SHORT COMMUNICATIONS

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On space-group frequencies.

By R. Srinivasan, *Department of Crystallography and Biophysics, University of Madras, Madras* 600 025, *India*

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Abstract

In compiling the space-group-frequency table of observed structures, retention of all the 230 space groups is advocated. This is based on some of the fundamental aspects of chirality. For cases both with space-group chirality (case *A*, *e.g.* $P4_1$, $P4_3$ *etc.*) and without (case *B*, *e.g.* $P2_1$, $P2_12_12_1$), possible asymmetric distribution of observed structures over mirror equivalents cannot be ruled out. The need to specify a possible physical attribute to characterize a given crystal and correlate this to the absolute structure in case *B* is pointed out.

The question of the treatment of enantiomeric structures and enantiomeric space groups in the context of space-group frequencies has attracted some debate (Donohue, 1985; Mighell, Himes & Rodgers, 1983; Srinivasan, 1991). Brock & Dunitz (1991) have recently argued that enantiomeric structures, even if experimentally observed and reported, are to be included only once since they are isometric and have equal probability of occurrence arising out of isoenergy consideration. I would like to advance here two principal arguments in support of my earlier contention (Srinivasan, 1991) that the statistics should be concerned only with observed data, including those enantiomeric structures that have been observed and reported but not those based on theoretical argument alone, as was proposed by Donohue. This applies to both (case *A*) pairs of enantiomeric space groups such as $P4_1$ and $P4_3$, $P6_1$ and $P6_5$ *etc.* and (case *B*) enantiomeric space groups such as $P2$, $P2_12_12_1$ *etc.*

The first argument is that conventional chirality of molecular species is a physical reality and it is now well established that its unique determination through X-ray anomalous scattering is, in principle, possible although it is not routinely practised, which is the cause of the uncertainty in space-group assignments in case *A*. The uncertainty, at present, in case *B* is of course in the assignment of the absolute configuration or structure. The argument based on isometry for elimination of one of the enantiomeric structures in counting statistics is no longer adequate, although, for all practical purposes, this might have sufficed up to now. The isometric argument hinges essentially on the equivalence of the corresponding vector sets of the enantiomers. Purely from physical arguments this criterion is insufficient since the two structures are distinct in three dimensions and are separate chiral entities each demanding a physical identity in its own right.

The second argument in this regard is that the statistics over the observed data set are to be interpreted as containing information on the global distribution of observed structures. Since these are essentially organic chemical structures, the observed data (allowing for some fraction of chemically laboratory-synthesized enantiomeric structures) are by and large a reflection of the statistical distribution, at the global level, of the way organic structures resort to space-group preference (including chiral space-group preference in case *A*). Although current listings may not be reliable due to experimental limitations and uncertainty in assignment, there is no reason why precise data cannot be built up, at least in the future, for all the space groups.

In this context some of the findings during the last decade and more on the significance of chirality at subatomic and subnuclear levels and their implications at the molecular and biological evolutionary aspects assume importance. Although the breakdown of the isoenergy assumption on chiral molecules was mooted as early as 1959 (Ulbricht, 1959) based on the discovery of parity nonconservation, more recent work based on the electroweak force seems to provide even more convincing evidence in this respect. In fact, the slight preference, based on energy considerations, for L-amino acids has been calculated* [for a concise review refer to Mason (1984)]. Even though the difference between the L and D forms works out to one in 10^{14} (J mol^{-1}), this has evolutionary significance as far as biomolecules are concerned, in view of the very large time scale involved. From this point of view, for the observed protein structures, natural peptides *etc.* based on L-amino acids, the global absence of corresponding enantiomeric structures are to be construed as an extension of this argument. Although proteins do not at present form part of the current listings, there is no reason to exclude the possibility that other organic structures will be influenced by such an asymmetric distribution, particularly because of the complex biochemical pathways involved in the bio-organic synthesis. In fact, a critical assessment of the choice of space group among chiral pairs and correlation, if any, on chirality at the molecular level would seem highly desirable.

These arguments lead us to conclude that the optimum strategy may be the following.

1. The statistics should be over only observed data sets including enantiomeric structures.
2. Unique space-group assignments (case *A*) and absolute configuration/structure (case *B*) through techniques such as anomalous scattering *etc.* should be

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* Although only organic molecules are cited here, examples from the inorganic world, such as quartz, are also available (see, for example, Mason 1984).

systematically emphasized and encouraged in structure reports.

3. Where uncertainty arises in assignment, a given structure may be incorporated in both enantiomeric space groups but with half the weight (which takes care of the probability aspect and keeps the observed data set unaltered).

If these are acceptable it could raise a moot point whether or not it is desirable to include in case B two subdivisions such as $P2^+/P2^-$ where the +, − symbols refer to, for example, chirality at the molecular level where such a distinction is possible (such as known L- or D-amino acids). Since such prior distinction may not always be possible it is necessary to adopt a more specific and experimentally determinable physical attribute such as optical rotation in the solid state for the specific crystal used for X-ray studies. Although the latter may be difficult from the experimental point of view, the need for such an identification/characterization is felt to be highly desirable.

I would like to thank Professors Brock and Dunitz for a preprint of their letter and Professor K. S. Chandrasekaran for bringing to my attention recent work at the particle-physics level on chirality.

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Use of the Debye–Waller approximation in diffraction-pattern calculation.

By JANUSZ WOLNY, *Faculty of Physics and Nuclear Techniques, Academy of Mining and Metallurgy, al. Mickiewicza* 30, 30-059 *Kraków, Poland*

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Abstract

A new method of diffraction-pattern calculation is proposed and tested on quasicrystals. With use of an appropriately defined reference lattice, a structure factor can be well approximated by a rapidly convergent series expansion of a variable u that describes nearest distances between atomic positions and points of the reference lattice. Only the first few terms are significant for diffraction-pattern calculation. The possibility of using the Debye–Waller approximation is discussed. In this case an appropriate shift of the reference structure is required. Calculations based on the Debye–Waller formula in real and phason spaces give similar results.

Introduction

A new approach to the calculation of diffraction patterns has recently been proposed (Wolny, 1991; Wolny & Pytlik, 1992). The diffraction intensity is calculated in real space using a distribution of atomic positions around a periodic reference lattice of points with period equal to the wavelength for a given scattering wave vector.

For each scattering vector $\mathbf{k}$, a one-dimensional reference lattice of points $\{\boldsymbol{\lambda}_l\}$ can be defined such that

$$\mathbf{k}\cdot\boldsymbol{\lambda}_l = k\lambda_l = 2\pi l, \tag{1}$$

where l is an integer. The vectors $\boldsymbol{\lambda}_l$ are parallel to the scattering vector $\mathbf{k}$ and their lengths are given by

$$\lambda_l = \lambda_0 l, \tag{2}$$

where $\lambda_0 = 2\pi/k$ is the wavelength for scattering vector $\mathbf{k}$. It should be noted that the vectors $\boldsymbol{\lambda}_l$ depend on $\mathbf{k}$, which can be expressed by writing $\boldsymbol{\lambda}_l = \boldsymbol{\lambda}_l(\mathbf{k})$. For any position vector $\mathbf{r}_n$ and its component $\mathbf{r}_n^k$ parallel to $\mathbf{k}$, one can choose a vector $\boldsymbol{\lambda}_l$ such that (Fig. 1)

$$\mathbf{r}_n^k = \boldsymbol{\lambda}_l + \mathbf{u}_n, \tag{3}$$

where the length of $\mathbf{u}_n$ is less than or equal to $\lambda_0/2$. Vectors $\mathbf{r}_n^k$, $\boldsymbol{\lambda}_l$ and $\mathbf{u}_n$ are all parallel. With use of (1) and (3), the structure factor for a finite arrangement of N particles at positions $\mathbf{r}_n$ and with form factor f_n can be written as

$$F(\mathbf{k}) = \sum_{n=1}^{N} f_n \exp(iku_n) = \sum_{n=1}^{N} f_n \sum_{m=0}^{\infty} (iku_n)^m/m!, \tag{4}$$

and since

$$ku_n \le \pi \tag{5}$$

this series expansion is rapidly convergent and the first few terms are dominant.

The real and imaginary parts of the structure factor are given by

$$\mathrm{Re}\,[F(\mathbf{k})] = N(1 - k^2\langle u^2\rangle/2! + k^4\langle u^4\rangle/4! - k^6\langle u^6\rangle/6! + \ldots), \tag{6a}$$

$$\mathrm{Im}\,[F(\mathbf{k})] = N(k\langle u\rangle - k^3\langle u^3\rangle/3! + k^5\langle u^5\rangle/5! - \ldots), \tag{6b}$$

where

$$\langle u^m\rangle = (1/N) \sum_{n=1}^{N} f_n (u_n)^m \tag{7}$$

is an mth moment of variable u. Finally, the intensity of the diffraction pattern for a given scattering vector that is

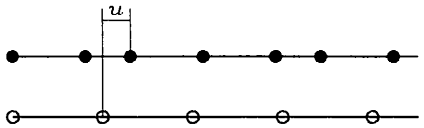

Fig. 1. The variable u describes the shortest distance of the projection of the atomic position (filled circles) from the reference lattice ('wave lattice' - open circles).

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