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On the unified treatment of complete orthonormal sets of functions in coordinate, momentum, and four dimensional spaces and their expansion and one-range addition theorems

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The new formulas have been established for the expansion and one-range addition theorems for the complete orthonormal sets of functions in coordinate, momentum, and four-dimensional spaces. These theorems enable us to derive the formulas for the overlap integrals over STOS, Ψ^{α}-ETOs, Φ^{α}-MSOs, and Z^{α}-HSHs which can be useful in the study of different quantum mechanical problems in both the theory and practice of calculations dealing with atoms, molecules, and solids when the coordinate, momentum or four-dimensional spaces employed. This work presents the development of our previous paper (I.I. Guseinov, J. Math. Chem., (2007) DOI: 10.1007/s10910-006-9154-1).

KEY WORDS: one-range addition theorems, exponential-type orbitals, momentum space orbitals, hyperspherical harmonics

1. Introduction

In a previous paper [1], by the use of Ψ^{α}, Φ^{α}, and Z^{α} basis sets, where $\alpha = 1, 0, -1, \ldots$, the expansion and one-range addition theorems were derived for the complete orthonormal sets of functions in coordinate, momentum or four-dimensional spaces. The aim of this work is to establish the new expansion and one-range addition theorems using $\bar{\Psi}^{\alpha}$, $\bar{\Phi}^{\alpha}$, and $\bar{Z}^{\alpha}$ basis sets which are orthonormal with respect to the functions Ψ^{α}, Φ^{α}, and Z^{α}, respectively.

2. Expansion and addition theorems

In order to establish the formulas in the $\bar{\Psi}^{\alpha}$, $\bar{\Phi}^{\alpha}$, and $\bar{Z}^{\alpha}$ basis sets for the expansion and addition theorems of complete sets of functions in coordinate, momentum, and four-dimensional spaces, we use the method set out in [1].

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Then, carrying through calculations analogous to those for the Ψ^α, Φ^α, and Z^α basis sets described in [1], we obtain the following results:

2.1. Expansion theorems

2.1.1. Expansion theorems for ETOs

$$\bar{\Psi}^{\alpha *}_{nlm}(\zeta,\vec{r})\Psi^{\alpha}_{n'l'm'}(\zeta',\vec{r}) = \frac{(2z)^{3/2}}{\sqrt{4\pi}} \sum_{N=1}^{n+n'-1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} \bar{B}^{\alpha NLM}_{nlm,n'l'm'}(\eta)\bar{\Psi}^{\alpha *}_{NLM}(z,\vec{r}), \quad (1)$$

where

$$\bar{B}^{\alpha NLM}_{nlm,n'l'm'}(\eta) = \frac{\sqrt{4\pi}}{(2z)^{3/2}} \int \bar{\Psi}^{\alpha *}_{nlm}(\zeta,\vec{r})\Psi^{\alpha}_{n'l'm'}(\zeta',\vec{r})\Psi^{\alpha}_{NLM}(z,\vec{r})\mathrm{d}^3\vec{r} \quad (2a)$$

$$= (2L+1)^{1/2}C^{L|M|}(lm,l'm')A^{M}_{mm'}\bar{B}^{\alpha NL}_{nl,n'l'}(\eta), \quad (2b)$$

$$\bar{B}^{\alpha NL}_{nl,n'l'}(\eta) = \bar{N}^{\alpha}_{nl}N^{\alpha}_{n'l'}N^{\alpha}_{NL} \times \sum_{s=0}^{q-p} \sum_{s'=0}^{q'-p'} \sum_{S=0}^{Q-P} \gamma^{p}_{qs}\gamma^{p'}_{q's'}\gamma^{P}_{QS}(l+s-\alpha+l'+s'+L+S+2)! \times \left(\frac{1}{1+1/\eta}\right)^{l+s-\alpha+\frac{3}{2}} \left(\frac{1}{1+\eta}\right)^{l'+s'+\frac{3}{2}}. \quad (3)$$

2.1.2. Expansion theorems for MSOs

$$\bar{\Phi}^{\alpha *}_{nlm}(\zeta,\vec{k})\Phi^{\alpha}_{n'l'm'}(\zeta,\vec{k}) = \frac{1}{4\pi\zeta^{3/2}} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} \bar{D}^{\alpha NLM}_{nlm,n'l'm'}\bar{\Phi}^{\alpha *}_{NLM}(\zeta,\vec{k}), \quad (4)$$

where

$$\bar{D}^{\alpha NLM}_{nlm,n'l'm'} = 4\pi\zeta^{3/2} \int \bar{\Phi}^{\alpha *}_{nlm}(\zeta,\vec{k})\Phi^{\alpha}_{n'l'm'}(\zeta,\vec{k})\Phi^{\alpha}_{NLM}(\zeta,\vec{k})\mathrm{d}^3\vec{k} \quad (5a)$$

$$= (-1)^{(l-l'-L)/2}(2L+1)^{1/2}C^{L|M|}(lm,l'm')A^{M}_{mm'}\bar{D}^{\alpha NL}_{nl,n'l'}, \quad (5b)$$

$$\bar{D}^{\alpha NL}_{nl,n'l'} = 2^{l+l'+L+2} l! l'! L! \bar{N}^{\alpha}_{nl} N^{\alpha}_{n'l'} N^{\alpha}_{NL} \sum_{s=0}^{q-p} \sum_{s'=0}^{q'-p'} \sum_{S=0}^{Q-P} (s-\alpha+1)! \gamma^{p}_{qs} (s'+1)!$$
$$\times \gamma^{p'}_{q's'} (S+1)! \gamma^{P}_{QS}$$
$$\times \sum_{i} (-1/4)^i F_i \left(\frac{1}{2}(l+l'+L+2) \right) \sum_{k} (-1)^k d^{l+1,l'+1,L+1}_{s-\alpha+1,s'+1,S+1,k}$$
$$\times F_{\frac{1}{2}(l+l'+L)+s-\alpha+s'+S+i-k+4}$$
$$\times \left(2\left[\frac{1}{2}(l+l'+L) + s - \alpha + s' + S + i - k + 4 \right] - 1 \right), \qquad (6)$$

where $0 \leqslant i \leqslant \frac{1}{2}(l+l'+L+2)$ and $0 \leqslant k \leqslant E\left(\frac{s-\alpha+1}{2}\right) + E\left(\frac{s'+1}{2}\right) + E\left(\frac{S+1}{2}\right)$.

2.1.3. Expansion theorems for HSHs

$$\bar{Z}^{\alpha *}_{nlm}(\zeta, \beta\theta\varphi) Z^{\alpha}_{n'l'm'}(\zeta, \beta\theta\varphi) = \frac{1}{4\pi \zeta^{3/2}} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} \bar{D}^{\alpha NLM}_{nlm,n'l'm'} \bar{Z}^{\alpha *}_{NLM}(\zeta, \beta\theta\varphi) \qquad (7)$$

where the expansion coefficients $\bar{D}^{\alpha NLM}_{nlm,n'l'm'}$ are determined by equations (5b) and (6).

2.2. Addition theorems

2.2.1. Addition theorems for ETOs

$$\Psi^{\alpha}_{nlm}(\zeta, \vec{r} - \vec{R}) = \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} {}^{a}\bar{S}^{\alpha}_{n'l'm',nlm}(\vec{G}) \Psi^{\alpha}_{n'l'm'}(\zeta, \vec{r}). \qquad (8)$$

Here, the quantities ${}^{a}\bar{S}^{\alpha}_{nlm,n'l'm'}(\vec{G}) \equiv {}^{a}\bar{S}^{\alpha}_{nlm,n'l'm'}(\zeta, \zeta; \vec{R})$ are the two-center overlap integrals with the same screening constants:

$${}^{a}\bar{S}^{\alpha}_{nlm,n'l'm'}(\zeta, \zeta; \vec{R}) = \int \bar{\Psi}^{\alpha *}_{nlm}(\zeta, \vec{r}) \Psi^{\alpha}_{n'l'm'}(\zeta, \vec{r} - \vec{R}) \mathrm{d}^3\vec{r} \qquad (9a)$$
$$= \frac{\sqrt{4\pi}}{(2\zeta)^{3/2}} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} \bar{D}^{\alpha NLM}_{nlm,n'l'm'} \bar{\Psi}^{\alpha}_{NLM}(\zeta, -\vec{R}) \qquad (9b)$$

$$= G^{-\alpha} e^{-G/2} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} \bar{A}^{\alpha NLM}_{nlm,n'l'm'} L^{P}_{Q}(G) \times T_{LM}(-\vec{G}), \tag{9c}$$

where

$$\bar{A}^{\alpha NLM}_{nlm,n'l'm'} = (2L+1)^{1/2} \bar{N}^{\alpha}_{NL} \bar{D}^{\alpha NLM}_{nlm,n'l'm'} \tag{10}$$

2.2.2. Addition theorems for MSOs

$$\Phi^{\alpha}_{nlm}(\zeta, \vec{k} - \vec{p}) = \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} {}^{b}\bar{S}^{\alpha}_{n'l'm',nlm}(\vec{\mathcal{F}}) \Phi^{\alpha}_{n'l'm'}(\zeta, \vec{k}). \tag{11}$$

The ${}^{b}S^{\alpha}_{nlm,n'l'm'}(\vec{\mathcal{F}}) \equiv {}^{b}S^{\alpha}_{nlm,n'l'm'}(\zeta, \zeta; \vec{p})$ occurring in equation (11) are the two-center overlap integrals in momentum space:

$${}^{b}\bar{S}^{\alpha}_{nlm,n'l'm'}(\zeta, \zeta; \vec{p}) = \int \bar{\Phi}^{\alpha^*}_{nlm}(\zeta, \vec{k}) \Phi^{\alpha}_{n'l'm'}(\zeta, \vec{k} - \vec{p}) \mathrm{d}^3\vec{k} \tag{12a}$$

$$= 4\pi (2\zeta)^{3/2} \sum_{N=1}^{n+n'-1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} \bar{B}^{\alpha NLM}_{nlm,n'l'm'} \bar{\Phi}^{\alpha^*}_{NLM}(2\zeta, \vec{p}) \tag{12b}$$

$$= \sum_{N=1}^{n+n'-1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} \bar{\kappa}^{\alpha NLM}_{nlm,n'l'm'} \sum_{S=0}^{Q-P} (S-\alpha+1)! \times \gamma^{P}_{QS}(2x_p)^{L+S-\alpha+3} C^{L+1}_{S-\alpha+1}(x_p) \tilde{T}_{LM}(\vec{F}), \tag{12c}$$

where

$$\bar{\kappa}^{\alpha NLM}_{nlm,n'l'm'} = 2^L (2L+1)^{1/2} L! \bar{N}^{\alpha}_{NL} \bar{B}^{\alpha NLM}_{nlm,n'l'm'}. \tag{13}$$

2.2.3. Addition theorems for HSHs

$$Z^{\alpha}_{nlm}(\zeta, \beta_{k'}\theta_{k'}\varphi_{k'}) = \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} {}^{c}\bar{S}^{\alpha}_{n'l'm',nlm}(\vec{\mathcal{F}}) Z^{\alpha}_{n'l'm'}(\zeta, \beta_k\theta_k\varphi_k). \tag{14}$$

Here, the ${}^{c}\bar{S}^{\alpha}_{nlm,n'l'm'}(\vec{\mathcal{F}}) \equiv {}^{c}\bar{S}^{\alpha}_{nlm,n'l'm'}(\zeta,\zeta;\beta_p\theta_p\varphi_p)$ are the overlap integrals in four-dimensional space:

$$
{}^{c}\bar{S}^{\alpha}_{nlm,n'l'm'}(\zeta,\zeta;\beta_p\theta_p\varphi_p) = \int \bar{Z}^{\alpha *}_{nlm}(\zeta,\beta_k\theta_k\varphi_k) Z^{\alpha}_{n'l'm'}(\zeta,\beta_{k'}\theta_{k'}\varphi_{k'})\mathrm{d}\Omega \tag{15a}
$$

$$
= 4\pi(2\zeta)^{3/2} \sum_{N=1}^{n+n'-1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} \bar{B}^{\alpha NLM}_{nlm,n'l'm'} \times \bar{Z}^{\alpha *}_{NLM}(2\zeta,\beta_p\theta_p\varphi_p) \tag{15b}
$$

$$
= \sum_{N=1}^{n+n'-1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} \bar{\kappa}^{\alpha NLM}_{nlm,n'l'm'} \sum_{S=0}^{Q-P} (S-\alpha+1)! \times \gamma^{P}_{QS}(2\kappa^{p}_{4})^{L+S-\alpha+3} C^{L+1}_{S-\alpha+1}(\kappa^{p}_{4}) \tilde{T}_{LM}(\vec{\mathcal{F}}). \tag{15c}
$$

3. Use of expansion and addition theorems for ETOs in the evaluation of overlap integrals over STOs

Using equations (9b) and (9c) for the overlap integrals between Ψ^{α}-ETOs derived in this study with the help of expansion and addition theorems for ETOs, one can establish the relations for the two-center overlap integrals of complex or real STOs with the same screening constant which have the form

$$
S_{nlm,n'l'm'}(\zeta,\zeta;\vec{R}) = \int \chi^{*}_{nlm}(\zeta,\vec{r})\chi_{n'l'm'}(\zeta,\vec{r}-\vec{R})\mathrm{d}^3\vec{r}, \tag{16}
$$

where $\vec{r}=\vec{r}_a, \vec{r}-\vec{R}=\vec{r}_b, \vec{R}=\vec{R}_{ab}$ and

$$
\chi_{nlm}(\zeta,\vec{r}) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1}\mathrm{e}^{\zeta r} S_{lm}(\theta,\varphi). \tag{17}
$$

In order to evaluate the integral (16), we use the following relations between STOs and ETOs:

$$
\chi_{nlm}(\zeta,\vec{r}) = \sum_{\mu=l+1}^{n} \bar{\omega}^{\alpha l}_{n\mu} \Psi^{\alpha}_{\mu lm}(\zeta,\vec{r}), \tag{18a}
$$

$$
\Psi^{\alpha}_{nlm}(\zeta,\vec{r}) = \sum_{\mu=l+1}^{n} \omega^{\alpha l}_{n\mu} \chi_{\mu lm}(\zeta,\vec{r}), \tag{18b}
$$

$$\chi_{nlm}(\zeta,\vec{r}) = [[2\,(n+\alpha)]!/\,(2n)!]^{1/2} \sum_{\mu=l+1}^{n+\alpha} \frac{\bar{\omega}^{\alpha l}_{n+\alpha\mu}}{(2\mu)^{\alpha}} \bar{\Psi}^{\alpha}_{\mu lm}(\zeta,\vec{r}), \tag{19a}$$

$$\bar{\Psi}_{nlm}(\zeta,\vec{r}) = (2n)^{\alpha} \sum_{\mu=l+1-\alpha}^{n-\alpha} [(2\mu)!/\,[2\,(\mu+\alpha)]!]^{1/2} \times \omega^{\alpha l}_{n\mu+\alpha} \chi_{\mu lm}(\zeta,\vec{r}). \tag{19b}$$

See [2] for the exact definition of coefficients $\omega^{\alpha l}$ and $\bar{\omega}^{\alpha l}$.

Using equations (18a) and (19a) in (16) one gets the desired result,

$$S_{nlm,n'l'm'}(\vec{G}) = [[2\,(n+\alpha)]!/\,(2n)!]^{1/2} \sum_{\mu=l+1}^{n+\alpha} \sum_{\mu'=l'+1}^{n'} \frac{1}{(2\mu)^{\alpha}} \bar{\omega}^{\alpha l}_{n+\alpha\mu} \bar{\omega}^{\alpha l'}_{n'\mu'} \times {}^{a}\bar{S}^{\alpha}_{\mu lm,\mu'l'm'}(\vec{G}). \tag{20}$$

Now we take into account equations (18b) and (19b) in (9a). Then, we obtain for the transformation of $\bar{S}^{\alpha}$-overlap integral into S-integral the expression

$${}^{a}\bar{S}^{\alpha}_{nlm,n'l'm'}(\vec{G}) = (2n)^{\alpha} \sum_{\mu=l+1-\alpha}^{n-\alpha} \sum_{\mu'=l'+1}^{n'} [(2\mu)!/\,[2\,(\mu+\alpha)]!]^{1/2}\, \omega^{\alpha l}_{n\mu+\alpha} \omega^{\alpha l'}_{n'\mu'} \times S_{\mu lm,\mu'l'm'}(\vec{G}). \tag{21}$$

The result of the calculation for the overlap integrals over STOs and the comparative values obtained from the literature [3] are represented in table 1.

As can be seen from equation (20), the two-center overlap integrals with the same screening parameters of STOs are expressed in terms of overlap integrals between complete orthonormal sets of ETOs by the finite linear combinations. It is well known that the two-center overlap integrals of STOs with the same screening constant can be utilized as a basis in the calculation of multicenter integrals over exponential type orbitals which play a significant role in the theory and application to quantum mechanics of atoms, molecules and solids [4]. Thus, the formulas presented in this paper for two-center overlap integrals can be used in the evaluation of multicenter integrals over STO and ETO basis functions. We notice that, with the help of expansion and one-range addition theorems for the complete orthonormal sets of ETOs, Φ^{α}-MSOs, Z^{α}-HSHs, and STOs obtained in our works, the arbitrary multicenter integrals arising in coordinate, momentum, and four-dimensional spaces can be reduced to the overlap integrals with the same screening constant of Ψ^{α}-ETOs, Φ^{α}-MSOs, Z^{α}-HSHs, and STOs.

Table 1
Comparison of methods of computing two-center overlap integrals of STOs for $\theta = \varphi = 0$.

n	l	m	n'	l'	m'	$G = 2\zeta R$	Equation (20) $\alpha = 1$	Equation (20) $\alpha = 0$	Reference [3]
3	2	1	3	2	1	50	−1.5574859499788381265740682E-06	−1.5574859499788381265740682E-06	–
7	3	2	4	3	2	300	−2.8249115584238567327670235E-52	−2.8249115584238567327670235E-52	–
10	9	9	10	9	9	30	1.1666305403972297056003121E-02	1.1666305403972297056003121E-02	–
15	14	14	15	14	14	30	3.7472249703818919543060838E-02	3.7472249703818919543060838E-02	3.7472249703 8189195430E-02
16	15	15	16	15	15	70	1.2168652185901981885690611E-06	1.2168652185901981885690611E-06	1.2168652185 9019818856E-06

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