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ORIGINAL PAPER

Expansion formulae for two-center charge densities of integer and noninteger *n* generalized exponential type orbitals with hyperbolic cosine and their use in evaluation of multicenter multielectron integrals

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Abstract The expansion formulae are derived for the two-center charge densities of integer and noninteger *n* generalized exponential type orbitals with hyperbolic cosine (GETOHC) in terms of corresponding charge densities of generalized exponential type orbitals (GETO) presented in our previous paper. The general formulae obtained for the GETOHC charge densities are utilized for the evaluation of multicenter multielectron integrals appearing in the Hartree–Fock–Roothaan (HFR) and explicitly correlated theories when the GETOHC are employed as basis functions.

Keywords Charge densities · Generalized exponential functions · ψ^{α}-Exponential type orbitals · Multicenter multielectron integrals

1 Introduction

It is well known that the Gaussian type orbitals (GTO) and Slater type orbitals (STO) are widely used as basis functions in HFR approximation. However, the integer and noninteger *n* GETO and GETOHC are more efficient than GTO and STO [1–4]. Therefore, it is desirable to use GETO and GETOHC basis functions in electronic structure calculations of atoms and molecules. In a previous paper [5], the series expansion formulae were presented for two-center charge densities of integer and noninteger *n* GETO in terms of complete orthonormal sets of ψ^{α}-ETO [6]. The aim of this work is to establish the formulae for GETOHC charge densities and evaluate the multicenter multielectron integrals over GETOHC.

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2 Definitions and basic formulas

The normalized GETOHC functions are defined as

$$\Phi^{\kappa}_{n^*lm}(\zeta,\beta,\gamma;\vec{r}) = R_{n^*}(\kappa,\zeta,\beta,\gamma;r)\,S_{lm}(\theta,\varphi) \tag{1}$$

$$R_{n^*}(\kappa,\zeta,\beta,\gamma;r) = A_{n^*}(\kappa,\zeta,\beta,\gamma)\,r^{n^*-1}e^{-\zeta r^{\kappa}}\cosh\left(\beta r^{\kappa}+\gamma\right). \tag{2}$$

Here, the parameter γ can be either positive, zero or negative, $\kappa > 0, \zeta > 0, -\zeta < \beta < \zeta$,

$\cosh(\beta r^{\kappa}+\gamma) = \frac{1}{2}\left(e^{\beta r^{\kappa}+\gamma} + e^{-\beta r^{\kappa}-\gamma}\right)$ and

$$A_{n^*}(\kappa,\zeta,\beta,\gamma) = \left\{\frac{1}{4\kappa}\Gamma\left(\frac{2n^*+1}{\kappa}\right)\sum_{i=-1}^{1}(1+\delta_{i0})\frac{e^{-i\gamma}}{[2(\zeta+i\beta)]^{\frac{2n^*+1}{\kappa}}}\right\}^{-1/2}. \tag{3}$$

We notice that the Φ^{κ}-GETOHC functions are not orthogonal with respect to the principal quantum numbers, i.e.,

$$\begin{aligned}
&\int \Phi^{\kappa^*}_{n^*lm}(\zeta,\beta,\gamma;\vec{r})\Phi^{\kappa}_{n'^*l'm'}(\zeta,\beta,\gamma;\vec{r})\,d^3\vec{r}\\
&= \delta_{ll'}\delta_{mm'}\frac{1}{4\kappa}A_{n^*}(\kappa,\zeta,\beta,\gamma)\,A_{n'^*}\left(\kappa,\zeta',\beta',\gamma'\right)\Gamma\left(\frac{n^*+n'^*+1}{\kappa}\right)\\
&\quad\times\sum_{i=-1}^{1}{}'\sum_{i'=-1}^{1}{}'\frac{e^{-i\gamma-i'\gamma'}}{[(\zeta+\zeta'+i\beta+i'\beta')]^{\frac{n^*+n'^*+1}{\kappa}}}.
\end{aligned} \tag{4}$$

The special cases of Φ^{κ}-GETOHC for $\beta = 0$ and $\gamma = 0$ correspond to the φ^{κ}-GETO, χ-STO and G-GTO, i.e.,

$$\Phi^{\kappa}_{n^*lm}(\zeta,0,0;\vec{r}) = \begin{cases}\varphi^{\kappa}_{n^*lm}(\zeta,\vec{r}) & \text{for}\quad \kappa > 0\\ \chi^{\kappa}_{n^*lm}(\zeta,\vec{r}) & \text{for}\quad \kappa = 1.\\ G^{\kappa}_{n^*lm}(\zeta,\vec{r}) & \text{for}\quad \kappa = 2\end{cases} \tag{5}$$

3 Use of φ^{κ}-GETO in evaluation of multicenter multielectron integrals of Φ^{κ}-GETOHC

The two-center charge densities and multicenter integrals of GETOHC examined in this work have the following form:

$$\mathrm{P}^{\kappa}_{p^*p'^*}\left(\zeta,\beta,\gamma,\vec{r}_a;\zeta',\beta',\gamma',\vec{r}_c\right) = \Phi^{\kappa}_{p^*}(\zeta,\beta,\gamma;\vec{r}_a)\,\Phi^{\kappa^*}_{p'^*}\left(\zeta',\beta',\gamma';\vec{r}_c\right) \tag{6}$$

$$\begin{aligned}
&Q^{\kappa acbd\ldots ef}_{p_1^*p_1'^*,p_2^*p_2'^*,\ldots,p_s^*p_s'^*}\left(\zeta_1\beta_1\gamma_1\zeta_1'\beta_1'\gamma_1',\zeta_2\beta_2\gamma_2\zeta_2'\beta_2'\gamma_2',\ldots,\zeta_s\beta_s\gamma_s\zeta_s'\beta_s'\gamma_s'\right)\\
&= \int F^{(s)}\mathrm{P}^{\kappa^*}_{p_1^*p_1'^*}\left(\zeta_1,\beta_1,\gamma_1,\vec{r}_{a1};\zeta_1',\beta_1',\gamma_1',\vec{r}_{c1}\right)
\end{aligned}$$

$$\times \mathrm{P}^{\kappa}_{p_2^* p_2'^*}\left(\zeta_2, \beta_2, \gamma_2, \vec{r}_{b2}; \zeta_2', \beta_2', \gamma_2', \vec{r}_{d2}\right)$$
$$\times \cdots \times \mathrm{P}^{\kappa}_{p_s^* p_s'^*}\left(\zeta_s, \beta_s, \gamma_s, \vec{r}_{es}; \zeta_s', \beta_s', \gamma_s', \vec{r}_{fs}\right) \mathrm{d}v_1 \mathrm{d}v_2 \ldots \mathrm{d}v_s, \tag{7}$$

where $p^* \equiv n^* lm$, $p'^* \equiv n'^* l'm'$, $p_i^* \equiv n_i^* l_i m_i$, $p_i'^* \equiv n'^*{}_i l'{}_i m'{}_i$, $s = 1, 2, \ldots$ Here, $F^{(s)}$ is the arbitrary s-electron operator (see [6–9]).

In order to obtain the formulae for multicenter charge densities and integrals of Φ^{κ}-GETOHC functions we use the following relation for Φ^{κ}-GETOHC in terms of φ^{κ}-GETO:

$$\Phi^{\kappa}_{n^* lm}(\zeta, \beta, \gamma; \vec{r}) = \frac{1}{2} A_{n^*}(\kappa, \zeta, \beta, \gamma) \sum_{i=-1}^{1}{}' \frac{e^{-i\gamma}}{A_{n^*}(\kappa, \zeta_i)} \varphi^{\kappa}_{n^* lm}(\zeta_i, \vec{r}), \tag{8}$$

where $\zeta_i = \zeta + i\beta$.

Taking into account Eq. (8) in (6) and (7) we obtain:

$$\mathrm{P}^{\kappa}_{p^* p'^*}\left(\zeta, \beta, \gamma, \vec{r}_a; \zeta', \beta', \gamma', \vec{r}_c\right)$$
$$= \frac{1}{4} A_{n^*}(\kappa, \zeta, \beta, \gamma) A_{n'^*}\left(\kappa, \zeta', \beta', \gamma'\right)$$
$$\times \sum_{i=-1}^{1}{}' \sum_{i'=-1}^{1}{}' \frac{e^{-i\gamma - i'\gamma'}}{A_{n^*}(\kappa, \zeta_i) A_{n'^*}\left(\kappa, \zeta_{i'}'\right)} \times \rho^{\kappa}_{p^* p'^*}\left(\zeta_i, \vec{r}_a; \zeta_{i'}', \vec{r}_c\right) \tag{9}$$

$$Q^{\kappa acbd \ldots ef}_{p_1^* p_1'^*, p_2^* p_2'^*, \cdots, p_s^* p_s'^*}\left(\zeta_1\beta_1\gamma_1\zeta_1'\beta_1'\gamma_1', \zeta_2\beta_2\gamma_2\zeta_2'\beta_2'\gamma_2', \ldots, \zeta_s\beta_s\gamma_s\zeta_s'\beta_s'\gamma_s'\right)$$
$$= \frac{1}{4} A_{n_1^*}(\kappa, \zeta_1, \beta_1, \gamma_1) A_{n_1'^*}\left(\kappa, \zeta_1', \beta_1', \gamma_1'\right)$$
$$\times \sum_{i_1=-1}^{1}{}' \sum_{i_1'=-1}^{1}{}' \frac{e^{-i_1\gamma_1 - i_1'\gamma_1'}}{A_{n_1^*}\left(\kappa, \zeta_{i_1}\right) A_{n_1'^*}\left(\kappa, \zeta_{i'_1}'\right)}$$
$$\times \frac{1}{4} A_{n_2^*}(\kappa, \zeta_2, \beta_2, \gamma_2) A_{n_2'^*}\left(\kappa, \zeta_2', \beta_2', \gamma_2'\right)$$
$$\times \sum_{i_2=-1}^{1}{}' \sum_{i_2'=-1}^{1}{}' \frac{e^{-i_2\gamma_2 - i_2'\gamma_2'}}{A_{n_2^*}\left(\kappa, \zeta_{i_2}\right) A_{n_2'^*}\left(\kappa, \zeta_{i_2'}'\right)}$$
$$\times \cdots \times \frac{1}{4} A_{n_s^*}(\kappa, \zeta_s, \beta_s, \gamma_s) A_{n_s'^*}\left(\kappa, \zeta_s', \beta_s', \gamma_s'\right)$$
$$\times \sum_{i_s=-1}^{1}{}' \sum_{i_s'=-1}^{1}{}' \frac{e^{-i_s\gamma_s - i_s'\gamma_s'}}{A_{n_s^*}\left(\kappa, \zeta_{i_s}\right) A_{n_s'^*}\left(\kappa, \zeta_{i_s'}'\right)}$$
$$\times \mathrm{I}^{\kappa acbd \ldots ef}_{p_{i_1}^* p'^*_{i_1'}, p_{i_2}^* p'^*_{i_2'}, \ldots, p_{i_s}^* p'^*_{i_s'}}\left(\zeta_{i_1}\zeta_{i_1'}', \zeta_{i_2}\zeta_{i_2'}', \ldots, \zeta_{i_s}\zeta_{i_s'}'\right). \tag{10}$$

See [5] for the exact definition of quantities ρ^{κ} and $\mathrm{I}^{\kappa acbd \ldots ef}$. Thus, the formulae derived for the two-center charge densities and multicenter multielectron integrals of

φ^{κ}-GETO in a previous paper [5] can be used in the evaluation of arbitrary multicenter multielectron integrals arising in the HFR approximation and explicitly correlated methods when the Φ^{κ}-GETOHC, φ^{κ}-GETO, χ-STO and G-GTO are employed as basis functions.

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