ORIGINAL PAPER

Calculation of two-center overlap integral in molecular coordinate system over Slater type orbital using Löwdin α-radial and Guseinov rotation–angular functions

B. A. Mamedov · H. Koç

Abstract By use of Löwdin and Guseinov relations for the radial and angular part of two-center overlap integrals, respectively, the computer calculations of overlap integrals over Slater type orbitals (STOs) in molecular coordinate system are performed. The results of calculations are valid for arbitrary principal quantum numbers, screening constants and location of STOs. Excellent agreement with benchmark results and stability of the technique are demonstrated.

Keywords Slater type orbitals · Overlap integrals · Hartree–Fock · Wave function · Löwdin α function · Guseinov rotational transformation function

1 Introduction

The Löwdin α [1] and Guseinov rotational transformation [2–4] functions play a decisive role in the calculation of multicenter integrals over STOs in molecular coordinate system. The different approaches of Löwdin α function method for solving multicenter integrals with STOs are available in the literature [5–19]. There is a long history (started by Jones [5–10], Sharma [11–14] and Suzuki [15]) of systematic attempts to obtain accurate and fast evaluation of molecular integrals using Löwdin α function. Unfortunately, they were not entirely successful in the evaluation of multicenter integrals for high quantum numbers. The aim of this report is to calculate the overlap integrals over STOs in molecular coordinate system for high quantum numbers using the analytical approaches for Löwdin α–radial and Guseinov rotation–angular functions presented in Refs. [15] and [2–4], respectively. It should be noted that the overlap integrals arise not only in the Hartree–Fock–Roothaan equations for molecules, but

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are also central to the calculation of arbitrary multicenter integrals based on the Guseinov's series expansion formulas about a new center [20] and one-range addition theorems for STOs [21] which necessitate to accurately calculate the overlap integrals especially for large quantum numbers. The overlap integrals over STOs are also used in all of the semiempirical methods [22].

2 Definition

The two-center overlap integrals over STOs with respect to molecular coordinate system (nonlined-up coordinate systems) are defined as

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

where $\vec{R} \equiv \vec{R}_{ab} = \vec{r}_a - \vec{r}_b$ and

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

Here, the complex and real spherical harmonics S_{lm} are determined by

$$
S_{lm}(\theta, \varphi) = P_{l|m|}(\cos \theta) \Phi_m(\varphi), \tag{3}
$$

where $P_{l|m|}$ are the normalized associated Legendre functions [23,24] and for complex spherical harmonics (SH)

$$
\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \tag{4}
$$

for real spherical harmonics

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

We notice that our definition of phases for complex spherical harmonics ($Y_{lm}^{*} = Y_{l-m}$) differs from the Condon–Shortley phases ($Y_{lm}^{*} = (-1)^m Y_{l-m}$) by the sign factor [25].

3 Löwdin α-radial function for overlap integrals

In order to calculate the integral (1) in molecular coordinate system, we use the following relation for the radial parts of overlap integrals obtained by Jones [5] with the help of Löwdin α method:

$$S_{nl\lambda,n'l'\lambda}(\zeta,\zeta',R) = N_{nl,n'l'\lambda}(-1)^{l'+\lambda}\left(\frac{\zeta'}{\zeta}\right)^{n'+\frac{1}{2}}$$

$$\times \sum_{i=0}^{n+l+l'}\sum_{j=0}^{n+l'}(n'-l'+j)!C_{l'}^{nl\lambda}(i,j)(\zeta a)^{n'-2l'-l+i+j}$$

$$\times\left[e^{-\zeta R}\left(\frac{(-1)^j}{[R(\zeta'-\zeta)]^{n'-l'+j+1}}-\frac{1}{[R(\zeta'+\zeta)]^{n'-l'+j+1}}\right)\right.$$

$$\left.+e^{-\zeta'R}\sum_{k=0}^{n}\frac{1}{(n'-l'+j-k)!}\left(\frac{(-1)^i}{[R(\zeta'+\zeta)]^{k+1}}-\frac{(-1)^j}{[R(\zeta'-\zeta)]^{k+1}}\right)\right] \text{ for } \zeta \neq \zeta'$$

$$(6)$$

Here, $\lambda = |m| = |m'|$ and

$$N_{nl,nl'\lambda} = (-1)^{\lambda}2^{n'+n}\left[\frac{(2l+1)(2l'+1)(l+\lambda)!(l'-\lambda)!}{(2n')!(2n)!(l'+\lambda)!(l-\lambda)!}\right]^{\frac{1}{2}}, \quad (7)$$

$$C_{l'}^{nl\lambda}(i,j)$$

$$=\begin{cases}\dfrac{(l-\frac{1}{2})!(l'-\frac{1}{2})!}{(l+\lambda)!(l'-\lambda)!}\displaystyle\sum_{K=0}^{\min\{[i/2],l+l'\}}\sum_{k=0}^{\min\{[j/2],l+l'-K\}}\dfrac{(n+l+2l'-2K-2k)!}{(i-2K)!(j-2k)!} \\ \times b_{l+l'-K-kk}(l\lambda\backslash l') & \text{for } i+j \leq n+l-\lambda+2l' \\ 0 & \text{for } i+j > n+l-\lambda+2l'\end{cases}$$

$$(8)$$

where

$$b_{Kk}(l\lambda\backslash l') = \frac{(l-\lambda)!(l+\lambda)!(l'-\lambda)!(l'+\lambda)!(l-K-\frac{1}{2})!(l'-k-\frac{1}{2})!}{(l+l'-K-k)!(l-\frac{1}{2})!K!(l'-\frac{1}{2})!k!}$$

$$\times\sum_{s=0}^{l-\lambda}\frac{(-l+K+k+s-\frac{1}{2})!}{s!(l-\lambda-s)!(l'-l+s)!(-l+s-\frac{1}{2})!(l+\lambda-s)!} \quad (9)$$

In Eqs. 8 and 9 the factorial $(p-1/2)!$ has the form [15]

$$(p-1/2)! = \begin{cases}(p-1/2)(p-3/2)\ldots 1/2 & \text{for a positive integer } p \\ 1/[(-1)^{-p}(-p-1/2)!] & \text{for a negative integer } p\end{cases} \quad (10)$$

with $(-1/2)! \equiv 1$. Thus the following relation holds [15]:

$$(p-1/2)!(-p-1/2)! = (-1)^p. \quad (11)$$

4 Guseinov rotation–angular function for overlap integrals

The explicit expressions of for the Guseinov rotational transformation functions $T^{\lambda}_{lm,l'm'}(\theta, \varphi)$ in terms of Clebsch–Gordan coefficients and spherical harmonics have the following form [2–4]:
for complex SH

$$
T^{\lambda}_{lm,l'm'}(\theta, \varphi) = \frac{2}{1+\delta_{\lambda 0}} \sum_{L=|l-l'|}^{l+l'} {}^{(2)}C^{ll'L}_{m,-m',m-m'} C^{ll'L}_{\lambda,-\lambda,0} \left(\frac{4\pi}{2L+1}\right)^{1/2}
$$
$$
\times Y_{L,m-m'}(\theta, \varphi), \tag{12}
$$

for real SH

$$
T^{\lambda}_{lm,l'm'}(\theta, \varphi) = \frac{2(-1)^{\gamma+\gamma'}}{(1+\delta_{\lambda 0})\left[(1+\delta_{m0})(1+\delta_{m'0})\right]^{1/2}} \sum_{i=-1}^{1} {}^{(2)} \sum_{L=|l-l'|}^{l+l'} {}^{(2)} (\varepsilon_{m0})^{\delta_{i,\varepsilon_{mm'}}}
$$

$$
\times C^{ll'L}_{i\gamma,\gamma',i\gamma+\gamma'} C^{ll'L}_{\lambda,-\lambda,0} \left[\frac{2\pi(1+\delta_{M_i 0})}{2L+1}\right]^{1/2} S_{LM_i}(\theta, \varphi), \tag{13}
$$

where $\gamma = |m|, \gamma' = |m'|$, $M_i = \varepsilon_{mm'}|i\gamma + \gamma'|$ and $\varepsilon_{mm'} = \pm 1$. The sign of the symbol $\varepsilon_{mm'}$ is determined by the product of the signs m and m' (the sign of zero is regarded as positive). 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. 13 should be equated to zero. The quantities $C^{ll'L}$ occurring in Eqs. 12 and 13 are the Clebsch–Cordan coefficients in the case of our phases (see Ref. [2]).

In the case of lined-up coordinate systems the functions $T^{\lambda}_{lm,l'm'}(\theta, \varphi)$ are determined by

$$
T^{\lambda}_{lm,l'm'}(\theta, \varphi) = \delta_{mm'}\delta_{\lambda|m'|} \begin{cases} 1 & \text{for } \theta = 0, \varphi = 0 \\ (-1)^{l+l'} & \text{for } \theta = \pi, \varphi = 0 \end{cases}. \tag{14}
$$

Following properties hold for the rotational transformation functions [4]:

$$
\sum_{m=-l}^{l} T^{\lambda}_{lm,lm}(\theta, \varphi) = \frac{2}{1+\delta_{\lambda 0}}, \tag{15}
$$

$$
\sum_{\lambda=0}^{l} T^{\lambda}_{lm,lm'}(\theta, \varphi) = \delta_{mm'}, \tag{16}
$$

$$\sum_{m=-l}^{l} \sum_{m'=-l'}^{l'} T_{lm,l'm'}^{*\lambda}(\theta, \varphi) T_{lm,l'm'}^{\lambda'}(\theta, \varphi) = \frac{2}{1 + \delta_{\lambda 0}} \delta_{\lambda \lambda'}. \tag{17}$$

We notice that the matrices of the rotational transformation functions are Hermitian, i.e.,

$$T_{lm,l'm'}^{\lambda}(\theta, \varphi) = T_{l'm',lm}^{*\lambda}(\theta, \varphi). \tag{18}$$

To evaluate the overlap integrals, in molecular coordinate system we use Eqs. 6 and 13 in (1). Then we obtain:

$$S_{nlm,n'l'm'}(\zeta, \zeta'; \vec{R}) = \sum_{\lambda=0}^{\min(l,l')} T_{lm,l'm'}^{*\lambda}(\theta, \varphi) S_{nl\lambda,n'l'\lambda}(\zeta, \zeta'; R). \tag{19}$$

5 Numerical results and discussion

In this paper, we performed the computation of overlap integrals over STOs for high values of quantum numbers using Löwdin α and Guseinov rotational transformation functions. We note that the Guseinov rotational transformation function is very important for evaluation of multicenter integrals in molecular coordinate system. Moreover, the multicenter integrals can be directly evaluated in molecular coordinate system by using Guseinov function. Also, the formulas can easily be implemented with an algebraic computer language. The comparative results of overlap integrals calculations on a Mathematica 5.0 international mathematical software and Turbo Pascal 7.0 language packages for various values of parameters obtained in the lined-up and nonlined-up coordinate systems are represented in Tables 1 and 2, respectively. The numerical results obtained from the formulas (6) and (19) using Mathematica 5.0 international mathematical software are seen to be very accurate: these results exactly agree with the results of Ref. [27]. We see that the accuracy of overlap integrals strongly depends on the presented formulas and especially on the used program language packages. We note that, the difference between the numerical results of Eq. 5 of Ref. [26] and Eq. 19 arises only after 45th 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.

We notice that the algorithm used in this study is of a completely general type and can be utilized to calculate any overlap integral for the arbitrary values of quantum numbers, screening constants and location of STOs, and internuclear distances. We believe that the Löwdin α-radial and Guseinov rotation–angular formulas are important for the ab initio calculations of atoms and molecules. The ultimate purpose of this study is to perform the molecular ab initio calculations using Löwdin–Guseinov approach for overlap integrals arising in the Guseinov method for the expansion of STOs about a displaced center (see Ref. [20]).

Table 1 The comparative values of the two-center overlap integrals over STOs in lined-up coordinate systems (in a.u.)

n	l	n'	l'	λ	p	t	Equations 6 and 4 of Ref. [26] in Mathematica procedure	Ref. [27] in Mathematica procedure	Equation 4 in Turbo Pascal procedure of Ref. [26]
3	2	3	2	1	25	0.6	−4.422877669882608806795415E − 04	−4.4228776698260880679E − 04	−4.4228776698826988261E − 04
4	2	4	3	1	80	0.4	4.035059503263829810896077E − 17	4.03505950326382298108E − 17	4.0350595032638232382E − 17
5	4	5	4	4	100	0.7	1.562006027457891037452179E − 14	1.56200602745789103745E − 14	1.562005991539766E − 14
7	3	4	3	2	150	0.7	−1.768610506922648590808884E − 18	−1.76861050692264859080E − 18	−1.768610506977887E − 18
9	5	8	4	3	45	0.2	−5.465102430227040173824997E − 08	−5.46510243022704017382E − 08	−5.465102430228677E − 08
10	7	8	2	1	60	0.2	−1.841890261731981064243984E − 10	−1.84189026173198106424E − 10	−1.841890261735588E − 10
10	9	10	9	9	15	0.6	6.231223181911249464756102E − 04	6.23122318191124946475E − 04	6.231223181968666E − 04
13	12	13	12	12	25	0.01	1.353105780247123818618686E − 04	1.35310578702471238186E − 04	1.353105603921893E − 04
14	13	14	13	13	15	0.4	4.535512851067909115523032E − 03	4.53551285106790911552E − 03	4.535513121565253E − 03
17	8	8	7	4	50	0.1	−1.006400641171881723467400E − 06	−1.00640064117188172346E − 06	−1.006400613542583E − 06
17	16	17	16	16	25	−0.5	3.067703255790193609380388E − 05	3.06770325579019360938E − 05	3.067695651855753E − 05
18	12	18	12	12	20	−0.6	6.639318136966506077513212E − 05	6.63931813696650677513E − 05	6.639318136512403E − 05
27	8	9	8	7	35	−0.2	−1.744238075196959091936618E − 04	−1.74423807519695909193E − 04	−1.733009827996991E − 04
37	8	12	10	6	10	−0.6	3.982280043770915735962091E − 14	3.98228004377091573596E − 14	3.982198490042594E − 14
40	4	12	4	3	15	0.6	9.483792208322556785384419E − 02	9.48379220832255678538E − 02	9.483792655998103E − 02
43	10	18	8	6	60	−0.4	−1.158256532671748146605545E − 04	−1.15825653267174814660E − 04	−1.159076871231043E − 04
50	4	50	4	4	25	0.7	1.843958799324363403100208E − 12	1.84395879932436340310E − 12	1.843959010372283E − 12

Table 2 The comparative values of the two-center overlap integrals over STOs in nonlined-up coordinate systems (in a.u.)

n	l	m	n′	l′	m′	p	t	θ	φ	Equation 19 in Mathematica procedure	Equation 5 in Mathematica procedure of Ref. [26]	Equation 5 in Turbo Pascal procedure of Ref. [26]
2	1	0	2	1	0	25	0.5	60	120	−2.01912763169782351044068597E−05	−2.01912763169782351044068597E−05	−2.01912763028473E−05
5	4	2	5	4	0	150	0.7	45	210	−2.27511176683283043597258533E−17	−2.27511176683283043597258533E−17	−2.27511175896203E−17
7	4	1	5	3	1	200	0.7	45	210	−2.00183868910395189767894518E−23	−2.00183868910395189767894518E−23	−2.00183867476671E−23
14	11	7	13	10	6	12	−0.6	15	10	4.48032190106317531036390097E−05	4.48032190106317531036390097E−05	4.48032207619290E−05
19	9	8	14	13	7	15	0.8	18	300	2.18261954539413971517851094E−05	2.18261954539413971517851094E−05	2.18261954784081E−05
20	13	5	20	9	5	40	−0.5	120	225	1.70386203434124448885557620E−03	1.70386203434124448885575620E−03	1.70386168880515E−03
28	14	10	28	16	16	20	0.7	30	60	−4.73504506786453315953195544E−10	−4.73504506786453315953195544E−10	−4.73486792914621E−10
46	2	1	14	1	1	10	0.5	15	24	3.16442030563724283564008724E−01	3.16442030563724283564008724E−01	3.16455689731464E−01
50	4	4	50	4	4	22	0.7	45	210	1.41805173022101706099860032E−11	1.41805173022101706099860032E−11	1.41805162040407E−11

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