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RESEARCH PAPER

Convergence of Slater-Type Orbitals in Calculations of Basic Molecular Integrals

Selda Akdemir[1]

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Abstract The relationship between real Slater-type orbitals with the distinct scaling constants is examined analytically via the Fourier transform method. The convergence of the formula that we have derived in terms of infinite sums of Slater-type orbitals is analyzed numerically. Subsequently, the analytical expression is applied to basic molecular integrals. Numerical calculations performed to demonstrate the accuracy of the obtained formulas are compared with results in the literature. Numerical results are also presented in tables.

Keywords Fourier transform method · Slater-type orbitals · Overlap integrals · Taylor expansions

1 Introduction

For the evaluation of molecular integrals, which occur in the electronic structure calculations of atomic and molecular systems, the choice of basis functions to be used as atomic orbitals is of major importance. These functions should represent in the best way the physical and chemical structure of the system. In addition, the efficiency of the algorithms developed depends strongly on the basis functions used.

The wave functions obtained from the exact solution of the Schrödinger equation satisfy the cusp condition at the nucleus and decay exponentially at large distances. Accordingly, among exponential-type orbitals (ETOs), Slater-type orbitals (STOs), which correctly exhibit the behavior of the wave functions near nuclei and at large distances from them, are frequently used in the calculation of molecular integrals. In addition, that STOs have a simple analytical structure in configuration space and all other ETOs can be expressed in terms of STOs are reasons to prefer them as basis functions. In recent calculations of electronic structure, the use of STOs continues (Guseinov et al. 2001; Öztekin et al. 2001; Öztekin 2004; Özcan and Öztekin 2009; Özay and Öztekin 2013; Harris 2002; Safouhi and Hoggan 2003; Safouhi 2004; Özdoğan and Orbay 2002; Barnett 2003; Antolovic and Silverstone 2004). For computing molecular integrals with STOs, many package programs have been developed over the past 40 years (Bouferguene et al. 1996; Fernandez Rico et al. 1998, 2001, 2004; Guidotti et al. 2003).

The Fourier transform method, primarily suggested by Prosser and Blanchard (1962), is one of the most important methods used to simplify the calculation of many-center molecular integrals. Through this method, in which integrals are transformed into inverse Fourier integrals, two-dimensional integrals in configuration space with non-separable integration variables can be expressed as one-dimensional integrals in momentum space with easily separable integration variables.

In this paper, we prefer to use the Fourier transform of STOs (FTSTOs) in ETOs. These functions have a relatively complicated analytical structure in momentum space (Geller 1963; Silverstone 1966; Kaijser and Smith 1977; Weniger and Steinborn 1983b). However, the use of partial fraction decompositions and Taylor expansions of rational functions makes the analytic process easier (Weniger et al. 1986). In Sect. 2, we shall discuss the relevant properties of STOs using the Fourier transform method. Particular emphasis will be given to the relationship between STOs

✉ Selda Akdemir
sozcan@sinop.edu.tr

[1] Department of Science Education, Faculty of Education, Sinop University, Sinop, Turkey

with distinct scaling constants. In the remaining sections, we shall develop all mathematical tools that we need for the derivation of closed-form expressions for the overlap integrals for one- or two-center molecular functions over the identical and distinct scaling constants. With the help of these tools, analytical representations for overlap integrals, which are mostly new, will be derived and numerical results in agreement with those in the literature are presented.

In the last years, Sturmian orbitals that their Fourier transform are hyperspherical harmonics have been used as a basis function to solve one and two-center molecular integrals in momentum space (Avery 2000; Aquilanti et al. 2001; Calderini et al. 2012; Coletti et al. 2013; Avery and Avery 2015). The evaluation of molecular integrals has been already done for STOs (Fernandez Rico et al. 1998, 2001, 2004; Silverstone 1966; Kaijser and Smith 1977; Todd et al. 1970). However, we think that the problems associated with these integrals are now much better understood and that considerable progress could be achieved. In our opinion, this is mainly a consequence of the investigation of properties of STOs.

2 Fourier Transform of STOs

In this section, we shall discuss only those properties of STOs that will be required for the derivation of closed-form relationships for the two-center molecular integrals. More complete treatments of the mathematical properties of STOs and their Fourier transform were given elsewhere (Weniger and Steinborn 1983b; Guseinov et al. 2001; Öztekin et al. 2001; Öztekin 2004; Özcan and Öztekin 2009; Özay and Öztekin 2013).

We shall use the symmetric version of the Fourier transformation in this paper. Accordingly, STOs $\chi_{nl}^{m}(\alpha,\mathbf{r})$ and their Fourier transform $U_{nl}^{m}(\alpha,\mathbf{p})$ related to each other by the relations

$$\begin{aligned}\chi_{n\,l}^{m}(\alpha,\mathbf{r}) &= (2\pi)^{-3/2}\int e^{i\,r\cdot p}U_{n\,l}^{m}(\alpha,\mathbf{p})\mathrm{d}\mathbf{p},\\ U_{n\,l}^{m}(\alpha,\mathbf{p}) &= (2\pi)^{-3/2}\int e^{-i\,r\cdot p}\chi_{nl}^{m}(\alpha,\mathbf{r})\mathrm{d}\mathbf{r}.\end{aligned} \tag{1}$$

The normalized STOs are defined according to the following relationship,

$$\chi_{nl}^{m}(\alpha,\mathbf{r}) = \frac{(2\alpha)^{n+1/2}}{\sqrt{(2n)!}}r^{n-1}e^{-\alpha r}Y_{l}^{m}(\theta,\phi), \tag{2}$$

where n, l, and m are quantum numbers and α a scaling constant. $Y_{l}^{m}(\theta,\phi)$ is the complex or real spherical harmonic of degree l and order m (Arfken and Weber 2001).

To evaluate FTSTOs, we need the well-known Rayleigh expansion of a plane wave in terms of spherical Bessel functions and spherical harmonics (Edmonds 1960).

$$e^{\pm i\mathbf{p}\cdot\mathbf{R}} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(\pm i)^{l}j_{l}(pR)\left(Y_{l}^{m}(\theta_p,\phi_p)\right)^{*}Y_{l}^{m}(\theta_R,\phi_R). \tag{3}$$

The spherical Bessel functions in Eq. (3) are defined in terms of modified Bessel functions (Arfken and Weber 2001),

$$j_l(xy) = \sqrt{\frac{\pi}{2xy}}J_{l+1/2}(xy). \tag{4}$$

Using Eq. (2) and the plane-wave expansion given by Eq. (3), we have for the FTSTOs.

$$\begin{aligned}U_{nl}^{m}(\alpha,\mathbf{p}) = \frac{2^{n+1}\alpha^{n+1/2}}{\sqrt{\pi(2n)!}}&\sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'}(-i)^{l'}Y_{l'}^{m'}(\theta_p,\phi_p)\\ &\times\int_{r=0}^{\infty}j_{l'}(rp)r^{n+1}e^{-\alpha r}dr\\ &\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}Y_{l}^{m}(\theta,\phi)\left(Y_{l'}^{m'}(\theta,\phi)\right)^{*}\sin\theta\mathrm{d}\theta\mathrm{d}\phi\end{aligned} \tag{5}$$

To obtain an analytical expression for the FTSTOs in terms of the radial integral, we use the orthogonality of the spherical harmonics and Eq. (4) to express the FTSTOs as

$$U_{n\,l}^{m}(\alpha,\mathbf{p}) = (-i)^{l}\frac{2^{n+1}\alpha^{n+1/2}}{\sqrt{\pi(2n)!}}Y_{l}^{m}(\theta_p,\phi_p)\,I_{n}^{l}(\alpha), \tag{6}$$

where

$$I_{n}^{l}(\alpha) = \sqrt{\frac{\pi}{2p}}\int_{0}^{\infty}e^{-\alpha r}J_{l+1/2}(pr)\,r^{n+1/2}\mathrm{d}r\,. \tag{7}$$

The remaining radial integral $I_{n}^{l}(\alpha)$ in Eq. (7) can be expressed in terms of a hypergeometric series. One has to compute radial integrals of the type (Gradshteyn and Ryzhik 2000),

$$\begin{aligned}\int_{0}^{\infty}e^{-ar}J_{\nu}(br)r^{\mu-1}\mathrm{d}r &= \frac{(b/2a)^{\nu}\Gamma(\nu+\mu)}{a^{\mu}\Gamma(\nu+1)}\\ &{}_2F_1\left(\frac{\nu+\mu}{2},\frac{\nu+\mu+1}{2};\nu+1;-\frac{b^2}{a^2}\right)\end{aligned} \tag{8}$$

$$\begin{aligned}&= \frac{(b/2a)^{\nu}\,\Gamma(\nu+\mu)a^{\mu-1}}{\Gamma(\nu+1)(a^2+b^2)^{\mu-1/2}}\\ &{}_2F_1\left(\frac{\nu-\mu+1}{2},\frac{\nu-\mu}{2}+1;\nu+1;-\frac{b^2}{a^2}\right)\end{aligned} \tag{9}$$

$$= \frac{\Gamma(\nu+\mu)}{\sqrt{(a^2+b^2)^{\mu}}}P_{\mu-1}^{-\nu}\left(a\Big/\sqrt{(a^2+b^2)}\right). \tag{10}$$

The hypergeometric series is defined as (Gradshteyn and Ryzhik 2000)

$$
{}_pF_q\left(a_1, a_2, \ldots, a_p; b_1, b_2, \ldots, b_q; x\right) = \sum_{k=0}^{\infty} \frac{(a_1)_k (a_2)_k \ldots (a_p)_k x^k}{(b_1)_k (b_2)_k \ldots (b_q)_k k!}, \tag{11}
$$

where $(a)_k = \Gamma(a+k)/\Gamma(a)$ is the Pochhammer symbol and $\Gamma(x)$ denotes the Gamma function.

If Eq. (9) is used for the computation of the radial integral in Eq. (7), we can establish the following formula for the FTSTOs (Weniger and Steinborn 1983a);

$$
U^m_{n\,l}(\alpha, \mathbf{p}) = \frac{2^{n-l}(n+l+1)!\, S^m_l(-i\mathbf{p})}{\sqrt{(2n)!}\,\alpha^{l+3/2}\,(l+1/2)!}\left(\frac{\alpha^2}{\alpha^2+p^2}\right)^{n+1} {}_2F_1\left(\frac{l-n}{2}, \frac{l-n+1}{2}; l+\frac{3}{2}; -\frac{p^2}{\alpha^2}\right), \tag{12}
$$

where $S^m_l(\mathbf{p}) = p^l Y^m_l(\mathbf{p}/p)$ denotes the regular solid spherical harmonic. The representation in Eq. (12) appears in (Kaijser and Smith 1977; Weniger and Steinborn 1983b).

For FTSTOs, an identical expression can be derived (Weniger and Steinborn 1983b) with the help of the transformation formulae of the hypergeometric series given below (Gradshteyn and Ryzhik 2000)

$$
{}_2F_1(a, b; c; x) = \frac{F_a(c-1)}{F_a(b-1)(1-x)^a}\, {}_2F_1\left(a, c-b; a-b+1; \frac{1}{1-x}\right) + \frac{F_b(c-1)}{F_b(a-1)(1-x)^b}\, {}_2F_1\left(b, c-a; b-a+1; \frac{1}{1-x}\right), \tag{13}
$$

where $F_a(b)$ denotes the binomial coefficients.

Now, we have a new relation for all values of $n-l$ with no distinction between even and odd degree. Analogously, we obtain an expression for the FTSTOs in terms of hypergeometric functions:

$$
U^m_{n\,l}(\alpha, \mathbf{p}) = N^{l\,l'}_n(\alpha)\, S^m_l(i\mathbf{p})\left(\frac{\alpha^2}{\alpha^2+p^2}\right)^{(n+l+l'+2)/2} {}_2F_1\left(\frac{l-n+l'}{2}, \frac{n+l+l'+2}{2}; l'+\frac{1}{2}; \frac{\alpha^2}{\alpha^2+p^2}\right), \tag{14}
$$

where

$$
l' = \delta_{\left[\frac{n-l+1}{2}\right], \frac{n-l+1}{2}}
$$

$$
\left[\frac{n-l}{2}\right] = \frac{n-l}{2} - \left(1-(-1)^{n-l}\right)\Big/4 \tag{15}
$$

$$
N^{l\,l'}_n(\alpha) = \frac{i^{n+l+3l'}(n+l+1)!(n-l+l')!}{\sqrt{\pi(2n)!}\,\alpha^{l+3/2}\left(\frac{n-l+l'}{2}\right)!\,(1/2)_{(n+l-l'+2)/2}}.
$$

If we use following relations between Gegenbauer polynomials and hypergeometric functions (Gradshteyn and Ryzhik 2000),

$$
C^\lambda_{2k}(x) = \frac{(-1)^k}{(\lambda+k)B(\lambda, k+1)}\, {}_2F_1\left(-k, k+\lambda; \frac{1}{2}; x^2\right), \tag{16}
$$

$$
C^\lambda_{2k+1}(x) = \frac{(-1)^k\, 2x}{B(\lambda, k+1)}\, {}_2F_1\left(-k, k+\lambda+1; \frac{3}{2}; x^2\right),
$$

we obtain another expression for the FTSTOs in terms of Gegenbauer polynomials for even and odd values of n–l,

$$
U^m_{n\,l}(\alpha, \mathbf{p}) = g^{l'}_{n,l}(\alpha) f_{n,l}(\alpha, p) Y^m_l(\theta_p, \phi_p), \tag{17}
$$

where

$$
g^{l'}_{n,l}(\alpha) = i^{n-l'} N^{l\,l'}_n(\alpha)\, B\left(l+1, \frac{n-l-l'+2}{2}\right)\left(1+\left(1+(-1)^{l'}\right)(n+l+1)/2\right)/2, \tag{18}
$$

$$
f_{n,l}(\alpha, p) = \left(\frac{\alpha^2}{\alpha^2+p^2}\right)^{(n+l+2)/2} C^{l+1}_{n-l}\left(\frac{\alpha}{\sqrt{\alpha^2+p^2}}\right) p^l, \tag{19}
$$

with $B(p,q)$ denoting the beta function (Arfken and Weber 2001). Equation (17) is a general formula of FTSTOs for all values of the quantum numbers.

The FTSTOs consists of three parts as can be seen in Eq. (17). The factor $g^{l'}_{n,l}(\alpha)$ is the normalization coefficient, $f_{n,l}(\alpha, p)$ the radial part, and $Y^m_l(\theta, \phi)$ the angular part. The term that is difficult to compute in numerical calculations is the radial part. To store and retrieve it from memory in the computations, the position of the radial part $f_{n,l}(\alpha, p)$ in memory is determined by the following relation (Özay and Öztekin 2013)

$$
k^l_n = \frac{n(n-1)}{2} + l + 1. \tag{20}
$$

If we use Eq. (47) of Weniger et al. (1986) and the series expansion of the Gegenbauer polynomials in Eq. (19), we obtain the following expression for the radial part of the FTSTOs in terms of distinct scaling constants,

$$
f_{n,l}(\alpha, p) = \sum_{s=0}^{\left[\frac{n-l}{2}\right]} A^s_{n,l}(\alpha) p^l \left(\beta^2+p^2\right)^{-n+s-1} {}_1F_0\left(n-s+1; \frac{\beta^2-\alpha^2}{\beta^2+p^2}\right), \tag{21}
$$

where

$$A^{s}_{n,l}(\alpha) = (-1)^{s} \frac{2^{n-l-2s}\,\alpha^{2(n-s+1)}\,(n-s)!}{l!s!(n-l-2s)!}. \tag{22}$$

The FTSTOs are then written as

$$U^{m}_{n\,l}(\alpha, \mathbf{p}) = g^{l'}_{n,l}(\alpha) \sum_{s=0}^{\left[\frac{n-l}{2}\right]} A^{s}_{n,l}(\alpha) \frac{S^{m}_{l}(\mathbf{p})}{(\beta^2 + p^2)^{n-s+1}} \, {}_1F_0\left(n - s + 1; \frac{\beta^2 - \alpha^2}{\beta^2 + p^2}\right), \tag{23}$$

where $\beta \neq \alpha$, i.e., the scaling constants are distinct, and ${}_1F_0(a, x)$ is the generalized hypergeometric series. The generalized hypergeometric series ${}_1F_0(a, x)$ in Eq. (11) converges absolutely and uniformly for all $p \in R$ provided that $\beta \in (0, \sqrt{2}\,\alpha)$ (Weniger et al. 1986). After some algebra, we obtain the following expression for the FTSTOs

$$U^{m}_{n\,l}(\alpha, \mathbf{p}) = g^{l'}_{n,l}(\alpha) \sum_{k=0}^{\infty} \frac{(\beta^2 - \alpha^2)^k}{k!} \sum_{s=0}^{\left[\frac{n-l}{2}\right]} A^{s}_{n,l}(\alpha) \frac{(n-s+1)_k S^{m}_{l}(\mathbf{p})}{(\beta^2 + p^2)^{n+k-s+1}}. \tag{24}$$

Hence, we only have to use the inverse Fourier transform of FTSTOs given by Eq. (1) in Eq. (24) to derive

$$\chi^{m}_{n\,l}(\alpha, \mathbf{r}) = \frac{g^{l'}_{n,l}(\alpha)}{(2\pi)^{3/2}} \sum_{k=0}^{\infty} \frac{(\beta^2 - \alpha^2)^k}{k!} \sum_{s=0}^{\left[\frac{n-l}{2}\right]} (n-s+1)_k A^{s}_{n,l}(\alpha) \int e^{i\,r.p} \frac{S^{m}_{l}(\mathbf{p})}{(\beta^2 + p^2)^{n+k-s+1}} \,\mathrm{d}\mathbf{p}. \tag{25}$$

Using the radial integral formula in Gradshteyn and Ryzhik (2000), in Eq. (25), we establish the following expression for the STOs in configuration space,

$$\int e^{i\,\mathbf{r}\cdot\mathbf{p}} \frac{S^{m}_{l}(\mathbf{p})}{(\beta^2 + p^2)^n} \mathrm{d}\mathbf{p} = (i)^l \pi^2 \frac{\beta^{l-2n+3/2}}{2^{2n-5/2}} \sum_{q=1}^{n-l-1} \frac{(2n-2l-q-3)!\sqrt{(2(q+l))!}}{(n-1)!(q-1)!(n-l-q-1)!} \chi^{m}_{q+l\,l}(\beta, \mathbf{r}). \tag{26}$$

By analyzing this representation of the inverse Fourier transform of FTSTOs according to Eqs. (25) and (26), we learn about the properties of STOs, such as

$$\chi^{m}_{n\,l}(\alpha, \mathbf{r}) = \sum_{k=0}^{\infty} \left(1 - \frac{\alpha^2}{\beta^2}\right)^k \sum_{s=0}^{\left[\frac{n-l}{2}\right]} P^{s,k}_{n,l}(\alpha, \beta) \sum_{q=1}^{n+k-s-l} Q^{q\,s}_{n\,k\,l}\, \chi^{m}_{q+l\,l}(\beta, \mathbf{r}), \tag{27}$$

where

$$P^{s,k}_{n,l}(\alpha, \beta) = \frac{i^l \sqrt{\pi}\beta^{l-2n+2s-1/2}}{k!(n-s)!\,2^{2n+2k-2s+1}} A^{s}_{n,l}(\alpha) g^{l'}_{n,l}(\alpha) \tag{28}$$

and

$$Q^{q\,s}_{n\,k\,l} = \frac{(2(n+k-s-l)-q-1)!\sqrt{(2(q+l))!}}{(q-1)!(n+k-s-l-q)!}. \tag{29}$$

In Eq. (27), the STO is expressed in terms of infinite sums of STOs of a distinct scaling constant. This remarkable property of STOs could be used quite profitably in connection with two-center molecular integrals with distinct scaling constants. In these cases, only closed form expressions for the two-center molecular integrals over STOs have to be derived, which can be obtained more easily than the corresponding integrals over nonscalar functions.

To analyze the convergence of Eq. (27) when we take $n = \alpha = r = 1$ and $l = m = 0$, Eq. (27) essentially represents the expansion of $1/e = 0.367879$ in terms of STOs with distinct scaling constants

$$1/e = \sum_{k=0}^{\infty} P^{0,k}_{1,0}(1, \beta) \left(1 - \frac{1}{\beta^2}\right)^k \sum_{q=1}^{k+1} Q^{q\,0}_{1\,k\,0}\, \chi^{0}_{q\,0}(\beta, \mathbf{r}). \tag{30}$$

In Table 1, we list partial sums of Eq. (30) for some values of the scaling constant β. These results show quite convincingly that the series in Eq. (30) rapidly converges when α and β differ only slightly. However, convergence alone is not sufficient to make the series Eq. (27) numerically useful if one tries to evaluate it by a direct summation of the series terms.

3 Overlap Integrals

We shall need some distribution theory for the derivation of analytical expressions for the two-center overlap integrals over STOs via the Fourier transform method:

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; \mathbf{R}) = \int \left(\chi_{n_1 l_1}^{m_1}(\alpha, \mathbf{r})\right)^* \chi_{n_2 l_2}^{m_2}(\beta, \mathbf{r} - \mathbf{R})\, d\mathbf{r}$$

$$= \int e^{-i\mathbf{R}.\mathbf{p}} \left(U_{n_1 l_1}^{m_1}(\alpha, \mathbf{p})\right)^* U_{n_2 l_2}^{m_2}(\beta, \mathbf{p})\, d\mathbf{p} \tag{31}$$

Overlap integrals with distinct and identical scaling constants can be represented by finite and infinite sums of corresponding STOs via Eq. (31).

3.1 One-Center Overlap Integrals over STOs

In this section, we discuss analytical problems that occur if one-center overlap integrals over STOs are to be evaluated using Eq. (31)

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; 0) = \int \left(\chi_{n_1 l_1}^{m_1}(\alpha, \mathbf{r})\right)^* \chi_{n_2 l_2}^{m_2}(\beta, \mathbf{r})\, d\mathbf{r}. \tag{32}$$

3.2 Two-Center Overlap Integrals with Identical Scaling Constants

The well-known compact representation of the two-center overlap integrals with the identical scaling constants (Filter and Steinborn 1978) in momentum space is written

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \alpha; \mathbf{R}) = \int e^{-iR.p} \left(U_{n_1 l_1}^{m_1}(\alpha, \mathbf{p})\right)^* U_{n_2 l_2}^{m_2}(\alpha, \mathbf{p})\, d\mathbf{p}. \tag{35}$$

Using the FTSTOs given by Eq. (17) and the Taylor expansion given by Eq. (4.2) of Weniger et al. (1986) to simplify the denominator of the integral, the two-center overlap integrals with identical scaling constants can be obtained as follows:

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \alpha; \mathbf{R}) = \sum_{l=|l_1-l_2|}^{l_1+l_2}{}^{(2)} \sum_{m=-l}^{l} a_{l, n_1 l_1 m_1}^{m, n_2 l_2 m_2}(\alpha) \sum_{r=0}^{\left[\frac{n_1-l_1}{2}\right]} \sum_{s=0}^{\left[\frac{n_2-l_2}{2}\right]} b_{n_1 l_1 r}^{n_2 l_2 s} \times \left\{ \int e^{-i\mathbf{R}.\mathbf{p}} p^{l_1+l_2} Y_l^m(\theta_p, \phi_p) d\mathbf{p} - \sum_{k=0}^{n_1+n_2-r-s+1} \alpha^{2k} \int e^{-i\mathbf{R}.\mathbf{p}} \frac{p^{l_1+l_2+2} Y_l^m(\theta_p, \phi_p)}{(\alpha^2 + p^2)^{k+1}} d\mathbf{p} \right\}, \tag{36}$$

From the orthogonality of the spherical harmonics, the one-center overlap integrals can be reduced to a radial integral that then yields a representation in terms of factorial functions. Accordingly, the following two well-known expressions for the one-center overlap integrals can be easily obtained:

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; 0) = \delta_{l_1, l_2} \delta_{m_1, m_2} 2^{n_1+n_2+1} \frac{(n_1 + n_2)!}{\sqrt{(2n_1)!(2n_2)!}} \frac{\alpha^{n_1+1/2} \beta^{n_2+1/2}}{(\alpha + \beta)^{n_1+n_2+1}}, \tag{33}$$

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \alpha; 0) = \delta_{l_1, l_2} \delta_{m_1, m_2} \frac{(n_1 + n_2)!}{\sqrt{(2n_1)!(2n_2)!}}. \tag{34}$$

These two relations were also derived in Weniger and Steinborn (1983a) by considering the limiting case $R \to 0$ in some representations of the two-center overlap integrals, which are based upon the orthogonality of spherical harmonics over Bessel-type orbitals. Equations (33) and (34) are very simple to apply numerically for all quantum numbers and angles specifying the STOs.

where

$$a_{l, n_1 l_1 m_1}^{m, n_2 l_2 m_2}(\alpha) = (-1)^{l_2} \frac{i^{l_1+l_2} 2^{2n_1+2n_2+2} \langle l_1 m_1 | l_2 m_2 | l m \rangle A_{m_1 m_2}^m}{\alpha^{l_1+l_2+3} \pi F_{l_1}(n_1) F_{l_2}(n_2) \sqrt{F_{n_1}(2n_1) F_{n_2}(2n_2)}}, \tag{37}$$

$$b_{n_1 l_1 r}^{n_2 l_2 s} = (-1)^{r+s} \frac{a_r(l_1 + 1, n_1 - l_1)\, a_s(l_2 + 1, n_2 - l_2)}{2^{2(r+s)}}, \tag{38}$$

$$a_m(b, c) = F_{b-1}(b + c - m - 1) F_m(c - m). \tag{39}$$

In Eq. (37) $\langle l_1 m_1 | l_2 m_2 | l m \rangle$, is called the Gaunt coefficient, and $A_{m_1 m_2}^m$ are coefficients obtained with the integration of the product of three real spherical harmonics. These coefficients can be found in (Gaunt 1929; Guseinov 1970).

When the plane wave expansion given by Eq. (5) and orthogonality relation of the spherical harmonics are used for the integrals of Eq. (36), only radial integrals in terms of modified Bessel functions remain. The first radial integral obtained can be evaluated easily using the following integral formula (Gradshteyn and Ryzhik 2000)

$$\int_0^{\infty} x^{\mu} J_v(ax)dx = 2^{\mu} a^{-\mu-1} \frac{\Gamma((v+\mu+1)/2)}{\Gamma((v-\mu+1)/2)}. \tag{40}$$

To calculate the second radial integral in Eq. (36), we use the following integral equality (Gradshteyn and Ryzhik 2000),

$$\int_0^{\infty} \frac{t^{2m+a+1} J_a(zt)}{(t^2+\alpha^2)^{\mu+1}} \mathrm{d}t = \sqrt{\frac{\pi}{2}} \frac{(-1)^m \alpha^{2m-2\mu+a}}{2^{\mu}} \sum_{q=0}^{m} (-2)^q F_q(m) \frac{(\alpha z)^a}{\Gamma(\mu-q+1)} \hat{k}_{\mu-a-q}(\alpha z). \tag{41}$$

Here $\hat{k}_{\mu-a-q}(\alpha z)$ is the reduced Bessel function. Using the series expansion for the reduced Bessel function, the integral in the second part of Eq. (36) can be written in terms of linear combinations of STOs,

$$\begin{aligned} S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \alpha; \mathbf{R}) = & \sum_{l=|l_1-l_2|}^{l_1+l_2}{}^{(2)} \sum_{m=-l}^{l} a^{m, n_2 l_2 m_2}_{l, n_1 l_1 m_1}(\alpha) \sum_{r=0}^{\left[\frac{n_1-l_1}{2}\right]} \sum_{s=0}^{\left[\frac{n_2-l_2}{2}\right]} b^{n_2 l_2 s}_{n_1 l_1 r} \\ & \times \left\{ (-i)^l \pi^{3/2} Y_l^m(\theta_R, \phi_R) \left(\frac{2}{R}\right)^{l_1+l_2+3} \frac{\Gamma[(l_1+l_2+l+3)/2]}{\Gamma[(l-l_1-l_2)/2]} \right. \\ & + (-i)^l (-1)^L \pi^2 \alpha^{l_1+l_2+3/2} \sum_{k=0}^{n_1+n_2-r-s+1} \sum_{t=0}^{L+1} (-1)^t \frac{F_t(L+1)}{2^{2(k-t)-1/2}} \\ & \left. \times \sum_{q=1}^{k-t-l} \frac{(2(k-t-l)-q-1)! \sqrt{(2(q+l))!}}{(k-t)!(q-1)!(k-t-q-l)!} \chi^m_{q+l\, l}(\alpha, \mathbf{R}) \right\}. \end{aligned} \tag{42}$$

Over the range of values for the l index, the first part of Eq. (42) is always zero because the factorial in the denominator is negative. Consequently, for the two-center overlap integrals with identical scaling constants, a new analytical expression is obtained

$$\begin{aligned} S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \alpha; \mathbf{R}) = & \sum_{r=0}^{\left[\frac{n_1-l_1}{2}\right]} \sum_{s=0}^{\left[\frac{n_2-l_2}{2}\right]} b^{n_2 l_2 s}_{n_1 l_1 r} \sum_{l=|l_1-l_2|}^{l_1+l_2}{}^{(2)} \sum_{m=-l}^{l} a^{m, n_2 l_2 m_2}_{l, n_1 l_1 m_1}(\alpha) \\ & \times (-i)^l (-1)^L \pi^2 \alpha^{l_1+l_2+3/2} \sum_{k=0}^{n_1+n_2-r-s+1} \sum_{t=0}^{L+1} \frac{(-1)^t F_t(L+1)}{2^{2(k-t)-1/2}(k-t)!} \\ & \times \sum_{q=1}^{n} \frac{(2n-q-1)! \sqrt{(2(q+l))!}}{(q-1)!(n-q)!} \chi^m_{q+l\, l}(\alpha, \mathbf{R}), \end{aligned} \tag{43}$$

where

$$n = k-t-l, \; 2L = l_1 + l_2 - l. \tag{44}$$

3.3 Two-Center Overlap Integrals with Distinct Scaling Constants

Now, we come to the main part of this paper concerning STOs. In this section, analytical and numerical properties of the two-center overlap integrals given by Eq. (31) over real STOs with distinct scaling constants are discussed.

Using STOs obtained in terms of infinite sums given by Eq. (28) via the Fourier transform method, we write two different series expansions of the overlap integral with distinct scaling constants in terms of the overlap integrals with identical scaling constants,

$$\begin{aligned} S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta; \mathbf{R}) = & \sum_{k=0}^{\infty} \left(1 - \frac{\beta^2}{\alpha^2}\right)^k \sum_{s=0}^{\left[\frac{n_2-l_2}{2}\right]} P^{s,k}_{n_2 l_2}(\beta, \alpha) \\ & \sum_{q=1}^{n_2-l_2+k-s} Q^{q,s}_{n_2 k l_2} S^{q+l_2\, l_2 m_2}_{n_1 l_1 m_1}(\alpha, \alpha; \mathbf{R}) \quad for\, \alpha\, \beta, \end{aligned} \tag{45}$$

$$\begin{aligned} = & \sum_{k=0}^{\infty} \left(1 - \frac{\alpha^2}{\beta^2}\right)^k \sum_{s=0}^{\left[\frac{n_1-l_1}{2}\right]} P^{s,k}_{n_1 l_1}(\alpha, \beta) \sum_{q=1}^{n_1-l_1+k-s} \\ & Q^{q,s}_{n_1 k l_1} S^{n_2 l_2 m_2}_{q+l_1\, l_1 m_1}(\beta, \beta; \mathbf{R}) \quad for\, \beta\, \alpha, \end{aligned} \tag{46}$$

The numerical calculation of these two analytical expressions depends on the rate of convergence of the infinite series. The infinite series in Eq. (45) converges when $\left|1-(\beta/\alpha)^2\right| < 1$ and in Eq. (46) converges when $\left|1-(\alpha/\beta)^2\right| < 1$(Filter and Steinborn 1978; Antolovic and Delhalle 1980; Weniger and Steinborn 1983a; Weniger et al. 1986).

4 Results and Discussion

In this study, two-center overlap integrals with distinct scaling constants over STOs have been written in terms of infinite series sums of two-center overlap integrals with identical scaling constants via the Fourier transform method. Similar expressions were obtained using Bessel-type orbitals in (Filter and Steinborn 1978; Weniger and Steinborn 1983a).

First, analytical expressions of FTSTOs, which can be found in the literature, have been derived in terms of hypergeometric functions and Gegenbauer polynomials. Using the Taylor expansions in Weniger et al. (1986) and some mathematical manipulations, FTSTOs have been obtained in terms of infinite series, Eq. (24). Then, by the inverse Fourier transform of the FTSTOs in Eq. (24), STOs have been expressed in configuration space in terms of infinite sums of STOs with different scaling constants given by Eq. (27). The dependence of the convergence of this equation on scaling constants α and β has been analyzed. For $n = \alpha = r = 1$ and $l = m = 0$, the upper limit of the infinite series in Eq. (30) has been determined for different values of β and the results obtained have been

Table 1 Convergence of the series expansion of Eq. (30)

β	Number of terms	β	Number of terms
0.71	360	1.6	24
0.75	51	1.7	28
0.80	21	1.8	32
0.85	13	1.9	37
0.90	9	2.0	41
0.95	5	2.5	69
1.0	1	3.0	102
1.3	13	4.0	186
1.5	20	5.0	294

We have $n = \alpha = r = 1$ and $l = m = 0$ in Eq. (27)

given in Table 1. For $\alpha = \beta$, the infinite series terminates after the first term.

Two-center overlap integrals with distinct scaling constants are more complicated than overlap integrals with identical scaling constants. To perform this calculation, the representation of the STOs with different scaling constants in Eq. (27) has been used and the two-center overlap integrals with distinct scaling constants have been written in terms of two-center overlap integrals with identical scaling constants. These equations, Eqs. (45) and (46), contain infinite series. These two new infinite series expansions for the overlap integrals with distinct scaling constants have been analyzed numerically using program

Table 2 Comparative values for two-center overlap integrals over STOs with distinct scaling constants

n_1/n_2	l_1/l_2	m_1/m_2	α/β	R	θ	ϕ	N	Numerical results
1/1	0/0	0/0	2.2/1.5	2	45	0	57	$2.313\,711\,058\,327\,530 \times 10^{-1}$
								$2.313\,711\,058\,327\,53 \times 10^{-1}$ [a]
1/1	0/0	0/0	5.5/1.5	2	45	0	430	$5.912\,593\,860\,893\,338 \times 10^{-2}$
								$5.912\,593\,860\,893\,39 \times 10^{-2}$ [a]
1/2	0/1	0/0	1.02/1.01	1	0	0	9	$-4.338\,568\,004\,883\,413 \times 10^{-1}$
								$-4.338\,568\,004\,883\,410 \times 10^{-1}$ [b]
2/2	1/1	−1/−1	2.4/4.1	2.5	0	0	90	$2.542\,056\,225\,953\,330 \times 10^{-2}$
								$2.542\,056\,225\,95 \times 10^{-2}$ [c]
2/3	1/2	1/1	4.2/4.4	2.5	0	0	16	$1.292\,136\,453\,370\,558 \times 10^{-2}$
								$1.292\,136\,453\,370\,6 \times 10^{-2}$ [d]
3/3	2/2	−1/−1	1.2/4.5	2.5	0	0	140	$1.874\,186\,225\,439\,111 \times 10^{-1}$
								$1.874\,186\,225\,44 \times 10^{-1}$ [c]
3/3	2/2	2/2	5.8/4.5	8.7	0	0	67	$7.934\,310\,549\,472\,991 \times 10^{-15}$
								$7.934\,310\,549\,473\,0 \times 10^{-15}$ [d]
3/3	2/2	−2/−2	6.3/4.2	0.2	0	0	65	$8.04\,628\,483\,321\,906 \times 10^{-1}$
								$8.046\,628\,483\,32 \times 10^{-1}$ [c]
4/4	0/1	0/0	0.5/0.4	1.4	0	0	44	$-1.230\,350\,868\,942\,323 \times 10^{-1}$
								$-1.230\,350\,868\,942\,32 \times 10^{-1}$ [e]
5/5	2/2	2/2	1.5/1.4	1	0	0	21	$9.389\,786\,330\,449\,060 \times 10^{-1}$
								$9.389\,786\,330\,449\,057 \times 10^{-1}$ [b]
5/5	3/3	2/2	1.1/0.9	7	45	360	45	$-5.154\,764\,486\,478\,074 \times 10^{-3}$
								$-5.154\,764\,486\,473\,70 \times 10^{-3}$ [f]
6/6	5/5	−4/−5	1.02/0.98	15	120	360	16	$-3.601\,030\,586\,243\,642 \times 10^{-2}$
								$-3.601\,030\,586\,080\,59 \times 10^{-2}$ [f]
7/6	5/5	4/4	1.1/0.9	1	54	90	36	$8.609\,474\,596\,835\,023 \times 10^{-1}$
								$8.609\,474\,596\,835\,02 \times 10^{-1}$ [f]
10/10	0/0	0/0	2.5/3	3	0	0	50	$-1.677\,485\,114\,440\,529 \times 10^{-1}$
								$-1.677\,485\,114 \times 10^{-1}$ [g]
10/10	0/5	0/0	2.5/2.3	3	0	0	30	$1.937\,326\,997\,951\,603 \times 10^{-1}$
								$1.937\,326\,998 \times 10^{-1}$ [g]
13/13	12/12	12/12	1.01/0.99	2.5	0	0	14	$1.353\,105\,787\,024\,712 \times 10^{-4}$
								$1.353\,105\,787\,024\,712 \times 10^{-4}$ [h]
17/8	8/7	4/4	5.5/4.5	10	0	0	50	$-1.006\,400\,641\,171\,882 \times 10^{-6}$
								$-1.006\,400\,641\,171\,882 \times 10^{-6}$ [h]

[a] (Fernandez Rico et al. 1988); [b] (Jones 1997); [c] (Magnasco et al. 1999); [d] (Barnett 2003); [e] (Bhattacharya and Dhabal 1986); [f] (Guseinov et al. 2002); [g] (Bouferguene and Rinaldi 1994); [h] (Barnett 2001)

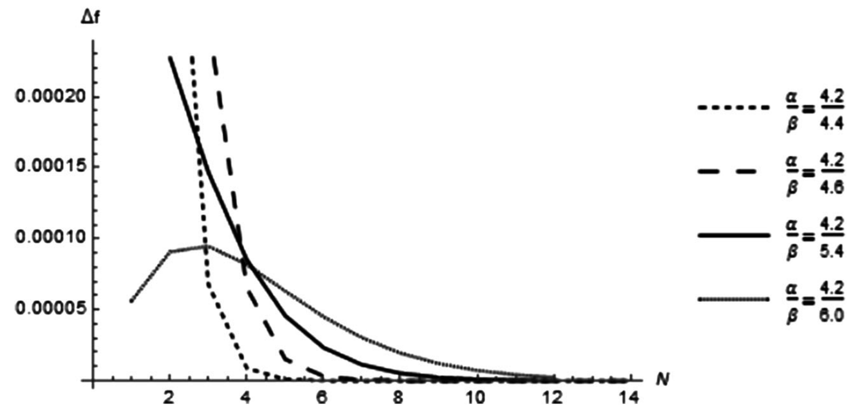

Fig. 1 Convergence of the series in Eq. (46) as a function of the upper limit of the index k for $S_{211}^{321}(\alpha,\ \beta;\ 2.5, 0, 0)$

(written in MATHEMATICA 10.0 language) that evaluate Eqs. (45) and (46). The computer program stops when the best approximation has been obtained. For N, the number of terms in Eqs. (45) and (46), the stopping criterion is

$$\left|\frac{S_{n_1\,l_1\,m_1}^{n_2\,l_2\,m_2^N}(\alpha,\ \beta;\ \mathbf{R}) - S_{n_1\,l_1\,m_1}^{n_2\,l_2\,m_2^{N-1}}(\alpha,\ \beta;\ \mathbf{R})}{S_{n_1\,l_1\,m_1}^{n_2\,l_2\,m_2^N}(\alpha,\ \beta;\ \mathbf{R})}\right| < 10^{-15}. \tag{47}$$

Subject to this criterion, comparative values up to 15 decimal digits for the two-center overlap integrals over STOs have been given in Table 2. From this table, our numerical results are in agreement with those in the literature. In addition, the convergence of the series in Eqs. (45) and (46) for various values of the scaling constants in the overlap integral $S_{211}^{321}(\alpha,\ \beta;\ 2.5, 0, 0)$ is shown in Fig. 1. Δf represents the difference between the values of the overlap integral in the previous and next terms. As can be seen from Fig. 1, when the two scaling constants are numerically close the convergence of Δf is more rapid. For larger differences of scaling constants the convergence rate is deteriorated.

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