the lowest e.s.d. values, in some cases by a factor of 2 or more, but in the light of the work of Taylor & Kennard (1986) this may not be unrealistic.

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On the Harker–Kasper Inequalities

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Abstract

It is shown that two unitary structure factors generate a two-parameter family of Harker–Kasper inequalities and that the strongest of these coincides with the third-order determinant Karle–Hauptman inequality.

Inequality relationships among structure factors are called Harker–Kasper (HK) inequalities when they are obtained by the Cauchy–Schwartz inequality (Harker & Kasper, 1948). Their derivation requires algebraic manipulations of the unitary structure-factor (u.s.f.) expressions. Thus, HK inequalities in general have considerably different expressions, as is illustrated by, for instance, equations (6), (15) and (16) of Woolfson (1988). Moreover, Woolfson showed that some HK inequalities can be more effective that the lowest determinant Karle–Hauptman (Karle & Hauptman, 1950) inequalities. Since it is commonly believed that HK inequalities are contained within the *complete* set of determinant inequalities, the former result does not conflict with this idea. This paper reports explicit proof of this in the case of the lowest-order inequality. More definitely, it is shown that a *two*-parameter family of HK inequalities, involving three reflexions, can be constructed from *two* unitary structure factors and that the strongest of these inequalities, *viz* the one that holds true whatever the parameter values, is the third-order determinant Karle–Hauptman (Karle & Hauptman, 1950) inequality, in the form obtained by Goedkoop (1950). [For a recent review, see Hauptman (1991).]

Since the analysis is derived from that of Woolfson (1988; hereinafter referred to as I), his notation is adopted. In order to prove the above statement, the effect of translations on the derivation of the HK inequality [equation (6*a*) of I] is first analysed. Translation of the origin by **a** implies that the u.s.f. $U(\mathbf{h})$ [whose modulus $|U(\mathbf{h})|$ is denoted $\mu(\mathbf{h})$, so that $U(\mathbf{h}) = \exp i\varphi(\mathbf{h})\,\mu(\mathbf{h})$] becomes

$$\begin{aligned} U_{\mathbf{a}}(\mathbf{h}) &= \sum_{j=1}^{N} n_j \exp[i2\pi\mathbf{h}\cdot(\mathbf{r}_j + \mathbf{a})] \\ &= \exp[i2\pi\mathbf{a}\cdot\mathbf{h}]U(\mathbf{h}) \\ &\equiv \exp[i\phi_{\mathbf{a}}(\mathbf{h})]U(\mathbf{h}). \end{aligned} \tag{1}$$

The same calculations of *I*, yielding inequality (6*a*) of I, can now be repeated bt starting with $U_{\mathbf{a}}(\mathbf{h})$ and $U_{\mathbf{a}}(\mathbf{k})$. They give

$$\begin{aligned} &|\exp[i\phi_{\mathbf{a}}(\mathbf{h})U(\mathbf{h})] + \exp[i\phi_{\mathbf{a}}(\mathbf{k})]U(\mathbf{k})|^2 \\ &\quad \le 2\{1 + \mu(\mathbf{h}-\mathbf{k})\cos[\varphi(\mathbf{h}-\mathbf{k}) + 2\pi\mathbf{a}\cdot(\mathbf{h}-\mathbf{k})]\}. \end{aligned} \tag{2}$$

With the definition

$$\delta \equiv \varphi(\mathbf{h}-\mathbf{k}) + 2\pi\mathbf{a}\cdot(\mathbf{h}-\mathbf{k}), \tag{3}$$

inequality (2) becomes

$$|\exp[i\varphi_3(\mathbf{h},\bar{\mathbf{k}}) + \delta]\mu(\mathbf{h}) + \mu(\mathbf{k})|^2 \leq 2[1 + \mu(\mathbf{h}-\mathbf{k})\cos(\delta)], \quad (4)$$

where

$$\varphi_3(\mathbf{h},\bar{\mathbf{k}}) = \varphi(\mathbf{h}) - \varphi(\mathbf{k}) - \varphi(\mathbf{h}-\mathbf{k})$$

is the triple-phase structure invariant of the involved u.s.f's. Since the arbitrariness of **a** implies that of δ, the strongest HK inequality resulting from (4) will be the one that is fulfilled for whatever $\delta \in [0, 2\pi)$. In order to work out this relation, it is convenient to write inequality (4) as

$$2\{\mu(\mathbf{h})\mu(\mathbf{k})\cos[\varphi_3(\mathbf{h},\bar{\mathbf{k}}) + \delta] - \mu(\mathbf{h}-\mathbf{k})\cos\delta\} \leq 2 - [\mu^2(\mathbf{h}) + \mu^2(\mathbf{k})]. \quad (5)$$

From the addition formula for circular functions and the definitions

$$M \equiv \{[\mu(\mathbf{h})\mu(\mathbf{k})\cos\varphi_3(\mathbf{h},\bar{\mathbf{k}}) - \mu(\mathbf{h}-\mathbf{k})]^2 + [\mu(\mathbf{h})\mu(\mathbf{k})\sin\varphi_3(\mathbf{h},\bar{\mathbf{k}})]^2\}^{1/2}, \quad (6a)$$

$$\cos\tau \equiv [\mu(\mathbf{h})\mu(\mathbf{k})\cos\varphi_3(\mathbf{h},\bar{\mathbf{k}}) - \mu(\mathbf{h}-\mathbf{k})]/M, \quad (6b)$$

$$\sin\tau \equiv [\mu(\mathbf{h})\mu(\mathbf{k})\sin\varphi_3(\mathbf{h},\bar{\mathbf{k}})]/M, \quad (6c)$$

the left hand side (l.h.s.) of inequality (5) becomes $2M\cos(\delta + \tau)$. Inequality (5) reads

$$\cos(\delta + \tau) \leq [2 - \mu^2(\mathbf{h}) - \mu^2(\mathbf{k})]/2M.$$

This constraint is fulfilled for any δ, *i.e.* for any translation, if and only if

$$[2 - \mu^2(\mathbf{h}) - \mu^2(\mathbf{k})]/2M \geq 1.$$

Simple algebraic manipulations convert this inequality into

$$\cos\varphi_3(\mathbf{h},\bar{\mathbf{k}}) \geq \{[\mu^2(\mathbf{h}) + \mu^2(\mathbf{k}) + \mu^2(\mathbf{h}-\mathbf{k}) - 1] \times [2\mu(\mathbf{h})\mu(\mathbf{k})\mu(\mathbf{h}-\mathbf{k})]^{-1}\} - \{[\mu^2(\mathbf{h}) - \mu^2(\mathbf{k})]^2[8\mu(\mathbf{h})\mu(\mathbf{k})\mu(\mathbf{h}-\mathbf{k})]^{-1}\}, \quad (7)$$

which represents the strongest HK inequality with respect to all possible translations. Of course, the inequality is structure invariant and refers to the symmetry group $P1$. However, it is weaker than the third-order determinant Karle–Hauptman inequality (Goedkoop, 1950)

$$\cos\varphi_3(\mathbf{h},\bar{\mathbf{k}}) \geq [\mu^2(\mathbf{h}) + \mu^2(\mathbf{k}) + \mu^2(\mathbf{h}-\mathbf{k}) - 1] \times [2\mu(\mathbf{h})\mu(\mathbf{k})\mu(\mathbf{h}-\mathbf{k})]^{-1} \quad (8)$$

involving the same reflexions. In fact, constraint (7) becomes equal to (8) only when $\mu(\mathbf{h}) = \mu(\mathbf{k})$.

From a mathematical point of view, inequality (7) has been obtained because all linear combinations, with unitary coefficients, of contributions $U(\mathbf{h})$ and $U(\mathbf{k})$ have been considered of the l.h.s. of (2). Thus, in a certain sense, the vectorial structure assumed by Kitajgorodskij (1961) in working out the Karle–Hauptman relations has been exploited, though only in part, owing to the unimodularity constraint set on the coefficients. Consequently, the question arises as to whether an inequality stronger than (7) may not be obtained starting from the most general linear combination $zU(\mathbf{h}) + wU(\mathbf{k})$, where z and w are complex numbers. This is exactly what happens and the resulting inequality is the Karle–Hauptman combination. To clarify this point, put

$$z \equiv |z|\exp[i\arg(z)], \quad (9a)$$

$$w \equiv |w|\exp[i\arg(w)], \quad (9b)$$

$$\Omega \equiv \arg(z) - \arg(w), \quad (9c)$$

$$\rho \equiv (|z|^2 + |w|^2)^{1/2}, \quad (10a)$$

$$\sin\tau \equiv |z|/\rho, \quad (10b)$$

$$\cos\tau \equiv |w|/\rho, \quad (10c)$$

where τ obeys the constraint

$$0 \leq \tau \leq \pi/2. \quad (11)$$

The result is

$$zU_{\mathbf{a}}(\mathbf{h}) + wU_{\mathbf{a}}(\mathbf{k}) = \rho\exp[i\arg(z)] \times \{\sin\tau\exp[i\phi_{\mathbf{a}}(\mathbf{h})]U(\mathbf{h}) + \cos\tau\exp\{i[\phi_{\mathbf{a}}(\mathbf{k}) - \Omega]\}U(\mathbf{k})\}.$$

The use of the Cauchy–Schwartz inequality and simple calculations yield

$$\begin{aligned}|\sin\tau\exp[i\phi_{\mathbf{a}}(\mathbf{h})]U(\mathbf{h}) &+ \cos\tau\exp\{i[\phi_{\mathbf{a}}(\mathbf{k}) - \Omega]\}U(\mathbf{k})|^2\\ &\leq \sum_{j=1}^{N} n_j\{1 + 2\sin\tau\cos\tau \times \cos[2\pi(\mathbf{h}-\mathbf{k})\cdot(\mathbf{r}_j + \mathbf{a}) + \Omega]\}\\ &= 1 + 2(\sin\tau\cos\tau)\Re[U_{\mathbf{a}}(\mathbf{h}-\mathbf{k})\exp(i\Omega)]\\ &= 1 + 2\mu(\mathbf{h}-\mathbf{k})(\sin\tau\cos\tau)\cos[\varphi(\mathbf{h}-\mathbf{k}) + 2\pi\mathbf{a}\cdot(\mathbf{h}-\mathbf{k}) + \Omega].\end{aligned}$$

With $\delta \equiv \varphi(\mathbf{h}-\mathbf{k}) + 2\pi\mathbf{a}\cdot(\mathbf{h}-\mathbf{k}) + \Omega$,

$$|\mu(\mathbf{h})\sin\tau\exp\{i[\varphi_3(\mathbf{h},\bar{\mathbf{k}}) + \delta]\} + \mu(\mathbf{k})\cos\tau|^2 \leq 1 + 2\mu(\mathbf{h}-\mathbf{k})\sin\tau\cos\tau\cos\delta. \quad (12)$$

This is the family of the HK inequalities based on *two* reflexions and involving only *three* reflexions. It depends on the *two* parameters δ and τ. The inequality that holds true whatever $\delta \in [0, 2\pi)$ and $\tau \in [0, \pi/2]$ is now obtained.

With

$$M_1(\mathbf{h}, \tau) \equiv \mu(\mathbf{h}) \sin \tau, \qquad (13a)$$
$$M_2(\mathbf{k}, \tau) \equiv \mu(\mathbf{k}) \cos \tau \qquad (13b)$$

and

$$M_3(\mathbf{h} - \mathbf{k}, \tau) \equiv 2\mu(\mathbf{h} - \mathbf{k}) \sin \tau \cos \tau, \qquad (13c)$$

inequality (12) becomes

$$\begin{aligned} 2M_1(\mathbf{h}, \tau)M_2(\mathbf{k}, \tau) \cos[\varphi_3(\mathbf{h}, \bar{\mathbf{k}}) + \delta] \\ \leq 1 - M_1^2(\mathbf{h}, \tau) - M_2^2(\mathbf{k}, \tau) \\ + M_3(\mathbf{h} - \mathbf{k}, \tau) \cos \delta \end{aligned} \qquad (14)$$

This can be written as

$$\cos[\varphi_3(\mathbf{h}, \bar{\mathbf{k}}) + \delta] - \mathcal{N} \cos \delta \leq \mathcal{M}(\tau) \qquad (15)$$

where

$$\begin{aligned} \mathcal{M}(\tau) \equiv [1 - M_1^2(\mathbf{h}, \tau) - M_2^2(\mathbf{k}, \tau)] \\ \times [2M_1(\mathbf{h}, \tau)M_2(\mathbf{k}, \tau)]^{-1} \end{aligned} \qquad (16a)$$

and

$$\begin{aligned} \mathcal{N} &\equiv M_3(\mathbf{h} - \mathbf{k}, \tau)[2M_1(\mathbf{h}, \tau)M_2(\mathbf{k}, \tau)]^{-1} \\ &= \mu(\mathbf{h} - \mathbf{k})/\mu(\mathbf{h})\mu(\mathbf{k}). \end{aligned} \qquad (16b)$$

Constraint (15) is formally quite similar to (5). Thus, with

$$\begin{aligned} \mathcal{A} &\equiv \{[\cos \varphi_3(\mathbf{h}, \bar{\mathbf{k}}) - \mathcal{N}]^2 + \sin^2 \varphi_3(\mathbf{h}, \bar{\mathbf{k}})\}^{1/2} \\ &= [1 - 2\mathcal{N} \cos \varphi_3(\mathbf{h}, \bar{\mathbf{k}}) + \mathcal{N}^2]^{1/2}, \end{aligned} \qquad (17a)$$

$$\cos \psi \equiv [\cos \varphi_3(\mathbf{h}, \bar{\mathbf{k}}) - \mathcal{N}]/\mathcal{A}, \qquad (17b)$$

$$\sin \psi \equiv [\sin \varphi_3(\mathbf{h}, \bar{\mathbf{k}})]/\mathcal{A}, \qquad (17c)$$

inequality (15) becomes

$$\cos(\psi + \delta) \leq \mathcal{M}(\tau)/\mathcal{A}.$$

For this to be fulfilled for any δ, the result

$$\mathcal{M}(\tau) \geq \mathcal{A} \qquad (18)$$

must be obtained. Since $\mathcal{M}$ and $\mathcal{A}$ are always positive, the inequality can be squared and, owing to the condition $\mathcal{N} > 0$, becomes

$$\cos \varphi_3(\mathbf{h}, \bar{\mathbf{k}}) \geq (1 + \mathcal{N}^2 - \mathcal{M}^2)/2\mathcal{N}.$$

The inequality holds true for any $\tau \in [0, \pi/2]$ if and only if

$$\begin{aligned} \cos \varphi_3(\mathbf{h}, \bar{\mathbf{k}}) &\geq \max[1 + \mathcal{N}^2 - \mathcal{M}^2(\tau)]/2\mathcal{N} \\ &= \{1 + \mathcal{N}^2 - \min[\mathcal{M}^2(\tau)]\}/2\mathcal{N}. \end{aligned} \qquad (19)$$

In order to determine the mimimum value of $\mathcal{M}^2(\tau)$ in the interval $0 \leq \tau \leq \pi/2$, it is convenient to put $x = \sin^2 \tau$ and to write

$$\begin{aligned} \mathcal{M}^2(\tau) &= \mathcal{M}_1(x)/4\mu^2(\mathbf{h})\mu^2(\mathbf{k}) \\ &\equiv [1/4\mu^2(\mathbf{h})\mu^2(\mathbf{k})] \\ &\quad \times (\{1 - \mu^2(\mathbf{k}) - x[\mu^2(\mathbf{h}) \\ &\quad - \mu^2(\mathbf{k})]\}^2/x(1 - x)). \end{aligned}$$

It is straightforward to show that, at

$$x = x_0 \equiv [1 - \mu^2(\mathbf{k})]/[2 - \mu^2(\mathbf{h}) - \mu^2(\mathbf{k})],$$

$\mathcal{M}_1(x)$ takes its minimum value equal to

$$\mathcal{M}_1(x_0) = [1 - \mu^2(\mathbf{h})][1 - \mu^2(\mathbf{k})]/\mu^2(\mathbf{h})\mu^2(\mathbf{k}).$$

By substitution of this result into (19), the strongest HK inequality, involving only three reflexions,

$$\begin{aligned} \cos \varphi_3(\mathbf{h}, \bar{\mathbf{k}}) &\geq [\mu^2(\mathbf{h}) + \mu^2(\mathbf{k}) + \mu^2(\mathbf{h} - \mathbf{k}) - 1] \\ &\quad \times [2\mu(\mathbf{h})\mu(\mathbf{k})\mu(\mathbf{h} - \mathbf{k})]^{-1}, \end{aligned} \qquad (20)$$

is obtained. It coincides with the third-order determinant Karle–Hauptman inequality.

Finally, the constraint on the number of reflexions involved in the inequalities follows from the fact that the derivation of a HK inequality always requires an ingenious manipulation of the analytical expression relevant to the sum of the reflexions considered. Woolfson (1988) applied the Cauchy–Schwartz inequality to the moduli of two u.s.f.'s and derived two examples [see (15) and (18) of I] of HK inequalities that involve more than three reflexions. Can stronger inequalities also be obtained in these cases by combining Woolfson's factorization with a linear combination of the u.s.f. moduli? The answer, unfortunately, appears to be no, because the procedure in general does not yield a linear combination of the reflexions appearing on the right-hand sides of (15) and (18) of I. For the same reason, the generalization of the proof expounded above to the case of inequalities relevant to more than three reflexions does not appear to be trivial.

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