

Chapter 9.4

THMA

TLS-Analysis

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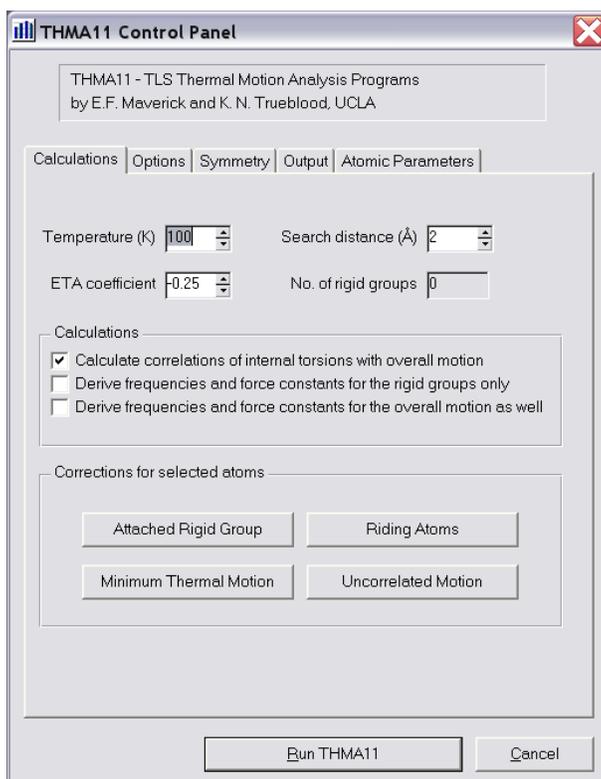
9.4 Programs THMA11 & THMA14c

These two programs are slightly different versions of THMA, a program which performs a TLS thermal motion analysis on experimentally measured *anisotropic displacement parameters* (ADPs). For an excellent introductory discussion on thermal motion analysis see *X-ray Analysis and the Structure of Organic Molecules* by J.D. Dunitz, VCH, Weinheim (1995), Ch. 5, pp 244-261. There are also two recent reviews on the subject:

Dunitz, J. D.; Schomaker, V.; Trueblood, K. N. *J. Phys. Chem.* 1988, **92**, 856-867.

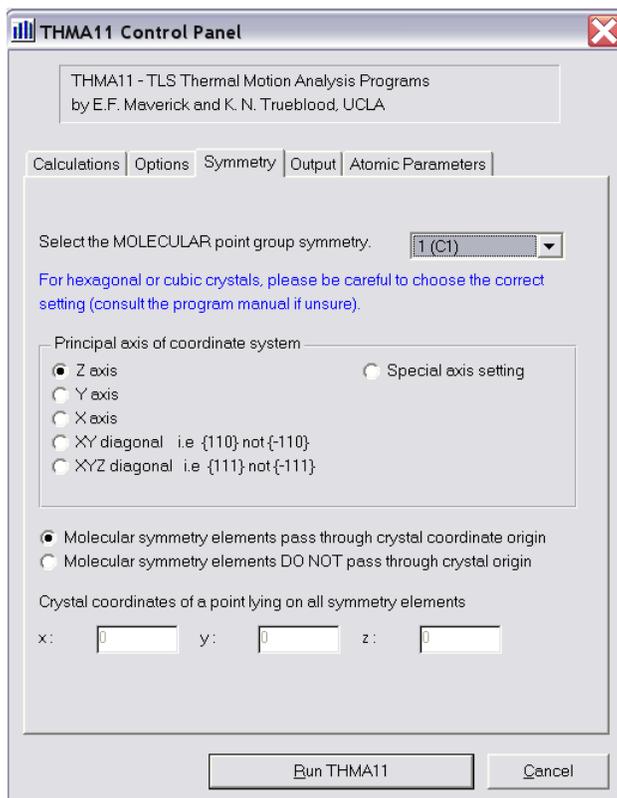
Dunitz, J. D.; Maverick, E. F.; Trueblood, K. N. *Angew. Chem., Int Ed. Engl.* 1988, **27**, 880-895.

THMA14c is the most recent version, but THMA11 has been more extensively tested. As implemented in *WinGX*, the input files for both programs (called THMA11.INPUT or THMA14.INPUT) are created automatically. The SHELXL.LST file is read to provide the standard uncertainties for the ADPs. Alternatively, a CIF containing atomic coordinates, U(ij)s and their errors may be used as input. Occasionally it may be necessary to manually edit these input files, e.g. if using relatively obscure options of the program, but the GUI now allows access to virtually all the documented features of the program. Full details of the file format and meaning of all the input parameters for THMA11 are given below, and the (very minor) differences between THMA11 and THMA14c given in Section 9.2.5. On selecting the THMA11 program a Window similar to the one shown below opens



A virtually identical window is shown for THMA14c.

For a default run there is no need to modify any parameters, except possibly to select the appropriate symmetry shown in the Window below. Note that the site symmetry refers to the



molecular rather than the crystallographic symmetry. For hexagonal or cubic crystals it is vital to choose the correct appropriate symmetry

The GUI allows the user to modify the input parameters, remove atoms from the list etc. Bubble help is available for several of the items. Only those atoms with *anisotropic* displacement parameters in the SHELX or CIF files will be passed to the GUI. If three or fewer atoms with ADPs are found, then a TLS analysis is not possible, and the program halts. The most common options which may need altering are the calculations of all pairs of MSDAs (default is to calculate all pairs) and options to cut down the voluminous output produced. The experienced user should note that it is always possible to manually edit the input files THMA11.INPUT/THMA14.INPUT, and directly run THMA using these files from WinGX.

Output from the programs is directed to the files THMA11.LST or THMA14.LST. This file is automatically opened when the program is finished. Both programs also generate two other files. THMA_SCF.OUT is suitable as input for the PEANUT

program of Hummel et al (this displays the difference $U(ij)s$) and THMA_CND.OUT, which is a pseudo SHELX file, can be used as input to Ortep for Windows, to visualise the principal axes of the T and L tensors. In addition, some other files may be written if selected on the GUI. The bubble help facility on the GUI explains the purpose of these files.

ADVICE : Users should first try a default run and check the values in the Δ MSDA table, which are a very useful guide as to the quality of the ADPs. Ideally the MSDAs between bonded atoms should be below 10 (i.e. $< 10^{-3} \text{ \AA}^2$), but certainly less than 2-3 times the average sigU. Much larger values between non-bonded atoms could indicate non-rigid parts of the molecule.

9.4.1 Summary of instruction file for THMA11

Optional cards are shown in parentheses and will only be required if certain parameters are set. Others are essential.

1. title (first 4 letters = "FREE" if free format input)
2. 6 cell dimen, IFMX, IFMB, ETA, DIS (up to 10 quantities)
3. control line: NTOT, NO, ISET, IB, NONRIG, NVIB, NS, ISIG, ISYM, ICORL, IWU, IFU, ICSVIB (up to 13 quantities)
- 4a. first option line: TEMP, IRECAL, ISIGX, IRIDE, IMIN, IUNC (up to 6 quantities)
- 4b. second option line: IFREQ, IATWT, IEIG, IMAT, IOUT, CONSLV (up to 6 quantities)
- 4c. infrequently used; only if ISET > 5; see control line, 3
- 5a,5b. pairs of lines for atomic parameters:
 - 5a. X, Y, Z, ATOMNAME, WEIGHT, MULT (order depends on format used; see lines 1 and 2)
 - 5b. anisotropic displacement parameters (order may vary with format used; see lines 1 and 2), NUORB
- 5c. ISIG lines of sigmas of displacement parameters; if no sigmas input, ISIG = 0; see control line, 3
- 6a. NAFA, LBAT1, LBAT2, NONSY, AXMOM; and
- 6b. a total of NAFA names; 6a and 6b may be omitted, depending on NONRIG, see control line, 3
- 6c. LBAT3, LBAT4, LBAT5; may omit depending on NAFA, see line 6a
- 6d. pairs of atom names; may be omitted, depending on IRIDE; see option line 4a)
- 6e. pairs of atom names; may be omitted, depending on IMIN; see option line 4a)
- 6f. pairs of atom names and equivalent positions; may be omitted, depending on IUNC; see option line 4a)
7. SYML(i), i=1,3 may be omitted, depending on ISYM; see control line, 3
- 8a. NVIB pairs of atom names and equivalent positions, if NVIB is positive; see control line, 3
- (8b. 2 x ICSVIB lines if ICSVIB is not 0; see control line, 3)
- (9, 10 etc. data for another calculation or for another compound; whether these lines are called for depends on NS (control line, 3) and IRECAL (option line 4a))

NOTE: some other input may also be required, depending on the values of ISET, NONRIG, NVIB, NS, ISIG, ISYM, ICSVIB, IRECAL, ISIGX, IRIDE, IMIN, IUNC and NAFA. In the default input files created by the WinGX implementation, lines 9 & 10 will never be used (since only single calculations are carried out).

9.4.2 Comments

- Frequency calculations (controlled by IFREQ, 2nd option line) should be viewed with great scepticism.
- Riding motion corrections and corrections for anharmonicity of the potential function are automatic for bonds to (anisotropic) hydrogen or deuterium atoms. **CAUTION:** If the "anharmonic" correction is positive, the data are suspect. It will be positive whenever the H or D has a lower MSDA than the "heavy atom" to which it is bonded (e.g., C,N,O) along the bonding direction. Normally the MSDA in this direction for H or D should be 0.040-0.060 Å² larger than that of the C, N or O to which it is bonded. When NVIB is negative, check the printed Δ MSDA matrix concerning this point - see Jeffrey and Ruble (1984). *ACA Trans.*, **20**, 129-131.
- The default is to include internal and overall correlations if internal libration is included. To bypass these correlations, deselect this GUI item on the Parameters page (making ICORL negative - control line, 3)
- Free-format input is used throughout except that, for atomic position and displacement parameters and their esds, it is optional. In this way, parameter sets from other programs may be used.

9.4.3 Restrictions on this version

1. No more than 7 *attached rigid groups* (ARGs) if the point group for the molecule is centrosymmetric, or 6 if it is acentric. No atom may be affected by the motion of more than 3 attached rigid groups. No more than 150 atoms are allowed.
2. This version uses the quadratic approximation of Schomaker and Trueblood (1968), *Acta Cryst.* B24, 63-76, for the rigid-body motion and the approximation of Dunitz and White (1973), *Acta Cryst.* A29, 93-94, for the libration of attached rigid groups on the molecule, including correlations of the internal and overall motion - see Schomaker & Trueblood, (1998) *Acta Cryst.*, **B54**, 507-514. For discussion of force constants, frequencies and barriers see also Trueblood and Dunitz (1983) *Acta Cryst.* B39, 120-133. Other useful references (reviews) are: Dunitz, Schomaker and Trueblood (1988) *J. Phys. Chem.* **92**, 856-867 and Dunitz, Maverick and Trueblood (1988) *Angew. Chem. (Int. Engl. Edn.)* **27**, 880-895

9.4.4 Full details of input instructions

Atom names (4-character strings) are included in input with atom parameters and are later used to identify sigU lines and for various instructions. These later names must be identical, including spaces (e.g., left adjustment), to those used initially. If not, there may be an error message, or just an unexplained failure, e.g., a

divide-by-zero stop, because the program could not find the atom you thought you were designating. All names are converted to uppercase .

LINE (1) title line

Up to 80 characters. If cols 1-4 of title line are "FREE", free-format input assumed for atomic parameters and sigUs, as well as for all other input. (These four characters will not be printed as part of title.)

LINE (2) six cell dimensions, IFMX, IFMB, ETA, DIS

Now always in free format with list-directed input. You need only separate items by spaces, by commas, or by spaces and commas. Use "/" to terminate list if all items are not included, e.g., if some are default zeros.

Options for cell dimensions:

1. real cell with either angles or cosines of angles. Sequence a, b, c, alpha, beta, gamma or a, b, c, cos(alpha), cos(beta), cos(gamma)
2. reciprocal cell with either angles or cosines of angles. Sequence analogous to that for real cell.

IFMX, IFMB are input format controls for atomic parameters. They are irrelevant if free-format input used.

IFMX

IFMX = 0 format for x,y,z is a4,23x,3f9.6,2f5.1 for name, x,y,z, atomic weight, multiplicity
 = 1 SHELX input for x,y,z and ADPs:
 line 1: (a4,f5.0,6f10.5,1x,i1) for name, at wt,x,y,z,mult,u11,u22,NUORB. As indicated below, SHELX parameter lines can usually be used unmodified, unless an atom is in a special position; see 5a,5b).
 line 2: (5x, 4f10.5) for U33, U23, U13, U12 (note order!)
 when IFMX = 1, IFMB is ignored
 > 1 format for x,y,z is 3f8.5,14x,a4,4x,2f5.1 for x,y,z, name,atomic weight, multiplicity
 < 0 format for x,y,z, is a4,5x,5f9.6 for name, atomic weight, multiplicity, x,y,z (see also lines (5) below)

IFMB

Value is irrelevant for SHELX input, IFMX = 1, or when free-format input used for atomic parameters. When IFMX \neq 1 and IFMB = 0, format for ADPs is 6f9.6,i1. If IFMB \neq 0 format for anisotropic displacement parameters is 6f10.6,i1 (see also lines (5) below)

ETA

The Hirshfeld-Shmueli [*Acta Cryst* A28, (1972) 648-652] correlation coefficient between mutually perpendicular mean-square amplitudes. This value should be that appropriate for the data input (see printed table, discussed below).

Recommended: Use the default value if you have any doubt. This will give what are presumably the most meaningful values for the sigUs of the U(i,j) in the absence of specific information about correlations. Alternatively, one can use unit weights, but when the sigUs vary widely, this seems questionable.

ETA is needed (and is used by the program) for transformation of sigUs from one co-ordinate system to another, in the absence of specific information on the covariances of the ADPs. The approximation used is that the covariances are isotropic, and that the only important terms are among the $U(i,i)$ and the $U(i,j)$ of a given atom. The actual value of ETA used seems to be important only for non-orthogonal axes. When NS (control line) is non-negative, a table is printed to indicate how appropriate the Hirshfeld-Shmueli assumptions and/or the value of ETA that was input are. Inspection of this table (see the legend accompanying it) may make it reasonable to try another input value. Whatever the value input, once a reasonably constant overall variance (s) is found, it is used with the standard ETA (-0.25) and the interaxial angles to estimate covariances. Hirshfeld and Shmueli recommend an ETA of -0.25, and this is the default if ETA is input as blank or zero. To get ETA = 0.0, use ETA = 99.0 for input. Experience has indicated that if the sigUs of the $U(i,j)$ (off-diagonal elements) are significantly smaller than one-half those of the $U(i,i)$, an ETA value of about 0.75 is implied. This is $(1 - 0.25)$, and we have found quite small values of the esds of the $U(i,j)$ when an overall isotropic B has been included as a parameter in the refinement. This has the effect of introducing a strong positive correlation among the $U(i,i)$. The Hirshfeld-Shmueli recommendation of -0.25 presumed no such correlation. If the variance-covariance matrix, or the related matrix of correlation coefficients for the l.s. refinement of the structure with $U(i,j)$ (or B or beta) has been printed out, it should be inspected to check on the typical correlation coefficients between the different $U(i,i)$ of a given atom. They are of the form

$$ETA + (1 - ETA) * \cos^2(ANGLE)$$

where ANGLE is the angle between the corresponding reciprocal axes. Usually the second term is very small, so this correlation coefficient is about ETA.

DIS

All distances in Å smaller than DIS from any input atom to any other input atom or any atom generated by symmetry will be listed when NS (control line) is not -2 or -4. Default of DIS (i.e., when DIS is input as zero) is 2.0 Å. DIS also is the upper limit for distances to be corrected for the effects of internal and/or overall motion. These distances are measured from the second axis-defining atom to each of the atoms affected by the internal motion.

A separate list of atoms with no neighbours or only one neighbour within this distance DIS is also printed, as well as a list of the connections (by this DIS criterion) between different asymmetric units. This option permits checking that a single molecule has been input (not several disconnected fragments).

LINE (3) control line NTOT, NO, ISET, IB, NONRIG, NVIB, NS, ISIG, ISYM, ICORL, IWU, IFU, ICSVIB

Now free format (list-directed). Spaces required between each integer.

NTOT number of atoms to be input (max = 150)

If the molecule (ion) whose motion is to be analysed has 2-fold or higher site-symmetry in the crystal, only those atoms comprising the asymmetric unit need be input. Those equivalent by symmetry will be generated by the program. If the total number of atoms, including any generated by symmetry exceeds 150, the job will be terminated with an error message. The limit for the number of atoms is given by

$$ntot + (na + na1) * (nmult - 1) \leq 150$$

na = number of atoms to be included in analysis of the motion + those with weight 800.0 (na is calculated by the program from the input data. You need not supply it.)

na1 = additional atoms included in setting up the system of inertia (wt negative as discussed under (5) below). (na1 is also calculated by the program)

nmult = no. of sym operations of the point group (nmult is also calculated by the program; it includes the identity operation)

NO control variable for site symmetry.

A number corresponding to the site symmetry of the molecule in the crystal. It is the number of the corresponding space group in Vol I of the *International Tables for X-ray Crystallography*.

Caution: The site symmetry of *the molecule* - the molecule's point group in the crystal - is what is wanted here. The space group of the crystal containing the molecule may be quite irrelevant. If the molecule comprises the asymmetric unit of the crystal (or only part of it because there are several molecules in the asymmetric unit), then the point-group number to use is necessarily 1, since the molecule has no internal symmetry.

The only permitted values of **NO** are as follows; they are grouped below, for convenience, in different symmetry classes:

site symmetry	number	site symmetry	number
1 (C1)	1	2/m (C2h)	10
1bar (Ci)	2	222 (D2)	16
P2 (C2)	3	mm2 (C2v)	25
m (Cs)	6	mmm (D2h)	47
4 (C4)	75	4mm (C4v)	99
4bar (S4)	81	(4bar)2m (D2d)	111
4/m (C4h)	83	4/mmm (D4h)	123
4222 (D4)	89		

The next group of site symmetries is to be used only for crystals indexed on hexagonal axes. If you have a molecule or ion with 3-fold symmetry indexed with

rhombohedral axes, you must first transform the positions (and U(ij)s or B(ij)s) to hexagonal axes.

site symmetry	number	site symmetry	number
3 (C3)	143	6 (C6)	168
3bar (C3i)	147	6bar (C3h)	174
312 (D3)	149	6/m (C6h)	175
321 (D3)	150	6222 (D6)	177
3m1 (C3v)	156	6mm (C6v)	183
31m (C3v)	157	(6bar)m2 (D3h)	187
(3bar)1m (D3d)	162	(6bar)2m (D3h)	189
(3bar)m1 (D3d)	164	6/mmm (D6h)	191

The final group of site symmetries listed here is to be used only for cubic crystals:

site symmetry	number	site symmetry	number
3 (C3)	146	3m (C3v)	160
3bar (C3i)	148	(3bar)m (D3d)	166
32 (D3)	155		
23 (T)	195	(4bar)3m (Td)	215
m3 (Th)	200	m3m (Oh)	221
432 (O)	207		

NOTE: as indicated, the *R* space-group numbers (146, 148, 155, 160, 166) are to be used only for molecules with the indicated point-group symmetry that are found in cubic crystals. Note that the coordinates must correspond to the 3-fold axis lying along the diagonal (ISET=5). If a molecule with such point-group symmetry is found in a trigonal crystal, use corresponding hexagonal axes and the point-group number appropriate to those axes.

ISET setting of principal axis in crystal coord. system

- if ISET = 1 principal axis z
- if ISET = 2 principal axis x
- if ISET = 3 principal axis y
- if ISET = 4 principal axis xy-diagonal (this means [110], not [-1,1,0], etc)
- if ISET = 5 principal axis xyz-diagonal (this means [111], not [-1,1,1], etc)
- if ISET > 5, special setting needed (e.g., for a molecule that has mmm symmetry with the axes oriented at 45 degrees to x and y). See (4c) below for input of matrices.

The 'principal axis' is the unique axis (if any) of the point group. For molecules with symmetry elements of order higher than 2 it is assumed that the principal axis will be along the z-direction (ISET = 1) except for groups with 3-fold symmetry elements in cubic crystals for which the *R*-space group number (146,148, 155,160, or 166) corresponding to the appropriate point-group symmetry should be used.

Use ISET = 5 for such groups and only for such groups. Thus, when (e.g.) you have a 2-fold axis parallel to the b-axis (i.e., y), make ISET = 3, or the symmetry operations appropriate to the point-symmetry chosen will not be correct.

use ISET = 1 for C1 and Ci (NO = 1 and 2).

use ISET = 3 for monoclinic crystals with b as the unique axis

IB indicator of ADP type

IB is the same index used by ORTEP to denote the kind of anisotropic displacement parameter. Only indices 0, 1, 4, and 8 are used here. Any other value will cause the program to exit. NOTE : in the WinGX implementation IB is ALWAYS 8 and should not be changed

IB = 0 dimensionless B(i,j), explicit 2 with cross terms

IB = 1 dimensionless B(i,j), no factor 2 with cross terms

Thus anisotropic displacement parameter for IB = 1 is:

$$\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}h*k + b_{13}h*l + b_{23}k*l)$$

For IB = 4 and 8, anisotropic displacement parameters are assumed to be U(i,j) (Å²), with an explicit factor of 2 included with the cross terms. The form is:

$$\exp -d*(r_a(i)*r_a(j)*u(i,j)*h(i)*h(j))$$

with r_a meaning reciprocal axis length and h meaning reflection index. Summation over i,j is assumed.

IB = 8 d = 2.0*π²

IB = 4 d = 0.25

NONRIG control variable for attached rigid groups (ARGs)

If NONRIG ≠ 0, input follows for attached rigid groups (i.e., input concerning internally moving groups). NONRIG defines number of attached rigid groups to be considered moving (max = 7 in THMA11). Six extra parameters are determined per group (one parameter if ICORL < 0).

NVIB control variable for MSDA calculations

If NVIB < 0, mean square displacement amplitudes are to be calculated along interatomic lines for all unique pairs of atoms (omitting isotropic atoms). Matrices of differences of msda values are output regardless of the value of NS, but if NVIB < -1 and NS ≥ 0, a complete list (including all atoms in the asymmetric unit and those atoms generated by symmetry) of amplitudes will be included in the output.

If NVIB > 0, mean square displacement amplitudes are to be calculated only for selected pairs of atoms, along lines defined by these pairs. The atom pairs are read on line (8a). NVIB is defined as a positive integer, equal to the number of pairs of atoms for which mean square amplitudes along the corresponding interatomic lines are wanted. NVIB cannot exceed 40 (there is no limit on the number of pairs if NVIB is negative - see above).

NS control variable for output.

If NS is greater than 0, another set of data follows starting with title line.

NS negative gives shorter output, specifically:
NS = -1, somewhat shorter, no compound follows
NS = -2, much shorter output, no compound follows
NS = -3, somewhat shorter, another compound follows
NS = -4, much shorter, another compound follows

Use *much shorter* in second and later runs of the same data, when trying variations; in initial runs, use either full output or shorter. *Much shorter* skips output of such things as principal-axis setting, input sigUs, transformation matrices, Cartesian co-ordinates, information about the inertia tensor, intramolecular distances, correlation coefficients, comparison of observed and calculated U(ij)s, and a few other items. Some of these are also skipped when NS = -1 or -3. The long detailed listing of MSDA differences can be obtained only when $NS \geq 0$ and $NVIB \leq -2$. When NS is negative, only 5 lines are skipped between pages, rather than going to an actual new sheet.

ISIG control variable for sigUs

If ISIG = 0, no sigUs (or Bs) to be provided. If sigUs (or Bs) are to be given, they need not be given for more than the number of atoms whose U(ij)s are to be used in the analysis of the motion. The absolute value of ISIG should be the number of atoms whose U(ij) are to be used. More sigUs may be input (and ISIG increased accordingly), but the program will ignore them. Thus they need not be given for atoms with negative weights or dummy atoms with weight 800.0 or 999.9. ISIG may be positive or negative.

If ISIG is positive, input is sigBs or sigUs and the working weights will be:

- if $IWU \neq 1$, $wu(i,k) = [\text{average sigU}(i,k)]/\text{sigU}(i,k)$ (average not including sigmas of 0.0 or atoms with weight 800.; sigmas of atoms with weight 999.9 or < 0 always ignored)
- if $IWU = 1$, then $wu(i,k) = 1.0$ and the sigUs are used only to calculate the mean standard deviation of U observed values

If ISIG is negative, the input is treated as working weights $wu(i,k)$ for the observational equations. Weights must be those appropriate for U(ij)s in the Cartesian system (in which calculations are done), not the input crystal system. No transformation done. If you wish to put in 'working weights' appropriate for the crystal system, and have them transformed to working system, use sigUs proportional to inverse of the weights (with ISIG positive).

ISYM control variable for symmetry setting

If ISYM = 0 or blank, origin of crystal system lies on the molecular symmetry elements, i.e., the molecular symmetry elements pass through (0,0,0) of the co-ordinate system used.

If $ISYM \neq 0$, then the crystal origin does not lie on the molecular symmetry elements. When $ISYM \neq 0$ an additional line is read with the co-ordinates of a point on the symmetry elements. See (7) below.

ICORL control variable for calculation of correlations

If ICORL is less than 0, then calculation of correlations of internal torsions with overall motion is bypassed (Dunitz-White method). Bypass is automatic for groups with only one atom ($NAFA(i) = 1$) since there are too few $U(i,j)$ to determine 6 parameters.

IWU control variable for weights

If $IWU \geq 0$, ignored unless $ISIG \geq 0$ (see ISIG above)

IFU control variable for output

If $IFU \neq 0$, then detailed information is requested for each atom. The output gives an atom-by-atom comparison of observed and calculated $U(ij)$ s in the inertial system, their eigenvalues and eigenvectors, the angles between the latter, and the angles between the eigenvectors of U_{obs} and those of L and T .

ICSVIB control variable for MSDA calculations

ICSVIB is non-zero if mean square displacement amplitudes are to be calculated for individual specified atoms along directions that are defined by input direction cosines. ICSVIB must be a positive integer (no larger than 10) and is the number of directions for which the calculations are to be made. The direction cosines and atom names are read in on lines (8b). The maximum number of atoms for any direction is 12. A given direction may be used more than once.

LINE (4) three option lines (free format).

The options in line 4a will probably be more generally used, those in 4b are for less common situations, 4c is rarely required. However all three lines are given by the GUI in default mode.

LINE (4a) TEMP, IRECAL, ISIGX, IRIDE, IMIN, IUNC

TEMP

If entered as 0.0, the default temperature of 296 K is assumed. Otherwise TEMP is the Kelvin temperature, a floating point number, e.g., 115.0 or 239.0.

IRECAL

If IRECAL $\neq 0$ signifies that a second calculation is wanted with the same atomic parameters. To start it, use new title line, omit cell dimensions, include control and option lines, omit atomic parameters and esds, include other lines if specified on control line or option line. **This parameter is not used in the WinGX version, and should not be changed from default value of 0 ! (unless you prepare an input file by hand and you know what you are doing)**

ISIGX

ISIGX \neq 0, implies that lines including esds of x,y,z are intermixed with sigmas of U(ij)s or B(ij)s (see under lines (5c) below). This parameter is not used in the WinGX version, and should not be changed from default value of 0 ! (unless you prepare an input file by hand and you know what you are doing).

IRIDE

IRIDE \neq 0 means up to 20 pairs of atoms to be input at line (6d) below for riding-correction calculation. All bonds to (anisotropic) H and D atoms will automatically have riding correction calculated, so use IRIDE \neq 0 only if such corrections are to be applied to other atoms. Note that if less than 20 atoms pairs are given, the list MUST be terminated with a "/" (the GUI does this automatically).

IMIN

IMIN \neq 0 means up to 20 pairs of atoms to be input at line (6e) below to define distances for the minimal thermal motion correction [see Busing & Levy (1964), *Acta Cryst* 17, 142]. Note that if less than 20 atoms pairs are given, the list MUST be terminated with a "/" (the GUI does this automatically).

IUNC

IUNC \neq 0 means up to 20 pairs of atoms to be input at line (6f) below for correction for uncorrelated (independent) motion [see Busing & Levy (1964), *Acta Cryst.* 17, 142]. The first atom of each pair of atoms is assumed to be one of the atoms input; the 2nd may be related to an input atom by a centre of symmetry at the origin and by translation. Note that if less than 20 atoms pairs are given, the list MUST be terminated with a "/" (the GUI does this automatically).

LINE (4b) IFREQ, IATWT, IEIG, IMAT, IOUT, CONSLV**IFREQ**

If IFREQ = 0, no frequency, force constant or barrier estimations will be made. If $>$ 0, estimated frequencies, force constants and barriers for internal motion only, i.e., for motion of attached rigid groups. If IFREQ $<$ 0 estimated frequencies for overall motion also. A minor source of errors in frequencies will arise if H atoms are not included in the attached groups, because the moments of inertia will be low (by as much as 20 or 25 percent for groups such as methyl or t-butyl).

IATWT

If IATWT = 0, atomic weights to be assigned by program. If \neq 0, no atomic weights to be assigned by program. When IATWT = 0, atomic weights generated from the chemical symbol (first non-blank characters in cols 1-4 of atom name) for elements 1-53 and also D, W, Re, Os, Ir, Pt (excluding, however He, Ne, Ar, Kr, Tc), unless atom already has negative wt or wt 800.0 or 999.9. Either upper or lower case letters (or mixture) OK for atom names. To preassign wt to a particular atom

(other than its atomic weight, or special value), change its symbol to something non-standard. Isotropic atoms are assigned negative weights by the program (unless $wt = 800.$, 999.9 or a negative wt is input).

Note that if an atom has been identified as Ca (or CA), implying carbon α or carbon alpha, the program will identify it as calcium. For any atoms not in the "standard list" given above, use the desired wt as input value (program will retain the input value for any atom it does not recognise). As mentioned above, program will override any assigned weight for a 'common atom' unless $IATWT \neq 0$ or weight input as $800.$, 999.9 or negative. In the WinGX version, atomic weights will be assigned automatically to element type.

IEIG

If $IEIG > 0$ write out the matrix of normal equations for later analysis by an eigenvalue/eigenvector program. Inspection of the eigenvectors under this situation can be helpful in understanding the interdependence of different variables. This unformatted binary file is called THMA_MAT.OUT and has the first record integer N , followed by the matrix $((AN(i,j),j=1,N),i=1,N)$ as double precision real.

IMAT

This variable is used only for special checking of the matrix of normal equations. When the matrix or its inverse is printed, the accompanying vector is the last element listed in each row. Whenever the matrix of normal equations is printed, the corresponding solution vector is also printed (one element per line) immediately after.

IMAT = 100 or more provides special options for checking matrix of normal equations and effects of contracting it.

IMAT ≥ 250 do not contract matrix or delete any rows or columns

IMAT ≥ 200 print matrix, after contraction and deletion.

IMAT = 175 or IMAT = 225, print inverse matrix

IMAT ≥ 100 print matrix first with contributions of unique atoms only, then with all. Print solution vector (one element per line) and esds (similarly)

IOUT

If $IOUT \neq 0$, output co-ordinates corrected for rigid-body (but not internal) motion. These corrected co-ordinates will have format (a4,23x,3f9.6), which is the format appropriate for the Oak-Ridge programs, and are written to a file called THMA_COR.OUT

CONSLV

This may be ignored except on machines with relatively small word size (e.g., some VAX), and even then may be ignored most of the time. It is set to .01 by the program unless some non-zero value is input. Needed only when an overflow error occurs in subroutine MATINV, which may (rarely) happen with high-symmetry space groups (or possibly very large structures) on the VAX. Try $conslv = 0.005$ or 0.001 if

overflow occurs. It is used to reduce size of terms in the matrix at start of subroutine SOLVE. In the WinGX version this should never happen, but if another value of CONSLV is required, a manual edit of the THMA11.INPUT file will be needed.

LINE (4c) title, TMat, RTMat

If on the control line ISET is larger than 5, insert 1 line with title of special setting format (20a4) and input 9 components of the transformation matrix, (by rows, i.e., with columns varying fastest; see example below), and 9 components of the inverse transformation matrix. There may be up to 9 values per line, or (for easier visualising) 3 per line. All values are free format.

Note that throughout this program all matrices premultiply vectors, even when the latter are contravariant.

TMat is the transformation matrix, as a prefactor, to be applied to the standard setting (z-axis as unique axis) to transform it to the particular setting in the crystal of interest. See also the comments under ISET (line (3) above).

RTMat matrix for backtransformation

example original setting z-axis, desired principal axis = x

```
(TMat(I,J),J=1,3)      input: 0., 0., 1., 1., 0., 0., 0., 1., 0.
                        (or the same numbers spread over 3 lines), which is
                        equivalent to:
                        tmat(1,j) 0. 0. 1.
                        tmat(2,j) 1. 0. 0.
                        tmat(3,j) 0. 1. 0.
```

```
(RTMat(I,J),J=1,3)
  rtmat(1,j) 0. 1. 0.
  rtmat(2,j) 0. 0. 1.
  rtmat(3,j) 1. 0. 0.
```

This case is implemented in the program, ISET = 2. This TMat, as a prefactor multiplying x,y,z will produce

```
new x = old z
new y = old x
new z = old y
```

The program (in subroutine SYMPOS) gets the symmetry operations appropriate to the specified setting of the principal axis from those that are stored (in SYMET) by applying **tmat** as a prefactor and **rtmat** as a postfactor in a triple matrix multiplication. The stored symmetry operations are those appropriate for the z-axis as the principal axis; they are internally modified as needed when ISET is not 1.

LINE (5) atomic parameter lines**LINE (5a) position parameters.**

These may be formatted or free format:

Formatted input: [formats given above, under line (2)] as either

atomname, x, y, z, weight, mult (IFMX = 0)

SHELX format: (IFMX = 1)

atomname,wt,x,y,z,mult,u11,u22

x, y, z, atomname, weight, mult (IFMX > 1)

atomname, weight, mult, x, y, z (IFMX < 0)

Free-format input (if columns 1-4 of title line were "free"). Order is then:

atomname, x, y, z, wt, mult

mult will be set to 1.0 if input as 0.0 (see below). Hence it need be given only when atom is in a special position).

wt need be given only when program is not assigning atomic wts *i.e.* IATWT \neq 0 on 2nd option line, or if atom is in special position, so **mult** is to be input. Value for **wt** irrelevant if atomic weights to be set by program, regardless of values of **mult**.

x, y, z are fractional co-ordinates along a, b, c

atomname is a four-character name, which must begin with the chemical symbol for the element if atomic wts are to be assigned by the program. The identical name must be used for the same atom for input of sigU and non-rigid group information (see below).

CAUTION: be sure the x, y, z values used correspond (after symmetry operations, if any) to a single molecule, not parts of several separate molecules. If you are uncertain, use NS \geq -1 the first time, and check the printed list of input distances and pairs of bonded asymmetric units. Submit fractional co-ordinates for one complete asymmetric unit.

Input lines of position co-ordinates and anisotropic displacement parameters are read pairwise for each atom, 1st line co-ordinates, 2nd line U(ij)s or B(ij)s (except for SHELX input, IFMX=1, when U11,U22 are on first line). The sequence of the atoms is irrelevant (except for easy interpretation of the MSDA matrix - see comments on NVIB on the control line)

Atom names may be upper case, lower case, or mixed (in any case they are converted internally to uppercase). There are various special weights that may be used for special purposes. See the discussion and table below.

With SHELX input, if mult is input as 10.0 or greater, it will be diminished by 10.0; similarly, if x,y,z, or any U value has been fixed by having had 10.0 added to it, it

will be automatically corrected by this program. With SHELX input, 'AFIX' lines are automatically skipped, so they need not be removed from the file.

Standard format (when IFMX = 0) is a4,23x,3f9.6,2f5.1 . Other formats possible when IFMX \neq 0. see above.

weights:

These are relative weights of the atoms, to be used EITHER for calculation of the inertia tensor, OR as signals to the program to treat the atom in a special way. They are NOT weightings for the least squares calculation, which are either inverse variances of the displacement parameters, or special weights that the user may input.

The following table summarises the way in which atoms with different input weights are treated. Positions and U(ij)s or B(ij)s must be input for all atoms, but the U or B values are irrelevant for those atoms not included in analysis of the motion, except insofar as you may be interested in their comparison with the U(ij)s calculated by the program. These will be listed, for all input atoms, in the crystal system when NS is not negative, and in the Cartesian crystal system (if different) when NS is not -2 or -4 when IFU is positive (control line), detailed atom-by-atom comparisons are made in the inertial system. See discussion of IFU above.

weight	U(ij)s used in analysis of motion	Reproduced by symmetry operations	Included in inertial system	SigUs of atom(#) "interpreted" when IFU \neq 0	U(ij)s (B(ij)s) need to be input (##)
0.0 (*)	yes	yes	no	yes	yes
negative	no	yes	yes(**)	yes(***)	no
800.	no	yes	no	no	no
999.9	no	no	no	yes	no
other	yes	yes	yes	yes	yes

(*) if program is assigning atomic wts (IATWT = 0), you must give an unrecognisable name to the atom to keep the input weight = 0.0 (e.g., CX, NX, OX, ...)

(**) negative weight is made positive by subroutine INERT

(***) isotropic atoms are given negative wt by program, but they will not be "interpreted" by subroutine ATINT

(#) U(ij)s corresponding to the derived motion will be calculated for these atoms in the inertial system and compared with those input when yes appears in this column, except for isotropic atoms

(##) when ISIG is non-zero, that is, when any sigUs or sigB's input

Dummy atoms

Dummy atoms should be given weight 800.0. Such atoms are useful for defining libration axes that do not lie along any interatomic line in the molecule. Although wt 999.9 can be used for dummy atoms when the symmetry is only 1 (NO = 1), atoms with weight 999.9 are not reproduced by symmetry operations. Note that atoms of wt 800.0 will be reproduced by the symmetry operations. U(ij)s or B(ij)s must be given for 800.0 atoms, but the specific values are not used (they may all be zero). Esds are optional, even if included for others. Alternatively, dummy atoms may be given wt 0.0, so that they do not contribute to the inertial tensor and given sigUs (or sigBs) higher by a factor of 1000 or more than those of other atoms. These two steps have the same effect as weight 800.0: the atoms contribute nothing to the inertial tensor and negligibly to the matrix of normal equations, but they are reproduced by the symmetry operations because they have $wt \geq 0.0$. If this option is used, however, these atoms will add to the 'number of independent observations' through their NUORB values, so esds will be estimated too low. If there are no atoms with either positive or zero weight the job will be terminated

Atoms in special positions:

Note that atoms in special positions will be given their normal atomic weights, for the weight of each atom is adjusted for multiplicity in the calculation of the inertia tensor. There is no adjustment for multiplicity in calculating the contributions to the normal equations, that is, the U(ij)s of atoms in special positions are given the same relative weight for least squares. as atoms in general positions, taking into account whatever variation there may be in the sigmas of individual components of the U(ij)s if sigu is used for weighting.

A user who wants to exclude a particular component from the analysis can do this with the option ISIG < 0 (on control line, (3)), inserting sigU(i,j) = 0. for this component, for all the others, sigU = 1.

mult

The multiplicity of the position for the atom. All atoms in general positions have mult = 1.0. *mult is used only for calculation of the inertia tensor, and has no effect on the kinematic calculations*

If **mult** is input as 0.0 or blank, it is changed to 1.0, so that effective input value of mult is always greater than or equal to 1.0. For atoms in special positions, calculate mult as follows: examine the listing of the positions in Vol I of the *International Tables* for the space group appropriate for the point group. If NG = the number of general positions (always listed first in the Tables) and NS = the number of special positions, then **mult** = ng/ns

Note that the program immediately converts **mult** into its reciprocal (still calling it **mult(i)**). This is why **mult** (despite its name) is not regarded by the program as an integer and why it is to be input as f5.1 (see format), e.g. as 1.0, 4.0, etc.

Example D2h number 47, Pmmm, NG = 8) all atoms in general positions have mult = 1.0 (since for these positions NS = NG). An atom in a position of site-symmetry m has NS = 4, and thus has mult = 8/4 = 2.0. An atom in a position of site-symmetry mmm has NS = 1 and thus has mult = 8/1 = 8.0

Example in a cubic crystal: a group with sym $D3d [(3\bar{6})m]$, use $NO = 166$, as specified for NO (on control line) since space group 166 is $R(3\bar{6})m$, $NG = 12$. An atom in a position of site-symmetry $3m$ has $NS = 2$, so $mult = 12/2 = 6.0$

LINE(5b) atomic displacement parameters

Standard format is (6f9.6,i1) but if $IFMB \neq 0$, format is 6f10.6,i1 (again, format changes may be made in subroutine RDIN) or free-format input (see earlier comments)

ADPs as indicated with IB (line(3)). $B(ij)$ s are converted to $U(ij)$ s (subroutine CONVER).

Sequence B11, B22, B33, B12, B13, B23, NUORB(i)
 or U11, U22, U33, U12, U13, U23, NUORB(i)
 or (SHELX) U33,U23,U13,U12 (U11,U22,NUORB with x,y,z)

NUORB(i) is number of independent ADPs of the atom I. If blank, 6 is assumed

NOTE: It is usually unnecessary to give NUORB, which needs to be explicitly input only for atoms in special positions.

Program calculates the number of independent observations:

$$ninobs = \text{sum}(NUORB(i))$$

(NUORB is used only in calculation of sigUs, so if they have not been adjusted for symmetry the only effect is that the calculated sigUs are too low)

If sigUs are provided, they follow after the complete set of input data for coordinates and anisotropic displacement parameters

LINE (5c) input of sigU (or sigB), atname format (6f10.5,a4)

Sequence: sigU11,sigU22,sigU33,sigU12,sigU13,sigU23,atname

Free-format input will be used here if it is used for the position and displacement parameters

NOTES:

1. Abs(ISIG) input lines of sigUs (sigBs) MUST be given
2. Atom names must be identical to those used above. Sequence of atoms irrelevant, sorted by program.
3. If ISIGX (1st option line) is non-zero, sigmas of x,y,z intermixed with sigUs or sigBs, sigmas of x,y,z being first line of each pair. The sigmas of x,y,z are not used by the program

4. Format for sigUs (or sigBs) is not variable, but it could be altered in subroutine RDIN (rdin5)
5. The sigmas of the displacement parameters will be taken to be sigBs if IB = 0 or 1 and will be converted to sigUs. They are not listed until after they have been converted to sigU
6. If sigUs are to be used to calculate least square wts (ISIG > 0), any sigma = 0.0 is set = average sigma
7. If no sigUs input, wu is set to 1.0 for all atoms and all U(ij)
8. When ISIG positive and IWU \neq 1, sigUs for equivalent atoms are generated, and sigUs are transformed to Cartesian (working) system.

LINES (6a, 6b, 6c) Input concerning attached rigid groups, assumed to be undergoing torsional or other motion ('non-rigid' input)

All atomic names must be identical with the names used in the input for the coordinates, including spacing and blanks. If not an error message is printed and calculation stops.

Limitations:

- No atom may be in more than 3 attached rigid groups (ARGs)
- A maximum of 7 attached rigid groups is allowed, each containing at the most 40 *affected atoms*, i.e., atoms whose positions are affected by motion of the group about its prescribed axis. An atom lying on the axis is not affected by the motion, so do not consider the axis-defining atoms as *affected atoms*.
- If these dimensions are exceeded, the job will be terminated.

For each ARG, input lines 6a, 6b (and 6c if needed). Then follow with similar lines for the next ARG. All input free format. For each ARG:

line (6a) NAFA, LBAT1, LBAT2, NONSY, AXMOM

(NONSY, AXMOM usually not needed; use "/" if omitting them)

NAFA

Number of affected atoms (no more than 40). Note especially that this number does not include the two atoms that define the libration axis and it includes only the unique affected atoms, not those generated by any symmetry operations that affect the attached rigid group. If NAFA is input as a negative number (it is made positive), it means that three more atom names are to be read (see line (6c) below), and that direction of axis of attached rigid group is to be defined as the vector product of the vector from LBAT1 to LBAT2 with the vector from LBAT3 to LBAT4, the axis passing through the atom whose name is given by LBAT5, i.e., (LBAT1→LBAT2) x (LBAT3→LBAT4), through LBAT5

LBAT1, LBAT2

LBAT1 - name of atom 1 defining the libration axis

LBAT2 - name of atom 2 defining the libration axis

LBAT2 should be the axis-defining atom that is closest to the other atoms in the group, since corrected distances to it (but not to LBAT1) that are less than or equal to DIS (input line 2) are calculated and printed.

Parameter NRBCON was once (pre-1985) in cols 31-35; it is no longer used. If using free format input with a pre-existing input set, be sure to remove it.

NONSY

You can ignore this parameter if doing no frequency calculations, (IFREQ = 0, 2nd option line) or if symmetry is only P1 or P1bar.

NONSY = 0 if this ARG lies on any symmetry element, = non-zero if ARG lies on no symmetry element, when symmetry is higher than P1bar. This is used only in subroutine NRCOR. The program usually calculates the moment of inertia for an ARG in making frequency and force constant calculations. However, when symmetry is higher than P1bar, moment of inertia calculated by the program for a group lying on a symmetry element will be wrong, so calculation is skipped in these circumstances unless a non-zero value of AXMOM has been input for the group.

AXMOM

Only used when NONSY is zero. The moment of inertia of the attached group, in units of atomic weights and \AA^2 , about the symmetry axis. Typical values are 2.9 for $-\text{NH}_3^+$, 3.2 for CH_3 , 40.0 for a carboxylate group, 76.0 for t-butyl (not including H atoms), 88.0 for trifluoro-methyl, 89.0 for phenyl (including H atoms)

line (6b) names of the affected atoms

Up to 40 names, always free format. Submit a total of NAFA names.

line (6c) LBAT3, LBAT4, LBAT5

When NAFA input as negative number for a given ARG, three atom names are read here, free format: LBAT3, LBAT4, LBAT5

for example, C8 O4 N2 (see discussion under NAFA above)

Additional lines 6a, 6b, 6c for 2nd and further ARGs, if any.

LINES (6d, 6e, 6f) input concerning riding, minimal thermal motion and correlation corrections**line (6d) Riding correction**

When IRIDE (1st option line) is non-zero, read here up to a maximum of 20 pairs of atom names, in free format, for the application of riding correction. There is no

need for this for bonds involving (anisotropic) H or D atoms - riding corrections for these will be calculated automatically.

- First atom of each pair is the atom assumed to be riding
- Second atom of each pair is the atom that is being ridden

example: C15 Cu1 C16 Ru1 O19 Ru2/

Note that either space(s) or a comma must be between each item in the list. **If less than 20 pairs are entered, the list MUST be terminated by a "/"** .

line (6e) minimal thermal correction

When IMIN (option line) $\neq 0$, read here up to a maximum of 20 pairs of atom names, free format, for application of the minimal thermal motion correction to the distance between the atoms. **If less than 20 pairs are entered, the list MUST be terminated by a "/"** .

line (6f) independent motion correction

When IUNC (option line) $\neq 0$, read here up to a maximum of 20 pairs of atom names, with an equivalent position for 2nd atom, for correction of a distance for uncorrelated (independent) motion. The equivalent position may only be one related by translational symmetry or by combination of a centre of symmetry at the origin and translation. The distance may be larger than the limiting distance specified by DIS on the cell-dimension line. All input is free format. **If less than 20 pairs are entered, the list MUST be terminated by a "/"**.

For each pair, the following is needed:

atomname 1 atomname 2 NUNC (TUNC(i),i=1,3)

If 2nd atom is related to input position by a centre of symmetry at the origin, NUNC is negative; if not, NUNC is zero or positive. TUNC(i) are translational components, which may be fractional for centred lattices and thus are input with decimal point, as in this example:

C15 O17 0 0. -1. 2.

C18 N2 -1 0.5 2. 1.5

Here for first pair, O17 is related to input O17 by x , $y - 1.$, $z + 2.$ and for the second pair, N2 is related to the input N2 by $0.5 - x$, $2. - y$, $1.5 - z$

LINE (7) input concerning symmetry

When ISYM $\neq 0$, read in one line here (free format)

SYML(i), $i = 1,3$

SYML(i) are the co-ordinates of a point lying on all the molecular symmetry elements. If there is a unique point, they are the (crystal) co-ordinates of that point, which is the invariant point of the molecular point group. If no unique point, then the arbitrary co-ordinates may be given any value, most conveniently 0. For

example, for point group C_s (m) with the m perpendicular to the b -axis, at say $y = 0.25$, the values of SYML(i) would be 0.0, 0.25, 0.0 (although any other values could be used for x and z). For point group C_{2v} with the principal axis along the a -axis of the crystal at $y = 0.25$ and $z = 0.50$, with x arbitrary, SYML(i) would be 0.0, 0.25, 0.50.

LINE (8a), (8b) input concerning MSDA calculations

LINE (8a)

If $NVIB \leq 0$ (line 3), no input is needed here. When $NVIB < 0$, calculation is done for every unique pair of atoms. When $NVIB > 0$, such calculations done only for specified pairs of atoms. Each pair of atoms defines a direction for which mean square displacement amplitudes will be calculated for the atoms from the U_{obs} and, for atoms in the asymmetric unit input, the U_{calc} as well. The values from the U_{obs} give a measure of the quality of the data if the atoms define a 'bond' that would be expected to be 'rigid'. The values from the U_{calc} for any pair of atoms within a rigid body or within any librating group should be identical. They are output for checking and for comparison with the 'observed' amplitudes. MSDA calculated between an atom in the framework and one in a librating attached group (or between atoms in different groups of this kind) reflect the internal motion.

When $NVIB > 0$ (line (3)), read $NVIB$ pairs of atom names in free format, each name being accompanied by the number of its equivalent position (= 1 if atom is in the asymmetric unit input).

example atname1, eqposn1, atname2, eqposn2

The equivalent positions are listed in order early in the output. If unsure about this order, try one run with $NVIB = 0$ to check the order. As always, atom names must be identical to those used on atom parameter lines.

LINE (8b)

If $ICSVIB \neq 0$ (on line (3)), read 2 x $ICSVIB$ lines here. $ICSVIB$ may be no larger than 10. The lines come in pairs.

- First line of each pair contains direction cosines (relative to the Cartesian crystal axes) and the number of atoms whose names are to be read on the following line (no more than 12) and for which the displacement amplitudes in the specified direction are to be calculated. Free format (four values: 3 direction cosines, and no. of atoms to be read).
- Second line of each pair contains the names of up to 12 atoms for which amplitudes are to be calculated in the specified direction. Calculations may be made only for atoms in the asymmetric unit input..

9.4.5 Differences between THMA14c and THMA11

Version THMA14c differs from THMA11 in a number of small ways. The major difference is that THMA14c calculates the correlations between internal and overall motion (as outlined in the paper by Schomaker & Trueblood, (1998) *Acta Cryst. B54*, 507-514) in the Cartesian coordinate system. THMA14c has been reasonably well tested, but still does not do several things properly. In particular, when the molecule has symmetry higher than -1 and an attached rigid group (ARG) is in a general position, the values for the motion of that group may not always be correct. All 2-atom ARGs should lead to a singular, or nearly singular, matrix when correlations of internal and overall motion are included. If you want to determine the mean-square torsional amplitude for a 1-atom or 2-atom ARG, you will find that unless the group is on a site of special symmetry, it will only be done without correlations of internal and overall motion, because a 1-atom or 2-atom ARG in a general position leads to a singularity if one tries to include those correlations. All 1-atom and 2-atom ARGs *must follow* other ARGs if correlations of internal and overall motion are being done for the larger ARGs.

If problems with THMA14c are experienced, the user is advised to try THMA11. In terms of the input files the only differences are in the following two lines;

- 4a. first option line: TEMP, *ISCM*, *MSD8*, IRECAL, ISIGX, IRIDE, IMIN, IUNC (up to 8 quantities)
- 4b. second option line: IFREQ, *IBYP*, IATWT, *IEXU*, IEIG, IMAT, IOUT, CONSLV (up to 8 quantities)

The meaning of the new *italicised* items are :

ISCM

If entered as zero, no screening or filtering of the MSDA difference matrix is done. If ISCM is not set to zero, MSDA differences not greater than $2.5 \times (\text{ISCM})$ will be changed to blanks. If the mean esd of the MSDA difference is input as ISCM, only values of the difference significant at about the one percent level will be printed in the screened matrix, which is printed third, after the unscreened and bonded MSDA-difference matrices. [Note that the GUI merely sets ISCM to 1 if screening is requested. If you require another value of ISCM, then the THMA14.INPUT file will have to be manually edited.](#)

MSD8

If entered as non-zero number, table(s) of MSD for all pairs of atoms output in a file THMA_MSD.OUT (this file is always written with THMA11).

IBYP

If set to zero, the path through program includes calculations in the INERTIAL system, with ORIGIN at the centre of mass. If non-zero, then bypass inertial

system but shift origin to unweighted centroid. If set equal to 2 leave origin as input.

IEXU

If non zero (meaning *experienced users*) less explanatory material is given in the listing output

The remaining items of input have the same meaning as in THMA11.

THMA14c also accepts a "new" format instruction set. These are also automatically written by the GUI when running THMA14c and are called THMA14_NEW.INS (instructions), THMA14_NEW.PAR (atomic parameters) and THMA14_NEW.SIG (sigUs). While the program can only be run from the menu using the "old" format instructions, it is a trivial matter to set up a user defined menu item to run THMA14 using the "new" instruction set. Use the File-System-User Menu Item to set-up a new menu item (normally in the Analyse menu). The program executable is (assuming a default installation of WinGX) "c:\wingx\bin\thma14.exe" and the command line is "thma14_new.ins". A summary of the "new" format is given below.

TITL	Title, up to 76 characters after TITL
COMM	Any number of comment lines, which will be echoed only at the start of a run. EACH LINE must begin COMM
CELL	a,b,c in Angstroms; alpha, beta, gamma in degrees; free format, with at least one space between each entry. The following quantities have defaults (shown in blue), so that the line is not needed if the default value is wanted. More details on the implications of the more subtle of the following may be found in the full instructions given above. In those instructions, many variable names differ from the usually 4-character mnemonic names used with the NEW input. Most OLD names can be ignored, but you may find it helpful in considering the molecular point group to know that NO is the OLD name for what is now referred to as NPTG.
FRMX	Specify the format for position parameters, S for SHELX A4,F5.0,6F10.5,2X,I1 for ATOM,AtWt,x,y,z, U 1,1 ,U 2,2 ,MULT,NUORB no. independent U values OR for A4,5X,5F9.6 for ATOM,AtWt,MULT,x,y,z OM for A4,23X,3F9.6,2F5.1 for ATOM,x,y,z,AtWt,MULT T for 3F8.5,14X,A4,4X,2F5.1 for x,y,z,ATOM,AtWt,MULT T is the original THM format . or F for FREE FORMAT input ATOM, x,y,z, AtWt, MULT DEFAULT is SHELX so one never NEEDS to reply S [NOTE: Atomic Wt may be ignored if program is to generate it which is the DEFAULT, if IBYP = 0 and MULT may be ignored if it is 0 or 1, unless the atom is in a special position. The program sets values of 0 to 1 automatically. This usually means that there is no need to distinguish between formats OR which implies ORTEP and OM which implies ORTEP MODIFIED , if program is assigning atomic weights. User needs to adjust MULT only if it is not = 1.0.
FRMU	Specify the format for displacement parameters. If reply to FRMX was F or S the latter either explicit or by default , FRMU is irrelevant. Note that the program takes account of the different order of U(ij) in SHELX. O for 6F9.6,I1 ORTEP The I1 is for NUORB, the number of independent U

	<p>values for that atom; as before, if NUORB entered as 0 it is automatically set to 6 T for 6F10.6,I1 Original THM format I1 for NUORB DEFAULT: 0</p> <p>[NOTE: esds of displacement parameters are always read in the order 11,22,33,12,13,23, atom name, either formatted 6F10.6,A4, OR free format IF free format input has been specified by FRMX.]</p>
DIST	Max. distance to be considered for 'bonds' DEFAULT: 2.00 A
NPTG	Point group number, from International Tables DEFAULT: 1
IORT	ORTEP type of anisotropic displacement parameter: 0,1,4,or 8 DEFAULT: 8
NARG	Number of attached rigid groups DEFAULT: 0
OUTP	Do you want output to be full F , somewhat short S , or very short V ? DEFAULT: S
FOLL	Does another compound follow? DEFAULT: No N
SIGU	Are esds of displacement parameters input? DEFAULT: Yes Y
SIGX	Are esds of x,y,z included in ESD file input DEFAULT: N
SYML	Coordinates of a point through which all symmetry elements pass DEFAULT: 0.0, 0.0, 0.0
ISET	Desired setting of principal axis: X, Y, Z, XY = [110], XYZ = [111], or SP for SPecial DEFAULT: Z, but one may want Y in monoclinic crystals
TMAT	Special input matrix, TMAT, when ISET = SP
RTMA	Special input matrix, RTMAT, when ISET = SP
CORL	Do you want correlations of internal and overall motion DEFAULT: Y
TEMP	Temperature of measurement (K) DEFAULT: 296 K
MSDA	Do you want to calculate MSDA differences for ALL unique atom pairs? DEFAULT: Y so for none, use MSDA N, or NVIB 0
NVIB	Do you want to calculate MSDA differences for certain pairs of atoms? If so, include this line, with a number anywhere that indicates the number of such pairs. They then follow any ARG input, in a fashion given in the detailed instructions; they may include atoms in equivalent positions outside the asymmetric unit.
ISCM	Do you want MSDA matrix screened? DEFAULT: 0 no If ISCM.NE.0, MSDA differences not greater than 3.5x ISCM will be changed to blanks. If then the mean esd of Uii is input as ISCM, only values of the MSDA difference that are significant at about the 1% level will be printed in the SCREENED matrix, which is printed third, after unscreened and bonded MSDA-difference matrices. This assumes esd of MSDA diff is about 1.4x mean esd of Uii; often, there are, of course, significant variations in esd of Uii.
MSD8	Do you want MSDA matrices written out on UNIT 8 ? Respond with any number if so. DEFAULT: 0 no
RECA	Do you want another calculation with same atomic parameters? DEFAULT: N
ATWT	Do you want the program to calculate atomic weights from the symbols for the atoms? DEFAULT: Y
RIDE	Riding corrections wanted for atoms other than H,D? The atoms are given after ARG input if answer is Y DEFAULT: N
MINC	Minimum correction wanted for any atom pairs? The atoms are given after ARG input if answer is Y DEFAULT: N
UNCR	Uncorrelated corrections wanted for selected atom pairs ? The atoms are given after ARG input if answer is Y DEFAULT: N
FREQ	Frequency calculations wanted? I = internal motions only, B = both internal and overall motions: DEFAULT: N
ATUC	Do you want detailed atom-by-atom comparisons of Uobs and Ucalc in inertial system, including their eigenvalues and angles between their eigenvectors? If so, reply Y the program will set IFU = 1 . DEFAULT: N i.e., IFU = 0

	The program will also handle the following LINES, but they will not normally be mentioned for most users. BYIN and EXUS are new; the others are described in the full instructions. RKW corresponds to ISIG negative there; UNWT corresponds to IWU = 1 there; and ICSV is ICSVIB there.
IOUT	Do you want to output librationaly-corrected coordinates? 1 if you do DEFAULT: 0
BYIN	Do you want to bypass all inertial-system calculations? Respond with an integer. If 0, no bypass. DEFAULT: 0 If BYIN = 0, origin shifted to center of mass by program; if it is $\neq 0$ and $\neq 2$, origin is shifted to unweighted centroid. If BYIN = 2, origin left as input
EXUS	"Experienced user" - avoids printing much explanatory material and lists of parameters and the like, even for NS > 0 Y or N
ETA	Hirshfeld-Shmueli correlation coefficient DEFAULT: -0.25
WRKW	Do you want the 'esds' of displacement parameters used to weight the observational equations directly, rather than using their inverses? DEFAULT: N
UNWT	Do you want unit weights even when sigU input? If Y program sets IWU = 1. DEFAULT: N i.e., IWU = 0
ICSV	The number of special directions for which the MSDA of up to 12 atoms are to be calculated. ICSV.LE.10 DEFAULT: 0
CONS	Do you want CONSLV other than 0.01? DEFAULT: N
IMAT	Do you want to output matrix of normal equations? DEFAULT: 0
IEIG	Do you want eigenvalues of the matrix? DEFAULT: 0

9.4.6 Sample default input file for THMA11

```

Mn2(CO)10 at 100K multipole refinement
 14.1260   6.8790  14.2890  90.0000 105.1400  90.0000  0  0 -0.25  2.00
 11   1   1   8   0  -2   0  11   0   0   0   0   0
100.00   0   0   0   0   0   0   0   0   0   0   0
 0   0   0   0   0   0   0   0   0   0.000000
MN1
 0.010820 0.012420 0.012580 0.002650 0.001280-0.000510
O1
 0.023000 0.053100 0.034400 0.013300-0.016100-0.004400
O2
 0.022600 0.027000 0.024700 0.007200 0.010800-0.002800
O3
 0.040400 0.022500 0.021300 0.001000 0.017700-0.006900
O4
 0.027000 0.017100 0.036400 0.000400 0.013400 0.005500
O5
 0.028600 0.014100 0.018300-0.001500 0.003700-0.000600
C1
 0.016300 0.027200 0.023400 0.008100-0.004500-0.001400
C2
 0.014300 0.017200 0.019200 0.003900 0.005300-0.001100
C3
 0.022900 0.015100 0.015600 0.001200 0.007100-0.002500
C4
 0.016700 0.014800 0.023400 0.003300 0.007500 0.002500
C5
 0.017800 0.013600 0.013400 0.000700 0.001100-0.002000
 0.00006  0.00006  0.00007  0.00004  0.00003  0.00004MN1
 0.00060  0.00120  0.00080  0.00090  0.00060  0.00080O1
 0.00040  0.00040  0.00040  0.00030  0.00030  0.00030O2
 0.00050  0.00030  0.00040  0.00030  0.00040  0.00040O3
 0.00040  0.00030  0.00050  0.00030  0.00040  0.00030O4
 0.00040  0.00030  0.00030  0.00020  0.00030  0.00030O5
 0.00020  0.00030  0.00030  0.00020  0.00020  0.00020C1
 0.00020  0.00020  0.00030  0.00020  0.00020  0.00020C2
 0.00030  0.00020  0.00020  0.00020  0.00020  0.00020C3
 0.00020  0.00020  0.00030  0.00020  0.00020  0.00020C4
 0.00020  0.00020  0.00020  0.00020  0.00020  0.00020C5

```