Targeting Real chemical accuracy at the EXascale

Recent developments in SAPT(MC)

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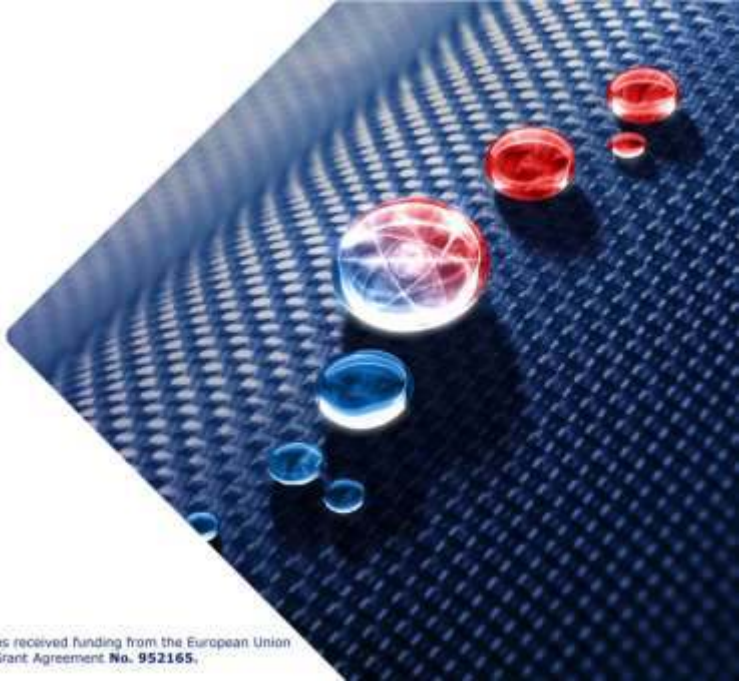
February 8, 2024

University of Warsaw, Poland

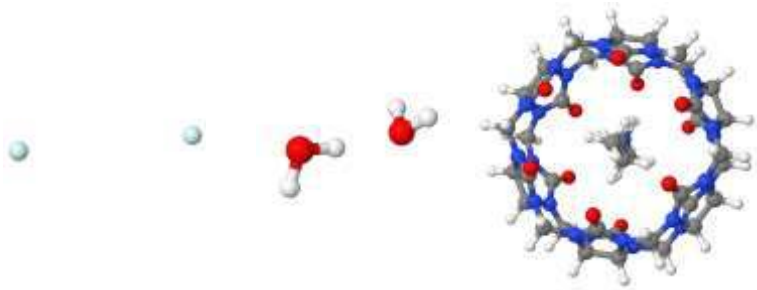


Targeting Real Chemical Accuracy at the Exascale project has received funding from the European Union Horizoon 2020 research and innovation programme under Grant Agreement **No. 952165.**

- Introduction
- SAPT
  - general
  - Many-body SAPT
  - SAPT(DFT)
  - Multicon gurational SAPT
  - SAPT(MC-srDFT)
  - interactions in ground vs. excited states

- Interaction energy for weakly interacting subsystems A and B

$$E_{int} = E_{AB} - E_A - E_B$$

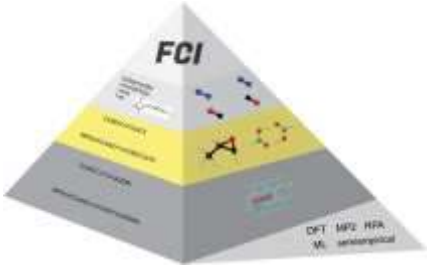


-0.02 kcal/mol -5.01 kcal/mol -82.2 kcal/mol

$$E_{int} = E_{AB} - E_A - E_B$$

Accuracy:

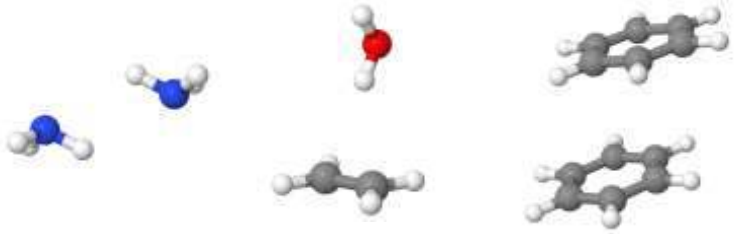
- covalent interactions:
  - 1 kcal/mol (chemical accuracy)
- noncovalent interactions:
  - 0.1 kcal/mol
  - 0.001 kcal/mol (spectroscopic accuracy)



Supermolecular CC: platinum, gold, ... standards

M. Kodrycka, K. Patkowski, JCP, 151, 070901 (2019)

- Interpretation: E_{int} is a single number



-3.14 kcal/mol -2.56 kcal/mol -2.73 kcal/mol

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Symmetry-adapted perturbation theory (SAPT)

- high-accuracy
- E_{int} decomposed into physically-meaningful terms

$$E_{int}^{SAPT} = E_{elst}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{exch-ind}^{(2)} + E_{disp}^{(2)} + E_{exch-disp}^{(2)} + \ldots$$

- MB-SAPT, SAPT(DFT), SAPT(MC), ...

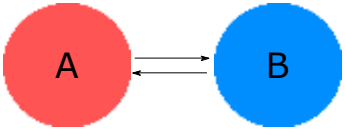
B. Jeziorski, R. Moszynski, K. Szalewicz, Chem. Rev. 94, 1887 (1994)
G. Jansen, WIREs Comput Mol Sci. 4:127 (2014)
K. Patkowski, WIREs Comput Mol Sci. 10:e1452 (2020)
T. Korona et al, Adv. Quant. Chem. 87, 37 (2023)

- perturbation expansion in orders of V

$$H = \underbrace{H_A + H_B}_{H_0} + V$$

$$V = \sum_{i\in A}\sum_{k\in B}\frac{1}{r_{ik}} - \sum_{i\in A}\sum_{\beta\in B}\frac{Z_\beta}{|r_i - R_\beta|} - \sum_{k\in B}\sum_{\alpha\in A}\frac{Z_\alpha}{|r_k - R_\alpha|} + \sum_{\alpha\in A}\sum_{\beta\in B}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}$$

B. Jeziorski, R. Moszynski, K. Szalewicz, Chem. Rev. 94, 1887 (1994)



- incomplete antisymmetry of $\Psi_A^{(0)}\Psi_B^{(0)}$
  - $A \overset{e}{\leftrightarrow} B$ exchange tunneling missing
  - symmetry forcing required
- exact $\Psi_A^{(0)}$ and $\Psi_B^{(0)}$ not known

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- developed in 1990s
- double-perturbation theory

$$H = \underbrace{F_A + F_B}_{=H_0} + \zeta W + \lambda V$$

$$W = \underbrace{W_A + W_B}_{\text{fluctuation potential}}$$

$$= (H_A - F_A) + (H_B - F_B)$$

- gives rise to a whole family of methods (SAPT0, SAPT2, ...)

$$E_{int}^{SAPT0} = E_{elst}^{(10)} + E_{exch}^{(10)} + E_{ind}^{(20)} + E_{exch-ind}^{(20)} + E_{disp}^{(20)} + E_{exch-disp}^{(20)} + \delta_{HF}$$

S. Rybak, B. Jeziorski, K. Szalewicz, JCP 95, 6576 (1991)
E. G. Hohenstein, C. D. Sherrill, WIREs 2:304 (2012)

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$$E_{int}^{SAPT2} = E_{int}^{SAPT0} + E_{elst}^{(12)} + E_{exch}^{(11)} + E_{exch}^{(12)} + {}^{t}E_{ind}^{(22)} + {}^{t}E_{exch\text{-}ind}^{(22)}$$

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$$E_{int}^{SAPT2+} = E_{int}^{SAPT2} + E_{disp}^{(21)} + E_{disp}^{(22)}$$

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$$E_{int}^{SAPT2+} = E_{int}^{SAPT2} + E_{disp}^{(21)} + E_{disp}^{(22)}$$

$$E_{int}^{SAPT2+(3)} = E_{int}^{SAPT2+} + E_{elst}^{(13)} + E_{disp}^{(30)}$$

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E. G. Hohenstein, C. D. Sherrill, WIREs 2:304 (2012)

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\begin{aligned}
E_{int}^{SAPT(DFT)} &= E_{elst}^{(1)} + E_{exch}^{(1)} \\
&+ E_{ind}^{(2)} + E_{exch-ind}^{(2)} \\
&+ E_{disp}^{(2)} + E_{exch-disp}^{(2)} \\
&+ \delta_{HF}
\end{aligned}
$$

- response properties from TDKS with asymptotic correction for KS potentials

A. Hesselmann, G. Jansen, M. Sch tz, JCP 122, 014103 (2005)
A. Misquitta, R. Podeszwa, B. Jeziorski, K. Szalewicz, JCP 123, 214103 (2005)

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$$E_{int}^{SAPT(DFT)} = E_{elst}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{exch-ind}^{(2)} + E_{disp}^{(2)} + E_{exch-disp}^{(2)} + \delta_{HF}$$

- response properties from TDKS

- terms depending on ρ and $\delta\rho$: accurate
- exchange terms: approximate

$$E_{elst}^{(1)} = \int \rho_A^{tot}(r_1)\frac{1}{|r_1 - r_2|}\rho_B^{tot}(r_2)dr_1dr_2$$

$$E_{ind}^{(2)}(A \leftarrow B) = \frac{1}{2}\int \omega_B(r_1)\omega_B(r_2)\alpha_A(r_1, r_2|0)dr_1dr_2$$

$$E_{disp}^{(2)} = -\frac{1}{4\pi}\int \frac{\alpha_A(r_1, r_2|i\omega)\alpha_B(r_1', r_2'|i\omega)}{|r_1 - r_2||r_1' - r_2'|}drd\omega$$

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- $\alpha_X(r, r|\omega)$: density susceptibility

- terms depending on ρ and $\delta\rho$: accurate
- exchange terms: approximate

$$E_{elst}^{(1)} = \int \rho_A^{tot}(r_1)\frac{1}{|r_1 - r_2|}\rho_B^{tot}(r_2)dr_1dr_2$$

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- rely on reduced density matrices

- terms depending on ρ and $\delta\rho$: accurate
- exchange terms: approximate

$$E_{exch}^{(1)}(S^2) = E_{exch}^{(1)}[\gamma_A, \gamma_B, \Gamma_A, \Gamma_B]$$
$$E_{exch-ind}^{(2)}(S^2) = E_{exch-ind}^{(2)}[\gamma_X, \gamma_X^v, \Gamma_X, \Gamma_X^v]$$
$$E_{exch-disp}^{(2)}(S^2) = E_{exch-disp}^{(2)}[\gamma_X, \gamma_X^v, \Gamma_X, \Gamma_X^v]$$

A. Hesselmann, G. Jansen, JPCA 105, 11156 (2001)
A. Misquitta, R. Podeszwa, B. Jeziorski, K. Szalewicz, JCP 123, 214103 (2005)

- near-CCSD(T) accuracy at N^5 cost (up to 3000 basis set functions)
- full PESs for water, CO, benzene, acetylene, ... dimers

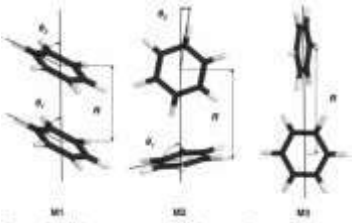


Figure 1. Minimum structures of the benzene dimer.

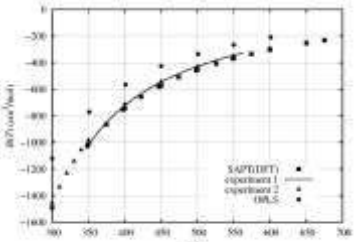
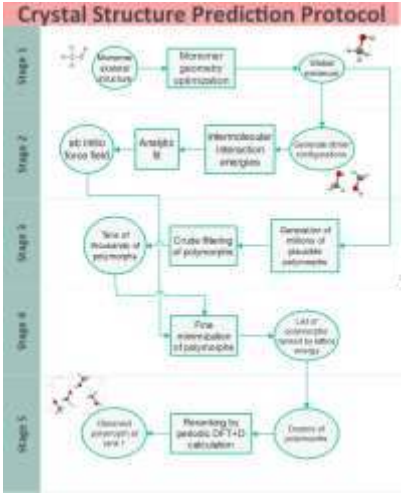


Figure 8. Second virial coefficient of benzene. SAPT(DFT): this work. Experiment 1: ref 71. Experiment 2: ref 72. OPLS: calculated with the empirical potential of ref 62.

R. Podeszwa, R. Bukowski, K. Szalewicz, JPCA 110, 094106 (2006)

- automated generation of site-site potentials (AutoPES program)
  - PES sampling limited to short-range
  - long-range from asymptotic expansion
- SAPT(DFT)-based force fields → crystal structure prediction (CSP)



R. Metz, K. Piszczatowski, K. Szalewicz, JCTC 12, 5895 (2016)
R. Nikhar, K. Szalewicz, Nat. Comm. 13 3095 (2022)

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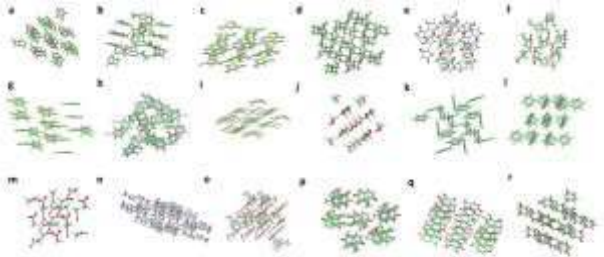
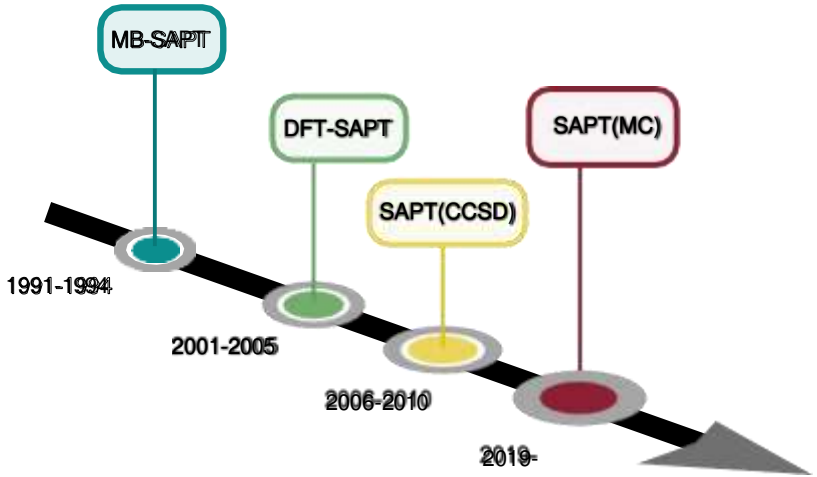


Fig. 2 Overlaps of crystal structures. Overlap of the experimental crystal structure (element-specific colors) with the closest calculated crystal structure (green) using SAPT(DFT)-based vdW's for: spirones **a** and **b**, I **c** II, **d** IV, **e** VIII, **f** XII, **g** XIII, **h** XVI, **i** XXII, **j** methanol, **k** and **l** benzene, **m** nitromethane, **n** CINIT, **o** THB, **p** and **q** Deltarones, **r** fluoranil.

R. Metz, K. Piszczatowski, K. Szalewicz et al., JCTC 12, 5895 (2016)
R. Nikhar, K. Szalewicz, Nat. Comm. 13 3095 (2022)

SAPT timeline



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&+ \delta_{\text{HF}}
\end{aligned}
$$

- response from extended RPA

- relies on one- and two-particle reduced density matrices (γ, Γ) of monomers
- may be applied with any MC wave function (CAS, GVB-PP, DMRG, CIPSI, . . .)

K. Chatterjee, K. Pernal, JCP 12, 137, 204109 (2012)
M. Hapka, M. Przybytek, K. Pernal, JCTC 15, 1116/6712 (2019)
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- N^6 scaling with the system size
- accuracy limited by
  - quality of γ, Γ
  - quality of γ^V, Γ^V
  - S^2 approximation

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- N^6 scaling with the system size → $E_{DISP}^{(2)}$
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N^6 scaling in SAPT(MC)

- evaluation of the $E^{(2)}_{\mathrm{disp}}$ formula
- solution of ERPA equations $(\Upsilon_\nu, \omega_\nu)$

$$E^{(2)}_{\mathrm{disp}} = -\frac{8}{\pi}\int_0^\infty d\omega\, \mathrm{Tr}\left[g^T C^A(\omega) C^B(\omega)^T g \right]$$

$$[C^X(\omega)]^{p'q'}_{pq} = 2 \sum_\nu \left[\Upsilon^X_\nu\right]_{pq} \left[\Upsilon^X_\nu\right]_{p'q'} \frac{\omega^X_\nu}{(\omega^X_\nu)^2 + \omega^2}$$

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N^5 scaling achieved by

- Cholesky decomposition of integrals
- recursive formula for $\tilde{C}(\omega)$

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g_{pq}

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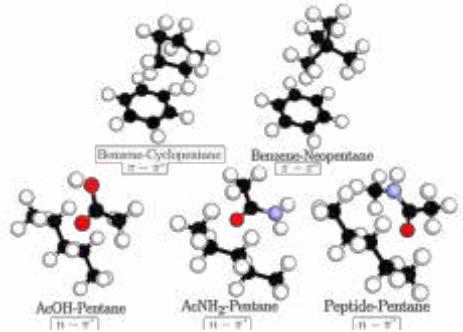
g_{pq}

- 1200 basis functions (2 hrs @4 CPUs for $E_{disp}^{(2)}$)



M. Hapka, A. Krzemi ska, M. Modrzejewski, M. Przybytek, K. Pernal, JPCL 14, 6895 (2023)

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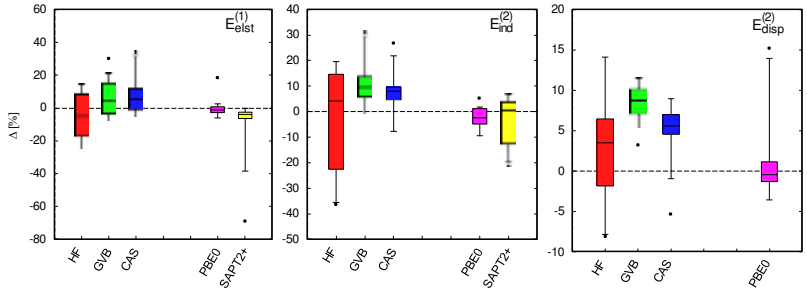
  - S^2 approximation

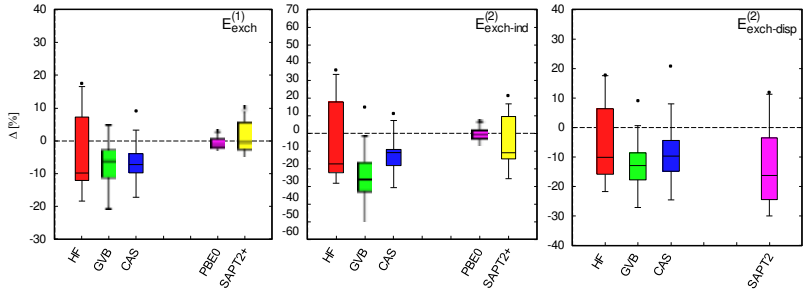
K. Chatterjee, K. Pernal, JCP 12, 137, 204109 (2012)
M. Hapka, M. Przybytek, K. Pernal, JCTC 15, 1116/6712 (2019)
M. Hapka, M. Przybytek, K. Pernal, JCTC 17, 5538 (2021)



rel. % errors wrt SAPT(CCSD)/avtz

A24 dataset: J. e z , P. Hobza, JCTC (2013)

- a ordable active space too small to recover intramonomer correlation



rel. % errors wrt SAPT(CCSD)/avtz

A24 dataset: J. e z , P. Hobza, JCTC (2013)

- a ordable active space too small to recover intramonomer correlation

- Introduction
- SAPT
  - general
  - Many-body SAPT
  - SAPT(DFT)
  - Multicon gurational SAPT
  - SAPT(MC-srDFT)
    - correlated electron densities of monomers
    - improved rst-order terms in SAPT
  - interactions in ground vs. excited states

- MC analogue of SAPT(DFT)
- single-perturbation theory

$$E_{int}^{SAPT(MCsrDFT)} = E_{elst}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{exch-ind}^{(2)} + E_{disp}^{(2)} + E_{exch-disp}^{(2)} + \delta_{HF}$$

- response properties from ERPA

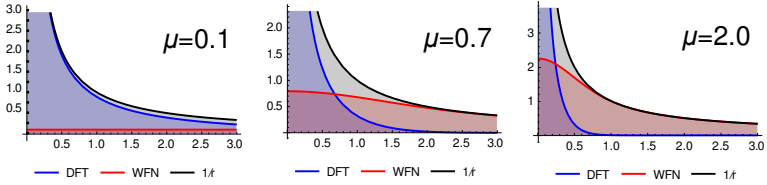
- terms depending on ρ and $\delta\rho$: accurate
- exchange terms: approximate

- ◇ nominal N^6 scaling
- ◇ SAPT(MC) accuracy limits
  - ◇ quality of γ, Γ → improved by srDFT
  - ◇ quality of γ^v, Γ^v → improved by xc kernel
  - ◇ S^2 approximation

H. Stoll and A. Savin, in Density Functional Methods in Physics, 177-207 (1985)

Separation of the electron-electron interaction operator

$$\frac{1}{r} = \underbrace{\frac{1-\mathrm{erf}(\mu r)}{r}}_{DFT} + \underbrace{\frac{\mathrm{erf}(\mu r)}{r}}_{WFN}$$



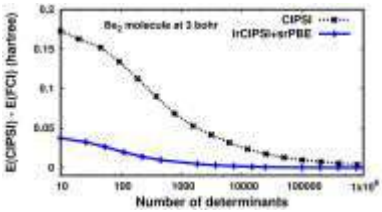
H. Stoll and A. Savin, in Density Functional Methods in Physics, 177-207 (1985)
A. Savin, in Recent Developments of Modern Density Functional Theory 327 (1996)

$$E_o = \min_{\Psi}^{nD} \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{LR} | \Psi \rangle^{E} + E_{Hxc}^{SR}[\rho_\Psi],$$

$$\hat{H}_{LR}\ \Psi^{LR} = E^{LR}\ \Psi^{LR}$$

$$\hat{H}_{LR} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{LR} + \hat{V}_{Hxc}^{SR}[\rho_\Psi^{LR}]$$

- static correlation described via WF
- removal of electron-electron cusp from Ψ^{LR}
  - faster convergence with basis-set size
  - more compact wave function



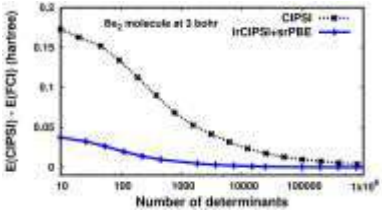
A. Fert , E. Giner, J. Toulouse, JCP 150, 084103 (2019)

$$\hat{H}_{LR} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{LR,\mu} + \hat{V}_{Hxc}^{SR,\mu}[\rho_{\Psi}^{LR}]$$

$$\hat{H}_{LR} \xrightarrow{\mu \to 0} \hat{H}_{KS-DFT}$$

$$\hat{H}_{LR} \xrightarrow{\mu \to \infty} \hat{H}_{CASSCF}$$

- static correlation described via WF
- removal of electron-electron cusp from Ψ^{LR}
  - faster convergence with basis-set size
  - more compact wave function



A. Fert , E. Giner, J. Toulouse, JCP 150, 084103 (2019)

$$v_{xc}(r) \xrightarrow{r \to \infty} -\frac{1}{r}$$

SAPT(DFT)

- asymptotic corrections
- optimal tuning of μ (LRC-DFT)
  - IP-tuning (ω_{IP})

$$IP(\omega_{IP}) = -\varepsilon_{HOMO}(\omega_{IP})$$

  - global density-dependent (ω_{GDD})

W. Cencek, K. Szalewicz, JCP 139, 024104 (2013)
R. Baer, et al., Annu. Rev. Phys. Chem. 61, 85 (2010)
M. Modrzejewski, et al., JPCA 117, 11580 (2013)

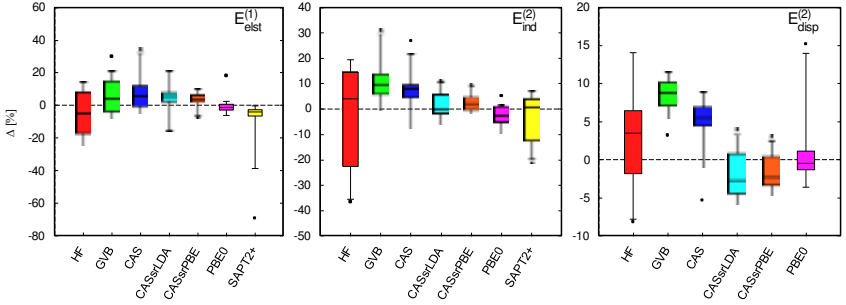
SAPT(MC-srDFT)

- range-separation of electron-electron interaction applied in monomer Hamiltonians
- optimal μ value from extended Koopmans theorem

$$\rho(r) \xrightarrow[r \to \infty]{} \exp\left(-2\sqrt{2\,IP_{EKT}}\,r\right)$$

D. W. Smith, O. W. Day, JCP 62, 113 (1975)

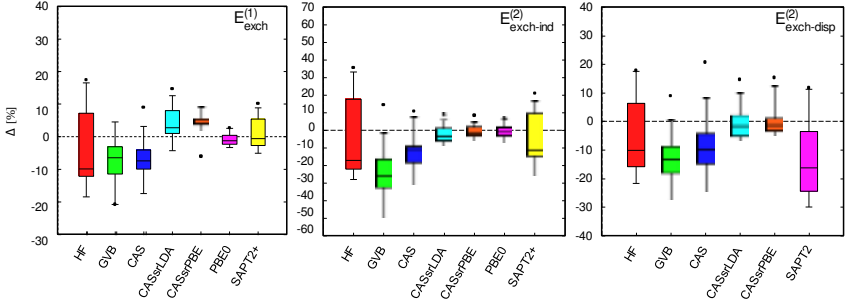
Polarization: rel. % errors wrt SAPT(CCSD)/avtz; A24 dataset



SAPT(CAS-srDFT):

- improvement over SAPT(CAS)/SAPT(GVB)
- polarization components close to SAPT(PBE0)

Exchange: rel. % errors wrt SAPT(CCSD)/avtz; A24 dataset



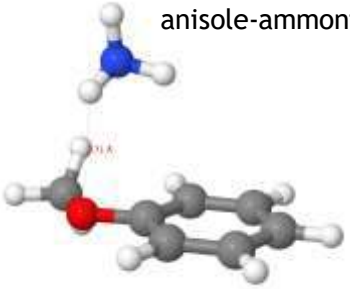
SAPT(CAS-srDFT):

- improvement over SAPT(CAS)/SAPT(GVB)
- $E^{(1)}_{exch}$ most sensitive to μ value

- Introduction
- SAPT
  - general
  - Many-body SAPT
  - SAPT(DFT)
  - Multicon gurational SAPT
  - SAPT(MC-srDFT)
    - correlated electron densities of monomers
    - improved rst-order terms in SAPT
  - interactions in ground vs. excited states

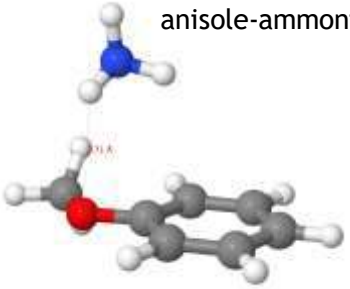
anisole-water

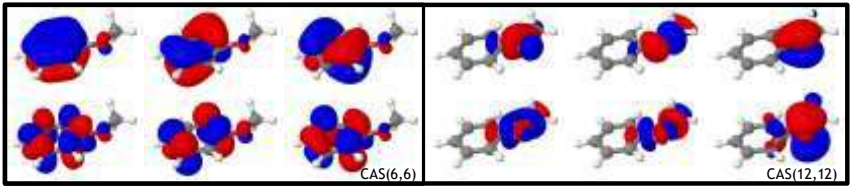
anisole-ammonia



anisole-water

anisole-ammonia





	Anisole-H_2O / ground state				
SAPT	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF					
CAS(6,6)					
CAS(12,12)					
CASsrPBE					
PBE0					
SAPT2+(3)					
supermolecular					
CAS+DISP					
CCSD(T)					

aug-cc-pVTZ; milliHartee

	Anisole-H_2O / ground state				
SAPT	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF					
CAS(6,6)					
CAS(12,12)					
CASsrPBE					
PBE0					
SAPT2+(3)					
supermolecular					
CAS+DISP					
CCSD(T)					

aug-cc-pVTZ; milliHartee

$$E_{IND} = E^{(2)}_{ind} + E^{(2)}_{exch-ind} + \delta_{HF}$$

	Anisole-H_2O / ground state				
SAPT	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF					
CAS(6,6)					
CAS(12,12)					
CASsrPBE					
PBE0					
SAPT2+(3)					
supermolecular					
CAS+DISP					
CCSD(T)					

aug-cc-pVTZ; milliHartee

$$E^{(2)}_{DISP} = E^{(2)}_{disp} + E^{(2)}_{exch-disp}$$

	Anisole-H_2O / ground state				
SAPT	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF					
CAS(6,6)					
CAS(12,12)					
CASsrPBE					
PBE0					
SAPT2+(3)					
supermolecular					
CAS+DISP					
CCSD(T)					

aug-cc-pVTZ; milliHartee

CAS+DISP= $E_{int}^{CASSCF} + E^{(2)}_{DISP}$

	Anisole-H_2O / ground state				
SAPT	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF	−11.84	10.95			
CAS(6,6)	−12.38	11.73			
CAS(12,12)	−11.30	11.53			
CASsrPBE					
PBE0					
SAPT2+(3)					

aug-cc-pVTZ; milliHartee

Anisole-H_2O / ground state					
SAPT	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF	−11.84	10.95			
CAS(6,6)	−12.38	11.73			
CAS(12,12)	−11.30	11.53			
CASsrPBE	−11.64	13.22			
PBE0					
SAPT2+(3)					

aug-cc-pVTZ; milliHartee

	Anisole-H_2O / ground state				
SAPT	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF	−11.84	10.95			
CAS(6,6)	−12.38	11.73			
CAS(12,12)	−11.30	11.53			
CASsrPBE	−11.64	13.22			
PBE0	−11.18	12.78			
SAPT2+(3)	−11.57	12.98			

- CASsrPBE > CAS(12,12) > CAS(6,6)

aug-cc-pVTZ; milliHartee

SAPT	Anisole-H_2O / ground state				
	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF	−11.84	10.95	−3.62	−4.75	−9.26
CAS(6,6)	−12.38	11.73	−3.63	−4.94	−9.22
CAS(12,12)	−11.30	11.53	−3.50	−4.93	−8.19
CASsrPBE	−11.64	13.22	−3.57	−4.87	−6.86
PBE0	−11.18	12.78	−3.55	−5.17	−7.11
SAPT2+(3)	−11.57	12.98	−3.99	−5.51	−8.09

- CAS(6,6) close to HF
- CASsrPBE close to PBE0

aug-cc-pVTZ; milliHartee

Anisole-H_2O / ground state					
SAPT	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF	−11.84	10.95	−3.62	−4.75	−9.26
CAS(6,6)	−12.38	11.73	−3.63	−4.94	−9.22
CAS(12,12)	−11.30	11.53	−3.50	−4.93	−8.19
CASsrPBE	−11.64	13.22	−3.57	−4.87	−6.86
PBE0	−11.18	12.78	−3.55	−5.17	−7.11
SAPT2+(3)	−11.57	12.98	−3.99	−5.51	−8.09
supermolecular					
CAS+DISP					−8.65
CCSD(T)					−7.70

aug-cc-pVTZ; milliHartee

SAPT	Anisole-NH_3 / ground state				
	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF	−5.69	5.79	−1.06	−5.35	−6.30
CAS(6,6)	−5.53	5.92	−1.03	−5.39	−6.04
CAS(12,12)	−5.63	5.96	−1.04	−5.41	−6.13
CASsrPBE	−5.59	6.57	−1.04	−5.47	−5.53
PBE0	−5.55	6.57	−1.04	−5.66	−5.68
SAPT2+(3)	−5.52	6.34	−1.09	−6.04	−6.31

- CASsrPBE > CAS(12,12) ≈ CAS(6,6)

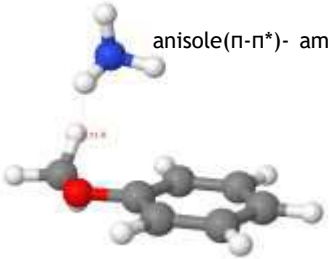
aug-cc-pVTZ; milliHartee

	Anisole-NH_3 / ground state				
SAPT	$E^{(1)}_{elst}$	$E^{(1)}_{exch}$	E_{IND}	$E^{(2)}_{DISP}$	E_{int}
HF	−5.69	5.79	−1.06	−5.35	−6.30
CAS(6,6)	−5.53	5.92	−1.03	−5.39	−6.04
CAS(12,12)	−5.63	5.96	−1.04	−5.41	−6.13
CASsrPBE	−5.59	6.57	−1.04	−5.47	−5.53
PBE0	−5.55	6.57	−1.04	−5.66	−5.68
SAPT2+(3)	−5.52	6.34	−1.09	−6.04	−6.31
supermolecular					
CAS+DISP					−6.24
CCSD(T)					−5.83

aug-cc-pVTZ; milliHartee

anisole(π-π*)- water

anisole(π-π*)- ammonia



- How does the interaction change upon vertical excitation?

vertical exc.	$\Delta E_i = E_i^{es} - E_i^{gs}$			
	a-H_2O		a-NH_3	
	CASSCF	CASsrPBE	CASSCF	CASsrPBE
$\Delta E^{(1)}_{elst}$				
$\Delta E^{(1)}_{exch}$				
ΔE_{IND}				
$\Delta E^{(2)}_{DISP}$				
ΔE^{SAPT}_{int}				

aug-cc-pVTZ; milliHartee

- stabilization

+ destab.

vertical exc. $\Delta E_i = E_i^{es} - E_i^{gs}$

	a-H_2O		a-NH_3	
	CASSCF	CASsrPBE	CASSCF	CASsrPBE
$\Delta E^{(1)}_{elst}$	0.83	2.52	0.12	−0.21
$\Delta E^{(1)}_{exch}$	-0.13	-0.06	−0.08	0.21
ΔE_{IND}	0.10	0.16	0.01	−0.07
$\Delta E^{(2)}_{DISP}$	-0.02	-0.32	0.03	−0.12
ΔE^{SAPT}_{int}	0.78	2.29	0.08	−0.19

- destabilization of ES due to $\Delta E^{(1)}_{elst}$

aug-cc-pVTZ; milliHartee

- stabilization + destab.

vertical exc.	$\Delta E_i = E_i^{es} - E_i^{gs}$			
	a-H_2O		a-NH_3	
	CASSCF	CASsrPBE	CASSCF	CASsrPBE
$\Delta E^{(1)}_{elst}$	0.83	2.52	0.12	-0.21
$\Delta E^{(1)}_{exch}$	−0.13	−0.06	-0.08	0.21
ΔE_{IND}	0.10	0.16	0.01	-0.07
$\Delta E^{(2)}_{DISP}$	−0.02	−0.32	0.03	-0.12
ΔE^{SAPT}_{int}	0.78	2.29	0.08	-0.19

- stabilization of ES due to $\Delta E^{(n>1)}$

aug-cc-pVTZ; milliHartee

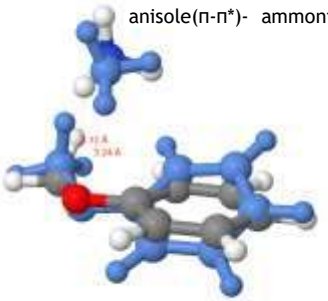
- stabilization | + destab.

vertical exc.	$\Delta E_i = E_i^{es} - E_i^{gs}$			
	a-H_2O		a-NH_3	
	CASSCF	CASsrPBE	CASSCF	CASsrPBE
$\Delta E_{elst}^{(1)}$	0.83	2.52	0.12	−0.21
$\Delta E_{exch}^{(1)}$	−0.13	−0.06	−0.08	0.21
ΔE_{IND}	0.10	0.16	0.01	−0.07
$\Delta E_{DISP}^{(2)}$	−0.02	−0.32	0.03	−0.12
ΔE_{int}^{SAPT}	0.78	2.29	0.08	-0.19
$\Delta E_{int}^{CAS+DISP}$	0.73		0.09	
ΔE_{int}^{CC2}		1.70		-0.46

$\Delta E_{int}^{CC2} = E_{int,gs}^{CCSD(T)} + {}^{'}\omega_{(AB)}^{CC2} * - \omega_{A^*}^{CC2}$

anisole(π-π*)- water

anisole(π-π*)- ammonia



- How does the interaction change upon adiabatic excitation?

adiabatic exc.	$\Delta E_i = E_i^{es} - E_i^{gs}$			
	a-H_2O		a-NH_3	
	CASSCF	CASsrPBE	CASSCF	CASsrPBE
$\Delta E^{(1)}_{elst}$	2.12	3.00	−2.52	−4.12
$\Delta E^{(1)}_{exch}$	-3.37	-3.47	4.87	5.25
ΔE_{IND}	1.16	1.21	−1.05	−1.40
$\Delta E^{(2)}_{DISP}$	0.51	0.25	−1.16	−1.42
ΔE^{SAPT}_{int}	0.42	1.00	0.15	−1.69

- destabilization of ES due to $\Delta E^{(n>1)}$

aug-cc-pVTZ; milliHartee

- stabilization + destab.

adiabatic exc. $\Delta E_i = E_i^{es} - E_i^{gs}$	a-H_2O		a-NH_3	
	CASSCF	CASsrPBE	CASSCF	CASsrPBE
$\Delta E^{(1)}_{elst}$	2.12	3.00	-2.52	-4.12
$\Delta E^{(1)}_{exch}$	−3.37	−3.47	4.87	5.25
ΔE_{IND}	1.16	1.21	-1.05	-1.40
$\Delta E^{(2)}_{DISP}$	0.51	0.25	-1.16	-1.42
ΔE^{SAPT}_{int}	0.42	1.00	0.15	-1.69

- stabilization of ES due to $\Delta E^{(n>1)}$

aug-cc-pVTZ; milliHartee

- stabilization + destab.

adiabatic exc. $\Delta E_i = E_i^{es} - E_i^{gs}$	a-H_2O		a-NH_3	
	CASSCF	CASsrPBE	CASSCF	CASsrPBE
$\Delta E^{(1)}_{elst}$	2.12	3.00	−2.52	−4.12
$\Delta E^{(1)}_{exch}$	−3.37	−3.47	4.87	5.25
ΔE_{IND}	1.16	1.21	−1.05	−1.40
$\Delta E^{(2)}_{DISP}$	0.51	0.25	−1.16	−1.42
ΔE^{SAPT}_{int}	0.42	1.00	0.15	-1.69
$\Delta E^{CAS+DISP}_{int}$	0.31		-0.25	
ΔE^{CC2}_{int}		0.78		-2.14

SAPT variant for multireference systems

E ciency

- nominal N^6 scaling
  - new algorithm for $E^{(2)}_{disp}$(MC)
    - tensor hypercontraction (THC)

M. Hapka, et al, JPCL 14, 6895 (2023)

GAMMCOR

Accuracy

- intramonomer correlation
  - SAPT(MC-srDFT)
    - perturbative corrections to γ, Γ

Applicability

- SAPT(DMFT)
  - degenerate SAPT

Acknowledgements

Lodz University of Technology

- Katarzyna Pernal
- Agnieszka Krzemi ska
- Ewa Pastorczak
- Mohammad Reza Jangrouei
- Dominik Cie li ski
- Micha Przybytek
- Marcin Modrzejewski