approximate c.p.d.f. of Φ at the ith point. In most computations, $n_\Phi = 19$ and Φ was varied from 0 to 90° in steps of 5°. The approximations considered are: (i) Cochran's (1955) c.p.d.f. of Φ, based on the central limit theorem; (ii) the c.p.d.f. of Φ based on the new algorithm described in this paper; and (iii) the c.p.d.f. of Φ based on an improved polynomial approximation based on the method of Posner *et al.* (1993).

The agreement of approximations (ii) and (iii) with the exact c.p.d.f. is very good throughout the range $15 \leq N \leq 70$, as can be seen from Table 3. The discrepancy of Cochran's (1955) c.p.d.f. and the exact one is quite considerable in this range of N, although it decreases slowly with increasing N. Both new approximations have a similar behaviour: the value of R is highest at the low end of the N range and decreases with increasing N; their performance is similar and, in general, very good.

References

COCHRAN, W. (1955). *Acta Cryst.* **8**, 473–478.
POSNER, Y., SHMUELI, U. & WEISS, G. H. (1993). *Acta Cryst.* **A49**, 260–265.
SHMUELI, U., RABINOVICH, S. & WEISS, G. H. (1989*a*). *Acta Cryst.* **A45**, 361–367.
SHMUELI, U., RABINOVICH, S. & WEISS, G. H. (1989*b*). *Acta Cryst.* **A45**, 367–371.

Acta Cryst. (1994). **A50**, 636–643

Rotation of Real Spherical Harmonics

BY ZHENGWEI SU AND PHILIP COPPENS

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214-3094, *USA*

(*Received* 7 *January* 1994; *accepted* 18 *March* 1994)

Abstract

Formulae for the rotation of real spherical harmonic functions are presented. To facilitate their application, values of the matrices $d^{(l)}_{m'm}(\pi/2)$, which occur in the equations, are tabulated for $1 \leq l \leq 8$ and $0 \leq m', m \leq l$. The application of the equations to spherical harmonic functions with normalization commonly used in charge-density analysis is described.

Introduction

The real spherical harmonic functions are extensively used for the description of atomic orbitals and as density basis functions in the analysis of experimental charge densities. In order to recognize the local or global symmetry of a particular site, it is often necessary to rotate the coordinate system after completion of a theoretical calculation or an experimental charge-density analysis. In the multipole analysis of charge densities, for example, application of local symmetry constraints requires the use of a local coordinate system on each of the atoms (Hansen & Coppens, 1978). For subsequent calculation of molecular properties, such as molecular electrostatic moments, it is necessary to rotate the functions to a common coordinate system.

The treatment given starts with the equations by Steinborn & Ruedenberg (1973) for the rotation of complex spherical harmonic functions and is similar to that described earlier by Cromer, Larson & Stewart (1976); however, expressions are given for both unnormalized and normalized spherical harmonic functions, the latter with normalization appropriate for either wave functions or density functions. Explicit numerical values are given for the matrices (up to $l = 8$) that occur in the equations, thus facilitating their application. In addition, a number of inadvertent errors in the earlier publication have been eliminated.

Coordinate-system rotations

Let (r, θ, φ) and (r, θ', φ') be the spherical coordinates of a vector

$$\mathbf{X} = (x_1, x_2, x_3)\begin{pmatrix}\mathbf{e}_1\\ \mathbf{e}_2\\ \mathbf{e}_3\end{pmatrix} = (x'_1, x'_2, x'_3)\begin{pmatrix}\mathbf{e}'_1\\ \mathbf{e}'_2\\ \mathbf{e}'_3\end{pmatrix}.$$

The unitary matrix that transforms the two right-handed Cartesian bases $\mathbf{e}$ and $\mathbf{e}'$ can be written in terms of Eulerian angles α, β and γ (Arfken, 1970; Edmonds, 1974; Steinborn & Ruedenberg, 1973), such that

$$\begin{pmatrix}\mathbf{e}'_1\\ \mathbf{e}'_2\\ \mathbf{e}'_3\end{pmatrix} = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix}\begin{pmatrix}\mathbf{e}_1\\ \mathbf{e}_2\\ \mathbf{e}_3\end{pmatrix} = \mathbf{R}\begin{pmatrix}\mathbf{e}_1\\ \mathbf{e}_2\\ \mathbf{e}_3\end{pmatrix}. \quad (1)$$

Acta Crystallographica Section A
ISSN 0108-7673 ©1994

That is, the transformation is represented as successive rotations of γ, β, α about the $\mathbf{e}_3$, $\mathbf{e}_2$ and $\mathbf{e}_3$ axes. A positive rotation is a counterclockwise rotation.* Since $\mathbf{R}$ is unitary, it follows that the Cartesian coordinates transform as

$$\begin{pmatrix}x'_1\\ x'_2\\ x'_3\end{pmatrix} = \mathbf{R}\begin{pmatrix}x_1\\ x_2\\ x_3\end{pmatrix}. \quad (2)$$

The Eulerian angles have domain of definition $0 \leq \alpha \leq 2\pi$, $0 \leq \beta \leq \pi$ and $0 \leq \gamma \leq 2\pi$. From (1) and (2), α, β and γ can be expressed in terms of the elements of $\mathbf{R}$:

$$\beta = \arccos(R_{33}), \quad (3a)$$

$$\alpha = \begin{cases} \arccos(R_{31}/\sin\beta) & \text{if } R_{32} \geq 0 \\ 2\pi - \arccos(R_{31}/\sin\beta) & \text{if } R_{32} < 0 \end{cases}, \quad (3b)$$

$$\gamma = \begin{cases} \arccos(-R_{13}/\sin\beta) & \text{if } R_{23} \geq 0 \\ 2\pi - \arccos(-R_{13}/\sin\beta) & \text{if } R_{23} < 0 \end{cases}. \quad (3c)$$

Equations (3*b*) and (3*c*) are valid if $R_{33} \neq \pm 1$. If $R_{33} = \pm 1$, then $\beta = \left\{\begin{matrix}0\\ \pi\end{matrix}\right.$. We set $\gamma = 0$ and find α from

$$\alpha = \begin{cases} \arccos(R_{11}/R_{33}) & \text{if } R_{12}/R_{33} \geq 0 \\ 2\pi - \arccos(R_{11}/R_{33}) & \text{if } R_{12}/R_{33} < 0 \end{cases}. \quad (4)$$

Equations (3) and (4) ensure that the angles are within the domain of definition and are unambiguously defined.

Rotation of spherical harmonic functions

Rotation of complex spherical harmonics

The complex spherical harmonic functions are defined for $l \geq 0$ and $-l \leq m \geq l$ by

$$Y^m_l(\theta,\varphi) = (-1)^m\{[(2l+1)/4\pi][(l-m)!/(l+m)!]\}^{1/2} \times P^m_l(\cos\theta)\exp(im\varphi) \quad (5)$$

[where $P^m_l(x)$ is an associated Legendre function (Arfken, 1970)]. The $Y^m_l(\theta,\varphi)$ as defined here contain the Condon–Shortley phase factor $(-1)^m$ (Condon & Shortley, 1957). They transform under rotation according to (Steinborn & Ruedenberg, 1973; Rose, 1957)

$$Y^m_l(\theta',\varphi') = \sum_{m'=-l}^{l} Y^{m'}_l(\theta,\varphi)D^{(l)}_{m'm}(\alpha,\beta,\gamma), \quad (6)$$

where the $D^{(l)}$ are $(2l+1)\times(2l+1)$ matrices, which form the $(2l+1)$-dimensional irreducible representation of the rotation group. We may write

$$D^{(l)}_{m'm}(\alpha,\beta,\gamma) = \exp(-im'\alpha)d^{(l)}_{m'm}(\beta)\exp(-im\gamma). \quad (7a)$$

$D^{(l)}_{m'm}(\alpha,\beta,\gamma)$ are the matrix elements of $\exp(-i\alpha L_z)\exp(-i\beta L_y)\exp(-i\gamma L_z)$, where L_z and L_y are the Cartesian components of the angular momentum operator $\mathbf{L}$; $L_z = \mathbf{L}\cdot\mathbf{e}_3$, $L_y = \mathbf{L}\cdot\mathbf{e}_2$. $D^{(l)}_{m'm}(\alpha,\beta,\gamma)$ are related to Wigner's (1959) $\mathrm{D}^{(l)}(\{\alpha_1\alpha_2\alpha_3\})_{m'm}$ by

$$D^{(l)}_{m'm}(\alpha,\beta,\gamma) = \mathrm{D}^{(l)}(\{-\gamma,-\alpha,-\beta\})_{m'm}, \quad (7b)$$

where $\mathrm{D}^{(l)}(\{\alpha_1,\alpha_2,\alpha_3\})_{m'm}$ are the matrix elements of $\exp(i\alpha_1L_z)\exp(i\alpha_2L_y)\exp(i\alpha_3L_z)$. Note that the transformation given in (1) is written as $\{\gamma\beta\alpha\}$ with Wigner's notation.

The elements $d^{(l)}_{m'm}(\beta)$ can be calculated by (Steinborn & Ruedenberg, 1973; Rose, 1957)

$$\begin{aligned} d^{(l)}_{m'm}(\beta) = {} & [(l+m')!(l-m')!/(l+m)!(l-m)!]^{1/2} \\ & \times(-1)^{m'-m}\sum_k(-1)^k\binom{l+m}{k} \\ & \times\binom{l-m}{l-m'-k}[\cos(\beta/2)]^{2l-m'+m-2k} \\ & \times[\sin(\beta/2)]^{2k-m+m'}, \end{aligned} \quad (8)$$

with the range of integer k defined by

$$\max(0, m-m') \leq k \leq \min(l-m', l+m)$$

and $\binom{a}{b} = a!/(a-b)!b!$.

Rotation of real spherical harmonics

The real spherical functions with normalization $\int y^2_{lmp}\,d\Omega = 1$ are defined by

$$\begin{aligned} Y_{lm+}(\theta,\varphi) &= \{[(2l+1)/2\pi(1+\delta_{m0})] \\ &\quad\times[(l-m)!/(l+m)!]\}^{1/2} \\ &\quad\times P^m_l(\cos\theta)\cos(m\varphi) \\ &\equiv N_{lm}P^m_l(\cos\theta)\cos(m\varphi) \end{aligned} \quad (9a)$$

and

$$y_{lm-}(\theta,\varphi) = N_{lm}P^m_l(\cos\theta)\sin(m\varphi) \quad (9b)$$

with $0 \leq m \leq l$. $y_{l0}(\theta,\varphi)$ is defined as $y_{l0+}(\theta,\varphi)$.

* α, β, and γ are related to the diffractometer angles ω, χ and φ, except that, in the conventional definition, the rotation β is around the y axis rather than the x axis.

The real spherical harmonics are related to the complex spherical harmonics by

$$y_{l0}(\theta,\varphi) = Y_l^0(\theta,\varphi) \tag{10a}$$

for $m = 0$ and

$$y_{lm+} = [(-1)^m Y_l^m + Y_l^{-m}]/2^{1/2} \tag{10b}$$

and

$$y_{lm-} = [(-1)^m Y_l^m - Y_l^{-m}]/2^{1/2} i \tag{10c}$$

for $m > 0$. In other words, the functions y_{lm+} and y_{lm-} are derived from the real and imaginary parts of the complex spherical harmonics, respectively. It then follows from (5) that the rotation of the real spherical harmonics is described by

$$\begin{aligned} y_{lm+}&(\theta',\varphi') \\ &= (-1)^m d^{(l)}_{0m}(\beta)\cos(m\gamma)2^{1/2}y_{l0}(\theta,\varphi) \\ &\quad + \sum_{m'=1}^{l}\{[(-1)^{m+m'}d^{(l)}_{m'm}(\beta)\cos(m\gamma+m'\alpha) \\ &\quad + (-1)^m d^{(l)}_{-m'm}(\beta)\cos(m\gamma-m'\alpha)]y_{lm'+}(\theta,\varphi) \\ &\quad + [(-1)^{m+m'}d^{(l)}_{m'm}(\beta)\sin(m\gamma+m'\alpha) \\ &\quad - (-1)^m d^{(l)}_{-m'm}(\beta)\sin(m\gamma-m'\alpha)]y_{lm'-}(\theta,\varphi)\}, \end{aligned} \tag{11a}$$

and

$$\begin{aligned} y_{lm-}&(\theta',\varphi') \\ &= (-1)^{m+1} d^{(l)}_{0m}(\beta)\sin(m\gamma)2^{1/2}y_{l0}(\theta,\varphi) \\ &\quad + \sum_{m'=1}^{l}\{[(-1)^{m+m'+1}d^{(l)}_{m'm}(\beta)\sin(m\gamma+m'\alpha) \\ &\quad + (-1)^{m+1} d^{(l)}_{-m'm}(\beta)\sin(m\gamma-m'\alpha)]y_{lm'+}(\theta,\varphi) \\ &\quad + [(-1)^{m+m'}d^{(l)}_{m'm}(\beta)\cos(m\gamma+m'\alpha) \\ &\quad - (-1)^m d^{(l)}_{-m'm}(\beta)\cos(m\gamma-m'\alpha)]y_{lm'-}(\theta,\varphi)\} \end{aligned} \tag{11b}$$

for $m > 0$ and

$$\begin{aligned} y_{l0}(\theta',\varphi') &= d^{(l)}_{00}(\beta)y_{l0}(\theta,\varphi) \\ &\quad + 2^{-1/2}\sum_{m'=1}^{l}\{[(-1)^{m'}d^{(l)}_{m'0}(\beta) \\ &\quad + d^{(l)}_{-m'0}(\beta)]\cos(m'\alpha)y_{lm'+}(\theta,\varphi) \\ &\quad + [(-1)^{m'}d^{(l)}_{m'0}(\beta) + d^{(l)}_{-m'0}(\beta)] \\ &\quad \times \sin(m'\alpha)y_{lm'-}(\theta,\varphi)\} \end{aligned} \tag{11c}$$

for $m = 0$. For the unnormalized real spherical harmonics, the corresponding equations are:

$$\begin{aligned} P_l^m&[\cos(\theta')]\cos(m\varphi') \\ &= \sum_{m'=0}^{l}[(l-m')!/(l-m)!](2-\delta_{0m'})/2 \\ &\quad \times \{[\cos(m\gamma+m'\alpha)s^{(l)}_{m'm}(\beta) \\ &\quad + (-1)^{m'}\cos(m\gamma-m'\alpha)s^{(l)}_{-m'm}] \\ &\quad \times P_l^{m'}(\cos\theta)\cos(m'\varphi) \\ &\quad + [\sin(m\gamma+m'\alpha)s^{(l)}_{m'm}(\beta) \\ &\quad - (-1)^{m'}\sin(m\gamma-m'\alpha)s^{(l)}_{-m'm}(\beta)] \\ &\quad \times P_l^{m'}(\cos\theta)\sin(m'\varphi)\} \end{aligned} \tag{12a}$$

for $m \geq 0$;

$$\begin{aligned} P_l^m&[\cos(\theta')]\sin(m\varphi') \\ &= \sum_{m'=0}^{l}[(l-m')!/(l-m)!](2-\delta_{0m'})/2 \\ &\quad \times \{-[\sin(m\gamma+m'\alpha)s^{(l)}_{m'm}(\beta) \\ &\quad + (-1)^{m'}\sin(m\gamma-m'\alpha)s^{(l)}_{-m'm}(\beta)] \\ &\quad \times P_l^{m'}(\cos\theta)\cos(m'\varphi) \\ &\quad + [\cos(m\gamma+m'\alpha)s^{(l)}_{m'm}(\beta) \\ &\quad - (-1)^{m'}\cos(m\gamma-m'\alpha)s^{(l)}_{-m'm}(\beta)] \\ &\quad \times P_l^{m'}(\cos\theta)\sin(m'\varphi)\} \end{aligned} \tag{12b}$$

for $m > 0$, where the $s^{(l)}_{m'm}(\beta)$ are directly related to $d^{(l)}_{m'm}(\beta)$ and given by

$$\begin{aligned} S^{(l)}_{m'm}(\beta) &= \sum_k (-1)^k \binom{l+m}{k}\binom{l-m}{l-m'-k} \\ &\quad \times [\cos(\beta/2)]^{2l-m'+m-2k} \\ &\quad \times [\sin(\beta/2)]^{2k-m+m'} \end{aligned} \tag{13}$$

for $l \geq m'$, $m \geq -l$.

Equations (12) and (13) are different from (A7) and (A8) of Cromer, Larson & Stewart (1976). A simple test, *i.e.* the rotation of $P_l^m(\cos\theta)\cos(m\varphi)$, $m \leq 1$, shows that the present results are correct.

Application to multipole density functions

The density-function spherical harmonics are defined by the normalization $\int|d_{lmp}|\mathrm{d}\Omega = 2 - \delta_{l0}$ (Coppens, 1993).* They are related to the real spherical harmonics y_{lmp}, defined by (9), by

$$d_{lmp}(\theta,\varphi)/y_{lmp}(\theta,\varphi) = L_{lmp}/M_{lmp} \tag{14}$$

and to the unnormalized functions $u_{lm\pm}(\theta,\varphi) = P_l^m(\cos\theta)\begin{smallmatrix}\cos m\varphi\\ \sin m\varphi\end{smallmatrix}$ by

$$d_{lmp}(\theta,\varphi)/u_{lmp}(\theta,\varphi) = L_{lmp}/C_{lmp}, \tag{15}$$

where L_{lmp}, C_{lmp} and M_{lmp} are normalization factors (Coppens, 1993).

The equations for the rotation of d_{lmp} follow by inserting the ratios of the normalization factors in front of each of the terms on both sides of (11) or

* The real spherical harmonic density functions, $d_{lmp}(\theta,\varphi)$, are not to be confused with the elements $d^{(l)}_{m'm}(\beta)$ defined by Steinborn & Ruedenberg (1973) and Edmonds (1974).

(12):

$$\begin{aligned} d_{lm+}&(\theta',\varphi') \\ &= (L_{lm+}/C_{lm+})\sum_{m'=0}^{l}[(l-m')!/(l-m)!](2-\delta_{0m'})/2 \\ &\quad \times \{[\cos(m\gamma+m'\alpha)s^{(l)}_{m'm}(\beta) \\ &\quad + (-1)^{m'}\cos(m\gamma-m'\alpha)s^{(l)}_{-m'm}] \\ &\quad \times (C_{lm'+}/L_{lm'+})d_{lm'+}(\theta,\varphi) \\ &\quad + [\sin(m\gamma+m'\alpha)s^{(l)}_{m'm}(\beta) \\ &\quad - (-1)^{m'}\sin(m\gamma-m'\alpha)s^{(l)}_{-m'm}(\beta)] \\ &\quad \times (C_{lm'-}/L_{lm'-})d_{lm'-}(\theta,\varphi)\} \end{aligned} \tag{16}$$

or, in terms of $d^{(l)}_{m'm}$ rather than $s^{(l)}_{m'm}$,

$$\begin{aligned} d_{lm+}(\theta',\varphi') &= (L_{lm+}/M_{lm+})(-1)^m d^{(l)}_{0m}(\beta) \\ &\quad \times \cos(m\gamma)2^{1/2}(M_{l0}/L_{l0})d_{l0}(\theta,\varphi) \\ &\quad + (L_{lm+}/M_{lm+}) \\ &\quad \times \sum_{m'=1}^{l}\{[(-1)^{m+m'}d^{(l)}_{m'm}(\beta) \\ &\quad \times \cos(m\gamma+m'\alpha) \\ &\quad + (-1)^m d^{(l)}_{-m'm}(\beta)\cos(m\gamma-m'\alpha)] \\ &\quad \times (M_{lm'+}/L_{lm'+})d_{lm'+} \\ &\quad + [(-1)^{m+m'}d^{(l)}_{m'm}(\beta)\sin(m\gamma+m'\alpha) \\ &\quad - (-1)^m d^{(l)}_{-m'm}(\beta)\sin(m\gamma-m'\alpha)] \\ &\quad \times (M_{lm'-}/L_{lm'-})d_{lm'-}(\theta,\varphi)\}, \end{aligned} \tag{17}$$

with $m > 0$ and, similarly, analogous to ($11b$) and ($12b$) for $d_{lm-}(\theta',\varphi')$.

The ratios L_{lmp}/M_{lmp} and L_{lmp}/C_{lmp} are listed in Table 1. They were obtained from the normalization factors given in the literature (Coppens, 1993) for $l \leq 7$. For $l = 8$, the normalization factors for $d_{8m\pm}(\theta,\varphi)$ were calculated numerically using Gaussian quadrature as discussed elsewhere (Su & Coppens, 1994).

Transformation of population parameters

Let $\mathbf{f}$, $\mathbf{P}$ and $\mathbf{f}'$, $\mathbf{P}'$ be $(2l+1)\times 1$ matrices representing the density-function-normalized spherical harmonics and their population parameters before and after rotation, respectively. Then, by using the ratios in Table 1 and (11) or (12), we construct a $(2l+1)\times(2l+1)$ matrix $\mathbf{M}$ such that

$$\mathbf{f}' = \mathbf{M}\mathbf{f}. \tag{18}$$

The population parameters transform according to

$$\mathbf{P}' = (\mathbf{M}^{-1})^T\mathbf{P}. \tag{19}$$

For the dipolar terms, $\mathbf{M}$ is unitary and $(\mathbf{M}^{-1})^T = \mathbf{M}$, but this is not the case for the higher moments. For the dipolar populations, the expressions are

Table 1. *Ratios of normalization factors*

lmp	$d_{lmp}(\theta,\varphi)/y_{lmp}(\theta,\varphi) = L_{lmp}/M_{lmp}$	$d_{lmp}(\theta,\varphi)/u_{lmp}(\theta,\varphi) = L_{lmp}/C_{lmp}$
00	0.28209	0.079577
11+, 11−, 10	0.65147	0.31831
20	0.65553	0.41350
21+, 21−	0.68647	0.25000
22+, 22−	0.68647	0.12500
30	0.65613	0.48971
31+, 31−	0.70088	0.21356
32+, 32−	0.69190	0.066667
33+, 33−	0.71929	0.028294
40	0.65620	0.55534
41+, 41−	0.70847	0.18960
42+, 42−	0.69880	0.044079
43+, 43−	0.70616	0.011905
44+, 44−	0.74900	0.0044643
50	0.65617	0.61391
51+, 51−	0.71306	0.17226
52+, 52−	0.70407	0.032143
53+, 53−	0.70548	0.0065743
54+, 54−	0.72266	0.0015873
55+, 55−	0.77592	0.00053894
60	0.65611	0.66733
61+, 61−	0.71609	0.15894
62+, 62−	0.70801	0.024846
63+, 63−	0.70703	0.0041354
64+, 64−	0.71555	0.00076411
65+, 65−	0.73945	0.00016835
66+, 66−	0.80049	0.000052610
70	0.65605	0.71677
71+, 71−	0.71823	0.14829
72+, 72−	0.71100	0.019977
73+, 73−	0.70894	0.002810
74+, 74−	0.71345	0.00060076
75+, 75−	0.72696	0.000072579
76+, 76−	0.75587	0.000014800
77+, 77−	0.82308	0.0000043072
80	0.65599	0.76299
81+, 81−	0.71977	0.13953
82+, 82−	0.71331	0.016527
83+, 83−	0.71082	0.0020272
84+, 84−	0.71311	0.00026256
85+, 85−	0.72154	0.000036841
86+, 86−	0.73881	0.0000058208
87+, 87−	0.77172	0.0000011101
88+, 86−	0.84400	0.0000030351

particularly simple ($\mathbf{M} = \mathbf{R}$):

$$\begin{pmatrix} P'_{11+} \\ P'_{11-} \\ P'_{10} \end{pmatrix} = \mathbf{R}\begin{pmatrix} P_{11+} \\ P_{11-} \\ P_{10} \end{pmatrix}, \tag{20}$$

where $\mathbf{R}$ is defined in (1).

Alternative computation of $d^{(l)}_{m'm}(\beta)$ and $s^{(l)}_{m'm}(\beta)$

Following Edmonds (1974), the $d^{(l)}_{m'm}(\beta)$ can be related to their values at $\beta = \pi/2$:

$$\begin{aligned} d^{(l)}_{m'm}(\beta) &= 2\sum_{m''=1}^{l}\Delta^{(l)}_{m''m'}\Delta^{(l)}_{m''m}\cos[m''\beta - (\pi/2)n] \\ &\quad + \Delta^{(l)}_{0m'}\Delta^{(l)}_{0m}\cos(\pi/2n), \end{aligned} \tag{21}$$

where

$$\begin{aligned}\Delta^{(l)}_{m'm} &= d^{(l)}_{m'm}(\pi/2)\\ &= D^{(l)}_{m'm}(0,\pi/2,0)\\ &= \mathrm{D}^{(l)}(\{0,-\pi/2,0\})_{m'm}\\ &= \mathrm{D}^{(l)}(\{0,\pi/2,0\})_{mm'} \qquad (22)\end{aligned}$$

and

$$n = m' - m. \qquad (23)$$

The symmetries of the $d^{(l)}_{m'm}(\beta)$,

$$\begin{aligned}d^{(l)}_{mm'(\beta)} &= d^{(l)}_{m'm}(-\beta)\\ &= d^{(l)}_{-m',-m}(\beta)\\ &= (-1)^{m'-m} d^{(l)}_{-m,-m'}(\beta)\\ &= (-1)^{m'-m} d^{(l)}_{m'm}(\beta)\\ &= (-1)^{l-m'} d^{(l)}_{-mm'}(\pi-\beta)\\ &= (-1)^{l+m} d^{(l)}_{m',-m}(\pi-\beta)\\ &= (-1)^{l-m'} d^{(l)}_{-m'm}(\pi-\beta)\\ &= (-1)^{l+m} d^{(l)}_{m,-m'}(\pi-\beta), \qquad (24)\end{aligned}$$

can be used to simplify the calculations. Thus, it suffices to give $\Delta^{(l)}_{m'm}$ for $0 \le m', m \le l$. Table 2 shows the values of $\Delta^{(l)}_{m'm}$* for $0 \le m', m \le l$, $1 \le l \le 8$.

$s^{(l)}_{m'm}(\beta)$ can be calculated from $d^{(l)}_{m'm}(\beta)$ by the use of

$$\begin{aligned}s^{(l)}_{m'm}(\beta) &= (-1)^{m'-m}\{(l+m)!(l-m)!\\ &\quad \times [(l+m')!(l-m')!]^{-1}\}^{1/2} d^{(l)}_{m'm}(\beta). \qquad (25)\end{aligned}$$

Example of application of the expressions

Fully deuterated benzene crystallizes in the orthorhombic space group *Pbca* (Jeffrey, Ruble, McMullan & Pople, 1987). A local Cartesian coordinate for atom C(1) is defined as follows: $\mathbf{e}_3$ is along the vector from C(1) to D(1), $\mathbf{e}_2$ is in the plane of C(1), C(2) and D(1) and $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$ form a right-handed system. This system is related to the Cartesian coordinate system, defined by $\mathbf{e}'_1 = \mathbf{a}/|\mathbf{a}|$, $\mathbf{e}'_2 = \mathbf{b}/|\mathbf{b}|$ and $\mathbf{e}'_3 = \mathbf{c}/|\mathbf{c}|$ (where $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are the crystallographic axes), by

$$\begin{pmatrix}\mathbf{e}'_1\\ \mathbf{e}'_2\\ \mathbf{e}'_3\end{pmatrix} = \begin{pmatrix}-0.679841 & -0.660441 & -0.318801\\ -0.251076 & -0.198832 & 0.947326\\ -0.689041 & 0.724074 & -0.030647\end{pmatrix}\begin{pmatrix}\mathbf{e}_1\\ \mathbf{e}_2\\ \mathbf{e}_3\end{pmatrix}. \qquad (26)$$

From (3), we get $\alpha = 133.580$, $\beta = 91.7562$ and $\gamma = 71.4005°$. Take $y_{21+}(\theta',\varphi')$ as an example. We have $l = 2$ and $m = 1$. $d^{(2)}_{m'1}$ are evaluated with (8) or (21):

$$\begin{aligned}&[d^{(2)}_{01}(\beta)\; d^{(2)}_{11}(\beta)\; d^{(2)}_{-11}(\beta)\; d^{(2)}_{21}(\beta)\; d^{(2)}_{-21}(\beta)]\\ &\quad = (-0.037517 \;\; -0.514384 \;\; 0.483737\\ &\qquad -0.484449 \;\; 0.515081). \qquad (27)\end{aligned}$$

Substitution of (27) and the values of α and γ into (11*a*) gives

$$\begin{aligned}y_{21+}(\theta',\varphi') &= (0.016922 \;\; 0.240505 \;\; -0.210597\\ &\quad 0.946645 \;\; -0.037180)\begin{bmatrix}y_{20}(\theta,\varphi)\\ y_{21+}(\theta,\varphi)\\ y_{21-}(\theta,\varphi)\\ y_{22+}(\theta,\varphi)\\ y_{22-}(\theta,\varphi)\end{bmatrix}. \qquad (28)\end{aligned}$$

Discussion

Since the Euler angles are related to the rotation matrix $\mathbf{R}$ by (3) and (4), the formulae for the rotation of real spherical harmonics presented in the present paper are general. There are, of course, other parametrizations of the rotation group, *e.g.* the parametrization using an angle of rotation and the direction cosines of the rotation axis (Corio, 1966, 1977; Courant & Hilbert, 1953). Corresponding formulae for the rotation of real spherical harmonics can be expressed in terms of the alternative parameters instead of the Eulerian angles but are not discussed here.

Fortran subroutine *ROTYLMP*

A Fortran subroutine *ROTYLMP* for rotating real spherical harmonics has been written and incorporated into the program *MOLPROP*94 (Su, 1994), which calculates electrostatic potential, the electric field, the electric-field gradient and the electrostatic potential derived atomic charges using the multipole description of the charge density derived from X-ray diffraction data (Su & Coppens, 1992; Su, 1993). *ROTYLMP* and *MOLPROP*94 are available from the authors on request.

Support of this work by the National Science Foundation (CHE9021069 and CHE9317770) is gratefully acknowledged.

* It should be noted that the values of $\Delta^{(l)}_{m'm} = D^{(l)}_{m'm}(0,\pi/2,0)$ in Table 2 differ from the values given by Edmonds, which, in Wigner's notation [7(*b*)], are $\mathrm{D}^{(l)}(\{0,\pi/2,0\})_{m'm}$ (Edmonds, 1974).

Table 2. *Special values of the representation matrix elements* $\Delta^{(l)}_{m'm} \equiv d^{(l)}_{m'm}(\pi/2) = D^{(l)}_{m'm}(0,\pi/2,0)$

$l = 1$

m' \ m	0	1
0	0	$\frac{2^{1/2}}{2}$
1	$-\frac{2^{1/2}}{2}$	$\frac{1}{2}$

$l = 2$

m' \ m	0	1	2
0	$-\frac{1}{2}$	0	$\frac{6^{1/2}}{4}$
1	0	$-\frac{1}{2}$	$\frac{1}{2}$
2	$\frac{6^{1/2}}{4}$	$-\frac{1}{2}$	$\frac{1}{4}$

$l = 3$

m' \ m	0	1	2	3
0	0	$-\frac{3^{1/2}}{4}$	0	$\frac{5^{1/2}}{4}$
1	$\frac{3^{1/2}}{4}$	$-\frac{1}{8}$	$-\frac{10^{1/2}}{8}$	$\frac{15^{1/2}}{8}$
2	0	$\frac{10^{1/2}}{8}$	$-\frac{1}{2}$	$\frac{6^{1/2}}{8}$
3	$-\frac{5^{1/2}}{4}$	$\frac{15^{1/2}}{8}$	$-\frac{6^{1/2}}{8}$	$\frac{1}{8}$

$l = 4$

m' \ m	0	1	2	3	4
0	$\frac{3}{8}$	0	$-\frac{10^{1/2}}{8}$	0	$\frac{70^{1/2}}{16}$
1	0	$\frac{3}{8}$	$-\frac{2^{1/2}}{8}$	$-\frac{7^{1/2}}{8}$	$\frac{14^{1/2}}{8}$
2	$-\frac{10^{1/2}}{8}$	$\frac{2^{1/2}}{8}$	$\frac{1}{4}$	$-\frac{14^{1/2}}{8}$	$\frac{7^{1/2}}{8}$
3	0	$-\frac{7^{1/2}}{8}$	$\frac{14^{1/2}}{8}$	$-\frac{3}{8}$	$\frac{2^{1/2}}{8}$
4	$\frac{70^{1/2}}{16}$	$-\frac{14^{1/2}}{8}$	$\frac{7^{1/2}}{8}$	$-\frac{2^{1/2}}{8}$	$\frac{1}{16}$

$l = 5$

m' \ m	0	1	2	3	4	5
0	0	$\frac{30^{1/2}}{16}$	0	$-\frac{35^{1/2}}{16}$	0	$\frac{3(7^{1/2})}{16}$
1	$-\frac{30^{1/2}}{16}$	$\frac{1}{16}$	$\frac{7^{1/2}}{8}$	$-\frac{42^{1/2}}{32}$	$-\frac{21^{1/2}}{16}$	$\frac{210^{1/2}}{32}$
2	0	$-\frac{7^{1/2}}{8}$	$\frac{1}{4}$	$\frac{6^{1/2}}{16}$	$-\frac{3^{1/2}}{4}$	$\frac{30^{1/2}}{16}$
3	$\frac{35^{1/2}}{16}$	$-\frac{42^{1/2}}{32}$	$-\frac{6^{1/2}}{16}$	$\frac{13}{32}$	$-\frac{9(2^{1/2})}{32}$	$\frac{3(5^{1/2})}{32}$
4	0	$\frac{21^{1/2}}{16}$	$-\frac{3^{1/2}}{4}$	$\frac{9(2^{1/2})}{32}$	$-\frac{1}{4}$	$\frac{10^{1/2}}{32}$
5	$-\frac{3(7^{1/2})}{16}$	$\frac{210^{1/2}}{32}$	$-\frac{30^{1/2}}{16}$	$\frac{3(5^{1/2})}{32}$	$-\frac{10^{1/2}}{32}$	$\frac{1}{32}$

Table 2 (*cont.*)

$l = 6$

m' \ m	0	1	2	3	4	5	6
0	$-\frac{5}{16}$	0	$\frac{105^{1/2}}{32}$	0	$-\frac{3(14^{1/2})}{32}$	0	$\frac{231^{1/2}}{32}$
1	0	$-\frac{5}{16}$	$\frac{10^{1/2}}{32}$	$\frac{3(10^{1/2})}{32}$	$-\frac{3^{1/2}}{8}$	$-\frac{66^{1/2}}{32}$	$\frac{3(22^{1/2})}{32}$
2	$\frac{105^{1/2}}{32}$	$-\frac{10^{1/2}}{32}$	$-\frac{17}{64}$	$\frac{9}{32}$	$\frac{30^{1/2}}{64}$	$-\frac{165^{1/2}}{32}$	$\frac{3(55^{1/2})}{64}$
3	0	$\frac{3(10^{1/2})}{32}$	$-\frac{9}{32}$	$-\frac{1}{32}$	$\frac{30^{1/2}}{16}$	$-\frac{165^{1/2}}{32}$	$\frac{55^{1/2}}{32}$
4	$-\frac{3(14^{1/2})}{32}$	$\frac{3^{1/2}}{8}$	$\frac{30^{1/2}}{64}$	$-\frac{30^{1/1}}{16}$	$\frac{13}{32}$	$-\frac{22^{1/2}}{16}$	$\frac{66^{1/2}}{64}$
5	0	$-\frac{66^{1/2}}{32}$	$\frac{165^{1/2}}{32}$	$-\frac{165^{1/2}}{43}$	$\frac{22^{1/2}}{16}$	$-\frac{5}{32}$	$\frac{3^{1/2}}{32}$
6	$\frac{231^{1/2}}{32}$	$-\frac{3(22^{1/2})}{32}$	$\frac{3(55^{1/2})}{64}$	$-\frac{55^{1/2}}{32}$	$\frac{66^{1/2}}{64}$	$-\frac{3^{1/2}}{32}$	$\frac{1}{64}$

$l = 7$

m' \ m	0	1	2	3	4	5	6	7
0	0	$-\frac{5(14^{1/2})}{64}$	0	$\frac{3(42^{1/2})}{64}$	0	$-\frac{462^{1/2}}{64}$	0	$\frac{858^{1/2}}{64}$
1	$\frac{5(14^{1/2})}{64}$	$-\frac{5}{128}$	$-\frac{15(6^{1/2})}{128}$	$\frac{9(3^{1/2})}{128}$	$\frac{3(33^{1/2})}{64}$	$-\frac{5(33^{1/2})}{128}$	$-\frac{858^{1/2}}{128}$	$\frac{3003^{1/2}}{128}$
2	0	$\frac{15(6^{1/2})}{128}$	$-\frac{5}{32}$	$-\frac{19(2^{1/2})}{128}$	$\frac{22^{1/2}}{16}$	$\frac{22^{1/2}}{128}$	$-\frac{143^{1/2}}{32}$	$\frac{2002^{1/2}}{128}$
3	$-\frac{3(42^{1/2})}{64}$	$\frac{9(3^{1/2})}{128}$	$\frac{19(2^{1/2})}{128}$	$-\frac{39}{128}$	$\frac{11^{1/2}}{64}$	$\frac{11(11^{1/2})}{128}$	$-\frac{3(286^{1/2})}{128}$	$\frac{1001^{1/2}}{128}$
4	0	$-\frac{3(33^{1/2})}{64}$	$\frac{22^{1/2}}{16}$	$-\frac{11^{1/2}}{64}$	$-\frac{1}{4}$	$\frac{25}{64}$	$-\frac{26^{1/2}}{16}$	$\frac{91^{1/2}}{64}$
5	$\frac{462^{1/2}}{64}$	$-\frac{5(33^{1/2})}{128}$	$-\frac{22^{1/2}}{128}$	$\frac{11(11^{1/2})}{128}$	$-\frac{25}{64}$	$\frac{43}{128}$	$-\frac{5(26^{1/2})}{128}$	$\frac{91^{1/2}}{128}$
6	0	$\frac{858^{1/2}}{128}$	$-\frac{143^{1/2}}{32}$	$\frac{3(286^{1/2})}{128}$	$-\frac{26^{1/2}}{16}$	$\frac{5(26^{1/2})}{128}$	$-\frac{3}{64}$	$\frac{14^{1/2}}{128}$
7	$-\frac{858^{1/2}}{64}$	$\frac{3003^{1/2}}{128}$	$-\frac{2002^{1/2}}{128}$	$\frac{1001^{1/2}}{128}$	$-\frac{91^{1/2}}{64}$	$\frac{91^{1/2}}{128}$	$-\frac{14^{1/2}}{128}$	$\frac{1}{128}$

Table 2 (*cont.*)

$l = 8$

m' \ m	0	1	2	3	4	5	6	7	8
0	$\frac{35}{128}$	0	$-\frac{3(35^{1/2})}{64}$	0	$\frac{3(154^{1/2})}{128}$	0	$-\frac{429^{1/2}}{64}$	0	$\frac{3(1430^{1/2})}{256}$
1	0	$\frac{35}{128}$	$-\frac{70^{1/2}}{128}$	$-\frac{1155^{1/2}}{128}$	$\frac{77^{1/2}}{64}$	$\frac{1001^{1/2}}{128}$	$-\frac{858^{1/2}}{128}$	$-\frac{715^{1/2}}{128}$	$\frac{715^{1/2}}{64}$
2	$-\frac{3(35^{1/2})}{64}$	$\frac{70^{1/2}}{128}$	$\frac{1}{4}$	$-\frac{3(66^{1/2})}{128}$	$-\frac{110^{1/2}}{64}$	$\frac{1430^{1/2}}{128}$	0	$-\frac{2002^{1/2}}{128}$	$\frac{2002^{1/2}}{128}$
3	0	$-\frac{1155^{1/2}}{128}$	$\frac{3(66^{1/2})}{128}$	$\frac{17}{128}$	$-\frac{5(15^{1/2})}{64}$	$\frac{195^{1/2}}{128}$	$\frac{910^{1/2}}{128}$	$-\frac{3(273^{1/2})}{128}$	$\frac{273^{1/2}}{64}$
4	$\frac{3(154^{1/2})}{128}$	$-\frac{77^{1/2}}{64}$	$-\frac{110^{1/2}}{64}$	$\frac{5(15^{1/2})}{64}$	$-\frac{9}{64}$	$-\frac{3(13^{1/2})}{64}$	$\frac{546^{1/2}}{64}$	$-\frac{455^{1/2}}{64}$	$\frac{455^{1/2}}{128}$
5	0	$\frac{1001^{1/2}}{128}$	$-\frac{1430^{1/2}}{128}$	$\frac{195^{1/2}}{128}$	$\frac{3(13^{1/2})}{64}$	$-\frac{45}{128}$	$\frac{7(42^{1/2})}{128}$	$-\frac{5(35^{1/2})}{128}$	$\frac{35^{1/2}}{64}$
6	$-\frac{429^{1/2}}{64}$	$\frac{858^{1/2}}{128}$	0	$-\frac{910^{1/2}}{128}$	$\frac{546^{1/2}}{64}$	$-\frac{7(42^{1/2})}{128}$	$\frac{1}{4}$	$-\frac{3(30^{1/2})}{128}$	$\frac{30^{1/2}}{128}$
7	0	$-\frac{715^{1/2}}{128}$	$\frac{2002^{1/2}}{128}$	$-\frac{3(273^{1/2})}{128}$	$\frac{455^{1/2}}{64}$	$-\frac{5(35^{1/2})}{128}$	$\frac{3(30^{1/2})}{128}$	$-\frac{7}{128}$	$\frac{1}{64}$
8	$\frac{3(1430^{1/2})}{256}$	$-\frac{715^{1/2}}{64}$	$\frac{2002^{1/2}}{128}$	$-\frac{273^{1/2}}{64}$	$\frac{455^{1/2}}{128}$	$-\frac{35^{1/2}}{64}$	$\frac{30^{1/2}}{128}$	$-\frac{1}{64}$	$\frac{1}{256}$

References

ARFKEN, G. (1970)]. *Mathematical Methods for Physicists*, 2nd ed. New York: Academic Press.

CONDON, E. V. & SHORTLEY, G. H. (1957). *The Theory of Atomic Spectra*. London, New York: Cambridge Univ. Press.

COPPENS, P. (1993). *International Tables for X-ray Crystallography*, Vol. *B*, edited by U. SHMUELI, pp. 10–22. Dordrecht: Kluwer Academic Publishers.

CORIO, P. L. (1966). *Structure of High-Resolution NMR Spectra*. New York: Academic Press.

CORIO, P. L. (1977). *J. Phys. Chem.* **81**, 2306.

COURANT, R. & HILBERT, D. (1953). *Methods of Mathematical Physics*. New York: Interscience.

CROMER, D. T., LARSON, A. C. & STEWART, R. F. (1976). *J. Chem. Phys.* **65**, 336–349.

EDMONDS, A. R. (1974). *Angular Momentum in Quantum Mechanics*, 2nd ed. Princeton Univ. Press.

HANSEN, N. K. & COPPENS, P. (1978). *Acta Cryst.* **A34**, 909–921.

JEFFREY, G. A., RUBLE, J. R., MCMULLAN, R. K. & POPLE, J. A. (1987). *Proc. R. Soc. London Ser. A*, **414**, 47–57.

ROSE, M. E. (1957). *Elementary Theory of Angular Momentum*. New York: Wiley.

STEINBORN, E. O. & RUEDENBERG, K. (1973). In *Advances in Quantum Chemistry*, Vol. 7, edited by P.-O. LÖWDIN. New York: Academic Press.

SU, Z. (1993). PhD thesis, State Univ. of New York at Buffalo, Buffalo, NY, USA.

SU, Z. (1994). *MOLPROP94, a Fortran Program for Deriving Experimental Molecular Electrostatic Properties*. State Univ. of New York at Buffalo, Buffalo, NY, USA.

SU, Z. & COPPENS, P. (1992). *Acta Cryst.* A**48**, 188–197.

SU, Z. & COPPENS, P. (1994). *Acta Cryst.* A**50**, 408–409.

WIGNER, E. D. (1959). *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra*. New York: Academic Press.