

extinction have been used: reflections with $k = 2 \pmod{4}$ are extinct. Equation (1) can be written as:

$$k = 2.$$

This can be reduced to

$$\frac{1}{4}k = \frac{1}{2} \pmod{1}$$

and

$$\frac{l'}{4} = \frac{1}{2} \pmod{1}.$$

It follows from (5) that $y' = \frac{1}{4}$ and $\frac{3}{4}$. This means that an atom at (x, y, z) is accompanied by an atom at $(x, y + \frac{1}{4}, z)$ or $(x, y + \frac{3}{4}, z)$.

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On the probability of measuring the intensity of a reflexion as negative. By A. J. C. WILSON, *Department of Physics, University of Birmingham, Birmingham B15 2TT, England*

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Infrequently quoted statistical results relating to taxi queues *etc.* are modified to obtain the probability of obtaining an observed number of counts $R_o = T_o - B_o$ when the 'true' numbers of counts are R , T and B for reflexion, total and background respectively and T_o and B_o have the expected Poisson distributions. The expression, valid for negative as well as positive values of R_o , is

$$p(R_o) = \exp\{-(B+T)\} (T/B)^{R_o/2} I_{R_o}\{2(BT)^{1/2}\},$$

where $I_n(x)$ is the hyperbolic Bessel function of the first kind. If the negative values of R_o are included, R_o is an unbiased estimator of R . In no case is $R_o^{1/2}$ an unbiased estimator of $R^{1/2}$, so that Patterson and R_2 methods are preferred to usual electron-density and R_1 methods in structure determination whenever they are appropriate.

In the absence of drift and other disturbing influences, the number of counts recorded during the counting interval used in diffractometers working in the fixed-time mode fluctuates in accordance with the Poisson probability distribution. If the 'true' number of counts to be expected in the interval is N , the probability that the number actually observed will be N_o is given by

$$p(N_o) = \exp(-N) N^{N_o} / N_o!. \quad (1)$$

The quantities p , N and N_o are necessarily non-negative. The intensity of a reflexion, say R , is given by the difference between the 'true' number of counts T expected when the diffractometer is set to receive the reflexion and the 'true' number of counts expected when the diffractometer is set to receive the immediate background:

$$R = T - B; \quad (2)$$

for simplicity it is assumed that the counting times for reflexion and background are the same. The observed values, T_o and B_o , will fluctuate with probabilities given by equations like (1), so that the observed value R_o will sometimes be negative, though the 'true' value R must be zero or positive. What is the probability $p(R_o)$ of obtaining any particular observed difference R_o ? The answer is not well known, and is to be found in comparatively few text-books. For the *sum*

$$S_o = T_o + B_o, \quad (3)$$

4. Limitations

The above-mentioned equations can be used if only one translational vector between pairs of atoms is present. Only in simple cases may a limited number of solutions of (5) be helpful for a structure determination. However, errors in space-group determination can be avoided by successful interpretations of pseudo-extinctions.

References

- NIGGLI, A. (1959a). *Z. Kristallogr.* **111**, 269–282.
 NIGGLI, A. (1959b). *Z. Kristallogr.* **111**, 283–287.
 SCHULZ, H. & SCHRÖDER, F. A. (1973). *Acta Cryst.* **A29**, 322–333.

the result is immediate: the sum of two Poisson-distributed variables is itself Poisson-distributed, with parameter S equal to the sum of the parameters T and B of its components, but obviously the converse is not true for the *difference*. It is easy to write down a formal expression:

$$p(R_o) = \sum p(B_o)p(T_o), \quad (4)$$

the summation being over all B_o and T_o related by

$$R_o = T_o - B_o. \quad (5)$$

Substitution from equation (1) gives

$$p(R_o) = \sum_{B_o=0}^{\infty} \exp\{-(B+T)\} B^{B_o} T^{B_o+R_o} / B_o!(B_o+R_o)!. \quad (6)$$

The summation was carried out in a special case by Irwin (1937) and in general by Skellam (1946); it results in the Bessel function I_n , related to the ordinary Bessel function J_n in the same way as the hyperbolic functions cosh and sinh are related to the trigonometric functions cos and sin. The required probability distribution for the observed number of counts in a reflexion is thus

$$p(R_o) = \exp\{-(B+T)\} (T/B)^{R_o/2} I_{R_o}\{2(BT)^{1/2}\}. \quad (7)$$

Extensive tables of I_n exist (for example, in Abramowitz & Stegun, 1964). As is fairly obvious intuitively, the mean value

of R_o , negative values included, is $R = T - B$ and its variance, again with negative values included, is $S = T + B$. In fact, all the odd semi-invariants of the distribution (7) are R and the even ones are S . The skewness of the distribution is thus (Cramér, 1945, pp. 184, 187)

$$\gamma_1 = \kappa_3/\kappa_2^{3/2} = R/S^{3/2} \quad (8)$$

and the excess is

$$\gamma_2 = \kappa_4/\kappa_2^2 = 1/S. \quad (9)$$

The skewness and excess both approach zero as the total number of counts S increases – the skewness more rapidly in fact than for the Poisson distribution – so that for strong reflexions or high background the distribution approaches the normal (Gaussian), though the approximation is not as good in the ‘tails’ as it is near the peak. It is amusing that the same distribution applies to the length of the queue of customers waiting at a taxi rank (or the length of the queue of taxis waiting for customers) when taxis and customers arrive at random (Kendall, 1951).

Since R_o , negative values included, is an unbiased estimator of R , whereas R_o , positive values only or values greater than 3σ only, is not, the above considerations reinforce the recommendations of Hirshfeld & Rabinovich (1973) and Wilson (1976) that structure determination, scaling, etc. should be carried out with all the measured intensities, rather than on a set with weak intensities excluded

or on the structure factors as ordinarily defined – the square roots of the measured intensities are not unbiased estimates of the true structure factors (Ibers & Hamilton, 1964). One thus prefers Patterson syntheses and refinement in R_2 whenever possible. However, electron-density syntheses must be used when determination of the details of electron density is the focus of interest, as in attempts to study bonding electrons or the non-sphericity of atoms. One is thus left with the question, not yet satisfactorily answered: if only T_o and B_o are known, is there an objective real unbiased estimator of $R^{1/2}$?

References

- ABRAMOWITZ, M. & STEGUN, I. A. (1964). *Handbook of Mathematical Functions*. Washington, DC: US Government Printing Office.
- CRAMÉR, H. (1945). *Mathematical Methods of Statistics*. Uppsala: Almqvist and Wiksells.
- HIRSHFELD, F. L. & RABINOVICH, D. (1973). *Acta Cryst.* **A29**, 510–513.
- IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781–782.
- IRWIN, J. O. (1937). *J. R. Stat. Soc.* **100**, 415–416.
- KENDALL, D. G. (1951). *J. R. Stat. Soc.* **B13**, 151–185.
- SKELLAM, J. G. (1946). *J. R. Stat. Soc.* **109**, 296.
- WILSON, A. J. C. (1976). *Acta Cryst.* **A32**, 994–996.

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A simple refinement of density distributions of bonding electrons. VIII. Comparison of experimental and theoretical scattering curves for bond charges in urea and thiourea. BY C. SCHERINGER, A. KUTOGLU, D. MULLEN and E. HELLNER, *Institut für Mineralogie der Universität Marburg, D-3550 Marburg, Federal Republic of Germany*

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Gaussian scattering curves for bond charges in urea and thiourea whose parameters were determined from 123 K X-ray data are compared with those derived theoretically. A fairly close agreement among the different scattering curves was found.

In a previous paper (Hellner, 1977) the refinement of a density model composed of atomic cores, bonded and non-bonded electrons was described. The charge clouds in the bonds are, like the temperature factor, represented by Gaussian distributions. Such a model was applied to urea and thiourea; for both compounds accurate X-ray data were collected at 123 K (Mullen & Hellner, 1978). At the end of the refinement the thermal smearing of the charge clouds was eliminated from the bond charges (Scheringer, Mullen & Hellner, 1978), and the Gaussian charge cloud at rest was so obtained. Its Fourier transform, i.e. its scattering curve, is also described by the parameters of the distribution. Since these parameters were obtained from the refinement, we acquired an experimental scattering curve for the charge clouds of the bonding electrons in urea and thiourea. It is

interesting to compare the scattering curves obtained with other proposed curves.

Fritchie (1966) derived form factors for C–C bond charges from two-centre orbital products by considering the overlap integrals. Fritchie’s scattering curves are not spherically symmetric but only have the rotational symmetry of the bond. Cromer & Larson (1974) derived spherically symmetric bond scattering factors of Gaussian shape for various pairs of atoms. Their derivation is based on a spherically symmetric approximation of the scattering factors for two-centre orbital products (Stewart, 1969).

The various scattering curves for bond charges are shown in Figs. 1 and 2. Fritchie’s (1966) curves refer to a C–C bond, whereas all the other curves refer to C–N bonds. All scattering curves are normalized to a total charge of one