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# Unified treatment of complete orthonormal sets of nonrelativistic, quasirelativistic and relativistic sets of spinor wave functions, and Slater spinor orbitals in coordinate, momentum and four-dimensional spaces

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**Abstract** Using the properties of tensor spherical harmonics introduced by the author in previous paper (Guseinov, Phys Lett A 372:44, 2007) and complete orthonormal scalar basis sets of nonrelativistic $\psi^{\alpha}$-exponential type orbitals ($\psi^{\alpha}$-ETO), $\phi^{\alpha}$-momentum space orbitals ($\phi^{\alpha}$-MSO) and $z^{\alpha}$-hyperspherical harmonics ($z^{\alpha}$-HSH) for particles with spin s $= 0$ the new analytical relations for the quasirelativistic and relativistic spinor wave functions and Slater spinor orbitals in coordinate, momentum and four-dimensional spaces are derived, where $\alpha = 1, 0, -1, -2, \ldots$. The 2-component quasirelativistic and 4-component relativistic spinor wave functions obtained are complete without the inclusion of the continuum. The relativistic spinor wave function sets and Slater spinor orbitals are expressed through the corresponding quasirelativistic spinor wave functions and Slater spinor orbitals, respectively. The analytical formulas for overlap integrals over quasirelativistic and relativistic Slater spinor orbitals with the same screening constants in coordinate space are also derived.

**Keywords** Tensor spherical harmonics · Spinor wave functions · Slater spinor orbitals · Overlap integrals

## 1 Introduction

It is well known that the solutions of the Schrödinger equation for the hydrogen-like atom play a significant role in theory and application to quantum mechanics of atoms, molecules and nuclei. However, the Schrödinger's nonrelativistic hydrogen-like orbitals and their extensions to momentum and four-dimensional spaces by Fock [1,2] are awkward to use as basis sets because they are not complete unless the continuum is

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included. To achieve completeness, Hylleraas, Shull and Löwdin in Refs. [3–6] introduced the so-called Lambda and Coulomb Sturmian functions for the particles with spin s = 0 in coordinate space. The orthonormality and completeness properties of Coulomb Sturmians have been studied by Weniger [7]. He has shown that such a set forms basis of a Sobolev space. Avery and Antonsen [8] have developed method for constructing relativistic one-electron Coulomb Sturmian basis set and discussed its potential-weighted orthonormality relations obeyed by the members of such a set.

In Refs. [9–11] and [12] we have developed the method for constructing complete orthonormal sets for tensor wave functions, and Slater tensor orbitals for particles with spin s = 0 and s = 1/2, 1, 3/2, 2, ..., respectively, in coordinate, momentum and four-dimensional spaces. In this article, using these functions for s = 0 and s = 1/2 we obtain a large number of quasirelativistic and relativistic spinor wave functions and Slater spinor orbitals in coordinate, momentum and four-dimensional spaces.

## 2 Quasirelativistic and relativistic spherical spinors

With the derivation of formulas for the sets of quasirelativistic and relativistic spinor wave functions and Slater spinor orbitals for a particle with spin 1/2 in coordinate, momentum and four-dimensional spaces we use the following eigenvalue equations of spherical spinors (see Sect. 7.2. of Ref. [13]):

$$\hat{j}^2\Omega^l_{jm_j}(\theta,\varphi) = j(j+1)\Omega^l_{jm_j}(\theta,\varphi) \tag{1}$$

$$\hat{j}_z\Omega^l_{jm_j}(\theta,\varphi) = m_j\Omega^l_{jm_j}(\theta,\varphi) \tag{2}$$

$$\hat{l}^2\Omega^l_{jm_j}(\theta,\varphi) = l(l+1)\Omega^l_{jm_j}(\theta,\varphi) \tag{3}$$

$$\hat{s}^2\Omega^l_{jm_j}(\theta,\varphi) = \frac{3}{4}\Omega^l_{jm_j}(\theta,\varphi), \tag{4}$$

where

$$\Omega^l_{jm_j}(\theta,\varphi) = Y^{l1/2}_{jm_j}(\theta,\varphi). \tag{5}$$

Here, the $Y^{l1/2}_{jm_j}(\theta,\varphi)$ is the tensor spherical harmonic of rank 1/2. Taking into account Eq. 10 of Ref. [12] for s = 1/2 in (5) we can express the spherical spinors $\Omega^l_{jm_j}$ through the scalar spherical harmonics $Y_{lm_l}(\theta,\varphi)$

$$\Omega^l_{jm_j}(\theta,\varphi) = \begin{pmatrix} a^l_{jm_j}(0)Y_{lm_l(0)}(\theta,\varphi) \\ a^l_{jm_j}(1)Y_{lm_l(1)}(\theta,\varphi) \end{pmatrix}, \tag{6}$$

where $m_l(\lambda) = m_j - \frac{1}{2} + \lambda$, $0 \le \lambda \le 1$ and

$$a^l_{jm_j}(\lambda) = \left( l \frac{1}{2} m_l(\lambda) \frac{1}{2} - \lambda \middle| l \frac{1}{2} j m_j \right) \tag{7}$$

The spherical spinors $\Omega^l_{jm_j}(\theta, \varphi)$ satisfy the orthonormality relationship, i.e.,

$$\int_0^{\pi} \int_0^{2\pi} \Omega^{l+}_{jm_j}(\theta, \varphi) \Omega^{l'}_{j'm'_j}(\theta, \varphi) \sin\theta d\theta d\varphi = \delta_{ll'} \delta_{jj'} \delta_{m_j m'_j}. \tag{8}$$

We notice that the spherical spinors $\Omega^l_{jm_j}(\theta, \varphi)$ are not eigenfunctions of the operators $\hat{l}_z$ and $\hat{s}_z$. i.e., the quantum numbers $m_l$ and $m_s$ can not be used to characterize them.

## 3 Quasirelativistic spinor wave functions and Slater spinor orbitals

In order to derive the formulas for quasirelativistic spinor wave functions and Slater spinor orbitals in coordinate, momentum and four-dimensional spaces we use Eqs. 11 and 16 of Ref. [12] for s = 1/2. Then, finally we obtain: for spinor wave functions

$$K^{\alpha l}_{njm_j} = K^{\alpha l 1/2}_{njm_j} = \begin{pmatrix} a^l_{jm_j}(0) k^{\alpha}_{nlm_l(0)} \\ a^l_{jm_j}(1) k^{\alpha}_{nlm_l(1)} \end{pmatrix}. \tag{9}$$

$$\bar{K}^{\alpha l}_{njm_j} = \bar{K}^{\alpha l 1/2}_{njm_j} = \begin{pmatrix} a^l_{jm_j}(0) \bar{k}^{\alpha}_{nlm_l(0)} \\ a^l_{jm_j}(1) \bar{k}^{\alpha}_{nlm_l(1)} \end{pmatrix}, \tag{10}$$

for Slater spinor orbitals

$$K^{l}_{njm_j} = K^{l 1/2}_{njm_j} = \begin{pmatrix} a^l_{jm_j}(0) k_{nlm_l(0)} \\ a^l_{jm_j}(1) k_{nlm_l(1)} \end{pmatrix}, \tag{11}$$

where

$$a^l_{jm_j}(\lambda) = a^{l1/2}_{jm_j}(\lambda) = \left( l \frac{1}{2} m_l(\lambda) \frac{1}{2} - \lambda \middle| l \frac{1}{2} j m_j \right). \tag{12}$$

Here $n \geq 1$, $1/2 \leq j \leq n-1/2$, $-m_j \leq j \leq m_j$, $j-1/2 \leq l \leq \min(j+1/2, n-1)$, $m_l(\lambda) = m_j - \frac{1}{2} + \lambda, \quad 0 \leq \lambda \leq 1$ and

$$K^{\alpha l}_{njm_j} = \psi^{\alpha l}_{njm_j}(\zeta, \vec{r}), \quad \Phi^{\alpha l}_{njm_j}(\zeta, \vec{k}), \quad Z^{\alpha l}_{njm_j}(\zeta, \beta\theta\varphi) \tag{13}$$

$$\bar{K}^{\alpha l}_{njm_j} = \bar{\psi}^{\alpha l}_{njm_j}(\zeta, \vec{r}), \quad \bar{\Phi}^{\alpha l}_{njm_j}(\zeta, \vec{k}), \quad \bar{Z}^{\alpha l}_{njm_j}(\zeta, \beta\theta\varphi) \tag{14}$$

$$k^{\alpha}_{nlm_l} = \psi^{\alpha}_{nlm_l}(\zeta, \vec{r}), \quad \phi^{\alpha}_{nlm_l}(\zeta, \vec{k}), \quad z^{\alpha}_{nlm_l}(\zeta, \beta\theta\varphi) \tag{15}$$

$$\bar{k}^{\alpha}_{nlm_l} = \bar{\psi}^{\alpha}_{nlm_l}(\zeta, \vec{r}), \quad \bar{\phi}^{\alpha}_{nlm_l}(\zeta, \vec{k}), \quad \bar{z}^{\alpha}_{nlm_l}(\zeta, \beta\theta\varphi) \tag{16}$$

$$K^{l}_{njm_j} = X^{l}_{njm_j}(\zeta, \vec{r}), \quad U^{l}_{njm_j}(\zeta, \vec{k}), \quad V^{l}_{njm_j}(\zeta, \beta\theta\varphi) \tag{17}$$

$$k_{nlm_l} = \chi_{nlm_l}(\zeta, \vec{r}), \quad u_{nlm_l}(\zeta, \vec{k}), \quad v_{nlm_l}(\zeta, \beta\theta\varphi) \tag{18}$$

The quasirelativistic spinor wave functions and Slater spinor orbitals are orthogonal with respect to the quantum numbers $(n, l, j, m_j)$ and $(l, j, m_j)$, respectively, i.e.,

$$\int K^{\alpha l^{\dagger}}_{njm_j}(\zeta, \vec{x}) \bar{K}^{\alpha l'}_{n'j'm'_j}(\zeta, \vec{x})\, d\vec{x} = \delta_{nn'}\delta_{ll'}\delta_{jj'}\delta_{m_j m'_j} \tag{19}$$

$$\int K^{l^{\dagger}}_{njm_j}(\zeta, \vec{x}) K^{l'}_{n'j'm'_j}(\zeta, \vec{x})\, d\vec{x} = \frac{(n+n')!}{[(2n)!\,(2n')!]^{1/2}} \delta_{ll'}\delta_{jj'}\delta_{m_j m'_j}, \tag{20}$$

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

The nonrelativistic scalar wave functions and Slater scalar orbitals satisfy the following orthogonality relations (see Ref. [11]):

$$\int k^{\alpha *}_{nlm_l}(\zeta, \vec{x}) \bar{k}^{\alpha}_{n'l'm'_l}(\zeta, \vec{x})\, d\vec{x} = \delta_{nn'}\delta_{ll'}\delta_{m_l m'_l}, \tag{21}$$

$$\int k^{*}_{nlm_l}(\zeta, \vec{x}) k_{n'l'm'_l}(\zeta, \vec{x})\, d\vec{x} = \frac{(n+n')!}{[(2n)!\,(2n')!]^{1/2}} \delta_{ll'}\delta_{m_l m'_l}. \tag{22}$$

## 4 Relativistic spinor wave functions and Slater spinor orbitals

For the construction of complete orthonormal sets of relativistic 4-component spinor wave functions, and Slater spinor orbitals in coordinate, momentum and four-dimensional spaces we use the quasirelativistic 2-component spinor wave functions $\left(K^{\alpha l}_{njm_j}, \bar{K}^{\alpha l}_{njm_j} \text{ and } K^{\alpha, l+t}_{njm_j}, \bar{K}^{\alpha, l+t}_{njm_j}\right)$ and Slater spinor orbitals $\left(K^{l}_{njm_j} \text{ and } K^{l+t}_{njm_j}\right)$ defined by Eqs. 9–11. Here, the parameter $t$ may have the values $\pm 1$ and is determined from the relation $j = l + \frac{1}{2}t$, namely,

$$t = \begin{cases} +1 & \text{for } j = l + 1/2 \\ -1 & \text{for } j = l - 1/2 \end{cases}. \tag{23}$$

Then, we finally establish the following formulas through the quasirelativistic and nonrelativistic functions: for relativistic wave functions

$$
{}^{t}K^{\alpha l}_{njm_j} = \frac{1}{\sqrt{2}}\begin{pmatrix} K^{\alpha l}_{njm_j} \\ K^{\alpha, l+t}_{njm_j} \end{pmatrix} \tag{24a}
$$

$$
= \frac{1}{\sqrt{2}}\begin{pmatrix} a^{l}_{jm_j}(0)k^{\alpha}_{nlm_l(0)} \\ a^{l}_{jm_j}(1)k^{\alpha}_{nlm_l(1)} \\ a^{l+t}_{jm_j}(0)k^{\alpha}_{n,l+t,m_l(0)} \\ a^{l+t}_{jm_j}(1)k^{\alpha}_{n,l+t,m_l(1)} \end{pmatrix} \tag{24b}
$$

$$
{}^{t}\bar{K}^{\alpha l}_{njm_j} = \frac{1}{\sqrt{2}}\begin{pmatrix} \bar{K}^{\alpha l}_{njm_j} \\ \bar{K}^{\alpha, l+t}_{njm_j} \end{pmatrix} \tag{25a}
$$

$$
= \frac{1}{\sqrt{2}}\begin{pmatrix} a^{l}_{jm_j}(0)\bar{k}^{\alpha}_{nlm_l(0)} \\ a^{l}_{jm_j}(1)\bar{k}^{\alpha}_{nlm_l(1)} \\ a^{l+t}_{jm_j}(0)\bar{k}^{\alpha}_{n,l+t,m_l(0)} \\ a^{l+t}_{jm_j}(1)\bar{k}^{\alpha}_{n,l+t,m_l(1)} \end{pmatrix}, \tag{25b}
$$

for relativistic spinor Slater orbitals

$$
{}^{t}K^{l}_{njm_j} = \frac{1}{\sqrt{2}}\begin{pmatrix} K^{l}_{njm_j} \\ K^{l+t}_{njm_j} \end{pmatrix} \tag{26a}
$$

$$
= \frac{1}{\sqrt{2}}\begin{pmatrix} a^{l}_{jm_j}(0)k_{nlm_l(0)} \\ a^{l}_{jm_j}(1)k_{nlm_l(1)} \\ a^{l+t}_{jm_j}(0)k_{n,l+t,m_l(0)} \\ a^{l+t}_{jm_j}(1)k_{n,l+t,m_l(1)} \end{pmatrix}. \tag{26b}
$$

Thus, in coordinate, momentum and four-dimensional spaces we have two kinds of independent complete orthonormal sets of relativistic spinor wave functions, and relativistic Slater spinor orbitals. These functions satisfy the following orthogonality relations:

$$
\int {}^{t}K^{\alpha l^{\dagger}}_{njm_j}(\zeta,\vec{x})\, {}^{t'}\bar{K}^{\alpha l'}_{n'j'm'_j}(\zeta,\vec{x})\, d\vec{x} = \delta_{nn'}\delta_{ll'}\delta_{jj'}\delta_{m_j m'_j}\delta_{tt'} \tag{27}
$$

$$\int {}^{t}K^{l^{\dagger}}_{njm_j}(\zeta,\vec{x})^{t'}K^{l'}_{n'j'm'_j}(\zeta,\vec{x})\,d\vec{x}=\frac{(n+n')!}{[(2n)!\,(2n')!]^{1/2}}\delta_{ll'}\delta_{jj'}\delta_{m_jm'_j}\delta_{tt'},\tag{28}$$

where $\alpha = 1, 0, -1, -2, \ldots$

As we see from the formulas presented in this work, all of the relativistic and quasirelativistic spinor wave functions and Slater spinor orbitals defined in coordinate, momentum and four-dimensional spaces are expressed through the corresponding nonrelativistic scalar functions. Thus, the expansion and one-range addition theorems obtained in [11] for the $\psi^{\alpha}$-ETO, $\phi^{\alpha}$-MSO, $z^{\alpha}$-HSH and $\chi$-STO can be also used in the case of relativistic and quasirelativistic spinor functions in coordinate, momentum and four-dimensional spaces, respectively.

## 5 Evaluation of overlap integrals over quasirelativistic and relativistic Slater spinor orbitals in coordinate space

As an example of application, we evaluate the two-center overlap integrals over quasirelativistic and relativistic Slater spinor orbitals with the same screening parameters in coordinate space which are defined as for quasirelativistic Slater spinor orbitals

$$S^{ll'}_{njm_j,n'j'm'_j}\left(\vec{G}\right)=\int X^{l^{\dagger}}_{njm_j}(\zeta,\vec{r})X^{l'}_{n'j'm'_j}\left(\zeta,\vec{r}-\vec{R}\right)d^3\vec{r},\tag{29}$$

for relativistic Slater spinor orbitals

$${}^{tt'}S^{ll'}_{njm_j,n'j'm'_j}\left(\vec{G}\right)=\int {}^{t}X^{l^{\dagger}}_{njm_j}(\zeta,\vec{r})^{t'}X^{l'}_{n'j'm'_j}\left(\zeta,\vec{r}-\vec{R}\right)d^3\vec{r},\tag{30}$$

where $\vec{r}=\vec{r}_a$, $\vec{r}-\vec{R}=\vec{r}_b$, $\vec{R}=\vec{R}_{ab}$, and $\vec{G}=2\zeta\vec{R}$. In order to evaluate these integrals we use Eqs. 11 and 26b. Then, we obtain for integrals (29) and (30) the following relations in terms of nonrelativistic overlap integrals:

$$\begin{aligned}S^{ll'}_{njm_j,n'j'm'_j}(\vec{G})&=a^{ll'}_{jm_j,j'm'_j}(0)s_{nlm_l(0),n'l'm'_l(0)}(\vec{G})\\&\quad+a^{ll'}_{jm_j,j'm'_j}(1)s_{nlm_l(1),n'l'm'_l(1)}(\vec{G})\end{aligned}\tag{31}$$

$$\begin{aligned}{}^{tt'}S^{ll'}_{njm_j,n'j'm'_j}(\vec{G})=\frac{1}{2}\Big[&a^{ll'}_{jm_j,j'm'_j}(0)s_{nlm_l(0),n'l'm'_l(0)}(\vec{G})\\&+a^{ll'}_{jm_j,j'm'_j}(1)s_{nlm_l(1),n'l'm'_l(1)}(\vec{G})\\&+a^{l+t,l'+t'}_{jm_j,j'm'_j}(0)s_{n,l+t,m_l(0),n',l'+t',m'_l(0)}(\vec{G})\\&+a^{l+t,l'+t'}_{jm_j,j'm'_j}(1)s_{n,l+t,m_l(1),n',l'+t,m'_l(1)}(\vec{G})\Big],\end{aligned}\tag{32}$$

**Table 1** The values of overlap integrals over quasirelativistic Slater spinor orbitals obtained from the different complete sets of nonrelativistic $\psi^{\alpha}$-ETO in molecular coordinate system

| $n$ | $l$ | $j$ | $m_j$ | $n'$ | $l'$ | $j'$ | $m'_j$ | $\theta$ | $\varphi$ | $G = 2\zeta R$ | $S^{ll'}_{njm_j,n'j'm'_j}(\vec{G})$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | $\alpha = 1$ | $\alpha = 0$ | $\alpha = -1$ |
| 3 | 0 | 1/2 | 1/2 | 3 | 0 | 1/2 | 1/2 | 0 | 0 | 20 | 6.9781133313E−02 | 6.9781133313E−02 | 6.9781133313E−02 |
| 5 | 3 | 5/2 | 1/2 | 4 | 1 | 3/2 | 1/2 | 0 | 0 | 50 | 1.6514703728E−04 | 1.6514703728E−04 | 1.6514703728E−04 |
| 7 | 4 | 9/2 | 5/2 | 5 | 3 | 5/2 | 5/2 | 0 | 0 | 10 | 1.7451839009E−01 | 1.7451839009E−01 | 1.7451839009E−01 |
| 8 | 6 | 11/2 | 7/2 | 8 | 5 | 9/2 | 7/2 | 0 | 0 | 8 | 4.5334741182E−01 | 4.5334741182E−01 | 4.5334741182E−01 |
| 11 | 8 | 17/2 | 15/2 | 10 | 7 | 15/2 | 15/2 | 0 | 0 | 60 | 2.6313526163E−05 | 2.6313526163E−05 | 2.6313526163E−05 |
| 17 | 15 | 29/2 | 29/2 | 17 | 15 | 29/2 | 29/2 | 0 | 0 | 70 | 1.0647022473E−06 | 1.0647022473E−06 | 1.0647022473E−06 |
| 3 | 1 | 3/2 | 1/2 | 3 | 1 | 3/2 | 1/2 | $\pi/3$ | $2\pi/3$ | 30 | −1.3245242725E−03 | −1.3245242725E−03 | −1.3245242725E−03 |
| 5 | 3 | 7/2 | 3/2 | 4 | 1 | 3/2 | 3/2 | $\pi$ | $\pi$ | 40 | 9.7661216381E−04 | 9.7661216381E−04 | 9.7661216381E−04 |
| 6 | 2 | 3/2 | 3/2 | 5 | 4 | 7/2 | 3/2 | $\pi/4$ | $5\pi/3$ | 90 | 6.0541291787E−11 | 6.0541291787E−11 | 6.0541291787E−11 |
| 8 | 5 | 11/2 | 7/2 | 6 | 4 | 9/2 | 9/2 | $\pi/7$ | $4\pi/5$ | 50 | −5.4660762593E−05 | −5.4660762593E−05 | −5.4660762593E−05 |
| 10 | 8 | 15/2 | 9/2 | 10 | 6 | 13/2 | 5/2 | $\pi/6$ | $\pi/4$ | 70 | 2.1357236307E−04 | 2.1357236307E−04 | 2.1357236307E−04 |
| 12 | 5 | 9/2 | 9/2 | 11 | 8 | 17/2 | 13/2 | $5\pi/8$ | $6\pi/5$ | 80 | 7.7998001404E−07 | 7.7998001404E−07 | 7.7998001404E−07 |

**Table 2** The values of overlap integrals over relativistic Slater spinor orbitals obtained from the different complete sets of nonrelativistic $\psi^{\alpha}$-ETO in molecular coordinate system

| $n$ | $l$ | $t$ | $j$ | $m_j$ | $n'$ | $l'$ | $t'$ | $j'$ | $m'_j$ | $\theta$ | $\varphi$ | $G = 2\zeta R$ | ${}^{tt'}S^{ll'}_{njm_j,n'j'm'_j}(\vec{G})$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | $\alpha = 1$ | $\alpha = 0$ | $\alpha = -1$ |
| 3 | 0 | 1 | 1/2 | 1/2 | 3 | 0 | 1 | 1/2 | 1/2 | 0 | 0 | 20 | 2.1686033117E−02 | 2.1686033117E−02 | 2.1686033117E−02 |
| 5 | 3 | −1 | 5/2 | 1/2 | 4 | 1 | 1 | 3/2 | 1/2 | 0 | 0 | 50 | −3.8795743525E−06 | −3.8795743525E−06 | −3.8795743525E−06 |
| 7 | 4 | 1 | 9/2 | 5/2 | 5 | 3 | −1 | 5/2 | 5/2 | 0 | 0 | 10 | 1.6745684860E−02 | 1.6745684860E−02 | 1.6745684860E−02 |
| 8 | 6 | −1 | 11/2 | 7/2 | 8 | 5 | −1 | 9/2 | 7/2 | 0 | 0 | 8 | 4.7810871366E−01 | 4.7810871366E−01 | 4.7810871366E−01 |
| 11 | 8 | 1 | 17/2 | 15/2 | 10 | 7 | 1 | 15/2 | 15/2 | 0 | 0 | 60 | 1.2674539035E−05 | 1.2674539035E−05 | 1.2674539035E−05 |
| 17 | 15 | −1 | 29/2 | 29/2 | 17 | 15 | −1 | 29/2 | 29/2 | 0 | 0 | 70 | 3.2656443489E−06 | 3.2656443489E−06 | 3.2656443489E−06 |
| 3 | 1 | 1 | 3/2 | 1/2 | 3 | 1 | −1 | 1/2 | 1/2 | $\pi/3$ | $2\pi/3$ | 30 | 3.8072490337E−04 | 3.8072490337E−04 | 3.8072490337E−04 |
| 5 | 3 | 1 | 7/2 | 3/2 | 4 | 1 | 1 | 3/2 | 3/2 | $\pi$ | $\pi$ | 40 | 3.2390814700E−04 | 3.2390814700E−04 | 3.2390814700E−04 |
| 6 | 2 | −1 | 3/2 | 3/2 | 5 | 4 | −1 | 7/2 | 3/2 | $\pi/4$ | $5\pi/3$ | 90 | −5.0113978450E−11 | −5.0113978450E−11 | −5.0113978450E−11 |
| 8 | 5 | 1 | 11/2 | 7/2 | 6 | 4 | 1 | 9/2 | 9/2 | $\pi/7$ | $4\pi/5$ | 50 | −2.3461470368E−05 | −2.3461470368E−05 | −2.3461470368E−05 |
| 10 | 8 | −1 | 15/2 | 9/2 | 10 | 6 | 1 | 13/2 | 5/2 | $\pi/6$ | $\pi/4$ | 70 | 3.2559146915E−05 | 3.2559146915E−05 | 3.2559146915E−05 |
| 12 | 5 | −1 | 9/2 | 9/2 | 11 | 8 | 1 | 17/2 | 13/2 | $5\pi/8$ | $6\pi/5$ | 80 | −1.3012419897E−05 | −1.3012419897E−05 | −1.3012419897E−05 |

where $a^{ll'}_{jm_j,j'm'_j}(\lambda) = a^{l}_{jm_j}(\lambda)a^{l'}_{j'm'_j}(\lambda)$. The overlap integrals over Slater scalar orbitals occurring on the right-hand side of Eqs. 31 and 32 are determined by

$$s_{nlm_l,n'l'm'_l}(\vec{G}) = \int \chi^*_{nlm_l}(\zeta,\vec{r})\chi_{n'l'm'_l}(\zeta,\vec{r}-\vec{R})d^3\vec{r} \tag{33a}$$

$$= \{[2(n+\alpha)]!/(2n)!\}^{1/2} \times \sum_{\mu=l+1}^{n+\alpha}\sum_{\mu'=l'+1}^{n'} \frac{1}{(2\mu)^{\alpha}}\bar{\omega}^{\alpha l}_{n+\alpha,\mu}\bar{\omega}^{\alpha l'}_{n'\mu'}s^{\alpha}_{\mu lm_l,\mu'l'm'_l}(\vec{G}), \tag{33b}$$

where

$$s^{\alpha}_{\mu lm_l,\mu'l'm'_l}\left(\vec{G}\right) = \int \bar{\psi}^{\alpha *}_{\mu lm_l}(\zeta,\vec{r})\psi^{\alpha}_{\mu'l'm'}\left(\zeta,\vec{r}-\vec{R}\right)d^3\vec{r}. \tag{34}$$

See Ref. [9] for the exact definition of coefficients $\bar{\omega}^{\alpha l}$. Hence, overlap integral of Slater scalar orbitals is given by a simple linear combination of overlap integrals over scalar $\psi^{\alpha}$-ETO. The analytical relations for the evaluation of nonrelativistic overlap integrals (34) were obtained in [11].

The results of calculation in atomic units for the quasirelativistic and relativistic overlap integrals over Slater spinor orbitals with the same screening parameters using Mathematica 5.0 international mathematical software obtained for different complete sets ($\alpha = 1, 0, -1$) are presented in Tables 1 and 2. As can be seen from the tables that the suggested approach guarantees a highly accurate calculation of the quasirelativistic and relativistic overlap integrals.

The nonrelativistic, quasirelativistic and relativistic overlap integrals with the same screening parameters play a significant role in the calculation of arbitrary multicenter integrals arising in coordinate, momentum and four-dimensional spaces when Hartree-Fock-Roothaan approximation is employed for the atomic and molecular systems. Thus, the relations for the nonrelativistic two-center overlap integrals over $\psi^{\alpha}$-ETO, $\phi^{\alpha}$-MSO, $z^{\alpha}$-HSH and $\chi$-STO can be used in the evaluation of multicenter integrals over corresponding quasirelativistic and relativistic spinor wave functions and Slater spinor orbitals. For this purpose, one has to use the expansion and one-range addition theorems for scalar $\psi^{\alpha}$, $\phi^{\alpha}$, $z^{\alpha}$ and $\chi$ obtained in our previous papers.

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