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Note

Evaluation of Electron Repulsion Integrals over Gaussian Lobe Basis Functions

The most time-consuming integral in molecular energy calculations using a gaussian lobe basis set is the electron repulsion integral

$$I = [aA_1bB_1 \mid r_{12}^{-1} \mid cC_2dD_2], \tag{1}$$

where, for example,

$$cC_2 = \exp[-c \mid \mathbf{r}_2 - \mathbf{C} \mid^2] \tag{2}$$

is a gaussian function for electron 2 centered on the point **C**. Boys [1] suggested evaluating this integral from the equation

$$I = f(aA, bB) f(cC, dD)(a + b + c + d)^{-1/2} F_0(t), \tag{3}$$

where

$$f(aA, bB) = (2\pi^{5/2})^{1/2} (a + b)^{-1} \exp[-ab \mid \mathbf{A} - \mathbf{B} \mid^2/(a + b)], \tag{4}$$

$$\mathbf{P} = (a\mathbf{A} + b\mathbf{B})/(a + b),$$

$$\mathbf{Q} = (c\mathbf{C} + d\mathbf{D})/(c + d),$$

$$t = (a + b)(c + d) \mid \mathbf{P} - \mathbf{Q} \mid^2/(a + b + c + d), \tag{5}$$

$$F_0(t) = t^{-1/2} \int_0^{t^{1/2}} e^{-x^2}\, dx. \tag{6}$$

Several suggestions [2] have been made for evaluating $F_0(t)$. For large values of t,

$$F_0(t) = \tfrac{1}{2}(\pi/t)^{1/2} \tag{7}$$

with an error of less than $e^{-t}/(2t)$. For $t > 31$, Eq. (7) has a relative error of less than 10^{-14}. For smaller values of t, F_0 may be evaluated from

$$F_0(t) = \sum_{m=0}^{k} F_m(t_0)(t_0 - t)^m/m!, \tag{8}$$

where

$$F_m(t) = t^{-(m+1/2)} \int_0^{t^{1/2}} x^{2m} e^{-x^2}\, dx. \tag{9}$$

If $F_m(t_0)$ is tabulated at intervals of 0.1, then $k = 6$ (i.e., a seven-term series) is sufficient to give 13 significant figures in $F_0(t)$ over the range $0 \leqslant t < 31$. This requires the pretabulation of 2170 coefficients $F_m(t_0)/m!$.

Shipman and Christoffersen [3] have suggested use of an eight-term Chebyshev series. They showed that this required only 32 intervals and hence only 256 coefficients to reach the same accuracy as (8). Speed in evaluation of $F_0(t)$ would be improved, however, by use of more intervals and fewer terms in the series. Consequently, we have examined the Chebyshev series for smaller intervals. Formally the Chebyshev series may be written on the interval $t_i \leqslant t \leqslant t_{i+1}$ as

$$F_0(t) = \sum_{n=0}^{\infty} a_n(i)\, T_n(y), \tag{10}$$

with

$$\begin{aligned} y &= 2(t - m_i)/d_i\,, \\ m_i &= (t_i + t_{i+1})/2, \\ d_i &= (t_{i+1} - t_i), \\ -1 &\leqslant y \leqslant 1. \end{aligned}$$

The coefficients $a_n(i)$ are given by

$$a_n(i) = (2 - \delta_{n,0})\, \pi^{-1} \int_{-1}^{1} F_0(t)\, T_n(y)(1 - y^2)^{-1/2}\, dy, \tag{11}$$

which may be evaluated by numerical integration from

$$a_n(i) = (2 - \delta_{n,0})\, N^{-1} \sum_{n=0}^{N}{}' F_0(z) \cos(n\pi k/N),$$

$$z = t_i + \tfrac{1}{2} d_i[\cos(n\pi k/N) + 1],$$

and $N = 20$. The prime on the sum indicates that the first and last terms are halved.

The results of examining this series were somewhat disappointing. At intervals $d_i = 0.1$, seven terms were still required for $0 < t < 2$. For $2 \leqslant t \leqslant 9$ only six terms are required, however, and for $10 < t < 31$ only five are needed. The basic difficulty with this approach seems to be that, for large t, F_0 behaves like $t^{-1/2}$ which is a difficult function to approximate.

A better alternative is to abandon (3) and avoid evaluation of F_0 altogether for large arguments. Equation (3) may be rewritten as

$$I = f(aA, bB)f(cC, dD)[(a + b)(c + d)| \mathbf{P} - \mathbf{Q} |^2]^{-1/2} G_0(t), \tag{12}$$

where

$$G_0(t) = \int_0^{t^{1/2}} e^{-x^2}\, dx = t^{1/2}F_0(t).$$

This expression for I has previously been avoided since it leads to an indeterminate form 0/0 as t approaches zero. For large arguments, however,

$$G_0(t) = \tfrac{1}{2}\pi^{1/2}$$

TABLE I

Number of Terms to Fit F_0 and G_0 with $d = 0.1$[a]

t	$G_0(t)$ (Chebyshev)	$F_0(t)$ (Chebyshev)	$F_0(t)$ (Taylor)
1	>10	7	7
2	8	6	7
3	7	6	7
4	6	6	7
5	6	6	7
6	6	6	7
7	6	6	7
8	6	6	7
9	5	6	7
10	5	5	7
11	5	5	7
12	5	5	7
13–17	4	5	7
18–22	3	5	7
23–26	2	5	7
27–31	1	5	7

[a] d is the interval for which a series is accurate to 3×10^{-14}.

TABLE II

Series and Interval Size for F_0 and G_0[a]

	No. of terms in series	Interval size	No. of coefficients to be stored
0–2	5	2^{-6}	640
2–3	5	2^{-5}	160
3–6	5	2^{-5}	480
6–8	4	2^{-6}	512
8–11	4	2^{-5}	384
11–12	4	2^{-4}	64
12–14	3	2^{-6}	384
14–16	3	2^{-5}	192
16–18	3	2^{-4}	96
18–20	2	2^{-6}	256
20–21	2	2^{-5}	64
21–22	2	2^{-4}	32
22–24	2	2^{-3}	32
24–25	1	2^{-6}	64
25–26	1	2^{-5}	32
26–30	1	2^{-3}	32

[a] F_0 is used for $0 < t < 3$; G_0 is used for $3 \leqslant t < 30$; $F_0 = 1$ is used for $t = 0$; $G_0 = \frac{1}{2}\pi^{1/2}$ is used for $30 \leqslant t < \infty$.

(to 14 significant figures for $t > 31$) so (12) can be evaluated by computing only one square root rather than the two square roots required by (3). For $t < 31$, G_0 may be expanded in a Chebyshev series. For $t < 7$, it was found that the G_0 series converged more slowly than the F_0 series, but for $t > 7$ the G_0 series converged much more rapidly. Table I shows the number of terms required in G_0 and F_0 to reach an accuracy of 3×10^{-14} with $d = 0.1$.

Clearly a compromise procedure is suggested which uses F_0 for small values of t and G_0 for large values. Our final choise of intervals is given in Table II. This choice requires storing 3424 coefficients, but no more than five terms are ever needed to evaluate I to an accuracy of 2×10^{-14}. The coefficients are, of course, tabulated for the actual working form of the equation,

$$\begin{Bmatrix} F_0 \\ G_0 \end{Bmatrix} = (\cdots (tc_k + c_{k-1})\, t + \cdots + c_1)\, t + c_0\,. \tag{13}$$

The coefficients are available from the authors upon request. On the average, this algorithm is about twice as fast as one using a comparable number of coefficients based on F_0 alone. No exact timing information can be given because the average time depends on the distribution of t among the different intervals.

Interval sizes which were inverse powers of 2 were used because this facilitated rapid location of the coefficients. If $[t]$ is the integer part of t, the first coefficient may be located by the algorithm

$$\begin{aligned} J &= [t], \\ K &= [(t - [t])\, 2^{N_J}], \\ \text{location} &= M_J + k_J(K - 1), \end{aligned}$$

where M_J, N_J and k_J (the number of terms required) are tables of integers for each $0 \leqslant J < 30$. The multiplication by 2^{N_J} was accomplished by addition of N_J to the exponent field of the floating point number $t - [t]$.

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