

Analysis of Orientationally Disordered Structures. I. Method

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A new method of analyzing the orientational structure of molecular solids is proposed. It is based on an expansion of the coherent scattering-length density of a molecule into a complete set of orthonormal functions. Explicit expressions for the structure factor are given in the three-dimensional case with use of symmetry-adapted cubic harmonics and for planar molecules with use of trigonometric functions. The method is especially well suited for analysis of plastic crystalline phases, orientationally disordered phases and ordered phases with molecules performing large librational motions. The treatment reveals a close analogy between orientationally ordered or disordered systems and magnetic systems.

I. Introduction

In structure analyses of neutron or X-ray data, the thermal motion of the atoms in a crystal is usually described by harmonic Debye–Waller factors, which may be anisotropic if the site symmetry of the specific atom is non-cubic. Such an approach is valid if the atoms perform small translational motions about well defined equilibrium positions. Deviations are to be expected if the atomic displacements are large and anharmonic effects become important. This occurs quite often in molecular crystals where large librational amplitudes have to be ascribed to molecules or molecular groups.

There have been several attempts to include such effects in the ensemble-averaged density distribution (also called probability density function: pdf). A review on this topic has been published recently (*Crystallographic Computing*, 1970). Principally two ways have been chosen: (i) inclusion of higher cumulants beyond bilinear terms in the Debye–Waller factor (Johnson, 1969); (ii) application of mechanistic models, which take into account librational amplitudes of molecules or molecular groups in a solid (Willis & Pawley, 1970; Pawley & Willis, 1970). There is, however, a large group of molecular solids for which neither method seems to be well suited, for instance the orientationally disordered crystals, where no well defined equilibrium positions exist for the atoms. Examples are the disordered phases of the ammonium halides or the group of crystals possessing a plastic (usually high-temperature) phase. Quite often these plastic phases are formed by molecules of high internal symmetry, (e.g. octahedral or tetrahedral symmetry).

The molecules can be treated as rigid units, if the frequencies of the internal modes of vibrations are high compared to those of the external (or lattice) modes. In dealing with the structure analysis of the plastic phase of a solid formed by rigid molecules, a method different from usual procedures seems to be worthwhile. Neutron-diffraction experiments are especially well suited, as the nuclear scattering can be described by delta functions at the position of the nuclei.

II. Method

In the following the coherent, elastic scattering function of a crystal which contains *essentially rigid* molecules performing rotational motions will be calculated. For neutron scattering the structure factor $F(\mathbf{Q})$ may be written as the Fourier transform of the scattering length density $b(\mathbf{r}')$

$$F(\mathbf{Q}) = \sum_{j=1}^N \sum_{\mu=1}^n \sum_{\nu=1}^{n_{\mu}} \int_{\text{vcell}} \exp(i\mathbf{Q} \cdot \mathbf{r}') b_{\nu}^j(\mathbf{r}') d\mathbf{r}' \quad (2.1)$$

\mathbf{Q} is the momentum transfer of the scattered neutrons, j enumerates the N molecules within the unit cell. The atoms in a molecule are arranged in n shells of atoms around the molecular centre and the μ th shell contains n_{μ} atoms enumerated by ν . $b_{\nu}^j(\mathbf{r}')$ is the ensemble-averaged scattering-length density of the specific atom, that is, its nuclear density weighted with its coherent neutron-scattering length. The scattering-length densities of the atoms within a shell are combined to a single quantity:

$$b_{\mu}^j(\mathbf{r}') = \sum_{\nu=1}^{n_{\mu}} b_{\nu}^j(\mathbf{r}') \quad (2.2)$$

\mathbf{r}' may be decomposed into $\mathbf{r}' = \mathbf{R} + \mathbf{r}$, where \mathbf{R} is a vector pointing to the centre of mass of a molecule. The scattering-length density of the (j, μ) th shell may then be written as:

$$b_{\mu}^j(\mathbf{r}') = \int p^j(\mathbf{R}) g_{\mu}^j(\mathbf{R} | \mathbf{r}') d\mathbf{R} \quad (2.3)$$

Here $p^j(\mathbf{R})$ is the probability of finding the centre of mass of the j th molecule at \mathbf{R} and $g_{\mu}^j(\mathbf{R} | \mathbf{r}')$ is the conditional probability (weighted by the scattering length) of finding a scatterer at \mathbf{r}' , if the molecular centre of mass is at \mathbf{R} . The influence of correlations between orientational motions and centre-of-mass translational motions has been discussed recently (Schomaker & Trueblood, 1968). We will consider a situation where such correlations may be neglected. Then $g_{\mu}^j(\mathbf{R} | \mathbf{r}')$ may be replaced by $a_{\mu}^j(\mathbf{r})$, a function

which depends only on the position relative to the instantaneous molecular centre.

$$g_{\mu}^j(\mathbf{R} | \mathbf{r}') = a_{\mu}^j(\mathbf{r}' - \mathbf{R}) = a_{\mu}^j(\mathbf{r}). \quad (2.4)$$

Inserting equations (2.2) to (2.4) into (2.1) and applying the convolution theorem we obtain:

$$F(\mathbf{Q}) = \sum_j \int_{\text{cell}} \exp(i\mathbf{Q}\mathbf{R}) p^j(\mathbf{R}) d\mathbf{R} \\ \times \sum_{\mu} \int_{\text{cell}} \exp(i\mathbf{Q}\mathbf{r}) a_{\mu}^j(\mathbf{r}) d\mathbf{r}. \quad (2.5)$$

Hence the translational and orientational motions may be treated separately. We will not go into the details of the translational part: generally, $p^j(\mathbf{R})$ will give rise to an anisotropic (harmonic) Debye-Waller factor; inclusion of higher cumulants may be necessary. We rewrite (2.5) as

$$F(\mathbf{Q}) = \sum_j \exp(i\mathbf{Q}\mathbf{R}_j^0) \exp[-W_j(\mathbf{Q})] \sum_{\mu} F_{j\mu}^{\text{rot}}(\mathbf{Q}) \quad (2.6)$$

where

$$F_{j\mu}^{\text{rot}}(\mathbf{Q}) = \int_{\text{cell}} \exp(i\mathbf{Q}\mathbf{r}) a_{\mu}^j(\mathbf{r}) d\mathbf{r} \quad (2.7)$$

is a 'rotational form factor'. To calculate it we have to find the 'rotational pdf' or the corresponding scattering length density $a_{\mu}^j(\mathbf{r})$ of a molecule interacting with the crystal field. The symmetry of this field is the site symmetry at the molecular position. $a_{\mu}^j(\mathbf{r})$ then will be expanded into the appropriate set of symmetry-adapted surface harmonics. If we calculate the rotational form factor of one shell in a single molecule, formula (2.7) simplifies to

$$F^{\text{rot}}(\mathbf{Q}) = \int_{\text{cell}} \exp(i\mathbf{Q}\mathbf{r}) a(\mathbf{r}) d\mathbf{r}. \quad (2.8)$$

In X-ray scattering $a(\mathbf{r})$ has to be replaced by the probability of finding an electron at \mathbf{r} .

(a) Three-dimensional case

In case of perfectly rigid molecules the convenient set of harmonics belongs to the irreducible representation of a group that contains both the elements of the site symmetry and the symmetry of the molecule itself. We will return to this topic in the next paragraph. For three-dimensional scatterers the set of (symmetry-adapted) cubic harmonics $K_{lm}(\Omega)$ (van der Lage & Bethe, 1947; Altmann & Cracknell, 1965) appears to be most useful. We may expand the scattering length density $a(\mathbf{r})$ into this complete set of orthonormal functions

$$a(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=1}^{2l+1} a_{lm}(r) K_{lm}(\Omega) \quad (2.9)$$

where $\Omega = (\theta, \varphi)$ denotes polar angles. When dealing with orientationally disordered molecules or molecules with large librational amplitudes, only a few

coefficients $a_{lm}(r)$ will be non-zero. For rigid molecules the nuclei are confined to a spherical shell of radius ϱ .

$$a_{lm}(r) = c_{lm} \delta(r - \varrho) / r^2. \quad (2.10)$$

We also expand $\exp(i\mathbf{Q}\mathbf{r})$:

$$\exp(i\mathbf{Q}\mathbf{r}) = 4\pi \sum_{l', m'} i^{l'} j_{l'}(Qr) K_{l', m'}(\Omega_Q) K_{l', m'}(\Omega). \quad (2.11)$$

Ω_Q denotes the polar angles of the scattering vector \mathbf{Q} in a coordinate system defined by the crystallographic axes. $j_l(Qr)$ are the spherical Bessel functions.

Inserting equations (2.9) to (2.11) into equation (2.8) and integrating over $d\mathbf{r}$, we obtain

$$F^{\text{rot}}(\mathbf{Q}) = 4\pi \sum_{l, m} i^l j_l(Q\varrho) c_{lm} K_{lm}(\Omega_Q). \quad (2.12)$$

Here the orthonormality of the harmonics has been used. We thus have performed all integrations analytically and have reduced the problem to a summation over the symmetry-allowed cubic harmonics. The trivial case $l=0$ brings us back to the Fourier transform of a spherically symmetric density distribution (*International Tables for X-ray Crystallography*, 1965). Then

$$F^{\text{rot}}(\mathbf{Q}) = 4\pi c_{01} j_0(Q\varrho) = 4\pi c_{01} \frac{\sin(Q\varrho)}{Q\varrho}. \quad (2.13)$$

Because of the orthonormality of the set of functions used, we have $4\pi \cdot c_{01} = n_{\mu} b$, where n_{μ} is the number of atoms confined to the shell and b their scattering length. The higher harmonics modulate the constant scattering-length density.

(b) Two-dimensional case

We now consider planar molecules that are confined to an essentially one-dimensional motion around their primary symmetry axis. The motion of the NO_3^- ion in solid KNO_3 may be an example for a crystal where this approximation applies. The scattering length density is then of the form:

$$a(\mathbf{r}) = \frac{1}{2\pi r} \delta(r - \varrho) \delta(z) f(\varphi_r). \quad (2.14)$$

We expand $f(\varphi_r)$:

$$f(\varphi_r) = \sum_{m=0}^{\infty} c_m \exp(im\varphi_r) + C \cdot C. \quad (2.15)$$

To calculate the structure factor

$$F^{\text{rot}}(\mathbf{Q}) = \int a(\mathbf{r}) \exp(i\mathbf{Q}\mathbf{r}) d\mathbf{r}$$

we write

$$\exp(i\mathbf{Q}\mathbf{r}) = \exp(iQ_z z) \exp[iQ_r r \cos(\varphi_Q - \varphi_r)] \quad (2.16)$$

and expand the second factor

$$\exp[iQ_r r \cos(\varphi_Q - \varphi_r)] \\ = J_0(Q_r r) + 2 \sum_{l=1}^{\infty} (i)^l J_l(Q_r r) \cos[l(\varphi_Q - \varphi_r)] \quad (2.17)$$

where $J_l(Q_r r)$ is a Bessel function. Integration over \mathbf{r} then yields:

$$F(\mathbf{Q}) = \sum_{l=0}^{\infty} (i)^l J_l(Q_r \varrho) [c_l \exp(i l \varphi_Q) + C. C.] \quad (2.18)$$

III. Formal development

To determine which coefficients in the expansion (2.9) of $a(\mathbf{r})$ vanish by symmetry, we perform this expansion in two coordinate systems.

The first (unprimed) one is referred to the crystal axes; the second (primed) one is fixed in the molecule. The atomic positions and therefore the coherent scattering-length density $b(\mathbf{r}')$ in the primed system is known. $b(\mathbf{r}')$ is expanded in cubic harmonics.

$$b(\mathbf{r}') = \sum_{l'm'} b_{l'm'}(r') K_{l'm'}(\theta' \varphi'). \quad (3.1)$$

The expansion coefficients $b_{l'm'}$ are given by

$$b_{l'm'}(r') = \int \sin \theta' d\theta' d\varphi' b(\mathbf{r}') K_{l'm'}^*(\theta' \varphi'). \quad (3.2)$$

The advantage of an expansion into symmetry-adapted functions is that most of the coefficients $b_{l'm'}(r')$ vanish.

In X-ray scattering $b(\mathbf{r}')$ has to be replaced by the electron density $\varrho(\mathbf{r}')$. All symmetry arguments are the same. The only difference is that $\varrho(\mathbf{r}')$ is not known exactly, so that (3.2) cannot be evaluated exactly. However, as numerical values for the $b_{l'm'}$ are not needed in the following, the formalism applies also for X-ray scattering.

To calculate the scattering-length (or electron) density in the unprimed coordinate system, we have to know the transformation properties of the cubic harmonics.

$$K_{l'm'}(\theta' \varphi') = \sum_{m''} K_{l'm''}(\theta \varphi) U_{m''m'}^{(l)}(\omega). \quad (3.3)$$

ω denotes the set of Euler angles that relate the primed coordinate system to the unprimed one. Equation (3.3) defines the cubic rotator functions (James & Keenan, 1959). These form an orthogonal and complete set. According to (3.2) for a definite orientation ω of the molecule the scattering length density in the unprimed system is

$$b(\mathbf{r}) = \sum_{l'm'm''} b_{l'm''}(r) K_{l'm'}(\theta \varphi) U_{m''m'}^{(l)}(\omega). \quad (3.4)$$

To obtain the pdf $a(\mathbf{r})$, we multiply by $f(\omega)$, the probability that the molecule is in an orientation specified by the Euler angles ω , and integrate over ω :

$$a(\mathbf{r}) = \int d\omega f(\omega) b(\mathbf{r}). \quad (3.5)$$

$f(\omega)$ may be expanded in cubic rotator functions:

$$f(\omega) = \sum_{lmm'} A_{lmm'}^{(l)} U_{lmm'}^{(l)}(\omega). \quad (3.6)$$

We insert (3.4) and (3.6) into (3.5) and perform the integration over ω :

$$a(\mathbf{r}) = \sum_{lmm'} A_{lmm'}^{(l)} b_{l'm'}(r) K_{l'm'}(\theta \varphi). \quad (3.7)$$

On the other hand $a(\mathbf{r})$ may directly be expanded in cubic harmonics:

$$a(\mathbf{r}) = \sum_{lm} a_{lm}(r) K_{lm}(\theta \varphi). \quad (3.8)$$

Again many of the expansion coefficients $a_{lm}(r)$ are zero. Only those $K_{lm}(\theta, \varphi)$ which are invariant under all operations belonging to the site symmetry, contribute in (3.8). Expansions (3.7) and (3.8) have to be identical. Therefore

$$a_{lm}(r) = \sum_{m'} A_{lmm'}^{(l)} b_{l'm'}(r). \quad (3.9)$$

From equation (3.9) we see that only a few terms contribute to the expansion of $f(\omega)$ in cubic rotator functions. The site symmetry determines which values of m are allowed for a given l and the molecular symmetry determines the allowed values of m' . In particular we notice, that all a_{lm} of a certain order l are zero, if there is no cubic harmonic of that order which is invariant under all symmetry operations of the molecule. This statement is independent of the site symmetry. It has been derived under the assumption of *perfectly rigid* molecules.

Molecules like adamantane and hexamethylenetetramine consist of several shells of atoms and every shell has at least the symmetry of the molecule as a whole. We may expand the ensemble-averaged scattering-length density of each shell in cubic harmonics:

$$a_{\mu}(\mathbf{r}) = \sum_{lm} a_{lm}^{\mu}(r) K_{lm}(\theta \varphi). \quad (3.10)$$

The expansion coefficients $a_{lm}^{\mu}(r)$ then are not independent of each other. A generalization of (3.9) to several shells of atoms reads

$$a_{lm}^{\mu}(r) = \sum_{m'} A_{lmm'}^{(l)} b_{l'm'}^{\mu}(r). \quad (3.11)$$

The coefficients $A_{lmm'}^{(l)}$ do not depend on the shell index and the constants $b_{l'm'}^{\mu}(r)$ are easily calculated from the known atomic positions in the (primed) coordinate system fixed in the molecule. For tetrahedral symmetry of the molecule and full cubic site symmetry there is at most one non-vanishing $A_{lmm'}^{(l)}$, for $l < 12$, i.e. there is only one independent coefficient a_{lm}^{μ} of order l .

IV. Analogy to magnetic systems

There is an evident analogy between the arrangement of electric multipoles and the arrangement in magnetic systems (J. Sivardière, to be published). We shall briefly point out how this analogy enters into the diffraction patterns as obtained from the disordered and ordered phase of a solid which undergoes an orienta-

tional phase transition. It will be assumed that the Debye-Waller factor for the translational motion of the molecules under consideration may be treated as isotropic.

In magnetic systems undergoing a paramagnetic-to-antiferromagnetic phase transition there are 'nuclear' Bragg peaks, the intensity of which is the same above and below the transition temperature. Additional superlattice reflexions arising from the magnetic ordering arise at lattice points which have been zone-boundary points in the disordered phase. In case of ferromagnetic transitions the nuclear Bragg peaks are modulated by the additional magnetic contribution below T_c (which is less favourable for experimental work). Starting from almost spherical symmetry in the disordered phase, we may identify the reflexions due to the isotropic part of the density distribution with the nuclear Bragg peaks. These are almost unchanged with the transition to the orientationally ordered phase. Additional reflexions arise if an antiferro-ordering occurs. It turns out that a symmetry operation, which usually appears in context of magnetic systems only, becomes important, namely the parity of the cubic harmonics

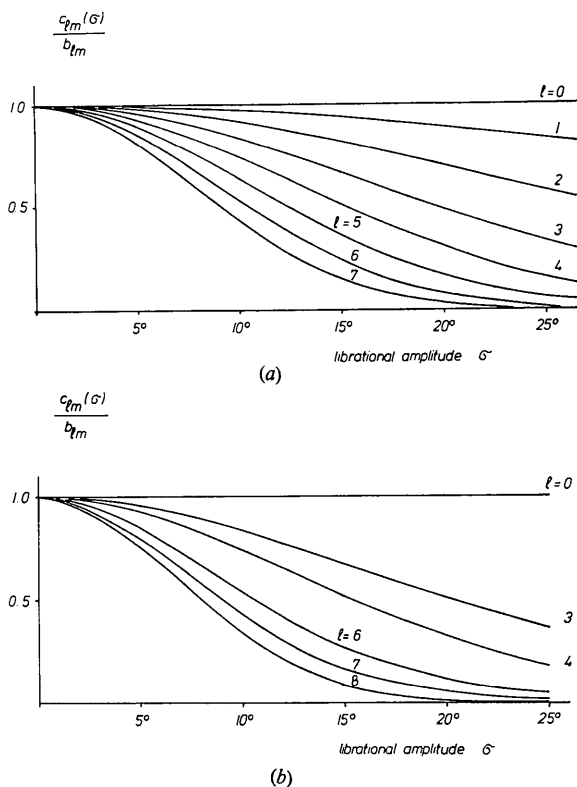


Fig. 1. (a) Expansion of a normalized Gaussian on the pole of a unit sphere in spherical harmonics. The expansion coefficients $c_{lm}(\sigma)$ are normalized by b_{lm} , their value for $\sigma=0$. If the half-width σ of the Gaussian is large, the expansion converges rapidly. (b) Expansion of four Gaussians, related by tetrahedral symmetry, in cubic harmonics. Explicit expressions of the relevant harmonics are listed in paper II.

which is $(-1)^l$ for harmonics of the order l . This may give rise to superlattice reflexions in the ordered phase which are well separated into those arising from harmonics of odd and even parity. (For more details, see the following paper (Press, 1973) referred to as paper II).

Magnetic form factors may certainly be treated in a way very similar to the one described in this paper (Moon, 1966; Moon, 1971; Watson & Freeman, 1961). A basic difference arises from the fact, that the r dependence of the pdf may not be described in such a simple way (δ -functions) as in the present case, which gives rise to r -dependent expansion coefficients $a_{lm}(r)$ or equivalently to averaged Bessel functions.

V. Discussion of the method

The question, under which conditions the present approach is equivalent or superior to conventional methods, has to be investigated. For brevity we confine ourselves to the discussion of the three-dimensional case. All conclusions are the same for two-dimensional molecules. An expansion of the pdfs in symmetry-adapted harmonics is certainly favourable if only a few harmonics contribute to $F_{j\mu}^{rot}(\mathbf{Q})$, since then the number of parameters entering into the problem is small. From equation (2.12) we find that two factors are multiplying $K_{lm}(\theta, \varphi)$, namely $j_l(Q\varrho)$ and c_{lm} .

The second factor has been discussed at length in § III. We have seen that not only high site symmetry but also (for rigid molecules) high molecular symmetry strongly reduces the number of non-vanishing coefficients. Symmetry does not decide, however, whether the series converges rapidly or whether there are important contributions from all orders of l . Rapid convergence is obtained if the orientational localization of the molecule is not too good. In this case only a few terms contribute to (3.6) whence it follows that (3.8) also converges rapidly. As explicit expressions for the rotator functions $U_{mm'}^{(l)}(\omega)$ for $l > 6$ are not found in the literature we discuss the convergence of the series (3.8) directly. Two simple examples have been treated numerically:

(i) a normalized Gaussian of increasing width on the pole of a unit sphere. The expansion has been performed in spherical harmonics $Y_{10}(\theta, \varphi)$ [Fig. 1(a)];

(ii) four Gaussians on the sphere, related by tetrahedral symmetry [Fig. 1(b)].

If the molecules are fixed with zero librational amplitude, the coefficients a_{lm} are identical with the expansion coefficients b_{lm} of equation (3.1). These are easily calculated. For a tetrahedron the following result is obtained: $b_{01}=1$, $b_{31}=\sqrt{35/9}$, $b_{41}=-\sqrt{7/3}$ etc. Fig. 1(b) shows the normalized quantity $c_{lm}(\sigma)/b_{lm}$ where σ is the half-width of the Gaussians. It may readily be seen that (3.8) converges rapidly for large librational amplitudes.

To discuss the influence of $j_l(Q\varrho)$ on the convergence of (2.11) some relevant low-order spherical Bessel func-

tions are represented in Fig. 2. As these functions approach zero as $(Q\rho)^l/1 \cdot 3 \cdot 5 \dots (2l+1)$ for small values of their argument, the coefficient of K_{0l} dominates for small Q . $K_{0l}(\Omega)$ is constant on the unit sphere. Deviations from spherical symmetry, *i.e.* deviations from complete orientational disorder, will therefore be visible at larger momentum transfers only. Inspection of Fig. 2 shows, that $j_l(Q\rho)$ is rising very slowly for higher orders of l . Whether a certain $K_{lm}(\Omega)$ can be seen at all in the scattered intensity depends on whether $j_l(Q\rho)$ attains an appreciable value within the range of Q vectors accessible in an experiment. This range is limited by the energy spectrum of the reactor and by the Debye-Waller factor for the translational motion of the molecules. Even if many coefficients c_{lm} are non-zero (*i.e.* for low site symmetry) only a few will effectively contribute to the rotational form factor if ρ is small. Examples are diatomic molecules like H_2 , N_2 , O_2 *etc.* (for details see paper II). On the other hand, if the radius ρ is small, only restricted information on the orientational structure is gained from experiments over a limited range of Q values. This lack of information cannot be circumvented by other methods of data analysis. Quite often, different mechanistic models lead to equivalent fits of neutron-scattering data. If the molecular radius is small and if the low-order terms of an expansion in cubic harmonics are the same for different models, the coincidence is not surprising.

A clear-cut condition for the superiority of our approach over conventional methods cannot be given. The following criteria are in favour of our method:

- (i) high symmetry (molecular or site symmetry);
- (ii) large librational amplitudes;
- (iii) small molecular radii.

Furthermore the approach gives a satisfying physical picture if the site symmetry is higher than the molecular symmetry. Up to now this has been described in a somewhat artificial way by oscillations about two or more different equilibrium orientations.

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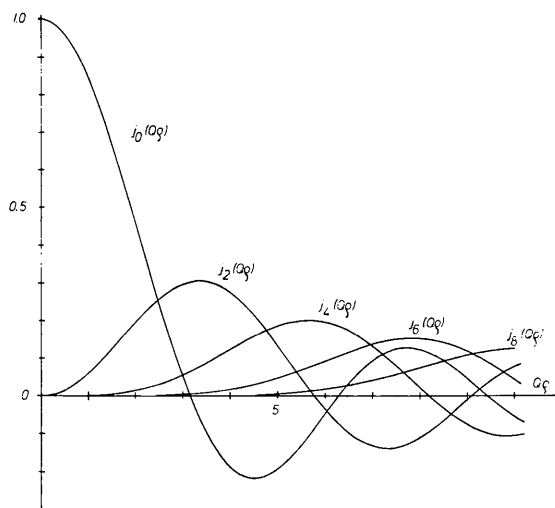


Fig. 2. Spherical Bessel functions of integer order. For small molecular radii ρ only few of them assume appreciable values within the range of experimentally accessible Q values.

References

- ALTMANN, S. L. & CRACKNELL, A. P. (1965). *Rev. Mod. Phys.* **37**, 19–32.
- Crystallographic Computing* (1970). Topic F. Edited by F. R. AHMED. Copenhagen: Munksgaard.
- International Tables for X-ray Crystallography* (1965). Vol. II. Birmingham: Kynoch Press.
- JAMES, H. M. & KEENAN, T. A. (1959). *J. Chem. Phys.* **31**, 12–41.
- JOHNSON, C. K. (1969). *Acta Cryst.* **A25**, 187–194.
- LAGE, F. C. VON DER & BETHE, H. A. (1947). *Phys. Rev.* **71**, 61–71.
- MOOK, H. A. (1966). *Phys. Rev.* **148**, 495–501.
- MOON, R. M. (1971). *Int. J. Magn.* pp. 219–231.
- PAWLEY, G. S. & WILLIS, B. T. M. (1970). *Acta Cryst.* **A26**, 260–262.
- PRESS, W. (1973). *Acta Cryst.* **A29**, 257–263.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- WATSON, R. E. & FREEMAN, A. J. (1961). *Acta Cryst.* **14**, 27–37.
- WILLIS, B. T. M. & PAWLEY, G. S. (1970). *Acta Cryst.* **A26**, 254–259.