Unified treatment of one-range addition theorems for integer and non-integer n-STO, -GTO and -generalized exponential type orbitals with hyperbolic cosine in position, momentum and four-dimensional spaces

I. I. Guseinov†

Department of Physics, Faculty of Arts and Sciences, Onsekiz Mart University, Çanakkale, Turkey

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The simpler formulas are derived for one-range addition theorems for the integer and noninteger n generalized exponential type orbitals, momentum space orbitals, and hyperspherical harmonics with hyperbolic cosine (GETO HC, GMSO HC, and GHSH HC) in position, momentum and four-dimensional spaces, respectively. The final results are expressed in terms of one-range addition theorems of complete orthonormal sets of ψ^{α}-exponential type orbitals, ϕ^{α}-momentum space orbitals and z^{α}-hyperspherical harmonics. We notice that the one-range addition theorems for integer and noninteger n-Slater type orbitals and Gaussian type orbitals in position, momentum and four dimensional spaces are the special cases of GETO HC, GMSO HC, and GHSH HC. The theorems presented can be useful in the accurate study of electronic structure of atomic and molecular systems.

Keywords: electronic structure, generalized exponential type orbitals, one-range addition theorems, Hartree–Fock–Roothaan equations

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1. Introduction

It is well known that the electronic structure calculations from the Schrödinger equation are more accurate than from the Hartree–Fock (HF) equations. To improve the HF solutions, a variational method in which the interelectronic coordinates are explicitly included in the wave functions was first introduced by Hylleraas.[1,2] It should be noted that it is difficult to evaluate the multicentre integrals that arise from Hylleraas theory. Thus, the Hylleraas method has been used only to calculate the ground state energies of two- and three-electron atomic and molecular systems.[3−13] Therefore, it is desirable to use the one-range addition theorems for exponential type orbitals (ETO) from which the problems of evaluation of multicentre integrals do not arise.

In previous papers,[14,15] the expansion formulae have been established for the one- and two-center charge densities of generalized exponential type orbitals (GETO) and GETO hyperbolic cosine (HC) functions in position space, respectively. In Ref. [16], the formulae were presented for the one-range addition theorems of generalized Coulomb- and Yukawa-like correlated interaction potentials. The aim of this work is to derive the one-range addition theorems for integer and noninteger n Ψ^{κ}-GETO HC, Φ^{κ}-generalized momentum space orbitals (GMSO) HC and Z^{κ}-generalized hyperspherical harmonics (GHSH) HC by using method given in Ref.[16]. The one-range addition theorems obtained are especially useful for computing the multicentre molecular integrals appearing in the determination of various properties of molecules when integer and non-integer n Ψ^{κ}-GETO HC, Φ^{κ}-GMSO HC and Z^{κ}-GHSH HC basis sets are used in the Hartree–Fock–Roothaan (HFR) theory.

2. Definitions and basic formulas

The normalized Ψ^{κ}-GETO HC functions in position space are defined as [15]

$$\Psi^{\kappa}_{n^*lm}(\zeta,\beta,\gamma;\boldsymbol{r}) = R^{\kappa}_{n^*}(\zeta,\beta,\gamma;r)\, S_{lm}(\theta,\varphi), \tag{1}$$

$$R^{\kappa}_{n^*}(\zeta,\beta,\gamma;r) = A^{\kappa}_{n^*}(\zeta,\beta,\gamma)\, r^{n^*-1}\, \mathrm{e}^{-\zeta r^{\kappa}} \times \cosh(\beta r^{\kappa}+\gamma), \tag{2}$$

$$A^{\kappa}_{n^*}(\zeta,\beta,\gamma) = \left\{ \frac{1}{4\kappa}\Gamma\left(\frac{2n^*+1}{\kappa}\right) \sum_{j=-1}^{1}(1+\delta_{j0}) \right.$$

†Corresponding author. E-mail: isguseinov@yahoo.com

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$$\times \frac{\mathrm{e}^{-j\gamma}}{[2(\zeta+j\beta)]^{\frac{2n^*+1}{\kappa}}}\Bigg\}^{-1/2}, \quad (3)$$

$$\cosh(\beta r^\kappa+\gamma) = \frac{1}{2}(\mathrm{e}^{\beta r^\kappa+\gamma}+\mathrm{e}^{-\beta r^\kappa-\gamma}). \quad (4)$$

Here, $\kappa>0$, $\zeta>0$, and $-\zeta<\beta<\zeta$; parameter γ can be either positive, zero, or negative.

We notice that the φ^κ-GETO is the special case of Ψ^κ-GETO HC for $\beta=\gamma=0$[14,15]

$$\begin{aligned}\varphi^\kappa_{n^*lm}(\zeta,\boldsymbol{r}) &= \Psi^\kappa_{n^*lm}(\zeta,0,0;\boldsymbol{r})\\ &= R^\kappa_{n^*}(\zeta,r)S_{lm}(\theta,\varphi), \end{aligned}\quad (5)$$

where

$$R^\kappa_{n^*}(\zeta,r) = R^\kappa_{n^*}(\zeta,0,0;r) = A^\kappa_{n^*}(\zeta)\, r^{n^*-1}\,\mathrm{e}^{-\zeta r^\kappa}, \quad (6)$$

$$\begin{aligned}A^\kappa_{n^*}(\zeta) &= A^\kappa_{n^*}(\zeta,0,0)\\ &= \left[\kappa(2\zeta)^{\frac{2n^*+1}{\kappa}}\Big/\Gamma\left(\frac{2n^*+1}{\kappa}\right)\right]^{1/2}. \end{aligned}\quad (7)$$

The slater type orbitals (STO) and Gaussian type orbitals (GTO) are the special cases of φ^κ-GETO for $\kappa=1$ and $\kappa=2$, respectively, i.e.,

$$\begin{aligned}\chi_{n^*lm}(\zeta,\boldsymbol{r}) &= \varphi^1_{n^*lm}(\zeta,\boldsymbol{r})\\ &= (2\zeta)^{n^*+\frac{1}{2}}\left[\Gamma(2n^*+1)\right]^{-1/2}\\ &\quad\times r^{n^*-1}\,\mathrm{e}^{-\zeta r}S_{lm}(\theta,\varphi), \end{aligned}\quad (8)$$

$$\begin{aligned}G_{n^*lm}(\zeta,\boldsymbol{r}) &= \varphi^2_{n^*lm}(\zeta,\boldsymbol{r})\\ &= \left[\frac{2(2\zeta)^{n^*+\frac{1}{2}}}{\Gamma\left(\frac{2n^*+1}{2}\right)}\right]^{1/2}\\ &\quad\times r^{n^*-1}\,\mathrm{e}^{-\zeta r^2}S_{lm}(\theta,\varphi). \end{aligned}\quad (9)$$

The normalized Ψ^κ-GETO HC, φ^κ-GETO, χ-STO and G-GTO with integer principal quantum numbers can be obtained from Eqs. (1), (5), (8), and (9) for $n^*=n$, where n is an integer.

3. Expressions for GETO HC in position, momentum and four-dimensional spaces

In order to obtain the formulae for GETO HC functions in position, momentum, and four-dimensional spaces, we use Eq. (1) in the following form:

$$\Psi^\kappa_{n^*lm}(\zeta,\beta,\gamma;\boldsymbol{r}) = \frac{1}{2}\mathrm{A}^\kappa_{n^*}(\zeta,\beta,\gamma) \times \sum_{j=-1}^{1}{}' \,\mathrm{e}^{-j\gamma}\Gamma^\kappa_{n^*lm}(\xi_j,\boldsymbol{r}), \quad (10)$$

where $\xi_j=\zeta+j\beta>0$ and

$$\Gamma^\kappa_{n^*lm}(\xi_j,\boldsymbol{r}) = r^{n^*-1}\,\mathrm{e}^{-\xi_j r^\kappa}S_{lm}(\theta,\varphi). \quad (11)$$

Function Γ^κ can be expanded into series over complete orthonormal sets of ψ^α-ETO introduced in Ref. [17] as

$$\begin{aligned}\Gamma^\kappa_{n^*lm}(\xi_j,\boldsymbol{r}) &= \Gamma^{\kappa\alpha}_{n^*lm}(\xi_j,\boldsymbol{r})\\ &= \sum_{n=l+1}^{\infty}\bar{\omega}^{\kappa\alpha l^*}_{n^*n}(\xi_j,\eta)\,\psi^\alpha_{nlm}(\eta,\boldsymbol{r}), \end{aligned}\quad (12)$$

where $-\infty<\alpha\le 2$, $\eta>0$, and

$$\begin{aligned}\bar{\omega}^{\kappa\alpha l}_{n^*n}(\xi_j,\eta) &= \int\Gamma^{\kappa^*\alpha}_{n^*lm}(\xi_j,\boldsymbol{r})\,\bar{\psi}^\alpha_{nlm}(\eta,\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}\\ &= \int_0^\infty r^{n^*+1}\,\mathrm{e}^{-\xi_j r^\kappa}\bar{R}^\alpha_{nl}(\eta,r)\,\mathrm{d}r. \end{aligned}\quad (13)$$

Now we take into account the relation in Ref. [17]

$$\begin{aligned}\bar{R}^\alpha_{nl}(\eta,r) &= \left(\frac{2n}{2\eta r}\right)^\alpha R^\alpha_{nl}(\eta,r)\\ &= (2n)^\alpha\sum_{u=l+1}^{n}\frac{\omega^{\alpha l}_{nu}}{\sqrt{(2u)!}}(2\eta)^{u-\alpha+\frac{1}{2}}\\ &\quad\times r^{u-\alpha-1}\,\mathrm{e}^{-\eta r}, \end{aligned}\quad (14)$$

then we obtain

$$\bar{\omega}^{\kappa\alpha l}_{n^*n}(\xi_j,\eta) = \frac{(2n)^\alpha}{(2\eta)^{n^*+\frac{1}{2}}}\sum_{u=l+1}^{n}\frac{\omega^{\alpha l}_{nu}}{\sqrt{(2u)!}}I^{\kappa\alpha}_{n^*u}(\xi_j,\eta), \quad (15)$$

$$I^{\kappa\alpha}_{n^*u}(\xi_j,\eta) = \int_0^\infty t^{n^*+u-\alpha}\,\mathrm{e}^{-\varepsilon_j^\kappa t^\kappa-\frac{t}{2}}\,\mathrm{d}t, \quad (16)$$

where

$$\varepsilon_j^\kappa = \frac{\xi_j}{(2\eta)^\kappa} = \frac{\zeta+j\beta}{(2\eta)^\kappa}.$$

See Eqs. (16), (19) and (20) of Ref. [14] for a exact definition of integral (16).

Using Fourier transforms of ψ^α-ETO[18,19] it is easy to obtain the formulae for functions $\Gamma^{\kappa\alpha}$ in momentum and four-dimensional spaces

$$\Gamma^{\kappa\alpha}_{n^*lm}(\xi_j,\boldsymbol{k}) = \sum_{n=l+1}^{\infty}\bar{\omega}^{\kappa\alpha l^*}_{n^*n}(\xi_j,\eta)\,\phi^\alpha_{nlm}(\eta,\boldsymbol{k}), \quad (17)$$

$$\Gamma^{\kappa\alpha}_{n^*lm}(\xi_j,\boldsymbol{\Omega}_k) = \sum_{n=l+1}^{\infty}\bar{\omega}^{\kappa\alpha l^*}_{n^*n}(\xi_j,\eta)\,z^\alpha_{nlm}(\eta,\boldsymbol{\Omega}_k), \quad (18)$$

where $\boldsymbol{\Omega}_k\equiv\boldsymbol{\Omega}_k(\beta\theta\varphi)$. Then, taking into account Eqs. (12), (17), and (18) we obtain for the functions $\Psi^{\kappa\alpha}$, $\Phi^{\kappa\alpha}$ and $Z^{\kappa\alpha}$ a large number of relations ($\alpha=2,\,1,\,0,\,-1,\,-2,\ldots$) in position, momentum, and four-dimensional spaces through the complete orthonormal

sets of ψ^α-ETO, ϕ^α-momentum space orbitals (ϕ^α-MSO), and Z^α-hyperspherical harmonics (Z^α-HSH):

$$\begin{aligned} & Q^{\kappa\alpha}_{n^*lm}(\zeta,\beta,\gamma;\boldsymbol{x}) \\ &= \frac{1}{2}A^{\kappa}_{n^*}(\zeta,\beta,\gamma)\sum_{n=l+1}^{\infty}\left[\sum_{j=-1}^{1}{}'\,\mathrm{e}^{-j\gamma}\bar{\omega}^{\kappa\alpha l\,*}_{n^*n}(\xi_j,\eta)\right] \\ &\quad\times f^{\alpha}_{nlm}(\eta,\boldsymbol{x}), \end{aligned} \tag{19}$$

where $Q^{\kappa\alpha}\equiv\Psi^{\kappa\alpha}, \Phi^{\kappa\alpha}, Z^{\kappa\alpha}$; $f^\alpha\equiv\psi^\alpha, \phi^\alpha, z^\alpha$; $\boldsymbol{x}\equiv\boldsymbol{r}$, $\boldsymbol{k}$, $\mathrm{d}\boldsymbol{\Omega}_k(\beta\theta\varphi)$.

4. One-range addition theorems of GETO HC, GMSO HC, and GHSH HC

The formulae for one-range addition theorems can be obtained by using Eq. (20) in the form of

$$\begin{aligned} & Q^{\kappa\alpha}_{n^*lm}(\zeta,\beta,\gamma;\boldsymbol{x}-\boldsymbol{y}) \\ &= \frac{1}{2}A^{\kappa}_{n^*}(\zeta,\beta,\gamma)\sum_{n=l+1}^{\infty}\left[\sum_{j=-1}^{1}{}'\,\mathrm{e}^{-j\gamma}\bar{\omega}^{\kappa\alpha l^*}_{n^*n}(\xi_j,\eta)\right] \\ &\quad\times f^{\alpha}_{nlm}(\eta,\boldsymbol{x}-\boldsymbol{y}), \end{aligned} \tag{20}$$

where $\boldsymbol{y}\equiv\boldsymbol{R}$, $\boldsymbol{p}$, $\mathrm{d}\boldsymbol{\Omega}_p(\beta\theta\phi)$. Now we use the formulae for one-range addition theorems of functions $f^\alpha\equiv\psi^\alpha$-ETO, ϕ^α-MSO and Z^α-HSH in position, momentum, and four-dimensional spaces, respectively. Then, we obtain for the one-range addition theorems the following combined relation:

$$\begin{aligned} & Q^{\kappa\alpha}_{n^*lm}(\zeta,\beta,\gamma;\boldsymbol{x}-\boldsymbol{y}) \\ &= \frac{1}{2}A^{\kappa}_{n^*}(\zeta,\beta,\gamma)\sum_{n'=1}^{\infty}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}\Bigg\{\sum_{n=l+1}^{\infty} \\ &\quad\times\left[\sum_{j=-1}^{1}{}'\,\mathrm{e}^{-j\gamma}\bar{\omega}^{\kappa\alpha l^*}_{n^*n}(\xi_j,\eta)\right] \\ &\quad\times\bar{S}^{\alpha}_{nlm,n'l'm'}(\eta,\eta;\boldsymbol{y})\Bigg\}f^{\alpha}_{n'l'm'}(\eta,\boldsymbol{x}), \end{aligned} \tag{21}$$

where

$$\begin{aligned} & \bar{S}^{\alpha}_{nlm,n'l'm'}(\eta,\eta;\boldsymbol{y}) \\ &= \int f^{\alpha\,*}_{nlm}(\eta,\boldsymbol{x}-\boldsymbol{y})\bar{f}^{\alpha}_{n'l'm'}(\eta,\boldsymbol{x})\,\mathrm{d}\boldsymbol{x} \end{aligned} \tag{22}$$

are the overlap integrals. The formulae for overlap integrals (22) in position, momentum, and four-dimensional spaces are presented in Refs. [20] and [21].

We can use Eqs. (21) and (22) for the determination of χ-STO, u-MSO and v-HSH. For this purpose one should take into account the following relations:[17]

$$f^{\alpha}_{nlm}(\eta,\boldsymbol{x})=\sum_{u=l+1}^{n}\omega^{\alpha l}_{nu}\varphi_{ulm}(\eta,\boldsymbol{x}), \tag{23}$$

$$\bar{f}^{\alpha}_{nlm}(\eta,\boldsymbol{x})=(2n)^{\alpha}\sum_{u=l+1}^{n}\omega^{\alpha l}_{nu}\varphi^{\alpha}_{ulm}(\eta,\boldsymbol{x}), \tag{24}$$

where $\varphi^{\alpha}_{nlm}=\frac{1}{(2\eta x)^\alpha}\varphi_{nlm}$, $\varphi_{nlm}\equiv\chi_{nlm}$, u_{nlm}, v_{nlm}, and $\boldsymbol{x}\equiv\boldsymbol{r},\boldsymbol{k},\boldsymbol{\Omega}_k(\beta\,\theta\,\varphi)$.

We can see from Eqs. (21)–(24) that the integer and non-integer n GETO HC, GMSO HC and GHSH HC can be determined with the help of one-range addition theorems of ψ^α-ETO and χ-STO in position, momentum, and four-dimensional spaces, respectively. These formulae can be used in the accurate electronic structure calculations when the GETO HC, GMSO HC, and GHSH HC are employed as basis functions in linear combination of atomic orbitals–molecular obital (LCAO–MO) approximation.

5. Conclusion

It is well-known that the quality of electronic structure calculations depends on the used basis functions. In this work, we construct the new combined wave functions in position, momentum, and four-dimensional spaces and their one-range addition theorems. These formulae can be useful for accurately calculating the electronic structures of atomic and molecular systems when HFR approximation is employed in position, momentum, and four-dimensional spaces.

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