14. ANOMALOUS DISPERSION
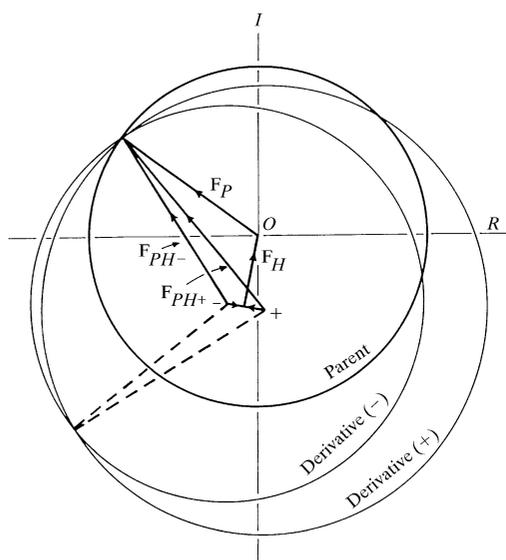

Fig. 14.1.7.2. Harker construction for a single isomorphous replacement with anomalous scattering, in the absence of errors.

Fig. 14.1.8.1. Vector diagrams illustrating lack of closure in the anomalous-scattering method.

The relation between the structure factors of the reflection hkl and its Friedel mate $\overline{hkl}$ is illustrated in Fig. 14.1.7.1(a). The situation can be conveniently represented (Fig. 14.1.7.1b) by reflecting the $\overline{hkl}$ diagram through the real axis onto the hkl diagram. In cases such as this, where Friedel's law breaks down, we shall refer to the difference $\Delta_{PH} = (F_{PH+} - F_{PH-})$ as the Bijvoet difference, or simply the anomalous-scattering difference. The Harker phase circles corresponding to Fig. 14.1.7.1(b) are shown in Fig. 14.1.7.2. It will be seen that, as in the case of single isomorphous replacement, and similarly with the anomalous-scattering data alone, there is an ambiguous phase determination. In the absence of error, the three phase circles (Fig. 14.1.7.2) will meet at a point, resolving the phase ambiguity and giving a unique solution for the phase of $\mathbf{F}_P$. The isomorphous-replacement method gives phase information symmetrical about the vector $\mathbf{F}_H$, whereas the anomalous-scattering phase information for $\mathbf{F}_{PH}$ is symmetrical about $\mathbf{F}_H''$, which, for heavy atoms of the same type, is at right angles to $\mathbf{F}_H$. In other words, the two methods complement each other, one method providing exactly that information which is not given by the other.

On average, the experimentally measured isomorphous-replacement difference, $(F_{PH} - F_P)$, will be larger than the anomalous-scattering difference, $(F_{PH+} - F_{PH-})$. The former, however, relies on measurements from different crystals and is also susceptible to errors due to non-isomorphism between the parent and derivative crystals. The latter can be obtained from measurements on the same crystal, under closely similar experimental conditions, and is not affected by non-isomorphism. Therefore, it is desirable to use methods that take into account the different sources of error in the respective measurements (Blow & Rossmann, 1961; North, 1965; Matthews, 1966b). One method is as follows.

14.1.8. The phase probability distribution for anomalous scattering

From Fig. 14.1.8.1, it can be seen that the most probable phase angle will be the one for which $\varepsilon_+ = \varepsilon_-$. At any other phase angle, there will be an 'anomalous-scattering lack of closure' which we define to be $(\varepsilon_+ - \varepsilon_-)$. The value of $(\varepsilon_+ - \varepsilon_-)$ can readily be calculated as a function of φ (Matthews, 1966b; Hendrickson, 1979). Thus, if the r.m.s. error in $(\varepsilon_+ - \varepsilon_-)$ is E', and the distribution of error is
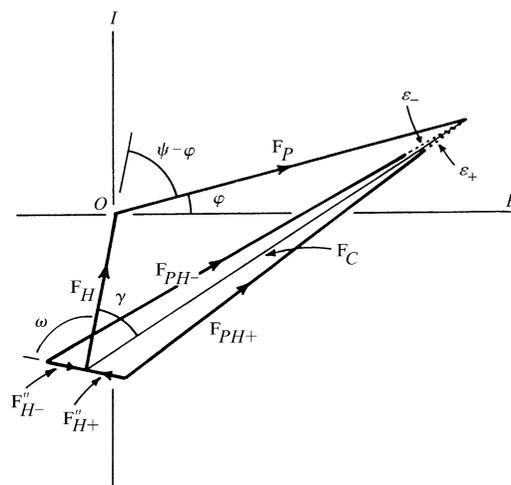
assumed to be Gaussian, then from measurements of anomalous scattering, the probability $P_{ano}(\varphi)$ of phase φ being the true phase of $\mathbf{F}_P$ can be estimated using an equation exactly analogous to equation (14.1.4.2).

An example of an anomalous-scattering phase probability distribution is shown by the dotted curve in Fig. 14.1.8.2. The asymmetry of the distribution arises from the fact that $P_{ano}(\varphi)$ is the phase probability distribution for F_P rather than that of F_{PH}, which would be symmetrical about the phase of F_H''. The overall probability distribution obtained by combining the anomalous-scattering data with the previous isomorphous-replacement data (Fig. 14.1.2.1b) is given by

$$P(\varphi) = N P_{iso}(\varphi) P_{ano}(\varphi) \qquad (14.1.8.1)$$
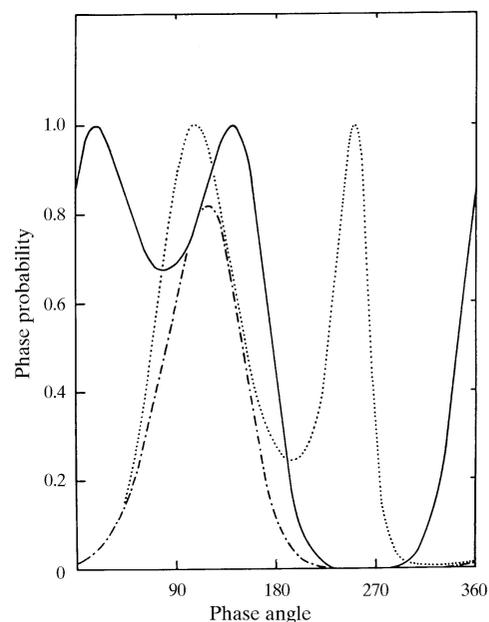
and is illustrated in Fig. 14.1.8.2.

Fig. 14.1.8.2. Combination of isomorphous replacement and anomalous-scattering phase probabilities for a single isomorphous replacement. $P_{iso}(\varphi)$ is drawn as a solid line, $P_{ano}(\varphi)$ as a dotted line, and the combined probability distribution is drawn as a dotted-and-dashed line.

296

references