

*Spin-component scaled MP2 – different parametrization  
for different problems*

**ACCURATE NON-COVALENT INTERACTION  
ENERGIES AND DISSOCIATION ENERGY CURVES**

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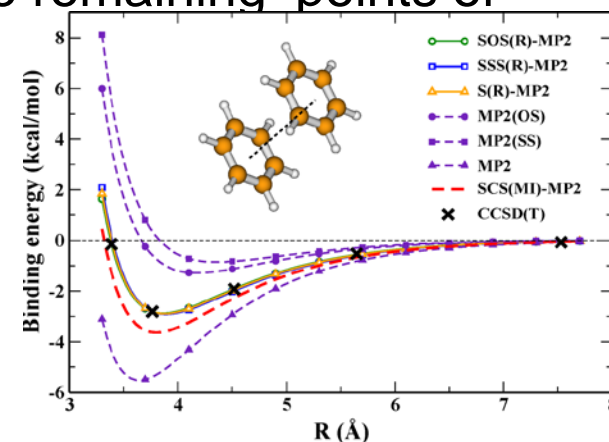


- Spin Component Scaled MP2

- A simple and non-empirical method to determine optimal scaling coefficients, within the (spin-component)-scaled MP2 approach, for calculating intermolecular potential energies of noncovalently-interacting systems.

### The key idea:

to compute with high accuracy (CCSD(T) ) a large portion of the dissociation curve at the max cost of a single CCSD(T) calculation. We do CCSD(T) calculation at some distance  $R$ , and the remaining points of the curve are calculated with the SOS MP2 ( $O(N^4)$ ).



I. Grabowski, E. Fabiano, F. Della Sala, PCCP , **15 (37)\*** (2013) , 15485

E. Fabiano, F. Della Sala, I. Grabowski, Chem. Phys. Lett. **635** (2015), 262



## Collaboration / research team

Eduardo Fabiano



Fabio Della Sala



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Mateusz Witkowski – student



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## Motivation

„Strange” behaviour and parametrization of the SCS MP2 methods for calculating the interaction energy curves for non covalently interacting systems and especially the difficulty in fixing optimal values of the scaling for the proper description of noncovalent interactions.



## Spin Component Scaled MP2 (SCS-MP2)

Introduce scaling factors to the **same-spin** and **opposite-spin** contributions of the MP2 correlation energy

$$E_C^{MP2} = c_{OS} \sum_{ijab} \frac{|(ia | jb)|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} + c_{SS} \sum_{ijab} \frac{(ia | jb)[(ia | jb) - (aj | bi)]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

SCS MP2 empirical parameters  $c_{OS}=6/5$  and  $c_{SS}=1/3$  proposed by S. Grimme (*S. Grimme, J. Chem. Phys.* **118** (2003) 9095.)

which have been obtained from a fit to a set of representative reaction energies (to reproduce QCISD(T) energies)

It was found that, with an appropriate choice of the  $c_{OS}$  and  $c_{SS}$  coefficients, a significant improvement over standard MP2 is possible on different levels and quantities (many applications !!!)



# SCS MP2

Method	$c_{OS}$	$c_{SS}$	Comment
MP2	1.00	1.00	
SCS-MP2	1.20	0.33	original, general purpose
SOS-MP2	1.30	0.00	$O(N^4)$ scaling with system size
MOS-MP2	1-2	0.00	$r_{12}$ dependent factors
O2	1.20	0.00	SOS-MP2 with optimized orbitals
SOS- $\pi$ -MP2	1.40	0.00	special version for $\pi$ -systems
FE2-MP2	1.12	0.84	Feenberg scaled version
SCS(MI)-MP2	0.40	1.29	special version for NCI <sup>a</sup>
SCSN-MP2	0.00	1.76	special version for NCI <sup>b</sup>
SCS-MP2-vdW	1.28	0.50	special version for NCI <sup>c</sup>
SCS-CCSD	1.27	1.13	general purpose
S2-MP	1.15	0.75	general purpose, new theoretical derivation

SOS-MP2 approach proposed by the Head-Gordon group with scaling factors of  $c_{OS}=1.3$  and  $c_{SS}=0.0$  (Y., Jung, R.C. Lochan, A.D. Dutoi, and M. Head-Gordon, *J. Chem. Phys.* **121** (2004) 9793.)

which scales  $O(N^4)$



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Application in DFT with orbital dependent functionals – correlated OEP DFT.

**SOS – OEP2 method** –  $c_{os}$  coefficients calculated on the fly,  $O(N^4)$  scaling - correlation and total energies, IP, KS correlation potentials and electron densities

I. Grabowski, E. Fabiano, F. Della Sala, Phys. Rev. B 87, 075103 (2013).

I. Grabowski, E. Fabiano, S. Śmiga, A. Buksztel, A. M. Teale, F. Della Sala, J. Chem. Phys. 141,24113-1 (2014)

S. Śmiga, F. Della Sala, A. Buksztel, I. Grabowski, E. Fabiano, J. Comput. Chem \*37\* 2081 - 2090 (2016)

A. Buksztel, S. Śmiga, I. Grabowski, Adv. Quantum Chem. \*73\* 263 - 283 (2016)



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Distasio and Head-Gordon (SCS(MI)-MP2 method)

Grant Hill and Platts

„Strange” parametrization of the SCS MP2 methods for calculating the interaction energy curves for non covalently interacting systems. The lack of an agreement with “standard” SCS-MP2 or SOS-MP2 values nor with the values suggested by theoretical arguments.





## Motivation

„Strange” behaviour and parametrization of the SCS MP2 methods for calculating the interaction energy curves for non covalently interacting systems.

- The „gold standard” for the simulation of noncovalently interacting complexes is the CCSD(T) approach scales as  $O(N^7)$
- In the case of the determination of a potential energy surface (PES) or for geometry optimizations - numerous single-point calculations are required.
- $O(N^4)$  or even  $O(N^3)$  scaling for the SOS MP2 method



Two classes of methods are used for studying the intermolecular forces:

Supermolecular approach - 90% of applications

Symmetry-adapted perturbation theory

Interaction energy is defined as:

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

 $E_{AB}$ 

dimer energy

 $E_A$ 

energy of isolated A

 $E_B$ 

and B monomers

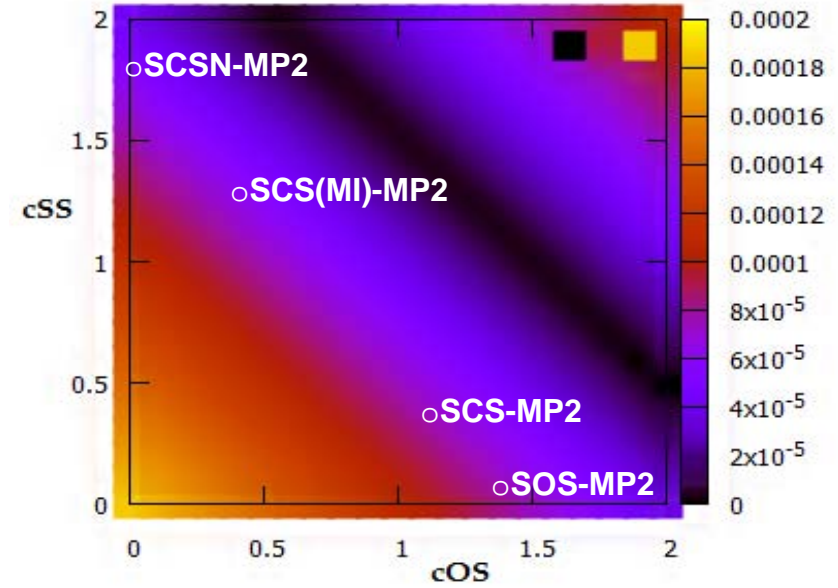
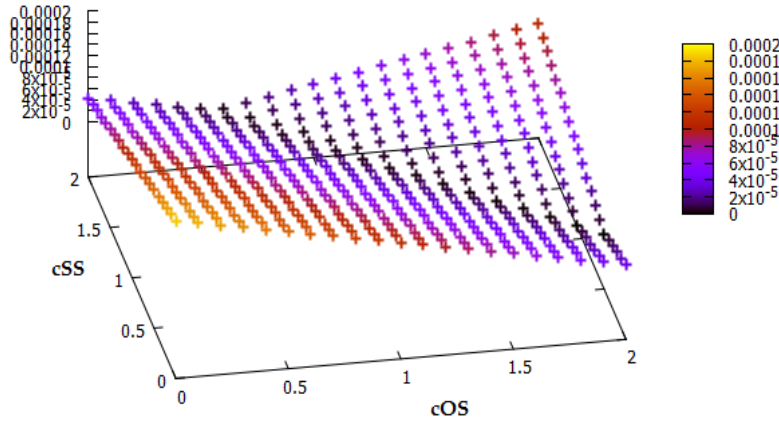


## Noncovalently interacting complexes

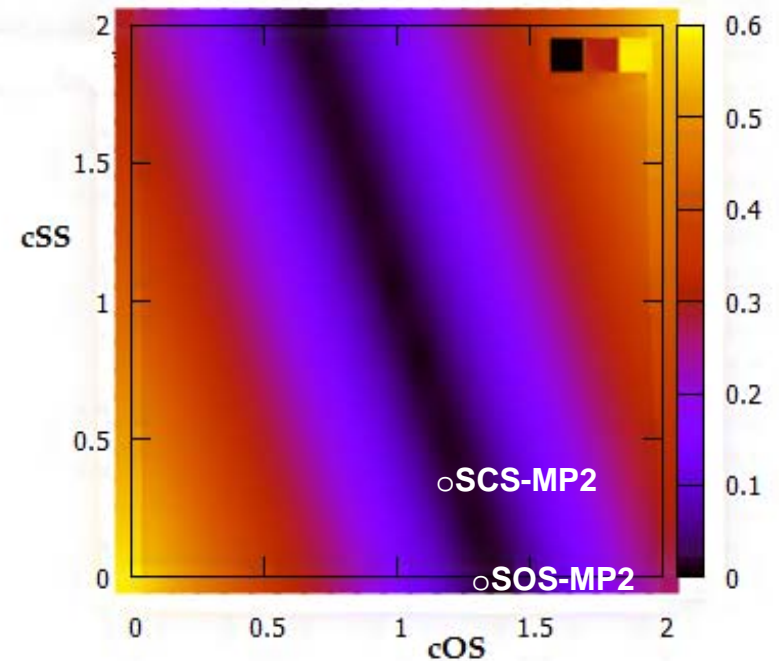
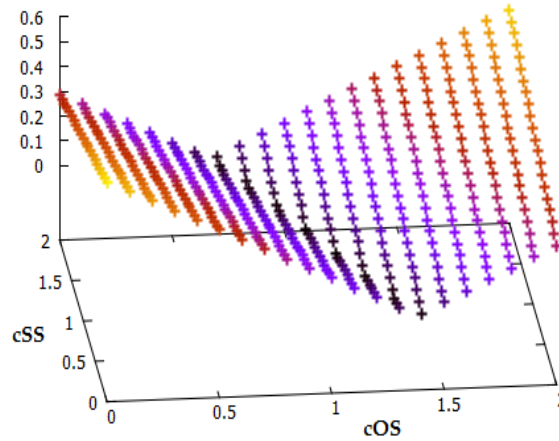
- Correlated methods are necessary, extremely sensitive for the quality of the methods and basis set.
- The „gold standard” for the simulation of noncovalently interacting complexes is the CCSD(T) approach scales as  $O(N^7)$
- MP2 – large error
- DFT – huge effort, some kind of progress, ... , ? , large calculations!
- SCS MP2 - high level of empiricism, unsatisfactory results.



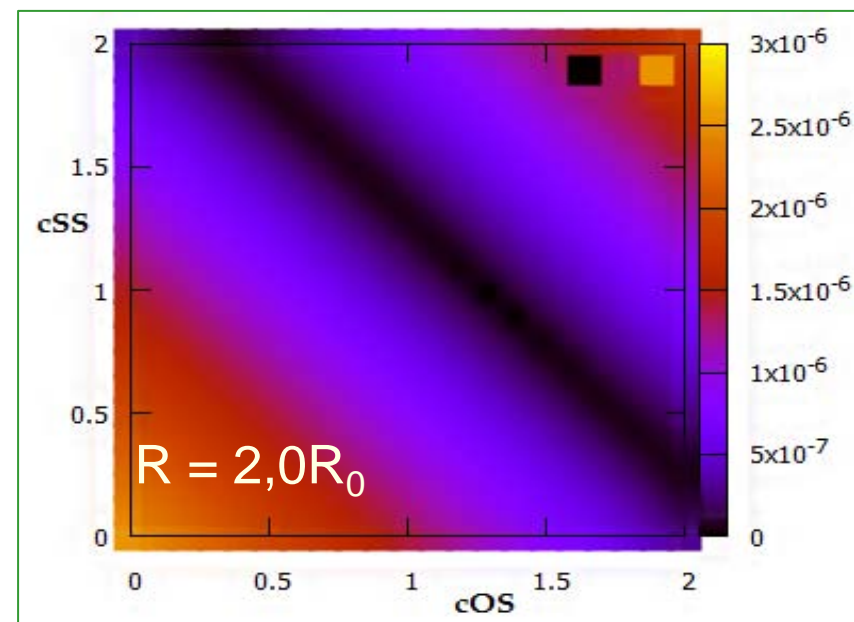
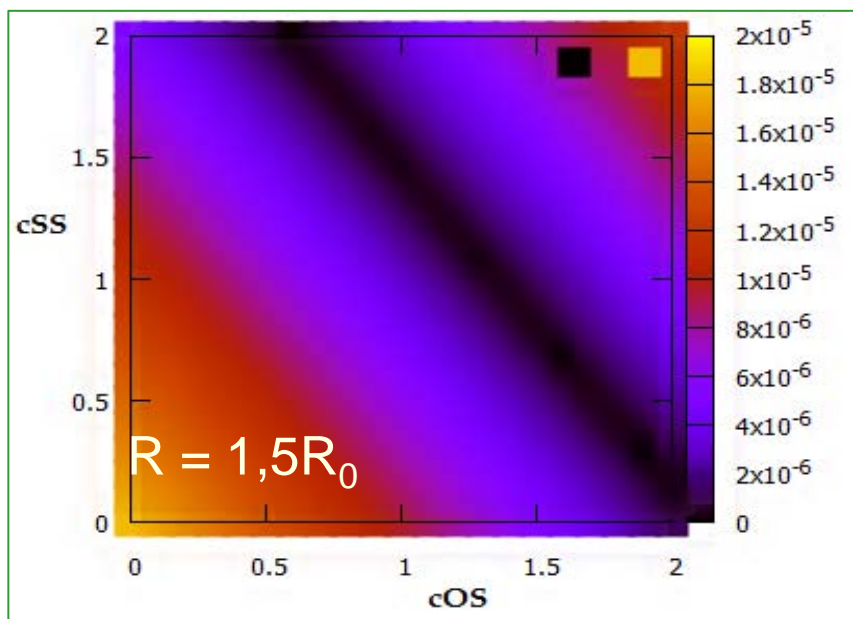
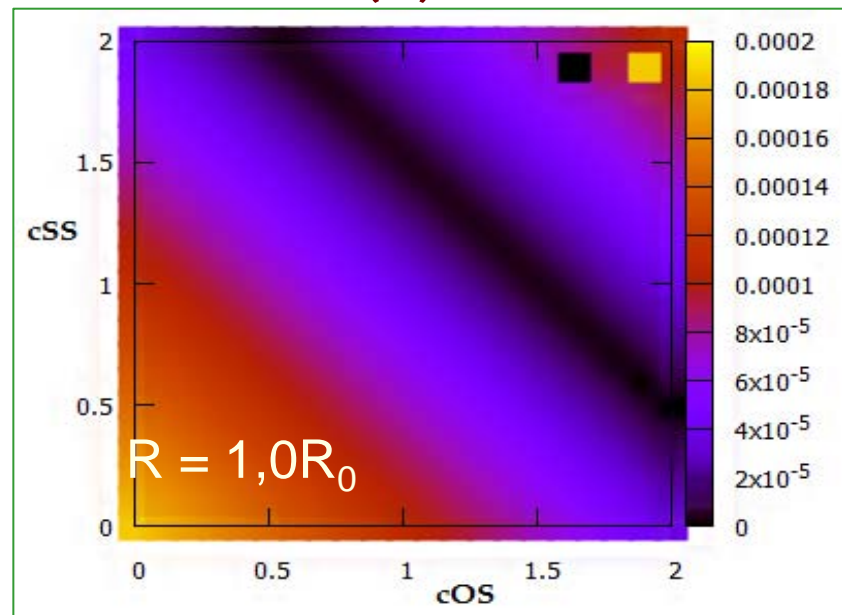
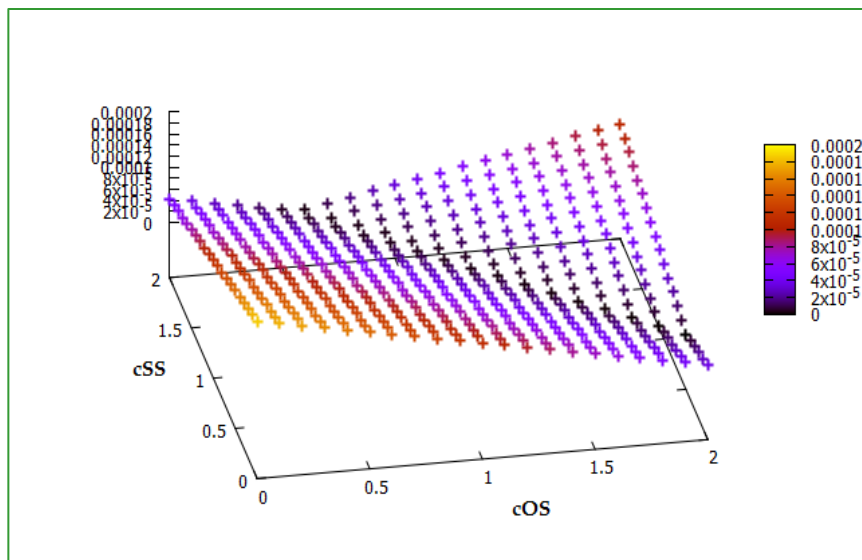
# Ne<sub>2</sub> SCS-MP2 correlation interaction energies with respect to CCSD(T)



# Ne<sub>2</sub> SCS-MP2 correlation energies with respect to CCSD(T)



# Ne<sub>2</sub> Scan of errors of SCS-MP2 correlation interaction energies with respect to CCSD(T)



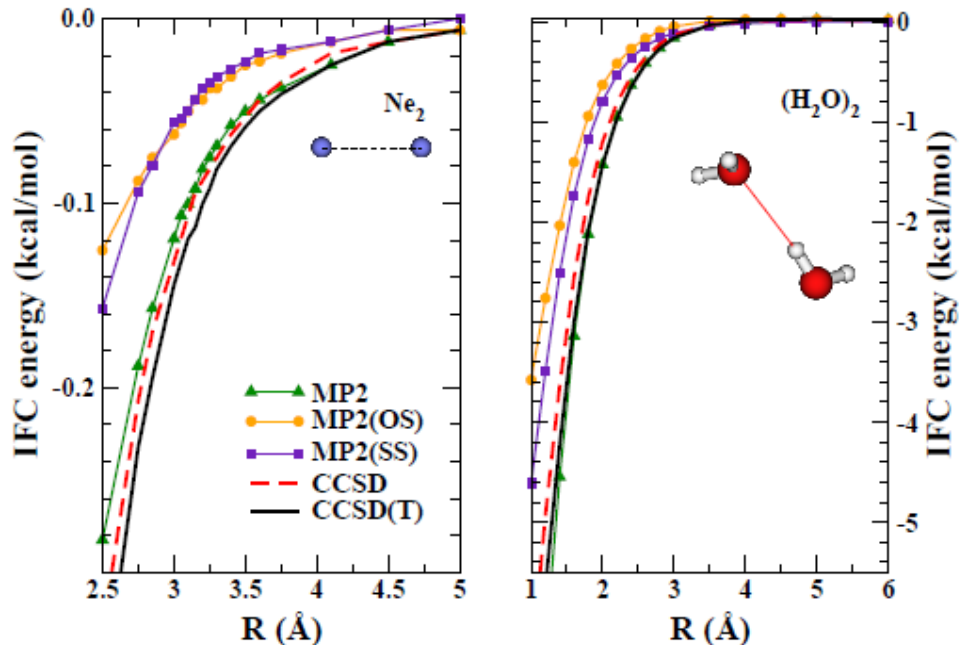
## Proposed procedure

- Our procedure is based on the observation that there exist a well defined proportionality between same/opposite–MP2 correlation interaction energies and the energy computed by CCSD(T), and is almost independent on the intermolecular distance.
- Thus, the **scaling parameter can be fixed once** by using the information from only one expensive high–level calculations at some distance  $R$  and successively the whole PES can be computed with high accuracy by performing only relatively cheap MP2 type calculations.



## Proportionality of IFC

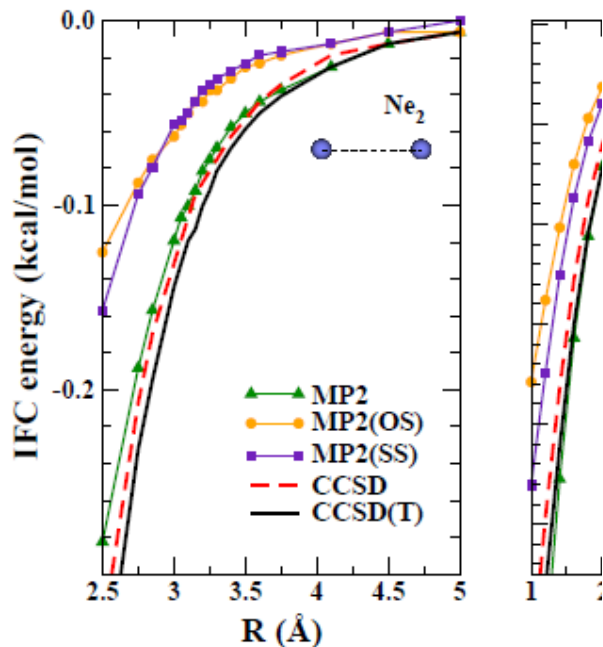
We observed that for noncovalent interactions, with good approximation, the correlation interaction energies computed at the MP2 (or equivalently MP2(SS) or MP2(OS)) level and at the CCSD(T) level are proportional to each other over a wide range of inter-fragment distances  $R$ .



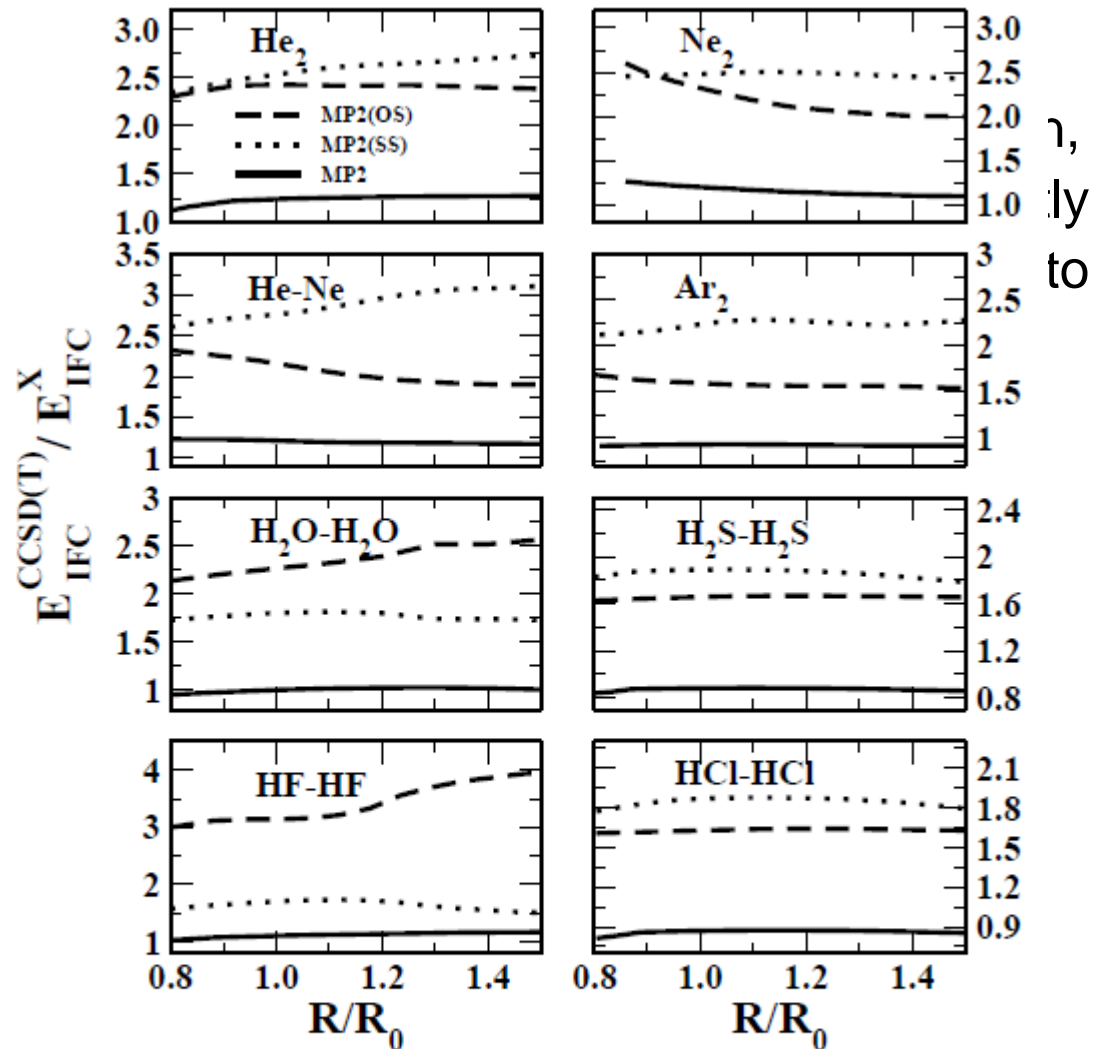
**Fig. 1** Inter-fragment correlation (IFC) energy of  $\text{Ne}_2$  and  $(\text{H}_2\text{O})_2$  as computed with different methods.



We observed that for non-  
the correlation interaction  
MP2(SS) or MP2(OS)) le  
each other over a wide ra



**Fig. 1** Inter-fragment correlation (IFC) energy as computed with different methods.



**Fig. 2** Ratio between different spin-resolved MP2 IFC energies and CCSD(T) ones, for various systems at several distances.  $R_0$  denotes the equilibrium distance of each complex.  $X = \text{MP2}$  [continuous line],  $\text{MP2(OS)}$  [dashed line], and  $\text{MP2(SS)}$  [dotted line].



## Proposed procedure

- Our procedure is based on the observation that there exist a well defined proportionality between same/opposite–MP2 correlation interaction energies and the energy computed by CCSD(T), and is almost independent on the intermolecular distance.
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## Method

How to fix the SCS coefficients?

$$E_{\text{int}}^{\text{CCSD}(T)}(R) \cong E_{\text{int}}^{\text{SCS-MP2}}(R)$$

Using the Interfragment correlation energy  $E_{\text{IFC}}$   
(correlation interaction energy) – the main quantity of interest here

$$E_{\text{IFC}}^X = E_{c,AB}^X - E_{c,A}^X - E_{c,B}^X$$

$$E_{\text{IFC}}^{\text{CCSD}(T)}(R) \cong E_{\text{IFC}}^{\text{SCS-MP2}}(R)$$



Assuming then we want to **have one scaling coefficient only in SCS MP2**,  
The coefficients are calculated at some distance  $R_0$

$$c_S = \frac{E_{IFC}^{CCSD(T)}(R_0)}{E_{IFC}^{MP2}(R_0)}$$

$$c_{OS} = \frac{E_{IFC}^{CCSD(T)}(R_0)}{E_{IFC}^{MP2(OS)}(R_0)}$$

$$c_{SS} = \frac{E_{IFC}^{CCSD(T)}(R_0)}{E_{IFC}^{MP2(SS)}(R_0)}$$

The correlation interaction energies

$$E_{IFC}^{S(R)-MP2}(R) = c_S E_{IFC}^{MP2}(R)$$

$$E_{IFC}^{SOS(R)-MP2}(R) = c_{OS} E_{IFC}^{MP2(OS)}(R)$$

$$E_{IFC}^{SSS(R)-MP2}(R) = c_{SS} E_{IFC}^{MP2(SS)}(R)$$



At one point (at some distance  $R_0$ ) the coefficients are calculated

$$c_S = \frac{E_{IFC}^{CCSD(T)}(R_0)}{E_{IFC}^{MP2}(R_0)}$$

$$c_{OS} = \frac{E_{IFC}^{CCSD(T)}(R_0)}{E_{IFC}^{MP2(OS)}(R_0)}$$

$$c_{SS} = \frac{E_{IFC}^{CCSD(T)}(R_0)}{E_{IFC}^{MP2(SS)}(R_0)}$$

For **the whole PES** we calculate MP2-like energies and scale them with the coefficients

$$E_{IFC}^{S(R)-MP2}(R) = c_S E_{IFC}^{MP2}(R)$$

$$E_{IFC}^{SOS(R)-MP2}(R) = c_{OS} E_{IFC}^{MP2(OS)}(R)$$

$$E_{IFC}^{SSS(R)-MP2}(R) = c_{SS} E_{IFC}^{MP2(SS)}(R)$$

SOS MP2 scales  $O(N^4)$



## Calculations

Representative set of small noncovalently interacting systems:

- $\text{He}_2$ ,  $\text{Ne}_2$ ,  $\text{He-Ne}$ ,  $\text{Ar}_2$  (dispersion interaction),
- $(\text{H}_2\text{O})_2$ ,  $(\text{HF})_2$  (hydrogen bond),  $(\text{H}_2\text{S})_2$ ,  $(\text{HCl})_2$  (dipole–dipole interaction).
- benzene–HCN, the stacked benzene dimer, and  $\text{Be}_2$

### ACES II, TURBOMOLE

For all systems an aug–cc–pVQZ basis set was used, except for  $\text{Ne}_2$  (uncontracted aug–cc–pVTZ),  $\text{Be}_2$  (cc–pV5Z), and  $\text{Ar}_2$  (aug–cc–pV5Z).

No correction for the basis set superposition error (BSSE) was included



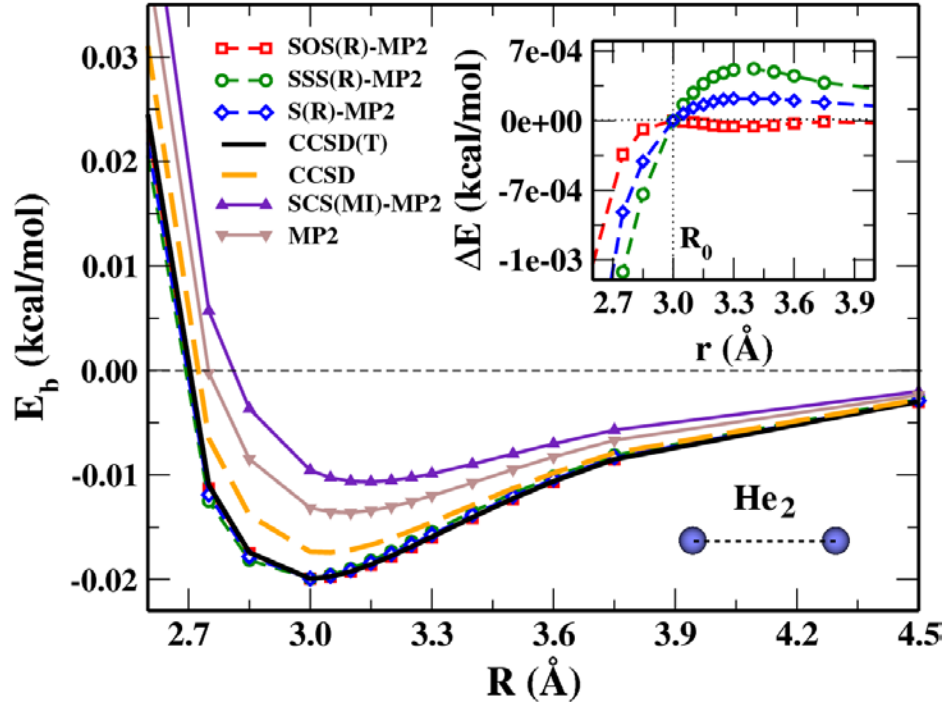
## Coefficients

**Table 1** Values of the  $c_{OS}$ ,  $c_{SS}$ , and  $c_S$  coefficients obtained via Eqs. (8), (9), (10) calculated at distance  $R_0$  for all the systems presented in this paper.

system	$c_{OS}$	$c_{SS}$	$c_S$	$R_0[\text{Å}]$
He <sub>2</sub>	2.43	2.53	1.24	3.0
He-Ne	2.15	2.76	1.21	3.0
Ne <sub>2</sub>	2.34	2.47	1.20	3.2
Ar <sub>2</sub>	1.60	2.24	0.93	3.7
H <sub>2</sub> S-H <sub>2</sub> S	1.66	1.89	0.88	2.8
HCl-HCl	1.63	1.87	0.87	2.5
HF-HF	3.14	1.71	1.11	1.8
H <sub>2</sub> O-H <sub>2</sub> O	2.27	1.80	1.00	2.0
Benzen HCN	1.27	1.35	0.66	2.34
Benzen dimer	1.39	1.66	0.76	3.765
Be <sub>2</sub>	1.79	3.03	1.13	2.4

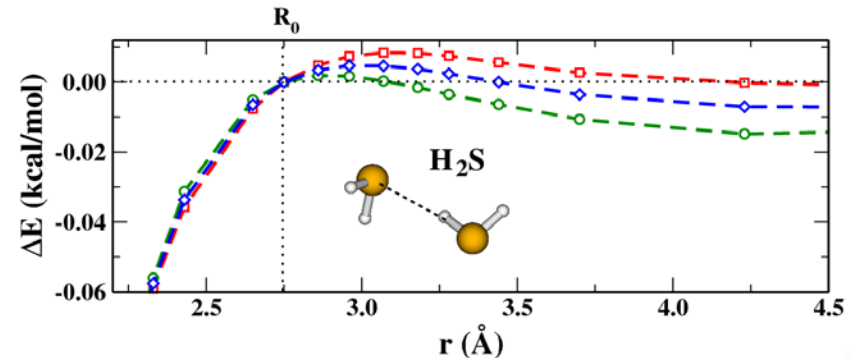
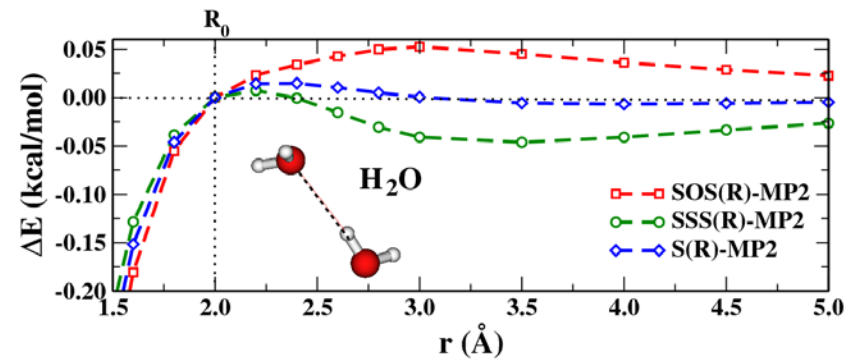
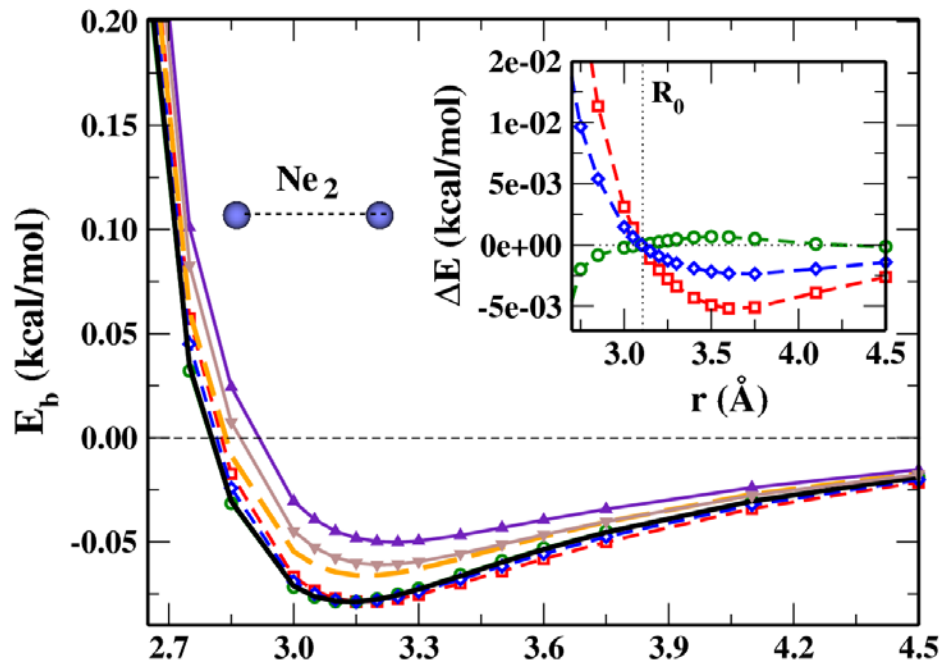
*The SCS coefficients are **strongly system dependent***

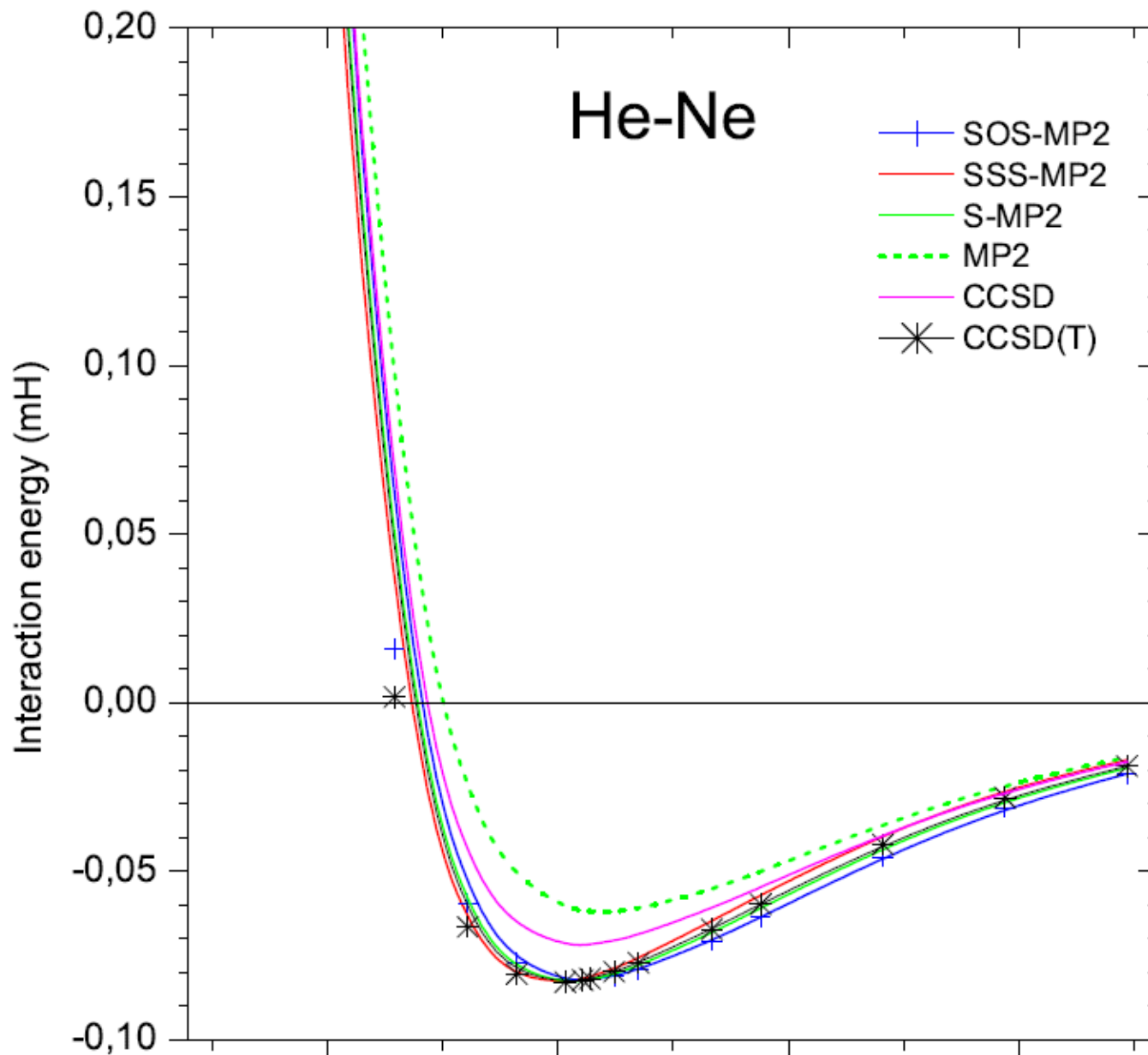




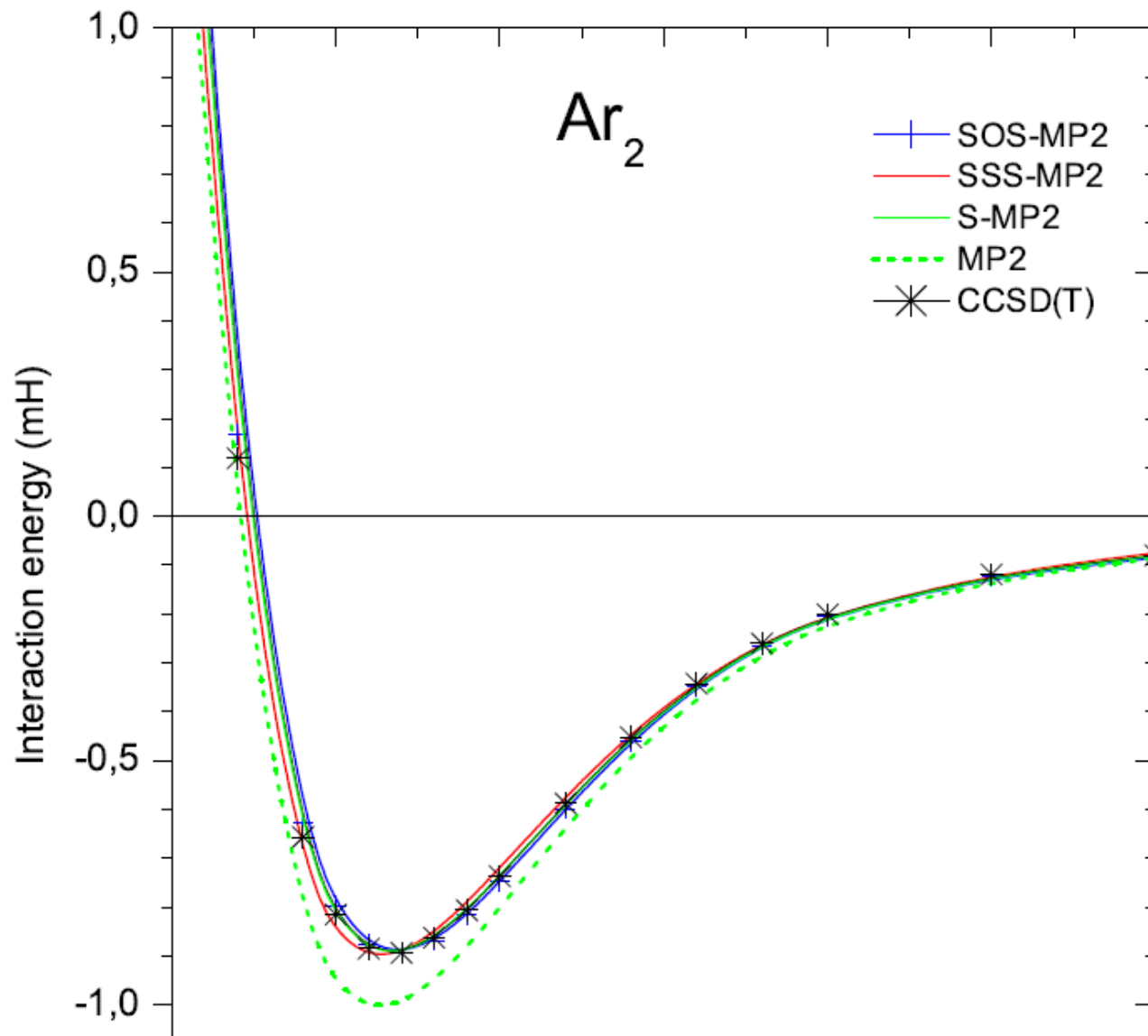
Binding energy of  $\text{He}_2$  and  $\text{Ne}_2$  as computed with different theoretical methods.

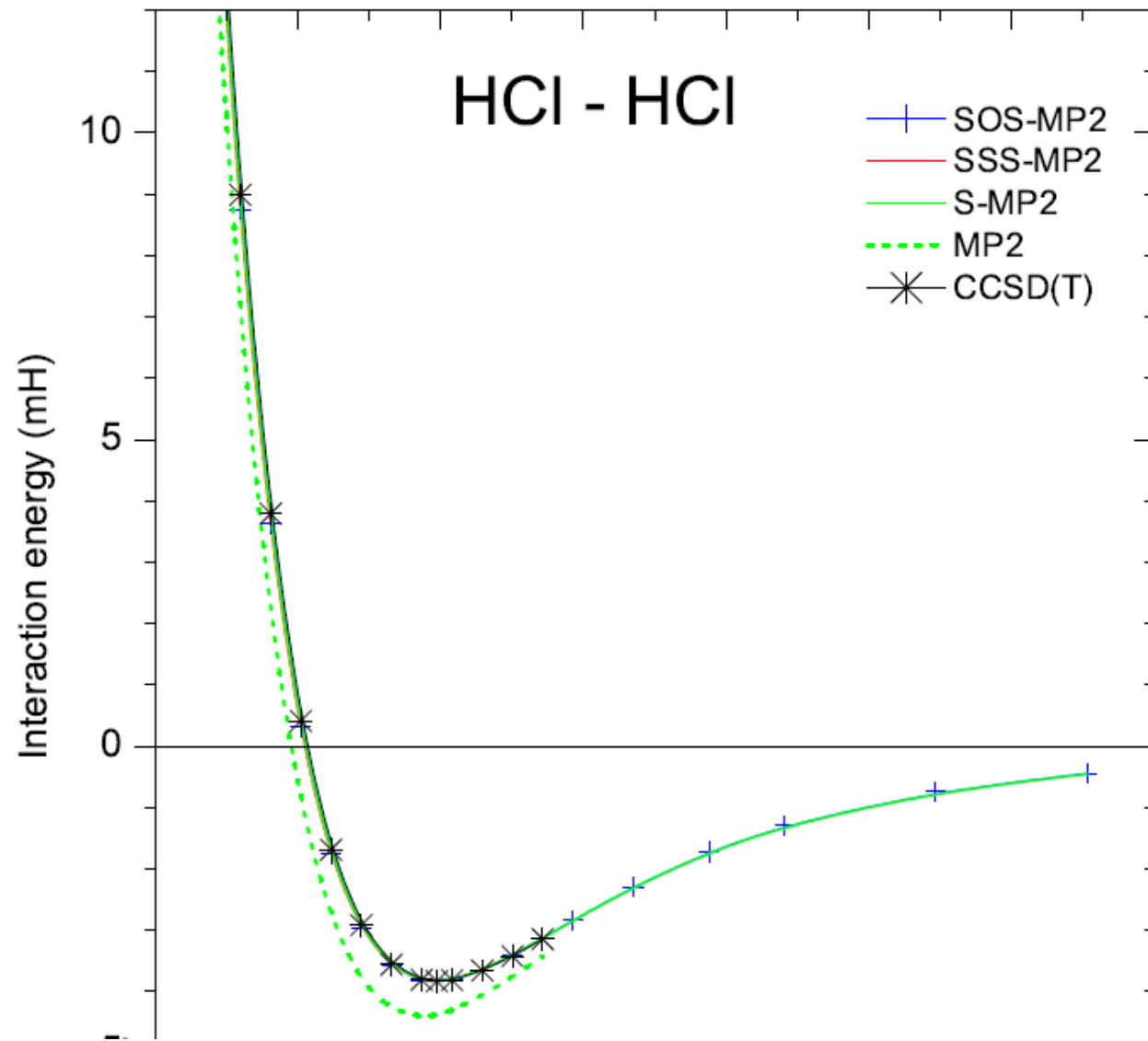
In the insets we report the difference between S(R)-MP2, SSS(R)-MP2, SOS(R)-MP2 and CCSD(T)

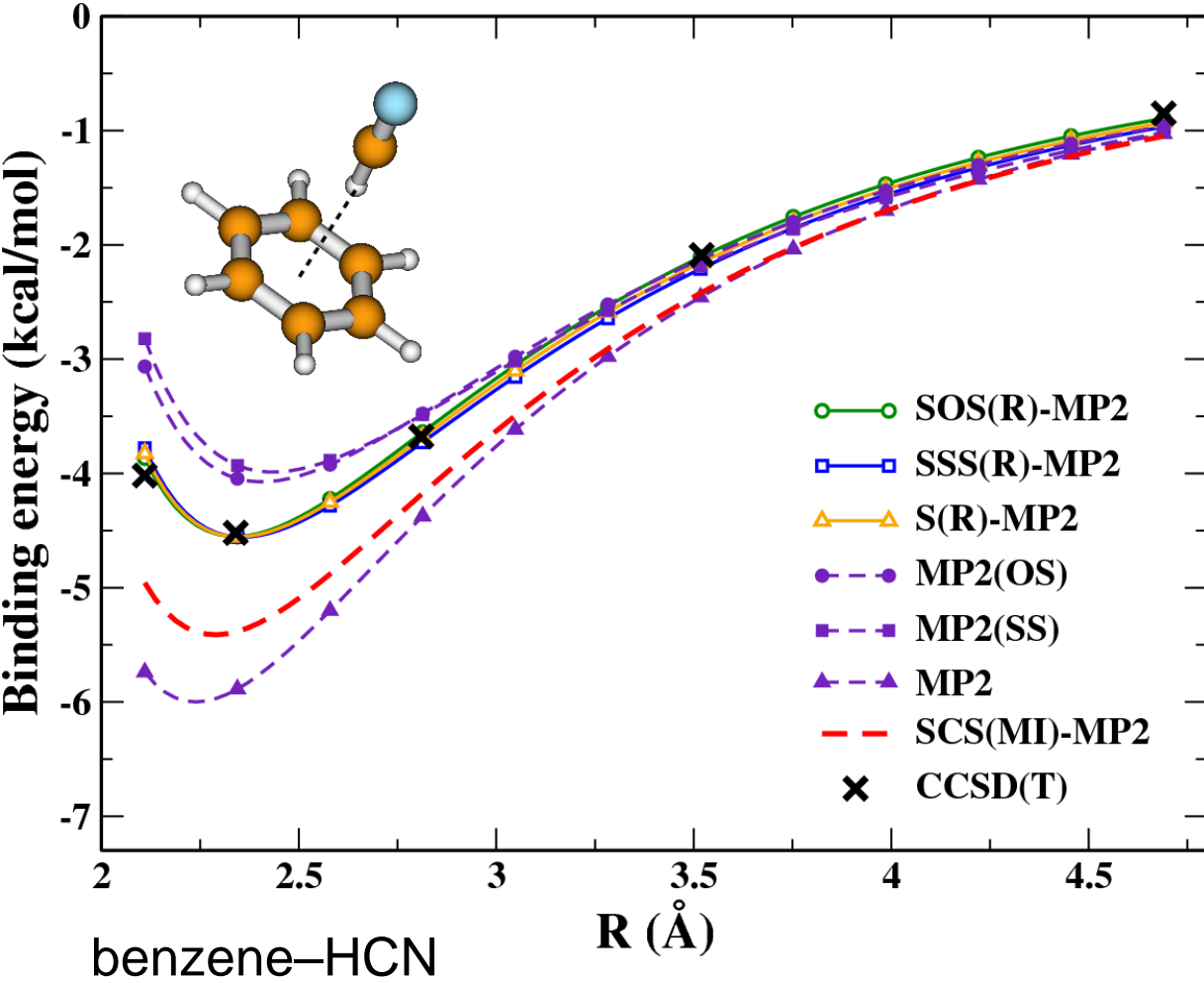


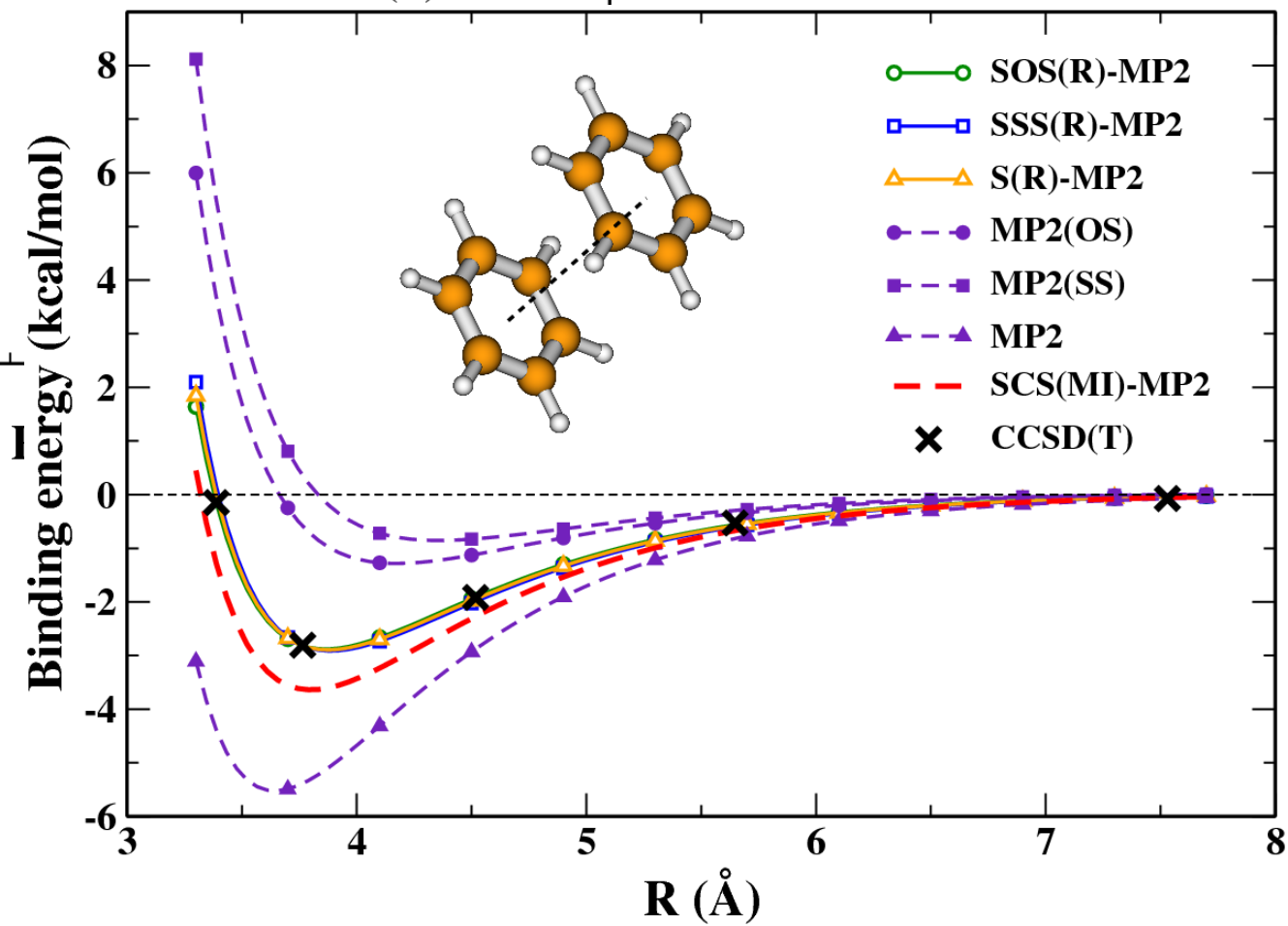
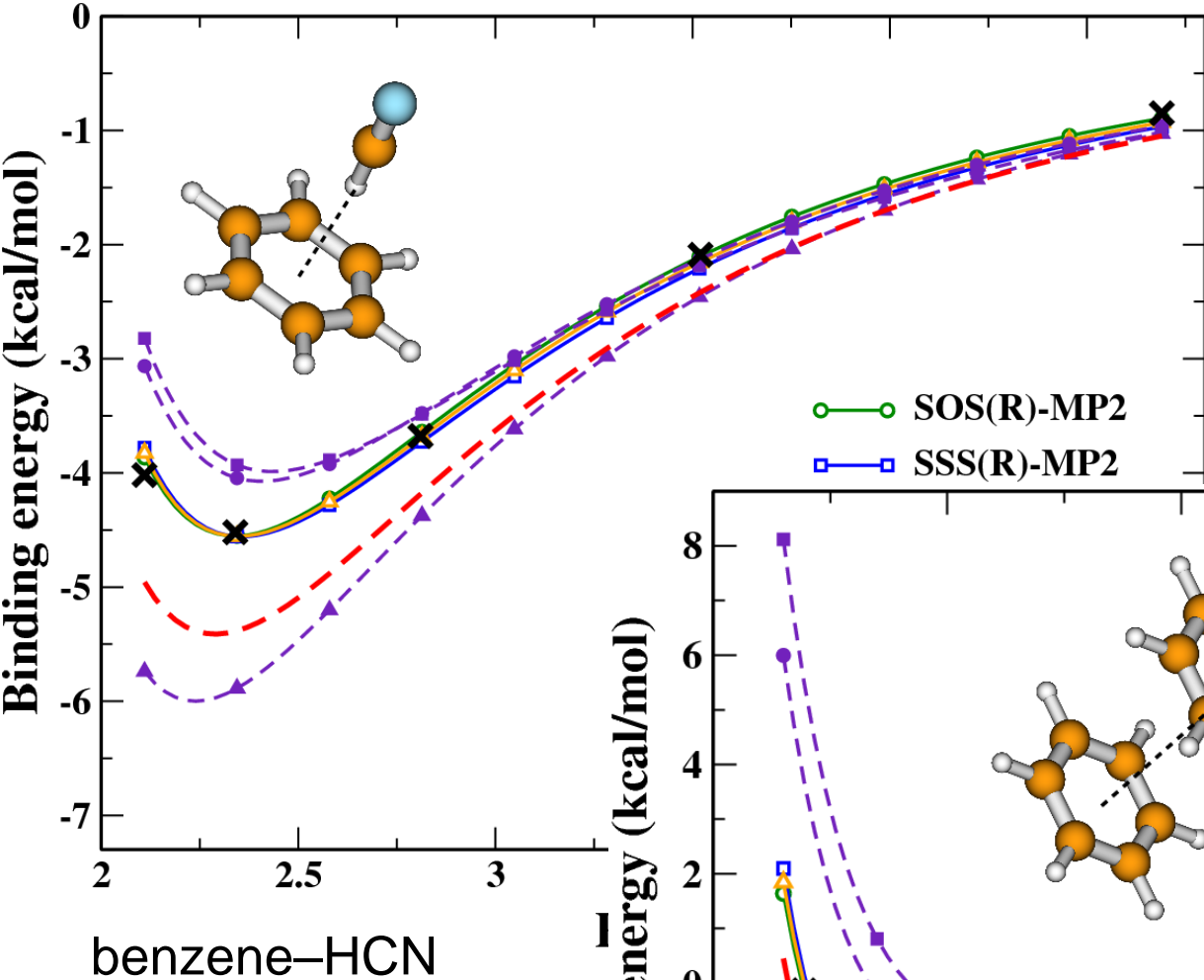


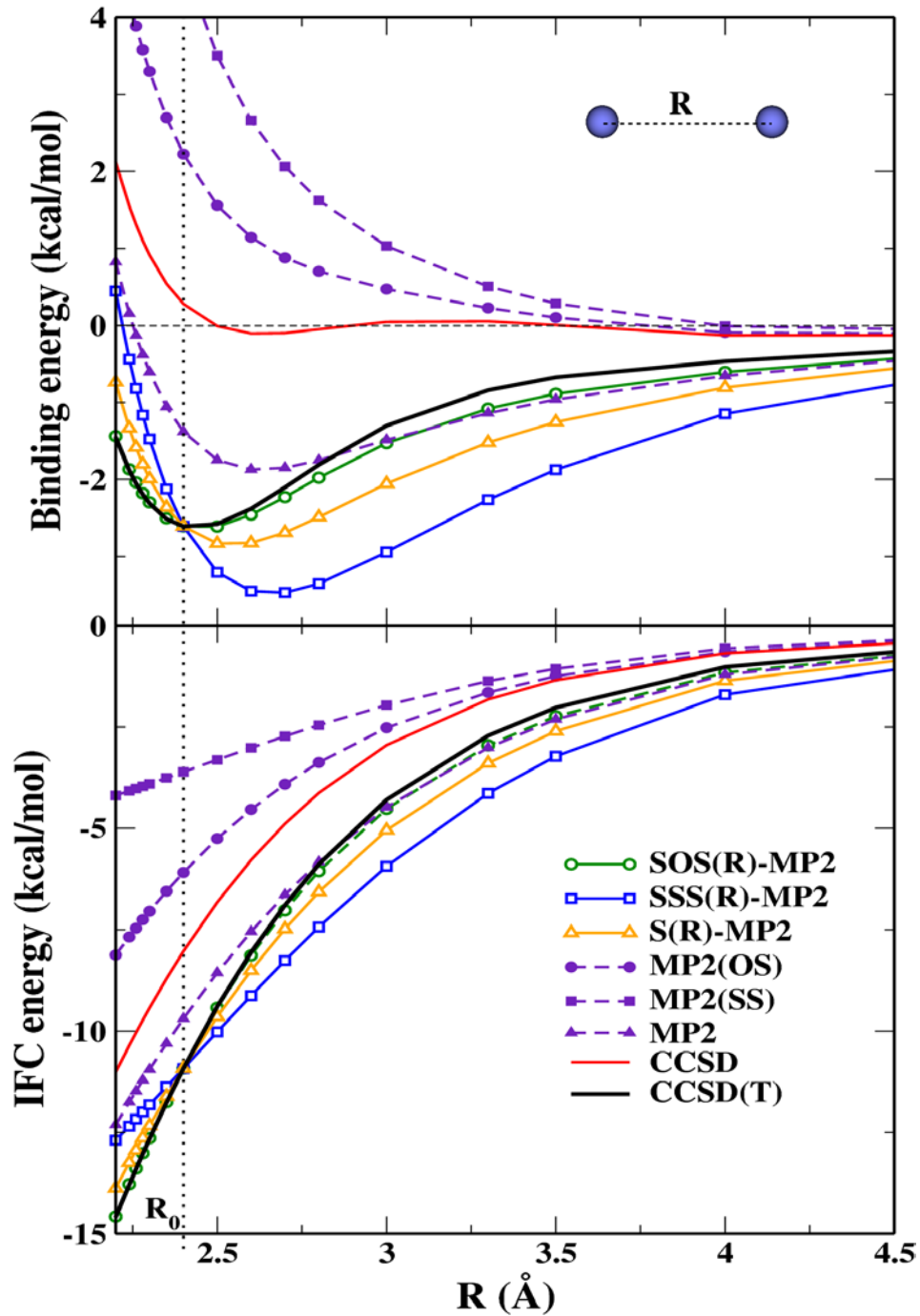












# Conclusions

- We have proposed a simple non-empirical procedure which can be used to calculate optimal scaling coefficients for (spin-resolved) MP2 calculations of the dissociation of noncovalent complexes.
- In all checked systems this procedure worked remarkably well – it is always the way to find SCS coefficient which scale the whole interacting energy curve.
- The proposed method is especially attractive because it allows to obtain a full dissociation curve of almost CCSD(T) quality at the cost of just a single CCSD(T) calculation (OS(MP2) –  $O(N^4)$  )
- The choice of the distance  $R$  where the coefficient is calculated is not very important



# Conclusions

- We can even replace the costly single point CCSD(T) calculation with a focal–point analysis (the  $\Delta$ CCSD(T) procedure) to obtain an estimate of the CCSD(T) correlation energy from a cheaper calculation.
- The coefficients in the SCS-MP2 method are **system dependent**, so it seems to better find the ansatz for calculating system dependent coefficient , then for looking for one universal coefficient / set of coefficients.
- Possible extension of the method to CBS limit



We want to use MP2 and CCSD(T) correlation energies, computed in relatively small basis sets, and fitted scaling coefficients to yield interaction energies of almost complete basis set limit CCSD(T) quality.

E. Fabiano, F. Della Sala, I. Grabowski, Chem. Phys. Lett. **635** (2015), 262





basis set aug-cc-pVnZ, with  $n = 2, 3, 4, 5$  i.e. D,T,Q,5, ...

$$c^{(n)} = \frac{\mathcal{E}_{CCSD(T)}^{(n)}(R_0)}{\mathcal{E}_{MP2}^{(n)}(R_0)}$$

$$\mathcal{E}_{CCSD(T)}^{(n)}(R) = c^{(n)} \mathcal{E}_{MP2}^{(n)}(R)$$

CBS:  $n = \infty$

$$c^{(\infty)} = \frac{\mathcal{E}_{CCSD(T)}^{(\infty)}(R_0)}{\mathcal{E}_{MP2}^{(\infty)}(R_0)}$$

$$\mathcal{E}_{S-MP2}^{(\infty)}(R) = c^{(\infty)} \mathcal{E}_{MP2}^{(\infty)}(R)$$



Simple ansatz derived from standard extrapolation formulas

(P.L. Fast, M.L. Sánchez, D.G. Truhlar, J. Chem. Phys. 111 (1999) 2921.)

Basis set evolution of the  $c^{(n)}$  factor: ( $A$  and  $\alpha$  – system dependent constants)

$$c^{(n)} = c^{(\infty)} + An^{-\alpha}$$

For  $n=2$  and  $n=3$

$$c_{approx}^{(\infty)} = \frac{c^{(3)} 3^\alpha - c^{(2)} 2^\alpha}{3^\alpha - 2^\alpha}$$



To evaluate  $\mathcal{E}_{MP2}^{(\infty)}$

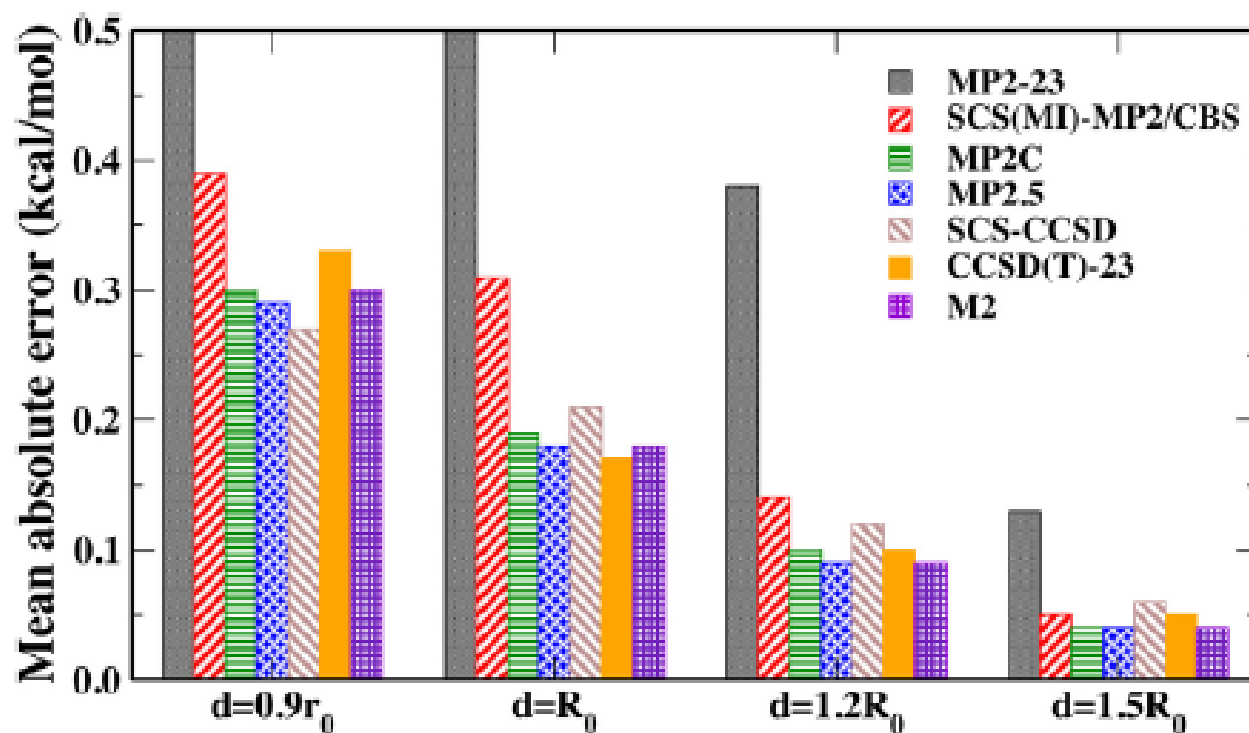
$$\mathcal{E}_{M2} = c_{M2}^{(\infty)} \frac{\mathcal{E}_{MP2}^{(3)} 3^\gamma - \mathcal{E}_{MP2}^{(2)} 2^\gamma}{3^\gamma - 2^\gamma}$$

$\gamma = 1.91$  (P.L. Fast, M.L. Sánchez, D.G. Truhlar, J. Chem. Phys. 111 (1999) 2921.)

$\alpha = 3.4$  (fitted to subset of S22)



S22 x 5 training set



**Figure 4.** Mean absolute errors (kcal/mol) with respect to accurate values [33] for the total interaction energies of non-covalent complexes of the  $S22 \times 5$  test set at different bonding distances  $d$  as obtained from several theoretical approaches. Accurate MP2C, MP2.5, and SCS-CCSD results are taken from Ref. [33].



Thank you

