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Errors in Deformation-Density and Valence-Density Maps: The Scale-Factor Contribution

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A formulation for the variance–covariance estimate of the deformation or valence density is given for a centrosymmetric crystal, taking into account correlations with the scale factor, when this is determined by the usual scaling procedure. It is shown that, when heavy atoms are present in the crystal, the scaling procedure is likely to result in better precision than an independent experimental determination of the scale factor.

Most experimental studies of the charge density distribution in crystals deal with the deformation density

$$\Delta\rho(\mathbf{r}) = \rho_o^u(\mathbf{r})/k - \rho_c(\mathbf{r}) \qquad (1)$$

where ρ_o^u is the Fourier transform of the unscaled observed structure factors $F_o^u \exp(i\alpha)$, k is a scale factor and ρ_c is the density calculated in the spherical-atom approximation. ρ_c depends on the positional and thermal parameters p_i, which are generally obtained by least-squares refinement from neutron or high-angle X-ray data.

In a previous study of the accuracy of $\Delta\rho$ (Rees, 1976), statistical independence of all the quantities F_o^u, p_i and k was assumed. However, when the usual scaling procedure is used to determine k, the correlation between k and the p_i's (especially the temperature parameters) cannot be neglected, as was emphasized by Stevens & Coppens (1976). A formulation taking such correlations into account will be given here.

ρ_o^u and ρ_c are obtained by Fourier transformation of F_o^u and F_c, respectively, at a given resolution characterized by $H_{\max} = 2 \sin \theta_{\max}/\lambda$:

$$\rho(\mathbf{r}) = \sum_{H<H_{\max}} C(\mathbf{H},\mathbf{r})\, F(\mathbf{H}) \qquad (2)$$

$$C(\mathbf{H},\mathbf{r}) = \frac{2}{V} \sum_{l=1}^{n} \cos 2\pi(\mathbf{H}_l \cdot \mathbf{r} - \alpha_l)$$

(sum over n crystallographically equivalent reflections).

When the same set of reflections as in the Fourier summations (2) is used to determine the scale factor k, the least-squares adjustment of the observed and calculated structure factors yields the value:

$$k = \sum_{H<H_{\max}} wF_o^uF_c \Big/ \sum_{H<H_{\max}} wF_c^2 \qquad (3)$$

with: $w = [\sigma(F_o^u)/k]^{-2}$.

By substitution into (1), differentiation, and some rearrangement, the following expression is obtained for the covariance of $\Delta\rho$ at two points $\mathbf{r}_A$ and $\mathbf{r}_B$, in the case of a centrosymmetric structure (in the non-centrosymmetric case, the error in the phases α must be considered):

$$\begin{aligned}\operatorname{cov}[\Delta\rho(\mathbf{r}_A), \Delta\rho(\mathbf{r}_B)] = &\sum_{H<H_{\max}} \{C(\mathbf{H},\mathbf{r}_A)\, C(\mathbf{H},\mathbf{r}_B)\\ &\times \sigma^2[F_o^u(\mathbf{H})]/k^2\} + [\rho_o(\mathbf{r}_A)\rho_o(\mathbf{r}_B) - \rho_o(\mathbf{r}_A)\rho_c(\mathbf{r}_B)\\ &- \rho_o(\mathbf{r}_B)\rho_c(\mathbf{r}_A)]\sigma_o^2(k)/k^2\\ &+ \sum_i \sum_j [A_i(\mathbf{r}_A)A_j(\mathbf{r}_B) \operatorname{cov}(p_i,p_j)] +\\ &+\rho_o(\mathbf{r}_A)\rho_o(\mathbf{r}_B)\, \sigma^2_{\text{model}}(k)/k^2 \end{aligned} \qquad (4)$$

where: $\rho_o = \rho_o^u/k$;

$$A_i(\mathbf{r}) = \sum_{H<H_{\max}} \left[C(\mathbf{H},\mathbf{r}) \frac{\partial F_c}{\partial p_i} \right] + \rho_o(\mathbf{r}) \frac{1}{k} \frac{\partial k}{\partial p_i}; \qquad (5)$$

$$\sigma_o^2(k)/k^2 = 1/ \sum_{H<H_{\max}} wF_c^2 \qquad (6)$$

$$\frac{1}{k}\frac{\partial k}{\partial p_i} = \sum_{H<H_{\max}} \left[w(F_o^u/k - 2F_c) \frac{\partial F_c}{\partial p_i} \right] \Big/ \sum_{H<H_{\max}} wF_c^2. \qquad (7)$$

Note that the contribution of $F(000)$, (the average electron density), which is known without error on an absolute scale, is not included in ρ_o in (2).

The variance of $\Delta\rho$ is given by (4) where $\mathbf{r}_A = \mathbf{r}_B$. This equation applies also when $\Delta\rho$ is the valence density: in this case F_c in (5) must be replaced by the structure factor of the core electrons.

$\sigma_o^2(k)$ is the part of the variance of k due to the uncertainty in the F_o^u's. The corresponding contribution to the uncertainty of $\Delta\rho$ is generally negative, because of the correlations introduced by the scaling procedure, which are responsible for the negative part in the second term of (4). The correlation between k and the p_i's is expressed by the second term of (5) and tends also to reduce the uncertainty, since the two terms of (5) are generally of opposite sign (an increase in ρ_c

Table 1. *Model dependence of the scale factor in* $Cr(CO)_6$

a, *b*, *c* and *d* are the centres of Gaussian charge distributions on the Cr–C–O bond axes, at the following distances from the Cr nucleus: (*a*) 0·65 Å (chromium asphericity), (*b*) 1·35 Å (carbon lone pair), (*c*) 2·50 Å (CO bonding), (*d*) 3·50 Å (oxygen lone pair).

	Charges							
Model	Cr	C	O	*a*	*b*	*c*	*d*	$(\Delta k/k)\times 10^3$
1	0	0	0	0	0	0	0	0
2	+0·20	0	0	0	0	0	0	2·1
3	0	+0·20	0	0	0	0	0	0·1
4	0	0	−0·20	0	0	0	0	−1·3
5	+0·15	+0·09	−0·12	0	0	0	0	0·8
6	−0·15	+0·25	+0·07	+0·05	−0·10	−0·15	−0·10	0·2
7	−0·57	+0·44	+0·25	+0·12	−0·22	−0·30	−0·20	−1·4

results in a decrease of k). The only part of the uncertainty of k which makes a positive contribution is thus that due to the inadequacy of the free-atom model used in the scaling procedure, and is expressed by the last term of (4).

The preceding equations were applied to the case of chromium hexacarbonyl (Rees & Mitschler, 1976). The deformation density $\Delta\rho$ was computed with a cut-off value $H_{\max} = 2 \sin \theta_{\max}/\lambda = 1{\cdot}52$ Å^{-1}.

$\sigma_{\rm model}(k)$ was estimated from structure-factor calculations with different models, which are summarized in Table 1. The spherical free-atom model (model 1) is taken as reference. Charged spherical atoms are considered in models 2 to 5. Scattering factors of a partially occupied valence shell (2p electrons for C and O, 3d for Cr) were used in those calculations. The charges of model 5 are the net atomic charges, as obtained by a numerical integration procedure (Rees & Mitschler, 1976). In models 6 and 7, spherical charge distributions were placed on the bond axes, at the locations experimentally observed in the deformation-density maps, with a Gaussian form factor, $\exp(-6 \sin^2 \theta/\lambda^2)$. The charges of model 6 result from an approximate integration of the corresponding peaks of the deformation density. Note that models 5, 6 and 7 describe a neutral molecule. From the dispersion of the values of the scale factor of the table, $\sigma_{\rm model}(k)/k = 0{\cdot}002$ seems a reasonable estimate.

Since the other contributions to $\sigma(k)$ can only reduce the error of $\Delta\rho$, it is interesting to note that the precision of the scaling procedure is better than that which can be reasonably expected from an experimental determination of the scale factor [$\sigma(k)/k \simeq 0{\cdot}01$ (Stevens & Coppens, 1975)]. This, however, is because of the presence of the heavy chromium atom. A test calculation on carbon monoxide ($H_{\max} = 1{\cdot}5$ Å^{-1}; mean square amplitude of motion: $U = 0{\cdot}015$ Å^2) showed that the scale factor obtained with the free-atom model was in excess by 3·8%, compared with the Hartree–Fock molecule (McLean & Yoshimine, 1967). This error is not very dependent on $H_{\max}$, but becomes somewhat smaller (2·5%) when a larger thermal motion ($U = 0{\cdot}06$ Å^2) is considered.

Fig. 1 shows the various contributions to the estimated standard deviation of $\Delta\rho$ along one of the bond axes in $Cr(CO)_6$. The dashed curves show the effect of the correlation of the scale factor with the observed intensities (curve *a*) and the parameters p_i (curve *b*). The former is seen to be negligible but the latter is important in the heavy-atom region. Both are negative, as discussed above. The contribution of $\sigma_{\rm model}(k)$ is predominant within about 0·3 Å from the chromium nucleus, but is generally negligible elsewhere.

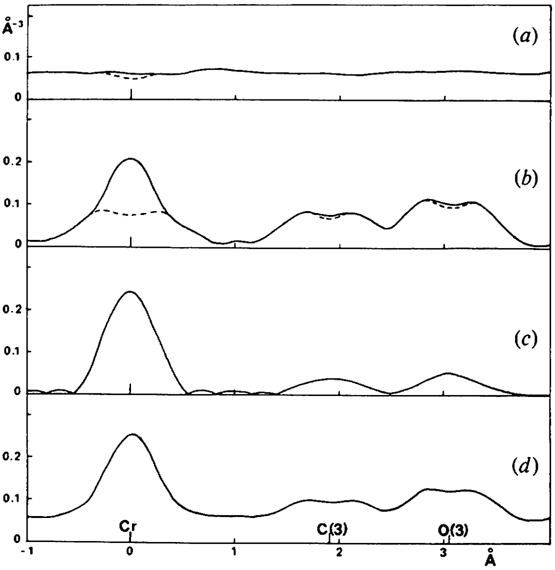

Fig. 1. Error estimate in $Cr(CO)_6$, along one bond axis, The different contributions to $\sigma(\Delta\rho)$ are shown. (*a*) Uncertainty due to errors in F_o. Full line: no correlation with the scale factor assumed. Dashed line: scale factor determined by least-squares fit. (*b*) Uncertainty due to errors in the positional and thermal parameters. Full line: no correlation with the scale factor. Dashed line: scale factor by least-squares fit. (*c*) Uncertainty due to the use of the free-atom model in the determination of the scale factor [$\sigma_{\rm model}(k)/k = 0{\cdot}002$]. (*d*) Total estimated standard deviation of $\Delta\rho$.

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Strukturmöglichkeiten für Pentahalogenide mit Doppeloktaeder-Molekülen $(MX_5)_2$ bei dichtester Packung der Halogenatome

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The crystal structures of the dimeric pentahalides $(MX_5)_2$ have a close-packed arrangement of halogen atoms in which one fifth of the octahedral holes are occupied by metal atoms. From considerations of the geometrical possibilities of arranging the molecules and thereby resulting symmetry restrictions, the possible space groups and structures are elucidated with the aid of group–subgroup relationships. It is shown that only certain space groups can be achieved. Among the centrosymmetric space groups these include: 1. $C2/m$, $C2/c$ and $C\bar{1}$ for hexagonal close packing when octahedral holes are occupied between layers A and B but not between B and A; 2. $Pnma$, $Pnmn$, $Pnab$, $C2/m$, $P2/m$, $P2_1/m$, $P2_1/a$ and $P\bar{1}$ for h.c.p. when holes between all pairs of layers are occupied; 3. $P2_1/m$, $P2_1/a$ and $P\bar{1}$ for the double hexagonal close packing; 4. $I4_1/a$, $Bbmb$, $Fddd$ and the monoclinic and triclinic space groups for cubic close packing. The more important arrangements are illustrated and their expected cell dimensions are given. The results are compared with the known structures of the pentachlorides of Nb, Ta, Mo, W, U and Re, $(NbBr_5)_2$, β-$(PaBr_5)_2$, and also $(WSCl_4)_2$ and $(WSBr_4)_2$. It is deduced that the previously published structure of niobium pentaiodide is probably in error. Predictions are made for likely structures of $(TaI_5)_2$, α-$(PaBr_5)_2$, $(PaI_5)_2$ and $(UBr_5)_2$.

Bei Bemühungen in der Vergangenheit, Verwandtschaftskriterien für Kristallstrukturen aufzustellen und die Strukturen systematisch zu ordnen, wurden Symmetriebeziehungen meist nur wenig beachtet. Erst nachdem Neubüser & Wondratschek (1966, 1969) eine Liste der Gruppe–Untergruppe-Beziehungen der kristallographischen Raumgruppen vorgelegt haben, wurde von Bärnighausen (1975) damit begonnen, systematische Strukturvergleiche aufgrund von Symmetriebetrachtungen anzustellen (Bärnighausen, Klee & Wondratschek, 1975). Die Anstrengungen konzentrierten sich bisher darauf, Strukturähnlichkeiten verschiedener Verbindungen aufzuzeigen, deren Symmetrie über Gruppe–Untergruppe-Beziehungen verwandt ist. Diese Beziehungen lassen sich aber auch heranziehen, um vorauszusagen, welche Raumgruppen überhaupt möglich sind, wenn eine Verbindung gegebener Zusammensetzung unter Einhaltung bestimmter Randbedingungen kristallisieren soll. Dies geschieht nachfolgend am Beispiel der Pentahalogenide mit dimerer Molekülstruktur $(MX_5)_2$. Diese Molekülstruktur ist charakteristisch für Metallpentahalogenide mit Ausnahme der Fluoride (weitere Ausnahmen sind bekannt, z.B. $SbCl_5$, $PaCl_5$).

Randbedingungen

Bei der Herleitung von möglichen Kristallstrukturen für $(MX_5)_2$-Moleküle sollen folgende Randbedingungen gelten:

1. Die Halogenatome X sollen eine hexagonal-, doppelt-hexagonal- oder kubisch-dichteste Kugelpackung annehmen.
2. Die Metallatome M sollen Oktaederlücken dieser Packung besetzen, wobei die Stöchiometrie festsetzt, dass es ein Fünftel aller Oktaederlücken sein muss.
3. Damit der Aufbau aus $(MX_5)_2$-Molekülen gewährleistet ist, müssen immer die Lücken zweier benachbarter Oktaeder mit gemeinsamer Kante besetzt werden, die Lücken aller weiteren Nachbaroktaeder müssen unbesetzt bleiben.

Bei Einhaltung dieser Randbedingungen sind nur

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