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Effect of Dispersion on the Probability Distribution of X-ray Reflexions

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Abstract

If dispersive atoms are present the structure factor of a centrosymmetric crystal is not purely real, and the probability distribution of the modulus of the structure factor becomes

$$P(F)\mathrm{d}F = (2F/\mu)\exp(-\Sigma F^2/\mu^2)I_0(SF^2/\mu^2)\mathrm{d}F,$$

where I_0 is the modified Bessel function of zero order, Σ is the sum of the squares of the moduli of the atomic scattering factors, S is the modulus of the sum of their squares, and μ is $(\Sigma^2 - S^2)^{1/2}$. For a non-centrosymmetric crystal the form of the distribution is not altered, but Σ must be defined as in the preceding sentence.

Introduction

Wilson (1949) used the central limit theorem to obtain probability distributions for the real and imaginary parts of the structure factor, the modulus of the structure factor, and the intensity of X-ray reflexions. His conscious assumptions were that the number of atoms per cell was sufficiently large, that the real and imaginary parts of the structure factor were uncorrelated, and that no atom or small group of atoms dominated the scattering. The expressions are thus the asymptotic forms for large numbers of atoms, N, per unit cell, and there have been many papers dealing with modifications needed when the number N is not large, when there are dominating atoms present, and when symmetry other than $P1$ or $P\bar{1}$ has to be taken into account. He also made the unconscious assumption that the atomic scattering factors were purely real. The expressions for the fourth moment of the moduli of the structure factors (Wilson, 1978) are asymptotically consistent with the Wilson (1949) distributions for non-centrosymmetric crystals, but not for centrosymmetric ones; this suggests that the probability distribution for dispersive centrosymmetric crystals will differ from that for non-dispersive crystals, though it does not prove that there will be no difference for non-centrosymmetric crystals.

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The calculation is closely parallel to that of Wilson (1949). If the atomic scattering factor of the ith atom is

$$\mathbf{f}_i = f_i + ig_i \tag{1}$$

and the trigonometric part of the structure factor of the Wyckoff position containing the ith atom (Wilson, 1978) is

$$\mathbf{J}_i = J_i + iK_i, \tag{2}$$

the contribution of the ith Wyckoff position to the real part of the structure factor is

$$\xi_i = f_iJ_i - g_iK_i \tag{3}$$

and to the imaginary part is

$$\eta_i = f_iK_i + g_iJ_i. \tag{4}$$

The mean-square values of these quantities, in the notation of Wilson (1949, 1978), are

$$\alpha_i^2 = \beta_i^2 = \tfrac{1}{2}p_i(f_i^2 + g_i^2) = \tfrac{1}{2}p_i|\mathbf{f}_i|^2 \tag{5}$$

for a non-centrosymmetric crystal, whereas for a centrosymmetric crystal ($K_i = 0$) they are

$$\alpha_i^2 = p_if_i^2, \tag{6}$$

$$\beta_i^2 = p_ig_i^2. \tag{7}$$

The covariance of ξ_i and η_i, zero under the assumptions of the Wilson (1949) paper, remains zero for non-centrosymmetric structures, but for centrosymmetric it becomes

$$\gamma_i = \langle\xi_i\eta_i\rangle = p_if_ig_i. \tag{8}$$

To the extent that the central limit theorem is applicable, therefore, the bivariate distribution of the real and the imaginary parts of the structure factor for a non-centrosymmetric crystal is unaltered by dispersion, the only change being the 'obvious' one that Σ is the sum of the squares of the moduli of the atomic structure factors instead of being the sum of the squares of the atomic scattering factors (Wilson, 1942), assumed wholly real. The bivariate distribution of the structure factor of a centrosymmetric crystal, on the other hand, is spread out over the whole complex plane, instead of being confined to the real axis (Wilson, 1949,

§2.2). The rest of this note is concerned with the resultant change in the probability distribution of the structure factors of a centrosymmetric crystal.

Distribution for a dispersive centrosymmetric crystal

We can write

$$A^2 = \sum_i \alpha_i^2, \tag{9}$$

$$B^2 = \sum_i \beta_i^2, \tag{10}$$

as in the first half of equations (11) and (13) of Wilson (1949), and define ρ, the correlation coefficient of the real and the imaginary parts of the structure factor, by

$$\rho AB = \sum_i \gamma_i. \tag{11}$$

The sum of the squares of the complex atomic scattering factors (Wilson, 1976, 1978) is

$$\mathbf{S} = \sum_i p_i(f_i^2 - g_i^2 + 2if_ig_i) \tag{12}$$

$$= A^2 - B^2 + 2i\rho AB. \tag{13}$$

It thus has the magnitude

$$S = [(A^2 - B^2)^2 + 4\,\rho^2A^2B^2]^{1/2} \tag{14}$$

$$= [(A^2 + B^2)^2 - 4A^2B^2(1 - \rho^2)]^{1/2} \tag{15}$$

$$= (\Sigma^2 - \mu^2)^{1/2}, \tag{16}$$

where

$$\mu = 2AB(1 - \rho^2)^{1/2}, \tag{17}$$

and has the phase δ given by

$$\tan\delta = 2\rho AB/(A^2 - B^2). \tag{18}$$

The central limit theorem (Cramér, 1945, pp. 285–290) then gives, asymptotically in N, the bivariate normal distribution for the real part of the structure factor,

$$x = \sum_i \xi_i, \tag{19}$$

and the imaginary part,

$$y = \sum_i \eta_i. \tag{20}$$

After a little reduction the expression is

$$P(x,y)\mathrm{d}x\,\mathrm{d}y = (\pi\mu)^{-1}\exp\{-2(B^2x^2 - 2\rho ABxy\ \ A^2y^2)/\mu^2\}\,\mathrm{d}x\mathrm{d}y. \tag{21}$$

We desire, however, to find $P(F)\mathrm{d}F$, the probability that $F = (x^2 + y^2)^{1/2}$ lies between F and $F + \mathrm{d}F$. With the substitution

$$x = F\cos\varphi, \qquad y = F\sin\varphi, \tag{22}$$

we obtain

$$P(F)\mathrm{d}F = (F/\pi\mu)\exp(-\Sigma F^2/\mu^2) \times \int_0^{2\pi} \exp\{(S^2F^2/\mu^2)\cos(2\varphi + \delta)\}\mathrm{d}\varphi\mathrm{d}F. \tag{23}$$

The integral gives a modified Bessel function of zero order (Abramowitz & Stegun, 1964, equation 9.6.16), so that

$$P(F)\mathrm{d}F = (2F/\mu)\exp(-\Sigma F^2/\mu^2)I_0(SF^2/\mu^2)\mathrm{d}F. \tag{24}$$

For non-zero μ this behaves quite differently from the distribution for a non-dispersive centrosymmetric crystal; in particular $P(0)$ is zero, whereas it is $(2/\pi\Sigma)^{1/2}$ in the non-dispersive case. By taking the limit as μ goes to zero the non-dispersive distribution is recovered; some care is required.

The distribution (24) resembles several of those found in cases of partial symmetry (Srinivasan & Parthasarathy, 1976, chapter III). The closest analogue is probably equation 3.84 of Srinivasan & Parthasarathy (1976), which is derived for the case of a non-centrosymmetric structure containing a centrosymmetric group. From the obverse point of view, dispersion can be regarded as introducing a certain degree of non-centrosymmetry into an otherwise centrosymmetric structure. With an appropriate reinterpretation of the scaling factors, Srinivasan & Parthasarathy's (1976) figure 3.10 would serve as a representation of the distribution (24) for different combinations of Σ, S, μ.

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