

## 'Peakiness' Test Functions

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### Abstract

A number of common functions have been tested to determine their efficiency in refining structures using the criteria of 'peakiness' and non-negativity of the electron density distribution. It is concluded that the best function to maximize, generally, is  $\int \rho^3 dv$ , although, in special cases, a higher power of  $\rho$  may be better. When there is a heavy atom in the structure the method is much less sensitive to the particular function used so long as it involves powers of  $\rho$  greater than  $\rho^2$ .

### Introduction

Cochran (1953) first noted that, for a correct structure, the integral of the cube of the electron density,  $\int \rho^3 dv$ , would be a maximum. Stanley (1979) showed that, using the criterion of the 'peakiness' of the correct electron density distribution, maximization of  $\int \rho^3 dv$  could be used both for the determination of an initial set of signs and for the refinement of the structure. It was pointed out at the time that, although  $\int \rho^3 dv$  was the simplest function to maximize, from the standpoint of both peakiness and non-negativity, there may be other, better, functions. A thorough investigation of the other possible functions has been conducted, using data from known, and published, structures and also using data from an artificial structure for various temperature coefficients and with a heavy atom at a variety of positions.

### Possible test functions

There does not seem to be any analytical approach to the determination of the most appropriate function for discriminating between 'peaky' and 'non-peaky' distributions, although the work of Hillstrom (1970) seems to suggest that the identification of 'peaky' distributions may be of more general interest. From the many possible functions whose integral could discriminate between 'peaky' and 'non-peaky' distributions the following have been tested:  $\rho$ ,  $\rho^2$ ,  $\rho^3$ ,  $\rho^4$ ,  $\rho^5$ ,  $\rho^6$ ,  $\rho^7$ ,  $\sinh(\rho)$  and  $\exp(\rho)$ . The last two functions

were soon rejected since they were indistinguishable from  $\rho$ . The odd functions,  $\int \rho^{2n-1} |\rho| dv$ , were also tested but usually were indistinguishable from  $\int \rho^{2n} dv$ , indicating that the criterion for 'peakiness' was much more important than that for non-negativity. The results are summarized in Table 1. It is observed that, in general, the best function to maximize is  $\int \rho^3 dv$ . An exception was triphenylphosphate (Davies & Stanley, 1962). In this structure the heavy atom is at a pseudo-special position, in projection. This made the original Fourier refinement very difficult. In this case it turns out that the best function to maximize is  $\int \rho^5 |\rho| dv$ .

In order to investigate further the efficiency of the various functions, the artificial structure of identical carbon-like atoms used in previous studies (Stanley, 1968, 1979), was used, various temperature coefficients were applied to the data and, in order to study the effect of the presence of a heavy atom, each atom, in turn, was replaced by a double-weight atom.

The number of incorrect signs, in all cases, was determined within the ranges of  $F_{\max}:F_{\min}$  of 100:1 and 10:1 using nine initially assigned signs. The results are summarized in Table 2. A change in the temperature coefficient changes the number of structure factors within each range and also changes their relative order of magnitude.

### Concluding remarks

From the results it is possible to draw several conclusions:

1.  $\int \rho^3 dv$  is generally the best function to maximize for both normalized (or unitary) structure factors and for observed structure factors.

2. For special, but unpredictable, reasons it may be that another function is as good (or better) in a particular case (e.g. for triphenylphosphate  $\int \rho^5 |\rho| dv$  turns out to be markedly superior).

3. The presence of a heavy atom makes the refinement much less sensitive to the function maximized provided that it is a function involving the integral of powers of  $\rho$  greater than two.

4. Since there is very little difference between  $\int \rho^{2n} dv$  and  $\int \rho^{2n-1} |\rho| dv$  it is concluded that 'peakiness' is a more sensitive criterion than non-negativity.

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Table 1. Refinement behaviour of several known structures using various maximizing functions

Data set	Signs	$\int \rho \, dv$	$\int \rho^2 \, dv$	$\int \rho  \rho  \, dv$	$\int \rho^3 \, dv$	$\int \rho^4 \, dv$	$\int \rho^3  \rho  \, dv$	$\int \rho^5 \, dv$	$\int \rho^6 \, dv$	$\int \rho^5  \rho  \, dv$	$\int \rho^7 \, dv$	$\int \exp(\rho) \, dv$	$\int \sinh(\rho) \, dv$
1. Number incorrect		58	17	14	0	16	16	44	44	44	44	55	58
*1st incorrect		7th	21st	21st		67th	67th	41st	41st	41st	41st	8th	7th
2. Number incorrect		26	27	20	12	28	24	26	26	26	26	26	26
*1st incorrect		25th	25th	40th	50th	41st	41st	41st	41st	41st	41st	25th	25th
3. Number incorrect		144	140	139	99	132	131	131	132	67	81	146	144
*1st incorrect		23rd	50th	50th	120th	40th	40th	40th	40th	168th	160th	23rd	23rd
4. Number incorrect		42	32	30	18	20	30	31	31	32	32	42	42
*1st incorrect		24th	30th	31st	43rd	40th	37th	30th	30th	30th	30th	24th	24th
5. Number incorrect		44	34	32	24	24	34	35	35	35	35	44	44
*1st incorrect		20th	24th	26th	44th	42nd	36th	36th	36th	36th	36th	20th	20th

## Two-dimensional data sets

1. Artificial structure (Stanley, 1968, 1979). 140 strongest reflections: 7 known signs.
2. Diphenylanthracene (Bennett & Hanson, 1953). 77 strongest reflections: 20 known signs.
3. Triphenylphosphate (Davies & Stanley, 1962). 300 strongest reflections: 11 known signs.
4. Roussin's red ethyl ester (Thomas, Robertson & Cox, 1958). 81 strongest reflections; 11 known signs.

## Three dimensional data set

5. Roussin's red ethyl ester (Thomas, Robertson & Cox, 1958). 125 strongest reflections: 14 known signs.

\* Data sets arranged in decreasing order of magnitude of  $F_s$ .

Table 2. Refinement behaviour of an artificial structure under various conditions

Function maximized	Data type	All carbon atoms		One heavy atom	
		$F_{\max} : F_{\min}$	$F_{\max} : F_{\min}$	$F_{\max} : F_{\min}$	$F_{\max} : F_{\min}$
		100:1	10:1	100:1	10:1
		Number incorrect	Number incorrect	Number incorrect	Number incorrect
		total number	total number	total number	total number
$\int \rho \, dv$	<i>E</i>	93/214	51/122	106/223	48/120
	<i>F</i> ( <i>B</i> = 1.0)	90/203	37/87	100/217	32/82
	<i>F</i> ( <i>B</i> = 2.0)	81/185	26/66	92/201	24/63
$\int \rho^2 \, dv$	<i>E</i>	60/214	29/122	52/223	23/120
	<i>F</i> ( <i>B</i> = 1.0)	82/203	27/87	62/217	12/82
	<i>F</i> ( <i>B</i> = 2.0)	76/185	19/66	84/201	19/63
$\int \rho^3 \, dv$	<i>E</i>	10/214	0/122	28/223	0/120
	<i>F</i> ( <i>B</i> = 1.0)	12/203	1/87	27/217	1/82
	<i>F</i> ( <i>B</i> = 2.0)	33/185	11/66	35/201	9/63
$\int \rho^4 \, dv$	<i>E</i>	46/214	8/122	29/223	1/120
	<i>F</i> ( <i>B</i> = 1.0)	46/203	7/87	27/217	1/82
	<i>F</i> ( <i>B</i> = 2.0)	50/185	13/66	66/201	12/63
$\int \rho^5 \, dv$	<i>E</i>	76/214	40/122	32/223	1/120
	<i>F</i> ( <i>B</i> = 1.0)	48/201	8/87	42/217	4/82
	<i>F</i> ( <i>B</i> = 2.0)	45/185	7/66	24/201	1/63
$\int \rho^6 \, dv$	<i>E</i>	76/214	40/122	32/223	1/120
	<i>F</i> ( <i>B</i> = 1.0)	48/201	10/87	45/217	6/82
	<i>F</i> ( <i>B</i> = 2.0)	47/185	8/87	29/201	3/63
$\int \rho^7 \, dv$	<i>E</i>	74/214	37/122	32/223	1/120
	<i>F</i> ( <i>B</i> = 1.0)	60/201	14/87	45/217	5/82
	<i>F</i> ( <i>B</i> = 2.0)	47/185	8/66	34/201	3/63
$\int \exp(\rho) \, dv$	<i>E</i>	90/214	47/122	96/233	42/120
	<i>F</i> ( <i>B</i> = 1.0)	81/201	34/87	100/217	30/82
	<i>F</i> ( <i>B</i> = 2.0)	76/185	21/66	89/201	32/63
$\int \sinh(\rho) \, dv$	<i>E</i>	99/214	54/122	96/223	48/120
	<i>F</i> ( <i>B</i> = 1.0)	79/201	33/87	93/217	30/82
	<i>F</i> ( <i>B</i> = 2.0)	76/185	22/66	93/201	21/63

5. As expected, it makes little difference which atom in the artificial structure is chosen as the double-weight atom. Thus, the position of a heavy atom, provided it is not at a special or pseudo-special position, is insignificant.

6. The lower the temperature coefficient the better the results. Best results are obtained using *E*s (or *U*s) rather than *F*s, whatever the temperature coefficient.

7. Once the initial set of signs is sufficiently large to define the structure (even if it cannot be recognized)

there is no point in extending it; refinement proceeds identically.

The superiority of  $\int \rho^3 \, dv$ , in most cases, is presumably because of the existence of the relationship due to Sayre (1953), namely,

$$\int \rho^3 \, dv = \sum_h \sum_k F(h)F(k)F(-h-k),$$

coupled with the probability of finding, within a reasonably extended set of data, sufficient closed sets,

$F(h)$ ,  $F(k)$ ,  $F(-h-k)$ , in which the triple product has significant magnitude. Other similar relationships may exist for more than three  $F$ s forming a closed set but it is less probable that these multiple products are sufficiently large. However, when such relationships exist it is to be expected that some function other than  $\int \rho^3 dv$  could be superior.

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## Diffraction d'un Faisceau de Rayons X en Incidence Très Rasante

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### Abstract

The penetration depth  $\tau$  of an X-ray beam ( $\lambda \approx 1 \text{ \AA}$ ) incident on a surface with an angle  $\alpha$  decreases rapidly when  $\alpha$  goes below  $\alpha_c$ , the critical angle of total reflexion. It is shown experimentally that at the same time the Bragg peaks have a stick-like shape perpendicular to the sample surface. The variation of the depth  $\tau$  as a function of  $\alpha$  has been determined by measuring the length of the stick. The variation of the Bragg intensity and the position of the peak as well as the depth are calculated precisely using the simple Fresnel formulae.

### Introduction

L'indice de réfraction d'un solide pour les longueurs d'onde X est légèrement inférieur à 1. Aussi, lorsqu'un faisceau X arrive sur une surface avec un angle d'incidence suffisamment faible (de l'ordre de quelques 1/10e degré), il est réfléchi totalement. On a établi dans le solide d'un système d'ondes évanescentes, et le faisceau transmis est absorbé fortement puisque sa pénétration n'est que de 20 à 50 Å selon le composé et la longueur d'onde X (Parratt, 1954). Si le solide est un composé monocristallin, l'onde transmise sera diffractée pour certaines positions du cristal. Les réflexions de Bragg seront donc sensibles aux constantes du cristal dans la couche irradiée, c'est-à-dire près de la surface. Marra, Eisenberger & Cho (1979) ont étudié l'interface entre deux cristaux épitaxiés par l'observation de certaines de ces réflexions. Par l'étude des réflexions de Bragg

en incidence rasante de monocristaux de silicium et alumine, nous avons déterminé la pénétration et la direction du faisceau transmis que nous avons comparé aux valeurs calculées par les formules de Fresnel.

### Intensité et formes des raies de Bragg

Rappelons brièvement le calcul de l'onde transmise. L'indice de réfraction pour les rayons X ( $\lambda \approx 1 \text{ \AA}$ ) se met sous la forme  $n = 1 + n' + in''$  avec  $n' < 0$ ,  $n'' < 0$ ,  $n' \approx 10^{-6}$  et  $0 < |n''| < 10^{-6}$  selon l'absorption du matériau.

Soit une onde plane incidente sur une surface selon une direction faisant un angle  $\alpha$  avec la surface. L'onde transmise se propage dans le solide selon une direction située à l'angle  $\alpha_s$  de la surface. Les angles  $\alpha$  et  $\alpha_s$  sont reliés par la loi de Descartes:  $\sin(\pi/2 - \alpha) = n \sin(\pi/2 - \alpha_s)$ .

Dans le cas où  $n'' = 0$  et lorsque l'angle d'incidence  $\alpha < \alpha_c = (-2n')^{1/2}$ , le faisceau est réfléchi totalement. Les amplitudes des ondes réfléchies et transmises sont données par les formules de Fresnel. Si nous nous limitons au cas d'une incidence très rasante ( $\alpha < 1/100 \text{ rad}$ ) la polarisation de l'onde incidente n'intervient pas et le vecteur champ électrique de l'onde transmise est, en un point de coordonnées  $x$  et  $z$  ( $x$  sur une direction parallèle à la surface et  $z$  sur la direction perpendiculaire) (voir par exemple Bruhat, 1954, ch. XVII).

$$E(x, z) = A(\alpha) \exp i\{\omega t - (2\pi/\lambda)n[x \cos \alpha_s + z \sin \alpha_s]\}.$$