SHORT COMMUNICATIONS

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Orthogonal bases of radial functions for charge density refinements.

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Abstract

Charge density determination from X-ray measurements necessitates the evaluation of the Fourier-Bessel transforms of the radial functions used to expand the charge density. Analytical expressions are given here for four sets of orthogonal functions which can substitute for the 'traditional exponential functions' set in least-squares refinements.

The charge density in crystals is usually expanded in terms of a series of nucleus-centered functions. The angular dependence of these functions is properly described in terms of spherical harmonics. To describe the radial dependence one can choose any arbitrary set of functions, as stated by Dawson (1967), mathematical simplicity being the main criterion. Several sets of radial functions have been proposed: harmonic-oscillator wavefunctions (Kurki-Suonio, 1968), exponential functions (Stewart, 1969), and Hartree-Fock-type functions (Hansen & Coppens, 1978). The charge density obtained from these multipole refinements has been used to calculate various electrical quantities such as atomic charges, molecular dipoles or electric field gradients. Recent work has shown that the choice of the radial functions may have some influence on the computed quantities (Restori & Schwarzenbach, 1986; Restori, Schwarzenbach & Schneider, 1987).

The expressions needed to implement a set of functions into existing least-squares programs are given explicitly for four sets of orthogonal functions satisfying the criterion of mathematical simplicity. This criterion can be formulated as: the Fourier-Bessel transforms of practically all radial function sets are given by hypergeometric functions ${}_mF_n(a_1, \ldots, a_m; b_1, \ldots, b_n: -x^2)$. Only for a few sets does the hypergeometric series have either a finite number of terms or represent a simple function (e^{-x}, for example). The four sets presented here are (1) the H-atom wavefunctions, (2) the harmonic-oscillator wavefunctions (Kurki-Suonio, 1968) (values of the normalization constants are explicitly given here), (3) the Laguerre functions, (4) a set of orthogonalized Lorentzians.

For these four sets as well as for the exponential functions introduced by Stewart (1969), both the charge density functions and the atomic scattering factors can be written in the form

$$f_{nl}(x) = N_{nl}x^l g_{nl}(x) \sum_{k=0}^{j} (-1)^k a_k^j [G(x)]^k, \tag{1}$$

where N_{nl} is a normalization constant, $g_{nl}(x)$ and $G(x)$ are simple analytical functions of x, a_k^j are numerical coefficients and j is related to $n-l$ (we will call it the 'order' of the function). Explicit expressions are given in Table 1 for the charge density functions and in Table 2 for the atomic scattering factors. The normalization constants N_{nl} can only be expressed in terms of a function of l $C_j(l)$ different for each 'order' j. The functions $C_j(l)$ are listed for $j=0$ through 5 in Table 3. The expression $\partial f/\partial \alpha$, the derivative of the atomic scattering factors with respect to the radial parameter α, is also needed in the least-squares procedure and given by

$$\frac{\partial f_{nl}}{\partial \alpha} = \frac{f_{nl}}{\alpha}[z(x) - x\Sigma'/\Sigma], \tag{2}$$

where Σ stands for $\sum_{k=0}^{j} (-1)^k a_k^j [G(x)]^k$, and Σ' for its derivative with respect to x. The functions $z(x)$ are also given in Table 2.

The use of the Laguerre functions should give the same results as the exponential functions proposed by Stewart (1969), since for any finite set of functions the population coefficients are related by a triangular matrix [$p_{\exp} = (M)p_{\rm Lag}$] provided that for a given l a complete set up to the same 'order' m is used in both sets. The H-atom wavefunctions are the only set for which x is dependent on n. The harmonic-oscillator wavefunctions are the only set for which the functions g and G are the same for the density and atomic scattering factor functions (Fourier invariant).

One can use any of the sets of radial functions given in Table 1 in a least-squares refinement of charge density distributions without noticeable change in the amount of CPU time needed for the refinement, or without having to invest much effort in programming (the five sets of functions have been implemented in a 120-line Fortran set of subroutines). It would be interesting to compare the results obtained for the electrical quantities from the refined parameters obtained for different sets of radial functions.

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Table 1. *Expressions for the charge density functions for the four sets of orthogonal functions mentioned in the text*

Corresponding expressions for the exponential functions are given for completeness.

	Exponentials	H-atom wavefunction	Harmonic-oscillator wavefunction	Laguerre	Lorentzian
j	$n-l$	$n-l-1$	$\frac{1}{2}(n-l)$	$n-l$	$n-l-1$
x	αr	$\frac{\alpha}{n} r$	αr	αr	αr
$g_{nl}(x)$	$\exp(-x)$	$\exp(-\frac{1}{2}x)$	$\exp(-\frac{1}{2}x^2)$	$\exp(-\frac{1}{2}x)$	$1/(1+x^2)^{n+1}$
$G(x)$	x	x	x^2	x	$1+x^2$
a^j_k	δ_{jk}	$\frac{(2l+j+1)!}{(2l+k+1)!(j-k)!k!}$	$\frac{2^k(2l+2j+1)!!}{(2l+2k+1)!!(j-k)!k!}$	$\frac{(2l+j+2)!}{(2l+k+2)!(j-k)!k!}$	$\frac{(2l+2j+3)!!(2l+2j+2-k)!}{2^k(2l+2j+3-2k)!!(2l+2j+2)!(j-k)!k!}$
N_{nl}	$\alpha^3\frac{(-1)^j}{(l+j+2)!}$	$\left(\frac{\alpha}{2n}\right)^3\frac{(-1)^j}{2^l(l+2)!C_j(l)}$	$\alpha^3\frac{(-1)^j}{(l+1)!!C_j(l)}q^*$	$\left(\frac{\alpha}{2}\right)^3\frac{(-1)^j}{2^l(l+2)!C_j(l)}$	$\alpha^3\frac{(-1)^j2^{l+2j+3}(l+j+1)!}{(l+1)!!(l-1)!!C_j(l)}q^\dagger$

* $q=(2/\pi)^{1/2}$, l even; $q=1$, l odd.
† $q=1/\pi$, l even; $q=1/2$, l odd.

Table 2. *Expressions for the atomic scattering factor functions for the four sets of orthogonal functions mentioned in the text*

Corresponding expressions for the exponential functions are given for completeness.

	Exponentials	H-atom wavefunction	Harmonic-oscillator wavefunction	Laguerre	Lorentzian
j	$n-l$	$n-l-1$	$\frac{1}{2}(n-l)$	$n-l$	$n-l-1$
x	$2\pi S/\alpha$	$4\pi nS/\alpha$	$2\pi S/\alpha$	$4\pi S/\alpha$	$2\pi S/\alpha$
$g_{nl}(x)$	$1/(1+x^2)^{l+j+2}$	$1/(1+x^2)^{l+j+2}$	$\exp(-\frac{1}{2}x^2)$	$1/(1+x^2)^{l+j+2}$	$\exp(-x)$
$G(x)$	x^2	x^2	x^2	x^2	x
a^j_k	$\frac{(j+1)}{2^k(j+1-2k)!(2l+2k+1)!!k!}$ *	$\frac{(2l+2j+1)!!}{(2l+2j+1-2k)!!(2l+2k+1)!!(j-k)!k!}$ †	$\frac{2^k(2l+2j+1)!!}{(2l+2k+1)!!(j-k)!k!}$	$\frac{(2l+2j+3)!!}{(2l+2j+3-2k)!!(2l+2k+1)!!(j-k)!k!}$	$\frac{2^k(2l+j+2)!}{(2l+k+2)!(j-k)!k!}$
N_{nl}	$\frac{(2l+j+2)!}{(l+j+2)!}$	$\frac{2(l+j+1)(2l+j+1)!}{(l+2)!C_j(l)}$	$\frac{1}{(l+1)!!C_j(l)}q^\dagger$	$\frac{(2l+j+2)!}{(l+2)!C_j(l)}$	$\frac{1}{(l+1)!!(l-1)!!C_j(l)}q^\ddagger$
$z(x)$	$2+j-(l+j+2)\frac{1-x^2}{1+x^2}$	$2+j-(l+j+2)\frac{1-x^2}{1+x^2}$	$-l+x^2$	$2+j-(l+j+2)\frac{1-x^2}{1+x^2}$	$-l+x$

* $a^j_k=0$ for $k\geq(j+3)/2$.
† $a^j_k=a^j_{j-k}$.
‡ $q=1$, l even; $q=(\pi/2)^{1/2}$, l odd.
§ $q=2$, l even; $q=\pi$, l odd.

Table 3. *Functions $C_j(l)$ appearing in the normalization constants N_{nl}*

j	H-atom wavefunction	Harmonic-oscillator wavefunction	Laguerre	Lorentzian
0	1	1	1	2
1	4	3	3	6
2	$l+9$	$\frac{1}{2}(4l+15)$	$l+6$	$2(l+6)$
3	$4(l+4)$	$\frac{1}{2}(12l+35)$	$3l+10$	$2(3l+10)$
4	$\frac{1}{2}[(l+9)(l+10)-40]$	$\frac{1}{8}[(4l+15)(4l+23)-30]$	$\frac{1}{2}[(l+6)(l+7)-12]$	$(l+3)(l+10)$
5	$2[(l+4)(l+5)-2]$	$\frac{1}{24}[(12l+35)(12l+59)+14]$	$\frac{1}{6}[(3l+10)(3l+13)-4]$	$(l+3)(3l+14)$

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