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Auxiliary functions for Slater molecular integrals

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Summary. Some types of recurrence relations are modified to overcome the cases in which their conventional application is unstable in both the forward and backward directions. The original recurrence relations – connecting adjacent elements – are replaced by more general ones, where the non-adjacent elements are connected by coefficients obtained by new sets of relations derived from the original ones. This modification can be helpful for the calculation of the complicated molecular integrals with Slater Type Orbitals (STOs).

As a simple test we prove that some auxiliary functions – previously evaluated by expensive expansions – appearing in two-center two-electron integrals can be thus calculated with very low computer cost and high accuracy.

Key words: Recurrence relations – Molecular integrals – Slater-type functions

1 Introduction

Some of the algorithms developed for the calculation of Slater molecular integrals [1–6] are based on their expression in terms of quantities depending on a small number of indices and variables, followed by the calculation of these quantities by means of recurrence relations [2–5].

One limitation of this approach is the presence of "unstabilities" in the recurrence relations which would necessitate a one by one calculation of these quantities. In this way the computer cost is always increased and the final accuracy of the results is often reduced so that the algorithms become unreliable. In this context it is clearly interesting to search modifications in the application of these relations oriented to overcome the cases in which the recurrence is unstable in both the forward and backward directions.

In this paper we present an example of such modifications. The basic idea is to replace the original recurrence relations – connecting contiguous elements – by more general ones in which no contiguous elements are connected by "coefficients" which are obtained by new sets of relations derived from the original sets. Our example deals with the case of a three-term inhomogeneous recurrence relation, often found in the calculations of auxiliary functions for two- and three-center Slater molecular integrals. The next section contains a detailed discussion of the algorithm. In the following section we test the algorithm by calculating some auxiliary functions which appear in some formulations of the calculation of two-center two-electron integrals with STOs. These have been selected among those for which the one by one calculation (by numerical [5] integrations or power series expansions [6]) becomes necessary because the conventional application of the recurrence relations fails in both forward and backward directions. The results show that in this case, our algorithm is extremely efficient and allows us to perform the calculation with very low computer cost and high accuracy.

The present investigation does however not consider the problems arising from the fact that, in every molecular calculation, *the simultaneous computation of all integrals is required.* This problem has been addressed by Ruedenberg and others [7] who have demonstrated that very large economies in computation can frequently be achieved by the so-called charge density vectorization, i.e. by calculating a relatively small number of *intermediate* quantities that are *common* to a very much larger number of integrals. As a result, the time to calculate all two-electron integrals of a molecule is no longer proportional to the number of integrals (i.e. the fourth power of the number of orbitals), but increases *much* more slowly. Unfortunately, one has to abandon the use of certain auxiliary functions, such as the W_l^m, in order to gain such economies.

2 Bisection algorithm

We will assume that the recurrence relations between the set of unknown functions $\{f_l\}_{l=0}^{\infty}$ with $f_l \equiv f_l(x_1, x_2, \ldots, x_n)$ can be written as:

$$P_l f_l = A_l f_{l+1} + B_l f_{l-1} + Q_l \tag{1}$$

where $P_l \equiv P_l(x_1, x_2, \ldots, x_n)$, $A_l \equiv A_l(x_1, x_2, \ldots, x_n)$, $B_l \equiv B_l(x_1, x_2, \ldots, x_n)$ and $Q_l \equiv Q_l(x_1, x_2, \ldots, x_n)$ are known functions of both the l index and the $(x_1, x_2, \ldots, x_n)$ variables.

Replacing first l by $l+1$ and later l by $l-1$ in Eq. (1), combining the resulting expressions with the original one and simplifying, f_l can be obtained in terms of f_{l+2} and f_{l-2}. This procedure can be repeated k times to get finally:

$$P_l^{(k)} f_l = A_l^{(k)} f_{l+2^k} + B_l^{(k)} f_{l-2^k} + Q_l^{(k)} \tag{2}$$

where $P_l^{(k)}$, $A_l^{(k)}$, $B_l^{(k)}$ and $Q_l^{(k)}$ can be obtained from the recurrence relations:

$$P_l^{(k+1)} = P_{l-2^k}^{(k)} P_l^{(k)} P_{l+2^k}^{(k)} - P_{l-2^k}^{(k)} A_l^{(k)} B_{l+2^k}^{(k)} - A_{l-2^k}^{(k)} B_l^{(k)} P_{l+2^k}^{(k)} \tag{3}$$

$$A_l^{(k+1)} = P_{l-2^k}^{(k)} A_l^{(k)} A_{l+2^k}^{(k)} \tag{4}$$

$$B_l^{(k+1)} = B_{l-2^k}^{(k)} B_l^{(k)} P_{l+2^k}^{(k)} \tag{5}$$

$$Q_l^{(k+1)} = P_{l-2^k}^{(k)} Q_l^{(k)} P_{l+2^k}^{(k)} - P_{l-2^k}^{(k)} A_l^{(k)} Q_{l+2^k}^{(k)} - Q_{l-2^k}^{(k)} B_l^{(k)} P_{l+2^k}^{(k)} \tag{6}$$

which start from known values of $P_l \equiv P_l^{(0)}$, $A_l \equiv A_l^{(0)}$, $B_l \equiv B_l^{(0)}$ and $Q_l \equiv Q_l^{(0)}$.

The algorithm proceeds in three steps. First, the central value, l_c, of l and the highest value of k, $k_{\max}$, are selected, and the sets of coefficients $P_l^{(k)}$, $A_l^{(k)}$, $B_l^{(k)}$ and $Q_l^{(k)}$ are obtained according to Eqs. (3) to (6). Then, the initial, $f_{l_c-2^{k_{\max}}}$, and final, $f_{l_c+2^{k_{\max}}}$, values of the f_l functions are calculated and, finally, the remaining functions are obtained by means of Eq. (2) in a sequential way. One starts by obtaining the central function f_c and, choosing this as frontier, partitioning the set of indices in two subintervals. The central one of each subinterval is calculated and four new subintervals are defined. This procedure is repeated until all the $2^{k_{\max}+1}$ functions f_l are evaluated. It should be noted that a very large amount of f_l functions can be obtained using small values of $k_{\max}$.

3 Applications

Although the algorithm can be applied to several auxiliary functions appearing in the calculation of molecular integrals with STOs, we choose the integrals:

$$L_l^m(n, \beta) = \int_1^\infty d\xi (\xi^2 - 1)^{m/2} Q_l^m(\xi) \xi^n e^{-\beta\xi} \tag{7}$$

where Q_l^m denotes an associated Legendre function of the second type [8], to test the behavior of the algorithm. These integrals are required for evaluating general two-center two-electron integrals in some formulations such as that proposed in a recent work by Maslen and Trefry [6].

We will start recalling attention on the existence of the recurrence relations:

$$L_l^{m+1}(n, \beta) = \frac{1}{2l+1}[(l-m)(l-m+1)L_{l+1}^m(n, \beta) - (l+m)(l+m+1)L_{l-1}^m(n, \beta)] \tag{8}$$

and

$$(2l+1)L_l^m(n+1, \beta) = (l-m+1)L_{l+1}^m(n, \beta) + (l+m)L_{l-1}^m(n, \beta) \tag{9}$$

which allow us to reduce the problem of the evaluation of the more simple functions:

$$L_l(\beta) \equiv L_l^0(0, \beta) = \int_1^\infty d\xi\, e^{-\beta\xi} Q_l(\xi) \tag{10}$$

Now, the use of:

$$(2l+1)Q_l(\xi) = \frac{d}{d\xi}(Q_{l+1}(\xi) - Q_{l-1}(\xi)) \tag{11}$$

combined with the integration by parts leads to the additional recurrence relation:

$$L_l(\beta) = \frac{\beta}{2l+1}[L_{l+1}(\beta) - L_{l-1}(\beta)] + \frac{e^{-\beta}}{l(l+1)} \tag{12}$$

which has just the form of Eq. (1).

Moreover, our study of the stability of this relation shows that (i) in the forward direction is always unstable from certain value l to the value of β; (ii) in the backward direction is unstable for all values of l and β.

In the application of the bisection algorithm we require the evaluation of the first and last elements. For the first one we choose $l = 0$ and we obtain, by direct integration:

$$L_0(\beta) = \frac{1}{2\beta}\{\Gamma(0, 2\beta)\, e^{\beta} + [C + \ln 2\beta]\, e^{-\beta}\} \tag{13}$$

where $\Gamma(0, 2\beta)$ denotes the incomplete gamma function [9] and C is the Euler's constant.

For the last one ($l = 2^{k_{\max}+1}$) we choose a few terms of the simple asymptotic formula:

$$L_l(\beta) = e^{-\beta} \sum_{k=0} (-2\beta)^k \frac{k!(l-k-1)!}{(l+k+1)!} \tag{14}$$

which can be easily derived integrating by parts.

Table 1 is representative of the results obtained with the bisection algorithm. All the results are obtained with an accuracy of at least fourteen figures working in double precision because the errors in the last ones are rapidly self-cancelled. In the assayed cases a unique additional step in k was sufficient to ensure the mentioned fourteen figures accuracy, as shown in Table 2.

Table 3 is indicative of the required computer time. It is clear from it that the calculation of one of these complicated functions becomes (even for moderate $l_{\max}$) less expensive than that of a single square root. We note, however, that the two-center integrals depend on the $L_l^m(n, \beta)$ functions through an intermediate set of auxiliary functions:

$$W_l^m(n, n'; \beta, \beta') = \int_1^\infty \int_1^\infty d\xi \, d\xi' \xi^n \xi'^{n'} e^{-(\beta\xi + \beta'\xi')} (\xi^2 - 1)^{m/2} \times (\xi'^2 - 1)^{m/2} P_l^m(\xi_<) Q_l^m(\xi_>) \tag{15}$$

where $\xi_<$ and $\xi_>$ stand for the smaller and the greater of ξ, ξ'.

Due to the existence of simple recurrence relations for increasing m [4] also here, we can restrict ourselves to the case with $m = 0$ for which these functions can be written:

$$W_l^0(n, n'; \beta, \beta') = w_l(n, n'; \beta, \beta') + w_l(n', n; \beta', \beta) \tag{16}$$

Table 1. $L_l(\beta)$ functions for several values of l and β

	$\beta = 0.1$	$\beta = 5.0$	$\beta = 30.0$
$l = 0$	0.208622255552380E + 01	0.200208937657724E − 02	0.731135715068053E − 14
$l = 1$	0.387695686388158E + 00	0.931528073846427E − 03	0.438471352527954E − 14
$l = 2$	0.144531876629154E + 00	0.539622121159458E − 03	0.307101701878840E − 14
$l = 3$	0.739777008795314E − 01	0.348159028491640E − 03	0.229720998151089E − 14
$l = 4$	0.447526663199247E − 01	0.240950944487782E − 03	0.178749488164424E − 14
$l = 5$	0.299492885109320E − 01	0.175455498651955E − 03	0.142981500067814E − 14
$l = 6$	0.214372030572620E − 01	0.132836928255816E − 03	0.116805090792353E − 14
$l = 7$	0.160984396532084E − 01	0.103720507411786E − 03	0.970501357644030E − 15
$l = 8$	0.125314955850551E − 01	0.830370041115965E − 04	0.817799535956249E − 15
$l = 9$	0.100310076387828E − 01	0.678654908788453E − 04	0.697441509175336E − 15
$l = 10$	0.821061998897917E − 02	0.564347739342667E − 04	0.601013097663727E − 15
$l = 11$	0.684431634666871E − 02	0.476244741649565E − 04	0.522665579522843E − 15
$l = 12$	0.579272708436864E − 02	0.407001111855425E − 04	0.458225071552139E − 15
$l = 13$	0.496612263761025E − 02	0.351651903783912E − 04	0.404646783976539E − 15
$l = 14$	0.430461468029557E − 02	0.306750304647807E − 04	0.359667579770796E − 15
$l = 15$	0.376699311176391E − 02	0.269846880517587E − 04	0.321577720459158E − 15
$l = 16$	0.332414769732633E − 02	0.239164655759769E − 04	0.289066901975751E − 15

Table 2. Accuracy as function of $k_{\max}$

β	$k_{\max}$	$L_{32}(\beta)$
0.5	4	0.573822253 E-03
0.5	5	0.57382225061349E-03
0.5	6	0.57382225061349E-03
1.0	4	0.34771215 E-03
1.0	5	0.34771214189268E-03
1.0	6	0.34771214189268E-03
2.0	4	0.12767574 E-03
2.0	5	0.12767570619541E-03
2.0	6	0.12767570619541E-03
4.0	4	0.1721471 E-04
4.0	5	0.17214670339269E-04
4.0	6	0.17214670339269E-04
8.0	4	0.312997 E-06
8.0	5	0.31299118111864E-06
8.0	6	0.31299118111864E-06
16.0	4	0.10352 E-09
16.0	5	0.10351297672707E-09
16.0	6	0.10351297672707E-09
32.0	4	0.1135 E-16
32.0	5	0.11339934085393E-16
32.0	6	0.11339934085393E-16
64.0	4	0.137 E-30
64.0	5	0.13679282691195E-30
64.0	6	0.13679282691195E-30

$$
\begin{aligned}
w_l(n, n'; \beta, \beta') = {} & L_l^0(n, \beta) K_l^0(n', \beta') \\
& - \sum_{i=0}^{n'-1} L_l^0(n+i, \beta+\beta') \frac{\beta'^l}{i!} \\
& \times \sum_{j=(0,1)}^{l} {}^{(2)} \frac{(-1)^{(l-j)/2}(l+j-1)!(n'+j)!}{(l-j)!j!\beta'^{n'+j+1}} \\
& - \sum_{l=0}^{l} L_l^0(n+n'+i, \beta+\beta') \frac{\beta'^i}{(n'+i)!} \\
& \times \sum_{j=(i,i+1)}^{l} {}^{(2)} \frac{(-1)^{(l-j)/2}(l+j-1)!(n'+j)!}{(l-j)!j!\beta'^{j+1}}
\end{aligned}
\tag{17}
$$

Table 3. Calculation time (in microseconds) per element $L_l(n, \beta)$

LMAX	NMAX	Time	LMAX	NMAX	Time	LMAX	NMAX	Time
16	5	28	32	5	23	64	10	14
16	10	20	32	10	17	64	20	12
16	15	19	32	15	14	64	30	11
			32	20	13	64	40	11
			32	25	13	64	50	10

A square root in double precision takes about 15 microseconds on an IBM 4381

where the summations over the j index run over values with the same parity as l. In this equation:

$$K_l^0(n, \beta) \equiv K_l(n, \beta) = \int_1^\infty d\xi\, e^{-\beta\xi} \xi^n P_l(\xi) \tag{18}$$

can be calculated (also with full accuracy) by the relations:

$$K_0(0, \beta) = \frac{e^{-\beta}}{\beta} \tag{19}$$

$$K_1(0, \beta) = \frac{e^{-\beta}}{\beta}(1 + 1/\beta) \tag{20}$$

$$K_{l+1}(0, \beta) = \frac{2l+1}{\beta} K_l(0, \beta) + K_{l-1}(0, \beta) \tag{21}$$

together with

$$(2l+1)K_l(n+1, \beta) = (l+1)K_{l+1}(n, \beta) + lK_{l-1}(n, \beta) \tag{22}$$

Equation (17) can be subject to cancellation errors in the summations. A quick look to that equation shows that these errors must be always important for small β and β' but it can become also severe for large β and β' if high values of the l index are needed, as it is shown in Table 4.

Table 4. Cancellation errors in $W_l^0(0, 0, \beta, \beta')$ functions

	$\beta = 1, \beta' = 1$	$\beta = 10, \beta' = 1$	$\beta = 10, \beta' = 10$
$l = 0$	0.73996409970089E−01	0.12864863856225E−05	0.30410608198259E−10
$l = 1$	0.20900007759504E−01	0.41689322656819E−06	0.14122085391963E−10
$l = 2$	0.91907927677545E−02	0.19403567160378E−06	0.81800434869322E−11
$l = 3$	0.50429705533407E−02	0.10922268722835E−06	0.52812601487281E−11
$l = 4$	0.315517144806 E−02	0.69216663380 E−07	0.36584000658839E−11
$l = 5$	0.215072855945 E−02	0.47517176964 E−07	0.26664861207873E−11
$l = 6$	0.155656041588 E−02	0.34536675088 E−07	0.20205351166307E−11
$l = 7$	0.11772582138 E−02	0.2619233318 E−07	0.15788458319192E−11
$l = 8$	0.92085536 E−03	0.205257218 E−07	0.12648123613838E−11
$l = 9$	0.73964498 E−03	0.16508176 E−07	0.10342825201113E−11
$l = 10$	0.6069438 E−03	0.1355939 E−07	0.8604690529064 E−12
$l = 11$	0.50689 E−03	0.1133249 E−07	0.7264161319500 E−12
$l = 12$	0.430 E−03	0.959 E−08	0.621000033889 E−12
$l = 13$	0.36 E−03	0.83 E−08	0.536695834304 E−12

4 Remarks

The bisection algorithm enables us to calculate the complicated functions $L_l^m(n, \beta)$ with high accuracy and a very low computer time. However, as regards the accurate calculation of the two-center two-electron integrals, the accurate computation of the $L_l(n, \beta)$ and $K_l(n, \beta)$ functions is not sufficient because the combinations of these functions in Eq. (17) often lead to important loss of accuracy, i.e. a decreasing in the number of accurate *significant* places. Nevertheless, this happens at the same time as the value of the integrals decreases so that the number of accurate *decimal* places remains almost constant.

However, when the auxiliary functions W_l^m of Eqs. (15–17) are used, then the total computation time is strictly proportional to the number of integrals calculated. Until the contrary has been demonstrated, it appears not too likely that such a method can outperform charge-density vectorized methods such as those mentioned in the introduction [7]. Of course, even in the context of charge-density vectorized methods, certain auxiliary functions and the recurrence relations between them play important roles.

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