Three-body intermolecular interactions with a combined density functional and symmetry-adapted perturbation theory approach

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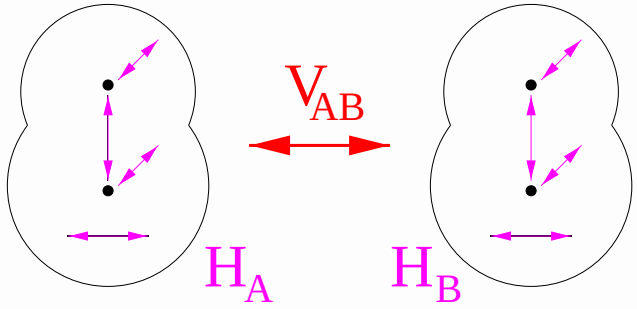
Symmetry-adapted perturbation theory (SAPT)

$$E_{\text{int}} = E_{\text{el}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)} + \cdots$$



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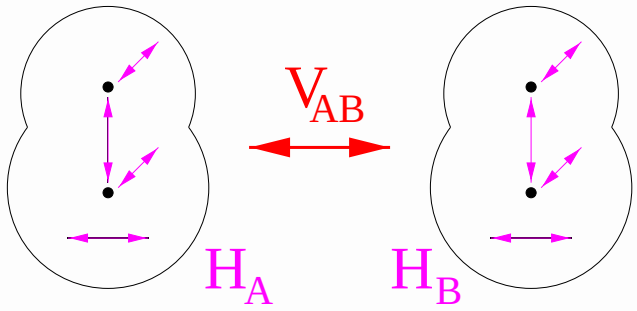

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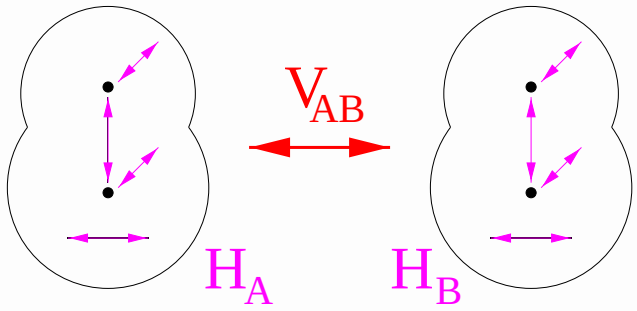

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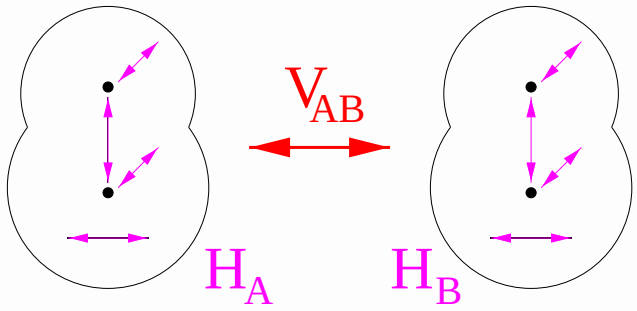
$$E_{\rm int} = E^{(1)}_{\rm el} + E^{(1)}_{\rm exch} + E^{(2)}_{\rm ind} + E^{(2)}_{\rm exch\text{-}ind} + E^{(2)}_{\rm disp} + E^{(2)}_{\rm exch\text{-}disp} + \ldots$$



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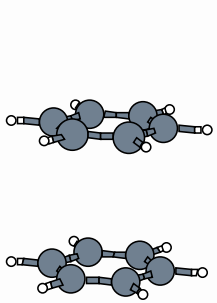
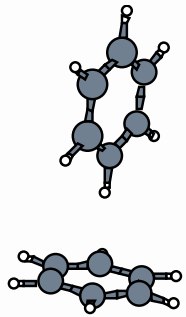
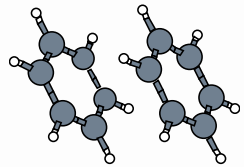
- Kohn-Sham densities, coupled response-densities, (coupled response-) density matrices for monomers:
  DFT-SAPT [G.J., Heßelmann , JPCA 105 (2001) 1115]

DFT-SAPT

Implementation of a density-fitting variant with Martin Schütz:

formal scaling $\mathcal{N}^6 \rightarrow \mathcal{N}^5$

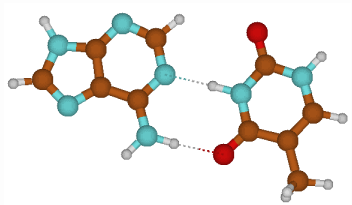
Application to $(\text{Benzene})_2$, up to 1512 GTOs (aug-cc-pVQZ), extrapolation to basis set limit:

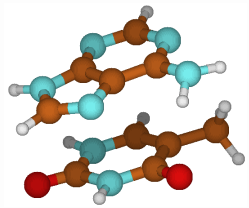




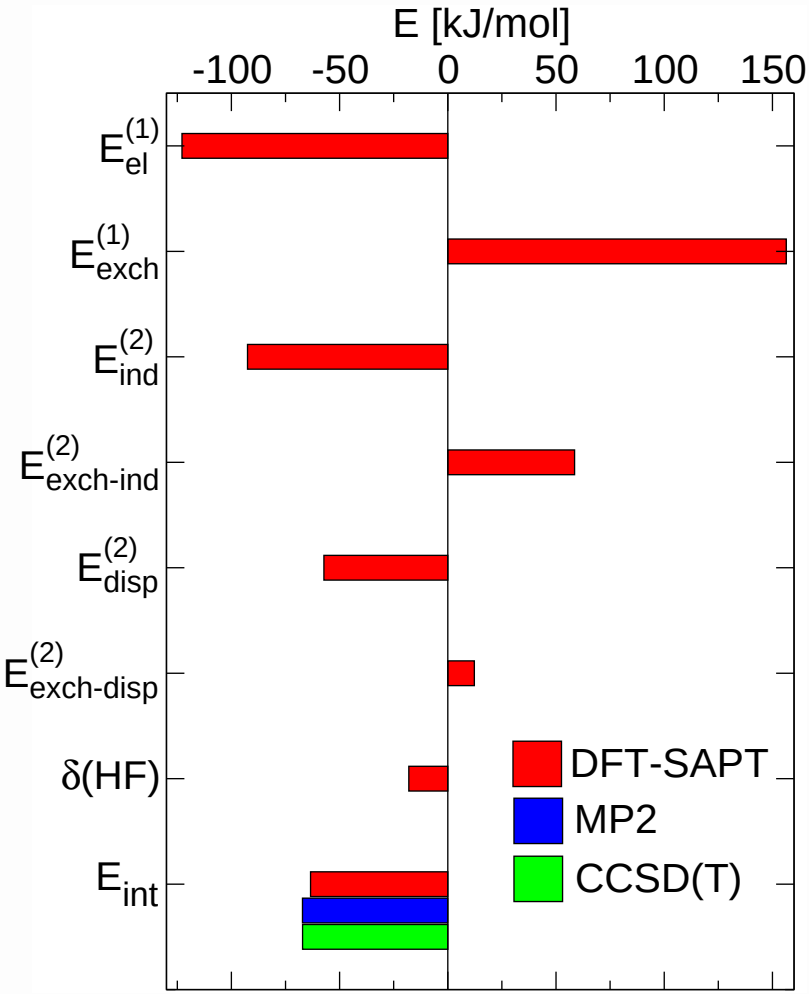
MP2	-14.4	-15.1	-20.3 kJ/mol
CCSD(T)	-6.7	-11.8	-11.4
DF-DFT-SAPT	-7.6	-11.9	-12.7

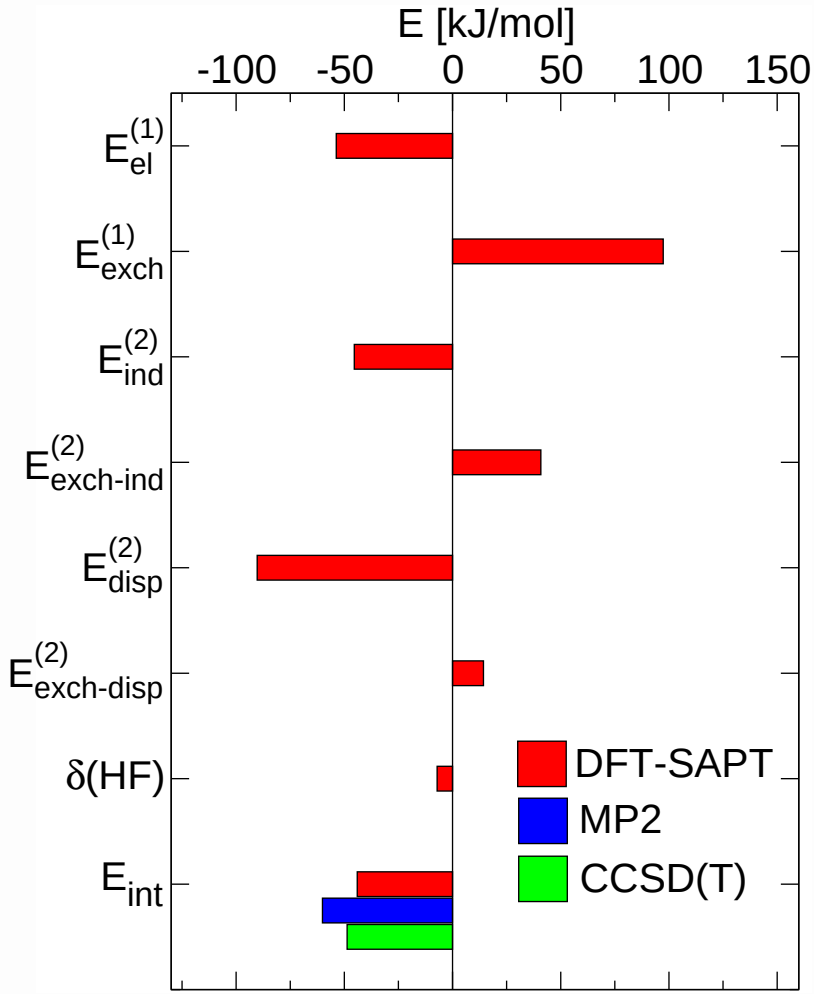
[A. Heßelmann, G.J., M. Schütz, JCP 122 (2005) 014103]

Adenine-Thymine









DF-DFT-SAPT up to aug-cc-pVQZ level

And what about larger aggregates?

$$E_{\rm int} = E_{\rm int}[2] + E_{\rm int}[3] + \ldots = \sum_{A<B} E_{\rm int}(A-B) + \sum_{A<B<C} E_{\rm int}(A-B-C) + \ldots$$

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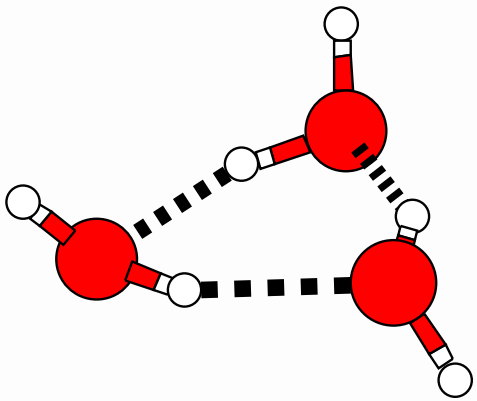

$E_{\rm int}[2] = -55.2$ kJ/mol

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[Mas et al., JCP 118 (2993) 4386]

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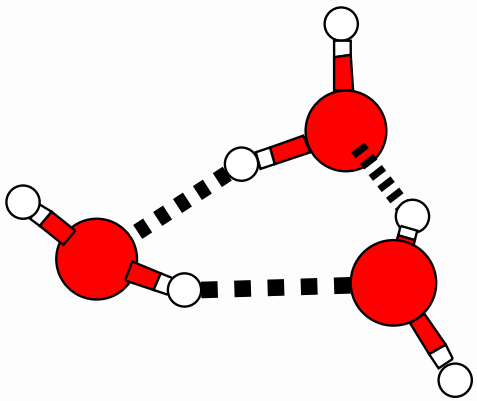

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Existing implementations [Jeziorski, Szalewicz, van der Avoird *et al.*]:

- intramonomer electron correlation only for $E^{(1)}_{\rm exch}$
- uncoupled Hartree-Fock for $E^{(2)}_{\rm exch-ind}$, $E^{(2)}_{\rm exch-disp}$

Project

- derivation and implementation of all three-body terms up to 2nd order ($E^{(1)}_{\mathrm{exch}}$, $E^{(2)}_{\mathrm{ind}}$, $E^{(2)}_{\mathrm{exch-ind}}$, $E^{(2)}_{\mathrm{exch-disp}}$) in DFT-SAPT framework

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- example application to $(H_2O)_3$

  $\Rightarrow$ improvement of polarizable force-fields

Outlook

- derivation and implementation of 3rd and higher order three-body terms

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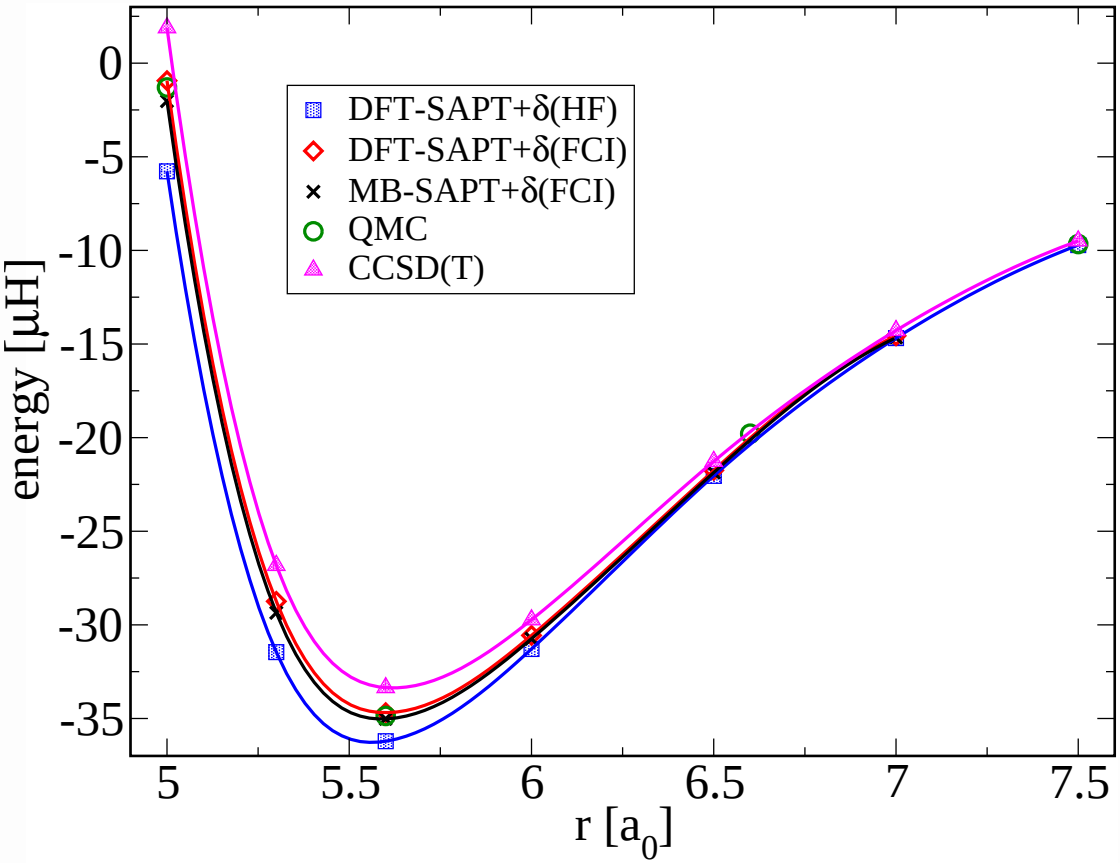
- derivation and implementation of 3rd and higher order three-body terms
- density-fitting implementation
- derivation of analytical representations useful in force-fields (e.g., for $\pi - \pi$-interactions)

$$\Downarrow$$

Simulations of condensed matter, biopolymers, . . .

DFT-SAPT for He_2 with exact xc-potential

- exact xc-potential for He atom used
- adiabatic local density approximation (ALDA) for xc-kernel
- 351 basis functions



	E_{int} [K]
DFT-SAPT+δ(HF)	-11.51
DFT-SAPT+δ(FCI)	-11.03
MB-SAPT+δ(FCI)	-11.059
FCI [cbs]	-11.008
QMC	-10.98
CCSD(T) [cbs]	-10.685

[A. Heßelmann and G.J., PCCP 5 (2003) 5010]