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ORIGINAL PAPER

Theory of complete orthonormal relativistic vector wave function sets and Slater type relativistic vector orbitals in coordinate, momentum and four-dimensional spaces

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Abstract The new analytical relations for the relativistic vector wave functions and Slater type relativistic vector orbitals in coordinate, momentum and four-dimensional spaces are derived using the properties of quasirelativistic vector spherical harmonics introduced by the author in previous paper (I.I. Guseinov, J. Math. Chem., 44, 197 (2008)) and complete orthonormal scalar basis sets of nonrelativistic ψ^α-exponential type orbitals (ψ^α-ETO), ϕ^α-momentum space orbitals (ϕ^α-MSO) and z^α-hyperspherical harmonics (z^α-HSH). The 6-component relativistic vector wave functions obtained are complete without the inclusion of the continuum. The relativistic vector wave function sets and Slater type relativistic vector orbitals are expressed through the corresponding quasirelativistic vector wave functions and Slater vector orbitals, respectively. The analytical formulas are also derived for overlap integrals over Slater type relativistic vector orbitals with the same screening constants in coordinate space.

Keywords Vector spherical harmonics · Slater type vector orbitals · Overlap integrals

1 Introduction

In Ref. [1] we have developed the method for constructing complete orthonormal sets of quasirelativistic vector wave functions and Slater type quasirelativistic vector orbitals for particles with spin $s = 1$ in coordinate, momentum and four-dimensional spaces. In this paper, using these functions we obtain a large number of relativistic vector wave functions and Slater type relativistic vector orbitals in coordinate,

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momentum and four-dimensional spaces. This work presents the development of previous paper [1].

2 Quasirelativistic vector orbitals in coordinate, momentum and four-dimensional spaces

In Ref. [1], we have introduced in coordinate, momentum and four-dimensional spaces the complete orthonormal sets for quasirelativistic vector wave functions and Slater type quasirelativistic vector orbitals in terms of nonrelativistic scalar orbitals. These quasirelativistic orbitals are determined by the following relations:

For quasirelativistic vector wave functions

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

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

where

$$K^{\alpha l}_{njm_j} = \Psi^{\alpha l}_{njm_j}(\zeta, \vec{r}), \quad \Phi^{\alpha l}_{njm_j}(\zeta, \vec{k}), Z^{\alpha l}_{njm_j}(\zeta, \beta\theta\varphi) \tag{3}$$

$$\overline{K}^{\alpha l}_{njm_j} = \overline{\Psi}^{\alpha l}_{njm_j}(\zeta, \vec{r}), \quad \overline{\Phi}^{\alpha l}_{njm_j}(\zeta, \vec{k}), \overline{Z}^{\alpha l}_{njm_j}(\zeta, \beta\theta\varphi). \tag{4}$$

For quasirelativistic Slater type vector orbitals

$$K^{l}_{njm_j} = \begin{pmatrix} a^l_{jm_j}(0)k_{nlm_l(0)} \\ a^l_{jm_j}(1)k_{nlm_l(1)} \\ a^l_{jm_j}(2)k_{nlm_l(2)} \end{pmatrix}, \tag{5}$$

where

$$K^{l}_{njm_j} = \mathrm{X}^{l}_{njm_j}(\zeta, \vec{r}), \quad U^{l}_{njm_j}(\zeta, \vec{k}), V^{l}_{njm_j}(\zeta, \beta\theta\varphi) \tag{6}$$

and

$$n \geq 1, \quad 1 \leq j \leq n, \quad -j \leq m_j \leq j,$$
$$j-1 \leq l \leq \min(j+1, n-1),$$

$$m_l(\lambda) = m_j - 1 + \lambda, \quad 0 \leq \lambda \leq 2.$$

Here, the complete orthonormal sets of scalar functions ($k^{\alpha}_{nlm_l}, \overline{k}^{\alpha}_{nlm_l}$), and Slater type scalar orbitals k_{nlm_l} are defined as

$$k^{\alpha}_{nlm_l} = \psi^{\alpha}_{nlm_l}(\zeta, \vec{r}), \quad \phi^{\alpha}_{nlm_l}(\zeta, \vec{k}), \quad z^{\alpha}_{nlm_l}(\zeta, \beta\theta\varphi) \tag{7}$$

$$\overline{k}^{\alpha}_{nlm_l} = \overline{\psi}^{\alpha}_{nlm_l}(\zeta, \vec{r}), \quad \overline{\phi}^{\alpha}_{nlm_l}(\zeta, \vec{k}), \quad \overline{z}^{\alpha}_{nlm_l}(\zeta, \beta\theta\varphi) \tag{8}$$

$$k_{nlm_l} = \chi_{nlm_l}(\zeta, \vec{r}), \quad u_{nlm_l}(\zeta, \vec{k}), \quad v_{nlm_l}(\zeta, \beta\theta\varphi). \tag{9}$$

See Refs. [2–5] for exact definition of functions $\psi^{\alpha}_{nlm_l}, \overline{\psi}^{\alpha}_{nlm_l}, \phi^{\alpha}_{nlm_l}, \overline{\phi}^{\alpha}_{nlm_l}, z^{\alpha}_{nlm_l}, \overline{z}^{\alpha}_{nlm_l}, \chi_{nlm_l}, u_{nlm_l}$ and v_{nlm_l} occurring in these formulas.

The quasirelativistic and nonrelativistic functions satisfy the following orthonormality relations:

$$\int K^{\alpha l\dagger}_{njm_j}(\zeta, \vec{x}) \overline{K}^{\alpha l'}_{n'j'm'_j}(\zeta, \vec{x}) d^3\vec{x} = \delta_{nn'}\delta_{ll'}\delta_{jj'}\delta_{m_jm'_j} \tag{10}$$

$$\int K^{l\dagger}_{njm_j}(\zeta, \vec{x}) K^{l'}_{n'j'm'_j}(\zeta, \vec{x}) d^3\vec{x} = \frac{(n+n')!}{[(2n)!(2n')!]^{1/2}} \delta_{ll'}\delta_{jj'}\delta_{m_jm'_j}, \tag{11}$$

$$\int k^{\alpha *}_{nlm_l}(\zeta, \vec{x}) \overline{k}^{\alpha}_{n'l'm'_l}(\zeta, \vec{x}) d^3\vec{x} = \delta_{nn'}\delta_{ll'}\delta_{m_lm'_l}, \tag{12}$$

$$\int k^{*}_{nlm_l}(\zeta, \vec{x}) k_{n'l'm'_l}(\zeta, \vec{x}) d^3\vec{x} = \frac{(n+n')!}{[(2n)!(2n')!]^{1/2}} \delta_{ll'}\delta_{m_lm'_l} \tag{13}$$

where $\vec{x} \equiv \vec{r}, \vec{k}, \beta\theta\varphi$

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

3 Relativistic vector wave functions and Slater type relativistic vector orbitals

For the construction of the complete orthonormal sets of relativistic 6-component vector wave functions, and Slater type relativistic vector orbitals in coordinate, momentum and four-dimensional spaces we use the quasirelativistic 3-component vector wave functions $\left(K^{\alpha l}_{njm_j}, \overline{K}^{\alpha l}_{njm_j} \text{ and } K^{\alpha, l+t}_{njm_j}, \overline{K}^{\alpha, l+t}_{njm_j}\right)$, and quasirelativistic Slater type vector orbitals $\left(K^{l}_{njm_j}\ \text{ and }\ K^{l+t}_{njm_j}\right)$ defined by Eqs. 1, 2 and 5. Here, the values of parameter t are determined from the relation

$$j = l + t, \tag{14}$$

where $t = 0, \pm 1$.

Using these relations we obtain the following relativistic formulae through the quasirelativistic and nonrelativistic functions:

For relativistic vector wave functions

$$K^{\alpha lt}_{njm_j} = \frac{1}{\sqrt{2}}\begin{pmatrix} K^{\alpha l}_{njm_j} \\ K^{\alpha,l+t}_{njm_j} \end{pmatrix} \tag{15a}$$

$$= \frac{1}{\sqrt{2}}\begin{pmatrix} a^{l}_{jm_j}(0)k^{\alpha}_{nlm_l(0)} \\ a^{l}_{jm_j}(1)k^{\alpha}_{nlm_l(1)} \\ a^{l}_{jm_j}(2)k^{\alpha}_{nlm_l(2)} \\ a^{l+t}_{jm_j}(0)k^{\alpha}_{n,l+t,m_{l+t}(0)} \\ a^{l+t}_{jm_j}(1)k^{\alpha}_{n,l+t,m_{l+t}(1)} \\ a^{l+t}_{jm_j}(2)k^{\alpha}_{n,l+t,m_{l+t}(2)} \end{pmatrix} \tag{15b}$$

$$\overline{K}^{\alpha lt}_{njm_j} = \frac{1}{\sqrt{2}}\begin{pmatrix} \overline{K}^{\alpha l}_{njm_j} \\ \overline{K}^{\alpha,l+t}_{njm_j} \end{pmatrix} \tag{16a}$$

$$= \frac{1}{\sqrt{2}}\begin{pmatrix} a^{l}_{jm_j}(0)\overline{k}^{\alpha}_{nlm_l(0)} \\ a^{l}_{jm_j}(1)\overline{k}^{\alpha}_{nlm_l(1)} \\ a^{l}_{jm_j}(2)\overline{k}^{\alpha}_{nlm_l(2)} \\ a^{l+t}_{jm_j}(0)\overline{k}^{\alpha}_{n,l+t,m_{l+t}(0)} \\ a^{l+t}_{jm_j}(1)\overline{k}^{\alpha}_{n,l+t,m_{l+t}(1)} \\ a^{l+t}_{jm_j}(2)\overline{k}^{\alpha}_{n,l+t,m_{l+t}(2)} \end{pmatrix}. \tag{16b}$$

For Slater type relativistic vector orbitals

$$K^{lt}_{njm_j} = \frac{1}{\sqrt{2}}\begin{pmatrix} K^{l}_{njm_j} \\ K^{l+t}_{njm_j} \end{pmatrix} \tag{17a}$$

$$= \frac{1}{\sqrt{2}}\begin{pmatrix} a^{l}_{jm_j}(0)k_{nlm_l(0)} \\ a^{l}_{jm_j}(1)k_{nlm_l(1)} \\ a^{l}_{jm_j}(2)k_{nlm_l(2)} \\ a^{l+t}_{jm_j}(0)k_{n,l+t,m_{l+t}(0)} \\ a^{l+t}_{jm_j}(1)k_{n,l+t,m_{l+t}(1)} \\ a^{l+t}_{jm_j}(2)k_{n,l+t,m_{l+t}(2)} \end{pmatrix}. \tag{17b}$$

The relativistic vector wave functions and Slater type relativistic vector orbitals obtained satisfy the following orthogonality relations:

$$\int K^{\alpha lt\dagger}_{njm_j}(\zeta,\vec{x})\overline{K}^{\alpha l't'}_{n'j'm'j}(\zeta,\vec{x})d^3\vec{x} = \delta_{nn'}\delta_{ll'}\delta_{jj'}\delta_{m_jm'_j}\delta_{tt'} \tag{18}$$

$$\int K^{lt\dagger}_{njm_j}(\zeta,\vec{x})K^{l't'}_{n'j'm'_j}(\zeta,\vec{x})d^3\vec{x} = \frac{(n+n')!}{[(2n)!(2n')!]^{1/2}}\delta_{ll'}\delta_{jj'}\delta_{m_jm'_j}\delta_{tt'} \tag{19}$$

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

We see from the formulas presented in this work, all of the relativistic vector wave functions and Slater type relativistic vector orbitals defined in coordinate, momentum and four-dimensional spaces are expressed through the corresponding nonrelativistic and quasirelativistic functions. Thus, all of the formulae obtained in [5] for the scalar orbitals in coordinate, momentum and four-dimensional spaces can be also used in the case of relativistic functions.

4 Overlap integrals of Slater type relativistic vector orbitals in coordinate space

We evaluate, as an example of application, the two-center overlap integrals over Slater type relativistic vector orbitals with the same screening parameters defined in coordinate space as

$$S^{lt,l't'}_{njm_j,n'j'm'_j}(\vec{G}) = \int X^{lt\dagger}_{njm_j}(\zeta,\vec{r})X^{l't'}_{n'j'm'_j}(\zeta,\vec{r}-\vec{R})d^3\vec{r}, \tag{20}$$

where $\vec{r} = \vec{r}_a$, $\vec{r} - \vec{R} = \vec{r}_b$, and $\vec{G} = 2\zeta\vec{R}$. For the evaluation of these integrals we use Eq. 17b for $K^{lt}_{njm_j} = \mathrm{X}^{lt}_{njm_j}$. Then, we can express integral (20) in terms of nonrelativistic overlap integrals:

$$S^{lt,l't'}_{njm_j,n'j'm'j}(\vec{G}) = \frac{1}{2}\sum_{\lambda=0}^{2}\left\{a^{l,l'}_{jm_j,j'm'_j}(\lambda)s_{nlm_l(\lambda),n'l'm'_l(\lambda)}(\vec{G}) + a^{l+t;l'+t'}_{jm_j;j'm'_j}(\lambda)s_{n,l+t,m_{l+t}(\lambda);n',l'+t',m'_{l'+t'}(\lambda)}(\vec{G})\right\}, \tag{21}$$

where $a^{l,l'}_{jm_j,j'm'_j}(\lambda) = a^{l}_{jm_j}(\lambda)a^{l'}_{j'm'_j}(\lambda)$. The nonrelativistic overlap integrals over Slater type scalar orbitals occurring on the right-hand side of Eq. 21 are defined by

$$\begin{aligned} s_{nlm_l,n'l'm'_l}(\vec{G}) &= \int \chi^*_{nlm_l}(\zeta,\vec{r})\chi_{n'l'm'_l}(\zeta,\vec{r}-\vec{R})d^3\vec{r} \\ &= \{[2(n+\alpha)]!/(2n)!\}^{1/2} \end{aligned} \tag{22a}$$

Table 1 The values of overlap integrals over Slater type relativistic vector 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	$G = 2\zeta R$	$S^{lt,l't'}_{njmj,n'j'm'j}(\vec{G})$		
													$\alpha = 1$	$\alpha = 0$	$\alpha = -1$
3	1	1	2	0	2	0	1	1	0	0	0	20	3.3691107660E-02	3.3691107660E-02	3.3691107660E-02
4	2	0	2	1	3	1	0	1	1	0	0	40	−4.6431835972E-04	−4.6431835972E-04	−4.6431835972E-04
5	2	−1	1	1	4	2	0	2	1	0	0	50	3.3683518204E-05	3.3683518204E-05	3.3683518204E-05
7	4	0	4	2	5	4	−1	3	2	0	0	60	2.2810175518E-05	2.2810175518E-05	2.2810175518E-05
8	5	1	6	4	7	6	0	6	4	0	0	75	3.1922967909E-08	3.1922967909E-08	3.1922967909E-08
4	3	−1	2	1	3	1	1	2	0	$\pi/4$	$5\pi/3$	10	−1.1017484210E-02	−1.1017484210E-02	−1.1017484210E-02
5	3	0	3	1	4	2	0	2	1	$\pi/5$	$2\pi/7$	25	−4.2418161877E-02	−4.2418161877E-02	−4.2418161877E-02
6	3	1	4	2	5	2	−1	1	1	$\pi/6$	$\pi/4$	35	2.2188910614E-03	2.2188910614E-03	2.2188910614E-03
7	5	1	6	4	7	4	0	4	2	$3\pi/7$	$\pi/6$	70	1.0702380841E-06	1.0702380841E-06	1.0702380841E-06
8	6	0	6	5	8	5	1	6	4	$5\pi/8$	$6\pi/5$	80	1.8329996850E-06	1.8329996850E-06	1.8329996850E-06

$$\times \sum_{\mu=l+1}^{n+\alpha} \sum_{\mu'=l'+1}^{n'} \frac{1}{(2\mu)^{\alpha}} \overline{\omega}_{n+\alpha,\mu}^{\alpha l} \overline{\omega}_{n'\mu'}^{\alpha l'} s_{\mu l m_l, \mu' l' m_l'}^{\alpha}(\vec{G}), \tag{22b}$$

where

$$s_{\mu l m_l, \mu' l' m_l'}^{\alpha}(\vec{G}) = \int \overline{\psi}_{\mu l m_l}^{\alpha^*}(\zeta, \vec{r}) \psi_{\mu' l' m_l'}^{\alpha}(\zeta, \vec{r} - \vec{R}) d^3\vec{r}. \tag{23}$$

The relation for the coefficients $\overline{\omega}^{\alpha l}$ is given in Ref. [2]. In Eq. 22b, the overlap integral over Slater type scalar orbitals are expressed in terms of overlap integrals over complete orthonormal sets of scalar ψ^{α}-ETO. The analytical relations for the nonrelativistic overlap integrals over ψ^{α}-ETO are presented in [5].

The values of overlap integrals of Slater type relativistic vector orbitals with the same screening parameters obtained with the help of complete orthonormal sets of ψ^{1}-, ψ^{0}- and ψ^{-1}-ETO using Mathematica 5.0 international mathematical software are presented in Table. As can be seen from this table that the suggested approach guarantees a highly accurate calculation of the overlap integrals over Slater type relativistic vector orbitals.

We notice that the overlap integrals over Slater type relativistic vector orbitals with the same screening parameters may be played a significant role in the calculation of arbitrary multicenter relativistic integrals arising in the study of different problems in Relativistic quantum mechanics. Thus, the relations for the nonrelativistic overlap integrals over scalar ψ^{α}-ETO, ϕ^{α}-MSO, z^{α}-HSH and χ-STO presented in our previous papers can be used in the evaluation of multicenter integrals over corresponding quasirelativistic and relativistic vector wave functions and Slater vector orbitals.

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