$$\varrho(r\theta) = \frac{1}{2\pi}\int_0^{2\pi}\varrho(\mathbf{r})\,d\varphi$$

$$= \frac{1}{V}\sum_{\mathbf{h}}\sum_{n=0}^{\infty}F(\mathbf{h})a_n j_n(\alpha r)P_n(\cos\theta_h)P_n(\cos\theta), \quad (7)$$

which is not a function of φ_h. The weighted projection $\varrho(r\varphi)$ is defined by

$$\varrho(r\varphi) = \frac{1}{2}\int_0^{\pi}\varrho(\mathbf{r})\sin\theta\,d\theta$$

$$= \frac{1}{V}\sum_{\mathbf{h}}\sum_{n=0}^{\infty}F(\mathbf{h})a_n j_n(\alpha r)\left\{\sum_{m=1}^{n}L_n^m\cos m(\varphi-\varphi_h)\right\}, \quad (8)$$

where L_n^m is a numerical constant. In the case of O_h, L_n^m-values for (n, m) are:

$(4, 4) =$	$0{\cdot}3333,$	$(6, 4) =$	$-0{\cdot}4000,$
$(8, 4) =$	$0{\cdot}04444,$	$(8, 8) =$	$0{\cdot}2063,$
$(10, 4) =$	$-0{\cdot}07619,$	$(10, 8) =$	$-0{\cdot}2159,$
$(12, 4) =$	$0{\cdot}01682,$	$(12, 8) =$	$0{\cdot}4140,$
$(12, 12) =$	$0{\cdot}1515\,.$		

By following the example given above, one can derive the results for other space groups.

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Some Improvements in the Method of Generalized Projections

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Elimination of termination of series error in generalized projections can be achieved by use of $(F_o - F_c)$ Fourier coefficients. Use of a particular kind of average is capable of minimizing the somewhat smaller errors in co-ordinates arising from inaccurately known temperature factors.

Introduction

Since the first use of generalized projections (Clews & Cochran, 1949; Hughes & Pfeiffer, 1949) the detailed theory (Cochran & Dyer, 1952) has become useful in applications in which three-dimensional information is obtainable by use of computational methods normally used in two-dimensional studies. Of the numerous applications (Dyer (1951), Raeuchle & Rundle (1952), Zussman (1953), Curtis & Pasternak (1955), White & Clews (1956), Huber (1957), Bryden (1957), Shoemaker, Shoemaker & Wilson (1957), Sutor (1958), Bryden (1958), Brunton, Steinfink & Beck (1958)) those of most interest here are: (a) the difference method (Zachariasen, 1954) to locate hydrogen atoms at specific levels in the unit cell; (b) the 'modulus projection' employed by Fridrichsons & Mathieson (1955), as well as by Philips (1956) to sharpen atoms viewed in projection by a suitable combination of the two possible generalized projections; (c) the proof (Speakman, 1953) of non-planarity of a nearly planar molecule; (d) an improved method to determine the shape of overcrowded molecules (Rossmann (1958), Trotter (1958)) and capable of demonstrating the slight, but unexpected, non-planarity in 2:3–8:9 dibenzperylene (Robertson & Rossmann, 1958). Since it is by no means obvious that the method of generalized projections could have been developed to the extent indicated by these latter examples, we have felt it desirable to report these recent improvements.

Reduction of series-termination error

We follow the notation of Cochran & Dyer (1952) who modify the ordinary electron density, e.g. $\varrho(x, z)$ when $K = 0$, to give the generalized density,

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$$\sigma_K(x-x_n, z-z_n) = \frac{1}{A} \sum_h \sum_l f(hkl)$$
$$\times \cos 2\pi[h(x-x_n)+l(z-z_n)]$$

near an atom at (x_n, z_n). Thus σ_K is exactly ϱ when $K = 0$, and differs but little for small K (Philips, 1954). The products $\sigma_K \sin 2\pi Ky$ and $\sigma_K \cos 2\pi Ky$ are the weighted sine or cosine densities, respectively.

The errors due to termination of series are minimized by the use of difference methods. The resulting cosine and sine projections are

$$C_K^D = \frac{1}{A} \sum_h \sum_l (|F_o|-|F_c|) \cos (\theta-\alpha),$$

$$S_K^D = -\frac{1}{A} \sum_h \sum_l (|F_o|-|F_c|) \sin (\theta-\alpha),$$

where $\theta = 2\pi(hx+lz)$, and α is the usual phase angle for a plane. Errors of up to 10% in peak heights of the ordinary $|F_o|$ synthesis, if interpreted as changes in $\sin 2\pi Ky$ or $\cos 2\pi Ky$, can cause large errors in the y co-ordinates. Such errors can be greatly reduced by the use of difference syntheses.

The difference between the observed and calculated weighted densities is

$$C_K^D = \sigma_{K,o} \cos 2\pi Ky_o - \sigma_{K,c} \cos 2\pi Ky_c \qquad (1)$$

for the cosine series, with a similar expression for the sine series. Thus the new value of y_o can be found more accurately if the temperature factor is nearly correct, so that $\sigma_{K,o} = \sigma_{K,c}$ is a valid approximation. Moreover, an approximate value of $\sigma_{K,o}$ is usually available from the known electron density, ϱ, of the zero layer line projection. In non-centrosymmetric structures equation (1) tends to underestimate the correction to y, so that it is sometimes helpful to double the value of C_K^D and S_K^D, as was done in the refinement of the $(h1l)$ reflections of $1:9–5:10$ diperi-naphthylene anthracene (Rossmann, 1958), or to double the resulting shift (y_o-y_c) as was done by Trotter (1958) in the refinement using the $(h1l)$ planes of dinaphtha $(7':1'–1:13)(1'':7''–6:8)$ pero-pyrene (Clar, Kelly, Robertson & Rossmann, 1956).

Reduction of error due to inaccurate temperature factors

Suppose the temperature factor is wrong in such a way that $\sigma_{K,o} > \sigma_{K,c}$. Then equation (1), and the corresponding equation for the sine function, gives values of $\cos 2\pi Ky_o$ and $\sin 2\pi Ky_o$ which are too large when calculated on the basis that $\sigma_{K,o} = \sigma_{K,c}$. But these trigonometric functions vary in opposite senses. Hence an averaging process between the refined co-ordinates, $\theta_o^c/2\pi K$ and $\theta_o^s/2\pi K$, of the separate cosine and sine series, respectively, can be used to minimize the effect due to choosing an incorrect temperature factor. Let

$$\gamma = \{(\cos^2 \theta_o^c + \sin^2 \theta_o^s)^{\frac{1}{2}} - 1\}.$$

Had no error been made in choosing the value of $\sigma_{K,o}$ to determine θ_o^c and θ_o^s then $\gamma = 0$. However, if $\sigma_{K,o}$ was chosen too small, it follows that γ is positive. That means if too much thermal motion was assumed for an atom, γ is positive, and vice versa. The co-ordinates θ_o^c and θ_o^s, obtained during refinement can therefore be corrected by means of the formulae

$$\cos \overline{\theta_o^c} = \frac{1}{1+\gamma} \cos \theta_o^c \quad \text{and} \quad \sin \overline{\theta_o^s} = \frac{1}{1+\gamma} \sin \theta_o^s.$$

It should, however, be noted that the sine generalized projection is accurate near 0 or π, while the cosine projection is accurate near $\pi/2$ or $3\pi/2$. Thus it is necessary to take a mean between $\overline{\theta_o^c}$ and $\overline{\theta_o^s}$ in order to obtain roughly the same accuracy in all parts of the unit cell. We have found that a useful averaging function is

$$\theta_{\text{final}} = (\overline{\theta_o^s} \cos \overline{\theta_o^c} + \overline{\theta_o^c} \sin \overline{\theta_o^s})/(\cos \overline{\theta_o^c} + \sin \overline{\theta_o^s}).$$

The strength of the expression for γ is demonstrated in Fig. 2 which shows a plot of γ against the distance of atoms from the molecular center in $2:3–8:9$ dibenzperylene. Further, the y co-ordinates obtained by the method described above are in excellent agreement with an exhaustive least-squares refinement of the $(h0l)$ and $(h1l)$ data, as shown in Table 1.

Table 1. *The y co-ordinates of the carbon atoms in one asymmetric unit of $2:3–8:9$ dibenzperylene expressed as fractions of the cell edge b (5·23 Å).*

Estimated standard deviations of y co-ordinates determined by generalized projections and by least squares are 0·02 Å (0·004 of b) and 0·012 Å (0·002 of b), respectively

Atom	Planar	Gen. proj.	Least-sq.
A	0·436	0·435	0·443
B	0·254	0·258	0·250
C	0·073	0·066	0·063
D	−0·111	−0·111	−0·109
E	−0·274	−0·274	−0·284
F	−0·290	−0·280	−0·289
G	0·608	0·614	0·613
H	0·612	0·617	0·610
I	0·788	0·795	0·788
J	0·775	0·785	0·787
K	0·612	0·611	0·602
L	0·452	0·428	0·419
M	0·449	0·435	0·432
N	0·262	0·274	0·266

Comparison with the best planar model shows clearly that the molecule is non-planar, especially around atoms L and M (Fig. 1). Comparison of experimental bond lengths for the planar and non-planar structures with the lengths expected from molecular orbital calculations also favors the non-planar model. Thus the experimental non-planar structure and the best planar model show average deviations of bond lengths of 0·02 Å and 0·04 Å, respectively, when compared with the MO model.
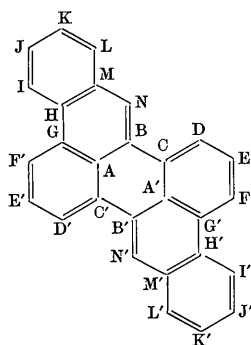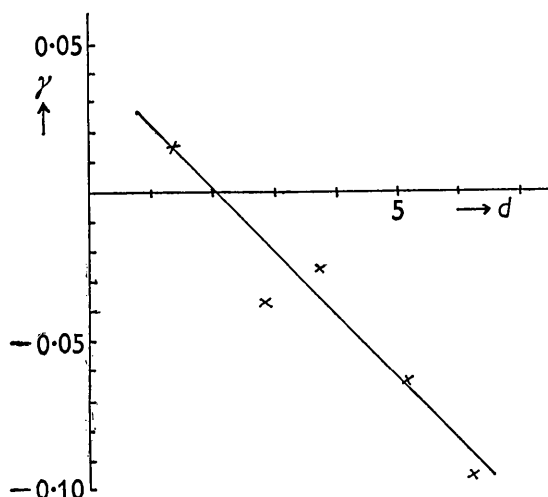
Fig. 1. The 2 : 3–8 : 9 dibenzperyline molecule.

Fig. 2. Graph showing relationship between γ and the distance, d, of atoms from the molecular center in Å, of 2 : 3–8 : 9 dibenzperylene. γ is a measure of the discrepancy between the y co-ordinates determined from the cosine and sine generalized projections.

An alternative method of refinement

If, instead of refining the cosine and sine series quite separately, both series are refined simultaneously, then it is possible to refine the x, y, z and B parameters all at the same time, and the effects of random errors of structure factors will be much reduced. The maximum gradients of a certain function, deduced below, gives the direction and size of the atomic shifts parallel to the plane of projection at each site, while the value of another function at each atomic position is a measure of the correctness of the temperature factors applied to the atoms.

An expression useful for the refinement of the co-ordinates parallel to the direction of projection can be obtained from equation (1) and its corresponding sine function:

$$S_K^D \cos 2\pi K y_c - C_K^D \sin 2\pi K y_c = \sigma_{K,o} \sin 2\pi K (y_o - y_c) .$$

The quantity S_K^D is most accurate when $2\pi K y_c$ is nearer 0 or π, i.e., when $\cos 2\pi K y_c$ has a value ap-

proaching unity. Similarly C_K^D is most accurate when $\sin 2\pi K y_c$ is near unity. Thus in evaluating $(y_o - y_c)$ by means of the equation above, the greater weight is given to the more accurate difference function. The effect of any error in the value assigned to $\sigma_{K,o}$ is small since only the shift in the atomic co-ordinate is calculated, hence the left-hand side is roughly proportional to $(y_o - y_c)$ when the latter is small.

Again from equation (1) and its equivalent sine function, we may derive another expression useful to refine the temperature factors:

$$S_K^D \sin 2\pi K y_c + C_K^D \cos 2\pi K y_c$$
$$= \sigma_{K,o} \cos 2\pi K (y_o - y_c) - \sigma_{K,c} .$$

When $(y_o - y_c)$ is small the right-hand term becomes $(\sigma_{K,o} - \sigma_{K,c})$, which is proportional to $-\Delta B$. The effect of an error, ΔB, in the temperature factor in S_K^D will be proportional to the value of $\sin 2\pi K y_c$ and that of C_K^D to $\cos 2\pi K y_c$. The above equation preserves this weighting. The expression $(\sigma_{K,o} - \sigma_{K,c})$ in a difference generalized projection is similar to $(\varrho_o - \varrho_c)$ in an ordinary difference synthesis and the corrections to B can be applied by the usual methods for difference projections.

Lastly, a comparison with the zero-layer projection (Cochran, 1951) gives us a function for the refinement of the co-ordinates parallel to the direction of projection. We have

$$\Delta (r) \sin 2\pi K y_c = \left(\frac{dS_K^D}{dr} \right)_{r=0} \Big/ (2p\sigma_{K,o}) ,$$

$$\Delta (r) \cos 2\pi K y_c = \left(\frac{dC_K^D}{dr} \right)_{r=0} \Big/ (2p\sigma_{K,o}) ,$$

when $\Delta (r)$ is the required shift in the atomic co-ordinates in the plane normal to the direction of projection. The direction of shift of the atom is along the line of maximum gradient but will be in the positive or negative sense depending on the sign of $\sin 2\pi K y_c$ or $\cos 2\pi K y_c$, respectively. By combining the above two expressions we have

$$\Delta (r) = \left\{ \frac{d}{\partial r} (S_K^D \sin 2\pi K y_c + C_K^D \cos 2\pi K y_c) \right\}_{r=0} \Big/ 2p\sigma_{K,o} .$$

The accuracy of the atomic shifts, determined from S_K^D and C_K^D, are weighted in a physically reasonable way by the magnitudes of $\sin 2\pi K y_c$ and $\cos 2\pi K y_c$, respectively. Thus the function

$$(S_K^D \sin 2\pi K y_c + C_K^D \cos 2\pi K y_c)$$

may be plotted in the vicinity of atomic sites. The maximum gradients then give the direction and size of the atomic shifts parallel to the plane of projection at each site.

It can be proved that the use of this function for the refinement of x, z and B, together with the function given above for the refinement of y, is equivalent to a least-squares procedure. In a proof of this state-

ment it is necessary to assume that the expression $\sum_{q} \omega(|F_o|-|F_c|)^2$ is being minimized over the same q terms as employed for the generalized projection work, where ω is the weight applied to each reflection. It then follows that $\omega = 1/\hat{f}$ in the case of positional parameters, or $\omega = \hat{f}^{-1}.\lambda^2/\sin^2\theta$ for temperature factor parameters if the two methods are to be strictly analogous. ($\hat{f}$ is the unitary scattering factor for each plane.)

The calculation of difference weighted generalized densities

Two co-ordinates per atom are generally known to a fair degree of accuracy when a difference generalized projection is about to be calculated. The third co-ordinates and the temperature factors can then be deduced from the peak heights at atomic sites. For instance, the difference cosine weighted generalized density of diperinaphthylene anthracene $(P2_1)$ when $K = 1$, is given by

$$C_1^D(x_n, z_n)$$
$$= \frac{2}{A} \sum_h \sum_l [\{(|F_o|-|F_c|)\sin\alpha\}\sin 2\pi(hx_n+lz_n)] .$$

The quantity $\sin 2\pi(hx_n+lz_n)$ was listed for the N independent atoms for every observed (hll) plane (see Table 2). Then every row, corresponding to the

Table 2. *Corner of table showing arrangement of* $\sin 2\pi(hx_n+lz_n)$ *quantities for* $1:9–5:10$ *diperinaph-thylene anthracene*

hll	Atoms					
	A_1	B_1	C_1	D_1	E_1	F_1
110	0·56	0·24	0·95	1·00	0·64	0·33
210	0·93	0·48	0·59	0·$\overline{17}$	0·$\overline{98}$	0·$\overline{60}$
310	0·97	0·68	0·$\overline{59}$	0·$\overline{97}$	0·86	0·83
410	0·68	0·85	0·$\overline{95}$	0·33	0·$\overline{33}$	0·$\overline{96}$
510	0·16	0·95	0·00	0·91	0·36	1·00

values of $\sin 2\pi(hx_n+lz_n)$ for a particular plane, must be multiplied by the common factor

$$\left\{ \frac{2}{A}(|F_o|-|F_c|)\sin\alpha \right\} .$$

This could be done very quickly on a slide rule as only two figure accuracy was required. Finally all columns

(each column corresponding to a particular atom) were added up to give the difference generalized density C_1^D at the atomic sites.

From the same table listing $\sin 2\pi(hx_n+lz_n)$ both real and imaginary parts of the structure factors could also be calculated. Every column (corresponding to a certain carbon atom) was multiplied by the common factor $\sin 2\pi y_n$ or $\cos 2\pi y_n$. Finally all rows were added to give the values of $A(hll)$ or $B(hll)$, respectively.

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