Evaluation of the Boys function using analytical relations

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The analytical relations for Boys function $F_m(x)$ are presented. These relations are useful in the fast and more accurate calculations of multicenter molecular integrals over Gaussian type orbitals (GTOs). The formulas obtained are numerically stable for all values of m and x.

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

1. Introduction

One of the remarkable advances in quantum chemistry was the Gaussian expansion of Slater type orbitals (STOs) basis sets of which were labeled STO-NG. The common link between almost all the methods to develop STO-NG sets is the use of the Boys function [1]

$$F_m(x) = \int_0^1 t^{2m} e^{-xt^2} dt. \tag{1}$$

It is easy to express the Boys function through the complete and incomplete gamma functions:

$$F_m(x) = \frac{1}{2x^{m+1/2}} \begin{cases} \gamma(m+1/2, x), & (2) \\ \Gamma(m+1/2) - \Gamma(m+1/2, x), & (3) \end{cases}$$

where $x \geqslant 0$, $m = \alpha - 1/2$, $\alpha = n + \varepsilon$, $0 < \varepsilon < 1$, $n = 0, 1, 2, \ldots$ and the gamma functions are defined as [2]

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$$\gamma(\alpha, x) = \int_0^x t^{\alpha-1} e^{-t} dt, \tag{4}$$

$$\Gamma(\alpha, x) = \int_x^\infty t^{\alpha-1} e^{-t} dt, \tag{5}$$

$$\Gamma(\alpha) = \int_0^\infty t^{\alpha-1} e^{-t} dt = \gamma(\alpha, x) + \Gamma(\alpha, x). \tag{6}$$

Thus, by the use of the method set out in our paper [3] for the gamma functions, the analytical relations can be established for the Boys function.

The accurate numerical calculation of Boys function is more important for large molecules like proteins than for small organic molecules, because the enormous number of calculation results in considerable accumulation of numerical errors [4–8]. It should be noted that, 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 which require the fast and accurate evaluation of the Boys function. In literature, for improving the accurate evaluation of $F_m(x)$ function, the different methods have been proposed [9–23]. The protein calculations in a Hartree-Fock level will be often performed in the near future, and accurate Boys function calculation is required particularly for such larger calculations. In this article, we introduce a new general and exact, yet simple, analytical algorithm for the evaluation of the Boys function $F_m(x)$ with arbitrary integer or non-integer values of m.

2.   Upward and downward recurrences

In order to establish the analytical formulas for Boys function, equation (1), we shall use the following recursive relations [9]:
upward recurrence

$$F_m(x) = \frac{1}{2x}[(2m-1)F_{m-1}(x) - e^{-x}] \tag{7}$$

downward recurrence

$$F_m(x) = \frac{1}{2m+1}(2x F_{m+1}(x) + e^{-x}). \tag{8}$$

Taking into account the formulas for starting terms of gamma functions presented in Ref. [3] in equations (2) and (3) it is easy to obtain the following relations for the starting terms of Boys function:

$$F_{\varepsilon+1/2}(x) = \begin{cases} \frac{1}{2x}(1 - e^{-x}) & \text{for} \quad \varepsilon = 0 \\ \frac{1}{2} \sum_{m=0}^{\infty} \frac{(-1)^m x^m}{m!(1+\varepsilon+m)} & \text{for} \quad 0 < \varepsilon < 1. \end{cases} \tag{9}$$

Using the method set out in Ref. [24] we can show that as a result of having d significant digits in $F_m(x)$, the downward recursion should be started from the even value of n_t satisfying

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

$$F_{n_t+\varepsilon-1/2}(x) \cong \frac{1}{x^{n_t-1}} F_{\varepsilon+1/2}(x). \tag{11}$$

3.   Analytical relations

The analytical formulas for the Boys function in terms of starting values, equations (9) and (11), can be established from its recurrence relations (7) and (8). For this purpose we use the method set out in Ref. [3]. Then we obtain:

$$F_m(x) = \frac{1}{x^k}[(m+1/2)_k F_{m-k}(x) - \frac{1}{2}e^{-x} \sum_{i=1}^{k} (m+1/2)_{k-i} x^{i-1}] \tag{12}$$

and

$$F_{m-k}(x) = \frac{1}{(m+1/2)_k}[x^k F_m(x) + \frac{1}{2}e^{-x} \sum_{i=1}^{k} (m+1/2)_{k-i} x^{i-1}], \tag{13}$$

where $m = n + \varepsilon - 1/2$ and $0 \leqslant k \leqslant n$. See Ref. [3] for the exact definition of the coefficients $(m+1/2)_k$.

In special cases of equations (12) and (13) for $k = n-1$ and $n = n_t$, respectively, we obtain for the Boys function the following analytical relations in terms of initial values:

$$F_{n+\varepsilon-1/2}(x) = \frac{1}{x^{n-1}}[(n+\varepsilon)_{n-1} F_{\varepsilon+1/2}(x) - \frac{1}{2}e^{-x} \sum_{i=1}^{n-1} (n+\varepsilon)_{n-i-1} x^{i-1}] \tag{14}$$

and

$$F_{m_t-k}(x) = \frac{1}{(m_t+1/2)_k}[x^k F_{m_t}(x) + \frac{1}{2}e^{-x} \sum_{i=1}^{k} (m_t+1/2)_{k-i} x^{i-1}, \tag{15}$$

where $m_t = n_t + \varepsilon - 1/2$ and $0 \leqslant k \leqslant n_t$.

4.   Numerical results and discussion

Analytical formulae have been presented for computation of the Boys function that arise in molecular calculations with the help of Gaussian types orbitals (GTOs). This analytical algorithm can be used for the arbitrary values of parameters m and x. The computer results obtained in this work were compared with those provided by other methods.

The results of calculations for various values of parameters on a PENTIUM III 800 MHz (using Turbo Pascal language), Maple 7 and Mathematica 4 international software are given in Tables 1 and 2. Extensive tests were performed for a variety of parameters. As can be seen from the tables, the accuracy of computer results in all of the calculations are satisfactory under range of parameters m and x.

Table 1

Computational results for $F_m(x)$ obtained from equation (12).

m	x	Mathematica 4	Maple 7	Turbo pascal
0.5	6.8	7.34475165333247E-02	7.34475165333247E-02	7.34475165333247E-02
13	14.1	1.56775160456192E-07	1.56775160456192E-07	1.56775160456192E-07
20.6	32.4	2.17602798734846E-14	2.17602798734846E-14	2.17602798734846E-14
25	6.4	4.28028518677348E-05	4.28028518677348E-05	4.28028518677348E-05
64	50	5.67024356263279E-24	5.67024356263282E-24	5.67024356263277E-24
75.5	40.8	2.63173492081630E-20	2.6317349205857E-20	2.63173492073033E-20
80.3	78.2	6.35062774057122E-36	6.35062774057123E-36	6.35062774057123E-36

Table 2

Computational results for $F_m(x)$ obtained from equation (14).

m	x	Mathematica 4	Maple 7	Turbo pascal
4	7	8.03538503977806E-04	8.03538503977806E-04	8.03538503977806E-04
8.5	3.6	2.31681539108704E-03	2.31681539108704E-03	2.31681539108704E-03
15.3	20.7	5.40914879973724E-10	5.40914879973724E-10	5.40914879973724E-10
1.8	25.3	3.45745419193244E-04	3.45745419193244E-04	3.45745419193244E-04
30	26	3.57321060811178E-13	3.57321060811177E-13	3.57321060811181E-13
46.8	37.6	1.91851951160577E-18	1.91851951160577E-18	1.91851951160577E-18
100	125.1	7.75391047694625E-55	7.75391047694625E-55	7.75391047670974E-55

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