

## Variance and Covariance in Experimental Electron Density Studies, and the Use of Chemical Equivalence

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Expressions are derived for the estimation of the variance and the covariance in the deformation electron density  $q_o/k - q_c$ , for a centrosymmetric crystal structure. The uncertainty in the calculated density  $q_c$  depends strongly on the distance to the nuclei. The uncertainty in the observed density  $q_o$  is fairly constant, except in the vicinity of a symmetry element, where it depends on the same correlation function as the covariance between observed densities. This correlation function is itself dependent on the resolution  $\lambda/(2 \sin \theta)_{\max}$ , the choice of which is of basic importance in any electron density study. The variance-covariance matrix may be used in an averaging procedure of electron densities at chemically, but not crystallographically, equivalent points. The method is applied to the results of X-ray and neutron diffraction studies of chromium hexacarbonyl  $\text{Cr}(\text{CO})_6$ .

### Introduction

An increasing number of crystallographic studies are concerned with precise electron density determination. Most of them consider the deformation electron density  $\Delta q = q_o/k - q_c$  where  $q_o$  is the unscaled observed electron density obtained from X-ray diffraction data,  $k$  the scale factor relating diffracted amplitudes and structure factors, and  $q_c$  a density calculated for a model, generally consisting of spherical atoms in their ground-state. The question of the meaningfulness of the results is essential. Three sources of errors may affect  $\Delta q$ : (a) the errors in the experimental diffracted amplitudes which affect  $q_o$ ; (b) the errors in the parameters on which depends the model, and which affect  $q_c$ ; (c) the error in the scale factor  $k$ .

If the three quantities are not statistically correlated, the variance of  $\Delta q$  is:

$$\sigma^2(\Delta q) = \sigma^2(q_o)/k^2 + \sigma^2(q_c) + (q_o/k)^2[\sigma(k)/k]^2. \quad (1)$$

The first term of (1) has been discussed by several authors: Cruickshank (1949); Cruickshank & Rollett (1953); Coppens & Hamilton (1968), who also considered the error in the electron density integrated over a parallelepiped; Maslen (1968), who considered principally the effect of phase errors, and also the effect of the error in the scale factor. A discussion including all three terms was given by Becker, Coppens & Ross (1973), who estimated an average variance of  $\Delta q$  throughout the crystal.

One may be interested not only in the variance, but also in the covariance between densities at two points defined by the vectors  $\mathbf{r}_A$  and  $\mathbf{r}_B$ . The expression corresponding to (1) is:

$$\text{cov}(\Delta q_A, \Delta q_B) = \text{cov}(q_{oA}, q_{oB})/k^2 + \text{cov}(q_{cA}, q_{cB}) + (q_{oA}/k)(q_{oB}/k)[\sigma(k)/k]^2 \quad (2)$$

where  $\Delta q_A, q_{oA}, \dots$  stand for  $\Delta q(\mathbf{r}_A), q_o(\mathbf{r}_A), \dots$

A knowledge of the covariance is useful if one wants to compare electron densities at two points in the same crystal. Another important case where the estimation of covariances is required is the use of chemical equivalence to compute an average deformation electron density which may give more precise information. The complete variance-covariance matrix between the densities at the equivalent points is needed for a proper weighting. Additionally, the discrepancy between the equivalent observations provides then a check of the individual variance estimations.

As an example of application of the methods of variance-covariance estimation and of electron density averaging, the results of an analysis of chromium hexacarbonyl will be considered.

### Assumptions and approximations

The following assumptions will be made throughout this paper:

(1) The crystal structure is centrosymmetric and the anomalous dispersion effects have been subtracted from the observed structure factors  $F_o$ , which are therefore all real. We assume furthermore that all signs are known without ambiguity, so that  $\sigma(F_o) = \sigma(|F_o|)$ . The errors arising from the uncertainty in the phase of complex structure factors have been discussed by Maslen (1968) and by Coppens (1974).

(2) The correlations between  $q_o$ ,  $q_c$  and  $k$  are negligible, so that equations (1) and (2) apply. This could not be true for two reasons: first,  $k$  is often determined from  $q_o$  and  $q_c$  (or from the corresponding structure factors), by a scaling procedure; second, systematic effects such as thermal diffuse scattering may induce a correlation between  $q_o$  and  $q_c$  even if they are determined from independent X-ray and neutron diffraction experiments (Coppens, 1974).

(3) There is no correlation between the observed

(unscaled) structure factors. This assumption of independent errors is true if the errors are random, but may break down if systematic errors are left uncorrected.

(4) The limit  $H_{\max} = (2 \sin \theta/\lambda)_{\max}$ , in the fraction of reciprocal space in which X-ray data are collected, is the same in all directions.

(5) The correlation between positional or thermal parameters used in the calculation of  $\varrho_o$  is negligible, and their variances are isotropic (except at special positions, where the variance is zero in certain directions).

(6) The effect on  $\varrho_c$  of the errors in the spherical atom scattering factors (including anomalous scattering) may be neglected.

### Uncertainty in the observed structure factors

The estimation of  $\sigma(F_o)$  must be deduced from that of  $\sigma(F_o^2)$ , which has been discussed by several authors [see *e.g.* Abrahams (1974) and McCandlish, Stout & Andrews (1975)]. If  $F_o$  is normally distributed around the mean  $F$ :

$$\sigma^2(F_o)/\sigma(F_o^2) = (u^2 + \frac{1}{2})^{1/2} - u, \quad (3)$$

where  $u = F^2/\sigma(F_o^2)$  [see *e.g.* Hamilton (1964) p. 34]. The assumption of a normal distribution of  $F_o^2$ , which is proportional to the actual measure, seems in fact better justified, and leads to:

$$\sigma^2(F_o)/\sigma(F_o^2) = \int_0^\infty x\varphi(x)dx - \left[ \int_0^\infty x^{1/2}\varphi(x)dx \right]^2 \quad (4)$$

with  $\varphi(x) = (2\pi)^{-1/2} \exp[-(x-u)^2/2]$ . The first integral of (4) is simply related to the cumulative normal distribution. The second may be calculated numerically.

Only for large values of the ratio  $u$  do both equations (3) and (4) reduce to the familiar equation, obtained from a first-order Taylor expansion:

$$\sigma(F_o) = \sigma(F_o^2)/(2F). \quad (5)$$

The curves corresponding to the three equations are represented on Fig. 1. For practical purposes, equation (4) may be replaced by the simple scheme:

$$\begin{aligned} \sigma(F_o) &= \sigma(F_o^2)/(2F_o) \text{ when } F_o^2 > \sigma(F_o^2) \\ \sigma(F_o) &= \sigma^{1/2}(F_o^2)/2 \text{ when } F_o^2 < \sigma(F_o^2). \end{aligned} \quad (4')$$

### Variances and covariances in the unscaled observed electron density

Since the  $F_o$ 's are uncorrelated:

$$\text{cov}(\varrho_{oA}, \varrho_{oB}) \simeq \sum_{\mathbf{H}} \frac{\partial \varrho_{oA}}{\partial F_o(\mathbf{H})} \frac{\partial \varrho_{oB}}{\partial F_o(\mathbf{H})} \sigma^2[F_o(\mathbf{H})], \quad (6)$$

where the summation is carried over the same set of structure factors as in the synthesis of  $\varrho_o$  and  $\Delta\varrho$ .  $\sigma^2(\varrho_o)$  is obtained from (6) as the particular case where  $\mathbf{r}_A \equiv \mathbf{r}_B$ .

This calculation may be quite time-consuming if a large set of points is considered, and it is therefore

useful to derive simplified expressions. In space group  $P\bar{1}$ , (6) may be written:

$$\begin{aligned} \text{cov}(\varrho_{oA}, \varrho_{oB}) &= \frac{2}{V^2} \sum_{1/2} \sigma^2(F_o) \\ &\times [\cos 2\pi(\mathbf{r}_A - \mathbf{r}_B) \cdot \mathbf{H} + \cos 2\pi(\mathbf{r}_A + \mathbf{r}_B) \cdot \mathbf{H}] \quad (7) \end{aligned}$$

where  $V$  is the volume of the crystal unit cell, and  $\sum_{1/2}$  means that the summations are carried over one hemisphere in reciprocal space, up to a radius  $H_{\max} = (2 \sin \theta/\lambda)_{\max}$ . Unless the vector  $\mathbf{r}_A + \mathbf{r}_B$  is very near to a direct lattice translation (which means  $\mathbf{r}_A$  and  $\mathbf{r}_B$  nearly related by an inversion centre), the second cosine term becomes rapidly negligible as  $H_{\max}$  increases. Furthermore, if  $\sigma^2(F_o)$  does not vary in a systematic way with  $\mathbf{H}$ , the first cosine term may be replaced by the average:

$$\langle \cos 2\pi(\mathbf{r}_A - \mathbf{r}_B) \cdot \mathbf{H} \rangle = 3(\sin u - u \cos u)/u^3 = C(u) \quad (8)$$

where  $u = 2\pi|\mathbf{r}_A - \mathbf{r}_B|H_{\max}$ .

An approximate form of equation (7), is thus:

$$\text{cov}(\varrho_{oA}, \varrho_{oB}) \simeq \frac{2}{V^2} C(u) \sum_{1/2} \sigma^2(F_o). \quad (9)$$

Similarly:

$$\sigma^2(\varrho_o) = \frac{2}{V^2} \sum_{1/2} \sigma^2(F_o), \quad (10)$$

which is the relation derived by Cruickshank (1949). Comparing (9) and (10),  $C$  is recognized as the correlation coefficient between  $\varrho_{oA}$  and  $\varrho_{oB}$ . The function  $C(u)$  calculated by (8) is represented on Fig. 2 [curve (a)]. As shown below,  $C(u)$  is closely related to the resolution function due to series termination.

Other space groups are deduced from  $P\bar{1}$  by adjunction of symmetry elements. If the measurements are still carried over one hemisphere, the moduli of the

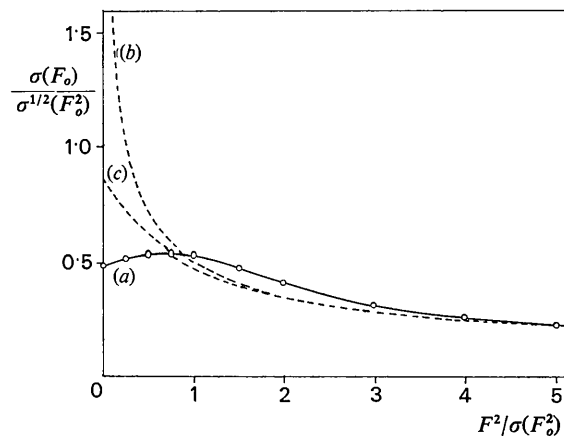


Fig. 1. Relation between  $\sigma(F_o)$  and  $\sigma(F_o^2)$ , (a) assuming a normal distribution of  $F_o^2$  [equation (4) in the text] (b) from first-order Taylor expansion [equation (5)] (c) assuming a normal distribution of  $F_o$  [equation (3)].  $F_o$  is the experimental determination of the true structure factor  $F$ .

structure factors of equivalent reflexions may be averaged (after correcting anisotropic effects like absorption or extinction), and the errors are reduced accordingly. As shown by Cruickshank (1949), at a sufficient distance from any symmetry element, the variance is given by a relation similar to (10):

$$\sigma^2(\rho_{oG}) = \frac{2}{V^2} \sum_{1/2} \sigma^2(\bar{F}_o) \quad (11)$$

where the summation is taken over the averaged structure factors.

The easiest way to derive the covariance between the densities  $\rho_{oA}$  and  $\rho_{oB}$  at two points  $\mathbf{r}_A$  and  $\mathbf{r}_B$  in a crystal which belongs to any centrosymmetric space group, is to assume that the densities are calculated as for  $P\bar{1}$ , and then averaged over the  $n$  symmetry-equivalent positions  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$ . This leads to:

$$\text{cov}(\rho_{oA}, \rho_{oB}) = \sigma^2(\rho_{oG}) \sum_{i=1}^n C(2\pi|\mathbf{r}_{A1} - \mathbf{r}_{B1}|H_{\max}) \quad (12)$$

$$\sigma^2(\rho_o) = \sigma^2(\rho_{oG}) \left[ 1 + \sum_{i=2}^n C(2\pi|\mathbf{r}_1 - \mathbf{r}_i|H_{\max}) \right]. \quad (13)$$

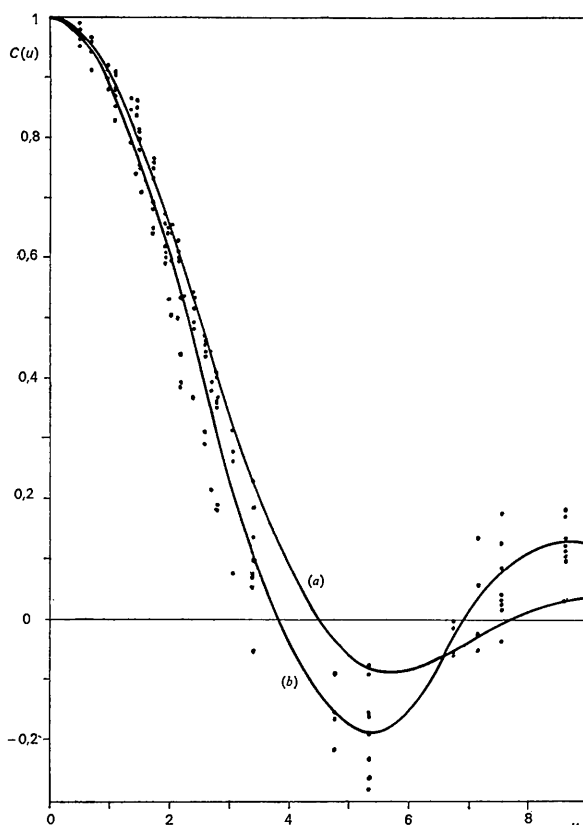


Fig. 2. Correlation coefficient in observed electron densities:  $\text{cov}(\rho_{oA}, \rho_{oB}) = C(2\pi|\mathbf{r}_A - \mathbf{r}_B|H_{\max})\sigma(\rho_{oA})\sigma(\rho_{oB})$ , (a)  $C(u) = 3(\sin u - u \cos u)/u^3$  (b) 'true' correlation coefficient in  $\text{Cr}(\text{CO})_6$ . The points represent values calculated from equation (6).

Thus in the vicinity of a symmetry element, even the variance of  $\rho_o$  depends on the correlation coefficient  $C$ . At special positions and for large values of  $H_{\max}$ , equation (13) reduces to the relation derived by Cruickshank & Rollett (1953).

### Variations and covariances of the calculated electron density

Let  $p_{ik}$  be positional or thermal parameters on which depends the density  $\rho_{ci}$ , calculated for the atom  $i$ . If the correlations between the parameters are neglected:

$$\text{cov}(\rho_{cA}, \rho_{cB}) \simeq \sum_i \sum_k \frac{\partial \rho_{ci}(\mathbf{r}_A)}{\partial p_{ik}} \frac{\partial \rho_{ci}(\mathbf{r}_B)}{\partial p_{ik}} \sigma^2(p_{ik}). \quad (14)$$

This relation must be modified when two crystallographically equivalent atoms  $i$  and  $j$  overlap at one of the considered positions  $\mathbf{r}_A$  or  $\mathbf{r}_B$ , since  $p_{ik}$  and  $p_{jk}$  are then completely correlated.

Relation (14) is simplified when the errors are isotropic, as assumed at the beginning. It is easily shown that this condition is fulfilled when, in orthonormal axes:

$$\begin{aligned} \sigma^2(X_1) &= \sigma^2(X_2) = \sigma^2(X_3) = \sigma_X^2 \\ \sigma^2(U_{11}) &= \sigma^2(U_{22}) = \sigma^2(U_{33}) = 2\sigma^2(U_{12}) = 2\sigma^2(U_{13}) \\ &= 2\sigma^2(U_{23}) = \sigma_U^2. \end{aligned} \quad (15)$$

If this is true, it may also be shown that the  $\sigma^2(X_k)$  and  $\sigma^2(U_{ki})$  are invariant in any change of the orthonormal axes. The simplest form for the derivatives  $\partial \rho_c / \partial p$  is obtained if they are referred to the principal axes of the thermal-motion tensor, so that the non-diagonal terms  $U_{ki}$  vanish (but not, of course, the corresponding derivatives).

### Weighted average of electron density

Let  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_m$  be chemically (but not crystallographically) equivalent points. The best average  $\bar{\Delta \rho}$  of the deformation electron densities  $\Delta \rho_i$  may be obtained by a standard least-squares procedure (Hamilton, 1964, p. 124). The weight-matrix  $\mathbf{P}$  is the inverse of the variance-covariance matrix, determined as above:

$$(P^{-1})_{ij} = \text{cov}(\Delta \rho_i, \Delta \rho_j). \quad (16)$$

The weighted average and its estimated variance are:

$$\bar{\Delta \rho} = \sum_{i=1}^m \Delta \rho_i \sum_{j=1}^m P_{ij} / \sum_i \sum_j P_{ij} \quad (17)$$

$$\sigma^2(\bar{\Delta \rho}) = s^2 / \sum_i \sum_j P_{ij}, \quad (18)$$

where:

$$s^2 = \left[ \sum_i \sum_j \Delta \rho_i \Delta \rho_j P_{ij} - \bar{\Delta \rho}^2 \sum_i \sum_j P_{ij} \right] / (m-1). \quad (19)$$

$s$  is the standard deviation of an observation of unit weight and should on average be equal to 1. A large

departure from 1 would indicate either a bad estimate of the variances and covariances of the  $\Delta\rho_i$ 's, or the inadequacy of the assumption of chemical equivalence.

### Error due to the scale factor

This part of the error has not been considered in the averaging procedure above, since it affects in the same manner the density at equivalent points and cannot be reduced by averaging. It has been discussed recently by Stevens & Coppens (1975), who showed that with the present techniques, the scale factor could be measured with an accuracy of about 1%. The corresponding uncertainty in  $\rho_o$  is thus  $|\rho_o|/100$  in the most favorable cases, which may be very large in the vicinity of the nuclei, especially those of heavy atoms.

However, it should be noted that this may not be too dramatic when the electron densities  $\Delta\rho_A$  and  $\Delta\rho_B$  at two points in the crystal are compared. Since the errors due to  $k$  are completely correlated, the corresponding part of the standard deviation of the difference  $\Delta\rho_A - \Delta\rho_B$  is:

$$\sigma_k(\Delta\rho_A - \Delta\rho_B) = [|\rho_{oA} - \rho_{oB}|/k] [\sigma(k)/k]. \quad (20)$$

If the total densities  $\rho_{oA}$  and  $\rho_{oB}$  are nearly the same, this term is very small. The situation is of course quite different for other problems as, for example, in the determination of the integrated charge of an atom.

### Example of application

The averaging procedure described above was applied to the experimental data of chromium hexacarbonyl,  $\text{Cr}(\text{CO})_6$ . The free molecule belongs to the symmetry group  $O_h$ , but only a mirror plane is retained in the crystal (see Fig. 3). The molecular symmetry is still very close to  $O_h$  and an averaging procedure thus seems justified. Neutron diffraction data (Jost, Rees & Yelon, 1975) and X-ray diffraction data were collected at liquid-nitrogen temperature. All X-ray reflexions, up to  $H_{\text{max}} = 1.52 \text{ \AA}^{-1}$ , were used in the computation of deformation densities. The electronic structure of this complex will be discussed elsewhere (Rees & Mitschler, 1976); only the discussion of the achieved precision is relevant here.

The variance-covariance estimation by the approximate equations (12) and (13) was compared to the exact calculation (6). From (11),  $\sigma(\rho_o)$  is  $0.066 \text{ e \AA}^{-3}$ . The results of the exact calculation for a number of points far from symmetry elements, were equal to this value within about 30%. This agrees with the model calculations of Coppens & Hamilton (1968), but in contrast to these calculations, no apparent relation between the fluctuations of  $\sigma(\rho_o)$  and the nuclear positions was evidenced. Covariances, as calculated by (6), were of importance only between points closer than about  $0.7 \text{ \AA}$  (for a value of  $H_{\text{max}}$  of  $1.52 \text{ \AA}^{-1}$ ). For larger distances, the magnitude of the correlation coefficient was always less than 0.2. The covariances cal-

culated by (12) were found to be correct provided that the theoretical value of the correlation coefficient  $C$  [equation (8)] was substituted by a somewhat steeper function, also represented on Fig. 2 [curve (b)]. This probably indicates the breakdown of the hypothesis, that  $\sigma(F_o)$  does not vary systematically with  $H$ . In fact, since the structure factors decrease for larger values of  $H$ ,  $\sigma(F_o)$  is also, on average, a decreasing function.

To calculate the derivatives of equation (14), cylindrical symmetry of the thermal motion around the Cr-C-O bond axes was assumed. The calculated density of each independent atom was expressed as a Fourier series in a cubic lattice ( $a^* = 0.15 \text{ \AA}^{-1}$ ), with axes along the three bond directions. Relations (15) were found to be approximately verified, except of course for those parameters which have a value fixed by the crystal symmetry.  $\sigma(\rho_o)$  behaves very differently from  $\sigma(\rho_c)$ : it is large in the vicinity of a nucleus and decreases rapidly when the distance to the nucleus increases. The covariance between the calculated densities at two points not too far from the same nucleus may be large, even for a relatively large distance between the two points.

The average deformation density  $\bar{\Delta\rho}$  was calculated in a plane defined by two perpendicular Cr-C-O bonds. As shown on Fig. 3, each value of  $\bar{\Delta\rho}$  results from the averaging over 12 chemically equivalent but crystallographically independent points.

The root-mean-square value of  $s$ , as calculated by (19), was 1.09. This indicates the correctness of the assumption of chemical equivalence and of the estimation of variances and covariances.

$\Delta\rho$  is shown on Fig. 4(a);  $\sigma(\Delta\rho) = [\sigma^2(\rho_o)/k^2 + \sigma^2(\rho_c)]^{1/2}$  in one plane before averaging, is shown on

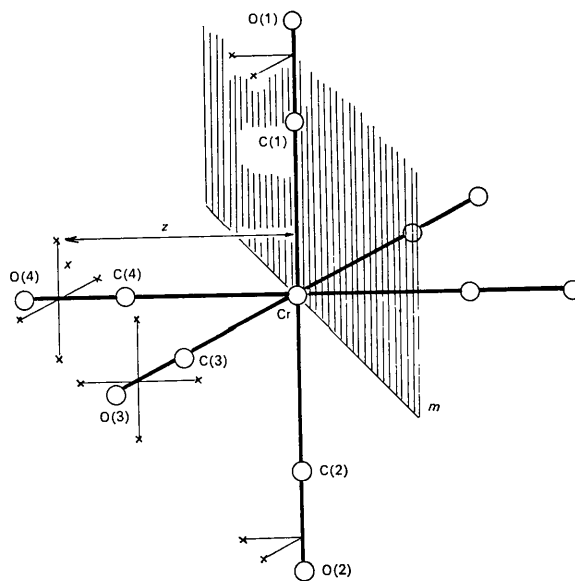


Fig. 3. Chemically equivalent points in  $\text{Cr}(\text{CO})_6$ .  $m$  is the crystallographic mirror plane.

Fig. 4(b) (note the larger value of  $\sigma$  in the vicinity of the mirror plane), and may be compared to  $\sigma(\Delta\bar{q})$  of Fig. 4(c). The improvement in precision due to averaging is obvious. When all correlations are small, the

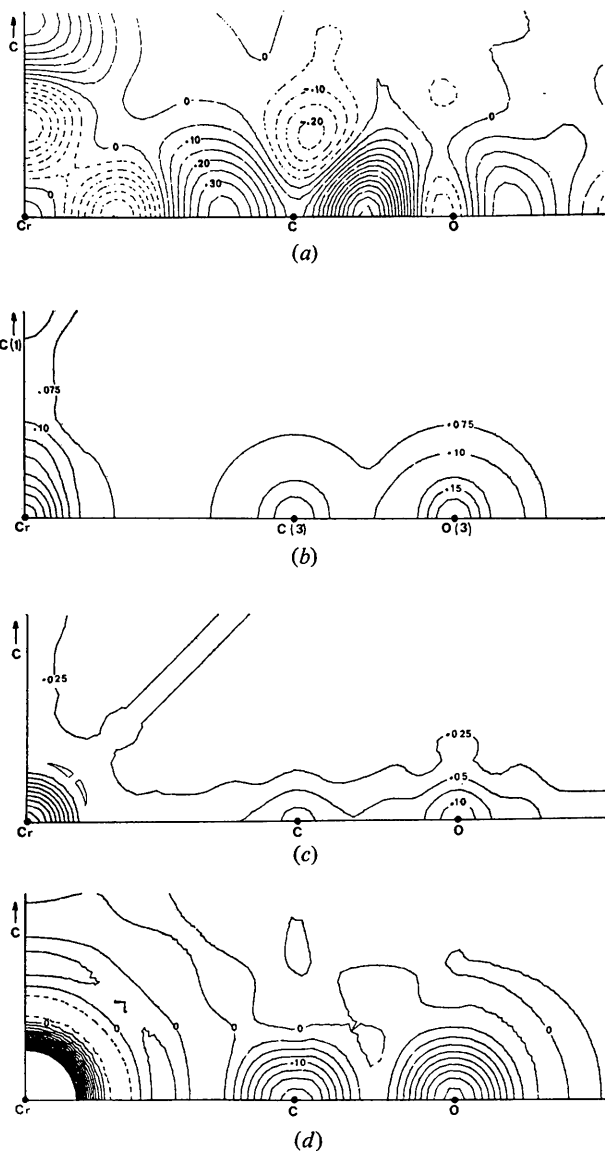


Fig. 4. Deformation electron density  $\Delta q = q_o/k - q_c$  in  $\text{Cr}(\text{CO})_6$  at a resolution  $\lambda/(2 \sin \theta)_{\max} = 0.66 \text{ \AA}$ , (a) Average deformation density  $\Delta\bar{q}$ . Contour intervals at  $0.05 \text{ e \AA}^{-3}$ , negative contours dotted. (b) Standard deviation  $\sigma(\Delta q)$  (not including the error in the scale factor) before averaging. Cr and C(1) are on the mirror plane. Contour intervals at  $0.025 \text{ e \AA}^{-3}$ . (c) Standard deviation  $\sigma(\Delta\bar{q})$  (not including the error in the scale factor) after averaging. Contours as in (b). (d)  $(q_o/k)/100$ . The contribution of  $F(000)$  is omitted. Contours up to  $0.4 \text{ e \AA}^{-3}$  are represented, with the same interval as in (b). The height of the peak at the chromium nucleus is  $1.21 \text{ e \AA}^{-3}$ .  $|q_o/k|/100$  is approximately the standard deviation of the error in  $\Delta q$  due to the imprecision in the scale factor.

standard deviation is divided by  $\sqrt{12}$ :  $0.019 \text{ e \AA}^{-3}$  instead of  $0.066 \text{ e \AA}^{-3}$ , far from the nuclei. The improvement is of course less in the regions of strong correlations, *i.e.* near to the bond axes or to their bisector.

An estimation of the error due to the scale factor is seen on Fig. 4(d). No experimental determination of the scale factor was attempted for the X-ray data of  $\text{Cr}(\text{CO})_6$ . From the scaling of observed and calculated structure factors with two different methods, a value of  $\frac{1}{100}$  seemed a reasonable estimation of  $\sigma(k)/k$ . Fig. 4(d) shows a map of  $q_o/100k$ . In this map, the contribution of  $F(000)$  is omitted, since this term is not included in the calculation of  $\Delta\bar{q}$ . Note that  $q_o/100k$  is the quantity which is added to  $\Delta\bar{q}$  of Fig. 4(a) when the scale factor is reduced by 1%.

#### Remark on the effect of series termination

All the formulae derived so far for the estimation of variances and covariances show the essential importance of the reciprocal-sphere limit  $H_{\max} = (2 \sin \theta/\lambda)_{\max}$ , in the synthesis of electron density. When more and more terms are added in the summation, the variance increases indefinitely. This has been considered as an absurdity, but the paradox is only apparent. It should be kept in mind that the determined electron density (which may be  $q_o$ ,  $q_c$  or  $\Delta q$ ) is in fact the convolution  $q_{H_{\max}}$  of the corresponding density for complete resolution,  $q_{\infty}$  by a resolution function depending on  $H_{\max}$ :

$$q_{H_{\max}}(\mathbf{r}) = \int q_{\infty}(\mathbf{r} - \mathbf{t}) g_{H_{\max}}(\mathbf{t}) d^3t. \quad (21)$$

$g_{H_{\max}}(\mathbf{t})$  is the Fourier transform of the step function  $G_{H_{\max}}(\mathbf{H})$ , equal to 1 inside the sphere of radius  $H_{\max}$ , and to 0 outside. It is spherically symmetric, and may be expressed as a function of  $u = 2\pi t H_{\max}$ :

$$g_{H_{\max}}(u) = V_{\max} C(u) \quad (22)$$

where  $V_{\max}$  is the volume of the reciprocal sphere and  $C(u)$  is the theoretical correlation coefficient given by equation (8).  $g_{H_{\max}}/V_{\max}$  is thus represented by the curve of Fig. 2(a). This is not surprising, since the covariance in  $q_o$  is precisely due to the convolution (21).

The choice of  $H_{\max}$  must result from a compromise between the best possible resolution and the lowest possible imprecision. For an optimal value of  $H_{\max}$ , the derivatives  $\partial \sigma[q_{H_{\max}}(\mathbf{r})]/\partial H_{\max}$  and  $\partial |q_{H_{\max}}(\mathbf{r})|/\partial H_{\max}$  should be approximately equal: when  $H_{\max}$  becomes larger than the optimal value, the first derivative becomes larger than the second. The gain in resolution is then overcompensated by the increase in errors, and one adds essentially background fluctuations to the density function. But since both derivatives depend on  $\mathbf{r}$ , the optimal value of  $H_{\max}$  would depend on the region which is considered in the crystal: it would be larger for regions of high curvature than for regions of low curvature, so that the definition of a unique optimal value of  $H_{\max}$  is difficult. Anyhow, the necessity should be emphasized of a clear specification of  $H_{\max}$

or, as for example in protein structure work, of the resolution  $\lambda/(2 \sin \theta)_{\max}$ , whenever experimental electron density maps are published.

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## X-ray Diffraction from a 6H Structure Containing Intrinsic Faults

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The theory of X-ray diffraction from a one-dimensionally disordered 6H structure (*ABCACB*) containing a random distribution of 14 unique intrinsic fault configurations has been developed. An exact expression for the diffracted intensity has been derived in terms of the coefficients of the characteristic equation and the boundary conditions by applying Holloway's method of analytic solution. This expression is then used to obtain the diffracted intensity in reciprocal space as a function of the 14 fault probabilities, assuming these to be small. Observable diffraction effects like peak broadening, peak shift and the change in the peak intensity are discussed for different single-crystal reflexions. A unique evaluation of all 14 fault probabilities is not possible from an experimental measurement of diffraction effects. However, it is often possible to neglect certain fault probabilities on the basis of physical considerations such as the stacking-fault energy and the mechanism of formation of faults in the 6H structure.

### Introduction

Recently we have shown (Pandey & Krishna, 1975*a*, *b*, *c*, *d*) that all the observed polytype structures in lead iodide, cadmium iodide and silicon carbide can result from spiral growth round a single screw dislocation created in a basic structure containing random stacking faults. The basic structures, which are the more commonly found small-period modifications, are different in different materials (Verma & Krishna, 1966). Thus the basic structure in  $\text{PbI}_2$  is type  $2H(A\gamma B)$ ; those in  $\text{CdI}_2$  are  $2H(A\gamma B)$  and  $4H(A\gamma BC\alpha B)$  while those in SiC are  $6H(A\alpha B\beta C\gamma A\alpha C\gamma B\beta)$ ,  $15R(A\alpha B\beta C\gamma B\beta A\alpha B\beta C\gamma A\alpha C\gamma B\beta C\gamma A\alpha B\beta A\alpha C\gamma)$  and  $4H(A\alpha B\beta C\gamma B\beta)$ . The range of interaction, as defined by Jagodzinski (1949*a*), extends to two, three, four and six layers for the  $2H$ ,  $4H$ ,  $6H$  and  $15R$  structures respectively. Stacking-fault energy in all these materials is very low (Stevens, 1972; Prasad & Srivastava, 1970) and the basic structures frequently contain a random distribution of stacking faults. This produces diffuse streaks connecting X-ray diffraction maxima that orig-

inate from reciprocal-lattice rows parallel to  $c^*$ . The concentration of stacking faults varies considerably from one crystal to another but the average value of the fault-order degree, as measured experimentally, is reported to be 0.12 for SiC and 0.26 for  $\text{CdI}_2$  (Jagodzinski, 1954; Jain & Trigunayat, 1970). The theory of X-ray diffraction from randomly faulted close-packed structures with a range of interaction up to three layers has been developed by several workers (Wilson, 1942; Hendricks & Teller, 1942; Jagodzinski, 1949*a*, *b*; Paterson, 1952; Gevers, 1954; Kakinoki & Komura, 1952; Kakinoki, 1967; Johnson, 1963; Holloway, 1969; Prasad & Lele, 1971).

Gevers (1954) has developed the theory of X-ray diffraction from close-packed structures with a four-layer range of interaction. Lele (1974*a*, *b*, *c*) has extended the theory to a stage where the fault probabilities are directly related to the experimentally observable diffraction effects for the structures  $6H$ ,  $9R$  and  $12R$ . We have shown in an earlier publication that there are 18 possible intrinsic fault configurations that can occur in the  $6H$  structure (Pandey & Krishna, 1975*c*, *d*). Of