J Math Chem (2011) 49:1011–1013
DOI 10.1007/s10910-010-9792-1

ORIGINAL PAPER

Unified treatment of complex and real rotation-angular functions for two-center overlap integrals over arbitrary atomic orbitals

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Received: 2 November 2010 / Accepted: 6 December 2010 / Published online: 29 December 2010

Abstract The new combined formulas have been established for the complex and real rotation-angular functions arising in the evaluation of two-center overlap integrals over arbitrary atomic orbitals in molecular coordinate system. These formulas can be useful in the study of different quantum mechanical problems in both the theory and practice of calculations dealing with atoms, molecules, nuclei and solids when the integer and noninteger n complex and real atomic orbitals basis sets are emploed. This work presented the development of our previous paper (I.I. Guseinov in Phys Rev A 32:1864, 1985).

Keywords Atomic orbitals · Overlap ıntegrals · Rotation-angular functions

1 Introduction

In a previous paper [1], the independent formulas have been derived for the rotation-angular functions (RAF) of overlap integrals in terms of complex Y_{lm} and real S_{lm} spherical hormonics (SH), respectively. The aim of this work is to establish the combined relations for these funstions which are especially useful for the calculation of two-center overlap integrals over arbitrary atomic orbitals (AO) with respect to the molecular coordinate system.

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2 Definition

The two-center overlap integrals over arbitrary complex and real normalized AO are defined as

$$S^{c}_{nlm,\,n'l'm'}(\vec{p},t) = \int \phi^{*}_{nlm}(\zeta,\vec{r}_a)\phi_{n'l'm'}(\zeta',\vec{r}_b)dv \tag{1}$$

$$S^{R}_{nlm,\,n'l'm'}(\vec{p},t) = \int \chi^{*}_{nlm}(\zeta,\vec{r}_a)\chi_{n'l'm'}(\zeta',\vec{r}_b)dv, \tag{2}$$

where $\vec{p} = \frac{1}{2}(\zeta+\zeta')\vec{R}_{ab}$, $t = \frac{\zeta-\zeta'}{\zeta+\zeta'}$ and

$$\phi_{nlm}(\zeta,\vec{r}) = R_{nl}(\zeta,r)Y_{lm}(\theta,\varphi) \tag{3}$$

$$\chi_{nlm}(\zeta,\vec{r}) = R_{nl}(\zeta,r)S_{lm}(\theta,\varphi). \tag{4}$$

Here, the complex and real SH are determined by

$$Y_{lm}(\theta,\varphi) = P_{l|m|}(\cos\theta)\,\frac{1}{\sqrt{2\pi}}e^{im\varphi} \tag{5}$$

$$S_{lm}(\theta,\varphi) = P_{l|m|}(\cos\theta)\,\frac{1}{[\pi\,(1+\delta_{m0})]^{\frac{1}{2}}}\begin{cases}\cos|m|\,\varphi & \text{for } m \geq 0\\ \sin|m|\,\varphi & \text{for } m < 0,\end{cases} \tag{6}$$

where $P_{l|m|}(\cos\theta)$ are the normalized associated Legendre functions.

We notice that our definition of phases for complex SH differs from the Conden-Shortley phases $\left(Y^{*}_{lm} = (-1)^m Y_{l-m}\right)$ [2] by the sign factor $\left(Y^{*}_{lm} = Y_{l-m}\right)$ [3].

3 Expressions for RAF in terms of SH

In order to establish the combined formulas for RAF, we use the following relationships between complex and real SH:

$$S_{lm} = \frac{(-i)^{\delta_{m,-|m|}}}{[2\,(1+\delta_{m0})]^{\frac{1}{2}}}\left(Y_{l|m|} + \varepsilon_m Y_{l-|m|}\right) \tag{7}$$

$$Y_{lm} = \frac{1}{(2-\delta_{m0})^{\frac{1}{2}}}\left(S_{l|m|} + i\,\eta_m S_{l-|m|}\right), \tag{8}$$

where

$$\varepsilon_m = \begin{cases}+1 & \text{for} \quad m \geq 0\\ -1 & \text{for} \quad m < 0\end{cases} \tag{9}$$

$$\eta_m = \begin{cases}m/|m| & \text{for} \quad m \neq 0\\ 0 & \text{for} \quad m = 0.\end{cases} \tag{10}$$

Now we use the method set out in [1]. Then, we obtain the following combined relation for the overlap integral of complex and real AO:

$$S^{C,R}_{nlm,\,n'l'm'}(\vec{p},t) = \sum_{\lambda=0}^{\min(l,l')} T^{\lambda}_{lm,l'm'}(\theta,\phi) S^{C,R}_{nl\lambda,\,n'l'\lambda}(p,t), \tag{11}$$

where $S^{C}_{nl\lambda,n'l'\lambda}(p,t) = S^{R}_{nl\lambda,n'l'\lambda}(p,t)$ are the two-center overlap integrals with respect to lined-up coordinate systems. For the calculation of these integrals, the efficient computer programs in the case of Slater type orbitals are avaible in our group [4].

The rotation-angular functions T_λ occuring in Eq. (11) are determined by

$$T^{\lambda}_{lm,\,l'm'}(\theta,\varphi) = \sum_{L=|l-l'|}^{l+l'} T^{\lambda L}_{lm,\,l'm'} Y_{LM}(\theta,\varphi). \tag{12}$$

Here, $M = -m + m'$ and

$$T^{\lambda L}_{lm,\,l'm'} = \begin{cases} D^{\lambda L}_{lm,\,l'm'} & \text{for complex SH} \\ d^{\lambda L}_{lm,\,l'm'} & \text{for real SH} \end{cases}, \tag{13}$$

where

$$D^{\lambda L}_{lm,\,l'm'} = \frac{2}{1+\delta_{\lambda 0}} C^{ll'L}_{-mm'M} C^{ll'L}_{-\lambda\lambda 0} \left(\frac{4\pi}{2L+1}\right)^{1/2} \tag{14}$$

$$d^{\lambda L}_{lm,\,l'm'} = \frac{(i)^{\delta_{m,-|m|}}(-i)^{\delta_{m',-|m'|}}}{2\left[(1+\delta_{m0})(1+\delta_{m'0})\right]^{1/2}} \left(D^{\lambda L}_{l|m|,\,l'|m'|} + \varepsilon_m D^{\lambda L}_{l-|m|,\,l'|m'|} + \varepsilon_{m'} D^{\lambda L}_{l|m|,\,l'-|m'|} + \varepsilon_m \varepsilon_{m'} D^{\lambda L}_{l-|m|,\,l'-|m'|}\right). \tag{15}$$

Thus, we have established the new combined relations for the rotational transformation functions of two-center overlap integrals over arbitrary AO in terms of spherical harmonics. The formulae obtained in this study are of a completely general type and can be utilized to calculate in molecular coordinate system any overlap integral for the arbitrary values of quantum numbers, screening constants and location of arbitrary atomic orbitals, and internuclear distances.

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