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Evaluation of two- and three-center overlap integrals over complete orthonormal sets of Ψ^{α}-ETOs using their addition theorems

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With the help of addition theorems for complete orthonormal sets of Ψ^{α}-ETOs in momentum space ($\alpha = 1, 0, -1, -2, \ldots$) introduced by the author, the general expansion formulas are established for the two- and three-center overlap integrals occurring when Hartree-Fock–Roothaan and explicitly correlated methods, respectively, are employed. The relationships obtained are valid for the arbitrary quantum numbers, screening constants and location of Ψ^{α}-ETOs.

KEY WORDS: complete orthonormal sets of exponential-type orbitals, addition theorems, momentum space, overlap integrals

AMS subject classification: 81-V55, 81V45

1. Introduction

It is well known that the complete orthonormal sets of exponential-type orbitals play a significant role in quantum mechanics of atoms, molecules, and solids [1,2]. In particular, one of the most promising methods is based upon the use of complete orthonormal sets of Ψ^{α}-ETOs as basis functions in the MO LCAO theory:

$$u_i^{\alpha} = \sum_p \Psi_p^{\alpha} c_{pi}^{\alpha}, \tag{1}$$

where $\alpha = 1, 0, -1, -2, \ldots$. Therefore, a large number of different sets of Hartree-Fock-Roothan (HFR) equations can be obtained with the help of a single analytical relation of Ψ^{α}-ETOs [3] which has the further advantage that the basis Ψ^{α}-ETOs, 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 set will determine the rate of convergence of the resulting series expansions. Using addition theorems for interaction potentials introduced

in Refs. [4,5] it is easy to show that the arbitrary multicenter multielectron integral over Ψ^α-ETOs that arises in the solution of atomic and molecular problems occurring in HFR and explicitly correlated theories can be expressed in terms of two and three-center overlap integrals. Therefore, the elaboration of algorithms for the evaluation of matrix elements in the MO LCAO theory with Ψ^α-ETOs necessitates progress in the development of methods to calculate two- and three-center overlap integrals over Ψ^α-ETOs.

The purpose of the present paper is to derive formulae for the two- and three-center overlap integrals with complete orthonormal sets of Ψ^α-ETOs appearing in the determination of atomic and molecular multielectron properties when the Ψ^α-ETOs basis in HFR and explicitly correlated theories is employed.

2. Definitions and basic formulas

The overlap integrals examined in this work have the following form: two-center overlap integrals

$$S^{\alpha}_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ab}) = \int \Psi^{\alpha *}_{nlm}(\zeta,\vec{r})\overline{\Psi}^{\alpha}_{n'l'm'}(\zeta',\vec{r}-\vec{R}_{ab})d^3\vec{r} \tag{2}$$

three-center overlap integrals

$$S^{\alpha}_{p_1p_2p_3}(\zeta_1\zeta_2\zeta_3;\vec{R}_{ac},\vec{R}_{cb}) = \sqrt{4\pi}\int \Psi^{\alpha *}_{p_1}(\zeta_1,\vec{r})\Psi^{\alpha}_{p_2}(\zeta_2,\vec{r}-\vec{R}_{ac})\overline{\Psi}^{\alpha}_{p_3}(\zeta_3,\vec{r}-\vec{R}_{ab})d^3\vec{r}, \tag{3}$$

where $p_i \equiv n_i l_i m_i$ $(i = 1,2,3)$, $\vec{r} = \vec{r}_a$, $\vec{r} - \vec{R}_{ac} = \vec{r}_c$ and $\vec{r} - \vec{R}_{ab} = \vec{r}_b$. The functions Ψ^α and $\overline{\Psi}^\alpha$ are the Ψ^α-ETOs determined by [6]

$$\Psi^{\alpha}_{nlm}(\zeta,\vec{r}) = R^{\alpha}_{nl}(\zeta,r)S_{lm}(\theta,\varphi) \tag{4}$$

$$\overline{\Psi}^{\alpha}_{nlm}(\zeta,\vec{r}) = \left(\frac{n}{\zeta r}\right)^{\alpha}\Psi^{\alpha}_{nlm}(\zeta,\vec{r}) \tag{5}$$

$$R^{\alpha}_{nl}(\zeta,r) = (-1)^{\alpha}\left[\frac{(2\zeta)^3(n-l-1)!}{(2n)^{\alpha}((n+l+1-\alpha)!)^3}\right]^{1/2}(2\zeta r)^l e^{-\zeta r}L^{2l+2-\alpha}_{n+l+1-\alpha}(2\zeta r), \tag{6}$$

where $\alpha = 1, 0, -1, -2, \ldots$. Here, the functions $L^p_q(x)$ and $S_{lm}(\theta,\varphi)$ are the generalized Laguerre polynomials, and the normalized complex ($S_{lm} \equiv Y_{lm}$) or real spherical harmonics, respectively.

For the evaluation of three-center overlap integrals, equation (3), we shall use the following addition theorems for complete orthonormal sets of exponential-type orbitals in the momentum representation [6]:

$$\Phi^{\alpha}_{nlm}(\zeta, \vec{k} - \vec{p})$$
$$= (4\pi z)^{3/2} \sum_{\mu=1}^{\infty} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} \left(\sum_{N=1}^{n+\mu+1} \sum_{L=0}^{N-1} \sum_{M=-L}^{L} B^{\alpha NLM}_{nlm,\mu\nu\sigma} \Phi^{\alpha *}_{NLM}(z, \vec{p}) \right) \bar{\Phi}^{\alpha}_{\mu\nu\sigma}(\zeta, \vec{k}) \quad (7)$$

where $\alpha = 1, 0, -1, -2, \ldots$ and $z = 2\zeta$. The Φ^{α}_{nlm} and $\bar{\Phi}^{\alpha}_{nlm}$ are the Fourier transforms of the functions (4) and (5), respectively. See Ref. [6] for the exact definition of the coefficients $B^{\alpha NLM}_{nlm,\mu\nu\sigma}$.

3. Evaluation of two-center overlap integrals with Ψ^{α}-ETOs

In order to evaluate the two-center overlap integrals of Ψ^{α}-ETOs we transform the Ψ^{α} – and $\overline{\Psi}^{\alpha}$-ETOs occurring in equation (2) into the STOs by taking into account the following linear combinations [6]:

$$\Psi^{\alpha}_{nlm}(\zeta, \vec{r}) = \sum_{\mu=l+1}^{n} \omega^{\alpha l}_{n\mu} \chi_{\mu lm}(\zeta, \vec{r}) \quad (8)$$

$$\overline{\Psi}^{\alpha}_{nlm}(\zeta, \vec{r}) = (2n)^{\alpha} \sum_{\mu=l+1}^{n} \omega^{\alpha l}_{n\mu} [(2(\mu - \alpha))!/(2\mu)!]^{1/2} \chi_{\mu-\alpha lm}(\zeta, \vec{r}), \quad (9)$$

where $\chi_{nlm}(\zeta, \vec{r})$ are the normalized STOs determined by

$$\chi_{nlm}(\zeta, \vec{r}) = (2\zeta)^{n+\frac{1}{2}} [(2n)!]^{-\frac{1}{2}} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \varphi). \quad (10)$$

See Ref. [6] for the exact definition of the coefficients $\omega^{\alpha l}_{n\mu}$.

Now using equations (8) and (9) we finally obtain from equation (2) for the expansion of overlap integrals with Ψ^{α}-ETOs in terms of overlap integrals over STOs the following relations:

$$S^{\alpha}_{nlm,n'l'm'}(\zeta, \zeta'; \vec{R}_{ab}) = \sum_{\mu=l+1}^{n} \sum_{\mu'=l'+1}^{n'} \omega^{\alpha l}_{n\mu} \omega^{\alpha l'}_{n'\mu'} (2n')^{\alpha}$$
$$\times [(2(\mu' - \alpha))!/(2\mu')!]^{1/2} S_{\mu\, lm, \mu'-\alpha\, l'm'}(\zeta, \zeta'; \vec{R}_{ab}). \quad (11)$$

Here $S_{nlm,n'l'm'}(\zeta, \zeta'; \vec{R}_{ab})$ are the two-center overlap integrals of STOs defined as

$$S_{nlm,n'l'm'}(\zeta, \zeta'; \vec{R}_{ab}) = \int \chi^{*}_{nlm}(\zeta, \vec{r}) \chi_{n'l'm'}(\zeta', \vec{r} - \vec{R}_{ab}) d^3\vec{r}. \quad (12)$$

The analytical and numerical aspects of overlap integrals over STOs have recently been investigated in our papers (see Ref. [7] and references quoted therein to our papers for overlap integrals of STOs.

4. Evaluation of three-center overlap integrals over Ψ^{α}-ETOs

For the evaluation of three-center overlap integrals, equation (3), we use in equations (2) and (3) the Fourier transform convolution theorem. Then, we obtain for the two- and three-center overlap integrals in the momentum space the relations

$$S^{\alpha}_{p_1 p_2}(\zeta_1\zeta_2;\vec{R}_{ab}) = \int e^{-i\vec{k}.\vec{R}_{ab}}\Phi^{\alpha *}_{p_1}(\zeta_1,\vec{k})\bar{\Phi}^{\alpha}_{p_2}(\zeta_2,\vec{k})d^3\vec{k} \tag{13}$$

$$S^{\alpha}_{p_1 p_2 p_3}(\zeta_1\zeta_2\zeta_3;\vec{R}_{ac},\vec{R}_{cb}) = \sqrt{4\pi}(2\pi)^{-3/2}\int e^{-i\vec{k}_1.\vec{R}_{ac}+i\vec{k}_3.\vec{R}_{cb}}\Phi^{\alpha *}_{p_1}(\zeta_1,\vec{k}_1)\Phi^{\alpha}_{p_2}(\zeta_2,\vec{k}_1-\vec{k}_3) \times\bar{\Phi}^{\alpha}_{p_3}(\zeta_3,\vec{k}_3)d^3\vec{k}_1 d^3\vec{k}_3 \tag{14}$$

In the derivation of these formulae we have taken into account the following properties of Fourier transforms:

$$\begin{aligned}\Psi^{\alpha}_{p}(\zeta,\vec{r}) &= (2\pi)^{-3/2}\int e^{i\vec{k}.\vec{r}}\Phi^{\alpha}_{p}(\zeta,\vec{k})d^3\vec{k},\\ \Phi^{\alpha}_{p}(\zeta,\vec{k}) &= (2\pi)^{-3/2}\int e^{-i\vec{k}.\vec{r}}\Psi^{\alpha}_{p}(\zeta,\vec{r})d^3\vec{r}\end{aligned} \tag{15}$$

$$\begin{aligned}\overline{\Psi}^{\alpha}_{p}(\zeta,\vec{r}) &= (2\pi)^{-3/2}\int e^{i\vec{k}.\vec{r}}\bar{\Phi}^{\alpha}_{p}(\zeta,\vec{k})d^3\vec{k},\\ \bar{\Phi}^{\alpha}_{p}(\zeta,\vec{k}) &= (2\pi)^{-3/2}\int e^{-i\vec{k}.\vec{r}}\bar{\Psi}^{\alpha}_{p}(\zeta,\vec{r})d^3\vec{r}\end{aligned} \tag{16}$$

Now we take in equation (14) into account equation (7) for the addition theorems of the functions $\Phi^{\alpha}_{p_2}(\zeta_2,\vec{k}_1-\vec{k}_3)$ and equation (13) for the Fourier transform of two-center overlap integrals. Then we obtain finally for the three-center overlap integrals in terms of the product of two-center overlap integrals of Ψ^{α}-ETOs the following series expansion formulae:

$$S^{\alpha}_{p_1 p_2 p_3}(\zeta_1\zeta_2\zeta_3;\vec{R}_{ac},\vec{R}_{cb}) = \sqrt{4\pi}(2z_2)^{3/2}\sum_{\mu=1}^{\infty}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}S^{\alpha}_{p_1 q}(\zeta_1\zeta_2;\vec{R}_{ac}) \times\left(\sum_{n=1}^{n_2+\mu+1}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}B^{\alpha p}_{p_2 q}S^{\alpha}_{p p_3}(z_2\zeta_3;\vec{R}_{cb})\right), \tag{17}$$

where $p\equiv nlm$, $q\equiv\mu\nu\sigma$, $z_2 = 2\zeta_2$ and $\alpha = 1, 0, -1, -2, \ldots$.

As can be seen from equations (11) and (17), the two- and three-center overlap integrals of Ψ^{α}-ETOs can be calculated by the use of two-center overlap integrals with STOs for the computation of which efficient computer programs

especially useful for the large quantum numbers are available in our group. Thus, the two-center overlap integrals over STOs can be utilized in the calculation of multicenter multielectron integrals of Ψ^{α}-ETOs, therefore, in the study of molecular electronic structure when Ψ^{α}-ETOs is employed as a basis in HFR and correlated methods.

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