The very heavy mercury atoms lie at symmetry centres and dominate half the reflexions while making no contribution to the remainder. These latter should conform to the theoretical distributions since they are due to the phenyl groups only. They are, however, so very much weaker than the 'mercury' reflexions that their intensities and the average are on the extreme lower limit measurable. As a result it is not possible in this case to derive the significant low-intensity end of the $N(z)$ curves.

It is hoped to discuss elsewhere the way in which the present statistical treatment should be modified to deal with the group of strong reflexions; this being a typical case of the general problem of the effects on the normal Gaussian functions produced by heavy atoms and pseudosymmetry.

I. *Eucryptite*

Intensities from powder data by Winkler (1948).

Space group $C6_22$; $a=5{\cdot}27$, $c=11{\cdot}25$ A.; three molecules of $LiAlSiO_4$ per unit cell.

The experimental distribution does not agree with either of the two theoretical possibilities; the substance produces an unusually high proportion of accidental absences, attributable to the structural pseudosymmetry. The top and bottom halves of the cell differ only in that one contains Al+Li where the other contains Si. Thus all reflexions with l odd are extremely weak.

5. Conclusions

The results confirm the Gaussian distribution found empirically by Hughes (1949) for the structure amplitudes of a centrosymmetric structure; they also provide quantitative verification of Wilson's theoretical distributions.

Only drastic departures from the conditions (i) and (ii) (§ 3) seem to disturb the distributions sufficiently to cause doubt in interpretation. The method may, therefore, be applied to a wide range of substances, being particularly suitable for the more complex organic compounds.

As a consequence of the ability to decide whether a unit cell or its projection possesses a centre of symmetry, the number of space groups distinguishable by X-ray means alone is considerably increased (Rogers, 1949).

Finally, it seems profitable to adopt the statistical survey of intensities as part of the routine procedure leading to Patterson and Fourier syntheses; in addition to the space-group information obtained, large systematic errors in the intensities may be revealed, and the data derived are of immediate use in converting the intensities to the absolute scale (Wilson, 1942).

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References

Dunitz, J. D. (1949). *Acta Cryst.* **2**, 1.
Fowweather, F. & Hargreaves, A. (1950). *Acta Cryst.* **3**, 81.
Gossner, B. & Neff, H. (1933). *Z. Krystallogr.* **86**, 32.
Hargreaves, A. & Taylor, W. H. (1941). *J. Sci. Instrum.* **18**, 138.
Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Howells, E. R., Phillips, D. C. & Rogers, D. (1949). *Research, Lond.*, **2**, 338.
Hughes, E. W. (1949). *Acta Cryst.* **2**, 34.
Jahnke, E. & Emde, F. (1938). *Tables of Functions.* Leipzig: Teubner.
Powell, H. M. & Stanger, G. B. (1939). *J. Chem. Soc.* p. 1105.
Rogers, D. (1949). *Research, Lond.*, **2**, 342.
Wilson, A. J. C. (1942). *Nature, Lond.*, **150**, 152.
Wilson, A. J. C. (1949). *Acta Cryst.* **2**, 318.
Winkler, H. G. F. (1948). *Acta Cryst.* **1**, 27.

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On the Derivation of Harker–Kasper Inequalities

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Group theory leads to an easy and straightforward method of finding Harker–Kasper inequalities.

1. In deriving inequality relations between structure factors, Harker & Kasper (1948), in their well-known paper, applied Schwarz's inequality to the so-called simplified structure factor, which is written as far as

possible in the form of cosine and/or sine products. The essential part of the inequalities derivation is, then, the transcription of the square of this goniometric factor into a sum of terms, each of which represents the goniometric part of a structure factor with indices different from the original one. Except for the simplest space groups this process is laborious and rather clumsy.

Also, it is evident from an inspection of Harker & Kasper's results that the constant factor in the right-hand side of the inequality is always equal to the reciprocal value of the symmetry number of the space group under consideration; the significance of this is not clear from the derivation given by Harker & Kasper. The attempt to prove this fact has led to a straightforward method of derivation, based on group theory; this method can easily be applied even to the most complicated space groups.

2. We start from the general formula

$$F(\bar{h})=\oint\rho(\bar{r})\exp[2\pi i(\bar{h}\cdot\bar{r})]\,dv(\bar{r}). \tag{1}$$

Let the symmetry number of the space group be n. A point $\bar{r}$ is equivalent to $n-1$ other points within a unit cell, at distances $\bar{r}_i$ from the origin, which can be symbolized by operators C_i as follows:*

$$C_i\cdot\bar{r}=\bar{r}_i\quad(i\text{ from }0\text{ to }(n-1)).$$

(Note that $C_0=I=$ identity, so $C_0\cdot\bar{r}\equiv\bar{r}$.)

Since $\rho(\bar{r})=\rho(C_i\cdot\bar{r})$, we may write

$$F(\bar{h})=\frac{1}{n}\oint\rho(\bar{r})\sum_{i=0}^{n-1}\exp[2\pi i(\bar{h}\cdot C_i\cdot\bar{r})]\,dv(\bar{r}).$$

Proceeding exactly as in Harker & Kasper's paper, we find

$$\left.\begin{aligned}|F(\bar{h})|^2&\leqslant\frac{1}{n^2}\oint\rho(\bar{r})\,dv(\bar{r})\\&\qquad\times\oint\rho(\bar{r})\left|\sum_{i=0}^{n-1}\exp[2\pi i(\bar{h}\cdot C_i\cdot\bar{r})]\right|^2dv(\bar{r}),\\|F(\bar{h})|^2&\leqslant\frac{1}{n^2}\cdot Z\cdot\oint\rho(\bar{r})\\&\qquad\times\sum_i^{n-1}\sum_j{}_0\exp[2\pi i(\bar{h}\cdot(C_i-C_j)\cdot\bar{r})]\,dv(\bar{r}).\end{aligned}\right\}\tag{2}$$

Now $(C_i-C_j)\cdot\bar{r}$, that is the distance between the two equivalent points r_i and r_j, can always be written in the form $(C_k-I)\cdot C_j\cdot\bar{r}$, where $C_k=C_i\cdot C_j^{-1}$. In other words, by the group definition there is, for any pair of equivalent points $\bar{r}_i$ and $\bar{r}_j$, an operator in the group which transforms $\bar{r}_j$ into $\bar{r}_i$. The integral in (2) can therefore be transformed as follows:

$$\begin{aligned}&\oint\rho(\bar{r})\sum_i^{n-1}\sum_j{}_0\exp[2\pi i(\bar{h}\cdot(C_i-C_j)\cdot\bar{r})]\,dv(\bar{r})\\&=\oint\rho(\bar{r})\sum_j\sum_k\exp[2\pi i(\bar{h}\cdot(C_k-I)\cdot C_j\cdot\bar{r})]\,dv(\bar{r})\\&=\oint\sum_{j=0}^{n-1}\rho(C_j\cdot\bar{r})\sum_{k=0}^{n-1}\exp[2\pi i(\bar{h}\cdot(C_k-I)\cdot C_j\cdot\bar{r})]\,dv(C_j\cdot\bar{r})\\&=n\oint\rho(\bar{r})\sum_{k=0}^{n-1}\exp[2\pi i(\bar{h}\cdot(C_k-I)\cdot\bar{r})]\,dv(\bar{r}).\end{aligned}\tag{3}$$

Now let us split the operators into a dyadic ϕ (rotation, mirror, etc.) and a translational part t (translation component of screw axis or glide plane, also translations in non-primitive cell):

$$C_k\cdot\bar{r}=\bar{t}_k+\phi_k\cdot\bar{r}. \tag{4}$$

Then $\qquad\bar{h}\cdot(C_k-I)\cdot\bar{r}=\bar{h}\cdot\bar{t}_k+\bar{h}\cdot(\phi_k-I)\cdot\bar{r}.$

Thus for any space group the fundamental Harker–Kasper inequality is given by

$$\left.\begin{aligned}|F(\bar{h})|^2&\leqslant\frac{Z}{n}\sum_{k=0}^{n-1}\exp[2\pi i(\bar{h}\cdot\bar{t}_k)]\\&\qquad\times\oint\rho(\bar{r})\exp[2\pi i(\bar{h}\cdot(\phi_k-I)\cdot\bar{r})]\,dv(\bar{r}),\\|F(\bar{h})|^2&\leqslant\frac{Z}{n}\sum_{k=0}^{n-1}\exp[2\pi i(\bar{h}\cdot\bar{t}_k)]\cdot F(h\cdot(\phi_k-I)).\end{aligned}\right\}\tag{5}$$

The transformed $\bar{h}_k$, defined by

$$\bar{h}_k=\bar{h}\cdot(\phi_k-I),$$

are easily found, as shown in the example given below. In particular, it may be remarked that $\bar{h}_0=\bar{h}\cdot(I-I)\equiv 0$, so that the series in the right-hand side of (5) starts in all cases with $F(000)=Z$. This is the origin of the term $1/n$ in the Harker–Kasper inequalities.

Without making use of group notation the result (5) can be written as follows:

$$\begin{aligned}|F(\bar{h})|^2&\leqslant\frac{Z}{n}\sum_{k=0}^{n-1}\oint\rho(\bar{r})\exp[2\pi i(\bar{h}\cdot(\bar{r}_k-\bar{r}))]\,dv(\bar{r})\\&\leqslant\frac{Z}{n}\sum_{k=0}^{n-1}\oint\rho(\bar{r})\exp[2\pi i(hx_k+ky_k+lz_k\\&\qquad\qquad-hx-ky-lz)]\,dv(\bar{r}).\end{aligned}\tag{5a}$$

Now, x_k, y_k and z_k are linear combinations of x, y, z, plus eventually a translational part; the exponent can therefore be written in the form

$$2\pi i(h_kx+k_ky+l_kz+ht_x^k+kt_y^k+lt_z^k),$$

so $\qquad|F(\bar{h})|^2\leqslant\frac{Z}{n}\sum_{k=0}^{n-1}F(\bar{h}_k)\cdot\exp[2\pi i(\bar{h}\cdot\bar{t}_k)],$

as before.

To show how the inequalities are found with the help of (5), let us take the space group $P\bar{4}2c$ as an example (Table 1).

The same result can be derived by making use of (5a) instead of via the matrices.

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* We follow mainly Zachariasen's notation (Zachariasen, 1945). Contrary to Zachariasen, we use operators as prefactors to $\bar{r}$, in order to be able to keep the conventional notation $\bar{h}\cdot\bar{r}$ instead of $\bar{r}\cdot\bar{h}$.

Table 1. *Application of equation* (5) *to space group* $P\bar{4}2c$

k	Components of r_k	ϕ_k	t_k	$\phi_k - I$	Components of $h_k = h\cdot(\phi_k - I)$
0	x, y, z	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}=I$	0	$\begin{pmatrix}0&0&0\\0&0&0\\0&0&0\end{pmatrix}$	000
1	$\bar{y}, x, \bar{z}$	$\begin{pmatrix}0&\bar{1}&0\\1&0&0\\0&0&\bar{1}\end{pmatrix}$	0	$\begin{pmatrix}\bar{1}&\bar{1}&0\\1&\bar{1}&0\\0&0&\bar{2}\end{pmatrix}$	$-h+k,\ -h-k,\ -2l$
2	$\bar{x}, \bar{y}, z$	$\begin{pmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{pmatrix}$	0	$\begin{pmatrix}\bar{2}&0&0\\0&\bar{2}&0\\0&0&0\end{pmatrix}$	$-2h,\ -2k,\ 0$
3	$y, \bar{x}, \bar{z}$	$\begin{pmatrix}0&1&0\\\bar{1}&0&0\\0&0&\bar{1}\end{pmatrix}$	0	$\begin{pmatrix}\bar{1}&1&0\\\bar{1}&\bar{1}&0\\0&0&\bar{2}\end{pmatrix}$	$-h-k,\ h-k,\ -2l$
4	$\bar{x}, y, \frac{1}{2}-z$	$\begin{pmatrix}\bar{1}&0&0\\0&1&0\\0&0&\bar{1}\end{pmatrix}$	$\frac{1}{2}c$	$\begin{pmatrix}\bar{2}&0&0\\0&0&0\\0&0&\bar{2}\end{pmatrix}$	$-2h,\ 0,\ -2l$
5	$y, x, \frac{1}{2}+z$	$\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$	$\frac{1}{2}c$	$\begin{pmatrix}\bar{1}&1&0\\1&\bar{1}&0\\0&0&0\end{pmatrix}$	$-h+k,\ h-k,\ 0$
6	$x, \bar{y}, \frac{1}{2}-z$	$\begin{pmatrix}1&0&0\\0&\bar{1}&0\\0&0&\bar{1}\end{pmatrix}$	$\frac{1}{2}c$	$\begin{pmatrix}0&0&0\\0&\bar{2}&0\\0&0&\bar{2}\end{pmatrix}$	$0,\ -2k,\ -2l$
7	$\bar{y}, \bar{x}, \frac{1}{2}+z$	$\begin{pmatrix}0&\bar{1}&0\\\bar{1}&0&0\\0&0&1\end{pmatrix}$	$\frac{1}{2}c$	$\begin{pmatrix}\bar{1}&\bar{1}&0\\\bar{1}&\bar{1}&0\\0&0&0\end{pmatrix}$	$-h-k,\ -h-k,\ 0$

3. According to Harker & Kasper, inequalities derived from linear combinations of structure factors are often useful. They can be derived as before. Starting from

$$F(\bar{h}) \pm F(\bar{h}') = \frac{1}{n}\left\{\oint \rho(\bar{r}) \sum_{i=0}^{n-1} \exp\left[2\pi i(\bar{h}\cdot C_i\cdot\bar{r})\right] dv(\bar{r}) \right.$$
$$\left. \pm \oint \rho(\bar{r}) \sum_{i=0}^{n-1} \exp\left[2\pi i(\bar{h}'\cdot C_i\cdot \bar{r})\right] dv(\bar{r})\right\},$$

one obtains

$$|F(\bar{h}) \pm F(\bar{h}')|^2 \leqslant \frac{Z}{n}\sum_{k=0}^{n-1} F(\bar{h}\cdot(\phi_k - I))\cdot\exp\left[2\pi i(\bar{h}\cdot\bar{t}_k)\right]$$
$$+ F(\bar{h}'\cdot(\phi_k - I))\cdot\exp\left[2\pi i(\bar{h}'\cdot\bar{t}_k)\right]$$
$$\pm 2\,\mathrm{Re}\,F(\bar{h}\cdot I - \bar{h}'\cdot\phi_k)\cdot\exp\left[(-2\pi i(h'\cdot t_k)\right].$$

This treatment can be extended to linear combinations of any number of structure factors.

4. Harker & Kasper showed that in many cases alternate forms of inequalities can be derived, namely, when it is possible to write the goniometric part of the structure factor as a product of two factors. Evidently, this is equivalent to the condition that the sum

$$\sum_{i=0}^{n-1} \exp\left[2\pi i(\bar{h}\cdot C_i\cdot\bar{r})\right]$$

can be written in the form

$$\sum_{j=0}^{p-1} \exp\left[2\pi i(\bar{h}\cdot(C_j' - I)\cdot\bar{r})\right]\cdot\sum_{k=0}^{q-1} \exp\left[2\pi i(\bar{h}\cdot C_k''\cdot\bar{r})\right],$$

where C' and C'' are subgroups of C:

$$(C) = (C')\cdot(C''), \quad \text{and} \quad pq = n. \tag{7}$$

It is easily seen that this can be done only if the matrix parts of C' and C'' are of the form

$$\begin{pmatrix}C_{11}&C_{12}&0\\C_{21}&C_{22}&0\\0&0&1\end{pmatrix} \quad \text{and} \quad \begin{pmatrix}1&0&0\\0&1&0\\0&0&C_{33}\end{pmatrix}$$

respectively. That is, if the group contains at most one more-than-twofold axis, and a symmetry plane perpendicular to it. (Of course, in groups of the class $2/m\,2/m\,2/m$ any one of the twofold axes can be singled out.) Schwarz's inequality can then be applied in the form

$$|F(\bar{h})|^2 \leqslant \frac{1}{n^2}\oint \rho(\bar{r})\left|\sum_{j=0}^{p-1}\exp\left[2\pi i(\bar{h}\cdot(C_j' - I)\cdot\bar{r})\right]\right|^2 dv(\bar{r})$$
$$\times \oint \rho(\bar{r})\left|\sum_{k=0}^{q-1}\exp\left[2\pi i(\bar{h}\cdot C_k''\cdot\bar{r})\right]\right|^2 dv(\bar{r}).$$

Proceeding exactly as before, and making use of (7), one finds

$$|F(\bar{h})|^2 \leqslant \frac{1}{n}\sum_{j=0}^{p-1} F(\bar{h}\cdot(\phi_j' - I))\cdot\exp\left[2\pi i(\bar{h}\cdot\bar{t}_j')\right]$$
$$\times \sum_{k=0}^{q-1} F(\bar{h}\cdot(\phi_k'' - I))\cdot\exp\left[2\pi i(\bar{h}\cdot\bar{t}_k'')\right]. \tag{8}$$

Again, the transformed h_j and h_k are easily found.

5. A few final remarks may be made.

All inequalities can, of course, be derived just as well introducing the presence of spherical atoms, that is, working with F in the form of a sum instead of an integral and applying Cauchy's inequality (Harker & Kasper, 1948).

As already remarked by Buerger, the transformations $h_k = h\cdot(\phi_k - I)$ are exactly the same as those which lead from Patterson to implication space (Buerger, 1948*a*, *b*). This is evident: in both cases the problem is to transform from a Harker vector, i.e. distance between two structurally equivalent points, to a vector from the origin to one of these points. There must be a connexion between inequalities and implication theory, since both try to find the relation between F^2 and F, that is between vector space and crystal space.

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References

Buerger, M. J. (1948*a*). *Acta Cryst.* **1**, 259.
Buerger, M. J. (1948*b*). *Proc. Nat. Acad. Sci., Wash.*, **34**, 277.
Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Zachariasen, W. H. (1945). *Theory of X-ray Diffraction in Crystals*. New York: Wiley.

Acta Cryst. (1950). **3**, 217

The Structure of Tetraphenylmethane*

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The crystal structure of tetraphenylmethane is reported. The C–C distances in the six-membered rings are 1·39 A. and the bond lengths about the central carbon atoms are 1·47 A. The crystallographic data are in agreement with previous work by George. The structure is a loose packing of molecules so arranged as to account for the observed planes in the crystal habit.

Introduction

The structure of tetraphenyl methane was undertaken as a part of a program to study spectroscopically and by X-rays a series of compounds wherein two, three and four phenyl groups are attached to the same carbon atom. These compounds are interesting because they frequently have a very low density and also because their bond character is easily altered by the substitution of active groups to form colored compounds such as crystal violet, and malachite green.

Tetraphenylmethane was first studied by George (1926), whose crystallographic findings are in agreement with the present work; but the conclusions pertaining to structure are somewhat at variance, mostly because structure determination was not the main object of his work.

A comparison of the crystallographic data of George and the present authors is shown in Table 1.

Table 1. *Crystallographic data*

Density by flotation (g.cm.$^{-3}$)	Cell dimensions (A.)		Molecules per unit cell	Space group	Authors
	a	*c*			
1·173	10·86	7·26	1·91	$P\bar{4}2_1c$	George
—	10·87	7·23	1·89	$P\bar{4}2_1c$	Sumsion & McLachlan

Experimental

From a sample of purified tetraphenylmethane a prismatic, needle-like crystal, having dimensions of 0·02 cm. in the two short directions and about 0·25 cm. in the longest direction, was selected and was exposed to filtered cobalt radiation to produce powder, rotation and Weissenberg pictures. Five layer lines were observed on the rotation picture and from this picture data were taken for the adjustment of the Weissenberg camera in taking equi-inclination photographs of each layer. Rotation pictures using copper and also molybdenum radiation were then taken, but no further data were obtained. The intensities were determined by visual methods, using the multiple-film technique (Robertson, 1943*a*). The Lorentz and polarization factors were taken from the tables of Buerger & Klein (1946), while the temperature factors were according to Debye and Waller.

Determination of structure

Since $P\bar{4}$ is a subgroup of $P\bar{4}2_1c$ it is logical to suspect that the tetraphenylmethane molecule might be in this configuration (see Fig. 1). Also, since the $P\bar{4}2_1c$ space group requires eight equivalent points, and the two molecules per unit cell furnish a total of eight phenyl groups but only two central carbon atoms, it was therefore suspected that the central carbon atoms of the molecule are in the special position 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, while the atoms of the phenyl groups are in the eight general positions, with the restriction that they conform to $P\bar{4}$ in sets of four. As a preliminary guess it was assumed that the distances between the central carbon atom and its nearest atoms in the phenyl groups are 1·49 A., while the distances between the carbon atoms in the ring are 1·39 A. These restrictions reduce the structure to a two-parameter problem, the angle (θ) of rotation of the phenyl groups about the tetragonal

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