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ORIGINAL PAPER

Evaluation of the auxiliary function G_{-ns}^{q} using basic overlap integrals over Slater type orbitals

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Abstract This paper presents a computationally efficient formula in terms of basic overlap integrals over Slater type orbitals (STOs) for the evaluation of auxiliary function G_{-ns}^{q} which plays a central role in calculations of multicenter molecular integrals. The basic overlap integrals are calculated with the help of recurrence relations. The resulting simple analytical formula for the auxiliary function $G_{-ns}^{q}(p_a, p, pt)$ is completely general for $p_a \leq 1.2$ and arbitrary values of parameters p and pt. The efficiency of calculation of auxiliary function G_{-ns}^{q} is compared with other method.

Keywords Auxiliary function · Overlap integrals · Slater type orbitals

1 Introduction

For improving the accurate evaluation of the multicenter integrals with Slater type orbital (STOs) the different kinds of the auxiliary functions have been proposed in literature [1–8]. One of the important auxiliary functions is the function G_{-ns}^{q} introduced in Refs. [9,10]. The calculation results of multicenter electron-repulsion integrals over STOs demonstrated that the computational accuracy is strongly depend on the accurate evaluation of the auxiliary function G_{-ns}^{q} which constitutes the basic building block of the two-center Coulomb and hybrid integrals occurring in the quantum mechanical calculations of the electronic structure of molecules. Particularly, the two-center exchange and three-four center integrals of STOs can be expressed through the two-center Coulomb and hybrid integrals using the expansion of STOs in terms of STOs

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at a displaced center [11,12]. By making use of these expansion formulas, all of the molecular integrals appearing in the Hartree-Fock-Roothaan approximation are expressed through the auxiliary function G^q_{-ns} [13,14]. This algorithm is especially useful for the computation of the auxiliary function G^q_{-ns} for large quantum numbers of STOs appearing in the series expansion formulas for molecular integrals. In this report, the auxiliary function G^q_{-ns} is expressed through the basic overlap integrals $S_{n00,n'00}(p,t)$ for calculation of which we use their recurrence relations.

2 Expansion for auxiliary function G^q_{-ns} in terms of basic overlap integrals

The auxiliary function G^q_{-ns} is defined by [9]

$$G^q_{-ns}(p_a,p,pt) = \int\limits_1^{\infty}\int\limits_{-1}^{1} \frac{(\mu\nu)^q(\mu-\nu)^s}{(\mu+\nu)^n}\left(1-e^{-p_a(\mu+\nu)}\sum_{k=0}^{n-1}\frac{[p_a(\mu+\nu)]^k}{k!}\right) \times e^{-p\mu-pt\nu}d\mu d\nu, \tag{1}$$

where $p_a>0,\ p>0\ and -p\le pt\le p$. The indices n, s and q are all non-negative integers. In Refs. [15,16] the function G^q_{-ns} were all calculated from the recurrence relations which are particularly unsuited for numerical computations for small values of p_a and pt, because of a serious loss of significant figures in each upward recurrence step. As can be seen from Ref. [16], the auxiliary function G^q_{-ns} becomes numerically unstable in the case of small values of parameters p_a and pt. In these cases, only infinite-form expressions for auxiliary function can be obtained easily from the following series expansion [17]:

$$e^{-x}=\sum_{k=0}^{\infty}\frac{(-x)^k}{k!}. \tag{2}$$

Taking into account (2) in Eq. 1, we obtain the following series expansion formula:

$$G^q_{-ns}(p_a,p,pt)=\lim_{N\to\infty}\sum_{k=0}^{N}\frac{(-1)^k p_a^{n+k}}{(n-1)!k!(n+k)}Q^q_{ks}(p,pt), \tag{3}$$

where the index N is the upper limit of summation. For the derivation of Eq. 3 we have taken into account the relation:

$$\frac{1}{x^n}\left(1-e^{-x}\sum_{s=0}^{n-1}\frac{x^s}{s!}\right)=\sum_{k=0}^{\infty}\frac{(-x)^k}{(n-1)!k!(n+k)}. \tag{4}$$

As can be seen from Eq. 3, the auxiliary function G^q_{-ns} is expressed through the auxiliary function Q^q_{ns} determined by [18,19]

$$Q_{ns}^{q}(p,pt)=\int\limits_{1}^{\infty}\int\limits_{-1}^{1}(\mu\nu)^{q}(\mu+\nu)^{n}(\mu-\nu)^{s}e^{-p\mu-pt\nu}d\mu d\nu. \tag{5}$$

In order to obtain the formula for the auxiliary function Q_{ns}^{q} in terms of basic overlap integrals we utilize the binomial expansion theorem in (5). Then, we find the expression in terms of auxiliary functions $Q_{nn'}^{0}$:

$$Q_{ns}^{q}(p,pt)=\frac{1}{4^{q}}\sum_{m=0}^{q}(-1)^{m}F_{m}(q)Q_{n+2q-2m,s+2m}^{0}(p,pt). \tag{6}$$

By the use of Eq. 15 of Ref. [19] the auxiliary function $Q_{nn'}^{0}$ can be expressed in terms of the basic overlap integrals $S_{n00,n'00}(p,t)$

$$Q_{nn'}^{0}(p,pt)=\frac{2}{N_{nn'}(p,pt)}S_{n00,n'00}(p,pt), \tag{7}$$

where

$$N_{nn'}(p,pt)=\frac{(p+pt)^{n+1/2}(p-pt)^{n'+1/2}}{\sqrt{(2n)!(2n')!}}. \tag{8}$$

The basic overlap integrals $S_{nn'}(p,t)\equiv S_{n00,n'00}(p,pt)$ occurring in Eq. 7 are determined from the following relations [20]:

for $n\geq 0, n'\geq 0$ and $t\neq 0$

$$\begin{aligned}S_{nn'}(p,t)=\frac{1}{t}\Bigg\{&\sqrt{\frac{n}{2(2n-1)}}(1+t)^{2}\left[S_{n-1n'}(p,t)-\sqrt{\frac{n-1}{2(2n-3)}}S_{n-2n'}(p,t)\right]\\&-\sqrt{\frac{n'}{2(2n'-1)}}(1-t)^{2}\times\left[S_{n,n'-1}(p,t)-\sqrt{\frac{n'-1}{2(2n'-3)}}S_{n,n'-2}(p,t)\right]\\&+\eta_{nn'}(p,t)\left[\delta_{n0}e^{-p(1-t)}-\delta_{n'0}e^{-p(1+t)}\right]\Bigg\},\end{aligned} \tag{9}$$

for $n'\geq 0$ and $t=0$

$$\begin{aligned}S_{0n'}(p,0)=&\left[\frac{n'}{2(2n'-1)}\right]^{1/2}S_{0n'-1}(p,0)+\left[\frac{2(2n'+1)}{n'+1}\right]^{1/2}\\&\times\eta_{0n'+1}(p,0)e^{-p},\end{aligned} \tag{10}$$

for $1 \le n \le n'$ and $t = 0$

$$S_{nn'}(p,0) = \left[\frac{n\left(2n'-1\right)}{(2n-1)(n'+1)}\right]^{1/2} S_{n-1n'+1}(p,0) - \left[\frac{n(n-1)\left(2n'+1\right)}{2(2n-1)(2n-3)(n'+1)}\right]^{1/2} S_{n-2n'+1}(p,0) + \left[\frac{n'}{2(2n'-1)}\right]^{1/2} S_{nn'-1}(p,0). \tag{11}$$

Here,

$$\eta_{nn'}(p,t) = \frac{[2p(1+t)]^{n+1/2}[2p(1-t)]^{n'+1/2}}{4p^2[(2n)!(2n')!]^{1/2}}. \tag{12}$$

With the aid of recurrence relations (9), (10) and (11) the basic overlap integrals $S_{n,n'}(p,t)$ can be expressed in terms of the functions $S_{00}(p,t)$ and $S_{00}(p,0)$ for the calculation of which we can use the following analytical formulas:

$$S_{00}(p,t) = \frac{1}{t}\eta_{00}(p,t)\left\{e^{-p(1-t)} - e^{-p(1+t)}\right\} \tag{13}$$

$$S_{00}(p,0) = e^{-p}. \tag{14}$$

Table 1 The comparative values of the auxiliary function $G^{q}_{-ns}(p_a, p, pt)$ for $N = 50$

n	s	q	p_a	p	pt	Ref. [14] in Turbo Pascal procedure	Eq. 3 in Mathematica procedure
10	6	8	0.3	2	1.0	5.37660254969285E-07	5.37660254969283383926797145703E-07
2	20	20	0.03	20	0.6	6.54028788640490E-07	6.54028788640016866493396181403E-07
6	5	4	0.8	20	14	9.31873241207543E-08	9.31873241207543218797869834953E-08
8	10	8	0.07	6	0.6	4.32621788285232E-13	4.32621788285231983727884293831E-13
10	10	10	0.03	0.8	0.08	4.30438163691663E-03	4.30438163691663084455320738376E-03
12	12	10	0.01	0.5	0.15	2.54034200229606E-06	2.54034200229606181645604418640E-06
17	12	16	3	22	15.4		9.69765047852047228601826070137E-07
20	25	25	0.6	15	1.05		−1.38252334309055119101897403309E-17
45	35	43	0.8	55	44		−7.42274283714507460522919058569E-58
37	42	36	5	54	27		7.78341116454117110739775764697E-20
65	76	66	1.2	24	9.6		4.41492024301361687153586994018E-33
86	86	86	0.9	32	22.4		2.38289436649041864191746010458E-71
100	100	100	0.2	12	9.6		3.03896549641696007999546E-67

Table 2 Convergence of the series expansion relations for auxiliary function $G^{q}_{-ns}(p_a, p, pt)$as a function of summation limits for N

N	Eq. 3 for $G^{15}_{-9,12}(0.2, 8, 4.8)$	Eq. 3 for $G^{10}_{-13,10}(0.6, 13, 10.4)$	N	Eq. 3 for$G^{17}_{-15,16}(1.3, 12, 6)$
14	−7.3012039730056977562 21E-8	3.89164667093518846405E-13	21	−3.69249257769822801908 80
15	−7.30120397300569173822 9E-8	3.89164667093517154705E-13	22	−3.69249258229813342171 26
16	−7.30120397300569207053 5E-8	3.89164667093517143568 E-13	25	−3.69249258146739771230 26
17	−7.30120397300569205269 9E-8	3.89164667093517144414 E-13	30	−3.69249258147507457256 55
18	−7.30120397300569205363 2E-8	3.89164667093517144414 E-13	35	−3.69249258147507221419 18
19	−7.30120397300569205358 4E-8	3.89164667093517144351 E-13	40	−3.69249258147507221472 75
20	−7.30120397300569205358 7E-8	3.89164667093517144356 E-13	45	−3.69249258147507221472 75
21	−7.30120397300569205358 7E-8	3.89164667093517144355 E-13		
22	−7.30120397300569205358 7E-8	3.89164667093517144355E-13		

3 Numerical results and discussion

In this section, the numerical examples are given for demonstration of computational efficiency of Eq. 3. On the basis of Eq. 3 and the recurrence relations for basic overlap integrals presented in this work we constructed a program for the computation of auxiliary function G^q_{-ns} using Mathematica 5.0 international mathematical software. The examples of computer calculation are shown in Tables 1 and 2. Table 1 contains compared values obtained in Ref. [14] for the complete expressions of the auxiliary function G^q_{-ns}. As can be seen from Table 1, the results of calculation for the auxiliary function show good agreement with values in Ref. [14]. As is clear from our test calculations, the Eq. 3 yields significant accuracy for $p_a \leq 1.2$. As shown in Table 2, the series in Eq. 3 converges more rapidly for $p_a \leq 1.2$, but the situation is reversed for $p_a > 1.2$. Thus, Eq. 3 is general, simple and stable for $p_a \leq 1.2$ and arbitrary values of p and pt. We see from Table 2 that the Eq. 3 display the most rapid convergence to the numerical result, with 21 digits stable and correct by the 21th terms in the infinite summations. It should be noted that the use of memory of the computer for calculation of binomial coefficients may extend the limits of large arguments to the users and result in speedier calculation, should such limits be reached in practice.

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