NCI for solids: the CRITIC2 program

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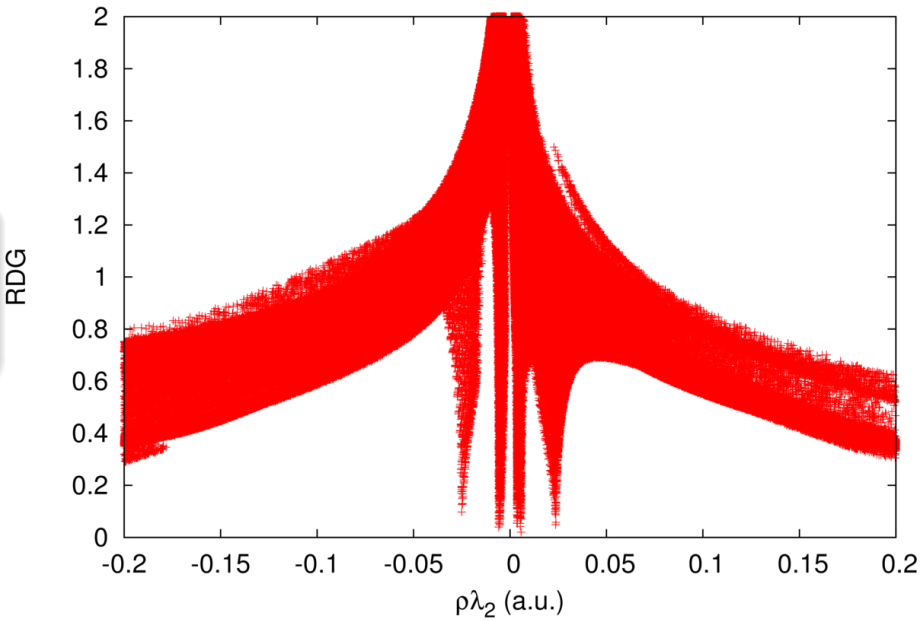
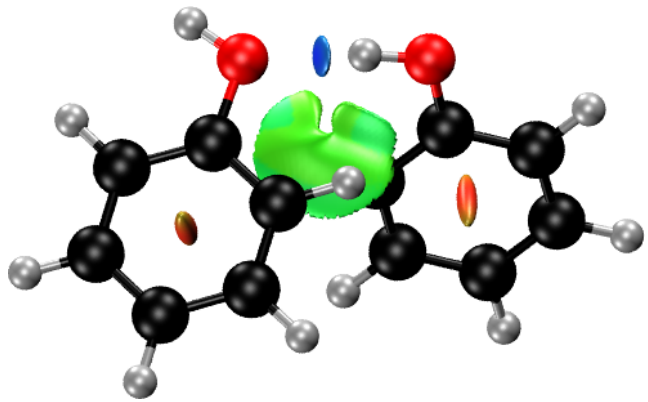
NCI basics

Reduced density gradient (RDG):

$$s = \frac{1}{2(3\pi^2)} \frac{|\nabla\rho|}{\rho^{4/3}}$$



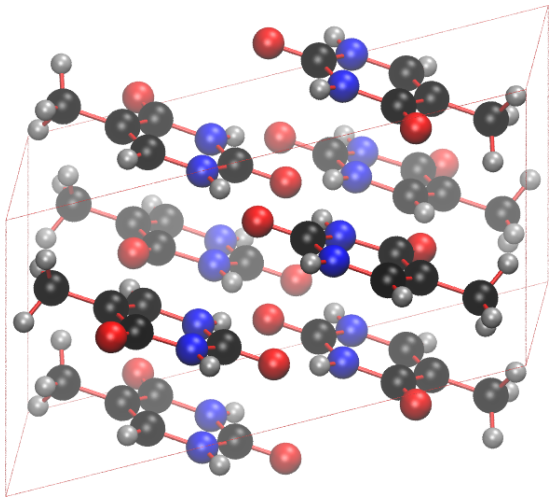
- Maps intermolecular contacts (i.e. Pauli repulsion zones).
- Simpler to calculate than Bader's topology.
- Color-mapping and region extent: strength of the interaction.

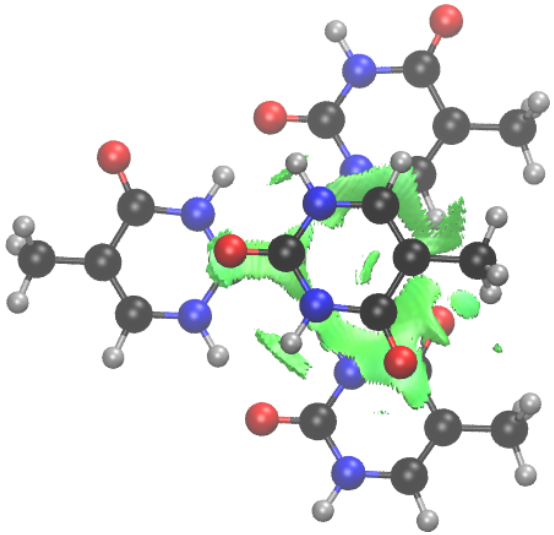


Johnson et al., J. Am. Chem. Soc. **132** (2010) 6498–6506.

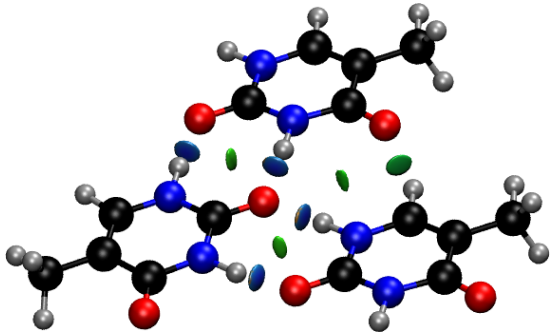
Contreras-García et al., J. Chem. Theory Comput. **7** (2011) 625–632.

NCI in solids





- Molecular contacts in crystal packing.
- Related to low-frequency intermolecular phonons.

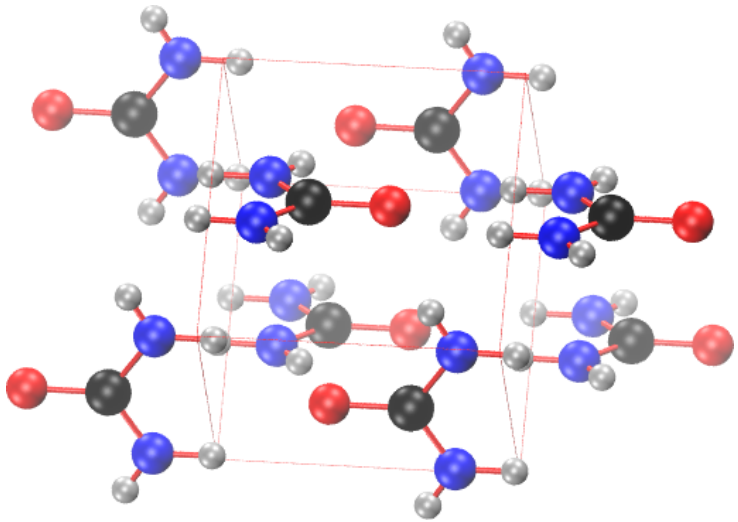


Otero-de-la-Roza et al., Phys. Chem. Chem. Phys. **14** (2012) 12165–12172.

NCI in solids: how it's done

1. Ingredients:
   - Crystal structure
   - ρ from a calculation...
   - ...or promolecular density
2. Calculate ρ and RDG on a grid
3. Eliminate the uninteresting parts.
   - Intramolecular (define fragments)
   - Crystal voids.
4. Generate the plots.

Example: **urea**

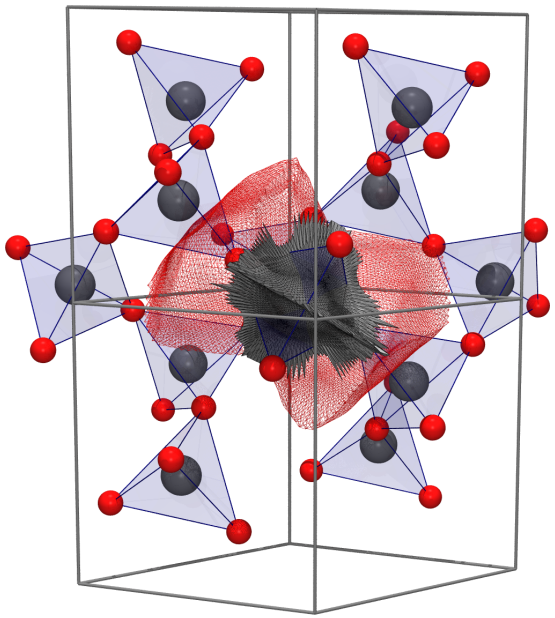


Critic2

CRITIC2 can do:

- NCI plots
- Bader integration (Q, V,...)
- Critical points of ρ...
  and other fields (ELF, MEP,...)
- Arithmetics with fields
- Graphical representations:
  basins, planes, cubes,...

```
 ____ ____ ____ ____ ____ ____ ____
||C |||R |||I |||T |||I |||C |||2 ||
||__|||__|||__|||__|||__|||__|||__||
|/__\|/__\|/__\|/__\|/__\|/__\|/__\|

* CRITIC2: analysis of real-space scalar fields in solids
  (c) 1996-2013 A. Otero-de-la-Roza, A. Martin-Pendas, V. Luana
  Distributed under GNU GPL v.3 (see COPYING for details)
  Bugs, requests and rants: alberto@carbono.quimica.uniovi.es
  If you find this software useful, please cite:
  A. Otero-de-la-Roza et al., Comput. Phys. Commun. 180 (2009) 157-166.
  A. Otero-de-la-Roza et al., submitted (2013)
```



Otero-de-la-Roza et al., Comput. Phys. Commun. **180** (2009) 157–166.

Otero-de-la-Roza et al., Comput. Phys. Commun. (submitted)

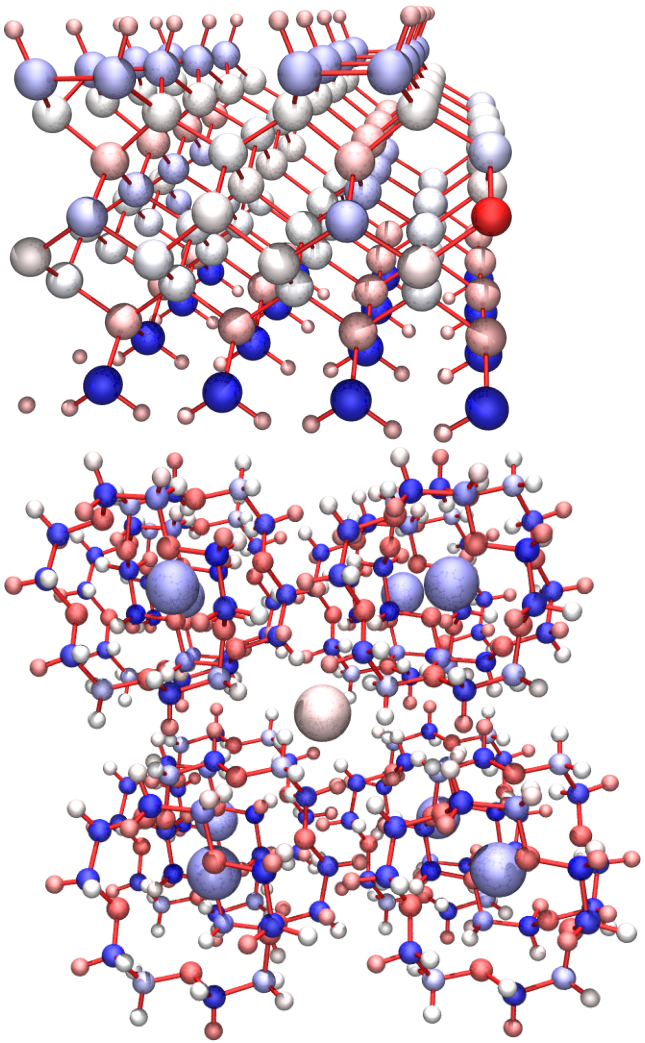
Critic2: basin integration, YT algorithm

- A P-doped Si surface
  176 atoms
  84 seconds (1 cpu).

```
crystal POSCAR Si H P
load CHGCAR
zpsp Si 4 H 1 P 5
yt
```

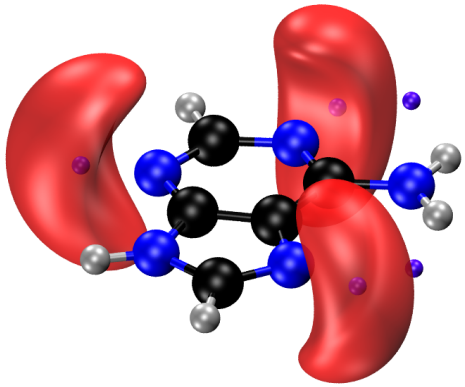
- An electride:
  71 atoms + 2 nnms
  14 seconds (1 cpu).

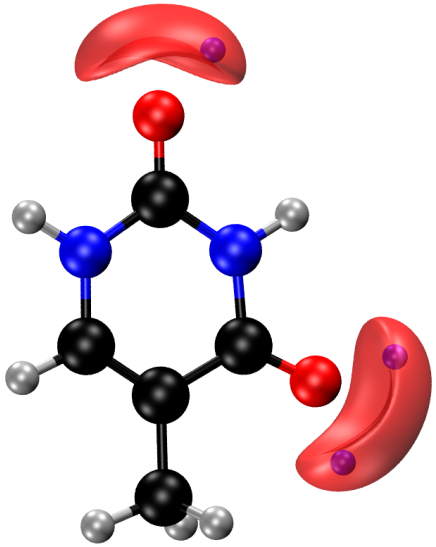
```
crystal TAGFEM.scf.out
load TAGFEM.rho.cube
zpsp cs 9 c 4 o 6 h 1
yt
```

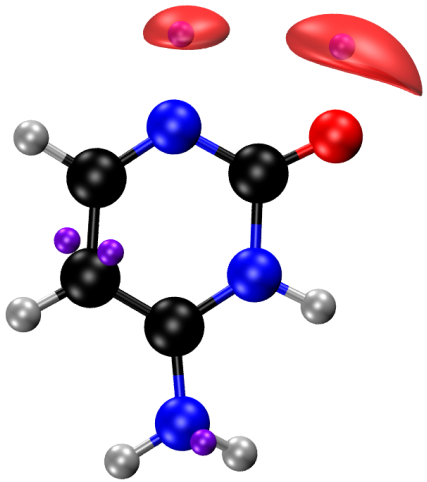


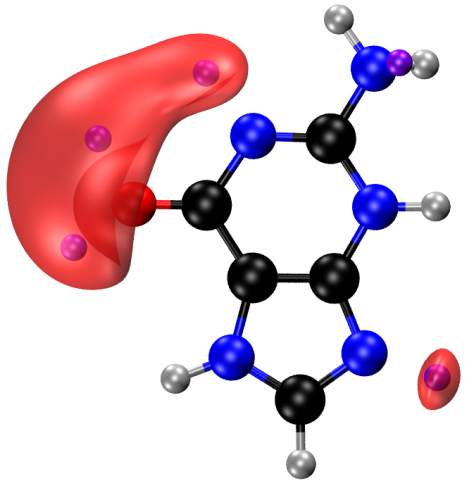
Yu, M. and Trinkle, D. R., J. Chem. Phys. **134** (2011) 064111

Critic2: critical points of the MEP









Critic2: other features

- **Crystal structure formats**: CIF, QE (scf.out), VASP (POSCAR), WIEN2k (struct), elk (GEOMETRY.OUT), abinit (DEN), cube files. Also, input by hand, maybe using a space group.
- **Field formats**: QE, VASP, abinit, WIEN2k, elk, PI, Gaussian,...
- Format conversion (e.g. CIF to QE).

Crystal structure

```
crystal BZDMAZ01.cif
crystal BZDMAZ01.struct
crystal POSCAR h c n
crystal BZDMAZ01.scf.out
crystal BZDMAZ01_o_DEN
crystal GEOMETRY.OUT
crystal BZDMAZ01.cube
```

Fields

```
load BZDMAZ01.cube
load CHGCAR
load BZDMAZ01_o_DEN
load BZDMAZ01.clmsum
BZDMAZ01.struct
load STATE.OUT GEOMETRY.OUT
load c.ion C h.ion H...
```

Copy the files

> scp -r
`workshop_nci@hydrogene.lct.jussieu.fr:transfer/NCI-solid/*/ .`

Password: **nciws2013**

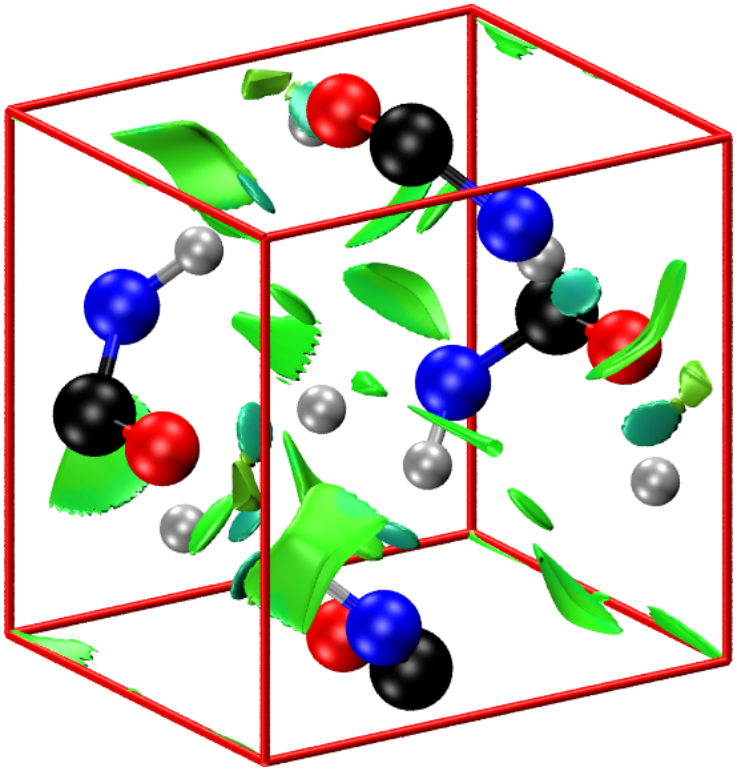
Urea: crystal structure and promolecular

Obtain the crystal structure

- Download CIF file
- From the literature
- ???

urea00.incritic

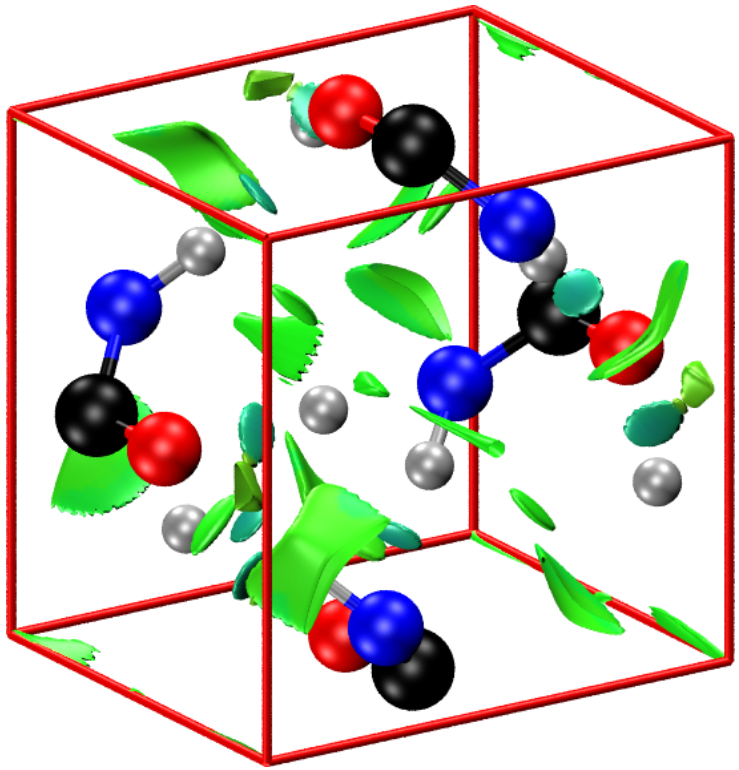
```
# Read structure:  CIF file
crystal urea.cif
# NCIplot (promolecular)
nciplot
endnciplot
```



Urea: format conversion

urea00.incritic

```
# Read structure:  CIF file
crystal urea.cif
# Convert CIF to other formats
write urea_bleh.scf.in
write urea_bleh.xyz molmotif
write POSCAR
write urea.abin
write urea.elk
```



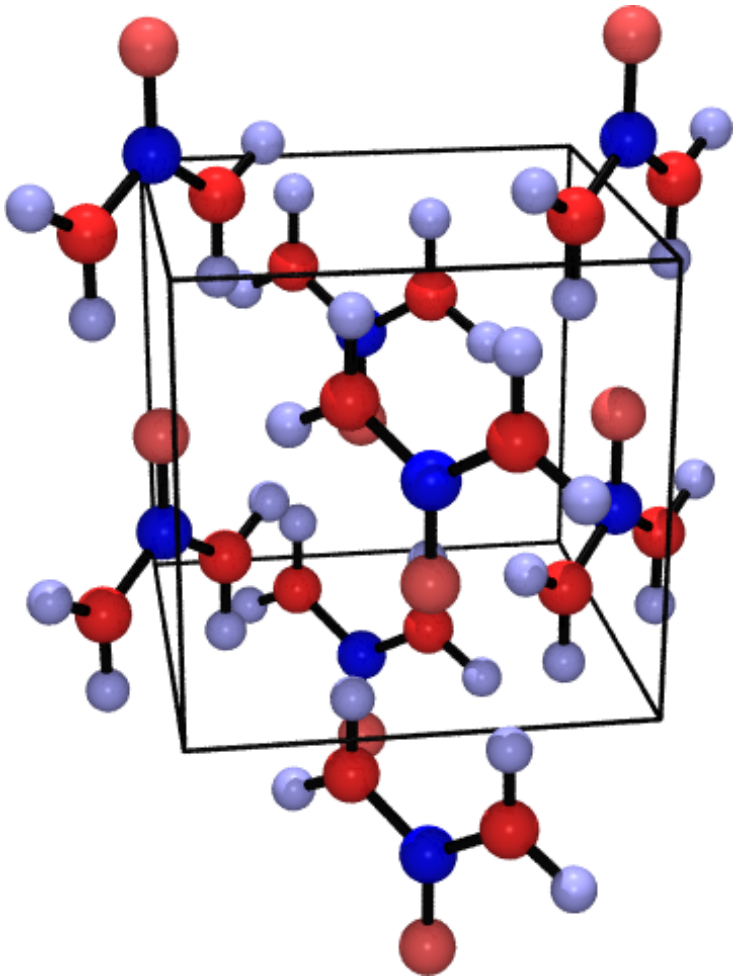
Urea: the SCF calculation

Calculation (QE) of the density

```
pw.x < urea.scf.in
pp.x < urea.pp.in
```

urea01.incritic

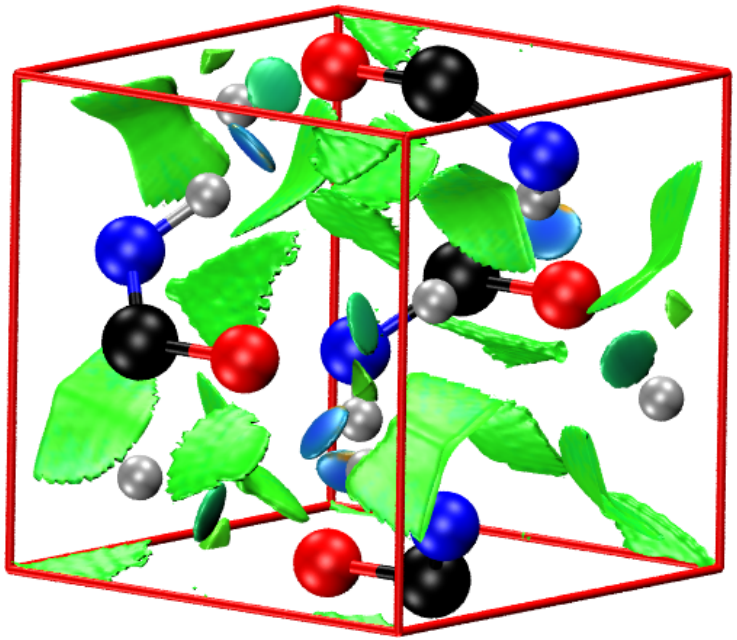
```
# Read structure and density
# from the cube file
crystal urea.rho.cube
load urea.rho.cube
# Pseudopotential Z
zpsp C 4 H 1 N 5 O 6
# Atomic charges and volumes
yt
```



Urea: simple nciplot

urea02.incritic

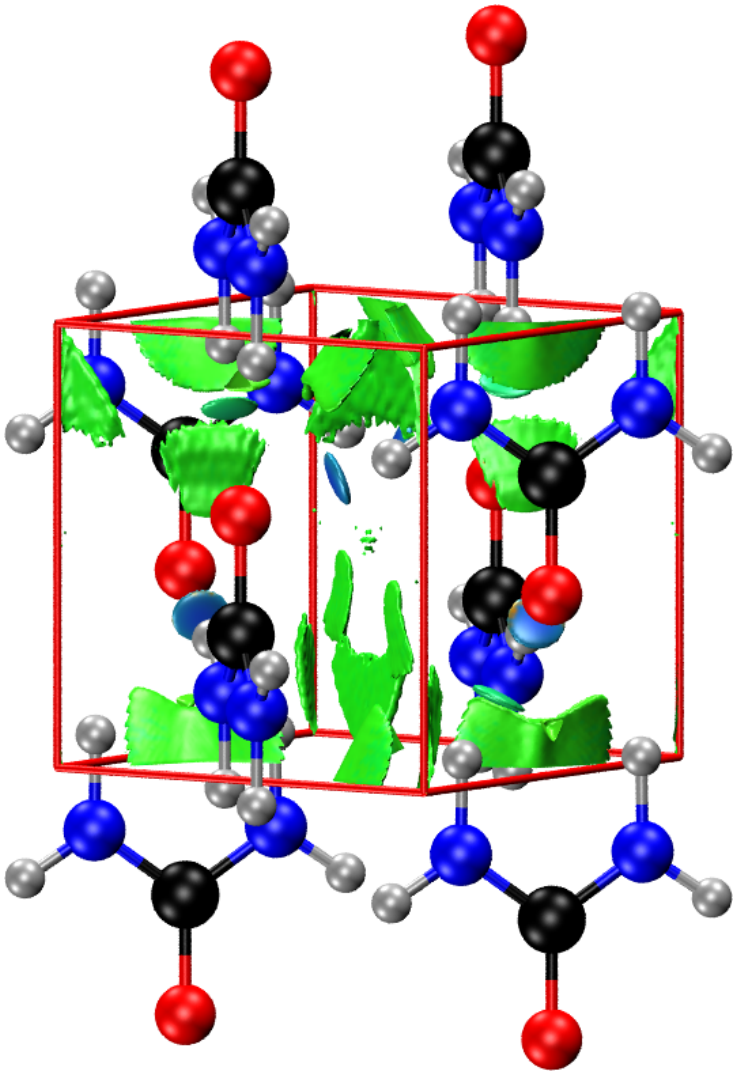
```
# Read structure and density
crystal urea.rho.cube
load urea.rho.cube

# Default nciplot
nciplot
endnciplot
```



Urea: simple nciplot

urea03.incritic

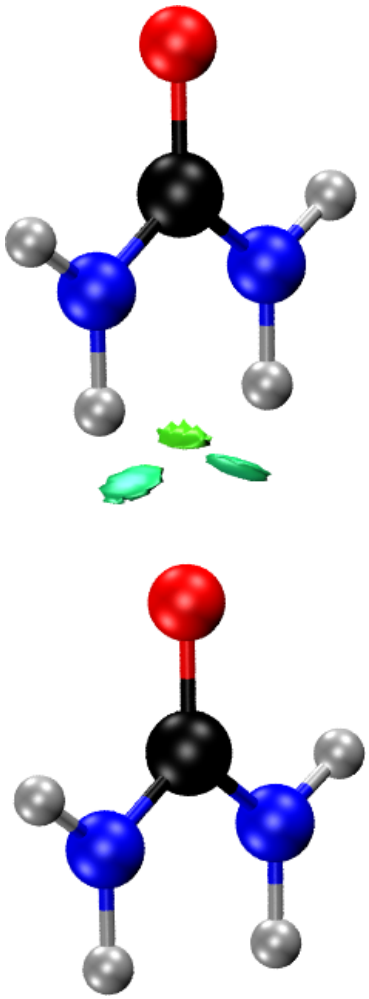
```
# Read structure and density
crystal urea.rho.cube
load urea.rho.cube

# Default nciplot
nciplot
  # Complete the molecules
  molmotif
endnciplot
```



Urea: fragments

urea04.incritic

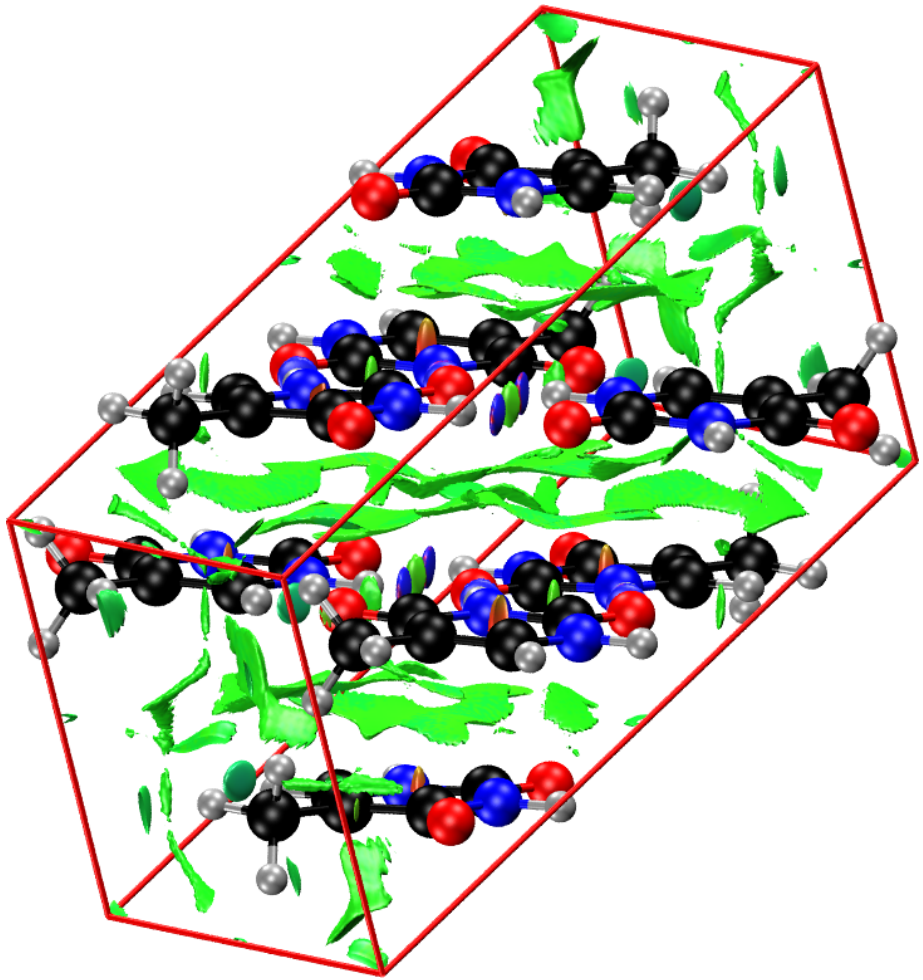
```
# Read structure and density
crystal urea.rho.cube
load urea.rho.cube
# Cut the fragments
# write urea.xyz molmotif
nciplot
  molmotif
  # 2 fragments
  fragment frag1.xyz
  fragment frag2.xyz
  # smaller grid
  nstep 40 40 120
endnciplot
```



Thymine: simple nciplot

thymine01.incritic

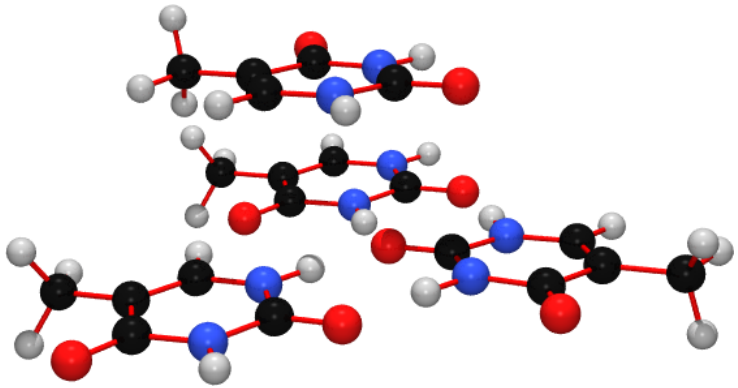
```
# Read structure and density
crystal rho.cube
load rho.cube
# Default nciplot
nciplot
  molmotif
endnciplot
```



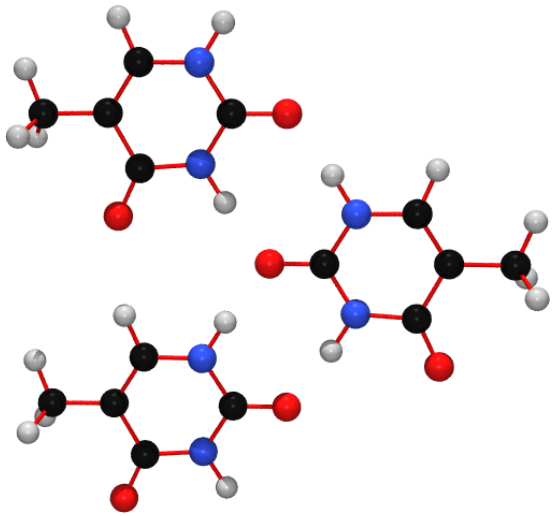
Thymine: cut the fragments

thymine02.incritic

```
# Read crystal structure
crystal rho.cube
# Write an xyz file
# Complete the molecules
write crystal.xyz molmotif
```



fragment 1

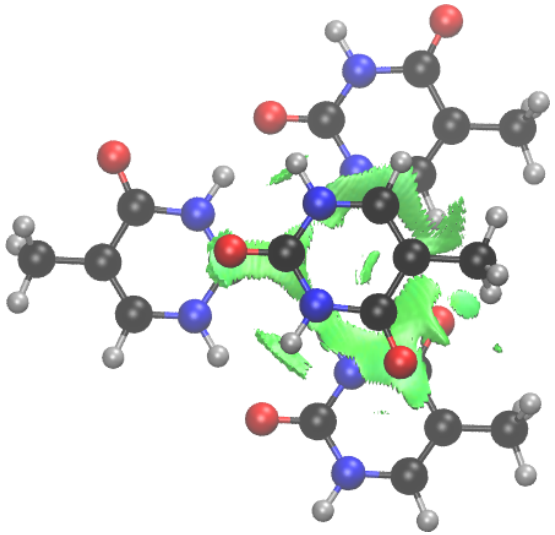


fragment 2

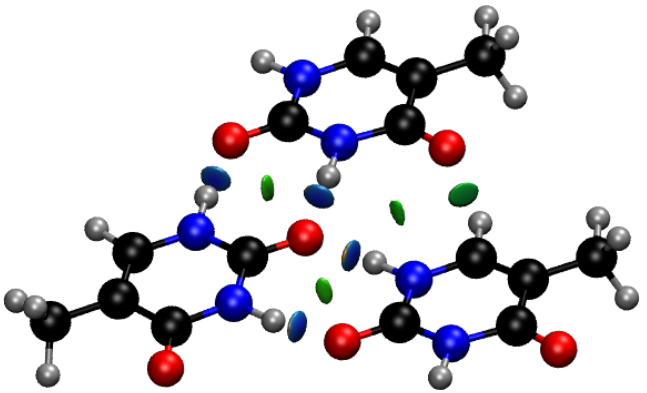
Thymine: fragment NCIplot

thymine03.incritic

```
# Read crystal structure
crystal rho.cube
load rho.cube
# First plot
nciplot
  fragment fragment_1a.xyz
  fragment fragment_1b.xyz
  rhoparam2 0.95
  oname thymine_inter
  nstep 120 120 120
endnciplot
# Second plot
nciplot
  fragment fragment_2a.xyz
  fragment fragment_2b.xyz
  fragment fragment_2c.xyz
  rhoparam2 0.95
  oname thymine_intra
  nstep 120 120 120
endnciplot
```



fragment 1

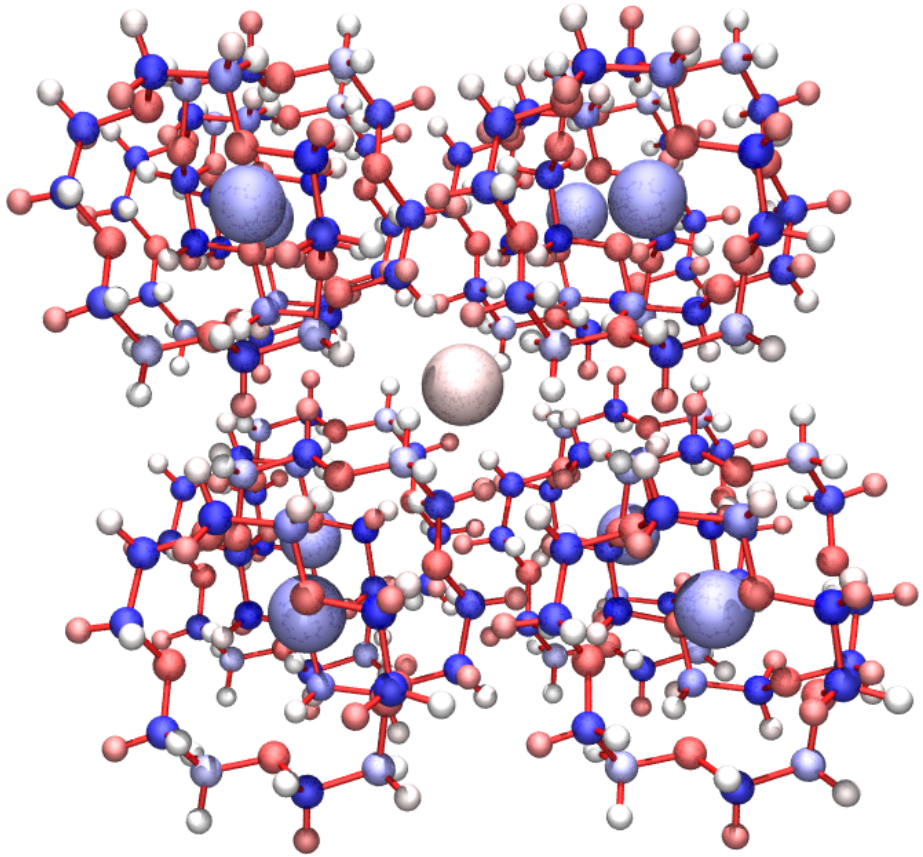


fragment 2

Electride (bis(15-crown-5)-cesium): atomic charges

TAGFEM01.incritic

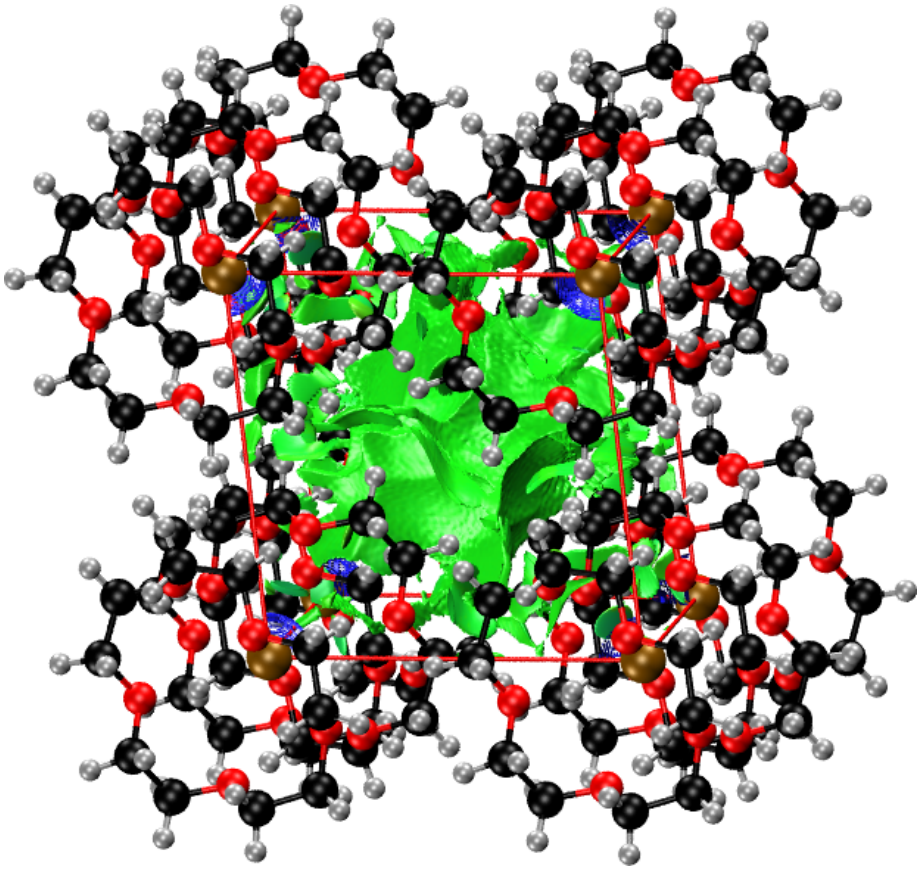
```
# Read structure
crystal TAGFEM.rho.cube
# Then the density
load TAGFEM.rho.cube
# Pseudopotential Z
zpsp cs 9 c 4 o 6 h 1
# Atomic charges
yt
```



Electride (bis(15-crown-5)-cesium): simple nciplot

TAGFEM02.incritic

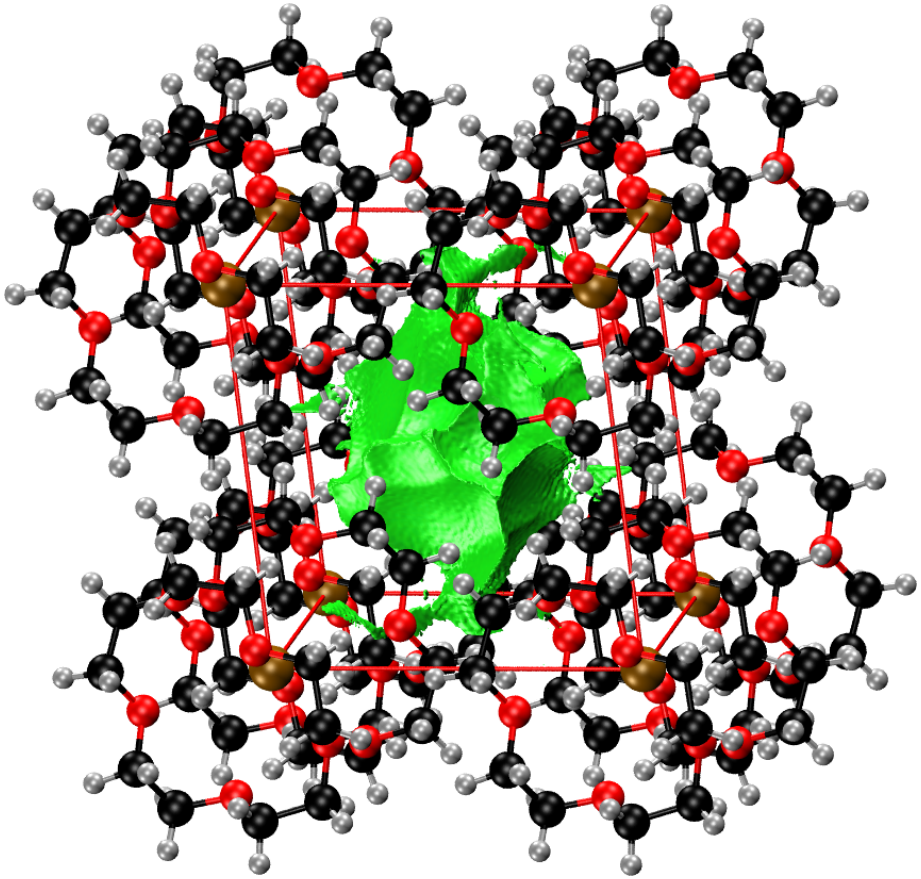
```
# Read structure
crystal TAGFEM.rho.cube
# Then the density
load TAGFEM.rho.cube
# Simple nciplot
nciplot
  molmotif
endnciplot
```



Electride (bis(15-crown-5)-cesium): crystal voids

TAGFEM03.incritic

```
# Read structure
crystal TAGFEM.rho.cube
# Then the density
load TAGFEM.rho.cube
nciplot
  molmotif
  # Only the voids
  void 0.0025
endnciplot
```



Closing remarks

Download CRITIC2 and the examples in this tutorial from:

`http://azufre.quimica.uniovi.es/software.html`

- Fully documented, with examples.
- Free licence (GNU/GPL v3).
- Contact: `aoterodelaroza@ucmerced.edu`