TOPAS-Academic

Technical Reference

Version 8

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Ab initio solution of proteins at atomic resolution, Fast simultaneous refinement of 1000s of data sets, Amazon EC2 cloud computing (experimental), PDF Generation, Deconvolution, Capillary aberration, LP-Search, Sine Transform, DPI awareness, Peak fitting, Pawley & Le Bail refinement, Rietveld refinement, PDF Generation, PDF refinement, Magnetic structures, CW Neutron refinement, TOF refinement, Stacking-faults, Laue refinement, Indexing, Charge flipping, Structure solution, Deconvolution and $K\alpha_1$ stripping, Penalties, Restraints.

Contents

1. ..INTRODUCTION

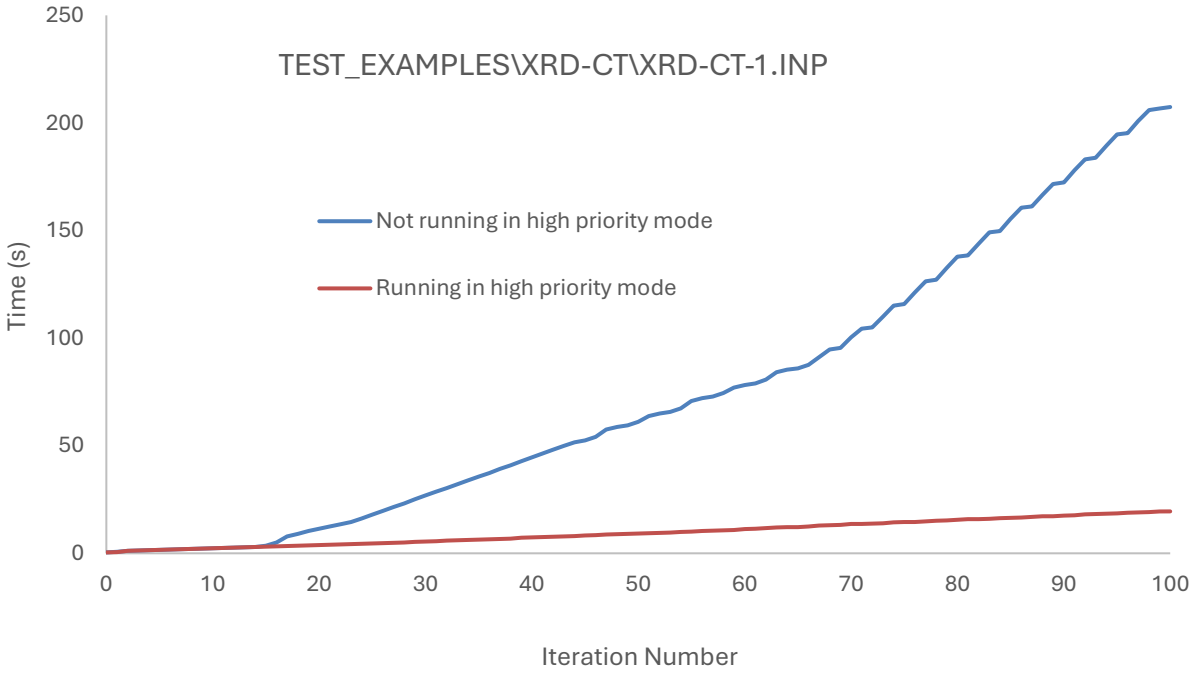
This document describes the kernel operation of TOPAS-Academic including its macro language. The kernel is written in ANSI c++ with internal data structures comprising a tree similar to an XML representation. Individual tree nodes correspond to c++ objects; understanding the internal structures facilitates program operation. Input is through an input file (*.INP) comprising readable keywords and macros, the latter being groupings of keywords. The kernel pre-processes the INP file expanding macros as required; the resulting pre-processed file (written to TOPAS.LOG) comprises keywords that are operated on by the kernel. On parsing the INP file the kernel creates its internal data structures. The main tree-node objects are:

xdd...
- bkg : Background.
- str... : Structure information for Rietveld refinement.
- xo_Is... : 2θ-I values for single line or whole powder pattern fitting.
- d_Is... : d-I values for single line or whole powder pattern fitting.
- hkl_Is... : Lattice information for Le Bail or Pawley fitting.
- fit_obj... : User defined fit models.

str, xo_Is, d_Is and hkl_Is are referred to as "phases" and the peaks of these "phase peaks". A listing of the data structures is given in section 21.1.

1.1..... Running TOPAS in high priority mode

Windows is becoming more guarded with the compiler not producing EXE files that run in a high priority mode. This slows down TOPAS appreciably when running large refinements, especially when accompanied by large memory usage. The solution is to run the program in high-priority-mode. Below shows a factor of 10+ difference in running-time when running XRD-CT-1.INP using TC.EXE.



When not running in high priority mode, time per iteration slows downs appreciably after iteration 16.

1.1.1 ..... Running TA.EXE in high priority mode (TOPASH.BAT)

Run the following from the command line:

```
start "" /high "ta"
```

Or, run the batch file TOPAS-HIGH-PRIORITY.BAT or **TAH.BAT**.

1.1.2 ..... Running TC.EXE in high priority mode

From the command prompt, use the following to start the command prompt:

```
start /high "cmd"
```

Or, run the command as an administrator from the start menu by typing ‘command’ and then choose the “Run as administrator”.

1.2 ..... Conventions

- Keywords look like this.
- Macros look like this.
- Keywords enclosed in square brackets [ ] are optional.
- Keywords ending in ... indicate that multiple keywords of that type are allowed.
- Text beginning with the character # corresponds to a number.
- Text beginning with the character $ corresponds to a string.
- E after keyword: corresponds to an equation (i.e. = a+b;) or constant (i.e. 1.245) or a parameter name with a value (i.e. lp 5.4013) that can be refined.
- !E after keyword: corresponds to an equation or constant or a parameter name with a value that cannot be refined.

To avoid input errors, it is useful to differentiate between keywords, macros, parameter names, and reserved parameter names. The conventions followed are:

Keywords :	all lower case
Parameter names :	first letter in lower case
Macro names :	first letter in upper case
Reserved parameter names :	first letter in upper case

1.3 ..... Input file example (INP format)

The following is an example input file for Rietveld refinement of corundum and fluorite:

```
' Rietveld refinement comprising two phases
xdd File_Name.xy
    CuKa5(0.001)                          ' Emission profile
    Radius(217.5)                         ' Diffractometer radius
    LP_Factor(26.4)                       ' Lorentz polarization
    Slit_Width(0.1)                       ' Receiving slit width
    Divergence(1)                         ' Equatorial divergence
    Full_Axial_Model(12, 15, 12, 2.3, 2.3) ' Axial divergence
    Zero_Error(@, 0)
    bkg @ 0 0 0 0 0 0
    STR(R-3C, "Corundum Al2O3")
        Trigonal(@ 4.759, @ 12.992)
        site Al x 0         y 0  z @ 0.3521  occ Al+3 1  beq @ 0.3
        site O  x @ 0.3062  y 0  z   0.25    occ O-2  1  beq @ 0.3
        scale @ 0.001
        CS_L(@, 100)
        r_bragg 0
    STR(Fm-3m, Fluorite)
        Cubic(@ 5.464)
        site Ca    x 0      y 0     z 0      occ Ca 1   beq @ 0.5
        site F     x 0.25   y 0.25  z 0.25   occ F  1   beq @ 0.5
        scale @ 0.001
        CS_L(@, 100)
        r_bragg 0
```

The format is case sensitive. Optional indentation can be used to show tree dependencies. Placement of keywords within a tree level is not important. For example, the keyword str signifies that all information (pertaining to str) occurring between this keyword and the next level of the same type (in this case str) applies to the first str. All input text streams can have line and/or block comments. A line comment is indicated by the character ' and a block comment by an opening /* and closing */. Text from the line comment character to the end of the line is ignored. Text within block comments is ignored; block comments can be nested. Here are some examples:

```
' This is a line comment
space_group C2/c ' This is also a line comment
/* This is a block comment.
    A block comment can comprise any number of lines. */
```

On termination of refinement an output file (*.OUT) similar-to the input file is created with refined values updated.

1.4..... Test examples

The directory TEST_EXAMPLES contain examples that can act as templates for creating INP files. In addition, charge-flipping examples are found in the CF directory and indexing examples in the INDEXING directory.

1.5..... TC-INPS.BAT and the aac$ macro

The batch file TC-INPS.BAT runs over 180 test examples in a few minutes. These examples play an important role in program testing. Arguments passed via the command line to the test

examples can contain the aac$ macro. If defined, aac$ is expanded at the bottom of the INP file. For example, to terminate refinement after 100 iterations the following could be used:

```
tc test_examples\pdf\alvo4\rigid "macro aac$ { iters 100 verbose 0 }"
```

1.6..... TOPAS is 64 bit

The command line TC.EXE and the GUI TA.EXE both run on the Windows 64-bit operating system.

2. ..PARAMETERS

2.1..... When is a parameter refined

A parameter is flagged for refinement by giving it a name. The first character can be an upper or lower-case letter. Subsequent characters can include the underscore character '_' and the numbers 0 through 9. For example:

```
site Zr x 0 y 0 z 0 occ Zr+4 1 beq b1 0.5
```

Here b1 is the name given to the beq parameter. No restrictions are placed on the length of parameter names. The character ! placed before b1, as in !b1, signals that b1 is not to be refined, for example:

```
site Zr x 0 y 0 z 0 occ Zr+4 1 beq !b1 0.5
```

A parameter can also be flagged for refinement by placing the @ character at the start of its name. Internally the parameter is given a unique name and treated as an independent parameter. The b1 text in the following is ignored:

```
     site Zr x 0 y 0 z 0 occ Zr+4 1 beq @ 0.5
or, site Zr x 0 y 0 z 0 occ Zr+4 1 beq @b1 0.5
```

2.2..... User defined parameters - the prm/local keywords

The [prm|local E] keywords defines a new parameter. For example:

```
prm b1 0.2 ‘ b1 is the name given to this parameter
           ‘ 0.2 is the initial value
site Zr x 0 y 0 z 0 occ Zr+4 0.5  beq = 0.5 + b1;
                    occ Ti+4 0.5  beq = 0.3 + b1;
```

Here b1 is a new parameter that will be refined; this example demonstrates adding a constant to a set of beq's. Note the use of the '=' sign after the beq keyword; this indicates that the parameter is in the form of an equation. In the following example, b1 is used but not refined:

```
prm !b1 0.2
site Zr x 0 y 0 z 0 occ Zr+4 0.5  beq = 0.5 + b1;
                    occ Ti+4 0.5  beq = 0.3 + b1;
```

2.3..... Parameter attributes

The following optional parameter attributes can be assigned to a parameter:

[min !E] [max !E] [del !E] [update !E] [stop_when !E] [val_on_continue !E] [_rem !E]

_rem is described in section 15.6. Attributes are equations and cannot have a parameter name; they can however be a function of other parameter names. The min and max attributes can be used to limit parameter values during refinement, for example:

```
prm a 0.1 min 0 max = 10;
prm b 0.2 min = a; max = 10;
```

Here b is constrained to within the range 0.1 and 10. Limits are effective in refinement stabilization. del is used for calculating numerical derivatives with respect to the calculated pattern; typically, internal default del values are adequate in most circumstances. Parameter values are updated at the end of an iteration as follows:

new_Val = old_Val + *Change*

When update is defined then the following is used:

new_Val = “update equation”

update can additionally be a function of the reserved parameter names *Change* and *Val*. The use of update does not negate min and max. stop_when is a conditional statement used as a stopping criterion. In this case convergence is determined when stop_when evaluates to a non-zero value for all defined stop_when attributes, as defined for independent parameters, and when the chi2_convergence_criteria condition has been met. val_on_continue is evaluated when continue_after_convergence is defined. It provides a means of changing parameter values after refinement convergence where:

new_Val = val_on_continue

Here are example attribute equations as applied to the x parameter:

```
x @ 0.1234
    min       = Val - 0.2;
    max       = Val + 0.2;
    update    = Val + Rand(0, 1) Change;
    stop_when = Abs(Change) < 0.000001;
```

2.4..... Parameter constraints

Equations can be a function of parameter names; this provides a mechanism for introducing linear and non-linear constraints, for example:

```
site Zr x 0 y 0 z 0 occ Zr+4 zr 1    beq 0.5
                    occ Ti+4 = 1-zr; beq 0.3
```

Here the zr parameter is used in the equation "= 1-zr;"; this equation defines the Ti+4 site occupancy. Note, equations start with an equal sign and end in a semicolon. Limiting zr with min/max can be performed as follows:

```
site Zr x 0 y 0 z 0 occ Zr+4 zr 1 min 0 max 1  beq 0.5
                    occ Ti+4 = 1 - zr;         beq 0.3
```

Here zr will be constrained to within 0 and 1. An example constraining the lattice parameters a, b, c to the same value as required for a cubic lattice is as follows:

```
a lp 5.4031b lp 5.4031c lp 5.4031
```

Parameters with names that are the same must have the same value. An exception is thrown if the above lp parameters were defined with values that were all not the same. Another means of constraining the three lattice parameters to the same value is by using equations with the parameter lp defined once, or,

```
a lp 5.4031    b = lp;    c = lp;
```

More general again is the use of the Get function as used in the Cubic macro:

```
a @ 5.4031 b = Get(a);    c = Get(a);
```

Here the constraints are formulated without the need for a parameter name.

2.5..... The *local* keyword

The local keyword is used for defining parameters as local to the top, xdd or phase level; local can simplify complex INP files. The following code fragment:

```
xdd    local a 1
xdd    local a 2
```

has two 'a' parameters; one dependent on the first xdd and the other dependent on the second xdd. Internally two independent parameters are generated, one for each of the 'a' parameters; this is necessary as the parameters require separate positions in the **A** matrix for minimization, correlation matrix, errors etc... In the code fragment:

```
local a 1              ' top level
xdd gauss_fwhm = a;    ' 1st xdd
xdd gauss_fwhm = a;    ' 2nd xdd
      local a 2        ' xdd level
```

the 1st xdd is convoluted with a Gaussian with a FWHM of 1 and the 2nd with a Gaussian with a FWHM of 2. In other words, the 1st gauss_fwhm equation uses the 'a' parameter from the top level and the second gauss_fwhm equation uses the 'a' parameter defined in the 2nd xdd. This is analogous, for example, to the scoping rules found in the c programming language. The following is not valid as b1 is defined twice but in a different manner.

```
xdd    local a 1  prm b1 = a;
xdd    local a 2  prm b1 = a;
```

The following comprises 4 separate parameters and is valid:

```
xdd    local a 1  local b1 = a;
xdd    local a 2  local b1 = a;
```

2.6..... Defining local parameters using $

The $ character can also be used to signal that a parameter is local. The following two lines are similar but not entirely equivalent:

```
xdd … local sc 0.01 min 1e-10 scale = sc;
xdd … scale $sc 0.01
```

The benefit of using $ is that the default scale parameter attributes of min, max and del are retained. The $ character can also be used with the prm keyword resulting in the parameter being defined as local. The following two lines are equivalent:

```
prm $cs 100
local cs 100
```

Use of $ also simplifies the writing of macros when using "for { }" loops. For example, the following:

```
for strs { CS_L(@, 100) }
```

expands to:

```
for strs {
    prm m67cff550_1 100 min .3 max = Min(Val 2 + .3, 10000);
    lor_fwhm = 0.1 57.2957795130823 Lam / (Cos(Th) (m67cff550_1));
}
```

Here, there's only one CS_L parameter, named m67cff550_1, for all strs within the loop. If on the other hand the intention was to have one unique CS_L for each str then the following can be used.

```
for strs { CS_L($cs, 100) }
```

which expands to:

```
for strs {
    prm $cs 100 min .3 max = Min(Val 2 + .3, 10000);
    lor_fwhm = 0.1 57.2957795130823 Lam / (Cos(Th) ($cs));
}
```

In the above each str has one unique cs parameter due to the use of the $ character. The problem with local parameters within the for loop, is that only one cs parameters is updated in the OUT file with the *cs* parameters being lost. This situation can be remedied by using the keyword load_save_locals.

2.7..... Reporting on equation values

The value of the equation can be obtained by placing " : 0" after the equation, for example:

```
occ Ti+4 = 1-zr; : 0
```

After refinement, the '0' is replaced by the value of the equation. The associated error is also reported when do_errors is defined.

2.8..... Naming of equations

Equations can be given a parameter name, for example:

```
prm !a1 = a2 + a3/2; : 0
```

Here the a1 parameter represents the equation “a2 + a3/2”. If the value of the equation evaluates to a constant, then a1 would be an independent parameter, otherwise a1 is treated as a dependent parameter. If the equation evaluates to a constant, then a1 will be refined if the character ‘!’ is not used. The following equation is valid even though it doesn’t have a parameter name; its value and error are also reported on termination of refinement.

```
prm = 2 a1^2 + 3; : 0
```

Equations in general are not evaluated sequentially, the following:

```
prm a2 = 2 a1; : 0
prm a1 = 3;
```

gives on termination of refinement:

```
prm a2 = 2 a1; : 6
prm a1 = 3;
```

Parameters with the same name must have identical values or equations. This allows for non-sequential evaluation of parameters. The following leads to redefinition errors:

```
prm a1 = 2;     prm a1 = 3;  ‘ redefinition error
prm b1 = 2 b3;  prm b1 = b3; ‘ redefinition error
```

2.9..... existing_prm

[existing_prm E]...

Evaluated sequentially and allows for the modification of an existing prm/local parameters, see for example the macro K_Factor_WP in TOPAS.INC. The following:

```
local a 1
existing_prm a += 1;
existing_prm a /= 2;
existing_prm a = 3 (a + 1);
prm = a; : 0
```

gives:

```
prm = a; : 6.00000
```

Allowed operators for existing_prm are +=, -=, *-, /= and ^=.

2.10 ... String, Concat, To_String and To_Prm functions

String assigns a string attribute to text that would otherwise be a parameter. To_String evaluates a parameter and converts the result to a string. To_Prm converts a string to a parameter name. Together these macros provide flexibility in the creation of INP files. Concat(a, b, c, ...) concatenates strings. Concat and To_Prm arguments can be parameters or strings. If an argument is a parameter, then the value of the parameter is converted to a string. For example, the following are all equivalent:

```
prm abc = 7;
prm  = To_Prm(a, b, c); :  7
prm  = To_Prm(a, "b", "c"); :  7
prm  = To_Prm(Concat("a", "b", "c")); :  7
prm  = To_Prm(Concat(a, "b", "c")); :  7
prm  = To_Prm(String(abc)); :  7
prm  = To_Prm("abc"); :  7
```

2.11 ... Starting a parameter with a random number

The pre-processor *#out* command (see section 22.1.2) can be used to start parameters at random values, for example:

```
#prm a_start = Rand(5.4, 5.6);
a @ #out a_start
```

This is pre-processed to (as seen in TOPAS.LOG):

```
a @ 5.58537511
```

2.12 ... Using the % equation character to define a parameter name

A parameter name can be defined using a % equation as seen in the following:

```
Create_XDDs(3)
prm i 1
for xdds {
    xdd_file = Concat("ceo2-", i, ".xdd")
    …
    str
        site  Ce1                       occ Ce+4  1 beq %Concat("bCe", i); 0.2
        site  O1  x 0.25 y 0.25 z 0.25  occ O-2   1 beq %Concat("bO", i);  0.4
        existing_prm i += 1;
        …
}
```

The above loads three xdds ceo2-1.xdd, ceo2-2.xdd and ceo2-3.xdd. Each has a structure with two beq parameters created using the %Concat sequence; the names created are bCe1, bO1, bCe2, bO2, bCe3 and bO3. These can be used in equations as normal. If the bCe_ parameters were the same as the bO_ parameters then the following could be used:

```
site  Ce1                       occ Ce+4  1 beq %Concat("b1", i); 0.2
site  O1  x 0.25 y 0.25 z 0.25  occ O-2   1 beq %Concat("b1", i); 0.2
```

or, using To_Prm:

```
site  Ce1                       occ Ce+4  1 beq %Concat("b1", i); 0.2
site  O1  x 0.25 y 0.25 z 0.25  occ O-2   1 beq = To_Prm(Concat("b1", i));
```

2.13 ... dummy and dummy_prm keywords

The dummy keyword reads a word from the input stream. dummy_prm is similar except it reads parameter dependent text. For example, the following purple text is loaded by dummy_prm and is ignored by the Kernel.

```
load xo dummy_prm I
   {
      10   = 1/Max(0.00023, 0.0001); min 10 max = Val 2; @ 100
      ...
```

2.14 ... Parameter errors and correlation matrix

When do_errors is defined, parameter errors and the correlation matrix are generated at the end of refinement, see also section 4.9. Errors are appended to parameter values as follows:

```
a lp 5.4031_0.0012
```

Here the error in lp is 0.0012. The correlation matrix is identified by C_matrix_normalized; it is appended to the OUT file if it does not already exist, or updated if it does exist.

2.15 ... Default parameter limits and LIMIT_MIN / LIMIT_MAX

Parameters with internal default min/max attributes are shown in Table 2-1. These limits avoid invalid numerical operations and equally important they stabilize refinement by directing the minimization process towards lower χ^2 values. Hard limits are avoided where possible and instead parameter values move within a range during a refinement iteration. User defined min/max limits override default limits. Parameters defined using prm/local should be defined with user defined min/max limits. Functionality is often realized through the standard macros defined in TOPAS.INC; this is an important file to view. Almost all prm's defined within this file have min/max limits. For example, the CS_L macro defines a crystallite size parameter with a min/max of 0.3 and 10000 nm respectively. On termination of refinement, independent parameters that refined close to their limits are identified by the text "_LIMIT_MIN_#" or "_LIMIT_MAX_#" appended to the parameter value. The '#' corresponds to the limiting value. These warnings can be suppressed using no_LIMIT_warnings.

Table 2-1. Default parameter limits.

Parameter	min	max
la	1e-5	2 *Val* + 0.1

lo	Max(0.01, *Val*-0.01)	Min(100, *Val*+0.01)
lh, lg	0.001	5
a, b, c	Max(1.5, 0.995 *Val* - 0.05)	1.005 *Val* + 0.05
al, be, ga	Max(1.5, *Val* - 0.2)	*Val* + 0.2
scale	1e-11	
sh_Cij_prm	-2 Abs(*Val*) - 0.1	2 Abs(*Val*) + 0.1
occ	0	2 *Val* + 1
beq	Max(-10, *Val*-10)	Min(20, *Val*+10)
pv_fwhm, h1, h2, spv_h1, spv_h2	1e-6	2 Val + 20 *Peak_Calculation_Step*
pv_lor, spv_l1, spv_l2	0	1
m1, m2	0.75	30
d	1e-6	
xo	Max(*X1*, *Val* - 40 *Peak_Calculation_Step*)	Min(*X2*, *Val* + 40 *Peak_Calculation_Step*)
l	1e-11	
z_matrix distance	Max(0.5, *Val* .5)	2 *Val*
z_matrix angles	*Val* – 90	*Val* + 90
rotate	*Val* – 180	*Val* + 180
x, ta, qa, ua	*Val* - 1/Get(a)	*Val* + 1/Get(a)
y, tb, qb, ub	*Val* - 1/Get(b)	*Val* + 1/Get(b)
z, tc, qc, uc	*Val* - 1/Get(c)	*Val* + 1/Get(c)
u11, u22, u33	*Val* If(*Val* < 0, 2, 0.5) - 0.05	*Val* If(*Val* < 0,0.5,2) + 0.05
u12, u13, u23	*Val* If(*Val* < 0, 2, 0.5) - 0.025	*Val* If(*Val* < 0,0.5,2) + 0.025
filament_length	0.0001	2 *Val* + 1
sample_length, receiving_slit_length, primary_soller_angle, secondary_soller_angle		

2.16 ... Reserved parameter names

Table 2-2 and Table 2-4 lists reserved parameter names that are internally updated when needed. Table 2-3 details dependences for certain reserved parameter names. An exception is thrown when a reserved parameter name is used for a User defined parameter name. An example for weighting using the reserved parameter names of *Yobs*, *Ycalc* and *X* is as follows:

```
weighting = Abs(Yobs-Ycalc) / (Max(Yobs+Ycalc,1) Max(Yobs,1) Sin(X Deg / 2));
```

Table 2-2. Reserved parameter names.

Name	Description
A_star, *B_star*, *C_star*	Corresponds to the lengths of the reciprocal lattice vectors.

Change	Returns the change in a parameter at the end of a refinement iteration. *Change* can only appear in the equations update and stop_when.
D_spacing	Corresponds to the d-spacing of phase peaks in Å.
H, *K*, *L*, *M*	hkl and multiplicity of phase peaks.
Iter, *Cycle*, *Cycle_Iter*	Returns the current iteration, the current cycle and the current iteration within the current cycle respectively. Can be used in all equations.
Lam	Corresponds to the wavelength lo of the emission profile line with the largest la value.
Lpa, *Lpb*, *Lpc*	Corresponds to the a, b and c lattice parameters respectively.
Mi	An iterator used for multiplicities. See the PO macro of TOPAS.INC for an example of its use.
Peak_Calculation_Step	Return the calculation step for phase peaks, see x_calculation_step.
QR_Removed, *QR_Num_Times_Consecutively_Small*	Can be used in the quick_refine_remove equation.
R, *Ri*	The distance between two sites *R* and an iterator *Ri*. Used in the equation part of atomic_interaction, box_interaction and grs_interaction.
Rp, *Rs*	Primary and secondary diffractometer radius respectively.
T	Corresponds to the current temperature, can be used in all equations.
Th	Corresponds to the Bragg angle (in radians) of hkl peaks.
X, *X1*, *X2*	Corresponds to the measured x-axis, the start and the end of the x-axis respectively. *X* is used in fit_obj's equations and the weighting equation. *X1* and *X2* can be used in all xdd dependent equation.
Xo	Corresponds to the current peak position; this corresponds to 2Th degrees for x-ray data.
Val	Returns the value of the corresponding parameter.
Yobs, *Ycalc*, *SigmaYobs*	Observed, Calculated and estimated standard deviation in *Yobs*; can be used in the weighting equation.

Table 2-3. Parameters that operate on phase peaks; dependencies are not shown.

Keywords that can be a function of *H*, *K*, *L*, *M*, *Xo*, *Th* and *D_spacing*.

lor_fwhm gauss_fwhm	user_defined_convolution th2_offset	phase_out, phase_out_X scale_top_peak

hat one_on_x_conv exp_conv_const circles_conv stacked_hats_conv	scale_pks h1, h2, m1, m2 spv_h1, spv_h2, spv_l1, spv_l2 pv_lor, pv_fwhm pk_xo	set_top_peak_area
		ymin_on_ymax la, lo, lh, lg modify_peak_eqn current_peak_min_x current_peak_max_x

Table 2-4. Phase intensity reserved parameter names.

Name	Description
A01, *A11*, *B01*, *B11*	Used for reporting structure factor details as defined in equations (20-5a) and (20-5b), see the macros Out_F2_Details and Out_A01_A11_B01_B11.
Iobs_no_scale_pks *Iobs_no_scale_pks_err*	Returns the observed integrated intensity of a phase peak and its associated error without any scale_pks applied. *Iobs_no_scale_pks* for phase peak *p* is calculated using the Rietveld decomposition formulae, or, ^{1}*Iobs_no_scale_pks* = Get(scale) $\frac{I_P \sum_x P_{x,p} Y_{obs,x}}{Y_{calc,x}}$ where $P_{x,p}$ is the phase peak *p* calculated at the x-axis position *x*. The summation Σ_x extends over the x-axis extent of the peak *p*. A good fit to the observed data results in an *Iobs_no_scale_pks* being approximately equal to *I_no_scale_pks*.
I_no_scale_pks	The Integrated intensity without scale_pks equations, or, ^{1}*I_no_scale_pks* = Get(scale) I
I_after_scale_pks	The Integrated intensity with scale_pks equations applied. ^{1}*I_after_scale_pks* = Get(scale) I Get(all_scale_pks) returns the cumulative value of all scale_pks equations applied to a phase.
^{1}) I corresponds to I of hkl_Is, xo_Is and d_Is phases or (M F_{obs}^2) for str phases.	

2.17 ... Val and Change reserved parameter names

Val is a reserved parameter name corresponding to the numeric value of a parameter during refinement. *Change* is a reserved parameter name corresponding to the change of a parameter at the end of an iteration as determined by non-linear least squares. *Val* can only be used in the attribute equations min, max, del, update, stop_when and val_on_continue. *Change* can only be used in the attribute equations update and stop_when. Here are some examples:

```
min 0.0001
max = 100;
max = 2 Val + 0.1;
```

```
del = Val 0.1 + 0.1;
update = Val + Rand(0,1) Change;
stop_when = Abs(Change) < 0.000001;
val_on_continue = Val + Rand(-Pi, Pi);
x @ 0.1234 update = Val + 0.1 ArcTan(Change 10); min=Val-.2; max=Val+.2;
```

2.17.1 ..... The "load { }" keyword and attribute equations

"load { }" allows for loading keywords of the same type by typing the keywords once, for example, exclude in the following input segment:

```
xdd   exclude 20 22   exclude 32 35   exclude 45 47
```

can be rewritten using "load { }" as follows:

```
xdd   load exclude { 20 22 32 35 45 47 }
```

In some cases, attribute equations are loaded by the parameter itself. For example, in the following:

```
prm t 0.01  val_on_continue = Rand(-Pi, Pi); min 0.4 max 0.5
```

the prm will load the attribute. In the following, however, load will load the min/max attributes:

```
load sh_Cij_prm {
   y00 !sh_c00 1
   y20  sh_c20 0.26202642  min 0 max 1
   y40  sh_c40 0.06823548
   ...
}
```

In this case load does not contain min/max and the parameter will load its attributes.

2.17.2 ..... The "move_to $keyword" keyword

move_to provides a means of entering parameter attributes without having to first load the parameter, see Keep_Atom_Within_Box macro. The site dependent ADPs_Keep_PD macro, defines min/max limits; here's part of that macro:

```
move_to u12
    min = -Sqrt(Get(u11) Get(u22));
    max =  Sqrt(Get(u11) Get(u22));
```

$keyword of move_to can be any object in the internal data tree.

2.18 ... Automatically saving and loading parameters - load_save_locals

[load_save_locals]	**Examples** TEST_EXAMPLES\LOAD-SAVE-LOCALS \LSL.INP

Parameters given unique names using the local keyword defined within "for {}" loops can be automatically saved and reloaded for subsequent refinements using the load_save_locals keyword. For example,

```
load_save_locals
xdd…
    str… phase_name p1
    str… phase_name p2
    for strs {
        site Ca1 x $ca1x 0.123 …
    }
```

In the above, there are two str's and two local x coordinate parameters defined using the $ character. However, only one value is defined and thus only one value is saved to the OUT file. load_save_locals can be used to save both values to a file called INP_FILE.OUT_SL; notice the OUT_SL file extension. On rerunning the INP file, a check is made for the existence of a file called INP_FILE.SL, and if the file exists then parameter values are read from the file if. The GUI copies INP_FILE.OUT_SL to INP_FILE.SL when parameter values are kept after refinement. Parameters are identified by the xdd file name and the phase name. If the file is a RAW file, then the range number is also saved to INP_FILE.SL. Alternatively, the xdd dependent keyword xdd_tag can be used to identify the parameter instead of the xdd file name/range number. This is useful when xdd file names are the same as in the following:

```
    XDD(..\ceo2) finish_X 50 …
    XDD(..\ceo2) start_X  50 … ' Same file name as first xdd, need to use xdd_tag
    prm i 0
    for xdds {
        xdd_tag = Load_Eval(i);
        existing_prm i += 1;
        …
    }
```

Phase names within a particular xdd needs to be unique. The Load_Eval function evaluates the parameter i when loading and places the value into the xdd dependent xdd_tag. A more complete example, LOAD-SAVE-LOCALS \LSL.INP, defines all refined values as local and is as follows:

```
load_save_locals
do_errors
XDD(..\ceo2) finish_X 50 str phase_name p1 str phase_name p2
XDD(..\ceo2) start_X  50 str phase_name p3 str phase_name p4
prm i 0
for xdds {
    xdd_tag = Load_Eval(Concat("tag", i)); ' Evaluate on load
    existing_prm i += 1;
    CuKa2(0.0001)
    Radius(173)
    LP_Factor(17)
    Full_Axial_Model(12, 20, 12, 5.1, $sl 5)
    Divergence(1)
    Slit_Width(0.1)
    Zero_Error($ze, 0)
    bkg $bkg  0 0 0 0 0
    One_on_X($onex, 0) ' This is a fit_obj phase which owns the its locals
    for strs {
        space_group FM3M
        scale $sc 0.001
        Cubic($a 5.4102)
        site  Ce1                       occ Ce+4  1 beq $b1  0.5
        site  O1  x 0.25 y 0.25 z 0.25  occ O-2   1 beq $b1  0.5
        CS_L($cs, 100)
    }
}
```

The above is the simplest way of refining on many similar xdds.

2.19 ... Using local to assist in using "for ... {}" loops

The following parameters have global scope:

```
march_dollase $Name
spherical_harmonics_hkl $Name
sites_geometry $Name
sites_distance $Name
sites_angle $Name
sites_flatten $Name
```

The march_dollase parameter, as used in the PO macro, can be constrained to the same value across two or more structures by giving them the same name. To have two different parameters, the $ can be used to make the parameter local to the str, see PO-CONSTRAINED-CREATE.INP and PO-FOR.INP in the TEST_EXAMPLES\PO-CONSTRAINED directory, for example:

```
str… str…
for strs { PO($po1, 0.8, , 1 0 4) }
```

The $Name in spherical_harmonics_hkl is local but the spherical harmonics coefficients are global. In the following:

```
PO_Spherical_Harmonics(sh2, 8 load sh_Cij_prm {
```

```
        k00   !sh2_c00  1.0000
        k41   sh2_c41   0.1000
        k61   sh2_c61  -0.2000
        k62   sh2_c62   0.3000
        k81   sh2_c81  -0.4000
    } )
```

the sh2 parameter is local to the str and the coefficients k00, k41 etc... are global. This allows the constraining of coefficients across different structures within 'for strs'; see POSH-CONSTRAINED-CREATE.INP and POSH-FOR.INP in the TEST_EXAMPLES\PO-CONSTRAINED directory.

2.20 ... out_dependences and out_dependences_for

[out_dependences $user_string]
[out_dependences_for $user_string $object_name]

out_dependences outputs dependences for the most previously defined prm or local. For example, the following:

```
    iters 1
    prm d 1 prm e 1 prm f 1
    prm c = e + f;
    prm b = d + e;
    prm a = b + c;
    out_dependences a_tag
    penalty = a^2;
```

produces on refinement termination the following in standard output:

```
out_dependences a_tag prm_10
   Object name followed by prm name
       prm_10   e
       prm_10   f
       prm_10   d
```

out_dependents_for is similar except that it names an object that is not a parameter, for example, the following lists independent refined parameters associated with the most recently defined rigid body:

```
    rigid ...   out_dependents_for tag_1 rigid
```

Many $object_name's can be tagged, these include x, y, z, occ, beq, u11, u22, u33, u12, u13, u23, a, b, c, al, be, ga, etc. In addition, non-parameters can be tagged, these include site, rigid, sites_restrain, lat_prms, gauss_conv, lor_conv, all_scale_pks, th2_offset_eqn etc.

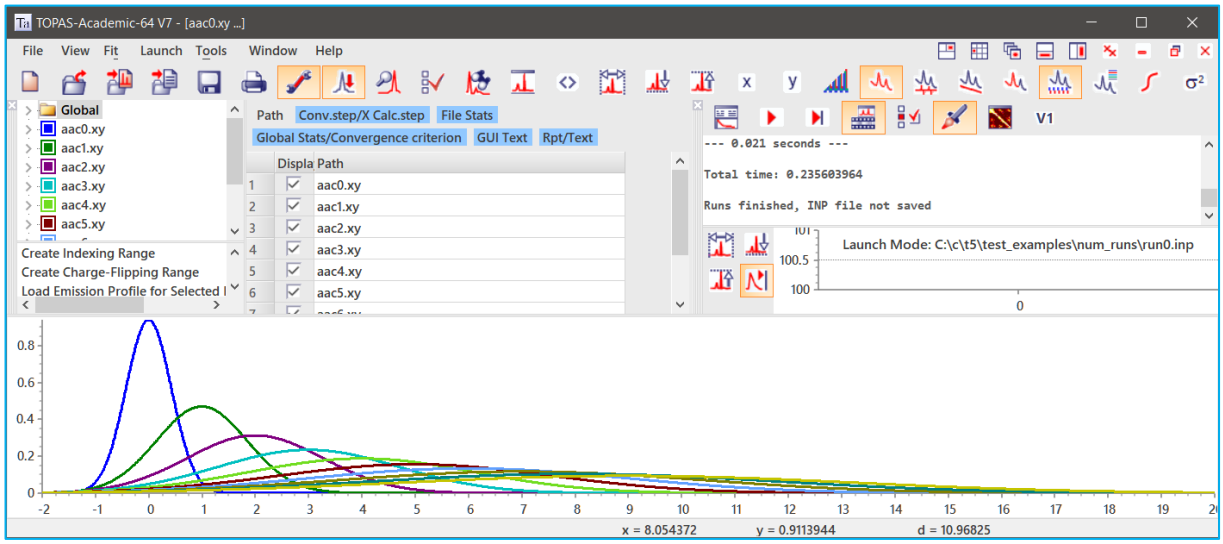
2.21 ... The num_runs keyword and preprocessor specifics

[num_runs #]
[out_file = $E]
[system_before_save_OUT { $system_commands }]...
[system_after_save_OUT { $system_commands }]...

Typically, an INP file is run once; num_runs change's this behaviour where the refinement is restarted and performed again until it is performed num_runs times. Information from one run to the next can be exchanged via the out keyword and the *#include* directive. The INP file is read each Run but not updated when both num_runs > 1 and out_file is empty. Equations could simplify to a constant during a run, or indeed, the Constant function can be used such that a parameter is not refined. From TA.EXE and Launch mode the Rwp graphical plot is appended such that it looks like continue_after_convergence. The following INP segment:

```
num_runs 10
yobs_eqn aac##Run_Number##.xy = Gauss(Run_Number, 1 + Run_Number);
    min -2 max 20 del 0.01
```

produces on execution the following:



out_file determines the name of the output file updated on refinement termination. The OUT file comprises the INP file but with parameter values updated. out_file defaults to the name of the INP file but with an OUT extension. If num_runs is greater than 1, and out_file is not defined, then no OUT file is saved. This can speed up refinements when an OUT file is not needed. out_file is an equation that needs to evaluate to a string; here are some examples:

```
out_file   aac.out   ' This will throw an exception
out_file = aac.out; ' This will throw an exception
out_file = "aac.out";
out_file = String(aac.out);
out_file = If(Get(r_wp) < 10, "aac.out", "");
out_file = If(Get(r_wp) < 10, Concat(String(INP_File), ".OUT"), "");
```

The standard macro Save_Best uses out_file as follows:

```
macro Save_Best {
  #if (Run_Number == 0)
     prm Best_Rwp_ = 9999;
  #else
     prm Best_Rwp_ = #include Best_Rwp_.txt;
  #endif
  out Best_Rwp_.txt Out(If(Get(r_wp) < Best_Rwp_, Get(r_wp), Best_Rwp_))
  out_file = If(Get(r_wp) < Best_Rwp_, Concat(String(INP_File),".OUT"), "");
}
```

system_before_save_OUT executes system commands defined in $system_commands string just before the *.OUT file is updated. The system commands are executed from the directory of the INP file. $system_commands can comprise any operating system commands. The macro Backup_INP uses system_before_save_OUT; it is defined in TOPAS.INC as:

```
macro Backup_INP {
   system_before_save_OUT {
      copy INP_File##.inp INP_File##.backup
   }
}
```

system_after_save_OUT executes the system commands defined in $system_commands string just after the *.OUT file is updated.

2.21.1 ..... Reserved macro names

The following are internally generated macros that can be used in INP files.

ROOT : Returns the root directory of the program.
INP_File : Returns current INP file name without a path or extension.
Run_Number : Returns the current run number.
File_Can_Open($file) : Returns 1 if $file can be opened or 0 of it can't be opened.

Running an INP file called AAC.INP from TC.EXE where AAC.INP comprises:

```
ROOT INP_File Run_Number File_Can_Open(aac.xy)
```

and AAC.XY exists will produce in TC.LOG the following:

```
c:\topas-6\ aac 0 1
```

2.21.2 ..... The #list directive – creating arrays of macros

#list creates arrays of macros than can be expanded depending on the value of an implied argument. For example, the following creates three arrays of macros called File_Name, Temperature and Time.

```
#list File_Name & Temperature(, & la) Time {
   File0001.xy 300 0.0
   { File0002 .xy } 320 10.2     ' Line with curly brackets
   File0003.xy 340 21.0
   File0017.xy { 360 + la } 28.9 ' Line with curly brackets
   File0107.xy 380 101.2 }
```

The actual macro invoked depends on the first argument of the macro. The first argument is implied in the case of File_Name and Time. In the case of Temperature, the first argument is the implied argument. When the macro is invoked the first argument is a #type equation that must equate to an integer; here's an example for File_Name:

```
xdd File_Name(Run_Number)
```

Curly brackets, as seen in the above *#list*, can be used as delimiters; the following:

```
File_Name(1)
Temperature(1,)
Temperature(3, Get(la) + 0.01)
```

produces on expansion:

```
File0002 .xy
(320)
(360 + (Get(la) + 0.01))
```

Using curly brackets as delimiters allow for curly brackets themselves to be part of the macro body.

2.21.3 ..... Getting the number of items in a #list using #list_n

During the pre-processor phase of loading INP files, #list_n returns the number of items in a #list; for example:

```
#list Files { file1.xdd file2.xdd file3.xdd }
Create_XDDs(#list_n Files)
```

2.21.4 ..... The File_Variable and File_Variables macro

The File_Variable macro can be used to run a series of runs with initial parameters values changing in a user defined manner between runs; the macro is defined in TOPAS.INC as follows:

```
macro File_Variable(c, x_start, dx) {
   #if (Run_Number == 0)
      #prm c = x_start;
   #else
      #prm c = #include c##.txt;
   #endif
   #prm c##_next = c + dx;
   out c##.txt Out(#out c##_next)
}
```

Using File_Variable as follows:

```
File_Variable(occ, 0, 0.1)
```

will generate a file called OCC.TXT for each Run with values ranging from 0.1 to 1 in steps of 0.1. A *#prm* is defined each run with the corresponding values. *#out* can be used to place the *#prm* in the INP file, for example, the following:

```
iters 0
num_runs 11
File_Variable(occ, 0, 0.1)
macro Out_File { Occ##Run_Number##.Out }
out_file
system_after_save_OUT {
   #if (Run_Number)
      type Out_File >> aac.out
   #else
      type Out_File > aac.out
   #endif
}
yobs_eqn !aac.xy = 1;
   min 10 max 50 del 0.01
   CuKa1(0.0001)
   Out_X_Ycalc( occ##Run_Number##.xy )
   STR(F_M_3_M)
      scale @ 0.0014503208
      Cubic(5.41)
      site  Ce1                       occ Ce+4 = #out occ; beq  0.2028
      site  O1  x 0.25 y 0.25 z 0.25  occ O-2  1           beq  0.5959
```

results in eleven *.XY files each generated with a different occupancy for the Ce1 site as determined by the occ *#prm*. The names of the files would be OCC0.XY to OCC10.XY. Additionally, using system_after_save_OUT the file AAC.OUT will contain a concatenation of all the *.OUT files. To iterate over two variables, pa and pb say, then the File_Variables macro, defined in TOPAS.INC as:

```
macro File_Variables(a, a1, a2, da, b, b1, b2, db) {
   #if (Run_Number == 0)
      #prm a = a1;
      #prm b = b1;
   #else
      #prm a = #include a##.txt;
      #prm b = #include b##.txt;
   #endif
   #prm a##_next = If(b >= b2, a + da, a);
   #prm b##_next = If(b >= b2, b1, b + db);
   out a##.txt Out(#out a##_next)
   out b##.txt Out(#out b##_next)
}
```

can be used as follows:

```
iters 0
num_runs 36
File_Variables(pa, 0, 1, 0.2, pb, 0, 1, 0.2)
prm !pa = #out pa; prm !pb = #out pb;
out papb.txt append
   out_record out_eqn = pa; out_fmt "(%.1f, "
   out_record out_eqn = pb; out_fmt "%.1f) "
   #if (pb == 1) Out_String("\n") #endif
```

On running the above the PAPB.TXT File contains:

```
(0.0, 0.0) (0.0, 0.2) (0.0, 0.4) (0.0, 0.6) (0.0, 0.8) (0.0, 1.0)
(0.2, 0.0) (0.2, 0.2) (0.2, 0.4) (0.2, 0.6) (0.2, 0.8) (0.2, 1.0)
(0.4, 0.0) (0.4, 0.2) (0.4, 0.4) (0.4, 0.6) (0.4, 0.8) (0.4, 1.0)
(0.6, 0.0) (0.6, 0.2) (0.6, 0.4) (0.6, 0.6) (0.6, 0.8) (0.6, 1.0)
(0.8, 0.0) (0.8, 0.2) (0.8, 0.4) (0.8, 0.6) (0.8, 0.8) (0.8, 1.0)
(1.0, 0.0) (1.0, 0.2) (1.0, 0.4) (1.0, 0.6) (1.0, 0.8) (1.0, 1.0)
```

2.22 ... Ingesting files into an INP file using #ingest

[*#ingest* $file]	

#ingest is a pre-processor command than copies a file into an INP file, for example:

```
xdd…
    str…
       #ingest common_str.txt
```

The output file will contain the ingested text with refined parameters updated. In other words, ingested files are treated as part of the original INP file. Ingested files can be nested. $file can be a function of macros.

2.23 ... #external_INP - using external INP files

[*#external_INP* $file]	**Examples** TEST_EXAMPLES\EXTERNAL_INP\EXT_INP.INP

#external_INP is a pre-processor command than includes the file $file as part of the refinement without ingesting the text into the INP file. On refinement end, the extension of $file is changed to OUT and the contents of this OUT file updated with refined parameter values. Example usage is as follows:

```
xdd…
    #external_INP instrument.inp
    #external_INP str.inp
```

#external_INP cab ne nested (*#external_INP* file can contain *#external_INP* commands). $file can be a function of macros. When running Launch mode from the GUI (TA.EXE), all *#external_INP* OUT files are renamed to INPs if the question on refinement termination is answered in the affirmative.

3. ..EQUATION OPERATORS AND FUNCTIONS

Table 3-1. Operators and functions supported in equations (case sensitive). In addition, equations can be a function of User defined parameter names.

Arithmetic	
+, -, *, /	Plus, Minus, Multiply, Divide. Multiply is optional, x*y = x y
^	x^y, Calculates x to the power of y. Precedence: x^y^z = (x^y)^z, x^y*z = (x^y)*z, x^y/z = (x^y)/z
Conditional	
a == b	Returns 1 if a = b
a < b	Returns 1 if a < b
a <= b	Returns 1 if a ≤ b
a > b	Returns 1 if a > b
a >= b	Returns 1 if a ≥ b
And(a, b, ...)	Returns 1 if all arguments are non-zero
Or(a, b, ...)	Returns 1 if one or more argument is non-zero
Mathematical	
ArcCos(x)	Returns the arc cos of x (-1 <= x <= 1)
ArcSin(x)	Returns the arc sine of x (-1 <= x <= 1)
ArcTan(x)	Returns the arc tangent of x
ArcTan2(y,x)	Returns arc tangent of y/x
Cos(x)	Returns the cosine of x
Cosh(x)	Hyperbolic cosine
Erf_Approx(x)	Error function
Erfc_Approx	Complementary error function
Exp(x)	Returns the exponential e to the x
Gamma_Approx(x)	Return the Gamma of x
Gamma_Ln_Approx(x)	Returns the natural logarithm of the gamma function
Gamma_P(a, x)	Returns the incomplete Gamma function P(a, x)
Gamma_Q(a, x)	Returns the incomplete Gamma function Q(a, x) = 1-P(a,x)
Ln(x)	Returns the natural logarithm of x
Sin(x)	Returns the sine of x
Sinh(x)	Hyperbolic sine
Sqrt(x)	Returns the positive square root
Tan(x)	Returns the tangent of x
Tanh(x)	Hyperbolic tangent
Special	
For(*Mi* = 0, *Mi* < *M*, *Mi* = *Mi*+1 , ...)	
Get($keyword)	Gets the parameter associated with $keyword

If(conditional_test, return true_eqn, return false_eqn)	
Sum(returns summation_eqn, initializer, conditional_test, increment_eqn)	
Miscellaneous	
Abs(x)	Returns the absolute value of x
Break	Can be used to terminate loops implied by the equations atomic_interaction, box_interaction and grs_interaction.

Break_Cycle	Can be used to terminate a refinement cycle. For example, a refinement cycle can be terminated depending on the value of a penalty as follows:
	`atomic_interaction ai = (R - 1.3)^2;`
	`penalty = If(ai > 5, Break_Cycle, 0);`

Concat(a, b, c, ...)	Concatenates strings; the arguments can be parameters or strings. If an argument, then the value of the parameter is converted to a string.
Error(p)	Returns associated error of parameter p.
a = Load_Eval(b)	Evaluates b on loading and places the result in a.
Max(a,b,c ...)	Returns the max of all arguments.
Min(a,b,c ...)	Returns the min of all arguments.
Mod(x, y)	Returns the modulus of x/y. Mod(x, 0) returns 0.
Obj_There(a)	Returns 1 if object 'a' exists within the current scope.
Prm_There(a)	Returns 1 if prm/local 'a' exists.
Rand(a, b)	Returns a uniform deviate random number between a & b.
Rand_Normal(mean,std)	Returns a random number with a normal distribution with a mean of 'mean' and standard deviation of 'std'.

Round(x)	Examples:
	`prm = Round(.1);  : 0.00000`
	`prm = Round(.5);  : 0.00000`
	`prm = Round(1.6);  : 2.00000`
	`prm = Round(-.1);  : 0.00000`
	`prm = Round(-.5);  : 0.00000`
	`prm = Round(-1.6); : -2.00000`

To_Prm(a, b, c, ...)	Concatenates the arguments to form a parameter name and returns the corresponding parameter. If an argument is a parameter name, then the value of the parameter is converted to a string.
To_String(a)	Evaluates the parameter 'a' and converts the result to a string.
Sign(x)	Returns the sign of x, or zero if x = 0

In addition, the following functions are implemented:

AB_Cyl_Corr(μR), **AL_Cyl_Corr**(μR)

Returns A_B and A_L for cylindrical sample intensity correction (Sabine *et al.*, 1998). These functions are used in the macros Cylindrical_I_Correction and

Cylindrical_2Th_Correction. Example CYLCORR.INP demonstrates usage. For a more accurate alternative to the Sabine corrections see the capillary_diameter_mm convolution.

Bkg_at(x)

Returns the value of the Chubychev polynomial, defined by bkg, at the value x.

Constant(expression)

Evaluates 'expression' once and then replaces 'Constant(expression)' with the corresponding numeric value. Very useful when the expected change in a parameter insignificantly affects the value of a dependent equation, see for example the TOF_Exponential macro.

Ln_Normal_x_at_CD(u, s, v, toll)

Returns x value of a Ln normal distribution such that x is at the Cumulative Distribution value of 'cd' where u and s are the mean and standard deviation of the variable's natural logarithm. x is calculated with a tolerance in 'cd' of 'toll'; see TEST_EXAMPLES\WPPM\LN-NORMAL-1.INP.

PV_Lor_from_GL(gauss_FWHM, lorentzian_FWHM)

Returns the Lorentzian contribution of a pseudo-Voigt approximation to the Voigt where gauss_FWHM and lorentzian_FWHM are the FWHMs of the Gaussian and Lorentzian convoluted to form the Voigt.

Sites_Geometry_Distance($Name)
Sites_Geometry_Angle($Name)
Sites_Geometry_Dihedral_Angle($Name)

Value_at_X(object, x) : Returns the value of *object* at *X* = x. *object* could be a parameter or a user_y object. For example, to ensure background is close to the high angle end of a pattern during PDF-generation, the following could be implemented:

```
user_y u capillary.xy
fit_obj = (p0 + p1 X) u;
bkg @ 0 0 0
penalty = 1000 (Bkg_at(X2) + (p0 + p1 X2) Value_at_X(u, X2) - Yobs_at(X2))^2;
```

Voigt_Integral_Breadth_GL(gauss_FWHM, lorentzian_FWHM)

Returns the integral breadth resulting from the convolution of a Gaussian with a Lorentzian with FWHMs of gauss_FWHM and Lorentzian_FWHM respectively.

Voigt_FWHM_GL(gauss_FWHM, lorentzian_FWHM)

Returns the Voigt FWHM resulting from the convolution of a Gaussian with a Lorentzian with FWHMs of gauss_FWHM and Lorentzian_FWHM respectively.

Yobs_Avg(x1, x2)

Returns the average value of *Yobs* between x1 and x2. x1 and x2 is first set to the closest x-axis data point.

Ycalc_at(x)

Returns the value of *Ycalc* at x. Zero is returned if x < *X1* or x > *X2*.

Yobs_at(#x)

Returns the *Yobs* value at the x-axis position #x; can be used in all sub xdd dependent equations.

Yobs_dx_at(#x):

Returns the step size of the observed data at the x-axis position #x; can be used in all sub xdd dependent equations. If the step size in the x-axis is equidistant then *Yobs_dx_at* is converted to a constant corresponding to the step size in the data.

Yobs_Min(x1, x2)

Returns the minimum value of *Yobs* between x1 and x2.

3.1..... 'If' and nested 'If' statements

'If' statements can be used in parameter equations, for example:

```
prm a 0.1 prm b 0.1
lor_fwhm = If(Mod(H, 2) == 0, a Tan(Th), b Tan(Th));
```

'If' can also be nested:

```
prm cs 200 update = If(Val < 10, 10, If(Val > 10000, 10000, Val));
```

For those who are familiar with if/else statements, the IF THEN ELSE ENDIF macros, as defined in TOPAS.INC, can be used:

```
IF a > b THEN
    a ‘ return expression value
ELSE
    b ‘ return expression value
ENDIF
```

Min and Max functions can be used in equations, for example:

```
prm a 0.1 prm b 0.3
th2_offset = Min(Max(a, b, -0.2), 0.2);
```

3.2..... Floating point exceptions

An exception is thrown when an invalid floating-point operation is encountered, i.e.

Divide by zero

Sqrt(x) for x < 0

Ln(x) for x ≤ 0

ArcCos(x) for x < -1 or x > 1

Exp(x) produces an overflow for x ~> 700

(-x)^y for x > 0 and y not an integer

Tan(x) evaluates to Infinity for x = n Pi/2, Abs(n) = 1, 3, 5, …

min/max equations, Min/Max functions or 'If' functions can be used to avoid invalid floating-point operations. Equations can also be manipulated to yield valid floating-point operations, for example, Exp(-1000) can be used in place of 1/Exp(1000).

4. ..THE MINIMIZATION ROUTINES

TMinimization
[line_min] [use_extrapolation] [no_normal_equations] [use_LU]
[approximate_A]
[A_matrix_memory_allowed_in_Mbytes !E]
[A_matrix_elements_tollerance !E]
[A_matrix_report_on]
[approximate_A_check_for_must_be_zero #n]
[chi2 !E]
[*chi2_convergence_criteria* !E]
[continue_after_convergence]
[bootstrap_errors !Ecycles]
[fraction_of_yobs_to_resample !E]
[determine_values_from_samples]
[resample_from_current_ycalc]
[do_errors]
[do_errors_include_restraints]
[do_errors_include_penalties]
[only_penalties]
[percent_zeros_before_sparse_A #]
[penalty !E]...
[penalties_weighting_K1 !E]
[pen_weight !E]
[quick_refine !E [quick_refine_remove !E]]
[randomize_on_errors]
[restraint !E]
[save_best_chi2]
[use_LU_for_errors]

Get(number_independent_parameters)

The Newton-Raphson non-linear least squares method is used by default with the Marquardt method (1963) included for stability. The objective function χ^2 is written as:

$$\chi^2 = \chi_0^2 + \chi_P^2 + \chi_R^2 \tag{4-1}$$

$$where \quad \chi_0^2 = K \sum_{m=1}^{M} w_m \left(Y_{o,m} - Y_{c,m}\right)^2 \tag{4-2}$$

$$\chi_P^2 = KK_1K_P \sum_{p=1}^{N_p} P_p \qquad \chi_R^2 = KK_1K_R \sum_{r=1}^{N_R} R_r^2 \qquad K = \frac{1}{\sum_{m=1}^{M} w_m Y_{o,m}^2} \tag{4-3}$$

$Y_{o,m}$ and $Y_{c,m}$ are the observed and calculated data respectively at data point m, M the number of data points, w_m the weighting given to data point m which for counting statistics is given by

$w_m=1/\sigma(Y_{o,m})^2$ where $\sigma(Y_{o,m})$ is the error in $Y_{o,m}$, P_p are penalty functions, defined using penalty, and N_p the number of penalty functions. R_r are restraints, defined using restraint, and N_R the number of restraints. K_P and K_R are weights applied to the penalty functions and restraints respectively. K_1 corresponds to the user defined penalties_weighting_K1 (default value of 1), typical values range from 0.1 to 2. Penalty functions and Restraints are minimized when observed data Y_o is absent; see example ONLYPENA.INP.

The matrix equations are generated by the usual expansion of $Y_{c,m}$ to a first order Taylor series around the parameter vector **p**. The size of **p** corresponds to the number of independent parameters N. The penalty functions are expanded to a second order Taylor series around the parameter vector **p**. The restraints are expanded to a first order Taylor series around the parameter vector **p.** The resulting matrix equations are:

$$\mathbf{A}\,\Delta\mathbf{p} = \mathbf{Y} \tag{4-4}$$

where $\mathbf{A} = \mathbf{A}_0 + \mathbf{A}_P + \mathbf{A}_R$

and $\mathbf{Y} = \mathbf{Y}_0 + \mathbf{Y}_P + \mathbf{Y}_R$

$$A_{ij} = \sum_{m=1}^{M} w_m \frac{\partial Y_{c,m}}{\partial p_i}\frac{\partial Y_{c,m}}{\partial p_j} \qquad Y_{o,i} = \sum_{m=1}^{M} w_m \left(Y_{o,m} - Y_{c,m}\right)\frac{\partial Y_{c,m}}{\partial p_i} \tag{4-5}$$

$$A_{P,ij} = \frac{K_P}{2}\sum_{p=1}^{N_P}\frac{\partial^2 P_p}{\partial p_i \partial p_j} \qquad Y_{P,i} = -\frac{K_P}{2}\sum_{p=1}^{N_P}\frac{\partial P_p}{\partial p_i}$$

$$A_{R,ij} = K_R\sum_{r=1}^{N_R}\frac{\partial R_{r,i}}{\partial p_i}\frac{\partial R_{r,j}}{\partial p_j} \qquad Y_{R,i} = -K_R\sum_{r=1}^{N_R} R_r\frac{\partial R_r}{\partial p_i}$$

The Taylor coefficients $\Delta\mathbf{p}$ corresponds to changes in the parameters p. Eq. (4-4) represents a linear set of equations in $\Delta\mathbf{p}$ that are solved for each iteration of refinement. Off diagonal terms in $\mathbf{A}_P$ are not calculated and are instead set to zero. K_R and K_P are both set to 1 in the absence of χ_0^2. When χ_0^2 does exist then K_P is used to give approximate equal weights to the sum of the inverse error terms in the parameters, $\sigma_0(p_i)^2$ and $\sigma_P(p_i)^2$, calculated from χ_P^2 and χ_0^2 respectively. Neglecting the off-diagonal terms results in $\sigma_P(p_i)^2=1/A_{0,ii}$ and $\sigma_P(p_i)^2=1/A_{P,ii}$; however, to avoid numerical stabilities K_P is written as shown in Eq. (4-6).

$$K_P = \sum_{k=1}^{N_P} If\left(Y_{P,k} < 10^{-14}A_{0,kk}, 0, \frac{1.05A_{0,kk}}{\left(A_{P,k} + A_{0,kk}Min\left(Y_{P,kk}/Y_{o,kk}, 0.05\right)\right)}\right) \tag{4-6}$$

k corresponds to independent parameters that are a function of χ_P^2. Similarly, for K_R we have:

$$K_R = \sum_{k=1}^{N_R} If\left(Y_{R,k} < 10^{-14}A_{0,kk}, 0, \frac{1.05A_{0,kk}}{\left(A_{R,k} + A_{0,kk}Min\left(Y_{R,kk}/Y_{o,kk}, 0.05\right)\right)}\right) \tag{4-7}$$

K_R and K_P can be modified using pen_weight and the macro Pen_Wt. Pen_Wt calls the user defined macro Write_Pen_Wt; a definition that mimics the default is:

```
macro Write_Pen_Wt(Aii, Ai, Pii, Pi) {
    pen_weight = If(Pii < 1e-14 Aii,0,1.05 Aii/(Pii+Aii Min(Pi/Ai, 0.05)));
}
```

A_{ii} and A_i corresponds to $A_{0,ii}$ and $Y_{0,i}$ respectively. For K_P then P_{ii} and P_i corresponds to $A_{P,ii}$ and $Y_{P,i}$. For K_R then P_{ii} and P_i corresponds to $A_{R,ii}$ and $Y_{P,i}$. ShelX type restraints can be formulated as follows:

```
pen_weight = 1;
penalties_weighting_K1 = (Get(r_wp) / Get(r_exp))^2;
do_errors_include_restraints
save_best_chi2
restraint = Sqrt(w) (yt - y);
```

where Sqrt(w) is simply the square root of the restraint weight used by ShelX.

4.1..... The Conjugate Gradient Solution method

The Bounds Constrained Conjugate Gradient (BCCG) method (Coelho, 2005) incorporating min/max limits is used for solving the normal equations; it assists in convergence of the non-linear least squares process. min/max limits are dynamically recalculated and used to during the solution process. For example, to constrain site occupancies on three sites to full occupancy with three atomic species, each with occupancy of 1, then the following could be defined (see TEST_EXAMPLES\OCC-CONSTRAIN.INP):

```
site Ni x 0.11 y 0.22 z 0.33   occ Ni ni1  0.20000 min 0 max  1
                                   occ Zr zr1  0.30000 min 0 max = 1 - ni1;
                                   occ Ca ca1 = 1 - ni1 - zr1; :  0.50000

site Zr x 0.21 y 0.32 z 0.43   occ Ni ni2  0.40000 min 0 max = 1 - ni1;
                                   occ Zr zr2  0.50000 min 0 max = 1 - ni2;
                                   occ Ca ca2 = 1 - ni2 - zr2; :  0.10000

site Ca x 0.31 y 0.42 z 0.53   occ Ni ni3 = 1 - ni1 - ni2; :  0.40000
                                   occ Zr zr3 = 1 - zr1 - zr2; :  0.20000
                                   occ Ca ca3 = 1 - ca1 - ca2; :  0.40000

' Occupancy on sites add up to 1
prm = ni1 + zr1 + ca1; :  1.00000
prm = ni2 + zr2 + ca2; :  1.00000
prm = ni3 + zr3 + ca3; :  1.00000

' Individual species add up to 1
prm = ni1 + ni2 + ni3; :  1.00000
prm = zr1 + zr2 + zr3; :  1.00000
prm = ca1 + ca2 + ca3; :  1.00000
```

If the **A** matrix is not sparse then use_LU can be used to invoke LU-decomposition instead of the BCCG routine. LU-decomposition does not use min/max limits during the solution process and in addition it requires the full A matrix which, for problems with thousands of parameters,

may be memory intensive. LU-decomposition can also be slow when the number of parameters is greater than about one thousand. percent_zeros_before_sparse_A defines the percentage of the A matrix that can be zero before sparse matrix methods are invoked. The default value is 60%.

4.2..... The Marquardt method

The Marquardt (1963) method applies a scaling factor η, called the Marquardt constant, to the diagonal elements of the **A** matrix when the solution to the normal equations of Eq. (5-4) fails to reduce χ^2, or,

$$A_{ii,scaled} = A_{ii} (1 + \eta)$$

After applying the Marquardt constant, the normal equations are again solved and χ^2 recalculated. If χ^2 increases, then η is increased and the scaling process repeated. Repeated failure results in a very large Marquardt constant; taken to the limit the off-diagonal terms can be ignored and the solution to the normal equations can be approximated as:

$$\Delta p_i = Y_i / (A_{ii} (1 + \eta)) \qquad (4\text{-}8)$$

Improvements to the determination of the Levenberg-Marquardt constant ([c]Coelho, 2018) has been made. This is especially the case for objective functions that are far from quadratic and when the BFGS method is used.

4.3..... Approximating the A matrix - the BFGS method

approximate_A can be used to approximate the **A** matrix, Eq. (4-4), without the need to calculate the **A** matrix dot products; the approximation is based on the BFGS method (Broyden, 1970; Fletcher, 1970; Goldfarb, 1970; Shanno, 1970). Approximating A is useful when the calculation of the **A** matrix dot products is proving expensive. approximate_A may also improve convergence for the case where penalties dominate the refinement. approximate_A cannot be used with line_min or use_extrapolation. The single crystal refinement examples of AE14-APPROX-A.INP and AE1-APPROX-A.INP are cases where the use of approximate_A achieves convergence in less time than with the fully calculated A matrix. When using approximate_A, the **A** matrix can be made sparse by defining A_matrix_memory_allowed_in_Mbytes and/or A_matrix_elements_tollerance. This allows for refinements with large numbers of independent parameters. A_matrix_memory_allowed_in_Mbytes limits the memory used by the **A** matrix. A_matrix_elements_tollerance #tol removes elements in the **A** matrix with values less than #tol. The comparison is made againts normalized elements of **A** such that A_{ii}=1. Typical values for #tol range from 0.0001 to 0.01. A_matrix_memory_allowed_in_Mbytes and A_matrix_elements_tollerance can be used simultanuously. A_matrix_report_on displays the percentage of non-zero elements in the **A** matrix.

4.4..... Setting A-matrix elements that must-be-zero to zero

[approximate_A_check_for_must_be_zero #n]	**Example** TEST_EXAMPLES\XRD-CT\XRD-CT-1.INP

In using approximate_A, A-matrix elements that must-be-zero can still comprise non-zero values during the BFGS method. A_{ij} elements that must-be-zero include cases where parameter p_i and parameter p_j are from different xdd patterns. The keyword approximate_A_check_for_must_be_zero test for zero A matrix elements and sets them to zero. This improves convergence in large problems comprising 1000s of xdds. Importantly, sparse matrix methods are invoked and only non-zero A-matrix elements are stored reducing memory usage. In cases where there are 1000s of xdds, use of approximate_A_check_for_must_be_zero often negates the need for A_matrix_memory_allowed_in_Mbytes.

Checking for zero A-matrix elements requires a modest amount of computational effort; to minimize this, the check is only performed up to the nth iteration of a refinement cycle where n is the number defined after the approximate_A_check_for_must_be_zero keyword. After the nth iteration, A_{ij} elements that must-be-zero are set to those that were zero at the nth iteration. Example use is as follows:

```
    approximate_A_check_must_be_zero = Cycle_Iter < 4;
```

4.5..... Line minimization and Parameter extrapolation

Line minimization, also known as the steepest decent method, is invoked using line_min. It uses a direction in parameter space given by $\Delta p_i = Y_i/A_{ii}$ to minimize on $\chi^2(p + \lambda\Delta p)$ by adjusting λ. Parameter Extrapolation, use_extrapolation, uses parabolic extrapolation of the parameters as a function of iteration, or, λ is adjusted such that $\chi^2(\mathbf{a}\lambda^2 + \mathbf{b}\lambda + \mathbf{c})$ is minimized where for a particular parameter p_i at iteration k we have $a_i=(y_1-2y_2+y_3)/2$, $b_i=(y_3-y_1)/2$ and $c_i=y_2$ where $y_1=(p_{i,k-5}+p_{i,k-4})/2$, $y_2=(p_{i,k-3}+p_{i,k-2})/2$ and $y_3=(p_{i,k-1}+p_{i,k-0})/2$. Parameter Extrapolation encompasses the last six sets of parameter values. In cases where both exists then Parameter Extrapolation reduces possible oscillatory behaviour in χ_0^2 and χ_P^2. Parameter extrapolation when used with Line Minimization can increase the rate of convergence when refining on penalties only. Line minimization and Parameter Extrapolation have relatively small memory footprints and thus can be useful when the **A** matrix consumes too much memory. Alternatively, approximate_A can be used. Line minimization with the full **A** matrix calculation (approximate_A not defined) can increase the rate of convergence on problems like Pawley refinement. no_normal_equations prevents the use of normal equations in the minimization routine.

4.6..... Restraints and Penalties

penalty defines a penalty function that can be a function of parameters. Penalties, such as bond-length restraints, are useful for stabilizing refinements. Example HOCK.INP uses penalties to minimize on the Hock and Schittkowski problem number 65:

```
    prm x1 1 min -4.5 max 4.5  val_on_continue = Rand(-4.5, 4.5); del 0.01
    prm x2 1 min -4.5 max 4.5  val_on_continue = Rand(-4.5, 4.5); del 0.01
    prm x3 1 min -5.0 max 5.0  val_on_continue = Rand(-5.0, 5.0); del 0.01

    ' Hock and Schittkowski problem number 65 function
    penalty = (x1 - x2)^2 + (1/9) (x1 + x2 - 10)^2 + (x3 - 5)^2; : 0

    prm contraint_1 = x1^2 + x2^2 + x3^2;
    penalty = If(contraint_1 < 48, 0, (contraint_1 - 48)^2); : 0
```

To apply a penalty function to lattice and crystallite size parameters, which are expected to be 5.41011 Å and 200 nm respectively, the following can be used:

```
str
    Cubic(lp_ceo2 5.41011)
    CS_L(cs_l, 200)
    penalty = (lp_ceo2 - 5.41011)^2;
    penalty = (cs_l - 200)^2;
```

penalties_weighting_K1 defines the weighting K_1 in Eq. (4-3); the default value is 1. A restraint can be reformulated into a penalty by squaring the restraint, for example:

```
restraint = a (x - b);
```

This is equivalent to:

```
penalty = a^2 (x - b)^2;
```

In the case of the restraint, the off-diagonal terms $A_{R,ij}$ are calculated when approximate_A (the BFGS method) is not defined. In the case of the penalty the off-diagonal terms $A_{P,ij}$ is set to zero. Restraints often converge in less iterations than equivalent penalties due to the use of the off-diagonal terms (compare ROSENBROCK-10.INP with ROSENBROCK-10-RESTRAINT.INP). However, the time to convergence may be greater due to calculation of the off-diagonal restraint terms in the **A** matrix. Penalties are useful for functions that are not to be squared; these include negative functions such as the GRS series atomic interaction (see ALVO4-GRS-AUTO.INP). For efficiency the $\mathbf{A}_R$ matrix is treated as a sparse matrix which is combined with $\mathbf{A}_0$ (if it exists) where $\mathbf{A}_0$ could be either sparse or dense. When approximate_A is used then the off-diagonal elements of $\mathbf{A}_0$, $\mathbf{A}_P$, and $\mathbf{A}_R$ are not calculated; instead, they are approximated by the BFGS method. approximate_A when used with penalties and restraints, effectively, means that the restraints are treated as penalties. The following two cases will have similar but not identical convergence.

' Case 1	' Case 2

approximate_A
prm p1 1 prm r1 1
penalty !P1 = 5^2 (p1 - 7)^2;
penalty !P2 = 6^2 (p1 - 8)^2;
restraint !R1 = 7 (r1 - 9);
restraint !R2 = 8 (r1 - 10);
	prm p1 1 prm r1 1
	penalty !P1 = 5^2 (p1 - 7)^2;
	penalty !P2 = 6^2 (p1 - 8)^2;
	penalty !P3 = 7^2 (r1 - 9)^2;
	penalty !P4 = 8^2 (r1 - 10)^2;

Diagonal elements of the A matrix	
$A_{P,p1p1} = (½)\partial^2(P1+P2)/\partial p1^2$ $A_{R,r1r1} = (\partial R1/\partial r1)^2 + (\partial R2/\partial r1)^2$	$A_{P,p1p1} = (½)\partial^2(P1+P2)/\partial p1^2$ $A_{P,r1r1} = (½)\,\partial^2(R1^2+R2^2)/\partial r1^2$

The difference in behaviour between penalties and restraints can be seen by comparing ROSENBROCK-10.INP to ROSENBROCK-10-RESTRAINT.INP. In 500,000 iterations, the former results in 71 iterations on average to convergence and the latter 47 iterations on average to convergence. The restraints case converges faster as $A_{R,ij}$ elements are calculated. Approximating $A_{R,ij}$, by defining approximate_A in ROSENBROCK-10-RESTRAINT.INP, results in fastest

convergence, time wise, with 71 iterations on average to convergence. Many penalties however cannot be formulated as a restraint, RASTRGIN.INP for example, and in these cases, penalties are necessary.

4.7 ..... Minimizing on penalties only

When there are no observed data or when only_penalties is defined then by default the BFGS method is used, see examples ROSENBROCK-10.INP and HOCK.INP; this behaviour can be overridden with the use of line_min. For 'penalties only' the BFGS method typically converges faster than line_min/use_extrapolation.

4.8 ..... Saved refined values and save_best_chi2

Values saved on termination of refinement are determined as follows:

- If continue_after_convergence is NOT defined and save_best_chi2 is NOT defined then values saved corresponds to those of the last iteration.
- If continue_after_convergence is NOT defined and save_best_chi2 is defined then values saved corresponds to those that gave the best χ^2.
- If continue_after_convergence is defined and save_best_chi2 is NOT defined then values saved corresponds to those that gave the best Rwp.
- If continue_after_convergence and save_best_chi2 is defined then values saved corresponds to those that gave the best χ^2.

When there are no penalties or restraints then the best χ^2 corresponds to the best Rwp.

4.9 ..... Error calculation

Estimated standard deviations for refined independent parameters are calculated at the end of refinement. The correlation matrix, if defined using C_matrix_normalized, is updated. Otherwise, the correlation matrix is created and appended to the OUT file.

do_errors: Errors calculated; penalties and restraints NOT included in the **A** matrix.

do_errors_include_restraints: Errors calculated; restraints included in the **A** matrix.

do_errors_include_penalties: Errors calculated; penalties included in the **A** matrix.

4.10 ... Error determination using SVD and bootstrap errors

Singular Value Decomposition (SVD) is used for errors determination. These errors closely resemble those obtained by the boot strap method. bootstrap_errors are potentially more accurate as parameter limits are considered; for example, the fact that intensities are positive is not considered by matrix inversion. use_LU_for_errors forces the use of LU decomposition; LU-decomposition results in very large errors for intensities that are 100% correlated. The three means of determining errors are demonstrated in a Pawley refinement of Y_2O_3 in the

examples Y2O3A-LU.INP, Y2O3A-SVD.INP and Y2O3A-BOOT.INP found in the directory TEST_EXAMPLES\SVD-ERRORS.

bootstrap_errors use the bootstrap method of error determination (Efron & Tibshirani 1986, DiCiccio & Efron 1996, Chernick 1999). Bootstrapping comprises a series of refinements each with a fraction of *Yobs* modified to obtain a new bootstrap sample. The standard deviations of the refined values then become the bootstrap errors. !Ecycles corresponds to the number of refinement cycles to perform for bootstrapping, the default is 200. The resulting bootstrapping errors are written to the OUT file. fraction_of_yobs_to_resample corresponds to the fraction of the observed data that is to be replaced each refinement cycle, it defaults to 0.37. Replacement data is, by default, obtained randomly from *Ycalc* as determined in the first refinement cycle. If resample_from_current_ycalc is defined, then replacement data are obtained from the currently completed refinement cycle. The updated *Yobs* data is additionally modified such that the change in Rwp is unchanged with respect to the current *Ycalc*. Parameter values used at the start of each refinement cycle are obtained from the end of the first refinement cycle. val_on_continue can additionlly be used to change parameter values at the start of a cycle. If determine_values_from_samples is defined, then parameter values at the end of bootstrapping are updated with values determined from the bootstrapping refinement cycles. Parameter values obtained at the end of each bootstrap refinement cycle is written to disk in binary format. These values are then read and processed at the end of the bootstrap process without storing the values in memory; the bootstrap process therefore has a small memory footprint.

4.11 ... Error Propagation using prm_with_error

Parameter errors determined outside of refinement can be included and propagated to dependent parameters using prm_with_error. For example, consider the INP snippet (see TEST_EXAMPLES\PRM-WITH-ERROR.INP):

```
xo_Is
   xo 0 I = 10 t i;
   prm i  9.99999`_0.00065 min 1e-6
   prm_with_error !t  1_0.33
   prm t_squared = t^2; : 1.00000`_0.66000
```

Here *t* is defined using prm_with_error and with an error of 0.33; this error is used in determining errors for dependent parameters, such as t_squared, that are a function of *t*.

4.12 ... xdd_sum and xdd_array

[xdd_array !E] ... [xdd_sum !E] ...	**Example** TEST_EXAMPLES\PDF\GENERATE\I15-DECON.INP

xdd_array calculates and stores an array of values which can then be used in equations which can in turn be a function of the reserved parameter names of *X*, *Yobs*, *Ycalc* and *SigmaYobs*. For example, applying the Si atomic scattering factor correction to an xo_Is phase can be performed as follows:

```
xo_Is …
    xdd_array si_f0 =
        2 ( ' atomic scattering data from atmscat.cpp
        5.275329 Exp( -2.631338  (Sin(X Pi/360)/Lam)^2 ) +
        3.191038 Exp( -33.730728 (Sin(X Pi/360)/Lam)^2 ) +
        1.511514 Exp( -0.081119  (Sin(X Pi/360)/Lam)^2 ) +
        1.356849 Exp( -86.288643 (Sin(X Pi/360)/Lam)^2 ) +
        2.519114 Exp( -1.170087  (Sin(X Pi/360)/Lam)^2 ) +
        0.145073);
    scale_phase_X = si_f0; ' apply the atomic scatter factor
```

The above will give the same result if xdd_array is replaced by prm. The latter does not store the array and therefore the equation is calculated every time si_f0 is used. Because xdd_array is an equation, the program automatically keeps track of its dependencies; this means xdd_array array is recalculated only when the equation changes; changes can happen, for example, if the equation is a function of a refinable parameter and the refined parameter changes. This recalculation only occurs when the array is being referenced; it does not occur at the instance of a dependency change. Use of xdd_array therefore produces fast and efficient INP files.

xdd_sum is similar to xdd_array except an array is not stored; instead, the sum of the values of the array are calculated and stored. Similar to xdd_array, the summed value of xdd_sum is only recalculated when necessary. xdd_sum can be nested, for example, to normalize the intensities between *Yobs* and *Ycalc* the following is possible:

```
xdd_sum sum_yobs  = Yobs;
xdd_sum sum_ycalc = Ycalc;
xdd_sum = (Yobs – Ycalc sum_yobs / sum_ycalc)^2;
xdd_sum num_data_points = 1;: 0 ' 0 is replace by the number of data points
```

4.13 … Refining on an arbitrary Chi2

chi2 allows for the minimization of a User defined χ^2. It can be a function of the reserved parameter names *X*, *Yobs*, *Ycalc* and *SigmaYobs*. In addition, xdd_sum can also be a function of these reserved parameter names. For example, the following can be used to define a normal least squares refinement:

```
xdd ...
    xdd_sum denominator = Yobs;
    xdd_sum numerator = (Yobs - Ycalc)^2 / Max(Yobs, 1);
    chi2 = 100 Sqrt(numerator / denominator);
```

In refining on an arbitrary chi2, the first and second derivatives of chi2 with respect to each independent parameter are required. To do this fast, *Ycalc* within chi2 is approximated with a first order Taylor approximation around the parameter vector **p**. This approximation, for various formulations of chi2, has yielded good convergence even for non-linear parameters. To summarize:

- chi2 is treated as a penalty.
- For each independent parameter, a definite minimum in chi2 is bracketed; inverse parabolic interpolation is then used to determine the minima of chi2 with respect to that

parameter. In the calculation of chi2, *Ycalc* is replaced with its first order Taylor approximation and thus the full *Ycalc* is only calculated once per refinement iteration and not 100s of times.

- Finding the minima and the curvature of chi2 with respect to each parameter yields 1st and 2nd order derivatives of chi2 with respect to each parameter.
- The BFGS method (approximate_A) is then used to solve the resulting linear equations with off diagonal terms approximated according to the BFGS method.
- The BCCG method incorporating the Marquardt method with automatic Marquardt constant determination is used to solve the matrix equations.

The Rietveld refinement example of TEST_EXAMPLES\CHI2-CEO2.INP demonstrates various scenarios:

Case 1) Here's output when NOT using chi2.

```
  0  Time   0.05  Rwp   26.630    0.000 MC   0.00 0
  1  Time   0.06  Rwp   16.651   -9.979 MC   0.06 1
  2  Time   0.06  Rwp    7.510   -9.141 MC   0.02 1
  3  Time   0.08  Rwp    6.955   -0.556 MC   0.01 1
  4  Time   0.08  Rwp    6.943   -0.011 MC   0.00 1
  5  Time   0.08  Rwp    6.923   -0.020 MC   0.00 1
  6  Time   0.09  Rwp    6.923   -0.000 MC   0.18 1
--- 0.094 seconds ---
```

Case 2) Here's output when NOT using chi2 but using approximate_A.

```
  0  Time   0.05  Rwp   26.630    0.000 MC   0.00 0
  1  Time   0.06  Rwp   16.883   -9.747 MC   0.00 0
  ...
 16  Time   0.13  Rwp    6.950   -0.002 MC   0.04 1
 17  Time   0.14  Rwp    6.949   -0.002 MC   0.09 1
 18  Time   0.14  Rwp    6.949   -0.000 MC   0.29 1
--- 0.14 seconds ---
```

Case 3) Here's output using chi2 defined for normal least squares.

```
  0  Time   0.03  Rwp   26.630    0.000 MC   0.00 0 P   26.63020
  1  Time   0.06  Rwp   15.897  -10.733 MC   0.00 0 P   15.89696
 ...
 13  Time   0.33  Rwp    6.974   -0.021 MC   0.00 1 P    6.97366
 14  Time   0.34  Rwp    6.958   -0.016 MC   0.00 1 P    6.95755
 15  Time   0.38  Rwp    6.951   -0.006 MC   0.00 1 P    6.95122
```

The chi2 case (3) looks similar-to case (2); however, the path towards the minima is different as the chi2 procedure is very different to normal least squares refinement.

4.14 ... Reporting on unrefined parameters

Parameters that do not take part in refinement are reported, for example, the following, where *a* and *b* are not used in any equations:

```
prm a 1 prm b 1
```

will result in the output:

```
Number of independent parameters not taking part in refinement: 2
   prm_10:  a
   prm_10:  b
```

The val_on_continue attribute of unrefined parameters are executed at the end of convergence. It can be useful, for example,

```
prm a 1 val_on_continue = b = 2; ' this sets the b parameter to 2
```

4.15 ... Summary, Iteration and Refinement Cycle

Table 4-1 shows various keyword usages for typical refinement problems. The term "refinement cycle" is used to describe a single convergence. The reserved parameter *Cycle* returns the current refinement cycle with counting starting at zero. The reserved parameter *Cycle_Iter* returns the current iteration within the current *Cycle* with counting starting at zero.

Table 4-1. Keyword sequences for various refinement types.

Refinement type	Keywords to use	Comments
Rietveld refinement. No penalties.		Marquardt refinement. **A** matrix calculation.
Rietveld refinement with a moderate number of penalties.	line_min (Maybe)	Line minimization used if line_min. Marquardt refinement. **A** matrix calculation.
Rietveld refinement dominated by penalties.	approximate_A	BFGS method of refinement. **A** matrix approximation.
Pawley refinement.	line_min	Line minimization. Marquardt refinement. **A** matrix calculation.
Penalties only.		BFGS method of refinement. **A** matrix approximation.
Refinements with a large number of parameters and a few xdds.	approximate_A	BFGS method of refinement. **A** matrix approximation.
Refinements with a large number of xdds and parameters.	approximate_A_check_for_must_be_zero	BFGS method of refinement. **A** matrix approximation.

4.16 ... quick_refine and computational issues

The computationally dominant factor of Eq. (4-5) is problem dependent. For Rietveld refinement with a moderate number of parameters, the calculation of the peak parameter derivatives may well be the most expensive item. On the other hand, for Rietveld refinement with many structural parameters and data points then the calculation of the $A_{1,ij}$ dot products would be the dominant factor, where the number of operations scale by $M(N^2+N)/2$. Before the

development of the BCCG routine (Coelho, 2005), the solution to the normal equations, Eq. (4-4), was also very expensive. For structure solution from powder data by simulated annealing, yobs_to_xo_posn_yobs can be used to reduce the number of data points M which reduces the number of operations in the $A_{1,ij}$ dot products, see the Decompose macro in example CIME-DECOMPOSE.INP. quick_refine removes parameters during a refinement cycle thus shrinking the size of the **A** matrix by reducing N and hence speeding up refinement iterations. Parameters are removed if the condition defined in Eq. (4-9) is met for three consecutive iterations.

$$\Delta p_i < 0.01 \text{ quick\_refine}/(K\ N\ Y_i) \tag{4-9}$$

Alternatively, parameters can be removed or reinstated during a refinement cycle using quick_refine_remove. This keyword provides a means of performing block refining. If quick_refine_remove is not defined, then all parameters are reinstated at the start of refinement cycles. Use of quick_refine speeds up simulated annealing, see for example the Auto_T macro which is used in example AE1-AUTO.INP. All refined parameters are reinstated for refinement at the start of subsequent cycles. Large quick_refine values aggressively removes parameters and convergence to low χ^2 maybe hindered. A value of 0.1 works well. quick_refine has the following consequences:

- If parameters are not reinstated using quick_refine_remove then χ^2 does not get to its lowest possible value for a particular refinement cycle.
- The degree of parameter randomization increases with increasing values of quick_refine. Randomization should therefore be reduced as quick_refine increases. Alternatively randomize_on_errros can be used which automatically determines the amount a parameter is randomized.

If quick_refine_remove evaluates to a non-zero value then the associated parameter is removed from refinement, similarly parameters are reinstated if quick_refine_remove evaluates to zero. quick_refine_remove can be a function of the reserved parameters *QR_Removed* or *QR_Num_Times_Consecutively_Small* and additionally global reserved parameter names such as *Cycle_Iter*, *Cycle* and *T*. If quick_refine_remove is not defined, then the removal scheme of Eq. (4-9) is used and parameters are not reinstated until the next refinement cycle. In most refinements the following will produce close to the lowest χ^2 and in a short time (see for example PAWLEY1.INP).

```
quick_refine 0.1
   quick_refine_remove =
      IF QR_Removed THEN
         0 ' reinstate the parameter
      ELSE
         IF QR_Num_Times_Consecutively_Small > 2 THEN
            1 ' remove the parameter
         ELSE
            0 ' dont remove the parameter
         ENDIF
      ENDIF;
```

4.17 ... Simulated annealing and Auto_T

Refinement is continued after convergence when continue_after_convergence is defined. Before continuing the following actions are performed:

- val_on_continue equations for independent parameters are evaluated.
- randomize_on_errors processes are performed.
- rand_xyz processes are performed.

When val_on_continue is defined, the corresponding parameter is not randomized according to randomize_on_errors. Simulated annealing is invoked using continue_after_convergence. It is sometimes difficult to formulate optimum val_on_continue functions; this is especially true in structure solution using rigid bodies where optimum randomization of the rigid body parameters can be difficult to ascertain. randomize_on_errors is a means of automatically randomizing parameters based on the approximate errors in the parameters as given in Eq. (4-10), where *T* is the current temperature and K is as defined in Eq. (4-3).

$$\Delta p_i = Q\ Sign\big(Rand(-1,1)\big)\sqrt{0.02\ T/(K\ A_{ii})} \qquad (4\text{-}10)$$

Q is a scaling factor determined such that convergence to a previous parameter configuration occurs 7.5% of the time on average. When randomize_on_errors is used, relative variation in temperature(s) are significant and not absolute values. The Auto_T macro includes quick_refine, randomize_on_errors and a temperature regime. It has shown to be adequate for a wide range of simulated annealing examples, see example CIME-Z-AUTO.INP.

4.18 ... Adaptive step size using randomize_on_errors

Use of randomize_on_errors result in an adaptive-step-size determination during simulated annealing; in many cases the complex temperature regime found in the Auto_T macro can be replaced with a single temperature. The example CIME-Z-AUTO.INP demonstrates randomize_on_errors by using a very incorrect starting temperature of 0.1; the program quickly modifies the temperature to a more appropriate value. Output lines such as:

```
Breaking - randomize on errors revisit
```

indicate that a parameter configuration has been revisited and the temperature will be internally adjusted. Note, with randomize_on_errors, relative temperature values are pertinent and not absolute values.

4.19 ... Criteria of fit

Trwp
[r_p #] [r_wp #] [r_exp #] [gof #] [r_p_dash #] [r_wp_dash #] [r_exp_dash #]
[weighted_Durbin_Watson #]

Global and xdd dependent refinement indicators. Keywords ending in "_dash" correspond to background subtracted values.

Table 4-2. Criteria of fit (Young , 1993). $Y_{o,m}$ and $Y_{c,m}$ are the observed and calculated data respectively at data point m; Bkg_m the background, M the number of data points, N the number of parameters, w_m the weighting given to data point m; for counting statistics $w_m=1/\sigma(Y_{o,m})^2$ where $\sigma(Y_{o,m})$ is the error in $Y_{o,m}$. And $I_{o,k}$ and $I_{c,k}$ the observed and calculated intensities of the k^{th} reflection. [1]) background corrected.

R-pattern, Rp'	$R_p = \frac{\sum\lvert Y_{o,m} - Y_{c,m}\rvert}{\sum Y_{o,m}}$	$R'_p = \frac{\sum\lvert Y_{o,m} - Y_{c,m}\rvert}{\sum\lvert Y_{o,m} - Bkg_m\rvert}$
R-weighted pattern, R_{wp}, $^1R_{wp}$'	$R_{wp} = \sqrt{\frac{\sum w_m\left(Y_{o,m} - Y_{c,m}\right)^2}{\sum w_m Y_{o,m}^2}}$	$R'_{wp} = \sqrt{\frac{\sum w_m\left(Y_{o,m} - Y_{c,m}\right)^2}{\sum w_m\left(Y_{o,m} - Bkg_m\right)^2}}$
R-expected, $^1R_{exp}$'	$R_{exp} = \sqrt{\frac{M-N}{\sum w_m Y_{o,m}^2}}$	$R'_{exp} = \sqrt{\frac{M-N}{\sum w_m\left(Y_{o,m} - Bkg_m\right)^2}}$
Goodness of fit, GOF	$GOF = chi = \frac{R_{wp}}{R_{exp}} = \sqrt{\frac{\sum w_m\left(Y_{o,m} - Y_{c,m}\right)^2}{M-N}}$	
R-Bragg	$R_B = \frac{\sum\lvert I_{o,k} - I_{c,k}\rvert}{\sum I_{o,k}}$	
Durbin-Watson, d, 1971; Hill & Flack, 1987	$d = \frac{\sum_{m=2}^{M}(\Delta Y_m - \Delta Y_{m-1})^2}{\sum_{m=1}^{M}(\Delta Y_m)^2}$; $\Delta Y_m = Y_{o,m} - Y_{c,m}$	

5. ..PEAK GENERATION AND "PEAK_TYPE"

Convolution implies integration; a function analytically integrated is exact whereas numerical integration is an approximation with an accuracy dependent on the step size used for integration. Accurate numerical convolution is used when analytical convolution is not possible; this makes it possible to include complex functions in the generation of peak shapes. Laboratory instrument aberration functions mostly require numerical convolution. This process of convolution, from a fundamental-parameters perspective (Cheary & Coelho, 1992; Cheary *et al.*, 2004), is an approximation; second order effects and higher are typically neglected. These approximations are valid except for extreme cases that are unlikely to exist in practice, for example, axial divergence with Soller slits acceptance angles that are greater than about 12 degrees.

5.1..... Source emission profiles

Generation of the emission profile is the first step in peak generation. It comprises EM lines, EM_k, each of which is a Voigt comprising the parameters la, lo, lh and lg. The reserved parameter name *Lam* is assigned the lo value of the EM_k line with the largest la value, this EM_k will be called *EMREF*. It is used to calculate d-spacings. The interpretation of EM data is dependent on peak_type. For all peak types, the position $2\theta_k$ calculated for an emission line for a Bragg position of 2θ is determined as:

$$2\theta = ArcSin\left(\frac{EM(k,lo)}{2d}\right)\frac{360}{\pi} \qquad \text{where} \qquad 2d = \frac{EMREF(lo)}{Sin(\theta)}$$

2θ for xo_Is phases corresponds to the xo parameter. 2θ for d_Is phases is given by the Bragg equation 2θ = ArcSin(*Lam*/(2 d)) 360/Pi where d corresponds to the value of the d parameter. 2θ values for str and hkl_Is phases are calculated from the lattice parameters. The $FWHW_k$ in °2θ for an EM_k line is determined from the relations provided in Table 5-1. When no_th_dependence is defined then the calculation of $2\theta_k$ is determined from

$$2\theta_k = 2\theta + EM(lo, i)$$

The macro No_Th_Dependence can be used when refining on non-X-ray data or fitting to negative 2θ values (see example NEGX.INP). The x-axis extent (x1, x2) to which an EM line is calculated is determined by:

$$\frac{Intensity\ of\ EM(i, x = x1 = x2)}{Intensity\ of\ EMREF(x = 0)} = ymin\_on\_ymax$$

The default value for ymin_on_ymax is 0.001. Emission profile data have been taken from Hölzer *et al.* (1997) and are stored in *.LAM files in the LAM directory.

Table 5-1. $FWHW_k$ in °2θ for an EM_k line for the different peak types.

FP peak type	$FWHM_k = \left(\frac{EM(k,lh)}{LAM}\right)\frac{Tan(\theta)360}{\pi}$

PV peak type	$FWHM_k = \frac{\text{pv\_fwhm}\ \ EM(k,lh)}{EMREF(lh)}$
SPVII peak type	$FWHM_k = \frac{(h_1 + h_2)EM(k,lh)}{EMREF(lh)}$
SPV peak type	$FWHM_k = \frac{(spv_{h_1} + spv_{h_2})EM(k,lh)}{EMREF(lh)}$

5.2..... Peak generation and peak types

Phase peaks P are generated as follows:

$$P = Get(scale)\ Get(all\_scale\_pks)\ EM(peak\_type) \otimes Convolutions \quad (5\text{-}1)$$

where the emission profile (EM) is generated first with emission profile lines of type peak_type; the symbol ⊗ denotes convolution. Peaks are then convoluted with any defined convolutions, multiplied by the scale parameter, multiplied by any defined scale_pks, and then multiplied by an intensity parameter. For xo_ls, d_ls and hkl_ls phases the intensity is given by the I parameter. For str phases it corresponds to the square of the structure factor F^2(hkl). Convolutions are normalized and do not change the area under a peak except for the capillary_diameter_mm and lpsd_th2_angular_range_degrees convolutions. The area under the emission profile is determined by the sum of the la parameters; typically, they add up to 1. The definitions of the pseudo-Voigt and PearsonVII functions are provided in Table 5-2.

Table 5-2. Unit area peak types. *x* corresponds to $(2\theta - 2\theta_k)$ where $2\theta_k$ is the position of the k^{th} reflection. *fwhm* corresponds to the Full Width at Half Maximum. η is the PV mixing parameter. The '1' and '2' subscripts correspond to the left and right of the split functions.

Gaussian	$G_{UA}(x) = \left(\frac{g_1}{fwhm}\right) Exp\left(\frac{-g_2 x^2}{fwhm^2}\right), \quad g_1 = 2\sqrt{\frac{Ln(2)}{\pi}}, \quad g_2 = 4Ln(2)$
Lorentzian	$L_{UA}(x) = \frac{\left(\frac{l_1}{fwhm}\right)}{\left(1 + \frac{l_2 x^2}{fwhm^2}\right)}, \qquad l_1 = \frac{2}{\pi}, \qquad l_2 = 4$
PseudoVoigt	$PV = \eta L_{UA}(x) + (1 - \eta) G_{UA}(x)$

Split PearsonVII SPVII	$$SPVII = PVII_{Left} + PVII_{Right}$$ $$PVII_{Left} = a^{-1}(1 + b_1 x^2)^{-m_1}, \quad \text{for } (-\infty < x < 0)$$ $$PVII_{Right} = a^{-1}(1 + b_2 x^2)^{-m_2}, \quad \text{for } (0 < x < \infty)$$ $$a = ½\,\Gamma(½)\left(\frac{\Gamma(m_1 - ½)}{\Gamma(m_1)\sqrt{b_1}} + \frac{\Gamma(m_2 - ½)}{\Gamma(m_2)\sqrt{b_2}}\right)$$ $$b_1 = \left(2^{\frac{1}{m_1}} - 1\right) h_1^{-2}, \quad b_2 = \left(2^{\frac{1}{m_2}} - 1\right) h_2^{-2}$$ $$fwhm_1 = 2\,h_1, \quad fwhm_2 = 2\,h_2, \quad fwhm = h_1 + h_2$$
Split PseudoVoigt SPV	$$SPV = \frac{2\left(PV_{Left} + a\,PV_{Right}\right)}{1 + a}$$ $$PV_{Left} = PV(h_1, \eta_1), \quad \text{for } (-\infty < x < 0)$$ $$PV_{Right} = PV(h_2, \eta_2), \quad \text{for } (0 < x < \infty)$$ $$a = \frac{PV_{Left}(x = 0)}{PV_{Right}(x = 0)}$$ $$fwhm_1 = 2\,h_1, \quad fwhm_2 = 2\,h_2, \quad fwhm = h_1 + h_2$$

Lorentzian and Gaussian convolutions using lor_fwhm and gauss_fwhm equations are analytically convoluted with FP and PV peak types and numerically convoluted with the SPVII and SPV peak types. These numerical convolutions have a high degree of accuracy as they comprise analytical Lorentzian and Gaussian functions convoluted with straight line segments. For FP and PV peak types, the first defined hat convolution is convoluted analytically. Additional hat convolutions for all peak types are convoluted numerically. For classic analytical full pattern fitting the macros PV_Peak_Type, PVII_Peak_Type, TCHZ_Peak_Type can be used. These macros use the following relationships to describe profile width as a function of 2θ.

PV_Peak_Type	PVII_Peak_Type
$fwhm = ha + hb \tan(\theta) + hc/\cos(\theta)$	$fwhm_1 = fwhm_2 = ha + hb \tan(\theta) + hc/\cos(\theta)$
$\eta = lora + lorb \tan(\theta) + lorc/\cos(\theta)$	$m1 = m2 = 0.6 + ma + mb \tan(\theta) + mc/\cos(\theta)$
where *ha*, *hb*, *hc*, *lora*, *lorb*, *lorc* are refineable parameters.	where *ha*, *hb*, *hc*, *ma*, *mb*, *mc* are refineable parameters.

TCHZ_Peak_Type: The modified Thompson-Cox-Hastings pseudo-Voigt "TCHZ" is defined as (e.g. Young, 1993, see example ALVO4_TCH.INP):

$\eta = 1.36603\,q - 0.47719\,q^2 + 0.1116\,q^3$

where $q = \Gamma_L / \Gamma$

$\Gamma = (\Gamma_G^5 + A\Gamma_G^4\Gamma_L + B\Gamma_G^3\Gamma_L^2 + C\Gamma_G^2\Gamma_L^3 + D\Gamma_G\Gamma_L^4 + \Gamma_L^5)^{0.2} = fwhm$

A = 2.69269, B = 2.42843, C = 4.47163, D = 0.07842

$\Gamma_G = (U \tan^2\theta + V \tan\theta + W + Z / \cos^2\theta)^{0.5}$

$\Gamma_L = X \tan\theta + Y / \cos\theta$

with U, V, W, X, Y, Z as refined parameters.

5.3..... Convolution and the peak generation stack

The emission profile of a peak P0 of a certain peak type (i.e. FP, PV etc...) is first calculated and placed onto a 'Peak calculation stack'. P0 analytically includes lor_fwhm and gauss_fwhm convolutions for FP and PV peak types and additionally one hat convolution if defined; the hat convolution is included analytically only if its corresponding num_hats has a value of 1 and if it does not take part in stack operations. Further defined convolutions are convoluted with the top member of the stack. The last convolution should leave the stack with one entry representing the final peak shape. The following keywords allow for manipulation of the Peak calculation stack:

[push_peak]...
[bring_2nd_peak_to_top]...
[bring_n_peak_to_top !E]...
[add_pop_1st_2nd_peak]...
[scale_top_peak E]...
[set_top_peak_area E]...

push_peak duplicates the top of the stack; bring_2nd_peak_to_top brings the second entry to the top of the stack, bring_n_peak_to_top brings the n^{th} peak to the top (n=0 corresponds to the top of the stack) and add_pop_1st_2nd_peak adds the top entry to the second most recent entry and then pops the stack. scale_top_peak scales the peak at the top of the stack. As an example, consider the generation of back-to-back exponentials as required by GSAS time of flight peak shape 3:

```
push_peak
   prm a0  481.71904 del = 0.05 Val + 2;
   prm a1 -241.87060 del = 0.05 Val + 2;
   exp_conv_const = a0 + a1 / D_spacing;
bring_2nd_peak_to_top
   prm b0 -3.62905 del = 0.05 Val + 2;
   prm b1  6.44536 del = 0.05 Val + 2;
   exp_conv_const = b0 + b1 / D_spacing^4;
add_pop_1st_2nd_peak
```

The first statement push_peak pushes P0 onto the stack leaving two peaks on the stack:

Stack = P0, P0

The top member is then convoluted by the first exp_conv_const convolution, or,

Stack = P0, P0 ⊗ exp_conv_const

where ⊗ denotes convolution. bring_2nd_peak_to_top results in the following:

Stack = P0 ⊗ exp_conv_const, P0

and the next convolution results in:

Stack = P0 ⊗ exp_conv_const, P0 ⊗ exp_conv_const

Thus, the stack contains two peaks convoluted with exponentials. The last statement add_pop_1st_2nd_peak produces:

Stack = P0 ⊗ exp_conv_const + P0 ⊗ exp_conv_const

Convolutions applied to peaks are normalized after convolution. Thus, the following, from WIF David's macro wifd_mic_moderator, will give unintended peak shapes:

```
push_peak                          ' first peak
   scale_top_peak = 1 - storage
bring_2nd_peak_to_top              ' second peak
   exp_conv_const = -Ln(0.001) / (taus_0 + taus_1 / lam^2);
   scale_top_peak = storage;
add_pop_1st_2nd_peak
```

where the ratio of the areas of the first peak to the second peak won't be (1-storage)/storage. This can be remedied by normalizing the exp_conv_const aberration as follows:

```
push_peak
   scale_top_peak = 1 - storage;
bring_2nd_peak_to_top
   exp_conv_const = -Ln(0.001) / (taus_0 + taus_1 / lam^2);
   scale_top_peak = storage Yobs_dx_at(Xo);
add_pop_1st_2nd_peak
```

However, not all aberrations are easily normalized; set_top_peak_area overcomes this problem by normalizing the area itself in situ. The INP segment can now be written as:

```
push_peak
   set_top_peak_area = 1 - storage;
bring_2nd_peak_to_top
   exp_conv_const = -Ln(0.001) / (taus_0 + taus_1 / lam^2);
   set_top_peak_area = storage;
add_pop_1st_2nd_peak
```

5.4..... Speed / Accuracy and peak_buffer_step

For computational efficiency, phase peaks are calculated at predefined 2θ intervals in a "peaks buffer". In between peaks are determined by stretching and interpolating. Use of the peaks buffer dramatically reduces the number of peaks calculated. Typically, no more than 50 to 100 peaks are necessary to accurately describe peaks across a whole diffraction pattern. The following keywords affect the accuracy of phase peaks:

[peak_buffer_step !E]
[convolution_step #1]
[ymin_on_ymax #]
[aberration_range_change_allowed !E]

Default values for these are typically adequate. peak_buffer_step determines the maximum x-axis spacing between peaks in the peaks buffer, it has a default value of 500*Peak_Calculation_Step. A value of zero will force the calculation of a new peak in the peaks buffer for each peak of the phase. Note that peaks are not calculated for x-axis regions that are void of phase peaks. convolution_step defines an integer corresponding to the number of calculated data points per measurement data point used to calculate the peaks in the peaks buffer, see x_calculation_step. Increasing the value for convolution_step improves accuracy for data with large step sizes or for peaks that have less than 7 data points across the FWHM. ymin_on_ymax determines the x-axis extents of a peak (see also section 5.1). aberration_range_change_allowed describes the maximum allowed change in the x-axis extent of a convolution aberration before a new peak is calculated for the peaks buffer. For example, in the case of axial_conv the spacing between peaks in the peaks buffer should be small at low angles and large at high angles. aberration_range_change_allowed is a dependent of the peak type parameters and convolutions as shown in Table 5-3. Small values for aberration_range_change_allowed reduces the spacing between peaks in the peaks buffer and subsequently increase the number of peaks in the peaks buffer.

Table 5-3. Default values for aberration_range_change_allowed.

Parameter	**Default** aberration_range_change_allowed
m1, m2	0.05
pv_lor, spv_l1, spv_l2	0.01
h1, h2, pv_fwhm, spv_h1, spv_h2	*Peak_Calculation_Step*
hat, axial_conv, whole_hat, half_hat	*Peak_Calculation_Step*
one_on_x_conv, exp_conv_const, circles_conv	*Peak_Calculation_Step*
lor_fwhm, gauss_fwhm	*Peak_Calculation_Step*

5.5..... The peaks buffer, speed and memory considerations

Anisotropic peak shapes result in the peaks-buffer holding as many peaks as there are hkls. For problems with 100,000s of peaks the calculation time and storage of the peaks-buffer can be prohibitive. This situation can be mitigated using the phase dependent peak_buffer_based_on:

[str | hkl_Is | xo_Is | d_Is]
[peak_buffer_based_on !E [peak_buffer_based_on_tol !E]]...

When peak_buffer_based_on is defined, the usual means of determining the size of the peak buffer is over-ruled. Instead, peaks are grouped according to the peak_buffer_based_on criterion. For example, to insert a peak into the peak buffer at x-axis intervals of 1 then the following can be used:

```
peak_buffer_based_on = Xo; peak_buffer_based_on_tol 1
```

Thus, peaks with similar *Xo*'s, as defined by peak_buffer_based_on_tol, are grouped. Occasionally peaks that are a function of hkls have groups of hkls that are of the same peak shape and at a similar x-axis position. The following demonstrates how to group these peaks such that a single peak shape is calculated.

```
peak_buffer_based_on = Xo; peak_buffer_based_on_tol 0.01
peak_buffer_based_on = sh; peak_buffer_based_on_tol 1e-7
```

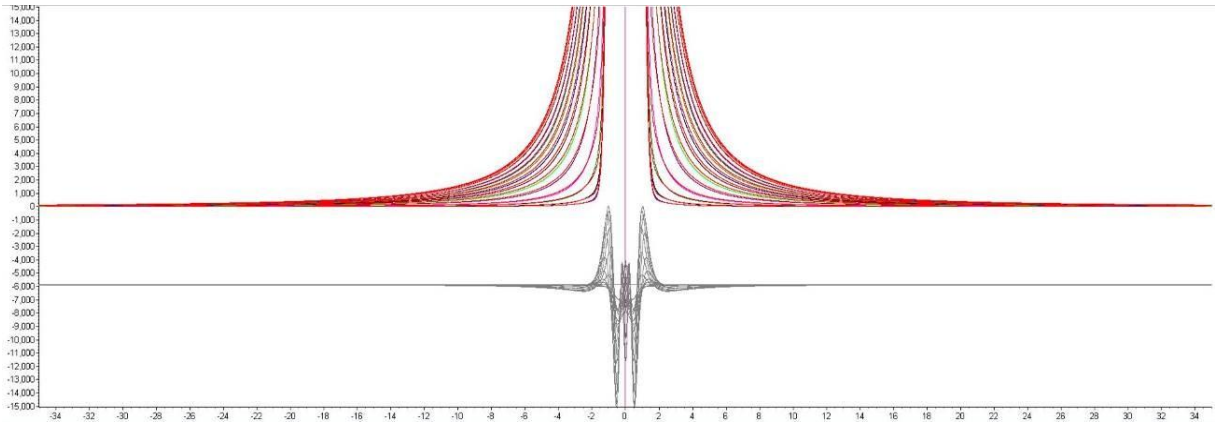
where sh can be a spherical harmonics parameter or an equation describing hkl dependence or a march_dollase parameter. When more than one peak_buffer_based_on is defined then peak groups obey all of the peak_buffer_based_on's. peak_buffer_based_on disables the peak stretching procedures and any defined aberration_range_change_allowed. peak_buffer_based_on can be a function of the reserved parameters *H*, *K*, *L*, *M*, *D_spacing*, *X*, *Xo*, *Th*.

Depending on the problem, smaller values such as 1e-7 can significantly reduce the number of peaks stored in the peaks buffer (a factor of 15 at times) without significantly affecting Rwp. A negative value for peak_buffer_based_on_tol will force a calculation for each peak resulting in independent hkl peak shapes, for example:

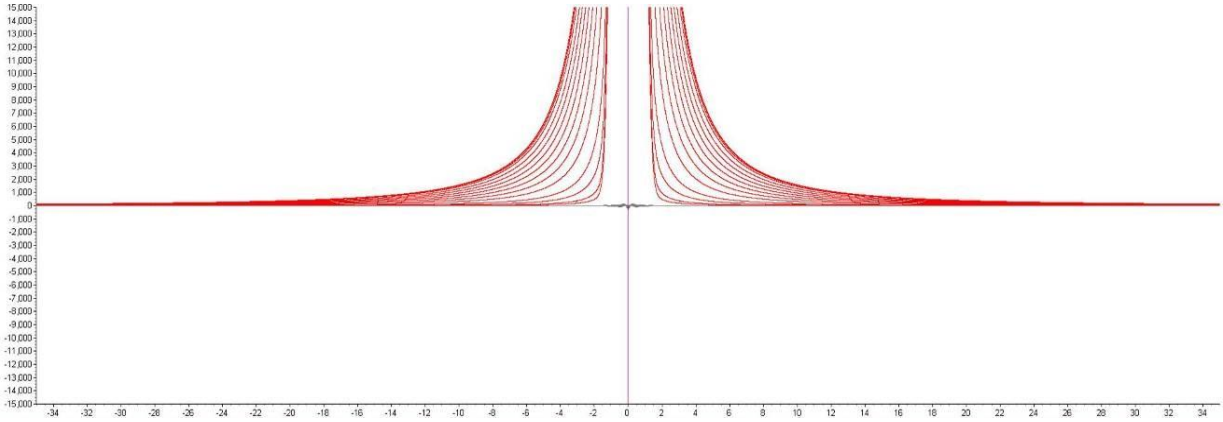
```
peak_buffer_based_on 1 peak_buffer_based_on_tol -1
```

5.6..... An Accurate Voigt

[more_accurate_Voigt] can be used to override the default Pseudo-Voigt approximation to the Voigt. It decreases the error (Voigt_approx – Voigt_true) by a factor of ~100. Defining G as the FWHM of a Gaussian and L as the FWHM of a Lorentzian; the screen shots below show fits to a range of G convoluted with L, resulting in Voigts, with L varying from 0.01 to 0.09 and G+L=1. Fitting to the Voigts using pseudo-Voigts we get



Fitting to the Voigts using the accurate calibration results in the small difference plots seen in the following:



The more_accurate_Voigt calibration is accurate and fast. It fits to each true Voigt the following:

```
fit_obj = a1 (2 Sqrt(Ln(2) / Pi) / f1) Exp(-4 Ln(2)(X / f1)^2);
fit_obj = a2 (2 Sqrt(Ln(2) / Pi) / f2) Exp(-4 Ln(2)(X / f2)^2);
fit_obj = a3 (2 / (Pi f3)) / (1 + 4 (X / f3)^2);
fit_obj = a4 (4 / (Pi f4)) / (1 + 4 (X / f4)^2)^2;
```

One thousand sets of a0, a1, a2, a3, f0, f1, f2, f3 parameters were determined by fitting to 1000 true Voigts with L varying from 0 to 1 in steps of 0.001.

numerical_lor_gauss_conv creates a 'true' Voigt by numerically convoluting Gaussians with Lorentzians; the extents to which these aberrations are calculated can be defined using numerical_lor_ymin_on_ymax (default of 0.0001). The CREATE.INP file in the TEST_EXAMPLES\VOIGT-APPROX directory uses numerical_lor_gauss_conv where the amount of Lorentzian is entered as a number out of a 1000. A value of 500 would yield a Voigt with a Lorentzian FWHM of 0.5 and a Gaussian FWHM of 0.5. The generated true Voigt is calculated by numerically convoluting a lor_fwhm with a gauss_fwhm. The generated true Voigt is saved to a file with the name VOIGTNNNN.XY, where NNNN corresponds to a number between 0 and 1000. The file generated contains 100,000 data points. The step size used in the convolutions is as small as 0.0005 when using a convolution_step of 4.

TOPAS uses an FFT to perform the double summation of the convolution. However, for lor > 500, the convolution itself comprises an analytical Lorentzian with a Gaussian comprising straight line segments. For lor < 500 then an analytical Gaussian is convoluted with a Lorentzian comprising straight line segments.

- The file FIT-PV.INP fits a pseudo-Voigt to the generated true Voigt.
- The file FIT-MORE.INP fits to the generated true Voigt using equivalent fit_obj's.
- The file FIT-OBJ.INP fits fit_obj's to the generated true Voigt.

The difference plot from FIT-PV.INP is in the order of 500 to 1000 times larger than the difference plot from FIT-MORE.INP.

5.7..... Stretching peaks

str...	**Examples**

[stretch_pks E]	STRETCH-PKS\STRETCH-1.INP

Refining 1000s of phases, where each has a peaks buffer that needs recalculation each iteration of the refinement, can be time consuming; as in XRT-CT refinements. In fact, many peak aberration parameters require the recalculation of the peaks buffer for each parameter derivative for each iteration of the refinement. The lor_fwhm and gauss_fwhm convolutions are two such parameters and typical usage is via the following macros:

```
CS_G(@, 100)
CS_L(@, 100)
```

When the values of the lor_fwhm and gauss_fwhm parameters are approximately known, then the shapes of the peaks can be approximated by stretching. For symmetric peaks the approximation is almost exact; asymmetric peaks, peaks with asymmetric convolutions, are not exact but if the values aren't too far off optimal values then the approximation can be good. The benefit of such an approximation is speed, where, using stretch_pks in the STRETCH-1.INP example speeds up refinement by a factor of 4.1. The usage of stretch_pks is as follows:

```
CS_L(100) ' not refined
CS_G(100) ' not refined
stretch_pks @ 1 min 0.001 max 10
```

The limits of a stretched peak, x1_s and x2_s, in terms of the unstretched limits x1 and x2, and the peak position Xo are:

x1_s = x0 – (Xo – x1) Get(stretch_pks)
x2_s = x0 + (x2 – Xo) Get(stretch_pks)

5.8..... transform_x without recalculating patterns

[transform_x E]	**Examples** TRANSFORM_X\TPX.INP

The transform_x keyword stretches a calculated phase pattern to form a final phase calculated pattern without recalculating peaks or summing peaks to Ycalc. The following:

```
prm tpx 0 transform_x = X + tpx Sin(X Pi / 360);
```

is an approximation to:

```
prm tpx 0 th2_ffset = tpx Sin(X Pi/ 360);
```

This approximation is accurate when the change in transform_X is smooth and when its largest value is in the order of what is expected from XRD-CT data. For two common strs residing in different xdds, then if th2_offset were to be used then two th2_offsets would need to be defined and the formation of the summation of the peaks to the calculated pattern performed twice. transform_X on the other hand allows for the reuse of a common calculated str pattern. A further description is given in section 6.

6. ..REUSING OBJECTS IN LARGE REFINEMENTS

lat_prms $name { ... } str_dets $name { ... } phase_dets $name { ... } use { ... }	**Examples** TEST_EXAMPLES\XRD-CT\XRD-CT-0.INP TEST_EXAMPLES\XRD-CT\XRD-CT-1.INP

The keywords lat_prms, str_dets and phase_dets can be used to define a set of lattice parameters, structural details and phase details that can be used multiple times within phases without recalculation of the corresponding item. The benefit is a reduction in memory usage and a speed up in refinement that is substantial when 100s of 1000s of phases are present. Similarly, derivatives of the common item are calculated once.

For a common phase with similar lattice parameters, then it is possible to use a commons set of hkls. Similarly, if the structure factors of the two phases are the same but the lattice parameters are different (but similar) then it is also possible to use a common set of structure factors. Absent the above keywords, the program automatically searches for common items in a global manner but with restrictions. For example, strs with hkls that are not identical cannot use a common str. However, defining the structure details in a str_dets object allows for a common structure even when the normal set of hkls generated would be vastly different.

XRD-CT-0.INP is a two str and two xdd example that highlights the use of the above keywords. It looks like:

```
' Change case_ to 0, 1
#prm case_ = 1;
iters 0
lam la 1 lo !lam 1 lg 0.3  ymin_on_ymax 0.001
str_dets s0 {
   space_group i41/amd:2
   site Zr x 0 y =3/4;      z =1/8;      occ Zr+4 1 beq !b1 1
   site Si x 0 y =1/4;      z =3/8;      occ Si   1 beq !b2 1
   site O  x 0 y !y1 0.066  z !z1 0.1951 occ O-2  1 beq !b3 2
}
lat_prms l0 { Tetragonal( 6, 4) }
lat_prms l1 { Tetragonal( 5, 7) }

prm !lor_ = Constant(0.1 Rad lam) / Cos(Th);
phase_dets pd0 { prm !cs0 140 min 10 max 500 lor_fwhm = lor_ / cs0; }
phase_dets pd1 { prm !cs1 100 min 10 max 500 lor_fwhm = lor_ / cs1; }

prm o10 0.01 min -0.1 max 0.1
prm o20 0.02 min -0.1 max 0.1
prm o11 0.03 min -0.1 max 0.1
prm o21 0.04 min -0.1 max 0.1
phase_dets ze0 { transform_X = o10 + o20 X + X; }
phase_dets ze1 { transform_X = o11 + o21 X + X; }

yobs_eqn aac1.xy = 1; min 30 max 60 del 0.01
   out_sfn4_ycalc = "xrd-ct-00.sfn4";
   bkg @ 100 -20 10
   #if case_ == 0;
      str scale @ 1 load use { l0 s0 pd0 ze0 }
   #elseif case_ == 1;
```

```
      str scale @ 1 load use { l0 s0 pd0 ze0 }
   #endif

yobs_eqn aac2.xy = 1; min 10 max 60 del 0.01
   out_sfn4_ycalc = "xrd-ct-01.sfn4";
   bkg @ 100 -20 10
   #if case_ == 0;
      str scale @ 1 load use { l1 s0 pd1 ze1 }
   #elseif case_ == 1;
      str scale @ 1 load use { l1 s0 pd0 ze1 }
   #endif
```

In the above, there are two strs and two xdds . In a real-world example this could extended to 100s of 1000s of xdds and strs resulting in an INP file comprising millions of lines. It is therefore efficient to define things once as is the case of lam. Modifying the preprocessor *case_ #prm* at the top of the file demonstrates capabilities. The *case_*=1 scenario is for the following:

- Two xdds each with one str
- The two strs use a common str_dets resulting in only one set of hkls being generated and on set of structure factor.
- The lattice parameters for the two strs are different and therefore two sets are used.
- The zero errors (transform_X) are different and therefore two sets used.
- The lor_fwhm peak shape convolutions (crystallite size) are different and therefore two sets are used.

*case_*=1 is an unrealistic example where the lattice parameters and x-axis of the two xdds are vastly different. The power of reusing object becomes apparent in a real-world sense where lattice parameters, amongst similar structures, are expected to be more similar. Important output from refinement for *case_*=1 is as follows:

```
Num data files: 2
Num hkl-sets/unique: 2 1
Num structure-factors-sets/unique: 2 1
Num m4_d2_inv unique: 1
Num peak buffers unique: 2
Num xo_ds unique: 2
Num bkg derivs unique: 2
Num transform_X/unique: 2 2
Num peak-shape-objects: 8
Num hkl_pk_dets/unique: 2 2
Num pk_sum_limits unique: 2

*** Warning: Lattice parameters not similar
    but using the same structure factors

   a 6 and 5
   b 6 and 5
   c 4 and 7
   al 90 and 90
   be 90 and 90
   ga 90 and 90
```

The unique items are shown in Red. Notice the warning which is due to the vastly different lattice parameters. *case_*=2 sets the peak shapes to be the same for the two phase and the output now looks like:

```
Num hkl-sets/unique: 2 1
Num peak buffers unique: 1
Num m4_d2_inv unique: 1
Num structure-factors-sets/unique: 2 1
```

Here we see one common peak buffer and thus only one is generated, and only derivatives for its parameters are calculated. Also seen is that one set of hkls is generated. The minimum/maximum x-axis values, used for the generation of the common hkls, corresponds to the minimum/maximum values of the the start_X/finish_X and extra_X_left/extra_X_right of all the common strs.

The example XRD-CT-1.INP refines on simulated data comprising 150,000 strs and 163,150 independent parameters. 20 iterations are completed in ~60s on an 8-core laptop. A few points to note when running XRD-CT-1.INP:

- Turn off animated fitting in the GUI, it cannot cope with 2000 xdd files and 150,000 strs.
- Run first with "#define CREATE_" to create the simulated data. The data files are created using the out_sfn4_ycalc keyword. This keyword outputs binary format files with a SFN4 extension. XY formats can also be outputted as well if desired.
- Do a first run with "*#define* SUBSET_" to see how things look (animated graphics can be turned on here).
- Then remove the *#define* and turn off animated graphics.
- 3.1 Gbytes of memory is used.

Output from the refinement looks like:

```
TOPAS-64 Version 8.38 (c) 1992-2020 Alan A. Coelho
   Maximum number of threads 8
Time   0.25, INP file pre-processed
approximate_A_check_must_be_zero On
Loading xyz's for fm-3m from file C:\w\sg\fm-3m.sg
Num hkls generated for C:\w\sg\fm-3m.sg 50
Loading xyz's for fm3m from file C:\w\sg\fm3m.sg
Num hkls generated for C:\w\sg\fm3m.sg 55
Loading xyz's for i41/amd:2 from file C:\w\sg\i41oamdq2.sg
Num hkls generated for C:\w\sg\i41oamdq2.sg 313
Num hkl-sets/unique: 150000 3
Num peak buffers unique: 3
Num independent parameters: 163150
Num data files: 2000
Num m4_d2_inv unique: 3
Num xo_ds unique: 3000
Num bkg derivs unique: 1
Num transform_X/unique: 150000 75
Num structure-factors-sets/unique: 150000 3
Num peak-shape-objects: 600000
Num stretch_pks/unique: 150000 3000
Num hkl_pk_dets/unique: 150000 3000
Num phase Ycalcs/unique (ignoring transform_X): 150000 3000
Num phase Ycalcs/unique derivs (ignoring transform_X): 150000 3000
Num pk_sum_limits unique: 3000
Num equiv posns for centrosymmetric fm-3m: 192
Num equiv posns for centrosymmetric fm3m: 192
Num equiv posns for centrosymmetric i41/amd:2: 32
```

```
  0  Time   5.37  Rwp   58.064    0.000 MC     0.00 0
  1  Time   7.12  Rwp   50.740   -7.325 MC     0.00 0
  2  Time  11.90  Rwp   45.643   -5.096 MC    11.10 3
  3  Time  15.77  Rwp   45.507   -0.137 MC   115.50 1
  4  Time  19.61  Rwp   43.351   -2.155 MC    30.34 1
approximate_A_check_must_be_zero: non-zero Aij elements now static
  5  Time  23.53  Rwp   25.599  -17.752 MC     8.31 1
  6  Time  26.62  Rwp   24.143   -1.457 MC    30.92 2
  7  Time  29.22  Rwp   14.654   -9.488 MC     8.05 1
  8  Time  32.26  Rwp   14.560   -0.094 MC   269.97 2
  9  Time  34.86  Rwp   14.480   -0.080 MC    68.26 1
 10  Time  37.48  Rwp   13.241   -1.239 MC    17.30 1
 11  Time  40.14  Rwp    5.025   -8.216 MC     4.67 1
 12  Time  43.23  Rwp    4.814   -0.211 MC    19.50 2
 13  Time  45.90  Rwp    4.097   -0.718 MC     5.18 1
 14  Time  48.98  Rwp    4.045   -0.051 MC    18.59 2
 15  Time  51.65  Rwp    3.783   -0.262 MC     4.85 1
 16  Time  54.30  Rwp    3.557   -0.226 MC     1.72 1
 17  Time  56.93  Rwp    3.512   -0.044 MC     3.51 1
 18  Time  59.62  Rwp    3.464   -0.048 MC    14.20 1
 19  Time  62.27  Rwp    3.374   -0.090 MC     3.29 1
--- 62.270 seconds ---
File C:\w\test_examples\xrd-ct\xrd-ct-1.out updated
    with parameters corresponding to best Rwp
```

Note the numbers in red. This is a large refinement that would not be possible without reusing objects and without the keyword approximate_A_check_must_be_zero. This refinement cannot be tested against Version 7 as the number of hkls alone, 62,700,000, would exhaust much of memory.

Objects reused are:

- hkls
- lattice parameters
- Ycalc
- Peak buffers
- Structure factors
- th2_offset
- transform_X
- stretch_pks
- gauss_fwhm
- and many other common arrays such as (Sin(Th)/Lam)^2.
- derivatives for common refined parameters.

7. ..DECONVOLUTION

[A0_matrix_is_constant] [create_pks_name $a_name] [create_pks_fn $fn_name]	Examples TEST_EXAMPLES\DECONVOLUTION\ PBSO4-DECON.INP

The deconvolution method of [a]Coelho (2018) has been implemented; it uses three macros found in TOPAS.INC: Deconvolution_Init, Deconvolution_Bkg_Penalty and Deconvolution_Intensity_Penalty. The method refines on linear parameters only; these linear parameters are peak intensity and background parameters; their derivatives are unchanging and hence the $\mathbf{A}_0$ matrix is unchanging. The keyword A0_matrix_is_constant informs the program that only linear parameters are being refined and hence the $\mathbf{A}_0$ matrix is calculated only once. Attempts to use A0_matrix_is_constant with quick_refine, approximate_A, chi2 or with refinement of non-linear parameters results in an exception being thrown.

create_pks_name is a xo_Is dependent keyword that creates a peak at each step along the x-axis with peak intensity parameter names starting with the string $a_name. Peaks are not created if peaks already exist for the xo_Is phase. If the '$' character is placed immediately after create_pks_name and if create_pks_name is within a macro then the output from create_pks_name is placed after the macro. create_pks_fn additionally appends a penalty to each peak with the penalty being written in terms of a function called fn_name. The OUT file is updated with peaks which looks something like:

```
xo 5.00 I a25_ 0.00217` penalty = dfn(5,a25_,a26_);
xo 5.02 I a26_ 0.00000` penalty = dfn(5.02,a26_,a27_);
xo 5.04 I a27_ 0.00000` penalty = dfn(5.04,a27_,a28_);
```

The dfn function takes arguments of x-axis position of the peak and two intensity parameter names, one at the x-axis position and the other at the next x-axis position. These keywords and functions are used in macros in the following manner:

```
Deconvolution_Init(0.5)
xdd …
   Deconvolution_Bkg_Penalty(0.5)
   xo_Is
      Deconvolution_Intensity_Penalty(a, afn)
```

The deconvolution process comprises three separate refinement runs. 1) Fitting the peaks to the diffraction pattern with peak shapes fixed to expected peak shapes, 2) creating a calculated pattern with a chosen peak shape, typically a peak shape comprising specimen contributions, and 3) a final run to produce a deconvoluted pattern with noise. The PBSO4-DECON.INP example is ready to run, it can be used as a template for other deconvolution processes, it is defined as:

```
#define DO_REFINEMENT_      ' Step 1
'#define DO_SPECIMEN_OUT_    ' Step 2
'#define DO_FINAL_DECON_     ' Step 3
macro Data_File { Pbso4 }
#ifdef DO_FINAL_DECON_
```

```
    RAW(..\##Data_File) ' load for comparison purposes
    xdd Data_File##-decon-specimen.xy
        x_calculation_step 0.025
        user_y d1 Data_File##-decon-specimen.xy
        user_y d2 Data_File##-diff.xy
        fit_obj = d1 + d2;
        Out_X_Ycalc(Data_File##-decon-final.xy) ' Final deconvoluted pattern
#else
    Deconvolution_Init(0.5)
    RAW(..\##Data_File)
        start_X 15
        bkg @ 0 0 0 0 0 0 0
        Deconvolution_Bkg_Penalty(0.5)
        'LP_Factor(17) ' Do not include when doing deconvolution
        CS_L(262.73494)
        Strain_L(0.03785)
        #ifdef DO_SPECIMEN_OUT_
            iters 0
            CuKa1(0.0001)
            Out_X_Ycalc(Data_File##-decon-specimen.xy)
        #else ' DO_REFINEMENT_
            Out_X_Difference(Data_File##-diff.xy)
            CuKa5(0.0001)
            Radius(173)
            Full_Axial_Model(10, 10, 10, 4.13679, 4.13679)
            Divergence(1)
            Slit_Width(0.2)
        #endif
        xo_Is
            Deconvolution_Intensity_Penalty(a, dfn)
#endif
```

Background should be less than all observed data and it should be graphically inspected during step 1. Background can be reduced by decreasing the *c* parameter of the Deconvolution_Bkg_Penalty macro; this parameter can range from 0.05 to 1. If the bases of the peaks are not matching *Yobs* then the background is still too high. Step 1 and 2 produces output XY files which are then used in step 3. The exclusion of LP_Factor, and similar peak scaling parameters, is important as peak intensities are used in a penalty inside the Deconvolution_Intensity_Penalty macro. The deconvolution process can be used for all types of data including neutron TOF; step (1) takes approximately 10 to 30 seconds on present laptops; steps (2) and (3) takes a trivial amount of time (< 1s). The deconvolution macros are as follows:

```
macro Deconvolution_Init(c) {
   process_times
   A0_matrix_is_constant       ' All parameters are linear
   penalties_weighting_K1 = c; ' A value of 0.5 seems sufficient
   save_best_chi2              ' We want best Chi2; not best Rwp
   chi2_convergence_criteria 1e-5
   continue_after_convergence  ' ~100 iterations is typically sufficient (~20s)
   pen_weight 1                ' Override the default
}
macro Deconvolution_Intensity_Penalty(i_name, fn_name) {
   fn fn_name(x, a0, a1) = (a0 - a1)^2 / ((a0 + a1) Yobs_at(x) + 1e-6);
   default_I_attributes 1e-6 min 0 val_on_continue = Val Rand(0.99, 1.01);
   create_pks_fn fn_name
```

```
    create_pks_name $ i_name
}
macro Deconvolution_Bkg_Penalty(& c, & w_min) {
    xdd_sum #m_unique pen = (Yobs - Get(bkg))^2 / Max(Get(bkg) Yobs, w_min^2);
    penalty = pen c;
}
macro Deconvolution_Bkg_Penalty(& c) { Deconvolution_Bkg_Penalty(c, 1) }
```

pen_weight over-rides the default; the default works but with slower convergence. Note, both the peak intensity and Bkg penalties are *Yobs* scale invariant where scaling of *Yobs* does not change the magnitude of the penalties relative to χ^2_0. Yobs_at is a new function that returns the value of *Yobs* at x. w_min in the Deconvolution_Bkg_Penalty macro allows for the setting of the expected minimum of *Yobs*Bkg*; a value of 1 for counting statistics. For XYE files, where *Yobs* is small and where *SigmaYobs* is used (tof data for example), then w_min should be reduced.

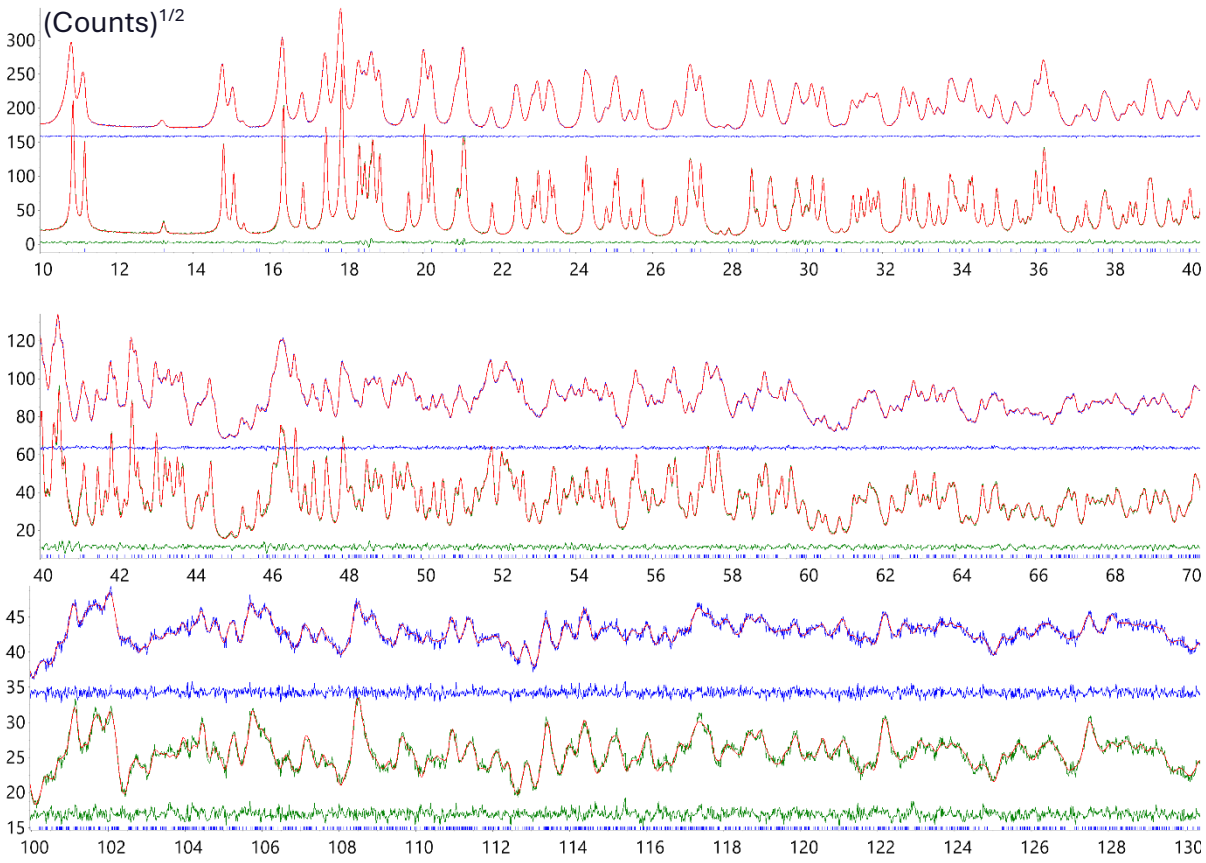
7.1..... Deconvolution – Simulated pattern

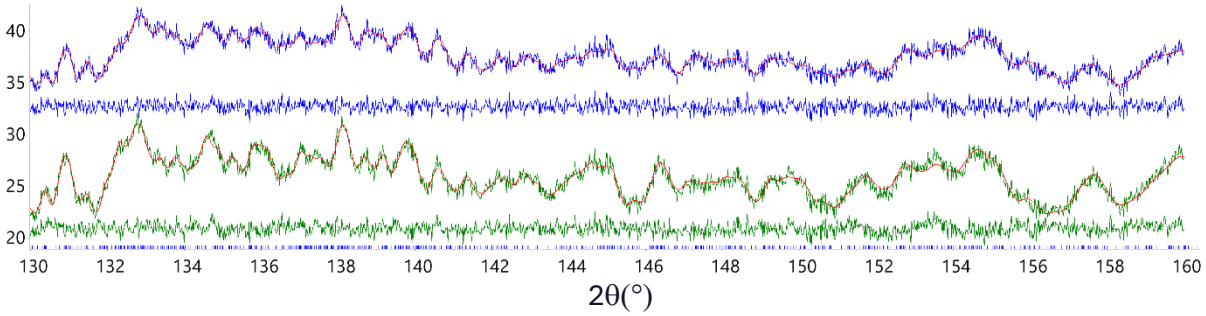
A simulated pattern was created with noise using SIM-CREATE.INP and the instrument contribution deconvoluted using SIM-DECON.INP; the latter INP file looks like:

```
/*  Three runs to produce the deconvoluted pattern.
    The name of the final deconvoluted pattern is:

        pbso4-decon-final.xy

    Define one at a time in the following:

        #define DO_REFINEMENT_    ' Run 1
        #define DO_SPECIMEN_OUT_  ' Run 2
        #define DO_FINAL_DECON_   ' Run 3
*/
#define DO_REFINEMENT_     ' Step 1
'#define DO_SPECIMEN_OUT_  ' Step 2
'#define DO_FINAL_DECON_   ' Step 3, Clear the GUI first

macro Data_File { Sim }
#ifdef DO_FINAL_DECON_
    xdd Data_File##-calc-rand.xy ' load for comparision purposes
    xdd Data_File##-calc-narrow.xy
        user_y d1 Data_File##-decon-specimen.xy
        user_y d2 Data_File##-diff.xy
        fit_obj = d1 + d2;
        Out_X_Ycalc(Data_File##-decon-final.xy)
#else
    Deconvolution_Init(0.5)
    xdd Data_File##-calc-rand.xy
        bkg @  259.381081  89.8339877  31.6429117 -34.4743462
                34.3097757 -55.7270435  30.631573
        Deconvolution_Bkg_Penalty(0.1)

        /* Specimen */
        CS_L(300)
        CS_G(300)
        Strain_L(0.05)
```

```
        Strain_G(0.05)

        #ifdef DO_SPECIMEN_OUT_
            iters 0
            CuKa1(0.001)
            Out_X_Ycalc(Data_File##-decon-specimen.xy)
        #else ' DO_REFINEMENT_
            num_cycles 20
            Out_X_Difference(Data_File##-diff.xy)

            /* Instrument */
            CuKa2(0.001)
            Radius(217)
            Full_Axial_Model(12, 12, 12, 2.3, 7)
            Divergence(1)
            Slit_Width(0.1)
            Absorption(60)
        #endif
        xo_Is
            Deconvolution_Intensity_Penalty(a, dfn)
#endif
```

The following figure is the deconvoluted pattern (green line, bottom plot) compared with the expected deconvoluted pattern (red line on top of green line). The top plot (blue line) is the original simulated pattern with noise and without noise (red line on top of blue line).





Parameter errors determined from refinement using the deconvoluted pattern are almost identical to errors produced using the original pattern, see [a]Coelho (2018).

8. ..PDF-GENERATION

[xdd...] [rebin_with_dx_of !E] [pdf_generate { [dr !E] [r_max !E] [gr_sst_file = “File”;] [hat !E [num_hats !E] [gr_to_fq !E] }]	**Examples** TEST_EXAMPLES\PDF\GENERATE\ FULLERENE\DECON.INP LIFEPO4\DECON.INP SILICON\DECON.INP TUNGSTEN\DECON.INP

PDF generation comprises an inverse Sine transform operating on an ideal diffraction pattern where background is absent, atomic scattering factors are constant, and 2θ and peak shapes symmetric. The task therefore becomes one of correcting real data such that it matches an ideal pattern as closely as possible. The corrections include determining a background, atomic scattering factors (if X-ray data), removing Lorentz polarization and removing asymmetry from peak shapes; for details see Coelho *et al*., 2021. To generate the PDF, a deconvolution process similar-to that described in section 7 is used. It allows for corrections in reciprocal space of peak asymmetry, instrument and emission profile aberrations, Lorentz polarization and atomic scattering factors corrections. The process comprises two operations described in a single INP file; these operations are:

- 0) Fit to the reciprocal space diffraction pattern - (Operation 0)
- 1) Generate *G*(*r*) - (Operation 1)
  - 1.0) Generate ideal pattern Ideal (2θ) from the parameters determined in step 0.
  - 1.1) Convert Ideal (2θ) to *Q* space to form *Ideal*(*Q*).
  - 1.2) Fit a polynomial to *Ideal*(*Q*) and save *F*(*Q*) = *Ideal*(*Q*) – *Poly*)
  - 1.3) Generate *G*(*r*) from *F*(*Q*)

Each operation requires running the INP file once. Steps 1.0 to 1.3 of operation 1 is performed with num_runs set to 4.

8.1..... PDF-Generating - LiFePO4

Fitting to the pattern, operation 0, follows the deconvolution process of [a]Coelho (2018). Lattice parameters are not required. A peak is laid down at each data point of the pattern together with a background and appropriate penalty functions. Approximate peak shapes from a preliminary peak fitting analysis, using a ‘standard’ for example, is recommended; once determined peak shapes are not refined. The data entry part of a typical INP file (see LIFEPO4\ DECON.INP for example) is as follows:

```
Include_PDF_Generate
'-------------------------------------------------------
'              START USER INPUT SECTION
'-------------------------------------------------------
macro Data_File         { LFP_0-8Kcap_AgFGM_2x4soll_Eiger1D_8h.xy }
```

```
macro Capillary_Scan    { capillary.xy }
macro Capillary_Rebin   { 0.1 } ' Smooth the capillary scan. Zero means no smoothing.
#prm operation = 0; ' Set to 0 to fit to reciprocal space data
                    ' Set to 1 to generate F(Q) and G(r)
                    ' Set to 2 to fit structure to G(r)
#prm use_narrow_peak_shape  = 1; ' A 0 means use full peak shapes in generating G(r)
'-------------------------------------------------------
' Inputs for reciprocal space fit, operation = 0
macro & Average_f           { f0_Li + f0_Fe + f0_P + 4 f0_O } ' formula of unit cell
#prm lab_no_monochromator   = 1; ' Set to 1 if using Laboratory instrument.
#prm use_Xo_Is_phase        = 1; ' Set to 0 if not fitting peaks
#prm use_bkg_penalty        = 1;
#prm use_simple_bkg_penalty = 1; ' Set to 1 if counting statistics is not right,
                                 ' or, maybe when there's Fluorescence.
macro & Bkg_Weighting               { 1 }
macro & Intensity_Penalty_Weighting { 1 }
macro & Scale_Peaks   { 1 } ' Useful if capillary absorption is inhibiting fitting.
macro & Scale_Yobs_By { 1 } ' Useful if data does not obey counting statistics.
prm pc0  1   ' Poly_Capillary coefficients; comment out if
prm pc1  0   ' not using Capillary as background.
inp_text fluorescence_bkg
   {
      bkg @ 3.49160163` -0.96682842`  0.292687899`
   }
inp_text fit_extra
   {
      penalty = 10000 (Bkg_at(X2) + (pc0 + pc1) Value_at_X(cap_, X2) - Yobs_at(X2))^2;
   }
macro Start_X       { 2.4  }
macro Finish_X      { 103  }
macro Step_X        { 0.02 } ' Set to zero to use measured step size.
                             ' Set to non-zero if scale_yobs_by is used.
                             ' Set to non-zero if unequal x-axis steps.
'-------------------------------------------------------------
' Inputs for generating F(Q), operation = 1
#prm poly_fq = 7;  ' Number of parameters for Poly when fitting Poly to F(Q).
                   ' View F(Q) plot, it needs to look right.
macro & Qmin                  { 0.1 }
macro & Qmax                  { 17.5 }
macro & Soper_Lorch_Constant  { 0 } ' best not to use
macro & Exp_Constant          { 0 } ' best not to use
macro & Lorch_Constant        { 0 } ' best not to use
inp_text fq_poly
   {
      bkg @  0 0 0 0 0 0 0 0  0
   }
macro FQ_Bkg_Penalty
   {
      weighting = If(X > (X2 - 1), 10, 1); ' Weigh the F(Q) data more at Qmax
      penalty   = Bkg_at(X1)^2;            ' Restrain F(Q=0) to 0
   }
'-------------------------------------------------------------
' Inputs for generating G(r) from F(Q), operation = 1
macro R_Max         { 100 }
macro dR            { 0.01 }
macro Num_Hats      { 3 } ' Best smoothing function for speed and accuracy
macro & Hat_Size    { 4.4934 / Qmax }
'-------------------------------------------------------------
```

```
' Reciprocal space peak details, operation = 0
macro Full_Emmision_Profile
   {
      lam ymin_on_ymax 0.001
         la 1 lo 0.5609 lg 1e-6
         la 0.55150 lo 0.5649441 lg 1e-6
   }
macro Deconvoluted_Emmision_Profile
   {
      lam ymin_on_ymax 0.0005 la 1 lo 0.5609 lg 1e-6
   }
macro Full_Peak_Shape_Specimen
   {
      CS_G(, 70)
      CS_L(, 45)
      Strain_L(, 0.042)
      Strain_G(, 0.42)
   }
macro Full_Peak_Shape
   {
      Full_Peak_Shape_Specimen
      Full_Axial_Model(10,10,10, 2.3, 5.73430)
   }
macro Deconvoluted_Peak_Shape
   {
      Deconvoluted_Emmision_Profile
      #if (use_Xo_Is_phase == 0)
         ' Using (Yobs - background); ie. no peak shape
      #elseif (use_narrow_peak_shape)
         ' Use Narrow peak shape
         ZE(, -0.00730929318) ' Set to negative of Rietveld fit
         gauss_fwhm 0.05
      #else ' Use Full peak shape specimen
         Full_Peak_Shape_Specimen
         ZE(, -0.00730929318) ' Set to negative of Rietveld fit
      #endif
   }
macro & LP_Factor_
   {
      #if (lab_no_monochromator)
         (1 + Cos(X Pi/ 180)^2)
      #endif
      1 / (Sin(X Pi/360)^2 Cos(X Pi/360)) ' Lorentz factor
   }
'-------------------------------------------------------
'              END USER INPUT SECTION
'-------------------------------------------------------
Include_PDF_Generate_Common
'-------------------------------------------------------
#if (And(use_Xo_Is_phase, Run_Number == 0, Or(fit_to_data, generate_fq_gr_from_fit)))
   xo_Is
      PDF_Generation_Intensity_Penalty(a,dfn, Intensity_Penalty_Weighting, Scale_Peaks)
#endif
'-------------------------------------------------------
```

Input is required for data such as the name of the data files etc... It is best to create a new directory for each data file. The PDF-GENERATE.INC file, included using the

Include_PDF_Generate macro, contains PDF generation specific macros. Capillary_Scan is the name of the file corresponding to a scan of the empty capillary sample holder. Typically, the capillary scan is collected in a short time leading to poor counting statistics; Capillary_Rebin can therefore be used to smooth the capillary scan. Setting the #prm called *operation* to 1 instructs the program to perform the fitting process. Setting *use_narrow_peak_shape* to 1 result in narrow peaks being used in the generation of the *Ideal*(2θ) (operation 1.0); this removes peak broadening as a function of 2θ.

8.1.1 ..... Operation 0 – Fitting peaks to the diffraction pattern

If *use_Xo_Is_phase*=0 then no peak fitting is performed and hence no deconvolution; the ideal pattern is created using (Yobs – Ycalc)/ (LP_Factor <f>), where Ycalc in this case is the background function. Also, *use_simple_bkg_penalty* should also be set to 1. When *use_Xo_Is_phase*=1, peaks are fitted. The program internally creates peaks and places them at the position of the xo_Is phase. *lab_no_monochromator*=1 instructs the program that the data is from a Laboratory instrument without a monochromator. Background is described as follows:

*Background = Poly_Capillary * Capillary_Scan + Poly_Fluorescence*

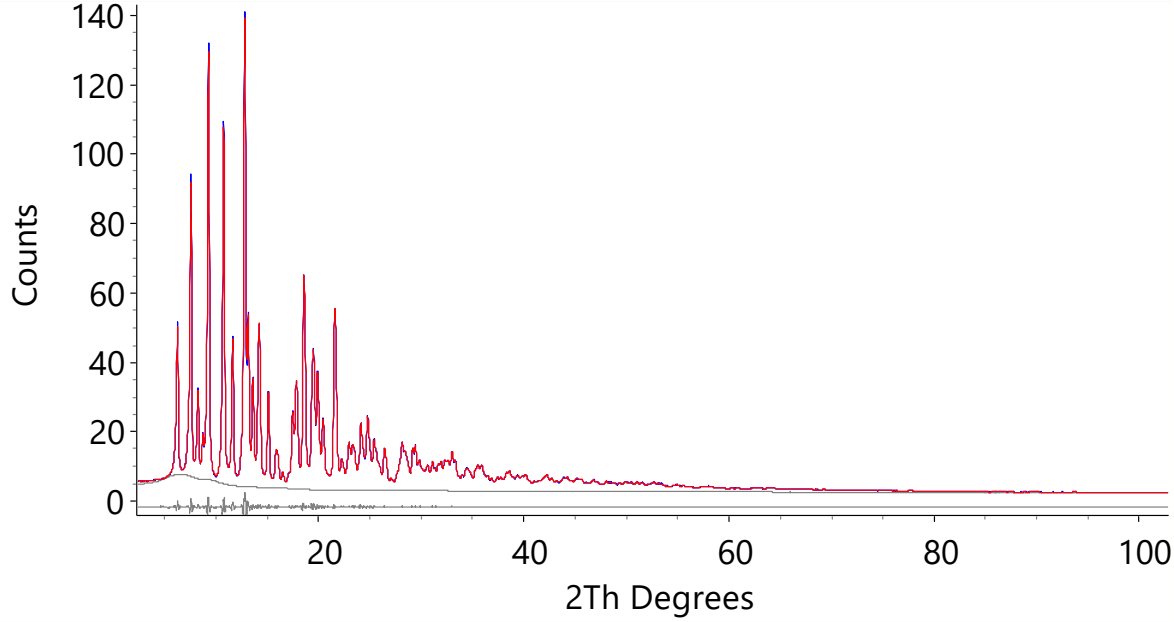
Poly_Capillary is a 1st order polynomial with coefficients defined by the pc0 and pc1 parameters. *Poly_Fluorescence* is also a nth order Chebyshev polynomial with coefficients defined by the user at the inp_text fluorescence_bkg {} construct; set this construct to blank when not using. $LiFePO_4$ fluoresces, and its best to use the smallest number of bkg parameters whilst producing a good background fit. In the case of $LiFePO_4$, the high angle peaks seem to vanish. This means that the background should be almost equal to *Yobs* at the highest angle *X2*. Such a condition can be enforced using a penalty as shown in the inp_text called *fit_extra*. The penalty describes the following:

$(Poly\_Capillary(X2) * Capillary\_Scan(X2) + Poly\_Fluorescence(X2) - Yobs\_at(X2))^2$

X2 is the reserved parameter name corresponding to the end of the diffraction pattern. *Poly_Capillary* at *X2* is simply (pc0 + pc1), see the X0_ macro in PDF-GENERATE_COMMON.INC, and *Poly_Fluorescence*(*X2*) corresponds to Bkg_at(*X2*). The penalty therefore looks like:

```
inp_text fit_extra
   {
      penalty = 10000 (Bkg_at(X2) + (pc0 + pc1) Value_at_X(cap_, X2) - Yobs_at(X2))^2;
   }
```

The fit for LiFePO4 looks like:



Notice the display of the background line as well as the small difference plot. When rerunning, *operation*=0, the peaks at the xo_Is phase is not recreated if already present. It may be necessary, therefore, to delete the peaks at the xo_Is phase when rerunning *operation*=0. When *use_simple_bkg_penalty*=0, the full background penalty is used which relies on counting statistics. For data that does not obey counting statistics, the macros Scale_Yobs_By can be used to scale the observed diffraction pattern. This scaling is performed using the user_y keyword as follows:

```
user_y data_file Data_File
yobs_eqn data.sst = data_file Scale_Yobs_By;
    min = Start_X; max = Finish_X; del = Step_X;
```

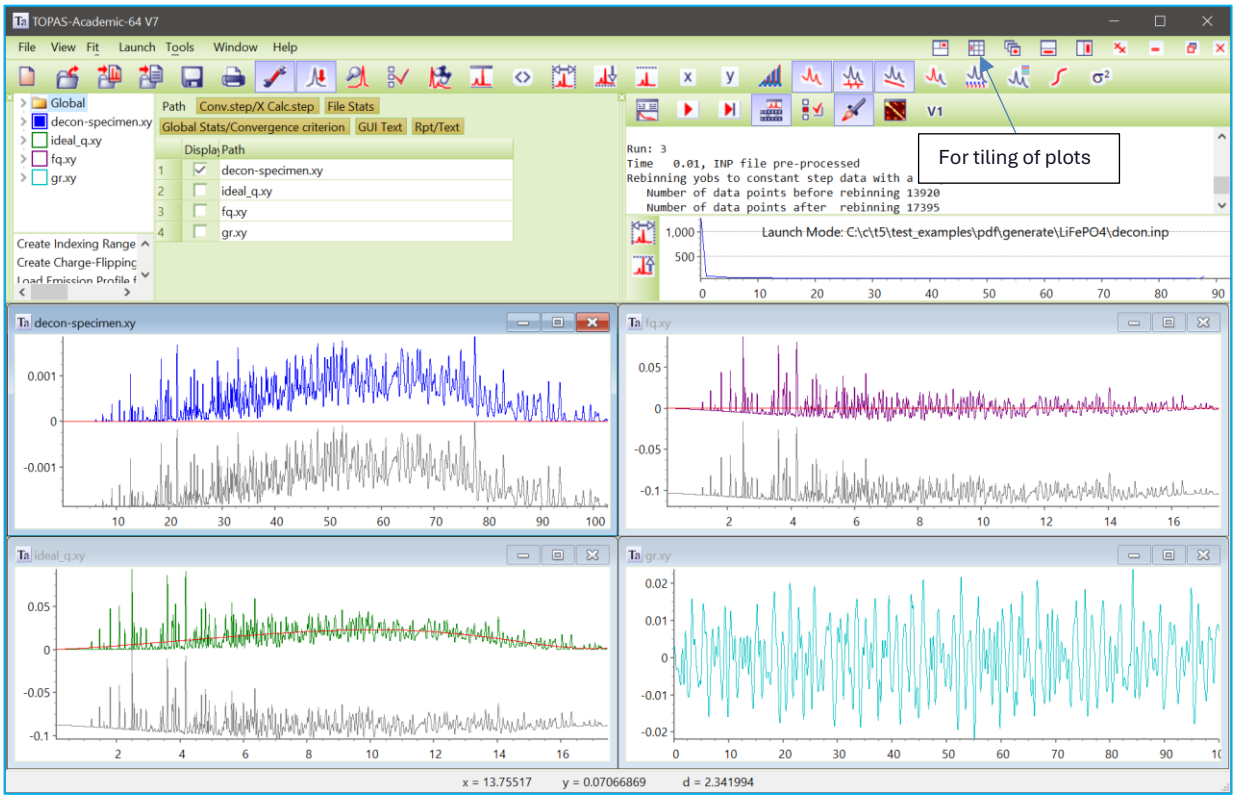
Note, user_y can also be a function of the reserved parameter *X*. The input created for the Kernel can be viewed in TOPAS.LOG.

8.1.2 ..... Operation 1 – Generation G(r) from the fitted peaks

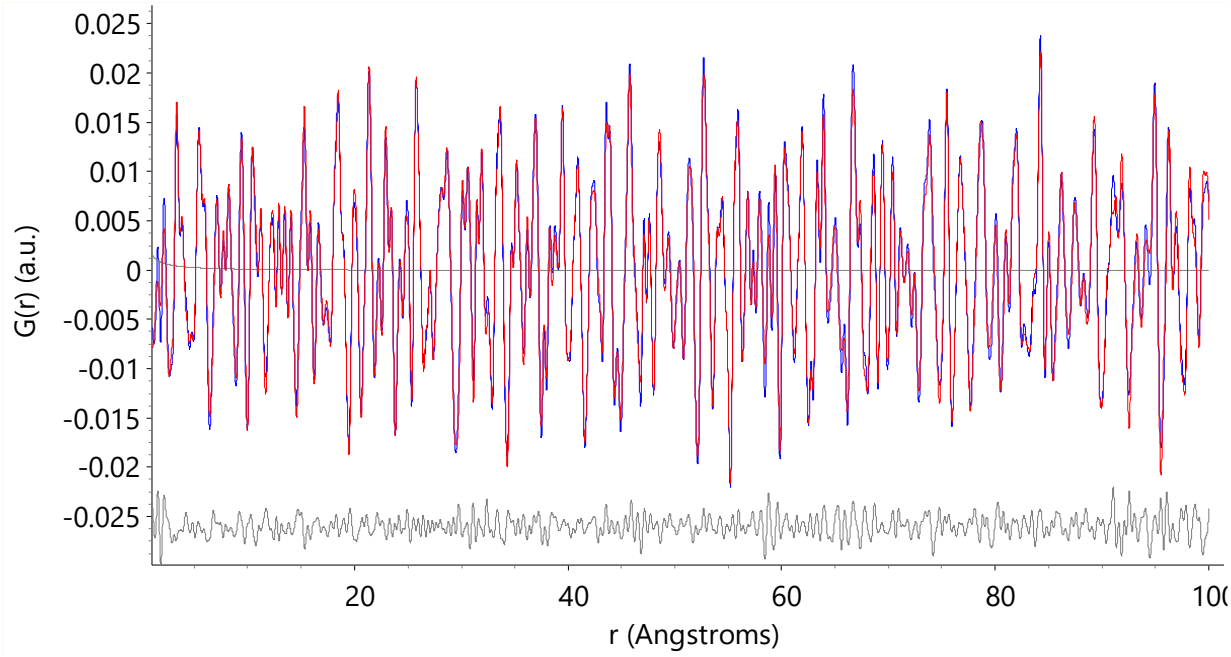
The Average_f macro is used to calculate the average atomic scattering factor <*f*> for operation 1.0. For X-ray data, a rough estimate of the atomic species is helpful; for neutron data an estimate is not required. Applying smoothing functions on *F*(*Q*) such as the Lorch and Soper-Lorch functions is not recommended. Instead, applying three hat convolutions directly to *G*(*r*) is faster and more accurate. At operation 1.1 the ideal pattern is converted to *Q* space. Operation 1.2 generates *F*(*Q*) by fitting a polynomial to *Ideal*(*Q*) where:

$$F(Q) = Ideal(Q) - Poly\_FQ$$

fq_poly describes *Poly_FQ* using the Chebyshev polynomial of bkg; the optimum number of coefficients is difficult to determine automatically. Its best to inspect the plots produced by operation 1; these are generated and loaded into the GUI and, using the GUI-Tiling option, looks like:



Changing *fq_poly* and rerunning operation 1 updates the four plots; this updating is achieved using the keyword gui_reload. Using the structure of $LiFePO_4$, the generated *G*(*r*) can be fitted-to by setting *operation*=2. With *use_narrow_peak_shape*=0 we get:



The grey line at the center of the plot is a correction added to the calculated *G*(*r*) using:

```
fit_obj = a1 Cos(a2 X + a3) / X;
```

If this grey line is significant in intensity, then the value of *F*(*Q*=0) is incorrect. Controlling the behaviour of *F*(*Q*) at the start and end of the Q range can be done from the FQ_Bkg_Penalty macro. For example, *F*(*Q*=0)=0 can be set using the following penalty:

```
       penalty = Bkg_at(X1)^2;
```

For *operation* 1; intermediate pre-processed text fed to the kernel can be sent to TOPAS.LOG (or TC.LOG) for viewing by setting *suspend_writing_to_log_file* to 0. For the current example, TOPAS.LOG for the operation 1.0 part is as follows (comments added):

```
iters 0
yobs_eqn aac.sst = 1; min 0.01 max = 103; del 0.0025
   gui_ignore
   Out_XDD_SST(decon.sst) ' Not expanded for clarity
      ' Output Ycalc / (polarization * <f>)
      = Ycalc / (( (1 + Cos(X 3.14159265358979/ 180)^2) 1 / (Sin(X 3.14159265358979/360)^2
        Cos(X 3.14159265358979/360))) (f0__(
        0.974637,0.158472,0.811855,0.262416,0.790108,0.002542,4.334946,0.342451,97.102966,201
        .363831,1.409234 ) + f0__( 12.311098,1.876623,3.066177,2.070451,6.975185,-
        0.304931,5.009415,0.014461,18.743040,82.767876,0.346506 ) + f0__(
        1.950541,4.146930,1.494560,1.522042,5.729711,0.155233,0.908139,27.044952,0.071280,67.
        520187,1.981173 ) + 4 f0__(
        2.960427,2.508818,0.637853,0.722838,1.142756,0.027014,14.182259,5.936858,0.112726,34.
        958481,0.390240 ))^2);
   lam ymin_on_ymax 0.0005 la 1 lo 0.5609 lg 1e-6
   th2_offset = (-0.00730929318);
   gauss_fwhm 0.05 ' Use narrow deconvoluted peak
   xo_Is
      extra_X_left = Max(X1 - Max(X1 - 1, 0.1), 0);
      extra_X_right = Max(Min(X2 + 1, 179.9) - X2, 0);
      fn dfn (x, a0, a1) = (a0 - a1)^2 / Max(a0 + a1, 1e-6);
      default_I_attributes 1e-6 min 0 val_on_continue = Val Rand(0.5, 2) + 1e-4;
      create_pks_fn dfn create_pks_name $ a
      xo 1.40009871 I a50_ 0.0178524321`
      xo 1.42009871 I a50_ 0.0178524321`
      xo 1.44009871 I a50_ 0.0178524321`
      …
```

The actual generation of *G*(*r*) occurs when Run_Number = 3; its INP text looks like:

```
    iters 0
    xdd fq.sst
        gui_reload
        lam ymin_on_ymax 0.0005 la 1 lo 0.5609 lg 1e-6
        rebin_with_dx_of 0.001
        pdf_generate {
            dr = 0.01;
            r_max = 100;
            gr_sst_file = "gr";
            hat = 4.4934 / (17.5); num_hats = 3;
        }
```

8.1.3 ..... Correcting the PDF due to a zero error in reciprocal space

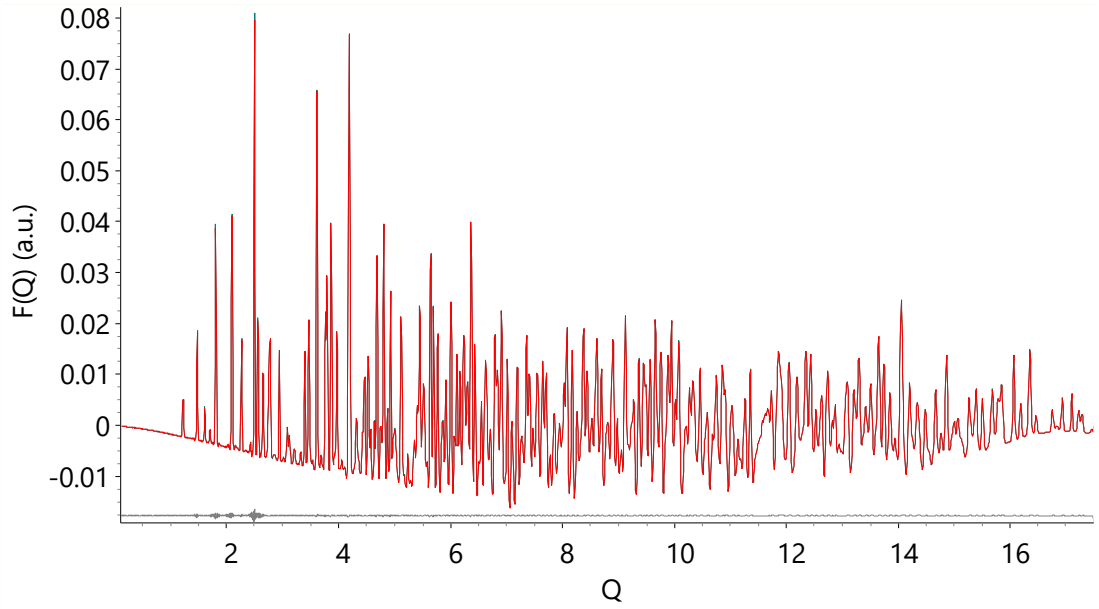
A zero-error added to peak positions in reciprocal can be subtracted from the deconvoluted pattern of operation 1.0. Thus, a zero-error determined from fitting to a standard in reciprocal space needs to be subtracted from the deconvoluted pattern from within the Deconvoluted_Peak_Shape macro.

8.1.4 ..... Generating F(Q) from G(r) - gr_to_fq

The LIFEPO4\GR-TO-FQ.INP file creates $G(r)$ from an $F(Q)$ file at Run_Number 0, then in Run_Number 1 it uses the newly created $G(r)$ to reproduce the original $F(Q)$ using gr_to_fq. The INP file is as follows:

```
num_runs 3
#if (Run_Number == 0)
   xdd fq-original.sst
      rebin_with_dx_of 0.005
      lam ymin_on_ymax 0.0005 la 1 lo 0.5609 lg 1e-6
      pdf_generate {
         dr = 0.01;
         r_max = 300;
         gr_sst_file = "gr-from-fq";
      }
#elseif (Run_Number == 1)
   xdd gr-from-fq.sst
      gui_ignore
      lam ymin_on_ymax 0.0005 la 1 lo 0.5609 lg 1e-6
      pdf_generate {
         dr = 0.00125;
         r_max = 17.5;
         gr_sst_file = "fq-from-gr";
         gr_to_fq 1
      }
#elseif (Run_Number == 2)
   xdd fq.sst
      rebin_with_dx_of 0.01
      user_y fq_from_gr fq-from-gr.sst

      prm a 1 min 1e-6
      fit_obj = fq_from_gr a;
#endif
```

Run_Number 3 fits the newly created $F(Q)$ to the original $F(Q)$; the result showing the reproduced $F(Q)$ (in red) and the original $F(Q)$ (in blue) has a small difference plot as seen in the following:



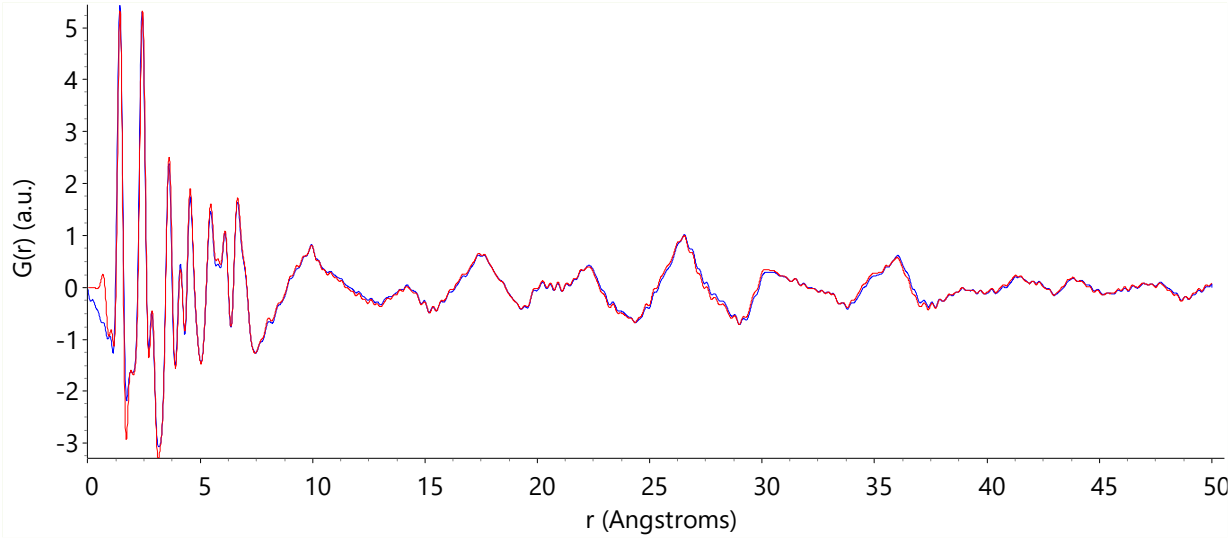
8.1.5 ..... PDF-Generation - Fullerene

In this example *G*(*r*) from TOPAS is compared to *G*(*r*) from GudrunX for Fullerene. The INP file is:

```
Include_PDF_Generate
'-------------------------------------------------------
'              START USER INPUT SECTION
'-------------------------------------------------------
macro Data_File        { i15-1-20401_tth_det2_0.xy }
macro Capillary_Scan   { i15-1-20398_tth_det2_0.xy}
macro Capillary_Rebin  { 0 } ' Smooth the capillary scan. Zero means no smoothing
#prm operation = 1; ' Set to 0 to fit to reciprocal space data
                    ' Set to 1 generate F(Q) and G(r)
                    ' Set to 2 to fit structure to G(r)

#prm use_narrow_peak_shape  = 1; ' Use narrow peak shapes in the generating G(r)
'-------------------------------------------------------
' Inputs for reciprocal space fit, operation == 0
#prm lab_no_monochromator   = 0; ' Set to 1 if using Laboratory instrument
#prm use_Xo_Is_phase        = 0; ' Set to 0 if not fitting peaks
#prm use_bkg_penalty        = 1;
#prm use_simple_bkg_penalty = 1; ' Set to 1 if counting statistics is not right
                                 ' or maybe when there's Fluorescence
macro & Bkg_Weighting                { 1 }
macro & Intensity_Penalty_Weighting { 1 }
macro & Scale_Peaks   { 1 } ' Useful if capillary absorption is inhibiting fitting.
macro & Scale_Yobs_By { 1 } ' Useful if data does not obey counting statistics.

prm pc0  1.09673044`     ' Multiplies Capillary by (pc0 + pc1 x0)
prm pc1  0.146927936     ' Comment out if not using Capillary as background.
inp_text fluorescence_bkg { }
inp_text fit_extra
   {
      penalty = 10000 (Bkg_at(X2) + (pc0 + pc1) Value_at_X(cap_, X2) - Yobs_at(X2))^2;
   }
macro Start_X       { 0.6    }
macro Finish_X      { 59.9   }
```

```
macro Step_X        { 0.02 } ' Set to 0 to use measured step size.
                             ' Set to non-zero if scale_yobs_by is use.
                             ' Set to non-zero if unequal x-axis.
'------------------------------------------------------
' Input for generating F(Q) - operation == 1
macro & Average_f             { f0_C }
macro & Qmin                  { 0.5 }
macro & Qmax                  { 25  }
macro & Soper_Lorch_Constant  { 1.1 } ' Used for comparison purposes
macro & Exp_Constant          { 0 }
macro & Lorch_Constant        { 0 }
inp_text fq_poly
   {
      bkg @  0 0 0 0 0 0 0 0 0
   }
macro FQ_Bkg_Penalty  { }
'------------------------------------------------------
' Inputs for generating G(r) from F(Q), operation == 1
macro R_Max         { 50 }
macro dR            { 0.01 }
macro Num_Hats      { 0 } ' Best smoothing funcion for speed and accuracy
macro & Hat_Size    { 4.4934 / Qmax }
'------------------------------------------------------
' Reciprocal space peak details, operation == 0
macro Full_Emmision_Profile
   {
      lam ymin_on_ymax 0.0005 la 1 lo 0.161669 lg 1e-6
   }
macro Deconvoluted_Emmision_Profile
   {
      Full_Emmision_Profile
   }
macro Full_Peak_Shape_Specimen { }
macro Full_Peak_Shape { }
macro Deconvoluted_Peak_Shape
   {
      Deconvoluted_Emmision_Profile
      #if (use_Xo_Is_phase == 0)
         ' Using (Yobs - background); ie. no peak shape
      #elseif (use_narrow_peak_shape)
         ' Use Narrow peak shape
         gauss_fwhm 0.05
      #else
         ' Use Full peak shape
         Full_Peak_Shape_Specimen
      #endif
   }
macro & LP_Factor_
   {
      #if (lab_no_monochromator) (1 + Cos(X Pi/ 180)^2) #endif
      1 / (Sin(X Pi/360)^2 Cos(X Pi/360)) ' Lorentz factor
   }
'------------------------------------------------------
'              END USER INPUT SECTION
'------------------------------------------------------
Include_PDF_Generate_Common
'------------------------------------------------------
```

In this example, peaks are not fitted and as such *use_Xo_Is_phase*=0 and *use_simple_bkg_penalty*=1. *fluorescence_bkg* is left empty as fluorescence is not present. *fit_extra* is used where a penalty is applied equating the bkg_tot to the *Yobs* value at the end of the diffraction pattern. Note, the use of the Value_at_X function. bkg_tot in this example comprises a fit_obj which corresponds to (pc0 + pc1 *X*)***Capillary*. In this example the Soper_Lorch_Constant was used to match GudrunX. *G*(*r*) generated for TOPAS (in red) and GudrunX (in Blue) is as follows:



9. ..PDF REFINEMENT

[xdd]...
  [pdf_data]
  [scale_phase_X[1] E]...
  [fit_obj[1] E]...
  [start_X #] [finish_X #]
  [rebin_with_dx_of[1] !E]
    [rebin_start_x_at !E]
  [weighting !E]
  [Tpdf_convolute]...
  [str]...
    [scale_phase_X1 E]...
    [scale E]
    [view_structure]
    [rigid]...
    [occ_merge $sites]...
    [pdf_scale_simple]
    [pdf_zero[1] E]
    [pdf_ymin_on_ymax 0.001]
    [pdf_info]
    [Tpdf_convolute]...
    [pdf_for_pairs $sites_1 $sites_2]...
      [pdf_only_eq_0]
      [pdf_gauss_fwhm[1] E]
      [Tpdf_convolute]...
    [pdf_partial_1 $sites]
    [pdf_partial_2 $sites]
    [pdf_partial_when !E1]

Tpdf_convolute
  [pdf_convolute[1] E]...
    [min_X !E]
    [max_X !E]
    [convolute_X_recal !E]

Examples

INP files

TEST_EXAMPLES\PDF\
  BEQ-2.INP
  BEQ-2-CREATE.INP
  BEQ-3.INP
  BEQ-3-CREATE.INP
  PDF-1.INP
  PDF-2.INP
  ALVO4\
    STRUCTURE-SOLUTION-CREATE.INP
    STRUCTURE-SOLUTION.INP
    RIGID.INP
  OCC-MERGE-PBSO4\
    CREATE.INP
    OCC-MERGE-TEST.INP
    OCC-MERGE.INP

Data files

TEST_EXAMPLES\PDF\
  BEQ-2.XY
  BEQ-3.XY
  ALVO4\ALVO4.XY
  OCC-MERGE-PBSO4\PBSO4.XY

[1]) Can be a function of the reserved parameter name *X*; *X* corresponds to r for PDF data.

PDF refinement as implemented operates at speed (Coelho, 2015). PDF patterns are treated as an xdd where most xdd keywords can be used. PDF patterns can be refined simultaneously with other types of xdd patterns where the latter can comprise x-ray dependent or x-ray independent phases. Penalties, restraints and keywords such as rigid, atomic_interaction, sites_geometry, sites_distance etc. can all be used. pdf_data tells the program that the data set is of $G(r)$ type. Let's write $G(r)$ as:

$$G(r) = s_1 S(r) / r - s_2 r$$

where r corresponds to the x-axis, s_1 and s_2 are constants and $S(r)$ are the pairs. pdf_scale_simple tells the program to calculate $S(r)/(N_p\ r)$ only. pdf_ymin_on_ymax defines the min/max value for the PDF Gaussians in-regards-to the x-axis extents of the Gaussians; the default value of 0.001 in typically sufficient. pdf_for_pairs can be used to select site pairs using the site name, for example:

```
pdf_for_pairs "V* Al* !O2" *
```

The '!' character excludes the O2 sequence from the wild card string, see section 20.26. Multiple pdf_for_pairs can be defined. pdf_only_eq_0 informs the parent pdf_for_pairs that only equivalent position 0 is to be considered. pdf_gauss_fwhm is used to write the width equation for the pairs selected by pdf_for_pairs. If all pairs are described by pdf_for_pairs then the associated beq's are not used; the user is informed of unused beq's. Consider the following abbreviated INP segment:

```
site Al1 ... beq 1
site O1  ... beq 1
pdf_for_pairs Al1 Al1 pdf_only_eq_0 pdf_gauss_fwhm 0.1 ' Line A
pdf_for_pairs Al1 O1  pdf_only_eq_0 pdf_gauss_fwhm 0.2 ' Line B
pdf_for_pairs Al1 O1                pdf_gauss_fwhm 0.3 ' Line C
```

The FWHMs of the interactions are as follows:

Al1-O1 : Interactions for equivalent-position-0 described using Line B.

Al1-O1 : Interactions excluding equivalent-position-0 described using Line C.

O1-O1 : Interactions described using beq's.

pdf_info displays the interactions in matrix form; for the above INP segment we have:

```
pdf_info
{
  - = No pdf_for_pairs defined hence beq's used
  0 = pdf_for_pairs defined with pdf_only_eq_0
  1 = pdf_for_pairs defined without pdf_only_eq_0
  2 = two pdf_for_pairs defined, one with and one without pdf_only_eq_0

     Al1    -2
     O1     2-
}
```

The matrix is in purple. pdf_for_pairs together with beq defaults offer great flexibility in describing peak widths. See PDF-1.INP, PDF-2.INP, BEQ-3.INP. scale_phase_X can be used to describe Gaussian dampening, for example:

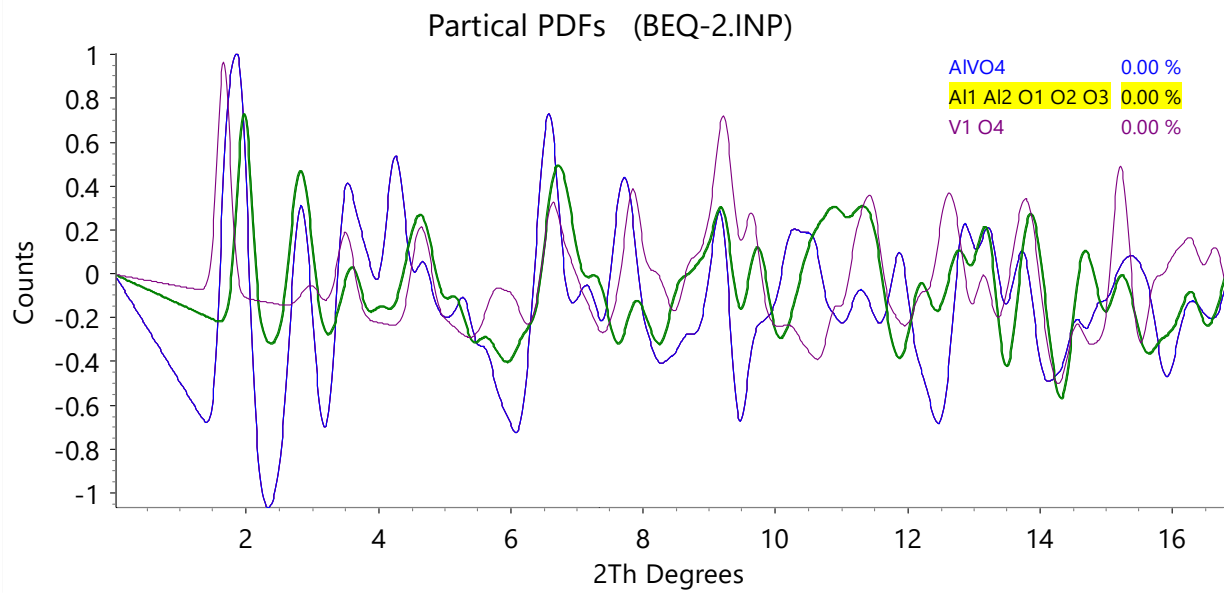
```
prm damp_fwhm 50 min 1e-6 max 200
prm damp = Gauss(0, damp_fwhm);
scale_phase_X = damp;
```

9.1..... Displaying partial PDFs

Partial PDFs can be dynamically displayed each iteration of refinement or at the end of refinement. A dummy structure mechanism is used as follows:

```
str…
    ' main PDF phase
dummy_str
    phase_name "Al1 Al2 O1 O2 O3"
    pdf_partial_1 "Al1 Al2 O1 O2 O3"
    pdf_partial_2 "Al1 Al2 O1 O2 O3"
    pdf_partial_when 0 ' Only at end of refinement
dummy_str
    phase_name "V1 O4"
    pdf_partial_1 "V1 O4"
        pdf_partial_2 "V1 O4"
    pdf_partial_when = Mod(Cycle_Iter, 2);
```

pdf_partial_1 and pdf_partial_2 are site identifying strings (see section 20.27) which can include the '*' wild card character and the negation character '!'. pdf_partial_when determines when to do the partial pdf calculation; the default value is non-zero which means the calculation is performed each iteration. A value of zero results in the calculation being performed at the end of refinement. The BEQ-2.INP example demonstrates this with the resulting GUI plot looking like:



9.2..... pdf_only_eq_0

Consider the space group *P*-1 with two equivalent positions, E0 and E1:

E0) x, y, z
E1) -x, -y, -z

The PDF comprises interactions between all atomic pairs. From symmetry, only interactions between E0 and the rest of the atoms are calculated. For a two-atom structure in *P-1*, with atoms A and B, the PDF comprises unique interactions between the following pairs:

A0-A0, A0-A1, A0-B0, A0-B1, B0-B0, B0-B1, B0-A1

Each interaction can be defined separately using a combination of beq and pdf_for_pairs. If the following is defined:

```
site A beq = a;
site B beq = b;
pdf_for_pairs A B                pdf_gauss_fwhm = ab;
pdf_for_pairs B B pdf_only_eq_0  pdf_gauss_fwhm = b0b0;
```

then the 7 types of interactions would have broadening as follows:

Pair	Gauss FWHM
A0-A0	Sqrt(a 2 Ln(2) / Pi^2)
A0-A1	Sqrt(a 2 Ln(2) / Pi^2)
A0-B0	ab
A0-B1	ab
B0-B0	b0b0
B0-B1	Sqrt(b 2 Ln(2) / Pi^2)
B0-A1	ab

For equivalent-position-0 and for distances within 10 Å then the following is required:

```
pdf_for_pairs * * pdf_only_eq_0
    pdf_gauss_fwhm = If(X < 10, something, 0);
```

pdf_info can be useful for specifying what is being used. Consider three sites A, B, C. For three sites there are (*N*^2+*N*)/2=6 types of atom-atom interactions:

A-A, A-B, A-C, B-B, B-C, C-C

Each of these can have broadening defined in three different ways, take A-A for example:

```
1)  site A ... beq
2)  pdf_for_pairs A A
3)  pdf_for_pairs A A pdf_only_eq_0
```

Use of pdf_only_eq_0 results in three types of A-A interactions:

i) interaction where none are equivalent position zero.

ii) interaction where both are equivalent position zero.

iii) interaction where one is equivalent position zero and the other not.

If case (2) is used then (i), (ii) and (iii) all use case (2); for example:

```
site A ... beq ... pdf_for_pairs A A ...
```

If case (3) is used, then beq is used for (i) and (iii) and case (3) is used for (ii); for example:

```
site A ... beq ... pdf_for_pairs A A pdf_only_eq_0...
```

If both case (2) and (3) are used then beq is ignored and case (2) is used (i) and (iii), and case (3) for (ii); for example:

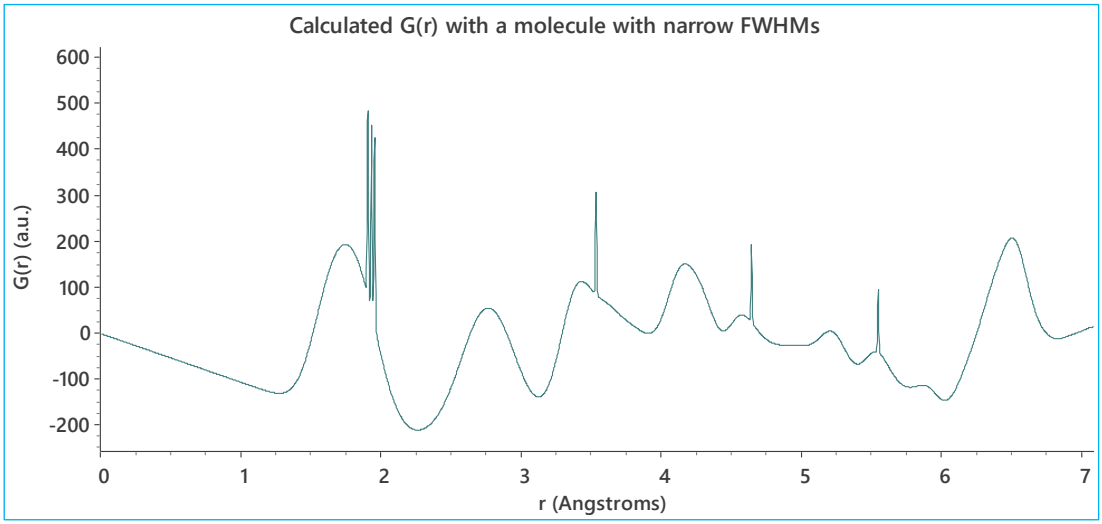
```
site A ... beq ...
    pdf_for_pairs A A...                ' (i) and (iii)
    pdf_for_pairs A A pdf_only_eq_0... ' (ii)
```

9.3..... Inter and Intra molecule FWHMs

pdf_for_pairs can be used to assign different interaction types between molecules. For example, to set the bond lengths for the atom Al1 of $AlVO_4$ (see PDF-2.INP) for equivalent-position-0 only, the following could be used:

```
prm intra_molec 0.01 min 1e-6
pdf_for_pairs Al1 "O1 O2 O3 O4 O5 O6" pdf_only_eq_0
    pdf_gauss_fwhm = intra_molec;
```

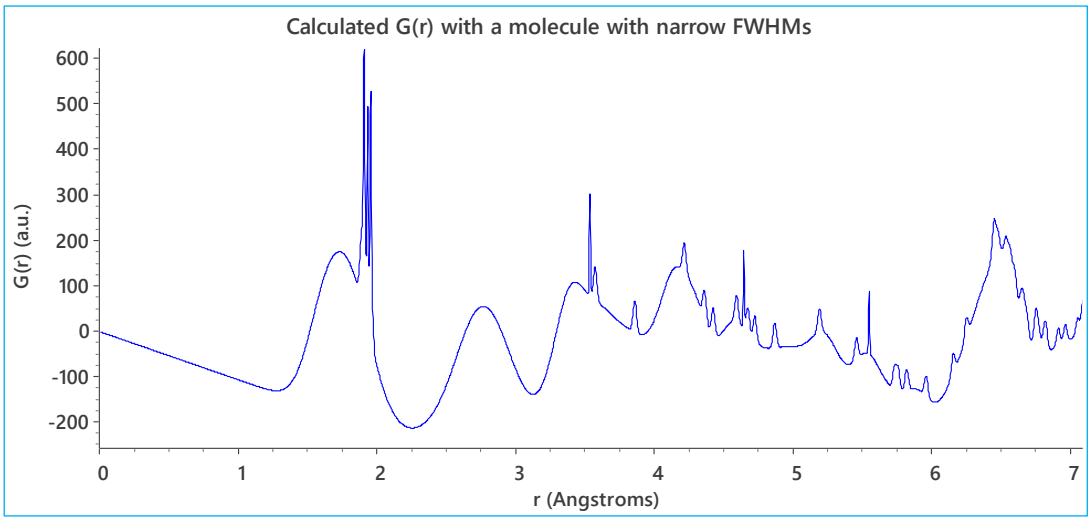
The calculated pattern from PDF-2.INP therefore becomes:



Notice the 6 spikes; they correspond to the Al1 bonds with narrow FWHMs. If we wanted Al1 bonds that are not equivalent-position-0 to be different to the beq's then we could use:

```
prm inter_molec 0.1  min 1e-6
prm intra_molec 0.01 min 1e-6
pdf_for_pairs Al1 "O1 O2 O3 O4 O5 O6" pdf_only_eq_0
    pdf_gauss_fwhm = intra_molec;
pdf_for_pairs Al1 "O1 O2 O3 O4 O5 O6"
    pdf_gauss_fwhm = inter_molec;
```

This gives the following calculated pattern where we see the various Al1 bonds.



The corresponding output from pdf_info becomes:

```
pdf_info
{
- = No pdf_for_pairs defined
0 = pdf_for_pairs defined with pdf_only_eq_0
1 = pdf_for_pairs defined without pdf_only_eq_0
2 = two pdf_for_pairs defined, one with pdf_only_eq_0 and one without pdf_only_eq_0

   Al1    ------222222------
   Al2    ------------------
   Al3    ------------------
   V1     ------------------
   V2     ------------------
   V3     ------------------
   O1     2-----------------
   O2     2-----------------
   O3     2-----------------
   O4     2-----------------
   O5     2-----------------
   O6     2-----------------
   O7     ------------------
   O8     ------------------
   O9     ------------------
   O10    ------------------
   O11    ------------------
   O12    ------------------
}
```

An exception is thrown if the same interaction is referenced in more than one pdf_for_pairs, for example, the following will throw an exception as Al1-O1 is referenced twice:

```
pdf_for_pairs Al1 "O1 O2 O3 O4 O5 O6" pdf_only_eq_0 ...
pdf_for_pairs Al1 O1 pdf_only_eq_0 ...
```

The following will not throw an exception:

```
pdf_for_pairs Al1 "O1 O2 O3 O4 O5 O6" pdf_only_eq_0 ...
pdf_for_pairs Al1 O1 ...
```

9.4..... Instrument Sinc function sinc-1.inp

In SINC-1.INP, pdf_convolute is used at the xdd level to convolute a Sinc function into phases:

```
pdf_convolute = Sin(Qmax X+q3)/If(Abs(X) < 0.5 Step_Size, If(X < 0,-q2,q2),X);
   min_X = -conv_max;
   max_X =  conv_max;
```

SINC-1.INP also uses an xo_Is phase defined as:

```
xo_Is
   NoThDependence(0.0001)
   xo 10 I @ 100
   peak_type pv
      pv_lor 0.5
      pv_fwhm 2
```

pdf_convolute operates on PDF type phases only; the xo_Is phase is untouched. Note the phase dependent use of an emission profile as defined in the NoThDependence macro. Multiple pdf_convolute's can be described at the global, xdd, str and pdf_for_pairs levels. Use of pdf_convolute as a dependent of pdf_for_pairs is slower than at the other levels; thus where possible use pdf_convolute outside of pdf_for_pairs.

9.5..... Weighting of PDF and 2-Theta type data

PDF and 2θ data can be of very different intensities; xdd_sum can be used to modifying the weighing of these data to give approximately similar weights to the patterns. For example:

```
xdd file1.xy
   xdd_sum !sum1 = Abs(Yobs);
   weighting = 1 / sum1;
xdd file2.xy
   xdd_sum !sum2 = Abs(Yobs);
   weighting = 1 / sum2;
   pdf_data
```

9.6..... Test_examples\pdf\beq-2.inp

BEQ-2-CREATE.INP generates a simulated pattern for BEQ-2.INP which:

- comprises the structure of $AlVO_4$,
- 3 types of beq parameters,
- beq is a function of *X* (ie. *X* = r) and hence peak widths are a function of *X*,
- demonstrates the use of pdf_zero,
- demonstrates the use of rebin_with_dx_of and rebin_start_x_at.

9.7..... Test_examples\pdf\beq-3.inp

BEQ-3-CREATE.INP generates a simulated pattern for BEQ-3.INP; it demonstrates the use of pdf_for_pairs.

9.8..... Speeding up refinement with rebin_with_dx_of

Increasing the x-axis step size of PDF data can speed up refinements; see BEQ-2.INP. The step size must be of equal size and the start of the x-axis needs to be an integral multiple of the step size. Data can therefore be rebinned to increase step size as follows:

```
    macro Rebin_Step    { 0.015 }
    rebin_with_dx_of Rebin_Step rebin_start_x_at Rebin_Step
```

Rebinning is akin to collecting the data at a larger step size. All data is included; counts after rebinning is equal to counts before rebinning. *esd*'s associated with the data are also rebinned. rebin_start_x_at can be used to place the start of the data at an integral multiple of the step size. In BEQ-2.INP parameters such as scale are written in terms of the rebin step size to reflect the fact that the scaling of the data is changed due to rebinning.

9.9..... Refining on beq parameters

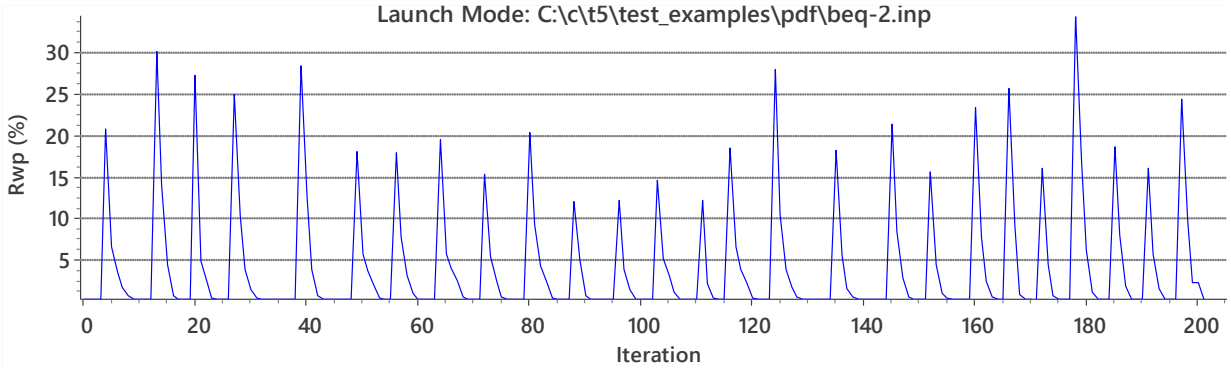
Modify the BB macro so that its empty as in the following:

```
macro BB {  } ' Enter ! to not refine, beq including low angle fwhm sharpening
```

This results in refinement of four independent beq parameters including the low angle sharpening parameter of erf_a as seen in the following:

```
macro Beq(c, v)
    {
        #m_argu c
        If_Prm_Eqn_Rpt(c, v, min 1e-6 max 10 val_on_continue = Rand(.1, 2); )
        beq = CeV(c, v) Erf_Approx( erf_a X);
    }
```

The Rwp plot is:



This type of convergence is indicative of correct derivative calculation. Convergence for coordinates, occupancies, lattice parameters and pdf_zero are similar.

9.10 ... Refining on ADPs in PDF refinement – Uij parameters

site... occ Zr 1 u11 @ .01 u22 @ .01 u33 @ .01 u12 @ 0 u13 @ 0 u23 @ 0
adps_scale @ 1

ADPs can now be used and refined in PDF refinement. The syntax is similar to reciprocal space refinement where the apds keyword, when used, generates the ADP parameters, for example, the following:

```
site Zr1 x # y # z # occ Zr 1 apds
```

becomes:

```
site Zr1 x # y # z # occ Zr 1 ADPs { u11 # u22 # u33 # u12 # u13 # u23 # }
```

This implementation is similar to PDFGui (Farrow *et al.*, 2007) where peaks are Gaussian even at low-*r*. ADP parameters will therefore correct for peak width but not asymmetry. Asymmetry does occur however and is noticeable when atomic displacement geometry is extreme.

adps_scale allows for the scaling of the Uij parameters and it can be a function of *X* where *X* corresponds to the distance between atoms.

```
prm !delt1 0.75 min 1e-6 max 5
prm !delt2 0 min 1e-5 max 1
prm !Qb  0.05 min 1e-6 max 1
prm aa 1 min 1 _v = Rand(0.5, 1.5);
adps_scale = 2 aa (Abs(1 - delt1 / X - delt2 / X^2 + (Qb^2) X^2));
```

The FWHM of a PDF peak for atom *i* and *j* is given by:

$$FWHM_{ij} = Sqrt(adp\_scale_i\ U_{cart,i} + adp\_scale_j\ U_{cart,j})$$

where U_{cart} is U_{ij} in cartesian coordinates. _v is an alternative to val_on_continue.

9.11 ... Multiatom approach to ADPs in PDF refinement

macro ADP_5 and ADP_7 See file PDF-ADPS.INC	**Examples** TEST_EXAMPLES\PDF-ADPS\ APPROX-1.INP FIT_TO_GR.INP

In many cases, anisotropic displacement parameters in PDF refinement can be described using 5 or 7 beq type sites, we will call these descriptions ADP_5 and ADP_7. ADP_5 comprises 7 parameters instead of the normal 6 unn parameters. These ADP_5 parameters can be transformed to unn parameters by fitting unn parameters to a pattern created from the ADP_5 parameters. The fit is reasonable considering the unn model has only 6 parameters. Some main points when using ADP_5 in PDF refinement:

- Number of ADP parameters become 7 instead of 6.

- Broadening due to ADPs in G(r) is implied.
- Asymmetry at low r is implied.
- This approach works in Version 7 (albeit slower)

Asymmetry seen at low r is typically difficult to model; the ADP_n approach however implicitly contains asymmetry. The computational effort increases as there are 7 atoms per ADP site; this is offset by the very fast calculation of PDF patterns using beq type sites. The file PDF-ADPS.INC contains the macros necessary for describing ADPs-7. APPROX-1.INP demonstrates the ability of the ADPs-7 approach to describe unn models in reciprocal space. It has three modes of operation:

1) CREATE_USING_unns: creates a simulated single crystal pattern from normal unn parameters for one atom. neutron_data is used the effects of atomic scattering factors.
2) FIT_USING_ADPs_5: fits to the simulated pattern using the ADPs-7 approach. This refinement then saves the calculated ADPs-7 pattern created to a file called SIM-2.HKL.
3) DETERMINE_unns_FROM_ADPs_5: fits normal unn parameters to SIM-2.HKL.

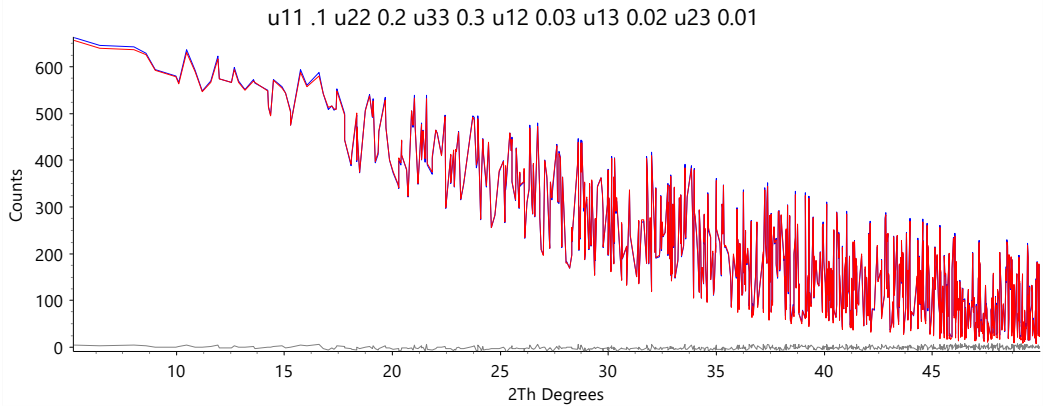
ADP_5 sites are described in the ADP_5 macro, and it looks like:

```
macro ADP_5_0(s, &x0, &y0, &z0, atom, &o, &x1, &y1, &z1, &x2, &y2, &z2, &bo)
{
site s x = x0;  y = y0;  z = z0;  occ atom = 0.2 o; beq = bo;
local #m_unique ns = Get(num_posns);
site s##_1p x = x0+x1; y = y0+y1; z = z0+z1; occ atom = 0.2 (ns / Get(num_posns)) o; beq = bo;
site s##_2p x = x0+x2; y = y0+y2; z = z0+z2; occ atom = 0.2 (ns / Get(num_posns)) o; beq = bo;
site s##_1m x = x0-x1; y = y0-y1; z = z0-z1; occ atom = 0.2 (ns / Get(num_posns)) o; beq = bo;
site s##_2m x = x0-x2; y = y0-y2; z = z0-z2; occ atom = 0.2 (ns / Get(num_posns)) o; beq = bo;
}
```

Two extreme cases have been performed; results for the first case, the refined and original Uij parameters are:

```
   ADPs {  0.39524 0.39690  0.40143 -0.18277 -0.19009 -0.19268 } ' refined
   ADPs {  0.4     0.4      0.4     -0.19    -0.19     -0.19 }   ' original
```

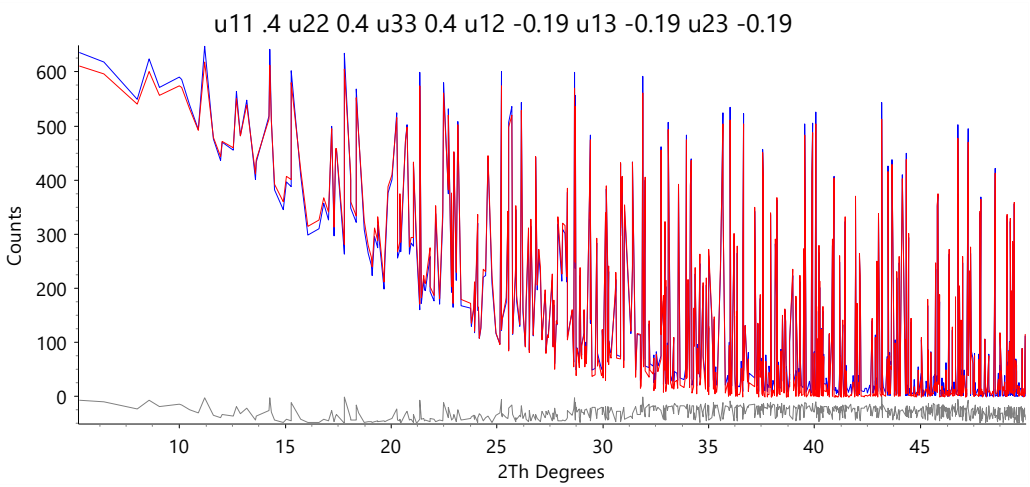
The refined values, from the DETERMINE_unns_FROM_ADPs_7 operation, shows good agreement with the original values. The FIT_USING_ADPs_7 operation produces a fit that looks like:



A further extreme example is:

```
ADPs {  0.39524 0.39690  0.40143 -0.18277 -0.19009 -0.19268 } ' refined
ADPs {  0.4     0.4      0.4     -0.19    -0.19     -0.19 }   ' original
```

The FIT_USING_ADPs_5 operation produces a fit that looks like:



9.11.1.1..... Multiatom approach to ADPs – fitting to G(r) patterns

This section generates describes the a reciprocal space pattern using unn parameters, then generates a G(r) pattern from the simulated data. Then fits to the G(r) pattern using either ADP_5 or Uij parameters. Additionally, a reciprocal space patterns can then be simulated using the fitted ADP_5 parameters and then finally the loop is complete with a unns fit to the reciprocal space pattern. The final unn parameters should match the original unn parameters reasonably well. The control parameters are as follows:

```
#prm generate_recip_space_pattern = 1;
#prm generate_Gr_created_from_sine_transform = 0;
#prm generate_Gr_calc_using_Uij = 0;
#prm ADP_5_fit_to_Gr_calc_using_Uij = 0;
#prm ADPs_fit_to_Gr_calc_using_Uij = 0;
#prm ADP_5_fit_to_Gr_created_from_sine_transform = 0;
#prm ADPs_fit_to_Gr_created_from_sine_transform = 0;
#prm create_recip_ADP_5_fit_to_Gr_calc_using_Uij = 0;
#prm create_recip_ADP_5_fit_to_Gr_created_from_sine_transform = 0;
#prm Fit_create_recip_ADP_5_fit_to_Gr_calc_using_Uij = 0;
#prm Fit_create_recip_ADP_5_fit_to_Gr_created_from_sine_transform = 0;
macro Append_to_File_Name { 1 } ' anything here to identify output files created
#prm include_resolution_broadening = 1;
```

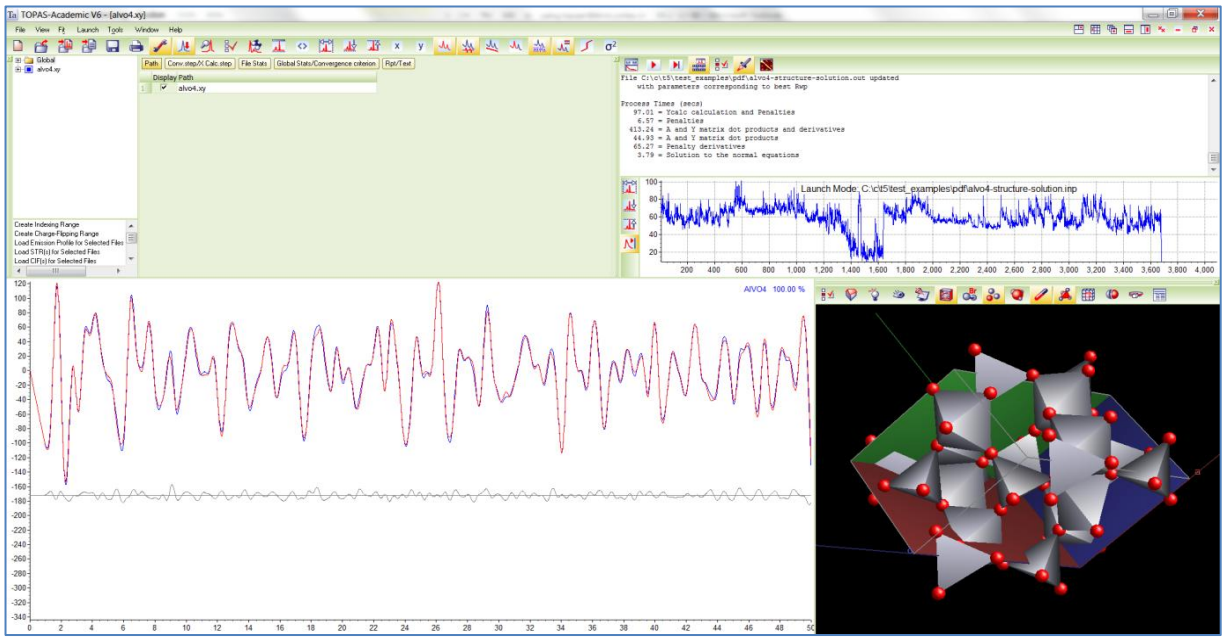
These need to be executed one at a time and in sequence; they should be self-explanatory. The main point is that the sine transform pattern created using generate_Gr_created_from_sine_transform comprises asymmetry whereas the calculated G(r) created using generate_Gr_calc_using_Uij does not. The former can be considered the ‘true’ G(r) pattern. Also of importance is that the pattern created using generate_Gr_created_from_sine_transform is generally better fitted using ADP_5 (or ADP_7) using than when using ADPs_fit_to_Gr_created_from_sine_transform. The reason is that the latter does not include asymmetry.

9.12 ... Structure Solution, Simulated Annealing

PDF\ALVO4\STRUCTURE-SOLUTION-CREATE.INP creates a simulated pattern for STRUCTURE-SOLUTION.INP. It's a simulated annealing refinement with all coordinates starting at zero and with anti-bump penalties applied using:

```
AI_Anti_Bump(O* , O* , 2.4, 1, 5)
AI_Anti_Bump(Al*, O* , 1.6, 1, 5)
AI_Anti_Bump(Al*, Al*, 2.8, 1, 5)
```

The correct solution is found as seen in the following:



The range of convergence for atomic coordinates are smaller than with reciprocal space as in normal Rietveld refinement. This is because the coordinates, in the PDF case, changes peak positions rather that peak intensities; with the former having a narrow range of convergence. It may be possible to increase the range of convergence for the PDF case by increasing the peak widths; this however comes at the expense of resolution and may also result in an even smaller range of convergence.

9.13 ... Rigid bodies with PDF data

PDF\ALVO4\RIGID.INP operates on simulated data created by STRUCTURE-SOLUTION-CREATE.INP. It demonstrates the use of rigid bodies with PDF data.

9.14 ... Occupancy merging with PDF data

PDF\OCC-MERGE-PBSO4\OCC-MERGE.INP operates on simulated data created by CREATE.INP. It demonstrates the use of occ_merge with PDF data.

9.15 ... Equivalence of pdf_gauss_fwhm and beq for one atom type

PDF\SI1.INP comprises an option to use beq or pdf_gauss_fwhm. For the beq case we have:

```
beq = width;
```

and for pdf_gauss_fwhm we have:

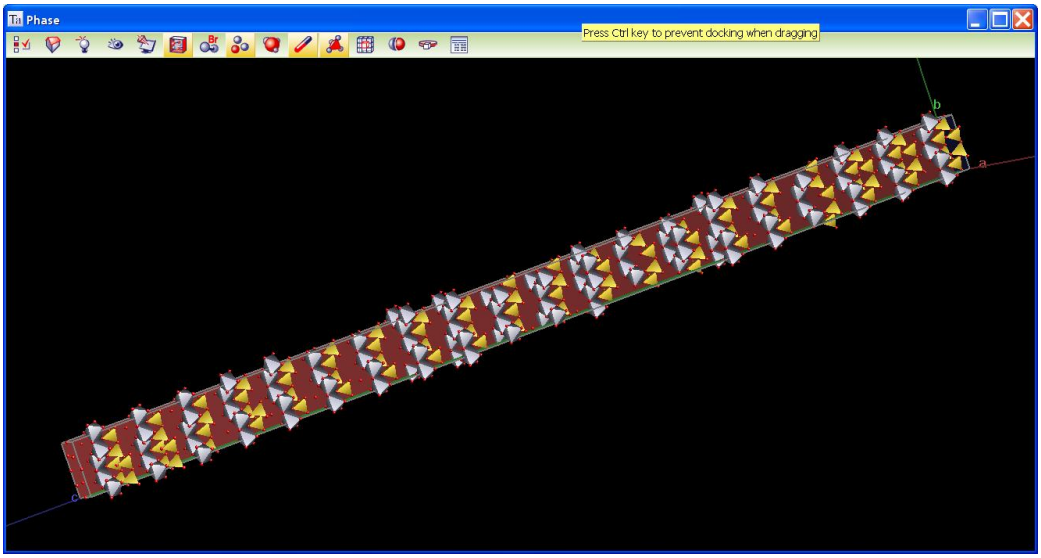
```
pdf_gauss_fwhm = Sqrt(width 2 Ln(2) / Pi^2);
```

The above cases are equivalent when all atoms are of the same type.

10. STACKING FAULTS

[site $name]...
    [layer $layer]
[stack $layer]...
    [sx E] [sy E] [sz E]
    [generate_these $sites]
        [generate_name_append $append_to_site_name]

The super cell approach to stacking faults has been implemented. layer identifies a site as belonging to a layer called $layer; stack applies a stacking vector { sx, sy, sz } to the named layer. Structures factors are generated in the usual manner with a shift applied corresponding to the stacking vector. stack operates in any space group. Sites that do not belong to a layer are treated as un-stacked and their structure factors are generated in the usual manner. generate_these generates the sites found in $sites for the stack with coordinates that reflect original $sites positions plus the stacking vector. generate_name_append appends $append_to_site_name to the generated site. The generated sites have occupancies set to zero which signals a dummy site. Dummy sites do not take part in structure factor calculations and hence speed is not hindered. The dummy sites allow for graphical display of the layers, i.e.



Importantly, penalties can operate on dummy sites which allow for restraints such as Distance_Restrain. The following rules govern the behaviour of sites marked with layer:

- A site marked with layer cannot take part in restraints.
- A site marked with layer is not displayed graphically.
- A site generated using generate_these can take part in restraints.
- A site not marked with layer can take part in restraints.

For example:

```
space_group P1
site O1 ... layer A
site O2 ... layer A
```

```
stack A
    sx ...
    generate_these 01
        generate_name_append _1
append_fractional
    in_str_format
```

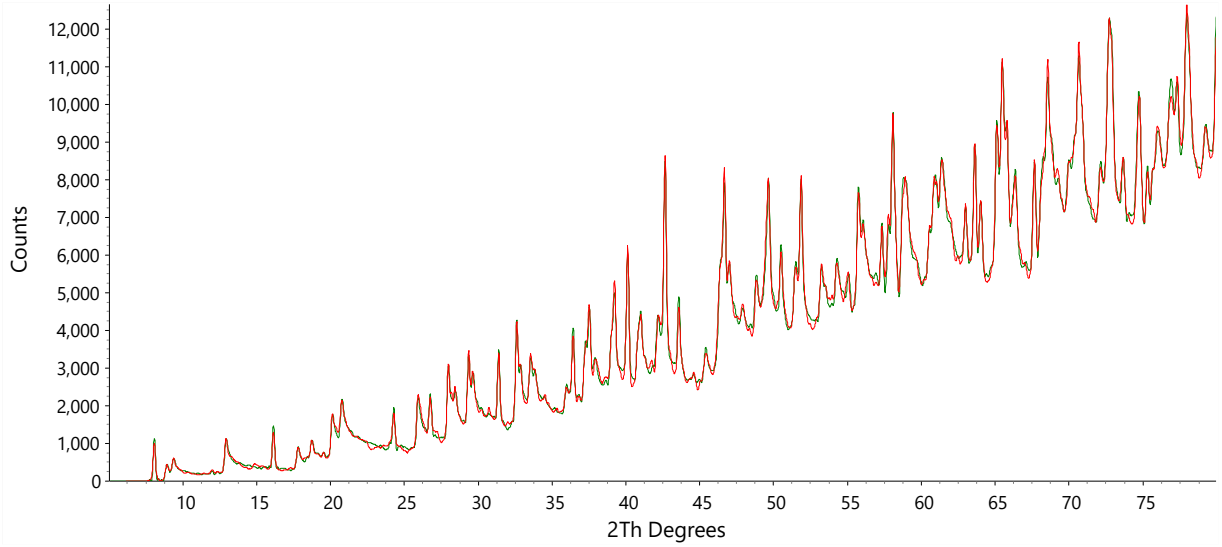
will output for append_fractional the following:

```
site 01 ...
site 02 ...
site 01_1 ... occ 0 0
```

The TEST_EXAMPLES\STACKING-FAULTS\KAOLINITE.INP shows how to simplify the setting up of layers with the use of simple macros. Speed of calculation for structure factors are very fast and the derivatives of the stacking vectors { sx, sy, sz } are very fast. The main bottle neck in speed is summing the peaks to *Ycalc*. The switch "*#define* Speed" in KAOLINITE.INP shows keywords that can speed things up in the early stages of determining the stacking vectors.

10.1 ... Fitting to a Debye-formulae pattern using 'stack'

A test pattern was generated using the Debye scattering equation. The structure comprised a single atom in an Orthorhombic unit cell with 40 layers (40x40x40 unit cells) in the a-b plane shifted according to {Round(Rand(0,2))/3, Round(Rand(0,2))/3, 0}. The blue line in the following is the generated pattern comprising the average of 30 runs of the Debye scattering equation. The red line corresponds to a Rietveld fit of 6 super cell structures (1x1x40) showing that the super cell approach is a good approximation to the Debye formulae for this example.



The example STACKING-FAULTS\DEBYE-NEW.INP corresponds to the Rietveld fit using the layer and stack keywords. The DEBYE-OLD.INP file corresponds to the same Rietveld fit but without the layer and stack keywords; instead, layers are explicitly defined using site in an enlarged unit cell.

There are two time-consuming bottle necks dealt with:

1) Summing peaks to *Ycalc*
2) Calculating structure factors for the stacked layers

The phase dependent [del_approx #] groups peaks from the peaks buffer whilst summing peaks to *Ycalc*; the peaks are grouped such that their 2Th positions all lie within:

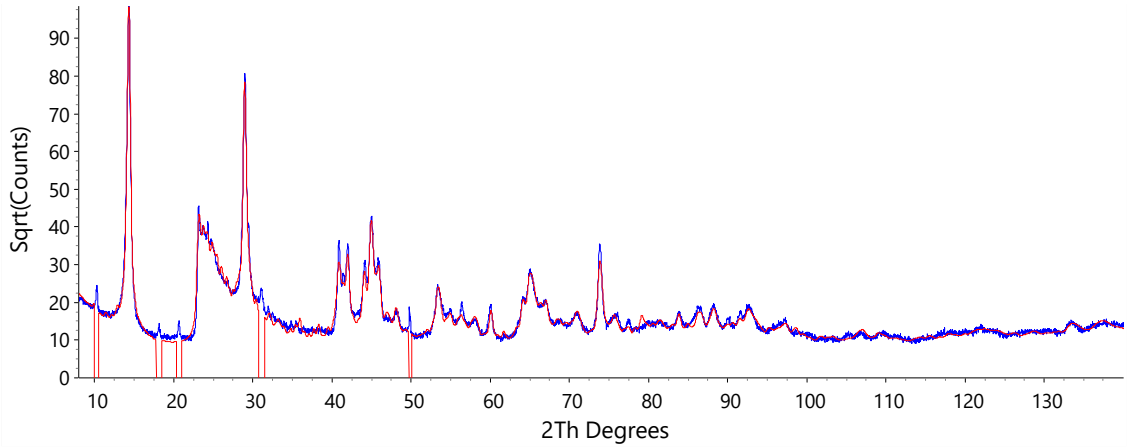
$$(-\text{del\_approx}\ \textit{Peak\_Calculation\_Step}) < 2\,\textit{Th} < (\text{del\_approx}\ \textit{Peak\_Calculation\_Step})$$

Once the group is found then only the two peaks with the smallest and largest 2Th is kept. The in-between peaks have their intensities appropriated to the kept peaks. The peak buffer stretching routines have also been optimized for both accuracy and speed. The following points should be noted when working with large super cells

- The layer and stack keywords increase computational speed and reduce memory usage.
- del_approx increase computation speed at a relatively small cost to accuracy; a value between 1 and 3, dependent on *Peak_Calculation_Step*, is typically acceptable.
- The graphical display of 10s of 1000s of hkl ticks (there's 51584 hkls in each phase of the DEBYE-NEW.INP) is time consuming; turning the graphical hkl-ticks option Off is worthwhile.

10.2 ... Fitting to Kaolinite data

STACKING-FAULTS\KAOLINITE.INP demonstrates the application of stack and layer with the following fit:



In this example the stacking vectors are refined in a simulated annealing process.

10.3 ... Stacking faults and generating sequences of layers

```
[generate_stack_sequences] {
    [number_of_sequences !E]
    [number_of_stacks_per_sequence !E]
    [save_sequences $file]
    [save_sequences_as_strs $file]
    [user_defined_starting_transition $tran-
        sition_name]
    [layers_tol !#0.5]
    [n_avg !E]
    [num_unique_vx_vy !N]
    [match_transition_matrix_stats {...}]
    [transition $transition_name]...
        [use_layer $layer]
        [height E]
        [n !N]
        [to $to_transition_name !E]...
            [ta E] [tb E] [tz E]
            [a_add E] [b_add E] [z_add E]
}
' Get(generated_c)
```

Examples

```
TEST_EXAMPLES\STACKING_FAULTS\
    FIT-1.INP
    FIT-2.INP
    FIT-3.INP
    RIETVELD-GENERATE\
        CREATE-SEQUENCES.INP
        RIETVELD-GENERATE.INP
        FIT-TO-RIETVELD-GENERATED.INP
        RIETVELD-GENERATED-200-2000.XY
        STRS-200-2000.TXT
```

Stacking fault generation and refinement can now be performed at speeds that make routine analysis possible (Coelho *et al.*, 2016). generate_stack_sequences generates sequences of stacks from the transition matrix described by the transition keyword. The opening and closing braces of { ... } corresponds to a block where keywords local to generate_stack_sequences can be used. Outside of the braces the generate_stack_sequences can't be used. After generation of the sequences, Get(generated_c) is updated with the average thickness of the generated sequences. It can be used to set the c lattice parameter.

On termination of refinement, num_unique_vx_vy reports on the number of unique { sx, sy } stacking vector coordinates for all layer types. transition defines a 'from' transition with the name $transition_name. The transition uses the layer defined in use_layer. to defines the to-transition. $to_transition_name must be a defined $transition_name. n returns the number of transitions generated for the corresponding to to-transition. height: can be used instead of z_add keywords. ta, tb: defines the stacking vector x and y coordinates in terms of the crystallographic **a** and **b** axes. a_add, b_add: defines the stacking vector x and y coordinates relative to the previous stacking vector in terms of the crystallographic **a** and **b** axes. tz: defines stacking vector z coordinate along the crystallographic **c** axis in Å. add_z: defines stacking vector z coordinate along the crystallographic **c** axis in Å relative to the previous stacking vector.

user_defined_starting_transition: if used, stacking begins at the transition with the name of $transition_name. Otherwise, stacking begins at the transition with the greatest probability according to the probability density matrix. layer_tol corresponds to *q* of Fig. 1 in the paper (Coelho, 2016); it describes the termination condition when generating the stacking sequence.

10.3.1 ..... Generating the same stacking sequences each run

The random number generator can be seeded with a constant seed using seed to generate the same set of stacking sequences each run, for example:

```
seed #number
```

#number is a constant integer. Each #number generates its own unique set of random numbers. Generating identical sets of stacking sequences is useful when changes in R_{wp}, that excludes stacking sequence variation, is required.

10.3.2 ..... The SF_Smooth macro

Stacking faulted calculated patterns can contain ripples when the peak shapes are small or when there are too few layers stacked. The SF_Smooth macro, defined in TOPAS.INC smooths these ripples such that small supercells can approximate large supercells; this increases computation speed and reduces memory usage. All stacking fault examples use SF_Smooth; typical usage is:

```
SF_smooth(@, 1, 1)
```

The refined parameter adjusts the width of a Gaussian convolution that is dependent on hkls and the intensities of the reflections. The last argument *s* (the '1') can be used to adjust the tolerance of peak_buffer_based_on used in the SF_Smooth macro; the definition of the latter is:

```
peak_buffer_based_on = idl;
    peak_buffer_based_on_tol = Max(0.01 idl, Peak_Calculation_Step 0.5 s);
```

Reducing *s* increases the number of peaks in the peaks buffer and increases the accuracy of the calculated pattern. *s*=1 is typically sufficient.

10.3.3 ..... Fitting to DIFFaX test diamond data

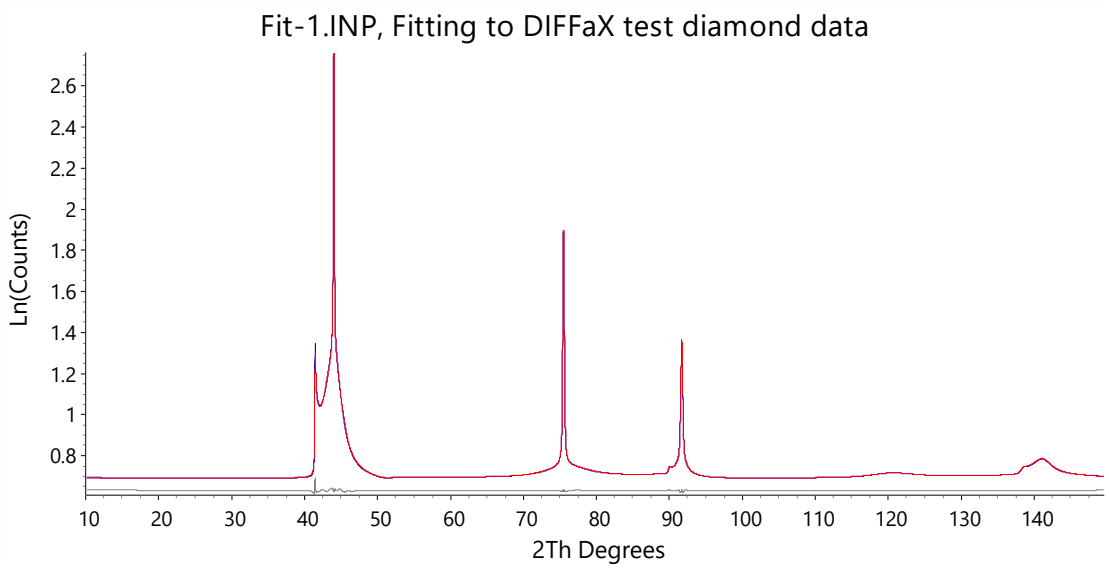
FIT-1.INP uses generate_stack_sequences to fit to data generated from the DIFFaX suite (Treacy, 1991); the INP segment that generates the sequences looks like:

```
generate_stack_sequences {
   number_of_sequences Nseqs 200
   number_of_stacks_per_sequence Nv 200
   num_unique_vx_vy  6
   Transition(1, lpc)
      to 1 = pa;     a_add = 2/3;  b_add = 1/3;   n !n1  349984
      to 2 = 1-pa;   a_add = 0;    b_add = 0;     n !n2  149781
   Transition(2, lpc)
      to 1 = 1-pa;   a_add = 0;    b_add = 0;     n !n3  149781
      to 2 = pa;     a_add = -2/3; b_add = -1/3;  n !n4  350254
}
```

The generated probability parameter pa can be determined using the n values as follows:

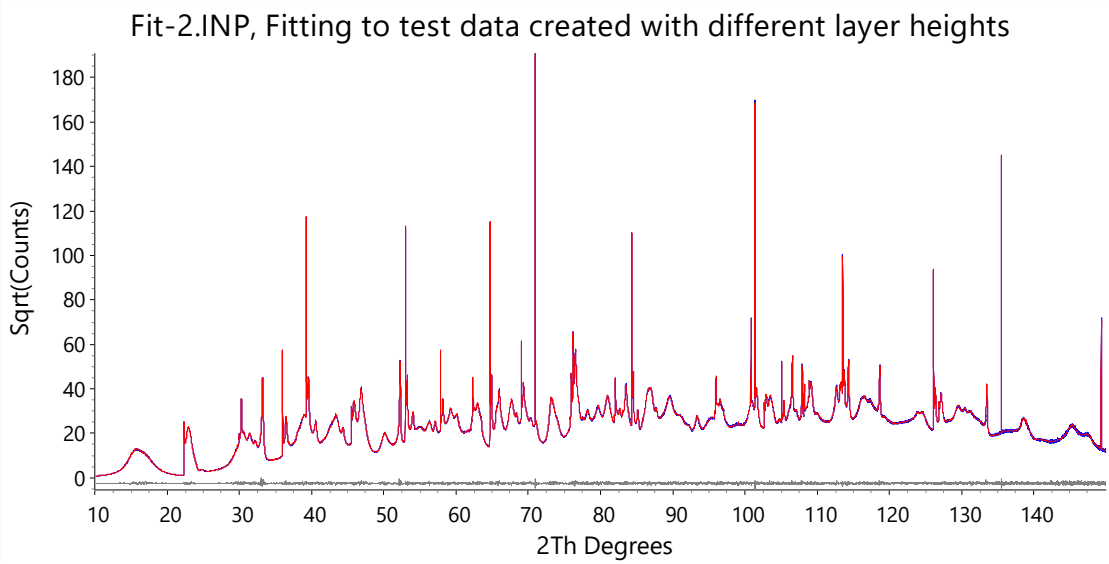
```
prm !pa_gen = (n1+n3)/(n1+n2+n3+n4); : 0.699974874
```

The fit to the DIFFaX data looks like:



10.3.4 ..... Stacking faults from layers of different layer heights

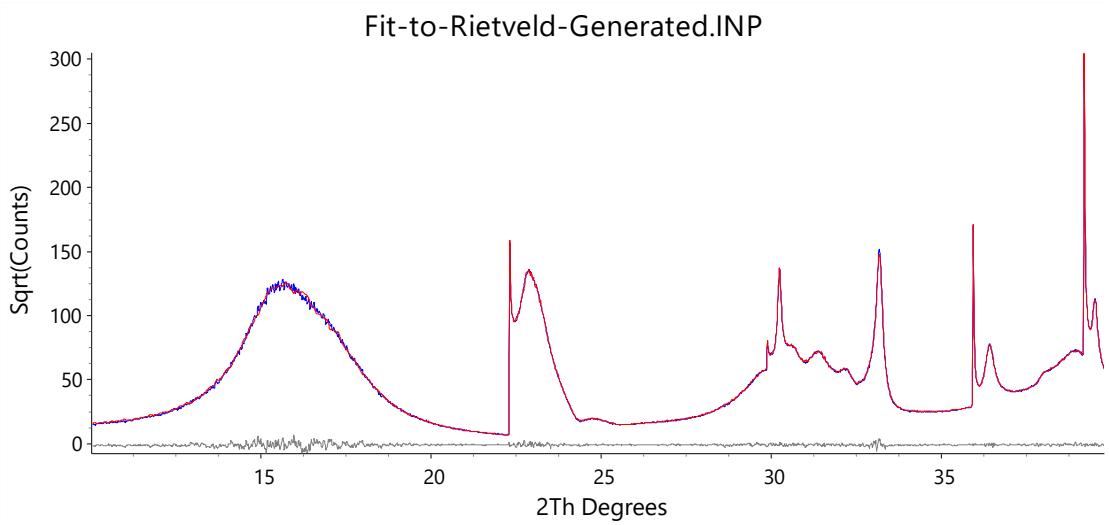
Layers of different thicknesses can be accurately modelled and with fast refinement. Here's a fit to simulated data (FIT-2.INP) for two different layer heights of 5 and 6Å.



10.3.5 ..... Rietveld-Generated example

The files in the RIETVELD-GENERATE directory can be used to create a stacking faulted test pattern using Rietveld refinement; the test pattern can then be refined against. CREATE-SEQUENCES.INP creates the INP format stacking sequences and places the result in the file STRS-200-2000.TXT. The file RIETVELD-GENERATE.INP can be used to create the test pattern RIETVELD-GENERATED-200-2000.XY. This test pattern can be fitted-to using FIT-TO-RIETVELD-GENERATED.INP; this INP file uses generate_stack_sequences and it demonstrates the

accuracy and speed of the stacking fault averaging procedure. The fit to the Rietveld generated stacking faulted pattern looks like:



10.3.6 ..... Refining on layer heights

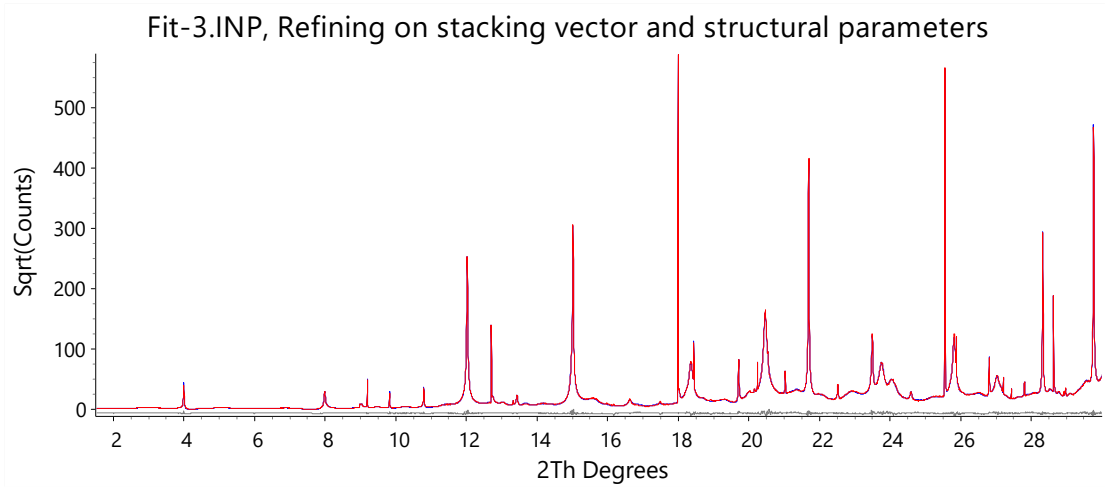
Layer heights can be refined by refining on parameters that are a function of the add_z or height keywords. The FIT-3.INP example refines on 3 height parameters as well as the z fractional atomic coordinates of the sites that comprise the layers. It also lists six types of transitions which operate on three unique layer types. The transitions points to the unique layer types using use_layer. The c lattice parameter is defined and refined using the following:

```
prm qq 0 c = Get(generated_c) + 0.0001 qq; : 1828.085117
```

Get(generated_c) is also used to initialize the z fractional coordinates of the sites as follows:

```
prm height_Se01 7.49691
prm !zSe01 = height_Se01 / Get(generated_c);
site Se01 x 0.5 y 0 z = zSe01; occ Se 1 beq !bval 1 layer cd00
```

The fit to the test data looks like:



11. QUANTITATIVE ANALYSIS

```
[xdd]...
    [mixture_MAC #]
    [mixture_density_g_on_cm3 #]
    [weight_percent_amorphous !E]
    [elemental_composition]
    [element_weight_percent $atom $Name #]...
    [element_weight_percent_known $atom #]...
    [prm = Get(sum_smvs)...]
    [prm = Get(mixture_MAC)... ]
    [prm = Get(mixture_density_g_on_cm3) ... ]
    [Mixture_LAC_1_on_cm(0)]
    [str]...
        [cell_mass !E] [cell_volume !E] [weight_percent !E]
            [spiked_phase_measured_weight_percent !E] [corrected_weight_percent !E]
        [phase_MAC !E]
        [prm = Get(sum_smvs)... ]
        [prm = Get(smv)... ]
        [prm = Get(sum_smvs_minus_this)... ]
        [prm = Get_Element_Weight(atom)... ]
        [Phase_LAC_1_on_cm(0)]
        [Phase_Density_g_on_cm3(0)]
```

Examples in TEST_EXAMPLES\QUANT

11.1 ... Summary of Quant examples

- QUANT-1.INP: shows the use of element_weight_percent_known etc.
- QUANT-2.INP: uses the Known_Weight_Percent macro
- QUANT-3.INP: uses elemental constraint using Get_Element_Weight
- QUANT-4.INP: uses Known_Weight_Percent on a hkl_Is phase.
- QUANT-5.INP: uses a dummy_str to describe an amorphous phase
- QUANT-6.INP: uses a hkl_Is phase; links a dummy_str to the hkl_Is phase.
- QUANT-7.INP: uses a fit_obj that is a function of a user_y object to describe a phase; links a dummy_str to a fit_obj to get QUANT info.

QUANT implementation, to a large extent, is written internally using the TOPAS Symbolic system; this allows great flexibility. Dependencies are determined automatically and unnecessary recalculations kept to a minimum. QUANT-1.INP uses many of the above keywords and additionally writes equivalent terms in the form of equations, for example:

```
prm = 100 Get(smv) / Get(sum_smvs); : 0 ' This is weight_percent

prm q = spiked_phase_measured_weight_percent /
        spiked_phase_measured_weight_percent_wt; : 0

prm = q Get(weight_percent); : 0   ' This is corrected_weight_percent
prm = 100 (1 - q); : 0             ' This is weight_percent_amorphous
```

11.2 ... Elemental weight percent constraint

If an elemental weight percent was known, and three phases of the mixture comprised this element then Get_Element_Weight can be used to get the weight of the element as a function of the structure, i.e.

```
str ...
    prm z1 = Get_Element_Weight(Zr);
    MVW(!m1 0, !v1 0,0)
str ...
    scale s2 0.001
    prm z2 = Get_Element_Weight(Zr);
    MVW(0, !v2 0,0)
str ...
    scale s3 0.001
    prm z3 = Get_Element_Weight(Zr);
    MVW(0, !v3 0,0)
```

Rearranging the formulae for element weight percent, the scale parameter of one of the phases, say the first one, can be written as:

```
scale = (0.01 known_Zr Get(sum_smvs_minus_this) - s2 v2 z2 - s3 v3 z3)
        / (v1 (z1 - 0.01 known_Zr m1));
```

Get(sum_smvs_minus_this) returns the sum of SMVs minus the phase where it is defined. QUANT-3.INP demonstrates this constraint with good convergence. It comprises 4 phases with three comprising Zr atoms. QUANT-2.INP demonstrates constraining a weight percent to a known value using the macro:

```
macro Known_Weight_Percent(& w)
{
    scale = (w / (100 - w)) Get(sum_smvs_minus_this) / (Get(cell_mass) Get(cell_volume));
}
```

11.3 ... Elemental composition and Restraints

The xdd dependent elemental_composition reports on the elemental composition of atoms within the structures of the xdd, for example:

```
' Before refinement
xdd ...
    elemental_composition
```

```
' After refinement
xdd ...
    elemental_composition
        {
                              Rietveld
           AL              0.875`_0.021
           O              26.135`_0.009
           SI              0.090`_0.003
           Y               6.289`_0.012
           ZR             66.612`_0.029
        }
```

The xdd dependent elemental_weight_percent returns the weight percent of an element within the corresponding str's of the xdd. Example usage:

```
    ' Before refinement
    penalties_weighting_K1 0.1
    xdd ...
        element_weight_percent Zr+4 zr  0
        restraint = (zr - 65); : 0
```

```
    ' After refinement
    penalties_weighting_K1 0.1
    xdd ...
        element_weight_percent Zr+4 zr 65.027
        restraint = (zr - 65); : 0.027525
```

In this example, zr is the name given to the element Zr+4, the restraint shows a known value of 65 (set for example by XRF results). The refinement obeys the restraint according to the value set for penalties_weighting_K1. A weight percent can be restrained using:

```
    xdd ...
        penalties_weighting_K1 0.2
        restraint = (Cubic_Zirconia_wt_percent - 36); : 0
        str ...
            MVW(0,0, !Cubic_Zirconia_wt_percent 0)
```

Note the name 'Cubic_Zirconia_wt_percent' which is given to weight_percent.

11.4 ... Amorphous phase composition

If spiked_phase_measured_weight_percent is defined then elemental_composition will report on Rietveld values, Corrected values, and values from the original un-spiked sample. If element_weight_percent_known keywords are defined then elemental_composition will additionally report on the elemental contents of the amorphous phase, for example, from QUANT-1.INP we have:

```
    elemental_composition
    {
                    Rietveld        Corrected         Original          Other
        AL       1.176`_0.042     1.059`_0.000     0.000`_0.000    0.000`_0.000
        O       26.271`_0.017    23.640`_0.832    23.162`_0.849    0.838`_0.849
        SI       0.104`_0.004     0.094`_0.005     0.096`_0.005    0.000`_0.000
        Y        6.182`_0.013     5.563`_0.204     5.676`_0.209    0.000`_0.000
        ZR      66.267`_0.055    59.631`_2.185    60.847`_2.229    2.153`_2.229
        Other    0.000`_0.000    10.015`_3.224    10.219`_3.290    7.228`_0.212
    }
```

The ‘Rietveld’ and ‘Corrected’ columns corresponds to elemental weight-percents as determined for the spiked phase; the ‘Original’ and ‘Other’ columns correspond to elemental weight-percents of the original phase. The ‘Rietveld’, ‘Corrected’ and ‘Original’ columns sum to 100%. The last row of the ‘Corrected’ column (purple number) corresponds to Get(weight_percent_amorphous). The last row of the ‘Other’ column (red number) is the amount of sample that is undefined; it comprises the number in Green minus the elements of the ‘Other’ column. Note the zeros for Al (blue number); this is due to the spiked phase (dummy test data) being the only phase containing Al.

11.5 ... Using a dummy_str phase to describe amorphous content

If it is known that the amorphous content (purple number) in the above table comprises a known composition, say TiO_2, then a dummy_str can be used to describe the amorphous content, or:

```
dummy_str
    phase_name "Amorphous"
    a 5 b 5 c 5
    space_group 1
    site Ti occ Ti 1
    site O occ O 2
    Known_Weight_Percent(10.0148)
    MVW(0, 0 ,0)
```

dummy_str’s that are void of MVW takes no part in Quantitative analysis. However, if its lattice parameters and chemistry correspond to a real structure then Mixture_LAC_1_on_cm and phase_LAC can be correctly calculated. In the case of using the Brindley correction these changed values will change the quantitative results. The space group entry can be different to *P1* so long as the chemistry is correct. Inclusion of the dummy_str produces:

```
elemental_composition
{
                      Rietveld         Corrected          Original
    AL             1.059`_0.038      1.059`_0.000      0.000`_0.000
    O             27.652`_0.015     27.652`_0.975     27.256`_0.995
    SI             0.094`_0.003      0.094`_0.005      0.096`_0.005
    TI             6.002`_0.000      6.002`_0.215      6.125`_0.219
    Y              5.563`_0.012      5.563`_0.204      5.676`_0.209
    ZR            59.631`_0.050     59.631`_2.185     60.847`_2.229
    Other          0.000`_0.000      0.000`_3.583      0.000`_3.656
}
```

Note that the ‘Other’ row becomes zero as the amorphous content is assigned to the dummy_str. The changes in mixture values are:

Without dummy_str:

```
Mixture_LAC_1_on_cm( 557.47740`_0.58665)
mixture_density_g_on_cm3  5.26713308`_0.00292681843
```

With dummy_str:

```
Mixture_LAC_1_on_cm( 608.85143`_0.76954)
mixture_density_g_on_cm3  5.86601008`_0.00407998952
```

If XRF results were entered for element_weight_percent_known, for example:

```
element_weight_percent_known Zr 63
element_weight_percent_known O  24
```

then we get:

```
elemental_composition
{
                Rietveld        Corrected         Original           Other
    AL       1.059`_0.038     1.059`_0.000     0.000`_0.000    0.000`_0.000
    O       27.652`_0.015    27.652`_0.975    27.256`_0.995   -3.256`_0.995
    SI       0.094`_0.003     0.094`_0.005     0.096`_0.005    0.000`_0.000
    TI       6.002`_0.000     6.002`_0.215     6.125`_0.219    0.000`_0.000
    Y        5.563`_0.012     5.563`_0.204     5.676`_0.209    0.000`_0.000
    ZR      59.631`_0.050    59.631`_2.185    60.847`_2.229    2.153`_2.229
    Other    0.000`_0.000     0.000`_3.583     0.000`_3.656    1.103`_0.431
}
```

The negative element weight percent for O for the amorphous content reflects the fact that the measured XRF value for O is lower than the refinement's value (this example is used for testing; XRF values here are fictitious).

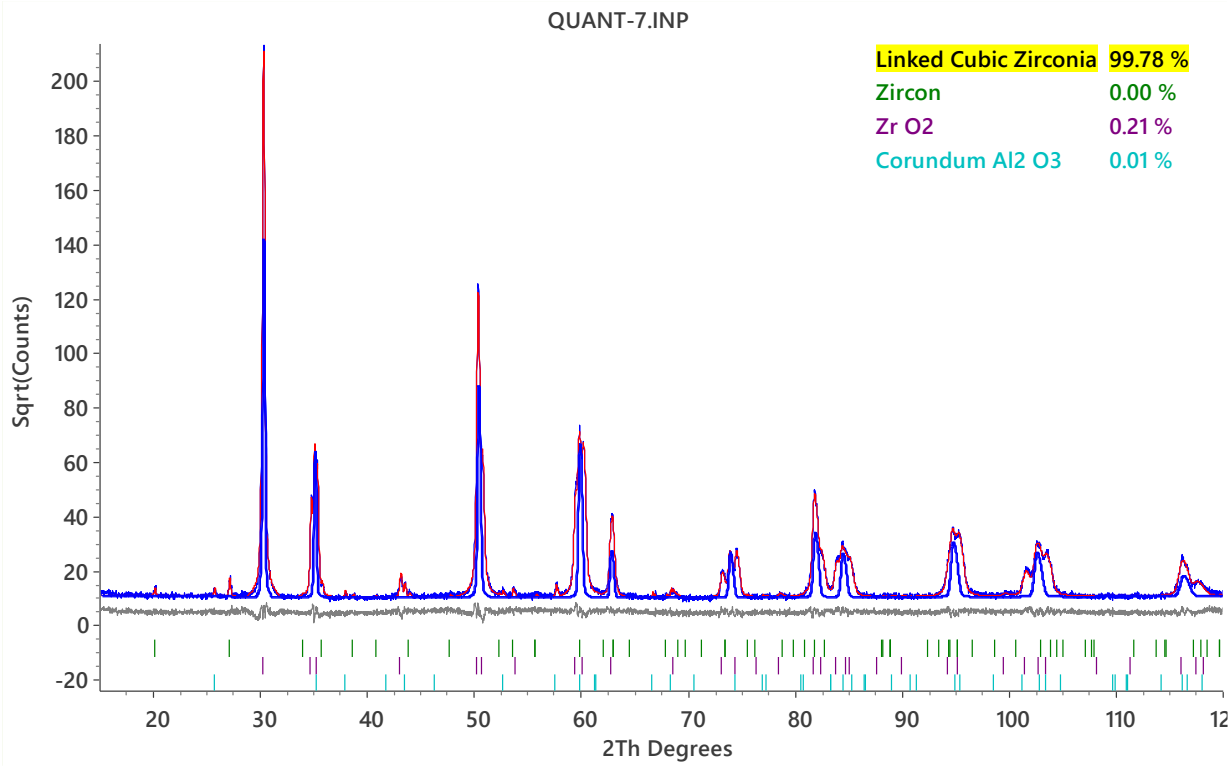
11.6 ... Quant using hkl_Is or other non-str phases

dummy_str's can be used to represent the quantitative results arising from non-str phases. For example, consider a phase where the structure is not known but the chemistry is known. If a calibration constant has been determined relating the hkl_Is intensities to the scale parameter of the hkl_Is phase, then a dummy_str can be written as follows (see QUANT-6.INP):

```
dummy_str
    phase_name "Linked Cubic Zirconia"
    Cubic(5.137866)
    space_group F_M_-3_M
    site Zr x 0     y 0     z 0      occ  Zr  0.85
                                     occ  Y   0.15
    site O  x 0.25  y 0.25  z 0.25   occ  O   0.96
    scale = hkl_scale;
    Phase_LAC_1_on_cm(0)
    Phase_Density_g_on_cm3(0)
    MVW(0, 0 ,0)
```

Note, in this case a space group has been entered with structural parameters that looks like a known structure; this could, for example, occur where the structure is known in an ordered state, but the diffraction pattern comprises a disordered state. In other cases, the *P1* space group may suffice with site occupancies corresponding to the appropriate chemistry. The dummy_str is linked to the hkl_Is phase by assigning the scale parameter of the dummy_str to

the scale parameters of the hkl_Is phase. QUANT-7.INP is a similar except that a fit_obj is linked to a dummy_str. Graphically the linked dummy_str is plotted with the calculated pattern of the hkl_Is phase or fit_obj, for example, QUANT-7.INP produces:



Here the blue line corresponds to the dummy_str which plots the calculated pattern of the linked fit_obj which in turn comprises a user_y object. The weight percent value determined by the dummy_str is also displayed.

11.7 ... External standard method

The method of O'Connor and Raven (1988) has been implemented in both GUI and Launch modes using the macros (see TEST_EXAMPLES\K-FACTOR):

```
macro K_Factor_MAC_K(mac, k, tot) {
    move_to xdd
    local !k_factor_mac_local_ mac
    local !k_factor_k_local_ k
    local !k_factor_sum_wps_ = 0; : tot
}
macro K_Factor_WP(result) {
    local k_factor_wp_ = 1.6605402 Get(smv) k_factor_mac_local_
                         / k_factor_k_local_; : result
    if Prm_There(k_factor_sum_wps_) {
        existing_prm k_factor_sum_wps_ += k_factor_wp_;
    }
}
```

11.8 ... QUANT Keywords

[cell_mass !E] [cell_volume !E] [weight_percent !E]

[spiked_phase_measured_weight_percent !E] [corrected_weight_percent !E]

cell_mass, cell_volume and weight_percent corresponds to the unit cell mass, volume, and weight percent of the phase within the mixture. spiked_phase_measured_weight_percent defines the weight percent of a spiked phase. It is used by the xdd dependent weight_percent_amorphous to determine amorphous weight percent. Only one phase per xdd is allowed to contain spiked_phase_measured_weight_percent. corrected_weight_percent is the weight percent after considering amorphous content as determined by weight_percent_amorphous. The weight fraction w_p for phase p is calculated as follows:

$$w_p = \frac{Q_p}{\sum_{p=1}^{N_p} Q_p}$$

where N_p = Number of phases.

$Q_p = S_p M_p V_p / B_p$

S_p = Rietveld scale factor for phase p.

M_p = Unit cell mass for phase p.

V_p = Unit cell volume for phase p.

B_p = Brindley correction for phase p,

The Brindley correction is a function of brindley_spherical_r_cm and the phase and mixture linear absorption coefficients; the latter two are in turn functions of phase_MAC and mixture_MAC respectively, or,

B_p is function of : (LAC_{phase}–$MAC_{mixture}$) brindley_spherical_r_cm

LAC_{phase} = linear absorption coefficient of phase p, packing density=1.

$MAC_{mixture}$= linear absorption coefficient of the mixture, packing density=1.

This makes B_p a function of the weight fractions w_p of all phases and thus w_p as written above cannot be solved analytically. Subsequently w_p is solved numerically using an iterative procedure.

[mixture_density_g_on_cm3 #]

Calculates the density of the mixture assuming a packing density of 1, see also mixture_MAC.

[mixture_MAC #]

Calculates the mass absorption coefficient in cm^2/g for a mixture as follows:

$$\left(\frac{\mu}{\rho}\right)_{mixture} = \sum_{i=1}^{N} \left(\frac{\mu}{\rho}\right)_i w_i$$

where w_i and $(\mu/\rho)_i$ is the weight percent and phase_MAC of phase i respectively. Errors are reported for phase_MAC and mixture_MAC. The following example calculates phase and mixture mass absorption coefficients.

```
xdd ...
```

```
        mixture_MAC 0
        str ...
            phase_MAC 0
```

The macros Mixture_LAC_1_on_cm, Phase_LAC_1_on_cm and Phase_Density_g_on_cm3 calculates the mixture and phase linear absorption coefficients (for a packing density of 1) and phase density, for example:

```
    xdd ...
        Mixture_LAC_1_on_cm(0)
        str ...
            Phase_Density_g_on_cm3(0)
            Phase_LAC_1_on_cm(0)
```

Errors for these quantities are also calculated. Mass absorption coefficients obtained from NIST at http://physics.nist.gov/PhysRefData/XrayMassCoef are used to calculate mixture_MAC and phase_MAC.

[phase_MAC !E]

Calculates the mass absorption coefficient in cm^2/g for the current phase. See description for mixture_MAC.

[weight_percent_amorphous !E]

Determines the amorphous content in a sample. The phase dependent spiked_phase_measured_weight_percent needs to be defined for weight_percent_amorphous to be calculated.

12. MAGNETIC STRUCTURE REFINEMENT

```
[str]...
    [mag_only_for_mag_sites]
    [mag_space_group $symbol]
    [site]...
        [mlx E] [mly E] [mlz E] [mg E]
        [mag_only]
        ' Site dependent macros
        MM_CrystalAxis_Display(mxc, myc, mzc)
        MM_CrystalAxis_Refine(mxc, mxv, myc, myv, mzc, mzv, mlx_v, mly_v, mlz_v)
        MM_Cartesian_Display(mxc, myc, mzc)
        MM_Cartesian_Refine(mxc, mxv, myc, myv, mzc, mzv, mlx_v, mly_v, mlz_v)
```

Thanks to Branton Campbell and John Evans for expert assistance during the implementation of magnetic structure refinement. Magnetic refinement is implemented using the keywords mlx, mly, mlz, mg and mag_space_group. See examples in the TEST_EXAMPLES\MAG directory as well as the tutorial by John Evans at:

http://www.dur.ac.uk/john.evans/topas_workshop/tutorial_lamno3_magnetic.htm

The Magnetic intensity is given by (* denotes conjugate gradient):

Magnetic intensity = **Fmagcperp . Fmagcperp*** = |**Fmagcperp**|

Fmagcperp = **Fmagc** - (**Fmagc** . **Qhat**) **Qhat**

Or in words, **Fmagcperp** is the component of the magnetic vector in the direction perpendicular to the scattering vector **Q**, where:

$\mathbf{Q} = (\mathbf{L}^{-1})^{T} * \mathbf{h}$

Qhat = Q / |Q|

L is the Cartesian lattice parameters in 3x3 matrix form

h is the Miller indices in vector form

* denotes matrix multiplication

Superscript $^{-1}$ denotes matrix inverse

Superscript ^{T} denotes matrix transpose

$(\mathbf{L}^{-1})^{T}$ = reciprocal lattice parameters

Fmagc in terms of the Cartesian lattice parameters is:

Fmagc = **L** * **Fmag**

Fmag for the plane **h** for a single site is:

$\mathbf{Fmag} = \sum_j (\mathbf{B}_j * \mathbf{m}) \exp(2\pi i U_j)$

where the summation is over the equivalent positions j and:

$U_j = \mathbf{h}.\mathbf{R}_j\,\mathbf{x} + \mathbf{h}.\mathbf{t}_j$

$\mathbf{x}$ = { x, y, z } = site fractional coordinates

$\mathbf{m}$ = { mlx, mly, mlz } = magnetic moment

$\mathbf{R}_j$ = rotation part of space group operator

$\mathbf{t}_j$ = translational part of space group operator

$d_j = s_j$ determinant($\mathbf{R}_j$) = s_j det($\mathbf{R}_j$)

$\mathbf{B}_j = s_j$ det($\mathbf{R}_j$) $\mathbf{R}_j$ = magnetic transformation matrix

The file MAGDATA.DAT (a GSAS file - permission for use granted by Robert Von Dreele, author of GSAS) comprises data for calculating magnetic form factors. The Lande splitting factor can be refined using the site dependent parameter mg; defaults for mg are obtained from MAGDATA.DAT. Shubnikov groups are obtained from the file SHUBNIKOVGROUPS.TXT. When mag_only is defined, the non-magnetic component to intensity for the site in question is ignored. When mag_only_for_mag_sites is defined then the non-magnetic component to intensity for all magnetic sites for the str in question is ignored.

12.1 ... Magnetic refinement warnings/exceptions

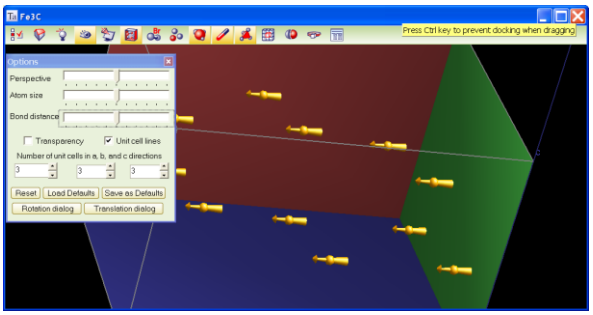
The following two messages:

1) Warning: Magnetic moment mlx of site Fe has no contribution to Fmag
2) Magnetic moment mlx of site Fe cannot be refined as it has no derivative

arise when for each group of equivalent positions of a special position, the first row of the matrix $\sum_j \mathbf{B}_j^*\mathbf{m}$ is zero where the *j*'s sum over the equivalent positions of a special position group. Similar messages for mly and mlz are given. Note, even though mlx, mly, mlz may not be refined, the warnring of (1) is still given dependening on associated constraints. Refinement terminates in the case of message (2) when mlx is being refined.

12.2 ... Displaying Magnetic moments

Magnetic moments (Occupancy $\mathbf{B}_j^*\mathbf{m}$) are displayed graphically when view_structure is defined. For the case where the atom balls are masking the display of the magnetic moment arrows, the "Atom size" can be varied as shown in the following:



12.3 ... 'Decomposing' Fmag for speed

When using magnetic space groups, equivalent positions for groups other than 1.1 are written in terms of other equivalent positions.

Let $C_j = \cos(U_j)$,

$S_j = \sin(U_j)$

$\mathrm{Exp}(i\,U) = C_j + i\,S_j$ = Euler's formulae

For two equivalent positions of a special position, we have:

$U_1 = U_2 = U$

$$\begin{aligned} \mathbf{Fmag}_1 + \mathbf{Fmag}_2 &= s_1 \det(\mathbf{R}_1)\ \mathbf{R}_1\,\mathbf{m}\,\mathrm{Exp}(i\,U) + s_2 \det(\mathbf{R}_2)\ \mathbf{R}_2\,\mathbf{m}\,\mathrm{Exp}(i\,U) \\ &= (s_1 \det(\mathbf{R}_1)\,\mathbf{R}_1 + s_2 \det(\mathbf{R}_2)\,\mathbf{R}_2)\,\mathbf{m}\,\mathrm{Exp}(i\,U) \\ &= \mathbf{c}\,\mathbf{m}\,\mathrm{Exp}(i\,U) \end{aligned}$$

c is independent of **x**. Note, a particular special position could have many equivalent positions.

If for two equivalent positions $\mathbf{R}_1 = -\mathbf{R}_2$ and $\mathbf{t}_1 = -\mathbf{t}_2$ then:

$U_1 = -U_2 = U$

$\mathbf{Fmag}_1 + \mathbf{Fmag}_2 =$	$s_1 \det(\mathbf{R})\,\mathbf{R}\,\mathbf{m}\,\mathrm{Exp}(i\,U) + s_2 \det(-\mathbf{R})\,(-\mathbf{R})\,\mathbf{m}\,\mathrm{Exp}(-i\,U)$
Now,	$\det(\mathbf{R})\,\mathbf{R} = \det(-\mathbf{R})\,(-\mathbf{R})$
or,	$\mathbf{Fmag}_1 + \mathbf{Fmag}_2 = \det(\mathbf{R})\,\mathbf{R}\,\mathbf{m}\,(s_1\,\mathrm{Exp}(i\,U) + s_2\,\mathrm{Exp}(-i\,U))$
For $s_1 = s_2$,	$\mathbf{Fmag}_1 + \mathbf{Fmag}_2 = s_1 \det(\mathbf{R})\,\mathbf{R}\,\mathbf{m}\,2\,C$
For $s_1 = -s_2$,	$\mathbf{Fmag}_1 + \mathbf{Fmag}_2 = s_1 \det(\mathbf{R})\,\mathbf{R}\,\mathbf{m}\,(2\,i\,S)$

If for two equivalent positions $\mathbf{R}_1 = \mathbf{R}_2$, then:

$$\begin{aligned} \mathbf{Fmag}_1 + \mathbf{Fmag}_2 &= s_1 \det(\mathbf{R})\,\mathbf{R}\,\mathbf{m}\,\mathrm{Exp}(i\,\mathbf{h}.\,\mathbf{R}\,\mathbf{x})\,\mathrm{Exp}(i\,\mathbf{h}.\mathbf{t}_1) + \\ &\quad s_2 \det(\mathbf{R})\,\mathbf{R}\,\mathbf{m}\,\mathrm{Exp}(i\,\mathbf{h}.\,\mathbf{R}\,\mathbf{x})\,\mathrm{Exp}(i\,\mathbf{h}.\mathbf{t}_2) \\ &= \det(\mathbf{R})\,\mathbf{R}\,\mathbf{m}\,(s_1\,\mathrm{Exp}(i\,\mathbf{h}.\mathbf{t}_1) + s_2\,\mathrm{Exp}(i\,\mathbf{h}.\mathbf{t}_2))\,\mathrm{Exp}(i\,\mathbf{h}.\,\mathbf{R}\,\mathbf{x}) \\ &= \mathbf{c}\,\mathrm{Exp}(i\,\mathbf{h}.\,\mathbf{R}\,\mathbf{x}) \end{aligned}$$

c is independent of **x** and is calculated only once. Many **R**'s can be the same for a particular space group with only the **t**'s changing.

Calculating C and S:

$\mathrm{Exp}(i\,(\mathbf{h}\,.\,\mathbf{R}\,\mathbf{x} + \mathbf{h}.\,\mathbf{t})) = \mathrm{Exp}(i\,\mathbf{h}\,.\,\mathbf{R}\,\mathbf{x})\,\mathrm{Exp}(i\,\mathbf{h}\,.\,\mathbf{t})$

$\mathrm{Exp}(i\,\mathbf{h}\,.\,\mathbf{t})$ is constant for a particular **h** and is calculated only once.

Only unique $\mathrm{Exp}(i\,\mathbf{h}\,.\,\mathbf{R}\,\mathbf{x})$ are calculated.

Trigonometric recurrence is used to calculate sines and cosines resulting in three cosine and three sine operations per unique equivalent r. In other words, a sin and cos are not calculated for each h; also a sin or cos function is equivalent to approximately 40 to 60 multiplies.

13. RIGID BODIES

```
[rigid]...
    [point_for_site $site [ux | ua E] [uy | ub E] [uz | uc E] ]...
        [in_cartesian] [in_FC]
    [z_matrix atom_1 [atom_2 E] [atom_3 E] [atom_4 E] ]...
    [rotate E [qx | qa E] [qy | qb E] [qz | qc E] ]...
        [operate_on_points $sites]
        [in_cartesian] [in_FC]
    [translate [tx | ta E] [ty | tb E] [tz | tc E] ]...
        [operate_on_points $sites]
        [in_cartesian] [in_FC]
        [rand_xyz !E]
        [start_values_from_site $unique_site_name]
```

Rietveld or Pair Distribution Function refinement can comprise rigid bodies. Rigid bodies comprise points in space defined using z_matrix or point_for_site keywords or both simultaneously. Operations can be performed on these points using rotate and translate. Rigid body operations include:

- Translating a rigid body or part of a rigid body.
- Rotating a rigid body or part of a rigid body around a point.
- Rotating a rigid body or part of a rigid body around a line.

ua, ub, uc, ta, tb, tc, qa, qb, qc and the parameters of z_matrix are all refinable parameters which can comprise parameter attributes such as min/max. The directory RIGID contains rigid body examples in *.RGD files. These files can be viewed and modified using the Rigid-Body-Editor of the GUI.

rigid defines the start of a rigid body. point_for_site defines a point in space with Cartesian coordinates given by the parameters ux, uy uz. Fractional equivalents can be defined using ua, ub and uc. $site is the site that the point_for_site represents. z_matrix defines a point in space with coordinates given in Z-matrix format as follows:

- E can be an equation, constant or a parameter name with a value.
- atom_1 specifies the site that the new Z-matrix point represents.
- The E after atom_2 specifies the distance in Å between atom_2 and atom_1. atom_2 must exist if atom_1 is preceded by at least one point.
- The E after atom_3 specifies the angle in degrees between atom_3, atom_2 and atom_1. atom_3 must exist if atom_1 is preceded by at least two points.
- The E atom_4 specifies the dihedral angle in degrees between the plane formed by atom_3-atom_2-atom_1 and the plane formed by atom_4-atom_3-atom_2. This angle is drawn using the righthand rule with the thumb pointing in the direction atom_3 to atom_2. atom_4 must exist if atom_1 is preceded by at least three sites of the rigid body.
- If atom_1 is the first point of the rigid body then it is placed at Cartesian (0, 0, 0). If atom_1 is the second point of the rigid body then it is placed on the positive z-axis at Cartesian (0,

0, E) where E corresponds to the E in [atom_2 E]. If $atom_1 is the third point of the rigid-body then it is placed in the x-y plane.

rotate rotates point_for_site's an amount as defined by the rotate E equation around the vector defined by the Cartesian vector qx, qy, qz. The vector can instead be defined in fractional coordinates using qa, qb and qc. translate performs a translation of point_for_site's an amount in Cartesian coordinates equal to tx, ty, tz. The amount can instead be defined in fractional coordinates using ta, tb and tc. rotate and translate operates on any previously defined point_for_site's; alternatively, point_for_site's operated-on can be identified using operate_on_points. operate_on_points must refer to previously defined point_for_site's (see section 20.26 for a description of how to identify sites). in_cartesian or in_FC can be used to signal coordinates are in Cartesian or fractional atomic coordinates respectively. When continue_after_convergence is defined, rand_xyz processes are initiated after convergence. It introduces a random displacement to the translate fractional coordinates (tx, ty, tz) that are independent parameters. The size of the random displacement is given by the current temperature multiplied by #displacement where #displacement is in Å. start_values_from_site initializes the values ta, tb, tc with corresponding values taken from the site named $unique_site_name.

13.1 ... Fractional, Cartesian and Z-matrix coordinates

Rigid bodies can be formulated using fractional or Cartesian coordinates. A Benzene ring without Hydrogens can be formulated as follows:

```
prm a 1.3 min 1.2 max 1.4
rigid
   point_for_site C1 ux =  a Sqrt(3) .5; uy =  a .5;
   point_for_site C2 ux =  a Sqrt(3) .5; uy = -a .5;
   point_for_site C3 ux = -a Sqrt(3) .5; uy =  a .5;
   point_for_site C4 ux = -a Sqrt(3) .5; uy = -a .5;
   point_for_site C5 uy =  a;
   point_for_site C6 uy = -a;
   Rotate_about_axies(@ 0, @ 0, @ 0) ' rotate previously defined points
   Translate(@ 0.1, @ 0.2, @ 0.3)    ' translate previously defined points
```

The last two statements rotate and translates the rigid body as a whole; their inclusion is implied if absent. A formulation of any complexity can be obtained from a) databases of existing structures using fractional or Cartesian coordinates of structure fragments or b) from sketch programs for drawing chemical structures. A Z-matrix representation of a rigid body explicitly defines the rigid body in terms of bond lengths and angles. A Benzene ring is typically formulated using two dummy atoms *X1* and *X2* as follows:

```
str ...
    site X1 ... occ C 0
    site X2 ... occ C 0
    rigid
        load z_matrix {
            X1
            X2   X1  1.0
            C1   X2  1.3   X1  90
            C2   X2  1.3   X1  90  C1  60
            C3   X2  1.3   X1  90  C2  60
            C4   X2  1.3   X1  90  C3  60
            C5   X2  1.3   X1  90  C4  60
            C6   X2  1.3   X1  90  C5  60
        }
```

Atoms with occupancies fixed to zero are dummy atoms and do not take part in structure factor calculations. Importantly however dummy atoms take part in penalties. The mixing of point_for_site and z_matrix keywords is possible as follows:

```
rigid
    point_for_site X1
    load z_matrix {
        X2   X1  1.0
        C1   X2  1.3   X1  90 ...
    }
```

Z-matrix parameters are like any other parameter; they can be equations and parameter attributes can be assigned. For example, the 1.3 bond distance can be refined as follows:

```
rigid
    point_for_site X1
    load z_matrix {
        X2   X1  1.0
        C1   X2  c1c2 1.3 min 1.2 max 1.4  X1  90
        C2   X2  = c1c2;   X1  90  C1  60
        C3   X2  = c1c2;   X1  90  C2  60
        C4   X2  = c1c2;   X1  90  C3  60
        C5   X2  = c1c2;   X1  90  C4  60
        C6   X2  = c1c2;   X1  90  C5  60
    }
```

This ability to constrain Z-matrix parameters using equations allow for great flexibility. For example, Z-matrix bond length parameter could be written in terms of other bond length parameters whereby the average bond length is maintained. Or, in cases where a bond length is expected to change as a function of a site occupancy, an equation relating the bond length as a function of the site occupancy parameter can be formulated.

13.2 ... Translating part of a rigid body

Once a starting rigid body model is defined, further translate and rotate statements can be included to represent deviations from the starting model. For example, if the C1 and C2 atoms are expected to shift by up to 0.1Å and as a unit then the following could be used:

```
rigid
   load z_matrix {
      X1
      X2   X1  1.0
      C1   X2  1.3   X1  90
      C2   X2  1.3   X1  90  C1  60
      C3   X2  1.3   X1  90  C2  60
      C4   X2  1.3   X1  90  C3  60
      C5   X2  1.3   X1  90  C4  60
      C6   X2  1.3   X1  90  C5  60
   }
   translate
      tx @ 0 min -0.1 max 0.1
      ty @ 0 min -0.1 max 0.1
      tz @ 0 min -0.1 max 0.1
      operate_on_points "C1 C2"
```

where the additional statements are in purple. The Cartesian coordinate representation allows an additional means of shifting the C1 and C2 atoms by refining on the ux, uy and uz coordinates directly, or,

```
prm a 1.3 min 1.2 max 1.4
prm t1 0 min -0.1 max 0.1
prm t2 0 min -0.1 max 0.1
prm t3 0 min -0.1 max 0.1
rigid
   point_for_site C1 ux = a Sqrt(3) 0.5 + t1; uy =  a 0.5 + t2; uz = t3;
   point_for_site C2 ux = a Sqrt(3) 0.5 + t1; uy = -a 0.5 + t2; uz = t3;
   point_for_site C3 ux =-a Sqrt(3) 0.5;      uy =  a 0.5;
   point_for_site C4 ux =-a Sqrt(3) 0.5;      uy = -a 0.5;
   point_for_site C5                          uy =  a;
   point_for_site C6                          uy = -a;
```

13.3 ... Rotating part of a rigid body around a point

Many situations require the rotation of part of a rigid body around a point. An octahedra (Fig. 13-1), for example, typically rotates around the central atom with three degrees of freedom. To implement such a rotation requires setting the origin at the central atom before rotation and then resetting the origin after rotation. This is achieved using the Translate_point_amount macro as follows:

```
prm r 2 min 1.8 max 2.2
rigid
    point_for_site A0
    point_for_site A1 ux =  r;
    point_for_site A2 ux = -r;
    point_for_site A3 uy =  r;
    point_for_site A4 uy = -r;
    point_for_site A5 uz =  r;
    point_for_site A6 uz = -r;
    Translate_point_amount(A0, -) operate_on_points "A* !A0"
    rotate @ 0 qa 1 operate_on_points "A* !A0"
    rotate @ 0 qb 1 operate_on_points "A* !A0"
    rotate @ 0 qc 1 operate_on_points "A* !A0"
```

```
        Translate_point_amount(A0, +) operate_on_points "A* !A0"
```

The point_for_site keywords could just as well be z_matrix keywords with the appropriate Z-matrix parameters. The first Translate_point_amount statement translates the specified points (A1 to A6) an amount equivalent to the negative position of A0. This sets the origin for these points to A0. The second resets the origin back to A0. If the A0 atom happens to be at Cartesian (0, 0, 0) then there would be no need for the Translate_point_amount statements.

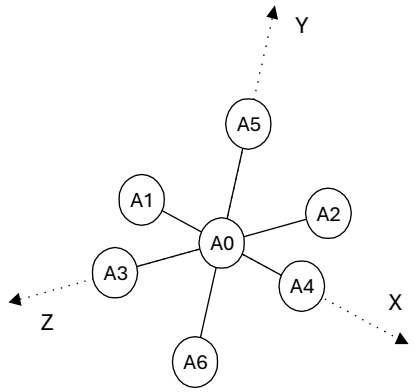


Fig. 13-1 Model of an ideal octahedron.

Further distortions are possible by refining on different bond-lengths between the central atom and selected outer atoms. For example, the following macro describes an orthorhombic bipyramid:

```
macro Orthorhombic_Bipyramide(s0, s1, s2, s3, s4, s5, s6, r1, r2) {
   point_for_site s0
   point_for_site s1 ux   r1
   point_for_site s2 ux  -r1
   point_for_site s3 uy   r1
   point_for_site s4 uy  -r1
   point_for_site s5 uz   r2
   point_for_site s6 uz  -r2
}
```

Note the two different lengths r1 and r2; with r1 = r2 this macro would describe a regular octahedron.

13.4 ... Rotating part of a rigid body around a line

Instead of explicitly entering fractional or Cartesian coordinates, rigid bodies can be created using the rotate and translate keywords. For example, two connected Benzene rings, a schematic without Hydrogens is shown in Fig. 13-2, can be formulated as follows:

```
prm r 1.3 min 1.2 max 1.4
rigid
   point_for_site C1 ux = r;
   load point_for_site ux rotate qz operate_on_points {
      C2 =r; 60  1 C2
      C3 =r; 120 1 C3
      C4 =r; 180 1 C4
      C5 =r; 240 1 C5
      C6 =r; 300 1 C6
```

```
   }
   point_for_site C7 ux = r;
   load point_for_site ux rotate qz operate_on_points {
      C8  =r; 60  1 C8
      C9  =r; 120 1 C9
      C10 =r; 300 1 C10
   }
   translate tx = 1.5 r; ty = r Sin(60 Deg);
      operate_on_points "C7 C8 C9 C10"
```

The points of the second ring can be rotated around the line connecting C1 to C2 with the following:

```
Rotate_about_points(@ 50 min -60 max 60, C1, C2, "C7 C8 C9 C10")
```

The min/max statements limit the rotations to ±30 degrees. C5 can be rotated around the line connecting C4 and C6 with the following:

```
Rotate_about_points(@ 40 min -50 max 50, C4, C6, C5)
```

Similar Rotate_about_points statements for each atom would allow for distortions of the Benzene rings without changing bond distances.

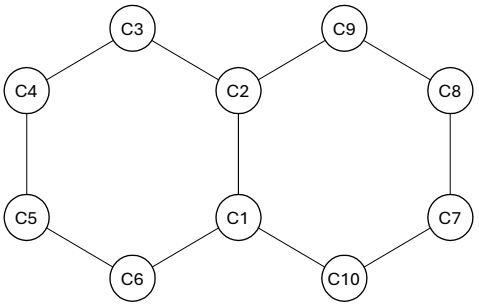


Fig. 13-2. Model of two connected Benzene rings

Another means of generating Fig. 13-2 and the one that requires the least thought is by using the Duplicate_Point and Duplicate_rotate_z macros as follows:

```
prm r 1.3 min 1.2 max 1.4
rigid
    point_for_site C1 ux = r;
    Duplicate_rotate_z(C2, C1, 60)
    Duplicate_rotate_z(C3, C2, 60)
    Duplicate_rotate_z(C4, C3, 60)
    Duplicate_rotate_z(C5, C4, 60)
    Duplicate_rotate_z(C6, C5, 60)
    Duplicate_Point(C7,  C3)
    Duplicate_Point(C8,  C4)
    Duplicate_Point(C9,  C5)
    Duplicate_Point(C10, C6)
    Rotate_about_points(180, C1, C2, "C7 C8 C9 C10")
```

13.4.1 ..... Using Z-matrix together with rotate and translate

Cyclopentadienyl (C5H5) is a well-defined molecular fragment which shows slight deviations from a perfect five-fold ring (Fig. 13-3). The rigid body definition using point_for_site keywords is as follows:

```
prm r1 1.19
prm r2 2.24
rigid
    load point_for_site ux { C1 =r1; C2 =r1; C3 =r1; C4 =r1; C5 =r1; }
    load point_for_site ux { H1 =r2; H2 =r2; H3 =r2; H4 =r2; H5 =r2; }
    load rotate qz operate_on_points { 72 1 C2  144 1 C3 216 1 C4 288 1 C5 }
    load rotate qz operate_on_points { 72 1 H2  144 1 H3 216 1 H4 288 1 H5 }
```

and using a typical Z-matrix representation:

```
    rigid
        load z_matrix {
            X1
            X2   X1 1
            C1   X2 1.19   X1  90
            C2   X2 1.19   X1  90   C1  72
            C3   X2 1.19   X1  90   C2  72
            C4   X2 1.19   X1  90   C3  72
            C5   X2 1.19   X1  90   C4  72
            X3   C1 1      X2  90   X1   0
            H1   C1 1.05   X3  90   X2 180
            H2   C2 1.05   C1 126   X2 180
            H3   C3 1.05   C2 126   X2 180
            H4   C4 1.05   C3 126   X2 180
            H5   C5 1.05   C4 126   X2 180
        }
```

This Z-matrix representation is typically used for Cyclopentadienyl; it allows for various torsion angles but does not allow for all possibilities. For example, no adjustment of a single Z-matrix parameter allows for displacement of the C1 atom without changing the C1-C2 and C1-C3 bond distances. The desired result however is possible using the Rotate_about_points macro:

```
    Rotate_about_points(@ 0, C2, C3, "C1 H1")
```

Thus, the ability to include rotate and translate together with z_matrix gives great flexibility in defining rigid bodies.

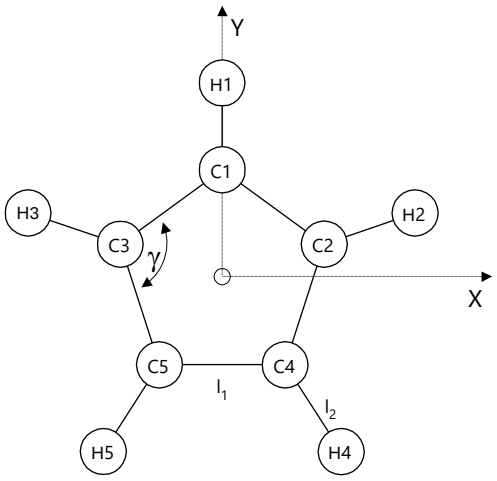


Fig. 13-3. Model of the idealized cyclopentadienyl anion (C_5H_5).

13.5 ... The simplest of rigid bodies

The simplest rigid body comprises an atom constrained to move within a sphere; for a radius of 1, this can be achieved as follows:

```
rigid
    point_for_site Ca uz @ 0 min -1 max 1
    rotate r1 10 qx 1
    rotate r2 10 qx = Sin(Deg r1); qy = -Cos(Deg r1);
```

The coordinates are in fact spherical coordinates where the rotation parameters r1 and r2 are communicative. When an atomic position is approximately known then constraining the atom to within a sphere is useful. Setting the distance between two sites, or two sites A and B a distance 2Å apart can be formulated as:

In Z-matrix form:

```
rigid
    z_matrix A                          ' line 1
    z_matrix B A 2                      ' line 2
    rotate @ 20 qa 1                    ' line 3
    rotate @ 20 qb 1                    ' line 4
    translate ta @ 0.1 tb @ 0.2 tc @ 0.3   ' line 5
```

In Cartesian form:

```
rigid
    point_for_site A                    ' line 1
    point_for_site B uz 2               ' line 2
    rotate @ 20 qa 1                    ' line 3
    rotate @ 20 qb 1                    ' line 4
    translate ta @ 0.1 tb @ 0.2 tc @ 0.3   ' line 5
```

Lines 1 and 2 defines the two points (note ux, uy and uz defaults to 0), line 3 and 4 rotates the two points around the a and then the b lattice vectors. Line 5 translates the two points to a position in fractional atomic coordinates of (0.1, 0.2, 0.3). Lines 3 to 5 contain the five parameters associated with this rigid body. The Set_Length macro can instead be used to set the distance between the two sites as follows:

```
Set_Length(A, B, 2, @, @, @, @ 30, @ 30)
```

where A and B are the site names, 2 is the distance in Å between the sites, arguments 4 to 6 the names given to the translation parameters, and arguments 7 and 8 are the rotational parameters. Set_Length is not supplied with the translate starting values; these are obtained from the A site with the use of start_values_from_site located in the Set_Length macro. min/max can be used to constrain the distance between the two sites, for example:

```
Set_Length(A, B, @ 2 min 1.9 max 2.1, @, @, @, @ 30, @ 30)
```

Note, this macro defines the distance between the two sites as a parameter that can be refined.

13.6 ... Generation of rigid bodies

A rigid body is constructed by the sequential processing of z_matrix, point_for_site, rotate and translate operations. The body is then converted to fractional atomic coordinates and then the symmetry operations of the space group applied. The conversion of Z-matrix coordinates to Cartesian is as follows:

- The first atom is paced at the origin.
- The second atom, if defined, is placed on the positive z-axis.
- The third atom, if defined, is placed in the x-z plane.

For Cartesian to fractional coordinates, in terms of the lattice vectors, we have:

- x-axis in the same direction as the **a** lattice vector.
- y-axis in the **a**-**b** plane.
- z-axis in the direction defined by the cross product of **a** and **b**.

Rotation operations are not commutative; the rotation of point A about the vector B-C and then about D-E is not the same as the rotation of A about D-E and then about B-C. By default, rotate and translate operate on all previously defined point_for_site's. Alternatively point_for_site's can be explicitly defined using operate_on_points. operate_on_points must refer to previously defined point_for_site's and it can refer to many sites at once by enclosing the site names in quotes and using the wild card character '*' or the negation character '!' (see section 20.26), for example:

```
operate_on_points "Si* O* !O2"
```

13.7 ... Rigid body parameter errors propagated to fractional coordinates

Errors for fractional coordinates for sites defined as part of a rigid body are propagated to the site fractional coordinates. The example RIGID-ERRORS\ANILINE_I_100K_X.INP (by Simon Parsons) demonstrates the equivalence of two refinements 1) using a rigid body and 2) hand coding the fractional coordinates in terms of rigid body parameters but not in fact using a rigid body. Errors and convergence behaviour in both cases are identical. Case (2), which has many computer algebra equations, takes approximately the same time per iteration as case (1); this

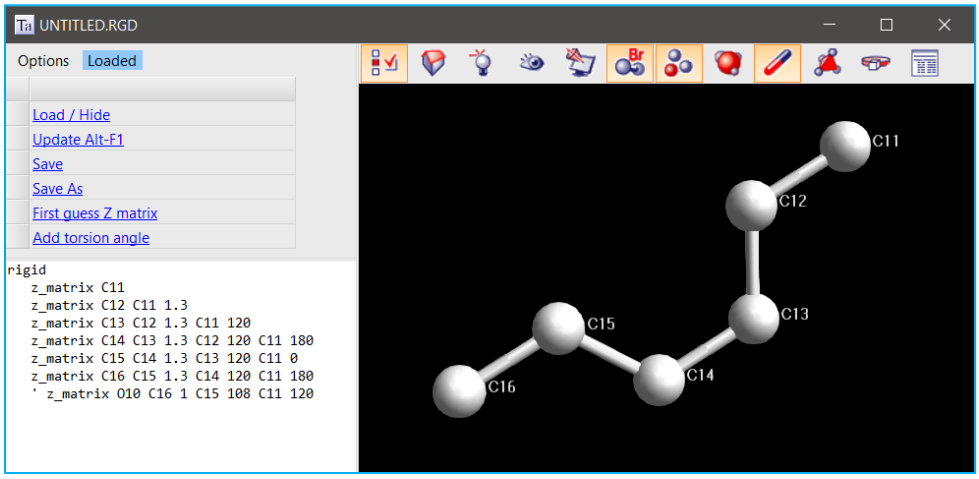
demonstrates that computer algebra often does not noticeably affect computational speed even in cases where its use is plentiful.

13.8 ... Z-matrix collinear error information

The Z-matrix collinear points exception can be deciphered using information displayed on detection of the error. The collinear error is due to three atoms on a z-matrix line which are collinear. The information displayed includes a snapshot of the rigid body operations pertaining to the error. The following is an example of the information displayed:

```
DB_x_CB Zero dot product - Z-matrix possible collinear points at atoms
    O10
    C16 8.91631604e-016 1.0912987e-014 5.2
    C15 3.72315026e-016 1.0912987e-014 3.9
    C11 0 0 0
Partial z-matrix in error:
    rigid
        z_matrix C11
        z_matrix C12 C11 1.3
        z_matrix C13 C12 1.3 C11 120
        z_matrix C14 C13 1.3 C12 120 C11 180
        z_matrix C15 C14 1.3 C13 120 C11 0
        z_matrix C16 C15 1.3 C14 120 C11 180
        z_matrix O10 C16 1   C15 108 C11 120
```

The rigid body fragment can be copied to the Rigid-body editor to investigate why the error occurs, i.e.



The O10 line is commented out as it is the line causing the error. Looking at the O10 line (using the OpenGL window), we see that atoms C16, C15, C11 lie on a straight line; this is invalid as it becomes impossible to form a dihedral angle in a non-degenerate manner. The best way to think about a z-matrix line with 4 atoms A, B, C, D, i.e.

```
z_matrix A B # C # D #
```

is to think of two triangles ABC and DBC hinged along the line BC. The angle between the triangles is the dihedral angle. If B,C,D are collinear then there's no triangle and the dihedral angle cannot be formed. Thus, for z-matrices both A,B,C and B,C,D must not be collinear. The program tests for a zero dot-product numerically with a tolerance of 10^{-15}.

13.9 ... Functions allowing access to rigid-body fractional coordinates

The standard macro Point(site_name, rx), see TOPAS.INC, returns the x Cartesian coordinate of the point called site_name; y and z Cartesian coordinates are returned by ry and rz objects respectively. These functions can only to be used in equations of the rigid body which encompass the keywords and their dependents of point_for_site, z_matrix, translate and rotate. The actual value returned by Point depends on where it is used in the rigid-body, for example, in the following:

```
rigid
   point_for_site O1
   translate tx 1
   point_for_site O2 ux = Point(O1, rx); ' Point here returns 1
   translate tx 2
   point_for_site O3 ux = Point(O1, rx); ' Point here returns 3
```

the final x Cartesian coordinate of site O3 becomes 3. To instead return fractional coordinates of points, the functions Point_rx_ua, Point_rx_ub and and Point_rx_ua can be used. These functions are passed the address of the point in question using the Point macro with one argument. Accompanying macros simplifying the call, as defined in TOPAS.INC, are:

```
macro Point_ua(site_name) { Point_rx_to_ua(Point(site_name)) }
macro Point_ub(site_name) { Point_ry_to_ub(Point(site_name)) }
macro Point_uc(site_name) { Point_rz_to_uc(Point(site_name)) }
```

These macros can return many different values for the same point in question depending on when they are called during the rigid body calculation.

13.10 . Determining the orientation of a known fragment

TEST_EXAMPLES\RIGID\MATCH.INP determines rotation and translation parameters for a known fragment. The known fragment is in fractional coordinates. To do the same for a fragment in Cartesian coordinates then change the lattice angles to 90 degrees and adjust the lattice parameter lengths. Also, see:

http://topas.dur.ac.uk/topaswiki/doku.php?id=rigid_body_-_matching_to_a_known_fragment

13.11 . Rigid body macros

Set_Length(s0, s1, r, xc, yc, zc, cva, cvb)

Fixes the distance between two sites.

[s0, s1]: Site names.

[r]: Distance in Å.

[xc, yc, zc]: The parameter names for the coordinates of s0.

[cva, cvb]: Parameter names and values for rotations about the x and y axes

Set_Lengths(s0, s1, s2, r, xc, yc, zc, cva1, cvb1, cva2, cvb2)
Set_Lengths(s0, s1, s2, s3, r, xcv, ycv, zcv, cva1, cvb1, cva2, cvb2, cva3, cvb3)

Sets the distance between two and three sites, respectively. The two sites case is defined as:

```
macro Set_Lengths(s0, s1, s2, r, xc, yc, zc,cva1, cvb1, cva2, cvb2)
{
   Set_Length(s0, s1, r, xc, yc, zc, cva1, cvb1)
   Set_Length(s0, s2, r, xc, yc, zc, cva2, cvb2)
}
```

Triangle(s1, s2, s3, r)
Triangle(s0, s1, s2, s3, r)
Triangle(s0, s1, s2, s3, r, xc, yc, zc, cva, cvb, cvc)

Defines a regular triangle without and with a central atom (s0).

[s0, s1, s2, s3]: Site names. s0 is the central atom of the triangle.

[r]: Distance in Å.

[xc, yc, zc]: Parameter names for the coordinates for the central atom.

[cva, cvb, cvc]: Parameter names and values for rotations about the x, y and z axes.

Tetrahedra(s0, s1, s2, s3, s4, r, xc, yc, zc, cva, cvb, cvc)

Defines a tetrahedra with a central atom.

[s0, s1, s2, s3, s4]: Site names. s0 is the central atom of the tetrahedra.

[r]: Distance in Å.

[xc, yc, zc]: Parameter names for the coordinates for the central atom.

[cva, cvb, cvc]: Parameter names and values for rotations about the x, y and z axes.

Octahedra(s0, s1, s2, s3, s4, s5, s6, r)
Octahedra(s0, s1, s2, s3, s4, s5, s6, r, xc, yc, zc, cva, cvb, cvc)

Defines an octahedra with a central atom.

[s0, s1, s2, s3, s4, s5, s6]: Site names. s0 is the central atom of the octahedra.

[r]: Distance in Å.

[xc, yc, zc]: Parameter names for the coordinates for the central atom.

[cva, cvb, cvc]: Parameter names and values for rotations about the x, y and z axes.

Hexagon_sitting_on_point_in_xy_plane(s1, s2, s3, s4, s5, s6, a)
Hexagon_sitting_on_side_in_xy_plane(s1, s2, s3, s4, s5, s6, a)

Defines a regular hexagon, where the hexagon is sitting on a point or on a side in the x-y plane, respectively.

[s1, s2, s3, s4, s5, s6]: Site names.

[a]: Distance in Å.

Translate(acv, bcv, ccv)
Translate(acv, bcv, ccv, ops)

Performs a translation of the rigid body.

[acv, bcv, ccv]: Amount of the translation in fractional coordinates.

[ops]: Operates on previously defined sites in “ops”.

Translate_with_site_start_values(s0, xc, yc, zc)

Performs a translation using the coordinates of s0 as start values.

[s0]: Site name.

[xc, yc, zc]: Parameter names for the coordinates of s0.

Rotate_about_points(cv, a, b)
Rotate_about_points(cv, a, b, pts)

Performs a rotation about a rotation vector specified by two sites.

[cv]: Amount the rigid body is rotated about the specified rotation vector in degrees.

[a, b]: Rotation vector defined by the sites a and b.

[pts]: Operates on previously defined point_for_site(s).

Note: Do not include points rotated about in the “operate on points” list of the Rotate_about_points macro. For example, in

```
Rotate_about_points(@ 1 0, C1, C2, " C3 C4 C5 C6 ")
```

the points C1 and C2 are not included in the “points operated on” list. Note also that Rotate_about_points without a “points operated on” list will operate on all previously defined point_for_site(s). Therefore, when an “operate on points” list is not defined then it is necessary to place the “points rotated about” after the Rotate_about_points macro. It is best to specify an “operate on points” list when in doubt.

Rotate_about_these_points(cv, a, b, ops)

Performs a rotation about a rotation vector specified by two sites.

[cv]: Amount the rigid body is rotated about the specified rotation vector in degrees.

[a, b]: Rotation vector defined by the sites a and b.

[ops]: Operates on previously defined point_for_site(s).

Rotate_about_axies(cva, cvb)
Rotate_about_axies(cva, cvb, cvc)

Performs a rotation about the axes.

14. INDEXING

The following algorithm is based on the iterative method of Coelho (2003). Unlike lp_serach it requires the extraction of d-spacings. The INDEXING directory contains example INP files, example usage is as follows:

```
index_zero_error
try_space_groups "2 75"
load index_d {
   8.912
   7.126
   4.296
   ...
}
```

Individual space groups can be tried or for simplicity all Bravais lattices can be tried using standard macros as follows:

```
Bravais_Cubic_sgs
Bravais_Trigonal_Hexagonal_sgs
Bravais_Tetragonal_sgs
Bravais_Orthorhombic_sgs
Bravais_Monoclinic_sgs
Bravais_Triclinic_sgs
```

To try all unique extinction subgroup space-groups, a more exhaustive approach, then the following macros can be used:

```
Unique_Cubic_sgs
Unique_Trigonal_Hexagonal_sgs
Unique_Tetragonal_sgs
Unique_Orthorhombic_sgs
Unique_Monoclinic_sgs
Unique_Triclinic_sgs
```

On termination of Indexing a *.NDX file is created, with a name corresponding to the name of the INP file and placed in the same directory as the INP file. The *.NDX file contains solutions as well as a detailed summary of the best 20 solutions. Here's an example of an NDX file:

```
' Indexing method - Alan Coelho (2003), J. Appl. Cryst. 36, 86-95
' Time: 2.015 seconds
     'Sg     Status UNI      Vol       Gof     Zero      Lps ...
Indexing_Solutions_With_Zero_Error_2 {
   0) P42/nmc    3   0    1187.321    38.82   0.0000    11.1924  ...
   1) P42/nmc    3   0    1187.057    38.64   0.0000    11.1896  ...
   2) P42/nmc    3   0    1187.458    38.61   0.0000    11.1914  ...
    ...
}
/*
=============================================================================
   0) P-1         0     985.652    30.80   0.0111     7.0877  ...

   h   k   l       dc       do    do-dc     2Thc     2Tho   2Tho-2Thc
   0   0   1   15.857   15.830   -0.027    5.569    5.578    0.009
```

```
          0   1   0    8.765    8.750   -0.015   10.084   10.101    0.017
           ...
       */
```

14.1 ... Figure of merit

The figure of merit *M* used in indexing is as follows:

$$M = \left[(1 + N_{uni}) d^2_{o,min} \left(\frac{N_c}{N_o} \right) \sum_i \left| d^2_{o,i} - d^2_{c,i} \right| Q_i \right]^{-1} \qquad \text{(14-1)}$$

$$\text{where} \quad Q_i = w_i N_o / \sum_j w_j$$

Where d_o and d_c are the observed and calculated d-spacings, N_o and N_c the number of observed and calculated lines used, N_{uni} the number of unindexed lines and the summations are over the used observed indexing lines. Q_i is a weighting that assists in the determination of extinction subgroups where w_i could for example be the inverse of the error in the peak positions from a Pawley refinement (see INDEXING\MGIR\INDEX.INP). index_I correspond to w_i. The formulation of Q_i is such that with or without Q_i the figure of merit *M* is of the same order of magnitude. The reciprocal-space lattice relationship solved during the indexing process (Coelho, 2000) includes *Q* as follows:

$$\left[X_{hh} h^2 + X_{kk} k^2 + X_{ll} l^2 + X_{hk} h\, k + X_{hl} h\, l + X_{kl} k\, l + \frac{4\,\pi Z_e}{360 \lambda^2} sin(2\theta) \right] W_{hkl} = \frac{W_{hkl}}{d^2_o} \qquad \text{(14-2)}$$

$$\text{where} \quad W_{hkl} = Q_{hkl} d^m_o |\Delta 2\theta_{hkl}|$$

14.2 ... Extinction subgroup determination

At the end of an indexing run further indexing runs are internally performed across extinction subgroups (see section 14.8) to determine the most likely subgroup. These internal runs are seeded with already determined lattice parameters and in most cases the correct extinction subgroup is obtained without the need for Q_i in Eq. (14-1). Extinction subgroups can be explicitly searched using the macros defined TOPAS.INC, see for example Unique_Orthorhombic_sgs.

14.3 ... Reprocessing solutions - DET files

Details of solutions can be obtained at a later stage by including solution lines, found in the NDX file, in the INP file. For example, supposing details of solutions 50 and 51 were sought then the following (see example INDEXING\EX10.INP) could be used:

```
index_lam 1.540596
index_zero_error
try_space_groups 2
Indexing_Solutions_With_Zero_Error_2 {
  50) P-1        1   0    2064.788     9.74   0.0000   ...
  51) P-1        3   0    3128.349     9.61   0.0115   ...
}
load index_d {
   15.83 good
    8.75
    7.91
    ...
}
```

After running this INP file, a *.DET file is created containing details of the supplied solutions.

14.4 ... Keywords and data structures

Tindexing
[index_lam !E1.540596]
[index_min_lp !E2] [index_max_lp !E]
[index_max_Nc_on_No !E5]
[index_max_number_of_solutions #3000]
[index_max_th2_error !E0.05]
[index_max_zero_error #0.2]
[index_th2 !E | index_d !E]...
[index_I E1 [good]]
[index_x0 !E]
[index_zero_error]
[no_extinction_subgroup_search]
[seed [#]]
[try_space_groups $]...
[x_angle_scaler #0.1]
[x_scaler #]

Values for most keywords are automatically determined or have defaults (appearing as numbers to the right) adequate for difficult indexing problems. In the following example from UPPW (service provided by Armel Le Bail to the SDPD mailing list at http://sdpd.univ-lemans.fr/uppw/), only a few keywords are necessary. Also note the use of dummy; this allows for the exclusion of 2θ and I values without having to edit the columns of data.

```
seed
index_lam  0.79776
index_zero_error
index_max_Nc_on_No 6
try_space_groups 3
load index_th2 dummy dummy index_I dummy  {
    ' d (A)  2Theta     Height      Area     FWHM
    1.724  26.50645    2758.3   23303.7    0.0450
    2.646  17.27733  150393.8  747063.6    0.0250
    3.235  14.13204   98668.8  493153.7    0.0250
    3.417  13.37776   11102.6   53185.0    0.0250
    5.190   8.80955     782.7    3910.9    0.0250
    ...
}
```

14.5 ... Keywords in detail

[index_lam !E1.540596]

Defines the wavelength in Å.

[index_min_lp !E2.5] [index_max_lp !E]

Defines the minimum and maximum allowed lattice parameters. The maximum is typically automatically determined.

[index_max_Nc_on_No !E5]

Determines the maximum ratio of the number of calculated to observed lines. The value of 6 allows for up to 83% of missing lines.

[index_max_number_of_solutions #1000]

The number of best solutions to keep.

[index_max_th2_error !E0.05]

Used for determining impurity lines (un-indexed lines UNI in *.NDX). Large values, 1 for example, forces the consideration of more observed input lines. For example, if it is known that there are none or maybe just one impurity line then a large value for index_max_th2_error will speed up the indexing procedure.

[index_max_zero_error !E0.2]

Excludes solutions with zero errors greater than index_max_zero_error.

[index_th2 !E | index_d !E]...
[index_I E1 [good]]

index_th2 or index_d defines a reflection entry in 2θ degrees or d-spacing in Å. index_I is typically set to the area under the peak; it is used to weight the reflection. good signals that the corresponding d-spacing is not an impurity line. A single use of good on a large d-

spacing decreases the number of possible solutions and hence speeds up the indexing process (see example INDEXING\EX10.INP).

[index_x0 !E]

Defines X_{hh} in the reciprocal lattice equation of (14-1). In a triclinic lattice the largest d-spacing can probably be indexed as 100 or 200 etc. Thus

```
index_x0 = 1/(dmax)^2;
```

speeds up the indexing process (if, in this case, the first line can be indexed as 100) and additionally the chance of finding the correct solution is enhanced, see EX13.INP. Note, if the data is in 2Th degrees then the following can be used:

```
index_x0 = (2 Sin(2Thmin Pi/360) / wavelength))^2;
```

The two macros Index_x0_from_d and Index_x0_from_th2 simplify the use of index_x0.

[index_zero_error]

Includes a zero error.

[no_extinction_subgroup_search]

By default, Extinction subgroup determination is performed at the end of an indexing run; this can be negated by defining no_extinction_subgroup_search.

[seed [#]]

Seeds the random number generator.

[try_space_groups $]...
[x_angle_scaler #0.1]
[x_scaler #]

Defines the space groups to be searched. The macros Bravais_Cubic_sgs etc... (see TOPAS.INC) defines lowest symmetry Bravais space groups. It is typically sufficient to use only these. Higher symmetry space groups for the Bravais lattices corresponding to the 10 best solutions is automatically searched at the end of an indexing run. Here are some examples of using try_space_groups.

Search	Use
Primitive monoclinic	`try_space_groups 3`
Monoclinic Bravais lattices of lowest symmetry	`Bravais_Monoclinic_sgs`
C-centered monoclinic of lowest symmetry	`try_space_groups 5`
All orthorhombic space groups individually	`Unique_Orthorhombic_sgs`

x_scaler is a scaling factor used for determining the number of steps to search in parameter space. x_scaler needs to be less than 1. Increasing x_scaler searches parameter space in finer detail. Default values are as follows:

Cubic	0.99	Orthorhombic	0.89
Hexagonal/Trigonal	0.95	Monoclinic	0.85
Tetragonal	0.95	Triclinic	0.72

x_angle_scaler is a scaling factor for determining the number of angular steps for monoclinic and triclinic space groups. Small values, 0.05 for example, increases the number of angular steps. The default value of 0.1 is usually adequate.

14.6 ... Identifying dominant zones

Here are two example output lines from an NDX file.

```
0) P42/nmc 3 0 1187.124  38.82 0.000 11.1904 11.1904 9.4799 90.00 90.00 90.00 ' ===  24 19
6) P-421c  3 0 1187.124  35.67 0.000 11.1904 11.1904 9.4799 90.00 90.00 90.00 ' ===  24 19
```

- The 1st column corresponds to the rank of the solution.
- The 2nd corresponds to the space group.
- The 3rd corresponds to the Status of the solution as follows:

  Status 1: Weighting applied as defined in Coelho (2003).

  Status 2: Zero error attempt applied.

  Status 3: Zero error attempt successful and impurity lines removal successful.

  Status 4: Impurity line(s) removed.
- The 4th column corresponds to the number of un-indexed lines.
- The 5th column corresponds to the volume of the lattice.
- The 6th corresponds to the goodness of fit value.
- The 7th corresponds to the zero error if index_zero_error is included.
- Columns 8 to 13 contains the lattice parameters.

The last two columns, let call them column Q_1 and Q_2, contain the number of non-zero ($h^2 + k^2 + h\,k$) and l^2 values, respectively, used in the indexed lines. Q_1 and Q_2 represent the hkl coefficient for X0 and X1 respectively for Trigonal/Hexagonal systems. When Q_1=-999 or Q_2=-999 then the corresponding lattice parameters are not represented. This facility is useful for identifying dominant zones. For example, if the smallest lattice parameter is 3Å and the smallest d-spacings is 4Å then it is impossible to determine the small lattice parameter. In such cases values of –999 will be obtained. The following table gives the hkl coefficients corresponding to the Xnn reciprocal lattice parameters for the 7 crystal systems.

	X0	X1	X2	X3	X4	X5
Cubic	$h^2+k^2+l^2$					
Hexagonal, Trigonal	$h^2+k^2+h\,k$	l^2				

Tetragonal	h^2+k^2	l^2				
Orhtorhombic	h^2	k^2	l^2			
Monoclinic	h^2	k^2	l^2	h l		
Triclinic	h^2	k^2	l^2	h k	h l	k l

14.7 ... *** Probable causes of Failure ***

The most probable cause of failure is the inclusion of too many d-spacings. If it is assumed that the smallest lattice parameter is greater than 3Å then it is problematic to include d-spacings with values less than about 2.5Å when there are already 30 to 40 reflections with d values greater than 2.5Å. Some of the problems caused by very low d-spacings are:

- The number of calculated lines increases dramatically and thus index_max_Nc_on_No will need to be increased.
- The low d-spacings are probably inaccurate due to peak overlap.

A situation where it is necessary to include low d-spacings is when there are only a few d-spacings available as in higher symmetry lattices.

14.8 ... Space groups with identical absences – Extinction subgroups

The following table lists spaces groups than have identical hkls. Typically, an indexing run will identify one space-group from the extinction group.

Space group numbers with identical hkls	Space group symbols with identical hkls
Triclinic	
1 2	P1 P-1
Monoclinic	
9 15	Cc C2/c
5 8 12	C2 Cm C2/m
14	P21/c
7 13	Pc P2/c
4 11	P21 P21/m
3 6 10	P2 Pm P2/m
Orthorhombic	
70	Fddd
43	Fdd2
22 42 69	F222 Fmm2 Fmmm
68	Ccca
73	Ibca
37 66	Ccc2 Cccm
45 72	Iba2 Ibam
41 64	Aba2 Cmca

46 74	Ima2 Imma
36 40 63	Cmc21 Ama2 Cmcm
39 67	Abm2 Cmma
20	C2221
23 24 44 71	I222 I212121 Imm2 Immm
21 35 38 65	C222 Cmm2 Amm2 Cmmm
52	Pnna
56	Pccn
60	Pbcn
61	Pbca
48	Pnnn
54	Pcca
50	Pban
33 62	Pna21 Pnma
34 58	Pnn2 Pnnm
32 55	Pba2 Pbam
30 53	Pnc2 Pmna
29 57	Pca21 Pbcm
27 49	Pcc2 Pccm
31 59	Pmn21 Pmmn
26 28 51	Pmc21 Pma2 Pmma
19	P212121
18	P21212
17	P2221
16 25 47	P222 Pmm2 Pmmm
Tetragonal	
142	I41/acd
110	I41cd
141	I41/amd
109 122	I41md I-42d
108 120 140	I4cm I-4c2 I4/mcm
88	I41/a
80 98	I41 I4122
79 82 87 97 107 119 121 139	I4 I-4 I4/m I422 I4mm I-4m2 I-42m I4/mmm
130	P4/ncc
126	P4/nnc
133	P42/nbc
103 124	P4cc P 4/mcc
104 128	P4nc P 4/mnc
106 135	P42bc P 42/mbc
137	P42/nmc
138	P42/ncm
134	P42/nnm
125	P4/nbm
114	P-421c
105 112 131	P42mc P-42c P42/mmc

102 118 136	P42nm P-4n2 P42/mnm
101 116 132	P42cm P-4c2 P42/mcm
100 117 127	P4bm P-4b2 P4/mbm
86	P42/n
85 129	P4/n P4/nmm
92 96	P41212 P43212
94	P42212
76 78 91 95	P41 P43 P4122 P4322
77 84 93	P42 P 42/m P4222
90 113	P4212 P-421m
75 81 83 89 99 111 115 123	P4 P-4 P4/m P422 P4mm P-42m P-4m2 P4/mmm
Trigonal & Hexagonal	
161 167	R3c R-3c
146 148 155 160 166	R3 R-3 R32 R3m R-3m
184 192	P6cc P6/mcc
159 163 186 190 194	P31c P-31c P63mc P-62c P63/mmc
158 165 185 188 193	P3c1 P-3c1 P63cm P-6c2 P63/mcm
169 170 178 179	P61 P65 P6122 P6522
144 145 151 152 153 154 171 172 180 181	P31 P32 P3112 P3121 P3212 P3221 P62 P64 P6222 P6422
173 176 182	P63 P63/m P6322
143 147 149 150 156 157 162 164 168 174 175 177 183 187 189 191	P3 P-3 P312 P321 P3m1 P31m P-31m P-3m1 P6 P-6 P6/m P622 P6mm P-6m2 P-62m P6/mmm
Cubic	
228	Fd-3c
219 226	F-43c Fm-3c
203 227	Fd-3 Fd-3m
210	F4132
196 202 209 216 225	F23 Fm-3 F432 F-43m Fm-3m
230	Ia-3d
220	I-43d
206	Ia-3
214	I4132
197 199 204 211 217 229	I23 I213 Im-3 I432 I-43m Im-3m
222	Pn-3n
218 223	P-43n Pm-3n
201 224	Pn-3 Pn-3m
205	Pa-3
212 213	P4332 P4132
198 208	P213 P4232
195 200 207 215 221	P23 Pm-3 P432 P-43m Pm-3m

14.9 ... Indexing Equations - Background

a, **b** and **c** lattice vectors can be converted to Cartesian coordinates with **a** collinear with the Cartesian *x* axis and **b** coplanar with the Cartesian *x*-*y* plane as follows:

$$\mathbf{a} = a_x\,\mathbf{i} \qquad \mathbf{b} = b_x\,\mathbf{i} + b_y\,\mathbf{j} \qquad \mathbf{c} = c_x\,\mathbf{i} + c_y\,\mathbf{j} + c_z\,\mathbf{k} \tag{14-3}$$

where

$a_x = a$

$b_x = b\cos(\gamma),\quad b_y = b\sin(\gamma)$

$c_x = c\cos(\beta),\quad c_y = c\,(\cos(\alpha) - \cos(\beta)\cos(\gamma)) / \sin(\gamma),\quad c_z^2 = c^2 - (c_x)^2 - (c_y)^2$

a, b, c are the lattice parameters and α, β, γ the lattice angles. The reciprocal lattice vectors **A**, **B**, and **C** calculated from the lattice vectors of Eq. (14-3) become:

$$\mathbf{A} = A_x\,\mathbf{i} + A_y\,\mathbf{j} + A_z\,\mathbf{k} \qquad \mathbf{B} = B_y\,\mathbf{j} + B_z\,\mathbf{k} \qquad \mathbf{C} = C_z\,\mathbf{k}$$

The equation relating d-spacing d_{hkl} to hkl in terms of the reciprocal lattice parameters is:

$$X_{hh}h^2 + X_{kk}k^2 + X_{ll}l^2 + X_{hk}h\,k + X_{hl}h\,l + X_{kl}k\,l = 1/d_{hkl}^2 \tag{14-4}$$

where

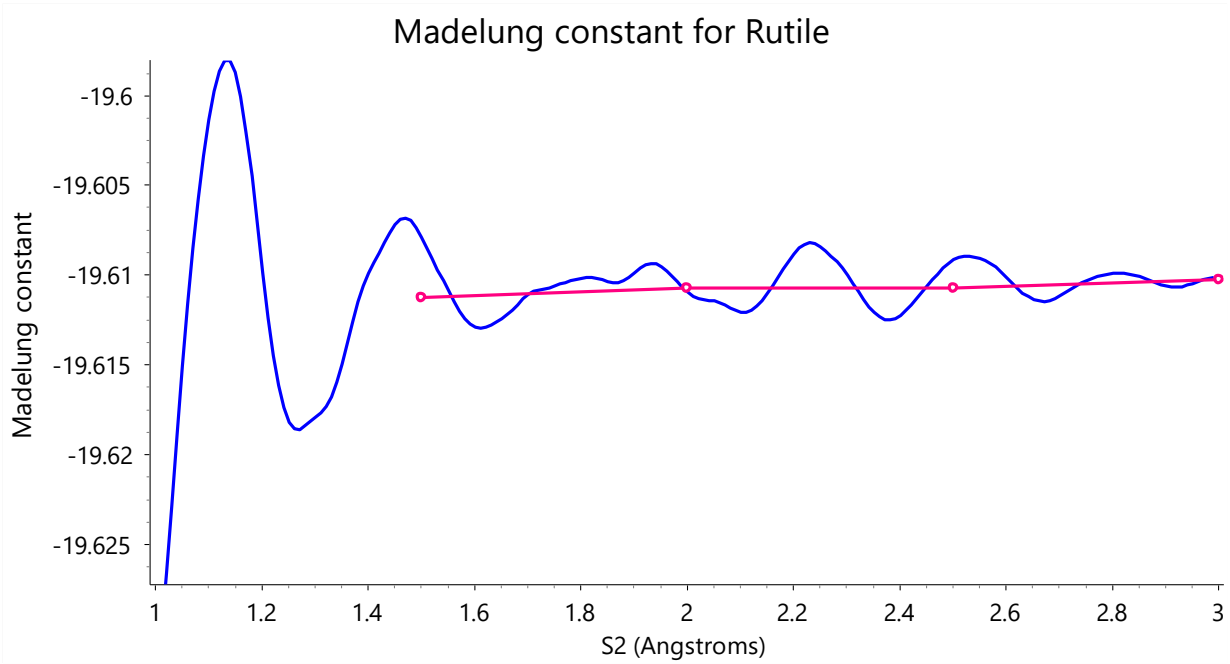
$$X_{hh} = A_x^2 + A_y^2 + A_z^2 \qquad X_{hk} = 2A_yB_y + 2A_zB_z$$
$$X_{kk} = B_y^2 + B_z^2 \qquad X_{hl} = 2A_zC_z$$
$$X_{ll} = C_z^2 \qquad X_{kl} = 2B_zC_z$$

15. ENERGY MINIMIZATION

15.1 ... Reporting on the Madelung constant

str... [madelung #]	**Examples** TEST_EXAMPLES\MADELUNG.INP

The madelung keyword reports on the Madelung constant of a structure (Madelung, 1918). It uses the method of Coelho & Cheary (1997) for calculating the electrostatic potentials. Atomic charges are from the occ keyword, see MADELUNG.INP. *#define show_GRS* in MADELUNG.INP creates an XY file with (S2-S1) of the GRS series set to 0.01. This is a small value that shows the behaviour of the GRS series which is as follows (blue line):



With the default values of S1 =1 and S2 = 1.5; the GRS series integrates between S1 and S2 to obtain an accurate value for the Madelung constant; this is seen in the first point of the Red line of the above plot. In energy minimization, the derivatives of the Madelung constant as a function of atomic coordinates constitutes the electrostatic force exerted on atoms.

15.2 ... Reporting on the Coulomb potential at a site

site ... [co #]	

The site dependent keyword co reports on the Coulomb potential at a site. The sum of all co values equates to the Madelung constant. From observation, atoms of the same species seem to have similar co values in an ionic crystal. Note, both the co and madelung keywords are independent of the grs_interaction keyword.

15.3 ... Enhancements to the grs_interaction

site ... [g !N q E s E] [repulsion_refine] [grs_interaction [qi !E qj !E] $s1 $s2 c !E]... [no_coulomb] [penalty = Get(grs_lp_rep);] [penalty = Get(grs_lp_refine);]	**Examples** TEST_EXAMPLES\ ALVO4-GRS-AUTO.INP (not new) GRS-ALVO4\SOLVE-1.INP GRS-ALVO4\REP-1.INP GRS-ALVO4\REP-2.INP

The site dependent keyword g reports on the difference in value between the sum of all grs_intercations with the site included, and the site excluded. In other words, it reports on the site's contribution to all grs_interactions.

When repulsion_refine is defined, then all grs_interactions are placed in a "repulsion refine" mode. In this mode, grs_interactions return the sum of the derivatives squared of the grs_interactions, with respect to the atomic coordinates, or, in pseudo code:

$$\text{Sum}(d\text{grs\_interaction}/df_i, i)^2$$

where f_i corresponds to the x, y and z coordinates of the sites associated with the grs_interaction. In this manner, a refinement will adjust repulsion parameters such that the derivatives of the grs_interactions with respect to independent repulsion parameters are a minimum.

Repulsion parameters include qi, qj, q, s and any other parameters defined in the grs_interaction equation. The new site dependent keyword, s, scales the equation part of grs_interactions. This simplifies the setting up of grs_interactions; consider the following:

```
grs_interaction qi = 3; qj = -2; Al* O* p1 = B1 / R^7; penalty = p1;
grs_interaction qi = 5; qj = -2; V*  O* p2 = B2 / R^7; penalty = p2;
grs_interaction qi = 3; qj =  5; Al* V* p3 = B3 / R^7; penalty = p3;
```

Here, there are three parameters B1, B2 and B3. In the repulsion_refine mode, fractional coordinates are not refined. However, their derivatives with respect to the grs_interaction equations are expensive and are required. The site dependent s parameters can be used to avoid this recalculation as follows:

```
site Al … q  3 s s1 1
site V …  q  5 s s2 1
site O …  q -2 s s3 1
repulsion_refine
grs_interaction * * c = 1/R^9;
penalty = c;
```

Note the reformulation where three grs_interactions become one. Here the program examines the equation, 1/R^9 in this case, and, if independent of refined parameters, the program stores the 1/R^9 values for use in the calculation of derivatives of the grs_intercations equations with respect to repulsion refined parameters. This results in a large speed up in computation. The three parameters s1, s2 and s3 are related to the B1, B2 and B3 values as follows:

B1 = s1 s3

B2 = s2 s3
B3 = s1 s2

These parameters are related to the minimum distance R_o between two isolated atoms *i* and *j*, and for the case of opposite q charges, as follows:

$$U_{ij} = q_i q_j / R + s_i s_j / R^n$$

Setting the derivative to zero:

$$dU_{ij}(R=R_o)/dR = 0$$

we get:

$$R_o = [(n-1) s_i s_j / (q_i q_j)]^{1/(n-1)}$$

15.4 ... Including lattice parameter in grs_interaction(s)

The default is to not include lattice parameters when repulsion_refine is defined. To include the minimization of derivatives of the grs_interactions with respect to the lattice parameters, the following can be used:

```
penalty = Get(grs_lp_rep); : 0
```

For normal refinement (repulsion_refine not defined), lattice parameters, flagged for refinement, are included in the derivatives of grs_interactions if the following is included:

```
penalty = Get(grs_lp_refine); : 0
```

15.5 ... Ignoring the Coulomb part of the grs_intercation

The Coulomb part of the grs_interaction can be ignored using the no_coulomb keyword. This is useful for materials that are not wholly ionic. Various version of the Lennard Jones potential, for example, can be implemented; consider a potential U of:

$$U = A / R^6 + B/R^{12}$$

To efficiency calculates this U, then two grs_intercations can be used:

```
site... q  1 s @ 1
site... q -1 s @ 1
grs_interaction … = 1 /R^4; no_coulomb
grs_interaction … = 1 /R^9; no_coulomb
```

Here, 1/R^4 and 1/R^9 values are stored in lookup tables which are calculated once at the start of refinement. This potential is used in describing the partly ionic structure of $AlVO_4$, see GRS-ALVO4\REP-2.INP.

The grs_interaction equation can also be set to zero. This may be useful when looking at dipole properties of a molecule where the centre of the electron cloud is at a different position from the nucleus, for example:

```
    site Al1       x x1 # y y1 # z z1 # …
    site Al1_shift x = dx1 x1; y = dy1 + y1; z = dz1 + z1; …
    grs_interaction … Al1 = 0;                      ' No repulsion equation
    grs_interaction … Al1_shift = 1 /R^9; no_coulomb ' No Coulomb potential
```

15.6 … _rem attribute - Removing/inserting parameters from refinement

The _rem parameter attribute is an equation that is evaluated at the start of a refinement iteration (note: attribute equations cannot be named). If non-zero, the associated parameter is removed from refinement for the duration of the iteration. The parameter can be reinstated in subsequent iterations if _rem evaluates to zero; for example, to reinstate the parameter after convergence and into a new Cycle, the following could be used:

```
    prm a 1 _rem = Mod(Cycle, 2);
```

15.7 … Using ok_to_continue and _rem

In version 7, the ALVO4-GRS-AUTO.INP test example was the fastest way of solving the $AlVO_4$ structure. In that example, the scattering power of the Al and V sites are allowed to refine within the scattering power range of Al+3 and V+5. An alternative to refining on the Al+3 occupancies, is to fix the occupancies for a certain number of Cycles and then change the occupancies on the Al+3 site without actually including them in the refinement. This is accomplished using the new keywords of ok_to_continue, q, s and the new _rem parameter attribute; it works as follows (see GRS-ALVO4\SOLVE-1.INP for details):

```
macro qal { 3 } ' Charge of Al+3
macro qv  { 5 } ' Charge of V+5
macro exp { 9 } ' Repulsion exponent

macro ro_al { 1.65 } ' Ro values from bond distances
macro ro_v  { 1.5 }
macro ro_oo { 2.4 }

' Change Ro values to s values
prm !so  = Sqrt((4 ro_oo^(exp-1)) / exp); :  22.1184
prm !sal = ((ro_al^(exp-1)) 6 / exp   ) / so; :  1.65587133
prm !sv  = ((ro_v^(exp-1)) 10 / exp) / so; :  1.28746033

macro S_ { If(Get(q) == qal, sal, sv) }
macro OCC { If(Get(q) == qal, 1, 1.85) }
macro VV { rand_xyz 1 } ' Randomize sites at start of cycle
macro VQ { _rem 1 val_on_continue = If(Mod(Cycle,10), If(Rand(0,1)<0.5,qal,qv), Val); }
prm q1 qal VQ
prm q2 qal VQ
prm q3 qal VQ
prm q4 qv  VQ
prm q5 qv  VQ
prm q6 = 3 qal + 3 qv - q1 - q2 - q3 - q4 - q5;

' Ensure scattering power equals 3*Al sites plus 3*V sites
ok_to_continue = Or(q6 == qal, q6 == qv);

Grs_(*, *, exp, 0) ' grs_interaction penalty
```

```
site Al   x @  0.0  y @  0.9  z @  0.8 occ Al+3 = OCC; q = q1; s = S_; VV
site Al   x @  0.1  y @  0.0  z @  0.9 occ Al+3 = OCC; q = q2; s = S_; VV
site Al   x @  0.2  y @  0.1  z @  0.0 occ Al+3 = OCC; q = q3; s = S_; VV
site Al   x @  0.3  y @  0.2  z @  0.1 occ Al+3 = OCC; q = q4; s = S_; VV
site Al   x @  0.4  y @  0.3  z @  0.2 occ Al+3 = OCC; q = q5; s = S_; VV
site Al   x @  0.5  y @  0.4  z @  0.3 occ Al+3 = OCC; q = q6; s = S_; VV

site O1   x @  0.6  y @  0.5  z @  0.4 occ O-2 1 q -2 s = so; VV
site O2   x @  0.7  y @  0.6  z @  0.5 occ O-2 1 q -2 s = so; VV
site O3   x @  0.8  y @  0.7  z @  0.6 occ O-2 1 q -2 s = so; VV
site O4   x @  0.9  y @  0.8  z @  0.7 occ O-2 1 q -2 s = so; VV
site O5   x @  0.0  y @  0.9  z @  0.8 occ O-2 1 q -2 s = so; VV
site O6   x @  0.1  y @  0.0  z @  0.9 occ O-2 1 q -2 s = so; VV
site O7   x @  0.2  y @  0.1  z @  0.0 occ O-2 1 q -2 s = so; VV
site O8   x @  0.3  y @  0.2  z @  0.1 occ O-2 1 q -2 s = so; VV
site O9   x @  0.4  y @  0.3  z @  0.2 occ O-2 1 q -2 s = so; VV
site O10  x @  0.5  y @  0.4  z @  0.3 occ O-2 1 q -2 s = so; VV
site O11  x @  0.6  y @  0.5  z @  0.4 occ O-2 1 q -2 s = so; VV
site O12  x @  0.7  y @  0.6  z @  0.5 occ O-2 1 q -2 s = so; VV
```

The above will change the scattering power on the Al* sites every 10th Cycle as defined in the VQ macro. Note, there's only one grs_interaction and the Grs_ macro looks like:

```
    macro Grs_(s1, s2, & n, v)
        {
            grs_interaction s1 s2 #m_unique c =
                If (R < rsm,
                    ((-n rsm^(-2 - n)/2) R^2 + rsm^(-n) + n/(2 rsm^n)),
                    1 / R^n
                );
            penalty = c; : v
        }
```

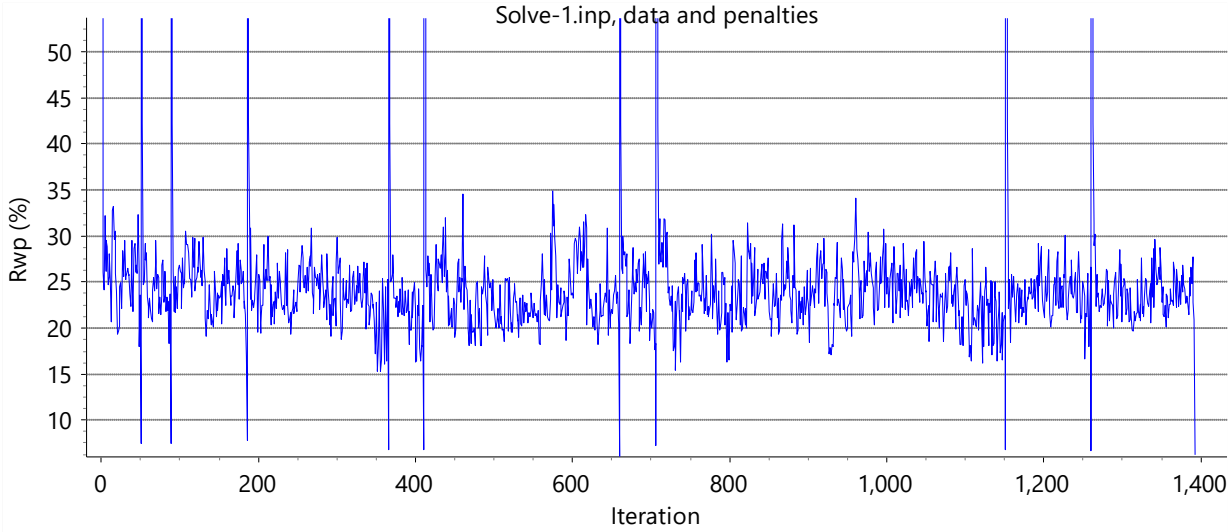
SOLVE-1.INP operates in three modes which can be chosen by the two control parameters (in Red) in the INP text at the top of the file and is as follows:

```
continue_after_convergence
#prm penalties_only_start_at_Rietveld_positions = 1;
#if penalties_only_start_at_Rietveld_positions;
    only_penalties
    verbose 1
    temperature 0.5 use_best_values
#else
    #prm solve_using_real_data_and_penalties = 1;
    #prm solve_using_penalties_only = solve_using_real_data_and_penalties == 0;
    verbose -1
    num_runs 10  ' Solve structure 10 times, change to 1 to see solution

    #if solve_using_real_data_and_penalties;
        ' Minimum energy at 5%
        temperature = If(Mod(Cycle, 200), 0.7, 10);
        iters = If(And(Cycle_Iter > 2, Get(r_wp) < 8), 0, 1000000000);
    #endif
    #if solve_using_penalties_only;
        ' Minimum energy at -423.5
```

```
        only_penalties
        temperature = If(Mod(Cycle, 200), Rand(0.35, 0.7), 10);
        iters = If(And(Cycle_Iter > 2, Get(r_wp) < -423), 0, 1e9);
    #endif
#endif
```

Running SOLVE-1.INP with *penalties_only_start_at_Rietveld_positions*=1 refines on the atomic coordinated with only_penalties defined. It also displaces the atomic positions by an amount of rand_xyz*temperature, or, 0.5 Å in a random direction at the start of each cycle. As can be seen whilst running, the structure returns to the Rietveld refined values after each cycle.

Running SOLVE-1.INP with *solve_using_real_data_and_penalties*=1 solves the structure 10 times and the Rwp plot looks like:



This is similar to ALVO4-GRS-AUTO.INP which refines on occupancies. ok_to_continue is evaluated at the start of each iteration. If it evaluates to zero, then val_on_continue of its independent parameters are executed. The process is repeated until all ok_to_continue(s) evaluates to non-zero. Note, more than one ok_to_continue can be defined.

15.8 ... Energy minimization-only resulting in the observed structure of AlVO4

Running SOLVE-1.INP with *solve_using_real_data_and_penalties*=0, achieves a minimum energy configuration that matches the Rietveld refined structure. only_penalties are refined; lattice parameters are not included. Even though $AlVO_4$ is partly ionic, the maximum atomic displacement at the energy minimum compared to the Rietveld refined positions is relatively small at ~0.22 Å with an average movement of ~0.14 Å. In other words, the energy minimization "pseudo-solved" the structure from a crude atomic interaction model.

Including lattice parameters as refinable parameters results in non-sensical atomic coordinates which means that the atomic interaction model is inadequate in a physical sense.

15.9 ... Determining repulsion parameters for AlVO4

REP-1.INP performs three types of operations/refinements as seen by the self-explanatory control statements at the top of the file of:

```
#prm determine_repulsion_parameters = 0;
#prm test_rep_prms = 0;
#prm bond_length_differences = 0;
```

Setting *determine_repulsion_parameters*=1 fixes the atomic coordinates to Rietveld refined values and then minimizes dU_{ij}/df_i=0 for $AlVO_4$ by varying three s repulsion parameters of *sal*, *sv* and *so* where:

$$U_{ij} = q_i\, q_j / R + s_i\, s_j / R^9$$

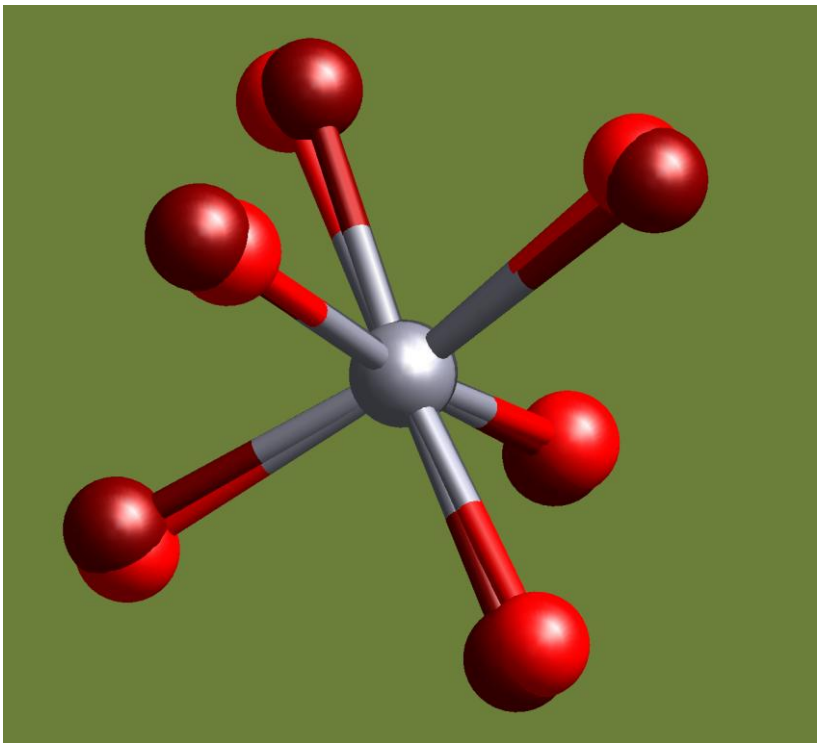
As seen in REP-1.INP, the sum of the derivatives squared of dU/df_i (where f_i is a fractional atomic coordinate) do not refine to zero. This is seen in the lines:

```
Grs_(*, *, 9, 0.465098047`)
penalty = Get(grs_lp_rep); :  2.6397897`
```

Also, seen in REP-1.INP is that the R_o values (distance between two isolated atoms) seem too large as in:

```
prm !ro_alo = ( (exp-1) Abs(sal so qal qo) )^(1/(exp-1)); :  2.18729482
prm !ro_vo  = ( (exp-1) Abs(sv  so qv  qo) )^(1/(exp-1)); :  2.4673052
prm !ro_oo  = ( (exp-1) Abs(so  so qo  qo) )^(1/(exp-1)); :  2.73559269
```

Performing another refinement with the three determined repulsion parameters *sal*, *sv* and *so* fixed, and instead refining on the atomic coordinates (*test_rep_prms*=1) results in a structure with average atomic movements of 0.14 Å from the Rietveld coordinates. The movement can be seen in the following Al octahedron (lighter atoms are the Rietveld determined positions):

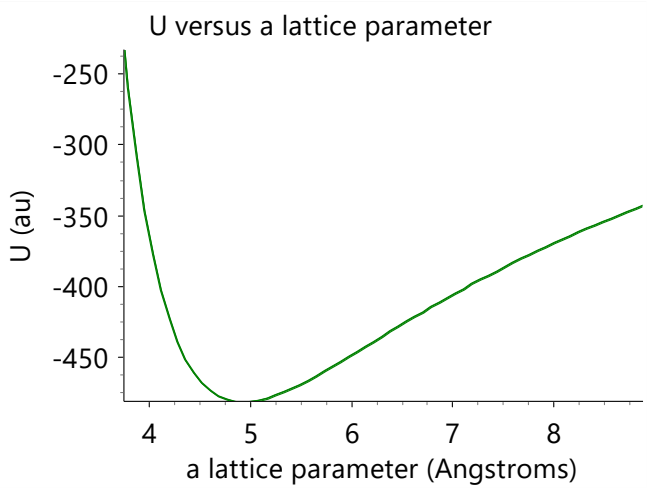


Setting *test_rep_prms*=1 and *output_U_vs_a*=1 executes the INP code of:

```
#if And(output_U_vs_a, test_rep_prms);
```

```
      verbose 1
      num_runs 100
      iters 0
      a = Ramp_Run_Number(6.54131-3, 6.54131+3, Get(num_runs));
      out a.xy append
         Out(Get(a))
         Out_String(" ")
         Out(Get(non_fit, r_wp))
         Out_String("\n")
   #else
      a  6.54131
   #endif
```

This produces the XY file of:



Here we see that the observed *a* lattice parameter of 6.54131 Å is far from the minimum; this was evident from the non-zero value for Get(*grs_lp_rep*) as seen above. Note the use of *Get(non_fit, r_wp)* instead of *Get(r_wp)*; the former gets the global Rwp and the latter the xdd dependent Rwp. Use of only_penalties does not update xdd dependent Rwp(s); hence the need to Get the *global r_wp*.

Lattice parameters were not refined in performing the *test_rep_prms*=1 operation; they could have been with the inclusion of the line:

```
   penalty = Get(grs_lp_refine); : 0
```

The refinement in such a case would have produced very incorrect results as indicated by the U versus *a* plot above. This demonstrates that a simple Coulomb sum and 1/R^9 repulsion term does not fully describe $AlVO_4$ and that another model is needed.

15.10 . A non-ionic model for AlVO4

Instead of using the Coulomb sum, a 1/R^4 term was used for atoms of opposite charge (Al-O and V-O) and a 1/R^9 for like charges, or,

$$U_{ij} = A_{ij} / R^4 + B_{ij}/R^9$$

This U choice was a guess and there may well be more physically meaningful models available. The following however does highlight the ability to quickly model such cases. The REP-2.INP test example uses this potential and it has three operational/refinement modes:

```
#prm repulsion_refine = 0;          ' set to 0 or non-zero
#prm bond_length_differences = 0;   ' set to 0 or non-zero
#prm test_repulsion_prms = repulsion_refine == 0;
```

Refining with *repulsion_refine*=1 results in a low value for *grs_lp_rep* and for grs_interactions:

```
penalty = Get(grs_lp_rep); : 0.000423118927`
Grs_(Al*,  O*, ea,  -a_alo, 0.000824217622`)
Grs_(V*,   O*, ea,  -a_vo,  0.00103650359`)
Grs_(O*,   O*, ea,  a_oo,   0.000721564661`)
Grs_(Al*, Al*, ea,  a_alal, 0.000102652961`)
Grs_(Al*,  V*, ea,  a_alv,  0.000417591887`)
Grs_(V*,   V*, ea,  a_vv,   0.000314938926`)
Grs_(Al*,  O*, er,  b_alo,  0.000824217622)
Grs_(V*,   O*, er,  b_vo,   0.00103650359)
Grs_(O*,   O*, er,  b_oo,   0.000721564661)
Grs_(Al*, Al*, er,  b_alal, 0.000102652961)
Grs_(Al*,  V*, er,  b_alv,  0.000417591887)
Grs_(V*,   V*, er,  b_vv,   0.000314938926)
```

These are low values compared to those obtained for REP-1.INP and it indicates near zero values for $(\mathrm{dgrs\_interaction}/\mathrm{d}f_i)^2$ where f_i is a fractional atomic coordinate or lattice parameter. The difference in lattice parameters between the observed values from Rietveld refinement and the energy minimization of REP-2.INP is:

```
Δa  = 0.353377, Δb  = 0.387755,  Δc = 0.501125
Δal = -0.92222, Δbe = -0.32539, Δga = -0.77862
```

The maximum bond length difference is 0.18 Å with an average difference of 0.08 Å.

16. MOLECULAR DYNAMICS (MD)

molecular_dynamics md_time_step !E (default = 0.002) md_time !E md_scale !E (default = 1) Parameter attributes: _md_k !E (default = 1) _mass !E (default = 1) _md_force !E (default = 0)	**Examples** TEST_EXAMPLES\GRS-ALVO4\ MD-1.INP MD-2.INP MD-3.INP MD-4.INP GRS-0.INP

16.1 ... Molecular dynamics in a general manner

Defining molecular_dynamics (MD) places the program in a non-refinement mode where parameters of any type can be updated in a time dependent manner. The Verlet (1967) algorithm is used for updating parameters. In the present implementation, parameters that are not typically associated with molecular dynamics can be updated in a MD manner. This is accomplished with the use of the parameter attributes of _md_k and _md_mass.

Molecular dynamics is basically the steepest decent method of refinement but with new parameters values accepted regardless of the change in the objective function (Rwp in the case of TOPAS), or, relating this to the Newtonian equations of motion for iteration *k* and parameter *p*, we have:

$$\text{Force}(k) = m\, a(k) = d\text{Rwp}/dp$$

$$\text{Velocity}(k+1) = \text{Velocity}(k) + (d\text{Rwp}(k)/dp) / m$$

In the Verlet algorithm, velocity is not considered explicitly and instead p is updated as follows:

$$p(k+1) = 2\,p(k) - p(k-1) + a(k)\,t^2$$

$$= 2\,p(k) - p(k-1) + (1/m)\,(d\text{Rwp}(k)/dp)\,t^2$$

where *t* is the time step of the molecular dynamics. The mass *m* is set using _mass. To introduce flexibility, the present implementation allows modifications of *p*(k+1) as follows:

$$p(k+1) = (p(k) - p(k-1) + (\text{\_md\_k} / \text{\_mass})\,(d\text{Rwp}(k)/dp)\,t^2)\ \text{md\_scale} + p(k)$$

This equates to the Verlet algorithm with the default value of 1 for _md_k, _mass and _md_scale. md_scale is a means of increasing or decreasing atomic movements (increasing or decreasing temperature).

16.2 ... Molecular dynamics for atoms

In the absence of the _mass attribute, mass is determined from the masses found in the ISOTOPES.TXT file for site occupancies, as defined by the occ keyword, and weighted by the occ values. In the absence of the _md_k attribute, md_k is determined for x, y and z coordinate parameters as follows:

```
md_k for x = ax
md_k for y = by
md_k for z = cz
where  ax = 1
       bx = Cos(Get(ga) Deg)
       by = Sin(Get(ga) Deg)
       cx = Cos(Get(be) Deg)
       cy = (Cos(Get(al) Deg) - cx bx) / by
       cz = Sqrt(1.0 - cx^2 - cy^2)
```

The following two sites are therefore equivalent:

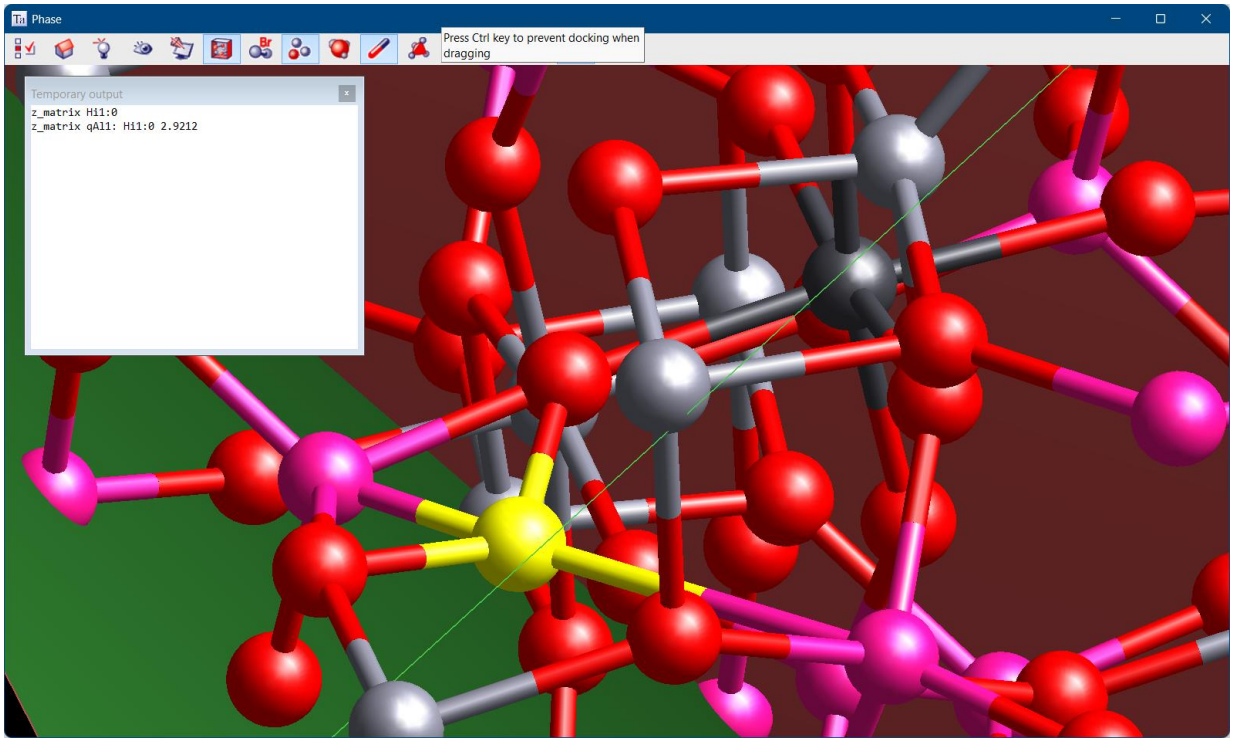
```
   site Al
      x @ # _mass = 26.981; _md_k = ax;
      y @ # _mass = 26.981; _md_k = by;
      z @ # _mass = 26.981; _md_k = cz;
      occ Al+3 1
' and
   site Al x @ # y @ # z @ # occ Al+3 1
```

The use of _md_k corrects the forces in case of non-orthogonal lattice parameters. grs_interaction can be used to calculate the forces for molecular dynamics; this is demonstrated in MD-1.INP. The display of the Rwp plot in the Fit dialog can take a lot of processing for long MD runs; not displaying the plot can speed up the simulation; and imilarly for the OpenGL 3D graphics.

MD-1.INP operates in the P-1 space group; this can be changed to P1 by outputting the fractional coordinates in P1 as follows:

```
   p1_fractional_to_file aac.txt
      in_str_format
      in_cart 0
      na 2 nb 2 nc 2
```

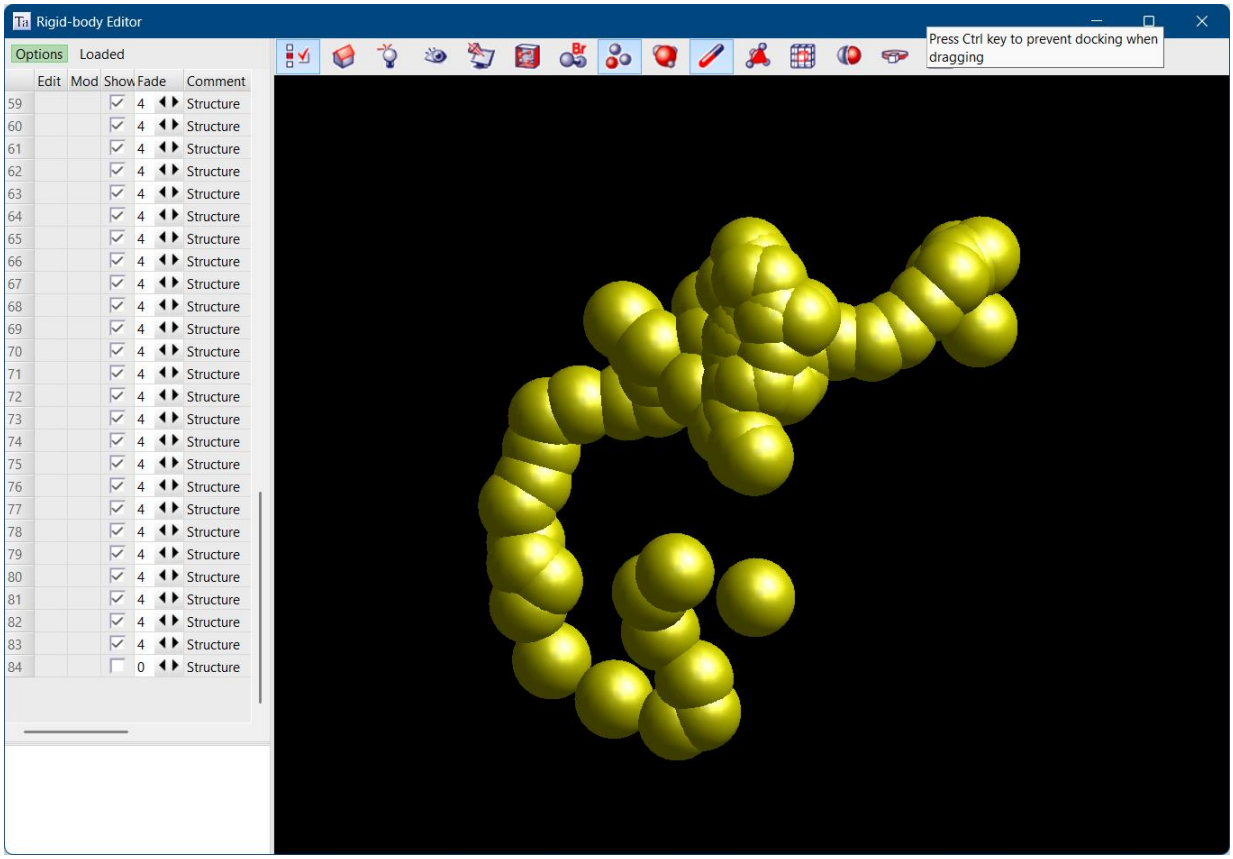
Here, a 2x2x2 unit cell is outputted in P1 to the AAC.TXT file. MD-2.INP describes such a unit cell comprising 288 atoms. One of the AL1 atoms is offset, and running the MD simulation results in the atom returning to its lowest energy configuration position. This return to the optimal position is due to the small offset of 2.92 Å. The following shows the starting configuration:



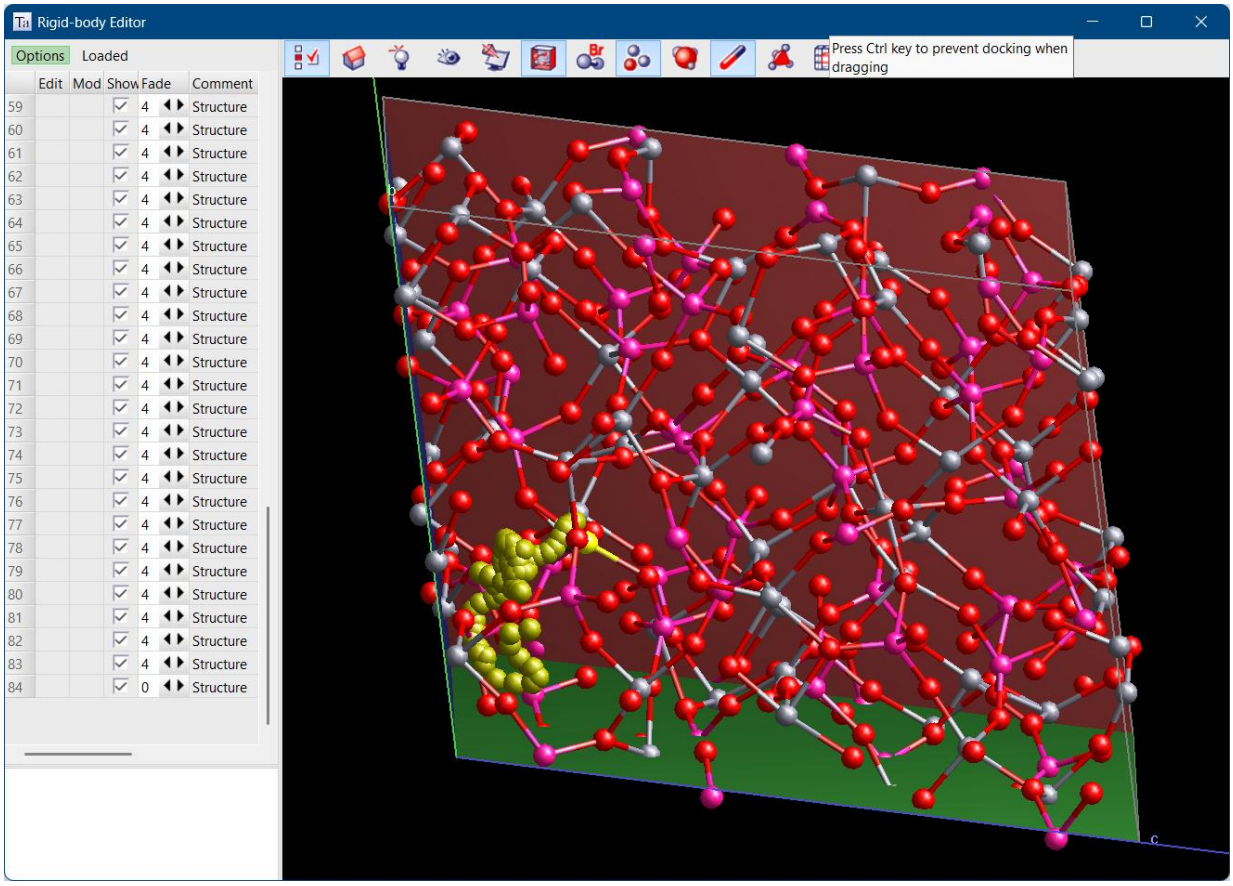
where the yellow atom is the Al1 atom's offset, and the dark grey atom is the original position of the Al1 atom. It is informative to watch the yellow atom migrate to the dark grey atom. The INP text that produces the coloured Al1 sites is:

```
track_buffer 100
site qAl1 x   0.37342 y   0.34930 z   0.20369  occ Al+3  1 ' original posn
site Hi1  x @ 0.2     y @ 0.2     z @ 0.1  occ Al+3  1 track = Mod(Cycle_Iter, 20) == 0;
```

The colours for the Al1 and Hi1sites is seen in the ATOM_COLORS.DEF file; this file can be edited for the purpose of changing atom colours. The original atom qAl1 does not take part in the only_penalties MD simulation as it is absent from the grs_interactions. The path of the Al1 atom looks like:



Note the last display has been disabled (item 84); it comprises all 288 atoms in the cell. Including line 84 produces:



MD-3.INP moves the Al1 atom 4 Å from the original position and in a random direction; the pertinent INP text is:

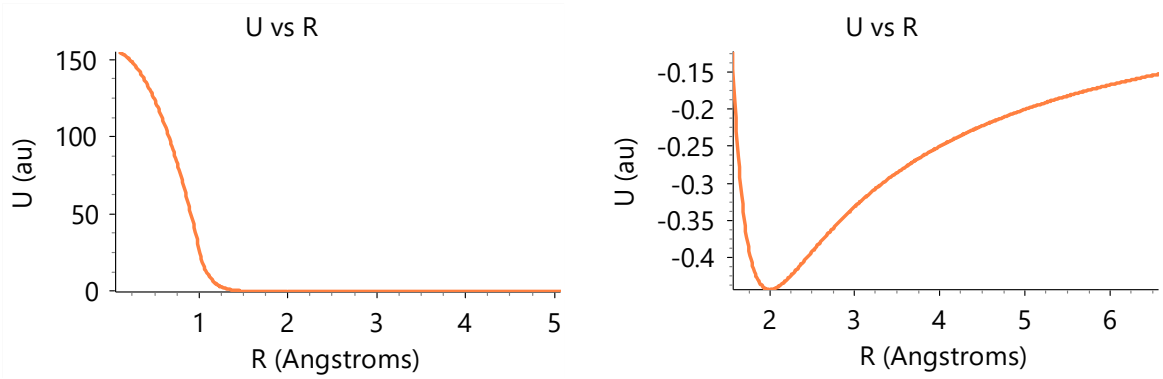
```
temperature 1
md_scale = If(Cycle_Iter < 2, 0.1, 1);
site Hi1 x @  0.37342 y @  0.34930  z @ 0.20369  occ Al+3 1 rand_xyz 4
```

Clicking on the Break icon; ie.

executes rand_xyz. Often the energy of the system (which is kept constant) is too great and the MD goes chaotic. This behaviour can be damped using md_scale as seen above. Also, repulsion terms such as $1/R^9$ can be very large when R is small; such small bond distances are unrealistic and modifying U_{ij} to avoid large values is beneficial. In the present work the equation used for the grs_interaction, rewritten in terms of a yobs_eqn, is given in GRS-0.INP, or,

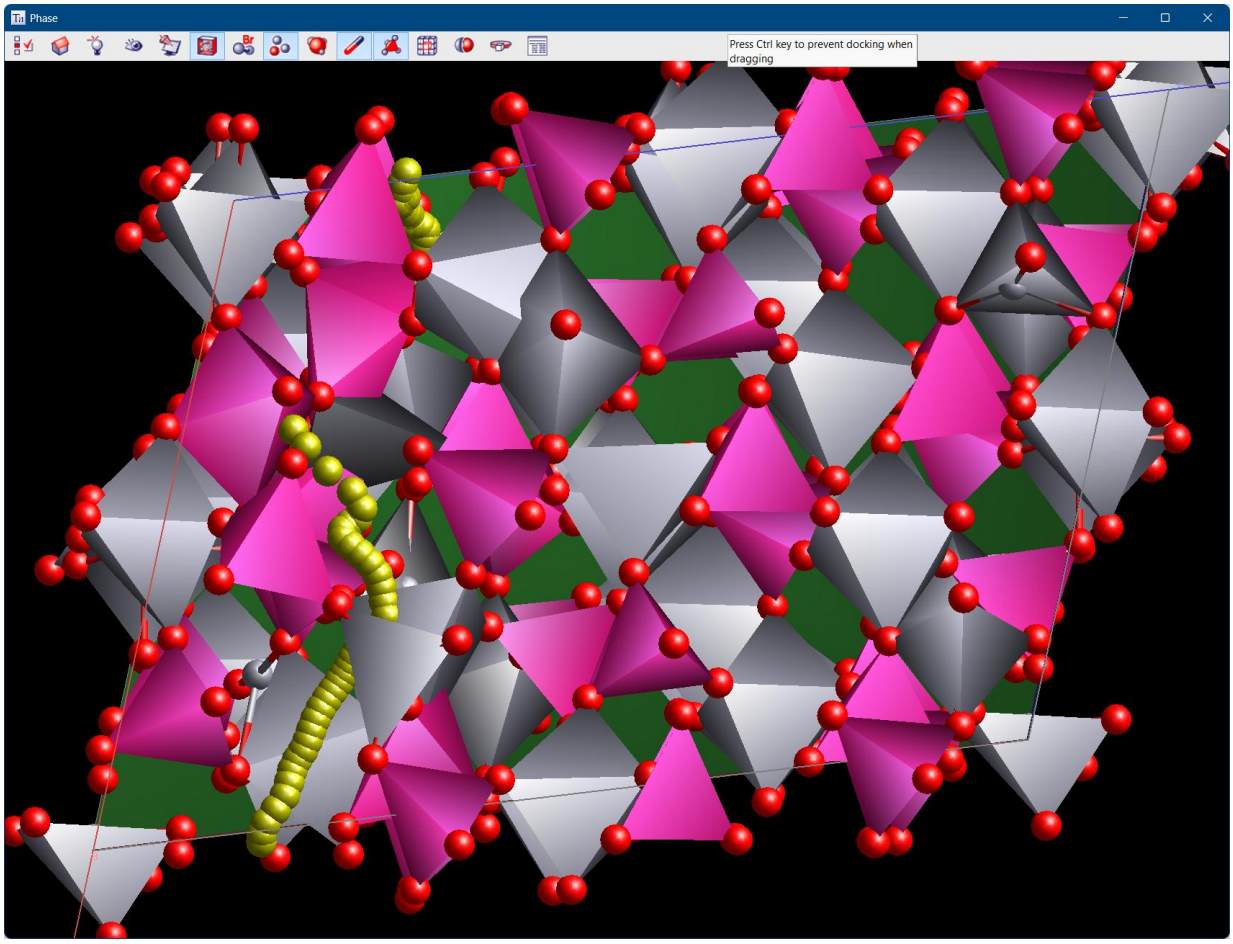
```
macro & n { 9 }
macro & q { -1 }
macro & ro { 2 }    ' x-axis value at the minimum
macro & rsm { 1 }
yobs_eqn aac.xy =
   If (X < rsm,
        (Abs( q ) / n) (ro^(n-1)) ( (-n rsm^(-2 - n)/2) X^2 + rsm^(-n) + n/(2 rsm^n)),
        (Abs( q ) / n) (ro^(n-1)) / X^n + q / X
   );
    min 0.1 max 7 del 0.01
```

Note, the rsm value of 1. For R < rsm, U is modified such that large values are not encountered. The following shows two views of the same yobs_eqn plot:



16.3 ... Applying a force on atoms

The _md_force attribute can be used to apply a force to atoms. The MD simulation in such a case maintains energy conservation by adjusting the kinetic energy of the system. For the case of $AlVO_4$ and for the crude potential used; it is interesting that for a force along the a-axis on an Al+3 atom, the structural integrity is maintained as seen below (see MD-4.INP):



The structure, however, loses its integrity for a similar force along the c-axis.

17. AMAZON EC2 CLOUD COMPUTING

TOPAS refinements can be run on the Amazon Web Services (AWS) cloud platform utilizing the Amazon Elastic Compute Cloud (Amazon EC2) computing platform: “TC-Cloud”. TC-Cloud is an optional, EXPERIMENTAL FEATURE within TOPAS and its use has following provisions:

- TC-Cloud is not part of the official TOPAS-Academic V8 feature set. TC-Cloud is provided to get early feedback for possible future products. Its use is for internal testing purposes.
- TC-Cloud is provided AS IS without warranty of any kind and without obligation to provide any support such as installation support, usage support, error corrections, and/or any enhancements to the feature.
- Using non-free AWS resources do incur AWS fees. The user is responsible for all AWS costs. Coelho software is not liable for any loss arising out of the use of TC-Cloud; any damages arising out of the use of TC-Cloud is borne by the User.
- The TC-Cloud feature can be cancelled at any time in future updates or upgrades, for any reason, and without notice.

TC-Cloud can be run on 100s of virtual computers on the Amazon Web Services (AWS) cloud platform. The process is driven from the GUI version of TOPAS/TOPAS-Academic, where launching an INP file on the cloud is a few mouse-clicks away. The Cloud gives access to large computing resources where 1000s of virtual machines (VMs) can be utilized in a relatively inexpensive manner. Large simulated-annealing problems taking weeks on a laptop can be done in minutes. The process typically involves working interactively with TOPAS in Launch mode and performing initial preliminary refinements. Once the User is satisfied, the Cloud version of the kernel, which we will call TC-Cloud, can be launched. Cloud operation is often performed in an interactive manner due to the speed of analysis; many Cloud runs need only last for 10 to 20 minutes depending on the number of VMs used.

The User does not install TC-Cloud; instead, TC-Cloud is pre-installed on a Virtual Machine image called an Amazon Machine Image (AMI). The AMI for TC-Cloud is called TC-AMI. TC-AMI can be used to create many virtual machines each corresponding to a virtual Linux computer; we will call these TC-VMs. Each TC-VM can run multiple instances of TC-Cloud. To summarize:

- TA.EXE is the GUI version of TOPAS running on a local computer.
- TC-Cloud is the cloud version of TOPAS running on a VM.
- TC-AMI is an image of a VM with TC-Cloud installed.
- TC-VM is a VM created from TC-AMI.
- Many TC-VMs (500 for example) can be created/deleted at once.

The user is given a choice of VM type when launching TC-AMI to create TC-VMs. A large TC-VM can run more than one instance of TC-Cloud.

17.1 ... Operation

TC-Cloud operates in a similar but not identical manner to TC.EXE. Importantly INP files are pre-processed before launching on the Cloud; this ensures the use of local files such as TOPAS.INC and other *#include* files. Since the local TOPAS.INC is used then local emission profiles are used. Data files referenced in the INP file must reside in the same local directory as the INP file. This is normal practise and INP files should therefore not contain file paths. For example,

- this is valid on the Cloud: xdd data.xy
- this is not valid on the Cloud: xdd data\data.xy

File names on Linux are case sensitive. It is therefore important to use the correct case when referring to file names within INP files. The following keywords can be included in INP files but have been disabled:

append_bond_lengths	do_errors_include_penalties	out_prm_vals_per_iteration
atom_out	do_errors_include_restraints	phase_out
A_matrix	index	phase_out_X
A_matrix_normalized	num_runs	process_times
bootstrap_errors	out	system_after_save_OUT
C_matrix	out_file	system_before_save_OUT
C_matrix_normalized	out_prm_vals_dependents_filter	verbose
do_errors	out_prm_vals_filter	view_structure
	out_prm_vals_on_convergence	xdd_out
	out_prm_vals_on_end	

Many of these refer to data output and as such are better left to the local computer.

17.2 ... Pre-requisites

Signing up with Amazon AWS is required, see https://aws.amazon.com/. Also, necessary is TOPAS/TOPAS-Academic and a local computer to run TOPAS. TC-AMI comes with TOPAS/Academic Version 7; access to TC-AMI can be obtained from Alan Coelho. TC-VMs are monitored and terminated depending on User defined conditions. For example, VMs can be terminated when the best goodness of fit parameter (GOF) from all TC-VMs drop below a User defined value. This reduces running times for the TC-VMs and consequently running costs. The following points are important:

- Signing up with AWS does not incur a fee.
- Using non-free AWS resources do incur AWS fees.
- The User is responsible for all AWS costs.
- AWS fees can be reduced by reducing the use of AWS services.
- VMs created as spot instances are often 60 to 70% cheaper.
- Services can be reduced by:
    - Turning off unused VMs.
    - Deleting unused VMs.

17.3 ... Pricing of AWS cloud resources

The following approximate pricing information are dependent on AWS and could change. Running TOPAS on AWS requires the use of VMs. Each VM in turn uses an EBS volume (a storage device). Use of both the VM and the EBS incur AWS fees, see:

For VMs: https://aws.amazon.com/ec2/pricing/on-demand/

For EBS volumes: https://aws.amazon.com/ebs/pricing/

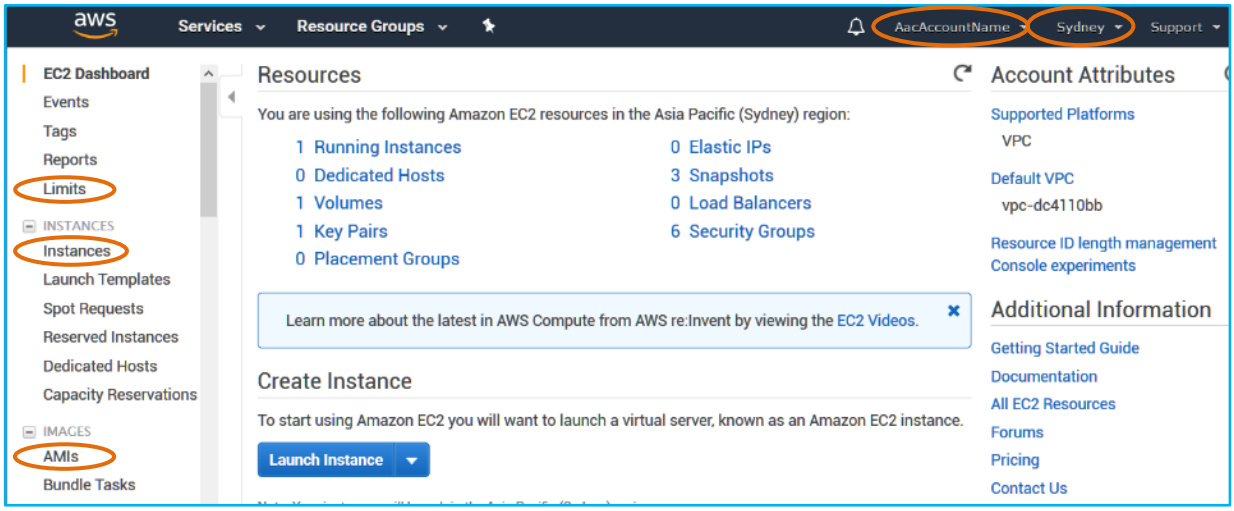
Limited usage of a single core VM on Amazon AWS are free of charge for a period of one year. Large VMs (ones with many cores) are not free with charges dependent on time usage. Pricing is on a per second basis for Linux VMs; the twin core VM *c5.large* is recommended for routine TC-Cloud usage; for the same core count, it is equivalent to an average high end laptop in computational speed and is priced at approximately ~0.034 cents USD (for spot instances) per hour. One hundred of these running for one hour will cost approximately $3.40 USD. Large saving, often up to 70%, can be realized by requesting *spot-instances*, see https://aws.amazon.com/ec2/spot/pricing/. The author has had no trouble getting regular access to 500 spot instances.

Each TV-VM is a Linux VM; it comes with an 8 Gbyte EBS volume which stores TC-Cloud and the operating system. EBS volumes are relatively inexpensive at 0.125 USD per Gbyte per month, or $1 USD per month for each TC-VM. For one hundred VMs this small charge becomes $100 USD per month. It is therefore recommended that VMs are deleted after use to reduce costs. Creating and starting VMs takes one to two minutes.

Cloud storage is required in addition to VMs and associated EBS volumes. This storage is used to transfer data from the local computer to the VMs and visa-versa. AWS S3 cloud storage is used; it is inexpensive and runs at approximately $0.02 per Gbyte per month, see https://aws.amazon.com/s3/pricing/. File manipulation of S3 storage is provided online via the AWS Dashboard. Running TC-Cloud typically requires a fraction of a Gbyte in S3 storage and hence common storage costs are negligible.

17.4 ... AWS dashboard and operating TC-Cloud

AWS includes a comprehensive browser dashboard called EC2 Dashboard https://ap-south-east-2.console.aws.amazon.com/ec2/. In the case of running TC-Cloud, the dashboard is primarily used to create TC-VMs from TC-AMI as well as deleting files created on the S3 cloud storage. The rest of TC-Cloud operations are performed from TA.EXE. The important parts of EC2 Dashboard are circled in the following:



Note: AWS web screens may change due to improvements etc...; the general operation however should remain the same. Clicking on the *Account* (circled on the top) brings up account options which includes real time billing information (AWS Cloud costs). Also on the top, is the AWS region being operated-on. AWS operates on a regional basis; regions chosen should be in close geographical proximity to the local computer. This reduces response times and data transfer costs. TC-VMs are created by clicking on *AMIs*. Once created, details of TC-VMs for the selected region can be viewed by clicking on *Instances*. AWS limits the number of VMs available to 20 on most VM types; request for increasing this number can be made from the circled 'Limits' item. The author had no trouble getting regular access to 500 spot instance VMs.

17.5 ... Installing AWS CLI on the local computer

For communicating with the TC-VMs; the local computer requires the installation of the AWS Command Line Interface (CLI). The CLI can be trivially installed and downloaded from:

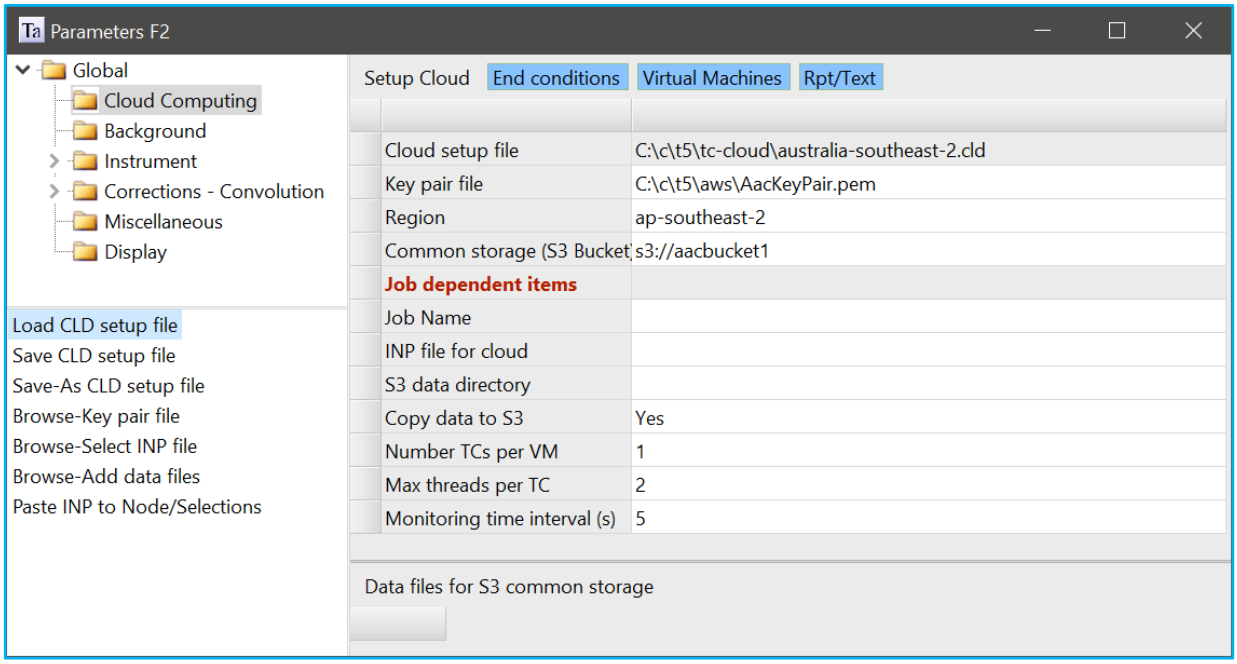
https://docs.aws.amazon.com/cli/latest/userguide/install-windows.html.

17.6 ... Operating TC-Cloud from TOPAS (GUI)

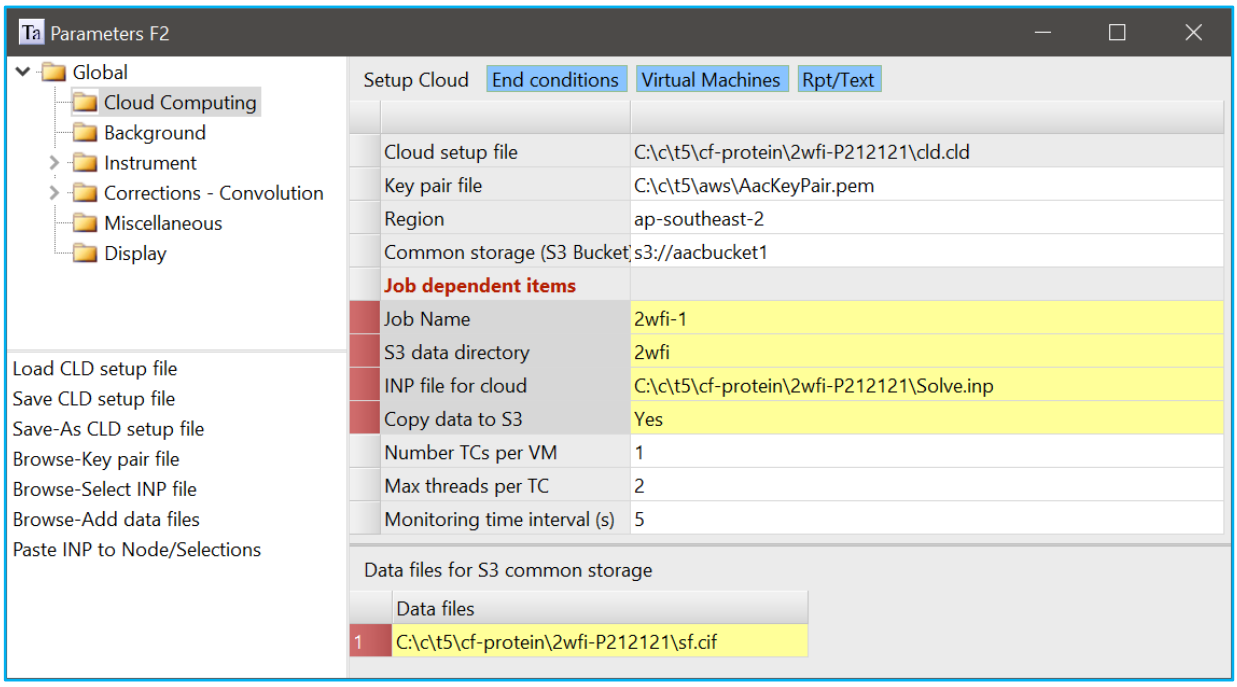
After the preliminary setting up and testing of an INP file with TA.EXE on the local computer, the INP file can be fed to AWS for parallel operation on many VMs. Summing up the process we have:

1) Set up INP file and ensure it runs as expected on TA.EXE on the local computer.
2) Create a small number of VMs (3 for example) and ensure that the INP file runs as expected on the VMs.
3) Create many more VMs (User determined) and run the INP file on the VMs.

Stage-1 is normal TOPAS operation. Stage-2 involves creating a *job* (*.CLD files) from the 'Setup Cloud' tab in the GUI. Before creating a job its best to create a template that can be used for all jobs in the AWS region. Enter your *'Key pair file'*, the AWS *Region* being used and your *S3* bucket name details in the *Setup Cloud* tab; it should look something like:



Save the details using '*Save-As CLD setup file*' to a file. Load this file when creating other CLD files. To run a job then enter the rest of the setup details; an example is:



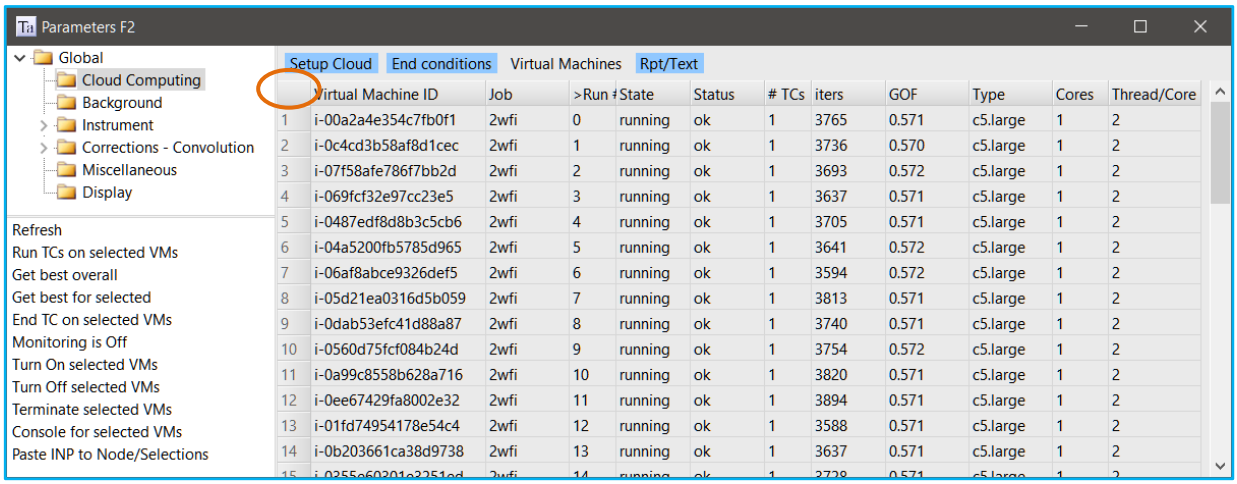
The highlighted lines require input of the INP file to be run on the Cloud as well as the necessary data files. In the above the INP file is placed in the S3 job directory called 2wfi-1 and the data file is placed in the S3 directory called 2wfi. S3 will therefore contain the following two directories:

s3://aacbucket1/swfi-1

s3://aacbucket1/swfi

The INP file as well as other communication files are copied to the job directory, 2wfi-1 in this case. The name of the INP file on S3 is changed to IN.INP; IN.INP is used in the retrieval of

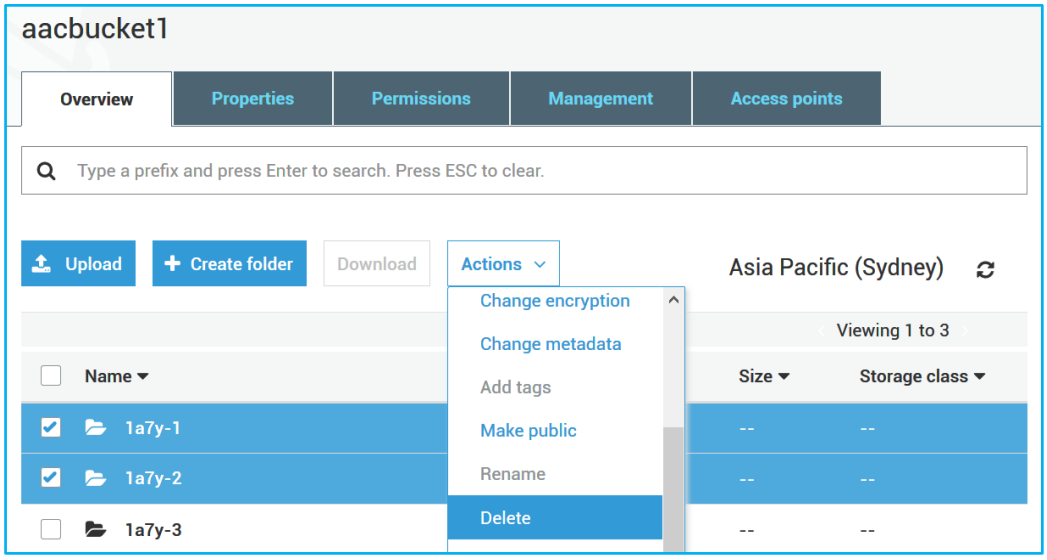
output from the VMs; it is unchanged during Cloud operation, and it can be also viewed as a backup for the job. Each run on the Cloud requires a unique job name; an exception is thrown otherwise. Many jobs, however, can use the same S3 data directory. In cases where many jobs are run sequentially, each using the same data files, then the '*Copy data to S3*' option can be set to No after the first job; this speeds-up processing as copying large data files over the internet can be slow. CLD files contain information necessary for launching the INP file on the cloud. Once the information is entered, it becomes possible to view the created VMs in the 'Virtual Machines' tab, or:



	Virtual Machine ID	Job	>Run #	State	Status	# TCs	iters	GOF	Type	Cores	Thread/Core
1	i-00a2a4e354c7fb0f1	2wfi	0	running	ok	1	3765	0.571	c5.large	1	2
2	i-0c4cd3b58af8d1cec	2wfi	1	running	ok	1	3736	0.570	c5.large	1	2
3	i-07f58afe786f7bb2d	2wfi	2	running	ok	1	3693	0.572	c5.large	1	2
4	i-069fcf32e97cc23e5	2wfi	3	running	ok	1	3637	0.571	c5.large	1	2
5	i-0487edf8d8b3c5cb6	2wfi	4	running	ok	1	3705	0.571	c5.large	1	2
6	i-04a5200fb5785d965	2wfi	5	running	ok	1	3641	0.572	c5.large	1	2
7	i-06af8abce9326def5	2wfi	6	running	ok	1	3594	0.572	c5.large	1	2
8	i-05d21ea0316d5b059	2wfi	7	running	ok	1	3813	0.571	c5.large	1	2
9	i-0dab53efc41d88a87	2wfi	8	running	ok	1	3740	0.571	c5.large	1	2
10	i-0560d75fcf084b24d	2wfi	9	running	ok	1	3754	0.572	c5.large	1	2
11	i-0a99c8558b628a716	2wfi	10	running	ok	1	3820	0.571	c5.large	1	2
12	i-0ee67429fa8002e32	2wfi	11	running	ok	1	3894	0.571	c5.large	1	2
13	i-01fd74954178e54c4	2wfi	12	running	ok	1	3588	0.571	c5.large	1	2
14	i-0b203661ca38d9738	2wfi	13	running	ok	1	3637	0.571	c5.large	1	2

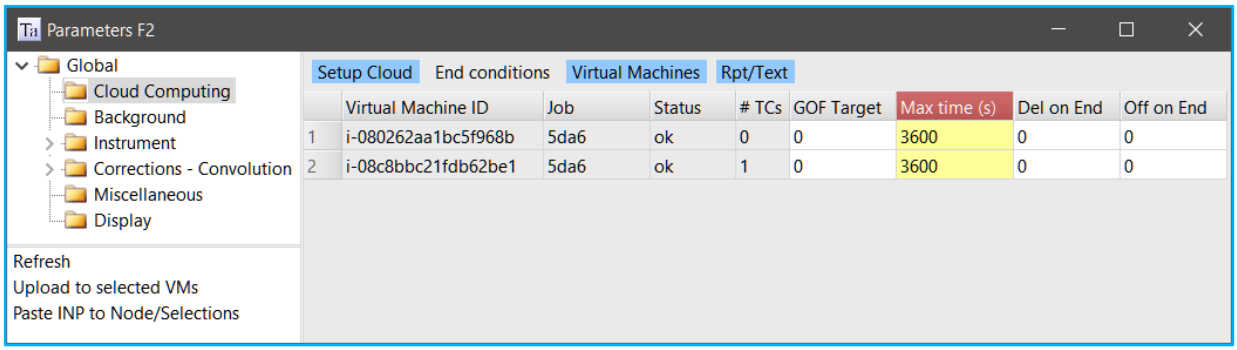
Data can be displayed in sorted order by double clicking on the column headings. To launch the INP file on a VM then select the VM and click *'Run TC on selected VMs'*. To select all VMs then click on the empty circled rectangle shown. Only VMs with an *ok* Status can be launched. If a selected VM is '*starting*' or '*pending*' then *Status* will not be *ok*. The number of TCs running on each VM (typically one) is shown in the *# TCs* column. This data as well as other VM details maybe out-of-date; to show the latest then click on the *Refresh* option. The *iters* column shows the total number of refinement iterations executed on the respective VM; this number supplies a means of determining if a VM is running in an expected manner. For example, if *iters* has stopped increasing in an expected manner and *#TCs* is not zero then the running TCs have stopped operating in an expected manner.

Due to the speed of analysis, Cloud operation is often performed interactively. Running many jobs to investigate a problem, each taking 10 to 20 minutes and comprising 500 VMs, is common. Each job creates a directory on S3 which can be deleted after use using the AWS S3 dashboard; it looks like:



17.7 ... Terminating/Stopping TC-VMs and tc-mon.a

Terminating or stopping TC-VMs reduces AWS fees. TC-VMs can be automatically stopped or terminated depending on *'End conditions'*, or:



These conditions are uploaded to the VMs when a job is launched. On launching a job, a small monitoring program, called *tc-mon.a*, is started on each VM. This monitoring program reads the End conditions and monitors the running TCs. VMs are in turn terminated/stopped depending on the End conditions. From the local machine, the end conditions can also be uploaded after a job has started using the *'Upload to selected VMs'* option. This option has no effect on VMs with a *Status* that is not *ok*. The *'Refresh'* option displays values as found on common storage for the job indicated in *'Setup cloud'* tab.

TCs running on VMs are terminated when the number or iters, as defined in the INP file, has been reached, or, when the CPU time allocated *'Max time (s)'* has been reached or when the overall best GOF falls below *'GOF Target'*. When there are no TCs running on a VM then the VM is stopped if *'Off on End'*=1; subsequently if *'Del on end'*=1 then the VM itself is terminated (deleted). Parameters for a typical job left unattended would be:

Max time (s) = 10 60 60 = 10 hrs of running

GOF Target = 10, Off_on_End = 1, Del_on_end = 1

For interactive use, the user can manually terminate TCs and VMs; the termination parameters could therefore look something like:

Max time (s) = 0

GOF_Target = 10, Off_on_End = 0, Del_on_end = 0

A *'Max time (s)'* of zero (the default) disables the ending of TCs on a time basis. *'Max time (s)'* on VMs can be entered as an equation by starting the equation with an equal sign. For example, '= 24 60 60' could be used to enter 24hrs.

17.8 ... Powering off TC-VMs after 100 minutes of inactivity

In addition to the terminating/stopping criteria of section 17.7, VMs are automatically powered off (stopped but not terminated) after 100 minutes of TC-Cloud inactivity including inactivity on VM start-up. The net effect is that VMs are stopped after 100 minutes of TC-cloud not being run. Situations where 100 minutes of inactivity is possible include internet-down situations as well as Users forgetting to power-off or terminate VMs. For example, the fee incurred for forgetting to turn off 100 spot instance VMs would be ~3.40 USD.

17.9 ... Retrieving the INP or FC file that gave the best GOF

Output from a job, corresponding to the best INP for Rietveld refinement, or the best structure factors for charge-flipping, is stored on the S3 job directory. This storage to S3 from a job is independent of the local computer. The *'Get best overall'* downloads the output from S3 to the local directory where INP file originated. The name given to the output is *Job-Name*.INP for Rietveld refinement or *Job-Name*.FC for charge-flipping. For example, for a job named 'PbSO4-1' and an input file with a path of C:\DATA\PBSO4.INP we get:

'INP File for cloud' = C:\DATA\PBSO4.INP

'Get best overall' places output in C:\DATA\PBSO4 -1.INP

Once retrieved, the best INP file can be run on the local computer; in other words, the best fit from the Cloud can be visually inspected with a few mouse clicks. If the VMs are available and not *stopped* or *terminated*, then output from the individual VMs can be retrieved using the *'Get best for selected'* option; output is placed in the local computer in an identical to that described for *'Get best overall'*. Typical interactive operation therefore comprise viewing and partially running intermediate Cloud results and making decisions based on those results.

17.10 . Monitoring, TC-Cloud is independent of the local computer

The running of VMs can be monitored by the local computer using the *'Monitoring is On/Off'* option. When On, the best overall GOF is displayed in the text output of the '*Fit Dialog'* window at time intervals as defined in *'Monitoring time interval'* option of *'Setup cloud'* tab. Whilst jobs are running, the local computer can be used to run refinements independent of Cloud jobs. Cloud jobs can be started on a laptop, left running overnight and results viewed the next day.

17.11 . Random number generator automatically seeded

The random number generator for both TC-Cloud (and TC.EXE on the local computer) is seeded such that the sequence of random numbers generated for any run is unique. Identical

sequences can be generated by using the seed keyword with an integer (corresponding to a seed number) placed after it.

17.12 . CLOUD__ #define and Get(cloud_run_number)

The pre-processor directive of '*#define* CLOUD__' is automatically included at the start of INP files running on VMs. This allows blocks of INP script to be conditionally included/excluded from Cloud runs making it easy to run the same INP file in both the Cloud and on the local computer. For example, the following is useful in the case of charge-flipping:

```
charge_flipping
    #ifdef CLOUD__
        randomize_initial_phases_by = Rand(-180, 180);
    #else
        set_initial_phases_to job-name.fc
    #endif
```

Here the state of the best FC file found on the VMs can be determined by first executing the *'Get best overall'* option and then locally running the INP file. Also, available is Get(cloud_run_number) which returns the run number assigned to the corresponding VM with counting starting at 0. Get(cloud_run_number) returns -1 when running on the local computer. Example usage in terms of stacking faults could be:

```
    macro & pa { Get(cloud_run_number+1)/102 }
    generate_stack_sequences {
        number_of_sequences 200
        number_of_stacks_per_sequence 200
        Transition(1, lpc)
            to 1 = pa;      a_add = 2/3;   b_add = 1/3;
            to 2 = 1-pa;    a_add = 0;     b_add = 0;
        Transition(2, lpc)
            to 1 = 1-pa;    a_add = 0;     b_add = 0;
            to 2 = pa;      a_add = -2/3;  b_add = -1/3;
    }
```

17.13 . 'Setup Cloud' details

Cloud setup file

File name containing cloud details for a job.

Key pair file

File name containing encrypted login information, see:

https://docs.aws.amazon.com/AWSEC2/latest/UserGuide/ec2-key-pairs.html

This file needs to be read/write protected so that only one user can access; use Windows Explorer and Right-Click on the file to change its properties.

Region

Geographical region where VMs reside.

S3 Bucket

The name of the bucket for transferring data to and from the TC-VMs. Buckets are created and manipulated at https://s3.console.aws.amazon.com/s3/. By default, S3 buckets are private to the User. Once a bucket is created, directories within the bucket corresponding to the job name are automatically created on launching the TC-VMs. For example, for a job named *job-1* and a bucket called *my-bucket* then the following directory on S3 is created:

s3://my-bucket/job-1

my-bucket are used for many jobs. Information stored on common storage are not deleted by TA.EXE running on the local computer; the User is therefore responsible for cleaning up unwanted files using the AWS S3 dash-board.

Job Name

Name of job. Job names cannot contain spaces.

S3 data directory

Directory where data files are stored. More than one job can use an S3 data directory.

INP file for cloud

Input file to run on the Cloud. The INP file can make use of the predefined pre-processor directive called CLOUD__. It can also make use of Get(cloud_run_number).

Number TCs per VM

Typically set to 1. The number of TC-Cloud instances to run on each TC-VM. The number of TCs per VM should not exceed the number of Cores as seen in the *Cores* column of the *Virtual Machines* tab. For example, the VM type of *c5.18xlarge* has 36 Cores each with 2 threads (intel hyper threading). The number of TCs therefore should not exceed 36. Information on EC2 instance types can be found at https://docs.aws.amazon.com/AWSEC2/latest/UserGuide/instance-optimize-cpu.html.

Max threads per TC

Typically set to 2 for *c5.large* VMs. The maximum number threads each TC can use. If zero, then each VM will be allowed to use the maximum number or threads. For VMs with more than one TC running then the maximum number threads should be set to:

Max_threads_per_TC = (Virtual Cores) / Number_TCs_per_VM

Monitoring time interval (s)

The time interval used when *'Monitoring is On'*.

17.14 . 'Virtual Machines' tab options

Refresh

Refreshes VMs details corresponding to the region defined in the *'Setup cloud'* tab.

Run TC on selected VMs

Launches TC-Cloud on selected VMs.

Get best overall

Gets and processes the best output from common storage for the job defined in *Setup cloud* and places the result in the directory where the original INP file came from. For Rietveld refinement the retrieved output is placed in a file called *job-name*.INP. For charge-clipping, the retrieved output (structure factors) is placed in a file called *job-name*.FC. Files placed in common storage persists and are therefore available even after the job's VMs are deleted.

Get best for selected

Gets and processes the best output from a selected VM and places the result in the directory of the original INP file. The selected VM must be *On*. For Rietveld refinement the retrieved output is placed in a file called *job-name*.INP. For charge-clipping, the retrieved output (structure factors) is placed in a file called *job-name*.FC.

End TC on selected VMs

Stops any TC-Clouds running on selected VMs. On termination of the TCs, the VMs are turned off if their corresponding Off_on_End=1; in turn VMs are terminated if their corresponding Del_on_End=1.

Monitoring is On/Off

Starts/Stops monitoring. When monitoring is On, the best GOF as found by the TC-VMs for the job defined in *'Setup cloud'* is displayed in the Fit Dialog.

Turn On selected VMs

Turns selected VMs On.

Turn Off selected VMs

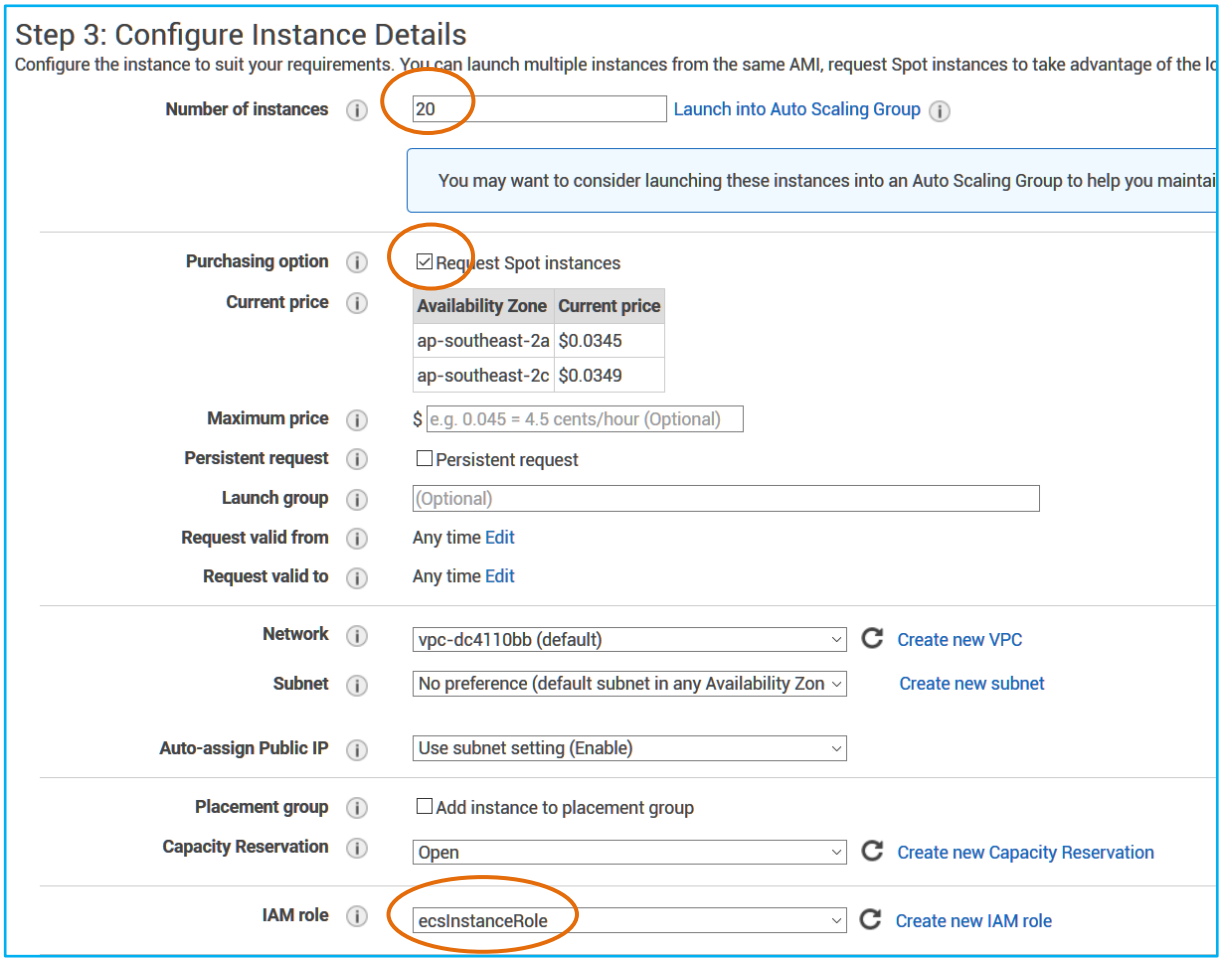
Turns selected VMs Off.

Console for selected VMs

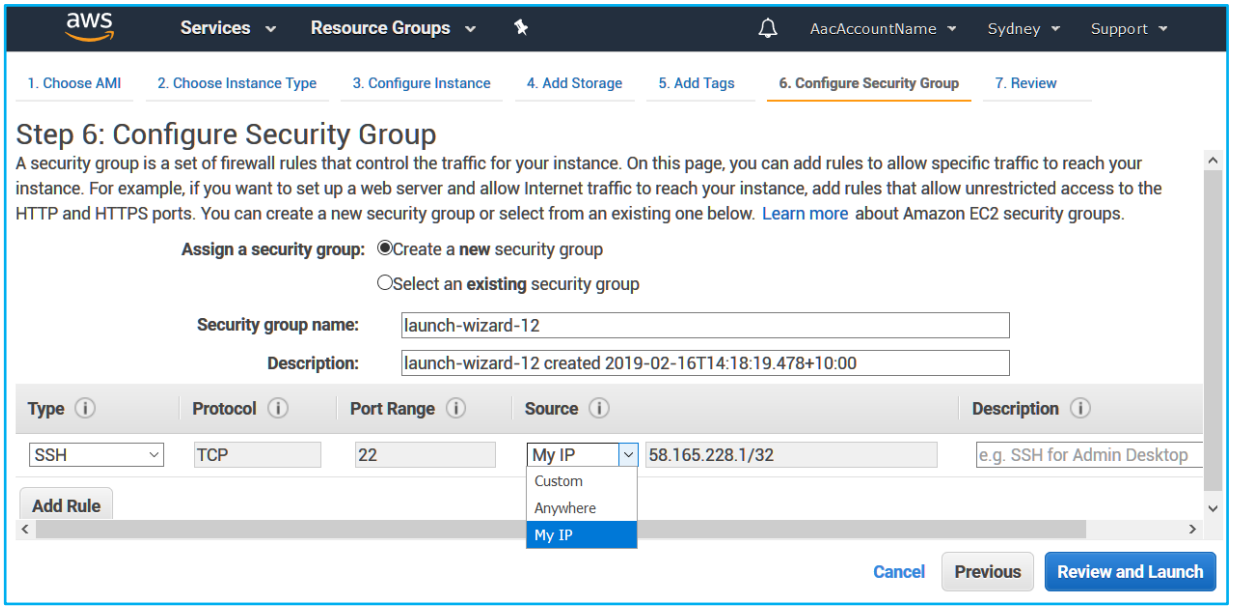
Log-in to the selected VMs creating terminal windows for each. Can be useful for trouble shooting.

17.15 . Creating TC-VMs – Spot Instances

TC-VMs are created from the EC2 dashboard. To create 200 VMs, for example, click on the *AMIs* option and then click on the *TC-AMI-n* AMI. *n* corresponds to the latest TC-AMI version. Then click on *Launch* to bring up *'Choose an Instance Type'* screen. Choose an appropriate VM type; for refinements that require less than 4Gbytes of memory then choose *c5.large*. The amount of memory required for each TC can be determined by first running the INP file on the local machine and viewing the Windows Task Manager. Once the VM type is chosen, proceed to the next screen *'Configure Instance Details'*:



Set *'Number of instances'* to 200 and set the '*IAM role'* to *'ecsInstanceRole'*. Select *'Request Spot instances'*. Spot instances are often 60 to 70% cheaper; the user is informed when spot instances are unavailable; the author has had no difficulty obtaining 500 spot instances on a regular basis. Proceed to the *'Configure Security Group'* screen' and set the *Source* to *'My IP'*; ie.



Click on *'Review and Launch'* to Launch the creation of the TC-VMs. Creation should take one to two minutes. Use the TA *Refresh* option of *'Virtual Machines'* to see the status of VMs; VMs with a *Status* of *ok* are ready to run. Once all the VMs are created, the *'Run TCs on selected VMs'* option from the *Virtual Machines* tab can be used to launch the job on the selected VMs.

17.16 . Choosing the optimum VM type

The most appropriate VM for TOPAS type problems are *c5.large* where memory usage is less than 4 Gbytes. However, a problem that uses 20 Gbytes of memory would need a larger VM; such problems could be a large charge flipping refinement, a large Rietveld refinement or a simulated annealing refinement with 1000s of parameters. Memory usage prior to launching on the Cloud can be determined using the local computer. The VM type chosen should therefore be one than has more memory than the maximum memory usage seen on the local computer. Only c* types (compute types) VMs should be chosen (see https://aws.amazon.com/ec2/pricing/on-demand/). For a problem that uses 20 Gbytes of memory, the *c5.4xlarge* is the smallest VM that will do the job. Max Number of threads should be set to zero allowing the maximum number of threads to be used which in this case is probably 16.

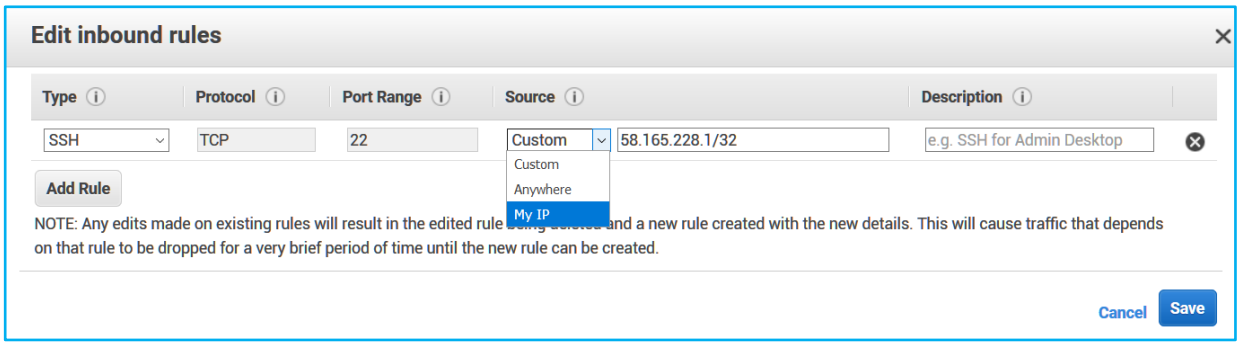
Note, TOPAS is threaded to a large extent, however, an excessive number of threads could slow down execution. For example, the large VM type of *c5.18xlarge* operating on the TEST_EXAMPLES\SINGLE-CRYSTAL\PN_O2_2-ADPS.INP (3970 parameters) produces the following as a function of number of threads:

# of Threads	approximate_A - 15 iterations		Full A matrix - one iteration	
	Time(s)	Gain	Time(s)	Gain
2	42.19	0.32		
4	22.28	0.60	186.98	0.36
8	8.41	1.59	61.93	1.09
16	4.11	3.25	31.65	2.12
32	2.77	4.82	17.92	3.75
48	2.89	4.62	15.18	4.43
64	2.95	4.53	13.71	4.91
70	3.06	4.37	13.73	4.90

The columns marked Gain are the times taken on a high-end laptop with 8 threads divided by the time taken on *c5.18xlarge*. The speedup due to number-of-threads is substantial up to about 32 threads. It is worth noting that TOPAS V7 for the approximate_A case is 1.9 times faster than V6.

17.17 . Unable to connect to TC-VMs after local computer restart

The IP address of the local computer may change when the local computer is powered off and restarted, or, when the connection to the internet changes. VMs created prior to the restart would therefore have an invalid local-computer-IP-address; communication with the VMs would therefore not be possible. This scenario is noticed when the *Refresh* or *'Run TCs on selected VMs'* options of the *'Virtual Machines'* tab is not responsive. In such a case it is necessary to instruct the VMs that the IP address has changed. This can be performed from the *Instances* of the *EC2 Dashboard*; from this screen click on the security group shown in the *'Security Groups'* column. This brings up details of the security group. Click on *Inbound* and then *Edit* and then change the Source to *My IP*, or,



18. PROTEIN REFINEMENT

18.1 ... Reading Protein Data Bank (PDB) CIF files

[pdb_cif_to_str_file $file] ... [pdb_ignode_adps !E0] [pdb_cif_sites $sites] [pdb_cif_to_str #0]	**Examples** CF-PROTEIN\2PVB-P212121\GEN.INP CF-PROTEIN\2PVB-P212121\MATCH.INP CF-PROTEIN\6Y84-C121\REFINE-MENT.INP

Protein Data Bank (PDB) PDBx/mmCIF fles from https://www.rcsb.org/ can be downloaded and converted to INP text using pdb_cif_to_str_file. The operation is performed when pdb_cif_to_str is 1; on termination of refinement pdb_cif_to_str is set to 0 in the OUT file. The INP text generated is placed in the INP file after the pdb_cif_to_str keyword, or:

```
pdb_cif_to_str_file cif.cif
   pdb_ignode_adps  1
   pdb_cif_to_str   0
xdd_scr sf.cif
   lam lo 0.9096
   str
      scale @ 1
      a 51.03
      b 49.81
      c 34.57
      space_group P212121
      site ACE_C_0_1_HETATM    x  0.07354 y  0.35529 z  0.47637 occ C  1.00 beq  6.24
      site ACE_O_0_2_HETATM    x  0.06210 y  0.34246 z  0.50194 occ O  1.00 beq  7.96
      site ACE_CH3_0_3_HETATM  x  0.06198 y  0.35666 z  0.43651 occ C  1.00 beq  8.20
      site SER_N_1_4_ATOM      x  0.09557 y  0.36858 z  0.48319 occ N  1.00 beq  6.66
      site SER_CA_1_5_ATOM     x  0.10676 y  0.36880 z  0.52155 occ C  0.46 beq  8.09
      ...
      rigid
         point_for_site SER_N_1_4_ATOM    ux  -1.40900 uy  0.28011 uz  -1.21189
         point_for_site SER_CA_1_5_ATOM   ux  -0.83800 uy  0.29111 uz   0.11411
         point_for_site SER_CA_1_6_ATOM   ux  -0.70700 uy  0.20011 uz   0.04411
         ...
         Rotate_about_axies(@ 0 RX_, @ 0 RY_, @ 0 RZ_)
         translate tx @    6.28600 ty @   18.07889 tz @   17.91589
```

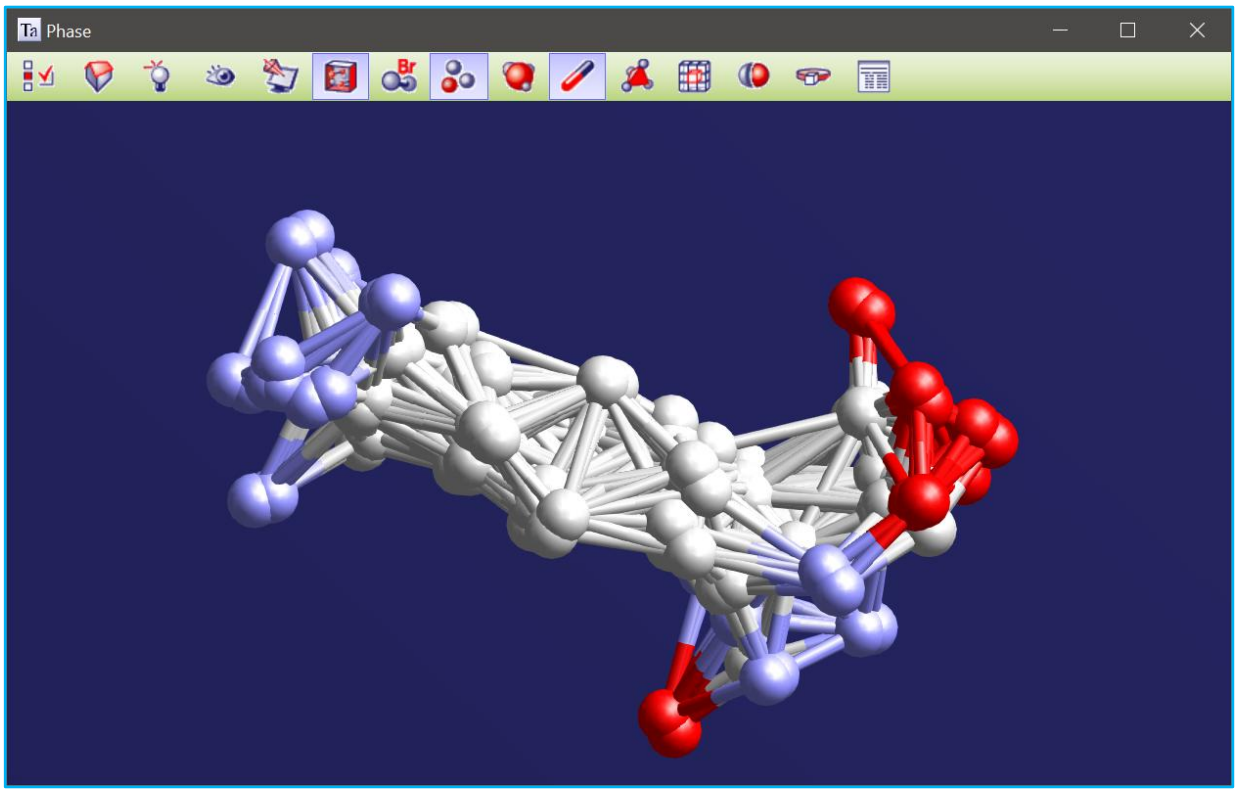
A rigid body is generated for each residue with coordinates set relative to its geometric center. Refinement can proceed on the generated INP text by setting the file name of xdd_scr to the name of the structure factor file 2PVB-SF.CIF, also downloaded from https://www.rcsb.org/. Running 2PVB\GEN.INP produces GEN.OUT; setting GEN.INP to GEN.OUT and running produces a fit.

pdb_cif_sites considers sites with names matching the site identifying string $sites. This can be used, for example, to extract all residues of the same type. The translate keywords of the rigid bodies can then be set to zero and the individual sites of the residues penalized such that sites of the same name are brought together; example INP text to do this is as follows:

```
      macro Match(s)
```

```
        {
            atomic_interaction s = R^2;
                ai_sites_1 s*
                ai_sites_2 s*
                ai_closest_N 1
                ai_only_eq_0
            penalty = s;
        }
    Match(LYS_N_)
    Match(LYS_CA_)
    Match(LYS_C_)
    Match(LYS_O_)
    Match(LYS_CB_)
    Match(LYS_CG_)
    …
```

Running example 2PVB\MATCH.INP produces the following showing overlay of LYS residues:

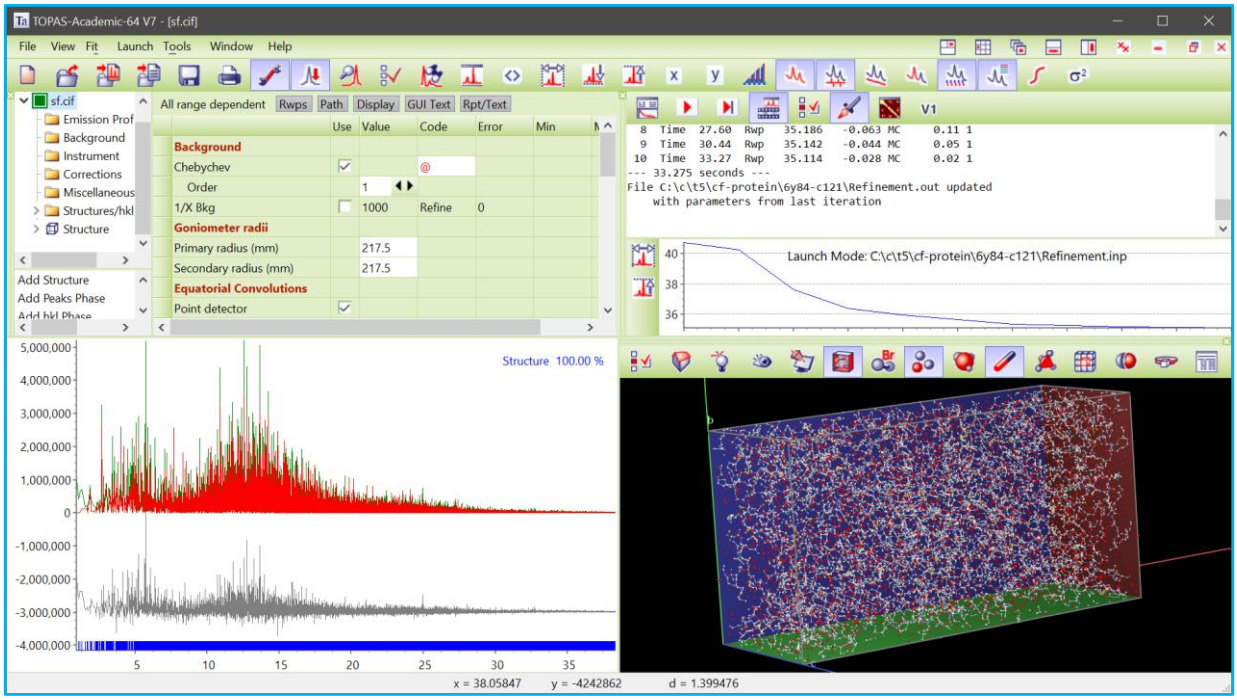


18.2 … Protein Refinement, 6y84, SARS-CoV-2 main protease

The structure factors and PDBx/mmCIF files for 6y84 can be downloaded from the PDB. To generate an initial INP file then create an INP file with the following (see 6Y84-C121\REFINEMENT.INP):

```
pdb_cif_to_str_file cif.cif
    pdb_ignode_adps  1
    pdb_cif_to_str 0
```

After refinement, the INP file can be updated with the structure generated from the CIF file. Refining on the updated INP file gives:



The refinement comprise 50348 unique reflections and 1826 parameters and the time to convergences is 33s on a laptop with all graphics operational. Restrains/constrains can of course be added.

19. SOLVING PROTEINS AT ATOMIC RESOLUTION

```
Include_Charge_Flipping
charge_flipping
    [cf_plot_histo !E]
    [cf_plot_fit !E]
    [add_to_phases_of_non_weak_reflections  !E]
    ...
    [scale_flipped !E]
    [cf_percent_ED_ge_H #]
    [pick_atoms $atom]...
        [choose_from !E]
        [choose_to !E]
        [choose_randomly !E]
        [with_symmetry !E]
        [omit !E]
        [insert !E]
        [pick_fwhm !E1]
        [omit_fwhm !E1]
        [insert_fwhm !E1]
    [insert_atoms {
        [activate !E1]
        [in_cartesian]
        [insert_atom] ...
            [x !E] [y !E] [z !E] [occ !E]
     }]...
     [cf_set_phases !E {
        #h #k #l #Re #im
     }]
     [prm N # val_on_continue !E] ...
```

Macros in CHARGE_FLIPPING.INC

Examples

CF-PROTEIN\

- 1A7Y-P1\SOLVE.INP
- 2ERL-C2\SOLVE.INP
- 1BYZ-P1\SOLVE.INP
- 2KNT-P21\SOLVE.INP
- 1AHO-P212121\SOLVE.INP
- 4LZT-P1\SOLVE.INP
- 1MC2-C121\SOLVE.INP
- 1DY5-P21\SOLVE.INP
- 2WFI-P212121\SOLVE.INP

- 1HHZ-P3221\SOLVE.INP
- 1C75-P212121\SOLVE.INP
- 1B0Y-P212121\SOLVE.INP
- 1CTJ-R3R\SOLVE.INP
- 2PVB-P212121\SOLVEINP
- 1CKU-P212121\SOLVE.INP
- 1SWZ-P3221\SOLVE.INP
- 5DA6-R32\SOLVE.INP

- 1CTJ-R3R\1-ATOM.INP
- 2PVB-P212121\1-ATOM.INP
- 1C75-P212121\1-ATOM.INP
- 5DA6-R32\1-ATOM.INP
- 1CKU-P212121\1-ATOM.INP
- 2WFI-P212121\1-ATOM.INP

- 4LZT-P1\2-ATOMS.INP

The largest proteins ever solved *ab initio* at atomic resolution can be solved using modified charging flipping strategies, see Coelho (2021) for details. Difficult or large structures can be solved in minutes, rather than days using Amazon AWS Cloud computing. New/modified charge_flipping keywords are shown above. A single strategy does not solve all structures; A strategy successful on one structure is not necessarily successful on another. However, it will be shown that only two strategies can solve a large range of the most difficult structures. New keywords allow for a variety of strategies. scale_flipped scales flipped electron density (ED) charge; it is applied each charge-flipping iteration. insert_atom inserts atoms in the ED when activate is non-zero. val_on_continue for prm(s) are evaluated at the end of each charge-flipping iteration. cf_percent_ED_ge_H returns the percentage of ED pixels greater than 1 where the maximum of the ED is set to number of electrons in the heaviest atom defined by f_atom_type. Values less than 1 often signal a Uranium atom situation where a single ED peak dominates. cf_percent_ED_ge_H is displayed during charge flipping in the Fit Dialog. cf_plot_histo plots a frequency distribution of the electron density pixel intensity.

When cf_set_phases is non-zero, the phases for the family of reflections (#h, #k, #l) are set to the phase corresponding to #Re and #Im. cf_set_phases is useful when phases are known or for setting origin defining phases; for triclinic structures, three origin defining phases are possible. Additionally, intensities of the reflections are scaled by the value evaluated by cf_set_phases.

Table 19-1 show difficult benchmark structures, as listed by Elser *et al*. (2017) and Burla *et al*. (2011), that have been solved *ab initio*; see corresponding SOLVE.INP files for details. It is best to do preliminary investigations on the local computer (non-Cloud) to determine which strategy might work best. Once a strategy is chosen, INP files can be fed to the Cloud for rapid structure solution. Up to 500 spot instance Virtual Machines (VMs) are easily obtained on the Amazon AWS system in Australia at a cost of ~0.035 USD cents per VM per hour, or, 3.40 USD per hour for 100 machines. These prices are Amazon AWS dependent. Prices are shown prior to the creation of the VMs. The times shown in **Table 19-1** can be easily doubled when one considers the preliminary analysis taken to arrive at the appropriate strategy. Typically, strategies are tried on the local computer before migrating the problem to the Cloud. Also, the structure solution process is normally halted after the first solution is found; for the investigative purposes, however, the structures in **Table 19-1** were each solved at least 5 times. The two strategies mentioned in **Table 19-1** are:

```
' S0 strategy
fraction_reflections_weak 0.5    add_to_phases_of_weak_reflections 90
fraction_density_to_flip  0.9    scale_flipped 0.6
```

S0 seems to work well for large structures with a relatively heavy atom. Non-triclinic structures with symmetry seems to succumb to the S1 strategy, or:

```
' S1 strategy
fraction_reflections_weak 0.5    add_to_phases_of_weak_reflections = Rand(-180, 180);
fraction_density_to_flip  0.97   scale_flipped 0.2
pick_atoms *
    pick_fwhm 3
    choose_randomly = If(Mod(Cycle_Iter, 50), 0, 10);
    with_symmetry 1
    insert 10       ' Increase if the most dominant atom does not change
symmetry_obey_0_to_1  0.25 find_origin 0
flip_regime_2 = Sine_Wave(10/4,-2,2,10); ' Used when there's not enough perturbation
```

S1T extends the S1 strategy with the addition of the tangent formula, or the inclusion of:

```
Tangent(0.5, 30)
```

Table 19-1. *Ab initio* structure solution strategies. Time indicates time to solution on average. Each structure was solved at least 5 times. *Num_VMs* greater than 8 refers to the number of VMs used on the Cloud; *Num_VMs*=9 corresponds to an 8 core local computer (a laptop). Cost corresponds to the average Cloud cost to a solution using the strategy indicated.

Solved	PDB code	Space group	N/Z	d_{min} (Å)	Time (min)	Num VMs	Cost USD	Strategy	N_p
yes	1a7y	*P*1	270	0.94	0.1	8	-	S0	-

yes	2erl	*C*2	303	1.00	1	200	0.10	S1	8
yes	1byz	*P*1	408	0.90	1	200	0.10	S0	-
yes	2knt	$P2_1$	460	1.20	16	200	2.00	S1T	7
yes	1aho	$P2_12_12_1$	500	0.96	1	200	0.10	S1	8
No	1w7q	$P6_5$	828	1.10	>240	200	>28	S0,S1	4
yes	4lzt	*P*1	1183	0.95	2	8	-	S1	10
yes	1mc2	*C*2	1254	0.80	2	200	0.20	S1	10
yes	1dy5	$P2_1$	1894	0.87	1	500	1.40	S1	30
yes	2wfi	$P2_12_12_1$	1920	0.75	18	500	5.10	S1	15
yes	1hhz	$P3_221$	354	0.99	7	200	1.00	S1	6
yes	1c75	$P2_12_12_1$	1184	0.92	1	8	-	S0	-
yes	1b0y	$P2_12_12_1$	837	0.93	1	8	-	S0	-
yes	1ctj	*R*3:R	918	1.10	1	200	0.10	S1	4
yes	2pvb	$P2_12_12_1$	1096	0.91	3	200	0.35	S1	5
yes	1cku	$P2_12_12_1$	1599	1.20	1	200	0.15	S1	8
yes	1swz	$P3_221$	1254	1.06	50	200	5.80	S1	15
yes	5da6	*R*32	1390	1.05	5	500	1.40	S1	15

PDB code	**Reference**
1a7y, 2erl, 1byz, 2knt, 1aho, 1w7q, 4lzt, 1mc2, 1dy5, 2wfi	Elser & Lan (2017)
1hhz, 1c75, 1b0y, 1ctj, 2pvb, 1cku, 1swz	Burla et al. (2011)
5da6	Mooers (2016)

PDB codes 1b0y, 1ctj, 1c75 and 1cku are easily solved (a few minutes) on a laptop using the S0 strategy. 2knt uses the tangent formula due to its relatively low-resolution data (1.2Å) as well as its relatively small number of non-hydrogen atoms in the asymmetric unit. 1w7q is a light element structure that was not solved *ab initio* after more than four hours. flip_regime_2 of S1 introduces perturbation and it should be used for cases where there the ED seems quiet during the charge flipping process; decreasing the absolute value of flip_regime_2 reduces perturbation. In the case of 1cm2, flip_regime_2 was set to oscillate between -1 and 1. Larger values clearly shows too much perturbation in the ED.

Graphically inspecting the ED or looking at the (%ED > H) output on the local can be used to determine if there's too little or too much perturbation, during charge flipping. (%ED > H) should typically range from 1 to 5. For example, setting fraction_reflections_weak to 0.9 results in too much perturbation. Or, using the Tangent formula macro on *P*1 structures, without the mitigation strategy of Fix_Uranium_3, results in too little perturbation resulting in uranium atom solutions. The value set for Fix_Uranium_3 should be just high enough to prevent Uranium atom solutions; a value of 1 seem to work in most cases. The number used for insert of pick_atoms should be just high enough to change the position of the highest intensity ED peak every 40 to 50 iterations as defined by choose_randomly; note pick_atoms is executed when

choose_randomly is greater than zero. add_to_phases_of_weak_reflections=90 results in a shifting origin and it should not be used with symmetry_obey_0_to_1; the latter prevents origin shifting. add_to_phases_of_weak_reflections should be set to Rand(-180,180) instead of 90 when using symmetry_obey_0_to_1. Further structure solution tips are:

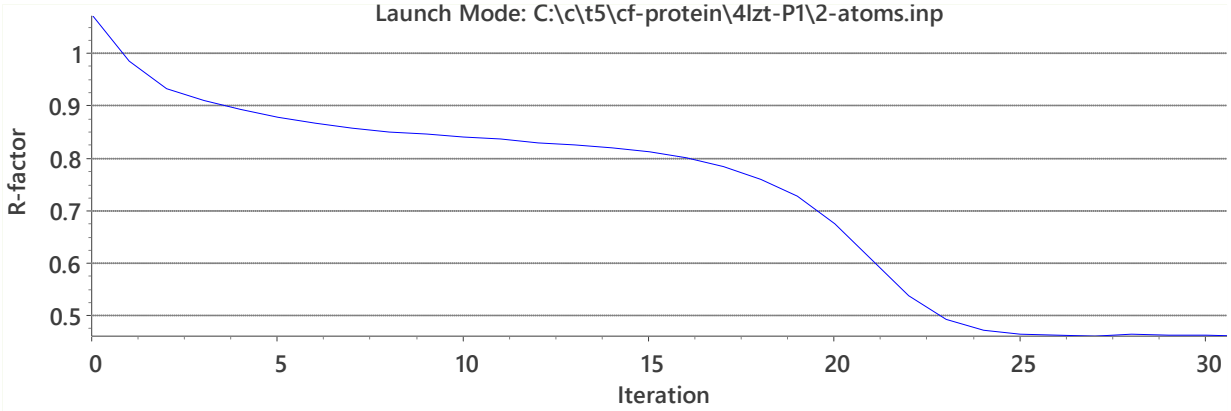
- Try the simple S0 strategy first for number of atoms less than about 300.
- If a heavy atom is present, then try S0.
- Inspect the ED graphically; if it does not show distinct atoms after a few iterations then change strategy.
- Use S1 for large difficult structures.
- Try the tangent formula when the number of non-hydrogen atoms in the asymmetric is less than ~500 atoms. The tangent formula reduces perturbation allowing lower resolution structure to be solved.

The range of convergence of structure factor phases can be investigated by loading optimum structure factor phases values, using set_initial_phases_to, and then adding to the optimal phases using randomize_initial_phases_by. High resolution data can have their optimal phases changed by an amount of 0.96*Rand(-180,180) whilst still being able to solve the structure within a few dozen charge flipping iterations. Most of the SOLVE.INP examples contain the following for investigating this range of convergence:

```
#if (0)
    set_initial_phases_to optimal.fc
    randomize_initial_phases_by = Rand(-180, 180) 0.9;
#endif
```

19.1 ... Ab initio solution of triclinic 4lzt

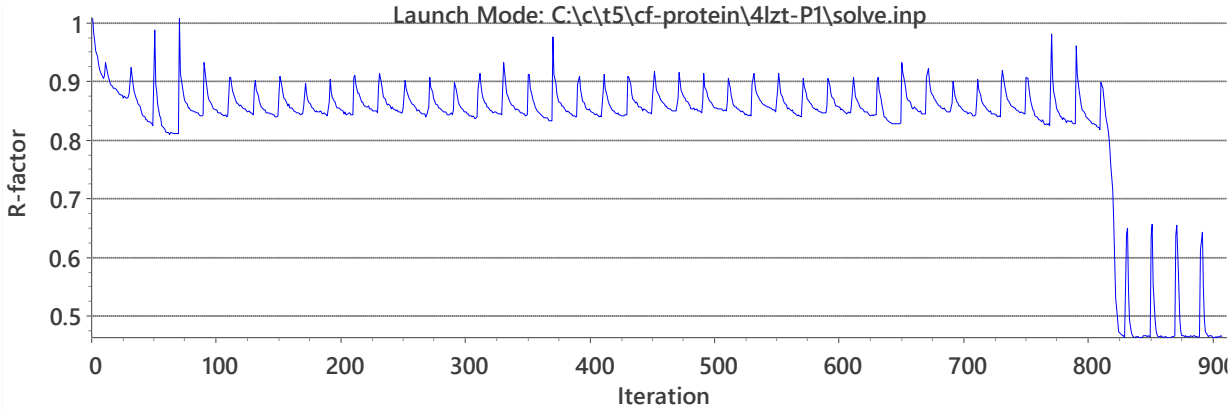
PDB code 4lzt comprises 1183 non-hydrogen atoms in the unit cell and is considered difficult to solve, see Elser *et al.*, 2017. 4lzt contains 10 Sulphur atoms and these are considered moderately heavy. If we were to insert ED peaks at positions corresponding to the highest two peaks of the optimum electron density, then charge flipping finds a solution and within a few iterations; 4LST\2-ATOMS.INP demonstrates this where an ED starting with the two highest optimal peaks, inserted using insert_atoms, produces and R-factor plot of:



In fact, any two of the five highest peaks produce similar R-factor plots. However, these optimal ED peak positions are unknown. The strategy that works therefore involves picking an atom randomly out of the 10 largest peaks in the electron density and setting the picked atom to a large density. The INP file looks like:

```
    fraction_reflections_weak 0.5
        add_to_phases_of_weak_reflections = Rand(-180, 180);
    fraction_density_to_flip 0.97
        scale_flipped 0.2
    pick_atoms *
        pick_fwhm 5 omit_fwhm 1 insert_fwhm 1
        choose_randomly = If(Mod(Cycle_Iter, 50), 0, 10);
        insert 10
    Fix_Uranium_3(0.5)
    ATP(1000, 1) ' Totally randomize phases after 1000 iterations
```

pick_atoms picks atoms with a FWHM of 5 Å, as defined by pick_fwhm; this relatively large value ensures that the picked atoms are approximately 5 Å apart. Once picked, pick_atoms removes the atoms with a FWHM as defined by omit_fwhm, and then inserts atoms with a FWHM of insert_fwhm. A solution of 4lzt takes a minute or two on a laptop computer and a typical R-factor plot looks like:



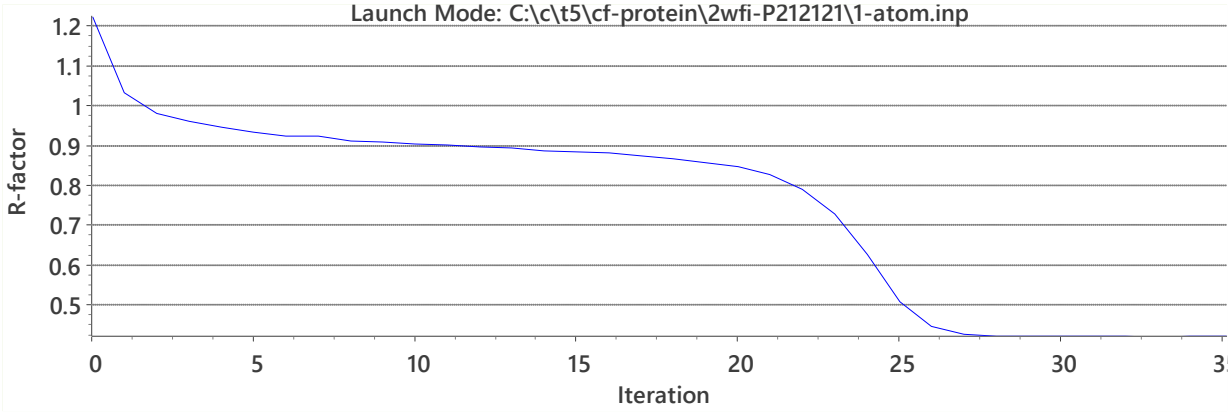
19.2 ... Solution of non-triclinic lattices using a known atomic position

Large non-triclinic structures with many origins are difficult to solve. However, because of symmetry, non-triclinic structures can often be solved when the position of a single atom is known within the ED. Atoms can be inserted in the ED using insert_atoms; for PDB code 2wfi we have:

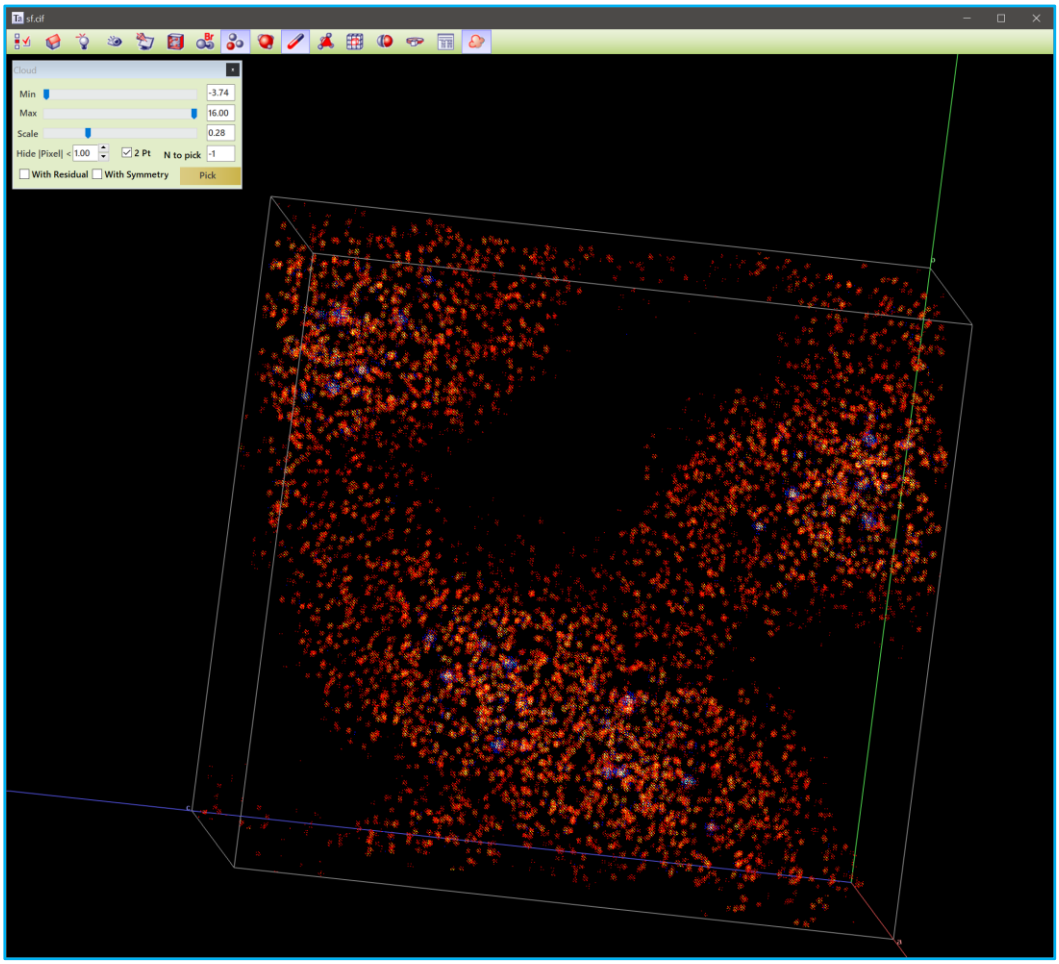
```
charge_flipping
    cf_hkl_file sf.cif ' Structure fact file from PDB
    space_group P212121
    a  37.544  b  65.144  c  69.680
    fraction_reflections_weak 0.5
        add_to_phases_of_weak_reflections = Rand(-180, 180);
    fraction_density_to_flip 0.97
        scale_flipped 0.2
    symmetry_obey_0_to_1 0.25 find_origin 0
    macro Occ_0 { 100 }
    insert_atoms {
```

```
            activate = Mod(Cycle_Iter, 100) == 0;
            load insert_atom x y z occ  {
                0.72697 0.77709 0.11312  100 ' Position of known atom
            }
        }
```

The x, y, z coordinates of insert_atom can be in Cartesian coordinates using the in_cartesian keyword at the insert_atoms level. The use of symmetry_obey_0_to_1 often assists in solution determination for non-triclinic structures. 2WFI can be solved *ab initio;* however, it can be easily solved if the position of one atom was known as seen by running 2WFI-P212121\1-ATOM.INP; it gives and R-factor plot that looks like:



The OpenGL plot (right) shows the solution.



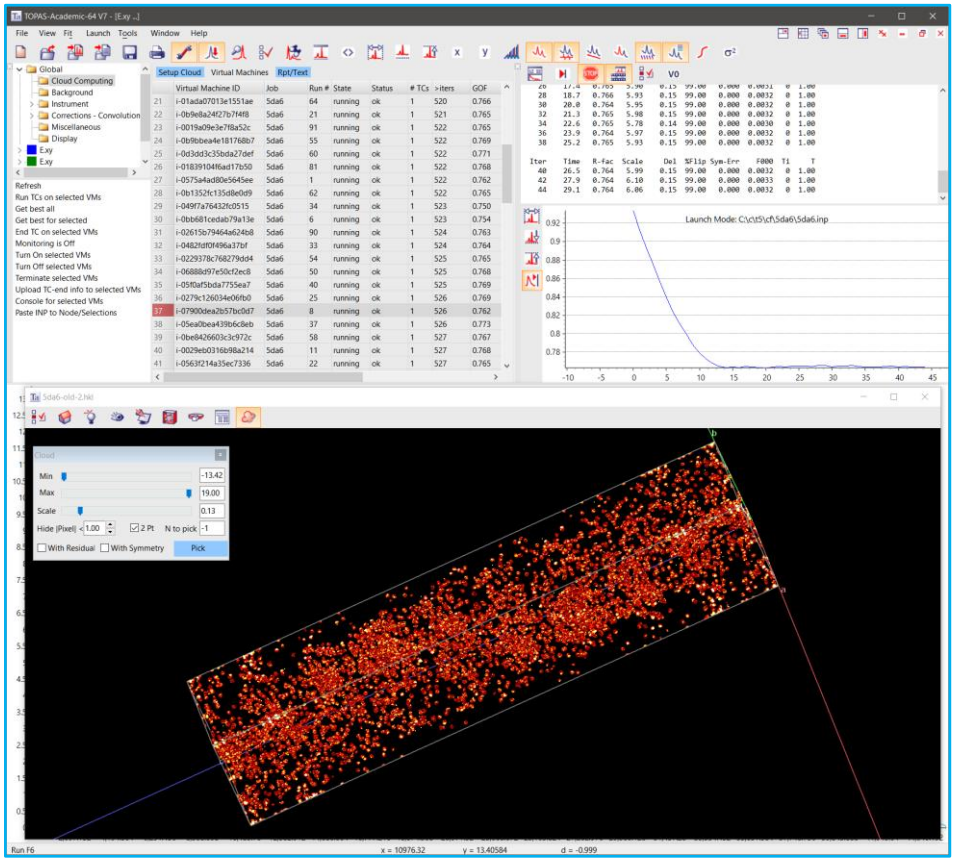
Using any one of the first six highest optimal ED peaks results in a solution. Many structures can be solved from knowing the position of just one atom. 1-ATOM.INP files, similar-to the 2wfi case, are given for 1ctj, 2pvb, 1c75, 5da6, 1cku, 2wfi.

19.3 … Ab initio solution of 5da6 in space group $R3_2$

PDB code 5da6 comprises 1390 atoms in the asymmetric unit. Placing an ED peak at any of its potassium sites result in the correct solution (see 5DA6-R32\1-ATOM.INP). 5da6 can also be solved *ab initio* using the following INP file (see 5DA6-R32\SOLVE.INP):

```
charge_flipping
    cf_hkl_file sf.cif ' Structure factor file from PDB
    space_group R32
    a  42.890  b  42.890  c  266.936  ga 120.00
    fraction_reflections_weak 0.5
        add_to_phases_of_weak_reflections = Rand(-180, 180);
    fraction_density_to_flip 0.97
        scale_flipped 0.2
    symmetry_obey_0_to_1 0.25 find_origin 0
    pick_atoms *
        pick_fwhm 5 omit_fwhm 1 insert_fwhm 1
        choose_randomly = If(Mod(Cycle_Iter, 50), 0, 15);
        insert 10
    flip_regime_2 = Sine_Wave(50 / 4, -2, 2, 50);
    ATP(1000, 1) ' Randomize all phases every 1000 iterations
```

It takes approximately six hours on average to solve 5da6 using the above INP file on an 8-core laptop computer. This time is reduced to 5 minutes on the Cloud where the INP file is run simultaneously on 500 VMs. The best solution on each VM computer or the best solution overall can be viewed during the process. Here's a typical Cloud run (right):



20. MISCELLANOUS

20.1 ... Outputting special characters

The characters ,(){}[] can be outputted to text files by enclosing them in double quotation marks. For example:

```
out aac.txt
    Out_String("a,b}c(d")
```

To output a single apostrophe or double quote character, the escape sequences of %A and %B can be used respectively, for example, the following:

```
do_errors
prm b -0.61427_0.01048
out aac.txt
    out_record
        out_fmt "%V g[h%Bh"
        out_eqn = b;
    out_record
        out_fmt "\n%s%A (brack}et"
        out_eqn = "abc";
```

produces in the AAC.TXT file:

```
-0.614(10) g[h"h
abc' (brack}et
```

The escape sequences themselves can be outputted by using two separate out_records. For example, to output %A use:

```
Out_String("%")
Out_String("A")
```

20.2 ... Iterating over internal data-tree nodes using 'for'

'for' can be used to iterate over all nodes of the internal data tree. For example, to iterate over the site_recs node the following can be used:

```
for site_recs {
    beq @ 1
}
```

20.3 ... Command prompt output during INP file loading using print

The keyword print is executed during the loading of INP files; it is useful for determining when an item is loaded for debugging purposes. For example:

```
print("Executed during the loading of INP files")
#prm a = 1.234;
print(#out a)
```

20.4 ... Sorting output by columns using _sort_dec or _sort_inc

Columns can be sorted in ascending or descending order using _sort_inc or _sort_dec respectively. For example, the following can be used to sort by d-spacing in descending order and then by I_no_scale_pks in ascending order:

```
xdd...
   str...
      phase_out aac.txt
         out_record
            out_fmt "  d = %9.5f"
            out_eqn = D_spacing; _sort_dec 1
         out_record
            out_fmt "  I_no_scale_pks = %9.5f"
            out_eqn = I_no_scale_pks; _sort_inc 2
         out_record
            out_fmt "  2Th = %9.5f\n"
            out_eqn = 2 Rad Th;
```

20.5 ... Creating many xdds at once using new and xdd_file

The new keyword can be used to create many xdds at once, for example:

```
macro Create_XDDs(n)
    {
       move_to xdds
       move_to xdd_recs
       new(xdd, n)
    }
```

See section **Error! Reference source not found.** for usage of the macro Create_XDDs.

20.6 ... seed, #seed_eqn, seed-tc.txt, seed-tb.txt, Rand

The command line TC.EXE increments the number in the file SEED-TC.TXT to seed the random number generator and then saves the incremented value back to SEED-TC.TXT file. If using the GUI version of the program TA.EXE, then the number in the file SEED-TB.TXT is used. *#seed* is similar except it is executed at the pre-processor stage of loading INP files. If a number occurs after either seed or *#seed* then the random number generator is seeded with that number.

#seed_eqn seeds the random number generator at the preprocessor stage with the equation value; here are examples:

```
#seed_eqn seed_1 = Rand(0,32767);
prm value_fed_to_random_number_generator = #out seed_1;
#seed_eqn seed_2 = Run_Number;
```

The rand function of c++ returns integers between 0 and 32767. This range is extended by the Rand function with the following code:

```
inline double Rand(double r1, double r2)
    {
        const double c0 = 1.0 / double(RAND_MAX);
        const double c1 = 1.0 / (1.0 + double(RAND_MAX));
        return (rand() + rand() * c0) * c1 * (r2 - r1) + r1;
    }
```

20.7 ... Threading

TOPAS is threaded; this allows for the utilization of multiple processors resulting in faster program execution. The degree of speedup is computer and problem dependent. For non-trivial problems, the gain is 2 to 4 for a 4-core laptop PC with four i7 processors. Attention is paid to reducing memory usage at the thread level. This is particularly apparent when using rigid bodies or occupancy merge. Except for some penalties all items are threaded; they include peak generation, all convolutions, all derivatives that are a function of *Ycalc*, equations that are a function of changing variables such as *X*, *Th*, *D_spacing* etc..., Pawley refinement, structure refinement, charge flipping, magnetic refinement, stacking faults, PDF refinement, conjugate gradient solution method and Indexing.

20.7.1 ..... Setting the maximum number of threads

The program defaults to using the maximum number of threads available. The user can limit this behaviour by editing the file MAXNUMTHREADS.TXT. This file is read on program start-up; it contains a single number, let's call it Max_Threads_File, which defines the maximum number of threads. Non-existence of the file or a Max_Threads_File of zero results in the program using the maximum number of threads available. If Max_Threads_File is negative, then the maximum number of threads is set to the following:

Max_Number_Threads = Max(1, Max_Threads_File + Max_Threads_Available);

20.8 ... Restraining background using the Bkg_at function

The Chebyshev background function, bkg, can sometimes misbehave during Pawley, Le Bail or deconvolution refinements. In the case of xdd deconvolution refinements, the Deconvolution_Bkg_Penalty macro stabilizes bkg in most cases. In cases of instability, however, the Bkg_at(x) function can be used in penalty functions to guide the shape of bkg. Bkg_at(x) returns the value of bkg at the x-axis position of x. Here's an example use of Bkg_at as applied to TOF data:

```
bkg  @  0.443519294`  0.0200324829`  0.0113774736`
penalty = 1000000 (Bkg_at(2036)  - 0.43)^2;
penalty = 1000000 (Bkg_at(9000)  - 0.50)^2;
penalty = 1000000 (Bkg_at(14600) - 0.50)^2;
```

The first penalty restrains the value of bkg at x=2036 to 0.43. Typically, only two to three Bkg_at penalties are necessary. The values of 0.43, 0.5 and 0.5 can be determined graphically.

20.9 ... Calculation of structure factors

The structure factor *F* for a site *s* with adps is the complex quantity:

$$F(\mathbf{h},\lambda,2\theta)=\sum_s\left\{\left(\sum_e T_{s,e}(\mathbf{h_e},2\theta)\,e^{2\pi\,i\,\mathbf{h_e}\,.\mathbf{r}_{s,e}}\right)\left(\sum_a\left(f_{o,s,a}(2\theta,\lambda)+f'_{s,a}(\lambda)+if''_{s,a}(\lambda)\right)\,O_{s,a}\right)\right\} \tag{20-1}$$

where

s corresponds to site *s*

e corresponds to the equivalent position of site *s*

a corresponds to atom *a*

$O_{s,a}$ corresponds to occupancy

$T_{s,e}$ corresponds to the anisotropic temperature factor

f' and f'' corresponds to anomalous dispersion coefficients

For a site with beq, *F* for a fixed λ becomes:

$$F(\mathbf{h},2\theta)=\sum_s\left\{\left(\sum_e e^{2\pi\,i\,\mathbf{h_e}\,.\mathbf{r}_{s,e}}\right)\left(\sum_a\left(f_{o,s,a}(2\theta)+f'_{s,a}+if''_{s,a}\right)\,e^{-beq_{s,a}\,sin^2(\theta)/\lambda^2}O_{s,a}\right)\right\} \tag{20-2}$$

Let

$$A_s=\sum_e\,cos\left(2\pi\,\mathbf{h_e}\,.\mathbf{r}_{s,e}\right),\quad B_s=\sum_e\,sin\left(2\pi\,\mathbf{h_e}\,.\mathbf{r}_{s,e}\right)$$

Separating the real and imaginary parts we get:

$$F(\mathbf{h},\lambda,2\theta) = \sum_s \left\{ A_s \left(\sum_a \left(f_{o,s,a}(2\theta,\lambda) + f'_{s,a}(\lambda) \right) \; e^{-beq_{s,a}\, sin^2(\theta)/\lambda^2} \right) O_{s,a} \right.$$
$$- \; B_s \left(\sum_a f''_{s,a}(\lambda) \; e^{-beq_{s,a}\, sin^2(\theta)/\lambda^2} O_{s,a} \right)$$
$$+ \; i \left(A_s \left(f''_{s,a}(\lambda) \; e^{-beq_{s,a} sin^2(\theta)/\lambda^2} \; O_{s,a} \right) \right.$$
$$\left. \left. + \; B_s \left(\sum_a \left(f_{o,s,a}(2\theta,\lambda) + f'_{s,a}(\lambda) \right) \; e^{-beq_{s,a}\, sin^2(\theta)/\lambda^2} O_{s,a} \right) \right) \right\}$$

Approximation 2θ with the Bragg angle and dropping subscripts and defining:

$$f_{o,s} = \Sigma_a \, f_{o,a} \, O_a, \quad f_s' = \Sigma_a \, f_a' \, O_a, \quad f_s'' = \Sigma_a \, f_a'' \, O_a \tag{20-3}$$

we have:

$$F = \Sigma_s \, (A_s + i \, B_s) \, (f_{o,s} + f_s' + i \, f_s'') \tag{20-4}$$
$$F = \Sigma_s \, (A_s \, (f_{o,s} + f_s') - B_s \, f_s'') + i \, \Sigma_s \, (A_s \, f_s'' + B_s \, (f_{o,s} + f_s'))$$
$$\text{or,} \quad F = A + i \, B$$

The intensity is proportional to the complex conjugate of the structure factor, or,

$$F^2 = A^2 + B^2 \tag{20-5a}$$

or,

$$F^2 = A_{01}^2 + B_{01}^2 + A_{11}^2 + B_{11}^2 + 2 \, B_{01} \, A_{11} - 2 \, A_{01} \, B_{11} \tag{20-5b}$$
$$\text{where } A_{01} = \Sigma_s \, A_s \, (f_{o,s} + f_s'), \quad A_{11} = \Sigma_s \, A_s \, f_s''$$
$$B_{01} = \Sigma_s \, B_s \, (f_{o,s} + f_s'), \quad B_{11} = \Sigma_s \, B_s \, f_s''$$
$$\text{and } A = A_{01} - B_{11}, \quad B = B_{01} + A_{11}$$

Atomic scattering factors, $f_{o,a}$, comprise 11 values per atom and are found in the file ATMSCAT_11.CPP. Correspondingly 9 values per atom, obtained from the International Tables, are found in the file ATMSCAT_9.CPP. Use of either 9 or 11 values can be invoked by running the batch files USE_9F0 and USE_11F0 respectively. Dispersion coefficients, f_a' and f_a'', are by default from http://www.cxro.lbl.gov/optical_constants/asf.html.

These data, found in the SSF directory, covers the energy range from 10 to 30000eV. The use of use_tube_dispersion_coefficients force the use of dispersion coefficients from the International Tables for X-ray Crystallography (1995), Vol.C, p384-391 and 500-502, and for O2- from Hovestreydt (1983). These data are in discrete energy steps corresponding to wavelengths typically found in laboratory X-ray tubes. For neutron diffraction data, $f_a' = f_a'' = 0$ and $f_{o,a}$ is replaced by the bound coherent scattering length (found in the NEUTSCAT.CPP file) for atom 'a'.

20.9.1 ..... Friedel pairs

For centrosymmetric structures, the intensities for a Friedel reflection pair are equivalent, or $F^2(h\ k\ l) = F^2(-h-k-l)$. This holds true regardless of the presence of anomalous scattering and regardless of the atomic species present in the unit cell. This equivalence in F^2 is due to $B_{01} = B_{11} = 0$ and thus:

$$F = A_{01} + i\,A_{11} \quad \text{and} \quad F^2 = A_{01}^2 + A_{11}^2 \tag{20-6}$$

For non-centrosymmetric structures and for the case of no anomalous scattering, or for the case where the unit cell comprises a single atomic species, then $F^2(h\ k\ l) = F^2(-h-k-l)$. Or, for a single atomic species we have:

$$B_{01}\,A_{11} = (f_0 + f')\,(\Sigma_S\,B_S)\,f''\,(\Sigma_S\,A_S), \quad A_{01}\,B_{11} = (f_0 + f')\,(\Sigma_S\,A_S)\,f''\,(\Sigma_S\,B_S) \tag{20-7}$$

$$\text{or } B_{01}\,A_{11} = A_{01}\,B_{11}$$

and thus, from cancellation in Eq. (20-5b) we get:

$$F^2(\mathbf{h}) = F^2(-\mathbf{h}) = A_{01}^2 + B_{01}^2 + A_{11}^2 + B_{11}^2 \tag{20-8}$$

For non-centrosymmetric structures and for the case of anomalous scattering and for a structure comprising more than one atomic species then $F^2(\mathbf{h}) \neq F^2(-\mathbf{h})$.

20.9.2 ..... Powder data

Friedel pairs are merged for powder diffraction data meaning that the multiplicities as determined by the hkl generator includes the reflections (h k l) and (-h -k -l); this improves computational efficiency. Eq. (20-5b) gives the correct intensity for unmerged Friedel pairs and thus it cannot be used for merged Friedel pairs. Using the fact that:

$$A_{01}(\mathbf{h}) = A_{01}(-\mathbf{h}), \qquad A_{11}(\mathbf{h}) = A_{11}(-\mathbf{h}) \tag{20-9}$$

$$B_{01}(\mathbf{h}) = B_{01}(-\mathbf{h}), \qquad B_{11}(\mathbf{h}) = B_{11}(-\mathbf{h})$$

then F^2 from Eq. (20-5b) in terms of $B_{01}(\mathbf{h})$ and $B_{11}(\mathbf{h})$ evaluates to:

$$F^2(\mathbf{h}) = Q_1 + Q_2 \tag{20-10}$$

$$F^2(-\mathbf{h}) = Q_1 - Q_2$$

$$\text{where } Q_1 = A_{01}^2 + B_{01}^2 + A_{11}^2 + B_{11}^2$$

$$\text{and } Q_2 = 2\,(B_{01}\,A_{11} - A_{01}\,B_{11})$$

and for merged Friedel pairs we get:

$$F^2(\mathbf{h}) + F^2(-\mathbf{h}) = 2\,Q_1 \tag{20-11}$$

The factor of 2 in Eq. (20-11) is dropped as its included in the multiplicity for **h** (as given by the hkl generator). Thus, the final equation describing F^2 for powder diffraction data for merged Friedel pairs is:

$$F^2(\mathbf{h})_{merged} = Q_1 \qquad (20\text{-}12)$$

The reserved parameter names of *A01*, *A11*, *B01* and *B11* can be used to obtain unmerged real, imaginary and F^2 components and the merged F^2. The following macros have been provided in TOPAS.INC:

```
macro F_Real_positive { (A01-B11) }
macro F_Real_negative { (A01+B11) }
macro F_Imaginary_positive { (A11+B01) }
macro F_Imaginary_negative { (A11-B01) }
macro F2_positive { (F_Real_positive^2 + F_Imaginary_positive^2) }
macro F2_negative { (F_Real_negative ^2 + F_Imaginary_negative^2) }
macro F2_Merged { (A01^2 + B01^2 + A11^2 + B11^2) }
```

Note that F2_Merged = (F2_positive + F2_negative) / 2. The reserved parameters *I_no_scale_pks* and *I_after_scale_pks* for str phases are equivalent to the following:

I_no_scale_pks = Get(scale) *M* F2_Merged

I_after_scale_pks = Get(all_scale_pks) Get(scale) *M* F2_Merged

In addition, the macros Out_F2_Details and Out_A01_A11_B01_B11 can be used to output F^2 details.

20.9.3 ..... Single crystal data

SHELX HKL4 single crystal data comprise unmerged equivalent reflections and thus Eq. (20-5b) is used for calculating F^2. Equivalent reflections are merged by default and can be unmerged using dont_merge_equivalent_reflections. For centrosymmetric structures, merging includes the merging of Friedel pairs and thus Eq. (20-12) is used for calculating F^2. For non-centrosymmetric structures, merging excludes the merging of Friedel pairs and thus (20-5b) is used for calculating F^2. dont_merge_Friedel_pairs prevent merging of Friedel pairs. ignore_differences_in_Friedel_pairs force the use of Eq. (20-12) for calculating F^2. The reserved parameter name *Mobs* returns the number of observed reflections belonging to a family of reflections.

Merging of equivalent reflections reduces computational effort and is useful in the initial stages of structure refinement. Only a single intensity is calculated for a set of equivalent reflections even in the absence of merging. Thus, equivalent reflections and Friedel pairs is remembered and intensities appropriated as required.

*.SCR data is typically generated from a powder pattern and comprises merged equivalent reflections including merged Friedel pairs. Consequently, Eq. (20-12) is used for calculating F^2; definitions of dont_merge_equivalent_reflections, dont_merge_Friedel_pairs and ignore_differences_in_Friedel_pairs are ignored.

20.9.4 ..... The Flack parameter

[Flack E]

For single crystal data and for non-centrosymmetric structures the Flack parameter (Flack, 1983) scales $F^2(\mathbf{h})$ and $F^2(-\mathbf{h})$ as follows (see the test example YLIDMA.INP):

$$F^2(\mathbf{h}) = Q_1 + (1 - 2\ \text{Flack})\ Q_2 \qquad (20\text{-}13)$$

$$F^2(-\mathbf{h}) = Q_1 - (1 - 2\ \text{Flack})\ Q_2$$

20.9.5 ..... Single Crystal Output

The macro Out_Single_Crystal_Details, see TOPAS.INC, outputs details for single crystal refinement, see test example YLIDMA.INP. *Mobs* corresponds to the number of observed reflections belonging to a family of planes. When Friedel Pairs are not merged then *Mobs* for **h** and –**h** will be different. Phase symmetry is considered in the values for A01, B01, A11 and B11.

20.9.6 ..... 2θ point by point calculation of f0 and beq

Structure factors for powder diffraction data typically writes beq and the atomic scattering factor fo as a function of the Bragg angle $2\theta_o$. A more accurate description can be realized using the str dependent point_by_point_beq_fo_etc which writes the structure factor in terms of 2θ. This calculates fo and beq on a 2θ point-by- point basis rather than $2\theta_o$. In routine Rietveld refinement the difference in structure factor values is small and difficult to detect. It can however be useful for analysing nanoparticles when extreme accuracy is required. The keyword only works with X-ray powder data and results in a slight increase in computational effort of ~5%. Reported structure factor values using the reserved parameter names of A01, B01, A11 and B11 are still written in terms of the Brang angle $2\theta_o$ and are therefore unchanged.

20.10 . Convolution

20.10.1..... Instrument and sample convolutions

Diffractometer instrument and sample aberration functions used in peak profile synthesis are generated from generic convolutions. For example, the 'simple' axial divergence model is described using the generic convolution circles_conv as defined in the Simple_Axial_Model macro. Table 20-1 lists instrument convolutions. In addition, the full axial divergence model of Cheary & Coelho (1998a, 1998b) is supported.

Table 20-1. Instrument and sample aberration functions in terms of $\varepsilon = 2\theta - 2\theta_k$, where 2θ is the measured angle and $2\theta_k$ the Bragg angle. R_P and R_S correspond to the primary and secondary radius of the diffractometer respectively. ε_m in $^o2\theta$

Aberrations	Name	Aberration function Fn(ε)
Instrument		

Equatorial divergence (fixed divergence slits)	EDFA [°]	$Fn(\varepsilon) = (4\varepsilon_m\varepsilon)^{-\frac{1}{2}}$ $for\ \varepsilon = 0\ to\ \varepsilon_m = -\left(\frac{\pi}{360}\right) cot(\theta_k)\ EDFA^2$
Equatorial divergence (variable divergence slits)	EDFL (mm)	$Fn(\varepsilon) = (4\varepsilon_m\varepsilon)^{-\frac{1}{2}}$ $for\ \varepsilon = 0\ to\ \varepsilon_m = -\frac{EDFL^2\ sin(2\theta_k)\left(\frac{180}{\pi}\right)}{4R_S^2}$
Size of source in the equatorial plane	TA (mm)	$Fn(\varepsilon) = HatShape, \quad for -\frac{\varepsilon_m}{2} < \varepsilon < \frac{\varepsilon_m}{2}$ where $\varepsilon_m = \frac{\left(\frac{180}{\pi}\right)TA}{R_S}$
Specimen tilt; thickness of sample surface as projected onto the equatorial plane	ST (mm)	$Fn(\varepsilon) = HatShape, \quad for -\frac{\varepsilon_m}{2} < \varepsilon < \frac{\varepsilon_m}{2}$ Where $\varepsilon_m = \frac{\left(\frac{180}{\pi}\right)\cos(\theta_k)ST}{R_S}$
Receiving slit length in the axial plane	SL (mm)	$Fn(\varepsilon) = \left(\frac{1}{\varepsilon_m}\right)\left(1 - \sqrt{\frac{\varepsilon_m}{\varepsilon}}\right)$ $for\ \varepsilon = 0\ to\ \varepsilon_m = -\left(\frac{90}{\pi}\right)\left(\frac{SL}{R_S}\right)^2 \cot(2\theta_k)$
Width of the receiving slit in the equatorial plane	SW (mm)	$Fn(\varepsilon) = HatShape, \quad for -\frac{\varepsilon_m}{2} < \varepsilon < \frac{\varepsilon_m}{2}$ where $\varepsilon_m = \frac{\left(\frac{180}{\pi}\right)SW}{R_S}$
Sample		
Linear absorption coefficient	AB (cm^{-1})	$Fn(\varepsilon) = \left(\frac{1}{\delta}\right) Exp\left(-\frac{\varepsilon}{\delta}\right)$ $for\ \varepsilon \leq 0$ and $\delta = 900\sin(2\theta_k)/(\pi\ AB\ R_S)$

20.10.2..... Convolutions in general

TOPAS performs convolution in various ways and the terms “FFT convolution” (Fast Fourier Transform) or “direct convolution” are simplifications. Typically, convolutions are broken down into double summations that can be calculated either directly or by using an FFT. The program uses the method that is fastest as determined by calculating the number of operations required by each method.

Response functions that are known to the program are treated analytically. Response functions that are unknown to the program (such as user defined convolutions) are treated as straight-line segments. Convolution therefore can be i) between two sets of line segments ii) one set of line segments and an analytical expression or iii) simply done analytically. When straight-line segments are used, a response function with N_r data points and a peak comprising N_p points, the extra cost of the piece wise integration is approximately 3 (N_r+N_p) operations. This is a small number of operations, and it produces a high degree of accuracy. Apart from

lor_fwhm and gauss_fwhm, the convolutions described below have discontinuities in 2Th space; associated Fourier transforms are therefore difficult to describe and hence convolution is performed in 2Th space. Response functions that are treated as line segments are:

user_defined_convolution, capillary_diameter_mm, lpsd_th2_angular_range_degrees

Response functions that are analytically convoluted with line segments are:

exp_conv_const, hat, stacked_hats_conv

Response functions that comprise a mixture of analytical and straight-line segments are:

axial_conv, one_on_x_conv, circles_conv

lor_fwhm and gauss_fwhm convolutions are convoluted analytically with the emission profile to form the base profile. Convolutions are calculated with an x-axis step size of:

Peak_Calculation_Step = x_calculation_step / convolution_step

For efficiency x_calculation_step should not be defined for data with equal x-axis steps; instead rebin_with_dx_of should be used. The following response functions are calculated at smaller step sizes without changing *Peak_Calculation_Step* or N_r:

axial_conv	: Step = *Peak_Calculation_Step* / 2
lpsd_th2_angular_range_degrees	: Step = *Peak_Calculation_Step* / 3
capillary_diameter_mm	: Step = *Peak_Calculation_Step* / 1 to 3

In this manner a high degree of accuracy is maintained and N_p*N_r is left unchanged. Typically, a laboratory diffraction pattern can be accurately synthesized with a *Peak_Calculation_Step* of 0.02 degrees 2Th. The next step to increasing accuracy would be to increase convolution_step to 2 and so on. The computational effort for direct convolution scales by (N_r * N_p). Convolutions that scale by (N_r+N_p) are very fast and are:

exp_conv_const, hat, stacked_hats_conv

Calculating derivatives of parameters that are a function of a convolution can be demanding. Most convolutions however that have multiple dependent parameters require only one recalculation of the convolution; exceptions are ft_conv, WPPM_ft_conv and user_defined_convolution. In the case of convolutions that comprise multiple convolution parameters, for example, axial_conv with its convolution parameters of primary_soller_angle etc..., then a recalculation for each of the convolution parameters is required. The following is an overview of convolutions and associated aberrations:

axial_conv	Full Axial divergence model
one_on_x_conv	Equatorial Divergence
circles_conv	Simple axial model
capillary_diameter_mm	Capillary sample
lpsd_th2_angular_range_degrees	LPSD detector
exp_conv_const	Sample penetration

hat	Receiving slit width, sample tilt
stacked_hats_conv	Tube tails

20.10.3..... Capillary convolution for a focusing convergent beam

The capillary convolution has been extended to include a focusing convergent beam (Coelho & Rowles, 2017); syntax is as follows:

[capillary_diameter_mm E]
    capillary_u_cm_inv E
    [capillary_convergent_beam] [capillary_divergent_beam] [capillary_parallel_beam]
    [capillary_focal_length_mm E]
    [capillary_xy_n #]

See examples LAB6-STOE.INP and LAB6-D8.INP in the directory TEST_EXAMPLES\CAPILLARY. If using a str phase then capillary_u_cm_inv can be set to the calculated linear absorption coefficient multiplied by a packing density, for example:

```
prm packing_density 0.31208
capillary_diameter_mm @ 0.57313
    capillary_u_cm_inv
        = Get(mixture_MAC) Get(mixture_density_g_on_cm3) packing_density;
    capillary_focal_length_mm @ 197.89657
    capillary_convergent_beam
```

If capillary_focal_length_mm is not defined, then it defaults to the diffractometer radius Rs.

20.10.4..... ft_conv

[ft_conv_re_im] ... [ft_conv_re E] [ft_conv_im E] [ft_min !E] [ft_x_axis_range !E] ‘ Get(ft_0) ‘ *FT_Break*	Examples TEST_EXAMPLES\FT\ ALVO4A.INP VOIGT.INP

Fourier Transform (FT) of a response function that is convoluted into phase peaks using a Fast Fourier Transform (FFT); for example, to convolute a Voigt into a phase, the following can be used:

```
ft_conv = Exp(-(Pi FT_K gfwhm)^2 / (4 Ln(2)) - Pi FT_K lfwhm);
    ft_min = 1e-8; ‘ this is the default; ft_min is optional
    ft_x_axis_range = 40 lfwhm;
```

ft_conv is equal to the two keywords [ft_conv_re_im ft_conv_re]. More than one transform can be defined. See ft_conv and WPPM_ft_conv for details. Here the convolution theorem is used by multiplying the FT of a Gaussian by the FT of a Lorentzian. If the Fourier transforms are separately defined, the program will internally use the convolution theorem. *FT_K* is a reserved

parameter; it returns the transform k divided by the x-axis range of the peak; this range includes ft_x_axis_range. ft_x_axis_range is a mandatory equation defined such that the transform decays to near zero; peak tails will otherwise be incorrect. A Lorentzian for example needs a large ft_x_axis_range for accurate tails. ft_min defines the smallest value to which the transform is calculated to. For example, an already broadened peak in x-axis space will have a relatively narrow transform; the calculation of the transform is therefore terminated when FT(k)/FT(k=0)<ft_min. Transform values for larger k are then set to zero. If(,,) constructs can instead be used within the transform equation for further control; for example:

```
ft_conv = If (FT_K > D, FT_Break, Sphere(FT_K, D));
```

Here the calculation of the FT is terminated when *FT_K*>D using *FT_Break*. Get(ft_0) returns FT(k=0) and can be used within the ft_conv equation, for example:

```
ft_conv = {
    def a = Exp(-Pi FT_K lf);
    return If(a < 1e-6 Get(ft_0), FT_Break, a);
}
```

ft_conv integrates with convolutions that are performed in direct space. It can be used within peak stack operations, and it can be a function of the reserved parameter names:

H, *K*, *L*, *M*, *Th*, *Xo*, *D_spacing*, *FT_K*

Multiple ft_conv (s) can be defined at either the xdd or phase level. When defined at the xdd level the convolution is applied to all phases of that xdd. The TEST_EXAMPLES\FT directory comprises examples that use ft_conv. For a typical Rietveld refinement, an ft_conv used to describe a Voigt is almost as fast as the analytical equivalent as seen in example FT\ALVO4A.INP. For high accuracy, the range of the peak, as defined with ft_x_axis_range, needs to be large, up to 400 FWHM for a Lorentzian; in these cases, the ft_conv is considerably slower as seen in FT\VOIGT.INP.

FT\ALVO4A.INP compares the use of spherical_harmonics_hkl with and without ft_conv as follows.

```
prm csl 50 min 3 max = Min(Val 2 + 0.1, 10000);
prm csg 50 min 3 max = Min(Val 2 + 0.1, 10000);
prm csl_fwhm = 0.1 Rad Lam / (csl Cos(Th));
prm csg_fwhm = 0.1 Rad Lam / (csg Cos(Th));
if 1 {
    ' Spherical Harmonics
    spherical_harmonics_hkl sh
        sh_order 2
        load sh_Cij_prm {
            y00   !sh_c00  1
            y20   sh_c20   0
            y21p  sh_c21p  0
            y21m  sh_c21m  0
            y22p  sh_c22p  0
            y22m  sh_c22m  0
        }
    existing_prm csl_fwhm *= sh;
```

```
        existing_prm csg_fwhm *= sh;
    }
    if 0 {
        ' use analytical Lorentzian and Gaussian convolution
        lor_fwhm = csl_fwhm;
        gauss_fwhm = csg_fwhm;
    } else {
        ' use Fourier Transform convolution
        ft_conv = Exp(-(Pi FT_K csg_fwhm)^2 / (4 Ln(2)) - Pi FT_K csl_fwhm);
            ft_x_axis_range = 45 csl_fwhm + 4 csg_fwhm;
    }
```

The speed of the analytical convolution is greater not simply because describing the peak analytically is faster but because derivatives of multiple parameters for lor_fwhm (or gauss_fwhm) requires only one peak calculation; whereas for ft_conv the peak is recalculated for each independent parameter that it is a function of.

20.10.4.1..... ft_conv compared to user_defined_convolution

If a response function is known in x-axis space, then it is often best to perform the convolution in x-axis space rather that describing the FT of the response function using ft_conv. user_defined_convolution can be used to perform convolution in x-axis space and the speed at which it operates is as fast or faster than ft_conv depending on the x-axis range of the response function; this is demonstrated in FT\LORENTZIAN.INP. For each peak, user_defined_convolution estimates the computational effort required to perform the convolution either directly or with an FFT and chooses the one with the least computational effort. Examples that use user_defined_convolution are as follows:

FT\LORENTZIAN.INP
TOF\TOF_BANK2_2.INP
WPPM\GAMMA.INP
UDEFA.INP

UDEFA.INP shows how to convolute a function with discontinuities, i.e.

```
    user_defined_convolution = Exp(-20 X^2); min = -.2; max = .5;
```

The FT for functions with such discontinuities often cannot be described analytically.

20.10.4.2.. FFT versus direct summation

Typically an FFT convolution for a response function that comprise histograms is quoted as comprising $O(N \log_2 N)$ operations (Cooley–Tukey algorithm for example). Direct convolution is quoted as comprising $O(N^2)$ operations and is only faster for $N<128$. However, in XRD work a direct convolution rather than an FFT working on real numbers is often faster for N ~< 256 to 512 as the comparison of the $O(N \log_2 N)$ versus $O(N^2)$ is not strictly correct. To see why consider a response function comprising 3 points and a peak comprising 5 points. A convolution can be pictured as the response function R moving along the peak P as follows:

```
P    0 0 0 1 1 1 1 1 0 0 0
R      - - x
R        - x x
R          x x x
R            x x x
R              x x x
R                x x -
R                  x - -
```

In this representation each 'x' can be considered a multiply; in direct convolution this makes a total of 15 multiplies (N_r*N_p) and not N^2 where $N/2 \leq (N_r+N_p) \leq N$. To perform such a convolution using an FFT, the number of operations is approximately $4*16*\log_2 16=256$ multiplies where 16 is the closest power of 2 to N_r+N_p. Of course, FFT routines typically also have special cases for small N; nonetheless N=256 to 512 is not small and many peaks in XRD work typically comprise less points and many of the response functions have a small N_r; these include axial divergence, equatorial divergence, receiving slit width, capillary convolution, LPSD convolution and often sample penetration. Another factor favouring direct convolution for modest N_r and N_p is the fact that modern processors such as the Intel i7 are very fast when data in cache memory are arranged sequentially and accessed sequentially. In fact, non-sequential operations can be as much as 8 times slower than for the sequential case.

20.10.5..... WPPM

[WPPM_ft_conv_re_im E]... [WPPM_ft_conv_re E] [WPPM_ft_conv_im E] WPPM_L_max E WPPM_th2_range E [WPPM_break_on_small !E] [WPPM_correct_Is]	Examples TEST_EXAMPLES\WPPM\ GAMMA.INP GAMMA-FIT-OBJ.INP SPHERE-FIT-OBJ.INP SUPER-LORENTZIAN.INP COMPARE-1.INP S-SPHERE-1.INP CUBE-LN-NORMAL-1.INP LN-NORMAL-1.INP

WPPM_ft_conv is equal to [WPPM_ft_conv_re_im WPPM_ft_conv_re].

20.10.5.1..... WPPM in 2Th space

The WPPM microstructure analysis (Scardi & Leoni, 2001; Leoni *et al*. 2004; David *et al*. 2010) for domains comprising spheres and a gamma distribution can be implemented using user_defined_convolution operating in 2Th space as shown in GAMMA.INP.

20.10.5.2..... WPPM using fit_obj(s)

For cases where microstructure broadening is far greater than instrument/emission profile broadening then fit_obj's can be used to describe the peak shape (see GAMMA-FIT-OBJ.INP and SPHERE-FIT-OBJ.INP), for example:

```
fn gamma_mu_variance(mu, v, xo) {
   def s = 2 ( Sin( X Pi/360) - Sin(xo Pi/360) ) / lam;
```

```
      def p0 = Pi s mu;
      def p = If(Abs(p0) < 1e-10, 1, p0);
      def q = 2 p / v;
      return mu v / p^4
         (
            2 p^2 / (2 + v) + (v/(2+ 3 v + v^2)) (1 - (1 + q^2)^(-.5 v)
            Cos(v ArcTan(q)) - 2 p (1 + q^2)^(-.5 (v+1)) Sin( (1 + v)
            ArcTan(q)))
         );
   }
```

Example SUPER-LORENTZIAN.INP is useful for asking the question; can spheres with a gamma distribution describe a 1/(1+x^2)^m type function? Example COMPARE-1.INP is useful for asking the question; can a Voigt fit to a particular case of spheres with a gamma distribution?

20.10.5.3..... WPPM using WPPM_ft_conv

WPPM_ft_conv describes a FT in *s* space and performs a convolution on phase peaks that have been interpolated to *s* space, for example:

```
WPPM_ft_conv = 1 - 1.5 WPPM_L / D + 0.5 (WPPM_L / D)^3;
    WPPM_L_max = D;
    WPPM_th2_range = 25 .1 Rad Lam / (D Cos(Th));
    WPPM_break_on_small 1e-7
    WPPM_correct_Is
```

The result is then interpolated back to 2Th space. Interpolations are scaled such that $I(s)ds = I(\theta)d\theta$ when WPPM_correct_Is is defined; the effects of this scaling is typically small at low angles and becomes noticeable at very high angles reaching a maximum at 180 degrees 2Th where the derivative of Cos(*Th*) is at a maximum.

When multiple WPPM_ft_conv(s) are defined then the program will internally use the convolution theorem.

WPPL_L is a reserved parameter name that returns the transform parameter.

WPPM_L_max defines the maximum *WPPL_L*.

Get(ft_0) and FT_Break can both be used in WPPM_ft_conv in a manner similar-to ft_conv.

The calculation of the Fourier transform is terminated when WPPM_ft_conv_re is less than WPPM_break_on_small multiplied by the value of WPPM_ft_conv_re evaluated at WPPM_L = 0. If WPPM_break_on_small is not defined, then no check is made to terminate the transform.

The tails of WPPM peaks extend for almost the whole diffraction pattern; they can be shortened using WPPM_th2_range; in the above example, this range has been written in terms of the fwhm as defined in the Scherrer equation. WPPM_ft_conv can be a function of the following reserved parameter names:

H, *K*, *L*, *M*, *Th*, *Xo*, *D_spacing*, *WPPM_L*

Example S-SPHERE-1.INP uses WPPM_ft_conv to fit to a synthesized WPPM generated peak with identical results. Example CUBE-LN-NORMAL-1.INP can be used to test these macros. Lattice parameters appearing within the macros are made constant using Constant; these convolutions are therefore made independent of lattice parameter changes and hence separate convolutions are not initiated whilst calculating lattice parameter derivatives.

WPPM_Ln_k is a reserved parameter name that returns Ln of an integer and is used to calculate Ln(Kc *WPPM_L*) in a fast manner.

The example LN-NORMAL-1.INP can be used for visualizing a Ln normal distribution. It uses the Ln_Normal_x_at_CD function to determine the limit of the distribution.

20.10.6..... Microstructure convolutions

The Double-Voigt approach (Balzar, 1999) is supported for modelling microstructure effects. Crystallite size and strain comprise Lorentzian and Gaussian component convolutions varying in 2θ as a function of $1/\cos(\theta)$ and $\tan(\theta)$ respectively.

20.10.6.1..... Preliminary equations

The following preliminary equations are based on the unit area Gaussian, $G_{UA}(x)$, Lorentzian, $L_{UA}(x)$, and pseudo-Voigt $PV_{UA}(x)$ functions as given in Table 5-2.

Height of $G_{UA}(x)$ and $L_{UA}(x)$ respectively:

$$G_{UAH} = G_{UA}(x=0) = g_1 / fwhm$$
$$L_{UAH} = L_{UA}(x=0) = l_1 / fwhm$$

Gaussian and Lorentzian respectively with area A:

$$G(x) = A\, G_{UA}(x)$$
$$L(x) = A\, L_{UA}(x)$$

Height of G(x) and L(x) respectively:

$$G_H = A\, G_{UA}$$
$$L_H = A\, L_{UAH}$$

Integral breadth of Gaussian and Lorentzian respectively:

$$\beta_G = A / G_H = 1 / G_{UAH} = fwhm / g_1$$
$$\beta_L = A / L_H = 1 / L_{UAH} = fwhm / l_1$$

Unit area Pseudo Voigt, PV_{UA}:

$$PV_{UAH} = \eta\, L_{UAH} + (1-\eta)\, G_{UAH}$$
$$\beta_{PV} = 1 / PV_{UAH}$$

A Voigt is the result of a Gaussian convoluted by a Lorentzian:

$$V = G(fwhm_G) \otimes L(fwhm_L)$$

where "⊗" denotes convolution and fwhmG and fwhmL are the FWHM of the Gaussian and Lorentzian components. A Voigt can be approximated using a Pseudo Voigt. This is done numerically where:

$$V(x) = G(fwhm_G) \otimes L(fwhm_L) = PV_{UA}(x, fwhm_{PV})$$

By changing units to s ($Å^{-1}$):

$$s = 1/d = 2 \sin(\theta) / \lambda$$

and differentiating and approximating $ds/d\theta = \Delta s / \Delta\theta$ we get:

$$\Delta s = (2 \cos(\theta) / \lambda) \Delta\theta$$

thus:

$$fwhm(s) = fwhm(2\theta) \cos(\theta) / \lambda$$
$$IB(s) = IB(2\theta) \cos(\theta) / \lambda$$

20.10.6.2..... Crystallite size and strain

Crystallite Size: Gaussian and Lorentzian component convolutions are:

$$fwhm(2\theta) \text{ of Gaussian} = (180/\pi) \lambda / (\cos(\theta) CS\_G)$$
$$fwhm(2\theta) \text{ of Lorentzian} = (180/\pi) \lambda / (\cos(\theta) CS\_L)$$
$$\beta(2\theta) \text{ of Gaussian} = (180/\pi) \lambda / (\cos(\theta) CS\_G\, g_1)$$
$$\beta(2\theta) \text{ of Lorentzian} = (180/\pi) \lambda / (\cos(\theta) CS\_L\, l_1)$$

or, according to Balzar (1999), in terms of s, βGS and βCS:

$$fwhm(s) \text{ of Gaussian} = (180/\pi) / CS\_G$$
$$fwhm(s) \text{ of Lorentzian} = (180/\pi) / CS\_L$$
$$\beta_{GS}(s) = \beta(s) \text{ of Gaussian} = (180/\pi) / (CS\_G\, g_1)$$
$$\beta_{CS}(s) = \beta(s) \text{ of Lorentzian} = (180/\pi) / (CS\_L\, l_1)$$

The macros CS_L and CS_G are used for calculating the CS_L and CS_G parameters respectively. Determination of the volume weighted mean column height LVol, LVol-IB and LVol-FWHM is as follows:

LVol-IB = k / Voigt_Integral_Breadth_GL (1/CS_G, 1/CS_L)
LVol-FWHM = k / Voigt_FWHM_GL(1/CS_G, 1/CS_L)

The macro LVol_FWHM_CS_G_L is used for calculating LVol-IB and LVol-FWHM.

Strain: Strain_G and Strain_L parameters corresponds to the fwhm(2θ) of a Gaussian and a Lorentzian that is convoluted into the peak, or,

fwhm(2θ) of Gaussian = Strain_G tan(θ)
fwhm(2θ) of Lorentzian= Strain_L tan(θ)
$\beta(2\theta)$ of Gaussian = Strain_G tan(θ) / g_1
$\beta(2\theta)$ of Lorentzian = Strain_L tan(θ) / l_1

or, according to Balzar (1999), in terms of s, β_{CD} and β_{GD}:

fwhm(s) of Gaussian = Strain_G sin(θ) / λ = Strain_G s / 2
fwhm(s) of Lorentzian = Strain_L sin(θ) / λ = Strain_L s / 2
$\beta_{GD}(s)/s_0$ s = β(s) of Gaussian = (Strain_G / g_1) s / 2
$\beta_{CD}(s)/s_0$ s = β(s) of Lorentzian = (Strain_L / l_1) s / 2

The macros Strain_L and Strain_G are used for calculating the Strain_L and Strain_G parameters respectively. From these equations we get:

$\beta_{GD}(s) = s_0$ Strain_G / (2 g_1)
$\beta_{CD}(s) = s_0$ Strain_L / (2 l_1)

According to Balzar (1999), equation (34):

$e = \beta_D(2\theta) / (4 \tan(\theta))$

where $\beta_D(2\theta)$ is the fwhm of a Voigt comprising a Gaussian with a fwhm = Strain_G Tan(θ) and a Lorentzian with a fwhm = Strain_L Tan(θ). The value for e0 is given by:

4 e0 Tan(θ)= FWHM of the Voigt from Strain_G and Strain_L
= Voigt_FWHM_GL(Strain_G, Strain_L) Tan(θ)

or,

e0 = Voigt_FWHM_GL(Strain_G, Strain_L) (π / 360) / 4

The macro e0_from_Strain calculates e0 using the equation function Voigt_FWHM_GL.

20.11 . Loading of INP files

20.11.1..... if {} else if {} else {}

'if' operates during the loading of pre-processed INP files, syntax is as follows (see TEST_EXAMPLES\ZRO2.INP):

```
    if expression {
    } else if expression {
    } else expression {
    }
```

expression can be any valid TOPAS equation without the semicolon; in addition, *expression* can contain the functions Prm_There(prm_name) and Obj_There(obj_name). The following is equivalent to a /* */ block comment:

```
    if 0 {
        ...
    }
```

A more complex construct could look something like:

```
xdd
    local aaa 1
    str ...
        local aaa 2
    str ...
        local aaa 3
    hkl_Is
        if Prm_There(aaa) {
            Out(aaa, "\nThis is the aaa at the xdd level %-1.6f")
            if aaa == 2 {
                Out_String("\nNot written to file as aaa at the xdd level is 1")
            }
        } else if Obj_There(hkl_Is) {
            Out_String("\nYes this is a hkl_Is phase")
        } else {
            Out_String("\naaa is not there and this is not a hkl_Is phase")
        }
for xdds {
   if And(Obj_There(neutron), Obj_There(pk_xo)) {
       ' Neutron TOF
} }
```

20.12 . Functions – fn, def, return, noinline

Functions can be defined using fn; here's an example of a recursive function:

```
    fn factorial(x) { return If(x == 1, 1, x factorial(x-1)); }
    prm = factorial(5); : 120
```

There's also the simple form where the return statement is implied:

```
    fn factorial(x) = If(x == 1, 1, x factorial(x-1));
```

The equation part of prm objects can have a function body (see the Robust_Refinement macro in TOPAS.INC), for example:

```
    prm = { def a = 2; return a; }
```

Most importantly, functions can reference parameters defined using prm; this simplifies the writing of prm equations and additionally memory usage can be greatly reduced when noinline is used. Equations called def objects can be used and defined within non-simple functions. Here's an example:

```
fn gauss(a, x, f, g) {
    def a1 = 2 Sqrt(Ln(2) / Pi) / f;
    def a2 = 4 Ln(2);
    def a3 = (x / f);
    return a1 Exp(-a2 a3^2);
}
```

A def object must be defined prior to its use. They can be assigned to other def objects but not to objects of prm type. In other words, prm objects are write-protected within functions. The arguments to functions can be def or prm objects. c-style braces can be used to scope variables; the following will throw an exception due to the attempted use of an uninitialized def object:

```
fn foo(x) { def a; { def a = x; } return a; }
prm = foo(3); : 0 ' Exception thrown
```

The following will not throw an exception as the simplification routines recognizes '0':

```
Fn a(x) = x undefined_name 0; prm = a(3); : 0
```

Functions can be nested, for example:

```
fn foo() {
    def a, b;
    a = 3; b = 2;
    fn nested(x, y) { return Sqrt(x^2 + y^2); }
    return nested(a, b);
}
prm = foo(); : 3.60555
```

def and prm objects have scope which determines the actual object used.

Here def 'a' is returned:

```
fn a(a) { def a = 2; return a; } prm = a(1) : 2
```

Here prm 'a' is returned:

```
prm a = 2; fn a() = a; prm = a(); : 2
```

Here the argument 'a' is returned:

```
prm a = 2; fn a(a) = a; prm = a(3); : 3
```

Function specifics:

- fn's are a kernel operation and not a pre-processor operation.
- fn's must be defined prior to their use.
- fn arguments are optional but parentheses must be used.
- a fn cannot be defined with a name of a previously defined fn name.
- fn's are inlined by default.
- Non-nested fn's can be prevented from being inlined with the noinline prefix.
- nested functions cannot be prefixed with noinline.

Use of noinline can often be slower than not using noinline; this is because a stack mechanism is used for the fn arguments, additionally the global simplification routines cannot simplify what's inside a noinline function. Functions are therefore 'inlined' (the word 'expand' is sometimes used) by default. A macro can be considered an inlined function and there's no difference in how the following is finally processed:

```
fn my_max(a, b, c) = Max(a, b, c);
macro & my_max(& a, & b, & c) { Max(a, b, c) }
```

The macro, by definition, is inlined in the pre-processed INP file. In the case of fn, the program will inline 'my_max'. Prefixing fn with noinline prevents in-lining, for example:

```
noinline fn gauss(x, f)=(2 Sqrt(Ln(2)/Pi)/f) Exp(-4 Ln(2)((X-x)/f)^2);
```

Its best to inline small functions as it gives the simplification routines a chance to simplify what's inside the function with regards to its surroundings. Consider the following:

```
noinline fn a(b, c) = b^2 + c^2;
prm  p1 1
prm !p2 1
prm  p3 1
prm !p4 1
prm  p5 = a(p1, p2) + a(p3, p4); : 0
```

Without inlining, the simplification routines won't see that p2 and p4 are constants inside the 'a' function and hence no simplification is performed; the 'a' function will be called twice, and the stack used twice. Note, stack here refers to the computer algebra stack. With inlining, p5 after simplification reduces to:

```
prm p5 = p1^2 + p3^2 + 2; : 0
```

In the case of large functions, not inlining may increase performance as the signalling of equation nodes for recalculation will be reduced. Inlined functions have scope allowing the use of the Get(...) function, for example:

```
fn lat(h, k, l) = h Get(a) + k Get(b) + l Get(c);
str ...
    lor_fwhm = lat(H, K, L) - lat(-H, -K, -L);
```

20.12.1..... Subject independent single crystal refinement

The example \FUNCTIONS\ALVO4-FN.INP performs a single crystal refinement using computer algebra. No subject dependent keywords are used and instead only the following six keywords are used:

fn, noinline, def, return, prm, restraint

The speed of ALVO4-FN.INP is 7.4 times slower than the comparable subject dependent equivalent of ALVO4-NORMAL.INP. Much of the difference in speed is in the calculation of the Cosines necessary for the structure factors. Importantly, convergence and the behaviour of the parameters are similar. The placement of noinline is important. Also used is out_refinement_stats which outputs the following:

```
First pass equation statistics excluding attribute equations
   Number of equations         : 534
   Number of nodes             : 99751
   Number of nodes if expanded : 12070283

Number of penalties/restraints: 532
Number of independent penalty/restraints parameters: 58
Number of penalties/restraints: 532
Number of independent penalty/restraints parameters: 58

Time   0.13
Second pass equation statistics excluding attribute equations
   Before/After equation simplification
     Number of equations         : 549  553
     Number of nodes             : 99766  8354
     Number of nodes if expanded : 12070298  228183
Number of objects taking part in refinement: 73
Number of dependent parameters with derivatives wrt to Ycalc: 15
```

The ALVO4-FN.INP demonstrates the ease at which an entire single crystal refinement can be performed; it should allow for user defined temperature factors etc.

20.12.2..... Computer algebra and out_refinement_stats

The computer algebra system CAS in version 5 (Coelho *et al.*, 2011) is around 2 to 4 times faster than version 4; compare with running ROSENBROCK-10.INP or PVS.INP. The CAS has been reworked and it now operates on a global level where equations are simplified across all objects. The out_refinement_stats keywords, for SERINE_I_EVANS_N_TA_BANG_ROT.INP for example, outputs the following equation statistics:

```
Second pass equation statistics excluding attribute equations
   Before/After equation simplification
     Number of equations         : 2707  3085
     Number of nodes             : 22941  16671
```

```
    Number of nodes if expanded : 1706390373  1070170132

Number of objects taking part in refinement: 2595
Number of dependent parameters with derivatives wrt to Ycalc: 2319
```

20.13 . CIF

The following macros and Get's can be used to output data in CIF format:

```
Out_CIF_STR(file)
Out_CIF_ADPs(file)
Out_CIF_STR(file, with_id)
Out_CIF_Bonds_Angles(file)
Get(number_of_parameters)
Get(refine_ls_shift_on_su_max)
Get(weighting)
Xi = a reserved parameter name
```

_refine_ls_shift / su_max can be accessed using Get(refine_ls_shift_on_su_max) when do_errors is defined and when continue_after_convergence is NOT defined. A message similar-to the following is displayed on calculation:

```
refine_ls_shift_on_su_max 0.409610469 corresponds to parameter m501b939c_3 of object prm_10
```

Get(weighting) and *Xi* can be used as follows:

```
xdd_out file append load out_record out_fmt out_eqn {
    " %9.0f" = Xi;
    " %11.5f" = X;
    " %11.5f" = Ycalc;
    " %11.5f" = Yobs;
    " %11.5f\n" = Get(weighting);
}
```

Get(weighting) returns weighting as defined by the User; if weighting is not defined then the following is returned:

1 / Max(1, *Yobs*), if *SigmaYobs* does not exist

1 / *SigmaYobs*^2, if *SigmaYobs* does exist

Get(weighting) returns zero for x-axis regions that are excluded using exclude. If weighting is a function of *Ycalc* etc... then it returns the last weighting calculated depending on recal_weighting_on_iter.

20.14 . Laue refinement

Single crystal Laue diffraction data can be refined; data files have the extension *.HKL-LAM; see directory TEST_EXAMPLES\LAUE. *Laue_Lam* is a reserved parameter name that can be used in hkl type equations; it returns the reflection dependent wavelength. The merging of equivalent reflections and Friedel_pairs are not allowed with Laue refinement; the following keywords are internally defined with Laue refinement:

```
dont_merge_equivalent_reflections
dont_merge_Friedel_pairs
```

and the following messages reported:

```
Equivalent reflections not merged
Friedel pairs not merged
```

20.15 . Learnt Shapes for Background or Otherwise

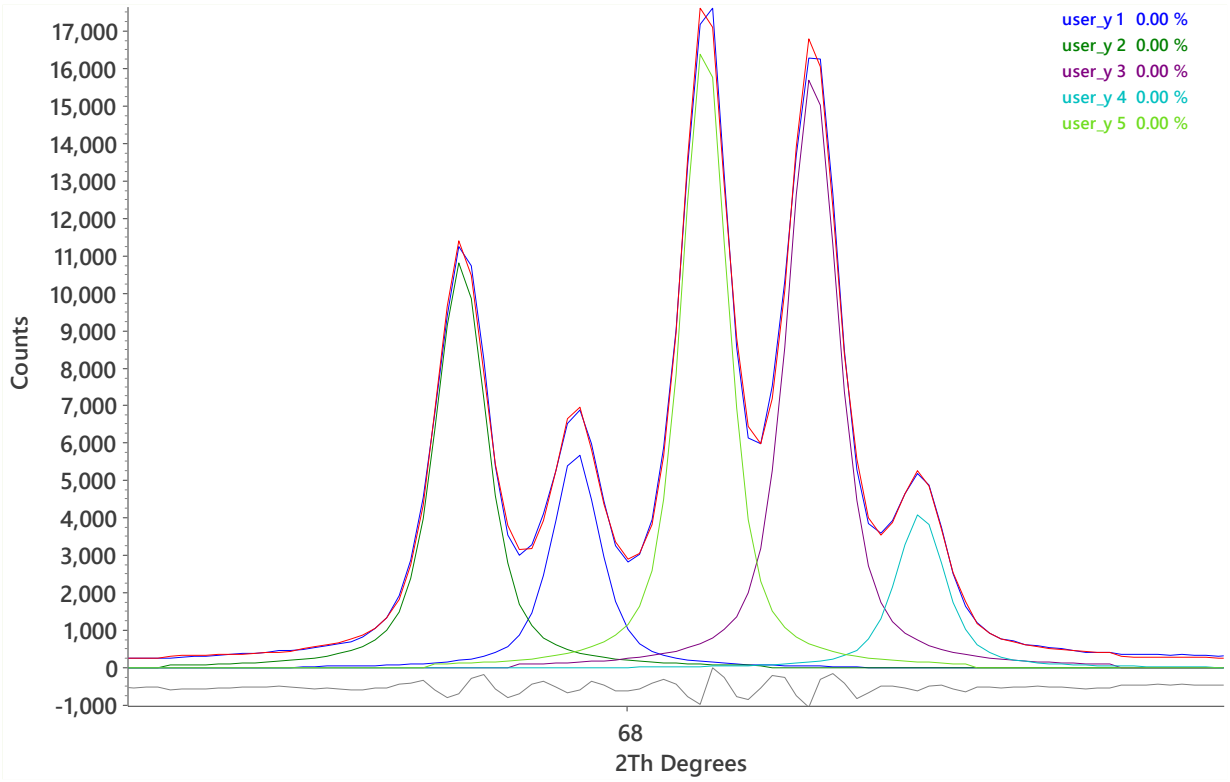
[xdd]... [user_y $name { *#include* $file }]... | [user_y $name $file]... [[1]xye_format] [[1]rebin_with_dx_of !E] [[1]user_y_hat E] ... [[1]user_y_gauss_fwhm E] ... [[1]user_y_lor_fwhm E] ... [[1]user_y_exp_conv_const E [user_y_exp_limit E]...	Examples TEST_EXAMPLES\USER_Y\ USER_Y_CONVOLUTION.INP

[1]New user_y dependents. user_y_hat, user_y_gauss_fwhm, user_y_lor_fwhm and user_y_exp_conv_const are identical to the hat, gauss_fwhm and lor_fwhm and exp_conv_const convolutions except they are applied to user_y data.

user_y can be used to add, multiply and in general manipulate data files of different x-axis steps. For example, to add two data files, square the result and then multiply by the x-axis reserved parameter *X*, the following can be used:

```
user_y f1 file1.xy
user_y f2 file2.xy
yobs_eqn result.sst = X (f1 + f2)^2; min 10 max 100 del 0.01
```

The test example USER_Y\USER_Y.INP fits five fit objects to the quartz triplet using a learnt peak shape defined using user_y; the fit with the individual fit_obj's displayed, using the Plot_Fit_Obj macro, looks like:



The test example USER_Y\USER_Y_CONVOLUTION.INP fits five fit objects to a simulated pattern using a learnt peak shape defined using user_y convoluted with user_y_exp_conv_const and user_y_gauss_fwhm; the INP file looks like:

```
'#define CREATE_SIMULATED_
continue_after_convergence

macro FO_Peak(& p, & pe, & a, & x, & s)
   {
      fit_obj = a p;
         min_X = -pe s + x; max_X = pe s + x;
           fo_transform_X = (X - x) / s;
   }

prm !peak_extent 2

#ifdef CREATE_SIMULATED_
    iters 0
    user_y peak { _xy -0.01 0 0 100 0.01 0  }
        user_y_exp_conv_const @ 1    min 0.5 max 2
        user_y_gauss_fwhm     @ 0.1  min 0.1 max 2
   yobs_eqn = 1; min 66 max 70 del 0.01
        gui_ignore ' don't load data file into GUI
        Out_X_Ycalc(user_y_convolution.xy)
#else
    ' Fit to the simulated peak
    user_y peak { _xy -0.01 0 0 100 0.01 0  }
        user_y_exp_conv_const @ 1   min 0.5 max 2 val_on_continue = Rand(0.5, 2);
        user_y_gauss_fwhm     @ 0.1 min 0.1 max 1 val_on_continue = Rand(0.1, 1);
    xdd user_y_convolution.xy
#endif
      start_X  66
      finish_X 70
```

```
bkg @ 100
prm a1 1000 min 1.0e-6 val_on_continue = Rand(1, 100);
prm a2 2000 min 1.0e-6 val_on_continue = Rand(1, 100);
prm a3 3000 min 1.0e-6 val_on_continue = Rand(1, 100);
prm a4 2000 min 1.0e-6 val_on_continue = Rand(1, 100);
prm a5 1500 min 1.0e-6 val_on_continue = Rand(1, 100);
prm x1 67.7 val_on_continue = Val + Rand(-0.01, 0.01) 5; min 67 max 69
prm x2 67.9 val_on_continue = Val + Rand(-0.01, 0.01) 5; min 67 max 69
prm x3 68.1 val_on_continue = Val + Rand(-0.01, 0.01) 5; min 67 max 69
prm x4 68.3 val_on_continue = Val + Rand(-0.01, 0.01) 5; min 67 max 69
prm x5 68.5 val_on_continue = Val + Rand(-0.01, 0.01) 5; min 67 max 69
prm s1 0.7 val_on_continue = Rand(0.5, 2); min 0.5 max 2
prm s2 0.9 val_on_continue = Rand(0.5, 2); min 0.5 max 2
prm s3 1.1 val_on_continue = Rand(0.5, 2); min 0.5 max 2
prm s4 1.0 val_on_continue = Rand(0.5, 2); min 0.5 max 2
prm s5 0.8 val_on_continue = Rand(0.5, 2); min 0.5 max 2

FO_Peak(peak, peak_extent, a1, x1, s1) Plot_Fit_Obj("user_y 1")
FO_Peak(peak, peak_extent, a2, x2, s2) Plot_Fit_Obj("user_y 2")
FO_Peak(peak, peak_extent, a3, x3, s3) Plot_Fit_Obj("user_y 3")
FO_Peak(peak, peak_extent, a4, x4, s4) Plot_Fit_Obj("user_y 4")
FO_Peak(peak, peak_extent, a5, x5, s5) Plot_Fit_Obj("user_y 5")
```

fo_transform_X is a dependent of fit_obj and it can be used to transform *X* used within the fit_obj. This is useful for cases where the user_y x-axis is different to the *Yobs* x-axis. The user_y NAME {...} usage allow shapes to be typed directly into the INP file using the *_x1_dx* tag. A triangle for example is formulated as follows:

```
user_y NAME {
   _x1_dx -1 1 /* start and step */
   0 1 0       /* the shape data */
}
```

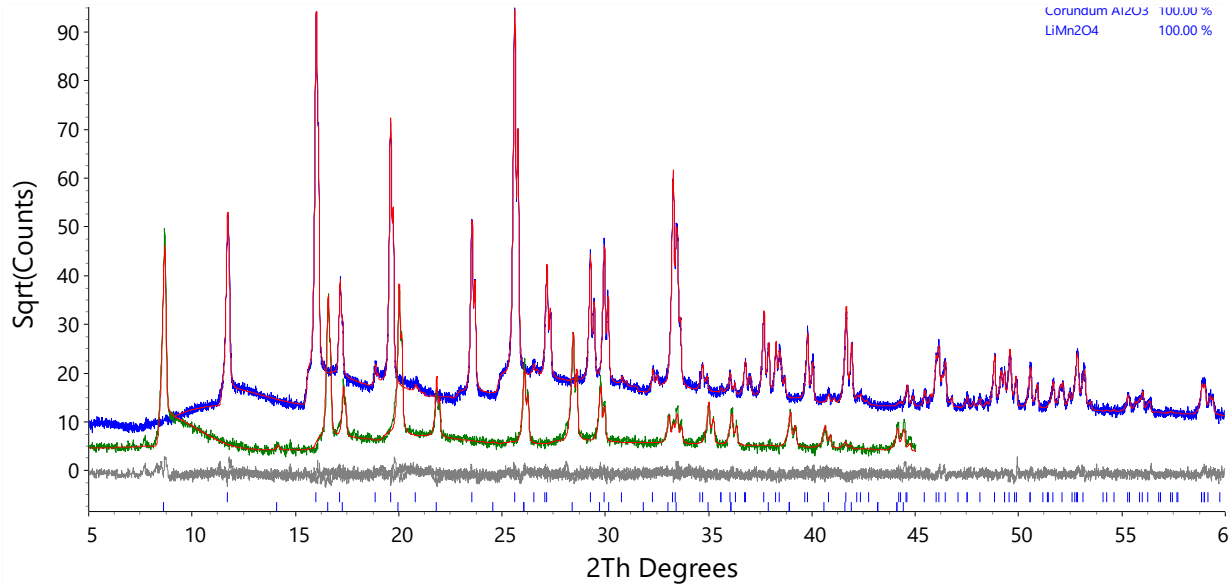
Multiple user_y(s) can be defined, and each can be used any number of times in equations that can be a function of *X*. The test example USER_Y.INP loads a single shape and stretches and scales it five different ways onto a diffraction pattern to fit the Quartz triplet. Convergence is as fast as with any other refinement.

20.16 . Emission Profile with Absorption Edges

[modify_peak] [modify_peak_apply_before_convolutions] [modify_peak_eqn !E] [current_peak_min_x !E] [current_peak_max_x !E] Get(current_peak) Get(current_peak_x)	Examples TEST_EXAMPLES\ABSORPTION-EDGE \ AL2O3-PAM.INP SPINNEL-PAM.INP

modify_peak can be used to modify peak profiles either before convolutions or after. Functionality is realized by using the internal data objects of Get(current_peak_x) and Get(current_peak); these two objects return the x-axis wavelength being processed and the current

calculated peak intensity respectively. Here are plots from AL2O3-PAM.INP and SPINNEL-PAM.INP that has an identical absorption edge modelled for both Al2O3 and Spinnel samples:



When no_th_dependence is defined then Get(current_peak_x) returns the x-axis of the point being calculated; when no_th_dependence is not defined then Get(current_peak_x) returns the wavelength of the point being calculated.

20.17 . scale_phase_X keyword

[scale_phase_X E]...	Examples TEST_EXAMPLES\ SCALE_PHASE_X.INP

Scales *Ycalc* point by point. It can be used, for example, to define the Lorentz Polarization factor on an x-axis basis rather than on a peak basis as is the case for scale_pks. Some main points for scale_phase_X:

- Can be a function of *X*
- Multiple definitions allowed and each applied to the pattern.
- Can occur at the xdd and/or phase level.

Here's an example:

```
xdd ...
    scale_phase_X ...
    str       scale_phase_X ...
    hkl_Is    scale_phase_X ...
```

The first str is multiplied by the first and second scale_phase_X; the hkl_Is phase is multiplied by the first and third scale_phase_X.

20.18 . Refining on f0, f' and f"

[f0_f1_f11_atom]... [f0 E] [f1 E] [f11 E]	**Examples** TEST_EXAMPLES\F0-F1-F11\ XRAY-POWDER.INP TOF.INP

User defined atomic scattering factors, f0, and anomalous dispersion coefficients, f1 and f11. Example usage:

```
report_on_str
load f0_f1_f11_atom f1 f11 {
    Ba @ -0.160127754 2.3954287
    Ge 0.184162081 1.86162161
}
```

High correlations exist between f1, f11, scale and beq parameters. f0_f1_f11_atom can be used at the str, xdd and global levels. f1 and f11 can be defined and refined independently. Defaults are used when f1 or f11 are not defined. The examples XRAY-POWDER.INP and TOF.INP demonstrates the use of f0, f1 and f11. The f0 parameter can be a function of the reserved parameter *D_spacing*, *Th* and *X*; for example:

```
prm a1 25 min -50 max 50
load f0_f1_f11_atom f0 f11 {
    Pb+2
    = a1         Exp(1.058874   (-0.25) / D_spacing^2) +
      16.496822  Exp(0.106305   (-0.25) / D_spacing^2) +
      19.984501  Exp(6.708123   (-0.25) / D_spacing^2) +
      6.813923   Exp(24.395554  (-0.25) / D_spacing^2) +
      5.233910   Exp(1.058874   (-0.25) / D_spacing^2) +
      4.065623; ' this is f0 for Pb
      @ 5       ' this is f11 for Pb
}
```

For X-ray data f0 is by default obtained from the file ATMSCAT.CPP. For neutron data f0 corresponds to the neutron scattering length from the NEUTSCAT.CPP file. Neutron scattering lengths can be refined, see example TOF.INP. no_f11 instructs the program to ignore f11. This increases speed with little change in *Ycalc*. report_on_str reports on f1 and f11, or neutron scattering lengths used. No values are reported when d_spacing_to_energy_in_eV_for_f1_f11 is used. To disable the effects of f0, f1 and f11, for say CeO_2, then the following could be used:

```
load f0_f1_f11_atom f0 f1 f11 {
    Ce+4 1 0 0
    O-2  1 0 0
}
```

20.18.1..... Using a user defined table to input f0 values via user_y

Atomic scattering factors f0 can be defined in a *.XY file and used via the user_y keyword as follows:

```
xdd ...
    user_y C_f0_table C_f0_table.xy ' x-axis are the D_spacings
    str
        load f0_f1_f11_atom f0 f1 f11 { C = C_f0_table; 0 0 }
        …
```

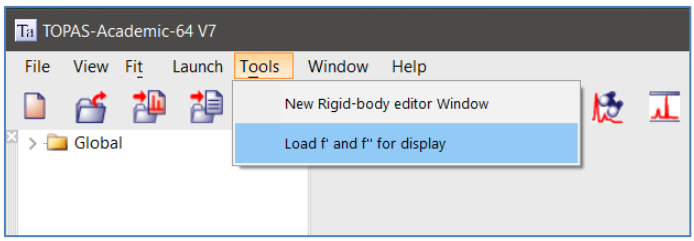
Here the C_F0_TABLE.XY file comprises D_spacing and f0 value pairs which are used to describe f0 values for the C atoms within the structure. In the above example, f1 and f11 are set to zero.

20.19 . Invalid f1 and f11

The following message is displayed when there are no valid entries for f' and f" in the corresponding NFF file:

```
Invalid f1 and f11 for O in file ...\ssf\o.nff
   for the wavelength 0.399826.
   Setting value(s) to zero
```

In such cases the user may choose to manually define f' and f'' using f1 and f11 respectively. Also useful is to view f' and f'' NFF files found in the ssf directory using the GUI Tools menu:



20.20 . Isotopes and Atom Names

ISOTOPES.TXT is used for obtaining isotope weights. The same atom names can be used for both neutron_data and x-ray data as the program will do the appropriate conversion. For example:

```
site ...  occ Mg ...
site ...  occ Mg+2 ...
site ...  occ 24Mg ...
site ...  occ 26Mg ...
site ...  occ 26Mg+2 ...
```

In the cases of 'Mg' and 'Mg+2' the atomic weight used is the 'Standard Weight' as defined in ISOTOPES.TXT. In the cases of '26Mg' and '26Mg+2' the atomic weight used is the isotope weight as defined in ISOTOPES.TXT. Note the '+2' is dropped when searching that file. The atomic weight for 24Mg is not the same as that for Mg. When 24Mg is used then the isotope weight for 24Mg is used. When Mg is defined then the standard weight is used. The standard weight corresponds to the mean weight of the naturally occurring Mg isotopes.

In the case of x-rays:

- atomic scattering factors used (from file ATMSCAT.CPP) for 26Mg and 26Mg+2 corresponds to those of Mg or Mg+2 respectively. Numbers occurring at the start of the symbol are dropped when searching ATMSCAT.CPP.
- f' and f'' corrections (files in SSF directory) correspond to that for Mg. In other words, the numbers occurring at the start of the symbol as well as the charge (i.e. '+2' in this case) are dropped.

In the case of neutrons:

- scattering lengths used are from the NEUTSCAT.CPP file; the charge '+2' is dropped when searching NEUTSCAT.CPP.

Internally the program converts 'D' and 'T' to '2H' and '3H' respectively.

20.21 . Atomic data files and associated sources

Table 20-2. Files read when atomic data is sought. The references refer to the source of the data. In many cases the format of the data file corresponds to the original source format.
ANOMDISP.CPP : f' and f'' for Laboratory X-ray tubes. File is read if there are no associated SSF*.NFF file or if use_tube_dispersion_coefficients is defined.
ATMSCAT.CPP : f0 or Elastic Photon-Atom Scattering, relativistic form factors; data from http://www.esrf.fr/computing/expg/subgroups/theory/DABAX/dabax.html
ATOM_COLORS.DEF : Red, Green, Blue (RGB) CPK atom colors from http://www.bio.cmu.edu/Courses/BiochemMols/Periodic/ElemList.htm. Used for assigning colors to atoms when displaying in OpenGL.
ATOM_RADIUS.DEF : Atomic radii and Covalent radii from http://www.esrf.fr/cgi-bin/periodic.
ISOTOPES.TXT : Atomic Weights and Isotopic Compositions for All Elements from http://physics.nist.gov/PhysRefData/Compositions/
MAGDATA.DAT : Data from GSAS data file via the International tables. Data correction for V entry made by Robert Von Dreele.
NEUTSCAT.CPP : Neutron scattering lengths from http://www.ccp14.ac.uk/ccp/web-mirrors/neutrons/n-scatter/n-lengths/LIST~1.HTM
NO_POLYHEDRA.DEF : Disables drawing of polyhedral for atoms listed.
SSF*.NFF : Anomalous scattering factors f' and f'' for a range of wavelengths from http://www-cxro.lbl.gov/optical_constants/asf.html The present data is in three columns "E(eV),f1,f2" where f'=f1–Z and f''= f2 and the conversion from wavelength to energy scale is: E(eV)=10^5/(8.065541*Lambda(Ang)).

MAC\ZNN.HTML : X-Ray Mass Attenuation Coefficients from http://www.nist.gov/pml/data/xraycoef/index.cfm

20.22 . Removing Phases during refinement

[remove_phase !E]	Examples TEST_EXAMPLES\REMOVE-PHASE.INP

Allows for phase removal during refinement through use of the Remove_Phase macro. Typical usage is:

```
for strs {
   Remove_Phase(0.3, 0.5)
}
```

Here a phase is removed if its weight percent is below 0.3% and if the error in the weight percent is greater than 0.5 times the weight percent. The phase removal process is executed at the end of a *Cycle*. The following text is displayed on removal of a phase:

```
*** Deleting phase: Corundum ***
*** Deleting phase: Zincite ***
    etc...
```

Refinement is terminated when no phases are removed during a *Cycle*.

20.23 . Numerical Lorentzian and Gaussian Convolutions

For fundamental and pseudo-Voigt peak types, Lorentzian and Gaussian convolutions are performed analytically during the calculation of the emission profile Voigt. Therefore, lor_fwhm and gauss_fwhm are still calculated at the emission profile level even when defined between push_peak and add_pop_1st_2nd_peak keywords.

20.24 . Space groups, hkls and symmetry operators

[space_group $symbol]

Used to define the space group where $symbol can be any symbol (case insensitive) occurring in the file SGCOM5.CPP, it can also be a space group number; here are some examples:

```
space_group "I a -3"
space_group ia-3
space_group P_63_M_C
space_group I_41/A_M_D
space_group I_41/A_M_D:2 ' defines second setting of I_41/A_M_D
space_group 206
space_group 222:2        ' defines second setting of 222
```

Symmetry operators are generated by SGCOM6.EXE and placed into a SG*.SG file with a name similar-to the name of the space group. Space group details for space groups with names

containing the characters '/' or ':' are placed in files with file names similar-to the space group but with the characters replaced by 'o' and 'q' respectively. The reason for this is that file names containing these characters are not allowed on some operating systems. hkl generation uses information in *.sg files.

20.24.1..... User defined rotational matrices

Space group generator - User defined rotational matrices can be added to the file SGROTS3.CPP found in the main TA directory.

20.25 . Defining hkls using use_hklm

hkls are automatically generated for str phases. This behaviour can be changed using the use_hklm keyword such that hkls become User-defined; for example:

```
    str…
       load use_hklm {
         2   2   0  12
         2   2   2   8
         …
       }
```

20.26 . Cross correlation function

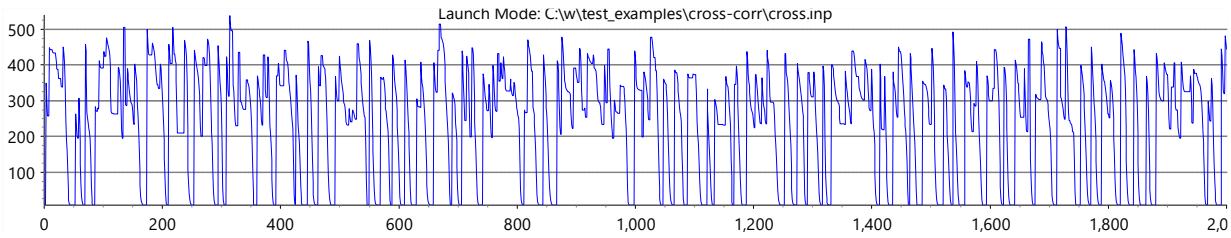
[cross_corr $name #value cross_corr_s !E	**Examples** CROSS-CORR\CROSS.INP

cross_corr calculates the cross-correlation function for a triangle of x-axis width cross_corr_s. cross_corr_s can be an equation that can be a function of *Cycle_Iter* which allows for changing the width of the triangle in situ. $name is a name that can be given to the function and #value is the value of the cross-correlation function. $name can be used in the chi2 keyword for obtaining lattice parameters. However, as can be seen in the example CROSS.INP, using normal refinement with a triangle convolution is much faster than using the cross-correlation function. CROSS.INP is an informative example and it looks like:

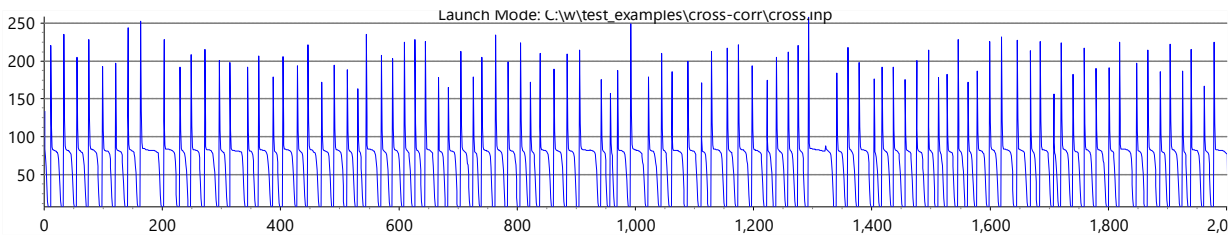
```
#prm USE_CROSS_CORRELATION = 1; ' Set to zero to see normal refinement
#prm INCLUDE_HATS = 1;          ' This is for normal refinement
macro DEL_ { Rand(-1, 1) 0.5 }  ' Change in lattice parameters at the start of a Cycle
macro AA { }

continue_after_convergence
verbose 1
iters 2000

RAW(..\pbso4)
   rebin_with_dx_of 0.01
   CuKa5(0.0001)
   LP_Factor(17)
   Radius(173)
   Full_Axial_Model(10, 10, 10, !sol  3.77616`, !sol  3.77616`)
   Divergence(1)
   Slit_Width(0.2)
```

```
bkg AA -792.524948 767.974856 -305.050785 121.658117 -45.020282 18.2136589
One_on_X(AA, 22265.9137`)

ZE(AA,-0.0110740988)

finish_X 60
extra_X_right 10

#if (USE_CROSS_CORRELATION)
   cross_corr corr 0
      cross_corr_s 3
   chi2 = -Ln(corr); : 0
   macro SCALE_ {  }
#else
   ' Normal refinement
   #if (INCLUDE_HATS)
      hat @ 1 val_on_continue 2 max 2 num_hats 2
   #endif
   macro SCALE_ { @ }
#endif

STR(P_b_n_m) ' PbSO4
   space_group P_b_n_m
   macro LP_(v) { v val_on_continue = v + DEL_; min = v - 3; max = v + 3;
   a  @  LP_(6.962377)
   b  @  LP_(8.483133)
   c  @  LP_(5.400478)
   site Pb x AA 0.16717 y  AA 0.18778 z 0.25       occ Pb+2 1 beq AA 1.47495
   site S  x AA 0.18429 y  AA 0.43563 z 0.75       occ S    1 beq AA 0.85254
   site O1 x AA 0.09441 y  AA 0.59667 z 0.75       occ O-2  1 beq AA 1.05681
   site O2 x AA 0.03611 y  AA 0.31151 z 0.75       occ O-2  1 beq AA 1.63474
   site O3 x AA 0.31549 y  AA 0.42069 z AA 0.97553 occ O-2  1 beq AA 1.49181

   CS_L(AA, 274.77)
   Strain_L(AA, 0.035898)
   scale SCALE_  0.000335087199
```

Running cross.inp with USE_CROSS_CORRELATION set to 1 gives an Rwp plot of:



Running cross.inp with USE_CROSS_CORRELATION set to 0 (normal refinement) gives an Rwp plot of:



20.27 . Site identifying strings

Keywords such as operate_on_points use a site identifying string which can contain the wild card character * and the negation character !. The wild card character * used in O* means that sites with names starting with O are considered. In addition to using the wild card character, site names can be written explicitly within double quotation marks. Table 20-3 shows some operate_on_points strings and the corresponding sites identified.

Table 20-3. operate_on_points strings and corresponding sites identified.

```
str
   site Pb1 ...
   site S1 ...
   site O1 ...
   site O2 ...
   site O31 ...
   site O32 ...
   site O4 ...
```

$sites	Sites identified
*	Pb1, S1, O1, O2, O31, O32, O4
Pb*	Pb1
“Pb1 S*”	Pb1, S1
O*	O1, O2, O31, O32, O4
“O* !O3*”	O1, O2, O4
“O* !O1 !O2”	O31, O32, O4

20.28 . Occupancies and symmetry operators

Only unique positions are generated from symmetry operators. Fully occupied sites therefore require site occupancy values of 1. A comparison of atomic positions is performed in the generation of the unique positions with a tolerance in fractional coordinates of 10^{-15}. It is therefore necessary to enter fractions in the form of equations when entering fractional atomic coordinates that have recurring values such as 0.33333..., 0.66666... etc., for example:

use:
```
x = 1/3;  y = 1/3;  z = 2/3;
```
instead of:
```
x 0.33333 y 0.33333 z 0.66666
```

20.29 . Pawley and Le Bail extraction

[lebail #]

Use the following input segment for Le Bail intensity extraction (see example LEBAIL1.INP):

```
hkl_Is    space_group p-1    lebail 1 ...
```

Use the following input segment for Pawley intensity extraction (see example PAWLEY1.INP):

```
hkl_Is    space_group p-1 ...
```

hkls are generated in the absence of hkl_m_d_th2 keywords. After refinement, details for the generated hkl’s are appended after the space_group keyword. For the Pawley method, once the hkl details are generated, parameter equations can be applied in the usual manner to the I parameters.

20.30 . Anisotropic refinement models

Keywords that can be a function of *H*, *K*, *L* and *M*, as shown in Table 2-3, allow for the refinement of anisotropic models including preferred orientation, and peak broadening. An important consideration when dealing with hkls in equations is whether to work with hkls or whether to work with their multiplicities. The Multiplicities_Sum macro can be used when working with multiplicities, for example:

```
prm a 0 th2_offset = Multiplicities_Sum(If(Mod(L, 2) == 0, a Tan(Th), 0));
```

L here corresponds to the *L*'s of the multiplicities. A completely different viewpoint than to refine on half widths is to consider the distribution of lattice metric parameters within a sample. Each crystallite is regarded as having its own lattice parameters, with a multi-dimensional distribution throughout the powder sample. This can be achieved by adding the same structure several times to the input file.

20.30.1..... Spherical harmonics

spherical_harmonics_hkl can be applied to both peak shapes, for anisotropy, and intensities for a preferred orientation correction. Preferred orientation can be described using the PO_Spherical_Harmonics(sh, order) macro, where "sh" is the parameter name and "order" the order of the spherical harmonics. scale_pks is used to correct peak intensities as follows:

```
macro PO_Spherical_Harmonics(sh, order) {
   spherical_harmonics_hkl sh
      sh_order order
      scale_pks = sh;
}
```

Example clay.inp uses spherical_harmonics_hkl for describing anisotropic peak broadening using the exp_conv_const convolution as follows:

```
str ...
   spherical_harmonics_hkl sh
      sh_order 8
   exp_conv_const = (sh-1) Tan(Th);
```

20.30.2..... Miscellaneous models using User defined equations

Anisotropic Gaussian broadening as a function of *L* (see example CEO2HKL.INP):

```
str ...
   prm a 0.1 min 0.0001 max 5
   prm b 0.1 min 0.0001 max 5
   gauss_fwhm = If(L==0, a Tan(Th) + 0.2, b Tan(Th));
```

Anisotropic peak shifts as a function of *L* (th2_offset):

```
str ...
   prm at 0.07 min 0.0001 max 1
   prm bt 0.07 min 0.0001 max 1
   th2_offset = If(L == 0, at Tan(Th), bt Tan(Th));
```

Description of anisotropic peak broadening using the March (1932) relation and str_hkl_angle:

```
str ...
   str_hkl_angle ang1 1 0 0
   prm p1 1    min 0.0001 max 2
   prm p2 0.01 min 0.0001 max 0.1
   lor_fwhm = p2 Tan(Th) Multiplicities_Sum(((p1^2 Cos(ang1)^2 +
              Sin(ang1)^2 / p1)^(-1.5)));
```

20.31 . Simulated annealing and structure determination

Defining continue_after_convergence and a temperature regime is analogous to defining a simulated annealing process (Coelho, 2000). After convergence, a new refinement cycle is initiated with parameter values changed according to any defined val_on_continue attributes and rand_xyz or randomize_on_errors processes. Simulated annealing is therefore not specific to structure solution, see for example ONLYPENA.INP and ROSENBROCK-10.INP. Convergence is determined when the change in χ^2 is less than chi2_convergence_criteria for three consecutive cycles and when all defined stop_when parameter attributes evaluate to true. Example:

```
chi2_convergence_criteria = If(Cycle_Iter < 10, 0.001, 0.01);
```

For structure solution in real space, the need for computation efficiency is critical. In many cases computation speed can be increased by up to a factor of 20 or more with the appropriate choice of keywords. Keywords that facilitate speed are:

```
chi2_convergence_criteria...
quick_refine...
yobs_to_xo_posn_yobs...
```

Another category is one that facilitate structure solution by changing the form of χ^2:

```
penalties_weighting_K1...
penalty...
occ_merge...
rigid...
```

Further keywords and processes typically used are:

```
file_name_for_best_solutions
seed
temperature !E ...
   move_to_the_next_temperature_regardless_of_the_change_in_rwp
   save_values_as_best_after_randomization
   use_best_values
xdd ... or xdd_scr ...
   str ...
```

```
site ... rand_xyz ...
```

20.31.1..... Penalties used in structure determination

Introducing suitable penalties can reduce the number of local minima in χ^2 and correspondingly increase the chances of obtaining a global minimum. The structure factor for a reflection with Miller indices 10 0 0 for a two-atom triclinic unit cell with fractional atomic coordinates of (0,0,0) and (x, 0,0) is given by 4 $\cos(\pi hx)^2$; here there are 10 local minima for 0<x<1. If it was known that the bond length distance is half the distance of the *a* lattice parameter then a suitable penalty would reduce the number of minima to one. In this trivial example the number of minima increases as the Miller indices increase. For non-trivial structures and for the important d spacing range near inter-atomic distances of 1 to 2Å the number of local minima is very large. Bragg reflections with large Miller indices that are heavily weighted are expected to contain many false minima; by applying an appropriate weighting scheme to the diffraction data the search for the global minimum can be facilitated. For powder data the default weighting scheme is:

```
weighting = If(Yobs <= 1, 1, 1 / Yobs);
```

For single crystal data the following, which is proportional to 1/d, works well:

```
weighting = 1 / (Sin(X Deg / 2) Max(Yobs,1));
```

A more elaborate scheme which also works well for single crystal data is:

```
weighting = ( Abs(Yobs-Ycalc) / Abs(Yobs+Ycalc) + 1) / Sin(X Deg / 2);
```

Two penalty functions that have shown to facilitate the determination of structures are the anti-bumping (AB) penalty and the potential energy penalty U. The anti-bumping penalty is written as:

$$AB_i = \begin{cases} \sum (r_{ij} - r_o)^2, & \text{for } r_{ij} < r_o \quad \text{and } i \neq j \\ 0, & \text{for } r_{ij} > r_o \end{cases} \qquad \text{(20-14)}$$

where r_0 is a bond length distance, r_{ij} the distance between atoms *i* and *j* including symmetry equivalent positions and the summation is over all atoms of type *j*. The ai_anti_bump and box_interaction keywords are used to implement the penalty of Eq. (20-15) using the AI_Anti_Bump and Anti_Bump macros respectively. Typically, Anti bump constraints are applied to heavy atoms; an overuse of such constraints can in fact hinder simulated annealing in finding the global minimum. Applying the constraint for the first few iterations of a refinement cycle can also be beneficial; this is achieved in the AI_Anti_Bump macro by writing the penalty in terms of the reserved parameter *Cycle_Iter*; see for example CIME-DECOMPOSE.INP.

The grs_interaction can be used to calculate the Lennard-Jones or Born-Mayer potentials and it is suited to ionic atomic models (see example ALVO4-GRS-AUTO.INP). For a site i they comprise a Coulomb term C_i and a repulsive term *Ri* and is written as:

$$U_i = C_i + R_i \qquad \text{(20-15)}$$

$$\text{where} \quad C_i = A\sum_{i,j}\frac{Q_iQ_j}{r_{i,j}}, \qquad i \neq j$$

$$R_i = \sum_{i,j}\frac{B_{i,j}}{r_{i,j}^n}, \qquad \text{for Leonard Jones and } i \neq j$$

$$R_i = \sum_{i,j} c_{i,j}\, exp\left(-d\, r_{i,j}\right), \qquad \text{for Born} - \text{Mayer and } i \neq j$$

where A = $e^2/(4\pi\varepsilon_0)$ and $\varepsilon 0$ is the permittivity of free space, Q_i and Q_j are the ionic valences of atoms *i* and *j*, $r_{i,j}$ is the distance between atoms *i* and *j* and the summation is over all atoms to infinity. The repulsive constants $B_{i,j}$, *n*, $c_{i,j}$ and *d* is characteristic of the atomic species and their potential surrounds. The equation part of the grs_interaction is typically used to describe the repulsive terms.

20.31.2..... Bond length restraints

Example ALVO4-GRS-AUTO.INP defines a bond length restraint using the GRS series between an Aluminum site and three Oxygen sites. Valence charges have been set to +3 and –2 for Aluminum and Oxygen, respectively. The expected bond length is 2 Å between for O-O bonds and 1.5 Å for Al-O bonds:

```
site Al  x @ 0.7491  y @ 0.6981  z @ 0.4069  occ Al+3 1  beq 0.25
site O1  x @ 0.6350  y @ 0.4873  z @ 0.2544  occ  O-2 1  beq 1
site O2  x @ 0.2574  y @ 0.4325  z @ 0.4313  occ  O-2 1  beq 1
site O3  x @ 0.0450  y @ 0.6935  z @ 0.4271  occ  O-2 1  beq 1
Grs_Interaction(O*, O*, -2, -2, oo,  2.0, 5)  penalty = oo;
Grs_Interaction(Al, O*,  4, -2, alo, 1.5, 5)  penalty = alo;
```

The following example defines a bond length restraint using the AI_Anti_Bump macro between a Potassium site and three Carbon sites. The expected bond length is 4 Å between Potassium sites and 1.3 Å between Carbon sites.

```
site K   x @ 0.14305  y @ 0.21812  z @ 0.12167  occ K 1  beq 1
site C1  x @ 0.19191  y @ 0.40979  z @ 0.34583  occ C 1  beq 1
site C2  x @ 0.31926  y @ 0.35428  z @ 0.32606  occ C 1  beq 1
site C3  x @ 0.10935  y @ 0.30991  z @ 0.39733  occ C 1  beq 1
AI_Anti_Bump(K , K , 4  , 1)
AI_Anti_Bump(C*, C*, 1.3, 1)
```

Unlike the first example, there's no explicit definition of a penalty function as the AI_Anti_Bump macro includes the penalty function.

20.32 . Not saving extrapolated peaks when doing intensity derivatives

str... [dont_save_extrapolated_pks]	

The process of adding peaks to a calculated profile from the peaks buffer can be computationally intensive. This process occurs many times during a refinement iteration when, for example, calculating the derivatives of a site fractional atomic coordinate. An in-between step is therefore performed where interpolated peak data is stored. The memory requirements for the interpolated data can be large and in cases where memory is an issue then the keyword dont_save_extrapolated_pks can be used.

20.33 . Applying lp_search to TOF data

lp_search cannot be directly applied to TOF data. However, it is relatively easy to convert the TOF data to 2Th data where lp_search can be used. The examples TEST_EXAMPLES\TOF\TOF-TO-Q.INP is an example that converts the data to 2Th and then applies lp_search. The conversion is as follows:

I(Q) = Intensity(TOF) dTOF/dQ

Q = 2 Pi / d

d = 2 Pi / Q

TOF = t0 + t1 d + t2 d^2 = t0 + t1 2 Pi / Q + t2 (2 Pi)^2 / Q^2

dTOF/dd = t1 + 2 t2 d;

dd/dQ = -2 Pi / Q^2;

dTOF/dQ = dTOF/dd dd/dQ

If t0 = t2 = 0 we get:

dTOF/dQ = -t1 2 Pi / Q^2 = -t1 D_spacing^2 / (2 Pi)

Or in INP format we have:

```
xdd TOF-DATA.XY
   x_calculation_step = Yobs_dx_at(Xo) .5;prm !t0 0
   prm !t1 6171.89377
   prm !t2 0
   prm !d = X / t1;
   prm !Q = 2 Pi / d;
   prm !dtof_dd = t1 + 2 t2 d;
   prm !dd_dQ = -2 Pi / Q^2;
   prm !dtof_dQ = dtof_dd dd_dQ;
   xdd_out TOF-to_Q.xy load out_record out_fmt out_eqn
      {
          " %11.6f  " = 2 Pi / d;
          " %11.6f\n" = Yobs Abs(dtof_dQ);
      }
```

20.34 . Correction for dispersion using modify_peak_eqn

Example: TEST_EXAMPLES\DISPERSION\DISP.INP

The shape of the emission profile changes with 2θ due to dispersion such that:

I(lam) dlam = I(th) dth

or,

I(th) = I(lam) dlam_dth

Differentiating Bragg's with respect to θ we have:

dlam_dth = 2 d Cos(th)

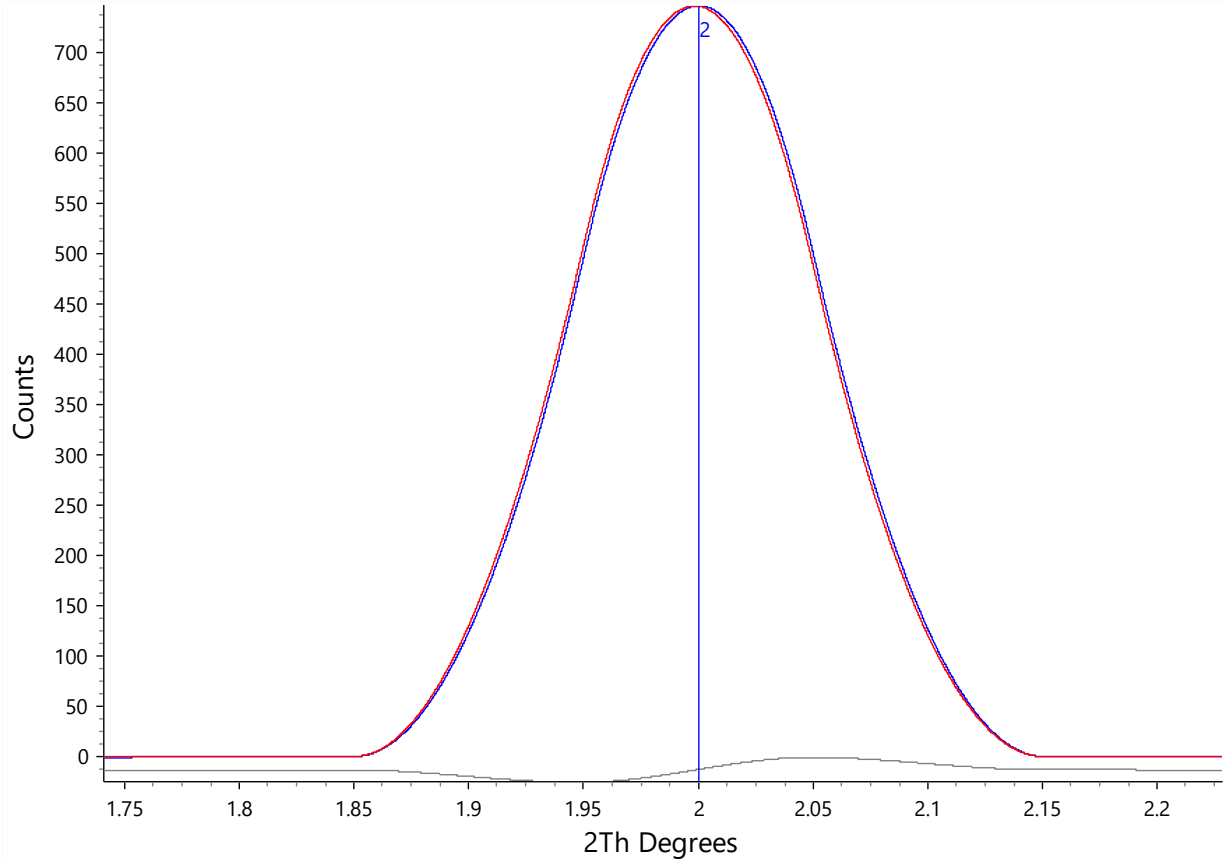
or,

I(th) = I(lam) 2 d Cos(th)

Rearranging we get:

I(th) = lam I(lam) Cot(th)

The point by point intensity of the emission profile therefore changes as function of Cot(th). DISP.INP show difference between correcting for and not correcting for dispersion as follows:



The peak shape of the above is as follows:

```
hat 0.1 num_hats 3 ' specimen/instrument
lam ymin_on_ymax 0.0000001 la 1 lo !lam_0 1.540596 lh 0.5
    modify_peak_eqn =
        Get(current_peak)
```

```
        If (And(Get(current_peak_x)>(lam_0-1.5),Get(current_peak_x)<(lam_0+ 1.5)),
            1 / Tan(ArcSin(Get(current_peak_x) / (2 D_spacing))),
            0
        );
    modify_peak_apply_before_convolutions
```

20.35 . File types and formats

Table 20-4. File types.	
*.PRO	Project files.
*.INP	Input file in INP format.
*.OUT	Output file created on termination of refinement in INP format.
*.STR	Structure data. Same format as *.INP.
*.LAM	Source emission profile data. Same format as *.INP.
*.DEF	Program defaults. Same format as *.INP.
*.LOG	TOPAS.LOG and TC.LOG. Useful for tracking input errors.
Measurement Data	

*.SST	Implies an equal x-axis and has the format of "*start, step, data points....*" SST files can be used instead of *.XY files. As x-axis values are not used, they save space on creation as well as on loading. For equal x-axis data then the macro Out_XDD_SST can be used in the following manner:
	`xdd …`
	`  Out_XDD_SST(filename.sst) = Ycalc;  ' outut Ycalc`
	`  Out_XDD_SST(filename.sst) = Yobs - Ycalc; ' output difference plot`

*.RAW	Bruker AXS binaries (DIFFRAC AT and DIFFRAC^{plus})
*.DAT, *.XDD, *.CAL, *.XY, *XYE	ASCII file formats, see Table 20-5
*.SCR	ASCII file format comprising lines of h, k, l, m, d, 2θ, and Fo.
*.HKL	ShelX HKL4 format.
Structure and structure factor data	
*.CIF	Crystallographic Information File; International Union for Crystallography.
*.FCF	CIF file representation of structure factor details suitable for generating Fourier maps using ShelX.

Table 20-5. ASCII input data file formats. *.XY, *.XYE, *.XDD and *.CAL are white space delimited and can contain line and block comments.		
*.DAT, LHPM/RIET7/CSRIET		
	Line 1-4	Comments
	Line 5	Start, Step and Finish angle
	Line 6 ...	Observed XRD data points

GSAS ("std - const", "alt - ralf"), use gsas_format		
	Line 1	Legend
	Line 2	Item 3: Number of data points
	Line 3 ...	Depending on item10 and item5
	For item10 = "STD" and item5 = "CONST" xmin = item6/div step =item7/div read(10(i2,F6.0) iww(i),y(i) i=1, npts sigma(i)=sqr(y(i)/iww(i)) i=1, npts For item10 = "ALT" and item5 = "RALF" xmin = item6/32 step = item7/32 read(4(F8.0,F7.4,F5.4) x(i), y(i), sigma(i) i=1, npts x(i) = x(i)/32 i=1, npts do i = 1, npts-1 div = x(i+1)-x(i) y(i) =1000 * y(i)/div sigma(i) = 1000 * sigma(i)/div end do rk (constant wavelength data): div = 100 rk (time of flight data): div = 1	
FullProf (INSTRM = 0: free format file), use fullprof_format		
	Line 1	Start angle, step width, finish angle, comments
	Line 2 ...	Observed XRD data points (any number of rows)
*.XDD, *.CAL	Line 1	Optional line for comments
	Line 2 ...	Start, Step and Finish angle
		Next three numbers are unused
		Observed XRD data points
*.XY		2θ and intensity data values
*.XYE		2θ, intensity and intensity error values.

20.36 . Batch mode operation – TC.EXE

The command line program tc.exe provides for batch mode operation. Running tc.exe without arguments displays help information. Running an INP file called PBSO4.INP is as follows:

```
tc pbso4
```

Macros can be passed to the command line. Passing a file name to an INP file is as follows:

1) Create a TEMPLATE.INP file with the required refinement details, this could look like the following:

```
        xdd FILE
            etc...
```

2) TEMPLATE.INP is fed to TC.EXE at the command line; the word FILE (within TEMPLATE.INP) is expanded to whatever the macro on the command line contains; for example:

```
tc ...\file_directory\template.inp "macro FILE { file.xy }"
```

The macro called FILE is described on the command line within quotation marks. On running tc.exe the word 'FILE' occurring in TEMPATE.INP is expanded to 'file.xy'. More than one macro can be described on the command line. To process a whole directory of data files, say *.XY file for example, then:

1) Execute the following DOS command from the file directory:

```
dir *.xy > ...\main_ta_directory\xy.bat
```

The XY.BAT file will then reside in the main TA directory.

2) Edit ...\MAIN_TA_DIRECTORY\XY.BAT to look like the following:

```
tc ...\file_directory\template "macro FILE { file1.xy }"
copy ...\file_directory\template.out ...\file_directory\file1.out
tc ...\file_directory\template.inp "macro FILE { file2.xy }"
copy ...\file_directory\template.out ...\file_directory\file2.out
etc...
```

After each run of TC.EXE a TEMPLATE.OUT file is created containing refined results. This file is copied to files FILE1.OUT, FILE2.OUT etc.... After running XY.BAT a number of *.OUT files is created one for each *.XY file. In summary tc.exe receives TEMPLATE.INP to process. Words occurring in TEMPLATE.INP are expanded depending on the macros described on the command line.

21. KEYWORDS

21.1 ... Data structures

The following describes keyword dependencies. Trailing '...' implies that more than one node of that type can be inserted under its parent. Items enclosed in square brackets are optional. Items beginning with a capital T corresponds to keyword groups analogous to complex types in XML.

Ttop
- Tcomm_1
- Tcomm_2
- Ttop_xdd
- Tglobal
- Txdd
- Txdd_scr
- Tindexing
- Tcharge_flipping

Ttop_xdd
- [convolution_step #1]
- [Rp !E] [Rs !E]
- [x_calculation_step !E]

Tglobal
- TMinimization
- Trwp
- [A_matrix] [C_matrix] [A_matrix_normalized] [C_matrix_normalized]
- [conserve_memory]
- [file_name_for_best_solutions $file]
- [force_positive_fwhm]
- [inp_text $name] ...[inp_text_insert $name { ... }]...
- [iters #]
- [no_LIMIT_warnings]
- [num_cycles #]
- [out_A_matrix $file]
- [out_refinement_stats]
- [out_rwp $file]
- [out_prm_vals_per_iteration $file]... | [out_prm_vals_on_convergence $file]...
- [out_prm_vals_on_end $file]...
- [process_times]
- [randomise_file_out_normal $file]
- [seed [#]]
- [suspend_writing_to_log_file #1]
- [temperature !E]...
- [use_tube_dispersion_coefficients]
- [verbose #1]

Txdd
[xdd $file [{$data}] [range #] [xye_format] [gsas_format] [fullprof_format]]...
Ttop_xdd
Txdd_comm_1
Tcomm_1
Tcomm_2
Tmin_max_rc
Trwp
[gui_add_bkg !E]
[xdd_sum !E] and [xdd_array !E]
[xo_ls]...
[xo E I E]...
Tcomm_1_2_phase_1_2
[d_ls]...
[d E I E]...
Tcomm_1_2_phase_1_2
[lebail #]
[hkl_ls]...
[lp_search !E]
[l_parameter_names_have_hkl $start_of_parameter_name]
[hkl_m_d_th2 # # # # # # # E I E]...
Tspace_group
Tcomm_1_2_phase_1_2
Thkl_lat
[lebail #]
[str | dummy_str]...
Tstr_details
Thkl_lat
Tcomm_1_2_phase_1_2
Tmin_max_rs
[rigid]...
Tspace_group

Tcomm_1_2_phase_1_2
Tcomm_1
Tcomm_2
Tphase_1
Tphase_2

Txdd_scr
[xdd_scr $file] ...
Txdd_comm_1
Tcomm_2
Ttop_xdd
Tmin_max_r
[str]...
Tstr_details

Tphase_1
Tcomm_2
Thkl_lat
Tmin_max_r
[rigid]...
Tspace_group
Tscr_1

Tscr_1
[Flack E]
[i_on_error_ratio_tolerance #]
[num_highest_I_values_to_keep #]

Txdd_comm_1
[bkg [@] # # #...]
[*degree_of_crystallinity* #]
[d_spacing_to_energy_in_eV_for_f1_f11 !E]
[exclude #ex1 #ex2]...
[extra_X_left !E] [extra_X_right !E]
[fit_obj E [min_X !E] [max_X !E]]...
[neutron_data]
[rebin_with_dx_of !E]
[smooth #]
[start_X !E] [finish_X !E]
[weighting !E [recal_weighting_on_iter]]
[xdd_out $file [append]]...
Tout_record
[yobs_eqn !N E]
[yobs_to_xo_posn_yobs !E]

Tcomm_1
[axial_conv]...
[capillary_diameter_mm E]...
[lpsd_th2_angular_range_degrees E]...
[circles_conv E]...
[exp_conv_const E [exp_limit E]]...
[ft_conv E]...
[gauss_fwhm E]...
[h1 E h2 E m1 E m2 E]
[hat E [num_hats #1]]...
[modify_peak]
[more_accurate_Voigt]
[lor_fwhm E]...
[numerical_lor_gauss_conv]
[numerical_lor_ymin_on_ymax #0.0001]
[one_on_x_conv E]...
[pk_xo E]
[push_peak]...

[pv_lor E pv_fwhm E]
[spv_h1 E spv_h2 E spv_l1 E spv_l2 E]
[stacked_hats_conv [whole_hat E [hat_height E]]...[half_hat E [hat_height E]]...]...
[th2_offset E]...
[user_defined_convolution E min E max E]...
[WPPM_ft_conv E]...

Tcomm_2
[f0_f1_f11_atom]...
[lam [ymin_on_ymax #] [no_th_dependence] [Lam !E] [calculate_Lam]]
[scale_pks E]...
[scale_phase_X E]
[prm|local E [min !E][max !E][del !E][update !E][stop_when !E][val_on_continue !E]]...
[existing_prm E]...
[penalty !E]...
[out $file [append]]...
Tout_record

Tphase_1
[atom_out $file [append]]...
Tout_record
[auto_scale !E]
[del_approx !E]
[phase_name $phase_name]
[phase_out $file [append]]...
[phase_out_X $file [append]] ...
[brindley_spherical_r_cm !E]
[r_bragg #]
[remove_phase !E]
[scale E]

Tphase_2
[peak_buffer_step E [report_on]]
[peak_type $type]
[numerical_area E]

Tstr_details
[append_cartesian] [append_fractional [in_str_format]]
[append_bond_lengths [consider_lattice_parameters]]
[atomic_interaction N E] | [ai_anti_bump N]...
[box_interaction [from_N #] [to_N #] [no_self_interaction] $site_1 $site_2 N E]...
[fourier_map !E]
[grs_interaction [from_N #][to_N #][no_self_interaction] $site_1 $site_2 qi # qj # N E]...
[hkl_plane $hkl]...
[no_f11]
[normalize_FCs]
[occ_merge $sites [occ_merge_radius !E]]...
[p1_fractional_to_file $file] [in_str_format]...

[site $site]...
[adps] [u11 E] [u22 E] [u33 E] [u12 E] [u13 E] [u23 E]
Tmin_r_max_r
[sites_distance N] | [sites_angle N] | [sites_flatten N [sites_flatten_tol !E]]...
[sites_geometry N]...
[siv_s1_s2 # #]
[report_on_str]
[view_structure]

Thkl_lat
[a E] [b E] [c E] [al E] [be E] [ga E]
[normals_plot !E]...
[phase_penalties $sites N [hkl_Re_Im #h #k #l #Re #Im]...]...
[spherical_harmonics_hkl $name]...
[str_hkl_angle N h k l]...
[omit_hkls !E]

Tout_record
[out_record]...

Tmin_r_max_r
[min_r #] [max_r #]

Tspace_group
[space_group $symbol]

Miscellanous
[aberration_range_change_allowed !E]
[default_l_attributes !E]
load, move_to, for

21.2 ... Alphabetical listing of keywords

[a E] [b E] [c E] [al E] [be E] [ga E]

Lattice parameters in Å and lattice angles in degrees.

[adps] [u11 E] [u22 E] [u33 E] [u12 E] [u13 E] [u23 E]

adps generates the *unn* atomic displacement parameters with considerations made for special positions (see TEST_EXAMPLES\SINGLE-CRYSTAL\AE14-ADPS.INP). On termination of refinement the adps keyword is replaced with the *unn* parameters; see example AE1-ADPS.INP. Instead of using the adps keyword the *unn* parameters can be manually entered. The *unn* matrix can be kept positive definite with the site dependent macro of ADPs_Keep_PD; this can stabilize refinement. The ADPs_Keep_PD macro can be used after the *unn* parameters are created. For determining adp constraints the 3x3 eigen value determination routine of Kopp (2006) has been used.

[amorphous_phase]

In the calculation of degree_of_crystallinity, phases with amorphous_phase are treated as amorphous in the calculation.

[A_matrix] [C_matrix] [A_matrix_normalized] [C_matrix_normalized]

Generates the un-normalized and normalized A and correlation matrices. If do_errors is defined then C_matrix_normalized is automatically generated and appenedd to the OUT file.

[append_cartesian] [append_fractional [in_str_format]]

Appends site fractional coordinates in Cartesian or fractional coordinates respectively to the *.OUT file at the end of a refinement. For the case of append_fractional, in_str_format produces output in INP format.

[append_bond_lengths [consider_lattice_parameters]]

Appends bond lengths the *.OUT file at the end of refinement. A number corresponding to equivalent positions is appended to site names. consider_lattice_parameters includes lattice parameter errors in the calculation of bond length and bond angle errors. An example of bond lengths output is as follows:

```
Y1:0    O1:0    2.23143
        O2:0    2.23143    88.083
        O3:0    2.28045    109.799    99.928
```

The first line gives the distance between the sites Y1 and O2. The first number in the second line gives the distance between sites Y1 and O2. The third number of 88.083 gives the angle between the vectors Y1 to O1 and Y1 to O2. The first number on the third line contains the distance between sites Y1 and O3. The second number in the third line contains the angle between the vectors Y1 to O3 and Y1 to O2. The third number in line three contains the angle between the vectors Y1 to O3 and Y1 to O1. Bond lengths, therefore, correspond to the first number in each line and bond angles start from the second number. The numbers after the site name and after the ':' character corresponds to the site equivalent position as found in the *.SG space group files found in the SG directory

[atomic_interaction N E] | [ai_anti_bump N]...
ai_sites_1 $sites_1 ai_sites_2 $sites_2
[ai_no_self_interation]
[ai_closest_N !E]
[ai_radius !E]
[ai_exclude_eq_0]
[ai_only_eq_0]

Defines an atomic interaction with the name N between sites identified by $site_1 and $site_2. For atomic_interaction, E is the site interaction equation that can be a function of *R* and *Ri*. *R* returns the distance in Å between two atoms; these distances are updated when dependent fractional atomic coordinates are modified. The name of the

atomic_interaction N can be used in equations including penalty equations. For ai_anti_bump, an internal c++ anti-bump interaction equation is used. For anti-bumping only, ai_anti_bump is faster than using atomic_interaction. The AI_Anti_Bump macro uses ai_anti_bump. no_self_interaction prevents interactions between equivalent positions of a site. This is useful when a general position is used to describe a special position.

ai_closest_N: interactions between $sites_1 and $sites_2 are sorted by distance and only the first ai_closest_N number of interactions are considered.

ai_radius: only the interactions between $sites_1 and $sites_2 that are within the distance ai_radius is considered.

When ai_radius and ai_closest_N are both defined then interactions from both sets of corresponding interaction are considered.

ai_exclude_eq_0: only interactions that is not the first equivalent positions in $sites_2 are considered. For example, in the following:

```
atomic_interaction ...
    ai_exclude_eq_0
    ai_sites_1 Pb
    ai_sites_2 "O1 O2"
```

the following interactions are considered:

```
Pb:0 and O1:n      (n ≠ 0)
Pb:0 and O2:n      (n ≠ 0)
```

where the number after the ':' character corresponds to the equivalent positions of the sites. ai_only_eq_0: only interactions between equivalent positions 0 are considered.

Functions

The atomic_interaction equation can be a function of the following functions:

AI_R(#ri): Returns the distance between the current site and the atom defined with *Ri*=#ri.

AI_R_CM: A function of no arguments that returns the geometric center of the current atom and the atoms defined in $sites_2.

AI_Flatten(#toll): A function that returns the sum of distances of the current atom and those defined in $sites_2 to an approximate plane of best fit. The plane of best fit is constructed such that the sum of the perpendicular distances to the current atom plus those defined in $sites_2 are at the minimum

AI_Cos_Angle(#ri1, #ri2): Returns the Cos of the angle between the atom define as *Ri*=#ri1, the current atom and the atom defined as *Ri*=#ri2.

AI_Angle(#ri1, #ri2) : Similar-to AI_Cos_Angle except that the value returned is the angle in degrees.

Examples BENZENE_AI1.INP, BENZENE_AI2.INP and BENZENE_AI3.INP demonstrates the use of the atomic_interation functions. atomic_interaction's are used to apply geometric restraints. For example, anti-bumping between molecules for the first ten iterations of a refinement cycle can be formulated as follows:

```
atomic_interaction ai1 = If(R < 3, (R-3)^2, 0);
    ai_exclude_eq_0
    ai_sites_1 C*
    ai_sites_2 C*
    ai_radius 3
penalty = If(Cycle_Iter < 10, ai1, 0);
```

[atom_out $file [append]]...

Used for writing site dependent details to file. See out for a description of out_record. The Out_CIF_STR macro uses atom_out

[axial_conv]...
filament_length E sample_length E receiving_slit_length E
[primary_soller_angle E]
[secondary_soller_angle E]
[axial_n_beta !E]

Full axial divergence model using the method of Cheary & Coelho (1998b). filament_length, sample_length and receiving_slit_length define the lengths of the tube-filament, sample and receiving slit in the axial plane in mm. primary_soller_angle and secondary_soller_angle define Soller slit angles in degrees. axial_n_beta defines the number of rays emanating from a point X-ray source in the axial plane. Larger values for axial_n_beta increases both accuracy and calculation time. The Full_Axial_Model macro simplifies the use of axial_conv.

[bkg [@] # # # ...]

Defines a Chebyshev polynomial where the number of coefficients is equal to the number of numeric values appearing after bkg.

[box_interaction [from_N #] [to_N #] [no_self_interaction] $site_1 $site_2 N E]...

Defines a site interaction with the name N between sites identified by $site_1 and $site_2. E represents the site interaction equation which can be a function of *R* and *Ri*. *R* returns the distance in Å between two atoms; these distances are updated when dependent fractional atomic coordinates are modified. The name of the box_interaction N can be used in equations including penalty equations. When either from_N or to_N are defined, the interactions between $site_1 and $site_2 are sorted by distance and only the interactions between the from_N and to_N are considered. no_self_interaction prevents any interactions between equivalent positions of the same site. This is useful when a general position is used to describe a special position. For example, the following could be used to iterate from the nearest atom to the third atom from a site called Si1:

```
str
```

```
site Si1 ...
site O1 ...
site O2 ...
site O3 ...
box_interaction Si1 O* to_N 2 !si1o = (R-2)^2;
penalty = !si1o;
```

In this example the nearest three oxygen atoms are soft constrained to a distance of 2 Å by use of the penalty function. Counting starts at zero and thus to_N is set to 2 to iterate up to the third nearest atom.

The wild card character '*' used in "O*" means that sites with names starting with 'O' are considered. In addition to using the wild card character, the site names can be explicitly written within double quotation marks, for example:

```
box_interaction Si1 "O1 O2 O3" to_N 3 etc...
```

Interactions between Si1 and the three oxygen atoms O1, O2, O3 may not all be included, for example, if Si1 has as its nearest neighbours the following:

Si1-O1,1 at a distance of 1.0 Å
Si1-O2,3 at a distance of 1.1 Å
Si1-O2,1 at a distance of 1.2 Å
Si1-O1,2 at a distance of 1.3 Å

then two equivalent positions of site O1 and two equivalent positions of O2 would be included in the interaction equation; thus, interactions between Si1-O3 are not considered. To ensure that each of the three oxygens has Si1 included in an interaction equation then the following could be used:

```
box_interaction "O1 O2 O3" Si1 to_N 0 etc...
```

Thus, the order of $site_1 and $site_2 is important when either from_N or to_N is defined. The reserved parameters *Ri* and *Break* can also be used in interaction equations when either from_N or to_N is defined. *Ri* returns the index of the current interaction being operated on with the first interaction starting at *Ri* = 0.

box_interaction is used for example by the Anti_Bump macro.

[brindley_spherical_r_cm !E]

Applies the Brindley correction for spherical particles. The macro Apply_Brindley_Spherical_R_PD is defined as:

```
macro Apply_Brindley_Spherical_R_PD(& R, & PD) {
    brindley_spherical_r_cm = R PD;
}
```

R is the radius of the particle in cm and PD is the packing density. Here's an example:

```
xdd ...
```

```
        str
            Apply_Brindley_Spherical_R_PD(R, PD)
            MVW(0,0,0)
        str
            Apply_Brindley_Spherical_R_PD(R, PD)
            MVW(0,0,0)
```

Use of phase_MAC or MVW is optional as they are created when needed. The Brindley correction can be applied to all phases including xo_Is. In the case of phases that do not have lattice parameters or sites, definitions of cell_volume, cell_mass and phase_MAC is required for the Brindley correction to work and for weight_percent(s) to be calculated. This allows for the incorporation of non-structural phases in quantitative analysis; for example, the following is valid as necessary information have been included:

```
    xo_Is
        Apply_Brindley_Spherical_R_PD(0.002, 0.6)
        MVW(654, 230, 0)
        phase_MAC 200
```

[capillary_diameter_mm E]...
capillary_u_cm_inv E
[capillary_convergent_beam] [capillary_divergent_beam] [capillary_parallel_beam]
[capillary_focal_length_mm E]
[capillary_xy_n #]

Examples for the capillary convolution (Coelho & Rowles, 2017) are LAB6-STOE.INP and LAB6-D8.INP as found in the directory TEST_EXAMPLES\CAPILLARY. If using a str phase then capillary_u_cm_inv can be set to the calculated linear absorption coefficient multiplied by a packing density, for example:

```
    prm packing_density 0.31208
    capillary_diameter_mm @ 0.57313
        capillary_u_cm_inv
            = Get(mixture_MAC) Get(mixture_density_g_on_cm3) packing_density;
        capillary_focal_length_mm @ 197.89657
        capillary_convergent_beam
```

If not defined, capillary_focal_length_mm defaults to the diffractometer radius Rs.

[circles_conv E]...

Defines ε_m in the convolution function:

$$(1 - |\varepsilon_m / \varepsilon|^{1/2}) \qquad \text{for } \varepsilon = 0 \text{ to } \varepsilon_m$$

that is convoluted into phase peaks. ε_m can be greater than or less than zero. circles_conv is used for example by the Simple_Axial_Model macro.

[cloud $sites]...
    [cloud_population !E]
    [cloud_save $file]
    [cloud_save_xyzs $file]
    [cloud_load_xyzs $file]
        [cloud_load_xyzs_omit_rwps !E]
    [cloud_formation_omit_rwps !E]
    [cloud_try_accept !E]
    [cloud_gauss_fwhm !E]
    [cloud_extract_and_save_xyzs $file]
        [cloud_number_to_extract !E]
        [cloud_atomic_separation !E]

cloud allows for the tracking of atoms defined in $sites in three dimensions. It can be useful for determining the average positions of heavy atoms or rigid bodies during refinement cycles. For example, a dummy atom, “site X1” say, can be placed at the center of a benzene ring and then tracked as follows:

```
continue_after_convergence
...
cloud “X1”
    cloud_population 100
    cloud_save SOME_FILE.CLD
```

On termination of refinement the CLD file is saved; it can be viewed using the rigid body editor of the GUI; see examples AE14-12.INP for a cloud example. cloud_population is the maximum number of population members. Each population member comprises the fractional coordinates of $sites and an associated Rwp value.

cloud_save_xyzs saves a cloud population to file.

cloud_load_xyzs loads and reuses previously saved populations. cloud_load_xyzs_omit_rwps can be used to exclude population membes whilst loading; it can be a function of Get(Cloud_Rwp) where Cloud_Rwp is the associated Rwp of a population member.

cloud_formation_omit_rwps can be used to limit population membes in the formation of CLD files; it can be a function of Get(Cloud_Rwp).

cloud_try_accept accepts population members if it evaluates to non-zero and if the best Rwp since the last acceptance is less than a present population member or if the number of members is less than cloud_population. If the number of population members equals cloud_population then the population member with the lowest Rwp is discarded. cloud_try_accept is evaluated at the end of each refinement cycle; it default value is true. Here’s are some examples:

```
cloud_try_accept = And(Cycle, Mod(Cycle, 50);
cloud_try_accept = T == 10;
```

cloud_gauss_fwhm is the full width at half maximum of a three-dimensional Gaussian that is used to fill the cloud.

cloud_extract_and_save_xyzs searches the three-dimensional cloud for high densities and extracts xyz positions; these are then saved to $file. cloud_number_to_extract defines the number of positions to extract and cloud_atomic_separation limits the atomic separation during the extraction. The actual number of positions extracted may be less than cloud_number_to_extract depending on the cloud.

[conserve_memory]

Deletes temporary arrays used in intermediate calculations as often as possible; memory savings of up to 70% can be expected on some problems with subsequent lengthening of execution times by up to 40%. When approximate_A is used on dense matrices then conserve_memory can reduce memory usage by up to 90%.

[convolution_step #1]

An integer defining the number of calculated data points per measured data point. Increasing convolution_step when the measurement step is large improves convolution accuracy. Only when the measurement step is greater than about 0.03 degrees 2Th or when high precision is required is it necessary to increase convolution_step.

[default_I_attributes E]

Changes the attributes of the I parameter, for example:

```
xo_Is...   default_I_attributes 0 min 0.001 val_on_continue 1
```

Useful when randomizing lattice parameters during Le Bail refinements with continue_after_convergence.

[degree_of_crystallinity #]
[crystalline_area #]
[amorphous_area #]

Reports on the degree of crystallinity which is calculated as follows:

100 * Get(crystalline_area) / (Get(crystalline_area) + Get(amorphous_area))

crystalline_area and amorphous_area corresponds to the sum of the numerical areas under the crystalline and amorphous phases respectively. Phases with amorphous_phase are treated as amorphous in the calculation.

[d_Is]...
[d E I E]...

Defines a phase type that uses d-spacing values for generating peak positions. d corresponds to the peak position in d-space in Å and I is the intensity parameter before applying any scale_pks equations.

[d_spacing_to_energy_in_eV_for_f1_f11 !E]

Used for refining on energy dispersive data (see example ED_SI_STR.INP). Can be a function of the reserved parameter *D_spacing*. f′ and f″ (see section 20.12) values used corresponds to energies given by d_spacing_to_energy_in_eV_for_f1_f11. For example:

```
' E(eV) = 10^5 / (8.065541 Lambda(A))
prm !detector_angle_in_radians = 7.77 Deg_on_2;
prm wavelength = 2 D_spacing Sin(detector_angle_in_radians);
prm energy_in_eV = 10^5 / (8.065541 wavelength);
pk_xo = 10^-3 energy_in_eV + zero;
d_spacing_to_energy_in_eV_for_f1_f11 = energy_in_eV;
```

[exclude #x1 #x2]...

Excludes an x-axis region between #x1 and #x2. The macro Exclude simplifies usage; see example CEO2.INP.

[exp_conv_const E [exp_limit E]]...

Defines ε_m in the aberration function:

$$A = \mathrm{Exp}(\mathrm{Ln}(0.001)\ \varepsilon / \varepsilon_m) \quad \text{for } \varepsilon = 0 \text{ to exp\_limit}$$

that is convoluted into phase peaks. Used by the Absorption and Absorption_With_Sample_Thickness_mm macros. The ε range of A is:

$$(0 < \varepsilon < \varepsilon_{limit}) \text{ for } \varepsilon_m < 0, \quad \text{or,} \quad (\varepsilon_{limit} < \varepsilon < 0) \text{ for } \varepsilon_m > 0$$

where $A(\varepsilon_{limit}) = 0.001$. Alternatively, ε_{limit} can be defined using exp_limit.

[extra_X_left !E] [extra_X_right !E]

Determines the extra x-axis range for hkl generation. For TOF data extra_X_left is typically used. For x-ray data then extra_X_right is typically used. Both defaults to 0.5.

[file_name_for_best_solutions $file]

Appends INP file details to $file during refinement with independent parameter values updated. The operation is performed when convergence results in the best Rwp.

[force_positive_fwhm]

Forces Lorentzian and/or Gaussian FWHM values to be positive. The following INP snippets are equivalent:

```
force_positive_fwhm
xdd ...
    str ...
        lor_fwhm = Rand(-1,1);
```

```
xdd ...
    str ...
        lor_fwhm = Abs(Rand(-1.1,));
```

[fit_obj E [min_X !E] [max_X !E]]...
[fo_transform_X !E]
[fit_obj_phase !E]

Defines a User defined function added to *Ycalc*, see example PVS.INP. fit_obj's can be a function of *X*. min_X and max_X define the x-axis range of the fit_obj; if min_X is omitted then the fit_obj is calculated from the start of the x-axis; similarly, if max_X is omitted then the fit_obj is calculated to the end of the x-axis. fo_transform_X is a dependent of fit_obj and it can be used to transform *X* used within the fit_obj.

[fourier_map !E]
[fourier_map_formula !E]
[extend_calculated_sphere_to !E]
[min_grid_spacing !E]
[correct_for_atomic_scattering_factors !E]
[f_atom_type $type f_atom_quantity !E]...

If fourier_map is non-zero then a Fourier map is calculated on refinement termination and shown in the OpenGL window; maps can be calculated for x-ray or neutron single crystal or powder data, see test examples FOURIER-MAP-AE14.INP and FOURIER-MAP-CIME.INP. The type of map is determined by fourier_map_formula which can be a function of the reserved parameter names *Fcalc*, *Fobs* and *D_spacing*; here are some examples:

```
        fourier_map_formula = Fobs; ' The default
        fourier_map_formula = 2 Fobs - Fcalc;
```

For single crystal data, *Fobs* corresponds to the observed structure moduli; powder data *Fobs* is calculated from the Rietveld decomposition formula. Structure factor phases are determined from *Fcalc*. Reflections that are missing from within the Ewald sphere are included with *Fobs* set to *Fcalc*. If extend_calculated_sphere_to is defined, then the Ewald sphere is extended. scale_pks definitions are removed from *Fobs*. If scale_pks evaluates to zero for a particular reflection, then *Fobs* is set to *Fcalc*; the number of *Fobs* reflections set to *Fcalc* is reported on.

[gauss_fwhm E]...

Defines the FWHM of a Gaussian function convoluted into phase peaks; see CS_G and Strain_G macros.

[hkl_plane $hkl]...

Used by the OpenGL viewer to display hkl planes, see the CEO2.STR file in the RIGID directory. Here are some examples:

```
str ...
   hkl_plane 1 1 1
   hkl_plane "2 -2 0"
```

[grs_interaction [from_N #] [to_N #] [no_self_interaction] $site_1 $site_2 qi # qj # N E]...

Defines a GRS interaction with the name N between sites identified by $site_1 and $site_2. E represents the GRS interaction equation that can be a function of *R*; *R* returns the distance in Å between two atoms; these distances are updated when dependent fractional atomic coordinates are modified. The name N of the grs_interaction can be used in equations including penalty equations. When either from_N or to_N are defined, the interactions between $site_1 and $site_2 are sorted by distance and only the interactions between the from_N and to_N are considered. no_self_interaction prevents any interactions between equivalent positions of the same site. This is useful when a general position is used to describe a special position. qi and qj corresponds to the valence charges used to calculate the Coulomb sum for the $site_1 and $site_2 sites respectively. grs_interaction is typically used for applying electrostatic restraints in inorganic materials. The GRS_Interaction macro simplifies the use of grs_interaction.

[hat E [num_hats #1]]...

Defines the x-axis extent of an impulse function that is convoluted into phase peaks. num_hats correspond to the number of hats to be convoluted. hat is used for example by the Slit_Width and Specimen_Tilt macros.

[hkl_Is]...
[lp_search !E]
[l_parameter_names_have_hkl $start_of_parameter_name]
[hkl_m_d_th2 # # # # # # l E]...

Defines a phase type that uses hkls for generating peak positions. lp_search uses an indexing algorithm that is independent of d-spacing extraction ([b]Coelho, 2017); see LP-SEARCH-PBSO4.INP. lp_search minimizes on a figure of merit function that gives a measure of correctness for a particular set of lattice parameters. The method avoids difficulties associated with extracting d-spacings from complex patterns comprising heavily overlapped lines; the primary difficulty being that of ascertaining the number of lines present. l_parameter_names_have_hkl assigns names to generated Intensity parameters that start with $start_of_parameter_name and end with the corresponding hkl. The numbers after hkl_m_d_th2 define h k l m d and 2θ values, where

h, k, l	: Miller indices
m	: multiplicity.
d and th2	: d and 2θ values.
l	: Peak intensity parameter before applying any scale_pks.

If no hkl_m_d_th2 keywords are defined, then hkls are generated using the space group. Generated hkl_m_d_th2 details are placed after the space_group keyword on refinement termination. Intensity parameters are given an initial starting value of 1. If lebail is not defined, then the intensity parameters are given the code of @. For example, the following:

```
xdd quartz.xdd
   ...
   hkl_Is
      Hexagonal(4.91459, 5.40603)
      space_group P_31_2_1
```

generates in the OUT file the following:

```
xdd quartz.xdd
   ...
   hkl_Is
      Hexagonal(4.91459, 5.40603)
      space_group P_31_2_1
      load hkl_m_d_th2 I {
         1   0   0   6    4.25635   20.85324 @ 3147.83321
         1   0   1   6    3.34470   26.62997 @ 8559.23955
         1   0  -1   6    3.34470   26.62997 @ 8559.23955
         ...
      }
```

The Create_hklm_d_Th2_Ip_file macro creates an hkl file listing in the "load hkl_m_d_th2 I" format as shown above. Even though the structure would have no sites, weight_percent can still be used; it uses whatever value is defined by cell_mass to calculate weight_percent.

[inp_text $name] ...
[inp_text_insert $name { ... }]...

inp_text provides a means of defining INP text at one place in a file and having that text inserted at another place in the INP file, or in an #include file, using inp_text_insert. The inp_text is updated on refinement termination. inp_text is very useful for simplifying complicated INP files where placing control parameters at the top of the file is of benefit; see test_example INP-TEXT.INP. An example is as follows:

```
inp_text back_ground {
   bkg @  17.365576`  14.5555883`  14.038067`
}
xdd …
   inp_text_insert back_ground
```

More than one inp_text can be of the same name; in such cases inp_text_insert will use the most recent inp_text.

[iters #]

The maximum number of refinement iterations, default is 10^9.

[lam [ymin_on_ymax #] [no_th_dependence] [Lam !E] [calculate_Lam]]
[la E lo E [lh E] | [lg E] [lo_ref]]...

Defines an emission profile (see section 5) where each la determines an emission profile line, where:

la: Area under the emission profile line
lo: Wavelength in Å of the emission profile line
lh: HW in mÅ of a Lorentzian convoluted into the emission profile line.
lg: HW in mÅ of a Gaussian convoluted into the emission profile line.

ymin_on_ymax determines the x-axis extent to which an emission profile line is calculated; default value is 0.001. no_th_dependence defines an emission profile that is 2θ independent; it allows use of non-X-ray data or fitting to negative 2θ values. By default, the program calculates d-spacings using the wavelength of the emission profile line with the highest la parameter. However, if la parameters are refined the reference wavelength could change causing confusion. To avoid this lo_ref can be used to identify the reference wavelength.

Lam defines the value to be used for the reserved parameter *Lam*. When Lam is not defined then the reserved parameter *Lam* is defined as the wavelength of the emission profile line with the largest la value. Note that Lam is used to determine the Bragg angle.

calculate_Lam calculates Lam such that it corresponds to the wavelength at the peak of the emission profile. Lam needs to be set to an approximate value corresponding to the peak of the emission profile.

[lor_fwhm E]...

Defines the FWHM of a Lorentzian that is convoluted into phase peaks; see for example the CS_L and Strain_L macros.

[lpsd_th2_angular_range_degrees E]...
lpsd_equitorial_divergence_degrees E
lpsd_equitorial_sample_length_mm E

Convolutes the aberration for a Linear Position Sensitive Detector (Cheary & Coelho, 1994) into phase peaks. lpsd_th2_angular_range_degrees correspond to the angular range of the LPSD in 2Th degrees. lpsd_equitorial_divergence_degrees is the equatorial divergence in degrees of the primary beam and lpsd_equitorial_sample_length_mm the length of the sample in the equatorial plane. lpsd_th2_angular_range_degrees corrects peak shapes, intensities and 2Th shifts, see example LPSD-SIMULATED.INP.

[min_r #] [max_r #]

Defines the minimum and maximum radii for calculating bond lengths, defaults are 0 and 3.2 Å respectively.

[neutron_data]

Signals the use of neutron atomic scattering lengths. Scattering lengths for isotopes can be used by placing the isotope name after "occ" as in:

```
occ 6Li 1
occ 36Ar 1
```

The scattering lengths data, contained in the file NEUTSCAT.CPP.

Constant wavelength neutron diffraction requires a Lorentz correction using the Lorentz_Factor macro (defined in TOPAS.INC); it is defined as follows:

```
scale_pks = 1 / (Sin(Th)^2 Cos(Th));
```

[no_LIMIT_warnings]

Suppresses LIMIT_MIN and LIMIT_MAX warnings.

[normalize_FCs]

Normalizes site fractional coordinates. Normalization does not occur for coordinates with min/max limits, is part of a rigid body or is part of a site constraint of any kind.

[numerical_area E]

Returns the numerically calculated area under the phase.

[num_cycles #]

Determines the number of cycles to process when continue_after_convergence is defined. The number of iterations, defined using iters, is still adhered to. Thus, to set number of cycles to 100 then using something like:

```
continue_after_convergence
iters 1000000000
num_cycles 100
```

[occ_merge $sites [occ_merge_radius !E]]...

Rewrites site occupancies of sites defined in $sites in terms of their fractional atomic coordinates (Favre-Nicolin and R. Cerny 2002). This is useful during structure solution for merging rigid bodies such as octahedra. It is also useful for identifying special positions as seen in the example PBSO4-DECOMPOSE.INP. In the present implementation $sites are thought of as spheres with a radius occ_merge_radius. When two atoms approach with a distance less than the sum of their respective occ_merge_radius's then the spheres intersect. The occupancies of the sites, occ_xyz, become:

occ_xyz = 1 / (1 + Intersecting_fractional_volumes)

In this way any number of sites can be merged. Sites appearing in $sites cannot have their occupancies refined. On termination of refinement the occ parameter values are updated with their corresponding occ_xyz.

[omit_hkls !E]

Allows for the filtering of hkls using the reserved parameter names of *H*, *K*, *L* and *D_spacing*. More than one omit_hkls can be defined, for example:

```
omit_hkls = If(And(H==0, K==0), 1, 0);
```

```
omit_hkls = And(H==0, K==1);
omit_hkls = D_spacing < 1;
```

[one_on_x_conv E]...

Defines ε_m in the convolution function:

$$(4 \mid \varepsilon_m \varepsilon \mid)^{-1/2} \qquad \text{for } \varepsilon = 0 \text{ to } \varepsilon_m$$

that is convoluted into phase peaks. ε_m can be greater than or less than zero, see for example the Divergence macro.

[out_A_matrix $file]
[A_matrix_prm_filter $filter]

Outputs the least squares **A** matrix to the file $file; used in the macro Out_for_cf. Output can be limited by using A_matrix_prm_filter, here's an example for outputting **A** matrix elements corresponding to parameters with names starting with 'q':

```
out_A_matrix file.a A_matrix_prm_filter q*
```

[out $file [append]]...
[out_record]
[out_eqn !E]
[out_fmt $c_fmt_string]
[out_fmt_err $c_fmt_string]...

Used for writing parameter details to a file. The details are appended to $file when append is defined. out_eqn defines the equation or parameter to be written to $file using the out_fmt. $c_fmt_string describes a format string in c syntax containing a single format specified for a double precision number. out_fmt_err defines the $c_fmt_string used for formatting the error of eqn. Both out_fmt and out_fmt_err requires an out_eqn definition. out_fmt can be used without out_eqn for writing strings. The order of out_fmt and out_fmt_err determines which is written to file first. The following illustrates the use of out using the Out macros (see OUT-1.INP):

```
xdd ...
    out "sample output.txt" append
    str ...
        CS_L(cs_l, 1000)
        Out_String("\tCrystallite Size Results:\n")
        Out_String("\t=========================\n")
        Out(cs_l, "\tCrystallite Size (nm):\t%11.5f",
                  "\tError in Crystallite Size:\t%11.5f\n")
```

[out_rwp $file]

Outputs a list of R_{wp} values encountered during refinement to the file $file in XDD format.

[out_prm_vals_per_iteration $file [append]]... | [out_prm_vals_on_convergence $file [append]]...
[out_prm_vals_filter $filter]
[out_prm_vals_dependents_filter $filter_dependents]

Outputs refined independent parameter values per iteration or on convergence into the file $file. out_prm_vals_filter can be used to filter the parameters; $fliter can contain the wild card character '*' and the negation character '!', for example:

```
out_prm_vals_per_iteration PRM_VALS.TXT out_prm_vals_filter "* !u*"
```

More than one out_prm_vals_per_iteration/out_prm_vals_on_convergence can be defined for outputting different parameters into different files depending on the corresponding out_prm_vals_filter. out_prm_vals_dependents_filter allows dependent parameters to be outputted according to $filter_dependents.

[out_prm_vals_on_end $file [append]]...

Allows for output only at the end of refinement, for example:

```
str…
    prm wtp = Get(weight_percent);
        out_prm_vals_on_end aac2.txt append
        out_prm_vals_filter wtp
        out_prm_vals_dependents_filter wtp
```

The following example shows how to add items to the out_prm_vals_on_end file.

```
#list Files { file1.xy file2.xy }
num_runs #list_n Files
do_errors
out_prm_vals_on_end results.txt #if (Run_Number > 0) append #endif
xdd Files(Run_Number)
    str…
    out results.txt append
        load out_record out_fmt out_eqn {
            "%d " = Run_Number;
            " %s  " = Files(Run_Number);
            }
```

The above will output the following into the file RESULTS.TXT.

```
Cycle Iter Rwp second_soll1FCF42E6640_ Err bkg1FCF3E90F18 Err ...
    0      7  7.026593e+00  7.437574e+00  3.511447e-02  1.208843e+01 ...
    0  file1.xy
Cycle Iter Rwp second_soll1FCF42E6640_ Err bkg1FCF3E90F18 Err ...
    0      7  7.026593e+00  7.437574e+00  3.511447e-02  1.208843e+01 ...
    1  file2.xy
```

[p1_fractional_to_file $file] [in_str_format]

Structure dependent. Saves atomic positions corresponding to space group *P*1 to the file $file. The original space group can be any space group. If in_str_format is defined, then the structural data is saved in INP format.

[peak_type $type]
[pv_lor E pv_fwhm E]
[h1 E h2 E m1 E m2 E]
[spv_h1 E spv_h2 E spv_l1 E spv_l2 E]

Sets the peak type for a phase, see section 5. The following peak_type's are available:

Peak type	$type	Parameters
Fundamental Parameters	fp	
Pseudo-Voigt	pv	pv_lor: the Lorentzian fraction of the peak profile(s). pv_fwhm: the FWHM of the peak profile(s).
Split-PearsonVII	spvii	The sum of h1 and h2 gives the FWHM of the composite peak. m1, m2 are the PearsonVII exponents of the left and right composite peak.
Split-PseudoVoigt	spv	The sum of spv_h1 and spv_h2 gives the full width at half maximum of the composite peak. spv_l1, spv_l2 are the left and right Lorentzian fractions.

[peak_buffer_step E [report_on]]

Peaks shapes typically change in a gradual manner over a short 2θ range; a new peak shape, therefore, is calculated only if the position of the last peak shape calculated is more than the distance defined by peak_buffer_step. Various stretching and interpolation procedures are used to calculate in-between peaks, see also section 5.4. The default setting is as follows:

peak_buffer_step = 500**Peak_Calculation_Step*.

When the reserved parameter names of *H*, *K*, *L*, *M,* or parameter names associated with sh_Cij_prm and hkl_angle, are used in peak convolution equations, then irregular peak shapes are possible over short 2θ ranges. In such cases, separate peak shapes are calculated for each peak irrespective of peak_buffer_step. report_on displays the number of peaks in the peaks buffer.

A value of zero for peak_buffer_step forces the calculation of a separate peak shape for each peak.

[phase_out $file [append]]...

Used for writing phase dependent details to file. See out for a description of out_record. The Create_hklm_d_Th2_Ip_file uses phase_out.

[phase_out_X $file [append]]...

Phase dependent keyword that writes phase Ycalc details to a file. The out_eqn can contain reserved parameter names occurring in xdd_out as well as Get(phase_ycalc); for example:

```
phase_out_X Phase.txt load out_record out_fmt out_eqn {
    " %9.0f" = Xi;
    " %11.5f" = X;
    " %11.5f" = Get(phase_ycalc);
    " %11.5f" = Ycalc;
    " %11.5f" = Yobs;
    " %11.5f\n" = Get(weighting);
}
```

The x-axis extent of the output corresponds to the x-axis range of the phase. If conserve_memeory is used, then the message "phase_out_X: No data" is outputted.

[pk_xo E]

Applied to all phase types except for xo_Is phases; provides a mechanism for transforming peak position to an x-axis position. For example, the peak position for neutron time-of-flight data is typically calculated in time-of-flight space, *tof,* or,

$$tof = t_0 + t_1\, d_{hkl} + t_2\, d_{hkl}^2$$

where t_0 and t_1 and t_2 are diffractometer constants. See examples TOF_BALZAR_SH1.INP and TOF_BALZAR_BR1.INP.

[phase_name $phase_name]

The name given to a phase; used for reporting purposes.

[phase_penalties $sites N]...[hkl_Re_Im #h #k #l #Re #Im]...
[accumulate_phases_and_save_to_file $file]
[accumulate_phases_when !E]

phase_penalties for a single hkl is defined as follows:

$$Pp_{hkl} = \begin{cases} 0, & if\ \varphi_{s,hkl} - 45° < \varphi_c < \varphi_{s,hkl} + 45° \\ d\, I_{c,hkl}^2 \left(\varphi_{s,hkl} - \varphi_{c,hkl}\right), & if\ \varphi_c < \varphi_{s,hkl} - 45° or\ \varphi_c > \varphi_{s,hkl} + 45° \end{cases}$$

where φ_s assigned phase, φ_c = calculated phase, I_c = calculated intensity and d is the reflection d-spacing. The name N returns the sum of the phase_penalties and it can be used in equations and in particular penalty equations. φ_c is calculated from sites identified in $sites.

#h, #k, #l are user defined hkls; they are used for formulating the phase penalties. #Re and #Im are the real and imaginary parts of φ_s. An example usage of phase penalties (see examples AE14-12.INP and AE5-AUTO.INP) is as follows:

```
penalty = pp1;
```

```
phase_penalties * pp1
load hkl_Re_Im {
    0   1   2   1  0
    1   0  -2   1  0
    1  -2  -1   1  0
}
```

hkls chosen for phase penalties should comprise those that are of high intensity, large d-spacing and isolated from other peaks to avoid peak overlap. Origin defining hkls are typically chosen.

accumulate_phases_and_save_to_file saves the average phases collected to $file. Phases are collected when accumulate_phases_when evaluates to true; accumulate_phases_when defaults to true. Here's an example use:

```
load temperature { 1 1 1 1 10 }
   move_to_the_next_temperature_regardless_of_the_change_in_rwp
accumulate_phases_and_save_to_file SOME_FILE.TXT
    accumulate_phases_when = T == 10;
```

Here phases with the best Rwp since the last accumulation are accumulated when the current temperature is 10.

[process_times]

Displays process times on termination of refinement.

[rand_xyz !E]

If continue_after_convergence is defined, then rand_xyz is executed at the end of a refinement cycle. It adds the vector **u** to the site fractional coordinate, the direction of which is random and the magnitude in Å is:

$$|\mathbf{u}| = T \, \text{rand\_xyz}$$

where T is the current temperature. To add a shift to an atom between 0 and 1 Å the following could be used:

```
temperature 1
    site... occ 1 C beq 1 rand_xyz = Rand(0,1);
```

Only fractional coordinates (x, y, z) that are independent parameters are considered.

[r_bragg #]

Reports on the R-Bragg value. R-Bragg is independent of hkl's and thus can be calculated for all phase types that contain phase peaks.

[rebin_with_dx_of !E]
[rebin_start_x_at !E]

Rebins the observed data (and *SigmaYobs* if it exists), see example CLAY.INP. It can be a function of the reserved parameter *X* as demonstrated in TOF_BANK2_1.INP. If rebin_with_dx_of evaluates to a constant, then the observed data is re-binned to equal x-axis steps. For observed data that is of unequal x-axis steps then re-binning provides a means of converting to equal x-axis steps. Some points about rebin_with_dx_of:

- It changes the data.
- It uses all data and uses it once.
- Errors are similar if the fit to the new data is similar.
- If a hat convolution is included in *Ycalc* then the fit is potentially the same.

rebin_with_dx_of creates a new x-axis with points determined by the rebin_with_dx_of equation, or,

x[i+1] = x[i] + rebin_with_dx_of

The new x-axis can be at x-axis intervals that are unequal. The position of the first x[i] value defaults to the start of the original x-axis; this can be changed using rebin_start_x_at. Intensities at the new x-axis are determined by the following integration:

Intensity at x[i] = Integrate *Yobs* from (x[i] + x[i-1])/2 to (x[i] + x[i+1])/2

Yobs is considered as line segments; integration is therefore simply the area under the line segments. The integration implies convolution and rebin_with_dx_of can be thought of as a resampling of the data. If rebin_with_dx_of is a constant, then the x-axis intervals are equal, then the integration can be included in *Ycalc* using a hat function, or,

```
rebin_with_dx_of 0.02
hat 0.02
```

[Rp #] [Rs #]

Primary and secondary diffractometer radii in mm; defaults to 217mm.

[scale E]

Rietveld scale factor; can be applied to all phase types.

[scale_pks E]...

Scales phase peaks; the following defines a Lorentz-Polarisation correction:

```
scale_pks = (1 + Cos(c Deg)^2 Cos(2 Th)^2) / (Sin(Th)^2 Cos(Th));
```

See LP_Factor, Preferred_Orientation and Absorption_With_Sample_Thickness_mm_Intensity macros.

[seed [#]]

Initializes the random number generator with a seed based on the computer clock. To initialize the random number generator at the pre-processor stage then use *#seed*.

[site $site [x E] [y E] [z E]]...
[occ $atom E [beq E] [scale_occ E]]...
[num_posns #] [rand_xyz !E] [inter !E #]

Defines a site where $site is a User defined string used to identify the site. x, y, and z define the fractional atomic coordinates, see also section 20.28. occ and beq defines the site occupancy factor and the equivalent isotropic temperature factor respectively. $atom corresponds to a valid atom symbol or isotope contained in the file ATMSCAT.CPP for x-ray data and NEUTSCAT.CPP for neutron_data. num_posns corresponds to the number of unique equivalent position generated from the space group; it is updated on refinement termination. inter corresponds to the sum of all GRS interactions which are a function of the site. The value of inter can represent the site electrostatic potential depending on the type of GRS interactions defined. A site fully occupied by Calcium is written as:

```
site Al1  x 0       y 0    z 0.3521  occ Ca+2 1    beq 0.3
```

A site occupied by two cations is:

```
site Fe2  x 0.9283  y 0.25 z 0.9533  occ Fe+3 0.5  beq 0.25
                                       occ Al+3 0.5  beq 0.25
```

scale_occ is occ dependent and it scales occ. It and can be a function of *H*, *K*, *L*, *D_spacing*, *Xo* and *Th*. The occ keyword remains single valued for QUANT purposes and thus cannot be a function of *H*, *K*, *L* etc. The following is valid:

```
occ Pb+2 1
   prm q1 1 min 1e-6
   prm q2 1 min 1e-6
   prm q3 1 min 1e-6
   prm q4 1 min 1e-6
   scale_occ = q1 / D_spacing + 1 / (q2 H^2 + q3 K^2 + q4 L^2);
```

scale_occ is a child of occ, the keyword therefore needs to occur after the occ keyword. The following two definitions will produce identical structure factors but different QUANT results:

```
site Pb occ Pb+2 1   beq 1
site Pb occ Pb+2 0.5 beq 1 scale_occ 2
```

scale_occ works with magnetic data, neutron data, x-ray data etc. but not PDF data.

Symmetry: The user is responsible for obeying symmetry. If not working in *P*1 then the Multiplicities_Sum macro could be used. The spherical_harmonics_hkl keyword can also be used, for example:

```
spherical_harmonics_hkl sh sh_order 6
site Pb occ Pb+2 1 beq 1
   prm q 1 min 1e-6
   scale_occ = q sh;
```

[sites_distance N] | [sites_angle N] | [sites_flatten N [sites_flatten_tol !E]]...
[site_to_restrain $site [#ep [#n1 #n2 #n3]]]...

When used in equations the name N of sites_distance and sites_angle returns the distance in Å between two sites and angle in degrees between three sites respectively. The sites considered are defined by site_to_restrain. N can be used in penalty equations to restrain bond lengths. N of sites_flatten returns a restraint term that decreases as the sites become coplanar; it is defined as follows:

$$\text{sites\_flatten}=\frac{6}{n(n-1)(n-2)}\sum_{i=1}^{n}\sum_{j=i+1}^{n}\sum_{k=j+1}^{n}\left(\left|b_i\, x\, b_j\, .\, b_k\right|-tol\right)^2, if\ \left|b_i\, x\, b_j\, .\, b_k\right|>tol$$

where *tol* corresponds to sites_flatten_tol, *n* corresponds to the number of sites defined by site_to_restrain, **b** are Cartesian unit length vectors between the sites and the geometric center of the sites.

#eq, #n1, #n2 and #n3 correspond to the site equivalent position and fractional offsets to add to the sites. This is useful if the structure is already known and constraints are required, for example, in the bond length output (see append_bond_lengths):

```
Zr1:0  O1:20  0  0 -1  2.08772
       O1:7   0 -1  0  2.08772  89.658
       O1:10  0  0 -1  2.08772  90.342   90.342
       O1:15 -1  0  0  2.08772  180.000  89.658   89.658
       O1:18 -1  0  0  2.08772  90.342   89.658   180.000 90.342

P1:0   O1:4   0  0  0  1.52473
       O1:8   0  0  0  1.52473  112.923
       O1:0   0  0  0  1.52473  112.923  112.923
       O2:0   0  0  0  1.59001  105.749  105.749  105.749
```

Example constraints using macros looks like:

```
Angle_Restrain(O1 P1 O1 8, 112, 112.92311, 0, 0.001)
Angle_Restrain(O1 18 -1 0 0 Zr1 O1 10 0 0 -1, 89, 89.65750, 0, 0.001)
Distance_Restrain(Zr1 O1 20 0 0 -1, 2.08, 2.08772, 0, 1)
```

BENZENE.INP demonstrates the use of the restraint macros Distance_Restrain, Angle_Restrain and Flatten. OpenGL viewing is recommended. Note, for more than ~6 sites then sites_flatten becomes computationally expensive.

[sites_geometry $Name]...
[site_to_restrain $site [#ep [#n1 #n2 #n3]]]...

Defines a grouping of up to four sites; $Name is the name given to the grouping. The sites that are part of the group is defined using site_to_restrain, for example:

```
sites_geometry some_name
   load site_to_restrain { C1 C2 C3 C4 }
```

Three functions, Sites_Geometry_Distance($Name), Sites_Geometry_Angle($Name) and Sites_Geometry_Dihedral_Angle($Name) can be used in equations to obtain the distance between sites C1 and C2, the angle between C1-C2-C3 and the dihedral angle formed between the planes C1-C2-C3 and C2-C3-C4. The convention used are the same as for z-matrices, see example SITES_GEOMETRY_1.INP.

If $Name contains only two sites, then only Sites_Geometry_Distance($Name) can be used. Three sites defined additionally allows the use of Sites_Geometry_Angle($Name) and four sites defined additionally allows the use of Sites_Geometry_Dihedral_Angle($Name).

Examples SITES_GEOMETRY_1.INP And SITES_GEOMETRY_2.INP demonstrates the use of sites_geometry.

[siv_s1_s2 # #]

Defines the s_1 and s_2 integration limits for the spherical interaction volume of the GRS series.

[smooth #num_pts_left_right]

Performs a Savitzky-Golay smoothing on the observed data. The smoothing encompasses (2 * #num_pts_left_right + 1) points.

[spherical_harmonics_hkl $name]...
[sh_Cij_prm $Yij E]...
[sh_alpha !E]
[sh_order #]

Defines a hkl dependent symmetrized spherical harmonics series (see section 20.30.1) with a name of $name. When $name is used in equations, it returns the value of the associated spherical-harmonics series.

sh_Cij_prm is the spherical harmonics coefficients which can be defined by the User, or alternatively, if there are no coefficients defined, then the sh_Cij_prm parameters are generated. Only the coefficients allowed by the selection rules of the point group are generated (Järvinen, 1993). At the end of refinement, the generated sh_Cij_prm parameters are appended to sh_order. This allows for control over the sh_Cij_prm parameters in subsequent refinements. $Yij corresponds to valid symmetrized harmonics that has survived symmetrisation. It is internally generated when there are no sh_Cij_prm parameters defined by the User.

sh_alpha corresponds to the angle in degrees between the polar axis and the scattering vector; sh_alpha defaults to zero degrees which is required for symmetric reflection as is the case for Bragg-Brentano geometry.

sh_order corresponds to the order of the spherical harmonic series which are even numbers ranging from 2 to 8 for non-cubic and from 2 to 10 for cubic systems.

The PO_Spherical_Harmonics macro simplifies the use of spherical_harmonics_hkl. CLAY.INP demonstrates the use of spherical_harmonics_hkl for describing anisotropic peak shapes.

[stacked_hats_conv [whole_hat E [hat_height E]]...[half_hat E [hat_height E]...]...

Defines hat sizes for generating an aberration function comprising a summation of hats. whole_hat defines a hat with an x-axis extent of ±whole_hat/2. half_hat defines a hat with an x-axis range of half_hat to zero if half_hat<0; or zero to half_hat if half_hat> 0. hat_height defines the height of the hat; it defaults to 1. stacked_hats is used for example to describe tube tails using the Tube_Tails macro.

[start_X !E] [finish_X !E]

Defines the start and finish x-axis region to fit to.

[str | dummy_str]...

Defines a new structure node.

[str_hkl_angle N #h #k #l]...

Defines a parameter name N and a vector normal to the plane defined by h, k and l. When the parameter name is used in an equation, it returns angles (in radians) between itself and the normal to the planes defined by hkls.

[suspend_writing_to_log_file #1]

When num_runs > 0, then, by default, output to TOPAS.LOG (or TC.LOG if running TC.EXE) is suspended after the first run (Run_Number == 0). suspend_writing_to_log_file changes this behaviour.

[temperature !E]...
[move_to_the_next_temperature_regardless_of_the_change_in_rwp]
[save_values_as_best_after_randomization]
[use_best_values]

A temperature regime has no effect unless the reserved parameter *T* is used in val_on_continue attributes, or, if the temperature dependent keywords rand_xyz or randomize_on_errors are used. randomize_on_errors automatically determine parameter displacements without the need for rand_xyz or val_on_continue. It performs well on a wide range of problems. The reserved parameter *T* returns the current temperature. The first temperature defined becomes the starting temperature; subsequent temperature(s) become the current temperature. If χ_0^2 increases relative to a previous cycle, then the temperature is advanced to the next temperature. If χ_0^2 decreases relative to previous temperatures of lesser values, then the current temperature is rewound to a previous temperature such that its previous is of a greater value. move_to_the_next_temperature_regardless_of_the_change_in_rwp

forces the refinement to move to the next temperature regardless of the change in Rwp from the previous temperature. save_values_as_best_after_randomization saves the current set of parameters and gives them the status of “best solution”. Note, this does not change the global “best solution” which is saved at the end of refinement. use_best_values replaces the current set of parameters with those marked as “best solution”. The temperature regime defined in the Auto_T macro is sufficient for most problems. A typical temperature regime starts with a high value and then a series of annealing temperatures, for example:

```
temperature 2
    move_to_the_next_temperature_regardless_of_the_change_in_rwp
temperature 1 temperature 1 temperature 1
```

If the current temperature is the last one defined (the fourth one), and χ_0^2 decreased relative to the second and third temperatures, then the current temperature is set to the second temperature. The current temperature can be used in all equations using the reserved parameter *T*, for example:

```
x @ 0.123 val_on_continue = Val + T Rand(-.1, .1)
```

The following temperature regime will allow parameters to randomly walk for the first temperature. At the second temperature the parameters are reset to those that gave the "best solution".

```
temperature 1 temperature 1 use_best_values
temperature 1 temperature 1 use_best_values
temperature 1
temperature 10
   save_values_as_best_after_randomization
   move_to_the_next_temperature_regardless_of_the_change_in_rwp
```

Note, that when a "best solution" is found, the temperature is rewound to a position where the temperature decreased. For example, if the R_{wp} dropped at lines 2 to 5 then the next temperature will be set to "line 1". The following temperature regime will continuously use the "best solution" before randomisation; it has a tendency to remain in a false minimum.

```
temperature 1 use_best_values
```

[th2_offset E]...

Used for applying 2θ corrections to phase peaks. The following applies a sample displacement correction:

```
th2_offset = -2 Rad (c) Cos(Th) / Rs;
```

th2_offset is used for example in the Zero_Error and Specimen_Displacement macros.

[user_defined_convolution E min E max E]...

User defined convolutions are convoluted into phase peaks and can be a function of *X*. The min/max equations are mandatory, they define the x-axis extents of the

user_defined_convolution where min ≤ 0 and max ≥ 0. For example, a sinc function can be convoluted into phase peaks (example AU111.INP) as follows:

```
str ...
    prm k 10 min 0.001 max 100
    user_defined_convolution = If(Abs(X) < 10^(-10), 1, (Sin(k X) /(k X))^2);
        min -3 max 3
```

[use_tube_dispersion_coefficients]

Forces the use of Laboratory tube anomalous dispersion coefficients, see section 20.9.

[verbose #1]...

A value of 1 instructs the kernel to output in a verbose manner. A value of 0 reduces kernel output such that text output is initiated at the end of a refinement cycle. A value of -1 reduces kernel output further such that text output is initiated every second in time and only R_{wp} values at the end of a refinement cycle is kept. The Simulated_Annealing_1 macro has verbose set to -1; this ensures that long simulated annealing runs do not exhaust memory due to saving R_{wp} values in text output buffers.

[view_structure]

Informs the GUI to display the structure.

[weighting !E [recal_weighting_on_iter]]

Used for calculating the xdd dependent weighting function in χ_0^2. Can be a function of the reserved parameter names *X*, *Yobs*, *Ycalc* and *SigmaYobs*. The default is as follows:

```
    weighting = 1 / Max(Yobs, 1);
```

In cases where weighting is a function of *Ycalc* then recal_weighting_on_iter can be used to recalculate the weighting at the start of refinement iterations. Otherwise, the weighting is recalculated at the start of each refinement cycle. Note that some goodness of fit indicators such as r_wp are a function of weighting, see Table 4-2.

[x_calculation_step !E]

Calculation step used in the generation of phase peaks and fit_obj's. *Peak_Calculation_Step* is the actual step size used. For an x-axis with equidistant steps and x_calculation_step not defined then:

Peak_Calculation_Step = "Observed data step size" / convolution_step

otherwise

Peak_Calculation_Step = x_calculation_step / convolution_step

x_calculation_step can be a function of *Xo* and *Th*. In some situations, it may be computationally efficient to write x_calculation_step in terms of the function Yobs_dx_at and the

reserved parameter *Xo*. It is also mandatory to define x_calculation_step for data with unequal x-axis steps (*.XY or *.XYE data files). Example usage:

```
x_calculation_step 0.01
x_calculation_step = 0.02 (1 + Tan(Th));
x_calculation_step = Yobs_dx_at(Xo);
```

[xdd $file [{ $data }] [range #] [xye_format] [gsas_format] [fullprof_format]]...
[gui_reload]
[gui_ignore]

Defines the start of xdd dependent keywords and the file containing the observed data. {$data} allow for insertion of ASCII data directly into the INP file. range applies to Bruker AXS *.RAW data files; in multi-range files it defines the range to be refined with the first range starting at 1 (the default). xye_format (see section 20.35 as well) signals the loading of columns of x, y and error values. gsas_format and fullprof_format signals the loading of GSAS and FullProf file formats. The following will refine on the first range in the data file pbso4.raw:

```
xdd pbso4.raw
```

The following will refine on the third range:

```
xdd pbso4.raw range 3
```

To read data directly from an INP file, the following can be used:

```
xdd {
    1 1 10  ' start, step and finish (equidistant data)
    1 2 3 4 5 6 7 8 9 10
}
```

```
xdd {
    _xy ' switch indicating x-y format
    0.1 1   0.2 2   ...
}
```

When in Launch mode; data files by default are not reloaded if already loaded. gui_reload forces the reload of the data file. Data files are loaded/reloaded into the GUI under the following circumstances:

- The data file is not loaded into the GUI
- Any of the following keywords have been used at the xdd level:
  gui_reload, rebin_with_dx_of, smooth, yobs_eqn, yobs_to_xo_posn_yobs

gui_reload can be used in cases where the data file has been changed by a process not listed. gui_ignore informs the GUI to ignore the xdd data file; *Ycalc*, difference and other items associated with the data file is not retrieved from the Kernel.

[xdd_out $file [append]]...

Used for writing xdd dependent details to file. The out_eqn can contain the reserved parameter names of *X*, *Yobs*, *Ycalc* and *SigmaYobs*. See out for a description of out_record. The Out_Yobs_Ycalc_and_Difference macro is a good example of using xdd_out.

[xdd_scr $file] ...
[dont_merge_equivalent_reflections]
[dont_merge_Friedel_pairs]
[ignore_differences_in_Friedel_pairs]
[str]...
[auto_scale !E]
[i_on_error_ratio_tolerance #]
[num_highest_I_values_to_keep #num]

xdd_scr defines single crystal data from the file $file. The file can have extensions of *.HKL for ShelX HKL4 format or *.SCR for SCR format. All xdd and str keywords that are not dependent on powder data can be used by xdd_scr. Single crystal data is internally stored in 2θ versus F_o^2 format; this allows the use of start_X, finish_X and exclude keywords; a lam definition is required.

dont_merge_equivalent_reflections prevent merging of equivalent reflections, see also section 20.9.3. dont_merge_Friedel_pairs prevent merging of Friedel pairs. ignore_differences_in_Friedel_pairs force the use of Eq. (20-12) for calculating F^2. auto_scale rewrites the scale parameter in terms of F^2; this eliminates the need for the scale parameter. The value determined for auto_scale is updated at the end of refinement. i_on_error_ratio_tolerance filters out hkl's that does not meet the condition:

$$|F_o| > \text{i\_on\_error\_ratio\_tolerance} \mid \text{Sigma}(F_o) \mid$$

num_highest_I_values_to_keep removes all hkl's except for #num hkl's with the highest F_o values. An example input segment for single crystal data refinement is as follows:

```
xdd_scr ylidm.hkl
   MoKa2(0.001)
   finish_X 35
   weighting = 1 / (Sin(X Deg / 2) Max(1, Yobs));
   STR(P212121)
      a  5.9636
      b  9.0390
      c  18.3955
      scale @ 1.6039731906
      i_on_error_ratio_tolerance 4
      site S1  x @ 0.8090  y @ 0.1805  z @ 0.7402  occ S 1  beq 2
      site O1  x @ 0.0901  y @ 0.8151  z @ 0.2234  occ O 1  beq 2
      ...
```

The SCR format is white space delimited and consists of entries of h, k, l, m, d, 2θ, F_o^2 which is the format outputted by the Create_hklm_d_Th2_Ip_file macro.

[xo_Is]...
[xo E I E]...

Defines a phase type that uses x-axis space for generating peak positions, see example XOIS.INP. xo corresponds to the peak position, and I is the intensity parameter before applying scale_pks equations.

[yobs_eqn !N E min E max E del E]

Observed data is created via an equation; this is useful for approximating functions. The name !N given to the equation is used for identifying the plot in the GUI.

[yobs_to_xo_posn_yobs !E]

At the start of refinement, yobs_to_xo_posn_yobs decomposes an X-ray diffraction pattern into a new pattern comprising at most one data point per hkl. Fitting to the decomposed pattern in a normal Rietveld refinement manner is then possible due to the ability to refine data of unequal x-axis step sizes. This normal Rietveld manner of fitting is important in structure solution from simulated annealing as the background can still be refined and the problem of peak overlap avoided. These new data points are not extracted intensities and thus the problem of peak overlap, as occurs in intensity extraction, is avoided. The much smaller number of data points in the new diffraction pattern can greatly improve speed in structure solution; in other words, the calculation time in synthesizing the diffraction pattern becomes close to that of when dealing with single crystal data. If the distance between two hkls is less than the value of yobs_to_xo_posn_yobs then the proposed data point at one of these hkls is discarded. Thus, the final decomposed pattern may in fact have less data points than hkls. A reasonable value for yobs_to_xo_posn_yobs is *Peak_Calculation_Step*, or,

```
yobs_to_xo_posn_yobs = Peak_Calculation_Step;
```

yobs_to_xo_posn_yobs can be a function of the reserved parameter *X* with *X* being the value of the x-axis at the hkl. For refinement stability, all peak shape, zero error and lattice parameters should be determined and then fixed before using yobs_to_xo_posn_yobs. Also, if the original diffraction pattern is noisy then it may be best to smooth the pattern using smooth or re-binned using rebin_with_dx_of. Alternatively, a calculated pattern could be used as input into the yobs_to_xo_posn_yobs. Note that structure solution can be speed-up by preventing graphical output or by increasing the Graphics Response Time in the GUI. See examples CIME-DECOMPOSE.INP and PBSO4-DECOMPOSE.INP.

22. MACROS AND INCLUDE FILES

Macros appearing in INP files are expanded by the pre-processor. The pre-processor comprises two types of directives, global types and types that are invoked on macro expansion; directives begin with the character # and are:

Directives with global scope:

macro $user_defined_macro_name { ... }

#include $user_defined_macro_file_name

#delete_macros { $macros_to_be_deleted }

#define, *#undef*, *#if*, *#ifdef*, *#ifndef*, *#else*, *#elseif*, *#endif*, *#prm*

#seed – initializes the random number generator at the pre-processor stage.

Directives invoked on macro expansion:

#m_if, *#m_ifarg*, *#m_elseif*, *#m_else*, *#m_endif*

#m_code, *#m_eqn*, *#m_code_refine*, *#m_one_word*

#m_argu, *#m_first_word*, *#m_unique_not_refine*

22.1 ... The macro directive

Macros are defined using the *macro* directive; here's an example:

```
macro Cubic(cv) { a cv b = Get(a); c = Get(a); }
```

Macros can have multiple arguments or none; the Cubic macro above has one argument; here are some example uses of Cubic:

```
Cubic(4.50671)
Cubic(a_lp 4.50671  min 4.49671  max 4.52671)
Cubic(!a_lp 4.50671)
```

The first instance defines the a, b and c lattice parameters without a parameter name. The second defines the lattice parameters with a name indicating refinement of the a_lp parameter. In the third example, the a_lp parameter is preceded by the ! character. This indicates that the a_lp parameter is not to be refined; it can however be used in equations. The definition of macros need not precede its use. For example, in the segment:

```
xdd...
    Emission_Profile ' this is expanded
    macro Emission_Profile { CuKa2(0.001) }
```

Even though the Emission_Profile macro has been defined after its use, Emission_Profile is expanded to "CuKa2(0.001)".

Macro names need not be unique; in cases where more than one macro have the same name then the actual macro expanded is determined by the number of arguments. For example, if the macro Slit_Width(0.1) is used then the Slit_Width(v) macro is expanded. On the other hand

if the macro Slit_Width(sw, .1) is used then the Slit_Width(c, v) macro is expanded. Macros can also expand to macro names. For example, the Crystallite_Size macro expands to CS and since CS is a macro then the CS macro is expanded.

22.1.1 ..... Directives with global scope

#include $user_defined_macro_file_name

Include files are used to group macros. The file TOPAS.INC contains standard macros; it's a good place to view examples. Text within include files are inserted at the position of the *#include* directive, thus the following:

```
#include "my include file.inc"
```

inserts the text within "my include file.inc" at the position of the *#include* directive. The standard macro file TOPAS.INC is always included by default.

#delete_macros { $macros_to_be_deleted }

Macros can be deleted using *#delete_macros*, for example the following

```
#delete_macros { LP_Factor SW ZE }
```

will delete previously defined macros, irrespective of the number of arguments, with the names LP_Factor, SW and ZE.

#define, *#undef*, *#ifdef*, *#ifndef*, *#else*, *#endif*

The *#define* and *#undef* directives works similar-to the c pre-processor directives of the same name. *#define* and *#undef* is typically used with *#ifdef*, *#else*, *#endif* directives to control macro expansion in INP files. For example, the following:

```
#ifdef STANDARD_MACROS
    xdd ...
#endif
```

will expand to contain the xdd keyword if STANDARD_MACROS has been previously defined using a *#define* directive. The following will also expand to contain the xdd keyword if STANDARD_MACROS has not been defined using a *#define* directive,

```
#ifdef !STANDARD_MACROS
   #define STANDARD_MACROS
   xdd ...
#endif
```

or,

```
#ifndef STANDARD_MACROS
   #define STANDARD_MACROS
   xdd ...
#endif
```

Note the use of the '!' character placed before STANDARD_MACROS which means if STANDARD_MACROS is not defined.

22.1.2 ..... Pre-processor equations and #prm, #if, #elseif, #out

Pre-processor parameters, called hash parameters, are defined using the *#prm* directive. *#prm*'s can be a function of other *#prm*'s and they can be used in *#if*, *#elseif*, *#m_if* and *#m_elseif* pre-processor statements. *#prm*'s are only evaluated at the pre-processor stage of loading INP files (see TEST_EXAMPLES\HASH_PRM.INP); they are therefore unknown to the kernel and are totally separate to parameters defined using prm. Pre-processed output can be found in the TOPAS.LOG file, when running TA.EXE, or TC.LOG when running TC.EXE.

#out and *#m_out* allows pre-processor *#prm*'s values, which can be strings or numbers, to be placed into the pre-processed text. For example, the following:

```
#prm a = Constant(Rand(0,1));
#out a
```

will output a random number between 0 and 1 into the pre-processed file at the position of *#out*. INP files can therefore be manipulated with *#prm*'s and *#if* statements with a means of identifying the manipulation carried out. The following:

```
macro Ex1(a) {
    #m_if a == "b";
        Yes b
    #m_elseif a == "c";
        Yes c
    #m_endif
}
Ex1("b")
```

expands to:

```
Yes b
```

In the following:

```
#prm ran = Constant(Rand(0,1));
#if ran < 0.5;
    view_structure
#endif
#if ran < 0.5;
    view_structure
#endif
#if ran < 0.5;
    view_structure
#endif
```

each call to 'ran' in the *#if* statements would return the same value because of the use of Constant. More complicated INP file manipulation is shown in the following:

```
#prm space_group_number = 4;
```

```
#if And(space_group_number >= 75, space_group_number <= 142);
   ...
#elseif And(space_group_number >= 16, space_group_number <= 74);
   ...
#endif
```

22.1.3 ..... A macro that repeats text using #out

A macro that repeats and modifies text can be formulated as follows:

```
macro Repeat(& n)
   {
      #if (n > 0)
         A n
         Repeat(n-1)
      #endif
   }
Repeat(10)
```

Output from the above looks like:

```
A (10) A ((10)-1) A (((10)-1)-1) A ((((10)-1)-1)-1) A (((((10)-1)-1)-1)-1) A ((((((10)-1)-
1)-1)-1)-1) A (((((((10)-1)-1)-1)-1)-1)-1) A ((((((((10)-1)-1)-1)-1)-1)-1)-1) A
((((((((((10)-1)-1)-1)-1)-1)-1)-1)-1) A ((((((((((10)-1)-1)-1)-1)-1)-1)-1)-1)-1)
```

This output may be intended. However, what is often intended is:

```
macro Repeat(& n)
   {
      #if (n > 0)
         #prm a = n;
         #prm am1 = n - 1;
         A #out a
         Repeat(#out am1)
      #endif
   }
Repeat(10)
```

and the output is as follows:

```
A 10  A 9  A 8  A 7  A 6  A 5  A 4  A 3  A 2  A 1
```

More succinctly again is to use the Numeric macro as follow:

```
macro Numeric(& n)
    {
       #prm a = n; #out a
```

```
    }
macro Repeat(& n)
    {
       #if (n > 0)
          A Numeric(n)
          Repeat(Numeric(n-1))
       #endif
    }
Repeat(10)
```

22.1.4 ..... Directives invoked on macro expansion

#m_if, *#m_ifarg*, *#m_elseif*, *#m_else*, *#m_endif*, *#m_if*, *#m_out*

These are conditional directives that are invoked on macro expansion. *#m_ifarg* operates on two statements immediately following its use; the first must refer to a macro argument and the second can be any of the following: *#m_code*, *#m_eqn*, *#m_code_refine*, *#m_one_word* and "some string". *#m_ifarg* evaluates to true according to the rules of Table 22-1.

Table 22-1. *#m_ifarg* syntax and meaning.

	Evaluates to true if the following is true
#m_ifarg c *#m_code*	If the macro argument c has a letter or the character ! as the first character and if it is not an equation.
#m_ifarg c *#m_eqn*	If the macro argument c is an equation.
#m_ifarg c *#m_code_refine*	If the macro argument c has a letter as the first character and if it is not an equation.
#m_ifarg c "some_string"	If the macro argument c == "some_string".
#m_ifarg v *#m_one_word*	If the macro argument v consists of one word.

#m_argu, *#m_first_word*, *#m_unique_not_refine*

These operate on one macro argument with the intention of changing the value of the argument according to the rules of Table 22-2.

Table 22-2. Directives that change the value of a macro argument.

#m_argu c	Changes the macro argument c to a unique parameter name if it has @ as the first character.
#m_unique_not_refine c	Changes the macro argument c to a unique parameter name that is not to be refined.
#m_first_word $v	Replace the string macro argument $v with the first word occurring in $v.

22.1.5 ..... Defining unique parameters within macros

#m_unique $string assigns a unique parameter name to $string within a macro. This allows new unique parameters to be defined within macros whilst avoiding name clashes. In the example:

```
macro Some_macro(v) { prm #m_unique a = Cos(Th); : v }
```

'a' is assigned a unique parameter name and it has the scope of the macro body text. The Robust_Refinement and TCHZ_Peak_Type macros are good examples of its use, where for example, the former is defined as:

```
macro Robust_Refinement {
    ' Robust refinement algorithm
    prm #m_unique test = Get(r_exp);
    prm #m_unique N = 1 / test^2;
    prm #m_unique p0 = 0.40007404;
    prm #m_unique p1 = -2.5949286;
    prm #m_unique p2 = 4.3513542;
    prm #m_unique p3 = -1.7400101;
    prm #m_unique p4 = 3.6140845e-1;
    prm #m_unique p5 = -4.45247609e-2;
    prm #m_unique p6 = 3.5986364e-3;
    prm #m_unique p7 = -1.8328008e-4;
    prm #m_unique p8 = 5.7937184e-6;
    prm #m_unique p9 = -1.035303e-7;
    prm #m_unique p10 = 7.9903166e-10;
    prm #m_unique t = (Yobs - Ycalc) / SigmaYobs;
    weighting = If( t < 0.8,  N / Max(SigmaYobs^2, 1),  If( t < 21, N ((((((((((p10 t +
              p9) t + p8) t + p7) t + p6) t + p5) t + p4) t + p3) t + p2) t + p1) t + p0)
              / (Yobs - Ycalc)^2, N (2.0131 Ln(t) + 3.9183) / (Yobs - Ycalc)^2));
    recal_weighting_on_iter
}
```

22.1.6 ..... Superfluous parentheses and the '&' Type for macros

The pre-processor is an un-typed language meaning that it knows nothing about the type of text passed as macro arguments. This is flexible but problematic. For example, the following:

```
macro divide(a, b) { a / b }
prm e = divide(a + b, c - d);
```

expands to the unintended result of:

```
prm e = a + b / c - d;
```

The writer of the macro could solve this problem by rewriting the macro with parentheses:

```
macro divide(a, b) { (a) / (b) }
```

Alternatively, macro arguments can be prefixed with the & character signalling that the argument is of an equation type, for example:

```
macro divide(& a, & b) { a / b }
prm e = divide(a + b, c - d);
```

The program inspects &-type arguments and parentheses are included as needed. This results in the correct expansion of:

```
prm e = (a + b) / (c - d);
```

Even with the use of &-types for arguments, the following:

```
macro divide(& a, & b) { a / b }
prm e = divide(a + b, c - d)^2;
```

expands to the unintended:

```
prm e = (a + b) / (c - d)^2;
```

The writer of the macro could again rewrite the macro to include more parentheses:

```
macro divide(a, b) {  ((a) / (b))  }
```

Or define the expansion of the macro itself to have an &-type by placing the & character before the macro name itself:

```
macro & divide(& a, & b) {  a / b  }
```

Expansion of prm e = divide(a + b, c - d)^2 now becomes the intended:

```
prm e = ((a + b) / (c - d))^2;
```

With the use of the &-type, macros such as Ramp defined in Version 4 as:

```
macro Ramp(x1, x2, n) { ((x1)+((x2)-(x1)) Mod(Cycle_Iter,(n))/((n)-1)) }
```

can be written with less parentheses as follows:

```
macro & Ramp(& x1,& x2,& n) { x1 + (x2 - x1) Mod(Cycle_Iter, n) / (n-1) }
```

22.2 ... Overview

The file TOPAS.INC is included in INP files by default; it contains commonly used standard macros. The meaning of the macro arguments in TOPAS.INC can be readily determined from the following conventions:

Arguments called "c" correspond to a parameter name.
Arguments called "v" correspond to a parameter value.
Arguments called "cv" correspond to a parameter name and/or value.

For example, the Cubic(cv) macro requires a value and/or a parameter name as an argument, i.e.

```
Cubic(a_lp 10.604)
Cubic(10.604)
Cubic(@ 10.604  min 10.59 max 10.61)
```

Here are examples for the Slit_Width macro:

```
SW(@, 0.1)
SW(sw, 0.1  min = Val-.02; max = Val+.02;)
SW((ap+bp)/cp, 0) ' where ap, bp and cp are parameters defined elsewhere
```

22.2.1 ..... xdd macros

```
RAW(path_no_ext)
RAW(path_no_ext, range_num)
DAT(path_no_ext)
XDD(path_no_ext)
XY(path_no_ext, calc_step)
XYE(path_ext)
SCR(path_no_ext)
SHELX_HKL4(path_no_ext)
```

22.2.2 ..... Lattice parameters

```
Cubic(cv)
Tetragonal(a_cv, c_cv)
Hexagonal(a_cv, c_cv)
Rhombohedral(a_cv, al_cv)
```

22.2.3 ..... Emission profile macros

```
No_Th_Dependence                FeKa7_Holzer(yminymax)
CuKa1(yminymax)                 MnKa7_Holzer(yminymax)
CuK1sharp(yminymax)             NiKa5_Holzer(yminymax)
CuKa2_analyt(yminymax)          MoKa2(yminymax)
CuKa2(yminymax)                 CuKb4_Holzer(yminymax)
CuKa4_Holzer(yminymax)          CoKb6_Holzer(yminymax)
CuKa5(yminymax)                 CrKb5_Holzer(yminymax)
CuKa5_Berger(yminymax)          FeKb4_Holzer(yminymax)
CoKa3(yminymax)                 MnKb5_Holzer(yminymax)
CoKa7_Holzer(yminymax)          NiKb4_Holzer(yminymax)
CrKa7_Holzer(yminymax)
```

22.2.4 ..... Instrument and instrument convolutions

Radius(rp, rs)

Primary and secondary instrument radii (mm). For most diffractometers rp = rs.

Specimen_Tilt(c, v)

Specimen tilt in mm.

Slit_Width(c, v) or SW(c, v)

Aperture of the receiving slit in the equatorial plane in mm.

Sample_Thickness(dc, dv)

Sample thickness in mm in the direction of the scattering vector.

Divergence(c, v)

Horizontal divergence of the beam in degrees in the equatorial plane.

Variable_Divergence(c, v)
Variable_Divergence_Shape(c, v)
Variable_Divergence_Intensity

Constant illuminated sample length in mm for variable slits (i.e. variable beam divergence). This Variable_Divergence macro applies both a shape and intensity correction.

Simple_Axial_Model(c, v)

Receiving slit length mm for describing peak asymmetry due to axial divergence.

Full_Axial_Model(filament_cv, sample_cv, detector_cv, psol_cv, ssol_cv)

Accurate model for describing peak asymmetry due to axial divergence of the beam.

[filament_cv]: Tube filament length in [mm].

[sample_cv]: Sample length in axial direction in [mm].

[detector_cv]: Length of the detector (= receiving) slit in [mm].

[psol_cv, ssol_cv]: Aperture of the primary and secondary Soller slit in [°].

Finger_et_al(s2, h2)

Finger *et al.*, 1994. model for describing peak asymmetry due to axial divergence.

[s2, h2]: Sample length, receiving slit length.

Tube_Tails(source_width_c, source_width_v, z1_c, z1_v, z2_c, z2_v, 1z2_h_c, z1z2_h_v)

Model for description of tube tails (Bergmann, 2000).

[source_width_c, source_width_v]: Tube filament width in [mm].

[z1_c, z1_v]: Effective width of tube tails in the equatorial plane perpendicular to the X-ray beam - negative z-direction [mm].

[z2_c, z2_v]: Effective width of tube tails in the equatorial plane perpendicular to the X-ray beam - positive z-direction [mm].

[z1_z2_h_c, z1_z2_h_v]: Fractional height of the tube tails relative to the main beam.

UVW(u, uv, v, vv, w, wv)

Cagliotti relation (Cagliotti *et al.*, 1958).

[u, v, w]: Parameter names.

[uv, vv, wv]: Halfwidth value.

22.2.5 ..... Phase peak_type's

PV_Peak_Type(ha, hav, hb, hbv, hc, hcv, lora, lorav, lorb, lorbv, lorc, lorcv)
TCHZ_Peak_Type(u, uv, v, vv, w, wv, z, zv, x, xv, y, yv)
PVII_Peak_Type(ha, hav, hb, hbv, hc, hcv, ma, mav, mb, mbv, mc, mcv)

Pseudo-Voigt, TCHZ pseudo-Voigt and PearsonVII functions. For the definition of the functions and function parameters refer to section 5.2.

22.2.6 ..... Quantitative Analysis

Apply_Brindley_Spherical_R_PD(R, PD)

Applies the Brindley correction for quantitative analysis (Brindley, 1945).

MVW(m_v, v_v, w_v)

Returns cell mass, cell volume and weight percent.

22.2.7 ..... 2Th Corrections

Zero_Error or ZE(c, v)

Zero point error.

Specimen_Displacement(c, v) or SD(c, v)

Specimen displacement error.

22.2.8 ..... Intensity Corrections

LP_Factor(c, v)

Lorentz and *L*orentz-Polarisation factor.

[c, v]: Monochromator angle in [°2θ]

Values for most common monochromators (Cu radiation) are:

Ge	: 27.3°
Graphite	: 26.4°
Quartz	: 26.6°

Lorentz_Factor

Lorentz factor for fixed wavelength neutron data.

Surface_Roughness_Pitschke_et_al(a1c, a1v, a2c, a2v)
Surface_Roughness_Suortti(a1c, a1v, a2c, a2v)

Suortti and Pitschke *et al*. intensity corrections each with two parameters a1 and a2.

Preferred_Orientation(c, v, ang, hkl) or PO(c, v, ang, hkl)

Preferred orientation correction based on March (1932).

[c, v]: March parameter value.

[ang, hkl]: Lattice direction.

PO_Two_Directions(c1, v1, ang1, hkl1, c2, v2, ang2, hkl2, w1c, w1v)

Preferred orientation correction based on March (1932) considering two preferred orientation directions.

[c1, v1]: March parameter value for the first preferred orientation direction.

[ang1, hkl1]: Parameter name and lattice plane for the first preferred orientation direction.

[c2, v2]: March parameter value for the second preferred orientation direction.

[ang2, hkl2]: Lattice direction for the second preferred orientation direction.

[w1c, w1v]: Fraction of crystals oriented into first preferred orientation direction.

PO_Spherical_Harmonics(sh, order)

Preferred orientation correction based on spherical harmonics according to Järvinen (1993).

[(sh, order)]: Parameter name, spherical harmonics order.

22.2.9 ..... Bondlength penalty functions

Anti_Bump(ton, s1, s2, ro, wby)
AI_Anti_Bump(s1, s2, ro, wby, num_cycle_iters), AI_Anti_Bump(s1, s2, ro, wby)

Applies a penalty function as a function of the distance between atoms. The closer the atoms are the higher the penalty is.

[ton]: Sets to_N of box_interaction.

[s1, s2]: Sites.

[ro]: Distance.

[wby]: Relative weighting given to the penalty function.

For more details refer to box_interaction and ai_anti_bump.

Parabola_N(n1, n2, s1, s2, ro, wby)

Applies a penalty function as a function of the distance between atoms. The closer the atoms are the higher the penalty is.

[n1]: The closest n1 number of atoms of type s2 is soft constrained to a distance ro away from s1 .

[n2]: The closest n2 number of atoms of type s2 (excluding the closest n1 number of atoms of type s2) is repelled from s1, for distances between s1 and s2 less than ro.

[s1, s2]: Sites.

[ro]: Distance.

[wby]: Relative weighting given to the penalty function.

Grs_Interaction(s1, s2, wqi, wqj, c, ro, n)

Penalty function applying the GRS series according to Coelho & Cheary (1997).

[s1, s2]: Sites.

[wqi, wqj]: Valence charge of the atoms.

[c]: Name of the GRS.

[ro]: Distance.

[n]: The exponent of the repulsion part of the Lennard-Jones potential.

For more details refer to grs_interaction.

Grs_No_Repulsion(s1, s2, wqi, wqj, c)

Used for calculating the Madelung constants.

[s1, s2]: Sites.

[wqi, wqj]: Valence charge of the atoms.

[c]: Name of the GRS.

Grs_BornMayer(s1, s2, wqi, wqj, c, ro, b)

Uses the GRS series with a Born-Mayer equation for the repulsion term.

[s1, s2]: Sites.

[wqi, wqj]: Valence charge of the atoms.

[c]: Name of the GRS.

[ro]: Mean distance.

[b]: b-constant for the repulsion part of the Born-Mayer potential.

Distance_Restrain(sites, t, t_calc, tol, wscale)
Angle_Restrain(sites, t, t_calc, tol, wscale)
Flatten(sites, t_calc, tol, wscale)
Distance_Restrain_Keep_Within(sites, r, wby, num_cycle_iters)
Distance_Restrain_Keep_Out(sites, r, wby, num_cycle_iters)

Applies penalties restraining distances and angles between sites. 'sites' must comprise two sites for the distance restraints and three for the angle restraints. For Flatten, 'sites' must contain more than three sites. wby is a scaling constant applied to the penalty.

Keep_Atom_Within_Box(size).

Applies a min/max constraints such that the present site cannot more outside of a box with a length of 2*size.

22.2.10..... Reporting macros

Create_2Th_Ip_file(file)

Creates a file with positions (2θ) and intensities.

Create_d_Ip_file(file)

Creates a file with positions (d) and intensities.

Create_hklm_d_Th2_Ip_file(file)

Creates a file with the following information for each peak: h, k, l, multiplicity, positions d and 2θ and intensities.

Out_Yobs_Ycalc_and_Difference(file)

Outputs the x-axis, *Yobs*, *Ycalc* and difference.

Out_X_Yobs(file), Out_X_Ycalc(file), Out_X_Difference(file)

Outputs the x-axis, *Yobs*, *Ycalc* and difference to files.

Out_F2_Details(file), Out_A01_A11_B01_B11(file)

Outputs structure factor details, see section 20.9.2.

Out_FCF(file)

Outputs a CIF file representation of structure factor details suitable for generating Fourier maps using ShelX..

Out_CIF_STR(file)

Outputs structure details in CIF format.

Absorption_With_Sample_Thickness_mm_Shape_Intensity(u, uv, d, dv)

Corrects the peak intensity for absorption effects.

[u, uv]: Parameter name, absorption coefficient in cm-1.

[d, dv]: Parameter name, sample thickness in [mm].

CS_L(c,v) or Crystallite_Size(c, v) or CS(c, v)

Applies a Lorentzian convolution with a FWHM that varies according to the relation lor_fwhm = 0.1 Rad Lam / (c Cos(*Th*)).

[c, v]: Parameter name, crystallite size in [nm].

CS_G(c, v)

Applies a Gaussian convolution with a FWHM that varies according to the relation

```
gauss_fwhm = 0.1 Rad Lam / (c Cos(Th));
```

[c, v]: Parameter name, crystallite size in [nm].

Strain_L(c, v) or Microstrain(c, v) or MS(c, v)

Applies a Lorentzian convolution with a FWHM that varies according to the relation lor_fwhm = c Tan(*Th*).

Strain_G(c, v)

Applies a Gaussian convolution with a FWHM that varies according to the relation gauss_fwhm = c Tan(*Th*).

LVol_FWHM_CS_G_L(k, lvol, kf, lvolf, csgc, csgv, cslc, cslv)

Calculates FWHM and IB (integral breadth) based volume-weighted column heights (LVol). For details refer to section 20.13.

[k, lvol]: shape factor (fixed to 1), integral breadth based LVol.

[kf, lvolf]: shape factor (defaults to 0.89), FWHM based LVol.

[csgc, csgv]: Parameter name, Gaussian component.

[cslc, cslv]: Parameter name, Lorentzian component.

22.2.11..... Neutron TOF

TOF_XYE(path, calc_step), TOF_GSAS(path, calc_step)

Includes the neutron_data keyword and the calculation step size.

TOF_LAM(w_ymin_on_ymax)

Defines a simple emission profile suitable for TOF data

TOF_x_axis_calibration(t0, t0v, t1, t1v, t2, t2v)

Writes the pk_xo equation in terms of the three calibration constants t0, t1, t2 converting d-spacing to x-axis space.

TOF_Exponential(a0, a0v, a1, a1v, wexp, t1, lr)

An exponential convolution applied to the TOF peaks - see example TOF_BANK2_1.INP.

TOF_CS_L(c, v, t1), TOF_CS_G(c, v, t1)

Lorentzian and Gaussian components for crystallite size. t1 is the calibration constant appearing in the argument of the macro TOF_x_axis_calibration.

TOF_PV(fwhm, fwhmv, lor, lorv, t1)

A pseudo-Voigt used to describe the instrumental broadening t1 is the calibration constant appearing in the argument of the macro TOF_x_axis_calibration, see examples TOF_BALZAR_BR1.INP and TOF_BALZAR_SH1.INP.

22.2.12..... Miscalleneous

Temperature_Regime

Defines a temperature regime. See the temperature keyword.

STR(sg)

Signals the start of structure information with a space group of sg.

Exclude

Defines excluded regions. See exclude.

Decompose(diff_toll)

Decompose a diffraction pattern comprising data points at peak positions only. Data points closer than diff_toll to another data point is not included. Decompose also sets x_calculation_step to the value of diff_toll.

ADPs_Keep_PD

Mixture_LAC_1_on_cm(mlac)

Phase_Density_g_on_cm3(pd)

Phase_LAC_1_on_cm(u)

Gauss(xo, fwhm), Lorentzian(xo, fwhm)

An equation defines a unit area Gaussian or Lorentzian with a position of xo and a FWHM of fwhm

23. INDEXING

The following algorithm is based on the iterative method of Coelho (2003). Unlike lp_serach it requires the extraction of d-spacings. The INDEXING directory contains example INP files, example usage is as follows:

```
index_zero_error
try_space_groups "2 75"
load index_d {
   8.912
   7.126
   4.296
   ...
}
```

Individual space groups can be tried or for simplicity all Bravais lattices can be tried using standard macros as follows:

```
Bravais_Cubic_sgs
Bravais_Trigonal_Hexagonal_sgs
Bravais_Tetragonal_sgs
Bravais_Orthorhombic_sgs
Bravais_Monoclinic_sgs
Bravais_Triclinic_sgs
```

To try all unique extinction subgroup space-groups, a more exhaustive approach, then the following macros can be used:

```
Unique_Cubic_sgs
Unique_Trigonal_Hexagonal_sgs
Unique_Tetragonal_sgs
Unique_Orthorhombic_sgs
Unique_Monoclinic_sgs
Unique_Triclinic_sgs
```

On termination of Indexing a *.NDX file is created, with a name corresponding to the name of the INP file and placed in the same directory as the INP file. The *.NDX file contains solutions as well as a detailed summary of the best 20 solutions. Here's an example of an NDX file:

```
' Indexing method - Alan Coelho (2003), J. Appl. Cryst. 36, 86-95
' Time: 2.015 seconds
     'Sg     Status UNI      Vol       Gof     Zero      Lps ...
Indexing_Solutions_With_Zero_Error_2 {
   0) P42/nmc    3   0    1187.321    38.82   0.0000    11.1924  ...
   1) P42/nmc    3   0    1187.057    38.64   0.0000    11.1896  ...
   2) P42/nmc    3   0    1187.458    38.61   0.0000    11.1914  ...
    ...
}
/*
=============================================================================
   0) P-1         0     985.652    30.80   0.0111     7.0877  ...

   h   k   l       dc       do    do-dc     2Thc     2Tho   2Tho-2Thc
   0   0   1   15.857   15.830   -0.027    5.569    5.578    0.009
```

```
          0   1   0    8.765    8.750   -0.015   10.084   10.101    0.017
           ...
       */
```

23.1 ... Figure of merit

The figure of merit *M* used in indexing is as follows:

$$M = \left[(1 + N_{uni}) d^2_{o,min} \left(\frac{N_c}{N_o} \right) \sum_i \left| d^2_{o,i} - d^2_{c,i} \right| Q_i \right]^{-1} \qquad \text{(23-1)}$$

$$\text{where} \quad Q_i = w_i N_o / \sum_j w_j$$

Where d_o and d_c are the observed and calculated d-spacings, N_o and N_c the number of observed and calculated lines used, N_{uni} the number of unindexed lines and the summations are over the used observed indexing lines. Q_i is a weighting that assists in the determination of extinction subgroups where w_i could for example be the inverse of the error in the peak positions from a Pawley refinement (see INDEXING\MGIR\INDEX.INP). index_I correspond to w_i. The formulation of Q_i is such that with or without Q_i the figure of merit *M* is of the same order of magnitude. The reciprocal-space lattice relationship solved during the indexing process (Coelho, 2000) includes *Q* as follows:

$$\left[X_{hh} h^2 + X_{kk} k^2 + X_{ll} l^2 + X_{hk} h\, k + X_{hl} h\, l + X_{kl} k\, l + \frac{4\,\pi Z_e}{360 \lambda^2} sin(2\theta) \right] W_{hkl} = \frac{W_{hkl}}{d^2_o} \qquad \text{(23-2)}$$

$$\text{where} \quad W_{hkl} = Q_{hkl} d^m_o |\Delta 2\theta_{hkl}|$$

23.2 ... Extinction subgroup determination

At the end of an indexing run further indexing runs are internally performed across extinction subgroups (see section 14.8) to determine the most likely subgroup. These internal runs are seeded with already determined lattice parameters and in most cases the correct extinction subgroup is obtained without the need for Q_i in Eq. (14-1). Extinction subgroups can be explicitly searched using the macros defined TOPAS.INC, see for example Unique_Orthorhombic_sgs.

23.3 ... Reprocessing solutions - DET files

Details of solutions can be obtained at a later stage by including solution lines, found in the NDX file, in the INP file. For example, supposing details of solutions 50 and 51 were sought then the following (see example INDEXING\EX10.INP) could be used:

```
index_lam 1.540596
index_zero_error
try_space_groups 2
Indexing_Solutions_With_Zero_Error_2 {
  50) P-1        1   0    2064.788     9.74   0.0000   ...
  51) P-1        3   0    3128.349     9.61   0.0115   ...
}
load index_d {
   15.83 good
    8.75
    7.91
    ...
}
```

After running this INP file, a *.DET file is created containing details of the supplied solutions.

23.4 ... Keywords and data structures

Tindexing
[index_lam !E1.540596]
[index_min_lp !E2] [index_max_lp !E]
[index_max_Nc_on_No !E5]
[index_max_number_of_solutions #3000]
[index_max_th2_error !E0.05]
[index_max_zero_error #0.2]
[index_th2 !E | index_d !E]...
[index_I E1 [good]]
[index_x0 !E]
[index_zero_error]
[no_extinction_subgroup_search]
[seed [#]]
[try_space_groups $]...
[x_angle_scaler #0.1]
[x_scaler #]

Values for most keywords are automatically determined or have defaults (appearing as numbers to the right) adequate for difficult indexing problems. In the following example from UPPW (service provided by Armel Le Bail to the SDPD mailing list at http://sdpd.univ-lemans.fr/uppw/), only a few keywords are necessary. Also note the use of dummy; this allows for the exclusion of 2θ and I values without having to edit the columns of data.

```
seed
index_lam  0.79776
index_zero_error
index_max_Nc_on_No 6
try_space_groups 3
load index_th2 dummy dummy index_I dummy  {
    ' d (A)  2Theta     Height      Area     FWHM
    1.724  26.50645    2758.3   23303.7    0.0450
    2.646  17.27733  150393.8  747063.6    0.0250
    3.235  14.13204   98668.8  493153.7    0.0250
    3.417  13.37776   11102.6   53185.0    0.0250
    5.190   8.80955     782.7    3910.9    0.0250
    ...
}
```

23.5 ... Keywords in detail

[index_lam !E1.540596]

Defines the wavelength in Å.

[index_min_lp !E2.5] [index_max_lp !E]

Defines the minimum and maximum allowed lattice parameters. The maximum is typically automatically determined.

[index_max_Nc_on_No !E5]

Determines the maximum ratio of the number of calculated to observed lines. The value of 6 allows for up to 83% of missing lines.

[index_max_number_of_solutions #1000]

The number of best solutions to keep.

[index_max_th2_error !E0.05]

Used for determining impurity lines (un-indexed lines UNI in *.NDX). Large values, 1 for example, forces the consideration of more observed input lines. For example, if it is known that there are none or maybe just one impurity line then a large value for index_max_th2_error will speed up the indexing procedure.

[index_max_zero_error !E0.2]

Excludes solutions with zero errors greater than index_max_zero_error.

[index_th2 !E | index_d !E]...
[index_I E1 [good]]

index_th2 or index_d defines a reflection entry in 2θ degrees or d-spacing in Å. index_I is typically set to the area under the peak; it is used to weight the reflection. good signals that the corresponding d-spacing is not an impurity line. A single use of good on a large d-

spacing decreases the number of possible solutions and hence speeds up the indexing process (see example INDEXING\EX10.INP).

[index_x0 !E]

Defines X_{hh} in the reciprocal lattice equation of (14-1). In a triclinic lattice the largest d-spacing can probably be indexed as 100 or 200 etc. Thus

```
index_x0 = 1/(dmax)^2;
```

speeds up the indexing process (if, in this case, the first line can be indexed as 100) and additionally the chance of finding the correct solution is enhanced, see EX13.INP. Note, if the data is in 2Th degrees then the following can be used:

```
index_x0 = (2 Sin(2Thmin Pi/360) / wavelength))^2;
```

The two macros Index_x0_from_d and Index_x0_from_th2 simplify the use of index_x0.

[index_zero_error]

Includes a zero error.

[no_extinction_subgroup_search]

By default, Extinction subgroup determination is performed at the end of an indexing run; this can be negated by defining no_extinction_subgroup_search.

[seed [#]]

Seeds the random number generator.

[try_space_groups $]...
[x_angle_scaler #0.1]
[x_scaler #]

Defines the space groups to be searched. The macros Bravais_Cubic_sgs etc... (see TOPAS.INC) defines lowest symmetry Bravais space groups. It is typically sufficient to use only these. Higher symmetry space groups for the Bravais lattices corresponding to the 10 best solutions is automatically searched at the end of an indexing run. Here are some examples of using try_space_groups.

Search	Use
Primitive monoclinic	`try_space_groups 3`
Monoclinic Bravais lattices of lowest symmetry	`Bravais_Monoclinic_sgs`
C-centered monoclinic of lowest symmetry	`try_space_groups 5`
All orthorhombic space groups individually	`Unique_Orthorhombic_sgs`

x_scaler is a scaling factor used for determining the number of steps to search in parameter space. x_scaler needs to be less than 1. Increasing x_scaler searches parameter space in finer detail. Default values are as follows:

Cubic	0.99	Orthorhombic	0.89
Hexagonal/Trigonal	0.95	Monoclinic	0.85
Tetragonal	0.95	Triclinic	0.72

x_angle_scaler is a scaling factor for determining the number of angular steps for monoclinic and triclinic space groups. Small values, 0.05 for example, increases the number of angular steps. The default value of 0.1 is usually adequate.

23.6 ... Identifying dominant zones

Here are two example output lines from an NDX file.

```
0) P42/nmc 3 0 1187.124  38.82 0.000 11.1904 11.1904 9.4799 90.00 90.00 90.00 ' ===  24 19
6) P-421c  3 0 1187.124  35.67 0.000 11.1904 11.1904 9.4799 90.00 90.00 90.00 ' ===  24 19
```

- The 1st column corresponds to the rank of the solution.
- The 2nd corresponds to the space group.
- The 3rd corresponds to the Status of the solution as follows:

  Status 1: Weighting applied as defined in Coelho (2003).

  Status 2: Zero error attempt applied.

  Status 3: Zero error attempt successful and impurity lines removal successful.

  Status 4: Impurity line(s) removed.
- The 4th column corresponds to the number of un-indexed lines.
- The 5th column corresponds to the volume of the lattice.
- The 6th corresponds to the goodness of fit value.
- The 7th corresponds to the zero error if index_zero_error is included.
- Columns 8 to 13 contains the lattice parameters.

The last two columns, let call them column Q_1 and Q_2, contain the number of non-zero ($h^2 + k^2 + h\,k$) and l^2 values, respectively, used in the indexed lines. Q_1 and Q_2 represent the hkl coefficient for X0 and X1 respectively for Trigonal/Hexagonal systems. When Q_1=-999 or Q_2=-999 then the corresponding lattice parameters are not represented. This facility is useful for identifying dominant zones. For example, if the smallest lattice parameter is 3Å and the smallest d-spacings is 4Å then it is impossible to determine the small lattice parameter. In such cases values of –999 will be obtained. The following table gives the hkl coefficients corresponding to the Xnn reciprocal lattice parameters for the 7 crystal systems.

	X0	X1	X2	X3	X4	X5
Cubic	$h^2+k^2+l^2$					
Hexagonal, Trigonal	$h^2+k^2+h\,k$	l^2				

Tetragonal	h^2+k^2	l^2				
Orhtorhombic	h^2	k^2	l^2			
Monoclinic	h^2	k^2	l^2	h l		
Triclinic	h^2	k^2	l^2	h k	h l	k l

23.7 ... *** Probable causes of Failure ***

The most probable cause of failure is the inclusion of too many d-spacings. If it is assumed that the smallest lattice parameter is greater than 3Å then it is problematic to include d-spacings with values less than about 2.5Å when there are already 30 to 40 reflections with d values greater than 2.5Å. Some of the problems caused by very low d-spacings are:

- The number of calculated lines increases dramatically and thus index_max_Nc_on_No will need to be increased.
- The low d-spacings are probably inaccurate due to peak overlap.

A situation where it is necessary to include low d-spacings is when there are only a few d-spacings available as in higher symmetry lattices.

23.8 ... Space groups with identical absences – Extinction subgroups

The following table lists spaces groups than have identical hkls. Typically, an indexing run will identify one space-group from the extinction group.

Space group numbers with identical hkls	Space group symbols with identical hkls
Triclinic	
1 2	P1 P-1
Monoclinic	
9 15	Cc C2/c
5 8 12	C2 Cm C2/m
14	P21/c
7 13	Pc P2/c
4 11	P21 P21/m
3 6 10	P2 Pm P2/m
Orthorhombic	
70	Fddd
43	Fdd2
22 42 69	F222 Fmm2 Fmmm
68	Ccca
73	Ibca
37 66	Ccc2 Cccm
45 72	Iba2 Ibam
41 64	Aba2 Cmca

46 74	Ima2 Imma
36 40 63	Cmc21 Ama2 Cmcm
39 67	Abm2 Cmma
20	C2221
23 24 44 71	I222 I212121 Imm2 Immm
21 35 38 65	C222 Cmm2 Amm2 Cmmm
52	Pnna
56	Pccn
60	Pbcn
61	Pbca
48	Pnnn
54	Pcca
50	Pban
33 62	Pna21 Pnma
34 58	Pnn2 Pnnm
32 55	Pba2 Pbam
30 53	Pnc2 Pmna
29 57	Pca21 Pbcm
27 49	Pcc2 Pccm
31 59	Pmn21 Pmmn
26 28 51	Pmc21 Pma2 Pmma
19	P212121
18	P21212
17	P2221
16 25 47	P222 Pmm2 Pmmm
Tetragonal	
142	I41/acd
110	I41cd
141	I41/amd
109 122	I41md I-42d
108 120 140	I4cm I-4c2 I4/mcm
88	I41/a
80 98	I41 I4122
79 82 87 97 107 119 121 139	I4 I-4 I4/m I422 I4mm I-4m2 I-42m I4/mmm
130	P4/ncc
126	P4/nnc
133	P42/nbc
103 124	P4cc P 4/mcc
104 128	P4nc P 4/mnc
106 135	P42bc P 42/mbc
137	P42/nmc
138	P42/ncm
134	P42/nnm
125	P4/nbm
114	P-421c
105 112 131	P42mc P-42c P42/mmc

102 118 136	P42nm P-4n2 P42/mnm
101 116 132	P42cm P-4c2 P42/mcm
100 117 127	P4bm P-4b2 P4/mbm
86	P42/n
85 129	P4/n P4/nmm
92 96	P41212 P43212
94	P42212
76 78 91 95	P41 P43 P4122 P4322
77 84 93	P42 P 42/m P4222
90 113	P4212 P-421m
75 81 83 89 99 111 115 123	P4 P-4 P4/m P422 P4mm P-42m P-4m2 P4/mmm
Trigonal & Hexagonal	
161 167	R3c R-3c
146 148 155 160 166	R3 R-3 R32 R3m R-3m
184 192	P6cc P6/mcc
159 163 186 190 194	P31c P-31c P63mc P-62c P63/mmc
158 165 185 188 193	P3c1 P-3c1 P63cm P-6c2 P63/mcm
169 170 178 179	P61 P65 P6122 P6522
144 145 151 152 153 154 171 172 180 181	P31 P32 P3112 P3121 P3212 P3221 P62 P64 P6222 P6422
173 176 182	P63 P63/m P6322
143 147 149 150 156 157 162 164 168 174 175 177 183 187 189 191	P3 P-3 P312 P321 P3m1 P31m P-31m P-3m1 P6 P-6 P6/m P622 P6mm P-6m2 P-62m P6/mmm
Cubic	
228	Fd-3c
219 226	F-43c Fm-3c
203 227	Fd-3 Fd-3m
210	F4132
196 202 209 216 225	F23 Fm-3 F432 F-43m Fm-3m
230	Ia-3d
220	I-43d
206	Ia-3
214	I4132
197 199 204 211 217 229	I23 I213 Im-3 I432 I-43m Im-3m
222	Pn-3n
218 223	P-43n Pm-3n
201 224	Pn-3 Pn-3m
205	Pa-3
212 213	P4332 P4132
198 208	P213 P4232
195 200 207 215 221	P23 Pm-3 P432 P-43m Pm-3m

23.9 ... Indexing Equations - Background

a, **b** and **c** lattice vectors can be converted to Cartesian coordinates with **a** collinear with the Cartesian *x* axis and **b** coplanar with the Cartesian *x*-*y* plane as follows:

$$\mathbf{a} = a_x\,\mathbf{i} \qquad \mathbf{b} = b_x\,\mathbf{i} + b_y\,\mathbf{j} \qquad \mathbf{c} = c_x\,\mathbf{i} + c_y\,\mathbf{j} + c_z\,\mathbf{k} \tag{23-3}$$

where

$a_x = a$

$b_x = b\cos(\gamma),\quad b_y = b\sin(\gamma)$

$c_x = c\cos(\beta),\quad c_y = c\,(\cos(\alpha) - \cos(\beta)\cos(\gamma)) / \sin(\gamma),\quad c_z^2 = c^2 - (c_x)^2 - (c_y)^2$

a, b, c are the lattice parameters and α, β, γ the lattice angles. The reciprocal lattice vectors **A**, **B**, and **C** calculated from the lattice vectors of Eq. (14-3) become:

$$\mathbf{A} = A_x\,\mathbf{i} + A_y\,\mathbf{j} + A_z\,\mathbf{k} \qquad \mathbf{B} = B_y\,\mathbf{j} + B_z\,\mathbf{k} \qquad \mathbf{C} = C_z\,\mathbf{k}$$

The equation relating d-spacing d_{hkl} to hkl in terms of the reciprocal lattice parameters is:

$$X_{hh}h^2 + X_{kk}k^2 + X_{ll}l^2 + X_{hk}h\,k + X_{hl}h\,l + X_{kl}k\,l = 1/d_{hkl}^2 \tag{23-4}$$

where

$$X_{hh} = A_x^2 + A_y^2 + A_z^2 \qquad X_{hk} = 2A_yB_y + 2A_zB_z$$
$$X_{kk} = B_y^2 + B_z^2 \qquad X_{hl} = 2A_zC_z$$
$$X_{ll} = C_z^2 \qquad X_{kl} = 2B_zC_z$$

24. CHARGE-FLIPPING

The charge-flipping method of Oszlányi & Süto (2004) has been implemented (Coelho, 2007) using the keywords shown in Table 24-2. Also included is the use of the tangent formula (Hauptman & Karle, 1956) within the iterative charge-flipping process. Equations appearing in charge-flipping keywords can be functions of the items shown in Table 24-1. At the end of a charge flipping process a file with the same name as that given by cf_hkl_file is created but with a *.FC extension. Almost all charge-flipping keywords can be equations allowing for great flexibility in-regards to changing resolution etc... on the fly. Table 24-3 lists charge-flipping examples found in the CF directory.

Table 24-1. Items that can be used in charge-flipping equations

Get(Aij) Get(alpha_sum) Get(density) Get(cycles_since_last_best) Get(d_squared_inverse) Get(initial_phase) Get(iters_since_last_best) Get(F000) Get(max_density) Get(max_density_at_cycle_iter_0) Get(num_reflections_above_d_min) Get(phase_difference) Get(r_factor_1), Get(r_factor_2) Get(threshold)	These are updated internally each charge-flipping iteration or cycle or when needed.
Reserved parameter names: *Cycle_Iter*, *Cycle*, *Iter*, *D_spacing*	
Macros (see TOPAS.INC) Ramp, Ramp_Clamp, Cycle_Ramp, Tangent, Restart_CF, Pick, Pick_Best Out_for_cf(file) : Outputs the A matrix from a Pawley refinement for use in charge flipping; uses cf_in_A_matrix. See example CF-CIME-PAWLEY.INP.	

Table 24-2. Keywords that can be used in charge-flipping.

charge_flipping	**Default**
[a !E b !E c !E [al !E] [be !E] [ga !E]	al = be = ga = 90
[cf_hkl_file $file]	
[cf_in_A_matrix $file]	
[scale_Aij !E]	Get(Aij)^2
[break_cycle_if_true !E]	
[delete_observed_reflections !E]	
[extend_calculated_sphere_to !E]	
[f_atom_type $type f_atom_quantity !E]...	
[find_origin !E]	1

[fraction_density_to_flip !E]	0.75
[fraction_reflections_weak !E]	0
[min_d !E]	0
[min_grid_spacing !E]	
[neutron_data]	
[space_group $]	*P1*
[use_Fc]	
Electron density perturbations	
[flip_equation !E]	
[flip_regime_2 !E]	
[flip_regime_3 !E]	
[histogram_match_scale_fwhm !E]	
[hm_size_limit_in_fwhm !E]	1
[hm_covalent_fwhm !E]	1
[pick_atoms $atoms]...	
[activate !E]	1
[choose_from !E]	
[choose_to !E]	
[choose_randomly !E]	
[omit !E]	
[displace !E]	
[insert !E]	
[scale_density_below_threshold !E]	
[symmetry_obey_0_to_1 !E]	
Phase perturbations	
[add_to_phases_of_weak_reflections !E]	
[randomize_phases_on_new_cycle_by !E]	0
[set_initial_phases_to $file]	
[modify_initial_phases !E]	
[tangent_num_h_read !E]	
[tangent_num_k_read !E]	
[tangent_num_h_keep !E]	
[tangent_max_triplets_per_h !E]	30
[tangent_min_triplets_per_h !E]	1
[tangent_scale_difference_by !E]	1
[tangent_tiny !E]	0.01
Miscellaneous	
[apply_exp_scale !E]	1
[correct_for_atomic_scattering_factors !E]	1
[correct_for_temperature_effects !E]	1
[hkl_plane $hkl]...	
[randomize_initial_phases_by !E]	Rand(-180,180)
[scale_E !E]	1

[scale_F !E]	1
[scale_F000 !E]	0
[scale_weak_reflections !E]	
[user_threshold !E]	
[verbose #]	1
GUI Related	
[add_to_cloud_N !E [add_to_cloud_when !E]]	
[pick_atoms_when !E]	
[view_cloud !E]	1

24.1 ... Charge-flipping usage

CF works well on data at good resolution (<1Å resolution). For data at poor resolution or for difficult structures then inclusion of the tangent formula can facilitate solution and sharpen electron densities, see example CF-1A7Y.INP. Powder diffraction data usually fall under the poor resolution/data quality category and as such additional symmetry restraints using symmetry_obey_0_to_1 can sharpen electron densities. Example CF-ALVO4.INP demonstrates the use of the tangent formula on powder data.

The choice and amount of perturbation necessary for finding a solution are important considerations. Not enough perturbation leads to the system being trapped within a local parameter space; too much perturbation may lead to a solution not being found and in addition contrast in R-factors prior to and at convergence are diminished; this leads to difficult to identify solutions. Many of the examples in the CF directory use the Ramp macro to gradually vary control parameters, here are some examples:

```
fraction_density_to_flip = Ramp(0.85, 0.8, 100);
fraction_reflections_weak = Ramp(0.5, 0, 100);
flip_regime_2 = Ramp(1, 0, 200);
flip_regime_3 = Ramp(0.25, 0.5, 200);
symmetry_obey_0_to_1 = Ramp(0.5, 1, 100);
tangent_scale_difference_by = Ramp(0, 1, 100);
```

Choosing control parameters in this manner gradually decreases perturbation allowing for solutions to be found and identified. This is similar-to a simulated annealing process where temperatures start at high values and are then progressively lowered.

24.1.1 ..... Perturbations

Perturbations can be categorized as being of either phase, structure factor intensity or electron density perturbations as shown in Table 24-2. There are two built in flipping regimes, flip_regime_2 and flip_regime_3, and one user defined regime flip_equation. Only one can be used, and they all modify the electron density. In the absence of a flipping regime, the following is used where δ corresponds to the electron density threshold.

$$\rho = \begin{cases} -\rho & for\ \rho < \delta \\ \rho & for\ \rho \leq \delta \end{cases} \quad (24\text{-}1)$$

Using the tangent formula on either difficult structures or on data at poor resolution often leads to uranium atom solutions. Uranium atom solutions can be avoided by modifying the electron density using a flipping regime that dampens high electron densities or by using pick_atoms.

Using a large number of triplets per E_h value (a value for tangent_max_triplets_per_h greater than 100) reduces perturbation, increases occurrences of uranium atom solutions, and increases the chances of finding a solution after an initial phase randomization. A large number of triplets, would typically be used for poor resolution data; correspondingly a flipping regime that avoids uranium atom solutions should be chosen. Perturbations mostly increase randomness in the system with the exceptions of the tangent formula, scale_density_below_threshold and histogram_match_scale_fwhm.

24.1.2 ..... The Ewald sphere, weak reflections and CF termination

By default, CF uses the minimum observed *d* spacing to define the Ewald sphere; alternatively, min_d can be used. The Ewald sphere can be increased using extend_calculated_sphere_to; this inserts missing reflections and gives them the status of "weak". Weak reflections are also inserted for missing reflections within the Ewald sphere. Weak reflection phases and structure factors can be modified using scale_weak_reflections and add_to_phases_of_weak_reflections.

Reflections that have zero intensities according to the space group are not included in CF; correspondingly the number of observed reflections removed are reported. Structure factor intensities within a family of reflections are determined by averaging the observed structure factors intensities. This averaging is also performed on calculated intensities each CF iteration for weak reflections.

Changing the space group is possible; changing the space group to a higher symmetry from that as implied in the input hkl file often makes sense. Changing the space group to a lower symmetry implies less symmetry and is useful for checking whether a significantly better R-factor is realized.

Typically, a fraction of observed reflections is given the status of "weak" using fraction_reflections_weak. When a solution is found and CF terminates, a *.FC file is saved; this file comprises structures factors that produced the best R-factor. A new CF process can be initiated with phase information saved in the *.FC file using the Restart_CF macro. To further complete the structure, the new CF process may for example reduce perturbations to sharpen the electron density.

24.1.3 ..... Powder data considerations

For powder data it is usually best to maximize the number of constraints due to poor data quality; it is also best to use *.A files as generated by a Pawley refinement and to then use cf_in_A_matrix. No weak observed reflections within the observed Ewald sphere should be assigned by setting fraction_reflections_weak to zero. Instead, weak reflections can be included by extending the Ewald sphere with something like:

```
    extend_calculated_sphere_to 1
    add_to_phases_of_weak_reflections = 90 Ramp(1, 0, 100);
```

If the Ewald sphere is extended such that the weak reflections are many then some of these weak reflections could well be of high intensity. Subsequently offsetting high intensity weak reflections by a constant could lead to too much perturbation and thus the following may be preferential:

```
    extend_calculated_sphere_to 1
    add_to_phases_of_weak_reflections = Rand(-180,180) Ramp(1, 0, 100);
```

In a Pawley refinement the calculated intensities at the low *d*-spacing edge are often in error to a large extent; it is therefore best to remove these reflections using delete_observed_reflections, for example:

```
    delete_observed_reflections = D_spacing < 1.134;
```

A typical first try INP file template for powders is as follows:

```
    macro Nr { 100 }
    charge_flipping
        cf_in_A_matrix PAWLEY_FILE.A
        space_group $
        a # b # c al # be # ga #
        delete_observed_reflections = D_spacing < #;
        extend_calculated_sphere_to #
        add_to_phases_of_weak_reflections = 90 Ramp(1, 0, Nr);
        flip_regime_2 = Ramp(1, 0, Nr);
        symmetry_obey_0_to_1 = Ramp(0.5, 1, Nr);
        Tangent(0.3, 30)
        min_grid_spacing 0.3
        load f_atom_type f_atom_quantity { ... }
```

24.1.3.1..... Powder data, the A matrix and the Tangent formula

In the case of charge-flipping from powder data TOPAS uses the diagonally normalized A-matrix cf_in_A_matrix (see example CF\CF-CIME.INP), which we will call **D,** from a Pawley refinement (see example CF\CF-CIME-PAWLEY.INP) to modify normalized structure factors $\mathbf{E}_h$ calculated during the charge-flipping process; this produces better results than using reflections output in a SHELX format (Whitfield & Coelho, 2016). Equation (24-2) shows how the structure factors are modified.

$$\mathbf{E}_{h,calc,modified} = \mathbf{E}_{h,calc}\sqrt{\frac{I_{obs,h,w}}{I_{calc,h,w}}} \qquad (24\text{-}2)$$

$$\text{where} \quad I_{calc,h,w} = \sum_k \mathrm{D}^2_{h,k}\, I_{calc,k} \quad \text{and} \quad I_{obs,h,w} = \sum_k \mathrm{D}^2_{h,k}\, I_{obs,k}$$

The subscripts *h* and *k* correspond to reflections *h* and *k* respectively and the summation in *k* is over all reflections. $I_{calc,k}$ and $I_{obs,k}$ corresponds to observed and calculated intensities. Equation (1) modifies the calculated intensities to include intensities from overlapping peaks.

When there's no overlap $D_{i,i}$=1 and $D_{i,j}$=0 and the calculated intensities as well as $\mathbf{E}_h$ are not modified. When using the direct-methods tangent formula within the charge-flipping process as described by Coelho (2007), the **D** matrix is also used to modify E_h values used in triple phase relationships as shown in equation (2).

$$E_{obs,h,modified} = E_{obs,h}q_h + E_{calc,h}(1 - q_h) \qquad (24\text{-}3)$$
$$\text{where} \quad q_h = \sum_k \mathrm{D}_{h,k}^2$$

$E_{obs,h}$ and $E_{calc,h}$ corresponds to tangent formula E_h values calculated from the observed and calculated intensities respectively. $E_{calc,h}$ is typically not used in the tangent formula, however, intensities used for determining $E_{obs,h}$ can be grossly in error due to peak overlap. Equation (2) therefore influences triple phase relationships by weighing $E_{obs,h}$ by q_h; when there's no overlap q_h=1 resulting in no modification. When there's significant overlap then q_h is small and the influence of triple phase relationships using the h reflection is reduced. Equation (2) also includes a (1-q_h) portion of $E_{calc,h}$ thus stating that when there's significant overlap the calculated E_h is to be more trustworthy than the observed E_h. Equation (24-3) corrects for errors in E_h when I_{obs} is similar-to I_{calc}; this assists in reducing the goodness of fit value thus enhancing the chances of solving the structure.

24.1.3.2..... The algorithm of Oszlányi & Süto (2005) and F000

Normalized structure factors enhance the chances of finding a solution (Oszlányi & Süto, 2006) and are realized by inclusion of f_atom_type's and when correct_for_temperature_effects is non-zero. Example CF-1A7Y-GABOR.INP implements the algorithm of Oszlányi & Süto (2005) with normalized structure factors. In the original algorithm the amount of charge flipped is a function of the maximum electron density; this can be realized using:

```
user_threshold = 0.2 Get(max_density_at_cycle_iter_0);
```

Get(max_density_at_cycle_iter_0) is a different value at the start of each CF process as phases are chosen randomly. An alternative means of defining the threshold is:

```
fraction_density_to_flip 0.83
```

The CF process is sensitive to the threshold value. A value of 0.83 for fraction_density_to_flip is optimum for 1A7Y and produces a solution in ~1000 iterations. A solution is not found however at 0.75 or 0.85. To overcome this sensitivity the fraction_density_to_flip parameter could be ramped as a function of iteration from a high value to a low value, or,

```
fraction_density_to_flip = Ramp(0.85, 0.8, 100);
```

Implementation of such a ramp solves 1a7y in ~2000 iterations.

F000 is allowed to float when scale_F000 is set to 1. In the Oszlányi & Süto (2005) algorithm, a floating F000 produces the best results for some structures but not for others (see section 24.2.3). When the electron density is perturbed then a floating F000 often produces unfavourable oscillations in R-factors. In general, the electron density is best left unperturbed when

scale_F000 is non-zero. Example CF-1A7Y-GABOR.INP does not seem to solve at a lower resolution, try for example:

```
        delete_observed_reflections = D_spacing < 1.1;
```

On the other hand, when scale_F000 is zero then electron density perturbations are possible; CF_1A7Y.INP solves 1A7Y at 1.1 Angstrom (include "delete_observed_reflections = *D_spacing* < 1.1"); CF_1A7Y.INP uses flip_regime_2 and the tangent formula.

24.2 ... Charge-flipping Investigations / Tutorials

The effects of CF keywords can be investigated by inclusion/exclusion of keywords or by changing equations. This section lists some investigative examples and highlights the use of keywords necessary to solve examples found in the CF directory.

24.2.1 ..... Preventing uranium atom solutions using pick_atoms

Example CF-1A7Y-OMIT.INP uses pick_atoms to modify the peaks of the highest intensity atoms, or,

```
        pick_atoms *       choose_to 5    omit = Rand(1, 1.1);
```

This example additionally uses the tangent formula and 1A7Y solves in ~100 iterations and with a large contrast in R-factors before and at convergence. Another means to modify the peaks are:

```
        pick_atoms *       choose_to 5    insert = Rand(-.1, 1);
```

The insert case is slightly slower than the omit case as the 5 atoms are first omitted before insertion. Each case however solves 1A7Y in a similar number of iterations.

Example CF-1A7Y-NO-TANGENT.INP is similar but without the tangent formula, 1A7Y in this case solves in ~1000 iterations.

24.2.2 ..... The tangent formula on powder data

In CF-ALVO4.INP comment out the Tangent line as follows:

```
        ' Tangent(.5, 50)
```

Run CF-ALVO4.INP and turn on Octahedra viewing in the OpenGL window. Visual inspection of picked atoms should show electron densities that are not recognizable as correct solutions.

Include the Tangent line and rerun; after a minute or two and at the bottom of the Ramps visual inspection of picked atoms should show a well-defined solution.

Thus, use of the tangent formula assists in solving CF-ALVO4.INP.

24.2.3 ..... Pseudo symmetry – 441 atom oxide

CF works well on pseudo symmetric structures (Oszlányi *et al.*, 2006). Example CF-PN-02.INP is an oxide structure that contains 441 atoms in the asymmetric unit (Lister *et al.*, 2004); run CF to convergence. Pick atoms and turn on Octahedra viewing; all polyhedra should be well formed. Thus, CF works extremely fast and trivializes the solving of such structures. The contents of the INP file is as follows:

```
charge_flipping
    cf_hkl_file 020pn.hkl
    space_group Pn
    a 24.1332  b 19.5793  c 25.1091  be 99.962
    fraction_reflections_weak 0.4
    symmetry_obey_0_to_1 0.3
    Tangent(0.25, 30)
    load f_atom_type f_atom_quantity {
        MO = 42 2;
        P  = (126 - 42) 2;
        O  = (441 - 126) 2;
    }
```

The tangent formula is used to assist symmetry_obey_0_to_1 and to assist in finding the solution faster; it is not necessary however for this example. The Oszlányi & Süto (2005) algorithm can be used by replaceing symmetry_obey_0_to_1 and the Tangent line with the following:

```
scale_F000 1
fraction_reflections_weak 0.4
add_to_phases_of_weak_reflections 90
user_threshold = 0.15 Get(max_density_at_cycle_iter_0);
```

Slow convergence is observed due to the use of F000. This is opposite to the case of 1a7y in CF-1A7Y-GABOR.INP where F000 is necessary. Setting scale_F000 to zero greatly increases the rate of convergence.

24.2.4 ..... Origin finding and symmetry_obey_0_to_1

When symmetry_obey_0_to_1 is defined origin finding is performed each iteration of charge flipping. Symmetry elements of the space group are used in finding an origin. On finding an origin the electron density is shifted to a position that best matches the symmetry of the space group. Additionally, a restraint is placed on the electron density pixels forcing symmetry to be obeyed.

Run CF-AE14.INP to convergence; notice the *P-1* symmetry. Remove symmetry_obey_0_to_1 and run to convergence; the origin should now be arbitrary.

24.2.5 ..... symmetry_obey_0_to_1 on poor resolution data

Run CF-AE5.INP until a solution is found; terminate CF, this saves the phase information to the file AE5.FC. Copy AE5.FC to AE5-SAVE.FC. Place the following lines into the file CF-AE5-POOR.INP:

```
set_initial_phases_to ae5-save.fc
randomize_initial_phases_by 0
```

This simply starts CF with optimum phase values. Also include the following line:

```
symmetry_obey_0_to_1 0.75
```

Run CF-AE5-POOR.INP; the atom positions after picking should visually produce the correct result. Comment out symmetry_obey_0_to_1 and rerun CF-AE5-POOR.INP. R-factors should diverge and picked atoms should show a non-solution. Thus, symmetry_obey_0_to_1 assists in solving CF-AE5-POOR.INP.

Include symmetry_obey_0_to_1 and remove set_initial_phases_to and randomize_initial_phases_by and then rerun CF-AE5-POOR.INP. A solution should be obtained in a few minutes. Note that in this example the default flipping regime leads to regular occurrences of uranium atom solutions; this can be trivially ascertained by viewing the electron density. To reduce the occurrences of uranium atom solutions the following flipping regime is used:

```
flip_regime_3 0.5
```

24.2.6 ..... Sharpening clouds - extend_calculated_sphere_to

Example CF-AE9-POOR.INP demonstrates the limit to which the present CF implementation can operate. Single crystal data is purposely chosen to isolate resolution effects and not intensity errors. The tangent formula is critical where without it the CF process is extremely perturbed and unstable. 'flip_regime_3 0.5' is used due to occurrences of uranium atom solutions.

There are no ramps, instead the CF process is restarted when the R-factor fails to decrease for 100 consecutive iterations, or,

```
break_cycle_if_true = Get(iters_since_last_best) > 100;
randomize_phases_on_new_cycle_by = Rand(-180, 180);
```

Half of the observed reflections are considered weak and additionally missing reflections up to 1 Angstrom are included and considered weak using:

```
fraction_reflections_weak 0.5
extend_calculated_sphere_to 1
```

The intensities of weak reflections are left untouched and instead a Pi/2 phase shift is randomly applied to ~30% of weak reflections as follows:

```
add_to_phases_of_weak_reflections = If(Rand(0, 1) < .3, 90, 0);
```

A symmetry_obey_0_to_1 of 0.7 is used not merely to find an origin but rather to prevent the electron density from straying.

Run CF-AE9-POOR.INP and a solution should be clearly recognizable after a few minutes. Change/remove keywords and rerun to view effects. Examples CF-CIME-POOR.INP and CF-AE5-POOR.INP are similar.

24.2.7 ..... A difficult powder, CF-SUCROSE.INP

CF-SUCROSE.INP without scale_density_below_threshold=0 exhibits large oscillations in R-factors resulting in difficult to identify solutions; this can be prevented by increasing the amount of charge flipped and including scale_density_below_threshold=0, for example

```
fraction_density_to_flip 0.83
scale_density_below_threshold 0
```

When scale_density_below_threshold=0 is used the percentage of charge that is less than the threshold before the application of scale_density_below_threshold is reported; the difference between this reported value and (1-fraction_density_to_flip) gives the flipped pixels that survived scale_density_below_threshold. At fraction_density_to_flip of 0.83 approximately 23% of pixels survives scale_density_below_threshold=0 which in effect means that only 23% of pixels are flipped out of the original 83%.

The following can be used to omit 30% of atoms:

```
pick_atoms *
    activate = Cycle_Iter == 0;
    insert = If(Rand(0, 1) > 0.3, 10, 0);
```

Note that atoms are inserted at an intensity that is 10 times the average intensity. This increases the weight of inserted atoms relative to electron density noise. It also initially gives more weight to weak reflections.

Use of scale_density_below_threshold often results in CF requiring more iterations to solution; a solution however is preferable to no solution.

24.2.8 ..... Increasing contrast in R-factors

The act of flipping introduces an appreciable amount of unwanted high frequencies in the structure factors. This effect can be reduced by dampening high frequencies using apply_exp_scale which is ON by default. apply_exp_scale changes R-factors and not phases, directions taken by CF are unchanged.

Run CF-1A7Y.INP until convergence. The difference in R-factors before and at convergence should be ~0.39 (i.e. 0.81 and 0.42). Turn OFF apply_exp_scale by including the following line:

```
apply_exp_scale 0
```

Rerun CF-1A7Y.INP until convergence. The difference in R-factors before and at convergence should now be ~0.29 (0.81 and 0.52). Thus apply_exp_scale increases contrast in R-factors. Note that most of the increase seems to be realized from d-spacings less than 1 Angstrom.

24.3 ... Charge Flipping and neutron_data

neutron_data informs the charge flipping routine that neutron scattering lengths are to be used. It also results in the following default neutron flipping routine being used:

```
    flip_equation =
        If(And(Get(density)< Get(threshold),Get(density) > 0.4 Get(min_density)),
            -Get(density),
             Get(density)
        );
```

flip_neutron can be used to change the 0.4 value occurring in the above equation, for example:

```
        flip_neutron = 0.5;
```

The tangent formula is made less accurate due to the negative scattering of H atoms. However, if positive scattering lengths are dominant then the tangent formula can stabilize refinement. For example (see TEST_EXAMPLES\CF\NEUTRON-CIME\CF-NEUTRON.INP), try:

```
        Tangent(0.3, 30) tangent_scale_difference_by = Ramp(1, 0, Nc);
```

24.4 ... Charge-flipping Examples

Table 24-3. Examples found in the CF directory. Number of atoms corresponds to the number of non-hydrogen atoms within the asymmetric unit.

Single crystal data	Num atoms in asymmetric unit	Space group
CF-1A7Y.INP CF-1A7Y-GABOR.INP CF-1A7Y-OMIT.INP CF-1A7Y-NO-TANGENT.INP	314	*P1*
CF-AE14.INP	43	*P-1*
CF-AE5.INP CF-AE5-POOR.INP	23	*C2/c*
CF-AE9.INP CF-AE9-POOR.INP	53	*P-1*
CF-GEBAA.INP	17	$P4_12_12$
CF-PN-02.INP	441	*Pn*
CF-YLIDM.INP	17	$P2_12_12_1$
Powder data		
CF-ALVO4.INP CF-ALVO4-PAWLEY.INP	18	*P-1*
CF-CIME-PAWLEY.INP CF-CIME.INP CF-CIME-HISTO.INP CF-CIME-POOR.INP CF-CIME-POOR-HISTO.INP	17	$P2_1/a$
CF-SUCROSE.INP CF-SUCROSE-PAWLEY.INP	23	$P2_1$

24.5 ... Keywords in detail

[add_to_cloud_N !E]
[add_to_cloud_when !E]

The current cloud is added to the GUI cloud creating a running average cloud for display purposes. add_to_cloud_N corresponds to the number of most recent clouds to include in the running average. add_to_cloud_when determines when the current cloud is to be included in the running average; here's an example:

```
add_to_cloud_N 10 add_to_cloud_when = Mod(Cycle_Iter, 2);
```

Averaged clouds eliminate noise and is effective if the cloud remains stationery which is generally the case. Note that add_to_phases_of_weak_reflections can produce translations of the cloud and should not be included when averaging clouds.

[add_to_phases_of_weak_reflections !E]

Allows for modification to phases of weak reflections. For example, to add $\pi/2$ to the phases of weak reflections then the following could be used:

```
add_to_phases_of_weak_reflections 90
```

When add_to_phases_of_weak_reflections is defined then the intensities of weak reflections are not set to zero; instead they are left untouched meaning that their intensities are set to the values as determined by the inverse Fourier transform. See also scale_weak_reflections.

[apply_exp_scale !E]

Determines *a* and *b* each CF iteration such that the following is a minimum:

$$\text{R-factor} = \sum | a \exp(b / D\_spacing^2)\, Fc - Fo |$$

where *Fc* and *Fo* are the calculated and observed moduli respectively. Use of apply_exp_scale corrects R-factors in case of an incorrect temperature factor correction as applied when normalizing structure factors. Use of apply_exp_scale typically increases the difference between R-factors prior to and at convergence. apply_exp_scale is used by default, setting it to zero prevents its use.

[cf_hkl_file $file]

Defines the input hkl file.

[cf_in_A_matrix $file [scale_Aij !E]]

Data input is from a file created using out_A_matrix from a previous Pawley refinement. The correlations in $file are used to partition intensities during each iteration of charge-flipping. This partitioning is applied to structure factors as used by CF and as used by the tangent formula. scale_Aij can be used to modify the A matrix off-diagonal coefficients, here are some examples:

```
scale_Aij = Get(Aij);
scale_Aij = Get(Aij)^2; ' The default
scale_Aij = 0;          ' Equivalent to using a Pawley generated hkl file
```

CF on powder data can also be initiated using standard hkl files.

[break_cycle_if_true !E]

Interrupts charge flipping to execute randomize_phases_on_new_cycle_by. *Cycle_Iter* is set to zero and *Cycle* is incremented.

[correct_for_atomic_scattering_factors !E]

Structure factors are normalized when correct_for_atomic_scattering_factors is non-zero and when f_atom_type's are defined. Structure factors are normalized by default.

[correct_for_temperature_effects !E]

Attempts to remove isotropic temperature effects from the structure factors. correct_for_temperature_effects is ON by default, setting it to zero will prevent this correction. Normalized structure factors are realized when correct_for_temperature_effects is ON and the unit cell contents is defined using f_atom_type and f_atom_quantity.

[delete_observed_reflections !E]

Reflections are deleted before entering CF according to delete_observed_reflections; it can be a function of *D_spacing*, for example:

```
delete_observed_reflections = D_spacing < 1.1;
```

Once deleted, observed reflections cannot be reinstated by changing min_d.

[extend_calculated_sphere_to !E]

Used to sharpen electron density clouds by filling in missing reflections; added reflections are given the status of "weak". extend_calculated_sphere_to can be used in conjunction with scale_weak_reflections and add_to_phases_of_weak_reflections to modify "weak" reflection magnitudes and phases respectively (see section 24.2.6); here's an example:

```
extend_calculated_sphere_to 1
add_to_phases_of_weak_reflections = If(Rand(0, 1) < .3, 90, 0);
```

[f_atom_type $type f_atom_quantity !E]...

Defines atom types and number of atoms within the unit cell; used by the tangent formula in determining E_h values and by the OpenGL display for picking atoms. For the tangent formula then relative quantities are important.

[find_origin !E]

If defined and non-zero, then origin finding is turned ON. symmetry_obey_0_to_1 defines find_origin by default. symmetry_obey_0_to_1 can be used without find_origin by defining and setting find_origin to zero.

[flip_equation !E]

Allows for a user defined flip; here's an example:

```
flip_equation = If(Get(density)<Get(threshold),-Get(density), Get(density));
```

[flip_regime_2 !E]

The elctron density is modified according to Eq. (24-1) and then further modified using:

$$\rho = \rho - Get(\text{flip\_regime\_2})\rho^3/\rho_{max}^2$$

flip_regime_2 is typically ramped from 1 to 0.

[flip_regime_3 !E]

The electron density is modified according to Eq. (24-1) and then further modified using:

$$\rho = \begin{cases} \rho, & for\, \rho < \delta \\ Min(\rho, \rho_{max}\text{Get}(\text{flip\_regime\_3})), & \text{for } \rho \geq \delta \end{cases}$$

A value of 0.5 for flip_regime_3 introduces little perturbation whilst reducing the occurrence of uranium atom solutions. It is recommended that flip_regime_3 be used in cases where flip_regime_2 produces uranium atom solutions. An additional perturbation, such as "add_to_phases_of_weak_reflections=90;" may be necessary.

[fraction_density_to_flip !E]

The amount of charge flipped is fractionally based. A value of 0.6, for example, sets the threshold δ such that the sign of the lowest 60% of charge is changed. Get(threshold) can be used to retrieve δ.

[fraction_reflections_weak !E]

Defines the fraction of observed reflections to flag as "weak". When scale_weak_reflections, add_to_phases_of_weak_reflections and extend_calculated_sphere_to are all not defined then intensities of weak reflections are set to zero effectively removing them from the charge flipping process. Otherwise, intensities of weak reflections are not set to zero; instead, they are left untouched prior to scale_weak_reflections and add_to_phases_of_weak_reflections and space group family averaging.

[histogram_match_scale_fwhm !E]
[hm_size_limit_in_fwhm !E]
[hm_covalent_fwhm !E]

An implementation of Histogram Matching ([b]Baerlocher *et al*., 2007) where the distribution of pixels within the unit cell is restrained to one that matches Gaussian atoms with intensities corresponding to the atoms defined by f_atom_type's. The Histogram matching operation is performed when histogram_match_scale_fwhm evaluates to a non-zero value. Subsequently the full width at half maximum (FWHM) of the Gaussians (obtained from the file ATOM_RADIUS.DEF) is scaled by histogram_match_scale_fwhm. hm_size_limit_in_fwhm corresponds to the extent to which the Gaussians are calculated in units of FWHM. Covalent radii are used if hm_covalent_fwhm evaluates to a non-zero value otherwise ionic radii are used. Example usage is as follows:

```
histogram_match_scale_fwhm = If(Mod(Cycle_Iter, 3), 0, 1);
    hm_size_limit_in_fwhm 1
    hm_covalent_fwhm 1
```

Reported on is the fraction of pixels modified; values of 1 for both histogram_match_scale_fwhm and hm_size_limit_in_fwhm seem optimal where typically ~15 to 20% of pixels are modified. Use of histogram matching should produce R-factors at convergence that are equal to or than less R-factors produced when not using histogram matching. Histogram matching sharpens the electron density cloud for data at poor resolution (see examples CF-CIME-HISTO.INP and CF-CIME-POOR-HISTO.INP).

[min_d !E]

Determines in Å the resolution of observed reflections to work with; only observed reflections with a d-spacing above min_d are considered. min_d is evaluated each CF iteration. Get(num_observed_reflections_above_d_min) is updated when a change in min_d is detected. See also extend_calculated_sphere_to and delete_observed_reflections.

[min_grid_spacing !E]

If defined, then the grid spacing used is set to the smaller of min_d/2 and min_grid_spacing; useful for obtaining many grid points for graphical purposes.

[neutron_data]

Signals that the input data is of neutron type. Used in the picking of atoms and additionally E_h values are not corrected from any defined f_atom_type and f_atom_quantity keywords.

[pick_atoms $atoms]...
[activate !E]
[choose_from !E]
[choose_to !E]
[choose_randomly !E]
[omit !E]
[displace !E]
[insert !E]

pick_atoms modifies the electron density based on picked atoms. $atom corresponds to the atom types to be operated on; it can contain the wild card character '*' and the negation

character '!', see section 20.26 for details. The operations of pick_atoms are invoked when activate evaluates to a non-zero value, for example,

```
pick_atoms "O C"
    activate = Mod(Cycle_Iter, 20) == 0;
```

The picking routine attempts to locate the atom types found in $atom based on the intensities of picked atoms and the scattering power of the atoms defined in f_atom_type. For example,

```
load f_atom_type f_atom_quantity { Ca 2 O 10 C 12 }
pick_atoms "O C"
```

Here two Ca atoms are first picked and then 10 O atoms and then 12 C atoms. The picked atoms operated on will be the O and C atoms with the Ca atoms ignored.

choose_from and choose_to can be used to limit the number of atoms operated on. Note, that picked atoms within pick_atoms are sorted in decreasing intensity order. For example, to not operate on the first three O atoms and the last 2 C atoms then the following could be used:

```
choose_from 4
choose_to 20
```

choose_randomly further reduces the atoms operated on and is executed after choose_from and choose_to.

omit removes operated-on-atoms from the electron density. Atoms can be partially removed by setting omit to values less than 1. Values greater than 1 can also be used, the effect is to change the sign of the electron density. omit operating on a few of the highest intensity atoms is an extremely effective means of preventing the occurrence of uranium atom solutions, see CF-1A7Y-OMIT.INP; for example:

```
pick_atoms *
    choose_to 5
    omit = Rand(1, 1.1);
```

Omitting atoms randomly is a technique referred to as "random omit maps" in ShelXD, (Schneider and Sheldrick, 2002).

insert inserts operated on atoms; a value of 1 inserts the atoms with an intensity that is equal to the average of the picked atoms. Values of less than 1 decreases the intensity of the inserted atoms. When insert is defined then omit is internally defined if it does not already exist. Thus, atoms are removed before insertion by default.

displace displaces in Å atom positions from their picked positions; it is evaluated before insert. For example, to randomly displace atoms by 0.3 Å then the following could be used:

```
displace = Rand(0.4, 0.6);
insert 1
```

There can be more than one occurrence of pick_atoms, for example to limit uranium atom solutions then the following can be used:

```
pick_atoms *
    choose_to 5
    insert = Rand(-.1, 1);
```

To randomly remove a further ~33% of atoms then the following could be used:

```
Break_cycle_if_true = Get(iters_since_last_best) > 10;
pick_atoms *
    activate = Cycle_Iter == 0;
    insert = If(Rand(0, 1) > 0.33, 10, 0);
```

Note that in this example atoms are inserted at ten times the average picked intensity; this simply gives more weight to picked atoms relative to electron density noise. Additionally weak reflections are also given more weighting.

[pick_atoms_when !E]

Atoms are picked in the OpenGL display when pick_atoms_when evaluates to a non-zero value, here's an example:

```
pick_atoms_when = Mod(Cycle_Iter + 1, 10) == 0;
```

Note that picking can be manually initiated from the Cloud dialog of the OpenGL display. A text description of picked atoms can be obtained by opening the "Temporary output" text window of the OpenGL window.

[randomize_initial_phases_by !E]

Initializes phases. To start a process with already saved phase information then the following could be used:

```
set_initial_phases_to aleady_saved.fc
randomize_initial_phases_by 0 ' this has a default of 0
```

[randomize_phases_on_new_cycle_by !E]

```
randomize_phases_on_new_cycle_by = Rand(-180, 180); ' an example
```

[scale_density_below_threshold !E]

Electron density pixels that are less than the threshold value are scaled by scale_density_below_threshold. Values for scale_density_below_threshold that are less than 1 tends to sharpen the electron density and to reduce large oscillations in R-factors; the latter occurs for bad data, see example CF-SUCROSE.INP. A value of zero for scale_density_below_threshold results in "low density elimination" similar to that of Shiono & Woolfson (1992).

[scale_E !E]

Normalized structure factors (E_h values) are a function of correct_for_temperature_effects and unit cell contents. scale_E allows for an additional scaling of E_h values.

[scale_F !E]

CF works with normalized structure factors by default. scale_F is an additional scaling of structure factors. The defualt scale_F broadens electron density peaks to avoid pixilation effects and is given by:

```
scale_F = Exp(-0.2 Get(d_squared_inverse));
```

[scale_F000 !E]

Scale should be set to 1 for compliance with the algorithm of Oszlányi & Süto (2004). When scale_F000 is non_zero then modifications to the electron density produces unfavourable effects.

[scale_weak_reflections !E]

By default, weak reflection structure factors are set to zero; however, when either scale_weak_reflections or add_to_phases_of_weak_reflections is defined then weak reflection structure factors are instead modified accordingly, for example:

```
scale_weak_reflections = Rand(-0.2, 0.4);
```

scale_weak_reflections or add_to_phases_of_weak_reflections can be a function of *D_spacing*.

[set_initial_phases_to $file]
[modify_initial_phases !E]

Sets initial phases to those appearing in $file. Typically, $file corresponds to a *.FC file saved in a previous charge-flipping process. modify_initial_phases is executed each CF iteration; it can be used to restrain the phases of $file. For example,

```
modify_initial_phases = Get(initial_phase) + Min(Abs(Get(phase_difference)),45);
```

where phase_difference corresponds to the difference between the current phase and the initial phase; it has a value between ±90°. modify_initial_phases can be used to constrain phases to those as determined by high resolution transmission electron microscopy HRTEM ([a]Baerlocher *et al.*, 2007).

[space_group $]

If defined, then the cf_hkl_file is assumed to comprise merged hkls corresponding to the defined space group; otherwise, the cf_hkl_file is assumed to be of space group type *P1*.

[symmetry_obey_0_to_1 !E]

If a space group is defined, then symmetry is adhered to according to symmetry_obey_0_to_1. symmetry_obey_0_to_1 can be thought of as a real space electron density restraint; its value should range between 0 and 1. If 1 then symmetry is obeyed 100%; if 0 then for a particular set of equivalent grid points, as determined by the equivalent positions of the space group, an average density ρ_{avg} is obtained. The electron densities on the grid points are then adjusted as follows:

$$\rho_{new} = \rho\,(1 - \text{symmetry\_obey\_0\_to\_1}) + \text{symmetry\_obey\_0\_to\_1}\ \rho_{avg}$$

The text output 'symmetry error' as displayed when symmetry_obey_0_to_1 is used and is defined as follows:

$$'symmetry\ error' = \frac{\sum|\rho - \rho_{avg}|}{\sum|\rho|}$$

where the summation is over all electron density grid points. symmetry_obey_0_to_1 defines find_origin by default. find_origin is applied before symmetry_obey_0_to_1. find_origin shifts the electron density such that an approximate error in 'symmetry error' is minimized; thus find_origin assists in the symmetry_obey_0_to_1 restraint.

[tangent_num_h_read !E]
[tangent_num_k_read !E]
[tangent_num_h_keep !E]
[tangent_max_triplets_per_h !E]
[tangent_min_triplets_per_h !E]
[tangent_scale_difference_by !E]

tangent_num_h_read and tangent_num_k_read defines the number of highest *h* and highest *k* reflections to read in determining triplets. tangent_num_h_keep defines the number of highest *h* reflections to include for tangent formula updating. tangent_max_triplets_per_h and tangent_min_triplets_per_h defines the maximum and minimum number of triplets per reflection *h*. Reflections with less than tangent_min_triplets_per_h are not included for tangent formula updating. tangent_scale_difference_by corresponds to *S* in the following:

$$\emptyset_{h,new} = \emptyset_{h,cf} + S\ \alpha_h\left(\emptyset_{h,tf} - \emptyset_{h,cf}\right)$$

$$tan\left(\emptyset_{h,tf}\right) = T_h/B_h$$

$$T_h = \sum_k E_h E_k E_{h-k} sin(\emptyset_k - \emptyset_{h-k})$$

$$B_h = \sum_k E_h E_k E_{h-k} cos(\emptyset_k + \emptyset_{h-k})$$

$$\alpha_h = M_h/M_{h,max}\ ,\quad M_h = \sqrt{T_h^2 + B_h^2}$$

[user_threshold !E]

By default, Get(threshold) is determined using fraction_density_to_flip. When defined then user_threshold overrides fraction_density_to_flip. Electron density pixels are normalized to have a maximum value of 1, thus typical values for user_threshold range between 0 and 0.1.

[use_Fc]

Sets initial phases to those saved in a previous *.FC file. The FC file used corresponds to the same name as the data file, defined using cf_hkl_file or cf_in_A_matrix, but with a FC extension. use_Fc is similar-to set_initial_phases_to except that the file is implied.

[verbose #]

A value of 1 outputs text in a verbose manner. A value of 0 outputs text when the R-factor is less that a previous value encountered within a particular Cycle.

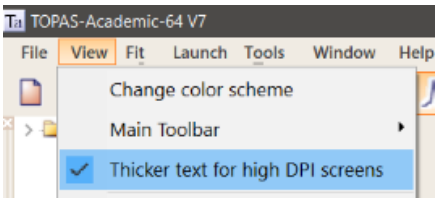
[view_cloud !E]

Informs a detected GUI to display the electron density. Here are some examples:

```
view_cloud 1 ‘ Update cloud every charge-flipping iteration
view_cloud = Mod(Cycle_Iter, 10) == 0;
```

25. GUI FUNCTIONALITY

1.1 .... TOPAS is DPI aware



Monitors with a high number of Dots Per Inch (DPI), often display text that are too small. Windows can scale fonts using Windows font scaling to enlarge text. This scaling is carried through to TOPAS where fonts and bitmaps scale to the required size. Additionally, a thicker-text option ("Segoe UI Semibold") can be enabled if the TOPAS text appears too thin. The option is saved for subsequent TOPAS loads and is enabled/disabled from the View menu:

1.2 .... Antialiasing and OpenGL

Enable Antialiasing on your graphics card to display smooth lines in OpenGL; this affects all OpenGL displays. Depending on the graphics card, Antialiasing can also be enabled on a program specific manner.

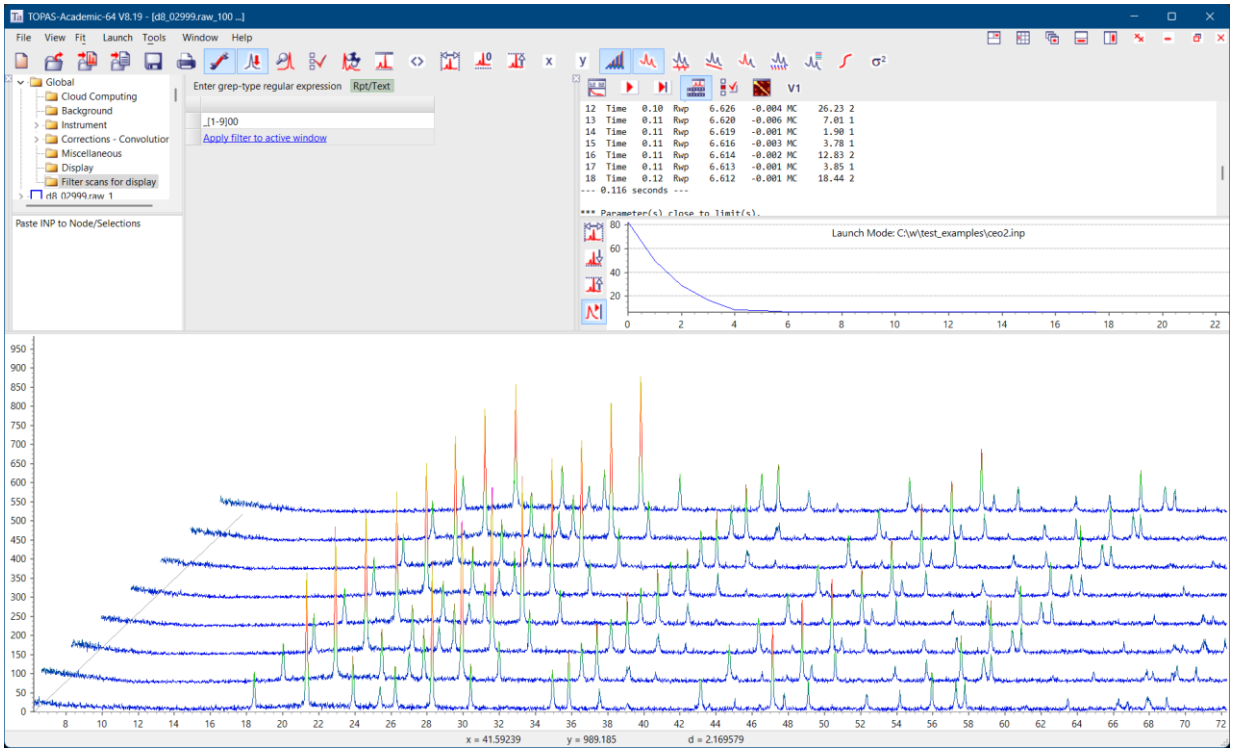
1.3 .... Scan-window viewing operations

The following described operation of the scan window where LMB and RMB corresponds to Left and Right mouse buttons.

	Operation
Mouse-Wheel	Scroll plots left/right
Shift Mouse-Wheel	Compress/expand x-axis
LMB forwards rectangle	Zoom
LMB backwards rectangle	Unzoom
LMB forwards/backwards rectangle towards 1st and 3rd quadrants	Change start/end of x-axis window depending on proximity to window limits.
RMB click	Context menu
RMB down and scroll	Panning, similar to scrolling using mouse wheel
LMB click on hkl tick mark or tick mark row	Highlight all tick marks from same phase. Display associated phase.
Mouse close to tick mark	Show hkl and d-spacing on screen
Mouse close to phase line	Highlights phase and associated tick marks.

1.4 .... Selecting files for display using grep regular expressions

Grep regular expressions can be used to simplify the selection of scans for display; this is useful when there are many patterns loaded. Grep can be accessed through the “Global/Filter scans for display” option in the TreeView pane as seen in the following:



In the above, every 100th scan is displayed using the regular expression of "_[1-9]00".

1.5 .... gui_text keyword now ignored by the kernel

For the commercial version of TOPAS, the gui_text keyword allows for INP format text to be used in GUI mode refinement. Previously, use of gui_text within INP files in Launch mode threw an exception. Version 8 does not throw an exception; instead, the keyword is ignored but with the INP text within the gui_text block included in the refinement. The means that INP files are GUI mode compliant and moving between GUI and Launch mode becomes a smooth operation. For example, the following INP file can be run in both Launch and GUI modes without modification:

```
XDD(ceo2)
   CuKa5(0.0001)
   Full_Axial_Model(12, 20, 12, 5.1, sl 5)
   Radius(173)
   LP_Factor(17)
   Divergence(1)
   Slit_Width(0.1)
   bkg  @ 0 0 0 0 0
   Zero_Error(@, 0)
   gui_text {
      prm b0 0
      prm b1 0
      fit_obj = b0 + b1 (X2-X1) / 2;
   }
   str
      space_group F_M_3_M
      scale @ 0.001
      Cubic(@ 5.410)
      site Ce1                        occ Ce+4 1 beq 1
      site O1  x 0.25 y 0.25 z 0.25   occ O-2  1 beq 1
```

```
CS_L(@, 100)
MVW(0,0,0)
```

1.6 .... Displaying a phase with and without background

Phases can be plotted with or without background by cycling through the three states of the phase-display icon.

1.7 .... How atoms are displayed in OpenGL

Atoms colours and radii are defined in the files ATOM_COLORS.DEF and ATOM_RADIUS.DEF respectively. A site defined as:

```
site S1 occ Al+3 1 beq 1
```

will be displayed as a Sulphur atom. If the Site Name, minus the numbers, is not found in ATOM_COLOURS.DEF then the atom type defined at the first site occupancy is used. Thus, a site defined as:

```
site _S1 occ Al+3 1 beq 1
```

will be displayed as an Aluminium atom.

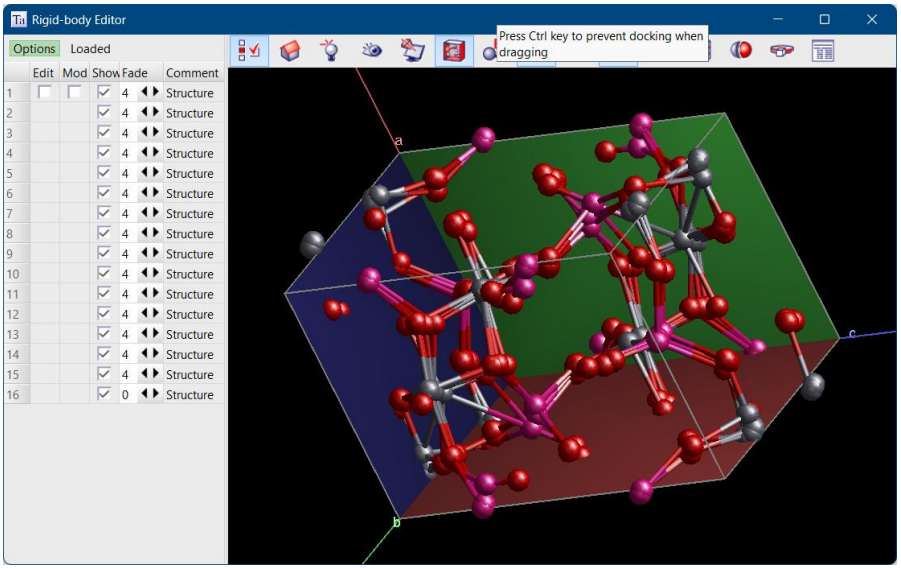
1.8 .... Tracking atomic movements graphically

[str...] [track_buffer !E] [site... track !E]	**Examples** TEST_EXAMPLES\ALVO4A.INP

Atomic movements can be tracked using the site dependent keyword track. For example, the following:

```
site AL1 … track = Mod(Cycle_Iter, 2) == 0;
```

will store the Al1 site position every second iteration. Doing this for every site in AlVO4 produces:



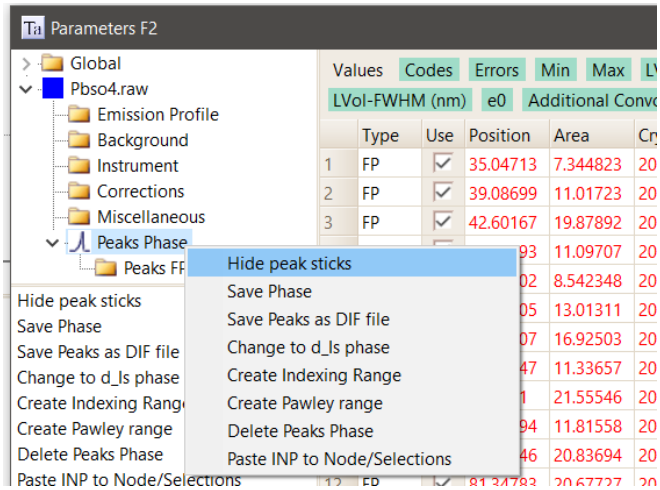
Saved positions are Faded with a Fade value of 4. A Fade value of 0 does nothing; a Fade value of 10 results in black atoms. The str dependent track_buffer keyword determines the number of previous atomic positions to keep; the default value is 10.

1.9 .... x_calculation_step deleted when constant x-axis step size detected

*.XY and *.XYE data files are converted to a constant x-axis step size when a constant step size is detected. When this occurs Version 7 removes the “Calc.Step” item from the GUI menus for the corresponding data file. A small calculation step size can still be used by increasing “Conv. Steps”. PRO files containing an x_calculation_step will still show an entry of x_calculation_step.

1.10... hide_peak_sticks

A GUI option that toggles the display of peak sticks in the scan window; the option can be found at the Peaks phase level as follows:



25.1 ... User defined phase colour, line width and point size (_clp)

_clp #red #green #blue #line_width #point_size	**Examples** TEST_EXAMPLES\ZRO2.INP

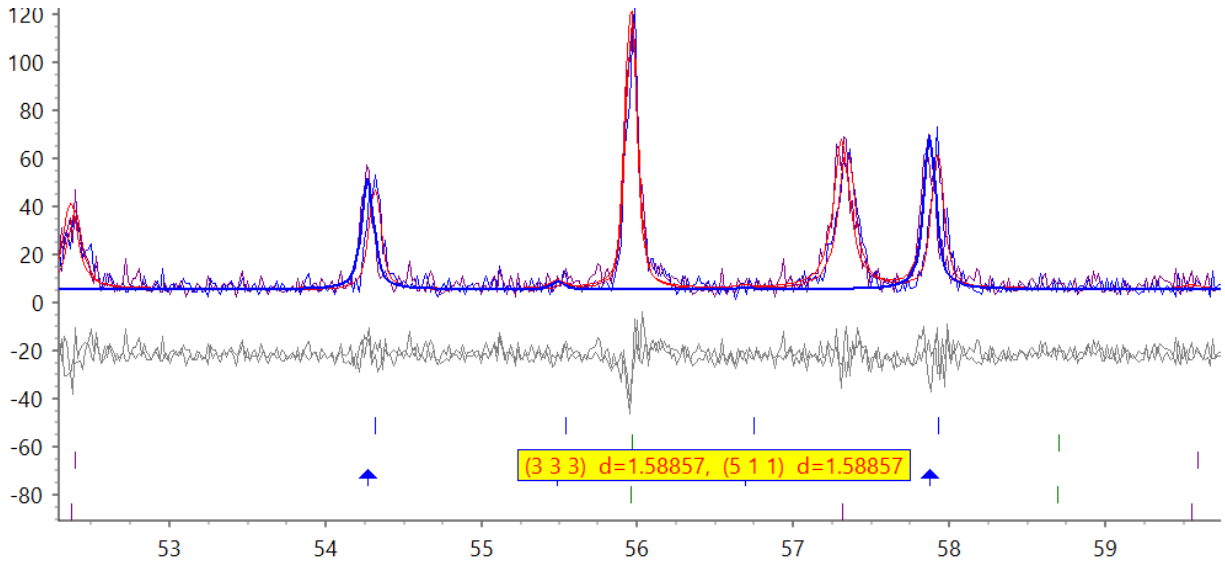
The colour, line width and data point size of phase plots can be entered in INP files using the phase or bkg dependent keyword _clp. The first three numbers correspond to red, green and blue colour weightings with value ranging between 0 and 1. #line_wdith and #point_size can be between 0 and 15. The file COLOURS.INC contains standard colours. Example usage is as follows:

```
#include colours.inc
bkg …
    _clp 0.5 0.5 0.5 3 2 ‘ Grey with a line width of 3 and a data point size of 2
str…
    _clp 0.2 0.2 1 1 0   ‘ Blueish with a line width of 1 and a data point size of 0
fit_obj !fs  = 1000 X;
    Plot_Fit_Obj(fs, Some_bkg)
           _clp Blue 2 2 ‘ Blue colour from colours.inc
```

25.2 ... Highlighting/displaying phases and hkl tick marks

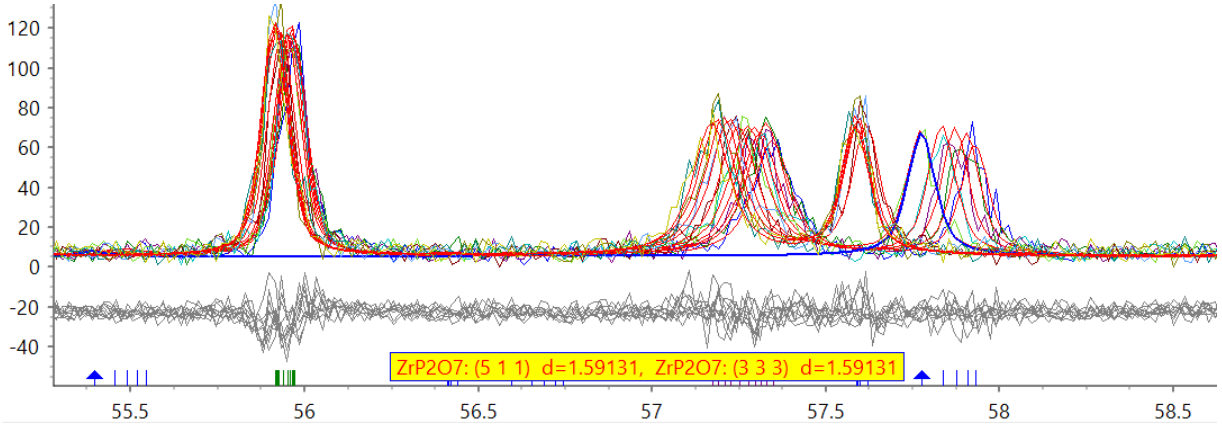
Highlighting a phase in a multi-phase pattern or patterns, can be performed in a many ways:

- Displaying phase names on the right of the plot window and moving the mouse over the phase name.
- Clicking on the row of the hkl tick marks. This displays the associated phase and tick marks highlighted, for example:

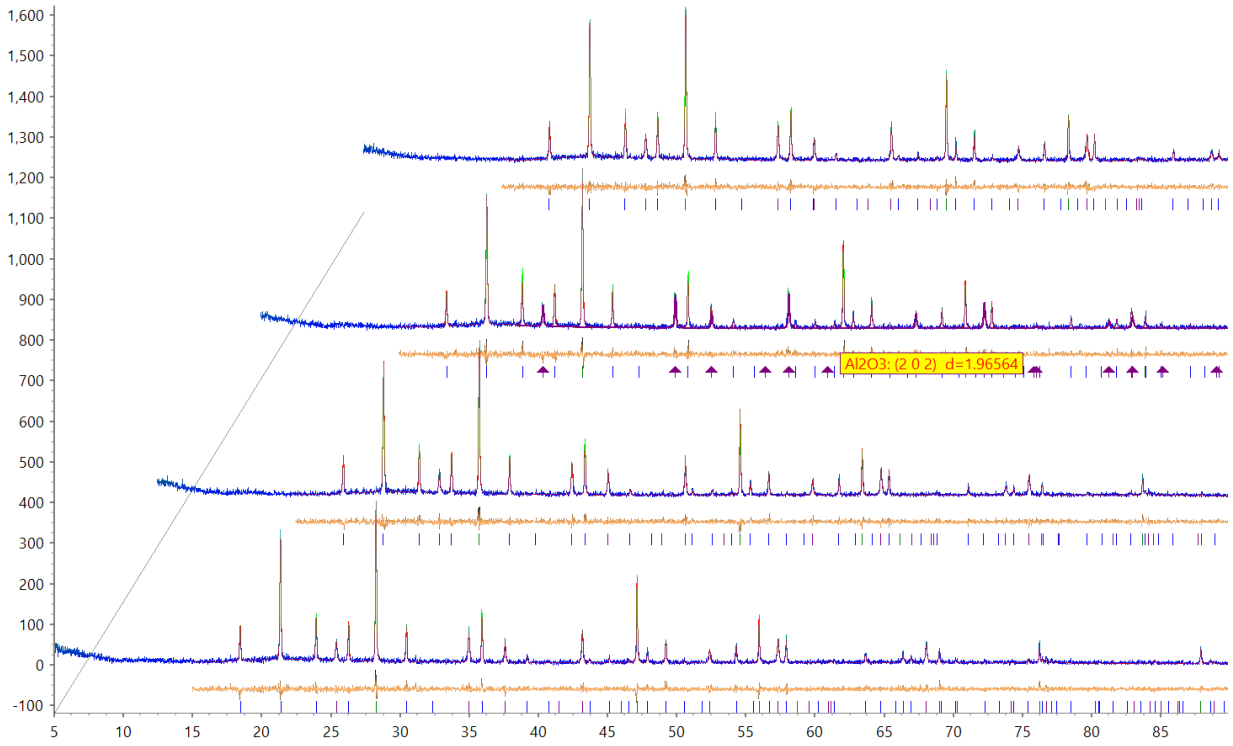


If individual phases are displayed using , then moving the mouse over the pattern highlights the pattern as well as ticks marks associated with the phase.

If there are too many tick rows, then the program displays all phase ticks from all patterns in one row. Moving the mouse close to a tick mark, displays tick mark information on the screen as well as displaying the associated range name on the status bar. Additionally clicking the left mouse button on a phase tick mark, highlights all tick marks associated with that phase additionally displays the phase pattern highlighted; for example:



hkl tick marks are also now displayed in 2D-Offset mode as seem in the following:



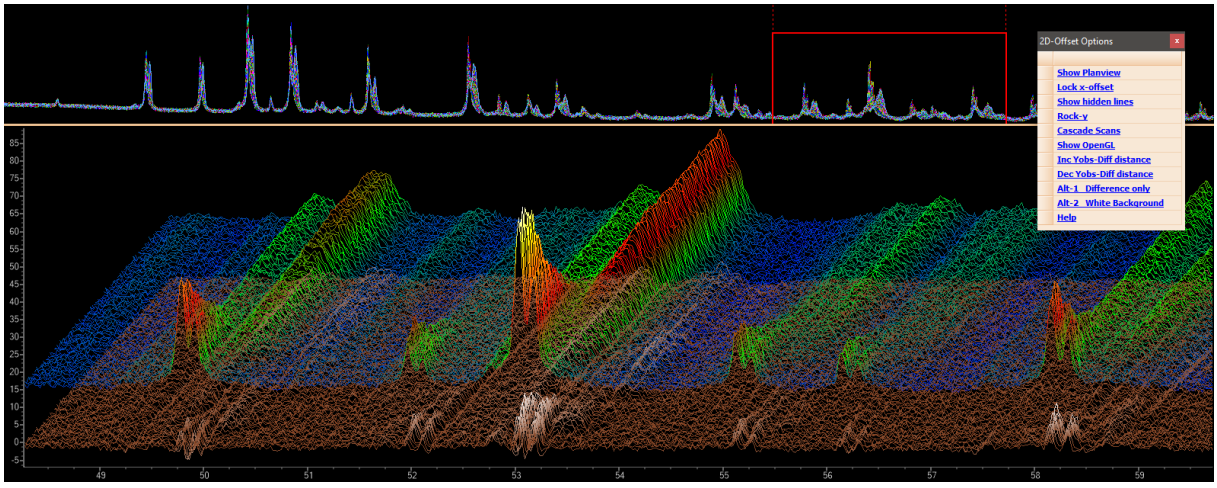
In 2D-offset mode, ticks marks from a particular pattern are placed on a common tick mark row. Clicking on an individual tick mark, highlights all ticks marks from the corresponding phase and highlights and displays the corresponding phase pattern. As in the non-2D-offset mode, a phase pattern and its associated tick marks are highlighted when the mouse is close to the phase pattern.

25.3 ... TOF x-axis can be displayed as d-spacing, Q or tof

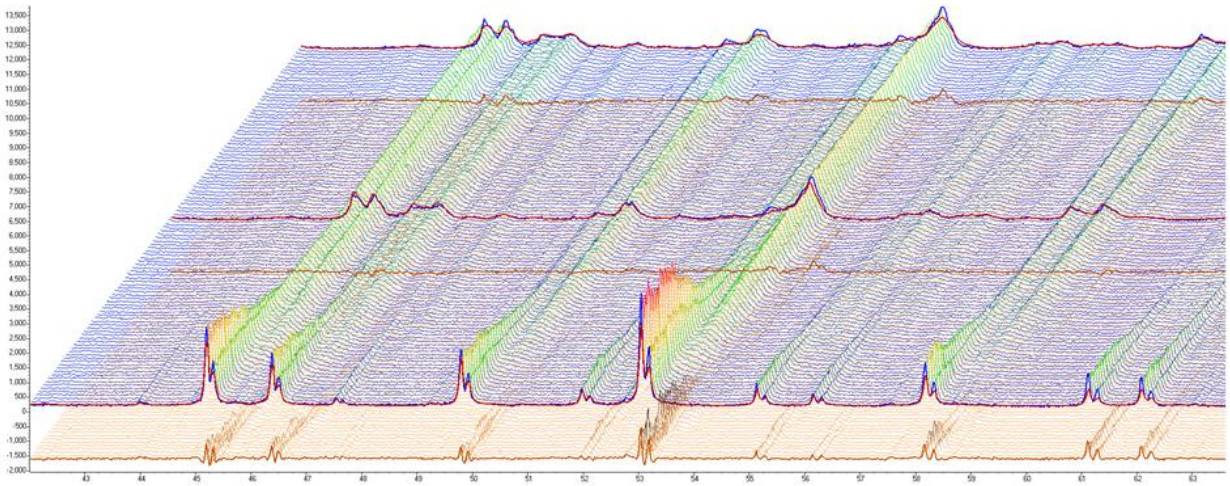
The x-axis of TOF data can be displayed as either tof, d-spacing or Q by cycling the x-axis button.

25.4 ... Surface plots – 2D with offsets

This icon displays scans offset from one another, for example (see files in the directory TEST_EXAMPLES\3D\):



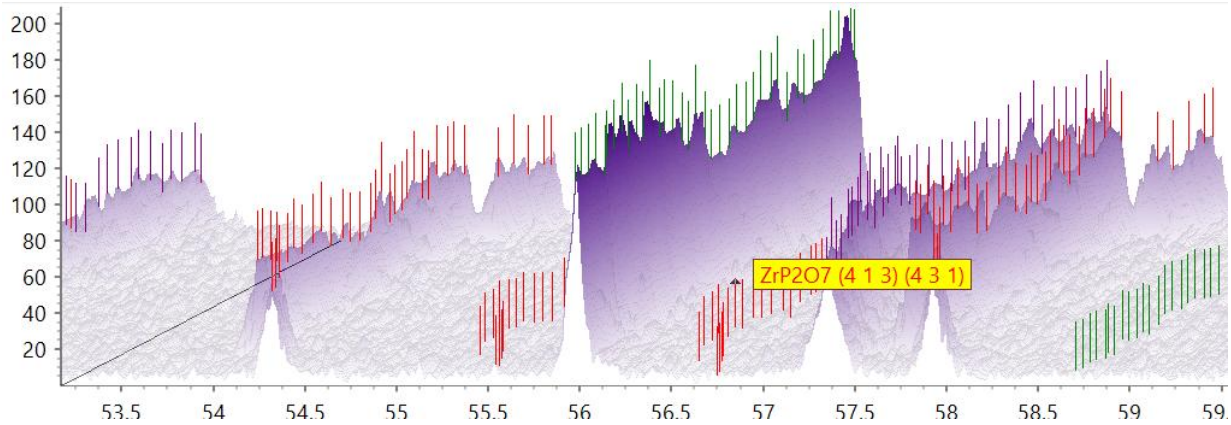
The Quickzoom window is operational in all 2D-offset plots.



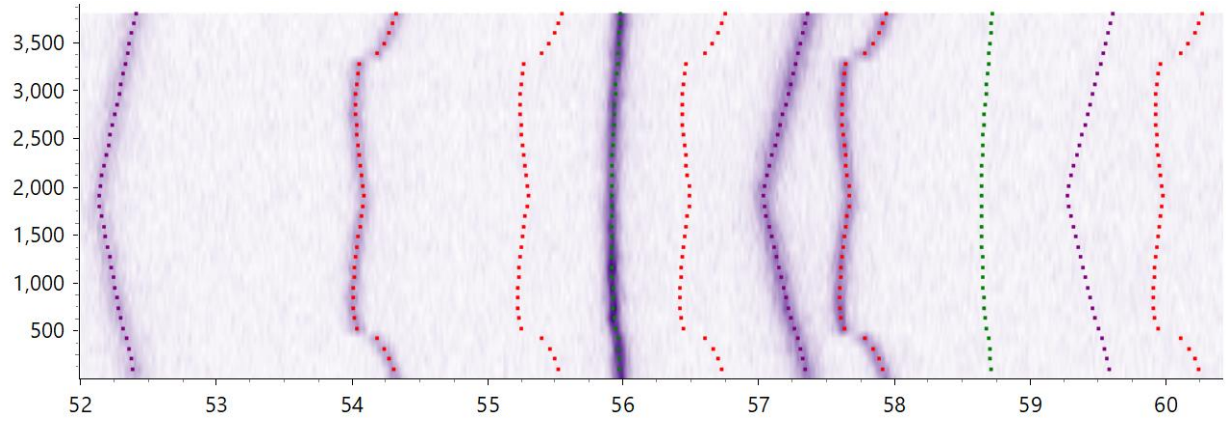
Pressing the Middle Mouse Button and moving the mouse changes the x and y offsets. This movement greatly assists in determining the curvature of the surface. The QuickZoom display is not offset allowing for two views of the same data.

25.4.1 ..... Display hkl ticks on Surface plots

hkl ticks with z-axis height can be displayed on surface plots as seen in the following for \TEST_EXAMPLES\JE-PARA\D8_02999_35_ANNOTATE_04.INP:

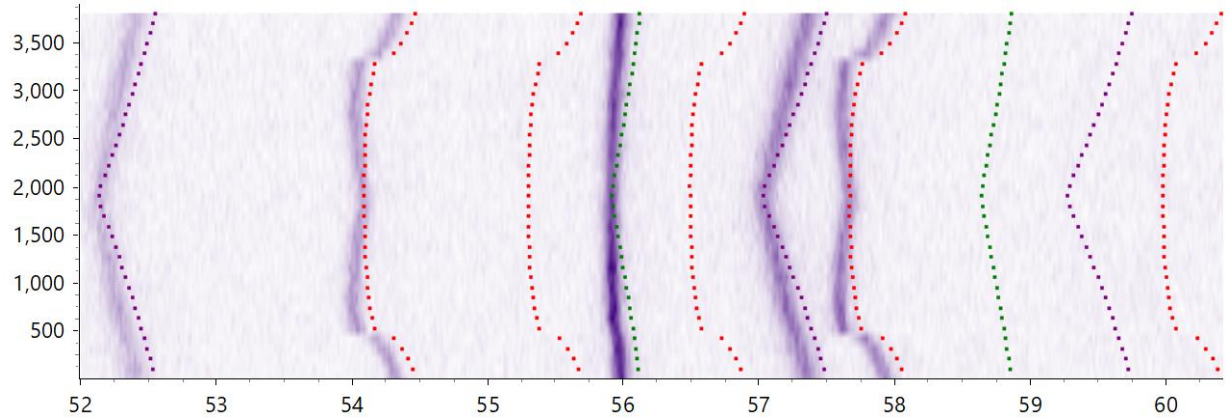


And in PlanView:



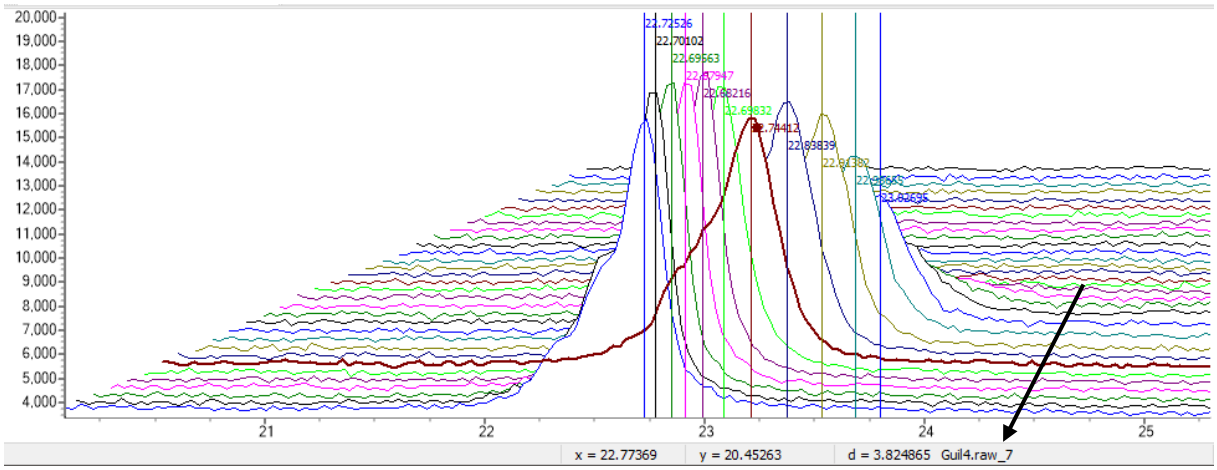
25.4.2 ..... hkl ticks are now corrected for zero errors

The display of hkl ticks in Surface or 1D plots are now corrected for th2_offset or transform_X. The corrected PlanView plot shown above, when uncorrected, looks like:



25.4.3 ..... Inserting peaks and identifying scans

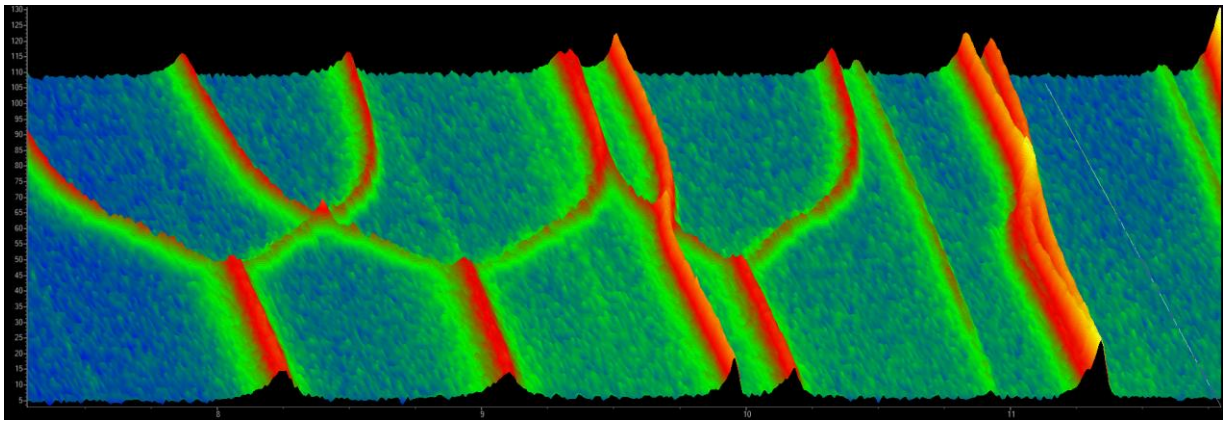
Peaks can be inserted by pressing the Ctrl-Key and clicking the RMB. When the Ctrl key is pressed a solid circle is displayed on the scan closest to the mouse. The circle is coloured to match the scan lines and in addition the closest scan is displayed with a thickened line. Displayed at the bottom of the plot is the name of the scan as seen by the arrow below. Peaks as well as excluded regions move with the offsets.



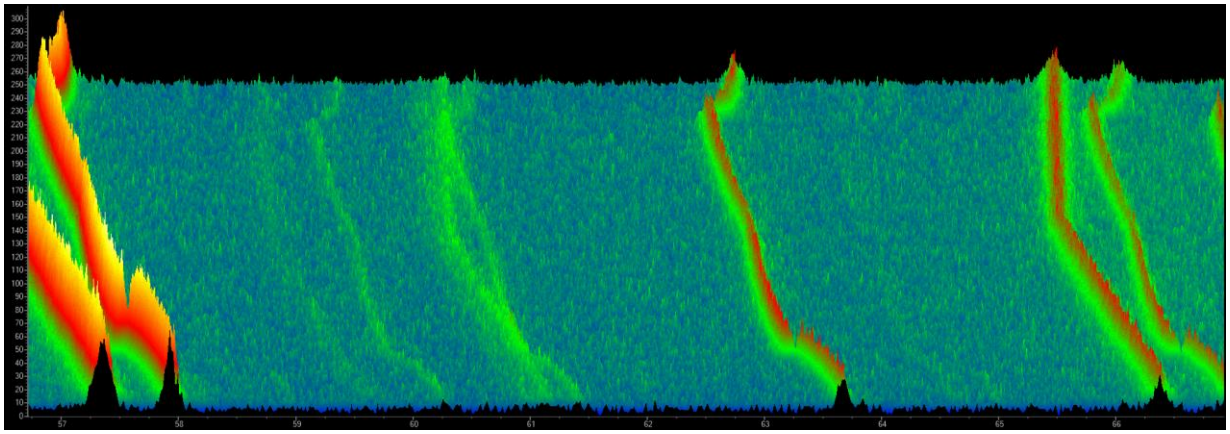
When the Ctrl-Key is pressed the x and y axis values displayed on the status line are offset to match the closest scan. Similarly, when the “For LAM Cursor” option is selected the LAM cursor is changed to match the axis of the closest scan.

25.4.4 ..... 2D-offset Surface plots

2D-offset plots can be displayed as a 3D-Surface, for example:

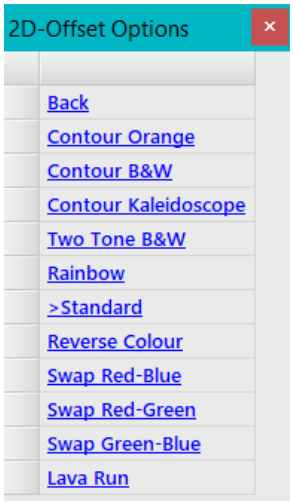


These plots can be manipulated in real time; the 871 file TEST_EXAMPLES\JE-PARA\D8_02999.RAW with over 4 million data points can be easily manipulated:

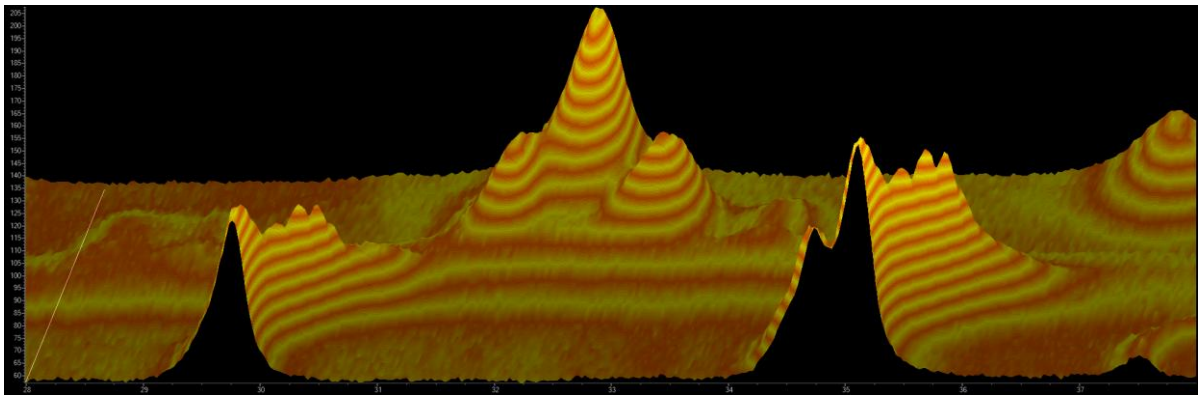


Pressing the Shift key whilst performing a Zoom (forming a box using the mouse) zooms into a region. Zooming in this manner deselects scans for display. An unzoom is performed by

performing an Unzoom whilst holding down the Shift key. Colour schemes can be changed by using the Colours options:

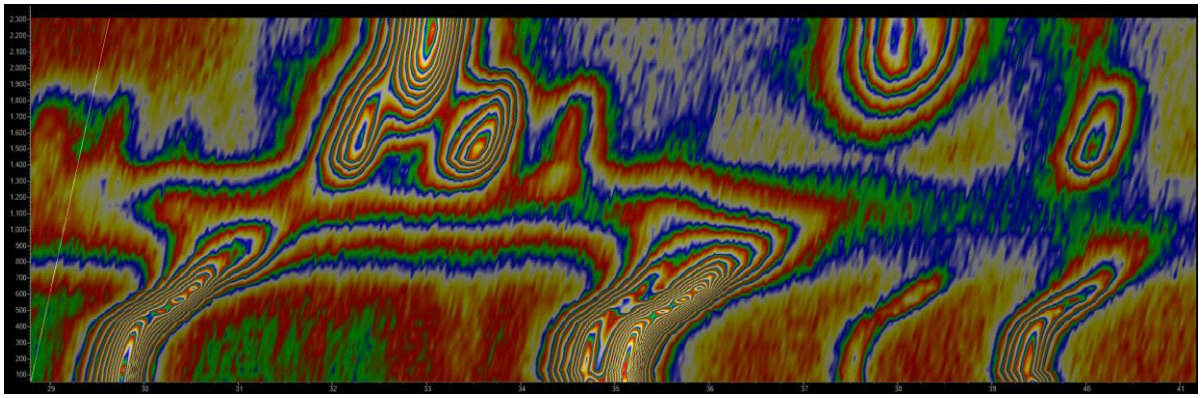


Contour-Orange-15 looks like:

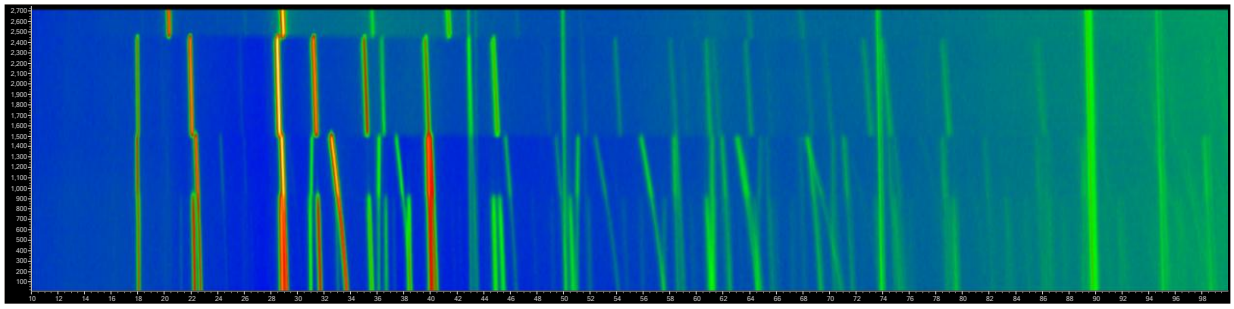


25.4.5 ..... 2D-offset Planview plots

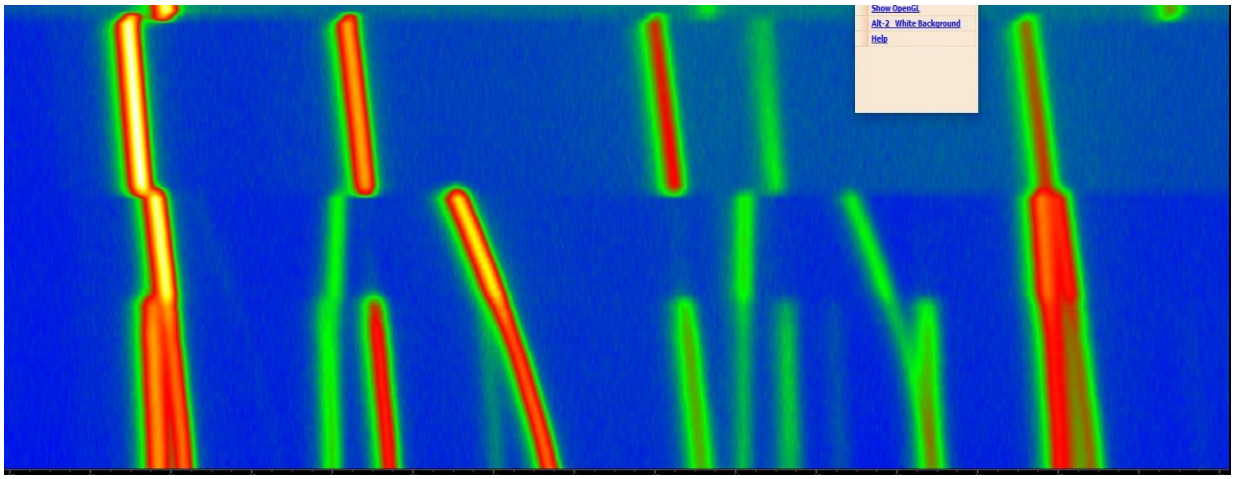
Moving the y-offset such that it's at a maximum automatically produces a Planview; a Kaleidoscope colour scheme gives:



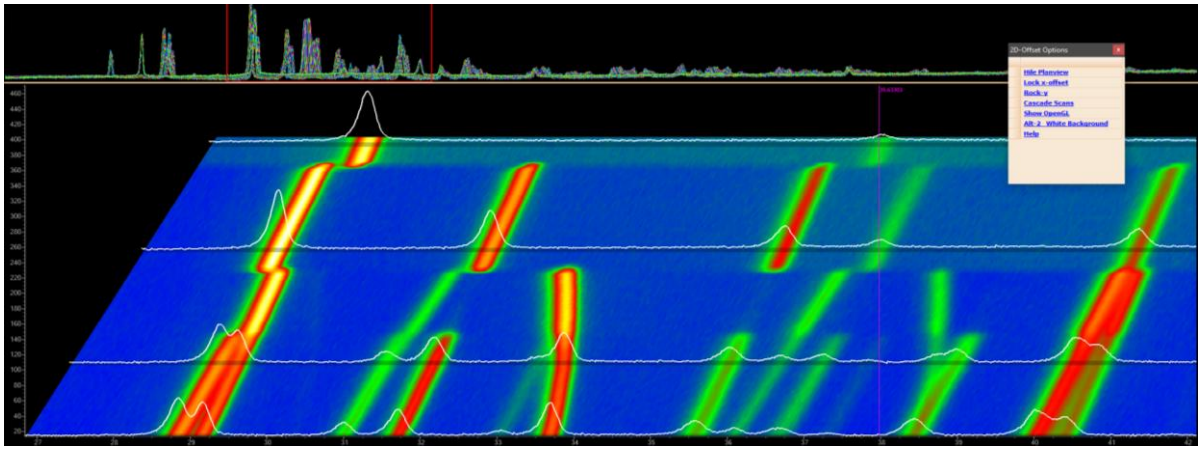
The Standard colour scheme gives:



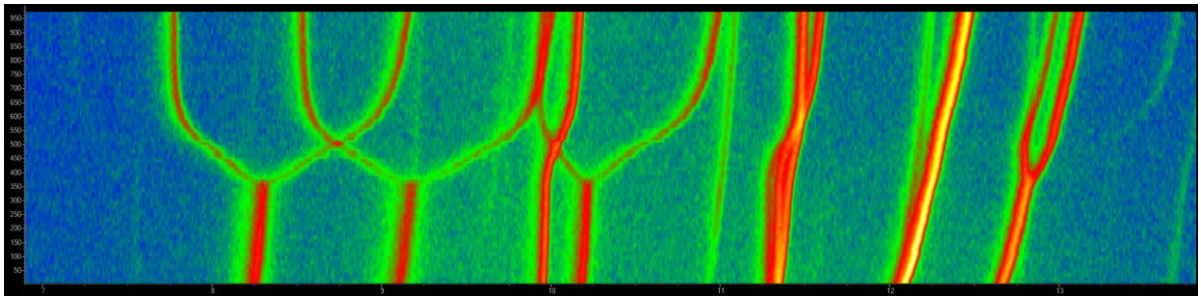
Zooming gives:



Planview can also have x-axis offsets with line scans overlain:

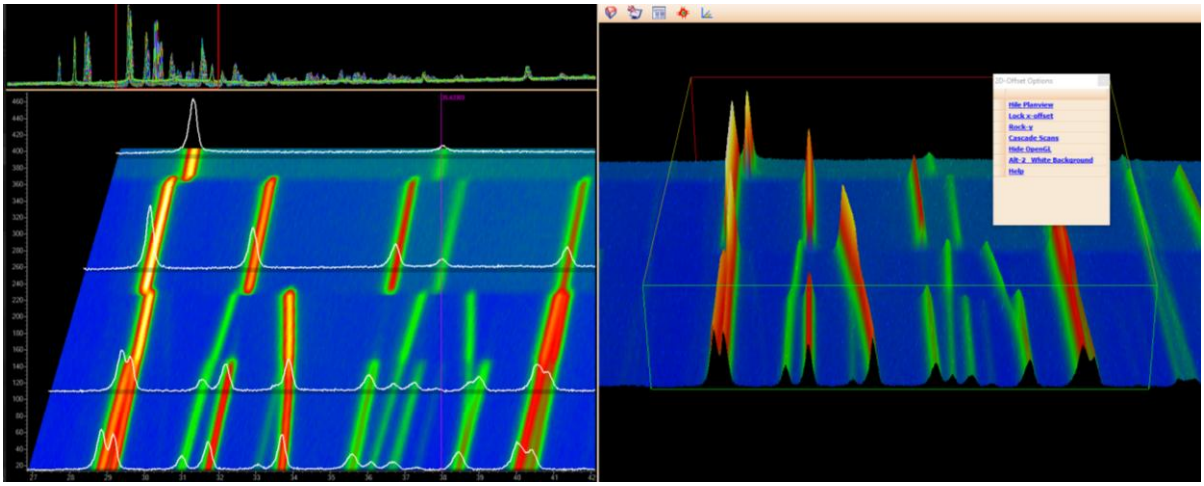


These line scans can include the calculated and/or difference patterns as well as patterns for individual phases. Beneath the displayed line scans are their shadows. Colours are blended across scans as well as across the x-axis to sharpen images.

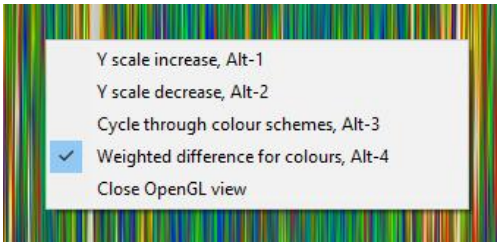


25.4.6 ..... OpenGL Surface plots

OpenGL surface plots can be displayed alongside 2D-offset plots:



The scans displayed in the chart area are displayed to the right as a surface plot. Use RMB on the surface plot for options; these are:



The OpenGL surface plot respects the 2D x-axis and y-axis display options. It is also aware of the QuickZoom window and scrolling. Scrolling can be performed from either the 2D or 3D displays using the Mouse Wheel. Navigation in the OpenGL window is as follows:

- Use the Moise Wheel to scroll the x-axis from either the 2D or 3D plots.
- RMB-Pressed and moving zooms.
- Pressing '**x**' whilst rotating allows rotation around an axis vertical to the screen.
- Pressing '**y**' whilst rotating allows rotation around an axis horizontal to the screen.
- Pressing '**z**' whilst rotating allows rotation around an axis perpendicular to the screen.
- Pressing the Mouse Wheel button (as opposed to rotating the mouse wheel) moves the object and hence the centre of rotation.

- When the Mouse is close to the Left or Right borders of the OpenGL window then rotation is around an axis perpendicular to the computer screen. Very useful for positioning 3D objects.

Opening the OpenGL Text Dialog and clicking on the 3D surface writes text into the Text Dialog; this text comprises the names of the two files bordering the polygon that has been clicked and the average x and y values of the polygon.

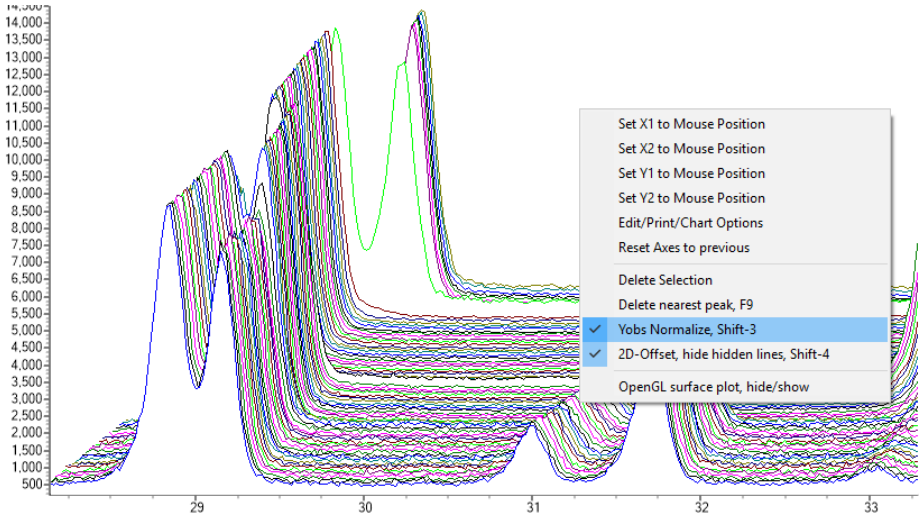
25.4.7 ..... OpenGL – Weighted difference for colours

The RMB "Weight difference for colours" option displays colours corresponding to:

WtDiff = Abs(*Yobs*–*Ycalc*) / Weighting

25.5 ... Normalizing scans within a Scan Window

Displayed scans can be normalized using the option "*Yobs* Normalize" which is activated using the RMB on the Scan window. Normalizing scales displayed scans such that the maximum values of the displayed data are all equal. Normalizing is temporary and can be toggled on/off by executing the "*Yobs* Normalize". The following shows scans normalized:



25.6 ... Plotting phases above background

[fit_obj E [min_X !E] [max_X !E]]...
    [fo_transform_X !E]
    [fit_obj_phase !E]

By default, phases are plotted on top of background where background comprises fit_obj's+bkg. The xdd dependent gui_add_bkg and the fit_obj dependent fit_obj_phase can be used to change the defaults, for example,

```
xdd ...
   gui_add_bkg !E
   fit_obj ...
      fit_obj_phase !E
```

gui_add_bkg defaults to 1; if its zero then phases are not plotted above background. fit_obj_phase defaults to 1. If gui_add_bkg=1 then the following is added to phases:

bkg + (and any fit_obj's that has fit_obj_phase =1)

QUANT\QUANT-7.INP shows the use of fit_obj_phase=1 where a fit_obj that is a function of a user_y object, that is supposed to be a phase, is plotted on top of background using a dummt_str; the dummy_str checks the status of the fit_obj's fit_obj_phase.

25.7 ... Plotting fit_objs

fit_obj's can be plotted using the following macros:

```
macro Plot_Fit_Obj(p, name) {
   dummy_str
      phase_name name
      scale = p;
}
```

```
macro Plot_Fit_Obj(name) {
   dummy_str
      phase_name name
}
```

See TEST_EXAMPLES\VOIGT-APPROX\FIT-OBJ.INP for example; i.e.

```
xdd ...
   fit_obj !f1 = ...
   Plot_Fit_Obj(f1, "Fit Obj")
```

Plotting is via a dummy_str with the scale parameter set to the name given to the fit_obj, which in this case is f1. At the plotting stage the dummy_str borrows the calculated pattern from the fit_obj. The scale parameter of the dummy_str has some intelligence built into it such that if scale is not a function of a fit_obj name then it will search the place of the item it is a function of for a calculated pattern. For example, in the following:

```
xdd ...
   Plot_Fit_Obj(a, "Fit Obj")
   fit_obj = a ...
      prm a ...
```

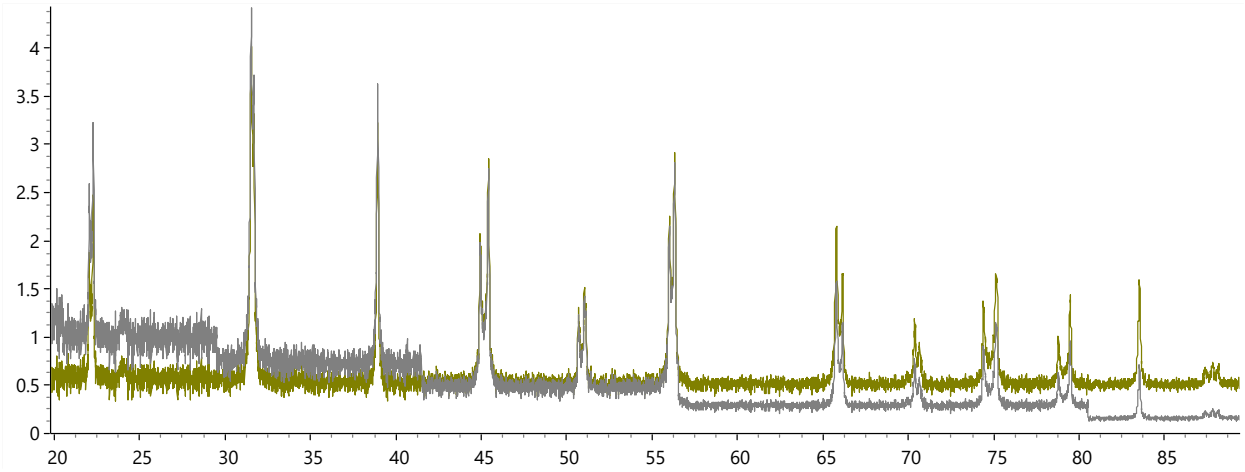
the 'a' parameter lives locally to the fit_obj as it is defined after the fit_obj. Defining the scale parameter of the dummy_str in terms of 'a' therefore allows the dummy_str to determine where to find the calculated pattern to display. In this way macros such as the PV macro can be used and plotted without having to define a name for the fit_obj, see TEST_EXAMPLES\PVS.INP. Sometimes the fit_obj has no name and no parameter that belongs to it; instead of naming the fit_obj or rearranging prm definitions the second Plot_Fit_Obj macro can be used:

```
xdd ...
   fit_obj = ...
   Plot_Fit_Obj("plot previously defined fit_obj")
```

Here the fit_obj defined prior to Plot_Fit_Obj is plotted.

25.8 ... Display of Normalized SigmaYobs^2

This icon displays normalized *SigmaYobs*^{2}; useful for checking anomalies from VCT or XYE files; here's an example:



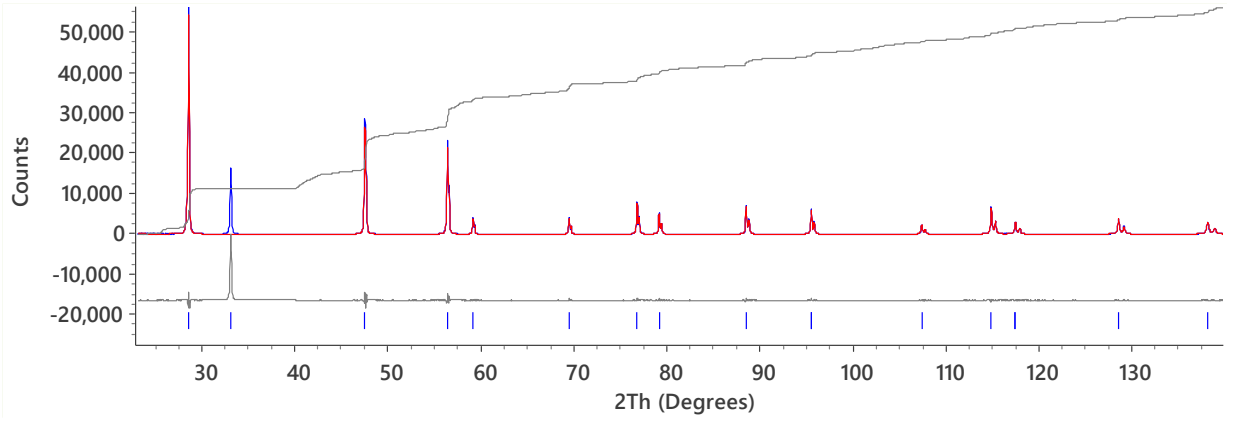
The normalization is as follows:

SigmaYobs^2 displayed = SigmaYobs^2 Sum[Yobs] / Sum[SigmaYobs^2]

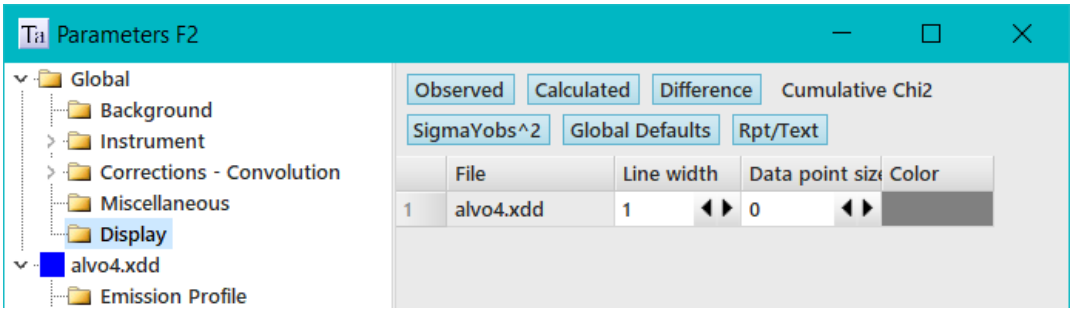
This puts the display of *SigmaYobs*^2 on a similar scale to *Yobs*. For normal x-ray data *SigmaYobs* = Sqrt(*Yobs*) and hence nothing is done as the displayed plot would simply be equal to *Yobs*. On some data sets, TOF for example, the magnitude of *SigmaYobs* can be small; therefore, when refining on multiple data sets from different sources, the weighting schemes may need modification to give the desired weight to the data sets.

25.9 ... Cumulative Chi2

A kernel operation that results in the following graphical display:

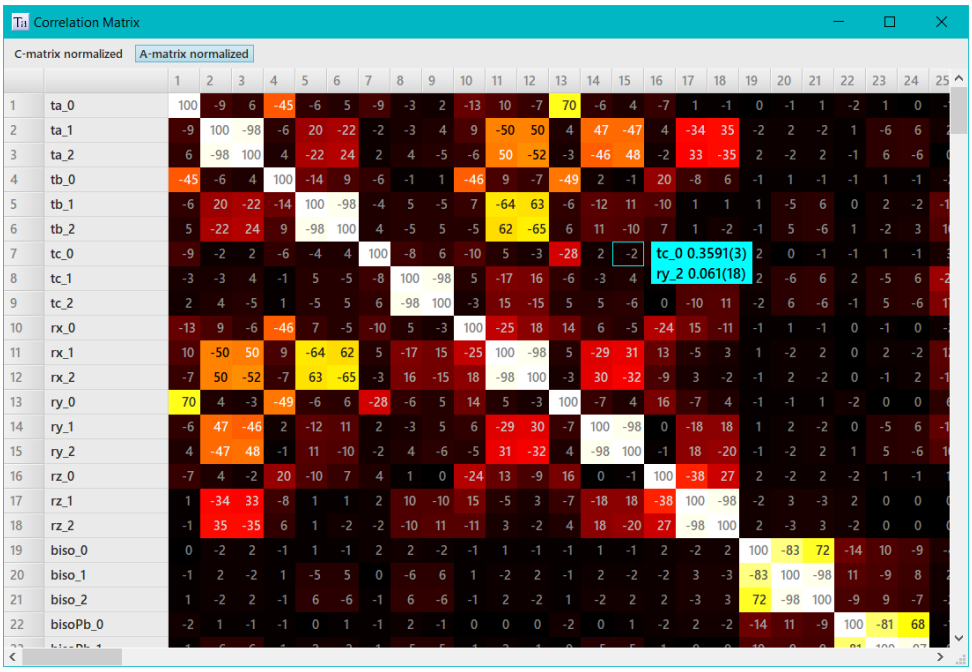


Uses the weighting from the kernel which can be User defined or otherwise. *SigmaYobs* is used in the weighting if it exists. The Cumulative Chi2 it is normalized to have the maximum intensity of *Yobs* within the display window. Data is obtained from the kernel; excluded regions are ignored as shown in the plot above. Tabs for Cumulative Chi2 has been included in the appropriate GUI tabs, i.e.

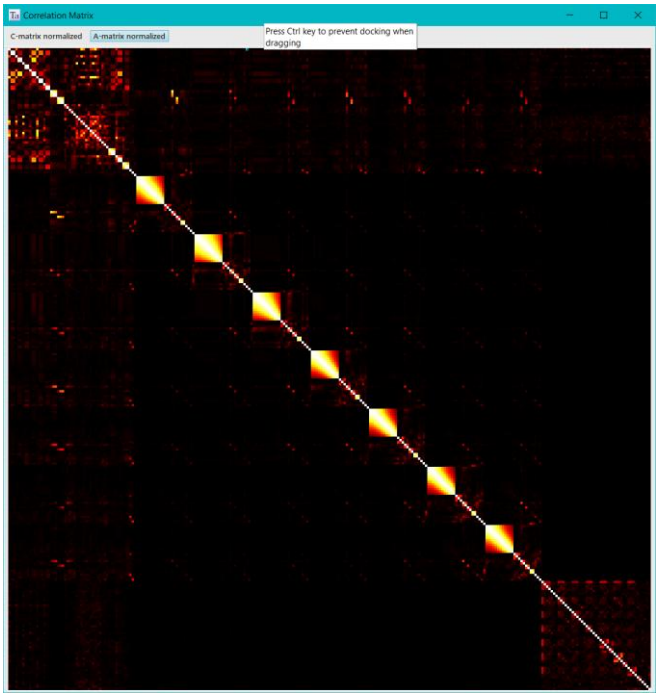


25.10 . Correlation Matrix display

A Correlation matrix window activated from the Fit Dialog; it operates in Launch and GUI modes. Example output is as follows:



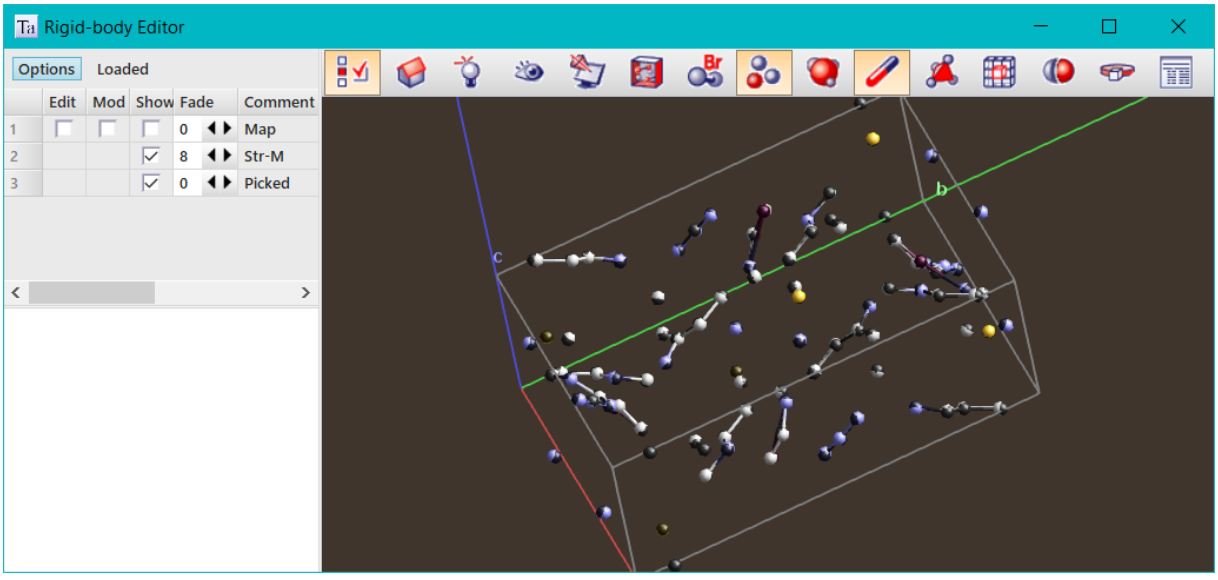
Both the A-matrix and the correlation matrix include penalties/restraints depending on whether do_errors_include_penalties and/or do_errors_include_restraints are defined. The display of the matrix can be zoomed using Ctrl-MouseWheel, here's an example:



MouseMove over the correlation matrix displays a Hint comprising the corresponding parameter name, value and error. Left Mouse button down and dragging translates the matrix.

25.11 . Fading a structure

The intensity of atom colours displayed in OpenGL can be adjusted using the Fade spin button of the OpenGL grid options, for example:



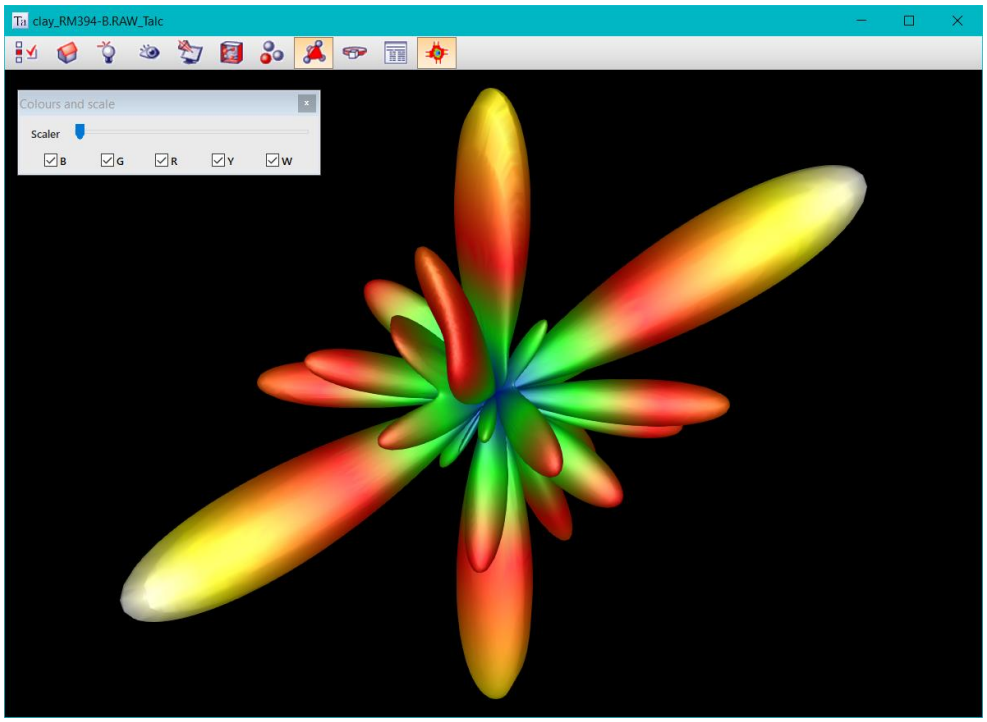
25.12 . Normals Plot

[normals_plot !E]...
    [normals_plot_min_d !E]

An OpenGL plot of lattice plane Normals with Normals lengths defined by normals_plot. For example:

```
normals_plot = Abs(H * K + L^2) + 1; normals_plot_min_d 0.3
```

normals_plot_min_d is optional; small values (ie. 0.1) could lead to millions of points and Users could blow up their computers. Here's output from the test example CLAY.INP:



The slider in the plot is activated by clicking on the  button. This slider multiplies the length of the normals_plot equation before generating the surface. The exact formulation for the multiplications is as follows.

Definitions:

s = multiplier which has a value (not shown to the user) that varies from 0 and 1.

N = diffraction vector directions with lengths given by the normals_plot equation.

N = Sqrt(**N** . **N**) = magnitude of **N**

N_{max} = maximum N

Before generating the shape, **N** is multiplied by:

For $s < 0.25$: $((N / N_{max})^{(4*s)}) * N_{max} / N$

For $0.25 \le s < 0.5$: $((N / N_{max})^{(4*(0.5-s))}) * N_{max} / N$

For $0.5 < s \le 0.75$: $(4*(0.5-s)) * N_{max} / N + (1-s)$

For $0.75 < s \le 1$: $(((4*(0.75-s)) + N_{max} / N$

25.13 . Improvements to the Grid

Data can be sorted by double clicking on column headings. Sorting alternates between ascending and descending order. On leaving a grid, the column most recently sorted is remembered. On re-entry of that grid, the data is again sorted according to the saved state. A small < or > sign is displayed to the left of the column heading name. Sorting works for all grids that

display data with rows that are similar in Type; i.e. Peak data, sites etc... Val and Error columns are sorted numerically. Hkls, F^2 and other obvious numeric columns are also sorted numerically. However, Min and Max are sorted using strings as they can be equations and hence their fields are strings.

CTRL-MouseWheel zooms/un-zooms the text of a grid.

MouseDownMouseMove for Panning.

25.14 . Mouse operation in OpenGL Graphics

First some definitions

LMB = Left Mouse Button

RMB = Right Mouse Button

MID = Mouse Wheel or Middle button on Laptops

MM = Mouse Moving

WM = Wheel moving

LMB-D = Left Mouse Button Down

RMB-D = Right Mouse Button Down

- MW-D = Mouse Wheel Down
- For example, LMB-D-MM is simply dragging with the LMD

Image rotation/translation operations are:

- LMB-D- MM rotates the image.
- LMB-D- MM and quick release initiates continuous rotation.
- LMD-D-MM on the first 10% of the viewport from the left, or, the last 10% from the right rotates around an axis perpendicular to the screen. This is another way of doing what Shift-LMB-D-MM does but without the need for keyboard input.
- MW zooms in addition to the usual RMB-D-MM.
- MID-D-MM translates the image in the plane of the screen.

Images are rotated around the centre of gravity (or centre of unit cell) unless there's a change using the RMB-D options.

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