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Expansion formulae for two-center integer and noninteger n STO charge densities and their use in evaluation of multi-center integrals

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Using complete orthonormal sets of Ψ^{α}-exponential type orbitals (Ψ^{α}-ETOs, $\alpha = 1, 0, -1, -2, \ldots$) introduced by the author, the series expansion formulae are derived for the two-center integer and noninteger n STO (ISTO and NISTO) charge densities in terms of integer n STOs at a third center. The expansion coefficients occurring in these relations are presented through the two-center overlap integrals between STOs with integer and noninteger principal quantum numbers. The general formulae obtained for the STO charge densities are utilized for the evaluation of two-center Coulomb and hybrid integrals of NISTOs appearing in the Hartee–Fock–Roothaan approximation. The final results are expressed in terms of both the overlap integrals and the one-center basic integrals over integer n STOs. It should be noted that the result for the multi-center multielectron integrals with two-center noninteger n STO charge densities presented in this paper were not appeared in our past publications.

KEY WORDS: Slater type orbitals, noninteger principal quantum numbers, charge densities, multi-center integrals

1. Introduction

It is well known that the STOs with integer and noninteger principal quantum numbers describe the physical situation more accurately than do GTOs because they satisfy the cusp condition at the nuclei [1] and exponential decay at large distances [2]. The main problem for the use of ISTOs and NISTOs basis in molecular calculations arises in the evaluation of the multi-center integrals. The large body of formulas developed by the use of the expansion methods for STOs about a displaced center [3–12], the Fourier transform method [13–15], the B-function method [16–17], and the ellipsoidal coordinates method (see [18] and references therein) for the evaluation of multi-center molecular integrals with ISTOs and NISTOs were not entirely successful. One of the most promising methods for the evaluation of multi-center molecular integrals over STOs is the use of complete orthonormal sets of Ψ^{α}-ETOs [19]. The aim of this report is

with the help of these functions to provide the general formulas for the expansion of ISTO and NISTO charge densities and to evaluate the multi-center multi-electron integrals. The series expansion relations obtained are especially useful for the computation of multi-center molecular integrals appearing in the determination of various properties of molecules when ISTO and NISTO basis is used in the Hartree–Fock–Roothaan theory. We notice that the method used in this work is an extension of the results of Ref. [19] to the case of NISTOs in which the formulas for the multi-center integrals over ISTOs have been established.

2. Expansion of NISTOs in terms of ISTOs at a new origin

The normalized NISTOs with nonintegral values of the principal quantum number n^* are defined by

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

In equation (1), ζ is the screening constant and $\Gamma(x)$ is the gamma function [20]. $S_{lm}(\theta, \varphi)$ is a complex or real spherical harmonic. The normalized ISTOs can be obtained from equation (1) for $n^* = n$, where n is an integer:

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

The procedure for expansion of NISTOs and ISTOs in terms of ISTOs at a displaced center is one and the same. Therefore for obtaining the expansion of NISTOs about a new center by the use of complete orthonormal sets of Ψ^α-ETOs we can use the method for the expansion of ISTOs set out in a previous paper [19]. Carrying through calculations for the NISTOs analogous to those for the ISTOs, we obtain finally the formulas for the expansion of NISTOs in terms of ISTOs at a new origin:

$$\chi_{n^*lm}(\zeta, \vec{r}_a) = \lim_{N\to\infty} \begin{cases} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} V^{*\alpha N}_{n^*lm,\mu\nu\sigma}(\zeta, \zeta; \vec{R}) \chi_{\mu\nu\sigma}(\zeta, \vec{r}_b) & \text{for} \quad R \neq 0, \\ \sum_{\mu=l+1}^{N} V^{*\alpha N}_{n^*l,\mu l} \chi_{\mu lm}(\zeta, \vec{r}_a) & \text{for} \quad R = 0, \end{cases} \tag{3a, b}$$

where $\vec{R} \equiv \vec{R}_{ab}$, $\alpha = 1, 0, -1, -2, \ldots$ and the expansion coefficients $V^{\alpha N}$ are determined as follows:

$$V^{\alpha N}_{n^*lm,\mu\nu\sigma}\left(\zeta,\zeta;\vec{R}\right) = \sum_{\mu'=\nu+1}^{N} \Omega^{\alpha\,\nu}_{\mu\mu'}(N) S_{n^*lm,\mu'-\alpha\,\nu\sigma}\left(\zeta,\zeta;\vec{R}\right), \tag{4a}$$

$$V^{\alpha N}_{n^*l,\mu l} = \sum_{\mu'=l+1}^{N} \Omega^{\alpha\,l}_{\mu\mu'}(N) \frac{\Gamma(n^*+\mu'-\alpha+1)}{\sqrt{\Gamma(2n^*+1)\Gamma(2(\mu'-\alpha)+1)}}, \tag{4b}$$

$$\Omega^{\alpha\nu}_{\mu\kappa}(N) = \left[\frac{[2(k-\alpha)]!}{(2\kappa)!}\right]^{1/2} \sum_{\mu'=\max(\mu,\kappa)}^{N} (2\mu')^{\alpha} \omega^{\alpha\,\nu}_{\mu\mu'}\,\omega^{\alpha\nu}_{\mu'\kappa}, \tag{5}$$

$$\omega^{\alpha\,\nu}_{\mu\mu'} = (-1)^{\mu'-\nu-1}\left[\frac{(\mu'+\nu+1)!}{(2\mu)^{\alpha}(\mu'+\nu+1-\alpha)!} F_{\mu'+\nu+1-\alpha}(\mu+\nu+1-\alpha)\right.$$
$$\left.\times F_{\mu'-\nu-1}(\mu-\nu-1)\; F_{\mu'-\nu-1}(2\mu')\right]^{1/2}. \tag{6}$$

Here $F_{\mu}(k) = k!/[\mu!(k-\mu)!]$ and the quantities $S_{n^*lm,\mu\nu\sigma}$ are the overlap integrals between the normalized NISTOs and ISTOs:

$$S_{n^*lm,\mu\nu\sigma}\left(\zeta,\zeta;\vec{R}\right) = \int \chi^{*}_{n^*lm}(\zeta,\vec{r}_a)\chi_{\mu\nu\sigma}(\zeta,\vec{r}_b)\mathrm{d}V. \tag{7}$$

We notice that for $n^* = n$ the expansion coefficients $V^{\alpha N}$ occurring in equation (3b) are reduced to the Konecker symbol, i.e.

$$V^{\alpha N}_{nl,\mu l} = \delta_{N\mu}\delta_{\mu n}. \tag{8}$$

As can be seen from equations (3a) and (4a), the coefficients for expansion of NISTOs for $R \neq 0$ are expressed through the noninteger n^* overlap integrals with the same screening constants defined by equation (7). It should be noted that the expansion formulas obtained in this paper can also be used in the case of integer values of n^*: for $n^* = n$, where n is an integer, equation (3a) becomes the series expansion formulas for translation of ISTOs (see, equation (15) of Ref. [19]).

3. Expansion of NISTO charge densities

For the evaluation of multi-center molecular integrals with NISTOs, we first obtain the expansion formulas for two-center charge density over NISTOs which is defined by

$$\rho_{p^*p'^*}(\zeta,\vec{r}_g\,;\zeta',\vec{r}_h) = \chi_{p^*}(\zeta,\vec{r}_g)\chi^{*}_{p'^*}(\zeta',\vec{r}_h), \tag{9}$$

where $\chi_{p^*}(\zeta, \vec{r}_g) \equiv \chi_{n^*lm}(\zeta, \vec{r}_g)$ and $\chi_{p'^*}(\zeta', \vec{r}_h) \equiv \chi_{n'^*l'm'}(\zeta', \vec{r}_h)$ are normalized real or complex NISTOs centered on nuclei g and h, respectively.

Taking into account equations (3a) and (3b) for the expansion of NISTOs and using the method set out in a previous paper [19], it is easy to obtain, for the expansion of the charge density in terms of ISTOs (for two- and three-center cases) and NISTOs (for one-center case) the following general formulas:

$$\rho_{p^*p'^*}(\zeta, \vec{r}_g\,; \zeta', \vec{r}_h) = \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} \chi_q(z, \vec{r}_a) \begin{cases} W^{\alpha N}_{p^*p'^*q}(\zeta, \zeta', z; \vec{R}_{hg}, \vec{R}_{ga}), \\ W^{\alpha N}_{p^*p'^*q}(\zeta, \zeta', z; \vec{R}_{ha}, \vec{R}_{ga}), \end{cases} \tag{10}$$

$$\rho_{p^*p'^*}(\zeta, \vec{r};\ \zeta', \vec{r}) = \frac{1}{\sqrt{4\pi}} \sum_{\nu=|l-l'|}^{l+l'} \sum_{\sigma=-\nu}^{\nu} W_{p^*p'^*q^*}(\zeta, \zeta', z)\chi_{q^*}(z, \vec{r}) \tag{11}$$

$$= \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{p^*p'^*q}(\zeta, \zeta', z; 0, 0)\chi_q(z, \vec{r}), \tag{12}$$

where $p^* \equiv n^*lm$, $p'^* \equiv n'^*l'm'$, $q \equiv \mu\nu\sigma$, $z = \zeta + \zeta'$, $q^* \equiv k^*\nu\sigma$, $k^* = n^* + n'^* - 1$, and

$$W^{\alpha N}_{p^*p'^*q}(\zeta, \zeta', z; 0, 0) = W_{p^*p'^*q^*}(\zeta, \zeta', z) V^{\alpha N}_{k^*\nu,\,\mu\nu}, \tag{13}$$

$$W_{p^*p'^*q^*}(\zeta, \zeta', z) = \frac{z^{3/2}}{2^{k^*}} \left[\frac{2\nu+1}{2} \frac{\Gamma(2k^*+1)}{\Gamma(2n^*+1)\Gamma(2n'^*+1)}\right]^{1/2} \times (1+t)^{n^*+\frac{1}{2}}(1-t)^{n'^*+\frac{1}{2}} C^{\nu|\sigma|} \times (lm, l'm') A^{\sigma}_{mm'} \delta_{k^*, n^*+n'^*-1}. \tag{14}$$

See Ref. [21] for the exact definition of generalized Gaunt coefficients $C^{\nu|\sigma|}(lm, l'm')$ and coefficients $A^{\sigma}_{mm'}$.

The quantities $W^{\alpha N}_{p^*p'^*q}$ occurring in equation (10) are the three-center expansion coefficients which can be expressed through the one of the two-center expansion coefficients, i.e.

$$W^{\alpha N}_{p^*p'^*q}(\zeta, \zeta', z;\ \vec{R}_{hg}, \vec{R}_{ga}) = \lim_{N'\to\infty} \sum_{\mu'=1}^{N'} \sum_{\nu'=0}^{\mu'-1} \sum_{\sigma'=-\nu'}^{\nu'} W^{\alpha N}_{p^*q'\,q}(\zeta, \zeta', z; 0, \vec{R}_{ga}) V^{\alpha N'}_{p'^*q'}(\zeta', \zeta'; \vec{R}_{hg}), \tag{15}$$

$$W^{\alpha N}_{p^*p'^*q}(\zeta,\zeta',z;\ \vec{R}_{ha},\vec{R}_{ga})$$

$$= \lim_{N'\to\infty}\sum_{\mu'=1}^{N'}\sum_{\nu'=0}^{\mu'-1}\sum_{\sigma'=-\nu'}^{\nu'} W^{\alpha N}_{q'p'^*q}(\zeta,\zeta',z;\vec{R}_{ha},0)V^{*\alpha N'}_{p^*q'}(\zeta,\zeta;\vec{R}_{ga}), \qquad (16)$$

where

$$W^{\alpha N}_{p^*p'^*q}(\zeta,\zeta',z;\ 0,\vec{R}_{ga})$$

$$= \lim_{N'\to\infty}\sum_{\mu'=1}^{N'}\sum_{\nu'=0}^{\mu'-1}\sum_{\sigma'=-\nu'}^{\nu'} W^{\alpha N}_{q'p'^*q}(\zeta,\zeta',z;0,0)V^{*\alpha N'}_{p^*q'}(\zeta,\zeta;\vec{R}_{ga}) \qquad (17)$$

$$= \sum_{\nu'=|l-l'|}^{l+l'}\sum_{\sigma'=-\nu'}^{\nu'} W_{p^*p'^*q'^*}(\zeta,\zeta',z)V^{*\alpha N}_{q'^*q}(z,z;\vec{R}_{ga}), \qquad (18)$$

$$W^{\alpha N}_{p^*p'^*q}(\zeta,\zeta',z;\ \vec{R}_{ha},0)$$

$$= \lim_{N'\to\infty}\sum_{\mu'=1}^{N'}\sum_{\nu'=0}^{\mu'-1}\sum_{\sigma'=-\nu'}^{\nu'} W^{\alpha N}_{p^*q'q}(\zeta,\zeta',z;0,0)V^{\alpha N'}_{p'^*q'}(\zeta',\zeta';\vec{R}_{ha}). \qquad (19)$$

4. Use of NISTO charge densities in evaluation of multi-center integrals

In the Hartree–Fock theory the matrix elements of arbitrary s-electron operators $F^{(s)}$, where $s = 1, 2, 3, \ldots$, between the determinantal wave functions of molecules are expressed through the multi-center integrals with the same operators. The $2s$-center molecular integrals of s-electron operators over normalized real or complex NISTOs are defined by

$$I^{s}_{p_1^*p'^*_1,\,p_2^*p'^*_2,\ldots,p_s^*p'^*_s}(\zeta_1,\zeta_1',\vec{R}_{ca},\ 0;\zeta_2,\zeta_2',\vec{R}_{db},\vec{R}_{ba};\ldots;\zeta_s,\zeta_s',\vec{R}_{fe},\vec{R}_{ea})$$

$$= \int F^{(s)}\rho^{*}_{p_1^*p'^*_1}(\zeta_1,\vec{r}_{a1};\ \zeta_1',\vec{r}_{c1})\rho_{p_2^*p'^*_2}(\zeta_2,\vec{r}_{b2};\ \zeta_2',\vec{r}_{d2})\ \ldots\rho_{p_s^*p'^*_s}$$

$$\times(\zeta_s,\vec{r}_{es};\ \zeta_s',\vec{r}_{fs})\mathrm{d}V_1\mathrm{d}V_2\ \ldots\ \mathrm{d}V_s. \qquad (20)$$

In order to evaluate these integrals we use the expansion formula (10) for all the electron charge densities which occur in equation (20). Then, we obtain the expression in terms of the multi-center charge-density expansion coefficients and the one-center s-electron basic integrals

$$I^{s}_{p_1^* p'^*_1,\, p_2^* p'^*_2,\ldots,p_s^* p'^*_s}(\zeta_1, \zeta'_1, \vec{R}_{ca},\ 0;\ \zeta_2, \zeta'_2, \vec{R}_{db}, \vec{R}_{ba};\ \ldots;\ \zeta_s, \zeta'_s, \vec{R}_{fe}, \vec{R}_{ea})$$

$$= \lim_{N_1, N_2, \ldots, N_s \to \infty} \sum_{\mu_1=1}^{N_1} \sum_{\nu_1=0}^{\mu_1-1} \sum_{\sigma_1=-\nu_1}^{\nu_1} W^{*\alpha N_1}_{p_1^* p'^*_1 q_1}(\zeta_1, \zeta'_1, z_1;\ \vec{R}_{ca}, 0)$$

$$\times \sum_{\mu_2=1}^{N_2} \sum_{\nu_2=0}^{\mu_2-1} \sum_{\sigma_2=-\nu_2}^{\nu_2} W^{\alpha N_2}_{p_2^* p'^*_2 q_2}(\zeta_2, \zeta'_2, z_2;\ \vec{R}_{db}, \vec{R}_{ba}) \ldots$$

$$\sum_{\mu_s=1}^{N_s} \sum_{\nu_s=0}^{\mu_s-1} \sum_{\sigma_s=-\nu_s}^{\nu_s} W^{\alpha N_s}_{p_s^* p'^*_s q_s}(\zeta_s, \zeta'_s;\ \vec{R}_{fe}, \vec{R}_{ea}) J^{s}_{q_1 q_2 \ldots q_s}(z_1, z_2, \ldots, z_s). \qquad (21)$$

Here, the quantities J^s are the one-center s-electron basic integrals with ISTOs which were defined and evaluated in a previous paper for the special cases of one- and two-electron operators $F^{(1)} = \frac{1}{r_{b1}}$ and $F^{(2)} = \frac{1}{r_{21}}$ appearing in the HFR equations for molecules (see equations (19) – (21) in Ref. [22]).

Taking into account the series expansion formulas obtained in this paper by the use of complete orthonormal sets of Ψ^α-ETOs, we can calculate all the molecular integrals with ISTOs and NISTOs arising in the determination of various properties for a given molecule when HFR approximation is employed.

It should be noted that we have the infinite series in formulas for the molecular integrals with an arbitrary multi-electron operator only from the expansion of ISTOs or NISTOs about a point displaced from the orbital center. In our previous works (see Ref. [23] and references therein to our papers), the convergence, accuracy and CPU time for these series have been tested by calculating concrete cases for arbitrary values of principal quantum numbers and screening constants of ISTOs and NISTOs, and internuclear distances. The formulas obtained in this study for the multi-center charge-density expansion coefficients with ISTOs and NISTOs can be used to calculate the different kinds of molecular integrals over NISTOs.

As can be seen from equations (4a) and (15)–(21), the overlap integrals with ISTOs and NISTOs occur in the multi-center integrals. The computer programs presented in Ref. [24] for these overlap integrals are used in the calculation of two-center Coulomb and hybrid electron-repulsion integrals. The result of the calculation in atomic units obtained with a pentium 233 MHz computer (using TURBO PASCAL 7.0 language) are represented in table 1. The comparative values obtained from equation (21) and Ref. [25] with the expansions of different Ψ^α-ETOs are shown in this table. We see from the table that the accurracy of the computer results for different expansion formulas obtained from Ψ^0-ETOs and Ψ^{-1}-ETOs are satisfactory.

Table 1
Comparison of methods of computing two-center Coulomb and hybrid integrals of NISTOs for $N_1 = N'_1 = 12$, $\nu_2 = \nu'_2 = 11$, $\sigma_2 = \sigma'_2 = 5$, $\theta_{ba} = 120°$, $\phi_{ba} = 144°$, $\theta_{da} = 45°$, $\phi_{da} = 150°$ in (a.u.).

																	Equation (21)		Ref. [25]
n_1^*	l_1	m_1	ζ_1	n'^*_1	l'_1	m'_1	ζ'_1	n_2^*	l_2	m_2	ζ_2	n'^*_2	l'_2	m'_2	ζ'_2	R_{ba}	R_{da}	$\alpha = 0$	$\alpha = -1$	$\alpha = 1$
2.5	1	0	7.5	2.5	1	0	7.5	2.5	1	0	7.5	2.8	1	0	8.7	0	1.4	−2.6312401180E-2	−2.6312413094E-2	−2.6312424618E-2
2.8	1	1	6.8	2.8	1	1	6.8	2.8	1	1	6.8	2.3	1	1	4.5	0	1.6	−9.4749167886E-2	−9.4749175693E-2	−9.4749149433E-2
2.78	1	−1	4.6	2.78	1	−1	4.6	2.78	1	−1	4.6	2.63	1	−1	6.2	0	0.8	3.4521171339E-1	3.4521175224E-1	3.4521172619E-1
3.8	1	1	6.4	3.8	1	1	6.4	3.8	1	1	6.4	3.6	1	1	8.6	0	0.6	3.6951779907E-1	3.6951776576E-1	3.6951779803E-1
2.38	1	0	7.6	2.38	1	0	7.6	2.46	1	0	9.8	2.46	1	0	9.8	0.8	0	9.8340995977E-1	9.8340894917E-1	9.8340830914E-1
2.8	1	1	4.5	2.8	1	1	4.5	2.6	1	0	5.6	2.6	1	0	5.6	1.1	0	5.7987538464E-1	5.7987550239E-1	5.7987554076E-1
2.5	1	1	3.4	2.5	1	1	3.4	2.1	1	1	1.5	2.1	1	1	1.5	0.9	0	4.7866999462E-1	4.7866978744E-1	4.7866971371E-1
2.7	1	−1	5.3	2.7	1	−1	5.3	2.9	1	−1	3.1	2.9	1	−1	3.1	0.5	0	6.7503032897E-1	6.7503171956E-1	6.7503044306E-1

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