The Three-Center Hybrid and Four-Center Electron Repulsion Integrals over Slater-Type Orbitals Using Guseinov Rotation-Angular Function

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Abstract: The three-center hybrid integral and the four-center electron repulsion integral are expressed in terms of the two-center overlap and two-center Coulomb integrals. The analytical evaluation of the two-center overlap integral over Slater-type orbitals by using Guseinov rotation-angular function obtained by the authors [13]. Therefore, it is recommended to use the expansion formulas for translation of Slater-type orbitals from one center to another center [3, 4, 14].

Keywords: hybrid integral, four-center electron repulsion integral, overlap integral, Coulomb integral, Slater-type orbitals, Guseinov rotation-angular function.
1. Introduction

One of the main difficulties in the study of the electronic structure of polyatomic molecules is the evaluation of the three and four-center molecular integrals over Slater-type orbitals.

For the calculation of these integrals several methods have been reported in the literature (The expansion methods for Slater-type orbitals about an arbitrary point [1,6,7,9,10], Gaussian transform methods [8, 12], etc.).

The aim of this paper is to present a simple general formula for three and four-center integrals over Slater-type orbitals using Guseinov rotation-angular function.

2. The three-center hybrid integral

The three-center hybrid integrals examined in the present paper have the following form

\[
\left[ (n_a l_a m_a) (n_b l_b m_b) (n_c l_c m_c) \right] \frac{1}{r_{12}} \left[ (n_b l_b m_b) (n_c l_c m_c) \right] = \int \chi_a (1) \cdot \chi'_a (1) \frac{1}{r_{12}} \chi_b (2) \cdot \chi_c (2) \, dv_1 \, dv_2
\]

\[
= \int \chi'_{n_a l_a m_a} (\zeta_a, r_a \theta_a \phi_a) \chi'_{n_b l_b m_b} (\zeta'_a, r_a \theta_a \phi_a) \frac{1}{r_{12}} \chi_{n_b l_b m_b} (\zeta_b, r_b \theta_b \phi_b) \chi_{n_c l_c m_c} (\zeta_c, r_c \theta_c \phi_c) \, dv_1 \, dv_2
\]

(1)

Where \( \chi_{n_i l_i m_i} (\zeta, r \theta \phi) \) and \( \chi'_{n_i l_i m_i} (\zeta', r' \theta' \phi') \) are four-center different real Slater-type orbitals (STO's) centered on the nuclei \( i = a, b, c \). And the real STO's \( \chi_{n_i l_i m_i} (\zeta, r \theta \phi) \) are defined by equations (8) to equations (11) in [14] by using the expansion of real real STO's at a new origin [3,4] whose coefficients represent itself overlap integrals between STO's.

Thus we can write \( \chi_{n_i l_i m_i} (\zeta, r \theta \phi) \) as

\[
\chi_{n_i l_i m_i} (\zeta, r \theta \phi) = \lim_{N \to \infty} \sum_{n_i^* = -N}^{N} \sum_{L_i = 0}^{L_i \text{max}} \sum_{m_i = -L_i}^{L_i} W_{n_i l_i m_i n_i^* l_i m_i^*} (\tilde{P}_{cb}) \cdot \chi_{n_i^* l_i m_i} (\zeta, r \theta \phi)
\]

(2)
Then using equation (2), we can express the three-center hybrid integral in the following expression

\[
\left[ (n_a l_a m_a)(n'_a l'_a m'_a) \right] \frac{1}{r_{12}} \left| \left( n_b l_b m_b \right) \left( n_c l_c m_c \right) \right| = \lim_{N \to \infty} \sum_{n_a=1}^{N} \sum_{l_a=0}^{n_a-1} \sum_{m_a=-l_a}^{l_a} W_{n_a l_a m_a a_b l_b m_b}^{N} (P_{cb}) \cdot \left( n_a l_a m_a \right) \left( n'_a l'_a m'_a \right) \left| \left( n_b l_b m_b \right) \left( n_c l_c m_c \right) \right|
\]

Where \(
\left[ (n_a l_a m_a)(n'_a l'_a m'_a) \right] \frac{1}{r_{12}} \left| \left( n_b l_b m_b \right) \left( n'_b l'_b m'_b \right) \right|
\) is the two-center Coulomb integral \([2, 4, 5]\) and \(W_{n_a l_a m_a a_b l_b m_b}^{N} (P_{cb})\) expressed through the two-center overlap integrals.

It should be noted that the general formula for the two-center overlap integral over STO's by using Guseinov rotation-angular function have been established by our work \([13]\).

### 3. The four-center electron repulsion integral

Now we can move on to the evaluation of multicenter electron repulsion integrals over real STO's which have the following form

\[
\left[ (n_a l_a m_a)(n_c l_c m_c) \right] \frac{1}{r_{12}} \left| \left( n_b l_b m_b \right) \left( n_d l_d m_d \right) \right| = \int \chi_a(1) \cdot \chi_c(1) \int \chi_b(2) \cdot \chi_d(2) \quad dv_1 \quad dv_2 \\
= \int \chi_{n_a l_a m_a} (\zeta_a, r, \theta, \phi_a) \chi_{n_c l_c m_c} (\zeta_c, r, \theta, \phi_c) \int \chi_{n_b l_b m_b} (\zeta_b, r, \theta, \phi_b) \chi_{n_d l_d m_d} (\zeta_d, r, \theta, \phi_d) \quad dv_1 \quad dv_2
\]

(4)

For this purpose we use the expansion formulas for the STO's \(\chi_a\) and \(\chi_d\) which we express through the STO's centered on the nuclear center \(a\) and \(b\).

\[
\chi_{n_a l_a m_a} (\zeta_a, r, \theta, \phi_a) = \lim_{N \to \infty} \sum_{n_a=1}^{N} \sum_{l_a=0}^{n_a-1} \sum_{m_a=-l_a}^{l_a} W_{n_a l_a m_a a_b l_b m_b}^{N} (P_{ca}) \cdot \chi_{n_d l_d m_d} (\zeta_a, r, \theta, \phi_a)
\]

(5)
Then we obtain for the four-center electron repulsion integrals over STO's the expression in terms of the overlap integral and the Coulomb integral.

\[
(X_{e_{a}, l_{a}, m_{a}, \phi_{a}, \theta_{a}, \rho_{a}}(r_{d}, \rho_{d}, \theta_{d}, \phi_{d})) = \lim_{N \to \infty} \sum_{n_{a}=1}^{N} \sum_{l_{a}=0}^{n_{a}-1} \sum_{m_{a}=-l_{a}}^{l_{a}} W_{n_{a}, l_{a}, m_{a}, n_{b}, l_{b}, m_{b}}^{N}(P_{db}) \cdot \chi_{n_{a}, l_{a}, m_{a}}(r_{d}, \rho_{d}, \theta_{d}, \phi_{d})
\]

(6)

(7)

Where, the auxiliary function \( \Omega_{n, n'}^{N}(N) \) has been discussed in appendix of our work [13].

As stated above, the three-center hybrid and the four-center electron repulsion integrals are expressed through the two-center overlap and the two-center Coulomb integrals for which the analytical formulas have been established in our previous works [5, 13, 14].
References:


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