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

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This article is dedicated to Professor Philip Coppens, whose X-ray studies of photoinduced excited states were recently selected by *Chemistry and Engineering News* as one of the top ten most important studies in the 100-year history of X-ray crystallography.

The widely used pseudoatom formalism [Stewart (1976). *Acta Cryst*. A**32**, 565–574; Hansen & Coppens (1978). *Acta Cryst*. A**34**, 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), A**44**, 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; Tsirelson & Ozerov, 1996; Coppens, 1992, 1997):

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

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

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

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

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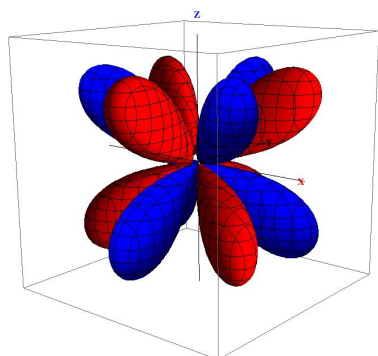
later in the Stewart model (Stewart & Spackman, 1983), the population (electron count) and the expansion–contraction of $\rho_\alpha^{\text{valence}}(\mathbf{r})$ can be adjusted in the course of the least-squares fit of the model [equation (1)] to the experimental (or theoretical) structure factors (Coppens, 1997). At this time we drop the index α, and consider expansion of $\Delta\rho(\mathbf{r})$ for a single pseudoatom. The deformation part of the pseudoatom density $\Delta\rho(\mathbf{r})$ is, in general, a sum of products of populations P_{lm}, and radial functions $R_{lm}(r)$ and angular functions $A_{lm}(\theta, \varphi)$ in the spherical polar coordinate system (r, θ, φ):

$$\Delta\rho(\mathbf{r}) = \Delta\rho(r, \theta, \varphi) = \sum_l \sum_m P_{lm} R_{lm}(r) A_{lm}(\theta, \varphi), \quad (3)$$

where l and m are the indices of summation. In the Hirshfeld model (Hirshfeld, 1971, 1977; Harel & Hirshfeld, 1975), the angular functions $A_{lm}(\theta, \varphi)$ are defined in terms of directional cosines, while in the Stewart (1976) and Hansen–Coppens (Hansen & Coppens, 1978; Coppens, 1992, 1997) formalisms, functions $A_{lm}(\theta, \varphi)$ are represented by real spherical harmonics with $l = 0, \ldots, \infty$, $m = -l, \ldots, l$, requiring a special normalization as discussed below. In general, the real spherical harmonic function $y_l^m(\theta, \varphi)$ is the normalized linear combination of complex spherical harmonics (or, simply, spherical harmonics) $Y_l^m(\theta, \varphi)$ (Pinchon & Hoggan, 2007; Romanowski et al., 2008):

$$y_l^m(\theta, \varphi) = \begin{cases} \dfrac{i}{\sqrt{2}}\left(Y_l^m(\theta, \varphi) - (-1)^m Y_l^{|m|}(\theta, \varphi)\right) & \text{if } m < 0, \\ Y_l^0(\theta, \varphi) & \text{if } m = 0, \\ \dfrac{1}{\sqrt{2}}\left(Y_l^{-m}(\theta, \varphi) + (-1)^m Y_l^m(\theta, \varphi)\right) & \text{if } m > 0. \end{cases}$$
$$(4)$$

In mathematics, spherical harmonics $Y_l^m(\theta, \varphi)$ are the angular part of the solutions for the Laplace equation (Arfken & Weber, 2001):

$$\nabla^2 f(r, \theta, \varphi) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\varphi^2} = 0. \quad (5)$$

Spherical harmonics $Y_l^m(\theta, \varphi)$ are normalized such that (Press et al., 1992)

$$\int_0^{2\pi}\int_0^\pi Y_l^m(\theta, \varphi)^* Y_{l'}^{m'}(\theta, \varphi)\sin\theta\,d\theta\,d\varphi = \delta_{ll'}\delta_{mm'}, \quad (6)$$

where the symbol '*' denotes the complex conjugate, and δ_{ij} is the Kronecker delta,

$$\delta_{ij} = \begin{cases} 0 \text{ if } i \neq j, \\ 1 \text{ if } i = j. \end{cases} \quad (7)$$

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

$$Y_l^m(\theta, \varphi) = \left[\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta)\exp(im\varphi), \quad (8)$$

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):

$$P_l^{|m|}(x) = (-1)^{|m|}(1-x^2)^{|m|/2}\frac{d^{|m|}P_l(x)}{dx^{|m|}},$$
$$P_l^{-|m|}(x) = (-1)^{-|m|}\frac{(l-|m|)!}{(l+|m|)!}P_l^{|m|}(x),$$
$$(9)$$

which makes it unnecessary to include the Condon–Shortley phase in the definition of $Y_l^m(\theta, \varphi)$. Note that Paturle & 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 $Y_l^m(\theta, \varphi)$, and thus excluded from the definition of the associated Legendre polynomial $P_l^m(x)$.

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

$$y_l^m(\theta, \varphi) = \begin{cases} \sqrt{2}\,\text{Im}\left[Y_l^{|m|}(\theta, \varphi)\right] & \text{if } m < 0, \\ Y_l^0(\theta, \varphi) & \text{if } m = 0, \\ \sqrt{2}\,\text{Re}\left[Y_l^{|m|}(\theta, \varphi)\right] & \text{if } m > 0. \end{cases} \quad (10)$$

The real spherical harmonics $y_l^m(\theta, \varphi)$ have the same orthonormality properties [equation (6)] as $Y_l^m(\theta, \varphi)$:

$$\int_0^{2\pi}\int_0^\pi y_l^m(\theta, \varphi)y_{l'}^{m'}(\theta, \varphi)\sin\theta\,d\theta\,d\varphi = \delta_{ll'}\delta_{mm'}. \quad (11)$$

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

$$y_l^{|m|}(\theta, \varphi) = \left[\frac{(2l+1)}{2\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)\cos(|m|\varphi)$$
$$\equiv N_{lm}P_l^{|m|}(\cos\theta)\cos(|m|\varphi),$$
$$y_l^{-|m|}(\theta, \varphi) = \left[\frac{(2l+1)}{2\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)\sin(|m|\varphi)$$
$$\equiv N_{lm}P_l^{|m|}(\cos\theta)\sin(|m|\varphi). \quad (12)$$

The functions

$$P_l^{|m|}(\cos\theta)\begin{Bmatrix} \cos(|m|\varphi) \\ \sin(|m|\varphi) \end{Bmatrix} := T_l^m(\theta, \varphi) \quad (13)$$

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

The spherical harmonics, both the real and complex, can be transformed from the spherical coordinate system (r, θ, φ) to the Cartesian frame (x, y, z) using well known relationships (Arfken & Weber, 2001):

$$x = r \sin\theta \cos\varphi,$$
$$y = r \sin\theta \sin\varphi,$$
$$z = r \cos\theta, \qquad (14)$$

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

$$r = \left(x^2 + y^2 + z^2\right)^{1/2},$$
$$\cos\theta = \frac{z}{(x^2+y^2+z^2)^{1/2}} = \frac{z}{r},$$
$$\tan\varphi = \frac{y}{x}. \qquad (15)$$

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 $y_l^m(\theta, \varphi)$ 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 $y_l^m(\theta, \varphi)$:

$$d_l^{|m|}(\theta, \varphi) = N'_{lm} P_l^{|m|}(\cos\theta)\cos(|m|\varphi),$$
$$d_l^{-|m|}(\theta, \varphi) = N'_{lm} P_l^{|m|}(\cos\theta)\sin(|m|\varphi). \qquad (16)$$

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

$$y_l^m(\theta, \varphi) = N_{lm} T_l^m(\theta, \varphi),$$
$$d_l^m(\theta, \varphi) = N'_{lm} T_l^m(\theta, \varphi). \qquad (17)$$

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

$$\int_0^{2\pi}\int_0^\pi \left|d_l^m(\theta, \varphi)\right| \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi = 1 \text{ for } l = 0,$$
$$\int_0^{2\pi}\int_0^\pi \left|d_l^m(\theta, \varphi)\right| \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi = 2 \text{ for } l > 0. \qquad (18)$$

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

$$\Delta\rho(\mathbf{r}) = \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} P_{lm} R_{lm}(r) d_l^m(\theta, \varphi). \qquad (19)$$

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

$$\Delta\rho(\mathbf{r}) = \sum_{l=0}^{l_{max}} R_l(r) \sum_{m=-l}^{l} P_{lm} d_l^m(\theta, \varphi). \qquad (20)$$

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

Table 1
Definitions of C_{lm}, $c_l^{|m|}(x, y, z)$ and L_{lm} used in the literature.

	Paturle & Coppens, 1988; Coppens, 1992			Coppens, 1997		
l, m	C_{lm}	$c_l^m(x, y, z)$	L_{lm}	C_{lm}	$c_l^m(x, y, z)$	L_{lm}
2, 2+	6	$(x^2 - y^2)/2$	0.750	3	$x^2 - y^2$	0.375
2, 2−	6	xy	0.750	3	$2xy$	0.375

written in several different forms (Paturle & Coppens, 1988; Coppens, 1992, 1997):

$$d_l^{|m|}(\theta, \varphi) = N'_{lm} P_l^{|m|}(\cos\theta)\cos(|m|\varphi) = L_{lm} c_l^{|m|}(x, y, z)$$
$$= N'_{lm} C_{lm} c_l^{|m|}(x, y, z)$$
$$d_l^{-|m|}(\theta, \varphi) = N'_{lm} P_l^{|m|}(\cos\theta)\sin(|m|\varphi) = L_{lm} c_l^{-|m|}(x, y, z)$$
$$= N'_{lm} C_{lm} c_l^{-|m|}(x, y, z), \qquad (21)$$

where $c_l^{|m|}(x, y, z)$ are the Cartesian functions and C_{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 C_{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'_{lm} and L_{lm} are available primarily for $l \le 4$ (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_{lm}, but should not be confused with the coefficients N_{lm} defined in equation (12)]. The authors extended the list of coefficients L_{lm} up to $l \le 7$ (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'_{lm} 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 $R_{lm}(r)$ 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 $T_l^m(\theta, \varphi)$ [equation (13)] is straightforward in *Mathematica*:

$$T_{l,m}[\theta\_, \varphi\_] := \text{If } [m \geq 0,$$
$$(-1)^m \text{LegendreP}[l, \text{Abs}[m], \text{Cos}[\theta]] \text{Cos}[\text{Abs}[m]\varphi], \quad (22)$$
$$(-1)^m \text{LegendreP}[l, \text{Abs}[m], \text{Cos}[\theta]] \text{Sin}[\text{Abs}[m]\varphi]];$$

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 $T_l^m(\theta, \varphi) \rightarrow T_l^m(x, y, z)$ are more complicated, as they involve evaluating functions of the form $\sin(|m|\varphi)$ and $\cos(|m|\varphi)$, where the angle φ is defined as $\tan \varphi = y/x$ [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

$$\text{CSin}(m\varphi) = \begin{cases} 0 & m = 0 \\ \text{Sin}\left(\text{ArcTan}\left(\frac{y}{x}\right)\right) = \frac{y}{\sqrt{x^2 + y^2}} & m = 1 \\ \text{CSin}(a)\text{CCos}(b) + \text{CCos}(a)\text{CSin}(b) & m > 1 \end{cases}$$
$$(23)$$

$$\text{CCos}(m\varphi) = \begin{cases} 0 & m = 0 \\ \text{Cos}\left(\text{ArcTan}\left(\frac{y}{x}\right)\right) = \frac{x}{\sqrt{x^2 + y^2}} & m = 1 \\ \text{CCos}(a)\text{CCos}(b) - \text{CSin}(a)\text{CSin}(b) & m > 1 \end{cases},$$
$$(24)$$

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

$$T_{l,m}[x\_, y\_, z\_] := \text{If } [m \geq 0,$$

$$(-1)^m \text{LegendreP}\left[l, \text{Abs}[m], \frac{z}{\sqrt{x^2 + y^2 + z^2}}\right]$$

$$\times \text{CCos}\left[\text{Abs}[m], \frac{x}{\sqrt{x^2 + y^2 + z^2}}, \frac{y}{\sqrt{x^2 + y^2 + z^2}}\right],$$

$$(-1)^m \text{LegendreP}\left[l, \text{Abs}[m], \frac{z}{\sqrt{x^2 + y^2 + z^2}}\right]$$

$$\times \text{CSin}\left[\text{Abs}[m], \frac{x}{\sqrt{x^2 + y^2 + z^2}}, \frac{y}{\sqrt{x^2 + y^2 + z^2}}\right]];$$
$$(25)$$

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}

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

$$N'_{lm} = \frac{1 + \delta_{l0}}{2(2 + (\pi - 2)\delta_{m0}) \int_{-1}^1 |P_l^{|m|}(z)| \, \mathrm{d}z}. \quad (26)$$

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} 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} 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 wavefunction-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 $R_l(r)$ [equation (20)] and incorporate it into $d_l^m(\theta, \varphi)$ (Volkov *et al.*, 2006):

$$R_l(r)d_l^m(\theta, \varphi) = \left[r^{-l}R_l(r)\right]\left[r^l d_l^m(\theta, \varphi)\right]. \qquad (27)$$

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

$$R_l(r) = N_R(n_l, \zeta)r^{n_l}\exp(-\zeta r), \qquad (28)$$

where ζ is the effective exponent and $N_R(n_l, \zeta)$ is the radial function normalization factor (Coppens, 1992, 1997), contain the r^{n_l} 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_l-l} always remains nonnegative. 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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