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# ERROR MATRICES IN GAS-ELECTRON DIFFRACTION
## II. INFLUENCE OF WEIGHT MATRIX

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ABSTRACT

The properties of three different forms of error matrices in electron diffraction are investigated, assuming the presence of stationary, Gaussian, Markovian noise in the primary data. The error matrices studied are $M_x^P$ based on the optimum weight matrix $P$, the bona fide error matrix $M_x^W$ based on the nonoptimum weight matrix $W$, and the false error matrix $M_x^0$ commonly calculated by diffractionists using the formula for the optimum error matrix while incorporating a nonoptimum weighting. Simple formulae relating the elements of the various matrices are derived in the case where $W$ is the best diagonal weight matrix and where geometric constraints are not imposed on parameters. The influence of geometric constraints is tested. Calculations indicate that diagonal weight matrices in ordinary circumstances give results imperceptibly inferior to the results obtained with the best nondiagonal weight matrices. Elements of $M_x^W$ closely approach those of $M_x^P$ whereas elements of the false error matrix, taken alone, may be very misleading.

## INTRODUCTION

A reliable procedure for error analysis in gas-phase electron diffraction continues to be an elusive goal. One long-standing problem, the influence of correlations between the intensity points, has been clarified to a considerable extent. Early crude treatments[1–3] were followed by important advances by

Kuchitsu et al.[4,5] and subsequent extensions involving more general weight matrices[6-9]. A considerable proportion of current least-squares refinements of data are based on convenient but nonoptimum diagonal weight matrices, and injudicious wordings in the literature have confused the significance of error matrices derived from diagonal weight matrices. It is common to derive a matrix defined by

$$\boldsymbol{M}_x^0 = \boldsymbol{B}^{-1}\boldsymbol{V}'\boldsymbol{W}\boldsymbol{V}/(n-m) \tag{1}$$

computed with an $n \times n$ arbitrary weight matrix $\boldsymbol{W}$ and least-squares intensity residuals $\boldsymbol{V}$, where the $m \times m$ information matrix $\boldsymbol{B} = \boldsymbol{A}'\boldsymbol{W}\boldsymbol{A}$ is based on the design matrix $\boldsymbol{A}$ and the arbitrary weight matrix. We shall denote $\boldsymbol{M}_x^0$ as the "zero-order error matrix" if $\boldsymbol{W}$ is non optimum. It was pointed out several years ago[6-8] that the zero-order error matrix is not a true error matrix at all but that the use of a non optimum weight matrix does not preclude the calculation of a bona fide error matrix $\boldsymbol{M}_x^w$ associated with nonoptimum weighting, provided the errors are statistically distributed (though not necessarily uncorrelated), if the appropriate relation is employed, namely

$$\boldsymbol{M}_x^w = \boldsymbol{B}^{-1}\boldsymbol{A}'\boldsymbol{W}\boldsymbol{M}_F\boldsymbol{W}\boldsymbol{A}\boldsymbol{B}^{-1} \tag{2}$$

where $\boldsymbol{M}_F$ with elements $[n/(n-m)]\langle V_i V_j\rangle$ is the matrix of errors in observations. A simple formula was given relating the diagonal elements of $\boldsymbol{M}_x^w$ with those of $\boldsymbol{M}_x^0$ when $\boldsymbol{W}$ is diagonal.

In the following we shall present a simple, more general treatment interrelating the elements, off-diagonal as well as diagonal, of the $\boldsymbol{M}_x^w$ matrix, the $\boldsymbol{M}_x^0$ matrix, and the optimum error matrix $\boldsymbol{M}_x^p$ based on the optimum weight matrix $\boldsymbol{P}$. The relations may prove to be useful to those who work with diagonal weight matrices.

## THEORETICAL TREATMENT

### *Intensity correlation function*

If a noise is stationary, Gaussian, and Markovian, it *must* correspond to the correlation function[10]

$$\rho(\Delta s) = \sigma^2 e^{-\gamma|s_i - s_j|} \tag{3}$$

where, in the case of diffraction intensities, we may associate $s_i$ with the conventional angular variable $s_i = (4\pi/\lambda)\sin(\phi_i/2)$. For our model calculations, let us assume that eqn. (3) is adequate and let us further assume that observations are evenly spaced with an interval $\Delta s = \Delta$. The matrix of errors in observations,

$M_F$, is then given by

$$M_F = \sigma^2 \begin{Vmatrix} 1 & \beta & \beta^2 & \dots & \beta^{n-1} \\ \beta & 1 & \beta & \dots & \beta^{n-2} \\ \vdots & & & & \\ \beta^{n-1} & & \dots & & 1 \end{Vmatrix} \tag{4}$$

where $\beta = e^{-\gamma\Delta}$, provided the intensity observations $sM(s)h(s)$ corresponding to the conventional reduced intensity $sM(s)$ are adjusted by the smooth modification function $h(s)$ to distribute the noise uniformly in $s$-space. Commonly $h(s)$ is a nearly constant or gently decreasing function of $s$. The results of the treatment are insensitive to $h(s)$ as long as it is smooth. The inverse of the moment matrix $M_F$ is

$$M_F^{-1} = \frac{1}{\sigma^2(1-\beta^2)} \begin{Vmatrix} 1 & -\beta & 0 & 0 & \dots & 0 \\ -\beta & (1+\beta^2) & -\beta & 0 & & \\ 0 & -\beta & (1+\beta^2) & -\beta & & \\ 0 & 0 & -\beta & \dots & & \\ \vdots & & & & & \\ \vdots & & & \vdots & (1+\beta^2) & -\beta \\ 0 & & & \cdot & -\beta & 1 \end{Vmatrix} \tag{5}$$

*Form of error matrices*

Let us first investigate the elements of the zero-order error matrix $M_x^0$ using the diagonal weighting $W = E$, the identity matrix. Such weighting would make $M_x^0$ correspond to the optimum error matrix in the absence of correlation between data (i.e., in the case of $\beta = 0$). From eqn. (1) we see, identifying $V'V/(n-m)$ with $\sigma^2$, that

$$M_x^0 = \sigma^2 B^{-1}. \tag{6}$$

The optimum error matrix, namely the matrix with minimum diagonal elements, is found by using a weight matrix $P$ proportional to $M_F^{-1}$. Substitution of $W = P = M_F^{-1}$ into eqn. (2) leads to extensive cancellation, yielding the error matrix

$$M_x^p = \mathscr{B}^{-1} \tag{7}$$

where $\mathscr{B} = A'PA$.

The elements of the inverse of the error matrix become, in view of eqns. (5)

and (7)

$$(M_x^{p-1})_{kl} = (\mathscr{B})_{kl}$$
$$= \sigma^2 \frac{(1+\beta^2)}{(1-\beta^2)} \left\{ \sum_{i=1}^{n} A'_{ki} A_{il} - \frac{\beta}{(1+\beta^2)} \sum_{i=1}^{n-1} [A'_{ki} A_{(i+1)l} + A'_{k(i+1)} A_{il}] \right.$$
$$\left. - \frac{\beta^2}{(1+\beta^2)} [A'_{k1} A_{1l} + A'_{kn} A_{nl}] \right\} \tag{8}$$

where the last term is trivial if $n$ is large (as it normally is).

The simplest and most appropriate arbitrary, diagonal weight matrix is $W = E$. It leads to the bona fide, nonoptimum error matrix, according to Equation (2), of

$$M_x^w = B^{-1} A' M_F A B^{-1}$$
$$\equiv B^{-1} \Xi B^{-1}. \tag{9}$$

To establish the form of the $\Xi$ matrix, eqn. (4) is introduced into the matrix $A'M_FA$ of eqn. (9) giving

$$\Xi_{kl} = \sum_i \sum_j A'_{ki} (M_F)_{ij} A_{jl}$$
$$= \sigma^2 \{ \sum_{i=1}^{n} A'_{ki} A_{il} + \beta \sum_{i=1}^{n-1} [A'_{ki} A_{(i+1)l} + A'_{k(i+1)} A_{il}]$$
$$+ \beta^2 \sum_{i=1}^{n-2} [A'_{ki} A_{(i+2)l} + A'_{k(i+2)} A_{il}] + \ldots \}. \tag{10}$$

It is possible to simplify eqns. (8)–(10) still further by adopting the expression

$$F(s) = sM(s)h(s)$$
$$= h(s) \sum_k C_k [\exp(-l_k^2 s^2/2)] \sin s r_k \tag{11}$$

to represent the modified intensity function explicitly.

*Error matrices in absence of geometric constraints*

In the event that internuclear distances and amplitudes of vibration are derived directly from the diffraction data as independent parameters, correlated only by the diffraction data and *not* by the additional application of geometric constraints, a great simplification results. The essence of the simplification is that the design matrix elements are expressible then as elementary derivatives of eqn. (11), and, hence are proportional to sine or cosine functions. The resultant oscillatory character of the $A_{ik}$ elements leads to virtual extinction of many of the sums in eqns. (8) and (10), particularly when the $k$ and $l$ parameters in $A'_{kl}A_{jl}$ correspond to quite different internuclear distances, and trigonometric identities render other

sums tractable. Furthermore, the $\boldsymbol{B}$ matrix can be inverted by inverting the small, mutually uncorrelated blocks of which it is composed.

Consistent with the above restrictions, the design matrix elements become

$$\begin{aligned} A_{ik} &\equiv \partial F(s_i)/\partial r_k \\ &= s_i \mathrm{h}(s_i) C_k [\exp(-l_k^2 s_i^2/2)] \cos s_i r_k \end{aligned} \tag{12}$$

for internuclear distances $r_k$ and

$$\begin{aligned} A_{ik} &\equiv \partial F(s_i)/\partial l_k \\ &= -s_i^2 l_k h(s_i) C_k [\exp(-l_k^2 s_i^2/2)] \sin s_i r_k \end{aligned} \tag{13}$$

for amplitudes of vibration, $l_k$.

To illustrate how the matrix elements can be evaluated, consider the case of a molecule with two internuclear distances $r_s = \bar{r} - \frac{1}{2}\varepsilon$ and $r_t = \bar{r} + \frac{1}{2}\varepsilon$, not necessarily of equal scattering power, differing by a small amount $\varepsilon$. Assume that all other internuclear distances in the molecule are quite different from $\bar{r}$. The parameters $r_s$ and $r_t$ are then appreciably correlated with each other, as are the parameters $\varepsilon$ and the amplitudes of vibration, but $r_s$ and $r_t$ are uncorrelated with other internuclear distances. Accordingly, the $\boldsymbol{B}^{-1}$ matrix contains a $4\times4$ block $\boldsymbol{b}^{-1}$ for parameters $r_s$, $r_t$, $l_s$ and $l_t$ which is just the inverse of the corresponding $4\times4$ block $\boldsymbol{b}$ in the full $\boldsymbol{B}$ matrix. As shown in the Appendix, if $\Delta$ is small, the general sums over square brackets in eqns. (8) and (10) reduce to

$$\sum_i [A'_{ki} A_{(i+p)l} + A'_{k(i+p)} A_{il}] = 2 \cos p\bar{r}\Delta \sum_i [A'_{ki} A_{il}] \tag{14}$$

whether $k$ and $l$ correspond to an isolated internuclear distance or to a close cluster with mean distance $\bar{r}$. Consequently, the $\Xi$ matrix elements of eqn. (10) become

$$\begin{aligned} \Xi_{kl} &= \sigma^2 \{ \sum_{i=1}^{n} A'_{ki} A_{il} + \beta \cos \bar{r}\Delta \sum_{i=1}^{n-1} A'_{ki} A_{il} + \beta^2 \cos 2\bar{r}\Delta \sum_{i=1}^{n-2} A'_{ki} A_{il} + \ldots \} \\ &\approx \sigma^2 ( \sum_{p=-n}^{n} \beta^p \cos p\bar{r}\Delta ) \sum_{i=1}^{n} A'_{ki} A_{il} = R_r \sigma^2 B_{kl} \end{aligned} \tag{15}$$

where the result is insensitive to the upper limits of the sums because $\beta^p$ becomes vanishingly small at large $p$, and where the $R_r$ factor in eqn. (15) can be further simplified, since the $\Delta s$ interval $\Delta$ is small, to

$$\begin{aligned} R_r &= \int_{-\infty}^{\infty} \beta^p \cos p\bar{r}\Delta \, \mathrm{d}p \\ &= 2 \int_0^{\infty} \mathrm{e}^{-p\gamma\Delta} \cos p\bar{r}\Delta \, \mathrm{d}p \\ &= 2\gamma/[\Delta(\gamma^2 + \bar{r}^2)]. \end{aligned} \tag{16}$$

Therefore, inserting result (15) into eqn. (9), we note for our block of correlated

parameters that

$$\begin{aligned}(M_x^w)_{kl} &= \sum_q \sum_r (B^{-1})_{kq} \Xi_{qr} (B^{-1})_{rl} \\ &= \sum_q (B^{-1})_{kq} [\sum_r R_r \sigma^2 B_{qr} (B^{-1})_{rl}] \\ &= R_r \sigma^2 \sum (B^{-1})_{kq} \delta_{ql} \\ &= R_r \sigma^2 (B^{-1})_{kl} \\ &= R_r (M_x^0)_{kl} \end{aligned} \tag{17}$$

We have shown that the elements of the $M_x^w$ and $M_x^0$ matrices are related by a factor completely analogous to the factor given in ref. 6 for a less general case.

An analogous result for the optimum error matrix can be obtained by applying formula (14) to eqn. (8) with the result

$$\begin{aligned}(M_x^{p-1})_{kl} &= \frac{(1+\beta^2)}{\sigma^2(1-\beta^2)} \left\{ \sum_{i=1}^{n} A'_{ki} A_{il} - \frac{2\beta \cos \bar{r}\Delta}{(1+\beta^2)} \sum_{i=1}^{n-1} A'_{ki} A_{il} \right\} \\ &\approx \sigma^{-2}[(1+\beta^2-2\beta \cos \bar{r}\Delta)/(1-\beta^2)] B_{kl}. \end{aligned} \tag{18}$$

Therefore, for the block of correlated parameters with a common value of $\bar{r}$, the optimum error matrix elements are

$$\begin{aligned}(M_x^p)_{kl} &= R'_r \sigma^2 (B^{-1})_{kl} \\ &= R'_r (M_x^0)_{kl} \end{aligned} \tag{19}$$

where, for small $\Delta$, the proportionality constant $(1-\beta^2)/(1+\beta^2-2\beta \cos \bar{r}\Delta)$ becomes

$$R'_r \approx 2\gamma/[\Delta(\gamma^2+\bar{r}^2)]. \tag{20}$$

Somewhat more precise but less simple formulae for $R_r$ and $R'_r$ have been derived[11]; they do not alter the conclusions outlined in the following. We observe that, to a good approximation discussed in the Appendix, the elements in the optimum matrix $M_x^p$ are related to the elements of the zero-order matrix by the same factor as are the elements of the nonoptimum matrix $M_x^w$. Therefore, a good diagonal weight matrix gives results scarcely inferior to the results of the best nondiagonal weight matrix, as long as the derived structure parameters are determined by least squares without the introduction of additional parameter correlations imposed by geometrical constraints among the distances.

The ratio of optimum to zero-order matrix elements for bond angles is readily calculated from the above results if the internuclear distances involved are uncorrelated. Let us treat two cases. In case (a) with two identical bonds of length $r$ forming a bond angle $\alpha$ and a nonbonded distance $R$ opposite angle $\alpha$, the ratio $(M_x)_{\alpha\alpha}/(M_x^0)_{\alpha\alpha}$ is given by

$$(R_\alpha)_a = \left[\frac{R_r (M_x^0)_{rr}}{r^2} + \frac{R_R (M_x^0)_{RR}}{R^2}\right] \Big/ \left[\frac{(M_x^0)_{rr}}{r^2} + \frac{(M_x^0)_{RR}}{R^2}\right] \tag{21}$$

In case (b) with bonds of length $r_1$ and $r_2$ forming an angle $\alpha$ and a nonbonded distance R the corresponding ratio is

$$(R_x)_b = \frac{R_{r1} D_1^2 (M_x^0)_{r1r1} + R_{r2} D_2^2 (M_x^0)_{r2r2} + R_R R^2 (M_x^0)_{RR}}{D_1^2 (M_x^0)_{r1r1} + D_2^2 (M_x^0)_{r2r2} + R^2 (M_x^0)_{RR}} \tag{22}$$

in which

$$D_1 = (r_2 \cos \alpha) - r_1$$

and

$$D_2 = (r_1 \cos \alpha) - r_2 .$$

*Effect on error matrices of geometric constraints*

If geometric constraints are imposed the theoretical problem is complicated so greatly that it is much less trouble to resort to numerical calculations than to work out a general theory. Such calculations have been performed[12] in the cases of $AsF_3$[13] [where the distances and amplitudes are virtually uncorrelated and where geometric constraints play no role in a $C_{3v}$ structure], and of $C(CH_3)_4$[14] and $(CH_3)_3PF_2$[15] [where geometric constraints play a significant role]. For all three molecules $M_x^0$, $M_x^w$, and $M_x^p$ were calculated.

First, it was verified that the parameter standard deviations $\sigma(\theta_k) = (M_x)_{kk}^{\frac{1}{2}}$ are only the order of a percent larger when the weight matrix is diagonal than when it is optimum. Secondly, it was found for the 87 parameter correlation coefficients

$$\rho_{kl} = (M_x)_{kl} / [(M_x)_{kk} (M_x)_{ll}]^{\frac{1}{2}}$$

encountered in $AsF_3$, $C(CH_3)_4$, and $(CH_3)_3PF_2$, that the $M_x^w$ and $M_x^p$ matrices gave identical values to within a few hundredths of a unit. The close correspondence of $M_x^w$ and $M_x^p$ is thus demonstrated, even in the presence of imposed geometric constraints. Finally, it was observed that the parameter standard deviations calculated from $M_x^0$ together with the $R_r$ factor $2\gamma/[\Delta(\gamma^2 + r^2)]$ were quite close to the bona fide standard deviations from $M_x^w$. The ratios $\sigma_k/\sigma_k^0$ embodied in $[(M_x^w)_{kk}/(M_x^0)_{kk}]^{\frac{1}{2}}$ agreed with our simplified theory to about 3 % in the cases of $AsF_3$, $(CH_3)_3PF_2$, and for $r_{CH}$ and the amplitudes of vibration in neopentane. The CC bond length in neopentane, however, which in the $T_d$ molecule is completely correlated with the strongly scattering C · · · C nonbonded distance, gave a ratio about 8 % lower than that calculated from $R_r$ with $r = 1.54$ (i.e., in the direction of $R_r$ with $r$ for the C · · · C (distance).

*Other nonoptimum weights*

If the influence of geometric constraints is disregarded, the present formalism permits a simple estimate of the influence of various nonoptimum weights. Con-

sider, for example, the case of a single internuclear distance uncorrelated with other distances and with $h(s) = s^{-1}$ [i.e., the case where $M(s)$ distributes the noise uniformly]. The standard deviations $\sigma(r_k)$ and $\sigma(l_k)$ are then derivable from

$$\sigma_k^2 = (M_x^w)_{kk} \approx \Xi_{kk}/B_{kk}^2. \tag{23}$$

Suppose that the decidedly nonoptimum diagonal weighting $W_i^* = s_i^2$ is adopted in the fitting of $M(s)$ [or, what is equivalent, $sM(s)$ is fitted with unit weight]. By replacing the sums representing $\Xi_{kk}$ and $B_{kk}$ by integrals from zero to infinity and adopting the design matrix elements of eqns. (12) and (13), it is easy to show that $\Xi_{kk}^*/(B_{kk}^*)^2$ is 3 times as large for $r_k$ and 5/3 times as large for $l_k$ as it is if the best diagonal weighting $W_i = 1$ is used. On the other hand, if $h(s) = 1$ [i.e., the case where $sM(s)$ distributes noise uniformly], then $W_i^* = s_i^2$ gives error matrix elements 5/3 times as large for $r_k$ and 7/5 times as large for $l_k$ as does the superior weight $W_i = 1$. These examples, of course, assume data are available to rather large values of $s$.

*Effect of the modulation function $h(s)$*

One noteworthy result of the above treatment is that the ratio $R_r$ relating $M_x^w$ and $M_x^0$ elements is independent of $h(s)$, the modulation function described beneath eqn. (4), as long as the curvature of $Ch(s)$ is small in comparison with the curvature of sin $sr$. This means that the proper ratio between bona fide error matrix elements $(M_x^w)_{kl}$ and zero-order elements $(M_x^0)_{kl}$ calculated with the same weight function is $2\gamma/[\Delta(\gamma^2+r^2)]$ irrespective of whether it is $M(s)$, $sM(s)$, or $sM(s)h(s)$ which distributes the noise uniformly in $s$-space. It is imperative, however, that $h(s)$ be known and used in weighting the residuals if the matrices $M_x^w$ and $M_x^0$ are to have any physical significance because both matrices rely on the validity of eqn. (4) as a proper representation of the matrix of errors in observations. Note also that the quantity $\sigma^2$ in eqn. (4) is

$$\sigma^2 = V'PV/(n-m) \tag{24}$$

where $V_i = s_i h(s_i)[M^0(s_i) - M^0(s_l)]$. If $h(s)$ is arbitrarily assigned, or if the model correlation function $\exp(-\gamma|s_i - s_j|)$ fails to represent faithfully the true data correlations, the above error formulas are invalid of course. On the other hand, $h(s)$ need not be arbitrary, and the plausibility of $\exp(-\gamma|s_i - s_j|)$ is supported by some empirical[6-9] as well as theoretical[10] evidence. Therefore, the simple results of the present analysis may be helpful. Certainly they justify the use of diagonal weight matrices in ordinary circumstances.

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## APPENDIX

In order to justify the key relationship, eqn. (14), it suffices to treat a representative term in which parameters $k$ and $l$ represent $r_k = \bar{r} - \frac{1}{2}\varepsilon$ and $r_l = \bar{r} + \frac{1}{2}\varepsilon$. Since $A_{ik}$ is proportional to cos $s_i r_k$, the term $[A'_{ki}A_{(i+p)l} + A'_{k(i+p)}A_{il}]$ encountered in the text involves the product terms (which can be factored from their coefficients if $\Delta$ is small)

$$\cos s_i(\bar{r} - \tfrac{1}{2}\varepsilon) \cos [(s_i + p\Delta)(\bar{r} + \tfrac{1}{2}\varepsilon)] + \cos [(s_i + p\Delta)(\bar{r} - \tfrac{1}{2}\varepsilon)] \cos s_i(\bar{r} + \tfrac{1}{2}\varepsilon),$$

which can be expressed as

$$\left\{\cos p\bar{r}\Delta \left[\cos p\frac{\varepsilon\Delta}{2} \cos s\varepsilon - \sin p\frac{\varepsilon\Delta}{2} \sin s\varepsilon\right]\right\}$$
$$+ \frac{1}{2}\left\{\cos\left(2sr + p\bar{r}\Delta + p\frac{\varepsilon\Delta}{2}\right) + \cos\left(2sr + p\bar{r}\Delta - p\frac{\varepsilon\Delta}{2}\right)\right\}.$$

The term enclosed by the second pair of curly brackets oscillates rapidly and, when its sum over s is carried out, its contribution virtually vanishes. If $\Delta$ and $\varepsilon$ are small, $\cos(p\varepsilon\Delta/2) \approx 1$ and $\sin(p\varepsilon\Delta/2) \approx 0$. Therefore, the only component of the product terms which contributes strongly in the sum over s is

$$\cos p\bar{r}\Delta \cos s\varepsilon,$$

in which the quantity cos $p\bar{r}\Delta$ can be factored from the $s$-dependent quantity as needed for eqn. (14) to hold. The relative contributions of the terms which are retained and the terms which are neglected can be investigated analytically by replacing the relevant sums by integrals from zero to infinity. If $h(s) \approx s^n$ with $n$ higher than zero or so, the difference between $s_{min}$ and zero in the sums is trivial if $r \gg l$ and if $rs_{max} \gg 2\pi$. If $\Delta$ is only as small as $\pi/10$ Å$^{-1}$, a common value, and $\varepsilon$ is as large as 0.3 Å, the neglected term involving sin $p\varepsilon\Delta/2$ may be of the order of one percent of the leading term. If $r = 2$ Å, for example, the expressions (16) and (20), derived from eqns. (15) and (18) in the limit of small $\Delta$, give an $R_r$ factor that is one percent lower than that of eqns. (15) and (18) if $\Delta = \pi/20$ and 4 % lower if $\Delta = \pi/10$. The influence of correlations introduced by geometric constraints is likely to be more serous than the above approximations if $\Delta$ is less than, say, $\pi/20$.

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