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Finite Analytical Expressions for Two-Centre Exchange Integrals between Slater Orbitals Having the Same Exponents

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Closed analytical expressions are derived for some two-centre exchange integrals between Slater orbitals. Integrals involving $1s$, $2s$ and $2p\sigma$ orbitals are considered with the restriction that the two orbitals have the same exponent. An expansion formula accurate for large values of R is also derived.

Für eine Reihe von Zweizentren-Austauschintegralen zwischen Slaterorbitalen werden geschlossene analytische Ausdrücke mitgeteilt, wobei allerdings nur $1s$-, $2s$- und $2p\sigma$-Orbitale mit gleichen Exponenten behandelt werden. Schließlich wird noch eine asymptotische Entwicklung für große R angegeben.

Obtention d'expressions analytiques compactes pour certaines intégrales d'échange bicentriques entre orbitales de Slater. On considère des intégrales impliquant des orbitales $1s$, $2s$ et $2p\sigma$ avec comme restriction l'égalité des exposants orbitaux. Un développement valable pour les grandes valeurs de R est aussi obtenu.

1. Introduction

Two-electron exchange integrals between Slater-type orbitals are usually evaluated by expansion methods in which the integral is expressed in terms of auxillary functions. A review of the most popular methods is given by Alder and coworkers [1]. The accuracy of any integral can always be improved by increasing the length of the expansion. However, the rate of convergence to the exact value will not be the same for all integrals and in particular it will depend strongly on the distance between the two orbital centres. We encountered difficulties in using the established procedure to calculate exchange integrals at large internuclear separations. These integrals were needed to evaluate interatomic energies in the van-der-Waals region and the problem encountered was that the integrals were small but one requires them with considerable accuracy because of a cancellation of terms that occurs in the total energy expression [2].

In 1931 Podolansky [3] showed that all exchange integrals could in principle be represented by closed analytical expressions which involve powers, exponentials, the logarithmic and the exponential integral. To our knowledge such an expression has only been obtained for the case of two $1s$ orbitals with equal exponents[1]. This is worked out in detail by Slater, who expresses the view that this is almost

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[1] The integral was first evaluated by Sugiura, Y.: Z. Physik **45**, 484 (1927).

the only case that can be treated in this way [4]. In this paper we show that closed analytical expressions can be obtained for other axially symmetric orbitals ($2s$, $2p\sigma$, etc.) with equal exponents. We also develop an expansion technique for these cases which has rapid convergence at large internuclear distances. We have not, as yet, extended the method to orbitals with different exponents, or to orbitals without axial symmetry.

We present our results partly with the aim of stimulating further research in this field. A general advance in developing analytical expressions for two-electron integrals in a Slater orbital basis, or in improving the expansion techniques, would have a considerable impact on the time required for molecular calculations and on the size of molecules susceptible to nonempirical calculations.

An additional justification for this work is that it provides exact expressions for a few cases against which the more widely applicable expansion techniques can be tested.

2. General Theory

We follow the symbolism used by Ruedenberg [5] and refer the reader to that paper for full definition of the terms introduced. The integral to be evaluated has the form

$$I = \int \Omega_{ab}(1) r_{12}^{-1}\, \Omega_{ab}(2) \mathrm{d}v_1 \mathrm{d}v_2 \,, \tag{1}$$

where $\Omega_{ab}(1)$ is a product of normalised Slater orbitals on diffrent centres. The integrals are most conveniently handled in elliptic co-ordinates (ξ, η, φ). The operator r_{12}^{-1} is written as the Neumann expansion in associated Legendre functions of the first and second kind $P_l^{|m|}$ and $Q_l^{|m|}$. We have used the definitions of these functions of Jahnke and Emde [6], as adopted by Ruedenberg [5]. We shall consider only the case of equal screening constants ($\beta = 0$) and axially symmetric orbitals ($m = 0$). After integration over the elliptic coordinates φ_1 and φ_2, η_1, η_2, and ξ_1, the integral to be evaluated has the form

$$I = \frac{\zeta}{4} \alpha^{2(n_a+n_b)+1} \sum_{l=0}^{\infty} (2l+1) \int_1^{\infty} Q_l(\xi_2)\, K_l(\xi_2)\, M_l(\xi_2, \alpha)\, e^{-\alpha\xi_2} \mathrm{d}\xi_2 \tag{2}$$

where

$$M_l(\xi_2, \alpha) = \int_1^{\xi_2} P_l(\xi_1)\, K_l(\xi_1)\, e^{-\alpha\xi_1} d\xi_1$$

and where K_l and M_l are just polynomials[2]. The summation over l does not in practice extend to infinity because of the orthogonality of the Legendre polynomials.

The functions $Q_l(\xi)$ are made up of logarithmic and polynomial terms. For example the first member is

$$Q_0 = \ln((\xi+1)/(\xi-1)) \,. \tag{3}$$

Detailed expressions for the higher members can be found in Ref. [6].

[2] If ζ_a and ζ_b are the exponents of the Slater orbitals whose product is Ω_{ab}, and R is the internuclear distance, then we have defined $\zeta = \frac{1}{2}(\zeta_a + \zeta_b)$ and $\alpha = \zeta R$.

The polynomial part can be easily integrated, but integrals involving the logarithmic function are more difficult. We first change the range of integration by introducing the variable $x = \xi - 1$. This leads to a number of terms each of which has the form

$$\int_0^\infty X(x_2) \ln((x_2+2)/x_2)\, e^{-\alpha x_2} \int_0^{x_2} Y(x_1)\, e^{-\alpha x_1} \mathrm{d}x_1 \mathrm{d}x_2 \tag{4}$$

the functions X and Y being polynomials. Each of these integrals is split into three parts by using the identity

$$\ln((x+2)/x) = \ln 2\alpha + \ln(1 + x/2) - \ln \alpha x\,, \tag{5}$$

where α is introduced for computational convenience. The integrals involving $\ln 2\alpha$ and $\ln \alpha x$ can be evaluated using the expressions

$$\int_0^\infty x^{n-1} e^{-\alpha x} \mathrm{d}x = \frac{\Gamma(n)}{\alpha^n} = \frac{(n-1)!}{\alpha^n} \tag{6}$$

and

$$\int_0^\infty x^{n-1} \ln \alpha x\, e^{-\alpha x} \mathrm{d}x = \frac{\Gamma'(n)}{\alpha^n}\,, \tag{7}$$

where Γ' is the derivative of the Γ-function the first member of which $\Gamma'(1)$ is Euler's constant. These may be evaluated from the recursion relation

$$\Gamma'(n+1) = \Gamma(n) + n\Gamma'(1)\,. \tag{8}$$

The remaining integral involving $\ln(1 + x/2)$ may be evaluated as a semi-convergent series or it may be expressed in terms of the exponential integral. We describe both methods.

3. The Series Expansion

We prove in the appendix that

$$\int_0^\infty x^{n-1} \ln(1+x)\, e^{-\alpha x} \mathrm{d}x = \sum_{i=1}^{r} (-1)^{i+1} \frac{(n+i-1)!}{i\alpha^{n+i}} + R_r(\alpha)\,, \tag{9}$$

where

$$|R_r(\alpha)| < \frac{(r+n)!}{(r+1)\,\alpha^{r+n+1}}\,. \tag{10}$$

Thus for large values of α the remainder decreases up to the term $r \approx \alpha - n$ and increases thereafter to infinity. If we terminate the summation at this value of r we have a value of the integral with an accuracy

$$|R(\alpha)| < \frac{\Gamma(\alpha+1)}{(\alpha-n+1)\,\alpha^{\alpha+1}}\,. \tag{11}$$

Table 1 [a]

k	A_k	B_k
	$2p\sigma - 2p\sigma$	
1	−0.215524446E−02	0.634920635E−02
2	−0.367409905E−01	0.380952381E−01
3	−0.298154438E 00	0.152380952E 00
4	−0.204927873E 02	0.952380952E 00
5	−0.112353809E 02	0.634285714E 01
6	−0.487369100E 02	0.325714286E 02
7	−0.176872781E 03	0.134000000E 03
8	−0.537397619E 03	0.464571429E 03
9	−0.126239734E 04	0.133628571E 04
10	−0.197965535E 04	0.300000000E 04
11	−0.139561611E 04	0.486000000E 04
12	0.130338781E 04	0.504000000E 04
13	0.309931186E 04	0.252000000E 04
14	0.204491629E 04	0.000000000E 00
15	−0.577867222E 04	0.000000000E 00

[a] In all tables the numbers are given in E Germat, that is NE—02 ≡ N × 10^{-2}.

After collecting the terms in I arising from these separate integrations the integral has the form[3]

$$I = \alpha^n \zeta \sum_{k=1} \alpha^{-k} [A_k + B_k \ln \alpha] e^{-2\alpha}, \tag{12}$$

where $n = 2n_a + 2n_b$ and A_k and B_k are coefficients which are characteristic of the orbital types occurring. In practice we found for $\alpha > 5$ that approximately 15 terms gives an accurate value of the integral. The coefficients A_k and B_k are given in Table 1 for the $2p\sigma - 2p\sigma$ integral, and in Table 3 we compare values of this integral with those obtained by the MIDIAT program[4]. The coefficients for the remaining integrals involving $1s$, $2s$ and $2p\sigma$ orbitals may be had from the authors on request. For $\alpha > 9$ the expansion gives integrals whose accuracy is determined by the accuracy of A_k and B_k, which in these calculations is given to nine significant figures.

4. Closed Expressions Involving the E_1 Function

The integral (9) may also be expressed in terms of the exponential integral

$$E_1(x) = \int_x^{\infty} \frac{e^{-t}}{t} \, dt. \tag{13}$$

[3] The $\ln \alpha$ arises from the term in (13) which is $\ln 2\alpha$.

[4] MIDIAT is a two-centre integral program originally written by Switendick and Corbato. The theory is described by an article in Ref. [1]. A modification has been made to run on the ICL 1905 computer, which is a relatively slow machine with small store (32 K). Each exchange integral requires several minutes with this program whereas they can be calculated at a rate of about ten a second from the expressions given in this paper.

Table 2

k	P_k	Q_k	R_k
		$1s-1s$	
1	0.102954220 E−01	0.133333333 E 00	0.266666666 E 00
2	−0.138227468 E 00	0.800000000 E 00	0.000000000 E 00
3	0.443132987 E−02	0.200000000 E 01	−0.800000000 E 00
4	0.201031760 E 01	0.240000000 E 01	0.000000000 E 00
5	0.692658798 E 00	0.120000000 E 01	0.240000000 E 01
		$2s-2s$	
1	−0.239471606 E−03	0.705467372 E−03	0.141093474 E−02
2	−0.598515769 E−02	0.776014109 E−02	0.000000000 E 00
3	−0.429793835 E−01	0.536155203 E−01	0.197530864 E−01
4	−0.176717113 E 00	0.251851852 E 00	0.000000000 E 00
5	−0.563571275 E 00	0.850793651 E 00	0.677248678 E−01
6	−0.657159359 E 00	0.209100529 E 01	0.000000000 E 00
7	−0.102134818 E 01	0.359365079 E 01	−0.457142857 E 00
8	0.256952782 E 01	0.382222220 E 01	0.000000000 E 00
9	0.110312336 E 01	0.191111103 E 01	0.382222222 E 01
		$2p\sigma-2p\sigma$	
1	−0.215524446 E−02	0.634920635 E−02	0.126984127 E−01
2	−0.415028947 E−01	0.380952381 E−01	0.000000000 E 00
3	−0.304900468 E 00	0.152380952 E 00	0.000000000 E 00
4	−0.201177873 E 01	0.952380952 E 00	0.000000000 E 00
5	−0.114795773 E 02	0.634285714 E 01	0.125714285 E 01
6	−0.477239636 E 02	0.325714286 E 02	0.000000000 E 00
7	−0.185108384 E 03	0.134000000 E 03	−0.514285716 E 01
8	−0.499450688 E 03	0.464571429 E 03	0.000000000 E 00
9	−0.138867495 E 04	0.133628571 E 04	0.325714286 E 02
10	−0.162835301 E 04	0.300000000 E 04	0.000000000 E 00
11	−0.223473187 E 04	0.486000000 E 04	−0.360000000 E 03
12	0.290916695 E 04	0.504000000 E 04	0.000000000 E 00
13	0.145458348 E 04	0.252000000 E 04	0.504000000 E 04
		$1s-2s$	
1	−0.219408680 E−02	0.126984127 E−01	−0.253968254 E−01
2	−0.297608489 E−01	0.107936508 E 00	0.000000000 E 00
3	−0.246867362 E 00	0.482539683 E 00	−0.253968254 E−01
4	−0.253791812 E 00	0.133333333 E 01	0.000000000 E 00
5	−0.474451871 E 00	0.234285714 E 01	−0.342857143 E 00
6	0.179503510 E 01	0.251428571 E 01	0.000000000 E 00
7	0.725642550 E 00	0.125714286 E 01	0.251428571 E 01
		$1s-2p\sigma$	
1	−0.658226038 E−02	0.380952381 E−01	0.761904762 E−01
2	−0.160361537 E 00	0.266666666 E 00	0.000000000 E 00
3	−0.804472103 E 00	0.990476191 E 00	−0.152380953 E 00
4	−0.256460679 E 01	0.297142857 E 01	0.000000000 E 00
5	−0.875282455 E 01	0.834285714 E 01	0.685714285 E 00
6	−0.115697504 E 02	0.194285714 E 02	0.000000000 E 00
7	−0.154849755 E 02	0.325714286 E 02	−0.342857143 E 01
8	0.197902514 E 02	0.342857143 E 02	0.000000000 E 00
9	0.989512568 E 01	0.171428571 E 02	0.342857143 E 02

Table 2 (continued)

k	P_k	Q_k	R_k
		$2p-2s\sigma$	
1	−0.718414819 E−03	0.211640212 E−02	−0.423280423 E−02
2	−0.116620815 E−01	0.179894180 E−01	0.000000000 E 00
3	−0.114717877 E 00	0.994708995 E−01	−0.253968254 E−01
4	−0.566686762 E 00	0.464550265 E 00	0.000000000 E 00
5	−0.295280898 E 01	0.204656085 E 01	−0.194708995 E 00
6	−0.977379385 E 01	0.816507937 E 01	0.000000000 E 00
7	−0.300916937 E 02	0.266222222 E 02	0.137142857 E 01
8	−0.409567646 E 02	0.653015874 E 02	0.000000000 E 00
9	−0.538044079 E 02	0.111380953 E 03	−0.134285714 E 02
10	0.681664211 E 02	0.118095239 E 03	0.000000000 E 00
11	0.340832102 E 02	0.590476201 E 02	0.118095238 E 03

For example, for $n=1$ in (9) we have

$$\begin{aligned}\int_0^\infty \ln(1+y)\,e^{-\alpha y}\,dy &= \left[\frac{\ln(1+y)\,e^{-\alpha y}}{-\alpha}\right]_0^\infty + \frac{1}{\alpha}\int_0^\infty \frac{e^{-\alpha y}\,dy}{1+y} \\ &= \frac{e^\alpha}{\alpha}\int_1^\infty \frac{e^{-\alpha x}}{x}\,dx = \frac{e^\alpha E_1(\alpha)}{\alpha} \equiv h(\alpha)\,.\end{aligned} \tag{14}$$

For $n>1$ the integration is tedious but not impossible. The final integrals take the form

$$I=\alpha^n \zeta \sum_{k=1}^{r} \alpha^{-k}[P_k + (\ln\alpha + (-1)^k h(4\alpha))\,Q_k + h(2\alpha)\,R_k]\,e^{-2\alpha}\,. \tag{15}$$

The coefficients P, Q, and R are given in Table 2. The value of r depends on the type of orbitals occurring in the integral.

Expression (15) is a closed analytical expression valid for all values of α. For a given accuracy of the coefficients P, Q, and R, greater accuracy can be obtained at large α than at small α because of the cancellation of large terms. The exponential integral has been tabulated. Alternatively a rapid method of evaluating $h(\alpha)$ is to use the expression

$$\alpha^2 h(\alpha) = \frac{\alpha^4 + a_1\alpha^3 + a_2\alpha^2 + a_3\alpha + a_4}{\alpha^4 + b_1\alpha^3 + b_2\alpha^2 + b_3\alpha + b_4} + \varepsilon(\alpha)\,. \tag{16}$$

The coefficients are listed in Ref. [7] to ten decimal places and give an accuracy of better than 2×10^{-8} for $1 \leqq \alpha < \infty$.

The results obtained from expression (15) for the $2p\sigma-2p\sigma$ integral are also shown in Table 3. The integrals are in agreement with those obtained by the expansion method to nine significant figures for $\alpha>9$, and we therefore believe that these integrals are accurate to nine figures.

Table 3. *Comparison of the expansion formula (12) and the exact formula (15) with values obtained from the* MIDIAT *program for the* $2p\sigma - 2p\sigma$ *exchange integral*

α	Expression (12)	Expression (15)	MIDIAT program
2	−0.306417211 E 00	0.439915223 E−01	0.439913419 E−01
4	0.783877950 E−01	0.785051035 E−01	0.785037689 E−01
6	0.294099453 E−01	0.294098744 E−01	0.294098740 E−01
8	0.431792303 E−02	0.431792294 E−02	0.431792278 E−02
10	0.392474239 E−03	0.392474240 E−03	0.392474238 E−03
15	0.324944134 E−06	0.324944134 E−06	0.324652299 E−06
20	0.115820626 E−09	0.115820626 E−09	0.115555747 E−09

The MIDIAT program gives an estimate of the accuracy to which any integral is calculated. For $\alpha = 2$, for example, this is only to give five significant figures. The result from expression (15) is the same as from MIDIAT to this accuracy and we believe it is much higher. As we have already emphasised, the accuracy depends only on the accuracy to which the coefficients in (15) and the exponential integral are evaluated.

Appendix

$$I_n(\alpha) = \int_0^\infty x^{n-1} \ln(1+x)\, e^{-\alpha x} \mathrm{d}x . \tag{1}$$

As $\ln(1+x)$ is analytical in the region $0 < x < \infty$, we can use the Taylor expansion formula

$$f(1+x) = \sum_{i=0}^{r} \frac{1}{i!} f^i(1)\, x^i + \frac{1}{(r+1)!} f^{(r+1)}(1+\xi)\, x^{r+1} , \tag{2}$$

where $0 < \xi < x$.

This gives

$$\ln(1+x) = \sum_{i=1}^{r} (-1)^{i+1} \frac{x^i}{i} + (-1)^r \frac{x^{r+1}}{(r+1)(1+\xi)^{r+1}} \tag{3}$$

Inserting (3) into (1) we get

$$I_n(\alpha) = \sum_{i=1}^{r} (-1)^{i+1} \frac{(n+i-1)!}{i\alpha^{n+i}} + R_r(\alpha) , \tag{4}$$

where

$$R_r(\alpha) = \frac{(-1)^r}{(r+1)} \int_0^\infty \frac{x^{r+n}}{(1+\xi)^{r+1}} e^{-\alpha x} \mathrm{d}x , \tag{5}$$

$$|R_r(\alpha)| \leqq \frac{1}{r+1} \int_0^\infty x^{r+n} e^{-\alpha x} \mathrm{d}x = \frac{(r+n)!}{(r+1)\,\alpha^{r+n+1}} . \tag{6}$$

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