From (7) it is seen that (8) and (9) can be written in the conventional form (Murnaghan, 1951; Nye, 1957):

$$\mathbf{\varepsilon} = \tfrac{1}{2}(\mathbf{\xi}+\mathbf{\xi}^{T})$$

$$\mathbf{\eta} = \tfrac{1}{2}(\mathbf{\xi}+\mathbf{\xi}^{T}+\mathbf{\xi}^{T}\mathbf{\xi}).$$

Finally, expressing $\mathbf{\xi}$ in these equations by (4), it can be shown that (Schlenker, Gibbs & Boisen, 1978; Catti, 1985)

$$\mathbf{\varepsilon} = \tfrac{1}{2}(\mathbf{O}'^{-1}\mathbf{O}+\mathbf{O}^{T}\mathbf{O}'^{-1T})-\mathbf{I}$$

$$\mathbf{\eta} = \tfrac{1}{2}(\mathbf{O}^{T}\mathbf{O}'^{-1T}\mathbf{O}'^{-1}\mathbf{O}-\mathbf{I}).$$

Concluding remarks

We can express all these matrix relations in the following tensor diagram which illustrates the one-to-one correspondence between the tensors $\mathbf{gS}$, $\mathbf{D}$ and $\mathbf{d}$ in the crystallographic reference frame and the tensors $\mathbf{\xi}$, $\mathbf{\eta}$ and $\mathbf{\varepsilon}$ in the Cartesian reference frame:
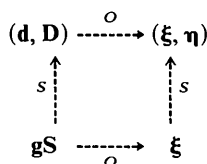
where O and S denote orthogonalization and symmetrization operations.

Therefore, mathematically we can visualize the homogeneous lattice deformation as a transformation of the basis vectors in the crystallographic reference frame or as a transformation of the atomic coordinates in the Cartesian reference frame.

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Calculation of the point-by-point error in protein crystallographic electron-density functions.

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Abstract

In protein crystallographic studies, the mean-square error at each point in the electron-density function is given, in space group $P1$, by

$$\sigma^{2}(\mathbf{x}) = (1/V^{2}) \sum_{\text{all } \mathbf{h}} F_{o}^{2}[1-m(\mathbf{h})^{2}]$$

$$+ (1/V^{2}) \sum_{\text{all } \mathbf{h}} F_{o}^{2}\{m_{2}(\mathbf{h}) \exp[i\alpha_{2}(\mathbf{h})]$$

$$- m(\mathbf{h})^{2} \exp[2i\alpha_{B}(\mathbf{h})]\} \exp(-4\pi i\mathbf{h}.\mathbf{x}).$$

Here, F_{o} is the observed structure-factor amplitude; $m(\mathbf{h}) \exp[i\alpha_{B}(\mathbf{h})] = \int P[\alpha(\mathbf{h})] \exp(i\alpha) \, d\alpha$ is the weighted phase factor in the 'best' Fourier coefficient of Blow & Crick; $m_{2}(\mathbf{h}) \exp(i\alpha_{2}) = \int P[\alpha(\mathbf{h})] \exp(2i\alpha) \, d\alpha$ is similar to a traditional second moment. $P[\alpha(\mathbf{h})] \, d\alpha$ is the probability that the phase angle for a given reflection has value between α and $\alpha + d\alpha$.

Introduction

It is common practice in protein crystallography to make estimates of the error in each structure factor $\mathbf{F}(\mathbf{h})$. The most commonly used error models lead to an estimate of $P[\alpha(\mathbf{h})]$, the probability density function for the phase $\alpha(\mathbf{h})$ (Blow & Crick, 1959; Hendrickson & Lattman, 1970). Errors in the structure-factor amplitudes are generally ignored. $P(\alpha)$ is of great importance in developing correct weights for the structure factors in Fourier syntheses. For example, the commonly used 'best' Fourier coefficient of Blow & Crick (1959) uses the centroid-weighted phase factor given in (7).

Little attention has been paid to the corresponding errors in the electron-density function $\rho(\mathbf{x})$. Yet there are many operations, such as solvent flattening and molecular averaging, in which appropriate weighting could be very important. An objective measure of the local quality of the electron-density map might help to distinguish structural

disorder from poor density. To accomplish this, appropriate errors must be associated with each point in the electron-density function. Here we obtain the function $\sigma^2(\mathbf{x})$, the variance of the electron density at point $\mathbf{x}$, given F_o and $P(\alpha)$ for each reflection.

Methods

Space group P1

Let $\mathbf{F_T} = F_T \exp(i\alpha_T)$ be the true or correct structure factor, which we do not know. Let $\mathbf{F_B} = mF_o \exp(i\alpha_B)$ be the structure factor for the best Fourier synthesis of Blow & Crick (Blundell & Johnson, 1976). The difference density between the best and true structures is

$$\Delta\rho = (1/V) \sum_{\mathbf{h}} (\mathbf{F_T} - \mathbf{F_B}) \exp(-2\pi i\mathbf{h}.\mathbf{x}). \qquad (1)$$

The square of $\Delta\rho$, the quantity we wish to estimate, is given by

$$\Delta\rho^2 = (1/V^2) \sum_{\mathbf{h}} (\mathbf{F_T} - \mathbf{F_B}) \exp(-2\pi i\mathbf{h}.\mathbf{x})$$
$$\times \sum_{\mathbf{k}} (\mathbf{F_T} - \mathbf{F_B}) \exp(-2\pi i\mathbf{k}.\mathbf{x}). \qquad (2)$$

Collecting Friedel mates, since these are not independent observations, one finds that

$$\Delta\rho^2 = (1/V^2) \left\{ \sum_{\substack{1/2 \\ \text{sphere}}} (\mathbf{F_T} - \mathbf{F_B}) \exp(-2\pi i\mathbf{h}.\mathbf{x}) \right.$$
$$\left. + (\mathbf{F_T^*} - \mathbf{F_B^*}) \exp(2\pi i\mathbf{h}.\mathbf{x}) \right\}$$
$$\times \left\{ \sum_{\substack{1/2 \\ \text{sphere}}} (\mathbf{F_T} - \mathbf{F_B}) \exp(-2\pi i\mathbf{k}.\mathbf{x}) \right.$$
$$\left. + (\mathbf{F_T^*} - \mathbf{F_B^*}) \exp(2\pi i\mathbf{k}.\mathbf{x}) \right\}. \qquad (3)$$

Consider initially terms in the product of the two summations for which $\mathbf{h} = \mathbf{k}$. The general term of this type is

$$(\mathbf{F_T} - \mathbf{F_B})^2 \exp(-4\pi i\mathbf{h}.\mathbf{x}) + (\mathbf{F_T^*} - \mathbf{F_B^*})^2 \exp(4\pi i\mathbf{h}.\mathbf{x})$$
$$+ 2(\mathbf{F_T} - \mathbf{F_B})(\mathbf{F_T^*} - \mathbf{F_B^*}).$$

We make the usual approximation that $|\mathbf{F_T}| = F_o$, thus assuming that all error is in the phases. The general term for $\mathbf{h} = \mathbf{k}$ then reduces to

$$F_o^2 \{ [\exp(i\alpha_T) - m \exp(i\alpha_B)]^2 \exp(-4\pi i\mathbf{h}.\mathbf{x})$$
$$+ [\exp(-i\alpha_T) - m \exp(-i\alpha_B)]^2 \exp(4\pi i\mathbf{h}.\mathbf{x})$$
$$+ 2[\exp(i\alpha_T) - m \exp(i\alpha_B)]$$
$$\times [\exp(-i\alpha_T) - m \exp(-i\alpha_B)] \}. \qquad (4)$$

Since we do not know α_T we follow the procedure of Blow & Crick, and compute expectation values for each reflection using $P(\alpha)$, which is assumed to be normalized. Consider the first term within the curly brackets in (4). Expanding the square yields

$$\{ \exp(2i\alpha_T) - 2m \exp(i\alpha_B) \exp(i\alpha_T) + m^2 \exp(2i\alpha_B) \}$$
$$\times \exp(-4\pi i\mathbf{h}.\mathbf{x}). \qquad (5)$$

We compute the expectation value of $\exp(2i\alpha_T)$ using

$$\int_0^{2\pi} P(\alpha) \exp(2i\alpha) \, d\alpha \equiv m_2 \exp(i\alpha_2), \qquad (6)$$

and of $\exp(i\alpha_T)$ by the definition

$$\int_0^{2\pi} P(\alpha) \exp(i\alpha) \, d\alpha \equiv m \exp(i\alpha_B). \qquad (7)$$

Thus the first term in the curly brackets in (4) becomes

$$F_o^2 \{ m_2 \exp(i\alpha_2) - m^2 \exp(2i\alpha_B) \} \exp(-4\pi i\mathbf{h}.\mathbf{x}). \qquad (8)$$

The second term is the complex conjugate of this. The third is

$$2|\mathbf{F_T} - \mathbf{F_B}|^2 = 2F_o^2 \{ \exp(i\alpha_T) - m \exp(i\alpha_B) \}$$
$$\times \{ \exp(-i\alpha_T) - m \exp(-i\alpha_B) \}$$
$$= 2F_o^2(1 - m^2). \qquad (9)$$

The last step makes use of the expectation value of $\exp(i\alpha_T)$ in (7). Thus - still ignoring terms for which $\mathbf{h} \neq \mathbf{k}$ - we can write the final form of (2) for the error in the electron-density function. We have introduced $\sigma^2(\mathbf{x})$ as the function name because it now represents the expected value of the squared error at each point, rather than the actual value, which is unknown.

$$\sigma^2(\mathbf{x}) = (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2 [1 - m(\mathbf{h})^2]$$
$$+ (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2 \{ m_2(\mathbf{h}) \exp[i\alpha_2(\mathbf{h})] - m(\mathbf{h})^2$$
$$\times \exp[2i\alpha_B(\mathbf{h})] \} \exp(-4\mathbf{h}.\mathbf{x}). \qquad (10)$$

Friedel's law has been used to restore the summation limits to a full sphere. The first term in (10) represents the familiar equation for the root-mean-square error in the electron density, averaged over the entire unit cell (Blundell & Johnson, 1976). It enters as the constant term in our series, and its appearance is a comforting suggestion that the calculation is on the right track. The second term in (10) is a Fourier synthesis in which the indices have been doubled, effectively halving the unit cell. One can rationalize this superficially counter-intuitive result by realizing that the error contributed by a single Fourier component does not depend on its sign, since the squared error is being calculated. Thus grid points that are separated by multiples of a half cycle of the component receive equal error contributions. The phase factor $[m_2 \exp(i\alpha_2) - m^2 \exp(2i\alpha_B)]$ contains the difference between the second moment of a distribution, and the square of its first moment - a familiar feature of statistical error or fluctuational analyses.

Terms for which $\mathbf{h} \neq \mathbf{k}$. It is easy to show that terms in (3) for which $\mathbf{h} \neq \mathbf{k}$ make no contribution to $\sigma(\mathbf{x})^2$. A typical term is given by

$$\{ F_T(\mathbf{h}) \exp[i\alpha_T(\mathbf{h})] - m(\mathbf{h}) F_o(\mathbf{h}) \exp[i\alpha_B(\mathbf{h})] \}$$
$$\times \{ F_T(\mathbf{k}) \exp[i\alpha_T(\mathbf{k})] - m(\mathbf{k}) F_o(\mathbf{k}) \exp[i\alpha_B(\mathbf{k})] \}$$
$$\times \exp[-2\pi i(\mathbf{h} + \mathbf{k}).\mathbf{x}]. \qquad (11)$$

The approximation that $F_T = F_o$ allows (11) to be simplified to

$$F_o F_o' \{ [\exp(i\alpha_T) - m \exp(i\alpha_B)]$$
$$\times [\exp(i\alpha_T') - m' \exp(i\alpha_B')] \}$$
$$\times \exp[-2\pi i(\mathbf{h} + \mathbf{k}).\mathbf{x}]. \qquad (12)$$

Expanding the square and replacing $\exp(i\alpha_T)$ and $\exp(i\alpha'_T)$ by their expectation values, as in (5), one gets

$$F_o F'_o \, mm'\{\exp[i(\alpha_B + \alpha'_B)] - \exp[i(\alpha_B + \alpha'_B)]$$
$$- \exp[i(\alpha_B + \alpha'_B)] + \exp[i(\alpha_B + \alpha'_B)]\} = 0. \quad (13)$$

Terms involving complex conjugates give the same result. Thus, (10) represents the final expression for $\sigma^2(\mathbf{x})$ in space group $P1$.

Other space groups

One can calculate $\sigma^2(\mathbf{x})$ for other space groups by a procedure similar to that used above. The main difference is that in (3), where Friedel mates are collected for space group $P1$, all symmetry mates have to be collected within the brackets, since they constitute the set of non-independent observations. A program that takes specific account of the space group is thus required. As a simple example, consider the space group $P2$. To make the notation more compact we introduce

$$\mathbf{W}_{\mathbf{h},\mathbf{x}} = \exp(2\pi i \mathbf{h} \cdot \mathbf{x}), \qquad \Delta \mathbf{F} = \mathbf{F}_T - \mathbf{F}_B,$$

$\mathbf{h}' =$ symmetry mate of $\mathbf{h} = (-h, k, -l)$.

$$\Delta \rho^2 = (1/V^2)\left\{ \sum_{\substack{\mathbf{h}=1/4 \\ \text{sphere}}} \Delta\mathbf{F} \cdot \mathbf{W}_{-\mathbf{h},\mathbf{x}} + \Delta\mathbf{F}^* \cdot \mathbf{W}_{\mathbf{h},\mathbf{x}} \right.$$

$$\left. + \Delta\mathbf{F}' \cdot \mathbf{W}_{-\mathbf{h}',\mathbf{x}} + \Delta\mathbf{F}'^* \cdot \mathbf{W}_{\mathbf{h}',\mathbf{x}} \right\}$$

$$\times (1/V^2)\left\{ \sum_{\substack{\mathbf{k}=1/4 \\ \text{sphere}}} \Delta\mathbf{F} \cdot \mathbf{W}_{-\mathbf{k},\mathbf{x}} + \Delta\mathbf{F}^* \cdot \mathbf{W}_{\mathbf{k},\mathbf{x}} \right.$$

$$\left. + \Delta\mathbf{F}' \cdot \mathbf{W}_{-\mathbf{k}',\mathbf{x}} + \Delta\mathbf{F}'^* \cdot \mathbf{W}_{\mathbf{k}',\mathbf{x}} \right\}. \quad (14)$$

As before, consider only terms for which $\mathbf{k} = \mathbf{h}$. The general term is

$$\Delta\mathbf{F}^2 \cdot \mathbf{W}_{-2\mathbf{h},\mathbf{x}} + \Delta\mathbf{F}^{*2} \cdot \mathbf{W}_{2\mathbf{h},\mathbf{x}} + \Delta\mathbf{F}'^2 \cdot \mathbf{W}_{-2\mathbf{h}',\mathbf{x}} + \Delta\mathbf{F}'^{*2} \cdot \mathbf{W}_{2\mathbf{h}',\mathbf{x}}$$

$$+ 2|\Delta\mathbf{F}|^2 + 2|\Delta\mathbf{F}'|^2 + 2\Delta\mathbf{F} \cdot \Delta\mathbf{F}'\mathbf{W}_{-\mathbf{h}-\mathbf{h}',\mathbf{x}}$$

$$+ 2\Delta\mathbf{F} \cdot \Delta\mathbf{F}'^* \mathbf{W}_{-\mathbf{h}+\mathbf{h}',\mathbf{x}} + 2\Delta\mathbf{F}^* \cdot \Delta\mathbf{F}'\mathbf{W}_{\mathbf{h}-\mathbf{h}',\mathbf{x}}$$

$$+ 2\Delta\mathbf{F}^* \cdot \Delta\mathbf{F}'^*\mathbf{W}_{\mathbf{h}+\mathbf{h}',\mathbf{x}}. \quad (15)$$

The first six terms represent twin sets of terms just like those in the $P1$ equation – one for each asymmetric unit. The remainder involves cross terms between the asymmetric units. Symmetry operations do not change the phase in $P2$. Setting $F_o = |\mathbf{F}_T|$ as before, and using (6)

and (7), we have

$$\sigma^2(\mathbf{x}) = (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2[1 - m(\mathbf{h})^2]$$

$$+ (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2 \{m_2(\mathbf{h}) \exp[i\alpha_2(\mathbf{h})]$$

$$- m(\mathbf{h})^2 \exp[2i\alpha_B(\mathbf{h})]\} \exp(-4\pi\mathbf{h} \cdot \mathbf{x})$$

$$+ (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2\{m_2(\mathbf{h}) \exp[i\alpha_2(\mathbf{h})]$$

$$- m(\mathbf{h})^2 \exp[2i\alpha_B(\mathbf{h})]\} \exp[-2\pi(\mathbf{h}+\mathbf{h}') \cdot \mathbf{x}]$$

$$+ (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2\{m_2(\mathbf{h}) \exp[i\alpha_2(\mathbf{h})]$$

$$- m(\mathbf{h})^2 \exp[2i\alpha_B(\mathbf{h})]\} \exp[-2\pi(\mathbf{h}-\mathbf{h}') \cdot \mathbf{x}]. \quad (16)$$

Crystal and Friedel symmetries have been used to re-expand the summation limits to a full sphere. For high-symmetry space groups the formula for $\sigma^2(\mathbf{x})$ will clearly contain many terms. However, the calculation is easily compressed and fully tractable.

Discussion

As yet little direct experience has been gained with the error function. However, a number of uses come readily to mind. High- and low-quality regions of electron-density maps may be distinguishable, giving guidance about chain tracing through difficult regions. In the case of non-crystallographic averaging, the factor $1/\sigma^2(\mathbf{x})$ provides the correct weight for each point in the average. Hitherto, unit weights have been used. For a set of points related by non-crystallographic symmetry, substantial disagreement between the $\sigma^2(\mathbf{x})$ values and the actual variance of the average could serve as a warning about a possibly misplaced symmetry operator. More speculatively, combining the Fourier transforms of the modified density and the concomitantly modified $\sigma^2(\mathbf{x})$ could allow one to phase the probability density function used in generating the coefficients for the map in the next cycle.

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Improved values of the forward X-ray scattering factor for metallic aluminium.

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Abstract

The real and imaginary parts of the forward X-ray scattering factor of metallic aluminium are reported for photon energies from 10 to 10^4 eV. The imaginary part of the scattering factor $f_2(\omega)$ was derived from the absorption database of Shiles, Sasaki, Inokuti & Smith [*Phys. Rev. B* (1980). **22**, 1612-1628] with the addition of solid-state struc-