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Evaluation of the rotation matrices in the basis of real spherical harmonics

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Abstract

Rotation matrices (or Wigner *D* functions) are the matrix representations of the rotation operators in the basis of spherical harmonics. They are the key entities in the generation of symmetry-adapted functions by means of projection operators. Although their expression in terms of ordinary (complex) spherical harmonics and Euler rotation angles is well known, an alternative representation using real spherical harmonics is desirable. The aim of this contribution is to obtain a general algorithm to compute the representation matrix of any point-group symmetry operation in the basis of the real spherical harmonics, paying attention to the use of recurrence relationships that allow the treatment of functions with high angular momenta. © 1997 Elsevier Science B.V.

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1. Introduction

The choice of real spherical harmonics (RSH) as basis functions in electronic-structure calculations has a number of advantages over other alternatives. Ordinary complex spherical harmonics are easier to manipulate theoretically, owing to a number of useful relationships that lose their simplicity when stated in terms of the RSH. However, they are complex functions requiring twice the computer memory needed by RSH, as well as a complete rewriting of quantum-mechanical programs to diagonalize Hermitian matrices instead of real ones.

A second alternative are the $x^i y^j z^k$ Cartesian functions. These are real functions and are used in most self-consistent field (SCF) programs. Once again, the expressions of integrals in terms of these functions are simpler than those in terms of the RSH, owing to their Cartesian tensorial character. However, these functions have two main problems: their use becomes more involved for high angular momenta, and they include undesired atomic symmetry-adapted functions when the index $l = i + j + k > 2$. Another problem associated to the use of these functions is their use along with Slater-type radial functions, since the best compilation of optimized exponents for Slater-type orbitals (STO), that of Clementi and Roetti [1], uses spherical harmonics which can be considered to be either real or complex, because of the spherical symmetry of the free atoms.

In addition to the advantages mentioned above, the real spherical harmonics are the symmetry-adapted

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functions for atoms under most point groups. In relation to this subject, McWeeny [2] points out: ''Although the complex functions provide the standard representations of the full group D_3, the real spherical harmonics are often just the correct combinations to carry irreducible representations of its subgroups — the point groups''. Appendix 1 of the same reference also gives an exhaustive list of the symmetry-adapted functions of the crystal point groups. The RSH are, therefore, the most adequate basis functions for calculations in which atomic symmetry is important, when high angular momenta are needed, or when using high-quality Slater-type radial basis functions.

In order to use the RSH the following three basic items are necessary: a definition suitable for recurrent evaluation of functions with high angular momenta, a set of rules for evaluation of the coupling coefficients between them (Gaunt coefficients), and a means of computing their rotation matrices in order to obtain symmetry functions. The first item is presented in Section 2, dedicated to the definition and basic properties of the RSH. The second item has been recently treated by Homeier and Steinborn [3]. The third item, obtaining in an efficient way the representation matrices of the symmetry operations in the basis of the RSH, is the main objective of this contribution, and will be addressed to in Section 3. Recently, Ivanic and Ruedenberg [4] developed a completely different method with the same goal. These authors deal directly with the rotation matrices, while in the present work we deal with their representation in terms of the Euler angles.

2. Definition and basic properties

Real spherical harmonics are defined in terms of their complex analogs. These are the eigenfunctions of the orbital angular momentum operators, $\hat{l}^2$ and $\hat{l}_z$, and can be labeled by two quantum numbers, l and m, related to the corresponding eigenvalues. The complex spherical harmonic Y_{lm} can be written as [5–7]

$$\begin{aligned} Y_{lm}(\theta,\phi) &= (-1)^m \Theta_{lm}(\theta)\, e^{im\phi} \\ &= (-1)^m N_{lm} P_l^m(\cos\theta)\, e^{im\phi} \end{aligned} \tag{1}$$

where l takes non-negative integer values, the possible values for m are the integers from $-l$ to l, θ and ϕ are the angular spherical coordinates, N_{lm} is the normalization factor

$$N_{lm} = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}} \tag{2}$$

and $P_l^m(x)$ are the Legendre associated polynomials, which can be defined through the Rodrigues formula,

$$P_l^m(x) = \frac{1}{2^l l!}(1-x^2)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l \tag{3}$$

From this definition one can derive [6]

$$Y_{lm}^*(\theta,\phi) = (-1)^m Y_{l\bar{m}}(\theta,\phi) \tag{4}$$

where $\bar{m}$ means $-m$. Introducing the notation $\hat{r} = (\theta,\phi)$ for the angular coordinates, one can also derive the parity property

$$Y_{lm}(-\hat{r}) = Y_{lm}(\hat{\imath}\hat{r}) = (-1)^l Y_{lm}(\hat{r}) \tag{5}$$

where $\hat{\imath}$ is the spatial inversion operator.

The complex dependence in ϕ, $e^{im\phi}$, is characteristic of the spherical symmetry of atoms, being the eigenfunction of $\hat{l}_z$. However, functions with different m are degenerate for effective Hamiltonians with spherical symmetry, so any linear combination of these functions will still be an eigenfunction of this kind of Hamiltonian. In particular, one can choose real functions by combining complex conjugate functions, corresponding to opposite values of m. In this way, the real spherical harmonics are defined as [7]

$$S_{lm}(\theta,\phi) = \begin{cases} \dfrac{(-1)^m}{\sqrt{2}}(Y_{lm}+Y_{lm}^*) = \Theta_{lm}(\theta)\sqrt{2}\cos m\phi, & m>0 \\ Y_{l0} = \Theta_{l0}(\theta), & m=0 \\ \dfrac{(-1)^m}{i\sqrt{2}}\left(Y_{l|m|}-Y_{l|m|}^*\right) = \Theta_{l|m|}(\theta)\sqrt{2}\sin|m|\phi, & m<0 \end{cases} \tag{6}$$

The $(-1)^m$ factor has been introduced following Chisholm [7], in order to obtain signless expressions for the real spherical harmonics (see Table 1). These functions can also be written as

$$S_{lm}(\theta,\phi) = \Theta_{l|m|}(\theta)\Phi_m(\phi) \tag{7}$$

Table 1
Real spherical harmonics with $l \le 2$. The factors $\sqrt{(2l+1)/4\pi}$ have been omitted for simplicity

l	s	p	d
$m = -2$			$\frac{\sqrt{3}}{2}\sin^2\theta\sin 2\phi = \sqrt{3}xy/r^2$
-1		$\sin\theta\sin\phi = y/r$	$\frac{\sqrt{3}}{2}\sin 2\theta\sin\phi = \sqrt{3}yz/r^2$
0	1	$\cos\theta = z/r$	$\frac{1}{2}(3\cos^2\theta - 1) = \frac{1}{2}(3z^2/r^2 - 1)$
1		$\sin\theta\cos\phi = x/r$	$\frac{\sqrt{3}}{2}\sin 2\theta\cos\phi = \sqrt{3}xz/r^2$
2			$\frac{\sqrt{3}}{2}\sin^2\theta\cos 2\phi = \frac{\sqrt{3}}{2}(x^2-y^2)/r^2$

by defining the azimuthal function as

$$\Phi_m(\phi) = \begin{cases} \sqrt{2}\cos m\phi, & m > 0 \\ 1, & m = 0 \\ \sqrt{2}\sin |m|\phi, & m < 0. \end{cases} \tag{8}$$

The real spherical harmonics for $l \le 2$ are presented in Table 1.

To obtain the real spherical harmonics one can use closed formulas for Legendre polynomials (see for example [5]), and then evaluate directly $\cos m\phi$ and $\sin m\phi$. However, this can lead to numerical instabilities, in addition to being inefficient when, as is usually the case, all the RSH up to a given l are needed. In this case, it is more efficient to use stable recurrence relationships, such as [8]

$$P_0^0(\cos\theta) = 1 \tag{9}$$

$$P_l^l(\cos\theta) = (2l-1)\sin\theta\, P_{l-1}^{l-1}(\cos\theta) \tag{10}$$

$$P_{l+1}^l(\cos\theta) = (2l+1)\cos\theta\, P_l^l(\cos\theta) \tag{11}$$

$$P_l^m(\cos\theta) = \frac{(2l-1)\cos\theta\, P_{l-1}^m(\cos\theta) - (l+m-1)P_{l-2}^m(\cos\theta)}{(l-m)} \tag{12}$$

For the ϕ functions, one can start with the $\sin\phi$ and $\cos\phi$ values, and then use the known trigonometric formulas:

$$\sin m\theta = \sin\phi\cos(m-1)\phi + \cos\phi\sin(m-1)\phi \tag{13}$$

$$\cos m\phi = \cos\phi\cos(m-1)\phi - \sin\phi\sin(m-1)\phi \tag{14}$$

With these recurrence relationships, one can obtain the ϕ and θ functions separately, so that no one expression is computed more than once, because only Legendre polynomials with $m \ge 0$ are needed, and ϕ functions for a given m are common for all l values. The normalization factors N_{lm} ($m \ge 0$) can be computed only once, at the very beginning of a calculation, and then used any time a spherical harmonic is evaluated.

Given their definition, Eq. (6), the RSH have the following properties. First of all, since they always involve complex spherical functions with the same l value, they share the same symmetry under inversion,

$$S_{lm}(-\hat{r}) = S_{lm}(\hat{\imath}\hat{r}) = (-1)^l S_{lm}(\hat{r}) \tag{15}$$

Secondly, it is easy to prove their orthonormality from that of their complex counterparts,

$$\langle S_{lm}|S_{l'm'}\rangle = \delta_{ll'}\delta_{mm'} \tag{16}$$

Thirdly, they are real functions,

$$S_{lm}^*(\hat{r}) = S_{lm}(\hat{r}) \tag{17}$$

Eq. (6) can be written in matrix form as

$$\vec{S}_l = \mathbf{C}^l \vec{Y}_l \tag{18}$$

where we define column vectors containing real and complex spherical harmonics, ordered by raising m values, and the transformation matrix between them for a given l is

$$\mathbf{C}^l = \frac{1}{\sqrt{2}}\begin{pmatrix} i & 0 & \cdots & 0 & \cdots & 0 & -i(-1)^l \\ 0 & i & \cdots & 0 & \cdots & -i(-1)^{l-1} & 0 \\ \vdots & \vdots & \ddots & \vdots & \iddots & \vdots & \vdots \\ 0 & 0 & \cdots & \sqrt{2} & \cdots & 0 & 0 \\ \vdots & \vdots & \iddots & \vdots & \ddots & \vdots & \vdots \\ 0 & 1 & \cdots & 0 & \cdots & (-1)^{l-1} & 0 \\ 1 & 0 & \cdots & 0 & \cdots & 0 & (-1)^l \end{pmatrix} \tag{19}$$

This matrix can be represented by a set of simple rules:

1. $C^l_{mm'} = 0$ if $|m| \neq |m'|$.
2. $C^l_{00} = 1$.
3. $C^l_{mm} = (-1)^m/\sqrt{2}$.
4. $C^l_{m\bar{m}} = 1/\sqrt{2}$.
5. $C^l_{\bar{m}m} = -i(-1)^m/\sqrt{2}$.
6. $C^l_{\bar{m}\bar{m}} = i/\sqrt{2}$.

In the last four rules, $m > 0$ is assumed. It can also be proved that $\mathbf{C}^l$ is a unitary matrix, that is,

$$(\mathbf{C}^l)^{-1} = (\mathbf{C}^l)^{\dagger} = \left[(\mathbf{C}^l)^t\right]^* \tag{20}$$

In this way, the matrix definition can be reversed to obtain

$$\vec{Y}_l = (\mathbf{C}^l)^{-1}\vec{S}_l = (\mathbf{C}^l)^{\dagger}\vec{S}_l \tag{21}$$

By using the previous relationship and the completeness of the complex functions, it is possible to demonstrate that the RSH constitute a complete basis set. Effectively, if a given function can be written as a linear combination of complex spherical harmonics of a given l, this can also be made in terms of the real ones, by making an appropriate transformation on the coefficients of the linear combination:

$$\begin{aligned}\sum_m c_{lm} Y_{lm} &= \sum_m c_{lm} \sum_{m'} (C^l_{mm'})^{-1} S_{lm'} \\ &= \sum_{m'}\left(\sum_m c_{lm}(C^l_{mm'})^{-1}\right) S_{lm'} = \sum_{m'} b_{lm'} S_{lm'}\end{aligned} \tag{22}$$

where $b_{lm'} = \sum_m c_{lm}(C^l_{mm'})^{-1}$. A special case of the previous expression occurs when the c_{lm} coefficients are in turn complex spherical functions of a different coordinate system than that of the initial expansion. In this case, if $c_{lm} = Y^*_{lm}(\hat{r}')$, then

$$\begin{aligned}b_{lm'} &= \sum_m Y^*_{lm}(\hat{r}')(C^l_{mm'})^{-1} = \left[\sum_m C^l_{m'm} Y_{lm}(\hat{r}')\right]^* \\ &= S^*_{lm'}(\hat{r}')\end{aligned} \tag{23}$$

which, being the RSH real functions, equals $S_{lm'}(\hat{r}')$, and so the interesting property follows:

$$\sum_m Y_{lm}(\hat{r}) Y^*_{lm}(\hat{r}') = \sum_m S_{lm}(\hat{r}) S_{lm}(\hat{r}') \tag{24}$$

which is very useful in the Laplace expansion of the Coulomb repulsion operator r_{12}^{-1}.

3. Symmetry transformations

The use of symmetry is fundamental for simplifying the quantum-mechanical determination of the electronic structure. Be it spatial or point symmetry, its use can greatly reduce the number of non-equivalent integrals to compute, and also the size of matrices in the program, by employing symmetry-adapted functions. In order to obtain these symmetry functions, it is necessary to know the transformation properties of the atomic basis functions under symmetry operations. In this work, we will restrict ourselves to point-symmetry groups, because they are the only ones needed for finite molecules.

First of all, let us see how point-symmetry operations are represented. Let $\hat{R}$ be a symmetry operation of the G point group, and $\vec{r}$ a point in the three-dimensional space. If we apply the symmetry operation to this point, we obtain a new point $\vec{r}'$ which relates to the original one through

$$\hat{R}\vec{r} = \vec{r}' = \mathbf{R}\vec{r} \tag{25}$$

where $\mathbf{R}$ is the matrix associated to the operation, i.e., the representation matrix of the $\hat{R}$ operation in the basis of the Cartesian coordinates. The operations are classified as proper or improper depending upon the determinant of their associated matrices: +1 and –1, respectively. Any improper operation can be seen as the product of a proper operation and the inversion:

$$\hat{S} = \hat{S}\hat{1} = \hat{S}\hat{\imath}\hat{\imath} = (\hat{S}\hat{\imath})\hat{\imath} = \hat{R}\hat{\imath} \tag{26}$$

where $\hat{S}$ is an improper operation and $\hat{R} = \hat{S}\hat{\imath}$ is the corresponding proper operation. Remembering that the representation of a product of operations is the product of the representations of each operation, **S** = **Ri**, and the **i** matrix is just the negative of the unit matrix, one can see that **R** = –**S**.

Up to this point, all representations are taken in the Cartesian basis. If we want to obtain the representation matrices in the basis of the real spherical harmonics, we must know what happens to these functions upon the symmetry transformation. It can be shown that, for point symmetry operations,

$$\hat{R}S_{lm'}(\hat{r}) = S_{lm'}(\mathbf{R}^{-1}\hat{r}) = \sum_m \Delta^l_{mm'}(\hat{R})S_{lm}(\hat{r}) \quad (27)$$

that is, the spherical harmonics of a given l are transformed into a linear combination of functions of the same l. It must be noted that, in this definition, the matrix $\boldsymbol{\Delta}^l(\hat{R})$ multiplies the spherical harmonics as row vectors, whereas the rotation matrices for Cartesian coordinates were defined multiplying column vectors [Eq. (25)]. This is the usual convention in both cases, and it should be remembered when relating them, as well as when obtaining the representation matrices of projection operators. $\boldsymbol{\Delta}^l(\hat{R})$ is the representation matrix of the symmetry operation $\hat{R}$ in the basis of the RSH of order l, and it can be expressed symbolically as

$$\Delta^l_{mm'}(\hat{R}) = \langle S_{lm}|\hat{R}|S_{lm'}\rangle \quad (28)$$

An important special case of representation matrix is that of the inversion. Remembering Eq. (15), we can write it as

$$\Delta^l_{mm'}(\hat{\imath}) = (-1)^l \delta_{mm'} \quad (29)$$

that is, $(-1)^l$ times the unit matrix. In this way, the matrix representation of an improper operation can be obtained as a function of the matrix of its corresponding proper operation as:

$$\Delta^l_{mm'}(\hat{S}) = (-1)^l \Delta^l_{mm'}(\hat{R}) \quad (30)$$

Taking into account that proper symmetry operations are equivalent to rotations in three-dimensional space, the problem of obtaining the representations of point-group symmetry operations is reduced to obtaining the representation of any rotation operation. The representation matrices of rotation operations are generically called rotation matrices of the selected basis set.

Usually, point-group symmetry operations are specified by their matrix representations in the basis of the Cartesian coordinates, so we shall focus on obtaining the representation matrices of the RSH, taking those of the Cartesian coordinates as a starting point. This will be specially useful in crystalline applications, where parallel coordinate systems are best suited for integral calculation, symmetry operations do not necessarily coincide with Cartesian axis, and the coordinate rotation matrices can be easily obtained from those of the space group. In order to relate both representations, it must be noted that S_{1m} functions transform in the same way as the Cartesian coordinates under point-group operations, and so

$$\boldsymbol{\Delta}^1(\hat{R}) = \begin{pmatrix} R_{yy} & R_{yz} & R_{yx} \\ R_{zy} & R_{zz} & R_{zx} \\ R_{xy} & R_{xz} & R_{xx} \end{pmatrix} \quad (31)$$

where

$$\mathbf{R} = \begin{pmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{zy} & R_{zz} \end{pmatrix} \quad (32)$$

is the matrix representation of the $\hat{R}$ operator in the Cartesian basis. This relationship gives us the matrix representation of the operation in the basis of p functions. Since the s spherical harmonic is a constant, it is invariant under any symmetry operation, and so

$$\Delta^0_{00}(\hat{R}) = 1 \quad (33)$$

for any $\hat{R}$. These two matrices, for s and p functions, will serve as the starting point of the recurrence relationships that will allow us to obtain the rotation matrices for the RSH of any order.

The traditional method for obtaining the representation matrices is to represent the functions, then apply the operation, and finally try to get the elements of the matrix by inspection. It is clear that this is not a computationally viable method, and so we must try to develop better ones. A similar method would be to obtain the RSH as a polynomial in Cartesian coordinates, and substitute the rotation matrix for them. However, this is still an inefficient method. Another possible method would be to obtain the rotation matrices of complex spherical harmonics, and then use the transformation matrices between real and

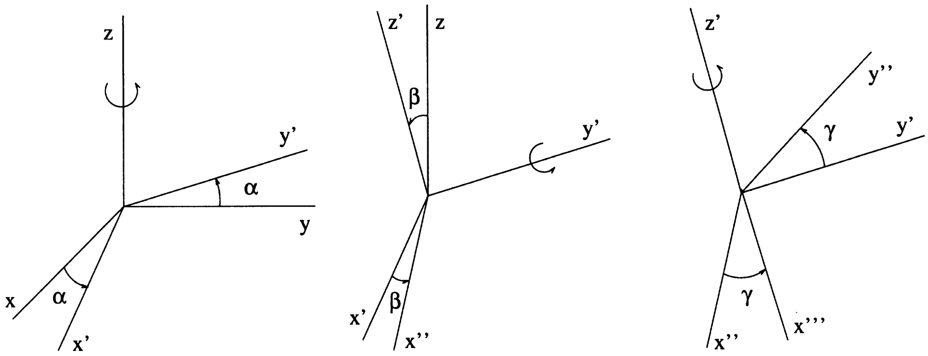

Fig. 1. Description of an arbitrary rotation in terms of Euler angles.

complex functions:

$$\Delta^l_{mm'}(\hat{R}) = \langle S_{lm}|\hat{R}|S_{lm'}\rangle = \sum_{m''m'''}\left(C^l_{mm''}\right)^* C^l_{m'm'''}\langle Y_{lm''}|\hat{R}|Y_{lm'''}\rangle = \sum_{m''m'''}\left(C^l_{mm''}\right)^* D^l_{m''m'''}(\hat{R})\left(C^l_{m'''m'}\right)^t \quad (34)$$

where $D^l_{mm'}(\hat{R})$ is the rotation matrix of complex spherical harmonics, also known as Wigner D function [5]. Writing the above expression in matrix form,

$$\mathbf{\Delta}^l(\hat{R}) = \left(\mathbf{C}^l\right)^*\mathbf{D}^l(\hat{R})\left(\mathbf{C}^l\right)^t \Rightarrow \mathbf{D}^l(\hat{R}) = \left(\mathbf{C}^l\right)^t\mathbf{\Delta}^l(\hat{R})\left(\mathbf{C}^l\right)^* \quad (35)$$

we make clear the transformation between rotation matrices. This is a better method than the preceding ones, but it still has a big drawback: it involves complex matrices in the intermediate steps of the calculation of $\mathbf{\Delta}^l$ matrices, which are real by definition.

The Wigner D functions are well known in the quantum theory of angular momentum [5], and their properties can be easily found in the literature. One of their most important properties is their expression in terms of Euler angles (see Fig. 1 for their definition): since any given rotation can be expressed in terms of these angles, the rotation matrix can be made dependent on them through

$$D^l_{mm'}(\alpha,\beta,\gamma) = \mathrm{e}^{-im\alpha} d^l_{mm'}(\beta)\,\mathrm{e}^{-im'\gamma} \quad (36)$$

The fact that $\mathbf{d}^l$ matrices are real makes viable a new scheme for obtaining the rotation matrices $\mathbf{\Delta}^l$. The $\mathbf{d}^l(\beta)$ matrix can be put in closed form as [5]:

$$d^l_{mm'}(\beta) = (-1)^{m-m'}[(l+m)!(l-m)!(l+m')!(l-m')!]^{1/2} \times \sum_k (-1)^k \frac{\left(\cos\frac{\beta}{2}\right)^{2l-2k-m+m'}\left(\sin\frac{\beta}{2}\right)^{2k+m-m'}}{k!(l-m-k)!(l+m'-k)!(m-m'+k)!} \quad (37)$$

where k runs through all integer values for which the factorials involved exist. However, as happened with the spherical harmonics, it is more interesting to obtain this matrix by means of recurrence relationships. To accomplish this task, the following relationships may be of use (the β dependence is omitted for the sake of simplicity):

$$d^l_{mm'} = d^l_{\bar{m}'\bar{m}} = (-1)^{m+m'}d^l_{\bar{m}\bar{m}'} = (-1)^{m+m'}d^l_{m'm} \quad (38)$$

$$\cos\beta\, d^l_{mm'} = \frac{\sqrt{[l^2-m^2][l^2-(m')^2]}}{l(2l+1)}d^{l-1}_{mm'} + \frac{mm'}{l(l+1)}d^l_{mm'} + \frac{\sqrt{[(l+1)^2-m^2][(l+1)^2-(m')^2]}}{(l+1)(2l+1)}d^{l+1}_{mm'} \quad (39)$$

$$\frac{m'-m\cos\beta}{\sin\beta}d^l_{mm'} = \frac{1}{2}\sqrt{(l+m)(l-m+1)}d^l_{m-1\,m'} + \frac{1}{2}\sqrt{(l-m)(l+m+1)}d^l_{m+1\,m'} \quad (40)$$

In addition, the following expressions for special values of the indices will be needed:

$$d^l_{lm} = \sqrt{\frac{(2l)!}{(l+m)!(l-m)!}}\left(\cos\frac{\beta}{2}\right)^{l+m}\left(-\sin\frac{\beta}{2}\right)^{l-m} \quad (41)$$

$$d^l_{l-1\,m} = (l\cos\beta - m)\sqrt{\frac{(2l-1)!}{(l+m)!(l-m)!}}\left(\cos\frac{\beta}{2}\right)^{l-1+m} \times \left(-\sin\frac{\beta}{2}\right)^{l-1-m} \quad (42)$$

The elements of $d^l_{mm'}$ for all values of the indices can then be computed by using the above expressions recursively, as we shall see below.

The scheme for obtaining the matrices $\boldsymbol{\Delta}^l$ in terms of $\mathbf{d}^l$ and the Euler angles will be obtained. Then we shall see how to obtain the trigonometric functions of Euler angles in terms of the $\boldsymbol{\Delta}^1$ matrix elements. In this way, we can compute $\mathbf{d}^0$ and $\mathbf{d}^1$ matrices, which combined with a set of recurrence rules allow us to obtain the rest of the $\mathbf{d}^l$ matrices, and with them the $\boldsymbol{\Delta}^l$ matrices, which constitute the aim of this work.

Eq. (34) will be the starting point of the following discussion. First we must note that, owing to the properties of $\mathbf{C}^l$, whose only non-zero elements are those in the two diagonals, each summation through m'' and m''' has two elements at most, giving a total maximum of four terms. So, it is affordable to particularize these elements and try to find simpler closed expressions that do not involve complex numbers. There are four possible cases, depending on which indices are zero ($m,m' \neq 0$):

$$\Delta^l_{00} = \left(C^l_{00}\right)^* D^l_{00} C^l_{00} \quad (43)$$

$$\Delta^l_{m0} = \left(C^l_{mm}\right)^* D^l_{m0} C^l_{00} + \left(C^l_{m\bar{m}}\right)^* D^l_{\bar{m}0} C^l_{00} \quad (44)$$

$$\Delta^l_{0m'} = \left(C^l_{00}\right)^* D^l_{0m'} C^l_{m'm'} + \left(C^l_{00}\right)^* D^l_{0\bar{m}'} C^l_{m'\bar{m}'} \quad (45)$$

$$\Delta^l_{mm'} = \left(C^l_{mm}\right)^* D^l_{mm'} C^l_{m'm'} + \left(C^l_{m\bar{m}}\right)^* D^l_{\bar{m}m'} C^l_{m'm'} + \left(C^l_{mm}\right)^* D^l_{m\bar{m}'} C^l_{m'\bar{m}'} + \left(C^l_{m\bar{m}}\right)^* D^l_{\bar{m}\bar{m}'} C^l_{m'\bar{m}'} \quad (46)$$

After replacing in the previous expressions the definition of $\mathbf{D}^l$ matrices [Eq. (36)], sorting the different cases for the $\mathbf{C}^l$ matrices, and a certain amount of algebra, the following relationship is obtained ($m,m' > 0$):

$$\Delta^l_{mm'} = \mathrm{sign}(m')\Phi_m(\alpha)\Phi_{m'}(\gamma)\frac{d^l_{|m'||m|} + (-1)^m d^l_{|m|(-|m'|)}}{2} - \mathrm{sign}(m)\Phi_{\bar{m}}(\alpha)\Phi_{\bar{m}'}(\gamma)\frac{d^l_{|m'||m|} - (-1)^m d^l_{|m|(-|m'|)}}{2} \quad (47)$$

where the definition in Eq. (8) has been used, and sign(0) = 1. In this way, knowing the $\mathbf{d}^l$ matrices and the Euler angles, the $\boldsymbol{\Delta}^l$ matrices can be obtained. In fact, it suffices with half the $\mathbf{d}^l$ matrices, since only elements with $m \geq 0$ are needed. It is possible to reduce these requirements even more by using the mirror symmetry of both diagonals of these matrices, so that the lower of the four triangles that the diagonals define is only needed.

Now we shall obtain the starting elements for the recurrence relationships. These will be the elements of the lower triangle of the $\mathbf{d}^0$ and $\mathbf{d}^1$ matrices; i.e., the d^0_{00}, d^1_{00}, $d^1_{1\bar{1}}$, d^1_{10} and d^1_{11} elements. The first one is the simplest,

$$d^0_{00} = 1 \quad (48)$$

which makes $\Delta^0_{00} = D^0_{00} = 1$, since the s function does not change upon rotations. To obtain the d^1_{00} element, we use Eq. (42):

$$d^1_{00} = \cos\beta \quad (49)$$

Eq. (41) is used for the remaining three elements:

$$d^1_{1\bar{1}} = \sin^2\frac{\beta}{2} \quad (50)$$

$$d^1_{10} = -\frac{1}{\sqrt{2}}\sin\beta \quad (51)$$

$$d^1_{11} = \cos^2\frac{\beta}{2} \quad (52)$$

The above expressions can be introduced in Eq. (47) to obtain the $\boldsymbol{\Delta}^1$ matrix:

$$\boldsymbol{\Delta}^1(\alpha,\beta,\gamma) = \begin{pmatrix} \begin{pmatrix} \cos\alpha\cos\gamma \\ -\sin\alpha\sin\gamma\cos\beta \end{pmatrix} & \sin\alpha\sin\beta & \begin{pmatrix} \cos\alpha\sin\gamma \\ +\sin\alpha\cos\gamma\cos\beta \end{pmatrix} \\ \sin\gamma\sin\beta & \cos\beta & -\cos\gamma\sin\beta \\ \begin{pmatrix} -\cos\alpha\sin\gamma\cos\beta \\ -\sin\alpha\cos\gamma \end{pmatrix} & \cos\alpha\sin\beta & \begin{pmatrix} \cos\alpha\cos\gamma\cos\beta \\ -\sin\alpha\sin\gamma \end{pmatrix} \end{pmatrix} \quad (53)$$

Relating this matrix to its expression in terms of the rotation matrix in the Cartesian basis, Eq. (31), it is possible to obtain the trigonometric functions of the Euler angles. Certainly, given $\beta \in [0,\pi]$, it can be established that

$$\cos\beta = \Delta^1_{00}(\hat{R}) = R_{zz} \tag{54}$$

so that $\sin\beta = \sqrt{1-R_{zz}^2}$. In the same way, the original elements of the $\mathbf{d}^l(\beta)$ matrix, $d^1_{00} = R_{zz}$, $d^1_{10} = -\sqrt{(1-R^2_{zz})/2}$ and $d^1_{1(\pm 1)} = (1 \pm R_{zz})/2$, can be obtained. When $0 < \beta < \pi$ ($\sin\beta \neq 0$), the following relationships can be found:

$$\cos\alpha = \frac{\Delta^1_{10}(\hat{R})}{\sin\beta} = \frac{R_{zx}}{\sqrt{1-R^2_{zz}}} \tag{55}$$

$$\sin\alpha = \frac{\Delta^1_{\bar{1}0}(\hat{R})}{\sin\beta} = \frac{R_{zy}}{\sqrt{1-R^2_{zz}}} \tag{56}$$

$$\cos\gamma = -\frac{\Delta^1_{01}(\hat{R})}{\sin\beta} = -\frac{R_{xz}}{\sqrt{1-R^2_{zz}}} \tag{57}$$

$$\sin\gamma = \frac{\Delta^1_{0\bar{1}}(\hat{R})}{\sin\beta} = \frac{R_{yz}}{\sqrt{1-R^2_{zz}}} \tag{58}$$

However, when $\sin\beta = 0$ these relationships fail. In this case, the $\mathbf{\Delta}^1$ matrix can be written as

$$\Delta^1\left(\alpha, \begin{Bmatrix} 0 \\ \pi \end{Bmatrix}, \gamma\right) = \begin{pmatrix} \cos(\alpha \pm \gamma) & 0 & \pm\sin(\alpha \pm \gamma) \\ 0 & \pm 1 & 0 \\ -\sin(\alpha \pm \gamma) & 0 & \pm\cos(\alpha \pm \gamma) \end{pmatrix} \tag{59}$$

so that there is a single independent rotation angle, $\alpha \pm \gamma$. Arbitrarily choosing $\gamma = 0$, we find:

$$\cos\alpha = \Delta^1_{\bar{1}\bar{1}}(\hat{R}) = R_{yy} \tag{60}$$

$$\sin\alpha = -\Delta^1_{1\bar{1}}(\hat{R}) = -R_{yx} \tag{61}$$

$$\cos\gamma = 1 \tag{62}$$

$$\sin\gamma = 0 \tag{63}$$

when $|R_{zz}| = 1$ ($\sin\beta = 0$). This particular case corresponds to rotations about the z axis. Since it can introduce problems in the application of recurrence relationships, we shall consider it separately in some cases. In this way, the trigonometric functions of Euler angles are obtained from $\mathbf{R}$ matrices for a given rotation, along with the starting elements of the $\mathbf{d}^1(\beta)$ matrix.

To continue, we need the particular recurrence relationships to use in the generation of $\mathbf{d}^l$ matrices. The first and most important rule is that relating the l-order matrix with those of orders $l-1$ and $l-2$, Eq. (39), which can be written in a more useful form as

$$d^l_{mm'} = \frac{l(2l-1)}{\sqrt{[l^2-m^2][l^2-(m')^2]}}\left\{\left(d^1_{00} - \frac{mm'}{l(l-1)}\right)d^{l-1}_{mm'} - \frac{\sqrt{[(l-1)^2-m^2][(l-1)^2-(m')^2]}}{(l-1)(2l-1)}d^{l-2}_{mm'}\right\} \tag{64}$$

This relationship gives access to all elements of the matrix of a given order once the previous two orders are known, with the exception of the first and last two rows and columns. The problem can be reduced to the computation of the last two rows by using the symmetry relationships in Eq. (38). To evaluate these elements by means of recurrence rules, Eq. (41) can be used to obtain

$$d^l_{ll} = \left(\cos^2\frac{\beta}{2}\right)^l = d^1_{11}d^{l-1}_{l-1\ l-1} \tag{65}$$

In the same way, Eq. (42) can be transformed into

$$d^l_{l-1\ l-1} = (l\cos\beta - l + 1)\left(\cos^2\frac{\beta}{2}\right)^{l-1} = (ld^1_{00} - l + 1)d^{l-1}_{l-1\ l-1} \tag{66}$$

To obtain the rest of the elements of the last two rows, we could use the general recurrence relationship, Eq. (40). However, this requires two previous elements for each new one, making it unnecessarily complicated to obtain these two rows: since there are particular expressions for them, eqns (41) and (42), it is more efficient to use such expressions to obtain descending recurrence rules for both. Thus, Eq. (65) can be used as the starting point for the last row, and then successively lower the second index by means of

$$d^l_{l\ m-1} = -\sqrt{\frac{l+m}{l-m+1}}\tan\frac{\beta}{2}d^l_{lm} \tag{67}$$

which can be obtained from Eq. (41), and where $\tan(\beta/2) = \sqrt{d^1_{1\bar{1}}/d^1_{11}}$. The same can be done starting from Eq. (66), stepping down through the second to last row by means of

$$d^l_{l-1\ m-1} = -\frac{l\cos\beta - m + 1}{l\cos\beta - m}\sqrt{\frac{l+m}{l-m+1}}\tan\frac{\beta}{2}d^l_{l-1\ m} \tag{68}$$

obtained from Eq. (42). Since $\lim_{\beta\to\pi}\tan(\beta/2)\to\infty$, these recurrence relationships are not valid. However, in this case eqns (41) and (42) can be used to prove that all elements of the last two columns are zero except $d^l_{l\bar{l}} = 1$ and $d^l_{l-1\ 1-l} = l-1$.

Collecting all the previous relationships, the following algorithm to obtain $\mathbf{d}^l$ matrices can be devised:

obtain $d^0_{00} = 1$.
obtain trigonometric functions of (α,β,γ) from **R**.
obtain d^1_{00}, $d^1_{1\bar{1}}$, d^1_{10} and d^1_{11} from **R**.
for $l = 2,3,\ldots$
  obtain $d^l_{mm'}$ ($m = 0,\ldots,l-2$; $m' = -m,\ldots,m$) using Eq. (64).
  obtain d^l_{ll} [Eq. (65)] and $d^l_{l-1\ l-1}$ [Eq. (66)].
  obtain $d^l_{lm'}$ for $m' = l-1,\ldots,-l$ [Eq. (67)].
  obtain $d^l_{l-1\ m'}$ for $m' = l-2,\ldots,1-l$ [Eq. (68)].
  end-for

In this way all the elements of the lower triangle of the $\mathbf{d}^l$ matrices of all orders can be computed. To obtain the rest of the elements with $m > 0$, the mirror properties through the diagonals [Eq. (38)] can be used, and so all necessary elements in Eq. (47) will be available. Since we also have the sine and cosine of the angles α and γ, along with the recurrence relationships, eqns (13) and (14), we are able to evaluate the rotation matrices of the RSH, $\mathbf{\Delta}^l$, for any order. Remembering that the representation matrix of the inversion operation is the unit matrix times $(-1)^l$, the representation matrices of any point symmetry operation in the basis of the real spherical harmonics can be obtained from its representation matrix in the Cartesian basis.

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References

[1] E. Clementi, C. Roetti, At. Data Nucl. Data Tables 14 (1974) 177–478.
[2] R. McWeeny, in: E.A. Guggenheim, J.E. Mayer, F.C. Tompkins (Eds.), The International Encyclopedia of Physical Chemistry and Chemical Physics, Vol. 3 of 1: Mathematical Techniques, 1st edn, Pergamon Press, London, 1963.
[3] H.H.H. Homeier, E.O. Steinborn, J. Mol. Struct. (Theochem) 368 (1996) 31–37.
[4] J. Ivanic, K. Ruedenberg, J. Phys. Chem. 100 (1996) 6342–6347.
[5] D.A. Varshalovich, A.N. Moskalev, V.K. Khersonskii. Quantum Theory of Angular Momentum, 1st edn, World Scientific, Singapore, 1988.
[6] G. Arfken, Mathematical Methods for Physicists, 3rd edn, Academic Press, San Diego, CA, 1985.
[7] C.D.H. Chisholm, Group Theoretical Techniques in Quantum Chemistry, Academic Press, London, 1976.
[8] W.H. Press, B. P. Flannery, S. A. Teukolski, W. T. Vetterling, Numerical Recipes, 1st edn, Cambridge University Press, Cambridge, 1986.