On the Accurate Evaluation of Overlap Integrals over Slater Type Orbitals Using Analytical and Recurrence Relations

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In this study, using the analytical and recurrence relations suggested by the authors in previous works, the new efficient and reliable program procedure for the overlap integrals over Slater type orbitals is presented. The proposed procedure guarantees a highly accurate evaluation of the overlap integrals with arbitrary values of quantum numbers, screening constants and internuclear distances. It is demonstrated that the computational accuracy of the proposed procedure is not only dependent on the efficiency of formulas, as has been discussed previously, but also on a number of other factors including the used program language package and solvent properties. The numerical results obtained, using the algorithm described in the present work, are in complete agreement with those obtained using the alternative evaluation procedure. We notice that the program works without any restrictions and in all ranges of integral parameters.

Key words: Slater Type Orbitals; Overlap Integrals; Recurrence Relations; Auxiliary Functions.

1. Introduction

In the study of the electronic structure of molecules, one has to evaluate overlap integrals over Slater type orbitals (STOs) accurately and efficiently. These integrals arise not only in the Hartree-Fock-Roothaan equations for molecules, but are also central to the calculation of arbitrary multicenter integrals based on the series expansion formulas about a new center and one-range addition theorems for STOs [1] which necessitate to accurately calculate the overlap integrals especially for the large quantum numbers. It should be noted that the overlap integrals over STOs are also used in all of the semiempirical methods [2].

The aim of this report is to calculate the overlap integrals over STOs using the analytical approach containing well-known auxiliary functions, A_k and B_k and the recurrence relations for the basic overlap integrals presented in our previous works [3 – 5]. These expressions are especially useful for computation of overlap integrals on the computer for high quantum numbers, internuclear distances and orbital exponents or vice versa.

In this work, the differences and similarities in organization of existing overlap integral programs are discussed, and a new strategy is developed. This method is computationally simple and numerically well behaved. On the basis of formulas obtained in the papers [3 – 5] we constructed a program for computation of the overlap integrals over STOs using Mathematica 5.0 international mathematical software and Turbo Pascal language packages. The numerical results demonstrate that the computational accuracy of the established formulas is not only dependent on the efficiency of formulas, but also strongly depends on the used program language packages. Excellent agreement with benchmark results and stability of the technique are demonstrated. Since the overlap integrals over STOs are of considerable importance in the evaluation of arbitrary multicenter integrals, it is hoped that the present work will prove useful in tackling more complicated molecular integrals appearing in the determination of various properties for molecules when the Hartree-Fock-Roothaan approximation is employed.

2. Definition

The two-center overlap integrals over STOs with respect to lined-up coordinate systems are defined as

$$S_{nl\lambda,n'l'\lambda}(p,t) = \int \chi^*_{nlm}(\zeta,\vec{r}_a)\chi_{n'l'm}(\zeta',\vec{r}_b)\mathrm{d}V, \quad (1)$$

Table 1. Comparison of our results with those of Barnett [12].

n	l	n'	l'	λ	p	t	Equations (3) and (7), Turbo Pascal procedure	Equations (3) and (7), Mathematica procedure	Ref. [12], Mathematica procedure
3	2	3	2	1	25	0.6	−4.42287766988261E-04	−4.42287766988260880679541 5E-04	−4.42287 76698 82608 80679E-04
4	2	4	3	1	80	0.4	4.03505950326382E-17	4.03505950326382981089607 7E-17	4.03505 95032 63822 98108E-17
5	4	5	4	4	100	0.7	1.56200599153976E-14	1.56200602745789103745217 9E-14	1.56200 60274 57891 03745E-14
7	3	4	3	2	150	0.7	−1.76861050697887E-18	−1.76861050692264859080888 4E-18	−1.76861 05069 22648 59080E-18
9	5	8	4	3	45	0.2	−5.46510243022867E-08	−5.46510243022704017382499 7E-08	−5.46510 24302 27040 17382E-08
10	7	8	2	1	60	0.2	−1.84189026173558E-10	−1.84189026173198106424398 4E-10	−1.84189 02617 31981 06424E-10
10	9	10	9	9	15	0.6	6.23122318196866E-04	6.23122318191124946475610 2E-04	6.23122 31819 11249 46475E-04
13	12	13	12	12	25	0.01	1.35310560392189E-04	1.35310578702471238186186 8E-04	1.35310 57870 24712 38186E-04
14	13	14	13	13	15	0.4	4.53551312156525E-03	4.53551285106790911552303 2E-03	4.53551 28510 67909 11552E-03
15	14	15	14	14	15	0	3.74722497038009E-02	3.74722497038189195430608 4E-02	3.74722 49703 81891 95430E-02
16	15	16	15	15	35	0	1.21686562253236E-06	1.21686521859019818856906 1E-06	1.21686 52185 90198 18856E-06
17	8	8	7	4	50	0.1	−1.00640061354258E-06	−1.00640064117188172346740 0E-06	−1.00640 06411 71881 72346E-06
17	16	17	16	16	25	−0.5	3.06769565185575E-05	3.06770325579019360938038 5E-05	3.06770 32557 90193 60938E-05
18	12	18	12	12	20	−0.6	6.63931813651240E-05	6.63931813696650677513212 0E-05	6.63931 81369 66506 77513E-05
21	10	9	8	6	45	0	5.38980685350612E-05	5.38980685338143773017272 0E-05	5.38980 68533 8143 773017E-05
27	8	9	8	7	35	−0.2	−1.73300982799699E-04	−1.74423807519695909193661 8E-04	−1.74423 80751 96959 09193E-04
30	10	14	10	8	35	0	1.35074709592800E-02	1.35074709593243338875633 5E-02	1.35074 70959 32433 38875E-02
37	8	12	10	6	10	−0.6	3.98219849004259E-14	3.98228004377091573596209 1E-14	3.98228 00437 70915 73596E-14
40	4	12	4	3	15	0.6	9.48379265599810E-02	9.48379220832255678538438 4E-02	9.48379 22083 22556 78538E-02
43	10	18	8	6	60	−0.4	−1.15907687123104E-04	−1.15825653267174814660554 5E-04	−1.158256 53267 1748 14660E-04
50	4	50	4	4	25	0.7	1.84395901037228E-12	1.84395879932436340310020 8E-12	1.84395 87993 24363 40310E-12

where

$$0 \le \lambda \le l, \quad m = \pm\lambda, \quad p = \frac{R}{2}(\zeta + \zeta'),$$
$$t = (\zeta - \zeta')/(\zeta + \zeta'), \quad \vec{R} \equiv \vec{R}_{ab} = \vec{r}_a - \vec{r}_b,$$

and

$$\chi_{nlm}(\zeta, \vec{r}) = (2\zeta)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}} r^{n-1} e^{-\zeta r} S_{lm}(\theta\varphi). \quad (2)$$

Here, S_{lm} is the complex ($S_{lm} = Y_{lm}$) or real spherical harmonic. It should be noted that our definition of phases for complex spherical harmonics $Y^*_{lm} = Y_{l-m}$ differs from the Condon-Shortley phases [6] by the sign factor.

3. Analytical Relations in Terms of Auxiliary Functions

In [3], using the auxiliary function method for the overlap integrals the following formula has been established:

$$S_{nl\lambda,n'l'\lambda}(p,t) = N_{nn'}(t) \sum_{a=-\lambda}^{l} {}^{(2)} \sum_{\beta=\lambda}^{l'} {}^{(2)} g^0_{\alpha\beta}(l\lambda, l'\lambda)$$
$$\cdot \sum_{q=0}^{\alpha+\beta} F_q(\alpha+\lambda, \beta-\lambda) \sum_{m=0}^{n+n'-\alpha-\beta} F_m(n-\alpha, n'-\beta)$$
$$\cdot A^{n+n'+1}_{n+n'-\alpha-\beta-m+q}(p) B_{m+q}(pt), \quad (3)$$

where $N_{nn'}(t)$, $F_m(N,N')$, and $A^k_n(p)$ are determined by

$$N_{nn'}(t) = \frac{[(1+t)]^{n+1/2}[(1-t)]^{n'+1/2}}{\sqrt{(2n)!(2n')!}}, \quad (4)$$

$$F_m(n,N') = \sum_{\sigma=\frac{1}{2}[(m-n)+|m-n|]}^{\min(m,N')} (-1)^\sigma F_{m-\sigma}(N) F_\sigma(N'), \quad (5)$$

$$A^k_n(p) = p^k A_n(p). \quad (6)$$

Here, $F_m(n) = n!/[m!(n-m)!]$ are the binomial coefficients and $k \ge n+1$. It should be noted that (5) for the generalized binomial coefficients with different notation $D^{NN'}_m$ firstly has been presented by Rosen [7]. The quantities $A_n(p)$ and $B_n(pt)$ occurring in (3) and (6) are well known auxiliary functions [8] (see also [9]).

The quantities $g^0_{\alpha\beta}(l\lambda, l'\lambda)$ in (3) are the expansion coefficients for a product of two normalized Legendre functions in elliptic coordinates. The relationship for these coefficients in terms of factorials was given in [10]. In [11], these coefficients were expressed in terms of binomial coefficients.

4. Use of Recurrence Relations for Basic Overlap Integrals

In [5], using the expansion formula for a product of two spherical harmonics both with the same center

Table 2. Comparative values of the two-center overlap integrals over STOs in lined-up coordinate systems for small and high values of integral parameters.

n	l	n'	l'	λ	p	t	Equations (3) and (7), Mathematica procedure	Equations (3) and (7), Turbo Pascal procedure
7	4	7	4	4	0.01	0.01	0.99924789827031604141 2006	0.999247898270316
7	4	7	4	4	0.1	0.001	0.99975776677973292939 3514	0.999757766779732
7	4	7	4	4	0.01	0.001	0.99999015239715781346358966	0.999990152397158
7	4	7	4	4	0.0	0.0	1.00000000000000000000000000	1.00000000000000000
7	4	7	4	4	0.001	0.1	0.92739329037943788468 4943	0.927393290379438
8	7	8	7	7	1E-4	1E-4	0.99999991470588556843130229397	0.999999914705885
8	7	8	7	7	1E-6	1E-6	0.99999999999147058823532627 2549	0.999999999991471
8	7	8	7	7	1E-6	−0.5	0.08670032767073938939427324 64838	0.0867003276707394
10	9	10	9	9	1E-8	0.6	9.22337203685477579394533784 86E-03	9.22337203685478E-03
10	9	10	9	9	0.0	0.0	1.00000000000000000000000000	1.000000000000000
10	9	10	9	9	1E-8	1E-8	0.99999999999999894761904761905	0.99999999999999
10	9	10	9	9	1E-5	−0.8	2.19369506403590528994511164E-05	2.19369506403591
12	10	12	10	10	1E-5	1E-5	0.99999999874817265352528614 0114	0.999999998748173
12	10	12	10	10	1E-6	1E-6	0.99999999998748172652811 2453	0.999999999987482
12	10	12	10	10	1E-6	0.1	0.88194181179889565501056834 1338	0.881941811798896
12	10	12	10	10	1E-4	−0.6	3.77789318590102512480044787 1E-03	3.77789318590103E-03
7	6	7	6	6	50	0.1	1.46022337829746637671 1404E-14	1.46022337769784E-14
10	9	16	10	9	60	0.1	−4.91326865764212881432637 55E-13	−4.91327027112068E-13
10	9	16	10	9	60	0.01	−1.81096789566647263861898 93E-13	−1.81096834940493E-13
13	10	13	10	10	35	0.1	9.76348508560255594773647305E-07	9.76348559116148E-07
7	4	7	4	4	100	0.1	2.72292316027798424617358955E-31	2.72292315888289E-31
75	30	75	20	18	1E-6	0.0	−8.19297549621687882025926 3E-78	−8.19297549621688E-78

[10], the overlap integrals (1) were expressed through the basic overlap integrals

$$S_{nl\lambda,n'l'\lambda}(p,t) = \sum_{l''=\lambda}^{l} \frac{[2p(1+t)]^l}{[2p(1-t)]^{l''}} \Big\{ \big[(2l+1)(2l'')!F_{2n'} \cdot (2n'+2l'')F_{l''+\lambda}(l+\lambda)F_{l''-\lambda}(l-\lambda)\big] \Big/ \big[(2l''+1)(2l)!F_{2n-2l}(2n)\big] \Big\}^{1/2} \cdot \sum_L \sqrt{2L+1}C^L(l'\lambda,l''\lambda)S_{n-l00,n'+l''L0}(p,t), \quad (7)$$

where $C^L(l'\lambda,l''\lambda)$ are the Gaunt coefficients. With the aid of recurrence relations given in [5], the basic overlap integrals $S_{n00,n'l'0}(p,t)$ appearing in (7) can be expressed in terms of the functions $S_{00}(p,t) \equiv S_{000,000}(p,t)$ and $S_{00}(p,0) \equiv S_{000,000}(p,0)$ for the calculation of which we can use the following analytical formulas:

$$S_{00}(p,t) = \frac{1}{t}\eta_{00}(p,t)\left\{e^{-p(1-t)} - e^{-p(1+t)}\right\}, \quad (8)$$

$$S_{00}(p,0) = e^{-p}. \quad (9)$$

5. Numerical Results and Discussion

On the basis of (3) and (7), obtained in our papers [3–5], we constructed the programs which were performed in the Mathematica 5.0 international mathematical software and Turbo Pascal 7.0 language packages. The computational results of overlap integrals by the use of the Turbo Pascal 7.0 language package program have been examined in our published papers [3–5]. The Barnett's data [12] and results of our calculation using Mathematica 5.0 international mathematical software and Turbo Pascal 7.0 language packages for various values of parameters are represented in Table 1. Barnett's data are reproduced by using our scheme with Mathematica while we get different results using the same scheme with Turbo Pascal. Thus, in this paper we show that the discrepancies can be arisen in the case of different programming environments. We note that, the difference between the numerical results of (3) and (7) arise only after forty five digits. It should be noted that for the comparison of the accuracy of computer results obtained from the formulas of overlap integrals, one should use the same program language packages.

It is well known from the expert of this field that the problems occuring in the evaluation of overlap integrals are as follows: small internuclear distances

and small orbital exponents, and high internuclear distances and high orbital exponents. The results of calculation in these cases are given in Table 2. As is clear from our tests that the recurrence and analytical formulas presented in this study are useful tools for the exact evaluation of the overlap integrals with arbitrary values of quantum numbers, internuclear distances and orbital parameters. Thus, our program calculates the overlap integrals over STOs with arbitrary quantum numbers (n, l, n', l', λ) and variables (p, t).

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