NOTE

The Recursive and Analytical Evaluation of Atomic Correlation Integrals

The calculation of correlation energy, CE, defined as the difference between the expectation value of the exact nonrelativistic hamiltonian of a system and its Hartree–Fock energy [1], is of fundamental importance in understanding the electronic interactions in atomic, and molecular systems. Such calculations are, however, not easy to carry out due to more complicated types of integrals which one has to calculate. All such integrals involve functions containing the interparticle distance, r_{12}, as one of the variables.

Recently [2] Calais and Löwdin discussed the evaluation of the following particular type of useful integral:

$$I_{k,l,m}(a, b, c) = \int_0^\infty r_1{}^k e^{-ar_1} dr_1 \int_0^\infty r_2{}^l e^{-br_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12}{}^m e^{-cr_{12}} dr_{12} . \tag{1}$$

Such integrals arise in CE calculation of atomic systems if one uses a correlation function of the $r_{12}^p e^{-cr_{12}}$ type.

In this note the evaluation of this integral has been looked into from a practical view point. Consider the following equation [3]:

$$I_{0,0,0}(a, b, c) = \int_0^\infty e^{-ar_1} dr_1 \int_0^\infty e^{-br_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} e^{-cr_{12}} dr_{12} ,$$

$$= 2(a + b)^{-1}(b + c)^{-1}(c + a)^{-1}, \tag{2}$$

where the subscripts on I refer to the powers of r_1, r_2 and r_{12} under the integral sign. By applying the operator $(-\partial/\partial a)^k (-\partial/\partial b)^l (-\partial/\partial c)^m$ to the above equation, one obtains the following equation:

$$I_{k,l,m}(a, b, c) = \int_0^\infty r_1{}^k e^{-ar_1} dr_1 \int_0^\infty r_2{}^l e^{-br_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12}{}^m e^{-cr_{12}} dr_{12} ,$$

$$= (-\partial/\partial a)^k(-\partial/\partial b)^l(-\partial/\partial c)^m 2(a + b)^{-1}(b + c)^{-1}(c + a)^{-1}. \tag{3}$$

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By carrying out the indicated differentiation, using Leibnitz theorem [4], it can be shown that ([2], [5])

$$I_{k,l,m}(a, b, c) = 2k!\, l!\, m! \sum_{p=0}^{k} \sum_{q=0}^{l} \sum_{r=0}^{m} \binom{p+q}{q}\binom{k-p+r}{r}\binom{l-q+m-r}{m-r}$$

$$\times (a+b)^{-p-q-1}(b+c)^{q+r-l-m-1}(c+a)^{p-k-r-1}. \tag{4}$$

This analytical expression for $I_{k,l,m}(a, b, c)$ can thus be used to evaluate any desired integral. As will be pointed out later on, sometimes it is more desirable to evaluate such integrals by means of appropriate recurrance relationships. Following the general treatment of Sack, Roothaan and Kolos [6], we will now derive these recurrance relationships for $I_{k,l,m}(a, b, c)$ starting with equation (3). Thus

$$I_{k,l,m}(a, b, c) = (-\partial/\partial a)^k(-\partial/\partial b)^l(a+b)^{-1}[(-\partial/\partial c)^m\, 2(b+c)^{-1}(c+a)^{-1}],$$

or

$$I_{k,l,m}(a, b, c) = \sum_{p=0}^{k} \sum_{q=0}^{l} \frac{k!\, l!}{p!\, q!} \left[\frac{(k-p+l-q)!}{(k-p)!\,(l-q)!} \right](a+b)^{k-p+l-q-1}$$

$$\times (-\partial/\partial a)^k(-\partial/\partial b)^l(-\partial/\partial c)^m\, 2(b+c)^{-1}(c+a)^{-1}. \tag{5}$$

Now, using the binomial coefficients recurrance relationship to the quantity in the square parenthesis of equation (5), which is true for all values of p and q except when $p = k$ and $q = l$, we get the following equation:

$$I_{k,l,m}(a, b, c) = (a+b)^{-1}\{kI_{k-1,l,m}(a, b, c) + lI_{k,l-1,m}(a, b, c) + 2J_{k,l,m}(a, b, c)\}, \tag{6}$$

where

$$2J_{k,l,m}(a, b, c) = (-\partial/\partial a)^k\, (-\partial/\partial b)^l\, (-\partial/\partial c)^m\, 2(a+c)^{-1}\, (b+c)^{-1}. \tag{7}$$

Now, equation (7) can be rewritten in the form

$$2J_{k,l,m}(a, b, c) = J_{k,m,l}(a, c, b) + J_{l,m,k}(b, c, a), \tag{8}$$

where

$$J_{k,m,l}(a, c, b) = (-\partial/\partial a)^k\, (-\partial/\partial c)^m\, (a+c)^{-1}\, [(-\partial/\partial b)^l\, (b+c)^{-1}]. \tag{9}$$

Again, on carrying out the indicated differentiation with respect to a and c, and applying the binomial coefficient recurrance relationship to the result, one obtains the following equation:

$$J_{k,m,l}(a, c, b)$$

$$= (a+c)^{-1}\{kJ_{k-1,l,m}(a, b, c) + mJ_{k,l,m-1}(a, b, c) + K_{k,l,m}(a, b, c)\}, \tag{10}$$

where

$$K_{k,l,m}(a, b, c)$$
$$= (-\partial/\partial a)^k (-\partial/\partial b)^l (-\partial/\partial c)^m (b + c)^{-1} = \delta_{k,0}(l + m)! (b + c)^{-l-m-1}. \quad (11)$$

Similarly

$$J_{l,m,k}(b, c, a) = (b + c)^{-1}\{lJ_{k,l-1,m}(a, b, c) + mJ_{k,l,m-1}(a, b, c)$$
$$+ \delta_{l,0}(k + m)! (a + c)^{-k-m-1}\}. \quad (12)$$

Thus the equations (6), (8), (10), and (12) form the basis for recursive calculation of the general integral, $I_{k,l,m}(a, b, c)$.

The numerical results obtained by either of the two methods are fairly accurate. However, the recursive method yields results which, in all trial cases, are accurate to at least six significant figures. The analytical method, on the other hand, shows significant differences in the 6th figure when compared with the "exact" answers. The typical results of Table I illustrate the relative accuracies of these two methods. The "exact" answers given in Table I were obtained either by direct hand calculation or by the analytical method using a "double-precision arithmatic" program in IBM 1620-Model II.

TABLE I

COMPARISON OF THE NUMERICAL ACCURACIES OF THE ANALYTICAL
AND RECURSIVE COMPUTATION METHODS

Integral	Exact value	$I(A)^a$	$\delta(A)^b$	$I(R)^c$	$\delta(R)^d$
$I_{2,2,2}(7, 8, 9)$	$.34467412E - 07$	$.34467401E - 07$	$1.1E - 14$	$.34467410E - 07$	$2E - 15$
$I_{8,8,2}(2, 3, 4)$	$.12425678E + 01$	$.12425666E + 01$	$1.2E - 6$	$.12425672E + 01$	$6E - 7$
$I_{8,8,3}(2, 3, 4)$	$.12220366E + 01$	$.12220353E + 01$	$1.3E - 6$	$.12220359E + 01$	$7E - 7$
$I_{8,8,4}(2, 3, 4)$	$.14976957E + 01$	$.14976908E + 01$	$4.9E - 6$	$.14976950E + 01$	$7E - 7$
$I_{8,8,5}(2, 3, 4)$	$.21961570E + 01$	$.21961524E + 01$	$4.6E - 6$	$.21961560E + 01$	$1E - 6$
$I_{8,8,6}(2, 3, 4)$	$.37464839E + 01$	$.37464642E + 01$	$1.97E - 5$	$.37464824E + 01$	$1.5E - 6$
$I_{8,8,7}(2, 3, 4)$	$.72845034E + 01$	$.72844749E + 01$	$2.85E - 5$	$.72845010E + 01$	$2.4E - 6$
$I_{8,8,8}(2, 3, 4)$	$.15892448E + 02$	$.15892344E + 02$	$1.04E - 4$	$.15892442E + 02$	$6E - 6$
$I_{8,8,8}(7, 8, 9)$	$.26698067E - 10$	$.26697829E - 10$	$2.38E - 16$	$.26698045E - 10$	$2.2E - 17$

[a] $I(A)$ is value obtained by the use of analytical formula.
[b] $\delta(A)$ is the error in $I(A)$.
[c] $I(R)$ is value obtained by the use of recursion formulae.
[d] $\delta(R)$ is the error in $I(R)$.

It is expected that the analytical method of computation is economical, timewise, provided only a few of such integrals are needed. However, in most practical

applications of these integrals in Quantum Chemistry a host of such integrals, with the indices varying from zero to a certain upper limit, are needed. In such circumstances it is much faster to calculate these integrals by the recursive method. Our investigation shows that the calculation of a given number of integrals by the analytical method takes about $1\frac{1}{2}$ times as much time as is needed to calculate the same number of integrals by the recursive method. This argument together with the one presented above about the numerical accuracies suggests that the recursive method of computation is a better choice for calculating the integrals, $I_{k,l,m}(a, b, c)$.

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