

Note

Evaluation of a Four-Electron Atomic Integral

In calculations of four-electron atomic states using either Hylleraas-type expansions [1] or a combination of Hylleraas-type and configuration-interaction wave functions [2] there arises the auxiliary integral which we designate by X :

$$X(a, b, c, d; \alpha, \beta, \gamma, \delta) \equiv \int_0^\infty x^a e^{-\alpha x} dx \int_x^\infty y^b e^{-\beta y} dy \int_y^\infty z^c e^{-\gamma z} dz \int_z^\infty w^d e^{-\delta w} dw. \quad (1)$$

Methods for evaluation of this integral and related three-, two-, and one-electron auxiliary integrals W , V , and A have been discussed by Sims and Hagstrom [3], who point out that the X integral exists provided

$$a \geq 0, \quad a + b \geq -1, \quad a + b + c \geq -2, \quad a + b + c + d \geq -3. \quad (2)$$

For nonnegative values of b , c , and d , the X integral can be suitably evaluated by use of recurrence relations based on pioneering work of James and Coolidge [4]. Cases arise, however, for which c and/or d is negative and use of recurrence relations leads to troublesome differencing error. For such cases, we have found it advantageous to use the series-summation scheme described below.

Derivation of the series will only be outlined. By repeated application of recurrence relation [5] involving the first argument, a , one can derive a series for the X integral each term of which is a product of a coefficient B_n and a three-electron W integral whose first argument increases with the index n . B_n is determined by a simple recurrence relation involving a , α , and n . By use of a recurrence relation on the W integral [5], one can then reexpress X as a series involving a two-electron V integral and a coefficient D_n , the recurrence relation for which involves B_n . Finally, a recurrence relation [5] on V leads to a series involving a coefficient E_n and a trivial one-electron integral.

The series expression, recurrence relations, and starting values are given below:

$$X(a, b, c, d; \alpha, \beta, \gamma, \delta) = \frac{(a + b + c + d + 3)!}{(a + 1)(\alpha + \beta + \gamma + \delta)^{a+b+c+d+4}} \sum_{n=3}^{\infty} Y_n, \quad (3)$$

$$Y_n = \frac{(a + b + c + d + n)}{(a + b + c + n)} \left[Z_{n-1} + \frac{(\alpha + \beta + \gamma)}{(\alpha + \beta + \gamma + \delta)} Y_{n-1} \right], \quad (4)$$

$$Z_n = \frac{(a + b + c + d + n)}{(a + b + n)} \left[W_{n-1} + \frac{(\alpha + \beta)}{(\alpha + \beta + \gamma + \delta)} Z_{n-1} \right], \tag{5}$$

$$W_n = \frac{(a + b + c + d + n)}{(a + n)} \frac{\alpha}{(\alpha + \beta + \gamma + \delta)} W_{n-1}, \tag{6}$$

$$Y_3 = \frac{1}{(a + b + c + 3)(a + b + 2)}, \tag{7}$$

$$Z_3 = \frac{1}{(a + b + 3)} \left[\frac{1}{(a + b + 2)} \frac{(\alpha + \beta)}{(\alpha + \beta + \gamma + \delta)} + \frac{1}{(a + 2)} \frac{\alpha}{(\alpha + \beta + \gamma + \delta)} \right], \tag{8}$$

$$W_3 = \frac{1}{(a + 3)(a + 2)} \left[\frac{\alpha}{(\alpha + \beta + \gamma + \delta)} \right]^2. \tag{9}$$

Some representative results are given in Table I. The series was terminated when Y_n became less than 10^{-M} times the running sum of the Y_n . For these results, M was taken as 8. A crude estimate of the number N of terms required for convergence

TABLE I

Calculated values of the auxiliary integral X . The number in parentheses is the power of 10 by which the decimal fraction should be multiplied. Also indicated is the actual number N , and the estimated number N_{est} , of terms required for convergence to eight decimal places.

a	b	c	d	α	β	γ	δ	$X(a, b, c, d; \alpha, \beta, \gamma, \delta)$	N	N_{est}
0	0	0	0	1.10	1.10	1.10	1.10	0.284589 (-1)	63	64
0	0	0	-1	7.40	7.40	1.92	1.92	0.107506 (-2)	133	169
0	0	1	-1	7.40	7.40	1.92	1.92	0.326148 (-3)	139	169
2	2	2	-1	7.40	7.40	1.92	1.92	0.123923 (-6)	145	169
0	0	0	-1	1.92	1.92	7.40	7.40	0.127515 (-3)	33	36
1	0	0	-1	1.92	1.92	7.40	7.40	0.545451 (-5)	33	36
0	0	1	-1	1.92	1.92	7.40	7.40	0.180190 (-4)	33	36

can be obtained by noting that for large values of n , Z_n becomes small compared to Y_n and the behavior of Y_n is dominated by the factor involving a ratio of sums of exponential parameters. This leads to the estimate

$$N_{est} = \frac{M}{\log_{10} \left[\frac{\alpha + \beta + \gamma + \delta}{\alpha + \beta + \gamma} \right]}. \tag{10}$$

Values of N_{est} and of the actual number N of terms required for convergence are listed in Table I.

The above method has been tested in various ways and incorporated into a computer program for calculating S states of four-electron atoms [1]. One simple test is based on the fact that for $a = b = c = d$ and $\alpha = \beta = \gamma = \delta$, the X integral is simply $(1/24)$ times the product of four identical one-electron integrals, where 24 arises as the number of permutations of four coordinates. An example is given in the first row of Table I. Of course one normally does not use the series-summation scheme unless at least one of the arguments b, c, d is negative, because of the greater computing time required as compared to that when using recurrence relations such as given by Sims and Hagstrom [3] and by James and Coolidge [4].¹

Analogous series-summation schemes for three-electron and two-electron auxiliary integrals have been given by Öhrn and Nordling [6], though their notation differs somewhat from that given above. In deriving the four-electron scheme, it did not seem possible to make use of the corresponding three-electron formulas.

REFERENCES

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5. The relevant recurrence relations for the W and V integrals are given in [4]; the corresponding relation for the X integral can be easily derived and is not given here.
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