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the screening of the nuclear charge by the electrons and therefore affects the radial dependence of the atomic electron distribution (Coulson, 1961). A change in radial dependence of the density may also occur in a purely covalent bond, as, for example, in the H_2 molecule (Ruedenberg, 1962). It can be expressed as

$$\rho'_{\text{valence}}(r) = \kappa^3 \rho_{\text{valence}}(\kappa r) \qquad (1.2.6.1)$$

(Coppens *et al.*, 1979), where ρ' is the modified density and κ is an expansion/contraction parameter, which is > 1 for valence-shell contraction and < 1 for expansion. The κ^3 factor results from the normalization requirement.

The valence density is usually defined as the outer electron shell from which charge transfer occurs. The inner or core electrons are much less affected by the change in occupancy of the outer shell and, in a reasonable approximation, retain their radial dependence.

The corresponding structure-factor expression is

$$F(\mathbf{H}) = \sum_j [\{P_{j,\,\text{core}} f_{j,\,\text{core}}(H) + P_{j,\,\text{valence}} f_{j,\,\text{valence}}(H/\kappa)\}$$
$$\times \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j)], \qquad (1.2.6.2)$$

where $P_{j,\,\text{core}}$ and $P_{j,\,\text{valence}}$ are the number of electrons (not necessarily integral) in the core and valence shell, respectively, and the atomic scattering factors $f_{j,\,\text{core}}$ and $f_{j,\,\text{valence}}$ are normalized to one electron. Here and in the following sections, the resonant-scattering contributions are incorporated in the core scattering.

1.2.7. Beyond the spherical-atom description: the atom-centred spherical harmonic expansion

1.2.7.1. Direct-space description of aspherical atoms

Even though the spherical-atom approximation is often adequate, atoms in a crystal are in a nonspherical environment; therefore, an accurate description of the atomic electron density requires nonspherical density functions. In general, such density functions can be written in terms of the three polar coordinates r, θ and φ. Under the assumption that the radial and angular parts can be separated, one obtains for the density function:

$$\Phi(r, \theta, \varphi) = R(r)\Theta(\theta, \varphi). \qquad (1.2.7.1)$$

The angular functions Θ are based on the spherical harmonic functions Y_{lm} defined by

$$Y_{lm}(\theta, \varphi) = (-1)^m \left[\left(\frac{2l+1}{4\pi} \right) \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^m(\cos\theta) \exp(im\varphi),$$
$$(1.2.7.2a)$$

with $-l \le m \le l$, where $P_l^m(\cos\theta)$ are the associated Legendre polynomials (see Arfken, 1970).

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

$$P_l(x) = \frac{1}{l!2^l} \frac{d^l}{dx^l}\left[(x^2-1)^l\right].$$

The real spherical harmonic functions y_{lmp}, $0 \le m \le l$, $p = +$ or $-$ are obtained as a linear combination of Y_{lm}:

$$y_{lm+}(\theta, \psi) = \left[\frac{(2l+1)(l-|m|)!}{2\pi(1+\delta_{m0})(l+|m|)!} \right]^{1/2} P_l^m(\cos\theta) \cos m\varphi$$
$$= N_{lm} P_l^m(\cos\theta) \cos m\varphi$$
$$= (-1)^m (Y_{lm} + Y_{l,-m}) \qquad (1.2.7.2b)$$

and

$$y_{lm-}(\theta, \psi) = N_{lm} P_l^m(\cos\theta) \sin m\varphi$$
$$= (-1)^m (Y_{lm} - Y_{l,-m})/(2i). \qquad (1.2.7.2c)$$

The normalization constants N_{lm} are defined by the conditions

$$\int y_{lmp}^2 \, d\Omega = 1, \qquad (1.2.7.3a)$$

which are appropriate for normalization of wavefunctions. An alternative definition is used for charge-density basis functions:

$$\int |d_{lmp}| \, d\Omega = 2 \text{ for } l > 0 \text{ and } \int |d_{lmp}| \, d\Omega = 1 \text{ for } l = 0.$$
$$(1.2.7.3b)$$

The functions y_{lmp} and d_{lmp} differ only in the normalization constants. For the spherically symmetric function d_{00}, a population parameter equal to one corresponds to the function being populated by one electron. For the nonspherical functions with $l > 0$, a population parameter equal to one implies that one electron has shifted from the negative to the positive lobes of the function.
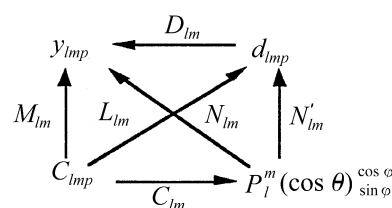
The functions y_{lmp} and d_{lmp} can be expressed in Cartesian coordinates, such that

$$y_{lmp} = M_{lm} c_{lmp} \qquad (1.2.7.4a)$$

and

$$d_{lmp} = L_{lm} c_{lmp}, \qquad (1.2.7.4b)$$

where the c_{lmp} are Cartesian functions. The relations between the various definitions of the real spherical harmonic functions are summarized by

in which the direction of the arrows and the corresponding conversion factors X_{lm} define expressions of the type (1.2.7.4). The expressions for c_{lmp} with $l \le 4$ are listed in Table 1.2.7.1, together with the normalization factors M_{lm} and L_{lm}.

The spherical harmonic functions are mutually orthogonal and form a complete set, which, if taken to sufficiently high order, can be used to describe any arbitrary angular function.

The spherical harmonic functions are often referred to as multipoles since each represents the components of the charge distribution $\rho(\mathbf{r})$, which gives nonzero contribution to the integral $\Theta_{lmp} = \int \rho(\mathbf{r}) c_{lmp} r^l \, d\mathbf{r}$, where Θ_{lmp} is an electrostatic multipole moment. Terms with increasing l are referred to as *monopolar* $(l = 0)$, *dipolar* $(l = 1)$, *quadrupolar* $(l = 2)$, *octapolar* $(l = 3)$, *hexadecapolar* $(l = 4)$, *triacontadipolar* $(l = 5)$ and *hexaconta-tetrapolar* $(l = 6)$.

Site-symmetry restrictions for the real spherical harmonics as given by Kara & Kurki-Suonio (1981) are summarized in Table 1.2.7.2.

In cubic space groups, the spherical harmonic functions as defined by equations (1.2.7.2) are no longer linearly independent. The appropriate basis set for this symmetry consists of the '*Kubic harmonics*' of Von der Lage & Bethe (1947). Some low-order terms are listed in Table 1.2.7.3. Both wavefunction and density-function normalization factors are specified in Table 1.2.7.3.

A related basis set of angular functions has been proposed by Hirshfeld (1977). They are of the form $\cos^n \theta_k$, where θ_k is the angle with a specified set of $(n+1)(n+2)/2$ polar axes. The Hirshfeld functions are identical to a sum of spherical harmonics

Table 1.2.7.1. *Real spherical harmonic functions (x, y, z are direction cosines)*

l	Symbol	C†	Angular function, c_{lmp}‡	Normalization for wavefunctions, M_{lmp}§		Normalization for density functions, L_{lmp}¶	
				Expression	Numerical value	Expression	Numerical value
0	00	1	1	$(1/4\pi)^{1/2}$	0.28209	$1/4\pi$	0.07958
1	11+	1	x	$(3/4\pi)^{1/2}$	0.48860	$1/\pi$	0.31831
	11−	1	y				
	10	1	z				
2	20	1/2	$3z^2 - 1$	$(5/16\pi)^{1/2}$	0.31539	$\dfrac{3\sqrt{3}}{8\pi}$	0.20675
	21+	3	xz	$(15/4\pi)^{1/2}$	1.09255	3/4	0.75
	21−	3	yz				
	22+	6	$(x^2 - y^2)/2$				
	22−	6	xy				
3	30	1/2	$5z^3 - 3z$	$(7/16\pi)^{1/2}$	0.37318	$\dfrac{10}{13\pi}$	0.24485
	31+	3/2	$x[5z^2 - 1]$	$(21/32\pi)^{1/2}$	0.45705	$[ar + (14/5) - (\pi/4)]^{-1}$††	0.32033
	31−	3/2	$y[5z^2 - 1]$				
	32+	15	$(x^2 - y^2)z$	$(105/16\pi)^{1/2}$	1.44531	1	1
	32−	15	$2xyz$				
	33+	15	$x^3 - 3xy^2$	$(35/32\pi)^{1/2}$	0.59004	$4/3\pi$	0.42441
	33−	15	$-y^3 + 3x^2y$				
4	40	1/8	$35z^4 - 30z^2 + 3$	$(9/256\pi)^{1/2}$	0.10579	‡‡	0.06942
	41+	5/2	$x[7z^3 - 3z]$	$(45/32\pi)^{1/2}$	0.66905	$\dfrac{735}{512\sqrt{7} + 196}$	0.47400
	41−	5/2	$y[7z^3 - 3z]$				
	42+	15/2	$(x^2 - y^2)[7z^2 - 1]$	$(45/64\pi)^{1/2}$	0.47309	$\dfrac{105\sqrt{7}}{4(136 + 28\sqrt{7})}$	0.33059
	42−	15/2	$2xy[7z^2 - 1]$				
	43+	105	$(x^3 - 3xy^2)z$	$(315/32\pi)^{1/2}$	1.77013	5/4	1.25
	43−	105	$(-y^3 + 3x^2y)z$				
	44+	105	$x^4 - 6x^2y^2 + y^4$	$(315/256\pi)^{1/2}$	0.62584	15/32	0.46875
	44−	105	$4x^3y - 4xy^3$				
5	50	1/8	$63z^5 - 70z^3 - 15z$	$(11/256\pi)^{1/2}$	0.11695	—	0.07674
	51+	15/8	$(21z^4 - 14z^2 + 1)x$	$(165/256\pi)^{1/2}$	0.45295	—	0.32298
	51−		$(21z^4 - 14z^2 + 1)y$				
	52+	105/2	$(3z^3 - z)(x^2 - y^2)$	$(1155/64\pi)^{1/2}$	2.39677	—	1.68750
	52−		$2xy(3z^3 - z)$				
	53+	105/2	$(9z^2 - 1)(x^3 - 3xy^2)$	$(385/512\pi)^{1/2}$	0.48924	—	0.34515
	53−		$(9z^2 - 1)(3x^2y - y^3)$				
	54+	945	$z(x^4 - 6x^2y^2 + y^4)$	$(3465/256\pi)^{1/2}$	2.07566	—	1.50000
	54−		$z(4x^3y - 4xy^3)$				
	55+	945	$x^5 - 10x^3y^2 + 5xy^4$	$(693/512\pi)^{1/2}$	0.65638	—	0.50930
	55−		$5x^4y - 10x^2y^3 + y^5$				

with $l = n, n - 2, n - 4, \ldots (0, 1)$ for $n > 1$, as shown elsewhere (Hirshfeld, 1977).

The radial functions $R(r)$ can be selected in different manners. Several choices may be made, such as

$$R_l(r) = \frac{\zeta^{n_l+3}}{(n_l + 2)!} r^{n(l)} \exp(-\zeta_l r) \qquad \text{(Slater type function)},$$

$$(1.2.7.5a)$$

where the coefficient n_l may be selected by examination of products of hydrogenic orbitals which give rise to a particular

multipole (Hansen & Coppens, 1978). Values for the exponential coefficient ζ_l may be taken from energy-optimized coefficients for isolated atoms available in the literature (Clementi & Raimondi, 1963). A standard set has been proposed by Hehre *et al.* (1969). In the bonded atom, such values are affected by changes in nuclear screening due to migrations of charge, as described in part by equation (1.2.6.1).

Other alternatives are:

$$R_l(r) = \frac{\alpha'^{n+1}}{n!} r^n \exp(-\alpha r^2) \qquad \text{(Gaussian function)} \quad (1.2.7.5b)$$

Table 1.2.7.1 (*cont.*)

l	Symbol	C†	Angular function, c_{lmp}‡	Normalization for wavefunctions, M_{lmp}§		Normalization for density functions, L_{lmp}¶	
				Expression	Numerical value	Expression	Numerical value
6	60	1/16	$231z^6 - 315z^4 + 105z^2 - 5$	$(13/1024\pi)^{1/2}$	0.06357	—	0.04171
	61+ 61−	21/8	$(33z^5 - 30z^3 + 5z)x$ $(33z^5 - 30z^3 + 5z)y$	$(273/256\pi)^{1/2}$	0.58262	—	0.41721
	62+ 62−	105/8	$(33z^4 - 18z^2 + 1)(x^2 - y^2)$ $2xy(33z^4 - 18z^2 + 1)$	$(1365/2048\pi)^{1/2}$	0.46060	—	0.32611
	63+ 63−	315/2	$(11z^3 - 3z)(x^3 - 3xy^2)$ $(11z^3 - 3z)(3x^2y - 3y)$	$(1365/512\pi)^{1/2}$	0.92121	—	0.65132
	64+ 64−	945/2	$(11z^2 - 1)(x^4 - 6x^2y^2 + y^4)$ $(11z^2 - 1)(4x^3y - 4xy^3)$	$(819/1024\pi)^{1/2}$	0.50457	—	0.36104
	65+ 65−	10395	$z(x^5 - 10x^3y^2 + 5xy^4)$ $z(5x^4y - 10x^2y^3 + y^5)$	$(9009/512\pi)^{1/2}$	2.36662	—	1.75000
	66+ 66−	10395	$x^6 - 15x^4y^2 + 15x^2y^4 - y^6$ $6x^5y - 20x^3y^3 + 6xy^5$	$(3003/2048\pi)^{1/2}$	0.68318	—	0.54687
7	70	1/16	$429z^7 - 693z^5 + 315z^3 - 35z$	$(15/1024\pi)^{1/2}$	0.06828	—	0.04480
	71+ 71−	7/16	$(429z^6 - 495z^4 + 135z^2 - 5)x$ $(429z^6 - 495z^4 + 135z^2 - 5)y$	$(105/4096\pi)^{1/2}$	0.09033	—	0.06488
	72+ 72−	63/8	$(143z^5 - 110z^3 + 15z)(x^2 - y^2)$ $2xy(143z^5 - 110z^3 + 15z)$	$(315/2048\pi)^{1/2}$	0.22127	—	0.15732
	73+ 73−	315/8	$(143z^4 - 66z^2 + 3)(x^3 - 3xy^2)$ $(143z^4 - 66z^2 + 3)(3x^2y - y^3)$	$(315/4096\pi)^{1/2}$	0.15646	—	0.11092
	74+ 74−	3465/2	$(13z^3 - 3z)(x^4 - 6x^2y^2 + y^4)$ $(13z^3 - 3z)(4x^3y - 4xy^3)$	$(3465/1024\pi)^{1/2}$	1.03783	—	0.74044
	75+ 75−	10395/2	$(13z^3 - 1)(x^5 - 10x^3y^2 + 5xy^4)$ $(13z^3 - 1)(5x^4y - 10x^2y^3 + y^5)$	$(3465/4096\pi)^{1/2}$	0.51892	—	0.37723
	76+ 76−	135135	$z(x^6 - 15x^4y^2 + 15x^2y^4 - y^6)$ $z(6x^5y + 20x^3y^3 - 6xy^5)$	$(45045/2048\pi)^{1/2}$	2.6460	—	2.00000
	77+ 77−	135135	$x^7 - 21x^5y^2 + 35x^3y^4 - 7xy^6$ $7x^6y - 35x^4y^3 + 21x^2y^5 - y^7$	$(6435/4096\pi)^{1/2}$	0.70716	—	0.58205

† Common factor such that $C_{lm}c_{lmp} = P_l^m(\cos\theta)^{\cos m\varphi}_{\sin m\varphi}$. ‡ $x = \sin\theta\cos\varphi$, $y = \sin\theta\sin\varphi$, $z = \cos\theta$. § As defined by $y_{lmp} = M_{lmp}c_{lmp}$ where c_{lmp} are Cartesian functions. ¶ Paturle & Coppens (1988), as defined by $d_{lmp} = L_{lmp}c_{lmp}$ where c_{lmp} are Cartesian functions. †† ar = arctan (2). ‡‡ $N_{\mathrm{ang}} = \{(14A_-^2 - 14A_+^5 + 20A_+^4 - 20A_-^3 + 6A_- - 6A_+)2\pi\}^{-1}$ where $A_\pm = [(30 \pm \sqrt{480})/70]^{1/2}$.

or

$$R_l(r) = r^l L_n^{2l+2}(\gamma r) \exp\left(-\frac{\gamma r}{2}\right) \quad \text{(Laguerre function)},$$

(1.2.7.5c)

where L is a Laguerre polynomial of order n and degree $(2l + 2)$.

In summary, in the multipole formalism the atomic density is described by

$$\rho_{\mathrm{atomic}}(\mathbf{r}) = P_c \rho_{\mathrm{core}} + P_v \kappa^3 \rho_{\mathrm{valence}}(\kappa r)$$
$$+ \sum_{l=0}^{l_{\mathrm{max}}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{l} \sum_p P_{lmp} d_{lmp}(\mathbf{r}/r),$$

(1.2.7.6)

in which the leading terms are those of the kappa formalism [expressions (1.2.6.1), (1.2.6.2)]; the subscript p is either + or −.

The expansion in (1.2.7.6) is frequently truncated at the hexadecapolar ($l = 4$) level. For atoms at positions of high site symmetry the first allowed functions may occur at higher l values.

For trigonally bonded atoms in organic molecules the $l = 3$ terms are often found to be the most significantly populated deformation functions.

1.2.7.2. Reciprocal-space description of aspherical atoms

The aspherical-atom form factor is obtained by substitution of (1.2.7.6) in expression (1.2.4.3a):

$$f_j(\mathbf{S}) = \int \rho_j(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r}.$$

(1.2.4.3a)

In order to evaluate the integral, the scattering operator $\exp(2\pi i \mathbf{S} \cdot \mathbf{r})$ must be written as an expansion of products of spherical harmonic functions. In terms of the complex spherical harmonic functions, the appropriate expression is (Weiss & Freeman, 1959; Cohen-Tannoudji et al., 1977)

$$\exp(2\pi i \mathbf{S} \cdot \mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(2\pi S r) Y_{lm}(\theta, \varphi) Y_{lm}^*(\beta, \gamma).$$

(1.2.7.7a)

Table 1.2.7.2. *Index-picking rules of site-symmetric spherical harmonics (Kara & Kurki-Suonio, 1981)*

λ, μ and j are integers.

Symmetry	Choice of coordinate axes	Indices of allowed y_{lmp}, d_{lmp}
1	Any	All $(l, m, \pm)$
$\bar{1}$	Any	$(2\lambda, m, \pm)$
2	$2\|z$	$(l, 2\mu, \pm)$
m	$m \perp z$	$(l, l - 2j, \pm)$
$2/m$	$2\|z, m \perp z$	$(2\lambda, 2\mu, \pm)$
222	$2\|z, 2\|y$	$(2\lambda, 2\mu, +), (2\lambda + 1, 2\mu, -)$
$mm2$	$2\|z, m \perp y$	$(l, 2\mu, +)$
mmm	$m \perp z, m \perp y, m \perp x$	$(2\lambda, 2\mu, +)$
4	$4\|z$	$(l, 4\mu, \pm)$
$\bar{4}$	$\bar{4}\|z$	$(2\lambda, 4\mu, \pm), (2\lambda + 1, 4\mu + 2, \pm)$
$4/m$	$4\|z, m \perp z$	$(2\lambda, 4\mu, \pm)$
422	$4\|z, 2\|y$	$(2\lambda, 4\mu, +), (2\lambda + 1, 4\mu, -)$
$4mm$	$4\|z, m \perp y$	$(l, 4\mu, +)$
$\bar{4}2m$	$\bar{4}\|z, 2\|x$	$(2\lambda, 4\mu, +), (2\lambda + 1, 4\mu + 2, -)$
	$m \perp y$	$(2\lambda, 4\mu, +), (2\lambda + 1, 4\mu + 2, +)$
$4/mmm$	$4\|z, m \perp z, m \perp x$	$(2\lambda, 4\mu, +)$
3	$3\|z$	$(l, 3\mu, \pm)$
$\bar{3}$	$\bar{3}\|z$	$(2\lambda, 3\mu, \pm)$
32	$3\|z, 2\|y$	$(2\lambda, 3\mu, +), (2\lambda + 1, 3\mu, -)$
	$2\|x$	$(3\mu + 2j, 3\mu, +),$
		$(3\mu + 2j + 1, 3\mu, -)$
$3m$	$3\|z, m \perp y$	$(l, 3\mu, +)$
	$m \perp x$	$(l, 6\mu, +), (l, 6\mu + 3, -)$
$\bar{3}m$	$\bar{3}\|z, m \perp y$	$(2\lambda, 3\mu, +)$
	$m \perp x$	$(2\lambda, 6\mu, +), (2\lambda, 6\mu + 3, -)$
6	$6\|z$	$(l, 6\mu, \pm)$
$\bar{6}$	$\bar{6}\|z$	$(2\lambda, 6\mu, \pm), (2\lambda + 1, 6\mu + 3, \pm)$
$6/m$	$6\|z, m \perp z$	$(2\lambda, 6\mu, \pm)$
622	$6\|z, 2\|y$	$(2\lambda, 6\mu, +), (2\lambda + 1, 6\mu, -)$
$6mm$	$6\|z, m\|y$	$(l, 6\mu, +)$
$\bar{6}m2$	$\bar{6}\|z, m \perp y$	$(2\lambda, 6\mu, +), (2\lambda + 1, 6\mu + 3, +)$
	$m \perp x$	$(2\lambda, 6\mu, +), (2\lambda + 1, 6\mu + 3, -)$
$6/mmm$	$6\|z, m \perp z, m \perp y$	$(2\lambda, 6\mu, +)$

The Fourier transform of the product of a complex spherical harmonic function with normalization $\int |Y_{lm}|^2 \, d\Omega = 1$ and an arbitrary radial function $R_l(r)$ follows from the orthonormality properties of the spherical harmonic functions, and is given by

$$\int Y_{lm} R_l(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\tau = 4\pi i^l \int j_l(2\pi Sr) R_l(r) r^2 \, dr Y_{lm}(\beta, \gamma),$$
(1.2.7.8a)

where j_l is the lth-order spherical Bessel function (Arfken, 1970), and θ and φ, β and γ are the angular coordinates of $\mathbf{r}$ and $\mathbf{S}$, respectively.

For the Fourier transform of the real spherical harmonic functions, the scattering operator is expressed in terms of the real spherical harmonics:

$$\exp(2\pi i \mathbf{S} \cdot \mathbf{r}) = \sum_{l=0}^{\infty} i^l j_l(2\pi Sr)(2 - \delta_{m0})(2l + 1) \sum_{m=0}^{l} \frac{(l - m)!}{(l + m)!}$$
$$\times P_l^m(\cos \theta) P_l^m(\cos \beta) \cos[m(\phi - \gamma)], \quad (1.2.7.7b)$$

which leads to

$$\int y_{lmp}(\theta, \varphi) R_l(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\tau = 4\pi i^l \langle j_l \rangle y_{lmp}(\beta, \gamma). \quad (1.2.7.8b)$$

Since y_{lmp} occurs on both sides, the expression is independent of the normalization selected. Therefore, for the Fourier transform of the density functions d_{lmp}

$$\int d_{lmp}(\theta, \varphi) R_l(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\tau = 4\pi i^l \langle j_l \rangle d_{lmp}(\beta, \gamma). \quad (1.2.7.8c)$$

In (1.2.7.8b) and (1.2.7.8c), $\langle j_l \rangle$, the *Fourier–Bessel transform*, is the radial integral defined as

$$\langle j_l \rangle = \int j_l(2\pi Sr) R_l(r) r^2 \, dr \quad (1.2.7.9)$$

of which $\langle j_0 \rangle$ in expression (1.2.4.3) is a special case. The functions $\langle j_l \rangle$ for Hartree–Fock valence shells of the atoms are tabulated in scattering-factor tables (*IT* IV, 1974). Expressions for the evaluation of $\langle j_l \rangle$ using the radial function (1.2.7.5a–c) have been given by Stewart (1980) and in closed form for (1.2.7.5a) by Avery & Watson (1977) and Su & Coppens (1990). The closed-form expressions are listed in Table 1.2.7.4.

Expressions (1.2.7.8) show that the Fourier transform of a direct-space spherical harmonic function is a reciprocal-space spherical harmonic function with the same l, m, or, in other words, the spherical harmonic functions are Fourier-transform invariant.

The scattering factors $f_{lmp}(\mathbf{S})$ of the aspherical density functions $R_l(r) d_{lmp}(\theta, \phi)$ in the multipole expansion (1.2.7.6) are thus given by

$$f_{lmp}(\mathbf{S}) = 4\pi i^l \langle j_l \rangle d_{lmp}(\beta, \gamma). \quad (1.2.7.8d)$$

The reciprocal-space spherical harmonic functions in this expression are identical to the functions given in Table 1.2.7.1, except for the replacement of the direction cosines x, y and z by the direction cosines of the scattering vector $\mathbf{S}$.

1.2.8. Fourier transform of orbital products

If the wavefunction is written as a sum over normalized Slater determinants, each representing an antisymmetrized combination of occupied molecular orbitals χ_i expressed as linear combinations of atomic orbitals φ_ν, i.e. $\chi_i = \sum_\nu c_{i\nu} \varphi_\nu$, the electron density is given by (Stewart, 1969a)

$$\rho(\mathbf{r}) = \sum_i n_i \chi_i^2 = \sum_\mu \sum_\nu P_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r}), \quad (1.2.8.1)$$

with $n_i = 1$ or 2. The coefficients $P_{\mu\nu}$ are the populations of the orbital product density functions $\phi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r})$ and are given by

$$P_{\mu\nu} = \sum_i n_i c_{i\mu} c_{i\nu}. \quad (1.2.8.2)$$

For a multi-Slater determinant wavefunction the electron density is expressed in terms of the occupied natural spin orbitals, leading again to (1.2.8.2) but with noninteger values for the coefficients n_i.

The summation (1.2.8.1) consists of one- and two-centre terms for which φ_μ and φ_ν are centred on the same or on different nuclei, respectively. The latter represent the overlap density, which is only significant if $\varphi_\mu(\mathbf{r})$ and $\varphi_\nu(\mathbf{r})$ have an appreciable value in the same region of space.

1.2.8.1. One-centre orbital products

If the atomic basis consists of hydrogenic type s, p, d, f, ... orbitals, the basis functions may be written as

$$\varphi(r, \theta, \varphi) = R_l(r) Y_{lm}(\theta, \varphi) \quad (1.2.8.3a)$$

or

$$\varphi(r, \theta, \varphi) = R_l(r) y_{lmp}(\theta, \varphi), \quad (1.2.8.3b)$$

which gives for corresponding values of the orbital products

$$\varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r}) = R_l(r) R_{l'}(r) Y_{lm}(\theta, \varphi) Y_{l'm'}(\theta, \varphi) \quad (1.2.8.4a)$$

and

$$\varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r}) = R_l(r) R_{l'}(r) y_{lmp}(\theta, \varphi) y_{l'm'p'}(\theta, \varphi), \quad (1.2.8.4b)$$

references