Intermolecular interactions II: Density-based methods

Electron deformation density(EDD)

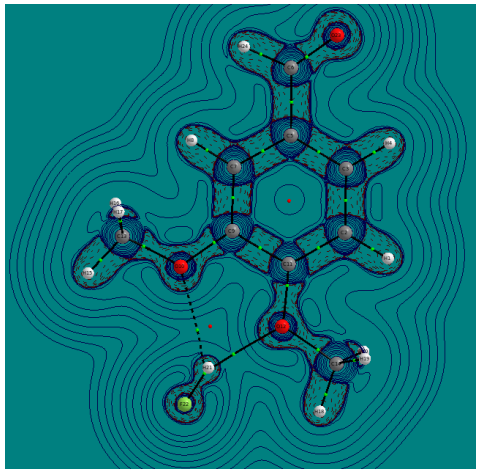
- Upon formation of complex redistribution of electron density occurs(polarisation, charge transfer):

$$\Delta\rho = \rho_{complex} - \sum \rho_{fragments} \tag{1}$$

- in inputs of both fragment the atoms of missing partner is represented by ghost centers (indicated by Bq label) $\Rightarrow$ preservation of occupied space
- cubgen utility produces 3D density output (*.cube format/xplor) by processing formatted checkpoint file (*.chk) from Gaussian SP calculation

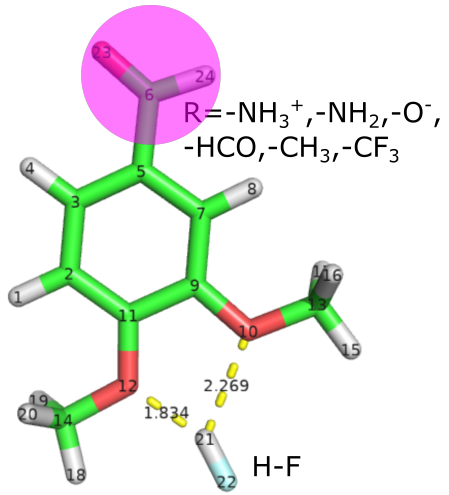
Topological analysis of electron density using QTAIM approach

- molecular space divided in atomic basins bordered by zero-flux surfaces $\nabla\rho \cdot n = 0$ of gradient of electron density
- Bond critical points (BCPs) = local stationary points of vanishing density gradient and maximized density in two directions perpendicular to interatomic vector A-B $\Rightarrow$ (3,-1) Hessian tensor
- various density-based descriptors can be analysed to evaluate character of interaction between atoms A and B (local density $\rho(r)$,Laplacian $\nabla^2\rho(r)$, delocalisation index *DI(A,B)*)



HOMEWORK: Bifurcated hydrogen bond

1. The aim is to analyze set of H-bonded complexes of HF attached to substituted dimethoxybenzene (see attached figure, BLYP/def2TZVPP optimized geometries of -NH_2 and -CHO derivatives available in IS)
2. Calculate interaction energies (ΔE for all 6 complexes and for 2 extremes plot the electron deformation energies($\Delta\rho$, slide 5) and map of Laplacian of electron density ($\nabla^2\rho$, slide 6).
3. Run basic QTAIM calculation for all complexes, extract values of density, Laplacian of electron density and delocalisation index (DI) associated with BCPs between (F)**H** and **O**(CH_3) atoms.
4. Try to correlate ΔE versus ρ, $\nabla^2\rho$, $\sum$DI, $\sum$DI/r(O-C)



Electron deformation density

Gaussian input for organic fragment

```
%chk=f1.chk
#p B3LYP/def2TZVPP scf=conver=6
Integral=UltraFine

SP of f1

0 1
  H        0.6778488    1.2270278    2.1895466
  C        0.1339051    1.3019980    1.2510536
  C       -1.2613796    1.3725016    1.2677278
  H       -1.7993284    1.3529764    2.2128579
  C       -1.9692784    1.4687435    0.0645759
  C       -3.3941682    1.5428919    0.0703788
  ...
  H-Bq     3.0768960    1.2302657   -1.6848812
  F-Bq     3.8684785    1.1731588   -2.2005430
  N       -4.5586668    1.6046640    0.0695014
```

run script

```
module add gaussian

#COMPLEX
g09 complex.com
formchk -3 complex.chk complex.fchk
cubgen "ncpus" density=SCF complex.fchk
complex.cube -3
#FRAGMENT 1
g09 f1.com
formchk -3 f1.chk f1.fchk
cubgen "ncpus" density=SCF f1.fchk f1.cube
-3
#FRAGMENT 2
g09 f1.com
formchk -3 f2.chk f2.fchk
cubgen "ncpus" density=SCF f2.fchk f2.cube
-3
```

use interactive tool CUBMAN for processing cube files:

1. **A**dd *f1.cube* and *f2.cube* to get temporary *sum.cube*.
2. **SU**bstract *complex.cube* minus *sum.cube* to get final difference map.
3. Use VMD isosurface representation to show positive and negative regions of $\Delta\rho$.

OTAIM

Gaussian input: BSSE-corrected interaction energy + generation of wavefunction file *wfx

```
%chk=complex.chk
#p B3LYP/def2TZVPP scf=conver=6
Integral=UltraFine Counterpoise=2 output=wfx

SP of complex

0 1 0 1 0 1
  H       0.6778488    1.2270278    2.1895466 1
  C       0.1339051    1.3019980    1.2510536 1
  C      -1.2613796    1.3725016    1.2677278 1
  ...
  H       3.0768960    1.2302657   -1.6848812 2
  F       3.8684785    1.1731588   -2.2005430 2
  N      -4.5586668    1.6046640    0.0695014 1

complex.wfx
```

Commands for performing QTAIM analysis in AIMALL program based on Gaussian wavefunction

```
module add gaussian
# start job
g16 complex.com
formchk -3 complex.chk complex.fchk

# clean
rm -f core

# QTAIM
module add aimall
aimqb.ish -nogui -nproc=3
-atlaprhocps=true -encomp=1 -usetwoe=0
complex.fchk
```

Plotting the Laplacian using Aimstudio GUI

1. Run in terminal `aimstudio.ish complex.sumviz`.
2. Use Counters/New 2D Grid option, select Function DelSqRho, copy coordinates of 3 ring atoms(right click on selected atom in structure).
3. Open *complex.g2dvi* in current window and export png picture.

Extracting data from *sumviz file

- Open *complex.sumviz* and find relevant BCPs (H–O, or O–H), save corresponding values of ρ, $\nabla^2\rho$.
- Find the section listing delocalisation indexes (table with DI(A,B) heading) and save these values.
- Extract H–O distances from structure.
- Prepare correlation plots.