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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 simpler formulas are derived for the complete orthonormal sets of exponential-type orbitals, momentum space orbitals and hyperspherical harmonics and their expansion and one-range addition theorems. The continuum states are not properly included in these functions. The analytical formulas are also obtained for the overlap integrals over Ψ^{α}-ETOs, their extensions to momentum and four-dimensional spaces and STOs with the same screening constants using addition and expansion theorems derived in this paper. The complete orthonormal sets of functions and their expansion and one-range addition theorems obtained can be useful in the study of different quantum mechanical problems when the coordinate, momentum or four-dimensional spaces employed.

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

1. Introduction

It is well known that the hydrogen-like orbitals and their extensions to momentum and four-dimensional spaces by Fock [1,2], i.e., the momentum space orbitals (MSOs) and hyperspherical harmonics (HSHs), are awkward to use as basis sets because they are not complete unless the continuum is included. To remedy this situation, in recent publications [3–5], we suggested the sets of Ψ^{α}-ETOs, Φ^{α}-MSOs and Z^{α}-HSHs which are complete without the inclusion of the continuum, where $-\infty < \alpha \leqslant 1$. For these functions, in [4,5], the analytical relations, and expansion and one-range addition theorems in terms of STOs were obtained. The aim of this work is to derive the new simpler formulas for functions Ψ^{α}, Φ^{α} and Z^{α}, their expansion and addition theorems and to yield the method for the calculation of multicenter integrals when the Hartree–Fock–Roothaan approximation and correlated methods are employed.

2. Expressions for Ψ^α-ETOs, Φ^α-MSOs, and Z^α-HSHs

In order to establish the formulas for the complete orthonormal sets of functions Ψ^α, Φ^α and Z^α in coordinate, momentum and four-dimensional spaces, respectively, we use the method set out in [5]. Then, we obtain the following results:

$$\Psi^\alpha_{nlm}(\zeta,\vec{r}) = R^\alpha_{nl}(\zeta,r)S_{lm}(\vec{r}/r), \tag{1a}$$
$$\overline{\Psi}^\alpha_{nlm}(\zeta,\vec{r}) = \overline{R}^\alpha_{nl}(\zeta,r)S_{lm}(\vec{r}/r), \tag{1b}$$

$$\Phi^\alpha_{nlm}(\zeta,\vec{k}) = \Pi^\alpha_{nl}(\zeta,k)\tilde{S}_{lm}(\vec{k}/k), \tag{2a}$$
$$\overline{\Phi}^\alpha_{nlm}(\zeta,\vec{k}) = \overline{\Pi}^\alpha_{nl}(\zeta,k)\tilde{S}_{lm}(\vec{k}/k), \tag{2b}$$

$$Z^\alpha_{nlm}(\zeta,\beta\theta\varphi) = P^\alpha_{nl}(\zeta,\beta)\tilde{S}_{lm}(\theta,\varphi), \tag{3a}$$
$$\overline{Z}^\alpha_{nlm}(\zeta,\beta\theta\varphi) = \overline{P}^\alpha_{nl}(\zeta,\beta)\tilde{S}_{lm}(\theta,\varphi). \tag{3b}$$

Here, S_{lm} and $\tilde{S}_{lm} = (-i)^l S_{lm}$ are the spherical (complex or reel) and modified spherical harmonics, respectively, and

$$R^\alpha_{nl}(\zeta,r) = (2\zeta)^{3/2}N^\alpha_{nl}t^l \mathrm{e}^{-\frac{1}{2}t}L^p_q(t), \tag{4a}$$
$$\overline{R}^\alpha_{nl}(\zeta,r) = (2\zeta)^{3/2}\overline{N}^\alpha_{nl}t^{l-\alpha} \mathrm{e}^{-\frac{1}{2}t}L^p_q(t), \tag{4b}$$

$$\Pi^\alpha_{nl}(\zeta,k) = \frac{2^l l! N^\alpha_{nl}}{\sqrt{4\pi}\zeta^{3/2}}(1-x^2)^{l/2}\sum_{s=0}^{q-p}(s+1)!\gamma^p_{qs}(2x)^{l+s+3}C^{l+1}_{s+1}(x), \tag{5a}$$

$$\overline{\Pi}^\alpha_{nl}(\zeta,k) = \frac{2^l l! \overline{N}^\alpha_{nl}}{\sqrt{4\pi}\zeta^{3/2}}(1-x^2)^{l/2}\sum_{s=0}^{q-p}(s-\alpha+1)!\gamma^p_{qs}(2x)^{l+s-\alpha+3}C^{l+1}_{s-\alpha+1}(x), \tag{5b}$$

$$P^\alpha_{nl}(\zeta,\beta) = \frac{2^l l! N^\alpha_{nl}}{\sqrt{4\pi}\zeta^{3/2}}\mathrm{Sin}^l\,\beta\sum_{s=0}^{q-p}(s+1)!\gamma^p_{qs}(2y)^{l+s+3}C^{l+1}_{s+1}(y), \tag{6a}$$

$$\overline{P}^\alpha_{nl}(\zeta,\beta) = \frac{2^l l! \overline{N}^\alpha_{nl}}{\sqrt{4\pi}\zeta^{3/2}}\mathrm{Sin}^l\,\beta\sum_{s=0}^{q-p}(s-\alpha+1)!\gamma^p_{qs}(2y)^{l+s-\alpha+3}C^{l+1}_{s-\alpha+1}(y), \tag{6b}$$

where $p = 2l+2-\alpha q = n+l+1-\alpha, -\infty < \alpha \leqslant 1, t = 2\zeta r, x = \zeta/\sqrt{\zeta^2+k^2}$, $y = \cos\beta$ and

$$N^\alpha_{nl} = (-1)^\alpha\left[\frac{(q-p)!}{(2n)^\alpha(q!)^3}\right]^{1/2}, \tag{7a}$$

$$\overline{N}^\alpha_{nl} = (-1)^\alpha\left[\frac{(2n)^\alpha(q-p)!}{(q!)^3}\right]^{1/2}. \tag{7b}$$

Here, C_n^k is the Gegenbauer polynomial. The Laguerre coefficients γ_{qs}^p occurring in these equations are determined by

$$L_q^p(t) = \sum_{s=0}^{q-p} \gamma_{qs}^p t^s, \tag{8}$$

$$\gamma_{qs}^p = (-1)^{p+s}(q-s)!F_s(q)F_{p+s}(q), \tag{9}$$

where

$$F_s(q) = \begin{cases} q!/[s!(q-s)!] & \text{for} \quad 0 \leqslant s \leqslant q, \\ 0 & \text{for} \quad s < 0, s > q. \end{cases} \tag{10}$$

The Ψ^α-ETOs, Φ^α-MSOs and Z^α-HSHs are orthonormal with respect to the functions $\overline{\Psi}^\alpha$-ETOs, $\overline{\Phi}^\alpha$-MSOs and $\overline{Z}^\alpha$-HSHs, respectively,

$$\int \Psi_{nlm}^{\alpha^*}(\zeta,\vec{r})\overline{\Psi}_{n'l'm'}^{\alpha}(\zeta,\vec{r})\mathrm{d}^3\vec{r} = \delta_{nn'}\delta_{ll'}\delta_{mm'}, \tag{11}$$

$$\int \Phi_{nlm}^{\alpha^*}(\zeta,\vec{k})\overline{\Phi}_{n'l'm'}^{\alpha}(\zeta,\vec{k})\mathrm{d}^3\vec{k} = \delta_{nn'}\delta_{ll'}\delta_{mm'}, \tag{12}$$

$$\int Z_{nlm}^{\alpha^*}(\zeta,\beta\theta\varphi)\overline{Z}_{n'l'm'}^{\alpha}(\zeta,\beta\theta\varphi)\mathrm{d}\Omega(\zeta,\beta\theta\varphi) = \delta_{nn'}\delta_{ll'}\delta_{mm'}, \tag{13}$$

where $\mathrm{d}\Omega(\zeta,\beta\theta\varphi) = \zeta^3 \frac{\mathrm{Sin}^2\beta}{\mathrm{Cos}^4\beta}\mathrm{d}\beta\mathrm{Sin}\theta\mathrm{d}\theta\mathrm{d}\varphi \quad (0 \leqslant \beta \leqslant \pi/2, 0 \leqslant \theta \leqslant \pi, 0 \leqslant \varphi \leqslant 2\pi)$.

3. Expansion theorems

3.1. *Expansion theorems for ETOs*

Let us obtain the expansion theorems for product of two ETOs, representing it as a finite sum of ETOs term. The results will enable us to get the addition theorems for the complete sets of functions in momentum and four-dimensional spaces.

The products of the ETOs are transformed to their linear combinations,

$$\Psi_{nlm}^{\alpha^*}(\zeta,\vec{r})\Psi_{n'l'm'}^{\alpha}(\zeta',\vec{r}) = \frac{(2z)^{3/2}}{\sqrt{4\pi}} \sum_{N=1}^{n+n'-1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L} B_{nlm,n'l'm'}^{\alpha NLM}(\eta)\Psi_{NLM}^{\alpha^*}(z,\vec{r}), \tag{14}$$

where $\eta = \zeta/\zeta'$ and $z = \zeta + \zeta'$. Using the orthonormality relation (11) for the expansion coefficients occurring in equation (14) one gets

$$B_{nlm,n'l'm'}^{\alpha NLM}(\eta) = \frac{\sqrt{4\pi}}{(2z)^{3/2}} \int \Psi_{nlm}^{\alpha^*}(\zeta,\vec{r})\Psi_{n'l'm'}^{\alpha}(\zeta',\vec{r})\overline{\Psi}_{NLM}^{\alpha}(z,\vec{r})\mathrm{d}^3\vec{r}. \tag{15}$$

Now we substitute equations (1a), (1b), (4a), and (4b) into the integral in equation (15), use equation (8) for the Laguerre polynomials and the following linearization formula for spherical harmonics:

$$S^{*}_{lm}(\theta,\varphi)S_{l'm'}(\theta,\varphi)=\sum_{L=|l-l'|}^{l+l'}\sum_{M=-L}^{L}\left(\frac{2L+1}{4\pi}\right)^{1/2}C^{L|M|}(lm,l'm')A^{M}_{mm'}S^{*}_{LM}(\theta,\varphi) \quad (16)$$

(see [6] for the exact definition of the Gaunt coefficients). Then, one gets the desired result,

$$B^{\alpha NLM}_{nlm,n'l'm'}(\eta)=(2L+1)^{1/2}C^{L|M|}(lm,l'm')A^{M}_{mm'}B^{\alpha NL}_{m,n'l'}(\eta), \quad (17)$$

where

$$B^{\alpha NL}_{nl,n'l'}(\eta)=N^{\alpha}_{nl}N^{\alpha}_{n'l'}\overline{N}^{\alpha}_{NL} \times\sum_{s=0}^{q-p}\sum_{s'=0}^{q'-p'}\sum_{S=0}^{Q-P}\gamma^{p}_{qs}\gamma^{p'}_{q's'}\gamma^{P}_{QS}(l+s+l'+s'+L +S-\alpha+2)!\left(\frac{1}{1+1/\eta}\right)^{l+s+3/2}\left(\frac{1}{1+\eta}\right)^{l'+s'+3/2}. \quad (18)$$

Here $p=2l+2-\alpha$, $q=n+l+1-\alpha$, $p'=2l'+2-\alpha$, $q'=n'+l'+1-\alpha$, $P=2L+2-\alpha$ and $Q=N+L+1-\alpha$. It should be noted that for $\zeta=\zeta'(\eta=1$ and $z=2\zeta)$, the coefficients $B^{\alpha NL}_{nl,n'l'}$ do not depend on the parameter ζ, i.e.

$$B^{\alpha NL}_{nl,n'l'}=N^{\alpha}_{nl}N^{\alpha}_{n'l'}\overline{N}^{\alpha}_{NL}\sum_{s=0}^{q-p}\sum_{s'=0}^{q'-p'}\sum_{S=0}^{Q-P}\gamma^{p}_{qs}\gamma^{p'}_{q's'}\gamma^{P}_{QS}(l+s+l'+s'+L+S-\alpha +2)!(1/2)^{l+s+l'+s'+3}, \quad (19)$$

where $B^{\alpha NL}_{nl,n'l'}\equiv B^{\alpha NL}_{nl,n'l'}(1)$.

3.2. Expansion theorems for MSOs

The formulas obtained in this section for the expansion theorems of MSOs are closely related to the addition theorems in the coordinate representation. Let us consider the expansion for product of MSOs:

$$\Phi^{\alpha^*}_{nlm}(\zeta,\vec{k})\Phi^{\alpha}_{n'l'm'}(\zeta,\vec{k})=\frac{1}{4\pi\zeta^{3/2}}\sum_{N=1}^{n+n'+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}D^{\alpha NLM}_{nlm,n'l'm'}\Phi^{\alpha^*}_{NLM}(\zeta,\vec{k}), \quad (20)$$

where

$$D^{\alpha NLM}_{nlm,n'l'm'} = 4\pi\zeta^{3/2}\int \Phi^{\alpha^*}_{nlm}(\zeta,\vec{k})\Phi^{\alpha}_{n'l'm'}(\zeta,\vec{k})\overline{\Phi}^{\alpha}_{NLM}(\zeta,\vec{k})\mathrm{d}^3\vec{k}. \tag{21}$$

In order to calculate this integral, we substitute the expressions (2a), (2b), (5a), and (5b) into the integral in (21), take into account equations (8), (16) and the following expansion relation for the product of Gegenbauer polynomials [4]:

$$C^{\beta}_{n}(x)C^{\beta'}_{n'}(x)C^{\beta''}_{n''}(x) = \sum_{s}(-1)^s \mathrm{d}^{\beta\beta'\beta''}_{\mathrm{nn'n'',s}}(2x)^{n+n'+n''-2s}, \tag{22}$$

$$\mathrm{d}^{\beta\beta'\beta''}_{nn'n'',s} = \sum_{m}\mathrm{d}^{\beta}_{nm}\sum_{m'}\mathrm{d}^{\beta'}_{n'm'}d^{\beta''}_{n''s-m-m'}, \tag{23}$$

where $0 \leqslant s \leqslant E(n/2)+E(n'/2)+E(n''/2)$, $0 \leqslant m \leqslant \min[E(n/2),s]$, $0 \leqslant m' \leqslant \min[E(n'/2), s-m]$, and $E(n/2) = \frac{1}{2}\left[n-\frac{1}{2}(1-(-1)^n)\right]$ (see [4] for the exact definition of Gegenbauer coefficients d^{β}_{nm}). Finally, using the result [7]

$$\int\limits_0^1 \frac{x^{2n}}{\sqrt{1-x^2}}\mathrm{d}x = \frac{(2n-1)!}{2^{2n}n!(n-1)!}\pi, \tag{24}$$

we obtain for the expansion coefficients occurring in equation (20) the following relation:

$$D^{\alpha NLM}_{nlm,n'l'm'} = (-1)^{(l-l'-L)/2}(2L+1)^{1/2}C^{L|M|}(lm,l'm')A^{M}_{mm'}D^{\alpha NL}_{nl,n'l'}, \tag{25}$$

where

$$\begin{aligned} D^{\alpha NL}_{nl,n'l'} = {} & 2^{l+l'+L+2}l!l'!L!N^{\alpha}_{nl}N^{\alpha}_{n'l'}\overline{N}^{\alpha}_{NL}\sum_{s=0}^{q-p}\sum_{s'=0}^{q'-p'}\sum_{S=0}^{Q-P}(s+1)!\gamma^{p}_{qs}(s'+1)!\gamma^{p'}_{q's'} \\ & (S-\alpha+1)!\gamma^{P}_{QS}\sum_{i}(-1/4)^i F_i\left(\frac{1}{2}(l+l'+L+2)\right) \\ & \sum_{j}(-1)^j \mathrm{d}^{l+1,l'+1,L+1}_{s+1,s'+1,S-\alpha+1,j} \times F_{\frac{1}{2}(l+l'+L)+s+s'+S-\alpha+i-j+4} \\ & \left(2\left[\frac{1}{2}(l+l'+L)+s+s'+S-\alpha+i-j+4\right]-1\right), \end{aligned} \tag{26}$$

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

3.3. Expansion theorems for HSHs

It is well known that the MSOs are identical with the HSHs arising in the four-dimensional representation, except the momentum space coordinates k_x, k_y and k_z have been replaced by β, θ, and φ. Therefore, the expansion theorems for products of HSHs are obtained from equation (20), i.e.

$$Z^{\alpha*}_{nlm}(\zeta, \beta\theta\varphi) Z^{\alpha}_{n'l'm'}(\zeta, \beta\theta\varphi) = \frac{1}{4\pi\zeta^{3/2}} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} D^{\alpha NLM}_{nlm,n'l'm'} Z^{\alpha*}_{NLM}(\zeta, \beta\theta\varphi). \quad (27)$$

Here, the expansion coefficients $D^{\alpha NLM}_{nlm,n'l'm'}$ are determined by equation (25).

4. Addition theorems

In order to obtain the addition theorems for ETOs, MSOs and HSHs, we shall use the following formulas on expansion of the exponentials into series over products of ETOs and MSOs [4]:

$$e^{-i\vec{k}\vec{r}} = (2\pi)^{3/2} \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \overline{\Phi}^{\alpha}_{n'l'm'}(\zeta, \vec{k}) \Psi^{\alpha*}_{n'l'm'}(\zeta, \vec{r}), \quad (28)$$

$$e^{i\vec{k}\vec{r}} = (2\pi)^{3/2} \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \overline{\Psi}^{\alpha}_{n'l'm'}(\zeta, \vec{r}) \Phi^{\alpha*}_{n'l'm'}(\zeta, \vec{k}), \quad (29)$$

where $0 < \zeta < \infty$.

4.1. Addition theorems for ETOs

Let us consider the Fourier transforms of the functions$\Psi^{\alpha}_{nlm}(\zeta, \vec{r} - \vec{R})$,

$$\Psi^{\alpha}_{nlm}(\zeta, \vec{r} - \vec{R}) = (2\pi)^{-3/2} \int e^{i\vec{k}(\vec{r}-\vec{R})} \Phi^{\alpha}_{nlm}(\zeta, \vec{k}) d^3\vec{k}. \quad (30)$$

Substitute the expansion (29) into the integral in (30), the result is

$$\Psi^{\alpha}_{nlm}(\zeta, \vec{r} - \vec{R}) = \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \overline{\Psi}^{\alpha}_{n'l'm'}(\zeta, \vec{r}) \left[\int e^{i\vec{k}\vec{R}} \Phi^{\alpha*}_{nlm}(\zeta, \vec{k}) \Phi^{\alpha}_{n'l'm'}(\zeta, \vec{k}) d^3\vec{k} \right]^*. \quad (31)$$

Next, we use equation (20) for the expansion theorems of MSOs and the Fourier transforms of the functions $\Psi^{\alpha}_{nlm}(\zeta, \vec{R})$ and $\overline{\Psi}^{\alpha}_{nlm}(\zeta, \vec{R})$. Then, one gets the desired result,

$$\Psi^{\alpha}_{nlm}(\zeta, \vec{r} - \vec{R}) = \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} {}^{a}S^{\alpha}_{n'l'm',nlm}(\vec{G}) \overline{\Psi}^{\alpha}_{n'l'm'}(\zeta, \vec{r}). \tag{32}$$

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

$$\begin{aligned} {}^{a}S^{\alpha}_{nlm,n'l'm'}(\zeta, \zeta; \vec{R}) &= \int \Psi^{\alpha *}_{nlm}(\zeta, \vec{r}) \Psi^{\alpha}_{n'l'm'}(\vec{\zeta}, \vec{r} - \vec{R}) \mathrm{d}^3 \vec{r} \\ &= \frac{\sqrt{4\pi}}{(2\zeta)^{3/2}} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} D^{\alpha NLM}_{nlm,n'l'm'} \Psi^{\alpha}_{NLM}(\zeta, -\vec{R}). \end{aligned} \tag{33}$$

Taking into account equations (4a) and (36) in (33), the overlap integrals can be expressed through the Laguerre polynomials and solid spherical harmonics:

$${}^{a}S^{\alpha}_{nlm,n'l'm'}(\zeta, \zeta; \vec{R}) = e^{-G/2} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} A^{\alpha NLM}_{nlm,n'l'm'} L^{P}_{Q}(G) T_{LM}(-\vec{G}), \tag{34}$$

where $\vec{G} = 2\zeta \vec{R}$ and

$$A^{\alpha NLM}_{nlm,n'l'm'} = (2L+1)^{1/2} N^{\alpha}_{NL} D^{\alpha NLM}_{nlm,n'l'm'}. \tag{35}$$

Here, $T_{lm}(\vec{r}) \equiv T_{lm}(x, y, z)$ are the complex or real regular solid spherical harmonics determined by

$$T_{\mathrm{lm}}(x, y, z) = \left(\frac{4\pi}{2l+1}\right)^{1/2} r^{l} S_{lm}(\theta, \varphi). \tag{36}$$

Thus, we have derived the desired addition theorems for ETOs: any ETOs having the difference of the radius vectors, $\vec{r} - \vec{R}$, as its argument is expanded into a series over products of Ψ^{α}- and $\overline{\Psi}^{\alpha}$-ETOs depending on $\vec{R}$ and $\vec{r}$, separately.

4.2. Addition theorems for MSOs

In order to get the addition theorems for MSOs we shall consider the Fourier transforms of $\Phi^{\alpha}_{nlm}(\zeta, \vec{k} - \vec{p})$,

$$\Phi^{\alpha}_{nlm}(\zeta, \vec{k} - \vec{p}) = (2\pi)^{-3/2} \int \mathrm{e}^{-i(\vec{k}-\vec{p})\vec{r}} \Psi^{\alpha}_{nlm}(\zeta, \vec{r}) \mathrm{d}^3\vec{r}. \tag{37}$$

Now, we take into account equations (28) and (14) for the expansion theorems of $e^{-i\vec{k}\vec{r}}$ and ETOs, respectively. Then, using the Fourier transform of the functions MSOs and the properties

$$\Phi^{\alpha}_{NLM}(\zeta,-\vec{p})=\Phi^{\alpha^*}_{NLM}(\zeta,\vec{p}), \tag{38}$$

we obtain for addition theorems the following expression:

$$\Phi^{\alpha}_{nlm}(\zeta,\vec{k}-\vec{p})=\sum_{n'=1}^{\infty}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}{}^{b}S^{\alpha}_{n'l'm',nlm}(\vec{\mathcal{F}})\overline{\Phi}^{\alpha}_{n'l'm'}(\zeta,\vec{k}). \tag{39}$$

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 (39) are the two-center overlap integrals in momentum space:

$$\begin{aligned}{}^{b}S^{\alpha}_{nlm,n'l'm'}(\zeta,\zeta;\vec{p})&=\int\Phi^{\alpha^*}_{nlm}(\zeta,\vec{k})\Phi^{\alpha}_{n'l'm'}(\zeta,\vec{k}-\vec{p})d^3\vec{k}\\&=4\pi(2\zeta)^{3/2}\sum_{N=1}^{n+n'-1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}B^{\alpha NLM}_{nlm,n'l'm'}\Phi^{\alpha^*}_{NLM}(2\zeta,\vec{p}).\end{aligned} \tag{40}$$

By the use of equations (5a), (8) and (43), the overlap integrals in momentum space can be expressed in terms of Laguerre coefficients, Gegenbauer polynomials and modified solid spherical harmonics:

$$\begin{aligned}{}^{b}S^{\alpha}_{nlm,n'l'm'}(\zeta,\zeta;\vec{p})=&\sum_{N=1}^{n+n'-1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}\kappa^{\alpha NLM}_{nlm,n'l'm'}\sum_{S=0}^{Q-P}(S+1)!\gamma^{P}_{QS}(2x_p)^{L+S+3}\\&\times C^{L+1}_{S+1}(x_p)\tilde{T}_{LM}(\vec{\mathcal{F}}),\end{aligned} \tag{41}$$

where $\vec{F}=2\zeta\vec{p}$, $x_p=2\zeta\Big/\sqrt{(2\zeta)^2+p^2}$ and

$$\kappa^{\alpha NLM}_{nlm,n'l'm'}=2^L(2L+1)^{1/2}L!N^{\alpha}_{NL}B^{\alpha NLM}_{nlm,n'l'm'}. \tag{42}$$

The quantities $\tilde{T}_{LM}$ occurring in this formula are the modified regular solid spherical harmonics determined as

$$\tilde{T}_{lm}(x,y,z)=\left(\frac{4\pi}{2l+1}\right)^{1/2}(1-x^2)^{1/2}\tilde{S}_{lm}(\theta,\varphi). \tag{43}$$

The expansion (40) enables one to formulate the theorems on representation of MSOs depending on the difference of the momentum vectors, $\vec{k}-\vec{p}$, in terms of product of Φ^{α}- and $\overline{\Phi}^{\alpha}$-MSOs depending on $\vec{p}$ and $\vec{k}$.

4.3. Addition theorems for HSHs

In order to obtain the addition theorems for HSHs, we use in equation (39) a Fock transformation of the radial momentums to the angular variables. Then, the relation (39) is reduced to the addition theorems of HSHs:

$$Z^{\alpha}_{nlm}(\zeta,\beta_{k'}\theta_{k'}\varphi_{k'})=\sum_{n'=1}^{\infty}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}{}^{c}S^{\alpha}_{n'l'm',nlm}(\vec{\mathcal{F}})\overline{Z}^{\alpha}_{n'l'm'}(\zeta,\beta_k\theta_k\varphi_k). \tag{44}$$

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

$$\begin{aligned}{}^{c}S^{\alpha}_{nlm,n'l'm'}\left(\zeta,\zeta;\beta_p\theta_p\varphi_p\right)&=\int Z^{\alpha^*}_{nlm}(\zeta,\beta_k\theta_k\varphi_k)Z^{\alpha}_{n'l'm'}(\zeta,\beta_{k'}\theta_{k'}\varphi_{k'})\mathrm{d}\Omega\\&=4\pi(2\zeta)^{3/2}\sum_{N=1}^{n+n'-1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}B^{\alpha NLM}_{nlm,n'l'm'}\\&\quad Z^{\alpha^*}_{NLM}(2\zeta,\beta_p\theta_p\varphi_p).\end{aligned} \tag{45}$$

Using equation (41), it is easy to express the overlap integrals in four-dimensional space through the Laguerre coefficients, Gegenbauer polynomials and modified solid spherical harmonics:

$$\begin{aligned}{}^{c}S^{\alpha}_{nlm,n'l'm'}(\zeta,\zeta;\beta_p\theta_p\varphi_p)&=\sum_{N=1}^{n+n'-1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}\kappa^{\alpha NLM}_{nlm,n'l'm'}\sum_{S=0}^{Q-P}\\&\quad(S+1)!\gamma^{P}_{QS}(2\kappa^{p}_{4})^{L+S+3}C^{L+1}_{S+1}(\kappa^{p}_{4})\tilde{T}_{LM}(\vec{\mathcal{F}}),\end{aligned} \tag{46}$$

where $\vec{k'}=\vec{k}-\vec{p},\vec{\mathcal{F}}=2\zeta\vec{\kappa}^{\mathrm{p}}$, $\kappa^{\mathrm{p}}_1=\sin\beta_{\mathrm{p}}\cos\varphi_{\mathrm{p}}\sin\theta_{\mathrm{p}}$, $\kappa^{\mathrm{p}}_2=\sin\beta_{\mathrm{p}}\sin\varphi_{\mathrm{p}}\sin\theta_{\mathrm{p}}$, $\kappa^{\mathrm{p}}_3=\sin\beta_{\mathrm{p}}\cos\theta_{\mathrm{p}}$, $\kappa^{\mathrm{p}}_4=\cos\beta_{\mathrm{p}}$, and

$$\tilde{T}_{lm}(\vec{\kappa}^{p})\equiv\tilde{T}_{lm}(\kappa^{p}_1,\kappa^{p}_2,\kappa^{p}_3)=\left(\frac{4\pi}{2l+1}\right)^{1/2}(\sin\beta_p)^{l}\tilde{S}_{lm}(\theta_p,\varphi_p). \tag{47}$$

The quantities $\kappa_1,\kappa_2,\kappa_3$, and κ_4 determined by relations

$$\begin{aligned}\kappa_1&=\frac{k_x}{\sqrt{\zeta^2+k^2}}, &\quad \kappa_2&=\frac{k_y}{\sqrt{\zeta^2+k^2}},\\ \kappa_3&=\frac{k_z}{\sqrt{\zeta^2+k^2}}, &\quad \kappa_4&=\frac{\zeta}{\sqrt{\zeta^2+k^2}}\end{aligned} \tag{48}$$

are the Cartesian components of the unit vector $\vec{r}/r$ in four-dimensional space which are connected to hyperspherical angles by means of following formulae:

$$\begin{aligned}\kappa_1&=\mathrm{Sin}\beta\cos\varphi\sin\theta, &\quad \kappa_2&=\mathrm{Sin}\beta\sin\varphi\sin\theta,\\ \kappa_3&=\mathrm{Sin}\beta\cos\theta, &\quad \kappa_4&=\cos\beta.\end{aligned} \tag{49}$$

We notice that the length of four-dimensional radius-vector κ is invariant with respect to the Lorentz transformations in the four-dimensional coordinate system (we note that the replacements $\vec{k} \to i\vec{k}$ and $\zeta \to c$ should be made).

Thus, we have considered the addition and expansion theorems for complete orthonormal sets of functions and overlap integrals in the coordinate, momentum and four-dimensional spaces, and have found the close relations between them.

5. Two-center overlap integrals over STOs with the same screening constants

As an example of application, we consider the two-center overlap integrals over STOs with the same screening parameters. By the use of equation (33), the two-center overlap integrals over STOs defined by

$$\mathrm{S}_{nlm,n'l'm'}(\vec{\mathrm{G}}) = \int \chi^{*}_{nlm}(\zeta, \vec{\mathrm{r}})\chi_{n'l'm'}(\zeta, \vec{\mathrm{r}} - \vec{\mathrm{R}})\mathrm{d}^3\vec{\mathrm{r}} \tag{50}$$

can be evaluated. For this purpose we use the following relation for the transformation χ-STOs into Ψ^{α}-ETOs (see equations (6) and (8) of Ref. 3):

$$\chi_{nlm}(\zeta, \vec{r}) = \sum_{\mu=l+1}^{n} \overline{\omega}^{\alpha l}_{n\mu} \Psi^{\alpha}_{\mu l m}(\zeta, \vec{r}). \tag{51}$$

We take into account equation (51) in (50). Then, one gets finally the desired result,

$$S_{nlm,n'l'm'}(\vec{G}) = \sum_{\mu=l+1}^{n} \sum_{\mu'=l'+1}^{n'} \overline{\omega}^{\alpha l}_{n\mu} \overline{\omega}^{\alpha l'}_{n'\mu'} \, {}^{a}S^{\alpha}_{\mu lm,\mu' l' m'}(\vec{G}), \tag{52}$$

where $-\infty < \alpha \leqslant 1$.

Using equation (5) of [3] in (33) it is easy to obtain for the transformation of S^{α}-overlap integrals into S- overlap integrals the expression

$${}^{a}S^{\alpha}_{nlm,n'l'm'}(\vec{G}) = \sum_{\mu=l+1}^{n} \sum_{\mu'=l'+1}^{n'} \omega^{\alpha l}_{n\mu} \omega^{\alpha l'}_{n'\mu'} S_{\mu lm,\mu' l' m'}(\vec{G}). \tag{53}$$

The results of the calculation in atomic units for the two-center overlap integrals over STOs with the same screening constants are represented in table 1. The comparative values obtained from the literature [8] are also given in this table.

The formulas derived for the two-center overlap integrals in coordinate, momentum and four-dimensional spaces can be used in the evaluation of arbitrary multicenter multielectron integrals arising in the Hartree–Fock–Roothaan

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

							Equation (52)			
n	l	m	n'	l'	m'	$G = 2\zeta R$	$\alpha = 1$	$\alpha = 0$	$\alpha = -1$	*Ref.* 8
5	4	0	5	4	0	2	0.768617016	0.768617016	0.768617016	0.768617011
5	4	4	5	4	4	2	0.955778746	0.955778746	0.955778746	0.955778746
5	4	0	5	4	0	10	−0.138257012	−0.138257012	−0.138257012	−0.138257012
5	4	4	5	4	4	10	0.356825987	0.356825987	0.356825987	0.356825987
8	0	0	8	0	0	2	0.989015721	0.989015721	0.989015721	0.989015721
8	0	0	8	0	0	10	0.785230850	0.785230850	0.785230850	0.785230850

approximation and correlated methods (see [9]). These multicenter integrals can be reduced to the overlap integrals with the same screening constants of Ψ^{α}-ETOs, Φ^{α}-MSOs, Z^{α}-HSHs, and STOs using the expansion and one-range addition theorems for the complete orthonormal sets of functions presented in this study.

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