EVALUATION OF TWO-CENTER OVERLAP INTEGRALS OVER SLATER-TYPE ORBITALS USING FOURIER TRANSFORM CONVOLUTION THEOREM

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Analytical expressions are presented for two-center overlap integrals over Slater-type orbitals using Fourier transform convolution theorem. The efficiency of calculation of these expressions is compared with those of other methods and good rate of convergence and great numerical stability is obtained for wide range of quantum numbers, orbital exponents and internuclear distances.

Keywords: Overlap integrals; Slater-type orbitals; Fourier transform convolution theorem; STO; LCAO; Quantum chemistry.

Slater-type orbitals (STOs) are able to satisfy the cusp condition[1] at the nuclei, and for large distances they behave as exact eigenstates of atomic and molecular Hamiltonians do[2]. Therefore, it is generally accepted that the use of STOs in molecular electronic structure calculations would be highly desirable. On the other hand, the notorious problems with the evaluation of multicenter molecular integrals which occur in the linear combination of atomic orbitals (LCAO) ansatz so far have prevented a systematic application of STOs. However, the search for manageable analytical expressions of multicenter molecular integrals over STOs has been continued. Among these multicenter integrals, two-center overlap integrals constitute the basic building blocks of many more complicated multicenter molecular integrals occurring in quantum mechanical calculation of the electronic structure of molecules. So, two-center overlap integrals over STOs have already been investigated by numerous authors with different algorithms (see refs[3–6] and references therein).

As is well known, the use of the Fourier transform convolution theorem[7] is one of the most important methods for the evaluation of the complicated multicenter molecular integrals. There is an extensive literature on the use of Fourier transform convolution theorem in the evaluation of

multicenter molecular integrals[8]. A large part of the literature are on Fourier transform of Bessel-type orbitals (BTOs)[8h–8m]. Although the Fourier transform of BTOs have a simple form, inefficiency arises in the evaluation of multicenter molecular integrals especially in the case of higher quantum numbers, nearly equal orbital exponents and high or low internuclear distances[8i]. In recent years, Geller[8a,8b], Silverstone[8c,8d], Steinborn[8h–8k] and some other workers[8] have used the Fourier transform convolution theorem in the evaluation of multicenter molecular integrals. Because of the form of STOs, to the best of the author's knowledge, there is no satisfactory computational method for the use of Fourier transform convolution theorem in the evaluation of multicenter molecular integrals over STOs except for the old works of Geller[8a,8b] and Silverstone[8c,8d] and recent works of Guseinov *et al.*[5d,8n] and Öztekin *et al.*[8o]. It can be easily seen that the formulae presented in works of Geller and Silverstone are complex in structure and therefore it is not easy to use them in molecular calculations. The algorithm presented in works of Guseinov *et al.*[5d,8n] is limited to only two-center overlap integrals over STOs with equal orbital exponents and it can be easily seen that their method fails even for smaller quantum numbers as well. More recently, Öztekin *et al.*[8o] have given some tables for two-center overlap integrals over STOs but we have noticed that some inconsistencies arise in case of very high quantum numbers. The purpose of this work is to present an accurate algorithm for the evaluation of two-center overlap integrals over STOs with arbitrary orbital exponents using the Fourier transform convolution theorem.

Atomic units (a.u.) are used throughout this work.

CALCULATIONS

Definition and Fourier Transform of a STO

Two-center overlap integrals examined in the present work have the following form:

$$S_{nlm,n'l'm'}(\zeta,\zeta';\boldsymbol{R}) = \int \chi^{*}_{nlm}(\zeta,\boldsymbol{r})\chi_{n'l'm'}(\zeta',\boldsymbol{r}-\boldsymbol{R})\,\mathrm{d}^3 r\,. \qquad (1)$$

Here $\chi_{nlm}(\zeta,\boldsymbol{r})$ are normalized complex or real STOs defined by

$$\chi_{nlm}(\zeta,\boldsymbol{r}) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}}\, r^{n-1}\, \mathrm{e}^{-\zeta r}\, S_{lm}(\theta,\varphi)\,, \qquad (2)$$

in which $S_{lm}(\theta,\varphi)$ is complex or real spherical harmonic[9] and ζ is orbital exponent.

By the use of Fourier transform convolution theorem, Eq. (*1*) can be written as

$$S_{nlm,n'l'm'}(\zeta,\zeta';\boldsymbol{R}) = \int \mathrm{e}^{-\mathrm{i}\boldsymbol{kR}}\, U^{*}_{nlm}(\zeta,\boldsymbol{k})\, U_{n'l'm'}(\zeta',\boldsymbol{k})\, \mathrm{d}^3\boldsymbol{k}\,, \tag{3}$$

where $\chi_{nlm}(\zeta,\boldsymbol{r})$ and $U_{nlm}(\zeta,\boldsymbol{k})$ are a pair of mutual Fourier transforms given by

$$\chi_{nlm}(\zeta,\boldsymbol{r}) = \frac{1}{(2\pi)^{3/2}} \int \mathrm{e}^{-\mathrm{i}\boldsymbol{kr}}\, U_{nlm}(\zeta,\boldsymbol{k})\, \mathrm{d}^3\boldsymbol{k} \tag{4}$$

and

$$U_{nlm}(\zeta,\boldsymbol{k}) = \frac{1}{(2\pi)^{3/2}} \int \mathrm{e}^{-\mathrm{i}\boldsymbol{kr}}\, \chi_{nlm}(\zeta,\boldsymbol{r})\, \mathrm{d}^3\boldsymbol{r}\,. \tag{5}$$

To evaluate $U_{nlm}(\zeta,\boldsymbol{k})$, we need the Rayleigh expansion of a plane wave in terms of spherical Bessel functions and spherical harmonics[10]:

$$\mathrm{e}^{\pm\mathrm{i}\boldsymbol{kr}} = 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (\pm\mathrm{i})^{L}\, j_L(kr)\, S_{LM}\left(\frac{\boldsymbol{r}}{r}\right) S_{LM}\left(\frac{\boldsymbol{k}}{k}\right), \tag{6}$$

where $j_{\mathrm{L}}(kr)$ is the spherical Bessel function.

Substituting Eq. (*6*) into Eq. (*5*) and solving the radial integral, the following expression is obtained for the Fourier transform of a STO [8n]:

$$U_{nlm}(\zeta,\boldsymbol{k}) = Q_{nl}(\zeta,k)\, S_{lm}\left(\frac{\boldsymbol{k}}{k}\right) \tag{7}$$

with

$$Q_{nl}(\zeta,k) = \frac{2^{n+l+1}\, l!\,(n-l)!\,(2k)^{2l+1/2}}{\sqrt{\pi(2n)!}\;\zeta^{3/2}}\, x^{n+2}\,(1-x^2)^{1/2}\, C^{l+1}_{n-1}(x) \tag{8}$$

In Eq. (*8*), $x = \zeta / \sqrt{\zeta^2 + k^2}$ and $C^{\alpha}_{n}(x)$ is the Gegenbauer polynomial defined by

$$C_n^{\alpha}(x) = \sum_{s=0}^{E\left(\frac{n}{2}\right)} (-1)^s a_s(\alpha,n)(2x)^{n-2s} \ , \tag{9}$$

in which

$$E\left(\frac{n}{2}\right) = \frac{n}{2} - \frac{1}{4}\left(1-(-1)^n\right), \tag{10}$$

$$a_s(\alpha,n) = F_{\alpha-1}(\alpha-1+n-s)\, F_s(n-s)\,. \tag{11}$$

In Eq. (*11*), $F_m(n) = n!/m!(n-m)!$ are usual binomial coefficients.

Two-Center Overlap Integrals Over STOs

With the help of formulas given in previous part, we obtain for two-center overlap integrals over complex and real STOs the following relations:

For two-center overlap integrals over complex STOs

$$S_{nlm,n'l'm'}(\zeta,\zeta';\boldsymbol{R}) = \sqrt{2\pi} \sum_{L=|l-l'|}^{l+l'}{}^{(2)} (-1)^{(L-|l-l'|)/2} \sqrt{2L+1}\; C^L(lm,l'm') \times$$

$$\times Q^L_{nl,n'l'}(\zeta,\zeta';R)\, S_{L,m-m'}(\theta,\varphi)\,. \tag{12}$$

For two-center overlap integrals over real STOs

$$S_{nlm,n'l'm'}(\zeta,\zeta';\boldsymbol{R}) = \sqrt{2\pi} \sum_{L=|l-l'|}^{l+l'}{}^{(2)} \sum_{M=-L}^{L} (-1)^{(L-|l-l'|)/2} \sqrt{2L+1}\; C^{L|M|}(lm,l'm') \times$$

$$\times A^M_{mm'} Q^L_{nl,n'l'}(\zeta,\zeta';R)\, S_{LM}(\theta,\varphi)\,. \tag{13}$$

In Eqs (*12*) and (*13*) the symbol $\sum^{(2)}$ indicates that the summation is to be performed in steps of two, and the summation limits of the L summation are direct consequences of the selection rules satisfied by the Gaunt coefficients $C^L(lm,l'm')$ (ref.[11]).

The quantities $C^{L|M|}(lm,l'm')$ and $A^{M}_{mm'}$ in Eq. (*13*) are defined by

$$C^{L|M|}(lm,l'm') = \begin{cases} C^{L}(lm,l'm') & \text{for } M = m - m' \\ C^{L}(lm,l' - m') & \text{for } M = m + m' \end{cases}, \tag{14}$$

$$A^{M}_{mm'} = \frac{1}{\sqrt{2}}\left(2 - |\eta^{m-m'}_{mm'}|\right)^{1/2} \delta_{M,\varepsilon|m-m'|} + \frac{1}{\sqrt{2}} \eta^{m-m'}_{mm'} \delta_{M,\varepsilon|m+m'|} . \tag{15}$$

In Eq. (*15*), the symbol ε may have the value ±1 and is determined by the product of the signs of m and m'. The symbols $\eta^{m\pm m'}_{mm'}$ may have the values ±1 and 0: if among the indices m, m' and $m \pm m'$ there occurs a value equal to zero, then $\eta^{m\pm m'}_{mm'}$ is also zero; if all the indices differ from zero, $\eta^{m\pm m'}_{mm'} = \pm 1$ and the sign is determined by the product of the sign of indices m, m' and $m \pm m'$. Thus the coefficients $A^{M}_{mm'}$ differ from zero only with the values $|M| = |m - m'|$, $|m + m'|$ (ref.[5a]).

The auxiliary function $Q^{L}_{nl,n'l'}(\zeta,\zeta';R)$ in Eqs (*12*) and (*13*) is defined by

$$Q^{L}_{nl,n'l'}(\zeta,\zeta';R) = \int_0^\infty \mathrm{d}k\, k^2 Q_{nl}(\zeta,k)\, Q_{n'l'}(\zeta',k)\, j_L(kR) . \tag{16}$$

Using Eqs (*8*) and (*9*) in Eq. (*16*), we get the following expression for the auxiliary function $Q^{L}_{nl,n'l'}$

$$Q^{L}_{nl,n'l'}(\zeta,\zeta';R) = N_{nl,n'l'}(\zeta,\zeta') \sum_{s=0}^{E\left(\frac{n-l}{2}\right)} \sum_{s'=0}^{E\left(\frac{n'-l'}{2}\right)} (-1)^{s+s'} \frac{a_s(l+1,n-l)\, a_s(l'+1,n'-l')}{\zeta^{2s}\, \zeta'^{2s'}} \times$$

$$\times\, G^{2l+2l'+5,L}_{(2n-l-2s+1)/2,(2n'-l'-2s'+1)/2}(\zeta,\zeta';R) , \tag{17}$$

where

$$N_{nl,n'l'}(\zeta,\zeta') = \frac{2^{2n+2n'+2l+2l'+3}\, n!\, n'!\, \zeta^{2n-l+1/2}\, \zeta'^{2n'-l'+1/2}}{\pi F_l(n) F'_l(n') \sqrt{(2n)!}\sqrt{(2n')!}} \tag{18}$$

and the function $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$ is defined by

$$G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R) = \int_0^\infty \mathrm{d}k\, \frac{k^\varepsilon}{(\zeta^2 + k^2)^{M+1} (\zeta'^2 + k^2)^{N+1}}\, j_L(kR) . \tag{19}$$

As it can be seen from Eq. (*17*), the auxiliary function $Q^{L}_{nl,n'l'}(\zeta,\zeta';R)$ appearing in Eqs (*12*) and (*13*) is through the function $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$. Therefore, the efficiency of overlap integrals depends on the accurate calculation of function $G^{\varepsilon,L}_{M,N}$.

Calculation of Function $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$

In this section, we will focus our attention on the efficient calculation of functions $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$. Therefore, we analyze the function $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$ in three possible cases.

1. Equal Orbital Exponents Case

For equal orbital exponents ($\zeta = \zeta'$), we express the function $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$ by

$$G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R) = g^{L}_{\varepsilon,M+N+2}(\zeta,R)\,. \tag{20}$$

2. Nearly Equal Orbital Exponents Case

For nearly equal orbital exponents ($\zeta \approx \zeta'$), we use the following Taylor series expansion in Eq. (*19*)

$$(\zeta'^2 + k^2)^{-N-1} = \sum_{q=0}^{\infty} f_q(N+q)(\zeta^2 - \zeta'^2)^q\,(\zeta^2 + k^2)^{-N-q-1} \tag{21}$$

and the relation below is obtained for $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$:

$$G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R) = \sum_{q=0}^{\infty} f_q(N+q)(\zeta^2 - \zeta'^2)^q\; g^{L}_{\varepsilon,M+N+2}(\zeta,R)\,. \tag{22}$$

3. Different Orbital Exponents Case

For the calculation of $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$, in which orbital exponents differ substantially, we use the following decomposition of denominator in Eq. (*19*)

$$(\zeta^2 + k^2)^{-M-1}(\zeta'^2 + k^2)^{-N-1} = \sum_{q=0}^{\infty} f_N(N+M-q)(\zeta^2 - \zeta'^2)^{q-N-M-1}\,(\zeta'^2 + k^2)^{-q-1} +$$

$$+\sum_{q=0}^{\infty} f_M(N+M-q)(\zeta'^2-\zeta^2)^{q-N-M-1}(\zeta'^2+k^2)^{-q-1}\,, \qquad (23)$$

and the relation below is obtained for $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$:

$$G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R) = g^{\varepsilon,L}_{M,N}(\zeta,\zeta';R) + g^{\varepsilon,L}_{N,M}(\zeta',\zeta;R)\,, \qquad (24)$$

in which

$$g^{\varepsilon,L}_{M,N}(\zeta,\zeta';R) = \sum_{q=0}^{\infty} f_M(N+M+q)(\zeta^2-\zeta'^2)^{q-N-M-1} g^{L}_{\varepsilon,q+1}(\zeta,R)\,. \qquad (25)$$

In Eqs (*21*)–(*25*) the function $f_m(N)$ is given by[5f]:

$$f_m(N) = \frac{\Gamma(N+1)}{\Gamma(m+1)\Gamma(N-m+1)}\,. \qquad (26)$$

As it can be seen from Eqs (*20*)–(*25*), the calculation of functions $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$ is reduced to basic integral $g^{L}_{M,N}(\zeta,R)$ defined by

$$g^{L}_{M,N}(\zeta) = \int_0^{\infty} \mathrm{d}k\, \frac{k^M}{(\zeta^2+k^2)^N}\, j_L(kR)\,. \qquad (27)$$

For the calculation of basic integral $g^{L}_{M,N}(\zeta,R)$, two different alternative formulas have been presented in Appendix, using two different formulations involving infinite series and the hypergeometric function ${}_2F_1$.

COMPUTATIONAL RESULTS AND DISCUSSION

In this study, a new method is developed for the evaluation of two-center overlap integrals over complex and real STOs using the Fourier transform convolution theorem. The expressions obtained here for two-center overlap integrals are in terms of Gaunt coefficients, spherical harmonics and auxiliary function $Q^{L}_{nl,n'l'}(\zeta,\zeta';R)$.

On the basis of Eq. (*13*), we have constructed a computer program in Turbo Pascal 7.0 programming language (on a Pentium 233 MHz computer)

for the evaluation of two-center overlap integrals over real STOs. In the calculations, the auxiliary function $Q^{L}_{nl,n'l'}$ and binomial coefficients $F_m(n)$ are evaluated at compile time for reducing calculation times. The binomial coefficients $F_m(n)$ are stored in a one-dimensional array induced by

$$f^{m,n} = \frac{n(n+1)}{2} + m + 1 . \qquad (28)$$

The efficiency of the formulas for two-center overlap integrals given in this work depends critically on the rate of convergence of the efficient calculation of function $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$ appearing in the calculation of auxiliary function $Q^{L}_{nl,n'l'}(\zeta,\zeta';R)$. Therefore, the function $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$ is analyzed in three possible cases. For the different orbital exponents case, the expression for $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$ involves one infinite sum. For nearly equal orbital exponents, the function $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$ converges as in the case of different orbital exponents. On the other hand, for equal orbital exponents, the infinite sum disappears and we express $G^{\varepsilon,L}_{M,N}$ with an analytical relation. The convergence limit for $G^{\varepsilon,L}_{M,N}$ is determined for 18-decimal-digit accuracy, with typically at most 20–40 terms in infinite sums in the whole calculations.

Some comparative values of two-center overlap integrals over STOs have been listed in Table I for wide range of quantum numbers, orbital exponents and internuclear distances. As it can be seen from Table I, the accuracy is in all cases 13 significant figures at least with refs[3–6], but some discrepancies appear with the results in ref.[8o] for principal quantum numbers n, $n' \geq 55$.

In order to test the accuracy of the presented method, we have constructed a computer program in Maple 6 symbolic programming language. Computer results obtained from programs constructed in Maple 6 have been added to Table I. Comparing these values with the data in literature it can be seen that the presented method gives more accurate results than older literature[3–6,8o]. We think that the discrepancies with results in ref.[8o] may result from the error in the starting point of the recurrence relations given in ref.[8o], which will increase with increasing quantum numbers. To strengthen our claim, we also compare the computer results of this study with the formula obtained by the ellipsoidal coordinate method[5f], and at least five-decimal-digit accuracy is obtained up to n, $n' \leq 83$. Therefore, we think that the stability region of recurrence schemes in ref.[8o] should be well analyzed.

Another important of the presented algorithm is the speed. For testing the speed of the presented algorithm, we compared our CPU times with the available literature for same set of parameters. We found that our algorithm

TABLE I
The comparative values of two-center overlap integrals over STOs for various quantum sets

n	*l*	*m*	*n′*	*l′*	*m′*	ζ	ζ′	*R*	θ	φ	Eq. (*13*)	Literature
2	1	0	2	1	0	7.5	2.5	5.0	60	120	–2.01912763169782E-05	–2.01912763028473E-05[5a]
3	2	2	3	2	2	5.8	4.5	8.7	0	0	7.93431005494730E-15	7.934310054948E-15[6]
3	2	1	3	2	1	8.0	2.0	5.0	0	0	–4.42287766988260880679541502 43E-04[a]	–4.42287766988261E-04[8o]
4	3	3	4	3	2	3.0	2.0	20	30	60	3.75545611854747E-02	–
5	4	2	5	4	0	8.5	1.5	30	45	210	–2.27511175118464E-02	–2.27511175896203E-17[5a]
7	3	2	4	3	2	8.5	1.5	30	0	0	1.76861050692264859080888433 1E-18[a]	1.76861050697887E-18[8o]
8	7	–6	7	5	5	0.5	0.3	12	150	240	–4.44987258245886E-02	–
10	0	0	10	2	0	2.5	3.0	3.0	0	0	–1.67748511444053E-01	–1.677485114E-01[4]
10	7	1	8	1	1	5.0	5.0	5.0	0	0	1.52138456890820E-02	1.52138456890819E-02[5c]
11	9	5	11	5	5	1.0	1.0	1.0	0	0	6.69780683306607E-05	6.697806833065E-05[3]
13	12	11	13	12	11	4.0	4.0	2.5	0	0	–4.01371353397628E-01	–4.01371353397597E-01[5c]
14	13	13	14	13	13	7.0	3.0	3.0	0	0	4.53551285106790911552303162 3E-03[a]	4.53551312156525E-03
15	4	4	8	4	4	5.0	5.0	5.0	0	0	2.54324132559905E-03	2.5432413255908E-03[8o]
17	8	4	8	7	4	5.5	4.5	10	0	0	–1.00640064117188172346739998 5E-06[a]	–1.00623367113747E-06[8o]
18	10	9	18	17	9	4.0	4.0	5.0	0	0	–1.14908694660295E-02	–1.14908694660295E-02[8o]
21	10	10	15	8	–8	7.5	2.5	2.0	20	22.5	–1.39037489991391E-03	–1.39037497955321E-03[5a]
25	12	9	24	10	7	1.5	0.5	7.5	45	60	1.16035989847285E-05	–
28	14	10	28	16	16	8.5	1.5	4.0	30	60	–4.73506211475728E-10	–4.73486792914621E-10[5a]
32	7	5	16	8	–8	8.5	1.5	3.0	45	210	–6.27346727994947E-04	–
34	14	10	34	12	10	3.0	3.0	25	0	0	1.3527925684325E-04	1.30016393590254E-04[8o]
37	10	9	16	12	5	0.02	0.08	20	120	75	–1.0605662552466E-19	–

TABLE I
(*Continued*)

n	*l*	*m*	*n′*	*l′*	*m′*	ζ	ζ′	*R*	θ	φ	Eq. (*13*)	Literature
40	8	7	30	7	7	9.5	0.5	6.0	0	0	–4.70039559672119E-17	–4.70039545616601E-17[5b]
42	5	0	5	4	0	7.0	3.0	6.0	60	30	5.77870505957353E-03	5.77870507539378E-03[5d]
45	8	3	24	9	4	0.9	0.1	30	37.5	150	–2.10439953384112E-06	–
47	3	1	22	5	1	8.5	1.5	1.6	45	210	5.38928092697445E-04	5.38928092481825E-04[5d]
50	4	4	50	4	4	8.5	1.5	4.5	45	210	1.41805161985255E-11	1.41805162040407E-11[5d]
50	15	11	15	13	11	1.0	1.0	10	0	0	2.90100707200582E-04	2.90100707205215E-04[8o]
52	10	6	53	8	5	6.5	3.5	3.0	60	120	–2.70310289655582E-04	–
55	20	20	52	23	20	5.0	5.0	7.0	0	0	–2.58332568976321E-01	–1.78167728016314E-01[8o]
58	19	11	57	15	10	5.5	4.5	4.0	45	60	–1.76802362523849E-03	–
60	14	12	52	17	12	5.0	5.0	7.0	0	0	–2.62097248323569E-02	–7.50777781146405E-02[8o]
60	35	35	60	35	35	1.2	1.2	1.6	0	0	9.90918020468622E-01	–
62	19	15	52	17	15	1.0	1.0	10	0	0	3.16515414846025E-01	3.16515414845183E-01[8o]
65	24	18	65	20	18	0.01	0.01	1.0	0	0	2.95687254441400E-14	–1.26130790353512E-10[8o]
67	15	6	68	25	3	7.0	3.0	2	75	240	–7.81143508118869E-05	–
70	15	10	65	13	10	0.01	0.01	0.01	0	0	–3.46058313255987E-06	3.65666732448635E-03[8o]
73	8	2	72	13	1	6.0	4.0	3.0	30	60	–5.0805351459805E-03	–
75	30	18	75	20	18	0.001	0.001	0.001	0	0	–5.25685560022314E-64	–4.92600264607547E-08[8o]
77	15	6	78	12	5	8.0	2.0	1.0	120	150	–7.26999914679803E-18	–
80	4	3	80	5	4	0.9	0.1	4	75	120	–1.11271886601600E-31	–
83	12	11	80	15	11	3.5	3.5	1.4	0	0	–4.03480512144507E-04	–

[a] These values have been obtained from the computer program constructed in Maple 6 symbolic programming language.

is substantially faster than algorithms in prior literature. For example, since the calculation of the integral $S_{766,766}$ requires 0.3 ms in our algorithm, this time is higher in ref.[8o] and other available literature[3–6].

It can also be seen from Table I that the algorithm presented in this work is not affected by the canceling singularities arising for higher quantum numbers, nearly equal or equal orbital exponents, and higher or lower internuclear distances, as arise using BTOs in the evaluation of multicenter molecular integrals[8i]. On the contrary, it must be noted that the convergence of two-center overlap integrals with equal orbital exponents is more accurate and somewhat faster than in nearly equal and different orbital exponents cases. Also, the presented algorithm permits to avoid the use of rotation of overlap integrals as we encountered recently[5f].

It should be noted that the possible numerical instabilities may encountered in our algorithm is related to the calculation of integral $G^{\varepsilon,L}_{M,N}(\zeta,\zeta';R)$ arising in the calculation of auxiliary function $Q^{L}_{nl,n'l'}(\zeta,\zeta';R)$. To achieve the best results, one can give more accurate formulas for this integral.

CONCLUSIONS

Consequently, it may be concluded that the approach presented in this work allows to attain high accuracy in the whole range of quantum numbers, orbital exponents, and internuclear distances. Also, we note that this algorithm provides a rapid and sufficiently accurate method for the calculation of multicenter molecular integrals arising in the Hartree–Fock–Roothaan approximation based on the translation formulas for STOs. Work is in progress for the evaluation of the multicenter molecular integrals over STOs based on the computer results for two-center overlap integrals given in this work.

APPENDIX

In this section we confine ourselves to the accurate calculation of the basic integral $g^{L}_{M,N}(\zeta,R)$. Two different alternative formulations are given in the following.

1. The first approximation for the calculation of basic integral $g^{L}_{M,N}(\zeta,R)$ is based on the series expansion of spherical Bessel function $j_L(kR)$ (ref.[9]). From this point of view, we obtain

$$g^{L}_{M,N}(\zeta,R) = (2R)^{L} \sum_{u=0}^{\infty} \frac{(-1)^{u} f_u(N+u)}{\Gamma(N+2u+1)\, f_N(2N+2u+1)} R^{2u} g_{L+M+2u,N}(\zeta) , \qquad (29)$$

where $g_{M,N}(\zeta)$ is the integral of the form

$$g_{M,N}(\zeta) = \int_0^\infty \mathrm{d}k \, \frac{k^M}{(\zeta^2 + k^2)^N} \,. \tag{30}$$

We express the function $g_{M,N}(\zeta)$ for even and odd M, respectively, as in the following:

$$g_{2M,N}(\zeta) = \frac{\pi}{\zeta^{2N-2M-1}} \frac{f_{N-1}(2N-2M-3)\, f_M(2M-1)}{2^{2N-3} f_{N-2M-2}(N-M-2)} \tag{31}$$

and

$$g_{2M+1,N}(\zeta) = \frac{1}{2\zeta^{2N-2M-2}(N-M-1)\, f_M(N-1)} \,. \tag{32}$$

2. The alternative formulation for the calculation of integral $g^L_{M,N}(\zeta,R)$ is in terms of the hypergeometric function ${}_2F_1$, which can be obtained using formula in ref.[9]:

$$g^L_{M,N}(\zeta,R) = \frac{\sqrt{\pi}}{\zeta^{2N-M-1}} \left[\frac{x^L}{\Gamma_r(N)\,\Gamma(L+3/2)} \; {}_2F_1(r;r-N-1,L+3/2;x^2) + \right.$$

$$\left. + \frac{x^{2N-M-1}}{4\Gamma_{s-N}(N+s+1)\,\Gamma(2N+1)} \; {}_2F_1(N;N+s+1,N-r+1;x^2) \right], \tag{33}$$

where

$$x = \zeta R/2\,, \qquad r = (L+M+1)/2\,, \qquad s = (L-M)/2\,. \tag{34}$$

We define the function $\Gamma_m(N)$ and hypergeometric function ${}_2F_1(a,b,c;x)$ as

$$\Gamma_m(N) = \frac{\Gamma(N)}{\Gamma(m)\,\Gamma(N-m)} \tag{35}$$

and

$$ {}_2F_1(a,b,c;x) = \sum_{h=0}^{\infty} \frac{f_h(a)}{f_h(b)\, f_h(c)}\, x^h \quad . \tag{36} $$

The function $f_m(N)$ is given in Eq. (*26*). The convergence limit for the hypergeometric function ${}_2F_1(a,b,c;x)$ is determined for twenty-decimal-digit accuracy in all calculations.

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REFERENCES

1. Kato T.: *Commun. Pure Appl. Math.* **1951**, *10*, 151.
2. Agmon S.: *Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations: Bound on Eigenfunctions of N-Body Schrödinger Operators*. Princeton University Press, Princeton (NJ) 1982.
3. Rico J. F., Lopez R., Ramirez G.: *J. Comput. Chem.* **1988**, *9*, 790.
4. Bouferguene A., Rinaldi D.: *Int. J. Quantum Chem.* **1994**, *30*, 21.
5. a) Guseinov I. I.: *J. Phys. B: At., Mol. Opt. Phys.* **1970**, *3*, 1399; b) Guseinov I. I., Mamedov B. A.: *J. Mol. Struct. (THEOCHEM)* **1999**, *465*, 1; c) Guseinov I. I., Mamedov B. A.: *Theor. Chem. Acc.* **2000**, *105*, 93; d) Guseinov I. I., Öztekin E., Hüseyin S.: *J. Mol. Struct. (THEOCHEM)* **2001**, *536*, 59; e) Guseinov I. I., Mamedov B. A., Orbay M., Özdogan T.: *Commun. Theor. Phys.* **2000**, *33*, 161; f) Özdogan T., Orbay M.: *Int. J. Quantum Chem.* **2002**, *87*, 15; g) Özdogan T., Orbay M., Gümüş S.: *Commun. Theor. Phys.* **2002**, *37*, 711; h) Özdogan T.: *Int. J. Quantum Chem.* **2003**, *52*, 419; i) Gümüş S., Özdogan T.: *J. Chin. Chem. Soc.* **2003**, in press.
6. Magnasco V., Rapallo A., Casanova M.: *Int. J. Quantum Chem.* **1999**, *73*, 333.
7. Carrier G. F., Krook M., Pearson C. E.: *Functions of a Complex Variable*. McGraw–Hill, New York 1966.
8. a) Geller M.: *J. Chem. Phys.* **1962**, *36*, 2424; b) Geller M.: *J. Chem. Phys.* **1963**, *39*, 84; c) Silverstone H. J.: *J. Chem. Phys.* **1966**, *45*, 4337; d) Silverstone H. J.: *J. Chem. Phys.* **1967**, *46*, 4368; e) Edwards S. A., Gottlieb H. P. W., Doddrell D. M.: *Mol. Phys.* **1979**, *38*, 1147; f) Kaijser P., Smith V. H.: *Adv. Quantum Chem.* **1977**, *10*, 37; g) Henneker W. H., Cade P. E.: *Chem. Phys. Lett.* **1968**, *2*, 575; h) Filter E., Steinborn E. O.: *J. Math. Phys.* **1978**, *19*, 79; i) Trivedi H. P., Steinborn E. O.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1983**, *27*, 670; j) Weniger E. J., Steinborn E. O.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1983**, *28*, 2026; k) Weniger E. J., Steinborn E. O.: *J. Chem. Phys.* **1983**, *78*, 6121; l) Weniger E. J., Steinborn E. O.: *Theor. Chim. Acta* **1988**, *73*, 323; m) Antlovic D., Delhalle J.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1980**, *21*, 1815; n) Guseinov I. I., Ilik A., Allahverdiyev S. I.: *Int. J. Quantum Chem.* **1996**, *60*, 637; o) Öztekin E., Yavuz M., Atalay Ş.: *Theor. Chem. Acc.* **2001**, *106*, 264.
9. Gradshteyn I. S., Ryzhik I. M.: *Tables of Integrals, Series and Products*. Academic Press, New York 1995.
10. Weisbluth M.: *Atoms and Molecules*. Academic Press, New York 1978.
11. Condon E. U., Shortley G. H.: *The Theory of Atomic Spectra*. Cambridge University Press, Cambridge 1970.