Convergence accelerators in the computation of molecular integrals over Slater-type basis functions in the two-range one-center expansion method

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The so-called nonlinear transformations may be of substantial help in many practical problems including the so-called multicenter integrals. In this work Wynn's epsilon algorithm and the Levin's u transformation have been used to improve the convergence of the series representation of three-center two-electron integrals obtained via the so-called two-range one-center expansion method.

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I. INTRODUCTION

It is well known that except for a few simple systems (e.g., hydrogenlike atoms, hydrogen molecular ions, etc.), the Schrödinger equation cannot be fully solved, that is to say, it is not possible to write its eigenfunctions in an explicit closed analytical form. However, some early works about such an equation revealed some important intrinsic properties regarding the eigenfunctions. Indeed, it has been found that such eigenfunctions always satisfy the following boundary conditions: the cusp condition [1] at the origin (i.e., nuclei) and an exponential decrease at infinity [2,3]. Thus, from a mathematical point of view, functions exhibiting the same singularities, among which we find Slater-type functions (STF's), which will be defined later, are expected to fit the exact eigenfunctions better than any other kind of functional. However, these functions have not been used extensively in the quantum chemistry area, though they constitute the most natural and suitable basis of functions in the linear combination of atomic orbitals and molecular orbitals [4] approach, from the self-consistent-field (SCF) as well as from density-functional theory [5] standpoint. Indeed, within the framework of these approaches, we face the notorious problem of the evaluation of multicenter integrals over STF's which raise many cumbersome mathematical and computational difficulties. This is particularly due to the absence of a simple multiplication theorem involving two STF's located at two distinct points. Hence, in the beginning of the computational era, it became of crucial importance to find another strategy in order to circumvent the limitations of the computational tools. This has been done by Boys [6], who introduced a new kind of basis set function called Gaussian-type functions (GTF's). Nowadays, calculations with such functions become preponderant in quantum chemistry in spite of their inadequate representation of electronic density close to the nuclei and at a large distance therefrom since such functions do not satisfy the above criteria. This fact is largely due to the ease of the mathematical expressions of multicenter integrals since GTF's obey a multiplication theorem allowing to express a product of two GTF's centered on two points A and B as a GTF located on a point C lying on the segment joining A to B, the position of which is determined in a quite easy way.

However, quantum chemistry followed the boom in computer power with considerable effort directed at programming multicenter integrals for STF's. Not only do these programs require very powerful machines (e.g., parallel architectures), but also the design of new mathematical approaches appropriate to such basis sets. These currently fall into two categories, those based on the so-called one-center expansion methods [7–32] and those founded on the use of integral transforms [33–47].

The most promising approaches using the integral transform are the Gaussian integral transform [36–38] proposed by Shavitt and Karplus [37,38] and the Fourier integral transform of the convolution product of two particular STF's called B functions [48–50]. The usefulness of the latter has been pointed out by Bonham, Peacher, and Cos [33,34], but its development and application are largely indebted to Steinborn *et al.* [43–47,51–57].

With regard to the one-center expansion methods, they consist in expanding an STF or a product of two STF's centered on various nuclei about a chosen fixed center by means of some fundamental properties of Hilbert spaces. These methods are certainly the most accessible both theoretically and formally in their application.

II. BASIC IDEAS AND GENERAL PROPERTIES OF THE ONE-CENTER EXPANSION

Before discussing the numerical aspects of the two-range one-center expansion method, it would be advisable to recall some of its fundamental and general features.

Let $\{\varphi_n\}_{n=1,2,\ldots}$ be a sequence in the Hilbert space $\mathcal{H}$. Such a sequence is called complete if the only element of $\mathcal{H}$ which is orthogonal to every φ_n is the null element, that is,

$$(f,\varphi_n)=0 \Longrightarrow f=\Theta \ . \tag{1}$$

Here Θ stands for the zero element of $\mathcal{H}$.

If $\{\varphi_n\}_{n=1,2,\ldots}$ is assumed to be a complete sequence in some Hilbert space $\mathcal{H}$, then every function in $\mathcal{H}$ may be approximated to any desired degree of accuracy by the expansion

$$f=\sum_n a_n\varphi_n \ , \tag{2}$$

where $\{a_n\}_{n=1,2,\ldots}$ represents a sequence of coefficients (usually scalars). In other words, when $\{\varphi_n\}_{n=1,2,\ldots}$ is complete but not orthogonal, the most we can say about f is that for a given ϵ, there is some finite sequence of coefficients $\{a_n\}_{n=1,2,\ldots}$ such that

$$\left|\left| f - \sum_n a_n \varphi_n \right|\right| < \epsilon \ . \tag{3}$$

If a new ϵ is given, the whole set of coefficients may have to be changed. Conversely, when $\{\varphi_n\}_{n=1,2,\ldots}$ is a complete and orthogonal sequence, the following lemma holds.

Lemma 2.1 (best approximation). For any f in $\mathcal{H}$ (i) $\|f-\sum_n a_n\varphi_n\|$ is smallest when a_n has the value $C_n=(f,\varphi_n)$ and (ii) $\sum_n |C_n|^2 \le \|f\|^2$.

The quantities C_n are called the Fourier coefficients of f with respect to $\{\varphi_n\}_{n=1,2,\ldots}$. Moreover, f can have at most one such expansion, that is to say, that f determines its Fourier coefficients uniquely by the formula $C_n=(f,\varphi_n)$.

From the preceding lemma it may readily be observed that the use of a complete and orthogonal sequence of functions is computationally much more advantageous than a nonorthogonal one. In addition, such a lemma may be considered as the starting point of any one-center expansion method that may be developed. Indeed, let $f^M_{N,L}(\mathbf{r})$ be an element of the exponential-type function (ETF) set that is defined in its most general case as follows:

$$f^M_{N,L}(\mathbf{r}) = \mathcal{P}_{N,L}(\zeta,r) e^{-\zeta r} Y^M_L(\theta_r,\phi_r) \ , \tag{4}$$

where ζ is a positive real number, usually called the Slater exponent, and $\mathcal{P}_{N,L}$ a polynomial of the variable r. With regard to the term Y^M_L, it denotes the surface spherical harmonic of Lth degree and of Mth order which, according to the phase convention of Condon and Shortley [58], may be defined as

$$Y^M_L(\theta_r,\phi_r) = i^{M+|M|} \left[\frac{(2L+1)}{4\pi} \frac{(L-|M|)!}{(L+|M|)!} \right]^{1/2} \times P_L^{|M|}(\cos\theta_r) e^{iM\phi_r} \ . \tag{5}$$

Here $P_L^{|M|}$ represents the Legendre associated functions of Lth degree and $|M|$th order.

Perhaps the best known class of complete and orthogonal functions that has been used *in extenso* by physicists in classical as well as in quantum mechanics is the surface spherical harmonics [59]. Indeed, many addition theorems involve such functions (e.g., Laplace-Neumann expansion of the Coulomb repulsion operator [60], the Gegenbauer addition theorem [61], a special case of which is the addition theorem of the Yukawa potential, etc.).

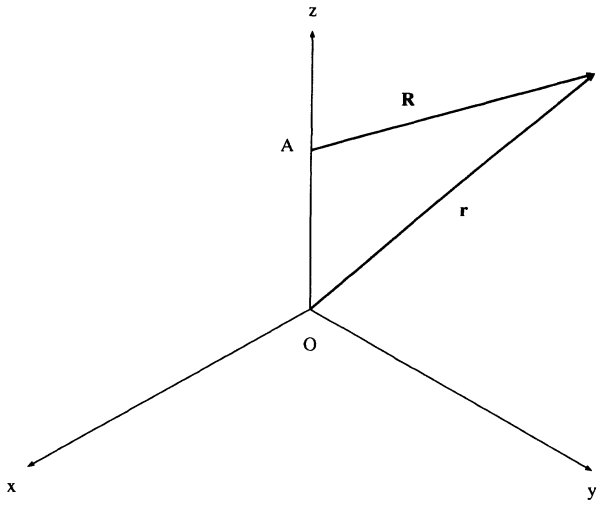

FIG. 1. Coordinate system.

Besides, in an early work of Coolidge [62] such functions have also been used to carry out the evaluation of multicenter integrals involved in the quantum chemical treatment of the water molecule. In order to illustrate this, let us consider the ETF $f^M_{N,L}(\mathbf{r}-\mathbf{R})$, centered on some point of the three-dimensional Euclidean space $\mathcal{E}_3$ defined by the vector $\mathbf{R}$. Therefore, in order to separate the variables $\mathbf{r}$ and $\mathbf{R}$, the function $f^M_{N,L}$ is expanded in terms of the surface spherical harmonics as follows:

$$f^M_{N,L}(\mathbf{r}-\mathbf{R}) = \sum_{l=0}^{+\infty} \sum_{m=-l}^{l} A^{N,L,M}_{l,m}(\mathbf{R}) Y^m_l(\theta_r,\phi_r) \ , \tag{6}$$

where the Fourier coefficients $A^{N,L,M}_{l,m}$ are determined by the following relationship:

$$A^{N,L,M}_{l,m}(\mathbf{R}) = \langle Y^m_l(\theta_r,\phi_r) | f^M_{N,L}(\mathbf{r}-\mathbf{R}) \rangle \ . \tag{7}$$

Furthermore, it should be emphasized that, although the mathematical background of such an expansion remains the same for all the approaches based on the use of surface spherical harmonics, its originality rests in the way it is used to evaluate the above Fourier coefficients [8,10–12,17].

Derivation of the two-range one-center expansion

Now let us consider a special STF, namely, an unnormalized Slater orbital, centered on an arbitrary point A of $\mathcal{E}_3$, which may explicitly be defined as follows (cf. Fig. 1):

$$\begin{aligned} \chi^M_{N,L}(\zeta\mathbf{R}) &= \chi^M_{N,L}[\zeta(\mathbf{r}-\mathbf{r}_{OA})] \\ &= |\mathbf{r}-\mathbf{r}_{OA}|^{N-1} e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|} Y^M_L(\theta_{\mathbf{r}-\mathbf{r}_{OA}},\varphi_{\mathbf{r}-\mathbf{r}_{OA}}) \\ &= (|\mathbf{r}-\mathbf{r}_{OA}|^{N-L-1} e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|})[|\mathbf{r}-\mathbf{r}_{OA}|^L Y^M_L(\theta_{\mathbf{r}-\mathbf{r}_{OA}},\varphi_{\mathbf{r}-\mathbf{r}_{OA}})] \end{aligned} \tag{8}$$

where $N=1,2,\ldots$, $L=0,1,\ldots,N-1$, and $-L \le M \le L$.

Here O is assumed to be the origin of the reference system but it may also be any point of $\mathscr{E}_3$. In this equation, the second term enclosed between brackets may readily be translated using the well-known addition theorem of the solid spherical harmonics as follows [see, for instance, Ref. [14], Eq. (2.19)]:

$$\mathcal{Y}_L^M(\mathbf{r}-\mathbf{r}_{OA})=|\mathbf{r}-\mathbf{r}_{OA}|^L Y_L^M(\theta_{\mathbf{r}-\mathbf{r}_{OA}},\varphi_{\mathbf{r}-\mathbf{r}_{OA}})$$
$$=4\pi(2L+1)!!\sum_{l'=0}^{L}\sum_{m'=-l'}^{l'}\frac{\langle LM|l'm'|L-l'M-m'\rangle}{(2l'+1)!![2(L-l')+1]!!}\mathcal{Y}_{l'}^{m'}(\mathbf{r})\mathcal{Y}_{L-l'}^{M-m'}(-\mathbf{r}_{OA}) , \tag{9}$$

where the double factorials are determined by the relationship

$$(2l+1)!!=1\times3\times5\times7\times\cdots\times(2l+1)=\frac{(2l+1)!}{2^l l!} . \tag{10}$$

With regard to the first term involved in Eq. (8), its expansion is carried out in two steps. First, let us recall a particular case of the Gegenbauer addition theorem [61] of the modified Bessel functions that states

$$\frac{e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}}{|\mathbf{r}-\mathbf{r}_{OA}|}=\sum_{\lambda=0}^{+\infty}(2\lambda+1)\frac{I_{\lambda+1/2}(\zeta\rho_<)}{\sqrt{\rho_<}}\frac{K_{\lambda+1/2}(\zeta\rho_>)}{\sqrt{\rho_>}}\times P_\lambda[\cos\angle(\mathbf{r},\mathbf{r}_{OA})] , \tag{11}$$

where I_ν and K_ν denote the modified Bessel functions of the second kind [63] while P_λ stands for the Legendre polynomials of the λth degree. The symbols $\rho_<$ and $\rho_>$ refer to $\min(r,|\mathbf{r}_{OA}|)$ and $\max(r,|\mathbf{r}_{OA}|)$, respectively.

Now, the second step consists in taking the $(N-L)$th derivative with respect to ζ of both sides of the preceding equation. This yields

$$\left[\frac{d}{d\zeta}\right]^{N-L}\frac{e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}}{|\mathbf{r}-\mathbf{r}_{OA}|}$$
$$=(-1)^{N-L}|\mathbf{r}-\mathbf{r}_{OA}|^{N-L-1}e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}$$
$$=\left[\frac{d}{d\zeta}\right]^{N-L}\sum_{\lambda=0}^{+\infty}(2\lambda+1)\frac{I_{\lambda+1/2}(\zeta\rho_<)}{\sqrt{\rho_<}}\frac{K_{\lambda+1/2}(\zeta\rho_>)}{\sqrt{\rho_>}}\times P_\lambda[\cos\angle(\mathbf{r},\mathbf{r}_{OA})] . \tag{12}$$

Thus, combining Eqs. (9) and (12) leads one to the analytical expression describing the translation of an unnormalized Slater orbital from point A to O.

It is clear that since Eq. (9) represents a finite combination of solid spherical harmonics with well-behaved coefficients (i.e., not too large), the numerical behavior (e.g., rate of convergence, numerical stability, etc.) of the two-range one-center expansion under study is therefore highly dependent of the two-range series given by Eq. (12). Hence, for our convergence analysis, it will be sufficient to restrict our study to the expansion of the pure radial term (i.e., the unnormalized scalar Slater orbital), that is,

$$|\mathbf{r}-\mathbf{r}_{OA}|^{N-L-1}e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}$$
$$=(-1)^{N-L}\left[\frac{d}{d\zeta}\right]^{N-L}\frac{e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}}{|\mathbf{r}-\mathbf{r}_{OA}|} . \tag{13}$$

Now let us establish the best computationally suitable representation of the two-range one-center expansion of the pure radial term given by Eq. (12). For such a purpose, we recall that instead of using the closed analytical form of the modified Bessel functions of the second kind $I_{\lambda+1/2}$ and $K_{\lambda+1/2}$, it has been found more convenient [64] to use their integral representations [65]:

$$I_{\lambda+1/2}(\zeta\rho_<)=\frac{1}{\lambda!\sqrt{\pi}}\left[\frac{\zeta\rho_<}{2}\right]^{\lambda+1/2}\times\int_{-1}^{+1}(t^2-1)^\lambda e^{\pm\zeta\rho_< t}dt , \quad \lambda\geq0$$
$$K_{\lambda+1/2}(\zeta\rho_>)=\frac{\sqrt{\pi}}{\lambda!}\left[\frac{\zeta\rho_>}{2}\right]^{\lambda+1/2}\times\int_{1}^{+\infty}(1-t^2)^\lambda e^{-\zeta\rho_> t}dt . \tag{14}$$

Subsequently inserting the product of the previous integral representations into Eq. (12) and using the Leibniz rule of derivation yields

$$|\mathbf{r}-\mathbf{r}_{OA}|^{N-L-1}e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}=(-1)^{N-L}\left[\frac{d}{d\zeta}\right]^{N-L}\frac{e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}}{|\mathbf{r}-\mathbf{r}_{OA}|}$$
$$=(-1)^{N-L}\sum_{\lambda=0}^{+\infty}(2\lambda+1)\frac{1}{\lambda!}\left[\frac{\zeta\rho_<}{2}\right]^{\lambda+1/2}\frac{1}{\lambda!}\left[\frac{\zeta\rho_>}{2}\right]^{\lambda+1/2}$$
$$\times\left[\sum_{k=0}^{N-L}\binom{N-L}{k}\frac{(2\lambda+1)!}{(2\lambda+1-k)!}\times\int_{-1}^{+1}\int_{1}^{+\infty}(1-x^2)^\lambda(y^2-1)^\lambda\frac{(\pm x\rho_<-y\rho_>)^{N-L-k}}{\zeta^k}\times e^{(\pm x\rho_<-y\rho_>)\zeta}dy\,dx\right]P_\lambda[\cos\angle(\mathbf{r},\mathbf{r}_{OA})] . \tag{15}$$

For computational work, it should be noted that the evaluation of the double integral involved in the above expression is carried out numerically [64] by means of some Gauss quadrature routines which are readily available from a wide variety of mathematical libraries [66–68].

III. SOME CONVERGENCE ASPECTS OF THE TWO-RANGE ONE-CENTER EXPANSION

In an early work by Löwdin [69], it has been pointed out that the convergence of the two-range one-center expansion under consideration is rather poor near and at the cusp. The aim of the present section is to generalize the Löwdin's formula [70] to arbitrary orbitals. For such a purpose, let us rewrite Eq. (12):

$$\left[\frac{d}{d\zeta}\right]^{N-L}\frac{e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}}{|\mathbf{r}-\mathbf{r}_{OA}|}=\sum_{\lambda=0}^{+\infty}(2\lambda+1)A_\lambda^{N-L}(\zeta\rho_<,\zeta\rho_>)\times P_\lambda[\cos\angle(\mathbf{r},\mathbf{r}_{OA})]\ , \tag{16}$$

where the function A_λ^{N-L} is defined by the following relationship:

$$A_\lambda^{N-L}=\left[\frac{d}{d\zeta}\right]^{N-L}\left[\frac{I_{\lambda+1/2}(\zeta\rho_<)}{\sqrt{\rho_<}}\frac{K_{\lambda+1/2}(\zeta\rho_>)}{\sqrt{\rho_>}}\right]\ . \tag{17}$$

In the following, for the sake of simplicity but without loss of generality, point A is assumed to lie on the Z axis. Therefore, the angle $\angle(\mathbf{r},\mathbf{r}_{OA})$ is no more than the polar angle θ (cf. Fig. 1). Now, taking the norm of both sides of Eq. (16) in the Hilbert space $L_2([0,\pi)\times[0,2\pi])$ and making use of the orthogonality condition of the Legendre polynomials yields

$$\langle|\mathbf{r}-\mathbf{r}_{OA}|^{N-L-1}e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}||\mathbf{r}-\mathbf{r}_{OA}|^{N-L-1}e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}\rangle_{\theta,\varphi}=\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}[|\mathbf{r}-\mathbf{r}_{OA}|^{2(N-L-1)}e^{-2\zeta|\mathbf{r}-\mathbf{r}_{OA}|}]\sin\theta\,d\theta\,d\varphi=4\pi\sum_{\lambda=0}^{+\infty}(2\lambda+1)|A_\lambda^{N-L}(\zeta\rho_<,\zeta\rho_>)|^2\ . \tag{18}$$

From the above equation, it is clear that the term enclosed between brackets is nothing but a scalar Slater orbital the quantum parameters of which are $[2(N-L)-1,0,0]$ and hence may readily be expanded following the same scheme as that given by Eq. (16). This yields

$$|\mathbf{r}-\mathbf{r}_{OA}|^{2(N-L-1)}e^{-2\zeta|\mathbf{r}-\mathbf{r}_{OA}|}=\sum_{\lambda=0}^{+\infty}(2\lambda+1)A_\lambda^{2(N-L)-1}(2\zeta\rho_<,2\zeta\rho_>)P_\lambda(\cos\theta)\ . \tag{19}$$

Now, putting this least equation into Eq. (18) and taking once again the orthogonality condition of the Legendre polynomials into account, one obtains

$$\langle|\mathbf{r}-\mathbf{r}_{OA}|^{N-L-1}e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}||\mathbf{r}-\mathbf{r}_{OA}|^{N-L-1}e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}\rangle_{\theta,\varphi}=4\pi A_0^{2(N-L)-1}(2\zeta\rho_<,2\zeta\rho_>)\ . \tag{20}$$

In order to discuss the rate of convergence of the two-range expansion given by Eq. (16), we recall that, from practical standpoint, only a finite number of terms is used in any numerical evaluation involving series expansions. For this purpose, let us evaluate the following difference:

$$\begin{aligned}E_\mu^{N,L}(\zeta,\mathbf{r}_{OA};\mathbf{r})&=\left|\left||\mathbf{r}-\mathbf{r}_{OA}|^{N-L-1}e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}-\sum_{\lambda=0}^{\mu}(2\lambda+1)A_\lambda^{N-L}(\zeta\rho_<,\zeta\rho_>)P_\lambda(\cos\theta)\right|\right|^2\\&=4\pi\sum_{\lambda=\mu+1}^{+\infty}(2\lambda+1)|A_\lambda^{N-L}(\zeta\rho_<,\zeta\rho_>)|^2\\&=4\pi\sum_{\lambda=0}^{+\infty}(2\lambda+1)|A_\lambda^{N-L}(\zeta\rho_<,\zeta\rho_>)|^2-4\pi\sum_{\lambda=0}^{\mu}(2\lambda+1)|A_\lambda^{N-L}(\zeta\rho_<,\zeta\rho_>)|^2\\&=4\pi A_0^{2(N-L)-1}(2\zeta\rho_<,2\zeta\rho_>)-4\pi\sum_{\lambda=0}^{\mu}(2\lambda+1)|A_\lambda^{N-L}(\zeta\rho_<,\zeta\rho_>)|^2\ .\end{aligned} \tag{21}$$

Clearly this last equation in fact represents the mean-square error of the two-range expansion of an unnormalized Slater orbital over the surface spherical harmonics basis set, when such an expansion is truncated after μ terms (see Fig. 8 in Ref. [69]).

IV. IMPROVING THE CONVERGENCE OF THE TWO-RANGE ONE-CENTER EXPANSION

According to Fig. 8 of Ref. [69], it may readily be seen that the rate of convergence of the two-range one-center expansion is not satisfactory near the cusp. Therefore, when such a method is used to carry out multicenter integrals, it is expected that many terms of the series given by Eq. (16) have to be computed in order to achieve an acceptable accuracy. In other words, the leading packages will certainly be very time consuming. Fortunately, in a previous work [71], we have shown that the use of some nonlinear accelerating algorithm [72–75] may be of substantial help in the improvement of the rate of convergence of the series describing multicenter integrals. Among the most powerful convergence accelerators, spe-

cialists of the field usually quote the so-called Levin's transformations and Wynn's epsilon algorithm.

A. Shanks transformation and Wynn's epsilon algorithm

The first and certainly the oldest nonlinear convergence accelerating transformation, which is a special case of the generalized epsilon algorithm, is the well known Aitken Δ^2 process [76,77]. Such an algorithm consist in transforming a convergent sequence $\{S_n\}_{n=0,1,\ldots}$, the limit of which is S, into a new sequence denoted by $\{e_1(S_n)\}_{n=0,1,\ldots}$ that is determined by the following relationship:

$$e_1(S_n)=\frac{S_nS_{n+1}-S_{n+1}^2}{S_{n+2}-2S_{n+1}+S_n}\ ,\quad n=0,1,2,\ldots\ . \tag{22}$$

Since we are dealing with infinite series of the form $\sum_{\mu=0}^{+\infty}c_\mu$, the terms S_n of the sequence involved in all the equations of the present section correspond in fact to the partial sums of such series, that is to say, $S_n=\sum_{\mu=0}^{n}c_\mu$. An important result regarding Aitken's Δ^2 process, which may readily be proved, is that if the sequence $\{S_n\}_{n=0,1,\ldots}$ satisfies the following linear difference equation:

$$a_0(S_n-S)+a_1(S_{n+1}-S)=0\ , \tag{23}$$

where $a_0+a_1\neq 0$. Therefore

$$e_1(S_n)=S\ ,\quad \forall n>N\ . \tag{24}$$

The generalization of Aitken's Δ^2 process is due to Shanks [72,78–80] and has led to the so-called Shanks transformation. Indeed, let $\{S_n\}_{n=0,1,\ldots}$ be a convergent sequence, whose limit is S and which satisfies the following linear difference equation:

$$\sum_{i=0}^{k}a_i(S_{\mu+i}-S)=0\ ,\quad \mu=n,n+1,\ldots,n+k \tag{25}$$

where as for Aitken's process $\sum_{i=0}^{n}a_i\neq 0$. Thus for any $n>N$, the transformation of order k, which is usually referred to as $e_k(S_n)$, equals S:

$$e_k(S_n)=S\ ,\quad \forall n>N\ . \tag{26}$$

In the following, for the sake of simplicity but without any loss of generality, we assume that

$$\sum_{i=0}^{k}a_i=1\ . \tag{27}$$

Now taking into account this last equation, the identity given by Eq. (25) may be written in a more explicit fashion as follows:

$$\begin{array}{lllll} a_0 & +a_1 & +\cdots+ & a_k & =1,\\ a_0S_n & +a_1S_{n+1} & +\cdots+ & a_kS_{n+k} & =S,\\ a_0S_{n+1} & +a_1S_{n+2} & +\cdots+ & a_kS_{n+k+1} & =S,\\ \vdots & \vdots & & \vdots & \vdots\\ a_0S_{n+k-1} & +a_1S_{n+k+1} & +\cdots+ & a_kS_{n+2k} & =S. \end{array} \tag{28}$$

After some straightforward linear combinations of the equations involved in the above system, one obtains the limit S of the sequence under consideration by means of Cramer's rule. This yields

$$S=e_k(S_n)=\frac{\begin{vmatrix} S_n & S_{n+1} & \cdots & S_{n+k}\\ \Delta S_n & \Delta S_{n+1} & \cdots & \Delta S_{n+k}\\ \vdots & \vdots & \ddots & \vdots\\ \Delta S_{n+k-1} & \Delta S_{n+k} & \cdots & \Delta S_{n+2k-1}\end{vmatrix}}{\begin{vmatrix} 1 & 1 & \cdots & 1\\ \Delta S_n & \Delta S_{n+1} & \cdots & \Delta S_{n+k}\\ \vdots & \vdots & \ddots & \vdots\\ \Delta S_{n+k-1} & \Delta S_{n+k} & \cdots & \Delta S_{n+2k-1}\end{vmatrix}}\ . \tag{29}$$

Obviously, as mentioned above, Aitken's Δ^2 process is just a special case of the Shanks transformation, namely, $e_1(S_n)$:

$$\begin{aligned} e_1(S_n)&=\frac{\begin{vmatrix} S_n & S_{n+1}\\ \Delta S_n & \Delta S_{n+1}\end{vmatrix}}{\begin{vmatrix} 1 & 1\\ \Delta S_n & \Delta S_{n+1}\end{vmatrix}}\\ &=\frac{S_n\Delta S_{n+1}-S_{n+1}\Delta S_n}{\Delta S_{n+1}-\Delta S_n}\\ &=\frac{S_nS_{n+2}-S_{n+1}^2}{\Delta^2 S_n}\ ,\quad n=0,1,\ldots \end{aligned} \tag{30}$$

where the differences $\Delta^k S_n$ are generally defined recursively as follows:

$$\Delta S_n=S_{n+1}-S_n\ ,\quad \Delta^{k+1}S_n=\Delta^k S_{n+1}-\Delta^k S_n\ . \tag{31}$$

From a computational standpoint, this determinant solution is exceedingly unwieldy. Indeed, it is well known that the determinant may involve large numbers with alternate signs, and upon subtraction of large numbers the relative error may soar to a point that makes the result worthless. But much more important is that the computation of an nth-order determinant requires the evaluation of $n!$ terms, which ultimately implies that the above determinantal representation has little practical interest since it is computationally very time consuming.

The epsilon algorithm proposed by Wynn [72,80–82] is a recursive algorithm based on the Shanks transformation that allows us to avoid the evaluation of the determinants. This method obeys the following rules:

$$\begin{aligned} &\epsilon_{-1}^{(n)}=0\ ,\quad \epsilon_0^{(n)}=S_n\ ,\quad n=0,1,2,\ldots\\ &\epsilon_{k+1}^{(n)}=\epsilon_{k-1}^{(n+1)}+\frac{1}{\epsilon_k^{(n+1)}-\epsilon_k^{(n)}}\ ,\quad k,n,=0,1,2,\ldots\ . \end{aligned} \tag{32}$$

B. Levin's u transformation

At the present time, the specialists of convergence accelerating techniques agree that Levin's sequence transformation [72,83–85] is undoubtedly the most powerful

accelerator. Such a sequence transformation has been elaborated to give the exact limit of any sequence S_n, which obeys the following identity:

$$S_\mu = S + \omega_\mu \sum_{i=0}^{k-1} \frac{a_i}{(\mu+\beta)^i} \quad \text{with } \mu = n, n+1, \ldots, n+k;\ k = 1,2,\ldots \tag{33}$$

where ω_μ are arbitrary functions of n which must be different from zero for all n while β is a constant.

In order to deduce the general expression of Levin's transformation, we first begin by rewriting the above identity in such a way as to obtain a linear system where the unknowns are the k coefficients a_i and of course the limit S of the sequence under consideration. This yields

$$\begin{aligned}
S + \omega_n a_0 + \frac{\omega_n}{n+\beta} a_1 + \cdots + \frac{\omega_n}{(n+\beta)^{k-1}} a_{k-1} &= S_n , \\
S + \omega_{n+1} a_0 + \frac{\omega_{n+1}}{n+1+\beta} a_1 + \cdots + \frac{\omega_{n+1}}{(n+1+\beta)^{k-1}} a_{k-1} &= S_{n+1} , \\
\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\
S + \omega_{n+k} a_0 + \frac{\omega_{n+k}}{n+k+\beta} a_1 + \cdots + \frac{\omega_{n+k}}{(n+k+\beta)^{k-1}} a_{k-1} &= S_{n+k} .
\end{aligned} \tag{34}$$

Once again, by means of the well-known Cramer's rule, one may express the so-called Levin transformation as the ratio of two determinants as follows:

$$S = L_k(S_n) = \frac{\begin{vmatrix} S_n & \omega_n & \frac{\omega_n}{n+\beta} & \cdots & \frac{\omega_n}{(n+\beta)^{k-1}} \\ S_{n+1} & \omega_{n+1} & \frac{\omega_{n+1}}{n+1+\beta} & \cdots & \frac{\omega_{n+1}}{(n+1+\beta)^{k-1}} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ S_{n+k} & \omega_{n+k} & \frac{\omega_{n+k}}{n+k+\beta} & \cdots & \frac{\omega_{n+k}}{(n+k+\beta)^{k-1}} \end{vmatrix}}{\begin{vmatrix} 1 & \omega_n & \frac{\omega_n}{n+\beta} & \cdots & \frac{\omega_n}{(n+\beta)^{k-1}} \\ 1 & \omega_{n+1} & \frac{\omega_{n+1}}{n+1+\beta} & \cdots & \frac{\omega_{n+1}}{(n+1+\beta)^{k-1}} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & \omega_{n+k} & \frac{\omega_{n+k}}{n+k+\beta} & \cdots & \frac{\omega_{n+k}}{(n+k+\beta)^{k-1}} \end{vmatrix}} . \tag{35}$$

However, as mentioned in the case of the Shanks transformation, this determinantal representation is not suitable for numerical work. Fortunately, the above ratio may be expressed in a more computationally attractive form according to [86]

$$L_k(S_n) = \frac{\sum_{i=0}^{k} (-1)^i \binom{k}{i} \frac{(\beta+n+i)^{k-1}}{(\beta+n+k)^{k-1}} \frac{S_{n+i}}{\omega_{n+i}}}{\sum_{i=0}^{k} (-1)^i \binom{k}{i} \frac{(\beta+n+i)^{k-1}}{(\beta+n+k)^{k-1}} \frac{1}{\omega_{n+i}}} , \quad k,n = 1,2,\ldots . \tag{36}$$

At this stage, the problem that has to be dealt with is to find the best sequence $\{\omega_\mu\}$ corresponding to the sequence Levin's transformation is applied to.

In one of his first works, Levin [83] suggested some simple sequences $\{\omega_\mu\}$, including the following:

$$\omega_n = (\beta+n) a_n , \quad n = 1,2,\ldots . \tag{37}$$

This sequence is well adapted to logarithmically convergent sequences, that is to say, that

TABLE I. Evaluation of the series given by Eq. (40) for $\zeta = 9.715$ and $\mathbf{r}_{OA} = (4.46\ \text{a.u.}, 0, 0)$ at the cusp (i.e., $\mathbf{r} = \mathbf{r}_{OA}$). Numbers in brackets denote powers of 10.

λ	S_λ[a]
0	0.266 326 681 097 793 464 52[−03]
1	0.106 402 998 617 201 167 41[−02]
2	0.238 929 670 203 779 508 52[−02]
3	0.423 582 770 122 378 152 51[−02]
4	0.659 492 074 978 688 091 56[−02]
5	0.945 558 343 806 063 423 52[−02]
10	0.307 569 184 373 050 353 67[−01]
20	0.100 139 985 924 731 714 67[+0]
30	0.186 733 476 196 503 289 46[+0]
40	0.273 649 769 458 445 734 36[+0]
50	0.352 535 651 455 190 818 38[+0]
100	0.605 744 539 970 459 244 56[+0]
200	0.789 272 795 159 040 147 14[+0]
300	0.857 518 454 614 059 233 21[+0]
400	0.892 573 020 054 584 812 05[+0]
500	0.913 836 720 611 728 460 51[+0]
600	0.928 091 909 776 676 684 19[+0]
700	0.938 307 576 062 560 558 15[+0]
800	0.945 985 439 566 309 427 97[+0]

[a]Partial sums of the series given by Eq. (40).

$$\lim_{n\to+\infty}\frac{S_{n+1}-S}{S_n-S}=1\ . \tag{38}$$

Thus the use of the special sequence $\{\omega_n\}$ given by Eq. (37) yields the well-known Levin's u transformation which is defined by the following relationship:

$$u_k(S_n)=\frac{\sum_{i=0}^{k}(-1)^i\binom{k}{i}\frac{(\beta+n+i)^{k-2}}{(\beta+n+k)^{k-1}}\frac{S_{n+i}}{a_{n+i}}}{\sum_{i=0}^{k}(-1)^i\binom{k}{i}\frac{(\beta+n+i)^{k-2}}{(\beta+n+k)^{k-1}}\frac{1}{a_{n+i}}}\ . \tag{39}$$

Besides, according to the numerous studies [87,88] on Levin's u transformation, it should be emphasized that such a transformation is certainly the best suited accelerating technique for monotonic as well as alternating sequences.

C. Numerical experiments

In Sec. IV it was stated that the convergence rate of the two-range one-center expansion method is not sufficiently satisfactory near and at the cusp. In order to illustrate this fact numerically, let us consider the expansion of a special case, namely, an unnormalized 1s Slater orbital, which according to Eq. (12) may be written explicitly as follows:

$$e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}=-\left[\frac{d}{d\zeta}\right]\frac{e^{-\zeta|\mathbf{r}-\mathbf{r}_{OA}|}}{|\mathbf{r}-\mathbf{r}_{OA}|}=\sum_{\lambda=0}^{+\infty}(2\lambda+1)\frac{\rho_{>}I_{\lambda+1/2}(\zeta\rho_{<})K_{\lambda+3/2}(\zeta\rho_{>})-\rho_{<}I_{\lambda-1/2}(\zeta\rho_{<})K_{\lambda+1/2}(\zeta\rho_{>})}{\sqrt{\rho_{<}}\sqrt{\rho_{>}}}$$
$$\times P_\lambda[\cos\angle(\mathbf{r},\mathbf{r}_{OA})]\ . \tag{40}$$

As it may be seen from the values listed in Table I, the convergence of the above series at the cusp is still unsatisfactory, after having computed 800 terms. In addition, since the numerical evaluation of the Bessel functions $I_{\lambda+1/2}(z)$ and $K_{\lambda+1/2}(z)$ has been done recursively, it has been necessary to use the SCRATCHPAD II [89] computer algebra system in order to avoid the internal round off errors. Indeed, for such a calculation, the accuracy has been set to 1800 exact digits.

Conversely, from the values reported in Tables II and III, it may be observed that convergence accelerating techniques may be of substantial help for the evaluation of the series given by Eq. (40), which, of course, is always involved in the analytical expressions of multicenter integrals evaluated via the two-range one-center expansion method.

Furthermore, regarding Levin's u transformation, it follows from Table III that within a suitable choice of the constant β the values produced by such a transformation are in good agreement with the exact value (i.e., 1.0). It should also be noticed that compared to the epsilon algorithm, the later transformation is far and away the best one, since using the same number of partial sums, the u transformation yields better accuracy.

TABLE II. Selected subsequences obtained by applying the epsilon algorithm [Eq. (32)] to the first 20 terms of the series given by Eq. (40) at the cusp (i.e., $\mathbf{r}=\mathbf{r}_{OA}$) for $\zeta=9.715$ and $\mathbf{r}_{OA}=(4.46$ a.u. 0,0). Numbers in brackets denote powers of 10.

n	S_n	$\epsilon_8^{(n)}$	$\epsilon_{14}^{(n)}$	$\epsilon_{20}^{(n)}$
0	0.266 326 681 097 793 464 52[−03]			
1	0.106 402 998 617 201 167 41[−02]			
2	0.238 929 670 203 779 508 52[−02]			
3	0.423 582 770 122 378 152 51[−02]			
4	0.659 492 074 978 688 091 56[−02]	0.178 339 206 573 833 795 88		
5	0.945 558 343 806 063 423 52[−02]	0.189 289 484 922 574 719 88		
6	0.128 046 733 876 709 839 20[−01]	0.204 046 710 720 549 360 20		
7	0.166 270 622 831 939 396 57[−01]	0.223 501 981 127 387 367 32	−0.237 876 105 116 476 611 30	
8	0.209 058 198 100 395 985 94[−01]	0.248 551 228 362 275 006 36	−1.472 731 341 430 522 600 7	
9	0.256 224 132 640 763 653 36[−01]	0.279 916 403 394 932 853 88	2.888 521 284 563 294 630 2	
10	0.307 569 184 373 050 353 67[−01]	0.317 892 686 065 261 664 62	1.280 238 848 713 023 715 7	1.001 301 022 551 704 013 8
11	0.362 882 373 736 410 350 98[−01]	0.362 073 467 648 155 560 03	1.005 471 556 936 549 484 5	
12	0.421 943 187 184 824 775 75[−01]	0.411 163 801 171 646 792 24	0.903 568 234 635 371 552 98	
13	0.484 523 766 382 964 170 83[−01]	0.463 015 869 315 864 126 65	0.856 288 300 583 650 103 76	
14	0.550 391 046 407 418 818 45[−01]	0.514 953 233 666 771 874 91		
15	0.619 308 810 580 879 747 59[−01]	0.564 301 924 263 379 442 39		
16	0.691 039 634 421 818 474 34[−01]	0.608 917 977 832 648 225 11		
17	0.765 346 696 338 517 427 43[−01]			
18	0.841 995 437 910 852 607 55[−01]			
19	0.920 755 061 690 411 183 40[−01]			
20	0.100 139 985 924 731 714 67[+0]			

TABLE III. Application of Levin's u transformation [Eq. (39)] to the first 20 terms of the series given by Eq. (40) at the cusp (i.e., $\mathbf{r}=\mathbf{r}_{OA}$) for $\zeta=9.715$ and $\mathbf{r}_{OA}=(4.46$ a.u., 0,0). Numbers in brackets denote powers of 10.

n	S_n	k	$u_k(S_{20-k})^a$	$u_k(S_{20-k})^b$	$u_k(S_{20-k})^c$
0	0.266 326 681 097 793 464 52[−03]	0	0.100 139 985 924 731 714 67[+0]	0.100 139 985 924 731 714 67[+0]	0.100 139 985 924 731 714 67[+0]
1	0.106 402 998 617 201 167 41[−02]	1	−0.255 831 066 932 378 656 36[−01]	−0.298 948 654 809 435 417 35[−01]	−0.340 983 296 954 714 869 05[−01]
2	0.238 929 670 203 779 508 52[−02]	2	0.575 314 621 960 390 694 37[−01]	0.575 314 621 960 390 694 37[−01]	0.575 314 621 960 390 694 37[−01]
3	0.423 582 770 122 378 152 51[−02]	3	0.490 512 674 722 642 624 13[+0]	0.746 008 489 800 911 531 09[+0]	0.152 573 964 849 793 522 58[+1]
4	0.659 492 074 978 688 091 56[−02]	4	0.933 066 598 090 926 756 09[+0]	0.993 705 081 500 548 665 07[+0]	0.993 631 986 236 840 745 04[+0]
5	0.945 558 343 806 063 423 52[−02]	5	0.994 714 610 890 144 403 05[+0]	0.999 941 564 367 678 059 40[+0]	0.100 010 572 573 728 356 38[+1]
6	0.128 046 733 876 709 839 20[−01]	6	0.998 801 856 903 337 691 67[+0]	0.999 008 019 897 425 631 27[+0]	0.998 751 420 723 187 560 03[+0]
7	0.166 270 622 831 939 396 57[−01]	7	0.998 488 813 125 711 877 20[+0]	0.998 291 699 739 087 132 32[+0]	0.998 077 244 313 094 844 15[+0]
8	0.209 058 198 100 395 985 94[−01]	8	0.998 092 790 526 337 483 76[+0]	0.997 924 854 988 151 173 00[+0]	0.997 794 820 373 213 905 25[+0]
9	0.256 224 132 640 763 653 36[−01]	9	0.997 913 960 281 620 761 58[+0]	0.997 840 625 302 182 426 92[+0]	0.997 826 233 551 166 544 54[+0]
10	0.307 569 184 373 050 353 67[−01]	10	0.997 921 423 353 977 111 47[+0]	0.997 964 633 098 054 294 13[+0]	0.998 082 853 911 345 052 32[+0]
11	0.362 882 373 736 410 350 98[−01]	11	0.998 059 865 942 719 532 43[+0]	0.998 227 683 563 704 149 72[+0]	0.998 482 213 760 298 977 04[+0]
12	0.421 943 187 184 824 775 75[−01]	12	0.998 279 376 948 031 369 83[+0]	0.998 570 572 635 927 932 25[+0]	0.998 954 197 497 592 000 52[+0]
13	0.484 523 766 382 964 170 83[−01]	13	0.998 539 365 741 269 788 34[+0]	0.998 946 187 997 575 366 44[+0]	0.999 444 082 298 690 123 18[+0]
14	0.550 391 046 407 418 818 45[−01]	14	0.998 808 789 365 689 404 64[+0]	0.999 319 642 792 534 733 35[+0]	0.999 912 899 482 887 722 58[+0]
15	0.619 308 810 580 879 747 59[−01]	15	0.999 065 209 862 099 418 23[+0]	0.999 667 077 591 085 822 97[+0]	0.100 033 593 359 538 527 62[+1]
16	0.691 039 634 421 818 474 34[−01]	16	0.999 293 317 607 191 534 45[+0]	0.999 973 709 130 025 427 26[+0]	0.100 070 014 553 492 538 12[+1]
17	0.765 346 696 338 517 427 43[−01]	17	0.999 483 285 969 052 221 16[+0]	0.100 023 159 562 407 586 49[+1]	0.100 100 117 846 277 818 04[+1]
18	0.841 995 437 910 852 607 55[−01]	18	0.999 629 208 856 823 676 31[+0]	0.100 043 745 792 936 259 71[+1]	0.100 124 042 440 196 340 87[+1]
19	0.920 755 061 690 411 183 40[−01]	19	0.999 727 786 880 797 916 33[+0]	0.100 059 077 238 855 311 48[+1]	0.100 142 244 477 940 933 40[+1]
20	0.100 139 985 924 731 714 67[+0]	20	0.999 777 362 930 856 971 95[+0]	0.100 069 225 341 856 070 96[+1]	0.100 155 288 434 073 302 32[+1]

[a]Using Eq. (39) with $\beta=1$.
[b]Same as a, but using the value $\beta=2$.
[c]Same as a, but using the value $\beta=3$.

V. APPLICATION TO THE THREE-CENTER TWO-ELECTRON COULOMB INTEGRALS

In this section, we want to show how the accelerating techniques presented above might be used to improve the rate of convergence of the series representation of the three-center two-electron integrals. However, before addressing the application of such accelerators, let us first begin by establishing the formulas that will be used to carry out the evaluation of these integrals within the framework of the two-range one-center expansion approach.

The three-center one- and two-electron Coulomb integrals are among the most difficult integrals that are needed in the SCF approximation. However, there is not an extensive literature about the latter in contrast to the former, which has been studied in detail in many works. The three-center two-electron Coulomb integrals are generally defined as follows:

$$\left\langle \chi^{m_1}_{n_1,l_1}[\xi_1(\mathbf{R}_1-\mathbf{r}_{OA})]\chi^{m_3}_{n_3,l_3}[\xi_3(\mathbf{R}_2-\mathbf{r}_{OB})] \left| \frac{1}{|\mathbf{R}_1-\mathbf{R}_2|} \right| \chi^{m_2}_{n_2,l_2}[\xi_2(\mathbf{R}_1-\mathbf{r}_{OA})]\chi^{m_4}_{n_4,l_4}[\xi_4(\mathbf{R}_2-\mathbf{r}_{OC})] \right\rangle . \tag{41}$$

By a suitable change of variable (i.e., $\mathbf{r}_1=\mathbf{R}_1-\mathbf{r}_{OA}$ and $\mathbf{r}_2=\mathbf{R}_2-\mathbf{r}_{OA}$), the previous definition may be rewritten in a somewhat simpler fashion as follows:

$$\mathcal{J}^{n_3,l_3,m_3,n_4,l_4,m_4}_{n_1,l_1,m_1,n_2,l_2,m_2}(\xi_1,\xi_2,\xi_3,\xi_4;\mathbf{r}_{AB},\mathbf{r}_{AC})=\langle \chi^{m_3}_{n_3,l_3}[\xi_3(\mathbf{r}_2-\mathbf{r}_{AB})]|V(\mathbf{r}_2)|\chi^{m_4}_{n_4,l_4}[\xi_4(\mathbf{r}_2-\mathbf{r}_{AC})]\rangle_{\mathbf{r}_2} , \tag{42}$$

where $V(\mathbf{r}_2)$ stands for the so-called one-center charge distribution potential which is defined as

$$V(\mathbf{r}_2)=\left\langle \chi^{m_1}_{n_1,l_1}(\xi_1\mathbf{r}_1) \left| \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \right| \chi^{m_2}_{n_2,l_2}(\xi_2\mathbf{r}_1) \right\rangle_{\mathbf{r}_1} . \tag{43}$$

Now expanding the Coulomb operator by means of the well-known Laplace-Neumann addition theorem yields

$$V(\mathbf{r}_2)=\mathcal{N}_1\mathcal{N}_2\sum_{l=0}^{+\infty}\frac{4\pi}{2l+1}\langle l_1m_1|lm|l_2m_2\rangle \times\left\langle r_1^{n_1-1}e^{-\xi_1r_1}\left|\frac{r_<^l}{r_>^{l+1}}\right|r_1^{n_2-1}e^{-\xi_2r_1}\right\rangle \times[Y_l^m(\theta_{\mathbf{r}_2},\varphi_{\mathbf{r}_2})]^* , \tag{44}$$

where $r_<$ and $r_>$ represent $\min(r_1,r_2)$ and $\max(r_1,r_2)$, respectively. The terms $\mathcal{N}_1$ and $\mathcal{N}_2$ are nothing but the normalization factors of the Slater orbitals which are determined by

$$\mathcal{N}_i=\frac{(2\xi_i)^{n_i+1/2}}{\sqrt{(2n_i)!}} . \tag{45}$$

In addition, taking the nonvanishing conditions of the Gaunt coefficients into account, which are

$$\langle l_1m_1|lm|l_2m_2\rangle\neq 0 \Longleftrightarrow \begin{cases} |l_1-l_2|\le l\le l_1+l_2 \\ m=m_1-m_2 \\ l_1+l+l_2 \text{ is even} , \end{cases} \tag{46}$$

allow us to rewrite the energies given by Eq. (44) as a finite sum such that

$$V(\mathbf{r}_2)=\mathcal{N}_1\mathcal{N}_2\sum_{l=|l_1-l_2|}^{l_1+l_2}{}'\frac{4\pi}{2l+1}\langle l_1m_1|lm|l_2m_2\rangle V_l(r_2) \times[Y_l^{m_1-m_2}(\theta_{\mathbf{r}_2},\varphi_{\mathbf{r}_2})]^* , \tag{47}$$

where the symbol $\sum'$ indicates that the summation is to be performed in steps of two. The pure radial functions [i.e., $V_l(r_2)$] may readily be expressed using Roothaan's notation [90] as

$$V_l(r_2)=r_2^{n_1+n_2}\{E_{n_1+n_2+l}[(\xi_1+\xi_2)r_2] + A_{n_1+n_2-l-1}[(\xi_1+\xi_2)r_2]\} , \tag{48}$$

where the auxiliary functions $E_n(\alpha)$ and $A_n(\alpha)$, defined for $n\ge 0$, are such that

$$E_n(\alpha)=\int_0^1 x^ne^{-\alpha x}dx , \tag{49}$$

$$A_n(\alpha)=\int_1^{+\infty} x^ne^{-\alpha x}dx . \tag{50}$$

The numerical evaluation of these two functions is greatly simplified by the use of the recurrence relations, relating E_n to E_{n-1} and A_n to A_{n-1}. However, the calculation of the "first" terms involved in such relations (i.e., E_0 and A_0 for the upward calculation $E_{n\max}$ and $A_{n\max}$ for the backward calculation) may be computed by means of the closed analytical formula:

$$\int x^ne^{-\alpha x}dx=-\frac{n!}{\alpha^{n+1}}e^{-\alpha x}\sum_{m=0}^{n}\frac{(\alpha x)^m}{m!} \tag{51}$$

or by a series expansion, namely, Kummer functions [91], which from a numerical standpoint exhibit a better numerical stability:

$${}_1F_1(1;n+2;\alpha)=(n+1)e^{\alpha}E_n(\alpha) , \tag{52}$$

$$U(1;n+2;\alpha)=e^{\alpha}A_n(\alpha) . \tag{53}$$

Hence, substituting Eq. (47) into Eq. (42) yields

$$\mathcal{J}^{n_3,l_3,m_3,n_4,l_4,m_4}_{n_1,l_1,m_1,n_2,l_2,m_2}(\xi_1,\xi_2,\xi_3,\xi_4;\mathbf{r}_{AB},\mathbf{r}_{AC})$$
$$=\mathcal{N}_1\mathcal{N}_2\sum_{l=|l_1-l_2|}^{l_1+l_2{}'}\frac{4\pi}{2l+1}\langle l_1m_1|lm|l_2m_2\rangle\langle\chi^{m_3}_{n_3,l_3}[\xi_3(\mathbf{r}_2-\mathbf{r}_{AB})|V_l(r_2)[Y_l^{m_1-m_2}(\theta_{\mathbf{r}_2},\varphi_{\mathbf{r}_2})]^*|\chi^{m_4}_{n_4,l_4}[\xi_4(\mathbf{r}_2-\mathbf{r}_{AC})]\rangle_{\mathbf{r}_2}\ . \tag{54}$$

The next step consists in translating the Slater orbital $\chi^{m_3}_{n_3,l_3}$ and $\chi^{m_4}_{n_4,l_4}$ in such a way as to separate the variables $\mathbf{r}_2$, $\mathbf{r}_{AB}$, and $\mathbf{r}_{AC}$. For such a purpose, let us begin by making use of the solid spherical harmonics addition theorem given by Eq. (9). Thus one obtains

$$\mathcal{J}^{n_3,l_3,m_3,n_4,l_4,m_4}_{n_1,l_1,m_1,n_2,l_2,m_2}(\xi_1,\xi_2,\xi_3,\xi_4;\mathbf{r}_{AB},\mathbf{r}_{AC})$$
$$=(-1)^{n_3-l_3+n_4-l_4}$$
$$\times\mathcal{N}_1\mathcal{N}_2\mathcal{N}_3\mathcal{N}_4\sum_{l=|l_1-l_2|}^{l_1+l_2{}'}\frac{4\pi}{2l+1}\langle l_1m_1|lm|l_2m_2\rangle$$
$$\times4\pi(2l_3+1)!!\sum_{l_3'=0}^{l_3}\sum_{m_3'=-l_3'}^{l_3'}\frac{\langle l_3m_3|l_3'm_3'|l_3-l_3'm_3-m_3'\rangle}{(2l_3'+1)!![2(l_3-l_3')+1]!!}[\mathcal{Y}^{m_3-m_3'}_{l_3-l_3'}(-\mathbf{r}_{AB})]^*$$
$$\times4\pi(2l_4+1)!!\sum_{l_4'=0}^{l_4}\sum_{m_4'=-l_4'}^{l_4'}\frac{\langle l_4m_4|l_4'm_4'|l_4-l_4'm_4-m_4'\rangle}{(2l_4'+1)!![2(l_4-l_4')+1]!!}\mathcal{Y}^{m_4-m_4'}_{l_4-l_4'}(-\mathbf{r}_{AC})$$
$$\times P^{m_1,m_2,m_3',m_4'}_{n_3,l_3,l_3',l,n_4,l_4,l_4'}(\xi_1,\xi_2,\xi_3,\xi_4;\mathbf{r}_{AB},\mathbf{r}_{AC})\ , \tag{55}$$

where the functions P are defined as follows:

$$P^{m_1,m_2m_3',m_4'}_{n_3,l_3,l_3',l,n_4,l_4,l_4'}(\xi_1,\xi_2,\xi_3,\xi_4;\mathbf{r}_{AB},\mathbf{r}_{AC})=\langle|\mathbf{r}_2-\mathbf{r}_{AB}|^{n_3-l_3-1}e^{-\xi_3|\mathbf{r}_2-\mathbf{r}_{AB}|}\mathcal{Y}^{m_3'}_{l_3'}(\mathbf{r}_2)$$
$$\times|V_l(r_2)[Y_l^{m_1-m_2}(\theta_{\mathbf{r}_2},\varphi_{\mathbf{r}_2})]^*||\mathbf{r}_2-\mathbf{r}_{AC}|^{n_4-l_4-1}e^{-\xi_4|\mathbf{r}_2-\mathbf{r}_{AC}|}\mathcal{Y}^{m_4'}_{l_4'}(\mathbf{r}_2)\rangle\ . \tag{56}$$

Now applying the addition theorem given by Eq. (12) to the functions $|\mathbf{r}_2-\mathbf{r}_{AB}|^{n_3-l_3-1}e^{-\xi_3|\mathbf{r}_2-\mathbf{r}_{AB}|}$ and $|\mathbf{r}_2-\mathbf{r}_{AC}|^{n_4-l_4-1}e^{-\xi_4|\mathbf{r}_2-\mathbf{r}_{AC}|}$ allows us to separate the variables $\mathbf{r}_2$, $\mathbf{r}_{AB}$, and $\mathbf{r}_{AC}$ as follows:

$$P^{m_1,m_2,m_3',m_4'}_{n_3,l_3,l_3',l,n_4,l_4,l_4'}(\xi_1,\xi_2,\xi_3,\xi_4;\mathbf{r}_{AB},\mathbf{r}_{AC})=\sum_{\lambda=0}^{+\infty}(2\lambda+1)\sum_{\lambda'=0}^{+\infty}(2\lambda'+1)R\,\Omega\ , \tag{57}$$

where the functions R and Ω stand for the pure radial integral and the pure angular integral, which are determined by the following relationships:

$$R=\left\langle r_2^{l_3'}\left[\frac{d}{d\xi_3}\right]^{n_3-l_3}\left[\frac{I_{\lambda+1/2}(\xi_3\rho_<)}{\sqrt{\rho_<}}\frac{K_{\lambda+1/2}(\xi_3\rho_>)}{\sqrt{\rho_>}}\right]|V_l(r_2)|r_2^{l_4'}\left[\frac{d}{d\xi_4}\right]^{n_4-l_4}\left[\frac{I_{\lambda'+1/2}(\xi_3\rho'_<)}{\sqrt{\rho'_<}}\frac{K_{\lambda'+1/2}(\xi_3\rho'_>)}{\sqrt{\rho'_>}}\right]\right\rangle_{r_2}\ . \tag{58}$$

Here the variables $\rho_<$, $\rho_>$, $\rho'_<$, and $\rho'_>$ stand for $\min(r_2,a)$, $\max(r_2,a)$, $\min(r_2,c)$, and $\max(r_2,c)$, respectively, where, for brevity and convenience, the modulus of the vectors $\mathbf{r}_{AB}$ and $\mathbf{r}_{AC}$ are referred to as a and c:

$$\Omega=\langle P_\lambda[\cos\angle(\mathbf{r}_2,\mathbf{r}_{AB})]Y^{m_3'}_{l_3'}(\theta_{\mathbf{r}_2},\varphi_{\mathbf{r}_2})|[Y_l^{m_1-m_2}(\theta_{\mathbf{r}_2},\varphi_{\mathbf{r}_2})]^*|P_{\lambda'}[\cos\angle(\mathbf{r}_2,\mathbf{r}_{AC})]Y^{m_4'}_{l_4'}(\theta_{\mathbf{r}_2},\varphi_{\mathbf{r}_2})\rangle\ . \tag{59}$$

For dealing with this pure angular integral, let us first apply the surface spherical harmonics multiplication theorem in order to linearize the product of the three spherical harmonics $[Y^{m_3'}_{l_3'}]^*$, $[Y_l^{m_1-m_2}]^*$, and $Y^{m_4'}_{l_4'}$:

$$[Y^{m_1}_{l_1}(\theta,\varphi)]^*Y^{m_2}_{l_2}(\theta,\varphi)=\sum_{l=|l_1-l_2|}^{l_1+l_2{}'}\langle l_2m_2|l_1m_1|lm_2-m_1\rangle Y_1^{m_2-m_1}(\theta,\varphi)\ . \tag{60}$$

Thus one obtains

$$[Y_{l'_3}^{m'_3}(\theta_{r_2},\varphi_{r_2})]^*[Y_l^{m_1-m_2}(\theta_{r_2},\varphi_{r_2})]^* Y_{l'_4}^{m'_4}(\theta_{r_2},\varphi_{r_2})$$
$$= \sum_{l'_{34}=|l'_3-l'_4|}^{l'_3+l'_4}{}' \langle l'_4 m'_4 | l'_3 m'_3 | l'_{34} m'_4 - m'_3 \rangle \sum_{l''_{34}=|l'_{34}-l|}^{l'_{34}+l}{}' \langle l'_{34} m'_4 - m'_3 | l m_1 - m_2 | l''_{34} (m'_4 - m'_3) - (m_1 - m_2) \rangle$$
$$\times Y_{l''_{34}}^{(m'_4-m'_3)-(m_1-m_2)}(\theta_{r_2},\varphi_{r_2}) . \tag{61}$$

It turns out that the Legendre polynomials involved into Eq. (59) may readily be expanded according to the following addition theorem:

$$P_\lambda[\cos\angle(\mathbf{r},\mathbf{R})] = \frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} Y_\lambda^\mu(\theta_r,\varphi_r)[Y_\lambda^\mu(\theta_R,\varphi_R)]^* . \tag{62}$$

Hence, by taking once again the nonvanishing conditions of the Gaunt coefficients into account, the angular integral Ω may be rewritten as

$$\Omega = \frac{4\pi}{(2\lambda+1)} \frac{4\pi}{(2\lambda'+1)} \sum_{l'_{34}=|l'_3-l'_4|}^{l'_3+l'_4}{}' \langle l'_4 m'_4 | l'_3 m'_3 | l'_{34} m'_4 - m'_3 \rangle$$
$$\times \sum_{l''_{34}=|l'_{34}-l|}^{l'_{34}+l}{}' \langle l'_{34} m'_4 - m'_3 | l m_1 - m_2 | l''_{34} (m'_4 - m'_3) - (m_1 - m_2) \rangle$$
$$\times \sum_{\mu=-\lambda}^{\lambda} \langle \lambda\mu | l''_{34} (m'_4 - m'_3) - (m_1 - m_2) | \lambda' \mu - (m'_4 - m'_3) + (m_1 - m_2) \rangle$$
$$\times Y_\lambda^\mu(\theta_{r_{AB}},\varphi_{r_{AB}})[Y_{\lambda'}^{\mu-(m'_4-m'_3)+(m_1-m_2)}(\theta_{r_{AC}},\varphi_{r_{AC}})]^* . \tag{63}$$

It should be mentioned that according to the nonvanishing conditions of the Gaunt coefficients of Eq. (46), the running index λ' occurring in Eq. (57) is such that

$$|\lambda - l''_{34}| \le \lambda' \le \lambda + l''_{34} ,$$
$$\lambda + l''_{34} + \lambda' \text{ is even} . \tag{64}$$

As a special case of the series representation given by Eq. (55), let us assume that points A, B, and C are aligned (i.e., $\theta_{r_{AB}} = \theta_{r_{AC}} = 0$, linear molecules). Therefore, the three-center two-electron integrals vanish unless the following equality holds: $m_4 - m_3 = m_1 - m_2$. Indeed, linearizing the product of the surface spherical harmonics depending on the angular parameters of the vectors $\mathbf{r}_{AB}$ and $\mathbf{r}_{AC}$ by means of the multiplication theorem of Eq. (60) and taking into account the following relationships:

$$\mathcal{Y}_l^m(-\mathbf{R}) = |\mathbf{R}|^l Y_l^m(\pi-\theta_R,\pi+\varphi_R)$$
$$= (-1)^l |\mathbf{R}|^l Y_l^m(\theta_R,\varphi_R) , \tag{65}$$
$$Y_l^m(0,\varphi) = \left[\frac{2l+1}{4\pi}\right]^{1/2} \delta_{m,0} ,$$

where δ stands for the Kronecker symbol, immediately yields the above-mentioned additional condition.

In Table IV selected integrals have been computed by means of the series representation given by Eq. (55). As may be seen from the first set of values, good convergence is obtained by the computation of only 20 terms of such a series. However, by using Levin's u transformation fewer terms may produce the exact value. This is due to the fact that in this case, the sequence of partial sums increases monotonically and hence is well adapted to such a nonlinear transformation. Conversely, from the last set of values it may be seen that the epsilon algorithm produce better values than the Levin's u transformation though it is less efficient in comparison to the latter. This is essentially due to the fact that in this case, the partial sums obtained from the original series do not constitute either a monotonic or an alternating sequence. In fact, these partial sums increase in magnitude and then decrease towards the exact value of the integral.

VI. CONCLUSION

At the present time, it is still too early to claim that the algorithms based on the use of Slater-type orbitals may complete the *ab initio* programs using Gaussian-type orbitals. There are nevertheless two points in favor of these alternative algorithms. The first is related to the fact that with the huge technological advance in computer science area such algorithms will certainly benefit from the new architectures (e.g., massively parallel machines). With regard to the second point, it concerns the method itself. Indeed, in the present work we have focused our attention on the improvement of the numerical algorithm by means of some nonlinear transformations, namely, the epsilon algorithm and also Levin's u transformation. However, such numerical devices are not sufficient to obtain efficient packages. Indeed, the examination of the three-center two-electron integrals given above shows clearly that the most time-consuming step corresponds to the evaluation of the derivatives of the product of the modified Bessel functions of the second kind. Therefore,

TABLE IV. Three-center two-electron repulsion integrals with normalized Slater orbitals [Eq. (41)]. The present values correspond to the linear molecule LiCCH, the geometrical parameters of which are (see [94]) Li (0,0,0), C (3.55,0,0), C′ (5.8196,0,0), and H (7.8284,0,0). Lengths are in a.u. Numbers in brackets denote powers of 10.

Integral	ζ_1	ζ_2	ζ_3	ζ_4	I^{a}	$\epsilon_{20}^{(n)}$	I^{b}	$u_3(S_{12})$
$\langle 1s^{C'}1s^{H}\|1s^{C}1s^{C}\rangle$	7.968 97	0.454 41	5.230 90	5.230 90	0.188 877 912[−01]	0.188 877 949[−01]	0.188 877 949[−01]	0.188 877 949[−01]
$\langle 1s^{C'}1s^{H}\|1s^{C}2s^{C}\rangle$	7.968 97	0.454 41	5.230 90	1.167 82	0.275 256 626[−02]	0.275 256 680[−02]	0.275 256 680[−02]	0.275 256 680[−02]
$\langle 1s^{C'}1s^{H}\|1s^{C}2p_z^{C}\rangle$	7.968 97	0.454 41	5.230 90	1.255 72	0.484 255 956[−03]	0.484 256 051[−03]	0.484 256 051[−03]	0.484 256 051[−03]
$\langle 1s^{C'}1s^{H}\|2p_z^{C}3d_z^{C}\rangle$	7.968 97	0.454 41	2.726 25	2.015 91	0.477 576 493[−02]	0.477 576 604[−02]	0.477 576 604[−02]	0.477 576 604[−02]
$\langle 2s^{C'}1s^{H}\|1s^{C}1s^{C}\rangle$	1.167 82	0.454 41	5.230 90	5.230 90	0.231 915 790[+00]	0.231 915 790[+00]	0.231 915 790[+0]	0.231 915 790[+0]
$\langle 2s^{C'}1s^{H}\|1s^{C}2s^{C}\rangle$	1.167 82	0.454 41	5.230 90	1.167 82	0.335 758 750[−01]	0.335 758 750[−01]	0.335 758 750[−01]	0.335 758 750[−01]
$\langle 2s^{C'}1s^{H}\|1s^{C}2p_z^{C}\rangle$	1.167 82	0.454 41	5.230 90	1.255 72	0.318 914 301[−02]	0.318 914 301[−02]	0.318 914 301[−02]	0.318 914 301[−02]
$\langle 2s^{C'}1s^{H}\|2p_z^{C}3d_{zz}^{C}\rangle$	1.167 82	0.454 41	2.726 25	2.015 91	0.247 693 208[−01]	0.247 693 208[−01]	0.247 693 208[−01]	0.247 693 208[−01]
$\langle 2s^{C'}1s^{H}\|1s^{Li}1s^{Li}\rangle$	1.167 82	1.337 61	2.433 09	2.433 09	0.752 785 341[−01]	0.752 720 784[−01]	0.752 720 787[−01]	0.572 907 876[−01]
$\langle 2s^{C'}1s^{H}\|1s^{Li}2s^{Li}\rangle$	1.167 82	1.337 61	2.433 09	0.450 00	0.778 300 824[−02]	0.778 234 078[−02]	0.778 234 081[−02]	0.778 427 516[−02]
$\langle 2s^{C'}1s^{H}\|2s^{Li}2s^{Li}\rangle$	1.167 82	1.337 61	0.450 00	0.450 00	0.713 556 031[−01]	0.713 495 636[−01]	0.713 495 640[−01]	0.713 665 009[−01]
$\langle 2s^{C'}2s^{C}\|1s^{Li}1s^{Li}\rangle$	1.167 82	1.167 82	4.517 69	4.517 69	0.150 148 053[+00]	0.150 148 075[+00]	0.150 148 075[+0]	0.150 147 841[+0]
$\langle 2s^{C'}2s^{C}\|2s^{Li}2s^{Li}\rangle$	1.167 82	1.167 82	0.850 00	0.850 00	0.143 404 274[+00]	0.143 404 295[+00]	0.143 404 295[+0]	0.143 404 064[+0]

[a]Computed values by means of the series representation (55). These values have been obtained with 20 terms of the original series.
[b]Comparative values, obtained from the ALCHEMY II (Ref. [95]) package.

we intend to investigate this point in a further study of the method.

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