Korean J. Crystallography
Vol.8, No.1, pp.64~65, 1997

Calculation of Estimated Standard Deviations (ESDs)

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標準偏差의 槪算

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Abstract

A method for calculation of the estimated standard deviation (ESD) of physical quantities which are functions of experimentally observed variables has been shown.

槪 要

實驗的으로 測定된 變數의 函數인 物理量의 標準偏差의 槪算法이 提示되었다

1. Introduction

Crystallographic papers require ESDs of many quantities such as bond distance, bond angle, average bond length, average bond angle, least-square plane, angle between least-squares planes, coordinates of centroids of aromatic rings, hydrogen atomic position between donor and acceptor, newly transformed cell parameters, etc.
This paper shows how to calculate ESDs of such quantities which are functions of experimentally observed variables.

2. Theory

When a quantity Q has a functional relation Q =f (a, b, c, ...) with variables a, b, c, ... which are actually measured, the standard deviation σ_Q of the quantity Q is expressed only in terms of the variances as the Eq. (1)[1] assuming the fluctuations in the observations of a, b, c, ... are either uncorrelated or very small:

$$\sigma_Q^2=\sigma_a^2\left(\frac{\partial Q}{\partial a}\right)^2+\sigma_b^2\left(\frac{\partial Q}{\partial b}\right)^2+\sigma_c^2\left(\frac{\partial Q}{\partial c}\right)^2+\cdots \qquad (1)$$

where σ_a, σ_b, σ_c are the standard deviations of a, b, c.

Three examples for the calculation of ESDs are given below.

(1) ESDs of average bond length, average bond angle and coordinates of centroid of any ring

The equation for average bond length, average bond angle and coordinates of centroid of any ring are expressed as

$$B(b_1, b_2, b_3, \cdots b_n) = (b_1+b_2+b_3+\cdots+ b_n)/n,$$

where the fluctuations in the observations of b_1, b_2, b_3, $\cdots$ b_n are uncorrelated.

Substituting this equation into Eq. (1), the ESD of B is given as:

$$\sigma_B^2=\frac{1}{n^2}(\sigma_{b_1}^2+\sigma_{b_2}^2+\sigma_{b_3}^2+\cdots+\sigma_{b_n}^2)$$

ex. 1) The ESD of the average bond length of S-C=1.633(4) and S'-C'=1.704(3)Å?

The average bond length of S-C=(1/2)(1.633+1.704)=1.669Å

Its ESD: $\sigma^2=\frac{1}{4}[(0.004)^2+(0.003)^2]=$

0.00000625

σ=0.0025≒0.003

∴The mean value of S-C: 1.669(3)Å

ex. 2) Find the ESD for x-coordinate of the centroid of a benzene ring C_1, C_2, C_3, C_4, C_5, C_6 whose coordinates are

	x	y	z
C1	-0.04933(31)	0.58841(28)	-0.15595(25)
C2	-0.12290(31)	0.61114(28)	-0.12224(26)
C3	-0.23982(31)	0.58223(30)	-0.17269(28)
C4	-0.28157(36)	0.52896(30)	-0.25383(30)
C5	-0.20855(34)	0.50127(33)	-0.28750(28)
C6	-0.09457(34)	0.53227(31)	-0.23741(26).

The x-coordinate of the centroid is

$$x_c=\frac{1}{6}(x_{C1}+x_{C2}+x_{C3}+x_{C4}+x_{C5}+x_{C6})=-0.16612.$$

Its ESD is $\sigma_{x_c}^2=\frac{1}{36}(\sigma_{x_{c_1}}^2+\sigma_{x_{c_2}}^2+\sigma_{x_{c_3}}^2+\sigma_{x_{c_4}}^2+\sigma_{x_{c_5}}^2+\sigma_{x_{c_6}}^2)$

$\sigma_{x_c}=0.00013$

∴The x-coordinate of the centroid:
x=−0.16612(13).

(2) ESD of hydrogen atomic position between donor and acceptor

The x coordinate of the hydrogen atomic position between a donor oxygen and an acceptor nitrogen is a function of x_O and x_N as shown below[2]:

$$x_H=x_O+\frac{d_{O-H}}{d_{O-N}}(x_N-x_O)$$

where x_H, x_O and x_N are the x-coordinates of hydrogen, oxygen and nitrogen, and d_{O-H} and d_{O-N} are the distances between O-H and O-N, respectively.

The estimated standard deviation of x_H is calculated by Eq. (1) as follows:

$$\sigma_{x_H}^2=\sigma_{x_O}^2\left(1-\frac{d_{O-H}}{d_{O-N}}\right)^2+\sigma_{x_N}^2\left(\frac{d_{O-N}}{d_{O-N}}\right)^2$$

ex. 3) When O: x=−0.4015(3), y=0.5071(3), z=−0.2996(2), N: x=−0.5232(3), y=0.5767(3), z=−0.2074(2), d_{O-N}=2.892Å, d_{O-H}=0.9Å, find x_H and σ_{x_H}.

$$x_H=-0.4015+\frac{0.9}{2.892}(-0.5232+0.4015)=-0.4394$$

$$\sigma_{x_H}^2=(0.0003)^2\left(1-\frac{0.9}{2.892}\right)^2+(0.003)^2\left(\frac{0.9}{2.892}\right)^2$$

$$=4.27\times10^{-8}+8.72\times10^{-9}=5.1\times10^{-8}$$

σ_{x_H}=0.0002

∴The x-coordinate of hydrogen atom:
x=−0.4394(2)

3. Concluding remarks

ESDs of all quantities which have dependence on common variables can be obtained by using the Eq. (1). However in the Eq. (1), the covariance terms are omitted so that there must be a certain amount of errors in case the fluctuations in the observation of the variables are correlated to each other.

References

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