CROATICA CHEMICA ACTA CCACAA 49 (1) 69—74 (1977)

YU ISSN 0011—1643
539.19

CCA-976

Note

Gaussian Quadrature for Computation of the Auxiliary Integral $B_n(y)$

L. Jakab

State Committee for Nuclear Energy, Institute of Stable Isotopes, P. O. Box 243, Cluj-Napoca, Romania

Received January 19, 1976

The Gauss-Legendre quadrature formula is suggested to be used for computation of the auxiliary integral $B_n(y)$ in case when y takes values near to zero. It is analytically shown and numerically tested that the precision of the results raises as y approaches zero. Owing to this property, this numerical procedure may be helpful in computing overlap integrals over Slater type orbitals with nearly equal exponents.

Despite of computationally simple Gaussian basis orbitals, the Slater orbitals still remain of interest[1]. Frequently, molecular integrals over Slater type orbitals are reducible to some auxiliary integrals which in principle can be evaluated by a recursive or an expansive computation formula[2]. One of these auxiliary integrals

$$B_n(y) = \int_{-1}^{1} \exp(-yx)\, x^n\, dx \tag{1}$$

demands special attention since it is evaluated with considerable error when the argument y is less than one and near to zero. Then either the equation

$$B_n(y) = n!/y^{n+1} \left(\exp(y) \sum_{k=0}^{n} (-y)^n/(k!) - \exp(-y) \sum_{k=0}^{n} y^k/(k!)\right)$$

or the recursive formula

$$B_n(y) = 1/y\,(nB_{n-1}(y) - \exp(-y) + (-1)^n \exp(y))$$

is used for computation. This case is met, for example, when one wants to compute the overlap integral of Slater type orbitals with nearly equal exponents.

A couple of years ago an alternative solution aiming to improve this situation was proposed by using the infinite sums[3]

$$B_n(y) = 2 \sum_{k=0}^{\infty} y^k/(k!\,(k+n+1)) \qquad \text{for } n \text{ even, } k \text{ even}$$

and

$$B_n(y) = -2 \sum_{k=1}^{\infty} y^k/(k!\,(k+n+1)) \qquad \text{for } n \text{ odd, } k \text{ odd}$$

values.

The aim of this note is to present our results obtained when the integral defined in Eq (1) is computed by a Gauss-Legendre quadrature formula[4]

$$\int_{-1}^{1} f(x)\,dx = \sum_{i=1}^{N} w_i f(x_i) + R_N(f) \tag{2}$$

where N is the number of quadrature points on the interval (—1, 1), x_i are the abscissae for which the value of the function f (x) is required and w_i are weighting factors. The term R_N (f) represents the remainder or the absolute error caused by approximating the integral with the N term sum. Details concerning the deduction of Eq (2) are beyond our interests here, but they can be found in the literature[5]. We shall pay our attention only to the expression of the remainder which is given as

$$R_N(f) = Q_N f^{(2N)}(x) \qquad (-1 < x < 1) \tag{3}$$

where Q_N is a constant depending only on the number of quadrature points

$$Q_N = 2^{2N+1} (N!)^4/((2N+1)((2N)!)^3) \tag{4}$$

and $f^{(m)}(x)$ represents the m th derivative of the function f (x) with respect to x. For the validity of Eq (3) it is neccessary for $f^{(m)}(x)$ to be a continuous function of x in the interval (—1, 1). In the more general case when this requirement is not guaranteed we have the inequality

$$|R_N(f)| \leqslant Q_N F_{2N} \tag{5}$$

where

$$F_{2N} = \sup_{-1 \leqslant x \leqslant 1} |f^{(2N)}(x)|$$

We can observe that R_N (f) is equal to zero when f (x) is a polynomial of order less or equal to 2N-1.

In our case the integrand in Eq (1) may be written as a product of two functions u and v where $u = \exp(-yx)$ and $v = x^n$. By using Leibnitz's theorem for the differentiation of a product the following equations will result for the expression of the remainder

$$R_N(B_1) = Q_N \exp(-yx)(-y)^{2N-1}(-yx + 2N)$$
$$R_N(B_2) = Q_N \exp(-yx)(-y)^{2N-2}(y^2x^2 - 4Nyx + 2N(2N-1))$$
$$\begin{aligned} R_N(B_n) = Q_N \exp(-yx)(-y)^{2N-n}\Big((-yx)^n &+ \binom{N}{1} n (-yx)^{n-1} \\ &+ \binom{2N}{2} n(n-1)(-yx)^{n-2} + \ldots \\ &+ \binom{2N}{i} n(n-1)\ldots(n-i+1)(-yx)^{n-i} + \ldots \\ &+ \binom{2N}{n} n!\Big) \end{aligned}$$

where x belongs to the interval (—1, 1) and $\binom{k}{j}$ means $k!/(j!(k-j)!)$.

From these equations the following conclusions may be drawn:

1. In contrast to evaluations based on recursive or expansive formulas, in our case the precision of the results rises as y becomes smaller and smaller. The function behaves then essentially like x^n over the interval (—1, 1), hence is exactly integrable with a Gauss-Legendre grid. For example, using six quadrature points, the integral for B_8 (1.0) is computed to four digits accuracy only, but for B_8 (0.02) we could obtain ten exact digits with the same number of quadrature points.

TABLE I

Values of the Auxiliary Integral $B_n(y)$ Computed with a Gauss-Legendre Quadrature Formula Using Eighty Points for Integration

y	k	$B_{2k}(y)$	$B_{2k+1}(y)$
.02	0	.2000133336D+01	—.1333386667D—01
	1	.6667466686D+00	—.8000380958D—02
	2	.4000571443D+00	—.5714582015D—02
	3	.2857587314D+00	—.4444686873D—02
	4	.2222585869D+00	—.3636568768D—02
	5	.1818489519D+00	—.3077100858D—02
	6	.1538728213D+00	—.2666823532D—02
	7	.1333568634D+00	—.2353081530D—02
	8	.1176681121D+00	—.2105390144D—02
	9	.1052822061D+00	—.1904877849D—02
.04	0	.2000533376D+01	—.2667093358D—01
	1	.6669866971D+00	—.1600304781D—01
	2	.4002285951D+00	—.1143094195D—01
	3	.2858920829D+00	—.8890828414D—02
	4	.2223676932D+00	—.7274368412D—02
	5	.1819412730D+00	—.6155268476D—02
	6	.1539528331D+00	—.5334588325D—02
	7	.1334274622D+00	—.4707005241D—02
	8	.1177312795D+00	—.4211542263D—02
	9	.1053393576D+00	—.3810451414D—02
.06	0	.2001200216D+01	—.4001440185D—01
	1	.6673868210D+00	—.2401028715D—01
	2	.4005144057D+00	—.1715085832D—01
	3	.2861143839D+00	—.1333987978D—01
	4	.2225495780D+00	—.1091463023D—01
	5	.1820951769D+00	—.9235569993D—02
	6	.1540862174D+00	—.8004235976D—02
	7	.1335451549D+00	—.7062613620D—02
	8	.1178365839D+00	—.6319218609D—02
	9	.1054346334D+00	—.5717416668D—02
.08	0	.2002134016D+01	—.5336747447D—01
	1	.6679471544D+00	—.3202438702D—01
	2	.4009146650D+00	—.2287611079D—01
	3	.2864257072D+00	—.1779329713D—01
	4	.2228043030D+00	—.1455858639D—01
	5	.1823107171D+00	—.1231907330D—01
	6	.1542730213D+00	—.1067670876D—01
	7	.1337099836D+00	—.9420749763D—02
	8	.1179840635D+00	—.8429181991D—02
	9	.1055680682D+00	—.7626470094D—02
.10	0	.2003335000D+01	—.6673335715D—01
	1	.6686678575D+00	—.4004763757D—01
	2	.4014294976D+00	—.2860848076D—01
	3	.2868261546D+00	—.2225253808D—01
	4	.2231319543D+00	—.1820747032D—01
	5	.1825879683D+00	—.1540684741D—01
	6	.1545133109D+00	—.1335294995D—01
	7	.1339220074D+00	—.1178225768D—01
	8	.1181737716D+00	—.1054219605D—01
	9	.1057397108D+00	—.9538308946D—02

y	k	$B_{2k}(y)$	$B_{2k+1}(y)$
.20	0	.2013360025D+01	—.1338674291D+00
	1	.6746857341D+00	—.8038154544D—01
	2	.4057291167D+00	—.5743963868D—01
	3	.2901708651D+00	—.4468727928D—01
	4	.2258688541D+00	—.3656912042D—01
	5	.1849040042D+00	—.3094732254D—01
	6	.1565206730D+00	—.2682381036D—01
	7	.1356933005D+00	—.2367001683D—01
	8	.1197586789D+00	—.2117984779D—01
	9	.1071737240D+00	—.1916377460D—01
.40	0	.2053761629D+01	—.2709577867D+00
	1	.6989726957D+00	—.1630666412D+00
	2	.4230952167D+00	—.1166716499D+00
	3	.3036868803D+00	—.9084145446D—01
	4	.2369325398D+00	—.7437971447D—01
	5	.1942687673D+00	—.6297075726D—01
	6	.1646389111D+00	—.5459724877D—01
	7	.1428579220D+00	—.4818978586D—01
	8	.1261701947D+00	—.4312858252D—01
	9	.1129754155D+00	—.3902962512D—01
.60	0	.2122178607D+01	—.4145863822D+00
	1	.7402239998D+00	—.2504307284D+00
	2	.4526404176D+00	—.1795472478D+00
	3	.3267061289D+00	—.1399792240D+00
	4	.2557889534D+00	—.1147164270D+00
	5	.2102381570D+00	—.9718451492D—01
	6	.1784883088D+00	—.8430403605D—01
	7	.1550844328D+00	—.7443990847D—01
	8	.1371143812D+00	—.6664326040D—01
	9	.1228807952D+00	—.6032554528D—01
.80	0	.2220264955D+01	—.5682561714D+00
	1	.7996245269D+00	—.3449953899D+00
	2	.4952880061D+00	—.2480373275D+00
	3	.3599849991D+00	—.1937186236D+00
	4	.2830787193D+00	—.1589517739D+00
	5	.2333677814D+00	—.1347803712D+00
	6	.1985593877D+00	—.1169973162D+00
	7	.1728119227D+00	—.1033638147D+00
	8	.1529886612D+00	—.9257831608D—01
	9	.1372528437D+00	—.8383232726D—01
1.00	0	.2350402387D+01	—.7357588823D+00
	1	.8788846226D+00	—.4495074018D+00
	2	.5523727800D+00	—.3242973697D+00
	3	.4046181691D+00	—.2538340857D+00
	4	.3197297018D+00	—.2085939537D+00
	5	.2644628501D+00	—.1770699184D+00
	6	.2255633663D+00	—.1538375075D+00
	7	.1966772817D+00	—.1360020449D+00
	8	.1743696694D+00	—.1218768903D+00
	9	.1566183613D+00	—.1104124044D+00

2. Since, the factor Q_N decreases very quickly as N increases, for a given y and n we can find a proper N for which the desired precision is attainable for almost all practical cases of interest. We found, for example, twelve quadrature points sufficient to compute the integral $B_n(y)$ to nine exact digits when y is not greater than one and n is less than twenty. In Table I a series of values is given for the integral $B^n(y)$ computed by an eighty point quadrature formula. Since we arrived to the same results when the computation was repeated with fourty and with twenty quadrature points, we consider every item given in the Table to be exact to ten digits.

3. By increasing the order n of the integral $B_n(y)$ and keeping the parameter y at a constant value the accuracy of the results decreases if the same number of quadrature points is used during computation. For example, $B_7(0.1)$ is computed to ten, but $B_{11}(0.1)$ to five exact digits only, using in both cases six quadrature points for the integration. In Figure 1 the limiting values of n are represented against variations of y when the integral $B_n(y)$ is computed at least to six exact digits using four, six or eight quadrature points.

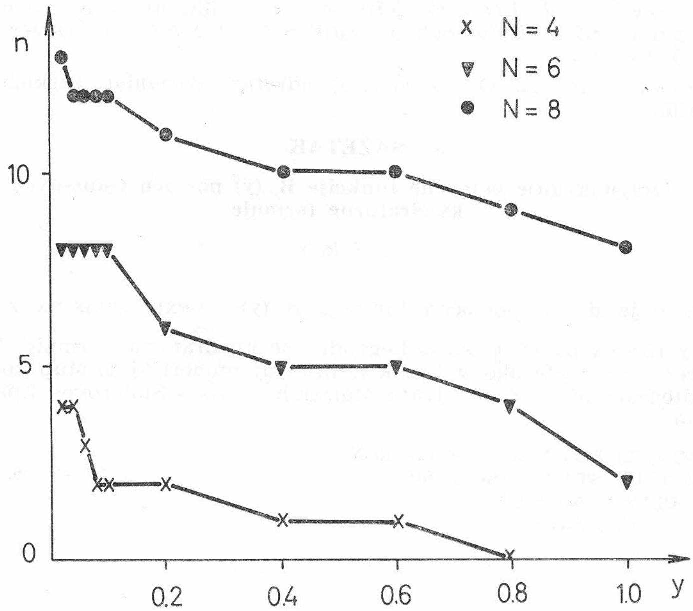

Figure 1. The maximum value of n is represented against variations of y when the integral $B_n(y)$ is computed at least to six exact digits using N quadrature points for the integration.

4. The upper limit of the remainder can be estimated in advance. For example, we found, before doing the integration for $B_2(1.0)$ and $B_4(1.0)$, as upper limit for the remainder 3.52×10^{-5} and 8.55×10^{-4}, respectively, by putting in Eq (3) and Eq (4) $x = -1$ and $N = 4$. After performing the integration with four quadrature points and comparing the results with those given in Table I we observed that the remainder was only 2.37×10^{-6} for $B_2(1.0)$ and 1.02×10^{-4} for $B_4(1.0)$.

Acknowledgements. Thanks are due to Professor Dr. Doc. Victor Mercea for the possibility of doing this work in his Institute.

The author would like to express his appreciation for the helpful cooperation of the Teritory Computer Centre of Cluj-Napoca where the computations were performed.

For numerous suggestions leading to the improvement of the manuscript the author is very much indebted to the anonymous referees.

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SAŽETAK

Izračunavanje pomoćne funkcije $B_n(y)$ pomoću Gaussove kvadraturne formule

L. Jakab

Predloženo je da se pomoćna funkcija $B_n(y) = \int_{-1}^{+1} \exp(-yx)x^n dx$ za male vrijednosti od y računa pomoću Gauss-Legendreove kvadraturne formule. Pokazano je da točnost rezultata raste ako y teži k nuli. Ovaj numerički pristup koristan je za računanje integrala prekrivanja dvaju atomskih orbitala Slaterovog tipa sa sličnim eksponentima.

STATE COMMITTEE FOR NUCLEAR ENERGY
INSTITUTE OF STABLE ISOTOPES
CLUJ — NAPOCA
ROMANIA

Prispjelo 19. veljače 1976.