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## One-range addition theorems for derivatives of Slater-type orbitals

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**Abstract** Using addition theorems for STOs introduced by the author with the help of complete orthonormal sets of  $\psi^\alpha$ -ETOs (Guseinov II (2003) J Mol Model 9:190–194), where  $\alpha=1, 0, -1, -2, \dots$ , a large number of one-range addition theorems for first and second derivatives of STOs are established. These addition theorems are especially useful for computation of multicenter-multielectron integrals over STOs that arise in the Hartree–Fock–Roothaan approximation and also in the Hylleraas function method, which play a significant role for the study of electronic structure and electron–nuclei interaction properties of atoms, molecules, and solids. The relationships obtained are valid for arbitrary quantum numbers, screening constants and location of STOs.

**Keywords** Addition theorems · Slater-type orbitals · Multicenter-multielectron integrals

### Introduction

For the calculation of multicenter integrals, it is often necessary to transform Slater-type orbitals (STOs), which depend upon the coordinates of two particles, in such a way that the coordinates of the particles appear in a computationally more convenient form. In most cases this requires a separation of variables, which can be accomplished with the help of so-called addition theorems. In order to separate the integration variables from those related to the geometry of the molecule, the earliest approaches for the evaluation of multicenter integrals consist of using the relatively complicated addition theorems of STOs. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17] One of the most promising methods for

the evaluation of multicenter-multielectron integrals is the extension of Fock's method [18, 19] for the momentum space solution of the Schrödinger equation for hydrogen-like atoms and the theory of hyperspherical harmonics to the multicenter case by Shibuya and Wulfman [20] (see also [21, 22, 23]). Unfortunately, the convergence of the expansion derived by Shibuya and Wulfman is not guaranteed since the continuum states of the hydrogen spectrum are not included in the expansion properly. Recently, in [24] we introduced the new complete orthonormal sets of  $\psi^\alpha$ -ETOs ( $\alpha=1, 0, -1, -2, \dots$ ) for which the problems with the continuum states do not occur. The great progress made in both applied mathematics and computer science has led a number of researchers to focus their efforts on the elaboration of new approaches directed to computing multicenter integrals over STOs.

To our knowledge, many authors (see [25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35] and references therein) have considered this problem and, although many improvements have been made in the past few years by the use of computers, an efficient general program for the calculation of multicenter integrals over STOs is not yet available. In previous work [36] addition theorems for STOs were derived using complete orthonormal sets of  $\psi^\alpha$ -ETOs

The aim of this report is to establish one-range addition theorems for derivatives of STOs. The addition theorems for STOs and their derivatives obtained in [36] and in this work, are useful for the calculation of electronic structure and electron–nuclei interaction properties of a molecule when the Hartree–Fock–Roothaan and Hylleraas approaches are employed.

### Addition theorems for derivatives of STOs

We shall use the addition theorems for STOs in the following form: [36]

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$$\chi_{nlm}(\zeta, \vec{r}_{b1}) = \frac{\sqrt{4\pi}}{\zeta^{3/2}} \lim_{k \rightarrow \infty} \sum_{n'=1}^k \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \left[ \sum_{N=1}^{k+n-\alpha+1} \sum_{L=0}^{N-1} \sum_{M=-L}^L Y_{nlm,n'l'm'}^{\alpha k, NLM} \chi_{NLM}^*(\zeta, \vec{R}_{ab}) \right] \chi_{n'l'm'}(\zeta, \vec{r}_{a1}) \quad (1)$$

where  $\alpha = 1, 0, -1, -2, \dots$ ,  $\vec{R}_{ab} = \vec{r}_{a1} - \vec{r}_{b1}$  and  $\chi_{nlm}(\zeta, \vec{r}) = R_n(\zeta, r) S_{lm}(\theta, \varphi)$  (2)

$$R_n(\zeta, r) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} e^{-\zeta r} \quad (3)$$

$$Y_{nlm,n'l'm'}^{\alpha k, NLM} = (-1)^L Z_{nlm,n'l'm'}^{\alpha k, NLM} \quad (4)$$

See Eq. (17) of [36] for the exact definition of the coefficients  $Z_{nlm,n'l'm'}^{\alpha k, NLM}$ . Here  $S_{lm}$  are complex ( $S_{lm} \equiv Y_{lm}$ ) or real spherical harmonics determined by the relation

$$S_{lm}(\theta, \phi) = P_{l|m}(\cos \theta) \Phi_m(\phi) \quad (5)$$

where  $P_{l|m}$  are normalized associated Legendre functions and for complex spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (6)$$

for real spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{\pi(1 + \delta_{m0})}} \begin{cases} \cos |m|\phi & \text{for } m \geq 0 \\ \sin |m|\phi & \text{for } m < 0. \end{cases} \quad (7)$$

The derivatives of  $\chi_{nlm}(\zeta, \vec{r}_{b1})$  with respect to Cartesian coordinates  $(X, Y, Z)$  of the nucleus  $b$  are defined by

$$\frac{\partial \chi_{nlm}(\zeta, \vec{r}_{b1})}{\partial X^i} = \frac{\sqrt{4\pi}}{\zeta^{3/2}} \lim_{k \rightarrow \infty} \sum_{n'=1}^k \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \cdot \left[ \sum_{N=1}^{k+n-\alpha+1} \sum_{L=0}^{N-1} \sum_{M=-L}^L Y_{nlm,n'l'm'}^{\alpha k, NLM} \chi_{NLM}^{i*}(\zeta, \vec{R}) \right] \chi_{n'l'm'}(\zeta, \vec{r}_{a1}) \quad (8)$$

$$\frac{\partial^2 \chi_{nlm}(\zeta, \vec{r}_{b1})}{\partial X^i \partial X^j} = \frac{\sqrt{4\pi}}{\zeta^{3/2}} \lim_{k \rightarrow \infty} \sum_{n'=1}^k \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \cdot \left[ \sum_{N=1}^{k+n-\alpha+1} \sum_{L=0}^{N-1} \sum_{M=-L}^L Y_{nlm,n'l'm'}^{\alpha k, NLM} \chi_{NLM}^{ij*}(\zeta, \vec{R}) \right] \chi_{n'l'm'}(\zeta, \vec{r}_{a1}) \quad (9)$$

Here  $i, j = 1, -1, 0$ ,  $\vec{R} = \vec{R}_{ab}$ ,  $R = (X^2 + Y^2 + Z^2)^{1/2}$ ,  $X^1 = X$ ,  $X^{-1} = Y$ ,  $X^0 = Z$  and

$$\chi_{NLM}^i(\zeta, \vec{R}) = \frac{\partial}{\partial X^i} \chi_{NLM}(\zeta, \vec{R}) = \gamma_{NL}(\zeta) \frac{\partial}{\partial X^i} F_{NLM}(\zeta, \vec{R}) \quad (10)$$

$$\begin{aligned} \chi_{NLM}^{ij}(\zeta, \vec{R}) &= \frac{\partial^2}{\partial X^i \partial X^j} \chi_{NLM}(\zeta, \vec{R}) \\ &= \gamma_{NL}(\zeta) \frac{\partial^2}{\partial X^i \partial X^j} F_{NLM}(\zeta, \vec{R}) \end{aligned} \quad (11)$$

where

$$\gamma_{NL}(\zeta) = (2\zeta)^{N+1/2} [(2N)!]^{-1/2} \left( \frac{2L+1}{4\pi} \right)^{1/2} \quad (12)$$

$$F_{NLM}(\zeta, \vec{R}) = T_{LM}(X, Y, Z) f_{NL}(\zeta, R) \quad (13)$$

$$\begin{aligned} T_{LM}(X, Y, Z) &= R^L \bar{S}_{LM}(\theta, \varphi), \quad \bar{S}_{LM}(\theta, \varphi) \\ &= \left( \frac{4\pi}{2L+1} \right)^{1/2} S_{LM}(\theta, \varphi) \end{aligned} \quad (14)$$

$$f_{NL}(\zeta, R) = R^{N-L-1} e^{-\zeta R} \quad (15)$$

As can be seen from Eqs. (10), (11), (13), (14) and (15), for the determination of addition theorems, Eqs. (8) and (9), we need the derivatives of the functions  $T_{LM}(X, Y, Z)$  and  $f_{NL}(\zeta, R)$ . Then, using the method set out in our previous paper (see [37], Eqs. (19), (20) and (21)) for the determination of the derivatives of the function  $T_{LM}(X, Y, Z)$ , we finally find for the derivatives of STOs in terms of STOs the following relations:

$$\begin{aligned} \chi_{NLM}^i(\zeta, \vec{R}) &= 2\zeta \left\{ \eta_{NL}^{11} \sum_{M'=-L-1}^{L-1} a_{LM, M'}^i \chi_{N-1L-1M'}(\zeta, \vec{R}) \right. \\ &\quad \left. + \frac{X^i}{R} \left[ (N-L-1) \eta_{NL}^{10} \chi_{N-1LM'}(\zeta, \vec{R}) - \frac{1}{2} \chi_{NLM}(\zeta, \vec{R}) \right] \right\} \end{aligned} \quad (16)$$

$$\begin{aligned} \chi_{NLM}^{ij}(\zeta, \vec{R}) &= (2\zeta)^2 \left\{ \eta_{NL}^{22} \sum_{M'=-L-2}^{L-2} a_{LM, M'}^{ij} \chi_{N-2L-2M'}(\zeta, \vec{R}) \right. \\ &\quad + \sum_{M'=-L-1}^{L-1} \left[ a_{LM, M'}^i \left( \frac{X^j}{R} \right) + a_{LM, M'}^j \left( \frac{X^i}{R} \right) \right] \\ &\quad \times [(N-L-1) \eta_{NL}^{21} \chi_{N-2L-1M'}(\zeta, \vec{R}) \\ &\quad - \frac{1}{2} \eta_{NL}^{11} \chi_{N-1L-1M'}(\zeta, \vec{R})] + \left( \frac{X^i}{R} \right) \left( \frac{X^j}{R} \right) [(N-L-1) \\ &\quad \times (N-L-3) \eta_{NL}^{20} \chi_{N-2LM}(\zeta, \vec{R}) \\ &\quad - \frac{1}{2} (2N-2L-3) \eta_{NL}^{10} \chi_{N-1LM}(\zeta, \vec{R}) \\ &\quad + \frac{1}{4} \chi_{NLM}(\zeta, \vec{R})] + \delta_{ij} [(N-L-1) \eta_{NL}^{20} \chi_{N-2LM}(\zeta, \vec{R}) \\ &\quad - \frac{1}{2} \eta_{NL}^{10} \chi_{N-1LM}(\zeta, \vec{R})] \left. \right\} \end{aligned} \quad (17)$$

where

$$\eta_{NL}^{kk'} = \left[ \frac{[2(N-k)!(2L+1)]^{1/2}}{(2N)![2(L-k') + 1]} \right] \quad (18)$$

$$a_{lm,m'}^1 = -\frac{\varepsilon_m}{2} \left\{ [(1 + \delta_{m0})(1 - \delta_{m,-1})(l - m) \cdot (l - m - 1)]^{1/2} \delta_{m',m+1} - [(1 - \delta_{m0})(1 + \delta_{m1})(l + m) \cdot (l + m - 1)]^{1/2} \delta_{m',m-1} \right\} \quad (19)$$

$$a_{lm,m'}^{-1} = -\frac{\varepsilon_m}{2} \left\{ [(1 + \delta_{m0})(1 + \delta_{m,-1})(l - m) \cdot (l - m - 1)]^{1/2} \delta_{m',-m-1} + [(1 - \delta_{m0})(1 - \delta_{m1})(l + m) \cdot (l + m - 1)]^{1/2} \delta_{m',-m+1} \right\} \quad (20)$$

$$a_{lm,m'}^0 = [(l + m)(l - m)]^{1/2} \delta_{m',m} \quad \text{for } l \geq 1 \quad (21)$$

$$a_{lm,m'}^{ij} = a_{lm,m'}^{ji} = \sum_{m''=-l-1}^{l-1} a_{lm,m''}^i a_{l-1,m'',m'}^j \quad \text{for } l \geq 2 \quad (22)$$

Here  $a_{lm,m'}^i \equiv 0$  for  $l = 0$ ,  $a_{lm,m'}^{ij} \equiv 0$  for  $l = 0, 1$  and  $\varepsilon_m = \pm 1$ . The sign of the symbol  $\varepsilon_m$  is determined by the sign of  $m$ , i.e.  $\varepsilon_m = +1$  for  $m \geq 0$  and  $\varepsilon_m = -1$  for  $m < 0$ . It should be noted that the superscripts  $i, j, k$  and  $k'$  occurring in Eqs. (16), (17) and (18) are the indices.

As can be seen from the formulae of this study obtained by the use of complete orthonormal sets of  $\Psi_{nlm}^1, \Psi_{nlm}^0, \Psi_{nlm}^{-1}, \Psi_{nlm}^{-2}, \dots$ -ETOs, all the one-range addition theorems of STOs and their derivatives are expressed through the STOs. Work is in progress for the calculation of multicenter-multielectron integrals appearing in the Hartree-Fock-Roothaan theory based on the one-range addition theorems presented in this article.

## Application

According to the Hellmann-Feynman theorem of electrostatics, [38] the electric field and its gradient induced at the nuclei of a molecule by electrons can be studied by differentiating the electronic energy (or the adiabatic potential function) with respect to Cartesian coordinates of the nuclei. The values of these derivatives at the nuclei are very sensitive to minor errors in the electronic energy of a molecule. Thus, the use of the Hylleraas electronic correlation approach in the Hartree-Fock-Roothaan theory for the study of electron-nuclei interaction properties would be desirable since it is capable of producing highly accurate results for the adiabatic potential function of a molecule. Then, the required electronic energies for the  $N$ -electron atomic and molecular systems can be expressed through the matrix elements of the Hartree-Fock-Roothaan equations and the following multicenter-multielectron correlation integrals (see Eq. (6) of [36]).

$$I_{p_1 p'_1 p_2 p'_2 p_3 p'_3 \dots p_t p'_t}^{ac, bd, gh, \dots, ef}(\zeta_1 \zeta'_1, \zeta_2 \zeta'_2, \zeta_3 \zeta'_3, \dots, \zeta_t \zeta'_t; \eta) = \int \chi_{p_1}^*(\zeta_1, \vec{r}_{a1}) \chi_{p'_1}(\zeta'_1, \vec{r}_{c1}) \chi_{p_2}(\zeta_2, \vec{r}_{b2}) \chi_{p'_2} \cdot (\zeta'_2, \vec{r}_{d2}) \chi_{p_3}(\zeta_3, \vec{r}_{g3}) \chi_{p'_3}(\zeta'_3, \vec{r}_{h3}) \dots \chi_{p_t}(\zeta_t, \vec{r}_{et}) \cdot \times \chi_{p'_t}(\zeta'_t, \vec{r}_{ft}) O_\tau(\eta, \vec{r}_{123\dots t}) dv_1 dv_2 dv_3 \dots dv_t \quad (23)$$

where  $2 \leq t \leq N$ ,  $p_i \equiv n_i l_i m_i$ ,  $p'_i \equiv n'_i l'_i m'_i$ ,  $\tau \equiv uvst$ ,  $p \equiv nlm$  and  $O_\tau(\eta, \vec{r}_{123\dots t})$  is the  $t$ -electron correlation operator (See Eq. (1) of [36]). The derivatives of these functions with respect to the Cartesian coordinates of the nucleus  $b$  are determined by

$$\frac{\partial}{\partial X^i} I_{p_1 p'_1 p_2 p'_2 p_3 p'_3 \dots p_t p'_t}^{ac, bd, gh, \dots, ef} = \frac{\sqrt{4\pi}}{\zeta^{3/2}} \lim_{k \rightarrow \infty} \sum_{n'=1}^k \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \cdot \left[ \sum_{N=1}^{k+n-\alpha+1} \sum_{L=0}^{N-1} \sum_{M=-L}^L Y_{nlm, n'l'm'}^{\alpha k, NLM} \chi_{NLM}^{i*}(\zeta, \vec{R}_{db}) \right] \cdot \times I_{p_1 p'_1 p_2 p'_2 p_3 p'_3 \dots p_t p'_t}^{ac, dd, gh, \dots, ef} \quad (24)$$

$$\frac{\partial^2}{\partial X^i \partial X^j} I_{p_1 p'_1 p_2 p'_2 p_3 p'_3 \dots p_t p'_t}^{ac, bd, gh, \dots, ef} = \frac{\sqrt{4\pi}}{\zeta^{3/2}} \lim_{k \rightarrow \infty} \sum_{n'=1}^k \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \cdot \left[ \sum_{N=1}^{k+n-\alpha+1} \sum_{L=0}^{N-1} \sum_{M=-L}^L Y_{nlm, n'l'm'}^{\alpha k, NLM} \chi_{NLM}^{ij*}(\zeta, \vec{R}_{db}) \right] \cdot \times I_{p_1 p'_1 p_2 p'_2 p_3 p'_3 \dots p_t p'_t}^{ac, bd, gh, \dots, ef} \quad (25)$$

where  $p' \equiv n'l'm'$ . The derivatives  $\chi_{NLM}^{i*}(\zeta, \vec{R}_{db})$  and  $\chi_{NLM}^{ij}(\zeta, \vec{R}_{db})$  occurring in these equations can be determined by the use of addition theorems, Eqs. (16) and (17).

In [36], we established the general formulae for the multicenter  $t$ -electron correlation integrals of Yukawa-like central and noncentral interaction potentials, Eq. (23), in terms of two- and three-center overlap integrals. Thus, the multicenter-multielectron integrals and their derivatives, Eqs. (23), (24) and (25), are determined solely from the two- and three-center overlap integrals over STOs.

The results of calculation for the three-center overlap integrals  $S^{acb}$  (see Eqs. (31) and (32) of [36]) with a Pentium III 800-MHz computer (using Turbo Pascal 7.0) are shown in Table 1. The comparative values obtained from the expansions in terms of complete orthonormal sets of  $\psi^0$ -ETOs and  $\psi^1$ -ETOs are given in this table. As can be seen from the table, the computation time and accuracy of the computer results for different expansion formulae are satisfactory.

**Table 1** Comparison of methods of computer three-center overlap integrals  $S^{acb}$  (in a.u.):  $N=15$ 

$n$	$l$	$m$	$\zeta$	$n'$	$l'$	$m'$	$\zeta'$	$\mu'$	$\nu'$	$\sigma'$	$z'$	$R_{bc}$	$\theta_{bc}$	$\varphi_{bc}$
1	0	0	5.6	2	1	0	2.3	2	1	0	4.2	0.7	360	40
1	0	0	7.5	1	0	0	5.2	1	0	0	3.4	0.5	90	80
2	1	0	3.7	2	1	0	1.5	1	0	0	3.3	1.2	135	100
2	1	0	4.3	2	1	0	2.1	2	1	1	4.3	0.6	180	140
$R_{ca}$	$\theta_{ca}$	$\varphi_{ca}$	$\alpha=0$				$\alpha=-1$				CPU (ms)			
0.7	180	120	4.8588666043E-01				4.8588586165E-01				13.6			
1.1	225	120	1.5142553575E-01				1.5142552710E-01				9.2			
0.8	270	72	1.3668666543E-01				1.3670021222E-01				16.7			
0.6	315	90	1.3784469477E-01				1.3784371500E-01				19.1			

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