COMBINED OPEN SHELL HARTREE-FOCK THEORY of ATOMIC-MOLECULAR and NUCLEAR SYSTEMS, COMPLETE ORTHONORMAL SETS of EXPONENTIAL TYPE ORBITALS and THEİR APPLICATIONS

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CONTENTS

1. COMBINED OPEN SHELL HARTREE-FOCK THEORY of ATOMIC-MOLECULAR and NUCLEAR SYSTEMS (J.Math.Chem, 2007)

Abstract

In this study, the combined Hartree-Fock and Hartree-Fock-Roothaan equations are derived for multideterminantal single configuration states with any number of open shells of atoms, molecules and nuclei. It is shown that the postulated orbital-dependent energy and Fock operators are invariant to the unitary transformation of orbitals. This new methodology is based entirely on the spin-restricted Hartree-Fock theory. As an application of combined open shell theory of atomic-molecular and nuclear systems presented in this paper we have solved Hartree-Fock-Roothaan equations for the ground state of electronic configuration $C(1s^2 2s^2 2p^2)$ using Slater type orbitals as a basis.

Keywords: Hartree-Fock theory, Open-shell systems, Multideterminantal states

1. Introduction

The main application of Hartree-Fock (HF) method was, in atomic and molecular physics, the study of Coulomb systems (atoms, ions and molecules) with a purely Coulombic Hamiltonian of electrons interacting with static nuclei. In nuclear physics, the use of HF method to compute the ground state of nuclei is more recent and we refer, for example, to papers [1-5] and the references therein. Roothaan's open shell HF theory [6] is commonly used to evaluate the various properties of certain states of atoms, molecules and nuclei (see, e. g., Refs. [7-15]). This approach does not seem to have been extended to arbitrary open-shell states. In Roothaan's treatment, which is an extension of HF theory for closed shell systems [16], and in the extensions to open-shell states by others [17-23], there are well-known complicating features which do not occur in the closed-shell equations. In Ref.[24], we eliminated these difficulties and derived HF and Hartree-Fock-Roothaan (HFR) equations applicable to any multideterminantal state of a single configuration of atomic and molecular systems that has arbitrary open-shells. The aim of this report is to derive the combined HF and HFR equations of atomic-molecular and nuclear systems applicable to any multideterminantal state of a single configuration that has any number of open shells of any symmetry.

2. Definitions and basic formulas

In the present paper, we use the combined Hamiltonian of the atomic-molecular and nuclear systems of N particles (electrons or nucleons) in the following form:

$$\hat{H}^{\omega}=\sum_{\mu=1}^{N}\left(-\frac{1}{2m^{\omega-1}}\nabla_{\mu}^{2}-\delta_{\omega 1}\sum_{a}\frac{Z_{a}}{r_{a\mu}}\right)+\sum_{\mu=1}^{N-1}\sum_{\nu=\mu+1}^{n}f^{\omega}\left(x_{\mu\nu}\right), \tag{1}$$

where $f^{\omega}(x_{\mu\nu})$ are the repulsion or attraction interaction potentials for electrons $(\omega=1)$ and nucleons$(\omega=2)$, respectively; m is the mass of nucleon. Thus we deal in both cases with fermions, i. e., particles which obey the Pauli exclusion principle. This means that the particles of atomic-molecular and nuclear systems will be described by antisymmetric wave functions-Slater determinants. The general form of Slater determinants for an N - particle open shell system may be written as [25]

$$U\left(u_{n_{N-k+1}}(x_{N-k+1})\ \ldots\ u_{n_N}(x_N)\right)\equiv U\left(u_{n_1}(x_1)u_{n_2}(x_2)\ \ldots\ u_{n_{N-k}}(x_{N-k})u_{n_{N-k+1}}(x_{N-k+1})\ \ldots\ u_{n_N}(x_N)\right)=$$

$$=\frac{1}{\sqrt{N!}}\begin{vmatrix} u_{n_1}(x_1) & u_{n_2}(x_1) & \ldots & u_{n_{N-k}}(x_1) & u_{n_{N-k+1}}(x_1) & \ldots & u_{n_N}(x_1) \\ u_{n_1}(x_2) & u_{n_2}(x_2) & \ldots & u_{n_{N-k}}(x_2) & u_{n_{N-k+1}}(x_2) & \ldots & u_{n_N}(x_2) \\ . & . & \ldots & . & . & \ldots & . \\ . & . & \ldots & . & . & \ldots & . \\ . & . & \ldots & . & . & \ldots & . \\ u_{n_1}(x_N) & u_{n_2}(x_N) & \ldots & u_{n_{N-k}}(x_N) & u_{n_{N-k+1}}(x_N) & \ldots & u_{n_N}(x_N) \end{vmatrix}, \tag{2}$$

where $n\equiv im_t^{\omega-1}m_s$ and $x\equiv xyz\kappa^{\omega-1}\sigma$. Here, $u_n(x)\equiv u_i(xyz)\upsilon_{m_t}^{\omega-1}(\kappa)u_{m_s}(\sigma)$ is the isospin-spin orbital; $\mathrm{u_i(xyz)}$, $\upsilon_{m_t}(\kappa)$ and $\mathrm{u_{m_s}}(\sigma)$ are the spatial, isospin and spin wave functions, respectively. The spin orbital $u_n(x)\equiv u_i(xyz)u_{m_s}(\sigma)$ for atoms and molecules is the special case of isospin-spin orbital for $\omega=1$. $(u_{n_1},u_{n_2},\ \ldots,\ u_{n_{N-k}})$ *and* $(u_{n_{N-k+1}},\ldots,\ u_{n_N})$ occurring in Eq.(2) are the sets of orthonormal isospin-spin orbitals for closed and open shells, respectively, where $0\le k\le N$. All of the orthonormal and independent Slater determinants for a given configuration can be obtained from Eq.(2). The first $N-k$ orthonormal and independent isospin-spin orbitals in these determinants are the same (closed shells), and all other k isospin-spin orbitals are different (open shells). The orbitals and Slater determinants form the orthonormal sets:

$$\int u_i^{*}u_s\,dv=\delta_{is} \tag{3a}$$

$$\sum_{k}v_{m_t}^{*}(\kappa)\,v_{m_t'}(\kappa)=\delta_{m_t m_t'} \tag{3b}$$

$$\sum_{\sigma}u_{m_s}^{*}(\sigma)\,u_{m_s'}(\sigma)=\delta_{m_s m_s'} \tag{3c}$$

$$\int U^{*}U'd\tau=\delta_{UU'} \tag{3d}$$

3. Combined orbital dependent energy expression

The postulated energy expectation value for a single configuration multideterminantal state of combined atomic-molecular and nuclear systems with a given space, spin and isospin symmetry can be written in the following form:

$$E^{\omega} = \omega\left[2\sum_{i}^{n} f_i h_i + \sum_{ijkl}^{n}(2\omega A_{kl}^{ij} J_{kl}^{ij} - B_{kl}^{ij} K_{kl}^{ij})\right]. \quad (4)$$

Here $n = n_c + n_o$ is the number of occupied orbitals belonging to closed (n_c) and open (n_o) shells, $1 \le i, j, k, l \le n$ and $\omega = 1,2$. For $\omega = 1$ and for $\omega = 2$ Eq.(4) denotes the energy expectation value of atomic-molecular and nuclear systems, respectively; f_i is the fractional occupancy of shell i which is determined by

$$f_i = \frac{N_i}{N_{0i}}, \quad (5)$$

where N_{0i} and N_i are number of states and particles in shell i, respectively. It should be noted that the orbital occupation numbers can also be determined by the use of MCSCF or CASSCF approaches, which are well suited for open-shell problems and routine these days (see, e. g., Ref.[7]). In MCSCF and CASSCF orbital optimizations, the orbital occupation numbers are the result of calculations and not some arbitrary numbers selected before the calculation is performed.

In Eq.(4), the coefficients A_{kl}^{ij} and B_{kl}^{ij} are the coupling-projection constants. For closed-closed and closed-open shell interaction energies $(1 \le i, j \le n_c, 1 \le k, l \le n \; and \; 1 \le i, j \le n, 1 \le k, l \le n_c)$ the coupling-projection coefficients A_{kl}^{ij} and B_{kl}^{ij} are determined by

$$A_{kl}^{ij} = B_{kl}^{ij} = f_i f_k \delta_{ij} \delta_{kl}. \quad (6)$$

In the case of open-open shell interaction energies ($n_c + 1 \le i, j \le n \; and \; n_c + 1 \le k, l \le n$) the values of coefficients A_{kl}^{ij} and B_{kl}^{ij} depend on the state under study. We notice that the possibility of writing the combined energy of atomic-molecular and nuclear systems in form (4) is based on the assumption that the energy E^{ω} is the average expectation value for all the degenerate total orthonormal sets of multideterminantal wave functions $\Psi_{M_\Gamma}^{\Gamma}$ for state with the irreducible representation Γ:

$$E_{\Gamma}^{\omega} = \frac{1}{N_{\Gamma}} \sum_{M_{\Gamma}} \int \Psi_{M_{\Gamma}}^{\Gamma *} \hat{H} \Psi_{M_{\Gamma}}^{\Gamma} d\tau \;, \quad (7)$$

where

$$\Psi_{M_\Gamma}^{\Gamma}=\begin{cases}\Psi_{M_L M_T M_S}^{LTS}\\ \Psi_{M_L M_S}^{LS}\\ \Psi_{M_\Lambda M_S}^{\Lambda S}\\ \Psi_{M_\Gamma M_S}^{\Gamma S}\end{cases},N_\Gamma=\begin{cases}(2L+1)(2T+1)(2S+1) & \text{for Nuclei}\\ (2L+1)(2S+1) & \text{for Atoms}\\ (2-\delta_{\Lambda 0})(2S+1) & \text{for Linear Molecules}\\ \Gamma_d(2S+1) & \text{for Nonlinear Molecules.}\end{cases} \quad (8)$$

Here, the quantities L, T and S are the total orbital, isospin and spin quantum numbers, respectively.

In Eq.(4), h_i, J_{kl}^{ij} and K_{kl}^{ij} are defined by

$$h_i=\int u_i^*(\vec{r}_1)\hat{h}u_i(\vec{r}_1)dv_1 \quad (9)$$

$$J_{kl}^{ij}=\int u_i^*(\vec{r}_1)\hat{J}_{kl}(\vec{r}_1)u_j(\vec{r}_1)dv_1=\int u_k^*(\vec{r}_2)\hat{J}_{ij}(\vec{r}_2)u_l(\vec{r}_2)dv_2 \quad (10)$$

$$K_{kl}^{ij}=\int u_i^*(\vec{r}_1)\hat{K}_{kl}(\vec{r}_1)u_j(\vec{r}_1)dv_1=\int u_k^*(\vec{r}_2)\hat{K}_{ij}(\vec{r}_2)u_l(\vec{r}_2)dv_2\,, \quad (11)$$

where

$$\hat{h}=-\frac{1}{2m^{\omega-1}}\nabla_1^2-\delta_{\omega 1}\sum_a\frac{Z_a}{r_{a1}} \quad (12)$$

$$\hat{J}_{kl}(\vec{r}_1)\varphi(\vec{r}_1)=(\int u_k^*(\vec{r}_2)f(x_{21})u_l(\vec{r}_2)dv_2)\varphi(\vec{r}_1) \quad (13)$$

$$\hat{K}_{kl}(\vec{r}_1)\varphi(\vec{r}_1)=(\int u_k^*(\vec{r}_2)f(x_{21})\varphi(\vec{r}_2)dv_2)u_l(\vec{r}_1)\,. \quad (14)$$

Here, $\hat{K}_{kl}$ is the exchange operator. See Ref.[24] for the definition of symmetrical properties of square n^2-dimensional supermatrices A, B, J and K.

In the single-determinantal closed shell case, one has $f_i=f_k=1$ and $A_{kl}^{ij}=B_{kl}^{ij}=\delta_{ij}\delta_{kl}$. Then, the formula for E^ω, Eq.(4), can be rewritten using integrals h_i, J_{kk}^{ii} and K_{kk}^{ii},

$$E^\omega=\omega\left[2\sum_i^n h_i+\sum_{ik}^n(2\omega J_{kk}^{ii}-K_{kk}^{ii})\right], \quad (15)$$

where J_{kk}^{ii} and K_{kk}^{ii} are the ordinary 2-indexed integrals of Roothaan's closed shell HF theory [16].

4. Use of modified Slater's determinantal method in evaluation of coupling-projection coefficients

For the evaluation of coupling-projection coefficients occurring in the combined energy expression, Eq. (4), we have to find independent Slater determinants and orthonormal multideterminantal wave functions of terms. For this purpose we use the determinantal method presented in Refs. [26, 27]. However, by the use of Slater's determinantal method it is not only difficult, in general, to find independent Slater determinants but also to simplify the construction of multideterminantal wave functions for open-shell systems. In this section we have modified Slater's determinantal method for the evaluation of independent Slater determinants, which are useful for the construction of multideterminantal wave functions and for the evaluation of coupling-projection coefficients.

We have now to consider the problem of determining which of the independent Slater determinants occur in a given configuration. According to Refs. [25] we can write down the N individual sets comprising each complete set, which occurs in the configuration. The number and nature of the closed shells is without effect on the values of quantum numbers in the open-shell spin-orbitals. We denote here a set of quantum numbers for open-shell spin-orbitals by n_i (where i = 1,2,…,k), namely,

$$n_i \equiv 1,2,...,N_i, \tag{16}$$

where N_i is the number of spin-orbitals in the open shell i.

In order to obtain from Eq. (2) all of the independent Slater determinants for a given electronic or nucleonic configuration we modified the Slater's determinantal method for the states of the same open-shell by taking into account in Eq. (2) only those values of n_i in the following form:

$$n_1 < n_2 < ... < n_k. \tag{17}$$

We refer to the Slater rule based on the inequality (17) as modified Slater's determinantal method for the evaluation of independent determinantal wave functions. It should be noted that in the case of different open-shells the sets of quantum numbers in Eq. (2) are independent. Therefore it is easy to obtain the independent determinantal wave functions for these systems by the use of modified determinantal method.

Now we can move on, as an example, to an application of modified determinantal method for the determination of Slater determinants for atoms. Having made a list of the complete sets which belong to an atomic electronic configuration we may classify them by values of $\sum m_l = M_L$ and $\sum m_s = M_S$. To make the argument concrete, let us consider the configuration $C(1s^2 2s^2 2p^2)$ in which two electrons occur outside closed shells. The complete sets for these electrons classified by M_L, M_S values and the independent determinants obtained from Eq. (2) by modified determinantal method are shown in Table 1.

It is easy to find from Table 1 the terms and the orthonormal sets of multideterminantal wave functions $\Psi^{LS}_{M_L M_S}$ which are egienfunctions of operators $\hat{L}^2$, $\hat{L}_Z$, $\hat{S}^2$, and $\hat{S}_z$. The results are given in Table 2.

For the calculation of coupling-projection coefficients A^{ij}_{kl} and B^{ij}_{kl} for open shell electrons we have to take into account Table 2 for wave functions $\Psi^{LS}_{M_L M_S}$ in Eq. (7) and to compare the results with Eq. (4). The obtained results for $C(1s^2 2s^2 2p^2)$ are presented in Table 3, where

nlm:100 200 211 210 21−1

i: 1 2 3 4 5

and $n_c = 2$, $n_0 = 3$, $n = n_c + n_0 = 5$, $f_1 = f_2 = 1$, $f_3 = f_4 = f_5 = \frac{2}{6}$.

5. Hartree-Fock and Hartree-Fock-Roothaan equations

The formula (4) for E^{ω} seems to be completely general, for a single configuration with any number of open shells. The use of symmetrical and Hermitian properties of the $A^{ij}_{kl}, B^{ij}_{kl}, \hat{J}_{kl}$ *and* $\hat{K}_{kl}$ (see Eqs.(11)-(14) of Ref.[24]) simplifies the derivation of combined HF equations.

We now apply the variational principle to the total energy, Eq.(4), in order to obtain the combined HF equations for the spatial orbitals u_i of atoms, molecules and nuclei. This derivation closely parallels the derivation of HF equations in Ref.[24] for the atomic and molecular systems. If we take into account the subsidiary conditions (3a) by the method of the Lagrangian undetermined multipliers, denote the Lagrangian multiplier by $-2\omega\varepsilon_{si}$ and make use of the symmetrical and Hermitian properties of $A^{ij}_{kl}, B^{ij}_{kl}, \hat{h}, \hat{J}_{kl}$ *and* $\hat{K}_{kl}$, then the variation of energy E^{ω}, Eq.(4), gives the following equations for the orbitals;

$$\hat{F}^i u_i = \sum_s u_s \varepsilon_{si}\,, \tag{18}$$

Where ε is a Hermitian matrix of Lagrangian multipliers and $\hat{F}^i$ is the Fock operator defined by

$$\hat{F}^i = f_i \hat{h} + \hat{G}^i\,. \tag{19}$$

Here, the total particle interaction operator $\hat{G}^i$ is determined by

$$\hat{G}^i = \sum_{j,kl}^{n} (2\omega \hat{A}^{ij}_{kl} \hat{J}_{kl} - \hat{B}^{ij}_{kl} \hat{K}_{kl})\,. \tag{20}$$

The quantities $\hat{A}^{ij}_{kl}$ and $\hat{B}^{ij}_{kl}$ occurring in Eq.(20) are the coupling-projection operators, defined by

$$\hat{A}^{ij}_{kl} u_i = A^{ij}_{kl} u_j \tag{21}$$

$$\hat{B}_{kl}^{ij}u_i = B_{kl}^{ij}u_j . \qquad (22)$$

The operator $\hat{F}^i$, which is defined in terms of the orbitals u_i, is easily shown to be invariant when orbitals are subjected to the unitary transformation by means of a unitary matrix Q [24]:

$$u_i(\vec{r}) = \sum_{i'} u'_{i'}(\vec{r})Q^+_{i'i} , \quad u'_{i'}(\vec{r}) = \sum_i u_i(\vec{r})Q_{ii'} \quad . \qquad (23)$$

It is easy to show that the energy expression, Eq.(4), is also invariant to such changes of the orbitals.

Accordingly, the orbitals $u'_{i'}$ satisfy

$$\hat{F}^{i'}u_{i'} = \sum_{s'} u'_{s'}\varepsilon'_{s'i'} , \qquad (24)$$

where

$$\varepsilon' = Q^+ \varepsilon Q . \qquad (25)$$

Eq.(25) shows that the Fock operator can be diagonalized using the unitary combinations of the original orbitals. Since the matrix ε is Hermitian, there exists a unitary matrix Q so that $\varepsilon' = Q^+ \varepsilon Q$ is a diagonal matrix with real diagonal elements. It is therefore no loss of generality if we assume that our set of orbitals satisfies the simpler equations

$$\hat{F}^i u_i = \varepsilon_i u_i , \qquad (26)$$

where the operator $\hat{F}^i$ is defined by Eq.(19).

It should be noted that the orbital-dependent Fock operators and total energy in Roothaan's open shell HF theory defined by [6]

$$E = 2\sum_k H_k + \sum_{kl}(2J_{kl} - K_{kl}) + f[2\sum_m H_m + f\sum_{mn}(2aJ_{mn} - bK_{mn}) + 2\sum_{km}(2J_{km} - K_{km})] \qquad (27)$$

are not invariant to the unitary transformation of orbitals and, therefore, the Fock operators of Roothaan's approach can not be diagonalized.

The combined HF equations for closed-shell atomic-molecular and nuclear systems can be obtained from Eq.(26) using Eq.(6) for $f_i = f_k = 1$:

$$\hat{F}u_i = \varepsilon_i u_i , \qquad (28)$$

where

$$\hat{F} = \hat{h} + \hat{G} \qquad (29)$$

$$\hat{G} = \sum_k^n (2\omega \hat{J}_{kk} - \hat{K}_{kk}) . \qquad (30)$$

Using Eqs.(4), (19), (20) and (26) we can express the total energy in terms of the orbital energies ε_i and the one-particle integrals h_i:

for open-shell systems

$$E^{\omega} = \omega \sum_{i}^{n} (f_i h_i + \varepsilon_i)\,, \tag{31}$$

for closed-shell systems

$$E^{\omega} = \omega \sum_{i}^{n} (h_i + \varepsilon_i)\,. \tag{32}$$

It is well known that the orbitals u_i, occurring in the atomic-molecular and nuclear structure theories, usually are defined as linear combinations of arbitrary basic atomic or nuclear orbitals (LCAO or LCNO) [16]:

$$u_i = \sum_{q} \chi_q C_{qi}\,. \tag{33}$$

In order to obtain the HFR equations for the coefficients C_{qi} we have to minimize the expression (4) by varying the coefficients C_{qi} within the limits permitted by the requirement that the orbitals (33) form an orthonormal set, as expressed by Eq.(3a). We restrict ourselves here to writing down the results for the combined open shell HFR equations of atomic-molecular and nuclear systems:

$$\sum_{q} (\hat{F}^{i}_{pq} - \varepsilon_i S_{pq}) C_{qi} = 0\,, \tag{34}$$

where

$$S_{pq} = \int \chi^{*}_{p} \chi_q dv \tag{35}$$

$$\hat{F}^{i}_{pq} = f_i h_{pq} + \hat{G}^{i}_{pq} \tag{36}$$

$$h_{pq} = \int \chi^{*}_{p} \Big(-\frac{1}{2m^{\omega-1}} \nabla^{2}_{1} - \delta_{\omega 1} \sum_{a} \frac{Z_a}{r_{a1}}\Big) \chi_q dv_1 \tag{37}$$

$$\hat{G}^{i}_{pq} = \sum_{j,rs} \Big(2\omega\, \hat{a}^{ij}_{rs}\, I^{pq}_{rs} - \hat{b}^{ij}_{rs}\, K^{pq}_{rs} \Big). \tag{38}$$

Here, the $\hat{a}^{ij}_{rs}$ and $\hat{b}^{ij}_{rs}$ are the coupling-projection operators of HFR equations determined through the matrix elements of the square n- dimensional density matrices $\hat{a}^{ij}$ and $\hat{b}^{ij}$ by the following formulas:

$$\hat{a}^{ij} = C \hat{A}^{ij} C^{+} \tag{39}$$

$$\hat{b}^{ij} = C \hat{B}^{ij} C^{+}\,, \tag{40}$$

where the operators $\hat{a}^{ij}$ and $\hat{b}^{ij}$ are defined by

$$\hat{a}^{ij} C_{qi} = a^{ij} C_{qj} \tag{41}$$

$$\hat{b}^{ij} C_{qi} = b^{ij} C_{qj} . \tag{42}$$

The quantities I_{rs}^{pq} and K_{rs}^{pq} occurring in Eq.(38) are defined by

$$I_{rs}^{pq} = \iint \chi_p^*(x_1)\chi_r^*(x_2) f(x_{21}) \chi_q(x_1) \chi_s(x_2) dv_1 dv_2 \tag{43}$$

$$K_{rs}^{pq} = \iint \chi_p^*(x_1)\chi_r^*(x_2) f(x_{21}) \chi_s(x_1) \chi_q(x_2) dv_1 dv_2 . \tag{44}$$

Taking into account Eq.(6) for $f_i = f_k = 1$ in Eq.(33) it is easy to obtain for the combined closed shell HFR equations the following formulas:

$$\sum_q (F_{pq} - \varepsilon_i S_{pq}) C_{qi} = 0 , \tag{45}$$

where

$$F_{pq} = h_{pq} + G_{pq} \tag{46}$$

$$G_{pq} = \sum_{rs} \rho_{rs}^* \left(2\omega I_{rs}^{pq} - K_{rs}^{pq} \right) \tag{47}$$

$$\rho = CC^+ . \tag{48}$$

We see from the Tables 1-3 that the modified determinantal method can be of considerable importance in the simplification and calculation of independent Slater determinants, multideterminantal wave functions and coupling-projection coefficients for open-shell systems. As an application of modified determinantal method, we have solved combined HFR equations for the ground state of an $C(1s^2 2s^2 2p^2)$ atom using Slater-type atomic orbitals as a basis. The results of computer calculations for the linear-combination coefficients, orbital energies, total energy and virial coefficient are given in Table 4 (the data for the screening constants of Slater atomic orbitals were taken from Ref. [28]**.** The results given in this table agree well with published data [28, 29].
It should be noted that the modified determinantal method presented in this paper can also be used to obtain the coupling-projection coefficients for open-shell nuclei and molecules. Work is in progress in our group for the computation of structure of atomic-molecular and nuclear systems with multideterminantal state of a single configuration that has arbitrary open-shells.

6. Conclusion

It is well-known that in the Roothaan's HF theory the orbital-dependent energy functional, Eq. (27), and Fock operators are not invariant to unitary transformation of orbitals [24]. Therefore Roothaan's Fock operators are not diagonalized. In this study, the new formulas are introduced for the combined total energy, Eq. (4), and Fock operators (Eq.(19)) of open shell atomic-molecular and nuclear systems which are invariant with respect to unitary transformation of orbitals. The variational principle is applied to the energy functional and the new forms of HF and HFR equations are derived for spatial orbitals u_i and coefficients C_{qi}. For this purpose we have minimized the postulated energy functional with respect to the orbitals u_i and coefficients C_{qi}, subject to the orthonormality constraints the Lagrangian multipliers of which are designated with $-2\omega\varepsilon_{si}$. We conclude that the Lagrangian multipliers form a Hermitian matrix, $\varepsilon_{si} = \varepsilon_{is}^{*}$, and the resulting equations have the off-diagonal coefficients ε_{si}.

It is shown that the operator $\hat{F}^i$ is invariant with respect to the unitary transformation of orbitals. We may therefore diagonalize the matrix ε, so that all the orbitals u_i and coefficients C_{qi} satisfy the HF and HFR equations, respectively, $\hat{F}^i u_i = \varepsilon_i u_i$ and $\sum_q (\hat{F}^i_{pq} - \varepsilon_i S_{pq}) C_{qi} = 0$. Thus, in this paper we have established the combined HF and HFR equations for open shell atomic-molecular and nuclear systems.

We notice that in the case of integer and noninteger n-STOs, the multicenter integrals occuring in the combined HFR approach for atomic and molecular systems ($\omega = 1$) can be calculated by the use of expansion and one-range addition theorems for STOs, Ψ^{α}-ETOs and Coulomb-Yukawa like central and noncentral interaction potentials established by the author in Refs. [30].

Table 1. The independent determinantal wave functions for the electronic configuration $C(1s^2 2s^2 2p^2)$

$n_5 : m_{l_5}\ m_{s_5}$	$n_6 : m_{l_6}\ m_{s_6}$	M_L	M_S	$U(21m_{l_5}m_{s_5}\ 21m_{l_6}m_{s_6})$
$1:1\ \frac{1}{2}$	$2:1-\frac{1}{2}$	2	0	$U_1(211\ \frac{1}{2}\quad 211\ -\frac{1}{2})$
	$3:0\ \frac{1}{2}$	1	1	$U_2(211\ \frac{1}{2}\quad 210\ \frac{1}{2})$
	$4:0-\frac{1}{2}$	1	0	$U_3(211\ \frac{1}{2}\quad 210\ -\frac{1}{2})$
	$5:-1\ \frac{1}{2}$	0	1	$U_5(211\ \frac{1}{2}\quad 21-1\ \frac{1}{2})$
	$6:-1-\frac{1}{2}$	0	0	$U_6(211\ \frac{1}{2}\quad 21-1-\frac{1}{2})$
$2:1-\frac{1}{2}$	$3:0\ \frac{1}{2}$	1	0	$U_4(211\ -\frac{1}{2}\quad 210\ \frac{1}{2})$
	$4:0-\frac{1}{2}$	1	-1	$U_9(211\ -\frac{1}{2}\quad 210\ -\frac{1}{2})$
	$5:-1\ \frac{1}{2}$	0	0	$U_7(211\ -\frac{1}{2}\quad 21-1\ \frac{1}{2})$
	$6:-1-\frac{1}{2}$	0	-1	$U_{10}(211\ -\frac{1}{2}\quad 21-1-\frac{1}{2})$
$3:0\ \frac{1}{2}$	$4:0-\frac{1}{2}$	0	0	$U_8(210\ \frac{1}{2}\quad 210\ -\frac{1}{2})$
	$5:-1\ \frac{1}{2}$	-1	1	$U_{11}(210\ \frac{1}{2}\quad 21-1\ \frac{1}{2})$
	$6:-1-\frac{1}{2}$	-1	0	$U_{12}(210\ \frac{1}{2}\quad 21-1-\frac{1}{2})$
$4:0-\frac{1}{2}$	$5:-1\ \frac{1}{2}$	-1	0	$U_{13}(210\ -\frac{1}{2}\quad 21-1\ \frac{1}{2})$
	$6:-1-\frac{1}{2}$	-1	-1	$U_{14}(210\ -\frac{1}{2}\quad 21-1-\frac{1}{2})$
$5:-1\ \frac{1}{2}$	$6:-1-\frac{1}{2}$	-2	0	$U_{15}(21-1\ \frac{1}{2}\quad 21-1-\frac{1}{2})$

Table 2. The terms of electronic configuration $C(1s^2 2s^2 2p^2)$ and their multideterminantal wave functions

Terms	$\Psi^{LS}_{M_L M_S}$		
^1S	$\Psi^{00}_{00} = \frac{1}{\sqrt{3}}(U_6 - U_7 - U_8)$		
^1D	$\Psi^{20}_{20} = U_1$	$\Psi^{20}_{10} = \frac{1}{\sqrt{2}}(U_3 - U_4)$	$\Psi^{20}_{00} = \frac{1}{\sqrt{6}}(U_6 - U_7 + 2U_8)$
	$\Psi^{20}_{-10} = \frac{1}{\sqrt{2}}(U_{12} - U_{13})$	$\Psi^{20}_{-20} = U_{15}$	
^3P	$\Psi^{11}_{11} = U_2$	$\Psi^{11}_{10} = \frac{1}{\sqrt{2}}(U_3 + U_4)$	$\Psi^{11}_{1-1} = U_9$
	$\Psi^{11}_{01} = U_5$	$\Psi^{11}_{00} = \frac{1}{\sqrt{2}}(U_6 + U_7)$	$\Psi^{11}_{0-1} = U_{10}$
	$\Psi^{11}_{-11} = U_{11}$	$\Psi^{11}_{-10} = \frac{1}{\sqrt{2}}(U_{12} + U_{13})$	$\Psi^{11}_{-1-1} = U_{14}$

Table 3. The values of coupling-projection coefficients A_{kl}^{ij} and B_{kl}^{ij} for electronic configuration $C(1s^2 2s^2 2p^2)$.

Closed-closed and closed-open shells Eqs. (5) and (6)		Open-open shells Eqs. (4) and (7)	
$A_{11}^{11}=1$	$B_{11}^{11}=1$	$A_{44}^{33}=A_{33}^{44}=\frac{1}{12}$	$B_{44}^{33}=B_{33}^{44}=\frac{1}{6}$
$A_{22}^{11}=A_{11}^{22}=1$	$B_{22}^{11}=B_{11}^{22}=1$	$A_{55}^{33}=A_{33}^{55}=\frac{1}{12}$	$B_{55}^{33}=B_{33}^{55}=\frac{1}{6}$
$A_{33}^{11}=A_{11}^{33}=\frac{1}{3}$	$B_{33}^{11}=B_{11}^{33}=\frac{1}{3}$	$A_{55}^{44}=A_{44}^{55}=\frac{1}{12}$	$B_{55}^{44}=B_{44}^{55}=\frac{1}{6}$
$A_{44}^{11}=A_{11}^{44}=\frac{1}{3}$	$B_{44}^{11}=B_{11}^{44}=\frac{1}{3}$		
$A_{55}^{11}=A_{11}^{55}=\frac{1}{3}$	$B_{55}^{11}=B_{11}^{55}=\frac{1}{3}$		
$A_{22}^{22}=1$	$B_{22}^{22}=1$		
$A_{33}^{22}=A_{22}^{33}=\frac{1}{3}$	$B_{33}^{22}=B_{22}^{33}=\frac{1}{3}$		
$A_{44}^{22}=A_{22}^{44}=\frac{1}{3}$	$B_{44}^{22}=B_{22}^{44}=\frac{1}{3}$		
$A_{55}^{22}=A_{22}^{55}=\frac{1}{3}$	$B_{55}^{22}=B_{22}^{55}=\frac{1}{3}$		

Table 4. Numerical linear combination coefficients of Slater atomic orbitals $(u_i=\sum_{q=1}^{5}\chi_q C_{qi})$ for the ground state of $C(1s^2 2s^2 2p^2, {}^3P)$ and orbital energies (in a.u.).

χ_q	ζ_q	$\varepsilon_1=\varepsilon_{1s}$ -11.301550	$\varepsilon_2=\varepsilon_{2s}$ -6.774946	$\varepsilon_3=\varepsilon_{2p_x}$ -1.338743	$\varepsilon_4=\varepsilon_{2p_z}$ -1.338743	$\varepsilon_5=\varepsilon_{2p_y}$ -1.338743
$\chi_1=C(1s)$	5.6727	0.997438	-0.235078	0.000000	0.000000	0.000000
$\chi_2=C(2s)$	1.6083	0.011438	1.024702	0.000000	0.000000	0.000000
$\chi_3=C(2p_x)$	1.5679	0.000000	0.000000	1.000000	0.000000	0.000000
$\chi_4=C(2p_z)$	1.5679	0.000000	0.000000	0.000000	1.000000	0.000000
$\chi_5=C(2p_y)$	1.5679	0.000000	0.000000	0.000000	0.000000	1.000000

Total energy	Kinetic energy	Virial ratio
-37.622389	37.622691	-1.999992
-37.622389 (from [28])		
-37.579018 (from [29])		

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2.COMPLETE ORTHONORMAL SETS of Ψ^{α}-ETOs in COORDINATE, MOMENTUM and FOUR-DIMENSIONAL SPACES, and ONE-RANGE ADDITION THEOREMS for Ψ^{α}-ETOs and STOs (Int.J. Quantum Chem., 90 (2002) 114 ,…)

It is well known that the exponential type orbitals (ETOs) would be desirable for basis sets in molecular calculations because they can satisfy the cusp condition at the nuclei [6] and the exponential decay for large distances [7-8]. However, the difficulties in calculation of multicenter molecular integrals have restricted the use of ETOs in quantum chemistry. In the literature there is renewed interest in developing efficient methods for the calculation of multicenter molecular integrals by employing ETOs as basis sets [9-17]. Older works mainly using STOs are reviewed in Refs. [18-22].

One of the most promising methods for the evaluation of multicenter molecular integrals is the expansion of STOs in terms of complete orthonormal sets of ETOs placed at shifted center. In Ref. [17] we derived the two kinds of expansion formulas for one-range addition theorems of STOs using so-called Coulomb Sturmian and Lambda ETOs, which into atomic and molecular calculations were introduced in Refs. [23-26], respectively (see also Refs. [27-28]). It should be noted that Coulomb Sturmian and Lambda ETOs are based upon the generalized Laguerre polynomials L_{n+1}^{2l+1} and L_{n+l+1}^{2l+2}, respectively. Utilizing relations for these ETOs presented in Refs. [23-26] we are able to find in Ref. [2] the following single analytical formula for the complete orthonormal sets of $\psi^{\alpha}-ETOs$ which are composed of an exponential, a regular solid spherical harmonic, and the non-standard generalized Laguerre polynomials L_{n+1}^{2l+1}, $L_{n+l+1}^{2l+2}, L_{n+l+2}^{2l+3},\ldots$

$$\psi_{nlm}^{\alpha}(\zeta,\vec{r}) = R_{nl}^{\alpha}(\zeta,r)S_{lm}(\theta,\varphi) \tag{2.1}$$

$$R_{nl}^{\alpha}(\zeta,\vec{r}) = (-1)^{\alpha}\left[\frac{(2\zeta)^3(q-p)!}{(2n)^{\alpha}(q!)^3}\right]^{1/2} x^l e^{-x/2}L_q^p(x), \tag{2.2}$$

where $x = 2\zeta r$, $p = 2l+2-\alpha$, $q = n+l+1-\alpha$ and α = 1, 0,−1,−2,−3, ... The following relation determines the generalized Laguerre polynomials

$$L_q^p(x) = \sum_{i=1}^{q-p}\beta_{qi}^p x^i, \tag{2.3}$$

where

$$\beta_{qi}^p = (-1)^{p+i}(q-i)!F_i(q)F_{p+i}(q). \tag{2.4}$$

$$F_i(q) = \begin{cases} q!/[i!(q-i)!] & for \quad 0 \le i \le q \\ 0 & for \quad i<0 \quad and \quad i>q. \end{cases} \tag{2.5}$$

The generalized Laguerre polynomials satisfy the orthonormality relation

$$\int_0^{\infty} e^{-x}x^p L_q^p(x)L_{q'}^p(x)dx = \frac{(q!)^3}{(q-p)!}\delta_{qq'}. \tag{2.6}$$

The functions S_{lm} occurring in Eq. (2.1) are the normalized complex ($S_{lm}\equiv Y_{lm}$)or real spherical harmonics. We notice that our definition of phases for the complex spherical harmonics differs from the Condon–Shortley phases [29] by the sign factor. We use phases according to the relation $Y_{lm}^{*}(\theta,\varphi) = Y_{l-m}(\theta,\varphi)$. It should be noted that the Lambda and Coulomb Sturmian ETOs introduced in Refs. [23-26] are the special cases of the $\psi^{\alpha}-ETOs$ for α = 0 and α = 1, respectively; i.e., $\psi_{nlm}^{0}\equiv\Lambda_{nlm}$ and $\psi_{nlm}^{1}\equiv\psi_{nlm}$ (see Eqs. (1) and (2) of Ref. [17]).

The $\psi^{\alpha}-ETOs$ are orthonormal with respect to the weight function $(n/\zeta r)^{\alpha}$:

$$\int\psi_{nlm}^{\alpha^*}(\zeta,\vec{r})\bar{\psi}_{n'l'm'}^{\alpha}(\zeta,\vec{r})dV = \delta_{nn'}\delta_{ll'}\delta_{mm'}, \tag{2.7}$$

where

$$\bar{\psi}_{nlm}^{\alpha}(\zeta,\vec{r}) = \bar{R}_{nl}^{\alpha}(\zeta,r)S_{lm}(\theta,\varphi) \tag{2.8}$$

$$\bar{R}_{nl}^{\alpha}(\zeta,\vec{r}) = \left(\frac{n}{\zeta r}\right)^{\alpha}R_{nl}^{\alpha}(\zeta,r). \tag{2.9}$$

By the representing the generalized Laguerre polynomial in terms of powers of the $x=2\zeta r$ according to Eq. (2.3) it is easy to obtain for the transformation of $\psi^{\alpha}-and\ \bar{\psi}^{\alpha}-ETOs$ into STOs the expressions

$$\psi^{\alpha}_{nlm}(\zeta,\vec{r})=\sum_{n'=l+1}^{n}\omega^{\alpha l}_{nn'}\chi_{n'lm}(\zeta,\vec{r}) \tag{2.10}$$

$$\bar{\psi}_{nlm}(\zeta,\vec{r})=(2n)^{\alpha}\sum_{n'=l+1-\alpha}^{n-\alpha}\left[(2n')!/\left[2(n'+\alpha)\right]!\right]^{1/2}\omega^{\alpha l}_{nn'+\alpha}\chi_{n'lm}(\zeta,\vec{r}), \tag{2.11}$$

where the quantities $\omega^{\alpha l}_{nn'}$ are determined by

$$\omega^{\alpha l}_{nn'}=(-1)^{n'-l-1}\left[\frac{(n'+l+1)!}{(2n)^{\alpha}(n'+l+1-\alpha)!}F_{n'+l+1-\alpha}(n+l+1-\alpha)F_{n'-l-1}(n-l-1)F_{n'-l-1}(2n')\right]^{1/2} \tag{2.12}$$

Here, the $\chi_{nlm}(\zeta,\vec{r})$ are the normalized STOs defined as

$$\chi_{nlm}(\zeta,\vec{r})=(2\zeta)^{n+1/2}\left[(2n)!\right]^{-1/2}r^{n-1}e^{-\zeta r}S_{lm}(\theta,\varphi). \tag{2.13}$$

We notice that if factorials of negative number occur in these equations, they should be equated to zero, i.e., $\omega^{\alpha l}_{nn'}=0$ for $n<n'$.

1. One-Range Addition Theorems for Ψ^{α}-ETOs, STOs and Coulomb-Yukawa Like CIPs

The aim of this section is to establish the one-range addition theorems for $\psi^{\alpha}-ETOs$, STOs and Coulomb-Yukawa like CIPs. These addition theorems can be used for the calculation of multicenter multielectron integrals arising in HFR approximation and correlated interaction potentials approaches.

2. Ψ^{α}-ETOs

To derive the unsymmetrical one-range addition theorems for $\psi^{\alpha}-ETOs$ we expand the $\psi^{\alpha}-ETOs$ in terms of $\psi^{\alpha}-ETOs$ at a displaced center and use Eq. (2.7) for orthonormality relation. Then, we get the desired result,

$$\psi^{\alpha}_{nlm}\left(\zeta,\vec{r}_{a1}\right)=\sum_{n'=1}^{\infty}\sum_{l'=0}^{n-1}\sum_{m'=-l'}^{l'}S^{\alpha^*}_{nlm,n'l'm'}\left(\zeta,\zeta';\vec{R}_{ab}\right)\psi^{\alpha}_{n'l'm'}\left(\zeta',\vec{r}_{b1}\right), \tag{3.1}$$

where the overlap integrals of $\psi^{\alpha}-ETOs$ are determined as

$$S^{\alpha}_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ab})=\int\Psi^{\alpha^*}_{nlm}(\zeta,\vec{r}_{a1})\bar{\Psi}^{\alpha}_{n'l'm'}(\zeta',\vec{r}_{b1})dv_1. \tag{3.2}$$

Using Eqs. (2.10) and (2.11) in (3.2) we obtain for the expansion coefficients in terms of overlap integrals over STOs the following relation:

$$S^{\alpha}_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ab}) = (2n')^{\alpha} \sum_{n''=l+1}^{n} \sum_{\mu'=l'+1-\alpha}^{n'-\alpha} \left[(2\mu')!/\left[2(\mu'+\alpha)\right]!\right]^{1/2} \omega^{\alpha l}_{nn''} \omega^{\alpha l'}_{n'\mu'+\alpha} S_{n''lm,\mu'l'm'}(\zeta,\zeta';\vec{R}_{ab}), \quad (3.3)$$

where the $S_{n''lm,\mu'l'm'}(\zeta,\zeta';\vec{R}_{ab})$ are the overlap integrals of STOs defined by

$$S_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ab}) = \int \chi^{*}_{nlm}(\zeta,\vec{r}_{a1}) \chi_{n'l'm'}(\zeta',\vec{r}_{b1}) dv_1 . \quad (3.4)$$

See Sec. 5 for the evaluation of overlap integrals $S_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ab})$.

The formulae for symmetrical one-range addition theorems of $\psi^{\alpha}-ETOs$ are presented in Ref. [30]:

$$\Psi^{\alpha}_{nlm}(\zeta,\vec{r}_{a1}) = \left(\frac{2\pi}{\bar{\zeta}}\right)^{3/2} \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \left(\sum_{N=1}^{\infty} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} D^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta',\bar{\zeta}) \Psi^{\alpha *}_{NLM}(\bar{\zeta},\vec{R}_{ab}) \right) \bar{\Psi}^{\alpha}_{n'l'm'}(\zeta',\vec{r}_{b1}), \quad (3.5)$$

where $\bar{\zeta} = (\zeta+\zeta')/2$ and

$$D^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta',\bar{\zeta}) = \frac{1}{2\pi}(2L+1)^{1/2} C^{L|M|}(lm,l'm') A^{M}_{mm'}$$

$$\times (2N)^{\alpha} \sum_{s=l+1}^{n} \sum_{s'=l'+1}^{n'} \sum_{S=L+1}^{N} \omega^{\alpha l}_{ns} \omega^{\alpha l'}_{n's'} \omega^{\alpha L}_{NS} \frac{[(2(S-\alpha))!]^{1/2}}{[(2S)!]^{1/2}} Q^{S-\alpha L}_{sl,s'l'}(\zeta,\zeta',\bar{\zeta}). \quad (3.6)$$

It should be noted that for $\zeta = \zeta'$, the coefficients $D^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta',\bar{\zeta})$ determined by the relations (3.6) do not depend on the parameters ζ, i.e.,

$$D^{\alpha NLM}_{nlm,n'l'm'} = D^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta,\zeta). \quad (3.7)$$

Thus, Eqs. (3.1) and (3.5) determine all the unsymmetrical and symmetrical one-range addition theorems of $\psi^{\alpha}-ETOs$, respectively.

3. STOs

In previous works [31-32] the unsymmetrical and symmetrical one-range addition theorems for STOs were derived using complete orthonormal sets of $\Psi^{\alpha}-ETOs$.

In order to obtain the unsymmetrical one-range addition theorems for STOs we expand STOs in terms of complete orthonormal sets of Ψ^{α}-ETOs at a displaced center:

$$\chi_{nlm}(\zeta,\vec{r}_{a1}) = \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} M^{\alpha *}_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}) \Psi^{\alpha}_{n'l'm'}(\zeta',\vec{r}_{b1}), \quad (3.8)$$

where $\vec{R} = \vec{R}_{ab}$ and

$$M^{\alpha}_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}) = \int \chi^{*}_{nlm}(\zeta,\vec{r}_{a1}) \bar{\Psi}^{\alpha}_{n'l'm'}(\zeta',\vec{r}_{b1}) dv_1 . \quad (3.9)$$

Here, we have taken into account the orthonormality relation (2.7) for Ψ^{α}-ETOs.

In order to express the right-hand side of eq.(3.8) in terms of STOs we use a particular method suggested in previous publucation[31]. Using this method, we write Eq.(3.8) in the following form:

$$\chi_{nlm}\left(\zeta,\vec{r}_{a1}\right)=\lim_{N\to N_{\max}}\sum_{n'=1}^{N}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}M_{nlm,n'l'm'}^{\alpha*}\left(\zeta,\zeta';\vec{R}\right)\Psi_{n'l'm'}^{\alpha}\left(\zeta',\vec{r}_{b1}\right) \tag{3.10}$$

where $N_{\max}<\infty$.

Now we rearrange the order of summations in (3.10) using Eq. (2.10) and characteristics of the coefficients $\omega_{nn'}^{\alpha l}$. Then, it is easy to prove for $1\le N<\infty$ the following identity:

$$\begin{aligned}&\sum_{n'=1}^{N}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}M_{nlm,n'l'm'}^{\alpha*}\left(\zeta,\zeta';\vec{R}\right)\Psi_{n'l'm'}^{\alpha}\left(\zeta',\vec{r}_{b1}\right)\\&\qquad=\sum_{n'=1}^{N}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}\left(\sum_{n''=n'}^{N}\omega_{n''n'}^{\alpha l'}M_{nlm,n''l'm'}^{\alpha*}\left(\zeta,\zeta';\vec{R}\right)\right)\chi_{n'l'm'}\left(\zeta',\vec{r}_{b1}\right).\end{aligned} \tag{3.11}$$

We take into account Eq.(2.10) in Eqs.(3.9) and (3.11). Then, we obtain finally for the unsymmetrical one-range addition theorems of STOs the following relation:

$$\chi_{nlm}\left(\zeta,\vec{r}_{a1}\right)=\lim_{N\to N_{\max}}\sum_{n'=1}^{N}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}V_{nlm,n'l'm'}^{\alpha N*}\left(\zeta,\zeta';\vec{R}\right)\chi_{n'l'm'}\left(\zeta',\vec{r}_{b1}\right). \tag{3.12}$$

Here, the expansion coefficients $V^{\alpha N}$ for translation of STOs are determined by

$$V_{nlm,n'l'm'}^{\alpha N}\left(\zeta,\zeta';\vec{R}\right)=\sum_{n''=l'+1}^{N}\Omega_{n'n''}^{\alpha l'}\left(N\right)S_{nlm,n''-\alpha l'm'}\left(\zeta,\zeta';\vec{R}\right), \tag{3.13}$$

where

$$\Omega_{n\kappa}^{\alpha l}\left(N\right)=\left[\frac{[2(k-\alpha)]!}{(2\kappa)!}\right]^{\frac{1}{2}}\sum_{n'=\max(n,\kappa)}^{N}(2n')^{\alpha}\,\omega_{n'n}^{\alpha l}\,\omega_{n'\kappa}^{\alpha l}. \tag{3.14}$$

The quantities $S_{nlm,n'l'm'}$ occurring in Eq. (3.13) are the overlap integrals between the normalized STOs defined by Eq. (3.4)

It can be seen from Eq.(3.13) that the expansion coefficients for the unsymmetrical one-range addition theorems of STOs are expressed through the overlap integrals with STOs.

The symmetrical one-range addition theorems of STOs are given in Ref. [33]:

$$\chi_{\mu\nu\sigma}(\zeta,\vec{r}_{a1})=\frac{1}{\eta^{3/2}}\lim_{\substack{N\to N_{\max}\\N'\to N'_{\max}}}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\left[\sum_{u=1}^{N+N'-\alpha+1}\sum_{\upsilon=0}^{u-1}\sum_{s=-\upsilon}^{\upsilon}D_{\mu\nu\sigma,nlm}^{\alpha u\upsilon s}(N,N';t)\chi_{u\upsilon s}^{*}(\eta,\vec{R}_{ab})\right]\chi_{nlm}(\eta,\vec{r}_{b1}), \tag{3.15}$$

where $\eta>0$ and

$$D^{\alpha u v s}_{\mu\nu\sigma,nlm}(N,N';t)=\sum_{n'=l+1}^{N}\Omega^{\alpha l}_{nn'}(N)\sum_{\mu'=\nu+1}^{N'}g^{\alpha u v s}_{\mu'\nu\sigma,n'-\alpha lm}\sum_{\mu''=\nu+1}^{N'}\frac{(\mu+\mu''-\alpha)!}{\{(2\mu)![2(\mu''-\alpha)]!\}^{1/2}} \times\Omega^{\alpha\nu}_{\mu'\mu''}(N')(1+t)^{\mu+1/2}\left(1-t\right)^{\mu''-\alpha+1/2}. \tag{3.16}$$

Here, $t=\dfrac{\zeta-\eta}{\zeta+\eta}$ and $g^{\alpha u v s}_{\mu'\nu\sigma,n'-\alpha lm}\equiv 0\ \ for\ u>\mu'+n'-\alpha+1$.

The unsymmetrical and symmetrical one-range addition theorems can also be established for noninteger n STOs. For this purpose one should take into account Eq. (3.12) and (3.15) in Eq. (4.27) for the one-center expansion formulas.

4. Coulomb-Yukawa Like CIPs

It is well known that the determination of multielectron properties for atoms and molecules requires the more accurate solutions of Hartree-Fock (HF) equations [34]. In order to obtain better approximate solutions in HF theory, Hylleraas first introduced the two standard variational approaches in a series of papers on heliumlike systems: (1) the Hylleraas (Hy) method [23,35], in which the interelectronic coordinates r_{ij} are explicitly included in the terms of the wave function; (2) the configuration interaction (CI) method [36,37], in which the wave function is determined by the linear combination of determinantal functions arising from different configurations [38]. There are theoretical grounds [38-39] for thinking that both the CI and the Hy methods are general methods capable of yielding variational solutions that converge to the exact solution of the Schrödinger equation with any desired degree of accuracy if a sufficient number of terms are included. We notice that the CI expansions converge much more slowly than the Hy-method expansions. Recent work on the hybrid technique Hy-CI [40], which avoids many of the complicated integrals, converges rather quickly for small systems. A drawback in the Hy-type expansions, however, is the complexity of the calculation of multicenter multielectron integrals. The Hy method first developed by James and Coolidge [41] has been used for determination of the ground state energy of H_2 molecule [42, 43] and is still valid for two- and three-electron atomic and molecular systems (see, e.g., Refs.[44, 45] and references quoted therein).

In this section, using the complete orthonormal sets of $\psi^{\alpha}-ETOs$ a large number of unsymmetrical and symmetrical one-range addition theorems for Coulomb-Yukawa like CIPs are presented. The addition theorems derived are especially useful for the computation of multicenter multielectron integrals of CIPs occurring in the HFR approximation and explicitly correlated methods.

In Ref. [46], we introduced the CIPs method, in which the positive indices μ, screening parameter ξ and the interelectronic coordinates x_{ij}, y_{ij} *and* z_{ij} are explicitly included in the terms of the CIPs. The combined Coulomb (for $\xi = 0$) and Yukawa (for $\xi > 0$) like CIPs are defined as [32, 46]:

$$f_{\mu\nu\sigma}(\xi,\vec{r}) = f_{\mu}(\xi,r)\left(\frac{4\pi}{2\nu+1}\right)^{1/2} S_{\nu\sigma}(\theta,\varphi), \tag{3.17}$$

where $\mu \geq 0$, $\xi \geq o$ and $S_{\nu\sigma}(\theta,\varphi)$ are the complex (for $S_{\nu\sigma} \equiv Y_{\nu\sigma}$) or real spherical harmonics and

$$f_{\mu}(\xi,r) = f_{\mu 00}(\xi,r) = r^{\mu-1}e^{-\xi r}. \tag{3.18}$$

In order to derive the unsymmetrical one-range addition theorems for Coulomb-Yukawa like CIPs, we expand the function (3.17) in terms of complete orthonormal sets of $\psi^{\alpha}-ETOs$ at a displaced center. Then, using the method set out in section (3.2) we finally obtain:

$$f_{\mu\nu\sigma}(\xi,\vec{r}_{a1}) = \sqrt{4\pi}\lim_{N\to N_{\max}}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} W^{\alpha N^{*}}_{\mu\nu\sigma,nlm}\left(\xi,\eta;\vec{R}_{ab}\right)\chi_{nlm}(\eta,\vec{r}_{b1}), \tag{3.19}$$

where $\eta > 0$ and

$$W^{\alpha N}_{\mu\nu\sigma,nlm}\left(\xi,\eta;\vec{R}_{ab}\right) = \sum_{n'=l+1}^{N}\Omega^{\alpha l}_{nn'}\left(N\right)U_{\mu\nu\sigma,n'-\alpha lm}\left(\xi,\eta;\vec{R}_{ab}\right). \tag{3.20}$$

Here, $\alpha = 1,0,-1,-2,...$ and $U_{\mu\nu\sigma,n'-\alpha lm}\left(\xi,\eta;\vec{R}_{ab}\right)$ are the overlap integrals between CIPs and STOs:

$$U_{\mu\nu\sigma,n'-\alpha lm}\left(\xi,\eta;\vec{R}_{ab}\right) = \frac{1}{\sqrt{4\pi}}\int f^{*}_{\mu\nu\sigma}\left(\xi,\vec{r}_{a1}\right)\chi_{n'-\alpha lm}\left(\eta,\vec{r}_{b1}\right)dv_{1}. \tag{3.21}$$

The unsymmetrical one-range addition theorems of Coulomb and Yukawa potentials are obtained from Eq. (3.19) for $\mu = \nu = \sigma = 0$, $\xi = 0$ and $\mu = \nu = \sigma = 0$, $\xi > 0$, respectively,

for Coulomb potential

$$\frac{1}{r_{a1}} = \sqrt{4\pi}\lim_{N\to N_{\max}}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} W^{\alpha N^{*}}_{000,nlm}\left(0,\eta;\vec{R}_{ab}\right)\chi_{nlm}\left(\eta,\vec{r}_{b1}\right) \tag{3.22}$$

$$W^{\alpha N}_{000,nlm}\left(0,\eta;\vec{R}_{ab}\right) = \sum_{n'=l+1}^{N}\Omega^{\alpha l}_{nn'}(N)U_{000,n'-\alpha lm}\left(0,\eta;\vec{R}_{ab}\right) \tag{3.23}$$

$$U_{000,n'-\alpha lm}\left(0,\eta;\vec{R}_{ab}\right) = \frac{1}{\sqrt{4\pi}}\int\frac{1}{r_{a1}}\chi_{n'-\alpha lm}\left(\eta,\vec{r}_{b1}\right)dv_{1}, \tag{3.24}$$

for Yukawa potential

$$\frac{e^{-\xi r_{a1}}}{r_{a1}} = \sqrt{4\pi}\lim_{N\to N_{\max}}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} W^{\alpha N^{*}}_{000,nlm}\left(\xi,\eta;\vec{R}_{ab}\right)\chi_{nlm}\left(\eta,\vec{r}_{b1}\right) \tag{3.25}$$

$$W^{\alpha N}_{000,nlm}\left(\xi,\eta;\vec{R}_{ab}\right)=\sum_{n'=l+1}^{N}\Omega^{\alpha l}_{nn'}(N)U_{000,n'-\alpha lm}\left(\xi,\eta;\vec{R}_{ab}\right) \tag{3.26}$$

$$U_{000,n'-\alpha lm}\left(\xi,\eta;\vec{R}_{ab}\right)=\frac{1}{\sqrt{4\pi}}\int\frac{e^{-\xi r_{a1}}}{r_{a1}}\chi_{n'-\alpha lm}\left(\eta,\vec{r}_{b1}\right)dv_1\,. \tag{3.27}$$

The analytical relation for two-center basic Coulomb potential function, Eq. (3.24), is given in previous work [47]

$$U_{nlm}(\eta,\vec{r})=\frac{2^{n+1}(n+l+1)!}{(2l+1)[(2n)!(2\eta)]^{1/2}(\eta r)^{l+1}}(1-e^{-\eta r}\sum_{\sigma=0}^{n+l}\gamma^{l}_{\sigma}(n)(\eta r)^{\sigma})S_{lm}(\theta,\varphi)\,, \tag{3.28}$$

$$\gamma^{l}_{\sigma}(n)=\frac{1}{\sigma!}-\frac{(n-l)!}{(n+l+1)!(\sigma-2l-1)!}\,. \tag{3.29}$$

Here $U_{nlm}\left(\eta,\vec{r}\right)\equiv U_{000,nlm}\left(0,\eta;\vec{r}\right)$, $\gamma^{l}_{\sigma}(n)=0$ *for* $\sigma<0$ *and* $\sigma>n+l$. In Eq.(3.29) terms with negative factorials should be equated to zero.

We notice that the expression for two-center basic Yukawa potential function, Eq. (3.27), could be obtained by the use of formula for two-center overlap integrals of STOs (see Sec. 5).

The formulae for the symmetrical one-range addition theorems of Coulomb-Yukawa like CIPs have been derived in Ref. [33]:

$$f_{\mu\nu\sigma}(\xi,\vec{r}_{21})=\frac{2^{3/2}}{(2\eta)^{\mu+2}}\lim_{\substack{N\to N_{\max}\\ N'\to N'_{\max}}}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\left[\sum_{u=1}^{N+N'-\alpha+1}\sum_{\upsilon=0}^{u-1}\sum_{s=-\upsilon}^{\upsilon}\left(-1\right)^{\nu}B^{\alpha u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';\xi,\eta)\chi^{*}_{u\upsilon s}(\eta,\vec{r}_2)\right] \times\chi_{nlm}(\eta,\vec{r}_1), \tag{3.30}$$

where $\alpha=1,0,-1,-2,...$ and

$$B^{\alpha u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';\xi,\eta)=\left(\frac{4\pi}{2\nu+1}\right)^{1/2}\sum_{n'=l+1}^{N}\Omega^{\alpha l}_{nn'}(N)\sum_{\mu'=\nu+1}^{N'}g^{\alpha u\upsilon s}_{\mu'\nu\sigma,n'-\alpha lm}\sum_{\mu''=\nu+1}^{N'}\frac{(\mu+\mu''-\alpha)!}{\{[2(\mu''-\alpha)]!\}^{1/2}} \times\Omega^{\alpha\nu}_{\mu'\mu''}(N')\left(\frac{2\eta}{\xi+\eta}\right)^{\mu+\mu''-\alpha+1}. \tag{3.31}$$

In the case of symmetrical addition theorems for Coulomb like CIPs ($\xi=0$) the coefficient $B^{\alpha u\upsilon s}$ does not depend on the parameter η, i.e., $B^{\alpha u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';0,\eta)=B^{\alpha u\upsilon s}_{\mu\nu\sigma,nlm}(N,N')$.

We notice that in our published papers, the series expansion formulae were also derived for the derivatives of unsymmetrical and symmetrical one-range addition theorems of $\Psi^{\alpha}-ETOs$, STOs and Coulomb-Yukawa like CIPs. These derivatives can be useful especially in the study of electric field and its gradient created by the electrons within the molecule. Weniger, however, claims that *"Guseinov did not derive completely symmetrical one-range addition theorems" [3, p.16]*. This statement of Weniger is completely unacceptable. He had failed to understand our theory behind unsymmetrical one-range addition theorems.

5. Use of one-range addition theorems for Coulomb potential in evaluation of multicenter integrals of HFR equations

The series expansion formulae obtained in Section 3 for the unsymmetrical and symmetrical one-range addition theorems of STOs and Coulomb-Yukawa like CIPs can be used in the derivation of relations for the multicenter integrals of an arbitrary t-electron operator that arises in calculations of atoms and molecules with N electrons, where $2 \le t \le N$. As an example of application, we calculate in this Section, the multicenter integrals of integer and noninteger n STOs appearing in the HFR equations.

5.1. Multicenter integrals of integer n STOs

The multicenter integrals over integer n STOs examined in this work have the following form:

One-electron multicenter integrals

$$J^{ab,c}_{p_1 p_1'}(\zeta_1,\zeta_1') = \int \chi^*_{p_1}(\zeta_1,\vec{r}_{a1})\chi_{p_1'}(\zeta_1',\vec{r}_{b1})\frac{1}{r_{c1}}dv_1, \tag{4.1}$$

Two-electron multicenter integrals

$$J^{ab,cd}_{p_1 p_1', p_2 p_2'}(\zeta_1,\zeta_1',\zeta_2,\zeta_2') = \int\int \chi^*_{p_1}(\zeta_1,\vec{r}_{a1})\chi_{p_1'}(\zeta_1',\vec{r}_{b1})\frac{1}{r_{21}}\chi_{p_2}(\zeta_2,\vec{r}_{c2})\chi_{p_2'}(\zeta_2',\vec{r}_{d2})dv_1 dv_2, \tag{4.2}$$

where $p_1 \equiv n_1 l_1 m_1$, $p_1' \equiv n_1' l_1' m_1'$, $p_2 \equiv n_2 l_2 m_2$ and $p_2' \equiv n_2' l_2' m_2'$. Here the $\chi_p(\zeta,\vec{r}_{g1})$ denotes that the STO is located at a center g, where $g = a,b,c,d$.

In order to evaluate the one- and two-electron multicenter integrals, Eqs. (4.1) and (4.2), we use the relation (3.22) for the unsymmetrical one-range addition theorems of Coulomb potential in the following form:

$$\frac{1}{r_{21}} = 4\pi \lim_{N\to N_{\max}} \sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}[\sum_{n'=l+1}^{N}(-1)^l \Omega^{\alpha l}_{nn'}(N)U^*_{n'-\alpha lm}(\eta,\vec{r}_2)]\chi_{nlm}(\eta,\vec{r}_1), \tag{4.3}$$

where $\alpha = 1,0,-1,-2...$ Then, we obtain:

$$J^{ab,c}_{p_1 p_1'}(\zeta_1,\zeta_1',\eta) = \sqrt{4\pi} \lim_{N\to N_{\max}} \sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}(-1)^l S^{abb}_{p_1 p_1' p}(\zeta_1,\zeta_1',\eta)\sum_{n'=l+1}^{N}\Omega^{\alpha l}_{nn'}(N)U^*_{p'}(\eta,\vec{R}_{bc}) \tag{4.4}$$

$$J^{ab,cd}_{p_1p_1',p_2p_2'}(\zeta_1,\zeta_1',\zeta_2,\zeta_2',\eta)=\lim_{N\to N_{\max}}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}(-1)^l S^{abc}_{p_1p_1'p}(\zeta_1,\zeta_1',\eta)\sum_{n'=l+1}^{N}\Omega^{\alpha l}_{nn'}(N)U^{c,cd}_{p',p_2p_2'}(\eta,\zeta_2,\zeta_2'), \tag{4.5}$$

where $p\equiv nlm$, $p'\equiv n'-\alpha lm$ and

$$U_{p'}(\eta,\vec{R}_{bc})=\frac{2^{n'-\alpha+1}(n'-\alpha+l+1)!}{(2l+1)\{[2(n'-\alpha)]!(2\eta)\}^{1/2}(\eta R_{bc})^{l+1}}(1-e^{-\eta R_{bc}}\sum_{\sigma=0}^{n'-\alpha+l}\gamma^l_\sigma(n'-\alpha)(\eta R_{bc})^\sigma)S_{lm}(\theta_{bc},\varphi_{bc}) \tag{4.6}$$

$$S^{abc}_{p_1p_1'p}(\zeta_1,\zeta_1',\eta)=\sqrt{4\pi}\int\chi^*_{p_1}(\zeta_1,\vec{r}_{a1})\chi_{p_1'}(\zeta_1',\vec{r}_{b1})\chi_p(\eta,\vec{r}_{c1})dv_1 \tag{4.7}$$

$$U^{c,cd}_{p',p_2p_2'}(\eta,\zeta_2,\zeta_2')=\sqrt{4\pi}\int U^*_{p'}(\eta,\vec{r}_{c2})\chi_{p_2}(\zeta_2,\vec{r}_{c2})\chi^*_{p_2'}(\zeta_2',\vec{r}_{d2})dv_2 \tag{4.8}$$

The relationship for two- and three-center overlap integrals of three STOs occurring in Eqs. (4.4) and (4.5), respectively, are presented in Refs. [48] and [49].

Taking into account Eq. (4.6) in (4.8) for $b\to c, c\to 2$ and $\vec{R}_{bc}=\vec{r}_{c2}$ we obtain for the two-center functions $U^{c,cd}_{p',p_2p_2'}$ the following relation:

$$\begin{aligned}U^{c,cd}_{p',p_2p_2'}(\eta,\zeta_2,\zeta_2')=&\frac{2^{n'-\alpha}(n'-\alpha+l+1)!}{(2l+1)\{[2(n'-\alpha)]!(2\eta)\}^{1/2}}\frac{N_{n_2n_2'}(p_2,p_2t_2)}{p_a^{l+1}}\sum_L(2L+1)^{1/2}C^{L|m_2'|}(lm,l_2m_2)A^{m_2'}_{mm_2}\\&\times\sum_{\alpha\beta q}g^q_{\alpha\beta}(L\lambda_2',l_2'\lambda_2')\begin{cases}G^q_{-(l+1+\alpha-n_2),n_2'-\beta}(p_a;p_2,p_2t_2)-\sum\limits_{\sigma=l+1+\alpha-n_2}^{n'-\alpha+l}\gamma^l_\sigma(n'-\alpha)p_a^\sigma Q^q_{\sigma-(l+1+\alpha-n_2),n_2'-\beta}(p,pt) & for \quad l+1+\alpha-n_2>0\\ Q^q_{|l+1+\alpha-n_2|,n_2'-\beta}(p_2,p_2t_2)-\sum\limits_{\sigma=0}^{n'-\alpha+l}\gamma^l_\sigma(n'-\alpha)p_a^\sigma Q^q_{\sigma+|l+1+\alpha-n_2|,n_2'-\beta}(p,pt) & for \quad l+1+\alpha-n_2\le 0\end{cases},\end{aligned} \tag{4.9}$$

where $\lambda_2'=|m_2'|$, $p_a=\frac{\eta}{2}R_{cd}$, $p_2=\frac{R_{cd}}{2}(\zeta_2+\zeta_2')$, $p_2t_2=\frac{R_{cd}}{2}(\zeta_2-\zeta_2')$, $p=p_a+p_2$, $pt=p_a+p_2t_2$

and

$$N_{n_2n_2'}(p_2,p_2t_2)=\frac{(p_2+p_2t_2)^{n_2+1/2}(p_2-p_2t_2)^{n_2'+1/2}}{[(2n_2)!(2n_2')!]^{1/2}} \tag{4.10}$$

$$Q^q_{NN'}(p,pt)=\int_1^\infty\int_{-1}^1(\mu\nu)^q(\mu+\nu)^N(\mu-\nu)^{N'}e^{-p\mu-pt\nu}d\mu d\nu \tag{4.11}$$

$$G^q_{-NN'}(p_a;p,pt)=\int_1^\infty\int_{-1}^1\frac{(\mu\nu)^q(\mu-\nu)^{N'}}{(\mu+\nu)^N}(1-e^{-p_a(\mu+\nu)}\sum_{\sigma=0}^{N-1}\frac{[p_a(\mu+\nu)]^\sigma}{\sigma!})e^{-p\mu-pt\nu}d\mu d\nu \tag{4.12}$$

The analytical and recurrence relations for auxiliary functions $Q^q_{NN'}$ and $G^q_{-NN'}$ are presented in previous paper [50].

Carrying through calculations for the one-center functions $U^{c,cc}_{p',p_2p_2'}$ analagous to those for the two-center case, we obtain the following formula:

$$U^{c,cc}_{p',p_2p'_2}(\eta,\zeta_2,\zeta'_2)=\frac{2^{n'-\alpha}(n'-\alpha+l+1)!}{\{(2l+1)[2(n'-\alpha)]!(2\eta)\}^{1/2}k_2^{l+1}}N_{n_2n'_2}(1,t_2)C^{l|m|}(l_2m_2,l'_2m'_2)A^{m}_{m_2m'_2}$$
$$\times\begin{cases}F_{-(l+1-n_2-n'_2)}(k_2)-\sum\limits_{\sigma=l+1-n_2-n'_2}^{n'-\alpha+l}\gamma^l_\sigma(n'-\alpha)k_2^\sigma\dfrac{[\sigma-(l+1-n_2-n'_2)]!}{(k_2+1)^{\sigma-(l-n_2-n'_2)}} & for \quad l+1-n_2-n'_2>0\\ |l+1-n_2-n'_2|!-\sum\limits_{\sigma=0}^{n'-\alpha+l}\gamma^l_\sigma(n'-\alpha)k_2^\sigma\dfrac{(\sigma+|l+1-n_2-n'_2|)!}{(k_2+1)^{\sigma+|l+1-n_2-n'_2|+1}} & for \quad l+1-n_2-n'_2\le 0\end{cases}, \quad (4.13)$$

where $k_2=\dfrac{\eta}{\zeta_2+\zeta'_2}$ and

$$\begin{aligned}F_{-N}(k)&=\int_0^\infty\frac{1}{x^N}(1-e^{-kx}\sum_{\sigma=0}^{N-1}\frac{(kx)^\sigma}{\sigma!})e^{-x}dx\\&=\frac{(-1)^{N-1}}{(N-1)!}[\ln(k+1)+\sum_{i=1}^{N-1}\frac{(-k)^i}{i}].\end{aligned} \quad (4.14)$$

For the small values of k, the function $F_{-N}(k)$ can be calculated by the use of series expansion relation

$$F_{-N}(k)=\sum_{\sigma=0}^{\infty}\frac{(-1)^\sigma k^{N+\sigma}}{(N-1)!(N+\sigma)}. \quad (4.15)$$

For the derivation of Eq. (6.15) we have taken into account the following formula [49]:

$$\frac{1}{x^N}(1-e^{-x}\sum_{\sigma=0}^{N-1}\frac{x^\sigma}{\sigma!})=\sum_{\sigma=0}^{\infty}\frac{(-x)^\sigma}{(N-1)!\sigma!(N+\sigma)}. \quad (4.16)$$

From Eqs. (4.4) and (4.5), it can be seen that the three-center nuclear attraction and four-center electron-repulsion integrals of HFR equations are expressed through the two- and three-center overlap integrals of three STOs, respectively, for which the analytical formulas have been established in our previous works [48, 49]. The auxiliary functions $Q^q_{NN'}$ and $G^q_{-NN'}$ occurring in Eq. (4.9) for the two-center functions $U^{c,cd}_{p',p_2p'_2}$, therefore, arising in the case of four-center electron-repulsion integrals have been studied in recently published paper [50]. It should be noted that all the one-, two- and three-center multicenter integras appearing in HFR equations can also be calculated from the formulas (4.4) and (4.5). For this purpose we must calculate one- and two-center overlap integrals of three STOs and use Eqs. (4.9), (4.13), (4.14) and (4.15).

The convergence properties of the series expansion relation for three-center nuclear attraction integral $J^{ab,c}_{211,211}(3.8,4.6,4.6)$ obtained by the use of unsymmetrical one-range addition theorems of the Coulomb potential for $\alpha=-1$ are shown in tables 4.1, 4.2 and 4.3. These tables list the partial summations in Eq. (4.4) corresponding to progressively increasing upper summations limits denoted by N, L and M. As can be seen from tables 4.1 and 4.2, the Eq. (4.4) displays the most rapid convergence to the numerical results with twelve digits stable as a function of summation limits L and M. We see that the convergence of the series with respect to L and M is rapid; therefore, we can include only a few terms obtained from the summation over indices l and m. Table 4.3 shows that the accuracy of computer calculations obtained in the present algorithm is satisfactory for $N=15$. Greater accuracy is attainable by the use of more terms in the expansion in Eq. (4.4).

Carrying through calculations for the symmetrical case analogous to those for the unsymmetrical one-range addition theorems, we obtain for the multicenter integrals of HFR equations the following symmetrical formulas:

$$J^{ab,c}_{p_1p'_1}(\zeta_1,\zeta'_1,\eta)=\frac{\sqrt{4\pi}}{\eta^2}\lim_{\substack{N\to N_{\max}\\ N'\to N'_{\max}}}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\left[\sum_{u=1}^{N+N'-\alpha+1}\sum_{v=0}^{u-1}\sum_{s=-v}^{v}B^{\alpha q}_{p}(N,N')\chi_q(\eta,\vec{R}_{bc})\right]S^{abc}_{p_1p'_1p}(\zeta_1,\zeta'_1,\eta) \quad (4.17)$$

$$\begin{aligned}J^{ab,cd}_{p_1p'_1,p_2p'_2}(\zeta_1,\zeta'_1,\zeta_2,\zeta'_2,\eta)=&\lim_{\substack{N\to N_{\max}\\ N'\to N'_{\max}}}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\sum_{u=1}^{N+N'-\alpha+1}\sum_{v=0}^{u-1}\sum_{s=-v}^{v}(-1)^{v}B^{\alpha q}_{p}(N,N')\\ &\times S^{abc}_{p_1p'_1p}(\zeta_1,\zeta'_1,\eta)S^{ccd}_{qp_2p'_2}(\eta,\zeta_2,\zeta'_2)\end{aligned} \quad (4.18)$$

where $p\equiv nlm, q\equiv uvs$ and

$$B^{\alpha q}_{p}(N,N')=\sum_{n'=l+1}^{N}\Omega^{\alpha l}_{nn'}(N)\sum_{\mu'=1}^{N'}g^{\alpha uvs}_{\mu'00,n'-\alpha lm}\sum_{\mu''=1}^{N'}\frac{(\mu''-\alpha)!}{\{[2(\mu''-\alpha)]!\}^{1/2}}\Omega^{\alpha 0}_{\mu'\mu''}(N')2^{\mu''-\alpha+1} \quad (4.19)$$

The quantities S^{abc} and S^{ccd} occurring in Eqs. (4.17) and (4.18) are the multicenter overlap integrals of three STOs. We see from Eq. (4.17) that the multicenter one-electron integrals are expressed through the products of STOs and multicenter overlap integrals. The two-electron multicenter integrals, Eq. (4.18), are the function of the products of multicenter overlap integrals.

Thus, for the calculation of multicenter integrals of HFR equations obtained by the use of symmetrical and unsymmetrical one-range addition theorems of Coulomb potential one can use the formulae for overlap integrals, and auxiliary functions and overlap integrals, respectively.

5.2. Multicenter integrals of noninteger n STOs

The multicenter integrals over noninteger n STOs arising in HFR equations are defined as

One-electron multicenter integrals

$$J^{ab,c}_{p_1^*p_1'^*}(\zeta_1,\zeta'_1)=\int\chi^*_{p_1^*}(\zeta_1,\vec{r}_{a1})\chi_{p_1'^*}(\zeta'_1,\vec{r}_{b1})\frac{1}{r_{c1}}dv_1, \quad (4.20)$$

Two-electron multicenter integrals

$$J^{ab,cd}_{p_1^*p_1'^*,p_2^*p_2'^*}(\zeta_1,\zeta'_1,\zeta_2,\zeta'_2)=\int\int\chi^*_{p_1^*}(\zeta_1,\vec{r}_{a1})\chi_{p_1'^*}(\zeta'_1,\vec{r}_{b1})\frac{1}{r_{21}}\chi_{p_2^*}(\zeta_2,\vec{r}_{c2})\chi_{p_2'^*}(\zeta'_2,\vec{r}_{d2})dv_1dv_2, \quad (4.21)$$

where $p_1^*\equiv n_1^*l_1m_1$, $p_1'^*\equiv n_1'^*l'_1m'_1$, $p_2^*\equiv n_2^*l_2m_2$, $p_2'^*\equiv n_2'^*l'_2m'_2$ and

$$\chi_{n^*lm}(\zeta,\vec{r})=(2\zeta)^{n^*+1/2}[\Gamma(2n^*+1)]^{-1/2}r^{n^*-1}e^{-\zeta r}S_{lm}(\theta,\varphi). \quad (4.22)$$

Here, $\Gamma(x)$ is the gamma function [51]. The normalized integer n STOs, Eq. (2.13), can be obtained from Eq. (4.22) for $n^* = n$, where n is an integer.

Taking into account Eqs. (3.22) and (4.3) for the one-range addition theorems of Coulomb potential in Eqs. (4.20) and (4.21) we obtain for the one- and two-electron multicenter integrals of noninteger n STOs the following relations:

$$J^{ab,c}_{p_1^* p_1'^*}(\zeta_1,\zeta_1',\eta) = \sqrt{4\pi} \lim_{N\to N_{\max}} \sum_{n=1}^{N} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} (-1)^l S^{abb}_{p_1^* p_1'^* p}(\zeta_1,\zeta_1',\eta) \sum_{n'=l+1}^{N} \Omega^{\alpha l}_{nn'}(N) U^*_{p'}(\eta,\vec{R}_{bc}) \tag{4.23}$$

$$J^{ab,cd}_{p_1^* p_1'^*, p_2^* p_2'^*}(\zeta_1,\zeta_1',\zeta_2,\zeta_2',\eta) = \lim_{N\to N_{\max}} \sum_{n=1}^{N} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} (-1)^l S^{abc}_{p_1^* p_1'^* p}(\zeta_1,\zeta_1',\eta) \sum_{n'=l+1}^{N} \Omega^{\alpha l}_{nn'}(N) U^{c,cd}_{p',p_2^* p_2'^*}(\eta,\zeta_2,\zeta_2'), \tag{4.24}$$

where $U_{p'}(\eta,\vec{R}_{bc})$ is determined by Eq. (4.6) and

$$S^{abc}_{p_1^* p_1'^* p}(\zeta_1,\zeta_1',\eta) = \sqrt{4\pi} \int \chi^*_{p_1^*}(\zeta_1,\vec{r}_{a1}) \chi_{p_1'^*}(\zeta_1',\vec{r}_{b1}) \chi_p(\eta,\vec{r}_{c1}) dv_1 \tag{4.25}$$

$$U^{c,cd}_{p',p_2^* p_2'^*}(\eta,\zeta_2,\zeta_2') = \sqrt{4\pi} \int U^*_{p'}(\eta,\vec{r}_{c2}) \chi_{p_2^*}(\zeta_2,\vec{r}_{c2}) \chi^*_{p_2'^*}(\zeta_2',\vec{r}_{d2}) dv_2\,. \tag{4.26}$$

With the calculation of these integrals we use the one-center expansion formula for noninteger n STOs in terms of integer n STOs established with the aid of complete orthonormal sets of $\psi^\alpha - ETOs$ [52]:

$$\chi_{n^*lm}(\zeta,\vec{r}) = \lim_{N\to N_{\max}} \sum_{n=l+1}^{N} V^{\alpha N}_{n^*l,nl} \chi_{nlm}(\zeta,\vec{r}), \tag{4.27}$$

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

$$V^{\alpha N}_{n^*l,nl} = \sum_{n'=l+1}^{N} \Omega^{\alpha l}_{nn'}(N) \frac{\Gamma(n^* + n' - \alpha + 1)}{[\Gamma(2n^*+1)\Gamma(2n'-2\alpha+1)]^{1/2}} \tag{4.28}$$

We notice that in the case of integer values of n^* the coefficient $V^{\alpha N}_{n^*l,nl}$ are reduced to the Kronecker symbol, i.e

$$V^{\alpha N}_{n^*l,nl} = \delta_{nn^*} \delta_{Nn^*} \tag{4.29}$$

Now we take into account the one-center expansion relation (4.27) in Eqs. (4.25) and (4.26). Then, we obtain the following expressions through the integer n integrals:

$$S^{abc}_{p_1^* p_1'^* p}(\zeta_1,\zeta_1',\eta) = \lim_{\substack{N_1\to N_{1\max} \\ N_1'\to N_{1\max}'}} \sum_{n_1=l_1+1}^{N_1} \sum_{n_1'=l_1'+1}^{N_1'} V^{\alpha N_1}_{n_1^* l_1, n_1 l_1} V^{\alpha N_1'}_{n_1'^* l_1', n_1' l_1'} S^{abc}_{p_1 p_1' p}(\zeta_1,\zeta_1',\eta) \tag{4.30}$$

$$U^{c,cd}_{p',p_2^* p_2'^*}(\eta,\zeta_2,\zeta_2') = \lim_{\substack{N_2\to N_{2\max} \\ N_2'\to N_{2\max}'}} \sum_{n_2=l_2+1}^{N_2} \sum_{n_2'=l_2'+1}^{N_2'} V^{\alpha N_2}_{n_2^* l_2, n_2 l_2} V^{\alpha N_2'}_{n_2'^* l_2', n_2' l_2'} U^{c,cd}_{p',p_2 p_2'}(\eta,\zeta_2,\zeta_2') \tag{4.31}$$

As can be seen from the formulas of this section obtained by the use of one-range addition theorems of Coulomb potential, the evaluation of one- and two-electron multicenter integrals over integer and noninteger n STOs is reduced to the calculation of integer n integrals $S^{aaa}, S^{abb}, S^{abc}, U^{c,cd}$ and $U^{c,cc}$. In order to calculate the three-center overlap integrals S^{abc} we should use the one-range addition theorems for STOs.

Thus, all of the integer and noninteger multicenter integrals arising in HFR equations are evaluated by the use of one-range addition theorems for the Coulomb potential and Slater orbitals. It should be noted that the one-range addition theorems for the STOs and Coulomb potential are the special classes of one-range addition theorems obtained by the use of $\psi^{\alpha} - ETOs$ which belong to the corresponding Hilbert spaces.

Weniger is very sceptical about all addition theorems for Slater type functions with nonintegral principal quantum number [3, p.28]. This claim can be rejected with the help of calculation of multicenter integrals over noninteger n STOs for different values of indices α. The results of calculation for three-center nuclear attraction integrals over noninteger n STOs, Eq. (4.23), for various values of parameters are presented in Table 4.4. As can be seen from this table that the accuracy of computer results for $\alpha = 0$ and $\alpha = -1$ are satisfactory.

3.TWO-CENTER OVERLAP and MULTICENTER INTEGRALS over Ψ^{α}-ETOs and STOs

Overlap integrals over integer and noninteger n STOs arise not only in the HFR equations for molecules, but are also central to the calculation of arbitrary multicenter multielectron integrals based on the series expansion formulas obtained by the use of unsymmetrical and symmetrical one-range addition theorems for STOs and correlated interaction potentials which necessitate to accurately calculate the overlap integrals especially for the large quantum numbers.

1. Overlap Integrals of Integer n STOs

The two-center overlap integrals over integer n STOs with respect to lined-up coordinate systems are defined as

$$S_{nl\lambda,n'l'\lambda}(p,t) = \int \chi^{*}_{nlm}(\zeta,\vec{r}_a)\chi_{n'l'm}(\zeta',\vec{r}_b)\,dV, \quad (5.1)$$

where $0 \le \lambda \le l, m = \pm\lambda, p = \frac{R}{2}(\zeta+\zeta'), t = (\zeta-\zeta')/(\zeta+\zeta')$ and $\vec{R} \equiv \vec{R}_{ab} = \vec{r}_a - \vec{r}_b$.

We calculate the overlap integrals over integer n STOs using the analytical approach containing well-known auxiliary functions A_k and B_k and the recurrence relations for the basic overlap integrals presented in our previous works [53] and [54, 55], respectively. These expressions are especially useful for computation of overlap integrals on the computer for high quantum numbers, internuclear distances and orbital exponents or vice versa.

In this section, the differences and similarities in organization of existing overlap integral programs are discussed, and a new strategy is developed. This method is computationally simple and numerically well behaved. On the basis of formulas obtained in papers [53-55] we constructed a program for computation of the overlap integrals over integer n STOs using Mathematica 5.0 international mathematical software and Turbo Pascal language packages. The numerical results demonstrate that the computational accuracy of the established formulas is not only dependent on the efficiency of formulas, but also strongly dependent on the used program language packages. Excellent agreement with benchmark results and stability of the technique are demonstrated. Since the overlap integrals over integer n STOs are of considerable importance in the evaluation of arbitrary multicenter integrals by the use of one-range addition theorems, for STOs and potential, it is hoped that the present work will prove useful in tackling more complicated molecular integrals appearing in the determination of various properties for molecules when the HFR approximation is employed.

1.A. Analytical Relations in Terms of Auxiliary Functions

In Ref. [53], using the auxiliary function method for the overlap integrals have been established the following formula:

$$\begin{aligned} S_{nl\lambda,n'l'\lambda}\left(p,t\right) &= N_{nn'}(t)\sum_{\alpha=-\lambda}^{l}{}^{(2)}\sum_{\beta=\lambda}^{l'}{}^{(2)} g_{\alpha\beta}^{0}(l\lambda,l'\lambda)\sum_{q=0}^{\alpha+\beta}F_q(\alpha+\lambda,\beta-\lambda) \\ &\times \sum_{m=0}^{n+n'-\alpha-\beta}F_m(n-\alpha,n'-\beta)A_{n+n'-\alpha-\beta-m+q}^{n+n'+1}(p)B_{m+q}(pt), \end{aligned} \tag{5.2}$$

where A_n and B_n are the auxiliary functions defined by [56]

$$A_n(p)=\int_1^{\infty}\mu^n e^{-p\mu}d\mu=\frac{n!e^{-p}}{p^{n+1}}\sum_{s=0}^{n}\frac{p^s}{s!} \tag{5.3}$$

$$B_n(pt)=\int_{-1}^{1}\nu^n e^{-pt\nu}d\nu=(-1)^{n+1}A_n(-pt)-A_n(pt) \tag{5.4}$$

and

$$A_n^k(p)=p^kA_n(p)=n!e^{-p}\sum_{s=k-(n+1)}^{k-1}\frac{p^s}{(s-k+n+1)!}\qquad for\ \ k\geq n+1 \tag{5.5}$$

In our previous paper [57], the new analytical relations have been suggested for the fast evaluation of auxiliary functions A_n and B_n.

The coefficients $N_{nn'}(t)$ and $F_m(N,N')$ occurring in Eq.(5.2) are determined by

$$N_{nn'}(t)=\frac{[(1+t)]^{n+1/2}[(1-t)]^{n'+1/2}}{\sqrt{(2n)!(2n')!}} \tag{5.6}$$

$$F_m(N,N')=\sum_{\sigma=\frac{1}{2}[(m-n)+|m-n|)}^{\min(m,N')}(-1)^{\sigma}F_{m-\sigma}(N)F_{\sigma}(N'), \tag{5.7}$$

where $F_m(n)=n!/[m!(n-m)!]$ are the binomial coefficients. It should be noted that, Eq. (5.7) for the generalized binomial coefficients with different notation $D_m^{NN'}$ firstly has been presented by N. Rosen in Ref. [58].

The quantities $g_{\alpha\beta}^{0}(l\lambda,l'\lambda)$ in Eq.(5.2) are the expansion coefficients for a product of two normalized Legendre functions in elliptic coordinates. The relationship for these coefficients in terms of factorials was given in [59]. In Ref.[60], these coefficients were expressed in terms of binomial coefficients:

$$g_{\alpha\beta}^{0}(l\lambda,l'\lambda)=\left[\sum_{i=0}^{\lambda}(-1)^{i}F_i(\lambda)D_{\alpha+2\lambda-2i}^{l\lambda}\right]D_{\beta}^{l'\lambda}, \tag{5.8}$$

where

$$D_{\beta}^{l\lambda}=\frac{(-1)^{(l-\beta)/2}}{2^{l}}\left[\frac{2l+1}{2}\frac{F_l(l+\lambda)}{F_{\lambda}(l)}\right]^{1/2}F_{(l-\beta)/2}(l)F_{\beta-\lambda}(l+\beta). \tag{5.9}$$

1.B. Use of Recurrence Relations for Basic Overlap Integrals

In Ref. [55], using the expansion formula for product of two spherical harmonics both with the same center [59], the overlap integrals, Eq.(5.1), were expressed through the basic overlap integrals:

$$S_{nl\lambda,n'l'\lambda}(p,t)=\sum_{l''=\lambda}^{l}\frac{[2p(1+t)]^{l}}{[2p(1-t)]^{l''}}\left[\frac{(2l+1)(2l'')!F_{2n'}(2n'+2l'')F_{l''+\lambda}(l+\lambda)F_{l''-\lambda}(l-\lambda)}{(2l''+1)(2l)!F_{2n-2l}(2n)}\right]^{1/2}$$
$$\times\sum_{L}\sqrt{2L+1}C^{L}(l'\lambda,l''\lambda)S_{n-l00,n'+l''L0}(p,t), \tag{5.10}$$

where $C^{L}(l'\lambda,l''\lambda)$ are the Gaunt coefficients. The basic overlap integrals $S_{n,n'l'}\equiv S_{n00,n'l'0}$ appearing in Eq.(5.10) are determined by the following recurrence relationships:

$$S_{n,n'l'}\left(p,t\right)=-a_{l'-1}\left\{\frac{p\left(1-t\right)}{\left[\left(2n'-1\right)2n'\right]^{1/2}}S_{n,n'-1l'-1}\left(p,t\right)+\frac{\left[\left(2n'+1\right)\left(2n'+2\right)\right]^{1/2}}{4p\left(1-t\right)}S_{n,n'+1l'-1}\left(p,t\right)\right.$$

$$\left.-\frac{\left(1-t\right)}{4p\left[\left(1+t\right)\right]^{2}}\left[\frac{\left(2n+1\right)\left(2n+2\right)\left(2n+3\right)\left(n+2\right)}{\left(2n'-1\right)n'}\right]^{1/2}S_{n+2,n'-1l'-1}\left(p,t\right)\right\}-b_{l'-1}S_{n,n'l'-2}\left(p,t\right),\quad (5.11)$$

where $n \geq 1, n' \geq l' + 1, l' \geq 1, -1 < t < 1$ and the coefficients a_l and b_l are determined by

$$a_l = \frac{1}{l+1}\left[(2l+1)(2l+3)\right]^{1/2}\ ,\ \ b_l = \frac{l}{l+1}\left(\frac{2l+3}{2l-1}\right)^{1/2}. \qquad (5.12)$$

The recurrence relations (5.11) allow us to express $S_{n,n'l'}$ in terms of the integrals $S_{n,n'} \equiv S_{n00,n'00}$ for the calculation of which one can use the following recurrence relations:

for $n \geq 0, n' \geq 0$ and $t \neq 0$

$$S_{nn'}\left(p,t\right)=\frac{1}{t}\left\{\sqrt{\frac{n}{2\left(2n-1\right)}}\left(1+t\right)^{2}\left[S_{n-1n'}\left(p,t\right)-\sqrt{\frac{n-1}{2\left(2n-3\right)}}S_{n-2n'}\left(p,t\right)\right]-\sqrt{\frac{n'}{2\left(2n'-1\right)}}\left(1-t\right)^{2}\right.$$

$$\left.\times\left[S_{n,n'-1}\left(p,t\right)-\sqrt{\frac{n'-1}{2\left(2n'-3\right)}}S_{n,n'-2}\left(p,t\right)\right]+\eta_{nn'}\left(p,t\right)\left[\delta_{n0}e^{-p(1-t)}-\delta_{n'0}e^{-p(1+t)}\right]\right\}, \qquad (5.13)$$

for $n' \geq 0$ and $t = 0$

$$S_{0n'}\left(p,0\right)=\left[\frac{n}{2\left(2n'-1\right)}\right]^{1/2}S_{0n'-1}\left(p,0\right)+\left[\frac{2\left(2n'+1\right)}{n'+1}\right]^{1/2}\eta_{0n'+1}\left(p,0\right)e^{-p}, \qquad (5.14)$$

for $1 \leq n \leq n'$ and $t = 0$

$$S_{nn'}\left(p,0\right)=\left[\frac{n\left(2n'-1\right)}{\left(2n-1\right)\left(n'+1\right)}\right]^{1/2}S_{n-1n'+1}\left(p,0\right)-\left[\frac{n\left(n-1\right)\left(2n'+1\right)}{2\left(2n-1\right)\left(2n-3\right)\left(n'+1\right)}\right]^{1/2}S_{n-2n'+1}\left(p,0\right)$$

$$+\left[\frac{n'}{2\left(2n'-1\right)}\right]^{1/2}S_{nn'-1}\left(p,0\right). \qquad (5.15)$$

Here,

$$\eta_{nn'}\left(p,t\right)=\frac{\left[2p\left(1+t\right)\right]^{n+1/2}\left[2p\left(1-t\right)\right]^{n'+1/2}}{4p^{2}\left[(2n)!(2n')!\right]^{1/2}}. \qquad (5.16)$$

With the aid of recurrence relations (5.11), (5.13), (5.14) and (5.15) the basic overlap integrals $S_{n,n'l'}(p,t)$ can be expressed in terms of the functions $S_{00}(p,t)$ and $S_{00}(p,0)$ for the calculation of which we can use the following analytical formulas:

$$S_{00}(p,t)=\frac{1}{t}\eta_{00}(p,t)\left\{e^{-p(1-t)}-e^{-p(1+t)}\right\} \tag{5.17}$$

$$S_{00}(p,0)=e^{-p}. \tag{5.18}$$

By the use of calculations we can answer to the following Weniger's comment: *"Moreover, Guseinov should know that an observed agreement of different floating point computations up to a certain number of digits does not necessarily prove anything (see for example [61]) " [3, p.23].* On the basis of Eqs.(5.2) and (5.10), obtained in our papers [53-55], we constructed the programs which were performed in the Mathematica 5.0 international mathematical software and Turbo Pascal 7.0 language packages. The computational results of overlap integrals by the use of Turbo Pascal 7.0 language package program have been examined in our published papers [53-55]. The Barnett's data [61] and results of our calculation using Mathematica 5.0 international mathematical software and Turbo Pascal 7.0 language packages for various values of parameters are represented in Table 5.1. Barnett's data are reproduced by using our scheme with Mathematica while we get different results using the same scheme with Turbo Pascal. Thus, in this paper we show that the discrepancies can be arisen in the case of different programming environments. We note that, the difference between the numerical results of Eqs.(5.2) and (5.10) arise only after forty fifth digits. It should be noted that for the comparison of the accuracy of computer results obtained from the formulas of overlap integrals, one should use the same program language packages.

It is well known from the expert of this field that the problems occur in the evaluation of overlap integrals are as follow: small internuclear distances and small orbital exponents, and high internuclear distances and high orbital exponents. The results of calculation in these cases are given in Table 5.2. As is clear from our tests that the recurrence and analytical formulas presented in this study are useful tool for exact evaluation of the overlap integrals with arbitrary values of quantum numbers, internuclear distances and orbital parameters. Thus, our program calculates the overlap integrals over STOs with arbitrary quantum numbers (n,l,n',l',λ) and variables (p,t).

2. Overlap Integrals of Noninteger n STOs

The overlap integrals over noninteger n STOs are defined as

$$S_{n^*lm,\, n'^*l'm}\left(\zeta,\zeta';\vec{R}\right)=\int \chi^*_{n^*lm}\left(\zeta,\vec{r}_a\right)\chi_{n'^*l'm}\left(\zeta',\vec{r}_b\right)dV\ . \tag{5.19}$$

With the calculation of these integrals we use Eq. (4.27) in (5.19). Then, we obtain the series expansion relation in terms of overlap integrals with integer n STOs:

$$S_{n^*lm,\, n'^*l'm}\left(p,t\right)=\lim_{\substack{N\to N_{max}\\ N'\to N'_{\max}}}\sum_{n=l+1}^{N}\sum_{n'=l'+1}^{N'}V^{\alpha N}_{n^*l,nl}V^{\alpha N'}_{n'^*l',n'l'}S_{nlm,\,n'l'm}\left(p,t\right), \tag{5.20}$$

where $p=\dfrac{R}{2}(\zeta+\zeta'),\ t=\dfrac{\zeta-\zeta'}{\zeta+\zeta'},\quad S_{n^*lm,\,n'^*l'm}\left(p,t\right)\equiv S_{n^*lm,\,n'^*l'm}\left(\zeta,\zeta';R\right)$

and $S_{nlm,\,n'l'm}\left(p,t\right)\equiv S_{nlm,\,n'l'm}\left(\zeta,\zeta';R\right)$.

For the calculation of overlap integrals over integer n STOs, we can use the analytical formulas and sets of recurrence relations presented in sections (5.1A) and (5.1B). This algorithm is especially useful for the computation of overlap integrals for large quantum numbers of integer n STOs appearing in the series expansion formulas for the multicenter molecular integrals obtained by the use of one-range addition theorems. The overlap integrals with noninteger n STOs, Eqs. (5.20), can be calculated by the use of our computer programs for the overlap integrals over integer n STOs .

Thus, we proposed a new technique for the efficient computation of overlap integrals with noninteger n^* STOs, based on the usage of complete orthonormal sets of Ψ^{α}-ETOs. An analysis of the numerical aspects and several numerical tests confirmed that the convergence and the numerical stability of the relevant formulas are guaranteed. Besides having an excellent convergence rate, the proposed method is perfectly general, valid for arbitrary values of quantum numbers, screening constants and internuclear distances. On the basis of formulae (5.20) we constructed a program for the computation of overlap integrals over noninteger n STOs using Turbo Pascal 7.0 language and Mathematica 5.0 international mathematical software. One can determine the accuracy of computer results obtained in this work for the overlap integrals over noninteger n STOs using different sets of Ψ^{α}-ETOs. The examples of computer calculation are shown in Table 5.3. As can be seen from Table 4 that the calculated values of overlap integrals over noninteger n STOs for $\alpha=1,0,-1$ show a good rate of convergence with the literature for the arbitrary values of parameters. Greater accuracy is attainable by the use of more terms in the series expansion formula (5.20). The better accuracies can be obtained, if required, by the use of large number of summation terms.

Table 5.4 lists the partial summations corresponding to progressively increasing upper summation limits of Eq. (5.20) for $N = N'$. We see from this table that the Eq. (5.20) displays the most rapid convergence to the numerical results with eleven digits stable and correct by the 17th terms in the infinite summations.

4.UNIFIED TREATMENT of COMPLETE ORTHONORMAL SETS for EXPONENTIAL TYPE VECTOR ORBITALS of PARTICLES WITH SPIN 1 in COORDINATE, MOMENTUM and FOUR-DIMENSIONAL SPACES

(J.Math.Chem.(Online)

Abstract

The new formulas are obtained for complete orthonormal sets of exponential type vector orbitals of a particle with spin 1 in coordinate, momentum and four-dimensional spaces using the properties of spherical vectors and complete orthonormal scalar basis 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 by the author for particles with spin $s=0$, where $\alpha = 1, 0, -1, -2, ...$ These vector orbitals are complete without the inclusion of the continuum and, therefore, their group of transformation is the four-dimensional rotation group of O(4). For overlap integrals over vector Slater orbitals with the same screening constant the analytical relations in coordinate space are also derived. It should be noted that the new idea presented in this study is the combination of spherical vectors with complete orthonormal scalar sets for radial parts of ψ^{α}-, ϕ^{α}-, z^{α}- orbitals.

Key Words: Spherical vector, Exponential type vector orbitals, Overlap integral

1. Introduction

It is well known that the Schrödinger's hydrogen-like orbitals and their extensions to momentum and four-dimensional spaces by Fock [1,2] are awkward to use as basis because they are not complete unless the continuum is included. Hylleraas, Shull and Löwdin in Refs. [3-6] introduced the so-called Lambda and Coulomb Sturmian functions which are complete and orthonormal basis sets for the particles with spin s=0 in coordinate space. These functions later were used extensively by Filter, Steinborn [7] and Weniger [8]. The method for constructing relativistic Coulomb Sturmian basis set has been developed and discussed by Avery and Antonsen [9]. Recently, in Refs [10-12] we suggested in coordinate, momentum and four-dimensional spaces the scalar basis sets of ψ^{α}-ETO, ϕ^{α}-MSO and z^{α}-HSH for particles with spin $s=0$ which are complete without the inclusion of the continuum, where $\alpha = 1, 0, -1, -2, \ldots$. In the present work, we obtain a large number of new different complete and orthonormal sets for vector wave functions, and vector Slater orbitals in coordinate, momentum and four-dimensional spaces using complete orthonormal scalar basis sets of ψ^{α}-ETO, ϕ^{α}-MSO and z^{α}-HSH functions. It should be noted that the Lambda and Coulomb Sturmian functions introduced by Hylleraas, Shull and Löwdin are the special classes of ψ^{α}-ETO for $\alpha = 0$ and $\alpha = 1$, respectively (see Ref. [10]).

2. Spherical vectors and vector wave functions

For the derivation of relations for complete orthonormal sets of vector wave functions of a particle with spin $s=1$ in coordinate, momentum and four-dimensional spaces we use the following eigenvalue equations of spherical vectors (see Sec. 7.3. of Ref. [13]):

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

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

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

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

Here, $\hat{l}$-orbital angular momentum operator, $\hat{s}$-spin operator for s=1, $\hat{j} = \hat{l} + \hat{s}$-total angular momentum operator. The spherical vectors $Y^l_{jm_j}(\theta,\varphi)$ are expressed through the products of scalar spherical harmonics $Y_{lm_l}(\theta,\varphi)$ and basis spin functions u_{1m_s}, i.e.,

$$Y^l_{jm_j}(\theta,\varphi) = \sum_{m_l, m_s} (l1 m_l m_s | l1 j m_j) Y_{lm_l}(\theta,\varphi) u_{1m_s}, \tag{5}$$

where $(l1 m_l m_s | l1 j m_j)$ are the Clebsch-Gordan coefficients, $m_l = m_j - m_s$ and (see Sec. 6.1. of Ref. [13]):

$$u_{11} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, u_{10} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, u_{1-1} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \tag{6}$$

The complete sets of scalar spherical harmonics, basis spin functions and spherical vectors satisfy the following orthonormality relations:

$$\int_0^{\pi}\int_0^{2\pi} Y^*_{lm_l}(\theta,\varphi)Y_{l'm'_l}(\theta,\varphi)Sin\theta d\theta d\varphi = \delta_{ll'}\delta_{m_l m'_l} \tag{7}$$

$$u^+_{1m_s}u_{1m'_s} = \delta_{m_s m'_s} \tag{8}$$

$$\int_0^{\pi}\int_0^{2\pi} Y^{l+}_{jm_j}(\theta,\varphi)Y^{l'}_{j'm'_j}(\theta,\varphi)Sin\theta d\theta d\varphi = \delta_{jj'}\delta_{m_j m'_j}\delta_{ll'}. \tag{9}$$

We notice that the spherical vectors are not eigenfunctions of the operators $\hat{l}_z$ and $\hat{s}_z$, i.e., the quantum numbers m_l and m_s cannot be used to characterize them. This is important in derivation of relations for the complete orthonormal sets of vector wave functions in coordinate, momentum and four-dimensional spaces.

Taking into account Eqs. (6) for the basis spin functions u_{1m_s} in (5) we can express the spherical vectors $Y^l_{jm_j}(\theta,\varphi)$ only through the scalar spherical harmonics $Y_{lm_l}(\theta,\varphi)$, i.e.,

$$Y^l_{jm_j}(\theta,\varphi) = \begin{pmatrix} a^l_{jm_j}(0)Y_{lm_l(0)}(\theta,\varphi) \\ a^l_{jm_j}(1)Y_{lm_l(1)}(\theta,\varphi) \\ a^l_{jm_j}(2)Y_{lm_l(2)}(\theta,\varphi) \end{pmatrix}, \tag{10}$$

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

$$a^l_{jm_j}(\lambda) = (l1m_l1-\lambda | l1jm_j). \tag{11}$$

Now we move on to the derivation of vector wave functions. For this purpose we introduce the following complete and orthonormal sets of functions:

$$\psi_{nlm_l}(\vec{r}) = R_{nl}(r)Y_{lm_l}(\theta,\varphi) \tag{12}$$

These functions are complete and orthonormal with respect to an integration over the whole 3-dimensional space $\Re^3$ in a suitable Hilbert space of functions $F(\vec{r})$ by forming products of the (surface) spherical harmonics $Y_{lm_l}(\theta,\varphi)$, which are complete and orthonormal with respect to an integration over the surface of the unit sphere in $\Re^3$, and the radial functions $R_{nl}(r)$, which are complete and orthonormal with respect to an integration over the positive semiaxis $0 \le r < \infty$ in a suitable Hilbert space of radial functions $f(r)$.

It is obviously possible to expand a function $F(\vec{r})$ belonging to a suitable Hilbert space in terms of the complete and orthonormal functions $\psi_{nlm_l}(\vec{r})$ which are determined by Eq. (12):

$$F(\vec{r}) = \sum_{nlm_l} C_{nlm_l}\psi_{nlm_l}(\vec{r}) \tag{13}$$

$$C_{nlm_l} = \int \psi^*_{nlm_l}(\vec{r}) F(\vec{r}) d^3\vec{r}. \tag{14}$$

As long as the ψ_{nlm_l} are complete and orthonormal set of functions, the convergence of expansion (13) is guaranteed. Thus, the functions ψ_{nlm_l} constructed by the product of complete and orthonormal functions $R_{nl}(r)$ and $Y_{lm_l}(\theta,\varphi)$ also are the complete orthonormal functions in a suitable space of the radial functions and the (surface) spherical harmonics.

In this way, one can construct the vector wave functions. For this purpose, we multiply the scalar components of the spherical vectors by the complete orthonormal radial functions $R_{nl}(r)$. Then, we obtain the following complete orthonormal set of vector wave functions:

$$\begin{aligned}\psi^l_{njm_j}(\vec{r}) &= R_{nl}(r) Y^l_{jm_j}(\theta,\varphi)\\ &= \begin{pmatrix} a^l_{jm_j}(0)\psi_{nlm_{l(0)}}(r,\theta,\varphi) \\ a^l_{jm_j}(1)\psi_{nlm_{l(1)}}(r,\theta,\varphi) \\ a^l_{jm_j}(2)\psi_{nlm_{l(2)}}(r,\theta,\varphi) \end{pmatrix}.\end{aligned} \tag{15}$$

The vector wave functions also satisfy the orthonormality relation, i.e.,:

$$\int \psi^{l^+}_{njm_j}(\vec{r}) \psi^{l'}_{n'j'm'_j}(\vec{r}) d^3r = \delta_{nn'}\delta_{jj'}\delta_{m_j m'_j}\delta_{ll'}. \tag{16}$$

3. Complete orthonormal sets of exponential type vector orbitals

For the derivation of relations for the complete orthonormal sets of vector orbitals in coordinate, momentum and four-dimensional spaces we use the properties of spherical vectors (see Sec. 7.3. of Ref. [13]) and scalar basis sets of ψ^α-ETO, ϕ^α-MSO, z^α-HSH functions presented in [10-12]. Then, we obtain the following results:

for vector Ψ^α-ETO (Ψ^α-VETO) in coordinate space

$$\Psi^{\alpha l}_{njm_j}(\zeta,\vec{r}) = \begin{pmatrix} a^l_{jm_j}(0)\psi^\alpha_{nlm_l(0)}(\zeta,\vec{r}) \\ a^l_{jm_j}(1)\psi^\alpha_{nlm_l(1)}(\zeta,\vec{r}) \\ a^l_{jm_j}(2)\psi^\alpha_{nlm_l(2)}(\zeta,\vec{r}) \end{pmatrix} \tag{17a}$$

$$\bar{\Psi}^{\alpha l}_{njm_j}(\zeta,\vec{r}) = \begin{pmatrix} a^l_{jm_j}(0)\bar{\psi}^{\alpha l}_{nlm_l(0)}(\zeta,\vec{r}) \\ a^l_{jm_j}(1)\bar{\psi}^{\alpha l}_{nlm_l(1)}(\zeta,\vec{r}) \\ a^l_{jm_j}(2)\bar{\psi}^{\alpha l}_{nlm_l(2)}(\zeta,\vec{r}) \end{pmatrix}, \tag{17b}$$

for vector Φ^α-MSO (Φ^α-VMSO) in momentum space

$$\Phi^{\alpha l}_{njm_j}(\zeta,\vec{k})=\begin{pmatrix} a^l_{jm_j}(0)\phi^{\alpha}_{nlm_l(0)}(\zeta,\vec{k}) \\ a^l_{jm_j}(1)\phi^{\alpha}_{nlm_l(1)}(\zeta,\vec{k}) \\ a^l_{jm_j}(2)\phi^{\alpha}_{nlm_l(2)}(\zeta,\vec{k}) \end{pmatrix} \tag{18a}$$

$$\bar{\Phi}^{\alpha l}_{njm_j}(\zeta,\vec{k})=\begin{pmatrix} a^l_{jm_j}(0)\bar{\phi}^{\alpha}_{nlm_l(0)}(\zeta,\vec{k}) \\ a^l_{jm_j}(1)\bar{\phi}^{\alpha}_{nlm_l(1)}(\zeta,\vec{k}) \\ a^l_{jm_j}(2)\bar{\phi}^{\alpha}_{nlm_l(2)}(\zeta,\vec{k}) \end{pmatrix}, \tag{18b}$$

for vector Z^{α}-HSH (Z^{α}-VHSH) in four-dimensional space

$$Z^{\alpha l}_{njm_j}(\zeta,\beta\theta\varphi)=\begin{pmatrix} a^l_{jm_j}(0)z^{\alpha}_{nlm_l(0)}(\zeta,\beta\theta\varphi) \\ a^l_{jm_j}(1)z^{\alpha}_{nlm_l(1)}(\zeta,\beta\theta\varphi) \\ a^l_{jm_j}(2)z^{\alpha}_{nlm_l(2)}(\zeta,\beta\theta\varphi) \end{pmatrix} \tag{19a}$$

$$\bar{Z}^{\alpha l}_{njm_j}(\zeta,\beta\theta\varphi)=\begin{pmatrix} a^l_{jm_j}(0)\bar{z}^{\alpha}_{nlm_l(0)}(\zeta,\beta\theta\varphi) \\ a^l_{jm_j}(1)\bar{z}^{\alpha}_{nlm_l(1)}(\zeta,\beta\theta\varphi) \\ a^l_{jm_j}(2)\bar{z}^{\alpha}_{nlm_l(2)}(\zeta,\beta\theta\varphi) \end{pmatrix}. \tag{19b}$$

Here, the coefficients $a^l_{jm_j}(\lambda)$ are determined by Eq. (11) and

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

The functions $\psi^{\alpha}_{nlm_l}, \bar{\psi}^{\alpha}_{nlm_l}, \phi^{\alpha}_{nlm_l}, \bar{\phi}^{\alpha}_{nlm_l}, z^{\alpha}_{nlm_l}$ and $\bar{z}^{\alpha}_{nlm_l}$ occurring on the right-hand side of Eqs. (17a)- (19b) are the complete orthonormal sets of orbitals for particles with spin $s=0$ in coordinate, momentum and four-dimensional spaces.

The vector wave functions Ψ^{α}, Φ^{α} and Z^{α} are orthonormal with respect to the $\bar{\Psi}^{\alpha}$, $\bar{\Phi}^{\alpha}$ and $\bar{Z}^{\alpha}$, respectively, i.e.,

$$\int \bar{\Psi}^{\alpha l^+}_{njm_j}(\zeta,\vec{r})\Psi^{\alpha l'}_{n'j'm'_j}(\zeta,\vec{r})d^3\vec{r}=\delta_{nn'}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'} \tag{20}$$

$$\int \bar{\Phi}^{\alpha l^+}_{njm_j}(\zeta,\vec{k})\Phi^{\alpha l'}_{n'j'm'_j}(\zeta,\vec{k})d^3\vec{k}=\delta_{nn'}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'} \tag{21}$$

$$\int \bar{Z}^{\alpha l^+}_{njm_j}(\zeta,\beta\theta\varphi)Z^{\alpha l'}_{n'j'm'_j}(\zeta,\beta\theta\varphi)d\Omega(\zeta,\beta\theta\varphi)=\delta_{nn'}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'}\,. \tag{22}$$

4. Vector Slater orbitals

Carrying through the calculations for vector Slater orbitals analogous to those for the vector wave functions, we obtain the following relations through the scalar Slater orbitals:

for vector X-STO (X-VSTO) in coordinate space

$$\mathrm{X}^{l}_{njm_j}(\zeta,\vec{r})=\begin{pmatrix} a^{l}_{jm_j}(0)\chi_{nlm_l(0)}(\zeta,\vec{r}) \\ a^{l}_{jm_j}(1)\chi_{nlm_l(1)}(\zeta,\vec{r}) \\ a^{l}_{jm_j}(2)\chi_{nlm_l(2)}(\zeta,\vec{r}) \end{pmatrix}, \tag{23}$$

for vector U-MSO (U-VMSO) in momentum space

$$U^{l}_{njm_j}(\zeta,\vec{k})=\begin{pmatrix} a^{l}_{jm_j}(0)u_{nlm_l(0)}(\zeta,\vec{k}) \\ a^{l}_{jm_j}(1)u_{nlm_l(1)}(\zeta,\vec{k}) \\ a^{l}_{jm_j}(2)u_{nlm_l(2)}(\zeta,\vec{k}) \end{pmatrix}, \tag{24}$$

for vector V-HSH (V-VHSH) in four-dimensional space

$$V^{l}_{njm_j}(\zeta,\beta\theta\varphi)=\begin{pmatrix} a^{l}_{jm_j}(0)v_{nlm_l(0)}(\zeta,\beta\theta\varphi) \\ a^{l}_{jm_j}(1)v_{nlm_l(1)}(\zeta,\beta\theta\varphi) \\ a^{l}_{jm_j}(2)v_{nlm_l(2)}(\zeta,\beta\theta\varphi) \end{pmatrix}, \tag{25}$$

See Ref. [12] for the exact definition of Slater orbitals χ_{nlm_l}, u_{nlm_l} and v_{nlm_l} in coordinate, momentum and four-dimensional spaces occurring on the right-hide side of Eqs. (23) – (25).

The vector Slater orbitals determined by relations (23), (24) and (25) are orthogonal with respect to the quantum numbers j, m_j and l, i.e.,

$$\int \mathrm{X}^{l+}_{njm_j}(\zeta,\vec{r})\mathrm{X}^{l'}_{n'j'm'_j}(\zeta,\vec{r})d^3\vec{r}=\frac{(n+n')!}{[(2n)!(2n')!]^{1/2}}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'} \tag{26}$$

$$\int U^{l+}_{njm_j}(\zeta,\vec{k})U^{l'}_{n'j'm'_j}(\zeta,\vec{k})d^3\vec{k}=\frac{(n+n')!}{[(2n)!(2n')!]^{1/2}}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'} \tag{27}$$

$$\int V^{l+}_{njm_j}(\zeta,\beta\theta\varphi)V^{l'}_{n'j'm'_j}(\zeta,\beta\theta\varphi)d\Omega(\zeta,\beta\theta\varphi)=\frac{(n+n')}{[(2n)!(2n')!]^{1/2}}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'}. \tag{28}$$

5. Evaluation of overlap integrals over vector STO in coordinate space

As an example of application, we evaluate the two-center overlap integrals over vector Slater orbitals with the same screening parameters in coordinate space defined by

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

where $\vec{r}=\vec{r}_a$, $\vec{r}-\vec{R}=\vec{r}_b$, $\vec{R}=\vec{R}_{ab}$ and $\vec{G}=2\zeta\vec{R}$.

Now we take into account Eq. (23) in (29). Then, we obtain for integrals (29) the following relation in terms of overlap integrals over χ-STO:

$$S^{ll'}_{njm_j,n'j'm'_j}(\vec{G})=a^{ll'}_{jm_jj'm'_j}(0)s_{nlm_l(0),n'l'm'_l(0)}(\vec{G})+a^{ll'}_{jm_jj'm'_j}(1)s_{nlm_l(1),n'l'm'_l(1)}(\vec{G})+a^{ll'}_{jm_jj'm'_j}(2)s_{nlm_l(2),n'l'm'_l(2)}, \tag{30}$$

where $a^{ll'}_{jm_j j'm'_j}(\lambda) = a^{l}_{jm_j}(\lambda) a^{l'}_{j'm'_j}(\lambda)$ and $s_{nlm_l, n'l'm'_l}(\vec{G}) = \int \chi^*_{nlm_l}(\zeta, \vec{r}) \chi_{n'l'm'_l}(\zeta, \vec{r} - \vec{R}) d^3\vec{r}$.

(31)

In order to evaluate the overlap integrals over scalar STO, Eq. (31), we use the following expressions for STO in terms of complete orthonormal sets of ψ^{α} - and $\bar{\psi}^{\alpha}$ -ETOs:

$$\chi_{nlm_l}(\zeta, \vec{r}) = \sum_{\mu=l+1}^{n} \bar{\omega}^{\alpha l}_{n\mu} \psi^{\alpha}_{\mu l m_l}(\zeta, \vec{r}) \tag{32a}$$

$$= \{[2(n+\alpha)]!/(2n)!\}^{1/2} \sum_{\mu=l+1}^{n+\alpha} [\bar{\omega}^{\alpha l}_{n+\alpha\mu} / (2\mu)^{\alpha}] \bar{\psi}^{\alpha}_{\mu l m_l}(\zeta, \vec{r}) , \tag{32b}$$

See Ref. [10] for the exact definition of coefficients $\bar{\omega}^{\alpha l}$. Then, we obtain:

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

where $\alpha = 1, 0, -1, -2, \dots$ and

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

The analytical relations for the determination of integral (34) are available in Ref. [12].

The values overlap integrals over vector Slater orbitals with the same screening parameters obtained from the different complete sets of ψ^{α} -ETO ($\alpha = 1, 0, -1$) using Mathematica 5.0 international mathematical software are presented in table 1. As can be seen from the table that the presented in this work approach for a particle with spin 1 guarantees a highly accurate calculation of the X -VSTO overlap integrals.

It should be noted that the overlap integrals over vector STO with the same screening parameters play a significant role in the calculation of arbitrary multicenter integrals arising in coordinate, momentum and four-dimensional spaces. Thus, in the evaluation of multicenter integrals over vector orbitals for a particle with spin 1 the relations for the two-center overlap integrals over ψ^{α} -ETO, ϕ^{α} -MSO, z^{α} -HSH and χ -STO also can be used. For this purpose, one has to use the expansion and one-range addition theorems for scalar basis sets of ψ^{α} -ETO, ϕ^{α} -MSO, z^{α} -HSH and χ -STO presented in our previous papers.

Table1. The values of overlap integrals over X -VSTO obtained from the different complete sets of ψ^{α} -ETO in molecular coordinate system

n	j	m_j	l	n'	j'	m'_j	l'	θ	φ	$G=2\zeta R$	Eqs. (30) and (33)		
											$\alpha=1$	$\alpha=0$	$\alpha=-1$
3	1	0	0	2	1	0	0	0	0	100	2.7703550866E-16	2.7703550866E-16	2.7703550866E-16
5	3	2	2	4	2	2	2	0	0	120	1.3671541011E-17	1.3671541011E-17	1.3671541011E-17
6	4	3	4	7	4	3	4	0	0	70	6.1423669728E-07	6.1423669728E-07	6.1423669728E-07
8	7	5	6	8	5	5	6	0	0	80	1.3572606274E-08	1.3572606274E-08	1.3572606274E-08
9	6	4	7	6	4	4	4	0	0	40	-4.9503929717E-04	-4.9503929717E-04	-4.9503929717E-04
11	8	6	9	10	7	6	9	0	0	60	1.1296567011E-05	1.1296567011E-05	1.1296567011E-05
3	2	1	1	2	1	0	0	π/8	2π/3	50	-1.5925219197E-07	-1.5925219197E-07	-1.5925219197E-07
5	4	3	3	5	2	1	1	2π/5	5π/3	60	4.1403685342E-06	4.1403685342E-06	4.1403685342E-06
7	6	3	5	6	5	1	4	π/4	π	30	2.3106531352E-04	2.3106531352E-04	2.3106531352E-04
9	8	3	7	8	7	7	6	4π/5	π/7	100	1.4852955548E-09	1.4852955548E-09	1.4852955548E-09
11	8	5	7	10	9	9	8	π/8	9π/7	90	1.8690202487E-09	1.8690202487E-09	1.8690202487E-09
13	10	8	9	12	11	11	10	5π/6	5π/6	120	8.2938717076E-12	8.2938717076E-12	8.2938717076E-12

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5. UNIFIED TREATMENT of COMPLETE ORTHONORMAL SETS for WAVE FUNCTIONS, and SLATER ORBITALS of PARTICLES with ARBITRARY SPIN in COORDINATE, MOMENTUM and FOUR-DIMENSIONAL SPACES

(PHYSICS LETTERS A (Online))

Abstract

The new analytical relations of complete orthonormal sets for the tensor wave functions and the tensor Slater orbitals of particles with arbitrary spin in coordinate, momentum and four-dimensional spaces are derived using the properties of tensor spherical harmonics and complete orthonormal scalar basis sets of ψ^{α}-exponential type orbitals, ϕ^{α}-momentum space orbitals and z^{α}-hyperspherical harmonics introduced by the author for particles with spin $s=0$, where the $\alpha=1,0,-1,-2,...$ All of the tensor wave functions obtained are complete without the inclusion of the continuum and, therefore, their group of transformations is the four-dimensional rotation group $\mathrm{O}(4)$. The analytical formulas in coordinate space are also derived for the overlap

integrals over tensor Slater orbitals with the same screening constant. We notice that the new idea presented in this work is the combination of tensor spherical harmonics of rank s with complete orthonormal scalar sets for radial parts of ψ^{α}-, ϕ^{α}- and z^{α}- orbitals, where $s=\frac{1}{2},1,\frac{3}{2},2,...$

Key Words: Tensor spherical harmonic, Tensor wave function, Slater orbital, Overlap integral

1. Introduction

In atomic and molecular electronic structure calculations it is quite common to introduce the complete and orthonormal function sets for particles with arbitrary spin s in coordinate, momentum and four-dimensional spaces. The examples of complete and orthonormal functions for the particles with spin $s=0$ in coordinate space are the so-called Lambda and Coulomb Sturmian functions introduced by Hylleraas, Shull and Löwdin in Refs. [1-3] and [4], respectively. These functions later were used extensively by Filter, Steinborn [5] and Weniger [6]. Coulomb Sturmians-or rather their three-dimensional Fourier transforms- occur also in Fock's treatment of the hydrogen atom [7], albeit in a somewhat disguised form. Weniger [6] has shown that the Coulomb Sturmians are complete and orthonormal in Sobolev space. It should be noted that the eigenfunctions of the Schrödinger equation for the hydrogen-like atom and their extensions to momentum and four-dimensional spaces by Fock[7,8] are not complete unless the continuum is included.

The relativistic one-electron Coulomb Sturmian wave functions have been developed and discussed by Avery and Antonsen [9]. Recently, in Refs. [10-12] we have developed method for constructing complete orthonormal scalar basis sets of one-electron wave functions for the particles with spin $s=0$ in coordinate, momentum and four-dimensional spaces. In this paper, we obtain a large number of the new different complete and orthonormal sets for the particles with arbitrary spin in coordinate, momentum and four-dimensional spaces using complete orthonormal sets of ψ^{α}-exponential type orbitals ($\psi^{\alpha}-ETO$), ϕ^{α}-momentum space orbitals ($\phi^{\alpha}-MSO$) and z^{α}-hyperspherical harmonics ($z^{\alpha}-HSH$) introduced in our above-mentioned works for $s=0$, where $\alpha=1,0,-1,-2,...$ It should be noted that the Lambda and Coulomb Sturmian functions introduced by Hylleraas, Shull and Löwdin for $s=0$ in coordinate space are special cases of the $\psi^{\alpha}-ETO$ for $\alpha=0$ and $\alpha=1$, i.e., $\psi^{0}_{nlm_l}\equiv\Lambda_{nlm_l}$ and $\psi^{1}_{nlm_l}\equiv\psi_{nlm_l}$, where Λ_{nlm_l} and ψ_{nlm_l} are the Lambda and Coulomb-Sturmians, respectively.

2. Tensor spherical harmonics

In order to derive the formulas for the complete orthonormal sets of tensor wave functions of rank s, where $s = 0, 1/2, 1, 3/2, 2, \ldots$, in coordinate, momentum and four-dimensional spaces we use the following eigenvalue equations of tensor spherical harmonics (see Sec. 7.1. of Ref.[13]):

$$\hat{j}^2 Y^{ls}_{jm_j}(\theta,\varphi) = j(j+1) Y^{ls}_{jm_j}(\theta,\varphi) \tag{1}$$

$$\hat{j}_z Y^{ls}_{jm_j}(\theta,\varphi) = m_j Y^{ls}_{jm_j}(\theta,\varphi) \tag{2}$$

$$\hat{l}^2 Y^{ls}_{jm_j}(\theta,\varphi) = l(l+1) Y^{ls}_{jm_j}(\theta,\varphi) \tag{3}$$

$$\hat{s}^2 Y^{ls}_{jm_j}(\theta,\varphi) = s(s+1) Y^{ls}_{jm_j}(\theta,\varphi). \tag{4}$$

As can be seen from Eqs. (1)-(4) that the tensor spherical harmonics $Y^{ls}_{jm_j}$ defined by

$$Y^{ls}_{jm_j}(\theta,\varphi) = \sum_{m_l m_s} (ls\, m_l m_s | ls\, j\, m_j) Y_{lm_l}(\theta,\varphi) u_{sm_s} \tag{5}$$

are the eigenfunctions of $\hat{j}^2$, $\hat{j}_z$, $\hat{l}^2$ and $\hat{s}^2$ where $\hat{l}$ denotes the orbital angular momentum operator, $\hat{s}$ the spin operator, and $\hat{j} = \hat{l} + \hat{s}$.

Here, $(ls\, m_l m_s | ls\, j\, m_j)$ and u_{sm_s} are the Clebsch-Gordan coefficients and basis spin functions, respectively, where $m_l = m_j - m_s$. The complete sets of basis spin functions u_{sm_s} are determined by (see Sec. 6.1. in Ref. [13])

$$u_{ss} = \begin{pmatrix} 1 \\ 0 \\ . \\ . \\ . \\ 0 \\ 0 \end{pmatrix},\ u_{s\,s-1} = \begin{pmatrix} 0 \\ 1 \\ . \\ . \\ . \\ 0 \\ 0 \end{pmatrix}, \ldots, u_{s\,-s} = \begin{pmatrix} 0 \\ 0 \\ . \\ . \\ . \\ 0 \\ 1 \end{pmatrix}. \tag{6}$$

The scalar spherical harmonics $Y_{lm_l}(\theta,\varphi)$ and basis spin functions u_{sm_s} occurring in Eq. (5) satisfy the following orthonormality relations:

$$\int_0^{\pi}\int_0^{2\pi} Y^*_{lm_l}(\theta,\varphi) Y_{l'm'_l}(\theta,\varphi) \sin\theta d\theta d\varphi = \delta_{ll'}\delta_{m_l m'_l} \tag{7}$$

$$u^+_{sm_s} u_{sm'_s} = \delta_{m_s m'_s}. \tag{8}$$

The tensor spherical harmonics $Y^{ls}_{jm_j}\left(\theta,\varphi\right)$ for fixed s constructed from the angular momentum coupling of scalar spherical harmonics and spin functions also satisfy the orthogonality relationship, i.e.,

$$\int_0^{\pi}\int_0^{2\pi} Y^{ls^{+}}_{jm_j}(\theta,\varphi)Y^{l's}_{j'm'_j}(\theta,\varphi)\sin\theta d\theta d\varphi=\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'}\,. \tag{9}$$

It follows from Eq. (5) that the tensor spherical harmonics are not eigenfunctions of the operators $\hat{l}_z$ and $\hat{s}_z$, i.e., the magnetic quantum numbers m_l and m_s cannot be used to characterize them. This is important in construction of complete orthonormal sets of tensor wave functions of rank s in coordinate, momentum and four-dimensional spaces.

3. Tensor wave functions

For the construction of complete orthonormal sets of tensor wave functions in coordinate, momentum and four-dimensional spaces for particles with arbitrary spin we take into account Eqs. (6) for the basis spin functions u_{sm_s} in (5). Then, the tensor spherical harmonics $Y^{ls}_{jm_j}(\theta,\varphi)$ can be expressed only through the scalar spherical harmonics $Y_{lm_l}(\theta,\varphi)$:

$$Y^{ls}_{jm_j}(\theta,\varphi)=\begin{pmatrix} a^{ls}_{jm_j}(0)Y_{lm_l(0)}(\theta,\varphi)\\ a^{ls}_{jm_j}(1)Y_{lm_l(1)}(\theta,\varphi)\\ \vdots\\ a^{ls}_{jm_j}(2s-1)Y_{lm_l(2s-1)}(\theta,\varphi)\\ a^{ls}_{jm_j}(2s)Y_{lm_l(2s)}(\theta,\varphi)\end{pmatrix}, \tag{10}$$

where $m_l(\lambda)=m_j-s+\lambda$, $0\le\lambda\le 2s$ and

$$a^{ls}_{jm_j}(\lambda)=(lsm_l(\lambda)s-\lambda\left|lsjm_j\right.). \tag{11}$$

Now we introduce function sets

$$\psi_{nlm_l}(\vec{r})=R_{nl}(r)Y_{lm_l}(\theta,\varphi) \tag{12}$$

which are complete and orthonormal with respect to an integration over the whole three-dimensional real space, i.e., they belong to the Hilbert space $L^2(\Re^3)$. Then, any function $F(\vec{r})\in L^2(\Re^3)$ can be expanded in terms of functions $\psi_{nlm_l}(\vec{r})$:

$$F(\vec{r})=\sum_{nlm_l}C_{nlm_l}\psi_{nlm_l}(\vec{r}), \tag{13}$$

$$C_{nlm_l}=\int\psi^*_{nlm_l}(\vec{r})F(\vec{r})d^3\vec{r}. \tag{14}$$

The convergence of expansion (13) is guaranteed as long as the functions ψ_{nlm_l} are complete and orthonormal in $L^2(\Re^3)$. Thus, the ψ_{nlm_l} obtained from the product of complete and orthonormal radial functions $R_{nl}(r)$ and $Y_{lm_l}(\theta,\varphi)$ also are the complete orthonormal functions in a suitable Hilbert space of the radial functions and the (surface) spherical harmonics.

It is obviously possible to multiply the scalar components of the tensor spherical harmonics by the same complete orthonormal radial functions $R_{nl}(r)$. Then, we obtain the following complete orthonormal sets of tensor wave functions:

$$\Psi^{ls}_{njm_j}(\vec{r}) = R_{nl}(r)Y^{ls}_{jm_j}(\theta,\varphi) = \begin{pmatrix} a^{ls}_{jm_j}(0)\psi_{nlm_l(0)}(\vec{r}) \\ a^{ls}_{jm_j}(1)\psi_{nlm_l(1)}(\vec{r}) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)\psi_{nlm_l(2s-1)}(\vec{r}) \\ a^{ls}_{jm_j}(2s)\psi_{nlm_l(2s)}(\vec{r}) \end{pmatrix}. \tag{15}$$

The tensor wave functions determined by (15) also satisfy the orthonormality relationship:

$$\int \Psi^{ls\,+}_{njm_j}(\vec{r})\Psi^{l's}_{n'j'm'_j}(\vec{r})d^3\vec{r} = \delta_{nn'}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'}. \tag{16}$$

In order to derive the formulas for complete orthonormal sets of tensor wave functions of rank s, where s=1/2,1,3/2,2,…, in coordinate, momentum and four-dimensional spaces we take in (15) into account the radial parts of complete orthonormal scalar basis sets of functions $\psi^\alpha - ETO$, $\phi^\alpha - MSO$ and $z^\alpha - HSH$ presented in previous paper [12]. Then, we obtain:

for tensors Ψ^α-ETO (Ψ^α-TETO) in coordinate space $\Psi^{\alpha ls}_{njm_j}(\zeta,\vec{r}) = \begin{pmatrix} a^{ls}_{jm_j}(0)\psi^\alpha_{nlm_l(0)}(\zeta,\vec{r}) \\ a^{ls}_{jm_j}(1)\psi^\alpha_{nlm_l(1)}(\zeta,\vec{r}) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)\psi^\alpha_{nlm_l(2s-1)}(\zeta,\vec{r}) \\ a^{ls}_{jm_j}(2s)\psi^\alpha_{nlm_l(2s)}(\zeta,\vec{r}) \end{pmatrix}$ (17a)

$$\bar{\Psi}^{\alpha ls}_{njm_j}(\zeta,\vec{r}) = \begin{pmatrix} a^{ls}_{jm_j}(0)\bar{\psi}^\alpha_{nlm_l(0)}(\zeta,\vec{r}) \\ a^{ls}_{jm_j}(1)\bar{\psi}^\alpha_{nlm_l(1)}(\zeta,\vec{r}) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)\bar{\psi}^\alpha_{nlm_l(2s-1)}(\zeta,\vec{r}) \\ a^{ls}_{jm_j}(2s)\bar{\psi}^\alpha_{nlm_l(2s)}(\zeta,\vec{r}) \end{pmatrix}, \tag{17b}$$

for tensors Φ^α-MSO (Φ^α-TMSO) in momentum space

$$\Phi^{\alpha ls}_{njm_j}(\zeta,\vec{k})=\begin{pmatrix} a^{ls}_{jm_j}(0)\phi^{\alpha}_{nlm_l(0)}(\zeta,\vec{k}) \\ a^{ls}_{jm_j}(1)\phi^{\alpha}_{nlm_l(1)}(\zeta,\vec{k}) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)\phi^{\alpha}_{nlm_l(2s-1)}(\zeta,\vec{k}) \\ a^{ls}_{jm_j}(2s)\phi^{\alpha}_{nlm_l(2s)}(\zeta,\vec{k}) \end{pmatrix} \tag{18a}$$

$$\bar{\Phi}^{\alpha ls}_{njm_j}(\zeta,\vec{k})=\begin{pmatrix} a^{ls}_{jm_j}(0)\bar{\phi}^{\alpha}_{nlm_l(0)}(\zeta,\vec{k}) \\ a^{ls}_{jm_j}(1)\bar{\phi}^{\alpha}_{nlm_l(1)}(\zeta,\vec{k}) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)\bar{\phi}^{\alpha}_{nlm_l(2s-1)}(\zeta,\vec{k}) \\ a^{ls}_{jm_j}(2s)\bar{\phi}^{\alpha}_{nlm_l(2s)}(\zeta,\vec{k}) \end{pmatrix}, \tag{18b}$$

for tensors Z^{α}-HSH(Z^{α}-THSH) in four-dimensional space

$$Z^{\alpha ls}_{njm_j}(\zeta,\beta\theta\varphi)=\begin{pmatrix} a^{ls}_{jm_j}(0)z^{\alpha}_{nlm_l(0)}(\zeta,\beta\theta\varphi) \\ a^{ls}_{jm_j}(1)z^{\alpha}_{nlm_l(1)}(\zeta,\beta\theta\varphi) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)z^{\alpha}_{nlm_l(2s-1)}(\zeta,\beta\theta\varphi) \\ a^{ls}_{jm_j}(2s)z^{\alpha}_{nlm_l(2s)}(\zeta,\beta\theta\varphi) \end{pmatrix} \tag{19a}$$

$$\bar{Z}^{\alpha ls}_{njm_j}(\zeta,\beta\theta\varphi)=\begin{pmatrix} a^{ls}_{jm_j}(0)\bar{z}^{\alpha}_{nlm_l(0)}(\zeta,\beta\theta\varphi) \\ a^{ls}_{jm_j}(1)\bar{z}^{\alpha}_{nlm_l(1)}(\zeta,\beta\theta\varphi) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)\bar{z}^{\alpha}_{nlm_l(2s-1)}(\zeta,\beta\theta\varphi) \\ a^{ls}_{jm_j}(2s)\bar{z}^{\alpha}_{nlm_l(2s)}(\zeta,\beta\theta\varphi) \end{pmatrix}, \tag{19b}$$

where $n \geq 1$, $s \leq j \leq s+n-1$, $-j \leq m_j \leq j$ and $j-s \leq l \leq \min(j+s, n-1)$.

See Ref. [12] for the exact definition of complete scalar basis sets of orbitals ψ^{α}, $\bar{\psi}^{\alpha}$, ϕ^{α}, $\bar{\phi}^{\alpha}$, z^{α} and $\bar{z}^{\alpha}$ occurring on the right-hand side of Eqs. (17a)-(19b). Using the relation $a^{l0}_{jm_j}(0)=\left(l0m_l0 \middle| l0jm_j\right)=\delta_{jl}\delta_{m_jm_l}$ we can show that these orbitals are the complete orthonormal sets of wave functions for particles with spin $s=0$ in coordinate, momentum and four-dimensional spaces, i.e., $\psi^{\alpha} \equiv \Psi^{\alpha}$, $\bar{\psi}^{\alpha} \equiv \bar{\Psi}^{\alpha}$, $\phi^{\alpha} \equiv \Phi^{\alpha}$, $\bar{\phi}^{\alpha} \equiv \bar{\Phi}^{\alpha}$, $z^{\alpha} \equiv Z^{\alpha}$ and $\bar{z}^{\alpha} \equiv \bar{Z}^{\alpha}$ for s=0.

The tensor wave functions $\Psi^{\alpha ls}$, $\Phi^{\alpha ls}$ and $Z^{\alpha ls}$ are orthonormal with respect to the $\bar{\Psi}^{\alpha ls}$, $\bar{\Phi}^{\alpha ls}$ and $\bar{Z}^{\alpha ls}$ for fixed s and α, i.e.,

$$\int \bar{\Psi}^{\alpha ls\,+}_{njm_j}(\zeta,\vec{r})\Psi^{\alpha l's\,+}_{n'j'm'_j}(\zeta,\vec{r})d^3\vec{r} = \delta_{nn'}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'} \tag{20}$$

$$\int \bar{\Phi}^{\alpha ls\,+}_{njm_j}(\zeta,\vec{k})\Phi^{\alpha l's}_{n'j'm'_j}(\zeta,\vec{k})d^3\vec{k} = \delta_{nn'}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'} \tag{21}$$

$$\int \bar{Z}^{\alpha ls\,+}_{njm_j}(\zeta,\beta\theta\varphi)Z^{\alpha l's}_{n'j'm'_j}(\zeta,\beta\theta\varphi)d\Omega(\zeta,\beta\theta\varphi) = \delta_{nn'}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'}\,. \tag{22}$$

4. Tensor Slater orbitals

Carrying through the calculations for the tensor Slater orbitals analogous to those for the tensor wave functions we obtain:

for tensors X-STO (X-TSTO) in coordinate space

$$\mathrm{X}^{ls}_{njm_j}(\zeta,\vec{r}) = \begin{pmatrix} a^{ls}_{jm_j}(0)\chi_{nlm_l(0)}(\zeta,\vec{r}) \\ a^{ls}_{jm_j}(1)\chi_{nlm_l(1)}(\zeta,\vec{r}) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)\chi_{nlm_l(2s-1)}(\zeta,\vec{r}) \\ a^{ls}_{jm_j}(2s)\chi_{nlm_l(2s)}(\zeta,\vec{r}) \end{pmatrix}, \tag{23}$$

for tensors U-MSO (U-TMSO) in momentum space

$$U^{ls}_{njm_j}(\zeta,\vec{k}) = \begin{pmatrix} a^{ls}_{jm_j}(0)u_{nlm_l(0)}(\zeta,\vec{k}) \\ a^{ls}_{jm_j}(1)u_{nlm_l(1)}(\zeta,\vec{k}) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)u_{nlm_l(2s-1)}(\zeta,\vec{k}) \\ a^{ls}_{jm_j}(2s)u_{nlm_l(2s)}(\zeta,\vec{k}) \end{pmatrix}, \tag{24}$$

for tensors V-HSH $\left(V-THSH\right)$ in four dimensional space

$$V^{ls}_{njm_j}(\zeta,\beta\theta\varphi) = \begin{pmatrix} a^{ls}_{jm_j}(0)v_{nlm_l(0)}(\zeta,\beta\theta\varphi) \\ a^{ls}_{jm_j}(1)v_{nlm_l(1)}(\zeta,\beta\theta\varphi) \\ \vdots \\ a^{ls}_{jm_j}(2s-1)v_{nlm_l(2s-1)}(\zeta,\beta\theta\varphi) \\ a^{ls}_{jm_j}(2s)v_{nlm_l(2s)}(\zeta,\beta\theta\varphi) \end{pmatrix}. \tag{25}$$

The functions χ_{nlm_l}, u_{nlm_l} and v_{nlm_l} occurring on the right-hand side of Eqs. (23), (24) and (25) are the Slater orbitals for particles with spin $s=0$ in coordinate, momentum and four-dimensional spaces, respectively, i.e., $\chi \equiv \mathrm{X}$, $u \equiv U$ and $v \equiv V$ for s=0.

The tensor Slater orbitals determined by Eqs.(23), (24) and (25) are orthogonal with respect to the quantum numbers j , m_j and l, i.e.,

$$\int \mathrm{X}_{njm_j}^{ls^+}(\zeta,\vec{r})\mathrm{X}_{n'j'm'_j}^{l's}(\zeta,\vec{r})d^3\vec{r} = \frac{(n+n')!}{[(2n)!(2n')!]^{1/2}}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'} \tag{26}$$

$$\int U_{njm_j}^{ls^+}(\zeta,\vec{k})U_{n'j'm'_j}^{l's}(\zeta,\vec{k})d^3\vec{k} = \frac{(n+n')!}{[(2n)!(2n')!]^{1/2}}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'} \tag{27}$$

$$\int V_{njm_j}^{ls^+}(\zeta,\beta\theta\varphi)V_{n'j'm'_j}^{l's}(\zeta,\beta\theta\varphi)d\Omega(\zeta,\beta\theta\varphi) = \frac{(n+n')!}{[(2n)!(2n')!]^{1/2}}\delta_{jj'}\delta_{m_jm'_j}\delta_{ll'}\,. \tag{28}$$

5. Evaluation of overlap integrals over tensor STO in coordinate space

Now we evaluate, as an example of application, the two-center overlap integrals over tensor Slater orbitals with the same screening parameters defined in coordinate space by

$$S_{njm_j,n'j'm'_j}^{ls,l's}(\vec{G}) = \int \mathrm{X}_{njm_j}^{ls^+}(\zeta,\vec{r})\mathrm{X}_{n'j'm'_j}^{l's}(\zeta,\vec{r}-\vec{R})d^3\vec{r}\ , \tag{29}$$

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 this integral we take into account Eq. (23) in (29). Then, we obtain the following relation in terms of overlap integrals over χ-STO:

$$\begin{aligned} S_{njm_j,n'j'm'_j}^{ls,l's}(\vec{G}) &= a_{jm_j,j'm'_j}^{ls,l's}(0)s_{nlm_l(0),n'l'm'_l(0)}(\vec{G}) + a_{jm_j,j'm'_j}^{ls,l's}(1)s_{nlm_l(1),n'l'm'_l(1)}(\vec{G}) + \\ \ldots &+ a_{jm_j,j'm'_j}^{ls,l's}(2s-1)s_{nlm_l(2s-1),n'l'm'_l(2s-1)}(\vec{G}) + a_{jm_j,j'm'_j}^{ls,l's}(2s)s_{nlm_l(2s),n'l'm'_l(2s)}(\vec{G})\ , \end{aligned} \tag{30}$$

where $a_{jm_j,j'm'_j}^{ls,l's}(\lambda) = a_{jm_j}^{ls}(\lambda)a_{j'm'_j}^{l's}(\lambda)$ and

$$s_{nlm_l,n'l'm_l'}(\vec{G}) = \int \chi_{nlm_l}^{*}(\zeta,\vec{r})\chi_{n'l'm_l'}(\zeta,\vec{r}-\vec{R})d^3\vec{r}\,. \tag{31}$$

For the evaluation of integral (31) we utilize the following expressions for χ-STO in terms of complete sets of ψ^α - and $\bar{\psi}^\alpha$ -ETO:

$$\chi_{nlm_l}(\zeta,\vec{r}) = \sum_{\mu=l+1}^{n}\varpi_{n\mu}^{\alpha l}\psi_{\mu lm_l}^{\alpha}(\zeta,\vec{r}) \tag{32a}$$

$$= \{[2(n+\alpha)]!/(2n)!\}^{1/2}\sum_{\mu=l+1}^{n+\alpha}[\bar{\varpi}_{n+\alpha\mu}^{\alpha l}/(2\mu)^\alpha]\bar{\psi}_{\mu lm_l}^{\alpha}(\zeta,\vec{r}). \tag{32b}$$

See Ref. [10] for the exact definition of coefficients $\bar{\varpi}^{\alpha l}$. Taking into account Eqs. (32a) and (32b) in (31) we obtain:

$$s_{nlm_l,n'l'm_l'}(\vec{G})=\{[2(n+\alpha)]!/(2n)!\}^{1/2}\sum_{\mu=l+1}^{n+\alpha}\sum_{\mu'=l'+1}^{n'}[\bar{\omega}_{n+\alpha\mu}^{\alpha l}/(2\mu)^{\alpha}]\bar{\omega}_{n'\mu'}^{\alpha l'}s_{\mu lm_l,\mu'l'm_l'}^{\alpha}(\vec{G}), \tag{33}$$

where $\alpha=1,0,-1,-2,...$ and

$$s_{\mu lm_l,\mu'l'm_l'}^{\alpha}(\vec{G})=\int\bar{\psi}_{\mu lm_l}^{\alpha*}(\zeta,\vec{r})\psi_{\mu'l'm_l'}^{\alpha}(\zeta,\vec{r}-\vec{R})d^3\vec{r}. \tag{34}$$

For the calculation of this integral one can use the analytical relations presented in Ref. [12].

The results of calculation in atomic units for the overlap integrals over tensor Slater orbitals with the same screening parameters for $s=1/2$, $s=1$ and $s=3/2$ using Mathematica 5.0 international mathematical software which are obtained by the use of different complete sets ($\alpha=1,0,-1$) are given in tables 1,2 and 3. We see that the presented in this work approach guarantees a highly accurate calculation of the $X-TSTO$ overlap integrals.

We notice that the 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. Thus, the relations for the two center overlap integrals over $\psi^{\alpha}-ETO$, $\phi^{\alpha}-MSO$, $z^{\alpha}-HSH$ and $\chi-STO$ for the particles with spin $s=0$ can be used in evaluation of multicenter integrals over corresponding tensor orbitals for the particles with arbitrary spin. For this purpose, one has to use the expansion and one-range addition theorems for scalar basis sets of $\psi^{\alpha}-ETO$, $\phi^{\alpha}-MSO$, $z^{\alpha}-HSH$ and $\chi-STO$ functions which are available in our previous papers.

Table 1. The values of overlap integrals over X-TSTO for $s=1/2$ obtained from the different complete sets of ψ^{α}-ETO in molecular coordinate system

n	j	m_j	l	n'	j'	m'_j	l'	θ	φ	$G=2\zeta R$	Eqs. (30) and (33)		
											$\alpha=1$	$\alpha=0$	$\alpha=-1$
3	1/2	1/2	0	2	1/2	1/2	0	0	0	50	7.1275718501E-07	7.1275718501E-07	7.1275718501E-07
6	7/2	5/2	4	4	5/2	5/2	2	0	0	30	-8.8780952986E-03	-8.8780952986E-03	-8.8780952986E-03
7	9/2	7/2	4	6	7/2	7/2	4	0	0	60	2.2247734843E-06	2.2247734843E-06	2.2247734843E-06
8	5/2	3/2	3	6	7/2	3/2	4	0	0	40	-1.5538996817E-03	-1.5538996817E-03	-1.5538996817E-03
10	13/2	11/2	6	8	11/2	11/2	5	0	0	80	2.1034973256E-08	2.1034973256E-08	2.1034973256E-08
12	19/2	17/2	10	12	17/2	17/2	9	0	0	100	-4.0269693887E-08	-4.0269693887E-08	-4.0269693887E-08
3	3/2	1/2	1	2	1/2	1/2	0	π/6	π/3	50	8.3229206441E-07	8.3229206441E-07	8.3229206441E-07
4	3/2	-1/2	2	3	1/2	-1/2	1	2π/3	3π/2	40	3.7886261076E-04	3.7886261076E-04	3.7886261076E-04
6	7/2	5/2	3	5	5/2	-3/2	2	π/5	2π/7	60	-2.1379605958E-06	-2.1379605958E-06	-2.1379605958E-06
8	9/2	3/2	5	8	7/2	5/2	4	π/3	3π/8	20	-5.7251053173E-02	-5.7251053173E-02	-5.7251053173E-02
10	13/2	-9/2	7	9	11/2	7/2	6	π/4	5π/3	80	-3.8318079347E-05	-3.8318079347E-05	-3.8318079347E-05
13	23/2	11/2	11	12	21/2	15/2	10	3π/5	7π/4	100	-4.8916831109E-06	-4.8916831109E-06	-4.8916831109E-06

Table 2. The values of overlap integrals over X -TSTO for $s=1$ obtained from the different complete sets of ψ^{α} -ETO in molecular coordinate system

n	j	m_j	l	n'	j'	m'_j	l'	θ	φ	$G=2\zeta R$	Eqs. (30) and (33)		
											$\alpha=1$	$\alpha=0$	$\alpha=-1$
2	1	0	0	2	1	0	0	0	0	70	2.4395477541E-11	2.4395477541E-11	2.4395477541E-11
4	2	1	2	3	2	1	1	0	0	50	1.6573617805E-05	1.6573617805E-05	1.6573617805E-05
5	4	2	3	5	2	2	3	0	0	80	1.0252040078E-09	1.0252040078E-09	1.0252040078E-09
7	5	4	5	6	4	4	4	0	0	20	3.0946206702E-02	3.0946206702E-02	3.0946206702E-02
9	6	6	7	8	7	6	6	0	0	60	-5.1122825714E-06	-5.1122825714E-06	-5.1122825714E-06
10	8	7	8	10	7	7	7	0	0	40	-1.2488415956E-03	-1.2488415956E-03	-1.2488415956E-03
3	2	1	1	2	1	1	0	3π/4	5π/4	30	-1.1724258661E-03	-1.1724258661E-03	-1.1724258661E-03
4	3	-1	2	3	2	0	1	π/6	7π/6	50	2.6634696867E-06	2.6634696867E-06	2.6634696867E-06
6	5	5	4	5	4	3	3	2π/3	3π/2	60	-2.3995958731E-05	-2.3995958731E-05	-2.3995958731E-05
7	6	-1	5	9	7	-2	6	π/3	4π/3	40	-6.7143781343E-03	-6.7143781343E-03	-6.7143781343E-03
10	7	5	8	8	7	3	8	π/4	5π/3	70	-8.7789594896E-06	-8.7789594896E-06	-8.7789594896E-06
12	10	7	10	11	9	-8	9	π/6	5π/6	100	4.0504854462E-09	4.0504854462E-09	4.0504854462E-09

Table 3. The values of overlap integrals over X-TSTO for $s = 3/2$ obtained from the different complete sets of ψ^{α}-ETO in molecular coordinate system

n	j	m_j	l	n'	j'	m'_j	l'	θ	φ	$G = 2\zeta R$	Eqs. (30) and (33)		
											$\alpha = 1$	$\alpha = 0$	$\alpha = -1$
4	5/2	1/2	2	4	3/2	1/2	2	0	0	20	9.9761194058E-02	9.9761194058E-02	9.9761194058E-02
5	9/2	3/2	3	3	5/2	3/2	1	0	0	40	-5.0598748953E-04	-5.0598748953E-04	-5.0598748953E-04
6	7/2	1/2	4	4	1/2	1/2	2	0	0	50	-9.2565575272E-05	-9.2565575272E-05	-9.2565575272E-05
7	5/2	5/2	4	7	7/2	5/2	3	0	0	80	4.9898149210E-08	4.9898149210E-08	4.9898149210E-08
9	15/2	11/2	7	8	13/2	11/2	6	0	0	90	5.3294685074E-09	5.3294685074E-09	5.3294685074E-09
11	19/2	13/2	8	9	15/2	13/2	7	0	0	100	-1.3478479027E-09	-1.3478479027E-09	-1.3478479027E-09
3	3/2	1/2	0	2	3/2	1/2	0	π/6	5π/6	20	3.7387341932E-02	3.7387341932E-02	3.7387341932E-02
4	5/2	-3/2	2	3	3/2	-1/2	1	π/4	π/6	30	-2.8222062021E-03	-2.8222062021E-03	-2.8222062021E-03
5	3/2	-3/2	3	4	1/2	-1/2	2	2π/3	5π/4	60	-2.1846826945E-06	-2.1846826945E-06	-2.1846826945E-06
7	9/2	5/2	5	6	5/2	3/2	3	π/8	4π/3	70	-1.2002777687E-06	-1.2002777687E-06	-1.2002777687E-06
9	11/2	-7/2	7	7	9/2	5/2	5	π/6	7π/4	90	9.4942481083E-08	9.4942481083E-08	9.4942481083E-08
13	21/2	15/2	11	12	19/2	15/2	10	π/5	3π/2	110	- 3.4144983964E-08	- 3.4144983964E-08	- 3.4144983964E-08

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