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Short Communication

Efficient calculation of boys integrals

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An efficient procedure has been presented for the calculation of Boys integrals by dividing the integral region [0, 1] into several parts. The obtained formula includes factorials, exponentials and a well known auxiliary function that converges very well. A computer program has been constructed in Maple symbolic programming language for comparing our results with literature. It is seen that the computational results of the presented algorithm agree well with the numerical results obtained by direct integration with Maple and results in the available literature.

Key words: Boys function, molecular integrals, dividing methods.

INTRODUCTION

The efficiency of the theoretical calculations of atomic and molecular properties depends strictly on the choice of the basic functions. Among the basic functions, Slater type orbitals (STOs) and Gaussian type orbitals (GTOs) are extensively used. As is well known, GTOs cannot represent electron behavior exactly. Therefore, Gaussian expansion of STOs (STO-nG) is used for overcoming the calculation of numerous recondite matrix elements between wave functions (molecular integrals). The use of STO-nG causes a large number of Boys integrals which play a crucial role in the calculation of molecular integrals. For a rigorous *ab initio* calculation, Boys integrals must be calculated with a high accuracy and a fast computational algorithm.

Boys integral have the following form (Boys, 1950).

$$F_m(\alpha) = \int_0^1 x^{2m} e^{-\alpha x^2} dx \qquad (1)$$

where α is related to the exponential parameters and the coordinates of GTOs centers; 2*m* is related on the angular momentum of GTOs.

There is an extensive literature on the calculation of Boys integrals (Guseinov, 2006; Harris, 1983; Ishida, 1996; McMurchie and Davidson, 1978; Pople and Hehre, 1978; Primorac, 1998; Saunders, 1975; Sahvitt et al., 1963). The aim of this work is to present an efficient and fast analytical algorithm for the calculation of Boys integrals.

METHOD

For the calculation of Boys integral given by Equation (1), we investigate the following integral

$$G_m(\beta, u) = \int_0^u x^{2m} e^{-\beta x^2} dx \qquad (2)$$

and divide the integral region $[0,u]$ into as possible as high parts:

$$G_m(\beta,u) = \int_0^a x^{2m} e^{-\beta x^2} dx + \int_a^{2a} x^{2m} e^{-\beta x^2} dx + \int_{2a}^{3a} x^{2m} e^{-\beta x^2} dx + \ldots + \int_{(N-1)a}^{Na} x^{2m} e^{-\beta x^2} dx. \qquad (3)$$

where the integral region [0, *u*] is divided into Na parts ($Na = u$). Using some basic mathematical tricks we obtain the formula below:

$$F_m(\beta) = \lim_{Q\to\infty} \sum_{s=0}^{n-1} e^{-s^2 a^2} \sum_{k=0}^{Q} \frac{(-\beta^2)^k a^{2m+2k+1}}{k!} A_{2m+2k}^{(0,1)}(2\beta s a^2) \qquad (4)$$

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Table 1. Comparative values of Boys integrals for arbitrary parameters.

m	β	*N*	*Q*	This work, Equation 4	Numeric (maple)	Accuracy
2	2.8	5	3	0.03307915621	0.03307916220	-0.6×10^{-8}
7	10.7	5	2	0.03621074558	0.03621095972	-0.2×10^{-6}
4	1.4	4	5	0.3934693403	0.3934694197	-0.8×10^{-7}
2	2	4	5	0.05294281483	0.05294290536	-0.9×10^{-7}
2	10	4	6	0.002099244933	0.002099246874	-0.2×10^{-8}
1	25.6	5	9	0.003421015147	0.003421014955	-0.2×10^{-9}
5	5.8	4	3	0.001002592162	0.001003548282	-0.6×10^{-6}
6	12.3	5	4	0.00001154377536	0.00001154415522	-0.4×10^{-9}
3	20	4	6	0.00004644518330	0.00004645262434	-0.7×10^{-8}
4	14	3	8	0.00004042254373	0.00004042330408	-0.7×10^{-8}
2	20.5	5	7	0.0003493184389	0.0003493175502	-0.8×10^{-9}
12	4.7	1	36	0.0005487914431	0.0005487915385	-0.9×10^{-10}
16	5	1	30	0.000283606900	0.0002836073536	-0.4×10^{-9}
13	3	1	30	0.0023154841	0.002315483646	-0.4×10^{-9}
5	16.5	4	5	0.000005265462305	0.000005263445336	-0.2×10^{-8}
3	25.5	5	6	0.00001984520444	0.00001984588875	-0.6×10^{-9}
3	0.5	1	16	0.09722202443	0.09722202446	-0.3×10^{-10}
6	12	3	5	0.00001348269912	0.00001345816536	-02×10^{-7}

Here, the choice of N and a is arbitrary but for attaining higher accuracy *N* must be high; the auxiliary function $A_n^{(0,1)}(\alpha)$ is defined as follow (Magnasco and Rapallo 2000):

$$A_n^{(0,1)}(\alpha)=\int_0^1 x^n e^{-\alpha x}dx \tag{5}$$

and can be computed easily by the following formulae

$$A_n^{(0,1)}(\alpha)=n!e^{-\alpha}\sum_{k=0}^{\infty}\frac{\alpha^k}{(n+k+1)!} \quad \text{if} \quad n\geq\alpha \tag{6a}$$

$$A_n^{(0,1)}(\alpha)=\frac{n!-\Gamma(n+1,\alpha)}{\alpha^{n+1}} \quad \text{if} \quad n\leq\alpha \tag{6.b}$$

Or by following recursive relations (Silver and Ruedenberg, 1968)

$$A_n^{(0,1)}(\alpha)=\left[nA_{n-1}^{(0,1)}(\alpha)-e^{-\alpha}\right]/\alpha \tag{7}$$

with the starting value

$$A_n^{(0,1)}(\alpha)=\left(1-e^{-\alpha}/\alpha\right) \tag{8}$$

Whenever the following relation is satisfied

$$\alpha\geq(0.072+0.012n_{\max})n\max \tag{9}$$

For other cases Equation (6) are accurate. In Equation (6), the symbol $\Gamma(n,x)$ is incomplete gamma function (Abromowitz et al., 1965). Recursive relation (7) can be calculated with an accuracy of 10 significant figures.

Boys integrals are special cases of the obtained formula for $G_m(\alpha,u)$. That is

$$F_m(\alpha)=G_m(\alpha,1) \tag{10}$$

COMPUTATIONAL RESULTS AND DISCUSSION

An efficient procedure had been proposed for the calculation of Boys integrals. The obtained formula (Equation 4) includes factorials and a well known auxiliary function $A_n^{0,1}(\alpha)$ that converges very well. A computer program had been constructed in Maple symbolic programming language for comparing our results with literature. As can be seen from

Table 1, the procedure presented here for the calculation of Boys integrals agree well with the numerical results obtained by Maple. Our results agree well with the values in available literature. We arrive the result that the optimum values of N and *Q are* N = 5 and Q = 36 that give at least 6 correct decimal digits. Therefore, we conclude that our algorithm can be used in large scale *ab initio* calculations giving accurate results and high speed.

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