Calculation of multicenter nuclear attraction and electron repulsion integrals over Slater orbitals by Fourier transform method using Gegenbauer polynomials

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In this study, using complete orthonormal sets of exponential type orbitals (ETOs), a single closed analytical relation is derived for a large number of different expansions of overlap integrals over Slater type orbitals (STOs) with the same screening parameters in terms of Gegenbauer coefficients. The general formula obtained for the overlap integrals is utilized for the evaluation of multicenter nuclear attraction and electron repulsion integrals appearing in the Hartree–Fock–Roothaan equations for molecules. The formulas given in this study for the evaluation of these multicenter integrals show good rate of convergence and great numerical stability under wide range of quantum numbers, scaling parameters of STOs and internuclear distances.

KEY WORDS: exponential type orbitals, Slater type orbitals, overlap integrals, multicenter integrals

1. Introduction

The basis sets of functions for calculations in the theory of molecular structure are of prime importance since the quality of several molecular properties may depend strongly on the nature of these basis functions. As is well known, the Gaussian type orbitals (GTOs) are used almost exclusively as the basis sets for ab initio quantum chemistry. However, GTOs are unable to represent important properties of the exact electronic wave function at nuclei and at large distances. Thus, ETOs would be desirable for basis sets in molecular calculations because they satisfy the cusp condition at the nuclei [1] and the exponential decay for large distances [2]. Unfortunately, the large body of formulae of the expansion methods of ETOs about a displaced center [3–8], the Fourier transform methods [9–11] and the *B*-function method [12–15] developed for the evaluation of multicenter molecular integrals over ETOs is not quite satisfactory in the numerical aspects of multicenter integrals, especially in the calculation of three- and four-center electron

repulsion integrals of the Hartree–Fock–Roothaan equations for molecules. In the literature, the wide use of ETOs as basis sets has been pursued with considerable enthusiasm by growing number of workers because of the huge advance in applied mathematics and computer science (see [16–25] and references quoted therein).

One of the most promising methods for the evaluation of multicenter integrals is the extension of Fock's methods [26,27] for momentum-space solution of the Schrödinger equation for hydrogenlike atoms and theory of hyperspherical harmonics to the multicenter case by Shibuya and Wulfman [28] (see also [29–31]). Unfortunately, the convergence of the expansion derived by Shibuya and Wulfman is not guaranteed since the continuum states of the hydrogen spectrum are not included properly in the expansion. Recently, one of us in [32] introduced the new complete orthonormal sets of Ψ^α-ETOs (where $\alpha = 1, 0, -1, -2, \ldots$) for which the problems with the continuum states do not occur. For obtaining the translation formulas for STOs we have used these complete orthonormal sets of Ψ^α-ETOs. Using these translation formulas in [33] the different analytical expressions were derived for expansion of one- and two-center electron charge density over STOs in terms of STOs about a new center. The expansion coefficients in these formulas are expressed through the overlap integrals with the same screening parameters for the calculation of which the efficient computer programs are available in our group [34,35]. Therefore, using the computer programs for the overlap integrals based on auxiliary functions [34] and recurrence relations [35] one can calculate arbitrary multicenter integrals appearing in the determination of various properties for molecules when the Hartree–Fock–Roothaan approximation is employed. The aim of this paper is to establish a single relation for overlap integrals with the same screening parameters in terms of Gegenbauer coefficients using Fourier transform of Ψ^α-ETOs and to use this relation for the calculation of multicenter nuclear attraction and electron repulsion integrals. It should be noted that, there is not a close relationship of our work to those of [3–28].

2. Ψ^α-ETOs in momentum representation

The Ψ^α-ETOs in the coordinate representation are defined by [32]

$$\Psi^\alpha_{nlm}(\zeta, \mathbf{r}) = R^\alpha_{nl}(\zeta, r) S_{lm}(\theta, \varphi), \tag{1}$$

$$R^\alpha_{nl}(\zeta, \mathbf{r}) = (-1)^\alpha \left[\frac{(2\zeta)^3 (n-l-1)!}{(2n)^\alpha [(n+l+1-\alpha)!]^3} \right]^{1/2} (2\zeta r)^l \, \mathrm{e}^{-\zeta r} L^{2l+2-\alpha}_{n+l+1-\alpha}(2\zeta r), \tag{2}$$

where $\alpha = 1, 0, -1, -2, \ldots$ and L^p_q is the generalized Laguerre polynomial [36]. In [32], the Ψ^α-ETOs were represented as finite linear combinations of STOs:

$$\Psi^\alpha_{nlm}(\zeta, \mathbf{r}) = \sum_{n'=l+1}^{n} \omega^{\alpha l}_{nn'} \chi_{n'lm}(\zeta, \mathbf{r}), \tag{3}$$

$$\omega_{nn'}^{\alpha l} = (-1)^{n'-l-1}\left[\frac{(n'+l+1)!}{(2n)^{\alpha}(n'+l+1-\alpha)!}F_{n'+l+1-\alpha}(n+l+1-\alpha)\right.$$

$$\left.\times F_{n'-l-1}(n-l-1)F_{n'-l-1}(2n')\right]^{1/2}, \tag{4}$$

$$\chi_{nlm}(\zeta, \mathbf{r}) = R_n(\zeta, r)S_{lm}(\theta, \varphi), \tag{5}$$

$$R_n(\zeta, r) = (2\zeta)^{n+1/2}[(2n)!]^{-1/2}r^{n-1}e^{-\zeta r}. \tag{6}$$

Here $F_s(n) = n!/[s!(n-s)!]$ is the binomial coefficient. The spherical harmonics in equations (1) and (5) are determined by the relation

$$S_{lm}(\theta, \phi) = P_{l|m|}(\cos\theta)\Phi_m(\phi), \tag{7}$$

where $P_{l|m|}$ are normalized associated Legendre functions, and for complex spherical harmonics ($S_{lm} \equiv Y_{lm}$)

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi}, \tag{8}$$

for real spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}}\begin{cases} \cos|m|\phi & \text{for } m \geqslant 0, \\ \sin|m|\phi & \text{for } m < 0. \end{cases} \tag{9}$$

We notice that the definition of phases in this work for the complex spherical harmonics ($Y_{lm}^* = Y_{l-m}$) differs from the Condon–Shortley phases [37] by the sign factor $(-1)^m$.

We notice that the complete sets of Ψ^{α}-ETOs are orthonormal with recpect to the weight function $(n/\zeta r)^{\alpha}$, where $\alpha = 1, 0, -1, -2, \ldots$:

$$\int \Psi_{nlm}^{\alpha*}(\zeta, \mathbf{r})\left(\frac{n}{\zeta r}\right)^{\alpha}\Psi_{n'l'm'}^{\alpha}(\zeta, \mathbf{r})\,d^3\mathbf{r} = \delta_{nn'}\delta_{ll'}\delta_{mm'}. \tag{10}$$

The Ψ^{α}-ETOs and STOs in the momentum representation are defined as the Fourier transforms of the functions (1) and (5):

$$\Phi_{nlm}^{\alpha}(\zeta, \mathbf{k}) = (2\pi)^{-3/2}\int e^{-i\mathbf{kr}}\Psi_{nlm}^{\alpha}(\zeta, \mathbf{r})\,d^3\mathbf{r}, \tag{11}$$

$$U_{nlm}^{\alpha}(\zeta, \mathbf{k}) = (2\pi)^{-3/2}\int e^{-i\mathbf{kr}}\chi_{nlm}^{\alpha}(\zeta, \mathbf{r})\,d^3\mathbf{r}. \tag{12}$$

Substituting equations (1) and (5) into the integrals in equations (11) and (12) and using the method set out in [38] one gets for the Ψ^{α}-ETOs and STOs in momentum representation the following expressions:

$$\Phi_{nlm}^{\alpha}(\zeta, \mathbf{k}) = \sum_{n'=l+1}^{n}\omega_{nn'}^{\alpha l}U_{n'lm}(\zeta, \mathbf{k}), \tag{13}$$

$$U_{nlm}(\zeta, \mathbf{k}) = Q_{nl}(\zeta, k)S_{lm}\left(\frac{\mathbf{k}}{k}\right), \tag{14}$$

where $S_{lm}(\mathbf{k}/k)$ are the spherical harmonics and

$$Q_{nl}(\zeta, k) = \frac{2^{n+l+1}l!(n-l)!}{\zeta^{3/2}\sqrt{\pi(2n)!}}x^{n+2}(1-x^2)^{l/2}C_{n-l}^{l+1}(x). \qquad (15)$$

Here, $x = \zeta/\sqrt{\zeta^2 + k^2}$ and $C_n^\alpha(x)$ is the Gegenbauer polynomial defined by the relation [36]

$$C_n^\alpha(x) = \sum_{s=0}^{E(n/2)} (-1)^s a_s(\alpha, n)(2x)^{n-2s}, \qquad (16)$$

where

$$a_s(\alpha, n) = F_{\alpha-1}(\alpha - 1 + n - s)F_s(n - s). \qquad (17)$$

It should be noted that the functions $\Phi_{nlm}^\alpha(\zeta, \mathbf{k})$ obtained from the Fourier transformation of Ψ^α-ETOs are orthonormal with the weight $(n/\zeta k)^\alpha$, where $\alpha = 1, 0, -1, -2, \ldots$:

$$\int \Phi_{nlm}^{\alpha*}(\zeta, \mathbf{k})\left(\frac{n}{\zeta r}\right)^\alpha \Phi_{n'l'm'}^\alpha(\zeta, \mathbf{k})\, d^3\mathbf{k} = \delta_{nn'}\delta_{ll'}\delta_{mm'}. \qquad (18)$$

Thus, the Ψ^α-ETOs in the momentum representation are also complete orthonormal sets of functions and are expressed in terms of Fourier transforms of STOs by the finite linear combinations. As can be seen from equation (15), the STOs in the momentum representation are defined by the Gegenbauer polynomials.

3. Overlap integrals with the same screening parameters

For evaluation of overlap integrals over STOs defined by relation

$$S_{nlm,n'l'm'}(p, \theta, \phi) = \int \chi_{nlm}^*(\zeta, \mathbf{r})\chi_{n'l'm'}(\zeta, \mathbf{r} - \mathbf{R})\, d^3\mathbf{r}, \qquad (19)$$

we use the Fourier transform convolution theorem [39,40] which is expressed in the form

$$S_{nlm,n'l'm'}(p, \theta, \phi) = \int e^{-i\mathbf{k}\mathbf{R}}U_{nlm}^*(\zeta, \mathbf{k})U_{n'l'm'}(\zeta, \mathbf{k})\, d^3\mathbf{k}, \qquad (20)$$

where $p = \zeta R$. Here $\chi_{nlm}(\zeta, \mathbf{r})$ and $U_{nlm}(\zeta, \mathbf{k})$ are a pair of mutual Fourier transforms defined by equations (5) and (14), respectively.

In order to evaluate overlap integrals we shall fist expand the product of two functions in the right-hand side of equation (20) in terms of the Ψ^α-ETOs in the momentum representation:

$$U_{nlm}^*(\zeta, \mathbf{k})U_{n'l'm'}(\zeta, \mathbf{k}) = (2\pi\zeta)^{-3/2} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-l}^{L} M_{nlm,n'l'm'}^{\alpha NLM}\Phi_{NLM}^{\alpha*}(\zeta, \mathbf{k}), \qquad (21)$$

where $\alpha = 1, 0, -1, -2, \ldots$, and

$$M_{nlm,n'l'm'}^{\alpha NLM} = \int U_{nlm}^*(\zeta, \mathbf{k}) U_{n'l'm'}(\zeta, \mathbf{k}) \left(\frac{N}{\zeta k}\right)^\alpha \Phi_{NLM}^\alpha(\zeta, \mathbf{k}) \, \mathrm{d}^3 \mathbf{k}. \tag{22}$$

Here we have taken into account the orthonormality relation (18) for function Φ^α. Now we use equation (13) and characteristics of the coefficients $\omega_{nn'}^{\alpha l}$ (see [32]). Then it is easy to prove the following identity:

$$\sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-l}^{L} M_{nlm,n'l'm'}^{\alpha NLM} \Phi_{NLM}^{\alpha*}(\zeta, \mathbf{k})$$

$$= \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-l}^{L} \left(\sum_{N'=N}^{n+n'+1} \omega_{NN'}^{\alpha L} M_{nlm,n'l'm'}^{\alpha N'LM}\right) U_{NLM}^*(\zeta, \mathbf{k}). \tag{23}$$

We take into account equation (13) in equations (22) and (23). Then we obtain finally for the expansion of product of Fourier transforms in terms of their linear combinations the following relation:

$$U_{nlm}^*(\zeta, \mathbf{k}) U_{n'l'm'}(\zeta, \mathbf{k})$$

$$= (2\pi\zeta)^{-3/2} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-l}^{L} \left(\sum_{N'=L+1}^{n+n'+1} \Omega_{NN'}^{\alpha L}(n + n' + 1) T_{nlm,n'l'm'}^{N'-\alpha LM}\right) U_{NLM}^{\alpha*}(\zeta, \mathbf{k}), \tag{24}$$

where

$$\Omega_{n\kappa}^{\alpha l}(N) = \left[\frac{[2(k-\alpha)]!}{(2\kappa)!}\right]^{1/2} \sum_{n'=\max(n,\kappa)}^{N} (2n')^\alpha \omega_{n'n}^{\alpha l} \omega_{n'\kappa}^{\alpha l}, \tag{25}$$

$$T_{nlm,n'l'm'}^{NLM} = (2\pi\zeta)^{3/2} \int U_{nlm}^*(\zeta, \mathbf{k}) U_{n'l'm'}(\zeta, \mathbf{k}) U_{NLM}(\zeta, \mathbf{k}) \, \mathrm{d}^3 \mathbf{k}. \tag{26}$$

The expressions for the integral $T_{nlm,n'l'm'}^{NLM}$ in terms of Gaunt and Gegenbauer coefficients are given in [38]. As can be seen from equations (20) and (24), the Fourier transformation converts the function $U_{NLM}(\zeta, \mathbf{k})$ into the STOs $\chi_{NLM}(\zeta, \mathbf{R})$. Thus, we are able to obtain for the overlap integrals with the same screening parameters the following finite linear combinations of STOs:

$$S_{nlm,n'l'm'}(p, \theta, \phi) = \zeta^{-3/2} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-l}^{L} g_{nlm,n'l'm'}^{\alpha NLM} \chi_{NLM}^*(\zeta, \mathbf{R})$$

$$\text{for } \alpha = 1, 0, -1, -2, \ldots, \tag{27}$$

where

$$g_{nlm,n'l'm'}^{\alpha NLM} = \sum_{N'=1}^{n+n'+1} \Omega_{NN'}^{\alpha L}(n + n' + 1) T_{nlm,n'l'm'}^{N'-\alpha LM}. \tag{28}$$

In order to calculate the overlap integrals on a computer, we have modified these expressions in nonlined-up coordinate systems:

$$S_{nlm,n'l'm'}(p,\theta,\phi) = e^{-p} \sum_{L=|l-l'|}^{l+l'} \sum_{M=-L}^{L} \sum_{N=L+1}^{n+n'+1} p^{N-1} G_{nlm,n'l'm'}^{\alpha NLM} \sqrt{\frac{4\pi}{2L+1}} S_{LM}(\theta,\phi).$$

(29)

In lined-up coordinate systems

$$S_{nlm,n'l'm'}(p,\theta,\phi) \equiv S_{nlm,n'l'm'}(p,0,0) = \delta_{mm'} e^{-p} \sum_{L=|l-l'|}^{l+l'} \sum_{N=L+1}^{n+n'+1} p^{N-1} G_{nlm,n'l'm'}^{\alpha NL0}.$$

(30)

Here

$$\begin{aligned} G_{nlm,n'l'm'}^{\alpha NLM} &= 2^N \sqrt{\frac{2(2L+1)}{(2N)!}} g_{nlm,n'l'm'}^{\alpha NLM} \\ &= (-1)^{(l-l'-L)/2}(2L+1)C^{L|M|}(lm,l'm')A_{mm'}^{M}\frac{2^N}{\sqrt{(2N)!}} \\ &\quad \times \sum_{N'=L+1}^{n+n'+1} \Omega_{NN'}^{\alpha L}(n+n'+1)Q_{nl,n'l'}^{N'-\alpha L'} \end{aligned}$$

(31)

and

$$\begin{aligned} Q_{nl,n'l'}^{NL} &= \Big[F_l(n)F_{l'}(n')F_L(N)\sqrt{F_n(2n)F_{n'}(2n')F_N(2N)} \Big]^{-1} \\ &\quad \times \sum_{s=0}^{k} (-1)^s a_s(l+1,n-l;l'+1,n'-l';L+1,N-L)b_{n+n'+N+1-g-s,g}, \end{aligned}$$

(32)

where

$$k = E\left(\frac{n-l}{2}\right) + E\left(\frac{n'-l'}{2}\right) + E\left(\frac{N-L}{2}\right)$$

and

$$b_{i,j} = \sum_{m=0}^{j+1} (-1)^m 2^{2j+1-2m} F_m(j+1)F_{i+m}\big(2(i+m)-1\big).$$

(33)

The Gaunt coefficients $C^{L|M|}$ and coefficients $A_{mm'}^{M}$ in equation (31) have been defined in [41].

One can determine the accuracy of the computer results by using the following recurrence relation:

$$\begin{aligned} S_{nlm,n'l'm'}(p,\theta,\phi) &= \frac{\sqrt{3}}{4pS_{10}(\theta)\sqrt{\pi}} \Big[A_{nl\lambda}S_{n+1l+1m,n'l'm'}(p,\theta,\phi) + B_{nl\lambda}S_{n+1l-1m,n'l'm'}(p,\theta,\phi) \\ &\quad - A_{n'l'\lambda'}S_{nlm,n'+1l'+1m'}(p,\theta,\phi) + B_{n'l'\lambda'}S_{nlm,n'+1l'-1m'}(p,\theta,\phi) \Big]. \end{aligned}$$

(34)

Here the coefficients $A_{nl\lambda}$ and $B_{nl\lambda}$ are determined by

$$A_{nl\lambda} = \left[(2n+1)(2n+2)\frac{(l-\lambda+1)(l+\lambda+1)}{(2l-1)(2l+3)}\right]^{1/2}, \tag{35}$$

$$B_{nl\lambda} = \left[(2n+1)(2n+2)\frac{(l-\lambda)(l+\lambda)}{(2l-1)(2l+1)}\right]^{1/2}, \tag{36}$$

where $\lambda = |m|$ and $\lambda' = |m'|$. These formulas are obtained from equation (17) of [35] for $t = 0$.

4.   Multicenter nuclear attraction and electron repulsion integrals

In a previous paper [33], by the use of complete orthonormal sets of Ψ^α-ETOs we presented the different analytical expressions for the expansion of one- and two-center electron charge density over STOs in terms of STOs about a new center. Using these expansion formulas the multicenter nuclear attraction and electron repulsion integrals can be expressed in terms of overlap integrals with the same screening parameters.

- Multicenter nuclear attraction integrals:

$$
\begin{aligned}
I_{p_1 p_1'}^{ac,b}(\zeta_1, \zeta_1') &= \int \chi_{p_1}^*(\zeta_1, \mathbf{r}_{a1}) \chi_{p_1'}(\zeta_1', \mathbf{r}_{c1}) \frac{1}{r_{b1}} \, dV_1 \\
&= \lim_{N \to \infty} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W_{p_1 p_1' q}^{\alpha N}(\zeta_1, \zeta_1', z; \mathbf{R}_{ca}, 0) J_q(z, \mathbf{R}_{ab}),
\end{aligned}
\tag{37}
$$

where $p_1 \equiv n_1 l_1 m_1$, $p_1' \equiv n_1' l_1' m_1'$, $q \equiv \mu\nu\sigma$, $z = \zeta_1 + \zeta_1'$ and $J_q(z, \mathbf{R}_{ab})$ is the two-center nuclear attraction integral determined by [42]

$$
J_q(z, \mathbf{R}_{ab}) = 2^\mu \sqrt{\frac{2}{F_\mu(2\mu)z}}
\begin{cases}
\delta_{\nu 0}\delta_{\sigma 0} & \text{for } \mathbf{R}_{ab} = 0, \\[2ex]
\dfrac{F_\mu(\mu+\nu+1)}{\eta_{\nu+1}(2p)} \\[2ex]
\quad \times \left[1 - e^{-2p}\displaystyle\sum_{k=0}^{\mu+\nu}\gamma_k(\mu,\nu)\eta_k(2p)\right] \\[2ex]
\quad \times \dfrac{\sqrt{4\pi}}{2\nu+1}S_{\nu\sigma}^*(\theta,\phi) & \text{for } \mathbf{R}_{ab} \neq 0,
\end{cases}
\tag{38}
$$

where $2p = zR$ and $\eta_k(x) = x^k/k!$.

- Multicenter electron repulsion integrals:

$$I_{p_1 p_1'; p_2 p_2'}^{ac;bd}(\zeta_1, \zeta_1'; \zeta_2, \zeta_2')$$

$$= \int \chi_{p_1}^*(\zeta_1, \mathbf{r}_{a1}) \chi_{p_1'}(\zeta_1', \mathbf{r}_{c1}) \frac{1}{r_{21}} \chi_{p_2}(\zeta_2, \mathbf{r}_{b2}) \chi_{p_2'}^*(\zeta_2', \mathbf{r}_{d2}) \, dV_1 \, dV_2$$

$$= \lim_{N \to \infty} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W_{p_1 p_1' q}^{\alpha N *}(\zeta_1, \zeta_1', z; \mathbf{R}_{ca}, 0)$$

$$\times \lim_{N' \to \infty} \sum_{\mu'=\nu+1}^{N'} W_{p_2 p_2' q'}^{\alpha N'}(\zeta_2, \zeta_2', z'; \mathbf{R}_{db}, \mathbf{R}_{ba}) J_{\mu\nu, \mu'\nu}(z, z'), \qquad (39)$$

where $p_i \equiv n_i l_i m_i$, $p_i' \equiv n_i' l_i' m_i'$ $(i = 1, 2)$, $q' \equiv \mu'\nu'\sigma'$, $z = \zeta_1 + \zeta_1'$ and $z' = \zeta_2 + \zeta_2'$ and $J_{\mu\nu, \mu'\nu}$ are the one-center basic Coulomb integrals defined by [42]

$$J_{\mu\nu, \mu'\nu}(z, z') = \frac{2^{\mu+\mu'+1}}{z'\sqrt{zz'}x^{\nu+1}} \left[\frac{(2\nu + 2)F_{\mu-\nu-1}(\mu + \nu + 1)}{(2\nu + 1)F_{\mu+\nu+1}(2\mu)F_{\mu'-\nu}(2\mu')F_{\mu'-\nu}(\mu' + \nu)} \right]^{1/2}$$

$$\times \left[1 - \sum_{k=0}^{\mu+\nu} \gamma_k(\mu, \nu) F_k(\mu' - \nu + k) \frac{x^k}{(1 + x)^{\mu'-\nu+k+1}} \right], \qquad (40)$$

where $x = z/z'$ and

$$\gamma_k(\mu, \nu) = 1 - \frac{F_{2\nu+1}(k)}{F_{\mu-\nu}(\mu + \nu + 1)}. \qquad (41)$$

The quantities $W^{\alpha N}$ in equations (37) and (39) are the charge density expansion coefficients which are expressed in terms of overlap integrals with the same screening parameters (see [33]).

5.   Discussion

As can be seen from equations (37) and (39) of this article, the charge density expansion coefficients occur in the multicenter nuclear attraction and electron repulsion integrals over STOs. Using Ψ^α-ETOs for these coefficients the formulas in terms of overlap integrals with the same screening parameters have recently been established in [33]. Therefore, equations (29) and (30) for overlap integrals can be used in the calculation of multicenter nuclear attraction and electron repulsion integrals.

In order to calculate the overlap integrals with the same screening parameters, the values of the Gaunt coefficients, the normalized associated Legendre functions and the Gegenbauer coefficients are required. The normalized associated Legendre functions and the Gaunt coefficients were calculated using the method in [34,42], respectively,
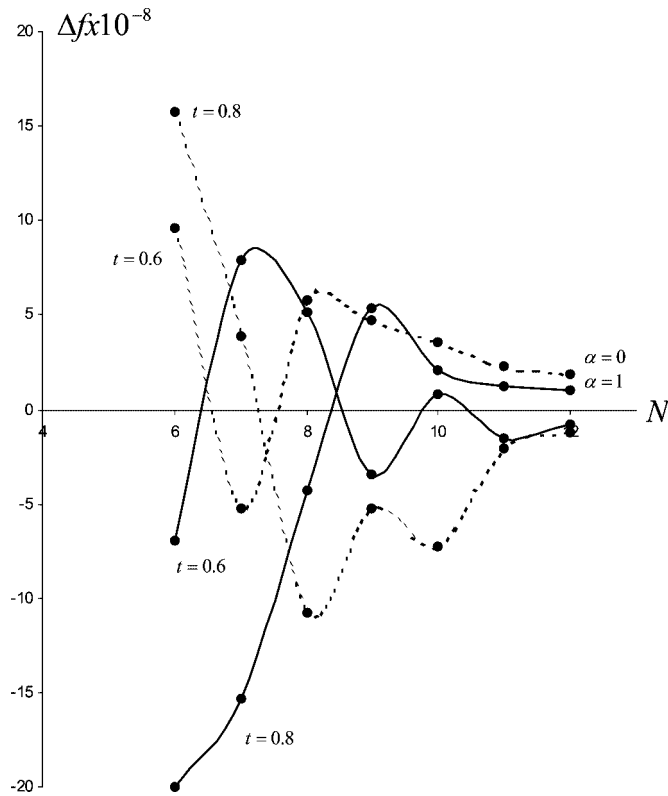
Figure 1. The convergence of the series in equation (37) for the nuclear attraction integral $I_{211,211}$ with different expansion coefficients for translation of STOs (in a.u.); $R_{ab} = 2.4$, $\theta_{ab} = 60°$, $\phi_{ab} = 120°$, $R_{cb} = 0.3$, $\theta_{cb} = 135°$, $\phi_{cb} = 270°$.

while the Gegenbauer coefficients were calculated using equations (13), (21) and (22) of [38].

The accuracy of the overlap integrals given in equations (29) and (30) was checked for various quantum numbers using equation (34). The results for $\alpha = 0, 1, -1$ are given in table 1. It is seen from table 1 that the right-hand side (RHS) and the left-hand side (LHS) of equation (34) are consistent with each other. The comparative values of the overlap integrals with the same screening parameters of STOs, the number of correct decimal figures Δf and CPU time in milliseconds are also tabulated in table 1. The LHS and the RHS of equation (34) are in agreement with each other to at least 19 decimal digits.

The convergence of the series in equations (37) and (39) for $L \leqslant N - 1$ and $M \leqslant N - 1$ was tested, where N, L and M are the upper limits of indices μ, ν and σ, respectively. The results of tests on series accuracy $\Delta f_{NLM} = f_{N\,N-1\,N-1} - f_{N\,N-1\,M}$ for the three-center integral $I_{211,211}$ are shown in figure 1. Here the quantities $f = f_{N\,N-1\,N-1}$ are the values of integrals for $L = N - 1$ and $M = N - 1$. As can be seen from figure 1, the convergence of the series with respect to σ is rapid. Therefore, it is

Table 1

The values of overlap integrals obtained from equation (29) for $\alpha = 1$, $\alpha = 0$ and $\alpha = -1$.

n	l	m	n'	l'	m'	p	θ	ϕ	For $\alpha = 1$	Δf	For $\alpha = 0$	Δf	For $\alpha = -1$	Δf	CPU (ms)
3	2	2	3	2	2	18	0	0	2.6089825587249E−5	20	2.6089825587249E−5	20	2.6089825587249E−5	20	–
5	4	3	4	3	3	100	0	0	1.44519305167894E−35	48	1.44519305167894E−35	48	1.44519305167867E−35	46	–
7	6	6	8	7	6	55	0	0	−1.41040741874206E−15	28	−1.41040741874206E−15	28	−1.41040741874206E−15	28	0.3
12	10	9	13	11	9	25	0	0	5.928674286808893E−3	20	5.928674286808893E−3	19	5.928674286808893E−3	19	0.7
14	12	10	13	11	10	15	0	0	−2.58408151011941E−1	22	−2.58408151011941E−1	19	−2.58408151011941E−1	18	2.5
16	14	13	15	14	13	0.15	0	0	9.83248855471735E−1	21	9.83248855471735E−1	20	9.83248855471735E−1	18	5.3
30	14	13	25	14	13	0.01	0	0	7.98096184616459E−1	19	7.98096184616459E−1	19	7.98096184616459E−1	17	8.1
60	10	8	60	10	8	1.2	0	0	−3.87575725482831E−6	20	−3.87575725482842E−6	18	−3.87575725482653E−6	16	6.4
26	12	10	16	12	10	40	0	0	2.32953664607847E−3	19	2.32953664607847E−3	17	2.32953664607847E−3	17	2.17
2	1	1	2	1	1	25	$\pi/6$	$\pi/8$	−6.85069172874667E−8	22	−6.85069172874667E−8	22	−6.85069172874667E−8	22	–
4	3	2	4	2	2	150	$\pi/3$	$\pi/4$	−1.91854492882121E−54	70	−1.91854492882121E−54	66	−1.91854492877643E−54	60	–
5	4	2	5	4	2	5	$\pi/5$	$2\pi/3$	−1.44686204869417E−1	21	−1.44686204869417E−1	20	−1.44686204869417E−1	19	–
10	9	8	12	9	8	12	π	$3\pi/5$	−2.63733203794235E−1	19	−2.63733203794235E−1	18	−2.63733203794235E−1	16	1.34
19	12	11	18	12	8	30	$\pi/7$	$4\pi/5$	−4.82993344792702E−3	19	−4.82993344792702E−3	17	−4.82993344792702E−3	16	5.3
25	20	18	25	20	18	20	$2\pi/7$	π	1.60648815611516E−2	20	1.60648815611516E−2	18	1.60648815611388E−2	17	6.1
80	20	8	25	20	8	20	$2\pi/7$	π	−1.18040862548839E−6	22	−1.18040862548855E−6	18	−1.18040862548719E−6	16	3.7
35	25	24	35	25	24	0.2	$3\pi/7$	$6\pi/5$	9.95321109892458E−1	18	9.95321109892458E−1	17	9.95321109892466E−1	16	8.3

Table 2
Comparison of methods of computing two- and three-center nuclear attraction integrals (equation (37)) with different expansion coefficients for translation of STOs (in a.u.); $N = 15$, $\nu = 14$, $\sigma = 5$, $\Delta f = f(c \to a) - f(a \to c)$.

n	l	m	ζ	n'	l'	m'	ζ'	R_{ac}	θ_{ac}	ϕ_{ac}	R_{ab}	θ_{ab}	ϕ_{ab}	For $\alpha = 0$		For $\alpha = -1$		
														$c \to a$	Δf	$a \to c$	Δf	CPU (ms)
3	2	2	11.6	3	2	2	6.7	0	0	0	6.7	$\pi/8$	$2\pi/7$	1.14942754737854E−1	–	1.14942754737854E−1	–	–
3	2	2	9.1	4	3	3	5.6	0	0	0	7	$\pi/4$	$3\pi/7$	−4.69050318233664E−4	–	−4.69050318233664E−4	–	–
4	3	2	4.9	4	3	2	8.5	0	0	0	2.3	0	0	3.09548435943587E−1	–	3.09548435943587E−1	–	0.4
6	5	4	8.4	4	3	3	1.8	0	0	0	4.2	$5\pi/8$	$5\pi/7$	1.69945040558276E−1	–	1.69945040558276E−1	–	0.8
6	5	4	5.8	6	5	4	10.8	0	0	0	0.1	$3\pi/4$	$6\pi/7$	7.44825814826279E−1	–	7.44825814826279E−1	–	1.4
10	8	7	6.5	10	8	6	2.3	0	0	0	1.2	$3\pi/4$	π	−1.71989089125151E−3	–	−1.71989089125146E−3	–	8.3
15	14	13	3.6	15	13	13	4.2	0	0	0	4.3	0	0	1.58285587294791E−1	–	1.58285587294791E−1	–	10.4
35	14	10	5.3	25	10	10	2.4	0	0	0	7.4	0	0	5.52182976263269E−5	–	5.52182976263269E−5	–	16.7
5	4	4	7.5	5	4	3	4.2	7.4	$\pi/3$	$2\pi/9$	0	0	0	−3.28819545225970E−9	–	−3.28819545225970E−9	–	–
8	6	6	17.5	7	6	5	12.4	1.8	$2\pi/3$	$\pi/3$	0	0	0	1.14100479768397E−3	–	1.14100479768397E−3	–	2.2
13	10	10	21.5	13	10	10	10.4	0.3	π	$4\pi/9$	0	0	0	9.10734555540533E−22	–	9.10734555540533E−22	–	4.31
20	15	14	7.2	23	11	11	3.1	0.9	$3\pi/4$	$5\pi/9$	0	0	0	−1.16829459508 54E−8	–	−1.16829459508 54E−8	–	10.3
12	11	11	8.7	12	11	11	4.2	7.1	0	0	0	0	0	1.36774085017597E−25	–	1.36774085017597E−25	–	2.4
20	12	8	4.8	20	12	8	6.4	2.7	0	0	0	0	0	−6.17920462974650E−16	–	−6.17920462974650E−16	–	8.8
40	12	10	3.4	30	12	10	1.6	4.2	0	0	0	0	0	−1.64017094722951E−17	–	−1.64017094722951E−17	–	15.6
8	7	7	3.9	8	7	7	2.5	1.4	0	0	0	0	0	1.45390300835789E−1	–	1.45390300835789E−1	–	–
2	1	1	1.1	1	0	0	0.4	3.5	$2\pi/3$	π	1.5	$2\pi/5$	$\pi/2$	−8.50197388994751E−2	12	−8.50197388994577E−2	10	2.5
3	2	1	10.5	3	1	1	7.3	5.4	$\pi/6$	$3\pi/4$	3.7	$4\pi/5$	$\pi/2$	5.15035443599671E−11	15	5.15035441049 6275E−11	14	22.1
2	1	1	5.5	2	1	1	3.0	8.1	$\pi/3$	$\pi/4$	6.1	$3\pi/5$	$3\pi/2$	1.81664800623076E−8	13	1.81664802742 6477E−9	12	36.8
3	2	2	7.6	3	2	2	3.4	1.5	π	$4\pi/5$	0.3	$\pi/5$	π	4.88592699084623E−2	10	4.88592678936050E−2	10	67.4

Table 3

The values of multicenter electron repulsion integrals (equation (39)) in molecular coordinate system in a.u. for $N = N' = 12$, $\nu = 11$, $\sigma = 5$, $\theta_{ca} = 120°$, $\phi_{ca} = 180°$, $\theta_{db} = 60°$, $\theta_{db} = 135°$, $\phi_{db} = 60°$, $\theta_{ba} = 30°$, $\phi_{ba} = 45°$, $\Delta f = f(c \to a, d \to b, b \to a) - f(c \to a, b \to d, d \to a)$.

n_1	l_1	m_1	ζ_1	n_1'	l_1'	m_1'	ζ_1'	n_2	l_2	m_2	ζ_2	n_2'	l_2'	m_2'	ζ_2'	R_{ca}	R_{db}	R_{ba}	For $\alpha=1$ $c \to a, d \to b, b \to a$	Δf	For $\alpha=0$ $c \to a, d \to b, b \to a$	Δf	CPU (ms)
3	2	2	7.6	3	2	2	5.3	3	2	2	7.6	5	4	2	2.55	0	0	0	-3.20774914908047E-3	–	–	–	–
6	4	4	17.6	6	5	4	15.3	5	3	3	11.8	5	3	3	6.0	0	0	0	8.83439539045330E-2	–	–	–	–
6	5	5	5.5	5	6	5	5.5	6	5	5	5.5	6	5	5	5.5	0	0	0	8.53631451458682E-1	–	–	–	–
7	6	5	9.1	6	7	6	8.8	6	5	5	9.1	6	5	5	8.8	0	0	0	1.26892403759967E-1	–	–	–	–
1	0	0	1.8	2	0	0	1.8	2	0	0	3.5	2	0	0	2.5	0	5.6	0	1.34794435119887E-4	11	1.34794435117724E-4	10	25.7
2	1	0	7.4	2	1	0	5.1	2	1	0	8.3	2	1	0	4.2	0	10.5	0	-1.25613345978908E-7	11	-1.25613345976171E-7	11	38.2
2	1	1	12.7	2	1	1	10.5	2	1	1	9.8	2	1	1	6.4	0	0.8	0	-9.94672463995942E-2	10	-9.94672463996853E-2	9	46.3
3	2	2	5.1	3	2	2	9.5	3	2	1	2.9	3	2	1	1.6	0	3.4	8.3	7.40047199995075E-3	10	7.40047199995203E-3	10	79.5
2	1	1	3.5	2	0	0	7.9	2	0	0	11.2	2	0	0	9.1	0	0	12.8	7.53745201386896E-2	11	7.53745201386923E-2	10	20.9
2	1	1	10.3	2	1	1	6.7	2	1	1	9.2	2	1	1	4.8	0	0	0.83	5.36998171441876E-2	11	5.36998171443621E-2	10	28.4
3	2	1	1.5	2	1	1	1.5	2	1	1	1.5	2	1	1	1.5	0	0	6	4.42400487665858E-1	10	4.42400487652409E-1	9	56.3
3	2	2	8.3	3	2	2	4.7	2	2	2	9.1	2	2	2	9.1	1.5	1.5	0	1.25749561609601E-1	10	1.25749561607448E-1	10	100.5
1	0	0	5.5	1	0	0	3.4	1	0	0	5.5	1	0	0	3.4	7.3	7.3	0	2.10871303537709E-3	11	2.10871303535124E-3	11	72.1
2	1	0	10.5	2	1	0	8.3	2	1	0	10.5	2	1	0	8.3	2.3	1.7	0	5.68506283070020E-18	25	5.68506267210036E-18	22	75.7
2	1	0	10.5	2	1	0	8.3	2	1	0	10.5	2	1	0	2.15	3.2	0.1	0	1.00047716918933E-6	11	1.00047716753453E-7	9	88.3
2	1	1	8.1	2	1	1	4.8	2	1	1	8.1	2	1	1	7.2	0	3.0	2.8	-9.01319409848109E-4	10	-9.01319424226110E-4	8	68.3
1	0	0	6.8	2	1	0	6.8	2	1	0	2.4	2	1	0	7.2	0	1.3	0.2	1.47269919783122E-5	9	1.47269934557704E-5	8	75.7
2	1	1	4.6	2	1	0	4.6	2	1	0	5.2	2	1	0	7.2	0	0.8	0.2	-3.83784737129254E-2	9	-3.83784737009938E-2	9	113.4
2	1	1	7.4	2	1	1	7.4	3	1	1	3.5	3	1	1	1.7	3.2	0.8	0.2	3.17170225981866E-1	9	3.17170244914704E-1	7	194.6
1	0	0	7.4	2	1	0	3.5	1	0	0	1.7	1	0	0	1.7	4.3	2.3	0.2	-1.59434193890076E-4	10	-1.59434190383338E-4	9	79.4
2	1	0	8.7	2	1	1	6.3	2	1	0	7.1	2	1	0	4.1	2.3	4.3	0.2	4.67267546648838E-7	9	4.67267437863893E-7	9	312.4
2	1	1	5.6	2	1	1	8.6	2	1	1	9.7	2	1	1	4.4	2.4	1.2	1.8	3.69799231624762E-8	12	3.69799436922550E-8	10	576.2

sufficient to include only a few terms in the summation over indices σ. The full and broken lines in figure 1 represent the results of calculations using equation (37) obtained for $\alpha = 1$ and $\alpha = 0$, respectively.

The results of calculations for two-, three-center nuclear attraction and one-, two-, three-, four-center electron repulsion integrals on a Pentium III 800 MHz computer (using Turbo Pascal 7.0 language) are represented in tables 2 and 3, respectively. The comparative values, the number of correct decimal figures Δf and the CPU time are given in these tables. As can be seen from the tables, in all the calculations, the CPU time and the accuracy of computer results for the $(c \rightarrow a,\ d \rightarrow b,\ b \rightarrow a)$ and $(c \rightarrow a,\ b \rightarrow d,\ d \rightarrow a)$ translations of STOs in equations (37) and (39) are satisfactory. It should be noted that the algorithm presented above can be used to calculate any two-, three-center nuclear attraction and one-, two-, thee-, and four-center electron repulsion integrals for the arbitrary values of screening constants, quantum numbers and location of STOs.

References

[1] T. Kato, Commun. Pure Appl. Math. 10 (1957) 151.
[2] S. Agmon, *Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations: Bounds on Eigenfunctions of N-Body Schrödinger Operators* (Princeton University Press, Princeton, NJ, 1982).
[3] A.S. Coolidge, Phys. Rev. 42 (1932) 189.
[4] R. Landshoff, Z. Phys. 102 (1936) 201.
[5] P.O. Löwdin, Ark. Mat. Fys. Astron. A 35 (1947) 9.
[6] M.P. Barnett and C.A. Coulson, Philos. Trans. Roy. Soc. London Ser. A 243 (1951) 221.
[7] F.E. Harris and H.H. Michels, J. Chem. Phys. 43 (1965) S165; 45 (1966) 116.
[8] R.R. Sharma, Phys. Rev. A 13 (1976) 517.
[9] H.J. Silverstone, J. Chem. Phys. 47 (1967) 537.
[10] H.J. Silverstone and R.K. Moats, J. Chem. Phys. 16 (1977) 1731.
[11] K.G. Kay and H.J. Silverstone, J. Chem. Phys. 51 (1969) 4287.
[12] E.O. Steinborn and E. Filter, Theor. Chim. Acta. 38 (1975) 247.
[13] E. Filter and E.O. Steinborn, J. Math. Phys. 21 (1980) 2725.
[14] E.J. Weniger and E.O. Steinborn, J. Chem. Phys. 78 (1983) 6221.
[15] H.P. Trivedi and E.O. Steinborn, Phys. Rev. A 27 (1983) 670.
[16] H.W. Jones, Int. J. Quant. Chem. 61 (1997) 881.
[17] A. Bouferguene and H.W. Jones, J. Chem. Phys. 109 (1998) 5718.
[18] H. Safouhi and P.E. Hoggan, J. Phys. A: Math. Gen. 31 (1998) 8941.
[19] H. Safouhi, J. Phys. A: Math. Gen. 34 (2001) 881; 34 (2001) 2801.
[20] H. Safouhi, J. Comput. Phys. 165 (2000) 473.
[21] H.L. Kennedy and Y. Zhao, Int. J. Quant. Chem. 71 (1999) 1.
[22] V. Magnasco and A. Rapallo, Int. J. Quant. Chem. 79 (2000) 91.
[23] M.P. Barnett, Int. J. Quant. Chem. 76 (2000) 464.
[24] J.F. Rico, J.J. Fernandez, I. Ema, R. Lopez and G. Ramirez, Int. J. Quant. Chem. 81 (2001) 16.
[25] I.I. Guseinov, Int. J. Quant. Chem. 81 (2001) 126.
[26] V.A. Fock, Z. Phys. 98 (1935) 145.
[27] V.A. Fock, Kgl. Norske Vidensk. Forh. 31 (1958) 138.
[28] T. Shibuya and C.E. Wulfman, Proc. Roy. Soc. A 286 (1965) 376.

[29] B.R. Judd, *Angular Momentum Theory for Diatomic Molecules* (Acadmic Press, New York, 1975).
[30] J. Avery, *Hyperspherical Harmonics and Generalized Sturmians* (Kluwer Academic, Dordrecht, Netherlands, 2000).
[31] J. Avery and R. Shim, Int. J. Quant. Chem. 83 (2001) 1.
[32] I.I. Guseinov, Int. J. Quant. Chem. 90 (2002) 114.
[33] I.I. Guseinov, Int. J. Quant. Chem. 90 (2002) 980.
[34] I.I. Guseinov, A. Özmen, Ü. Atav and H. Yüksel, Int. J. Quant. Chem. 67 (1998) 199.
[35] I.I. Guseinov and B.A. Mamedov, J. Mol. Struct. (Theochem) 465 (1999) 1.
[36] I.S. Gradshteyn and I.M. Ryzhik, *Tables of Integrals, Sums, Series and Products*, 4th ed. (Academic Press, New York, 1980).
[37] E.U. Condon and G.H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1970).
[38] I.I. Guseinov, A.Ilık and S.I. Allahverdiyev, Int. J. Quant. Chem. 60 (1996) 637.
[39] F.P. Prosser and C.H. Blanchard, J. Chem. Phys. 36 (1962) 1112.
[40] H.J. Silverstone, J. Chem. Phys. 45 (1966) 4337.
[41] I.I. Guseinov, J. Phys. B 3 (1970) 1399.
[42] I.I. Guseinov, J. Mol. Struct. (Theochem) 417 (1997) 117.