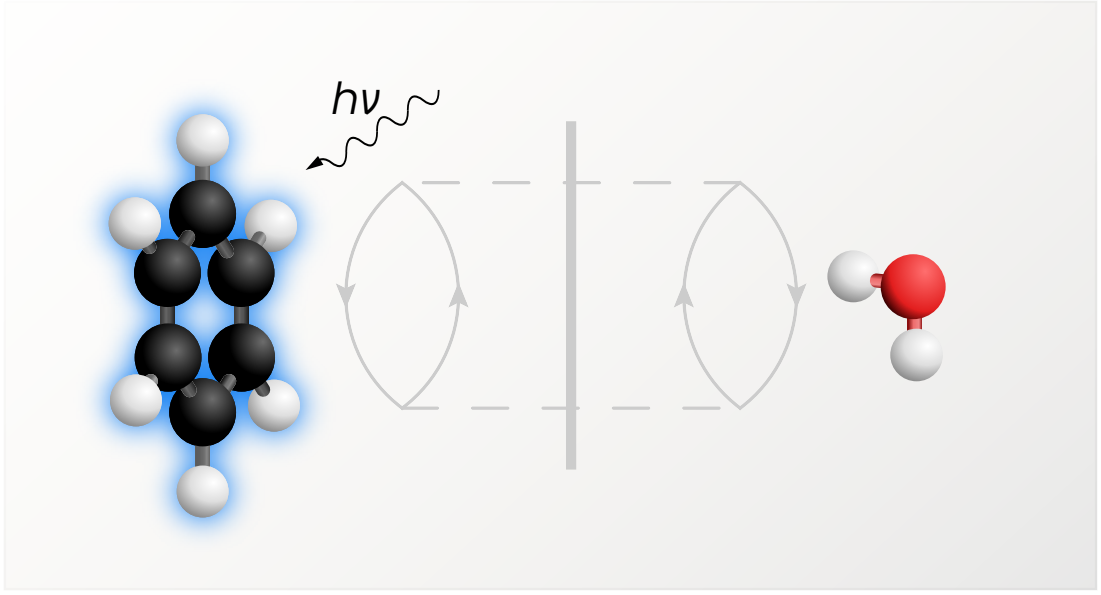
Dispersion Interactions in Exciton-Localized States. Theory and Applications to $\pi - \pi^*$ and $n - n^*$ Excited States



Michał Hapka, Katarzyna Pernal

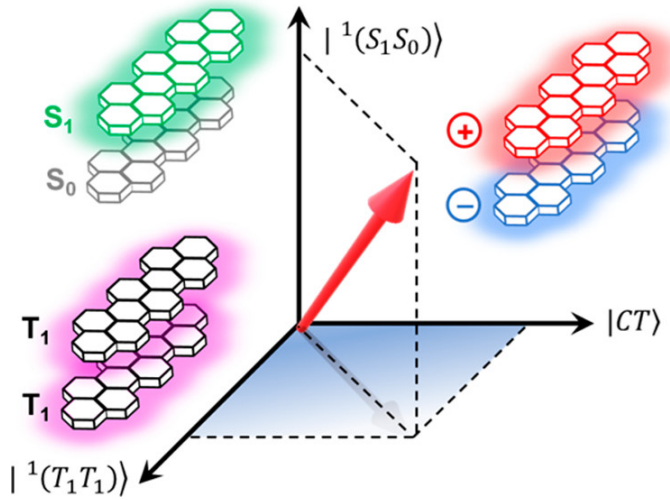
Quantum Chemistry Group
Lodz University of Technology

08.06.2022

Dispersion Interactions in Exciton-Localized States

Outline

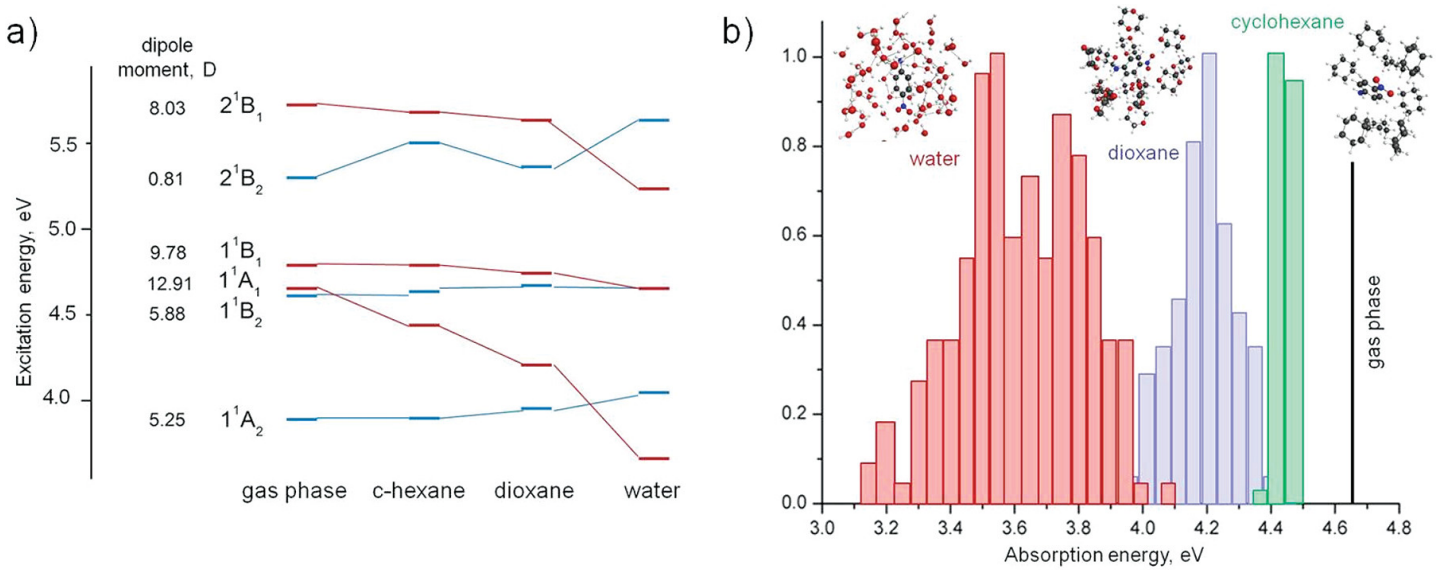
- Introduction
- Theory
  - dispersion energy for ES
- Results
  - energy decomposition
  - comparison of CASSCF-based approaches



R. M. Young, M. R. Wasilewski, *Acc. Chem. Res.* 53, 1957 (2020)

Interactions involving excited-state molecules

- understanding of charge/energy-transfer processes
- design of optoelectronic materials
  - organic LEDs, solar cells, molecular switches, ...
- solvent effects on absorption/emission bands



Effective fragment potential: A. DeFusco et al., *J. Phys. Chem. Lett*, 2, 2184 (2011)

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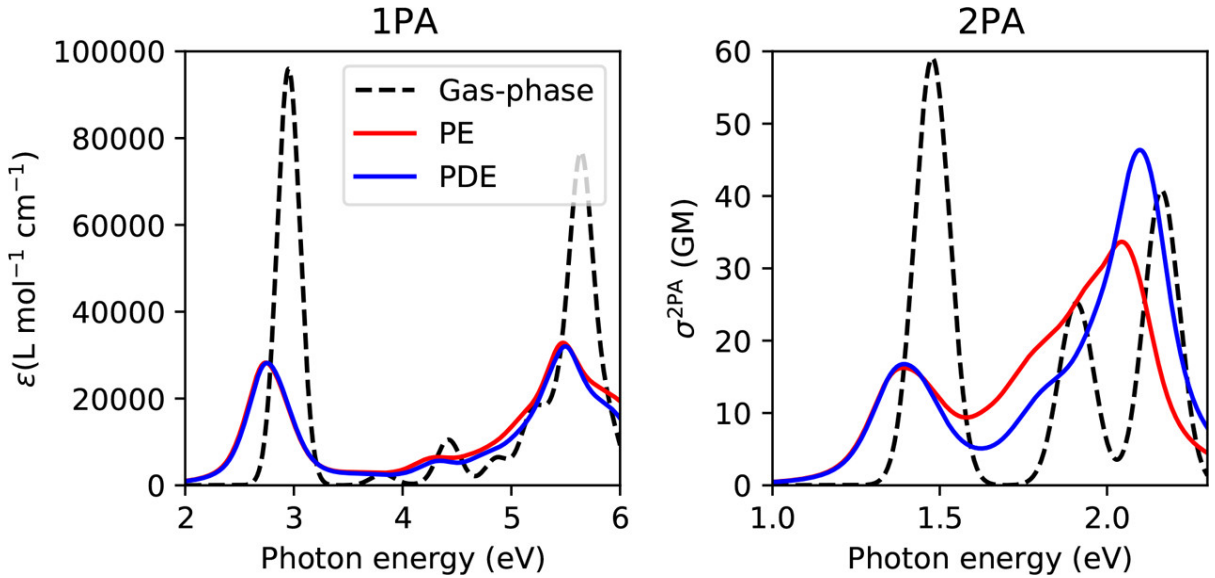

Polarizable embedding: P. Reinholdt et al., *J. Chem. Theory Comput.*, 16, 5999 (2020)

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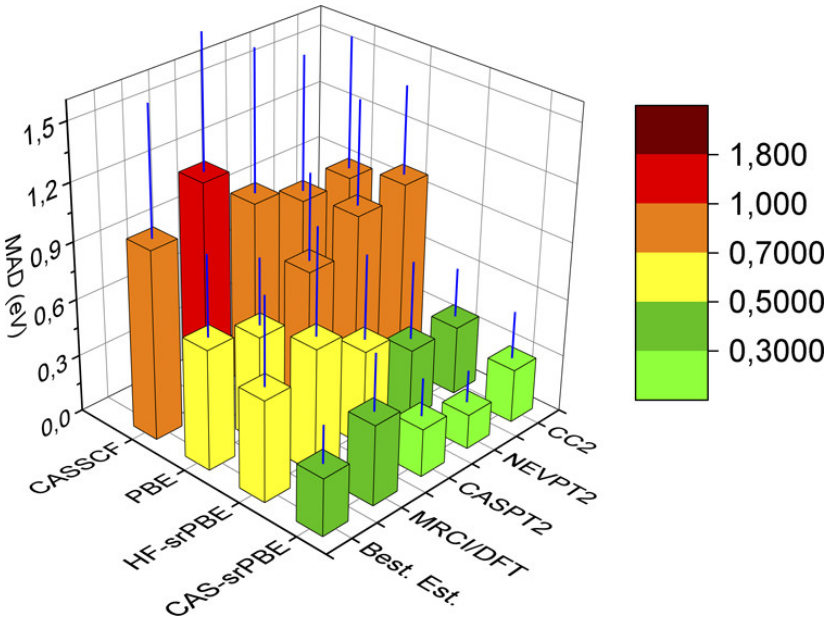
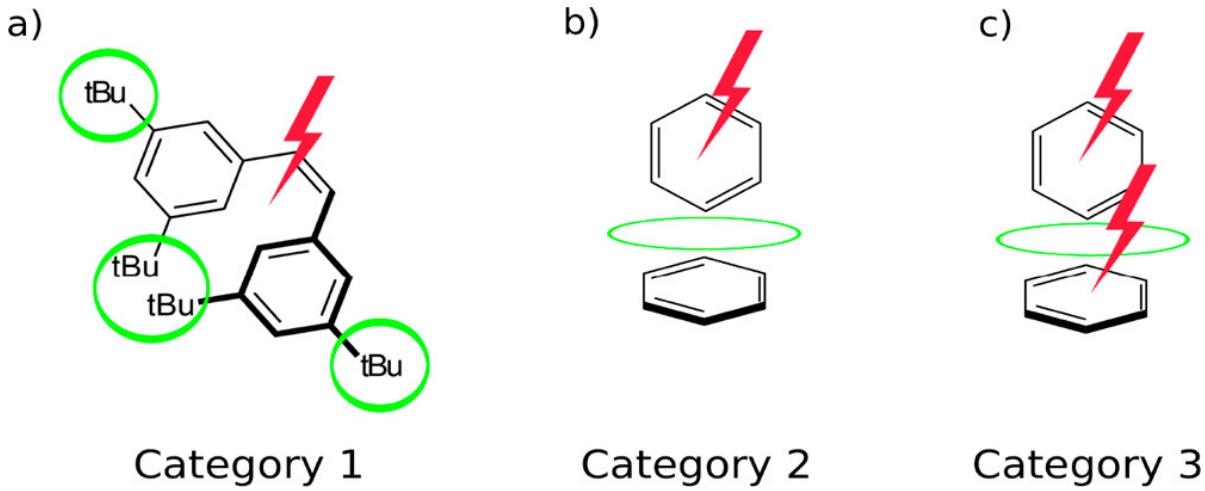


M. Hubert et al. *J. Chem. Theory Comput.*, 12, 2203 (2016)

Challenges for *ab initio* approaches

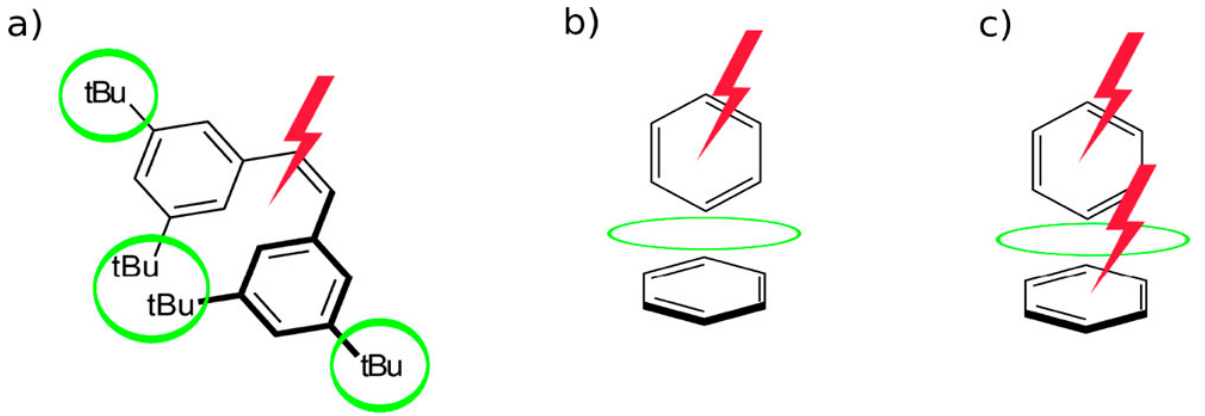
- multireference PT-based methods (CASPT2, NEVPT2)
  - size-inconsistency, intruder states
- coupled-cluster response (CC2, CC3)
  - limited to small- and medium-size systems
- time-dependent DFT
  - dispersion corrections designed for ground states



A. Fabrizio, C. Corminboeuf, *J. Phys. Chem. Lett.* 9 464 (2018)

Motivation

- direct calculations of London dispersion in electronically excited vdW complexes
- study of vdW complexes: low-lying π-π^* and n-π^* states



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Motivation

- direct calculations of London dispersion in electronically excited vdW complexes
- study of vdW complexes: low-lying π-π^* and n-π^* states
- excition localized on one of the monomers
  - no need for degenerate PT

Outline

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Dispersion energy for excited states

$$\lim_{R_{AB}\to\infty} |\Psi^{AB}\rangle = |\Psi_I^A \Psi_J^B\rangle\,, \quad \text{if } |\Psi_I^A \Psi_J^B\rangle \text{ nondegerate}$$

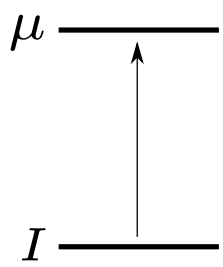
$$E_{\text{disp}}^{(2)}(A_I B_J) = -\sum_{\mu\neq I,\nu\neq J} \frac{1}{\omega_\mu^{A_I} + \omega_\nu^{B_J}} \left(\int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \frac{\rho_\mu^{A_I}(\mathbf{r}_1)\rho_\nu^{B_J}(\mathbf{r}_2)}{r_{12}} \right)^2 ,$$

where $I \to \mu$ transition energies and density are

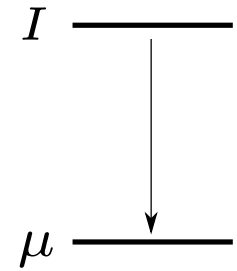
$$\omega_\mu^{A_I} = E_\mu^A - E_I^A$$

$$\rho_\mu^{A_I}(\mathbf{r}) = N_A \sum_\sigma \int \Psi_I^A(\mathbf{x}, \mathbf{x}_2, ...)^* \Psi_\mu^A(\mathbf{x}, \mathbf{x}_2, ...) \mathrm{d}\mathbf{x}_2 ... \mathrm{d}\mathbf{x}_{N_A}$$

Dispersion energy for excited states



$\forall_{\mu>I}\ \omega_\mu^{A_I} > 0$



$\forall_{\mu<I}\ \omega_\mu^{A_I} < 0$

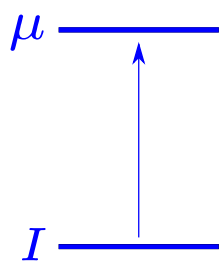
$$E^{(2)}_{\rm disp}(A_I B_J) = \sum_{\mu>I,\nu>J} W_{\mu\nu}^{A_I B_J} + \sum_{\mu<I,\nu<J} W_{\mu\nu}^{A_I B_J}$$

$$+ \sum_{\mu>I,\nu<J} W_{\mu\nu}^{A_I B_J} + \sum_{\mu<I,\nu>J} W_{\mu\nu}^{A_I B_J}\ ,$$

where

$$W_{\mu\nu}^{A_I B_J} = -\frac{1}{\omega_\mu^{A_I} + \omega_\nu^{B_J}} \left(\int\int \frac{\rho_\mu^{A_I}(\mathbf{r}_1)\rho_\nu^{B_J}(\mathbf{r}_2)}{r_{12}} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \right)^2$$

Dispersion energy for excited states



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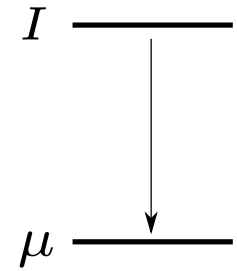

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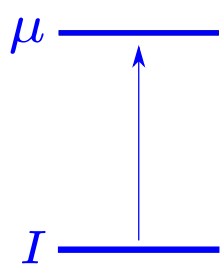

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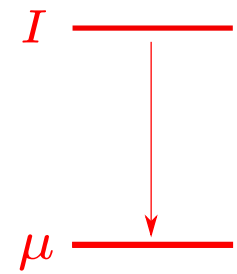

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$E^{(2)}_{\text{disp}}$ for excited states with SAPT(MC)

$$\underbrace{\{\gamma,\,\Gamma\}}_{} \rightarrow \underbrace{\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{B} & \mathcal{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} \mathcal{N} & \mathbf{0} \\ \mathbf{0} & -\mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix}}_{\text{ERPA}} \rightarrow \underbrace{\{\gamma^{0\nu}, \Gamma^{0\nu}, \omega_\nu\}}_{} \rightarrow E^{\text{SAPT}}_{\text{int}}$$

ERPA: K. Chatterjee, K. Pernal, *J. Chem. Phys.* 137 (2012)

SAPT(MC) $\equiv$ multiconfigurational SAPT

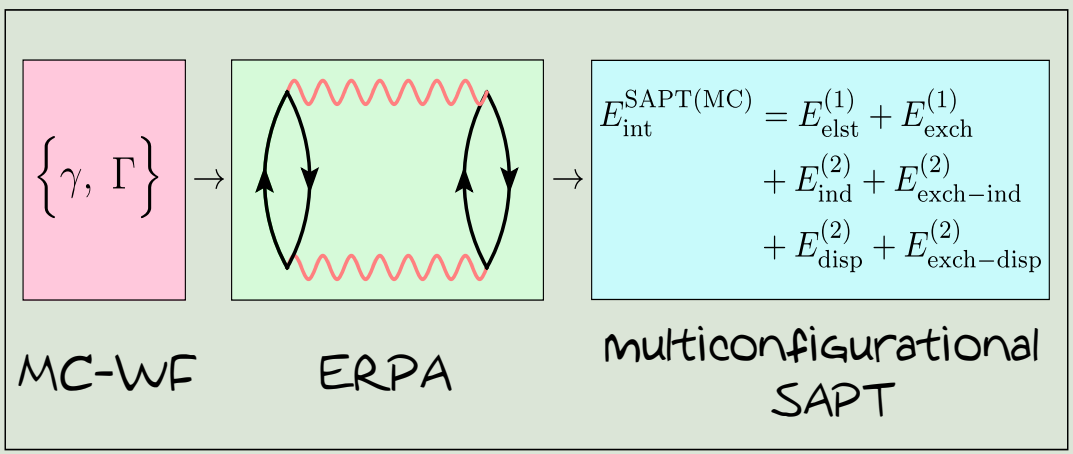
- requires only one- and two-particle reduced density matrices (γ, Γ) of the monomers
- 2nd order based on response properties from extended random phase approximation (ERPA)
- may be applied with any MC wavefunction (CAS, DMRG, GVB-PP, CIPSI...)

$E^{(2)}_{\text{disp}}$ for excited states with SAPT(MC)

$$\underbrace{\{\gamma,\ \Gamma\}}_{\text{MC-WF}} \rightarrow \underbrace{\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{B} & \mathcal{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} \mathcal{N} & \mathbf{0} \\ \mathbf{0} & -\mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix}}_{\text{ERPA}} \rightarrow \underbrace{\{\gamma^{0\nu}, \Gamma^{0\nu}, \omega_\nu\}}_{\text{E}^{\text{SAPT}}_{\text{int}}}$$

M. Hapka, M. Przybytek, K. Pernal, JCTC, 15, 6712 (2019), 17, 5538 (2021)

SAPT(MC) ≡ multiconfigurational SAPT



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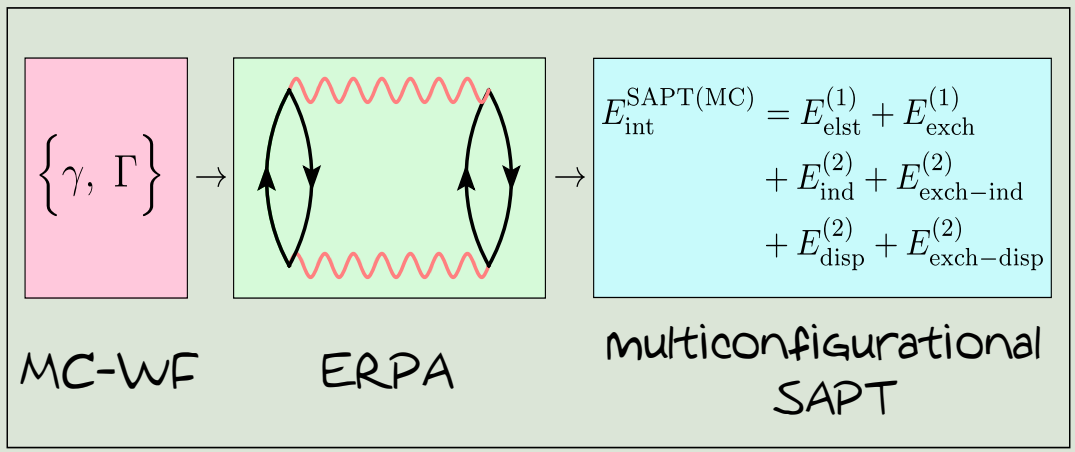

GammCor, `https://github.com/pernalk/GAMMCOR`

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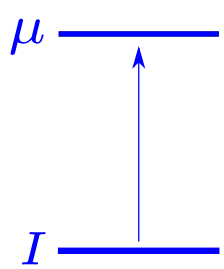

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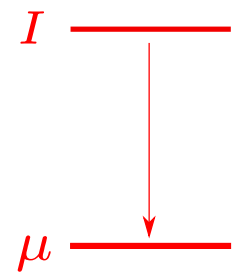

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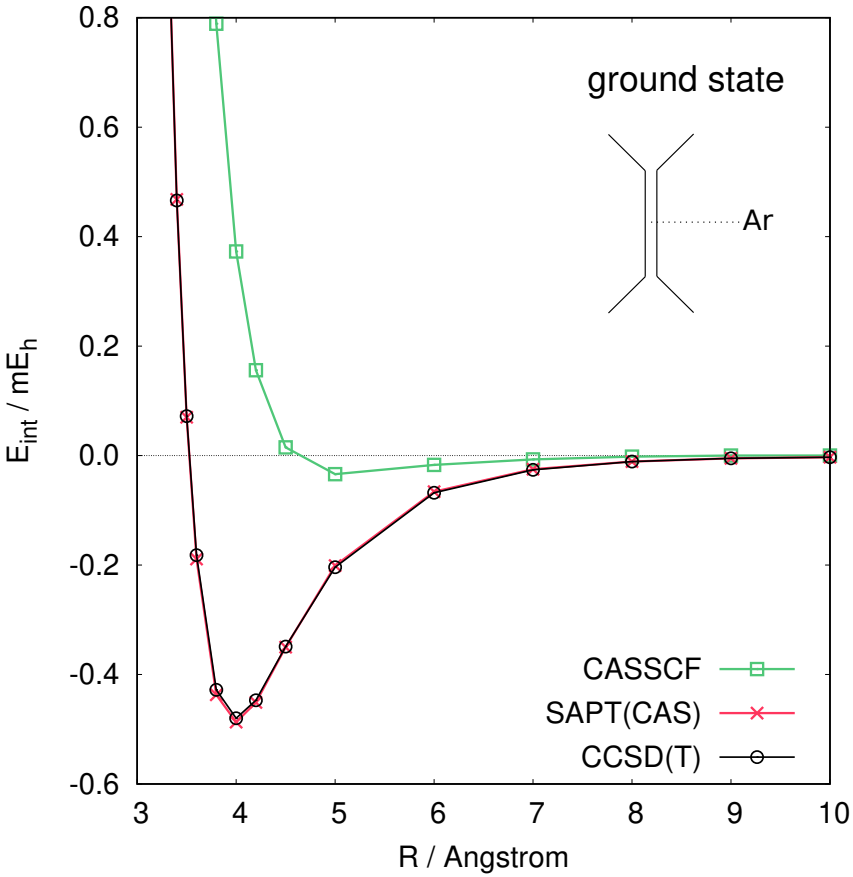
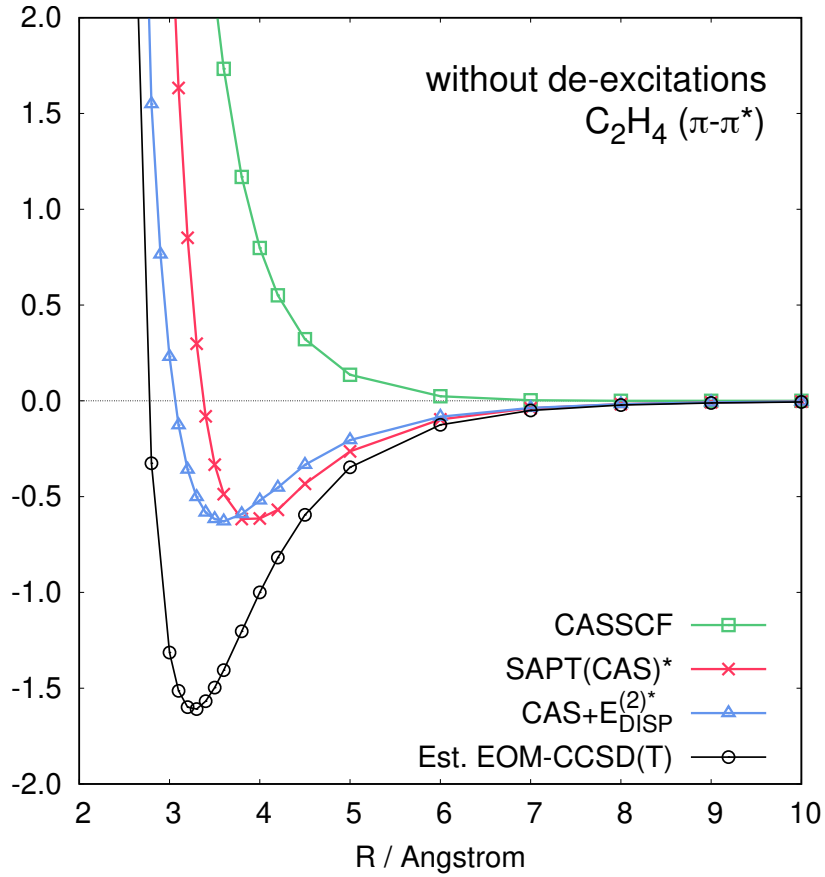
- can $W_{\mu\nu}^{A_I B_J}$ terms be relevant?

Example: $Ar\cdots C_2H_4$ and $C_2H_4(\pi \rightarrow \pi^*)$





M. Hapka, M. Przybytek, K. Pernal, *J. Chem. Theory Comput.*, 17, 5538 (2021)

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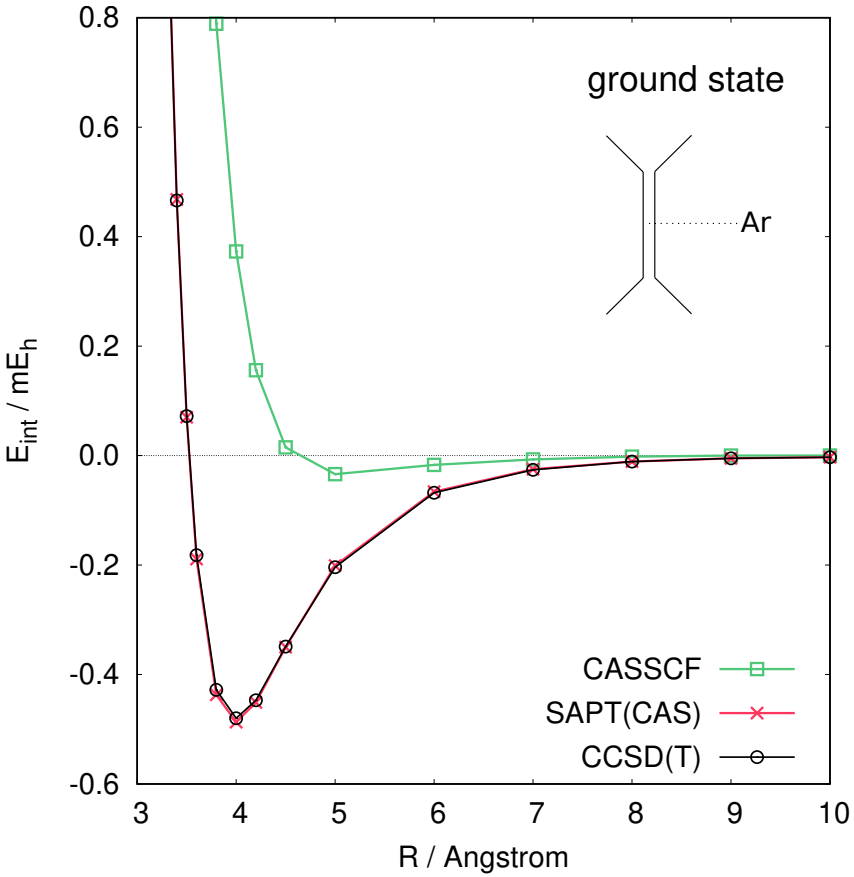

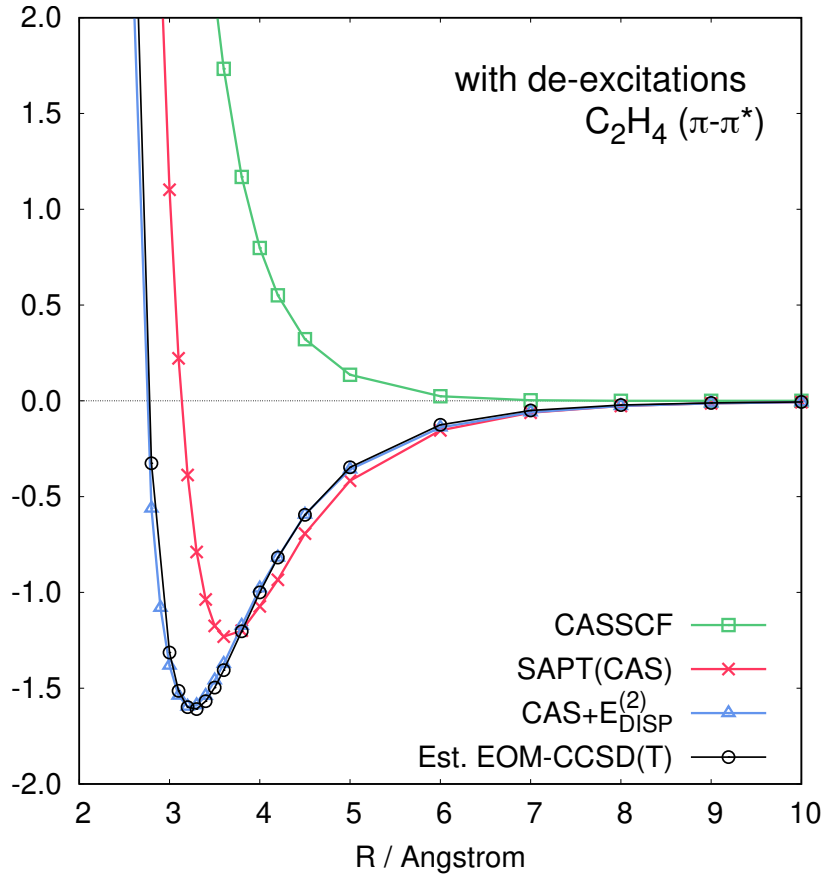

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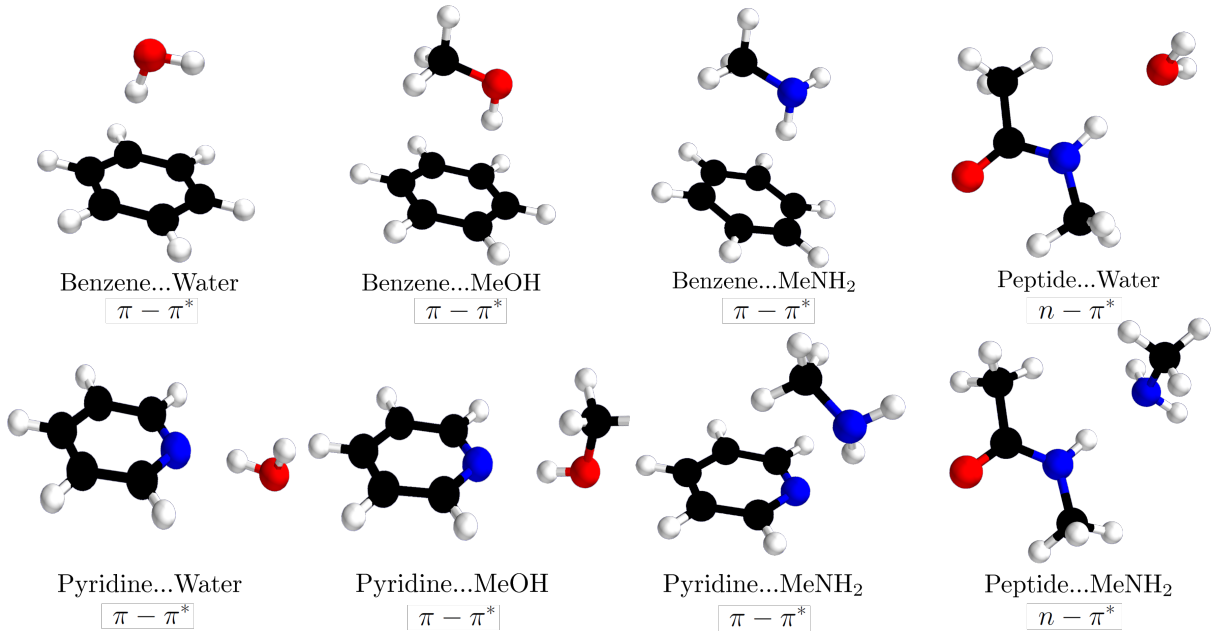
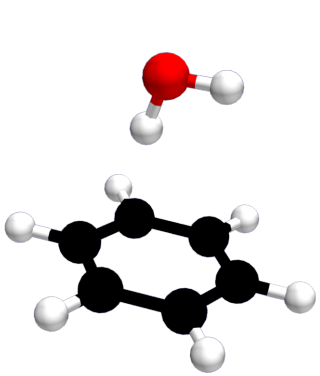


S66: J. Řezáč et al., *J. Chem. Theory Comput.* 7, 2427 (2011)

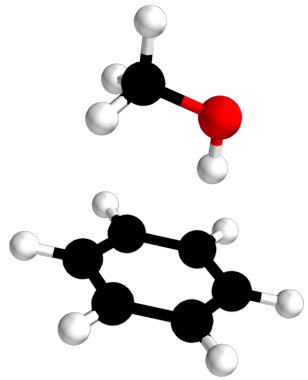
- energy decomposition
  - SAPT(CAS)
- assessment of CASSCF-based approaches
  - CAS+dispersion
  - multireference adiabatic connection (AC) methods

Benzene$\cdots H_2O$, $\cdots$MeOH, $\cdots MeNH_2$



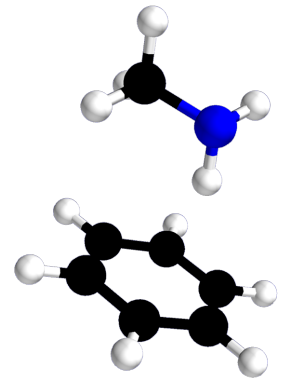
Benzene...Water

$\pi - \pi^*$



Benzene...MeOH

$\pi - \pi^*$



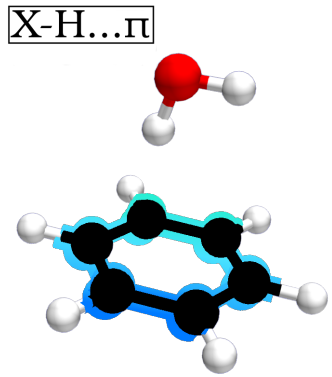
Benzene...$MeNH_2$

$\pi - \pi^*$

	ground state			excited state		
	H_2O	MeOH	$MeNH_2$	H_2O	MeOH	$MeNH_2$
$E^{(2)}_{\text{disp}}$	−3.06	−4.89	−4.86	−2.88	−4.63	−4.62
$E^{(1)}_{\text{elst}}$	−2.74	−3.08	−2.22	−1.85	−2.10	−1.68
disp/elst	1.1	1.6	2.2	1.6	2.2	2.8

kcal/mol

Benzene$\cdots$$H_2O$, $\cdots$MeOH, $\cdots$$MeNH_2$



Benzene...Water

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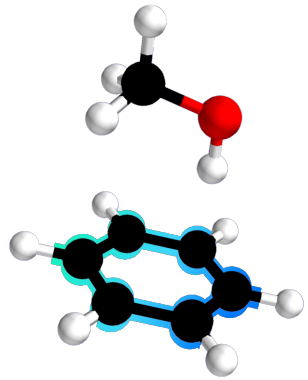
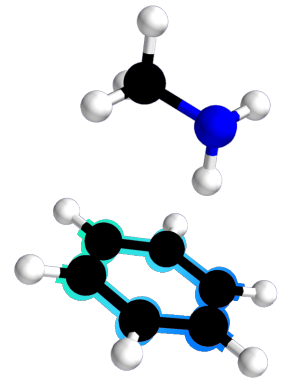


Benzene...MeOH

$\pi - \pi^*$



Benzene...$MeNH_2$

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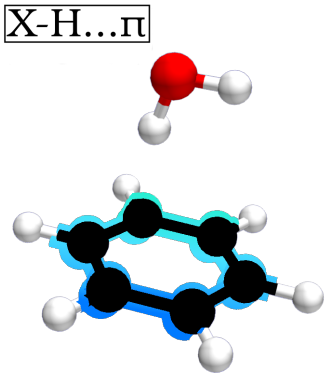
Benzene$\cdots$H$_2$O, $\cdots$MeOH, $\cdots$MeNH$_2$

X-H...π



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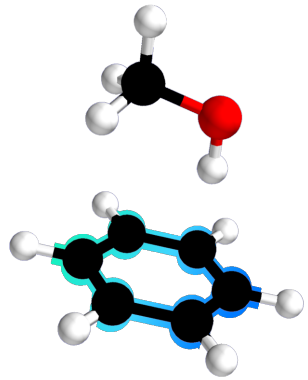
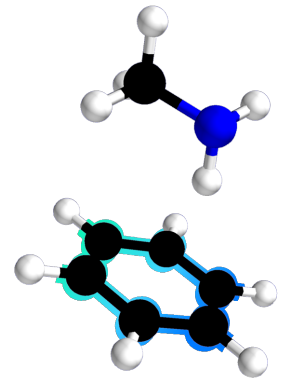


Benzene...MeOH

$\pi - \pi^*$



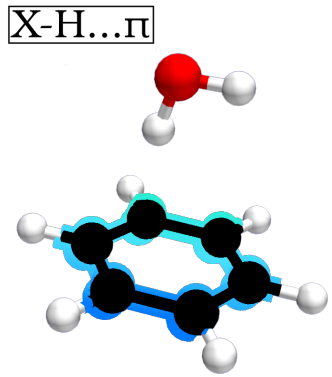
Benzene...MeNH$_2$

$\pi - \pi^*$

	ground state			excited state		
	H_2O	MeOH	$MeNH_2$	H_2O	MeOH	$MeNH_2$
$E^{(2)}_{\text{disp}}$	−3.06	−4.89	−4.86	−2.88	−4.63	−4.62
$E^{(1)}_{\text{elst}}$	−2.74	−3.08	−2.22	−1.85	−2.10	−1.68
disp/elst	1.1	1.6	2.2	1.6	2.2	2.8

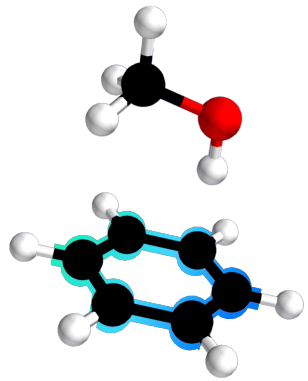
kcal/mol

Benzene$\cdots H_2O$, $\cdots$MeOH, $\cdots MeNH_2$



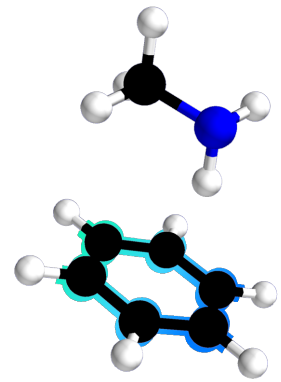
Benzene...Water

$\pi - \pi^*$



Benzene...MeOH

$\pi - \pi^*$



Benzene...$MeNH_2$

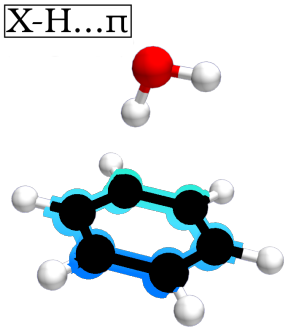
$\pi - \pi^*$

	ground state			excited state		
	H_2O	MeOH	$MeNH_2$	H_2O	MeOH	$MeNH_2$
$E^{(2)}_{\text{disp}}$	−3.06	−4.89	−4.86	−2.88	−4.63	−4.62
$\varepsilon^{1\to0}_{\text{disp}}$				−0.04	−0.06	−0.02
disp/elst	1.1	1.6	2.2	1.6	2.2	2.8

$\varepsilon^{1\to0}_{\text{disp}}$: non-CP terms; kcal/mol

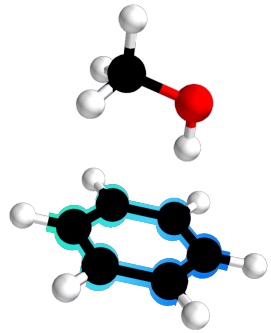
Benzene$\cdots$ H_2O, $\cdots$ MeOH, $\cdots$ $MeNH_2$

X-H...π



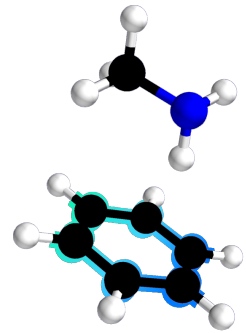
Benzene...Water

$\pi - \pi^*$



Benzene...MeOH

$\pi - \pi^*$



Benzene...$MeNH_2$

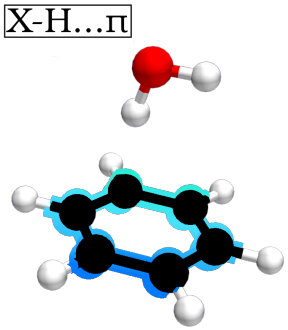
$\pi - \pi^*$

	$E_{es} - E_{gs}$		
	H_2O	MeOH	$MeNH_2$
$\Delta E^{(1)}_{elst}$	0.88	0.98	0.54
$\Delta E^{(1)}_{exch}$	−0.35	−0.45	−0.25
$\Delta E^{(2)}_{ind}$	0.11	0.15	0.08
$\Delta E^{(2)}_{exch-ind}$	−0.05	−0.08	−0.03
$\Delta E^{(2)}_{disp}$	0.17	0.24	0.22
$\Delta E^{(2)}_{exch-disp}$	−0.05	−0.07	−0.05
ΔE^{SAPT}_{int}	0.72	0.77	0.50

- stabilization | + destab. | kcal/mol

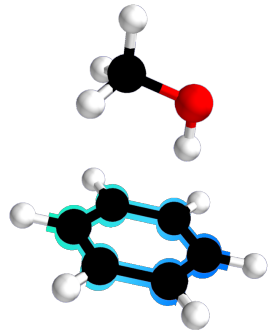
Benzene$\cdots$ H_2O, $\cdots$ MeOH, $\cdots$ $MeNH_2$

X-H...π



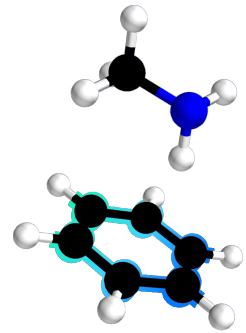
Benzene...Water

$\pi - \pi^*$



Benzene...MeOH

$\pi - \pi^*$



Benzene...$MeNH_2$

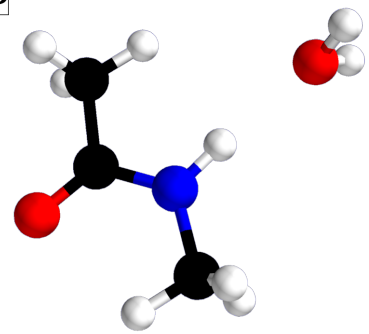
$\pi - \pi^*$

	$E_{es} - E_{gs}$		
	H_2O	MeOH	$MeNH_2$
$\Delta E^{(1)}_{elst}$	0.88	0.98	0.54
$\Delta E^{(1)}_{exch}$	-0.35	-0.45	-0.25
$\Delta E^{(2)}_{ind}$	0.11	0.15	0.08
$\Delta E^{(2)}_{exch-ind}$	-0.05	-0.08	-0.03
$\Delta E^{(2)}_{disp}$	0.17	0.24	0.22
$\Delta E^{(2)}_{exch-disp}$	-0.05	-0.07	-0.05
ΔE^{SAPT}_{int}	0.72	0.77	0.50

- stabilization | + destab. | kcal/mol

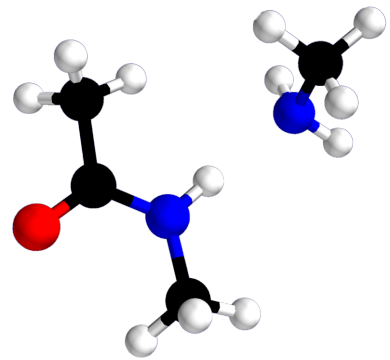
Peptide$\cdots$H$_2$O, $\cdots$MeNH$_2$

HB



Peptide...Water

$n - \pi^*$



Peptide...MeNH$_2$

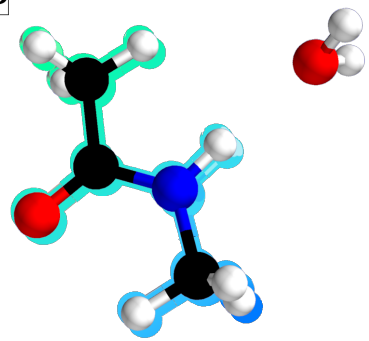
$n - \pi^*$

	ground state		excited state	
	H$_2$O	MeNH$_2$	H$_2$O	MeNH$_2$
$E^{(2)}_{\text{disp}}$	-2.93	-5.70	-2.93	-5.80
$E^{(1)}_{\text{elst}}$	-6.71	-10.55	-5.99	-9.84
disp/elst	0.4	0.5	0.5	0.6

kcal/mol

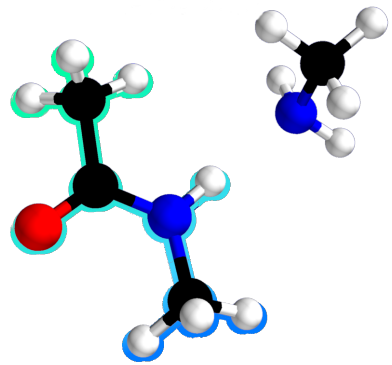
Peptide$\cdots$H$_2$O, $\cdots$MeNH$_2$

HB



Peptide...Water

$n - \pi^*$



Peptide...MeNH$_2$

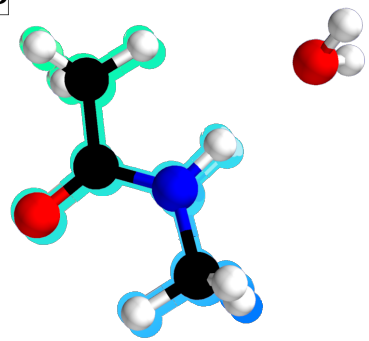
$n - \pi^*$

	ground state		excited state	
	H$_2$O	MeNH$_2$	H$_2$O	MeNH$_2$
$E^{(2)}_{\text{disp}}$	-2.93	-5.70	-2.93	-5.80
$E^{(1)}_{\text{elst}}$	-6.71	-10.55	-5.99	-9.84
disp/elst	0.4	0.5	0.5	0.6

kcal/mol

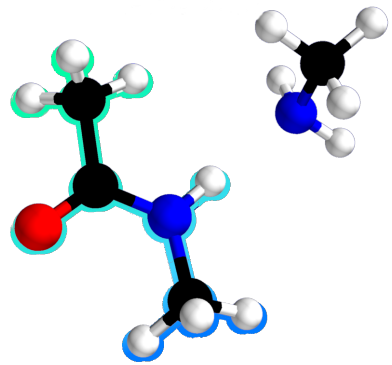
Peptide$\cdots H_2O$, $\cdots MeNH_2$

HB



Peptide...Water

$n - \pi^*$



Peptide...$MeNH_2$

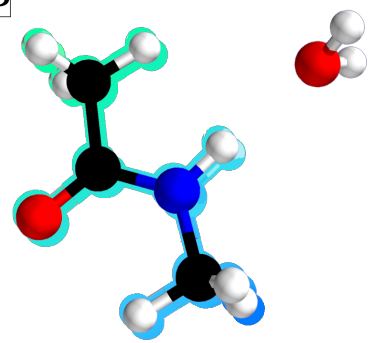
$n - \pi^*$

	ground state		excited state	
	H_2O	$MeNH_2$	H_2O	$MeNH_2$
$E^{(2)}_{\text{disp}}$	−2.93	−5.70	−2.93	−5.80
$E^{(1)}_{\text{elst}}$	−6.71	−10.55	-5.99	−9.84
disp/elst	0.4	0.5	0.5	0.6

kcal/mol

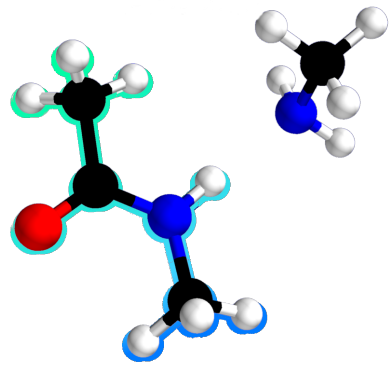
Peptide$\cdots H_2O$, $\cdots MeNH_2$

HB



Peptide...Water

$n - \pi^*$



Peptide...$MeNH_2$

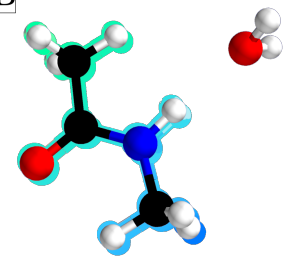
$n - \pi^*$

	ground state		excited state	
	H_2O	$MeNH_2$	H_2O	$MeNH_2$
$E^{(2)}_{\text{disp}}$	-2.93	-5.70	-2.93	-5.80
$\varepsilon^{1\to0}_{\text{disp}}$			0.00	0.00
disp/elst	0.4	0.5	0.5	0.6

$\varepsilon^{1\to0}_{\text{disp}}$: non-CP terms; kcal/mol

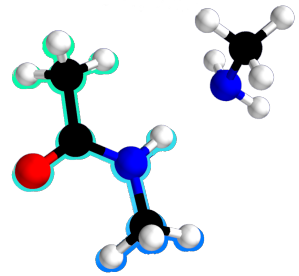
Peptide$\cdots$H$_2$O, $\cdots$MeNH$_2$

HB



Peptide...Water

$n - \pi^*$



Peptide...MeNH$_2$

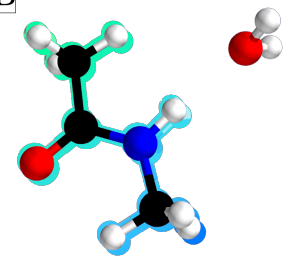
$n - \pi^*$

	$E_{es} - E_{gs}$	
	H$_2$O	MeNH$_2$
$\Delta E^{(1)}_{elst}$	0.71	0.71
$\Delta E^{(1)}_{exch}$	−0.03	0.05
$\Delta E^{(2)}_{ind}$	0.12	−0.12
$\Delta E^{(2)}_{exch-ind}$	−0.03	0.32
$\Delta E^{(2)}_{disp}$	−0.01	−0.10
$\Delta E^{(2)}_{exch-disp}$	0.01	0.05
ΔE^{SAPT}_{int}	0.77	0.91

- stabilization | + destab. | kcal/mol

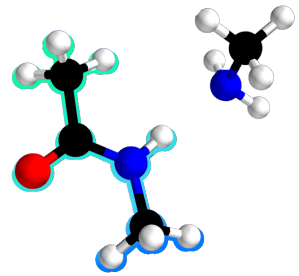
Peptide$\cdots$H$_2$O, $\cdots$MeNH$_2$

HB



Peptide...Water

$n - \pi^*$



Peptide...MeNH$_2$

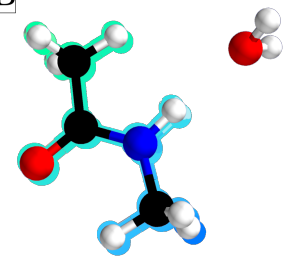
$n - \pi^*$

	$E_{es} - E_{gs}$	
	H$_2$O	MeNH$_2$
$\Delta E^{(1)}_{elst}$	0.71	0.71
$\Delta E^{(1)}_{exch}$	−0.03	0.05
$\Delta E^{(2)}_{ind}$	0.12	−0.12
$\Delta E^{(2)}_{exch-ind}$	−0.03	0.32
$\Delta E^{(2)}_{disp}$	−0.01	−0.10
$\Delta E^{(2)}_{exch-disp}$	0.01	0.05
ΔE^{SAPT}_{int}	0.77	0.91

- stabilization + destab. kcal/mol

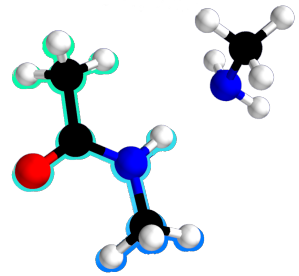
Peptide$\cdots$H$_2$O, $\cdots$MeNH$_2$

HB



Peptide...Water

$n - \pi^*$



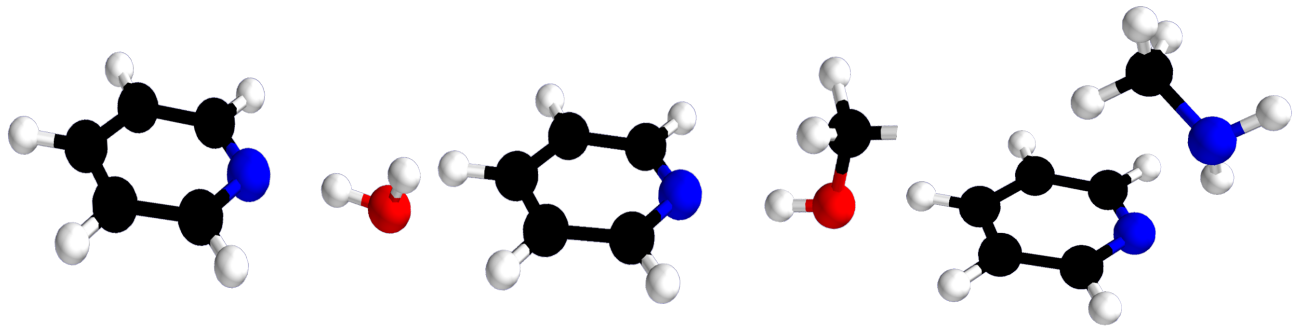
Peptide...MeNH$_2$

$n - \pi^*$

	$E_{es} - E_{gs}$	
	H$_2$O	MeNH$_2$
$\Delta E^{(1)}_{elst}$	0.71	0.71
$\Delta E^{(1)}_{exch}$	-0.03	0.05
$\Delta E^{(2)}_{ind}$	0.12	-0.12
$\Delta E^{(2)}_{exch-ind}$	-0.03	0.32
$\Delta E^{(2)}_{disp}$	-0.01	-0.10
$\Delta E^{(2)}_{exch-disp}$	0.01	0.05
ΔE^{SAPT}_{int}	0.77	0.91

- stabilization + destab. kcal/mol

Pyridine$\cdots$H$_2$O, $\cdots$MeOH, $\cdots$MeNH$_2$



Pyridine...Water
$\pi - \pi^*$

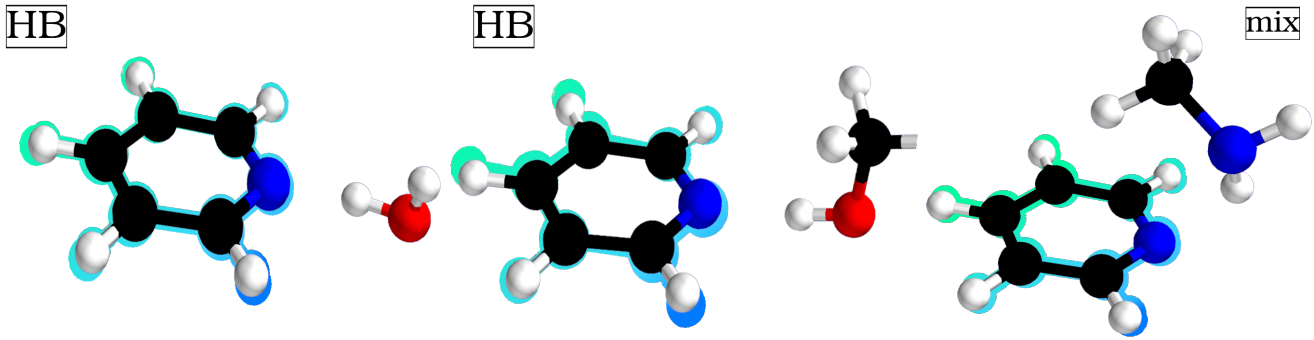
Pyridine...MeOH
$\pi - \pi^*$

Pyridine...MeNH$_2$
$\pi - \pi^*$

	ground state			excited state		
	H$_2$O	MeOH	MeNH$_2$	H$_2$O	MeOH	MeNH$_2$
$E^{(2)}_{\text{disp}}$	-4.09	-5.00	-5.17	-4.05	-4.95	-5.01
$E^{(1)}_{\text{elst}}$	-11.2	-11.8	-4.1	-11.2	-11.8	-3.9
disp/elst	0.4	0.4	1.3	0.4	0.4	1.3

kcal/mol

Pyridine$\cdots$H$_2$O, $\cdots$MeOH, $\cdots$MeNH$_2$



Pyridine...Water
$\pi - \pi^*$

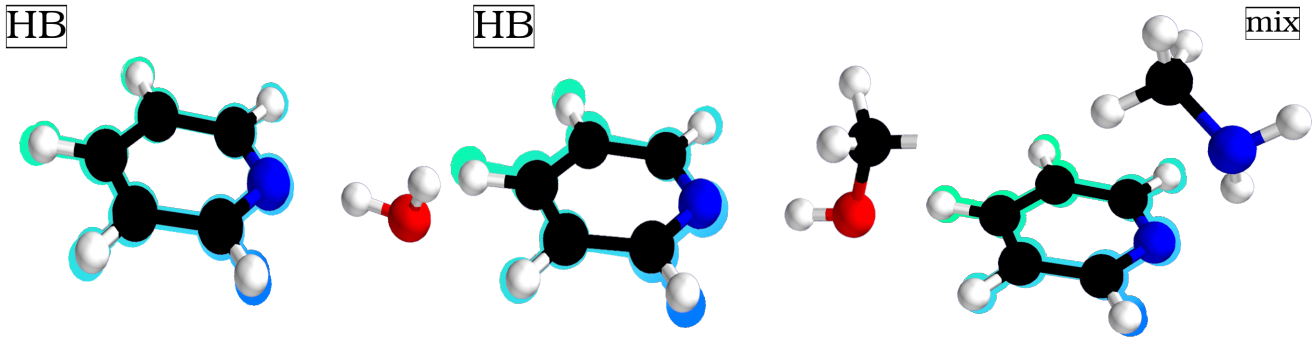
Pyridine...MeOH
$\pi - \pi^*$

Pyridine...MeNH$_2$
$\pi - \pi^*$

	ground state			excited state		
	H$_2$O	MeOH	MeNH$_2$	H$_2$O	MeOH	MeNH$_2$
$E^{(2)}_{\text{disp}}$	-4.09	-5.00	-5.17	-4.05	-4.95	-5.01
$E^{(1)}_{\text{elst}}$	-11.2	-11.8	-4.1	-11.2	-11.8	-3.9
disp/elst	0.4	0.4	1.3	0.4	0.4	1.3

kcal/mol

Pyridine$\cdots H_2O$, $\cdots$MeOH, $\cdots MeNH_2$



Pyridine...Water
$\pi - \pi^*$

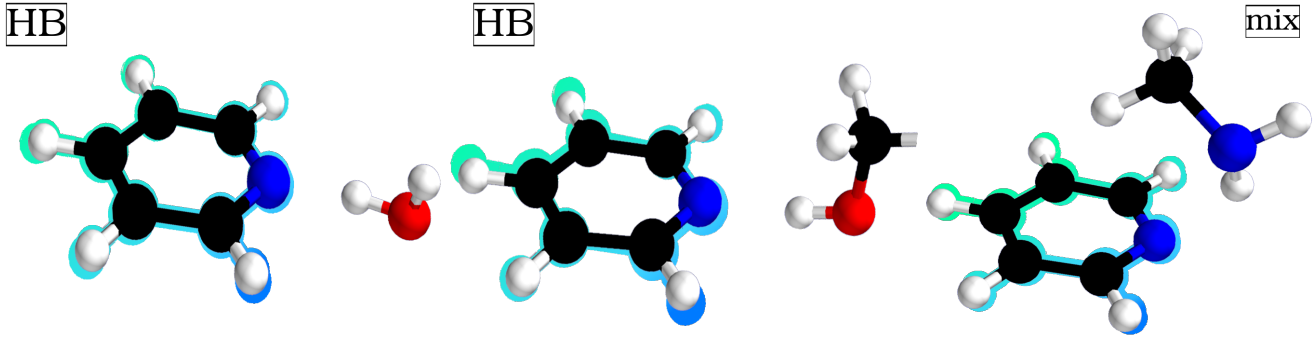
Pyridine...MeOH
$\pi - \pi^*$

Pyridine...$MeNH_2$
$\pi - \pi^*$

	ground state			excited state		
	H_2O	MeOH	$MeNH_2$	H_2O	MeOH	$MeNH_2$
$E^{(2)}_{\text{disp}}$	-4.09	-5.00	-5.17	-4.05	-4.95	-5.01
$E^{(1)}_{\text{elst}}$	-11.2	-11.8	-4.1	-11.2	-11.8	-3.9
disp/elst	0.4	0.4	1.3	0.4	0.4	1.3

kcal/mol

Pyridine$\cdots H_2O$, $\cdots$MeOH, $\cdots MeNH_2$



Pyridine...Water
$\pi - \pi^*$

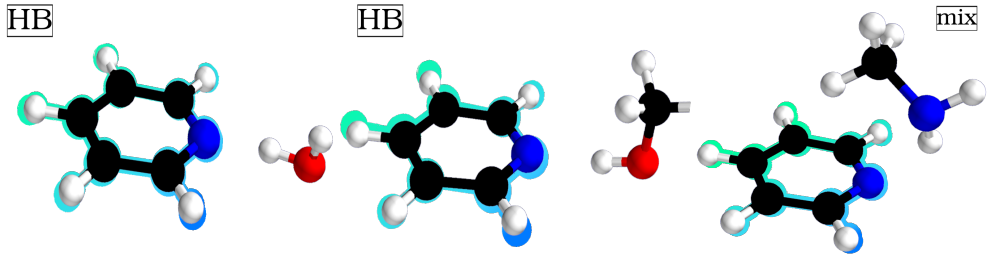
Pyridine...MeOH
$\pi - \pi^*$

Pyridine...$MeNH_2$
$\pi - \pi^*$

	ground state			excited state		
	H_2O	MeOH	$MeNH_2$	H_2O	MeOH	$MeNH_2$
$E^{(2)}_{\text{disp}}$	-4.09	-5.00	-5.17	-4.05	-4.95	-5.01
$\varepsilon^{1\to0}_{\text{disp}}$				-0.07	-0.08	-0.08
disp/elst	0.4	0.4	1.3	0.4	0.4	1.3

$\varepsilon^{1\to0}_{\text{disp}}$: non-CP terms; kcal/mol

Pyridine$\cdots$H$_2$O, $\cdots$MeOH, $\cdots$MeNH$_2$



Pyridine...Water
$\pi - \pi^*$

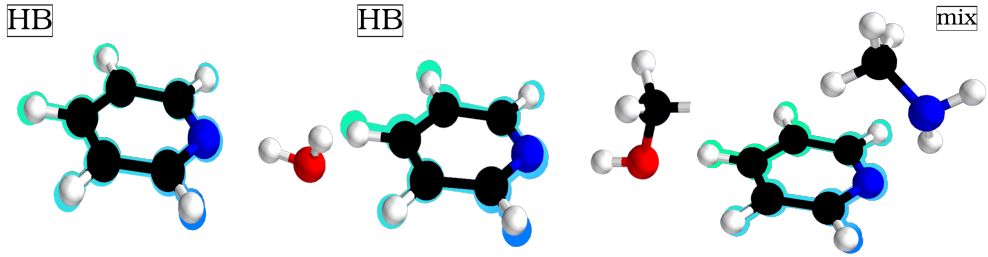
Pyridine...MeOH
$\pi - \pi^*$

Pyridine...MeNH$_2$
$\pi - \pi^*$

	$E_{es} - E_{gs}$		
	H$_2$O	MeOH	MeNH$_2$
$\Delta E^{(1)}_{elst}$	0.04	0.03	0.17
$\Delta E^{(1)}_{exch}$	0.02	0.02	−0.15
$\Delta E^{(2)}_{ind}$	0.02	0.02	0.04
$\Delta E^{(2)}_{exch-ind}$	0.01	0.01	−0.04
$\Delta E^{(2)}_{disp}$	0.02	0.04	0.15
$\Delta E^{(2)}_{exch-disp}$	0.00	0.00	−0.03
ΔE^{SAPT}_{int}	0.03	0.04	0.14

- stabilization | + destab. | kcal/mol

Pyridine$\cdots$H$_2$O, $\cdots$MeOH, $\cdots$MeNH$_2$



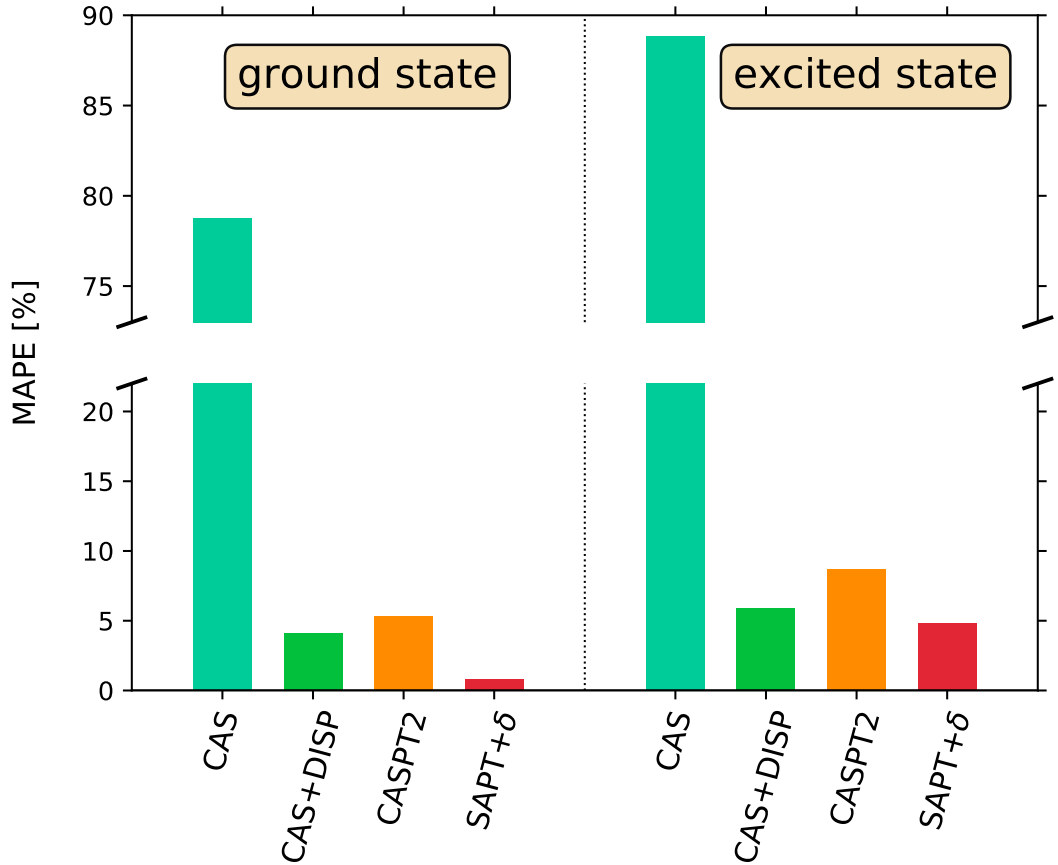
	$E_{es} - E_{gs}$		
	H$_2$O	MeOH	MeNH$_2$
$\Delta E^{(1)}_{elst}$	0.04	0.03	0.17
$\Delta E^{(1)}_{exch}$	0.02	0.02	-0.15
$\Delta E^{(2)}_{ind}$	0.02	0.02	0.04
$\Delta E^{(2)}_{exch-ind}$	0.01	0.01	−0.04
$\Delta E^{(2)}_{disp}$	0.02	0.04	0.15
$\Delta E^{(2)}_{exch-disp}$	0.00	0.00	−0.03
ΔE^{SAPT}_{int}	0.03	0.04	0.14

- stabilization | + destab. | kcal/mol

Outline

- Introduction
- Theory
  - dispersion energy for ES
- Results
  - energy decomposition
  - comparison of CASSCF-based approaches

Interaction energies: mean absolute % errors



- SAPT > CAS+DISP > CASPT2

Conclusions

$E^{(2)}_{\text{disp}}$ for excited states

- generalized Casimir-Polder formula
  - involves "de-excitation" terms
- can be obtained in SAPT(MC)

Numerical demonstration: $\pi \to \pi^*$, $n \to \pi^*$

- SAPT(CAS) useful for $E^{\text{ES}}_{\text{int}}$ decomposition
- $\Delta E^{(2)}_{\text{disp}}$ cannot be neglected

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M. R. Jangrouei et al., *J. Chem. Theory Comput.*, 10.1021/acs.jctc.2c00221

GammCor, `https://github.com/pernalk/GAMMCOR`

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Thank you for your attention!