Combined theory of two- and four-component complete orthonormal sets of spinor wave functions and Slater type spinor orbitals in position, momentum and four-dimensional spaces

I. I. Guseinov

Abstract   By the use of complete orthonormal sets of nonrelativistic scalar orbitals introduced by the author in previous papers the new complete orthonormal basis sets for two- and four-component spinor wave functions, and Slater spinor orbitals useful in the quantum-mechanical description of the spin-1/2 particles by the two- and four-component relativistic equations are established in position, momentum and four-dimensional spaces. These function sets are expressed through the corresponding nonrelativistic orbitals. The analytical formulas for overlap integrals over four-component relativistic Slater spinor orbitals with the same screening constants in position space are also derived. The relations obtained in this study can be useful in the study of different problems arising in the relativistic quantum mechanics when the position, momentum and four dimensional spaces are employed.

1 Introduction

It is well known that the eigenfunctions of the Schrödinger equation of the hydrogen-like atom and their extensions to momentum and four-dimensional spaces by Fock [1,2] are not complete unless the continuum is included. In atomic and molecular electronic structure calculations it is quite common to introduce the complete and orthonormal function sets. The examples of complete and orthonormal functions in position space for the particles with spin $s = 0$ are so-called Lambda and Coulomb Sturmian orbitals introduced by Hylleraas, Shull and Löwdin in Refs. [3–6].

I. I. Guseinov (✉)
Department of Physics, Faculty of Arts and Sciences, Onsekiz Mart University, Çanakkale, Turkey
e-mail: isguseinov@yahoo.com

The relativistic one-electron Coulomb Sturmian wave functions have been developed and discussed by Avery and Antonsen [7].

Vast majority of modern relativistic calculations are being done within numerically more convenient Gaussian type orbitals (GTO) (see [8] and references quoted therein). In the case of the point nuclear model, the GTO do not allow an adequate representation of important properties of the electronic wave function, such as the cusps at the nuclei [9] and the exponential decay at large distances [10]. Therefore, it is desirable to perform the relativistic calculations with the help of exponential type orbitals (ETO), when the point-like nuclear model is used. The Gaussian-type basis sets are the natural and preferable choice when the Gaussian nuclear charge distribution is used. Certainly, this is a better model for reality than the point nucleus.

It should be noted that the straightforward use of relativistic equations for two- or more- particle systems in the calculations with finite basis sets, independent for large and small components, could cause numerical instability known as the Brown-Ravenhall disease [11]. A possible solution of this problem is to use "kinetically balanced" basis sets for the small components [12]. The similar so-called variational collapse arising in the one-particle level can also be avoided by the use of "kinetically balanced" basis sets [13]. We notice that all of these problems are of no practical relevance in todays 4-component calculations, since there are efficient ways to avoid them.

The aim of this work is to derive the new complete orthonormal basis sets for two- and four-component exponential type spinor orbitals arising in relativistic quantum theory of atomic-molecular and nuclear systems. We notice that the definition of phases in this work for the complete spherical harmonics ($Y_{lm}^* = Y_{l,-m}$) differs from the Condon–Shortley phases [14] by the sign factor $(-1)^m$.

2 Nonrelativistic scalar wave functions and Slater orbitals

To construct in position, momentum and four-dimensional spaces the complete orthonormal sets of two- and four-component relativistic spinor wave functions, and Slater spinor orbitals for the spin-1/2 particles we shall use the following nonrelativistic scalar orbitals:

ψ^α-exponential type orbitals (ψ^α-ETO)

$$\psi_{nlm}^\alpha(\zeta, \vec{r}) = R_{nl}^\alpha(\zeta, r) S_{lm}(\vec{r}/r) \tag{1}$$

$$\overline{\psi}_{nlm}^\alpha(\zeta, \vec{r}) = \overline{R}_{nl}^\alpha(\zeta, r) S_{lm}(\vec{r}/r), \tag{2}$$

ϕ^α-momentum space orbitals (ϕ^α-MSO)

$$\phi_{nlm}^\alpha(\zeta, \vec{k}) = \Pi_{nl}^\alpha(\zeta, k) \tilde{S}_{lm}(\vec{k}/k) \tag{3}$$

$$\overline{\phi}_{nlm}^\alpha(\zeta, \vec{k}) = \overline{\Pi}_{nl}^\alpha(\zeta, k) \tilde{S}_{lm}(\vec{k}/k), \tag{4}$$

z^α-hyperspherical harmonics (z^α-HSH)

$$z^{\alpha}_{nlm}(\zeta, \beta\theta\varphi) = P^{\alpha}_{nl}(\kappa_4)\tilde{T}_{lm}(\kappa_1, \kappa_2, \kappa_3) \tag{5}$$

$$\overline{z}^{\alpha}_{nlm}(\zeta, \beta\theta\varphi) = \overline{P}^{\alpha}_{nl}(\kappa_4)\tilde{T}_{lm}(\kappa_1, \kappa_2, \kappa_3), \tag{6}$$

χ-Slater type orbitals (χ-STO)

$$\chi_{nlm}(\zeta, \vec{r}) = R_n(\zeta, r)S_{lm}(\vec{r}/r), \tag{7}$$

Slater type u-momentum space orbitals (u-MSO)

$$u_{nlm}(\zeta, \vec{k}) = Q_{nl}(\zeta, k)\tilde{S}_{lm}(\vec{k}/k), \tag{8}$$

Slater type v-hyperspherical harmonics (v-HSH)

$$v_{nlm}(\zeta, \beta\theta\varphi) = \frac{1}{\zeta^{3/2}}\Gamma_{nl}(\kappa_4)\tilde{T}_{lm}(\kappa_1, \kappa_2, \kappa_3). \tag{9}$$

See Refs. [15–20] for the exact definition of quantities occurring on the right-hand sides of Eqs. 1–9. We notice that the quantities $\kappa_1, \kappa_2, \kappa_3$ and κ_4 occurring in Eqs. 5, 6 and 9 are the Cartesian coordinates on the four-dimensional space. They can be obtained from the components of the momentum vector $\vec{k}$ by the following relations:

$$\begin{aligned}
\kappa_1 &= k_x/\sqrt{\zeta^2 + k^2} = \sin\beta\cos\varphi\sin\theta \\
\kappa_2 &= k_y/\sqrt{\zeta^2 + k^2} = \sin\beta\sin\varphi\sin\theta \\
\kappa_3 &= k_z/\sqrt{\zeta^2 + k^2} = \sin\beta\cos\theta \\
\kappa_4 &= \zeta/\sqrt{\zeta^2 + k^2} = \cos\beta,
\end{aligned} \tag{10}$$

where the angles β, θ, φ ($0 \leq \beta \leq \frac{\pi}{2}, 0 \leq \theta \leq \pi, 0 \leq \varphi \leq 2\pi$) are spherical coordinates on the four-dimensional unit sphere; θ and φ have the meaning of the usual spherical coordinates in momentum space. The surface element of the four-dimensional sphere is determined by

$$d\Omega(\zeta, \beta\theta\varphi) = \zeta^3 d\Omega. \tag{11}$$

This surface element is connected with the volume element in momentum space by the relation:

$$d^3\vec{k} = dk_x dk_y dk_z = d\Omega(\zeta, \beta\theta\varphi), \tag{12}$$

where

$$d\Omega = d\Omega(1, \beta\theta\varphi) = \frac{\sin^2\beta}{\cos^4\beta}d\beta\sin\theta d\theta d\varphi. \tag{13}$$

In this study, using functions (1–9) we introduce in position, momentum and four-dimensional spaces the new complete orthonormal basis sets for two- and four-component spinor wave functions, and Slater spinor orbitals. We notice that the spinor wave functions obtained are complete without the inclusion of the continuum.

3 Two- and four-component spinor wave functions and Slater type spinor orbitals

In order to construct the formulas for the two- and four-component spinor wave functions, and Slater spinor orbitals in position, momentum and four-dimensional spaces we use for the spherical spinors the following independent relations:

$$\Omega_{jm_j}^l(\theta, \varphi) = \begin{pmatrix} ta_{jm_j}^l(0)\beta_{m(0)}Y_{lm(0)}(\theta, \varphi) \\ -ta_{jm_j}^l(1)\beta_{m(1)}Y_{lm(1)}(\theta, \varphi) \end{pmatrix} \tag{14}$$

$$\Lambda_{jm_j}^{l_t}(\theta, \varphi) = \begin{pmatrix} -ia_{jm_j}^{l_t}(1)\beta_{m(0)}Y_{l_tm(0)}(\theta, \varphi) \\ -ia_{jm_j}^{l_t}(0)\beta_{m(1)}Y_{l_tm(1)}(\theta, \varphi) \end{pmatrix}. \tag{15}$$

Then, by the use of Eqs. 1–9, 14 and 15 one can construct for the two- and four-component of exponential type spinor orbitals in position, momentum and four dimensional spaces the following relations:

Complete orthonormal sets of two-component spinor wave functions

$$K_{njm_j}^{\alpha l}(\zeta, \vec{r}) = R_{nl}^\alpha(\zeta, r)\Omega_{jm_j}^l(\theta, \varphi) = \begin{pmatrix} ta_{jm_j}^l(0)\beta_{m(0)}k_{nlm(0)}^\alpha(\zeta, \vec{r}) \\ -ta_{jm_j}^l(1)\beta_{m(1)}k_{nlm(1)}^\alpha(\zeta, \vec{r}) \end{pmatrix} \tag{16a}$$

$$\overline{K}_{njm_j}^{\alpha l}(\zeta, \vec{r}) = \overline{R}_{nl}^\alpha(\zeta, r)\Omega_{jm_j}^l(\theta, \varphi) = \begin{pmatrix} ta_{jm_j}^l(0)\beta_{m(0)}\overline{k}_{nlm(0)}^\alpha(\zeta, \vec{r}) \\ -ta_{jm_j}^l(1)\beta_{m(1)}\overline{k}_{nlm(1)}^\alpha(\zeta, \vec{r}) \end{pmatrix} \tag{16b}$$

$$K_{njm_j}^{\alpha l_t}(\zeta, \vec{r}) = R_{nl_t}^\alpha(\zeta, r)\Lambda_{jm_j}^{l_t}(\theta, \varphi) = \begin{pmatrix} -ia_{jm_j}^{l_t}(1)\beta_{m(0)}k_{nl_tm(0)}^\alpha(\zeta, \vec{r}) \\ -ia_{jm_j}^{l_t}(0)\beta_{m(1)}k_{nl_tm(1)}^\alpha(\zeta, \vec{r}) \end{pmatrix} \tag{17a}$$

$$\overline{K}_{njm_j}^{\alpha l_t}(\zeta, \vec{r}) = \overline{R}_{nl_t}^\alpha(\zeta, r)\Lambda_{jm_j}^{l_t}(\theta, \varphi) = \begin{pmatrix} -ia_{jm_j}^{l_t}(1)\beta_{m(0)}\overline{k}_{nl_tm(0)}^\alpha(\zeta, \vec{r}) \\ -ia_{jm_j}^{l_t}(0)\beta_{m(1)}\overline{k}_{nl_tm(1)}^\alpha(\zeta, \vec{r}) \end{pmatrix}, \tag{17b}$$

Slater type two-component spinor orbitals

$$K_{njm_j}^l(\zeta, \vec{r}) = R_{nl}(\zeta, r)\Omega_{jm_j}^l(\theta, \varphi) = \begin{pmatrix} ta_{jm_j}^l(0)\beta_{m(0)}k_{nlm(0)}(\zeta, \vec{r}) \\ -ta_{jm_j}^l(1)\beta_{m(1)}k_{nlm(1)}(\zeta, \vec{r}) \end{pmatrix} \tag{18}$$

$$K_{njm_j}^{l_t}(\zeta, \vec{r}) = R_{nl_t}(\zeta, r)\Lambda_{jm_j}^{l_t}(\theta, \varphi) = \begin{pmatrix} -ia_{jm_j}^{l_t}(1)\beta_{m(0)}k_{nl_tm(0)}(\zeta, \vec{r}) \\ -ia_{jm_j}^{l_t}(0)\beta_{m(1)}k_{nl_tm(1)}(\zeta, \vec{r}) \end{pmatrix}, \tag{19}$$

complete orthonormal sets of four-component spinor wave functions

$$
K_{njm_j}^{\alpha lt}(\zeta, \vec{r}) = \frac{1}{\sqrt{2 - \delta_{nl_t}}} \begin{pmatrix} K_{njm_j}^{\alpha l}(\zeta, \vec{r}) \\ K_{njm_j}^{\alpha l_t}(\zeta, \vec{r}) \end{pmatrix} \tag{20a}
$$

$$
= \frac{1}{\sqrt{2 - \delta_{nl_t}}} \begin{pmatrix} ta_{jm_j}^{l}(0)\beta_{m(0)}k_{nlm(0)}^{\alpha}(\zeta, \vec{r}) \\ -ta_{jm_j}^{l}(1)\beta_{m(1)}k_{nlm(1)}^{\alpha}(\zeta, \vec{r}) \\ -ia_{jm_j}^{l_t}(1)\beta_{m(0)}k_{nl_tm(0)}^{\alpha}(\zeta, \vec{r}) \\ -ia_{jm_j}^{l_t}(0)\beta_{m(1)}k_{nl_tm(1)}^{\alpha}(\zeta, \vec{r}) \end{pmatrix} \tag{20b}
$$

$$
\overline{K}_{njm_j}^{\alpha lt}(\zeta, \vec{r}) = \frac{1}{\sqrt{2 - \delta_{nl_t}}} \begin{pmatrix} \overline{K}_{njm_j}^{\alpha l}(\zeta, \vec{r}) \\ \overline{K}_{njm_j}^{\alpha l_t}(\zeta, \vec{r}) \end{pmatrix} \tag{21a}
$$

$$
= \frac{1}{\sqrt{2 - \delta_{nl_t}}} \begin{pmatrix} ta_{jm_j}^{l}(0)\beta_{m(0)}\overline{k}_{nlm(0)}^{\alpha}(\zeta, \vec{r}) \\ -ta_{jm_j}^{l}(1)\beta_{m(1)}\overline{k}_{nlm(1)}^{\alpha}(\zeta, \vec{r}) \\ -ia_{jm_j}^{l_t}(1)\beta_{m(0)}\overline{k}_{nl_tm(0)}^{\alpha}(\zeta, \vec{r}) \\ -ia_{jm_j}^{l_t}(0)\beta_{m(1)}\overline{k}_{nl_tm(1)}^{\alpha}(\zeta, \vec{r}) \end{pmatrix}, \tag{21b}
$$

Slater type four-component spinor orbitals

$$
K_{njm_j}^{lt}(\zeta, \vec{r}) = \frac{1}{\sqrt{2 - \delta_{nl_t}}} \begin{pmatrix} K_{njm_j}^{l}(\zeta, \vec{r}) \\ K_{njm_j}^{l_t}(\zeta, \vec{r}) \end{pmatrix} \tag{22}
$$

$$
= \frac{1}{\sqrt{2 - \delta_{nl_t}}} \begin{pmatrix} ta_{jm_j}^{l}(0)\beta_{m(0)}k_{nlm(0)}(\zeta, \vec{r}) \\ -ta_{jm_j}^{l}(1)\beta_{m(1)}k_{nlm(1)}(\zeta, \vec{r}) \\ -ia_{jm_j}^{l_t}(1)\beta_{m(0)}k_{nl_tm(0)}(\zeta, \vec{r}) \\ -ia_{jm_j}^{l_t}(0)\beta_{m(1)}k_{nl_tm(1)}(\zeta, \vec{r}) \end{pmatrix}. \tag{23}
$$

The functions containing in these formulas are defined as

$$
k_{nlm}^{\alpha} = \psi_{nlm}^{\alpha}(\zeta, \vec{r}), \phi_{nlm}^{\alpha}(\zeta, \vec{k}), z_{nlm}^{\alpha}(\zeta, \beta\theta\varphi) \tag{24a}
$$

$$
\overline{k}_{nlm}^{\alpha} = \overline{\psi}_{nlm}^{\alpha}(\zeta, \vec{r}), \overline{\phi}_{nlm}^{\alpha}(\zeta, \vec{k}), \overline{z}_{nlm}^{\alpha}(\zeta, \beta\theta\varphi) \tag{24b}
$$

$$
k_{nlm} = \chi_{nlm}(\zeta, \vec{r}), u_{nlm}(\zeta, \vec{k}), v_{nlm}(\zeta, \beta\theta\varphi) \tag{25}
$$

$$
K_{njm_j}^{\alpha l} = \Psi_{njm_j}^{\alpha l}(\zeta, \vec{r}), \Phi_{njm_j}^{\alpha l}(\zeta, \vec{k}), Z_{njm_j}^{\alpha l}(\zeta, \beta\theta\varphi) \tag{26a}
$$

$$
\overline{K}_{njm_j}^{\alpha l} = \overline{\Psi}_{njm_j}^{\alpha l}(\zeta, \vec{r}), \overline{\Phi}_{njm_j}^{\alpha l}(\zeta, \vec{k}), \overline{Z}_{njm_j}^{\alpha l}(\zeta, \beta\theta\varphi) \tag{26b}
$$

$$
K_{njm_j}^{l} = X_{njm_j}^{l}(\zeta, \vec{r}), U_{njm_j}^{l}(\zeta, \vec{k}), V_{njm_j}^{l}(\zeta, \beta\theta\varphi) \tag{27}
$$

$$K_{njm_j}^{\alpha lt} = \Psi_{njm_j}^{\alpha lt}(\zeta, \vec{r}), \Phi_{njm_j}^{\alpha lt}(\zeta, \vec{k}), Z_{njm_j}^{\alpha lt}(\zeta, \beta\theta\varphi) \tag{28a}$$

$$\overline{K}_{njm_j}^{\alpha lt} = \overline{\Psi}_{njm_j}^{\alpha lt}(\zeta, \vec{r}), \overline{\Phi}_{njm_j}^{\alpha lt}(\zeta, \vec{k}), \overline{Z}_{njm_j}^{\alpha lt}(\zeta, \beta\theta\varphi) \tag{28b}$$

$$K_{njm_j}^{lt} = X_{njm_j}^{lt}(\zeta, \vec{r}), U_{njm_j}^{lt}(\zeta, \vec{k}), V_{njm_j}^{lt}(\zeta, \beta\theta\varphi). \tag{29}$$

The functions $\psi_{nlm}^{\alpha}, \overline{\psi}_{nlm}^{\alpha}, \phi_{nlm}^{\alpha}, \overline{\phi}_{nlm}, \ z_{nlm}^{\alpha}, \overline{z}_{nlm}^{\alpha}, \chi_{nlm}, u_{nlm}$ and v_{nlm} occurring in these formulas are determined by Eqs. 1–9. It should be noted that the radial parts of orbitals $\psi_{nl_t m}^{\alpha}, \overline{\psi}_{nl_t m}^{\alpha}, \phi_{nl_t m}^{\alpha}, \overline{\phi}_{nl_t m}, z_{nl_t m}^{\alpha}, \overline{z}_{nl_t m}^{\alpha}, \ \chi_{nl_t m}, u_{nl_t m}$ and $v_{nl_t m}$ with $l_t = n$ arising in the two- and four-component cases must be equated to zero.

The quantities containing in Eqs. 14–23 are determined by

$$1 \le n < \infty; \ j = l + \frac{1}{2}t \ (t = \pm 1); \ \frac{1}{2} \le j \le n - \frac{1}{2}; \ -j \le m_j \le j;$$

$$j - \frac{1}{2} \le l \le \min\left(j + \frac{1}{2}, n - 1\right); \tag{30}$$

$$l_t = l + t; \ m(\lambda) = m_j + \lambda - \frac{1}{2}; \ 0 \le \lambda \le 1;$$

$$\beta_{m(\lambda)} = (-1)^{[|m(\lambda)| - m(\lambda)]/2} = i^{|m(\lambda)| - m(\lambda)}$$

and

$$a_{jm_j}^l(\lambda) = \left(l\frac{1}{2}m(\lambda)\frac{1}{2} - \lambda \left| l\frac{1}{2}jm_j\right.\right) = t^{1-\lambda}\left[\frac{l + (-1)^{\lambda}tm_j + \frac{1}{2}}{2l + 1}\right]^{1/2}. \tag{31}$$

The coefficients $a_{jm_j}^l(\lambda)$ satisfy the orthonormality relation

$$\sum_{\lambda=0}^{1} a_{jm_j}^l(\lambda) a_{j'm_j}^l(\lambda) = \delta_{jj'}. \tag{32}$$

In the special case of position space the four-component spinor orbitals, Eqs. 20b, 21b and 23, have the following form:
For complete orthonormal sets of spinor wave functions

$$\Psi_{njm_j}^{\alpha lt}(\zeta, \vec{r}) = \frac{1}{\sqrt{2 - \delta_{nl_t}}}\begin{pmatrix} t a_{jm_j}^l(0)\beta_{m(0)}\psi_{nlm(0)}^{\alpha}(\zeta, \vec{r}) \\ -t a_{jm_j}^l(1)\beta_{m(1)}\psi_{nlm(1)}^{\alpha}(\zeta, \vec{r}) \\ -i a_{jm_j}^{l_t}(1)\beta_{m(0)}\psi_{nl_t m(0)}^{\alpha}(\zeta, \vec{r}) \\ -i a_{jm_j}^{l_t}(0)\beta_{m(1)}\psi_{nl_t m(1)}^{\alpha}(\zeta, \vec{r}) \end{pmatrix} \tag{33}$$

$$\overline{\Psi}_{njm_j}^{\alpha lt}(\zeta, \vec{r}) = \frac{1}{\sqrt{2 - \delta_{nl_t}}}\begin{pmatrix} t a_{jm_j}^l(0)\beta_{m(0)}\overline{\psi}_{nlm(0)}^{\alpha}(\zeta, \vec{r}) \\ -t a_{jm_j}^l(1)\beta_{m(1)}\overline{\psi}_{nlm(1)}^{\alpha}(\zeta, \vec{r}) \\ -i a_{jm_j}^{l_t}(1)\beta_{m(0)}\overline{\psi}_{nl_t m(0)}^{\alpha}(\zeta, \vec{r}) \\ -i a_{jm_j}^{l_t}(0)\beta_{m(1)}\overline{\psi}_{nl_t m(1)}^{\alpha}(\zeta, \vec{r}) \end{pmatrix}, \tag{34}$$

for the Slater type spinor orbitals

$$
X_{njm_j}^{lt}(\zeta, \vec{r}) = \frac{1}{\sqrt{2 - \delta_{nl_t}}}
\begin{pmatrix}
ta_{jm_j}^{l}(0)\beta_{m(0)}\chi_{nlm(0)}(\zeta, \vec{r}) \\
-ta_{jm_j}^{l}(1)\beta_{m(1)}\chi_{nlm(1)}(\zeta, \vec{r}) \\
-ia_{jm_j}^{l_t}(1)\beta_{m(0)}\chi_{nl_tm(0)}(\zeta, \vec{r}) \\
-ia_{jm_j}^{l_t}(0)\beta_{m(1)}\chi_{nl_tm(1)}(\zeta, \vec{r})
\end{pmatrix}.
\tag{35}
$$

The first few four-component spinor wave functions defined by Eq. 33 are shown in Table 1.

Using method set out in Ref. [21] it is easy to show that the independent spherical spinors, Eqs. 14 and 15, for the given values of j have the following properties:

$$
\vec{\sigma}\hat{\vec{p}}[R_{nl}^{\alpha}(\zeta, r)\Omega_{jm_j}^{l}(\theta, \varphi)] = \hbar \left[\frac{dR_{nl}^{\alpha}(\zeta, r)}{dr} + (1 - \kappa)\frac{R_{nl}^{\alpha}(\zeta, r)}{r}\right]\Lambda_{jm_j}^{l_t}(\theta, \varphi),
\tag{36}
$$

$$
\vec{\sigma}\hat{\vec{p}}[R_{nl_t}^{\alpha}(\zeta, r)\Lambda_{jm_j}^{l_t}(\theta, \varphi)] = -\hbar \left[\frac{dR_{nl_t}^{\alpha}(\zeta, r)}{dr} + (1 + \kappa)\frac{R_{nl_t}^{\alpha}(\zeta, r)}{r}\right]\Omega_{jm_j}^{l}(\theta, \varphi)
\tag{37}
$$

where $\zeta > 0$, $-\infty < \alpha \leq 1$, the three Cartesian components of $\vec{\sigma}$ are the Pauli spin matrices and

$$
\kappa = t(j + 1/2).
\tag{38}
$$

Equations 36 and 37 are important in the reduction of the Dirac equation to the radial form.

The nonrelativistic scalar wave functions, and the two- and four-component relativistic spinor orbitals satisfy the following orthonormality relations:

$$
\int k_{nlm}^{\alpha*}(\zeta, \vec{x})\overline{k}_{n'l'm'}^{\alpha}(\zeta, \vec{x})\, d\vec{x} = \delta_{nn'}\delta_{ll'}\delta_{mm'}
\tag{39}
$$

$$
\int k_{nlm}^{*}(\zeta, \vec{x})k_{n'l'm'}(\zeta, \vec{x})\, d\vec{x} = \frac{(n + n')!}{[(2n)!\,(2n')!]^{1/2}}\delta_{ll'}\delta_{mm'}
\tag{40}
$$

$$
\int K_{njm_j}^{\alpha l\dagger}(\zeta, \vec{x})\overline{K}_{n'j'm_j'}^{\alpha l'}(\zeta, \vec{x})\, d\vec{x} = \delta_{nn'}\delta_{ll'}\delta_{jj'}\delta_{m_jm_j'}
\tag{41}
$$

$$
\int K_{njm_j}^{l\dagger}(\zeta, \vec{x})K_{n'j'm_j'}^{l'}(\zeta, \vec{x})\, d\vec{x} = \frac{(n + n')!}{[(2n)!\,(2n')!]^{1/2}}\delta_{ll'}\delta_{jj'}\delta_{m_jm_j'}
\tag{42}
$$

$$
\int K_{njm_j}^{\alpha l\dagger t}(\zeta, \vec{x})\overline{K}_{n'j'm_j'}^{\alpha l't}(\zeta, \vec{x})\, d\vec{x} = \delta_{nn'}\delta_{ll'}\delta_{jj'}\delta_{m_jm_j'}
\tag{43}
$$

$$
\int K_{njm_j}^{l\dagger t}(\zeta, \vec{x})K_{n'j'm_j'}^{l't}(\zeta, \vec{x})\, d\vec{x} = \frac{(n + n')!}{[(2n)!\,(2n')!]^{1/2}}\delta_{ll'}\delta_{jj'}\delta_{m_jm_j'}
\tag{44}
$$

Table 1 The four-component spinor wave functions for $1 \leq n \leq 3$

n	l	t	j	m_j	$\tilde{\Psi}_{njm_j}^{\alpha lt}(\zeta,\vec{r})$
1	0	+1	1/2	1/2	$\left(\psi_{100}^{\alpha}\ \ 0\ \ 0\ \ 0\right)$
				−1/2	$\left(0\ \ -\psi_{100}^{\alpha}\ \ 0\ \ 0\right)$
2	0	+1	1/2	1/2	$\frac{1}{\sqrt{2}}\left(\psi_{200}^{\alpha}\ \ 0\ \ \frac{-i}{\sqrt{3}}\psi_{210}^{\alpha}\ \ -i\sqrt{\frac{2}{3}}\psi_{211}^{\alpha}\right)$
				−1/2	$\frac{1}{\sqrt{2}}\left(0\ \ -\psi_{200}^{\alpha}\ \ i\sqrt{\frac{2}{3}}\psi_{21-1}^{\alpha}\ \ \frac{-i}{\sqrt{3}}\psi_{210}^{\alpha}\right)$
	1	−1	1/2	1/2	$\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{3}}\psi_{210}^{\alpha}\ \ \sqrt{\frac{2}{3}}\psi_{211}^{\alpha}\ \ -i\psi_{200}^{\alpha}\ \ 0\right)$
				−1/2	$\frac{1}{\sqrt{2}}\left(-\sqrt{\frac{2}{3}}\psi_{21-1}^{\alpha}\ \ \frac{1}{\sqrt{3}}\psi_{210}^{\alpha}\ \ 0\ \ i\psi_{200}^{\alpha}\right)$
		+1	3/2	3/2	$\left(\psi_{211}^{\alpha}\ \ 0\ \ 0\ \ 0\right)$
				1/2	$\left(\sqrt{\frac{2}{3}}\psi_{210}^{\alpha}\ \ -\frac{1}{\sqrt{3}}\psi_{211}^{\alpha}\ \ 0\ \ 0\right)$
				−1/2	$\left(-\frac{1}{\sqrt{3}}\psi_{21-1}^{\alpha}\ \ -\sqrt{\frac{2}{3}}\psi_{210}^{\alpha}\ \ 0\ \ 0\right)$
				−3/2	$\left(0\ \ \psi_{21-1}^{\alpha}\ \ 0\ \ 0\right)$
3	0	+1	1/2	1/2	$\frac{1}{\sqrt{2}}\left(\psi_{300}^{\alpha}\ \ 0\ \ -\frac{i}{\sqrt{3}}\psi_{310}^{\alpha}\ \ -i\sqrt{\frac{2}{3}}\psi_{311}^{\alpha}\right)$
				−1/2	$\frac{1}{\sqrt{2}}\left(0\ \ -\psi_{300}^{\alpha}\ \ i\sqrt{\frac{2}{3}}\psi_{31-1}^{\alpha}\ \ -\frac{i}{\sqrt{3}}\psi_{310}^{\alpha}\right)$
	1	−1	1/2	1/2	$\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{3}}\psi_{310}^{\alpha}\ \ \sqrt{\frac{2}{3}}\psi_{311}^{\alpha}\ \ -i\psi_{300}^{\alpha}\ \ 0\right)$
				−1/2	$\frac{1}{\sqrt{2}}\left(-\sqrt{\frac{2}{3}}\psi_{31-1}^{\alpha}\ \ \frac{1}{\sqrt{3}}\psi_{310}^{\alpha}\ \ 0\ \ i\psi_{300}^{\alpha}\right)$
		+1	3/2	3/2	$\frac{1}{\sqrt{2}}\left(\psi_{311}^{\alpha}\ \ 0\ \ -\frac{i}{\sqrt{5}}\psi_{321}^{\alpha}\ \ -\frac{2i}{\sqrt{5}}\psi_{322}^{\alpha}\right)$
				1/2	$\frac{1}{\sqrt{2}}\left(\sqrt{\frac{2}{3}}\psi_{310}^{\alpha}\ \ -\frac{1}{\sqrt{3}}\psi_{311}^{\alpha}\ \ -i\sqrt{\frac{2}{5}}\psi_{320}^{\alpha}\ \ -i\sqrt{\frac{3}{5}}\psi_{321}^{\alpha}\right)$
				−1/2	$\frac{1}{\sqrt{2}}\left(-\frac{1}{\sqrt{3}}\psi_{31-1}^{\alpha}\ \ -\sqrt{\frac{2}{3}}\psi_{310}^{\alpha}\ \ i\sqrt{\frac{3}{5}}\psi_{32-1}^{\alpha}\ \ -i\sqrt{\frac{2}{5}}\psi_{320}^{\alpha}\right)$
				−3/2	$\frac{1}{\sqrt{2}}\left(0\ \ \psi_{31-1}^{\alpha}\ \ -\frac{2i}{\sqrt{5}}\psi_{32-2}^{\alpha}\ \ \frac{i}{\sqrt{5}}\psi_{32-1}^{\alpha}\right)$
	2	−1	3/2	3/2	$\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{5}}\psi_{321}^{\alpha}\ \ \frac{2}{\sqrt{5}}\psi_{322}^{\alpha}\ \ -i\psi_{311}^{\alpha}\ \ 0\right)$
				1/2	$\frac{1}{\sqrt{2}}\left(\sqrt{\frac{2}{5}}\psi_{320}^{\alpha}\ \ \sqrt{\frac{3}{5}}\psi_{321}^{\alpha}\ \ -i\sqrt{\frac{2}{3}}\psi_{310}^{\alpha}\ \ \frac{i}{\sqrt{3}}\psi_{311}^{\alpha}\right)$
				−1/2	$\frac{1}{\sqrt{2}}\left(-\sqrt{\frac{3}{5}}\psi_{32-1}^{\alpha}\ \ \sqrt{\frac{2}{5}}\psi_{320}^{\alpha}\ \ \frac{i}{\sqrt{3}}\psi_{31-1}^{\alpha}\ \ i\sqrt{\frac{2}{3}}\psi_{310}^{\alpha}\right)$
				−3/2	$\frac{1}{\sqrt{2}}\left(\frac{2}{\sqrt{5}}\psi_{32-2}^{\alpha}\ \ -\frac{1}{\sqrt{5}}\psi_{32-1}^{\alpha}\ \ 0\ \ -i\psi_{31-1}^{\alpha}\right)$
		+1	5/2	5/2	$\left(\psi_{322}^{\alpha}\ \ 0\ \ 0\ \ 0\right)$
				3/2	$\left(\frac{2}{\sqrt{5}}\psi_{321}^{\alpha}\ \ -\frac{1}{\sqrt{5}}\psi_{322}^{\alpha}\ \ 0\ \ 0\right)$
				1/2	$\left(\sqrt{\frac{3}{5}}\psi_{320}^{\alpha}\ \ -\sqrt{\frac{2}{5}}\psi_{321}^{\alpha}\ \ 0\ \ 0\right)$
				−1/2	$\left(-\sqrt{\frac{2}{5}}\psi_{32-1}^{\alpha}\ \ -\sqrt{\frac{3}{5}}\psi_{320}^{\alpha}\ \ 0\ \ 0\right)$
				−3/2	$\left(\frac{1}{\sqrt{5}}\psi_{32-2}^{\alpha}\ \ \frac{2}{\sqrt{5}}\psi_{32-1}^{\alpha}\ \ 0\ \ 0\right)$
				−5/2	$\left(0\ \ -\psi_{32-2}^{\alpha}\ \ 0\ \ 0\right)$

where

$$\vec{x} = \vec{r}, \vec{k}, \beta\theta\varphi \text{ and } d\vec{x} = d^3\vec{r}, d^3\vec{k}, d\Omega \,(\zeta, \beta\theta\varphi). \tag{45}$$

As can be seen from the formulas presented in this work, all of the two- and four-component spinor wave functions and Slater type spinor orbitals are expressed through the corresponding nonrelativistic scalar functions defined in position, momentum and four-dimensional spaces. Thus, the expansion and one-range addition theorems obtained in [19] for the ψ^α-ETO, ϕ^α-MSO, z^α-HSH and χ-STO can be also used in the case of two- and four-component relativistic functions in position, momentum and four-dimensional spaces.

4 Evaluation of overlap integrals over Slater type four-component spinor orbitals in position space

Now, we evaluate the two-center overlap integrals over four-component Slater type spinor orbitals with the same screening parameters defined as

$$S_{njm_j,n'j'm'_j}^{lt,l't'}\left(\vec{G}\right) = \int X_{njm_j}^{lt\dagger}(\zeta,\vec{r}) X_{n'j'm'_j}^{l't'}\left(\zeta,\vec{r}-\vec{R}\right) d^3\vec{r}, \tag{46}$$

where $\vec{r} = \vec{r}_a$, $\vec{r} - \vec{R} = \vec{r}_b$, $\vec{R} = \vec{R}_{ab}$ and $\vec{G} = 2\zeta\vec{R}$. By the use of Eq. 29 for $K_{njm_j}^{lt} \equiv X_{njm_j}^{lt}$ we obtain for integral (46) the following relation:

$$S_{njm_j,n'j'm'_j}^{lt,l't'}(\vec{G}) = \frac{1}{2}\sum_{\lambda=0}^{1}\{tt'a_{jm_j,j'm'_j}^{l,l'}(\lambda)\beta_{m(\lambda),m'(\lambda)}s_{nlm(\lambda),n'l'm'(\lambda)}(\vec{G})$$
$$+a_{jm_j;j'm'_j}^{l_t,l'_{t'}}(1-\lambda)\beta_{m(\lambda),m'(\lambda)}s_{nl_tm(\lambda);n'l'_{t'}m'(\lambda)}(\vec{G})\}, \tag{47}$$

where $a_{jm_j,j'm'_j}^{l,l'}(\lambda) = a_{jm_j}^l(\lambda)a_{j'm'_j}^{l'}(\lambda)$, $a_{jm_j,j'm'_j}^{l_t,l'_t}(\lambda) = a_{jm_j}^{l_t}(\lambda)a_{j'm'_j}^{l'_t}(\lambda)$ and $\beta_{m(\lambda),m'(\lambda)} = \beta_{m(\lambda)}\beta_{m'(\lambda)}$. The quantities $s_{nlm(\lambda),n'l'm'(\lambda)}(\vec{G})$ are the overlap integrals over Slater nonrelativistic orbitals. They are determined by

$$s_{nlm,n'l'm'}(\vec{G}) = \int \chi_{nlm}^*(\zeta,\vec{r})\chi_{n'l'm'}(\zeta,\vec{r}-\vec{R}) d^3\vec{r} \tag{48}$$

It is easy to show that

$$s_{nlm,n'l'm'}(\vec{G}) = \{[2(n+\alpha)]!/(2n)!\}^{1/2}$$
$$\times \sum_{\mu=l+1}^{n+\alpha}\sum_{\mu'=l'+1}^{n'}\frac{1}{(2\mu)^\alpha}\overline{\omega}_{n+\alpha,\mu}^{\alpha l}\overline{\omega}_{n'\mu'}^{\alpha l'}s_{\mu lm,\mu'l'm'}^\alpha(\vec{G}), \tag{49}$$

where

$$s^{\alpha}_{\mu lm, \mu' l'm'} \left(\vec{G} \right) = \int \overline{\psi}^{\alpha *}_{\mu lm} \left(\zeta, \vec{r} \right) \psi^{\alpha}_{\mu' l'm'} \left(\zeta, \vec{r} - \vec{R} \right) d^3 \vec{r}. \qquad (50)$$

See Ref. [16] for the exact definition of coefficients $\overline{\omega}^{\alpha l}$.

As we see from Eq. 49, the overlap integrals of Slater scalar orbitals are expressed in terms of overlap integrals over nonrelativistic ψ^{α}-ETO. The analytical relations for the evaluation of nonrelativistic overlap integrals over ψ^{α}-ETO were obtained in [19].

The results of calculations for the overlap integrals over Slater type four-component spinor orbitals with the same screening parameters obtained from the complete sets of $\psi^{1}-$, $\psi^{0}-$ and $\psi^{-1}-$ETO using Mathematica 5.0 international mathematical software are presented in Table 2. As we see from the table that the suggested approach guarantees a highly accurate calculation of the overlap integrals over relativistic Slater spinor orbitals which are obtained by the use of nonrelativistic overlap integrals.

Thus, the relations for the nonrelativistic overlap integrals over scalar orbitals presented in our previous papers also can be used in the evaluation of arbitrary multi-center multielectron integrals over two- and four-component relativistic spinor wave functions and Slater spinor orbitals. We note that the corresponding approach for the evaluation of nonrelativistic multicenter multielectron integrals using nonrelativistic overlap integrals have been described in previous papers [22–25]. For the calculation of nonrelativistic overlap integrals, the efficient computer programs especially for large quantum numbers are available in our group [26]. Therefore by using these programs and formulae presented in this study one can calculate the multicenter multielectron integrals arising in atomic and molecular electronic structure calculations when the complete orthonormal spinor wave functions or the Slater spinor orbitals basis sets are employed.

5 Conclusion

It is well known that the eigenstates of the matrix representation of the Dirac operator do not lead to the correct Schrödinger and Pauli limits in the same basis (and to the exact results for a complete basis). These wrong Schrödinger and Pauli limits are the main reason for the so-called "variational collapse" which can be avoided by the use of "kinetically balanced" basis sets. In the majority of works published in the literature, the relativistic calculations were performed with the help of "kinetically balanced" basis sets, and this creates some difficulty in calculating the atomic and molecular structures. In order to overcome the "variational collapse" appearing in the Schrödinger and Pauli limits, the necessity thus arises of using the four-component complete orthonormal spinor wave functions and Slater spinor orbitals basis sets which are expressed through the corresponding nonrelativistic scalar orbitals, and this is one of the main advantages of the present article.

Table 2 The values of overlap integrals over Slater type four-component spinor orbitals obtained from the different complete sets of nonrelativistic ψ^α-ETO in molecular coordinate system

n	l	t	j	m_j	n'	l'	t'	j'	m'_j	θ	φ	$G = 2\zeta R$	$S^{lt,l't'}_{njm_j,n'l'm'_j}(\vec{G})$		
													$\alpha = 1$	$\alpha = 0$	$\alpha = -1$
3	1	1	3/2	1/2	2	1	−1	1/2	1/2	0	0	10	−2.4887810380E-01	−2.4887810380E-01	−2.4887810380E-01
5	4	1	9/2	5/2	4	3	1	7/2	5/2	0	0	25	−5.0974610445E-02	−5.0974610445E-02	−5.0974610445E-02
6	3	1	7/2	1/2	5	2	1	5/2	−1/2	0	0	40	7.9055124161E-03	7.9055124161E-03	7.9055124161E-03
6	4	−1	7/2	−1/2	5	3	−1	5/2	−1/2	0	0	40	−2.1886363326E-03	−2.1886363326E-03	−2.1886363326E-03
7	6	1	13/2	9/2	7	6	1	13/2	9/2	0	0	50	4.4862520946E-04	4.4862520946E-04	4.4862520946E-04
3	0	1	1/2	1/2	2	0	1	1/2	1/2	π/4	π/6	15	5.8206200380E-02	5.8206200380E-02	5.8206200380E-02
4	3	1	7/2	7/2	4	3	1	7/2	1/2	3π/5	2π/7	30	−9.0944010952E-03	−9.0944010952E-03	−9.0944010952E-03
5	3	−1	5/2	3/2	4	2	−1	3/2	1/2	2π/5	5π/3	45	−3.7793727920E-06	−3.7793727920E-06	−3.7793727920E-06
9	8	1	17/2	17/2	8	7	1	15/2	15/2	4π/5	π/3	70	1.0551134090E-07	1.0551134090E-07	1.0551134090E-07
12	10	−1	19/2	15/2	10	6	1	13/2	9/2	π/6	π/4	90	−6.1611871954E-07	−6.1611871954E-07	−6.1611871954E-07

References

1. V.A. Fock, Z. Phys. **98**, 145 (1935)
2. V.A. Fock, Kgl Norske Videnskab Forh. **31**, 138 (1958)
3. E.A. Hylleraas, Z. Phys. **54**, 347 (1929)
4. H. Shull, P.O. Löwdin, J. Chem. Phys. **23**, 1362 (1955)
5. P.O. Löwdin, H. Shull, Phys. Rev. **101**, 1730 (1956)
6. E.A. Hylleraas, Z. Phys. **48**, 469 (1928)
7. J. Avery, F. Antonsen, J. Math. Chem. **24**, 175 (1998)
8. P. Pyykkö, *Relativistic Theory of Atoms and Molecules I–III*. (Springer, Berlin, 1986, 1993 and 2000)
9. T. Kato, Commun Pure Appl. Math. **10**, 151 (1957)
10. S. Agmon, *Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations: Bounds on Eigenfunctions of N-body Shrödinger Operators* (Princeton University Press, Princeton, NJ, 1982)
11. G.E. Brown, D.G. Ravenhall, Proc. Roy. Soc. Lond. A **208**, 552 (1951)
12. R.E. Stanton, S. Havriliak, J. Chem. Phys. **81**, 1910 (1984)
13. W. Kutzelnigg, Int. J. Quantum Chem. **25**, 107 (1984)
14. E.U. Condon, G.H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1970)
15. I.I. Guseinov, Phys. Lett. A **372**, 44 (2007)
16. I.I. Guseinov, Int. J. Quantum Chem. **90**, 114 (2002)
17. I.I. Guseinov, J. Mol. Model. **9**, 135 (2003)
18. I.I. Guseinov, J. Mol. Model. **12**, 757 (2006)
19. I.I. Guseinov, J. Math. Chem. **42**, 991 (2007)
20. I.I. Guseinov, J. Math. Chem. **44**, 839 (2008)
21. H.A. Bethe, E.E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957)
22. I.I. Guseinov, J. Math. Chem. **42**, 415 (2007)
23. I.I. Guseinov, J. Theor. Comput. Chem. **7**, 257 (2008)
24. I.I. Guseinov, Chin. Phys. Lett. **25**, 4240 (2008)
25. I.I. Guseinov, J. Theor. Comput. Chem. **9** (2009) (in press)
26. I.I. Guseinov, B.A. Mamedov, Z. Naturforsch, **62a**, 467 (2007)