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On the Strong Equivalence of Structure Invariants

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The triangle in reciprocal space associated with a given structure invariant is employed to introduce the concept of the strong equivalence of structure invariants and to describe its relationship to the earlier theory of equivalence. It is assumed that the collection of interatomic triangles in a crystal structure may be partitioned into subsets in such a way that the interatomic triangles in each subset are congruent, lie in the same or parallel planes, and are randomly oriented about a common normal. For structures satisfying these conditions, two structure invariants which are equivalent to each other in the strong sense are also approximately equal, especially if the sides of the associated triangle are small. This result may find application in the solution of the problem of direct phase determination for extremely complex structures satisfying our assumptions.

1. Introduction

In the determination of crystal structures, powerful use is usually made of some previously known structural information. If the crystal structure determination is carried out by the so-called direct method, *i.e.* by finding first the phases of the structure factors, it is not always clear just what *a priori* structural knowledge has been utilized or how it has been employed. The study of this matter is important because its clarification leads to a strengthening of the direct method of phase determination. Thus, once it was recognized that the inequality relationships among the structure factors (Harker & Kasper, 1948) were based on the nonnegative character of the electron density distribution, it became possible to extend considerably the class of known inequalities (Karle & Hauptman, 1950). Again the Sayre (1952) relationship was appreciably sharpened by means of algebraic and probability methods which deliberately exploited the essential discreteness of the electron density distribution, the structural feature upon which the equation of Hughes (1953) and its probability counterpart (Zachariasen, 1952; Hauptman & Karle, 1953; Woolfson, 1954) depend. More recently, it has been found possible to utilize previous knowledge of partial or complete molecular structure as an aid in phase determination (Hauptman, 1964). Finally, for extremely complex structures having the property that many of the interatomic triangles are congruent to each other and are randomly oriented in space (a situation which obtains, for example, in certain protein structures), the theory of the equivalence of structure invariants yields additional relationships among the structure factors (Hauptman, 1966). In view of the latter development, it is natural to ask whether anything can be salvaged if it should happen that interatomic triangles are congruent but not necessarily randomly oriented in space. It is our purpose in the present paper to give an affirmative answer to this question. To this end we introduce the theory of strong equivalence, relate it to the earlier one on the equivalence of structure invariants, and show how it leads to the relationships we seek.

2. Preliminary definitions

Denote by N the number of atoms in the unit cell and by Z_j and $\mathbf{r}_j$ the atomic number and position vector respectively of the atom labeled j. The normalized structure factor $E_{\mathbf{h}}$ and its phase $\varphi_{\mathbf{h}}$ are defined by

$$E_{\mathbf{h}} = |E_{\mathbf{h}}| \exp(i\varphi_{\mathbf{h}}) = \frac{1}{\sigma_2^{1/2}} \sum_{j=1}^{N} Z_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) \quad (2.1)$$

where

$$\sigma_2 = \sum_{j=1}^{N} Z_j^2 . \quad (2.2)$$

If we assume that

$$\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0 \quad (2.3)$$

and introduce the abbreviations

$$\varphi_i = \varphi_{\mathbf{h}_i},\ i = 1,2,3, \quad (2.4)$$

then the linear combinations of the phases

$$\varphi_1 + \varphi_2 + \varphi_3 , \quad (2.5)$$

are known as structure invariants since their values are uniquely determined by the crystal structure and are independent of the choice of origin.

Instead of (2.5) we shall be particularly interested in the variant

$$V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} = |E_1 E_2 E_3| \cos(\varphi_1 + \varphi_2 + \varphi_3) \quad (2.6)$$

in which the abbreviations

$$E_i = E_{\mathbf{h}_i},\ i = 1,2,3 \quad (2.7)$$

have been employed. Under the assumption (2.3), the $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$, like (2.5), are evidently structure invariants. They are important because it is their values, rather than those of the individual phases $\varphi_{\mathbf{h}}$, which are, in general, uniquely determined by the known magnitudes $|E_{\mathbf{h}}|$ of the structure factors. In addition, the values of the $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ lead directly, by means of simple arithmetic, space-group dependent procedures for fixing the origin and enantiomorph (Hauptman & Karle, 1956; Karle & Hauptman, 1956, 1957), to the values of all the phases $\varphi_{\mathbf{h}}$.

3. The concept of strong equivalence

Def. 3.1. In view of (2.3), the structure invariant $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ determines a triangle, $\Delta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$, said to be the triangle associated with $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and having a definite orientation in reciprocal space, whose sides are the vectors $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$. The lengths of its sides are denoted by

$$q_{\mathbf{h}_i}=|\mathbf{h}_i|\ ,\ \ i=1,2,3\ . \tag{3.1}$$

Def. 3.2. Two invariants $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $V_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ are said to be equivalent in the strong sense if their associated triangles, $\Delta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $\Delta_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$, are congruent and coplanar. We assume naturally that $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0$.

The notion of approximate strong equivalence is particularly important in application. Thus $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $V_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ are considered to be approximately equivalent in the strong sense if their associated triangles, $\Delta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $\Delta_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ are approximately congruent and approximately coplanar.

Since the equivalence of structure invariants requires only the congruence (not necessarily the coplanarity) of the associated triangles (Hauptman, 1966), it follows that two structure invariants which are equivalent to each other in the strong sense are also equivalent.

The relationship of strong equivalence induces a partition of the set of structure invariants (2.6) into mutually exclusive subsets having the property that any two invariants which belong to the same subset are equivalent to each other in the strong sense while two invariants belonging to different subsets are not equivalent to each other in the strong sense. The importance of the concept of strong equivalence stems from the fact that, for structures satisfying certain conditions, two structure invariants which are equivalent to each other in the strong sense are approximately equal. Thus the notion of strong equivalence facilitates the solution of the problem of direct phase determination.

4. The structure invariants $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$

The starting point of our investigation is the equation (Hauptman & Karle, 1962)

$$V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}-\frac{1}{N^{1/2}}(|E_{\mathbf{h}_1}|^2+|E_{\mathbf{h}_2}|^2+|E_{\mathbf{h}_3}|^2-2)$$
$$=\frac{(N-1)\,(N-2)}{N^{1/2}}\langle\cos 2\pi(\mathbf{h}_1\cdot\mathbf{r}_{\mu\nu}-\mathbf{h}_3\cdot\mathbf{r}_{\nu\rho})\rangle_{\mu\nu\rho}\ , \tag{4.1}$$

in which $\mathbf{r}_{\mu\nu}$ and $\mathbf{r}_{\nu\rho}$ are adjacent interatomic vectors,

$$\mathbf{r}_{\mu\nu}=\mathbf{r}_\mu-\mathbf{r}_\nu\ ,\quad \mathbf{r}_{\nu\rho}=\mathbf{r}_\nu-\mathbf{r}_\rho\ ,\quad \mathbf{r}_{\rho\mu}=\mathbf{r}_\rho-\mathbf{r}_\mu\ , \tag{4.2}$$

and the average of the cosine is defined by

$$\langle\cos 2\pi(\mathbf{h}_1\cdot\mathbf{r}_{\mu\nu}-\mathbf{h}_3\mathbf{r}_{\nu\rho})\rangle_{\mu\nu\rho}$$
$$=\frac{\sum\limits_{\mu\neq\nu\neq\varrho\neq\nu=1}^{N}\cos 2\pi(\mathbf{h}_1\cdot\mathbf{r}_{\mu\nu}-\mathbf{h}_3\cdot\mathbf{r}_{\nu\rho})}{N(N-1)\ (N-2)}\ . \tag{4.3}$$

Equation (4.1), which expresses the structure invariant $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ in terms of the interatomic vectors, is valid if the crystal structure consists of N identical atoms in the unit cell. It will be clear however that our final result retains approximate validity even if this requirement is relaxed somewhat, provided that 'heavy-atom' structures are excluded.

Next, we attempt to estimate the average (4.3) by replacing each term in the sum on the right hand side by its average value. Which average shall we choose? In order to answer this question we observe that there corresponds to each term in the sum an interatomic triangle having sides $\mathbf{r}_{\mu\nu}$, $\mathbf{r}_{\nu\rho}$, $\mathbf{r}_{\rho\mu}$ since, in view of (4.2), $\mathbf{r}_{\mu\nu}+\mathbf{r}_{\nu\rho}+\mathbf{r}_{\rho\mu}=0$. In other words, the sum in (4.3) is taken over all the interatomic triangles. Since the crystal structure is fixed, the planes of the interatomic triangles, the magnitudes of the interatomic vectors, and the angle between any pair of adjacent interatomic vectors, while perhaps not known, are nevertheless also fixed. These facts suggest that we fix the vectors $\mathbf{h}_1$, $\mathbf{h}_3$ and the plane and the magnitudes r and r' of the vectors $\mathbf{r}$ and $\mathbf{r}'$ respectively (to be identified later with a pair of adjacent interatomic vectors) as well as the angle φ_r between $\mathbf{r}$ and $\mathbf{r}'$. We imagine all orientations in a fixed plane of the triangle determined by r, r', and φ_r to be equally probable and, under these conditions, require the average value of $\cos 2\pi(\mathbf{h}_1\cdot\mathbf{r}-\mathbf{h}_3\cdot\mathbf{r}')$. Denoting by α the angle between the plane of $\mathbf{r}$ and $\mathbf{r}'$ and that of $\mathbf{h}_1$ and $\mathbf{h}_3$ and referring to equations (17) and (13) of an earlier paper (Hauptman, 1965) we find this average to be

$$\langle\cos 2\pi(\mathbf{h}_1\cdot\mathbf{r}-\mathbf{h}_3\cdot\mathbf{r}')\rangle=C(r_\pm;\alpha)$$
$$=J_0\left(2\pi r_+\sin^2\frac{\alpha}{2}\right)J_0\left(2\pi r_-\cos^2\frac{\alpha}{2}\right)\ , \tag{4.4}$$

where

$$r_\pm=\{q_{\mathbf{h}_1}^2r^2+2q_{\mathbf{h}_1}rq_{\mathbf{h}_3}r'\cos(\varphi_{r}\pm\varphi_h)+q_{\mathbf{h}_3}^2r'^2\}^{\frac{1}{2}}\ , \tag{4.5}$$

$q_{\mathbf{h}_1}$ and $q_{\mathbf{h}_3}$ are the magnitudes of $\mathbf{h}_1$ and $\mathbf{h}_3$ respectively, and $\varphi_{\mathbf{h}}$ is the angle between $\mathbf{h}_1$ and $-\mathbf{h}_3$. Substituting from (4.4) into (4.1) we find

$$V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}-\frac{1}{N^{\frac{1}{2}}}(|E_{\mathbf{h}_1}|^2+|E_{\mathbf{h}_2}|^2+|E_{\mathbf{h}_3}|^2-2)$$
$$\approx\frac{(N-1)\,(N-2)}{N^{\frac{1}{2}}}\langle C(r_{\pm\mu\nu\rho};\alpha_{\mu\nu\rho})\rangle_{\mu\nu\rho} \tag{4.6}$$

where $C(r_{\pm\mu\nu\rho};\alpha_{\mu\nu\rho})$ is obtained from (4.4); the $r_{\pm\mu\nu\rho}$ are found from (4.5) by replacing r by $r_{\mu\nu}=|\mathbf{r}_{\mu\nu}|$, r' by $r_{\nu\rho}=|\mathbf{r}_{\nu\rho}|$, and φ_r by $\varphi_{\mu\nu\rho}$, the angle between $\mathbf{r}_{\mu\nu}$ and $\mathbf{r}_{\rho\nu}$; $\alpha_{\mu\nu\rho}$ is the angle between the plane of the interatomic triangle determined by $\mathbf{r}_{\mu\nu}$, $\mathbf{r}_{\nu\rho}$, $\mathbf{r}_{\rho\mu}$ and the plane of $\mathbf{h}_1$ and $\mathbf{h}_3$; and the average of $C(r_{\pm\mu\nu\rho};\alpha_{\mu\nu\rho})$ is defined by

$$\langle C(r_{\pm\mu\nu\rho};\,\alpha_{\mu\nu\rho})\rangle=\frac{\sum\limits_{\substack{\mu\neq\nu\neq\varrho\neq\mu\\1}}^{N} C(r_{\pm\mu\nu\rho}\,;\,\alpha_{\mu\nu\rho})}{N(N-1)\,(N-2)}\,. \quad (4.7)$$

There remains the problem of determining the precise conditions under which the average of (4.4) may be substituted for that appearing in (4.1). In view of the meaning of the average in (4.4) we formulate the following [which we call hypothesis II in order to distinguish it from the hypothesis of our earlier paper (Hauptman, 1966)]:

Hypothesis II. The set of all interatomic triangles may be decomposed into mutually exclusive subsets with the property that the interatomic triangles in any subset are congruent to each other and coplanar, in the sense that they lie in the same or parallel planes. Furthermore, the triangles in any such collection of congruent, coplanar interatomic triangles are randomly oriented about their common normal. (It is to be noted that no restriction on the number of such families of congruent, coplanar interatomic triangles is imposed.)

We show next that, except for the errors inherent in finite sampling, (4.6) is valid if the crystal structure fulfils the requirements of hypothesis II. In order to prove this it is sufficient to group the terms in the numerator of the right hand side of (4.3) into sets, the terms in each set corresponding to all those interatomic triangles which are congruent to some specified one and which lie in planes parallel or identical to the plane of the specified interatomic triangle. Since the interatomic triangles in any such set are assumed to be randomly oriented about their common normal (hypothesis II), the sum of the cosine terms corresponding to each such set in the numerator of (4.3) is equal to the number of terms in the set multiplied by the appropriate average $C(r_{\pm\mu\nu\rho};\,\alpha_{\mu\nu\rho})$. In this way we arrive at (4.6) and (4.7).

It is clear that even if hypothesis II is relaxed somewhat, in particular for the larger interatomic triangles whose corresponding terms in (4.3) would then tend to cancel each other and for which the values of $C(r_{\pm\mu\nu\rho};\,\alpha_{\mu\nu\rho})$ are small anyhow, (4.6) still retains approximate validity.

There remains only the problem of showing that, for structures satisfying hypothesis II, the right hand side of (4.6) has the same value for any two structure invariants which are equivalent to each other in the strong sense. To this end let $V_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ be any structure invariant equivalent to $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ in the strong sense. Then

$$\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0\,,\quad q_{\mathbf{k}_i}=|\mathbf{k}_i|=|\mathbf{h}_i|=q_{\mathbf{h}_i}\,,\quad i=1,2,3,$$

and the plane determined by $\mathbf{k}_1$ and $\mathbf{k}_3$ is parallel to that determined by $\mathbf{h}_1$ and $\mathbf{h}_3$. For this invariant (4.6) becomes

$$V_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}-\frac{1}{N^{\frac{1}{2}}}\left(|E_{\mathbf{k}_1}|^2+|E_{\mathbf{k}_2}|^2+|E_{\mathbf{k}_3}|^2-2\right)$$
$$\approx\frac{(N-1)\,(N-2)}{N^{\frac{1}{2}}}\,\langle C(r'_{\pm\mu\nu\rho};\,\alpha'_{\mu\nu\rho})\rangle_{\mu\nu\rho}\,,\quad (4.8)$$

where $r'_{\pm\mu\nu\rho}$ and $\alpha'_{\mu\nu\rho}$ are obtained from $r_{\pm\mu\nu\rho}$ and $\alpha_{\mu\nu\rho}$ respectively by replacing $\mathbf{h}_1$ by $\mathbf{k}_1$, $\mathbf{h}_3$ by $\mathbf{k}_3$, and $\varphi_{\mathbf{h}}$, the angle between $\mathbf{h}_1$ and $-\mathbf{h}_3$, by $\varphi_{\mathbf{k}}$, the angle between $\mathbf{k}_1$ and $-\mathbf{k}_3$. Since $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $V_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ are equivalent in the strong sense, the associated triangles $\Delta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $\Delta_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ are congruent so that $q_{\mathbf{k}_1}=q_{\mathbf{h}_1}$, $q_{\mathbf{k}_3}=q_{\mathbf{h}_3}$, and $\varphi_{\mathbf{k}}=\varphi_{\mathbf{h}}$. In view of (4.5), $r'_{\pm\mu\nu\rho}=r_{\pm\mu\nu\rho}$ for all μ, ν, ϱ. Furthermore, $\Delta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $\Delta_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ lie in parallel planes so that $\alpha_{\mu\nu\rho}$, the angle between the plane of the interatomic triangle $\mathbf{r}_{\mu\nu}$, $\mathbf{r}_{\nu\rho}$, $\mathbf{r}_{\rho\mu}$ and that of $\Delta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$, is equal to $\alpha'_{\mu\nu\rho}$, the angle between the plane of $\mathbf{r}_{\mu\nu}$, $\mathbf{r}_{\nu\rho}$, $\mathbf{r}_{\rho\mu}$ and that of $\Delta_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$, for all μ, ν, ϱ. Since $r_{\pm\mu\nu\rho}=r'_{\pm\mu\nu\rho}$ and $\alpha_{\mu\nu\varrho}=\alpha'_{\mu\nu\rho}$ for all μ, ν, ϱ, it follows that the right hand sides of (4.6) and (4.8) are equal to each other. Finally, for large N, the second terms of the left hand sides of (4.6) and (4.8) are relatively small. Thus we arrive at the main result of this paper:

Theorem. For structures satisfying hypothesis II, two structure invariants, equivalent to each other in the strong sense, are approximately equal.

5. Concluding remarks

As has already been observed, our theorem retains approximate validity even if hypothesis II is relaxed somewhat. It is an important fact that, in the event that the sides of the associated triangle are small, then the error resulting from the relaxation of hypothesis II is particularly small. Conversely, the theorem tends to lose validity as the sides of the associated triangle increase. Intuitively this is seen to be a consequence of the fact that interatomic triangles which are almost congruent or almost coplanar 'appear' to be more precisely congruent or coplanar when viewed from the low resolution inherent in the small size of the triangle with sides $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$. It is not difficult to give a more rigorous justification based on a closer analysis of the terms of (4.3). However, the argument is so similar to the corresponding one given in our earlier paper (1966) that we do not repeat it here.

We observe next that crystal structures satisfying our earlier hypothesis (1966) also satisfy the present hypothesis II, but not necessarily conversely. Thus hypothesis II imposes a milder restriction on the structure than the earlier one. For this reason we anticipate that our present theorem should yield fewer relationships among the structure factors than were obtained in the earlier paper. That this does indeed turn out to be the case is a consequence of the fact that two structure invariants which are equivalent to each other in the strong sense are obviously also equivalent, but not necessarily conversely.

If, for structures satisfying hypothesis II, it should happen that the molecular structure is partially or completely known and if the orientations of many interatomic planes are also known, then (4.6) may be used directly to obtain initial estimates of the invariants $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$. Standard techniques (*e.g.*, Karle & Hauptman, 1956, 1957, 1958) may then be employed to determine more accurately the values of all the phases.

We note finally that complex crystal structures, in particular protein structures, often satisfy (at least approximately) the present hypothesis II, as well even as our earlier hypothesis (1966). We therefore anticipate that the methods described here and in the earlier paper may eventually find application in the elucidation of such structures.

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The Influence of Intensity Errors on the Higher-Moment Test for Centrosymmetry*

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The sensitivity of the higher-moment test for detection of centrosymmetry to errors in the intensity data is examined. The errors considered are (1) random errors proportional to I, (2) systematic errors of the type $I_o = k\Sigma\,[1-\exp(-I/k\Sigma)]$, (3) errors associated with the non-observance of very weak reflexions, and (4) errors systematic in $\sin\theta$. Mathematical expressions are obtained in a compact form for $\langle z^n\rangle$ including the effect of errors in all the cases except (4). Tables of $\langle z^n\rangle$ with errors are given. It is found that it would not be profitable to use moments of very high order such as $\langle z^4\rangle$ or $\langle z^5\rangle$ but that the higher-moment test is relatively safe for crystals whose weighted reciprocal lattice contains a large percentage of very weak reflexions.

Introduction

Various statistical criteria based on the statistical distribution of X-ray intensities have been used to distinguish between centrosymmetric and non-centrosymmetric crystals (or projections). Deviations from Wilson's (1949) distributions occur for various reasons such as the presence of a few dominating atoms, pseudo-symmetry, *etc.*, and the distributions of intensities in these special cases have been considered by various authors. The distributions obtained in practical cases may also deviate from Wilson's distributions (even in the absence of the above mentioned disturbing features which are structural in nature) because of the use of inaccurate intensity data, *i.e.* intensity data with errors of observation. Rogers, Stanley & Wilson (1955, hereafter referred to as R–S–W) have considered the effect of errors of various kinds in the original intensity data on the statistical criteria such as the cumulative distribution function $N(z)$, the test-ratio ϱ of Wilson, and the specific variance, v, with the aim of finding a rough upper limit for the discrepancy that can be allowed in practical cases where intensities with the errors of observation are involved. This enables one to avoid correlating such deviations (*i.e.* the statistical anomalies arising from the use of inaccurate intensity data) with structural peculiarities. In the present paper we shall study the effect of errors in the intensity data on the higher-moment test which has been proposed by Foster & Hargreaves (1963*a*,*b*) and independently by Srinivasan & Subramanian (1964). The additional advantage of the higher-moment test over other statistical criteria is that the exact theoretical values of the higher moments can be obtained under very general conditions (Foster & Hargreaves, 1963*a*,*b*). We shall however consider here only the equal-atom-random-position case as has been done by R–S–W since this would suffice to show the influence of intensity errors on the higher-moment test.

A second aim of the present investigation is to study the sensitivity of the various higher moments to the errors of intensity data; such a study may therefore provide some guidance regarding the choice of a particular higher moment as optimum in practical cases.

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