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Convergence analysis of the addition theorem of Slater orbitals and its application to three-center nuclear attraction integrals

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The mathematical foundation of the methods using addition theorems to evaluate multicenter integrals over Slater-type orbitals is actually well understood. However, many numerical aspects of such approaches still require further investigations. In the framework of these methods, multicenter integrals are generally represented by infinite series which under certain circumstances are very slowly convergent. Accordingly, the determination of the convergence type of such series is of great importance since it allows one to choose adequately the convergence accelerator to be used in the summation procedure. In this work, the convergence of the two-range addition theorem proposed by Barnett and Coulson [Philos. Trans. R. Soc. London, Ser. A **243**, 221 (1951)] is analyzed. The results obtained from this study are then applied to study the convergence of three-center nuclear integrals, and most importantly, to discuss the choice of the convergence accelerator to be used in the summation procedure. © *1998 American Institute of Physics.* [S0021-9606(98)00538-8]

I. INTRODUCTION

The Schrödinger equation is known to be exactly soluble only for some few quantum mechanical systems, among which is the well-known hydrogen atom. Although an age-old problem, the hydrogen atom is still giving rise to very interesting studies,[1–3] the mathematical results of which could eventually be used in the treatment of more complicated systems, namely many electron atoms. Indeed, in the latter case things become much more difficult, since it is impossible to construct the exact solutions of the Schrödinger equation. Therefore, we have no choice but to turn to approximation methods; the most commonly used in the realm of quantum chemistry is the variational technique.

Fortunately, early works about the Schrödinger equation have shown that its solutions must, on the one hand, satisfy the Kato cusp condition[4] at the origin, and on the other hand, decrease exponentially at infinity.[5,6] Accordingly, it is natural to expect that the trial function used in the variational procedure should converge rapidly to the exact solution if it has the above mentioned asymptotic behavior. In the case of molecular systems, prior to the application of the suitable variational algorithm is the construction of the molecular trial wave function. For such a purpose, theorists usually combine linearly the atomic orbitals according to the well-known LCAO (linear combination of atomic orbitals) scheme.[7] It is clear that within the framework of such an approach, the molecular wave function inherits the singularities of the atomic orbitals. In an early work on atomic wave functions, Slater[8] proposed to use in the variational procedure a simplified form of the hydrogenlike functions, henceforth known as Slater-type orbitals (STOs) in order to simplify the leading numerical work. However, although STOs are well suited functions from their asymptotic behavior standpoint, they have not been used extensively in the widely diffused molecular computational programs. This was essentially due to the difficulty of computing the notorious multicenter integrals over such functions. To circumvent this difficulty, a different basis of functions was introduced to describe quantum chemical phenomena, namely the Gaussian-type orbitals (GTOs).[9] In fact these functions do not possess the required asymptotic behavior, but their superior advantage stems essentially from the drastic simplifications they provide in the mathematics involved in the computation of multicenter integrals. GTOs are nowadays considered as the cornerstone of almost all quantum chemistry packages.

With the great progress made in both applied mathematics and computer science, an efficient evaluation of multicenter integrals over STOs appears to be an accessible task. This has led a number of researchers worldwide to focus their efforts on the elaboration of new and viable approaches directed to computing these quantities. These studies have led to two types of approach. The first and perhaps the earliest one consists of using an addition theorem to separate the integration variables from those related to the geometry of the molecule.[10–31] In other words, atomic orbitals (AOs) occurring in a given multicenter integral are first translated (using an addition theorem) to a suitable origin before evaluating the integral itself. In this work, displaced STOs are represented by infinite series over spherical harmonics in which the Fourier coefficients are functionals of r. In addition, these coefficients are described by two different analytical forms, hence leading to the so-called two-range addition theorem.[25] In contrast, if the off-center STOs are expanded over functions of $L_2(IR^3)$ or $W_2^{(1)}(IR^3)$[1–3,17,24,25] we are led to a one-range addition theorem, since in this case the Fourier coefficients are scalars. These scalars may be written

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as overlap integrals between the basis functions and the STO being translated.[17,24] A detailed methodology allowing one to derive one-range addition theorems was given in Ref. 25, where weakly convergent expansions of a plane wave in connection with the Fourier transform method were used.

Regarding the second method, it is essentially based on the use of suitable integral transformations. The best known are the Fourier and the Gaussian integral transforms. The latter consists of representing the term $\exp(-\zeta\mathbf{r})$, which is closely related to the modified Bessel function $\mathbf{K}_{1/2}(\zeta\mathbf{r})$, as a semi-infinite integral whose integrand involves a Gaussian-type function.[32–34] The advantage of this approach is that it reduces the multicenter integrals problem to manipulating the already well-known Gaussian functions. It does, however, suffer from a major drawback since it requires evaluating multiple integrals which take prohibitive calculation time. Conversely, the second transformation implies solving the multicenter integral problem in momentum space rather than in direct coordinate space. Mathematical simplifications led Steinborn's group to new basis functions denoted by *B* (Ref. 35), which in spite of their complexity in coordinate space have a very simple Fourier transform.[36–47]

In the present work, use is made of the two-range addition theorem. Within the framework of such an approach, multicenter integrals are usually expressed as infinite series, the summation of which may become a challenging problem in numerical analysis. Indeed, in an early work of Löwdin[12] it was pointed out that the two-range addition theorem of STOs (also called α function expansion) suffers from poor convergence as one approaches the cusp. Such a bad behavior is usually inherited by multicenter integrals based on this expansion. To circumvent this difficulty, Peterson and McKoy[48] have used a convergence accelerator which allowed the authors to improve substantially the efficiency of their computational algorithms. However, the application of these numerical accelerating methods cannot be effective without a rigorous knowledge of the convergence type of the series that are being summed. For such a purpose we derive in the first part of this work asymptotic forms of the Barnett-Coulson ζ functions (or equivalently Löwdin α functions) from which we determine the convergence nature of the addition theorem of STOs. In the second part we apply these results to the three-center nuclear attraction integral which appears in various fields of computational chemistry and physics, e.g., electron-molecule scattering, *ab initio* calculations (including density functional theory). From this study, a clear explanation of the poor convergence pointed out by Flygare *et al.*[49] will straightforwardly follow.

II. GENERAL DEFINITIONS

In the following, we would like to begin this work by a brief recall of some fundamental definitions which hopefully will facilitate the comprehension of the succeeding paragraphs. In the most general case, a STO is defined as follows:

$$\chi_{n,l}^{m}(\zeta,\mathbf{R}) = \mathcal{N} R^{n-l-1} \exp(-\zeta R) \quad \mathcal{Y}_l^m(\mathbf{R}) \qquad \text{with} \quad \begin{cases} n = 1,2,3,\ldots \\ l = 0,1,\ldots,n-1 \\ m = -l,-l+1,\ldots,l \end{cases}, \tag{2.1}$$

where $\mathcal{N} = (2\zeta)^{n+1/2}/\sqrt{(2n)!}$ is the normalization constant, while $\mathcal{Y}_l^m(\mathbf{R})$ stands for the solid spherical harmonic of degree l and order m which is related to the surface spherical harmonic $Y_l^m(\theta,\varphi)$ according to

$$\mathcal{Y}_l^m(\mathbf{R}) = R^l \; Y_l^m(\theta,\varphi). \tag{2.2}$$

Regarding the surface spherical harmonics, their definition may be written using the Condon and Shortley phase convention[50] as,

$$Y_l^m(\theta,\varphi) = i^{m+|m|} \quad \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}} \quad P_l^{|m|}(\cos\theta) e^{im\varphi}, \tag{2.3}$$

where the associated Legendre function $P_l^{|m|}(z)$ is defined as follows:[51]

$$P_l^{|m|}(z) = (1-z^2)^{|m|/2} \quad \left(\frac{d}{dz}\right)^{|m|} \quad P_l(z)$$

$$= (-1)^l \; (1-z^2)^{|m|/2} \quad \left(\frac{d}{dz}\right)^{l+|m|} \left[\frac{(1-z^2)^l}{2^l \; l!}\right]. \tag{2.4}$$

Now, when the Slater orbital is centered on some arbitrary point defined by the position vector $\mathbf{a}$ (relative to the origin), the expression given in Eq. (2.1) can be rewritten with respect to this origin as follows:

$$\chi_{n,l}^{m}(\zeta,\mathbf{r}-\mathbf{a}) = \mathcal{N}|\mathbf{r}-\mathbf{a}|^{n-l-1} \exp(-\zeta|\mathbf{r}-\mathbf{a}|) \; \mathcal{Y}_l^m(\mathbf{r}-\mathbf{a}). \tag{2.5}$$

A. The addition theorem of Slater orbitals

The difficulty arising from STOs when they are employed in multicenter integrals stems essentially from the absence of a simple addition theorem which would permit separation of the variables $\mathbf{r}$ and $\mathbf{a}$ in Eq. (2.5). In fact, only the function $|\mathbf{r}-\mathbf{a}|^{n-l-1} \exp(-\zeta|\mathbf{r}-\mathbf{a}|)$ poses serious problems because the remaining term, i.e., $\mathcal{Y}_l^m(\mathbf{r}-\mathbf{a})$, can be expanded in a simple way according to the following relation:[52]

$$\mathcal{Y}_l^m(\mathbf{r}-\mathbf{a}) = 4\pi \; (2\lambda+1)!! \times \sum_{l'=0}^{l} \sum_{m'=-l'}^{l'} \frac{\langle l \; m | l' \; m' | l-l' \; m-m' \rangle}{(2l'+1)!! \quad [2(l-l')+1]!!} \times \mathcal{Y}_{l'}^{m'}(\mathbf{r}) \quad \mathcal{Y}_{l-l'}^{m-m'}(-\mathbf{a}), \tag{2.6}$$

where the double factorial $(2\nu+1)!!$ is related to the factorial function according to,

$$(2\nu+1)!! = \prod_{p=0}^{\nu} \quad (2p+1) = \frac{(2\nu+1)!}{2^\nu \; \nu!}. \tag{2.7}$$

Regarding the symbol $\langle l_1 \; m_1 | l_2 \; m_2 | l_3 \; m_3 \rangle$, it is known as the Gaunt coefficient and is defined by,

$$\langle l_1\ m_1|l_2\ m_2|l_3\ m_3\rangle = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}[Y_{l_1}^{m_1}(\theta,\varphi)]^* \times Y_{l_2}^{m_2}(\theta,\varphi)\ \ Y_{l_3}^{m_3}(\theta,\varphi)d\theta\ d\varphi. \quad (2.8)$$

Here, it is worth noticing that from an analytical standpoint, the expansion of the function $|\mathbf{r}-\mathbf{a}|^{n-l-1}\exp(-\zeta|\mathbf{r}-\mathbf{a}|)$ over a complete set of surface spherical harmonics may easily be done by successively differentiating the Gegenbauer addition theorem[34] of the Yukawa potential with respect to ζ (Ref. 11). Thus, one obtains,

$$|\mathbf{r}-\mathbf{a}|^{n-l-1}\exp(-\zeta|\mathbf{r}-\mathbf{a}|) = \frac{1}{\sqrt{ar}}\sum_{\lambda=0}^{+\infty}(2\lambda+1)\ \ \mathcal{A}_{\lambda+1/2}^{n-l}(\zeta,a,r)\ P_\lambda\left(\frac{\mathbf{a}\cdot\mathbf{r}}{a\ r}\right), \quad (2.9)$$

where the functions $\mathcal{A}_{\lambda+1/2}^{n-l}(\zeta,a,r)$, which from now on will be referred to as Barnett-Coulson-Löwdin functions (BCLFs), are defined as follows:

$$\mathcal{A}_{\lambda+1/2}^{n-l}(\zeta,a,r) = \left(-\frac{\partial}{\partial\zeta}\right)^{n-l}\left[\frac{\mathbf{I}_{\lambda+1/2}(\zeta\rho_<)}{\sqrt{\rho_<}}\frac{\mathbf{K}_{\lambda+1/2}(\zeta\rho_>)}{\sqrt{\rho_>}}\right], \quad (2.10)$$

where $\rho_<$ and $\rho_>$ stand for $\min(a,r)$ and $\max(a,r)$, respectively. As regards the functions $\mathbf{I}_{\lambda+1/2}(z)$ and $\mathbf{K}_{\lambda+1/2}(z)$, they represent the modified Bessel functions of the second kind.[34] Note that the major advantage of the series expansion Eq. (2.9) lies in the fact that each of its terms can be written explicitly because the order of the Bessel functions is half-integral and hence could be expanded in finite closed forms according to Ref. 34.

III. CONVERGENCE ANALYSIS OF THE ADDITION THEOREM OF STOS

In the foregoing section, an addition theorem allowing us to expand a Slater orbital about an arbitrary origin was derived from the well-known Gegenbauer addition theorem of modified Bessel functions of the second kind. Now, we want to derive the asymptotic forms of the functions $\mathcal{A}_{l+1/2}^{n}(\zeta,a,r)$ for large values of l. These asymptotics will, then, be used to determine the convergence type of the addition theorem under consideration. Here it would be worthwhile reviewing some basic definitions related to the convergence of infinite series. More detailed discussions are to be found in the excellent review paper of Weniger[53] and in the article of Weniger *et al.*[54] and in a more recent textbook of Brezinski and Redivo-Zaglia.[55]

Let $S=\Sigma_{k=0}^{+\infty}a_k$, be a convergent series, the limit of which is s, and let ρ be the ratio that is defined by,

$$\lim_{n\to+\infty}\frac{S_{n+1}-s}{S_n-s}=\rho, \quad (3.1)$$

where S_n stands for the nth partial sum of S such that $S_n=\Sigma_{k=0}^{n}a_k$.

Then, according to Wimp,[56] the series S converges linearly if $0<|\rho|<1$ and logarithmically if $\rho=1$. From a computational point of view, a linearly convergent series may be evaluated by a direct summation procedure, though there exist better ways to carry out such a task, while for logarithmic convergent series the direct summation procedure should definitely be avoided since it is extremely difficult to achieve an acceptable numerical accuracy in a reasonable amount of CPU time. In the latter case, use of convergence accelerating techniques is a crucial issue to the computational algorithm. In fact, according to Weniger *et al.*,[54] the definition (3.1) is of very little use since it assumes the knowledge of the limit s and the analytical form of the partial sum S_n. Fortunately, it was shown that, if for very large values of the index n, the term a_n has a Poincaré-type asymptotic expansion of the form,

$$a_n=\lambda^n\ n^\Theta\left[\alpha_0+\frac{\alpha_1}{n}+\frac{\alpha^2}{n^2}+\ \ldots\right] \quad \text{with}\ \begin{cases}\alpha_0\neq 0\\ n\to+\infty.\end{cases} \quad (3.2)$$

Therefore, S converges linearly if $|\lambda|<1$ and logarithmically if $\lambda=1$ and $\mathrm{Re}(\Theta)<-1$.

In what follows, our first task is devoted to elaborating the asymptotic representations of the modified Bessel functions $\mathbf{I}_\nu(z)$ and $\mathbf{K}_\nu(z)$ for large values of ν and finite values of the argument z. Thus, in the former case, that is for the function $\mathbf{I}_\nu(z)$, our starting point will be its series representation[51] that may be written as,

$$\mathbf{I}_\nu(z)=\sum_{p=0}^{+\infty}\frac{\left(\frac{z}{2}\right)^{\nu+2p}}{p!\ \Gamma(\nu+p+1)} =\frac{\left(\frac{z}{2}\right)^{\nu}}{\Gamma(\nu+1)}\sum_{p=0}^{+\infty}\frac{\left(\frac{z}{2}\right)^{2p}}{p!\ (\nu+1)_p}, \quad (3.3)$$

where the symbol $(a)_n$ stands for the Pochhammer coefficient defined as,

$$(a)_0=1, \quad \text{and}$$

$$(a)_n=\frac{\Gamma(a+n)}{\Gamma(a)}=a\times(a+1)\times\ \ldots(a+n-1). \quad (3.4)$$

At this point, if we approximate the Pochhammer coefficient involved in Eq. (3.3) by the leading term of the asymptotic expansion of the ratio $\Gamma(z+\alpha)/\Gamma(z+\beta)$, that is,[51]

$$\frac{\Gamma(z+\alpha)}{\Gamma(z+\beta)}\sim z^{\alpha-\beta}\ \ \text{with}\ \ z\to+\infty, \quad (3.5)$$

we immediately obtain an asymptotic representation of the Bessel function under study which may be written in a closed analytical form as,

$$\mathbf{I}_\nu(z)\sim\frac{\left(\frac{z}{2}\right)^{\nu}}{\Gamma(\nu+1)}\ \ \exp\left\{\frac{z^2}{4\nu}\right\} \quad \text{with}\ \ \nu\to+\infty\ \ \text{and}\ \ \frac{z^2}{4}\ll\nu. \quad (3.6)$$

Regarding the asymptotic behavior of the Bessel function $\mathbf{K}_\nu(z)$, the forms given by Grosswald,[57] may directly be used. However, in order to simplify the mathematics involved in the next section, we prefer to derive a simplified asymptotic representation that is valid only for $z^2/4 \ll \nu$, as was the case for the function $\mathbf{I}_\nu(z)$. Thus, to obtain such a representation, it is sufficient to start with the following definition:[34]

$$\mathbf{K}_\nu(z) = \frac{\pi}{2\sin(\nu\pi)}\left[\mathbf{I}_{-\nu}(z) - \mathbf{I}_\nu(z)\right]. \tag{3.7}$$

Now, substituting for the Bessel functions $\mathbf{I}_{-\nu}(z)$ and $\mathbf{I}_\nu(z)$ their series representations, and making use of the identity[51] relating $\Gamma(1-z)$ to $\Gamma(z)$, that is,

$$\Gamma(1-z)\,\Gamma(-z) = \frac{\pi}{\sin(\pi z)}, \tag{3.8}$$

we are able to write the following expansion:

$$\mathbf{K}_\nu(z) = \frac{\pi}{2\sin(\nu\pi)}\left(\frac{z}{2}\right)^{-\nu} \sum_{p=0}^{+\infty} \frac{\left(\frac{z}{2}\right)^{2p}}{p!} \times\left[(-1)^p \frac{\sin(\nu\pi)}{\pi}\,\Gamma(\nu-p) - \frac{(z^2/4)^\nu}{\Gamma(\nu+p+1)}\right]. \tag{3.9}$$

A brief survey of this last equation shows that for large values of ν and with the assumption $z^2/4 \ll \nu$, the expression enclosed between brackets may be approximated by its first term. This finally allows us to write the asymptotic representation of $\mathbf{K}_\nu(z)$,

$$\mathbf{K}_\nu(z) \sim \frac{1}{2}\left(\frac{2}{z}\right)^\nu \Gamma(\nu) \sum_{p=0}^{p_{\max}} (-1)^p \frac{\Gamma(\nu-p)}{\Gamma(\nu)} \frac{\left(\frac{z}{2}\right)^{2p}}{p!}, \tag{3.10}$$

where the upper bound integer $p_{\max}$ satisfies the inequality $p_{\max} \leqslant [\nu]$, the symbol $[\nu]$ being the largest integer less than or equal to ν.

Furthermore, if in the above expansion ν is large enough to apply the approximation given by Eq. (3.5), the summation over p may therefore be approximated by a single exponential term. This yields

$$\mathbf{K}_\nu(z) \sim \frac{1}{2}\left(\frac{2}{z}\right)^\nu \Gamma(\nu)\,\exp\left\{-\frac{z^2}{4\,\nu}\right\}, \quad \text{with } \nu \to +\infty \text{ and } \frac{z^2}{4} \ll \nu. \tag{3.11}$$

Now that we have derived the asymptotic representations of the modified Bessel functions $\mathbf{I}_\nu(z)$ and $\mathbf{K}_\nu(z)$ for large values of ν and for $z^2/4 \ll \nu$, the next step of the present work is to establish the asymptotics of BCLFs, i.e., $\mathcal{A}^n_{l+1/2}(\zeta,a,r)$.

The first asymptotic form, and certainly the simplest, of the functions $\mathcal{A}^n_{l+1/2}(\zeta,a,r)$ (for large values of ν and $z^2/4 \ll \nu$) may straightforwardly be obtained by differentiating n times the product of the expressions given by Eqs. (3.6) and (3.11) (see Appendix A). Thus one obtains,

$$\mathcal{A}^n_\nu(\zeta,a,r) \sim \frac{1}{2\nu}\left(\frac{\rho_<}{\rho_>}\right)^\nu \left(-\frac{\partial}{\partial\zeta}\right)^n \exp\left\{-\zeta^2\,\frac{|a^2-r^2|}{4\nu}\right\}, \tag{3.12}$$

where from now on we prefer to write ν instead of $l+1/2$ to simplify the writing.

In this last equation, the nth derivative of the exponential function may be explicitly written using the Hermite polynomials, since according to Rodrigues formulas,[51] these polynomials are defined as follows:

$$H_n(z) = (-1)^n \exp(z^2)\left(\frac{d}{dz}\right)^n \exp(-z^2). \tag{3.13}$$

Now, taking the above definition into account, the first asymptotic representation of BCLFs follows at once,

$$\mathcal{A}^n_\nu(\zeta,a,r) \sim \frac{1}{2\nu}\left(\frac{\rho_<}{\rho_>}\right)^\nu \left(\frac{|a^2-r^2|}{4\nu}\right)^{n/2} \times H_n\left(\zeta\sqrt{\frac{|a^2-r^2|}{4\nu}}\right) \exp\left\{-\zeta^2\,\frac{|a^2-r^2|}{4\nu}\right\}. \tag{3.14}$$

On the other hand, substituting for the Hermite polynomial involved in the above equation its explicit definition, which according to Ref. 51 may be written as follows:

$$H_n(z) = n! \sum_{p=0}^{[n/2]} (-1)^p \frac{(2z)^{n-2p}}{p!\,(n-2p)!}, \tag{3.15}$$

we finally obtain after some straightforward algebraic manipulations a Poincaré-type asymptotic expansion of the function $\mathcal{A}^n_\nu(\zeta,a,r)$ valid for large values of ν and finite values of ζa and ζr that satisfy the conditions $(\zeta a)^2/4 \ll \nu$ and $(\zeta r)^2/4 \ll \nu$. Such an expansion may be written as,

$$\mathcal{A}^n_\nu(\zeta,a,r) \sim (-1)^{[n/2]} \frac{n!}{(2\zeta)^n} (\zeta\sqrt{|a^2-r^2|})^{2[(n+1)/2]} \frac{\left(\frac{\rho_<}{\rho_>}\right)^\nu}{2\nu^{[(n+1)/2]+1}} \times \sum_{p=0}^{[n/2]} (-1)^p \frac{1}{([n/2]-q)!\,(n-2[n/2]+2q)!} \times \frac{(\zeta\sqrt{|a^2-r^2|})^p}{\nu^p}. \tag{3.16}$$

Here, it is convenient to notice that according to the above equation, the Poincaré-type asymptotic expansions of the functions $\mathcal{A}^{2n-1}_\nu(\zeta,a,r)$ and $\mathcal{A}^{2n}_\nu(\zeta,a,r)$ are similar, since in both cases the leading terms of such expansions may be written as

$$\mathcal{A}_{\nu}^{2n-1}(\zeta,a,r)\sim C\,\frac{\left(\frac{\rho_<}{\rho_>}\right)^{\nu}}{\nu^{n+1}},$$

and (3.17)

$$\mathcal{A}_{\nu}^{2n}(\zeta,a,r)\sim C'\,\frac{\left(\frac{\rho_<}{\rho_>}\right)^{\nu}}{\nu^{n+1}},$$

where C and C' are two constants independent of ν.

Despite its simple analytical form, the asymptotic representation given by Eq. (3.16) is only valid in the case where $\rho_<\neq\rho_>$. In other words, this means that at the cusp, i.e., $\rho_<=\rho_>=a$, it is necessary to derive another form since Eq. (3.14) gives zero. For such a purpose, our starting point is the expansions given by Eqs. (3.3) and (3.10). Hence, proceeding in the same way as in the previous case, that is differentiating n times the product of such expansions with respect to ζ (see Appendix A), yields, after simplifications,

$$\begin{aligned}\mathcal{A}_{\nu}^{n}(\zeta,a,r)\sim{}&\frac{(-1)^n}{\zeta^n}\,\frac{1}{2\nu}\left(\frac{\rho_<}{\rho_>}\right)^{\nu}\\&\times\sum_{s=[(n+1)/2]}^{+\infty}(-1)^s\,\frac{(2s)!}{(2s-n)!}\left(\frac{\zeta\rho_>}{2}\right)^{2s}\\&\times\left[\sum_{p=0}^{\min(s,[\nu])}(-1)^p\right.\\&\left.\times\frac{\Gamma(\nu-s+p)}{\Gamma(\nu+p+1)\;(s-p)!}\,\frac{\left(\frac{\rho_<}{\rho_>}\right)^{2p}}{p!}\right].\end{aligned}\tag{3.18}$$

With a view to providing another asymptotic representation when $\rho_<\neq\rho_>$, two separate cases will be considered in the above equation. The first case we consider corresponds to $\rho_<\neq\rho_>$, for which the above expression may be approximated by a closed form straightforwardly obtained if we assume that on one hand ν is large enough to apply the identity of Eq. (3.5) and on the other hand $\min(s,[\nu])=s$. Thus one obtains,

$$\begin{aligned}\mathcal{A}_{\nu}^{n}(\zeta,a,r)\sim{}&\frac{(-1)^n}{\zeta^n}\,\frac{1}{2\,\nu}\left(\frac{\rho_<}{\rho_>}\right)^{\nu}\\&\times\sum_{s=[(n+1)/2]}^{[\nu]}(-1)^s\,\frac{(2s)!}{(2s-n)!}\\&\times\frac{\left[\left(\frac{\zeta\rho_>}{2}\right)^2-\left(\frac{\zeta\rho_<}{2}\right)^2\right]^s}{s!}\,\frac{1}{\nu^s}.\end{aligned}\tag{3.19}$$

Here, it is worth noticing that the terms involved in the above expansion are identical to the first $[\nu]$ terms obtained by substituting for the exponential term occurring in Eq. (3.14) its Taylor series representation. However, the terms whose order s is strictly greater than $[\nu]$ are different, since in such a case, the summation over p in Eq. (3.18) cannot be reduced by the Newton binomial formula.

As regards the second case, that is, that corresponding to the cusp for which $\rho_<=\rho_>=a$, the use of the following identity [see Ref. 18, Eq. (5)],

$$\sum_{\mu}\,(-1)^{\mu}\,\frac{(a-\mu)!}{\mu!\;(b-\mu)!\;(c-\mu)!}=\frac{(a-b)!\;(a-c)!}{b!\;c!\;(a-b-c)!},\tag{3.20}$$

allows us to perform the summation over p involved in Eq. (3.18). Therefore, the asymptotic representation of the BCLF $\mathcal{A}_{\nu}^{n}(\zeta,a,a)$ may finally be written as,

$$\begin{aligned}\mathcal{A}_{\nu}^{n}(\zeta,a,a)\sim{}&\frac{\pi^{-1/2}}{\zeta^n}\,\frac{1}{2\nu}\sum_{s=[(n+1)/2]}^{+\infty}(-1)^s\,\frac{(2s)!}{(2s-n)!}\\&\times\Gamma\left(s+\frac{1}{2}\right)\frac{\Gamma(\nu-s)}{\Gamma(\nu+s+1)}\,\frac{(\zeta a)^{2s}}{s!}.\end{aligned}\tag{3.21}$$

Here, if once again the parameter ν is large enough to justify the use of the approximation (3.5), the above expansion may therefore be written as a Poincaré-type series. Thus one obtains,

$$\begin{aligned}\mathcal{A}_{l}^{n}(\zeta,a,a)\sim{}&(-1)^{[(n+1)/2]}\,\frac{(\zeta a)^{2[(n+1)/2]}}{2\pi\;\zeta^n}\\&\times\frac{1}{\nu^{2[(n+1)/2]+1}}\sum_{q=0}^{+\infty}(-1)^q\\&\times\frac{[\Gamma(q+[(n+1)/2]+\frac{1}{2})]^2}{(2q+2[(n+1)/2]-n)!}\,\frac{(\zeta a)^{2q}}{\nu^{2q}}.\end{aligned}\tag{3.22}$$

As a consequence of the asymptotic representations of BCLFs [c.f. Eqs. (3.16) and (3.22)], it is clear that the asymptotic behavior of the terms, $a_l^n=(2l+1)\;\mathcal{A}_{l+1/2}^{n}(\zeta,a,r)\;P_l[(\mathbf{ar})/(ar)]$, involved in the addition theorem of Eq. (2.9), may be deduced in a straightforward way. Indeed, remembering that $\nu=l+1/2$, it may readily be seen that for large values of l, the leading term of the asymptotic expansion of a_l^n may be written as,

$$a_l^n\sim C\,\frac{\left(\frac{\rho_<}{\rho_>}\right)^{l+1/2}}{(l+\frac{1}{2})^{[(n+1)/2]}}\,P_l\left(\frac{\mathbf{a}\cdot\mathbf{r}}{ar}\right),\quad\text{for }\rho_<\neq\rho_>\tag{3.23}$$

and,

$$a_l^n\sim C'\,\frac{1}{(l+\frac{1}{2})^{2[(n+1)/2]}}\,P_l\left(\frac{\mathbf{a}\cdot\mathbf{r}}{ar}\right),\quad\text{for }\rho_<=\rho_>=a,\tag{3.24}$$

where C and C' are two constants independent of l.

As a special case of these equations, attention should be drawn to the fact that when the vectors $\mathbf{r}$ and $\mathbf{a}$ are parallel, that is to say $P_l[(\mathbf{ar})/(ar)]=(\pm1)^l$, then according to Wimp,[56] the convergence of the two-range addition theorem of Eq. (2.9) is linear for $r\neq a$ and logarithmic otherwise.

IV. THREE-CENTER NUCLEAR ATTRACTION INTEGRALS

Three-center nuclear attraction integrals are by far the most difficult one-electron quantities that are required when solving the Schrödinger equation within the LCAO-MO (molecular orbitals) ansatz. In fact many works were devoted to the evaluation of these integrals using either the Fourier integral transform method[45,58,59] or the method based on addition theorems.[31,60–62] This work essentially aims at highlighting one of the most important difficulties encountered when multicenter integrals over STOs are evaluated within the framework of the method based on the two-range addition theorem Eq. (2.9). Indeed, when using the two-range addition theorem we are usually led to an infinite series which under certain circumstances may be slowly convergent.[49] Three-center nuclear attraction integrals are generally defined as follows:

$$\mathcal{T}=\left\langle \chi^{M_1}_{N_1,L_1}(\alpha,\mathbf{r}) \left| \frac{1}{|\mathbf{r}-\mathbf{c}|} \right| \chi^{M_2}_{N_2,L_2}[\beta,\mathbf{r}-\mathbf{a}] \right\rangle. \tag{4.1}$$

Now expanding the Coulomb attraction operator and using the product of the addition theorems of Eqs. (2.6) and (2.9) yields after some simple algebra,

$$\begin{aligned}\mathcal{T}=&\mathcal{N}_1\,\mathcal{N}_2\,(4\pi)^3\,(2L_2+1)!!\sum_{L_2'=0}^{L_2}\sum_{M_2'=-L_2'}^{L_2'}\frac{\langle L_2\,M_2|L_2'\,M_2'|L_2-L_2'\,M_2-M_2'\rangle}{(2L_2'+1)!!\,[2(L_2-L_2')+1]!!}\,\mathcal{Y}^{M_2-M_2'}_{L_2-L_2'}(-\mathbf{a})\\ &\times\sum_{L=|L_1-L_2'|}^{L_1+L_2'}{}''\,\langle L_2'M_2'|L_1M_1|LM_2'-M_1\rangle\sum_{l=0}^{+\infty}\frac{1}{2l+1}\sum_{\lambda=|l-L|}^{l+L}{}''\,\mathcal{R}_l(N_1,N_2,L_2,L_2',\alpha,\beta,a)\\ &\times\sum_{m=-l}^{l}\langle l\;m|LM_2'-M_1|\lambda\,m-(M_2'-M_1)\rangle[\mathcal{Y}^{m-(M_2'-M_1)}_{\lambda}(\mathbf{a}/a)]^*\mathcal{Y}^m_l(\mathbf{c}/c),\end{aligned} \tag{4.2}$$

where the radial function $\mathcal{R}_l(N_1,N_2,L_2,L_2',\alpha,\beta,a)$, which for simplicity will be referred to as $\mathcal{R}_l$, is defined according to,

$$\mathcal{R}_l(N_1,N_2,L_2,L_2',\alpha,\beta,a)=\left\langle r^{N_1+L_2'-1}\exp(-\alpha r)\left|\frac{r_<^l}{r_>^{l+1}}\right|\frac{A^{N_2-L_2}_{\lambda+1/2}(\beta,a,r)}{\sqrt{ar}}\right\rangle, \tag{4.3}$$

where $r_<$ and $r_>$ stand for $\min(a,c)$ and $\max(a,c)$ respectively. For numerical purposes the evaluation of these quantities may be carried out using two main schemes. The first and perhaps the most advantageous, since it requires no further mathematical developments, is based on numerical integration techniques, whereas the second is more classical in the sense that $\mathcal{R}_l$ is evaluated analytically. As a matter of fact such an analytical calculus is made possible by using the **C** matrix representation of BCLFs. In the present work we confine ourselves to applying the first method, namely Gauss quadratures. In so doing, the radial integral $\mathcal{R}_l$ is evaluated as the sum of three terms over the ranges $[0,\min(a,c)]$, $\min(a,c),\max(a,c)]$ and $[\max(a,c),+\infty)$.

A. Convergence analysis of three-center nuclear attraction integrals

In this paragraph it is our aim to highlight some convergence aspects of three-center nuclear attraction integrals by examining in details the special case corresponding to *s* type orbitals. Generalization of this case to a linear system might be done quite straightforwardly. In fact, such a case not only allows us to simplify the mathematics but is of great practical interest since these orbitals are involved in all atomic and molecular systems. Hence, from Eq. (4.3) one obtains, after some straightforward simplifications, including the use of the orthogonality property of surface spherical harmonics, the following expansion:

$$\mathcal{T}_{s,s}=\mathcal{N}_1\,\mathcal{N}_2\sum_{l=0}^{+\infty}\langle r^{N_1-1}\exp(-\alpha r)|\times\frac{r_<^l}{r_>^{l+1}}\left|\frac{\mathcal{A}^{N_2}_{l+1/2}(\beta,a,r)}{\sqrt{ar}}\right\rangle P_l\left(\frac{\mathbf{a}\cdot\mathbf{c}}{a\;c}\right). \tag{4.4}$$

In order to derive the convergence type of the above infinite expansion we are required to determine the asymptotic form of its terms for large values of *l*. Before doing so, it should be pointed out that in a paper devoted to molecular integrals over STOs, LaBudde and Sahni[63,64] established the asymptotic form of many integrals, including the one under study. Using some special inequalities satisfied by modified Bessel functions,[63] the authors succeeded in deriving a set of inequalities satisfied by the terms of the series (4.4) (for arbitrary values of *l*). In this work, our approach is more restrictive, since we mainly focus on the behavior of the terms of (4.4) for large values of *l*. Of course, the generality of LaBudde and Sahni's inequalities makes it possible to derive very simply an asymptotic form of the terms of the above series that is equivalent to that obtained below. To start our derivation, we first express the radial integral of Eq. (4.4) as a sum of three terms $\mathcal{R}_1$, $\mathcal{R}_2$ and $\mathcal{R}_3$ such that,

$$\mathcal{R}_1=\frac{1}{\sqrt{a}c^{l+1}}\int_0^{\min(a,c)}\frac{\mathcal{A}^{N_2}_{l+1/2}(\beta,a,r)}{\sqrt{r}}r^{N_1+l+1}\exp(-\alpha r)dr \tag{4.5}$$

$$\mathcal{R}_2=\frac{1}{\sqrt{a}}\int_{\min(a,c)}^{\max(a,c)}\frac{\mathcal{A}^{N_2}_{l+1/2}(\beta,a,r)}{\sqrt{r}}\frac{[\min(c,r)]^l}{[\max(c,r)]^{l+1}}r^{N_1+1}\times\exp(-\alpha r)dr \tag{4.6}$$

$$\mathcal{R}_3=\frac{c^l}{\sqrt{a}}\int_{\max(a,c)}^{+\infty}\frac{\mathcal{A}^{N_2}_{l+1/2}(\beta,a,r)}{\sqrt{r}}r^{N_1-l}\exp(-\alpha r)dr. \tag{4.7}$$

From the above equations it follows that in contrast to $\mathcal{R}_1$ and $\mathcal{R}_3$ the integral $\mathcal{R}_2$ has two different forms according to whether $\min(a,c)=a$ or c. However, as may be seen later, the derivation of its Poincaré-type asymptotic expansion is straightforward.

For large values of the subscript l the introduction of the asymptotic form of BCLFs (3.18) [for which $\rho_<=r$ and $\rho_>=\min(a,c)$] in the definition of $\mathcal{R}_1$ yields

$$\mathcal{R}_1\sim\frac{(-1)^{N_2}}{(2l+1)\beta^{N_2}}\frac{1}{(ac)^{l+1}}\times\sum_{s=[(N_2+1)/2]}^{+\infty}(-1)^s\frac{(2s)!}{(2s-N_2)!}\left(\frac{\beta a}{2}\right)^{2s}\times\sum_{p=0}^{\min(s,l)}(-1)^p\frac{\Gamma(l-s+p+1/2)}{\Gamma(l+p+3/2)(s-p)!}\frac{a^{-2p}}{p!}\times\int_0^{\min(a,c)}r^{N_1+2l+2p+1}\exp(-\alpha r)dr. \tag{4.8}$$

Now using the fact that for large values of l and finite values of $\alpha\ \min(a,c)$ the above integral over r may be approximated by,

$$\int_0^{\min(a,c)}r^{N_1+2l+2p+1}\exp(-\alpha r)dr\sim\frac{[\min(a,c)]^{N_1+2l+2p+2}}{N_1+2l+2p+2}\frac{\exp[-\alpha\ \min(a,c)]}{1-\dfrac{\alpha\ \min(a,c)}{2l}}. \tag{4.9}$$

Now inserting the above approximate into Eq. (4.8) and using some straightforward simplifications, we obtain

$$\mathcal{R}_1\sim\frac{(-1)^{N_2}}{(2l+1)\beta^{N_2}}\left[\frac{\min(a,c)}{\max(a,c)}\right]^{l+1}\frac{[\min(a,c)]^{N_1}}{1-\eta}\times\exp[-\alpha\ \min(a,c)]\sum_{s=[(N_2+1)/2]}^{+\infty}(-1)^s\times\frac{(2s)!}{(2s-N_2)!}\left(\frac{\beta a}{2}\right)^{2s}\sum_{p=0}^{\min(s,l)}(-1)^p\times\frac{\Gamma(l-s+p+1/2)}{\Gamma(l+p+5/2)(s-p)!}\frac{[\min(a,c)/a]^{2p}}{p!}, \tag{4.10}$$

where η stands for the ratio $[\alpha\ \min(a,c)]/(2l)$. At this stage, it turns out that the integral $\mathcal{R}_1$ has in fact two different Poincaré-type expansions according to whether $\min(a,c)=a$ or $\min(a,c)=c$. Indeed in the former case the innermost summation, i.e., over p, may be performed using the identity [see Ref. 18, Eq. (5)],

$$\sum_\delta(-1)^\delta\frac{(a+\delta)!}{\delta!(b-\delta)!(c+\delta)!}=(-1)^\delta\frac{a!(a-c)!}{b!(b+c)!(a-b-c)!}. \tag{4.11}$$

From this point, use of Eq. (3.5) allows one to obtain the following asymptotic expansion for the integral $\mathcal{R}_1$:

$$\mathcal{R}_1\sim\frac{(-1)^{N_2}}{2(2l+1)\beta^{N_2}}\left(\frac{a}{c}\right)^{l+1}\frac{a^{N_1}}{1-\eta}\exp(-\alpha a)\times\sum_{s=[(N_2+1)/2]}^{+\infty}\left[(-1)^s\frac{(2s)!}{(2s-N_2)!}\frac{(2s+1)!}{(s+1)!}\frac{\left(\dfrac{\beta a}{2}\right)^{2s}}{s!}\right]\times\frac{1}{(l+1/2)^{2s+2}}. \tag{4.12}$$

Now, in the case where $\min(a,c)=c$, use of Eq. (3.5) yields a summation over p which could easily be performed since it represents in fact the standard Newton expansion of the term $[1-(c/a)^2]^s$. Some simple algebraic work leads afterward to the following Poincaré-type expansion:

$$\mathcal{R}_1\sim\frac{(-1)^{N_2}}{4\beta^{N_2}}\left(\frac{c}{a}\right)^{l+1}\frac{c^{N_1}}{1-\eta}\exp(-\alpha c)\times\sum_{s=[(N_2+1)/2]}^{+\infty}\left[(-1)^s\frac{(2s)!}{(2s-N_2)!}\times\frac{\left[\left(\dfrac{\beta a}{2}\right)^2-\left(\dfrac{\beta c}{2}\right)^2\right]^s}{s!}\right]\frac{1}{(l+\frac{1}{2})^{s+2}}. \tag{4.13}$$

Here, it should be pointed out that in both cases, i.e., $\min(a,c)=a$ and $\min(a,c)=c$, the leading term of the Poincaré-type expansion of the integral $\mathcal{R}_1$ has the same form, that is,

$$\mathcal{R}_1\sim\mathcal{K}_1\frac{\left(\dfrac{\min(a,c)}{\max(a,c)}\right)^{l+1}}{(l+\frac{1}{2})^{[(N_2+1)/2]+2}}, \tag{4.14}$$

where $\mathcal{K}_1$ is a constant independent of l.

According to the introductory remark of this section, the integral $\mathcal{R}_2$ has two different definitions according to whether $\min(a,c)=a$ or $\min(a,c)=c$. In what follows we will restrict ourselves to consider only the former case, since the latter may be treated exactly in the same way. In this case the following equalities hold: $\rho_<=a$ and $r_<=r$. Thus inserting

the asymptotic expansion of $\mathcal{A}^{N_2}_{l+1/2}(\beta,a,r)$ (3.18) into Eq. (4.6), and collecting all the powers of the variable r, yields the following radial integral:

$$\int_a^c r^{N_1+2s-2p+1}\exp(-\alpha r)dr. \tag{4.15}$$

From the above expression, it is clear that the above integral could be considered as a constant independent of l, and hence for large values of such a parameter use of Eq. (3.5) yields after simplifications the following leading term of the Poincaré asymptotic expansion for $\mathcal{R}_2$:

$$\mathcal{R}_2 \sim \frac{\mathcal{K}_2}{\max(a,c)}\frac{\left(\dfrac{\min(a,c)}{\max(a,c)}\right)^l}{(l+\frac{1}{2})^{[(N_2+1)/2]+2}}. \tag{4.16}$$

Regarding the integral $\mathcal{R}_3$, it is theoretically forbidden to directly substitute the asymptotic form of BCLFs given by Eq. (3.18) into the definition of such an integral since its upper limit is not finite. In order to circumvent this difficulty, it is sufficient to approximate $\mathcal{R}_3$ by an integral where the upper limit was set equal to a large but finite value $r_{\max}$. This approach is well justified, since for large values of r the integrand behaves like $r^p\exp[-(\alpha+\beta)r]$. In other words, this means that beyond such a suitably chosen limit the following approximate holds:

$$\int_{r_{\max}}^{+\infty}\frac{\mathcal{A}^{N_2}_{l+1/2}(\beta,a,r)}{\sqrt{r}}r^{N_1-l}\exp(-\alpha r)\approx 0. \tag{4.17}$$

Hence, substituting the asymptotic form of Eq. (3.18) into the approximate definition of $\mathcal{R}_3$ yields,

$$\begin{aligned}\mathcal{R}_3 \sim{}& \frac{(-1)^{N_2}}{2\beta^{N_2}}(ac)^l\sum_{s=[(N_2+1)/2]}^{+\infty}\frac{(2s)!}{(2s-N_2)!}\left(\frac{\beta a}{2}\right)^{2s}\\ &\times\sum_{q=0}^{\min(s,l)}(-1)^q\frac{\Gamma(l-q+1/2)}{q!(s-q)!\Gamma(l+s-q+3/2)}b^{-2q}\\ &\times\int_{\max(a,c)}^{r_{\max}}\frac{\exp(-\alpha r)}{r^{2l-2q-N_1+1}}dr.\end{aligned} \tag{4.18}$$

Since l is a large number, the radial integral involved in the above equation may be approximated by the first term of the expansion obtained by an integration by part where $u=\exp(-\alpha r)$ and $dv=dr/r^{2l-2q-N_1+1}$. Thus, one obtains

$$\begin{aligned}&\int_{\max(a,c)}^{r_{\max}}\frac{\exp(-\alpha r)}{r^{2l-2q-N_1+1}}\,dr\\ &\quad=\frac{1}{2l-2q-N_1}\left[\frac{\exp[-\alpha\ \max(a,c)]}{[\max(a,c)]^{2l-2q-N_1}}-\frac{\exp[-\alpha r_{\max}]}{r_{\max}^{2l-2q-N_1}}\right]\\ &\qquad-O\left(\frac{1}{l^2}\right)\sim\frac{1}{2l-2q-N_1}\frac{\exp[-\alpha\ \max(a,c)]}{[\max(a,c)]^{2l-2q-N_1}}.\end{aligned} \tag{4.19}$$

In addition, use of the approximation $\Gamma(l-q+1/2)/(2l-2q-N_1)\approx 1/2\ \Gamma(l-q-1/2)$ enables us to obtain the following asymptotic representation for $\mathcal{R}_3$:

$$\begin{aligned}\mathcal{R}_3 \sim{}& \frac{(-1)^{N_2}}{4\beta^{N_2}}\left[\frac{\min(a,c)}{\max(a,c)}\right]^l[\max(a,c)]^{N_1}\\ &\times\exp[-\alpha\ \max(a,c)]\\ &\times\sum_{s=[(N_2+1)/2]}^{+\infty}\frac{(2s)!}{(2s-N_2)!}\left(\frac{\beta a}{2}\right)^{2s}\sum_{q=0}^{\min(s,l)}(-1)^q\\ &\times\frac{\Gamma(l-q-1/2)}{(s-q)!\Gamma(l+s-q+3/2)}\frac{\left[\dfrac{\max(a,c)}{a}\right]^{2q}}{q!}.\end{aligned} \tag{4.20}$$

As in the case of $\mathcal{R}_1$, the above asymptotic form may be simplified differently according to whether $\min(a,c)=a$ or $\min(a,c)=c$. In the former case use of Eq. (3.20) with Eq. (3.5) yields after some simplifications the following Poincaré-type asymptotic expansion:

$$\begin{aligned}\mathcal{R}_3 \sim{}& \frac{(-1)^{N_2}}{4\beta^{N_2}}\left[\frac{\min(a,c)}{\max(a,c)}\right]^l[\max(a,c)]^{N_1}\exp[-\alpha\max(a,c)]\\ &\times\sum_{s=[(N_2+1)/2]}^{+\infty}\left[(-1)^s\frac{(2s)!}{(2s-N_2)!}\frac{(2s+1)!}{(s+1)!}\frac{\left(\dfrac{\beta a}{2}\right)^{2s}}{s!}\right]\\ &\times\frac{1}{(l+\frac{1}{2})^{2s+2}}\quad\text{for }\min(a,c)=a,\end{aligned} \tag{4.21}$$

and

$$\begin{aligned}\mathcal{R}_3 \sim{}& \frac{(-1)^{N_2}}{4\beta^{N_2}}\left[\frac{\min(a,c)}{\max(a,c)}\right]^l[\max(a,c)]^{N_1}\\ &\times\exp[-\alpha\ \min(a,c)]\\ &\times\sum_{s=[(N_2+1)/2}^{+\infty}\left[(-1)^s\frac{(2s)!}{(2s-N_2)!}\frac{\left[\left(\dfrac{\beta c}{2}\right)^2-\left(\dfrac{\beta a}{2}\right)^2\right]^s}{s!}\right]\\ &\times\frac{1}{(l+\frac{1}{2})^{s+2}}\quad\text{for}\quad\min(a,c)=c.\end{aligned} \tag{4.22}$$

From the above equations it is clear that in both cases the leading term of the Poincaré-type expansion may be written as follows:

$$\mathcal{R}_3=\mathcal{K}_3\frac{\left(\dfrac{\min(a,c)}{\max(a,c)}\right)^l}{(l+\frac{1}{2})^{[(N_2+1)/2]+2}}, \tag{4.23}$$

where $\mathcal{K}_3$ is a constant independent of l.

At this stage it may readily be seen from Eqs. (4.14), (4.16) and (4.23) that for large values of l the terms of the series representation of the three-center nuclear attraction integral (4.4) behave like

TABLE I. Selected three-center nuclear attraction integrals in the case of a linear molecule. Numbers in parentheses represent powers of 10.

Atomic orbitals	Integral	D_{exc}	This work	ALCHEMY [b]	DTEST [c,d]
1 : (H) $1s$[1.24]	$\langle 1\|2\rangle$	5	2.945 496 054(−1)	2.945 496 054(−2)	2.945 494 454(−2)
2 : (C) $1s$[5.67]	$\langle 1\|3\rangle$	11	1.606 646 078(−1)	1.606 646 041(−1)	1.606 645 937(−1)
3 : (C) $2s$[1.61]	$\langle 1\|4\rangle$	7	−1.163 866 018(−1)	−1.163 866 018(−1)	−1.163 865 846(−1)
4 : (C) $2p_0$ [1.56]	$\langle 2\|6\rangle$	2	3.710 041 454(−5)	3.710 041 454(−5)	3.710 152 495(−5)
5 : (C) $2p_1$ [1.54]	$\langle 2\|7\rangle$	6	2.695 528 880(−2)	2.695 528 880(−2)	2.695 532 230(−2)
6 : (N) $1s$[6.66]	$\langle 2\|8\rangle$	6	−4.621 491 513(−2)	−4.621 491 513(−2)	−4.621 497 451(−2)
7 : (N) $2s$[1.94]	$\langle 3\|6\rangle$	2	1.408 177 370(−2)	1.408 177 370(−2)	1.408 441 969(−2)
8 : (N) $2p_0$ [1.92]	$\langle 3\|7\rangle$	3	1.467 233 406(−1)	1.467 233 406(−1)	1.467 232 649(−1)
9 : (N) $2p_1$ [1.80]	$\langle 3\|8\rangle$	4	−1.530 415 963(−1)	−1.530 415 963(−1)	−1.530 415 938(−1)
	$\langle 5\|9\rangle$	4	1.009 914 329(−1)	1.009 914 329(−1)	1.009 914 330(−1)

[a]This work: Values obtained after accelerating the initial series expansion using the ϵ algorithm. D_{exc} represents the number of exact digits obtained after the summation of 17 terms of the original series. Our values correspond to the term ϵ_{16}^{16} of the ϵ algorithm. The molecule is along the Z axis and such that d(H, C)=2.0143 and d(H, N)=4.1934.
[b]See Ref. 67.
[c]DTEST: These values were obtained using the so−called Legendre Möbius quadrature (LRM) (Ref. 68) method for which the parameters are: LRM 90 | 30, 20; 1(-6) | 20, 16; 1(-7) | 10, 10; 1(-8).
[d]See Ref. 59.

$$a_l^n \sim \mathcal{K} \frac{\left(\frac{\min(a,c)}{\max(a,c)}\right)^l}{(l+\frac{1}{2})^{[(N_2+1)/2]+2}} \; \mathrm{P}_l\left(\frac{\mathbf{a}\cdot\mathbf{c}}{\alpha c}\right) \quad \text{with} \quad l \to +\infty, \tag{4.24}$$

where $\mathcal{K}$ is a constant independent of l.

As a conclusion of this section, it is obvious for linear molecules, that is to say $\mathrm{P}_l[(\mathbf{ac})/(ac)]=(\pm 1)^l$, the convergence of the above series is linear for $a \neq c$ and logarithmic otherwise. However, it is clear that for $a \approx c$ the convergence of Eq. (4.4) will deteriorate since though still linear (from a mathematical standpoint) this region is close to the case $a=c$ where the convergence is definitely logarithmic. This study provides in fact a rigorous explanation to what was pointed out by Flygare *et al.* in Ref. 49. In addition to this remark, it should be pointed out that since N_2 appears as a power of $(l+1/2)$, the convergence of the series (4.4) is expected to improve with high values of this parameter.

V. NUMERICAL RESULTS

In this section we present some numerical values of three-center nuclear attraction integrals and show the improvement in the convergence obtained with the help of two different nonlinear convergence accelerators, namely the Levin u transformation and the Wynn ϵ algorithm. It should be mentioned that Peterson and McKoy[48] have applied the latter method to circumvent the difficulties arising from the summation of the slowly convergent series representing four-center integrals. According to Fessler, Ford and Smith the u transformation may be defined as follows:

$$u_k(S_n)=\frac{\sum_{i=0}^{k}(-1)^i\binom{k}{i}\frac{(1+n+i)^{k-2}}{(1+n+k)^{k-1}}\frac{S_{n+i}}{a_{n+i}}}{\sum_{i=0}^{k}(-1)^i\binom{k}{i}\frac{(1+n+i)^{k-2}}{(1+n+k)^{k-1}}\frac{1}{a_{n+i}}}. \tag{5.1}$$

For numerical purposes the evaluation of the above quantity may lead to severe numerical instabilities[54] because of the existence of alternating terms in both numerator and denominator. We will, therefore, apply the recursive algorithm advised by Smith and Ford to evaluate these quantities. Such an algorithm is defined as,

$$Q_{k,n}=Q_{k-1,n+1}-\frac{n+1}{n+k}\left(\frac{n+k}{n+k+1}\right)^k Q_{k-1,n} \quad \text{with} \quad k \geqslant 1, n \geqslant 0, \tag{5.2}$$

where the starting value $Q_{0,n}$ is defined by,

$$Q_{0,n}=\begin{cases}\dfrac{S_n}{(n+1)^2 a_n} & \text{for the numerator} \\ \dfrac{1}{(n+1)^2 a_n} & \text{for the denominator.}\end{cases} \tag{5.3}$$

Regarding the so-called Wynn ϵ algorithm, it is a computational procedure allowing one to calculate recursively the quantities required by Shanks.[65] The ϵ algorithm is defined as

$$\epsilon_{k+1}^{(n)}=\epsilon_{k-1}^{(n+1)}+\frac{1}{\epsilon_k^{(n+1)}-\epsilon_k^{(n)}}, \tag{5.4}$$

where the procedure is initialized with the terms $\epsilon_{-1}^{(n)}=0$ and $\epsilon_0^{(n)}=S_n$. According to Wimp,[56] the ϵ algorithm may also suffer from numerical instabilities, but in our case such an algorithm has exhibited a good numerical behavior since it always converges to the right value.

In Table I it may be seen that after summing 17 terms of the series expansion (4.4) only a few accurate digits are obtained (c.f. column labeled D_{exc}). It should also be noticed that according to the concluding remark of the previous section, the convergence of Eq. (4.4) generally improves for increasing values of N_2 (c.f. lines 1, 5 and 6). Furthermore,

TABLE II. Comparison to previous values for linear and nonlinear systems. In this table, the orbitals are assumed to be on the Z axis, i.e., $\mathbf{a}(0,0,a)$ [see Eq. (4.1)]. Calculations are carried out using the same approach as in Table (I). Numbers in parentheses represent powers of 10.

Geometry	Integral	This work	Rico *et al.*[a]	D_{TEST}[b]
$a=3$, $\mathbf{c}(3,4,5)$	$\langle 2p_x[4.0] \vert 3d_{xz}[3.0]\rangle$	−3.020 076 721(−3)	−3.020 076 72(−3)	−3.028 935 052(−3)
$a=5$, $\mathbf{c}(3,4,5)$	$\langle 2p_x[4.0] \vert 3d_{xz}[3.0]\rangle$	−2.587 578 890(−5)	−2.587 578 60(−5)	−2.600 519 879(−5)
$a=5$, $\mathbf{c}(0,0,7)$	$\langle 2p_x[4.0] \vert 3d_{xz}[3.0]\rangle$	−2.818 653 000(−5)	−2.818 657 00(−5)	−2.818 654 096(−5)
$a=5$, $\mathbf{c}(-2,5,4)$	$\langle 2s[3.0] \vert 2p_z[3.0]\rangle$	−1.333 583 172(−3)	−1.333 596 00(−3)	−1.333 586 292(−3)
$a=5$, $\mathbf{c}(-3,6,5)$	$\langle 2s[3.0] \vert 2p_z[3.0]\rangle$	−1.045 218 434(−4)	−1.045 219 17(−4)	−1.045 222 323(−4)
$a=5$, $\mathbf{c}(-4,7,6)$	$\langle 2s[3.0] \vert 2p_z[3.0]\rangle$	−8.531 955 275(−5)	−8.531 955 79(−5)	−8.531 988 486(−5)
$a=2$, $\mathbf{c}(0,0,9)$	$\langle 2s[4.0] \vert 1s[1.0]\rangle$	−2.630 240 914(−2)	2.630 240 91(−2)	2.630 314 167(−2)
$a=5$, $\mathbf{c}(0,0,9)$	$\langle 2s[4.0] \vert 1s[1.0]\rangle$	1.538 280 150(−3)	1.538 280 15(−3)	1.538 316 674(−3)
$a=8$, $\mathbf{c}(0,0,9)$	$\langle 2s[4.0] \vert 1s[1.0]\rangle$	7.945 638 156(−5)	7.945 637 90(−5)	7.945 820 427(−5)

[a]Reference 69.
[b]Reference 59.

in all cases, namely those involving s type orbitals as well as those which do not, a spectacular improvement of the accuracy is achieved by applying the above accelerating techniques.

In the case of nonlinear molecules (see Table II), the convergence of the series under study is, theoretically, neither linear nor logarithmic. This results from the presence of the Legendre polynomial, which makes it impossible to obtain for the coefficient Eq. (4.24) a Poincaré-type expansion similar to that of Eq. (3.2). In this case, the failure of Levin u transformation was observed, whereas the ϵ algorithm allowed us to achieve the accuracy needed in *ab initio* quantum chemical calculations. In fact, such a good behavior of the ϵ algorithm may be predicted by noticing that the series Eq. (4.4) is an infinite expansion in terms of Legendre polynomials, $\mathrm{P}_l(\cos\theta)$. For large values of l, these polynomials have the following asymptotic form:[51]

$$\mathrm{P}_l(\cos\theta) \sim \frac{1}{\sqrt{\pi \sin\theta}} \frac{1}{l^{1/2}} \{\cos[(l+\tfrac{1}{2})\theta] + \sin[(l+\tfrac{1}{2})\theta]\} \quad \text{with} \quad \begin{cases} 0<\theta<\pi \\ l\to+\infty \end{cases}. \tag{5.5}$$

From this equation, it is clear that Legendre polynomials behave asymptotically like a Fourier series. Accordingly, the difficulties encountered when accelerating the convergence of the expansion Eq. (4.4) are similar to those occurring when dealing with a Fourier series, in which case only very few accelerators can be used. Fortunately, the ϵ algorithm belongs to this class of successful algorithms because of the form of its kernel,[55] which includes special Fourier series of the form

$$\sum_i [B_i(n)\cos(\beta_i n) + C_i \sin(\beta_i n)] \exp(w_i n). \tag{5.6}$$

The special case of a molecule in which atoms are located on the vertices of an equilateral triangle is of interest since in such a case the cusp plays an important role. The integrals listed in Table III were obtained with the molecular system C_3. These values show that, in this special case, 17 partial sums are generally not sufficient to achieve more than five to six accurate digits.

VI. CONCLUDING REMARKS

The first part of this work aimed at examining the convergence of the two-range addition theorem (as derived by Barnett and Coulson[11]). It is shown that for arbitrary vectors $\mathbf{r}$ and $\mathbf{a}$ [c.f. Eq. (2.9)] the terms of this orthogonal expansion are represented asymptotically as a product involving a Legendre polynomial Eq. (2.9). For the special case in which $\mathbf{r}$ and $\mathbf{a}$ are parallel, we show that the series representation Eq. (2.9) converges logarithmically when $r=a$ and linearly otherwise. This study hence provides a rigorous proof to the observation reported by Löwdin in one of his early works on the addition theorem of STOs.[12]

Strictly speaking, the evaluation of the series Eq. (2.9) is not required when computing multicenter integrals over STOs since it is generally combined with other expansions, e.g., Laplace expansion of the Coulomb operator. However, as shown in Sec. IV, the knowledge of the asymptotic form of the terms defining the series Eq. (2.9) helps one to derive the asymptotic representation of the terms involved in the series describing multicenter integrals.

As an application of this approach, we have considered the case of three-center nuclear attraction integrals in which only s type orbitals are used. Thus, after some algebra one obtains an orthogonal expansion Eq. (2.9), the terms of which are

TABLE III. Convergence of the series expansion Eq. (4.4) for an equilateral geometry. The atoms are located at: (0., 0., 0.), (0., 0., 2.51900), (2.18152, 0., 1.25950). Calculations are carried out using the same approach as in Table (I). Numbers in parentheses represent powers of 10.

Atomic orbitals	Integral	This work	D_{TEST}[a]
$1:1s[5.67]$	$\langle 1 \vert 5\rangle$	2.320 346 76(−5)	2.320 320 39(−5)
$2:2s[1.61]$	$\langle 2 \vert 5\rangle$	2.036 349 67(−2)	2.036 346 71(−2)
$3:2p_0\,[1.56]$	$\langle 3 \vert 5\rangle$	3.594 130 07(−2)	3.594 125 61(−2)
$4:2p_1\,[1.54]$	$\langle 4 \vert 5\rangle$	−4.891 573 90(−4)	−4.891 139 61(−4)
	$\langle 2 \vert 6\rangle$	1.949 350 00(−1)	1.949 349 28(−1)
	$\langle 3 \vert 6\rangle$	2.052 678 19(−1)	2.052 682 43(−1)
	$\langle 4 \vert 6\rangle$	−4.328 212 00(−2)	−4.328 219 90(−2)
$5:1s[5.67]$	$\langle 1 \vert 7\rangle$	−3.594 136 80(−2)	−3.594 125 61(−2)
$6:2s[1.61]$	$\langle 2 \vert 7\rangle$	−2.052 682 14(−1)	−2.052 682 43(−1)
$7:2p_0\,[1.56]$	$\langle 3 \vert 7\rangle$	−1.667 138 73(−1)	−1.667 138 08(−1)
$8:2p_1\,[1.54]$	$\langle 4 \vert 7\rangle$	4.607 731 36(−2)	4.607 729 24(−2)

[a]Reference 59.

asymptotically represented by a product involving a Legendre polynomial Eq. (2.9). In the case of linear molecules, i.e., **a** parallel to **c**, it is shown that the series Eq. (2.9) converges logarithmically for $a=c$ and linearly elsewhere. In order to highlight the importance of this analysis, several examples are presented throughout Secs. IV and V. The numerical values listed in Table I correspond to a linear molecule and show that a very good accuracy is achieved with the epsilon algorithm operating on the first 17 terms of the expansion Eq. (2.9). It should be emphasized that though our analysis of Sec. IV was restricted to integrals with s type orbitals, the accuracy obtained with nonspherical orbitals, e.g., p, is very satisfactory.

In the case of nonlinear molecules, two different examples were studied. In the first instance (Table II), we have considered the case in which the cusp does not play an important role. Hence, starting with 17 partial sums, of the series Eq. (2.9) and using the epsilon algorithm, we obtain numerical values which agree favorably with those of other authors (even when nonspherical orbitals are involved). As regards the values of Table III, they correspond to a nonlinear molecular system, namely C_3, in which the atoms are located on the vertices of an equilateral triangle. In this case, it appears that 17 partial sums of the initial series Eq. (2.9) yield after using the epsilon algorithm to only six accurate digits (at least when nonspherical orbitals are involved). This observation suggests that an improvement of the accuracy will require the computation of more partial sums, especially when nonspherical orbitals are involved in multicenter integrals.

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APPENDIX: FURTHER REMARKS ON THE DERIVATION OF THE ASYMPTOTIC EXPANSION OF BCLFS

Throughout Sec. III, we have established the asymptotic expansion of BCLFs, i.e., $\mathcal{A}_\nu^n(\zeta,a,r)$, by differentiating n times, that represent $\mathcal{A}_\nu^0(\zeta,a,r)$. It is clear that such a derivation is only allowed under special circumstances which in the case of interest hold. Indeed, according to Bromwich,[66] it is stated that,

(i) Differentiation of the asymptotic representation of a function f may not lead to the asymptotic expansion of f' unless we know from independent reasoning that f' is asymptotically developable.

(ii) If the asymptotic representation of f is a convergent series, we can then apply the test of uniform convergence[66] directly to the differentiated series and hence infer that the derived function has an expansion.

Before applying the above statements, let us write the asymptotic representation of $\mathcal{A}_\nu^0(\zeta,a,r)$, which according to Sec. III, is the product of Eqs. (3.6) and (3.11). Thus, one obtains

$$\mathcal{A}_\nu^0(\zeta,a,r)\sim\frac{1}{2\nu}\left(\frac{\rho_<}{\rho_>}\right)^\nu\exp\left\{-\zeta^2\frac{|a^2-r^2|}{4\nu}\right\}$$
$$=\frac{1}{2\nu}\left(\frac{\rho_<}{\rho_>}\right)^\nu\sum_{p=0}^{+\infty}\left(-\zeta^2\frac{|a^2-r^2|}{4\nu}\right)^p\Big/\,p!. \tag{A1}$$

Here, it is clear that use of the second of the above statements allows one to obtain the asymptotic expansion of BCLFs [c.f. Eq. (3.14)] as the nth derivative of Eq. (A1). This immediately follows from the absolute-convergence property of the series representation of the exponential function.

An alternative way to show that in our case differentiation of Eq. (A1) will lead to the Poincaré-type expansion of BCLFs is to apply the first of the above statements. Accordingly, one needs to show that for any positive integer n, BCLF is asymptotically developable. For such a purpose we start by forming the product of the infinite series given by Eqs. (3.3) and (3.9) and then differentiating term by term with respect to ζ. After simplifications, this yields

$$\mathcal{A}_\nu^n(\zeta,a,r)=\frac{\zeta^{-n}}{2\nu}\left(\frac{\rho_<}{\rho_>}\right)^\nu\frac{\pi}{\sin(\nu\pi)}\sum_{s=0}^{+\infty}(\zeta\rho_</2)^{2s}$$
$$\times\sum_{q=0}^{s}\frac{1}{q!(s-q)!\;(\nu+1)_{s-q}}\left(\frac{\rho_>}{\rho_<}\right)^{2q}$$
$$\times\left[(-1)^q\frac{\sin(\nu\pi)}{\pi}\frac{(2s)!\;\Gamma(\nu-q)}{(2s-n)!\Gamma(\nu)}\right.$$
$$\left.-\frac{(2\nu+2s)!}{(2\nu+2s-n)!\Gamma(\nu)\Gamma(\nu+q+1)}(\zeta\rho_>/2)^{2\nu}\right]. \tag{A2}$$

Now bearing in mind that for $\zeta\rho_>\ll\nu$ the second term appearing in brackets can be neglected [as for Eq. (3.9)], one obtains after some algebraic manipulations (including Eq. (3.5) and the well-known binomial expansion) the following expansion:

$$\mathcal{A}_\nu^n(\zeta,a,r)\sim\frac{\zeta^{-n}}{2\nu}\left(\frac{\rho_<}{\rho_>}\right)^\nu\sum_{s=[(n+1)/2]}^{+\infty}(-1)^s$$
$$\times\frac{(2s)!}{(2s-n)!}\frac{1}{s!}\left(\frac{\zeta^2|a^2-r^2|}{4\nu}\right)^s. \tag{A3}$$

From this equation, it clearly appears that BCLFs are expandable asymptotically in a Poincaré-type series, which in

other words means that differentiation of the asymptotic representation of $\mathcal{A}_\nu^0(\zeta,a,r)$ will give (in a more straightforward manner) the asymptotic expansion of $\mathcal{A}_\nu^n(\zeta,a,r)$ [c.f. Eqs. (3.12) and (3.18).]

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