Expansion of Slater-type orbitals about a new origin and analytical evaluation of multicenter electron-repulsion integrals

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A general version of the formulas given by the author for the expansion of Slater-type orbitals (STO) in terms of STO's at a new origin is derived. By the use of these formulas multicenter electron-repulsion integrals are evaluated analytically. The final results are expressed in terms of both the overlap integrals and the usual A and B functions.

In a previous paper we presented a particular method for obtaining the expansions of Slater-type orbitals (STO's) with the screening parameter ζ in terms of STO's with the same ζ at a new origin which has been utilized for the evaluation of molecular three- and four-center two-electron integrals.[1] In this note we wish to give more general formulas, based on our treatment of the expansion problem, and to establish simpler expressions for the multicenter electron-repulsion integrals, suitable for machine computation.

With the aid of the method set out in our paper,[1] we can easily obtain a more general formula for the expansion of real STO's in terms of STO's at a new origin:

$$X_{nlm}(\zeta;r_a\theta_a\varphi_a)=\sum_{n'=1}^{\infty}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}\sum_{n''=l'+1}^{n'}M_{nlm,n'l'm'}^{n-1,l'}(p,t)\omega_{n'n''}^{l'}X_{n''l'm'}(\zeta';r_b\theta_b\varphi_b)\,, \tag{1}$$

where

$$M_{nlm,n'l'm'}^{n-1,l'}(p,t)=\sum_{n''=l'+1}^{n'}\omega_{n'n''}^{l'}(nlm\,|\,n''l'm')\,. \tag{2}$$

Here $(nlm)\equiv X_{nlm}(\zeta;r_a\theta_a\varphi_a)$ and $(n'l'm')\equiv X_{n'l'm'}(\zeta';r_b\theta_b\varphi_b)$ are real STO's with the screening parameters ζ and ζ', respectively.

Now we can move on to the evaluation of multicenter electron-repulsion integrals over real STO's. For this purpose we use the expansion formula (1) for the Slater-type orbitals X_b, X_c, and X_d which we express through the STO's centered on the nuclear center a. Then we obtain for the four-center electron-repulsion integrals over real STO's the expression in terms of the overlap integrals and the one-center two-electron integrals for $\overline{\zeta}_1=\overline{\zeta}_2$ [see Eq. (2) of Ref. 2]:

$$\begin{aligned}[(n_al_am_a)(n_cl_cm_c)|(n_bl_bm_b)(n_dl_dm_d)]=&\sum_{n_1l_1m_1,n_1'}M_{n_cl_cm_c,n_1l_1m_1}^{n_c-1,l_1}(p_{ca},t_{ca})\omega_{n_1n_1'}^{l_1}\\&\times\sum_{n_2l_2m_2,n_2'}M_{n_bl_bm_b,n_2l_2m_2}^{n_b-1,l_2}(p_{ba},t_{ba})\omega_{n_2n_2'}^{l_2}\\&\times\sum_{n_3l_3m_3,n_3'}M_{n_dl_dm_d,n_3l_3m_3}^{n_d-1,l_3}(p_{da},t_{da})\omega_{n_3n_3'}^{l_3}\cdot 2\overline{\zeta}_2N_{n_an_1'}(1,t_1)N_{n_2'n_3'}(1,t_2)\\&\times[(n_al_am_a)(n_1'l_1m_1)|(n_2'l_2m_2)(n_3'l_3m_3)]'\,,\end{aligned} \tag{3}$$

where $(n_i'l_im_i)\equiv X_{n_ial_iam_ia}'(\zeta_{ia};r_a\theta_a\varphi_a)$. In Eq. (3) one of the screening parameters of STO's at the new origin (ζ_{1a}, ζ_{2a}, and ζ_{3a}) must be calculated from the relation $\zeta_a+\zeta_{1a}=\zeta_{2a}+\zeta_{3a}$ and

$$\begin{aligned}[(n_1l_1m_1)(n_1'l_1'm_1')|(n_2l_2m_2)(n_2'l_2'm_2')]'=&\sum_{LM}C^{L\,|M|}(l_1m_1,l_1'm_1')\\&\times C^{L\,|M|}(l_2m_2,l_2'm_2')A_{m_1m_1'}^{M}A_{m_2m_2'}^{M}f^{L}(n_1+n_1'-1,n_2+n_2'-1)\,,\end{aligned} \tag{4}$$

where

$$f^{L}(N_1,N_2)=(N_1+L+1)!\,(N_2-L)!\left[1-\sum_{S=0}^{N_1+L}(0.5)^{N_2-L+1+S}\gamma_S^L(N_1)(N_2-L+S)!\,\Big/(N_2-L)!\right]. \tag{5}$$

Let us now consider the expressions for the expansion of complex STO's about a point displaced from

TABLE I. Three-center methane integrals and their convergence as a function of number of summation terms.

Integral	Number of terms 3×12	6×12	9×12	12×12	Comparison values
$h_1h_1;h_2h_3$	0.109 820 92	0.095 050 46	0.095 624 24	0.095 704 85	
$cc;h_1h_2$	0.155 592 10	0.165 250 70	0.166 270 67	0.166 535 83	
$xc;h_1h_2$	0.001 593 37	0.002 394 04	0.002 359 19	0.002 370 19	0.002 370 04
$zc;h_1h_2$	−0.003 416 79	−0.001 684 82	−0.001 678 80	−0.001 675 18	−0.001 675 81
$xx;h_1h_2$	0.112 465 20	0.122 875 76	0.141 889 46	0.141 922 71	0.141 922
$xz;h_1h_2$	−0.000 945 34	−0.001 389 32	−0.001 413 29	−0.001 435 79	−0.001 435 79
$yy;h_1h_2$	0.109 318 98	0.121 171 34	0.136 218 29	0.136 758 18	0.136 758
$zz;h_1h_2$	0.155 425 32	0.128 093 28	0.139 653 61	0.140 911 77	0.140 912
$h_1h_2;h_1h_3$	0.036 005 44	0.035 669 60	0.035 688 89	0.035 693 39	
$ch_1;ch_2$	0.006 612 75	0.011 608 03	0.011 316 92	0.011 128 72	
$ch_1;xh_2$	0.013 545 75	0.020 296 13	0.020 039 37	0.019 804 02	0.019 809 03
$ch_1;zh_2$	0.002 484 28	0.006 459 78	0.006 000 26	0.005 884 71	0.005 885 22
$xh_1;xh_2$	0.038 344 59	0.034 939 86	0.035 607 03	0.035 568 51	0.035 568 58
$xh_1;zh_2$	0.000 682 30	0.001 399 16	0.001 500 91	0.001 489 06	0.001 489 40
$yh_1;yh_2$	0.016 963 86	0.019 220 94	0.022 171 74	0.022 318 98	0.022 319 59

the orbital's center. Carrying through calculations for the case of complex STO's analogous to those for real STO's, we obtain

$$\varphi_{nlm}(\zeta;r_a\theta_a\varphi_a)=\sum_{n'=1}^{\infty}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}\sum_{n''=l'+1}^{n'}L^{n-1,l'}_{nlm,n'l'm'}(p,t)\omega^{l'}_{n'n''}\varphi_{n''l'm'}(\zeta';r_b\theta_b\varphi_b), \tag{6}$$

where

$$L^{n-1,l'*}_{nlm,n'l'm'}(p,t)=\sum_{n''=l'+1}^{n'}\omega^{l'}_{n'n''}(\{nlm\}^*|\{n''l'm'\}). \tag{7}$$

We notice that the overlap integrals on the right-hand sides of Eqs. (2) and (7) can be determined by the formulas of our previous works [see Eqs. (16), (21), (22) of Ref. 1 and Eqs. (14) and (15) of Ref. 3].

When one takes Eq. (6) into account, it is easy to establish for the multicenter electron-repulsion integrals over complex STO's the following expression:

$$\begin{aligned}(\{n_al_am_a\}^*\{n_cl_cm_c\}|\{n_bl_bm_b\}\{n_dl_dm_d\}^*)&=\sum_{n_1l_1m_1,n'_1}L^{n_c-1,l_1}_{n_cl_cm_c,n_1l_1m_1}(p_{ca},t_{ca})\omega^{l_1}_{n_1n'_1}\\&\times\sum_{n_2l_2m_2,n'_2}L^{n_b-1,l_2}_{n_bl_bm_b,n_2l_2m_2}(p_{ba},t_{ba})\omega^{l_2}_{n_2n'_2}\\&\times\sum_{n_3l_3m_3,n'_3}L^{n_d-1,l_3*}_{n_dl_dm_d,n_3l_3m_3}(p_{da},t_{da})\omega^{l_3}_{n_3n'_3}\\&\times 2\xi_2N_{n_an'_1}(1,t_1)N_{n'_2n'_3}(1,t_2)(\{n_al_am_a\}^*\{n'_1l_1m_1\}|\{n'_2l_2m_2\}\{n'_3l_3m_3\}^*)',\end{aligned} \tag{8}$$

where $(\{n_1l_1m_1\}^*\{n'_1l'_1m'_1\}|\{n_2l_2m_2\}\{n'_2l'_2m'_2\}^*)'$ can be calculated from Eq. (4) for $A^M_{m_1m'_1}\to\delta_{M,m_1-m'_1}$ and $A^M_{m_2m'_2}\to\delta_{M,m_2-m'_2}$.

It should be noted that for the evaluation of two- and three-center electron-repulsion integrals we can also use Eqs. (3) and (8). For this purpose we must go to the limit in Eqs. (3) and (8) for $R_{ka}\to 0$ and replace the quantities $M^{n_k-1,l_i}_{n_kl_km_k,n_il_im_i}(0,t_{ka})$ and $L^{n_k-1,l_i}_{n_kl_km_k,n_il_im_i}(0,t_{ka})$ by the Kronecker symbols, where $k=b,c,d$.

From Eqs. (2)–(5), (7), and (8) and the above-mentioned formulas of Ref. 1 and 3 it can be seen that the multicenter electron-repulsion integrals over STO's are expressed through the overlap integrals or the well-known auxiliary functions A_k and B_k. It should be noted that formulas (3) and (8) contain quantities $C^{L|M|}(lm,l'm')$, $f^L(N_1,N_2)$, and $\omega^l_{nn'}$ (independent of the screening parameters and the coordinates of nuclei) which can be calculated once and for all, thereby making the evaluation of

multicenter electron-repulsion integrals for large-scale quantum-mechanical calculation economical.

Since the author is inexperienced in efficient programming, it is difficult to make a general statement on the practicableness of the proposed method. It is, however, possible to test the convergence of the expansions (1) and (6) by calculating concrete cases. The results of tests on expansion accuracy are given in Table I for several three-center methane integrals which contains two infinite summations. The last column gives the comparison values of the integrals contained in Ref. 4. As we see from the table, the accuracy was assessed by increasing the number of terms taken in the infinite summations. An overall accuracy of between 10^{-5} and 10^{-6} hartree was sought for 12×12 terms. Greater accuracy is easily attainable by the use of more terms of the expansion.

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