

Chapter 5

XDGEOM – Geometry Functions, Errors and Tables

5.1 Overview

This program computes various functions of the atomic coordinates together with standard uncertainties (s.u.s) obtained from the variance-covariance matrix. The method is fully described by Busing, Martin and Levy [1], and is given in outline below. Errors in the unit cell parameters are applied if they are provided in the form of a CELLS entry in the Master File (see example). Torsion angle s.u.s are calculated by the method of Stanford and Waser [2]. An algorithm due to Rollett [3] is used to generate space-group symmetry-related atoms automatically, where relevant.

Additionally, CIF (Crystallographic Information File [4]) listings of the functions and atomic parameters are produced in the file `xd_geo.cif`. The rhoCIF specifications [5] for multipole population coefficients are used. Note that in a future release of XD, it is planned to move listings of all refined parameters to `xd_lsm.cif`.

5.1.1 Mathematical method

A function l of the n nuclear positions may be defined as

$$l = f(p_1, p_2, \dots, p_n)$$

and its estimated standard uncertainty as

$$\sigma(l) = f(u_1, u_2, \dots, u_n)$$

where

$$u_i = \frac{\partial l}{\partial p_i}$$

The derivative of a function of several variables is given by

$$dl = \frac{\partial l}{\partial p_1} dp_1 + \frac{\partial l}{\partial p_2} dp_2 + \dots + \frac{\partial l}{\partial p_n} dp_n$$

so that

$$\sigma^2(l) = \left[\sum_{i=1}^n u_i c_i \right]^2$$

where $c_i = \sigma(p_i)$. Hence

$$\sigma^2(l) = \sum_{i=1}^n \sum_{j=1}^n u_i u_j c_i c_j$$

which is a quadratic form. So the variance of l may be written

$$\sigma^2(l) = \mathbf{u}^T \mathbf{C} \mathbf{u}$$

and the matrix \mathbf{C} is the variance-covariance matrix. Its diagonal elements are the variance of the parameters:

$$C_{ii} = c_i^2$$

and its off-diagonal elements are covariances:

$$C_{ij} = \text{cov}(p_i, p_j) = c_i c_j r_{ij}$$

where r_{ij} is a correlation coefficient.

5.2 Files used and created by XDGEOM

Input: `xd.mas`, `xd.res`, `xd.cov`
 Output: `xd_geo.cif`, `xd.tex`, `xd_geo.out`

5.3 Input instructions for XDGEOM

5.3.1 SELECT

SELECT (*)**rmin** *rmin* (*)**rmax** *rmax* (*)**ato** (*)**bon** (*)**ang** (*)**tor** (*)**loc** (*)**non**

(*)**rmin** *rmin* [0.01] (*)**rmax** *rmax* [use radii from databank

Internuclear separations in Å defining bonded atoms, and atoms in van der Waals contact, may be given here. Bond and contact distances and angles are calculated according to the connectivity so defined. If **non** is selected, **rmin** and **rmax** define the range of van der Waals contacts. Distances less than *rmin* are then taken to be bonding distances.

Alternatively, the default action is to use the covalent and van der Waals radii from `xd.bnk_*` (the chosen system databank file) to define bond and contact distances. In this case **rmin** and **rmax** are not selected. A special case is the selection of an **rmin** value of exactly zero, in conjunction with **non**. Then bonds are defined by covalent radii and contacts by the selected value of **rmax**.

(*)**ato**

Generates a list of atomic coordinates, displacement amplitudes, multipole population coefficients, and their estimated standard deviations.

(*)**bon**

Generates a list of bond distances and their s.u.'s.

(*)**ang**

Generates a list of bond angles and their s.u.'s.

(*)**tor**

Generates a list of torsion angles and their s.u.'s

(*)**loc**

Lists the "local geometry" at each atom. This is a list of all bonds and angles and their s.u.s for each atom in turn, together with the symmetry operations used to generate the connected atoms.

(*)**non**

Generates a list of van der Waals contacts and their s.u.s, with the symmetry operations used to generate the contacting atoms.

5.4 Example Master File segment for XDGEOM

```
TITL      HCONH2  Formamide 123K
CELL      3.6130      9.0570      6.9730      90.000      100.360      90.000
CELLSD    .005 .003 .003 0.0 0.06 0.0
WAVE      0.71069
LATT      C      P
SYMM      1/2 - X, 1/2 + Y, 1/2 - Z
.
.
MODULE    XDGEOM
SELECT    *rmin 1.6 *rmax 4.0 *ato *bon *ang *tor *non
END      XDGEOM
```

Bibliography

1. W.R. Busing, K.O. Martin and H. Levy, *ORFFE – A Fortran Crystallographic Function and Error Program*, Oak Ridge National Laboratory (1964), ORNL-TM-306.
2. R.H. Stanford and J. Waser *Acta Cryst.* **A28**, 213-215, (1972)
3. J.S. Rollett, in *Computing Methods in Crystallography*, Ed. Rollett, J.S., Pergamon Press, 1965.
4. S. R. Hall, F. H. Allen and I. D. Brown *Acta Cryst.* **A47**, 655-685 (1991).
5. P. R. Mallinson and I. D. Brown, *International Tables for X-ray Crystallography*, Vol. G, Sect 3.5, Kluwer Academic Publishers, to be published.

