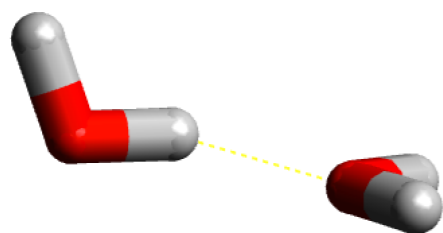
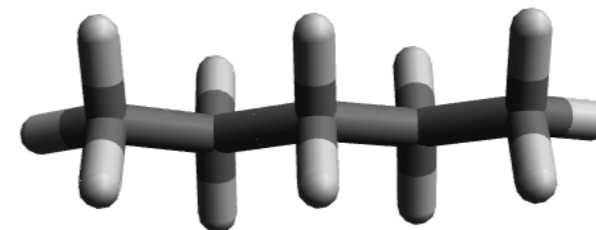


Insight From Numbers: Analyzing Intramolecular Non-Covalent Interactions With IntraSAPT

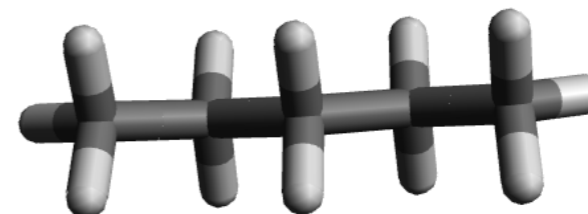
Ewa Pastorczak,
Antonio Prlj, Jerome Gonthier, Clemence Corminboeuf

Intermolecular interactions

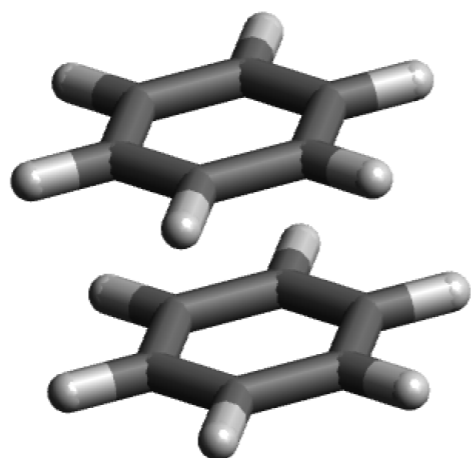
van der Waals (dispersion) complexes



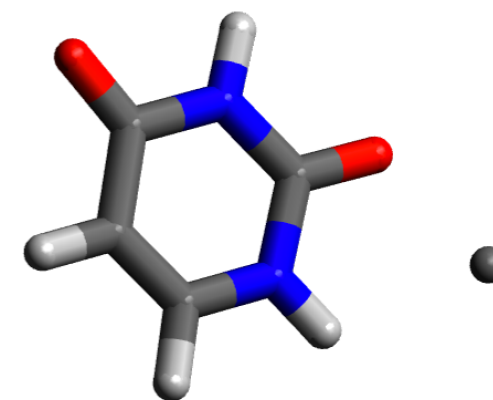
Hydrogen bonds



Charge-transfer



π - π stacking



others...

Symmetry-adapted perturbation theory (SAPT)

Treats the interaction between monomers as a perturbation

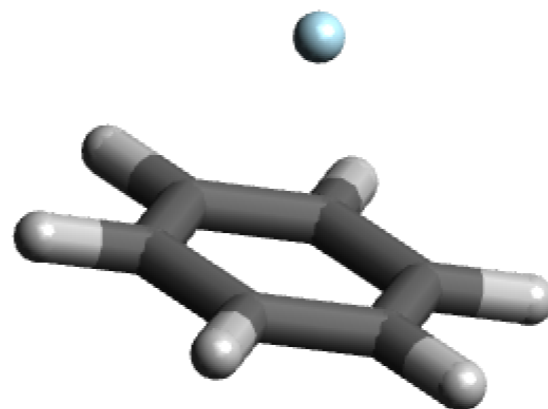
Interaction energy of dimers:

$$E_{int} = E_{elst} + E_{exch} + E_{ind,resp} + E_{exch-ind,resp} + E_{disp} + E_{exch,disp} + \dots$$

SAPT makes it possible to compute, decompose and interpret
the intermolecular interaction energy

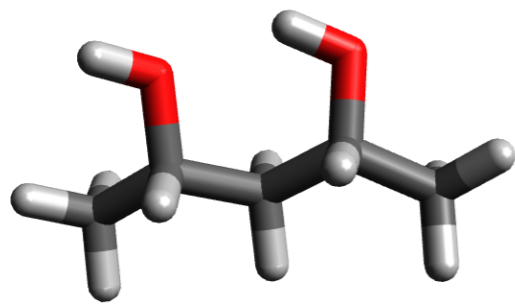
Key features of SAPT

- Interaction energy emerges from a **single** computation (no BSSE)
- Exchange interaction is introduced through antisymmetrization of the product of the monomer wavefunctions
- Can describe non-covalently bound dimers (or trimers)
- Gives accurate interaction energies
- Non-empirical definition of dispersion at all ranges

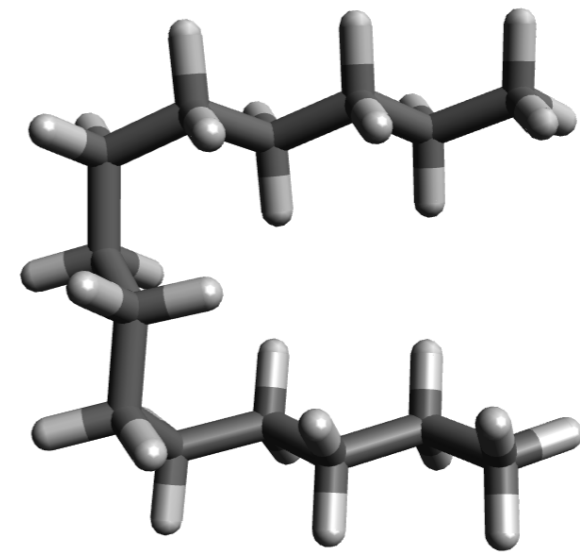


Intramolecular interactions

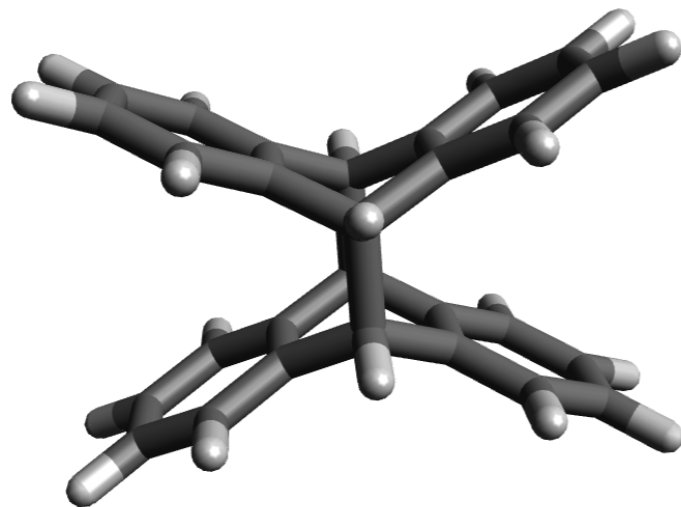
van der Waals (dispersion)



Hydrogen bonds



Charge-transfer

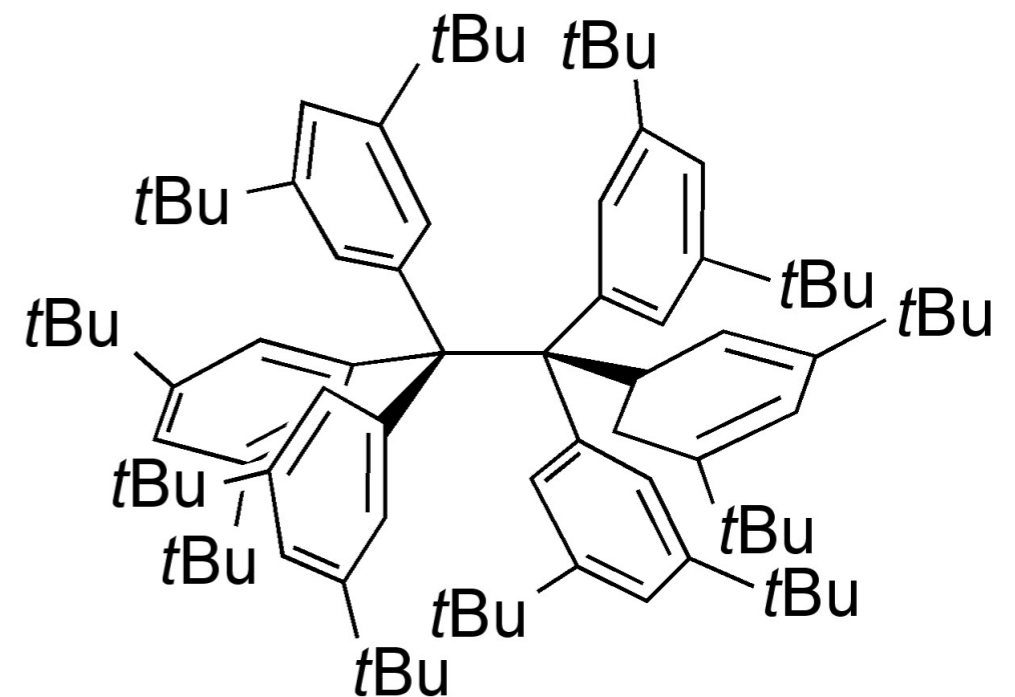
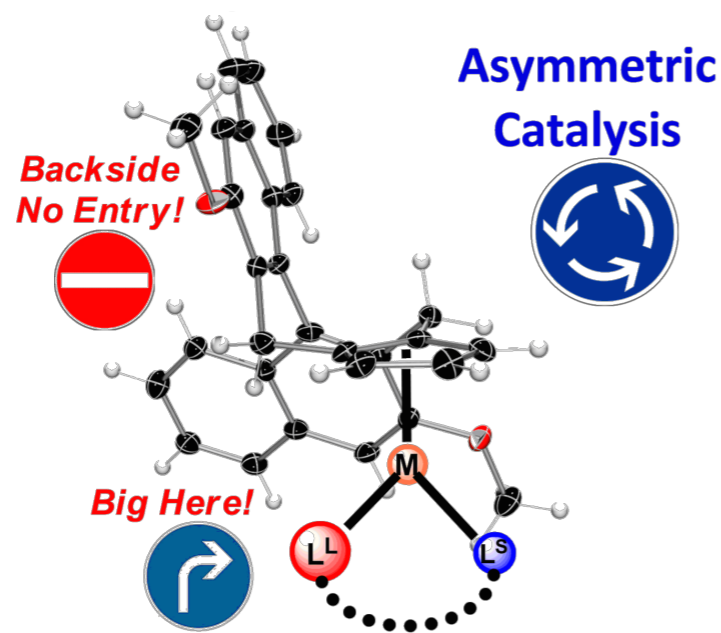


π - π stacking

others...

What are we interested in?

- Computing interaction energies of particular groups
- Exchange/dispersion balance



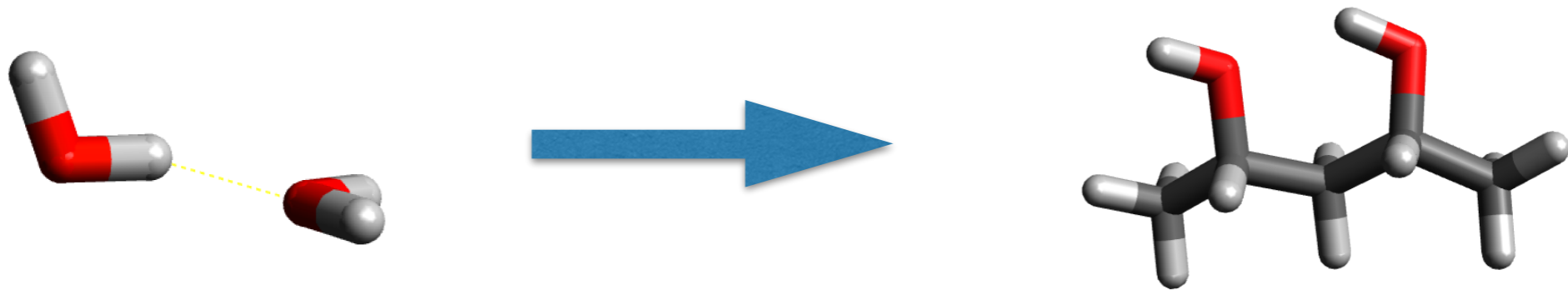
C. G. Newton *et al.*, *J. Am. Chem. Soc.* **2016**, 138, 3935-3941

P. R. Schreiner *et al.*, *Nature*, **2011**, 477, 308-312

- Explaining stability of certain molecules
- Designing new molecules by promoting some interactions

The challenge for intramolecular SAPT

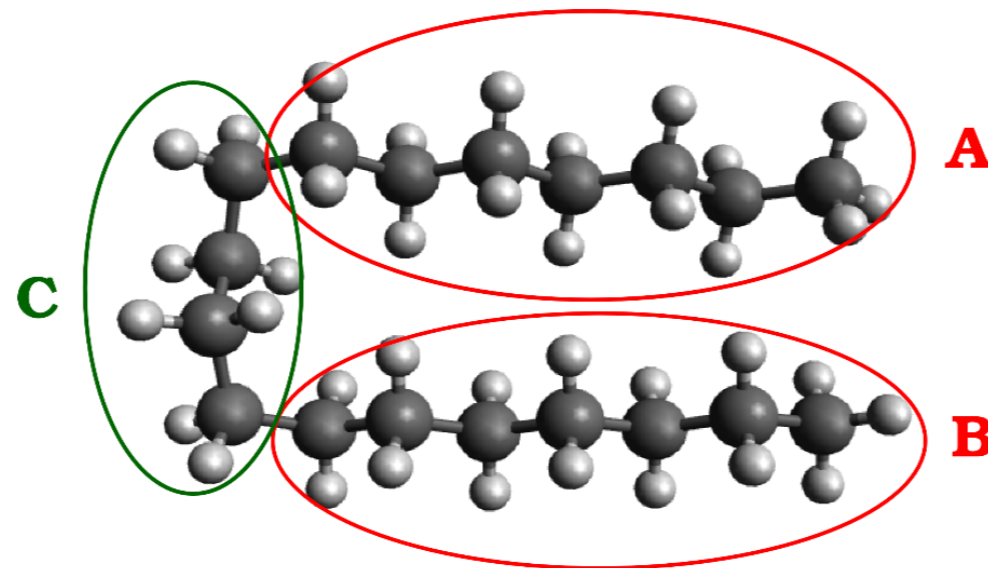
No monomers, just **arbitrarily** chosen fragments



How to choose the fragments?

Can we associate the interactions with the fragments?

How to partition the molecule?



1. Choose the nuclei
2. Take advantage of the atom-centered basis set to partition the basis functions¹
3. Localize the orbitals on fragments using strictly localized orbitals²

¹I. Mayer, *Int. J. Quantum Chem.* **23(2)**, 41-363 (1983)

²H. Stoll, G. Wagenblast, H. Preuss, *Theor. Chem. Acc.* **57(2)**, 169-178 (1980)

Removing the interfragment interactions - zeroth order Hamiltonian

The integrals where the product of the operator and the ket represent an interaction between A and B are removed, e.g.

$$-\sum_{I \in A} \left\langle \tilde{i} \left| \frac{Z_I}{R_{1I}} \right| b \right\rangle, \quad b \in B$$

For integrals representing interactions within fragment B
the bra basis functions on fragment A
are projected out, e.g.

$$\langle \tilde{i}\tilde{j} | \frac{1}{r_{12}} | bc \rangle \longrightarrow \langle \tilde{i}\tilde{j} | (\hat{P}_{BC}(1)\hat{P}_{BC}(2)) \frac{1}{r_{12}} | bc \rangle$$

biorthogonal orbitals

Bring back the interaction - perturbative corrections - single-determinant wavefunction

For interaction \widehat{W}_{AB} between fragments A and B:

Electrostatics + exchange

$$E^{(1)} = \left\langle \tilde{\Psi}_0 \left| \widehat{W}_{AB} \right| \Psi_0 \right\rangle + \sum_{I \in A, J \in B} \frac{Z_I Z_J}{R_{IJ}}$$

Induction (polarization+delocalization) + dispersion

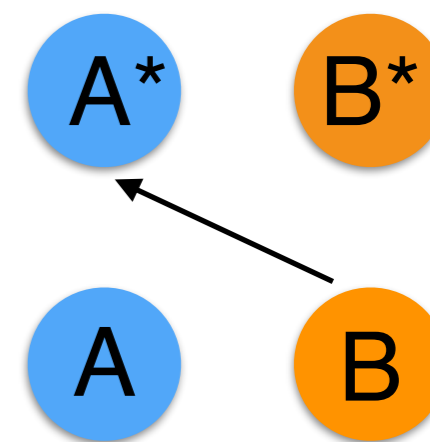
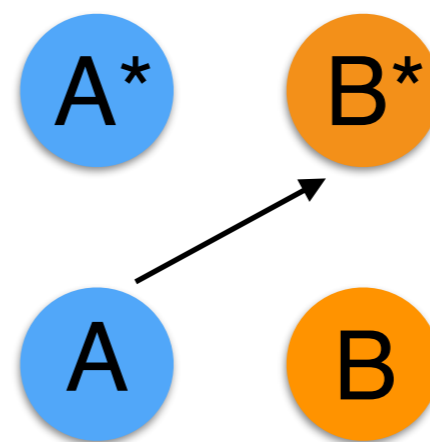
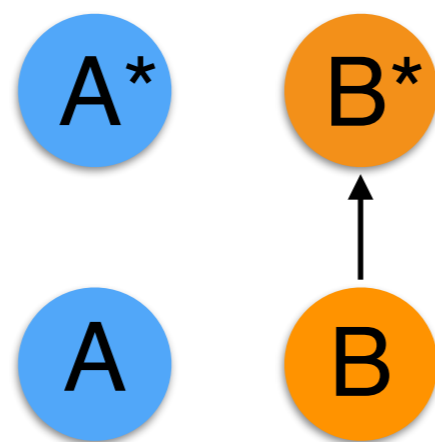
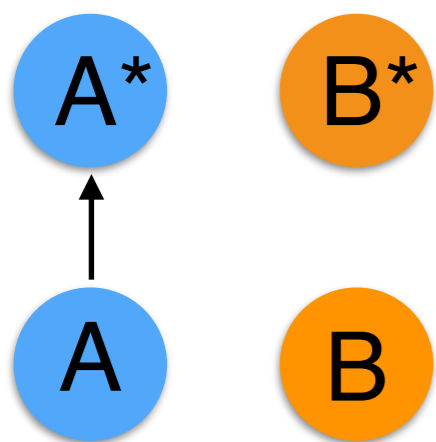
$$E^{(2)} = - \sum_{exc} \frac{\left\langle \tilde{\Psi}_{exc} \left| \widehat{W}_{AB} \right| \Psi_0 \right\rangle \left\langle \tilde{\Psi}_0 \left| \widehat{W}_{AB} \right| \tilde{\Psi}_{exc} \right\rangle}{E_{exc}^{(0)} - E_0^{(0)}}$$

Second order corrections - contributing excitations

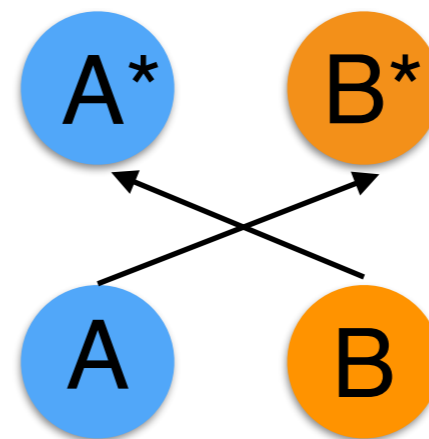
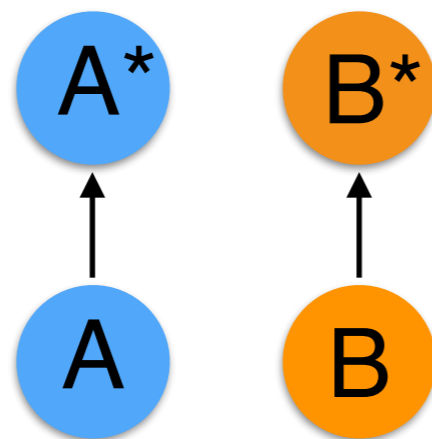
Induction

Polarization

Delocalization



Dispersion

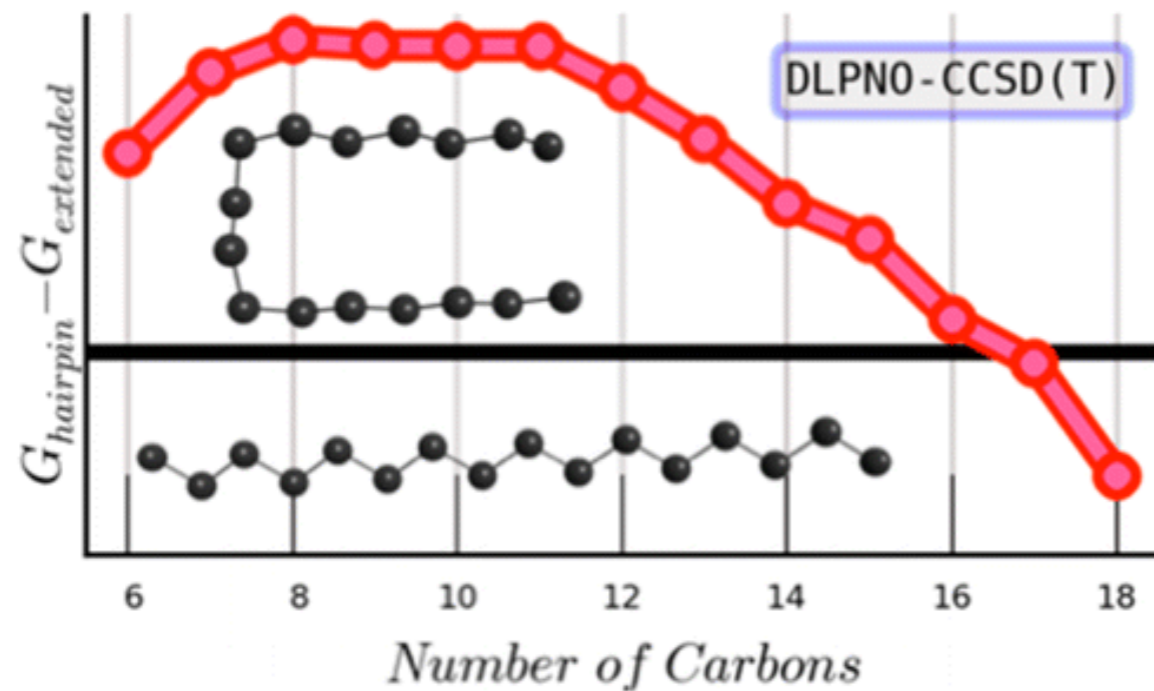


Key features of intraSAPT

- Interaction energy emerges from one computation
- Wavefunction is antisymmetric
 - no need to introduce exchange
- Non-empirical dispersion
- It's an extension of Surjan *et al.*¹ theory for intermolecular interactions
 - able to treat inter- and intramolecular interactions on equal footing

¹P.R. Surjan, I. Mayer & I. Lukovits, *Chem. Phys. Lett.* **119(6)**, 538-542, 1985

Hairpin alkanes conformations

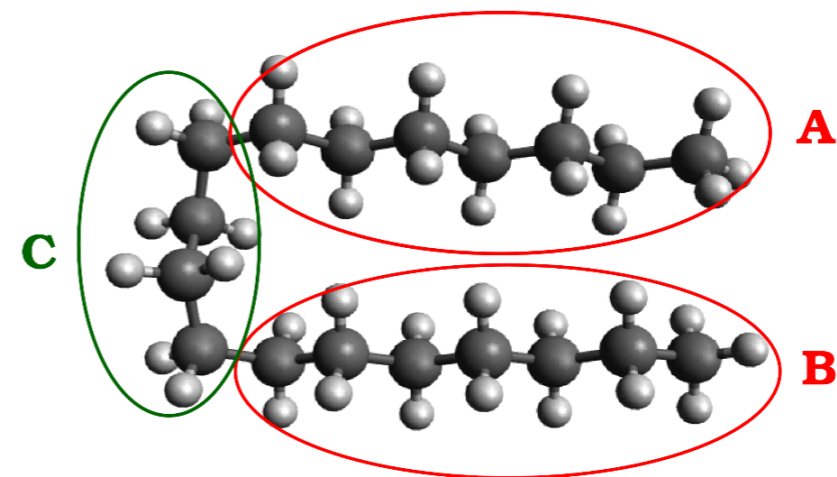
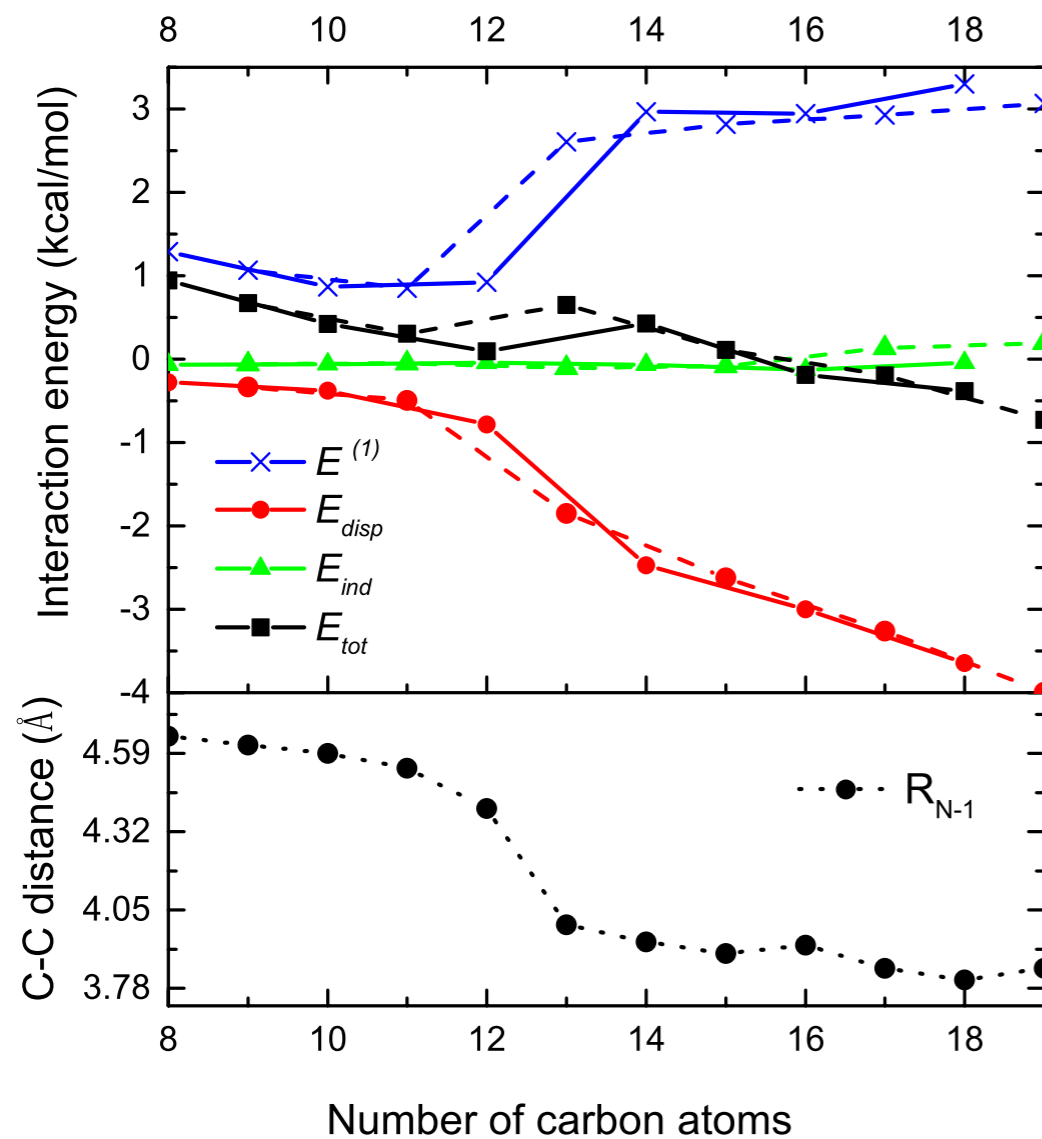


Short alkanes prefer a linear conformation, long ones - a folded one.

Why is that?

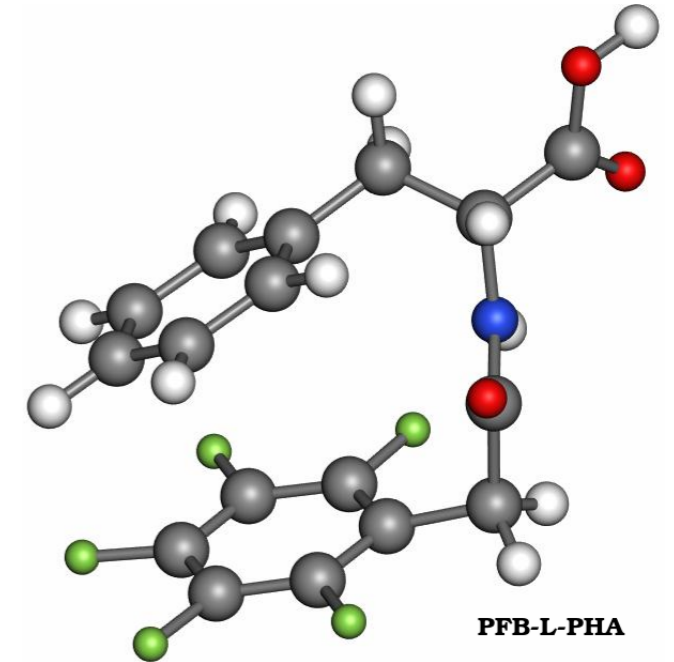
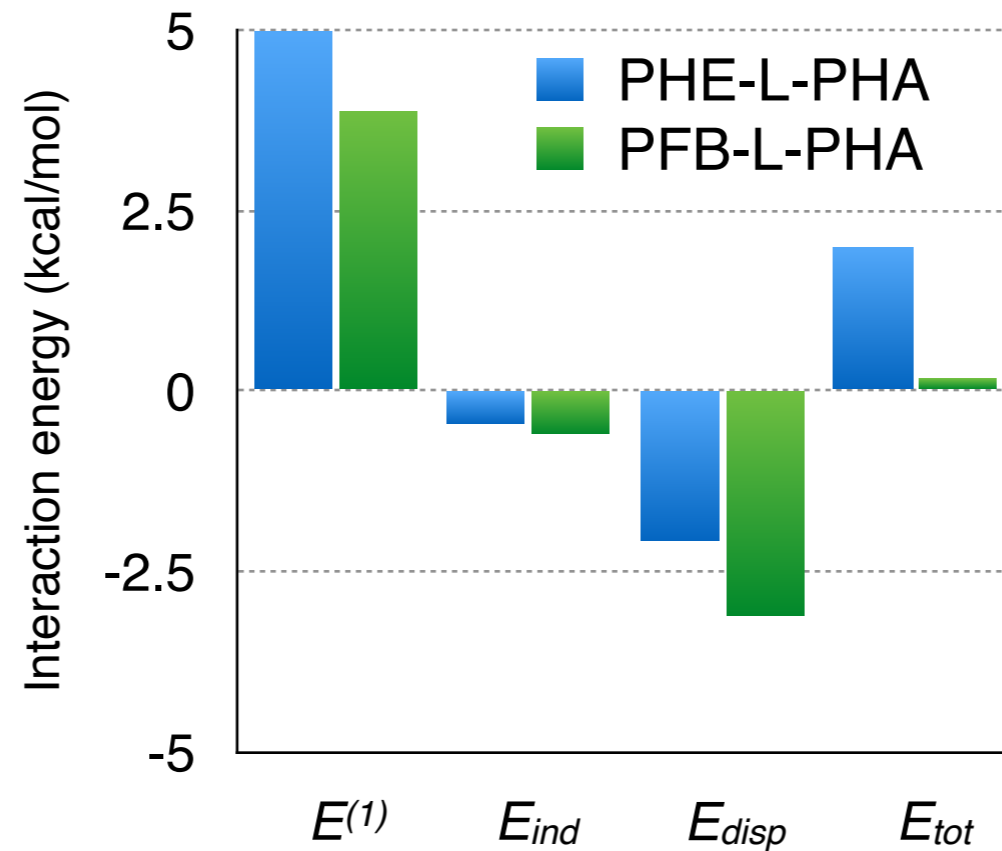
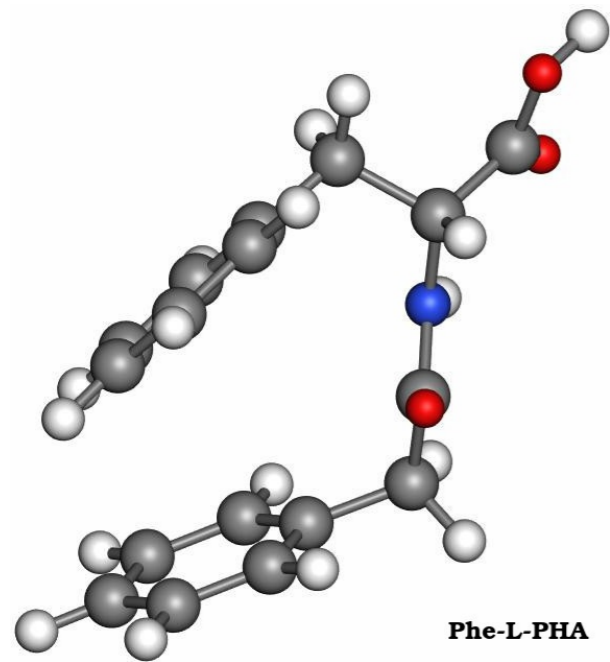
Hairpin alkanes

- a classic example of intramolecular dispersion



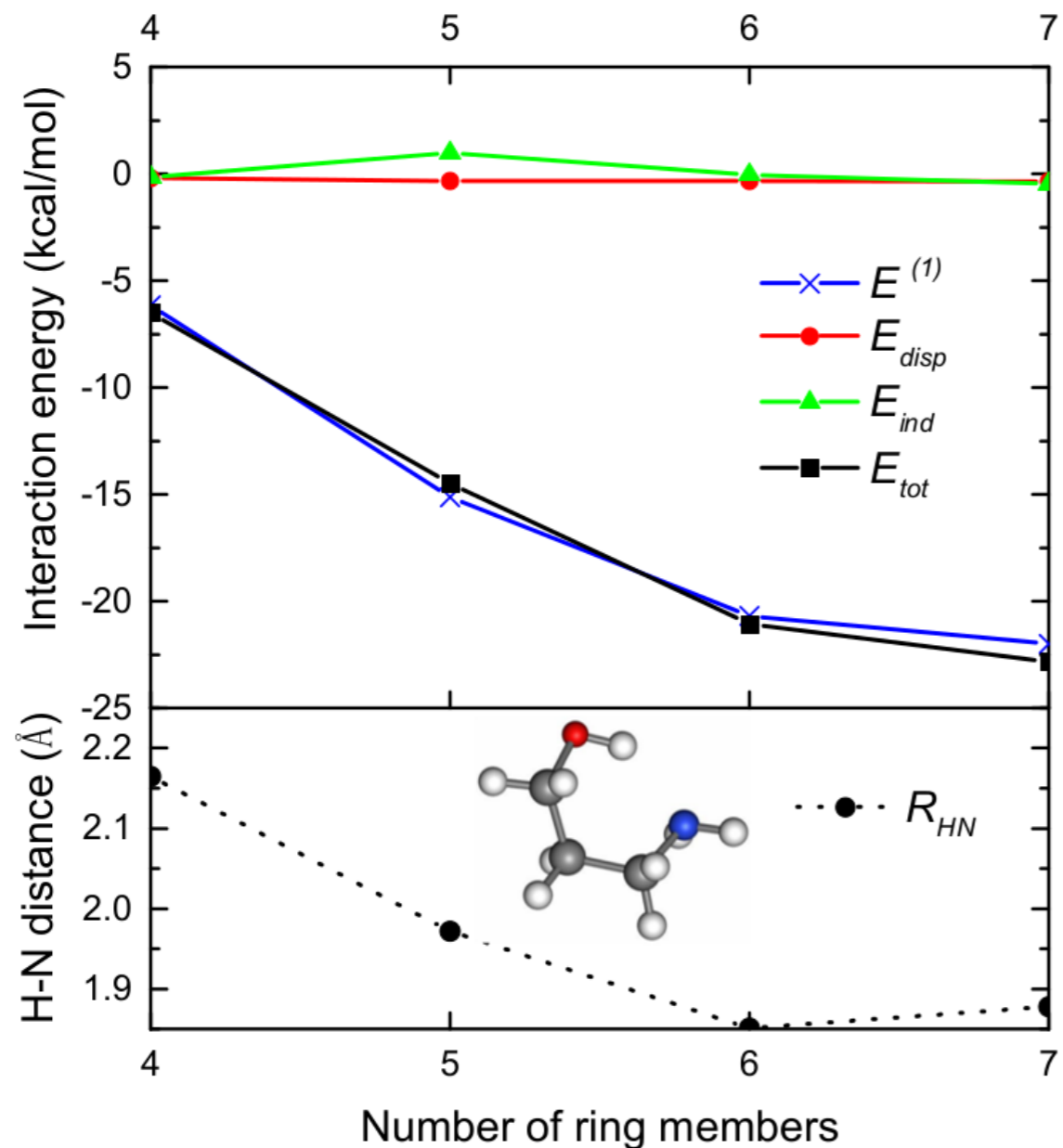
- Dispersion between the chains compensates for the Pauli repulsion
- With chain elongation molecule gains more freedom and tends towards its van der Waals minimum

Intramolecular π - π stacking



- The interaction between the rings is slightly repulsive
- The linker does not significantly influence the π - π interactions
- Dipole-dipole interactions between C-H and C-F pairs lower the repulsion in $E^{(1)}$

Hydrogen bonds in aminoalcohol molecules



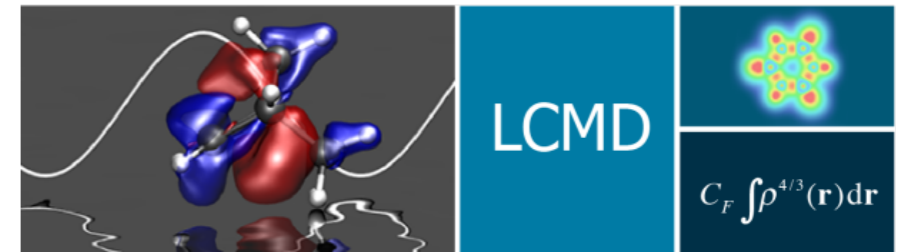
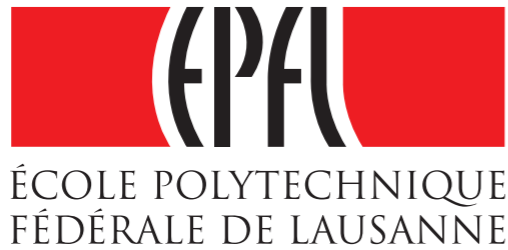
- Strong electrostatic attraction
- Induction and dispersion play no role
- Larger rings tend towards the maximization of the $\text{NH}_2\text{-OH}$ interaction
- Trend consistent with spectroscopic measurements
- Pauli repulsion slightly underestimated

Conclusions

- IntraSAPT is able to describe various types of intramolecular interactions
- A direct computation and interpretation of each energy component is possible
- A spin-coupling scheme is required

Different attempts to develop intramolecular SAPT

- intraSAPT (Corminboeuf): based on Chemical Hamiltonian approach
J. Chem. Phys., 140, 154107, 2014, J. Chem. Phys. 143, 224107 (2015)
- ISAPT (Parrish): SAPT0 & HF-in-HF density matrix embedding
J. Chem. Phys., 143, 051103 (2015)
- Hesselmann: incremental fragmentation method
J. Chem. Phys. 144, 084109 (2016)



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