# Intermolecular interactions

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

# Quantum Theory of "Atoms in Molecules" (QTAIM)

- Works with electron density and its derivatives
- Observable property
- Lower dependence of results on basis set
- No mathematical[1] tricks (Transformations etc.)
- Prone to overanalysis (properties of LCPs)

[1] Read magical.

# Task 1: $\sigma$-hole interactions

- Analyze the $\sigma$-hole bonding between bromide and pentafluorobromobenzene
- Calculate the *binding* and *interaction* energies
- Perform AIM calculation on the wavefunction (use output=wfn in the route section of Gaussian job)
- Use M062X/Def2TZVP level of theory
- AIMAll package for the processing of wavefunction
- `http://aim.tkgristmill.com/manual/aimqb/aimqb.html`

# Inspection of AIM results

- Going through the output (.sum)
- Visualizing the molecular graph/contour maps/surfaces
- Visualize the electron density and Laplacian of electron density

# Extraction of numbers

- Extract data from the .sum file:
  - Properties of LCP between bromines
  - Charge on bromide anion
  - Delocalization indices between atomic (bonded) pairs:
    - C-C
    - C-F
    - C-Br
    - Br-Br

# 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 $\lambda_2$ is indicator of “attractive” (negative) vs “repulsive” (positive) density
- Manual of NCIplot:
- `http://www.lct.jussieu.fr/pagesperso/contrera/nciplot-manual.pdf`

# Task 2: Perform NCI analysis on the .wfn

- Calculate the NCI cube files
- Visualize the cubes using the generated .vmd file
- Plot the RDG vs $\rho$ using gnuplot