MiCMoS
Milano Chemistry Molecular Simulation
Description and User Manual

Tutorials

T5. Lattice energy by *Pixelc*

PURPOSE: In this tutorial, it is described how to use module ***Pixelc*** to compute static charge density-based interaction energies and lattice energies of the test case used in Tutorials T1, T2 and T4.

REFERENCE to main manual: Sections 3.2 (***Pixelc***); 3.2.4 (input/output); 3.2.5 (how to run); 3.2.6 (pixpar.*par*); 3.2.7 (input file format); 3.2.8 (output).

FILES: You can find all the files you need to run this tutorial here:
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T5/SAMPLExxa.den
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T5/pixpar.par
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T5/sample.inp
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T5/sample.oeh
For PIXEL calculations, a molecular charge density file computed at the MP2/6-31G** level of theory (extension .*den*) and the corresponding input (extension .*inp*) are required; you should have obtained both while working on Tutorial T2 for acetylsalicylic acid. A valid structure .*oeh* file is also needed; it has been built in Tutorial T1. Place .*oeh*, .*den* and .*inp* files, plus pertinent (Windows/Unix) macros, into your working directory.

The ***Pixmt2*** module (manual, Section 3.2.5) can produce the input for the ***Pixelc*** calculation, sample.*inp*, through the procedure shown in Tutorial T2. See manual, Section 3.2.7 for detailed explanations on the various entries in this file.

The sample.*inp* file used in this exercise is printed on the next page.

Note that atomic polarizabilities are all zero because defaults are taken, so that the atom list is just an indicator of atom types. Then follow the cutoff and the two matrix/vector pairs $\mathbf{M}_1/\mathbf{t}_1$ and $\mathbf{M}_2/\mathbf{t}_2$ (see also Appendix, Section A4), which relate the coordinates of every electron density pixel in the Gaussian standard orientation to those in the crystallographic reference system. Information on space group symmetry closes the input, in the usual format.

CAUTION: If the *nosym* keyword was used in the Gaussian calculation of the cube .*den* file (manual, Section 3.2.5), the local inertial molecular reference frame corresponds to standard orientation: $\mathbf{M}_1$ is the unit matrix and $\mathbf{t}_1$ = [0 0 0]. ***Pixmt2*** takes care of computing the correct matrices and there is usually no need to modify them.

sample.inp file for acetylsalicylic acid, to be given as input to ***Pixelc***

```
#SAMPLExx 'P 21/c'
   1   0  21   0
   0.000
   1  12  0.0000  0.0000    C
   2  12  0.0000  0.0000    C
   3  12  0.0000  0.0000    C
   4  12  0.0000  0.0000    C
   5  12  0.0000  0.0000    C
   6  12  0.0000  0.0000    C
   7  10  0.0000  0.0000    C
   8  10  0.0000  0.0000    C
   9  13  0.0000  0.0000    C
  10  28  0.0000  0.0000    O
  11  27  0.0000  0.0000    O
  12  23  0.0000  0.0000    O
  13  27  0.0000  0.0000    O
  14   2  0.0000  0.0000    H
  15   2  0.0000  0.0000    H
  16   2  0.0000  0.0000    H
  17   2  0.0000  0.0000    H
  18   3  0.0000  0.0000    H
  19   3  0.0000  0.0000    H
  20   3  0.0000  0.0000    H
  21   6  0.0000  0.0000    H
     0.000    16.000
   11.4300    6.5910   11.3950   90.0000   95.6800   90.0000
  1.000  0.000  0.000  0.000  1.000  0.000  0.000  0.000  1.000
  0.000  0.000  0.000
    0.406859 -0.733256 -0.544794
    0.436051  0.679948 -0.589516
    0.802698  0.002292  0.596381
    2.538629    3.970265    0.297080
   4
   1.00   0.00   0.00   0.00   1.00   0.00   0.00   0.00   1.00
  0.000000  0.000000  0.000000
  -1.00   0.00   0.00   0.00   1.00   0.00   0.00   0.00  -1.00
  0.000000  0.500000  0.500000
  -1.00   0.00   0.00   0.00  -1.00   0.00   0.00   0.00  -1.00
  0.000000  0.000000  0.000000
   1.00   0.00   0.00   0.00  -1.00   0.00   0.00   0.00   1.00
  0.000000 -0.500000 -0.500000
```

To proceed, open a new pixpar.*par* file:

```
vi pixpar.par
```

and type in the parameters for the PIXEL run according with manual (Section 3.2.6), as detailed also in the box below.

```
0.00  3.000   150.0   4800.0   1200.0  0
   5 0 0.000000  0.0
   5 0 0.000000  0.0
 3.0  0
```

The first line contains general limits and damping parameters. Second and third lines specify electron density trimmers for molecule A and B (if the crystal contains only a chemical specie, the third line is ineffective). The last line gives the threshold for printing molecule-molecule energies in the output and a flag (0) to have intermolecular distance referring to their centres of mass. Default quantities should be chosen in most cases; among these parameters, the

contraction level 5 in second and third lines is the only to be really crucial, as it governs to what extent adjacent pixels of charge density are averaged to produce the final operational grid (see manual, Section 3.2.2). Larger values mean cheaper but less accurate calculations. We here recommend a value of 5 for speed up the calculation, although for crystals a value of 4 is preferred; all other parameters are the default values of the Pixel theory.

The running command to use sample.*inp*, the SAMPLExxa.*den* density file and to have samplep as output prefix is:

```
./run.pixelc sample samplep SAMPLExxa
```

The program prints on screen the following information:

***Pixelc**, printout on screen*

```
  +++++++++  MiCMoS 1.0 jan 2020  +++++++++
           This is the Pixelc module


  SAMPLExx 'P 21/c'
 First molecule ( A ), total charge     0.00

   Condensation level    5
   Density steps,original  100  140  160 and condensed   20   28   32
 steps and pixel vol(A)     0.4000   0.4000   0.4000   0.06400
 original electron number  68.00129  remaining-pixels    68.00055   8084
 accept q min and max  0.1000E-05   9999.00
 screening: electrons out low and high  0.7466E-03  0.0000E+00
 renormalized total charges     68.000000  -68.000000

 ===== Start energy calculations =====
  collision parameter     0.200
   center of mass distance limits    0.00   16.00
 cells along a,b,c for lattice search    7    9    7
       76 symm operations included
 A...A energies
 i,j,d,edisp,erep
    1    2    8.273   -9.19    7.07
...
```

It is essentially a short summary of relevant computational parameters and molecule-molecule energies. In the end, ***Pixelc*** produces as output files sampleppix.*pri* (regular printout) and samplep.*mlc* (list of molecule-molecule energies). The file sampleppix.*pri* stores all the information displayed on screen, and other parameters detailed in the description below.

After the obvious echo of input atomic data, the relevant part of is as follows:

***Pixelc** output, regular printout (excerpt)*

```
   Condensation level    5
   Density steps,original  100  140  160 and condensed   20   28   32
 steps and pixel vol(A)     0.4000   0.4000   0.4000   0.06400
original electron number  68.00117  remaining-pixels    68.00045   8084
```

Note that the calculation runs with 8084 condensed pixels, each occupying 0.064 Å^3 of space. This is less accurate than for contraction 4, but good enough: note that the electron count is very close to that estimated from the original, uncondensed pixel array, and both are also very

close to the expected integer electron count printed below (68). Also note that the number of condensed density steps equals the original ones, divided by the condensation level.

Other working parameters are then summarized for checking:

Pixelc *output, regular printout (excerpt)*

```
accept q min and max  0.1000E-05   9999.00
 screening: electrons out low and high  0.7201E-03  0.0000E+00
nuclear charge,n.of electrons,input charge    68.0000   68.0012    0.0000
 polarizability,raw, tot, renorm  0.17844E+02  0.17370E+02  0.17370E+02
 renormalized total charges     68.000000  -68.000000
```

Then, the number of charge points (pixels) per atom is displayed. You can appreciate that each atom is described with 300-500 point charges.

Pixelc *output, regular printout (excerpt)*

```
no. of charge points per atom
   1  232   2  204   3  460   4  512   5  532   6  440   7  308   8  241
   9  659  10  414  11  649  12  314  13  596  14  324  15  348  16  332
  17  257  18  278  19  327  20  331  21  326
```

In the subsequent output block, the parameters related to the energy calculation are printed. First, cutoffs and cell parameters and the symmetry operations are reported.

Pixelc *output, regular printout (excerpt)*

```
===== Start energy calculations =====
  collision parameter     0.200
   center of mass distance limits    0.00   16.00
  cell parameters  11.430   6.591  11.395   90.00   95.68   90.00
 Space group matrices
   1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0    0.000  0.000  0.000
  -1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0 -1.0    0.000  0.500  0.500
  -1.0  0.0  0.0  0.0 -1.0  0.0  0.0  0.0 -1.0    0.000  0.000  0.000
   1.0  0.0  0.0  0.0 -1.0  0.0  0.0  0.0  1.0    0.000 -0.500 -0.500
 cells along a,b,c for lattice search    7    9    7
       76 symm operations included
```

The last two lines inform you that the calculation will be performed on a cluster spanning 7x9x7 unit cells, resulting in 76 surrounding molecules in the cluster when the 16 Å center of mass distance cutoff is applied.

Then, dipole energy contributions are shown:

Pixelc *output, regular printout (excerpt)*

```
 Computing cell dipole energy
 cell dipole moment components and module,debye
     0.000   0.000   0.000     0.000 energy       -0.0
```

As you are dealing with a centrosymmetric structure, such contributions are exactly 0, as expected. Finally, the coulombic and dispersion/repulsion terms are printed for the whole cluster above defined:

***Pixelc** output, regular printout (excerpt)*

```
   A molecule, Epol,damp,no-damp   -44.3  -648.3
   A...A  A...B  B...B total energies
   (Coulombic part not significant for ionic species)
 coul    -100.2     0.0     0.0  -100.2
 disp     -96.1     0.0     0.0   -96.1
 rep      124.0     0.0     0.0   124.0
 Pixel coul,pol,disp,rep,celdip,tot.,per mol.in as.un
   SAMPLExx ---   -100.2   -44.3   -96.1   124.0    -0.0  -116.6
   SAMPLExx cell dip moment(D) and Eceldip./molecule    0.000    -0.0
```

CAUTION: as noted in the output, all energies are expressed per molecule in the asymmetric unit (ASU). As in this case Z' = 1 (one molecule per ASU), the total energy (-116.6) corresponds to the molar heat of sublimation of aspirin in kJ/mol.

Note that the total lattice energy is within a few kJ/mol from the CLP and LJC values, but the coulombic and repulsion energies are largely different from the atom-atom values. As an added bonus, the energy contributions are partitioned among A···A, A···B and B···B interactions, where B is another molecule possibly present in the asymmetric unit. As in this case the asymmetric unit contains only one molecule, A···B and B···B contributions are 0.

More information is contained in the final part of the output with molecule-molecule energies (also detailed in the samplep.*mlc* file) larger than 3.0 kJ/mol:

***Pixelc** output, regular printout (excerpt)*

```
  molecule-molecule energy data for E>    3.0
   symmetry,distance,ec,epol,edisp,erep,etot
 distances between centers of mass
  a...a energies
-1  0  0  0  1  0  0  0 -1  0.000  0.500  0.500  8.273   -5.9   -2.9   -9.3    7.1  -11.0
 1  0  0  0  1  0  0  0  1  0.000 -1.000  0.000  6.591   -8.2   -3.0  -16.5    7.9  -19.8
 1  0  0  0  1  0  0  0  1  0.000  1.000  0.000  6.591   -8.2   -3.0  -16.5    7.9  -19.8
-1  0  0  0  1  0  0  0 -1  0.000 -0.500  0.500  8.273   -5.9   -2.9   -9.3    7.1  -11.0
-1  0  0  0 -1  0  0  0 -1  0.000  1.000  0.000  5.287   -0.8   -3.0  -22.6   12.5  -13.9
-1  0  0  0 -1  0  0  0 -1  0.000  2.000  0.000  7.322 -138.1  -68.3  -22.1  155.8  -72.7
-1  0  0  0 -1  0  0  0 -1  1.000  1.000  0.000  6.522   -9.6   -3.4  -19.5   10.5  -21.9
-1  0  0  0 -1  0  0  0 -1  1.000  2.000  0.000  8.257  -10.4   -2.6   -6.6    5.6  -14.0
 1  0  0  0 -1  0  0  0  1  0.000  0.500 -0.500  7.351   -2.7   -1.1  -10.3    3.4  -10.6
 1  0  0  0 -1  0  0  0  1  0.000  0.500  0.500  7.351   -2.7   -1.1  -10.3    3.4  -10.6
 1  0  0  0 -1  0  0  0  1  0.000  1.500 -0.500  6.021   -4.1   -3.8  -18.1   12.5  -13.5
 1  0  0  0 -1  0  0  0  1  0.000  1.500  0.500  6.021   -4.1   -3.8  -18.1   12.5  -13.5
```

Each row corresponds to a molecular pair; energies are always computed with respect to the reference molecule at x, y, z, and symmetry operations here displayed correspond to transforms that produce its various symmetry-related images. Energies are expressed in kJ/mol; these values compare in a proportional way with the results of the atom-atom calculations.

The samplep.*mlc* file lists all the 76 molecule-molecule pairs in the cluster. For each pair, first a table of symmetry operations is printed; it is followed by a full list of interaction energies, included those not shown in the regular .*pri* output.