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Letter

Calculation of overlap integrals over Slater-type orbitals using translational and rotational transformations for spherical harmonics

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Abstract. Using translation and rotation formulas for spherical harmonics the finite sums through the basic overlap integrals and spherical harmonics are derived for the arbitrary overlap integrals over Slater-type orbitals (STOs). The recurrence relations for the evaluation of basic overlap integrals have been established recently [Guseinov II, Mamedov BA (1999) *J Mol Struct* (*THEOCHEM*) 465:1]. By the use of the derived expressions the overlap integrals can be calculated most efficiently and accurately, especially for large quantum numbers of STOs.

Key words: Slater-type orbitals – Overlap integrals – Spherical harmonics

1 Introduction

Overlap integrals constitute the basic building block of many more complicated multicenter molecular integrals occurring in quantum mechanical calculations of the electronic structure of molecules. Particularly, these integrals are of fundamental importance in the approach based on the expansion of Slater-type orbitals (STOs) in terms of STOs at a displaced center [1]. By making use of these expansion formulas, all the molecular integrals appearing in the Hartree–Fock–Roothaan approximation were expressed through the overlap integrals over STOs [2]. The overlap integrals are defined with respect to a molecular coordinate system (non-lined-up coordinate systems) by

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

where $p = \frac{1}{2}(\zeta+\zeta')R, t = (\zeta-\zeta')/(\zeta+\zeta')$ and $(R,\ \theta,\ \phi)$ are the spherical-polar coordinates of radius vector $\vec{R} \equiv \vec{R}_{ab} = \vec{r}_a - \vec{r}_b$; $\chi_{nlm}(\zeta,\vec{r}_a)$ and $\chi_{n'l'm'}(\zeta',\vec{r}_b)$ are normalized STOs centered on the nuclei a and b, respectively,

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

Here the functions S_{lm} are complex or real spherical harmonics defined by

$$S_{lm}(\theta,\phi) = P_{l|m|}(\cos\theta)\Phi_m(\phi) \quad , \qquad (3)$$

where $P_{l|m|}$ are normalized associated Legendre functions [3] and for complex spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}\mathrm{e}^{im\varphi} \qquad (4)$$

and for real spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}}\begin{cases}\cos|m|\phi & \text{for } m \geq 0\\ \sin|m|\phi & \text{for } m < 0\end{cases} \qquad (5)$$

In this letter, using translation and rotation formulas for spherical harmonics, the arbitrary overlap integrals are expressed through the basic overlap integrals $S_{n00,n'l'0}(p,t) \equiv S_{n00,n'l'0}(p,t;0,0)$, the recurrence relations for which were established in Ref. [4]. This algorithm is especially useful for the computation of overlap integrals for large quantum numbers of STOs appearing in the series expansion formulas for molecular integrals.

2 Expansions in terms of basic overlap integrals and spherical harmonics

For deriving the expression of the integral in Eq. (1) in terms of basic overlap integrals $S_{n00,n'l'0}$ and spherical harmonics we take into account the well-known relations for translational and rotational transformations of the spherical harmonics [5–10]. For this purpose we use Eqs. (1), (14) and (15) of Ref. [9] for translation and Eqs. (2), (6), (7) and (16) of Ref. [8] for rotation of spherical harmonics centered on the nucleus a. Then, by the use of expansion formulas for the product of two spherical harmonics both with the same center [11], it is easy to

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obtain for the overlap integrals with respect to non-lined-up coordinate systems the following relations.

For overlap integrals over complex STOs

$$S_{nlm,n'l'm'}(p,t;\theta,\phi) = \sqrt{4\pi}\sum_{v=0}^{l+l'} D^{v}_{nlm,n'l'm'}(p,t)\,Y^{*}_{vm-m'}(\theta,\phi) \ , \tag{6}$$

$$D^{v}_{nlm,n'l'm'}(p,t) = \sum_{l''=0}^{l}\sum_{L=|l'-l''|}^{l'+l''} d^{v,l''L}_{nlm,n'l'm'}\frac{[2p(1+t)]^{l}}{[2p(1-t)]^{l''}} \times S_{n-l00,n'+l''L0}(p,t) \ , \tag{7}$$

$$d^{v,l''L}_{nlm,n'l'm'} = \left[\frac{F_{2n'}(2n'+2l'')(2v+1)(2l+1)(2l'')!}{F_{2n-2l}(2n)[2(l-l'')+1](2l''+1)(2l)!}\right]^{\frac{1}{2}} \times \sum_{m''=l''}^{l''}(-1)^{m'-m''}\Lambda_{lm,l''m''}C^{L}(l'm',l''m'') \times C^{v}(l-l''m-m'',Lm'-m'') \ . \tag{8}$$

For overlap integrals over real STOs

$$S_{nlm,n'l'm'}(p,t,\theta,\phi) = \sqrt{4\pi}\sum_{v=0}^{l+l'}\sum_{\sigma=-v}^{v} \times D^{v\sigma}_{nlm,n'l'm'}(p,t)S^{*}_{v\sigma}(\theta,\phi) \ , \tag{9}$$

$$D^{v\sigma}_{nlm,n'l'm'}(p,t) = \sum_{l''=0}^{l}\sum_{L=|l'-l''|}^{l'+l''} d^{v\sigma,l''L}_{nlm,n'l'm'}\frac{[2p(1+t)]^{l}}{[2p(1-t)]^{l''}} \times S_{n-l00,n'+l''L0}(p,t) \ , \tag{10}$$

$$d^{v\sigma,l''L}_{nlm,n'l'm'} = \left[\frac{F_{2n'}(2n'+2l'')(2v+1)(2l+1)(2l'')!}{F_{2n-2l}(2n)[2(l-l'')+1](2l''+1)(2l)!}\right]^{\frac{1}{2}} \times \sum_{m''=-l''}^{l''}\sum_{i=\pm1}\Lambda^{i}_{lm,l''m''}\sum_{M=-L}^{L}(-1)^{M}C^{L|M|} \times (l'm',l''m'')A^{M}_{m'm''}C^{v|\sigma|}(l-l''m_i,LM)A^{\sigma}_{m_iM} \ . \tag{11}$$

Here $m_i = \varepsilon_{mm''}|i\gamma + \gamma''|$, $\gamma = |m|$, $\gamma'' = |m''|$ and $F_k(n) = \frac{n!}{k!(n-k)!}$. The coefficients $\Lambda_{lm,l'm'}$ and $\Lambda^{i}{}_{lm,l'm}$ in Eqs. (8) and (11) are determined by Eqs. (6) and (7) of Ref. [10]. We note that the quantity $\varepsilon_{i\gamma+\gamma',m}$ in Eq. (7) of Ref. [10] must be replaced by the symbol ε_{m0}. (See Ref. [11] for the exact definitions of the quantities $\varepsilon_{\mathrm{mm}'}$, $A^{M}{}_{mm'}$ and the Gaunt coefficients C^{L} and $C^{L|M|}$ appearing in Eqs. 8, 11.)

For deriving the expression for overlap integrals in terms of basic overlap integrals with respect to lined-up coordinate systems. We use in Eqs. (6) and (9) the properties of spherical harmonics for $\theta = 0$, $\phi = 0$ and $\theta = \pi$, $\phi = 0$. Then, for overlap integrals over real or complex STOs it is easy to obtain the following formula (see Eqs. 4, 5 and 8 of Ref. [4]):

$$S_{nlm,n'l'm'}(p,t;\theta,\phi) = \delta_{mm'}S_{nl\lambda,n'l'\lambda}(p,t) \times \begin{cases} 1 & \text{for } \theta = 0,\ \phi = 0 \\ (-1)^{l+l'} & \text{for } \theta = \pi,\ \phi = 0 \end{cases} , \tag{12}$$

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

Table 1. The values of overlap integrals obtained from Eqs. (9), (12) and (13) in the molecular coordinate system (in atomic units). *LHS* and *RHS* represent left-hand side and right.hand side, respectively

n	l	m	n'	l'	m'	p	t	θ	ϕ	LHS of Eq. (17) in Ref. [4]	RHS of Eq. (17) in Ref. [4]	Δf	Computing time (ms)
4	3	2	3	2	1	1.5	0.5	120	90	$687153968850948 \times 10^{-11}$	$6.87153968853261 \times 10^{-11}$	22	0.01
5	4	3	5	3	−2	30	0.3	150	35	$-3.76528714570421 \times 10^{-6}$	$-3.76528714570237 \times 10^{-6}$	18	2.0
6	5	1	6	5	1	50	0.8	150	270	$-4.52554470357060 \times 10^{-6}$	$-4.52554470357043 \times 10^{-6}$	18	6.0
10	9	8	12	10	8	20	0.4	30	360	$1.50981944685389 \times 10^{-3}$	$1.50981944685389 \times 10^{-3}$	20	7.85
12	10	9	12	10	8	20	0.7	45	0	$-4.97337842055340 \times 10^{-6}$	$-4.97337842055340 \times 10^{-6}$	20	10.98
13	6	4	12	5	4	60	0.7	15	0	$2.58664616427115 \times 10^{-6}$	$2.58664616427115 \times 10^{-6}$	23	0.65
14	3	2	14	6	2	200	0.9	7.5	0	$1.31943525439935 \times 10^{-5}$	$1.31943525439937 \times 10^{-5}$	18	0.16
14	13	12	14	13	12	70	0.5	135	0	$-2.18765647986679 \times 10^{-5}$	$-2.18765647986679 \times 10^{-5}$	19	10.86
16	12	6	17	12	6	10	0.6	120	0	$-2.20845885527976 \times 10^{-5}$	$-2.20845885527976 \times 10^{-5}$	20	9.72
20	10	8	20	10	8	35	0.2	0	45	$2.41391679719113 \times 10^{-2}$	$2.41391679719113 \times 10^{-2}$	18	21.35
22	12	6	18	10	6	50	0.4	0	180	$-1.28993134351658 \times 10^{-3}$	$-1.28993134351658 \times 10^{-3}$	19	18.5
24	8	5	20	7	5	60	0.4	0	240	$-7.03048781165857 \times 10^{-4}$	$-7.03048781165857 \times 10^{-4}$	18	5.74
15	10	10	15	10	10	40	0.6	45	210	$5.47546324620556 \times 10^{-7}$	$5.47546324620556 \times 10^{-7}$	21	19.5
26	9	8	15	10	8	10	0.8	0	150	$-5.39739018697043 \times 10^{-5}$	$-5.39739018697043 \times 10^{-5}$	19	38
26	12	−6	20	10	−6	22	0.9	0	270	$1.34710397904560 \times 10^{-13}$	$1.34710397105807 \times 10^{-13}$	22	40
32	6	4	20	5	4	34	0.7	0	300	$4.44505406036585 \times 10^{-4}$	$4.44505406046589 \times 10^{-4}$	18	16
34	8	5	27	7	5	30	0.6	0	180	$4.47327103267062 \times 10^{-4}$	$4.47327103267066 \times 10^{-4}$	18	43
34	12	10	27	10	10	12	0.5	0	180	$7.98319684824242 \times 10^{-2}$	$7.98319684824242 \times 10^{-2}$	22	55.5
38	10	8	30	10	8	20	0.7	0	0	$1.36385965917645 \times 10^{-6}$	$1.36385965917645 \times 10^{-6}$	21	58.6
40	8	7	30	7	7	30	0.9	0	0	$-4.70039545616601 \times 10^{-17}$	$-4.70039545616618 \times 10^{-17}$	30	40
42	6	6	30	6	6	29	0.5	0	180	$1.54941633286238 \times 10^{-2}$	$1.54941633286238 \times 10^{-2}$	20	32
48	7	2	28	6	2	29	0.6	45	30	$3.43880694721407 \times 10^{-3}$	$3.43880694721407 \times 10^{-3}$	18	43
50	5	2	50	5	2	20	0.6	180	90	$-5.64314946989160 \times 10^{-6}$	$-5.64314946989160 \times 10^{-6}$	19	32

$$S_{nl\lambda,n'l'\lambda}(p,t) = \sum_{l''=\lambda}^{l} \sum_{L=|l'-l''|}^{l'+l''} d_{nl\lambda,n'l'\lambda}^{l''L} \times \frac{[2p(1+t)]^l}{[2p(1-t)]^{l''}} S_{n-l00,n'+l''L0}(p,t) \ , \quad (13)$$

$$d_{nl\lambda,n'l'\lambda}^{l''L} = \left[\frac{F_{2n'}(2n'+2l'')(2l+1)(2L+1)(2l'')!}{F_{2n-2l}(2n)(2l''+1)(2l)!} \times F_{l''+\lambda}(l+\lambda) F_{l''-\lambda}(l-\lambda) \right]^{\frac{1}{2}} C^L(l'\lambda, l''\lambda) \ . \quad (14)$$

3 Discussion

As stated previously, for arbitrary overlap integrals we have the relations through the basic overlap integrals and Gaunt coefficients in the form of finite sums. The basic overlap integrals and Gaunt coefficients can be calculated by making use of computer programs presented in Refs. [4] and [12], respectively. With the aid of recurrence relations for the overlap integrals over STOs (see Eq. 17 in Ref. [4]) one can determine the accuracy of results which are obtained from Eqs. (6), (9) and (13).

On the basis of Eqs. (9) and (13) we constructed a program for evaluating the overlap integrals over real STOs. The results of calculations on a Pentium 233 MHz computer (using Turbo Pascal 7.0 language) for various values of parameters of overlap integrals are presented in Table 1. The comparative values obtained from Eqs. (9) and (13), the number of correct decimal figures Δf and the computation time in milliseconds are given in this table. In all of the calculations (up to $n = n' = 50$) the left-hand side and the right-hand side of Eq. (17) in Ref. [4] are in agreement with each other for at least 18 decimal digits.

As can be seen from Table 1, the accuracy and the computation time of the results obtained from Eqs. (9) and (13) for the arbitrary values of quantum numbers, screening constants and locations of STOs are satisfactory. Therefore, the algorithm presented in this letter can be useful for the calculation of multicenter molecular integrals in the Hartree–Fock–Roothaan approximation based on the translation formulas for STOs.

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