Unified Treatment for Two-Center One-Electron Molecular Integrals Over Slater Type Orbitals with Integer and Noninteger Principal Quantum Numbers

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A unified expression has been obtained for two-center one-electron molecular integrals over Slater type orbitals with integer and noninteger principal quantum numbers by the use of the expansion formula for the product of two normalized associated Legendre functions. The presented expression for two-center one-electron molecular integrals contains the expansion coefficients $d_{us}^{kk'}$ and Mulliken integrals A_n and B_n. The efficiency of the presented calculation has been compared with that of other methods, indicating good convergence and great numerical stability for a wide range of quantum numbers, orbital exponents and internuclear distances.

Key words: Slater Type Orbitals; Noninteger Principal Quantum Numbers; Overlap Integrals; Nuclear Attraction Integrals.

1. Introduction

The evaluation of multicenter integrals over various basis functions or orbitals contained in the Hartree-Fock-Roothaan (HFR) approximation plays a decisive role in the calculation of various molecular parameters. Common basis types include Gaussian [1], Slater [2, 3] and, less often, Laguerre functions [4]. The methods of evaluating these integrals depend strongly on the orbital type. Since the integrals for Gaussian-type orbitals (GTOs) may be evaluated easily, these are the common choice for quantum chemistry. Slater-type orbitals (STOs) are less popular, since their multicenter integrals are difficult to evaluate.

It is desirable to replace GTOs with STOs, because the latter approximate the correct form of the solutions to the molecular Schrödinger equation more closely. They satisfy the cusp condition [5] and behave asymptotically as $\exp(-r)$ [6]. GTOs satisfy neither condition [7]. Thus there is continued interest in multicenter integrals over STOs.

Two-center one-electron molecular integrals (overlap and nuclear attraction integrals) represent a fundamental class of molecular integrals in calculating multicenter integrals for the HFR approximation by the Slater function translation method. In the literature, there are a number of formulas [8], and the large body of them consists of STOs with integer principal quantum numbers.

As is known from earlier works [9, 10], STOs with noninteger principal quantum numbers (noninteger *n*-STOs) provide a more flexible basis for molecular calculations and also the orbital energies obtained by noninteger *n*-STOs are lower than those obtained by integer *n*-STOs [10]. A detailed discussion of the use of noninteger *n*-STOs in molecular calculations can be found in an excellent review article of Bishop [9g)].

In our previous papers we evaluated overlap and nuclear attraction integrals over integer and noninteger *n*-STOs [11 – 17]. The aim of this work is to present a unified formula for the evaluation of two-center one-electron molecular integrals (overlap and nuclear attraction integrals) over integer and noninteger *n*-STOs. Atomic units are used from this point onwards.

2. Definitions

The two-center one-electron molecular integrals examined in the present work have the following form:

Overlap Integrals:

$$S_{nl\lambda,n'l'\lambda}\left(\zeta,\zeta';\vec{R}\right)=\int\chi^{*}_{nl\lambda}\left(\zeta,\vec{r}_a\right)\chi_{n'l'\lambda}\left(\zeta',\vec{r}_b\right)\mathrm{d}V. \tag{1}$$

Nuclear Attraction Integrals:

$$U^{(A)}_{nl\lambda,n'l'\lambda}\left(\zeta,\zeta';\vec{R}\right)=\int\chi^{*}_{nl\lambda}\left(\zeta,\vec{r}_a\right)\frac{1}{r_a}\chi_{n'l'\lambda}\left(\zeta',\vec{r}_b\right)\mathrm{d}V, \tag{2}$$

$$U^{(B)}_{nl\lambda,n'l'\lambda}\left(\zeta,\zeta';\vec{R}\right)=\int\chi^{*}_{nl\lambda}\left(\zeta,\vec{r}_a\right)\frac{1}{r_b}\chi_{n'l'\lambda}\left(\zeta',\vec{r}_b\right)\mathrm{d}V, \tag{3}$$

where $\vec{R}\equiv\vec{R_{ab}}=\vec{r}_a-\vec{r}_b$, $\lambda=|m|=|m'|$. In (1)–(3), $\chi_{nlm}(\zeta,\vec{r}_a)$ and $\chi_{nlm}(\zeta,\vec{r}_b)$ are Slater type orbitals located on centers a and b. Other types of nuclear attraction integrals are not the aim of this work and therefore will not be studied here.

In the most general case, any STO is defined by

$$\chi_{nlm}\left(\zeta,\vec{r}\right)=R_n\left(\zeta,r\right)S_{lm}(\theta,\varphi), \tag{4}$$

where the radial part is given by

$$R_n\left(\zeta,r\right)=\frac{(2\zeta)^{n+\frac{1}{2}}}{\sqrt{\Gamma\left(2n+1\right)}}r^{n-1}\exp\left(-\zeta r\right), \tag{5}$$

in which $\Gamma(n)$ indicates the gamma function [18], ζ is the orbital exponent, and the angular part $S_{lm}(\theta,\varphi)$ is a complex or real spherical harmonic [19], defined by

$$S_{lm}(\theta,\varphi)=P_{l|m|}(\cos\theta)\Phi_m(\varphi). \tag{6}$$

In (3), $P_{l|m|}$ is a normalized associated Legendre function, which we re-defined recently as [20]

$$P_{lm}(\cos\theta)=\\(-1)^{\frac{1}{2}(|m|-m)}\sum_{k=\frac{1}{2}(|m|-m)}^{E\left(\frac{l-m}{2}\right)}C^{k}_{lm}(\sin\theta)^{2k+m}(\cos\theta)^{l-(2k+m)} \tag{7}$$

with

$$E\left(\frac{n}{2}\right)=\frac{n}{2}-\frac{1}{4}\left(1-(-1)^n\right) \tag{8}$$

and

$$C^{k}_{lm}=\frac{(-1)^k}{2^{2k+m}}\left[\frac{2l+1}{2}F_{l-k}(l+m)F_{k+m}(l-k)\cdot F_{2k}(l-m)F_k(2k)\right]^{\frac{1}{2}}, \tag{9}$$

in which $F_m(n)=\frac{n!}{m!(n-m)!}$ indicates the usual binomial coefficient. Similar expressions for Legendre functions can be found in [8h), 8i)].

The orthonormal function $\Phi_m(\varphi)$ in (6) is given by

$$\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}\exp(im\varphi) \tag{10}$$

for complex spherical harmonics, and

$$\Phi_m(\varphi)=\frac{1}{\sqrt{\pi\left(1+\delta_{m0}\right)}}\begin{cases}\cos m\varphi & \text{for } m\geq 0\\ \sin|m|\varphi & \text{for } m<0\end{cases} \tag{11}$$

for real spherical harmonics, in which δ_{mn} indicates the kronecker delta function.

3. The Expansion of the Product of two Normalized Associated Legendre Functions

For the evaluation of multicenter integrals as also (1)–(3) it is necessary to have an equation for the expansion of the product of two normalized associated Legendre functions centered on the nuclei a and b. Therefore we shall require, first, the product

$$T^{l\lambda,l'\lambda}\left(\theta_a,\theta_b\right)=P_{l\lambda}\left(\cos\theta_a\right)P_{l'\lambda}\left(\cos\theta_b\right). \tag{12}$$

Using the definition of the normalized associated Legendre function in (7) and the interrelation between elliptic and spherical polar coordinates, we have presented recently [12, 13] the following formula for the product of two normalized associated Legendre functions:

$$T^{l\lambda,l'\lambda}(\mu\nu)=P_{l\lambda}\left(\frac{l+\mu\nu}{\mu+\nu}\right)P_{l'\lambda}\left(\frac{l-\mu\nu}{\mu-\nu}\right)=\\ \sum_{k,k'}\sum_{u,s}a^{kk'}_{us}(l\lambda,l'\lambda)\frac{(\mu\nu)^s}{(\mu+\nu)^{l-2(k+k'+\lambda-u)}(\mu-\nu)^{l'}}, \tag{13}$$

where the expansion coefficients $a^{kk'}_{us}(l\lambda,l'\lambda)$ are

$$a^{kk'}_{us}(l\lambda,l'\lambda)=(-1)^u C^{k}_{l\lambda}C^{k'}_{l'\lambda}F_u(k+k'+\lambda)\cdot F_s(l-2k+2u,l'-2k'-\lambda), \tag{14}$$

and $F_m(N,N')$ is the expansion coefficient in

$$(\mu+\nu)^N(\mu-\nu)^{N'}=\sum_{m=0}^{N+N'}F_m(N,N')\mu^{N+N'-m}\nu^m, \tag{15}$$

defined by [20]

$$F_m(N,N') = \sum_{i=0}^{m}\sum_{j=0}^{m}(-1)^{N'-j}\delta_{m,(i+j)}F_i(n)F_j(N'). \quad (16)$$

The ranges of the summation indices are as follows:

$$\begin{aligned} &0 \le k \le E\left(\frac{l-\lambda}{2}\right),\ 0 \le k' \le E\left(\frac{l'-\lambda}{2}\right),\\ &0 \le u \le (k+k'+\lambda),\\ &0 \le s \le (l+l') - 2(k+k'+\lambda-u). \end{aligned} \quad (17)$$

The symmetry properties and recurrence relations for the expansion coefficients $a_{us}^{kk'}$ are given in the Appendix. Some different expansion formulae for the product of two associated Legendre functions can be found in [8j), 8k)]. Despite these different expansion formulae can be transformed into one another, they can not enable one to have the same satisfactory results due to their mathematical structure. It will be seen from the next Sections of this paper that our expansion formula enables us to obtain higher accuracy for arbitrary molecular parameters.

4. Unified Formula for Two-Center One-Electron Molecular Integrals over Integer and Noninteger *n*-STOs

Substituting (13) and (14) in the integrals given by (1) – (3), we express the two-center one-electron molecular integrals (overlap and nuclear attraction integrals) over integer and noninteger *n*-STOs in a lined-up coordinate system by the following unified formula:

$$I^{(i,j)}_{nl\lambda,n'l'\lambda}\left(\zeta,\zeta';\vec{R}\right) = I^{(i,j)}_{nl\lambda,n'l'\lambda}(p,t) = \left(\frac{2}{R}\right)^{i+j} N_{nn'}(p,t)(-1)^{l'-\lambda}\sum_{k,k'}\sum_{u,s}a^{kk'}_{us}(l\lambda,l'\lambda)Q^s_{N-i,N'-j}(p,t), \quad (18)$$

where

$$\begin{aligned} &N = (n+n')-(l+l')+2(k+k'+\lambda-u)+s-h,\\ &N' = s+h, \quad p = R(\zeta+\zeta')/2,\\ &t = (\zeta-\zeta')/(\zeta+\zeta'), \end{aligned} \quad (19)$$

$$N_{nn'}(p,t) = \frac{[p(1+t)]^{n+\frac{1}{2}}[p(1-t)]^{n'+\frac{1}{2}}}{\sqrt{\Gamma(2n+1)\Gamma(2n'+1)}}, \quad (20)$$

and the function $Q^s_{N,N'}(p,t)$ is an integral of the form

$$Q^s_{N,N'}(p,t) = \int_1^{\infty}\int_{-1}^{+1}(\mu+\nu)^N(\mu+\nu)^{N'}(\mu\nu)^s \cdot e^{-p\mu-pt\nu}\mathrm{d}\mu\mathrm{d}\nu. \quad (21)$$

The accuracy of our formula for two-center one-electron molecular integrals given by (18) depends strongly on the efficient calculation of the function $Q^s_{N,N'}(p,t)$. Using the expansion in (15), this function can be easily expanded as

$$Q^s_{N,N'}(p,t) = \sum_{m=0}^{N+N} F_m(N,N')A_{N+N'+s-m}(p)B_{s+m}(pt)$$

for integer N,N',

$$Q^s_{N,N'}(p,t) = \lim_{Q\to\infty}\sum_{m=0}^{Q} f_m(N,N')A_{N+N'+s-m}(p) \cdot B_{s+m}(pt) \quad (22)$$

for noninteger N,N',

where the functions $A_k(p)$ and $B_k(pt)$ are well-known Mulliken's integrals [21]. A detailed discussion of these functions can be found in [22] and the Appendix of [12]. The auxiliary function $Q^s_{NN'}(p,t)$ for integers N and N' has been described first in [8j)] and some usefull recurrence relations for this function can be seen in [8j)].

The presented expression (18) for two-center one-electron molecular integrals is a unified formula for two-center overlap and two types of nuclear attraction integrals depending on the values of the couple $(i,\, j)$. That is, the couples $(i,\, j)$ in (18) are: (0,0) for two-center overlap integrals, (1,0) for two-center nuclear attraction integrals $U^{(A)}$, and (0,1) for two-center nuclear attraction integrals $U^{(B)}$.

In the nonintegral case of (22), $f_m(N,N')$ is given by

$$f_m(N,N') = \sum_{\sigma=0}^{m}(-1)^{\sigma}f_{m-\sigma}(N)f_{\sigma}(N'), \quad (23)$$

where

$$f_m(N) = \frac{\Gamma(N+1)}{m!\,\Gamma(N-m+1)}. \quad (24)$$

Table 1. Comparative values of two-center overlap integrals over integer *n*-STOs (in a. u.).

n	l	n'	l'	λ	ζ	ζ'	R	**This work-Eq. (18) for $i=0, j=0$**	**Literature**	
2	0	1	0	0	1.3	6.2	1.0	1.46701781424007 E-01	—	
3	2	3	2	2	5.8	4.5	8.7	7.934310054947300E-15	7.934310054948 E-15	[8a)]
4	2	3	2	1	5	5	5	−5.655544714928136E-06	−5.65554471492814E-06	[8g)]
5	4	4	3	3	5.1	7.2	2.6	2.17961200414942 E-03	—	
7	4	7	4	4	1.0	3.0	1.0	1.10110477764970 E-01	1.10110477764970E-01	[8b)]
10	0	10	2	0	2.5	3.0	3.0	−1.67748511444053 E-01	−1.677485114 E-01	[8c)]
10	7	8	1	1	5.0	5.0	5.0	1.52138456890820 E-02	1.52138456890819E-02	[8d)]
10	9	11	10	9	1.5	0.5	2.4	−1.69505145438257 E-02	—	
11	8	9	5	5	20	1.0	1.0	−5.65362429908826 E-10	−5.65362430 E-10	[8f)]
11	9	11	5	5	1.0	1.0	1.0	6.69780683306607 E-05	6.697806833065 E-05	[8f)]
13	12	13	12	11	4.0	4.0	2.5	−4.01371353397628 E-01	−4.01371353397597E-01	[8d)]
15	4	8	4	4	5	5	5	2.54324132559905 E-03	2.5432413255908 E-03	[8g)]
15	11	13	9	5	5.5	4.5	3.2	4.70059291056680 E-02	—	
18	10	18	17	9	4	4	5	−1.14908694660295 E-02	−1.14908694660295E-02	[8g)]
18	17	19	18	17	7.5	2.5	1.2	−2.50431130553536 E-03	—	
25	20	23	21	20	7.0	3.0	0.8	−2.07368720040068 E-02	—	
29	25	28	26	25	6.0	4.0	0.4	−1.08326409521208 E-01	—	
34	14	34	12	10	3	3	25	1.3527925684325 E-04	1.30016393590254E-04	[8g)]
38	13	36	20	8	5.3	4.1	2.1	−1.05816984077981 E-02	—	
40	8	30	7	7	9.5	0.5	6.0	−4.70039559672119 E-17	−4.70039545616601E-17	[8e)]
46	6	49	11	5	8.0	2.0	3.0	−1.48044811194617 E-13	—	
50	15	15	13	11	1	1	10	2.90100707200582 E-04	2.90100707205215E-04	[8g)]
55	20	52	23	20	5	5	7	−2.58332568976321 E-01	−1.78167728016314E-01	[8g)]
56	4	58	5	3	6.0	4.0	1.0	−2.67785477132371 E-04	—	
60	14	52	17	12	5	5	7	−2.62097248323569 E-02	−7.50777781146405E-02	[8g)]
62	19	52	17	15	1	1	10	3.16515414846025 E-01	3.16515414845183E-01	[8g)]
65	24	65	20	18	0.01	0.01	1	2.95687254441400 E-14	−1.26130790353512E-10	[8g)]
68	1	70	2	0	5.5	4.5	2.0	−1.22049329384116 E-05	—	
70	15	65	13	10	0.01	0.01	0.01	−3.46058313255987 E-06	3.65666732448635E-03	[8g)]
75	30	75	20	18	0.001	0.001	0.001	−5.25685560022314 E-64	−4.92600264607547E-08	[8g)]

Taking into account the asymptotic behavior of the gamma function [12] for $m \to \infty$, the function $f_m(N)$ takes the form

$$\lim_{m\to\infty} f_m(N) = \frac{(-1)^m \Gamma(m-N)}{m!\,\Gamma(-N)}. \tag{25}$$

5. Computational Results and Discussion

We have established a unified expression for the evaluation of two-center one-electron molecular integrals by the use of the expansion formula for the product of two normalized associated Legendre functions centered on the nuclei a and b. The obtained expression includes the expansion coefficients $a_{us}^{kk'}(l\lambda, l'\lambda)$, $F_m(N,N')$, $f_m(N,N')$ and an auxiliary function $Q^s_{N,N'}(p,t)$, which includes the Mulliken integrals $A_n(p)$ and $B_n(pt)$.

On the basis of the unified expression given by (18), we constructed computer programs for the evaluation of two-center one-electron molecular integrals over integer and noninteger *n*-STOs. The coefficients $F_m(N,N')$, $f_m(N,N')$, $a_{us}^{kk'}(l\lambda, l'\lambda)$, and the auxiliary functions A_k and B_k are stored in the memory of the computer before the calculations and retrived from the memory during the calculation for reducing the computation time.

The comparative values of two-center overlap integrals over integer and noninteger *n*-STOs are given in Tables 1 and 2, respectively, for a wide range of quantum numbers, orbital exponents and internuclear distances. As can be seen from Table 1, the computer results for two-center overlap integrals over integer *n*-STOs are found to agree completely with the literature data [8a – f]. There arise some discrepancies with very high quantum numbers in [8g], in which three different algorithms have been presented for the evaluation of two-center overlap integrals over integer *n*-STOs with equal orbital exponents, and agreement between their two algorithms is found. Investigating the algorithm presented in [8g], it is understood that both algorithms start with the same set of auxiliary functions and starting points. At the same time, the staring point in the

Table 2. Comparative values of two-center overlap integrals over noninteger n-STOs (in a. u.).

n	l	n'	l'	λ	ζ	ζ'	R	**This work-Eq. (18) for $i=0, j=0$**	**[10d)]**
1.7	0	1.7	0	0	0.3	0.2	0.2	9.13962955185213E-01 (48)	—
2.4	1	2.4	1	0	2.3	1.2	0.12	7.33749238098386E-01 (46)	—
3.6	2	4.8	3	1	4.8	3.6	1.4	1.17732795279297E-01 (44)	—
3.8	0	5.5	0	0	2.2	1.1	1.4	2.90802046505185E-01 (49)	2.90802069369 E-01
4.5	3	5.4	2	1	3.4	2.8	0.4	1.93177056647043E-01 (30)	—
5.7	1	3.8	1	1	2.1	1.3	1.4	8.66889506327292E-01 (47)	8.66889476942 E-01
7.3	4	7.3	4	4	3.0	1.0	1.0	1.01734314959567E-01 (12)	1.01734314960 E-01
7.7	4	6.6	4	4	0.9	1.5	5.0	2.34831461283908E-01 (47)	2.34831448531 E-01
8.4	5	7.2	4	3	6.0	4.0	1.8	−1.67049133111712E-03 (30)	
9.5	8	8.7	7	7	1.2	1.5	2.4	5.01119569690299E-01 (13)	—
9.8	2	8.3	4	1	1.5	0.5	0.14	1.83392891636172E-06 (7)	—
11.3	8	13.7	6	4	2.3	1.8	2.1	7.39040600721031E-02 (19)	—
15.7	14	18.2	16	13	3.1	1.4	0.8	4.75031165481152E-03 (8)	—
18.5	9	17.6	8	3	5.2	4.8	3.0	3.15950816741387E-02 (24)	—
18.7	5	16.4	5	4	7.0	3.0	0.6	1.03539437523603E-03 (14)	—
20.3	9	11.3	8	6	8.0	2.0	1.7	1.40804977117408E-04 (24)	—
24.9	21	23.8	21	20	1.3	1.1	1.7	8.11254512604098E-01 (7)	—
32.2	21	35.7	20	15	3.2	3.6	0.2	1.46808686307348E-01 (7)	—
37.3	11	39.8	12	4	5.5	4.5	3.2	1.84721225622118E-01 (26)	—
49.7	5	49.1	5	5	5.5	4.5	0.14	6.4186085308399 E-01 (7)	—

The numbers in parantheses denote the upper limit of the summation indices Q in (22).

Table 3. Two-center nuclear attraction integrals over integer n-STOs (in a. u.).

n	l	n'	l'	λ	ζ	ζ'	R	$U^{(A)}$**(Eq. (18) for $i=1, j=0$)**	$U^{(B)}$**(Eq. (18) for $i=0, j=1$)**
4	3	5	4	2	9	1	0.8	4.24534017683082E-03	2.18066558934826E-03
5	4	6	3	2	6	4	3	2.31925894422871E-02	1.79934638013278E-02
8	4	7	5	3	7	3	2	−1.15088507166162E-01	−1.00593845425167E-01
10	9	10	8	8	8	2	1.6	−1.04550467576996E-03	−1.12874460630165E-03
12	10	13	5	2	7.5	2.5	1.4	−4.35457130833401E-06	1.09803124016626E-05
15	12	13	12	12	6.5	3.5	0.5	−1.42672063462406E-01	−1.42130861520079E-01
20	9	13	8	8	4	6	1.5	−2.04362216593653E-02	−2.32188069444587E-02
23	20	25	23	18	1.2	3.8	0.9	6.06040723190944E-07	4.44921766119358E-07

Table 4. Two-center nuclear attraction integrals over noninteger n-STOs (in a. u.).

n	l	n'	l'	λ	ζ	ζ'	R	$U^{(A)}$**(Eq. (18) for $i=0, j=0$)**	$U^{(B)}$**(Eq. (18) for $i=0, j=0$)**
10	0	1.3	0	0	1.2	3.8	0.9	3.78534217246586E-01 (3)	6.86114372414011E-01 (2)
2.3	1	2.7	1	0	3	2	3.8	−8.86457891398012E-02 (4)	−3.12407060352115E-02 (4)
3.8	2	2.3	2	1	1.5	1.5	2.0	−6.34167203084412E-02 (44)	−4.48501537580678E-02 (44)
4.7	3	5.3	3	3	6	4	2.5	7.96038841339142E-03 (9)	7.23965763701582E-03 (9)
5.3	3	6.4	4	2	1.6	0.4	1.8	−5.02978305305875E-03 (35)	−4.11119047441547E-03 (37)
8.7	6	7.6	4	4	5.5	4.5	1.5	1.91779893207921E-01 (35)	2.62105967096993E-01 (34)
12.5	10	10.7	6	4	8.5	1.5	0.2	−2.14380494481450E-09 (13)	−5.35990573368964E-09 (12)
19.8	18	20.3	18	18	1.5	0.5	2.3	9.78428512486167E-05 (7)	9.74967147175635E-05 (6)

The numbers in parantheses denote the upper limit of the summation indices Q in (22).

two algorithms has been obtained with the recurrence relation. These two important points may be the cause of the discrepancies with our results.

The computer results for two-center overlap integrals over noninteger n-STOs have been given in Table 2. Comparison with the study of Mekelleche and Baba-Ahmed [10] was made because of the scarcity of the literature on the evaluation of two-center overlap integrals over noninteger n-STOs. It is seen from Table 2 that the computer results agree well with their more recent results [10d)].

Numerical results for two-center nuclear attraction integrals over integer n-STOs are listed in Table 3. Our computer results for two-center nuclear attraction integrals over integer n-STOs are in best agreement with the literature [10c), 23 – 25]. Some examples of two-center nuclear attraction integrals over noninteger n-STOs are presented in Table 4 with no comparison because of the scarcity of the literature. The computer results for two center nuclear attraction integrals over integer n-STOs have been compared with the limiting case of noninteger n-STOs for checking our values, and best agreement has been obtained. Also, we note that our computer results for two-center overlap and nuclear attraction integrals agree well with the results obtained via the formula we presented recently [12, 13, 23].

The computer time required for the calculation of two-center one-electron integrals is not given in the Tables because comparison can not be made for the different computers used in the literature. It is seen from the algorithm presented for two-center one-electron integrals that our CPU times are satisfactory. For instance: for two-center integrals with the quantum sets $n = n' = 7.3$, $l = l' = 4$, $\lambda = 4$, $\zeta = 3$, $\zeta' = 1$, and $R = 1$, the CPU time takes about 2.3 milliseconds. So, the algorithm presented in this work is faster than others.

Consequently, the unified formulae given in this study for the evaluation of two-center one-electron molecular integrals over integer and noninteger n-STOs show a good rate of convergence and great numerical stability for a wide range of quantum numbers, orbital exponents and internuclear distances. Work is in progress for the evaluation of the multicenter molecular integrals over integer and noninteger n-STOs based on the computer results for two-center one-electron molecular integrals given in this paper.

The computer program is written in the Turbo Pascal 7.0 programming language on a Pentium 233 MHz computer. In all parts of the program double precision arithmetic is used.

Appendix

In the evaluation of two-center molecular integrals the following symmetry and recurrence relations are taken into account for reducing the computing time.

A) Symmetry Properties for the Expansion Coefficients $a_{us}^{kk'}(l\lambda, l'\lambda)$

$$a_{us}^{kk'}(l\lambda, l'\lambda) = a_{us}^{k'k}(l'\lambda, l\lambda), \tag{26}$$

$$a_{us}^{k'k}(l'\lambda, l\lambda) = (-1)^s a_{us}^{k'k}(l\lambda, l'\lambda). \tag{27}$$

B) Recurrence Relations for the Expansion Coefficients $a_{us}^{kk'}(l\lambda, l'\lambda)$

For reducing the computing time, the following recurrence relations for the expansion coefficients $a\,_{us}^{kk'}(l\lambda, l'\lambda)$ can be used:

$$a_{us}^{kk'}(l\lambda, l'\lambda) = \gamma_{us}^{kk'}(l\lambda, l'\lambda)\, a_{us}^{k-1k'}(l\lambda, l'\lambda), \tag{28}$$

$$a_{us}^{kk'}(l\lambda, l'\lambda) = \gamma_{us}^{k'k}(l'\lambda, l\lambda)\, a_{us}^{kk'-1}(l\lambda, l'\lambda), \tag{29}$$

with

$$\begin{aligned}\gamma_{us}^{kk'}(l\lambda, l'\lambda) = &-\frac{(l-\lambda-2k+1)(l-\lambda-2k+2)}{(l-\lambda-2k+2u+1)(l-\lambda-2k+2u+2)}\,\frac{(k+k'+\lambda)}{4k(k+\lambda)(k+k'+\lambda-u)}\\ &\cdot\sum_{\sigma=0}^{s}(l-2k-\lambda+2u-s+\sigma+1)(l-2k-\lambda+2u-s+\sigma+2).\end{aligned} \tag{30}$$

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