Journal of Mathematical Chemistry Vol. 38, No. 1, July 2005 (© 2005)
DOI: 10.1007/s10910-005-4527-4

Fast evaluation of molecular auxiliary functions A_α and B_n by analytical relations

I.I. Guseinov*

Department of Physics, Faculty of Arts and Sciences, Onsekiz Mart University, Çanakkale, Turkey
E-mail: iguseinov@cheerful.com

B.A. Mamedov

Department of Physics, Faculty of Arts and Sciences, Gaziosmanpaşa University, Tokat, Turkey

Received 11 January 2005; revised 21 January 2005

Analytical relations through the initial values are derived for the molecular auxiliary functions $A_\alpha(x)$ and $B_n(x)$, where $\alpha = n+\varepsilon$, $0 \leqslant \varepsilon < 1$ and $n = 0, 1, 2, \ldots$. These relations are useful in the fast calculation of multicenter molecular integrals over integer and noninteger n Slater type orbitals. It is shown that the formulas obtained are numerically stable for all values of n, ε *and* x.

KEY WORDS: molecular auxiliary functions, Slater type orbitals, overlap integrals, multicenter integrals

PACS No: 31.15.+q, 31.20.Ej

AMS subject classification: 81-V55, 81-V45

1. Introduction

It is known that the multicenter molecular integrals over integer and noninteger n Slater type orbitals (STOs) can be calculated using series expansion formulas in which the individual terms are expressed through the overlap integrals [1,2], which involve the auxiliary functions [3]

$$A_\alpha(x) = \int_1^\infty t^\alpha e^{-xt} dt, \tag{1}$$

$$B_n(x) = \int_{-1}^1 t^n e^{-xt} dt. \tag{2}$$

Recent works in this area [4–7] discuss the efficient evaluation of these functions. The methods presented in references [4–7] are based on the use of upward and

*Corresponding author.

downward recursion relations, therefore, require more computational effort. The purpose of this paper is to present an accurate algorithm for the fast evaluation of auxiliary functions $A_\alpha(x)$ and $B_n(x)$ with arbitrary values of parameters α, n *and* x using analytical formulas.

2. Recursion relations

In order to establish the analytical formulas for auxiliary functions, equations (1) and (2), we shall use the following recursive relations [8,9]:

Upward recurrences

$$A_\alpha(x) = (\alpha A_{\alpha-1}(x) + \mathrm{e}^{-x})/x, \tag{3a}$$

$$C(\alpha, x) = \alpha C(\alpha-1, x) + x^\alpha, \tag{3b}$$

$$B_n(x) = (nB_{n-1}(x) + (-1)^n \mathrm{e}^x - \mathrm{e}^{-x})/x, \tag{4}$$

where

$$A_\alpha(x) = \mathrm{e}^{-x} C(\alpha, x)/x^{\alpha+1}. \tag{5}$$

Downward recurrences

$$A_\alpha(x) = (xA_{\alpha+1}(x) - \mathrm{e}^{-x})/(\alpha+1), \tag{6a}$$

$$C(\alpha, x) = (C(\alpha+1, x) - x^{\alpha+1})/(\alpha+1), \tag{6b}$$

$$B_n(x) = (xB_{n+1}(x) + (-1)^n \mathrm{e}^x + \mathrm{e}^{-x})/(n+1). \tag{7}$$

The starting points in upward recurrences are given by

$$A_\varepsilon(x) = \begin{cases} \mathrm{e}^{-x}/x & \text{for} \quad \varepsilon = 0, \\ \frac{1}{x^{1+\varepsilon}}(\Gamma(1+\varepsilon) - \gamma(1+\varepsilon, x)) & \text{for} \quad 0 < \varepsilon < 1, \end{cases} \tag{8a}$$

$$C(\varepsilon, x) = \mathrm{e}^x x^{1+\varepsilon} A_\varepsilon(x), \tag{8b}$$

$$B_0(x) = (\mathrm{e}^x - \mathrm{e}^{-x})/x, \tag{9}$$

where Γ and γ are the complete and incomplete gamma functions, respectively [10]. The downward recursion of auxiliary functions $B_n(x)$ should be started from the even value of n_t determined as [5]

$$n_t \geqslant \begin{cases} \frac{d}{|\log(n_{\max}/x)|} + n_{\max} & \text{for} \quad n_{\max} \neq x, \quad (10a) \\ n_{\max}^2 & \text{for} \quad n_{\max} = x, \quad (10b) \end{cases}$$

at which point

$$B_{n_t}(x) = B_0(x)/x^{n_t}. \tag{11}$$

3. Analytical relations

The analytical formulas for auxiliary functions $A_\alpha(x)$ and $B_n(x)$ in terms of starting values can be obtained from their recurrence relations presented in Section 2. For this purpose we use the method set out in our previous paper [11]. Then, we obtain:

$$A_\alpha(x) = \frac{1}{x^k}\left[(\alpha+1)_k A_{\alpha-k}(x) + \mathrm{e}^{-x}\sum_{i=1}^{k}(\alpha+1)_{k-i}x^{i-1}\right], \tag{12a}$$

$$C(\alpha,x) = (\alpha+1)_k C(\alpha-k,x) + \sum_{i=1}^{k}(\alpha+1)_{k-i}x^{\alpha-k+i}, \tag{12b}$$

$$B_n(x) = \frac{(n+1)_k}{x^k}\left\{B_{n-k}(x) + \sum_{i=1}^{k}\frac{(n+1)_{k-i}}{(n+1)_k}\left((-1)^{n-k+i}\mathrm{e}^{x} - \mathrm{e}^{-x}\right)x^{i-1}\right\} \tag{13}$$

and

$$A_{\alpha-k}(x) = \frac{1}{(\alpha+1)_k}\left[x^k A_\alpha(x) - \mathrm{e}^{-x}\sum_{i=1}^{k}(\alpha+1)_{k-i}x^{i-1}\right], \tag{14a}$$

$$C(\alpha-k,x) = \frac{1}{(\alpha+1)_k}\left[C(\alpha,x) - \sum_{i=1}^{k}(\alpha+1)_{k-i}x^{\alpha-k+i}\right], \tag{14b}$$

$$B_{n-k}(x) = \frac{x^k}{(n+1)_k}B_n(x) - \sum_{i=1}^{k}\frac{(n+1)_{k-i}}{(n+1)_k}\left((-1)^{n-k+i}\mathrm{e}^{x} - \mathrm{e}^{-x}\right)x^{i-1}, \tag{15}$$

where $0 \leqslant k \leqslant n$ and $(\alpha)_k$ is the Pochhammer symbol defined by

$$(\alpha)_k = \begin{cases} 1 & \text{for} \quad k = 0, & (16a) \\ (\alpha-1)(\alpha-2)\ldots(\alpha-k) & \text{for} \quad 1 \leqslant k \leqslant n-1, & (16b) \end{cases}$$

$$(n)_k = (n-1)!/(n-1-k)! \quad \text{for} \quad \alpha = n(\varepsilon = 0). \tag{17}$$

In special cases of equations (12a), (12b), (13) and (15) for $k = n$ and $n = n_t$, respectively, we obtain for the molecular auxiliary functions $A_\alpha(x)$ and $B_n(x)$ the following analytical relations in terms of initial values:

$$A_{n+\varepsilon}(x) = \frac{1}{x^n}\left[(n+\varepsilon+1)_n A_\varepsilon(x) + \mathrm{e}^{-x}\sum_{i=1}^{n}(n+\varepsilon+1)_{n-i}x^{i-1}\right], \quad (18a)$$

$$C(n+\varepsilon, x) = (n+\varepsilon+1)_n C(\varepsilon, x) + \sum_{i=1}^{n}(n+\varepsilon+1)_{n-i}x^{\varepsilon+i}, \quad (18b)$$

$$B_n(x) = \frac{n!}{x^n}\left\{B_0(x) + \sum_{i=1}^{n}\frac{1}{i!}[(-1)^i\mathrm{e}^x - \mathrm{e}^{-x}]x^{i-1}\right\}, \quad (19a)$$

$$= \frac{n!}{x^n}\sum_{i=0}^{n}\frac{1}{i!}[(-1)^i\mathrm{e}^x - \mathrm{e}^{-x}]x^{i-1} \quad (19b)$$

and

$$B_{n_t-k}(x) = \frac{x^k}{(n_t+1)_k}B_{n_t}(x) - \sum_{i=1}^{k}\frac{(n_t+1)_{k-i}}{(n_t+1)_k}[(-1)^{n_t-k+i}\mathrm{e}^x - \mathrm{e}^{-x}]x^{i-1} \quad (20)$$

4. Discussion

A novel technique is introduced to accurately calculate the molecular auxiliary functions A_α and B_n by the use of analytical formulas obtained from the upward and downward recurrences.

On the basis of formulas (equations (12a)–(19b)) obtained in this paper we constructed a program for computation of auxiliary functions on a Mathematica 5.0 international mathematical software. One can determine the accuracy of computer results obtained from analytical relations (12a) and (13) by the use of upward and downward recurrences, equations (6a)–(7). The examples of computer calculation of equations (12a) and (13) for the A_α and B_n are shown in tables 1 and 2.

The calculation results based on the use of upward and downward analytical relations for auxiliary functions A_α and B_n show good rate of convergence and numerical stability with literature [4,7] under arbitrary values of parameter x. The accuracy of the computer results obtained from the analytical relations can be determined with the help of upward or downward recurrences. The number of correct decimal figures m occurring in $\Delta f_\mathrm{u} = 10^{-m_\mathrm{u}}$ and $\Delta f_\mathrm{d} = 10^{-m_\mathrm{d}}$ are presented in tables 1 and 2, where $\Delta f = \left|f^\mathrm{L} - f^\mathrm{R}\right|$ and $m = m_\mathrm{u}$ and $m = m_\mathrm{d}$. The values f^L and f^R are determined from the left- and right-hand side (LHS and RHS) of analytical formulas derived from the upward and downward relations. The advantage of the algorithm described in this work is in its general applicability: indeed, the proposed algorithm could be useful in the fast evaluation of molecular properties involving auxiliary functions A_α and B_n.

Table 1
Computational results and numbers of correct decimal figures for $A_\alpha(x)$ obtained from equation (12a).

α	$x = 45.7$	m	$x = 88.3$	m	$x = 100.6$	m	$x = 156.8$	m
30	8.2724084848442E-22	∞	7.62944712344975E-41	∞	2.87516184087968E-46	∞	6.290884014811274E-71	∞
48.6	4.1643824413431E-21	∞	1.09905727831202E-40	∞	3.86132529173347E-46	∞	7.356051242853456E-71	∞
75.3	2.02600102815814E-17	∞	2.70417126475659E-40	∞	7.37382651002109E-46	∞	9.7002484449169E-71	∞
100	2.08193634880702E-10	43	2.41383295074105E-39	∞	2.56378641724850E-45	∞	1.367998538934625E-70	∞
120	9.45221602808358E-03	28	2.31157591274040E-37	∞	3.15865859424409E-44	∞	2.02108576294880E-70	∞
153.4	7.69155040714605E+13	36	5.25705534176673E-31	∞	9.46121233739903E-40	∞	6.791343282934481E-70	∞

Table 2
Computational results and numbers of correct decimal figures for $B_n(x)$ obtained from equation (13).

n	$x = 70$	m	$x = 90$	m	$x = 120$	m	$x = 150$	m
40	2.279139966728097E+28	∞	9.36531245924842E+36	∞	8.1382938742304E+49	∞	7.327126714697923E+62	∞
70	1.790302140485578E+28	64	7.606574379099845E+36	∞	6.850737054846059E+49	∞	6.325837536724039E+62	∞
85	−1.617108964573127E+28	∞	−6.954317517800445E+36	72	6.348942869217614E+49	∞	−5.921515156793208E+62	∞
100	1.474542858225349E+28	∞	6.405343261219855E+36	∞	5.915811343082898E+49	∞	5.565889981743682E+62	∞
120	1.3195011903013358E+28	∞	5.795609482489004E+36	85	5.422742443767506E+49	∞	5.15336941385952E+62	∞

Acknowledgment

This work was supported by the TÜBITAK Project No. TBAG-2396 (103T172).

References

[1] I.I. Guseinov, Phys. Rev. A, 31 (1985) 2851.
[2] I.I. Guseinov and B.A. Mamedov, J. Mol. Model. 8 (2002) 272.
[3] R.S. Mulliken, C.A. Rieke, D. Orloff and H. Orloff, J. Chem. Phys.,17 (1949) 1248.
[4] F.E. Harris, Int. J. Quantum Chem. 100 (2004) 142.
[5] I.I. Guseinov, A. Özmen, Ü. Atav and H. Yüksel, Int. J. Quantum Chem. 67 (1998) 199.
[6] I.I. Guseinov, B.A. Mamedov, M. Kara and M. Orbay, Pramana J. Phys. 56 (2001) 691.
[7] I.I. Guseinov, Pramana J. Phys. 61 (2003) C781.
[8] C. Zener and V. Guillemin, Phys. Rev. 34 (1929) 999.
[9] F.J. Corbato, J. Chem. Phys. 24 (1956) 452.
[10] I.S. Gradshteyn and I.M. Ryzhik, *Tables of Integrals, Sums, Series and Products 4-th ed.* (New York, Academic Press, 1980).
[11] I.I. Guseinov and B.A. Mamedov, J. Math. Chem. 36 (2004) 341.