Journal of Mathematical Chemistry 8(1991)333-344

EXPRESSION OF THE $SU(2)$ ROTATION MATRICES $\mathbf{D}^{(j)}$ IN TERMS OF NORMALIZED IRREDUCIBLE TENSORIAL MATRICES

M.L. ELLZEY, Jr.
Department of Chemistry, The University of Texas at El Paso, El Paso, TX 79968-0513, USA

Received 16 January 1991; revised 2 May 1991

Abstract

The $SU(2)$ rotation matrices $\mathbf{D}^{(j)}$, specified in terms of axis and angle of rotation, are expressed as linear combinations of normalized irreducible tensorial matrices (NITM) of rank $l = 0$ to $2j$ rotated to the polar angles of the axis. The rotated NITM are constructed from spherical harmonics of the same rank. Since this formulation requires no matrix products, it may be computationally more efficient than Euler angle formulas, particularly for large j. Rotated NITM and formulas for the $\mathbf{D}^{(j)}$ with $j = 1/2$ and $j = 1$ are written out explicitly. A formula for the structure constants of the products of conformable NITM is also given in terms of $3-j$ and $6-j$ symbols.

1. Introduction

The $\mathbf{D}^{(j)}$ rotation matrices [1], which are the irreducible representations of $SU(2)$, are given here as linear combinations of normalized irreducible tensorial matrices (NITM) [2-4]. Sometimes called Wigner rotation matrices when expressed in terms of Euler angles, the $\mathbf{D}^{(j)}$ are important in chemistry and physics in that they give the behavior under rotations of a number of important quantities, including spherical harmonics, spinors, and terms in multipole expansions. They are an essential tool in quantum mechanics [5-8].

For a rotation specified in terms of an axis and angle of rotation, the representation $\mathbf{D}^{(j)}$ is a linear combination of rank $l = 0$ to $2j$ NITM rotated to the polar angles of the rotation axis. The rotated NITM are expressed in terms of spherical harmonics of the same rank having as arguments the polar angles of the rotation axis. Since this formulation does not require matrix products, it can offer computational advantages over the Euler angle formulation, particularly for large j.

Different conventions for rotations proliferate in the literature [9,10]. In the present work, the form of a positive rotation about the z-axis is necessarily determined to be $e^{-i\phi j_z}$ by the P_R convention for transforming functions.

Normalized irreducible tensorial matrices have previously been employed for the construction of effective superposition Hamiltonians in quantum chemistry, and tables of selected NITM are included in these references [2,3]. The orientation of various interaction Hamiltonians was facilitated by the tensorial property [11,12] of the NITM. A formula for the multiplication of conformable NITM is presented here for the first time.

The organization of this paper is as follows: Useful properties of the NITM, including multiplicative structure constants, are summarized in the second section. Representations of rotations and elements of $SU(2)$ are related to transformations of coordinates, functions and spherical harmonics in the third section. In the fourth section, rotation matrices are expressed as linear combinations of rotated NITM. In the fifth section, rotated NITM and formulas of $\mathbf{D}^{(j)}$ for $j = 1/2$ and $j = 1$ are given explicitly. The matrix $\mathbf{d}^{(j)}(\beta) = \mathbf{D}^{(j)}(\hat{j}, \beta)$ corresponding to the second Euler angle β is also given for the values of j. The Euler-angle expression of $\mathbf{D}^{(j)}$ consistent with the present development is given in the sixth section for comparison. The seventh section is a discussion.

2. Normalized irreducible tensorial matrices

The NITM are defined in terms of the $SU(2)$ $3-j$ symbols (proportional to Clebsch–Gordan coupling coefficients), which are conventionally adapted to the $SU(1)$ subgroup [5,13]. Normalized irreducible tensorial matrices of rank k, $[n_q^{(k)}]^{(jj')}$, $q = -k, -k+1, \ldots, k$, are $(2j+1)$ by $(2j'+1)$ matrices with elements given by [2–4]

$$\left[n_q^{(k)}\right]_{mm'}^{(jj')} \equiv (-1)^{j-m}\sqrt{2k+1}\begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix}. \tag{2.1}$$

The choice of phase in (2.1) corresponds to the conventional statement of the Wigner–Eckart theorem for $SU(2)$ [12,13]. The $3-j$ symbols are preferred to coupling coefficients by virtue of their useful symmetries under permutations of columns. The orthogonality relations of the $3-j$ symbols result in orthonormality of the NITM under the trace:

$$\mathrm{tr}\left\{\widetilde{\left[n_q^{(k)}\right]}^{(jj')}\left[n_{q'}^{(k')}\right]^{(jj')}\right\} = \delta(k,k')\,\delta(q,q'). \tag{2.2}$$

The matrix space $M(n \times n')$ consisting of all $n \times n'$ matrices is spanned by the NITM $[n_q^{(k)}]^{(jj')}$, $q = -k, -k+1, \ldots, k$; $k = |j-j'|, |j-j'|+1, \ldots, j+j'$, where $2j+1 = n$ and $2j'+1 = n'$. A general matrix $[X]^{(jj')}$ in $M(2j+1 \times 2j'+1)$ is expressed as

$$[X]^{(jj')} = \sum_{k=|j-j'|}^{j+j'} \sum_q (X)_q^{(jj';k)}\left[n_q^{(k)}\right]^{(jj')}, \tag{2.3}$$

where the coefficients $(X)_q^{(jj';k)}$ are given by the trace

$$(X)_q^{(jj';k)} = \mathrm{tr}\left\{ \widetilde{\left[n_q^{(k)}\right]}^{(jj')} [X]^{(jj')} \right\}. \tag{2.4}$$

By virtue of the Wigner–Eckart theorem [6], the NITM transform under rotations according to the $\mathbf{D}^{(j)}$ representation in the special form

$$\mathbf{D}^{(j)}(R)\left[n_q^{(k)}\right]^{(jj')}\mathbf{D}^{(j')}(R^{-1}) = \sum_{q'} \mathbf{D}^{(k)}(R)_{q'q}\left[n_{q'}^{(k)}\right]^{(jj')}, \tag{2.5}$$

which is characteristic of tensorial operators.

Using relation (2.19) from Rotenberg et al. [13], it can be shown that conformable NITM multiply according to

$$\left[n_{q_1}^{(k_1)}\right]^{(j_1 j_2)}\left[n_{q_2}^{(k_2)}\right]^{(j_2 j_3)}$$
$$= \sum_{k_3=|k_1-k_2|}^{k_1+k_2} \gamma(j_1, k_1, j_2, k_2, j_3, k_3; q_1, q_2)\left[n_{q_1+q_2}^{(k_3)}\right]^{(j_1 j_3)}, \tag{2.6}$$

where the structure constants are given by

$$\gamma(j_1, k_1, j_2, k_2, j_3, k_3; q_1, q_2) = (-1)^{j_1+j_3+k_1+k_2-k_3-q_1+q_2}$$
$$\times \sqrt{(2k_1+1)(2k_2+1)(2k_3+1)} \begin{Bmatrix} k_1 & k_2 & k_3 \\ j_3 & j_1 & j_2 \end{Bmatrix} \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & -q_1-q_2 \end{pmatrix}. \tag{2.7}$$

The second factor from the right in (2.7) is a $6-j$ symbol [13] and the last factor is a $3-j$ symbol. The presence of a $3-j$ symbol in the structure constant is expected since the product on the left of (2.6) transforms under rotations according to the direct product $\Gamma^{(k_1)} \times \Gamma^{(k_2)}$, while $[n_q^{(k_3)}]^{(j_1 j_3)}$ transforms according to $\Gamma^{(k_3)}$. The m-sum rule obviates summation over q_3.

Other properties of the NITM follow from those of the $3-j$ symbols. By the m-sum rule, all elements $[n_q^{(k)}]_{mm'}^{(jj')}$ are zero unless $m = q + m'$. That is, the only nonzero elements of $[n_q^{(k)}]^{(jj')}$ lie along one of the diagonals. If $q = 0$, this is the main diagonal with $m' = m$. In this case, the nonzero elements are related by

$$\left[n_0^{(k)}\right]_{mm}^{(jj')} = (-1)^{j+j'+k-2m}\left[n_0^{(k)}\right]_{-m\,-m}^{(jj')}, \tag{2.8}$$

so that diagonal elements of $q = 0$ NITM which differ in the sign of the index m have the same absolute value. The sign difference is then given by $(-1)^{j+j'+k-2m}$.

3. Rotation matrices

A rotation in Cartesian three-space is uniquely specified by an axis $\boldsymbol{r}$ and an angle v, $R(\boldsymbol{r}, v)$. The rotation angle v is positive if a right handed screw turned through v will advance in the direction of $\boldsymbol{r}$. Since the only significance of a rotation axis $\boldsymbol{r}$ is its orientation, its length may conveniently be taken to be one. A rotation through v about another axis $\boldsymbol{r}'$ is related to the first by the equivalence transformation

$$R(\boldsymbol{r}', v) = R(\boldsymbol{r} \to \boldsymbol{r}')\, R(\boldsymbol{r}, v)\, R(\boldsymbol{r} \to \boldsymbol{r}')^{-1}, \tag{3.1}$$

where $R(\boldsymbol{r} \to \boldsymbol{r}')$ is a rotation which carries vector $\boldsymbol{r}$ into vector $\boldsymbol{r}'$. The rotation $R(\boldsymbol{r} \to \boldsymbol{r}')$ is not uniquely determined by the two vectors $\boldsymbol{r}$ and $\boldsymbol{r}'$ since the final position of $\boldsymbol{r}'$ is unspecified. Relation (3.1) holds, however, for any rotation of this type.

On the other hand, a rotation is also uniquely specified by its effect on the three Cartesian basis vectors. For example, a rotation about the z-axis is given by

$$R(\hat{\boldsymbol{k}}, v)\{\hat{\boldsymbol{i}}, \hat{\boldsymbol{j}}, \hat{\boldsymbol{k}}\} = \{\hat{\boldsymbol{i}}, \hat{\boldsymbol{j}}, \hat{\boldsymbol{k}}\}[R(\hat{\boldsymbol{k}}, v)]^{\mathrm{c}}, \tag{3.2}$$

where

$$[R(\hat{\boldsymbol{k}}, v)]^{\mathrm{c}} = \begin{bmatrix} \cos v & -\sin v & 0 \\ \sin v & \cos v & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{3.3}$$

is the matrix representation of $R(\hat{\boldsymbol{k}}, v)$ on this basis. A vector $\boldsymbol{r}$ in this space is represented by a column matrix $[\boldsymbol{r}]^{\mathrm{c}}$ with the three coordinates as elements. Then, $\boldsymbol{r}' = R\boldsymbol{r}$ if and only if

$$[\boldsymbol{r}']^{\mathrm{c}} = [R\boldsymbol{r}]^{\mathrm{c}} = [R]^{\mathrm{c}}[\boldsymbol{r}]^{\mathrm{c}}. \tag{3.4}$$

Scalar functions of the Cartesian coordinates $f(\boldsymbol{r})$ are here taken to transform under R according to

$$\begin{aligned} P_R\, f([\boldsymbol{r}']^{\mathrm{c}}) &= f'([\boldsymbol{r}']^{\mathrm{c}}) \\ &= f'([R\boldsymbol{r}]^{\mathrm{c}}) \\ &= f(\boldsymbol{r}), \end{aligned} \tag{3.5}$$

which leads to

$$f(\boldsymbol{r}') = P_{R^{-1}} f(\boldsymbol{r}). \tag{3.6}$$

The $\mathbf{D}^{(j)}$ are irreducible representations of $SU(2)$ given by

$$\mathbf{D}^{(j)}(\hat{\boldsymbol{k}}, v)_{mm'} = \langle jm | P_{R(\hat{\boldsymbol{k}}, v)} | jm' \rangle, \tag{3.7}$$

where $R(\hat{\boldsymbol{k}},\nu)$ is an element of $SU(2)$. The representations with half-integer j are the double-valued representations of $SU(2)$. The representations with integer j are single-valued representations of $SU(2)$ and also serve as the irreducible representations of the rotation group $R(3)$, giving the transformation properties of spherical harmonics under rotations:

$$P_R Y_{lm} = \sum_{m'} \mathbf{D}^{(l)}(R)_{m'm} Y_{lm'}. \tag{3.8}$$

The symbol l is used to indicate integer values.

Expressions of the spherical harmonics as functions of rotated coordinates are obtained using (3.6) and (3.8). Let the polar angles of $\boldsymbol{r}$ be θ, ϕ, and those of $\boldsymbol{r}'$ be θ', ϕ'. Then,

$$\begin{aligned} Y_{lm}(\theta'\phi') &= P_{R(\boldsymbol{r}\to\boldsymbol{r}')^{-1}} Y_{lm}(\theta\phi) \\ &= \sum_{m'} \mathbf{D}^{(l)}(\boldsymbol{r}\to\boldsymbol{r}')^{-1}_{m'm} Y_{lm'}(\theta\phi) \\ &= \sum_{m'} \mathbf{D}^{(l)}(\boldsymbol{r}\to\boldsymbol{r}')^{*}_{mm'} Y_{lm'}(\theta\phi), \end{aligned} \tag{3.9}$$

where the last equality follows from the unitary property of the $\mathbf{D}^{(j)}$. An important special case of (3.9) is rotation from the basis vector $\hat{\boldsymbol{k}}$ with polar angles $\theta = 0$ and $\phi = 0$, to $\boldsymbol{r}$ with polar angles $\theta' = \theta$ and $\phi' = \phi$. Since the only nonzero spherical harmonics with zero arguments are those with zero m, it follows that

$$Y_{lm'}(00) = \delta(m',0)\sqrt{(2l+1)/4\pi}, \tag{3.10}$$

so that eq. (3.9) becomes

$$\begin{aligned} Y_{lm}(\theta\phi) &= \sum_{m'} \mathbf{D}^{(l)}(\hat{\boldsymbol{k}}\to\boldsymbol{r})^{*}_{mm'} Y_{lm'}(00) \\ &= \mathbf{D}^{(l)}(\hat{\boldsymbol{k}}\to\boldsymbol{r})^{*}_{m0}\sqrt{(2l+1)/4\pi}. \end{aligned} \tag{3.11}$$

Consequently, if $R(\hat{\boldsymbol{k}}\to\boldsymbol{r})$ is any rotation which transforms $\hat{\boldsymbol{k}}$ into $\boldsymbol{r}$, the elements of the middle columns of its representations $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}}\to\boldsymbol{r})$ must be proportional to spherical harmonics with arguments which are polar angles of $\boldsymbol{r}$:

$$\begin{aligned} \mathbf{D}^{(l)}(\hat{\boldsymbol{k}}\to\boldsymbol{r})_{m0} &= Y_{lm}(\theta\phi)^{*}\sqrt{4\pi/(2l+1)} \\ &= (-1)^{-m} Y_{l-m}(\theta\phi)\sqrt{4\pi/(2l+1)}. \end{aligned} \tag{3.12}$$

The last equality in (3.12) follows from the conventions of Condon and Shortley for spherical harmonics [14]. The representations $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{r})$ are further treated in the appendix.

For a positive rotation about the z-axis, the expression of P_R consistent with (3.12) is

$$P_{R(\hat{k},\, \nu)} = \mathrm{e}^{-\mathrm{i}\nu j_z}, \tag{3.13}$$

where j_z is the infinitesimal generator of the Lie algebra of $SU(2)$. The corresponding representations are then diagonal:

$$\begin{aligned}\mathbf{D}^{(j)}(\hat{\boldsymbol{k}}, \nu)_{mm'} &= \langle jm \,|\, \exp(-\mathrm{i}\,\nu j_z) \,|\, jm' \rangle \\ &= \delta(m, m')\mathrm{e}^{-\mathrm{i}\nu m}.\end{aligned} \tag{3.14}$$

4. Expansion of rotation matrices in terms of NITM

The representation matrices $\mathbf{D}^{(j)}$ can be expanded in terms of NITM according to (2.3). In particular, for rotations about the z-axis,

$$\mathbf{D}^{(j)}(\hat{\boldsymbol{k}}, \nu) = \sum_{k=0}^{2j} \sum_{q} \left[n_q^{(k)}\right]^{(jj)} (\nu)_q^{(jj;k)}, \tag{4.1}$$

where

$$(\nu)_q^{(jj;k)} = \mathrm{tr}\left\{ \widetilde{\left[n_q^{(k)}\right]}^{(jj)} \mathbf{D}^{(j)}(\hat{\boldsymbol{k}}, \nu) \right\}. \tag{4.2}$$

Since the diagonal NITM are those with $q = 0$ and since by (3.14) the $\mathbf{D}^{(j)}(\hat{\boldsymbol{k}}, \nu)$ are diagonal, the coefficients in (4.2) are zero unless $q = 0$. Furthermore, by combining (2.8) with (3.14), these nonzero coefficients are written out as:

$$(\nu)_0^{(jj;k)} = \left[n_0^{(k)}\right]_{00}^{(jj)} + 2 \sum_{m>0}^{j} \left[n_0^{(k)}\right]_{mm}^{(jj)} \cos(m\nu), \tag{4.3a}$$

for even k and integer j;

$$(\nu)_0^{(jj;k)} = 2 \sum_{m>0}^{j} \left[n_0^{(k)}\right]_{mm}^{(jj)} \cos(m\nu), \tag{4.3b}$$

for even k and half-integer j; and

$$(\nu)_0^{(jj;k)} = -2\mathrm{i} \sum_{m>0}^{j} \left[n_0^{(k)}\right]_{mm}^{(jj)} \sin(m\nu), \tag{4.3c}$$

for odd k and all j.

The representation of the general element of $SU(2)$ with axis $\boldsymbol{r}$ and rotation angle ν is obtained from these relations by applying the equivalence transformation (3.1) to $\mathbf{D}^{(j)}(\hat{\boldsymbol{k}}, \nu)$:

$$\mathbf{D}^{(j)}(\boldsymbol{r}, \nu) = \mathbf{D}^{(j)}(\hat{\boldsymbol{k}} \to \boldsymbol{r})\mathbf{D}^{(j)}(\hat{\boldsymbol{k}}, \nu)\mathbf{D}^{(j)}(\hat{\boldsymbol{k}} \to \boldsymbol{r})^{-1}$$

$$= \sum_{k=0}^{2j} \left[n(\theta\phi)_0^{(k)}\right]^{(jj)} (\nu)_0^{(jj;k)}, \tag{4.4}$$

where $[n(\theta\phi)_0^{(k)}]^{(jj)}$ is a rotated NITM given by

$$\left[n(\theta\phi)_0^{(k)}\right]^{(jj)} = \mathbf{D}^{(j)}(\hat{\boldsymbol{k}} \to \boldsymbol{r})\left[n_0^{(k)}\right]^{(jj)}\mathbf{D}^{(j)}(\hat{\boldsymbol{k}} \to \boldsymbol{r})^{-1}$$

$$= \sum_q \left[n_q^{(k)}\right]^{(jj)} \mathbf{D}^{(k)}(\hat{\boldsymbol{k}} \to \boldsymbol{r})_{q0}$$

$$= \sum_q \left[n_q^{(k)}\right]^{(jj)} Y_{kq}(\theta\phi)^* \sqrt{4\pi/(2k+1)} \tag{4.5}$$

using relations (2.5), (3.1) and (3.12). In effect, (4.5) is a contraction between contragradient tensors as would be expected from the invariance relation (3.5). The rotated NITM exhibit all the properties of the original NITM, including the same multiplicative structure constants. The expansion coefficients in (4.1) and (4.2) are the same as those of $\mathbf{D}^{(j)}(\boldsymbol{r}, \nu)$ expanded over the rotated NITM:

$$(\nu)_q^{(jj;k)} = \mathrm{tr}\left\{\widetilde{\left[n(\theta\phi)_q^{(k)}\right]^{(jj)}}\mathbf{D}^{(j)}(\hat{\boldsymbol{r}}, \nu)\right\}. \tag{4.6}$$

The rotated NITM in (4.4) and (4.5) are independent of the specific nature of the rotation $R(\hat{\boldsymbol{k}} \to \boldsymbol{r})$ employed in (4.4). This follows since only the middle column of $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{r})$ is required to transform the $q = 0$ terms occurring in (4.4), and by (3.12) the elements of this column are indeed independent of the detailed form of $R(\hat{\boldsymbol{k}} \to \boldsymbol{r})$. Therefore, this development is valid for any $R(\hat{\boldsymbol{k}} \to \boldsymbol{r})$ which rotates $\hat{\boldsymbol{k}}$ to $\boldsymbol{r}$.

5. Rotation matrices for $j = 1/2$ and $j = 1$

The formulas for $\mathbf{D}^{(1/2)}$ and $\mathbf{D}^{(1)}$ are here written out explicitly in terms of rotated NITM obtained from matrices tabulated in ref. [2]. The rows and columns of the matrices are ordered from $m = -j$ at the top and left to $+j$ at the bottom and right. For a positive rotation through angle ν about axis $\boldsymbol{r}$ with polar angles θ and ϕ, the $j = 1/2$ matrix is

$$\mathbf{D}^{(1/2)}(\boldsymbol{r}, \nu) = \sqrt{2}\cos(\nu/2)\left[n(\theta\phi)_0^{(0)}\right]^{(1/2,1/2)} - \sqrt{2}\,\mathrm{i}\sin(\nu/2)\left[n(\theta\phi)_0^{(1)}\right]^{(1/2,1/2)}$$
$$= \sqrt{2}\cos(\nu/2)\begin{bmatrix} 1/\sqrt{2} & 0 \\ 0 & 1/\sqrt{2} \end{bmatrix} - \sqrt{2}\,\mathrm{i}\sin(\nu/2)\begin{bmatrix} -\cos\theta/\sqrt{2} & \sin\theta\, \mathrm{e}^{\mathrm{i}\phi}/\sqrt{2} \\ \sin\theta\, \mathrm{e}^{-\mathrm{i}\phi}/\sqrt{2} & \cos\theta/\sqrt{2} \end{bmatrix}. \tag{5.1}$$

The $j = 1$ matrix is

$$\mathbf{D}^{(1)}(\boldsymbol{r}, \nu) = \frac{1+2\cos\nu}{\sqrt{3}}\left[n(\theta\phi)_0^{(0)}\right]^{(1,1)} - \sqrt{2}\,\mathrm{i}\sin\nu\left[n(\theta\phi)_0^{(1)}\right]^{(1,1)} + \sqrt{2/3}\,(\cos\nu - 1)\left[n(\theta\phi)_0^{(2)}\right]^{(1,1)}$$

$$= \frac{1+2\cos\nu}{\sqrt{3}}\begin{bmatrix} 1/\sqrt{3} & 0 & 0 \\ 0 & 1/\sqrt{3} & 0 \\ 0 & 0 & 1/\sqrt{3} \end{bmatrix}$$

$$- \sqrt{2}\,\mathrm{i}\sin\nu\begin{bmatrix} -\cos\theta/\sqrt{2} & \sin\theta\, \mathrm{e}^{\mathrm{i}\phi}/2 & 0 \\ \sin\theta\, \mathrm{e}^{-\mathrm{i}\phi}/2 & 0 & \sin\theta\, \mathrm{e}^{\mathrm{i}\phi}/2 \\ 0 & \sin\theta\, \mathrm{e}^{-\mathrm{i}\phi}/2 & \cos\theta/\sqrt{2} \end{bmatrix} + \sqrt{2/3}\,(\cos\nu - 1)$$

$$\times \begin{bmatrix} (3\cos^2\theta - 1)/\sqrt{24} & -\sqrt{3/4}\,\sin\theta\cos\theta\, \mathrm{e}^{\mathrm{i}\phi} & \sqrt{3/8}\,\sin^2\theta\, \mathrm{e}^{2\mathrm{i}\phi} \\ -\sqrt{3/4}\,\sin\theta\cos\theta\, \mathrm{e}^{-\mathrm{i}\phi} & -(3\cos^2\theta - 1)/\sqrt{6} & \sqrt{3/4}\,\sin\theta\cos\theta\, \mathrm{e}^{\mathrm{i}\phi} \\ \sqrt{3/8}\,\sin^2\theta\, \mathrm{e}^{-2\mathrm{i}\phi} & \sqrt{3/4}\,\sin\theta\cos\theta\, \mathrm{e}^{-\mathrm{i}\phi} & (3\cos^2\theta - 1)/\sqrt{24} \end{bmatrix}. \tag{5.2}$$

Matrices for rotations through angle β about the $\hat{j}$-axis are the $\mathbf{d}^{(j)}(\beta)$ corresponding to the second Euler angle [1]. They are obtained from (5.1) and (5.2) by setting both θ and ϕ equal to 90° and ν equal to β. Then,

$$\begin{aligned}
\mathbf{D}^{(1/2)}(\hat{j},\beta) &= \sqrt{2}\cos(\beta/2)\begin{bmatrix} 1/\sqrt{2} & 0 \\ 0 & 1/\sqrt{2} \end{bmatrix} \\
&\quad - \sqrt{2}\,\mathrm{i}\sin(\beta/2)\begin{bmatrix} 0 & \mathrm{i}/\sqrt{2} \\ -\mathrm{i}/\sqrt{2} & 0 \end{bmatrix} \\
&= \begin{bmatrix} \cos(\beta/2) & \sin(\beta/2) \\ -\sin(\beta/2) & \cos(\beta/2) \end{bmatrix};
\end{aligned} \tag{5.3}$$

$$\begin{aligned}
\mathbf{D}^{(1)}(\hat{j},\beta) &= \frac{1+2\cos\beta}{\sqrt{3}}\begin{bmatrix} 1/\sqrt{3} & 0 & 0 \\ 0 & 1/\sqrt{3} & 0 \\ 0 & 0 & 1/\sqrt{3} \end{bmatrix} \\
&\quad - \sqrt{2}\,\mathrm{i}\sin\beta\begin{bmatrix} 0 & \mathrm{i}/2 & 0 \\ -\mathrm{i}/2 & 0 & \mathrm{i}/2 \\ 0 & -\mathrm{i}/2 & 0 \end{bmatrix} \\
&\quad + \sqrt{2/3}\,(\cos\beta - 1)\begin{bmatrix} -1/\sqrt{24} & 0 & -\sqrt{3/8} \\ 0 & 1/\sqrt{6} & 0 \\ -\sqrt{3/8} & 0 & -1/\sqrt{24} \end{bmatrix} \\
&= \begin{bmatrix} (1+\cos\beta)/2 & \sin\beta/\sqrt{2} & (1-\cos\beta)/2 \\ -\sin\beta/\sqrt{2} & \cos\beta & \sin\beta/\sqrt{2} \\ (1-\cos\beta)/2 & -\sin\beta/\sqrt{2} & (1+\cos\beta)/2 \end{bmatrix}.
\end{aligned} \tag{5.4}$$

6. Comparison with Euler angles

The conventions employed here agree with Steinborn and Ruedenberg [9]. With the Euler angles α, β, γ in that reference – and most of the others – the elements of the matrix $\mathbf{D}^{(j)}(\alpha, \beta, \gamma)$ are given by

$$\begin{aligned}
\mathbf{D}^{(j)}(\alpha,\beta,\gamma)_{mm'} &= \langle jm|\exp(-\mathrm{i}\alpha j_z)\exp(-\mathrm{i}\beta j_y)\exp(-\mathrm{i}\gamma j_z)|jm'\rangle \\
&= \mathrm{e}^{-\mathrm{i}\alpha m}\mathbf{d}^{(j)}(\beta)_{mm'}\mathrm{e}^{-\mathrm{i}\gamma m'}.
\end{aligned} \tag{6.1}$$

This representation is related to that of Wigner [1] by a sign change in the three angles:

$$\mathbf{D}^{(j)}(\alpha, \beta, \gamma) = \mathbf{D}^{(j)}(-\alpha, -\beta, -\gamma) \text{ (Wigner)}. \tag{6.2}$$

There are other conventions in the literature, as surveyed by Steinborn and Ruedenberg [9], Wolf [10], and Silver [12], but it is unnecessary to consider them in this development.

7. Discussion

A number of points can be made concerning the NITM expansion of the rotation $\mathbf{D}^{(j)}(\boldsymbol{r}, \nu)$:

$$\mathbf{D}^{(j)}(\boldsymbol{r}, \nu) = \sum_{k=0}^{2j} \left[n(\theta\phi)_0^{(k)}\right]^{(jj)} (\nu)_0^{(jj;k)}. \tag{7.1}$$

The rotation angle ν occurs only in the expansion coefficients, while the orientation – polar angles – of the axis $\boldsymbol{r}$ is confined to the rotated NITM. In some applications, it might be efficient to set up the required rotated NITM at the beginning of a calculation.

Being diagonal, the original $q = 0$ NITM commute with each other. This commutativity is also seen in the structure constants (2.7) by setting all $q = 0$ and all j equal to each other. In this particular case, the product contains only those $[n_0^{(k_3)}]^{(jj)}$ for which $k_1 + k_2 + k_3$ is even and, consistent with commutativity of the $q = 0$ NITM, the nonzero structure constants are invariant to exchange of k_1 and k_2. Since they are related to the original NITM by an equivalence transformation (4.5), the NITM rotated to a particular set of polar angles have identically the same structure constants. In particular, the rotated $q = 0$ NITM commute with each other, consistent with the fact that the group of all rotations about a given axis is Abelian. NITM rotated to different axes do not in general commute.

All square NITM, except $[n_0^{(0)}]^{(jj)}$, have zero trace, so that setting $\nu = 0$ in (4.3) zeroes all coefficients but the first in the expansion (7.1). This term is then the identity matrix. The $q = 0$ NITM are self-adjoint and the rotation matrix is unitary. The inverse rotation corresponding to $-\nu$ is therefore obtained by changing the signs of the pure imaginary terms which are those with odd k.

Appendix

The representations $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})$ of rotations which send the $\hat{\boldsymbol{k}}$ axis into a vector $\boldsymbol{u}$ at polar angles ϕ and θ were shown in (3.12) to have middle column elements proportional to conjugated spherical harmonics. Since there are infinitely many rotations which send $\hat{\boldsymbol{k}}$ into $\boldsymbol{u}$, it is remarkable that they should all have the same middle column. These representations are further examined in this appendix.

To determine $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})$ in general, its columns will be demonstrated to be nondegenerate eigenvectors of the unitary operator $\mathbf{D}^{(l)}(\boldsymbol{u}, \zeta)$, where ζ is any angle. This is done by transforming $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}}, \zeta)$ into $\mathbf{D}^{(l)}(\boldsymbol{u}, \zeta)$ with $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})$ using (3.1):

$$\mathbf{D}^{(l)}(\boldsymbol{u}, \zeta) = \mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})\, \mathbf{D}^{(l)}(\hat{\boldsymbol{k}}, \zeta)\, \mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})^{-1}. \tag{A.1}$$

By (3.14), rotations about the $\hat{\boldsymbol{k}}$-axis are diagonal:

$$\mathbf{D}^{(l)}(\hat{\boldsymbol{k}}, \zeta)_{mm'} = \delta(m, m')\, \mathrm{e}^{-\mathrm{i}m\zeta}. \tag{A.2}$$

Multiplying both sides of (A.1) from the right by $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})$ yields

$$\mathbf{D}^{(l)}(\boldsymbol{u}, \zeta)\, \mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u}) = \mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})\, \mathbf{D}^{(l)}(\hat{\boldsymbol{k}}, \zeta). \tag{A.3}$$

This is in the form of an eigenvalue equation, where $\mathbf{D}^{(l)}(\boldsymbol{u}, \zeta)$ is a unitary operator, $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})$ is the matrix of eigenvectors, and $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}}, \zeta)$ is the diagonal eigenvalue matrix.

Since there are no degenerate eigenvalues in (A.2), relation (A.3) determines the columns of the unitary matrix $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})$ up to a set of phase factors. If a particular $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})$ satisfying (A.3), say $\mathbf{D}^{(l)}(R_1)$, is determined, then any other $\mathbf{D}^{(l)}(R_2)$ also satisfying (A.3) will differ from $\mathbf{D}^{(l)}(R_1)$ only in the phases of its columns. Consequently, the two matrices are related by

$$\mathbf{D}^{(l)}(R_2) = \mathbf{D}^{(l)}(R_1)\, [P], \tag{A.4}$$

where $[P]$ is a diagonal matrix given by

$$[P] = \mathbf{D}^{(l)}(R_1)^{-1}\mathbf{D}^{(l)}(R_2). \tag{A.5}$$

By group closure, $[P]$ must be a rotation matrix and, being diagonal, must have the form $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}}, \xi)$. Therefore,

$$\mathbf{D}^{(l)}(R_2) = \mathbf{D}^{(l)}(R_1)\, \mathbf{D}^{(l)}(\hat{\boldsymbol{k}}, \xi), \tag{A.6}$$

where

$$\mathbf{D}^{(l)}(\hat{\boldsymbol{k}}, \xi)_{mm'} = \delta(m, m')\, \mathrm{e}^{-\mathrm{i}m\xi}. \tag{A.7}$$

Since $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}}, \xi)_{00} = 1$, relation (A.6) verifies that the middle columns of all $\mathbf{D}^{(l)}(\hat{\boldsymbol{k}} \to \boldsymbol{u})$ are identical.

Acknowledgement

Initial support for this research by the Robert Welch Foundation of Houston, Texas is gratefully acknowledged.

References

[1] E.P. Wigner, *Group Theory* (Academic Press, New York–London, 1959).
[2] M.L. Ellzey, Jr., Int. J. Quant. Chem. 40(1991)347–360.
[3] M.L. Ellzey, Jr., J. Math. Chem. 4(1990)117–126.
[4] M.L. Ellzey, Jr., Croat. Chem. Acta 57(1984)1107.
[5] B.R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw–Hill, New York, 1963).
[6] L.C. Biedenharn and J.D. Louck, *Angular Momentum in Quantum Physics. Theory and Applications*, Encyclopedia of Mathematics and its Applications, Vol. 8, Ser. ed. G.-C. Rota (Addison–Wesley, New York, 1981).
[7] C.D.H. Chisholm, *Group Theoretical Techniques in Quantum Chemistry* (Academic Press, New York–London, 1976).
[8] H.A. Buckmaster, R. Chatterjee and Y.H. Shing, Phys. Stat. Sol. A13(1972)9.
[9] E.O. Steinborn and K. Ruedenberg, Adv. Quant. Chem. 7(1973)2.
[10] A.A. Wolf, Amer. J. Phys. 37(1969)531.
[11] G. Racah, Phys. Rev. 63(1943)367.
[12] B.L. Silver, *Irreducible Tensor Methods* (Academic Press, New York, 1976).
[13] M. Rotenberg, R. Bivens, N. Metropolis and J.K. Wooten, Jr., *The 3-j and 6-j Symbols* (MIT Press, Cambridge, MA, 1963).
[14] E.U. Condon and G.H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1951).