As can be seen from the Table, there is a notable difference in the results, yet one common attribute persists, *i.e.*, all approximations yield scattering factors larger than experiment. This qualitative result held true in the band model calculations of Arlinghaus (1965). One can see that the MHFS–WT approximation yield values closest to the HF results. Whether this is generally true remains to be ascertained.

All the Slater approximation SCF calculations listed herein were performed with a program written by the author in conjunction with Dr R.A. Moore. Much helpful correspondence with him is gratefully acknowledged.

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## Further developments in a likelihood ratio method for the precise and accurate determination of lattice parameters.

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A likelihood ratio method (LRM) was developed by Beu, Musil & Whitney in 1962 which accounted for $e_i$, the variable component of systematic error in Bragg angle in the process of calculating $\hat{\hat{a}}_0$, the maximum likelihood estimate of the lattice parameter (for cubic materials) under the hypothesis of 'no remaining variable systematic errors' in Bragg angle. In this note, the LRM has been generalized to include the constant component $e$. $\overset{*}{a}_0$, now under two hypotheses of 'no remaining variable systematic errors' and 'no remaining constant systematic error', may be estimated provided the LRM test statistics $W_m$ and $U$ are both less than the corresponding critical values of the $\chi^2$ distribution; in this case, $\hat{\hat{a}}_0$ is the maximum likelihood estimate of the lattice parameter, free of total (variable plus constant) systematic error within the precision of the Bragg angle measurements.

A likelihood ratio method (LRM) has been developed for evaluating in a valid statistical manner the extent of systematic error removal from corrected Bragg angle measurements to aid in the calculation of precise and accurate lattice parameters. (Beu, Musil & Whitney, 1962; hereafter called reference 1; Beu, Musil & Whitney, 1963). The original LRM was based on a hypothesis $H$ of 'no remaining (variable) systematic errors' ('variable' was not explicitly stated in $H$ of reference 1) in the corrected Bragg angle data and on an assumption that the algebraic sum of the variable error components ($e_i$) is zero, namely $\sum_i e_i=0$. Such an assumption is required to keep the maximum likelihood estimates $\hat{\hat{a}}_0$, $\hat{a}_0$, $\hat{e}_i$, *etc.* (reference 1) from becoming indeterminate and to provide unique values for these estimates. In so doing, however, the $e_i$ automatically become only one component of the total systematic error, namely, the variable component. The purpose of this note is to introduce the constant component $e$ into LRM theory so as to complete the generality of the LRM. With $e$, the LRM becomes completely general since $e'_i$, the total remaining systematic error, can be determined from $e_i$ and $e$ alone according to: $e'_i=e_i+e$.

A brief review of the original LRM theory is given to introduce the modification based on $e$. Complete details including additional definitions, derivations, calculation procedure and an example are given in a comprehensive report available from the authors (Beu & Whitney, 1965). The pertinent assumptions of the original LRM are:

$$E(\psi_{i\alpha})=\theta_i+e_i \tag{1}$$

$$\sum_i e_i=0 \tag{2}$$

where

$E(\psi_{i\alpha})$ is the expected or mean value of $\psi_{i\alpha}$ ($\alpha$th measurement of the $i$th Bragg angle) corrected for all known systematic errors.
$\psi_i$ is the average of $n_i$ measurements of $\psi_{i\alpha}$.
$\theta_i$ is the true but unknown value of the $i$th Bragg angle.
$e_i$ is the unknown variable systematic error remaining in the measured $i$th Bragg angle after correcting for all known systematic errors.
$E(\psi_{i\alpha})$, $\psi_i$, $\theta_i$, and $e_i$ are all measured in degrees $\theta$.

The maximum likelihood estimate of the lattice parameter $\hat{\hat{a}}_0$ (for cubic materials) under the hypothesis $(H_1)$* of 'no remaining variable systematic errors' in the $\psi_i$ is calculated using a test statistic ($W_m$) which is distributed like $\chi^2$ (Mood, 1950). $W_m$ is based on $H_1$, on assumptions (1) and (2), and on the maximum likelihood estimates $\hat{a}_0$, $\hat{\theta}_i$, $\hat{e}_i$, and $\hat{\sigma}_i$ (standard deviation estimate of the $i$th Bragg angle). By comparing the numerical value of $W_m$ with $w_\varepsilon$ (a critical value of the $\chi^2$ distribution), $H_1$ is or is not re-

* $H_1$ in this note is identical with $H$ in reference 1.

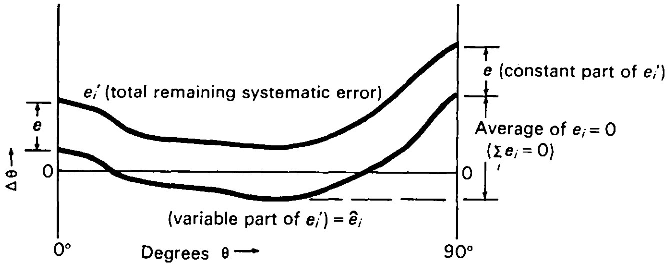


Fig. 1. Illustration of hypothetical variable and constant components of a generalized systematic error function.

jected at the $\varepsilon$ significance level if $W_m$ is respectively larger or smaller than $w_\varepsilon$.

The original LRM based on $H_I$ thus includes explicitly only the variable component of systematic error $e_i$. To include the constant component explicitly, assumption (1) could be recast as follows:

$$E(\psi_{i\alpha}) = \theta_i + e_i + e \tag{3}$$

where the total remaining systematic error is defined by:

$$e_i' = e_i + e . \tag{4}$$

Again an indeterminacy arises if assumption (3) is used directly. The technique by which this difficulty is circumvented and LRM theory is generalized to include $e$, along with $e_i$, follows.

Fig. 1 shows the relation of $e_i'$, $\hat{e}_i$, and $e$ for a completely general systematic error function. $e_i'$ represents a systematic error function of $\theta$ which can be constant or variable; it can be all positive, all negative, or a mixture; it can be an analytical function of $\theta$; it can have a purely empirical relation to $\theta$, such as the diffractometer angular scale calibration error; it can be a single error; or it can be a combination of any or all errors. $e_i'$ can also represent the total systematic error remaining in the Bragg angle data after all known systematic error corrections have been applied; in this sense, $e_i'$ is used for practical LRM applications. $\hat{e}_i$ rather than arbitrary $e_i$ are represented in Fig. 1 since it is the $\hat{e}_i$ which enter into the analytical development of LRM theory. The difference between $e_i'$ and $\hat{e}_i$, namely $e$, is the constant component of $e_i'$.

In the original LRM theory, if $W_m \geq w_\varepsilon$, $H_I$ is rejected and the investigator seeks additional possible sources of error, both variable and constant. He then makes additional corrections to his data (using the $e_i$ to tell him if they are useful corrections) until $W_m < w_\varepsilon$. At this point, $H_I$ is not rejected at the $\varepsilon$ confidence level when there are 'no remaining variable systematic errors', but the possibility of $e$ type errors remaining in the corrected data still exists. To determine whether $e$ type error remains in the corrected data, the assumption is made that:

$$E(\psi_{i\alpha}) = \theta_i + e \tag{5}$$

subject to $\theta_i = \arcsin(K_i/a_0)$ (for cubic crystals) where $K_i = (n\lambda/2)\sqrt{h_i^2 + k_i^2 + l_i^2}$ and the hypothesis ($H_{II}$) is made that there is 'no remaining constant systematic error' or:

$$e = 0 . \tag{6}$$

A function of $a_0$ and $e$ is derived based on (5) and (6):

$$T(a_0, e) = \sum_i n_i \ln\left(1 + \frac{(\psi_i - \theta_i - e)^2}{s_i^2}\right) \tag{7}$$

where $s_i^2$ is the variance of the $n_i$ measurements cf the $\psi_{i\alpha}$.

The minimum value of $T(a_0, e)$ is designated $T_m$ and a likelihood ratio function, $U$, based on $W_m$ and $T_m$, is given by:

$$U = W_m - T_m . \tag{8}$$

Like $W_m$, $U$ is distributed like $\chi^2$; it has one degree of freedom, and is numerically compared to $u_\varepsilon$, a critical value of the $\chi^2$ distribution at the $\varepsilon$ significance level. If $U \geq u_\varepsilon$, $H_{II}$ (that $e = 0$) is rejected and the investigator needs to reexamine his data to determine his error in making the constant correction to his Bragg angle data. If $U < u_\varepsilon$, $H_{II}$ is not rejected and, since $H_I$ was not rejected previously, the investigator is now satisfied that he has indeed removed both variable and constant systematic error components from his Bragg angle measurements in a valid statistical manner. In this case, $\hat{\hat{a}}_0$, the maximum likelihood estimate of $a_0$ under both $H_I$ and $H_{II}$ has been determined.

In other words, if both $H_I$ and $H_{II}$ are not rejected, then $\hat{\hat{a}}_0$ is the best estimate of $a_0$ free of systematic error (both variable and constant) in Bragg angle within measurement precision. If wavelength precision and accuracy* are comparable to, or better than, Bragg angle precision and accuracy, then $\hat{\hat{a}}_0$ is also a precise and accurate estimate of the lattice parameter, at the chosen significance level, on an absolute length scale.

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* Precision and accuracy of one part in 200,000 or better have been claimed recently (Bearden, 1964) on an absolute length scale for peak wavelengths such as Cu $K\alpha_1$.

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