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ORIGINAL PAPER

Use of Filter-Steinborn B and Guseinov Q_{ns}^{q} auxiliary functions in evaluation of two-center overlap integrals over Slater type orbitals

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Abstract An efficient method for computing overlap integral over Slater type orbitals based on the B Filter-Steinborn and Guseinov Q_{ns}^{q} auxiliary functions is presented. The final results are expressed through the binomial coefficients with the help of which the overlap integrals can be evaluated efficiently and accurately. The results of calculation are in good agreement with those obtained by other method for arbitrary principal quantum numbers and different screening constants.

Keywords Slater type orbitals · Overlap integrals · Auxiliary functions

1 Introduction

It is well known that the calculation of multicenter molecular integrals over exponential type orbitals (ETOs) is the great importance for accurate evaluation of problems in quantum chemistry and physics. Among the ETOs commonly used are the Gaussian type orbitals (GTOs) and Slater type orbitals (STOs). The STOs represent the real situation for the electron density in the valence region and beyond, but are not so good nearer to the nucleus. Many calculations over the years have been carried out with STOs, particularly for diatomic molecules. However, it soon became clear that there was a practical problem arising in evaluation of the necessary multicenter integrals over STOs when the orbitals in the integrals are centered on three or four different atoms.

In Ref. [1], Boys pointed out that the multicenter integrals over GTOs which contain the exponential $\exp(-r^2)$ are very easy to evaluate. They are mathematically simpler than the STOs, but less accurate. Since the early years of quantum chemistry, the

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evaluation of molecular integrals over STOs has been attracted the attention [2–28]. The calculation of these integrals, particularly of overlap integrals, within various approximations has been developed with different techniques, including analytic [29–31]. The method that uses the recurrence relation has also been suggested [19,28]. The aim of this report is to calculate the overlap integrals over STOs in lined-up coordinate systems for high quantum numbers using the analytical approaches for B and Q_{ns}^{q} auxiliary functions described in Refs. [32,33] and [34], respectively. It should be noted that the overlap 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 Guseinov's series expansion formulas about a new center [35] and one-range addition theorems for STOs [24] which necessitate to accurately calculate the overlap integrals especially for large quantum numbers. In this work we present a simple analytical approach to obtain the formula for overlap integral over STOs. The results of this calculation have been compared with those obtained in literature.

2 Definition and basic formulas

The STOs are determined as

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

where the S_{lm} are the complex or real spherical harmonics:

$$S_{lm}(\theta,\varphi) = P_{l|m|}(\cos\theta)\Phi_m(\varphi). \tag{2}$$

Here, $P_{l|m|}$ are the normalized associated Legendre functions [36] and for complex spherical harmonics

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \tag{3}$$

for real spherical harmonics

$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} \begin{cases} \cos|m|\varphi & \text{for} \quad m \geq 0 \\ \sin|m|\varphi & \text{for} \quad m < 0 \end{cases}. \tag{4}$$

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 [37].

The STOs can be expressed through the B functions [2]:

$$\chi_{nlm}(\zeta,r) = \frac{(2\zeta)^{n+\frac{1}{2}}\left[(2n)!\right]^{-\frac{1}{2}}}{\zeta^{n-1}} \times \sum_{p=\tilde{p}}^{n-l} \frac{(-1)^{n-l-p}\, 2^{2p+2l-n}(n-l)!(l+p)!}{(2p-n+l)!\,(n-l-p)!} B_{p,l}^{m}(\zeta,r) \tag{5}$$

with $p = \frac{n-l}{2} + \frac{1}{4}\left(1 - (-1)^{n-l}\right)$. In Eq. (5), the quantities $B^m_{p,l}(\zeta, r)$ are the B functions and defined by

$$B^m_{n,l}(\zeta, r) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!} k_{n-1/2}(\zeta r) S_{lm}(\theta, \varphi). \tag{6}$$

Here, $k_{n-1/2}(\zeta r)$ is the Bessel functions determined by the relation

$$k_{n-1/2}(z) = \sum_{j=1}^{n} \frac{(2n-j-1)!}{(j-1)!(n-j)!} \frac{z^{j-1}e^{-z}}{2^{n-j}}. \tag{7}$$

3 Expressions in terms of B and Q^q_{ns} auxiliary functions

The overlap integrals over STOs in lined-up coordinate systems are defined as

$$S_{nl\lambda,n'l'\lambda}(p, t) = \int \chi^*_{nlm}(\zeta, \vec{r}_a)\chi_{n'l'm}\left(\zeta', \vec{r}_b\right) dV, \tag{8}$$

where $0 \le \lambda \le l, m = \pm\lambda, p = \frac{R}{2}(\zeta + \zeta')$ and $t = (\zeta - \zeta')/(\zeta + \zeta')$. In order to calculate the integral (8) we use Eq. 5, and Eq. 16 in Ref. [34] for the auxiliary functions Q^q_{ns}. Then we obtain:

$$\begin{aligned} &S_{nl\lambda,n'l'\lambda}(\zeta, \zeta', R) \\ &= N_{nl,n'l'}(p,t) \sum_{p_1=\tilde{p}}^{n-l} \omega^p_{nl} \sum_{j=1}^{p} F_{j-1}(2p-j-1)F_{p-j}(2p-2j)(p-j)!(\zeta R)^j \\ &\quad\times \sum_{p'=\tilde{p}_1}^{n'-l'} \omega^{p'}_{n'l'} \sum_{j'=1}^{p'} F_{j'-1}(2p'-j'-1) \\ &\quad\times F_{p'-j'}(2p'-2j')(p'-j')!(\zeta' R)^{j'} \\ &\quad\times \sum_{\alpha=-\lambda}^{l}{}^{(2)} \sum_{\beta=\lambda}^{l'}{}^{(2)} \sum_{q=0}^{\alpha+\beta} g^q_{\alpha\beta}(l\lambda, l'\lambda) Q^q_{l+j-\alpha,l'+j'-\beta}(p,t), \end{aligned} \tag{9}$$

where $F_m(n) = n!/[m!(n-m)!]$ are the binomial coefficients. The auxiliary functions Q^q_{ns} are determined as:

$$\begin{aligned} Q^q_{nn'}(p,t) &= \int_1^{\infty}\int_{-1}^{1} (\mu\nu)^q(\mu+\nu)^n(\mu-\nu)^{n'}e^{-p\mu-pt\nu}d\mu d\nu \\ &= \sum_{k=0}^{n+n'} F_k(n,n')A_{q+n+n'-k}(p)B_{q+k}(pt) \end{aligned} \tag{10}$$

where A_n and B_n are the auxiliary functions defined by [38]

$$A_n(p) = \int_1^{\infty} \mu^n e^{-p\mu} d\mu = \frac{n! e^{-p}}{p^{n+1}} \sum_{s=0}^{n} \frac{p^s}{s!}, \tag{11}$$

$$B_n(pt) = \int_{-1}^{1} \nu^n e^{-pt\nu} d\nu = (-1)^{n+1} A_n(-pt) - A_n(pt). \tag{12}$$

In Ref. [39], the new analytical relations have been suggested for the fast evaluation of auxiliary functions A_n and B_n.

The coefficients $N_{nn'}(t)$, ω_{nl}^{p} and $F_m(N, N')$ occurring in Eqs. 9 and 10 are determined by

$$N_{nl,n'l'}(t) = \frac{[p(1+t)]^{l+1/2}[p(1-t)]^{l'+1/2}}{\sqrt{(2n)!(2n')!}}, \tag{13}$$

$$\omega_{nl}^{p} = (-1)^{n-l-p} F_{2p-n+l}(n-l) F_{n-l-p}(2n-2l-2p)(n-l-p)!, \tag{14}$$

$$F_m(N, N') = \sum_{\sigma=\frac{1}{2}[(m-n)+|m-n|)}^{\min(m,N')} (-1)^{\sigma} F_{m-\sigma}(N) F_{\sigma}(N'). \tag{15}$$

It should be noted that, Eq. 15 for the generalized binomial coefficients with different notation $D_m^{NN'}$ firstly has been presented by Rosen in Ref. [40].

The quantities $g_{\alpha\beta}^{q}(l\lambda, l'\lambda)$ in Eq. 9 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 [34]. In Ref. [30], these coefficients were expressed in terms of binomial coefficients:

$$g_{\alpha\beta}^{0}(l\lambda, l'\lambda) = \left[\sum_{i=0}^{\lambda} (-1)^i F_i(\lambda) D_{\alpha+2\lambda-2i}^{l\lambda}\right] D_{\beta}^{l'\lambda}, \tag{16}$$

where

$$D_{\beta}^{l\lambda} = \frac{(-1)^{(l-\beta)/2}}{2^l} \left[\frac{2l+1}{2} \frac{F_l(l+\lambda)}{F_{\lambda}(l)}\right]^{1/2} F_{(l-\beta)/2}(l) F_{\beta-\lambda}(l+\beta). \tag{17}$$

4 Numerical results and discussion

In this section we describe the technicalities of our algorithm for computing the overlap integrals over STOs in lined-up coordinate systems. The calculation is based on the

Table 1 The comparative values of the two-center overlap integrals over STOs in lined-up coordinate systems

n	l	n'	l'	λ	ς	ς'	R	Eq. 9	Eq. 4 in Ref. [28]
2	1	2	1	1	2.5	1.5	3	9.135405785379490643193673E-02	9.135405785379490643193673E-02
3	2	3	2	2	2	1.8	10	1.219055962648290145871361E-05	1.219055962648290145871361E-05
4	3	2	1	1	8	2	0.8	8.445354518381718842801487E-02	8.445354518381718842801487E-02
4	3	4	3	3	7	3	0.2	4.356744418101780218870684E-01	4.356744418101780218870684E-01
5	2	5	2	2	6	7	4	4.755215502404319303711083E-06	4.755215502404319303711083E-06
5	4	5	4	4	8.5	1.5	20	1.562006027457891037452179E-14	1.562006027457891037452179E-14
10	9	10	9	9	8	2	3	6.231223181911249464756102E-04	6.231223181911249464756102E-04
13	12	13	12	12	50.5	49.5	0.5	1.353105787024712381861868E-04	1.353105787024712381861868E-04
14	13	14	13	13	7	3	3	4.535512851067909115523032E-03	4.535512851067909115523032E-03
17	16	17	16	16	2.5	7.5	5	3.067703255790193609380388E-05	3.067703255790193609380388E-05
18	12	18	12	12	2	8	4	6.639318136966506775132120E-05	6.639318136966506775132120E-05
27	8	9	8	7	4	6	7	−1.744238075196959091936618E-04	−1.744238075196959091936618E-04
37	8	12	10	6	2	8	2	3.982280043770915735962091E-14	3.982280043770915735962091E-14
3	2	3	2	2	9.7	6.4	0.3	5.929114517943846451955691E-01	5.929114517943846451955691E-01
5	4	3	2	2	4	6	0.1	1.545257360857200864599668E-02	1.545257360857200864599668E-02
6	5	4	3	3	5	4	3	1.954052017485978203448938E-02	1.954052017485978203448938E-02
7	4	7	2	2	8	2	5	1.071866355210529370563238E-03	1.071866355210529370563238E-03

reformulation of two center overlap integrals as the summation of products of binomial coefficients. On the basis of formula Eq. 9 obtained we constructed a program in the Mathematica 5.0 international mathematical software. The computations were performed for wide range of parameters. We present some results of various numerical computations that suggest what level of accuracy of the algorithm one could expect. We compared the numerical results obtained in this paper with Ref. [28]. As seen from Table 1, the calculation results yields significantly high accuracy for arbitrary values of integral parameters.

We notice that the exact and rapid calculations of the overlap integrals need to avoid the use of factorials with large values. Therefore, in this study, the final expression (Eq. 9) have been expressed in terms of binomial coefficients. For quick calculations, the binomial coefficients are stored in the memory of the computer. For the binomial coefficients we use the following recurrence expression:

$$F_m(n) = F_m(n-1) + F_{m-1}(n-1). \tag{18}$$

In order to put these coefficients into or to get them back from the memory, the positions of certain coefficients $F_m(n)$ are determined by the following relation:

$$F(n, m) = n(n+1)/2 + m + 1. \tag{19}$$

This approach provides a considerable reduction of computational time in comparison to the earlier established in Ref. [28] formula.

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