Intermolecular interactions

Intermolecular interactions

- “Noncovalent” interactions
- Usually weaker than covanlent bonding (thus reversible)
- Hydrogen bonding, stacking, ion-ion, ion-dipole...
- Halogen/chalcogen/pnicogen bonds (σ-hole)
- Ion-π, π-hole ...

Stabilization energy

- Upon formation of stable complex, energy is released:

$$\Delta E = E_{complex} - \sum E_{monomers} \tag{1}$$

- Binding vs Interaction energy
- Basis Set Superposition Error (BSSE)

Nature of stabilization

- Mainly discussion of chemists
- **To what degree are Quantum or Classical stabilizations responsible for the complex formation?**
- Consequences:
  - How the interactions with EM radiation differ?
  - Can the interaction be modeled by MM?
  - Can the electrostatic potential be used as guide to modeling?
  - Difficulty of transferring the properties between various systems
- QM stabilization present for formally “noncovalent” interactions

Analysis of bonding

- EDA-NOCV
- NBO
- SAPT
- IQA
- NCI
- Electrostatic - Orbital - Dispersion - Pauli - Polarization - XC
- **All include certain degree of arbitrariness**

HOMEWORK: σ-hole interaction

- Analyze the σ-hole bonding between bromide and $C_6F_5Br.Br^-$ (structure available in IS)
- Calculate the *interaction* energy (M062X and B3LYP/def2tzvpp/BSSE in Gaussian). Explain different DFT values.
- Reoptimize the C_6F_5Br, calculate difference in single point energy of both free and bound form and estimate *deformation energy* (use Gaussian setup). What is the relation of interaction with bond deformation?
- Perform EDA analysis in ADF2018 using M062X/TZVP, compare the individual terms (Electrostatic, Pauli, Orbital) with $C_6F_6.Br^-$. *Input see bellow.*
- Generate complex.wfn file from single-point calculation in Gaussian on $C_6F_5Br.Br^-$ (in *.com file keyword *output=wfn* and put name of wfn at the end of *.com file), run NCI-analysis of reduced gradient of electron density, prepare visualization of cube file in VMD (use session file vmd -e *vmd). *Input see bellow.*. Interpret the results.

ADF-EDA

Input for *adf_compl.inp*

```
Atoms
C -3.0298060 0.6213630 -0.0000060 f=m
...
Br -1.7821970 6.2717390 0.0000290 f=n
End

ZlmFit
Quality good
End

charge -1
fragments
m t21.frag1
n t21.frag2
end

Basis
Type TZ2P
Core none
End

integration
accint 7
end

Symmetry Nosym

XC
MetaHybrid M062X
End

SAVE TAPE21

End Input
```

ADF-EDA run script

Input for *run.sh*

```
module add adf:2018.104

adf < adf1.inp > adf1.out
mv TAPE21 t21.frag1

adf < adf2.inp > adf2.out
mv TAPE21 t21.frag2

adf < adf_compl.inp > adf_compl.out
```

NonCovalent Interactions (NCI)

- Analysis of reduced density gradient:

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

- vs electron density multiplied by the sign of second eigenvalue of Laplacian:

$$sign(\lambda_2)\rho(r) \tag{3}$$

- Sign of λ_2 is indicator of “attractive” (negative) vs “repulsive” (positive) density
- Manual of NCIplot:
- `http://www.lct.jussieu.fr/pagesperso/contrera/nciplot-manual.pdf`

NCI plot

Input for *nci.sh*

```
module add nciplot
nciplot < nci.inp > nci.out
```

Input for *nci.inp*

```
1
complex.wfn
CUTOFFS 1.0 1.0
```