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On the evaluation of Boys functions using downward recursion relation

B.A. Mamedov

Department of Physics, Faculty of Arts and Sciences, Gaziosmanpaşa University, Tokat, Turkey
E-mail: bamamedov@yahoo.com

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A new, simple, and efficient technique is presented for the accurate evaluation of the Boys functions $F_m(x)$ (BFs) with integer and noninteger values of m appearing for the calculation of multicenter multielectron molecular integrals in a mixed Gaussian and plane-wave basis set. The extensive test calculations show that the proposed in this work algorithm is the most efficient in practical computations.

KEY WORDS: Boys function, incomplete gamma functions, Gaussian type orbitals, molecular integrals

1. Introduction

It is well known that the multicenter molecular integrals, appearing in the mathematical expressions of physical and chemical properties of molecules, are evaluated by the use of two types of orbitals: Gaussian-type orbitals (GTOs) and Slater-type orbitals (STOs). The applicability of Slater-type functions to other than trivial molecular problems are hindered by the enormous computational complexity of the resulting expressions for matrix elements of the Hamiltonian. Boys found a more tractable choice in Ref. [1] as he introduced GTOs and developed into highly efficient algorithm [2–4]. Much simpler expressions for the matrix elements more than compensate for improper behavior of GTOs at the origin and infinity. Indeed, an s-type Gaussian (Gaussian function with $l+m+n$ equal 0) is smooth at the origin, whereas an s-type STOs has a cusp at the origin (nonzero derivative with respect to r). Also, GTOs decay with r much faster that STOs. However, a fact that a given STOs can be well represented as a linear combination of only few GTOs with different exponents was noticed early on, thus STO-nG basis sets were introduced, in which a single STOs is represented as a linear combination of n GTOs.

One important note to make before we move on to mathematical details is the value of efficient algorithms for computing integrals. Normally, in a typical high accuracy calculation only a small portion of CPU time is spent in computing

molecular integrals and the major part is spent in computing wavefunction parameters. It is well known that the fast and accurate computation of the multicenter multielectron integrals over GTOs and electron scattering theory requires the evaluation of the BFs function [5–15]. In literature, variational methods have been proposed for improving the accurate evaluation of the BFs [16–37].

This paper introduced a new general and exact, yet simple, algorithm for the evaluation of the BFs. This proposed algorithm would be also useful for the estimation of results already known from experiments and theory.

2. Definitions and computational method of the BFs

The BFs are defined by [1]

$$F_m(x) = \int_0^1 t^{2m} e^{-xt^2} \mathrm{d}t, \tag{1}$$

where m are arbitrary integer or noninteger values and x is a nonnegative real number depending on coordinates of four orbitals. This function satisfies the following recursive relations [13]:
upward recurrence for $F_m(x)$

$$F_m(x) = \frac{1}{2x}[(2m-1)F_{m-1}(x) - \mathrm{e}^{-x}], \tag{2}$$

downward recurrence for $F_m(x)$

$$F_m(x) = \frac{1}{2m+1}(2xF_{m+1}(x) + \mathrm{e}^{-x}), \tag{3}$$

$$F_0(x) = \frac{1}{2\sqrt{x}}\gamma(1/2, x), \tag{4}$$

where $\gamma(\sigma, x)$ is well known incomplete gamma function defined by [38]

$$\gamma(a, x) = \int_0^x t^{a-1}\mathrm{e}^{-t}\ \mathrm{d}t. \tag{5}$$

One of the efficient methods for the calculation of BFs in the intermediate region of $x(10^{-8} < x < 35)$, has been proposed as [13]

$$F_m(x) = \mathrm{e}^{-x} \lim_{N\to\infty} \sum_{i=0}^{N} \frac{(2x)^i}{(2m+1)(2m+3)\cdots(2m+2i+1)}. \tag{6}$$

When $x \geqslant 35$, the $F_0(x)$ is evaluated by [8]

$$F_0(x) = \frac{\sqrt{\pi}}{2\sqrt{x}} \tag{7}$$

and $F_m(x)$ are computed by a recursion formula

$$F_m(x) \approx (2m-1)F_{m-1}(x)/x, \tag{8}$$

where $m = 1, 2, 3, \ldots$. Another efficient method for calculation of BFs for large enough x (approximately more than 60) has been proposed in Ref. [26] as

$$F_m(x) \approx \frac{1}{2}\sqrt{\frac{\pi}{z}}\frac{(2m-1)!!}{(2x)^m}. \tag{9}$$

Using Equations (2), (6), (7) and (9) the numerical aspects of BFs for various values of parameters have been investigated in Refs. [16–37] and references quoted therein. It should be noted that the algorithms presented in these works are not of completely general types and can not be used to calculate the BFs for arbitrary values of parameters. This difficulty can be overcome by using the downward recursive relation. In the downward recursion, the error made in the initial value decreases by a factor $x/(m+1)$. Starting from a sufficiently large value of m_t, the initial value can be chosen arbitrary. As mentioned, all values of $F_m(x)$ have the same order of magnitude; therefore, in the downward recursion, $F_0(x)$ (equation (4)) may be taken as the initial value.

As a result of having d significant digits in $F_m(x)$, we should start the downward recursion with an even value of m_t satisfied

$$m_t \geqslant \begin{cases} \dfrac{d}{|\log(m_{\max}/x)|} + m_{\max} & \text{for} \quad m_{\max} \neq x, \\ \dfrac{d}{|\log(m_{\max})|} + m_{\max} & \text{for} \quad m_{\max} = x. \end{cases} \tag{10}$$

One can determine the accuracy of the computer results obtained from the downward recurrences.

We notice that, by means of downward recurrence relations for B_k auxiliary functions presented in Refs. [39, 40] we have had considerable success in the calculation of multicenter nuclear attraction and electron repulsion integrals over STOs [41–44].

3. Numerical results and discussion

A novel technique is introduced to accurately calculate the BFs by the use of downward recursive formula equation (3). The method is completely general and free of any restrictions on its application. To verify the accuracy of the proposed method the results of different geometries are presented. An excellent agreement between our method and the other investigations can be observed in tables. It can be seen that the results compare very well to each other.

The calculations were performed on a computer Pentium III 800 MHz (using Turbo Pascal language) in double precision with an accuracy of significant

digits. The results for the BFs are shown in Tables 1–4. As can be seen from the tables, our results are in excellent agreement with the literatures [8,13,26].

It should be noted that the algorithm, presented in this paper is general and can be used to calculate the BFs for arbitrary values of parameters.

Table 1
The values of $F_m(x)$ function obtained for $10^{-8} < x < 35$.

m	x	Equation (3)	Equation (6)
8	16	4.02308592502660E−07	4.02308592502660E−07
15	27	1.08359515555596E−11	1.08359515555596E−11
20	30	1.37585444267909E−03	1.37585444267909E−03
25	13	8.45734447905704E−08	8.45734447905704E−08
31	34	2.90561943091301E−16	2.90561943091301E−16
11	38	4.04561442253925E−12	4.04561442253925E−12
42	32	5.02183610419087E−16	5.02183610419086E−16
75	30	1.01429517438537E−15	1.01429517438537E−15
100	33	3.42689684943483E−17	3.42689684943483E−17
20	1.4E−3	2.43577075309547E−02	2.43577075309547E−02
45	6.4E−5	1.09883228385254E−02	1.09883228385254E−02
100	2.6E−7	4.97512309732144E−03	4.97512309732144E−03

Table 2
The values of $F_m(x)$ function obtained for $36 < x \leqslant 60$.

m	x	Equation (3)	Equation (8)	Equation (6)
8	42	1.11826597752251E−10	1.11826597760535E−10	1.11826597752251E−10
16	50	2.40509456111904E−16	2.40509458873868E−16	2.40509456111904E−16
21	56	1.43739730342730E−19	1.43739736976764E−19	1.43739730342730E−19
12	60	4.05791663779760E−15	4.05791663779769E−15	4.05791663779760E−15
15	53	3.14434039868936E−16	3.14434039992514E−16	3.14434039868935E−16
18	58	1.78336953967902E−18	1.78336954046990E−18	1.78336953967902E−18

Table 3
The values of $F_m(x)$ integrals obtained for $x > 60$.

m	x	Equation (3)	Equation (9)	Equation (6)
8	63	3.56261924865627E−12	3.56261924865627E−12	3.56261924865627E−12
14	68	3.09783511327517E−17	3.09783511327517E−17	3.09783511327517E−17
20	73	1.71295886102040E−21	1.71295886102059E−21	1.71295886102040E−21
33	85	1.74268831008018E−29	1.74268831019472E−29	1.74268831008018E−29
36	100	3.08919970425521E−33	3.08919975617600E−33	3.08919970425521E−33
100	120	4.97723065221079E−53	5.13707096722718E−53	4.97723065221079E−53

Table 4
The values of $F_m(x)$ function obtained for noninteger m.

m	x	Equation (3)	Equation (6)
5.7	13.3	9.02296149898981E−06	9.02296149898981E−06
0.5	23.6	2.11864406767677E−02	2.11864406767677E−02
23.8	3.4	7.92593349658604E−04	7.92593349658604E−04
25.8	0.4	1.29331240687006E−02	1.29331240687006E−02
28.3	0.002	1.73275865107165E−02	1.73275865107165E−02
36.6	42.7	7.12651246345736E−02	7.12651246345735E−02
43.2	54.2	1.53021328677383E−24	1.53021328677383E−24
64.3	75.4	5.52165865464571E−34	5.52165865464571E−34
104.6	115.4	1.26350192129925E−51	1.26350192129925E−51
115.6	5.4	2.03911971791491E−05	2.03911971791491E−05

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