Vol. 39 (2008) *ACTA PHYSICA POLONICA B* No 8

TRANSFORMATION OF REAL SPHERICAL HARMONICS UNDER ROTATIONS

Zbigniew Romanowski

Interdisciplinary Centre for Materials Modelling
Pawińskiego 5a, 02-106 Warsaw, Poland

Stanisław Krukowski

Institute of High Pressure Physics of the Polish Academy of Sciences
Sokołowska 29/37, 01-142 Warsaw, Poland

Abraham F. Jalbout

Department of Chemistry, The University of Arizona, Tucson, AZ USA

(Received February 8, 2008)

The algorithm rotating the real spherical harmonics is presented. The convenient and ready to use formulae for $\ell = 0, 1, 2, 3$ are listed. The rotation in $\mathbb{R}^3$ space is determined by the rotation axis and the rotation angle; the Euler angles are not used. The proposed algorithm consists of three steps. *(i)* Express the real spherical harmonics as the linear combination of canonical polynomials. *(ii)* Rotate the canonical polynomials. *(iii)* Express the rotated canonical polynomials as the linear combination of real spherical harmonics. Since the three step procedure can be treated as a superposition of rotations, the searched rotation matrix for real spherical harmonics is a product of three matrices. The explicit formulae of matrix elements are given for $\ell = 0, 1, 2, 3$, what corresponds to s, p, d, f atomic orbitals.

PACS numbers: 31.15.Ar, 31.15.Fx, 71.15.Mb, 71.15.Dx

1. Introduction

In the previous paper [1] the algorithm rotating the complex spherical harmonics was presented. The proposed algorithm has the following properties:

- It does not use the Euler angles [2–4].
- The rotation is determined by the rotation axis and one rotation angle [5].

- For fixed angular momentum number, ℓ, the rotation matrix, $\boldsymbol{D}_\ell$, which rotates the complex spherical harmonic, is a product of three matrices.

The main idea of the algorithm is to split the rotation into three steps:

1. Express the complex spherical harmonics as the linear combination of canonical polynomials, matrix $\boldsymbol{B}_\ell$.
2. Rotate the canonical polynomials, matrix $\boldsymbol{C}_\ell$.
3. Express the rotated canonical polynomials as the linear combination of complex spherical harmonics, matrix $\boldsymbol{A}_\ell$.

It was shown in Ref. [1], that if $\boldsymbol{B}_\ell$ is invertible, then $\boldsymbol{B}_\ell = \boldsymbol{A}_\ell^{-1}$, and the searched rotation matrix $\boldsymbol{D}_\ell$ is a product:

$$\boldsymbol{D}_\ell = \boldsymbol{A}_\ell^{-1}\boldsymbol{C}_\ell\boldsymbol{A}_\ell\,. \tag{1}$$

From the above, it follows that the matrix $\boldsymbol{C}_\ell$ depends only on the canonical polynomials.

In the present paper, the three steps procedure, for real spherical harmonics is applied. Let us denote (for fixed ℓ) the rotation matrix for real spherical harmonics by $\boldsymbol{D}_\ell^{\mathrm{r}}$. Further, let denote by $\boldsymbol{A}_\ell^{\mathrm{r}}$ the matrix expressing the rotated canonical polynomials as the linear combination of real spherical harmonics. Since the matrix $\boldsymbol{C}_\ell$ depends only on the canonical polynomials, then:

$$\boldsymbol{D}_\ell^{\mathrm{r}} = (\boldsymbol{A}_\ell^{\mathrm{r}})^{-1}\boldsymbol{C}_\ell\boldsymbol{A}_\ell^{\mathrm{r}}\,. \tag{2}$$

Since the matrix $\boldsymbol{C}_\ell$ was derived in Ref. [1] for $\ell = 0, 1, 2, 3$, then the only thing required to define the rotation matrices for real spherical harmonics is the definition of matrix $\boldsymbol{A}_\ell^{\mathrm{r}}$. In the present paper the matrix $\boldsymbol{A}_\ell^{\mathrm{r}}$ is derived for $\ell = 0, 1, 2, 3$, what corresponds to s, p, d, f atomic orbitals.

2. Definitions

According to the Condon–Shortley phase conventions [4,12], the complex spherical harmonics are defined for $|m| \leq \ell$ as:

$$Y_\ell^m(\theta,\varphi) = N_\ell^m \mathcal{P}_\ell^{|m|}(\cos(\theta))e^{\mathrm{i}m\varphi}\,, \tag{3}$$

where N_ℓ^m is a normalization factor:

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

and $\mathcal{P}_\ell^{|m|}(v)$ is an associated Legendre function defined by Rodrigues' formula [6, Eq. 22.11] valid for $|v| \leq 1$ and $m \geq 0$:

$$\mathcal{P}_\ell^m(v) = \frac{(1-v^2)^{m/2}}{2^\ell \ell!} \frac{d^{m+\ell}}{dv^{m+\ell}} (v^2-1)^\ell \,. \tag{5}$$

Real spherical harmonic, $\mathcal{Y}_\ell^m(\theta,\varphi)$, is defined [7] as a linear combination of complex spherical harmonics:

$$\mathcal{Y}_\ell^m(\theta,\varphi) = \begin{cases} \frac{1}{\sqrt{2}}[Y_\ell^{-m}(\theta,\varphi) + (-1)^m Y_\ell^m(\theta,\varphi)] & \text{for} \quad m>0\,, \\ Y_\ell^m(\theta,\varphi) & \text{for} \quad m=0\,, \\ \frac{\mathrm{i}}{\sqrt{2}}[Y_\ell^m(\theta,\varphi) - (-1)^m Y_\ell^{-m}(\theta,\varphi)] & \text{for} \quad m<0\,. \end{cases} \tag{6}$$

In Ref. [1] it was shown, that $r^\ell Y_\ell^m(\theta,\varphi)$ for $m \geq 0$ is a complex polynomial of x, y, z:

$$r^\ell Y_\ell^m(\theta,\varphi) \equiv r^\ell Y_\ell^m(x,y,z) = N_\ell^m (x+\mathrm{i}y)^m \sum_{k=0}^{\lfloor(\ell-m)/2\rfloor} \gamma_{\ell,k}^{(m)} r^{2k} z^{\ell-2k-m}\,, \tag{7}$$

where (x,y,z) is a point in Cartesian coordinate system defined by the point (r,θ,φ) in the spherical coordinate system, hence, relations hold: $r^2 = x^2+y^2+z^2$, $z = r\cos(\theta)$, $y = r\sin(\theta)\sin(\varphi)$ and $x = r\sin(\theta)\cos(\varphi)$. In Eq. (7), the coefficient $\gamma_{\ell,k}^{(m)}$ is defined as

$$\gamma_{\ell,k}^{(m)} = (-1)^k 2^{-\ell} \binom{\ell}{k} \binom{2\ell-2k}{\ell} \frac{(\ell-2k)!}{(\ell-2k-m)!} \tag{8}$$

and $\lfloor(\ell-m)/2\rfloor$ is the largest integer number less than $(\ell-m)/2$. Multiplying Eq. (6) by r^ℓ and substituting Eq. (7) we obtain the real polynomial of x, y, z:

$$\begin{aligned} r^\ell \mathcal{Y}_\ell^m(\theta,\varphi) &\equiv r^\ell \mathcal{Y}_\ell^m(x,y,z) \\ &= r^\ell \begin{cases} \frac{1}{\sqrt{2}}[Y_\ell^{-m}(x,y,z) + (-1)^m Y_\ell^m(x,y,z)] & \text{for} \quad m>0\,, \\ Y_\ell^m(x,y,z) & \text{for} \quad m=0\,, \\ \frac{\mathrm{i}}{\sqrt{2}}[Y_\ell^m(x,y,z) - (-1)^m Y_\ell^{-m}(x,y,z)] & \text{for} \quad m<0\,. \end{cases} \end{aligned} \tag{9}$$

The function $\mathcal{Y}_\ell^m(x,y,z)$ is a Cartesian representation of the real spherical harmonic. For example, for $\ell = 1$ we get:

$$\begin{aligned} \mathcal{Y}_1^{-1}(x,y,z) &= \sqrt{3/(4\pi)}\, y/r\,, \\ \mathcal{Y}_1^{0}(x,y,z) &= \sqrt{3/(2\pi)}\, z/r\,, \\ \mathcal{Y}_1^{1}(x,y,z) &= \sqrt{3/(4\pi)}\, x/r\,. \end{aligned}$$

3. Rotation of real spherical harmonics in $\mathbb{R}^3$

Let us introduce the sphere of any radius and the center located at the origin of coordinate system, and denote by (θ, φ) and (θ', φ') two points located on it. It was proved [2–4], that for complex spherical harmonics the relation holds:

$$Y_\ell^m(\theta, \varphi) = \sum_{M=-\ell}^{\ell} d_{m,M}^{(\ell)} Y_\ell^M(\theta', \varphi') \,. \tag{10}$$

This relation means, that for fixed ℓ, the set of functions $S_\ell = \{Y_\ell^m(\theta, \varphi)\}$ for $m = -\ell, \ldots, \ell$ is complete. By definition (6), real spherical harmonic, $\mathcal{Y}_\ell^m(\theta, \varphi)$ is a linear combination of two complex spherical harmonics $Y_\ell^m(\theta, \varphi)$ and $Y_\ell^{-m}(\theta, \varphi)$ with the same angular momentum number ℓ. Thus, because of completeness of set S_ℓ, we have

$$\mathcal{Y}_\ell^m(\theta, \varphi) = \sum_{M=-\ell}^{\ell} \tilde{d}_{m,M}^{(\ell)} \mathcal{Y}_\ell^M(\theta', \varphi') \,, \tag{11}$$

where $\tilde{d}_{m,M}^{(\ell)}$ denotes the element of (searched) rotation matrix $\boldsymbol{D}_\ell^{\mathrm{r}}$.

As was indicated in Section 1, the only required thing to define the matrix $\boldsymbol{D}_\ell^{\mathrm{r}} = (\boldsymbol{A}_\ell^{\mathrm{r}})^{-1} \boldsymbol{C}_\ell \boldsymbol{A}_\ell^{\mathrm{r}}$ is to find the matrix $\boldsymbol{A}_\ell^{\mathrm{r}}$. The elements $\tilde{a}_{k,m}^{(\ell)}$ of matrix $\boldsymbol{A}_\ell^{\mathrm{r}}$ are defined by the equation [1]:

$$Q_\ell^k(x, y, z) = r^\ell \sum_{m=-\ell}^{\ell} \tilde{a}_{k,m}^{(\ell)} \mathcal{Y}_\ell^m(x, y, z) \,. \tag{12}$$

In this equation, the canonic polynomial, $Q_\ell^k(x, y, z)$ for $k = -\ell, \ldots, \ell$, is represented as a linear combination of real spherical harmonics. Due to the specific selection of $Q_\ell^k(x, y, z)$, the elements $\tilde{a}_{k,m}^{(\ell)}$ can be easily found from the polynomial representation of $\mathcal{Y}_\ell^m(x, y, z)$, defined in Eq. (9). Since the real spherical harmonic for $\ell = 0$ is constant, then $\tilde{d}_{0,0}^{(0)} = 1$. The results obtained for $\ell = 1, 2, 3$ are presented in the following subsections.

3.1. Expansion coefficient for $\ell = 1$

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

$$Q_1^{-1}(x, y, z) = x \,, \tag{13a}$$
$$Q_1^{0}(x, y, z) = y \,, \tag{13b}$$
$$Q_1^{1}(x, y, z) = z \,. \tag{13c}$$

Then, based on Eqs. (7), (9) and (12) the matrix $\boldsymbol{A}_1^{\mathrm{r}}$ has the form:

$$\boldsymbol{A}_1^{\mathrm{r}} = \sqrt{\frac{4\pi}{3}} \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & 0 \end{bmatrix} . \tag{14}$$

The matrix $\boldsymbol{A}_1^{\mathrm{r}}$ is invertible.

3.2. Expansion coefficient for $\ell = 2$

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

$$Q_2^{-2}(x,y,z) = yz\,, \tag{15a}$$
$$Q_2^{-1}(x,y,z) = xz\,, \tag{15b}$$
$$Q_2^{0}(x,y,z) = xy\,, \tag{15c}$$
$$Q_2^{1}(x,y,z) = x^2 - y^2\,, \tag{15d}$$
$$Q_2^{2}(x,y,z) = 2z^2 - x^2 - y^2 = 3z^2 - r^2\,. \tag{15e}$$

Then, based on Eqs. (7), (9) and (12), the matrix $\boldsymbol{A}_2^{\mathrm{r}}$ has the form:

$$\boldsymbol{A}_2^{\mathrm{r}} = \sqrt{\frac{4\pi}{15}} \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & \sqrt{6} & 0 & 0 \end{bmatrix} . \tag{16}$$

The matrix $\boldsymbol{A}_2^{\mathrm{r}}$ is invertible.

3.3. Expansion coefficient for $\ell = 3$

Let recall the “general set” of canonical polynomials $Q_3^k(x,y,z)$, for $k = -3,\ldots,3$

$$Q_3^{-3}(x,y,z) = x(4z^2 - x^2 - y^2)\,, \tag{17a}$$
$$Q_3^{-2}(x,y,z) = y(4z^2 - x^2 - y^2)\,, \tag{17b}$$
$$Q_3^{-1}(x,y,z) = z(2z^2 - 3x^2 - 3y^2)\,, \tag{17c}$$
$$Q_3^{0}(x,y,z) = xyz\,, \tag{17d}$$
$$Q_3^{1}(x,y,z) = y(3x^2 - y^2)\,, \tag{17e}$$
$$Q_3^{2}(x,y,z) = x(x^2 - 3y^2)\,, \tag{17f}$$
$$Q_3^{3}(x,y,z) = z(x^2 - y^2)\,. \tag{17g}$$

Applying Eqs. (7), (9) and (12) it can be verified that the matrix $\boldsymbol{A}_3^{\mathrm{r}}$ has the form:

$$\boldsymbol{A}_3^{\mathrm{r}} = 4\sqrt{\frac{2\pi}{21}} \begin{bmatrix} 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3}/2 & 0 & 0 & 0 \\ 0 & 1/\sqrt{40} & 0 & 0 & 0 & 0 & 0 \\ \sqrt{3/5} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{3/5} \\ 0 & 0 & 0 & 0 & 0 & 1/\sqrt{10} & 0 \end{bmatrix} . \qquad (18)$$

The matrix $\boldsymbol{A}_3^{\mathrm{r}}$ is invertible.

4. Possible application

In Density Function Theory (DFT) [8,9] the fundamental equation is the Kohn–Sham eigenproblem

$$\hat{H}_{\mathrm{KS}}\,\psi_\mu = \varepsilon_\mu \psi_\mu \, . \qquad (19)$$

For molecular systems, this equation is often solved by Linear Combination of Atomic Orbitals (LCAO), with $\psi_\mu(\boldsymbol{r}) = \sum_j c_{\mu,j}\chi_j(\boldsymbol{r})$, where $\chi_j(\boldsymbol{r})$ are so called basis functions and $c_{\mu,j}$ are the expansion coefficients. The LCAO method transforms the Kohn–Sham functional eigenproblem, Eq. (19), to the algebraic generalized eigenproblem $\boldsymbol{Hc} = \boldsymbol{\varepsilon S}$, where the elements of matrices $\boldsymbol{H}$ and $\boldsymbol{S}$ are given by

$$h_{j,k} = \int\limits_{\mathbb{R}^3} \chi_j^*(\boldsymbol{r})\hat{H}_{\mathrm{ks}}\chi_k(\boldsymbol{r})d\boldsymbol{r}\, , \qquad s_{j,k} = \int\limits_{\mathbb{R}^3} \chi_j^*(\boldsymbol{r})\chi_k(\boldsymbol{r})d\boldsymbol{r}\, , \qquad (20)$$

where * denotes conjugate complex. The main cost of LCAO method is:

- Evaluation of integrals $h_{j,k}$ and $s_{j,k}$.
- Solution of generalized algebraic eigenproblem $\boldsymbol{Hc} = \boldsymbol{\varepsilon S}$.

Often, the basis function $\chi_j(\boldsymbol{r})$ is represented as a product of the radial part and the spherical part: $\chi_j(\boldsymbol{r}) \equiv \chi_j(r,\theta,\varphi) = R_j(r)U_j(\theta,\varphi)$. When spherical part is a complex spherical harmonic, *i.e.* $U_j(\theta,\varphi) \equiv Y_\ell^m(\theta,\varphi)$, then matrices $\boldsymbol{H}$ and $\boldsymbol{S}$ are complex. When spherical part is a real spherical harmonic, *i.e.* $U_j(\theta,\varphi) \equiv \mathcal{Y}_\ell^m(\theta,\varphi)$, then matrices $\boldsymbol{H}$ and $\boldsymbol{S}$ are real. Since the solution cost of generalized eigenproblem is four times higher for the complex matrices than for the real matrices [10,11], it is desirable to apply the real spherical harmonics to save the computational time.

The evaluation of the matrix elements $h_{j,k}$ is a very complicated task. Generally, the integrals $h_{j,k}$ can be classified as one-, two-, three- and four-center integrals. The evaluation of these integrals can be substantially simplified, when the rotations and translations of basis functions $\chi_j(\boldsymbol{r})$ are used. Since the radial part of $\chi_j(\boldsymbol{r})$ does not change under rotations, then to rotate $\chi_j(\boldsymbol{r})$ only the spherical part $\mathcal{Y}_\ell^m(\theta,\varphi)$ must be rotated. When the spherical part of $\chi_j(\boldsymbol{r})$ is represented by a real spherical harmonic, then the algorithm described in the present paper might be useful.

5. Summary

The rotation of the real spherical harmonic was analyzed. The rotation was defined by the rotation axis and the rotation angle. The real spherical harmonic defined in the fixed coordinate system was expanded as a linear combination of the real spherical harmonic in the rotated coordinate system. The present manuscript heavily depends on the previous paper, where the rotation of the complex spherical harmonics was considered. For both cases, the rotation matrix is determined by two matrices. Since one matrix $\boldsymbol{C}_\ell$ is the same for complex and real spherical harmonics, the only difference is in the matrices $\boldsymbol{A}_\ell$ and $\boldsymbol{A}_\ell^{\mathrm{r}}$, which were easily obtained. The present algorithm might be useful in computational quantum chemistry.

REFERENCES

[1] Z. Romanowski, S. Krukowski, *J. Phys.* **A40**, 15071 (2007).

[2] M.E. Edmonds, *Angular Momentum in Quantum Mechanics*, Princeton University Press, New York 1974.

[3] D.A. Varshalovitch, A.N. Moskalev, V.K. Khersonskii, *Quantum Theory of Angular Momentum Techniques*, World Scientific, Singapore 1989.

[4] E.O. Steinborn, K. Ruedenberg, *Adv. Quant. Chem.* **7**, 1 (1973).

[5] J.D. Foley, A. van Dam, S.K. Feiner, J.F. Hughes, R.L. Phillips, *Introduction to Computer Graphics*, Addison–Wesley Professional, New York 1993.

[6] M. Abramowitz, I.A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, Dover Publications, New York 1972, `http://www.math.sfu.ca/ cbm/aands/toc.htm`

[7] E.O. Steinborn, *Adv. Quant. Chem.* **7**, 83 (1973).

[8] R.G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford 1989.

[9] W. Koch, M.C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Ed. Wiley, New York 2000.

[10] J. Stoer, R. Bulirsch, *Introduction to Numerical Analysis*, Springer, NY 2004.

[11] G.H. Golub, C.F. Van Loan, *Matrix Computation*, The Johns Hopkins University Press, Baltimore 1996.

[12] E.U. Condon, G.H. Shortley, *The Theory of Atomic Spectra*, Ed. Cambridge University Press, UK Cambridge 1970.