Short Communications

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A priori estimates of the errors in experimental electron densities. By E. D. STEVENS and P. COPPENS, *Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214, *U.S.A.*

A priori estimates of the suitability of a particular crystal for charge density analysis are discussed in terms of a simple criterion based on core electron concentration and a more detailed evaluation of the anticipated errors in the final deformation density maps. Predictions are compared with the results obtained in a series of studies and the implications for the design of a charge density analysis are discussed. It is found that counting statistics has often been a major contributor to the standard deviation of the charge density.

Experimental charge density analysis leads to information on the distortion of the valence electron distribution relative, for example, to the distribution corresponding to a superposition of spherical atoms. The electrons in the inner shells are essentially unperturbed within the resolution of the X-ray experiment (Groenewegen, Zeevalkink & Feil, 1971; Bentley & Stewart, 1974) and their presence results in charge density measurements being increasingly difficult when heavier atoms are present.

If we write the atomic scattering factors as a sum of the core and valence scattering:

$$f = f_{core} + f_{valence} \qquad (1)$$

then, to a first approximation

$$\langle F_{core}^2 \rangle = \sum_{unit\ cell} f_{core}^{\prime 2} = \sum_{unit\ cell} n_{core}^2 \qquad (2)$$

where n is the number of core electrons. When different crystals are compared the volume V of the unit cell has to be accounted for which leads to

$$S = \frac{V}{(\sum n_{core}^2)} \qquad (3)$$

as a possible measure for the core electron contribution to the observed structure factors and therefore as a suitability criterion for charge density analysis. S represents an inverse square core electron distribution and its value varies from typically 3–5 for first-row atom organic crystals to 0·1–0·3 for metals and alloys (Table 1).

Table 1. *Suitability factors for various crystals*

	V	V/Z	$\sum n_{core}^2$	S
Formamide	223·6	55·9	12	4·7
α-Glycylglycine	579·0	144·8	36	4·0
α-Deuterooxalic acid dihydrate	255·4	127·7	32	4·0
Tetracyanoethylene	897·8	149·6	40	3·7
Cr(CO)$_3$C$_6$H$_6$	419·5	209·8	372	0·56
Cr$_2$(O$_2$C$_2$H$_3$)$_4$.2H$_2$O	1392·2	348·1	720	0·48
Ni$_2$(C$_2$H$_2$) (C$_5$H$_5$)$_2$	1058·6	264·7	696	0·38
Cl$_2$	225·2	56·3	200	0·28
S$_8$ (orthorhombic)	3292·9	205·8	800	0·26
Si	157·5	19·7	100	0·19
Al	66·4	16·6	100	0·17
V$_3$Si	105·7	52·85	1072	0·05

However, a more complete *a priori* estimate of errors in the charge deformation is possible. In order to obtain significant results from an electron density distribution study by diffraction methods, the experiment must be designed so that the error $\sigma(\Delta\varrho)$ in the deformation density

$$\Delta\varrho = \frac{\varrho_{obs}}{k} - \varrho_{calc} \qquad (4)$$

is sufficiently less than the magnitude of density features. Since bond and lone pair peaks are often 0·30 to 0·50 e Å^{-3}, the total $\sigma(\Delta\varrho)$ in these areas should be less than 0·10 e Å^{-3}. Here, a number of approximations are considered for the contributions to the error in $\Delta\varrho$ in order to estimate in advance the suitability of a particular crystal structure for electron density studies and to aid in the design of the experiment. After completion of the experiment, the error distribution can be calculated without approximation as described by Rees (1976).

Assuming the errors in the observed structure factors, refined parameters, and scale factor k to be uncorrelated, the variance is given by

$$\sigma^2(\Delta\varrho) = \frac{\sigma^2(\varrho_{obs})}{k^2} + \sigma^2(\varrho_{calc}) + \left[\frac{\sigma^2(k)}{k^2}\right]\left[\frac{\varrho_{obs}^2}{k^2}\right]$$

$$= \sigma^2(\varrho_{obs}^\prime) + \sigma^2(\varrho_{calc}) + (\varrho_{obs}^\prime)^2\left[\frac{\sigma^2(k)}{k^2}\right] \qquad (5)$$

where $\varrho_{obs}^\prime = \varrho_{obs}/k$ and k is defined by $F_{obs} = kF_{calc}$.

The contribution to $\sigma(\Delta\varrho)$ due to the error in the scale factor $\sigma(k)$ depends on the value of ϱ_{obs} at the point of interest. Approximating $\varrho_{obs}^\prime$ by

$$\varrho_{obs}^\prime = \sum_i \varrho_i \text{ (spherical atom)} \qquad (6)$$

where ϱ_i is the contribution of the *i*th atom to the density at the point of interest, and using the atomic scattering factors expressed as a sum of Gaussian terms (*International Tables for X-ray Crystallography*, 1974)

$$f_i(\sin \theta/\lambda) = \sum_{j=1}^{5} A_{ij} \exp(-B_{ij} \sin^2 \theta/\lambda^2), \qquad (7)$$

the thermally smeared atomic density can be obtained analytically

$$\varrho_i(x,y,z)=\int\limits_\infty^\infty\int\int \sum_j A_{i,j} \exp\left(-B_{i,j}\sin^2\theta/\lambda^2\right)$$

$$\times \exp\left(-T_i\sin^2\theta/\lambda^2\right)\exp[2\pi i(hx+ky+lz)]dhdkdl \quad (8)$$

$$=\sum_j A_{i,j}\left(\frac{4\pi}{B_{i,j}+T_i}\right)^{3/2}\exp-[4\pi^2(x^2+y^2+z^2)/(B_{i,j}+T_i)], \quad (9)$$

where T_i is an isotropic temperature factor; x,y,z are coordinates in Å in a Cartesian coordinate system, and h,k,l are the corresponding reciprocal space coordinates.

The contribution from errors in the refined positional and thermal parameters, U_m, in the approximation that correlations are negligible, is given by

$$\sigma^2(\varrho_{calc})=\sum_m\left(\frac{\partial\varrho_{calc}}{\partial U_m}\right)^2\sigma^2(U_m). \quad (10)$$

The derivatives can be obtained in analytical form from expression (9). Average values of $\sigma(x)$ and $\sigma(T)$ for each type of atom can be estimated from previous experience. There is often, however, substantial correlation between thermal parameters and the scale factor, which can be included explicitly

$$\sigma^2(\varrho_{calc})=\sum_m\left(\frac{\partial\varrho_{calc}}{\partial U_m}\right)^2\sigma^2(U_m)$$

$$+2\sum_m\left(\frac{\partial\varrho_{calc}}{\partial U_m}\right)\sigma(U_m)\varrho_{obs}'\frac{\sigma(k)}{k}\gamma(U_m,k) \quad (11)$$

where the $\gamma(U_m,k)$ are correlation coefficients. Since the $(\partial\varrho_{calc}/\partial U_m)$ for thermal parameters are negative near the nuclear positions, and the correlation coefficients are positive, the total error in these areas is not as large as predicted from considering $\sigma(\varrho_{calc})$ and $\sigma(k)$ alone.

In Table 2, values of $\sigma(\varrho_{calc})$ and $\varrho_{obs}'[\sigma(k)/(k)]$ are tabulated for various positions in the structure of chromous acetate $[Cr_2(O_2C_2H_3)_4.2H_2O]$. The contribution to $\sigma(\Delta\varrho)$ from the error in the scale factor and errors in the positional and thermal parameters are largest at the atom centers. As has been noted earlier, experimental electron density maps suffer an unmanageable bias near the nuclear positions (Stewart, 1968) and no significance can be attached to experimental deformation densities in this region. Also tabu-

lated in Table 2 is the total contribution from $\sigma(\varrho_{calc})$ and $\sigma(k)$ including the correlation between the thermal parameters and the scale factor.

The contributions to the variance due to errors in the observations on a centrosymmetric crystal

$$\sigma^2(\varrho_{obs}')=\frac{1}{V^2}\sum_{hkl}\sigma^2(F)\cos^2 2\pi(hx+ky+lz) \quad (12)$$

can be approximated (Cruickshank, 1949) for a point in a general position by

$$\sigma^2(\varrho_{obs}')=\frac{2}{V^2}\sum_{1/2}\sigma^2(F), \quad (13)$$

provided that all observable Fourier coefficients have been measured so that series termination effects can be neglected, otherwise F_{calc} should replace $\sigma(F)$ in (13) for these terms. The variance of a measurement is often estimated by

$$\sigma^2(I)=I+C^2I^2. \quad (14)$$

An estimate of the constant C may be obtained from the internal agreement of measurements of symmetry-related reflections of strong intensity. Apart from intensity correction factors, the value of F^2 is related to the intensity by $I=F^2k^2$ where the scale factor k depends on crystal size, incident beam intensity, and details of the measurement technique.

Since

$$\sigma^2(F)=\sigma^2(F^2)/4F^2$$

$$\sigma^2(F)=\frac{1}{4k^2}+\frac{C^2F^2}{4}, \quad (15)$$

then, in the approximation of expression (13):

$$\sigma^2(\varrho_{obs}')=\frac{1}{V^2}\left(\frac{N}{4k^2n_1}+\frac{C^2\sum F^2}{4n_1}\right) \quad (16)$$

where n_1 is the number of symmetry-equivalent reflections included in the average and N is the number of reflections in the sphere of radius $2\sin(\theta_{max})/\lambda$,

$$N=\tfrac{4}{3}\pi\left(\frac{2\sin\theta_{max}}{\lambda}\right)^3 V/n_2 \quad (17)$$

with n_2 being equal to the multiplicity factor due to centering of the cell. The sphere is assumed to be large enough to include all observable reflections. Since the average value

Table 2. *Estimates of $\sigma(\varrho_{calc})$ and $\varrho_{obs}'[\sigma(k)/k]$ for the structure of* $Cr_2(O_2C_2H_3)_4.2H_2O$ *at 80K in units of* e Å^{-3}
(*DeLucia, Stevens & Coppens*, 1976)

Calculated using the following estimated standard deviations obtained from least-squares refinement: $\sigma(k)/k=0.0017$; $\bar\sigma_x(Cr)=0.001$, $\bar\sigma_x(O)=0.007$, $\bar\sigma_x(C)=0.008$, $\bar\sigma_x(H)=0.04$ Å; $\bar\sigma_T(Cr)=0.002$, $\bar\sigma_T(O)=0.012$, $\bar\sigma_T(C)=0.012$, $\bar\sigma_T(H)=1.0$ Å^2.

	I	II	III	IV
				Total including correlation between
Atom center	$\sigma(\varrho_{calc})$	$\varrho_{obs}'\left[\dfrac{\sigma(k)}{k}\right]$	Total $\sqrt{(I^2+II^2)}$	k and T
Cr	2·897	1·023	3·072	2·208
O	0·2627	0·1427	0·2990	0·2375
C	0·1791	0·1039	0·2071	0·1628
H	0·0005	0·0019	0·0019	0·0016
Bond midpoint				
Cr–Cr	0·0001	0·0005	0·0006	0·0004
Cr–O	0·0003	0·0009	0·0009	0·0008
O–C	0·0010	0·0039	0·0040	0·0031
C–H	0·0006	0·0028	0·0029	0·0024

Table 3. *Comparison of $\sigma(\varrho'_{obs})$ estimated for recently completed charge density studies with $\sigma(\varrho'_{obs})$ found*

	I	I	III	IV	V	VII	VIII	IX
	$\sigma(\varrho'_{obs})$ found e Å^{-3}	$\sigma(\varrho'_{obs})$ estimate* e Å^{-3}	$\dfrac{1}{V}\left(\dfrac{N}{4k^2n_1}\right)^{1/2}$ e Å^{-3}	$\dfrac{1}{V}\left(\dfrac{C^2\sum F^2}{4n_1}\right)^{1/2}$ e Å^{-3}	C_{exp}	$\dfrac{\sin\theta_{max}}{\lambda}$ Å^{-1}	n_1	n_2
Formamide[a]†	0·028	0·020	0·019	0·005	0·038	0·85	2	1
Glycylglycine[b]†	0·056	0·041	0·040	0·008	0·015	0·85	3	1
KN$_3^a$	0·025	0·023	0·019	0·013	0·015	1·20	5	2
Cr$_2$(O$_2$C$_2$H$_3$)$_4$.2H$_2$O[c]†	0·066	0·058	0·055	0·020	0·025	1·25	4	2
Cl$_2^a$†	0·049	0·038	0·035	0·015	0·050	1·20	6	2
S$_8^a$	0·056	0·060	0·023	0·055	0·022	0·70	4	4

* With $C = 0·02$. † Low-temperature study.
(a) Stevens (1976). (b) Griffin & Coppens (1975). (c) DeLucia, Stevens & Coppens (1976). (d) Coppens, Blessing, Yang & Larsen (1976).

of F^2 is $\langle F^2\rangle = \sum_i f_i^2$, the sum $\sum\langle F^2\rangle$ can be obtained from the scattering factors expressed in analytical form

$$\sum\langle F^2\rangle = \sum_i(\sum_i f_i^2) = V\int\int\int^{\infty}\sum_i\sum_{jk}A_{ij}A_{ik}$$

$$\times\exp[-(B_{ij}+B_{ik}+2T_i)\sin^2\theta/\lambda^2]dhdkdl \quad (18)$$

$$=\sum_i\sum_{jk}A_{ij}A_{ik}\left(\frac{4\pi}{B_{ij}+B_{ik}+2T_i}\right)^{3/2}V, \quad (19)$$

where h,k,l are Cartesian reciprocal coordinates in Å^{-1}.

If the measurement conditions remain the same, the scale factor can be estimated from the volume of the crystal and previous experience. Thus, taking a typical value for C ($\sim 0·02$), all of the contributions to $\sigma(\Delta\varrho)$ can be estimated before the start of the experiment with only a general knowledge of the structure and the appropriate temperature parameter. If the estimate of $\sigma(\Delta\varrho)$ is larger than an acceptable amount in the region of interest, the experiment can be changed, *i.e.* slower scans and more measurements of symmetry equivalents for $\sigma(\varrho_{obs})$, more careful collection of neutron or high-order X-ray data for $\sigma(\varrho_{calc})$, and careful experimental measurement of the scale factor to reduce $\sigma(k)$.

The suitability criterion, S, described earlier is an approximation to expression (16). Neglecting the first term in this expression and using $\langle\sum f_i^2\rangle = \sum\langle F^2\rangle/N$, it can be shown that

$$\frac{1}{\sigma^2(\varrho'_{obs})}\simeq \text{constant}\times\frac{V}{\langle\sum f_i^2\rangle} \quad (20)$$

in which the average value of $\sum f_i^2$ is approximately equal to $\sum n_{core}^2$. Therefore, S is simply related to an estimate of one contribution to the error that can be expected in a $\Delta\varrho$ map.

In order to test the approximations given by expressions (16), (17), and (19) predicted values of $\sigma(\varrho'_{obs})$ have been calculated for a number of recently completed charge density studies. In Table 3 the results are compared with the values of $\sigma(\varrho'_{obs})$ given by expression (13). Also included are

experimental details such as C, the constant in expression (14), and n_1 and n_2.

The values of $\sigma(\varrho'_{obs})$ in Table 3 do not correlate well with S values for two reasons. First, experimental precision as represented by the proportionality constant C differs between experiments. In addition the contribution to $\sigma(\varrho'_{obs})$ of the first term in expression (16) (Table 3, column III) is dominant when S is large as for formamide and glycylglycine. This implies that increased accuracy (and better correlation with S) would be achieved in these cases if the experiment could be designed such as to increase k, and thereby improve counting statistics. The scale factor k will be smaller for more complicated structures (fewer unit cells per unit volume), but is also dependent on beam intensity, scan speed and crystal size. Thus, in these cases a slower scan or the use of a larger crystal, at least in measuring the weaker reflections, will be needed to lower error estimates in the experimental electron density.

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