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Transformation of complex spherical harmonics under rotations

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Abstract

The algorithm rotating the complex spherical harmonics is presented. The convenient and ready to use formulae for $\ell = 0, 1, 2, 3$ are listed. Any rotation in $\mathbb{R}^3$ space is determined by the rotation axis and the rotation angle. The complex spherical harmonics defined in the fixed coordinate system is expanded as a linear combination of the spherical harmonics defined in the rotated coordinate system having $2\ell + 1$ terms, which are given explicitly. The derived formulae could be applied in quantum molecular calculations. The algorithm is based on the Cartesian representation of the spherical harmonics. The possible application of the algorithm to the evaluation of molecular integrals between slater type orbitals (STO) is described.

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1. Introduction

In the molecular linear combination of atomic orbitals method, the basis function is usually the product of the radial part and spherical harmonic [1, 2]. In order to represent the wavefunction or the molecular charge distribution, the atomic orbitals of s, p, d and f types are mainly applied. Typically, the rotations of the atomic orbitals are required to align the local (atomic) coordinate system axis with the unique inter-atomic direction. In the rotated coordinate system the integral evaluation can be easily performed. Since the radial part of the atomic orbital does not change under the rotation, only the spherical harmonic must be rotated.

The general algorithm rotating the complex spherical harmonic has been extensively discussed in [3–5]. In these articles the rotations in $\mathbb{R}^3$ space are defined by Euler angles, and the rotated spherical harmonic is expressed as a linear combination of the spherical harmonics in a fixed coordinate system. The expansion coefficients depend on the angular and magnetic quantum numbers and Euler angles. Since algebraic representation of the

expansion coefficients is lengthy, its application is inconvenient and leads to the inefficient implementation [6], although well-documented procedures exist [7–9].

Recently, the rotation of the spherical harmonic has been discussed without the explicit use of the Euler angles [10, 11]. In [10, 11], the rotation matrix is derived for complex and real spherical harmonics. The elements of the rotation matrix are obtained by the recursive relations with respect to the angular momentum number ℓ. The presentation relies on the recurrence relation and the integral formulae for spherical harmonics. Moreover, the elements of the rotation matrix are determined by the matrix $\mathcal{R}$, which determines the relation between fixed, $\boldsymbol{e}_k$, and rotated, $\hat{\boldsymbol{e}}_k$, coordinate system versors:

$$\hat{\boldsymbol{e}}_k = \sum_{j=0}^{3} \mathcal{R}_{jk} \boldsymbol{e}_j.$$

Although the algorithm presented in [10, 11] is general and works for all ℓ, its efficient implementation is quite involved.

In the present paper, we describe the algorithm representing the complex spherical harmonic defined in the fixed coordinate system, as a linear combination of the complex spherical harmonic defined in the rotated coordinate system. The rotation in $\mathbb{R}^3$ is represented by the rotation axis and the rotation angle. The Euler angles are not used. The explicit algebraic formulae are derived for expansion coefficients for angular momentum $\ell = 0, 1, 2, 3$, which are most often used in the molecular LCAO calculations. The obtained relations are simple, compact and contain only basic algebraic manipulations. The derivation of the expansion coefficient is based on the Cartesian representation of the spherical harmonic.

The organization of the manuscript is as follows. In section 2.1 Cartesian representation of the complex spherical harmonics is defined. In section 2.2 the rotations in $\mathbb{R}^3$ space are discussed. The main result is presented in section 3, which also contains the expansion coefficient evaluated for $\ell = 0, 1, 2, 3$.

2. Definitions

2.1. Complex spherical harmonics

The complex spherical harmonics $Y_\ell^m(\theta, \varphi)$ are defined in the spherical coordinate system (θ, φ). According to the Condon–Shortley phase conventions [5, 12], the complex spherical harmonics are defined for $|m| \leqslant \ell$ as

$$Y_\ell^m(\theta, \varphi) = N_\ell^m \mathcal{P}_\ell^{|m|}(\cos(\theta))\, \mathrm{e}^{\mathrm{i}m\varphi} \tag{1}$$

where N_ℓ^m is a normalization factor:

$$N_\ell^m = \mathrm{i}^{m+|m|} \left[\frac{2\ell+1}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{1/2} \tag{2}$$

and $\mathcal{P}_\ell^{|m|}(v)$ is an associated Legendre function defined by Legendre polynomial $P_\ell(v)$, for $|v| \leqslant 1$:

$$\begin{aligned} \mathcal{P}_\ell^{|m|}(v) &= (1-v^2)^{|m|/2} \frac{\mathrm{d}^{|m|}}{\mathrm{d}v^{|m|}} P_\ell(v) \\ \mathcal{P}_\ell^{|m|}(\cos(\theta)) &= \sin^{|m|}(\theta) \frac{\mathrm{d}^{|m|}}{\mathrm{d}(\cos(\theta))^{|m|}} P_\ell(\cos(\theta)). \end{aligned} \tag{3}$$

The Legendre polynomial, $P_\ell(v)$, is defined by Rodrigues' formula [13, equation (22.11)]:

$$P_\ell(v) = \frac{1}{2^\ell \ell!} \frac{\mathrm{d}^\ell}{\mathrm{d}v^\ell} (v^2-1)^\ell \tag{4}$$

or defined explicitly [[13], equation (22.3)]:

$$P_\ell(v) = \sum_{k=0}^{\lfloor \ell/2 \rfloor} \gamma_{\ell,k}^{(0)} v^{\ell-2k} \tag{5}$$

where $\lfloor \ell/2 \rfloor$ is the largest integer number less than $\ell/2$ and

$$\gamma_{\ell,k}^{(m)} = (-1)^k 2^{-\ell} \binom{\ell}{k} \binom{2\ell-2k}{\ell} \frac{(\ell-2k)!}{(\ell-2k-m)!}. \tag{6}$$

Based on this representation one can obtain the mth derivative (for $m \geqslant 0$):

$$\frac{\mathrm{d}^m}{\mathrm{d}v^m} P_\ell(v) = \sum_{k=0}^{\lfloor (\ell-m)/2 \rfloor} \gamma_{\ell,k}^{(m)} v^{\ell-2k-m}. \tag{7}$$

Since $z = r\cos(\theta)$ where $r^2 = x^2 + y^2 + z^2$, it follows that this derivative, times an appropriate power of r, is a simple polynomial of z variable:

$$r^{\ell-m} \frac{\mathrm{d}^m}{\mathrm{d}(\cos(\theta))^m} P_\ell(\cos(\theta)) = \sum_{k=0}^{\lfloor (\ell-m)/2 \rfloor} \gamma_{\ell,k}^{(m)} r^{2k} z^{\ell-2k-m}. \tag{8}$$

Further, since $x = r\sin(\theta)\cos(\varphi)$ and $y = r\sin(\theta)\sin(\varphi)$, then the expression

$$\begin{aligned} r^m \sin^m(\theta)\, \mathrm{e}^{\mathrm{i}m\varphi} &= [r\sin(\theta)\, \mathrm{e}^{\mathrm{i}\varphi}]^m = [r\sin(\theta)(\mathrm{i}\sin(\varphi) + \cos(\varphi))]^m \\ &= [\mathrm{i}r\sin(\theta)\sin(\varphi) + r\sin(\theta)\cos(\varphi)]^m = (x + \mathrm{i}y)^m \end{aligned} \tag{9}$$

is a complex polynomial of x, y. Multiplying equations (8), (9) by sides and applying equations (1), (3), we obtain

$$r^\ell Y_\ell^m(\theta, \varphi) = N_\ell^m (x + \mathrm{i}y)^m \sum_{k=0}^{\lfloor (\ell-m)/2 \rfloor} \gamma_{\ell,k}^{(m)} r^{2k} z^{\ell-2k-m} = r^\ell Y_\ell^m(x, y, z). \tag{10}$$

Thus, $r^\ell Y_\ell^m(x, y, z)$ is a polynomial of x, y, z. The function $Y_\ell^m(x, y, z)$ is a Cartesian representation of the complex spherical harmonic. For example, for $\ell = 1$ we get

$$\begin{aligned} Y_1^{-1}(x, y, z) &= \sqrt{3/(8\pi)}(x - \mathrm{i}y)/r \\ Y_1^0(x, y, z) &= \sqrt{3/(4\pi)}z/r \\ Y_1^1(x, y, z) &= -\sqrt{3/(8\pi)}(x + \mathrm{i}y)/r. \end{aligned}$$

Equation (10) was proved for $m \geqslant 0$. Moreover, we have

$$Y_\ell^{-m}(\theta, \varphi) = (-1)^m [Y_\ell^m(\theta, \varphi)]^\dagger \qquad \text{for} \quad m \geqslant 0 \tag{11}$$

where † denotes the conjugate complex. Thus, equation (10) is also valid for $m < 0$. In the present manuscript the Cartesian form of the complex spherical harmonics, $Y_\ell^m(x, y, z)$, is used.

2.2. *Rotations in* $\mathbb{R}^3$

Let us introduce the Cartesian coordinate system $\mathcal{C}$. Let us denote the coordinates of the point P in $\mathcal{C}$ as $P = (p_x, p_y, p_z)$. Let us define the rotation axis passing through the origin of the system $\mathcal{C}$ by vector $\boldsymbol{u} = (u_x, u_y, u_z)$ of unitary length $|\boldsymbol{u}| = 1$. Let us denote by α the rotation angle around this axis. Then, the coordinates of the point $P' = (p'_x, p'_y, p'_z)$, resulting from

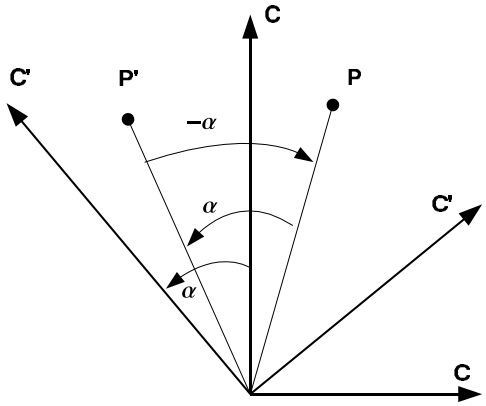

Figure 1. Relative position of the two Cartesian coordinate systems $\mathcal{C}$ and $\mathcal{C}'$. Rotation of point P creates point P'. Rotation of $\mathcal{C}$ creates $\mathcal{C}'$. Rotation axis points to the reader. Rotation is by angle α.

the rotation of point P, are given by [14]

$$(p'_x, p'_y, p'_z)^T = \mathcal{R}(\boldsymbol{u}, \alpha) \cdot (p_x, p_y, p_z)^T. \tag{12}$$

The rotation matrix $\mathcal{R}(\boldsymbol{u}, \alpha)$ around axis $\boldsymbol{u}$ by an angle α is given as

$$\mathcal{R}(\boldsymbol{u}, \alpha) = \begin{bmatrix} u_x^2 + \left(1 - u_x^2\right)c_\alpha & u_x u_y (1 - c_\alpha) - u_z s_\alpha & u_z u_x (1 - c_\alpha) + u_y s_\alpha \\ u_x u_y (1 - c_\alpha) + u_z s_\alpha & u_y^2 + \left(1 - u_y^2\right)c_\alpha & u_y u_z (1 - c_\alpha) - u_x s_\alpha \\ u_z u_x (1 - c_\alpha) - u_y s_\alpha & u_y u_z (1 - c_\alpha) + u_x s_\alpha & u_z^2 + \left(1 - u_z^2\right)c_\alpha \end{bmatrix}, \tag{13}$$

where $c_\alpha = \cos(\alpha)$ and $s_\alpha = \sin(\alpha)$. The matrix is valid for the right-handed coordinate systems and the counterclockwise rotation orientation. The positive rotations are counterclockwise, if the observer looks along the $\boldsymbol{u}$ axis from its positive end toward the origin. For example, if one wants to rotate the point $Q = (q_x, q_y, q_z) = \boldsymbol{q}$ to be on the coordinate axis Z, then the rotation axis $\boldsymbol{u}$ and the rotation angle α are defined as

$$\boldsymbol{u} = \frac{\boldsymbol{q} \times \boldsymbol{e}_z}{|\boldsymbol{q} \times \boldsymbol{e}_z|} \qquad \cos(\alpha) = \frac{\boldsymbol{q} \cdot \boldsymbol{e}_z}{|\boldsymbol{q} \cdot \boldsymbol{e}_z|}, \tag{14}$$

where $\boldsymbol{e}_z = (0, 0, 1)$ denotes versor along the coordinate axis Z.

In the above, the rotation of the point in the fixed system $\mathcal{C}$ is described. Now, the opposite, the coordinate system is rotated. Let us denote by $\mathcal{C}'$ the new coordinate system created by the rotation of $\mathcal{C}$ around the axis $\boldsymbol{u}$ by angle α, see figure 1. Let us denote by P' the new point created in $\mathcal{C}$ by the rotation of P around the axis $\boldsymbol{u}$ by angle α. The coordinates of P' are given by equation (12). It is clear that the coordinates of P' in $\mathcal{C}'$ are equal to the coordinates of P in $\mathcal{C}$. Let us denote the coordinates of P in $\mathcal{C}'$ as $(\tilde{p}_x, \tilde{p}_y, \tilde{p}_z)$. Then, the coordinates of P in $\mathcal{C}'$ can be obtained by the rotation of P' by angle $(-\alpha)$ see [14]. Since the coordinates of P' in $\mathcal{C}'$ are (p_x, p_y, p_z), then the coordinates of P in $\mathcal{C}'$ are given by

$$\begin{aligned} (\tilde{p}_x, \tilde{p}_y, \tilde{p}_z)^T &= \mathcal{R}(\boldsymbol{u}, -\alpha) \cdot (p_x, p_y, p_z)^T \\ (p_x, p_y, p_z)^T &= \mathcal{R}^{-1}(\boldsymbol{u}, -\alpha) \cdot (\tilde{p}_x, \tilde{p}_y, \tilde{p}_z)^T. \end{aligned} \tag{15}$$

Since $\mathcal{R}(\boldsymbol{u}, \alpha)$ is unitary, i.e. $\mathcal{R}^{-1}(\boldsymbol{u}, \alpha) = \mathcal{R}^T(\boldsymbol{u}, -\alpha)$, then

$$(p_x, p_y, p_z)^T = \mathcal{R}^T(\boldsymbol{u}, -\alpha) \cdot (\tilde{p}_x, \tilde{p}_y, \tilde{p}_z)^T. \tag{16}$$

The matrix $\mathcal{R}^T(\boldsymbol{u}, -\alpha)$ is used throughout the present paper.

3. Rotation of complex spherical harmonic in $\mathbb{R}^3$

Let us introduce two coordinate systems $\mathcal{C}$ and $\mathcal{C}'$ with a common origin. Let us define the rotation axis $\boldsymbol{u}$ passing through the origin of $\mathcal{C}$. Let us assume that $\mathcal{C}'$ is created as a rotation of $\mathcal{C}$ around the axis $\boldsymbol{u}$ by angle α, see figure 1. Let us introduce the point P, which in $\mathcal{C}$ has the coordinates $(x, y, z) = (r, \theta, \varphi)$ and in $\mathcal{C}'$ has the coordinates $(x', y', z') = (r', \theta', \varphi')$ and $r' = r$. Then, based on equation (16), we have

$$(x, y, z)^T = \mathcal{R}^T(\boldsymbol{u}, -\alpha)(x', y', z')^T. \tag{17}$$

For short, let us denote the elements of the matrix $\mathcal{R}^T(\boldsymbol{u}, -\alpha)$ as

$$\mathcal{R}^T(\boldsymbol{u}, -\alpha) = \begin{bmatrix} r_1 & r_2 & r_3 \\ r_4 & r_5 & r_6 \\ r_7 & r_8 & r_9 \end{bmatrix}. \tag{18}$$

The goal of our investigation is to represent the value at the point P of the complex spherical harmonic defined in $\mathcal{C}$ as a linear combination of the complex spherical harmonic defined in $\mathcal{C}'$. It was proved [3–5] that the sum is finite and runs over all allowed magnetic quantum numbers, M

$$Y_\ell^m(\theta, \varphi) = \sum_{M=-\ell}^{\ell} d_{m,M}^{(\ell)} Y_\ell^M(\theta', \varphi'). \tag{19}$$

Since the complex spherical harmonics are orthonormal,

$$\oint_\Omega Y_\ell^{m\dagger}(\theta, \varphi) Y_{\ell'}^{m'}(\theta, \varphi)\, \mathrm{d}\Omega = \delta_{\ell,\ell'}\delta_{m,m'}, \tag{20}$$

then the expansion coefficients $d_{m,M}^{(\ell)}$ fulfill the relation

$$\sum_{M=-\ell}^{\ell} \left| d_{m,M}^{(\ell)} \right|^2 = 1. \tag{21}$$

Since the representations of the complex spherical harmonic in spherical and Cartesian coordinates are equivalent, we have

$$Y_\ell^m(x, y, z) = \sum_{M=-\ell}^{\ell} d_{m,M}^{(\ell)} Y_\ell^M(x', y', z'). \tag{22}$$

From equation (17) it follows that the coordinates (x, y, z) are linear combinations of the coordinates (x', y', z'). This property is used to obtain the coefficients $d_{m,M}^{(\ell)}$ for the specific angular quantum number ℓ. Since the complex spherical harmonic for $\ell = 0$ is constant, then $d_{0,0}^{(0)} = 1$. The algorithm for $\ell > 0$ is as follows:

- Choose the angular quantum number $\ell > 0$.
- Select $2\ell + 1$ canonical polynomials, $Q_\ell^k(x, y, z)$, of order ℓ, for $k = -\ell, \ldots, \ell$. $Q_\ell^k(x, y, z)$ are polynomials allowing us to express spherical harmonics using Cartesian coordinates. Express them as a linear combination of $r^\ell Y_\ell^M(x, y, z)$

$$Q_\ell^k(x, y, z) = r^\ell \sum_{M=-\ell}^{\ell} a_{k,M}^{(\ell)} Y_\ell^M(x, y, z). \tag{23}$$

- By proper selection of $Q_\ell^k(x, y, z)$ we are sure that the inverse representation exists:

$$Y_\ell^m(x, y, z) = r^{-\ell} \sum_{k=-\ell}^{\ell} b_{m,k}^{(\ell)} Q_\ell^k(x, y, z). \tag{24}$$

- Since the rotation of the coordinate system is equivalent to the multiplication by the matrix (equation (17)), then any polynomial of order ℓ in the rotated coordinate system is also the polynomial of order ℓ, hence:

$$Q_\ell^k(x, y, z) = \sum_{j=-\ell}^{\ell} c_{k,j}^{(\ell)} Q_\ell^j(x', y', z') \tag{25}$$

- Substitute equation (25) into equation (24). Then, in the obtained result, substitute equation (23) for 'primed' variables x', y', z'

$$Y_\ell^m(x, y, z) = \sum_{k=-\ell}^{\ell} b_{m,k}^{(\ell)} \sum_{j=-\ell}^{\ell} c_{k,j}^{(\ell)} \sum_{M=-\ell}^{\ell} a_{j,M}^{(\ell)} Y_\ell^M(x', y', z'). \tag{26}$$

Let us introduce, for fixed ℓ, the vectors of $2\ell + 1$ components:

$$\begin{aligned} \boldsymbol{y}_\ell &= \left\{Y_\ell^{-m}(x, y, z), \ldots, Y_\ell^m(x, y, z)\right\}^T \\ \boldsymbol{y}'_\ell &= \left\{Y_\ell^{-m}(x', y', z'), \ldots, Y_\ell^m(x', y', z')\right\}^T \\ \boldsymbol{q}_\ell &= \left\{Q_\ell^{-m}(x, y, z), \ldots, Q_\ell^m(x, y, z)\right\}^T \\ \boldsymbol{q}'_\ell &= \left\{Q_\ell^{-m}(x', y', z'), \ldots, Q_\ell^m(x', y', z')\right\}^T. \end{aligned} \tag{27}$$

Further, let us introduce the matrices $\mathbf{A}_\ell, \mathbf{B}_\ell, \mathbf{C}_\ell, \mathbf{D}_\ell$, which are defined by equations (23), (24), (25), (22), respectively. Then, we have

$$\boldsymbol{q}_\ell = r^\ell \mathbf{A}_\ell \boldsymbol{y}_\ell, \qquad \boldsymbol{y}_\ell = r^{-\ell} \mathbf{B}_\ell \boldsymbol{q}_\ell, \qquad \boldsymbol{q}_\ell = \mathbf{C}_\ell \boldsymbol{q}'_\ell, \qquad \boldsymbol{y}_\ell = \mathbf{D}_\ell \boldsymbol{y}'_\ell. \tag{28}$$

If $\mathbf{A}_\ell$ is invertible, then $\mathbf{B}_\ell^{-1} = \mathbf{A}_\ell$ and finally:

$$\boldsymbol{y}_\ell = \mathbf{A}_\ell^{-1} \mathbf{C}_\ell \mathbf{A}_\ell \boldsymbol{y}'_\ell \quad \Longrightarrow \quad \mathbf{D}_\ell = \mathbf{A}_\ell^{-1} \mathbf{C}_\ell \mathbf{A}_\ell. \tag{29}$$

Thus, the needed expansion coefficients, $\mathbf{D}_\ell$, are fully defined by the two square matrices $\mathbf{A}_\ell$ and $\mathbf{C}_\ell$ of size $2\ell + 1$. Matrix $\mathbf{A}_\ell$ can be easily obtained from equation (23), if the explicit representation of the canonical polynomials $Q_\ell^k(x, y, z)$ is known. Hence, the problem of rotating the complex spherical harmonics has been reduced to the problem of rotating the canonical polynomials. Matrix $\mathbf{C}_\ell$ can be obtained based on the uniqueness of the polynomial representation, formulated in the following theorem:

Theorem 1. *Let $p(x, y, z)$ and $q(x, y, z)$ be the two polynomials of order n:*

$$p(x, y, z) = \sum_{0 \leqslant i+j+k \leqslant n} p_{i,j,k} x^i y^j z^k \qquad q(x, y, z) = \sum_{0 \leqslant i+j+k \leqslant n} q_{i,j,k} x^i y^j z^k,$$

where $p_{i,j,k}, q_{i,j,k} \in \mathbb{C}$ and $i, j, k \geqslant 0$. If $p(x, y, z) = q(x, y, z)$, then the coefficients are equal: $p_{i,j,k} = q_{i,j,k}$.

This theorem, applied to the canonical polynomials for $\ell = 1, 2, 3$, leads to the compact analytical expressions. The results are presented in the following sections.

3.1. Expansion coefficient for $\ell = 1$

Let us introduce the canonical polynomials, $Q_1^k(x, y, z)$, for $k = -1, 0, 1$

$$Q_1^{-1}(x, y, z) = x \qquad Q_1^0(x, y, z) = y \qquad Q_1^1(x, y, z) = z. \tag{30}$$

Then, based on equation (10), the matrix $\mathbf{A}_1$ has the form

$$\mathbf{A}_1 = \sqrt{\frac{2\pi}{3}} \begin{bmatrix} 1 & 0 & -1 \\ \mathrm{i} & 0 & \mathrm{i} \\ 0 & \sqrt{2} & 0 \end{bmatrix}. \tag{31}$$

The matrix $\mathbf{A}_1$ is invertible, and to determine matrix $\mathbf{D}_1$ from equation (29), only the matrix $\mathbf{C}_1$ is required. Since vector $\boldsymbol{q}_1$ contains only linear polynomials, equation (30), then based on equation (17) we obtain

$$\mathbf{C}_1 = \begin{bmatrix} r_1 & r_2 & r_3 \\ r_4 & r_5 & r_6 \\ r_7 & r_8 & r_9 \end{bmatrix}. \tag{32}$$

3.2. Expansion coefficient for $\ell = 2$

Let us introduce the canonical polynomials, $Q_2^k(x, y, z)$, for $k = -2, -1, 0, 1, 2$

$$\begin{aligned} Q_2^{-2}(x, y, z) &= yz \\ Q_2^{-1}(x, y, z) &= xz \\ Q_2^0(x, y, z) &= xy \\ Q_2^1(x, y, z) &= x^2 - y^2 \\ Q_2^2(x, y, z) &= 2z^2 - x^2 - y^2. \end{aligned} \tag{33}$$

Then, based on equation (10), the mattrix $\mathbf{A}_2$ has the form

$$\mathbf{A}_2 = \sqrt{\frac{2\pi}{15}} \begin{bmatrix} 0 & \mathrm{i} & 0 & \mathrm{i} & 0 \\ 0 & 1 & 0 & -1 & 0 \\ \mathrm{i} & 0 & 0 & 0 & -\mathrm{i} \\ 2 & 0 & 0 & 0 & 2 \\ 0 & 0 & 4\sqrt{3/2} & 0 & 0 \end{bmatrix}. \tag{34}$$

The matrix $\mathbf{A}_2$ is invertible, hence only the matrix $\mathbf{C}_2$ is required. The elements of the matrix $\mathbf{C}_2$ are obtained in the following manner. Based on equation (17), express the coordinates (x, y, z) by (x', y', z'), substitute into equation (25) and expand the left-hand side. Based on theorem 1, the coefficients for $y'z'$, and $x'z'$, and $x'y'$ and $2z'^2$ can be obtained by comparison of left- and right-hand sides, which are the searched coefficients of $Q_2^k(x', y', z')$ for $k = -2, -1, 0, 2$ (except $k = 1$), see equation (33). The last required coefficient for $x'^2 - y'^2$ is obtained by subtracting the obtained expansion and applying theorem 1 again. The result of this procedure is the matrix $\mathbf{C}_2$, presented below:

$$\mathbf{C}_2 = \begin{bmatrix} r_6r_8 + r_5r_9 & r_6r_7 + r_4r_9 & r_5r_7 + r_4r_8 & r_6r_9/2 & r_4r_7 + r_6r_9/2 \\ r_3r_8 + r_2r_9 & r_3r_7 + r_1r_9 & r_2r_7 + r_1r_8 & r_3r_9/2 & r_1r_7 + r_3r_9/2 \\ r_3r_5 + r_2r_6 & r_3r_4 + r_1r_6 & r_2r_4 + r_1r_5 & r_3r_6/2 & r_1r_4 + r_3r_6/2 \\ v_1 & v_2 & v_3 & v_4 & v_5 \\ w_1 & w_2 & w_3 & w_4 & w_5 \end{bmatrix}, \tag{35}$$

where the two auxiliary vectors $\boldsymbol{v}$, $\boldsymbol{w}$ are

$$\boldsymbol{v} = \begin{bmatrix} 2(r_2r_3 - r_5r_6) \\ 2(r_1r_3 - r_4r_6) \\ 2(r_1r_2 - r_4r_5) \\ \left(r_3^2 - r_6^2\right)/2 \\ r_1^2 - r_4^2 + \left(r_3^2 - r_6^2\right)/2 \end{bmatrix} \qquad \boldsymbol{w} = \begin{bmatrix} 4r_8r_9 - 2(r_2r_3 + r_5r_6) \\ 4r_7r_9 - 2(r_1r_3 + r_4r_6) \\ 4r_7r_8 - 2(r_1r_2 + r_4r_5) \\ r_9^2 - \left(r_3^2 + r_6^2\right)/2 \\ r_9^2 - r_1^2 - r_4^2 + 2r_7^2 - \left(r_3^2 + r_6^2\right)/2 \end{bmatrix}.$$

3.3. Expansion coefficient for $\ell = 3$

There are two common sets of the canonical polynomials for $\ell = 3$. The results will be presented for 'general set' [15]:

$$\begin{aligned} Q_3^{-3}(x, y, z) &= x(4z^2 - x^2 - y^2) \\ Q_3^{-2}(x, y, z) &= y(4z^2 - x^2 - y^2) \\ Q_3^{-1}(x, y, z) &= z(2z^2 - 3x^2 - 3y^2) \\ Q_3^{0}(x, y, z) &= xyz \\ Q_3^{1}(x, y, z) &= y(3x^2 - y^2) \\ Q_3^{2}(x, y, z) &= x(x^2 - 3y^2) \\ Q_3^{3}(x, y, z) &= z(x^2 - y^2). \end{aligned} \tag{36}$$

Applying equation (10) it can be verified that the matrix $\mathbf{A}_3$ has the form

$$\mathbf{A}_3 = \sqrt{\frac{2\pi}{105}} \begin{bmatrix} 0 & 0 & 2\sqrt{10} & 0 & -2\sqrt{10} & 0 & 0 \\ 0 & 0 & 2\mathrm{i}\sqrt{10} & 0 & 2\mathrm{i}\sqrt{10} & 0 & 0 \\ 0 & 0 & 0 & 2\sqrt{30} & 0 & 0 & 0 \\ 0 & \mathrm{i} & 0 & 0 & 0 & -\mathrm{i} & 0 \\ 2\mathrm{i}\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 2\mathrm{i}\sqrt{6} \\ 2\sqrt{6} & 0 & 0 & 0 & 0 & 0 & -2\sqrt{6} \\ 0 & 2 & 0 & 0 & 0 & 2 & 0 \end{bmatrix}. \tag{37}$$

The matrix $\mathbf{A}_3$ is invertible, hence only the matrix $\mathbf{C}_3$ is required. In order to obtain the elements of the matrix $\mathbf{C}_3$, theorem 1 is applied. First, the coordinates (x, y, z) are expressed by (x', y', z') and substituted into equation (25). Using expansion of the left-hand side, the coefficients of terms $4x'z'^2$, and $4y'z'^2$, and $2z'^3$ and $x'y'z'$ could be obtained, which are the searched coefficients of $Q_3^k(x', y', z')$ for $k = -3, -2, -1, 0$ (see equation (36)). The other three needed coefficients (for $k = 1, 2, 3$) are found by subtracting already obtained terms and applying the theorem 1 to $-y'^3$, and x'^3 and $z'x'^2$. The result (not as concise as for $\ell = 2$) of this procedure is the matrix $\mathbf{C}_3$ presented in the row form

$$\mathbf{C}_3 = [\boldsymbol{u}_1 \quad \boldsymbol{u}_2 \quad \boldsymbol{u}_3 \quad \boldsymbol{u}_4 \quad \boldsymbol{u}_5 \quad \boldsymbol{u}_6 \quad \boldsymbol{u}_7]^T, \tag{38}$$

where the rows of the matrix $\mathbf{C}_3$ are given by vectors $\boldsymbol{u}_j^T$, for $j = 1, \ldots, 7$ listed below:

$$\boldsymbol{u}_1^T = \begin{bmatrix} (2r_3r_7 + r_1r_9)r_9 - \left(3r_1r_3^2 + 2r_3r_4r_6 + r_1r_6^2\right)/4 \\ (2r_3r_8 + r_2r_9)r_9 - \left(3r_2r_3^2 + 2r_3r_5r_6 + r_2r_6^2\right)/4 \\ -r_3\left(r_3^2 + r_6^2 - 4r_9^2\right)/2 \\ -2[(3r_1r_2 + r_4r_5)r_3 + (r_2r_4 + r_1r_5)r_6 - 4(r_3r_7r_8 + r_2r_7r_9 + r_1r_8r_9)] \\ r_2\left(4r_2^2 + 3r_3^2 + 4r_5^2 + r_6^2 - 16r_8^2 - 4r_9^2\right)/4 + r_3(r_5r_6 - 4r_8r_9)/2 \\ r_1\left(-4r_1^2 - 3r_3^2 - 4r_4^2 - r_6^2 + 16r_7^2 + 4r_9^2\right)/4 - r_3(r_4r_6 - 4r_7r_9)/2 \\ r_3\left(-6r_1^2 - 3r_3^2 - 2r_4^2 - 3r_6^2 + 8r_7^2 + 12r_9^2\right)/2 - 2r_1(r_4r_6 - 4r_7r_9) \end{bmatrix}$$

$$\boldsymbol{u}_2^T = \begin{bmatrix} \left(-r_3^2r_4 - 2r_1r_3r_6 - 3r_4r_6^2\right)/4 + (2r_6r_7 + r_4r_9)r_9 \\ \left(-r_3^2r_5 - 2r_2r_3r_6 - 3r_5r_6^2\right)/4 + (2r_6r_8 + r_5r_9)r_9 \\ -r_6\left(r_3^2 + r_6^2 - 4r_9^2\right)/2 \\ -2[(r_2r_4 + r_1r_5)r_3 + (r_1r_2 + 3r_4r_5)r_6 - 4(r_6r_7r_8 + r_5r_7r_9 + r_4r_8r_9)] \\ r_5\left(4r_2^2 + r_3^2 + 4r_5^2 + 3r_6^2 - 16r_8^2 - 4r_9^2\right)/4 + r_6(r_2r_3 - 4r_8r_9)/2 \\ r_4\left(-4r_1^2 - r_3^2 - 4r_4^2 - 3r_6^2 + 16r_7^2 + 4r_9^2\right)/4 - r_6(r_1r_3 - 4r_7r_9)/2 \\ r_6\left(-2r_1^2 - 3r_3^2 - 6r_4^2 - 3r_6^2 + 8r_7^2 + 12r_9^2\right)/2 - 2r_4(r_1r_3 - 4r_7r_9) \end{bmatrix}$$

$$\boldsymbol{u}_3^T = \begin{bmatrix} -3\left[\left(r_3^2 + r_6^2\right)r_7 + 2\left(r_1r_3r_9 + r_4r_6r_9 - r_7r_9^2\right)\right]/4 \\ -3\left[\left(r_3^2 + r_6^2\right)r_8 + 2\left(r_2r_3r_9 + r_5r_6r_9 - r_8r_9^2\right)\right]/4 \\ -r_9\left(3r_3^2 + 3r_6^2 - 2r_9^2\right)/2 \\ -6[(r_2r_3 + r_5r_6)r_7 + (r_1r_3 + r_4r_6)r_8 + (r_1r_2 + r_4r_5 - 2r_7r_8)r_9] \\ \left[r_8\left(12r_2^2 + 3r_3^2 + 12r_5^2 + 3r_6^2 - 8r_8^2\right) + 6r_9(r_2r_3 + r_5r_6 - r_8r_9)\right]/4 \\ \left[r_7\left(-12r_1^2 - 3r_3^2 - 12r_4^2 - 3r_6^2 + 8r_7^2 + 6r_9^2\right) - 6r_9(r_1r_3 + r_4r_6)\right]/4 \\ -3r_9\left(2r_1^2 + 3r_3^2 + 2r_4^2 + 3r_6^2 - 4r_7^2 - 2r_9^2\right)/2 - 6r_7(r_1r_3 + r_4r_6) \end{bmatrix}$$

$$\boldsymbol{u}_4^T = \begin{bmatrix} (r_3r_6r_7 + r_3r_4r_9 + r_1r_6r_9)/4 \\ (r_3r_6r_8 + r_3r_5r_9 + r_2r_6r_9)/4 \\ r_3r_6r_9/2 \\ (r_3r_5 + r_2r_6)r_7 + (r_3r_4 + r_1r_6)r_8 + (r_2r_4 + r_1r_5)r_9 \\ -[r_8(4r_2r_5 + r_3r_6) + r_9(r_3r_5 + r_2r_6)]/4 \\ [r_7(4r_1r_4 + r_3r_6) + r_9(r_3r_4 + r_1r_6)]/4 \\ r_7(r_3r_4 + r_1r_6) + r_9(2r_1r_4 + 3r_3r_6)/2 \end{bmatrix}$$

$$\boldsymbol{u}_5^T = \begin{bmatrix} 3\left(r_3^2r_4 + 2r_1r_3r_6 - r_4r_6^2\right)/4 \\ 3\left(r_3^2r_5 + 2r_2r_3r_6 - r_5r_6^2\right)/4 \\ r_6\left(3r_3^2 - r_6^2\right)/2 \\ 6[r_4(r_2r_3 - r_5r_6) + r_1(r_3r_5 + r_2r_6)] \\ -r_5\left(12r_2^2 + 3r_3^2 - 4r_5^2 - 3r_6^2\right)/4 - (3/2)r_2r_3r_6 \\ r_4\left(12r_1^2 + 3r_3^2 - 4r_4^2 - 3r_6^2\right)/4 + (3/2)r_1r_3r_6 \\ 6r_1r_3r_4 + (3/2)r_6\left(2r_1^2 + 3r_3^2 - 2r_4^2 - r_6^2\right) \end{bmatrix}$$

$$\boldsymbol{u}_6^T = \begin{bmatrix} 3\left(r_1 r_3^2 - 2r_3 r_4 r_6 - r_1 r_6^2\right)/4 \\ 3\left(r_2 r_3^2 - 2r_3 r_5 r_6 - r_2 r_6^2\right)/4 \\ r_3\left(r_3^2 - 3r_6^2\right)/2 \\ 6[r_3(r_1 r_2 - r_4 r_5) - r_6(r_2 r_4 + r_1 r_5)] \\ -r_2\left(4r_2^2 + 3r_3^2 - 12r_5^2 - 3r_6^2\right)/4 + (3/2) r_3 r_5 r_6 \\ r_1\left(4r_1^2 + 3r_3^2 - 12r_4^2 - 3r_6^2\right)/4 - (3/2) r_3 r_4 r_6 \\ (3/2) r_3\left(2r_1^2 + r_3^2 - 2r_4^2 - 3r_6^2\right) - 6r_1 r_4 r_6 \end{bmatrix}$$

$$\boldsymbol{u}_7^T = \begin{bmatrix} \left[r_7\left(r_3^2 - r_6^2\right) + 2r_9(r_1 r_3 - r_4 r_6)\right]/4 \\ \left[r_8\left(r_3^2 - r_6^2\right) + 2r_9(r_2 r_3 - r_5 r_6)\right]/4 \\ \left(r_3^2 - r_6^2\right) r_9/2 \\ 2[r_7(r_2 r_3 - r_5 r_6) r_7 + r_8(r_1 r_3 - r_4 r_6) + r_9(r_1 r_2 - r_4 r_5)] \\ -r_8\left(4r_2^2 + r_3^2 - 4r_5^2 - r_6^2\right)/4 - r_9(r_2 r_3 - r_5 r_6)/2 \\ r_7\left(4r_1^2 + r_3^2 - 4r_4^2 - r_6^2\right)/4 + r_9(r_1 r_3 - r_4 r_6)/2 \\ r_9\left(2r_1^2 + 3r_3^2 - 2r_4^2 - 3r_6^2\right)/2 + 2r_7(r_1 r_3 - r_4 r_6) \end{bmatrix}$$

The solution seems to be lengthy, but it is extremely simple and can be efficiently implemented, as it contains only multiplication and addition operations.

4. Possible application

One of the possible applications of the expansion coefficient matrix for spherical harmonic, discussed in the present manuscript, is the evaluation of the molecular integrals between slater type orbitals (STO) [1, 2]. This subject was extensively studied by Steinbor's group [16–20]. However, the application of rotations and reflections significantly reduces the complexity of the problem, since the general case can be transformed to the diatomic case with the two coordinate systems of specific mutual orientation. For this diatomic case, Roothaan's group developed a set of compact and efficient algorithms presented in [21–25]. The reduction to this diatomic case is described below.

Let us introduce two Cartesian coordinate systems $\mathcal{C}_a$ and $\mathcal{C}_b$, with origins separated by vector $\boldsymbol{q}$ and parallel axes, as is typical configuration in quantum molecular calculations. Let us create two spherical coordinate systems $\mathcal{S}_a$ and $\mathcal{S}_b$, associated with $\mathcal{C}_a$ and $\mathcal{C}_b$, respectively. Further, let us create two atomic orbitals $f_a(\boldsymbol{r}) = R_a(r) Y_{\ell_a}^{m_a}(\theta, \varphi)$, $f_b(\boldsymbol{r}) = R_b(r) Y_{\ell_b}^{m_b}(\theta, \varphi)$, centered at the origins of $\mathcal{S}_a$ and $\mathcal{S}_b$, where $R_a(r)$, $R_b(r) : \mathbb{R}^+ \mapsto \mathbb{R}$ are the radial parts of atomic orbitals.

Let us introduce two rotations, which transform $\mathcal{S}_a$ to $\mathcal{S}'_a$ and $\mathcal{S}_b$ to $\mathcal{S}'_b$, such that Z axis of $\mathcal{S}'_a$ and Z axis of $\mathcal{S}'_b$ align along vector $\boldsymbol{q}$. These rotations can be accomplished according to equation (14). After these rotations, the X, Y, Z axes of $\mathcal{S}'_a$ and $\mathcal{S}'_b$ are still parallel. Further, since the X, Y, Z axes of $\mathcal{S}_a$ and $\mathcal{S}_b$ are parallel, then, according to equation (14), the rotation angles are equal. Finally, let us introduce the reflection, and change the right-hand coordinate system $\mathcal{S}'_b$ to the left-hand coordinate system $\mathcal{S}''_b$ by changing the direction of the axis Z od $\mathcal{S}'_b$. Then, we obtain the coordinate system which is considered in [21–25].

The rotations of spherical harmonics can be accomplished by the present algorithm. The reflection of spherical harmonics can be easily done, if one observes that the following relations hold:

$$x'' = x' \qquad y'' = y' \qquad z'' = -z' \tag{39}$$

$$r'' = r' \qquad \theta'' = \theta' + \pi \qquad \varphi'' = \varphi', \tag{40}$$

where $(x'', y'', z'') \equiv (r'', \theta'', \varphi'')$ and $(x', y', z') \equiv (r', \theta', \varphi')$ are the coordinates of the same point in $\mathcal{S}_b''$ and $\mathcal{S}_b'$, respectively. Since $\cos(\theta' + \pi) = -\cos(\theta')$, then based on the definition of complex spherical harmonic, equation (1), one has

$$Y_\ell^m(\theta'', \varphi'') = Y_\ell^m(\theta' + \pi, \varphi') = (-1)^\ell Y_\ell^m(\theta', \varphi'). \tag{41}$$

Hence, the complex spherical harmonic, defined in $\mathcal{S}_b''$, is expressed by the complex spherical harmonic defined in $\mathcal{S}_b'$. Thus, having the efficient rotation algorithm for spherical harmonic (like the presented), one can obtain all the molecular integrals, which can be obtained for diatomic systems.

5. Summary

In the present paper the complex spherical harmonic in the rotated coordinate system was analyzed. The rotation is defined by the rotation axis and the rotation angle. The complex spherical harmonic defined in the fixed coordinate system was expanded as a linear combination of the complex spherical harmonic in the rotated coordinate system. It was proved that the expansion coefficients matrix has the simple form $\mathbf{D} = \mathbf{A}^{-1}\mathbf{C}\mathbf{A}$. Since it can be treated as a similarity transformation, the rotation of the complex spherical harmonics can be viewed as a three-step procedure:

(i) Express the complex spherical harmonics as the canonical polynomials.
(ii) Rotate the canonical polynomials.
(iii) Express the rotated canonical polynomials as the complex spherical harmonics.

The general algorithm was presented and the explicit form of the expansion coefficients was evaluated for $\ell = 0, 1, 2, 3$.

Our algorithm resembles the algorithm developed in [10, 11]. However, the algorithm developed in [10, 11] depends on the recursive relations between spherical harmonics. On the other hand, our algorithm is based on the Cartesian representation of spherical harmonic described in section 2.1. From the numerical point of view both algorithms are comparable and are superior as compared to the algorithms based on Euler angles [3–5], since the factorial terms are avoided. If one is interested in the rotation of spherical harmonics for $\ell = 1, 2, 3$, then our method is much easier to implement. The presented algorithm requires only two matrix multiplications $\mathbf{D} = \mathbf{A}^{-1}\mathbf{C}\mathbf{A}$, where matrix $\mathbf{A}$ does not depend on the rotation angle. Moreover, the expressions are compact and ready for efficient implementation.

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