Now we consider hypothetical three-dimensional periodic functions $\Phi^*_{aL}(\mathbf{X})$ and $\Phi_{bL}(\mathbf{X})$ composed of φ^*_a and φ_b respectively. Then $\varrho_{BL}(\mathbf{X})$ is given by

$$\varrho_{BL}(\mathbf{X})=\Phi^*_{aL}(\mathbf{X}) \,.\, \Phi_{bL}(\mathbf{X}).$$

We define $\Phi^*_{aL}(\mathbf{X})$ and $\Phi_{bL}(\mathbf{X})$ as,

$$\Phi^*_{aL}(\mathbf{X})=(1/V)\sum_{\mathbf{H}} G^*_a(\mathbf{H}) \exp(2\pi i\mathbf{H} \,.\, \mathbf{X}) \,, \qquad (7)$$

$$\Phi_{bL}(\mathbf{X})=(1/V)\sum_{\mathbf{H}} G_b(\mathbf{H}) \exp(-2\pi i\mathbf{H} \,.\, \mathbf{X}) \,,$$

where

$$G^*_a(\mathbf{H})=\sum_j g^*_{aj} \exp(-2\pi i\mathbf{H} \,.\, \mathbf{X}_j) \,,$$

$$G_b(\mathbf{H}) =\sum_j g_{bj} \exp(2\pi i\mathbf{H} \,.\, \mathbf{X}_j) \,. \qquad (8)$$

Equations (7) and (8) correspond to equations (5) and (6) respectively, that is, $G(\mathbf{H})$ is a 'structure factor of the atomic wave function' and g_j is the Fourier transform of the jth atomic wave function as defined by equation (3). Using the convolution theory we have

$$F_B(\mathbf{H})= \frac{1}{V} \sum_{\mathbf{K}} G^*_a(\mathbf{K}) \,.\, G_b(\mathbf{K}\text{–}\mathbf{H}) \,. \qquad (9)$$

If the Fourier transforms of the atomic wave function, g's, are obtained, the bond structure factor can be calculated from equations (8) and (9).

As a simple example, we consider a hypothetical crystal composed of H_2 molecules which are located at corners of unit cells of a simple cubic lattice with their molecular axis along the **a** direction. The lattice constant of 20 atomic units (a.u.) and the H–H distance of 1·4 a.u. were assumed, then the fractional coordinate of the hydrogen nucleus is $x=0{\cdot}70/20=0{\cdot}035$. From equations (8) and (9) we obtain

$$F_B(hkl)=(1/V)\sum_{h',k',l'} g^*(h',k',l')g(h'-h,k'-k,l'-l) \times \cos 2\pi(2h'-h)\,x \,. \qquad (10)$$

$g(hkl)$ is given from the Slater wave function,

$$\varphi(1s)\ (1/\sqrt{\pi}) \exp(-r),$$

by

$$g(hkl)=8\sqrt{\pi}(1+4\pi^2 d^{*2}_{hkl})^{-1} \,, \qquad (11)$$

where d^*_{hkl} is the reciprocal of the spacing of reflection plane (hkl). Calculated values of $F_B(hk0)$ for **a*** and **b*** directions in which $g(h'k'l')$ is taken from $h',k',l'=0$ to $h',k',l'=10$ are shown in Fig. 1. It is found that the contour map of $F_B(hk0)$ which is identical with the bond scattering factor f_B in the simple cubic lattice has an anisotropy enlongated in the **b*** direction.

In order to see the contribution of the bond scattering factor f_B, we consider the structure factor $F_0(hkl)$ without the contribution of f_B. $F_0(hkl)$ of the crystal is given by

$$F_0(hkl)=2f_H \cos 2\pi hx \,, \qquad (12)$$

where

$$f_H=\int \varphi^*(1s)\varphi(1s) \exp(2\pi i\mathbf{H} \,.\, \mathbf{X})\mathrm{d}\mathbf{X}=(1+\pi^2 d^{*2}_{hkl})^{-1} \,.$$

From equation (1) we obtain

$$F_{\mathrm{VB}}(hkl)=(n_a+n_b)\, f_H \cos 2\pi hx+(n_{ab}/S_{ab})f_B, \qquad (13)$$

where $n_a=n_b=1/(1+S_{ab})^2=0{\cdot}6382$ and $n_{ab}=2S^2_{ab}/(1+S^2_{ab})=0{\cdot}7235$ $(n_a+n_b+n_{ab}=2)$ using the VB method, and $S_{ab}=\int\varphi^*_a(1s)\varphi_b(1s)\mathrm{d}r=0{\cdot}7529$. The comparison between $F_{\mathrm{VB}}(hk0)$ and $F_0(hk0)$ for the **a*** and **b*** directions is shown in Fig. 1. We can see clearly that the contribution of bond electrons for the **a*** direction is larger than that for the **b*** direction. This result is reasonable because the molecular axis of H_2 is assumed to lie along the **a** direction, and is similar to the result of McWeeny (1952).

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References

McWeeny, R. (1952). *Acta Cryst.* **5**, 463.
McWeeny, R. (1953). *Acta Cryst.* **6**, 631.
McWeeny, R. (1954). *Acta Cryst.* **7**, 180.
Raccah, P. M., Euwema, R. N., Stukel, D. J. & Collins, T. C. (1970). *Phys. Rev.* **B1**, 756.
Stewart, R. T. (1969). *J. Chem. Phys.* **51**, 4569.
Tomiie, Y. (1958). *J. Phys. Soc. Japan*, **13**, 1030.

Acta Cryst. (1971). A**27**, 186

Small-angle X-ray scattering by solutions: the calculation of radial electron density distributions for long cylinders.

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It is pointed out that a method recently suggested for evaluating the radial density distribution of long rods is not new and the necessary conditions for its application are emphasized by a simple treatment.

Fedorov & Aleshin (1966) described a Hankel transform method of calculating the radial electron density distribution $\varrho(r)$ for long rigid cylindrical molecules with a cylindrical symmetry of $\varrho(r)$ about the rod axis. Carlson & Schmidt (1969), using this method, have examined the relationship between theoretical models for $\varrho(r)$ and calculated distributions when data for the intensity of scattering by dilute solutions are available over a limited range of scattering angle ($s=0$ to $s=s_{\max}$, $s=2 \sin \theta/\lambda$, θ being the Bragg angle).

It is the purpose of the present note to point out that Fedorov & Aleshin's method is not a new one and that the complexities of their analysis can be avoided. In consequence the necessary assumptions for the method to be valid are clarified.

The Fedorov & Aleshin method is a variant of the Fourier—Bessel transform method used, for example, to deduce $\varrho(r)$ from *oriented* preparations of tobacco mosaic virus (Franklin & Holmes, 1958; see for general aspects Vainshtein, 1966).

The expression used by Franklin & Holmes is

$$\varrho(r) = 2\pi \int_0^{s_{\max}} F(s) J_0(2\pi sr) s\,ds \qquad (1)$$

where $F(s)$ is the continuous cylindrically symmetrical equatorial structure factor of the rod (with amplitude and phase) and J_0 is a zero order Bessel function. To apply this equation to the scattering by a dilute solution it is necessary to establish the relationship between $F(s)$ and the observed intensity of scattering by the solution $I(s)$.

This relationship is presented by Burge & Draper (1967) for the special cases of long rigid rods with $\varrho(r) = \text{constant}$, e^{-ar^2}, $r^2e^{-ar^2}$. These results imply the general result

$$I(s) \propto \frac{1}{s} |F(s)|^2 . \qquad (2)$$

Thus equation (1) becomes

$$\varrho(r) \propto \int_0^{s_{\max}} [I(s)]^{1/2} J_0(2\pi sr) s^{3/2} ds \qquad (3)$$

which is essentially the equation of Fedorov & Aleshin (1966).

The necessary conditions for the validity of equation (3) are those for equation (2). These are: (i) $s \gg 1/L$ with L the rod length; the problem of extrapolating $sI(s)$ to zero scattering angle has been considered by Luzzati (1960). (ii) The scattering corresponds entirely (in practice predominantly) to $F(s)$, *i.e.* at a given radius the cylindrically symmetrical rod density is assumed to be constant along its length.

References

BURGE, R. E. & DRAPER, J. C. (1967). *Acta Cryst.* **22**, 6.

CARLSON, R. D. & SCHMIDT, P. W. (1969). *J. Appl. Cryst.* **2**, 297.

FEDOROV, B. A. & ALESHIN, V. G. (1966). *Vysokomol. Soed.* **8**, 1506. English translation in *Polymer Sci. USSR* (1967). **8**, 1657.

FRANKLIN, R. E. & HOLMES, K. C. (1958). *Acta Cryst.* **11**, 581.

LUZZATI, V. (1960). *Acta Cryst.* **13**, 939.

VAINSHTEIN, B. K. (1966). *Diffraction of X-rays by Chain Molecules.* London: Elsevier.

Acta Cryst. (1971). A**27**, 187

The application of direct methods to centrosymmetric structures containing heavy atoms.

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For those reflexions of which the sign is determined by a relatively small number of heavy atoms, the known heavy-atom contribution is subtracted from the observed structure factor to obtain the magnitude and the sign of the light-atom contribution. Thereafter the signs of the reflexions that do not have appreciable heavy atom contributions are found using the triple product sign relationship.

As the solution of structures with a relatively small number of heavy atoms is straightforward in most cases, direct methods of sign determination have been used only rarely for these structures. It will be shown in this communication that the solution can easily be obtained by using the well-known triple product sign relationship

$$S_{\mathbf{h}+\mathbf{h}'} \sim S_{\mathbf{h}} \,.\, S_{\mathbf{h}'} \,. \qquad (1)$$

The procedure described below is similar to the method used by Subramanian (1967) to solve a structure in projection. It is assumed that the positions of the heavy atoms are known and that there is a sufficient number of reflexions whose signs are determined by the heavy atoms. These reflexions do not obey the probability relation (1). On subtracting the heavy atom contribution from the observed structure factors of these reflexions, one obtains the *magnitude* and the *sign* of the light atom contributions for these reflexions. Thereafter one can solve the remaining light atom structure by applying equation (1) to obtain the signs of the reflexions that do not have appreciable contributions from the heavy atoms.

The procedure was used to solve the structure of the complex $Au[S_2C_2(CN)_2]_2Au[S_2CN(C_4H_9)_2]_2$ (to be published). The space group was found to be $P2_1/c$, with two formula units per unit cell. The reflexions hkl ($h=2n$, $k+l=2n$) were all very strong and the gold atoms were placed at the (special) positions 000, $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$. 1337 observed 'strong' reflexions (with equal positive contributions from the gold atoms) and 538 observed 'weak' reflexions (without any contributions from the gold atoms) were used.

The first step was a calculation of the Wilson plot. The following expression (Parthasarathy, 1966) was used:

$$\begin{aligned} \langle I \rangle_{\mathbf{h}} = {} & K_L \langle \textstyle\sum_i^L f_i^2 \exp(-2B_L \sin^2\theta/\lambda^2) \rangle_{\mathbf{h}} \\ & + K_H \langle |F_H|^2 \exp(-2B_H \sin^2\theta/\lambda^2) \rangle_{\mathbf{h}} \end{aligned} \qquad (2)$$

where $I = (K|F_{\text{obs}}|^2)$ is the observed intensity on a relative scale, $K = K_L = K_H$ is the scale factor, $\sum^L$ denotes a summation over all light atoms in the unit cell, F_H is the heavy atom contribution to the structure factor and B_L and B_H are the overall temperature factor parameters of the light and heavy atoms respectively. The average is taken over reflexions $\mathbf{h}$ within a given $\sin\theta$ interval.

For the 'weak' reflexions ($F_H = 0$) the second term in equation (2) vanishes and a Wilson plot for these reflexions gave the scale factor K_L (1·29) and the value of B_L (3·24 Å^2). On substituting these results in equation (2) a Wilson plot for the 'strong' reflexions gave the scale factor K_H (1·26) and the value of B_H (2·91 Å^2). A small difference in K_L and K_H will not effect the following steps.

The second step is the calculation of the normalized structure factors E. The formulae normally used for the calculation of E values do not make sense for a structure containing heavy atoms. For the corresponding light atom