MiCMoS
Milano Chemistry Molecular Simulation
Description and User Manual

Tutorials

T4. Calculation of atom-atom lattice energies

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

REFERENCE to main manual: Sections 2.1 (CLP and LJC potentials); 3.1 (**Crysaa**); 3.1.2 (crypar.*par*).

FILES: Click here to download the materials for this exercise:
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T4/crypar_CLP.par
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T4/crypar_LJC.par
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T4/sample.oeh
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T4/samplesp.oeh
You need *runcrysaa* macro available in the batch directory of the package. Files sample.*oeh* and samplesp.*oeh* can be also obtained from Tutorials T1 and T2. They both refer to ACSALA01, the $P2_1/c$ structure of acetylsalicylic acid, and differ by the atomic charges, which are compatible either to the CLP parametrization (sample.*oeh*) or the LJC one (samplesp.*oeh*). Place .*oeh* files, plus pertinent (Windows/Unix) macros, into your working directory.

First, an intervention on the crypar.*par* file is needed. Create it as a new file with any text editor; vi works fine in a Unix/Linux environment:

```
vi crypar.par
```

Then, write down instructions according to manual, Section 3.1.2, as shown in the box below. The first line specifies the print level (=1) and the type of potential (=0 CLP, =1 LJC):

crypar.par file, for CLP potentials

```
1 0                                    ipri and ipot
0.41 235.0 650.0 77000.0               standard CLP scaling parameters, eq. (2.1)
40.0 10. 3.0 0.9 999.0                 cutoff and printout limits
```

The atom-atom lattice energy calculation routine for the CLP potentials is now called:

```
./run.crysaa sample
```

In a fraction of a second, the program answers:

```
normal end of operation, crystals read     1
 Thank you for using Crysaa
```

The calculation has ended correctly and an output samplecry.*pri* file has been created.
Let's repeat the calculation with the LJC potentials. First, change the potential indicator ipot in crypar.*par* to 1:

crypar.par file, for LJC potentials

```
1 1                                         ipri and ipot
0.41 235.0 650.0 77000.0                    standard CLP scaling parameters, eq. (2.1)
40.0 10. 3.0 0.9 999.0                      cutoff and printout limits
```

Second, call again **Crysaa** against the input bearing LJC-consisent charges (see Tutorial T2 to see how to produce it).

```
                        ./run.crysaa samplesp
```

The output will be printed in samplespcry.*pri*.

CAUTION: Note that samplesp.*oeh* must be filled with a 0 line at the end, meaning that no supplementary LJC potentials are needed (manual, Section 1.4.3).

Let's now examine the first output, samplecry.*pri*:

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

     CRYS-AA Lattice energy ------   #SAMPLExx 'P 21/c'
 T/K, date, R-factor      0.0     0.    0.00
 Coulomb-London-Pauli potential coefficients
      0.410   235.000   650.000    77000.0
  cell parameters      11.4300  6.5910  11.3950   90.00   95.68   90.00
        21 atom information, fragm.,species,charge
   1   0.1534   0.5640   0.0674   1  12 -0.0218
   2   0.2462   0.4877   0.0095   1  12  0.2360
 ........
  19   0.4582   0.9604  -0.1500   1   3  0.1266
  20   0.4380   0.7283  -0.2264   1   3  0.1442
  21   0.0732   0.9878  -0.0627   1   6  0.2738
 symmetry operator matrices    4
```

After listing all atoms, each with its specie indicator (manual, Table 1.1) and charge, a sequence of the 4 symmetry operations of P2$_1$/c is given, plus estimated molecular volume (Å^3), net charge, crystal density and packing coefficient. The molecular volume is computed as a plain superposition of interpenetrating van der Waals spheres.

```
   1   1.0   0.0   0.0   0.0   1.0   0.0   0.0   0.0   1.0   0.0000   0.0000   0.0000   TR
   2  -1.0   0.0   0.0   0.0   1.0   0.0   0.0   0.0  -1.0   0.0000   0.5000   0.5000   SC
   3  -1.0   0.0   0.0   0.0  -1.0   0.0   0.0   0.0  -1.0   0.0000   0.0000   0.0000   IN
   4   1.0   0.0   0.0   0.0  -1.0   0.0   0.0   0.0   1.0   0.0000  -0.5000  -0.5000   GL
 fragm.,n.at,weight,charge+,-    1   21      180.16     2.4921  -2.4921
 fragm.,volume    1     158.4
 cell volume, density, packing coeff.
 #SAMPLExx 'P 21/c'        ---       854.23   1.401   0.742
 max c.o.m. dist vector, cells on a,b,c   40.00     5     8     5
```

The symmetry operations S are listed as 3x3 matrices with elements organized in rows in the usual order (S(1,1), S(1,2), S(1,3), S(2,1), S(2,2), S(2,3), S(3,1), S(3,2), S(3,3)) and followed by translation vector components. For example, the 4th operation correspond to +x, -1/2-y, -1/2+z. A label is also assigned to each operation, with the following meaning:

TR: pure translation (or identity);
MI: mirror plane;
AX: twofold axis;
SC: screw axis;
GL: glide plane;
IN: inversion;
CE: centering;
CI: inversion-centering;
UK: unknown operator or operator above orthorhombic system.

A block of molecule-molecule energies follows. For each molecular pair, the following quantities are indicated, in this order: first fragment id number; second fragment id number; centre-of-mass distance (Å), symmetry operation number (among those listed above), translation vector, Coulomb, polarization, dispersion, repulsion and total energies, according to eq. (2.1) in the manual.

CAUTION: All energies are always given in kJ/mol.

fragm/fragm,dist.,symm.op,Translation   Ec   Ep   Ed   Er   Etot
```
   1   1   8.394    2   0.00  -0.50  -0.50    -1.2   -1.0   -0.9    0.0    -3.1
   1   1   6.591    1   0.00  -1.00   0.00    -3.5   -4.1  -16.2    6.6   -17.1
   1   1   8.273    2   0.00  -0.50   0.50    -2.0   -2.0   -8.3    6.5    -5.8
   1   1   8.394    2   0.00   0.50  -0.50    -1.2   -1.0   -0.9    0.0    -3.1
   1   1   8.273    2   0.00   0.50   0.50    -2.0   -2.0   -8.3    6.5    -5.8
   1   1   6.591    1   0.00   1.00   0.00    -3.5   -4.1  -16.2    6.6   -17.1
   1   1   5.287    3   0.00   1.00   0.00     0.3   -6.0  -25.8    8.0   -23.5
   1   1   7.351    4   0.00   0.50  -0.50     0.3   -2.0   -9.3    2.8    -8.3
   1   1   7.351    4   0.00   0.50   0.50     0.3   -2.0   -9.3    2.8    -8.3
```

When short atom-atom contacts are present, the program prints specific parameters. More in detail, the following quantities are indicated, in this order: first fragment id number, atom id number; second first fragment id number, atom id number; labels of involved atoms; actual atom-atom distance (Å); van der Waals contact distance (Å); "energy" of atom-atom contact.

fragm./atom, fragm/atom labels   dist.   R°   "energy"
```
   1    7    1   21   C10   H 6   2.550   2.870    82.3
   1   10    1   11   O28   O27   2.649   3.160   106.4
   1   11    1   21   O27   H 6   1.653   2.680  -120.5  HB
```

The last line says that atom O11 of fragment 1, species 27, and atom H21 of fragment 1, species 6, are at a short distance of 1.653 Å against a sum of standard radii of 2.680. **Crysaa** recognizes this contact as a possible hydrogen bond and in fact adds a "HB" label. The formal atom-atom energy is -120.5 kJ/mol (mostly, however, a physically meaningless number).

CAUTION: be careful in attaching a precise physical significance to atom-atom energy. This number comes just from the crude sum of atom-atom potentials, and does not necessarily correlate with accurate quantum mechanical estimates of the molecular interaction energy, neither necessarily bears a physically sound meaning. In this example, we could just say that the first two contacts highligted above are mostly repulsive, whereas the last one is strongly attractive.

The first line after atom-atom short contacts indicates to which molecular pair they belong. In this case, it is:

```
    1  1  7.322   3  0.00  2.00  0.00    -48.3  -10.9  -47.4   58.1  -48.5
```

The above line says that for units 1, 1 (there is only one chemical unit in the crystal) there is a molecule-molecule contact at 7.322 Å distance between centers of mass, by symmetry operation n.3 (inversion center), translation vector T = [0 2 0], with the listed Coulombic, polarization, dispersion, repulsion and total interaction energies. This molecular pair hosts the three short atom-atom contacts listed straight above. A cyclic, double H-bond over a COOH group is worth about 50 kJ/mol. Note that the Coulombic energy is very nearly equal to the total energy because of cancellation of other terms.

CAUTION: The need for such a long translation (2 cell units along y) is due to the highly criticizable practice of some authors to have all atomic coordinates positive, with the result that in many cases the fundamental unit is not entirely in the 0,0,0 unit cell. This makes the crystal packing search much more laborious.

The last molecule-molecule relevant interactions are then reported, and the output ends with a short summary of overall parameters.

```
    1  1  6.021   4  0.00  1.50 -0.50    -5.0   -5.1  -17.3    7.8  -19.6
    1  1  6.021   4  0.00  1.50  0.50    -5.0   -5.1  -17.3    7.8  -19.6
    1  1  6.522   3  1.00  1.00  0.00    -6.6   -4.9  -17.3    7.7  -21.1
    1  1  8.257   3  1.00  2.00  0.00   -10.2   -3.3   -6.7    6.0  -14.2


     1239 fragment pairs     1239 within cutoff    40.00
 AA-CLP energies,Coul-pol-disp-rep-celldip-tot
  per entire molecule in asymmetric unit
#SAMPLExx 'P 21/c'       ---    -41.6  -40.3 -108.5   64.1   -0.0 -126.2

  Cell dip module and E/molecule   0.0000    -0.0
 normal end of operation, crystals read    1
```

The string that opens with "`#SAMPLExx 'P 21/c'`" contains the total energies in the following order: Coulomb, polarization, dispersion, repulsion, Kroon & van Eijck correction for polar groups (manual, Section 3.1.5), and lattice energy.
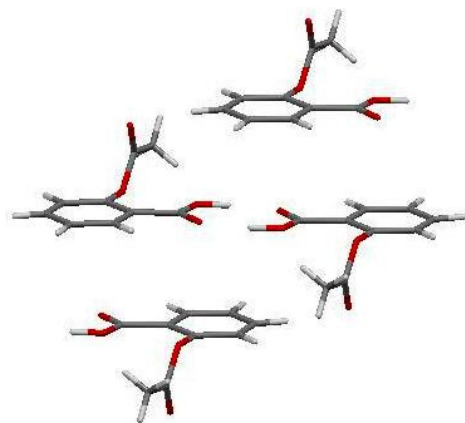
The crystal structure of aspirin (see Figure) is stabilized by a substantial Coulomb-polarization contribution, due to the cyclic hydrogen bonds, but in spite of this the main stabilization comes by far from dispersion, mostly due to interactions between stacked aromatic rings. This physically relevant fact is often neglected in casual discussions of crystal packing based only on the most appearing features, like hydrogen bonds.

Please note the richness of information that can be gathered by a procedure that takes a few minutes from the *.cif* file, and fractions of a second for the actual lattice energy calculation.

To conclude, examine the samplespcry.*pri* output, obtained in the LJC framework (see above) with ipot=1 in clppar.*par*. It looks similar to the output above commented, but now the following lines are printed, which provide a complete list of 6-12 potentials (see manual, Section 2.1.2).

Output from a Crysaa LJC calculation (excerpt)

```
library+extra 6-12 coefficients
 hydrogen non H-bonding
      73.8    0.14500E+05
 hydrogen H-bonding, zero 6-12 potential
 carbon, any
    2280.0    0.45000E+07
 nitrogen, any
    2200.0    0.23200E+07
 oxygen, any
    1650.0    0.12200E+07
 water oxygen ?? untested
    2600.0    0.26000E+07
 sulfur, any
   10000.0    0.13000E+08
 fluorine, chlorine, bromine, iodine
    1080.0    0.76000E+06
    6400.0    0.76500E+07
   11900.0    0.15800E+08
   14280.0    0.19000E+08
fragm.,volume    1    158.4
 cell volume, density, packing coeff.
 #SAMPLExx 'P 21/c'  esp ---      854.23   1.401  0.742
 max c.o.m. dist vector, cells on a,b,c   40.00    5    8    5
```

Then, the energy analysis is reported. First, molecule-molecule energies and short contacts are shown:

```
   1   1  6.591   1   0.00 -1.00   0.00     -6.0    0.0  -21.5    8.7  -18.7
   1   1  8.273   2   0.00 -0.50   0.50     -3.3    0.0  -10.6    5.7   -8.2
   1   1  8.273   2   0.00  0.50   0.50     -3.3    0.0  -10.6    5.7   -8.2
   1   1  6.591   1   0.00  1.00   0.00     -6.0    0.0  -21.5    8.7  -18.7
   1   1  5.287   3   0.00  1.00   0.00      2.7    0.0  -38.5   18.1  -17.7
   1   1  7.351   4   0.00  0.50  -0.50     -1.6    0.0  -12.2    3.4  -10.4
   1   1  7.351   4   0.00  0.50   0.50     -1.6    0.0  -12.2    3.4  -10.4
 1   7   1  21  C10  H 6  2.550  2.870  155.3
 1  10   1  11  O28  O27  2.649  3.160  149.1
 1  11   1  21  O27  H 6  1.653  2.680 -187.9 HB
   1   1  7.322   3   0.00  2.00   0.00    -72.3    0.0  -20.6   25.5  -67.5
   1   1  6.021   4   0.00  1.50  -0.50     -1.0    0.0  -22.2    9.2  -14.0
   1   1  6.021   4   0.00  1.50   0.50     -1.0    0.0  -22.2    9.2  -14.0
   1   1  6.522   3   1.00  1.00   0.00     -6.0    0.0  -23.3    9.1  -20.3
   1   1  8.257   3   1.00  2.00   0.00     -7.6    0.0   -9.2    4.4  -12.5

      1239 fragment pairs     1239 within cutoff    40.00
```

Eventually, the final lattice energies are printed:

```
AA-CLP energies,Coul-pol-disp-rep-celldip-tot
  per entire molecule in asymmetric unit
 #SAMPLExx 'P 21/c'  esp ---    -53.2    0.0 -124.1   56.0   -0.0 -121.4

  Cell dip module and E/molecule   0.0000    -0.0
 normal end of operation, crystals read    1
```

Comparing with CLP, there is no polarization energy; Coulombic energies are larger, the distribution of energies is somewhat different but the relative energies are comparable; the total lattice energy is the same within a few kJ/mol, i.e. within computational accuracy.