Density- and wavefunction-normalized Cartesian spherical harmonics for $l \leq 20$

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The widely used pseudoatom formalism [Stewart (1976). Acta Cryst. A32, 565–574; Hansen & Coppens (1978). Acta Cryst. A34, 909–921] in experimental X-ray charge-density studies makes use of real spherical harmonics when describing the angular component of aspherical deformations of the atomic electron density in molecules and crystals. The analytical form of the density-normalized Cartesian spherical harmonic functions for up to $l \leq 7$ and the corresponding normalization coefficients were reported previously by Paturle & Coppens [Acta Cryst. (1988), A44, 6–7]. It was shown that the analytical form for normalization coefficients is available primarily for $l \leq 4$ [Hansen & Coppens, 1978; Paturle & Coppens, 1988; Coppens (1992). International Tables for Crystallography, Vol. B, Reciprocal space, 1st ed., edited by U. Shmueli, ch. 1.2. Dordrecht: Kluwer Academic Publishers; Coppens (1997). X-ray Charge Densities and Chemical Bonding. New York: Oxford University Press]. Only in very special cases it is possible to derive an analytical representation of the normalization coefficients for $4 < l \leq 7$ (Paturle & Coppens, 1988). In most cases for $l > 4$ the density normalization coefficients were calculated numerically to within seven significant figures. In this study we review the literature on the density-normalized spherical harmonics, clarify the existing notations, use the Paturle–Coppens (Paturle & Coppens, 1988) method in the Wolfram Mathematica software to derive the Cartesian spherical harmonics for $l \leq 20$ and determine the density normalization coefficients to 35 significant figures, and computer-generate a Fortran90 code. The article primarily targets researchers who work in the field of experimental X-ray electron density, but may be of some use to all who are interested in Cartesian spherical harmonics.

1. Introduction

In experimental X-ray charge-density studies the static electron density $\rho(\mathbf{r}) = \rho(x, y, z)$ is described by the superposition of aspherical nucleus-centered atom-like densities $\rho^{PA}(\mathbf{r})$, called pseudoatoms (PAs) (Hirshfeld, 1971; Stewart, 1972, 1976; Hirshfeld, 1977; Hansen & Coppens, 1978; Tsirolel & Ozerov, 1996; Coppens, 1992, 1997):

$$\rho(\mathbf{r}) = \sum_{\alpha} \rho^{PA}_{\alpha}(\mathbf{r}). \quad (1)$$

Regardless of the formalism, the general mathematical form of the electron density of the pseudoatom $\rho^{PA}_{\alpha}(\mathbf{r})$ is represented as a sum of spherical core $\rho^{core}_{\alpha}(\mathbf{r})$ and valence $\rho^{valence}_{\alpha}(\mathbf{r})$ densities, and the deformation density $\Delta \rho_{\alpha}(\mathbf{r})$:

$$\rho^{PA}_{\alpha}(\mathbf{r}) = \rho^{core}_{\alpha}(\mathbf{r}) + \rho^{valence}_{\alpha}(\mathbf{r}) + \Delta \rho_{\alpha}(\mathbf{r}). \quad (2)$$

The spherical core and valence contributions are usually based on neutral ground-state non-interacting spherically averaged atomic densities obtained from accurate quantum-mechanical calculations. In the Hansen–Coppens formalism (Hansen & Coppens, 1978; Coppens et al., 1979; Coppens, 1992, 1997) and
In mathematics, spherical harmonics

\[ P_l^m(\theta, \phi) = \frac{1}{\sqrt{2\pi}} \int_0^{2\pi} \int_0^\pi P_l^m(\theta, \phi) \sin \theta \, d\theta \, d\phi = \delta_{l\theta} \delta_{mn}, \]  

where the symbol \( \delta \) denotes the Kronecker delta,

\[ \delta_{ij} = \begin{cases} 0 & \text{if } i \neq j, \\ 1 & \text{if } i = j. \end{cases} \]

Spherical harmonics \( Y_l^m(\theta, \phi) \) that obey equation (6) are often called 'wavefunction normalized'. The general form of \( Y_l^m(\theta, \phi) \) is given by (Press et al., 1992)

\[ Y_{l \theta}^m(\theta, \phi) = \frac{(-1)^m}{\sqrt{2\pi}} \frac{(2l+1)}{2} \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta) \exp(im\phi), \]

where the functions \( P_l^m(x) \) are the associated Legendre polynomials (Press et al., 1992). Note that here we follow the notation used in Mathematica (Wolfram Research, Inc., 2012; Tam, 2008) according to which the Condon–Shortley phase \((-1)^m\) (Condon & Shortley, 1951) is included in the definition of the associated Legendre polynomials (Abramowitz & Stegun, 1972; Press et al., 1992):

\begin{align*}
  P_l^m(x) &= (-1)^m(1-x^2)^{m/2} \frac{d^mP_l(x)}{dx^m}, \\
  P_l^{-m}(x) &= (-1)^{-m} \frac{(l-m)!}{(l+m)!} P_l^m(x),
\end{align*}

which makes it unnecessary to include the Condon–Shortley phase in the definition of \( Y_l^m(\theta, \phi) \). Note that Paturel & Coppens (1988) and Coppens (1992, 1997) follow the Arfken notation (Arfken & Weber, 2001), in which the Condon–Shortley phase \((-1)^m\) is included in the definition of \( Y_l^m(\theta, \phi) \), and thus excluded from the definition of the associated Legendre polynomial \( P_l^m(x) \).

Upon the separation of a complex function \( Y_l^m(\theta, \phi) \) into the real \( \text{Re}[Y_l^m(\theta, \phi)] \) and imaginary \( \text{Im}[Y_l^m(\theta, \phi)] \) parts, the real spherical harmonic function \( y_l^m(\theta, \phi) \) can be also defined as (Homeier & Steinborn, 1996)

\[ y_l^m(\theta, \phi) = \begin{cases} \sqrt{2} \text{Im}[Y_l^m(\theta, \phi)] & \text{if } m = 0, \\
\sqrt{2} \text{Re}[Y_l^m(\theta, \phi)] & \text{if } m > 0. \end{cases} \]

The real spherical harmonics \( y_l^m(\theta, \phi) \) have the same ortho-normality properties [equation (6)] as \( Y_l^m(\theta, \phi) \):

\[ \int_0^{2\pi} \int_0^\pi y_l^m(\theta, \phi) y_l^m(\theta, \phi) \sin \theta \, d\theta \, d\phi = \delta_{l\theta} \delta_{mn}. \]

The real spherical harmonics with \( m > 0 \) differ from those with \( m < 0 \) by multiplication of the cosine or sine functions, respectively:

\[ y_l^{-m}(\theta, \phi) = \begin{cases} \left[ \frac{(2l+1)}{2\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta) \cos(m\phi), \\
\left[ \frac{(2l+1)}{2\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta) \sin(m\phi), \end{cases} \]

The functions

\[ y_l^{-m}(\theta, \phi) = \begin{cases} \cos(m\phi) & \text{if } m = 0, \\
\sin(m\phi) & \text{if } m > 0, \end{cases} \]

are often called the tesseract harmonics (Abramowitz & Stegun, 1972; Stewart, 1976; Whittaker & Watson, 1990). Note that because no well established notation exists for tesseract harmonics, we shall denote these functions as \( T_l^m(\theta, \phi) \).

The spherical harmonics, both the real and complex, can be transformed from the spherical coordinate system \((r, \theta, \phi)\) to the Cartesian frame \((x, y, z)\) using well known relationships (Arfken & Weber, 2001):
\[ x = r \sin \theta \cos \varphi, \]
\[ y = r \sin \theta \sin \varphi, \]
\[ z = r \cos \theta, \]

(14)

where \( \theta \in [0, \pi] \) and \( \varphi \in [0, 2\pi) \). Of course, the reverse transformations are given by

\[ r = \left( x^2 + y^2 + z^2 \right)^{1/2}, \]
\[ \cos \theta = \frac{z}{\left( x^2 + y^2 + z^2 \right)^{1/2}} = \frac{z}{r}, \]
\[ \tan \varphi = \frac{y}{x}. \]

(15)

In both the Hansen–Coppens (Hansen & Coppens, 1978; Coppens, 1992, 1997) and Stewart (1976) formalisms, the real spherical harmonic functions are normalized in a different way than the functions \( y_m^l(\theta, \varphi) \) defined in equation (11). They are called the density-normalized real spherical harmonics and labeled as \( d_l^m(\theta, \varphi) \) (Paturle & Coppens, 1988; Coppens, 1992, 1997) to distinguish them from the wavefunction-normalized functions \( y_m^l(\theta, \varphi) \):

\[ d_l^m(\theta, \varphi) = N_l^mP_l^m(\cos \theta) \cos(m \varphi), \]
\[ d_l^{-m}(\theta, \varphi) = N_l^mP_l^{-m}(\cos \theta) \sin(m \varphi). \]

(16)

Using tesseral harmonics \( T_l^m(\theta, \varphi) \) [equation (13)], functions \( d_l^m(\theta, \varphi) \) and \( y_l^m(\theta, \varphi) \) can be rewritten simply as

\[ y_l^m(\theta, \varphi) = N_l^mT_l^m(\theta, \varphi), \]
\[ d_l^m(\theta, \varphi) = N_l^{-m}T_l^{-m}(\theta, \varphi). \]

(17)

The functions \( d_l^m(\theta, \varphi) \) are normalized as follows (Hansen & Coppens, 1978; Paturle & Coppens, 1988; Coppens, 1992, 1997):

\[ \int_0^{2\pi} \int_0^\pi \left| d_l^m(\theta, \varphi) \right| \sin \theta \, d\theta \, d\varphi = 1 \quad \text{for} \quad l = 0, \]
\[ \int_0^{2\pi} \int_0^\pi \left| d_l^m(\theta, \varphi) \right| \sin \theta \, d\theta \, d\varphi = 2 \quad \text{for} \quad l > 0. \]

(18)

Note that in the original paper by Hansen & Coppens (1978), both the density- and wavefunction-normalized spherical harmonics were called \( y_l^m(\theta, \varphi) \). Using functions \( d_l^m(\theta, \varphi) \), the expansion for \( \Delta \rho(\mathbf{r}) \) of a given pseudopotom becomes (Stewart, 1976; Hansen & Coppens, 1978; Coppens, 1992, 1997):

\[ \Delta \rho(\mathbf{r}) = \sum_{l=0}^{\text{max}} \sum_{m=-l}^{l} P_l^m R_{lm}(\mathbf{r}) d_l^m(\theta, \varphi). \]

(19)

Historically, it has been customary to assume that the radial functions \( R_{lm}(\mathbf{r}) \) are independent of \( m \) (Stewart, 1976; Hansen & Coppens, 1978; Coppens, 1992, 1997), so the expansion for \( \Delta \rho(\mathbf{r}) \) becomes

\[ \Delta \rho(\mathbf{r}) = \sum_{l=0}^{\text{max}} R_l(\mathbf{r}) \sum_{m=-l}^{l} P_l^m d_l^m(\theta, \varphi). \]

(20)

While functions \( d_l^m(\theta, \varphi) \) are uniquely defined via equations (16)–(18), their analytical representation can be somewhat confusing, because over the years these functions have been written in several different forms (Paturle & Coppens, 1988; Coppens, 1992, 1997):

\[ d_l^m(\theta, \varphi) = N_l^m T_l^m(\cos \theta) \cos(m \varphi) = L_{lm} c_l^m(x, y, z), \]
\[ d_l^{-m}(\theta, \varphi) = N_l^m T_l^{-m}(\cos \theta) \sin(m \varphi) = L_{lm} c_l^{-m}(x, y, z), \]

(21)

where \( c_l^m(x, y, z) \) are the Cartesian functions and \( L_{lm} \) are the so-called ‘common factors’ (Paturle & Coppens, 1988; Coppens, 1992, 1997). Unfortunately, neither functions \( c_l^m(x, y, z) \) nor pre-factors \( L_{lm} \) can be uniquely defined, which ultimately affects the values of the normalizations coefficients \( L_{lm} \) (Table 1).

Note that the two definitions give the same function \( d_l^m(\theta, \varphi) \). Additional problems arise from the fact that the analytical forms of coefficients \( N_l^m \) and \( L_{lm} \) are available primarily for \( l \leq 4 \) (Hansen & Coppens, 1978; Paturle & Coppens, 1988; Coppens, 1992, 1997) – only in very special cases can the analytical form of \( L_{lm} \) for \( l > 4 \) be obtained (Paturle & Coppens, 1988). For higher orders of \( l \), Paturle & Coppens (1988) proposed a simple numerical procedure for calculation of coefficients \( L_{lm} \) [note that in the original paper these were called \( N_l^m \), but should not be confused with the coefficients \( N_l^m \) defined in equation (12)]. The authors extended the list of coefficients \( L_{lm} \) up to \( l \leq 7 \) (Paturle & Coppens, 1988; Coppens, 1992, 1997), but unfortunately the numerical techniques used (ZROOTS and QROMB; Press et al., 1986) were able to reproduce no more than seven decimal points in cases where the coefficients could not be expressed analytically.

The advent of the 64-bit computer architecture, however, allows for double-precision floating-point numbers which can accurately express up to 15 significant figures of a real-valued number. While this architecture did not become readily available to workstations and servers until the 1990s (Kohn & Margulis, 1989), 32-bit operating systems were able to simulate double-precision floating-point numbers by utilizing more than one register in the 32-bit processor, albeit at higher computational cost. In the future, the 128-bit computer architecture will allow for quad precision (up to 34 digit representations) and will require far more accurate values of \( N_l^m \) and \( L_{lm} \) for use in scientific computer applications.

Aside from the accuracy of the normalization coefficients, recent studies (Koritsanszky et al., 2012; Koritsanszky & Michael, 2015) suggest that a higher multipole expansion
in \( l \) converges if the radial density functions \( R_m(r) \) are \( m \) dependent. For this reason it becomes necessary to determine and implement normalization coefficients that are much more accurate than those previously reported for \( l \leq 7 \).

2. Calculation of the tesseral harmonics in the Cartesian frame \( T_l^m(x, y, z) \)

The calculation of the tesseral harmonics in the spherical polar coordinate system \( T_l^m(\theta, \phi) \) [equation (13)] is straightforward in Mathematica:

\[
T_{l,m}[\theta, \phi] := \text{If} \ [m \geq 0, \\
(-1)^m \text{LegendreP}[l, \text{Abs}[m], \text{Cos}[\theta] \text{Cos}[\text{Abs}[m] \phi], \\
(-1)^m \text{LegendreP}[l, \text{Abs}[m], \text{Cos}[\theta] \text{Sin}[\text{Abs}[m] \phi]]; \\
\text{where we multiply Mathematica's associated Legendre polynomials (Wolfram Research, Inc., 2012; Tam, 2008) by the Condon–Shortley phase \((-1)^m\) (Condon & Shortley, 1951) so as to remain consistent with the Arfken (Arfken & Weber, 2001) and Coppens (Paturle & Coppens, 1988; Coppens, 1992, 1997) notations.}
\]

Formulas for the tesseral harmonics in the Cartesian frame \( T_l^m(\theta, \phi) \rightarrow T_l^m(x, y, z) \) are more complicated, as they involve evaluating functions of the form \( \sin(m \phi) \) and \( \cos(m \phi) \), where the angle \( \phi \) is defined as \( \tan \phi = y/x \) [equation (15)]. To evaluate these trigonometric functions in a form which results in a polynomial of \( (x, y, z) \), it becomes necessary to define the Cartesian sine (CSin) and cosine (CCos) functions by recursive evaluation such that

\[
\begin{align*}
\text{CSin}(m \phi) &= \begin{cases} 
0 & m = 0 \\
\sin \left( \arctan \left( \frac{y}{\sqrt{x^2 + y^2}} \right) \right) & m = 1 \\
\text{CSin}(a) \text{CCos}(b) + \text{CCos}(a) \text{CSin}(b) & m > 1
\end{cases} \\
\text{CCos}(m \phi) &= \begin{cases} 
0 & m = 0 \\
\cos \left( \arctan \left( \frac{y}{\sqrt{x^2 + y^2}} \right) \right) & m = 1 \\
\text{CCos}(a) \text{CCos}(b) - \text{CSin}(a) \text{CSin}(b) & m > 1
\end{cases}
\end{align*}
\]

where \( a = \text{Floor}[m/2] \) and \( b = \text{Ceil}[m/2] \). The functions \( \text{Floor}[x] \) and \( \text{Ceil}[x] \) are the standard Mathematica functions (Wolfram Research, Inc., 2012) that retain the ‘greatest integer less than or equal to \( x \’ \) and ‘smallest integer greater than or equal to \( x \’ \) (Wolfram Research, Inc., 2012), respectively. These \( \text{CSin} \) and \( \text{CCos} \) functions are defined as modules in the provided Mathematica code and occur in the definition of \( T_l^m(x, y, z) \) as

\[
T_{l,m}[x, y, z] := \text{If} \ [m \geq 0, \\
(-1)^m \text{LegendreP}[l, \text{Abs}[m], \frac{z}{\sqrt{x^2 + y^2 + z^2}}] \\
\times \text{CCos} \left[ \text{Abs}[m], \frac{x}{\sqrt{x^2 + y^2 + z^2}}, \frac{y}{\sqrt{x^2 + y^2 + z^2}} \right], \\
(-1)^m \text{LegendreP}[l, \text{Abs}[m], \frac{z}{\sqrt{x^2 + y^2 + z^2}}] \\
\times \text{CSin} \left[ \text{Abs}[m], \frac{x}{\sqrt{x^2 + y^2 + z^2}}, \frac{y}{\sqrt{x^2 + y^2 + z^2}} \right];
\]

where \( (x, y, z) \) are evaluated as \( (x/r, \ y/r, \ z/r) \) so as to remain on the surface of a unit sphere.

3. Calculation of the normalization coefficients \( N_{lm}^m \)

For the calculation of \( N_{lm}^m \), we use the method described by Paturle & Coppens (1988), which requires evaluation of a one-dimensional integral:

\[
N_{lm}^m = \frac{1 + \delta_{l0}}{2(2 + (\pi - 2)\delta_{m0})} \int_{-1}^{1} |P_l^m(z)| \, dz.
\]

The one-dimensional integral in equation (26) is defined in terms of roots of a polynomial equation for large values of \( l \) and thus we invoke methods in the Mathematica (Wolfram Research, Inc., 2012) software package to perform this integration and report values of \( N_{lm}^m \) with 35 significant figures.

It should be noted that, via Mathematica’s sophisticated numerical integration algorithms, a working precision of 70 digits was used throughout the calculation so as to avoid the roundoff error and to make sure that the reported values truly achieve a 35-digit level of accuracy. The numerical integration methods employed by Mathematica make use of a global adaptive strategy (GSA), which recursively bisects the domain of integration and performs numerical integration with GSA on each subregion (Wolfram Research, Inc., 2014). Each implementation of GSA returns integral value and error estimates and the bisection continues until error estimates are within the requested accuracy level – in this case, 35 digits.

4. Results

The Cartesian tesseral spherical harmonic functions \( T_l^m(x, y, z) \) for \( l \leq 20 \) were calculated in Mathematica and reformatted into a Fortran90-type source code (available in the supporting information) via a simple parser program, also written in Fortran. We note that no attempt has been made to optimize the Mathematica-generated formulas.

The calculated \( N_{lm}^m \) values for \( l \leq 20 \) are provided in the supporting information in simple ASCII text format, and also in the form of a Fortran90-compatible module. For completeness, we also include a module with waveform-function-based normalized coefficients \( N_{lm} \) [equations (12) and (17)].
The generated Fortran source code has been incorporated in the program DenProp (Volkov et al., 2009; Michael, 2014), including modifications necessary to calculate derivatives at \( r = 0 \) (Volkov et al., 2006).

Functions \( d_l^m(\theta, \varphi) \) and their derivatives behave poorly near the origin, as they contain direction cosines, so we remove a factor \( r^l \) from the radial function \( R(r) \) [equation (20)] and incorporate it into \( d_l^m(\theta, \varphi) \) (Volkov et al., 2006):

\[
R(r)d_l^m(\theta, \varphi) = \left[r^{l}R(r)\right]\left[r^{l}d_l^m(\theta, \varphi)\right].
\]  

(27)

Note that the normalized radial density functions \( R(r) \), usually expressed as (Stewart, 1976; Hansen & Coppens, 1978)

\[
R_l = N_l(n_l, \xi) r^n \exp(-\xi r),
\]

(28)

where \( \xi \) is the effective exponent and \( N_l(n_l, \xi) \) is the radial function normalization factor (Coppens, 1992, 1997), contain the \( r^0 \) term with the condition \( n_l \geq l \) to 'ensure a proper solution of Poisson’s equation at \( r = 0 \) for a Coulomb potential' (Stewart, 1976). Thus, even if the radial function \( R(r) \) is multiplied by \( r^{-l} \), the power of \( r \) in \( r^{n-1} \) always remains non-negative. In the spirit of this technique, we have used Mathematica to generate a Fortran90 source code to calculate all derivatives of function (27) up to the order of four (Michael & Volkov, 2015). This code has been incorporated in DenProp (Volkov et al., 2009) and extensively used in benchmark studies of theoretical electron densities (Michael, 2014).

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References


