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ORIGINAL PAPER

Expansion formulae for two-center charge densities of integer and noninteger *n* generalized exponential type orbitals applied to evaluation of multicenter multielectron integrals

I. I. Guseinov

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Abstract The series expansion formulae in terms of complete orthonormal sets of Ψ^{α}-exponential type orbitals introduced by the author are derived for the two-center charge densities of integer and noninteger n generalized exponential functions. The expansion coefficients arising in these relations are the multicenter overlap integrals of three Ψ^{α}-functions. The charge density expansion formulae obtained are utilized for the evaluation of multicenter multielectron integrals appearing in the Hartree–Fock–Roothaan and explicitly correlated theories when the generalized exponential type orbitals are employed as basis functions.

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

1 Introduction

It is well known that the Slater and Gaussian type orbitals (STO and GTO) introduced in Refs. [1–3] are not orthogonal with respect to the principal quantum numbers that creates some difficulties arising in the solution of different atomic and molecular problems when the Hartree–Fock–Roothaan (HFR) and explicitly correlated theories are employed. Thus, the necessity for using the complete orthonormal sets of Ψ^{α}-exponential type orbitals (Ψ^{α}-ETO) arises in the atomic and molecular electronic structure calculations [4]. The aim of this paper is to derive the formulae for the expansion of integer and noninteger n generalized exponential type orbitals (GETO) charge densities in terms of Ψ^{α}-ETO and to evaluate the multicenter multielectron integrals over GETO. We notice that the method used in this work is the development of

I. I. Guseinov (✉)
Department of Physics, Faculty of Arts and Sciences, Onsekiz Mart University, Çanakkale, Turkey
e-mail: isguseinov@yahoo.com

previous paper [5] in which the formulae for expansion and multicenter multielectron integrals over integer and noninteger n STO have been established.

2 Definitions and basic formulas

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

charge density of φ^{κ}-GETO

$$\rho^{\kappa}_{p^* p'^*}\left(\zeta, \vec{r}_a; \zeta', \vec{r}_c\right) = \varphi^{\kappa}_{p^*}\left(\zeta, \vec{r}_a\right) \varphi^{\kappa}_{p'^*}{}^{*}\left(\zeta', \vec{r}_c\right), \tag{1}$$

multicenter multielectron integrals with φ^{κ}-GETO

$$\begin{aligned} &I^{\kappa\, acbd\ldots ef}_{p_1^* p_1'^*, p_2^* p_2'^*, \ldots, p_s^* p_s'^*}\left(\zeta_1\zeta_1', \zeta_2\zeta_2', \ldots, \zeta_s\zeta_s'\right) \\ &= \int F^{(s)} \rho^{\kappa *}_{p_1^* p_1'^*}\left(\zeta_1, \vec{r}_{a1}; \zeta_1', \vec{r}_{c1}\right) \rho^{\kappa}_{p_2^* p_2'^*}\left(\zeta_2, \vec{r}_{b2}; \zeta_2', \vec{r}_{d2}\right) \\ &\quad \ldots \rho^{\kappa}_{p_s^* p_s'^*}\left(\zeta_s, \vec{r}_{es}; \zeta_s', \vec{r}_{fs}\right) dv_1 dv_2 \ldots dv_s, \end{aligned} \tag{2}$$

where $p^* \equiv n^* lm$, $p'^* \equiv n'^* l'm'$, $p_i^* \equiv n_i^* l_i m_i$, $p_i'^* \equiv n_i'^* l_i' m_i'$, $s = 1, 2, 3, \ldots$ and $F^{(s)}$ is the arbitrary s-electron operator (see, e.g., Refs. [6–8]). Here, the $\varphi^{\kappa}_{p^*}\left(\zeta, \vec{r}_g\right)$ are the normalized GETO with noninteger n^* or integer n (for $n^* \equiv n$) principal quantum numbers which are centred on the nuclei $g (g \equiv a, c, b, d, \ldots, e, f)$ and $\kappa > 0$. These functions are defined by [9]

$$\varphi^{\kappa}_{n^* lm}(\zeta, \vec{r}) = R_{n^*}(\kappa, \zeta; r) S_{lm}(\theta, \varphi) \tag{3}$$

$$R_{n^*}(\kappa, \zeta; r) = A_{n^*}(\kappa, \zeta) r^{n^*-1} e^{-\zeta r^{\kappa}} \tag{4}$$

$$A_{n^*}(\kappa, \zeta) = \left[\kappa (2\zeta)^{\frac{2n^*+1}{\kappa}} \Big/ \Gamma\left(\frac{2n^*+1}{\kappa}\right)\right]^{\frac{1}{2}}, \tag{5}$$

where $\Gamma(x)$ and $S_{lm}(\theta, \varphi)$ are the gamma function and the complex ($S_{lm} \equiv Y_{lm}$) or real spherical harmonics, respectively. It should be noted that our definition of phases for the complex spherical harmonics ($Y^*_{lm} \equiv Y_{l-m}$) differs from the Condon-Shortley phases [10] by sign factor $(-1)^m$. In a previous paper [11] we have investigated the efficiency of noninteger n φ^{κ}-GETO in energy calculations for some atoms. As stated above, the φ^{κ}-GETO are not orthogonal with repect to the principal quantum numbers, i.e.,

$$\int \varphi^{\kappa *}_{n^* lm}(\zeta, \vec{r}) \varphi^{\kappa}_{n'^* l'm'}(\zeta, \vec{r}) d^3\vec{r} = \delta_{ll'}\delta_{mm'} \frac{\Gamma\left(\frac{n^*+n'^*+1}{\kappa}\right)}{\left[\Gamma\left(\frac{2n^*+1}{\kappa}\right)\Gamma\left(\frac{2n'^*+1}{\kappa}\right)\right]^{\frac{1}{2}}}. \tag{6}$$

The special cases of φ^{κ}-GETO for $\kappa = 1$ and $\kappa = 2$ correspond to the STO and GTO, respectively, i.e.,

$$\chi_{n^*lm}(\zeta,\vec{r}) = \varphi^{1}_{n^*lm}(\zeta,\vec{r}) = (2\zeta)^{n^*+\frac{1}{2}}\left[\Gamma\left(2n^*+1\right)\right]^{-\frac{1}{2}} r^{n^*-1}e^{-\zeta r}S_{lm}(\theta,\varphi) \tag{7}$$

$$G_{n^*lm}(\zeta,\vec{r}) = \varphi^{2}_{n^*lm}(\zeta,\vec{r}) = \left[2\,(2\zeta)^{n^*+\frac{1}{2}} \Big/ \Gamma\left(\frac{2n^*+1}{2}\right)\right]^{\frac{1}{2}} r^{n^*-1}e^{-\zeta r^2}S_{lm}(\theta,\varphi). \tag{8}$$

The normalized φ^{κ}-GETO, χ-*STO* and *G-GTO* with integer principal quantum numbers can be obtained from Eqs. 3, 7 and 8 for $n^* = n$, where n is an integer.

In the present paper, we report applications of complete orthonormal sets of Ψ^{α}-ETO determined by [4]

$$\Psi^{\alpha}_{nlm}(\zeta,\vec{r}) = (-1)^{\alpha}\left[\frac{(2\zeta)^3\,(q-p)!}{(2n)^{\alpha}\,(q!)^3}\right]^{1/2} x^l e^{-x/2}L^{p}_{q}(x)\,S_{lm}(\theta,\varphi) \tag{9}$$

to the study of charge densities and multicenter multielectron integrals of φ^{κ}-GETO.

Here $\alpha = 1, 0, -1, -2, \ldots$, $p = 2l+2-\alpha$, $q = n+l+1-\alpha$ and $x = 2\zeta r$; $L^{p}_{q}(x)$ are the generalized Laguerre polynomials [12]. The Ψ^{α}-ETO are orthonormal with respect to the weight function $(n/\zeta r)^{\alpha}$,

$$\int \Psi^{\alpha\,*}_{nlm}(\zeta,\vec{r})\,\overline{\Psi}^{\alpha}_{n'l'm'}(\zeta,\vec{r})d^3\vec{r} = \delta_{nn'}\delta_{ll'}\delta_{mm'}, \tag{10}$$

where

$$\overline{\Psi}^{\alpha}_{nlm}(\zeta,\vec{r}) = (n/\zeta r)^{\alpha}\,\Psi^{\alpha}_{nlm}(\zeta,\vec{r})\,. \tag{11}$$

3 Expansions of φ^{κ}-charge densities

For the evaluation of multicenter multielectron integrals of φ^{κ}-GETO, we first obtain the general expansion formulae for the two-center φ^{κ}-GETO charge densities in terms of Ψ^{α}-ETO at a third center. Taking into account Eqs. 9–11 and the properties of Ψ^{α}-ETO we obtain:

$$\rho^{\kappa}_{p^*p'^*}\left(\zeta,\vec{r}_a;\zeta',\vec{r}_c\right) = \frac{1}{\sqrt{4\pi}}\sum_{\mu=1}^{\infty}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} {}^{\kappa}W^{\alpha\;acb\,*}_{p^*p'^*q}\left(\zeta,\zeta',z\right)\Psi^{\alpha}_{q}(z,\vec{r}_b), \tag{12}$$

where $q \equiv \mu\nu\sigma$, $z = \zeta + \zeta'$ and

$${}^{\kappa}W^{\alpha\;acb}_{p^*p'^*q}\left(\zeta,\zeta',z\right) = \sqrt{4\pi}\int \varphi^{\kappa}_{p^*}{}^{*}(\zeta,\vec{r}_a)\varphi^{\kappa}_{p'^*}\left(\zeta',\vec{r}_c\right)\overline{\Psi}^{\alpha}_{q}(z,\vec{r}_b)\,d^3\vec{r}. \tag{13}$$

Using equations

$$\varphi^{\kappa}_{n^*lm}(\zeta,\vec{r}) = \sum_{n=l+1}^{\infty} \overline{\omega}^{\kappa\alpha l}_{n^*n}(\zeta)\Psi^{\alpha}_{nlm}(\zeta,\vec{r}) \tag{14}$$

$$\begin{aligned}\overline{\omega}^{\kappa\alpha l}_{n^*n}(\zeta) &= \int \varphi^{\kappa *}_{n^*lm}(\zeta,\vec{r})\overline{\Psi}^{\alpha}_{nlm}(\zeta,\vec{r})\,d^3\vec{r} \\ &= \frac{1}{(2\zeta)^{n^*+\frac{1}{2}}} A_{n^*}(\kappa,\zeta)\,\overline{N}^{\alpha}_{nl}\sum_{s=0}^{q-p}\gamma^{p}_{qs} I^{\kappa\alpha l}_{n^*s}(\zeta),\end{aligned} \tag{15}$$

where

$$I^{\kappa\alpha l}_{n^*s}(\zeta) = \int_0^{\infty} t^{n^*+l-\alpha+s+1} e^{-\beta_\kappa t^{\kappa}-\frac{1}{2}t}\,dt, \tag{16}$$

we obtain for the expansion coefficients ${}^{\kappa}W^{\alpha}$ the following relation in terms of three-center overlap integrals of Ψ^{α}-ETO:

$${}^{\kappa}W^{\alpha acb}_{p^*p'^*q}(\zeta,\zeta',z) = \sum_{\mu_1=l+1}^{\infty}\sum_{\mu_1'=l'+1}^{\infty} \overline{\omega}^{\kappa\alpha l}_{n^*\mu_1}(\zeta)\overline{\omega}^{\kappa\alpha l'}_{n'^*\mu_1'}(\zeta')S^{\alpha\,acb}_{q_1q_1'q}(\zeta,\zeta',z), \tag{17}$$

where $\beta_\kappa = \frac{\zeta}{(2\zeta)^{\kappa}}$, $q_1 \equiv \mu_1 lm$, $q_1' \equiv \mu_1' l'm'$, $\vec{r}_b = \vec{r}$, $\vec{r}_a = \vec{r} - \vec{R}_{ba}$, $\vec{r}_c = \vec{r} - \vec{R}_{bc}$ and

$$\begin{aligned}S^{\alpha\,acb}_{pp'q}(\zeta,\zeta',z) &= \sqrt{4\pi}\int \Psi^{\alpha *}_{p}(\zeta,\vec{r}_a)\Psi^{\alpha}_{p'}(\zeta',\vec{r}_c)\,\overline{\Psi}^{\alpha}_{q}(z,\vec{r}_b)\,d^3\vec{r} \\ &= \sqrt{4\pi}\int \Psi^{\alpha *}_{p}\left(\zeta,\vec{r}-\vec{R}_{ba}\right)\Psi^{\alpha}_{p'}\left(\zeta',\vec{r}-\vec{R}_{bc}\right)\overline{\Psi}^{\alpha}_{q}(z,\vec{r})\,d^3\vec{r}.\end{aligned} \tag{18}$$

Thus, the φ^{κ}-charge densities are expressed through the multicenter overlap integrals of three Ψ^{α}-ETO. See Ref. [13] for the exact definition of coefficients $\overline{N}^{\alpha}_{nl}$ and γ^{p}_{qs} occurring in Eq. 15.

In special cases of $\kappa = 1$ (for STO) and $\kappa = 2$ (for GTO), the integral $I^{\kappa\alpha l}_{n^*s}(\zeta)$ occurring in Eq. 15 can be reduced to the following analytical relations (see Ref. [12]):

$$I^{1\alpha l}_{n^*s}(\zeta) = \Gamma(n^*+l-\alpha+s+2) \tag{19}$$

$$\begin{aligned}I^{2\alpha l}_{n^*s}(\zeta) = (2\zeta)^{\frac{1}{2}(n^*+l-\alpha+s+2)}\,\Gamma(n^*+l-\alpha+s+2)e^{2\zeta/16} \\ \times D_{-(n^*+l-\alpha+s+2)}(\sqrt{2\zeta}/2),\end{aligned} \tag{20}$$

where $D_{-\nu}$ is the parabolic cylinder function [14].

We notice that, when n^* is restricted to be an integer ($n^* = n$), the expansion coefficients $\overline{\omega}^{\kappa\alpha l}_{n^* n}(\zeta)$ for $\kappa = 1$ have a form

$$\overline{\omega}^{1\alpha l}_{n\mu}(\zeta) = \begin{cases} \overline{\omega}^{\alpha l}_{n\mu} & \text{for } l+1 \le \mu \le n \\ 0 & \text{for } \mu < l+1, \mu > n. \end{cases} \tag{21}$$

See Ref. [4] for the exact definition of $\overline{\omega}^{\alpha l}_{n\mu}$.

In order to evaluate the multicenter overlap integrals of three Ψ^α-ETO we use the following one-range addition theorems [15]:

$$\Psi^\alpha_p\left(\zeta, \vec{r} - \vec{R}_{hg}\right) = \sum_{u=1}^{\infty} \sum_{v=0}^{u-1} \sum_{s=-v}^{v} \overline{S}^{\alpha *}_{pk}\left(\vec{G}_{gh}\right) \Psi^\alpha_k(\zeta, \vec{r}), \tag{22}$$

where $k \equiv uvs$, $\vec{G}_{gh} = 2\zeta \vec{R}_{gh}$ and

$$\overline{S}^{\alpha}_{pk}\left(\vec{G}_{gh}\right) = \int \Psi^{\alpha *}_p(\zeta, \vec{r}_g)\, \overline{\Psi}^\alpha_k(\zeta, \vec{r}_h)\, dv = \int \Psi^{\alpha *}_p(\zeta, \vec{r} - R_{hg})\, \overline{\Psi}^\alpha_k(\zeta, \vec{r})\, d^3\vec{r}. \tag{23}$$

The formulae for the two-center overlap integrals $\overline{S}^\alpha_{pk}\left(\vec{G}_{gh}\right)$ are presented in [15].

Using Eq. 22 in 18 we obtain for overlap integrals of three Ψ^α-ETO the following relations through the overlap integrals with two Ψ^α-ETO:
for three-center cases ($a \not\equiv b, a \not\equiv c, c \not\equiv b$)

$$\begin{aligned} &S^{\alpha\, acb}_{pp'q}(\zeta, \zeta', z) \\ &= (2z)^{\frac{3}{2}} \sum_{u=1}^{\infty} \sum_{v=0}^{u-1} \sum_{s=-v}^{v} \sum_{u'=1}^{\infty} \sum_{v'=0}^{u'-1} \sum_{s'=-v'}^{v'} B^{\alpha q}_{kk'}(\zeta, \zeta', z) \overline{S}^\alpha_{pk}\left(\vec{G}_{ab}\right) \overline{S}^{\alpha *}_{p'k'}\left(\vec{G}'_{cb}\right), \end{aligned} \tag{24}$$

for two-center cases ($a \not\equiv b, a \not\equiv c, c \equiv b; a \equiv b, a \not\equiv c$)

$$S^{\alpha\, abb}_{pp'q}(\zeta, \zeta', z) = (2z)^{3/2} \sum_{u=1}^{\infty} \sum_{v=0}^{u-1} \sum_{s=-v}^{v} B^{\alpha q}_{kp'}(\zeta, \zeta', z)\, \overline{S}^\alpha_{pk}\left(\vec{G}_{ab}\right) \tag{25a}$$

$$S^{\alpha\, bcb}_{pp'q}(\zeta, \zeta', z) = (2z)^{3/2} \sum_{u'=1}^{\infty} \sum_{v'=0}^{u'-1} \sum_{s'=-v'}^{v'} B^{\alpha q}_{pk'}(\zeta, \zeta', z)\, \overline{S}^{\alpha *}_{p'k'}\left(\vec{G}'_{cb}\right), \tag{25b}$$

for one-center case ($a \equiv b \equiv c$)

$$S^{\alpha\, bbb}_{pp'q}(\zeta, \zeta', z) \equiv S^\alpha_{pp'q}(\zeta, \zeta', z) = (2z)^{3/2} B^{\alpha q}_{pp'}(\zeta, \zeta', z), \tag{26}$$

where $k \equiv uvs$, $k' \equiv u'v's'$, $\vec{G}_{ab} = 2\zeta \vec{R}_{ab}$, $\vec{G}'_{cb} = 2\zeta' \vec{R}_{cb}$ and

$$B^{\alpha q}_{pp'}\left(\zeta, \zeta', z\right) = \frac{\sqrt{4\pi}}{(2z)^{3/2}} \int \Psi^{\alpha *}_{p}(\zeta, \vec{r}) \Psi^{\alpha}_{p'}\left(\zeta', \vec{r}\right) \overline{\Psi}^{\alpha}_{q}(z, \vec{r})\, d^3\vec{r}. \tag{27}$$

See Ref. [13] for the exact definition of coefficients $B^{\alpha q}_{pp'}\left(\zeta, \zeta', z\right)$.

4 Expression for multicenter multielectron integrals of φ^{κ}-GETO

In order to evaluate the 2s-center multielectron integrals we use Eq. 12 for all the φ^{κ}-charge densities which occur in Eq. 2. Then, we obtain the following expression in terms of the expansion coefficients ${}^{\kappa}W^{\alpha}$ and the one-center s-electron basic integrals:

$$\begin{aligned} &I^{\kappa\, acbd\ldots ef}_{p_1^* p_{1,}'^* p_2' p_2'^*, \ldots, p_s^* p_s'^*}(\zeta_1\zeta_1', \zeta_2\zeta_2', \ldots, \zeta_s\zeta_s') \\ &\quad = \sum_{\mu_1\nu_1\sigma_1} {}^{\kappa}W^{\alpha\, aca*}_{p_1^* p_1'^* q_1}\left(\zeta_1, \zeta_1', z_1; 0, \vec{R}_{ac}\right) \\ &\qquad \times \sum_{\mu_2\nu_2\sigma_2} {}^{\kappa}W^{\alpha\, bda}_{p_2^* p_2'^* q_2}\left(\zeta_2, \zeta_2', z_2; \vec{R}_{ab}, \vec{R}_{ad}\right) \ldots \\ &\qquad \times \sum_{\mu_s\nu_s\sigma_s} {}^{\kappa}W^{\alpha\, efa}_{p_s^* p_s'^* q_s}\left(\zeta_s, \zeta_s', z_s; \vec{R}_{ae}, \vec{R}_{af}\right) J^{\alpha}_{q_1 q_2 \ldots q_s}(z_1 z_2 \ldots z_s), \end{aligned} \tag{28}$$

where $1 \le \mu_i \le \infty, 0 \le \nu_i \le \mu_i - 1, -\nu_i \le \sigma_i \le \nu_i$ *and* $1 \le i \le s$. The one-center s-electron basic integrals are defined as

$$\begin{aligned} &J^{\alpha}_{q_1 q_2 \ldots q_s}(z_1 z_2 \ldots z_s) \\ &\quad = \frac{1}{(4\pi)^{\frac{s}{2}}} \int \Psi^{\alpha\,*}_{q_1}(z_1, \vec{r}_1) \Psi^{\alpha}_{q_2}(z_2, \vec{r}_2) \ldots \Psi^{\alpha}_{q_s}(z_s, \vec{r}_s)\, dv_1 dv_2 \ldots dv_s. \end{aligned} \tag{29}$$

Now we use the relation [4]

$$\Psi^{\alpha}_{nlm}(\zeta, \vec{r}) = \sum_{\mu=l+1}^{n} \omega^{\alpha l}_{n\mu} \chi_{\mu lm}(\zeta, \vec{r}), \tag{30}$$

where $\chi_{\mu lm}(\zeta, \vec{r})$ are the STO. Then, Eq. 29 can be expressed through the one-center s-electron basic integrals of STO (see Ref. [5]). The formulas presented in our previous papers for the multicenter integrals of STO can be also used to calculate multicenter multielectron integrals over complete orthonormal sets of Ψ^{α}-ETO.

Thus, by the use of the series expansion formulae for multicenter multielectron integrals of φ^{κ}-GETO presented in this study, one can calculate all the multielectron molecular integrals arising in the determination of various properties for a given molecule when the complete orthonormal sets of Ψ^{α}-ETO are used in HFR and explicitly correlated theories. We notice that the two- and three-center overlap integrals

with three Ψ^{α}-ETO appearing in expansion coefficients ${}^{\kappa}W^{\alpha}$ can be calculated using two-center ovelap integrals of two STO for the computation of which efficient computer programs are available in our group (see Ref. [16] and references quoted therein to our papers for overlap integrals of STO).

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