Expansion and one-range addition theorems for complete orthonormal sets of spinor wave functions and Slater spinor orbitals of arbitrary half-integral spin in position, momentum and four-dimensional spaces

I.I. Guseinov

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

Abstract

The analytical relations in position, momentum and four-dimensional spaces are established for the expansion and one-range addition theorems of relativistic complete orthonormal sets of exponential type spinor wave functions and Slater spinor orbitals of arbitrary half-integral spin. These theorems are expressed through the corresponding nonrelativistic expansion and one-range addition theorems of the spin-0 particles introduced by the author. The expansion and one-range addition theorems derived are especially useful for the computation of multicenter integrals over exponential type spinor orbitals arising in the generalized relativistic Dirac-Hartree-Fock-Roothaan theory when the position, momentum and four-dimensional spaces are employed.

Key words: Exponential type spinor orbitals, Slater type spinor orbitals, Addition theorems, Relativistic Dirac-Hartree-Fock-Roothaan theory

1. Introduction

The solutions of the Dirac equation for hydrogen-like systems play a significant role in theory and application to relativistic quantum mechanics of atoms, molecules and nuclei. However, the relativistic hydrogen-like position orbitals and their extensions to momentum and four-dimensional spaces cannot be used as basis sets because they are not complete unless the continuum is included [1-4]. In Ref. [5] we have constructed in position, momentum and four-dimensional spaces the complete orthonormal sets of two- and four-component relativistic spinor wave functions based on the use of complete orthonormal sets of nonrelativistic orbitals. By the use of this method, in a previous work [6], we introduced the new complete orthonormal sets of relativistic $\Psi^{\alpha i}$-exponential type spinor orbitals ($\Psi^{\alpha i}$-ETSO) and $X^\alpha$-Slater type spinor orbitals ($X^\alpha$-STSO) for particles with arbitrary half-integral spin in position, momentum and four-dimensional spaces through the corresponding
nonrelativistic $\psi^\alpha$-exponential type orbitals ($\psi^\alpha$-ETO) [7] and $\chi$-Slater type orbitals ($\chi$-STO). The elaboration of algorithm for the solution of generalized Dirac equations [8] in linear combination of atomic spinor orbitals (LCASO) approach necessitates progress in the development of theory for one-range addition theorems of spinor orbitals of multiple order.

Addition theorems play a more and more important role in nonrelativistic and relativistic atomic and molecular electronic structure calculations [9]. Two fundamentally different types of addition theorems occur in the literature. The first type of the addition theorems has the two-range form of Laplace expansion for the Coulomb potential. There is second class of addition theorems which can be constructed by expanding a function located at a center $a$ in terms of a complete orthonormal set located at a center $b$. The use of one-range addition theorems in electronic structure calculations would be highly desirable since they are capable of producing much better approximations than the two-range addition theorems. In Refs.[10-13] we have developed the method for constructing in position, momentum and four-dimensional spaces the one-range addition theorems of complete orthonormal sets of nonrelativistic $\psi^\alpha$-ETO and $\chi$-STO. The aim of this work is to derive the relevant expansion and one-range addition theorems of complete orthonormal sets of relativistic $\Psi^{\alpha s}$-ETSO and $\chi^s$-STSO in position, momentum and four-dimensional spaces through the corresponding theorems for nonrelativistic orbitals $\psi^\alpha$-ETO and $\chi$-STO. These theorems might be useful for the calculation of multicenter integrals which appear in relativistic MO LCASO theory of arbitrary half-integral spin particles when the spinor orbitals basis sets in position, momentum and four-dimensional spaces are employed.

2. Definitions and basic formulas

In order to derive the expansion and one-range addition theorems for 2(2s+1)-component spinor orbitals in position, momentum and four-dimensional spaces we use the following definitions:

Complete orthonormal sets of nonrelativistic orbitals

$$k_{\alpha l m}^{\alpha}(\zeta, \bar{x}) \equiv \psi_{\alpha l m}^{\alpha}(\zeta, \vec{r}), \phi_{\alpha l m}^{\alpha}(\zeta, \vec{k}), z_{\alpha l m}^{\alpha}(\zeta, \vec{\kappa})$$  \hspace{1cm} (1)

$$\bar{k}_{\alpha l m}^{\alpha}(\zeta, \bar{x}) \equiv \bar{\psi}_{\alpha l m}^{\alpha}(\zeta, \vec{r}), \bar{\phi}_{\alpha l m}^{\alpha}(\zeta, \vec{k}), \bar{z}_{\alpha l m}^{\alpha}(\zeta, \vec{\kappa})$$  \hspace{1cm} (2)
Slater type nonrelativistic spinor orbitals

\[ k_{nlm}(\zeta, \vec{x}) \equiv \chi_{nlm}(\zeta, \vec{r}), u_{nlm}(\zeta, \vec{k}), v_{nlm}(\zeta, \vec{\alpha}_k), \]  

(3)

Complete orthonormal sets of 2(2s+1)-component relativistic spinor orbitals

\[ {^t\mathbf{K}}_{nljm}^{(\alpha)}(\zeta, \vec{\alpha}_k) \equiv {^t\Psi}_{nljm}^{(\alpha)}(\zeta, \vec{r}), {^t\Phi}_{nljm}^{(\alpha)}(\zeta, \vec{k}), {^tZ}_{nljm}^{(\alpha)}(\zeta, \vec{\alpha}_k) \]  

(4a)

\[ {^t\mathbf{K}}_{nljm}^{(\zeta)}(\zeta, \vec{x}) \equiv {^t\Psi}_{nljm}^{(\zeta)}(\zeta, \vec{r}), {^t\Phi}_{nljm}^{(\zeta)}(\zeta, \vec{k}), {^tZ}_{nljm}^{(\zeta)}(\zeta, \vec{\alpha}_k) \]  

(4b)

\[ {^t\mathbf{R}}_{nljm}^{(\alpha)}(\zeta, \vec{x}) \equiv {^t\Psi}_{nljm}^{(\alpha)}(\zeta, \vec{r}), {^t\Phi}_{nljm}^{(\alpha)}(\zeta, \vec{k}), {^tZ}_{nljm}^{(\alpha)}(\zeta, \vec{\alpha}_k) \]  

(5a)

\[ {^t\mathbf{R}}_{nljm}^{(\zeta)}(\zeta, \vec{x}) \equiv {^t\Psi}_{nljm}^{(\zeta)}(\zeta, \vec{r}), {^t\Phi}_{nljm}^{(\zeta)}(\zeta, \vec{k}), {^tZ}_{nljm}^{(\zeta)}(\zeta, \vec{\alpha}_k) \]  

(5b)

Slater type 2(2s+1)-component relativistic spinor orbitals

\[ {^t\mathbf{K}}_{nljm}^{(\alpha)}(\zeta, \vec{x}) \equiv {^t\Psi}_{nljm}^{(\alpha)}(\zeta, \vec{r}), {^t\Phi}_{nljm}^{(\alpha)}(\zeta, \vec{k}), \]  

(6a)

\[ {^t\mathbf{K}}_{nljm}^{(\zeta)}(\zeta, \vec{x}) \equiv {^t\Psi}_{nljm}^{(\zeta)}(\zeta, \vec{r}), {^t\Phi}_{nljm}^{(\zeta)}(\zeta, \vec{k}), {^tZ}_{nljm}^{(\zeta)}(\zeta, \vec{\alpha}_k) \]  

(6b)

where \( \vec{x} \equiv \vec{r}, \vec{k}, \vec{\alpha}_k \) and \( \omega_k \equiv \beta_{\zeta} \theta \varphi \).

See Refs.[6] and [14-15] for the exact definition of quantities occurring in Eqs (1)-(6).

We shall also use the following formulas for 2(2s+1)-component spinor orbitals through the independent sets of two-component spinors defined as a product of complete orthonormal sets of radial parts of nonrelativistic scalar \( \psi^{(\alpha)} \) -ETO and modified Clebsch-Gordan coefficients appearing in two-component tensor spherical harmonics (see Refs.[6] and [14-15]):

for \( {^tK}_{nljm}^{text{ETSO}} \)

\[ {^tK}_{nljm}^{text{ETSO}}(\zeta, \vec{x}) = N_{nl} \begin{bmatrix} {^tK}_{nljm}^{text{ETSO}0}(\zeta, \vec{x}) \\ {^tK}_{nljm}^{text{ETSO2}(\zeta, \vec{x})} \\ : \\ : \\ {^tK}_{nljm}^{text{ETSO2}_s(\zeta, \vec{x})} \\ {^tK}_{nljm}^{text{ETSO2}_s}(\zeta, \vec{x}) \\ : \\ : \\ {^tK}_{nljm}^{text{ETSO2}_s}(\zeta, \vec{x}) \\ {^tK}_{nljm}^{text{ETSO0}}(\zeta, \vec{x}) \end{bmatrix} \]  

(7a)
\[ tK'_{nljm}^\alpha(\zeta, \bar{x}) = \begin{bmatrix} \eta_t a^{l_\nu}_{jm} (\lambda) k_{nljm(+)}^\alpha (\zeta, \bar{x}) \\ -\eta_t a^{l_\nu}_{jm} (\lambda + 1) k_{nljm(+1)}^\alpha (\zeta, \bar{x}) \end{bmatrix} \] (7b)

\[ tK'_{nljm}^{\alpha \lambda}(\zeta, \bar{x}) = \begin{bmatrix} -i t^{l_\nu}_{jm} (2s - \lambda) k_{nljm(+)}^\alpha (\zeta, \bar{x}) \\ -i t^{l_\nu}_{jm} (2s - (\lambda + 1)) k_{nljm(+1)}^\alpha (\zeta, \bar{x}) \end{bmatrix} \] (7c)

for \( K' - ETSO \)

\[ t\bar{K}_{nljm}^{\alpha}(\zeta, \bar{x}) = N_{nljm} \begin{bmatrix} t\bar{K}_{nljm}^{\alpha 0}(\zeta, \bar{x}) \\ t\bar{K}_{nljm}^{\alpha 2}(\zeta, \bar{x}) \\ \vdots \\ t\bar{K}_{nljm}^{\alpha 2s-1}(\zeta, \bar{x}) \\ t\bar{K}_{nljm}^{\alpha 2s}(\zeta, \bar{x}) \end{bmatrix} \] (8a)

\[ t\bar{K}_{nljm}^{\alpha \lambda}(\zeta, \bar{x}) = \begin{bmatrix} \eta_t t^{l_\nu}_{jm} (\lambda) \bar{k}_{nljm(+)}^\alpha (\zeta, \bar{x}) \\ -\eta_t t^{l_\nu}_{jm} (\lambda + 1) \bar{k}_{nljm(+1)}^\alpha (\zeta, \bar{x}) \end{bmatrix} \] (8b)

\[ t\bar{K}_{nljm}^{\alpha \lambda}(\zeta, \bar{x}) = \begin{bmatrix} -i t^{l_\nu}_{jm} (2s - \lambda) \bar{k}_{nljm(+)}^\alpha (\zeta, \bar{x}) \\ -i t^{l_\nu}_{jm} (2s - (\lambda + 1)) \bar{k}_{nljm(+1)}^\alpha (\zeta, \bar{x}) \end{bmatrix} \] (8c)

for \( K' - STSO \)

\[ tK_{nljm}^{\alpha}(\zeta, \bar{x}) = N_{nljm} \begin{bmatrix} tK_{nljm}^{\alpha 0}(\zeta, \bar{x}) \\ tK_{nljm}^{\alpha 2}(\zeta, \bar{x}) \\ \vdots \\ tK_{nljm}^{\alpha 2s-1}(\zeta, \bar{x}) \\ tK_{nljm}^{\alpha 2s}(\zeta, \bar{x}) \end{bmatrix} \] (9a)
2. Expansion and one-range addition theorems for ETSO and STSO

With the derivation of expansion and one-range addition theorems for 2(2s+1)-component spinor orbitals in position, momentum and four-dimensional spaces, we use the method set out in previous papers [16-17] described for the nonrelativistic cases. Then, using Eqs. (7)-(9) and carrying through calculations analogous to those for the nonrelativistic basis sets we obtain the following relations in terms of nonrelativistic cases:

EXTRACTION THEOREMS:

for ETSO

\[ iK^{sl}_{nljm} (\zeta, \bar{x}) = \sum_{\lambda=0}^{2s-1} \left[ \eta_i' a^{\lambda}_{jm} (\lambda) k^{sl}_{nljm} (\zeta, \bar{x}) \right] \]

\[ -\eta_i a^{\lambda+1}_{jm} (\lambda+1) k^{sl}_{nljm} (\zeta, \bar{x}) \]  

\[ iK^{sl}_{nljm} (\zeta, \bar{x}) = \left[ -i' a^{\lambda}_{jm} (2s-\lambda) k^{sl}_{nljm} (\zeta, \bar{x}) \right] \]

\[ -i' a^{\lambda+1}_{jm} (2s-\lambda+1) k^{sl}_{nljm} (\zeta, \bar{x}) \]  

where \( \lambda = 0, 2, \ldots, 2s-1 \).

for STSO

\[ iK^{s'}_{nljm} (\zeta, \bar{x}) = \sum_{\lambda=0}^{2s-1} \left[ \eta_i' a^{s'}_{jm} (\lambda) k^{s'}_{nljm} (\zeta, \bar{x}) \right] \]

\[ -\eta_i a^{s'}_{jm} (\lambda+1) k^{s'}_{nljm} (\zeta, \bar{x}) \]  

\[ iK^{s'}_{nljm} (\zeta, \bar{x}) = \left[ -i' a^{s'}_{jm} (2s-\lambda) k^{s'}_{nljm} (\zeta, \bar{x}) \right] \]

\[ -i' a^{s'}_{jm} (2s-\lambda+1) k^{s'}_{nljm} (\zeta, \bar{x}) \]
\[ n' F_{\nu,\mu,\nu',\mu'}(\zeta', \zeta, \bar{x}) = \left( a_{\nu,\mu}^{\nu'}(2s - \lambda) \right) \left( a_{\nu',\mu'}^{\nu}(2s - \lambda) \right) k_{n,m(\lambda)}(\zeta, \bar{x}) \]

\[ + \left( a_{\nu,\mu}^{\nu'}(2s - (\lambda + 1)) \right) \left( a_{\nu',\mu'}^{\nu}(2s - (\lambda + 1)) \right) k_{n,m(\lambda + 1)}(\zeta, \bar{x}). \]

\[ (11c) \]

**ONE-RANGE ADDITION THEOREMS:**

for **ETSO**

\[ k_{n,m}^{x}(\zeta, \bar{x} - \bar{y}) = \left[ \eta \left( a_{n,m}^{\nu}(\lambda) k_{n,m(\lambda)}(\zeta, \bar{x} - \bar{y}) \right) \right] \]

\[ (12a) \]

\[ k_{n,m}^{x}(\zeta', \bar{x} - \bar{y}) = \left[ -i \left( a_{n,m}^{\nu}(2s - \lambda) k_{n,m(\lambda)}(\zeta, \bar{x} - \bar{y}) \right) \right] \]

\[ (12b) \]

for **STSO**

\[ k_{n,m}^{\nu}(\zeta, \bar{x} - \bar{y}) = \left[ \eta \left( a_{n,m}^{\nu}(\lambda) k_{n,m(\lambda)}(\zeta, \bar{x} - \bar{y}) \right) \right] \]

\[ (13a) \]

\[ k_{n,m}^{\nu}(\zeta', \bar{x} - \bar{y}) = \left[ -i \left( a_{n,m}^{\nu}(2s - \lambda) k_{n,m(\lambda)}(\zeta, \bar{x} - \bar{y}) \right) \right] \]

\[ (13b) \]

where \( \bar{x} \equiv \bar{r}, \bar{k}, \partial_k \) and \( \bar{y} \equiv \bar{R}, \bar{p}, \partial_p \).

The formulas for the expansion and one-range addition theorems for quantities \( \left( k_{n,m}^{\nu}(\zeta, \bar{x}), k_{n,m(\lambda)}^{\nu}(\zeta', \bar{x}), k_{n,m(\lambda + 1)}^{\nu}(\zeta, \bar{x} - \bar{y}) \right) \) and \( \left( k_{n,m}^{\nu}(\zeta, \bar{x}), k_{n,m(\lambda)}^{\nu}(\zeta', \bar{x}), k_{n,m(\lambda + 1)}^{\nu}(\zeta, \bar{x} - \bar{y}) \right) \) occurring on the right hand sides of these equations have been established in previous works [16, 17] and [18, 19], respectively.

As can be seen from the formulas of this work, all of the expansion and one-range addition theorems of 2(2s+1)-component ETSO and STSO defined in position, momentum and four-dimensional spaces are expressed through the corresponding nonrelativistic expansion and one-range addition theorems. Thus, the relations of nonrelativistic expansion and one-range addition theorems derived in previous papers [16-19] can be also used in the case of 2(2s+1)-component spinor orbitals in position, momentum and four-dimensional spaces.
References

1. I.P. Grant, Relativistic Quantum Theory of Atoms and Molecules, Springer, 2006.
2. K.G. Dyall, K. Fægri, Introduction to Relativistic Quantum Chemistry, Oxford University Press, 2007.
3. I.P. Grant, H.M. Quiney, Adv. At. Mol. Phys., 23 (1998) 37.
4. R. Szmytkowski, J. Phys. A: Math. Gen., 31 (1998) 4963.
5. I.I. Guseinov, J. Math. Chem., 47 (2010) 391.
6. I.I. Guseinov, Comput. Phys. Commun.(submitted).
7. I.I. Guseinov, Int. J. Quantum Chem., 90 (2002) 114.
8. I.I. Guseinov, arXiv: 0805.1856v4.
9. I.N. Levine, Quantum Chemistry, 5th ed., Prentice Hall, New Jersey, 2000.
10. I.I. Guseinov, J. Mol. Model., 9 (2003) 135
11. I.I. Guseinov, J. Mol. Model., 9 (2003) 190.
12. I.I. Guseinov, J. Mol. Model., 11 (2005) 124.
13. I.I. Guseinov, J. Mol. Model., 12 (2006) 757.
14. I.I. Guseinov, Phys. Lett. A, 372 (2007) 44.
15. I.I. Guseinov, Phys. Lett. A, 373 (2009) 2178.
16. I.I. Guseinov, J. Math. Chem., 42 (2007) 991.
17. I.I. Guseinov, J. Math. Chem., 43 (2008) 1024.
18. I. I. Guseinov, J. Theor. Comput. Chem., 7 (2008) 257.
19. I. I. Guseinov, Chin. Phys. Lett., 25 (2008) 4240