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A geometric approach to the crystal structure problem.

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The structure factors for crystals are defined by

$$F_{hkl}=\sum_{j=1}^{N} f_j(\theta_{hkl})\exp\left[-2\pi i(hx_j+ky_j+lz_j)\right], \qquad (1)$$

where N is the number of atoms in the unit cell, θ_{hkl} is the angle of scattering for F_{hkl}, $f_j(\theta_{hkl})$ is the scattering factor for the jth atom and x_j, y_j, z_j are its co-ordinates in the unit cell. The vector F_{hkl} may be written

$$F_{hkl}=R_{hkl}\exp\left[i\phi_{hkl}\right] \quad (R_{hkl}\geqslant 0,\ -\pi<\phi_{hkl}\leqslant\pi), \qquad (2)$$

where R_{hkl} is the magnitude and ϕ_{hkl} is the phase of F_{hkl}. The crystal structure problem is the problem of solving the system of equations (1) for the atomic co-ordinates x_j, y_j, z_j when, in addition to $f_j(\theta_{hkl})$, only the magnitudes R_{hkl} of the structure factors are known. The problem is completely determinate (assuming the f_j are obtained from tables) if $3(N-1)$ independent magnitudes R_{hkl} are known.

The geometric interpretation of (1) leads to a means for evaluating the atomic co-ordinates.* Equations (1) may be written

$$\sum_{j=1}^{N} f_j\exp\left[-2\pi i(hx_j+ky_j+lz_j)\right]-R_{hkl}\exp\left[i\phi_{hkl}\right]=0. \qquad (3)$$

Equation (3) states that a sum of $N+1$ coplanar vectors of known magnitudes is equal to zero, i.e. the vectors form a closed polygon. In this interpretation

$$f_j\exp\left[-2\pi i(hx_j+ky_j+lz_j)\right]$$

is regarded as a vector whose magnitude is f_j and whose angle is $-2\pi(hx_j+ky_j+lz_j)$.

As an illustration of the solution by means of a geometric-mechanical construction we consider the three-atom problem in one dimension. The number of independent structure-factor magnitudes required to determine the one-dimensional problem is $N-1$. In the three-atom problem we use, for example, R_1 and R_2. The defining equations are

$$\left.\begin{aligned} R_1e^{i\phi_1}&=f_1(\theta_1)\,e^{-2\pi ix_1}+f_2(\theta_1)\,e^{-2\pi ix_2}+f_3(\theta_1)\,e^{-2\pi ix_3},\\ R_2e^{i\phi_2}&=f_1(\theta_2)\,e^{-4\pi ix_1}+f_2(\theta_2)\,e^{-4\pi ix_2}+f_3(\theta_2)\,e^{-4\pi ix_3}.\end{aligned}\right\} \qquad (4)$$

Given the magnitudes R_1, R_2 and the structure factors f_1, f_2, f_3 at the two different scattering angles, there is a unique construction of the two vector sums with the restriction that the phases of the components in the second sum be twice those of the first sum. This is shown in Fig. 1 which illustrates the vector sums (4). The magnitudes of the vectors are given on the rods which are joined together by free moving links. These permit some degree of relative rotation in the plane. If the criterion is imposed that $\alpha_2=2\alpha_1$, $\beta_2=2\beta_1$, as required by equations (4), there is a unique configuration for the two vector sums. We now may read from this configuration the co-ordinates of the atoms along the line as follows:

$x_1=0$ (arbitrarily set), $\quad x_2=-\alpha_1/2\pi, \quad x_3=-(\alpha_1+\beta_1)/2\pi.$

This represents the solution to the problem of three atoms in one dimension. It should be noted that the phases of R_1 and R_2 may be immediately read if desired from the geometric construction. The point to be emphasized is that the solution is obtained by construction from measured *magnitudes* only and tabulated values of the atomic scattering factors. The coupling restrictions on the angles α and β set by (4) determine the unique configuration. The values of α and β are not *known* previous to the construction.

This geometric procedure generalizes in a straightforward fashion. In order to determine the three-dimensional co-ordinates x_j, y_j, z_j, $3(N-1)$ independent experimental magnitudes, R_{hkl}, are required. There are N vectors corresponding to the N atoms in each of the $3(N-1)$ vector sums whose magnitudes are the atom scattering factors for the particular scattering angle. The coupling restrictions on the angles in the geometrical linkages determine the co-ordinates of the atoms in the unit cell. The angles $\alpha, \beta, \ldots$ are, in three dimensions, linear functions of the three atomic co-ordinates.

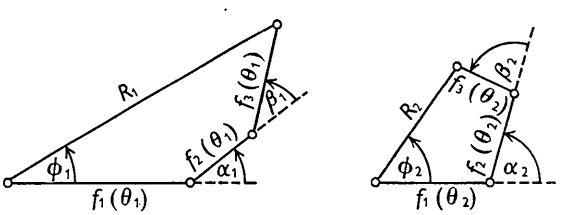

Fig. 1. Illustration of the vector sums of equations (4).

The practical aspects of the geometrical interpretation are apparent. The co-ordinates of the unit cell are obtained immediately by performing a simultaneous set of $3(N-1)$ vector summations subject to the coupling restrictions on the linkage angles $(\alpha_1, \beta_1, \ldots)$ given by equation (1). Since alternating currents combine in the same manner as vectors, an electrical model may be found for this construction.

The following pertinent remarks may be made:

(*a*) The geometric construction permits the immediate determination of the co-ordinates of the unit cell from measured magnitudes of the crystal structure factors and tabulated atomic scattering factors.

(*b*) Since more magnitudes are measured than are required for a solution, these afford a basis for adjusting the internal consistency of the data.

(*c*) The phases of the crystal structure factors are obtained immediately from the geometric construction. From this point of view, however, these phases are not required.

(*d*) No symmetry relations are required in these considerations. The formulation is valid for a triclinic crystal.

(*e*) If only relative intensities are measured an additional magnitude is required to determine the solution.

(*f*) The concept of vector summations with coupling restrictions on the angles joining the vectors lends itself to automatic computing techniques for obtaining the atomic co-ordinates.

* A similar interpretation of (1) was presented by Prof. J. M. Robertson at the Computer and Phase Conference, Pennsylvania State College, 7 April 1950.