

Evaluation of one-centre electron interaction integrals over Slater type atomic orbitals

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MS received 13 October 1986; revised 26 May 1987

Abstract. Simplified expressions for one-centre electron interaction integrals in general and Slater-Condon parameters as well as repulsion integrals of the type (*aa|aa*) in particular have been obtained over Slater-type atomic orbitals. Results calculated using these expressions are in agreement with those due to other authors.

Keywords. One-centre electron interaction integrals; integrals over STO's; MO theory; Slater-Condon parameters; atomic structure.

PACS No. 31·15

1. Introduction

In the prevalent *ab-initio* molecular orbital methodology, Slater type atomic orbitals are replaced by Gaussian functions (Habitx and Clementi 1983). While this makes evaluation of the integrals easy, the computer time required is appreciably enhanced. It is desirable to obtain analytical expressions for integrals over Slater type atomic orbitals to reduce computational labour on one hand and to increase accuracy on the other. A good deal of work has been done in this direction and different approaches to evaluate the various types of integrals developed (Roothaan 1951; Ruedenberg 1951; Deb and Coulson 1971; Kotani *et al* 1963; Yasui and Saika 1982; Guseinov 1985). Thulstrup and Lindenberg (1979) have obtained upper and lower bounds to the two electron Coulomb interaction integrals. Use of the above mentioned approaches usually involves quite a significant amount of complexity and recurrence relations. In view of the generally large number of integrals to be handled in a molecular orbital calculation on a molecule, the totality of these complexities increases the required computational work substantially. Thus, it is desirable to have as simple and as explicit expressions as possible for integrals over Slater type atomic orbitals involving the different operators while retaining accuracy fully. We have obtained such expressions for certain one-centre electron interaction integrals and these are presented here.

2. Evaluation of integrals

Atomic orbitals may be written as

$$\phi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi).$$

The radial part $R_n(r)$, for Slater type orbitals is given by

$$R_n(r) = (2\xi)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} \exp(-\xi r). \quad (1)$$

Let n_a, n_b, n_c, n_d and $\xi_a, \xi_b, \xi_c, \xi_d$ be the principal quantum numbers and Slater exponents (Pople and Beveridge 1970) for the orbitals ϕ_a, ϕ_b, ϕ_c and ϕ_d respectively. We have the following generalized one-centre electron interaction integral (in a.u)

$$(ab|cd) = \int \phi_a \phi_b (1/r_{12}) \phi_c \phi_d d\tau_1 d\tau_2. \quad (2a)$$

We also define the following one-centre integral

$$U^l(n_a, n_b, n_c, n_d; \xi_a, \xi_b, \xi_c, \xi_d) = \int R_{n_a l_a} R_{n_b l_b} (1/r_{12}) R_{n_c l_c} R_{n_d l_d} dr_1 dr_2. \quad (2b)$$

The $(1/r_{12})$ operator can be expanded in terms of spherical harmonics as usual (Pople and Beveridge 1970). Subsequent simplification of equation (2b) leads us to the following result

$$U^l(n_a, n_b, n_c, n_d; \xi_a, \xi_b, \xi_c, \xi_d) = \frac{xy(2n_2 + l)!}{(2\xi_2)^{2n_2 + l + 1}} \left[\frac{(2n_1 - l - 1)!}{(2\xi_1)^{2n_1 - l}} \right. \\ \left. - \sum_{l'=1}^{2n_2 + l + 1} \frac{(2\xi_2)^{2n_2 + l - l' + 1}}{(2n_2 + l - l' + 1)!} \frac{[2(n_1 + n_2) - l']!}{[2(\xi_1 + \xi_2)]^{2(n_1 + n_2) - l' + 1}} \right. \\ \left. + \sum_{l'=1}^{2n_2 - l} \frac{(2\xi_2)^{2n_2 + l - l' + 1} (2n_2 - l - 1)! [2(n_1 + n_2) - l']!}{(2n_2 + l)! (2n_2 - l - l')! [2(\xi_1 + \xi_2)]^{2(n_1 + n_2) - l' + 1}} \right],$$

where

$$x = \{ [2\xi_c]^{n_c + 1/2} [2\xi_d]^{n_d + 1/2} \} / \{ [(2n_c)! (2n_d)!]^{1/2} \};$$

$$y = \{ [2\xi_a]^{n_a + 1/2} [2\xi_b]^{n_b + 1/2} \} / \{ [(2n_a)! (2n_b)!]^{1/2} \};$$

$$n_1 = \frac{1}{2}[n_a + n_b]; \quad n_2 = \frac{1}{2}[n_c + n_d];$$

$$\xi_1 = \frac{1}{2}[\xi_a + \xi_b]; \quad \xi_2 = \frac{1}{2}[\xi_c + \xi_d]$$

and

$$|l_a - l_c| \leq l \leq |l_a + l_c|. \quad (3)$$

One-centre repulsion integrals $(ab|cd)$ may now be obtained as follows

$$(ab|cd) = \sum_{l=0}^{\infty} U^l(n_a, n_b, n_c, n_d; \xi_a, \xi_b, \xi_c, \xi_d) \\ \times C^l(l_a m_a, l_c m_c) C^l(l_b m_b, l_d m_d) \delta_{m_a + m_b, m_c + m_d}. \quad (4)$$

The integrals are zero unless (3) is satisfied. Definition of the C^l function and its values are available in the literature (Condon and Shortley 1967). It is obvious that the values

of the above integrals will depend on the magnetic quantum numbers m_a, m_b, m_c and m_d . Certain special cases of the integral U^l defined in (2b) are redefined as follows and called Slater-Condon parameters

$$F^l(n_a l_a; n_b l_b) = U^l(n_a, n_a, n_b, n_b; \xi_a, \xi_a, \xi_b, \xi_b)$$

and

$$G^l(n_a l_a; n_b l_b) = U^l(n_a, n_b, n_b, n_a; \xi_a, \xi_b, \xi_b, \xi_a).$$

Simplification of (3) leads us to the following results for certain cases of F^l and G^l which are frequently encountered in calculations on atoms and molecules. The purpose of giving the expressions in simplified form is to make the application easy.

$$F^0(1s, 1s) = 0.625 \xi_{1s}$$

$$F^0(1s, 2s) = 4\mu^3 \xi_{2s} \left[\frac{1}{(2\mu)^2} - \frac{1}{4} \sum_{l'=1}^5 \frac{(6-l')}{x^{7-l'}} + \frac{1}{16} \sum_{l'=1}^4 \frac{(6-l')!}{(4-l')! x^{7-l'}} \right],$$

$$F^1(1s, 2p) = 10\mu^3 \xi_{2p} \left[\frac{1}{2\mu} - \frac{1}{2} \sum_{l'=1}^6 \frac{1}{x^{7-l'}} + \frac{1}{120} \sum_{l'=1}^3 \frac{(6-l')!}{(3-l')! x^{7-l'}} \right],$$

$$F^0(1s, 3s) = 4\mu^3 \xi_{3s} \left[\frac{1}{(2\mu)^2} - \frac{1}{4} \sum_{l'=1}^7 \frac{(8-l')}{x^{9-l'}} + \frac{1}{24} \sum_{l'=1}^6 \frac{(8-l')!}{(6-l')! x^{9-l'}} \right],$$

$$F^1(1s, 3p) = 14\mu^3 \xi_{3p} \left[\frac{1}{2\mu} - \frac{1}{2} \sum_{l'=1}^8 \frac{1}{x^{9-l'}} + \frac{1}{420} \sum_{l'=1}^5 \frac{(8-l')!}{(5-l')! x^{9-l'}} \right],$$

$$F^2(1s, 3d) = 56\mu^3 \xi_{3d} \left[\frac{6}{8!} \sum_{l'=1}^4 \frac{(8-l')!}{(4-l')! x^{8-l'}} \right],$$

$$F^0(2s, 2s) = 0.3632812 \xi_{2s}; \quad F^1(2s, 2p) = 0.2408854 \xi_{2s}$$

$$F^0(2s, 3s) = \frac{4}{3} \mu^5 \xi_{3s} \left[\frac{6}{(2\mu)^4} - \frac{1}{16} \sum_{l'=1}^7 \frac{(10-l')!}{(7-l')! x^{11-l'}} + \frac{1}{96} \sum_{l'=1}^6 \frac{(10-l')!}{(6-l')! x^{11-l'}} \right],$$

$$F^1(2s, 3p) = \frac{14}{3} \mu^5 \xi_{3p} \left[\frac{2}{(2\mu)^3} - \frac{1}{8} \sum_{l'=1}^8 \frac{(10-l')!}{(8-l')! x^{11-l'}} + \frac{1}{1680} \sum_{l'=1}^5 \frac{(10-l')!}{(5-l')! x^{11-l'}} \right],$$

$$F^2(2s, 3d) = \frac{56}{3} \mu^5 \xi_{3d} \left[\frac{1}{(2\mu)^2} - \frac{1}{4} \sum_{l'=1}^9 \frac{(10-l')}{x^{11-l'}} + \frac{3}{2! 8!} \sum_{l'=1}^4 \frac{(10-l')!}{(4-l')! x^{11-l'}} \right],$$

$$F^2(2p, 2p) = 0.1757812 \xi_{2p}$$

$$F^3(2p, 3d) = 84\mu^5 \xi_{3p} \left[\frac{1}{2\mu} - \frac{1}{2} \sum_{l'=1}^{10} \frac{1}{x^{11-l'}} + \frac{1}{9!} \sum_{l'=1}^3 \frac{(10-l')!}{(3-l')! x^{11-l'}} \right],$$

$$F^0(3s, 3s) = 0.258138 \xi_{3s}; \quad F^1(3s, 3p) = 0.1809245 \xi_{3p}$$

$$F^2(3s, 3d) = 0.1362631 \xi_{3d}; \quad F^2(3p, 3p) = 0.136263 \xi_{3p}$$

$$F^3(3p, 3d) = 0.2160158 \xi_{3d}; \quad F^4(3d, 3d) = 0.0888667 \xi_{3d},$$

$$G^0(1s, 2s) = \frac{44 \xi_{1s}^3 \xi_{2s}^5}{(\xi_{1s} + \xi_{2s})^7}; \quad G^1(1s, 2p) = \frac{28 \xi_{1s}^3 \xi_{2p}^5}{(\xi_{1s} + \xi_{2p})^7},$$

$$G^0(1s, 3s) = \frac{74.400009 \xi_{1s}^3 \xi_{3s}^7}{(\xi_{1s} + \xi_{3s})^9}; \quad G^1(1s, 3p) = \frac{49.333333 \xi_{1s}^3 \xi_{3p}^7}{(\xi_{1s} + \xi_{3p})^9},$$

$$G^2(1s, 3d) = \frac{36.000026 \xi_{1s}^3 \xi_{3d}^7}{(\xi_{1s} + \xi_{3d})^9}; \quad G^1(2s, 2p) = 0.2408854 \xi_{2s};$$

$$G^0(2s, 3s) = \frac{514.66667 \xi_{2s}^5 \xi_{3s}^7}{(\xi_{2s} + \xi_{3s})^{11}}; \quad G^1(2s, 3p) = \frac{352 \xi_{2s}^5 \xi_{3p}^7}{(\xi_{2s} + \xi_{3p})^{11}},$$

$$G^2(2s, 3d) = \frac{261.33333 \xi_{2s}^5 \xi_{3d}^7}{(\xi_{2s} + \xi_{3d})^{11}}; \quad G^1(2p, 3s) = \frac{352 \xi_{3s}^7 \xi_{2p}^5}{(\xi_{3s} + \xi_{2p})^{11}},$$

$$G^2(2p, 3p) = \frac{261.33333 \xi_{2p}^5 \xi_{3p}^7}{(\xi_{2p} + \xi_{3p})^{11}}; \quad G^3(2p, 3d) = \frac{205.33345 \xi_{3p}^5 \xi_{3d}^7}{(\xi_{2p} + \xi_{3d})^{11}},$$

$$G^1(3s, 3p) = 0.1809244 \xi_{3s}; \quad G^2(3s, 3d) = 0.1362623 \xi_{3s};$$

$$G^3(3p, 3d) = 0.1080079 \xi_{3p}.$$

In these equations

$$\mu = \xi_{n_a} / \xi_{n_b}$$

where

$$n_a \leq n_b$$

and

$$x = 1 + \mu.$$

The integrals which are equal to any one of those given above [e.g. $F^2(2p, 3p) = F^2(2s, 3d)$] or which vanish [e.g. $F^1(2p, 2p)$] are not presented.

Simplified expressions for one-centre repulsion integrals of the type $(aa|aa)$ for certain important cases are as follows (in a.u.).

$$(1s\ 1s|1s\ 1s) = 0.625 \xi_{1s}$$

$$(2s\ 2s|2s\ 2s) = 0.3632812 \xi_{2s}$$

$$(2p\ 2p|2p\ 2p) = 0.3914062 \xi_{2p} \quad (m_i = 0)$$

$$(2p\ 2p|2p\ 2p) = 0.3703124 \xi_{2p} \quad (m_i = 1)$$

$$(2p\ 2p|2p\ 2p) = 0.3703124 \xi_{2p} \quad (m_i = -1)$$

$$(3s\ 3s|3s\ 3s) = 0.258138 \xi_{3s}$$

$$\begin{aligned}
(3p\ 3p|3p\ 3p) &= 0.27994\ \xi_{3p}\ (m_l = 0) \\
(3p\ 3p|3p\ 3p) &= 0.2635885\ \xi_{3p}\ (m_l = 1) \\
(3p\ 3p|3p\ 3p) &= 0.2635885\ \xi_{3p}\ (m_l = -1) \\
(3d\ 3d|3d\ 3d) &= 0.2765159\ \xi_{3d}\ (m_l = 0) \\
(3d\ 3d|3d\ 3d) &= 0.264143\ \xi_{3d}\ (m_l = 1) \\
(3d\ 3d|3d\ 3d) &= 0.264143\ \xi_{3d}\ (m_l = -1) \\
(3d\ 3d|3d\ 3d) &= 0.269463\ \xi_{3d}\ (m_l = 2) \\
(3d\ 3d|3d\ 3d) &= 0.269463\ \xi_{3d}\ (m_l = -2).
\end{aligned}$$

Similarly using the quantum numbers n and l associated with the orbitals ϕ_a , ϕ_b , ϕ_c and ϕ_d , other integrals of (3) and (4) can also be evaluated.

3. Results and discussion

The present formulas offer a very economical and convenient method of calculating the various one-centre electron interaction integrals U^l , F^l , G^l and $(ab|cd)$. We find that repulsion integrals of the type $(aa|aa)$ have extremely simple forms (constant \times Slater exponent). Numerical values of such integrals for certain cases calculated using (4) are presented in table 1. Results taken from the other sources (Yasui and Saika 1982, Pople

Table 1. One-centre repulsion integrals.

Atoms	Orbital ^a	Present value (a.u.)	From literature (a.u.)	Approx. time (sec)
Li	(2s2s 2s2s)	0.289615078125	0.289615078125 ^b	3
H	(1s1s 1s1s)	0.554843750000	0.554843750000 ^b	1
F	(2p _x 2p _x 2p _x 2p _x)	0.241301953125 $\times 10^1$	0.241301953125 $\times 10^1$ ^b	3
Be	(1s1s 1s1s)	0.386647500000 $\times 10^1$	0.386647500000 $\times 10^1$ ^b	1
Na	(1s1s 1s1s)	0.954725000000 $\times 10^1$	0.954725000000 $\times 10^1$ ^b	1
H	(1s1s 1s1s)	0.487687500000	0.487687500000 ^b	1
F	(1s1s 1s1s)	0.494868750000 $\times 10^1$	0.494868750000 $\times 10^1$ ^b	1
Sc	(1s1s 1s1s)	0.108062500000 $\times 10^2$	0.108062500000 $\times 10^2$ ^b	1
H	(1s1s 1s1s)	0.625000000000	0.625000000000 ^c	1
F	(2p _x 2p _x 2p _x 2p _x)	0.101765625000 $\times 10^1$	1.01766 ^c	3
F	(1s2s 2s1s)	0.146328213305	0.14633 ^c	1
F	(2p _x 2p _x 2p _x 2p _x)	0.054843750000	0.05484 ^c	3
F	(2s2p _x 2s2p _x)	0.208767361111	0.20877 ^c	3

^a x component corresponds to $m_l = 1$ while z component corresponds to $m_l = 0$.

^b From (Yasui and Saika 1982) using the following ξ values.

$\xi_{Li2s} = 0.79722$ (in LiH), $\xi_{Be1s} = 6.18636$ (in BeF⁺), $\xi_{H1s} = 0.88775$ (in LiH), $\xi_{F2p} = 6.165$ (in BeF⁺), $\xi_{Na1s} = 15.2756$ (in NaH), $\xi_{H1s} = 0.7803$ (in NaH), $\xi_{Sc1s} = 17.29$ (in ScF), $\xi_{F1s} = 7.9179$ (in ScF).

^c From (Pople and Beveridge 1970) using $\xi_{H1s} = 1.0$, $\xi_{F2p} = 2.6$, $\xi_{F2s} = 2.6$, $\xi_{F1s} = 8.7$ (in HF).

and Beveridge 1970) are compared with the present values in the same table. It may be noted that we used the same values of orbital exponents in our calculation as the other authors in order to make the numerical comparisons meaningful. We find that there is an almost perfect agreement between our values and those obtained by the other authors (Yasui and Saika 1982; Pople and Beveridge 1970) using different techniques.

We applied the present formulas for the Slater-Condon parameters F^l and G^l to certain orbitals of B , C , N and O . These integrals were also calculated using the formulas given by Slater in the basis of Morse functions (Slater 1960). This showed satisfactory agreement between the corresponding integral values despite the fact that the two basis sets are different. However, these calculated values are not being presented.

Use of the present analytical formulas, besides giving accuracy enhances computational speed as briefly explained below. An efficient computer program to evaluate two-electron interaction integrals has been made by Habitz and Clementi (1983). This program may take from about one to a few seconds to evaluate one-centre electron interaction integrals on an IBM 370/3033 computer. This system, as per available reports (Trickey and Purvis III 1984) is about two orders of magnitudes faster than an IBM PC/XT compatible system equipped with a co-processor which was used in the present calculation and which provides fairly good precision (64 bit processing). In our calculations presented above nearly 1 to 3 sec only were needed to compute the integrals using the general formula (4) on the IBM PC/XT compatible computer system. If, however, the specific formulas for the various cases were programmed, the computational speed would be enhanced further. The above considerations show that use of the present analytical formulas to evaluate the one-centre electron interaction integrals would provide substantial computational economy over an approach based on Gaussian expansions of Slater type atomic orbitals.

Acknowledgements

PCM thanks UGC, New Delhi for a project grant. Thanks are also due to Prof. B M Deb for discussions.

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