Evaluation of intermolecular interaction energy using one-range addition theorems for $\psi^\alpha - ETO$ and Coulomb-Yukawa like correlated interaction potentials with integer and noninteger indices

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Abstract   Using one-range addition theorems for complete orthonormal sets of ψ^α – exponential type orbitals ($\alpha = 1, 0, -1, -2, \ldots$) intruduced by the author, the series expansion relations are established for the energy of interaction between molecules which have any number of closed and open shells. The final results are expressed through the linear combination coefficients of molecular orbitals, the parameters of Coulomb-Yukawa like correlated interaction potentials with integer and noninteger indices and the multicenter overlap integrals. The formulas obtained are useful for the study of interaction between atomic-molecular systems when the ψ^α – exponential type orbital basis functions in Hartree-Fock-Roothaan and explicitly correlated methods are employed.

Keywords ψ^α – exponential type orbitals · One-range addition theorems · Coulomb-Yukawa like correlated interaction potentials · Hartree-Fock-Roothaan approximation · Intermolecular interaction energy

1 Introduction

In electronic structure calculations, the exponential type orbitals (ETO) are viable alternative to Gaussian type orbitals (GTO) because they behave as exact eigenstates of Hamiltonians of atomic and molecular systems [1,2]. However, the difficulties in the calculation of multicenter molecular integrals have restricted the use of ETO in quantum chemistry. As shown in the literature, there is now renewed interest in developing efficient methods for calculating molecular integrals by employing ETO as basis sets (see e.g. [3–9] and the bibliography quoted in these papers). The Slater type

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orbitals (STO), which are a special case of the ETO, are not orthogonal with respect to the principal quantum numbers that creates some difficulties in molecular electronic structure calculations. Thus, the necessity for using the complete orthonormal sets of $\psi^\alpha - ETO$ as basis functions arises [10]. A large number of different sets of molecular orbitals can be obtained for the different values of α, which have the further advantage that the basis sets of $\psi^\alpha - ETO$, which are required, can be chosen properly according to the nature of the problems under consideration. This is rather important because the choice of the basis sets will determine the rate of convergence of series expansions arising in atomic and molecular electronic structure calculations. Therefore, the complete orthonormal sets of $\psi^\alpha - ETO$ with different values of indices α could be universally used in electronic structure calculations of atoms and molecules.

The $\psi^\alpha - ETO$ basis functions can also be used for electronic structure calculations when the correlated interaction potentials with noninteger indices are employed. We notice that the use of potentials with noninteger indices considerably improves the effectiveness of calculations (see Ref. [11] and references quoted therein).

The aim of this work is to obtain the series expansion formulas for the energy of interaction between molecules when the $\psi^\alpha - ETO$ basis sets and the Coulomb-Yukawa like noninteger μ^* and integer μ (for $\mu^* = \mu$) correlated interaction potentials (NICIP and ICIP) approximations in Hartree-Fock-Roothaan (HFR) theory are employed. The results presented are especially useful for the investigation of interaction between atomic-molecular systems.

2 Definition and basic formulas

The $\psi^\alpha - ETO$ basis sets [10] and the Coulomb-Yukawa like NICIP [12] are defined as

$$\psi^\alpha_{nlm}(\zeta, \vec{r}) = (-1)^\alpha \left[\frac{(2\zeta)^3 (q-p)!}{(2n)^\alpha (q!)^3} \right]^{\frac{1}{2}} x^l e^{-\frac{x}{2}} L^p_q(x) S_{lm}(\theta, \varphi) \tag{1}$$

$$h^{\mu^* \nu \sigma}(\xi, \vec{r}) = \left(\frac{4\pi}{2\nu + 1} \right)^{\frac{1}{2}} r^{\mu^* - 1} e^{-\xi r} S_{\nu\sigma}(\theta, \varphi), \tag{2}$$

where $x = 2\zeta r$, $p = 2l + 2 - \alpha$, $q = n + l + 1 - \alpha$ and $\alpha = 1, 0, -1, -2, \ldots$ and $\mu^* \geq 0$; ζ and ξ are the scaling paramaters of $\psi^\alpha - ETO$ and potential, respectively ($\zeta > 0$ and $\xi \geq 0$); $L^p_q(x)$ is the generalized Laguerre polynomial. The $S_{lm}(\theta, \varphi)$ are the complex (for $S_{lm} \equiv Y_{lm}$) and reel spherical hormonics:

$$S_{lm}(\theta, \varphi) = P_{l|m|}(\cos \theta) \Phi_m(\varphi). \tag{3}$$

Here, $P_{l|m|}$ are the normalized associated Legendre functions and
for complex spherical harmonics

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \tag{4}$$

for real spherical harmonics

$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} \begin{cases} \cos|m|\varphi & for \quad m \geq 0 \\ Sin\,|m|\varphi & for \quad m < 0. \end{cases} \tag{5}$$

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

$$\int \Psi_{nlm}^{\alpha*}(\zeta,\vec{r})\bar{\Psi}_{n'l'm'}^{\alpha}(\zeta,\vec{r})dv = \delta_{nn'}\delta_{ll'}\delta_{mm'} \tag{6}$$

$$\bar{\Psi}_{nlm}^{\alpha}(\zeta,\vec{r}) = \left(\frac{n}{\zeta r}\right)^\alpha \Psi_{nlm}^{\alpha}(\zeta,\vec{r}). \tag{7}$$

We notice that the definition of phases in this work for the complex spherical harmonics $\left(Y_{lm}^* \equiv Y_{l-m}\right)$ differs from the Condon-Shortley phases [13] by the sign factor $(-1)^m$.

The Coulomb ($for\ \xi = 0$) and Yukawa ($for\ \xi > 0$) like NICIP, Eq. 2, can be expressed in terms of $\psi^\alpha - ETO$ [14]:

$$h^{\mu^*\nu\sigma}(\xi,\vec{r}) = \sqrt{4\pi} \lim_{M \to \infty} \sum_{\mu=\nu+1}^{M} E_{\mu^*\nu,\mu\nu}^{\alpha M}(\xi,\eta)\, \Psi_{\mu\nu\sigma}^{\alpha}(\eta,\vec{r}), \tag{8}$$

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

$$E_{\mu^*\nu,\mu\nu}^{\alpha M}(\xi,\eta) = \frac{1}{(2\nu+1)^{1/2}(\xi+\eta)^{\mu^*+1/2}}$$

$$\times \sum_{\mu'=\nu+1}^{M} \bar{\omega}_{\mu'\mu}^{\alpha\nu} \sum_{\mu''=\nu+1}^{M} \Omega_{\mu'\mu''}^{\alpha\nu}(M)\frac{\Gamma(\mu^*+\mu''-\alpha+1)}{[\Gamma(2\mu''-2\alpha+1)]^{1/2}}\left(\frac{2\eta}{\xi+\eta}\right)^{\mu''-\alpha+\frac{1}{2}}. \tag{9}$$

See Ref. [10] for the exact definition of coefficients $\bar{\omega}_{\mu'\mu}^{\alpha\nu}$ and $\Omega_{\mu'\mu''}^{\alpha\nu}(M)$.

3 Expressions for energy of interaction between molecules

In order to obtain the formulae for energy of interaction between molecules we introduce the common coordinate system OXYZ and the local coordinate systems $oxyz$ and $o'x'y'z'$ with origins o and o' anywhere within the system of charges of the molecules. The radius vectors of the electrons and nuclei of molecules in these coordinates are shown in Fig. 1. Now we regard one of the molecules as being in the field of the other. Then, we obtain for the operator of energy of the interaction between molecules the relation

$$\hat{U}^{\mu^*\nu\sigma}(\xi) = \hat{U}_{nn'}^{\mu^*\nu\sigma}(\xi) + \hat{U}_{ne'}^{\mu^*\nu\sigma}(\xi) + \hat{U}_{en'}^{\mu^*\nu\sigma}(\xi) + \hat{U}_{ee'}^{\mu^*\nu\sigma}(\xi). \tag{10}$$

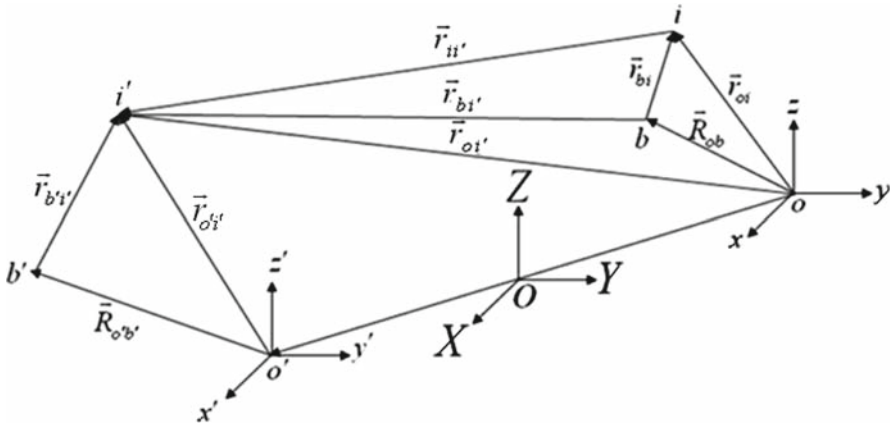Here, the operators of interactions between particles are denoted by

Fig. 1 The position of charges of molecules

for nuclei-nuclei

$$\hat{U}_{nn'}^{\mu^*\nu\sigma}(\xi) = \sum_b \sum_{b'} Z_b Z_{b'} h^{\mu^*\nu\sigma}\left(\xi, \vec{R}_{bb'}\right), \tag{11}$$

for electrons-nuclei

$$\hat{U}_{ne'}^{\mu^*\nu\sigma}(\xi) = -\sum_b \sum_{i'=1}^{N'} Z_b h^{\mu^*\nu\sigma}(\xi, \vec{r}_{bi'}) \tag{12}$$

$$\hat{U}_{en'}^{\mu^*\nu\sigma}(\xi) = -\sum_{i=1}^{N} \sum_{b'} Z_{b'} h^{\mu^*\nu\sigma}(\xi, \vec{r}_{ib'}), \tag{13}$$

for electrons-electrons

$$\hat{U}_{ee'}^{\mu^*\nu\sigma}(\xi) = \sum_{i=}^{N} \sum_{i'=1}^{N'} h^{\mu^*\nu\sigma}(\xi, \vec{r}_{ii'}). \tag{14}$$

The quantities $\vec{r}_{oi'}$ and $\vec{r}_{bi'}$ occurring in Fig. 1 are the radius-vectors of electrons of second molecule with respect to the origin of the coordinate system $oxyz$ and to the nuclei b for the first molecule, respectively ($b \equiv a, c, \ldots$); Z_b and $Z_{b'}$ are the charges of nuclei b and $b'(b' \equiv a', c', \ldots)$; N and N' are the number of electrons in first and second molecules, respectively. The Coulomb-Yukawa like NICIP containing in Eqs. 11–14 are defined by Eq. 2.

Now we use Eq. 8. Then, we can express the operators (10)–(14) through the corresponding operators with $\psi^{\alpha} - ETO$:

$$
\hat{U}^{\mu^{*}\nu\sigma}(\xi) = \lim_{M \to \infty} \sum_{\mu=\nu+1}^{M} E_{\mu^{*}\nu,\mu\nu}^{\alpha M}(\xi, \eta)[\hat{H}_{nn'}^{\alpha\mu\nu\sigma}(\eta)
$$
$$
+ \hat{H}_{ne'}^{\alpha\mu\nu\sigma}(\eta) + \hat{H}_{en'}^{\alpha\mu\nu\sigma}(\eta) + \hat{H}_{ee'}^{\alpha\mu\nu\sigma}(\eta)], \tag{15}
$$

where

$$
\hat{H}_{nn'}^{\alpha\mu\nu\sigma}(\eta) = \sqrt{4\pi} \sum_{b} \sum_{b'} Z_b Z_{b'} \Psi_{\mu\nu\sigma}^{\alpha}\left(\eta, \vec{R}_{bb'}\right) \tag{16}
$$

$$
\hat{H}_{ne'}^{\alpha\mu\nu\sigma}(\eta) = -\sqrt{4\pi} \sum_{b} \sum_{i'=1}^{N'} Z_b \Psi_{\mu\nu\sigma}^{\alpha}\left(\eta, \vec{R}_{bi'}\right) \tag{17}
$$

$$
\hat{H}_{en'}^{\alpha\mu\nu\sigma}(\eta) = -\sqrt{4\pi} \sum_{i=1}^{N} \sum_{b'} Z_{b'} \Psi_{\mu\nu\sigma}^{\alpha}(\eta, \vec{r}_{ib'}) \tag{18}
$$

$$
\hat{H}_{ee'}^{\alpha\mu\nu\sigma}(\eta) = \sqrt{4\pi} \sum_{i=1}^{N} \sum_{i'=1}^{N'} \Psi_{\mu\nu\sigma}^{\alpha}(\eta, \vec{r}_{ii'}). \tag{19}
$$

With the calculation of average expectation values of operators (15)–(19) one can use the method set out in previous paper [15]. Then, we obtain for the energies of interaction between particles of molecules which have the multideterminantal single electron configuration states with any number of closed and open shells the following relations:

$$
H_{nn'}^{\alpha\mu\nu\sigma}(\eta) = \sqrt{4\pi} \sum_{b} \sum_{b'} Z_b Z_{b'} \Psi_{\mu\nu\sigma}^{\alpha}\left(\eta, \vec{R}_{bb'}\right) \tag{20}
$$

$$
H_{ne'}^{\alpha\mu\nu\sigma}(\eta) = -2 \sum_{b} \sum_{i'=1}^{\kappa'} Z_b f_{i'} F_{i'}^{\alpha\mu\nu\sigma}(\eta, b) \tag{21}
$$

$$
H_{en'}^{\alpha\mu\nu\sigma}(\eta) = -2 \sum_{i=1}^{\kappa} \sum_{b'} f_i Z_{b'} F_i^{\alpha\mu\nu\sigma}\left(\eta, b'\right) \tag{22}
$$

$$
H_{ee'}^{\alpha\mu\nu\sigma}(\eta) = 4 \sum_{i=1}^{\kappa} \sum_{i'=1}^{\kappa'} f_i f_{i'} F_{ii'}^{\alpha\mu\nu\sigma}(\eta), \tag{23}
$$

where

$$
F_{i'}^{\alpha\mu\nu\sigma}(\eta, b) = \sqrt{4\pi} \int u_{i'}^{\alpha*}(\vec{r}_1) \Psi_q^{\alpha}(\eta, \vec{r}_{b1}) u_{i'}^{\alpha}(\vec{r}_1) dv_1 \tag{24}
$$

$$
F_i^{\alpha\mu\nu\sigma}(\eta, b') = \sqrt{4\pi} \int u_i^{\alpha*}(\vec{r}_1) \Psi_q^{\alpha}(\eta, \vec{r}_{b'1}) u_i^{\alpha}(\vec{r}_1) dv_1 \tag{25}
$$

$$F_{ii'}^{\alpha\mu\nu\sigma}(\eta) = \int \int u_i^{\alpha*}(\vec{r}_1) F_{i'}^{\alpha q}(\eta, \vec{r}_{12}) u_i^{\alpha}(\vec{r}_1) \, dv_1 dv_2$$

$$= \sqrt{4\pi} \int u_i^{\alpha*}(\vec{r}_1) \left[\int u_{i'}^{\alpha*}(\vec{r}_2) \Psi_q^{\alpha}(\eta, \vec{r}_{12}) u_{i'}^{\alpha}(\vec{r}_2) \, dv_2 \right] u_i^{\alpha}(\vec{r}_1) \, dv_1. \tag{26}$$

Here $\kappa = \kappa_c + \kappa_0$ is the number of occupied orbitals bilonging to closed (κ_c) and open (κ_0) shells, and f_i is the fractional occupancy of shell i. The molecular orbitals u_i^{α} and $u_{i'}^{\alpha}$ occurring in Eqs. 24–26 are defined as linear combinations of $\psi^{\alpha} - ETO$: for first molecule

$$u_i^{\alpha} = \sum_p \Psi_p^{\alpha} C_{pi}^{\alpha}, \tag{27}$$

for second molecule

$$u_{i'}^{\alpha} = \sum_{p'} \Psi_{p'}^{\alpha} C_{p'i'}^{\prime\alpha}. \tag{28}$$

The linear combination coefficients C_{pi}^{α} and $C_{p'i'}^{\prime\alpha}$ can be determined by solving the combined HFR equations for molecules (see Ref. [15]).

Taking into account Eqs. 27 and 28 in 24–26 we obtain:

$$F_{i'}^{\alpha q}(\eta, b) = \sum_{p_1' p_2'} C_{p_1' i'}^{\prime\alpha*} C_{p_2' i'}^{\prime\alpha} S_{p_1' p_2' q}^{\alpha \, a'c'b}(\zeta_1', \zeta_2', \eta) \tag{29}$$

$$F_i^{\alpha q}(\eta, b') = \sum_{p_1 p_2} C_{p_1 i}^{\alpha*} C_{p_2 i}^{\alpha} S_{p_1 p_2 q}^{\alpha \, acb'}(\zeta_1, \zeta_2, \eta) \tag{30}$$

$$F_{ii'}^{\alpha q}(\eta) = \sum_{p_1 p_2} C_{p_1 i}^{\alpha*} C_{p_2 i}^{\alpha} \sum_{p_1' p_2'} C_{p_1' i'}^{\prime\alpha*} C_{p_2' i'}^{\prime\alpha} I_{p_1 p_2, p_1' p_2', q}^{\alpha \, ac \, a'c'}(\zeta_1, \zeta_2; \zeta_1', \zeta_2'; \eta), \tag{31}$$

where $q \equiv \mu\nu\sigma$ and

$$S_{p_1' p_2' q}^{\alpha \, a'c'b}(\zeta_1', \zeta_2', \eta) = \sqrt{4\pi} \int \Psi_{p_1'}^{\alpha*}(\zeta_1', \vec{r}_{a'1}) \Psi_{p_2'}^{\alpha}(\zeta_2', \vec{r}_{c'1}) \Psi_q^{\alpha}(\eta, \vec{r}_{b1}) \, dv_1 \tag{32}$$

$$S_{p_1 p_2 q}^{\alpha \, acb'}(\zeta_1, \zeta_2, \eta) = \sqrt{4\pi} \int \Psi_{p_1}^{\alpha*}(\zeta_1, \vec{r}_{a1}) \Psi_{p_2}^{\alpha}(\zeta_2, \vec{r}_{c1}) \Psi_q^{\alpha}(\eta, \vec{r}_{b'1}) \, dv_1 \tag{33}$$

$$I_{p_1 p_2, p_1' p_2', q}^{\alpha \, ac \, a'c'}(\zeta_1, \zeta_2; \zeta_1', \zeta_2'; \eta) = \sqrt{4\pi} \int \left(\int \Psi_{p_1}^{\alpha*}(\zeta_1, \vec{r}_{a1}) \Psi_{p_2}^{\alpha}(\zeta_2, \vec{r}_{c1}) \Psi_q^{\alpha}(\eta, \vec{r}_{12}) \, dv_1 \right)$$
$$\times \Psi_{p_1'}^{\alpha*}(\zeta_1', \vec{r}_{a'2}) \Psi_{p_2'}^{\alpha}(\zeta_2', \vec{r}_{c'2}) dv_2. \tag{34}$$

For the evaluation of integral (34) we use the symmetrical one-range addition theorems for the $\psi^{\alpha} - ETO$ presented in previous papers [16,17]. See Ref. [18] for the

applicability of symmetrical one-range addition theorems. Then, we obtain the following two kinds of relations:

$$
I^{\alpha\,ac\,a'c'}_{p_1p_2,p_1'p_2',q}(\zeta_1,\zeta_2;\zeta_1',\zeta_2';\eta) = \frac{1}{(2\eta)^{\frac{3}{2}}} \sum_{u'=1}^{\infty}\sum_{v'=0}^{u'-1}\sum_{s'=-v'}^{v'} \bar{S}^{\alpha\,a'c'a}_{p_1'p_2'k'}(\zeta_1',\zeta_2',\eta)
$$
$$
\times \sum_{u=1}^{\mu+u'+1}\sum_{v=0}^{u-1}\sum_{s=-v}^{v} (-1)^v\,D^{\alpha k}_{qk'}\,S^{\alpha\,aca*}_{p_1p_2k}(\zeta_1,\zeta_2,\eta)
$$

$$(35)$$

$$
I^{\alpha\,ac\,a'c'}_{p_1p_2,p_1'p_2',q}(\zeta_1,\zeta_2;\zeta_1',\zeta_2';\eta) = \frac{1}{(2\eta)^{\frac{3}{2}}} \sum_{u'=1}^{\infty}\sum_{v'=0}^{u'-1}\sum_{s'=-v'}^{v'} \bar{S}^{\alpha\,a'c'a'}_{p_1'p_2'k'}(\zeta_1',\zeta_2',\eta)
$$
$$
\times \sum_{u=1}^{\mu+u'+1}\sum_{v=0}^{u-1}\sum_{s=-v}^{v} (-1)^v\,D^{\alpha k}_{qk'}\,S^{\alpha\,aca'*}_{p_1p_2k}(\zeta_1,\zeta_2,\eta),
$$

$$(36)$$

where $k \equiv uvs$ and $k' \equiv u'v's'$. Here, the quantities S^{α} and $\bar{S}^{\alpha}$ are the multicenter overlap integrals of three $\psi^{\alpha} - ETO$:

$$
S^{\alpha\,acb}_{pp'q}(\zeta,\zeta',\eta) = \sqrt{4\pi}\int \Psi^{\alpha*}_{p}(\zeta,\vec{r}_{a1})\Psi^{\alpha}_{p'}(\zeta',\vec{r}_{c1})\Psi^{\alpha}_{q}(\eta,\vec{r}_{b1})dv_1 \tag{37}
$$

$$
\bar{S}^{\alpha\,acb}_{pp'q}(\zeta,\zeta',\eta) = \sqrt{4\pi}\int \Psi^{\alpha*}_{p}(\zeta,\vec{r}_{a1})\Psi^{\alpha}_{p'}(\zeta',\vec{r}_{c1})\bar{\Psi}^{\alpha}_{q}(\eta,\vec{r}_{b1})dv_1. \tag{38}
$$

Thus, we have derived a large number of different ($\alpha = 1, 0, -1, -2, \ldots$) sets of series expansion relations for the energy of interaction between molecules in terms of multicenter overlap integrals with $\psi^{\alpha} - ETO$ and linear combination coefficients of molecular orbitals. In a previous paper [19], with the help of one-range addition theorems for the complete orthonormal sets of $\psi^{\alpha} - ETO$ in momentum space, the general expansion formulas for the multicenter overlap integrals (37) and (38) in terms of two-center overlap integrals over STO have been established. For the computation of two-center overlap integrals, the efficient computer programs especially useful for the large quantum numbers are available in our group [20]. Thus, by using the computer programs for the two-center overlap integrals of STO one can calculate the interaction energy between molecules having the multideterminantal single electron configuration states with any number of closed and open shells.

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