

Implementation and Application of Density Functional Theory based Symmetry-Adapted Perturbation Theory for Dimers, Trimers and Molecular Crystals

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Noncovalent Interaction

- ▶ Phase transition, stability of crystal structure
- ▶ Drug binding, DNA/RNA/protein structure
- ▶ Many-body Expansion for the energy of complex system:

$$E = \sum_A E_A + \sum_{AB} E_{AB}^{\text{int},2} + \sum_{ABC} E_{ABC}^{\text{int},3} + \cdots$$



Intermolecular Energies

- Supermolecular approach

$$E_{AB}^{\text{int},2} = E_{AB} - E_A - E_B$$

$$E_{ABC}^{\text{int},3} = E_{ABC} - E_{AB} - E_{AC} - E_{BC} + E_A + E_B + E_C$$

- Symmetry-Adapted Perturbation Theory (SAPT)

$$E^{\text{int},2} = E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$$

SAPT(DFT)

- ▶ Hamiltonian partitioning:

$$H = F_A + F_B + V_{AB} + W_A + W_B$$

$$H = K_A + K_B + V_{AB}$$

- ▶ “Uncoupled” sum-over-states approximation of $E_{\text{disp}}^{(2)}$ and in terms of frequency-dependent density susceptibility (FDDS):

$$\begin{aligned} E_{\text{disp,u}}^{(2)} &= -4 \sum_{ar \in A, bs \in B} \frac{|(ar|bs)|^2}{\epsilon_{ab}^{rs}} \\ &= -\frac{1}{2\pi} \int_0^\infty d\omega \int d\mathbf{r}_A d\mathbf{r}'_A d\mathbf{r}_B d\mathbf{r}'_B \\ &\quad \frac{1}{|\mathbf{r}_A - \mathbf{r}_B|} \frac{1}{|\mathbf{r}'_A - \mathbf{r}'_B|} \chi_0^A(\mathbf{r}_A, \mathbf{r}'_A | i\omega) \chi_0^B(\mathbf{r}_B, \mathbf{r}'_B | i\omega) \end{aligned}$$

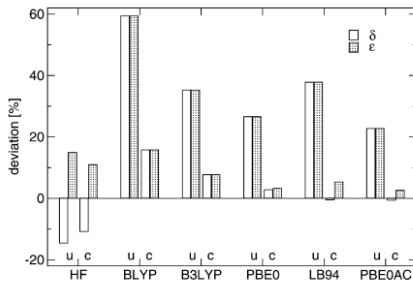
Uncoupled $E_{\text{disp}}^{(2)}$ 

Fig. 2. Mean (δ) and mean absolute (ϵ) percental deviations of the uncoupled (u) and coupled (c) second-order dispersion energies from the MP2 results.

Mean (δ) and mean absolute (ϵ) percentage deviations of uncoupled (u) and coupled (c) $E_{\text{disp}}^{(2)}$ from SAPT2+ results.

A. Heßelmann and G. Jansen, Chem. Phys. Lett. **367**, 778 (2003).



Coupled $E_{\text{disp}}^{(2)}$

- Replacing uncoupled FDDS with coupled FDDS, solved from the coupled Kohn–Sham (CKS) TDDFT equation:

$$\chi = \chi_0 + \chi_0 \mathbf{S}^{-1} \mathbf{W} (\mathbf{S} - \chi_0 \mathbf{S}^{-1} \mathbf{W})^{-1} \chi_0$$

- Exchange-correlation kernel term in \mathbf{W} approximated by adiabatic local-density approximation (ALDA) kernel:

$$\begin{aligned} W_{PQ} &= (P|r_{12}^{-1}|Q) + (P|f_{\text{xc}}|Q) \\ &\approx (P|r_{12}^{-1}|Q) + (P|f_{\text{xc}}^{\text{ALDA}}|Q) \end{aligned}$$

M. Pitoňák and A. Hesselmann, J. Chem. Theory Comput. **6**, 168 (2010).

Hybrid Functional

- ▶ Local Hartree–Fock (LHF) approach
 - ▶ Computing LHF potential in each KS SCF iteration
 - ▶ $O(N^4)$ with very large constant factor
 - ▶ Different set of KS orbitals with smaller occupied–virtual gap
- ▶ Hybrid ALDA kernel
 - ▶ Mixing CHF and CKS equations to solve for FDDS
 - ▶ CKS involves integral of form $(ar|a'r')$, $O(N^4)$ with density fitting
 - ▶ CHF involves $(aa'|rr')$ and $(ar'|a'r)$, $O(N^5)$



Coupled $E_{\text{exch-disp}}^{(2)}$

- Scaling from scaling uncoupled $E_{\text{exch-disp}}^{(2)}$

$$\tilde{E}_{\text{exch-disp},r}^{(2)} = E_{\text{exch-disp},u}^{(2)} \cdot \frac{E_{\text{disp},r}^{(2)}}{E_{\text{disp},u}^{(2)}}$$

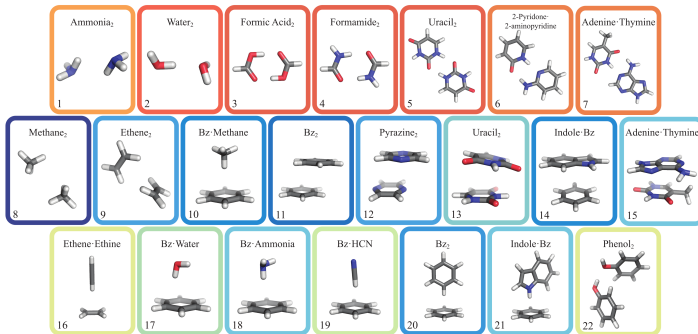
- Fixed scaling factor from fitting S22×5

$$\tilde{E}_{\text{exch-disp},r}^{(2)} = \alpha \cdot E_{\text{exch-disp},u}^{(2)} (\alpha = 0.686)$$

- Value of α above fitted from $E_{\text{exch-disp},u}^{(2)}$ *with LHF orbitals*

A. Heßelmann and T. Korona, J. Chem. Phys. **141**, 094107 (2014).

S22 Dimer Set



Coupled FDDS with Hybrid Kernel

- ▶ Recall coupled FDDS for pure ALDA kernel:

$$\chi = \chi_0 + \chi_0 \mathbf{S}^{-1} \mathbf{W} (\mathbf{S} - \chi_0 \mathbf{S}^{-1} \mathbf{W})^{-1} \chi_0$$

- ▶ Coupled FDDS for hybrid ALDA kernel, with $(aa'|rr')$ and $(ar'|a'r)$ contributions in χ'_0 and \mathbf{K}' :

$$\chi = \chi'_0 + (\chi'_0 \mathbf{S}^{-1} \mathbf{W} + \mathbf{K}') [\mathbf{S} - (\chi'_0 \mathbf{S}^{-1} \mathbf{W} + \mathbf{K}')]^{-1} \chi'_0$$

- ▶ Dispersion energy from integration over ω :

$$E_{\text{disp},r}^{(2)} = -\frac{1}{2\pi} \int_0^\infty d\omega \text{Tr} (\mathbf{S}^{-1} \chi^A \mathbf{S}^{-1} \chi)$$

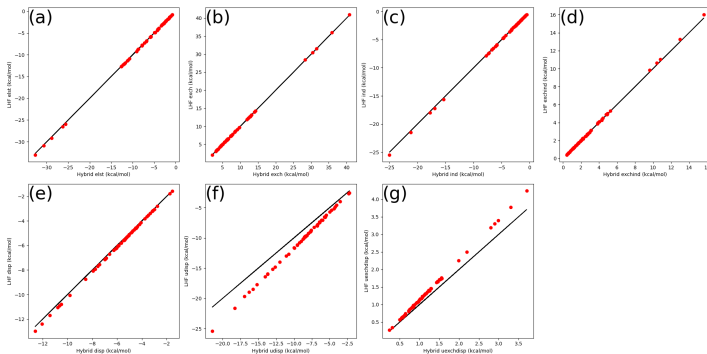
Refitting $E_{\text{exch-disp},r}^{(2)}$ for non-LHF Orbitals

- ▶ LHF vs. non-LHF orbitals: Only affects uncoupled second-order terms like $E_{\text{disp},u}^{(2)}$ and $E_{\text{exch-disp},u}^{(2)}$
- ▶ Similar $E_{\text{disp},r}^{(2)}$ for LHF + pure ALDA vs. non-LHF + hybrid ALDA, expect the same for $E_{\text{exch-disp},r}^{(2)}$
- ▶ Can fit non-LHF $E_{\text{disp},u}^{(2)}$ to LHF + pure ALDA $E_{\text{disp},r}^{(2)}$:

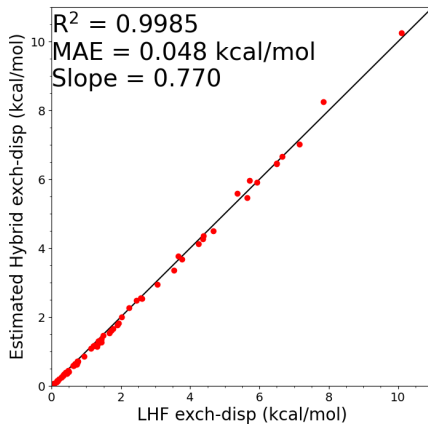
$$\begin{aligned} E_{\text{disp},r}^{(2)}(\text{hybrid}) &\approx E_{\text{disp},r}^{(2)}(\text{LHF}) \\ &\approx \alpha \cdot E_{\text{exch-disp},u}^{(2)}(\text{non-LHF}) \end{aligned}$$

- ▶ Fit for α using S22 \times 5 and test with S66 \times 8

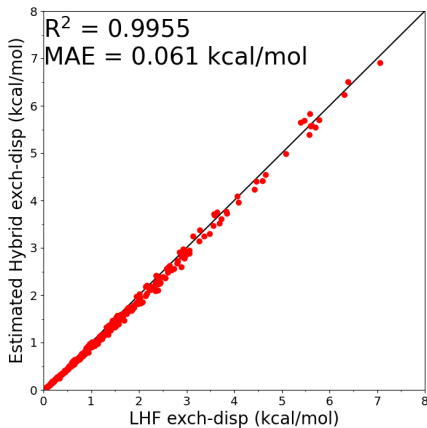
SAPT Terms: LHF vs non-LHF Orbitals



Hybrid vs. LHF values in kcal/mol for each term for S66 data set: (a) $E_{\text{elst}}^{(1)}$, (b) $E_{\text{exch}}^{(1)}$, (c) $E_{\text{ind}}^{(2)}$, (d) $E_{\text{exch-ind}}^{(2)}$, (e) $E_{\text{disp},r}^{(2)}$, (f) $E_{\text{disp},u}^{(2)}$, (g) $E_{\text{exch-disp},u}^{(2)}$

Fitting: S22 \times 5

Testing: S66×8



Computational Approach

- ▶ Benchmarking with S66 dimer set
- ▶ Using SAPT2+3(CCD) δ MP2/aug-cc-pVTZ as reference
- ▶ Compare electrostatics, exchange, induction, dispersion terms and total IE
- ▶ Using aug-cc-pVDZ for SAPT0 and SAPT2+, aug-cc-pVTZ for other methods

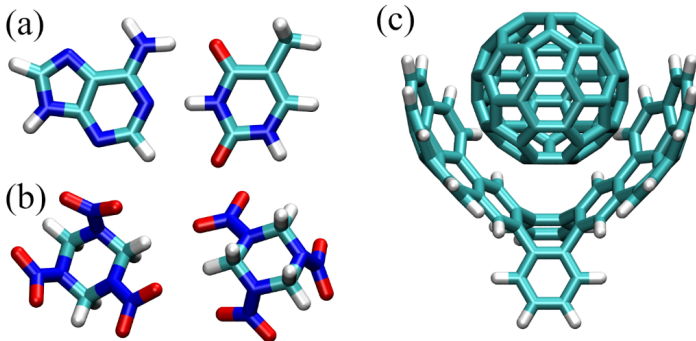
S66 Results

Method	Total	HB	MX	DD	Error Distribution						
					4	OB	1	0	1	UB	4
Electrostatics											
SAPT(DFT) hybrid	0.374	0.556	0.177	0.311							
SAPT(DFT) LHF	0.423	0.666	0.196	0.319							
SAPT0	0.613	1.034	0.439	0.297							
SAPT2+	0.236	0.270	0.136	0.263							
SAPT2+(3) δ MP2	0.000	0.000	0.000	0.000							
Exchange											
SAPT(DFT) hybrid	0.886	1.127	0.426	0.926							
SAPT(DFT) LHF	0.886	1.121	0.431	0.928							
SAPT0	0.675	0.942	0.263	0.658							
SAPT2+	0.337	0.467	0.222	0.277							
SAPT2+(3) δ MP2	0.000	0.000	0.000	0.000							
Induction											
SAPT(DFT) hybrid	0.211	0.201	0.212	0.220							
SAPT(DFT) LHF	0.224	0.223	0.223	0.225							
SAPT0	0.241	0.200	0.261	0.271							
SAPT2+	0.327	0.384	0.250	0.318							
SAPT2+(3) δ MP2	0.152	0.179	0.121	0.145							

S66 Results (cont.)

Method	Total	HB	MX	DD	Error Distribution						
					4	OB	1	0	1	UB	4
Dispersion											
SAPT(DFT) hybrid	0.370	0.260	0.219	0.573							
SAPT(DFT) LHF	0.308	0.200	0.173	0.499							
SAPT(DFT) non-hybrid	0.635	0.581	0.419	0.822							
SAPT0	0.443	0.862	0.162	0.195							
SAPT2+	0.235	0.397	0.169	0.115							
SAPT2+(3) δ MP2	0.093	0.129	0.056	0.080							
Total											
SAPT(DFT) hybrid	0.334	0.588	0.107	0.217							
SAPT(DFT) LHF	0.234	0.382	0.046	0.199							
SAPT(DFT) non-hybrid	0.604	0.955	0.389	0.385							
SAPT0	0.990	1.197	0.692	0.965							
SAPT2+	0.230	0.235	0.138	0.280							
SAPT2+(3) δ MP2	0.105	0.056	0.082	0.169							

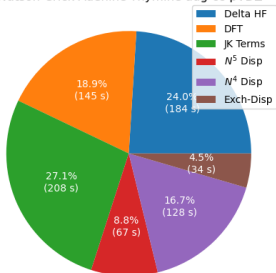
Timing Systems



Dimer systems for timing: (a) Watson-Crick adenine-thymine complex, (b) RDX dimer, (c) C_{60} -buckycatcher complex.

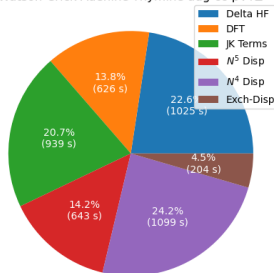
Watson-Crick Adenine-Thymine

(a) Watson-Crick Adenine-Thymine aug-cc-pVDZ



$$N_{bf} = 536$$

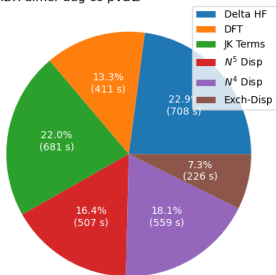
(b) Watson-Crick Adenine-Thymine aug-cc-pVTZ



$$N_{bf} = 1127$$

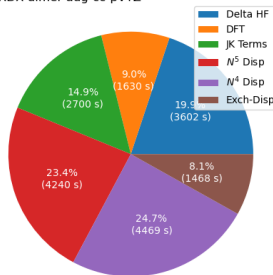
RDX Dimer

(c) RDX dimer aug-cc-pVDZ



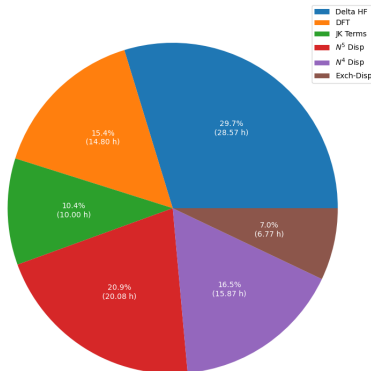
$$N_{bf} = 798$$

(d) RDX dimer aug-cc-pVTZ



$$N_{bf} = 1656$$

C₆₀–Buckycatcher Complex



$$N_{bf} = 3012$$

Conclusions

- ▶ Implemented SAPT(DFT) using hybrid xc kernel, applicable to up to 3000 basis functions
- ▶ Scaling factor of $E_{\text{exch-disp}}^{(2)}$ determined to be 0.770
- ▶ Accuracy of SAPT(DFT) comparable to SAPT2+ which scales as $O(N^7)$
- ▶ Iterative $O(N^4)$ terms not negligible; even dominating for smaller systems

Three-Body Interaction Energies

- ▶ Cheapest conventional methods to model three-body interaction energies scale as $O(N^6)$ [MP2.5, SCS(MI)-CCSD]
- ▶ MP2 lacks three-body dispersion interactions
- ▶ Combine supermolecular MP2 with three-body dispersion correction term
- ▶ Reduces computational cost for three-body interaction energies to the level of $O(N^5)$

CKS FDDS Dispersion

- ▶ Two-body FDDS dispersion term in SAPT(DFT):

$$E_{\text{disp,r}}^{(2)} = -\frac{1}{2\pi} \int_0^\infty d\omega \text{Tr} (\mathbf{S}^{-1} \boldsymbol{\chi}^A \mathbf{S}^{-1} \boldsymbol{\chi})$$

- ▶ Generalize to three-body case:

$$E_{\text{disp,r}}^{(3)} = \int_0^\infty d\omega \text{Tr} (\mathbf{S}^{-1} \boldsymbol{\chi}^A \mathbf{S}^{-1} \boldsymbol{\chi}^B \mathbf{S}^{-1} \boldsymbol{\chi}^C)$$

Axilrod–Teller–Muto Dispersion

- Dispersion energy of atom triplet:

$$E_{\text{ATM}}^{abc} = C_9^{abc} \frac{1 + 3\cos\theta_a\cos\theta_b\cos\theta_c}{(R_{ab}R_{bc}R_{ca})^3}$$

$$C_9^{abc} \approx \sqrt{C_6^{ab}C_6^{bc}C_6^{ca}}$$

- Sum over atom triplets:

$$E_{\text{ATM}}^{ABC} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} f_9^{abc} E_{\text{ATM}}^{abc}$$

Empirical Damping

Geometric Parameters

- ▶ Define geometrical parameters based on intermolecular distances
- ▶ R_{\min} : Smallest of three closest-contact distances
- ▶ R_{\max} : Largest of three closest-contact distances
- ▶ Analyze growth of three-body contribution to crystal lattice energy with respect to R_{\min} and R_{\max}

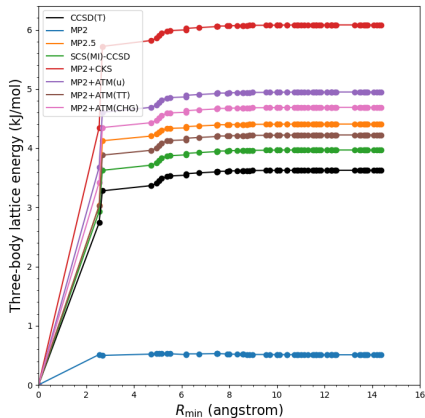
Computational Methods

- ▶ Crystalline benzene, carbon dioxide and triazine
- ▶ Using CCSD(T) with focal point approach as reference

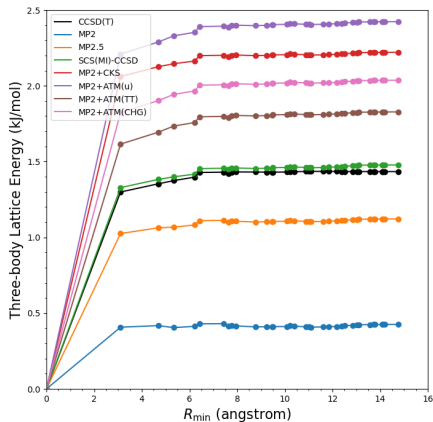
$$E = E^{\text{HF}}(\text{aQZ}) + \Delta E^{\text{MP2}}(\text{aTZ/aQZ}) + \Delta E^{\text{CCSD(T)}}(\text{aDZ})$$

- ▶ Compare three-body contribution to crystal lattice energies with various methods: MP2, MP2+ATM(undamped/TT/CHG), MP2+CKS, MP2.5, SCS(MI)-CCSD, CCSD(T)

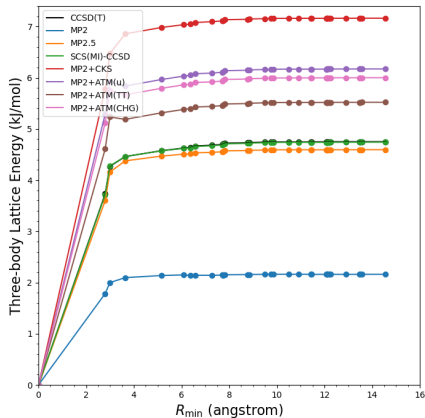
R_{\min} Dependence: Benzene



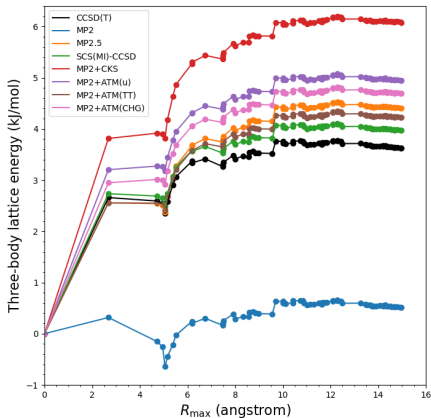
R_{\min} Dependence: Carbon Dioxide



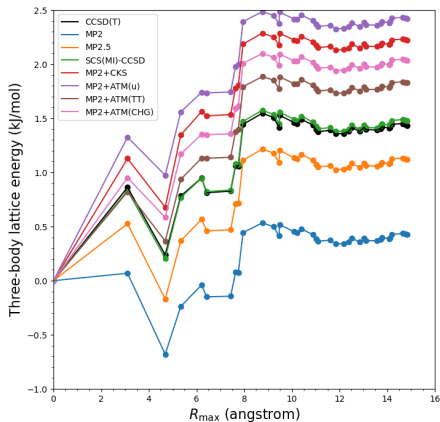
R_{\min} Dependence: Triazine



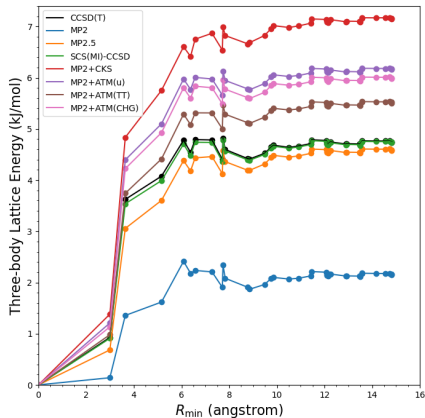
R_{\max} Dependence: Benzene



R_{\max} Dependence: Carbon Dioxide



R_{\max} Dependence: Triazine



Conclusions

- ▶ Three-body crystal lattice energies converge quickly as R_{\min} increases, less smooth for R_{\max} but can be cutoff at 10 Å
- ▶ Three-body dispersion contributions crucial to lattice energies for crystals studied
- ▶ CKS FDDS dispersion overestimates three-body dispersion, likely missing exchange-dispersion terms
- ▶ Performance of Tang-Toennies damped ATM comparable to MP2.5
- ▶ Can use CCSD(T) for trimers with small R_{\min} and MP2+ATM(TT) for larger ones



Acknowledgment