

discerned, some important fundamental features of bonding and structure will be apparent. Structural quadrics should be a useful concept for future work in crystallography.

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## On the Statistics of Atomic Deviations from the 'Best' Molecular Plane

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### Abstract

An expression for the variance of a deviation of an atom from the best plane of the group to which the atom belongs has been derived and a practical procedure for obtaining the variance, while neglecting correlations between different atoms, is suggested.

One of the results of a structural study, particularly relevant for unsaturated or aromatic organic compounds, is the degree of planarity of a group of atoms. The deviations of the atoms from the best plane of the group are often interpreted in terms of interatomic and/or intermolecular forces, and in order to put such interpretations on a sound basis, it is often of interest to find out how significant these deviations really are. Since the statistics of deviation of atoms from the best plane, and their implementation in practical calculations, have not been, to the author's knowledge, discussed in the crystallographic literature, it was thought desirable to deal with this subject as described in what follows. This can, of course, be presented in a general and rigorous manner, *e.g.* by discussing the transformation of the variance-covariance matrix to the coordinate system of interest (Cramér, 1951). It seems, however, that the evaluation of the variance of an atomic position along a given direction is more appropriate to the level of approximation usually adopted in crystallographic studies.

The usual statistical treatments of the linear transformation of a vector of random variables, and its variance-covariance matrix, assume that all the quantities are referred to a Cartesian system (*e.g.* Linnik, 1961). This is not suitable for our purpose, since the transformations involved include, at least in part, a transition from the triclinic to a Cartesian system and *vice versa*, but can be readily modified as shown below.

We assume here that the frequency distribution of the position of an atom (the outcome of a least-squares refinement) obeys the trivariate normal law (*e.g.* Cruickshank, 1967), with the true position as the mean.

Let

$$\xi^T = (\xi^1 \xi^2 \xi^3), \quad \mathbf{x}^T = (x^1 x^2 x^3) \quad (1)$$

be the possible (random) and mean atomic position vectors, expressed in contravariant components (Patterson, 1967). Then the expectation value

$$\mathbf{B} = E[(\xi - \mathbf{x})(\xi - \mathbf{x})^T] \quad (2)$$

is the variance-covariance matrix of such a position vector. In practice,  $B^{ij}$  is given by  $\lambda^{ij} \sigma(x^i) \sigma(x^j)$ , where  $\lambda^{ij}$  are the correlation coefficients and  $\sigma$  the estimated standard deviation.

Let now

$$\hat{\mathbf{k}}^T = (k_1 k_2 k_3) \quad (3)$$

be a constant unit vector, expressed in *covariant* components (in our case referred to the reciprocal-lattice basis vectors). The scalar product  $\hat{\mathbf{k}}^T(\xi - \mathbf{x})$  is

also a random variable, with zero mean and with variance

$$\begin{aligned}\sigma_{\hat{\mathbf{k}}}^2 &= E[\mathbf{k}^T(\boldsymbol{\xi} - \mathbf{x})(\boldsymbol{\xi} - \mathbf{x})^T \hat{\mathbf{k}}] = \hat{\mathbf{k}}^T \mathbf{B} \hat{\mathbf{k}} \\ &= \sum_{i=1}^3 \sum_{j=1}^3 k_i k_j B^{ij}.\end{aligned}\quad (4)$$

Hence, the standard deviation of an atomic position, taken in any direction  $\hat{\mathbf{k}}$ , is given by the square root of the quadratic form (4).

Turning to the deviations from the best plane, we define  $\mathbf{z}_{(n)} = \boldsymbol{\xi}_{(n)} - \mathbf{x}_{(n)}$  and  $\mathbf{z}_{(0)} = \boldsymbol{\xi}_{(0)} - \mathbf{x}_{(0)}$  as the vectors of statistical deviations of the  $n$ th atom and of the centroid of the group, respectively, from their average positions. We further take  $\hat{\mathbf{k}}$  as a unit vector, normal to the best plane. The mean deviation of the  $n$ th atom from the best plane is then given by

$$\bar{\Delta}_n = E[\hat{\mathbf{k}}^T(\mathbf{z}_{(n)} - \mathbf{z}_{(0)})] = \hat{\mathbf{k}}^T(\mathbf{x}_{(0)} - \mathbf{x}_{(n)}) \quad (5)$$

(Rollett, 1965) and the variance of this deviation is

$$\begin{aligned}\sigma^2(\Delta_n) &= D^2[\hat{\mathbf{k}}^T(\mathbf{z}_{(n)} - \mathbf{z}_{(0)})] \\ &= E[\hat{\mathbf{k}}^T(\mathbf{z}_{(n)} - \mathbf{z}_{(0)})(\mathbf{z}_{(n)} - \mathbf{z}_{(0)})^T \hat{\mathbf{k}}] \\ &= \hat{\mathbf{k}} \mathbf{B}_{(n)} \hat{\mathbf{k}} + \hat{\mathbf{k}}^T \mathbf{B}_{(0)} \hat{\mathbf{k}} - \hat{\mathbf{k}}^T [E(\mathbf{z}_{(n)} \mathbf{z}_{(0)}^T) \\ &\quad + E(\mathbf{z}_{(0)} \mathbf{z}_{(n)}^T)] \hat{\mathbf{k}},\end{aligned}\quad (6)$$

where  $\mathbf{B}_{(n)} = E(\mathbf{z}_{(n)} \mathbf{z}_{(n)}^T)$  and  $\mathbf{B}_{(0)} = E(\mathbf{z}_{(0)} \mathbf{z}_{(0)}^T)$  are the variance-covariance matrices of atom  $n$  and the centroid of the group respectively. The first two quadratic forms in the last line of (6) are, by analogy with (4), the variances of atom  $n$  and the centroid, along the plane normal  $\hat{\mathbf{k}}$ , while the last two quadratic forms in (6) depend primarily on correlations between positional uncertainties of different atoms. Interatomic correlations and hence the corresponding contributions to the variance of  $\Delta_n$  will be neglected in this paper.

It remains to relate the variance-covariance matrix of the centroid to the (usually available) atomic positional uncertainties. The deviation of the centroid from its mean position can be written as

$$\mathbf{z}_{(0)} = \boldsymbol{\xi}_{(0)} - \mathbf{x}_{(0)} = \sum_{p=1}^N \alpha_p (\boldsymbol{\xi}_{(p)} - \mathbf{x}_{(p)}) \quad (7)$$

where  $\alpha_p = w_p / \sum_{q=1}^N w_q$ ,  $w_q$  are the weights assigned to the atoms in the best-plane calculation (Rollett, 1965) and  $N$  is the number of atoms in the group which is tested for planarity. The contravariant components of  $\mathbf{B}_{(0)}$  are given by

$$\begin{aligned}B_{(0)}^{ij} &= E(z_{(0)}^i z_{(0)}^j) \\ &= E\left\{ \left[ \sum_p \alpha_p (\xi_{(p)}^i - x_{(p)}^i) \right] \left[ \sum_q \alpha_q (\xi_{(q)}^j - x_{(q)}^j) \right] \right\} \\ &= \sum_p \sum_q \alpha_p \alpha_q E[(\xi_{(p)}^i - x_{(p)}^i)(\xi_{(q)}^j - x_{(q)}^j)] \\ &= \sum_p \sum_q \alpha_p \alpha_q B_{(pq)}^{ij},\end{aligned}\quad (8)$$

and since the interatomic correlations are neglected, (8) reduces to

$$B_{(0)}^{ij} = \sum_p \alpha_p^2 B_{(p)}^{ij} = \sum_p w_p^2 B_{(p)}^{ij} / \left( \sum_q w_q \right)^2. \quad (9)$$

The following practical procedure follows from the above considerations, assuming that the atomic fractional coordinates and the (3 × 3) atomic positional variance-covariance matrices, referred to the crystal system, are available.

1. Carry out the best-plane calculation and refer the plane normal (unit vector)  $\hat{\mathbf{k}}$  to the reciprocal-lattice basis  $\mathbf{a}^*$ ,  $\mathbf{b}^*$ ,  $\mathbf{c}^*$  (see also Appendix, where a possible way of doing this is indicated).

2. Calculate the components of the centroid variance-covariance matrix from (9) and evaluate  $\sigma_{(0)\hat{\mathbf{k}}}^2 = \hat{\mathbf{k}}^T \mathbf{B}_{(0)} \hat{\mathbf{k}}$ .

3. Calculate the standard deviations of the deviations from the best plane as

$$\sigma(\Delta_n) = [\hat{\mathbf{k}} \mathbf{B}_{(n)} \hat{\mathbf{k}} + \sigma_{(0)\hat{\mathbf{k}}}^2]^{1/2}, \quad (10)$$

with the atomic variance-covariance matrices  $\mathbf{B}_{(n)}$ , and find the ratios  $\Delta_n / \sigma(\Delta_n)$  for assessing the statistical significance of the deviations from the best plane.

The method described above is still somewhat approximate, mainly because of the neglect of interatomic correlations and to a small extent due to an implicit error-free direction of the plane normal. A comparison of (8) and (9) indicates that the neglect of interatomic correlations may affect the variance of the centroid to a possibly large extent but even if all the correlations are allowed for, this variance can never exceed corresponding average variance of an atomic position, and will usually be appreciably smaller than the latter. It appears that the contribution of  $\mathbf{B}_{(0)}$  may be important when the number of the atoms involved is small. The procedure suggested in this paper has been programmed and is being used in this laboratory (e.g. Shaanan & Shmueli, 1980).

It should also be mentioned that a least-squares estimate of the standard deviation of the centroid can be obtained directly as a by-product of a constrained refinement calculation which is referred to the inertial system of the group considered (cf. Shmueli & Goldberg, 1974) and in which the position of the centroid is being refined.

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In any such calculation we evaluate or have access to the following transformation relating the crystal and the best-plane systems

## APPENDIX

The best-plane calculation is conveniently referred to a Cartesian system with origin at the centroid of the group of atoms involved, and with axes directed along the eigenvectors of a matrix which has the same functional form as that of the tensor of inertia (e.g. Rollett, 1965). Denoting the unit vectors of this Cartesian system by  $\hat{\mathbf{v}}_1, \hat{\mathbf{v}}_2, \hat{\mathbf{v}}_3$  and the crystal and reciprocal-lattice basis vectors by  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  and  $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$  respectively, we can express an atomic position vector as

$$\mathbf{r} = \sum_k X_k^I \hat{\mathbf{v}}_k = \sum_l x_l^{cc} \mathbf{a}_l, \quad (A1)$$

where  $X_k^I, k = 1, 2, 3$ , are Cartesian coordinates, referred to the best-plane system and  $x_l^{cc}, l = 1, 2, 3$ , are fractional coordinates, referred to the centroid of the group as origin and to the crystal system.

We further have the scalar products

$$\mathbf{r} \cdot \hat{\mathbf{v}}_p = \sum_k X_k^I \hat{\mathbf{v}}_k \cdot \mathbf{v}_p = \sum_k X_k^I \delta_{kp} = X_p^I \quad (A2)$$

and

$$\mathbf{r} \cdot \mathbf{a}_p^* = \sum_l x_l^{cc} \mathbf{a}_l \cdot \mathbf{a}_p^* = \sum_l x_l^{cc} \delta_{lp} = x_p^{cc} \quad (A3)$$

since  $\mathbf{v}_k$  are orthonormal and  $\mathbf{a}_l$  and  $\mathbf{a}_p^*$  are mutually reciprocal sets of basis vectors.

$$X_k^I = \sum_l R_{kl} x_l^{cc}. \quad (A4)$$

Comparing (A2) and (A3) with (A4) it is seen that the rows of the matrix  $\mathbf{R}$  contain the components of the vectors  $\hat{\mathbf{v}}_k, k = 1, 2, 3$ , referred to the reciprocal vectors  $\mathbf{a}_1^*, \mathbf{a}_2^*$  and  $\mathbf{a}_3^*$ . One of the  $\hat{\mathbf{v}}$  vectors corresponds to the plane normal, and its representation, required for evaluating the perpendicular variances, discussed in the text, is thus a by-product of a conventional best-plane calculation.

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## Hydrocarbon Chain Disorder in C-phase Potassium Caprate and its Associated Diffuse Scattering

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### Abstract

Structural studies of the crystalline monoclinic C phase of the potassium soap  $\text{K}^+ \cdot \text{C}_{10}\text{H}_{19}\text{O}_2^-$  (space group  $P2_1/a$ ,  $a = 8.145 \pm 0.044$ ,  $b = 5.726 \pm 0.010$ ,  $c =$

$28.309 \pm 0.061 \text{ \AA}$ ,  $\beta = 94^\circ 35' \pm 46'$ ,  $Z = 4$ ) stable above 349 K are reported. Analysis of the Bragg diffraction data demonstrates that the heavy end group and the first four carbon atoms in the hydrocarbon chain, C(1) to C(4), retain the ordered configuration of the room-temperature A phase. The remainder of the chain, C(5) to C(10), is disordered. The disordered segments of chain adopt an average parallel packing on

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