

**Note**

**Generalized Form of Atomic Two Electron Integrals  
over Hydrogenic Functions**

In this note, computationally useful form of atomic two electron integrals over hydrogenic functions is presented. Such integrals and their special cases are often needed in the perturbation treatment of atomic systems when the unperturbed atomic wavefunctions are chosen to be hydrogenic [1]. The formulas given are general enough to allow the variation of the exponential parameter should it be desired. Furthermore, the same formulas are valid when Slater type functions are used provided certain conditions, mentioned at the end, are fulfilled. The formulas presented are particularly suited for a high speed digital computer.

The general two-electron atomic integral  $I$  is of the form

$$I = \langle \chi_1(i) \chi_2(j) | r_{ij}^{-1} | \chi_3(i) \chi_4(j) \rangle, \tag{1}$$

where  $\chi_\alpha(i)$  is a hydrogenic function which has the following form:

$$\chi_\alpha(i) = R_\alpha(n_\alpha l_\alpha \zeta_\alpha | r_i) Y_{l_\alpha m_\alpha}(\theta_i, \phi_i). \tag{2}$$

Note that  $(r_i, \theta_i, \phi_i)$  are the coordinates of electron  $i$ ,  $r_{ij}$  is the distance between the electrons  $i$  and  $j$ ,  $Y_{l_\alpha m_\alpha}(\theta_i, \phi_i)$  are the well-known spherical harmonics, and  $R_\alpha(n_\alpha l_\alpha \zeta_\alpha | r_i) \equiv R_\alpha(r_i)$  is the radial function. The quantities  $(n_\alpha l_\alpha m_\alpha)$  and  $\zeta_\alpha$  are the quantum numbers and the exponent, respectively, characterizing the hydrogenic function  $\chi_\alpha$ . The usual procedure to evaluate (1) is to expand  $r_{ij}^{-1}$  in terms of spherical harmonics and carry out the integration over the angular coordinates of  $i$  and  $j$  [2]. This leads to the following expression for the integral  $I$ :

$$I = \sum_k D(l_1 l_3 k, \bar{m}_1 m_3 \bar{m}) D(l_2 l_4 k, \bar{m}_2 m_4 \bar{m}) \langle R_1(r_i) R_2(r_j) [r_{>}^{-k-1} r_{<}^k] R_3(r_i) R_4(r_j) \rangle, \tag{3}$$

where  $r_{>}$  stands for the larger of the two quantities  $r_i$  and  $r_j$ , and the limits on  $k$  along with the definitions of  $D$  coefficients are given elsewhere [3]. The radial

integral of (3) will be referred to as the  $R^k$  integral. To evaluate it we first expand each  $R_\alpha(r_i)$  function in the following convenient form [4]:

$$R_\alpha(r_i) \equiv R_\alpha(n_\alpha l_\alpha \zeta_\alpha | r_i) = N_\alpha(n_\alpha l_\alpha \zeta_\alpha) \sum_{\lambda_\alpha=0}^{n_\alpha-l_\alpha-1} K_\alpha(n_\alpha l_\alpha \lambda_\alpha \zeta_\alpha) r_i^{\lambda_\alpha} e^{-(\zeta_\alpha r_i)/2}, \quad (4)$$

where

$$N_\alpha \equiv N_\alpha(n_\alpha l_\alpha \zeta_\alpha) = \zeta_\alpha^{l_\alpha+1} [\zeta_\alpha(n_\alpha + l_\alpha)! (n_\alpha - l_\alpha - 1)!]^{1/2} (2n_\alpha)^{-1/2}, \quad \text{and} \quad (5)$$

$$K_\alpha \equiv K_\alpha(n_\alpha l_\alpha \lambda_\alpha \zeta_\alpha) = (-\zeta_\alpha)^{\lambda_\alpha} [\lambda_\alpha! (n_\alpha - l_\alpha - \lambda_\alpha - 1)! (2l_\alpha + \lambda_\alpha + 1)!]^{-1}. \quad (6)$$

Substitution of (4) in (3) and subsequent integration over  $r_i$  and  $r_j$  leads to, after considerable algebraic manipulations, the following analytical formula for the  $R^k$  integral:

$$\begin{aligned} R^k = & N_1 N_2 N_3 N_4 \sum_{\lambda_1} K_1 \sum_{\lambda_2} K_2 \sum_{\lambda_3} K_3 \sum_{\lambda_4} K_4 \left[ V(n_{24} + k + 2, \zeta_{24}) V(n_{13} - k + 1, \zeta_{13}) \right. \\ & - \zeta_{24}^{-1} V(n_{24} + k + 2, \zeta_{24}) \sum_{j_2} \{ V(n_{13} + j_2 - k + 1, \zeta_{13} + \zeta_{24}) / V(j_2, \zeta_{24}) \} \\ & \left. + \zeta_{24}^{-1} V(n_{24} - k + 1, \zeta_{24}) \sum_{i_2} \{ V(n_{13} + i_2 + k + 2, \zeta_{13} + \zeta_{24}) / V(i_2, \zeta_{24}) \} \right], \quad (7) \end{aligned}$$

where

$$\left. \begin{aligned} V(n, x) &= \int_0^\infty t^n e^{-xt} dt, \\ n_{ij} &= l_i + l_j + \lambda_i + \lambda_j, \quad \zeta_{ij} = (\zeta_i + \zeta_j)/2, \\ n_{24} + k + 2 \geq j_2 \geq 0, \quad \text{and} \quad n_{24} - k + 1 \geq i_2 \geq 0. \end{aligned} \right\} \quad (8)$$

Equations (3) and (7) then represent the analytical form of the integral  $I$ .

A computer program, written for the IBM/360 in FORTRAN IV, is now available for the computation of the  $R^k$  integral and the  $I$  integral. In Table I are presented some typical results for the  $R^k$  integrals. The calculations were carried out in double precision arithmetic at the computation center of the State University of New York at Stony Brook.

Note that when  $l_\alpha = n_\alpha - 1$  in the Eq. (4), the  $R_\alpha(r_i)$  function becomes identical with the normalized Slater type function [5], however, the same final formula, i.e., Eq. (7), is still true for the  $R^k$  integral within this restriction. In the above analysis we have used the following definition of  $\zeta_\alpha$ :  $\zeta_\alpha = 2Z/n_\alpha$ , where  $Z$  is the nuclear charge.

TABLE 1

 $R^k$  Integrals:  $\langle R_1(i)R_2(j)[r_{>}^{-k-1}r_{<}^k]R_3(i)R_4(j) \rangle^a$ 

$R_1(i)$	$R_2(i)$	$R_2(j)$	$R_4(j)$	$k$	$R^k$ integral
1s	1s	1s	1s	0	0.625 000 000 00
1s	1s	2s	1s	0	0.893 550 334-01
2s	1s	2s	1s	0	0.219 478 738-01
2s	1s	2s	2s	0	0.858 165 741-02
4s	1s	3s	2s	0	0.130 334 840-02
4p	3s	4f	3d	1	-0.565 850 300-03
4f	3s	6d	6p	3	-0.240 117 693-02
3p	2p	5p	4p	0	0.159 761 398-02
				1	0.118 571 421-02
				2	-0.417 933 967-03
4d	3d	6d	5d	0	0.127 981 079-04
				1	0.417 313 239-03
				2	-0.171 573 678-04
				3	-0.162 003 996-03
				4	-0.197 255 108-03
6d	5d	5f	4f	0	0.148 515 355-02
				1	0.113 039 677-02
				2	0.616 906 064-03
				3	0.288 619 386-03
				4	0.105 090 961-03

<sup>a</sup> Symbols such as 1s, 2p, etc. represent the corresponding radial part of the desired hydrogenic function. In the last column, the last two digits represent the power of 10, i.e., 0.105 090 961-03 stands for the number .000 105 090 961. Here we used  $Z = 1$ .

In a recent paper Lewis [6] reported a computer program for the calculation of hydrogenic  $R^k$  integrals presented in this note. His calculations are based upon (1) a closed-form expression for the  $R^k$  integrals involving a confluent hypergeometric function, and (2) an infinite series expansion of one of the four hydrogenic functions in  $R^k$ . Whereas method (1), in spite of its computationally tedious form, gives results identical with ours, method (2) is good only for large values of the principal quantum number of the hydrogenic function which is expanded in an infinite series. One of the main merits of using the concise analytical formula (7) is its easily programmable form which leads to a short and accurate subroutine. Our FORTRAN IV program for calculating the  $R^k$  integrals has a total length of about 215 cards compared to 1373 cards in Lewis' program.

Because of its short length we believe that the computing time needed per integral will be smaller for our program, although accurate time comparisons are difficult to make for programs used on different makes of computers. Our program can also be used to calculate the  $R^k$  integrals with fairly large values of principal quantum numbers of hydrogenic functions [7].

## REFERENCES

1. J. LINDERBERG AND H. SHULL, *J. Mol. Spectrosc.* **5** (1960), 1.
2. J. C. SLATER, "Quantum Theory of Atomic Structure," Vol. 1, p. 308, McGraw-Hill, New York, 1960.
3. B. D. JOSHI, *J. Chem. Phys.* **43** (1965), S40, Appendix 1. The limits on  $k$  follow from the properties of the D coefficients.
4. L. PAULING AND E. B. WILSON, "Introduction to Quantum Mechanics," Eqs. 20-9 and 20-11, McGraw-Hill, New York, 1935.
5. See Eq. (3) in C. C. J. ROOTHAAN, *Rev. Mod. Phys.* **32** (1960), 186.
6. M. N. LEWIS, *Comput. Phys. Comm.* **1** (1970), 325. We are grateful to the referee for bringing this work to our attention.
7. The only restriction regarding the use of large principal quantum number hydrogenic functions is that they should not cause an overflow in a double precision word of an IBM/360 during the computation of the radial integral. We have used values of principal quantum numbers as large as 20 without running into such difficulties.

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