Performance of Density Functional Theory for Describing the Interactions in $(H_2O)_6$

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Motivation

- Several recent studies have used low-energy isomers of $(H_2O)_6$ to investigate the performance of density functional methods for describing interactions in water.[1,2]

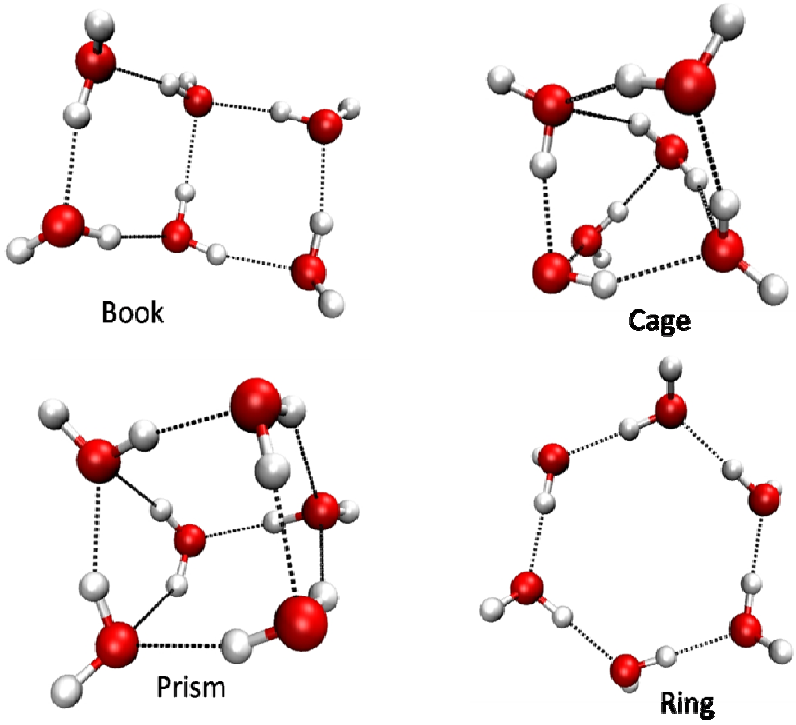
  The focus of these studies has been on correcting DFT for dispersion

- Objective of our work is to use energy decomposition analysis (EDA)[3] and symmetry-adapted perturbation theory (SAPT)[4] calculations to analyze in detail the 2- and 3-body interactions of four low energy isomers of $(H_2O)_6$

1. B. Santra, A. Michaelides, M. Funchs, A. Tkatchenko, C. Filippi, M. Scheffler, *J. Chem. Phys.*, 129, 194111 (2008)
2. A. K. Kelkkanen, B. I. Lundqvist, and J. K. Norskov, *J. Chem. Phys.*, 131, 046102 (2009)
3. R. Z. Khaliullin, E. A. Cobar, R. C. Lochan, A. T. Bell, and M. Head-Gordon, *J. Phys. Chem. A.*, 111, 8753 (2007)
4. S. Rybak, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.*, 95, 6576 (1991)

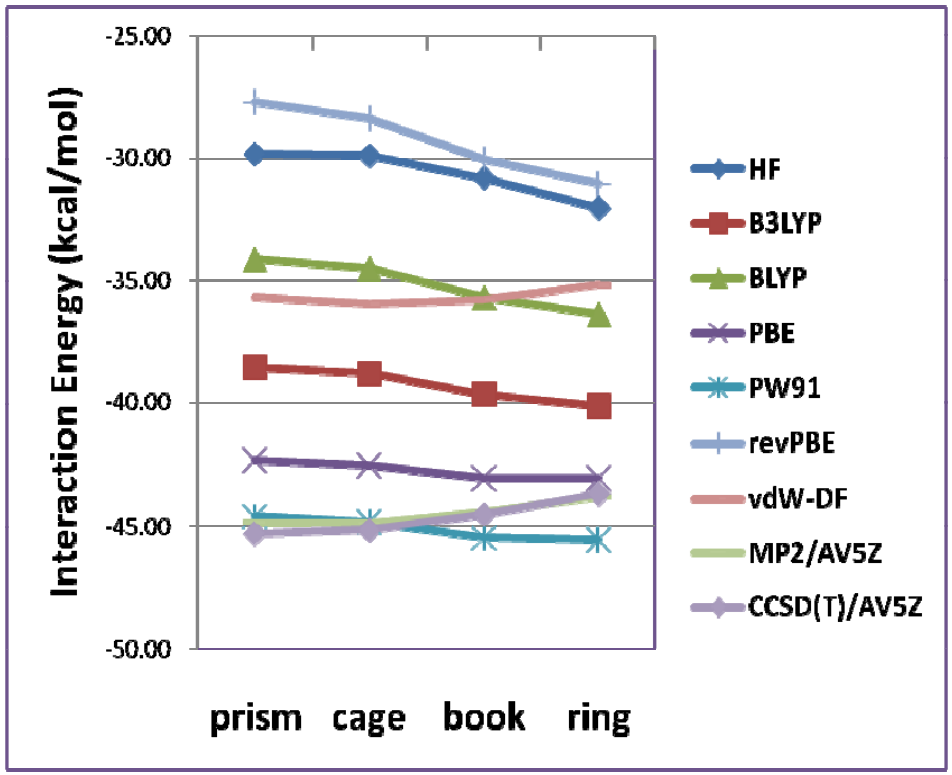
Tested Density Functionals

Method	Exchange		Correlation
	GGA	C_{HF}	
BLYP	B88	0	LYP
PW91	PW91	0	PW91
PBE	PBE	0	PBE
B3LYP	B88	0.2	LYP



Clusters considered

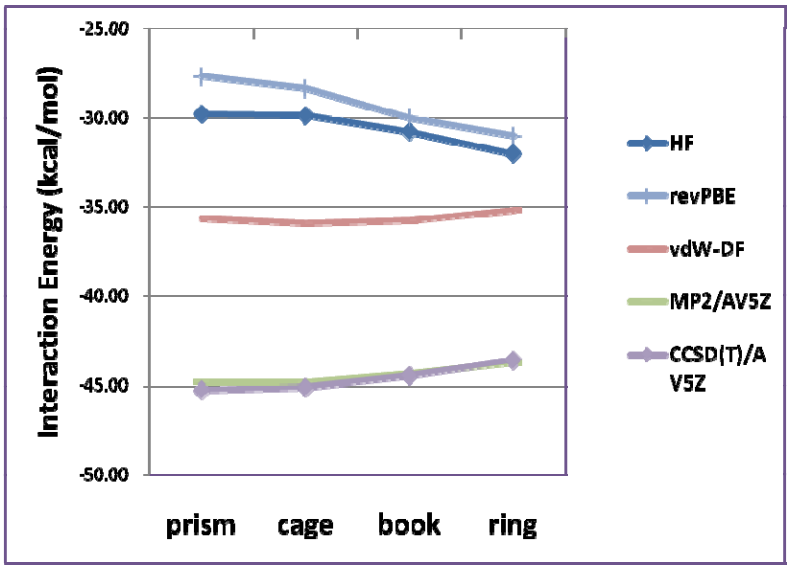
Net Interaction Energies of Isomers of $(H_2O)_6$

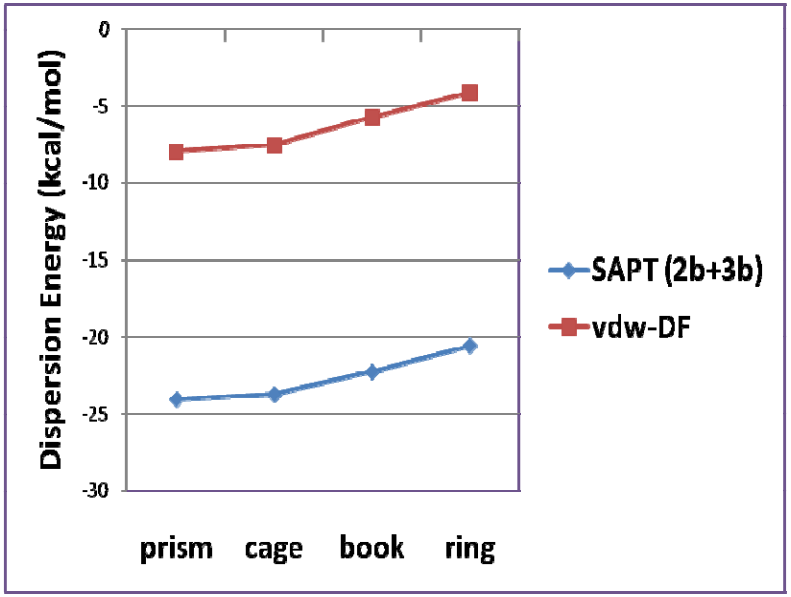


Standard DFT functionals incorrectly predict that the ring and book are more stable than the prism and ring isomers.

The vdW-DF functional largely remedies this problem.

vdW-DF





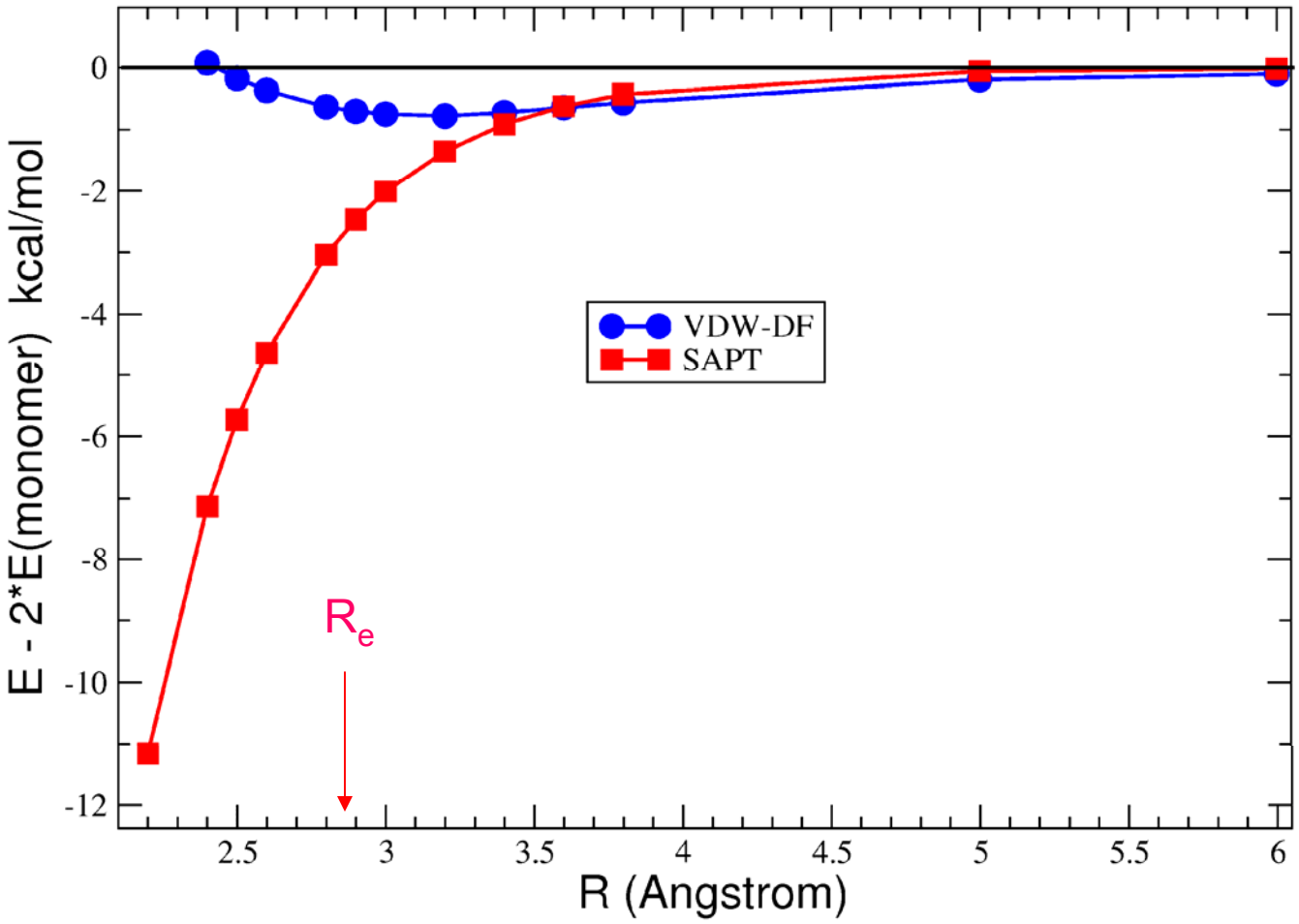
- vdW-DF§ is successful at predicting the relative dispersion energy contributions, although the magnitudes are much smaller than SAPT values.

- vdW-DF correctly predicts the ring to be the least stable isomer, but places the ring and book isomers about 0.5 kcal/mol closer to the cage and prism isomers than found from CSSD(T) calculations.

§ M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Letts.*, 92, 246401 (2004)

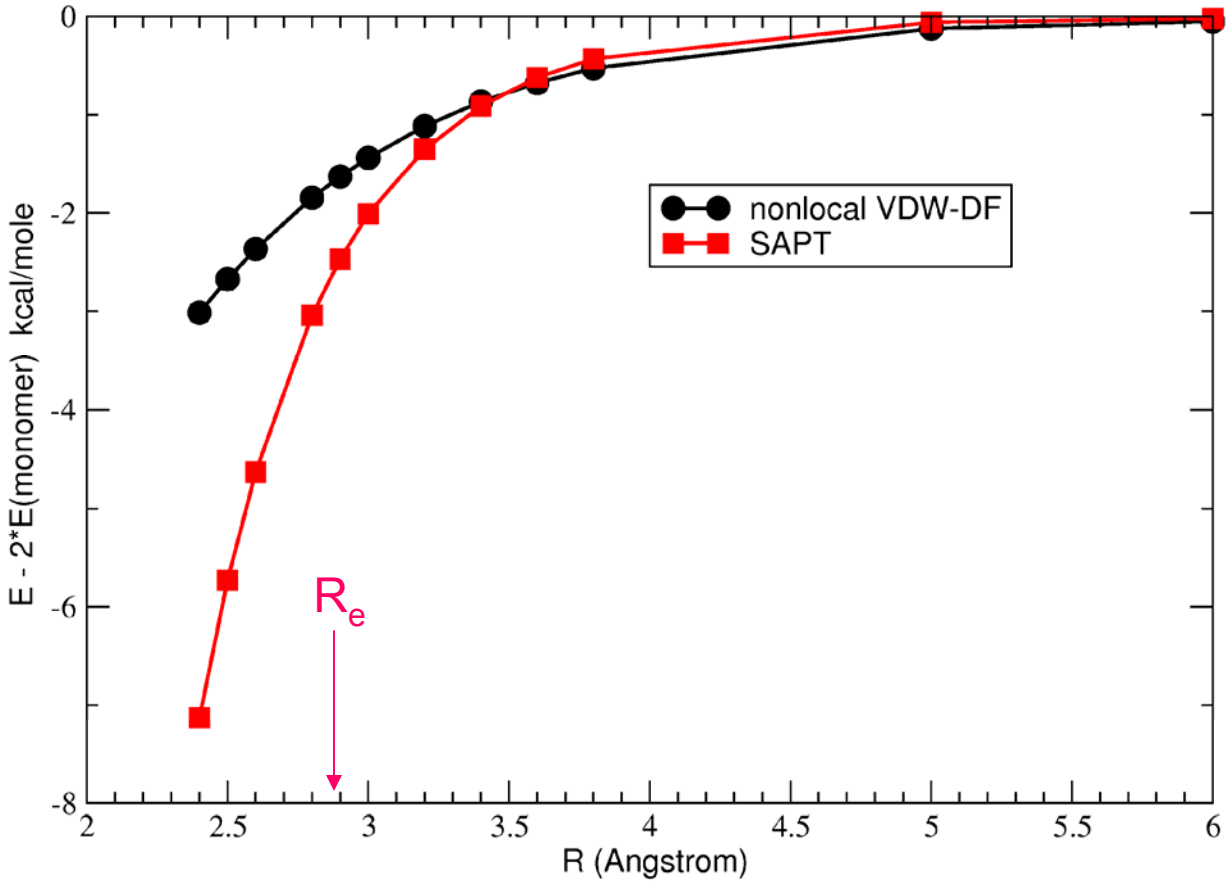
Dispersion energy for the water dimer

E(correl_vdw-df) = E(non-local vdW) + E(correl_LDA) - E(correl_revPBE)



SAPT calculations carried out using SAPT2008 of Szalewicz and co-workers.

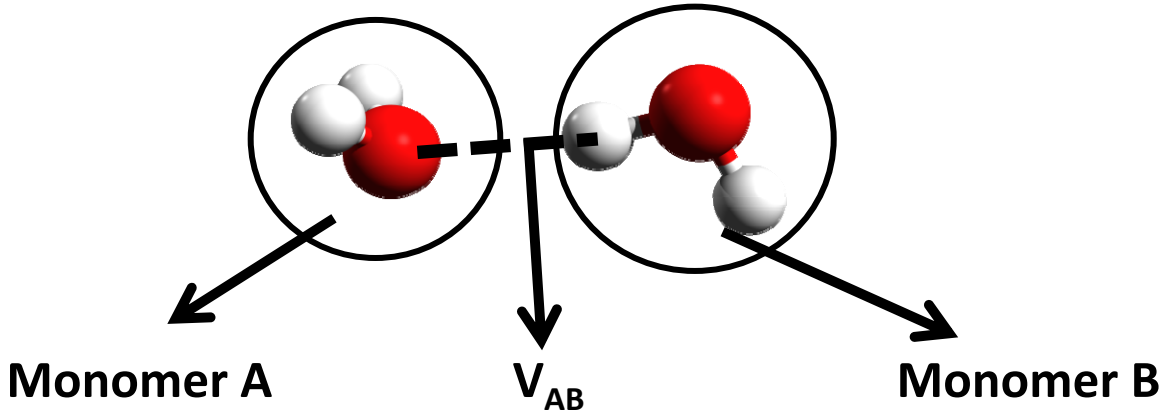
Now lets take a look at how the VDW-DF term alone for the water dimer



Is the discrepancy between vdW-DF and SAPT due to inadequate treatment of intramonomer correlation on the dispersion? (SAPT calculations suggest that this may be one of the factors at play.)

SAPT

Consider a dimer system (using water as an example)



$$H_{AB} = \left(F_A + W_A\right) + \left(F_B + W_B\right) + V_{AB}$$

Where:

H_{AB} is Hamiltonian of the dimer

$F_{A(B)}$ is the Fock operator of monomer A(B)

$W_{A(B)}$ describes intramolecular correlation of monomer A(B)

V_{AB} is the interaction between the two monomers

S. Rybak, B. Jeziorski and K. Szalewicz *J. Chem. Phys.* **95**, 6576 (1991)

Define the zeroth order wavefunction as:

$$\left|\Phi_{AB}\right\rangle = A\left|\Phi_A^0 \Phi_B^0\right\rangle$$

Where A is an *antisymmetrizer* that interchanges electrons between the two monomers.

Treat $W_{A(B)}$ and V_{AB} as perturbations:

$$H^0 = F_A + F_B$$

$$H^1 = \lambda V_{AB} + \eta W_A + \xi W_B$$

λ, η, and ξ are expansion parameters to be set equal to 1. By doing a triple perturbation theory expansion, the interaction energy can be written as:

$$E_{\text{int}} = \sum_{n,i,j=0}^{\infty} \left(E_{pol}^{(nij)} + E_{exch}^{(nij)} \right)$$

Where terms are expanded to n^{th} order in V_{AB} and $i(j)^{th}$ order in $W_{A(B)}$.

From perturbation expansion, one can write:

$$E_{pol}^{(2ij)} = E_{elst}^{(1ij)} + E_{ind}^{(2ij)} + E_{disp}^{(2ij)}$$

$$E_{exch}^{(2ij)} = E_{exch}^{(1ij)} + E_{ex-ind}^{(2ij)} + E_{ex-disp}^{(2ij)}$$

Furthermore, the total HF interaction energy can be written as

$$E_{\text{int}}^{HF} = E_{elst}^{(100)} + E_{exch}^{(100)} + E_{ind}^{(200)} + E_{ex-ind}^{(200)} + \delta(HF)$$

where δ(HF) the 3rd and higher order induction and exchange-induction terms.

This decomposition can be applied to the 2-, 3-, etc., body contributions to gain further insight into how various theoretical methods are doing

Contributions to the 2-body dispersion energies (kcal/mol)

	prism	cage	book	ring
E_{20}	-25.2	-25.0	-23.1	-21.9
E_{20}(ex-disp)	4.5	4.5	4.4	4.3
E_{21}	0.5	0.6	0.6	0.7
E_{22}	-4.7	-4.6	-4.2	-3.8
SAPT tot.	-24.9	-24.5	-22.7	-20.7
vdW-DF	-8.0	-7.6	-5.8	-4.1

E_{21} change in dispersion because of 1st order correction of wave function of one monomer

E_{22} allows both for first order correction of wave functions of both monomers as well as second order correction of the wave function of one monomer

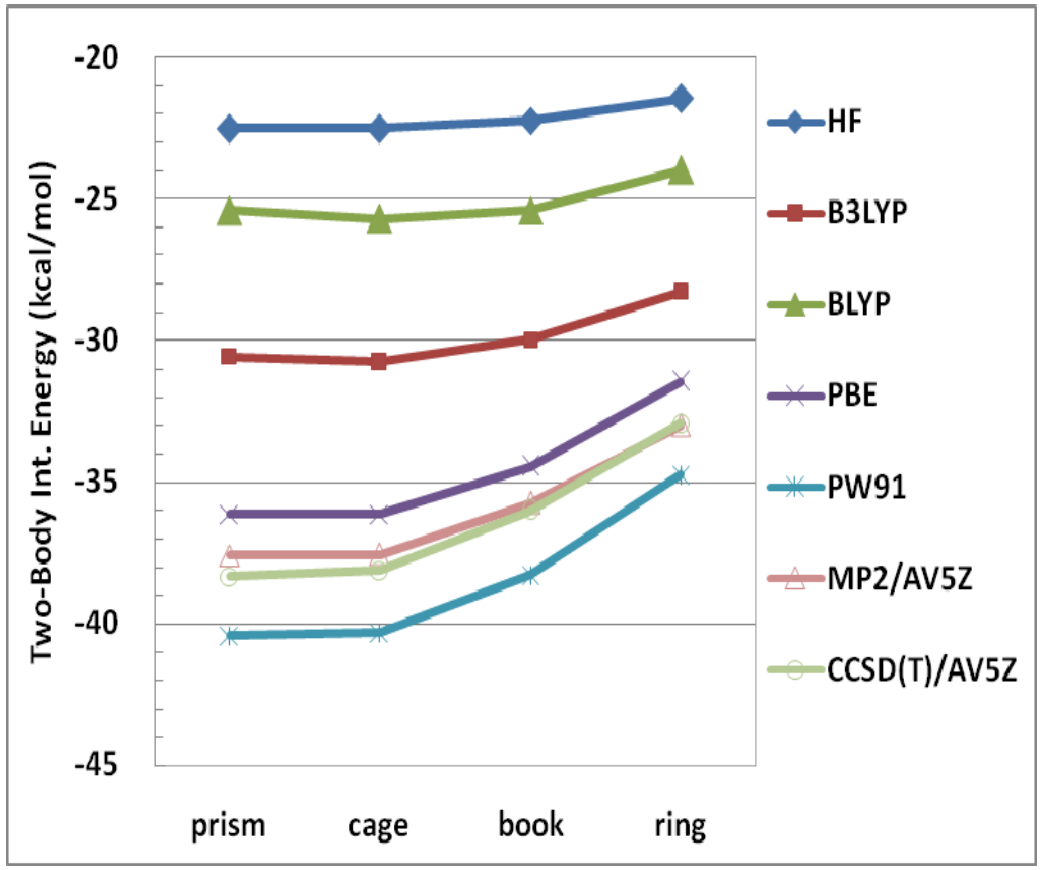
The latter term dominates

Detailed examination of the dispersion contributions to the interaction energies (kcal/mol) of the water and benzene dimers

	$(H_2O)_2$	$(Bz)_2$
E_{20}	-2.5	-6.4
E_{20}(ex-disp)	0.5	0.4
E_{21}	0.0	2.2
E_{211}	0.0	-0.2
E_{220}	-0.4	-1.1

Intramonomer correlation effects play fundamentally different roles in the dispersion energies of these two dimers

Net Two-Body Interaction Energies



- When only two-body interactions are included, all methods predict the prism and cage isomers to be the most stable.

- PBE, BLYP, and B3YP underestimate and PW91 overestimates the two-body energies in magnitude.

Heitler-London decomposition of the energy

$$\Delta E_{HL} = \Delta V_{electrostatic} + \Delta E_{HL}^{exchange-repulsion}$$

$$\Delta E_{HL}^{exchange-repulsion} = \Delta V_{HL} + \Delta T_{HL} + E_X^{HL}$$

$\Delta V \rightarrow$ Decrease in the electrostatic interaction energy due to the depletion of densities in the overlap region (with a corresponding increase of density around the monomers)

$\Delta T \rightarrow$ Increase in kinetic energy

Decomposition of DFT energies using fragment-based DFT (ADF)

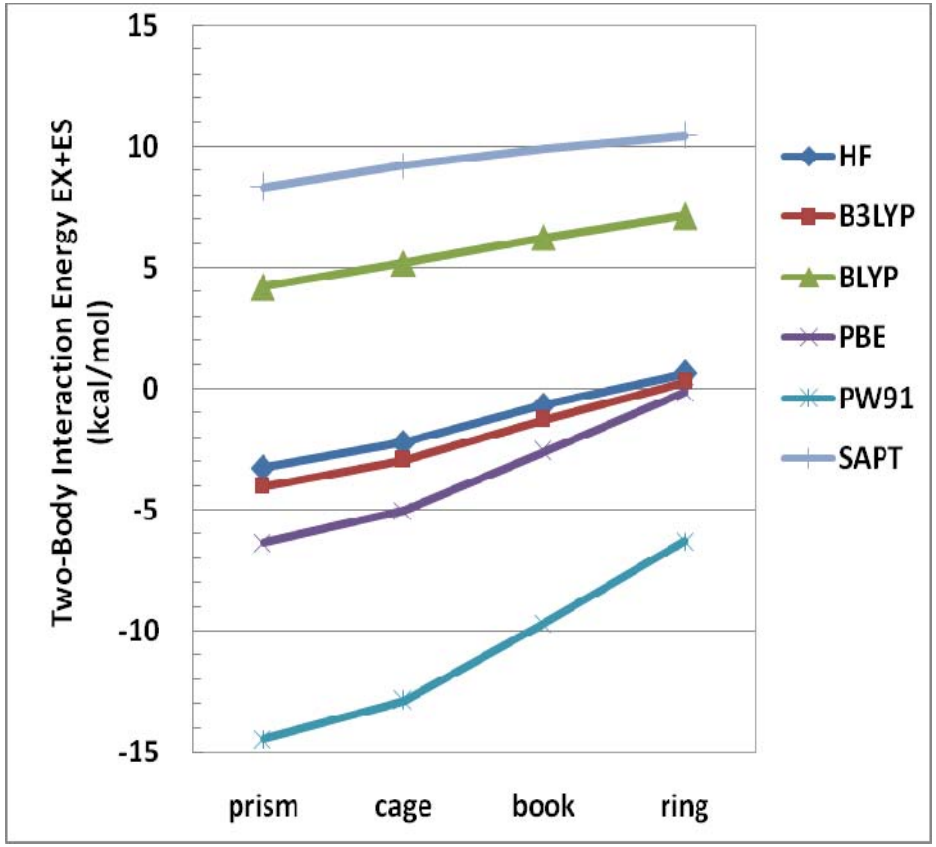
$$\Delta E = \Delta V_{electrostatic} + \Delta E_{Pauli} + \Delta E_{Orbital-interaction}$$

$$\Delta E_{Pauli} = \Delta V_{Pauli} + \Delta T_{Pauli} + E_{XC}(LDA) + E_X(GGA) + E_c(GGA)$$

Similar to Head-Gordon's EDA procedure

J.Langlet, J. Berges, and P. Reinhardt, *J. Mol. Struct.*, 685, 43-46 (2004)

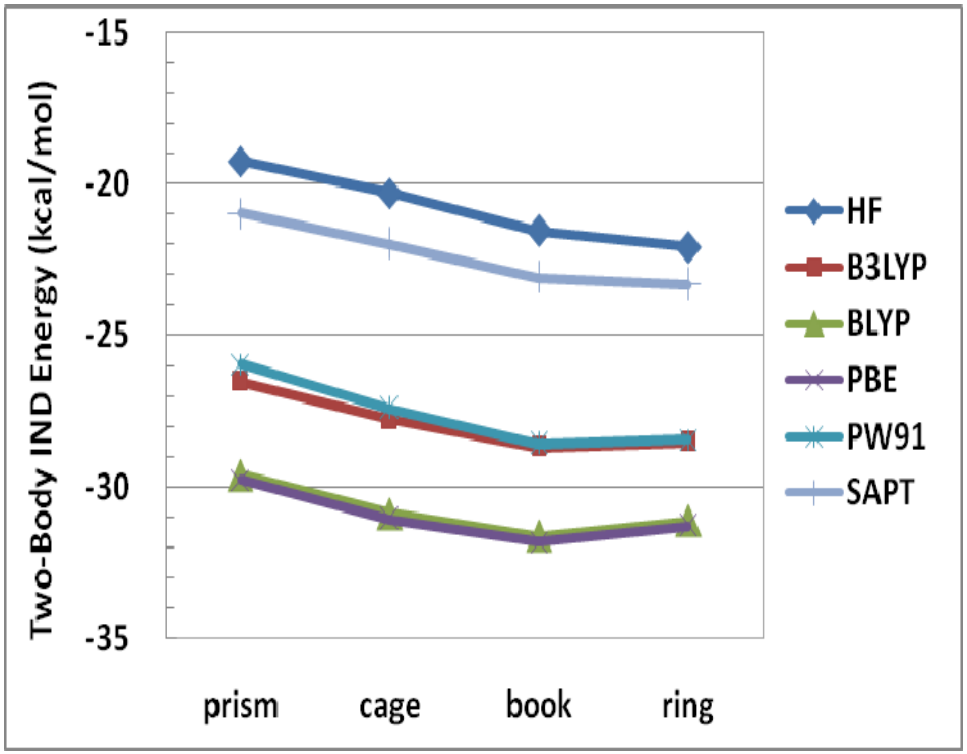
Two-Body Interaction Energy EX+ES



- All methods give similar values of the electrostatic interactions. Hence the differences in the EX+ES 2-body energies mainly reflect differences in the exchange-repulsion contributions.

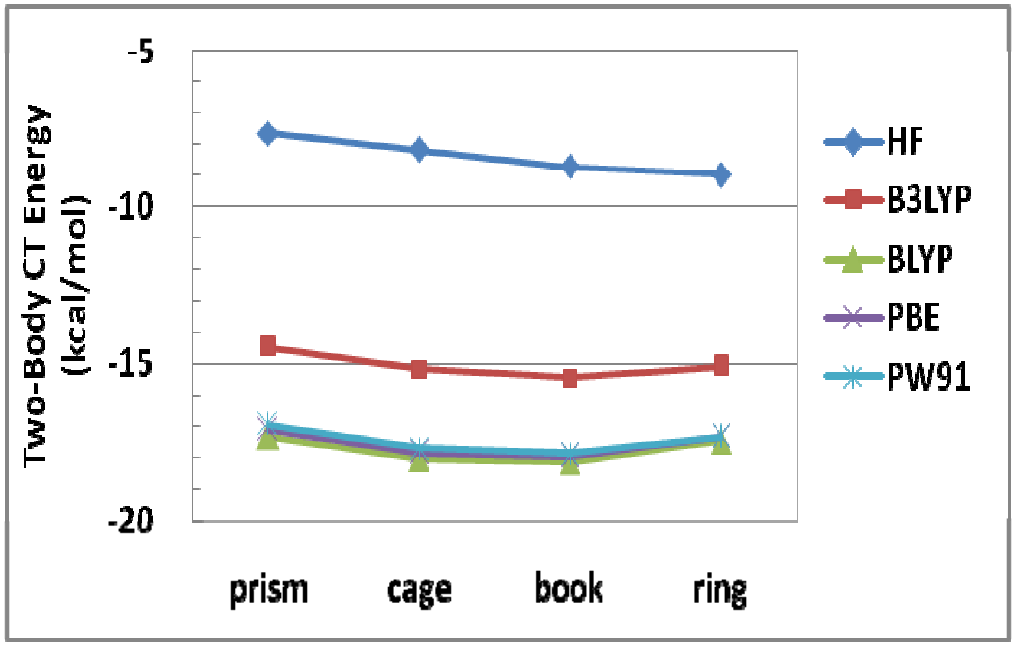
- Only the BLYP procedure gives two-body EX+ES interactions within 5 kcal/mol of the SAPT results.

Two-Body Induction Energy



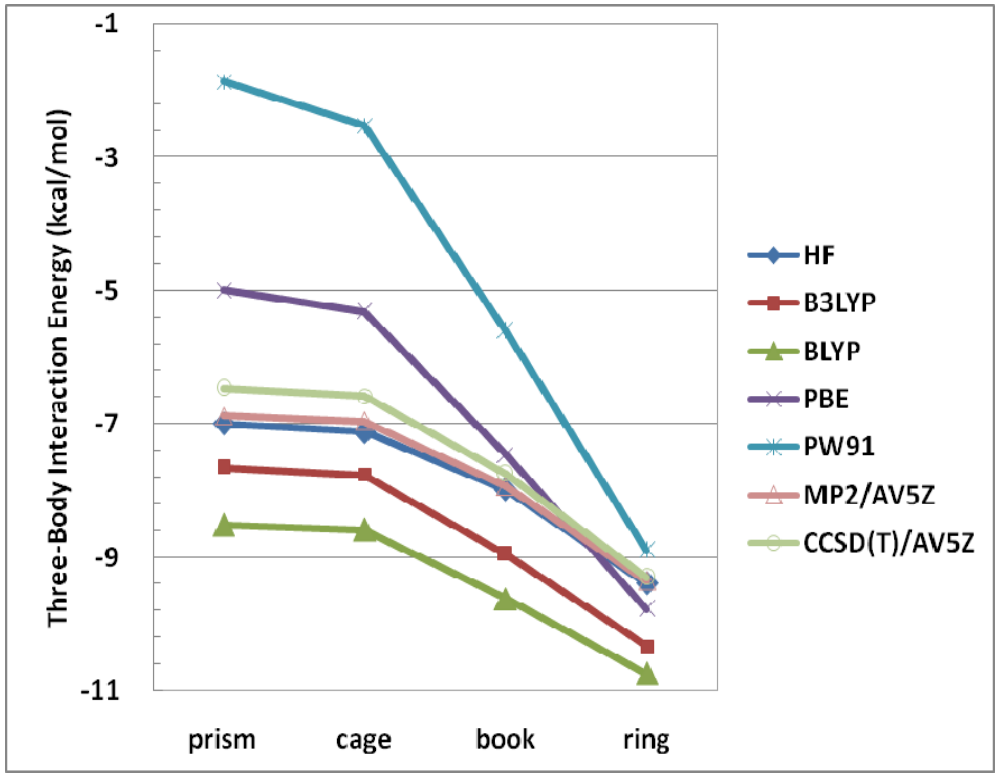
• All DFT methods give much greater (in magnitude) two-body induction energies than the SAPT calculations.

Two-Body Charge-Transfer Energy



• The overestimation in magnitude of the two-body induction energies in the DFT calculations is mainly due to the overestimation of charge-transfer contributions.

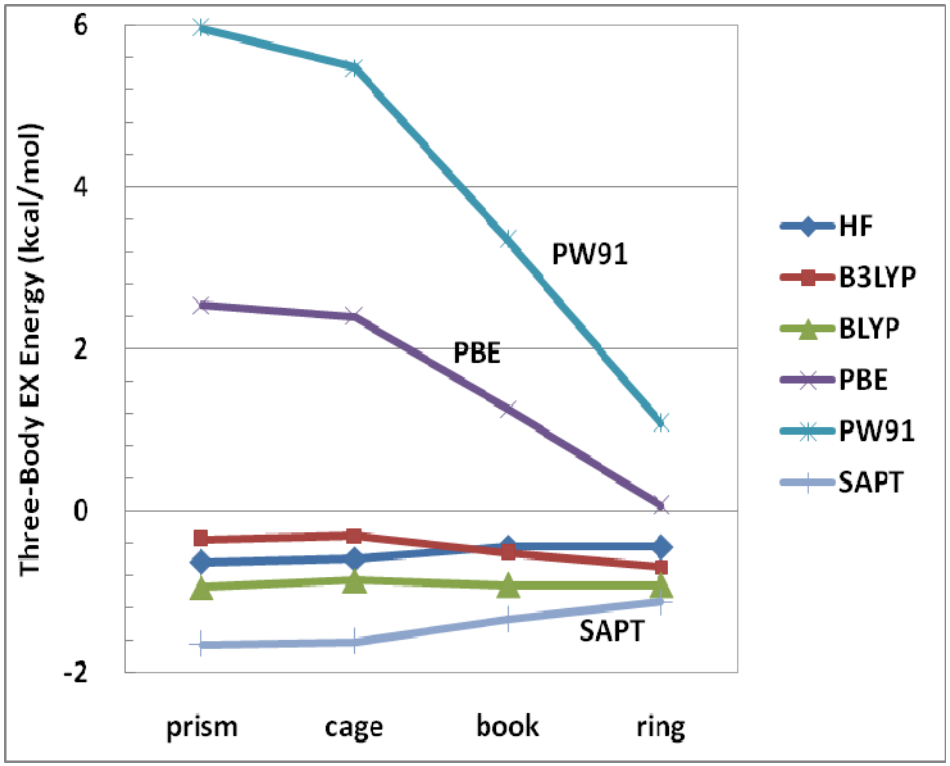
Net Three-Body Interaction Energy



- With the exception of the B3LYP method, none of the density functional methods considered give three-body energies close to the CCSD(T) results.

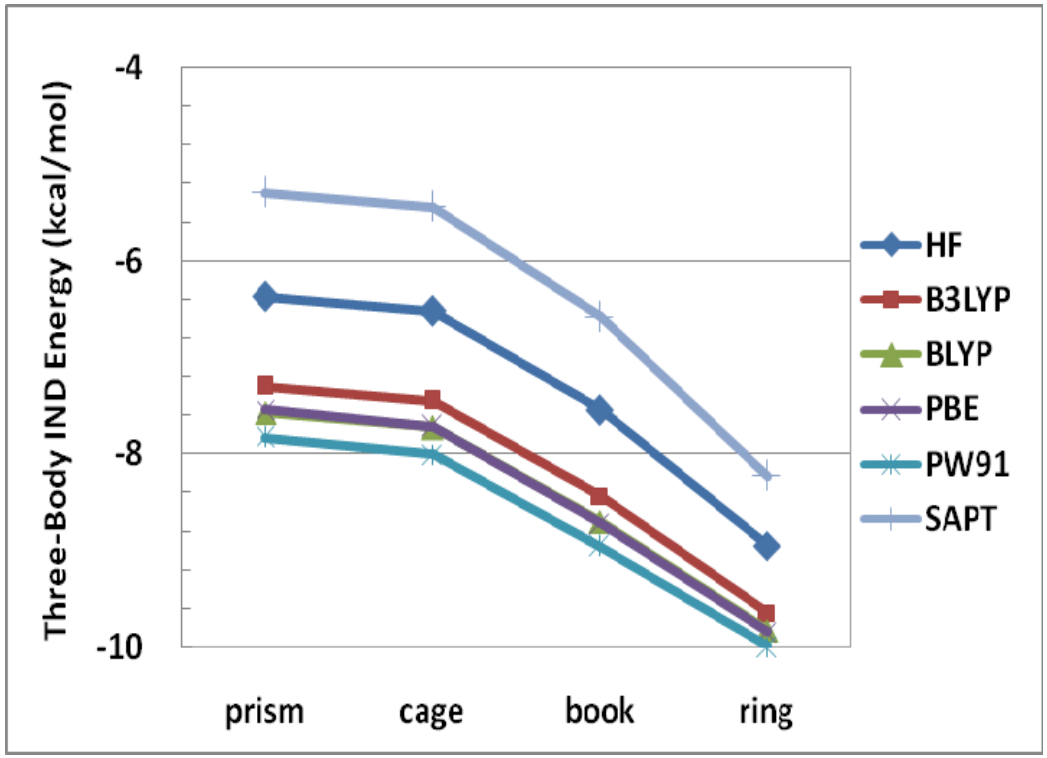
- PW91 and PBE functionals considerably underestimate the magnitude of the three-body energies of the prism and cage isomers.

Three-Body Exchange-Repulsion Energy



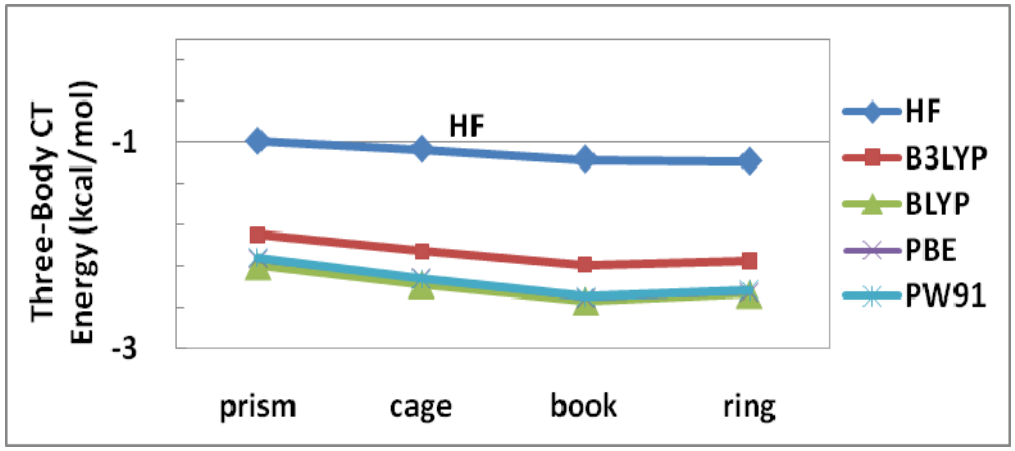
• None of the functionals properly account for the trends in the three-body exchange energies, with PW91 and PBE fairing especially poorly.

Three-Body Induction Energy



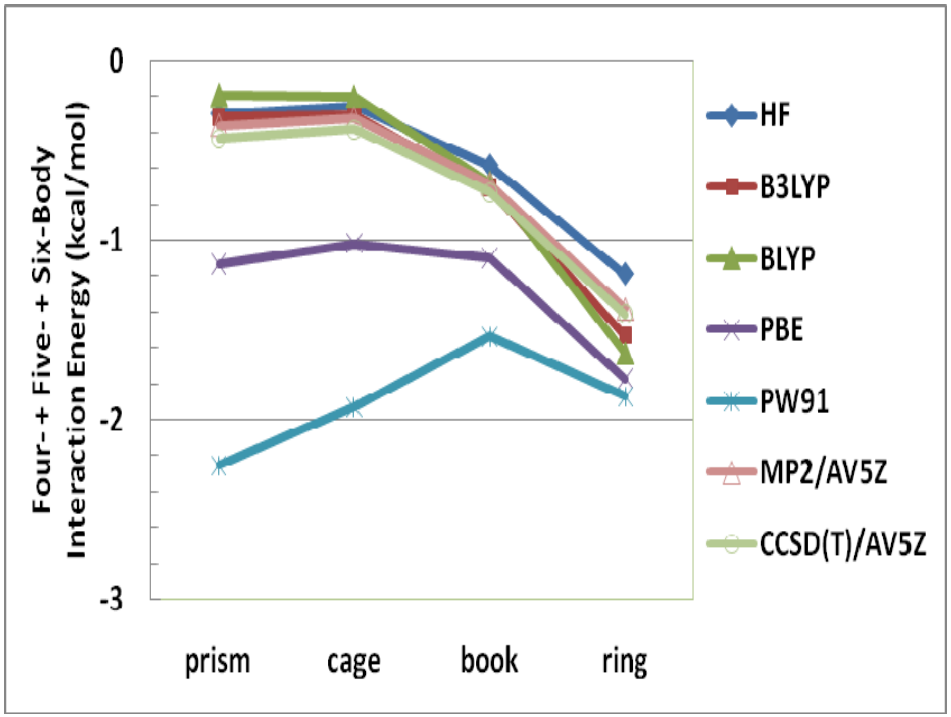
• All of the density functional methods give three-body induction energies that are larger in magnitude than those from the HF and SAPT calculations. (Here, HF is probably more useful than SAPT as the reference as the latter includes interactions only through third order.)

Three-Body Charge-Transfer Energy



• The overestimation of the three-body induction energies in the various DFT methods is mainly due to the overestimation of the charge-transfer contributions.

4+5+6- Body Energies



- The net 4+5+6-body contributions are quite small.
- BLYP, B3LYP give similar 4+5+6-body contributions to the CCSD(T) results.
- PW91 and PBE do not correctly predict the trends in the 4+5+6-body contributions.

Hybrid Functionals with Range Separation

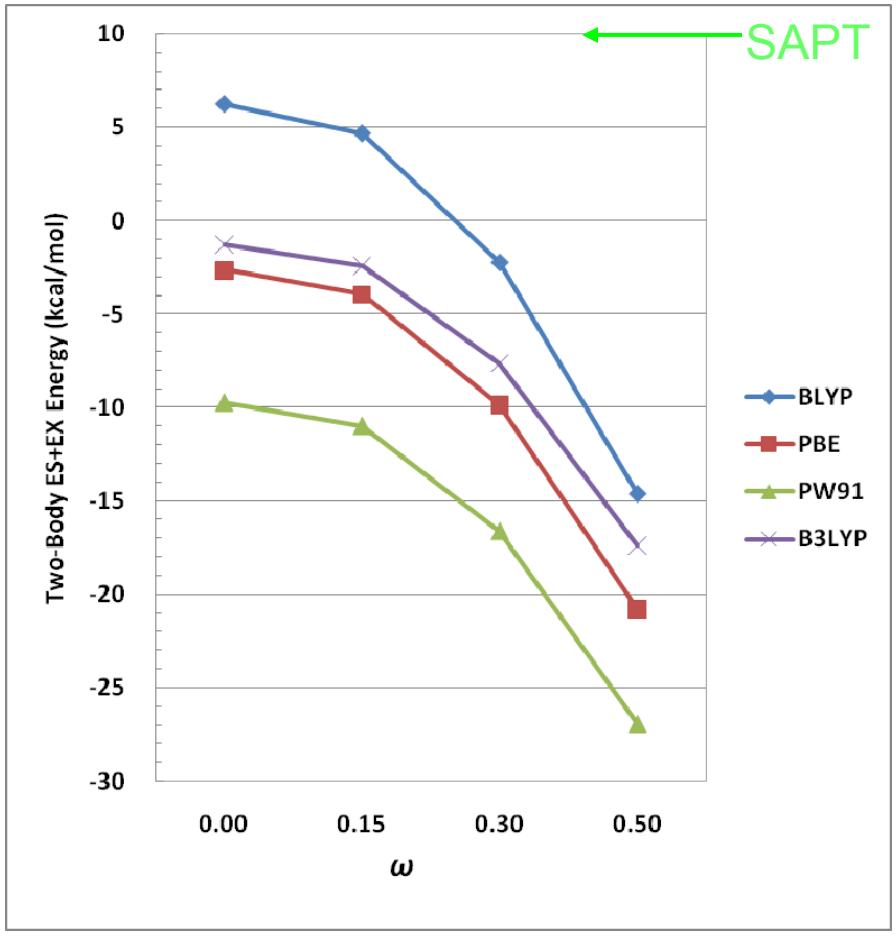
• Partition of the electron-electron Coulomb potential into long- and short-range components, using the error functional (erf):

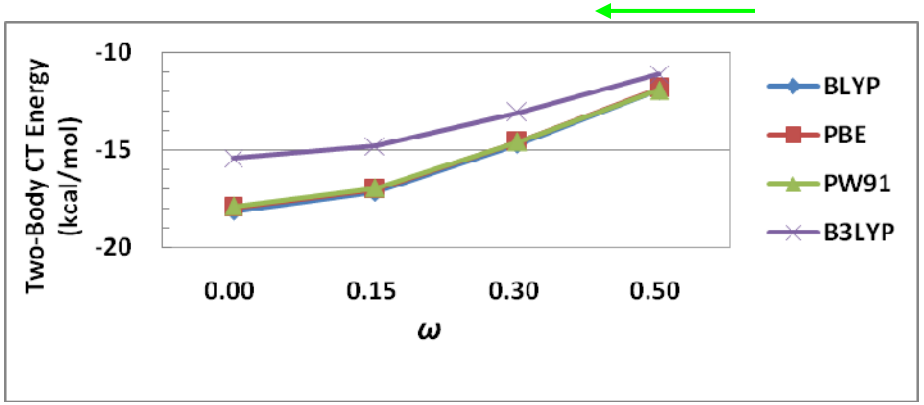
$$\frac{1}{r_{12}} = \frac{1-\mathrm{erf}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erf}(\omega r_{12})}{r_{12}}$$

• Full HF exchange using the long-range part of the Coulomb operator.

$$E_{\mathrm{XC}} = E_{\mathrm{C}} + E_{\mathrm{X}}^{\mathrm{GGA,SR}} + C_{\mathrm{HF}} E_{\mathrm{X}}^{\mathrm{HF,SR}} + E_{\mathrm{X}}^{\mathrm{HF,LR}}$$

Hybrid Functionals with Range Separation Tested on the Book Isomer





Although the use of range-separated functionals improves the description of CT, they worsen the characterization of the exchange-repulsion energy.

Summary

Standard DFT functionals

- do not properly describe the exchange and charge-transfer contributions to the interaction energies
- do not account for dispersion interactions.

This results in the incorrect ordering of the net interaction energies of isomers of the water hexamer.

The vdW-DF functional fares much better at predicting the relative energies of the isomers even though the magnitude of the dispersion energy is much smaller than SAPT values.

Range-separated functional do not fix the problems with the exchange-repulsion energies