Expansion of Slater-type orbitals about a displaced center and the evaluation of multicenter electron-repulsion integrals

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A simpler version of the formulas given by the author for the expansion of Slater-type orbitals (STO's) about a point displaced from the orbital center is derived. By utilizing these formulas, extremely compact analytical expressions are established for multicenter electron-repulsion integrals over STO's. The final results are of a simple structure and are, therefore, especially useful for machine computations.

In previous publications[1,2] we have presented a particular method for obtaining the expansions of Slater-type orbitals (STO's) about a new origin which has been utilized for the evaluation of three- and four-center electron-repulsion integrals. The aim of this paper is to present simpler formulas for the expansion of STO's in terms of STO's at a displaced center by means of which all multicenter electron-repulsion integrals are evaluated analytically.

For the calculation of the multicenter electron-repulsion integrals

$$[(n_a l_a m_a)(n_b l_b m_b) \mid (n_c l_c m_c)(n_d l_d m_d)]$$
$$=[(2n_a)!(2n_b)!(2n_c)!(2n_d)!]^{-1/2}[(\overline{n_a l_a m_a})(\overline{n_b l_b m_b}) \mid (\overline{n_c l_c m_c})(\overline{n_d l_d m_d})] \tag{1}$$

$$(\{n_a l_a m_a\}^*\{n_b l_b m_b\} \mid \{n_c l_c m_c\}\{n_d l_d m_d\}^*)$$
$$=[(2n_a)!(2n_b)!(2n_c)!(2n_d)!]^{-1/2}(\{\overline{n_a l_a m_a}\}^*\{\overline{n_b l_b m_b}\} \mid \{\overline{n_c l_c m_c}\}\{\overline{n_d l_d m_d}\}^*) \tag{2}$$

we shall require formulas for the expansions of unnormalized STO's determined by

$$(\overline{nlm}) \equiv \overline{\chi}_{nlm}(\zeta,r\theta\varphi)=\sqrt{(2n)!}\chi_{nlm}(\zeta,r\theta\varphi) , \tag{3}$$

$$\{\overline{nlm}\} \equiv \overline{\varphi}_{nlm}(\zeta,r\theta\varphi)=\sqrt{(2n)!}\varphi_{nlm}(\zeta,r\theta\varphi) , \tag{4}$$

where $(nlm) \equiv \chi_{nlm}(\zeta,r\theta\varphi)$ and $\{nlm\} \equiv \varphi_{nlm}(\zeta,r\theta\varphi)$ are normalized real and complex STO's, respectively.

The formulas for the expansions of STO's about a displaced center we wish to establish are

$$\overline{\chi}_{nlm}(\zeta,r_a\theta_a\varphi_a)=\lim_{N\to\infty}\sum_{n'=1}^{N}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'} V_{nlm,n'l'm'}^{N}(\mathbf{p}_{ab},t)\overline{\chi}_{n'l'm'}(\zeta',r_b\theta_b\varphi_b) , \tag{5}$$

$$\overline{\varphi}_{nlm}(\zeta,r_a\theta_a\varphi_a)=\lim_{N\to\infty}\sum_{n'=1}^{N}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'} W_{nlm,n'l'm'}^{N}(\mathbf{p}_{ab},t)\overline{\varphi}_{n'l'm'}(\zeta',r_b\theta_b\varphi_b) , \tag{6}$$

where $\mathbf{p}_{ab}=\frac{1}{2}(\zeta+\zeta')\mathbf{R}_{ab}$, $t=(\zeta-\zeta')/(\zeta+\zeta')$, and

$$V_{nlm,n'l'm'}^{N}(\mathbf{p},t)=\sum_{n''=l'+1}^{N}\Omega_{n'n''}^{l'}(N)[(\overline{nlm}) \mid (\overline{n''l'm'})] , \tag{7}$$

$$W_{nlm,n'l'm'}^{*N}(\mathbf{p},t)=\sum_{n''=l'+1}^{N}\Omega_{n'n''}^{l'}(N)(\{\overline{nlm}\}^* \mid \{\overline{n''l'm'}\}) , \tag{8}$$

$$\Omega_{nn'}^{l}(N)=\frac{(-1)^{n+n'}}{(n+l+1)!(n-l-1)!(n'+l+1)!(n'-l-1)!}\sum_{n''=\max(n,n')}^{N}\frac{(n''+l+1)!(n''-l-1)!}{(n''-n)!(n''-n')!} . \tag{9}$$

Here,

$$[(\overline{nlm})\,|\,(\overline{n'l'm'})] = \int \overline{\chi}_{nlm}(\zeta,r_a\theta_a\varphi_a)\overline{\chi}_{n'l'm'}(\zeta',r_b\theta_b\varphi_b)dv \;, \quad (10)$$

$$(\{\overline{nlm}\}^*\,|\,\{\overline{n'l'm'}\}) = \int \overline{\varphi}^*_{nlm}(\zeta,r_a\theta_a\varphi_a)\overline{\varphi}_{n'l'm'}(\zeta',r_b\theta_b\varphi_b)dv \quad (11)$$

are the overlap integrals with un-normalized STO's. It should be noted that for $R_{ab}=0$ and $t=0$ the expansion coefficients $V^N_{nlm,n'l'm'}$ and $W^N_{nlm,n'l'm'}$ are reduced to the Kronecker symbols, i.e.,

$$V^N_{nlm,n'l'm'}(0,0)=W^N_{nlm,n'l'm'}(0,0) =\delta_{nn'}\delta_{ll'}\delta_{mm'} \;. \quad (12)$$

The formulas (5) and (6) are simpler than our earlier expressions [see Eqs. (1) and (6) of Ref. 2]: there the use of the quantity $\Omega^l_{nn'}$ of Eq. (9) replaces one summation in Eqs. (1) and (6) of Ref. 2.

For the derivation of Eqs. (5)–(9) we have taken, in Eqs. (1) and (6) of Ref. 2, the following relationships into account:

$$\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} a^{R,C}_{nlm}\Psi^{R,C}_{nlm}(\zeta,r\theta\varphi) = \sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\left[\sum_{n'=n}^{N}\omega^l_{n'n}a^{R,C}_{n'lm}\right]\Phi^{R,C}_{nlm}(\zeta,r\theta\varphi) \quad (13)$$

$$\sum_{n'=n}^{N}\omega^l_{n'n}\Psi^{R,C}_{n'lm}(\zeta,r\theta\varphi) = \sum_{n'=l+1}^{N}\left[\sum_{n''=\max(n,n')}^{N}\omega^l_{n''n}\omega^l_{n''n'}\right]\Phi^{R,C}_{n'lm}(\zeta,r\theta\varphi) \;, \quad (14)$$

where $a^R_{n'l'm'}=M_{nlm,n'l'm'}(\mathbf{p},t)$, $a^C_{n'l'm'}=L_{nlm,n'l'm'}(\mathbf{p},t)$; $\Psi^{R,C}_{nlm}$ and $\Phi^{R,C}_{nlm}$ are real or complex wave functions with constant exponent and STO's, respectively.

The calculation of multicenter electron-repulsion integrals over STO's on a computer shows that, for the case of expansions of STO's with the screening parameter ζ in terms of STO's with the same ζ at a new origin, convergence of series is rapid. Therefore, with the analytical evaluation of integrals (1) and (2) we use the expansion formulas (5) and (6) for $\zeta=\zeta'$. Then expanding the STO's $\overline{\chi}_\kappa$ and $\overline{\varphi}_\kappa$ ($\kappa=b,c,d$) in Eqs. (1) and (2) in terms of the STO's centered on the nuclear a, we obtain for the four-center integrals the following expressions: for real STO's

$$[(\overline{n_al_am_a})(\overline{n_bl_bm_b})\,|\,(\overline{n_cl_cm_c})(\overline{n_dl_dm_d})] = \sum_{n_1=1}^{N}\sum_{l_1=0}^{n_1-1}\sum_{m_1=-l_1}^{l_1} V^N_{n_bl_bm_b,n_1l_1m_1}(\mathbf{p}_{ba})\sum_{n_2=1}^{N}\sum_{l_2=0}^{n_2-1}\sum_{m_2=-l_2}^{l_2} V^N_{n_cl_cm_c,n_2l_2m_2}(\mathbf{p}_{ca}) \times\sum_{n_3=1}^{N}\sum_{l_3=0}^{n_3-1}\sum_{m_3=-l_3}^{l_3} V^N_{n_dl_dm_d,n_3l_3m_3}(\mathbf{p}_{da}) \times[(\overline{n_al_am_a})(\overline{n_1l_1m_1})\,|\,(\overline{n_2l_2m_2})(\overline{n_3l_3m_3})] \;, \quad (15)$$

for complex STO's

$$(\{\overline{n_al_am_a}\}^*\{\overline{n_bl_bm_b}\}\,|\,\{\overline{n_cl_cm_c}\}\{\overline{n_dl_dm_d}\}^*) = \sum_{n_1=1}^{N}\sum_{l_1=0}^{n_1-1}\sum_{m_1=-l_1}^{l_1} W^N_{n_bl_bm_b,n_1l_1m_1}(\mathbf{p}_{ba}) \times\sum_{n_2=1}^{N}\sum_{l_2=0}^{n_2-1}\sum_{m_2=-l_2}^{l_2} W^N_{n_cl_cm_c,n_2l_2m_2}(\mathbf{p}_{ca}) \times\sum_{n_3=1}^{N}\sum_{l_3=0}^{n_3-1}\sum_{m_3=-l_3}^{l_3} W^N_{n_dl_dm_d,n_3l_3m_3}(\mathbf{p}_{da}) \times(\{\overline{n_al_am_a}\}^*\{\overline{n_1l_1m_1}\}\,|\,\{\overline{n_2l_2m_2}\}\{\overline{n_3l_3m_3}\}^*) \;, \quad (16)$$

where N is number of summation terms and

$$V^N_{nlm,n'l'm'}(\mathbf{p}) \equiv V^N_{nlm,n'l'm'}(\mathbf{p},0) ,$$

$$W^N_{nlm,n'l'm'}(\mathbf{p}) \equiv W^N_{nlm,n'l'm'}(\mathbf{p},0) ,$$

$$\zeta_1=\zeta_b , \quad \zeta_2=\zeta_c , \quad \zeta_3=\zeta_d ,$$

$$\mathbf{P}_{\kappa a}=\zeta_\kappa \mathbf{R}_{\kappa a} \quad (\kappa=b,c,d) .$$

From Eqs. (15) and (16), it can be seen that the four-center integrals for STO's are expressed through the two-center overlap and one-center Coulomb integrals for which the analytical formulas have been established in our previous works.[3,4] We notice that all the two- and three-center electron-repulsion integrals over STO's can also be calculated from the formulas of four-center integrals. For this purpose we must go to the limit in Eqs. (15) and (16) for $R_{ba} \rightarrow 0$, $R_{ca} \rightarrow 0$, or $R_{da} \rightarrow 0$ and use the relation (12).

It should be noted that with the evaluation of multi-center integrals for the linear molecules it will be convenient to use the coordinate systems the polar axes of which are placed along the line joining the centers. In this case the summations over m_1, m_2, and m_3 in Eqs. (15) and (16) must be replaced by the Kronecker symbols $\delta_{m_b m_1}$, $\delta_{m_c m_2}$, and $\delta_{m_d m_3}$.

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