

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  $3\sigma$  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  $R^{1/2}$ ?

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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

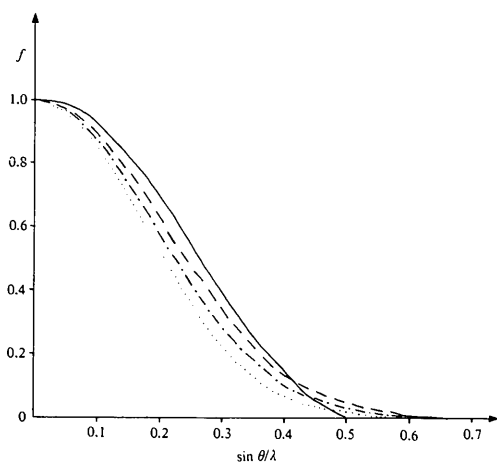


Fig. 1. Normalized scattering curves for bond charges in the direction of the bond. 1 (Full), C—C bond (Fritchie, 1966). 2 (Dashed) C—N bond (Cromer & Larson, 1974). 3 (Dotted) C—N bond, urea, experimental at 123 K. 4 (Dash-dotted) C—N bond, thiourea, experimental at 123 K.

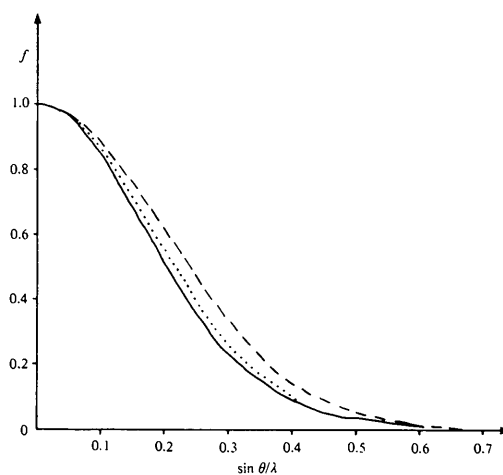


Fig. 2. Normalized scattering curves for bond charges perpendicular to the bond. Otherwise like Fig. 1. Curves 2 and 4 are indistinguishable in the scale of the drawing and are represented as one line (dashed).

electron. It can be seen that, in general, there is good agreement between the various scattering curves, which the authors consider underlines the usefulness and the physical sense of the proposed density model.

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**Effects of incorrect phases on difference density distributions.** By D. MULLEN and C. SCHERINGER, *Institut für Mineralogie der Universität Marburg, D-3550 Marburg/Lahn, Federal Republic of Germany*

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The effect of incorrect phases on difference density distributions is illustrated with the example of thiourea (space group  $P2_1ma$ ). Two difference density maps with phases from the free-atom model ( $R = 0.030$ ) and a molecular model of the charge distribution ( $R = 0.017$ ) are calculated. These maps show deviations as large as  $0.2 \text{ e } \text{Å}^{-3}$  in the peak heights.

The effect of incorrect phases on  $X-N$  maps of acentric structures was first discussed by Coppens (1974), who pointed out that a small phase error in the structure factors  $F_X$ , as is given by the use of phases  $\varphi_N$ , can lead to large errors in the amplitudes and phases of  $F_X - F_N$ . In the structure investigation of lithium formate monohydrate, Thomas, Tellgren & Almlöf found significant differences in two  $X-N$  maps with phases  $\varphi_N$ , on the one hand, and phases  $\varphi_X$ , on the other, where the phases  $\varphi_X$  were calculated from a fully refined free-atom model (room-temperature data without TDS correction). Recently Ito & Shibuya (1977) described a method for refining phases by a numerical Fourier transformation of difference electron density peaks. The method was applied to an artificial two-dimensional

structure, where the phases from a spherical free-atom model were used as a starting set. After 10 cycles of phase refinement the difference density could be significantly improved. In this paper we consider the effects of incorrect phases for the non-centrosymmetric structure of thiourea (space group  $P2_1ma$ , 1122 X-ray data at 123 K).

Two deformation density maps were calculated with identical scale factors but different phases  $\varphi_X$  for the observed  $F$ 's. In the first map (Fig. 1), the phases were those from the free-atom model ( $R = 0.030$ ). In the second (Fig. 2), the phases were those from a molecular model of the density distribution in which core and valence electron distributions were refined separately, and a better agreement between observed and calculated  $F$ 's was obtained ( $R =$