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A New Expression for Sharpening Patterson Functions

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A new modification function has been developed to sharpen Patterson functions. Its Fourier transform is equivalent to a weighted sum of the usual Patterson function, the 'gradient' function and functions derived from higher terms. It is shown that sharper peaks accompanied by less significant diffraction ripples can be obtained with this function than with other commonly used expressions.

It has been shown by Jacobson, Wunderlich & Lipscomb (1961) that the modification function $M_2(s)=s^2\exp(-\pi^2s^2/p)$ applied to structure amplitudes results in a vector distribution corresponding to the Patterson function of the gradient of the electron density. The negative excursions resulting from sharpening by $M_2(s)$ were significantly attenuated and the sharpness of main peaks enhanced by using the function $(k+s^2)\exp(-\pi^2s^2/p)$ which was equivalent to adding to the 'gradient' Patterson function a contribution from that sharpened in the usual way $[M(s)=\exp(-\pi^2s^2/p)]$.

Waser & Schomaker (1953) refer to the use of the function $M_4(s)=s^4\exp(-\pi^2s^2/p)$, 'which has proved most useful in affording a Patterson function with near maximal resolving power' and whose transform is virtually unaffected by finite cut-off. This function was used in the determination of the crystal structure of hydroxy-L-proline by Donohue & Trueblood (1952) and more recently by Hodgkin & Maslen (1961), who claim that, at least in three dimensions, the negative ripples were not sufficiently severe to be troublesome.

Modification functions of even order in s will clearly give still sharper transforms, but with increasingly important interference from subsidiary features. All such functions may be conveniently combined to give the function $M(s)=\cosh(as)\exp(-\pi^2s^2/p)$, which we may express as

$$(1+a^2s^2/2!+a^4s^4/4!+\ldots+a^ns^n/n!+\ldots)\exp(-\pi^2s^2/p)\,. \quad (1)$$

The transform of this function corresponds to a weighted sum of the normally sharpened Patterson distribution (first term), the 'gradient' Patterson function (term in s^2), the Waser & Schomaker modified Patterson function and those obtained by the use of higher powers of s^2. That is, the $\cosh(as)\exp(-\pi^2s^2/p)$ modification function is a simple and convenient generalization of the existing valuable techniques used to sharpen vector distributions.

The way in which the choice of the parameters a and p determine the weighting may be seen from the form of the coefficients, C_3^n, of the normalized three-dimensional complete transforms, $T_3^n(r)$, of the individual $(a^ns^n/n!)\exp(-\pi^2s^2/p)$ functions, namely:

$$C_3^n=(p/\pi)^{3/2}(a^2p/\pi^2)^{n/2}(n+1)/2^n(n/2)! \quad (2)$$

For $a=2$ Å and $p=2\cdot5\,\pi=7\cdot854$ Å^{-2}, say, we then have for the resultant function

$$\sum_n T_3^n(r)=3\cdot953\,T_3^0(r)+9\cdot437\,T_3^2(r)+6\cdot258\,T_3^4(r)$$
$$+2\cdot324\,T_3^6(r)+0\cdot584\,T_3^8(r)+0\cdot116\,T_3^{10}(r)$$
$$+0\cdot018\,T_3^{12}(r)+\ldots \quad (3)$$

The forms of $T_3^n(r)$ for $n=0,2,4$ and 8, are shown in Fig. 2, but the plot of $\sum_n T_3^n(r)$ for the first five terms of (3) lies so close to that of the transform of $\cosh(as)\exp(-\pi^2s^2/p)$ that only the latter is given. The curves are accompanied by the analytical expressions for $T_3^n(r)$ and for the one-, two- and three-dimensional transforms $T_i(r)$ $(i=1,2,3$ respectively) of $\cosh(as)$

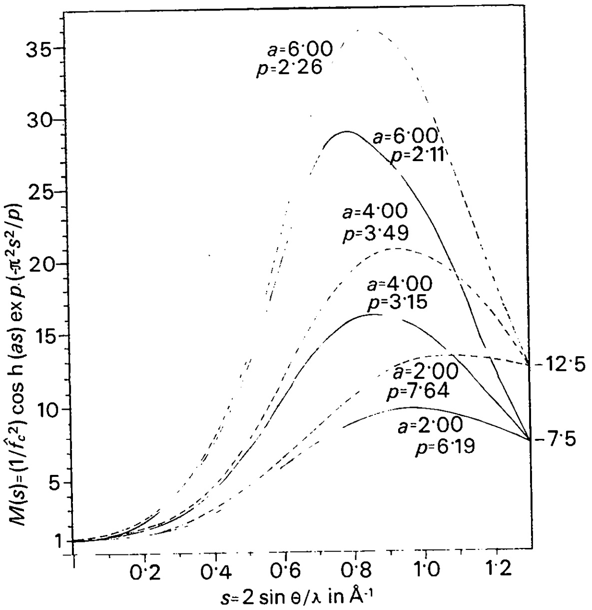

Fig. 1. Plots of $M(s)=1\hat{f}/\,_{c}{}^{2}\cosh(as)\exp(-\pi^2s^2/p)$ *versus s* for carbon atoms. Families for which $M(s)=7\cdot5$ and $12\cdot5$ at $s=1\cdot3$ Å^{-1} are represented by full lines and dashed lines respectively.

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$\exp(-\pi^2 s^2/p)$. The transforms of $T_2(r)$ and $T_1(r)$ are not plotted, but as would be expected the sharpness of the main peak and the importance of diffraction ripples increase inversely as the dimension. The effects of limiting the data to $s = 1{\cdot}3$ Å^{-1} have been calculated for the three-dimensional transforms of $\cosh(as)$ $\exp(-\pi^2 s^2/p)$ and $s^2 \exp(-\pi^2 s^2/p)$ for $a = 2$ Å and $p = 7{\cdot}854$ Å^{-2}. The curves pass through zero at $r = 0{\cdot}52$ and 0·48 Å and fall to $-0{\cdot}075$ at $r = 0{\cdot}65$ Å and $-0{\cdot}12$ at $r = 0{\cdot}6$ Å. It is clear from the series form in (1) that the contributions of the higher functions, $T_l^n(r)$, increasingly weight the influence of diffraction data at higher angles and that these contributions, and therefore the resultant peak shapes, are controlled according to (2) [and the example in (3)] by the values chosen for a and p. As a guide, the modification function $M(s) = 1/\hat{f}_C^2 \cosh(as) \exp(-\pi^2 s^2/p)$, where $\hat{f}_C$ is the unitary scattering factor for carbon, has been plotted in Fig. 1 for various values of a and p and arranged in the form of two families of curves for which $M(s) = 7{\cdot}5$ and $12{\cdot}5$ at $s = 1{\cdot}3$ Å^{-1}. The choice of parameters, on which both the shape of the curves and the position of the maxima depend, should always remain in accord with the spatial distribution of observed reflexions and on the standard deviations of the intensities.

The use of large values for both a and p results in divergent modification functions of the type studied by Abrahamsson & Maslen (1963), but the severe

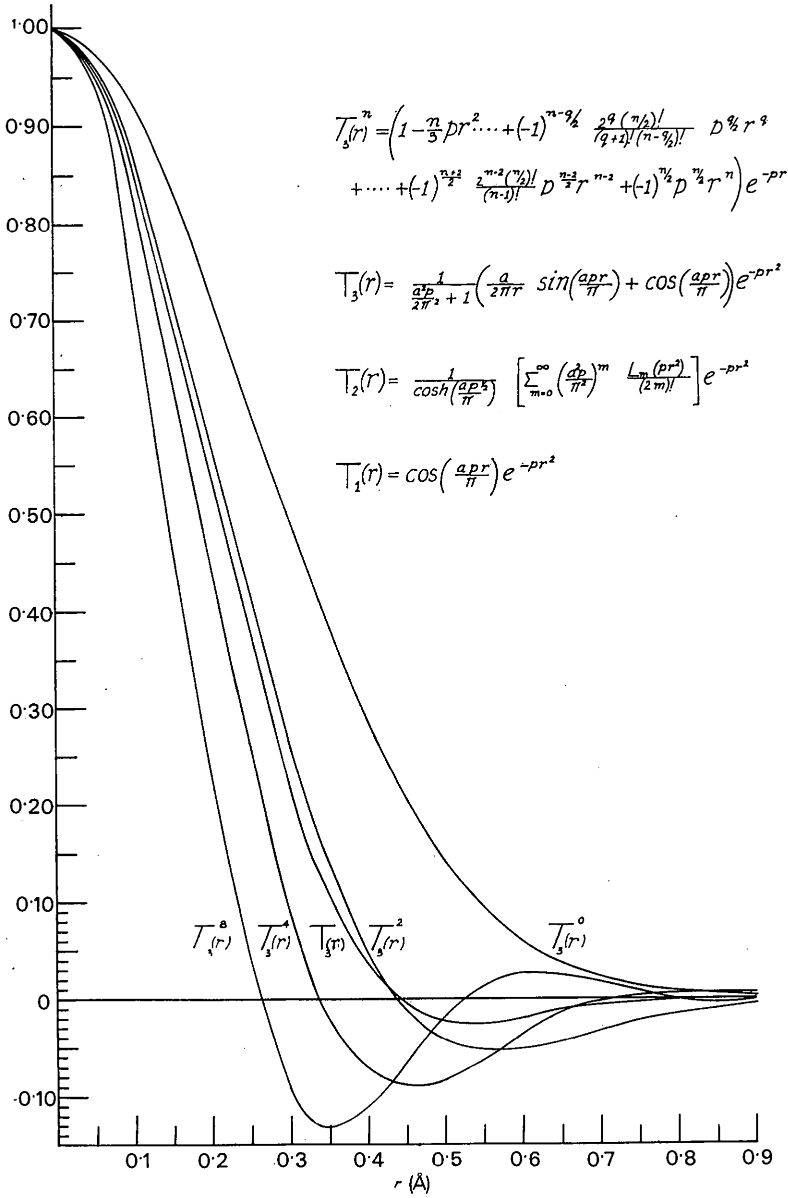

Fig. 2. Plots of $T_3^n(r)$ as a function of r for $n = 0,2,4$ and 8 and of $T_3(r)$, the three-dimensional complete transform of $\cosh(as)\exp(-\pi^2 s^2/p)$.

diffraction ripples and steep gradients could readily result in spurious peaks and significant displacement of main peaks.

It should be added finally that, for the purposes of computation, cosh $(as)\exp(-\pi^2s^2/p)$ is best expressed in the form

$$\tfrac{1}{2}[\exp(A-B)+\exp(-A-B)]\,, \qquad (4)$$

where $A=as$ and $B=(\pi^2/p)s^2$.

The factor $\frac{1}{2}$ may be absorbed outside the loop over the indices leaving an increase in computation of only three additions and one exponential term over that required to modify a structure amplitude in the usual way.

The author wishes to record his appreciation of fruitful discussions with Drs B. Dawson and A. McL. Mathieson and Mr A. F. Moodie, the latter having also derived the expression for the two-dimensional transform.

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The Crystal and Molecular Structure of Cyclopentadiene*

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The crystal structure of cyclopentadiene, C_5H_6, has been determined from X-ray diffraction photographs made at about −150 °C. The crystals are monoclinic, space group $P2_1/n$, with cell dimensions $a=7{\cdot}89$, $b=5{\cdot}65$, $c=10{\cdot}45$ Å, $\beta=114°\ 10'$. Intensities of 70 reflections recorded on four zero-level precession photographs were estimated visually and used in a least-squares refinement of the atomic coordinates. The final R index for these reflections is 0·10.

The five-membered ring of carbon atoms is planar; the values for the bond distances are in close agreement with those previously determined by electron diffraction techniques.

Introduction

Cyclopentadiene, C_5H_6, when irradiated with ultraviolet light at 77 °K, is damaged to form the very interesting cyclopentadienyl radical C_5H_5 (Liebling & Mc Connell, 1965). While trying to interpret electron paramagnetic resonance spectra of this radical we found that a knowledge of the crystal structure of the parent compound cyclopentadiene was necessary. Accordingly, the present investigation was undertaken.

Experimental

Cyclopentadiene (m.p. −80°C) was prepared by distilling dicyclopentadiene (Moffett, 1952). Single crystals were obtained by slowly lowering a sealed tube of cyclopentadiene from a dry-ice–acetone bath, at which temperature the compound is stable with respect to dimerization (Busler, Williams & Bonin, 1962), into a Dewar vessel of liquid nitrogen. The tube was then broken open under liquid nitrogen and clear monoclinic prisms, elongated along the **b** direction, were extracted from the frozen mass. All further operations on these crystals, including mounting and orientation, were carried out under liquid nitrogen.

A crystal about 2×1×1 mm in size was inserted into a 1 mm capillary which was then mounted on a goniometer head and transferred to a precession camera. During X-ray photography (Mo $K\alpha$ radiation) the capillary was kept in a steady stream of liquid nitrogen; although the nitrogen vaporized before reaching the crystal, it is estimated that the temperature of the crystal was about −150 °C.

A rather hasty (owing to the limited size of the liquid nitrogen reservoir) but systematic search of the reciprocal nets containing the b^* axis turned up four principal zones which were subsequently identified as $0kl$, $hk0$, $hk\bar{h}$, and $h,k,\bar{3}h$. Single photographs of the zero layer for each of these zones were prepared, the precession angle being 27°. Intensities were measured by visual comparison with a standard strip and were

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