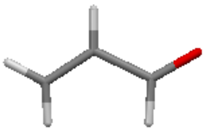
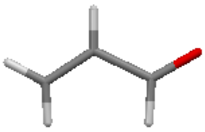
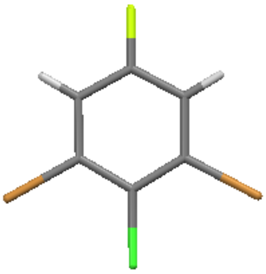
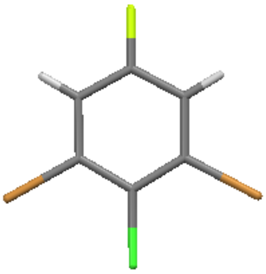
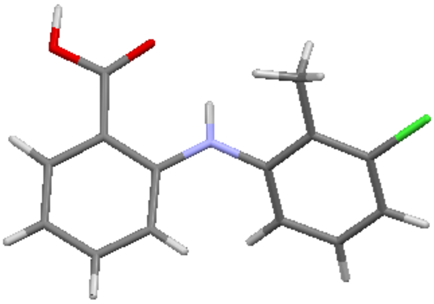
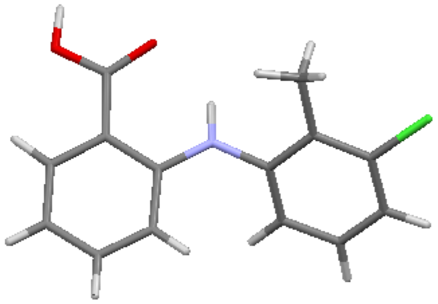
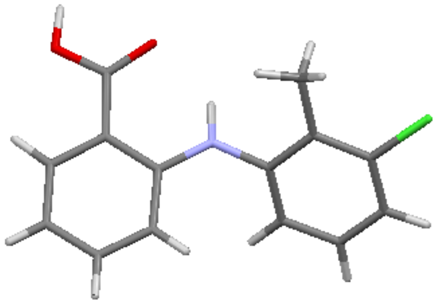
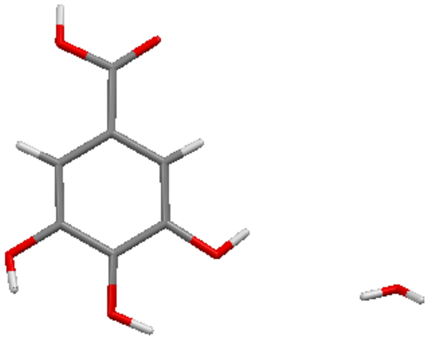
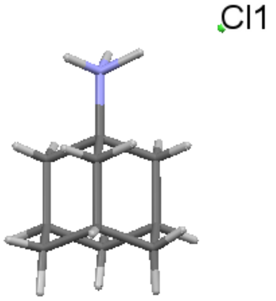
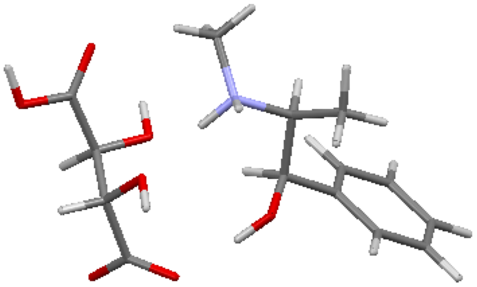
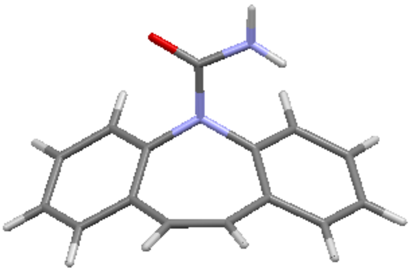
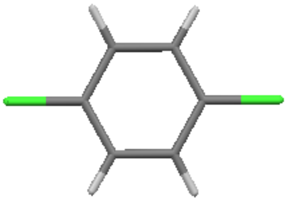
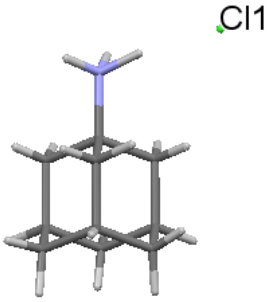
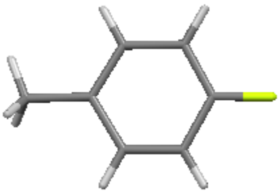
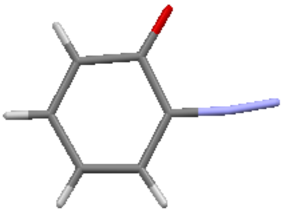
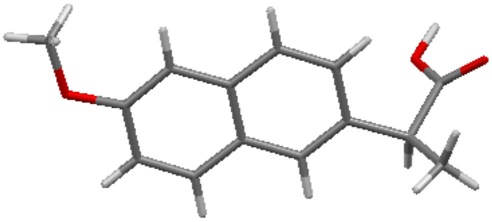
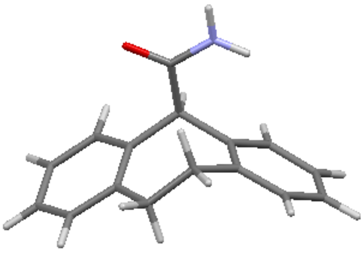
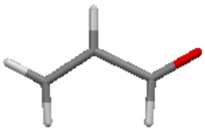
Test suite for NEIGHCRYS_2.3.0 and DMACRYS_2.3.0

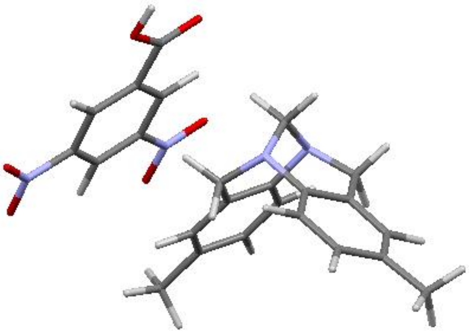
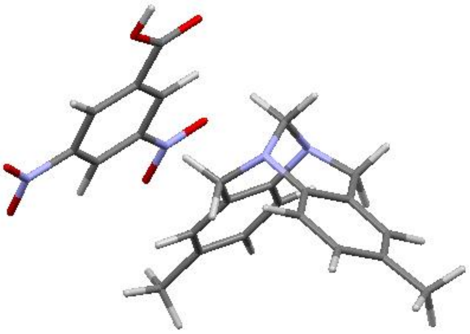
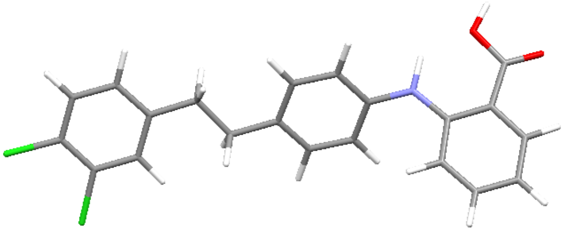
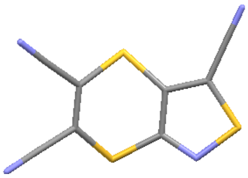
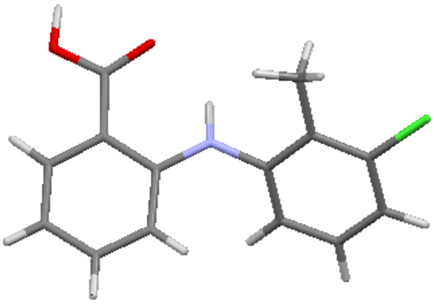
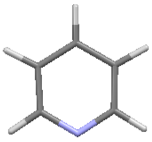
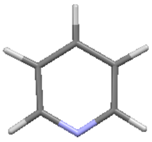
This suite provides a set of files for testing new installations of **`NEIGHCRYS_2.3.0`** and **`DMACRYS_2.3.0`** and above. The comments, instructions and examples below are to supplement information given in the paper describing the DMACRYS programme[1] and the associated manual, to act as illustrations for users (but not necessarily of best practice, as designed for fast testing).
The directory `test#_testing_REFCODE` contains a `README` and directories including `NEIGHCRYS_input`, which contains the input files:
`REFCODE.res` (Crystal structure), `bondlengths` (define molecule bonds), `dmacrys.dma` (Distributed multipoles) `dmacrys.mols` (Molecular Axes) `pote.dat`/`fit.pots`/`will01.pots` (repulsion-dispersion model).
If you want to run NEIGHCRYS interactively, then the answers you need are in `neighcrys_answers`.

All the test examples were created on Xenon using the above versions of the codes.

Test#_molecule#	Example of & crystal structure	Molecular diagram
01_I	Lattice energy minimization with **FIT exp-6 potential** and distributed multipoles. The example files are for a computational model corresponding to AXOSOW.	
02_I	Lattice energy minimization with **WILLIAMS potential**, where interaction sites on H are shifted, as contrast to 01. The example files are for a computational model corresponding to AXOSOW.	
03_II	Lattice energy minimization with a **custom potential** . The example files are for a computational model corresponding to SOXLEX.	
04_II	Lattice energy minimization with a custom potential and **without splines**. The example files are for a computational model SOXLEX. The input files for **`NEIGHCRYS`** are identical to example 3, but the output file (`SOXLEX_af395.dmain`) has been edited before running **`DMACRYS`**.	
05_III	Lattice energy minimization of a **large Z'>1 unit cell** with 15 Å cutoff. The example files are from the CSD entry KAXXAI02.	

06_III	Lattice energy minimization of **a large Z’>1** unit cell with 15 Å and **without splines**. The example files are from the CSD entry KAXXAI02. The input files for **NEIGHCRYS** are identical to example 5, but the output file (`KAXXAI02.dmain`) has been edited before running **DMACRYS**.	
07_III	Lattice energy minimization of a **large Z’>1 unit cell with 30 Å** and **without splines**. The example files are from the CSD entry KAXXAI02. The input files for **NEIGHCRYS** are identical to example 5, but the output file (`KAXXAI02.dmain`) has been edited before running **DMACRYS**.	
08_IV	Lattice energy minimization of a small **2 component system.** The example files are for a computational model corresponding to KONTIQ01.	
09_V	Lattice energy minimization of a crystal structure containing **a spherical ion**. The example files are for a computational model corresponding to FINVAZ.	
10_VI	Lattice energy minimization of a **complex salt**. The example files are for a computational model corresponding to WEMGEK.	
11_VII	**Properties** calculation of a crystal structure. The example files are for a computational model corresponding to CBMZPN10. The **NEIGHCRYS** output file (`CBMZPN_opt_III.dmain`) has been edited before running **DMACRYS**.	

12_VIII	**Properties** calculation of a crystal structure using an anisotropic repulsion **custom potential**. The example files are for a computational model corresponding to DCLBEN06. The **NEIGHCRYS** output file (`DCLBEN_beta_abi1.dmain`) has been edited before running **DMACRYS**.	
13_V	**Properties** calculation of a crystal structure containing **a spherical ion** FINVAZ. The example files are for a computational model corresponding to FINVAZ. This is also a large cell (C2/c Z=8), so takes longer to run.	
14_IX	Lattice energy minimization **with pressure**. The example files are for the experimentally observed form at high pressure (0.5 GPa) of 4-fluorotoluene (a redetermination was published as YICDIZ01, although the pressure wasn't specified in the CSD entry). The **NEIGHCRYS** output file (`YICDIZ.dmain`) has been edited before running **DMACRYS** to specify the pressure.	
15_X	Lattice energy minimization with **induction**. The example files are for a computational model corresponding to OBEQUJ.	
16_XI	**Symmetry reduction**. The example files are for a computational model corresponding to PAPTUX, which corresponds to a transition state. The run which required this symmetry reduction is given for information in the directory `reasons`.	
17_XII	**Pasting.** The example files are for TEVSOD, with a molecule optimized using **GAUSSIAN** being substituted for the crystallographically determined molecular structure.	
18_I	**Using default values.** This is a run of **NEIGHCRYS** which uses the default values for filenames. The example files are for a computational model corresponding to AXOSOW.	

19_XIII	**A large cubic cell.** This run of `NEIGHCRYS` has a Z'=1 two-component structure with 24 molecules in the whole cell. It failed with previous versions of the code.	
20_XIII	**Use of hessian.** This run of `DMACRYS` uses the hessian output from a previous run of `DMACRYS`. This would normally be used to speed up a minimisation, either as a restart or where there is a small change in the starting structure or potential model, so that the Hessian from another run is a reasonable approximation.	
21_XIV	**Use of extended mode of `NEIGHCRYS`.** This example has a long molecule, which the default settings of `NEIGHCRYS` cannot see all the atoms as connected. The extended mode of running `NEIGHCRYS` is required.	
22_XV	**Use of damped dispersion.** An example for use with non-empirical C_6, C_8 and C_{10} dispersion models.	
23_III	Lattice energy minimization of a **large Z'>1 unit cell with 30 Å** and **with splines**. In the case of example 7, the `NEIGHCRYS` output file (`KAXXAI02.dmain`) had to be edited manually to double the cutoff distance; this example **uses the extended mode of** `NEIGHCRYS` to get a 30 Å cutoff.	
24_XVI	**Use of non-empirical potentials.** Illustrating the use of more complex anisotropic repulsion terms and damped dispersion**.**	
25_XVI	**Energy refinement to include polarizability.**	

Notes on example sets.

`Data extracted from output files.`

I – AXOSOW **01.lem_fit_AXOSOW** & **02.lem_will01_AXOSOW**

This molecule was set as one of the challenges in the Fourth Blind Test of Crystal Structure Prediction.[2] The starting files are trial crystal structures generated by **MOLPAK**, with the distributed multipoles (dma) generated using **GAUSSIAN**[3] and **GDMA**,[4] as in all these examples.

The examples are given to show the differences in the FIT and Williams exp-6 potentials, whose coefficients are given in `pote.dat` (generic file type) file called `fit.pots` or `will01.pots` respectively. The two potentials do not only differ in the coefficients in pote.dat, but critically in the Williams potential has the hydrogen atom interaction sites moved in along the bonds by 0.1 Å to reflect the position of the centre of electron density. Further details of these two potentials, which are widely used for modelling organic crystals are given in the SI of the DMACRYS paper.[1] The wider range of atomic types and need for **NEIGHCRYS** to set up the shift the hydrogen interaction site positions for the Williams potential, leads to specific questions in the **NEIGHCRYS** input. The first difference in the output is the atomic types as seen in the `fort.21` (**NEIGHCRYS** output), which are used to describe the atoms in the `dmacrys.mols`, `dmacrys.dma` and potential (`fit.pots or will01.pots` in these examples).

I_1 – FIT potential

```
Inequivalent basis atoms


  atom    atomic         name         input  molecule  invert
 index    number                       name    number    flag
     1         6  C_F1_1____1_____      C1          1       F
     2         6  C_F1_2____2_____      C2          1       F
     3         6  C_F1_3____3_____      C3          1       F
     4         8  O_F1_1____4_____      O1          1       F
     5         1  H_F1_1____5_____      H1          1       F
     6         1  H_F1_2____6_____      H2          1       F
     7         1  H_F1_3____7_____      H3          1       F
     8         1  H_F1_4____8_____      H4          1       F
```

I_2 – Williams potential

```
Inequivalent basis atoms


  atom    atomic         name         input  molecule  invert
 index    number                       name    number    flag
     1         6  C_W3_1____1_____      C1          1       F
     2         6  C_W3_2____2_____      C2          1       F
     3         6  C_W3_3____3_____      C3          1       F
     4         8  O_W1_1____4_____      O1          1       F
     5         1  H_W1_1____5_____      H1          1       F
     6         1  H_W1_2____6_____      H2          1       F
     7         1  H_W1_3____7_____      H3          1       F
     8         1  H_W1_4____8_____      H4          1       F
```

The new hydrogen interactions sites required if Williams and foreshortening are requested in the **NEIGHCRYS** input are also given in `fort.21`

```
Hydrogen positions have been foreshortened.
 Positions of all atoms (with hydrogens not foreshortened)
 in the local axis system and centre of mass of the molecule
 with foreshortened hydrogens for molecule    1


basis No.  Species         x y z (Angstroms)       Mass

   1 C_W3_1____     -1.458147    -1.140153     0.000056    12.010700
   9 C_W3_2____     -0.777876     0.015814     0.000056    12.010700
  17 C_W3_3____      0.694209     0.015814     0.000056    12.010700
  25 O_W1_1____      1.379980     1.032476    -0.000193    15.999400
  33 H_W1_1____     -0.937054    -2.089416     0.001293     1.007940
  41 H_W1_2____     -2.537575    -1.172471     0.000375     1.007940
  49 H_W1_3____     -1.271827     0.978748    -0.001202     1.007940
  57 H_W1_4____      1.158373    -0.988909     0.000688     1.007940

.
.
.

Foreshortened hydrogen atom positions in the same
 local axis system

basis No.  Species         x y z (Angstroms)       Mass

  33 H_W1_1____     -0.985175    -2.001756     0.001179     1.007940
  41 H_W1_2____     -2.437620    -1.169478     0.000345     1.007940
  49 H_W1_3____     -1.226185     0.889771    -0.001086     1.007940
  57 H_W1_4____      1.116434    -0.898128     0.000631     1.007940
```

This data is used to calculate the distributed multipoles with the H nuclei in the foreshortened positions, using options in **GDMA**,[4] to analyse the ab initio wavefunction with the H nuclei in their true positions. Hence, the dma's in the two examples differ: not only in the H atom positions and multipoles, but also the non-hydrogen atoms will have the same positions (relative to the local axis system) but different multipoles because of the change in allocation of the electron density between the sites caused by the shift in H positions. However, as shown below, although the various contributions to the lattice energy change, the total electrostatic contribution to the initial lattice energy does not change by much compared with the difference in the repulsion-dispersion potential. Note that the change in potential does make a considerable difference to the structure at the lattice energy minimum.

FIT First evaluation of lattice energy

```
Contributions to lattice energy (eV per unit cell [kJ/mol])
 Z =         8
 Ewald summed charge-charge energy.......=  -0.90244160E+01[
-0.10883959E+03 ]
 Intra-molecular charge-charge energy....=  -0.78227800E+01[
-0.94347178E+02 ]
 Inter-molecular charge-charge energy....=  -0.12016360E+01[
-0.14492414E+02 ]
               Total charge-dipole energy=   0.20422449E+00[
0.24630636E+01 ]
               Total dipole-dipole energy=   0.17972682E+00[
0.21676078E+01 ]
 Total charge-dipole+dipole-dipole energy=   0.38395132E+00[
0.46306713E+01 ]
 Higher multipole interaction energy.....=  -0.75325700E+00[
-0.90847081E+01 ]
 Total isotropic repulsion-dispersion....=  -0.20073845E+01[
-0.24210199E+02 ]
 Total anisotropic repulsion energy......=   0.00000000E+00[
0.00000000E+00 ]
 Intermolecular induction energy.........=   0.00000000E+00[
0.00000000E+00 ]
 PV energy..(P =   0.00E+00 Pa).........     0.00000000E+00[
0.00000000E+00]
 Total lattice energy...................=  -0.35783261E+01[
-0.43156649E+02 ]
```

Williams First evaluation of lattice energy

```
Contributions to lattice energy (eV per unit cell [kJ/mol])
 Z =         8
 Ewald summed charge-charge energy.......=  -0.76909972E+01[
-0.92757803E+02 ]
 Intra-molecular charge-charge energy....=  -0.67563847E+01[
-0.81485844E+02 ]
 Inter-molecular charge-charge energy....=  -0.93461253E+00[
-0.11271959E+02 ]
               Total charge-dipole energy=   0.39674038E-02[
0.47849147E-01 ]
               Total dipole-dipole energy=   0.14317093E+00[
0.17267229E+01 ]
 Total charge-dipole+dipole-dipole energy=   0.14713833E+00[
0.17745720E+01 ]
 Higher multipole interaction energy.....=  -0.74209572E+00[
-0.89500967E+01 ]
 Total isotropic repulsion-dispersion....=  -0.21696973E+01[
-0.26167785E+02 ]
 Total anisotropic repulsion energy......=   0.00000000E+00[
0.00000000E+00 ]
 Intermolecular induction energy.........=   0.00000000E+00[
0.00000000E+00 ]
 PV energy..(P =   0.00E+00 Pa).........     0.00000000E+00[
0.00000000E+00]
 Total lattice energy...................=  -0.36992673E+01[
-0.44615268E+02 ]
```

II – SOXLEX **03.lem_custom_spli_SOXLEX** & **04.lem_custom_nospli_SOXLEX**

This example shows how the user makes their own definition of the atomic types, and uses an anisotropic atom-atom repulsion potential. This crystal structure was set as one of the challenges in the Fourth Blind Test of Crystal Structure Prediction.[2] The starting files are trial crystal structures generated by **MOLPAK**, with the dma generated using **GAUSSIAN**[3] and **GDMA**.[4] The repulsion dispersion potential was generated using **SAPT(DFT)**.[5]

A custom potential has different atomic types from FIT or WILLIAMS. The `labels` file lists all atoms from the input crystal structure file and assigns them the potential types which are used in the `dmacrys.mols`, `dmacrys.dma` and potential (`pote.dat`) files.

The `labels` file, defining atomic types

```
Br2    BR
Br1    BR
Cl     CL
F      FL
C1     CA
C3     CC
C4     CA
C5     CB
H1     HY
C6     CD
C2     CB
H2     HY
```

The anisotropic atom-atom repulsion potential requires the definition of a local axis system for each atom, and the anisotropic potential needs to be defined for every pair of atom types:

Starting excerpt from `dmacrys.mols` file, showing definition of local axis on a Cl atom

```
MOLX 1
X LINE   C_CC_2____   C_CD_5____   3
Y PLANE  C_CC_2____   C_CD_5____   3 C_CA_1____   1
ANIS
ClCL_1____
Z LINE C_CC_2____   ClCL_1____   1
X PLANE C_CC_2____   C_CA_1____   1 C_CB_6____   2
C_CC_2
```

Excerpt from `pote.dat` file, showing the anisotropic repulsion potential for Br…Br

```
BUCK  BrBR      BrBR
    2662.410975   0.330736   120.676039  0.0  70.0
ANIS  BrBR      BrBR
0 0 0 1 1  0.122057
0 0 1 0 1  0.122057
0 0 0 2 2 -0.237815
0 0 2 0 2 -0.237815
ENDS
```

The output has

```
Total isotropic repulsion-dispersion....=             -5.8978[            -142.2616 ]
Total anisotropic repulsion energy......=              2.7328[              65.9171 ]
```

which is slightly misleading as when a custom (anisotropic) repulsion is used, all the repulsion, isotropic and anisotropic, comes to 65.9171 kJ/mol and the dispersion contribution is -142.2616 kJ/mol.

NEIGHCRYS automatically sets up the limits used in summing the contributions to the lattice energy. These are a compromise between timing and accuracy and may need changing for different studies. Splines have been introduced rather than abrupt cutoffs in the direct space summations, so to give continuous first derivatives. The effect of splines using the default cutoff (see next example III) is shown, with examples 3 and 4 respectively. The line to bring the splines into play is automatically written out into the `*.dmain` file.

```
SPLI 2.0 4.0
```

This is manually removed from example 4, so that the repulsion-dispersion energy stops abruptly at 15 Å, which is only marginally longer than the *c* vector. The effect of the splines is expected to be much larger for this molecule than for III or other C/N/O/H molecules, because the dispersion coefficients for Br and Cl are much larger than for first row atoms, their repulsion is longer range, and they have significant atomic quadrupoles, so the inter atomic potentials at the cutoff can be much larger and not necessarily attractive.

II_3 – With splines

```
Initial Lattice Energy:        -84.6923 kJ/mol
Final Lattice Energy:          -85.1785 kJ/mol
                     a (Ang)     b (Ang)     c (Ang)   alpha (Deg)
beta (Deg) gamma (Deg)
   Initial =>      3.8052     13.7907     14.5314     90.0000
93.7800     90.0000
     Final =>      3.8430     14.0048     14.5186     90.0000
92.5989     90.0000
F =      8.374435
Total run time.........................          2.380000
```

II_4 – Without splines

```
Initial Lattice Energy:        -85.8975 kJ/mol
Final Lattice Energy:          -86.1616 kJ/mol
                     a (Ang)     b (Ang)     c (Ang)   alpha (Deg)
beta (Deg) gamma (Deg)
   Initial =>      3.8052     13.7907     14.5314     90.0000
93.7800     90.0000
     Final =>      3.8286     13.8841     14.6405     90.0000
94.4913     90.0000
F =      2.759047
Total run time.........................          1.600000
```

III – KAXXAI02 **05.largecell_KAXXAI** , **06.largecell_KAXXAI_nospli** and **07.largecell_KAXXAI_30ang**

This example illustrates the use of experimental X-ray structures as input, including when there are two symmetry independent molecules in the asymmetric unit cell. Test 5 uses summation defaults, which are contrasted with other treatments of the direct summation in tests 6 and 7. This molecule, tolfenamic acid, was studied as part of a series of fenamic acids.[6] The starting file was the crystal structure determination from the CSD, but with the atoms renumbered (to conform to the numbering scheme used in the rest of the series).

Since this is an experimental X-ray structure, the positions of the hydrogen atoms suffer from the systematic foreshortening of bonds to hydrogen. **NEIGHCRYS** has the question

```
Do you want to standardise bond lengths to hydrogen?
```

and the response

```
y(es)
```

will automatically change the hydrogen atomic positions by elongating the bond lengths to hydrogen to standard neutron values.[7] This can make a considerable difference to the results of the modelling. The hydrogen atom positions do not need correcting if the crystal structure has been determined by neutron diffraction, or the molecular structure obtained by ab initio optimisation, as the bond lengths to hydrogen should be similar or more accurate.

Although the two molecules in the asymmetric unit are the same, the axis system must be defined for each molecule, and the distributed multipoles calculated separately for each molecule to reflect the differences in conformation. Generating the dma for a two-component system requires generation of each dma separately (using **GAUSSIAN**[3] and **GDMA**[4]) and the two combined using **gdmaneighcrys** (supplied with the **DMACRYS**/**NEIGHCRYS** release bundle).

Definition of axis system for two molecules

```
MOLX 2
X LINE  C_F1_2____  C_F1_5____  3
Y PLANE C_F1_2____  C_F1_5____  3 N_F1_1____   2
X LINE  C_F1_16___  C_F1_19___  3
Y PLANE C_F1_16___  C_F1_19___  3 N_F1_2____   2
ENDS
```

Note that corresponding atoms have been used to define the axis system. However, as the molecules differ in the central torsion angle and hence centre of mass, there are differences in the coordinates of all atoms in the local axis system.

Contrasting the `.dma` entry for two equivalent atoms in the same molecule.

```
  2    C_F1_2____          -0.742683   5.289326   0.071526
Next   3    Limit  4
  -0.059318
   0.002371  -0.008579  -0.044884
  -1.263432  -0.020244  -0.019694   0.061451  -0.020968
  -0.015451  -0.320041  -0.143841   0.004144  -0.033650  -
1.111576   0.161357
  -1.713140  -0.048270  -0.074806   0.249255  -0.226941
0.032375  -0.002643
  -0.079820  -0.184937
```

```
 32    C_F1_16___          -0.518412   5.187897  -0.826132
Next  33    Limit  4
  -0.063162
   0.007418  -0.007997  -0.047917
  -1.276015  -0.042648  -0.007954   0.063306  -0.011778
  -0.016989  -0.312273  -0.146901   0.026483   0.015987  -
1.112546   0.153051
  -1.770809  -0.095468   0.051984   0.271955  -0.220172
0.021388  -0.011882
  -0.083770  -0.195849
```

The molecule itself is quite large, having a distance of 9.79 Å between the two most separated hydrogen atoms. The cutoff over which **DMACRYS** calculates intermolecular interactions is written in the `*.dmain` file by **NEIGHCRYS**. By default, the limit of the repulsion-dispersion potential is 15 Å, and the higher multipole contributions are calculated for all atoms in molecules whose centre of mass are within 15 Å. The limit of the repulsion-dispersion in the potential file can be greater than this (it is 70 Å in the files provided with the distribution), but it is overridden by the `*.dmain`. Ideally the summation limits should not be exactly an integer number of lattice vectors.

The three examples given for the lattice energy minimization of KAXXAI02 are (5) with **NEIGHCRYS** defaults of 15 Å cutoffs and splines, (6) with **NEIGHCRYS** default of 15 Å cutoffs, but no splines and (7) with a longer 30 Å cutoff and no splines. Note that since **DMACRYS** does not know that the two molecules in the asymmetric unit cell are the same molecule, all lattice energies need to be divided by 2 to be strictly in kJ/mol and comparable with the lattice energy of the Z'=1 polymorphs of tolfenamic acid.

III_5 – 15 Å cutoff and splines

```
CUTO   28.065000   0.534474
RDMA    0.534474
.
.
.
SPLI 2.0 4.0
```

```
Initial Lattice Energy:       -268.4195
kJ/mol
Final Lattice Energy:         -276.3210
kJ/mol
```

```
                          a (Ang)    b (Ang)
c (Ang)  alpha (Deg) beta (Deg) gamma
(Deg)
   Initial =>      7.6356    11.3050
28.0650    90.0000    93.0300
90.0000
     Final =>      7.7417    11.5427
27.8747    90.0000    91.2818
90.0000
```

```
F =    20.042020
```

```
Total run time...     24.500000
```

III_6 – 15 Å cutoff without splines

```
CUTO   28.065000   0.534474
RDMA    0.534474
.
.
.
```

```
Initial Lattice Energy:       -267.3524
kJ/mol
Final Lattice Energy:         -275.3161
kJ/mol
```

```
                          a (Ang)    b (Ang)
c (Ang)  alpha (Deg) beta (Deg) gamma
(Deg)
   Initial =>      7.6356    11.3050
28.0650    90.0000    93.0300
90.0000
     Final =>      7.7493    11.5629
27.8446    90.0000    91.2531
90.0000
```

```
F =    22.245230
```

```
Total run time....          17.740000
```

III_7 – 30 Å cutoff without splines

```
CUTO   28.065000   1.068948
RDMA    1.068948
.
.
.
```

```
Initial Lattice Energy:       -271.8905
kJ/mol
Final Lattice Energy:         -279.7492
kJ/mol
```

```
                          a (Ang)    b (Ang)
c (Ang)  alpha (Deg) beta (Deg) gamma
(Deg)
   Initial =>      7.6356    11.3050
28.0650    90.0000    93.0300
90.0000
     Final =>      7.7436    11.5457
27.8533    90.0000    91.2849
90.0000
```

```
F =    20.564110
```

```
Total run time            104.269997
```

When calculating the interatomic interactions over a larger number of molecules (example 7 with 30 Å limits to interaction calculation), the accuracy of the calculation is much greater as the longer range interactions are included, but the time taken is much longer. Increasing the cutoff or adding splines usually makes the lattice energy slightly lower because the attractive dispersion is the longest range contribution.

IV – KONTIQ01 **08.2comp_KONTIQ**

This illustrates using two different molecules in the asymmetric unit, with one being water. Gallic acid monohydrate was set as one of the challenges in the Fifth Blind Test of Crystal Structure Prediction,[8] to predict the structures of two new polymorphs, with this structure and that of another polymorph already published. It also had the complication of being a hydrate. Further screening resulted in characterising a further monohydrate, i.e. five polymorphs in all.[9]

The starting files in this example are from the end point of a **CrystalOptimizer** calculation, which optimizes the molecular conformation and crystal lattice together, including generating the .dma using **GAUSSIAN**[3] and **GDMA**[4] for sufficient conformations that a database can be used to speed these calculations over a large set of crystal structures.[10] Note that **gdmaneighcrys** has to be used as part of the process to combine the gallic acid and water dmas.

DMACRYS automatically assigns hydrogen atoms in water molecules as a different atomic type – H_Wa. The *exp-6* potential used for the water hydrogens was the same as for other polar hydrogen atoms in this case, but a different potential could have been chosen for H_Wa without the need to use a custom potential and `labels` file. Since the `pote.dat` *exp-6* input is required for each pair of atomic types, the **`crosspot`** utility supplied with the **`DMACRYS`**/**`NEIGHCRYS`** release bundle is useful for generating the unlike interaction parameters using the combining rules for extensions to the *exp-6* potentials of the FIT or Williams type.

V – FINVAZ **09.salt_FINVAZ** & **13.properties_FINVAZ**

Amantidine hydrochloride is an example of a lattice energy minimization, using the Williams potential, of a salt containing a spherical ion. In this case, the dma is generated for the molecular ion using **`GAUSSIAN`**[3] and **`GDMA`**[4] and the resulting `dmacrys.dma` file is manually edited to add the unit negative charge for the chloride ion. Rotations of the spherical chloride ion are meaningless; hence it does not require an axis system etc. It is also an example of a centred cell, C2/c (Z=8, Z′=1).

Salts such as FINVAZ have lattice energies that are orders of magnitude more stabilising than neutral systems, because of the high electrostatic interaction between the two species in the crystal. Nonetheless, as the properties calculation shows, such structures still have phonon modes of comparable frequencies to neutral organic molecules.

VI – Ephedrinium Tartrate **10.largesalt_WEMGEK**

Ephedrinium Tartrate is provided as an example of a lattice energy minimization of a salt with two large molecular components. It is a structure where the hydrogen atoms were positioned following a CSP study.[11] The same considerations as in previous examples should be made, namely it has large lattice energy, and the dma needs to be calculated separately for the two species and combined using **`gdmaneighcrys`**.

VII – CBMZPN10 **11.properties_CBMZPN**

`DMACRYS` can calculate the second derivative properties of the crystal at the lattice energy minimisation, namely the elastic constants[12] and k=0 phonon frequencies.[13] This is done with accurate second derivatives of the lattice energy, not the estimates made by updating the Hessian matrix used within the lattice energy minimisation. (These estimated second derivatives are used to calculate an approximate elastic constant matrix and eigenvalues of the Hessian to test whether the Born stability criterion is met, or whether the structure is a transition state, see **16.symmred_PAPTUX**). The elastic tensor is usually aligned so that *z* is along *c, x* is parallel to *a* and *y* is in the *ab* plane, but please check `fort.21` for higher symmetry space groups. The lowest eigenvalue and eigenvector of the shear submatrix is calculated as a guide to whether the crystal has a particularly weak plane. A range of properties of a microcrystalline aggregate, by various approximate averaging procedures,[14] are also reported.

The example of a properties calculation with the FIT potential is for the most stable polymorph of carbamazepine (form III). The example files here are a lattice energy minimum found in a rigid molecule CSP study of carbamazepine.

In order to calculate second derivative properties, it is usual to start at a lattice energy minimum (`fort.16` from a previous standard lattice energy minimisation run) to save the time in minimising with the more expensive and accurate 2nd derivatives calculation. This is why in the example output the lattice energy changes so very little in the `fort.12` and why the goodness of fit (F) is so low.

To run a properties calculation, following a **`NEIGHCRYS`** run starting from an estimated lattice energy minimum, the `*.dmain` must be edited to change the line that said "STAR PLUT" to say "STAR PROP" and remove the NOPR directive so that the program uses the most accurate second derivatives. It is also necessary to increase the accuracy of the Ewald summation by adding the line ACCM 100000000 in the section of the `*.dmain` file that deals with changes to default parameters.

<table>
<tr><th>Output from properties calculations</th><th></th></tr>
<tr><td><pre>
Zone Centre Phonon Frequencies
    THz   cm-1
  --------   --------
      0.0000   0.0000
      0.0000   0.0000
      0.0000   0.0000
</pre></td><td>The first 3 frequencies should be zero, to within numerical error.</td></tr>
</table>

```
      1.2704           42.3756
      1.3652           45.5384
      1.4234           47.4784
      1.5027           50.1256
      1.6125           53.7867
      1.6128           53.7961
      1.7326           57.7942
      2.0264           67.5939
      2.0904           69.7281
      2.2966           76.6065
      2.4722           82.4652
      2.5321           84.4618
      2.6035           86.8428
      2.7487           91.6871
      3.0024          100.1495
      3.0663          102.2815
      3.1597          105.3979
      3.2436          108.1949
      3.8337          127.8800
      3.9112          130.4624
      4.0285          134.3770
```

```
MECHANICAL PROPERTIES CALCULATIED FROM HESSIAN MATRIX


 Elastic stiffness tensor (Cij): GPa (10**10 DYNE/CM**2)
     16.88393      7.81752      9.43472      0.00000     -3.47841      0.00000
      7.81752     32.47090      3.46956      0.00000      0.32893      0.00000
      9.43472      3.46956     13.72289      0.00000     -0.68397      0.00000
      0.00000      0.00000      0.00000      5.99660      0.00000     -0.63703
     -3.47841      0.32893     -0.68397      0.00000     11.35118      0.00000
      0.00000      0.00000      0.00000     -0.63703      0.00000     11.39759

 Born stability criteria satisfied.
 Lowest eigenvalue of shear submatrix of Cij =    5.92248 GPa
 Corresponding eigenvector     0.99330   0.00000   0.11557 )


 Elastic compliance tensor (Sij): GPa^(-1) (10**-10 CM**2/DYNE)
      0.11605     -0.02046     -0.07303      0.00000      0.03176      0.00000
     -0.02046      0.03528      0.00480      0.00000     -0.00700      0.00000
     -0.07303      0.00480      0.12111      0.00000     -0.01522      0.00000
      0.00000      0.00000      0.00000      0.16776      0.00000      0.00938
      0.03176     -0.00700     -0.01522      0.00000      0.09711      0.00000
      0.00000      0.00000      0.00000      0.00938      0.00000      0.08826

 Mechanical properties calculated for a microcrystalline aggregate.
 Bulk modulus from elastic constants (Voigt averaging):    11.61348 GPa
 Bulk modulus from compliance constants (Reuss averaging):    10.52026 GPa
 Arithmetic mean:    11.06687 GPa
 Geometric mean:    11.05336 GPa

 Shear modulus from elastic constants (Voigt averaging):     8.57280 GPa
 Shear modulus from compliance constants (Reuss averaging):     5.99050 GPa
 Arithmetic mean:     7.28165 GPa
 Geometric mean:     7.16627 GPa

 Young's modulus from elastic constants (Voigt averaging):    20.63980 GPa
 Young's modulus from compliance constants (Reuss averaging):    15.10453 GPa
 Arithmetic mean:    17.87216 GPa
 Geometric mean:    17.65657 GPa

 Poisson's ratio from elastic constants (Voigt averaging):     0.20380 GPa
 Poisson's ratio from compliance constants (Reuss averaging):     0.26071 GPa
 Arithmetic mean:     0.23225 GPa
 Geometric mean:     0.23050 GPa

 Single crystal Young's modulus along optical axes     x-component:     8.61669 GPa
     y-component:    28.34411 GPa
     z-component:     8.25685 GPa
     arithmetic mean:    15.07255 GPa
```

Experimental elastic constants and phonon frequencies are often not available, and the main reason for calculating these properties is to estimate the zero-point vibrational energy and thermal contribution to the Helmholtz free energy. In this example, the resulting `*.dmaout` file has been automatically analysed to extract the phonon frequencies[13] and elastic constants.[12] More recent work by Nyman and Day[15, 16] has developed the use of **DMACRYS** to converge free energy differences between polymorphs, by using supercells to sample the Brilloiun zone. Their utilities **AutoLD**, and **AutoFree** for doing such calculations are included in the release bundle.

```
Average linearly extrapolated Debye frequency:
 (scaled by   1.00000000000000       )
                        wD (cm-1) =    59.8187608576981

 Average sinusoidaly extrapolated Debye frequency:
 (scaled by   1.00000000000000       )
                        wD (cm-1) =    45.4260764580391
 !! Using this value for the Debye frequency !!

 Zero-Point Energy Calculations:
 ZPE from optical modes (kJ/mol) =   2.57051461579617
 ZPE from acoustic modes (kJ/mol) =  0.152836113079392
 Total ZPE (kJ/mol) =    2.72335072887557
 -----------------------

 entropy worked out for T (K) =    298.000000000000
 -------------------------------------
 Entropy from optical modes (J/molK) =  -87.2146696803396
 Debye x =   0.219320687518172
 Debye function =   0.920152602545306
```

```
kD(x) bit =   -1.91265860137880
entropy from acoustical modes (J/molK) :
from Debye fiunction bit (J/molK) =   -2.07364893717513
from other bit (J/molK) =   -15.7096067768345
Total Entropy (J/molK) =   -104.997925394349

thermal energy worked out for T (K) =   298.000000000000
--------------------------------------------
thermal E from optical modes (kJ/mol) =  -15.3634642623644
thermal E from -kTD(x) (kJ/mol) = -0.569972263210882
thermal E from second bit (kJ/mol) =  -3.01950438657552
Total Thermal Energy (kJ/mol) =   -18.9529409121508
---------------------------------
Vibrational Free Energy (including ZPE):
                    Fvib (kJ/mol) =  -16.2295901832753
---------------------------------
```

VIII – DCLBEN06 **12.properties_DCLBEN**

This is an example of a properties calculation for the β triclinic P-1 Z′=0.5 polymorph of dichlorobenzene with a custom potential using a non-empirically derived atom-atom repulsion-dispersion potential for anisotropic chlorine.[17] This illustrates the more accurate type of potential that is likely to be needed for studying properties which are very sensitive to the 2nd derivatives, as shown by the comparison with the recorded low temperature spectrum.[18]

VIII_12 from `KONTIQ_A2312.dmaout` file	Experimental room temperature spectrum[18]
Zone Centre Phonon Frequencies (below)	cm^{-1} Three zero frequency modes, translating entire crystal 56 65 103 – Fortuitously close!

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

Only one molecule in the unit cell gives few lattice modes, but the triclinic cell has a full elastic tensor

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

IX - 4-fluorotoluene **14.press_YICDIZ**

The starting file in this example is a crystal structure determination where the liquid was forced to crystallize at high pressure and the X-ray data collected under those extreme conditions.[19]

Following the NEIGHCRYS run, the `YICDIZ.dmain` needs to be edited to add a line to include pressure. “PRES 0.5 GPa” after the CONP directive.

The resulting lattice energy from the `fort.12` is very high because it includes the PV term.

```
Initial Lattice Energy:       -11.4386 kJ/mol
Final Lattice Energy:         -11.9699 kJ/mol
```

X – OBEQUIJ **15.induction_OBEQUJ**

This illustrates the calculation of induction energy (sometimes called polarization energy, as we are using the long-range part of the induction energy, as calculated from point polarizabilities and multipoles) and lattice energy minimisation, including this term. The inclusion of damped induction and dispersion up to C_{10} are new features of **DMACRYS** for research work using non-empirical potentials.

This molecule was set as one of the challenges in the Fifth Blind Test of Crystal Structure Prediction.[20] The example uses the ab initio optimised molecular structure and has a non-empirical potential (c.f. SOXLEX[5] derived using **CamCASP**[21]) which has been fitted excluding the induction energy. The modelling of the induction energy using a distributed dipolar polarizability model[1] is the novel feature of this example. The molecular structure, atomic multipole moments, dipolar polarizability tensors and atom-atom isotropic C_6 dispersion coefficients were derived from the PBE0 exchange-correlation functional and the Sadlej pVTZ basis set with the Tozer-Handy asymptotic correction. The CUSTOM repulsion-dispersion model assumed that the parameters were transferable between all hydrogens and the four carbon atoms bonded to hydrogen (see `labels` file). This proved to be a lousy model potential, giving rise to considerable slippage in the *ab* plane, from deficiencies in the repulsion-dispersion potential. The *c* vector is large, so a larger cutoff should be used, but this significantly increases the computer time.

Note that the induction energy has to be iterated to convergence, so there is numerical noise in taking numerical derivatives. Hence the induction energy is only evaluated at a given structure. (i.e. in an optimisation, the induction energy is evaluated at the initial and final structure, and the forces from the induction energy are not used in the minimisation.)

The distributed dipolar polarizabilities are in the file `dmacrys.dma.pol`, which starts:

```
# Static polarizabilities

  1     C_C1_1____        -0.277986 -1.883193 -0.000535        RANK  1
    2.46610
    0.00000   14.52040
    0.00000    4.63450   12.08170

  2     C_C2_2____         0.816974  0.674908 -0.000979        RANK  1
    2.67470
    0.00000   23.67240
    0.00000    4.44500   17.25500
```

This is automatically read-in by **`NEIGHCRYS`** provided that the need for induction is specified near the start of the `dmacrys.mols` file by specifying the induction damping coefficient DIND, for example

```
MOLX 1
X LINE  C_C2_2____   N_N1_1____ 1
Y PLANE C_C2_2____   N_N1_1____ 1 O_O1_1____   2
DIND 1.0885
ANIS
C_C1_1____
Z LINE C_C1_1____   O_O1_1____   1
X PLANE C_C1_1____   O_O1_1____   1 C_C2_2____   1
```

In the `*.dmaout` file, the polarizabilities are written out, and the phrase “Induction damping has been requested” precedes the damping parameters. The induction calculation at the starting structure reports

```
First order induced moments (atomic units)
Atom Label          Q10           Q1c           Q1s
C_C1_1____1____  -0.003618019  0.011915082  0.075723632
C_C1I14___17___   0.003659108  0.012115435  0.075643569
C_C2_2____2____  -0.008601462  0.138004038  0.154284011
.
.
.
N_N1_1____7____  -0.009497820  0.016845367  0.049625221
N_N1I14___59___   0.009513033  0.016922579  0.049644818
N_N2_2____8____  -0.024434997 -0.047180778  0.040711153
N_N2I15___66___   0.024418822 -0.047173454  0.040708845
O_O1_1____9____   0.005452855 -0.012324706  0.096145953
O_O1I14___73___  -0.005383297 -0.012226963  0.096193965
.
.
.
H_H1_4____13___  -0.003580690 -0.001161334 -0.005492413
H_H1I17___101__   0.003580690 -0.001161334 -0.005492413
First-order induction energy  -6.72028888  kJ/mol.
Converged induced moments (atomic units)
Atom Label          Q10           Q1c           Q1s
C_C1_1____1____  -0.006422005  0.032483996  0.128535480
C_C1I14___17___   0.006461885  0.032705296  0.128461236
C_C2_2____2____  -0.013724200  0.185647096  0.218022713
.
.
.
N_N1_1____7____  -0.011628952  0.039485056  0.071653984
N_N1I14___59___   0.011638417  0.039596528  0.071663080
N_N2_2____8____  -0.023572019 -0.050642876  0.062891544
N_N2I15___66___   0.023529057 -0.050630339  0.062890475
O_O1_1____9____   0.010599723 -0.011842498  0.151069302
O_O1I14___73___  -0.010532090 -0.011733757  0.151117136
.
.
.
H_H1_4____13___  -0.002437387  0.001578367 -0.004484172
H_H1I17___101__   0.002440094  0.001584326 -0.004475367
Induction energy converged to  -9.64709323 kJ/mol with  17 iterations.
```

The induced dipole moments should be modest, reflecting the atoms which are most polarizable, with the induction energy being stabilising and converge in a reasonable number of iterations. The induction energy is written out as a component of the initial and final lattice energy. The initial energies and induced moments should be well reproduced, but minor discrepancies in the final structure and energy may just reflect numerical noise.

XI – PAPTUX **16.symmred_PAPTUX**

Lattice energy minimisation within the constraints of space group symmetry may lead to a structure which is not a true minimum, as detected by considering the eigenvalues of the second derivative matrix (~Born stability criterion). When this happens, then another run in a lower symmetry space-group, usually with more independent molecules in the asymmetric unit cell is required. This example shows the ability of **NEIGHCRYS** to generate the required new input files and run in lower symmetry.

The anti-inflammatory naproxen was studied because the structure of the marketed enantiopure form was known but not that of the racemate.[22] The crystal energy landscape showed that the racemic form was more stable, but experimentally it proved impossible to obtain single crystals, so this structure had to be determined from powder X-ray diffraction. A good match to the experimental data was obtained by the global minimum of the lattice energy landscape. However this Z'=1 structure had a negative eigenvalue of the Hessian, showing that it was a saddlepoint. This example demonstrates how the symmetry was lowered to give a true minimum, requiring a second run of **NEIGHCRYS** and **DMACRYS** to give a Z'=2 structure with the small energy lowering (~ 1 kJ/mol). Solid state NMR was used to confirm that structure was indeed *Pbca* Z'=1, confirming the estimate that even the zero-point motions would average over the Z'=2 $Pca2_1$ lattice energy minima.

The files in the directory `reason` are the original **NEIGHCRYS** and **DMACRYS** runs, showing the `fort.12` detects that the structure is not a true minimum.

```
 Warning - Non-zero eigenvalues found.
 A subgroup has a lower energy structure
```

To find the correct eigenvalue (~symmetry element) to remove, the `PAPTUX_CO1.dmaout` must be inspected. The relevant section looks like this.

```
 EIGENVALUES FOR REPRESENTATION    1
  0.54740738E+01  0.10484391E+02  0.21314702E+02  0.28925942E+02  0.32695686E+02
  0.58755977E+02
 EIGENVALUES FOR REPRESENTATION    2
  0.46788755E-13  0.41550997E+01  0.88608361E+01  0.26927779E+02  0.34219756E+02
  0.40828089E+02
 EIGENVALUES FOR REPRESENTATION    3
 -0.13293712E+01  0.20725220E-13  0.84737284E+01  0.15625808E+02  0.22016299E+02
  0.55803587E+02
 EIGENVALUES FOR REPRESENTATION    4
  0.80397293E+01  0.26443582E+02  0.30901556E+02  0.39325824E+02  0.63044816E+02
  0.74113852E+02  0.99367508E+02
 EIGENVALUES FOR REPRESENTATION    5
 -0.91065363E-14  0.10675599E+02  0.14989850E+02  0.24870560E+02  0.29247885E+02
  0.93156502E+02
 EIGENVALUES FOR REPRESENTATION    6
  0.91648862E+01  0.24404855E+02  0.39191727E+02  0.39637411E+02  0.50380072E+02
  0.79733633E+02  0.92081679E+02
 EIGENVALUES FOR REPRESENTATION    7
  0.75603086E+01  0.20745637E+02  0.32486537E+02  0.42178187E+02  0.48736699E+02
  0.73609246E+02  0.76396408E+02
 EIGENVALUES FOR REPRESENTATION    8
  0.93971337E+01  0.20082801E+02  0.28845175E+02  0.39408693E+02  0.45319387E+02
  0.71140469E+02  0.11491641E+03  0.15938635E+03  0.38729756E+03
```

In the next **NEIGHCRYS** run, the eigenvalue that is negative should be removed. In this case, the eigenvalue for representation *3* is negative and is the relevant one. (There are always 3 eigenvalues that are zero to within numerical error, for translation of the entire crystal. These are not exactly zero and so may also be negative, and are here in representations 2, 3 and 5). It can sometimes be the case that there are 2 negative eigenvalues, and it is recommended that you remove the larger magnitude one first, reminimize the structure, check the output, and run **NEIGHCRYS** again to remove the other if necessary. You should never need to remove the last representation on the list as this is the totally symmetric representation.

The subsequent run (**16.symmred_PAPTUX**) of **NEIGHCRYS** is distinguished by using this value *3* to answer the questions

```
Input zero for no symmetry subgroup or n to remove representation n
3
CVECTOR      5.51670
 Symmetry reduction for representation       3 complete
 input zero to end symmetry reduction or n to remove new representation n
0
```

which produces the files with parameters for two independent naproxen molecules: `dmacrys.new.mols` as a replacement to be used instead of the `dmacrys.mols` and `PAPTUX_C01.new.dma` instead of `dmacrys.dma`. These files are needed as input if it proves necessary to remove another representation. However, in this example, at the end of the run, a true minimum has been reached, with the `fort.12` summary file stating:

```
 Valid minimisation - converged on gradients

 Eigenvalue calculation is exact
 Minimum passed eigenvalue test
```

Change in Hessian matrix during run **16.symmred_PAPTUX**

At the start of the run with reduced symmetry, we have the negative eigenvalue appearing in the totally symmetric representation

```
EIGENVALUES FOR REPRESENTATION   1
  0.54749828E+01  0.91665656E+01  0.10486225E+02  0.21324804E+02  0.24408438E+02
  0.28940038E+02  0.32700849E+02  0.39198516E+02  0.39656679E+02  0.50404872E+02
  0.58785206E+02  0.79773166E+02  0.92096847E+02
 EIGENVALUES FOR REPRESENTATION   2
 -0.19184654E-12  0.41556496E+01  0.80411707E+01  0.88624634E+01  0.26448294E+02
  0.26940703E+02  0.30916946E+02  0.34226134E+02  0.39332327E+02  0.40848079E+02
  0.63075419E+02  0.74150025E+02  0.99385942E+02
 EIGENVALUES FOR REPRESENTATION   3
  0.28421709E-13  0.75617577E+01  0.10677549E+02  0.14992172E+02  0.20749220E+02
  0.24874684E+02  0.29262150E+02  0.32502922E+02  0.42184663E+02  0.48760752E+02
  0.73621962E+02  0.76433558E+02  0.93202329E+02
 EIGENVALUES FOR REPRESENTATION   4
 -0.13299736E+01 -0.14210855E-13  0.84752917E+01  0.93988285E+01  0.15629116E+02
  0.20086029E+02  0.22019776E+02  0.28859255E+02  0.39428316E+02  0.45327300E+02
  0.55830304E+02  0.71153052E+02  0.11497258E+03  0.15941309E+03  0.38736229E+03
```

In the final report of the eigenvalues in symmetry reduction, we have a true minimum (only 3 zero eigenvalues)

```
EIGENVALUES FOR REPRESENTATION   1
  0.62821481E+01  0.90017777E+01  0.10909412E+02  0.21923355E+02  0.24717232E+02
  0.25674871E+02  0.29355767E+02  0.37714874E+02  0.39091498E+02  0.51114580E+02
  0.60016101E+02  0.78624602E+02  0.95300860E+02
 EIGENVALUES FOR REPRESENTATION   2
  0.17763568E-13  0.43762867E+01  0.88027414E+01  0.90276714E+01  0.27077689E+02
  0.27322200E+02  0.30606861E+02  0.33087065E+02  0.35887132E+02  0.42707633E+02
  0.58616835E+02  0.74740580E+02  0.10569275E+03
 EIGENVALUES FOR REPRESENTATION   3
  0.42632564E-13  0.80571557E+01  0.10755696E+02  0.15344159E+02  0.21064826E+02
  0.23683924E+02  0.28396204E+02  0.34279322E+02  0.38682797E+02  0.49266106E+02
  0.69790339E+02  0.73566111E+02  0.92188150E+02
 EIGENVALUES FOR REPRESENTATION   4
 -0.56843419E-13  0.28814824E+01  0.88057206E+01  0.91321059E+01  0.16240193E+02
  0.19083826E+02  0.20499881E+02  0.28225705E+02  0.39943200E+02  0.42124144E+02
  0.50393546E+02  0.77415267E+02  0.11666586E+03  0.15461175E+03  0.39235526E+03
```

Note that in symmetry reduction, although the resulting structure is Z'=2, the lattice energy has not been doubled, but is only slightly lower (i.e. lattice energy at the saddle point is -134.1608 kJ/mol (Final energy in initial minimisation in `reason`) and at the minimum is -134.7353 kJ/mol). This is done so that automated symmetry reduction, as part of a CSP study, keeps all the structures on the same energy scale.

XII – TEVSOD **17.pasting_TEVSOD**

The **NEIGHCRYS** / **DMACRYS** combination is used for minimizing experimental crystal structures holding the conformation of the molecule rigid throughout. It is often desired to minimize a crystal structure with an alternative conformation of the molecule, such as the ab initio optimized conformation that is being used as input into a Crystal Structure Prediction study. **NEIGHCRYS** was written with the ability to change to a slightly different molecular structure within a crystal structure by aligning the molecule fixed axes of the new and original molecule. This will not work if there is a significant change in the molecular conformation, or the molecules are not identical. The use of the separate utility **optimalpaste** to produce a crystal structure which optimises the overlay of the two molecules is recommended in preference to this option.

The example chosen for this is Cyheptamide. Before beginning, **NEIGHCRYS** is run to set up the molecule in the local axis system. Text from the `fort.21` is then used for the **GAUSSIAN** input file, and **GAUSSIAN** is run specifying that the output should be written in atomic units. Alternatively, the output from **GAUSSIAN** in Angstroms can be used, but converted to Bohr with a utility such as http://bast.fr/angstrom-bohr/ The coordinates of the optimized geometry in atomic units are put into the `coord_to_paste_au` file with the atom labels generated by **NEIGHCRYS**. EVERY molecule in the crystal structure needs to appear in this file (with the sign of the Z coordinates inverted in inverted molecules), so it will look very similar to the end of the `fort.21` file.

When **NEIGHCRYS** is run pasting in a new molecule, the end of the `fort.21` file is first written out with the original coordinates and then with the new pasted coordinates.

I – AXOSOW **18.defaults_AXOSOW**

This example uses the same **NEIGHCRYS** input files as for **02.lem_will01_AXOSOW** but all the filenames have been changed. When **NEIGHCRYS** is run, d should be the answer to the first question, and most of the rest of the questions do not need any answers as the filenames are picked up automatically.

XIII – BT_XXV **19.largecubic_BTXXV**

This is example is of a large cell, where Z is 24. The cubic space group of Pa-3 caused problems with previous version of **NEIGHCRYS**, particularly as the two-component system is so large.

XIII – BT_XXV **20.largecubic_HESS_BTXXV**

This is an example of reuse of the hessian calculation from a previous run. Both example 19 and example 20 use exactly the same `*.dmain`, except that it has been edited to include the “HESS 1” directive in example 20, which instructs **DMACRYS** to write out the hessian at the end of the minimization, and use this file, if it exists, at the starting point of a new minimization. In this example, the `dmahessian` file is present in the files for example 20, which enables **DMACRYS** to set up the minimization using this hessian and so it runs with fewer iterations, and achieves exactly the same result for the minimization.

Results from **19.largecubic_BTXXV** (no use of hessian)

```
Number of Iterations:    25
 Lattice is P Centred. Calculated Lattice Energies
Initial Lattice Energy:      -206.0935 kJ/mol
Final Lattice Energy:        -206.4054 kJ/mol
.
.
F =      0.494052
```

```
Timing information

Program segment                               Time taken (CPU
seconds)

Time to set things up..................          4.090000
Reciprocal space part of Ewald sum......        29.169983
Real space part of Ewald sum............         1.940063
Short range potential calculation.......         0.419922

Higher multipole energy calculation

Energy calculation......................        76.470276
First derivative chain rule.............         1.339844
Second derivative chain rule............        49.269653
All other program sections..............       472.390285
Total run time..........................       635.090027
```

Results from **20.largecubic_HESS_BTXXV** (reuse of hessian)

```
Number of Iterations:    10
 Lattice is P Centred. Calculated Lattice Energies
Initial Lattice Energy:      -206.0935 kJ/mol
Final Lattice Energy:        -206.4054 kJ/mol
.
.
F =      0.494052
```

```
Timing information

Program segment                               Time taken (CPU
seconds)

Time to set things up..................          4.000000
Reciprocal space part of Ewald sum......        29.099991
Real space part of Ewald sum............         1.930038
Short range potential calculation.......         0.399963

Higher multipole energy calculation

Energy calculation......................        76.739655
First derivative chain rule.............         1.380096
Second derivative chain rule............        49.389481
All other program sections..............       130.330765
Total run time..........................       293.269989
```

This shows that the energies are exactly the same at the start and end of the minimization. There is in fact no difference in the output `fort.16` files. However, the time saving is made in reducing the number of steps required to minimize the structure, and the overall saving is over 50%.

Normally, the HESS directive is useful when the user is starting an optimization with a slightly different *.dmain file, e.g. with a slightly different molecular conformation, a slightly different dma, or a different cutoff, or to restart an optimization.

XIV – BT_XXIII **21.longcell_BTXXIII**

In this example, an unconventional cell setting has been used with an acute angle, resulting in the molecule spanning more than 3 unit cells. **NEIGHCRYS** does not assign the atoms to the same molecule if this happens. This is seen in the “reasons” folder, in the section of the `fort.21` headed “Inequivalent basis atoms”, where O_01_2 is not included in molecule 1.

```
Inequivalent basis atoms
```

```
  atom   atomic        name       input  molecule  invert
 index   number                   name   number    flag
     1       6  C_F1_1____1____     C1           1       F
     2       6  C_F1_2____2____     C2           1       F
⁞
    39       7  N_F1_1____39___     N1           1       F
    40       8  O_F1_1____41___     O2           1       F
    41       8  O_01_2____40___     O1           0       F
    42      17  ClF1_1____42___     Cl1          1       F
    43      17  ClF1_2____43___     Cl2          1       F
```

NEIGHCRYS is run in “extended mode” in this example, answering all the additional questions with the default values except

```
What value of MAXSCH do you want to use to locate whole molecules? [3]
4
```

The `fort.21` now has all the atoms in the molecule, and **DMACRYS** can run.
Note that this is not a real crystal structure, but a search-generated structure for the Blind Test, and so has many problems in the crystal structure itself. It is recommended crystal structures are reset to the conventional unit cell using a program such as **PLATON** (http://www.cryst.chem.uu.nl/spek/platon/) or **ISOCIF** (http://stokes.byu.edu/iso/isocif.php).

XV – BT_XXII **22. damped_C6_dispersion_BTXXII**

In this example, the damping parameter is included in the `dmacrys.mols` file. Note that the repulsion-dispersion potential is of the DBUC type, and so has $C_8^{\iota\kappa}$ and $C_{10}^{\iota\kappa}$ terms for each interaction, which are zero.

The `dmacrys.mols` file looks like:

```
MOLX 1
X LINE C_A1_1____ C_A6_4____ 3
Y PLANE  C_A1_1____ C_A6_4____ 3 C_A2_2____ 1
DDMP   2.47349488
ENDS
```

and the start of the `pote_same_as_CP.dat` looks like:

```
DBUC    C_A1   C_A1
        3.83545   0.3533404913   0.1704323228   0.0 0.0 0.0 70
ENDS
DBUC    C_A1   C_A2
        3.83431   0.3752002353   0.2174671841   0.0 0.0 0.0 70
ENDS
```

III – KAXXAI **23.largecell_KAXXAI_30ang**

This is exactly the same minimization as example 07, but rather than manually editing the `*.dmain` file, the larger cutoff is set with the extended question set of **NEIGHCRYS**. The extra question that is not answered with the default answer is:

```
What is the desired cutoff in Angstroms [15.0]
30
```

XVI – PYRDIN **24.dampedispersion_PYRDIN** and **25.polarizability_PYRDIN**

These illustrate the use of a non-empirical potential for pyridine in the solid state[23] where the model potential had been parameterised by using a state-of-the-art methods for defining the atomic multipoles, polarizabilities and dispersion coefficients and fitting the short range terms adequately required addition forms of anisotropic repulsion.[24]

As in example 22, the damped dispersion parameter is included in the `dmacrys.mols` file, and DBUC type repulsion-dispersion potentials are used, and anisotropy is included, for example:

```
DBUC  N_N1    N_N1
  526.634151   0.31473500    18.2665   139.6210   776.9042     0.00    70.00
ANIS  N_N1    N_N1
   0   0   0   1   1  0.05518400
   0   1   0   1   1 -0.00961700
   0   0   1   0   1  0.05518400
   1   0   1   0   1 -0.00961700
```

```
    0    0    0    2    2  0.06635000
    0    2    0    2    2 -0.08656300
    0    0    2    0    2  0.06635000
    2    0    2    0    2 -0.08656300
ENDS
DBUC   N_N1     C_C1
  650.973954    0.30405000      14.6176     92.5942   1046.8489      0.00     70.00
ANIS   N_N1     C_C1
    0    0    0    1    1  0.06924000
    0    1    0    1    1  0.01777100
    0    0    1    0    1  0.05518400
    1    0    1    0    1 -0.00961700
    0    0    0    2    2 -0.04085600
    0    2    0    2    2 -0.06018000
    0    0    2    0    2  0.06635000
    2    0    2    0    2 -0.08656300
ENDS
```

Furthermore, example 25 includes the induction energy, which is initiated through use of the `DIND 1.25` directive giving the induction damping coefficient in the `dmacrys.mols` file and the required `dmacrys.mols.pol` file with the polarizabilities.

Comparing the output from the optimisations **24.dampedispersion_PYRDIN** and **25.polarizability_PYRDIN**, it is seen that the unit cell is no different, but that the energy is different. This is because it is not possible to carry out the perfect lattice calculation in **DMACRYS** including the forces due to induction. (Expert use has shown that this approximation has very little effect on the structure.[25]) The lattice energy minimization part of the calculation is carried out neglecting the forces from the induction. However, **DMACRYS** calculates the induction energy both at the start and at the end, and adds this term to the total initial and final lattice energy.

25.dampedispersion_PYRDIN `PYR1opt.dmaout` first iteration

```
First order induced moments (atomic units)
Atom Label         Q10             Q1c             Q1s
N_N1_1____1____   0.008990743 -0.011086254 -0.028650718
C_C1_1____2____  -0.000663404 -0.039779257 -0.054350889
C_C2_2____3____  -0.003789783 -0.029083768 -0.012526122
C_C3_3____4____   0.001293661  0.024660883 -0.035313287
C_C2_4____5____  -0.003213832  0.016425376 -0.047905793
C_C1_5____6____  -0.000242076  0.075838134 -0.046018475
H_H1_1____7____   0.006698996 -0.011611686 -0.004945460
H_H2_2____8____  -0.001658823 -0.015424442 -0.003067456
H_H3_3____9____  -0.004643703  0.002112085 -0.010324937
H_H2_4____10___  -0.003659113  0.001953274 -0.007768117
H_H1_5____11___  -0.003774634  0.019094962 -0.000037930
First-order induction energy  -2.99010797  kJ/mol.
Converged induced moments (atomic units)
Atom Label         Q10             Q1c             Q1s
N_N1_1____1____   0.007457669 -0.007754083 -0.041300476
C_C1_1____2____  -0.000886896 -0.052311208 -0.076183412
C_C2_2____3____  -0.004847823 -0.034178550 -0.028088276
C_C3_3____4____  -0.000615048  0.025574195 -0.049755066
C_C2_4____5____  -0.005108418  0.022418894 -0.062840662
C_C1_5____6____  -0.002178751  0.091487579 -0.065569523
H_H1_1____7____   0.007820067 -0.014032519 -0.007400301
H_H2_2____8____  -0.001165530 -0.018095347 -0.005001532
H_H3_3____9____  -0.005597515  0.002049123 -0.012493107
H_H2_4____10___  -0.005414088  0.004487183 -0.009831232
H_H1_5____11___  -0.006524657  0.021953898 -0.002367676
Induction energy converged to  -3.84432644 kJ/mol with  14
iterations.
```

25.polarizability_PYRDIN `PYR1opt.dmaout` final iteration

```
First order induced moments (atomic units)
Atom Label         Q10             Q1c             Q1s
N_N1_1____1____   0.014226074  0.023260967 -0.038634199
C_C1_1____2____   0.006926994 -0.098149634 -0.075051120
C_C2_2____3____  -0.002777219 -0.050396623 -0.043408405
C_C3_3____4____  -0.004699829  0.006924179 -0.061537080
C_C2_4____5____   0.007121289  0.023226487 -0.066112972
C_C1_5____6____   0.003102491  0.079404706 -0.054878888
H_H1_1____7____   0.008676174 -0.020523308 -0.007068704
H_H2_2____8____  -0.003582663 -0.020731352 -0.011117880
H_H3_3____9____  -0.004164099  0.002336519 -0.011798518
H_H2_4____10___  -0.003261779  0.010213061 -0.011702622
H_H1_5____11___  -0.010716853  0.027068215  0.004596483
First-order induction energy  -4.82765443  kJ/mol.
Converged induced moments (atomic units)
Atom Label         Q10             Q1c             Q1s
N_N1_1____1____   0.014226075  0.023260967 -0.038634197
C_C1_1____2____   0.006926994 -0.098149634 -0.075051118
C_C2_2____3____  -0.002777219 -0.050396623 -0.043408404
C_C3_3____4____  -0.004699828  0.006924179 -0.061537080
C_C2_4____5____   0.007121289  0.023226487 -0.066112972
C_C1_5____6____   0.003102491  0.079404706 -0.054878887
H_H1_1____7____   0.008676173 -0.020523308 -0.007068704
H_H2_2____8____  -0.003582664 -0.020731352 -0.011117880
H_H3_3____9____  -0.004164099  0.002336519 -0.011798518
H_H2_4____10___  -0.003261779  0.010213061 -0.011702622
H_H1_5____11___  -0.010716852  0.027068215  0.004596483
Induction energy converged to  -4.82765443 kJ/mol with   2
iterations.
```

24.dampedispersion_PYRDIN `fort.12`

```
Initial Lattice Energy:         -58.1316 kJ/mol
Final Lattice Energy:           -61.9302 kJ/mol
```

```
Contributions to lattice energy (eV per primitive unit cell
[kJ/mol])  ( Z =          4)
Inter-molecular charge-charge energy....=                -
0.4502[          -10.8588 ]
Total charge-dipole+dipole-dipole energy=                -
0.0801[           -1.9319 ]
Higher multipole interaction energy.....=                -
0.1673[           -4.0349 ]
Total isotropic repulsion-dispersion....=                -
4.0616[          -97.9713 ]
Total anisotropic repulsion energy......=
2.1917[           52.8668 ]
Intermolecular induction energy.........=
0.0000[            0.0000 ]
PV energy..(P =    0.00E+00 Pa)..........=
0.0000[            0.0000 ]
```

25.polarizability_PYRDIN `fort.12`

```
Initial Lattice Energy:         -61.9760 kJ/mol
Final Lattice Energy:           -66.7578 kJ/mol
```

```
Contributions to lattice energy (eV per primitive unit cell
[kJ/mol])  ( Z =          4)
Inter-molecular charge-charge energy....=                -
0.4502[          -10.8588 ]
Total charge-dipole+dipole-dipole energy=                -
0.0801[           -1.9319 ]
Higher multipole interaction energy.....=                -
0.1673[           -4.0349 ]
Total isotropic repulsion-dispersion....=                -
4.0616[          -97.9713 ]
Total anisotropic repulsion energy......=
2.1917[           52.8668 ]
Intermolecular induction energy.........=                -
0.2001[           -4.8277 ]
PV energy..(P =    0.00E+00 Pa)..........=
0.0000[            0.0000 ]
```

Within the `PYR1opt.dmaout` file, the induced moments and induction energy are calculate for the initial crystal structure and the final crystal structure. These energies are included in the "Initial Lattice Energy" and "Final Lattice Energy" reports in the `fort.12`, and hence, as shown above, the lattice energy components differ only in the induction energy between **24.dampedispersion_PYRDIN** and **25.polarisability_PYRDIN**.

References

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