1.6. METHODS OF SPACE-GROUP DETERMINATION

this method is due to Buerger (1946) and later obtained only a one-sentence reference by Rogers (1950) and by Rossmann & Arnold (2001). The method is based on the observation that interatomic vectors between symmetry-related (other than by inversion in a point) atoms cause peaks to accumulate in the corresponding Harker sections and lines of the Patterson function. It is thus only necessary to find the location of those Harker sections and lines that have a high concentration of peaks to identify the corresponding symmetry operations of the space group. At the time of its discovery, it was not considered an economic method of space-group determination due to the labour involved in calculating the Patterson function. Subsequently it was completely neglected and there are no recent reports of its use. It is thus not possible to report on its strengths and weaknesses in practical modern-day applications.

1.6.2.2. Structure-factor statistics and crystal symmetry

Most structure-solving software packages contain a section dedicated to several probabilistic methods based on the Wilson (1949) paper on the probability distribution of structure-factor magnitudes. These statistics sometimes correctly indicate whether the intensity data set was collected from a centrosymmetric or noncentrosymmetric crystal. However, not infrequently these indications are erroneous. The reasons for this may be many, but outstandingly important are (i) the presence of a few very heavy atoms amongst a host of lighter ones, and (ii) a very small number of nearly equal atoms. Omission of weak reflections from the data set also contributes to failures of Wilson (1949) statistics. These erroneous indications are also rather strongly space-group dependent.

The well known probability density functions (hereafter p.d.f.'s) of the magnitude of the normalized structure factor E, also known as ideal p.d.f.'s, are

$$p(|E|) = \begin{cases} \sqrt{2/\pi}\exp\left(-|E|^2/2\right) & \text{for } P\bar{1}, \\ 2|E|\exp(-|E|^2) & \text{for } P1 \end{cases} \quad (1.6.2.3)$$

where it is assumed that all the atoms are of the same chemical element. Let us see their graphical representations.

It is seen from Fig. 1.6.2.1 that the two p.d.f.'s are significantly different, but usually they are not presented as such by the software. What is usually shown are the cumulative distributions of $|E|^2$, the moments: $\langle|E|^n\rangle$ for $n = 1, 2, 3, 4, 5, 6$, and the averages of low powers of $|E^2 - 1|$ for ideal centric and acentric distributions, based on equation (1.6.2.3). Table 1.6.2.2 shows the numerical values of several low-order moments of $|E|$ and that of the lowest power of $|E^2 - 1|$. The higher the value of n the
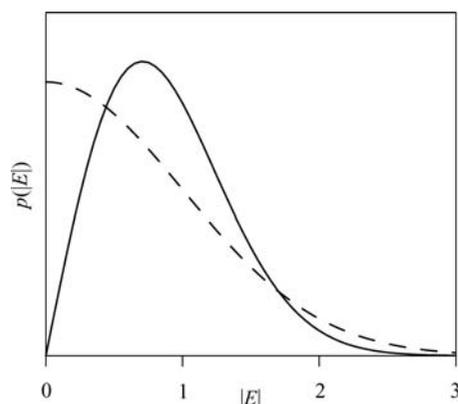

Figure 1.6.2.1
Ideal p.d.f.'s for the equal-atom case. The dashed line is the centric, and the solid line the acentric ideal p.d.f.

Table 1.6.2.2
The numerical values of several low-order moments of $|E|$, based on equation (1.6.2.3)

Moment	$P\bar{1}$	$P1$
$\langle|E|\rangle$	0.798	0.886
$\langle|E|^2\rangle$	1.000	1.000
$\langle|E|^3\rangle$	1.596	1.329
$\langle|E|^4\rangle$	3.000	2.000
$\langle|E|^5\rangle$	6.383	3.323
$\langle|E|^6\rangle$	15.000	6.000
$\langle|E^2 - 1|\rangle$	0.968	0.736

greater is the difference between their values for centric and acentric cases. However, it is most important to remember that the influence of measurement uncertainties also increases with n and therefore the higher the moment the less reliable it tends to be.

There are several ideal indicators of the status of centrosymmetry of a crystal structure. The most frequently used are: (i) the $N(z)$ test (Howells *et al.*, 1950), a cumulative distribution of $z = |E|^2$, based on equation (1.6.2.3), and (ii) the low-order moments of $|E|$, also based on equation (1.6.2.3). Equation (1.6.2.3), however, is very seldom used as an indicator of the status of centrosymmetry of a crystal stucture.

Let us now briefly consider p.d.f.'s that are valid for any atomic composition as well as any space-group symmetry, and exemplify their performance by comparing a histogram derived from observed intensities from a $P\bar{1}$ structure with theoretical p.d.f.'s for the space groups $P1$ and $P\bar{1}$. The p.d.f.'s considered presume that all the atoms are in general positions and that the reflections considered are general (see, *e.g.*, Section 1.6.3). A general treatment of the problem is given in the literature and summarized in the book *Introduction to Crystallographic Statistics* (Shmueli & Weiss, 1995).

The basics of the exact p.d.f.'s are conveniently illustrated in the following. The normalized structure factor for the space group $P\bar{1}$, assuming that all the atoms occupy general positions and resonant scattering is neglected, is given by

$$E(\mathbf{h}) = 2\sum_{j=1}^{N/2} n_j \cos(2\pi\mathbf{h}\mathbf{r}_j),$$

where n_j is the normalized scattering factor. The maximum possible value of E is $E_{\max} = \sum_{j=1}^{N} n_j$ and the minimum possible value of E is $-E_{\max}$. Therefore, $E(\mathbf{h})$ must be confined to the $(-E_{\max}, E_{\max})$ range. The probability of finding E outside this range is of course zero. Such a probability density function can be expanded in a Fourier series within this range (*cf.* Shmueli *et al.*, 1984). This is the basis of the derivation, the details of which are well documented (*e.g.* Shmueli *et al.*, 1984; Shmueli & Weiss, 1995; Shmueli, 2007). Exact p.d.f.'s for any centrosymmetric space group have the form

$$p(|E|) = \alpha\left\{1 + 2\sum_{m=1}^{\infty} C_m \cos(\pi m|E|\alpha)\right\}, \quad (1.6.2.4)$$

where $\alpha = 1/E_{\max}$, and exact p.d.f.'s for any noncentrosymmetric space group can be computed as the double Fourier series

$$p(|E|) = \tfrac{1}{2}\pi\alpha^2|E| \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} C_{mn} J_0[\pi\alpha|E|(m^2 + n^2)^{1/2}], \quad (1.6.2.5)$$

where $J_0(X)$ is a Bessel function of the first kind and of order zero. Expressions for the coefficients C_m and C_{mn} are given by

references