Evaluation of two-center overlap and nuclear-attraction integrals for Slater-type orbitals

I. I. Guseinov
Physical Faculty, Azerbaijan State University, 23 Lumumba Street, Baku, U.S.S.R.
(Received 11 February 1985)

General formulas are derived for the two-center overlap and nuclear-attraction integrals with the arbitrary location and screening constants of Slater-type orbitals. The final results are expressed in terms of the spherical harmonics and the usual A_k and B_k functions. Useful formulas have also been established for the radial parts of overlap and nuclear attraction integrals in the form of polynomials in $p=\zeta R$.

The evaluation of two-center overlap and nuclear-attraction integrals between Slater-type orbitals (STO's) is of fundamental importance in the study of molecular systems. These integrals arise not only in their own right, but are also central to the calculation of the multicenter electron-repulsion and three-center nuclear-attraction integrals based on the translation formulas given by the present author for the expansion of STO's about a new center.[1–3] It should be noted that two-center kinetic energy integrals and the integrals of nuclear attraction of type $(a\,|(1/r_b)|\,b)$ can also be expressed by overlap integrals.[4] Although the existing literature (see, e.g., Refs. 4–8 and references quoted in these works) contains a number of formulas, some further procedures for the evaluation of two-center overlap and nuclear-attraction integrals must be sought.

In a previous publication[9] we have presented general expressions for the overlap and nuclear-attraction integrals with respect to the coordinate systems a' and b', the polar axes of which are placed along the line joining the centers a and b. The aim of this Brief Report is to present more simple formulas for the rotation coefficients for the transformations of the two-center overlap and nuclear-attraction integrals from the original systems a and b, the axes of which are parallel to those of the common coordinate system (X,Y,Z), to a'- and b'-oriented systems.

The two-center integrals over STO's examined in this work have the following form: for overlap integrals,

$$\bar{S}^{c}_{nlm,n'l'm'}(\mathbf{p},t)=\int \bar{\phi}^{*}_{nlm}(\zeta,r_a\theta_a\phi_a)\bar{\phi}_{n'l'm'}(\zeta',r_b\theta_b\phi_b)\,dv\ , \tag{1}$$

$$\bar{S}^{R}_{nlm,n'l'm'}(\mathbf{p},t)=\int \bar{\chi}_{nlm}(\zeta,r_a\theta_a\phi_a)\bar{\chi}_{n'l'm'}(\zeta',r_b\theta_b\phi_b)\,dv\ , \tag{2}$$

and for nuclear-attraction integrals,

$$\bar{U}^{c}_{nlm,n'l'm'}(\mathbf{p},t)=\int \bar{\phi}^{*}_{nlm}(\zeta,r_a\theta_a\phi_a)\frac{1}{r_b}\bar{\phi}_{n'l'm'}(\zeta',r_a\theta_a\phi_a)\,dv\ , \tag{3}$$

$$\bar{U}^{R}_{nlm,n'l'm'}(\mathbf{p},t)=\int \bar{\chi}_{nlm}(\zeta,r_a\theta_a\phi_a)\frac{1}{r_b}\bar{\chi}_{n'l'm'}(\zeta',r_a\theta_a\phi_a)\,dv\ . \tag{4}$$

Here $\bar{\phi}_{nlm}=\sqrt{(2n)!}\,\phi_{nlm}$ and $\bar{\chi}_{nlm}=\sqrt{(2n)!}\,\chi_{nlm}$ are unnormalized complex and real STO's relative to a- and b-oriented coordinate systems, $\mathbf{p}=\frac{1}{2}(\zeta+\zeta')\mathbf{R}_{ab}$ and $t=(\zeta-\zeta')/(\zeta+\zeta')$.

The evaluation of the integrals (1)–(4) is conveniently performed by rotation of the axes of a and b to an orientation with polar axes Z_a' and Z_b' along the line joining centers. With the aid of the well-known relationship for rotational transformation of the complex spherical harmonics in terms of the Eulerian angles α, β, and γ (Ref. 10) we can show that the overlap and nuclear-attraction integrals over complex STO's are transformed by the formula

$$\bar{F}^{c}_{nlm,n'l'm'}(\mathbf{p},t)=\sum_{\lambda=0}^{l_-}D^{\lambda}_{lm,l'm'}(\Theta,\Phi)\bar{F}^{c}_{nl\lambda,n'l'\lambda}(p,t)\ , \tag{5}$$

where $\bar{F}^{c}=\bar{S}^{c}$ or $\bar{F}^{c}=\bar{U}^{c}$, l_- is the smaller of l and l', and

$$D^{\lambda}_{lm,l'm'}(\Theta,\Phi)=\frac{1}{1+\delta_{\lambda 0}}[D^{l*}_{m\lambda}(\alpha\beta 0)D^{l'}_{m'\lambda}(\alpha\beta 0)+D^{l*}_{m-\lambda}(\alpha\beta 0)D^{l'}_{m'-\lambda}(\alpha\beta 0)]\ . \tag{6}$$

The spherical angles $\Phi=\alpha$ and $\Theta=-\beta$ of the vector $\mathbf{R}_{ab}$ can be expressed through the coordinates (X_a,Y_a,Z_a) and (X_b,Y_b,Z_b) of the centers relative to a common axial frame, which is the same for all orbitals, by the relationships

$$\tan\Phi=\frac{Y_b-Y_a}{X_b-X_a},\quad \cos\Theta=\frac{Z_b-Z_a}{R_{ab}}\ ,$$
$$R_{ab}=[(X_b-X_a)^2+(Y_b-Y_a)^2+(Z_b-Z_a)^2]^{1/2}\ . \tag{7}$$

The overlap and nuclear-attraction integrals over complex STO's on the right-hand side of Eq. (5) can be expressed through the overlap and nuclear-attraction integrals over real STO's by the formulas [see Eqs. (15) and (21) of Ref. 9]

$$\bar{S}^{c}_{nl\lambda,n'l'\lambda}(p,t)=\bar{S}^{R}_{nl\lambda,n'l'\lambda}(p,t)=(-1)^{l'-\lambda}\bar{N}_{nn'}(p,t)\sum_{\alpha=-\lambda}^{l}\sum_{\beta=\lambda}^{l'}\sum_{q=0}^{\alpha+\beta}g^{q}_{\alpha\beta}(l\lambda,l'\lambda)Q^{q}_{n-\alpha,n'-\beta}(p,t)\ , \tag{8}$$

$$\bar{U}^{c}_{nl\lambda,n'l'\lambda}(p,t)=\bar{U}^{R}_{nl\lambda,n'l'\lambda}(p,t)=\frac{2}{R}N_{nn'}(p,t)\sum_{L}^{l+l'}\sum_{\alpha=0}^{\alpha}\sum_{q=0}^{\alpha}(2L+1)^{1/2}C^{L}(l\lambda,l'\lambda)g^{q}_{\alpha 0}(L0,00)Q^{q}_{n+n'-\alpha-1,0}(p,1)\ , \tag{9}$$

where

$$\bar{N}_{nn'}(p,t)=p^{n+n'+1}(1+t)^{n+1/2}(1-t)^{n'+1/2}$$

and

$$Q^{q}_{NN'}(p,t)=\sum_{m=0}^{N+N'}F_m(N,N')A_{N+N'+q-m}(p)B_{q+m}(pt) \quad . (10)$$

Here, A_K and B_K are the well-known auxiliary functions. [See Ref. 9 for the exact definitions of the quantities appearing in Eqs. (9) and (10).]

It should be mentioned that overlap integrals between STO's with equal screening constants play an important role in our procedure for evaluating multicenter integrals based on the expansion of STO's about a new center.[3] In this case, for the radial part of overlap integrals we can also use, instead of Eq. (8), the following formula in the form of polynomials in the parameters $p=\zeta R$ (where $t=0$):

$$\bar{S}^{R}_{nl\lambda,n'l'\lambda}(p,0)=e^{-p}\sum_{s=0}^{n+n'}a^{s}_{nl\lambda,n'l'\lambda}p^{s} \quad , \qquad (11)$$

where

$$a^{0}_{nl\lambda,n'l'\lambda}=(-1)^{l'-\lambda}(n+n')!\delta_{ll'}$$

and

$$a^{s}_{nl\lambda,n'l'\lambda}=(-1)^{l'-\lambda}(n+n'-s)! \times\sum_{\alpha=-\lambda}^{l}\sum_{\beta=\lambda}^{l'}\sum_{q=0}^{\alpha+\beta}\sum_{k=0}^{n-\alpha+n'-\beta}g^{q}_{\alpha\beta}(l\lambda,l'\lambda)\frac{1}{q+k+1}[1+(-1)^{q+k}] \times F_k(n-\alpha,n'-\beta)F_{s-(\alpha+\beta-q+k)}(n-\alpha+n'-\beta+q-k,0), \ \text{for } s\geqslant 1 \quad . \qquad (12)$$

For the derivation of Eq. (11) we have taken into account in (8) the characteristics of the auxiliary functions A_k and B_k.

In order to obtain the formula for the radial part of nuclear-attraction integrals in the form of polynomials in p we utilize Eq. (1) in Ref. 11 for $\theta_{a2}=\Theta=0$, $\phi_{a2}=\Phi=0$, and $r_{a2}=R_{ab}=R$. Then, using the characteristics of the spherical harmonics, we find, instead of the expression (9), the following formula for the radial part of nuclear-attraction integrals with the arbitrary values of the parameters p and t:

$$\bar{U}^{R}_{nl\lambda,n'l'\lambda}(p,t)=\frac{1}{R}\bar{N}_{nn'}(1,t)\sum_{L}C^{L}(l\lambda,l'\lambda)\frac{(n+n'+L)!}{(2p)^{L}}\left[1-e^{-2p}\sum_{\sigma=0}^{n+n'-1+L}(2p)^{\sigma}\gamma^{L}_{\sigma}(n+n'-1)\right] \quad . \qquad (13)$$

(See Ref. 11 for the exact definition of γ^{L}_{σ}.)

Now we can move on to the calculation of coefficients $D^{\lambda}_{lm,l'm'}$. For this purpose we use in (6) the relation (3.19) of Ref. 10 for the product of two functions $D^{l}_{m\lambda}(\alpha\beta\gamma)$ and the characteristics of the Clebsch-Gordan coefficients. Then we obtain for the rotation coefficients for the transformations of overlap and nuclear-attraction integrals over complex STO's the expression in terms of complex spherical harmonics:

$$D^{\lambda}_{lm,l'm'}(\Theta,\Phi)=\frac{1}{1+\delta_{\lambda 0}}\sum_{L=|l-l'|}^{l+l'}[1+(-1)^{l+l'-L}]C^{ll'L}_{-mm',-m+m'}C^{ll'L}_{-\lambda\lambda 0}\bar{Y}_{L,-m+m'}(\Theta,\Phi) , \qquad (14)$$

where

$$\bar{Y}_{LM}=\left[\frac{4\pi}{2L+1}\right]^{1/2}Y_{LM}$$

and

$$C^{j_1j_2J}_{m_1m_2M}=(-1)^{1/2(|m_1|+m_1+|m_2|+m_2+|M|+M)} \times(j_1j_2m_1m_2|j_1j_2JM) \quad . \qquad (15)$$

The Clebsch-Gordan coefficients $(j_1j_2m_1m_2|j_1j_2JM)$ in Eq. (15) can be determined from Eq. (2.9) of Ref. 10.

With the separation of angular contributions in Eqs. (2) and (4) for the overlap and nuclear-attraction integrals over real STO's, we use the following relationship between real and complex spherical harmonics:

$$S_{lm}=\frac{(-i)^{\delta_{m,-|m|}}}{\sqrt{2(1+\delta_{m0})}}(Y_{l|m|}+\epsilon_m Y_{l,-|m|}) \quad , \qquad (16)$$

where $Y_{l,-|m|}=Y^{*}_{l|m|}$ and $\epsilon_m\equiv\epsilon_{m0}$; the symbol $\epsilon_{mm'}$ may have the values ± 1 and the sign is determined by the product of the signs of m and m' (the sign of zero is regarded as positive). In Eq. (16) the symbol $\delta_{m,-|m|}$ may have the values $\delta_{m,-|m|}=0$ for $m\geqslant 0$ and $\delta_{m,-|m|}=1$ for $m<0$.

By use of (16) it is easy to express the product of

$$\bar{\chi}_{nlm}\bar{\chi}_{n'l'm'}=\bar{\chi}^{*}_{nlm}\bar{\chi}_{n'l'm'}$$

for the real STO's in terms of $\bar{\phi}^{*}_{nlm}\bar{\phi}_{n'l'm'}$. Then, carrying through the calculations in the same way as in the case of overlap and nuclear-attraction integrals for complex STO's, we obtain

$$\bar{F}^{R}_{nlm,n'l'm'}(\mathbf{p},t)=\sum_{\lambda=0}^{l_-}T^{\lambda}_{lm,l'm'}(\Theta,\Phi)\bar{F}^{R}_{nl\lambda,n'l'\lambda}(p,t) \quad , \qquad (17)$$

where $\bar{F}^{R}=\bar{S}^{R}$ or $\bar{F}^{R}=\bar{U}^{R}$ and

$$T^{\lambda}_{lm,l'm'}(\Theta,\Phi)=\frac{1}{(1+\delta_{\lambda 0})[(1+\delta_{m0})(1+\delta_{m'0})]^{1/2}}\sum_{i=\pm 1}\sum_{L=|l-l'|}^{l+l'}[1+(-1)^{l+l'-L}](\epsilon_m)^{\delta_{i,\epsilon_{mm'}}}C^{ll'L}_{i\gamma\gamma',i\gamma+\gamma'}C^{ll'L}_{-\lambda\lambda 0}$$
$$\times\bar{\mathscr{P}}_{L|i\gamma+\gamma'|}(\cos\Theta)\times\begin{cases}\cos(i\gamma+\gamma')\Phi & \text{for } \epsilon_{mm'}=+1\ ,\\ \sin(i\gamma+\gamma')\Phi & \text{for } \epsilon_{mm'}=-1\ .\end{cases}\quad (18)$$

Here $\gamma=|m|$, $\gamma'=|m'|$ and

$$\bar{\mathscr{P}}_{L|M|}=\left(\frac{2}{2L+1}\right)^{1/2}\mathscr{P}_{L|M|}\ .$$

(The quantity $\mathscr{P}_{L|M|}$ is the associated normalized Legendre function.)

Thus, the angular and radial parts of the overlap and nuclear-attraction integrals with the arbitrary screening constants of STO's relative to the common coordinate system are expressed in the form of finite sums through the spherical harmonics and the auxiliary functions A_k and B_k (or the polynomials in p), respectively.

For the linear molecule it will be convenient to take the polar axis Z of the common coordinate system (X,Y,Z) along the line joining the nuclei of the molecule. Then we find for the overlap and nuclear-attraction integrals with complex and real STO's, instead of Eqs. (5) and (17), the following expression;

$$\bar{F}^{c,R}_{nlm,n'l'm'}(\mathbf{p},t)=\delta_{mm'}\bar{F}^{R}_{nl\gamma,n'l'\gamma}(p,t)\begin{cases}1 & \text{for } \Theta=0,\Phi=0,\\ (-1)^{l+l'} & \text{for } \Theta=\pi,\Phi=0.\end{cases}\quad (19)$$

The overlap and nuclear-attraction integrals on the right-hand side of Eq. (19) are determined by the formulas (8)–(13).

[1]I. I. Guseinov, J. Chem. Phys. **69**, 4990 (1978).
[2]I. I. Guseinov, Phys. Rev. A **22**, 369 (1980).
[3]I. I. Guseinov, Phys. Rev. A **31**, 2851 (1985).
[4]C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).
[5]E. Filter and E. O. Steinborn, Phys. Rev. A **18**, 1 (1978).
[6]H. W. Jones, Int. J. Quantum Chem. **19**, 567 (1981); **21**, 1079 (1982).
[7]H. P. Trivedi and E. O. Steinborn, Phys. Rev. A **25**, 113 (1982).
[8]H. W. Jones, Phys. Rev. A **30**, 1 (1984).
[9]I. I. Guseinov, J. Phys. B **3**, 1399 (1970).
[10]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton Univ. Press, Princeton, 1957).
[11]I. I. Guseinov, J. Chem. Phys. **67**, 3837 (1977).