Unified analytical treatment of one- and two-electron multicenter integrals with Slater-type orbitals

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With the use of formulas given by the author for the expansion of Slater-type orbitals (STO's) in terms of STO's at a new origin [I.I. Guseinov, Phys. Rev. A **31**, 2851 (1985)], one- and two-electron multicenter integrals of $r^{\mu-1}e^{-\kappa r}S_{\nu\sigma}(\theta,\varphi)$ for $q=R$ and $r^{\mu-1}e^{-\kappa r}Y_{\nu\sigma}(\theta,\varphi)$ for $q=C$ are expressed in terms of the overlap integrals. The analytical formulas used for the evaluation of these integrals have recently been established by the author [I.I. Guseinov, J. Mol. Sci. (China), **5** (2) (1987)]. The relationships obtained are valid for general values of the STO parameters and for $\mu\geq-(\nu+1)$ and $\kappa\geq 0$.

The theoretical prediction of some one- and two-electron molecular properties requires computation of multicenter integrals of

$$f^q_{\mu\nu\sigma}(\kappa,\mathbf{r})=\mathbf{r}^{\mu-1}e^{-\kappa r}\begin{cases}S_{\nu\sigma}(\theta,\varphi) & \text{for } q=R\ ,\\ Y_{\nu\sigma}(\theta,\varphi) & \text{for } q=C\ ,\end{cases} \tag{1}$$

where $\mu\geq-(\nu+1)$ and $\kappa\geq0$; the quantities $S_{\nu\sigma}(\theta,\varphi)$ and $Y_{\nu\sigma}(\theta,\varphi)$ are the real and complex harmonics, respectively. Results for two- and three-center one-electron integrals over complex Slater-type orbitals (STO's) of this type for $\kappa=0$ have been given previously.[1] The aim of this note is to express all multicenter one- and two-electron integrals of $f^q_{\mu\nu\sigma}(\kappa,\mathbf{r})$ in terms of the overlap integrals over STO's.

The one- and two-electron multicenter integrals over unnormalized real (for $q=R$) and complex (for $q=C$) STO's examined in the present work have the following form:

$$\bar{U}^q_{abc}=\int [\bar{\chi}^q_{n_al_am_a}(\xi_a,\mathbf{r}_{a1})]^* f^q_{\mu\nu\sigma}(\kappa,\mathbf{r}_{B1})\times\chi^q_{n_cl_cm_c}(\xi_c,\mathbf{r}_{c1})dv_1\ , \tag{2}$$

$$\bar{I}^q_{acdb}=\int\int [\bar{\chi}^q_{n_al_am_a}(\xi_a,\mathbf{r}_{a1})]^*\bar{\chi}^q_{n_cl_cm_c}(\xi_c,\mathbf{r}_{c1})\times f^q_{\mu\nu\sigma}(\kappa,\mathbf{r}_{21})\bar{\chi}^q_{n_dl_dm_d}(\xi_d,\mathbf{r}_{d2})\times[\bar{\chi}^q_{n_bl_bm_b}(\xi_b,\mathbf{r}_{b2})]^* dv_1dv_2\ , \tag{3}$$

where $\mathbf{r}_{kj}=\mathbf{r}_{aj}-\mathbf{R}_{ak}$ and $\mathbf{r}_{21}=\mathbf{r}_{a1}-\mathbf{r}_{a2}$ ($j=1,2$ and $k=b,c,d$). Here $\bar{\chi}^R_{nlm}(\xi,\mathbf{r})=R_n(\xi,r)S_{lm}(\theta,\varphi)$ and $\chi^C_{nlm}(\xi,\mathbf{r})R_n(\xi,r)Y_{lm}(\theta,\varphi)$ are unnormalized real and complex STO's, where $R_n(\xi,r)=(2\xi)^{n+1/2}r^{n-1}e^{-\xi r}$.

To calculate the integrals (2) and (3), we use the translation formulas (5) and (6) of Ref. 2 for the STO's $\bar{\chi}^q_c$ and $\bar{\chi}^q_d$. Then we can express any multicenter one-electron integral in terms of a two-center nuclear attraction integral, and any multicenter two-electron integral in terms of either a one-center Coulomb or a two-center Coulomb and a two-center hybrid integral,

$$\bar{U}^q=\int [\bar{\chi}^q_{n_al_am_a}(\xi_a,\mathbf{r}_{a1})]^*\bar{\chi}^q_{n'_al'_am'_a}(\xi'_a,\mathbf{r}_{a1})\times f^q_{\mu\nu\sigma}(\kappa,\mathbf{r}_{b1})dv_1\ , \tag{4}$$

$$\bar{I}^q_i=\int\int [\bar{\chi}^q_{n_al_am_a}(\xi_a,\mathbf{r}_{a1})]^*\bar{\chi}^q_{n'_al'_am'_a}(\xi'_a,\mathbf{r}_{a1})\times f^q_{\mu\nu\sigma}(\kappa,\mathbf{r}_{21})\bar{\chi}^q_{n_il_im_i}(\xi_i,\mathbf{r}_{i2})\times[\bar{\chi}^q_{n_bl_bm_b}(\xi_b,\mathbf{r}_{b2})]^* dv_1dv_2\ . \tag{5}$$

We denote in Eq. (5) the center a and b by the symbols $i=+$ and $-$, respectively. It is easy to show that the combined equation (5) represents both the one- and two-center Coulomb (for $i=-$) and the two-center hybrid (for $i=+$) integrals.

For the calculation of the integrals (4) and (5) we use the expansion formula for the product of two unnormalized STO's both with one and the same center,

$$[\bar{\chi}^q_{n_al_am_a}(\xi_a,\mathbf{r}_{a1})]^*\bar{\chi}^q_{n'_al'_am'_a}(\xi'_a,\mathbf{r}_{a1})=\frac{\xi^{3/2}}{2^{n+1/2}}\beta_{n_an'_a}(t_a)\times\sum_{l,m}\left[\frac{2l+1}{4\pi}\right]^{1/2}C^{l\,|m|}(l_am_a,l'_am'_a)\times A^m_{m_am'_a}[\bar{\chi}^q_{nlm}(\xi,\mathbf{r}_{a1})]^*\quad\text{for } q=R\ , \tag{6}$$

where $\xi=\xi_a+\xi'_a$, $n=n_a+n'_a-1$, $t_a=(\xi_a-\xi'_a)/(\xi_a+\xi'_a)$, and

$$\beta_{nn'}(t)=(1+t)^{n+1/2}(1-t)^{n'+1/2}\ , \tag{7}$$

$$A^M_{mm'}=\frac{1}{\sqrt{2}}(2-|\eta^{m-m'}_{mm'}|)^{1/2}\delta_{m,\epsilon|m-m'|}+\frac{1}{\sqrt{2}}\eta^{m+m'}_{mm'}\delta_{m,\epsilon|m+m'|}\ , \tag{8}$$

$$C^{L\,|M|}(lm,l'm')=\begin{cases}C^L(lm,l'm') & \text{for } M=m-m'\\ C^L(lm,l'-m') & \text{for } M=m+m'\ .\end{cases} \tag{9}$$

Here C^L are the known Gaunt coefficients (See Ref. 3 for the exact definition of ϵ and $\eta_{mm'}^{m\pm m'}$). We notice that for $q=C$ the quantity $A_{m_a m_a'}^{m}$ in Eq. (6) must be replaced by the Kronecker symbol $\delta_{m,m_a-m_a'}$.

Taking into account (6) we can express Eqs. (4) and (5) in terms of the following two-center integrals:

$$\bar{U}_{nlm,\mu\nu\sigma}^{q}(\xi,\kappa,\mathbf{R}_{ab})=\int[\bar{\chi}_{nlm}^{q}(\xi,\mathbf{r}_{a1})]^{*}f_{\mu\nu\sigma}^{q}(\kappa,\mathbf{r}_{b1})dv_1 , \tag{10}$$

$$\bar{I}_{nlm,\mu\nu\sigma;n_il_im_i,n_bl_bm_b}^{q}(\xi,\kappa;\xi_i,\xi_b;\mathbf{R}_{ab})=\int \bar{U}_{nlm,\mu\nu\sigma}^{q}(\xi,\kappa,\mathbf{r}_{a2})\bar{\chi}_{n_il_im_i}^{q}(\xi_i,\mathbf{r}_{i2})\times[\bar{\chi}_{n_bl_bm_b}^{q}(\xi_b,\mathbf{r}_{b2})]^{*}dv_2 . \tag{11}$$

When calculating the two-center nuclear attraction integrals (10), and the Coulomb and hybrid integrals (11) we use the following formula for the one-center expansion of the function $f_{\mu\nu\sigma}^{q}(\kappa,\mathbf{r})$ in terms of the STO's [see Eqs. (5)–(8) of Ref. 2 for $\mathbf{R}_{ab}=0$ and $\mathbf{r}_a=\mathbf{r}_b=\mathbf{r}$]:

$$f_{\mu\nu\sigma}^{q}(\kappa,\mathbf{r})=\lim_{N\to\infty}\sum_{\mu'=\nu+1}^{N}\bar{F}_{\mu\nu,\mu'\nu}^{N}(\xi,t)\bar{\chi}_{\mu'\nu\sigma}^{q}(\xi,\mathbf{r}) , \tag{12}$$

where $\mu\geq-(\nu+1)$, $t=(\xi-\kappa)/(\xi+\kappa)$, and

$$\bar{F}_{\mu\nu,\mu'\nu}^{N}(\xi,t)=\sum_{\mu''=\nu+1}^{N}\Omega_{\mu'\mu''}^{\nu}(N)d_{\mu''\mu}(\xi,t) , \tag{13}$$

$$d_{\mu''\mu}(\xi,t)=\frac{(\mu''+\mu)!(1+t)^{\mu''+\mu+1}}{(2\xi)^{\mu+1/2}} , \tag{14}$$

$$\Omega_{\mu\mu'}^{\nu}(N)=\frac{(-1)^{\mu+\mu'}}{(\mu+\nu+1)!(\mu-\nu-1)!(\mu'+\nu+1)!(\mu'-\nu-1)!}\times\sum_{\mu''=\max(\mu,\mu')}^{N}\frac{(\mu''+\nu+1)!(\mu''-\nu-1)!}{(\mu''-\mu)!(\mu''-\mu')!} . \tag{15}$$

Using Eq. (12) of Ref. 2 we can show that for $\xi=\kappa$ ($t=0$) and $\mu\geq\nu+1$ the expansion coefficient $\bar{F}^N$ is reduced to the Kronecker symbol, i.e.,

$$\bar{F}_{\mu\nu,\mu'\nu}^{N}(\xi,0)=\frac{\delta_{\mu\mu'}}{(2\kappa)^{\mu+1/2}} \quad \text{for } \mu\geq\nu+1 . \tag{16}$$

Substituting (12) into (10) and (11), we obtain

$$\bar{U}_{nlm,\mu\nu\sigma}^{q}(\xi,\kappa;\mathbf{R}_{ab})=\lim_{N\to\infty}\sum_{\mu'=\nu+1}^{N}\bar{F}_{\mu\nu,\mu'\nu}^{N}(\xi,t)\bar{S}_{nlm,\mu'\nu\sigma}^{q}(\xi,\xi;\mathbf{R}_{ab}) , \tag{17}$$

$$\bar{I}_{nlm,\mu\nu\sigma;n_il_im_i,n_bl_bm_b}^{q}(\xi,\kappa;\xi_i,\xi_b;\mathbf{R}_{ab})=\lim_{N\to\infty}\sum_{\mu'=\nu+1}^{N}\bar{F}_{\mu\nu,\mu'\nu}^{N}(\xi,t)\times\bar{J}_{nlm,\mu'\nu\sigma;n_il_im_i,n_bl_bm_b}^{q}(\xi,\xi;\xi_i,\xi_b;\mathbf{R}_{ab}) , \tag{18}$$

where

$$\bar{S}_{nlm,\mu'\nu\sigma}^{q}(\xi,\xi;\mathbf{R}_{ab})=\int[\bar{\chi}_{nlm}^{q}(\xi,\mathbf{r}_{a1})]^{*}\bar{\chi}_{\mu'\nu\sigma}^{q}(\xi,\mathbf{r}_{b1})dv_1 , \tag{19}$$

$$J_{nlm,\mu'\nu\sigma;n_il_im_i,n_bl_bm_b}^{q}(\xi,\xi;\xi_i,\xi_b;\mathbf{R}_{ab})=\int S_{nlm,\mu'\nu\sigma}^{q}(\xi,\xi;\mathbf{r}_{a2})\bar{\chi}_{n_il_im_i}^{q}(\xi_i,\mathbf{r}_{i2})\times[\bar{\chi}_{n_bl_bm_b}^{q}(\xi_b,\mathbf{r}_{b2})]^{*}dv_2 . \tag{20}$$

As can be seen from Eqs. (18)–(20) the quantity $\bar{J}^q$ on the right-hand side of Eq. (18) depends on overlap integrals with the same screening parameters which can be expressed in terms of STO's (Ref. 4),

$$\bar{S}_{nlm,\mu\nu\sigma}^{q}(\xi,\xi;\mathbf{R})=\xi^{-3/2}\sum_{N=1}^{n+\mu+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}\bar{g}_{nlm,\mu\nu\sigma}^{NLM}\bar{\chi}_{NLM}^{q}(\xi,\mathbf{R}) , \tag{21}$$

where

$$\bar{g}_{nlm,\mu\nu\sigma}^{NLM}=\sum_{N'=1}^{n+\mu+1}\Omega_{NN'}^{L}(n+\mu+1)\bar{T}_{nlm,\mu\nu\sigma}^{N'LM} , \tag{22}$$

$$\bar{T}_{nlm,\mu\nu\sigma}^{NLM}=\sqrt{8\pi(2L+1)}C^{L|M|}(lm,\nu\sigma)A_{m\sigma}^{M}l!(n-l)!\mu!(\mu-\nu)!L!(N-L)!\times\sum_{s=0}^{E[(n-l)/2]+E[(\mu-\nu)/2]+E[(N-L)/2]}\sum_{m=0}^{g+1}(-1)^{s+m+1/2(l-\nu-L)}4^{g-m}\times a_s(l+1,n-l;\nu+1,\mu-\nu;L+1,N-L)F_m(g+1,0)F_k(2k-1,0) , \tag{23}$$

$$a_s(\alpha,n;\alpha',n';\alpha'',n'')=\sum_{m=0}^{E(n/2)}a_m(\alpha,n)\sum_{m'=0}^{E(n'/2)}a_{m'}(\alpha',n')a_{s-m-m'}(\alpha'',n'') . \tag{24}$$

Here $F_m(N,0)=N!/m!(N-m)!$, $g=\frac{1}{2}(l+\nu+L)$, $k=n+\mu+N+1-g-s+m$, $E(n/2)=n/2+\frac{1}{4}[(-1)^n-1]$, and $a_s(\alpha,n)=(\alpha-1+n-s)!/s!(\alpha-1)!(n-2s)!$.

Using Eq. (21) we obtain

$$\bar{J}_{nlm,\mu'\nu\sigma;n_il_im_i,n_bl_bm_b}^{q}(\xi,\xi;\xi_i,\xi_b;\mathbf{R}_{ab})=\xi^{-3/2}\sum_{k=1}^{n+\mu'+1}\sum_{s=0}^{k-1}\sum_{\tau=-s}^{s}\bar{g}_{nlm,\mu'\nu\sigma}^{ks\tau}\bar{G}_{ks\tau,n_il_im_i,n_bl_bm_b}^{q}(\xi,\xi_i,\xi_b;\mathbf{R}_{ab}) , \tag{25}$$

where

$$\bar G^q_{ks\tau,n_il_im_i,n_bl_bm_b}(\xi,\xi_i,\xi_b;\mathbf{R}_{ab}) = \int [\bar\chi^q_{ks\tau}(\xi,\mathbf{r}_{a2})]^* \bar\chi^q_{n_il_im_i}(\xi_i,\mathbf{r}_{i2})[\bar\chi^q_{n_bl_bm_b}(\xi_b,\mathbf{r}_{b2})]^* dv_2 \ . \quad (26)$$

Taking into account Eq. (6), it is easy to express the integrals in Eq. (26) in terms of the overlap integrals for $i=-$ and $i=+$, separately. For one- and two-center Coulomb integrals,

$$\bar G^q_{ks\tau,n_-l_-m_-,n_bl_bm_b}(\xi,\xi_-,\xi_b;\mathbf{R}_{ab}) = \frac{\zeta_-^{3/2}}{2^{N_-+1/2}}\beta_{n_-n_b}(t_-)\sum_{L,M}\left[\frac{2L+1}{4\pi}\right]^{1/2} C^{L|M|}(l_-m_-,l_bm_b)A^M_{m_-m_b}\bar S^q_{ks\tau,N_-LM}(\xi,\eta_-;\mathbf{R}_{ab}) \quad \text{for } R_{ab}\geq 0 \ , \quad (27)$$

and for two-center hybrid integrals,

$$\bar G^q_{ks\tau,n_+l_+m_+,n_bl_bm_b}(\xi,\xi_+,\xi_b;\mathbf{R}_{ab}) = \frac{\zeta_+^{3/2}}{2^{N_++1/2}}\beta_{kn_+}(t_+)\sum_{L,M}\left[\frac{2L+1}{4\pi}\right]^{1/2} C^{L|M|}(s\tau,l_+m_+)A^M_{\tau m_+}\bar S^q_{N_+LM,n_bl_bm_b}(\zeta_+,\xi_b;\mathbf{R}_{ab}) \quad \text{for } R_{ab}\geq 0 \ , \quad (28)$$

where

$$\zeta_-=\xi_-+\xi_b,\quad N_-=n_-+n_b-1,\quad t_-=\frac{\xi_--\xi_b}{\xi_-+\xi_b}\ ,$$

$$\zeta_+=\xi+\xi_+,\quad N_+=k+n_+-1,\quad t_+=\frac{\xi-\xi_+}{\xi+\xi_+}\ . \quad (29)$$

From Eqs. (2)–(5) and (17)–(28) it is evident that all one- and two-electron multicenter integrals of $f^q_{\mu\nu\sigma}(\kappa,\mathbf{r})$ are expressed in terms of the overlap integrals.

It should be noted that the formulas just obtained are correct in the case where $\mu=\nu=0$ and $\kappa=0$ $(t=1)$. This enables us to calculate the one- and two-electron multicenter integrals of Hartree-Fock-Roothaan equations.

As can be seen from Eqs. (16)–(18), when the screening parameters of the overlap integrals between the atomic orbitals and the function $f^q_{\mu\nu\sigma}(\kappa,\mathbf{r})$ centered on the nucleus a and b, respectively, are the same $(t=0)$, we obtain a finite sum for integrals $\bar U^q$ and $\bar I^q$ only when $\mu\geq\nu+1$. If the screening parameters are different $(t\neq 0)$ and $\mu\geq-(\nu+1)$ the expressions for two-center one- and two-electron integrals become an infinite series. The calculation of these integrals on a computer shows that for small values of the parameter t the convergence of series is rapid; therefore, it is sufficient to take into account only a few terms in Eqs. (17) and (18). The results of the convergence tests of Eq. (17) for different values of parameter t are shown in Fig. 1 for integral $\bar U^R_{211,32-2}$. Here the quantities $\Delta\bar U^R_N$ are the differences between the values of this integral for $\mu'_{\max}=\infty$ (exact value) and $\mu'_{\max}=N$, where N is the number of summation terms in Eq. (17).

It should be noted that the expressions for two-center one-electron integrals (10) for $\mu\geq\nu+1$ and $\kappa\neq\xi$ can also be obtained from the formulas of overlap integrals of STO's. In this case we utilize the following relationship between the function $f^q_{\mu\nu\sigma}(\kappa,\mathbf{r})$ and the unnormalized STO's:

$$f^q_{\mu\nu\sigma}(\kappa,\mathbf{r})=\frac{1}{(2\kappa)^{\mu+1/2}}\bar\chi^q_{\mu\nu\sigma}(\kappa,\mathbf{r}) \quad \text{for } \mu\geq\nu+1 \ . \quad (30)$$

From Eqs. (10) and (30), and Eq. (8) of Ref. 5, for the overlap integrals it is easy to show that the integrals $\bar U^q$ for $\mu\geq\nu+1$ can be expressed in terms of the two-center overlap integrals in which the factor $\beta_{n\mu}(t)=(1+t)^{n+1/2}(1-t)^{\mu+1/2}$ must be replaced by the factor $d_{n\mu}(\xi,t)/(n+\mu)!$, i.e.,

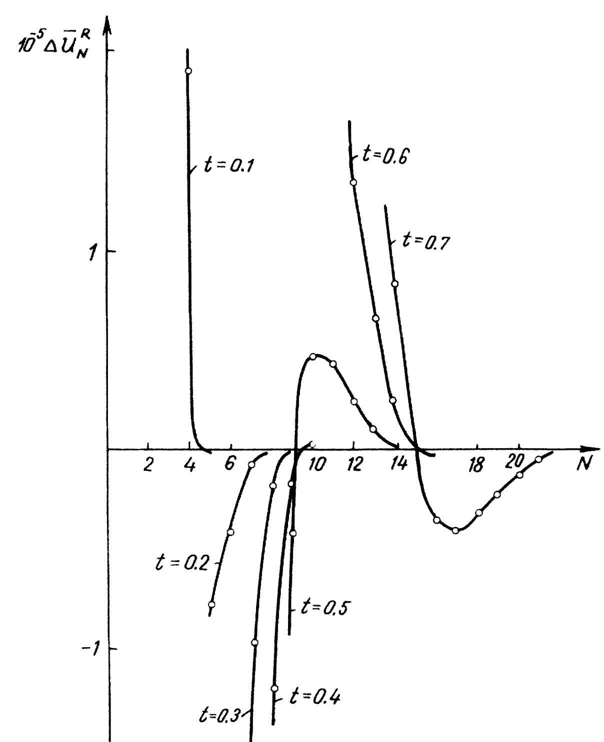

FIG. 1. Convergence of the series in Eq. (17) for different values of parameter t for integral $\bar U^R_{211,32-2}$ as a function of the number of summation terms $(X_a=Y_a=Z_a=0,\ X_b=-Y_b=-Z_b=-1.1547$ a.u.).

$$\bar{U}^q_{nlm,\mu\nu\sigma}(\xi,\kappa;\mathbf{R}_{ab})$$

$$=\bar{S}^q_{nlm},\mu\nu\sigma(\xi,\kappa;\mathbf{R}_{ab}) \quad \text{for } \beta_{n\mu}\rightarrow\frac{d_{n\mu}}{(n+\mu)1} \ . \qquad (31)$$

Here the quantity $d_{n\mu}(\xi,t)$ is defined by Eq. (14) and

$$t=(\xi-\kappa)/(\xi+\kappa).$$

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