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ORIGINAL PAPER

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Evaluation of overlap integrals with integer and noninteger *n* Slater-type orbitals using auxiliary functions

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Abstract The series expansion formulae are derived for the overlap integrals with arbitrary integer n and noninteger n^* Slater-type orbitals (ISTOs and NISTOs) in terms of a product of well-known auxiliary functions A_σ and B_k. The series becomes an ordinary closed expression when both principal quantum numbers n^* and n'^* of orbitals are integer $n^*=n$ and $n'^*=n'$. These formulae are especially useful for the calculation of overlap integrals for large quantum numbers. Accuracy of the results is satisfactory for values of integer and noninteger quantum numbers up to $n=n'=60$, $n^*=n'^*<33$ and for arbitrary values of screening constants of orbitals and internuclear distances.

Keywords Slater-type orbitals · Overlap integrals · Noninteger principal quantum numbers · Auxiliary functions

Introduction

It is well known that multicenter molecular integrals are evaluated by the use of two types of orbitals: Gaussian-type orbitals (GTOs) and Slater-type orbitals (STOs). GTOs do not represent important properties of the electronic wavefunction sufficiently, namely, the cusps at the nuclei [1] and exponential decay at large distances. [2] For problems in which the long part of the wavefunction or its behavior in the neighborhood of the nuclei is important, it is desirable to use STOs, which describe the physical situation more accurately than GTOs. It is well known that noninteger STOs (NISTOs) provide a simple but more flexible basis for molecular calculations than integer STOs (ISTOs). [3] The main problem for the use of a NISTO basis in molecular calculations arises in the evaluation of the multicenter integrals.

In [4] the multicenter multielectron molecular integrals over NISTOs with an arbitrary s-electron operator $F^{(s)}$ (s=1, 2, 3,...) appearing in the Hartree–Fock–Roothaan approximation and also in the Hyllaraas correlated wave functions method were expressed in terms of overlap integrals over NISTOs for the calculation of which we presented the analytical formulae through the overlap integrals with ISTOs. The overlap integrals with NISTOs can also be evaluated by the use of auxiliary functions A_σ and B_k. It is well known that the auxiliary function method in which elliptical coordinates are used has been studied extensively and employed in the calculation of overlap integrals over ISTOs (see, e.g. [5, 6, 7, 8] and the bibliography quoted in these papers). In this work, using the auxiliary function method, a unified treatment is described for the overlap integrals over ISTOs and NISTOs with respect to the molecular coordinate system (non-aligned coordinate systems):

$$S_{n^*lm,n'^*l'm'}(p,t;\theta,\varphi)=\int \chi^*_{n^*lm}(\zeta,\vec{r}_a)\chi_{n'^*l'm'}(\zeta',\vec{r}_b)\mathrm{d}V \qquad (1)$$

where

$$p=\tfrac{R}{2}(\zeta+\zeta'),\quad t=(\zeta-\zeta')/(\zeta+\zeta');$$

The quantities R, θ and φ are the spherical-polar coordinates of radius vector $\vec{R}\equiv\vec{R}_{ab}=\vec{r}_a-\vec{r}_b$; $\chi_{n^*lm}(\zeta,\vec{r}_a)$ and $\chi_{n'^*l'm'}(\zeta',\vec{r}_b)$ are normalized complex or real STOs on the nuclei a and b, respectively:

$$\chi_{n^*lm}(\zeta,\vec{r})=(2\zeta)^{n^*+\frac{1}{2}}[\Gamma(2n^*+1)]^{-\frac{1}{2}}r^{n^*-1}\mathrm{e}^{-\zeta r}S_{lm}(\theta,\varphi) \qquad (2)$$

Here n^* is an integer ($n^*=n$) or noninteger ($n^*\neq n$) principal quantum number, S_{lm} is a complex or real spherical harmonic and $\Gamma(x)$ is the gamma function. In the case of integer values of n^*, it is necessary to replace the function $\Gamma(2n^*+1)$ by the expression $\Gamma(2n^*+1)=(2n)!$.

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For θ=φ=0 (aligned coordinate systems) the overlap integrals are defined by

$$S_{n^*l\lambda,n'^*l'\lambda}(p,t) \equiv S_{n^*l\lambda,n'^*l'\lambda}(p,t,0,0) = \int \chi^*_{n^*l\lambda}(\zeta,\vec{r}_a)\chi_{n'^*l'\lambda}(\zeta',\vec{r}_b)\mathrm{d}V \quad (3)$$

where $\lambda = |m| = |m'|$.

Expressions in terms of auxiliary functions

In order to derive the expression for Eq. (3) in terms of auxiliary functions we use elliptical coordinates. Then integrating over the azimuthal angle $\varphi=\varphi_a=\varphi_b$ we obtain:

$$S_{n^*l\lambda,n'^*l'\lambda}(p,t) = N_{n^*n'^*}(p,t)\int_1^\infty\int_{-1}^1 (\mu+\nu)^{n^*}(\mu-\nu)^{n'^*}\cdot \cdot \mathrm{e}^{-p\mu-pt\nu}P_{l\lambda}\left(\frac{1+\mu\nu}{\mu+\nu}\right)P_{l'\lambda}\left(\frac{1-\mu\nu}{\mu-\nu}\right)\mathrm{d}\mu\mathrm{d}\nu \quad (4)$$

where $P_{l\lambda}$ and $P_{l'\lambda}$ are normalized associated Legendre polynomials and

$$N_{n^*n'^*}(p,t) = [\Gamma(2n^*+1)\Gamma(2n'^*+1)]^{-\frac{1}{2}}[p(1+t)]^{n^*+\frac{1}{2}}[p(1-t)]^{n'^*+\frac{1}{2}} \quad (5)$$

Now we use the expansion formulae for the product of two normalized associated Legendre polynomials both with different centers in Eq. (4). [9] Then it is easy to obtain for the overlap integrals over STOs with respect to aligned coordinate systems the following relation:

$$S_{n^*l\lambda,n'^*l'\lambda}(p,t) = N_{n^*n'^*}(p,t)\sum_{\alpha=-\lambda}^{l}\sum_{\beta=\lambda}^{l'}\sum_{q=0}^{\alpha+\beta} g^q_{\alpha\beta}(l\lambda,l'\lambda)Q^q_{n^*-\alpha,n'^*-\beta}(p,t) \quad (6)$$

where the quantity Q^q is the auxiliary function defined by

$$Q^q_{n^*n'^*}(p,t) = \int_1^\infty\int_{-1}^1 (\mu\nu)^q(\mu+\nu)^{n^*}(\mu-\nu)^{n'^*}\mathrm{e}^{-p\mu-pt\nu}\mathrm{d}\mu\mathrm{d}\nu \quad (7)$$

See [10] for the exact definition of coefficients $g^q_{\alpha\beta}$. The relationship for these coefficients in terms of binomial coefficients was given in [11]:

$$g^q_{\alpha\beta}(l\lambda,l'\lambda) = g^0_{\alpha\beta}(l\lambda,l'\lambda)F_q(\alpha+\lambda,\beta-\lambda) \quad (8)$$

$$g^0_{\alpha\beta}(l\lambda,l'\lambda) = \left[\sum_{i=0}^{\lambda}(-1)^i F_i(\lambda)D^{l\lambda}_{\alpha+2\lambda-2i}\right]D^{l'\lambda}_{\beta} \quad (9)$$

$$D^{l\lambda}_{\beta} = \frac{(-1)^{(l-\beta)/2}}{2^l}\left[\frac{2l+1}{2}\frac{F_l(l+\lambda)}{F_\lambda(l)}\right]^{1/2}\cdot \cdot F_{(l-\beta)/2}(l)F_{\beta-\lambda}(l+\beta) \quad (10)$$

Here the quantities $F_m(n,n')$ are the generalized binomial coefficients determined by the following relations:

$$(x+y)^n(x-y)^{n'} = \sum_{m=0}^{n+n'}F_m(n,n')x^{n+n'-m}y^m \quad (11)$$

$$F_m(n,n') = \sum_k (-1)^k F_{m-k}(n)F_k(n') \quad (12)$$

where $\frac{1}{2}[(m-n)+|m-n|] \le k \le \min(m,n')$. Here $F_m(n) = F_m(n,0) = n!/(m!(n-m)!)$ and $F_m(n,n')$ are the usual and generalized binomial coefficients. Generalized binomial coefficients have the following recursive relations and symmetry properties:

$$F_m(n,n') = F_m(n-2,n') + 2F_{m-1}(n-2,n') + F_{m-2}(n-2,n') \quad (13)$$

$$F_m(n,n') = F_m(n-1,n'-1) - F_{m-2}(n-1,n'-1) \quad (14)$$

$$F_m(n,n') = F_m(n-1,n') - F_{m-1}(n-1,n') \quad (15)$$

$$F_m(n,n') = F_m(n,n'-1) - F_{m-1}(n,n'-1) \quad (16)$$

and

$$F_m(n,n') = (-1)^m F_m(n',n) \quad (17)$$

$$F_i(n,n') = (-1)^{n'}F_{n+n'-i}(n,n') \text{ for} i = 0,1,\ldots,n+n' \quad (18)$$

Now we can move on to the calculation of overlap integrals relative to unaligned coordinate systems. For this purpose, we use Eqs. (5) and (17) of [10] for the rotation of two-center overlap integrals in the following form:

$$S_{n^*lm,n'^*l'm'}(p,t;\theta,\varphi) = \sum_{\lambda=0}^{\min(l,l')} T^{*\lambda}_{lm,l'm'}(\theta,\varphi)S_{n^*l\lambda,n'^*l'\lambda}(p,t) \quad (19)$$

where $S_{n^*l\lambda,n'^*l'\lambda}$ are the overlap integrals with respect to aligned coordinate systems determined by Eq. (6). The rotation coefficients T^λ in Eq. (19) are determined by the following relationships:

- for complex STOs

$$T^\lambda_{lm,l'm'}(\theta,\varphi) = \frac{2}{1+\delta_{\lambda 0}}\sum_{L=|l-l'|}^{l+l'}{}^{(2)}C^{ll'L}_{m,-m',m-m'}\cdot \cdot C^{ll'L}_{\lambda,-\lambda,0}\left(\frac{4\pi}{2L+1}\right)^{1/2}Y_{L,m-m'}(\theta,\varphi) \quad (20)$$

- for real STOs

$$T^\lambda_{lm,l'm'}(\theta,\varphi) = \frac{2(-1)^{\gamma+\gamma'}}{(1+\delta_{\lambda 0})[(1+\delta_{m0})(1+\delta_{m'0})]^{1/2}}\cdot \cdot \sum_{i=-1}^{1}{}^{(2)}\sum_{L=|l-l'|}^{l+l'}{}^{(2)}(\varepsilon_{m0})^{\delta_{i,\varepsilon_{mm'}}}\times C^{ll'L}_{i\gamma,\gamma',i\gamma+\gamma'}\cdot \cdot C^{ll'L}_{\lambda,-\lambda,0}\left[\frac{2\pi(1+\delta_{M_i0})}{2L+1}\right]^{1/2}S_{LM_i}(\theta,\varphi) \quad (21)$$

where $\gamma=|m|$, $\gamma'=|m'|$ and $M_i=\varepsilon_{mm'}|i\gamma+\gamma'|$. In Eqs. (20) and (21) the symbol $\sum^{(2)}$ indicates that the summation is to be performed in steps of two. For $\gamma=\gamma'$ and $\varepsilon_{mm'}=-1$ terms with a negative value of index i ($i=-1$) contained in Eq. (21) should be equated to zero. We notice that the symbol $\varepsilon_{mm'}$ in Eq. (21) may have the values ±1 and is determined by the product of the signs m and m' (the sign of zero is regarded as positive). The quantities C in Eqs. (20) and (21) are the Clebsch–Cordan coefficients in the case of our phases ($Y^*_{lm}=Y_{l-m}$, see [11]):

$$C^{l_1 l_2 L}_{m_1 m_2 M} = (-1)^{\frac{1}{2}(m_1+|m_1|+m_2+|m_2|+M+|M|)} \cdot (l_1 l_2 m_1 m_2 / l_1 l_2 L M) \tag{22}$$

where $(l_1 l_2 m_1 m_2 / l_1 l_2 L M)$ is a Clebsch–Cordan coefficient in Condon–Shortley phases.

For a linear molecule it is convenient to take the polar axes along the line joining the centers a and b. Then Eqs. (20) and (21) become

$$T^{\lambda}_{lm,l'm'}(\theta,\varphi) = \delta_{mm'}\delta_{\lambda|m|} \begin{cases} 1 \text{ for } \theta=0, \varphi=0 \\ (-1)^{l+l'} \text{ for } \theta=\pi, \varphi=0 \end{cases} \tag{23}$$

With the aid of Eq. (19) any overlap integral can be calculated in the molecular coordinate system from the overlap integrals with respect to aligned coordinate systems, which are expressed in terms of auxiliary functions Q^q by the relation (6). Thus, the computation of overlap integrals with STOs is reduced to the calculation of the auxiliary functions $Q^q_{n^*n'^*}$.

Evaluation of auxiliary functions

For the evaluation of auxiliary functions Q^q we use the following binomial relationship:

$$(\mu \pm \nu)^{n^*} = \sum_{m=0}^{\infty} (\pm 1)^m F_m(n^*) \mu^{n^*-m} \nu^m \tag{24}$$

where $F_0(n^*)=1$ and

$$F_m(n^*) \equiv F_m(n) = \frac{n!}{m!(n-m)!} \text{ for an integer } n* \tag{25}$$

$$F_m(n^*) = \frac{n^*(n^*-1)\ldots[n^*-(m-1)]}{m!} \text{ for a noninteger } n* \tag{26}$$

We notice that for $m>n$ the binomial coefficient $F_m(n)$ in Eq. (24) is zero, i.e., in the case of integer n^* terms with negative factorials do not contribute to the summation.

Taking into account Eq. (24) it is easy to show that

$$(\mu+\nu)^{n^*}(\mu-\nu)^{n'^*} = \lim_{N'\to\infty} \sum_{m=0}^{n+N'} F^{N'}_m(n^*,n'^*) \mu^{n^*+n'^*-m} \nu^m \tag{27}$$

where n is an integer part of principal quantum number n^* and

$$F^{N'}_m(n^*,n'^*) = \begin{cases} \delta_{N'n'} F_m(n,n') \text{ for } n^*=n, n'^*=n' \\ \sum_{\sigma=0}^{N'} (-1)^{\sigma} F_{m-\sigma}(n^*) F_{\sigma}(n'^*) \text{ for } n^* \\ = n, n'^* \neq n'; n^* \neq n, n'^* \\ = n'; n^* \neq n, n'^* \neq n' \end{cases} \tag{28}$$

The indices N' in Eqs. (27) and (28) arise from the expansion of $(\mu-\nu)^{n'^*}$. We notice that the quantities $F_m(n,n')$ are expansion coefficients in the identity (11).

Substituting Eq. (27) into Eq. (7) we finally obtain for auxiliary functions Q^q the following expressions:

- for noninteger n^* and n'^*

$$Q^q_{n^*n'^*}(p,t) = \lim_{N'\to\infty} \sum_{m=0}^{n+N'} F^{N'}_m(n^*,n'^*) A_{n^*+n'^*+q-m}(p) B_{q+m}(pt) \tag{29}$$

- for integer n^* and n'^*

$$Q^q_{nn'}(p,t) = \sum_{m=0}^{n+n'} F_m(n,n') A_{n+n'+q-m}(p) B_{q+m}(pt) \tag{30}$$

Here A_σ and B_k are the well-known auxiliary functions defined by

$$A_\sigma(p) = \int_1^{\infty} \mu^\sigma e^{-p\mu} d\mu \tag{31}$$

$$B_k(pt) = \int_{-1}^{1} \nu^k e^{-pt\nu} d\nu \tag{32}$$

where the index σ takes positive and negative integer and noninteger values; k is a positive integer number. The auxiliary functions $A_\sigma(p)$ and $B_k(pt)$ satisfy the following recursive relations:

$$A_\sigma(p) = \frac{1}{p}[\sigma A_{\sigma-1}(p) + e^{-p}] \tag{33}$$

$$B_k(pt) = \frac{1}{pt}[k B_{k-1}(pt) + (-1)^k e^{pt} - e^{-pt}] \text{ for } pt \neq 0 \tag{34}$$

$$B_k(0) = \frac{1}{k+1}[1+(-1)^k] \text{ for } pt = 0 \tag{35}$$

For integer values of the index σ in the auxiliary function $A_\sigma(p)$ is calculated from the recursive relation (33) which is stable for all values of σ and p. In the case of noninteger σ, the recursive relation (33) is only stable for small values of the parameter p. For noninteger values of σ, we have implemented an efficient procedure based on the use of the expression for the function $A_\sigma(p)$ through the incomplete gamma function [12]

$$A_\sigma(p) = p^{-\sigma-1}\Gamma(\sigma+1,p) \tag{36}$$

where

$$\Gamma(\sigma,p) = \int_p^{\infty} t^{\sigma-1} e^{-t} dt \tag{37}$$

For large values of parameter p we have used the algorithm given in [13] for the calculation of the incomplete gamma function. In our computational algorithm we used the routines GSER and GCF, which are available from the Fortran numerical recipes library. [14]

The simplest way of evaluating the integral $B_k(pt)$ is through its recurrence relation (34). Unfortunately, the recursive relation (34) for auxiliary functions $B_k(pt)$ becomes unstable when $k/|pt| > 1$. The absolute error made in the initial value $B_0(pt)$ in Eq. (34) grows with a factor $k/|pt|$ in each step. Since $B_k(pt)$ values have almost the same order of magnitude for all k, the relative error grows in each step by a factor $k/|pt|$. In [8] this difficulty was overcome by using the recursive relation downward for $k/|pt| > 1$. Therefore, in this study, for $k/|pt| > 1$ the calculation of auxiliary functions $B_k(pt)$ is performed by the use of the approach described in [8].

Using the identity [15]

$$\begin{aligned}\Delta f = S_{n^*lm,n^{*\prime}l'm'}(p,t;\theta,\varphi) - \{ & \frac{\sqrt{(2n+1)(2n+2)}}{2p(1+t)\cos\theta} \cdot \\ & \cdot [A_{l\lambda} S_{n^*+1l+1m,n^{*\prime}l'm'}(p,t;\theta,\varphi) \\ & + B_{l\lambda} S_{n^*+1l-1m,n^{*\prime}l'm'}(p,t;\theta,\varphi)] \\ & - \frac{\sqrt{(2n'+1)(2n'+2)}}{2p(1-t)\cos\theta} [A_{l'\lambda'} S_{n^*lm,n^{*\prime}+1l'+1m'}(p,t;\theta,\varphi) \\ & + B_{l'\lambda'} S_{n^*lm,n^{*\prime}+1l'-1m'}(p,t;\theta,\varphi)]\} \end{aligned} \quad (38)$$

one can determine the accuracy of computer results for the overlap integrals which are obtained from Eqs. (6) and (19). Here the coefficients $A_{l\lambda}$ and $B_{l\lambda}$ are defined by the relations:

$$A_{l\lambda} = \left[\frac{(l-\lambda+1)(l+\lambda+1)}{(2l+1)(2l+3)}\right]^{\frac{1}{2}}, \quad B_{l\lambda} = \left[\frac{(l-\lambda)(l+\lambda)}{(2l-1)(2l+1)}\right]^{\frac{1}{2}} \quad (39)$$

where $\lambda = |m|$ and $\lambda' = |m'|$.

Numerical results and discussion

As can be seen from Eqs. (6), (19) and (29), the overlap integrals with STOs are expressed in terms of auxiliary functions $A_\sigma(p)$ and $B_k(pt)$. The auxiliary functions occurring in the overlap integrals can be calculated by making use of computer programs presented in [8] and [14]. With the aid of identity (38) one can determine the accuracy of computer results that are obtained from Eqs. (6) and (19).

The coefficients $F_m(n^*,n'^*)$ and $D_\beta^{l\lambda}$ are stored in the memory of computer and used both in Eq. (6) and in the calculation of $g^0_{\alpha\beta}(l\lambda,l'\lambda)$ coefficients, respectively. In order to put these coefficients into or to get them back from the memory, the positions of certain coefficients $F_m(n^*,n'^*)$ and $D_\beta^{l\lambda}$ are determined by the following relations, respectively:

$$\begin{aligned} F^{n_1n_2m} = & \frac{1}{8}\{n_1(2n_1^2 - 11n_1 + 14) + 2[n_2(2n_1 + n_2 - 6) \\ & + \beta^{n_1 1} + \beta^{n_1 n_2} - 5] + \beta^{n_1 0}\} \\ & + \frac{1}{2}(2 - \delta_{n_1 n_2})m + \delta_{n_1 n_2} \end{aligned} \quad (40)$$

$$D^{l\lambda\beta} = \sum_{k=0}^{l-1} d^{kkk} + d^{l\lambda\beta} \quad (41)$$

Table 1 The values of overlap integrals over NSTOs obtained in the molecular coordinate system (in a.u.)

n^*	l	m	n'^*	l'	m'	p	t	θ	φ	Overlap integrals	[braceexΔ f[braceex	CPU (ms)	[17]
7.3	4	4	7.3	4	4	2	0.5	0	0	1.01734314959344E–01	14	12.6	1.101734314960E–01
3.8	0	0	5.5	0	0	2.31	11/33	0	0	2.90802046505438E–01	15	2.3	2.90802069369E–01
5.7	1	1	3.8	1	1	2.38	4/17	0	0	8.66889506331727E–01	16	3.1	8.66889476942E–01
6.4	1	0	6.4	0	0	5.1	–8/17	0	0	3.12099122165129E–01	14	2.5	3.12095409105E–01
7.7	4	4	6.6	4	4	6	–0.25	0	0	2.34831461718284E–01	13	12.5	2.34831448531E–01
4.1	2	2	3.7	2	2	10.25	5/41	0	0	2.93541966880792E–02	14	4.3	2.93217486171E–02
10.3	0	0	10.3	9	0	5.25	3/7	0	0	1.52927430062972E–05	12	7.7	1.52926483369E–05
3.6	2	1	2	1	1	0.8	0.3	72	180	6.49621736449485E–02	16	1.5	
4.5	3	2	3.2	2	2	12	0.1	0	0	1.69270199963546E–02	15	5.2	
5.38	4	2	4.2	3	2	0.08	0.4	144	60	–9.63888734685283E–03	15	8.3	
6.8	4	3	4.5	4	3	5	0.6	0	0	–2.35186756280448E–02	15	11.1	
6.3	5	4	5.5	4	4	15	0.1	120	240	1.85610753353492E–02	14	12.3	
7.6	3	2	7.2	4	3	25	0.01	150	300	–4.85856478885724E–04	13	8.3	
7.9	5	4	7.7	6	4	18	0.01	45	45	5.01350546208193E–06	14	13.1	
7.2	6	6	7.8	6	6	8	0.02	0	0	1.80791756875938E–01	13	16.5	
8.7	4	4	8.8	5	4	0.008	0.4	135	90	3.18346195817754E–04	16	21.1	
8.7	4	4	8.8	5	4	0.008	0.4	0	0	–4.50210194347972E–04	17	18.2	
8.7	7	7	8.8	7	7	0.002	0.7	180	225	1.80816109800210E–03	14	33.6	
9.5	7	3	9.8	7	3	0.002	0.7	0	0	8.27658561382520E–04	15	25.6	
9.6	8	6	9.2	8	5	0.02	0.1	135	45	1.47673938614477E–01	14	36.7	
11.6	8	7	7.4	5	4	0.03	0.2	135	180	5.49932834618303E–08	16	34.4	
12.4	10	9	10.2	9	9	3.3	0.02	20	270	1.62396868246811E–03	15	108.3	
13.2	7	6	11.5	7	6	0.06	0.1	0	0	9.84040136524412E–01	15	94.8	
32.5	10	8	30.2	10	8	0.05	0.3	100	180	5.51472012714084E–02	10	185.3	

Table 2 The values of overlap integrals over ISTOs obtained in the molecular coordinate system (in a.u.)

n	l	m	n'	l'	m'	p	t	θ	φ	Overlap integral	[braceexΔf[braceex	CPU (ms)
3	2	2	4.3	2	1	6	0.2	108	360	2.35433146098390E–02	16	1.3
4	3	2	3	2	2	28	0.5	36	90	1.31250973526034E–05	20	0.6
6	4	3	4.7	3	3	0.01	0.8	30	120	1.95914851453841E–06	12	7.1
6	5	4	5	4	3	100	0.9	30	120	3.22560055936252E–09	21	1.1
9	8	7	9	8	7	0.05	0.5	0	0	3.10284864728746E–02	18	7.4
13	11	10	13	11	10	3	0.5	40	45	8.94971276122572E–05	14	9.2
14	8	2	2	1	1	25	0.1	60	120	–3.44935857510066E–04	15	6.4
20	10	3	3	2	1	15	0.4	60	30	–1.91911299026405E–02	18	7.6
20	12	10	23	12	10	15	0.8	80	225	8.75180391158657E–11	18	11.8
30	9	2	5	4	2	1.3	0.5	180	60	3.80469836725469E–06	15	10.1
51	4	3	50	4	3	7	0.7	180	225	1.94567688548197E–11	17	5.1
60	3	2	60	3	2	4	0.1	30	45	6.47164982333689E–01	9	7.5

where

$$\beta^{n_1 n_2} = [1-(-1)^{n_1+n_2}]/2 \tag{42}$$

$$d^{l\lambda\beta} = d^{l\lambda-1\beta} + [\beta-\lambda-(1-(-1)^{l-\lambda})]/2+1 \tag{43}$$

$$d^{l0\beta} = [\beta-(1-(-1)^{l})]/2+1 \text{and} d^{000}=1 \tag{44}$$

Here, n_1 and n_2 are the integer parts of quantum numbers n^* and n'^*, respectively. We notice that the symmetry properties are taken into account in storing $F_m(n^*,n'^*)$. Computation time of overlap integrals is reduced by using Eqs. (40), (41), (42), (43) and (44) and the memory of the computer.

The results of calculations on a PENTIUM 233 computer (using Turbo Pascal 7.0 language) for various values of parameters are represented in Tables 1 and 2 obtained in the molecular coordinate system. The values of overlap integrals, the number of correct decimal figures [braceexΔf[braceex and the CPU time in milliseconds are given in these tables. As can be seen from the tables, in all of the calculations for $0<p$ and $-1<t<1$ the accuracy and CPU time of computer results are satisfactory.

In the literature, as far as we know, there are no studies on the evaluation of overlap integrals with NISTOs, with which to compare our results, except for the studies of [16] and [17]. The results of calculations had been checked with results of [17].

We notice that the algorithm presented in this work is of a completely general type and can be used to calculate any overlap integral for arbitrary values of integer and noninteger principal quantum numbers, screening constants and location of STOs, and internuclear distances. Therefore, this algorithm provides a rapid and sufficiently accurate method for the calculation of multicenter multielectron molecular integrals in the Hartree–Fock–Roothaan and Hyllaraas approximations based on the series expansion formulae for STOs obtained in [4].

Supporting information

The program is available from the authors on request.

References

1. Kato T (1957) Commun Pure Appl Math 10:151–160
2. Agmon S (1982) Lectures on exponential decay of solutions of second-order elliptic equations: bound on eigenfunctions of N-body Schrodinger operators. Princeton University Press, Princeton, pp 24–87
3. Silverstone HJ (1966) J Chem Phys 45:4337–4345
4. Guseinov II (2002) Int J Quantum Chem 90:114-118
5. Weatherford CA, Jones HW (1982) International Conference on ETO multicenter integrals. Reidel, Dordrecht, pp 1–65
6. Bouferguene A, Fares M, Hoggan PE (1996) Int J Quantum Chem 57:801–810
7. Rico JF, Lopez R, Aguado A, Ema I, Ramirez G (1998) J Comput Chem 19:1284–1293
8. Guseinov II, Özmen A, Atav Ü, Yüksel H (1998) Int J Quantum Chem 67:199–204
9. Guseinov II (1970) J Phys B 3:1399–1412
10. Guseinov II (1985) Phys Rev A 32:1864–1866
11. Guseinov II (1995) J Mol Struct (Theochem) 336:17–20
12. Gradshteyn IS, Ryzhik IM (1980) Tables of integrals, sums, series and products, 4th edn. Academic Press, New York, pp 300–320
13. Abramowitz M, Stegun IA (1972) Handbook of mathematical functions, 3rd edn. Dover Publications, New York, pp 253–265
14. Press WH, Flannery BP, Teukosky SA, Vatterling WT (1989) Numerical recipes (Fortran version). Cambridge University Press, Cambridge
15. Guseinov II, Mamedov BA (1999) J Mol Struct (Theochem) 465:1–6
16. Mekelleche SM, Baba-Ahmed A (1997) Int J Quant Chem 63:843–852
17. Mekelleche SM, Baba-Ahmed A (2000) Theor Chem Acc 103:463–468