Calculation of One-Electron Multicenter Integrals of Slater Type Orbitals and Coulomb–Yukawa Like Correlated Interaction Potentials with Integer and Noninteger Indices Using Unsymmetrical One-Range Addition Theorems

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Using expansion formulae for multicenter charge densities of integer and noninteger n Slater type orbitals (ISTO and NISTO) established by one of the authors with the help of unsymmetrical one-range addition theorems of complete orthonormal sets of Ψ^{α}-exponential type orbitals (Ψ^{α}-ETO), where α is the frictional quantum numbers ($\alpha = 1, 0, -1, -2, \ldots$), we perform the calculations for one-electron multicenter integrals of Slater type orbitals (STO) and Coulomb–Yukawa like correlated interaction potentials (CIP) with integer and noninteger indices (ICIP and NICIP). The convergence of the series is tested by calculating concrete cases for arbitrary values of indices and screening constants of orbitals and potentials. It should be noted that the results for one-electron multicenter integrals presented in this work were not shown in our previous publications. As an example of application, the calculations are performed for the ground state of electronic configuration of molecule BH_2 that has the open shell.

It is well known that the NISTO and Coulomb–Yukawa like NICIP describe the physical situation more accurately than do ISTO and ICIP (see Refs. 1–7 and 8 respectively). The main problem for the use of NISTO basis in electronic structure calculations arises in the evaluation of the multicenter integrals of Coulomb–Yukawa like NICIP. Most existing programs for multicenter integrals over ISTO and ICIP cannot be used in the cases of nonintegral values of indices. Thus, it is of interest to develop efficient algorithms for performing the computation of multicenter integrals of NISTO and NICIP. One of the most promising methods for the evaluation of these integrals is the use of multicenter charge density expansion formulae for NISTO[9] obtained with the help of unsymmetrical one-range addition theorems of Ψ^{α}-ETO.[10] We notice that the eigenfunctions Ψ^{α}-ETO correspond to the total centrally symmetric potential which contains the core attraction potantial and Lorentz potential of the field produced by the particle itself. The indices α arising from the use of total potential and occurring in the Ψ^{α}-ETO is the frictional quantum number.[11] In a previous paper,[12] we presented a particular method for evaluation of multicenter multielectron integrals using symmetric one-range addition theorems of STO. The aim of this work is, using the unsymmetrical one-range addition theorems for STO, to calculate the one-electron multicenter integrals of Coulomb–Yukawa like NICIP appearing in the determination of various properties of molecules when NISTO basis is used in the Hartree–Fock–Roothaan (HFR) theory.

Theoretical

Definition. The multicenter one-electron integrals with Coulomb–Yukawa like NICIP and NISTO are defined as

$$I^{ac;b}_{p_1{}^* p_1{}'^*;q^*}(\zeta_1, \zeta_1{}'; \xi) = \int \chi^*_{p_1{}^*}(\zeta_1, \vec{r}_{a1}) \chi_{p_1{}'^*}(\zeta_1{}', \vec{r}_{c1}) f_{q^*}(\xi, \vec{r}_{b1}) \mathrm{d}v_1 \quad (1)$$

where $p_1{}^* \equiv n_1{}^* l_1 m_1$, $p_1{}'^* \equiv n_1{}'^* l_1{}' m_1{}'$, $q^* \equiv \mu^* \nu \sigma$ and the combined Coulomb (for $\xi = 0$) and Yukawa (for $\xi > 0$) like NICIP are defined as:[13]

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

$$= \left(\frac{4\pi}{2\nu + 1}\right)^{1/2} \frac{[\Gamma(2\mu^* + 1)]^{1/2}}{(2\xi)^{\mu^* + 1/2}} \chi_{\mu^* \nu \sigma}(\xi, \vec{r}) \quad (2b)$$

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

$$f_{\mu^*}(\xi, r) = f_{\mu^* 00}(\xi, r) = r^{\mu^* - 1} e^{-\xi r} \quad (3)$$

In eq 1, the $\chi_{n^* lm}(\zeta, \vec{r})$ are the normalized NISTO determined by

$$\chi_{n^* lm}(\zeta, \vec{r}) = (2\zeta)^{n^* + 1/2} [\Gamma(2n + 1)]^{-1/2} r^{n^* - 1} e^{-\zeta r} S_{lm}(\theta, \varphi) \quad (4)$$

Here, the complex and real spherical harmonics S_{lm} are defined as

$$S_{lm}(\theta, \varphi) = P_{l|m|}(\cos\theta) \Phi_m(\varphi) \quad (5)$$

where $P_{l|m|}$ are the normalized associated Legendre functions[14] and for complex spherical harmonics

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \quad (6)$$

for real spherical harmonics

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$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} \begin{cases} \cos|m|\varphi & for\ m \geq 0 \\ \sin|m|\varphi & for\ m < 0 \end{cases} \quad (7)$$

It should be noted that our definition of phases for complex spherical harmonics ($Y^*_{lm} = Y_{l-m}$) differs from the Condon–Shortley phases[15] by the sign factor.

Use of Expansion Formulae for Multicenter Charge Densities of NISTO. With the evaluation of integral (1) we use the following expansion formulae for the unsymmetrical one-range addition theorems of multicenter charge densities over NISTO established in an earlier work[9]

$$\chi^*_{p_1{}^*}(\zeta_1, \vec{r}_{a1})\chi_{p_1{}'^*}(\zeta_1{}', \vec{r}_{c1}) = \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{n=1}^{N} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} \begin{bmatrix} W^{\alpha N}_{p_1{}^* p_1{}'^* p}(\zeta_1, \zeta_1{}', z; \vec{R}_{ca}, \vec{R}_{ab}) \\ W^{\alpha N}_{p_1{}^* p_1{}'^* p}(\zeta_1, \zeta_1{}', z; \vec{R}_{cb}, \vec{R}_{ab}) \end{bmatrix} \times \chi_p{}^*(z, \vec{r}_{b1}) \quad (8)$$

$$\chi^*_{p_1{}^*}(\zeta_1, \vec{r}_{a1})\chi_{p_1{}'^*}(\zeta_1{}', \vec{r}_{c1}) = \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{n=1}^{N} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} W^{\alpha N}_{p_1{}^* p_1{}'^* p}(\zeta_1, \zeta_1{}', z; \vec{R}_{ac}, 0) \times \chi_p{}^*(z, \vec{r}_{a1}) \quad (9)$$

$$\chi^*_{p_1{}^*}(\zeta_1, \vec{r}_{a1})\chi_{p_1{}'^*}(\zeta_1{}', \vec{r}_{b1}) = \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{n=1}^{N} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} W^{\alpha N}_{p_1{}^* p_1{}'^* p}(\zeta_1, \zeta_1{}', z; 0, \vec{R}_{ab}) \times \chi_p{}^*(z, \vec{r}_{b1}) \quad (10)$$

$$\chi^*_{p_1{}^*}(\zeta_1, \vec{r}_{b1})\chi_{p_1{}'^*}(\zeta_1{}', \vec{r}_{b1}) = \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{l=|l_1-l_1'|}^{l_1+l_1'} \sum_{m=-l}^{l} W_{p_1{}^* p_1{}'^* p^*}(\zeta_1, \zeta_1{}', z) \times \chi^*_{p^*}(z, \vec{r}_{b1}) \quad (11)$$

where $p^* \equiv n^* lm$, $n^* = n_1{}^* + n_1{}'^* - 1$, $p \equiv nlm$, and $z = \zeta_1 + \zeta_1{}'$. See Ref. 9 for the exact definition of multicenter expansion coefficients $W^{\alpha N}_{p_1{}^* p_1{}'^* p}(\zeta_1, \zeta_1{}', z; \vec{R}_{ca}, \vec{R}_{ab})$, $W^{\alpha N}_{p_1{}^* p_1{}'^* p}(\zeta_1, \zeta_1{}', z; \vec{R}_{ac}, 0)$, $W^{\alpha N}_{p_1{}^* p_1{}'^* p}(\zeta_1, \zeta_1{}', z; 0, \vec{R}_{ab})$, and $W_{p_1{}^* p_1{}'^* p^*}(\zeta_1, \zeta_1{}', z)$ occurring in these equations.

Taking into account eqs 8, 9, 10, and 11 in (1) we obtain for one-electron multicenter integrals of NISTO and Coulomb–Yukawa like NICIP the following formulae: for three-center integrals

$$I^{ac,b}_{p_1{}^* p_1{}'^*, q^*}(\zeta_1\zeta_1{}', \xi) = \frac{1}{(2\nu+1)^{1/2}} \lim_{N\to\infty} \sum_{n=1}^{N} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} W^{\alpha N}_{p_1{}^* p_1{}'^* p}(\zeta_1\zeta_1{}' z; \vec{R}_{ca}, 0) \times \Lambda_{pq^*}(z, \xi, \vec{R}_{ab}) \quad (12)$$

$$I^{ac,b}_{p_1{}^* p_1{}'^*, q^*}(\zeta_1, \zeta_1{}', \xi) = \frac{1}{(2\nu+1)^{1/2}(z+\xi)^{\mu^*+1/2}} \times \lim_{N\to\infty} \sum_{n=\nu+1}^{N} \begin{bmatrix} W^{\alpha N}_{p_1{}^* p_1{}'^*, n\nu\sigma}(\zeta_1, \zeta_1{}', z; \vec{R}_{ca}, \vec{R}_{ab}) \\ W^{\alpha N}_{p_1{}^* p_1{}'^*, n\nu\sigma}(\zeta_1, \zeta_1{}', z; \vec{R}_{cb}, \vec{R}_{ab}) \end{bmatrix} \times \frac{\Gamma(n+\mu^*+1)}{[\Gamma(2n+1)]^{1/2}} \left(\frac{2z}{z+\xi}\right)^{n+1/2} \quad (13)$$

for two-center integrals

$$I^{aa,b}_{p_1{}^* p_1{}'^*, q^*}(\zeta_1, \zeta_1{}'; \xi) = \left(\frac{4\pi}{2\nu+1}\right)^{1/2} \frac{[\Gamma(2\mu^*+1)]^{1/2}}{(2\xi)^{\mu^*+1/2}} \times \int \chi^*_{p_1{}^*}(\zeta_1, \vec{r}_{a1})\chi_{p_1{}'^*}(\zeta_1{}', \vec{r}_{a1})\chi_{q^*}(\xi, \vec{r}_{b1})\mathrm{d}v_1 \quad (14a)$$

$$= \frac{1}{(2\nu+1)^{1/2}} \sum_{l=|l_1-l_1'|}^{l_1+l_1'} \sum_{m=-l}^{l} W_{p_1{}^* p_1{}'^* p^*}(\zeta_1, \zeta_1{}', z) \times \Lambda_{p^* q^*}(z, \xi; \vec{R}_{ab}) \quad (14b)$$

$$I^{ab,b}_{p_1{}^* p_1{}'^*, q^*}(\zeta_1, \zeta_1{}'; \xi) = \left(\frac{4\pi}{2\nu+1}\right)^{1/2} \frac{[\Gamma(2\mu^*+1)]^{1/2}}{(2\xi)^{\mu^*+1/2}} \times \int \chi^*_{p_1{}'^*}(\zeta_1, \vec{r}_{a1})\chi_{p_1{}'^*}(\zeta_1{}', \vec{r}_{b1})\chi_{q^*}(\xi, \vec{r}_{b1})\mathrm{d}v_1 \quad (15a)$$

$$= \frac{1}{(2\nu+1)^{1/2}(z+\xi)^{\mu^*+1/2}} \times \lim_{N\to\infty} \sum_{n=\nu+1}^{N} W^{\alpha N}_{p_1{}^* p_1{}'^*, n\nu\sigma}(\zeta_1, \zeta_1{}', z; 0, \vec{R}_{ab}) \times \frac{\Gamma(n+\mu^*+1)}{[\Gamma(2n+1)]^{1/2}} \left(\frac{2z}{z+\xi}\right)^{n+1/2} \quad (15b)$$

for one-center integrals

$$I_{p_1{}^* p_1{}'^*, q^*}(\zeta_1, \zeta_1{}'; \xi) \equiv I^{bb,b}_{p_1{}^* p_1{}'^*, q^*}(\zeta_1, \zeta_1{}'; \xi) = \frac{\Gamma(n^*+\mu^*+1)(2z)^{n^*+\frac{1}{2}}}{[\Gamma(2n^*+1)(2\nu+1)]^{1/2}(z+\xi)^{n^*+\mu^*+1}} \times W_{p_1{}^* p_1{}'^* \kappa^*}(\zeta_1, \zeta_1{}', z) \quad (16)$$

where $\kappa^* \equiv n^* \nu\sigma$.

In eqs 12 and 14b, the quantities $\Lambda_{p^* q^*}(z, \xi, \vec{R}_{ab})$ are the modified overlap integrals of NISTO and Coulomb–Yukawa like NICIP defined as[9]

$$\Lambda_{n^* lm, n'^* l'm'}(z, \xi; \vec{R}_{ab}) = \frac{[\Gamma(2\mu^*+1)]^{1/2}}{(2\xi)^{\mu^*+1/2}} S_{n^* lm, n'^* l'm'}(z, \xi; \vec{R}_{ab}) \quad (17)$$

where

$$S_{n^* lm, n'^* l'm'}(z, \xi; \vec{R}_{ab}) = \int \chi^*_{n^* lm}(z, \vec{r}_a)\chi_{n'^* l'm'}(\xi, \vec{r}_b)\mathrm{d}v \quad (18)$$

Here, $S_{n^* lm, n'^* l'm'}(z, \xi; \vec{R}_{ab})$ are the overlap integrals over NISTO.[16–19]

Results and Discussion

On the basis of eqs 12, 14b, and 15b we constructed the programs which were performed in the Turbo Pascal 7.0 language packages on an Pentium® Dual-Core 2.6 GHz computer. Results of the calculation in atomic units are represented in Tables 1, 2, 3, 4, and 5. The convergence properties of the series expansion relation for one-electron three-center integral $I^{ab,c}_{211,211,210}(3.8, 4.6, 4.6)$ are shown in Tables 3, 4, and 5 for $\alpha = 0$. These tables list the partial summations in eq 12 corresponding to progressively increasing upper summation limits denoted by N, L, and M. As can be seen from Tables 3 and 4, the eq 12 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;

Table 1. Comparison of Methods of Computing Three-Center Integrals with NISTO and Coulomb–Yukawa Like NICIP for $N = 15$

n_1	l_1	m_1	ζ_1	n_1'	l_1'	m_1'	ζ_1'	μ	ν	σ	ξ	R_{ac}	θ_{ac}	φ_{ac}	R_{ab}	θ_{ab}	φ_{ab}	Equation 12	
																		$\alpha = 0$	$\alpha = 1$
1	0	0	4.3	1	0	0	3.1	0	0	0	0	0.6	120	180	0.7	30	45	8.666894506E-01	8.665312708E-01
1.8	0	0	6.4	1.5	0	0	1.3	0.1	0	0	0	0.8	36	360	0.2	60	90	6.029470678E-01	6.029585921E-01
1.8	0	0	8.6	1.5	0	0	3.1	0.6	0	0	1.5	0.4	54	54	0.7	20	135	1.853566283E-01	1.853541721E-01
2	1	0	7.4	1	0	0	5.3	0	0	0	3.6	0.8	60	18	0.4	60	90	−7.929402551E-04	−8.042110387E-04
2.1	1	0	10.8	1.5	0	0	5.3	0.3	0	0	3.1	0.6	90	72	0.2	50	72	5.880145086E-02	5.862508683E-02
2.4	1	1	5.6	2.2	1	0	3.4	1.8	1	0	1.2	0.3	80	162	0.27	110	104	−3.863502901E-02	−3.863799654E-02
2	1	0	8.7	2	1	0	2.5	1	0	0	4.3	0.3	150	36	1.1	40	270	3.134894169E-03	3.133574962E-03
2.1	1	0	9.3	2.1	1	0	4.5	0.2	0	0	5.3	0.1	126	108	0.4	126	90	1.100592954E-01	1.100546661E-01
2	1	1	10.8	2	1	1	5.2	2	1	0	6.4	0.1	180	54	0.5	60	360	−6.991840118E-03	−6.992408485E-03
2	1	1	12.3	2	1	−1	6.5	2	1	1	3.6	0.2	108	72	0.2	80	40	−2.290474025E-02	−2.289912527E-02
2	1	−1	10.6	2	1	−1	4.6	2	1	−1	2.3	0.5	126	90	0.08	100	50	−2.896546846E-02	−2.896149348E-02
3.2	1	0	8.5	2.7	1	0	7.3	1.2	1	1	4.1	0.25	120	72	0.01	120	180	8.530945269E-03	8.530964229E-03
3.5	2	0	4.2	2.4	1	1	2.7	1.2	1	1	3.4	0.04	140	90	0.2	130	234	−2.552943357E-03	−2.552324853E-03

Table 2. Comparison of Methods of Computing Two-Center Integrals with NISTO and Coulomb–Yukawa Like NICIP for $N = 15$

n_1	l_1	m_1	ζ_1	n_1'	l_1'	m_1'	ζ_1'	μ	ν	σ	ξ	R_{ab}	θ_{ab}	φ_{ab}	Equation 14b	Equation 15b
2	1	1	6.9	2	1	1	7.8	0.1	0	0	4.5	0.8	70	126	9.14302344775117E-03	−2.72677603888909E-02
2.5	1	1	10.6	2.7	1	0	9.7	0.4	0	0	6.4	1.8	100	144	2.32393497917036E-06	7.77207910748195E-07
3.2	1	1	12.4	2.4	1	1	7.9	2.4	1	1	5.6	1.3	20	162	−2.72549841557378E-04	3.54635297550039E-06
3.6	2	1	8.6	2.8	1	1	12.9	2.2	1	0	4.6	0.1	110	180	1.61947060714505E-02	1.35711153991336E-06
3.8	2	2	14.8	3.4	2	2	10.2	2.7	1	1	8.4	0.5	120	198	−2.12208976410640E-03	1.50270363093278E-04
4.3	3	2	8.4	4.4	3	2	3.6	0.7	0	0	9.8	0.7	130	216	3.07232532727479E-03	1.72645613057386E-03
4	3	3	8.4	4	3	2	3.6	0.5	0	0	0	0.6	130	216	−1.56109079264269E-02	9.03392959960546E-02

Table 3. Convergence of the Series Expansion Relation for Three-Center Integrals $I^{ac,b}_{211,211,210}(10.8, 5.2, 6.4)$ as a Function of Summation Limit L for $R_{ac} = 0.1$, $\theta_{ac} = 54°$, $\varphi_{ac} = 180°$, $R_{ab} = 0.7$, $\theta_{ab} = 30°$, $\varphi_{ab} = 45°$, and $N = 15$

L	$\alpha = 0$
1	−3.58431451848798E-03
2	−3.58423360050448E-03
3	−3.58421933169305E-03
4	−3.58427279013579E-03
5	−3.58428811781847E-03
6	−3.58428427419311E-03
7	−3.58428387641203E-03
8	−3.58428388202039E-03
9	−3.58428388264284E-03
10	−3.58428388264548E-03
11	−3.58428388264535E-03
12	−3.58428388264535E-03
13	−3.58428388264535E-03
14	−3.58428388264535E-03

Table 4. Convergence of the Series Expansion Relation for Three-Center Integrals $I^{ac,b}_{211,211,210}(10.8, 5.2, 6.4)$ as a Function of Summation Limit M for $R_{ac} = 0.1$, $\theta_{ac} = 54°$, $\varphi_{ac} = 180°$, $R_{ab} = 0.7$, $\theta_{ab} = 30°$, $\varphi_{ab} = 45°$, $N = 15$, and $L = 14$

M	$\alpha = 0$
1	−3.58428388264535E-03
2	−3.58428388264535E-03
3	−3.58428388264535E-03
4	−3.58428388264535E-03
5	−3.58428388264535E-03
6	−3.58428388264535E-03
7	−3.58428388264535E-03
8	−3.58428388264535E-03
9	−3.58428388264535E-03
10	−3.58428388264535E-03
11	−3.58428388264535E-03
12	−3.58428388264535E-03
13	−3.58428388264535E-03
14	−3.58428388264535E-03

therefore, we can include only a few terms obtained from the summation over indices l and m. Table 5 shows that the accuracy of computer calculations obtained in the present algorithm is satisfactory for $N = 15$. As can be seen from Tables 1 and 2, the calculated one-electron three-center integrals with the arbitrary values of parameters of Coulomb–Yukawa like NICIP and NISTO show a good rate agreement between $\alpha = 0$ and $\alpha = 1$. Greater accuracy is attainable by the use of more terms in the series expansion formula (12). The computer time required for the calculation of one-electron multicenter integrals of STO and Coulomb–Yukawa like CIP with integer and noninteger indices are not given in the tables due to the fact that the comparison cannot be made with the different computers used in the literature. For instance, the CPU time for $I^{ab,c}_{211,211,210}(3.8, 4.6, 4.6)$ takes about 2.27 ms. As is clear from our tests that the analytical formulae for the

Table 5. Convergence of the Series Expansion Relation for Three-Center Integrals $I^{ac,b}_{211,211,210}(10.8, 5.2, 6.4)$ as a Function of Summation Limit N for $R_{ac} = 0.1$, $\theta_{ac} = 54°$, $\varphi_{ac} = 180°$, $R_{ab} = 0.7$, $\theta_{ab} = 30°$, and $\varphi_{ab} = 45°$

N	$\alpha = 0$
8	−3.585573418E-03
9	−3.584692223E-03
10	−3.584346514E-03
11	−3.584251701E-03
12	−3.584252313E-03
13	−3.584271933E-03
14	−3.584283263E-03
15	−3.584283882E-03

Table 6. The Values of Coupling-Projection Coefficients

$i\ j$	$k\ l$	$A^{ij}_{kl} = A^{kl}_{ij}$	$B^{ij}_{kl} = B^{kl}_{ij}$
1 1	1 1	1	1
	2 2	1	1
	3 3	1	1
	4 4	1/2	1/2
2 2	2 2	1	1
	3 3	1	1
	4 4	1/2	1/2
3 3	3 3	1	1
	4 4	1/2	1/2

Table 7. The Orbital Energies and Linear Combination Coefficients D_{pi} for Symmetrized Molecular Orbitals ($u_i = \sum_p \varphi_p D_{pi}$) for Ground State Term $(1a_1^2 2a_1^2 1b_2^2 3a_1^1, {}^2A_1)$[a)]

$u_i = u_{ny}$:	$u_1 = u_{1a_1}$	$u_2 = u_{2a_1}$	$u_3 = u_{1b_2}$	$u_4 = u_{3a_1}$	$u_5 = u_{1b_1}$	$u_6 = u_{4a_1}$	$u_7 = u_{2b_2}$
ε_i:	ε_{1a_1}	ε_{2a_1}	ε_{1b_2}	ε_{3a_1}	ε_{1b_1}	ε_{4a_1}	ε_{2b_2}
φ_p	−7.76817	−0.68486	−0.54392	−0.18467	0.00000	0.00000	0.00000
$\varphi_1 = \varphi(1a_1)$	−0.05868	0.58062	0.00000	0.07543	0.00000	1.48021	0.00000
$\varphi_2 = \varphi(2a_1)$	0.99049	−0.17414	0.00000	0.06139	0.00000	0.19172	0.00000
$\varphi_3 = \varphi(3a_1)$	0.06880	0.50495	0.00000	−0.31599	0.00000	−1.41825	0.00000
$\varphi_4 = \varphi(1b_2)$	0.00000	0.00000	0.56874	0.00000	0.00000	0.00000	1.42909
$\varphi_5 = \varphi(1b_1)$	0.00000	0.00000	0.00000	0.00000	1.00000	0.00000	0.00000
$\varphi_6 = \varphi(2b_2)$	0.00000	0.00000	0.04970	0.00000	0.00000	0.00000	−1.4556
$\varphi_7 = \varphi(4a_1)$	−0.02364	−0.04165	0.00000	−0.94219	0.00000	0.59492	0.00000

a) $E = -25.644586$, $E = -25.602236$.[23]

unsymmetrical one-range addition theorems of multicenter charge densities are useful tool for exact evaluation of the one-electron multicenter integrals of Coulomb–Yukawa like NICIP for the arbitrary values of quantum numbers, internuclear distances and orbital parameters.

As an application of eqs 12, 14b, 15b, and 16 in the case of Coulomb interaction potential (for $\mu = \nu = \sigma = 0$ and $\xi = 0$), we have solved combined HFR eqs[19] for the ground state of BH_2 with C_{2v} symmetry. All the two-electron multicenter integrals arising in the combined HFR equations can be calculated by the use of computer programs presented in our previous papers.[20–22]

The general form of orthonormal Slater determinants of the electronic configuration $(1a_1^2 2a_1^2 1b_2^2 3a_1^1, {}^2A_1)$ of BH_2 is defined as

$$U(4m_{s7}) = \frac{1}{\sqrt{7!}} \hat{A}[u_{11/2}(x_1)u_{1-1/2}(x_2)u_{21/2}(x_3) \times u_{2-1/2}(x_4)u_{31/2}(x_5)u_{3-1/2}(x_6)u_{4m_{s7}}(x_7)] \quad (19)$$

Here, $x \equiv xyz\sigma$, $u_{im_s}(x) = u_i(x, y, z)u_{m_s}(\sigma)$ and $u_i(x, y, z)$ are the molecular spin and spatial orbitals, respectively. The molecular orbitals u_{ny} are the basis functions of the irreducible representation of the symmetry group C_{2v}. The Slater type orbitals χ_p are denoted as

χ_{nlm}:	$\chi_{100}(H_1)$	$\chi_{100}(H_2)$	$\chi_{100}(B)$	$\chi_{200}(B)$	$\chi_{211}(B)$	$\chi_{21-1}(B)$	$\chi_{210}(B)$
χ_p:	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7

(20)

The geometric parameters of BH_2 we take from:[23]

$$H_1(0, -0.9247076, 2.0290986),$$
$$H_2(0, -0.9247076, -2.0290986), B(0, 0, 0) \quad (21)$$

The atomic orbital exponents have been taken from Ref. 24.

The values of results of calculations for the coupling-projection coefficients and solutions of combined HFR equations for ground state of electronic configuration $(1a_1^2 2a_1^2 1b_2^2 3a_1^1, {}^2A_1)$ are presented in Tables 6 and 7, respectively. The symmetrized basis orbitals φ_p occurring in Table 7 are determined through the Slater type orbitals χ_q by the following relation:

$$\varphi_p = \sum_q \chi_q g_{qp} \quad (22)$$

where

$$g = \begin{pmatrix} 0.671172 & 0 & 0 & 0 & 0 & 7.490915 & 0 \\ 0.671172 & 0 & 0 & 0 & 0 & -7.490915 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \quad (23)$$

We see from Table 7 that, in the case of minimal basis set, the results of computer calculation obtained by the use of variational method[25–28] in the combined HFR approach for the molecule BH_2 are good. Work is in progress in our group for

the combined HFR calculations of small molecules with an arbitrary number of closed and open shells.

Conclusion

In summary, we present here an efficient method to calculate one-electron multicenter integrals of STO and Coulomb–Yukawa like CIP with integer and noninteger indices. The end formulae are established with the help of unsymmetrical one-range addition theorems of complete orthonormal sets of Ψ^{α}-ETO.[10] In this study, the results of calculations for ground state of BH_2 molecule are obtained by the use of closed and open shell CHFR eqs.[29] It can be concluded that this newly proposed approximation leads to reasonable results when used as a method of electronic structure calculations.

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