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Calculation of Overlap Integrals over Slater Orbitals with Nearly Equal Exponents

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A series expansion is derived for overlap integrals between Slater type orbitals with nearly equal screening constants and simple analytical expressions are obtained if both of them are equal. Unlike the known standard methods no numerical instabilities arise and also no restrictions exist with respect to the quantum numbers n, l and m of the orbitals.

INTRODUCTION

The methods of evaluating overlap integrals over Slater type orbitals can be divided into three different groups. The first one is based on the transformation to elliptical coordinates as carried out in the classical paper of Mulliken *et al.*[1], the second one uses a single-center expansion technique,[2,6] while the last one is founded on the Fourier transformation method.[3,4] Common to all these methods is the occurence of numerical instabilities when the screening constants of the Slater functions become almost equal requiring a special treatment in this case. For this reason, in a recent note[5] the single-center expansion technique has been applied to compute these overlap integrals with equal screening constants resulting in a collection of very lengthy and cumbersome formulas. Therefore, in this communication we shall show that much simpler expressions can be obtained for this case in deriving an analytical formula by the Fourier transformation method. Moreover, it has the additional advantage to be applicable without any numerical problems, even if the screening constants are slightly different. For this purpose, at first we give the general expression for overlap integrals obtained in this way, and afterwards we derive from this the desired limit when both of the screening constants approach each other.

OVERLAP INTEGRALS; GENERAL CASE

Starting with the Fourier representation of a like wave function[3]

$$\varphi_i (\vec{r} - \vec{R}) = R_i (|\vec{r} - \vec{R}|)\, Y_{L_i} (\widehat{r - R}) = \int d^3 k\, e^{i\vec{k}(\vec{r}-\vec{R})}\, \breve{\varphi}_i (\vec{k}) \qquad (1)$$

with the Fourier transformed

$$\breve{\varphi}_i (\vec{k}) = (2\pi^2 i^{l_i})^{-1}\, Y_{L_i} (\hat{k})\, \breve{R}_{i, l_i} (k) \qquad (2)$$

and the spherical Bessel transformed of order l_i

$$\breve{R}_{i,l_i}(k) = \int_0^\infty r^2\,dr\, j_{l_i}(kr)\, R_i(r) \tag{3}$$

the overlap integral takes the form

$$\begin{aligned} S_{ij}^{\mu\nu} &= \int d^3r\, \varphi_i^*(\vec{r} - \vec{R}_\mu)\, \varphi_j(\vec{r} - \vec{R}_\nu) \\ &= 4\pi \sum_L (-1)^{(l+l_i-l_j)/2}\, Y_L^*(\hat{R})\, G_L(L_iL_j)\, A_l(n_il_i, n_jl_j; R) \end{aligned} \tag{4}$$

Here, $G_L(L_iL_j)$ is a Gaunt number, $\vec{R} = \vec{R}_\mu - \vec{R}_\nu$, and the radial part is given as[3,4]

$$A_l(n_il_i, n_jl_j; R) = (2/\pi) \int_0^\infty k^2\,dk\, j_l(kR)\, \breve{R}_{i,l_i}(k)\, \breve{R}_{j,l_j}(k) \tag{5}$$

Assuming now the radial function to be a Slater-type orbital (STO), the spherical Bessel transformed, eq. (3), becomes

$$\breve{R}_{i,l_i}(k) = c_i\, k^{l_i} \sum_{n \geq n_{io}}^{n_i+1} (k^2 + \zeta_i^2)^{-n}\, B_n(n_i + 1, l_i; \zeta_i); \qquad n_{i0} = 1 + (n_i + l_i)/2 \tag{6}$$

with the normalization constant c_i and the B-coefficients being defined by the recurrence relations

$$\begin{aligned} &(1) && B_{n-m}(nl;\zeta) = 0 \text{ if } n \leq l + 2m;\ m = 0, \ldots, n \\ &(2) && B_n(nl;\zeta) = (2n-2)!!\,\zeta^{n-l-1};\ (2n)!! = 2 \cdot 4 \cdot \ldots \cdot 2n \\ &(3) && B_m(n+1, l; \zeta) = 2n\zeta B_{m-1}(nl;\zeta) - (n+l)(n-l-1)\, B_{m-1}(n-1, l; \zeta) \end{aligned} \tag{7}$$

where the last equation has been given in ref. 4 apart from a printing error; the first few members of these B-coefficients are listed in Table I.

The radial integral (5) may now be expressed by the following quadratic form

$$\begin{aligned} A_l(n_il_i, n_jl_j; R) &= c_ic_j \sum_{n' \geq n_{jo}}^{n_j+1} \sum_{n \geq n_{io}}^{n_i+1} B_n(n_i+1, l_i; \zeta_i)\, W_{nn'}^{l\lambda}(\zeta_i\zeta_j; R)\, B_{n'}(n_j+1, l_j; \zeta_j) \\ \lambda &= 1 + (l_i + l_j - l)/2 \end{aligned} \tag{8}$$

$W_{nn'}^{l\lambda}$ defined by

$$W_{nn'}^{l\lambda}(\zeta_i\zeta_j; R) = (2/\pi) \int dk\, \frac{k^{l+2\lambda}\, j_l(kR)}{(k^2 + \zeta_i^2)^n\, (k^2 + \zeta_j^2)^{n'}} \tag{9}$$

obeys the recurrence relations[4]

$$(1)\quad W_{n0}^{l1} = \left(\frac{R}{2\zeta}\right)^{n-1} \frac{\zeta^{l+1}}{(n-1)!}\, k_{n-2-l}(\zeta_i R) \tag{10}$$

$$(2)\quad W_{nn'}^{l,\lambda+1} = \frac{2l+3}{R}\, W_{nn'}^{l+1,\lambda} - W_{nn'}^{l+2,\lambda} \tag{11}$$

$$(3)\quad W_{nn'}^{l\lambda} = (W_{n,n'-1}^{l\lambda} - W_{n-1,n'}^{l\lambda})/(\zeta_j^2 - \zeta_i^2) \tag{12}$$

TABLE I

Coefficients of the Spherical Bessel Transformed of a Slater Function

$B_{n+l-\nu}(n+l, l)$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$
$\nu = 0$	$(2l)!!$	$(2l+2)!!\,\zeta$	$(2l+4)!!\,\zeta^2$	$(2l+6)!!\,\zeta^3$	$(2l+8)!!\,\zeta^4$	$(2l+10)!!\,\zeta^5$
$\nu = 1$	0	0	$-(2l+2)!!$	$-3\,(2l+4)!!\,\zeta$	$-6\,(2l+6)!!\,\zeta^2$	$-10\,(2l+8)!!\,\zeta^3$
$\nu = 2$	0	0	0	0	$3\,(2l+4)!!$	$15\,(2l+6)!!\,\zeta$

where $k_l(x)$ is the modified spherical Hankel function of the second kind. From these formulas, eqs. (7) and (10)—(12), the fast and efficient computation of the overlap integrals is guaranteed if $|\zeta_j^2 - \zeta_i^2| \geq 1$.

OVERLAP INTEGRALS FOR NEARLY EQUAL SCREENING CONSTANTS

In case that $|\zeta_j^2 - \zeta_i^2|$ is less than unity the application of eq. (12) leads to numerical instabilities. This can be avoided in the usual way by downward recursion from a certain n_{max}; however, in unfavourable cases ($|\zeta_j^2 - \zeta_i^2| \approx 1$) n_{max} may exceed values of larger than 100, making this procedure rather time consuming. This difficulty can be overcome in the following way. Let be without loss of generality $\zeta_j \geq \zeta_i$, i. e. $\zeta_i = \zeta_j - \varepsilon$ ($\varepsilon \geq 0$); then

$$(k^2 + \zeta_i^2)^n = (k^2 + (\zeta_j - \varepsilon)^2)^n = (k^2 + \zeta_j^2)^n \left(1 - \frac{\zeta_j^2 - \zeta_i^2}{k^2 + \zeta_j^2}\right)^n \tag{13}$$

Substituting this expression into the formula (9) for the W-coefficients, we obtain the series expansion

$$W_{nn'}^{l\lambda}(\zeta_i\,\zeta_j; R) = (2/\pi) \int_0^\infty dk \frac{k^{l+2\lambda} j_l(kR)}{(k^2 + \zeta_j^2)^{n+n'}} \left(1 - \frac{\zeta_j^2 - \zeta_i^2}{k^2 + \zeta_j^2}\right)^{-n}$$

$$= (2/\pi) \sum_{\mu=0}^{\infty} \binom{n-1+\mu}{n-1} (\zeta_j^2 - \zeta_i^2)^\mu \int_0^\infty \frac{k^{l+2\lambda} j_l(kR)\, dk}{(k^2 + \zeta_j^2)^{n+n'+\mu}}$$

$$= \sum_{\mu=0}^{\infty} W_{0,\, n+n'+\mu}^{l\lambda} \binom{n-1+\mu}{n-1} (\xi_j^2 - \zeta_i^2)^\mu \tag{14}$$

which is convergent for all k since $\zeta_j \geq \zeta_i$. For $\lambda = 1$ we can use eq. (10) to express W by Hankelfunctions ($\hat{n} = n + n' + 1$)

$$W_{nn'}^{l1} = (R/2\zeta_j)^{\hat{n}}\, \zeta_j^{l+1} \sum_{\mu=0}^{\infty} (1 - (\zeta_i/\zeta_j)^2)^\mu/\mu!\; (\zeta_j R/2)^\mu \frac{(n-1+\mu)!}{(n-1)!} \frac{k_{\hat{n}+\mu-l-1}(\zeta_j R)}{(\hat{n}+\mu)!} \tag{15}$$

In the special case $\zeta_i = \zeta_j = \zeta$ only the first term of the series survives yielding the simple result

$$W_{nn'}^{l1} = (R/2\zeta)^{\hat{n}}\, \zeta^{l+1}\, k_{\hat{n}-l-1}(\zeta R)/\hat{n}! \tag{16}$$

which can be used together with eq. (11) to calculate all the W-coefficients as will be shown in the next section. The main advantage of the series expansion (14), however, consists of the possibility of computing the overlap integrals fast and accurate when $0 < |\zeta_j^2 - \zeta_i^2| \leq 1$. For even in the unfavourable case $|\zeta_j^2 - \zeta_i^2| \approx 1$ only ten to fifteen terms are necessary to achieve an accuracy of ten significant figures. We have compared the computation time for this procedure with the single-center expansion method used previously by us[6] and found the former one to be more than four times faster.

APPLICATIONS AND CONCLUSION

A simple procedure for calculating overlap integrals between two Slater orbitals with nearly equal exponents has been described. Unlike the known standard methods no numerical instabilities occur, the integrals can be generated easily by a computer program without the need of additional storage space for any coefficients, and no restrictions exist with regard to the quantum numbers n, l, m. In the case of equal exponents the expressions become particularly simple. Therefore, the present analysis is of interest in view of the role which overlap integrals play in semiempirical theories of chemical bonding as Extended Hückel[7] or maximum overlap methods[8] where for qualitative discussions simple analytic formulas for overlap integrals and their derivatives[9] are useful which can be derived from eq. (4) choosing without loss of generality R parallel to the z-axis:

$$S_{ij}^{\mu\nu} = \sum_{L} [4\pi (-1)^{(l+l_i-l_j)} (2l+1)]^{1/2} G_{l0}(l_i m, l_j m) A_l(n_i l_i, n_j l_j; R) \tag{17}$$

With the appropriate values for the Gaunt integrals[10] one obtains:

$$(n_i s, n_j s; \sigma) = A_0(n_i 0, n_j 0; R)$$

$$\left.\begin{aligned}(n_i p, n_j p; \sigma) &= \\ (n_i p, n_j p; \pi) &= \end{aligned}\right\} A_0(n_i 1, n_j 1; R) - A_2(n_i 1, n_j 1; R) * \begin{Bmatrix} 2 \\ -1 \end{Bmatrix}$$

$$(n_i s, n_j p; \sigma) = 3\, A_1(n_i 0, n_j 1; R)$$

$$\left.\begin{aligned}(n_i d, n_j d; \sigma) &= \\ (n_i d, n_j d; \pi) &= \\ (n_i d, n_j d; \delta) &= \end{aligned}\right\} A_0(n_i 2, n_j 2; R) - 5/7\, A_2(n_i 2, n_j 2; R) * \begin{Bmatrix} 2 \\ 1 \\ -2 \end{Bmatrix} + 3/7\, A_4(n_i 2, n_j 2; R) * \begin{Bmatrix} 6 \\ -4 \\ 1 \end{Bmatrix}$$

$$(n_i s, n_j d; \sigma) = 5\, A_2(n_i 0, n_j 2; R)$$

$$\left.\begin{aligned}(n_i p, n_j d; \sigma) &= \\ (n_i p, n_j d; \pi) &= \end{aligned}\right\} 3/\sqrt{5}\, A_1(n_i 1, n_j 2; R) * \begin{Bmatrix} 2/\sqrt{3} \\ 1 \end{Bmatrix} - 3/\sqrt{5}\, A_3(n_i 1, n_j 2; R) * \begin{Bmatrix} \sqrt{3} \\ -1 \end{Bmatrix}$$

The $A_l(n_i l_i, n_j l_j; R)$ are easily calculated using eqs. (11) and (16) together with table I yielding the following results ($x = \zeta R$):

$$(1s, 1s; \sigma) = \frac{x^3}{3} k_2(x)$$

$$(2s, 2s; \sigma) = \frac{x^3}{9} [k_2(x) - x\, k_3(x) + \frac{x^2}{5} k_4(x)]$$

$$(3s, 3s; \sigma) = \frac{2x^5}{75} [k_4(x) - \frac{x}{3} k_5(x) + \frac{x^2}{42} k_6(x)]$$

$$(4s, 4s; \sigma) = \frac{x^5}{525} [k_4(x) - 2x\, k_5(x) + \frac{22}{21} x^2 k_6(x) - \frac{x^3}{7} k_7(x) + \frac{x^4}{189} k_8(x)]$$

$$(2p, 2p; \pi) = \frac{x^4}{15} k_3(x)$$

$$(2p, 2p; \sigma) = \frac{x^4}{15} [k_3(x) - x\, k_2(x)]$$

$$(3p, 3p; \pi) = \frac{2x^4}{225} [k_3(x) - x\, k_4(x) + \frac{3x^2}{14} k_5(x)]$$

$$(3p, 3p; \sigma) = (3p, 3p; \pi) - \frac{2x^5}{225} [k_2 (x) - x\, k_3 (x) + \frac{3x^2}{14} k_4 (x)]$$

$$(3d, 3d; \delta) = \frac{x^5}{105} k_4 (x)$$

$$(3d, 3d; \pi) = \frac{x^5}{105} [k_4 (x) - x \cdot k_3 (x)]$$

$$(3d, 3d, \sigma) = \frac{x^5}{105} [k_4 (x) - \frac{4}{3} x \cdot k_3 (x) + \frac{x^2}{3} k_2 (x)]$$

All overlap integrals with equal exponents are thus reduced to simple sums of Hankel functions of the second kind defined by the recurrence relations

$$k_{l+1} (x) = \frac{2l + 1}{x} k_l (x) + k_{l-1} (x)$$

$$k_0 (x) = e^{-x}/x; \quad k_1 (x) = (\frac{1}{x} + \frac{1}{x^2}) e^{-x}$$

Moreover, if both exponents are not too much different it is possible to evaluate the overlap integral to a good approximation by taking $\zeta_i = \zeta_j = (\zeta_i + \zeta_j)/2$.

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SAŽETAK

Računanje integrala prekrivanja Slaterovih orbitala s gotovo jednakim eksponentima

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Dobiveni su jednostavni analitički izrazi za računanje integrala prekrivanja Slaterovih orbitala s jednakim eksponentima. Ako se eksponenti međusobno malo razlikuju integrali se računaju s pomoću prikladnog razvoja u red. Prednost postupka sastoji se u tome da nema numeričkih nestabilnosti, koje se ponekad pojavljuju pri primjeni dosadašnjih metoda.