Symmetrized Multipole Analysis of Orientational Distributions

By Mikko Kara and Kaarle Kurki-Suonio

Department of Physics, University of Helsinki, Siltavuorenpenger 20 D, SF-00170 Helsinki 17, Finland

Abstract

A rigorous treatment of the constraints imposed by site and body symmetry on the orientational distribution of librating molecules is presented in terms of multipole expansions. Radial densities of the site-symmetric dynamic multipole expansion are linear combinations of the radial densities of the body-symmetric static multipole expansion of the same multipole order. The transformation from static to dynamic radial densities is transmitted by libration matrices, which can be included as parameters in a structure factor model. The matrix elements are connected to the rotational dynamics of the molecule. They are expansion coefficients of the orientational distribution in a basis obtained by site and body symmetrization of the real Wigner functions. Both symmetrizations are reduced to selecting terms from a general basis according to simple index rules. Independence of the kind of density function and Fourier invariance make the formalism useful in combined neutron and X-ray diffraction studies.

1. Introduction

Site-symmetric multipole expansions have gained increasing favour in X-ray and *X–N* studies of charge density (Kurki-Suonio, 1977*a,b*; Coppens, 1977; Coppens & Hansen, 1977; Coppens & Stevens, 1977; and references therein). In particular, they offer a suitable formalism for treatment of rigid molecules. There are several successful multipole studies of the motion and orientational disorder of molecules (Seymour & Pryor, 1970; Press & Hüller, 1973; Hüller & Press, 1979; Press, Grimm & Hüller, 1979; and references therein). At positions of high site symmetry, the assumption of rigidity and neglect of the coupling between librations and vibrations reduce the effect of orientational disorder − either dynamic or static − to one constant multiplier for each low-order multipole component (Press & Hüller, 1973; Kurki-Suonio, Merisalo, Vahvaselkä & Larsen, 1976). This leads to an extremely simple parametrization of the problem. On the other hand, these constants, the libration factors, can be derived from the experimental neutron scattering

amplitudes by direct analysis of the nuclear density (Vahvaselkä & Kurki-Suonio, 1975; Ahtee, Kurki-Suonio, Lucas & Hewat, 1979).

From the derivation of this basic result for the cubic case it is obvious that an analogous general theorem exists, which would allow the use of the multipole formalism in other site symmetries. The purpose of this paper is to derive this generalization, to give the rules necessary for its application in any symmetry and to discuss its consequences.

2. Site symmetry of orientational distributions

Multipole formulation of the problem

The relationship between the *static density* $\sigma(r)$ and the *dynamic density* $\rho(\mathbf{r})$ of a rigid librating molecule is defined by its *orientational distribution* $f(\alpha,\beta,\gamma) = f(\omega)$ through

$$\rho(\mathbf{r}) = \int f(\omega)\mathscr{R}(\omega)\sigma(\mathbf{r})\,d\omega, \qquad (1)$$

where $\mathscr{R}(\omega)$ denotes rotation through Eulerian angles α, β, γ about the centre of mass of the molecule. The integration is over all rotations, *i.e.*

$$\int d\omega = \int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} d\alpha \sin\beta\,d\beta\,d\gamma.$$

The density σ may be any kind of density function, particularly charge density or nuclear density observed by X-ray and neutron diffraction, respectively.

The distribution $f(\omega)$ is an orientational probability density. Accordingly, it is non-negative, $f \geq 0$, and normalized $\int f(\omega)\,d\omega = 1$. Further, it must possess the site symmetry of the molecular centre-of-mass site in its environment. This can be defined by the statement: *An orientational distribution $f(\omega)$ is site symmetric if it produces from any static density $\sigma(\mathbf{r})$ through* (1) *a site-symmetric dynamic density $\rho(\mathbf{r})$.*

The densities σ and ρ are properly expressed as multipole expansions

$$\sigma(\mathbf{r}) = \sum_{lmp} \sigma_{lmp}(r)y_{lmp}(\theta,\varphi) \qquad (2)$$

$$\rho(\mathbf{r}) = \sum_{lmp} \rho_{lmp}(r)\, y_{lmp}(\theta,\varphi) \qquad (3)$$

in terms of the *normalized real spherical harmonics*

$$y_{lm\pm}(\theta,\varphi) = \left[\frac{1}{1+\delta_{m0}}\frac{2l+1}{2\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2}$$

$$\times P_l^m(\cos\theta)\begin{cases}\cos m\varphi\\ \sin m\varphi\end{cases} \qquad (4)$$

$$l = 0, 1, \ldots; m = 0, 1, \ldots, l,$$

cf. Appendix.

In a coordinate system adapted to the symmetry the site symmetry of $\rho(\mathbf{r})$ can be defined by 'picking rules' of the indices lmp in (3) (Kurki-Suonio, Merisalo & Peltonen, 1979; Kurki-Suonio, 1977a). In the case of cubic symmetries the terms are further coupled together, within each multipole order l separately, yielding an expansion in terms of cubic harmonics. Again the symmetry is defined by systematic presence and absence of terms in this expansion.

Symmetric rotator basis for non-cubic sites

The stationary wave functions of a symmetric rotator or the Wigner functions form a natural orthogonal basis in the space of normalizable functions $f(\alpha,\beta,\gamma)$. According to Rose (1957), § 13, they can be written

$$D_{nm}^l(\alpha,\beta,\gamma) = e^{-ln\alpha}\, d_{nm}^l(\beta)\, e^{-lm\nu} \qquad (5)$$

with

$$d_{nm}^l(\beta) = [(l+n)!(l-n)!(l+m)!(l-m)!]^{1/2}$$

$$\times \sum_t \frac{(-1)^t(\cos\tfrac{1}{2}\beta)^{2l+n-m-2t}(\sin\tfrac{1}{2}\beta)^{2t+m-n}}{(l+n-t)!(l-m-t)!\,t!\,(t+m-n)!}, \qquad (6)$$

where t runs through all integer values for which the denominator is finite, *i.e.* from max $\{0, n-m\}$ to min $\{l+m, l-m\}$. The D_{nm}^l have the normalization

$$\int|D_{nm}^l|^2\, d\omega = 8\pi^2/(2l+1). \qquad (7)$$

The real benefit from the use of this basis comes from the fact that the functions (5) define the transformation properties of the spherical harmonics under rotations

$$\mathscr{R}(\alpha,\beta,\gamma)\, Y_l^m(\theta,\varphi) = \sum_{n=-l}^{l} D_{nm}^l(\alpha,\beta,\gamma) Y_l^n(\theta,\varphi); \qquad (8)$$

where Y_l^m are the *normalized spherical harmonics*:

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

$$\times P_l^m(\cos\theta)\, e^{lm\varphi}; \quad \text{for } m \geq 0$$

$$= (-1)^m\left(\frac{1+\delta_{m0}}{2}\right)^{1/2}(y_{lm+} + iy_{lm-}) \qquad (9)$$

$$Y_l^{-m}(\theta,\varphi) = (-1)^m(Y_l^m)^* = \left(\frac{1+\delta_{m0}}{2}\right)^{1/2}$$

$$\times(y_{lm+} - iy_{lm-})$$

(Rose, 1957, Appendix III). For the rotation of the real harmonics (4) this yields

$$\mathscr{R}(\alpha,\beta,\gamma)y_{lmp}(\theta,\varphi) = \sum_{nr} C_{nr\,mp}^l\,(\alpha,\beta,\gamma)\, y_{lnr}(\theta,\varphi), \qquad (10)$$

where

$$C_{nr\,mp}^l = \frac{(-1)^{m+n}}{(1+\delta_{m0})^{1/2}(1+\delta_{n0})^{1/2}}\begin{bmatrix}\mathrm{Re}\\ r\,\mathrm{Im}\end{bmatrix}\{D_{nm}^l$$

$$+ r(-1)^n D_{-nm}^l\}; \quad rp = \begin{bmatrix}+\\ -\end{bmatrix} \qquad (11)$$

$$= \frac{(-1)^{m+n}}{(1+\delta_{m0})^{1/2}(1+\delta_{n0})^{1/2}}\frac{1}{2}\begin{bmatrix}1\\ ip\end{bmatrix}$$

$$\times \{D_{nm}^l + p(-1)^m D_{n-m}^l + r(-1)^n D_{-nm}^l$$

$$+ pr(-1)^{n+m} D_{-n-m}^l\}; \quad rp = \begin{bmatrix}+\\ -\end{bmatrix} \qquad (11')$$

$$= \frac{(-1)^{m+n}}{(1+\delta_{m0})^{1/2}(1+\delta_{n0})^{1/2}}\left\{d_{nm}^l(\beta)\right.$$

$$\times\begin{bmatrix}\cos(n\alpha+m\gamma)\\ p\sin(n\alpha+m\gamma)\end{bmatrix} + (-1)^n d_{-nm}^l(\beta)$$

$$\left.\times\begin{bmatrix}r\cos(n\alpha-m\gamma)\\ \sin(n\alpha-m\gamma)\end{bmatrix}\right\}; \quad rp = \begin{bmatrix}+\\ -\end{bmatrix} \qquad (11'')$$

are *real Wigner functions*, *cf.* Appendix. The first expression (11) is obtained directly from (8) by noting that rotation of the real/imaginary part of a function necessarily yields the real/imaginary part of the rotated function.

The second form (11') follows then through the property $(D_{nm}^l)^* = (-1)^{m+n} D_{-n-m}^l$ of the Wigner functions. It shows that the functions $C_{nr\,mp}^l(\alpha,\beta,\gamma)$ form a complete orthogonal basis, since D_{nm}^l do, and have the same normalization

$$\int(C_{nr\,mp}^l)^2\, d\omega = 8\pi^2/(2l+1). \qquad (12)$$

The third form (11'') is obtained by substitution of (5). It gives, together with (6), the explicit expressions required in applications.

We can now represent the orientational distribution as a real expansion

$$f(\alpha,\beta,\gamma) = \sum_{lnrmp} a_{nr\,mp}^l\, C_{nr\,mp}^l(\alpha,\beta,\gamma) \qquad (13)$$

with the coefficients

$$a_{nr\,mp}^l = \frac{2l+1}{8\pi^2}\int f(\omega)C_{nr\,mp}^l(\omega)\, d\omega. \qquad (14)$$

Inserting (2), (10) and (13) in the integral (1) and applying the orthogonality and normalization (12) of the basis we get

$$\rho(\mathbf{r}) = \int \sum_{\substack{lnrmp \\ l'n'r'm'p'}} a^{l'}_{n'r'm'p'} \times C^{l''}_{n'r'm'p'}(\omega)\sigma_{lmp}(r)$$

$$\times C^l_{nrmp}(\omega)y_{lnr}(\theta,\varphi)\,\mathrm{d}\omega$$

$$= \sum_{lnr} \left[\frac{8\pi^2}{2l+1}\sum_{mp} a^l_{nrmp}\sigma_{lmp}(r)\right] y_{lnr}(\theta,\varphi)$$

or

$$\rho_{lnr}(r) = \frac{8\pi^2}{2l+1}\sum_{mp} a^l_{nrmp}\sigma_{lmp}(r). \tag{15}$$

Now, $\rho_{lnr} = 0$ for indices lnr violating the picking rule of the site symmetry. According to the basic definition, site symmetry of $f(\omega)$ requires this to be true irrespective of the radial densities σ_{lmp}. Thus the corresponding coefficients a^l_{nrmp} for all mp must vanish. This result implies that the functions $C^l_{nrmp}(\alpha,\beta,\gamma)$ (11) yield *a site-symmetric basis of orientational distributions* just by application of the same picking rule of lnr which makes the basis $\{y_{lnr}(\theta,\varphi)\}$ of density functions site symmetric. In this form the result concerns all of the 27 non-cubic site symmetries.

Cubic sites

To consider the five cubic (tetrahedral or octahedral) site symmetries [23 (T), $m3$ (T_h), 432 (O), $\bar{4}3m$ (T_d), $m3m$ (O_h)], we make a unitary transformation of the basis $\{y_{lmp}\}$ to obtain another *real orthonormal basis* $\{K_{lj}\}$,

$$K_{lj}(\theta,\varphi) = \sum_{mp} k^l_{mpj} y_{lmp}(\theta,\varphi), \tag{16}$$

which includes all *cubic harmonics* but is otherwise arbitrary (Von der Lage & Bethe, 1947; Bradley & Cracknell, 1972; *cf.* also Kurki-Suonio, 1977*a*; Kurki-Suonio *et al.*, 1979) *cf.* Appendix.

The rotated real harmonics can now be written

$$\mathscr{R}(\alpha,\beta,\gamma)y_{lmp}(\theta,\varphi) = \sum_j C^l_{jmp}(\alpha,\beta,\gamma) K_{lj}(\theta,\varphi) \tag{17}$$

with

$$C^l_{jmp}(\alpha,\beta,\gamma) = \sum_{nr} k^l_{nrj} C^l_{nrmp}(\alpha,\beta,\gamma). \tag{18}$$

Equation (18) presents a unitary transformation of the basis $\{C^l_{nrmp}\}$. Thus, $\{C^l_{jmp}\}$ is another real orthogonal basis with the same normalization

$$\int (C^l_{jmp})^2\,\mathrm{d}\omega = 8\pi^2/(2l+1).$$

With the expansion

$$f(\alpha,\beta,\gamma) = \sum_{lj\,mp} a^l_{j\,mp} C^l_{jmp}(\alpha,\beta,\gamma) \tag{19}$$

instead of (13), and (17) instead of (10) in the integral (1), we get the expansion

$$\rho(\mathbf{r}) = \sum_{lj} \left[\frac{8\pi^2}{2l+1}\sum_{nr} a^l_{j\,nr}\sigma_{lnr}(r)\right] K_{lj}(\theta,\varphi). \tag{20}$$

Owing to site symmetry of the orientational distribution (19) this is necessarily reduced to the site-symmetric cubic harmonic expansion

$$\rho(\mathbf{r}) = \sum_{lj} \rho_{lj}(r)K_{lj}(\theta,\varphi) \tag{21}$$

of the dynamic density, irrespective of the static radial densities $\sigma_{lnr}(r)$. Thus, the expansion coefficient $a^l_{j\,nr}$ of the orientational distribution must vanish identically unless the basis function $K_{lj}(\theta,\varphi)$ is a cubic harmonic of the site symmetry. This proves that one can pick out of the set $\{C^l_{jmp}(\alpha,\beta,\gamma)\}$ a *site-symmetric basis of orientational distributions for each of the five cubic point symmetries*. The relevant partial set follows automatically from the set of site-symmetric cubic harmonics. The basis functions C^l_{jmp}, equation (18), are linear combinations of the real Wigner functions C^l_{nrmp}, equation (11), just as the cubic harmonics, equation (16), are combinations of the real spherical harmonics, and the same coefficients will be applied.

3. Body symmetry of orientational distributions

The molecular symmetry defines the sequence of indices in the multipole expansion (2) of the static density. For molecules belonging to any of the tetrahedral or octahedral point groups we have to replace (2) by the expansion

$$\sigma(\mathbf{r}) = \sum_{lj} \sigma_{lj}(r)K_{lj}(\theta,\varphi) \tag{22}$$

in terms of the cubic harmonics, *cf.* (21). The rare case of an icosahedral molecule (Cotton, 1963) belonging to one of the two point groups 532 (Y) and $53m$ (Y_h) (Bradley & Cracknell, 1972) requires, correspondingly, use of the expansion

$$\sigma(\mathbf{r}) = \sum_{lj} \sigma'_{lj}(r)K'_{lj}(\theta,\varphi) \tag{23}$$

with the (totally symmetric) *normalized icosahedral harmonics*

$$K'_{lj}(\theta,\varphi) = \sum_{nr} k'^l_{nrj} y_{lnr}(\theta,\varphi) \tag{24}$$

as the basis (Cohan, 1958; Laporte, 1948), *cf.* Appendix.

A general treatment requires parallel discussion of the three different types of body symmetry, represented by the respective symmetric bases $\{y_{lmp}\}$, $\{K_{lj}\}$ and $\{K'_{lj}\}$, and of their coupling separately to the two different types of crystal site symmetry. Rotations of the real harmonics are represented by (10) and (17) in a non-cubic and a cubic site, respectively. Correspondingly, we can write for the rotated cubic harmonics

$$\mathscr{R}(\omega)K_{lj}(\theta,\varphi) = \sum_{nr} C^l_{nrj}(\omega)y_{lnr}(\theta,\varphi) \qquad (25)$$

$$= \sum_i C^l_{ij}(\omega)K_{li}(\theta,\varphi) \qquad (26)$$

and for the rotated icosahedral harmonics

$$\mathscr{R}(\omega)K'_{lj}(\theta,\varphi) = \sum_{nr} C'^l_{nrj}(\omega)y_{lnr}(\theta,\varphi) \qquad (27)$$

$$= \sum_i C'^l_{ij}(\omega)K_{li}(\theta,\varphi) \qquad (28)$$

in non-cubic and cubic sites, respectively, with the cubic-body rotators

$$C^l_{nrj}(\omega) = \sum_{mp} k^l_{mpj} C^l_{nr\,mp}(\omega), \qquad (29)$$

the totally cubic rotators

$$C^l_{ij}(\omega) = \sum_{nrmp} k^l_{nri} k^l_{mpj} C^l_{nrmp}(\omega), \qquad (30)$$

the icosahedral-body rotators

$$C'^l_{nrj}(\omega) = \sum_{mp} k'^l_{mpj} C^l_{nrmp}(\omega) \qquad (31)$$

and the icosahedral-body cubic-site rotators

$$C'^l_{ij}(\omega) = \sum_{nrmp} k^l_{nri} k'^l_{mpj} C^l_{nrmp}(\omega) \qquad (32)$$

in parallel with the general rotators, which are real Wigner functions, equation (11), and the cubic-site rotators, equation (18), *cf.* Appendix.

As in the discussion of the cubic site symmetry, if the bases $\{K_{lj}\}$, (16), and $\{K'_{lj}\}$, (24), are arbitrarily completed to form a complete (unsymmetrized) orthonormal basis for density functions, we find that the corresponding sets (29) to (32) of rotator functions are also completed to a complete orthogonal basis for orientational distributions with the normalization $\int (C^l)^2 \, d\omega = 8\pi^2/(2l+1)$. In these bases we can make

the expansions

$$f(\omega) = \sum_{lnrj} a^l_{nrj} C^l_{nrj}(\omega)$$

$$= \sum_{lij} a^l_{ij} C^l_{ij}(\omega)$$

$$= \sum_{lnrj} a'^l_{nrj} C'^l_{nrj}(\omega) \qquad (33)$$

$$= \sum_{lij} a'^l_{ij} C'^l_{ij}(\omega)$$

of the orientational distribution, insert them together with the relevant static expansion [equation (22) or (23)] and rotation equation [one of (25) to (28)] into the basic expression (1) to yield one of the dynamic expansions (3) or (21).

Switching now to the requirement of molecular symmetry, all radial densities σ_{lmp}, σ_{lj} or σ'_{lj}, except those of the body-symmetric terms, vanish identically, and we are left with the body-symmetric multipole expansion (2), (22) or (23), depending on the case. In the corresponding rotator functions, (11), (18), (29), (30), (31) or (32), this concerns the upper index l together with the last lower indices (mp) or j. If these indices do not match with the allowed indices of the body-symmetric static expansion, the rotator C^l has nothing to rotate. Those functions are, thus, unnecessary members of the $f(\omega)$ basis. Any such terms present in the expansion (13), (19) or (33) of $f(\omega)$ will have no effect on the resulting dynamic distribution. The corresponding coefficients a^l or a'^l are not genuine parameters of $f(\omega)$; their inclusion adds only a contribution of rotations $\mathscr{R}(\omega)$, which are identity transformations of the molecule.

The body symmetry of the orientational distributions $f(\omega)$ is, thus, most naturally defined in terms of the rotator basis. A general body-symmetric basis for orientational distributions of a rigid body is obtained from the set $\{C'^l_{nrj}\}$, (31), $\{C^l_{nrj}\}$, (29) or $\{C^l_{nrmp}\}$, (11) for icosahedral, cubic and other body symmetries, respectively, applying the index-picking rule of the relevant point symmetry to the indices (lj) or (lmp).

In non-cubic sites we get a basis, which is both body and site symmetrized, from the same sets by applying also the index-picking rule of the site symmetry to the indices (lnr). In cubic sites we have to transform first into the other sets $\{C'^l_{ij}\}$, (32), $\{C^l_{ij}\}$, (30), or $\{C^l_{lmp}\}$, (18), to obtain similarly the doubly symmetrized bases for orientational distributions of a molecule of icosahedral, cubic or other symmetry, respectively. [The doubly symmetrized basis functions C^l_{ij} for a cubic body at a cubic site are called in the literature cubic rotators (*cf.* Hüller & Press, 1979).]

4. Matrix formulation of the problem

The libration matrices

According to the results of the previous section we can now write the dynamical radial densities of a rigid librating molecule as linear combinations of the static radial densities of the same multipole order l for all site and molecular symmetries. At non-cubic sites we write

$$\rho_{lmp}(r) = \sum_j b'^{l}_{mp\,j}\, \sigma'_{lj}(r) \qquad \text{(icosahedral molecules)}$$

$$= \sum_j b^{l}_{mp\,j}\, \sigma_{lj}(r) \qquad \text{(cubic molecules)} \qquad (34)$$

$$= \sum_{nr} b^{l}_{mp\,nr}\, \sigma_{lnr}(r) \qquad \text{(other molecules)}$$

and at cubic sites

$$\rho_{li}(r) = \sum_j b'^{l}_{ij}\, \sigma'_{lj}(r) \qquad \text{(icosahedral molecules)}$$

$$= \sum_j b^{l}_{ij}\, \sigma_{lj}(r) \qquad \text{(cubic molecules)} \qquad (35)$$

$$= \sum_{nr} b^{l}_{i\,nr}\, \sigma_{l\,nr}(r) \qquad \text{(other molecules)}$$

or shortly

$$\rho_l(r) = \mathbf{B}_l\, \sigma_l(r), \qquad (36)$$

where ρ_l and σ_l are column vectors formed by the lth-order radial densities in the site- and body-symmetric expansions of $\rho(\mathbf{r})$ and $\sigma(\mathbf{r})$, respectively. The matrices $\mathbf{B}_l$ formed by the coefficients b (or b') in (34), (35) will be referred to as *libration matrices*.

The matrix elements b^l are related to the expansion coefficients a^l of the molecular orientational distribution $f(\omega)$ in the respective site- and body-symmetrized bases simply through

$$b^l = \frac{8\pi^2}{2l+1}\, a^l. \qquad (37)$$

The site symmetry defines the rows (mp) or (i) and the body symmetry defines the columns (nr) or (j) of $\mathbf{B}_l$ through the relevant index-picking rules. All matrix elements are genuine independent parameters of the orientational distribution, except for normalization $\int f(\omega)\, d\omega = 1$, which fixes the value $b^0_{00} = 1$, and for the condition $f(\omega) \geq 0$ (*cf.* Hüller & Press, 1979).

This is the general theorem we wished to formulate.

Examples

Take a hypothetical case of a molecule with the symmetry $4/mmm$ at a site of symmetry $\bar{6}m2$.

In a local Cartesian coordinate system with the z axis along the $\bar{6}$ axis and y axis perpendicular to the plane of reflexion, the site symmetry corresponds to the index rule $(l,mp) = (m + 2j, 3\mu+)$ yielding the sequence $(0,0+)$, $(2,0+)$, $(3,3+)$, $(4,0+)$, $(5,3+)$, $(6,0+)$, $(6,6+)$, $(7,3+)$, $(8,0+)$, $(8,6+)$, *etc.* for the indices of the dynamic multipole expansion (3).

In a body-fixed coordinate system with the z axis along the molecular 4 axis and all coordinate planes coinciding with planes of reflexion the body symmetry corresponds to the index rule $(l,nr) = (2\lambda,4\mu+)$ yielding the sequence $(0,0+)$, $(2,0+)$, $(4,0+)$, $(4,4+)$, $(6,0+)$, $(6,4+)$, $(8,0+)$, $(8,4+)$, $(8,8+)$, *etc.* for the indices of the static multipole expansion (2).

Zero rotation $(\alpha = \beta = \gamma = 0)$ is defined as the position in which the body axes coincide with the local axes.

Now, whatever the librational behaviour of the molecule (within the symmetry, of course), the static radial densities $\sigma_{lmp}(r)$ are transformed into the dynamic radial densities $\rho_{lmp}(r)$ by libration matrices $\mathbf{B}_l = (b^l_{mp\,nr})$ with rows mp and columns nr labelled by the first and the second sequence, respectively:

$$\mathbf{B}_0 = (b^0_{0+\,0+}) = (1), \qquad \mathbf{B}_2 = (b^2_{0+\,0+}),$$

$$\mathbf{B}_4 = (b^4_{0+\,0+} \quad b^4_{0+\,4+}),$$

$$\mathbf{B}_6 = \begin{pmatrix} b^6_{0+\,0+} & b^6_{0+\,4+} \\ b^6_{6+\,0+} & b^6_{6+\,4+} \end{pmatrix},$$

$$\mathbf{B}_8 = \begin{pmatrix} b^8_{0+\,0+} & b^8_{0+\,4+} & b^8_{0+\,8+} \\ b^8_{6+\,0+} & b^8_{6+\,4+} & b^8_{6+\,8+} \end{pmatrix}, \; etc.$$

The odd matrices vanish identically. The indices $l\,mp\,nr$ define at the same time that subset of functions $C^l_{mp\,nr}$ (11) which forms the doubly symmetrized basis for orientational distributions in this particular example. The matrix elements $b^l_{mp\,nr}$ define the expansion coefficients of the orientational distribution $f(\omega)$ in this basis:

$$f(\omega) = \sum_{lmpnr} \frac{2l+1}{8\pi^2}\, b^l_{mp\,nr}\, C^l_{mp\,nr}(\omega).$$

Correspondingly, at a cubic $\bar{4}3m$ site the possible orientational distributions of the same molecule would be defined by the matrices

$$\mathbf{B}_0 = (1), \quad \mathbf{B}_4 = (b^4_{1\,0+} \quad b^4_{1\,4+}),$$

$$\mathbf{B}_6 = (b^6_{1\,0+} \quad b^6_{1\,4+}),$$

$$\mathbf{B}_8 = (b^8_{1\,0+} \quad b^8_{1\,4+} \quad b^8_{1\,8+}),$$

etc. transforming the static multipole expansion (2) into the site-symmetric cubic harmonic expansion (21) of the dynamic density. The matrix elements give the

coefficients of $f(\omega)$ in the doubly symmetrized basis (18):

$$f(\omega) = \sum_{linr} \frac{2l+1}{8\pi^2} b_{inr}^l \, C_{inr}^l(\omega).$$

Obviously, orientational distributions of a low-symmetry molecule at a high-symmetry site are governed by row-like libration matrices (more columns than rows). A high-symmetry molecule at a low-symmetry site has column-like libration matrices (more rows than columns).

If the body and site symmetry are equal all libration matrices are square.

5. Application to diffraction studies

Structure factor formalism

The symmetrized libration matrix formalism is intended for diffraction studies of orientationally disordered molecular crystals.

It is presumed that the molecule behaves as a rigid body, *i.e.* there is a unique static density function $\sigma(r)$ representing the molecule at rest in the scattering process concerned. It may be smeared by internal vibrations independent of the external motion.

The second necessary condition is that the correlations between the translational and rotational motion are negligible. This means that formation of the observable dynamic density from the static density can be described in terms of two independent probability distributions, the translational probability density $\tau(R)$ of the centre of mass and the orientational probability density $f(\omega)$. The result is the convolution integral

$$\rho_{TR}(r) = \int \tau(R)\rho(r-R)\,d^3R, \qquad (38)$$

where $\rho(r)$ is the rotational dynamic density, equation (1).

The dynamic molecular form factor is correspondingly the product

$$F(S) = T(S)f(S) \qquad (39)$$

of the temperature factor $T(S)$ and the rotational form factor $f(S)$, the Fourier transforms of $\tau(R)$ and $\rho(r)$, respectively.

In this study the interest is focused on the rotational part of the problem. When expressed as a body-symmetric multipole expansion the static density $\sigma(r)$, (2), (22) or (23) is transformed by the rotations into the site-symmetric multipole expansion (3) or (21) of the rotational dynamic density. This transformation is transmitted by the libration matrices B_l through (36).

This representation is Fourier invariant (Kurki-Suonio, 1967, 1977*a*). The static form factor $g(S)$

becomes a multipole expansion,

$$g(S) = \sum_{lmp} g_{lmp}(S)y_{lmp}(\theta_S,\varphi_S), \qquad (40)$$

of exactly the same body-symmetric form (2), (22) or (23) as that of $\sigma(r)$ with the static radial form factors

$$g_{lmp}(S) = 4\pi i^l \int_0^\infty \sigma_{lmp}(r)j_l(2\pi Sr)\,r^2\,dr. \qquad (41)$$

The rotational form factor becomes correspondingly a multipole expansion

$$f(S) = \sum f_{lmp}(S)\,y_{lmp}(\theta_S,\varphi_S) \qquad (42)$$

of the same site-symmetric form (3) or (21) as that of $\rho(r)$ with the rotational radial form factors

$$f_{lmp}(S) = 4\pi i^l \int_0^\infty \rho_{lmp}(r)\,j_l(2\pi Sr)\,r^2\,dr. \qquad (43)$$

And, clearly, the same matrices B_l perform the transformation

$$f_l(S) = B_l\,g_l(S) \qquad (44)$$

from static to dynamic radial form factors.

If the static radial form factors are known or reliably modelled, the libration matrices B_l give immediately the proper parametrization of the rotational form factor for analysis of experimental structure factors. The vibrational part of the problem is included in $T(S)$ which must be parametrized separately. Strongly anharmonic vibrations cause a complication of the problem. In favourable cases, however, the experimental data can be understood to yield independent quantitative information on each dynamic radial form factor f_{lmp} up to some not too large multipole order l (Ahtee *et al.*, 1979; Vahvaselkä & Kurki-Suonio, 1975). This emphasizes the significance of molecular symmetry for the solvability of the problem. Low body symmetry makes each f_{lmp} a combination of many static g_{lnr}. The number of parameters (matrix elements of B_l) is, thus, large in view of the information contents of data. High body symmetry reduces some of the lowest-order libration matrices to just one column. There is then only one librational parameter for each ρ_{lmp} to be solved.

The number of significant parameters will depend on the convergence of the dynamic multipole expansion even more strongly than on the symmetry.

Neutron versus X-ray analysis

In the case of neutron diffraction one can start with the simple model where the static density is a known

array of δ functions

$$\sigma(\mathbf{r}) = \sum_i g_i \, \delta(\mathbf{r} - \mathbf{r}_i)$$

$$= \sum_i g_i \frac{\delta(r - r_i)}{r^2} \frac{\delta(\theta - \theta_i)}{\sin \theta} \delta(\varphi - \varphi_i), \quad (45)$$

where $r_i = (r_i, \theta_i, \varphi_i)$ is the position of the ith atom with respect to the molecular centre of mass and g_i its scattering length. This yields the radial densities

$$\sigma_{lmp}(r) = \sum_i g_i y_{lmp}(\theta_i, \varphi_i) r^{-2} \, \delta(r - r_i) \quad (46)$$

and the radial form factors

$$g_{lmp}(S) = 4\pi i^l \sum_i g_i y_{lmp}(\theta_i, \varphi_i) j_l(2\pi r_i S) \quad (47)$$

for the multipole expansions of the static density and the static form factor, respectively (Ahtee *et al.*, 1979). The convergence of these expansions is very slow. The convergence of the dynamic density and, thus, the number of significant parameters then depends critically on the orientational distribution. The favourable case is that of an almost freely rotating molecule with nearly isotropic and smooth $f(\omega)$.

In the case of X-ray diffraction the relevant static density is the molecular charge density. For a compact molecule the static multipole expansion may already converge rapidly, and reduce effectively the number of significant parameters (Vahvaselkä & Kurki-Suonio, 1975). The formalism can be applied to such cases independently of the nature of the rotational motions. It may then be useful to study the low-order libration matrices also from neutron data for use in interpretation of X-ray data or for comparison, irrespective of the slow convergence of the neutron form-factor expansion.

6. Discussion

The formalism proposed is purely representational. It leads only to a parametrization of the experimental information in terms of the rigid density function of the object and the orientational probability distribution. The parameters obtained are open for any kind of dynamical interpretations. In this respect it is parallel to the Fourier invariant treatment of anharmonic vibrations by Kurki-Suonio *et al.* (1979) and to the **TLS** formalism by Schomaker & Trueblood (1968), where the discrete pattern of atomic coordinates has the role of the density function of our formalism.

Because of the charge-density use of the formalism it would be useful to work out the libration matrices $\mathbf{B}_l$ corresponding to the **TL** matrix formalism of

Cruickshank (1956) for small librations. The corresponding general **TLS** formulation of Schomaker & Trueblood (1968) of small-amplitude rigid-body motion falls, however, beyond the present multipole treatment, because it explicitly involves correlation between translational and rotational motion (*cf.* Willis & Pryor, 1975, Ch. 6). An extension of the multipole formalism to include these correlations has been done by Press *et al.* (1979) for cubic sites. A generalization to include all body and site symmetries is under preparation.

It is possible, even quite common, to start right from the beginning from a dynamical model involving, for example, some potentials and force constants, to derive the structure factors from them within some of the conventional approximations of statistical mechanics, and to refine directly the dynamical parameters. The representational parametrization may still be useful as an intermediate step leaving the freedom for different dynamical modellings.

The most obvious and simple dynamical model to be coupled with the present formalism is obtained assuming the molecule to move in an effective one-body orientational potential $V(\omega)$. Since the potential must be both site and body symmetric we can expand it in the relevant doubly symmetrized basis (11), (18), (29), (30), (31) or (32) to obtain the expansion

$$V(\omega) = \sum_{lnrmp} V_{nrmp}^l \, C_{nrmp}^l(\omega)$$

(or some of the other forms depending on the case). The constant term V_{0+0+}^0 can always be chosen to vanish.

In the high-temperature classical limit the orientational distribution is the Boltzmann distribution

$$f(\omega) = \frac{1}{N} \exp\left[-\frac{V(\omega)}{kT} \right],$$

where N is the normalization constant to make $\int f(\omega) \, d\omega = 1$. This is also the limit of nearly free rotation where we expect the formalism to be best applicable. The limit suggests the approximation $e^{-x} \simeq 1 - x$ for the exponential. This yields

$$f(\omega) = \frac{1}{8\pi^2} \left[1 - \frac{V(\omega)}{kT} \right]$$

and gives, thus, the direct interpretation

$$a_{nrmp}^l = -\frac{1}{8\pi^2 \, kT} V_{nrmp}^l, \quad l > 0,$$

for the expansion coefficients of $f(\omega)$ in (13) or, according to (37),

$$b_{nrmp}^l = -\frac{1}{(2l+1)kT} V_{nrmp}^l, \quad l > 0,$$

for the libration matrix elements in terms of the potential coefficients.

This is a parallel of the one-particle-potential approach to anharmonic translational vibrations (*cf.* Willis & Pryor, 1975; Kurki-Suonio *et al.*, 1979). The most essential difference is in the nature of the basic approximation. In the translational case the main term is a Gaussian corresponding to harmonic approximation, which is of a localized nature and most valid for small vibrations close to the potential minimum. This gives a flavour of contradiction because the statistical treatment, on the other hand, assumes high temperature. This controversy does not occur here because the dominating term is the constant corresponding to complete isotropy, *i.e.* free rotation, and requires consistently high temperatures.

APPENDIX
Definitions and tables for symmetrized multipolar bases

Normalized real spherical harmonics

$$y_{lm\pm}(\theta,\varphi) = \frac{1}{N_{lm}}P_l^m(\cos\theta) \begin{cases} \cos m\varphi \\ \sin m\varphi \end{cases};$$

$$l = 0, 1, 2, \ldots; m = 0, 1, \ldots, l.$$

Normalization:

$$\int_0^\pi \int_0^{2\pi} [y_{lm\pm}(\theta,\varphi)]^2 \sin\theta \, d\theta \, d\varphi = 1,$$

$$N_{lm}^2 = (1 + \delta_{m0})\frac{2\pi}{2l + 1}\frac{(l + m)!}{(l - m)!},$$

$$P_l^0(z) = P_l(z) = \frac{1}{2^l \, l!}\frac{d^l}{dz^l}(z^2 - 1)^l,$$

$$P_l^m(z) = (1 - z^2)^{m/2}\frac{d^m}{dz^m}P_l(z).$$

Real Wigner functions

$$C_{nrmp}(\ ,\beta,\gamma) = \frac{(-1)^{m+n}}{(1 + \delta_{m0})^{1/2}(1 + \delta_{n0})^{1/2}}$$
$$\times \left\{ d_{nm}^l(\beta)\begin{bmatrix} \cos(n\alpha + m\gamma) \\ p\sin(n\alpha + m\gamma) \end{bmatrix} \right.$$
$$+ (-1)^n d_{-nm}^l(\beta)$$
$$\left. \times \begin{bmatrix} r\cos(n\alpha - m\gamma) \\ \sin(n\alpha - m\gamma) \end{bmatrix} \right\} ; \quad rp = \begin{bmatrix} + \\ - \end{bmatrix},$$

Table 1. *Index rules imposed by special symmetry elements*

Symmetry element	Index rule
Centre of symmetry, $\bar{1}$	$(2\lambda,m,p)$
n-fold axis, $n \| z$ axis	$(l,n\mu,p)$
n-fold inversion axis	
$\bar{n} \| z$ axis n even	$(m + 2j, \frac{n}{2}\mu, p)$
n odd	$(2\lambda,n\mu,p)$
2-fold axis $2 \| x$ axis	$[l,m,(-)^{l-m}]$
$2 \| y$ axis	$[l,m,(-)^n]$
Plane of reflexion, $m \perp x$ axis	$[l,m,(-)^m]$
$m \perp y$ axis	$(l,m,+)$
$m \perp z$ axis	$(l, l - 2j, p)$

The index rules specify the indices (lmp) of the real spherical harmonics $y_{lmp}(\theta,\varphi)$ occurring in the multipole expansions (2) and (3) of the body-symmetric static density and the site-symmetric dynamic density, respectively. The same rules apply to the indices (lnr) for site symmetry and to the indices (lmp) for body symmetry of the real rotators $C_{nr\,mp}^l(\alpha,\beta,\gamma)$ occurring in the expansion (13) of the orientational distribution. λ, μ and j in the rules denote any integers such that $l \geq m \geq 0$.

$$l = 0, 1, 2, \ldots; nr, mp = 0+, 1\pm, 2\pm, \ldots, 1\pm,$$
$$d_{nm}^l(\beta) = [(l + n)!(l - n)!(l + m)!(l - m)!]^{1/2}$$
$$\times \sum_t \frac{(-1)^t (\cos\frac{1}{2}\beta)^{2l+n-m-2t}(\sin\frac{1}{2}\beta)^{2t+m-n}}{(l + n - t)!(l - m - t)! \, t! \, (t + m - n)!}.$$

Normalization:

$$\int_0^{2\pi}\int_0^\pi\int_0^{2\pi} [C_{nrmp}(\alpha,\beta,\gamma)]^2 \, d\alpha \sin\beta \, d\beta \, d\gamma = \frac{8\pi^2}{2l + 1}.$$

Special relations:

$$d_{mn}^l(\beta) = (-1)^{n-m} d_{nm}^l(\beta),$$

$$C_{nr0+}^l(\alpha,\beta,\gamma) = \left(\frac{4\pi}{2l + 1}\right)^{1/2} y_{lnr}(\beta,\alpha),$$

$$C_{0+mp}^l(\alpha,\beta,\gamma) = p(-1)^m \left(\frac{4\pi}{2l + 1}\right)^{1/2} y_{lmp}(\beta,\gamma).$$

Table 1 shows the index rules imposed by special symmetry elements and Table 2 the index rules for non-cubic crystallographic point groups.

Normalized cubic harmonics

$$K_{lj}(\theta,\varphi) = \sum_{nr} k_{nrj}^l y_{lnr}(\theta,\varphi),$$

$$\int_0^\pi\int_0^{2\pi} [K_{lj}(\theta,\varphi)]^2 \sin\theta \, d\theta \, d\varphi = 1$$

Cubic-site rotators:

$$C_{lmp}^l(\alpha,\beta,\gamma) = \sum_{nr} k_{nri}^l C_{nrmp}^l(\alpha,\beta,\gamma),$$

$$C^l_{i0+}(\alpha,\beta,\gamma) = \left(\frac{4\pi}{2l+1}\right)^{1/2} K_{li}(\beta,\alpha).$$

Cubic-body rotators:

$$C^l_{nrj}(\alpha,\beta,\gamma) = \sum_{mp} k^l_{mpj}\, C^l_{nrmp}(\alpha,\beta,\gamma),$$

$$C^l_{0+j}(\alpha,\beta,\gamma) = (-1)^l \left(\frac{4\pi}{2l+1}\right)^{1/2} K_{lj}(\beta,\gamma).$$

Table 2. *Index rules for non-cubic crystallographic point groups*

Symmetry	Choice of axes	Index rule
1	Any	all (l,m,p)
$\bar{1}$	Any	$(2\lambda,m,p)$
2	$2\|x$	$[l,m,(-)^{l-m}]$
	$2\|y$	$[l,m,(-)^l]$
	$2\|z$	$[l,2\mu,p]$
m	$m\perp x$	$[l,m,(-)^m]$
	$m\perp y$	$(l,m,+)$
	$m\perp z$	$(l,\,l-2j,\,p)$
$2/m$	$2\|x, m\perp x$	$[2\lambda,m,(-)^m]$
	$2\|y, m\perp y$	$(2\lambda,m,+)$
	$2\|z, m\perp z$	$(2\lambda,2\mu,p)$
222	$2\|z, 2\|y, (2\|x)$	$[l,2\mu,(-)^l]$
$mm2$	$2\|x, m\perp z, (m\perp y)$	$(l,\,l-2j,\,+)$
	$2\|y, m\perp z, (m\perp x)$	$[l,\,l-2j,\,(-)^l]$
	$2\|z, m\perp y, (m\perp x)$	$(l,2\mu,+)$
mmm	$m\perp z, m\perp y, m\perp x$	$(2\lambda,2\mu,+)$
4	$4\|z$	$(l,4\mu,p)$
$\bar{4}$	$\bar{4}\|z$	$(l,\,2l-4j,\,p)$
$4/m$	$4\|z, m\perp z$	$(2\lambda,4\mu,p)$
422	$4\|z, 2\|y, (2 \simeq xyz \to yx\bar{z})$	$[l,4\mu,(-)^l]$
$4mm$	$4\|z, m\perp y, (m \simeq xy \to yx)$	$(l,4\mu,+)$
$\bar{4}2m$	$\bar{4}\|z, 2\|x, (m \simeq xy \to yx)$	$[l,\,2l-4j,\,(-)^l]$
	$m\perp y, (2 \simeq xyz\| \to yx\bar{z})$	$(l,\,2l-4j,\,+)$
$4/mmm$	$4\|z, m\perp z, m\perp x, (m \simeq xy \to yx)$	$(2\lambda,4\mu,+)$
3	$3\|z$	$(l,3\mu,p)$
$\bar{3}$	$\bar{3}\|z$	$(2\lambda,3\mu,p)$
32	$3\|z, 2\|y$	$[l,3\mu,(-)^l]$
	$2\|x$	$[l,3\mu,(-)^{l-m}]$
$3m$	$3\|z, m\perp y$	$(l,\,3\mu,+)$
	$m\perp x$	$[l,3\mu(-)^m]$
$\bar{3}m$	$\bar{3}\|z, m\perp y, (2\|y)$	$(2\lambda,3\mu,+)$
	$m\perp y, (2\|x)$	$[2\lambda,3\mu,(-)^m]$
6	$6\|z$	$(l,6\mu,p)$
$\bar{6}$	$\bar{6}\|z = (3\|z, m\perp z)$	$(m + 2j,\, 3\mu,\, p)$
$6/m$	$6\|z, m\perp z$	$(2\lambda,6\mu,p)$
622	$6\|z, 2\|y, (2\|x)$	$[l,6\mu,(-)^l]$
$6mm$	$6\|z, m\perp y, (m\perp x)$	$(l,6\mu,+)$
$6m2$	$6\|z, m\perp y, (2\|x)$	$(m + 2j,\, 3\mu\, +)$
	$m\perp x, (2\|y)$	$[m + 2j,\, 3\mu,\, (-)^l]$
$6/mmm$	$6\|z, m\perp z, m\perp y, (m\perp x, 2\|x, 2\|y)$	$(2\lambda,6\mu,+)$

See note below Table 1.

Totally cubic rotators:

$$C^l_{ij}(\alpha,\beta,\gamma) = \sum_{nrmp} k^l_{nri}\, k^l_{mpj}\, C^l_{nrmp}(\alpha,\beta,\gamma).$$

Normalization:

$$\int [C^l_{lmp}]^2\, d\omega = \int [C^l_{nrj}]^2\, d\omega$$

$$= \int [C^l_{ij}]^2\, d\omega = \frac{8\pi^2}{2l+1}.$$

Table 3 gives the cubic conversion factors up to tenth order.

Table 4 gives the index rules for cubic symmetries. These five symmetries are obtained from orthorhombic and tetragonal symmetries by introducing a threefold axis in the [111] direction as follows $222 \to 23$, $mmm \to m3$, $422 \to 432$, $\bar{4}2m \to \bar{4}3m$ and $4/mmm \to m3m$. Accordingly, the cubic harmonics are obtained from the relevant $y_{lmp}(\theta,\varphi)$ through symmetrization with respect to the threefold axis. They are, thus, naturally classified into four groups:

Even octahedral, O_e, derived from $(2\lambda,4\mu,+)$

Odd octahedral O_o, derived from $(2\lambda + 1,4\mu,-)$

Even tetrahedral T_e, derived from $(2\lambda, 4\mu + 2, +)$

Odd tetrahedral T_o, derived from $(2\lambda + 1, 4\mu + 2, -)$.

The index rules can be summarized by stating that

23 (T) involves all four classes O_e, O_o, T_e, T_o

$m3$ (T_h) involves O_e, T_e

432 (O) involves O_e, O_o

$\bar{4}3m$ (T_d) involves O_e, T_o

$m3m$ (O_h) involves only O_e.

These classes of cubic harmonics are equal to the four classes of tetrahedral harmonics of Laporte (1948). According to his results the number N_l of independent cubic harmonics of lth order fulfils the

Table 3. *Cubic conversion factors* k^l_{mpj} *up to tenth order*

Even

lj	0+	2+	4+	6+	8+	10+
0 1	1					
4 1	$\frac{1}{2}(\frac{7}{3})^{1/2}$		$\frac{1}{2}(\frac{5}{3})^{1/2}$			
6 1	$\frac{1}{2}(\frac{1}{2})^{1/2}$		$-\frac{1}{4}(\frac{7}{2})^{1/2}$			
6 2		$\frac{1}{4}11^{1/2}$		$-\frac{1}{8}5^{1/2}$		
8 1	$\frac{1}{8}33^{1/2}$		$\frac{1}{4}(\frac{7}{3})^{1/2}$		$\frac{1}{8}(\frac{65}{3})^{1/2}$	
10 1	$\frac{1}{8}(\frac{65}{6})^{1/2}$		$-\frac{1}{4}(\frac{11}{2})^{1/2}$		$-\frac{1}{8}(\frac{187}{6})^{1/2}$	
10 2		$\frac{1}{8}(\frac{247}{6})^{1/2}$		$\frac{1}{16}(\frac{19}{3})^{1/2}$		$-\frac{1}{16}85^{1/2}$

Odd

lj	2-	4-	6-	8-
3 1	1			
7 1	$\frac{1}{2}(\frac{13}{6})^{1/2}$		$\frac{1}{2}(\frac{11}{6})^{1/2}$	
9 1	$\frac{1}{4}3^{1/2}$		$-\frac{1}{4}13^{1/2}$	
9 2		$\frac{1}{2}(\frac{17}{6})^{1/2}$		$-\frac{1}{2}(\frac{7}{6})^{1/2}$

Table 4. *Index rules for cubic symmetries*

	Point group				
	23	m3	432	43m	m3m
lj	T	T_h	O	T_d	O_h
0 1	×	×	×	×	×
3 1	×			×	
4 1	×	×	×	×	×
6 1	×	×	×	×	×
6 2	×	×			
7 1	×			×	
8 1	×	×	×	×	×
9 1	×			×	
9 2	×		×		
10 1	×	×	×	×	×
10 2	×	×			

relation $N_{l+12} = N_l + 1$ for each class separately. With the addition that for $l = 11$ there is just one cubic harmonic $K_{11,1}(\theta,\varphi)$ which belongs to the class T_o, this completes the information about index rules of the five cubic groups.

Normalized icosahedral harmonics

$$K'_{lj}(\theta,\varphi) = \sum_{nr} k^{'l}_{nrj} y_{lnr}(\theta,\varphi),$$

$$\int_0^\pi \int_0^{2\pi} [K'_{lj}(\theta,\varphi)]^2 \sin\theta \, d\theta \, d\varphi = 1.$$

Icosahedral-body rotators:

$$C^{'l}_{nrj}(\alpha,\beta,\gamma) = \sum_{mp} k^{'l}_{mpj} C^l_{nr\,mp}(\alpha,\beta,\gamma).$$

Icosahedral-body cubic-site rotators:

$$C^{''l}_{lj}(\alpha,\beta,\gamma) = \sum_{nrmp} k^l_{nrl} k^{'l}_{mpj} C^l_{nr\,mp}(\alpha,\beta,\gamma).$$

Normalization:

$$\int [C^{'l}_{nrj}]^2 \, d\omega = \int [C^{''l}_{lj}]^2 \, d\omega = \frac{8\pi^2}{2l+1}.$$

Table 5. *Icosahedral conversion factors $k^{''l}_{mpj}$ up to tenth order corresponding to the coordinate axes chosen by Cohan* (1958)

The z axis is a fivefold axis. The xz plane contains in addition one fivefold axis above and two threefold axes below the positive x axis. The y axis is a twofold axis.

	mp		
lj	0+	5+	10+
0 1	1		
6 1	$\frac{1}{4}11^{1/2}$	$-\frac{1}{4}14^{1/2}$	
10 1	$\frac{1}{25}(\frac{247}{2})^{1/2}$	$\frac{1}{25}418^{1/2}$	$\frac{1}{25}(\frac{374}{2})^{1/2}$

Table 5 gives the icosohedral conversion factors up to tenth order. According to Laporte (1948) the number N_l of independent icosahedral harmonics of lth order fulfils the relation $N_{l+30} = N_l + 1$. From $l = 11$ to 29 there are no icosahedral harmonics for $l = 11$, 13, 14, 17, 19, 23, 29 and one for the other values of l. [Note that Laporte's (1948) expression in his Table 15 for the tenth-order harmonic is in error. It should read $153\varphi_{10} + 675\varphi_6 \, \varphi_2^2 - (4500/11) \, \varphi_2^5$.] The index rules for the icosahedral groups consist of the statement that all icosahedral harmonics belong to $532(Y)$ while only the even ones belong to $53m(Y_h)$.

References

Ahtee, M., Kurki-Suonio, K., Lucas, B. W. & Hewat, A. W. (1979). *Acta Cryst.* A35, 591–597.

Bradley, C. J. & Cracknell, A. P. (1972). *The Mathematical Theory of Symmetry in Solids.* Oxford: Clarendon Press.

Cohan, N. V. (1958). *Proc. Cambridge Philos. Soc.* 54, 28–38.

Coppens, P. (1977). *Isr. J. Chem.* 16, 159–162.

Coppens, P. & Hansen, N. K. (1977). *Isr. J. Chem.* 16, 163–167.

Coppens, P. & Stevens, E. D. (1977). *Isr. J. Chem.* 16, 175–179.

Cotton, F. A. (1963). *Chemical Applications of Group Theory.* New York: Wiley.

Cruickshank, D. W. J. (1956). *Acta Cryst.* 9, 754–756.

Hüller, A. & Press, W. (1979). *Acta Cryst.* A35, 876–880.

Kurki-Suonio, K. (1967). *Ann. Acad. Sci. Fenn. Ser. A6*, 263.

Kurki-Suonio, K. (1977a). *Isr. J. Chem.* 16, 115–123.

Kurki-Suonio, K. (1977b). *Isr. J. Chem.* 16, 132–136.

Kurki-Suonio, K., Merisalo, M. & Peltonen, H. (1979). *Phys. Scr.* 19, 57–63.

Kurki-Suonio, K., Merisalo, M., Vahvaselkä, A. & Larsen, F. K. (1976). *Acta Cryst.* A32, 110–115.

Laporte, O. (1948). *Z. Naturforsch. Teil A*, 3, 447–456.

Press, W., Grimm, H. & Hüller, A. (1979). *Acta Cryst.* A35, 881–885.

Press, W. & Hüller, A. (1973). *Acta Cryst.* A29, 252–256.

Rose, M. E. (1957). *Elementary Theory of Angular Momentum.* New York: Wiley.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B24, 63–76.

Seymour, R. S. & Pryor, A. W. (1970). *Acta Cryst.* B26, 1487–1491.

Vahvaselkä, A. & Kurki-Suonio, K. (1975). *Phys. Fenn.* 10, 87–99.

Von der Lage, F. C. & Bethe, H. A. (1947). *Phys. Rev.* 71, 612–622.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography.* Cambridge Univ. Press.