17. SHELXA: Empirical Absorption Corrections

The program **SHELXA** has been kindly donated to the system by an **anonymous user**. This applies "absorption corrections" by fitting the observed to the calculated intensities as in the program DIFABS. SHELXA is intended for **EMERGENCY USE ONLY**, eg. when the world's only crystal falls off the diffractometer before there is time to make proper absorption corrections by indexing crystal faces or by determining an absorption surface experimentally by measuring equivalent reflections at different azimuthal angles etc.

SHELXA reads an *.fcf* file written by SHELXL (using LIST 4 or LIST 6 and any combination of MERG, OMIT etc.) and a .raw file in SHELX HKLF 4 format containing "direction cosines", and writes a new SHELX *.hkl* file in HKLF 4 format**. THIS WILL OVERWRITE AN EXISTING .hkl FILE !** A SHELXL-93 .fcf file is not suitable because some information is missing. The following restrictions apply to the use of SHELXA:

(a) The structure should not be twinned (racemic twinning is allowed), the data should have been collected from one crystal (inter-batch scale factors should not have been refined), and there may not be a re-orientation matrix on the HKLF instruction. Otherwise there are no restrictions on the type of structure (SHELXA is equally (un)suitable for proteins) or the instructions used in the SHELXL refinement.

(b) It is understood that any structure determined by means of this scientifically dubious procedure **WILL NEVER BE PUBLISHED !** The anonymous author of SHELXA has no intention of ever writing a paper about it that could be cited and thereby ruin his reputation.

The absorption is modeled by spherical harmonic functions using full-matrix least-squares more or less by the method of Blessing (1995); nb. it is not this model that should be regarded as dubious, just the way SHELXA misuses it. Data are used for parameter determination if the I/σ(I) ratios for both the observed and calculated intensities exceed a given (by the -t switch) or assumed threshold (equal to 5.0). The -u switch specifies an artificial $\Delta U/\lambda^2$ value that is applied to the calculated intensities; this helps to prevent atoms going NPD, but the default value is zero. The -e and -o switches specify the highest even and odd order spherical harmonics to employ; the refinement could be unstable if these are too high, especially if only part of reciprocal space is sampled, eg. because only an asymmetric unit was collected for a high symmetry structure. Allowed values are (0,2,4,6,8) and (0,1,3,5,7) respectively. Thus:

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shelxa -t3 -u0.002 -e4 -o1 baddata
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would read baddata.raw and baddata.fcf and write baddata.hkl, with data with $I>3\sigma(I)$ used to fit the absorption parameters, a $\Delta U/\lambda^2$ of 0.002 effectively added to all current isotropic displacement parameters, and highest even and odd harmonics 4 and 1 respectively. Such UNIX switches will also be recognized under MSDOS, VMS etc.; no spaces are allowed between the letter and value. The values employed for these switches are summarized by the program (on the standard output device). The filename stem (here *baddata*) must come last. Usually the default values should prove sensible, ie:

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shelxa baddata
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The data may be re-processed when, for example, extra atoms are added; however, as with DIFABS, best results are obtained if the procedure is last run with the final ISOTROPIC model; re-running it after anisotropic refinement will result in a deterioration of the structure and (most important) the *R*-factors. The ΔU fudge should not be used repetitively, because the effects will be cumulative !

Note that all esd's estimated by SHELXL using data "corrected" in this way will be invalid unless the number of parameters used in the absorption model is input as the third L.S. parameter. This number depends on the settings of the -e and -o switches and is output by SHELXA.

The program can read either standard SHELX direction cosines (relative to the crystal reciprocal axes), or orthogonal direction cosines calculated by the method given in Blessing's paper. Siemens and Stoe write the SHELX .raw (HKLF 4) format as standard, for CAD4 diffractometers a suitable data reduction program is available from Klaus Harms at the University of Marburg. Users of other makes of diffractometer and area detectors will enjoy writing their own programs to generate direction cosines using Blessing's method; the anonymous author of SHELXA is of course not able to enter into any correspondence about this! For very large structures it may be necessary to change the number of reflections the program can handle by increasing the values of MR and MF in the PARAMETER statement at the start of the main program, and recompiling it.