One-range addition theorems for generalized integer and noninteger μ Coulomb, and exponential type correlated interaction potentials with hyperbolic cosine in position, momentum, and four-dimensional spaces

I. I. Guseinov†

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

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The formulae are established in position, momentum, and four-dimensional spaces for the one-range addition theorems of generalized integer and noninteger μ Coulomb, and exponential type correlated interaction potentials with hyperbolic cosine (GCTCP and GETCP HC). These formulae are expressed in terms of one-range addition theorems of complete orthonormal sets of Ψ^α-exponential type orbitals (Ψ^α-ETO), ϕ^α-momentum space orbitals (ϕ^α-MSO), and z^α-hyperspherical harmonics (z^α-HSH) introduced. The one-range addition theorems obtained can be useful in the electronic structure calculations of atoms and molecules when the GCTCP and GETCP HC in position, momentum, and four-dimensional spaces are employed.

Keywords: correlated interaction potentials, one-range additional theorems, complete orthonormal sets of orbitals, overlap integrals

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1. Introduction

Most electronic structure calculations of quantities for multielectron atomic and molecular systems require accurate solutions of the Hartree–Fock (HF) approximation.[1] To improve the HF solutions, one can use more accurate wave functions that include electron correlation by means of the Hylleraas correlated wave function (Hy) and configuration interaction (CI) approaches.[2−7] We notice that CI convergent expansion is much slower than Hy method expansions. The Hy method, first developed by James and Collidge,[8] is still valid for two- and three-electron atomic and molecular systems (see, e.g., Refs. [9]–[11] and references therein). A drawback in the Hy-type expansions, however, is the complexity of the calculation of multicenter multielectron integrals. There are other correlation approaches, such as the explicitly correlated interaction potential (CIP) methods.[12] The principal tools of the CIP methods are the one-range additional theorems. The use of one-range addition theorems is highly desirable since they are capable of simplifying subsequent integrations in multicenter integrals substantially. The one-range addition theorems established in our published papers using complete orthonormal sets of Ψ^α-ETO[13] could be utilized for the calculation of arbitrary multicenter multielectron integrals occurring in the explicitly correlated theories. The origin of Ψ^α-ETO, where $-\infty < \alpha \leq 2$, is the centrally symmetric potential which contains the core attraction potential and the quantum frictional potential of the field produced by the particle itself.[14] The quantum frictional forces are the analog of radiation damping or frictional forces suggested by Lorentz in classical electrodynamics.

In our previous papers,[15,16] using complete orthonormal basis sets of Ψ^α, ϕ^α, and z^α functions, the expansion formulae were derived for the two-center charge densities of integer and noninteger n generalized exponential-type orbitals with hyperbolic cosine (GETO HC) in position space. The aim of this work is to establish, using the method given in Refs. [15] and [16], the one-range addition theorems for the integer and noninteger μ GCTCP and GETCP HC in position, momentum, and four-dimensional spaces.

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

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2. Definitions and basic formulas

The integer and noninteger μ GCTCP (for $\xi = \delta = \tau = 0$) and GETCP HC ($\xi > 0$) in position space are defined as

$$V^{\kappa}_{\mu^*\nu\sigma}(\xi,\delta,\tau;\boldsymbol{r}) = V^{\kappa}_{\mu^*}(\xi,\delta,\tau;\boldsymbol{r})\bar{S}_{\nu\sigma}(\theta,\varphi), \quad (1)$$

where $V^{\kappa}_{\mu^*}$ and $\bar{S}_{\nu\sigma}$ are the radial and the angular parts of correlated potentials, respectively,

$$V^{\kappa}_{\mu^*}(\xi,\delta,\tau;r) = r^{\mu^*-1}\,\mathrm{e}^{-\xi r^{\kappa}}\cosh(\delta r^{\kappa}+\tau), \quad (2)$$

$$\bar{S}_{\nu\sigma}(\theta,\phi) = \Big(\frac{4\pi}{2\nu+1}\Big)^{1/2} S_{\nu\sigma}(\theta,\varphi). \quad (3)$$

Here, μ^* is the noninteger and integer (for $\mu^* = \mu$) indices, $\kappa > 0$, $\xi \geq 0$, $-\xi \leq \delta \leq \xi$, τ can be either positive, zero or negative and

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

The special cases of generalized GETCP HC for $\kappa = 1$ and $\kappa = 2$ correspond to the exponential and the Gaussian-type correlated potentials with hyperbolic cosine (ETCP HC and GTCP HC), respectively.[15] We notice that the GCTCP is the special case of GETCP HC for $\xi = \delta = \tau = 0$. Therefore, the GCTCP is defined as

$$V_{\mu^*\nu\sigma}(\boldsymbol{r}) = r^{\mu^*-1}S_{\nu\sigma}(\theta,\varphi). \quad (5)$$

With the derivation of one-range addition theorems in position space we rewrite Eq. (1) in the following form:

$$V^{\kappa}_{\mu^*\nu\sigma}(\xi,\delta,\tau;\boldsymbol{r}) = \frac{1}{2}\Big(\frac{4\pi}{2\nu+1}\Big)^{1/2}\sum_{i=-1}^{1}{}' \,\mathrm{e}^{-\mathrm{i}\,\tau}\mathscr{L}^{\kappa}_{\mu^*\nu\sigma}(\xi_i,\boldsymbol{r}), \quad (6)$$

where $\xi_i = \xi + \mathrm{i}\,\delta \geq 0$ and

$$\mathscr{L}^{\kappa}_{\mu^*\nu\sigma}(\xi_i,\boldsymbol{r}) = r^{\mu^*-1}\,\mathrm{e}^{-\xi_i r^{\kappa}}S_{\nu\sigma}(\theta,\varphi). \quad (7)$$

Now we expand the function $\mathscr{L}^{\kappa}$ into series over complete orthonormal sets of Ψ^{α}-ETO (see Refs. [15] and [16]):

$$\mathscr{L}^{\kappa}_{\mu^*\nu\sigma}(\xi_i,\boldsymbol{r}) = \sum_{\mu=\nu+1}^{\infty}\bar{\omega}^{\kappa\alpha\nu^*}_{\mu^*\mu}(\xi_i,\eta)\Psi^{\alpha}_{\mu\nu\sigma}(\eta,\boldsymbol{r}), \quad (8)$$

where $\eta > 0$ and

$$\bar{\omega}^{\kappa\alpha\nu}_{\mu^*}(\xi_i,\eta) = \int \mathscr{L}^{\kappa^*}_{\mu^*\nu\sigma}(\xi_i,\boldsymbol{r})\bar{\Psi}^{\alpha}_{\mu\nu\sigma}(\eta,\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} = \int_0^{\infty} r^{\mu^*+1}\,\mathrm{e}^{-\xi_i r^{\kappa}}\bar{R}^{\alpha}_{\mu\nu}(\eta,r)\,\mathrm{d}r. \quad (9)$$

Taking into account the relation[17]

$$\bar{R}^{\alpha}_{\mu\nu}(\eta,r) = (2\mu)^{\alpha}\sum_{u=\nu-\alpha+1}^{\mu-\alpha}\frac{1}{\sqrt{[2(u+\alpha)]!}}\omega^{\alpha\nu}_{\mu\,u+\alpha}(2\eta)^{u+1/2}r^{u-1}\,\mathrm{e}^{-\eta r}, \quad (10)$$

we obtain

$$\bar{\omega}^{\kappa\alpha\nu}_{\mu^*\mu}(\xi_i,\eta) = \frac{(2\mu)^{\alpha}}{(2\eta)^{\mu^*+1/2}}\sum_{u=\nu-\alpha+1}^{\mu-\alpha}\frac{\omega^{\alpha\nu}_{\mu\,u+\alpha}}{\sqrt{[2(u+\alpha)]!}}I^{\kappa}_{\mu^*+u}(\xi_i,\eta), \quad (11)$$

where $\gamma^{\kappa}_i = \dfrac{\xi_i}{(2\eta)^{\kappa}} = \dfrac{\xi+\mathrm{i}\,\delta}{(2\eta)^{\kappa}}$ and

$$I^{\kappa}_{\mu^*+u}(\xi_i,\eta) = \int_0^{\infty} t^{\mu^*+u}\,\mathrm{e}^{-\gamma^{\kappa}_i t^{\kappa}-t/2}\,\mathrm{d}t. \quad (12)$$

See Eqs. (16), (19), and (20) of Ref. [15] for the exact definition of integral (12).

The formulae for functions $\mathscr{L}^{\kappa}$ in momentum and four-dimensional spaces can be obtained by making use of Fourier transforms of Ψ^{α}-ETO:[18,19]

$$\mathscr{L}^{\alpha}_{\mu^*\nu\sigma}(\xi_i,\boldsymbol{k}) = \sum_{\mu=\nu+1}^{\infty}\bar{\omega}^{\kappa\alpha\nu^*}_{\mu^*\mu}(\xi_i,\eta)\phi^{\alpha}_{\mu\nu\sigma}(\eta,\boldsymbol{k}), \quad (13)$$

$$\mathscr{L}^{\alpha}_{\mu^*\nu\sigma}(\xi_i,\boldsymbol{\Omega}_k) = \sum_{\mu=\nu+1}^{\infty}\bar{\omega}^{\kappa\alpha\nu^*}_{\mu^*\mu}(\xi_i,\eta)z^{\alpha}_{\mu\nu\sigma}(\eta,\boldsymbol{\Omega}_k), \quad (14)$$

where $\boldsymbol{\Omega}_k \equiv \boldsymbol{\Omega}(\beta_k\theta_k\varphi_k)$. Then, using formulae (8), (13), and (14) we obtain a large number ($\alpha = 2,1,0,-1,-2,\ldots$) of relations for the interaction potentials V^{κ}, M^{κ}, and F^{κ} in position, momentum, and four-dimensional spaces

through the complete orthonormal sets of Ψ^{α}-ETO, ϕ^{α}-MSO, and z^{α}-HSH:

$$P^{\kappa}_{\mu^*\nu\sigma}(\xi,\delta,\tau;\boldsymbol{x}) = \frac{1}{2}\Big(\frac{4\pi}{2\nu+1}\Big)^{1/2} \sum_{\mu=\nu+1}^{\infty} \Big[\sum_{i=-1}^{1} \mathrm{e}^{-\mathrm{i}\,\tau} \bar{\omega}^{\kappa\alpha\nu *}_{\mu^*\mu}(\xi_i,\eta)\Big] f^{\alpha}_{\mu\nu\sigma}(\eta,\boldsymbol{x}), \tag{15}$$

where $P^{\kappa} \equiv V^{\kappa}$, M^{κ}, F^{κ}; $f^{\alpha} \equiv \Psi^{\alpha}$, ϕ^{α}, z^{α}; $\boldsymbol{x} \equiv \boldsymbol{r}$, $\boldsymbol{k}$, $\mathrm{d}\boldsymbol{\Omega}$ $(\beta_k\theta_k\varphi_k)$.

3. One-range addition theorems of GETCP HC

In order to establish the formulae for one-range addition theorems of GETCP HC we utilize Eq. (15) in the following form:

$$P^{\kappa}_{\mu^*\nu\sigma}(\xi,\delta,\tau;\boldsymbol{x}-\boldsymbol{y}) = \frac{1}{2}\Big(\frac{4\pi}{2\nu+1}\Big)^{1/2} \sum_{\mu=\nu+1}^{\infty} \Big[\sum_{i=-1}^{1}{}' \mathrm{e}^{-\mathrm{i}\,\tau} \bar{\omega}^{\kappa\alpha\nu^*}_{\mu^*\mu}(\xi_i,\eta)\Big] f^{\alpha}_{\mu\nu\sigma}(\eta,\boldsymbol{x}-\boldsymbol{y}), \tag{16}$$

where $\boldsymbol{y} \equiv \boldsymbol{R}$, $\boldsymbol{p}$, $\mathrm{d}\boldsymbol{\Omega}$ $(\beta_p\theta_p\varphi_p)$. Then, using formulae for one-range addition theorems of functions $f^{\alpha} \equiv \Psi^{\alpha}$-ETO, ϕ^{α}-MSO, and z^{α}-HSH, we obtain for the one-range addition theorems of GETCP HC the following relations:

$$\begin{aligned} &P^{\kappa}_{\mu*\nu\sigma}(\xi,\delta,\tau;\boldsymbol{x}-\boldsymbol{y}) \\ &= \frac{1}{2}\Big(\frac{4\pi}{2\nu+1}\Big)^{1/2} \sum_{\mu'=1}^{\infty} \sum_{\nu'=0}^{\mu'-1} \sum_{\sigma'=-\nu'}^{\nu'} \Big\{ \sum_{\mu=\nu+1}^{\infty} \Big[\sum_{i=-1}^{1}{}' \mathrm{e}^{-\mathrm{i}\,\tau} \bar{\omega}^{\kappa\alpha\nu\ *}_{\mu*\mu}(\xi_i,\eta)\Big] \bar{S}^{\alpha*}_{\mu\nu\sigma,\mu'\nu'\sigma'}(\eta,\eta;\boldsymbol{y})\Big\} f^{\alpha}_{\mu'\nu'\sigma'}(\eta,\boldsymbol{x}), \end{aligned} \tag{17}$$

where $\bar{S}^{\alpha}$ are the overlap integrals defined as

$$\bar{S}^{\alpha}_{\mu\nu\sigma,\mu'\nu'\sigma'}(\eta,\eta;\boldsymbol{y}) = \int f^{\alpha\,*}_{\mu\nu\sigma}(\eta,\boldsymbol{x}-\boldsymbol{y}) \bar{f}^{\alpha}_{\mu'\nu'\sigma'}(\eta,\boldsymbol{x})\,\mathrm{d}^3\boldsymbol{x}. \tag{18}$$

See Refs. [17] and [20] for the definition of overlap integrals (18) in position, momentum, and four-dimensional spaces.

It should be noted that Eqs. (17) and (18) can also be employed for the χ-Slater type orbitals (χ-STO), u-momentum space orbitals (u-MSO), and v-hyperspherical harmonics (v-HSH) in position, momentum, and four-dimensional spaces.[19] For this purpose one should use the following relations:[17,19]

$$f^{\alpha}_{nlm}(\eta,\boldsymbol{x}) = \sum_{\mu=l+1}^{n} \omega^{\alpha l}_{n\mu} \varphi_{\mu lm}(\eta,\boldsymbol{x}), \tag{19}$$

$$\bar{f}^{\alpha}_{nlm}(\eta,\boldsymbol{x}) = (2n)^{\alpha} \sum_{\mu=l-\alpha+1}^{n-\alpha} \Big\{(2\mu)!/[2(\mu+\alpha)]!\Big\}^{1/2} \omega^{\alpha l}_{n\mu+\alpha} \varphi_{\mu lm}(\eta,\boldsymbol{x}), \tag{20}$$

where $\varphi_{\mu lm} \equiv \chi_{\mu lm}$, $u_{\mu lm}$, $v_{\mu lm}$, and $\boldsymbol{x} \equiv \boldsymbol{r}, \boldsymbol{k}, \boldsymbol{\Omega}$ $(\beta_k\,\theta_k\,\varphi_k)$.

Thus, we have derived the formulae for one-range addition theorems of integer and noninteger μ GCTCP (for $\xi = \delta = \tau = 0$) and GETCP HC in terms of Ψ^{α}-ETO and χ-STO in position, momentum, and four-dimensional spaces. The final results are especially useful for the computations of multicenter integrals of GETCP HC using symmetrical and nonsymmetrical one-range addition theorems[21,22] when the Ψ^{α}-ETO and χ-STO basis functions in position, momentum, and four-dimensional spaces are employed. The formulae obtained can be used in the electronic structure calculations when the GETCP HC are employed as basis functions in Hartree–Fock–Roothaan approximation.

4. Conclusion

Accurate evaluation of the physical properties of atomic and molecular systems depends on the used basis sets of functions. The choice of basis functions is a prime importance, since the quality of calculations depends on their nature. For this purpose, we utilize in this work the method given in our previous papers for employing the correlated interaction potentials and their one-range addition theorems. Therefore, the algorithm presented in this study can be use-

ful for the accurate calculations of electronic structure when LCAO-MO approximation is employed.

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