Theoret. chim. Acta (Berl.) 31, 183—188 (1973)

Commentationes

The Numerical Integration of a Molecular Integral Using Two Different Techniques*

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Received March 30, 1973

A two-electron integral which commonly occurs in molecular calculations is evaluated numerically using the different methods of Boys and Conroy and the results are discussed.

Key words: Numerical Integration

1. Introduction

The purpose of the investigation was to consider an integral with a singular integrand which occurs quite often in electronic calculations and to evaluate it using the "diophantine-type" methods of Boys *et al.* [1, 2] and Conroy [3]. The integral chosen is the two-electron, one-centre integral

$$\int \frac{e^{-\alpha r_1 - \beta r_2}}{r_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 . \tag{1}$$

This integral has the advantage of being evaluated analytically to give

$$\frac{32\pi^2(\alpha^2 + 3\alpha\beta + \beta^2)}{\alpha^2\beta^2(\alpha+\beta)^3}, \tag{2}$$

thus making comparison with its numerical estimates possible.

2. The Co-Ordinate System

In both the numerical methods considered the spherical polar transformation of the co-ordinates of electron i ($i = 1, 2$) suggested by Boys and Handy [2] was employed i.e.

$$\begin{aligned} r_i &= A_i(q_{r_i}/1 - q_{r_i}) \\ \Theta_i &= \pi(6q_{\Theta_i}^5 - 15q_{\Theta_i}^4 + 10q_{\Theta_i}^3) \\ \phi_i &= 2\pi q_{\phi_i} . \end{aligned} \tag{3}$$

This reduces the integral to the standard form

$$\int_0^1 \cdots \int_0^1 f(q_{r_1}, q_{\Theta_1}, q_{\phi_1}, q_{r_2}, q_{\Theta_2}, q_{\phi_2})\, d\boldsymbol{q} . \tag{4}$$

* This paper was presented during the session on numerical integration methods for molecules of the 1970 Quantum Theory Conference in Nottingham. It has been revised in the light of the interesting discussion which followed.

Also in both the procedures the scale factors A_i $(i=1,2)$ were set equal to A in order to reduce the number of parameters.

3. Boys' Method

The transformation given by Eq. (3) transforms an integrand having a continuous derivative in polar co-ordinate space to an approximately periodic function. The Boys procedure gives an estimate of the integral by evaluating partial sums in which the integrand is evaluated at "diophantine" points in 3-space. Assuming that this procedure may be applied to integrands involving a singularity and generalizing it to the two-electron case, the partial sums are then given by

$$\frac{1}{N^2}\sum_{L_1=1}^{N}\sum_{L_2=1}^{N} f(L_1, L_2)\,\omega(L_1)\,\omega(L_2), \tag{5}$$

where

$$(q_{r_i}, q_{r_i}, q_{r_i}) = \left(\frac{L_i}{N}, \frac{DL_i}{N}, \frac{EL_i}{N}\right), \quad (i=1,2). \tag{6}$$

In (5), f is the integrand and ω a one-electron weight which is obtained from the one-electron contribution to the Jacobian of the transformation. Equation (6) involves N, the number of integration points per electron, and also fixed constants D and E both of which depend on N.

4. The Singularity

In order to prevent infinite contributions which arise when $r_{12}=0$, the method introduced by Boys and Cook [4] of coping with the singularity was used so that $1/r_{12}$ is replaced by

$$\left(r_{12}^3 + \frac{\omega^{\frac{1}{2}}(L_1)\,\omega^{\frac{1}{2}}(L_2)}{Z}\right)^{-\frac{1}{3}}. \tag{7}$$

The only modification employed in (7) is to regard Z as a parameter rather than setting $Z=3$ as suggested by Boys and Cook.

5. Results

The numerical estimate of the integral using Boys' method depends therefore on two parameters A and Z.

Figure 1 shows the variation with Z of the percentage errors in the estimates of the integral for $\alpha=1$, $\beta=2$; in this case the scale factor was fixed at 2 (c.f. Fig. 2). For the range $0<Z<25$, the integral estimates vary quite markedly with Z and give the correct result when $Z\simeq 16$. It would therefore seem that the estimate of Z as approximately 3 arrived at by Boys and Cook using an electrostatic argument is not as satisfactory as $Z=16$ as a parameter in the approximation for the $1/r_{12}$ singularity. In $Z>16$ the estimates become less accurate. This is to be expected since (7) approximates very closely to $1/r_{12}$ for large Z and thus introduces further inaccuracies into the calculation.

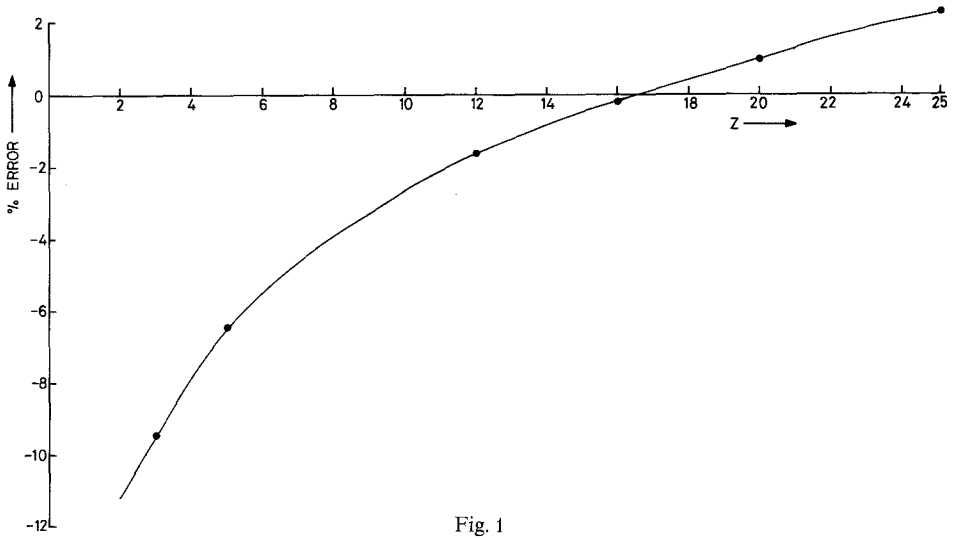

Fig. 1

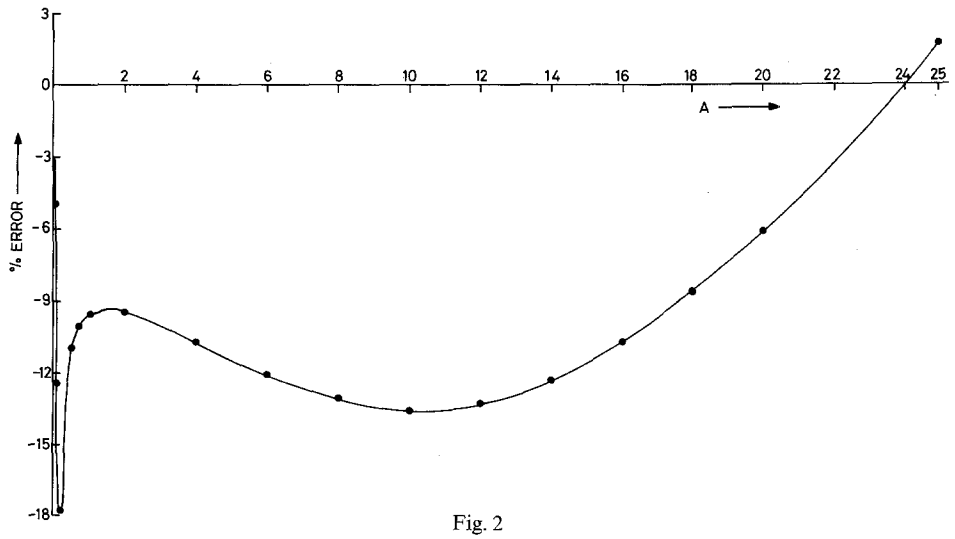

Fig. 2

Figure 2 shows the variation of the percentage error of the estimate with scale factor A. Again $\alpha = 1$, $\beta = 2$ and Z was chosen as the Boys and Cook estimate of 3. The error varies markedly with A, and the best estimates have an error of about 9–10% in the region $1 \leqq A \leqq 2$. It is in this region that the integral estimates are least sensitive to the scale factor.

Further calculation shows that if Z is increased to 16 the errors become much smaller and the integral estimates become much less sensitive to A. For example, when $Z = 16$, the percentage error is about 0.05 for $1 < A < 6$. These results were computed for $N = 80$ – i.e. using 6400 grid points. The previous results were

repeated for several different values of the parameters (α, β) confirming the fact that the choice of $Z = 3$ was far too small and that Z, in the neighbourhood of 16, gave much more accurate values of the estimates which were relatively insensitive to the choice of scale factor.

6. Conroy's Method

The method of Conroy [2] is based essentially on the approximation to this integral by the partial sum

$$\frac{1}{M} \sum_{L=1}^{M-1} g(L\boldsymbol{\alpha} - [L\boldsymbol{\alpha}]), \tag{8}$$

where g is the product of the integrand and the Jacobian of the transformation; M is the number of sample points. In expression (8)

$$\boldsymbol{\alpha} = \boldsymbol{p}/M, \tag{9}$$

where $\boldsymbol{p}$ is a six dimensional vector which is selected, having first chosen M, according to Conroy's prescription in which he lists optimised sets of M each with their respective optimised vector $\boldsymbol{p}$. In (8) because the integral parts are subtracted off each component of $L\boldsymbol{\alpha}$, the grid points lie inside the unit hypercube as is required from the transformation given by (3) (see also expression (4)).

The function g in expression (8) is evaluated in a six dimensional configuration space as opposed to the two three dimensional spaces of each electron as in the Boys method. It is therefore possible to order the components of $\boldsymbol{p}$ to correspond to the components of the vector $\boldsymbol{q}$ given by (3), in several different ways. Corresponding respectively to each of the components $p_1, p_2, \ldots, p_6$, the ordering $q_{r_1}, q_{\theta_1}, q_{\phi_1}, q_{r_2}, q_{\theta_2}, q_{\phi_2}$ and also the ordering $q_{r_1}, q_{r_2}, q_{\theta_1}, q_{\theta_2}, q_{\phi_1}, q_{\phi_2}$ were considered. It was generally found, however, that the former ordering gave better results than the latter, despite the fact that the latter ordering allows both the radial co-ordinates of the electrons to assume greater importance in the integral. This first ordering has been used in all subsequent results.

One further point to note is that this integration procedure is such that the choice of integration points does not make r_{12} small so that no special device for coping with the singularity need be introduced. The exceptional case, however, is that for which M is even in which case the point corresponding to $L = M/2$ makes r_{12} zero. In this case therefore the integration point corresponding to $L = M/2$ is omitted.

7. Results

Figure 3 shows the variation with the scale factor A of the percentage error of the integral estimate for a choice of 6044 and 9644 grid point respectively. For the choice of 6044 points the results are relatively insensitive to the scale factor and are particularly good for $2.5 \leqq A \leqq 10$ where the error is less than 1%. However, if the number of points used is increased to 9644 the results are much more sensitive to the scale factor particularly at values of A greater than 10 where there is marked oscillation. In this case the optimum results again occur in the region $2.5 \leqq A \leqq 10$ but, despite the increased number of points, there is no improvement in the accuracy.

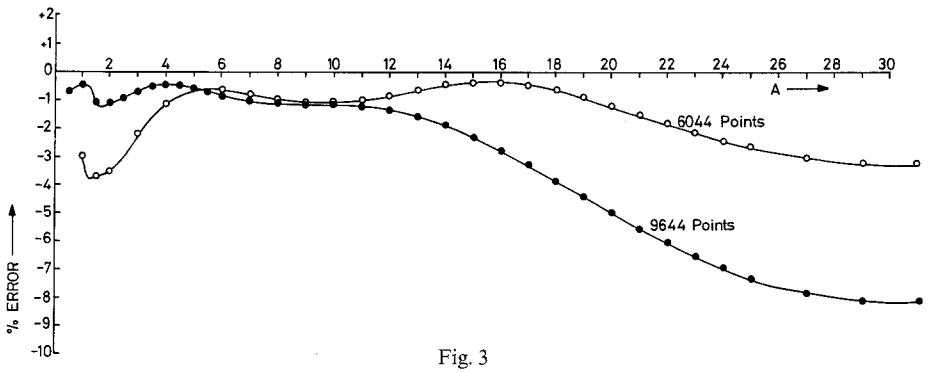

Fig. 3

8. Discussion and Conclusion

Both the methods of Conroy and Boys show that the results obtained are sensitive to the choice of scale factor (even for about 6000 grid points). It is, however, possible in estimating this integral to find for both methods ranges of A in which the estimates are optimum and least sensitive to the scale factor. In order to investigate the use of a different transformation from that given in (3), the alternative transformation

$$r_i = A(q_{r_i}/1 - q_{r_i})^2 \qquad (i = 1, 2) \tag{10}$$

was studied. The quadratic dependence of the r_i on q_i did in fact produce results which were less sensitive to A in both methods but the estimates were not as accurate. This alternative transformation did also predict the optimum value of Z for the Boys method as being approximately 22. Again confirming the choice of $Z = 3$ as being far too low. Concerning the Boys method generally, it is accepted that arguments in favour of this method as applied to a six dimensional integral are not as strong as those favouring its application to one of three dimensions, particularly if r_{12} occurs explicitly, and as a singularity, making the integrand and its derivatives no longer continuous. However it does seem that, although the method was not originally conceived with the idea of application to integrals with singularities such as $1/r_{12}$, this suggestion of coping with the singularity can be improved by using optimised parameters.

Whereas the Boys method is essentially a one-electron, or three dimensional procedure, Conroy's method is essentially a configuration-space procedure. For 6044 grid points, Conroy's procedure gave exceedingly accurate results for certain ranges of the scale factor. Further it has the advantage of requiring no special devices to deal with the singularity. However, the fact that at 9644 grid points the variation of the estimates with A were much larger than that for 6044 raises some quite serious objections. Any desirable numerical integration method using 9000 points should produce results which are relatively insensitive to the scale factor A. The integral for the Boys procedure was not estimated using 9000 points so that no comparison can be made.

In conclusion, *ab initio* molecular calculations in which very many integrals are numerically computed will certainly need procedures requiring a reduced number of integration points if the computing time is to be minimized.

The possibility of using optimum parameters necessitating a smaller number of grid points in numerical integration techniques should therefore be further explored.

Acknowledgments. The authors would like to thank Mr. Brian Ford and Mr. C. E. Solomon for their valuable help in the writing and execution of the programs.

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