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Analytical and numerical development for the two-centre overlap-like quantum similarity integrals over Slater-type functions

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Abstract

In molecular quantum similarity measure between two molecules, using the molecular electron density, the major task involves the accurate numerical evaluation of overlap between the two electron densities in the integral measure. By expanding the electron densities in terms of atomic orbitals, using the linear combination of atomic orbitals approach, a large number of overlap-like quantum similarity integrals over the basis functions in the two molecules will be required accurately for the calculation of a meaningful quantum similarity measure. Improvement of the computational methods of these integrals would be indispensable to a further development in computational studies of large molecular systems. Analytic expressions were obtained for these overlap-like quantum similarity integrals over Slater-type functions, in terms of the usual two-centre overlap integrals over B functions. Different approaches were developed for the numerical evaluation of these two-centre overlap integrals over B functions, which can be used for the numerical evaluation of the two-centre overlap-like quantum similarity integrals over Slater-type functions. In this work we present our approach which is based on the use of nonlinear transformations for improving convergence of highly oscillatory integrals. In the case of more complicated multicentre integrals, this approach is shown to be able to produce remarkably good results. We also present different representations, which were obtained by Steinborn group, and which can be used for a fast and accurate computation of the two-centre overlap-like quantum similarity integrals over Slater-type functions.

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1. Introduction

The concept of molecular similarity is used throughout chemistry. From a mathematical point of view, based on quantum chemical ideas, the concept of molecular similarity presents severe difficulties.

Many alternatives have been developed to quantify the similarity of two molecules and to align molecules [1–3]. Despite all these efforts, there is still no definite answer on how to express or evaluate molecular similarity. The complete theory of molecular quantum similarity was reviewed in several papers by Carbò *et al* [4–7].

Quantum molecular similarity measure (QSM) between two molecules can be expressed as an integral measure computation between the density functions attached to the involved molecules [4–9]:

$$Z_{12} = \int \rho_1(\vec{r})\rho_2(\vec{r})\,\mathrm{d}\vec{r}, \tag{1}$$

where $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$ refer to the electron density of molecules 1 and 2, respectively, at the point r in space, and they are given by

$$\begin{aligned}\rho_1(\vec{r}) &= \Psi_1^*(\vec{r})\Psi_1(\vec{r}) = \sum_{\mu=1}^{N_1}\sum_{\nu=1}^{N_1} c_\mu c_\nu \varphi_\mu^*(\vec{r})\varphi_\nu(\vec{r}) \\ \rho_2(\vec{r}) &= \Psi_2^*(\vec{r})\Psi_2(\vec{r}) = \sum_{\sigma=1}^{N_2}\sum_{\kappa=1}^{N_2} c_\sigma c_\kappa \varphi_\sigma^*(\vec{r})\varphi_\kappa(\vec{r}),\end{aligned} \tag{2}$$

where Ψ_1 and Ψ_2 stand for the wavefunctions. The coefficients c_μ, c_ν, c_σ and c_κ stand for the LCAO (linear combination of atomic orbitals) coefficients of the atomic orbitals φ_μ, φ_ν, φ_σ and φ_κ.

The element Z_{11} is called quantum self-similarity measure [4–9]. For a set of N molecules, all the element Z_{12} form a symmetrical matrix $Z(N \times N)$, which is called molecular quantum similarity matrix (MQSM), and where Z_{11} are the diagonal elements.

Carbò *et al* introduced the so-called Carbò similarity indices (CSI) [10], which is used to transform all the elements of the matrix Z into numbers lying in the interval]0, 1]. This transformation involves the calculation of the elements C_{12} given by

$$C_{12} = \frac{Z_{12}}{\sqrt{Z_{11}Z_{22}}}. \tag{3}$$

The diagonal elements of the obtained matrix C are equal to 1 and all other elements are in the interval]0, 1]. The elements C_{12} of the matrix C reflect the extent of similarity between the two molecules [11, 12].

By expressing the densities in terms of LCAO approach as in equation (2), one can express the integrals (1) in terms of overlap-like quantum similarity integrals as follows:

$$Z_{12} = \sum_{\mu=1}^{N_1}\sum_{\nu=1}^{N_1}\sum_{\sigma=1}^{N_2}\sum_{\kappa=1}^{N_2} c_\mu c_\nu c_\sigma c_\kappa \int \varphi_\mu^*(\vec{r})\varphi_\nu(\vec{r})\varphi_\sigma^*(\vec{r})\varphi_\kappa(\vec{r})\,\mathrm{d}\vec{r}. \tag{4}$$

The integrals occurring in the above equation, which will be referred to as $Z_{12}^{\mu\nu\sigma\kappa}$:

$$Z_{12}^{\mu\nu\sigma\kappa} = \int \varphi_\mu^*(\vec{r})\varphi_\nu(\vec{r})\varphi_\sigma^*(\vec{r})\varphi_\kappa(\vec{r})\,\mathrm{d}\vec{r}, \tag{5}$$

are the so-called overlap-like quantum similarity integrals. These integrals can be one-, two-, three- or four-centre terms.

It is clear that molecular quantum similarity measurements require a calculation of a large number of integrals, occurring in the calculation of the overlap.

In the present work, we used Slater-type functions (STFs) [13] as a basis set to represent atomic orbitals. These functions are better suited than Gaussian-type functions (GTFs) [14] to represent electron wave functions near the nucleus and at long range [15].

Using the fact that the product of two STFs centred at the same point can be expressed as a single STF centred at the same point, one can express the two-centre overlap-like quantum similarity integrals over STFs in terms of the usual two-centre overlap integrals over STFs. Such integrals have been studied by many authors and different approaches were developed for their analytic and numerical evaluation [16–29]. The numerical evaluation of these overlap-like quantum similarity integrals over STFs will probably benefice from the work previously done on the usual two-centre overlap integrals.

The two-centre overlap integrals over STFs are in their turn expressed in terms of overlap integrals over B functions [22, 30, 31]. These B functions have some remarkable mathematical properties applicable to multicentre integral problems [31, 32], their Fourier transform is of exceptional simplicity [16] and this is why they are well adapted to the Fourier transformation method [33, 34], which led to an analytic development for the overlap integrals over B functions [16, 19].

In the present work, we used an analytic expression obtained by Weniger and Steinborn [16], which involves semi-infinite spherical Bessel integrals. This analytic expression turned out to be very difficult to evaluate accurately due to the presence of the spherical Bessel function in the semi-infinite integral. The convergence problems could be solved by using appropriate mathematical techniques, such as convergence accelerators or nonlinear transformations for improving convergence of highly oscillatory integrals [35]. Among these nonlinear transformations, the $\overline{D}$ transformation of Sidi [36–38] is certainly one of the most powerful when dealing with integrals, whose integrands satisfy a certain type of linear differential equations.

In previous work [39–46], we showed that this nonlinear $\overline{D}$ transformation, combined with some extrapolation techniques, permits a remarkably efficient and reliable evaluation of complicated multi-centre integrals over B functions and over STFs. It is now shown that this approach can also be applied to the two-centre overlap integrals over B function [29]. The integrand of the semi-infinite spherical Bessel integrals satisfies all the conditions to apply the $\overline{D}$ transformation. This led to the development of highly accurate numerical evaluation of the two-centre overlap integrals over B functions, which is used for the numerical evaluation of the two-centre overlap-like similarity integrals.

The two-centre overlap integrals were thoroughly studied by Steinborn group [16–22]. Numerous different representations, which can be used for accurate and rapid computation of overlap integrals over B functions, were obtained. FORTRAN programs were developed by Homeier, Weniger and Steinborn [20]. These representations can also be used for the analytic development of the two-centre overlap-like quantum similarity integrals over STFs.

In this work, we used the code ACJU developed by Homeier, Weniger and Steinborn [20] for the numerical evaluation of the two-centre overlap integrals over B functions occurring in the analytic expression of the two-centre overlap-like similarity integrals over STFs.

Numerical results are obtained for the two-centre overlap-like similarity integrals of the first and second kinds. These results are in a complete agreement with those obtained using the one-centre two-range method [47] and also using the approach based on the epsilon algorithm of Wynn [48].

Comparisons with regard to accuracy and rapidity showed that the ACJU code gives highly efficient results and leads to the most rapid algorithm. Note that the algorithm using

the nonlinear $\overline{D}$ leads to a highly efficient numerical evaluation of the molecular integrals and the calculation times can be further reduced by developing extrapolation techniques specially suited to the two-centre overlap integrals.

2. General definitions and properties

The two-centre overlap-like quantum similarity integrals $Z_{12}^{n_1n_2n_3n_4}$ over Slater-type functions (STFs) are given by ($\vec{A}$, $\vec{B} \in \mathbb{R}^3$)

- the two-centre integrals of the first kind:

$$\int \chi_{n_1,l_1}^{m_1}(\zeta_1, \vec{r} - \overrightarrow{OA})^* \chi_{n_2,l_2}^{m_2}(\zeta_2, \vec{r} - \overrightarrow{OA}) \chi_{n_3,l_3}^{m_3}(\zeta_3, \vec{r} - \overrightarrow{OA})^* \chi_{n_4,l_4}^{m_4}(\zeta_4, \vec{r} - \overrightarrow{OB})\, \mathrm{d}\vec{r}. \quad (6)$$

- the first-type of the two-centre integrals of the second kind:

$$\int_{\vec{r}} \chi_{n_1,l_1}^{m_1}(\zeta_1, \vec{r} - \overrightarrow{OA})^* \chi_{n_2,l_2}^{m_2}(\zeta_2, \vec{r} - \overrightarrow{OA}) \chi_{n_3,l_3}^{m_3}(\zeta_3, \vec{r} - \overrightarrow{OB})^* \chi_{n_4,l_4}^{m_4}(\zeta_4, \vec{r} - \overrightarrow{OB})\, \mathrm{d}\vec{r}. \quad (7)$$

- the second type of the two-centre integrals of the second kind:

$$\int_{\vec{r}} \chi_{n_1,l_1}^{m_1}(\zeta_1, \vec{r} - \overrightarrow{OA})^* \chi_{n_2,l_2}^{m_2}(\zeta_2, \vec{r} - \overrightarrow{OB}) \chi_{n_3,l_3}^{m_3}(\zeta_3, \vec{r} - \overrightarrow{OA})^* \chi_{n_4,l_4}^{m_4}(\zeta_4, \vec{r} - \overrightarrow{OB})\, \mathrm{d}\vec{r}. \quad (8)$$

STFs are defined according to the following relationship [13]:

$$\widetilde{\chi}_{n,l}^{m}(\zeta, \vec{r}) = r^{n-1}\, \mathrm{e}^{-\zeta r} Y_l^m(\theta_{\vec{r}}, \varphi_{\vec{r}}), \quad (9)$$

where n, l, m are the quantum numbers and where $Y_l^m(\theta, \varphi)$ stands for the surface spherical harmonic and is defined explicitly using the Condon–Shortley phase convention as follows [49]:

$$Y_l^m(\theta, \varphi) = \mathrm{i}^{m+|m|} \left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right]^{\frac{1}{2}} P_l^{|m|}(\cos\theta)\, \mathrm{e}^{\mathrm{i}m\varphi}, \quad (10)$$

$P_l^m(x)$ is the associated Legendre polynomial of lth degree and mth order.
The normalized STFs are defined by

$$\chi_{n,l}^{m}(\zeta, \vec{r}) = \mathcal{N}(\zeta, n) \widetilde{\chi}_{n,l}^{m}(\zeta, \vec{r}), \quad (11)$$

where $N(\zeta, n)$ stands for the normalization factor and it is given by

$$\mathcal{N}(\zeta, n) = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}}. \quad (12)$$

The Gaunt coefficients are defined as [50–52]

$$\langle l_1 m_1 | l_2 m_2 | l_3 m_3 \rangle = \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \left[Y_{l_1}^{m_1}(\theta, \varphi) \right]^* Y_{l_2}^{m_2}(\theta, \varphi) Y_{l_3}^{m_3}(\theta, \varphi) \sin(\theta)\, \mathrm{d}\theta\, \mathrm{d}\varphi. \quad (13)$$

These coefficients linearize the product of two spherical harmonics:

$$\left[Y_{l_1}^{m_1}(\theta, \varphi) \right]^* Y_{l_2}^{m_2}(\theta, \varphi) = \sum_{l=l_{\min},2}^{l_1+l_2} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle Y_l^{m_2-m_1}(\theta, \varphi), \quad (14)$$

where the subscript $l = l_{\min,2}$ in the summation symbol implies that the summation index l runs in steps of 2 from $l_{\min}$ to $l_1 + l_2$. The constant $l_{\min}$ is given by [52]

$$l_{\min} = \begin{cases} \max(|l_1 - l_2|, |m_2 - m_1|), \\ \quad \text{if } l_1 + l_2 + \max(|l_1 - l_2|, |m_2 - m_1|) \quad \text{is even} \\ \max(|l_1 - l_2|, |m_2 - m_1|) + 1, \\ \quad \text{if } l_1 + l_2 + \max(|l_1 - l_2|, |m_2 - m_1|) \quad \text{is odd.} \end{cases} \quad (15)$$

By using equations (9) and (14), one can easily obtain

$$\widetilde{\chi}^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\widetilde{\chi}^{m_2}_{n_2,l_2}(\zeta_2,\vec{r}) = \sum_{l=l_{\min},2}^{l_1+l_2} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \widetilde{\chi}^{m_1-m_2}_{n_1+n_2-1,l}(\zeta_1+\zeta_2,\vec{r}). \tag{16}$$

STFs can be expressed as finite linear combinations of B functions [22]:

$$\widetilde{\chi}^{m}_{n,l}(\zeta,\vec{r}) = \frac{1}{\zeta^{n-1}} \sum_{p=\tilde{p}}^{n-l} \frac{(-1)^{n-l-p} 2^{2p+2l-n}(l+p)!}{(2p-n+l)!(n-l-p)!} B^{m}_{p,l}(\zeta,\vec{r}), \tag{17}$$

where

$$\tilde{p} = \begin{cases} \dfrac{n-l}{2} & \text{if} \quad n-l \quad \text{is even} \\ \dfrac{n-l+1}{2} & \text{if} \quad n-l \quad \text{is odd.} \end{cases} \tag{18}$$

The B functions are defined as follows [22, 31]:

$$B^{m}_{n,l}(\zeta,\vec{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!} \widehat{k}_{n-\frac{1}{2}}(\zeta r) Y^m_l(\theta_{\vec{r}},\varphi_{\vec{r}}), \tag{19}$$

where $\widehat{k}_{n-\frac{1}{2}}(z)$ stands for the reduced Bessel function [30, 31].
The spherical Bessel function $j_l(x)$ is defined by [53]

$$j_l(x) = (-1)^l x^l \left(\frac{\mathrm{d}}{x\,\mathrm{d}x}\right)^l \left(\frac{\sin(x)}{x}\right). \tag{20}$$

The spherical Bessel function and its first derivative satisfy the following recurrence relations [53]:

$$\begin{cases} x j_{l-1}(x) + x j_{l+1}(x) = (2l+1) j_l(x) \\ x j_{l-1}(x) - (l+1) j_l(x) = x j'_l(x). \end{cases} \tag{21}$$

For the following, we write $j^n_{l+\frac{1}{2}}$ with $n = 1, 2, \ldots$ for the successive positive zeros of $j_l(x)$. $j^0_{l+\frac{1}{2}}$ are assumed to be 0.
The Fourier transform $\overline{B}^{m}_{n,l}(\zeta,\vec{p})$ of $B^{m}_{n,l}(\zeta,\vec{r})$ is given by [16]

$$\overline{B}^{m}_{n,l}(\zeta,\vec{p}) = \sqrt{\frac{2}{\pi}} \zeta^{2n+l-1} \frac{(-\mathrm{i}|p|)^l}{(\zeta^2+|p|^2)^{n+l+1}} Y^m_l(\theta_{\vec{p}},\varphi_{\vec{p}}). \tag{22}$$

We defined $A^{(\gamma)}$ for certain γ, as the set of infinitely differentiable functions $p(x)$, which have asymptotic expansions in inverse powers of x as $x \to +\infty$, of the form

$$p(x) \sim x^{\gamma} \left(a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} + \cdots\right). \tag{23}$$

3. Two-centre overlap-like quantum similarity integrals

By using equation (16), one can express the two-centre overlap-like quantum similarity integrals as follow:

- The first kind:

$$\begin{aligned} Z^{n_1 n_2 n_3 n_4}_{12} = \prod_{i=1}^{4} \mathcal{N}(\zeta_i, n_i) \sum_{l_{12}=l_{12\,\min},2}^{l_1+l_2} & \langle l_2 m_2 | l_1 m_1 | l_{12} m_2 - m_1 \rangle \\ & \times \sum_{l'=l_{123\,\min},2}^{l_{12}+l_3} \langle l_3 m_3 | l_{12} m_2 - m_1 | l' m_3 - m_2 + m_1 \rangle \\ & \times \mathcal{S}^{n_4,l_4,m_4}_{n_1+n_2+n_3-2,l',m_3-m_2+m_1}(\zeta_1+\zeta_2+\zeta_3,\zeta_4,\overrightarrow{AB}). \end{aligned} \tag{24}$$

- First-type second kind:

$$Z_{12}^{n_1n_2n_3n_4} = \prod_{i=1}^{4}\mathcal{N}(\zeta_i,n_i)\sum_{l_{12}=l_{12\,\min},2}^{l_1+l_2}\langle l_1m_1|l_2m_2|l_{12}m_1-m_2\rangle \times \sum_{l_{34}=l_{34\,\min},2}^{l_3+l_4}\langle l_4m_4|l_3m_3|l_{34}m_4-m_3\rangle \times \mathcal{S}_{n_1+n_2-1,l_{12},m_1-m_2}^{n_3+n_4-1,l_{34},m_4-m_3}(\zeta_1+\zeta_2,\zeta_3+\zeta_4,\overrightarrow{AB}). \tag{25}$$

- Second-type second kind:

$$Z_{12}^{n_1n_2n_3n_4} = \prod_{i=1}^{4}\mathcal{N}(\zeta_i,n_i)\sum_{l_{13}=l_{13\,\min},2}^{l_1+l_3}\langle l_1m_1|l_3m_3|l_{13}m_1-m_3\rangle \times \sum_{l_{24}=l_{24\,\min},2}^{l_2+l_4}\langle l_4m_4|l_2m_2|l_{24}m_4-m_2\rangle \times \mathcal{S}_{n_1+n_3-1,l_{13},m_1-m_3}^{n_2+n_4-1,l_{24},m_4-m_2}(\zeta_1+\zeta_3,\zeta_2+\zeta_4,\overrightarrow{AB}). \tag{26}$$

In all the above equations (24)–(26), $\mathcal{S}_{n_i,l_i,m_i}^{n_j,l_j,m_j}(\zeta_i,\zeta_j,\vec{R})$ stand for two-centre overlap integrals over STFs, which are given by the following expression:

$$\mathcal{S}_{n_i,l_i,m_i}^{n_j,l_j,m_j}(\zeta_i,\zeta_j,\vec{R}) = \int_{\vec{r}}\left[\chi_{n_i,l_i}^{m_i}(\zeta_i,\vec{r})\right]^*\chi_{n_j,l_j}^{m_j}(\zeta_j,\vec{r}-\vec{R})\,\mathrm{d}\vec{r}. \tag{27}$$

The above integrals can be expressed in terms of the two-centre overlap integrals over B functions by using equation (17):

$$\mathcal{S}_{n_i,l_i,m_i}^{n_j,l_j,m_j}(\zeta_i,\zeta_j,\vec{R}) = \frac{1}{\zeta_i^{n_i-1}\zeta_j^{n_j-1}}\sum_{p_i=\tilde{p}_i}^{n_i-l_i}\frac{(-1)^{n_i-l_i-p_i}2^{2p_i+2l_i-n_i}(l_i+p_i)!}{(2p_i-n_i+l_i)!(n_i-l_i-p_i)!} \times \sum_{p_j=\tilde{p}_j}^{n_j-l_j}\frac{(-1)^{n_j-l_j-p_j}2^{2p_j+2l_j-n_j}(l_j+p_j)!}{(2p_j-n_j+l_j)!(n_j-l_j-p_j)!}\,{}_B\mathcal{S}_{p_i,l_i,m_i}^{p_j,l_j,m_j}(\zeta_i,\zeta_j,\vec{R}), \tag{28}$$

where $\tilde{p}_i$ and $\tilde{p}_j$ are given according to equation (18) and the integral ${}_B\mathcal{S}_{p_i,l_i,m_i}^{p_j,l_j,m_j}(\zeta_i,\zeta_j,\vec{R})$ is given by

$${}_B\mathcal{S}_{p_i,l_i,m_i}^{p_j,l_j,m_j}(\zeta_i,\zeta_j,\vec{R}) = \int_{\vec{r}}\left[B_{p_i,l_i}^{m_i}(\zeta_i,\vec{r})\right]^*B_{p_j,l_j}^{m_j}(\zeta_j,\vec{r}-\vec{R})\,\mathrm{d}\vec{r}. \tag{29}$$

With the help of the Fourier transform method, Weniger and Steinborn developed the following analytic expression for the overlap integrals over B functions [16]:

$${}_B\mathcal{S}_{p_i,l_i,m_i}^{p_j,l_j,m_j}(\zeta_i,\zeta_j,\vec{R}) = 8(-1)^{l_j}\mathrm{i}^{l_i+l_j}\zeta_i^{2n_i+l_i-1}\zeta_j^{2n_j+l_j-1} \times \sum_{\lambda=\lambda_{\min},2}^{l_i+l_j}(-\mathrm{i})^{\lambda}\langle l_jm_j|l_im_i|\lambda m_j-m_i\rangle Y_{\lambda}^{m_j-m_i}(\theta_{\vec{R}},\varphi_{\vec{R}}) \times \int_0^{+\infty}\frac{x^{n_x}}{\left(\zeta_i^2+x^2\right)^{k_1}\left(\zeta_j^2+x^2\right)^{k_2}}j_{\lambda}(Rx)\,\mathrm{d}x, \tag{30}$$

where

$$\begin{cases} R = \|\vec{R}\| \text{ the modulus of } \vec{R} \\ k_1 = p_i + l_i + 1 \\ k_2 = p_j + l_j + 1 \\ n_x = l_i + l_j + 2. \end{cases}$$

Now by using equations (30) and (28), one can obtain analytic expressions for the two-centre overlap-like quantum similarity integrals over STFs, which are given by equations (24)–(26).

- The first kind:

$$
\begin{aligned}
Z_{12}^{n_1n_2n_3n_4} = \prod_{i=1}^{4}\mathcal{N}(\zeta_i,n_i)\frac{1}{\zeta_{123}^{n_{123}-1}\zeta_4^{n_4-1}}\sum_{l_{12}=l_{12\,\min},2}^{l_1+l_2}\langle l_2m_2|l_1m_1|l_{12}m_2-m_1\rangle \\
\times\sum_{l'=l_{123\,\min},2}^{l_{12}+l_3}\langle l_3m_3|l_{12}m_2-m_1|l'm_3-m_2+m_1\rangle \\
\times\sum_{p_1=\tilde{p}_1}^{n_{123}-l'}\frac{(-1)^{n_{123}-l'-p_1}2^{2p_1+2l'-n_{123}}(l'+p_1)!}{(2p_1-n_{123}+l')!(n_{123}-l'-p_1)!} \\
\times\sum_{p_2=\tilde{p}_2}^{n_4-l_4}\frac{(-1)^{n_4-l_4-p_2}2^{2p_2+2l_4-n_4}(l_4+p_2)!}{(2p_2-n_4+l_4)!(n_4-l_4-p_2)!} \\
\times 8(-1)^{l_4}\mathrm{i}^{l'+l_4}\zeta_{123}^{2p_1+l'-1}\zeta_4^{2p_2+l_4-1} \\
\times\sum_{\lambda=\lambda_{\min},2}^{l'+l_4}(-\mathrm{i})^{\lambda}\langle l_4m_4|l'm_{123}|\lambda m_4-m_{123}\rangle Y_{\lambda}^{m_4-m_{123}}(\theta_{\vec{R}},\varphi_{\vec{R}}) \\
\times\int_0^{+\infty}\frac{x^{n_x}}{\left(\zeta_{123}^2+x^2\right)^{k_1}\left(\zeta_4^2+x^2\right)^{k_2}}j_{\lambda}(Rx)\,\mathrm{d}x,
\end{aligned}
\tag{31}
$$

where

$$
\begin{cases}
n_{123}=n_1+n_2+n_3-2\\
m_{123}=m_3-m_2+m_1\\
\zeta_{123}=\zeta_1+\zeta_2+\zeta_3.
\end{cases}
$$

- First-type second kind:

$$
\begin{aligned}
Z_{12}^{n_1n_2n_3n_4} = \prod_{i=1}^{4}\mathcal{N}(\zeta_i,n_i)\frac{1}{\zeta_{12}^{n_{12}-1}\zeta_{34}^{n_{34}-1}}\sum_{l_{12}=l_{12\,\min},2}^{l_1+l_2}\langle l_1m_1|l_2m_2|l_{12}m_1-m_2\rangle \\
\times\sum_{l_{34}=l_{34\,\min},2}^{l_3+l_4}\langle l_4m_4|l_3m_3|l_{34}m_4-m_3\rangle \\
\times\sum_{p_1=\tilde{p}_1}^{n_{12}-l_{12}}\frac{(-1)^{n_{12}-l_{12}-p_1}2^{2p_1+2l_{12}-n_{12}}(l_{12}+p_1)!}{(2p_1-n_{12}+l_{12})!(n_{12}-l_{12}-p_1)!} \\
\times\sum_{p_2=\tilde{p}_2}^{n_{34}-l_{34}}\frac{(-1)^{n_{34}-l_{34}-p_2}2^{2p_2+2l_{34}-n_{34}}(l_{34}+p_2)!}{(2p_2-n_{34}+l_{34})!(n_{34}-l_{34}-p_2)!} \\
\times 8(-1)^{l_{34}}\mathrm{i}^{l_{12}+l_{34}}\zeta_{12}^{2p_1+l_{12}-1}\zeta_{34}^{2p_2+l_{34}-1} \\
\times\sum_{\lambda=\lambda_{\min},2}^{l_{12}+l_{34}}(-\mathrm{i})^{\lambda}\langle l_{34}m_{43}|l_{12}m_{12}|\lambda m_{43}-m_{12}\rangle Y_{\lambda}^{m_{43}-m_{12}}(\theta_{\vec{R}},\varphi_{\vec{R}}) \\
\times\int_0^{+\infty}\frac{x^{n_x}}{\left(\zeta_{12}^2+x^2\right)^{k_1}\left(\zeta_{34}^2+x^2\right)^{k_2}}j_{\lambda}(Rx)\,\mathrm{d}x,
\end{aligned}
\tag{32}
$$

where

$$\begin{cases} n_{12} = n_1 + n_2 - 1 \\ n_{34} = n_3 + n_4 - 1 \\ m_{12} = m_2 - m_1 \\ m_{43} = m_4 - m_3 \\ \zeta_{12} = \zeta_1 + \zeta_2 \\ \zeta_{34} = \zeta_3 + \zeta_4. \end{cases}$$

- Second-type second kind:

$$\begin{aligned} Z_{12}^{n_1 n_2 n_3 n_4} = \prod_{i=1}^{4} N(\zeta_i, n_i) \frac{1}{\zeta_{13}^{n_{13}-1} \zeta_{24}^{n_{24}-1}} \sum_{l_{13}=l_{13\min},2}^{l_1+l_3} \langle l_1 m_1 | l_3 m_3 | l_{13} m_1 - m_3 \rangle \\ \times \sum_{l_{24}=l_{24\min},2}^{l_2+l_4} \langle l_4 m_4 | l_2 m_2 | l_{24} m_4 - m_2 \rangle \\ \times \mathcal{S}_{n_1+n_3-1, l_{13}, m_1-m_3}^{n_2+n_4-1, l_{24}, m_4-m_2}(\zeta_1 + \zeta_3, \zeta_2 + \zeta_4, \overrightarrow{AB}) \\ \times \sum_{p_1=\tilde{p}_1}^{n_{13}-l_{13}} \frac{(-1)^{n_{13}-l_{13}-p_1} 2^{2p_1+2l_{13}-n_{13}} (l_{13}+p_1)!}{(2p_1 - n_{13} + l_{13})!(n_{13} - l_{13} - p_1)!} \\ \times \sum_{p_2=\tilde{p}_2}^{n_{24}-l_{24}} \frac{(-1)^{n_{24}-l_{24}-p_2} 2^{2p_2+2l_{24}-n_{24}} (l_{24}+p_2)!}{(2p_2 - n_{24} + l_{24})!(n_{24} - l_{24} - p_2)!} \\ \times 8(-1)^{l_{24}} \mathrm{i}^{l_{13}+l_{24}} \zeta_{13}^{2p_1+l_{13}-1} \zeta_{24}^{2p_2+l_{24}-1} \\ \times \sum_{\lambda=\lambda_{\min},2}^{l_{13}+l_{24}} (-\mathrm{i})^{\lambda} \langle l_{24} m_{42} | l_{13} m_{13} | \lambda m_{42} - m_{13} \rangle Y_{\lambda}^{m_{42}-m_{13}}(\theta_{\vec{R}}, \varphi_{\vec{R}}) \\ \times \int_0^{+\infty} \frac{x^{n_x}}{\left(\zeta_{13}^2 + x^2\right)^{k_1} \left(\zeta_{24}^2 + x^2\right)^{k_2}} j_{\lambda}(Rx)\, \mathrm{d}x, \end{aligned} \tag{33}$$

where

$$\begin{cases} n_{13} = n_1 + n_3 - 1 \\ n_{24} = n_2 + n_4 - 1 \\ m_{13} = m_1 - m_3 \\ m_{42} = m_4 - m_2 \\ \zeta_{13} = \zeta_1 + \zeta_3 \\ \zeta_{24} = \zeta_2 + \zeta_4. \end{cases}$$

In equations (31)–(33), R stands for the modulus of the vector $\overrightarrow{AB}$ and $\lambda_{\min}$ is given according to equation (15).

The analytic expressions (31)–(33) turned out to be very difficult to evaluate accurately and rapidly, because of the presence of the spherical Bessel integrals, which will be referred to as $\mathcal{I}$:

$$\mathcal{I} = \int_0^{+\infty} \frac{x^{n_x}}{\left(\zeta_i^2 + x^2\right)^{k_1} \left(\zeta_j^2 + x^2\right)^{k_2}} j_{\lambda}(Rx)\, \mathrm{d}x. \tag{34}$$

For the following, the integrand of the above semi-infinite integral will be referred to as $\mathcal{F}(x)$.

The semi-infinite integral $\mathcal{I}$ can be transformed into an infinite series as follows:

$$\mathcal{I} = \sum_{n=0}^{+\infty} \int_{j_{\lambda,R}^{n}}^{j_{\lambda,R}^{n+1}} \mathcal{F}(x)\,\mathrm{d}x, \tag{35}$$

where $j_{\lambda,R}^{n} = \frac{j_{\lambda+\frac{1}{2}}^{l+1}}{R}$ for $l = 0, 1, 2, \ldots$, are the leading positive zeros of $j_\lambda(Rx)$. $j_{\lambda,R}^{0}$ is assumed to be 0.

The above infinite series is used to compute values of the semi-infinite integrals with a pre-determined number of correct digits. This approach is used for the computation of values with more than 12 correct digits of analytic expressions (31)–(33). These values are listed in tables 1–3 (Values$^{(\dagger)}$). For the computation of the finite integrals occurring in the above infinite series, we used Gauss–Legendre quadrature of order 92. This approach leads to a highly accurate numerical evaluation of the molecular integrals under consideration, but the calculation times are prohibitively long.

4. The $\overline{D}$ transformation and the development of the algorithm

Theorem 1 [38]. *Let $f(x)$ be integrable on $[0, +\infty[$ (i.e. $\int_0^{+\infty} f(t)\,\mathrm{d}t$ exists) and satisfies a linear differential equation of order m of the form*

$$f(x) = \sum_{k=1}^{m} p_k(x) f^{(k)}(x), \qquad \text{with} \quad p_k \in A^{(i_k)}, \quad i_k \leqslant k. \tag{36}$$

If for all $k = i, i+1, \ldots, m$; $i = 1, 2, \ldots, m$:

$$\lim_{x\to+\infty} p_k^{(i-1)}(x) f^{(k-i)}(x) = 0, \tag{37}$$

and for all $l \geqslant -1$:

$$\sum_{k=1}^{m} l(l-1)\cdots(l-k+1)p_{k,0} \neq 1, \tag{38}$$

where

$$p_{k,0} = \lim_{x\to+\infty} x^{-k} p_k(x), \qquad 1 \leqslant k \leqslant m, \tag{39}$$

then as $x \to +\infty$:

$$\int_x^{+\infty} f(t)\,\mathrm{d}t \sim \sum_{k=0}^{m-1} f^{(k)}(x) x^{j_k} \left(\beta_{0,k} + \frac{\beta_{1,k}}{x} + \frac{\beta_{2,k}}{x^2} + \cdots\right), \tag{40}$$

where

$$j_k \leqslant \max(i_{k+1}, i_{k+2} - 1, \ldots, i_m - m + k + 1), \quad k = 0, 1, \ldots, m-1.$$

The approximation $\overline{D}_n^{(m)}$ of $\int_0^{+\infty} f(t)\,\mathrm{d}t$, using the nonlinear $\overline{D}$ transformation, satisfies the $n(m-1)+1$ equations given by [37]

$$\overline{D}_n^{(m)} = F(x_l) + \sum_{k=1}^{m-1} f^{(k)}(x_l) x_l^{k+1} \sum_{i=0}^{n-1} \frac{\bar{\beta}_{k,i}}{x_l^i}, \qquad l = 0, 1, \ldots, nm, \tag{41}$$

where $\overline{D}_n^{(m)}$ and $\bar{\beta}_{k,i}$ are the unknowns of the above system. The x_l for $l = 0, 1, \ldots,$ are the leading positive zeros of $f(x)$. $F(x) = \int_0^x f(t)\,\mathrm{d}t$.

Table 1. Two-centre overlap-like integrals of the first kind Z_{AB}^{1234} where A is a carbon atom and B is a nitrogen. $n_1 = n_2 = 1, n_3 = n_4, l_1 = l_2 = l_3 = 0, m_1 = m_2 = m_3 = m_4 = 0$ and $\zeta_1 = \zeta_2 = 5.6727$. $A = (0, 0, 0)$ and $B = (0, 0, z_B)$.

n_4	l_4	ζ_3	ζ_4	z_B	Values$^{(\dagger)}$	Values$^{(\mathrm{ACJU})}$	Values$^{(\overline{D})}$	Values$^{(\ddagger)}$
1	0	5.6727	6.6651	0.5	0.858 425 675 391(0)	0.858 425 675 391(0)	0.858 425 675 370(0)	0.858 425 675 614(0)
1	0	5.6727	6.6651	1.0	0.347 537 588 663(−1)	0.347 537 588 663(−1)	0.347 537 588 659(−1)	0.347 537 588 654(−1)
1	0	5.6727	6.6651	1.5	0.129 121 127 852(−2)	0.129 121 127 852(−2)	0.129 121 127 001(−2)	0.129 121 127 837(−2)
1	0	5.6727	6.6651	2.0	0.469 994 519 133(−4)	0.469 994 519 132(−4)	0.469 994 462 638(−4)	0.469 994 519 184(−4)
2	0	1.6083	1.9237	0.5	0.501 691 891 384(−1)	0.501 691 891 384(−1)	0.501 691 891 384(−1)	0.501 691 891 246(−1)
2	0	1.6083	1.9237	1.0	0.390 207 911 608(−1)	0.390 207 911 608(−1)	0.390 207 911 607(−1)	0.390 207 911 404(−1)
2	0	1.6083	1.9237	1.5	0.230 014 520 894(−1)	0.230 014 520 894(−1)	0.230 014 520 893(−1)	0.230 014 520 892(−1)
2	0	1.6083	1.9237	2.0	0.119 332 536 417(−1)	0.119 332 536 417(−1)	0.119 332 536 417(−1)	0.119 332 536 431(−1)
2	1	1.6083	1.9170	0.5	−0.737 349 020 141(−1)	−0.737 349 020 141(−1)	−0.737 349 020 141(−1)	−0.737 349 020 146(−1)
2	1	1.6083	1.9170	1.0	−0.646 924 813 966(−1)	−0.646 924 813 966(−1)	−0.646 924 813 966(−1)	−0.646 924 813 973(−1)
2	1	1.6083	1.9170	1.5	−0.391 558 341 502(−1)	−0.391 558 341 502(−1)	−0.391 558 341 502(−1)	−0.391 558 341 738(−1)
2	1	1.6083	1.9170	2.0	−0.205 470 626 697(−1)	−0.205 470 626 697(−1)	−0.205 470 626 697(−1)	−0.205 470 626 552(−1)

$^{(\dagger)}$ Values are obtained using the infinite series (35) for the numerical evaluation of the semi-infinite integrals.
$^{(\mathrm{ACJU})}$ Two-centre overlap-like integrals of the first kind integral values obtained using the ACJU code [20] for the evaluation of the two-centre overlap integrals over B functions.
$^{(\overline{D})}$ The nonlinear $\overline{D}$ was used for the numerical evaluation of the semi-infinite integral occurring in the analytic expression of the two-centre overlap-like integrals of the first kind Z_{AB}^{1234}.
$^{(\ddagger)}$ Two-centre overlap-like integrals of the first kind integral values obtained in [47, 48].

Table 2. Two-centre overlap-like integrals of the first-type second kind Z_{AB}^{1234} where A is a carbon atom and C is a nitrogen. $n_1 = n_2 = 1, n_3 = n_4, l_1 = l_2 = l_3 = 0, m_1 = m_2 = m_3 = m_4 = 0$ and $\zeta_1 = \zeta_2 = 5.6727$. $A = (0, 0, 0)$ and $C = (0, 0, z_B)$.

n_4	l_4	ζ_3	ζ_4	z_B	Values$^{(\dagger)}$	Values$^{(\mathrm{ACJU})}$	Values$^{(\overline{D})}$	Values$^{(\ddagger)}$
1	0	5.6727	6.6651	0.5	0.392 518 041 234(0)	0.392 518 041 235(0)	0.392 518 041 235(0)	0.392 518 041 235(0)
1	0	5.6727	6.6651	1.0	0.287 291 441 055(−2)	0.287 291 441 056(−2)	0.287 291 441 058(−2)	0.287 291 441 058(−2)
1	0	5.6727	6.6651	1.5	0.142 141 502 022(−4)	0.142 141 502 024(−4)	0.142 141 554 478(−4)	0.142 141 502 118(−4)
1	0	5.6727	6.6651	2.0	0.600 438 754 995(−7)	0.600 438 755 929(−7)	0.600 439 980 628(−7)	0.600 438 413 711(−7)
2	0	1.6083	1.9237	0.5	0.185 319 053 139(−1)	0.185 319 053 140(−1)	0.185 319 053 139(−1)	0.185 319 053 140(−1)
2	0	1.6083	1.9237	1.0	0.266 806 719 446(−2)	0.266 806 719 446(−2)	0.266 806 719 218(−2)	0.266 806 719 446(−2)
2	0	1.6083	1.9237	1.5	0.206 888 508 259(−3)	0.206 888 508 260(−3)	0.206 888 508 167(−3)	0.206 888 508 260(−3)
2	0	1.6083	1.9237	2.0	0.115 769 691 749(−4)	0.115 769 691 749(−4)	0.115 769 691 379(−4)	0.115 769 691 756(−4)
2	1	1.6083	1.9170	0.5	−0.159 539 790 120(−1)	−0.159 539 790 121(−1)	−0.159 539 790 120(−1)	−0.159 539 790 121(−1)
2	1	1.6083	1.9170	1.0	−0.324 008 018 849(−2)	−0.324 008 018 850(−2)	−0.324 008 018 851(−2)	−0.324 008 018 850(−2)
2	1	1.6083	1.9170	1.5	−0.280 545 795 502(−3)	−0.280 545 795 502(−3)	−0.280 545 795 467(−3)	−0.280 545 795 503(−3)
2	1	1.6083	1.9170	2.0	−0.165 259 528 950(−4)	−0.165 259 528 951(−4)	−0.165 259 528 099(−4)	−0.165 259 528 957(−4)

$^{(\dagger)}$ Values are obtained using the infinite series (35) for the numerical evaluation of the semi-infinite integrals.
$^{(\mathrm{ACJU})}$ Two-centre overlap-like integrals of the first kind integral values obtained using the ACJU code [20] for the evaluation of the two-centre overlap integrals over B functions.
$^{(\overline{D})}$ The nonlinear $\overline{D}$ was used for the numerical evaluation of the semi-infinite integral occurring in the analytic expression of the two-centre overlap-like integrals of the first-type second kind Z_{AB}^{1234}.
$^{(\ddagger)}$ Two-centre overlap-like integrals of the first kind integral values obtained in [47, 48].

Table 3. Two-centre overlap-like integrals of the second-type second kind Z_{AB}^{1234} where A is a carbon atom and B is a nitrogen. $n_2 = n_1 = 1, l_1 = l_2 = 0, m_1 = m_2 = 0$ and $\zeta_2 = \zeta_1 = 5.6727$. $A = (0, 0, 0)$ and $B = (0, 0, z_B)$.

n_3	l_3	m_3	ζ_3	n_4	l_4	m_4	ζ_4	z_B	Values$^{(\dagger)}$	Values$^{(\mathrm{ACJU})}$	Values$^{(\overline{D})}$
1	0	0	5.6727	1	0	0	6.6651	0.5	0.380 763 574 385(0)	0.380 763 574 385(0)	0.380 763 574 386(0)
1	0	0	5.6727	1	0	0	6.6651	1.0	0.257 275 540 475(−2)	0.257 275 540 475(−2)	0.257 275 540 487(−2)
1	0	0	5.6727	1	0	0	6.6651	1.5	0.112 359 909 542(−4)	0.112 359 909 542(−4)	0.112 360 177 242(−4)
1	0	0	5.6727	1	0	0	6.6651	2.0	0.402 343 193 284(−7)	0.402 343 194 188(−7)	0.402 475 859 881(−7)
2	0	0	1.6083	2	0	0	1.9237	0.5	0.713 370 891 055(−1)	0.713 370 891 055(−1)	0.713 370 891 055(−1)
2	0	0	1.6083	2	0	0	1.9237	1.0	0.498 773 449 795(−1)	0.498 773 449 795(−1)	0.498 773 449 794(−1)
2	0	0	1.6083	2	0	0	1.9237	1.5	0.201 175 530 475(−1)	0.201 175 530 476(−1)	0.201 175 530 473(−1)
2	0	0	1.6083	2	0	0	1.9237	2.0	0.631 502 044 463(−2)	0.631 502 044 463(−2)	0.631 502 044 372(−2)
2	0	0	1.6083	2	1	0	1.9170	0.5	−0.111 091 841 731(0)	−0.111 091 841 731(0)	−0.111 091 841 731(0)
2	0	0	1.6083	2	1	0	1.9170	1.0	−0.838 714 636 018(−1)	−0.838 714 636 018(−1)	−0.838 714 636 018(−1)
2	0	0	1.6083	2	1	0	1.9170	1.5	−0.344 495 905 421(−1)	−0.344 495 905 422(−1)	−0.344 495 905 420(−1)
2	0	0	1.6083	2	1	0	1.9170	2.0	−0.109 079 091 615(−1)	−0.109 079 091 615(−1)	−0.109 079 091 613(−1)

$^{(\dagger)}$ Values are obtained using the infinite series (35) for the numerical evaluation of the semi-infinite integrals.

$^{(\mathrm{ACJU})}$ Two-centre overlap-like integrals of the first kind integral values obtained using the ACJU code [20] for the evaluation of the two-centre overlap integrals over B functions.

$^{(\overline{D})}$ The nonlinear $\overline{D}$ was used for the numerical evaluation of the semi-infinite integral occurring in the analytic expression of the two-centre overlap-like integrals of the second-type second kind Z_{AB}^{1234}.

Lemma 1. *Let $p(x)$ be in $A^{(\gamma)}$ for some γ. Then*

(i) If $\gamma \neq 0$ then $p'(x) \in A^{(\gamma-1)}$, otherwise $p'(x) \in A^{(\gamma-2)}$.
(ii) If $q(x) \in A^{(\delta)}$ then $p(x)q(x) \in A^{(\gamma+\delta)}$.
(iii) If $q(x) \in A^{(\delta)}$ and $\gamma - \delta > 0$ then the function $p(x) + q(x) \in A^{(\gamma)}$. If $\gamma = \delta$ then the function $p(x) + q(x) \in A^{(\gamma)}$.
(iv) The function $1/p(x) \in A^{(-\gamma)}$.

The proof of lemma 1 follows from the properties of asymptotic power series in the sense of Poincaré [54].

Corollary 1 [38]**.** *If f satisfies a linear mth order differential equation of the form given by equation (36) in theorem 1, and if $g \in A^{(\gamma)}$, then fg satisfies a linear differential equation of order m or less with coefficients that have asymptotic expansions in inverse powers of x.*

In [29], we showed that the integrand $\mathcal{F}(x)$, of the semi-infinite integral occurring in equations (31)–(33), satisfies a second-order linear differential of the form required to apply the nonlinear $\overline{D}$ transformation. This differential equation was obtained using the second-order linear differential equation satisfied by the spherical Bessel function $j_\lambda(Rx)$ [37].

The integrand $\mathcal{F}(x)$ is given by

$$\mathcal{F}(x) = g(x) j_\lambda(Rx), \tag{42}$$

where the function $g(x)$ is given by

$$g(x) = \frac{x^{n_x}}{\left(\zeta_i^2 + x^2\right)^{k_1} \left(\zeta_j^2 + x^2\right)^{k_2}}. \tag{43}$$

The spherical Bessel function satisfies a second-order linear differential equation given by [53]

$$j_\lambda(Rx) = q_1(x) j'_\lambda(Rx) + q_2(x) j''_\lambda(Rx), \tag{44}$$

where

$$q_1(x) = -\frac{2x}{(Rx)^2 - \lambda^2 - \lambda} \qquad \text{and} \qquad q_2(x) = \frac{x^2}{(Rx)^2 - \lambda^2 - \lambda}. \tag{45}$$

Using lemma 1, we showed that the coefficients $q_1(x)$ and $q_2(x)$ of the differential equation (44) are, respectively, in $A^{(-1)}$ and $A^{(0)}$. From equation (43), one can easily show that $g(x) \in A^{(n_x - 2(k_1+k_2))}$.

From the above arguments and the corollary, it follows that $g(x) j_\lambda(Rx)$ satisfies a second-order linear differential equation with coefficients that have asymptotic expansions in inverse powers of x. This differential equation, which is of the form required to apply the $\overline{D}$ transformation, can be obtained explicitly by replacing $j_\lambda(Rx)$ by $\frac{\mathcal{F}(x)}{g(x)}$ in equation (44):

$$\mathcal{F}(x) = p_1(x)\mathcal{F}'(x) + p_2(x)\mathcal{F}''(x), \tag{46}$$

where

$$p_1(x) = \frac{g(x)q_1(x) - 2q_2(x)g'(x)}{g(x)H(x)} \in A^{(-1)} \qquad \text{and} \qquad p_2(x) = \frac{q_2(x)}{H(x)} \in A^{(0)}, \tag{47}$$

and where $H(x)$ is given by

$$H(x) = 1 + \frac{q_1(x)g'(x)}{g(x)} - \frac{2q_2(x)(g'(x))^2}{g^2(x)} + \frac{q_2(x)g''(x)}{g(x)} \in A^{(0)}. \tag{48}$$

Using the fact that $p_1(x) \in A^{(-1)}$ and $p_2(x) \in A^{(0)}$, one can show that all the conditions of theorem 1 are fulfilled. Consequently, the approximation of this semi-infinite integral $\mathcal{I}$ (34), occurring in equations (31)–(33), can then be obtained by solving the linear system given by (41) with $m = 2$:

$$\overline{D}_n^{(2)} = \int_0^{x_l} \mathcal{F}(t)\,\mathrm{d}t + x_l^2 g(x_l) j'_\lambda(Rx_l) \sum_{i=0}^{n-1} \frac{\bar{\beta}_{1,i}}{x_l^i}, \qquad l = 0, 1, \ldots, n, \tag{49}$$

where $x_l = \frac{j_{\lambda+\frac{1}{2}}^{l+1}}{R}$ for $l = 0, 1, 2, \ldots$, are the leading positive zeros of $j_\lambda(Rx)$.

As we explained in [29], if x_l is a zero of $j_\lambda(Rx)$ then from equations (21) it follows that

$$j'_\lambda(Rx_l) = R j_{\lambda-1}(Rx_l). \tag{50}$$

From the above equation, it follows that one does not have to compute the first derivative of the spherical Bessel function for calculating the approximation $\overline{D}_n^{(2)}$. To use the expression (50), one should separate the case where $\lambda = 0$, where we can use the Cramer's rule as suggested by Sidi [37] for calculating the approximation $\overline{D}_n^{(2)}$, since the zeros of $j_0(Rx) = \frac{\sin(Rx)}{Rx}$ are equidistant. In this case, the expression of $\overline{D}_n^{(2)}$ is given by

$$\overline{D}_n^{(2)} = \frac{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+\mathrm{i})^n F(x_i) \Big/ \left[x_i^2 g(x_i)\right]}{\sum_{i=0}^{n+1} \binom{n+1}{i} (1+\mathrm{i})^n \Big/ \left[x_i^2 g(x_i)\right]}. \tag{51}$$

The computation of the above equation can be performed recursively using recurrence relations developed in [44, 45].

5. Two-centre overlap integrals over *B* functions

In this section, we present analytic developments of the two-centre overlap integrals over B functions, based on previous work by Steinborn group [16–21]. Different representations which can be used for the computation of these overlap integrals over B functions were obtained and with the help of equations (24)–(26) and (28), these representations can also be used for the computation of the two-centre overlap-like quantum similarity integrals over STFs.

The Fourier transform method in combination with the Fourier transformation of B functions (22) produces the following integral representation for the overlap integral [19]:

$$\begin{aligned} {}_B\mathcal{S}_{n_1,l_1,m_1}^{n_2,l_2,m_2}(\zeta_1, \zeta_2, \vec{R}) = {} & \frac{2}{\pi} \zeta_1^{2n_1+l_1-1} \zeta_2^{2n_2+l_2-1} \sum_{l=l_{\min}}^{l_{\max}} {}^{(2)}\langle l_2 m_2 | l_1 m_1 | l m_2 - m_2 \rangle \\ & \times \int \mathrm{e}^{-\mathrm{i}\vec{R}\cdot\vec{p}} \frac{p^{l_1+l_2-l} \mathcal{Y}_l^{m_2-m_1}(\vec{p})}{\left[\zeta_1^2 + p^2\right]^{n_1+l_1+1} \left[\zeta_2^2 + p^2\right]^{n_2+l_2+1}} \mathrm{d}^3\vec{p}. \end{aligned} \tag{52}$$

If the two scaling parameters in the above equation are equal, $\zeta_1 = \zeta_2$, then we only have to use the Fourier integral representation of a B function (22), together with [19]

$$p^{2\Delta l} = (-1)^{\Delta l} \zeta_1^{2\Delta l} \sum_{t=0}^{\Delta l} (-1)^t \binom{\Delta l}{t} \left(\frac{\zeta_1^2 + p^2}{\zeta_1^2}\right)^t, \tag{53}$$

which is essentially a reformulation of the binomial theorem, to obtain the overlap with the same scaling parameters [19]:

$$
\begin{aligned}
{}_B\mathcal{S}^{n_2,l_2,m_2}_{n_1,l_1,m_1}(\zeta_1,\zeta_2,\vec{R}) = {} & \frac{4\pi}{\zeta_1^3}\sum_{l=l_{\min}}^{l_{\max}} {}^{(2)}\langle l_2 m_2 | l_1 m_1 | l m_2 - m_2\rangle \\
& \times \sum_{t=0}^{\Delta l}(-1)^t \binom{\Delta l}{t} B^{m_2-m_1}_{n_1+n_2+2\Delta l-t+1,l}(\zeta_1,\vec{R}),
\end{aligned}
\tag{54}
$$

where

$$
\Delta l = \frac{l_1 + l_2 - 1}{2}.
$$

Note that the above equation was first derived by Filter and Steinborn [21], who obtained this expression via the addition theorem of the modified Helmholtz harmonics [21].

The overlap formula (54) is remarkably compact and a quadrature scheme will most likely be (much) less efficient than this explicit expression. Nevertheless, (54) contains one potential source of numerical instabilities: if Δl in (54) becomes large then it is quite likely that the sum $\sum_{t=0}^{\Delta l}$, which follows from (53), leads to a potential serious loss of significant digits since it contains large terms with strictly alternating signs. In such a case, a quadrature of the integral representation (52), or rather its radial part, may well be less likely to produce numerical instabilities than the otherwise almost trivial expression (54) for the overlap with equal scaling parameters.

The situation is more complicated in the case of different scaling parameters, $\zeta_1 \neq \zeta_2$. One possibility would be to use the partial fraction decomposition [16]:

$$
\begin{aligned}
& \left[\zeta_1^2 + p^2\right]^{-n_1-l_1-1}\left[\zeta_2^2 + p^2\right]^{-n_2-l_2-1} \\
& \quad = \frac{(-1)^{n_2+l_2+1}}{(n_2+l_2)!}\sum_{\nu=0}^{n_1+l_1}\frac{(n_1+n_2+l_1+l_2-\nu)!}{(n_1+l_1-\nu)!}\frac{\left[\zeta_1^2-\zeta_2^2\right]^{\nu-n_1-n_2-l_1-l_2-1}}{\left[\zeta_1^2+p^2\right]^{\nu+1}} \\
& \quad + \frac{(-1)^{n_1+l_1+1}}{(n_1+l_1)!}\sum_{\nu=0}^{n_2+l_2}\frac{(n_1+n_2+l_1+l_2-\nu)!}{(n_2+l_2-\nu)!}\frac{\left[\zeta_2^2-\zeta_1^2\right]^{\nu-n_1-n_2-l_1-l_2-1}}{\left[\zeta_2^2+p^2\right]^{\nu+1}}.
\end{aligned}
\tag{55}
$$

Inserting this into the integral representation (52) yields the so-called Jacobi polynomial representation of the overlap integral [22]:

$$
\begin{aligned}
{}_B\mathcal{S}^{n_2,l_2,m_2}_{n_1,l_1,m_1}(\zeta_1,\zeta_2,\vec{R}) = {} & (-1)^{l_2}4\pi\sum_{l=l_{\min}}^{l_{\max}} {}^{(2)}\langle l_2 m_2 | l_1 m_1 | l m_2 - m_2\rangle \\
& \times \left[\frac{(-1)^{n_1+l_1}(\zeta_1/\zeta_2)^{l_2}}{\zeta_2^3[1-(\zeta_1/\zeta_2)^2]^{n_2+l_2+1}}\sum_{s=0}^{n_1+l_1}(-1)^s P^{(s-n_1-\Delta l_2,n_2+\Delta l_1)}_{n_1+l_1+s}\left(\frac{\zeta_2^2+\zeta_1^2}{\zeta_2^2-\zeta_1^2}\right)\right. \\
& \times B^{m_2-m_1}_{s-l}(\zeta_1,\vec{R})\frac{(-1)^{n_2+l_2}(\zeta_2/\zeta_1)^{l_1}}{\zeta_1^3[1-(\zeta_2/\zeta_1)^2]^{n_1+l_1+1}} \\
& \left.\times \sum_{s=0}^{n_2+l_2}(-1)^s P^{(s-n_2-\Delta l_1,n_1+\Delta l_2)}_{n_2+l_2+s}\left(\frac{\zeta_1^2+\zeta_2^2}{\zeta_1^2-\zeta_2^2}\right) B^{m_2-m_1}_{s-l}(\zeta_2,\vec{R})\right],
\end{aligned}
\tag{56}
$$

where

$$
\Delta l_1 = \frac{l - l_1 + l_2}{2} \qquad \text{and} \qquad \Delta l_2 = \frac{l + l_1 - l_2}{2}.
$$

$P_n^{(\alpha,\beta)}(x)$ is a Jacobi polynomial [55]. For the special Jacobi polynomials in (56), a linear three-term recursion could be derived which permits a very convenient and effective computation of these polynomials [17].

The Jacobi polynomial representation (56) in combination with the recursive scheme mentioned above permits a remarkably efficient evaluation of the overlap integral with different scaling parameters. Unfortunately, (56) contains cancelling singularities as $R \to 0$ and $\zeta_1 \to \zeta_2$, which can create horrible numerical instabilities. Thus, (56) can only produce reliable results if R is sufficiently large and if the two scaling parameters are sufficiently different.

Thus, for small values of R and for $\zeta_1 \approx \zeta_2$, alternative representations have to be used. One possibility would be the Taylor expansion [16]:

$$[\gamma^2+p^2]^{-n-l-1} = [\delta^2+p^2]_1^{-n-l-1} F_0\left(n+l+1; [\delta^2-\gamma^2]/\left[\zeta_2^2+p^2\right]\right). \quad (57)$$

The generalized hypergeometric series ${}_1F_0$ in the above equation converges absolutely and uniformly for all $p \in \mathbb{R}$ provided that $\gamma \in [0, 2^{\frac{1}{2}}\delta)$. This Taylor expansions essentially equivalent to the multiplication theorem of B functions:

$$B_{n,l}^m(\gamma,\vec{r}) = (\gamma/\delta)^{2n+l-1} \sum_{\nu=0}^{+\infty} \frac{(n+l+1)_\nu}{\nu!} \left(\frac{\delta^2-\gamma^2}{\delta^2}\right)^\nu B_{n+\nu}^m(\delta,\vec{r}), \quad (58)$$

which was used by Filter and Steinborn [22] and which converges for $|1-(\gamma/\delta)^2| < 1$.

With the help of equation (57), we immediately obtain [19]

$$\left[\zeta_1^2+p^2\right]^{-n_1-l_1-1}\left[\zeta_2^2+p^2\right]^{-n_2-l_2-1}$$
$$= \left[\zeta_2^2+p^2\right]_1^{-n_1-n_2-l_1-l_2-2} F_0\left(n_1+l_1+1; \left[\zeta_2^2-\zeta_1^2\right]/\left[\zeta_2^2+p^2\right]\right) \quad (59)$$
$$= \left[\zeta_1^2+p^2\right]_1^{-n_1-n_2-l_1-l_2-2} F_0(n_2+l_2+1; \left[\zeta_1^2-\zeta_2^2\right]/\left[\zeta_1^2+p^2\right]). \quad (60)$$

The generalized hypergeometric series ${}_1F_0$ in (59) converges absolutely and uniformly for all $p \in \mathbb{R}$ provided that $\zeta_1 \in [0, 2^{\frac{1}{2}}\zeta_2)$, whereas the hypergeometric series ${}_1F_0$ in (60) requires $\zeta_2 \in [0, 2^{\frac{1}{2}}\zeta_1)$.

Inserting the power series expansions (59) and (60) into (52) yields [19]

$${}_B\mathcal{S}_{n_1,l_1,m_1}^{n_2,l_2,m_2}(\zeta_1,\zeta_2,\vec{R})$$
$$= \left(\frac{\zeta_1}{\zeta_2}\right)^{2n_1+l_1-1} \sum_{\nu=0}^{+\infty} \frac{(n_1+l_1+1)_\nu}{\nu!} \left(\frac{\zeta_2^2-\zeta_1^2}{\zeta_2^2}\right)_B^\nu \mathcal{S}_{n_1+\nu,l_1,m_1}^{n_2,l_2,m_2}(\zeta_2,\zeta_2,\vec{R}) \quad (61)$$
$$= \left(\frac{\zeta_2}{\zeta_1}\right)^{2n_2+l_2-1} \sum_{\nu=0}^{+\infty} \frac{(n_2+l_2+1)_\nu}{\nu!} \left(\frac{\zeta_1^2-\zeta_2^2}{\zeta_1^2}\right)_B^\nu \mathcal{S}_{n_1,l_1,m_1}^{n_2+\nu,l_2,m_2}(\zeta_1,\zeta_1,\vec{R}). \quad (62)$$

The series expansions (61) and (62), or also the power series (57) and (59), can be viewed to be different analytic continuations of the same function.

Nevertheless, the results in [17] showed that it would be desirable to have alternative series expansions that converge more rapidly than (61) and (62). This can be accomplished with the help of the following series expansion [19]:

$$\left[\zeta_1^2+p^2\right]^{-n_1-l_1-1}\left[\zeta_2^2+p^2\right]^{-n_2-l_2-1} = \left[\frac{\zeta_1^2+\zeta_2^2}{2}+p^2\right]^{-n_1-n_2-l_1-l_2-2}$$
$$\times \sum_{\nu=0}^{+\infty} {}_2F_0(-\nu, n_1+l_1+1; n_1+l_1+l_2+2; 2)$$
$$\times \frac{(n_1+n_2+l_1+l_2+2)_\nu}{\nu!} \left(\frac{\zeta_1^2-\zeta_2^2}{\zeta_1^2+\zeta_2^2+2p^2}\right)^\nu. \quad (63)$$

With the help of an estimate for the hypergeometric series ${}_2F_1$ [19], it can be shown that this series converges for all $\zeta_1, \zeta_2, p \in \mathbb{R}$.

At first sight, the series expansion (63) seems to be much more complicated than the series expansions (57) and (59). However, the terminating hypergeometric series ${}_2F_1$ in (63) can be computed conveniently with the help of the following three-term recursion that is stable in direction of increasing $\nu \in \mathbb{N}$ [19]:

$$\begin{aligned}(n+m+\nu+2)&{}_2F_1(-\nu-1, m+1; m+n+2; 2)\\ &= (n-m){}_2F_1(-\nu, m+1; m+n+2; 2)\\ &\quad + \nu\,{}_2F_1(-\nu+1, m+1; m+n+2; 2), \qquad n, m \in \mathbb{N}_0. \end{aligned} \tag{64}$$

Accordingly, the additional computational costs due to the terminating hypergeometric series ${}_2F_1$ in (63) are negligible. Inserting the series expansions (63) into (52) yields [19]

$$\begin{aligned}{}_B\mathcal{S}^{n_2,l_2,m_2}_{n_1,l_1,m_1}(\zeta_1, \zeta_2, \vec{R}) &= \frac{\zeta_1^{2n_1+l_1-1}\zeta_2^{2n_2+l_2-1}}{\left[(\zeta_1^2+\zeta_2^2)/2\right]^{n_2+n_2+(l_1+l_2)/2-1}}\\ &\quad\times \sum_{\nu=0}^{+\infty} {}_2F_1(-\nu, n_1+l_1+1; n_1+n_2+l_1+l_2+2; 2)\\ &\quad\times \frac{(n_1+n_2+l_1+l_2+2)_\nu}{\nu!}\left(\frac{\zeta_1^2-\zeta_2^2}{\zeta_1^2+\zeta_2^2}\right)^\nu\\ &\quad\times {}_B\mathcal{S}^{n_2,l_2,m_2}_{n_1+\nu,l_1,m_1}\left(\left[(\zeta_1^2+\zeta_2^2)/2\right]^{1/2}, \left[(\zeta_1^2+\zeta_2^2)/2\right]^{1/2}, \vec{R}\right). \end{aligned} \tag{65}$$

The numerical properties of this series expansion in combination with convergence acceleration methods were studied in [23, 18]. It is also possible to derive an integral representation for the overlap integral of two B functions with different scaling parameters that involves an integration over a nonphysical variable. The well-known Feynman identity [56] can be generalized to give [57]

$$a^{-m}b^{-m} = \frac{(m+n-1)!}{(m-1)!(n-1)!}\int_0^1 \frac{t^m(1-t)^n}{[at+b(1-t)]^{m+n}}\,\mathrm{d}t, \qquad m, n \in \mathbb{N}. \tag{66}$$

This yields for the characteristic denominators [18]:

$$\begin{aligned}\left[\zeta_1^2+p^2\right]^{-n_1-l_1-1}&\left[\zeta_2^2+p^2\right]^{-n_2-l_2-1}\\ &= \frac{(n_1+n_2+l_1+l_2+1)!}{(n_1+l_1)!(n_2+l_2)!}\int_0^1 \frac{t^{n_1+l_1}(1-t)^{n_2+l_2}}{\left[p^2+\zeta_1^2 t+\zeta_2^2(1-t)\right]^{n_1+n_1+l_1+l_2+2}}\,\mathrm{d}t. \end{aligned} \tag{67}$$

Combination of (54), (52) and (67) yields [18]

$$\begin{aligned}{}_B\mathcal{S}^{n_2,l_2,m_2}_{n_1,l_1,m_1}(\zeta_1, \zeta_2, \vec{R}) &= \zeta_1^{2n_1+l_1-1}\zeta_2^{2n_2+l_2-1}\frac{(n_1+n_2+l_1+l_2+1)!}{(n_1+l_1)!(n_2+l_2)!}\\ &\quad\times \int_0^1 \frac{t^{n_1+l_1}(1-t)^{n_2+l_2}}{[\gamma(\zeta_1,\zeta_2,t)]^{n_1+n_1+l_1+l_2+2}}\,{}_B\mathcal{S}^{n_2,l_2,m_2}_{n_1,l_1,m_1}(\gamma(\zeta_1,\zeta_2,t), \gamma(\zeta_1,\zeta_2,t), \vec{R})\,\mathrm{d}t, \end{aligned} \tag{68}$$

where $\gamma(\zeta_1, \zeta_2, t) = \sqrt{\zeta_1^2 t + \zeta_2^2(1-t)}$.

This integral representation was first used by Trivedi and Steinborn [33] in combination with an adaptive quadrature routine. Bhattacharya and Dhabal [58] used (68) in combination with Gauss–Legendre quadrature. Later, it was shown by Weniger and Steinborn [18] that Gauss–Jacobi gives better results than Gauss–Legendre. Homeier and Steinborn [24] also used this integral representation in combination with a so-called Möbius quadrature rule introduced in [59]. FORTRAN programs were published by Homeier, Weniger and Steinborn [20].

6. Numerical results and discussion

By using the fact that the integrand $\mathcal{F}(x)$ converges to 0 when $x \to +\infty$ and if $\lambda \neq 0$ then $\lim_{\alpha\to 0} j_\lambda(\alpha) = 0$, one can easily show that when $R \to 0$ and $\lambda \neq 0$ the semi-infinite spherical Bessel integrals occurring in equations (31)–(33) vanish. In the case when $\lambda = 0$ and $R \to 0$, we replaced $j_0(Rx)$ by its Taylor development and we obtained the following approximation for these semi-infinite integrals:

$$\int_0^{+\infty} \mathcal{F}(x)\,\mathrm{d}x \approx \int_0^{+\infty} g(x)\left(1 - \frac{R^2x^2}{3!} + \frac{R^4x^4}{5!} - \frac{R^6x^6}{7!} + \cdots\right)\mathrm{d}x. \tag{69}$$

The semi-infinite integral in the rhs of the above equation is evaluated using Gauss–Laguerre quadrature of order 48. In our algorithm, we used only the first term of the Taylor development, but one can increase the accuracy by including higher terms.

The linear system (49) is solved using the LU decomposition method. The finite integrals $\int_0^{x_l} \mathcal{F}(t)\,\mathrm{d}t$ occurring in equations (49) and (51) are transformed into a finite sum as follows:

$$\int_0^{x_l} \mathcal{F}(t)\,\mathrm{d}t = \sum_{i=0}^{l-1} \int_{x_i}^{x_{i+1}} \mathcal{F}(t)\,\mathrm{d}t, \tag{70}$$

and each term of the above finite sum is evaluated using Gauss–Legendre quadrature of order 24.

For the numerical evaluation of Gaunt coefficients which occur in the complete expressions of the integrals under consideration (31)–(33), we used the subroutine GAUNT.F developed by Weniger [52]. The spherical harmonics $Y_l^m(\theta, \varphi)$ are computed using the recurrence formulae presented in [52].

In tables 1–3, we listed values of the two-centre overlap-like quantum similarity integrals of the first and second kinds, over STFs.

Values$^{(\dagger)}$ are obtained using the infinite series (35) to evaluate the semi-infinite integrals $\mathcal{I}$, occurring in the analytic expressions of the integrals under consideration (31)–(33).

Values$^{(\mathrm{ACJU})}$ are obtained using the ACJU code [20] for the numerical evaluation of the two-centre overlap integrals over B functions occurring in the analytic expression of the two-centre overlap-like quantum similarity integrals.

Values$^{(\overline{D})}$ are obtained using the algorithm described in the present work for the numerical evaluation of the semi-infinite integral $\mathcal{I}$.

Values$^{(\ddagger)}$ are obtained using the one-centre two-range method [47] and using the approach based on the epsilon algorithm of Wynn [48].

From the numerical tables, one can note that the nonlinear $\overline{D}$ is able to reach a high accuracy in the numerical evaluation of the molecular integrals under consideration, more than 12 correct digits in most cases. Note that one can increase the accuracy by increasing the order of accuracy n (49) and (51). Our results are in a complete agreement with those obtained using the ACJU code and with those listed in [47, 48]. These arguments illustrate that introduction of the nonlinear transformations methods in molecular integral calculations constitutes an important step towards a development of highly accurate and fast algorithms for the molecular structure calculations.

We also compared the calculation times obtained from each approach described above. The use of the ACJU leads to the fastest algorithm compared with the nonlinear $\overline{D}$ transformation and the one-centre two-range method. For the calculation presented in table 1, the algorithm using the ACJU code requires less than 0.30 ms (calculations times are computed after the common blocks are initialized). The $\overline{D}$ transformation requires less than 0.85 ms. The approaches presented in [47, 48] require more than 1.6 ms.

It is clear that the ACJU code leads to a very fast and highly accurate algorithm for the numerical evaluation of the molecular integrals under consideration. The nonlinear $\overline{D}$ is faster compared to the alternatives presented in [47, 48]. The algorithm obtained from $\overline{D}$ could be further improved by developing extrapolation techniques suitable to the two-centre overlap integrals and by initializing all the common block in the program.

All the computations were done in FORTRAN double precision. We used Lahey ED compiler (15 significant decimals in double precision).

In all tables, the numbers in parentheses represent powers of 10 and all entries are in atomic units. Calculations were performed on a Workstation with an Intel Xeon Processor with 2.4 GHz.

7. Conclusion

STFs are used as a basis set of atomic orbitals. The two-centre overlap-like quantum similarity integrals are expressed in terms of the usual two-centre overlap integrals, which in their turn are expressed in terms of overlap integrals over the so-called B functions. Analytic expressions obtained using the Fourier transform method are used for the analytic development of the two-centre overlap-like quantum similarity integrals.

The obtained analytic expressions for the overlap-like quantum similarity integrals for the first and second kinds involve semi-infinite highly oscillatory spherical Bessel integral functions, which are the principal source in the numerical evaluation of the integrals under consideration.

With the help of the nonlinear $\overline{D}$ transformation, which is one of the most effective general approaches for increasing the rate of convergence of semi-infinite oscillatory integrals whose integrands satisfy linear differential equations with coefficients having asymptotic expansions in inverse powers of their argument x as $x \to +\infty$, the convergence of the semi-infinite spherical Bessel integrals is improved. An algorithm based on the $\overline{D}$ transformation is now developed and section 6 shows that this algorithm is capable to reproduce results from the literature with a high pre-determined accuracy.

The use of ACJU code developed by Homeier, Weniger and Steinborn leads to the development of highly accurate and rapid algorithm for the numerical evaluation of the two-centre overlap-like quantum similarity integrals. From this it follows that the use of the basis set of B functions in the analytic development of the molecular integrals under consideration or for the molecular integrals in general could lead to the development of highly efficient and rapid algorithms for accurate molecular structure calculations.

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