

1.2. The structure factor

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1.2.1. Introduction

The *structure factor* is the central concept in structure analysis by diffraction methods. Its modulus is called the *structure amplitude*. The structure amplitude is a function of the indices of the set of scattering planes h , k and l , and is defined as the amplitude of scattering by the contents of the crystallographic unit cell, expressed in units of scattering. For X-ray scattering, that unit is the scattering by a single electron (2.82×10^{-15} m), while for neutron scattering by atomic nuclei, the unit of scattering length of 10^{-14} m is commonly used. The complex form of the structure factor means that the phase of the scattered wave is not simply related to that of the incident wave. However, the observable, which is the scattered intensity, must be real. It is proportional to the square of the scattering amplitude (see, e.g., Lipson & Cochran, 1966).

The structure factor is directly related to the distribution of scattering matter in the unit cell which, in the X-ray case, is the electron distribution, time-averaged over the vibrational modes of the solid.

In this chapter we will discuss structure-factor expressions for X-ray and neutron scattering, and, in particular, the modelling that is required to obtain an analytical description in terms of the features of the electron distribution and the vibrational displacement parameters of individual atoms. We concentrate on the most basic developments; for further details the reader is referred to the cited literature.

1.2.2. General scattering expression for X-rays

The total scattering of X-rays contains both elastic and inelastic components. Within the first-order Born approximation (Born, 1926) it has been treated by several authors (e.g. Waller & Hartree, 1929; Feil, 1977) and is given by the expression

$$I_{\text{total}}(\mathbf{S}) = I_{\text{classical}} \sum_n \left| \int \psi_n^* \exp(2\pi i \mathbf{S} \cdot \mathbf{r}_j) \psi_0 \, d\mathbf{r} \right|^2, \quad (1.2.2.1)$$

where $I_{\text{classical}}$ is the classical Thomson scattering of an X-ray beam by a free electron, which is equal to $(e^2/mc^2)^2(1 + \cos^2 2\theta)/2$ for an unpolarized beam of unit intensity, ψ is the n -electron space-wavefunction expressed in the $3n$ coordinates of the electrons located at \mathbf{r}_j and the integration is over the coordinates of all electrons. \mathbf{S} is the scattering vector of length $2 \sin \theta/\lambda$.

The coherent elastic component of the scattering, in units of the scattering of a free electron, is given by

$$I_{\text{coherent, elastic}}(\mathbf{S}) = \left| \int \psi_0^* \sum_j \exp(2\pi i \mathbf{S} \cdot \mathbf{r}_j) \psi_0 \, d\mathbf{r} \right|^2. \quad (1.2.2.2)$$

If integration is performed over all coordinates but those of the j th electron, one obtains after summation over all electrons

$$I_{\text{coherent, elastic}}(\mathbf{S}) = \left| \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r} \right|^2, \quad (1.2.2.3)$$

where $\rho(\mathbf{r})$ is the electron distribution. The scattering amplitude $A(\mathbf{S})$ is then given by

$$A(\mathbf{S}) = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r} \quad (1.2.2.4a)$$

or

$$A(\mathbf{S}) = \hat{F}\{\rho(\mathbf{r})\}, \quad (1.2.2.4b)$$

where \hat{F} is the Fourier transform operator.

1.2.3. Scattering by a crystal: definition of a structure factor

In a crystal of infinite size, $\rho(\mathbf{r})$ is a three-dimensional periodic function, as expressed by the convolution

$$\rho_{\text{crystal}}(\mathbf{r}) = \sum_n \sum_m \sum_p \rho_{\text{unit cell}}(\mathbf{r}) * \delta(\mathbf{r} - n\mathbf{a} - m\mathbf{b} - p\mathbf{c}), \quad (1.2.3.1)$$

where n , m and p are integers, and δ is the Dirac delta function.

Thus, according to the Fourier convolution theorem,

$$A(\mathbf{S}) = \hat{F}\{\rho(\mathbf{r})\} = \sum_n \sum_m \sum_p \hat{F}\{\rho_{\text{unit cell}}(\mathbf{r})\} \hat{F}\{\delta(\mathbf{r} - n\mathbf{a} - m\mathbf{b} - p\mathbf{c})\}, \quad (1.2.3.2)$$

which gives

$$A(\mathbf{S}) = \hat{F}\{\rho_{\text{unit cell}}(\mathbf{r})\} \sum_h \sum_k \sum_l \delta(\mathbf{S} - h\mathbf{a}^* - k\mathbf{b}^* - l\mathbf{c}^*). \quad (1.2.3.3)$$

Expression (1.2.3.3) is valid for a crystal with a very large number of unit cells, in which particle-size broadening is negligible. Furthermore, it does not account for multiple scattering of the beam within the crystal. Because of the appearance of the delta function, (1.2.3.3) implies that $\mathbf{S} = \mathbf{H}$ with $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$.

The first factor in (1.2.3.3), the scattering amplitude of one unit cell, is defined as the structure factor F :

$$F(\mathbf{H}) = \hat{F}\{\rho_{\text{unit cell}}(\mathbf{r})\} = \int_{\text{unit cell}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r}. \quad (1.2.3.4)$$

1.2.4. The isolated-atom approximation in X-ray diffraction

To a reasonable approximation, the unit-cell density can be described as a superposition of isolated, spherical atoms located at \mathbf{r}_j .

$$\rho_{\text{unit cell}}(\mathbf{r}) = \sum_j \rho_{\text{atom}, j}(\mathbf{r}) * \delta(\mathbf{r} - \mathbf{r}_j). \quad (1.2.4.1)$$

Substitution in (1.2.3.4) gives

$$F(\mathbf{H}) = \sum_j \hat{F}\{\rho_{\text{atom}, j}\} \hat{F}\{\delta(\mathbf{r} - \mathbf{r}_j)\} = \sum_j f_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) \quad (1.2.4.2a)$$

or

$$\begin{aligned} F(h, k, l) &= \sum_j f_j \exp 2\pi i (hx_j + ky_j + lz_j) \\ &= \sum_j f_j \{ \cos 2\pi (hx_j + ky_j + lz_j) \\ &\quad + i \sin 2\pi (hx_j + ky_j + lz_j) \}. \end{aligned} \quad (1.2.4.2b)$$

$f_j(S)$, the spherical atomic scattering factor, or form factor, is the Fourier transform of the spherically averaged atomic density $\rho_j(r)$, in which the polar coordinate r is relative to the nuclear position. $f_j(S)$ can be written as (James, 1982)

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$$\begin{aligned}
 f_j(S) &= \int_{\text{atom}} \rho_j(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r} \\
 &= \int_{\nu=0}^{\pi} \int_{\varphi=0}^{2\pi} \int_{r=0}^{\infty} \rho_j(r) \exp(2\pi i S r \cos \vartheta) r^2 \sin \vartheta \, dr \, d\vartheta \, d\varphi \\
 &= \int_0^{\infty} 4\pi r^2 \rho_j(r) \frac{\sin 2\pi S r}{2\pi S r} \, dr \equiv \int_0^{\infty} 4\pi r^2 \rho_j(r) j_0(2\pi S r) \, dr \\
 &\equiv \langle j_0 \rangle,
 \end{aligned} \tag{1.2.4.3}$$

where $j_0(2\pi S r)$ is the zero-order spherical Bessel function.

$\rho_j(r)$ represents either the static or the dynamic density of atom j . In the former case, the effect of thermal motion, treated in Section 1.2.9 and following, is not included in the expression.

When scattering is treated in the second-order Born approximation, additional terms occur which are in particular of importance for X-ray wavelengths with energies close to absorption edges of atoms, where the participation of free and bound excited states in the scattering process becomes very important, leading to *resonance scattering*. [Resonance scattering is referred to as anomalous scattering in the older literature, but this misnomer is avoided in the current chapter.] Inclusion of such contributions leads to two extra terms, which are both wavelength- and scattering-angle-dependent:

$$f_j(S, \lambda) = f_j^0(S) + f_j'(S, \lambda) + i f_j''(S, \lambda). \tag{1.2.4.4}$$

The treatment of resonance effects is beyond the scope of this chapter. We note however (a) that to a reasonable approximation the S -dependence of f_j' and f_j'' can be neglected, (b) that f_j' and f_j'' are not independent, but related through the Kramers–Kronig transformation, and (c) that in an anisotropic environment the atomic scattering factor becomes anisotropic, and accordingly is described as a tensor property. Detailed descriptions and appropriate references can be found in Materlick *et al.* (1994) and in Section 4.2.6 of *IT C* (2004).

The structure-factor expressions (1.2.4.2) can be simplified when the crystal class contains nontrivial symmetry elements. For example, when the origin of the unit cell coincides with a centre of symmetry ($x, y, z \rightarrow -x, -y, -z$) the sine term in (1.2.4.2b) cancels when the contributions from the symmetry-related atoms are added, leading to the expression

$$F(\mathbf{H}) = 2 \sum_{j=1}^{N/2} f_j \cos 2\pi(hx_j + ky_j + lz_j), \tag{1.2.4.2c}$$

where the summation is over the unique half of the unit cell only.

Further simplifications occur when other symmetry elements are present. They are treated in Chapter 1.4, which also contains a complete list of symmetry-specific structure-factor expressions valid in the spherical-atom isotropic-temperature-factor approximation.

1.2.5. Scattering of thermal neutrons

1.2.5.1. Nuclear scattering

The scattering of neutrons by atomic nuclei is described by the atomic scattering length b , related to the total cross section σ_{total} by the expression $\sigma_{\text{total}} = 4\pi b^2$. At present, there is no theory of nuclear forces which allows calculation of the scattering length, so that experimental values are to be used. Two types of nuclei can be distinguished (Squires, 1978). In the first type, the scattering is a resonance phenomenon and is associated with the formation of a compound nucleus (consisting of the original nucleus plus a neutron) with an energy close to that of an excited state. In the second type, the compound nucleus is not near an

excited state and the scattering length is essentially real and independent of the energy of the incoming neutron. In either case, b is independent of the Bragg angle θ , unlike the X-ray form factor, since the nuclear dimensions are very small relative to the wavelength of thermal neutrons.

The scattering length is not the same for different isotopes of an element. A random distribution of isotopes over the sites occupied by that element leads to an incoherent contribution, such that effectively $\sigma_{\text{total}} = \sigma_{\text{coherent}} + \sigma_{\text{incoherent}}$. Similarly for nuclei with nonzero spin, a spin incoherent scattering occurs as the spin states are, in general, randomly distributed over the sites of the nuclei.

For free or loosely bound nuclei, the scattering length is modified by $b_{\text{free}} = [M/(m + M)]b$, where M is the mass of the nucleus and m is the mass of the neutron. This effect is of consequence only for the lightest elements. It can, in particular, be of significance for hydrogen atoms. With this in mind, the structure-factor expression for elastic scattering can be written as

$$F(\mathbf{H}) = \sum_j b_{j, \text{coherent}} \exp 2\pi i(hx_j + ky_j + lz_j) \tag{1.2.4.2d}$$

by analogy to (1.2.4.2b).

1.2.5.2. Magnetic scattering

The interaction between the magnetic moments of the neutron and the unpaired electrons in solids leads to magnetic scattering. The total elastic scattering including both the nuclear and magnetic contributions is given by

$$|F(\mathbf{H})|_{\text{total}}^2 = |F_N(\mathbf{H}) + \mathbf{Q}(\mathbf{H}) \cdot \hat{\lambda}|^2, \tag{1.2.5.1a}$$

where the unit vector $\hat{\lambda}$ describes the polarization vector for the neutron spin, $F_N(\mathbf{H})$ is given by (1.2.4.2b) and \mathbf{Q} is defined by

$$\mathbf{Q} = \frac{mc}{eh} \int \hat{\mathbf{H}} \times [\mathbf{M}(\mathbf{r}) \times \hat{\mathbf{H}}] \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r}. \tag{1.2.5.2a}$$

$\mathbf{M}(\mathbf{r})$ is the vector field describing the electron-magnetization distribution and $\hat{\mathbf{H}}$ is a unit vector parallel to \mathbf{H} .

\mathbf{Q} is thus proportional to the projection of \mathbf{M} onto a direction orthogonal to \mathbf{H} in the plane containing \mathbf{M} and \mathbf{H} . The magnitude of this projection depends on $\sin \alpha$, where α is the angle between \mathbf{Q} and \mathbf{H} , which prevents magnetic scattering from being a truly three-dimensional probe. If all moments $\mathbf{M}(\mathbf{r})$ are collinear, as may be achieved in paramagnetic materials by applying an external field, and for the maximum signal (\mathbf{H} orthogonal to \mathbf{M}), (1.2.5.2a) becomes

$$\mathbf{Q} = \mathbf{M}(\mathbf{H}) = \frac{mc}{eh} \int \mathbf{M}(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r} \tag{1.2.5.2b}$$

and (1.2.5.1a) gives

$$|F|_{\text{total}}^2 = |F_N(\mathbf{H}) - M(\mathbf{H})|^2 \tag{1.2.5.1b}$$

and

$$|F|_{\text{total}}^2 = |F_N(\mathbf{H}) + M(\mathbf{H})|^2$$

for neutrons parallel and antiparallel to $\mathbf{M}(\mathbf{H})$, respectively.

1.2.6. Effect of bonding on the atomic electron density within the spherical-atom approximation: the kappa formalism

A first improvement beyond the isolated-atom formalism is to allow for changes in the radial dependence of the atomic electron distribution.

Such changes may be due to electronegativity differences which lead to the transfer of electrons between the valence shells of different atoms. The electron transfer introduces a change in

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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 H₂ molecule (Ruedenberg, 1962). It can be expressed as

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

(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

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

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 apherical 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:

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

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

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

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

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

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

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

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

and

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

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

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

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

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

The functions y_{lm} and d_{lm} 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.

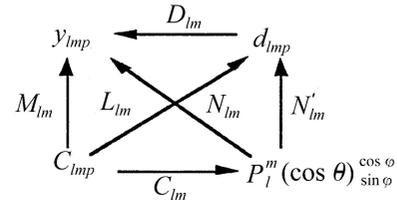
The functions y_{lm} and d_{lm} can be expressed in Cartesian coordinates, such that

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

and

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

where the c_{lm} 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_{lm} with $l \leq 4$ 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 $\Theta_{lm} = \int \rho(\mathbf{r}) c_{lm} r^l d\mathbf{r}$, where Θ_{lm} 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 *hexacontatetrapolar* ($l = 6$).

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

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

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

with $l = n, n - 2, n - 4, \dots (0, 1)$ 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

$$R_l(r) = \frac{\zeta^{n_l+3}}{(n_l + 2)!} r^{n(l)} \exp(-\zeta_l r) \quad (\text{Slater type function}), \quad (1.2.7.5a)$$

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:

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

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Table 1.2.7.1 (cont.)

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

† Common factor such that $C_{lm}c_{lmp} = P_l^m(\cos\theta) \frac{\cos m\varphi}{\sin m\varphi}$. ‡ $x = \sin\theta\cos\varphi$, $y = \sin\theta\sin\varphi$, $z = \cos\theta$. § 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. †† $\ar = \arctan(2)$. ‡‡ $N_{\text{ang}} = \{(14A_+^2 - 14A_-^2 + 20A_+^3 - 20A_-^3 + 6A_+ - 6A_-)2\pi\}^{-1}$ where $A_{\pm} = [(30 \pm \sqrt{480})/70]^{1/2}$.

or

$$R_l(r) = r^l L_n^{2l+2}(\gamma r) \exp\left(-\frac{\gamma r}{2}\right) \quad (\text{Laguerre function}), \quad (1.2.7.5c)$$

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

$$\rho_{\text{atomic}}(\mathbf{r}) = P_c \rho_{\text{core}} + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum_{l=0}^{l_{\text{max}}} \kappa^{l^3} R_l(\kappa' r) \sum_{m=0}^l \sum_p P_{lmp} d_{lmp}(\mathbf{r}/r), \quad (1.2.7.6)$$

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):

$$f_j(\mathbf{S}) = \int \rho_j(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r}. \quad (1.2.4.3a)$$

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)

$$\exp(2\pi i \mathbf{S} \cdot \mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l j_l(2\pi S r) Y_{lm}(\theta, \varphi) Y_{lm}^*(\beta, \gamma). \quad (1.2.7.7a)$$

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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

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

where j_l is the l th-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:

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

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

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

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 $\phi_{\mu\nu}(\mathbf{r}) \varphi_\nu(\mathbf{r})$ 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

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

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Table 1.2.7.3. 'Kubic harmonic' functions

(a) Coefficients in the expression $K_{ij} = \sum_{mp} k_{mpj}^l y_{lmp}$ with normalization $\int_0^\pi \int_0^{2\pi} |K_{ij}|^2 \sin \theta \, d\theta \, d\varphi = 1$ (Kara & Kurki-Suonio, 1981).

Even l		mp					
l	j	0+	2+	4+	6+	8+	10+
0	1	1					
4	1	$\frac{1}{2} \left(\frac{7}{3}\right)^{1/2}$ 0.76376		$\frac{1}{2} \left(\frac{5}{3}\right)^{1/2}$ 0.64550			
6	1	$\frac{1}{2} \left(\frac{11}{2}\right)^{1/2}$ 0.35355		$-\frac{1}{2} \left(\frac{7}{2}\right)^{1/2}$ -0.93541			
6	2		$\frac{1}{4} 11^{1/2}$ 0.82916		$-\frac{1}{4} 5^{1/2}$ -0.55902		
8	1	$\frac{1}{8} 33^{1/2}$ 0.71807		$\frac{1}{4} \left(\frac{7}{3}\right)^{1/2}$ 0.38188		$\frac{1}{8} \left(\frac{65}{3}\right)^{1/2}$ 0.58184	
10	1	$\frac{1}{8} \left(\frac{65}{6}\right)^{1/2}$ 0.41143		$-\frac{1}{4} \left(\frac{11}{2}\right)^{1/2}$ -0.58630		$-\frac{1}{8} \left(\frac{187}{6}\right)^{1/2}$ -0.69784	
10	2		$\frac{1}{8} \left(\frac{247}{6}\right)^{1/2}$ 0.80202		$\frac{1}{16} \left(\frac{19}{3}\right)^{1/2}$ 0.15729		$\frac{1}{16} 85^{1/2}$ 0.57622
l		j					
		2-		4-		8-	
3	1		1				
7	1		$\frac{1}{2} \left(\frac{13}{6}\right)^{1/2}$ 0.73598		$\frac{1}{2} \left(\frac{11}{16}\right)^{1/2}$ 0.41458		
9	1		$\frac{1}{4} 3^{1/2}$ 0.43301		$-\frac{1}{4} 13^{1/2}$ -0.90139		
9	2		$\frac{1}{2} \left(\frac{17}{6}\right)^{1/2}$ 0.84163		$-\frac{1}{2} \left(\frac{7}{6}\right)^{1/2}$ -0.54006		

(b) Coefficients k_{mpj}^l and density normalization factors N_{ij} in the expression $K_{ij} = N_{ij} \sum_{mp} k_{mpj}^l u_{lmp}$ where $u_{lm\pm} = P_l^m(\cos \theta)_{\sin m\varphi}^{\cos m\varphi}$ (Su & Coppens, 1994).

Even l		N_{ij}	mp					
l	j		0+	2+	4+	6+	8+	10+
0	1	$1/4\pi = 0.079577$	1					
4	1	0.43454	1		+1/168			
6	1	0.25220	1		-1/360			
6	2	0.020833		1		-1/792		
8	1	0.56292	1		1/5940		$\frac{1}{672} \times \frac{1}{5940}$	
10	1	0.36490	1		1/5460		$\frac{1}{4320} \times \frac{1}{5460}$	
10	2	0.0095165	1			1/43680		$-\frac{1}{456} \times \frac{1}{43680}$
l		j						
		2-		4-		8-		
3	1	0.066667		1				
7	1	0.014612		1		1/1560		
9	1	0.0059569		1		1/2520		
9	2	0.00014800			1		-1/4080	

(c) Density-normalized Kubic harmonics as linear combinations of density-normalized spherical harmonic functions. Coefficients in the expression $K_{ij} = \sum_{mp} k_{mpj}^l d_{lmp}$. Density-type normalization is defined as $\int_0^\pi \int_0^{2\pi} |K_{ij}|^2 \sin \theta \, d\theta \, d\varphi = 2 - \delta_{j0}$.

Even l		mp					
l	j	0+	2+	4+	6+	8+	10+
0	1	1					
4	1	0.78245		0.57939			
6	1	0.37790		-0.91682			
6	2		0.83848		-0.50000		
l		j					
		2-		4-		8-	
3	1	1					
7	1	0.73145		0.63290			

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Table 1.2.7.3 (cont.)

(d) Index rules for cubic symmetries (Kurki-Suonio, 1977; Kara & Kurki-Suonio, 1981).

l	j	23 T	$m\bar{3}$ T_h	432 O	$\bar{4}3m$ T_d	$m\bar{3}m$ O_h
0	1	×	×	×	×	×
3	1	×			×	
4	1	×	×	×	×	×
6	1	×	×	×	×	×
6	2	×	×			
7	1	×			×	
8	1	×	×	×	×	×
9	1	×			×	
9	2	×		×		
10	1	×	×	×	×	×
10	2	×	×			

respectively, where it has been assumed that the radial function depends only on l .

Because the spherical harmonic functions form a complete set, their products can be expressed as a linear combination of spherical harmonics. The coefficients in this expansion are the *Clebsch–Gordan coefficients* (Condon & Shortley, 1957), defined by

$$Y_{lm}(\theta, \varphi)Y_{l'm'}(\theta, \varphi) = \sum_L \sum_M C_{LL'}^{Mmm'} Y_{LM}(\theta, \varphi) \quad (1.2.8.5a)$$

or the equivalent definition

$$C_{LL'}^{Mmm'} = \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi Y_{LM}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) Y_{l'm'}(\theta, \varphi). \quad (1.2.8.5b)$$

The $C_{LL'}^{Mmm'}$ vanish, unless $L + l + l'$ is even, $|l - l'| < L < l + l'$ and $M = m + m'$.

The corresponding expression for y_{lmp} is

$$y_{lmp}(\theta, \varphi)y_{l'm'p'}(\theta, \varphi) = \sum_L \sum_M C'_{LL'}^{Mmm'} y_{LMP}(\theta, \varphi), \quad (1.2.8.5c)$$

with $M = |m + m'|$ and $|m - m'|$ for $p = p'$, and $M = -|m + m'|$ and $-|m - m'|$ for $p = -p'$ and $P = p \times p'$.

Values of C and C' for $l \leq 2$ are given in Tables 1.2.8.1 and 1.2.8.2. They are valid for the functions Y_{lm} and y_{lmp} with normalization $\int |Y_{lm}|^2 d\Omega = 1$ and $\int y_{lmp}^2 d\Omega = 1$.

By using (1.2.8.5a) or (1.2.8.5c), the one-centre orbital products are expressed as a sum of spherical harmonic functions. It follows that the one-centre orbital product density basis set is formally equivalent to the multipole description, both in real and in reciprocal space. To obtain the relation between orbital products and the charge-density functions, the right-hand side of (1.2.8.5c) has to be multiplied by the ratio of the normalization constants, as the wavefunctions y_{lmp} and charge-density functions d_{lmp} are normalized in a different way as described by (1.2.7.3a) and (1.2.7.3b). Thus

$$y_{lmp}(\theta, \varphi)y_{l'm'p'}(\theta, \varphi) = \sum_L \sum_M R_{LMP} C'_{LL'}^{Mmm'} d_{LMP}(\theta, \varphi), \quad (1.2.8.6)$$

where $R_{LMP} = M_{LMP}$ (wavefunction)/ L_{LMP} (density function). The normalization constants M_{lmp} and L_{lmp} are given in Table 1.2.7.1, while the coefficients in the expressions (1.2.8.6) are listed in Table 1.2.8.3.

1.2.8.2. Two-centre orbital products

Fourier transform of the electron density as described by (1.2.8.1) requires explicit expressions for the two-centre orbital product scattering. Such expressions are described in the literature for both Gaussian (Stewart, 1969b) and Slater-type (Bentley

& Stewart, 1973; Avery & Ørmen, 1979) atomic orbitals. The expressions can also be used for Hartree–Fock atomic functions, as expansions in terms of Gaussian- (Stewart, 1969b, 1970; Stewart & Hehre, 1970; Hehre *et al.*, 1970) and Slater-type (Clementi & Roetti, 1974) functions are available for many atoms.

1.2.9. The atomic temperature factor

Since the crystal is subject to vibrational oscillations, the observed elastic scattering intensity is an average over all normal modes of the crystal. Within the Born–Oppenheimer approximation, the theoretical electron density should be calculated for each set of nuclear coordinates. An average can be obtained by taking into account the statistical weight of each nuclear configuration, which may be expressed by the probability distribution function $P(\mathbf{u}_1, \dots, \mathbf{u}_N)$ for a set of displacement coordinates $\mathbf{u}_1, \dots, \mathbf{u}_N$.

In general, if $\rho(\mathbf{r}, \mathbf{u}_1, \dots, \mathbf{u}_N)$ is the electron density corresponding to the geometry defined by $\mathbf{u}_1, \dots, \mathbf{u}_N$, the time-averaged electron density is given by

$$\langle \rho(\mathbf{r}) \rangle = \int \rho(\mathbf{r}, \mathbf{u}_1, \dots, \mathbf{u}_N) P(\mathbf{u}_1, \dots, \mathbf{u}_N) d\mathbf{u}_1 \dots d\mathbf{u}_N. \quad (1.2.9.1)$$

When the crystal can be considered as consisting of perfectly following rigid entities, which may be molecules or atoms, expression (1.2.9.1) simplifies:

$$\langle \rho_{\text{rigid group}}(\mathbf{r}) \rangle = \int \rho_{\text{r.g., static}}(\mathbf{r} - \mathbf{u}) P(\mathbf{u}) d\mathbf{u} = \rho_{\text{r.g., static}} * P(\mathbf{u}). \quad (1.2.9.2)$$

In the approximation that the atomic electrons perfectly follow the nuclear motion, one obtains

$$\langle \rho_{\text{atom}}(\mathbf{r}) \rangle = \rho_{\text{atom, static}}(\mathbf{r}) * P(\mathbf{u}). \quad (1.2.9.3)$$

The Fourier transform of this convolution is the product of the Fourier transforms of the individual functions:

$$\langle f(\mathbf{H}) \rangle = f(\mathbf{H})T(\mathbf{H}). \quad (1.2.9.4)$$

Thus $T(\mathbf{H})$, the atomic temperature factor, is the Fourier transform of the probability distribution $P(\mathbf{u})$.

1.2.10. The vibrational probability distribution and its Fourier transform in the harmonic approximation

For a harmonic oscillator, the probability distribution averaged over all populated energy levels is a Gaussian, centred at the equilibrium position. For the three-dimensional isotropic harmonic oscillator, the distribution is

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Table 1.2.7.4. Closed-form expressions for Fourier transform of Slater-type functions (Avery & Watson, 1977; Su & Coppens, 1990)

$$\langle j_k \rangle \equiv \int_0^\infty r^N \exp(-Zr) j_k(Kr) dr, \quad K = 4\pi \sin \theta / \lambda.$$

k	N							
	1	2	3	4	5	6	7	8
0	$\frac{1}{K^2 + Z^2}$	$\frac{2Z}{(K^2 + Z^2)^2}$	$\frac{2(3Z^2 - K^2)}{(K^2 + Z^2)^3}$	$\frac{24Z(Z^2 - K^2)}{(K^2 + Z^2)^4}$	$\frac{24(5Z^2 - 10K^2Z^2 + K^4)}{(K^2 + Z^2)^5}$	$\frac{240Z(K^2 - 3Z^2)(3K^2 - Z^2)}{(K^2 + Z^2)^6}$	$\frac{720(7Z^6 - 35K^2Z^4 + 21K^4Z^2 - K^6)}{(K^2 + Z^2)^7}$	$\frac{40320(Z^7 - 7K^2Z^5 + 7K^4Z^3 - K^6Z)}{(K^2 + Z^2)^8}$
1		$\frac{2K}{(K^2 + Z^2)^2}$	$\frac{8KZ}{(K^2 + Z^2)^3}$	$\frac{8K(5Z^2 - K^2)}{(K^2 + Z^2)^4}$	$\frac{48KZ(5Z^2 - 3K^2)}{(K^2 + Z^2)^5}$	$\frac{48K(35Z^4 - 42K^2Z^2 + 3K^4)}{(K^2 + Z^2)^6}$	$\frac{1920KZ(7Z^4 - 14K^2Z^2 + 3K^4)}{(K^2 + Z^2)^7}$	$\frac{5760K(21Z^6 - 63K^2Z^4 + 27K^4Z^2 - K^6)}{(K^2 + Z^2)^8}$
2			$\frac{8K^2}{(K^2 + Z^2)^3}$	$\frac{48K^2Z}{(K^2 + Z^2)^4}$	$\frac{48K^2(7Z^2 - K^2)}{(K^2 + Z^2)^5}$	$\frac{384K^2Z(7Z^2 - 3K^2)}{(K^2 + Z^2)^6}$	$\frac{1152K^2(21Z^4 - 18K^2Z^2 + K^4)}{(K^2 + Z^2)^7}$	$\frac{11520K^2Z(21Z^4 - 30K^2Z^2 + 5K^4)}{(K^2 + Z^2)^8}$
3				$\frac{48K^3}{(K^2 + Z^2)^4}$	$\frac{384K^3Z}{(K^2 + Z^2)^5}$	$\frac{384K^3(9Z^2 - K^2)}{(K^2 + Z^2)^6}$	$\frac{11520K^3Z(3Z^2 - K^2)}{(K^2 + Z^2)^7}$	$\frac{11520K^3(33Z^4 - 22K^2Z^2 + K^4)}{(K^2 + Z^2)^8}$
4					$\frac{384K^4}{(K^2 + Z^2)^5}$	$\frac{3840K^4Z}{(K^2 + Z^2)^6}$	$\frac{3840K^4(11Z^2 - K^2)}{(K^2 + Z^2)^7}$	$\frac{46080K^4Z(11Z^2 - 3K^2)}{(K^2 + Z^2)^8}$
5						$\frac{3840K^5}{(K^2 + Z^2)^6}$	$\frac{46080K^5Z}{(K^2 + Z^2)^7}$	$\frac{40680K^5(13Z^2 - K^2)}{(K^2 + Z^2)^8}$
6							$\frac{46080K^6}{(K^2 + Z^2)^7}$	$\frac{645120K^6Z}{(K^2 + Z^2)^8}$
7								$\frac{645120K^7}{(K^2 + Z^2)^8}$

$$P(\mathbf{u}) = (2\pi \langle u^2 \rangle)^{-3/2} \exp\{-|\mathbf{u}|^2 / 2 \langle u^2 \rangle\}, \quad (1.2.10.1)$$

where $\langle u^2 \rangle$ is the mean-square displacement in any direction.

The corresponding trivariate normal distribution to be used for anisotropic harmonic motion is, in tensor notation,

$$P(\mathbf{u}) = \frac{|\sigma^{-1}|^{1/2}}{(2\pi)^{3/2}} \exp\{-\frac{1}{2} \sigma_{jk}^{-1} (u^j u^k)\}. \quad (1.2.10.2a)$$

Here σ is the variance-covariance matrix, with covariant components, and $|\sigma^{-1}|$ is the determinant of the inverse of σ . Summation over repeated indices has been assumed. The corresponding equation in matrix notation is

$$P(\mathbf{u}) = \frac{|\sigma^{-1}|^{1/2}}{(2\pi)^{3/2}} \exp\{-\frac{1}{2} (\mathbf{u})^T \sigma^{-1} (\mathbf{u})\}, \quad (1.2.10.2b)$$

where the superscript T indicates the transpose.

The characteristic function, or Fourier transform, of $P(\mathbf{u})$ is

$$T(\mathbf{H}) = \exp\{-2\pi^2 \sigma^{jk} h_j h_k\} \quad (1.2.10.3a)$$

or

$$T(\mathbf{H}) = \exp\{-2\pi^2 \mathbf{H}^T \sigma \mathbf{H}\}. \quad (1.2.10.3b)$$

With the change of variable $b^{jk} = 2\pi^2 \sigma^{jk}$, (1.2.10.3a) becomes

$$T(\mathbf{H}) = \exp\{-b^{jk} h_j h_k\}.$$

1.2.11. Rigid-body analysis

The treatment of rigid-body motion of molecules or molecular fragments was developed by Cruickshank (1956) and expanded into a general theory by Schomaker & Trueblood (1968). The theory has been described by Johnson (1970b) and by Dunitz (1979). The latter reference forms the basis for the following treatment.

The most general motions of a rigid body consist of rotations about three axes, coupled with translations parallel to each of the axes. Such motions correspond to screw rotations. A libration

around a vector λ ($\lambda_1, \lambda_2, \lambda_3$), with length corresponding to the magnitude of the rotation, results in a displacement $\delta \mathbf{r}$, such that

$$\delta \mathbf{r} = (\lambda \times \mathbf{r}) = \mathbf{D} \mathbf{r} \quad (1.2.11.1)$$

with

$$\mathbf{D} = \begin{bmatrix} 0 & -\lambda_3 & \lambda_2 \\ \lambda_3 & 0 & -\lambda_1 \\ -\lambda_2 & \lambda_1 & 0 \end{bmatrix}, \quad (1.2.11.2)$$

or in Cartesian tensor notation, assuming summation over repeated indices,

$$\delta r_i = D_{ij} r_j = -\varepsilon_{ijk} \lambda_k r_j \quad (1.2.11.3)$$

where the permutation operator ε_{ijk} equals +1 for i, j, k a cyclic permutation of the indices 1, 2, 3, or -1 for a noncyclic permutation, and zero if two or more indices are equal. For $i = 1$, for example, only the ε_{123} and ε_{132} terms occur. Addition of a translational displacement gives

$$\delta r_i = D_{ij} r_j + t_i. \quad (1.2.11.4)$$

When a rigid body undergoes vibrations the displacements vary with time, so suitable averages must be taken to derive the mean-square displacements. If the librational and translational motions are independent, the cross products between the two terms in (1.2.11.4) average to zero and the elements of the mean-square displacement tensor of atom n , U_{ij}^n , are given by

$$\begin{aligned} U_{11}^n &= +L_{22} r_3^2 + L_{33} r_2^2 - 2L_{23} r_2 r_3 + T_{11} \\ U_{22}^n &= +L_{33} r_1^2 + L_{11} r_3^2 - 2L_{13} r_1 r_3 + T_{22} \\ U_{33}^n &= +L_{11} r_2^2 + L_{22} r_1^2 - 2L_{12} r_1 r_2 + T_{33} \\ U_{12}^n &= -L_{33} r_1 r_2 - L_{12} r_3^2 + L_{13} r_2 r_3 + L_{23} r_1 r_3 + T_{12} \\ U_{13}^n &= -L_{22} r_1 r_3 + L_{12} r_2 r_3 - L_{13} r_2^2 + L_{23} r_1 r_2 + T_{13} \\ U_{23}^n &= -L_{11} r_2 r_3 + L_{12} r_1 r_3 - L_{13} r_1 r_2 - L_{23} r_1^2 + T_{23}, \end{aligned} \quad (1.2.11.5)$$

where the coefficients $L_{ij} = \langle \lambda_i \lambda_j \rangle$ and $T_{ij} = \langle t_i t_j \rangle$ are the elements of the 3×3 libration tensor \mathbf{L} and the 3×3 translation tensor \mathbf{T} , respectively. Since pairs of terms such as $\langle t_i t_j \rangle$ and $\langle t_j t_i \rangle$

1.2. THE STRUCTURE FACTOR

Table 1.2.8.1. *Products of complex spherical harmonics as defined by equation (1.2.7.2a)*

$Y_{00} Y_{00} = 0.28209479 Y_{00}$
$Y_{10} Y_{00} = 0.28209479 Y_{10}$
$Y_{10} Y_{10} = 0.25231325 Y_{20} + 0.28209479 Y_{00}$
$Y_{11} Y_{00} = 0.28209479 Y_{11}$
$Y_{11} Y_{10} = 0.21850969 Y_{21}$
$Y_{11} Y_{11} = 0.30901936 Y_{22}$
$Y_{11} Y_{11-} = -0.12615663 Y_{20} + 0.28209479 Y_{00}$
$Y_{20} Y_{00} = 0.28209479 Y_{20}$
$Y_{20} Y_{10} = 0.24776669 Y_{30} + 0.25231325 Y_{10}$
$Y_{20} Y_{11} = 0.20230066 Y_{31} - 0.12615663 Y_{11}$
$Y_{20} Y_{20} = 0.24179554 Y_{40} + 0.18022375 Y_{20} + 0.28209479 Y_{00}$
$Y_{21} Y_{00} = 0.28209479 Y_{21}$
$Y_{21} Y_{10} = 0.23359668 Y_{31} + 0.21850969 Y_{11}$
$Y_{21} Y_{11} = 0.26116903 Y_{32}$
$Y_{21} Y_{11-} = -0.14304817 Y_{30} + 0.21850969 Y_{10}$
$Y_{21} Y_{20} = 0.22072812 Y_{41} + 0.09011188 Y_{21}$
$Y_{21} Y_{21} = 0.25489487 Y_{42} + 0.22072812 Y_{22}$
$Y_{21} Y_{21-} = -0.16119702 Y_{40} + 0.09011188 Y_{20} + 0.28209479 Y_{00}$
$Y_{22} Y_{00} = 0.28209479 Y_{22}$
$Y_{22} Y_{10} = 0.18467439 Y_{32}$
$Y_{22} Y_{11} = 0.31986543 Y_{33}$
$Y_{22} Y_{11-} = -0.08258890 Y_{31} + 0.30901936 Y_{11}$
$Y_{22} Y_{20} = 0.15607835 Y_{42} - 0.18022375 Y_{22}$
$Y_{22} Y_{21} = 0.23841361 Y_{43}$
$Y_{22} Y_{21-} = -0.09011188 Y_{41} + 0.22072812 Y_{21}$
$Y_{22} Y_{22} = 0.33716777 Y_{44}$
$Y_{22} Y_{22-} = 0.04029926 Y_{40} - 0.18022375 Y_{20} + 0.28209479 Y_{00}$

Table 1.2.8.2. *Products of real spherical harmonics as defined by equations (1.2.7.2b) and (1.2.7.2c)*

$y_{00} y_{00} = 0.28209479 y_{00}$
$y_{10} y_{00} = 0.28209479 y_{10}$
$y_{10} y_{10} = 0.25231325 y_{20} + 0.28209479 y_{00}$
$y_{11\pm} y_{00} = 0.28209479 y_{11\pm}$
$y_{11\pm} y_{10} = 0.21850969 y_{21\pm}$
$y_{11\pm} y_{11\pm} = 0.21850969 y_{22\pm} - 0.12615663 y_{20} + 0.28209479 y_{00}$
$y_{11+} y_{11-} = 0.21850969 y_{22-}$
$y_{20} y_{00} = 0.28209479 y_{20}$
$y_{20} y_{10} = 0.24776669 y_{30} + 0.25231325 y_{10}$
$y_{20} y_{11\pm} = 0.20230066 y_{31\pm} - 0.12615663 y_{11\pm}$
$y_{20} y_{20} = 0.24179554 y_{40} + 0.18022375 y_{20} + 0.28209479 y_{00}$
$y_{21\pm} y_{00} = 0.28209479 y_{21\pm}$
$y_{21\pm} y_{10} = 0.23359668 y_{31\pm} + 0.21850969 y_{11\pm}$
$y_{21\pm} y_{11\pm} = \pm 0.18467439 y_{32\pm} - 0.14304817 y_{30} + 0.21850969 y_{10}$
$y_{21\pm} y_{11\mp} = 0.18467469 y_{32-}$
$y_{21\pm} y_{20} = 0.22072812 y_{41\pm} + 0.09011188 y_{21\pm}$
$y_{21\pm} y_{21\pm} = \pm 0.18022375 y_{42\pm} \pm 0.15607835 y_{22\pm} - 0.16119702 y_{40} + 0.09011188 y_{20} + 0.28209479 y_{00}$
$y_{21+} y_{21-} = -0.18022375 y_{42-} + 0.15607835 y_{22-}$
$y_{22\pm} y_{00} = 0.28209479 y_{22\pm}$
$y_{22\pm} y_{10} = 0.18467439 y_{32\pm}$
$y_{22\pm} y_{11\pm} = \pm 0.22617901 y_{33\pm} - 0.05839917 y_{31\pm} + 0.21850969 y_{11\pm}$
$y_{22\pm} y_{11\mp} = 0.22617901 y_{33-} \pm 0.05839917 y_{31-} \mp 0.21850969 y_{11-}$
$y_{22\pm} y_{20} = 0.15607835 y_{42\pm} - 0.18022375 y_{22\pm}$
$y_{22\pm} y_{21\pm} = \pm 0.16858388 y_{43\pm} - 0.06371872 y_{41\pm} + 0.15607835 y_{21\pm}$
$y_{22\pm} y_{21\mp} = 0.16858388 y_{43-} \pm 0.06371872 y_{41-} \mp 0.15607835 y_{21-}$
$y_{22\pm} y_{22\pm} = \pm 0.23841361 y_{44\pm} + 0.04029926 y_{40} - 0.18022375 y_{20} + 0.28209479 y_{00}$
$y_{22+} y_{22-} = 0.23841361 y_{44-}$

correspond to averages over the same two scalar quantities, the **T** and **L** tensors are symmetrical.

If a rotation axis is correctly oriented, but incorrectly positioned, an additional translation component perpendicular to the rotation axes is introduced. The rotation angle and the parallel component of the translation are invariant to the position of the axis, but the perpendicular component is not. This implies that the **L** tensor is unaffected by any assumptions about the position of the libration axes, whereas the **T** tensor depends on the assumptions made concerning the location of the axes.

The quadratic correlation between librational and translational motions can be allowed for by including in (1.2.11.5) cross terms of the type $\langle D_{ik} t_j \rangle$, or, with (1.2.11.3),

$$U_{ij} = \langle D_{ik} D_{jl} \rangle r_k r_l + \langle D_{ik} t_j + D_{jk} t_i \rangle r_k + \langle t_i t_j \rangle = A_{ijkl} r_k r_l + B_{ijk} r_k + \langle t_i t_j \rangle, \quad (1.2.11.6)$$

which leads to the explicit expressions such as

$$\begin{aligned} U_{11} &= \langle \delta r_1 \rangle^2 = \langle \lambda_3^2 \rangle r_2^2 + \langle \lambda_2^2 \rangle r_3^2 - 2 \langle \lambda_2 \lambda_3 \rangle r_2 r_3 \\ &\quad - 2 \langle \lambda_3 t_1 \rangle r_2 - 2 \langle \lambda_2 t_1 \rangle r_3 + \langle t_1^2 \rangle, \\ U_{12} &= \langle \delta r_1 \delta r_2 \rangle = - \langle \lambda_3^2 \rangle r_1 r_2 + \langle \lambda_1 \lambda_3 \rangle r_2 r_3 + \langle \lambda_2 \lambda_3 \rangle r_1 r_3 \\ &\quad - \langle \lambda_1 \lambda_2 \rangle r_3^2 + \langle \lambda_3 t_1 \rangle r_1 - \langle \lambda_1 t_1 \rangle r_3 \\ &\quad - \langle \lambda_3 t_2 \rangle r_2 + \langle \lambda_2 t_2 \rangle r_3 + \langle t_1 t_2 \rangle. \end{aligned} \quad (1.2.11.7)$$

The products of the type $\langle \lambda_i t_j \rangle$ are the components of an additional tensor, **S**, which unlike the tensors **T** and **L** is unsymmetrical, since $\langle \lambda_i t_j \rangle$ is different from $\langle \lambda_j t_i \rangle$. The terms involving elements of **S** may be grouped as

$$(\lambda_3 t_1) r_1 - (\lambda_3 t_2) r_2 + (\langle \lambda_2 t_2 \rangle - \langle \lambda_1 t_1 \rangle) r_3 \quad (1.2.11.8)$$

or

$$S_{31} r_1 - S_{32} r_2 + (S_{22} - S_{11}) r_3.$$

As the diagonal elements occur as differences in this expression, a constant may be added to each of the diagonal terms without changing the observational equations. In other words, the trace of **S** is indeterminate.

In terms of the **L**, **T** and **S** tensors, the observational equations are

$$U_{ij} = G_{ijkl} L_{kl} + H_{ijkl} S_{kl} + T_{ij}. \quad (1.2.11.9)$$

The arrays G_{ijkl} and H_{ijkl} involve the atomic coordinates $(x, y, z) = (r_1, r_2, r_3)$, and are listed in Table 1.2.11.1. Equations (1.2.11.9) for each of the atoms in the rigid body form the observational equations, from which the elements of **T**, **L** and **S** can be derived by a linear least-squares procedure. One of the diagonal elements of **S** must be fixed in advance or some other suitable constraint applied because of the indeterminacy of $\text{Tr}(\mathbf{S})$. It is common practice to set $\text{Tr}(\mathbf{S})$ equal to zero. There are thus eight elements of **S** to be determined, as well as the six each of **L** and **T**, for a total of 20 variables. A shift of origin leaves **L** invariant, but it intermixes **T** and **S**.

If the origin is located at a centre of symmetry, for each atom at **r** with vibration tensor **U**ⁿ there will be an equivalent atom at **-r** with the same vibration tensor. When the observational equations for these two atoms are added, the terms involving elements of **S** disappear since they are linear in the components of **r**. The other terms, involving elements of the **T** and **L** tensors, are simply doubled, like the **U**ⁿ components.

The physical meaning of the **T** and **L** tensor elements is as follows. $T_{ij} l_j$ is the mean-square amplitude of translational vibration in the direction of the unit vector **I** with components l_1, l_2, l_3 along the Cartesian axes and $L_{ij} l_j$ is the mean-square amplitude of libration about an axis in this direction. The quantity $S_{ij} l_j$ represents the mean correlation between libration

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table 1.2.8.3. Products of two real spherical harmonic functions y_{lmp} in terms of the density functions d_{lmp} defined by equation (1.2.7.3b)

$y_{00} y_{00} = 1.0000d_{00}$
$y_{10} y_{00} = 0.43301d_{10}$
$y_{10} y_{10} = 0.38490d_{20} + 1.0d_{00}$
$y_{11\pm} y_{00} = 0.43302d_{11\pm}$
$y_{11\pm} y_{10} = 0.31831d_{21\pm}$
$y_{11\pm} y_{11\pm} = 0.31831d_{22\pm} - 0.19425d_{20} + 1.0d_{00}$
$y_{11+} y_{11-} = 0.31831d_{22-}$
$y_{20} y_{00} = 0.43033d_{20}$
$y_{20} y_{10} = 0.37762d_{30} + 0.38730d_{10}$
$y_{20} y_{11\pm} = 0.28864d_{31\pm} - 0.19365d_{11\pm}$
$y_{20} y_{20} = 0.36848d_{40} + 0.27493d_{20} + 1.0d_{00}$
$y_{21\pm} y_{00} = 0.41094d_{21\pm}$
$y_{21\pm} y_{10} = 0.33329d_{31\pm} + 0.33541d_{11\pm}$
$y_{21\pm} y_{11\pm} = \pm 0.26691d_{32\pm} - 0.21802d_{30} + 0.33541d_{10}$
$y_{21\pm} y_{11\mp} = -0.26691d_{32-}$
$y_{21\pm} y_{20} = 0.31155d_{41\pm} + 0.13127d_{21\pm}$
$y_{21\pm} y_{21\pm} = \pm 0.25791d_{42\pm} \pm 0.22736d_{22\pm} - 0.24565d_{40} + 0.13747d_{20} + 1.0d_{00}$
$y_{21+} y_{21-} = 0.25790d_{42-} + 0.22736d_{22-}$
$y_{22\pm} y_{00} = 0.41094d_{22\pm}$
$y_{22\pm} y_{10} = 0.26691d_{32\pm}$
$y_{22\pm} y_{11\pm} = \pm 0.31445d_{33\pm} - 0.083323d_{31\pm} + 0.33541d_{11\pm}$
$y_{22\pm} y_{11\mp} = 0.31445d_{33-} \pm 0.083323d_{31-} \mp 0.33541d_{11-}$
$y_{22\pm} y_{20} = 0.22335d_{42\pm} - 0.26254d_{22\pm}$
$y_{22\pm} y_{21\pm} = \pm 0.23873d_{43\pm} - 0.089938d_{41\pm} + 0.22736d_{21\pm}$
$y_{22\pm} y_{21\mp} = 0.23873d_{43-} \pm 0.089938d_{41-} \mp 0.22736d_{21-}$
$y_{22\pm} y_{22\pm} = \pm 0.31831d_{44\pm} + 0.061413d_{40} - 0.27493d_{20} + 1.0d_{00}$
$y_{22+} y_{22-} = 0.31831d_{44-}$

about the axis l and translation parallel to this axis. This quantity, like $T_{ij}l_j$, depends on the choice of origin, although the sum of the two quantities is independent of the origin.

The nonsymmetrical tensor \mathbf{S} can be written as the sum of a symmetric tensor with elements $S_{ij}^S = (S_{ij} + S_{ji})/2$ and a skew-symmetric tensor with elements $S_{ij}^A = (S_{ij} - S_{ji})/2$. Expressed in terms of principal axes, \mathbf{S}^S consists of three principal screw correlations $\langle \lambda_{Ij} \rangle$. Positive and negative screw correlations correspond to opposite senses of helicity. Since an arbitrary constant may be added to all three correlation terms, only the differences between them can be determined from the data.

The skew-symmetric part \mathbf{S}^A is equivalent to a vector $(\boldsymbol{\lambda} \times \mathbf{t})/2$ with components $(\boldsymbol{\lambda} \times \mathbf{t})_i/2 = (\lambda_j t_k - \lambda_k t_j)/2$, involving correlations between a libration and a perpendicular translation. The components of \mathbf{S}^A can be reduced to zero, and \mathbf{S} made symmetric, by a change of origin. It can be shown that the origin shift that symmetrizes \mathbf{S} also minimizes the trace of \mathbf{T} . In terms of the coordinate system based on the principal axes of \mathbf{L} , the required origin shifts $\hat{\rho}_i$ are

$$\hat{\rho}_1 = \frac{\hat{S}_{23} - \hat{S}_{32}}{\hat{L}_{22} + \hat{L}_{33}}, \quad \hat{\rho}_2 = \frac{\hat{S}_{31} - \hat{S}_{13}}{\hat{L}_{11} + \hat{L}_{33}}, \quad \hat{\rho}_3 = \frac{\hat{S}_{12} - \hat{S}_{21}}{\hat{L}_{11} + \hat{L}_{22}}, \quad (1.2.11.10)$$

in which the carets indicate quantities referred to the principal axis system.

The description of the averaged motion can be simplified further by shifting to three generally nonintersecting libration axes, one each for each principal axis of \mathbf{L} . Shifts of the \mathbf{L}_1 axis in the \mathbf{L}_2 and \mathbf{L}_3 directions by

$${}^1\hat{\rho}_2 = -\hat{S}_{13}/\hat{L}_{11} \quad \text{and} \quad {}^1\hat{\rho}_3 = \hat{S}_{12}/\hat{L}_{11}, \quad (1.2.11.11)$$

respectively, annihilate the S_{12} and S_{13} terms of the symmetrized \mathbf{S} tensor and simultaneously effect a further reduction in $\text{Tr}(\mathbf{T})$ (the presubscript denotes the axis that is shifted, the subscript the direction of the shift component). Analogous equations for

Table 1.2.11.1. The arrays G_{ijkl} and H_{ijkl} to be used in the observational equations $U_{ij} = G_{ijkl}L_{kl} + H_{ijkl}S_{kl} + T_{ij}$ [equation (1.2.11.9)]

G_{ijkl}

ij	kl					
	11	22	33	23	31	12
11	0	z^2	y^2	$-2yz$	0	0
22	z^2	0	x^2	0	$-2xz$	0
33	y^2	x^2	0	0	0	$-2xy$
23	$-yz$	0	0	$-x^2$	xy	xz
31	0	$-xz$	0	xy	$-y^2$	yz
12	0	0	$-xy$	xz	yz	$-z^2$

H_{ijkl}

ij	kl								
	11	22	33	23	31	12	32	13	21
11	0	0	0	0	$-2y$	0	0	0	$2z$
22	0	0	0	0	0	$-2z$	$2x$	0	0
33	0	0	0	$-2x$	0	0	0	$2y$	0
23	0	$-x$	x	0	0	y	0	$-z$	0
31	y	0	$-y$	z	0	0	0	0	$-x$
12	$-z$	z	0	0	x	0	$-y$	0	0

displacements of the \mathbf{L}_2 and \mathbf{L}_3 axes are obtained by permutation of the indices. If all three axes are appropriately displaced, only the diagonal terms of \mathbf{S} remain. Referred to the principal axes of \mathbf{L} , they represent screw correlations along these axes and are independent of origin shifts.

The elements of the reduced \mathbf{T} are

$${}^I T_{II} = \hat{T}_{II} - \sum_{K \neq I} (\hat{S}_{KI})^2 / \hat{L}_{KK} \\ {}^I T_{JJ} = \hat{T}_{JJ} - \sum_K \hat{S}_{KI} \hat{S}_{KJ} / \hat{L}_{KK}, \quad J \neq I. \quad (1.2.11.12)$$

The resulting description of the average rigid-body motion is in terms of six independently distributed instantaneous motions – three screw librations about nonintersecting axes (with screw pitches given by $\hat{S}_{11}/\hat{L}_{11}$ etc.) and three translations. The parameter set consists of three libration and three translation amplitudes, six angles of orientation for the principal axes of \mathbf{L} and \mathbf{T} , six coordinates of axis displacement, and three screw pitches, one of which has to be chosen arbitrarily, again for a total of 20 variables.

Since diagonal elements of \mathbf{S} enter into the expression for ${}^I T_{II}$, the indeterminacy of $\text{Tr}(\mathbf{S})$ introduces a corresponding indeterminacy in ${}^I \mathbf{T}$. The constraint $\text{Tr}(\mathbf{S}) = 0$ is unaffected by the various rotations and translations of the coordinate systems used in the course of the analysis.

1.2.12. Treatment of anharmonicity

The probability distribution (1.2.10.2) is valid in the case of rectilinear harmonic motion. If the deviations from Gaussian shape are not too large, distributions may be used which are expansions with the Gaussian distribution as the leading term. Three such distributions are discussed in the following sections.

1.2.12.1. The Gram–Charlier expansion

The three-dimensional Gram–Charlier expansion, introduced into thermal-motion treatment by Johnson & Levy (1974), is an expansion of a function in terms of the zero and higher derivatives of a normal distribution (Kendall & Stuart, 1958). If D_j is the operator d/du^j ,

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Table 1.2.12.1. *Some Hermite polynomials (Johnson & Levy, 1974; Zucker & Schulz, 1982)*

$$\begin{aligned}
 H(\mathbf{u}) &= 1 \\
 H_j(\mathbf{u}) &= w_j \\
 H_{jk}(\mathbf{u}) &= w_j w_k - p_{jk} \\
 H_{jkl}(\mathbf{u}) &= w_j w_k w_l - (w_j p_{kl} + w_k p_{lj} + w_l p_{jk}) = w_j w_k w_l - 3w_j p_{kl} \\
 H_{jklm}(\mathbf{u}) &= w_j w_k w_l w_m - 6w_j p_{kl} w_m + 3p_{j(k} p_{lm)} \\
 H_{jklmn}(\mathbf{u}) &= w_j w_k w_l w_m w_n - 10w_j p_{kl} w_m w_n + 15w_j p_{jk} p_{lm} \\
 H_{jklmnp}(\mathbf{u}) &= w_j w_k w_l w_m w_n w_p - 15w_j p_{kl} w_l w_m w_n p_{jk} + 45w_j p_{jk} p_{lm} p_{np} \\
 &\quad - 15p_{j(k} p_{lm} p_{np)}
 \end{aligned}$$

where $w_j \equiv p_{jk} u^k$ and p_{jk} are the elements of σ^{-1} , defined in expression (1.2.10.2). Indices between brackets indicate that the term is to be averaged over all permutations which produce distinct terms, keeping in mind that $p_{jk} = p_{kj}$ and $w_j w_k = w_k w_j$ as illustrated for H_{jkl} .

$$\begin{aligned}
 P(\mathbf{u}) &= [1 - c^j D_j + \frac{1}{2!} c^{jk} D_j D_k - \frac{1}{3!} c^{jkl} D_j D_k D_l + \dots \\
 &\quad + (-1)^r \frac{c^{\alpha_1} \dots c^{\alpha_r}}{r!} D_{\alpha_1} D_{\alpha_2} \dots D_{\alpha_r}] P_0(\mathbf{u}), \quad (1.2.12.1)
 \end{aligned}$$

where $P_0(\mathbf{u})$ is the harmonic distribution, $\alpha_i = 1, 2$ or 3 , and the operator $D_{\alpha_1} \dots D_{\alpha_r}$ is the r th partial derivative $\partial^r / (\partial u^{\alpha_1} \dots \partial u^{\alpha_r})$. Summation is again implied over repeated indices.

The differential operators D may be eliminated by the use of three-dimensional Hermite polynomials $H_{\alpha_1 \dots \alpha_r}$ defined, by analogy with the one-dimensional Hermite polynomials, by the expression

$$D_{\alpha_1} \dots D_{\alpha_r} \exp(-\frac{1}{2} \sigma_{jk}^{-1} u^j u^k) = (-1)^r H_{\alpha_1 \dots \alpha_r}(\mathbf{u}) \exp(-\frac{1}{2} \sigma_{jk}^{-1} u^j u^k), \quad (1.2.12.2)$$

which gives

$$\begin{aligned}
 P(\mathbf{u}) &= \left[1 + \frac{1}{3!} c^{jkl} H_{jkl}(\mathbf{u}) + \frac{1}{4!} c^{jklm} H_{jklm}(\mathbf{u}) + \frac{1}{5!} c^{jklmn} H_{jklmn}(\mathbf{u}) \right. \\
 &\quad \left. + \frac{1}{6!} c^{jklmnp} H_{jklmnp}(\mathbf{u}) + \dots \right] P_0(\mathbf{u}), \quad (1.2.12.3)
 \end{aligned}$$

where the first and second terms have been omitted since they are equivalent to a shift of the mean and a modification of the harmonic term only. The permutations of j, k, l, \dots here, and in the following sections, include all combinations which produce different terms.

The coefficients c , defined by (1.2.12.1) and (1.2.12.2), are known as the *quasimoments* of the frequency function $P(\mathbf{u})$ (Kutznetsov *et al.*, 1960). They are related in a simple manner to the moments of the function (Kendall & Stuart, 1958) and are invariant to permutation of indices. There are 10, 15, 21 and 28 components of c for orders 3, 4, 5 and 6, respectively. The multivariate Hermite polynomials are functions of the elements of σ_{jk}^{-1} and of u^k , and are given in Table 1.2.12.1 for orders ≤ 6 (IT IV, 1974; Zucker & Schulz, 1982).

The Fourier transform of (1.2.12.3) is given by

$$\begin{aligned}
 T(\mathbf{H}) &= \left[1 - \frac{4}{3} \pi^3 i c^{jkl} h_j h_k h_l + \frac{2}{3} \pi^4 c^{jklm} h_j h_k h_l h_m \right. \\
 &\quad + \frac{4}{15} \pi^5 i c^{jklmn} h_j h_k h_l h_m h_n \\
 &\quad \left. - \frac{4}{45} \pi^6 c^{jklmnp} h_j h_k h_l h_m h_n h_p + \dots \right] T_0(\mathbf{H}), \quad (1.2.12.4)
 \end{aligned}$$

where $T_0(\mathbf{H})$ is the harmonic temperature factor. $T(\mathbf{H})$ is a power-series expansion about the harmonic temperature factor, with even and odd terms, respectively, real and imaginary.

1.2.12.2. The cumulant expansion

A second statistical expansion which has been used to describe the atomic probability distribution is that of Edgeworth (Kendall & Stuart, 1958; Johnson, 1969). It expresses the function $P(\mathbf{u})$ as

$$\begin{aligned}
 P(\mathbf{u}) &= \exp \left(\kappa^j D_j + \frac{1}{2!} \kappa^{jk} D_j D_k - \frac{1}{3!} \kappa^{jkl} D_j D_k D_l \right. \\
 &\quad \left. + \frac{1}{4!} \kappa^{jklm} D_j D_k D_l D_m - \dots \right) P_0(\mathbf{u}). \quad (1.2.12.5a)
 \end{aligned}$$

Like the moments μ of a distribution, the cumulants κ are descriptive constants. They are related to each other (in the one-dimensional case) by the identity

$$\exp \left\{ \kappa_1 t + \frac{\kappa_2 t^2}{2!} + \dots + \frac{\kappa_r t^r}{r!} + \dots \right\} = 1 + \mu_1 t + \frac{\mu_2 t^2}{2!} + \dots + \frac{\mu_r t^r}{r!}. \quad (1.2.12.5b)$$

When it is substituted for t , (1.2.12.5b) is the characteristic function, or Fourier transform of $P(t)$ (Kendall & Stuart, 1958).

The first two terms in the exponent of (1.2.12.5a) can be omitted if the expansion is around the equilibrium position and the harmonic term is properly described by $P_0(\mathbf{u})$.

The Fourier transform of (1.2.12.5a) is, by analogy with the left-hand part of (1.2.12.5b) (with t replaced by $2\pi i h$),

$$\begin{aligned}
 T(\mathbf{H}) &= \exp \left[\frac{(2\pi i)^3}{3!} \kappa^{jkl} h_j h_k h_l + \frac{(2\pi i)^4}{4!} \kappa^{jklm} h_j h_k h_l h_m + \dots \right] T_0(\mathbf{H}) \\
 &= \exp \left[-\frac{4}{3} \pi^3 i \kappa^{jkl} h_j h_k h_l + \frac{2}{3} \pi^4 \kappa^{jklm} h_j h_k h_l h_m + \dots \right] T_0(\mathbf{H}), \quad (1.2.12.6)
 \end{aligned}$$

where the first two terms have been omitted. Expression (1.2.12.6) is similar to (1.2.12.4) except that the entire series is in the exponent. Following Schwarzenbach (1986), (1.2.12.6) can be developed in a Taylor series, which gives

$$\begin{aligned}
 T(\mathbf{H}) &= \left\{ 1 + \frac{(2\pi i)^3}{3!} \kappa^{jkl} h_j h_k h_l + \frac{(2\pi i)^4}{4!} \kappa^{jklm} h_j h_k h_l h_m + \dots \right. \\
 &\quad \left. + \frac{(2\pi i)^6}{6!} \left[\kappa^{jklmp} + \frac{6!}{2!(3!)^2} \kappa^{jkl} \kappa^{mnp} \right] h_j h_k h_l h_m h_n h_p \right. \\
 &\quad \left. + \text{higher-order terms} \right\} T_0(\mathbf{H}). \quad (1.2.12.7)
 \end{aligned}$$

This formulation, which is sometimes called the Edgeworth approximation (Zucker & Schulz, 1982), clearly shows the relation to the Gram-Charlier expansion (1.2.12.4), and corresponds to the probability distribution [analogous to (1.2.12.3)]

$$\begin{aligned}
 P(\mathbf{u}) &= P_0(\mathbf{u}) \left\{ 1 + \frac{1}{3!} \kappa^{jkl} H_{jkl}(\mathbf{u}) + \frac{1}{4!} \kappa^{jklm} H_{jklm}(\mathbf{u}) + \dots \right. \\
 &\quad \left. + \frac{1}{6!} \left[\kappa^{jklmnp} + 10 \kappa^{jkl} \kappa^{mnp} \right] H_{jklmnp} \right. \\
 &\quad \left. + \text{higher-order terms} \right\}. \quad (1.2.12.8)
 \end{aligned}$$

The relation between the cumulants κ^{jkl} and the quasimoments c^{jkl} are apparent from comparison of (1.2.12.8) and (1.2.12.4):

$$\begin{aligned}
 c^{jkl} &= \kappa^{jkl} \\
 c^{jklm} &= \kappa^{jklm} \\
 c^{jklmn} &= \kappa^{jklmn} \\
 c^{jklmnp} &= \kappa^{jklmnp} + 10 \kappa^{jkl} \kappa^{mnp}. \quad (1.2.12.9)
 \end{aligned}$$

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The sixth- and higher-order cumulants and quasimoments differ. Thus the third-order cumulant κ^{jkl} contributes not only to the coefficient of H_{jkl} , but also to higher-order terms of the probability distribution function. This is also the case for cumulants of higher orders. It implies that for a finite truncation of (1.2.12.6), the probability distribution cannot be represented by a finite number of terms. This is a serious difficulty when a probability distribution is to be derived from an experimental temperature factor of the cumulant type.

1.2.12.3. The one-particle potential (OPP) model

When an atom is considered as an independent oscillator vibrating in a potential well $V(\mathbf{u})$, its distribution may be described by Boltzmann statistics.

$$P(\mathbf{u}) = N \exp\{-V(\mathbf{u})/kT\}, \quad (1.2.12.10)$$

with N , the normalization constant, defined by $\int P(\mathbf{u}) \, d\mathbf{u} = 1$. The classical expression (1.2.12.10) is valid in the high-temperature limit for which $kT \gg V(\mathbf{u})$.

Following Dawson (1967) and Willis (1969), the potential function may be expanded in terms of increasing order of products of the contravariant displacement coordinates:

$$V = V_0 + \alpha_j u^j + \beta_{jk} u^j u^k + \gamma_{jkl} u^j u^k u^l + \delta_{jklm} u^j u^k u^l u^m + \dots \quad (1.2.12.11)$$

The equilibrium condition gives $\alpha_j = 0$. Substitution into (1.2.12.10) leads to an expression which may be simplified by the assumption that the leading term is the harmonic component represented by β_{jk} :

$$P(\mathbf{u}) = N \exp\{-\beta'_{jk} u^j u^k\} \times \{1 - \gamma'_{jkl} u^j u^k u^l - \delta'_{jklm} u^j u^k u^l u^m - \dots\}, \quad (1.2.12.12)$$

in which $\beta' = \beta/kT$ etc. and the normalization factor N depends on the level of truncation.

The probability distribution is related to the spherical harmonic expansion. The ten products of the displacement parameters $u^j u^k u^l$, for example, are linear combinations of the seven octapoles ($l=3$) and three dipoles ($l=1$) (Coppens, 1980). The thermal probability distribution and the aspherical atom description can be separated only because the latter is essentially confined to the valence shell, while the former applies to all electrons which follow the nuclear motion in the atomic scattering model.

The Fourier transform of the OPP distribution, in a general coordinate system, is (Johnson, 1970a; Scheringer, 1985a)

$$T(\mathbf{H}) = T_0(\mathbf{H}) \left[1 - \frac{4}{3} \pi^3 i \gamma'_{jkl} G^{jkl}(\mathbf{H}) + \frac{2}{3} \pi^4 \delta'_{jklm} G^{jklm}(\mathbf{H}) + \frac{4}{15} \pi^5 i \varepsilon'_{jklmn} G^{jklmn}(\mathbf{H}) - \frac{4}{45} \pi^6 i \varphi'_{jklmnp} G^{jklmnp}(\mathbf{H}) \dots \right], \quad (1.2.12.13)$$

where T_0 is the harmonic temperature factor and G represents the Hermite polynomials in reciprocal space.

If the OPP temperature factor is expanded in the coordinate system which diagonalizes β_{jk} , simpler expressions are obtained in which the Hermite polynomials are replaced by products of the displacement coordinates u^j (Dawson *et al.*, 1967; Coppens, 1980; Tanaka & Marumo, 1983).

1.2.12.4. Relative merits of the three expansions

The relative merits of the Gram–Charlier and Edgeworth expansions have been discussed by Zucker & Schulz (1982), Kuhs (1983), and by Scheringer (1985b). In general, the Gram–Charlier expression is found to be preferable because it gives a better fit in

the cases tested, and because its truncation is equivalent in real and reciprocal space. The latter is also true for the one-particle potential model, which is mathematically related to the Gram–Charlier expansion by the interchange of the real- and reciprocal-space expressions. The terms of the OPP model have a specific physical meaning. The model allows prediction of the temperature dependence of the temperature factor (Willis, 1969; Coppens, 1980), provided the potential function itself can be assumed to be temperature independent.

It has recently been shown that the Edgeworth expansion (1.2.12.5a) always has negative regions (Scheringer, 1985b). This implies that it is not a realistic description of a vibrating atom.

1.2.13. The generalized structure factor

In the generalized structure-factor formalism developed by Dawson (1975), the complex nature of both the atomic scattering factor and the generalized temperature factor are taken into account. We write for the atomic scattering factor:

$$f_j(\mathbf{H}) = f_{j,c}(\mathbf{H}) + i f_{j,a}(\mathbf{H}) + f'_j + i f''_j \quad (1.2.13.1a)$$

$$T_j(\mathbf{H}) = T_{j,c}(\mathbf{H}) + i T_{j,a}(\mathbf{H}) \quad (1.2.13.1b)$$

and

$$F(\mathbf{H}) = A(\mathbf{H}) + iB(\mathbf{H}), \quad (1.2.13.2)$$

where the subscripts c and a refer to the centrosymmetric and noncentrosymmetric components of the underlying electron distribution, respectively. Substitution in (1.2.4.2) gives for the real and imaginary components A and B of $F(\mathbf{H})$

$$A(\mathbf{H}) = \sum_j (f_{j,c} + f'_j) [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c - \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a] - (f_{j,a} + f''_j) [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a + \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c] \quad (1.2.13.3a)$$

and

$$B(\mathbf{H}) = \sum_j (f_{j,c} + f'_j) [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a + \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c] + (f_{j,a} + f''_j) [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c - \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a] \quad (1.2.13.3b)$$

(McIntyre *et al.*, 1980; Dawson, 1967).

Expressions (1.2.13.3) illustrate the relation between valence-density anisotropy and anisotropy of thermal motion.

1.2.14. Conclusion

This chapter summarizes mathematical developments of the structure-factor formalism. The introduction of atomic asphericity into the formalism and the treatment of thermal motion are interlinked. It is important that the complexities of the thermal probability distribution function can often be reduced by very low temperature experimentation. Results obtained with the multipole formalism for atomic asphericity can be used to derive physical properties and d -orbital populations of transition-metal atoms (ITC, 2004). In such applications, the deconvolution of the charge density and the thermal vibrations is essential. This deconvolution is dependent on the adequacy of the models summarized here.

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