

# ADVANCED USERS DMACRYS manual

## Manual release July 2019, referring to

### Program release DMACRYS 2.3.0

The use of DMACRYS to calculate second derivative properties (including elastic constants and  $k=0$  phonons), minimize with fixed cell parameters, apply pressure and adjust some defaults for larger molecules or difficult optimizations, requires editing the .dmain file produced by NEIGHCRYST. These commonly changed directives are described in 2.3. Otherwise this technical manual is intended for expert users to allow deviations from the NEIGHCRYST system of producing DMACRYS input files.

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## NOTATION (Used for data input)

Throughout the manual the following notation is used.

- F The user must supply a floating point number in F format (Note that E format is not permitted).
- I The user must supply an integer.
- A The user must supply a character constant. Only the first four characters will be interpreted if it is a directive.
- F,I In some parts of the input dataset, the user has a choice of a real number or an integer.
- <...> Optional parameters are enclosed in angle brackets.
- *Italic script* will be used for items in the printed output that depend on the input dataset.

# 1 INTRODUCTION

This document describes the data input to the DMACRYS computer program. Normally the user will use the pre-processor NEIGHCRYS to write an input file template (file.dmain) and generate the symmetry file (fort.20). This manual provides details on the keywords for understanding the NEIGHCRYS generated DMACRYS input file (file.dmain), and making adaptations if there are problems with specific systems during the minimizations, including defining the error messages. It also shows additional options available in DMACRYS, including other potential forms, unusual crystal structures, additional printouts etc.

## 1.1.1 Outline of what the program does

It is possible to write an input file for DMACRYS without using NEIGHCRYS. This section outlines what needs to be input, greater detail follows in subsequent sections. (NB it is not possible to produce the additional file needed to use symmetry, described in Appendix H. In this case, the keyword SYMM must be omitted). Data describing the unit cell is first read in together with the multipole expansion of the charges on each atom. All data must be supplied in orthonormal coordinates rather than conventional crystallographic coordinates. Next, atom-atom potentials are read in which model the crystal structure. Details of the molecular bonding are also supplied. The perfect lattice is then modelled using this potential. The variables are the centre of mass translations and three independent rotations of each rigid molecule, together with the unit cell constants. The most expensive part of the calculation in terms of computer time is usually the calculation of the gradients of the energy. These are calculated at every iteration of the energy minimization. The minimization uses a Hessian update algorithm, hence the second derivative matrix need only be calculated and inverted once. The second derivative matrix can be calculated either analytically (although not all of the terms have been worked out analytically) or numerically by differences (although this is much more expensive). For energy minimization analytical second derivatives are preferred since the Hessian update algorithm gives a good approximation when the minimization is complete. For properties calculations no minimization is done and numerical second derivatives must be used. See NOPR directive below (Section 3.9.1). The matrix inversion step may be expensive for large unit cells. This is because the inversion increases as  $N^3$ , whereas the gradient and matrix calculation increase as approximately  $N^2$ .

## 2 PRELIMINARY COMMENTS

### 2.1 DATA INPUT

DMACRYS uses a free format input processor. Each line of data is read in as characters, which make up a number of data fields separated by one or more spaces. By default 120 characters per line are read in, although this may be reduced using the IREC directive. The characters are then interpreted as literal (character string), constants, integers or real numbers. Literals are input as a string of characters of which at least one must be alphabetic, which cannot contain any embedded spaces in the constant. Only the first four characters will be interpreted by the program for a directive.

Integer constants are input as a signed or unsigned integer, which again must not contain any embedded spaces.

Real constants may only be input in the F format (10.00), and the E format (1.00E+1) is prohibited. A real constant will therefore consist of an optional sign, followed by a floating point number containing a decimal point. Again there should be no embedded spaces, and the decimal point should always be included.

There is no end of record error message, so that attempting to read past the end of a line will not cause an error. If the program tries to read a literal constant and there are no more data fields in the record, four blank characters are input. Similarly for an integer the value 0 is input and for a real number the value 0.0.

### *Error Messages*

Error - Invalid format for I variable

The input processor encountered an invalid character in an integer data field.

Error - Invalid format for F variable

The input processor encountered an invalid character in a real data field.

These are both non-fatal errors, the program may carry on in order trying to find further errors.

End of file unit number 5 Program terminating

This is a fatal error - the input dataset is too short.

## 2.2 THE INPUT PROCESSOR

NEIGHCRY5 can be used to generate an input file for DMACRY5 (file.dmain and associated fort.20 symmetry file).

The DMACRY5 input dataset consists of a number of steps each containing one or more directives, which together form the main menu of the program. Each directive consists of a four-character keyword. Each of these directives may have data read in from the same record, or may instruct the program to read in further records before the next directive. These further records may consist of data, or they may be sub-directives instructing the program to choose one of several paths from a separate menu. For example, the potential input step has one directive, POTE, which instructs the program to read in potential information from subsequent records. The potential information is read in using a separate menu and records containing the data. The potential input menu contains a directive ENDS which instructs the program to return to the main menu. Care is needed in ordering the directives not to put a directive in the wrong place, for example a directive from the main menu when a sub-directive from the potential input menu is expected. Any errors detected in the input processor may not necessarily cause the program to stop immediately, to allow inexperienced users to find several errors in one run. A blank record is ignored if it is encountered when a directive from the main menu was expected, but not elsewhere. The steps in a DMACRY5 job are outlined in Table 3.1 in the order in which they should be run, together with the directives from the main menu used in each step. A number of the directives are redundant but are kept for compatibility or future developments. The main menu directives MOLE and STAR PLUT both have large sub-menus of directives.

## 2.3 COMMON CHANGES to \*.dmain as produced by NEIGHCRY5

There are certain directives and control parameters that are more frequently changed from the defaults that NEIGHCRY5 writes to file.dmain. These are listed in Table 2.1 with a brief description and link to the relevant section of the manual.

**Table 2.1 Commonly change directives from the defaults written out by NEIGHCRY5**

DIRECTIVE	COMMENT	SECTION
To optimize with fixed cell parameters		
CONV /CONP	CONV replaces CONP to minimize with constant lattice vectors, instead of under constant (default zero) pressure	3.9.1 CONV 3.9.1 CONP
To apply isotropic pressure		
PRES	Insert to run DMACRY5 for crystals under pressure	3.9.1 PRES
To calculate second derivatives properties (after rerunning NEIGHCRY5 on a successfully converged DMACRY5 minimization structure (fort.16))		
STAR PROP/PLUT NOPR	Change NEIGHCRY5 default of STAR PLUT to STAR PROP, and remove the NOPR line to stop the approximation of the second derivatives	3.10 PROPERTIES CALCULATIONS Contrast 3.9 PERFECT LATTICE CALCULATION 3.9.1 NOPR
To change the lattice summation parameters		
CUTO	The operand CUTPOT defines the repulsion-dispersion potential cutoff	3.2.4 CUTO
RDMA	The operand RDMA defines the cutoff for the higher multipoles. It	3.2.4 RDMA

	is usually set to equal CUTPOT	
SPLI	SMIN and SMAX are used to smooth the cutoffs of the multipole and repulsion-dispersion interactions. It can be removed for an abrupt cutoff.	3.6.3 SPLI
ACCM	To change Ewald summation	

### 3 JOB STEPS IN DMACRYS

Table 3.1: JOB STEPS IN A DMACRYS JOB.

JOB STEP	DIRECTIVES	COMMENTS
TITLE	TITL, ENDS	Optional
DEFAULT PARAMETER CHANGES	DUMP, PRIN, IREC, ACCU, ACCM, SCAL, SYMM, FDAT, CHGC, CLUS, ZVAL, EXTN, NOSY	Optional, order of steps may be varied
CUTOFFS	CUTO, RDMA	Mandatory
UNIT CELL SETUP including atomic multipoles	LATT BASI ENDS	Mandatory Order of directives must not be varied
ATOMIC POLARIZABILITIES	POLZ ENDS	Optional, requires DIND
SPLINE PARAMETERS	SPLI	Optional, but set by default in NEIGHCRY S
Other POTENTIAL INPUT	POTE ENDS	Mandatory
MOLECULE INPUT	MOLE ENDS	Mandatory
DAMPING PARAMETERS	DDMP DIND	Optional
PERFECT LATTICE CALCULATION	STAR PLUT	Either STAR PLUT or STAR PROP are needed
PROPERTIES CALCULATION	STAR PROP	
STOP	STOP	Mandatory

The full list of directives, including those that are seldom used or redundant, is given in Appendix A.

The order of the job steps should not be varied, although variation from this order is permitted in certain cases. Firstly, some of the directives to change default parameters may be more conveniently placed later in the dataset. Where this is so it will be discussed in the section on the individual directives, and the default directives should otherwise always be placed where indicated. Secondly, the title step may appear more than once, anywhere in the sequence given above.

#### **Error Messages**

**ERROR - Unidentified directive found in input data. The input line is as follows.**

This error does not cause the program to stop immediately. Further errors will be sought before the program stops. Check that the directive has been spelt correctly. Also this error message can arise if the input dataset is in the wrong order, and the input processor attempts to process either data or a directive from one of the sub-menus as a directive from the main menu.

#### **3.1 TITLE SECTION**

The title step has only one directive, TITL.

## TITL

Operands                      None

This directive instructs the program to read in and print a heading on the line printer output. Subsequent records will be read in and printed out exactly as input. The title is terminated with a record with the single word ENDS, which returns control to the main menu of the program. TITL directives may appear anywhere where a main menu directive can appear, but cannot be embedded in data.

### Example input

```
TITL
01.lem_fit_AXOSOW.res
ENDS
```

## 3.2 DEFAULT PARAMETER CHANGES

All of these directives are optional. They may be subdivided into two classes.

Printed output	DUMP, PRIN
Program control	IREC, ACCU, ACCM, CHGC, SCAL, CLUS, SYMM, FDAT, ZVAL

### 3.2.1 Printed output

#### DUMP

Operand type	I
Operand name	IDUMP

This is used in conjunction with the PRIN directive discussed below. IDUMP may have values 1 or 2. IDUMP = 1 produces output which may be useful if an error is suspected in the input dataset. IDUMP = 2 produces output useful for diagnostic purposes only.

#### PRIN

Operand types	A	I	[ A I ... ...]
Operand names	APRINT	MPRINT	

The APRINT name defines certain sections of the program for which additional printed output is required. The integers MPRINT define exactly what is printed. There are currently 6 print options for DMACRYS. Each of these will now be described in detail.

### PLUT

MPRINT is a 5 digit integer, with each digit controlling a different section of the perfect lattice calculation. Numbering the digits from the right (units digit) to left the digits have the following values and meanings.

#### Digit 1

0	No output
1	List the contributions to the lattice energy and the atom forces before the first iteration and after the last iteration.
2	List the contributions to the lattice energy after each iteration.

#### Digit 2

As for digit 1 but listing the elastic constant tensors.

<b>Digit 3</b>	
0	No output
<b>Digit 4</b>	
0	No output
1	List the force constant matrix and gradient vector before the first cycle and after the last cycle.
2	List the force constant matrix and gradient vector on every cycle of the perfect lattice iteration.
3	List the gradient vector only before the first cycle and after the last cycle
4	List the gradient vector only on every cycle
The force constants are scaled in internal program units. To convert to $(\text{eV } \text{\AA})^{-2}$ they must be multiplied by $14.3997584/\text{RLSCAL}^3$ , where RLSCAL is the lattice constant. The gradients must be scaled by $14.3997584/\text{RLSCAL}^2$ .	
<b>Digit 5</b>	
0	No output
1	Currently not used, formerly used to print the Madelung and repulsion-dispersion energies of each particle. (Use CCLS instead)

Default 00011 - NEIGHCRYST default is 00012

**LATT**

0	No output
> 0	The reciprocal lattice vectors are printed in the output.

Default 0

**BASI**

0	Print: Basis atoms as input Origin of the basis
> 0	In addition, print: The basis atoms after shift of origin The basis atoms after sorting into internal

	program order
< 0	Suppress printing of the basis atoms
Default 0	
<b>MINI</b>	
0	No output
1	Print information about progress of the minimization.
2	As 1
3	As 2 plus individual contributions to the lattice energy
4	As 3 plus first part of the hessian
Default 0 – NEIGHCRYST default is 2	
<b>MOLE</b>	
This APRINT option is used in DMACRYST to control output from the MOLE directive. Starting from version 2.1.0 this option also switches off the connectivity calculation, which can be very computationally expensive for large molecules. The default has been reset to 0 in version 2.1.0	
0	Do not print molecular bonding information.
1	Print molecular bonding information
Default 0	
<b>GEOM</b>	
0	No output
1	Print molecular local axis information
Default 1	

The full list of printing options, including those that are redundant, is given in Appendix B.

### Example input

```
PRIN BASI 0 PLUT 12 MOLE 1 BOND 2 TORS 2 MINI 2 GEOM 1
```

### Printed output

```
The printing options are as follows.
  PLUT  LATT  BASI  MINI  MOLE  GEOM
   12    0    0    2    1    1
```

## 3.2.2 Additional Input/Output

Table 3.2 gives a list of the additional FORTRAN unit numbers used by DMACRYST. Output is produced by default to fort.8, fort.12, fort.13, fort.15, and fort.16. Directives HESS, PHGR and R2ND are input as additional directives to STAR PLUT or STAR PROP.

**Table 3.2: ADDITIONAL FORTRAN UNIT NUMBERS USED BY PROGRAMS**

DIRECTIVE	UNIT	NATURE OF I/O	USE
STAR PLUT	8	FORMATTED WRITE	Provides an updated set of lattice and basis vectors from the perfect lattice relaxation

Default	12	FORMATTED WRITE	Summary file written to fort.12
Default	13	FORMATTED WRITE	Final cell written to fort.13
Default	15	FORMATTED WRITE	Final output in FDAT format
Default	16	FORMATTED WRITE	Final output in SHELX format
CCLS	17	FORMATTED WRITE	Output close contact list to fort.17
SYMM	20	FORMATTED READ	Read the symmetry information file fort.20 written by NEIGHCRYS
HESS	25	FORMATTED READ/WRITE	Read or write the inverted second derivative matrix. (unit 25 is called dmahessian)
PHGR	26	FORMATTED WRITE	Write a file suitable for graphical output of the phonon modes
R2ND	30	FORMATTED READ/WRITE	Temporary file used for restart runs.

### 3.2.3 Program Control

#### IREC

Operand type            I  
 Operand name            IRECL

The input processor reads 120 characters per card image by default. IRECL should be less than 120, and gives the number of characters read in per record.

#### ACCU

Operand type            F  
 Operand name            ACCLAT

ACCLAT is the limit below which numbers are taken as being equal. The default set in the program is 1.0E-06. ACCLAT is also used at various other points in the program for testing small quantities.

#### ACCM

Operand type            F <F>  
 Operand name            ACCMAD RLWGT

This directive changes the accuracy to which the Ewald sum is carried out. The default for ACCMAD is 1 part in  $10^6$  (Default value of ACCMAD = 1000000.0). This needs to be increased to 1 part in  $10^8$  for calculation of phonon frequencies. RLWGT changes the weighting towards carrying out the Ewald sum in reciprocal space as opposed to direct space and its default value is 1.0. RLWGT can be used to fine tune the Ewald sum, but altering its value from 1.0 should not make any significant difference to the calculation. Setting a larger value of RLWGT will carry out more of the calculation in reciprocal space, but the calculation may take longer. Values of RLWGT between 0.25 and 4.0 could be used. Setting a larger value of ACCMAD may change the perfect lattice properties slightly. It should also be noted that a larger value of ACCMAD will set a larger lattice sum cutoff and the calculation will take longer.

#### SCAL

Operand type            F  
 Operand name            SCALQQ

The charge and multipole interactions will be scaled by the factor SCALQQ. This is set by default in NEIGHCRYS to 1.0

#### SYMM

Operands                None

Instructs DMACRYS to read in the symmetry input file fort.20 that was written by NEIGHCRY5. This is set by default in NEIGHCRY5. If SYMM is removed, the structure will relax with no symmetry, however it is preferable to lower the symmetry to P1 in NEIGHCRY5 rather than use this option.

### FDAT

Operands	None
----------	------

A legacy option which instructs DMACRYS to read in the symmetry input file fort.20 that was written by NEIGHCRY5, but not to switch on symmetry for this run. This option is useful for producing a final relaxed structure dataset from a run with no symmetry. Note NOSY is now the preferred way to run with no symmetry.

### CHGC

Operands	None
----------	------

The program checks that the unit cell is neutral and will stop if it is not. Including the directive CHGC forces the program to continue with a non-neutral cell. DMAs generated by SCF programs often have a small residual charge, so this directive should be included and is set by NEIGHCRY5.

### CLUS

Operands	None
----------	------

This directive tells DMACRYS to switch off the Ewald sum and carry out charge-charge and charge-dipole interactions by direct summation. This can be used to work out the energy of a cluster by using a cell with artificially large lattice vectors. It is recommended to use this option without the SPLI directive, as this will force DMACRYS to use whole molecule summations which will converge faster.

### ZVAL

Operand type	I
Operand name	ZVAL

ZVAL is the user-defined number of formula units per cell, used to calculate energies in kilojoules per mole. If ZVAL is not supplied, DMACRYS will try to read it from the fort.20 file.

### EXTN

Operand type	F
Operand name	EXTH

This directive is used in conjunction with the Williams potential. If NEIGHCRY5 uses the Williams potential, EXTN 0.1 will be written.

The Williams potential uses artificially shortened hydrogen bond lengths by moving the positions of the hydrogen atoms. This is to take some account of the effect of thermal motion in the crystal. If NEIGHCRY5 is used to set up the dmain file, the hydrogen atoms can be foreshortened by using the appropriate option in the NEIGHCRY5 input. NEIGHCRY5 always foreshortens the H atom positions by 0.1 Angstroms. The directive EXTN instructs DMACRYS to extend the hydrogen bond lengths by an amount EXTH Angstroms. This will be done before the final fdat and res files are written to units 15 and 16 respectively so that the job may be restarted to carry out a symmetry reduction or properties calculation without cumulative reductions in the H bond length taking place. EXTH should be set to 0.1 for datasets written by NEIGHCRY5 but may need to be set to other values if the foreshortening is not 0.1.

### NOSY

Operands	<A>
Operand name	centering_type

This directive is used if you wish to run DMACRYS without a symmetry file fort.20. The optional operand can be one of P, A, B, C, I, F, R to give the centering type of the lattice, however the preferred method to give the centering type is to give a SHELX style LATT directive (see below). DMACRYS will regenerate a correctly centred output lattice but will output all equivalent basis atoms.

### Error message

Unreckognised lattice centering type read from NOSY directive

This is a fatal error.

## 3.2.4 CUTOFFS

### CUTO

Operand types	F	F	<F>	<F>
Operand names	RLSCAL	CUTPOT	ACCTH	CUTTH

### CUTOFFS

The repulsion-dispersion interactions which are calculated in DMACRYS are controlled by two cutoffs, CUTPOT and RDMA.

RLSCAL gives the lattice constant  $c$  in Å. (See LATT and BASI directives and the examples following). Certain quantities are input in units of RLSCAL, referred to as lattice units.

CUTPOT gives the repulsion-dispersion potential cutoff in lattice units. CUTPOT should not be equal to an interatomic distance in the crystal. This is because the test in the perfect lattice calculation may find one bond but leave out a symmetry related bond, giving perfect lattice tensor properties of the wrong symmetry. Usually it is safe just to ensure that CUTPOT does not equal an integral number of lattice vectors. (i.e. that CUTPOT is not an integer). NEIGHCRYST will set a default value of 15 Å.

The ACCTH operand is retained for future use, but is not used at present. Its value is ignored if the calculation does not use three-body forces. It gives the maximum permitted deviation of a bond angle from the value input on the BOHA sub-directive of the POTE directive. This maximum deviation is applied in the perfect lattice step to check that no spurious three-body interactions have been generated by the THBO directive.

The CUTTH operand is retained for future use, but is not used at present.

The cutoffs are used with the range parameters on the input potentials. The potentials may be input over a number of ranges, although usually only one range is used. The parameter defining the ranges is intended primarily as a separation of two ranges and not as a cutoff of the potential. Therefore the maximum range of the potential is always overridden by the value of CUTPOT. Thus if the maximum range is greater than CUTPOT, then interactions will only be calculated out to CUTPOT. If the maximum range is input as a value less than CUTPOT, its value is redefined and set to a value larger than CUTPOT.

### Example input

```
CUTO 6.999700 2.142949
RDMA 2.142949
```

### Printed Output

```
C-vector magnitude= RLSCAL Angstroms
Cut off for repulsion-dispersion potentials = Cutpot*RLSCAL Angstroms
```

### Example output

```
C-vector magnitude= 6.999700 Angstroms
Cut off for repulsion-dispersion potentials = 15.000000 Angstroms
```

### RDMA

Operand type	F
--------------	---

Operand name                    RANG

This gives the cutoff in lattice units for the higher multipoles. NEIGHCRY5 will set a default value of 15 Å. Higher multipoles are calculated for all atoms within two molecules whose centres of mass are within RDMA.

### Printed Output

```
Cut off for higher multipole summation =            RANG*RLSCAL Angstroms
```

### Example output

```
Cut off for higher multipole summation =            15.00000012 Angstroms
```

## 3.3 UNIT CELL SETUP

This section reads in the unit cell. These directives must be given in the order

LATT, BASI

### 3.3.1 LATTICE VECTOR INPUT

#### LATT

Operand type                    <I>  
Operand name                    centering\_type

This directive must be input once but may be input twice. The optional second input is used to input the lattice centering type in the SHELX format and must be followed by the optional integer I. If this option is used it must follow the NOSY directive for cases where the run does not have a fort.20 file. There are no additional records for the optional use of LATT. DMACRY5 will write a final output file in SHELX format with the correct centering but will include all equivalent basis atoms, although for centrosymmetric structures the basis atoms generated by the centre of symmetry will be omitted. The mandatory LATT directive instructs the program to call the lattice vector input routine and requires three additional records. The calculations are described in Appendix E. They are performed by the pre-processor NEIGHCRY5.

### Example input

```
LATT -4  
LATT  
          1.4092175378945    0.0000000000000    0.0000000000000  
          0.0000000000000    1.4485049359258    0.0000000000000  
          0.0000000000000    0.0000000000000    1.0000000000000
```

### Printed output

The lattice vectors are always printed by default. They are printed in rows, with the x, y, z components of each lattice vector in each row. If PRIN LATT MPRINT with MPRINT=1 is used, the reciprocal lattice vectors are also printed, again in rows.

```
START OF LATTICE VECTOR PROCESSING.  
THE LATTICE VECTORS ARE AS FOLLOWS.  
  
          XLAT(1,1)          XLAT(2,1)          XLAT(3,1)  
          XLAT(1,2)          XLAT(2,2)          XLAT(3,2)  
          XLAT(1,3)          XLAT(2,3)          XLAT(3,3)
```

### Example output

```
START OF LATTICE VECTOR PROCESSING.  
THE LATTICE VECTORS ARE AS FOLLOWS.  
  
          1.409217537894501    0.000000000000000    0.000000000000000  
          0.000000000000000    1.448504935925801    0.000000000000000  
          0.000000000000000    0.000000000000000    1.000000000000001
```

### Error messages

These error messages are from the optional second use of LATT

```
Error - LATT directive used to input SHELX format lattice must follow NOSY directive
```

This is a fatal error.

Unrecognised Lattice Centering Type read from LATT directive

This is a fatal error.

These error messages are from the mandatory use of LATT

ERROR - lattice vectors not defined before crystal basis.

This is a fatal error. The program decided that the lattice vectors are coplanar by working out the volume of the unit cell, which is equal to the determinant of the lattice vector matrix. This is tested to see if it is greater than ACCLAT (see ACCU directive).

Error - Invalid format for F variable

A fatal error, there is a format error in one of the lattice vector input records.

### 3.3.2 BASIS ATOM INPUT

#### BASI

Operands None

The BASI directive instructs the program to call the basis atom input routine. Usually the calculations described below will be carried out using the pre-processor NEIGHCRY. This reads in further records, which have one of three possible formats

Card format	A15	3F	< I >
	Long atom label	Atom coordinates	Optional molecule number
Card format	A	3F	
	CENT	Point group origin	
Card format	A		
	ENDS		

Only one CENT and ENDS record is permitted. The CENT record defines the basis origin. This record is not required for DMACRY, it may be omitted, in which case the basis origin is taken as the point 0.0 0.0 0.0. The ENDS record must be the last record, and instructs the subroutine to return to the main menu of directives.

There may be any number of atom records up to a maximum of MAXBAS (this includes the CENT record if present). The long atom label consists of an A15 field made up as follows. The first two characters are the element type and make the element label. Where an element has only 1 letter an underscore is used as the second character. The third and fourth characters denote the type of repulsion-dispersion potential, for example where the potential includes different terms for different types of hydrogen atom. The first four characters together make up the species label defining a unique element and potential type. The fifth character is \_ or I, where I denotes the atom is part of an inverted molecule. The sixth to tenth characters number the atoms, where equivalent atoms in different molecules have the same number. Where the atom number is shorter than 5 digits long, the remaining characters are filled with the underscore symbol. The number starts from the left. The first 10 characters make up the short atom label. The long atom label comprises the short atom label and 5 further characters denoting the number of the atom in the entire unit cell.

H\_F1\_1\_\_\_\_\_ would be the short atom label of a hydrogen atom with the F1 potential type, not in an inverted molecule, and the first hydrogen atom of this molecule.

Similar comments apply about the precision as for the lattice vectors, namely the coordinates must be given to at least 7 significant figures unless the ACCU directive has been used. The optional molecule number is used to indicate to which molecule it belongs. A value of zero, or leaving out the parameter all together, implies that intramolecular potentials will not be applied to this atom, and is used for isolated ions. Isolated ions should be put at the end of the list; NEIGHCRY will do this automatically.

The distributed multipoles must be given for the atoms.

Operand type A I

Operand name	LEVEL	ORDER
--------------	-------	-------

The record following the atom coordinates must begin with the keyword LEVEL or DUPL. Use LEVEL the first time an atom is encountered, use DUPL for duplications. LEVEL is followed by an integer indicating the pole order of the multipole on this atom, 0 for charge only up to 4 for hexadecapole. The atom's charge is given in units of  $|e|$  (The charge on the electron). The multipoles are then given in atomic units. The format is

Operand type	F
	F F F
	F F F F F
	F F F F F F F
	F F F F F F F F
	F F
Operand name	CHARGE

The operands are one charge, three dipole, five quadrupole, seven octopole and nine hexadecapole moments in the usual order. This will usually be input from the dma file in NEIGHCRY5.

It should be noted that adding or subtracting a lattice vector, or an integral multiple of a lattice vector, to a basis vector will have no effect on the program. In other words, basis atoms need not all be in the same unit cell.

The basis atoms will be sorted into an internal program order, but this will normally be done by NEIGHCRY5. The order into which they are sorted is determined by a number of rules.

1. All atoms in molecules come before free ions.
2. All atoms with the same element label are sorted together
3. All atoms with the same short atom label are sorted together.

The Ewald parameter is also calculated at this point, according to the formula

$$\eta = \left( \frac{\pi^3 \times NCOR}{V^2} \right)^{1/6}$$

where

NCOR = Number of atoms in the unit cell

V = Volume of the unit cell in (lattice units)<sup>3</sup>.

This is used with the parameter ACCMAD (see ACCM directive) to define the cutoffs in direct and reciprocal space for the Ewald sums.

$$\text{Direct space cutoff} = f / \eta$$

$$\text{Reciprocal space cutoff} = f \times \eta / \pi$$

$$f = \sqrt{\log ACCMAD}$$

### Example input

BASI						
C_F1_1_1	1.1101807730993	0.0115731054015	0.1185363100000	1		
LEVEL 4						
-0.083010						
0.000208	0.018691	0.030772				
-0.985535	0.000338	-0.000982	-0.038430	0.230443		
-0.001680	-0.163223	-0.177082	-0.000341	-0.002022	-2.077258	0.179549
-0.862134	-0.001088	0.000299	-0.508677	1.765922	-0.003956	-0.000607
0.964204	1.430481					
C_F1_1_9	0.4055720041520	0.7126793625614	0.8814636900000	2		
DUPL						

### Printed output

```

the x basis species are as follows.
all quantities are in lattice units

no.          orthogonal coordinates          label      molecule
           x          y          z
index        x          y          z          label      molecule

Origin of basis
0.0000000000000000  0.0000000000000000  0.0000000000000000
Basis origin shifted

```

### Example output

```

the 64 basis species are as follows.
all quantities are in lattice units

no.          orthogonal coordinates          label      molecule
           x          y          z
1          1.11018077  0.01157311  0.11853631  C_F1_1__1__  1
2          0.40557200  0.71267936  0.88146369  C_F1_1__9__  2
3          0.29903676  0.73582557  0.38146369  C_F1_1__10__ 3

!
Origin of basis
0.00000000  0.00000000  0.00000000
Basis origin shifted

```

The basis atoms and basis origin are printed as input by default. PRIN BASI -1 will suppress printing of the basis atoms. PRIN BASI 1 will print additionally the basis atoms after sorting and after the point group origin vector has been subtracted from them.

### Printed output

```

Cut off value for direct lattice sum = CUTLAT lattice units
Cut off value for reciprocal lattice sum = CUTRLT reciprocal lattice units
Values of the constants used in these summations are:
Eta parameter for division of sum between real and reciprocal lattice= HFCTO
PI/(ETA^2 * Vol.Cell) = GFCTO

```

### Example output

```

Cut off value for direct lattice sum = 1.330080 lattice units
Cut off value for reciprocal lattice sum = 3.306277 reciprocal lattice units
Values of the constants used in these summations are:
Eta parameter for division of sum between real and reciprocal lattice= 2.794510
PI/(ETA^2 * Vol.Cell) = 0.197079

```

This message is printed by default.

### Error messages

```
ERROR - lattice vectors not defined before crystal basis.
```

A LATT directive has been omitted or placed out of order, it should occur before the BASI directive.

```
ERROR - Maximum of maxbas basis atoms exceeded.
```

This error does not cause the program to terminate immediately.

```
ERROR - Basis atoms i and j are at equivalent lattice sites.
```

Two basis atoms have been found at the same lattice site. They may be at the same lattice site translated by an integral number of lattice vectors, so the coordinates are not necessarily the same.

## 3.4 INPUT POLARIZABILITIES FOR INDUCTION CALCULATION

### POLZ

Operands None

The POLZ directive instructs the program to read in the atom polarizabilities. Usually these will be read in by NEIGHCRYST. This reads in further records, which have one of two possible formats.

Card format	A15	3F	< I >
	Long atom label	Atom coordinates	Optional molecule

			number
Card format	A		
	ENDS		

The label and atom coordinates must be the same as one of the input basis atoms. The record following the atom coordinates must begin with the keyword LEVEL or DUPL. Use LEVEL the first time an atom is encountered, use DUPL for duplications. LEVEL is followed by the integer 2. The format is of the following records is

Operand type	F
	FF
	FFF

The operands are the components of the atomic polarizability in atomic units, defined relative to the molecular axis system.

### Example input

```
POLZ
N_N1_1___1___ 0.4249443989847 0.3489903884920 0.1195150000000 1
LEVEL 1
6.222150
0.000000 11.651800
0.000000 -0.013800 6.751630
N_N1_1___12___ 0.3139008792946 0.2598224434937 0.6195150000000 2
DUPL
```

### Example output

```
Atomic Polarizabilities
N_N1_1___ 6.222150 0.000000 0.000000
0.000000 11.651800 -0.013800
0.000000 -0.013800 6.751630
```

### Error messages

ERROR: Insufficient polarizabilities for number of atoms.
'ERROR: DUPL keyword found but no atoms to duplicate.
ERROR: Atom labels do not match for atom .....
'ERROR: Number of polarizability matrices is greater than number of basis atoms.
ERROR: Atom coordinates do not match for atom .....
ERROR: Polarizability model not supported. Read level .....
ERROR: Expected keyword ',I8,' in POLZ section

## 3.5 SPLINED POTENTIALS

An abrupt cutoff in the direct summation of energies can lead to discontinuities in the energy as atoms (or entire molecules for the higher multipole terms) move over the cutoff boundaries or in and out of the stored list of close contacts. Although the cutoffs (given by CUTPOT & RANG in units of  $c$ ) should be set such that these terms are very small, this produces noise in the numerical first derivatives which are used in

applications such as CrystalOptimizer or when optimizing the structure including the induction energy. Continuity in the numerical derivatives can be assured by introducing the command,

```
SPLI DSPL1 DSPL2
```

for example,

```
SPLI 2.0 4.0
```

directly above the POTE command. This adds a spline curve that matches the energy and first derivative of each term in the potential from its value at the cutoff and reduces to zero value and first derivative over a distance DSPL1 (default 2.0) Å. The close contacts list is calculated to DSPL2 (4.0) Å beyond the cutoff to ensure that this does not change during the calculation.

The inclusion of SPLI thus adds to the repulsion-dispersion contribution the spline energy for all atoms lying between CUTPOT and CUTPOT + DSPL1, which will be a stabilizing energy as all such contributions start from an attractive dispersion energy.

The addition of splines changes the way that the higher multipole energies are calculated. Without a splined function, all higher multipole interactions between **whole molecules** whose centres of mass are within the cutoff, RANG, are included. The table of molecules with centres within RANG is set up at the beginning of the run, and not changed during the run, to avoid discontinuities in the energies from molecules appearing in the summation. When SPLI is set, all higher multipole interactions with intermolecular **atom-atom** distances within RANG are evaluated, plus the spline energies over the atom-atom range RANG + DSPL1. The molecule table, set at the beginning of the run, is calculated out to a distance RANG + 0.5 (maximum intramolecular distance) + DSPL2. The holding of the additional molecules in this table means that any molecules moving so their centres of mass within RANG are now included in the higher multipole calculation. This aspect is a significant improvement on the original method for long molecules and small RDMA values (e.g. NEIGHCRY5 default 15 Å).

The spline is also applied to the electrostatic contributions calculated by Ewald summation. Hence the direct summation is out to the automatically determined direct summation limit + DSPL2, and differs from the true value by the difference between the true and spline values over the additional DSPL2 range. The cutoff value for the reciprocal lattice sum and the value of ETA are automatically adjusted to match the actual direct summation limit including DSPL2. The default accuracy of the Ewald summations means that the change in the Ewald summed terms is much smaller than the other terms.

Currently NEIGHCRY5 versions since 2.0.8 automatically adds the SPLI command.

### Printed output

```
Potentials will be cutoff with a spline terminating at      splmin Angstroms
with limit in expansion set to      splmax Angstroms

Cut off value for direct lattice sum =      CUTLAT lattice units
Cut off value for reciprocal lattice sum =      CUTRLT reciprocal lattice units
Values of the constants used in these summations are:
Eta parameter for division of sum between real and reciprocal lattice=      HFCTO
PI/(ETA^2 * Vol.Cell) =      GFCTO
```

### Example output

```
Potentials will be cutoff with a spline terminating at      2.00Angstroms
with limit in expansion set to      4.00 Angstroms

Cut off value for direct lattice sum =      1.901533 lattice units
Cut off value for reciprocal lattice sum =      2.312667 reciprocal lattice units
Values of the constants used in these summations are:
Eta parameter for division of sum between real and reciprocal lattice=      1.954697
PI/(ETA^2 * Vol.Cell) =      0.402803
```

This change in the Ewald summation parameters is written out after the original data without a spline.

## 3.6 POTENTIAL INPUT (other than multipoles & polarizabilities)

### 3.6.1 REPULSION-DISPERSION POTENTIAL INPUT

#### POTE

Operands                      None

This directive instructs the program to call the repulsion-dispersion potential input routine. This routine is menu driven with a menu of sub-directives. The sub-directives fall into seven classes: species data, repulsion & dispersion interactions, [core-shell interactions, three-body interactions, torsion interactions, restart sub-directives] and subroutine termination. Those in [] are not relevant to this version of DMACRYS but are retained for future use. Table 3.3 gives the sub-directives in each class.

**Table 3.3: DIRECTIVES FOR THE POTENTIAL INPUT SUBROUTINE**

Directive class	Directives
Species data	SPEC, ENDS
Repulsion-dispersion interactions	BUCK, MODI, LENN, MORS, BUC4, SPLP, MORQ, SPRI, COUL, VDWA, HULB, BUC7, NONE, BSPL,DBUC
Three-body interactions	BOHA, TRID, MOLD, QART, SIXT, BOHZ, THRH, RRHA
Four-body interactions	TOHA

The full list of potentials available is given in Appendix C.

The directive order for the initial call must be

Directives	Comments
SPEC	Followed by subdirectives (See below)
Others	May be given in any order
ENDS	

The limits on the numbers of potentials etc. are determined by a number of PARAMETER statements in the FORTRAN. These limits may be reset simply by changing every occurrence of the PARAMETER statement to the new limit. The variable names and default limits are given in Table 3.4.

**Table 3.4: POTENTIAL PARAMETERS LIMITS**

Variable	Default Value	Meaning
MAXPOT	1000	Maximum permitted number of potentials
MAXRNG	10	Maximum number of ranges for each potential
MAXTYP	1000	Maximum number of short atom labels permitted
MAXTHB	50	Maximum number of types of three-body bond
MAXTOR	50	Maximum number of types of torsions

Printed output and error messages from this section of the program are given below. Printed output may be suppressed using the option PRIN POTE 0 in the default parameter changes.

#### *Printed output*

```
START OF REPULSION-DISPERSION POTENTIAL PROCESSING
```

This is always output by the program.

#### *Error messages*

```
ERROR - Invalid directive given in above line
```

The line above began with an invalid directive.

```
ERROR - SPECIES MUST BE READ IN BEFORE POTENTIALS
```

The program has read in a valid potential input directive, but the species have not yet been read in using SPEC.

Only one SPEC directive is permitted.

### 3.6.2 SPECIES DATA INPUT

#### SPEC

Operands                      None

This should be the first directive after POTE. It instructs the program to read in the elements and atomic masses. The subsequent data cards have the formats

Card format	A	F	F
	Element label	Not used	Atomic mass
Card format	A		
	ENDS		

The element label is described in the BASI directive (3.3.2). The atomic mass is given in atomic mass units. A maximum of MAXTYP element labels may be read in. Element labels may be given which are superfluous to this particular job. The element input terminates with a directive ENDS, which returns control to the POTE menu of directives.

#### Example input

```
POTE
SPEC
C_ 0.0 12.010700
O_ 0.0 15.999400
H_ 0.0 1.007940
ENDS
```

#### Error messages

These should be self-explanatory.

Warning - A element has been given with zero or negative mass

Warning - no mass is given for element label A10 set to 1.0

ERROR - THE ELEMENT TYPE Lab Type IS DUPLICATED

ERROR - THE LIMIT OF Maxtyp ELEMENT IS EXCEEDED

### 3.6.3 REPULSION-DISPERSION INTERACTIONS

Repulsion-dispersion interactions need to be given between some or all of the possible species pairs. The repulsion-dispersion interaction is designed to be as flexible as possible, although for DMACRYS only a few options will normally be used. Different species pairs may have different repulsion-dispersion interaction types. The repulsion-dispersion interactions are given in one or more ranges for each species pair, up to a maximum of MAXRNG ranges. For each species pair, the ranges must be contiguous and there must be a range which starts at zero. Interactions which have a different analytic form in different ranges are permitted. In this case, overlapping ranges are not permitted. However it is permitted to split one of the interactions into two ranges so that a range is the sum of two potentials. The ranges, if more than one range is given, must be in ascending order. The maximum range is at present overridden by CUTPOT. (See section on cutoffs) A maximum of MAXPOT repulsion-dispersion interactions may be given.

The general format of a repulsion-dispersion interaction is given below. There are three types of input records. Species records indicate the start of a new two body interaction and give the two species involved. Species records begin with the type of interaction involved, and include the two species labels, which are the first 4 characters of the atom label. An interaction may have more than one species record, for example where different potential forms are required for different ranges. Range records give the parameters for the interaction in a given range. Finally, an ENDS record terminates the input for all potential forms and ranges for a particular species pair. The format of a species record is

Card format	A4	A4	A4	< F,I >
	Potential type	Species label A (see 3.3.2)	Species label B (see 3.3.2)	Additional Parameters for certain potential

				types only
Card format	F ...	< F >	F	
	Parameters	Optional RMIN	RMAX	

**RMIN and RMAX** define the minimum and maximum range for this potential. RMIN may be omitted; the program knows how many parameters there are on the record and can therefore determine whether an RMIN has been given. If RMIN is omitted, the program uses the following rules to decide which value it should have.

- If it is the first range record after a species record, the minimum range is assumed to be zero.
- If it is a subsequent range, the minimum range is taken as the maximum of the previous range.

If a second species record is given, the ranges must either coincide with ranges given after the first species record or must be new ranges, contiguous with the existing ranges but extending beyond the previous maximum. Overlapping ranges are not permitted. The limits of the ranges are given in Å so that no conversion needs to be done when the data is transferred to a different substance. (cf. the CUTPOT parameter, which is in lattice units.)

### Example input

```
BUCK C_F1 C_F1
      3832.147000 0.27777800 25.286950 0.00 70.00
ENDS
```

### Printed output

```
POTENTIAL BETWEEN SPECIES JSPECA AND JSPECB WITH JRANGF RANGES
```

```
LIST OF GENERAL INTERACTIONS
```

This indicates that the interaction is intermolecular.

### Error messages

A number of error messages will be given here as they do not depend on the keyword given in the species record.

```
ERROR - INVALID POTENTIAL GIVEN IN ABOVE LINE
```

This error message arises immediately after range records have been read in. The program expects either an ENDS record, or a new species record with a different potential type between the same two species. Neither of these two was found. Check that an ENDS record has not been omitted.

```
ERROR - IN ABOVE LINE AN INVALID SPECIES LABEL WAS GIVEN ON A POTENTIAL DIRECTIVE
```

The labels do not match anything given in the basis atom input.

```
ERROR - EACH POTENTIAL MUST BE MADE UP OF INTERACTIONS BETWEEN THE SAME TWO SPECIES.
CHECK THAT AN ENDS DIRECTIVE IS NOT MISSING
```

A species record immediately after a range record was found, with no intervening ENDS. The species labels must be the same as on the previous species record. Most probably a new interaction was intended and an ENDS record was omitted. If a second species record between the same species was intended, check that the species labels have been put in correctly.

```
ERROR - THE POTENTIAL BETWEEN THE ABOVE TWO SPECIES IS DUPLICATED.
CHECK THAT AN UNNECESSARY ENDS DIRECTIVE HAS NOT BEEN INCLUDED
```

A species record has just been read between two species for which a previous interaction has been read in. If you want to have an interaction with two different potential types, there must not be an ENDS record after the ranges of the first potential.

```
ERROR - IN ABOVE LINE A MINIMUM RANGE IS SUPPLIED WHICH MUST BE ZERO FOR FIRST RANGE OF FIRST POTENTIAL VALUE
READ IN IS F CHECK THE NUMBER OF PARAMETERS NEEDED FOR THIS POTENTIAL TYPE
```

The program found enough parameters on a range record to expect to have an RMIN parameter, but the value read in was not zero for the first range. Check that you have got the correct number of parameters for this potential type.

ERROR - IF MINIMUM OF RANGE IS GIVEN IT MUST BE THE SAME AS AN EXISTING MAXIMUM, VALUE IS F.

An RMIN parameter has been read in from the current range record. This was not the first range, and the value of RMIN read in was different from any of the previously read in values of RMAX. This makes the ranges overlapping. Split the appropriate previous range into two.

ERROR - POTENTIALS WHOSE RANGES OVERLAP MUST HAVE IDENTICAL RANGES

A second species record has been read in followed by a range record. The RMAX value on this record is less than the current maximum from the previous potential. There may also have been an RMIN read in. In either case, the next highest RMAX value read in from the previous potential does not match the current RMAX. This makes an overlapping range.

ERROR - TOO MANY POTENTIALS READ IN, MAXIMUM NUMBER OF POTENTIALS IS MAXPOT.

Increase the value of MAXPOT in all PARAMETER statements in the program and recompile it.

ERROR - RANGES MUST BE GIVEN IN ASCENDING ORDER

A range record has an RMAX value which is less than the previous record.

ERROR - THE MAXIMUM OF MAXRNG RANGES HAS BEEN EXCEEDED

Increase the value of MAXRNG in all PARAMETER statements in the program and recompile it.

Selected individual keywords will now be described.

## BUCK

There are no additional parameters to be read from the species record. Three parameters plus RMIN (optional) and RMAX must be read from the range records. The analytic form is

$$V(r) = A \times \exp(-r/B) - C/r^6$$

The parameters A, B and C must be read from the range record. Their units are given below

A	is in eV
B	is in Å
C	is in eV Å <sup>6</sup>

The ranges are terminated with an ENDS record or a new species record between the same species.

### Example input

```
BUCK C_F1 C_F1
      3832.147000 0.27777800 25.286950 0.00 70.00
ENDS
```

### Printed output

```
BUCKINGHAM POTENTIAL V(R) = A * EXP(-R/RHO) - C/R**6
      A          RHO          C          RMIN          RMAX
      A          RHO          C          RMIN          RMAX
```

### Example output

```
BUCKINGHAM POTENTIAL V(R) = A * EXP(-R/RHO) - C/R**6
      A          RHO          C          RMIN          RMAX
      0.38321470E+04 0.27777800E+00 0.25286950E+02 0.00000000E+00 0.70000000E+02
```

## ANIS

There are no additional parameters to be read from the species record. This potential type must be given immediately after the range record for a Buckingham potential or a damped Buckingham potential (i.e.

before the ENDS directive) and instructs DMACRYS to treat the repulsion part of the potential as an anisotropic potential. It is currently followed by up to 17 additional records which are not treated in the same way as other range records. The format of these anisotropic potential records is

5I	F
K1,K2,L1,L2,J	RHO

Where K1, K2, L1, L2, J define the S function used to define this component of the anisotropic potential and RHO is defined below. At present the only permitted values of K1, K2, L1, L2, J are given in the table below

K1	0	0	0	0	0	1	0	-1	0	1	0	-1	0	2	0	-2	0
K2	0	0	0	0	0	0	1	0	-1	0	1	0	-1	0	2	0	-2
L1	0	1	0	2	0	1	0	1	0	2	0	2	0	2	0	2	0
L2	0	0	1	0	2	0	1	0	1	0	2	0	2	0	2	0	2
J	0	1	1	2	2	1	1	1	1	2	2	2	2	2	2	2	2

The first S function is just the isotropic part. If it is not given the values input in the BUCK or DBUC record will be used. The next four terms are axially symmetric. The anisotropic repulsion term is

$$V(R) = \text{EXP}(-\text{ALPHA} * R) * \text{EXP}(\text{ALPHA} * \text{RHO})$$

$$\text{RHO} = \text{SIGMA} (\text{RHO}(\text{K1}, \text{K2}, \text{L1}, \text{L2}, \text{J}) * \text{S}(\text{K1}, \text{K2}, \text{L1}, \text{L2}, \text{J}))$$

ALPHA = 1/B where B is the B value read from the BUCK record.

The explicit forms of the S functions used are given in Appendix I. They are the same as are used for the multipole electrostatics.

### Example input (from example 04)

BUCK	BrBR	BrBR															
	2662.410975		0.33073600		120.676039		0.00		70.00								
ANIS	BrBR	BrBR															
	0	0	0	1	1	0.12205700											
	0	0	1	0	1	0.12205700											
	0	0	0	2	2	-0.23781500											
	0	0	2	0	2	-0.23781500											
ENDS																	

### Printed output

BUCKINGHAM POTENTIAL	V(R) = A * EXP(-R/RHO) - C/R**6																
A	RHO	C															
ANISOTROPIC REPULSION PARAMETERS	V(R) = EXP(-ALPHA*R) * EXP(ALPHA * RHO)																
RHO = SIGMA	(RHO(K1,K2,L1,L2,J) * S(K1,K2,L1,L2,J))																
	1.0/ALPHA	K1	K2	L1	L2	J											
	1.0/ALPHA	K1	K2	L1	L2	J											

### Example output (from example 04)

BUCKINGHAM POTENTIAL	V(R) = A * EXP(-R/RHO) - C/R**6																
A	RHO	C															
	0.00000000E+00	0.33073600E+00		0.12067604E+03										0.00000000E+00		0.70000000E+02	
ANISOTROPIC REPULSION PARAMETERS	V(R) = EXP(-ALPHA*R) * EXP(ALPHA * RHO)																
RHO = SIGMA	(RHO(K1,K2,L1,L2,J) * S(K1,K2,L1,L2,J))																
	1.0/ALPHA	K1	K2	L1	L2	J											
	0.33073600E+00	0	0	0	0	0								0.26085107E+01			
	0.33073600E+00	0	0	1	0	1								0.12205700E+00			
	0.33073600E+00	0	0	0	1	1								0.12205700E+00			
	0.33073600E+00	0	0	2	0	2								-0.23781500E+00			
	0.33073600E+00	0	0	0	2	2								-0.23781500E+00			

Note that the isotropic term is input as A but output as RHO(0,0,0,0,0), using the relationship  $A = \exp(\text{ALPHA} * \text{RHO}(0,0,0,0,0))$  where  $\text{ALPHA} = 1/\text{RHO}$ , with this equivalence where A = 1 energy unit being signalled by the output value of A being zero.

## DBUC

There are no additional parameters to be read from the species record. Five parameters plus RMIN (optional) and RMAX must be read from the range records. The repulsive part of the damped dispersion potential is the same as for the Buckingham potential. The damped dispersion is

$$U_{disp}^{MN} = \sum_{i \in M, k \in N} -f_6(\beta_{MN} R_{ik}) \frac{C_6^{ik}}{R_{ik}^6} - f_8(\beta_{MN} R_{ik}) \frac{C_8^{ik}}{R_{ik}^8} - f_{10}(\beta_{MN} R_{ik}) \frac{C_{10}^{ik}}{R_{ik}^{10}}$$

where  $f_n(\beta_{MN} R_{ik})$  is the Tang-Toennies damping function is given by

$$f_n(\beta_{MN} R_{ik}) = 1 - \left( \sum_{m=0}^n \frac{(\beta_{MN} R_{ik})^m}{m!} \right) \exp(-\beta_{MN} R_{ik})$$

The damping parameter  $\beta_{MN}$  is a constant for a molecule pair and its value is read in from the DDMP record (see below). If a value of 0 is input the function is undamped. The next record must read in 7 values. They are A, B,  $C_6^{ik}$ ,  $C_8^{ik}$ ,  $C_{10}^{ik}$  from the above equation, with the last 2 values as for BUCK. The units are given below.

<b>A</b>	is in eV
<b>B</b>	is in Å
$C_6^{ik}$	is in eV Å <sup>6</sup>
$C_8^{ik}$	is in eV Å <sup>8</sup>
$C_{10}^{ik}$	is in eV Å <sup>10</sup>

Note that this potential has been implemented for future use with non-empirical model potentials, and therefore has not been tested for a real system or one where the derivatives can readily be verified.

### Example input (from example 22)

```
DBUC C_A1 C_A1
      3.835450 0.35334049 0.1704 0.0000 0.0000 0.00 70.00
ENDS
!
DDMP 1 2.473495
```

The DDMP lines are generated by NEIGHCRYST and put in the \*.dmain after the molecule definition (axis system) section. There is one line per molecule and the format of this directive is described in 3.8.

### Example output

```
BUCKINGHAM WITH DAMPED VAN DER WAALS
V(R) = A * EXP(-R/RHO) - F6(BETA*R) * C/R**6 - F8(BETA*R) * D/R**8 - F10(BETA*R) * E/R**10
      A          RHO          C          D          RMIN          RMAX
      E
0.63091412E+04 0.21133000E+00 0.37945530E+01 0.13440326E+02 0.00000000E+00 0.70000000E+02
0.38920132E+02
```

## NONE

There are no additional parameters to be read from the species record. This is a dummy two-body potential which does nothing. It may be used where the true range of a potential is less than CUTPOT, and where a range needs to be put in so that the potential extends out as far as CUTPOT. This will most commonly occur for intramolecular potentials. The range record should contain the value of RMAX and (optionally) the value of RMIN.

## ENDS

This directive must be the last directive used to return control to the main menu of directives. Do not confuse this use of ENDS with previous ENDS terminating a repulsion-dispersion potential input. In some cases two consecutive ENDS directives are needed.

### **Error messages**

EXECUTION TERMINATING BECAUSE OF ABOVE ERRORS

The detection of an error does not necessarily cause an immediate stop, the program continues to try to detect as many errors as possible in one run. If you get this error, check the output for additional error messages.

## **3.7 INTRAMOLECULAR GEOMETRY SETUP**

### **MOLE**

Operands                      None

The aim of this directive is to set up a neighbour list to define which pairs of atoms will form part of a rigid unit. Atoms are considered to be neighbours if they are in the same molecule (defined by the molecule number in the basis species input) and if additional conditions defined by sub-directives given below are met. No potential will be applied between neighbours. Intermolecular potentials will be used

1. Within the same molecule between species which are not defined to be neighbours. Normally this should not be used.
2. Between different molecules with different molecule numbers.
3. Between an atom in a molecule and an atom with a molecule number of zero, which will be a free ion.

The sub-directives used to define the neighbour list are given below.

### **CUTM**

Operand types                F  
Operand names                CUTMOL

CUTMOL is the cutoff in Å used to limit intramolecular interactions. Starting from version 2.1.0, NEIGHCRY5 sets this to the maximum intramolecular size plus 0.1 Angstrom.

### **NBUR**

Operand types                I  
Operand names                NEBOUR

NEBOUR is an integer giving the maximum number of intramolecular bonds between species in the neighbour list. The value should be large enough to cover the whole molecule. NEIGHCRY5 sets this by default to 20

### **NNCU**

Operands                      None

This sub-directive instructs the program to read in nearest neighbour cutoffs between intramolecular species until terminated by an ENDS directive. The format of the subsequent records is

Card format	A2	A2	F
	LABELA	LABELB	BONDCUT
Card format	A		
	ENDS		

Where LABELA and LABELB are element labels in the usual format, and BONDCUT is the cutoff in Å between two atoms of the given type for the atoms to be treated as nearest neighbours within a molecule.

The ENDS directive returns control to the main menu of sub-directives.

### NFXP

Operands                      none

This directive turns off the intra-molecular COULOMB interaction.

### MOLX

Operand type                I  
Operand name                NAXES

This directive inputs the local axis system of the molecule.

NAXES is the number of different types of molecule. There are 2 x NAXES following records.

Card format	A1	A	A10	A10	I		
	Direction	'LINE'	LABELA	LABELB	NNBU1		
Card format	A1	A	A10	A10	I	A10	I
	Direction	'PLANE'	LABELA	LABELB	NNBU1	LABELC	NNBU2

where Direction is one of X, Y or Z. Labels are short atom labels defined in section 3.3.2. The first record defines a local axis to lie along the line joining two atoms which are NNBU1'th neighbours, the second record defines a local axis lying in a plane formed by the three atoms where the first and third are NNBU2'th neighbours, the third axis forms a right handed set. Normally the first direction will be X and the second Y. The mathematical formulae in DMACRYS always assume a right handed axis system, so special precautions are needed if the system contains two enantiomers. To avoid changing the formulae, a molecule related by a centre of symmetry to the first molecule in the unit cell will use a right handed axis system, but change the signs of all the odd-z multipole components in the distributed multipole. Frequently the crystal structure will not be one of two genuine enantiomers; rather rounding errors and limited precision will result in a structure which is not exactly superimposable on its mirror image. In such cases the odd z components of the multipolar expansion of the electrostatics should be zero. The program allows for the case where the multipolar expansion does not give exactly zero. NEIGHCRYST will label all such atoms with the letter 'I' as the fifth character of the label. This will only be valid if the axis order is X LINE and Y PLANE. If a different axis definition is used, the transformation of the multipole components may not be handled properly by NEIGHCRYST and should be checked and edited manually. If PRIN MOLE is set to 1, the values of NNBU1 and NNBU2 are checked with the connectivity found in the structure.

### ANIS

Operands                      None

This is followed by groups of three records which define the direction of the anisotropic axes used for the anisotropic repulsions. The anisotropic axes input is terminated by an ENDS record

Record 1

Card format	A10
	ATOM

ATOM is the short atom label for the atom for which the anisotropic axis is to be defined

Record 2

Card format	A1	A4	A10	A10	I
	AXIS	AXIS TYPE	ATOM 1	ATOM 2	SEPARATION

AXIS is the first axis which is defined. The first axis must be Z. AXIS TYPE is LINE which is the same as for molecular axes. The species defining the line do not have to include the species for which you are

constructing the axis. ATOM 1 and ATOM 2 are the short atom labels for the atoms defining the line and separation is the number of neighbours they are apart (1 for nearest neighbours and so on)

#### Record 2 (Alternative format)

Card format	A1	A4	A10	A10	I	A10	I
	AXIS	AXIS TYPE	ATOM 1	ATOM 2	SEPARATION 1	ATOM 3	SEPARATION 2

This format will seldom be needed. AXIS TYPE will be BIEX or BIIN to define the external or internal bisector of a bond angle. The atoms are in the order {centre of angle, end 1, separation 1, end 2, separation 2} so the bond angle is 2-1-3. These directives could be used for example to define the anisotropic axis system for the oxygen atom of a water molecule. The AXIS must be Z.

#### Record 3

Card format	A1	A4	A10	A10	I	A10	I
	AXIS	AXIS TYPE	ATOM 1	ATOM 2	SEPARATION 1	ATOM 3	SEPARATION 2

The second axis which must be a plane input in the same format as for MOLX. The second axis must be X. The sequence is terminated by an ENDS record; note that this will give you two ENDS records in a row. The calculated anisotropic axes are printed out.

As for the multipoles, care is needed where the unit cell has a centre of symmetry and there are two enantiomers, which may differ only slightly from being non-superimposable mirror images. The Z axis must be given first, rather than the X axis as was the case for the molecule local axes. Often only axially symmetric repulsion is necessary and only the first 4 anisotropic terms (plus the isotropic term) will be given. These 4 terms are most conveniently defined along the Z direction of the atomic axis. If non-axial terms are given the X axis must be given second. In the case of enantiomers, the sign of the odd y components of the anisotropic repulsion coefficients will be changed for inverted molecules. This is done internally in the program rather than in the input dataset so there is no way to change the axis order. As for the z components in the multipole case, these odd y components should be zero unless the crystal is a genuine racemate, however rounding errors in the repulsion coefficient calculation may give small non zero terms.

**ENDS**

This directive returns control to the main menu of directives.

#### *Example input*

```
MOLE
NFXP
CUTM      4.60
NBUR 20
NNCU
  C_  C_  1.600
  C_  O_  1.400
  C_  H_  1.300
ENDS
MOLX  2
X LINE C_F1_2___ C_F1_3___ 1
Y PLANE C_F1_2___ C_F1_3___ 1 C_F1_1___ 1
X LINE C_F1I10___ C_F1I11___ 1
Y PLANE C_F1I10___ C_F1I11___ 1 C_F1I9___ 1
ENDS
```

#### *Printed output*

If PRIN MOLE 1 is set, the following is output

```
START OF NEIGHBOUR LIST PROCESSING
```

```
CUTOFF FOR INTRAMOLECULAR INTERACTIONS SEARCH = CUTMOL  
NEIGHBOUR LIST WILL BE SET UP OUT TO NEBOUR NEIGHBOURS
```

```
THERE ARE MCUT NEAREST NEIGHBOUR CUTOFFS (IN ANGSTROMS)  
SPECIES TYPES CUTOFF
```

```
ITYPL(I) ITYPL(J) RTWO(IPOT)
```

```
LIST OF NEIGHBOURS
```

```
SPECIES NUMBERS AND TYPES MOLECULE LATTICE VECTORS SPACING DISTANCE
```

```
NA NB ATOMS(NA)%NAME ATOMS(NB)%NAME molecule_number JBARRS(2,JBARR) JBARRS(3,JBARR) JBARRS(4,JBARR)  
JBARRT(6,IJBARR) XDIST
```

### Example output

```
START OF NEIGHBOUR LIST PROCESSING
```

```
CUTOFF FOR INTRAMOLECULAR INTERACTIONS SEARCH = 0.63800000E+01  
NEIGHBOUR LIST WILL BE SET UP OUT TO 20 NEIGHBOURS
```

```
THERE ARE 5 NEAREST NEIGHBOUR CUTOFFS (IN ANGSTROMS)  
SPECIES TYPES CUTOFF
```

```
C_C1_1_____ C_C1_1_____ 0.16000000E+01  
C_C1_1_____ C_C1I14_____ 0.16000000E+01  
C_C1_1_____ C_C2_2_____ 0.16000000E+01  
C_C1_1_____ C_C2I15_____ 0.16000000E+01
```

```
LIST OF NEIGHBOURS
```

```
SPECIES NUMBERS AND TYPES MOLECULE LATTICE VECTORS SPACING DISTANCE
```

```
1 9 C_C1_1_____1_____ C_C2_2_____2_____ 1 0 0 0 1 1.48318083  
2 10 C_C1_1_____14_____ C_C2_2_____21_____ 2 0 0 0 1 1.48318083  
3 11 C_C1_1_____15_____ C_C2_2_____22_____ 3 0 0 0 1 1.48318083  
4 12 C_C1_1_____16_____ C_C2_2_____23_____ 4 0 0 0 1 1.48318083
```

### NA, NB

are the index of the basis atoms after sorting.

### ITYPL(I), ITYPL(J)

are short atom labels

### ATOMS(NA)%NAME, ATOMS(NB)%NAME

are long atom labels

### molecule\_number

is the molecule number as input in BASI section.

### JBARRS(2,JBARR), JBARRS(3,JBARR), JBARRS(4,JBARR)

give the number of lattice vector translations needed to be applied to the atom **NB** to bring it within the cutoff from atom **NA**.

### JBARRT(6,IJBARR)

gives the minimum number of covalent bonds between **NA** and **NB** moving along bonds. In other words, **NA** and **NB** are **JBARRT(6,IJBARR)**th neighbours.

### XDIST

gives the distance between the atoms in Angstroms.

### Error messages

```
ERROR - POTENTIAL INFORMATION MUST BE READ IN BEFORE TWO BODY BONDS
```

MOLE directive must come after POTE.

ERROR - IN ABOVE LINE AN INVALID SPECIES LABEL WAS GIVEN ON A MOLECULE CUTOFF DIRECTIVE

On a line following NNCU, an element label could not be recognised.

ERROR - THE CUTOFF BETWEEN THE ABOVE TWO SPECIES IS DUPLICATED

ERROR - MAXIMUM OF MAXBOND BOND CUTOFFS PERMITTED

ERROR, INSUFFICIENT MEMORY TO GENERATE NEIGHBOUR LIST, PROGRAM TERMINATING

UNIDENTIFIED MOLECULE KEYWORD KEYW PROGRAM TERMINATING

### Example input with anisotropic short range repulsions (from example 04)

```
MOLE
NFXP
CUTM      5.96
NBUR 20
NNCU
  Br C_ 2.200
  Cl C_ 1.800
  F  C_ 1.500
  C  C_ 1.600
  C  H_ 1.200
ENDS
MOLX 2
X LINE C_CC_2 C_CD_5 3
Y PLANE C_CC_2 C_CD_5 3 C_CA_1 1
X LINE C_CCI14 C_CDI17 3
Y PLANE C_CCI14 C_CDI17 3 C_CAI13 1
ANIS
ClCL_1
Z LINE C_CC_2 ClCL_1 1
X PLAN C_CC_2 C_CA_1 1 C_CB_6 2
C_CC_2
Z LINE C_CC_2 ClCL_1 1
X PLAN C_CC_2 C_CA_1 1 C_CB_6 2
!
C_CBI18
Z LINE C_CBI18 H_HYI14 1
X PLAN C_CBI18 C_CDI17 1 C_CBI16 2
ENDS
ENDS
```

### Example output (from example 04)

```
Local axis set for molecule: 1
x=>      0.052830      0.712390      -0.699792
y=>     -0.398380     -0.627556     -0.668930
z=>     -0.915698      0.314123      0.250648

QUARTERNION PARAMETERS
0.41107228D+00 -0.59785839D+00 -0.13130651D+00 0.67553203D+00
```

Gives the direction of the local axis for each molecule together with the quarternion parameters used to define the orientation. Symmetry related molecules should have symmetry related local axes, which gives a consistency check on the data input.

```
Atom positions in local axis system for molecule 1
basis No. Species x y z (Angstroms) Mass
1 BrBR_1 -0.507460 2.874834 0.000035 79.904000
5 BrBR_2 -0.506870 -2.874997 -0.000005 79.904000
```

Gives the atom positions in the local axis system. Symmetry related molecules should have positions which are related to each other by the appropriate symmetry element.

```
Molecule No. Centred at Total Mass
x y z (Angstroms)
1 2.713780 10.408734 3.318251 288.339183
2 1.083142 3.513384 3.696588 288.339183
3 1.083142 3.381966 10.962288 288.339183
4 2.713780 10.277316 10.583951 288.339183
```

Gives the initial centre of mass.

```

Molecule No.          Principal axes of inertia

   1                   0.78274495E-05 -0.69422841E-05  0.10000000E+01
                       0.99999999E+00  0.14094972E-03 -0.78264709E-05
                       -0.14094967E-03  0.99999999E+00  0.69433873E-05

Principal moments of inertia (amu.Ang**2) for molecule  1

  Ix =  0.20301856E+04, Iy =  0.14003934E+04, Iz =  0.62979224E+03

   2                   0.78274499E-05 -0.69422854E-05  0.10000000E+01
                       0.99999999E+00  0.14094972E-03 -0.78264713E-05
                       -0.14094967E-03  0.99999999E+00  0.69433887E-05

```

### The moments of inertia

```

Anisotropic short range potential axes in global axis system

  Index      Type                x(global)      y(global)      z(global)

   1         BrBR_1____1____  x(axis)  0.14094116E+00 -0.33312591E+00  0.93228896E+00
                                     y(axis) -0.91569225E+00  0.31411885E+00  0.25067320E+00
                                     z(axis) -0.37635528E+00 -0.88901995E+00 -0.26076854E+00

```

If the system has anisotropic short range potentials (example 04), the direction of the axes will be output.

### Printed output

```

Maximum intramolecular distance =  XDISTMAX Angstroms
Multipole tables are set up out to  RANG*RLSCAL Angstroms
Multipoles are calculated out to    RANG1*RLSCAL Angstroms
Splines are added out to           RANG2*RLSCAL Angstroms

```

### Example output (from example 01)

```

Maximum intramolecular distance =  0.46000000E+01 Angstroms
Multipole tables are set up out to  0.28200000E+02 Angstroms
Multipoles are calculated out to    0.15000000E+02 Angstroms
Splines are added out to           0.17000000E+02 Angstroms

```

The cutoffs used are summarized again here.

## 3.8 DAMPING PARAMETER INPUT

### DIND

```

Operand type      I, F
Operand name      Molno, mol_fdamp(MolNo)

```

If the run has induction damping, for each molecule there needs to be a record giving the molecule number followed by the induction damping parameter. These values will normally be set by NEIGHCRYST.

At the moment it is not possible to run a perfect lattice calculation including the forces due to induction. What DMACRYST is programmed to do is run the perfect lattice calculation as normal, and add the calculated induction energy to the final energy (N.B. it also calculates the induction energy at the start and includes this in the reported initial lattice energy, but this initial calculation has no effect on the course of the lattice energy minimization).

### Example input (example 25)

```

DIND      1      1.250000
DIND      2      1.250000
DIND      3      1.250000
DIND      4      1.250000

```

### Example output (example 25)

```

Induction damping has been requested
Molecule  Damping parameter
   1         0.1250E+01
   2         0.1250E+01
   3         0.1250E+01
   4         0.1250E+01

```

## Error message

```
DAMPing has been requested before POLZ section. Exiting.
```

### DDMP

Operand type            I, F  
Operand name            Molno, mol\_damping(MolNo)

If the run has dispersion damping, for each molecule there needs to be a record giving the molecule number followed by the dispersion damping parameter. These values will normally be set by NEIGHCRYST.

#### Example input (example 25)

```
DDMP            1            1.670000  
DDMP            2            1.670000  
DDMP            3            1.670000  
DDMP            4            1.670000
```

#### Example output (example 25)

```
Dispersion damping has been requested  
Molecule        Damping parameter  
      1            0.1670E+01  
      2            0.1670E+01  
      3            0.1670E+01  
      4            0.1670E+01
```

## 3.9 PERFECT LATTICE CALCULATION

The perfect lattice calculation step is invoked by the keywords STAR PLUT.

### STAR PLUT

#### 3.9.1 Perfect Lattice Relaxation Control Parameters

All of the directives are optional except the final start. The defaults are indicated.

### CONP

Operands                None

This instructs DMACRYST to relax the lattice vectors as well as the basis positions. There are 6 independent components of the bulk strain tensor which augment the  $3NBAS \times 3NBAS$  matrix of basis strain components. The relaxation of both cell and atom components is carried out simultaneously. Only one of CONV and CONP may be given; this is the default directive.

### CONV

Operands                None

This instructs the program to keep the lattice vectors fixed during the relaxation.

### PRES

Operand Type            F                            A  
Operand Name            Pressure                    units

This is used to change the pressure of the perfect lattice calculation. The units can be kPa, MPa or GPa. If only one operand is present, it is assumed that the units are Pa.

### MAXI

Operand Type            I  
Operand Name            NCYCLE

This defines the maximum number of iterations which will be carried out before a dump is written. The default is zero, which calculates the lattice properties at this configuration with no relaxation, although by default NEIGHCRYST sets NCYCLE to 1000.

### MAXD

Operand Type	F
Operand Name	DSPMAX

DSPMAX is the maximum permitted displacement of a coordinate per iteration. The default is 0.05 Angstroms, which is set small for most problems. By default, NEIGHCRYST sets DSPMAX to 0.5. A larger value may improve the speed at which a problem converges, but may allow the problem to reach a region in which the structure is physically unreasonable. DSPMAX is converted to a fraction of the c lattice constant RLSCAL.

The maximum rotation of a molecule is TORMAX radians, where TORMAX is set equal to DSPMAX.

### MAXU

Operand Type	I
Operand Name	MAXUPD

MAXUPD gives the number of times the Hessian will be updated before it is recalculated. It is recommended that for large unit cells MAXUPD should not be set too small; a value greater than 100 should be used. The default is 1000, which effectively means that the properties will only be recalculated when the structure converges or the calculation stops for another reason.

### LIMI

Operand Type	F
Operand Name	LIMIT

LIMIT gives the convergence test at which the relaxation stops with a valid minimization. The minimization will assume to have converged if all displacements in one cycle are less than LIMIT. The default is 1.0E-06 Angstroms, which is set very small. Most problems will be satisfactory with LIM I 0.0001.

### WCAL

Operand Type	A
Operand Name	WKEY

This forces the program to recalculate the Hessian rather than use the updating algorithm if the surface is abnormal. The default is no recalculation. The keyword WKEY can have two values, GDPO or NGCV. GDPO forces recalculation if an increase in energy is found after a Hessian update. NGCV forces recalculation if the curvature of the energy surface is negative. If both are required, the keyword WCAL may be given twice. This keyword is very seldom needed.

### ENGO

Operand Type	I
Operand Name	ICTRL

ICTRL is an integer which determines whether matrix properties will be calculated. It may have two values. ICTRL = 3 is the default and instructs the program to calculate matrix properties. ICTRL = 1 calculates lattice energy only. ENGO 1 in DMACRYST is only useful if no relaxation is being carried out (MAXI 0).

### LIMG

Operand Type	F
Operand Name	GLIMIT

GLIMIT gives the convergence test at which the relaxation stops with a valid minimization due to energy test being satisfied. The minimization will assume to have converged if the predicted change in energy, calculated as the scalar product of the gradient vector and displacement vector, is less than GLIMIT. The default is 1.0E-10, which is set very small. Most problems will be satisfactory with  $GLIMIT = 0.0001 \times LIMIT$ .

#### UDTE

Operand Type	F
Operand Name	USALP

USALP fine tunes the Hessian updating algorithm. The default value is 0.0, which will allow searching to continue in a given direction for a long way before updating. This can sometimes move into unphysical regions of the energy surface and give negative curvature. Setting a larger value will force the program to choose a new direction more often and may overcome this problem. It is suggested that a value of 0.1 for USALP would be suitable.

#### CCLS

Operand Types	F	< I >	< I >
Operand Names	RCCMAX	ICCMAX	ICCLS

Prints out the close contact list together with the energy subdivided by type of interaction. The information is written to fort.17 RCCMAX is the maximum separation to which information is written, ICCMAX is the maximum number of atom pairs and ICCLS is a flag. ICCLS=1 prints on the first and last cycle only, ICCLS=2 prints every 10 cycles and ICCLS=3 prints every cycle.

#### R2ND

Operands	None
----------	------

Switches on the storing or reading of the accurate second derivative matrix. Only useful if you may need to restart the run, which is seldom done. This only applies to the Properties calculation (STAR PROP)

#### SEIG

Operand Types	I	< F >	< F >	< I >	< I >	< I >	< I >	< I >
Operand Names	LSEIG	EIRNMI	EIRNMX	NEISTP	IREPS	IREPF	NEINS	NEINF

This will instruct DMACRYS to search along eigenvector directions for energies lower than the minimum which has been located. This is most useful if there is a negative eigenvalue belonging to a symmetry class which is not totally symmetric at the valid minimum for a particular run. LSEIG is a flag that takes values of 1 or 2. The search is done with displacements from EIRNMI to EIRNMX in NEISTP steps for representations from IREPS to IREPF for eigenvectors NEINS to NEINF. If LSEIG is 1 the search will be carried out only for the totally symmetric representation IREPA1 and only if one or more of its eigenvalue are negative. If LSEIG=1 the remaining parameters need not be given and the following defaults are used; EIRNMI=-1.0, EIRNMX=+1.0, NEISTP=20, IREPS=IREPA1, IREPF=IREPA1, NEINS=1, NEINF=0. LSEIG = 2 allows the search to be performed in all representations and for all eigenvectors.

#### NOPR

Operands	None
----------	------

The directive NOPR should normally be used as it instructs the program to use analytical expressions for the first derivatives and for some terms in the second derivative matrix. This is faster for structure optimizations but some of the second derivative matrix components are approximate. To calculate accurate analytical properties, this directive should be removed. The program will then calculate all terms of the matrix numerically, which is slower but more accurate.

## HESS

Operand Types            I  
Operand Names            IHESS

The directive HESS is used to instruct DMACRYS to either write out the inverted second derivative matrix or to read in a previously written version. This can save time if you need to restart from a slightly different starting position. Currently the only allowed value of IHESS is 1. The inverted second derivative matrix is written or read to a file dmahessian. If this file does not exist it will be written. If it already exists it will be read at the start and overwritten. Currently this option is only implemented if the SYMM directive is used. It can only be used for perfect lattice relaxation runs, (not properties runs, where R2ND should be used), without induction, although this restriction could be changed in a future release. (There must be no DIND directive and STAR PLUT must be used, not STAR PROP)

### Printed Output

```
Hessian will be written out for restart
```

This will be written if dmahessian does not exist.

```
Hessian will be read in and a new Hessian written out
```

This is written if dmahessian already exists.

## PHGR

Operands                None

A phonon graphics file is written to fort.26

## STAR

Operands                None

This must be the final sub-directive in the list. It starts the execution of the perfect lattice calculation and then returns control to the main menu of directives.

### Example input

```
STAR PLUT  
CONF  
NOPR  
MAXI 1000  
MAXD 0.5  
STAR  
STOP
```

### Printed Output

```
Commencing with PLUTO calculation.
```

```
Hessian will be updated when  
(1.0+UDTE*ALPHA2/ALPHAM)*(1.0-ABS(GD2/GD1)) > 0.75  
ALPHA2 = Greatest shift of an ion since last update  
ALPHAM = Maximum allowed shift per iteration  
UDTE =    USALP = User defined parameter (default ZERO)  
GD1 and GD2 = Energy changes in search direction.
```

This message is written if the UDTE option is used, and it describes how the Hessian update is modified.

```
Start variable-cell relaxation  
Start relaxation at constant volume
```

One of these messages is produced according to whether CONP (default) or CONV is given, respectively.

```
Maximum number of iterations =            NCYCLE  
Maximum relaxation of a coordinate per cycle (Angstroms) =    DSPMAX*RLSCAL  
Maximum rotation of a molecule per cycle (Degrees) =        TORMAX*RADDEG  
Maximum number of hessian updates before recalculation =      MAXUPD  
Iteration will terminate when all displacements are less than    ACCRLX  
Iteration will also terminate when dot product of gradient and displacement vectors is less than    GDRLX
```

This message is produced if NCYCLE greater than zero is given. Note the DSPMAX parameter has been scaled by the lattice parameter before it is printed.

### Example output

```
Maximum number of iterations = 1000
Maximum relaxation of a coordinate per cycle (Angstroms) = 0.50000000E+00
Maximum rotation of a molecule per cycle (Degrees) = 0.40927311E+01
Maximum number of hessian updates before recalculation = 1000
Iteration will terminate when all displacements are less than 0.14286327E-06
Iteration will also terminate when dot product of gradient and displacement vectors is less than 0.14286327E-10
```

### Printed output

```
Contributions to intra-molecular electrostatics
(eV per unit cell [kJ/mol])
```

The intramolecular multipolar energies are written out.

### Example output

```
Contributions to intra-molecular electrostatics
(eV per unit cell [kJ/mol])
Z = 8
CHAR-CHAR -7.8228 ( -94.3472 )
CHAR-DIPL -0.5625 ( -6.7844 )
DIPL-DIPL 1.6434 ( 19.8200 )
QUAD-CHAR 1.4251 ( 17.1870 )
QUAD-DIPL 12.1641 ( 146.7064 )
OCTO-CHAR 3.6191 ( 43.6485 )
QUAD-QUAD 24.2804 ( 292.8353 )
OCTO-DIPL 23.3706 ( 281.8632 )
HEXA-CHAR 2.7836 ( 33.5720 )
```

### Printed output

```
Number of Energy calculations =
```

The number of intramolecular interactions is written out.

### Example output

```
Number of Energy calculations = 224
```

### Printed output

```
Molecular dipole moments in local axis systems (eA)

Molecule          dipole          magnitude
                   x          y          z
M1 (DIPMOL(II,M1)*RLSCAL,II=1,3) DIPSIZ

Dipole per unit cell in global axis system (eA)
x          y          z          total dipole
(DIPTOT(II)*RLSCAL,II=1,3) DIPSIZ
```

The dipole moment for each molecule is written out followed by the total dipole per cell.

### Example output

```
Molecular dipole moments in local axis systems (eA)

Molecule          dipole          magnitude
                   x          y          z
1 -0.5204480 -0.5142307 0.0001551 0.7316416
2 -0.5204480 -0.5142307 0.0001551 0.7316416
i
Dipole per unit cell in global axis system (eA)
x          y          z          total dipole
0.0000000 0.0000000 0.0000000 0.0000000
```

### Printed output

```
Cutoffs used in original reciprocal sum
```

This gives the reciprocal space cutoffs used in the Ewald sum. A short direct space cell constant will give a small cutoff in reciprocal space. If the cell constants change a lot during the relaxation DMACRYS may recalculate the cutoffs to slightly different values, which could produce a small abrupt change in the energy.

## Example output

```
Cutoffs used in original reciprocal sum
      4      4      3
```

## Printed output

```
Contributions to inter-molecular electrostatics
(eV per unit cell [kJ/mol])
```

The intermolecular electrostatic energies are written out. The charge charge, charge dipole and dipole dipole energies are calculated by an Ewald sum and are not written out here.

```
Number of atom pairs calculated =
```

The number of intermolecular interactions is written out. This is written out again at the end of the calculation and should be the same. If the unit cell relaxes by a large amount, this may move the distance between two molecule centres of mass across the cutoff boundary, in which case restarting the job with the relaxed molecule positions will result in a slightly different energy.

## Example output

```
Contributions to inter-molecular electrostatics
(eV per unit cell [kJ/mol])
```

```
Z = 8
CHAR-CHAR      0.0000 ( 0.0000 )
CHAR-DIPL      0.0000 ( 0.0000 )
DIPL-DIPL      0.0000 ( 0.0000 )
QUAD-CHAR     -0.4849 ( -5.8484 )
QUAD-DIPL     -0.2427 ( -2.9272 )
OCTO-CHAR     -0.0984 ( -1.1869 )
QUAD-QUAD      0.0838 ( 1.0109 )
OCTO-DIPL     -0.0073 ( -0.0875 )
HEXA-CHAR     -0.0038 ( -0.0455 )
               0.0000 ( 0.0000 )
Number of atom pairs calculated = 60616
```

## Example output

```
First order induced moments (atomic units)
```

```
Atom Label      Q10      Q1c      Q1s
N_N1_1_1_1      0.008784710 -0.000223710 -0.031933831
C_C1_1_2_2      0.007661128 -0.059605627 -0.042854393
C_C2_2_3_3      0.000387439 -0.037451683 -0.019592931
C_C3_3_4_4      0.002308898 0.007518136 -0.042877699
C_C2_4_5_5      0.001037969 0.026020969 -0.041950207
C_C1_5_6_6     -0.000121835 0.057317585 -0.029450553
H_H1_1_7_7      0.007397176 -0.015557500 -0.002602166
H_H2_2_8_8     -0.001931694 -0.017964327 -0.006967515
H_H3_3_9_9      0.001042606 0.001773536 -0.010889367
H_H2_4_10_10   -0.003900347 0.010778306 -0.010907676
H_H1_5_11_11   -0.007505757 0.024167396 0.005266773
First-order induction energy -3.24602954 kJ/mol.
```

```
Converged induced moments (atomic units)
```

```
Atom Label      Q10      Q1c      Q1s
N_N1_1_1_1      0.010209149 0.000246732 -0.045533818
C_C1_1_2_2      0.009669262 -0.079718741 -0.068078799
C_C2_2_3_3      0.000952455 -0.048593373 -0.038268402
C_C3_3_4_4      0.002533031 0.004742404 -0.062148075
C_C2_4_5_5      0.001021180 0.030443546 -0.062949953
C_C1_5_6_6     -0.000985478 0.073073462 -0.048692936
H_H1_1_7_7      0.010412657 -0.019307530 -0.005062298
H_H2_2_8_8     -0.000903844 -0.022724949 -0.010454289
H_H3_3_9_9      0.001390565 0.001314198 -0.014026113
H_H2_4_10_10   -0.004909525 0.013354900 -0.013896190
H_H1_5_11_11   -0.010278534 0.027557972 0.003708171
Induction energy converged to -4.35911958 kJ/mol with 16 iterations.
```

This output will be produced if there is a DIND directive. It will be written for both the initial and the final structures.

## Printed output

```
Centralisation of forces (global axes)
and torques (global axes) for molecule: molecule
```

```
Basis No.  Species                                force (eV per Angstrom)
           x          y          z          magnitude
MAPX(J)  ITYPL(IABS(LBAS(MAPX(J))))  (G1(JBASE+JJ)*EVPERA,JJ=1,3)  GSIZE*EVPERA
```

Central force	$GSTIFF((I-1)*3+JJ)*EVP\text{PERA},JJ=1,3$	$G\text{SIZE}*EVP\text{PERA}$
Central torque	$GSTIFF(IT\text{BASE}+JJJ)*EVP\text{PERT},JJJ=1,3$	$G\text{SIZE}*EVP\text{PERT}$
(eV per radian) [	$G\text{LOCAL}(JJJ)*EVP\text{PERT},JJJ=1,3$	]

The force vector together with the total force on each atom in each molecule are written out. This is followed by the total force on the molecule centre of mass and the torque on the molecule. As a consistency check on data input, the forces and torques on symmetry equivalent molecules should be of the same magnitude, but the sign depends on the symmetry relation between the molecules.

### Example output

```
Centralisation of forces (global axes)
and torques (global axes) for molecule: 1

Basis No.  Species                                force (eV per Angstrom)
           x          y          z          magnitude
1  C_F1_1    -0.25612315E-01  -0.27546175E-02  -0.26987839E-02  0.25901004E-01
9  C_F1_2    -0.25861808E-01  -0.17797409E-01  -0.37804572E-01  0.49140274E-01
:          :          :          :          :
:          :          :          :          :

Central force      0.24075885E-03  -0.85637891E-03  -0.10741764E-02  0.13947059E-02
Central torque    -0.17519048E-02  -0.44469848E-03  -0.27510559E-03  0.18282806E-02
(eV per radian) [ -0.17964514E-02  0.79960003E-04  0.33011959E-03  ]
```

### Printed output

Strain derivatives for matrix deformation of form
---

The strain derivatives (stresses) on the unit cell are written out.

### Example output

```
Strain derivatives for matrix deformation of form:

      /
      |      E  1/2 E  1/2 E  |
      |      1      6      5  |
R =>  R + | 1/2 E      E  1/2 E  | R
      |      6      2      4  |
      | 1/2 E  1/2 E      E  |
      |      5      4      3/

dU/dE      dU/dE      dU/dE      dU/dE      dU/dE      dU/dE
  1          2          3          4          5          6
[ -0.0201    0.0455    -0.1011    0.0000    0.0000    0.0000
  -1.94      4.39      -9.76      0.00      0.00      0.00 ]

Units for strain derivatives : eV [kJ/mol].
```

### Printed output

Contributions to lattice energy (eV per unit cell [kJ/mol])		
Z =	INTZ	
Ewald summed charge-charge energy.....=	ECOULS*EVUNTS	[ ECOULS*RJUNTS ]
Intra-molecular charge-charge energy....=	ECOULV*EVUNTS	[ ECOULV*RJUNTS ]
Inter-molecular charge-charge energy....=	EQQS*EVUNTS	[ EQQS*RJUNTS ]
Total charge-dipole energy=	ECHDISS*EVUNTS	[ ECHDISS*RJUNTS ]
Total dipole-dipole energy=	EDIDISS*EVUNTS	[ EDIDISS*RJUNTS ]
Total charge-dipole+dipole-dipole energy=	EPOLSS*EVUNTS	[ EPOLSS*RJUNTS ]
Higher multipole interaction energy.....=	UES*EVUNTS	[ UES*RJUNTS ]
Total isotropic repulsion-dispersion....=	ESHRT*EVUNTS	[ ESHRT*RJUNTS ]
Total anisotropic repulsion energy.....=	EANIS*EVUNTS	[ EANIS*RJUNTS ]
Intermolecular induction energy.....=	EEIND*EVUNTS	[ EEIND*RJUNTS ]
PV energy..(P = 0.00E+00 Pa).....=	EPRESS*EVUNTS	[ EPRESS*RJUNTS ]
Total lattice energy.....=	E2*EVUNTS	[ E2*RJUNTS ]

Various contributions to the total lattice energy are written out.

### Example output

Contributions to lattice energy (eV per unit cell [kJ/mol])		
Z =	8	
Ewald summed charge-charge energy.....=	-0.90244160E+01[	-0.10883959E+03 ]
Intra-molecular charge-charge energy....=	-0.78227800E+01[	-0.94347178E+02 ]
Inter-molecular charge-charge energy....=	-0.12016360E+01[	-0.14492414E+02 ]
Total charge-dipole energy=	0.20422449E+00[	0.24630636E+01 ]
Total dipole-dipole energy=	0.17972682E+00[	0.21676078E+01 ]

```

Total charge-dipole+dipole-dipole energy= 0.38395132E+00[ 0.46306713E+01 ]
Higher multipole interaction energy.....= -0.75326526E+00[ -0.90848077E+01 ]
Total isotropic repulsion-dispersion....= -0.20073845E+01[ -0.24210199E+02 ]
Total anisotropic repulsion energy.....= 0.00000000E+00[ 0.00000000E+00 ]
Intermolecular induction energy.....= 0.00000000E+00[ 0.00000000E+00 ]
PV energy..(P = 0.00E+00 Pa).....= 0.00000000E+00[ 0.00000000E+00 ]
Total lattice energy.....= -0.35783344E+01[ -0.43156749E+02 ]

```

## Error messages

```
ERROR - NO ROUTE PARAMETER ON START DIRECTIVE CARD
```

The directive has the keyword STAR but not the keyword PLUT or PROP. Check that the keyword is correct.

```
ERROR - POTENTIAL FUNCTIONS NOT DEFINED BEFORE START OF PLUTO EXECUTION OR FILE INPUT
```

The POTE directive has been omitted or placed in the incorrect order. It should be before STAR PLUT

```
Execution terminated before PLUTO because of above errors
```

The STAR PLUT directive is one point where the program stops if it has detected a previous error. Look through the printed output for further error messages.

```
ERROR - Unrecognised keyword KEYW found whilst reading PLUT parameters
```

A keyword has been found which is not in the STAR PLUT menu.

```
ERROR - BASIS SPECIES NUMBERS i AND j
LABELS labeli labelj ARE SEPARATED BY LESS THAN CUTSHL
```

This error message is produced by inconsistencies between the species labels and the CUTSHL parameter. This message comes from two species lying within CUTSHL of each other in the perfect lattice relaxation. This means that the structure has moved to an unphysical geometry. Redefine MAXD to be smaller and resubmit the job.

## Printed output

If the relaxation vector is sufficiently small, DMACRYS will assume that a valid minimum has been found. Currently the distance used in this test is  $5.0 \times 10^{-6}$  lattice units, and the program terminates if all displacements of all symmetry adapted variables are less than this value.

If PRIN MINI is set to a value greater than one, the following output will be obtained.

```
MINIMISATION SETUP
```

This is printed every time the inner iterative loop is entered. Usually this will be once only on the first iteration, unless one of the Hessian recalculation options is used.

```
GD1 = F
```

This is written twice after the MINIMISATION SETUP message. The first value F is the value of G.DELTA, the second is the value of G.DELTA scaled if necessary to keep all of the elements of delta within RMAXSF. G.DELTA should be negative indicating a decrease of energy in the search direction. If the first value of GD1 is positive, the direction of the search is reversed to ensure that the energy decreases.

```
ALPHA= F1 ALPHA2= F2
```

This message occurs after MINIMISATION SETUP or after CHANGE DIRECTION (see below). ALPHA and ALPHA2 will both be one in this case. ALPHA is the current fraction of DELTA to be applied. ALPHA2 is the total fraction of DELTA applied since the last Hessian update.

```
GD1= F1 GD2= F2
```

This is printed every cycle except for MINIMISATION SETUP cycles. GD1 is the previous value of G.DELTA, GD2 is the value calculated at the position after the step in the search direction. If the minimization is working correctly, the magnitude of GD2 should be less than GD1.

If  $ABS(GD2/GD1)$  is less than 0.25, the following is printed.

```
CHANGE DIRECTION
```

```
GD1 = F1
```

```

ALPHA= F2 ALPHA2= F3
HESSIAN UPDATE COMPLETE ... GD1= F4 GD2= F5 IKIND= I1 DELMAX= F6 IN COMPONENT I2
Lattice energy = energy (in internal units) (Repulsion-dispersion cutoff = cuto lattice
units)

```

Where

F4	is the value of G.DELTA calculated from the updated Hessian and the new search direction DELTA. (DELTA = Hessian.G).
F5	is zero.
I1	is 0 if the Davidon-Fletcher-Powell algorithm has been used to update the Hessian.(R. Fletcher and M. J. D. Powell. Computer J. 6 (1963) 16) I1 is 1 if the Broyden, Fletcher and Shanno algorithm has been used. (C. G. Broyden. J. Inst. Maths. Applns. 6 (1970) 66 and 222. D. F. Shanno. Math. Computing 24 (1970) 647.)
F6	is the maximum displacement of a symmetry adapted variable. If F3 is greater than RMAXSF the search direction will be scaled so that the maximum displacement is RMAXSF.
I2	is the index of the variable with the maximum displacement.

```

GD1 = F1
ALPHA = F1 ALPHA2 = F2

```

These messages are described above under MINIMISATION SETUP.

If ABS(GD2/GD1) is greater than 0.25 then a further search in this direction is made before an update is carried out. There are three possible options.

1. If GD2 is less than GD1 (that is more negative), the system is in a region where the potential energy surface has negative curvature. Possible causes of this are that it is close to a saddle point and is moving away from it. Another point to look out for is that two atoms interacting with a BUCK repulsion-dispersion potential have not become too close. If the Van der Waals parameter is non-zero, the  $R^{-6}$  term eventually dominates the exponential term, leading to negative curvature in the energy surface. If this is the cause, either reduce RMAXSF or consider using the BUC4 potential instead.

```

NEGATIVE CURVATURE
ALPHA = F1 ALPHA2 = F2 ALPHA3 = F3 ALPHA4 = F4 GD1 = F5 GD2 = F6 GD3 = F7 GD4 = F8

```

These are the ALPHA values and corresponding G.DELTA values at four points in the search direction. ALPHA is the current step in the search direction. ALPHA2 is the total step since the last Hessian update or Hessian calculation. GD1 is the G.DELTA value for ALPHA = 1.0 GD2 is the G.DELTA value for the current step length ALPHA2. ALPHA3, ALPHA4, GD3 and GD4 are ALPHA and GD values from previous iterations in this search direction.

```

ALPHA2 TOO LARGE TO EXTRAPOLATE

```

Extrapolation in this direction would change one of the variables by more than RMAXSF, therefore a matrix update is carried out.

2. If GD2 is greater than zero, an interpolation is carried out.

```

LINEAR INTERPOLATION
ALPHA = F1 ALPHA2 = F2 ALPHA3 = F3 ALPHA4 = F4 GD1 = F5 GD2 = F6 GD3 = F7 GD4 = F8

```

This has the same meaning as above.

3. If GD2 is negative, a linear extrapolation is carried out.

```

LINEAR EXTRAPOLATION

```

```
ALPHA = F1 ALPHA2 = F2 ALPHA3 = F3 ALPHA4 = F4 GD1 = F5 GD2 = F6 GD3 = F7 GD4 = F8
```

This has the same meaning as described above.

If a further search is necessary in the same direction, additional printed output may be obtained.

```
QUADRATIC INTERPOLATION
```

```
ALPHA= F1 ALPHA2= F2 ALPHA3= F3 ALPHA4= F4  
GD1 = F5 GD2 = F6 GD3 = F7 GD4 = F8
```

```
QUADRATIC EXTRAPOLATION
```

```
ALPHA= F1 ALPHA2= F2 ALPHA3= F3 ALPHA4= F4  
GD1 = F5 GD2 = F6 GD3 = F7 GD4 = F8
```

These messages indicate that the results of two previous steps are being used to interpolate/extrapolate.

```
THREE INTERPOLATIONS
```

This indicates that three interpolations failed to reduce GD2 sufficiently and an update will be carried out in any case.

### ***Error messages***

```
INVALID MINIMISATION - PERSISTENT NEGATIVE CURVATURE
```

This indicates that the energy surface has negative curvature. It may not be possible to converge this dataset, however the values of RMAXSF and MAXUPD could be changed to alter the path taken by the minimization. Restarting from the final point of this minimization usually corrects this.

Three checks are now carried out to ensure that the minimization is proceeding properly. See section (3.9.13) below.

## **3.9.2 Successful minimization**

### ***Printed output***

```
On returning from minimiser proposed alterations are:
```

```
Molecular translations (Angstroms)
```

```
Molecule No.      x          y          z      magnitude
```

```
IMOL      (DEL(IBASE+IW)*RLSCAL,IW=1,3)  DELSIZ*RLSCAL
```

```
All will be scaled by a factor of      1.000000
```

```
Molecular rotations:
```

```
Molecule No. Global [local] rotation axis      magnitude  
                x          y          z      (Degrees)
```

```
IMOL      (UAAROT(IW),IW=1,3)  DELSIZ*RADDEG  
[      (AAROT(IW),IW=1,3)      ]
```

```
All will be scaled by a factor of      1.000000
```

This gives the shifts of the centres of mass of the molecules and rotations. If symmetry is conserved, these should be of the same magnitude but may differ in sign.

### ***Example output***

```
On returning from minimiser proposed alterations are:
```

```
Molecular translations (Angstroms)
```

```
Molecule No.      x          y          z      magnitude
```

```
1      0.000001      0.000001      -0.000001      0.000001
```

```

 2      0.000001      -0.000001      0.000001      0.000001
!
All will be scaled by a factor of      1.000000

Molecular rotations:

Molecule No. Global [local] rotation axis      magnitude
                x          y          z          (Degrees)

 1      -0.747137      -0.417699      -0.517024      0.000097
 [      -0.960588      0.005476      -0.277921 ]
!
All will be scaled by a factor of      1.000000

```

### Printed output

Strain matrix to be applied:

E	E	E	E	E	E
1	2	3	4	5	6
E1	E2	E3	E4	E5	E6

This is the final strain matrix and should be zero if the minimization is CONP.

Coordinates dumped

Cutoffs used in original reciprocal sum

This is described previously.

Contributions to inter-molecular electrostatics  
(eV per unit cell [kJ/mol])

This is described above and gives the final contributions to the electrostatics.

Number of atom pairs calculated =

This should be the same as was displayed previously.

Centralisation of forces (global axes)  
and torques (global axes) for molecule:

This is described above. The final centre of mass forces and torques should all be very close to zero, although individual atom forces will not be zero.

Strain derivatives for matrix deformation of form:

The final strain derivatives are written out. These should be zero for a CONP calculation.

```

Contributions to lattice energy (eV per unit cell [kJ/mol])
Z =      INTZ
Ewald summed charge-charge energy.....= ECOULS*EVUNTS [ ECOULS*RJUNTS ]
Intra-molecular charge-charge energy....= ECOULV*EVUNTS [ ECOULV*RJUNTS ]
Inter-molecular charge-charge energy...= EQQS*EVUNTS [ EQQS*RJUNTS ]
      Total charge-dipole energy= ECHDISS*EVUNTS [ ECHDISS*RJUNTS ]
      Total dipole-dipole energy= EDIDISS*EVUNTS [ EDIDISS*RJUNTS ]
Total charge-dipole+dipole-dipole energy= EPOLSS*EVUNTS [ EPOLSS*RJUNTS ]
Higher multipole interaction energy.....= UES*EVUNTS [ UES*RJUNTS ]
Total isotropic repulsion-dispersion...= ESHRT*EVUNTS [ ESHRT*RJUNTS ]
Total anisotropic repulsion energy.....= EANIS*EVUNTS [ EANIS*RJUNTS ]
Intermolecular induction energy.....= EEIND*EVUNTS [ EEIND*RJUNTS ]
PV energy..(P = 0.00E+00 Pa).....= EPRESS*EVUNTS [ EPRESS*RJUNTS ]
Total lattice energy.....= E2*EVUNTS [ E2*RJUNTS ]

```

These are written out as above.

Warning - NOPR directive was used - properties will only be approximate

In a perfect lattice minimization the NOPR directive will usually be switched on. In this case the elastic constants output will only be approximate, so will not be discussed in detail here. The following section on calculating the properties deals with the elastic constants and phonon frequencies, highlighting at the end those that are different when NOPR is switched on.

EIGENVALUES FOR REPRESENTATION

The program writes out the eigenvalues of the block diagonal matrices of the Hessian. There should be three components which are zero or close to zero. (If the crystal structure is high symmetry one of the representations may be two or three dimensional, so you need to take this into account when checking). The totally symmetric representation is always written last and should not have any negative eigenvalues. The other representations may have negative eigenvalues if the structure has converged to a saddle point. If this is the case, rerun NEIGHCRYST using the final structure from this DMACRYST run as a starting point (fort.15 or fort.16) and input the number of this representation in reply to the question.

**Example output (for example 01)**

```
EIGENVALUES FOR REPRESENTATION 1
 0.46992007E+00  0.75400646E+00  0.19545146E+01  0.19671835E+02  0.28378630E+02
 0.39229562E+02
EIGENVALUES FOR REPRESENTATION 2
-0.57779402E-13  0.28598497E+00  0.21937415E+01  0.27889473E+01  0.35149647E+02
 0.41375752E+02
!
```

A very small negative number, as in this example, is not indicative of convergence to a saddlepoint and can safely be ignored.

**Example output (for “reason” folder of example 16)**

```
EIGENVALUES FOR REPRESENTATION 1
 0.54740738E+01  0.10484391E+02  0.21314702E+02  0.28925942E+02  0.32695686E+02
 0.58755977E+02
EIGENVALUES FOR REPRESENTATION 2
-0.60919587E-13  0.41550997E+01  0.88608361E+01  0.26927779E+02  0.34219756E+02
 0.40828089E+02
EIGENVALUES FOR REPRESENTATION 3
-0.13293712E+01  0.29517738E-13  0.84737284E+01  0.15625808E+02  0.22016299E+02
 0.55803587E+02
!
```

This is indicative of convergence to a saddlepoint, and should be reminimized. See the test-suite supporting documentation and the NEIGHCRYST manual for further information.

On returning from minimiser proposed alterations are:

```
Molecular translations (Angstroms)
Molecule No.      x          y          z      magnitude
IMOL              (DEL (IBASE+IW) *RLSCAL, IW=1, 3)  DELSIZ*RLSCAL
All will be scaled by a factor of      1.000000

Molecular rotations:
Molecule No. Global [local] rotation axis      magnitude
                x          y          z      (Degrees)
IMOL              (UAAROT (IW) , IW=1, 3)          DELSIZ*RADDEG
 [              (AAROT (IW) , IW=1, 3)              ]
All will be scaled by a factor of      1.000000
```

This is printed out again, and should show that the proposed alterations are all negligible..

Strain matrix to be applied:

```

E          E          E          E          E          E
 1          2          3          4          5          6
E1         E2         E3         E4         E5         E6
```

The strain matrix should be zero.

**Example output**



Changes in structure during program run (Refer to centered cell)

Lattice vectors (Angstroms and Degrees)

	a	b	c	alpha	beta	gamma
Initial =>	SIZLAT (JJJ,1) *RLSCAL, JJJ=1,3			ANGLAT (JJJ,1), JJJ=1,3		
Final =>	SIZLAT (JJJ,2) *RLSCAL, JJJ=1,3			ANGLAT (JJJ,2), JJJ=1,3		
diff. (abs) =>	DIFLAT (JJJ) *RLSCAL, JJJ=1,3			DIFALP (JJJ), JJJ=1,3		
diff. (%) =>	100.0D+0*DIFLAT (JJJ) /SIZLAT (JJJ,1), JJJ=1,3			100.0D+0*DIFALP (JJJ) /ANGLAT (JJJ,1), JJJ=1,3		

Cell Volume ( Cubic Angstroms ) Cell density ( g/cubic cm)

Initial =>	VCELLI	DDENS1
Final =>	VCELLF	DDENS
diff. (abs) =>	VCELLF-VCELLI	DDENS-DDENS1
diff. (%) =>	(VCELLF-VCELLI)*100.0D+0/VCELLI	(DDENS-DDENS1)*100.0D+0/DDENS1

Dipole per unit cell in global axis system (eA)

	x	y	z	total dipole
--	---	---	---	--------------

Initial : DIPTOT (II) \*RLSCAL, II=1,3 DIPSZ1

Final : DPTOT2 (II) \*RLSCAL, II=1,3 DIPSZ2

The changes to the total crystallographic lattice are reported

### Example output

Changes in structure during program run (Refer to centered cell)

Lattice vectors (Angstroms and Degrees)

	a	b	c	alpha	beta	gamma
Initial =>	9.8641	10.1391	6.9997	90.0000	90.0000	90.0000
Final =>	9.8857	10.0951	7.0163	90.0000	90.0000	90.0000
diff. (abs) =>	0.0216	-0.0440	0.0166	0.0000	0.0000	0.0000
diff. (%) =>	0.2193	-0.4339	0.2376	0.0000	0.0000	0.0000

Cell Volume ( Cubic Angstroms ) Cell density ( g/cubic cm)

Initial =>	700.0617	1.0639
Final =>	700.2127	1.0636
diff. (abs) =>	0.1510	-0.0002
diff. (%) =>	0.0216	-0.0216

Dipole per unit cell in global axis system (eA)

	x	y	z	total dipole
--	---	---	---	--------------

Initial : 0.0000000 0.0000000 0.0000000 0.0000000

Final : 0.0000000 0.0000000 0.0000000 0.0000000

### Printed output

Initial crystallographic positions of molecule centres of mass

Molecule	a-vectors	b-vectors	c-vectors
----------	-----------	-----------	-----------

MOLWCH XTLCOM (JJJ), JJJ=1,3

Final crystallographic positions of molecule centres of mass

Molecule	a-vectors	b-vectors	c-vectors
----------	-----------	-----------	-----------

MOLWCH XTLCOM (JJJ), JJJ=1,3

The changes to the positions of the molecules' centres of mass are printed out.

### Example output

Initial crystallographic positions of molecule centres of mass

Molecule	a-vectors	b-vectors	c-vectors
----------	-----------	-----------	-----------

1 0.896521 0.156371 0.107545

2 0.396521 0.343629 0.892455

3 0.103479 0.656371 0.392455

4 0.603479 0.843629 0.607545

5 0.103479 0.843629 0.892455

6 0.603479 0.656371 0.107545

7 0.896521 0.343629 0.607545

```
8      0.396521      0.156371      0.392455
```

Final crystallographic positions of molecule centres of mass

Molecule	a-vectors	b-vectors	c-vectors
1	0.896612	0.156879	0.107226
2	0.396612	0.343121	0.892774
3	0.103388	0.656879	0.392774
4	0.603388	0.843121	0.607226
5	0.103388	0.843121	0.892774
6	0.603388	0.656879	0.107226
7	0.896612	0.343121	0.607226
8	0.396612	0.156879	0.392774

## Printed output

Direction cosines between axes before and after program run for molecule MOLWCH

```
new axis      old axis
||           X           Y           Z
//
LABAX (IAXIS) (DIRCOS (IAXIS, JAXIS), JAXIS=1, 3)
LABAX (IAXIS) (DIRCOS (IAXIS, JAXIS), JAXIS=1, 3)
LABAX (IAXIS) (DIRCOS (IAXIS, JAXIS), JAXIS=1, 3)
```

Actual angles between axes (Degrees):

```
new axis      old axis
||           X           Y           Z
//
LABAX (IAXIS) RADDEG*ACOS (DIRCOS (IAXIS, JAXIS)), JAXIS=1, 3
LABAX (IAXIS) RADDEG*ACOS (DIRCOS (IAXIS, JAXIS)), JAXIS=1, 3
LABAX (IAXIS) RADDEG*ACOS (DIRCOS (IAXIS, JAXIS)), JAXIS=1, 3
```

Euler (y-convention) angles of new system in old:

```
first rotation about z Phi = RADDEG* PHI
first rotation about y Theta= RADDEG*THETA
second rotation about z Psi = RADDEG*PSI
Equivalent to a single rotation of RADDEG*ACTANG degrees

around the global axis vector: RNORM (JJJ), JJJ=1, 3
```

```
[local axis {orig. system} vector: 0.503410 -0.802287 0.320802 ]
```

The changes to the positions of the molecular axes are printed out for each molecule.

## Example output

Direction cosines between axes before and after program run for molecule 1

```
new axis      old axis
||           X           Y           Z
//
X  0.999982  -0.005194  -0.002854
Y  0.005185  0.999981  -0.003226
Z  0.002871  0.003211  0.999991
```

Actual angles between axes (Degrees):

```
new axis      old axis
||           X           Y           Z
//
X  0.339568  90.297606  90.163514
Y  89.702921  0.349888  90.184839
Z  89.835529  89.816012  0.246784
```

Euler (y-convention) angles of new system in old:

```
first rotation about z Phi = 131.794159
first rotation about y Theta= 0.246784
second rotation about z Psi = -131.496815
```

Equivalent to a single rotation of 0.386414 degrees

```
around the global axis vector: 0.477247 -0.424397 0.769495
[local axis {orig. system} vector: 0.501013 -0.804490 0.319032 ]
```

## Printed output

```
Molecular movement including strains (Angstroms)
```

```
Mol.      | Dx |  
  
III      DELXML(III)  
  
RMS Aver.  RMS aver
```

The molecular movement for each molecule is printed out.

## Example output

```
Molecular movement including strains (Angstroms)
```

```
Mol.      | Dx |  
  
1         0.020376  
2         0.028127  
3         0.025353  
4         0.044647  
5         0.045576  
6         0.026685  
7         0.029722  
8         0.013028  
  
RMS Aver. 0.030994
```

## Printed output

```
Figure of shame as defined in Acta Cryst. B49 868 1993.  
in our case RMS values are used to take the place of symmetry independent factors so
```

```
F = | 0.5 RMS D THETA |2 + | 10 RMS Dx |2 + SUM (d=a,b,c) | 100 Dd |2
```

```
+ SUM (d= alpha,beta,gamma) Dd2
```

```
In this case: F= FSTOT
```

```
Terms in order are as follows:
```

```
FSANG   FSMOV   FSLAT   FSALPH
```

The Figure of shame is printed out.

## Example output

```
Figure of shame as defined in Acta Cryst. B49 868 1993.  
in our case RMS values are used to take the place of symmetry independent factors so
```

```
F = | 0.5 RMS D THETA |2 + | 10 RMS Dx |2 + SUM (d=a,b,c) | 100 Dd |2
```

```
+ SUM (d= alpha,beta,gamma) Dd2
```

```
In this case: F= 0.426189
```

```
Terms in order are as follows:
```

```
0.037329  0.096060  0.292800  0.000000
```

## Printed output

```
Initial crystallographic positions of atoms for molecule MOLWCH
```

```
No. Label Type      a-vectors      b-vectors      c-vectors  
MNA (MAPX (KATOM))  ITYPL (IABS (LBAS (MNA (MAPX (KATOM) ))) ) ) (XBASIT (JJJ, KATOM) , JJJ=1, 3)
```

```
Final crystallographic positions of atoms for molecule MOLWCH
```

```
No. Label Type      a-vectors      b-vectors      c-vectors  
MNA (MAPX (KATOM))  ITYPL (IABS (LBAS (MNA (MAPX (KATOM) ))) ) ) (XBASFN (JJJ, KATOM) , JJJ=1, 3)
```

Initial positions for each atom in each molecule are printed out, followed by the final positions of the same.

## Example output

```
Initial crystallographic positions of atoms for molecule 1
```

No.	Label	Type	a-vectors	b-vectors	c-vectors
1	C_F1_1		0.787799	0.007990	0.118536
9	C_F1_2		0.825944	0.131235	0.074278
17	C_F1_3		0.959006	0.181731	0.135252
25	O_F1_1		1.000471	0.293116	0.099920
33	H_F1_1		0.854020	-0.056139	0.199753
41	H_F1_2		0.690870	-0.031820	0.075890
49	H_F1_3		0.761901	0.197475	-0.006674
57	H_F1_4		1.021226	0.110836	0.217512

```
Final crystallographic positions of atoms for molecule 8
```

No.	Label	Type	a-vectors	b-vectors	c-vectors
8	C_F1I9		0.287123	0.008565	0.381576
16	C_F1I10		0.326029	0.132058	0.425948
24	C_F1I11		0.459124	0.181971	0.365151
32	O_F1I9		0.501260	0.293539	0.400592
40	H_F1I9		0.352744	-0.056194	0.300397
48	H_F1I10		0.190148	-0.030831	0.424092
56	H_F1I11		0.262595	0.198924	0.506866
64	H_F1I12		0.520707	0.110443	0.282919

## Printed output

```
Sorted displacements for molecule MOLWCH
```

No.	Label	Type	Displacement, including strain (Angstroms)			
			a-vectors	b-vectors	c-vectors	magnitude

```
MNA (MAPX (ISORT (IATOM))) ITYPL (IABS (LBAS (MNA (MAPX (ISORT (IATOM)))))) XBCHNG (JJJ, IATOM), JJJ=1, 4
```

The displacements for each atom are printed out.

## Example output

```
Sorted displacements for molecule 1
```

No.	Label	Type	Displacement, including strain (Angstroms)			
			a-vectors	b-vectors	c-vectors	magnitude

1	C_F1_1		-0.004733	0.004030	-0.000788	0.000000
9	C_F1_2		0.000594	0.005761	-0.001580	0.000000
17	C_F1_3		0.000827	0.001678	-0.002819	0.000000
25	O_F1_1		0.005525	0.002957	-0.003588	0.000000
33	H_F1_1		-0.008933	-0.000382	-0.001050	0.000000
41	H_F1_2		-0.005049	0.006924	0.000125	0.000000
49	H_F1_3		0.004860	0.010140	-0.001345	0.000000
57	H_F1_4		-0.003633	-0.002752	-0.003020	0.000000

## Printed output

```
STOP directive encountered. execution terminating.
```

The STOP directive was reached

Timing information follows.

## 3.9.3 Output from additional optional directives

```
Hessian will be recalculated if surface is abnormal
```

This message is written if directive WCAL is supplied.

```
Perfect lattice property calculation without relaxation
```

This is written if MAXI 0 is given.

## Example input (from example 16)

```
SEIG 1
```

## Printed Output

REPRESENTATION	EIGENVALUE	DISPLACEMENT	ENERGY
IREP	IWR	ALPHA2	E2

## Example output

REPRESENTATION	EIGENVALUE	DISPLACEMENT	ENERGY
			-0.85233812E+01
4	1	0.1053	-0.853592250539E+01
4	1	-0.1053	-0.853592250539E+01
4	1	0.2105	-0.854548149677E+01

The SEIG directive will be put in automatically by NEIGHCRY5 when a symmetry reduction is carried out. In this case, the value of REPRESENTATION will always be the final value in the list. Eigenvalue will usually have the value 1 corresponding to the negative value. If the representation has two or more negative eigenvalues, then all of them will be output in turn. The program selects progressively larger displacements, moves the structure along the eigenvector for this eigenvalue and calculates the energy for ten points in both directions. On the first row the energy at the unrelaxed position is printed; underneath the energies at the displaced positions are printed. The program looks for the lowest energy and starts the relaxation from this position. If a minimum is not found, the process is carried out a maximum of 3 times with smaller displacements.

The directive can be put in by editing the .dmain file by hand. You could use this for example to explore the energy surface without carrying out a relaxation in cases where there are multiple representations with negative eigenvalues. The best representation to remove first is usually the one giving the most negative energy.

Note that a symmetry reduction run of NEIGHCRY5 will not include the NOPR directive in the \*.dmain file. However, it is effectively present as symmetry reduction uses the approximate matrix with the non-analytical second derivatives being generated in the relaxation step, because this is faster and usually almost as accurate.

## Error messages

Error - cannot locate a lower energy along a negative eigenvalue

This indicates that even the smallest displacement selected by DMACRY5 was too large, and none of the points investigated were lower in energy than the original saddle point structure.

THE FORCE CONSTANT MATRIX IS AS FOLLOWS  
THE GRADIENT VECTOR IS AS FOLLOWS

The force constant matrix and gradient vector may be printed by setting PRIN PLUT 01000. If just the gradient vector is required, set PRIN PLUT 03000 (first and last cycle only) or PRIN PLUT 04000 (Each cycle). There are 6\*MOLS + 6 elements. The order of the elements is

x, y and z derivatives of each molecule in the sorted order. This is followed by the torsions for each molecule.

6 components of the bulk strain derivatives.

Note that there are mixed second derivatives between all three types. The elements of the matrix are not scaled to eV Angstrom units. To convert to eV Angstrom units, multiply

W or G	Position		Multiplication factor	Resulting Units
	From	To		
Gradient	1	6*MOLS	$\frac{14.3994584}{RLAT^2}$	$(\text{eV \AA})^{-1}$
	6*MOLS	ENDS	$\frac{14.3994584}{RLAT^3}$	$(\text{eV \AA})^{-2}$
Matrix	1,1	6*MOLS,6*MOLS	$\frac{14.3994584}{RLAT^3}$	$(\text{eV \AA})^{-2}$
	1,6*MOLS	6*MOLS,END	$\frac{14.3994584}{RLAT^4}$	$(\text{eV \AA})^{-3}$
	6*MOLS,6*MOLS	END,END	$\frac{14.3994584}{RLAT^5}$	$(\text{eV \AA})^{-4}$

The lattice vectors, basis species types and positions will be written to FORTRAN unit 8. This is by default for DMACRYS.

The force constants may be written out at several points in the program. Option PRIN PLUT 12010 will print out the force constants and gradient vector. The matrix before symmetry adaption is written out. The order of the elements is

- Translations of the rigid bodies, the x, y and z directions for rigid body 1, then rigid body 2 and so on.
- Translations of any free ions.
- Rotations of the rigid bodies about x, y and z axes.
- Unit cell strain components of the force constants.

If NOPR is used some of the terms will be zero as they are not calculated analytically.

### Example input

```
PRIN BASI 0 PLUT 12010 MOLE 0 BOND 2 TORS 2 MINI 2 GEOM 1
```

### Example output

```
The force constant matrix is as follows.
      1          2          3          4          5          6          7
8
  1    0.3184098D+02 -0.3310839D+01  0.4473320D+00 -0.1093008D+02  0.2707166D-11 -0.5339945D-11 -
0.5264660D+01  0.5161873D-11
  2    -0.3310839D+01  0.2364997D+02  0.2668241D+01  0.2707166D-11 -0.4996172D-01  0.2495639D+00
0.5161873D-11 -0.6548783D+01
!
The gradient vector is as follows
      1          2          3          4          5          6          7
8
  0.7881170D-03 -0.2935743D-02 -0.3657113D-02  0.7881170D-03  0.2935743D-02  0.3657113D-02 -0.7881170D-03 -
0.2935743D-02
!
```

PRIN MINI prints the progress of the minimisation. The output from MINI 3 and 4 is sometimes useful for looking at problematic minimisations. MINI 0 prints just the lattice energy each cycle. MINI 1 or 2 prints in addition quantities from the minimisation progress. GD1 which is printed is the product of the initial gradient vector and the step direction vector, and is the predicted energy to the minimum. GD2 is the same for the final gradient vector and should be numerically less than GD1. The ALPHA terms are the multiplication factors for the step vector. MINI 3 prints the eigenvalues of the inverse of the Hessian, the gradient vectors and the step vector DEL. The molecular translations, rotations and unit cell strains are printed. Finally the inter-molecular electrostatics are printed. MINI 4 prints the inverse of the Hessian before and after the Hessian update. For MINI 3 and 4 only the totally symmetric part of the symmetry adapted Hessian is printed. The order of the elements will be:

- Linear combinations of the translational part for rigid bodies
- Linear combinations of the translational part for free ions
- Linear combinations of the rotational part for rigid bodies.
- Unit cell strain components

The linear combinations used will be the translation and rotation functions for representation 1 printed in the fort.21 output from NEIGHCRYST. For the unit cell the representation 1 quadratic basis function is used. The symmetry adaption is applied to the Hessian, then the representation 1 (totally symmetric) part is inverted.

### Example output

The following section is printed for MINI >= 3

```
EIGENVALUES FOR REPRESENTATION 1
  0.47597337E+00  0.77296943E+00  0.19511596E+01  0.19844693E+02  0.27749771E+02
  0.39653737E+02
!
```

The following section is printed for MINI >= 1

```
GD1 = -0.1427E-03
```

ALPHA= 1.00000 ALPHA2= 1.00000

MINIMISATION SET-UP.

GD1 = -0.1427E-03

The following section is printed for MINI >= 3

G1  
0.2229131D-02 -0.8303534D-02 -0.1034388D-01 -0.2409472D-02 -0.6097552D-03  
-0.3836337D-03 -0.1007958D-01 0.2193225D-01 -0.4916001D-01  
DEL  
-0.5380197D-04 0.8052993D-03 0.3435313D-03 0.3270452D-02 0.1260930D-02  
-0.3172034D-03 0.1353046D-03 -0.1003562D-02 0.2042639D-02

The following section is printed for MINI = 4

W  
0.3497198D-01 0.9956483D-02 -0.5657340D-02 0.0000000D+00 0.0000000D+00  
0.0000000D+00 0.0000000D+00 0.0000000D+00 0.0000000D+00 0.9956483D-02

The following section is printed for MINI >= 3

On returning from minimiser proposed alterations are:

Molecular translations (Angstroms)

Molecule No.	x	y	z	magnitude
1	-0.000133	0.001993	0.000850	0.002171
2	-0.000133	-0.001993	-0.000850	0.002171

All will be scaled by a factor of 1.000000

Molecular rotations:

Molecule No.	Global [local] rotation axis	magnitude
	x y z	(Degrees)
1	0.929255 0.358276 -0.090129	0.071294
[	0.927015 0.168382 -0.335098 ]	
2	0.929255 -0.358276 0.090129	0.071294
[	0.927015 0.168382 -0.335098 ]	

All will be scaled by a factor of 1.000000

Strain matrix to be applied:

E	E	E	E	E	E
1	2	3	4	5	6
0.000135	-0.001004	0.002043	0.000000	0.000000	0.000000

Contributions to inter-molecular electrostatics  
(eV per unit cell [kJ/mol])

Z = 8

CHAR-CHAR	0.0000	(	0.0000	)
CHAR-DIPL	0.0000	(	0.0000	)
DIPL-DIPL	0.0000	(	0.0000	)
QUAD-CHAR	-0.4891	(	-5.8987	)
QUAD-DIPL	-0.2404	(	-2.8990	)
OCTO-CHAR	-0.0984	(	-1.1862	)
QUAD-QUAD	0.0823	(	0.9925	)
OCTO-DIPL	-0.0070	(	-0.0843	)
HEXA-CHAR	-0.0037	(	-0.0445	)
	0.0000	(	0.0000	)

Number of atom pairs calculated = 60568

### 3.10 PROPERTIES CALCULATIONS

The elastic stiffness tensor<sup>1</sup> and  $k=0$  phonon frequencies<sup>2</sup> of the perfect crystal at 0 K are estimated within DMACRYS from the second derivatives of the energy with respect to rigid body motions. The omission of the NOPR directive means that the full second derivative matrix is calculated numerically from the analytical gradients. The time taken to carry out the calculations is increased significantly. It is necessary to increase the accuracy to which the Ewald sum is carried out. The default is to 1 part in  $10^6$ , but this gives erroneous phonon frequencies. ACCMAD should be increased to 1 part in  $10^8$  for properties calculations.

The calculation should start from a lattice energy minimum; otherwise the relaxation may change the conventional Cartesian reference frame, leading to an error in the definition of the elastic constants. The restarting of the calculation may lead to **insignificant** small changes. The values that are changed very slightly by the NOPR directive being omitted are:

- Ewald summed charge-charge energy
- Inter-molecular charge-charge energy
- Total charge-dipole energy
- Total dipole-dipole energy
- Total charge-dipole+dipole-dipole energy
- Higher multipole interaction energy
- Total isotropic repulsion-dispersion
- The Eigenvalues for the representations
- The forces and torques are also changed slightly.

These insignificant changes arise from a number of causes. The relaxation may have moved the Cartesian axes so that they no longer follow the conventional definition (e.g. x is no longer along a\*), and so the restarted calculation will then run with a different Cartesian reference frame. The restart will be carried out from the fort.16 file output from the relaxation calculation which is written out to a lower precision which will result in discrepancies when the Cartesian coordinates are recalculated. The Ewald sum cutoffs will be slightly different because they are calculated once at the start of the calculation using an algorithm that depends on the unit cell volume. It may also be possible for an atom pair distance to cross the dispersion repulsion or multipole cutoff boundary during the relaxation, and since the list of possible interactions is set up once at the start of the calculation an interaction may be included or excluded from the restart. In principal the calculation can be restarted from exactly the same structure by editing the new .dmain file by hand, but the changes to the lattice energy summations will still give rise to insignificant differences in the components of the energies.

The  $k=0$  rigid body harmonic frequencies will include the low energy lattice modes observed by infrared (and teraHertz) and Raman spectroscopy, as well as inelastic neutron scattering. The symmetry assignments or spectroscopic activity of these modes are not included in the mode descriptions. However, the actual motions associated with each mode can be obtained from the harmonic modes entry, with each mode having the three Cartesian components of the x,y,z, translation for each molecule in the unit cell, and the rotation around the x,y,z, axis for each molecule in the unit cell, listed in that order, in order of ascending frequency. (i.e. there are  $6Z$  components to the eigenvector for each frequency given, with the first  $3Z$  defining the relative translations of the molecules within the unit cell, and the second  $3Z$  the relative rotations. The list starts with the 3 modes of zero frequency which correspond to a uniform translation of the unit cell). GM Day has a program Rudolph<sup>3</sup> for visualizing the modes, and scripts for calculating the thermodynamic quantities<sup>2,4</sup> from the properties output.

The likely accuracy of the estimated values of the elastic constants and normal modes must be interpreted in the context of the conformational flexibility of the molecule. The molecules will only move as rigid bodies, as assumed by these calculations, when there is a significant energy gap between the lattice modes given in harmonic frequencies and the vibrations of the isolated molecule. The lattice modes or elastic constants that

involve displacement of the intermolecular contacts involving flexible functional groups will be most affected by the mixing of inter and intramolecular modes (c.f. pentaerythritol).<sup>1</sup>

The properties calculation step is invoked by the keywords STAR PROP.

In this section, all examples are taken from example 12 unless otherwise stated.

## STAR PROP

### 3.10.1 Properties Calculations Control Parameters

Most control parameters for the Properties calculation are the same as for the perfect lattice relaxation. The exception is the accuracy to which the Ewald sum is calculated. This should be increased to 1 part in  $10^8$  as described in 3.9.1. Descriptions of all other control parameters are also given in that section.

#### Example input

```
SCAL 1.0
SYMM
CHGC
ACCM 100000000
  PRIN BASI 0 PLUT 12 MOLE 1 BOND 2 TORS 2 MINI 2 GEOM 1
```

#### Example output

```
Scaling factor for multipoles =      1.00000000

Symmetry Adapted

Number of formula units per primitive cell
(read from FDAT file and scaled by centring factor) =      1

Madelung sum accuracy redefined to    0.1000E+09

reciprocal space weighting =    0.1000E+01

The printing options are as follows.
  PLUT  LATT  BASI  MINI  MOLE  GEOM
    12    0    0    2    1    1
```

When the accuracy of the Ewald summation is changed, the output confirms this.

#### Example input

```
STAR PROP
CONF
MAXI 1000
MAXD 0.5
STAR
STOP
```

The lattice energy minimization calculation uses approximations for calculating the second derivative matrix. This is brought about by the use of the NOPR directive. In order to calculate these parameters more accurately, this directive must be omitted.

#### Printed output

```
Warning NOPR directive was used properties will only be approximate
```

If the NOPR directive was used this warning message is written out, the properties written out below will only be approximate.

### 3.10.2 Elastic Constants

The elastic constants are defined in a Cartesian reference frame, and NEIGHCRYST uses the conventional definition, which for most space groups has  $z$  parallel to  $c$  and  $x$  parallel to reciprocal  $a$ . The elastic stiffness gives all the elastic stiffness tensor  $C_{ij}$ , in order ( $C_{ij}$ ,  $i=1,6$ )  $j=1,6$ ), with the relationship of the Cartesian axes of this tensor to the crystal axes defined in elastic axis definition. There are up to 21 independent non-zero values of  $C_{ij}$ , depending on the crystal symmetry.

#### Printed output

```
MECHANICAL PROPERTIES CALCULATED FROM HESSIAN MATRIX
```

```
Elastic stiffness tensor (Cij): GPa (10**10 DYNE/CM**2)
(ELSTCN(I,J),J=1,6),I=1,6
```

### Example output

```
MECHANICAL PROPERTIES CALCULATED FROM HESSIAN MATRIX
```

```
Elastic stiffness tensor (Cij): GPa (10**10 DYNE/CM**2)
23.58876    9.62432    6.02847    3.21779    -2.34157    -3.50538
 9.62432   17.06762   6.37537   2.05584   -0.82018   -3.71365
 6.02847   6.37537  13.46004  -1.47659   0.10214   0.10800
 3.21779   2.05584  -1.47659   4.27730  -0.55820  -2.35944
-2.34157  -0.82018   0.10214  -0.55820   3.49188   2.78290
-3.50538  -3.71365   0.10800  -2.35944   2.78290   9.11696
```

The lowest eigenvalue of shear submatrix of  $C_{ij}$ , the lowest eigenvalue shear, gives a measure of how susceptible the crystal is to shear forces, and the corresponding eigenvector indicates the orientation of the plane of weakest shear stiffness, with reference to the elastic constant axis set.

Note that STAR PLUT and STAR PROP use different algorithms for obtaining the second derivative matrix. It is possible (but not a recommended usage) to run a STAR PLUT calculation with the NOPR directive omitted, and this will give slight differences in the elastic constants.

```
Born stability criteria satisfied.
```

### Error message

```
WARNING: Born stability criteria not met.
The elastic constant matrix is not positive definite.
Lowest eigenvalue:
```

If the elastic constants indicate that the crystal is not stable then this warning is written out instead of the message that the Born stability criteria are satisfied.

### Printed output

```
Lowest eigenvalue of shear submatrix of Cij = subEIGS(1)
Corresponding eigenvector eigVECT(I,1),I=1,3
```

The elastic tensor is transformed to give

```
Elastic compliance tensor (Sij): GPa(-1) (10**10 CM**2/DYNE)
GCOMPLI(I,J),J=1,6),I=1,6
```

### Example output

```
Born stability criteria satisfied.
Lowest eigenvalue of shear submatrix of Cij = 2.23826 GPa
Corresponding eigenvector 0.27544 -0.85460 0.44022 )
```

```
Elastic compliance tensor (Sij): GPa(-1) (10**10 CM**2/DYNE)
0.06715    -0.02263    -0.02475    -0.04704    0.03853    -0.00704
-0.02263    0.09406    -0.03755    -0.02780    -0.01936    0.02877
-0.02475    -0.03755    0.11113    0.07136    -0.01474    -0.00316
-0.04704    -0.02780    0.07136    0.34072    -0.04209    0.07077
0.03853    -0.01936    -0.01474    -0.04209    0.40224    -0.12657
-0.00704    0.02877    -0.00316    0.07077    -0.12657    0.17569
```

Several mechanical properties of a bulk polycrystalline aggregate that can be estimated from the elastic tensor data<sup>5</sup> are calculated. Voigt averaging assumes a uniform strain throughout the aggregate, whereas Reuss averaging assumes a uniform stress throughout the aggregate, and the two estimates can be seen as upper and lower bounds. However, since the morphologies of organic crystals are often needles or plates, which are likely to show a preferred orientation in aggregates, the fundamental assumption of random sampling of directions in aggregates behind these estimates is questionable. In a perfect lattice relaxation with the NOPR directive, these are only approximate.

### Printed output

```
Mechanical properties calculated for a microcrystalline aggregate.
Bulk modulus from elastic constants (Voigt averaging): Bv GPa
Bulk modulus from compliance constants (Reuss averaging): Br GPa
Arithmetic mean: Barith GPa
```

```

Geometric mean:      Bgeom GPa

Shear modulus from elastic constants (Voigt averaging):      Gv GPa
Shear modulus from compliance constants (Reuss averaging):    Gr GPa
Arithmetic mean:     Garith GPa
Geometric mean:      Ggeom GPa

Young's modulus from elastic constants (Voigt averaging):    Ev GPa
Young's modulus from compliance constants (Reuss averaging): Er GPa
Arithmetic mean:     Earith GPa
Geometric mean:      Egeom GPa

Poisson's ratio from elastic constants (Voigt averaging):    Pv GPa
Poisson's ratio from compliance constants (Reuss averaging): Pr GPa
Arithmetic mean:     Parith GPa
Geometric mean:      Pgeom GPa

Single crystal Young's modulus along optical axes      x-component:  Ex GPa
  y-component:     Ey GPa
  z-component:     Ez GPa
  arithmetic mean: Emean GPa

```

### Example output

```

Mechanical properties calculated for a microcrystalline aggregate.
Bulk modulus from elastic constants (Voigt averaging):      10.90808 GPa
Bulk modulus from compliance constants (Reuss averaging):    9.75864 GPa
Arithmetic mean:     10.33336 GPa
Geometric mean:      10.31737 GPa

Shear modulus from elastic constants (Voigt averaging):      5.51645 GPa
Shear modulus from compliance constants (Reuss averaging):    3.58423 GPa
Arithmetic mean:     4.55034 GPa
Geometric mean:      4.44660 GPa

Young's modulus from elastic constants (Voigt averaging):    14.16200 GPa
Young's modulus from compliance constants (Reuss averaging): 9.57985 GPa
Arithmetic mean:     11.87092 GPa
Geometric mean:      11.64774 GPa

Poisson's ratio from elastic constants (Voigt averaging):    0.28362 GPa
Poisson's ratio from compliance constants (Reuss averaging): 0.33639 GPa
Arithmetic mean:     0.31000 GPa
Geometric mean:      0.30888 GPa

Single crystal Young's modulus along optical axes      x-component:  14.89264 GPa
  y-component:   10.63190 GPa
  z-component:   8.99865 GPa
  arithmetic mean: 11.50773 GPa

```

### 3.10.3 Phonon frequencies

When the directive STAR takes the operand PROP instead of PLUT, the  $k=0$  phonon eigenvectors are also calculated. It is strongly advisable to start from a lattice energy minimum to avoid changes in the Cartesian axis system, though PROP will do a first minimization step. Since the rotational components of the second derivatives required for the dynamical matrix must be about the principal inertial axes, a change of molecular axis system is performed after the minimization, from the Cartesian axes used in the definition of the multipole moments and the analytical gradients. The phonon calculations change the molecular axis system in the rigid molecule approximation, so that each molecule is assigned a fixed axis system, with the origin at the centre of mass and the axes pointing along the principal inertial axes to be that of the inertia tensor.

There should be three zero frequencies. If there are any negative frequencies in the output, these correspond to imaginary frequencies and are a sign that the crystal is unstable. This type of instability should have been identified in the original minimization with NOPR, and Born stability criterion not being met. However, very rarely, the increased accuracy of the second derivatives matrix in a PROP calculation could show that a structure was unstable, although this was not apparent with NOPR switched on. Even more unusually, it is possible for there to be a  $k=0$  imaginary frequency for a mechanically stable crystal structure. This will occur only if the representations of the group in which the elastic constants transform do not include the representation which has the imaginary frequency.

### Printed output

```
Zone Centre phonon eigenvectors
```

```

For each mode:
molecule KJ      Trans(X),      Trans(Y),      Trans(Z),      Rot(X),      Rot(Y),      Rot(Z)
-----
IW      PHVECT(JW,IW) PHVECT(JW+1,IW) PHVECT(JW+2,IW) PHVECT(JW+3*MOLION,IW) PHVECT(JW+3*MOLION+1,IW)
                                                PHVECT(JW+3*MOLION+2,IW) JW=1,3,3

```

### Example output

```

Zone Centre phonon eigenvectors
For each mode:
molecule 1      Trans(X),      Trans(Y),      Trans(Z),      Rot(X),      Rot(Y),      Rot(Z)
-----
1          1.000000      0.000000      0.000000      0.000000      0.000000      0.000000
2          0.000000      1.000000      0.000000      0.000000      0.000000      0.000000
3          0.000000      0.000000      1.000000      0.000000      0.000000      0.000000
4          0.000000      0.000000      0.000000      -0.387472      0.903894      0.181223
5          0.000000      0.000000      0.000000      0.912990      0.349010      0.211288
6          0.000000      0.000000      0.000000      -0.127733      -0.247322      0.960477

```

### Printed output

```

Zone Centre Phonon Frequencies
THz          cm-1
-----
PHEIG(IW)    PHEIG(IW)*33.35640952d+0

```

### Example output

```

Zone Centre Phonon Frequencies
THz          cm-1
-----
0.0000      0.0000
0.0000      0.0000
0.0000      0.0000
1.4722      49.1063
2.0027      66.8034
3.1102      103.7450

```

DMACRYS takes the calculated final phonon eigenvectors and uses them to generate an input crystal structure with the atoms displaced. The energy of this structure is then calculated, and from it the phonon frequency is recalculated. This may be compared with the frequency calculated directly from the dynamical matrix. The two should agree closely. Any discrepancy may mean that accuracy parameters have not been set sufficiently high.

### Printed output

```

Cross check of phonon frequencies calculated from structures displaced by eigenvectors
ACCM may need to be at least 1.00000000 for check to work correctly
PHTEMP, PHTEMP*33.35640952

```

### Example output

```

Cross check of phonon frequencies calculated from structures displaced by eigenvectors
ACCM may need to be at least 1.00000000 for check to work correctly
0.0339      1.1291
-0.1043     -3.4802
0.0586      1.9557
1.4780      49.3015
1.9975      66.6279
3.1085      103.6890

```

The above Cross check example output was produced from the same input dataset as used to calculate the phonon frequencies from the dynamical matrix eigenvalues listed above as the Zone Centre Phonon Frequencies. As can be seen, 1.4780 is close to the dynamical matrix value 1.4722, and so on.

### Error message

This error message is written to fort.12.

```

Warning - ACCM is less than 10**8, phonon frequencies may not be accurate

```

### Example of incorrect output

The following example using a different dataset (which is not in the test suite) shows output which demonstrates the discrepancies if ACCM is not set to 10\*\*8.

### Example output

The first example has ACCM 10\*\*8

```

Zone Centre Phonon Frequencies
  THz          cm-1
-----
0.0000        0.0000
0.0000        0.0000
0.0000        0.0000
1.5626        52.1236
1.5934        53.1488
1.9850        66.2137
2.0489        68.3438
2.1516        71.7713
2.2846        76.2062
2.4207        80.7472
2.4212        80.7640
2.6077        86.9836

```

Cross check of phonon frequencies calculated from structures displaced by eigenvectors  
 ACCM may need to be at least 1.00000000 for check to work correctly

```

0.0674        2.2475
0.0515        1.7165
0.0982        3.2763
1.5626        52.1241
1.5932        53.1437
1.9847        66.2009
2.0496        68.3670
2.1517        71.7746
2.2834        76.1663
2.4183        80.6673
2.4213        80.7651
2.6081        86.9953

```

The same dataset with ACCM 10\*\*6

```

Zone Centre Phonon Frequencies
  THz          cm-1
-----
0.0000        0.0000
0.0000        0.0000
0.0000        0.0000
1.5313        51.0799
1.8194        60.6901
1.9961        66.5830
2.2195        74.0352
2.2357        74.5735
2.2933        76.4971
2.4268        80.9484
2.4273        80.9643
2.6176        87.3148

```

Cross check of phonon frequencies calculated from structures displaced by eigenvectors  
 ACCM may need to be at least 1.00000000 for check to work correctly

```

0.0000        0.0000
0.0701        2.3393
0.0476        1.5892
24.3904       813.5770
20.5713       686.1851
14.3105       477.3481
19.6247       654.6081
19.8445       661.9423
19.3092       644.0851
15.4398       515.0157
-18874.6685   -629591.2002
20.8314       694.8618

```

The phonon frequencies from the dynamical matrix differ only insignificantly if ACCM is increased to 10\*\*8, however the frequencies calculated from the eigenvectors are completely different.

If STAR PROP is used, but the NOPR directive is included, DMACRYS will not calculate the phonon frequencies, instead just carrying out the perfect lattice relaxation calculation.

At present properties calculations should not be attempted when the induction energy is included.

### 3.10.4 Phonon Graphics

A new functionality is to output coordinates suitable for use with Jmol for visualizing the phonon modes. In order to use this, the PHGR directive must be included somewhere between STAR PROP and STOP. An extra output file, fort.26, is written out. No output is produced if the directive is used between STAR PLUT and STOP.

#### *Example output*

```
This is an example of a fort.26 fileEIGENVECTOR      1
MOLECULE      1
  0.41877901   0.34198756   0.11874608
  0.41614793   0.25444494   0.19998341
  0.32391320   0.17098750   0.20884532
  ...
MOLECULE      2
  0.30655822   0.26265323   0.61783017
  0.30918930   0.35019584   0.69906750
  0.40142403   0.43365329   0.70792941
  ...
...
MOLECULE      1
  0.41878846   0.34200026   0.11930805
  0.41615738   0.25445764   0.20054537
  0.32392265   0.17100020   0.20940729
  ...
...
EIGENVECTOR    2
...
EIGENVECTOR    3
...
EIGENVECTOR    4
```

For the first eigenvector the atom coordinates are written out for each molecule. This is followed by the coordinates from a small positive displacement and a small negative displacement. This is repeated for all the eigenvectors in turn.

### 3.11 PRINT ANY ERROR MESSAGES

If the number of iterations exceeds the maximum permitted, (see section 3.3.2.2) the following is printed:

```
WARNING - MAXIMUM NUMBER OF I1 ITERATIONS HAS BEEN REACHED
```

## Appendix A. Full list of all directives written into the code

ICODE	Name	Description
1	TITL	Described in 3.1
2	PRIN	Described in 3.2.1
3	DIME	No longer in use
4	LATT	Described in 3.3.1
5	BASI	Described in 3.3.1
6	DEFE	No longer in use
7	ACCU	Described in 3.2.3
8	REGI	No longer in use
9	OPTI	No longer in use
10	THER	No longer in use here, but it is also a control parameter for the perfect lattice relaxation.
11	CUBI	No longer in use
12	HEXA	No longer in use
13	DUMP	Described in 3.2.1
14	POTE	Described in 3.4
15	MAXX	No longer in use
16	STAR	Described in 0
17	STOP	Described in 0
18		Blank directive, in case of blank line in input
19	FREE	No longer in use
20	REST	No longer in use
21	RESE	No longer in use
22	PLOT	No longer in use
23	IREC	Described in 3.2.3
24	REGN	No longer in use
25	CUTO	Described in 3.2.4
26	WRDU	No longer in use
27	REDU	No longer in use
28	PLDU	No longer in use
29	PLRE	No longer in use
30	ACCM	Described in 3.2.3
31	NOIO	Still in use, but not described in this manual
32	SMIV	No longer in use
33	THBO	No longer in use
34	JOBT	No longer in use
35	GAME	No longer in use
36	BLFN	No longer in use
37	REWI	Still in use, but not described in this manual
38	MOLE	Described in 3.7
39	PT13	Still in use, but not described in this manual
40	TORS	No longer in use here, but it is also a control parameter for the perfect lattice relaxation.
41	TEST	No longer in use
42	TEMP	No longer in use

43	DBAS	Still in use, but not described in this manual
44	CHGC	Described in 3.2.3
45	RANG	No longer in use
46	INFO	No longer in use
47	DEFS	No longer in use
48	STDC	No longer in use
49	DEFT	No longer in use
50	RDMA	Described in 3.2.4
51	SCAL	Described in 3.2.3
52	CLUS	Described in 3.2.3
53	SYMM	Described in 3.2.3
54	FDAT	Described in 3.2.3
55	ZVAL	Described in 3.2.3
56	EXTN	Described in 3.2.3
57	POLZ	Described in 3.2.3
58	DDMP	Described in 3.8
59	DIND	Described in 3.8
60	SPLI	Described in 3.5
61	VOID	Not used in version 2.3.0
62	NRIG	Not used in version 2.3.0
63	NOSY	Described in 3.2.3

The directives that are no longer in use, but which do not give an error message saying this are DIME, THER, REST and RESE.

THBO and TORS are historical placeholders for three-body and torsional forces as control parameters for the perfect lattice relaxation.

## Appendix B. Options for printed output

IPRINT		
1	REG1	Not in use
2	REG2	Not in use
3	RECI	Not in use
4	SYMM	Not in use
5	PLUT	Described in 3.2.1
6	CLAS	Not in use
7	LATT	Described in 3.2.1
8	BASI	Described in 3.2.1
9	STRU	Not in use
10	MATR	Not in use
11	ENGY	Not in use
12	MINI	Described in 3.2.1
13	BOND	Not in use
14	POTE	Not in use
15	TORS	Not in use
16	PHON	Not in use
17	MOLE	Described in 3.2.1
18	EPRS	Not in use
19	GEOM	Described in 3.2.1
20		Blank in case of mistakes in input

## Appendix C. Possible potentials

JCODF		
1	SPEC	Described in 3.6.2
2	ENDS	End of species data input
3	RELB	No longer in use
4	RETH	No longer in use
5	LCON	No longer in use
6	BOHA	3-body interaction
7	TRID	3-body interaction
8	MOLD	3-body interaction
9	QART	3-body interaction
10	SIXT	3-body interaction
11	BOHZ	3-body interaction
12	KUMA	3-body interaction (not in table)
13	THRH	3-body interaction
14	RRHA	3-body interaction
15	TOHA	4-body interaction
16	HARM	No longer in use
17	BUCK	Described in 3.6.3
18	MODI	Described below
19	LENN	Described below
20	MORS	Described below
21	BUC4	Described below
22	SPLP	Described below
23	MORQ	Described below
24	SPRI	Described below
25	COUL	Described below
26	VDWA	Described below
27	HULB	Described below
28	BUC7	Described below
29	NONE	There are no additional parameters
30	DBUC	Described in 3.6.3
31	BSPL	Described below
32	BVCK	No longer in use
33	DBVC	No longer in use
34	BUAH	No longer in use
35	ANIS	Described in 3.6.3 & Appendix I

The bits marked 3-body and 4-body interactions were determined by the old table in the old DMAREL manual.

The following sections give examples of input and output for the potential types that are no longer in use among the authors and close collaborators. If you use these potentials and wish this section to be updated, please provide example files of their usage for inclusion in this manual and the test-suite.

### MODI

There is one additional parameter read in from the species record. It has format I and operand name N. The analytic form of the potential is

$$V(r) = A \times \exp(-r/B) - C/r^N$$

The exponent N is read in from the MODI record. It is assumed that N remains the same for all ranges, if there is more than one. The parameters A, B and C must be read from the range record. The units of C are given below

**C**

is in eV Å<sup>N</sup>

The ranges are terminated with an ENDS record or a new species record between the same species.

**Example input**

```
MODI NA+ SHEL NA+ SHEL 8
7895.4 0.1709 29.06 20.0
ENDS
```

**Printed output**

```
MODIFIED BUCKINGHAM POTENTIAL V(R) = A * EXP(-R/RHO) - C/R**N.
A      RHO  C      N      RMIN      RMAX
A      rho  C      N      RMIN      RMAX
:      :    :      :      :        :
:      :    :      :      :        :
```

**LENN**

There are two additional parameters read in from the species record. They have format I and operand names N and M. The analytic form of the potential is

$$V(r) = A/r^N - B/r^M$$

The exponents N and M are read in on the LENN record. It is assumed that N and M remain the same for all ranges, if there is more than one. The parameters A and B must be read from the range record. The units of A and B are given below

**A**

is in eV Å<sup>N</sup>

**B**

is in eV Å<sup>M</sup>

The ranges are terminated with an ENDS record or a new species record between the same species.

**Example input**

```
LENN CL- SHEL CL- SHEL 12 6
8560.7 30.67 5.78 20.0
ENDS
```

**Printed output**

```
LENNARD-JONES POTENTIAL V(R) = A/R**N - B/R**M
A      B      N      M      RMIN      RMAX
A      B      N      M      RMIN      RMAX
:      :    :      :      :        :
:      :    :      :      :        :
```

**MORS**

There are no additional parameters read in from the species record. The analytic form of the potential is

$$V(r) = A \times [1 - \exp(-B \times (r - C))]^2 - A$$

This has the energy zero offset from the conventional spectroscopic definition, which defines the energy zero at the minimum. The new definition is consistent with the other potentials, which have the energy zero at infinity. The parameters A, B and C must be read from the range record. The units of A, B and C are given below

A	is in eV
B	is in $\text{\AA}^{-1}$
C	is in $\text{\AA}$

The ranges are terminated with an ENDS record or a new species record between the same species.

**Printed output**

```
MORSE POTENTIAL V(R) = A * (1.0-EXP(-B*(R-C)))**2-A
A      B      C      RMIN  RMAX
A      B      C      RMIN  RMAX
:      :      :      :      :
```

**BUC4**

There are no additional parameters read in from the species record. The analytic form of the potential is

5mm					
V(r)	=	A × exp (-r/B)	for	r < r <sub>b</sub>	5mm
V(r)	=	Fifth order polynomial	for	r <sub>b</sub> < r < r <sub>m</sub>	
V(r)	=	Third order polynomial	for	r <sub>m</sub> < r < r <sub>a</sub>	
V(r)	=	-C/r <sup>6</sup>	for	r <sub>a</sub> < r < r <sub>max</sub>	

There are 6 parameters read in from the range record. These are A, B, C, r<sub>b</sub>, r<sub>m</sub> and r<sub>a</sub>. Their units are given below

A	is in eV
B	is in $\text{\AA}$
C	is in eV $\text{\AA}^6$
R	are given in $\text{\AA}$

The ranges are terminated with an ENDS record. On input, the ranges must satisfy the condition

$$r_b < r_m < r_a$$

If r<sub>a</sub> is less than CUTPOT, the C/r<sup>6</sup> term will be calculated out to CUTPOT.

The polynomials are fitted so that the functions, first derivatives and second derivatives match at r<sub>b</sub>, r<sub>m</sub> and r<sub>a</sub>. At r<sub>m</sub> the potential has a minimum so that the first derivatives of both polynomials are zero. Only one ranges record is permitted for this interaction, since all of the ranges are given on the first record. Also, this potential must not overlap an existing potential.

**Printed output**

```
4 RANGE MODIFIED BUCKINGHAM POTENTIAL
RANGE 1 V(R) = A * EXP(-R/RHO),
RANGE 2 V(R) = A5*R**5+ B5*R**4 + C5*R**3 + D5*R**2 + E5*R + F5
RANGE 3 V(R) = A3*R**3 + B3*R**2 + C3*R + D3,
RANGE 4 V(R) = -C/R**6
                                     RMIN  RMAX
A      =  A      RHO      =      RHO      RMIN  r_b
A5     =  A5     B5      =      B5     C5     =      C5
D5     =  D5     E5      =      E5     F5     =      F5
A3     =  A3     B3      =      B3
C3     =  C3     D3      =      D3     E3     =      E3
                                     r_m  r_a
C      =  C                                          r_a  RMAX
```

## Error messages

ERROR - THE FOUR RANGE BUCKINGHAM POTENTIAL AND CUBIC SPLINE MUST NOT OVERLAP AN EXISTING POTENTIAL

ERROR - ONLY ONE PARAMETERS DIRECTIVE MUST BE GIVEN WITH THE FOUR RANGE BUCKINGHAM FORM

ERROR - THE RANGES ON THE FOUR RANGE BUCKINGHAM CARD ARE NOT GIVEN IN ASCENDING ORDER

## SPLP

There are two additional parameters on the species record, but they are both optional. They have format F, with operand names SMIN and SMAX. If only one F format number is given, the program interprets it as SMAX. If both are given, the program interprets them in the order SMIN then SMAX.

A cubic spline is defined in the following way. The energies  $E_i$  at  $n$  points  $r_i$  are given. The points need not be equally spaced. A cubic polynomial is then defined, polynomial  $P_i$  being between points  $i$  and  $i + 1$ . There are thus  $n - 1$  cubic polynomials. These are defined to be equal to  $E_i$  and  $E_{i+1}$  at  $r_i$  and  $r_{i+1}$  respectively. Also  $P_i$  and  $P_{i+1}$  will have the same first and second derivatives at  $r_{i+1}$ . A quick count of the number of parameters and equations shows that two more equations are required. These are taken to be that the second derivatives of  $P_1$  and  $P_{n-1}$  are zero at  $r_1$  and  $r_n$  respectively. It is also possible to define two more polynomials, which are in fact linear equations,  $P_0$  and  $P_n$ , to be extensions of the spline beyond the points  $r_1$  and  $r_n$ .

There are two parameters read in from the range record,  $E_i$  and  $r_i$ .  $E_i$  is in eV and  $r_i$  is in Å. The interpretation of the range records for the cubic spline potential is somewhat different to the other potentials. Usually this would be interpreted as the maximum of the range RMAX. For the cubic spline, it should be the value of  $r$  at which the energy is  $E$ . A value of RMIN is not permitted on the range record for a cubic spline. The program rearranges the input data so that it defines  $n - 1$  ranges each with an RMIN and RMAX. The usual convention that the potential must start at zero also applies to the cubic spline. There are two ways of doing this. Firstly, the energy at zero may be given on the first range card. The program will define  $n - 1$  ranges. If the energy at zero is not known, then input  $SMIN = 0.0$  on the species record and input a value for SMAX. The program will define  $n + 1$  ranges, with range 1 and  $n + 1$  being the linear functions  $P_0$  and  $P_n$  defined above. A third format is permitted, in which SMAX only is supplied. The cubic spline potential cannot have other potentials defined in the same range for the same species. It may, however, have different potential types defined in other ranges. A minimum of 3 and a maximum of  $MAXRNG - 1$  records defining the energy points must be given. The RMAX parameters must be in ascending order as usual. Care is needed if the ranges do not extend as far as CUTPOT. In this case the program will extend the last range out to CUTPOT. In general, however, the energy will not tend to zero as the range is extended. This may be overcome by adding extra ranges with zero energy.

## Printed output

```
CUBIC SPLINE POTENTIAL V(R)= A*R**3 + B*R**2 + C*R + D*R
A      B      C      D      RMIN      RMAX      E (RMIN)
A      B      C      D      RMIN      RMAX      E
:      :      :      :      :      :      :
```

## Error messages

ERROR - A MINIMUM RANGE MUST NOT BE GIVEN ON A CUBIC SPLINE PARAMETERS CARD

One of the range records has three parameters on it; the program assumes that an RMIN has been given.

ERROR - FOR CUBIC SPLINE THE FIRST PARAMETER CARD HAS A MINIMUM RANGE ON IT. THIS MUST BE ZERO FOR FIRST RANGE OF FIRST POTENTIAL

Either no SMIN has been given on the species record and the value of  $r$  on the first range record is not zero, or SMIN has been given but is not zero.

ERROR - THE CUBIC SPLINE MUST NOT EXCEED THE MAXIMUM NUMBER OF RANGES -1, MAXIMUM NUMBER OF RANGES IS MAXRNG

ERROR - THE FOUR RANGE BUCKINGHAM POTENTIAL AND CUBIC SPLINE MUST NOT OVERLAP AN EXISTING POTENTIAL

ERROR - THE CUBIC SPLINE MUST HAVE AT LEAST 3 RANGES, THE NUMBER INPUT IS N

ERROR - THE MAXIMUM FOR THE LINEAR EXTENSION OF THE CUBIC SPLINE IS LESS THAN THE LAST RANGE

This error message occurs when SMAX is given on the species record, but the value is less than the last RMAX given on the range records.

## MORQ

There are no additional parameters read in from the species record. The analytic form of the potential is

$$V(r) = A \times [1 - \exp(-B \times (r - C))]^2 - A - \frac{D \times Q_1 \times Q_2}{r}$$

The parameters A, B, C and D must be read from the range record.  $Q_1$  and  $Q_2$  are the charges on the species 1 and 2. This potential is intended to permit a Morse function for nearest neighbour interactions with no Coulomb term. To achieve this the parameter D must be set equal to 1.0 The effect of this additional term is to remove the Coulomb interaction between the species 1 and 2. The units of A, B, C and D are given below

A	is in eV
B	is in Å <sup>-1</sup>
C	is in Å
D	is dimensionless

The ranges are terminated with an ENDS record or a new species record between the same species.

### *Printed output*

COULOMB SUBTRACTED OFFSET MORSE POTENTIAL					
V(R)=A*(1.0-EXP(-B(R-C)))**2 - A -D*Q1*Q2/R					
A	B	C	D*Q1*Q2	RMIN	RMAX
A	B	C	D*Q1 *Q2	RMIN	RMAX
:	:	:	:	:	:
:	:	:	:	:	:

## SPRI

There are no additional parameters to be read in from the species record. The analytic form of the potential is

$$V(r) = A \times (r - B)^2 - \frac{C \times Q_1 \times Q_2}{r}$$

$Q_1$  and  $Q_2$  are the charges on the species 1 and 2. This potential is intended to permit a harmonic spring function for nearest neighbour interactions with no Coulomb term. The parameter B should be set equal to the bond length, and A to the spring constant. To achieve this the parameter C must be set equal to 1.0 Setting C equal to 0.0 will leave the Coulomb term in. The effect of this additional term is to remove the Coulomb interaction between the species 1 and 2. The units of A, B and C are given below

A	is in eV
B	is in Å
C	is dimensionless

The ranges are terminated with an ENDS record or a new species record between the same species.

### *Printed output*

HARMONIC SPRING CONSTANT BETWEEN DIFFERENT BASIS ATOMS WITH COULOMB TERM SUBTRACTED					
V(R) = 1/2*K*(R-R0)**2 - A*Q1*Q2/R					
K	R0	D*Q1*Q2	RMIN	RMAX	
K	R0	D*Q1 *Q2	RMIN	RMAX	
:	:	:	:	:	
:	:	:	:	:	

## COUL

There are no additional parameters to be read in from the species record. The analytic form of the potential is

$$V(r) = \frac{A \times Q_1 \times Q_2}{r}$$

$Q_1$  and  $Q_2$  are the charges on the species 1 and 2. This potential is intended to permit Coulomb subtraction between nearest neighbours. To achieve this the parameter A must be set equal to -1.0 The units of A are given below

A  
is dimensionless

The ranges are terminated with an ENDS record or a new species record between the same species.

### Printed output

```
COULOMB POTENTIAL V(R) = A*Q1*Q2/R
A*Q1*Q2      RMIN      RMAX
A*Q1*Q2      RMIN      RMAX
:             :           :
:             :           :
```

## VDWA

There is one additional parameter read in from the species record. It has format I and operand name N. The analytic form of the potential is

$$V(r) = A/r^N$$

The exponent N is read in on the VDWA record. It is assumed that N remains the same for all ranges, if there is more than one. The parameter A must be read from the range record. The units of A is given below

A  
is in eV Å<sup>N</sup>

The ranges are terminated with an ENDS record or a new species record between the same species.

### Printed output

```
VAN DER WAALS INTERACTION V(R) = A/R**N
A      N      RMIN      RMAX
A      N      RMIN      RMAX
:       :       :         :
:       :       :         :
```

## HULB

There are no additional parameters to be read in from the species record. The analytic form of the potential is

$$V(r) = A \times \left[ (1 - \eta_1)^2 + D \times \beta^3 \times \eta_2 \times (1 + E \times \beta) \right] - F - \frac{Q_1 \times Q_2}{r}$$

Where

$$\eta_1 = \exp(-\beta)$$

$$\eta_2 = \exp(-2 \times \beta)$$

$$\beta = B \times (r - C)$$

The parameters A, B, C, D, E and F must be read from the range record. The units of A, B, C, D, E and F are given below

A	is in eV
B	is in Å <sup>-1</sup>
C	is in Å
D	is dimensionless
E	is dimensionless
F	is in eV

The ranges are terminated with an ENDS record or a new species record between the same species.

### Printed output

COULOMB SUBTRACTED OFFSET HULBURT-HIRCHFELDER INTERACTION				
V(R) = A * ((1.0-EXP (-B*(R-C)))**2 + (D*(B**3) * ((R-C)**3) * EXP (-2.0 * B * (R-C)) * (1.0 + E * B * (R-C))))-F-QI*QJ/R				
A	B	C	RMIN	RMAX
D	E	F		
A	B	C	RMIN	RMAX
D	E	F		
⋮	⋮	⋮	⋮	⋮

## BUC7

There are no additional parameters read in from the species record. The analytic form of the potential is

V(r)	=	$A \times \exp(-r/B)$	for	$r < r_b$
V(r)	=	Fifth order polynomial	for	$r_b < r < r_m$
V(r)	=	Third order polynomial	for	$r_m < r < r_a$
V(r)	=	$-C/r^6$	for	$r_a < r < r_{\max}$

There are 6 parameters read in from the range record. These are A, B, C,  $r_b$ ,  $r_m$  and  $r_a$ . Their units are given below

A	is in eV
B	is in Å
C	is in eV Å <sup>6</sup>
R	are given in Å

The ranges are terminated with an ENDS record. On input, the ranges must satisfy the condition

$$r_b < r_m < r_a$$

If  $r_a$  is less than CUTPOT, the  $C/r^6$  term will be calculated out to CUTPOT.

The polynomials are fitted so that the functions, first derivatives, second derivatives and third derivatives match at  $r_b$ ,  $r_m$  and  $r_a$ . At  $r_m$  the potential has a minimum so that the first derivatives of both polynomials are zero. Only one ranges record is permitted for this interaction, since all of the ranges are given on the first record. Also, this potential must not overlap an existing potential.

## Printed output

```
4 RANGE MODIFIED BUCKINGHAM POTENTIAL WITH 7/4 SPLINE
RANGE 1 V(R) = A * EXP(-R/RHO)
RANGE 2 V(R) = A7*R**7 + B7*R**6 + C7*R**5 + D7*R**4 + E7*R**3 + F7*R**2 +G7*R + H7
RANGE 3 V(R) = A4*R**4 + B4*R**3 + C4*R**2 + D4*R + E4
RANGE 4 V(R) = -C/R**6
```

A	=	A	RHO	=	RHO			RMIN	RMAX
A7	=	A7	B7	=	B7	C7	=	RMIN	$r_b$
D7	=	D7	E7	=	E7	F7	=		
G7	=	G7	H7	=	H7			$r_b$	$r_m$
A4	=	A4	B4	=	B4	C4	=		
D4	=	D4	E4	=	E4			$r_b$	$r_m$
C	=	C						$r_a$	RMAX

## Error messages

```
ERROR - THE FOUR RANGE BUCKINGHAM POTENTIAL AND CUBIC SPLINE MUST NOT OVERLAP AN EXISTING POTENTIAL
ERROR - ONLY ONE PARAMETERS DIRECTIVE MUST BE GIVEN WITH THE FOUR RANGE BUCKINGHAM FORM
ERROR - THE RANGES ON THE FOUR RANGE BUCKINGHAM CARD ARE NOT GIVEN IN ASCENDING ORDER
```

## BSPL

There are no additional parameters on the species record. The program will fit a 5th. order spline between the points. There are two parameters read in from the range record,  $E_i$  and  $r_i$ .  $E_i$  is in eV and  $r_i$  is in Å. The interpretation of the range records for the quintic spline potential is somewhat different to the other potentials. Usually this would be interpreted as the maximum of the range RMAX. For the quintic spline, it should be the value of r at which the energy is E. A value of RMIN is not permitted on the range record for a quintic spline. The program rearranges the input data. In doing this ranges are redefined and extra ranges may be added. The quintic spline should not therefore be used with any other potential functions. The usual convention that the potential must start at zero also applies to the quintic spline.

## Printed output

```
B-SPLINE POTENTIAL. ORDER 5
SEPARATION SPLINE PARAMETER ENERGY, 1ST AND 2ND DERIVATIVESC
R      A      E      G      W
:      :      :      :      :
:      :      :      :      :
```

## Error messages

```
ERROR - FOR QUINTIC SPLINE THE NUMBER OF RANGES INPUT IS i AND MUST BE LESS THAN MAXRNG -6 WHERE MAXRNG =
maxrng
ERROR - THE NUMBER OF QUINTIC SPLINE KNOTS WHICH IS SET INTERNALLY IS TOO LARGE RESET MAXRNG TO i
```

The number of quintic spline points input was too large.

```
ERROR - SMOOT ERROR CODE i
```

User error - probably too few points.

## Appendix D. Authors recommended potentials

### The FIT and W99 empirical "repulsion-dispersion" potentials

Most of the crystal structure modelling using DMACRYS that has not derived a specific potential for the molecule<sup>1,2</sup> has supplemented the Distributed Multipole electrostatic model with an empirically fitted isotropic atom-atom potential of the form:

$$U = \sum_{i \in M, k \in N} \sqrt{A_{ii} A_{kk}} \exp\left(-\left(\frac{B_{ii} + B_{kk}}{2}\right) R_{ik}\right) - \frac{\sqrt{C_{ii} C_{kk}}}{R_{ik}^6}$$

where atom  $i$  of type  $\iota$  in molecule  $M$  is separated by  $R_{ik}$  from atom  $k$  of type  $\kappa$  in molecule  $N$ . Two widely used sets of parameters are tabulated below, with some notes and comments on their use and references to the definitive literature.

**W99** was derived<sup>3</sup> by fitting to a wide range of crystal structures and validated against peptide and nucleoside structures. A key feature is that the hydrogen interaction sites are moved by 0.1 Å into the H-X bond from their neutron or ab initio optimized positions. DMACRYS can perform this foreshortening, which has to also be used in the DMA analysis.

Potential	Atom pair	Description	$A_{ik} / \text{kJ mol}^{-1}$	$B_{ik} / \text{Å}^{-1}$	$C_{ik} / \text{kJ mol}^{-1} \text{Å}^6$
W99	C(2)⋯C(2)	C bonded to 2 atoms	103235	3.60	1435.09
W99	C(3)⋯C(3)	C bonded to 3 atoms	270363	3.60	1701.73
W99	C(4)⋯C(4)	C bonded to 4 atoms	131571	3.60	978.36
W99	H(1)⋯H(1)	H bonded to C	12680	3.56	278.37
W99	H(2)⋯H(2)	H in alcoholic group	361.30	3.56	0
W99	H(3)⋯H(3)	H in carboxyl group	115.70	3.56	0
W99	H(4)⋯H(4)	H in N-H group	764.90	3.56	0
W99	N(1)⋯N(1)	N in triple bond	96349	3.48	1407.57
W99	N(2)⋯N(2)	other N with no bonded H	102369	3.48	1398.15
W99	N(3)⋯N(3)	N bonded to 1 H atom	191935	3.48	2376.55
W99	N(4)⋯N(4)	N with 2 bonded H atoms	405341	3.48	5629.82
W99	O(1)⋯O(1)	O bonded to 1 other atom	241042	3.96	1260.73
W99	O(2)⋯O(2)	O bonded to 2 other atoms	284623	3.96	1285.87

This potential was successfully used in a large survey of crystal structure predictions in conjunction with both a point charge<sup>4</sup> and Distributed Multipole model.<sup>5</sup> However problems have been observed in underestimating hydrogen bond distances when combined with a Distributed Multipole Model, presumably because the electrostatic forces can be stronger than with the point charge model used in Williams' parameterization. In certain cases, of (carboxylate)O⋯H-O and N⋯H-O hydrogen bonds the underestimate has led to the hydrogen bonds becoming within the covalent bond range. (An ad hoc fix for the latter<sup>6</sup> is to replace the purely repulsive, Williams potential between pyridine nitrogen and carboxylic proton (N(2).H(3)) to  $A=75719.47 \text{ kJ mol}^{-1}$  and  $B=5.1765 \text{ Å}^{-1}$  used to model the cocrystal of 4-aminobenzoic acid with 4-nitrophenylacetic acid. This potential is much steeper at unphysically short distances without penalizing the lattice energy at typical contacts compared with the original Williams parameterization.) Graeme Day's group noted that O-H(3)⋯N(2) distances were unreasonably short for the cocrystal in the 2007 blind test,<sup>7</sup> and found substituting the alcohol H(2) parameters for H(3) in this carboxylic acid produced more reasonable results.

**FIT** has evolved through using Williams older parameterizations, which were fitted to crystals which had each element and C and H only. The H nuclei are used as the interaction sites, although whether Williams corrected for the X-ray foreshortening in the parameterization is unclear. Note that NEIGHBOURS does not distinguish between H-O and H-N and so many papers have use the  $H_N (=H_p)$  parameters for any polar hydrogen, including in hydrates and ice.<sup>8</sup>

Reference	Atom pair	Description	$A_{ik} / \text{kJ mol}^{-1}$	$B_{ik} / \text{Å}^{-1}$	$C_{ik} / \text{kJ mol}^{-1} \text{Å}^6$
9	C⋯C	Any C atom	369743	3.60	2439.8

9	H...H	H bonded to C	11971	3.74	136.4
10	H <sub>N</sub> ...H <sub>N</sub>	H bonded to N	5029.68	4.66	21.50
11	H <sub>O</sub> ...H <sub>O</sub>	H bonded to O	2263.3	4.66	21.50
9	N...N	Any N atom	254529	3.78	1378.4
12	O...O	Any O atom	230064.1	3.96	1123.59
13	F...F	Any F atom	363725	4.16	844
14	Cl...Cl	Any Cl Atom	924675	3.51	7740.48
Other parameters that have been used in conjunction with FIT for a few applications					
15	S...S	S in SO <sub>2</sub>	236501.5	2.9	8397.115
15	O...O	O in SO <sub>2</sub>	202983.6	3.96	640.8628
7	S...S	S in blind test (C=S and thioether)	401034	3.30	5791

NEIGHCRYST will automatically provide the FIT or W99 typing and can allow a user specified typing, allowing the ability of DMACRYST to use more atomic types for a given atom to be applied without manual editing of the input file. The extent to which the parameters in combination have been tested beyond<sup>10</sup> is limited, though there has been some validation for the F parameters in Ashley Hulme's thesis and for the isotropic chlorine in situations without close Cl...Cl contacts.<sup>16</sup> There are various failures: problems in stacking of some rigid aromatics differences led Tom Lewis to reduce the C parameters by 25% in his studies.<sup>17</sup>

Both these empirically fitted potentials are effectively modelling the total intermolecular potential with the electrostatic component removed, as well as it is sampled in the crystal structures used for fitting and validation. It is not surprising that the results can be sensitive to the quality of the electrostatic model used, and may be very poor for atypical short contacts. Since they are empirically based, the choice of which to use can only be made by empirical testing on related crystal structures. If neither are satisfactory, or the study warrants greater accuracy and confidence in the model potential, then a molecule specific, anisotropic atom-atom potential should be derived.

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## Appendix E. Possible control parameters for perfect lattice relaxation

1	CONV	Described in 3.9.1
2	CONP	Described in 3.9.1
3	MAXI	Described in 3.9.1
4	MAXD	Described in 3.9.1
5	MAXU	Described in 3.9.1
6	LIMI	Described in 3.9.1
7	WCAL	Described in 3.9.1
8	CORE	No longer in use
9	SHEL	No longer in use
10	ALL	No longer in use
11	NONE	No longer in use
12	FIX	No longer in use
13	STDC	No longer in use
14	SUBS	No longer in use
15	ENGO	Described in 3.9.1
16	TIDY	No longer in use
17	LIMG	Described in 3.9.1
18	UDTE	Described in 3.9.1
19	FITE	Used in DMAFIT, no longer used in DMACRYS
20	FITW	Used in DMAFIT, no longer used in DMACRYS
21	TSTG	No longer in use
22	TSTW	No longer in use
23	NTOQ	No longer in use
24	FLOP	No longer in use
25	ACCG	No longer in use
26	COUR	Used in DMAFIT, no longer used in DMACRYS
27	SHTR	Used in DMAFIT, no longer used in DMACRYS
28	THBR	Used in DMAFIT, no longer used in DMACRYS
29	TORR	Used in DMAFIT, no longer used in DMACRYS
30	ELLR	Used in DMAFIT, no longer used in DMACRYS
31	DMAR	Used in DMAFIT, no longer used in DMACRYS
32	COUW	Used in DMAFIT, no longer used in DMACRYS
33	SHTW	Used in DMAFIT, no longer used in DMACRYS
34	THBW	Used in DMAFIT, no longer used in DMACRYS
35	TORW	Used in DMAFIT, no longer used in DMACRYS
36	ELLW	Used in DMAFIT, no longer used in DMACRYS
37	DMAW	Used in DMAFIT, no longer used in DMACRYS
38	VIDE	No longer in use
39	MAXT	No longer in use
40	CCLS	Described in 3.9.1
41	R2ND	Described in 3.9.1
42	SEIG	Described in 3.9.1
43	NOPR	Described in 3.9.1
44	STAR	Described in 3.9.1
45	PRES	Described in 3.9.1
46	HESS	Described in 3.9.1
47	PHGR	Described in 3.9.1

## Appendix F. Lattice Vector and Basis input

The LATT directive reads in three records. The format of each record is

3F

Each record refers to one lattice vector, and gives the orthonormal  $\mathbf{x}, \mathbf{y}, \mathbf{z}$  coordinates of the lattice vectors.

The orthonormal lattice vector components must be given to a sufficiently high precision for all the symmetry elements of the lattice point group to be found. By default, at least seven significant figures must be given, unless the ACCU directive is used. (See examples after the BASI directive).

The following section describes how to calculate orthonormal lattice vectors from the conventional crystallographic unit cell. Firstly the general case will be given, although this should normally only be used for triclinic and monoclinic unit cells. The matrix given below (the normalizing matrix  $\mathbf{N}$ ) defines an orthonormal coordinate system with the  $\mathbf{z}$  axis parallel to the crystallographic  $\mathbf{c}$  axis, the  $\mathbf{x}$  axis parallel to the reciprocal  $\mathbf{a}$  axis and the  $\mathbf{y}$  axis forming a right-handed set with  $\mathbf{x}$  and  $\mathbf{z}$ . The matrix is normalized so that one unit = the crystallographic  $c$  spacing. This value should therefore be used for the value RLSCAL on the REGI directive.

$$N = \begin{matrix} 1/(a^* \times c) & 0 & 0 \\ \frac{a \times (\cos \gamma - \cos \alpha \times \cos \beta)}{c \times \sin \alpha} & \frac{b \times \sin \alpha}{c} & 0 \\ \frac{a \times \cos \beta}{c} & \frac{b \times \cos \alpha}{c} & 1 \end{matrix}$$

The unit cell is defined by three cell lengths  $a, b, c$ , and by three angles  $\alpha, \beta, \gamma$ .  $a^*$  above is the length of the reciprocal  $a$  lattice vector. A general expression for the length of  $a^*$  is

$$a^* = b \times c \times (\sin \alpha) / V$$

$$V = 2 \times a \times b \times c \times \sqrt{\sin s \times \sin(s - \alpha) \times \sin(s - \beta) \times \sin(s - \gamma)}$$

$$s = \frac{(\alpha + \beta + \gamma)}{2}$$

Whilst this matrix will work for any crystal, care is needed if comparison is to be made with perfect lattice tensor properties. (Elastic and dielectric constants). These will have been measured with respect to an orthogonal coordinate system which is not necessarily the same as that given above. Reference to the experimental papers may be necessary to find out the coordinate system used to measure the tensor properties. The above matrix should be used for triclinic and monoclinic crystals. For tetragonal, orthorhombic and cubic crystals a simpler matrix is used, which defines  $\mathbf{x}$  parallel to  $\mathbf{a}$  instead of  $\mathbf{a}^*$

$$N = \begin{matrix} a/c & 0 & 0 \\ 0 & b/c & 0 \\ 0 & 0 & 1 \end{matrix}$$

For trigonal and hexagonal crystals,  $\mathbf{x}$  is again defined parallel to  $\mathbf{a}$  giving the matrix.

$$N = \begin{matrix} a/c & -a/2c & 0 \\ 0 & \sqrt{3} \times a/2c & 0 \\ 0 & 0 & 1 \end{matrix}$$

At present NEIGHCRYS cannot handle P3 and P6 space groups.

The normalizing matrix  $\mathbf{N}$  defined above will transform any vector defined in crystallographic units into orthonormal coordinates. The vector may be a unit cell vector or a basis atom vector. If the unit cell is primitive, (P), the unit cell vectors in crystallographic coordinates are simply given by the identity matrix.

$$L = \begin{matrix} & a & b & c \\ \begin{matrix} 1 \\ 0 \\ 0 \end{matrix} & 0 & 0 & 0 \\ \begin{matrix} 0 \\ 1 \\ 0 \end{matrix} & 0 & 1 & 0 \\ \begin{matrix} 0 \\ 0 \\ 1 \end{matrix} & 0 & 0 & 1 \end{matrix}$$

Multiplying this by the normalizing matrix  $\mathbf{N}$  forms the orthogonal lattice vectors  $\mathbf{O} = \mathbf{N} \cdot \mathbf{L}$ . Hence the columns of the normalizing matrix given above are the lattice vectors needed by DMACRYS. Note that the input to DMACRYS and the printed output from DMACRYS give the lattice vectors in rows, so the normalizing matrix given above will be transposed.

If the unit cell is centred, then the centred lattice vectors should be used. It is recommended that this is always done, so NEIGHCRYST does this automatically. The non-primitive cell may be used, and the same answers will be produced. However there will be more basis atoms per unit cell if this is done, and the perfect lattice calculation will take correspondingly longer to run. The centred lattice vectors in crystallographic units may conveniently be taken as the columns of the matrices  $\mathbf{L}$  given in Table 3.5. (Other choices are possible).

**Table 3.5: LATTICE VECTORS FOR CENTRED CELLS**

Centring type	A	B	C
A	1	0	0
	0	1	1/2
	0	0	1/2
B	1	0	1/2
	0	1	0
	0	0	1/2
C	1	1/2	0
	0	1/2	0
	0	0	1
I	-1/2	1/2	1/2
	1/2	-1/2	1/2
	1/2	1/2	-1/2
F	0	1/2	1/2
	1/2	0	1/2
	1/2	1/2	0
R	2/3	-1/3	-1/3
	1/3	1/3	-2/3
	1/3	1/3	1/3

The orthonormal lattice vectors required by DMACRYS are then formed by the matrix product  $\mathbf{O} = \mathbf{N} \cdot \mathbf{L}$ . Again the matrix  $\mathbf{O}$  must be transposed to be input to DMACRYS. At the end of the DMACRYS calculation, output files are produced in fdat format (fort.15) and SHELX format (fort.16). The output will be converted back to the centred cell from the primitive cell. DMACRYS must have read the input from NEIGHCRYST from fort.20 either using the directive SYMM or FDAT for this to be carried out correctly.

## Appendix G. Minimization Methods

DMACRYS uses a Newton Raphson method to carry out minimization. The first step in the minimization needs an approximation to the second derivative matrix. As some of the components of the second derivative matrix are difficult to calculate analytically, they are initially set to zero. Subsequent steps in the iteration use the current and previous gradient vectors to update the inverse of the second derivative matrix to obtain a better approximation of the true matrix. When the structure has converged the matrix will be a closer approximation to the correct second derivative matrix inverse. When the user is doing a minimization calculation this will be adequate, and this procedure is used when the keyword NOPR is present.

In order to calculate accurate properties the updated matrix at the minimum is not sufficiently accurate. If NOPR is omitted, all elements of the second derivative matrix are calculated numerically so that an accurate matrix is obtained and accurate properties can be derived. It is very time consuming to carry out the numerical calculation so this should not be used for routine minimizations.

## Appendix H. Symmetry

This section is intended to briefly describe how symmetry is used in DMACRYS. Firstly we will discuss some of the problems that can arise if symmetry is not used, (i.e. SYMM omitted) for perfect lattice optimization. In principle, the perfect lattice calculation will conserve the space group symmetry of the input unit cell. In practice, rounding errors can permit the symmetry to change, although this rarely happens. Secondly, the perfect lattice relaxation is always carried out keeping the first molecule centre of mass fixed. This is to remove the translational invariance of the force constant matrix. The fixing of the first molecule centre of mass has important consequences for the symmetry. For example, this position may be related to a second by a two-fold axis. Relaxing the perfect lattice will relax these two positions keeping the first one fixed, so that the two-fold axis will move. It is possible that this two-fold axis initially passes through the point group origin, but will not after relaxation.

Including the keyword SYMM will carry out a symmetry-constrained DMACRYS relaxation, however NEIGHCRY5 must be used to write the symmetry information file fort.20. This file contains a set of symmetry adapted vectors which can be used to reduce the second derivative matrix to a block diagonal form, with each block corresponding to one of the irreducible representations of the space group. The block corresponding to the totally symmetric representation can then be used to carry out the minimization. This ensures that the space group symmetry is preserved, however the conventional direction and position of symmetry axes are not necessarily preserved. For this reason it is recommended that a properties calculation is always carried out by rerunning NEIGHCRY5 using the final structure written by DMACRYS.

The symmetry adapted vectors for all representations of the space group are used to check that the relaxed structure is a minimum and not a saddle point. The eigenvalues and eigenvectors of all of the symmetry adapted blocks of the final matrix are calculated. There should be three eigenvalues which are zero or close to zero corresponding to the translational invariance of the crystal, however these will not necessarily be in the totally symmetric representation. None of the eigenvalues should be negative. A negative eigenvalue indicates that the final structure is a saddle point with a lower energy configuration in a lower symmetry space group.

## Appendix I. Anisotropic repulsion

$\mathbf{z}_1$  is unit vector along (local) z axis on atom 1 etc,  $\mathbf{R}$  is unit vector from site 1 to site 2. The forms of anisotropy included and the required definition of the axes has the  $\mathbf{z}_1$  axis along the bonds, e.g. along C-Cl. Note that the values of K1 and K2 are not the original complex values, but the real components, with  $K > 0$  for cosine and  $K < 0$  for the sine combinations.

K1	K2	L1		L2	J	Function	K1	K2	L1	L2	J	Function
0	0	1		0	1	$\mathbf{z}_1 \cdot \mathbf{R}$	0	0	0	1	1	$-\mathbf{z}_2 \cdot \mathbf{R}$
1	0	1		0	1	$\mathbf{x}_1 \cdot \mathbf{R}$	0	1	0	1	1	$-\mathbf{x}_2 \cdot \mathbf{R}$
-1	0	1		0	1	$\mathbf{y}_1 \cdot \mathbf{R}$	0	-1	0	1	1	$-\mathbf{y}_2 \cdot \mathbf{R}$
0	0	2		0	2	$(3(\mathbf{z}_1 \cdot \mathbf{R})^2 - 1) / 2$	0	0	0	2	2	$(3(\mathbf{z}_2 \cdot \mathbf{R})^2 - 1) / 2$
1	0	2		0	2	$\sqrt{3}(\mathbf{z}_1 \cdot \mathbf{R})(\mathbf{x}_1 \cdot \mathbf{R})$	0	1	0	2	2	$\sqrt{3}(\mathbf{z}_2 \cdot \mathbf{R})(\mathbf{x}_2 \cdot \mathbf{R})$
-1	0	2		0	2	$\sqrt{3}(\mathbf{z}_1 \cdot \mathbf{R})(\mathbf{y}_1 \cdot \mathbf{R})$	0	-1	0	2	2	$\sqrt{3}(\mathbf{z}_2 \cdot \mathbf{R})(\mathbf{y}_2 \cdot \mathbf{R})$
2	0	2		0	2	$\sqrt{3}((\mathbf{x}_1 \cdot \mathbf{R})^2 - (\mathbf{y}_1 \cdot \mathbf{R})^2) / 2$	0	2	0	2	2	$\sqrt{3}((\mathbf{x}_2 \cdot \mathbf{R})^2 - (\mathbf{y}_2 \cdot \mathbf{R})^2) / 2$
-2	0	2		0	2	$\sqrt{3}(\mathbf{x}_1 \cdot \mathbf{R})(\mathbf{y}_1 \cdot \mathbf{R})$	0	-2	0	0	2	$\sqrt{3}(\mathbf{x}_2 \cdot \mathbf{R})(\mathbf{y}_2 \cdot \mathbf{R})$