17. X−5 CRYSTALLOGRAPHIC STATISTICS AND THE DEVELOP-
MENT OF DIRECT METHODS. By J. Karle, Laboratory for
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The earliest probability considerations in crystal struc-
ture analysis were introduced by Wilson (Nature (1942)
150, 152) who showed that intensity data could be cor-
rected for vibrational effects and placed on an absolute
scale by use of a statistical relationship between the
intensities and the atomic scattering factors. This
relationship is employed for the preparation of experi-
mental data for direct phase determining procedures.
Wilson pointed out that the expected values for absolute
intensities is given by

$$\langle I_h \rangle = \sum_{j=1}^{N} f_{jh}^2$$

where f_{jh} is the atomic scattering factor for the jth

atom in a unit cell containing N atoms. He also noted
that the observed intensities I_{hobs} will differ from the

I_h by a scale factor, k independent of θ, and a tempera-

ture factor. By use of the above relation the observed
data can be rescaled and corrected for positional dis-
order. Wilson (Acta Cryst. (1949) 2, 318) also found,
to a very good approximation, probability distributions
for the intensities in non-centrosymmetric and centro-
symmetric crystals that could be used to determine the
presence or absence of a center of symmetry. A number
of studies followed in the attempt to take account of
the presence of heavy atoms, special positions, and the
regularities that occur in crystal structures. One such
study invoked the use of the joint probability distribu-
tion (Hauptman and Karle, Acta Cryst. (1953) 6, 136).
It had an additional purpose, namely, to develop a facil-
ity in deriving joint probability distributions to be
associated with phase determining relations.

The basic phase determining relations, used in proce-
dures for phase determination have had their origins in
inequality theory (Harker and Kasper, Acta Cryst.(1948)
1, 70; Karle and Hauptman, Acta Cryst. (1950) 3, 181).
Inequality theory per se. is only applicable to simple
structures. However, it was apparent that the inequality
relationships could be extended as probabilistic formulas
in order to have formulas applicable to complex struc-
tures. For example, it was observed by Gillis (Acta
Cryst. (1948) 1, 174) that inequalities of Harker and
Kasper still gave correct phase indications even when the
appropriate structure factor magnitudes were of too small
a magnitude to satisfy the conditions of application of
the inequalities. The appropriate mathematical tool for
developing the probabilistic aspects of the inequality
theory was the joint probability distribution. The first
series of investigations concerned centrosymmetric crys-
tals (Hauptman and Karle (1953) Monograph No. 3, American
Crystallographic Association, Polycrystal Book Service:
Western Springs). Further application of probability
theory continued over the years, thus establishing the
mathematical foundations of direct methods. The devel-
opment involves the non-negativity of the electron den-
sity distribution, atomicity and the overdeterminacy of
the experimental data. The foundation mathematics which
is comprised of the phase determining formulas from in-
equality theory and their probabilistic implications
takes proper account of the presence of atoms of unequal
atomic number in crystals.

17. X−6 FOURIER REPRESENTATIONS OF PROBABILITY
DISTRIBUTIONS IN INTENSITY STATISTICS. By G. H.
Weiss[1], U. Shmueli[2], J. E. Kiefer[1], and A. J. C.
Wilson[3], 1. National Institutes of Health, Bethesda, MD
USA; 2. Tel-Aviv University, Tel-Aviv, Israel; 3.
Crystallographic Data Centre, Cambridge, England.

The study of intensity statistics has heretofore been
based on a Gaussian distribution for the normalized
structure factor, or on expansions in terms of polyno-
mials orthogonal with respect to the Gaussian. These
expansions are necessarily approximate and necessitate
increasingly complicated calculations as the degree of
heterogeneity increases. Barakat has shown that exact
solutions of the corresponding random walk problems can
be written as a Fourier or Fourier-Bessel series expan-
sion, the coefficients of which are readily computable
for many space groups. We show, in particular that the
series for space groups P1 and P1̄ are expressible in
terms of products of Bessel functions, and that the
resulting series present no serious numerical problems
for even large degrees of heterogeneity. These results
are readily generalized to deal with the bicentric dis-
tribution for the P1̄ space group. When the atoms in
the unit cell are all equal one can readily derive the
known Rogers-Wilson approximation, but our results are
exact for any degree of heterogeneity. Other space
groups can also be analyzed by the Fourier series
technique.

17. X−7 CENTRIC, PARTIALLY BICENTRIC AND BICENTRIC
INTENSITY STATISTICS IN THE PRESENCE OF HEAVY ATOMS.
By Uri Shmueli, Department of Chemistry, Tel Aviv
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Generalized statistical methods, capable of dealing with
problems due to heterogeneous atomic composition, ef-
fects of space-group symmetry and others, fall into two
classes: (1) expansions of the probability density func-
tions (pdf's) for the normalized structure amplitude,
$|E|$, in terms of orthogonal polynomials and coefficients
depending on the problem (e.g., Shmueli & Wilson, Acta
Cryst. A 37, 342-353 (1981)), and (2) Fourier series for
$|E|$, based on the exact solution to the problem of ran-
dom walk, with steps of unequal size (Shmueli, Weiss,
Kiefer & Wilson (1984)). The pdf's of class (1) are now
available for all the space groups, as four-term expan-
sions, for the case of atoms in general positions and no
hypersymmetry. However, these four terms may not suffice
for extreme atomic heterogeneities, especially in space
groups of the lowest symmetries. This gap of applica-
bility is now very effectively filled by the exact pdf's
of class (2), which are available for low-symmetry space
groups.

The random-walk approach has recently been extended
to the treatment of bicentric distributions and work on
partially bicentric distributions is now in progress.

The above two approaches will be compared with res-
pect to their performance. The test distributions com-
prise (i) computer simulations, (ii) $|E|$ values recal-
culated from published structures and (iii) experimental
distributions pertaining to centric and partially bicen-
tric organometallic structures.