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Calculations of overlap integrals over Slater type orbitals using recurrence relations for expansion coefficients

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Abstract

Using formulas for the expansion of overlap integrals with the same screening constants in terms of Slater type orbitals (STOs), sets of recurrence relations are established for the expansion coefficients. These recurrence relations are especially useful in the calculation of overlap integrals for large quantum numbers, which occur in the series expansion formulas for multicenter multielectron integrals of integer- and noninteger-n STOs. An accuracy of the computer results is satisfactory for arbitrary quantum numbers, screening constants and location of atomic orbitals.

Keywords: Slater type orbitals, Overlap integrals, Recurrence relations, Screening constants

I. Introduction

The calculation of overlap integrals of integer n STOs with the same screening constants is of fundamental importance in the study of arbitrary multicenter multielectron molecular integrals over integer- and noninteger n STOs [1]. Probably, this was the reason why overlap integrals have been examined thoroughly in the literature (see Refs.[2-4] and references therein). It is not very difficult to calculate overlap integrals with the same screening constants for small quantum numbers, though various difficulties arise for large quantum numbers appearing in the series expansion formulas for the above-mentioned multicenter integrals.

The overlap integrals with the same screening constants in the nonaligned (molecular) and aligned coordinate systems are defined by

$$S_{nlm,n'l'm'}(\vec{p}) = \int \chi^*_{nlm}(\zeta,\vec{r}_a)\chi_{n'l'm'}(\zeta,\vec{r}_b)dV \tag{1}$$

and

$$S_{nl\lambda,n'l'\lambda}(\vec{p}) = \int \chi^*_{nl\lambda}(\zeta,\vec{r}_a)\chi_{n'l'\lambda}(\zeta,\vec{r}_b)dV\,, \tag{2}$$

where $\lambda = |m| = |m'|$, $\vec{p} = \zeta\vec{R}$, $\vec{R} \equiv \vec{R}_{ab} = \vec{r}_a - \vec{r}_b$ and

$$\chi_{nlm}(\zeta,\vec{r}) = R_n(\zeta,r)S_{lm}(\theta,\varphi)\,,\quad R_n(\zeta,r) = (2\zeta)^{n+\frac{1}{2}}\left[(2n)!\right]^{-\frac{1}{2}}\, r^{n-1}e^{-\zeta r}. \tag{3}$$

Here the spherical harmonics S_{lm} are determined by the relation [5]

$$S_{lm}(\theta,\varphi) = P_{l|m|}(\cos\theta)\Phi_m(\varphi)\,, \tag{4}$$

where $P_{l|m|}$ are normalized associated Legendre functions and

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi} \qquad \text{for complex SH,} \tag{5}$$

$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}}\begin{cases}\cos|m|\varphi & for\ \ m \geq 0\\ \sin|m|\varphi & for\ \ m < 0\end{cases} \qquad \text{for real SH.} \tag{6}$$

In Refs.[6] and [7], using the Fourier transform convolution theorem and the auxiliary function method the following formulas have been established for overlap integrals in terms of STOs:

$$S_{nlm,n'l'm'}(\vec{p}) = \sqrt{4\pi}\sum_{N=1}^{n+n'+1}\sum_{L=|l-l'|}^{l+l'}\sum_{M=-L}^{L} g^{NLM}_{nlm,n'l'm'}\chi^*_{NLM}(1,\vec{p}) \tag{7}$$

and

$$S_{nl\lambda,n'l'\lambda}(p) = \sqrt{4\pi}\sum_{N=1}^{n+n'+1}\sum_{L=|l-l'|}^{l+l'}(2L+1)^{1/2}g^{NL0}_{nl\lambda,n'l'\lambda}\chi^*_{N00}(1,p) \tag{8}$$

$$= e^{-p}\sum_{N=1}^{n+n'+1} a^N_{nl\lambda,n'l'\lambda}p^{N-1}\quad , \tag{9}$$

where

$$a^{N}_{nl\lambda,n'l'\lambda} = \frac{2^{N+1/2}}{\sqrt{(2N)!}} \sum_{L=|l-l'|}^{l+l'} (2L+1)^{1/2} g^{NL0}_{nl\lambda,n'l'\lambda} \ . \tag{10}$$

The analytical formulas for the expansion coefficients $g^{NLM}_{nlm,n'l'm'}$ *and* $a^{N}_{nl\lambda,n'l'\lambda}$ are determined by Eqs.(62) and (12) of Refs.[6] and [7], respectively. The aim of this work is to derive the recurrence relations for basic expansion coefficients $a^{N}_{n00,n'l'0}$ in terms of which to express the coefficients $g^{NLM}_{nlm,n'l'm'}$ *and* $a^{N}_{nl\lambda,n'l'\lambda}$, and to calculate the overlap integrals from Eqs.(7) and (9).

2. Use of expansion relation for translation of spherical harmonics

In order to obtain the expressions for $a^{N}_{nl\lambda,n'l'\lambda}$ in terms of basic expansion coefficients $a^{N}_{n00,n'l'0}$ we use Eqs.(1), (14) and (15) of Ref.[8] for the translation of spherical harmonics centered on the nucleus a in Eqs.[2] and (9). Then using the expansion formula for the product of two spherical harmonics both with the same center [9], it is easy to obtain the following relations:

$$a^{N}_{nl\lambda,n'l'\lambda} = \sum_{l''=\lambda}^{l} \sum_{L=|l-l'|}^{l+l'} 2^{l-l''} \left[\frac{(2l+1)(2L+1)F_{2n'}(2n'+2l'')F_{l''+\lambda}(l+\lambda)F_{l''-\lambda}(l-\lambda)}{(2l''+1)(2l-2l'')!F_{2l''}(2l)F_{2n-2l}(2n)} \right]^{1/2}$$
$$\times C^{L}(l'\lambda, l''\lambda) a^{N-l+l''}_{n-l00,n'+l''L0} \tag{11}$$

$$a^{N}_{nl0,n'00} = \sum_{l''=0}^{l} 2^{l-l''} \left[\frac{(2l+1)F_{2n'}(2n'+2l'')F_{l''}(l)F_{l''}(l)}{(2l''+1)(2l-2l'')!F_{2n-2l}(2n)F_{2l''}(2l)} \right]^{1/2} a^{N-l+l''}_{n-l00,n'+l''l''0} \tag{12}$$

Here the quantities $C^{L}(l'\lambda, l''\lambda)$ are Gaunt coefficients [10] and

$$F_k(n) = \begin{cases} \dfrac{n!}{k!(n-k)!} & \text{for } 0 \le k \le n \\ 0 & \text{for } k<0,\ k>n \end{cases} \ . \tag{13}$$

Now we derive the relation for the coefficients $g^{NLM}_{nlm,n'l'm'}$ in terms of $a^{N}_{nl\lambda,n'l'\lambda}$. For this purpose we take into account Eqs.(17) and (18) of Ref.[7] for the rotation of two-center overlap integrals in Eqs.(1) and (7). Then, integrating over spherical angles we obtain:

$$g^{NLM}_{nlm,n'l'm'} = \frac{\sqrt{(2N)!}}{2^{N+1/2}} \sum_{\lambda=1}^{\min(l,l')} T^{\lambda,LM}_{lm,l'm'} a^{N}_{nl\lambda,n'l'\lambda} \ , \tag{14}$$

where

$$T_{lm,l'm'}^{\lambda,LM} = \frac{1}{\sqrt{4\pi}} \int T_{lm,l'm'}^{\lambda *}(\theta,\varphi) S_{LM}(\theta,\varphi) d\Omega = \frac{2}{(1+\delta_{\lambda 0})(2L+1)^{1/2}} C_{\lambda,-\lambda,0}^{ll'L}$$

$$= \begin{cases} C_{m,-m',m-m'}^{ll'L}\delta_{M,m-m'} & \text{for complex } SH \quad (15) \\ [(1+\delta_{m0})(1+\delta_{m'0})]^{-1/2} \sum_{i=\pm 1} (\varepsilon_{m0})^{\delta_{i,\varepsilon_{mm'}}} C_{i\gamma,\gamma',i\gamma+\gamma'}^{ll'L} [(1+\delta_{M_i 0})/2]^{1/2} \delta_{MM_i} & \text{for real } SH \quad (16) \end{cases}$$

Here the quantities $T_{lm,l'm'}^{\lambda}$ are relation coefficients of overlap integrals (see Ref.[7]) and

$$C_{m_1 m_2 M}^{j_1 j_2 J} = (-1)^{(|m_1|+m_1+|m_2|+m_2+|M|+M)/2} (j_1 j_2 m_1 m_2 / j_1 j_2 LM), \tag{17}$$

where $\gamma = |m|$, $\gamma' = |m'|$, $M_i = \varepsilon_{mm'}|i\gamma + \gamma'|$. For $\gamma = \gamma'$ and $\varepsilon_{mm'} = -1$ terms with a negative value of index i (i= -1) contained in Eq.(16) should be equated to zero. The Clebsh-Gordan coefficients $(j_1 j_2 m_1 m_2 / j_1 j_2 LM)$ in Eq.(17) can be determined from Eq.(2.9) of Ref.[11]. The relationships for Clebsh-Gordan and Gaunt coefficients through the binomial coefficients are given in Ref.[12].

It is easy to show that the coefficients $T_{lm,l'm'}^{\lambda,LM}$ have the following orthonormality relations:

$$T_{lm,l'm'}^{\lambda,00} = \delta_{mm'}\delta_{\lambda|m|} \tag{18}$$

$$\sum_{L=|l-l'|}^{l+l'} (2L+1)^{1/2} T_{l\lambda,l'\lambda}^{\lambda',L0} = \delta_{\lambda\lambda'} \tag{19}$$

Taking into account Eqs.(18) and (19) we get from Eq.(14):

$$g_{nlm,n'l'm'}^{N00} = \delta_{mm'} \frac{\sqrt{(2N)!}}{2^{N+1/2}} a_{nl\lambda,n'l'\lambda}^{N}, \tag{20}$$

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

By the use of Eqs.(11), (12), (14) and (20), all of the coefficients $g_{nlm,n'l'm'}^{NLM}$ and $a_{nl\lambda,n'l'\lambda}^{N}$ can be calculated from the basic coefficients $a_{n00,n'l'0}^{N}$.

3. Recurrence relations for basic expansion coefficients

For lowering the indices l' of the basic expansion coefficients $a_{n,n'l'}^{N} \equiv a_{n00,n'l'0}^{N}$ we take into account in Eqs.(2) and (9) the relation $R \equiv R_{ab} = Z_a - Z_b$ in the aligned up coordinate systems and the recurrence relations for the normalized associated Legendre functions [5]. Then, it is easy to obtain:

$$a^N_{n,n'l'} = -A_{l'-1}\{\frac{1}{[(2n'-1)2n']^{1/2}}a^N_{n,n'-1l'-1} + \frac{1}{4}[(2n'+1)(2n'+2)]^{1/2}a^{N+1}_{n,n'+1l'-1}$$
$$-\frac{1}{4}[\frac{(2n+1)(2n+2)(2n+3)(2n+4)}{(2n'-1)2n'}]^{1/2}a^{N+1}_{n+2,n'-1l'-1}\} - B_{l'-1}a^N_{n,n'l'-2}\ , \tag{21}$$

where $n \ge l,\ n' \ge l'+1,\ l' \ge 1,\ a^0 = a^{-1} \equiv 0$ and the coefficients $A_l \equiv A_{l0}$ *and* $B_l \equiv B_{l0}$ are determined by Eq.(27) for $\lambda = 0$.

By the use of Eq.(21) we can express $a^N_{n,n'l'}$ through the coefficients $a^N_{n,n'} \equiv a^N_{n00,n'00}$ for the calculation of which one can utilize the following recurrence relations:

$$[\frac{n}{2(2n-1)}]^{1/2}a^N_{n-1n'} - \frac{1}{2}[\frac{n(n-1)}{(2n-1)(2n-3)}]^{1/2}a^N_{n-2n'} - [\frac{n'}{2(2n'-1)}]^{1/2}a^N_{nn'-1} + \frac{1}{2}[\frac{n'(n'-1)}{(2n'-1)(2n'-3)}]^{1/2}a^N_{nn'-2}$$
$$+\frac{2^{n+n'-1}}{[(2n)!(2n')!]^{1/2}}\delta_{N,n+n'}(\delta_{n0}-\delta_{n'0}) = 0 \quad \text{for} \quad n>0 \text{ and } n' \ge 0\ (a^N_{nn'} \equiv 0 \text{ for } N > n+n'+1) \tag{22}$$

$$a^N_{0n'} = [\frac{n'}{2(2n'-1)}]^{1/2}a^N_{0n'-1} + 2^{n'}[\frac{2(2n'+1)}{(n'+1)[2(n'+1)]!}]^{1/2}\delta_{N,n'+1} \quad \text{for} \quad n' \ge 0 \tag{23}$$

$$a^N_{nn'} = [\frac{n(2n'+1)}{(2n-1)(n'+1)}]^{1/2}a^N_{n-1n'+1} - [\frac{n(n-1(2n'+1)}{2(2n-1)(2n-3)(n'+1)}]^{1/2}a^N_{n-2n'+1}$$
$$+[\frac{n'}{2(2n'-1)}]^{1/2}a^N_{nn'-1} \qquad \text{for} \quad 1 \le n \le n' \tag{24}$$

Using the recurrence relations (21), (22), (23) and (24), the basic expansion coefficients $a^N_{n00,n'l'0}$ can be calculated from the coefficients $a^N_{000,000}$ determined by

$$a^N_{000,000} = \delta_{N1} \tag{25}$$

For the derivation of Eqs.(22), (23) and (24) we have taken into account in Eq.(9) the recurrence relations for the auxiliary functions $Q^0_{nn'}(p,0)$ (see Ref.[9]) and Eq.(8) of Ref.[7] for $l = l' = \lambda = 0$.

Taking into account the recurrence relation

$$[\frac{1}{3}(2L+1)]^{1/2}\sum_{L'=|L-1|}^{L+1} C^L(L'M,10)g^{NL'M}_{nlm,n'l'm'} = [\frac{(2n+1)(2n+2)}{(2N+1)(2N+2)}]^{1/2}(A_{l\lambda}g^{N+1LM}_{n+1l+1m,n'l'm'}$$
$$+B_{l\lambda}g^{N+1LM}_{n+1l-1m,n'l'm'}) - [\frac{(2n'+1)(2n'+2)}{(2N+1)(2N+2)}]^{1/2}(A_{l'\lambda'}g^{N+1LM}_{nlm,n'+1l'+1m'} + B_{l'\lambda'}g^{N+1LM}_{nlm,n'+1l'-1m'}) \tag{26}$$

one can determine the accuracy of computer results for the expansion coefficients obtained from Eqs.(11), (12) and (14) and recurrence relations (Eqs.(21)-(24)). The coefficients $A_{l\lambda}$ *and* $B_{l\lambda}$ in Eq.(26) are determined by

$$A_{l\lambda}=[\frac{(l-\lambda+1)(l+\lambda+1)}{(2l+1)(2l+3)}]^{1/2},\quad B_{l\lambda}=[\frac{(l-\lambda)(l+\lambda)}{(2l-1)(2l+1)}]^{1/2}\ . \tag{27}$$

4. Discussion

As can be seen from the formulas of this study, the calculation of overlap integrals with the same screening constants can be reduced to the calculation of basic expansion coefficients $a^{N}_{n00,n'l'0}$ followed by the application of several recurrence relations. Taking as starting point the coefficient $a^{N}_{000,000}$ (Eq.25), all the expansion coefficients are obtained by repeated application of recurrence relations (Eqs.(21)-(24)) and analytical formulas (Eqs.(11)-(16)).

The basic expansion coefficients obtained from the recurrence relations are stored in memory and, then, they are used in the calculation of overlap integrals. In order to put these coefficients into, or get them back from the memory the positions of coefficients $a^{N}_{nn'}$ *and* $a^{N}_{n,n'l'}$ are determined by the relations:

$$P_{nn'}(N)=(2N-n+1)/2+n'+1 \qquad \text{for } a^{N}_{nn'} \tag{28}$$

where $N=\max(n,n')$

$$\begin{aligned}P_{L'NN'}(l'nn')&=\frac{L'-1}{2}[(l'+1)(l'+2)-(2l'+3)L'/2+L'(2L'-1)/6]\\&+\frac{i-1}{2}[2(l'-L'+2)-i]+i' \qquad \text{for} \quad a^{N'}_{n,n'l'}\end{aligned} \tag{29}$$

where $1\le L'\le l'$, $n\le N\le n+2l'-2L'$, $n'-l'+L'\le N'\le l'+n+n'-(L'+N)$, $i=(N-n)/2$ and $i'=(N'-(n'-l'+L'))/2+1$. Computation time of overlap integrals is reduced by using Eqs.(28) and (29), and the memory of the computer.

The accuracy of the expansion coefficients is checked with the use of Eq.(26). The Clebsch-Gordan and Gaunt coefficients and their symmetries are calculated from the formulas of Ref.[12] through the binomial coefficients.

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

n	l	m	n'	l'	m'	p	θ	φ	Eq.(7) and Eq.(8) Values	CPU (ms)	Ref.[13] Values
3	2	2	4	3	2	15	0	0	-1.48601950777581E-03	-	-1.48601950777581E-03
5	4	3	5	3	3	150	0	0	4.45601963708570E-55	-	4.45601963708573E-55
7	6	5	8	7	5	0.4	0	0	-1.34430597076390E-01	-	-1.34430597076390E-01
9	7	7	9	8	7	35	0	0	-1.00287352354768E-07	-	-1.00287352354768E-07
11	10	9	12	10	9	55	0	0	-1.55891802859646E-12	-	-1.55891802859646E-12
16	13	11	16	12	11	80	0	0	-2.49482004579593E-17	0.3	-2.49482004579593E-17
20	18	18	23	20	18	18	0	0	1.74097713182219E-01	0.8	1.74097713182219E-01
25	24	24	25	24	24	45	0	0	1.16288667850577E-01	1.3	1.16288667850577E-01
35	31	26	35	27	26	25	0	0	.9.47469674279908E-03	2.7	9.4746974279925E-03
45	25	20	50	27	20	13	0	0	1.07993070672457E-01	5.3	1.07993070672463E-01
65	15	15	50	17	15	8	0	0	7.62832269444606E-03	7.4	7.62832269444621E-03
100	15	2	100	17	2	12	0	0	2.71142396999548E-01	9.8	2.71142396999475E-01
100	25	4	100	25	4	12	0	0	-3.52042197923267E-01	10.3	-3.52042197923411E-01
5	4	4	5	4	4	200	60	36	1.26049931675009E-71	-	1.26049931675009E-71
7	6	6	8	7	6	120	120	72	-1.21521800695026E-34	-	-1.21521800695026E-34
12	10	10	13	11	10	63	180	108	2.16797386103057E-15	-	2.16797386103057E-15
18	17	16	19	18	16	21	45	144	8.59628952224478E-03	0.6	8.59628952224478E-03
24	20	18	20	18	18	34	45	144	1.22791238391418E-04	1.8	1.22791238391431E-04
30	25	20	26	22	20	24	135	180	1.82818761513606E-02	8.5	1.82818761513749E-02
40	27	22	36	22	22	32	60	216	1.41901468218836E-03	8.3	1.41901468218711E-03
67	20	6	60	20	6	13	80	252	-7.17221353592014E-02	9.7	-7.17221353592255E-02
77	12	5	80	6	5	16	100	45	-6.28258066445188E-06	6.4	-6.28258066445394E-06
100	6	5	100	6	5	6	120	90	9.43352601649184E-01	3.4	9.43352601649348E-01

The results of calculations for overlap integrals on a PENTİUM III 800 MHz computer (using Turbo Pascal language) are represented in Table 1. The comparative values obtained from the use of auxiliary function method [13] and the CPU time in milliseconds are given in this table. As can be seen from the table, the accuracy and the CPU time are satisfactory.

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