

## 1.2. THE STRUCTURE FACTOR

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

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)]

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

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

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

The sixth- and higher-order cumulants and quasimoments differ. Thus the third-order cumulant  $\kappa^{jkl}$  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  $\beta_{jk}$ :

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

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)

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

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  $\beta_{jk}$ , 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 acentric components, respectively. Substitution in (1.2.4.2) gives for the real and imaginary components  $A$  and  $B$  of  $F(\mathbf{H})$

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

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*, 1999). 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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