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Addition theorems for Slater-type orbitals in momentum space and their application to three-center overlap integrals

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Abstract Using addition theorems for complete orthonormal sets of exponential type orbitals in the momentum representation introduced by the author, the addition theorems are established for Slater type orbitals in momentum space. With the help of these addition theorems, the general series expansion formulae in terms of the product of two-center overlap integrals are established for the three-center overlap integrals that arise in the solution of atomic and molecular problems occurring when explicitly correlated methods are employed. The formulae obtained for addition theorems and three-center overlap integrals are valid for arbitrary location and parameters of orbitals.

Keywords Slater type orbitals · Addition theorems · Momentum representation · Three-center overlap integrals

Introduction

Complete orthonormal sets of exponential-type orbitals play a significant role in the theory and application to quantum mechanics of atoms, molecules and solids [1, 2]. The importance of these orbitals is due to the fact that their addition theorems are very useful in the calculation of multicenter multielectron integrals over Slater type orbitals (STOs) appearing in the determination of various properties of molecules. Approaches presented in the literature for the evaluation of multicenter integrals consist of using the relatively complicated addition theorems of STOs to separate the integration variables from those related to the geometry of the molecule [3–24]. We will give improvements on some of the existing results. In previous work [25], by the use of addition theorems for STOs in coordinate representation, all the multicenter multielectron integrals were expressed in terms of two-center and three-center overlap integrals, the evaluation of which was presented in Ref. [26]. The purpose of this work is to establish the addition theorems for STOs in momentum space, and to yield a new method for calculation of three-center overlap integrals appearing in the theory of multicenter multielectron integrals.

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Addition theorems for STOs in momentum space

In order to establish addition theorems for STOs in momentum space, we shall use the following addition relations for complete orthonormal sets of exponential-type orbitals in the momentum representation [27]:

$$\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}-\vec{p}\right)=\left(4\pi z\right)^{3/2}\sum_{\mu=1}^{\infty}\sum_{v=0}^{\mu-1}\sum_{\sigma=-v}^{v}\left(\sum_{N=1}^{n+\mu+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}B^{\alpha NLM}_{nlm,\mu v\sigma}\Phi^{\alpha *}_{NLM}\left(z,\vec{p}\right)\right)\bar{\Phi}^{\alpha}_{\mu v\alpha}\left(\zeta,\vec{k}\right),\qquad(1)$$

where $\alpha = 1,0,-1,-2,\ldots$, and $z=2\zeta$. The Φ^{α}_{nlm} and $\bar{\Phi}^{\alpha}_{nlm}$ are represented as finite linear combinations of STOs in the momentum space by

$$\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)=\sum_{\mu=l+1}^{n}\omega^{\alpha l}_{n\mu}U_{\mu lm}\left(\zeta,\vec{k}\right),\qquad(2)$$

$$\bar{\Phi}^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)=(2n)^{\alpha}\sum_{\mu=l+1}^{n}\omega^{\alpha l}_{n\mu}\left[(2(\mu-\alpha))!/(2\mu)!\right]^{1/2}U_{\mu-\alpha lm}\left(\zeta,\vec{k}\right)\qquad(3)$$

and, conversely,

$$U_{nlm}(\zeta,\vec{k}) = \sum_{\mu=l+1}^{n} \bar{\omega}_{n\mu}^{\alpha l}\Phi_{\mu lm}^{\alpha}(\zeta,\vec{k}) = \sum_{\mu=l+1}^{n} \bar{\omega}_{n\mu}^{\alpha l}\left(\frac{\zeta k}{\mu}\right)^{\alpha}\bar{\Phi}_{\mu lm}^{\alpha}(\zeta,\vec{k}). \quad (4)$$

See Refs. [27] and [28] for the exact definition of coefficients $B_{nlm,\mu\ \nu\sigma}^{\alpha NLM}$, $\omega_{n\mu}^{\alpha l}$ and $\bar{\omega}_{n\mu}^{\alpha l}$ occurring in Eqs. 1, 2, 3 and 4.

Taking into account Eqs. 1, 2 and 3 in Eq. 4 we obtain:

$$U_{nlm}\left(\zeta,\vec{k}-\vec{p}\right) = (4\pi z)^{3/2}\sum_{\mu=1}^{\infty}\sum_{v=0}^{\mu-1}\sum_{\sigma=-v}^{v} \left(\sum_{N=1}^{n+\mu+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L} D_{nlm,\mu v\sigma}^{\alpha NLM}\Phi_{NLM}^{\alpha *}(z,\vec{p})\right)\bar{\Phi}_{\mu v\sigma}^{\alpha}\left(\zeta,\vec{k}\right), \quad (5)$$

where

$$D_{nlm,\mu v\sigma}^{\alpha NLM} = \sum_{\mu'=l+1}^{n} \bar{\omega}_{n\mu'}^{\alpha l}B_{nlm,\mu' v\sigma}^{\alpha NLM}. \quad (6)$$

Now we use the following identity:

$$\sum_{N=1}^{n+\mu+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L} D_{nlm,\mu v\sigma}^{\alpha NLM}\Phi_{NLM}^{\alpha}(z,\vec{p}) = \sum_{N=1}^{n+\mu+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}\left(\sum_{N'=N}^{n+\mu+1}\omega_{N'N}^{\alpha L}D_{nlm,\mu v\sigma}^{\alpha N'LM}\right)U_{NLM}(z,\vec{p}). \quad (7)$$

Then, we obtain finally for the addition theorems of STOs in the momentum space the following relations:

$$U_{nlm}\left(\zeta,\vec{k}-\vec{p}\right) = (4\pi z)^{3/2}\sum_{\mu=1}^{\infty}\sum_{v=0}^{\mu-1}\sum_{\sigma=-v}^{v}\sum_{\mu'=v+1}^{\mu} \left(\sum_{N=1}^{n+\mu+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L} K_{nlm,\mu v\sigma}^{\alpha NLM}(\mu')U_{NLM}^{*}(z,\vec{p})\right)U_{\mu'-\alpha v\sigma}\left(\zeta,\vec{k}\right), \quad (8)$$

where $\alpha = 1, 0, -1, -2, \ldots$, and

$$K_{nlm,\mu v\sigma}^{\alpha NLM}(\mu') = (2\mu)^{\alpha}\left[\frac{(2(\mu'-\alpha))!}{(2\mu')!}\right]^{1/2} \omega_{\mu\mu'}^{\alpha v}\sum_{\mu''=l+1}^{n}\bar{\omega}_{n\mu''}^{\alpha l}\sum_{N'=N}^{n+\mu+1}\omega_{N'N}^{\alpha L}B_{\mu''lm,\mu v\sigma}^{\alpha N'LM}. \quad (9)$$

Now we can move on to the evaluation of three-center overlap integrals occurring in the multicenter multielectron integrals over STOs.

Evaluation of three-center overlap integrals

Three-center overlap integrals in the molecular coordinate system are as follows

$$S_{p_1p_2p_3}(\zeta_1,\zeta_2,\zeta_3;\vec{R}_{ab},\vec{R}_{cb}) = \sqrt{4\pi}\int \chi_{p_1}^{*}(\zeta_1,\vec{r})\chi_{p_2}(\zeta_2,\vec{r}-\vec{R}_{ac})\chi_{p_3}(\zeta_3,\vec{r}-\vec{R}_{ab})d^3\vec{r}, \quad (10)$$

where $p_i \equiv n_i l_i m_i (I = 1,2,3), \vec{r} = \vec{r}_a, \vec{r}-\vec{R}_{ac} = \vec{r}_c, \vec{r}-\vec{R}_{ab} = \vec{r}_b$ and $\chi_{p_1}(\zeta_1,\vec{r}_a), \chi_{p_2}(\zeta_2,\vec{r}_b)$ and $\chi_{p_3}(\zeta_3,\vec{r}_c)$ are the normalized complex or real STOs centered on the nuclei a, c and b, respectively, defined by

$$\chi_{nlm}(\zeta,\vec{r}) = (2\zeta)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}}r^{n-1}e^{-\zeta r}S_{lm}(\theta,\varphi). \quad (11)$$

Here the functions S_{lm} are complex ($S_{lm} \equiv Y_{lm}$) or real spherical harmonics (SH) defined by [29]

$$S_{lm}(\theta,\phi) = P_{l|m|}(\cos\theta)\Phi_m(\phi), \quad (12)$$

where

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\theta} \quad (13)$$

for complex SH and

$$\Phi_m(\phi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}}\begin{cases}\cos|m|\phi & \text{for} \quad m\geqslant 0,\\ \sin|m|\phi & \text{for} \quad m<0\end{cases} \quad (14)$$

for real SH. In Eq. 12, $P_{l\ |\ m|}$ are normalized associated Legendre functions.

In order to evaluate three-center overlap integrals, we use in Eq. 10 the Fourier transform convolution theorem. Then we obtain:

$$S_{p_1p_2p_3}(\zeta_1,\zeta_2,\zeta_3;\vec{R}_{ab},\vec{R}_{cb}) = \sqrt{4\pi}(2\pi)^{-3/2}\int e^{-i\vec{k}_1\cdot\vec{R}_{ab}+i\vec{k}_2\cdot\vec{R}_{cb}} U_{p_1}^{*}\left(\zeta_1,\vec{k}_1\right)U_{p_2}\left(\zeta_2,\vec{k}_2\right)\times U_{p_3}\left(\zeta_3,\vec{k}_1-\vec{k}_2\right)d^3\vec{k}_1 d^3\vec{k}_2, \quad (15)$$

where $\chi_{nlm}(\zeta,\vec{r})$ and $U_{nlm}\left(\zeta,\vec{k}\right)$ are a pair of mutual Fourier transforms given by

$$\chi_{nlm}(\zeta,\vec{r}) = (2\pi)^{-3/2}\int e^{i\vec{k}\cdot\vec{r}}U_{nlm}\left(\zeta,\vec{k}\right)d^3\vec{k}, \quad (16)$$

$$U_{nlm}\left(\zeta,\vec{k}\right) = (2\pi)^{-3/2}\int e^{i\vec{k}\cdot\vec{r}}\chi_{nlm}(\zeta,\vec{r})d^3\vec{r}. \quad (17)$$

To evaluate the integral in Eq. 15 we need the following relation for the Fourier transform of two-center overlap integrals:

$$S_{nlm,n'l'm'}(\zeta,\zeta',\vec{R}) = \int \chi_{nlm}^{*}(\zeta,\vec{r})\chi_{n'l'm'}(\zeta',\vec{r}-\vec{R})d^3\vec{r} = \int e^{i\vec{k}\cdot\vec{R}}U_{nlm}^{*}\left(\zeta,\vec{k}\right)U_{n'l'm'}\left(\zeta',\vec{k}\right)d^3\vec{k}. \quad (18)$$

Now we take Eq. 18 into account in Eq. 15 for the addition theorems of the function $U_{p_3}\left(\zeta_3,\vec{k}_1-\vec{k}_2\right)$ and Eq. 18 for the Fourier transform of two-center overlap integrals. Then, we obtain finally for the three-center overlap integrals in terms of the product of two-center overlap integrals the following series expansion formulae:

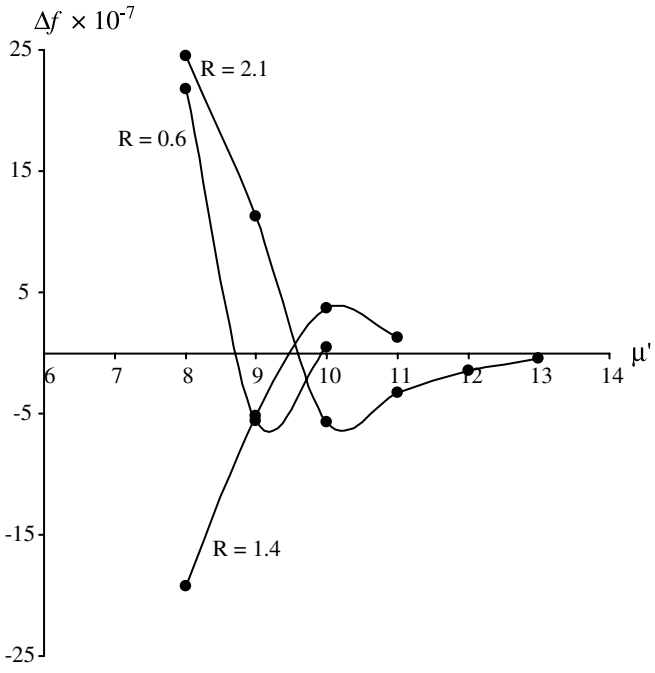

Fig. 1 Convergence of the series in Eq. 19 for the three-center overlap integrals $S_{210,\ 211,\ 100}$ for various values of $R = R_{ab}$ as a function of the number of summation terms $\alpha = 1$, $\zeta_1 = 4.3$, $\zeta_2 = 6.4$, $\zeta_3 = 2.3$, $\theta_{ab\text{-}45°}$, $\phi\_ab = 150$ °, $R\_bc = 0.6$, $\theta bc = 60°$, $\phi\_bc = 120°$

$$S_{p_1p_2p_3}(\zeta_1,\zeta_2,\zeta_3;\vec{R}_{ab},\vec{R}_{cb}) = \sqrt{4\pi}(2z_3)^{3/2}\sum_{\mu=1}^{\infty}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}\sum_{\mu'=\nu+1}^{\mu}$$
$$S_{n_1l_1m_1,\mu'-\alpha\nu\sigma}(\zeta_1\zeta_3;\vec{R}_{ab}) \times \left(\sum_{N=1}^{n_3+\mu+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L} K^{\alpha NLM}_{n_3l_3m_3,\mu\nu\sigma}(\mu')\right.$$
$$\left. S^{*}_{n_2l_2m_2,NLM}(\zeta_2z_3;\vec{R}_{cb})\right), \qquad (19)$$

where $\alpha = 1, 0, -1, -2, \ldots$

As can be seen from Eq. 19, with the help of the addition theorems for STOs in momentum space that have been established in this work, we can calculate the three-center overlap integrals by the use of two-center overlap integrals, for the computation of which efficient computer programs specially useful for large quantum numbers are available in our group [30]. Thus, the two-center overlap integrals can be utilized as a basis in the calculation of three-center overlap integrals, therefore, in the evaluation of multicenter multielectron integrals of arbitrary central and noncentral potentials.

Numerical results and discussion

Analytical formulae have been presented for computation of the three-center overlap integrals, which occur as part of the overall integration problem that arises in electronic structure computations using Slater-orbital basis functions. The two-center overlap integrals can be utilized as a basis in the calculation of these integrals, therefore, in the solution of multielectron problem when a correlated potentials approximation is employed.

Three-center overlap integrals have not been studied in the literature so far. For these integrals in this work we obtained analytical formulae in terms of two-center overlap integrals. The accuracy of the resulting calculations of three-center overlap integrals was tested by the use of different methods in which we utilize the different complete orthonormal sets of Ψ^1,Ψ^0 and Ψ^{-1} ETOs introduced in Ref. [28].

The convergence of the series in Eq. 19 for $\nu' \leqslant \mu' - 1$ and $\sigma' \leqslant \mu' - 1$ was tested, where μ', ν' and σ' are the upper limits of indices μ,ν and σ, respectively. The results of series accuracy $\Delta f_{\mu'\nu'\sigma'} = f_{\mu'\mu'-1\mu'-1} - f_{\mu'\nu'\sigma'}$ for $S_{210,211,100}$ are shown in Fig. 1. Here, the quantities $f = f_{\mu'\mu'-1\mu'-1}$ are the values of integrals for $\nu' = \mu' - 1$ and $\sigma' = \mu' - 1$.

The results of calculations for three-center overlap integrals on a Pentium III 800 Mhz computer (using Turbo Pascal) are given in Table 1. The comparative values obtained from Ψ^1 and Ψ^0-ETOs and the CPU time in milliseconds are given in the table. As can be seen from the table, the accuracy and the CPU time are satisfactory. Figure 1 shows that the convergence for a given α, is more rapid for small R, and it deteriorates as R increases. An accuracy of 10^{-5} is obtained for $\mu = 12$. Greater accuracy is easily attainable by the use of more terms of expansion in Eq. 19.

It should be noted that the algorithm presented in this study can be used to calculate any multicenter multielectron integral of arbitrary central and noncentral potential for the arbitrary values of screening constants, quantum numbers and location of STOs (see Ref. [25]).

Table 1 Comparison of methods of computing three-center overlap integrals S^{acb} for $\mu = 12$ (in au)

n	l	m	ζ	n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	R_{bc}	θ_{bc}	ϕ_{bc}	R_{ca}	θ_{ca}	ϕ_{ca}	$\alpha = 0$	$\alpha = 1$	CPU (ms)
2	0	0	5.8	2	0	0	3.6	2	0	0	2.7	0.4	100	240	0.8	144	140	7.8435843096E-01	7.843586656E-01	8.3
2	1	0	2.4	2	0	0	1.3	1	0	0	4.2	0.2	60	90	0.7	120	180	−1.5504804913E-01	−1.5504683691E-01	11.9
2	1	0	7.2	2	1	0	3.1	1	0	0	5.4	0.4	20	270	0.7	45	45	4.1310616384E-01	4.1310534138E-01	14.1
2	1	1	8.5	1	0	0	6.4	1	0	0	7.2	0.6	80	360	0.5	126	100	2.3374656418E-01	2.3375835540E-01	17.7
2	1	0	5.7	2	1	0	4.3	2	1	0	2.5	0.2	60	180	0.4	36	160	−6.5394921686E-01	−6.5394529848E-01	20.5

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