and Smith [19]. In fact, completeness in some Hilbert space is not sufficient for a set of functions to be suitable for quantum mechanical applications. For instance the so-called Sturmians

$$\Phi_{n,l}^{m}(\zeta,\mathbf{r}) = \mathcal{N}_{n,l}(\zeta)\exp(-\zeta r)L_{n-l-1}^{2l+1}(2\zeta r)\mathcal{Y}_{l}^{m}(2\zeta\mathbf{r}) \qquad \text{with}$$
$$\mathcal{N}_{n,l} = (2\zeta)^{3/2}\sqrt{\frac{(n-l-1)!}{2n(n+l)!}} \tag{4}$$

form a complete orthonormal set in $L_{1/r}^{2}(\mathbb{R}^3)$ but according to [9] the latter is not suited quantum mechanics. However, because Sturmians are also complete and orthonormal with respect to the weight $\zeta^2 - \nabla^2$ they form a complete orthonormal set in the Sobolev space $W_2^{(1)}(\mathbb{R}^3)$ [6, 9]. And this makes Sturmians acceptable candidates for atomic/molecular physics applications. Hydrogenlike functions,

$$W_{n,l}^{m}(Z,\mathbf{r}) = \mathcal{N}_{n,l}\exp(-Z/nr)L_{n-l-1}^{2l+1}(2Z/nr)\mathcal{Y}_{l}^{m}(2Z/n\mathbf{r}) \tag{5}$$

which are closely related to Sturmians form a complete orthonormal set in $L^2(\mathbb{R}^3)$ only if the eigenfunctions of the continuous spectrum are included [20, 21]. The continuum functions being complicated mathematically would, however, lead to difficult mathematical and computational problems. Regarding two-range addition theorems of physical interest these can generally be interpreted as rearranged three-dimensional Taylor expansions in the Cartesian components of $\mathbf{r} = (x, y, z)$ which converge pointwise. These questions were discussed in a very detailed way by Weniger [22, 23]. In the context of multicentre integrals, two-range addition theorems are usually obtained by expanding the quantity of interest in terms of spherical harmonics [24–55].

The Fourier integral transform [56–66] is amongst the most promising approach that was proposed to solve the multicentre integrals problem. More recently, Maslov *et al* [67] have proposed a numerical procedure allowing one to approximate a two-centre charge distribution in terms of one-centre quantities which of course simplify the whole calculation. However, obtaining the required approximates still needs further investigations in order for the method to be used for an accurate evaluation of multicentre integrals. Another excellent approach which has recently led to a complete package combines STOs and Gaussian type orbitals (GTOs) [68, 69]. Indeed, for one- and two-centre integrals STO-based working formulae are derived while for three- and four-centre repulsion integrals, STOs are first expanded over an appropriate large Gaussian basis set. It is clear that when proceeding this way, one can profitably use the powerful algorithms already designed to handle multicentre integrals over GTOs [70, 71].

The present investigation constitutes the second part of a work in which various facets (analytical and numerical) of the two-range expansion are examined. It must be emphasized that numerous papers were devoted to study algorithms and procedures that could potentially be used for the computation of BCLFs [41, 42, 46–52]. This work examines two additional procedures that will be added to the arsenal of methods that can be used to evaluate BCLFs. Hence, our main purpose is to study two types of series representations of BCLFs so as to elaborate the most appropriate strategy that should be used for computing such functions. Needless to say that in our approach, the success of multicentre integrals algorithms depends to a large extent on how fast can BCLFs be evaluated. In the original addition theorem of STOs, BCLFs are intrinsically non-symmetrical since two different analytical forms are used in order to fully specify such functions in the whole space. It is clear that use of such a non-symmetrical definition in multicentre integrals requires splitting the integration ranges

by introducing the cusp distances. Regarding the second class of series representations, they have the advantage of being completely symmetrical with respect to the variables of interest. The convergence of these series representations will also be considered from a numerical point of view and the advantage of using the Levin u [72–75] transformation is highlighted.

2. General properties

A Slater orbital centred on some point defined by its location vector, $\mathbf{a}$, is usually defined as

$$\chi_{n,l}^{m}(\zeta|\mathbf{r}-\mathbf{a}|) = \mathcal{N}|\mathbf{r}-\mathbf{a}|^{n-l-1}\exp(-\zeta|\mathbf{r}-\mathbf{a}|)\mathcal{Y}_{l}^{m}(\mathbf{r}-\mathbf{a}) \tag{6}$$

in which the $\mathcal{N} = (2\zeta)^{n+1/2}/\sqrt{(2n)!}$ is the normalization factor and $\mathcal{Y}_{l}^{m}(\mathbf{r})$ represents the solid spherical harmonic of degree l and order m which using the Condon and Shortley phase convention [76] can be expressed as

$$\mathcal{Y}_{l}^{m}(\mathbf{r}) = \|\mathbf{r}\|^{l}Y_{l}^{m}(\theta_{\mathbf{r}},\phi_{\mathbf{r}}) = \|\mathbf{r}\|^{l}i^{m+|m|}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_{l}^{|m|}(\cos\theta_{\mathbf{r}})\,\mathrm{e}^{im\phi} \tag{7}$$

where $P_{l}^{m}(z)$ is the associated Legendre function and is defined as

$$P_{l}^{m}(z) = (1-z^{2})^{|m|/2}\left(\frac{\mathrm{d}}{\mathrm{d}z}\right)^{|m|}P_{l}(z) = (-1)^{l}(1-z^{2})^{|m|/2}\left(\frac{\mathrm{d}}{\mathrm{d}z}\right)^{l+|m|}\left[\frac{(1-z^{2})^{l}}{2^{l}l!}\right]. \tag{8}$$

In previous work, it was shown that in order to have a better insight into the analytical and numerical properties of the two-range addition theorem of STOs, it is advisable to expand the radial and the angular parts of such functions separately. BCLFs are thus introduced in connection to the expansion of the radial part as follows:

$$|\mathbf{r}-\mathbf{a}|^{n-l-1}\exp(-\zeta|\mathbf{r}-\mathbf{a}|) = \frac{1}{\sqrt{ar}}\sum_{\lambda=0}(2\lambda+1)\mathcal{A}_{\lambda+1/2}^{n-l}(\zeta,a,r)\mathrm{P}_{\lambda}\left(\frac{\mathbf{a}\cdot\mathbf{r}}{ar}\right) \qquad \text{with}$$
$$\begin{cases} n = 1, 2, \ldots \\ l = 0, 1, \ldots, n-1 \end{cases} \tag{9}$$

where $\mathrm{P}_{n}(z)$ represents the Legendre polynomial of degree n and $\mathcal{A}_{\lambda+1/2}^{n}(\zeta,a,r)$ the so-called BCLF which may be defined using a recursive scheme such that

$$\begin{cases} \mathcal{A}_{\lambda+1/2}^{0}(\zeta,a,r) = \mathbf{I}_{\lambda+1/2}(\zeta\rho_{<})\mathbf{K}_{\lambda+1/2}(\zeta\rho_{>}) \\ \mathcal{A}_{\lambda+1/2}^{n}(\zeta,a,r) = -\partial/\partial\zeta\,\mathcal{A}_{\lambda+1/2}^{n-1}(\zeta,a,r) \end{cases} \tag{10}$$

where $\mathbf{I}_{l+1/2}(z)$ and $\mathbf{K}_{l+1/2}(z)$ represent the modified Bessel functions of the first and second kinds which may be described by finite expansions since they involve half integral orders [77] (p 79). The variables $\rho_{<}$ and $\rho_{>}$ stand for $\min(a,r)$ and $\max(a,r)$ respectively. An arbitrary STO is in fact constructed as the product of equation (9) by a solid spherical harmonic which obeys the following addition theorem [78]:

$$\mathcal{Y}_{l}^{m}(\mathbf{r}-\mathbf{a}) = 4\pi(2l+1)!!\sum_{l'=0}^{l}\sum_{m'=-l'}^{l'}\frac{\langle lm|l'm'|l-l'm-m'\rangle}{(2l'+1)!![2(l-l')+1]!!}\mathcal{Y}_{l'}^{m'}(\mathbf{r})\mathcal{Y}_{l-l'}^{m-m'}(\mathbf{a}) \tag{11}$$

where $(2l+1)!! = 1\times3\times\cdots\times(2l+1)$ and $\langle l_1m_1|l_2m_2|l_3m_3\rangle$ is the so-called Gaunt coefficient [79–88]. Note has to be taken that Dunlap [79–81] addresses complicated generalizations of Gaunt coefficients which occur in molecular multicentre integrals over spherical Gaussian orbitals.

In the many variations of the two-range addition theorem of STOs that appeared in the literature, the mathematical foundations used to set up the formalism were generally similar if not identical. However, the differences between each method lie in the manner with which the expansion coefficients are handled from both analytical and numerical standpoints. In his work, Sharma [35] succeeded in establishing a suitable analytical form for BCLFs when the location of the STO is on the z axis. Later, Rashid [36] and Suzuki [46–52] have independently simplified Sharma's formulation making it more tractable for further mathematical analysis and for numerical experiments. In the meantime, starting with Sharma's expansion, Jones and co-workers [38–44] have led to another form of BCLFs which is well adapted to integer arithmetic widely available nowadays through many well-known systems, e.g. mathematica, maple and the like. The latter was recently improved and some advantages of the new formulae, namely their generality and the ease of their practical use, were highlighted [89]. In the present work, the following items will be addressed:

1. Derive series expansions for the Fourier coefficients, i.e. BCLFs, involved in the expansion given by equation (10).
2. Compare various techniques used to evaluate BCLFs. It should be noted that our numerical study will mainly focus on $\mathcal{A}^0_{\lambda+1/2}(\zeta, a, r)$ and $\mathcal{A}^1_{\lambda+1/2}(\zeta, a, r)$ since as will be shown in what follows the expansion of an arbitrary order STOs requires either the expansion of the 1s orbital or the Yukawa potential.
3. Present some numerical experiments illustrating our findings.

As a last comment, it should be noted that in our numerical experiments, emphasis will be put on the series involving $\mathcal{A}^0_{\lambda+1/2}(\zeta, a, r)$ and $\mathcal{A}^1_{\lambda+1/2}(\zeta, a, r)$. This choice is motivated by the fact that an arbitrary STO can always be written as

$$|\mathbf{r}-\mathbf{a}|^{n-l-2}\exp(-\zeta|\mathbf{r}-\mathbf{a}|)\mathcal{Y}_l^m(\mathbf{r}-\mathbf{a}) = |\mathbf{r}-\mathbf{a}|^{n-l-1-2\lfloor(n-l-1)/2\rfloor} \times \exp(-\zeta|\mathbf{r}-\mathbf{a}|)\underbrace{|\mathbf{r}-\mathbf{a}|^{2\lfloor(n-l-1)/2\rfloor}\mathcal{Y}_l^m(\mathbf{r}-\mathbf{a})}_{\text{Finite}} \tag{12}$$

where $\lfloor x \rfloor$ represents the integral part of x (floor function). The term labelled 'Finite' can indeed be represented by a finite number of terms by combining equation (11) with the expansion of the radial term which is finite since the exponent is an even number.

3. Symmetrical representation of BCLFs

In previous investigations on the application of the two-range addition theorem to the evaluation of multicentre integrals, it was found that a hybrid method which combines analytical and numerical integration was the most effective from a computational perspective. Of course, for numerical integration the first pre-requisite is to have a robust procedure allowing one to evaluate BCLFs especially for large λs (cf equation (10)) since such functions are at the heart of all kinds of multicentre integrals. Usually, BCLFs can be computed by means of two different procedures according to whether the multicentre integral under study is represented by a finite sum, e.g. overlaps, or an infinite expansion, e.g. three-centre nuclear attraction and exchange integrals. In the first case, it is generally possible to directly use any of the method already described in the literature which date as back as 1967 [90] and in essence are all equivalent since using a finite number of terms. Conversely, for multicentre integrals that are described by infinite series, use of a finite representation of BCLFs leads to severe numerical instabilities [24]. These instabilities are mainly due to the fact that finite representations of BCLFs involve huge numbers with nearly equal magnitudes which are subtracted from each other during the calculation. As a result use of fixed precision arithmetic for differencing

such numbers makes the numerical algorithm become highly unstable. On the other hand, because the coefficients in the finite expansion are integers, they are well suited for carrying benchmark computations using symbolic algebra systems with high precision arithmetic.

To avoid the aforementioned drawbacks inherent in the finite representation of BCLFs, the most obvious choice is to use some infinite series whose terms are in general numerically stable. In the case of interest, an infinite series may readily be obtained by combining the infinite series representation of the modified Bessel function $\mathbf{I}_\nu(z)$ with the closed analytical form of $\mathbf{K}_\nu(z)$ involved in equation (10). This yields

$$\mathcal{A}^n_{l+1/2}(\zeta,a,r) = (-1)^n \frac{2}{\zeta^n}\left(\frac{\rho_<}{\rho_>}\right)^{l+1/2} \exp(-\zeta\rho_>) \sum_{p=0}^{+\infty} \sum_{s=\max(0,n-2p)}^{l+n} \mathbf{T}^{l,n}_{p,s} (\zeta\rho_<)^{2p} (\zeta\rho_>)^s \quad (13)$$

where

$$\mathbf{T}^{l,n}_{p,s} = n! \frac{(l+p+1)!}{p!(2l+2p+2)!} \frac{(-1)^s}{(2p-n+s)!} \left[\sum_{q=q_{\min}}^{q_{\max}} (-1)^q \frac{2^q (2l-q)!}{q!(l-q)!} \frac{(2p+q)!}{(s-q)!(n-s+q)!} \right] \quad (14)$$

in which, $q_{\min} = \max(0, s-n)$ and $q_{\max} = \min(l, s)$. The above expansion, albeit stable for numerical purposes, presents two unappealing features [1]. The series involves $\rho_<$ and $\rho_>$ meaning that during the final computational step, one has to split the integration domain $[0, \infty)$ into several subdomains. As a result, the number of domains that need to be considered grows (in the worst case) as 2^B, where B is the number of BCLFs involved in the final radial integral [2]. The definition of $\mathbf{T}$ matrix elements is complicated making any convergence analysis of the corresponding series representation of BCLFs rather difficult.

In the following, it is our aim to investigate the possibility and advantages of using a symmetrical representation of $\mathcal{A}^n_{\lambda+1/2}(\zeta,a,r)$, i.e. in which the variables $\rho_<$ and $\rho_>$ are interchangeable. According to [10, p 98], $\mathcal{A}^0_{\lambda+1/2}(\zeta,a,r)$ may be represented by various semi-infinite integrals whose integrands have the property of being symmetrical with respect to the variables r and a. Hence, starting with the following integral representation of $\mathcal{A}^0_{l+1/2}(\zeta,a,r)$:

$$\mathcal{A}^0_{l+1/2}(\zeta,a,r) = \frac{1}{2}\int_0^{+\infty} \mathbf{I}_{l+1/2}\left[\frac{ar}{2u}\right] \exp\left\{-\zeta^2 u - \frac{a^2+r^2}{4u}\right\} \frac{\mathrm{d}u}{u} \quad (15)$$

it may readily be seen that its derivatives of arbitrary orders with respect to ζ may be obtained effortlessly by noting that the differentiation operator $(-\partial/\partial\zeta)^n$ will only act on the first part of the exponential term leading to a Hermite polynomial which enters the formalism under the well-known Rodrigues form,

$$\mathrm{H}_n(z) = (-1)^n \exp(z^2)\left(\frac{\mathrm{d}}{\mathrm{d}z}\right)^n \exp(-z^2) = n! \sum_{m=0}^{\lfloor n/2 \rfloor} (-1)^m \frac{(2z)^{n-2m}}{m!2^m(n-2m)!}. \quad (16)$$

Further straightforward algebraic manipulations and simplifications finally yield

$$\mathcal{A}^n_{l+1/2}(\zeta,a,r) = \frac{1}{2}\int_0^{+\infty} \sqrt{u^n}\mathrm{H}_n(\zeta\sqrt{u})\mathbf{I}_{l+1/2}\left(\frac{ar}{2u}\right) \exp\left\{-\zeta^2 u - \frac{a^2+r^2}{4u}\right\} \frac{\mathrm{d}u}{u}. \quad (17)$$

Now, if the modified Bessel function $\mathbf{I}_{l+1/2}(z)$ occurring in the above equation is expanded according to [10, p 66] one obtains an infinite series involving a semi-infinite integral [10, p 85] that is related to the Bessel function $\mathbf{K}_\nu(z)$. After some elementary simplifications

one obtains a pointwise converging series that can be written as

$$\mathcal{A}^n_{l+1/2}(\zeta,a,r) = n!\left[\zeta\frac{ar}{2\sqrt{a^2+r^2}}\right]^{l+1/2}\sqrt{(a^2+r^2)^n}\sum_{p=0}^{\lfloor n/2\rfloor}(-1)^p\frac{(2\zeta\sqrt{a^2+r^2})^{-p}}{p!(n-2p)!}$$
$$\times\sum_{q=0}^{+\infty}\frac{1}{q!\Gamma(l+q+3/2)}\left[\zeta\frac{ar}{2\sqrt{a^2+r^2}}\right]^{2q}\mathbf{K}_{l+p-n+2q+1/2}[\zeta\sqrt{a^2+r^2}]. \tag{18}$$

In the same context, another pointwise converging series representation of BCLFs might be obtained from equation (17). Indeed, substituting to the function $\exp(-z)\mathbf{I}_{l+1/2}(z)$ its series representation [10, p 283] and following the same method used in the previous case, we arrive at

$$\mathcal{A}^n_{l+1/2}(\zeta,a,r) = \frac{n!}{\sqrt{\pi}}\left[2\zeta\frac{ar}{a+r}\right]^{l+1/2}(a+r)^n\sum_{p=0}^{\lfloor n/2\rfloor}(-1)^p\frac{[2\zeta(a+r)]^{-p}}{p!(n-2p)!}$$
$$\times\sum_{q=0}^{+\infty}\frac{(l+q)!}{(2l+q+1)!}\left[2\zeta\frac{ar}{a+r}\right]^q\mathbf{K}_{l-n+p+q+1/2}\left[\zeta(a+r)\right]. \tag{19}$$

Here, it is worth noting that in contrast to the series given in equation (13), the above infinite expansions are symmetrical with respect to r and a. This may be of some advantage when computing multicentre integrals since the above representations, i.e. integral and series forms, would allow us to use the same analytical form of BCLFs over the whole integration range. The usefulness of the symmetrical integral (17) and series (18) representations will be addressed in a subsequent section devoted to numerical experiments. As a last note, let us mention that the integral representation (17) is a suitable tool to check for recurrence relations among BCLFs of various orders. For instance, using the recurrence relations between Hermite polynomials and modified Bessel functions,

$$\mathrm{H}_{n+1}(x) = 2x\mathrm{H}_n(x) - 2n\mathrm{H}_{n-1}(x) \qquad \text{and} \qquad \mathbf{I}_{\nu-1} - \mathbf{I}_{\nu+1} = \frac{2\nu}{z}\mathbf{I}_\nu(z) \tag{20}$$

we can derive the following:

$$\mathcal{A}^{n+1}_l(\zeta,a,r) = \frac{ar}{2(2l+1)}\int_0^\infty[\zeta\sqrt{u^n}\mathrm{H}_n(\zeta\sqrt{u}) - \sqrt{u^{n-1}}\mathrm{H}_{n-1}(\zeta\sqrt{u})]$$
$$\times\left[\mathbf{I}_{l-1/2}\left(\frac{ar}{2u}\right) - \mathbf{I}_{l+3/2}\left(\frac{ar}{2u}\right)\right]$$
$$= \frac{ar}{2l+1}\left[\mathcal{A}^n_{l-1/2}(\zeta,a,r) - \mathcal{A}^n_{l+3/2}(\zeta,a,r) - \mathcal{A}^{n-1}_{l-1/2}(\zeta,a,r) - \mathcal{A}^{n-1}_{l+3/2}(\zeta,a,r)\right]. \tag{21}$$

It appears, however, that BCLFs do not satisfy a recurrence relation in which only the parameter l varies. This makes the quest for an efficient numerical procedure to evaluate BCLFs even more important since such a procedure will be called thousands of times in a real case calculation, i.e. molecular property determination.

4. Numerical evaluation of generalized Löwdin alpha functions

Combination of addition theorems, namely those of equations (11) and (10) with the Laplace expansion [91 (equations 12.180 and 12.181)] of the Coulomb operator $1/|\mathbf{r}-\mathbf{r}'|$ is at the heart of the so-called single centre expansion method for evaluating multicentre integrals. This approach allows multicentre integrals to be expressed as infinite series, the terms of

which involve a radial integral (RI), that is to say an integral (simple or double) over the radial variable(s) of the electron(s). An efficient algorithm directed to the evaluation of such integrals is therefore one of the first problems that should be dealt with. To be more precise, the difficulties related to the elaboration of such an algorithm stem from the analytical complexity of the integrand occurring in RIs which may involve, amongst other functions, one, two or three BCLFs. In fact, such complexity makes it impossible to obtain simple closed forms for RIs and this leaves one no choice but to rely on numerical integration techniques to perform the numerical work. In this respect, the evaluation of the integrand (involving BCLFs) in the RIs must be done efficiently.

4.1. Convergence analysis of the symmetrical series expansion of BCLFs

To start, let us first recap two principal results regarding the convergence of a sequence of numbers,

1. $$\lim_{n\to+\infty} \frac{S_{n+1}-s}{S_n-s} = \rho \tag{22}$$

   where $S_n = \sum_{k=0}^{n} a_k$ stands for the nth partial sum of the series a convergent series the limit of which is S. According to Wimp [92, p 6], the series S converges linearly if $0 < |\rho| < 1$ and logarithmically if $\rho = 1$.
2. The value of the previous definition is more theoretical than practical since the limit of the series is assumed to be known. For practical purposes, Wimp has also shown that if term a_n of the series to be summed has a Poincaré type asymptotic expansion of the form,

   $$a_n = \lambda^n n^{\Theta}\left[\alpha_0 + \frac{\alpha_1}{n} + \frac{\alpha^2}{n^2} + \cdots\right] \qquad \text{with} \qquad \begin{cases}\alpha_0 \neq 0\\ n \to +\infty\end{cases} \tag{23}$$

   then the series converges linearly if $|\lambda| < 1$ and logarithmically if $\lambda = 1$ and $\mathrm{Re}(\Theta) < -1$.

From a computational standpoint, a linearly convergent series can be evaluated by direct summation of its terms although it is always advantageous to select an appropriate method to speed up the process. As for logarithmic convergent series, direct summation cannot yield the accuracy required in practice within a reasonable time and for such particular cases use of convergence acceleration techniques is crucial.

In the following, let us first establish a Poincaré type asymptotic representation for the terms involved in the expansion (18). For such a purpose we will make use of the asymptotic representation of the modified Bessel function $\mathbf{K}_\nu(z)$ the leading term of which can be written as [93, 94]

$$\mathbf{K}_\nu(z) \sim \frac{1}{2}\left(\frac{2}{z}\right)^{\nu}\Gamma(\nu) \tag{24}$$

in which, $\nu \to +\infty$. At this point the qth term of the series expansion (18) can be expanded asymptotically as

$$\mathcal{A}^n_{l+1/2}\big|_q \sim \frac{\Gamma(l+2q+1/2)}{q!\Gamma(l+q+3/2)}\left[\left(\frac{ar}{a^2+r^2}\right)\right]^q \times \sum_{p=0}^{\lfloor n/2\rfloor}\frac{(-)^p}{p!(n-2p)!}\frac{\Gamma(l+p-n+2q+1/2)}{\Gamma(l+2q+1/2)}[\zeta\sqrt{a^2+r^2}]^{n-2p} \tag{25}$$

where $q \to +\infty$. Now, if the ratio $\Gamma(z+\alpha)/\Gamma(z+\beta)$ as $z \to +\infty$ is approximated by the leading term of its asymptotic expansion that is

$$\frac{\Gamma(z+\alpha)}{\Gamma(z+\beta)} \sim z^{\alpha-\beta} \qquad \text{as} \quad z \to +\infty \tag{26}$$

the inner sum, i.e. over p, involved in the asymptotic expansion of $\mathcal{A}^n_{l+1/2}\big|_q$ can then be written as,

$$S_{n,l,q,p} \sim \sum_{p=0}^{\lfloor n/2 \rfloor} \frac{(-1)^p}{p!(n-2p)!} \left(l+2q+\frac{1}{2}\right)^{p-n} [\zeta^2\sqrt{a^2+r^2}]^{n-2p}. \tag{27}$$

Keeping in mind that $p-n<0$, the term $(l+2q+1/2)^{p-n} \sim (l+2q+1/2)^{-\lfloor (n+1)/2 \rfloor}$ for large values of q (which is the leading term of the terms depending on p). With the previous approximation in hand, we can finally derive the asymptotic form of the term $S_{n,l,q,p}$ as

$$S_{n,l,q,p} \sim \left(l+2q+\frac{1}{2}\right)^{-\lfloor (n+1)/2 \rfloor} \underbrace{\sum_{p=0}^{\lfloor n/2 \rfloor} (-1)^p \frac{1}{p!(n-2p)!} [\zeta^2\sqrt{a^2+r^2}]^{n-2p}}_{\text{Constant}}. \tag{28}$$

Inserting the above asymptotic expansion back into equation (25) yields the following:

$$\mathcal{A}^n_{l+1/2}\big|_q \sim \left(l+2q+\frac{1}{2}\right)^{-\lfloor (n+1)/2 \rfloor} \frac{\Gamma(l+2q+1/2)}{q!\Gamma\left(l+q+\frac{3}{2}\right)} \left[\left(\frac{ar}{a^2+r^2}\right)^2\right]^q \tag{29}$$

in which the constant due the summation over p was deliberately omitted. We next use the Sterling asymptotic expansion of the Γ functions [95] (equation 6.137),

$$\Gamma(z) \sim \sqrt{2\pi} z^{z-1/2} \exp(-z) \left[1+\frac{1}{12z}+\frac{1}{288z^2}+\cdots\right] \qquad z \to +\infty \tag{30}$$

to finally obtain, after some algebraic simplifications, the Poincaré asymptotic representation of the general term of the series (18),

$$\mathcal{A}^n_{l+1/2}\big|_q \sim q^{-[(n+1)/2]-3/2} \left[\left(\frac{2ar}{a^2+r^2}\right)^2\right]^q \left[1-\frac{1}{6q}-\cdots\right] \tag{31}$$

where the multiplying constant terms have been omitted. Comparing the above equation with equation (23), it is clear that for $(2ar)/(a^2+r^2)<1$, i.e. $r \neq a$, the series converges linearly and for $(2ar)/(a^2+r^2)=1$ corresponding to $a=r$, the convergence will be logarithmic. Note that using the exact same approach as developed above, we can show that the series of equation (19) behave in the same way as (18) as far as convergence is concerned. As for the computational procedure to be used in order to compute the terms of the series (18) and (19), it appears that this could be done recursively. Indeed, after some analysis, it was found that high order terms in both series can conveniently be generated by means of two auxiliary sequences. As a side note, we point out that it is also possible to use a single recurrence relation involving four consecutive terms. Thus, in the case of the series (18) these sequences are the following:

$$\begin{cases} U_q = \dfrac{1}{q!\Gamma(l+q+3/2)} \left[\zeta \dfrac{ar}{2\sqrt{a^2+r^2}}\right]^{2q} \mathbf{K}_{l+p-n+2q+1/2}[\zeta\sqrt{a^2+r^2}] \\ V_q = \dfrac{1}{q!\Gamma(l+q+3/2)} \left[\zeta \dfrac{ar}{2\sqrt{a^2+r^2}}\right]^{2q} \mathbf{K}_{l+p-n+2q+3/2}[\zeta\sqrt{a^2+r^2}]. \end{cases} \tag{32}$$

Now, using the 3-term recurrence relation of the modified Bessel functions $\mathbf{K}_\nu(z)$ [10, p 67] and after simple algebraic simplifications one obtains

$$\begin{cases} U_{q+1} = \dfrac{[(\zeta ar)/(2\sqrt{a^2+r^2})]^2}{(q+1)(l+q+3/2)} U_q + \dfrac{[(\zeta ar)/(2\sqrt{a^2+r^2})]^2}{(q+1)(l+q+3/2)} \dfrac{2(l+p-n+2q+3/2)}{\zeta\sqrt{a^2+r^2}} V_q \\ V_{q+1} = \dfrac{[(\zeta ar)/(2\sqrt{a^2+r^2})]^2}{(q+1)(l+q+3/2)} V_q + \dfrac{2(l-p+n+2q+5/2)}{\zeta\sqrt{a^2+r^2}} U_{q+1}. \end{cases} \tag{33}$$

As for the initialization of the procedure, the values of U_0 and V_0 have to be computed and this can also be done recursively. Indeed, using the recurrence relation connecting $\mathbf{K}_{\nu-1}(z)$, $\mathbf{K}_\nu(z)$ and $\mathbf{K}_{\nu+1}(z)$ [77, p 79] we obtain

$$W_{l+1} = \frac{1}{(l+3/2)(l+1/2)} W_{l-1} + \frac{2(l+p-n)+1}{l+3/2} \frac{1}{\zeta\sqrt{a^2+r^2}} W_l. \tag{34}$$

Clearly the above relationship can be used to compute both U_0 and V_0 since $U_0 = W_l$ while $V_0 = (l+1/2)W_{l+1}$. To summarize the computational procedure, the values of U_0 and V_0 are first computed using equation (34) which is then followed by the evaluation of the terms $U_1, V_1, U_2, V_2, \ldots$ by means of equation (33).

5. Numerical results

Since the most difficult multicentre integrals, i.e. three-centre one-electron and exchange integrals are represented by infinite series which ultimately will involve high order BCLFs an important question to ask is: how fast can such functions be calculated? In our first experiment, cf table 1, we have used the series representation of equation (18) to evaluate $\mathcal{A}^1_{1/2}(1.5, 3, r)$ and $\mathcal{A}^1_{10+1/2}(1.5, 3, r)$ for various values of r. The values of r were chosen to be the nodes of a Gauss–Legendre quadrature allowing us to simulate what happens in practice, i.e. numerical integration within adjacent subdomains. As predicted by the analysis in the previous section, the convergence of the series representation (18) deteriorates badly as one goes near the cusp since the series becomes logarithmically convergent. The discussion about linear and logarithmic convergence being somewhat abstract, it is of interest to give a simple example that can help illustrate the difficulties. For such a purpose, let r_n be the residual between the limit of the series to be summed and its nth partial sum. Equation (22) can then be re-written as

$$\frac{r_{n+1}}{r_n} = \rho_n. \tag{35}$$

Now, using the above equation, one can estimate the number of terms p to be computed in order to gain an extra significant digit. Indeed, assuming that the ratio of equation (35) is approximately constant for n larger than some N we can write

$$\frac{r_{n+1}}{r_n} = \tilde{\rho}, \qquad \text{for} \quad n > N \quad \Longrightarrow \quad r_{N+p} = \tilde{\rho}^p r_N. \tag{36}$$

Using the second of the above equations, we can estimate the number of extra terms, p, to be computed in order to gain an extra significant digit which in other words corresponds to a reduction of the residual error by a factor of 10 at least, i.e. $r_{N+p} \approx 0.1 r_N$ one obtains.

$$p \approx -\frac{1}{\log_{10}\tilde{\rho}}. \tag{37}$$

Table 1. Effect of the u transformation on the convergence rate of the infinite series (18) representing the BCLFs $\mathcal{A}^1_{l+1/2}(3/2, 3, r)$ where $\lambda = 0$ and $\lambda = 10$. The values of r are a subset of the nodes generated by a Gauss–Legendre quadrature of order 32 in the interval [0, 3]. Numbers between parentheses denote powers of 10.

r	$\mathcal{A}^1_{1/2}$	N_0	u_9 (S_{70})	$\mathcal{A}^1_{10+1/2}$	N_{10}	u_9 (S_{70})
1.002 197	2.336 841 375 2977 (−2)	35	2.336 841 375 2977 (−2)	1.807 316 606 7480 (−7)	29	1.807 316 606 7482 (−7)
1.141 069	2.625 491 120 1400 (−2)	43	2.625 491 120 1400 (−2)	6.935 626 032 4428 (−7)	37	6.935 626 032 4430 (−7)
1.283 292	2.946 993 614 9620 (−2)	54	2.946 993 614 9620 (−2)	2.329 367 006 7865 (−6)	48	12.329 367 006 7866 (−6)
1.427 539	3.302 749 829 4499 (−2)	68	3.302 749 829 4499 (−2)	6.941 543 421 5744 (−6)	62	6.941 543 421 5745 (−6)
1.572 461	3.692 048 350 4673 (−2)	87	3.692 048 350 4673 (−2)	1.855 643 089 3949 (−5)	81	1.855 643 089 3949 (−5)
1.716 708	4.111 464 578 6874 (−2)	113	4.111 464 578 6874 $(-2)_9$	4.489 204 357 3348 (−5)	107	4.489 204 357 3348 $(-5)_9$
1.858 931	4.554 367 606 9479 (−2)	149	4.554 367 606 9479 $(-2)_9$	9.898 270 763 2397 (−5)	143	9.898 270 763 2397 $(-5)_7$
1.997 803	5.010 671 832 2757 (−2)	201	5.010 671 832 2757 $(-2)_7$	2.000 589 293 5521 (−4)	195	2.000 589 293 5521 $(-4)_6$
2.132 027	5.466 990 958 0880 (−2)	276	5.466 990 958 0880 $(-2)_5$	3.723 885 674 2346 (−4)	270	3.723 8856742345 $(-4)_4$
2.260 350	5.907 338 974 9205 (−2)	389	5.907 338 974 9209 $(-2)_4$	6.408 377 776 2497 (−4)	383	6.408377776 3127 $(-4)_3$
2.381 574	6.314 459 694 9428 (−2)	566	6.314 459 695 0975 $(-2)_3$	1.022 888 434 2960 (−3)	560	1.022888435 5859 $(-3)_3$
2.494 566	6.671 746 331 7550 (−2)	855	6.671 746 344 0424 $(-2)_2$	1.518 791 623 3106 (−3)	849	1.5187917 193934 $(-3)_2$
2.598 273	6.965 546 420 6049 (−2)	1 351	16.965 546 852 1449 $(-2)_2$	2.103 730 331 5661 (−3)	1 345	2.1037337 047017 $(-3)_1$
2.691 726	7.187 470 075 7783 (−2)	2 265	7.187 477 517 8110 $(-2)_2$	2.726 887 164 1746 (−3)	2 259	2.726 946 771 1057 $(-3)_1$
2.774 051	7.336 188 064 6265 (−2)	4 102	7.336 252 344 6038 $(-2)_1$	3.320 748 940 8629 (−3)	4 096	3.321 283 792 4541 $(-3)_1$
2.844 482	7.418 185 122 3704 (−2)	8 262	7.418 458 077 4215 $(-2)_1$	3.819 582 876 8676 (−3)	8 256	3.821 956 446 7457 $(-3)_1$
2.902 359	7.447 070 889 4180 (−2)	19 441	7.447 614 609 6178 $(-2)_1$	4.180 531 008 8260 (−3)	19 435	4.185 461 548 5184 $(-3)_0$
2.947 143	7.441 348 437 9159 (−2)	58 663	7.441 820 624 6767 $(-2)_1$	4.397 473 238 8610 (−3)	58 657	4.401 892 143 8087 $(-3)_0$
2.978 417	7.420 938 912 2025 (−2)	280 690	7.421 085 631 1962 $(-2)_1$	4.499 606 282 0439 (−3)	280 684	4.500 995 911 7665 $(-3)_0$
2.995 896	7.403 141 092 6667 (−2)	4201 290	7.403 142 125 7652 $(-2)_1$	4.533 762 739 0897 (−3)	4201 283	4.533 756 099 4439 $(-3)_0$

[1] Columns (3) and (6) represent the number of terms required to achieve an accuracy of 10^{-15}.
[2] Subscripts occurring in columns (4) and (7) indicate the number of exact digits obtained after 70 terms.
[3] Underlined figures correspond to exact digits.

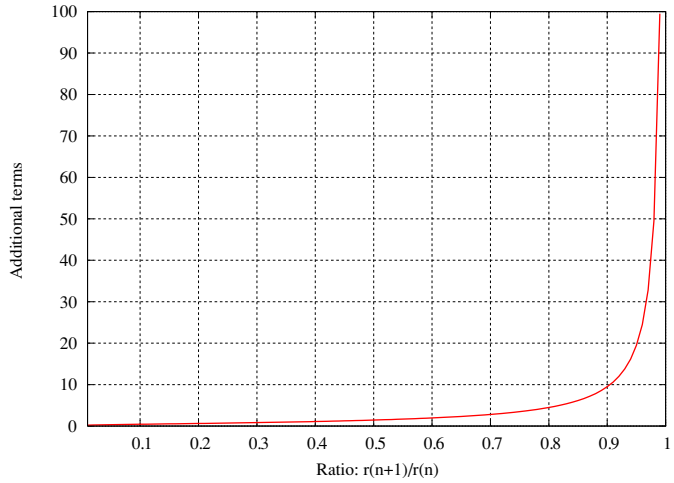

Figure 1. Number of terms to be evaluated to gain an extra significant digit as a function of the ratio (36). Note the extreme computational difficulty as the series goes becomes logarithmically convergent.

A plot (figure 1) of the above relationship clearly demonstrates the immense computational challenge one faces when direct summation is used to estimate the limit of an infinite series especially when it is logarithmically convergent. Even for linearly convergent series direct summations can be time consuming because of the number of terms required to ensure an accurate result. To remedy the difficulties inherent to direct summation procedures, the option is to make use of a suitable convergence accelerator.

In the case under study, equation (18) represents a sum of monotonic series and such a situation is ideal for the application of the so-called Levin u transformation which is defined as

$$u_k(S_n) = \frac{N_{k,n}}{D_{k,n}} \tag{38}$$

where $N_{k,n}$ and $D_{k,n}$ are computed recursively using the following 3-term relationship [96 (equation 7.2-8)]:

$$\mathcal{L}_{k+1}^{(n)}(\beta) = \mathcal{L}_k^{(n+1)}(\beta) - \frac{\beta+n}{\beta+n+k+1}\left(\frac{\beta+n+k}{\beta+n+k+1}\right)^{k-1}\mathcal{L}_k^{(n)}. \tag{39}$$

As for the initialization of the above relationship, the following is used:

$$\mathcal{L}_{0,n} = \begin{cases} \dfrac{S_n}{(\beta+n)^l a_n} & \text{for the numerator} \quad N_{k,n} \\ \dfrac{1}{(\beta+n)^l a_n} & \text{for the denominator} \quad D_{k,n}. \end{cases} \tag{40}$$

It is important to note that the above equation yields the Levin u transformation if $l = 1$ holds. Mild extensions of the general Levin transformation can be obtained for $l > 1$ [96, equation (7.1-8)]. For the numerical experiments considered in table 1, the parameters β and l occurring as part of the initialization step were respectively set to 1 and 3. Note that such a value was experimentally determined after trying $l = 1$ and $l = 2$ and noting that $l = 3$ gave slightly better results than in other cases. As a result of applying the Levin u transformation, a dramatic improvement in the convergence can be noted as can be seen from the results shown in columns 4 and 7 of table 1. However, in the vicinity of the cusp

the accuracy is still far from acceptable since even after applying the u transformation to the first 70 terms of the series (18), we only gained 3 to 4 additional significant digits. Of course, computing more terms of the original series is always an option that would produce more exact digits but this would slow the resulting computational procedures making them too much time consuming to be used in practice. On the other hand, since equation (18) involves monotonic series with positive terms, it may be used for benchmarking because of its numerical stability.

As an alternative to the symmetrical series expansion (18), one can use the integral representation (17) of BCLFs for their evaluation. Needless to say that in such a case an appropriate numerical integration technique is of paramount importance. This approach is expected to be faster (on average) since the number of operations involved in the computation is constant regardless of the values taken by r, i.e. near or away from the cusp. As a case study, the BCLF $\mathcal{A}^1_{l+1/2}(\zeta, a, r)$ is chosen since as mentioned in section 2 when an arbitrary STO is expanded within the one-centre expansion method it always amounts to expanding either the 1s orbital or the Yukawa potential. When considering the integral representation of $\mathcal{A}^1_{l+1/2}(\zeta, a, r)$,

$$\mathcal{A}^1_{l+1/2}(\zeta, a, r) = \zeta \int_0^{+\infty} \mathbf{I}_{l+1/2}\left[\frac{ar}{2u}\right] \exp\left\{-\zeta^2 u - \frac{a^2+r^2}{4u}\right\} \mathrm{d}u \tag{41}$$

it can be seen that the integrand goes to zero for $u \longrightarrow 0$ and $u \longrightarrow +\infty$ which indicates that the integrand has at least one extremum in the domain $[0, +\infty)$. As a confirmation of this, the integrand in the above equation was plotted for different values of λ and for two different values of r. Figure 2 clearly shows that the function to be integrated has a distorted bell shape which is the major contributor to the integral and as one goes farther the contribution becomes negligible. As a consequence, it is expected that a crude Gauss–Laguerre quadrature will not be sufficiently accurate since several nodes are located in the regions which contribute marginally to the final result.

To increase the accuracy of our computation, we have chosen a hybrid method which combines Gauss–Legendre and Gauss–Laguerre quadratures. To maximize the performance of such an approach, it is advisable to first determine, albeit approximately, the location of the extremum of the integrand so to concentrate the node within such a region. Of course, the issue of locating the maximum of the integrand at a low computational cost is an issue that needs to be resolved first. Because in practice, only BCLFs of the form $\mathcal{A}^0_{l+1/2}(\zeta, a, r)$ and $\mathcal{A}^1_{l+1/2}(\zeta, a, r)$ are needed, we will use the last of these to illustrate the method used to approximately locate the maximum of the integrand. Starting with the derivative we have

$$\mathcal{F}'_{l+1/2}(\zeta, a, r|u) = \frac{\mathrm{d}}{\mathrm{d}u}\mathbf{I}_{l+1/2}\left[\frac{ar}{2u}\right] + \left(-\zeta^2 u - \frac{a^2+r^2}{4u}\right)\mathbf{I}_{l+1/2}\left[\frac{ar}{2u}\right] \tag{42}$$

in which the exponential term was removed since it does not affect the sign of the derivative. Using the recurrence relations[77, p 79],

$$\mathbf{I}'_\nu(z) = \frac{\nu}{z}\mathbf{I}_\nu(z) + \mathbf{I}_{\nu+1}(z) \qquad \text{and} \qquad \mathbf{I}'_\nu(z) = -\frac{\nu}{z}\mathbf{I}_\nu(z) + \mathbf{I}_{\nu-1}(z) \tag{43}$$

and the fact that modified Bessel functions $\mathbf{I}_\nu(z)$ decrease with increasing values of ν, we can finally bracket the derivative of the integrand as follows:

$$\begin{aligned}\left(-\zeta^2 - \frac{l+1/2}{u} + \frac{(a-r)^2}{4u^2}\right)\mathbf{I}_\nu\left[\frac{ar}{2u}\right] &< \mathcal{F}'_{l+1/2}(\zeta, a, r|u) \\ &< \left(-\zeta^2 + \frac{l+1/2}{u} + \frac{(a-r)^2}{4u^2}\right)\mathbf{I}_\nu\left[\frac{ar}{2u}\right].\end{aligned} \tag{44}$$

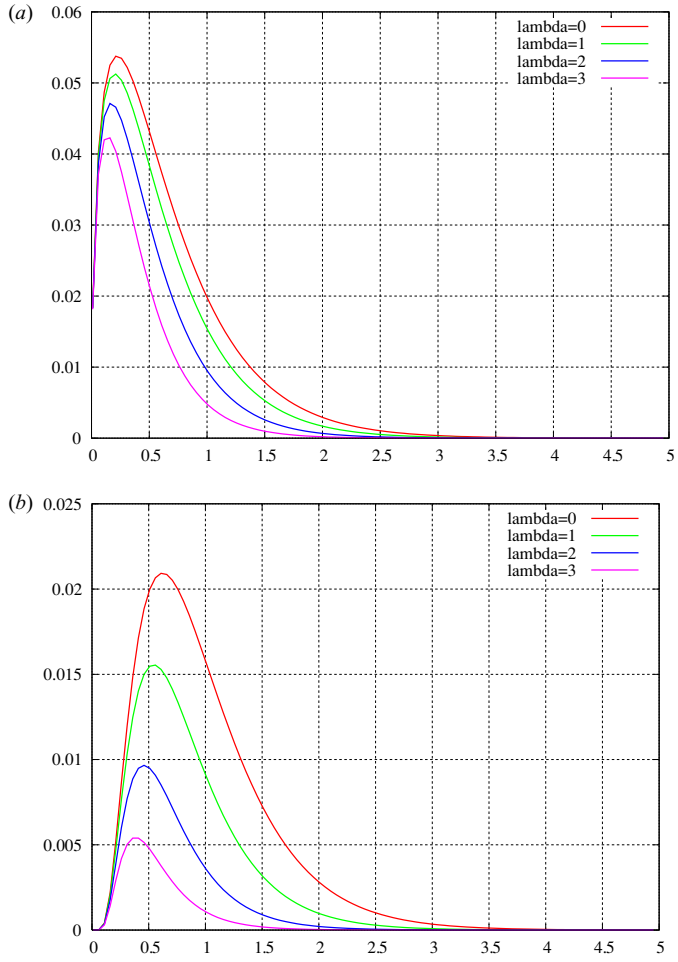

Figure 2. Shape of the integrand occurring in equation (17) for $n = 1$. (a) $\zeta = 1, \alpha = 3$ and $r = 1.5$, (b) $\zeta = 1, a = 3$ and $r = 2.99$.

The positive roots of the bracketing functions can easily be computed as

$$\begin{cases} u_0^{\text{lower}} = \dfrac{-(l+1/2) + \sqrt{(l+1/2)^2 + \zeta^2(a^2+r^2)}}{2\zeta^2} \\ u_0^{\text{upper}} = \dfrac{(l+1/2) + \sqrt{(l+1/2)^2 + \zeta^2(a^2+r^2)}}{2\zeta^2}. \end{cases} \tag{45}$$

From a computational standpoint, $u_{\max}$ can, as a first guess, be approximated by the positive root of either the lower or the upper bracketing functions (44). Refining such an extremum using a standard method for root finding is only costly when ran for the first time, i.e. the first value of the r. In fact, since the interest is to generate BCLFs for a set of increasing values of r, i.e. $\{r_1 < r_2 < \cdots < r_n\}$, it was found that (cf figure 2) the root of $\mathcal{F}'_{l+1/2}(\zeta, a, r_i|u)$ can be used as an approximation to the root of $\mathcal{F}'_{l+1/2}(\zeta, a, r_{i+1}|u)$. In such a case, the computational cost of the refinement procedure becomes marginal. In table 2, we have listed the

Table 2. Comparison of the numerical quadrature obtained by: (1) a combination Gauss–Legendre/Gauss–Laguerre and (2) a pure Gauss–Laguerre quadrature(s)

r	$\mathcal{A}^1_{1/2}$	LL(80, 16)[a]	Lag(64)[b]	$\mathcal{A}^1_{10+1/2}$	LL(80, 16)[a]	Lag(64)[b]
1.002 197	2.336 841 375 2977 (−2)	2.336 841 375 2977 (−2)	2.336 851 3605 (−2)	1.807 316 606 7480 (−7)	1.807 316 606 7480 (−7)	1.756 470 005 (−7)
1.141 069	2.625 491 120 1400 (−2)	2.625 491 120 1400 (−2)	2.625 499 3278 (−2)	6.935 626 032 4428 (−7)	6.935 626 032 4428 (−7)	6.910 219 9494 (−7)
1.283 292	2.946 993 614 9620 (−2)	2.946 993 614 9620 (−2)	2.946 983 0771 (−2)	2.329 367 006 7865 (−6)	2.329 367 006 7865 (−6)	2.340 333 9920 (−6)
1.427 539	3.302 749 829 4499 (−2)	3.302 749 829 4499 (−2)	3.302 712 7694 (−2)	6.941 543 421 5744 (−6)	6.941 543 421 5744 (−6)	7.016 642 2937 (−6)
1.572 461	3.692 048 350 4673 (−2)	3.692 048 350 4670 (−2)	3.692 021 6251 (−2)	1.855 643 089 3949 (−5)	1.855 643 089 3949 (−5)	1.878 274 7233 (−5)
1.716 708	4.111 464 578 6874 (−2)	4.111 464 578 6873 (−2)	4.111 525 4373 (−2)	4.489 204 357 3348 (−5)	4.489 204 357 3348 (−5)	4.524 139 0098 (−5)
1.858 931	4.554 367 606 9479 (−2)	4.554 367 606 9472 (−2)	4.554 514 6573 (−2)	9.898 270 763 2397 (−5)	9.898 270 763 2397 (−5)	9.894 376 5548 (−5)
1.997 803	5.010 671 832 2757 (−2)	5.010 671 832 2760 (−2)	5.010 687 3211 (−2)	2.000 589 293 5521\ (−4)	2.000 589 293 5525 (−4)	1.986 111 9797 (−4)
2.132 027	5.466 990 958 0880 (−2)	5.466 990 958 0862 (−2)	5.466 631 5712 (−2)	3.723 885 674 2346 (−4)	3.723 885 674 2349 (−4)	3.695 358 8880 (−4)
2.260 350	5.907 338 974 9205 (−2)	5.907 338 974 9210 (−2)	5.906 909 8196 (−2)	6.408 377 776 2497 (−4)	6.408 377 776 2492 (−4)	6.401 259 0114 (−4)
2.381 574	6.314 459 694 9428 (−2)	6.314 459 694 9409 (−2)	6.314 867 713 4 (−2)	1.022 888 434 2960 (−3)	1.022 888 434 2935 (−3)	1.029 773 8798 (−3)
2.494 566	6.671 746 331 7550 (−2)	6.671 746 331 7542 (−2)	6.673 136 3671 (−2)	1.518 791 623 3106 (−3)	1.518 791 623 3165 (−3)	1.530 748 2344 (−3)
2.598 273	6.965 546 420 6049 (−2)	6.965 546 420 6102 (−2)	6.966 080 4110 (−2)	2.103 730 331 5661\ (−3)	2.103 730 331 5628 (−3)	2.103 932 2756 (−3)
2.691 726	7.187 470 075 7783 (−2)	7.187 470 075 7726 (−2)	7.185 523 4665 (−2)	2.726 887 164 1746 (−3)	2.726 887 164 1742 (−3)	2.704 428 1610 (−3)
2.774 051	7.336 188 064 6265 (−2)	7.336 188 064 6301 (−2)	7.333 539 6327 (−2)	3.320 748 940 8629 (−3)	3.320 748 940 8630 (−3)	3.295 148 8466 (−3)
2.844 482	7.418 185 122 3704 (−2)	7.418 185 122 3851 (−2)	7.417 675 4988 (−2)	3.819 582 876 8676 (−3)	3.819 582 876 8682 (−3)	3.816 825 3305 (−3)
2.902 359	7.447 070 889 4180 (−2)	7.447 070 889 4205 (−2)	7.448 723 5156 (−2)	4.180 531 008 8260 (−3)	4.180 531 008 8459 (−3)	4.199 012 5597 (−3)
2.947 143	7.441 348 437 9159 (−2)	7.441 348 437 9175 (−2)	7.443 498 8721 (−2)	4.397 473 238 8610 (−3)	4.397 473 238 8298 (−3)	4.420 453 7948 (−3)
2.978 417	7.420 938 912 2025 (−2)	7.420 938 912 2001 (−2)	7.422 788 8807 (−2)	4.499 606 282 0439 (−3)	4.499 606 282 0445 (−3)	4.519 406 8730 (−3)
2.995 896	7.403 141 092 6667 (−2)	7.403 141 092 5701 (−2)	7.404 832 3493 (−2)	4.533 762 739 0897 (−3)	4.533 762 739 0751 (−3)	4.551 938 9339 (−3)

[a] Computation using a combination of Gauss–Legendre of order 64 within $[0, 2u_{\max}]$ and Gauss–Laguerre in $[2u_{\max}, +\infty)$.
[b] Computation using a Gauss–Laguerre of order 64 within $[0, +\infty)$.
Underlined figures correspond to exact digits.

computations performed with the methods described above, i.e. Gauss–Laguerre and the hybrid Gauss–Legendre/Laguerre quadratures. Clearly, the hybrid method yields the accuracy required by subsequent calculations of multicentre integrals and more importantly the complexity of the algorithm does not change regardless of the value of r being far or close to the cusp.

6. Concluding remarks

Within the framework of the so-called one-centre expansion method, the evaluation of multicentre integrals is carried out following two main approaches. In the first, multicentre integrals are first represented by closed analytical formulae or infinite series. Such closed formulae or series are then evaluated using suitable numerical procedures. As for the second category of methods, they combine to a certain extent numerical integration and analytical methods. As a consequence it becomes necessary to evaluate the Fourier coefficients (which only depend on ζ, a and r) occurring in the infinite series describing the displaced STO. In the present work, some analytical and numerical aspects of such coefficients, which are referred to as BCLFs, $\mathcal{A}^n_{l+1/2}(\zeta, a, r)$, were investigated. This work was motivated by the need to simplify the expressions of multicentre integrals which previously [89] had to be written as a sum of integrals. Because in each of these integrals a special analytical form had to be used, the computational procedures were rather cumbersome. In this paper, we have considered alternative routes in which BCLFs were represented by symmetrical forms allowing one to avoid splitting the radial integration domain $[0, +\infty)$, into several subdomains. The first of such symmetrical forms is a series expansion (18) in terms of Bessel functions $\mathbf{K}_\nu(\zeta\sqrt{a^2+r^2})$ which was found to be linearly convergent for $r \neq a$ and logarithmically convergent on the cusp $r = a$. From a numerical standpoint such a series cannot be efficiently used in practice since as one gets closer to the cusp the convergence deteriorates badly and even a convergence accelerator such as Levin u transformation would require a large number of terms to achieve an acceptable accuracy. For benchmarking purposes, we expect that the series expansion (18) can be safely used because of its numerical stability. The second symmetrical form we examined was the integral representation (17). It was found that by appropriately mixing Gauss–Legendre and Gauss–Laguerre numerical quadratures, BCLFs can in general be accurately computed (ten significant digits at least). To achieve such an accuracy, the range $[0, +\infty)$ is divided into two intervals $[0, 2u_{\max}]$ and $[2u_{\max}, +\infty)$ where Gauss–Legendre and Gauss–Laguerre quadratures were respectively applied. As for $u_{\max}$, it corresponds to the only extremum of the integrand in equation (41) which is first approximated by the one of the roots in equation (45) and then refined to be sufficiently close to the true extremum of the function to be integrated.

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