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On the computation of molecular auxiliary functions A_n and B_n

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Abstract. Molecular auxiliary functions $A_n(p)$ and $B_n(pt)$, arising in the Hartree–Fock–Roothaan (HFR) approximation for molecules, Ewald's crystal lattice theory, electromagnetic stopping theory, and other approximate methods, are evaluated and analysed in the range of $17 \leq n \leq 60$ and $25 \leq pt \leq 60$.

Keywords. Auxiliary functions; overlap integrals.

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1. Introduction

Computation of molecular integrals over STO's arising in the calculation of molecular properties by the use of HFR approximation is one of the most important problems of quantum chemistry. Numerical analysis of error occurrence and propagation in these problems are naturally followed with interest [1]. In the literature the molecular integrals over STO's are computed by translation of STO's to the new center [2]. The coefficients of translation formulas are two-center overlap integrals quantum members of which are the variables of infinite series.

If the overlap integrals for large quantum numbers contained in the series expansion formulas are calculated accurately, then the results will be more efficient and satisfactory. The overlap integrals can be evaluated analytically by using $A_n(p)$ and $B_n(pt)$ auxiliary functions [3]. In the literature the calculation of auxiliary functions $A_n(p)$ and $B_n(pt)$ for $n > 17$ and $pt > 25$ are not much satisfactory. For $1 \leq n \leq 17$ and $0.01 \leq pt \leq 25$ some molecular integrals have been evaluated by series and recursive formulas [4].

The aim of this report is to show that for large n and pt the downward relation of $B_n(pt)$ gives more accurate results.

2. Theory and computational method

The auxiliary functions $A_n(p)$ and $B_n(pt)$ are defined by [5]

$$A_n(p) = \int_1^\infty \mu^n \mathrm{e}^{-p\mu} \mathrm{d}\mu, \quad B_n(pt) = \int_{-1}^1 \nu^n \mathrm{e}^{-pt\nu} \mathrm{d}\nu. \tag{1}$$

These functions satisfy the following recursive relations [6]:

$$A_n(p) = \frac{1}{p}\left[nA_{n-1}(p) + \mathrm{e}^{-p}\right], \tag{2}$$

$$A_0(p) = \frac{\mathrm{e}^{-p}}{p} \tag{3}$$

and

$$B_n(pt) = \frac{1}{pt}\left[nB_{n-1}(pt) - 2\cosh(pt)\right] \quad \text{for odd } n, \tag{4}$$

$$B_n(pt) = \frac{1}{pt}\left[nB_{n-1}(pt) + 2\sinh(pt)\right] \quad \text{for even } n, \tag{5}$$

$$B_n(0) = \frac{1+(-1)^n}{n+1} \quad \text{for } t = 0. \tag{6}$$

Computation of $A_n(p)$ for small internuclear distances is very difficult [7]. In the calculation of molecular properties, the values of p for $p < 0.01$ are seldom used.

For $p \geq 0.01$ values, the auxiliary functions $A_n(p)$ are calculated from the recursive relation (2). The recursive relation (5) for auxiliary functions $B_n(pt)$ becomes unstable when $n/(pt) > 1$. The absolute error made in the initial value $B_0(pt)$ in eq. (5) grows with a factor $n/(pt)$ in each step. Since $B_n(pt)$ values have almost the same order of magnitude for all n, the relative error grows in each step by a factor $n/(pt)$. Corbato overcame this difficulty with an indirect approach by using the modified Bessel functions [8]. In this study, we used a direct approach as described below.

It could easily be shown that if the error made in the initial value is ε_0, then the error in $B_n(pt)$ is

$$\varepsilon_n = \frac{n!}{(pt)^n}\varepsilon_0. \tag{7}$$

The recursion could be used upward for $n/(pt) \leq e$ while keeping the magnitude of the error at the same level with ε_0. However, for large values of n, this relation can not be used upward.

This difficulty can be overcome by using the recursive relation downward for $n/(pt)>1$. For this purpose, in the downward recursion, the error made in the initial value decreases by a factor $(pt)/(n+1)$. Therefore, starting with a sufficiently large value of n_{top}, the initial value can be chosen arbitrarily. As mentioned, all $B_n(pt)$ values have the same order of magnitude; therefore, in the downward recursion, $B_0(pt)$ may be taken as the initial value.

In the downward recursion, the relative error made in the $n_{\max}$-th step is

$$\varepsilon_r = \frac{(pt)^{n_{\text{top}}-n_{\max}} n_{\max}!}{n_{\text{top}}!}. \tag{8}$$

As a result of having d significant digits in $B_{n_{\max}}(pt)$, we should start the downward recursion with an even value of n_{top} satisfying

$$n_{\text{top}} \geq d/\log\left(\frac{n_{\max}}{pt}\right) + n_{\max}. \tag{9}$$

For $pt \leq 0.01$ values, eqs (4) and (5) give more sufficient results.

3. Results and discussion

It is shown that the overlap integrals for large quantum numbers can be computed by using auxiliary functions $A_n(p)$ and $B_n(pt)$. Therefore, by the use of translation formulas for STO's multi-center molecular integrals for $17 \leq n \leq 60$ and $25 \leq pt \leq 60$ can easily be calculated in terms of auxiliary functions.

The result of computer calculation $A_n(p)$ and $B_n(pt)$ auxiliary functions for large pt are shown in tables 1 and 2, respectively. The graphics of $A_n(p)$ versus p for $n > 17$ is shown in figure 1. Besides, the graphics of $B_n(pt)$ versus pt for odd and even n, and $n > 17$ can

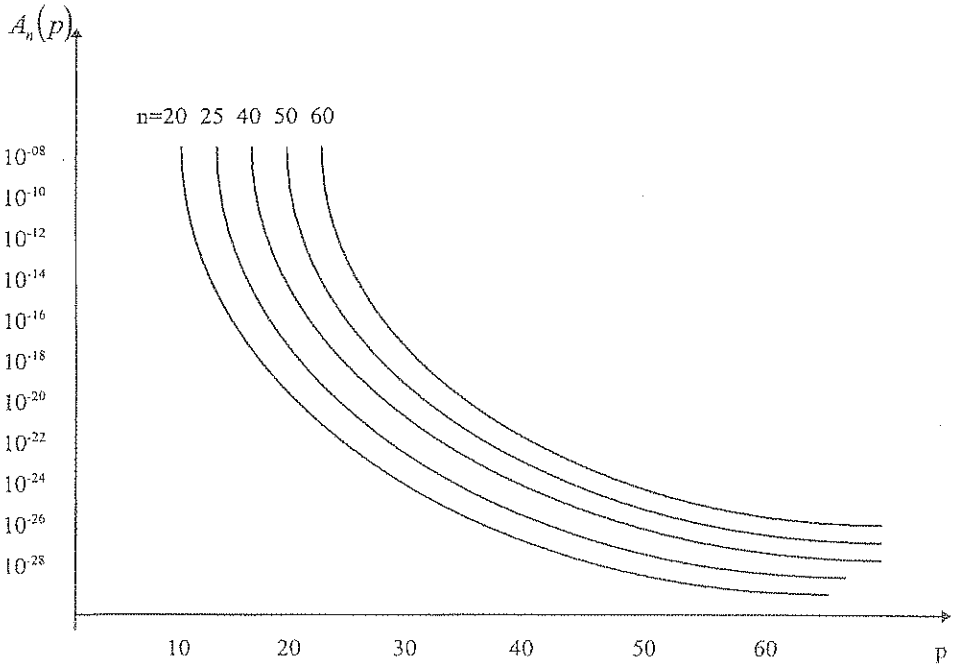

Figure 1. The graphics of $A_n(p)$ versus p.

be seen from figure 2. From the adequacy of graphics in figures 1 and 2, it is understood that the results are satisfactory.

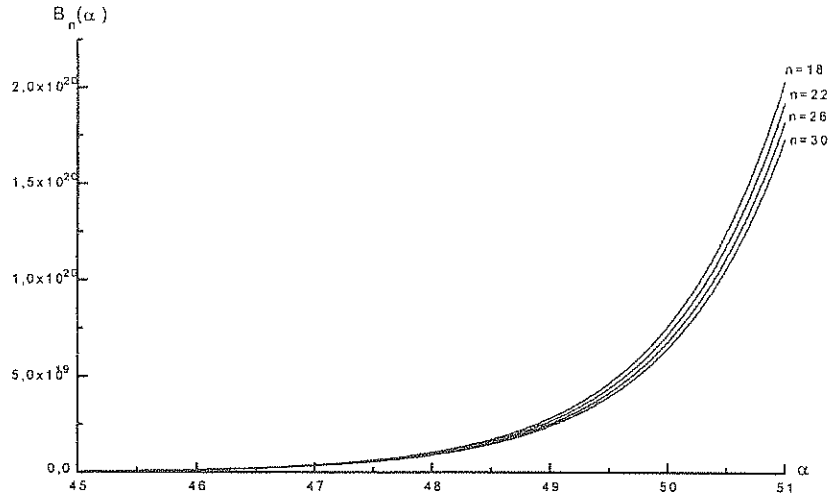

Figure 2a. The graphics of $B_n(pt)$ versus pt for even n.

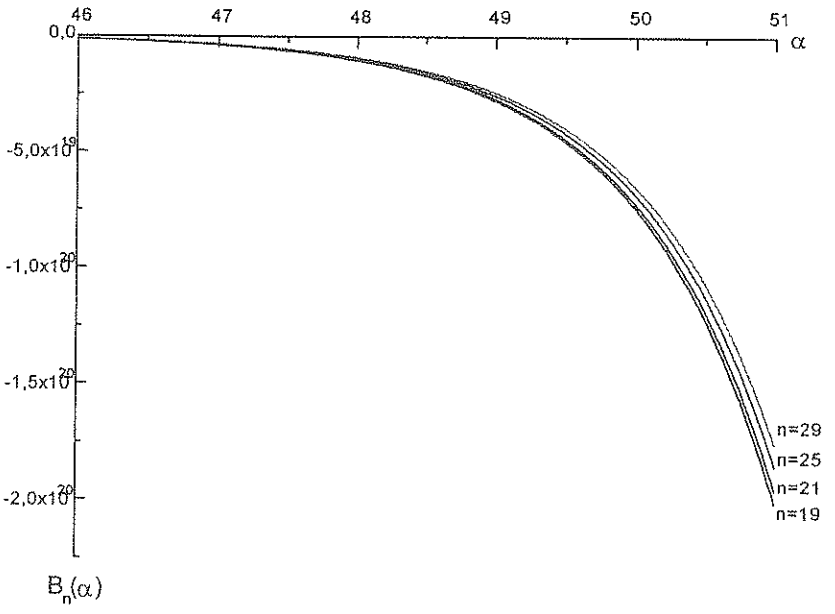

Figure 2b. The graphics of $B_n(pt)$ versus pt for odd n.

Table 1. Computation results of $B_n(pt)$ auxiliary function.

n	$pt = 30$	$pt = 40$	$pt = 50$	$pt = 60$
25	−1.92675188775215E+11	−3.59960238182083E+15	−6.88180140340171E+19	−1.3388271373405E+24
30	1.76611423075051E+11	3.34184827605494E+15	6.45016766196352E+19	1.2641446824000E+24
35	−1.63037431376783E+11	−3.11878604755608E+15	−6.06983803826688E+19	−1.19740685925734E+24
40	1.51412739520710E+11	2.92381220528587E+15	5.73212467782796E+19	1.13740263869122E+24
45	−1.41343521906220E+11	−2.75190798881541E+15	−5.43020697444211E+19	−1.08315652778228E+24
50	1.26245577534467E+11	2.59918865663824E+15	5.15865307427441E+19	1.03387368478154E+24
55	−1.19178342626757E+11	−2.46259896911232E+15	−4.91308199555929E+19	−9.88899766307868E+23
60	1.17859134130635E+11	2.33970216867924E+15	4.68992021129314E+19	9.47691071938667E+23

Table 2. Computation results of $A_n(p)$ auxiliary function.

n	$p = 30$	$p = 40$	$p = 50$	$p = 60$
25	1.27145768726688E−14	2.60599639963822E−19	7.45387488237306E−24	2.44591650723281E−28
30	2.35483360249446E−14	3.54849625091219E−19	9.07999690770193E−24	2.83448564015613E−28
35	5.80092767499976E−14	5.30433583029004E−19	1.21470685616151E−23	3.34200542965338E−28
40	2.16476156695732E−13	9.14364051172308E−19	1.65206145614830E−23	4.05166320151543E−28
45	1.34434887275401E−12	1.95591342530596E−18	2.24639270060226E−23	5.09850740583554E−28
50	1.41176183470790E−11	5.68245280007923E−18	3.68126096524700E−23	6.75285763235690E−28
55	2.42596343513057E−10	2.4215713596777E−17	7.176902229768891E−23	9.61177800778752E−28
60	6.54301802517065E−09	1.56312419792013E−16	1.78023605338362E−22	1.51601411741968E−27

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