

ADVANCED USERS DMACRYS & NEIGHCRYS manual

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This technical manual is intended for expert users to allow deviations from the NEIGHCRYS 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 NEIGHCRYST 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 NEIGHCRYST generated DMACRYS input file (file.dmain), and making adaptations if there are problems with specific systems during the minimisations, 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 NEIGHCRYST. 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 [Section??](#) so 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 minimisation. The minimisation 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 minimisation analytical second derivatives are preferred since the Hessian update algorithm gives a good approximation when the minimisation is complete. For properties calculations no minimisation is done and numerical second derivatives must be used. See NOPR directive below (Section 3.6.1) 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 80 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

<p>Error - Invalid format for I variable The input processor encountered an invalid character in an integer data field.</p>
<p>Error - Invalid format for F variable The input processor encountered an invalid character in a real data field.</p>

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

<p>End of file unit number 5 Program terminating</p>
--

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

2.2 THE INPUT PROCESSOR

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

The DMACRYS 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 DMACRYS 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.

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, POLZ, DAMP	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
POLARIZABILITY	POLZ ENDS	Optional
Other POTENTIAL INPUT	POTE ENDS	Mandatory
MOLECULE INPUT	MOLE ENDS	Mandatory
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	starting.res.dmain A1776_CrystalOptimizer
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.
Digit 3		
	0	No output
Digit 4		
	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 $14.3997584/RLSCAL^3$, where $RLSCAL$ is the lattice constant. The gradients must be scaled by $14.3997584/RLSCAL^2$.
Digit 5		
	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 - NEIGHCRY 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
MINI	
0	No output
1	Print information about progress of the minimisation.
2	As 1 plus lattice energies
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
MOLE	
	This APRINT option is used in DMACRYST to control output from the MOLE directive.
0	Do not print molecular bonding information.
1	Print molecular bonding information
	Default 1
GEOM	
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 DMACRYS. Output is produced by default to fort.8, fort.12, fort.13, fort.15, and fort.16.

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
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 80 characters per card image by default. IRECL should be less than 80, 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). 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

SYMM	
Operands	None

Instructs DMACRYS to read in the symmetry input file fort.20 that was written by NEIGHCRY5.

FDAT	
Operands	None

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.

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.

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.

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.

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 NEIGHCRYS is used to set up the dmain file, the hydrogen atoms can be foreshortened by using the appropriate option in the NEIGHCRYS input. NEIGHCRYS 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 but NEIGHCRYS but may need to be set to other values if the foreshortening is not 0.1.

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). NEIGHCRYS 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 10.323800 1.452953
RDMA 1.452953
```

Printed Output

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

RDMA	
Operand type	F
Operand name	RDMA

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 = RDMA 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	
Operands	None

This directive is required. The LATT directive instructs the program to call the lattice vector input routine. The calculations are described in appendix E. They are performed by the pre-processor NEIGHCRY5.

Example input

```
LATT
1.7073583288025 0.000000000000 0.7454652295501
0.0000000000000 0.6019682674984 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.
  0.837091464883601   0.000000000000000   -0.234665349082900
  0.000000000000000   0.459812859884801   0.000000000000000
  0.000000000000000   0.000000000000000   1.000000000000001
```

Error messages

```
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 NEIGHCRYST. 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 DMACRYST, 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 has 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
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 Punch file in `NEIGHCRY`.

It should be noted that adding or subtracting a lattice vector, or an intergal 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 `NEIGHCRY`. 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)³.

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 0.5103944548314 0.3025354180139 0.2253913193378 1
LEVEL 4
-0.287695
0.002275 -0.125772 -0.352452
0.702515 -0.024263 0.015752 -0.650375 0.476748
-0.000858 -0.421466 -1.163540 0.024966 0.028870 -0.028323 0.083639
-0.043519 0.029332 -0.006590 0.694422 -0.824759 0.019325 0.048927
-0.098391 1.137938

```

Printed output

```

the x basis atoms 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

```

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.

```

Cut off value for direct lattice sum = x lattice units
Cut off value for reciprocal lattice sum = y reciprocal lattice units
Values of the constants used in these summations are:
Eta parameter for division of sum between real and reciprocal lattice= z1
PI/(ETA^2 * Vol.Cell) = z2

```

This message is printed by default. The constants $Z1$ and $Z2$ are η and $\pi/(\eta^2 \times V)$.

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 POTENTIAL INPUT (other than multipoles & polarizabilities)

3.4.1 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, SPLI, MORQ, SPRI, COUL, VDWA, HULB, BUC7, NONE, BSPL
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	500	Maximum permitted number of potentials
MAXRNG	10	Maximum number of ranges for each potential
MAXTHB	50	Maximum number of types of three-body bond
MAXTYP	500	Maximum number of short atom labels permitted
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.

```
ERROR - ABOVE LINE CONTAINS A SPEC DIRECTIVE - ONLY ONE IS PERMITTED
```

Only one SPEC directive is permitted.

3.4.2 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
  S_ 0.0 32.066000
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
```

3.4.3 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

A	A A	A A	< F,I >
KEYW	LABELA	LABELB	Additional Parameters

Where

KEYW	is a 4 character keyword giving the potential type. These are described in detail below.
LABELA,LABELB	are species labels in the format described in 3.3.2
Additional Parameters	These are required for certain of the potential types only.

The format of a range record is

F ...	< F >	F
Parameters	Optional RMIN	RMAX

Where

Parameters	These are the parameters needed to define the repulsion-dispersion potential. The number of parameters depends on the particular potential type, defined by KEYW on the species record.
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. <ul style="list-style-type: none">• 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	25.286949	0.00	70.00
ENDS						
BUCK	C_F1	H_F1				
	689.536713		0.27248000	5.978972	0.00	70.00
ANIS	C_F1	H_F1				
	0	0	1	1	-0.68558800	
	0	0	1	0	1	-0.68558800
	0	0	2	2	1.44650200	
	0	0	2	0	2	1.44650200
ENDS						

Printed output

POTENTIAL BETWEEN SPECIES *Lab1Typ1* AND *Lab2Typ2* WITH *Nrange* 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 on 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 a 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.

The 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 ⁶

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

Example input

```
BUCK O F1 H wa
      352.561760 0.23201900 1.610837 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
```

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 (i.e. before the ENDS directive) and instructs DMACRYS to treat the repulsion part of the Buckingham potential as an anisotropic potential. It is currently followed by up to five 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
K2	0	0	0	0	0
L1	0	1	0	2	0
L2	0	0	1	0	2
J	0	1	1	2	2

The first S function is just the isotropic part. If it is not given the values input on the BUCK record will be used. 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.

Example input

```

BUCK  C_C1  C_C1
      14469.681037      0.25533300      15.674900      0.00      70.00
ANIS  C_C1  C_C1
      0  0  0  1  1 -0.68558800
      0  0  1  0  1 -0.68558800
      0  0  0  2  2  1.44650200
      0  0  2  0  2  1.44650200
ENDS
```

Printed output

```

BUCKINGHAM POTENTIAL V(R) = A * EXP(-R/RHO) - C/R**6
      A              RHO              C              RMIN
RMAX
      0.00000000E+00      0.25533300E+00      0.15674900E+02      0.00000000E+00
0.70000000
E+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      RHO(K1,K2,L1,L2,J)
0.25533300E+00      0      0      0      0      0      0.24460418E+01
0.25533300E+00      0      0      1      0      1      -0.68558800E+00
0.25533300E+00      0      0      0      1      1      -0.68558800E+00
0.25533300E+00      0      0      2      0      2      0.14465020E+01
0.25533300E+00      0      0      0      2      2      0.14465020E+01
```

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^N

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
```

Probably needs updating, but I've never used this potential type so can't do it

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^N

B
is in eV Å^M

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 Å ⁻¹
C	is in Å

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)	=	$A \times \exp(-r/B)$	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	$r_a < r < r_{max}$

5mm

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 ⁶
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 and second 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									
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									
A	=	A	RHO	=	RHO			RMIN	RMAX
A5	=	A5	B5	=	B5	C5	=	C5	
D5	=	D5	E5	=	E5	F5	=	F5	
A3	=	A3	B3	=	B3			r_b	r_m
C3	=	C3	D3	=	D3	E3	=	E3	
C	=	C						r_m	r_a
								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

SPLI

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 \AA^{-1}
C	is in \AA
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 ^N

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

$$\begin{aligned} \eta_1 &= \exp(-\beta) \\ \eta_2 &= \exp(-2 \times \beta) \\ \beta &= B \times (r - C) \end{aligned}$$

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 ⁻¹
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 ⁶
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
```

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.

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.

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 2 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.

3.5 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. NEIGHCRYS sets this to 20 Å, which should normally be sufficient.

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 DMACRY5 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. NEIGHCRY5 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 NEIGHCRY5 and should be checked and edited manually.

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

Operand type	A10
Operand name	ATOM

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

Record 2

Operand types	A1 A4 A10 A10 I
Operand names	AXIS, AXIS TYPE, ATOM 1 ATOM 2 SEPARATION

AXIS is the first axis which is defined, (X, Y or Z, usually X) 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)

Operand types	A1 A4 A10 A10 I A10 I A10 I
Operand names	AXIS, AXIS TYPE, ATOM 1 ATOM 2 SEPARATION1 ATOM 3 SEPARATION 2

This format will seldom be needed. AXIS TYPE will be BIEY 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.

Record 3

Operand types	A1 A4 A10 A10 I A10 I A10 I
Operand names	AXIS, AXIS TYPE, ATOM 1 ATOM 2 SEPARATION1 ATOM 3 SEPARATION 2

The second axis which must be a plane input in the same format as for MOLX. 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.

ENDS

This directive returns control to the main menu of directives.

Example input

```
MOLE
NFXP
CUTM 20.0
NBUR 20
NNCU
  C_ C_ 1.600
  C_ S_ 1.800
  C_ Cl 1.800
  C_ O_ 1.500
  C_ N_ 1.500
  C_ H_ 1.300
  S_ O_ 1.500
  N_ N_ 1.200
ENDS
MOLX 2
X LINE S_S1_1___ C_F1_7___ 1
Y PLANE S_S1_1___ C_F1_7___ 1 C_F1_1___ 1
X LINE S_S1I24___ C_F1I30___ 1
Y PLANE S_S1I24___ C_F1I30___ 1 C_F1I24___ 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 i NEAREST NEIGHBOUR CUTOFFS (IN ANGSTROMS)
ATOM TYPES CUTOFF

LABELI LABELJ BOND CUT
LIST OF NEIGHBOURS

ATOM NUMBERS AND TYPES MOLECULE LATTICE VECTORS SPACING DISTANCE
i j LABELIL LABELJL nmole la lb lc nbur r
```

ij

are the index of the basis atoms after sorting.

LABELI LABELJ

are short atom labels

LABELIL LABELJL

are long atom labels

nmole

is the molecule number as input in BASI section.

la lb lc

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

nbur

gives the minimum number of covalent bonds between i and j moving along bonds. In other words, i and j are n burth neighbours.

r

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

```
MOLE
NFXP
CUTM 20.0
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
```

Example input with anisotropic short range repulsions

```
MOLX 2
X LINE C_C2_2_____ N_N1_1_____ 1
Y PLANE C_C2_2_____ N_N1_1_____ 1 O_O1_1_____ 2
X LINE C_C2I15_____ N_N1I14_____ 1
Y PLANE C_C2I15_____ N_N1I14_____ 1 O_O1I14_____ 2
ANIS
C_C1_1_____
Z LINE C_C1_1_____ O_O1_1_____ 1
X PLAN C_C1_1_____ O_O1_1_____ 1 C_C2_2_____ 1
C_C2_2_____
Z LINE C_C2_2_____ N_N1_1_____ 1
X PLAN C_C2_2_____ N_N1_1_____ 1 C_C3_3_____ 1
C_C3_3_____
Z LINE C_C3_3_____ H_H1_1_____ 1
X PLAN C_C3_3_____ H_H1_1_____ 1 C_C3_4_____ 1
C_C3_4_____
Z LINE C_C3_4_____ H_H1_2_____ 1
X PLAN C_C3_4_____ H_H1_2_____ 1 C_C3_5_____ 1
C_C3_5_____
Z LINE C_C3_5_____ H_H1_3_____ 1
X PLAN C_C3_5_____ H_H1_3_____ 1 C_C3_6_____ 1
C_C3_6_____
Z LINE C_C3_6_____ H_H1_4_____ 1
X PLAN C_C3_6_____ H_H1_4_____ 1 C_C1_1_____ 1
O_O1_1_____
Z LINE C_C1_1_____ O_O1_1_____ 1
X PLAN C_C1_1_____ O_O1_1_____ 1 C_C2_2_____ 1
H H1 1
```

```

Z LINE C_C3_3 H_H1_1 1
X PLAN C_C3_3 H_H1_1 1 C_C3_4 1
H_H1_2
Z LINE C_C3_4 H_H1_2 1
X PLAN C_C3_4 H_H1_2 1 C_C3_5 1
H_H1_3
Z LINE C_C3_5 H_H1_3 1
X PLAN C_C3_5 H_H1_3 1 C_C3_6 1
H_H1_4
Z LINE C_C3_6 H_H1_4 1
X PLAN C_C3_6 H_H1_4 1 C_C1_1 1
N_N1_1
Z LINE C_C2_2 N_N1_1 1
X PLAN C_C2_2 N_N1_1 1 C_C3_3 1
N_N2_2
Z LINE N_N1_1 N_N2_2 1
X PLAN N_N1_1 C_C2_2 1 C_C3_3 1
C_C1I14
Z LINE C_C1I14 O_O1I14 1
X PLAN C_C1I14 O_O1I14 1 C_C2I15 1
C_C2I15
Z LINE C_C2I15 N_N1I14 1
X PLAN C_C2I15 N_N1I14 1 C_C3I16 1
C_C3I16
Z LINE C_C3I16 H_H1I14 1
X PLAN C_C3I16 H_H1I14 1 C_C3I17 1
C_C3I17
Z LINE C_C3I17 H_H1I15 1
X PLAN C_C3I17 H_H1I15 1 C_C3I18 1
C_C3I18
Z LINE C_C3I18 H_H1I16 1
X PLAN C_C3I18 H_H1I16 1 C_C3I19 1
C_C3I19
Z LINE C_C3I19 H_H1I17 1
X PLAN C_C3I19 H_H1I17 1 C_C1I14 1
O_O1I14
Z LINE C_C1I14 O_O1I14 1
X PLAN C_C1I14 O_O1I14 1 C_C2I15 1
H_H1I14
Z LINE C_C3I16 H_H1I14 1
X PLAN C_C3I16 H_H1I14 1 C_C3I17 1
H_H1I15
Z LINE C_C3I17 H_H1I15 1
X PLAN C_C3I17 H_H1I15 1 C_C3I18 1
H_H1I16
Z LINE C_C3I18 H_H1I16 1
X PLAN C_C3I18 H_H1I16 1 C_C3I19 1
H_H1I17
Z LINE C_C3I19 H_H1I17 1
X PLAN C_C3I19 H_H1I17 1 C_C1I14 1
N_N1I14
Z LINE C_C2I15 N_N1I14 1
X PLAN C_C2I15 N_N1I14 1 C_C3I16 1
N_N2I15
Z LINE N_N1I14 N_N2I15 1
X PLAN N_N1I14 C_C2I15 1 C_C3I16 1
ENDS
ENDSMOLE
NFXP
CUTM 20.0
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

```

Additional printed output

```

Local axis set for molecule: 1
x=> 0.959988 0.022530 0.279134
y=> -0.248172 0.530254 0.810704
z=> -0.129747 -0.847539 0.514629

QUATERNION PARAMETERS
0.86672818D+00 0.47830546D+00 -0.11793829D+00 0.78081424D-01

```

Gives the direction of the local axis for each molecule together with the quaternion 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 C_C1_1 -0.157298 -0.997097 -0.000025 12.010700
9 C_C2_2 0.456473 0.353141 -0.000131 12.010700
17 C_C3_3 -0.272684 1.577771 0.000097 12.010700
25 C_C3_4 -1.633698 1.520706 0.000332 12.010700

```

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	16.052882	6.793217	1.565032	120.108840
2	7.393482	4.127983	7.329768	120.108840

Gives the initial centre of mass.

```

Molecule No. Principal axes of inertia
1 0.89121989E-04 -0.62225071E-04 0.99999999E+00
0.13342984E+00 0.99105826E+00 0.49777138E-04
0.99105826E+00 -0.13342983E+00 -0.96627765E-04

Principal moments of inertia (amu.Ang**2) for molecule 1
Ix = 0.48362847E+03, Iy = 0.31983833E+03, Iz = 0.16379014E+03

```

The moments of inertia

```

Anisotropic short range potential axes in global axis system
Index Type x(global) y(global) z(global)
1 C_C1_1_1_1 x(axis) 0.67131855E+00 0.30700956E+00
0.67459361E+00 y(axis) -0.12959148E+00 -0.84753361E+00 0.51467740E+00
z(axis) 0.72975164E+00 -0.43293407E+00 -0.52917921E+00

```

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

3.6 PERFECT LATTICE CALCULATION

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

STAR PLUT

3.6.1 Perfect Lattice Relaxation Control Parameters

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

CONP	
Operands	none

This instructs DMACRYS 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.

MAXI	
Operand Type	I
Operand Name	MAXIT

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.

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. 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 MAXU 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 minimisation. The minimisation will assume to have converged if all displacements in one cycle are less than LIM I. 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 DMACRYS is only useful if no relaxation is being carried out (MAXI 0). **ICTRL = 0 is used for induction calculations.**

LIMG	
Operand Type	F
Operand Name	GLIMIT

GLIMIT gives the convergence test at which the relaxation stops with a valid minimisation due to energy test being satisfied. The minimisation 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 *LIMG* = 0.0001×*LIMI*.

UDTE	
Operand Type	F
Operand Name	UPDATE

UPDATE 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 UPDATE 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.

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. If LSEIG is zero (default), the search will be carried out by default only for the totally symmetric representation if one or more eigenvalue is negative. LSEIG = 1 allows the search even if these conditions are not met. If LSEIG=0, the following defaults are used; EIRNMI=-1.0, EIRNMX=+1.0, NEISTP=20, IREPS=IREPA1, IREPF=IREPA1, NEINS=1, NEINF=0. The search is done with displacements from EIRNMI to EIRNMX in NEISTP steps for representations from IREPS to IREPF (IREPA1 is the totally symmetric representation) for eigenvectors NEINS to NEINF.

NOPR	
Operands	None

NOPR switches off the calculation of elastic properties at the end of the calculation. (This calculation is slow as it uses numerical derivatives).

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
COMP
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 = UPDATE = 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 = MAXIT
Maximum relaxation of a coordinate per cycle (Angstroms) = MAXD
Maximum rotation of a molecule per cycle (Degrees) = 22222
Maximum number of hessian updates before recalculation = MAXU
Iteration will terminate when all displacements are less than LIMIT
Iteration will also terminate when dot product of gradient and displacement
vectors is less than GLIMIT
```

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

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

The intramolecular multipolar energies are written out.

```
Number of Energy calculations =
```

The number of intramolecular interactions is written out.

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

Molecule      dipole      magnitude
               x        y        z
molecule x    y        z        μ

Dipole per unit cell in global axis system (eA)
x    y    z    total dipole
x    y    z        μ
```

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

```
Cutoffs used in original reciprocal sum
9    3    5
```

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.

```
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.

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

Basis No.  Species      force (eV per Angstrom)
index      labeli         x          y          z          magnitude
          x          y          z          magnitude (eV)

Central force      x          y          z          magnitude (eV)
Central torque     x          y          z          magnitude (eV)
(eV per radian)
[ x          y          z          ]
```

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.

```
Strain derivatives for matrix deformation of form
```

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

```
Contributions to lattice energy (eV per unit cell [kJ/mol])
Z =      molecules
Ewald summed charge-charge energy.....=
Intra-molecular 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
      Total anisotropic repulsion energy....=
Total lattice energy.....=
```

Various contributions to the total lattice energy are written out.

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 5.0×10^{-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 minimisation 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.GELTA 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

QUADRATIC EXTRAPOLATION

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 minimisation.

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

3.6.2 Successful minimisation

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

```
Molecular translations (Angstroms)
```

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

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

```
Molecular rotations:
```

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

```
  molecule          x          y          z          deg
                  [ x          y          z ]
```

```
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.

```
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 minimisation is CONP.

```
Coordinates dumped
```

```
Cutoffs used in original reciprocal sum
  9      3      5
```

This bit is next, and needs to be described

```
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 =          molecules
Ewald summed charge-charge energy.....=
Intra-molecular 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
      Total anisotropic repulsion energy...=
Total lattice energy.....=

```

These are written out as described above.

```

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.

```

MECHANICAL PROPERTIES CALCULATED FROM HESSIAN MATRIX

Elastic stiffness tensor (Cij): GPa (10**10 DYNE/CM**2)
  C1      C2      C3      C4      C5      C6

```

Do we need to write something about this?

```

Born stability criteria satisfied.

```

This is good

```

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.

```

Lowest eigenvalue of shear submatrix of Cij =
Corresponding eigenvector  x      y      z

```

What do we need to write here??

```

Elastic compliance tensor (Sij): GPa^(1) (10**10 CM**2/DYNE)
  S1      S2      S3      S4      S5      S6

```

The elastic constant tensor is printed in units of 10^{11} Dynes cm^{-2} . The rows and columns refer to the xx yy zz yz xz xy components of the tensor. Note that the values printed depend on the choice of orthonormal coordinate system. The symmetry reflects that of the unit cell.

```

Mechanical properties calculated for a microcrystalline aggregate.
Bulk modulus from elastic constants (Voigt averaging): 12.49788 GPa
Bulk modulus from compliance constants (Reuss averaging): 11.17574 GPa
Arithmetic mean: 11.83681 GPa
Geometric mean: 11.81834 GPa

Shear modulus from elastic constants (Voigt averaging): 10.31534 GPa
Shear modulus from compliance constants (Reuss averaging): 8.92612 GPa
Arithmetic mean: 9.62073 GPa
Geometric mean: 9.59562 GPa

Young's modulus from elastic constants (Voigt averaging): 24.26907 GPa

```

```

Young's modulus from compliance constants (Reuss averaging):    21.14801 GPa
Arithmetic mean:      22.70854 GPa
Geometric mean:      22.65486 GPa

Poisson's ratio from elastic constants (Voigt averaging):    0.17636 GPa
Poisson's ratio from compliance constants (Reuss averaging):  0.18461 GPa
Arithmetic mean:      0.18049 GPa
Geometric mean:      0.18044 GPa

Single crystal Young's modulus along optical axes    x-component:    40.60911 GPa
y-component:    16.61765 GPa
z-component:    18.36004 GPa

```

All of the calculated elastic properties of the crystal are written out.

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

```

On returning from minimiser proposed alterations are:

Molecular translations (Angstroms)

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

All will be scaled by a factor of    1.000000

Molecular rotations:

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

molecule      x        y        z    deg
                [ x        y        z ]

All will be scaled by a factor of    1.000000

```

This appears again...

```

Strain matrix to be applied:

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

```

This also appears again.

```

Final lattice vectors are
1.708863226751663    0.000000000000000    0.744921804539825
0.000000000000000    0.602522041765577    0.000000000000000
0.000241666177688    0.000000000000000    0.998717148260084

```

The lattice vectors are printed out.

```

Final basis positions are
label    x        y        z    molecule

```

The final basis positions of all atoms in all molecules are printed out.

```
Final molecular centres of mass
Molecule   Centre of mass cords
molecule  x           y           z
```

The centres of mass of each of the molecules are printed out.

```
Final molecular axes
Axes for molecule           1
x           y           z
```

The molecular axes for each of the molecules are printed out.

```
Number of iterations =
```

The number of iterations is printed out.

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

Lattice vectors (Angstroms and Degrees)
      a           b           c           alpha  beta  gamma
Initial =>      a           b           c           alpha  beta  gamma
Final   =>      a           b           c           alpha  beta  gamma
diff.(abs) =>   Δa           Δb           Δc           Δα    Δβ    Δγ
diff.(%)  =>   Δa           Δb           Δc           Δα    Δβ    Δγ

      Cell Volume ( Cubic Angstroms )   Cell density ( g/cubic cm)
Initial =>           V                   d
Final   =>           V                   d
diff.(abs) =>       ΔV                   Δd
diff.(%)  =>       ΔV                   Δd

Dipole per unit cell in global axis system (eA)
      x           y           z           total dipole
Initial :      x           y           z           total
Final   :      x           y           z           total
```

The changes to the total crystallographic lattice are reported

```
Initial crystallographic positions of molecule centres of mass
Molecule   a-vectors   b-vectors   c-vectors
index       a-vector    b-vector    c-vector
.
.
.
Final crystallographic positions of molecule centres of mass
Molecule   a-vectors   b-vectors   c-vectors
index       a-vector    b-vector    c-vector
.
.
.
```

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

Direction cosines between axes before and after program run for molecule *index*

```

new axis      old axis
||           X           Y           Z
//
X   0.999998  -0.000164  0.001765
Y   0.000167  0.999998  -0.001776
Z   -0.001765  0.001776  0.999997

```

Actual angles between axes (Degrees):

```

new axis      old axis
||           X           Y           Z
//
X   0.101585  90.009416  89.898852
Y   89.990404  0.102201  90.101749
Z   90.101131  89.898234  0.143471

```

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

```

first rotation about z Phi = 45.179428
first rotation about y Theta= 0.143471
second rotation about z Psi = -45.169922

```

Equivalent to a single rotation of 0.143785 degrees

around the global axis vector: 0.707708 0.703406 0.066111

[local axis (orig. system) vector: -0.834833 0.058109 0.547428]

The changes to the molecular axes are printed out for each molecule. Things that are variables need to be shown as such.

Molecular movement including strains (Angstroms)

```

Mol.      | Dx |
index     Dx
.
.
RMS Aver.  RMS aver

```

The molecular movement for each molecule is printed out.

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

$$F = \left| 0.5 \text{ RMS } D \text{ THETA} \right|^2 + \left| 10 \text{ RMS } D_x \right|^2 + \text{SUM } (d=a,b,c) \left| 100 D_d \right|^2$$

$$+ \text{SUM } (d= \alpha,\beta,\gamma) D_d^2$$

In this case: $F = F$

Terms in order are as follows:

$$\left| 0.5 \text{ RMS } D \theta \right|^2 \quad \left| 10 \text{ RMS } D_x \right|^2 \quad \sum_{(d=a,b,c)} \left| 100 D_d \right|^2 \quad \sum_{(d=\alpha,\beta,\gamma)} D_d^2$$

The Figure of shame is printed out.

Initial crystallographic positions of atoms for molecule *index*

```

No. Label Type      a-vectors      b-vectors      c-vectors
index label         a-vector       b-vector       c-vector
.
.
.

```

Final crystallographic positions of atoms for molecule *index*

No.	Label	Type	a-vectors	b-vectors	c-vectors
index	label		a-vector	b-vector	c-vector
.					
.					
.					

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

STOP directive encountered. execution terminating.

The STOP directive was reached

Timing information follows.

The stuff below was already here, and I'm not sure where it should go.

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. (This is the default).

THE LATTICE ENERGY IS *e* EV

This message is always printed. According to the value of the MPRINT parameter on the PRIN PLUT MPRINT record, various other quantities may be printed, either before the first cycle and after the last cycle, or every cycle of iteration.

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	$\frac{14.3994584}{RLAT^2}$	$(\text{eV } \text{\AA})^{-1}$
	6*MOLS	ENDS	$\frac{14.3994584}{RLAT^3}$	$(\text{eV } \text{\AA})^{-2}$
Matrix	1,1	6*MOLS,6*MOLS	$\frac{14.3994584}{RLAT^3}$	$(\text{eV } \text{\AA})^{-2}$
	1,6*MOLS	6*MOLS,END	$\frac{14.3994584}{RLAT^4}$	$(\text{eV } \text{\AA})^{-3}$
	6*MOLS,6*MOLS	END,END	$\frac{14.3994584}{RLAT^5}$	$(\text{eV } \text{\AA})^{-4}$

.....

If a perfect lattice relaxation is carried out (MAXIT > 1), the lattice energy is printed out on each cycle of iteration. The final lattice vectors and basis positions are printed out after the final cycle of iteration. The basis positions are in the sorted order. The lattice vectors, basis species types and positions will be written to FORTRAN unit 8. This is by default for DMACRYS.

3.7 PROPERTIES CALCULATIONS

Some description?

Example input

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

The lattice energy minimization calculation uses approximations for calculating **stuff**. This is brought about by the use of the NOPR directive. In order to calculate these parameters more accurately, this directive must be omitted. 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 time taken to carry out the calculations is increased significantly.

When the directive STAR takes the operand PROP instead of PLUT, the k=0 phonon eigenvectors are calculated.

Printed output

```

k=0 phonon eigenvectors
For each mode:  molecule 1 - Trans(X), Trans(Y), Trans(Z)
                molecule 2 - Trans(X), Trans(Y), Trans(Z)
                molecule 3 - Trans(X), Trans(Y), Trans(Z)
                molecule 4 - Trans(X), Trans(Y), Trans(Z)
                molecule 1 - Rot(X) , Rot(Y) , Rot(Z)
                molecule 2 - Rot(X) , Rot(Y) , Rot(Z)
                molecule 3 - Rot(X) , Rot(Y) , Rot(Z)
                molecule 4 - Rot(X) , Rot(Y) , Rot(Z)

-----
0.36114424E+00 -0.42291172E-03 -0.34579569E+00
0.36114424E+00 -0.42291179E-03 -0.34579569E+00

      F/c          cm-1
-----
-0.574812091517E-05 -0.191736675217E-03

```

The forces and torques on each atom within each molecule are changed slightly, although the overall force remains the same. Other values that are changed are:

- Elastic stiffness tensor (Cij)
- Lowest eigenvalue of shear submatrix of Cij and the corresponding eigenvector
- Elastic compliance tensor (Sij)
- Bulk modulus
- Shear modulus
- Young's modulus
- Poisson's ratio
- Single crystal Young's modulus along optical axes
- The Eigenvalues for the representations
- The time taken to carry out the calculations

This needs to be written.

3.8 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 11 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 3.6
17	STOP	Described in 3.6
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 3.5
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	DAMP	Described in 3.2.3

The directives that are no longer in use (according to Maurice), but which do not give any errors are as follows:

DIME, THER, REST, RESE

THBO and TORS are allowed to be used, but are 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 3.4.2
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 3.4.3
18	MODI	Described in 3.4.3
19	LENN	Described in 3.4.3
20	MORS	Described in 3.4.3
21	BUC4	Described in 3.4.3
22	SPLI	Described in 3.4.3
23	MORQ	Described in 3.4.3
24	SPRI	Described in 3.4.3
25	COUL	Described in 3.4.3
26	VDWA	Described in 3.4.3
27	HULB	Described in 3.4.3
28	BUC7	Described in 3.4.3
29	NONE	There are no additional parameters
30	DBUC	No longer in use
31	BSPL	Described in 3.4.3
32	BVCK	No longer in use
33	DBVC	No longer in use
34	BUAH	No longer in use
35	ANIS	Not written up yet

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

Appendix D. Possible control parameters for perfect lattice relaxation

iwchky		
1	CONV	Described in 3.6.1
2	CONP	Described in 3.6.1
3	MAXI	Described in 3.6.1
4	MAXD	Described in 3.6.1
5	MAXU	Described in 3.6.1
6	LIMI	Described in 3.6.1
7	WCAL	Described in 3.6.1
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 3.6.1
16	TIDY	No longer in use
17	LIMG	Described in 3.6.1
18	UDTE	Described in 3.6.1
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 3.6.1
41	R2ND	Described in 3.6.1
42	SEIG	Described in 3.6.1
43	NOPR	Described in 3.6.1
44	STAR	Described in 3.6.1

45	PRES	To be written?
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Appendix E. 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 normalising 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 normalised so that one unit = the crystallographic c spacing. This value should therefore be used for the value RLSCAL on the REGI directive.

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

The unit cell is defined by three cell lengths a, b, c , and by three angles α, β, γ . 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}^*

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

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

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

At present NEIGHCRYS cannot handle P3 and P6 space groups.

The normalising matrix 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.

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

Multiplying this by the normalising matrix N forms the orthogonal lattice vectors $\mathbf{O} = \mathbf{N} \cdot \mathbf{L}$. Hence the columns of the normalising 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 normalising 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 NEIGHCRYS 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 NEIGHCRY from fort.20 either using the directive SYMM or FDAT for this to be carried out correctly.

Appendix F. Minimization Methods

DMACRYS uses a Newton Raphson method to carry out minimisation. The first step in the minimisation 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 minimisation 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 minimisations.

Appendix G. 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 optimisation. 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 minimisation. 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.