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Combining wave-function and density-functional theories: range-separated hybrids, multiconfigurational hybrids, and double hybrids

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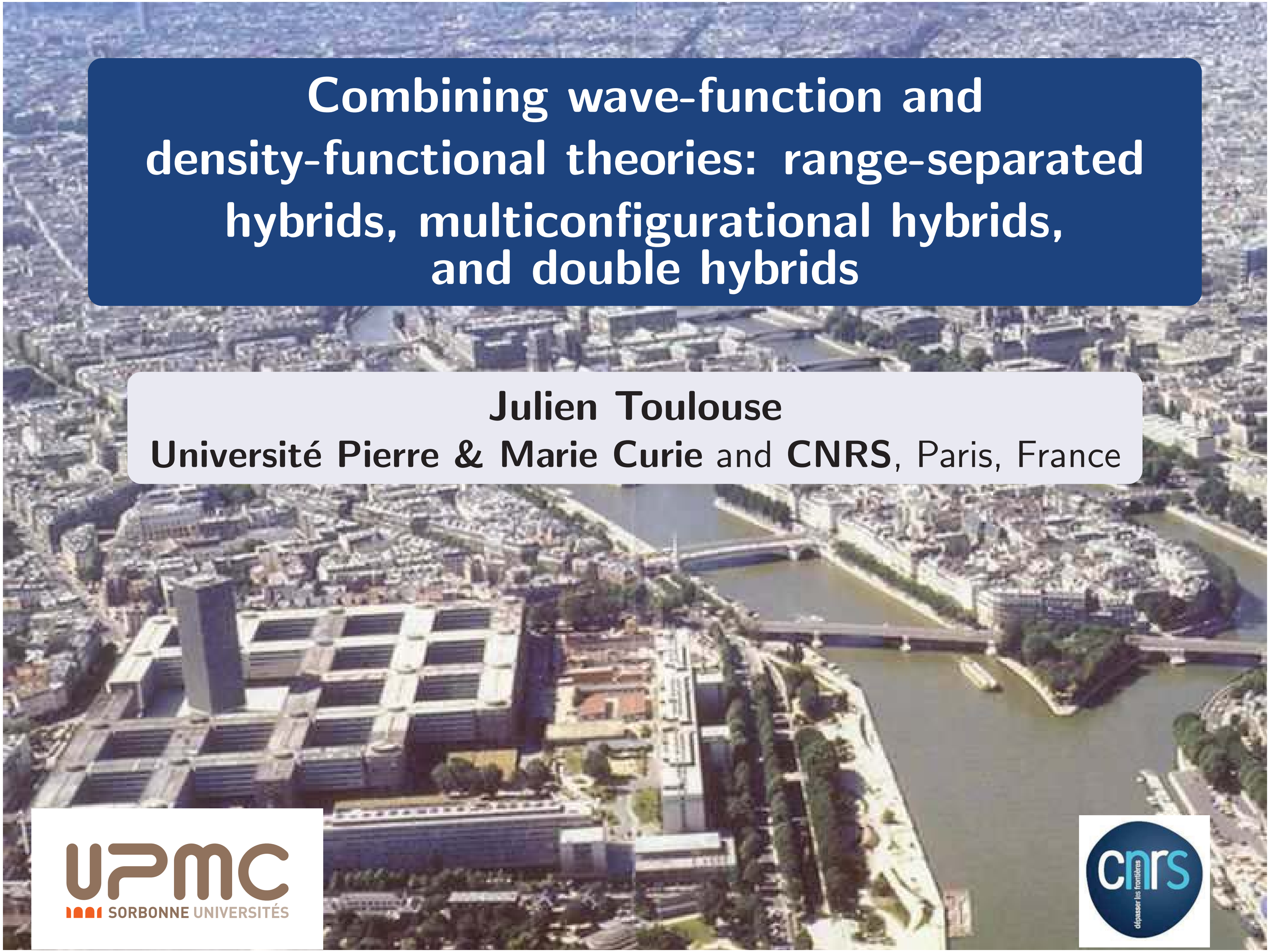


Combining wave-function and density-functional theories: range-separated hybrids, multiconfigurational hybrids, and double hybrids

Julien Toulouse
Université Pierre & Marie Curie and **CNRS**, Paris, France

1. Range-separated hybrids
2. Multiconfigurational hybrids
3. Double hybrids

1. Range-separated hybrids

   with W. Zhu, A. Savin, J. Ángyán, and G. Jansen

2. Multiconfigurational hybrids

3. Double hybrids

van der Waals dispersion interactions in DFT

$\longrightarrow$ **long-range interactions between quantum charge fluctuations**

Some approaches for vdW in DFT:

- Semiempirical asymptotic corrections ($-C_6/R^6 + \cdots$) with dispersion coefficients calculated *ab initio* or taken from reference data
- Highly parametrized hybrid density functionals
- Nonlocal correlation density functionals
- Orbital-dependent functionals (e.g., based on the adiabatic-connection fluctuation-dissipation theorem)

Here, we use a type of **range-separated hybrid**:
short-range DFT + **long-range perturbation theory**

Range-separated DFT

Extension of Kohn-Sham scheme to multideterminant wavefunction

$$E_{\text{exact}} = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{\text{lr}} | \Psi \rangle + E_{\text{Hxc}}^{\text{sr}}[n_{\Psi}] \right\}$$

long-range
interaction $\displaystyle\sum_{i<j} \frac{\text{erf}(\mu r_{ij})}{r_{ij}}$

short-range
density functional

Single-determinant approximation

$$E_0 \quad = \quad \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{\text{lr}} | \Phi \rangle + E_{\text{Hxc}}^{\text{sr}}[n_{\Phi}] \right\}$$

This is a hybrid DFT with HF exchange at long range

srLDA
srPBE, etc...

All what is missing is the **long-range correlation energy**

$$E_{\text{exact}} = E_0 + E_c^{\text{lr}}$$

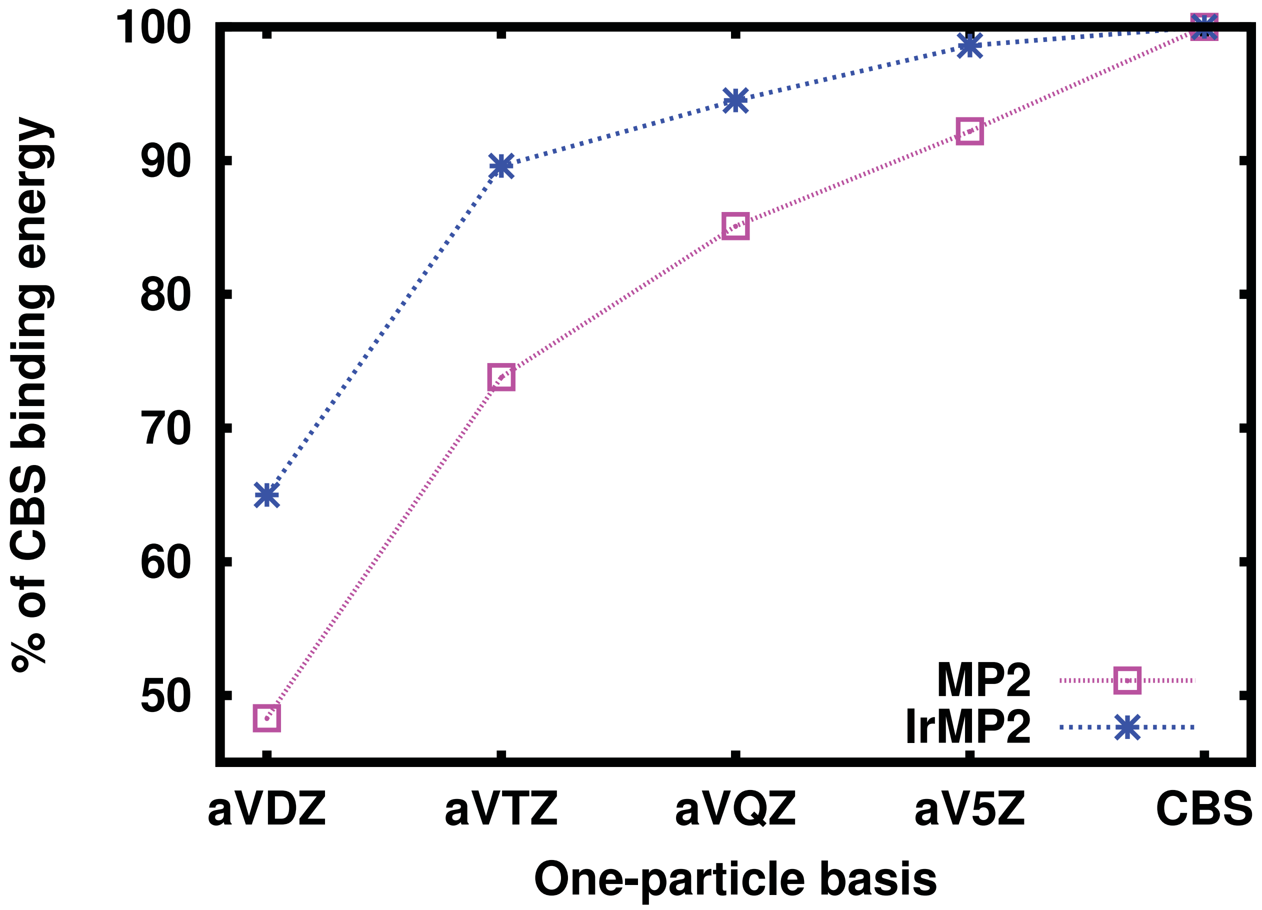
lrMP2
lrRPA
lrCC

Toulouse, Colonna, Savin, PRA 70, 062505 (2004)

Ángyán, Gerber, Savin, Toulouse, PRA 72, 012510 (2005)

Fast basis convergence of long-range perturbation theory

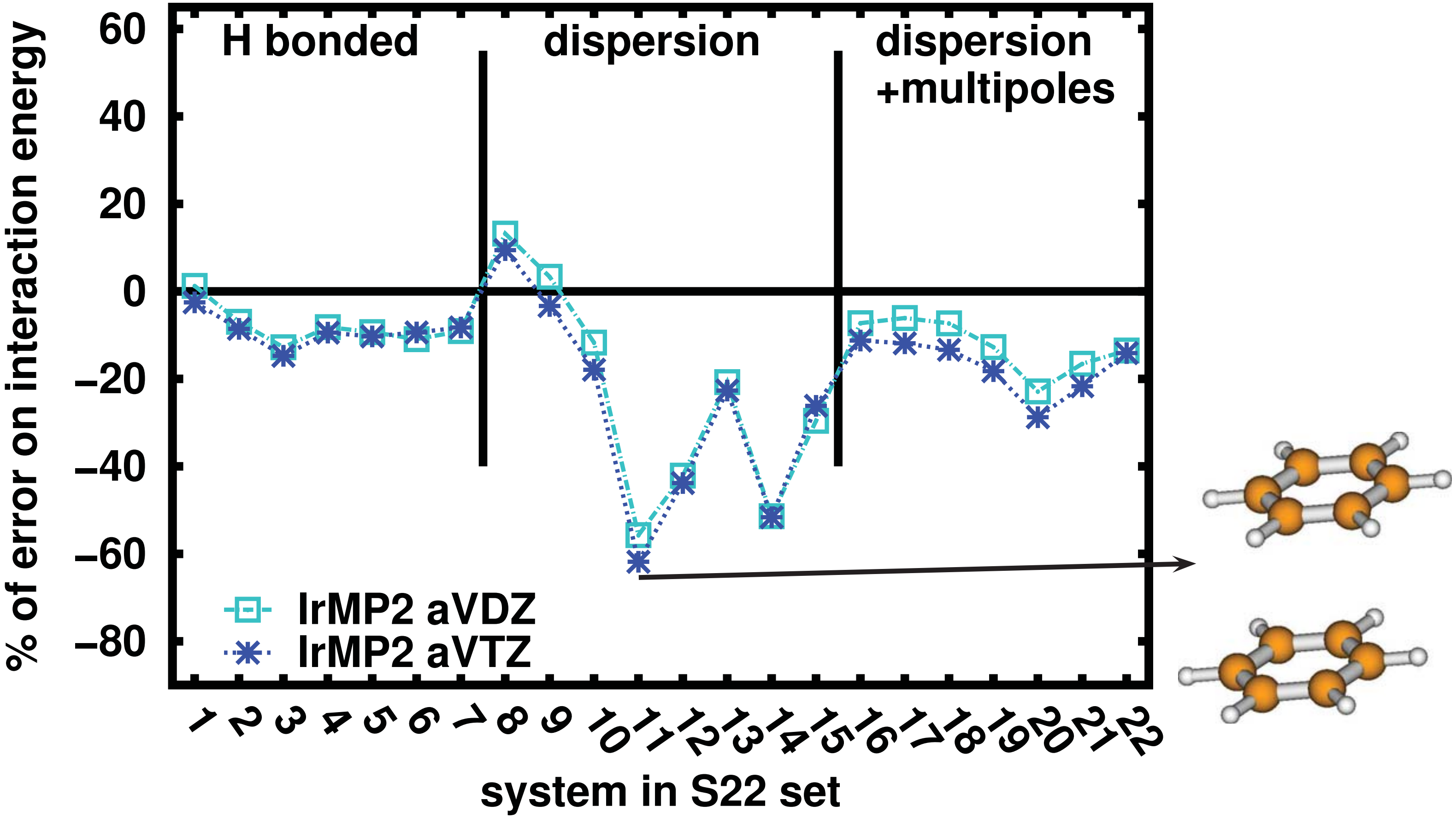
Convergence of binding energy of Ar_2 with aug-cc-pVnZ basis sets, $\mu = 0.5$ bohr^{-1}, srPBE functional:



Toulouse, Zhu, Ángyán, Savin, PRA 82, 032502 (2010)

IrMP2 is not accurate enough for dispersion interactions

S22 set: Equilibrium interaction energies of 22 weakly-interacting molecular systems from water dimer to DNA base pairs ($\mu = 0.5$ bohr^{-1}, srPBE functional):



Zhu, Toulouse, Savin, Ángyán, JCP 132, 244108 (2010)

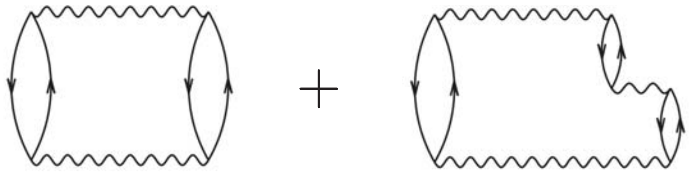
Long-range RPA variants from ring coupled cluster doubles

- *direct* RPA as *direct* ring CCD (without exchange):

$$E^{\mathrm{lr}}_{c,\mathrm{dRPA}} = \frac{1}{2}\sum_{ia,jb}\langle ab|ij\rangle^{\mathrm{lr}}\left(T^{\mathrm{lr}}_{\mathrm{drCCD}}\right)_{ia,jb}$$

Scuseria *et al.* 08

$=$



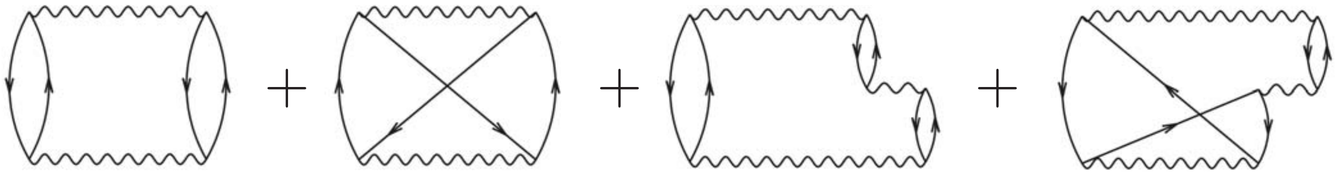
$+ \cdots$

- dRPA + second-order screened exchange (SOSEX)

Grüneis *et al.* 09
Paier *et al.* 10

$$E^{\mathrm{lr}}_{c,\mathrm{dRPA+SOSEX}} = \frac{1}{2}\sum_{ia,jb}\langle ab||ij\rangle^{\mathrm{lr}}\left(T^{\mathrm{lr}}_{\mathrm{drCCD}}\right)_{ia,jb}$$

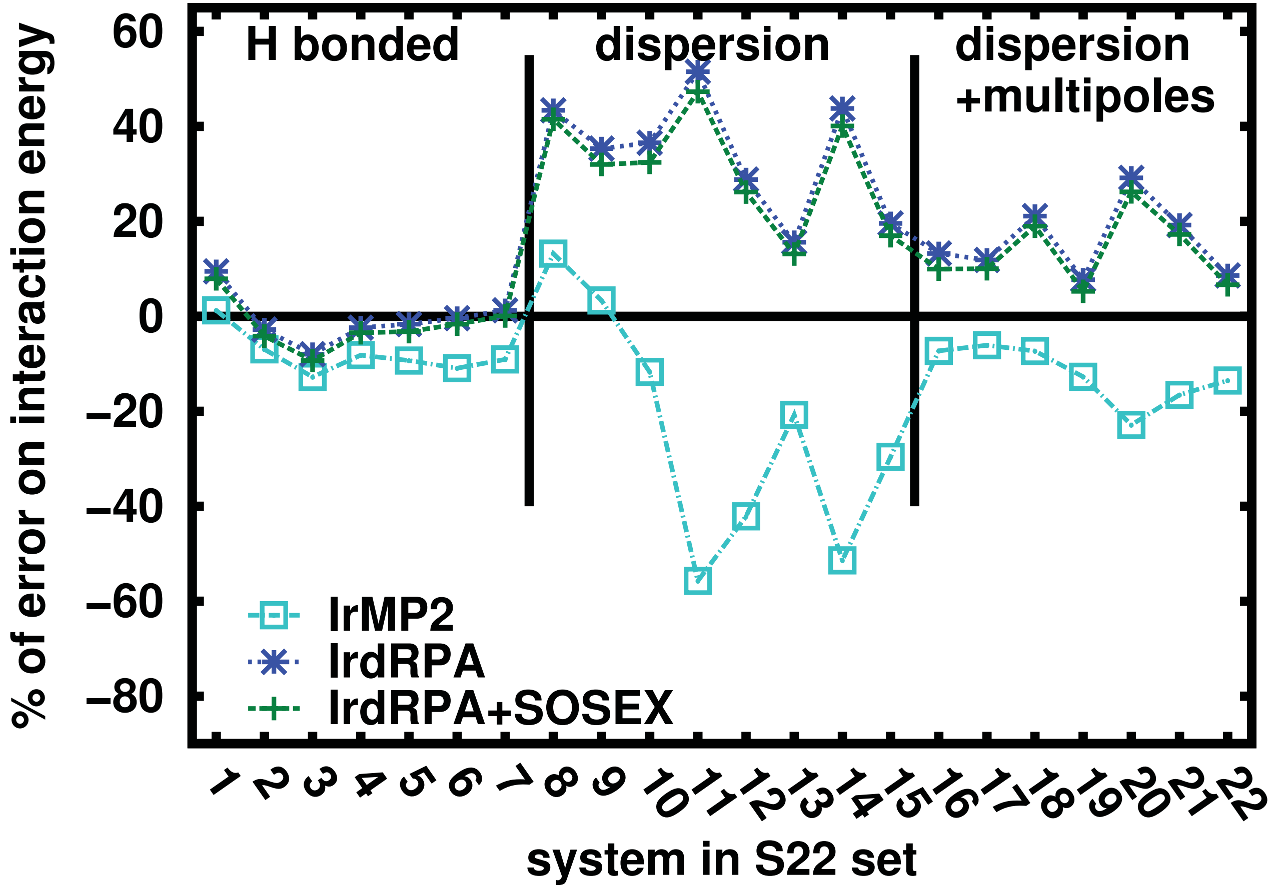
$=$



$+ \cdots$

lrdRPA and lrdRPA+SOSEX tested on S22 set

Equilibrium interaction energies of 22 weakly-interacting molecular systems from water dimer to DNA base pairs (aug-cc-pVDZ, $\mu = 0.5$ bohr^{-1}, srPBE functional):



Zhu, Toulouse, Savin, Ángyán, JCP 132, 244108 (2010)

Toulouse, Zhu, Savin, Jansen, Ángyán, JCP 135, 084119 (2011)

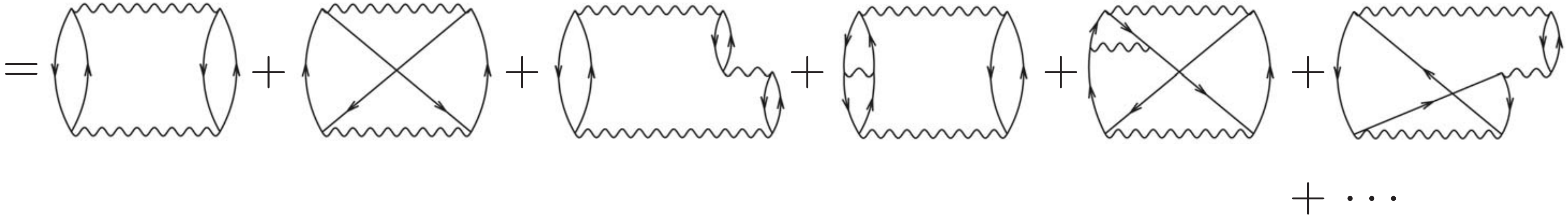
Long-range RPA from ring CCD with exchange (rCCDx)

- With *antisymmetrized* integrals: RPA variant of McLachlan-Ball 1964 (equivalent to TDHF plasmon formula)

$$E_{c,\text{RPAx-II}}^{\text{lr}} = \frac{1}{4} \sum_{ia,jb} \langle ab||ij\rangle^{\text{lr}} \left(T_{\text{rCCDx}}^{\text{lr}}\right)_{ia,jb}$$

- With *non-antisymmetrized* integrals, RPA variant of Szabo-Ostlund 1977

$$E_{c,\text{RPAx-SO2}}^{\text{lr}} = \frac{1}{2} \sum_{ia,jb} \langle ab|ij\rangle^{\text{lr}} \left(T_{\text{rCCDx}}^{\text{lr}}\right)_{ia,jb}$$

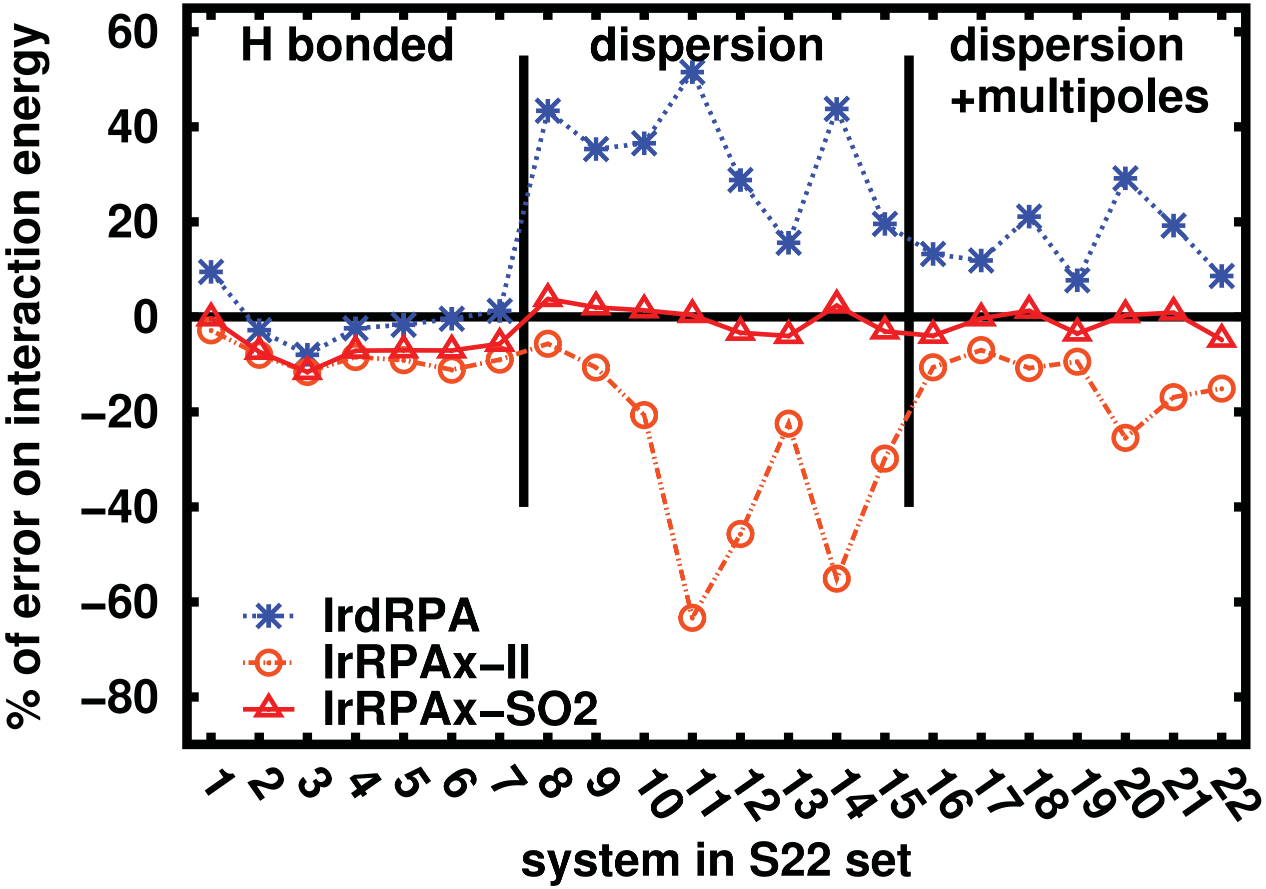


Heßelmann, JCP 134, 204107 (2011)

Toulouse, Zhu, Savin, Jansen, Ángyán, JCP 135, 084119 (2011)

lrRPAx variants tested on S22 set

Equilibrium interaction energies of 22 weakly-interacting molecular systems from water dimer to DNA base pairs (aug-cc-pVDZ, $\mu = 0.5$ bohr^{-1}, srPBE functional):

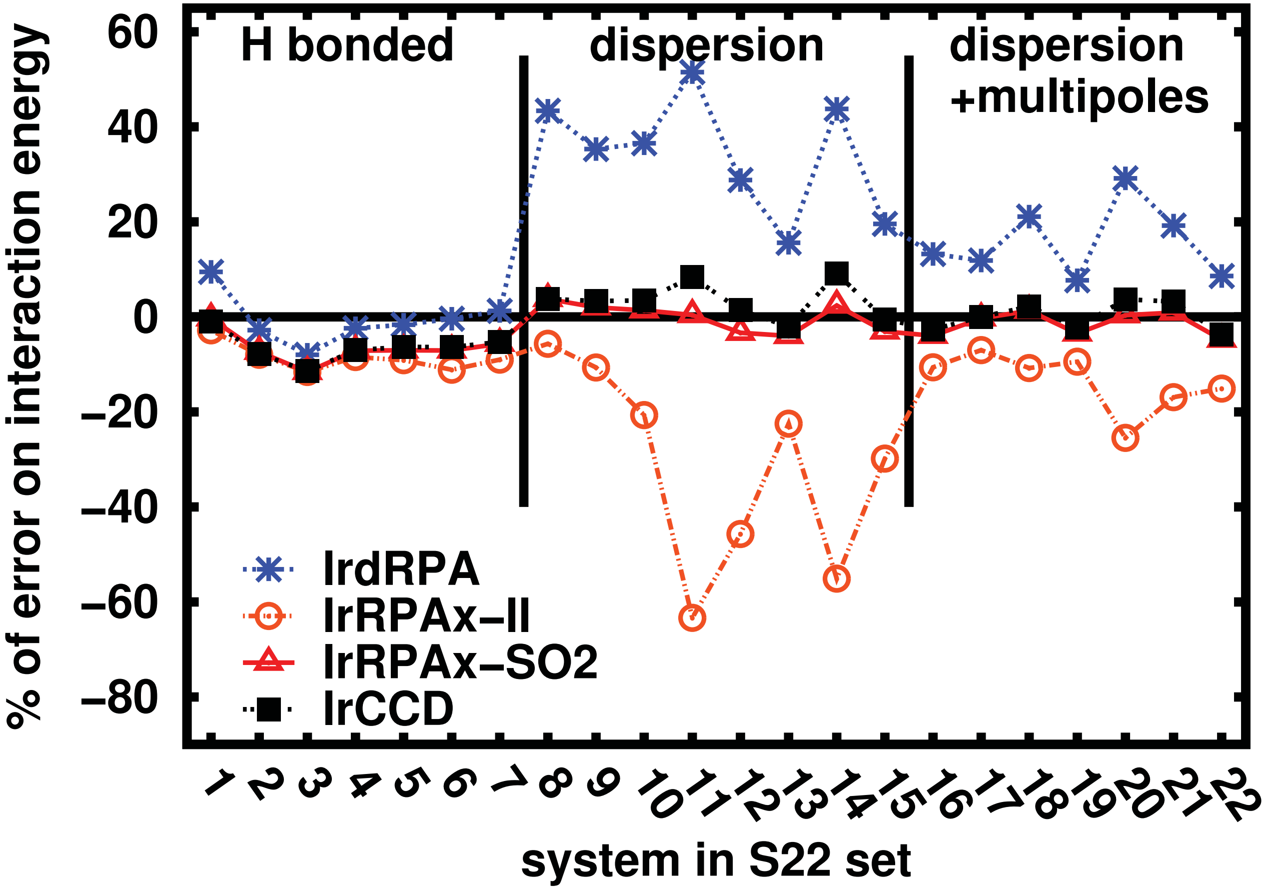


$\Longrightarrow$ **lrRPAx-SO2/aVDZ gives a MAE of $\sim$ 4% wrt CCSD(T)/CBS**

Toulouse, Zhu, Savin, Jansen, Ángyán, JCP 135, 084119 (2011)

IrRPAx variants tested on S22 set

Equilibrium interaction energies of 22 weakly-interacting molecular systems from water dimer to DNA base pairs (aug-cc-pVDZ, $\mu = 0.5$ bohr^{-1}, srPBE functional):



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Toulouse, Zhu, Savin, Jansen, Ángyán, JCP 135, 084119 (2011)

1 Range-separated hybrids

2 Multiconfigurational hybrids

with K. Sharkas, A. Savin and H. J. Aa. Jensen

3 Double hybrids

Static (or strong) correlation in DFT

⟶ **systems with partially filled near-degenerate orbitals**

Some approaches for static correlation in DFT:

- Artificial breaking of spin symmetry (unrestricted Kohn-Sham)
- DFT with ensembles or fractional orbital occupation numbers
- Configuration-interaction schemes with Hamiltonian matrix elements from DFT
- Standard correlated wave-function calculation + correlation density functional

Here, we use a **multiconfigurational hybrid**: **MCSCF+DFT** based on the linear decomposition of the e-e interaction

Multiconfigurational hybrid DFT

Based on a **linear** decomposition of e-e interaction

$$E_{\text{exact}} = \min_{\Psi}\left\{\langle\Psi|\hat{T} + \hat{V}_{ne} + \lambda\hat{W}_{ee}|\Psi\rangle + \bar{E}^{\lambda}_{\text{Hxc}}[n_{\Psi}]\right\}$$

with the λ-complement density functional $\bar{E}^{\lambda}_{\text{Hxc}}[n]$

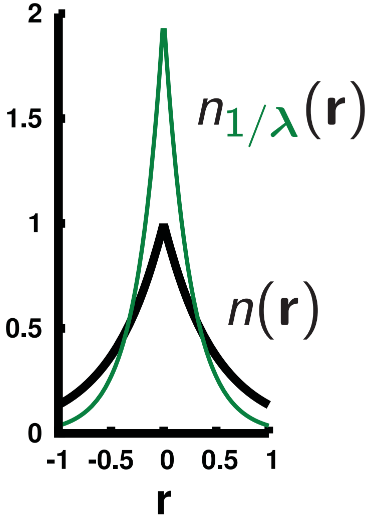
- Hartree and exchange contributions:

$$\bar{E}^{\lambda}_{\text{Hx}}[n] = (1-\lambda)E_{\text{Hx}}[n]$$

- Correlation contribution:

$$\bar{E}^{\lambda}_{c}[n] = E_c[n] - \lambda^2 E_c[n_{1/\lambda}]$$

with the scaled density $n_{1/\lambda}(\mathbf{r}) = (1/\lambda)^3 n(\mathbf{r}/\lambda)$



- In practice, approximations for Ψ and $E_{xc}[n]$

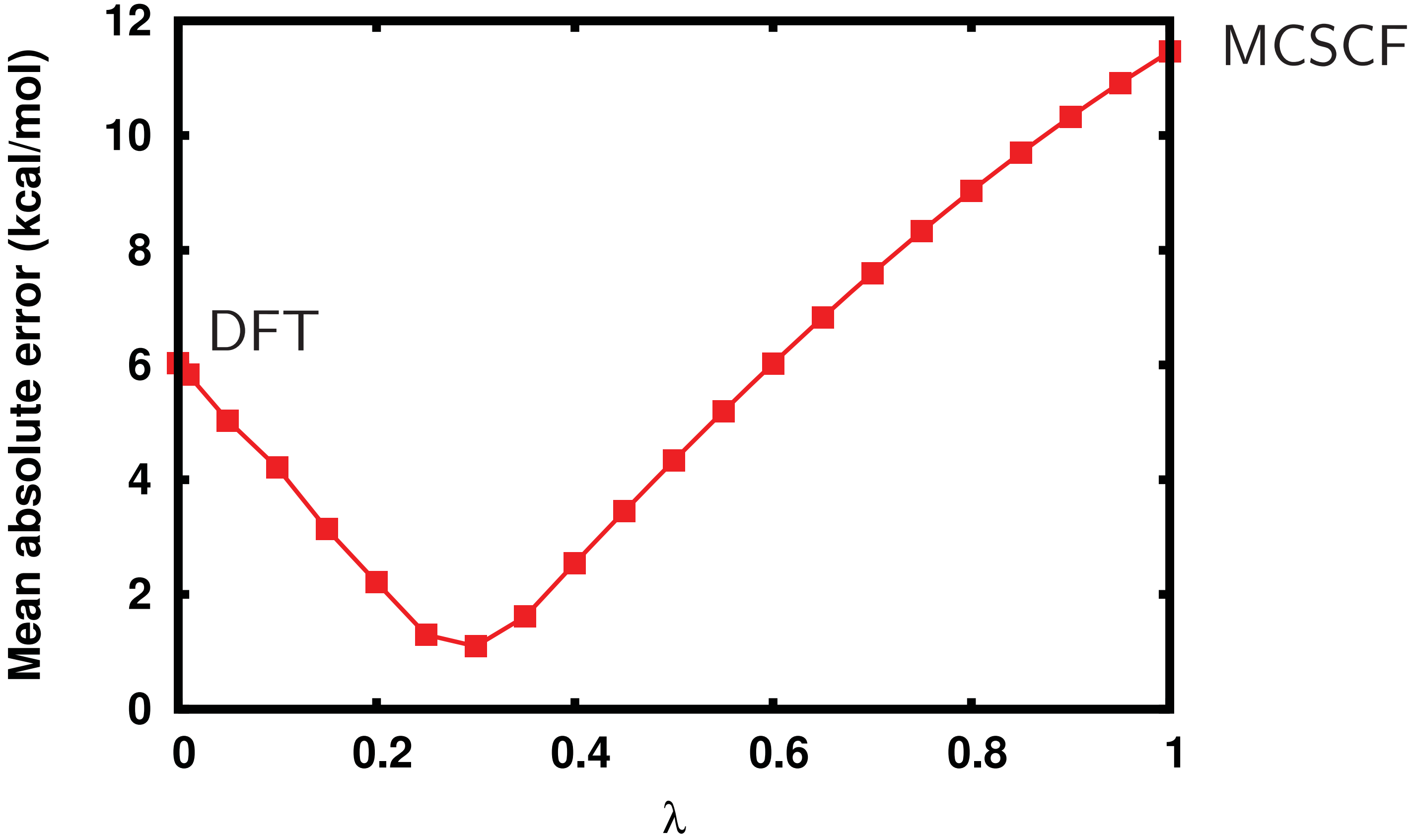
MCSCF: $\Psi = \sum_I c_I \Phi_I$

BLYP, PBE, etc...

Sharkas, Savin, Jensen, Toulouse, JCP 137, 044104 (2012)

What value for the empirical parameter λ?

O3ADD6 set of Grimme *et al.* 2010: 6 energy differences for cycloaddition reactions of ozone with ethylene or acetylene (aug-cc-pVTZ basis, BLYP functional):

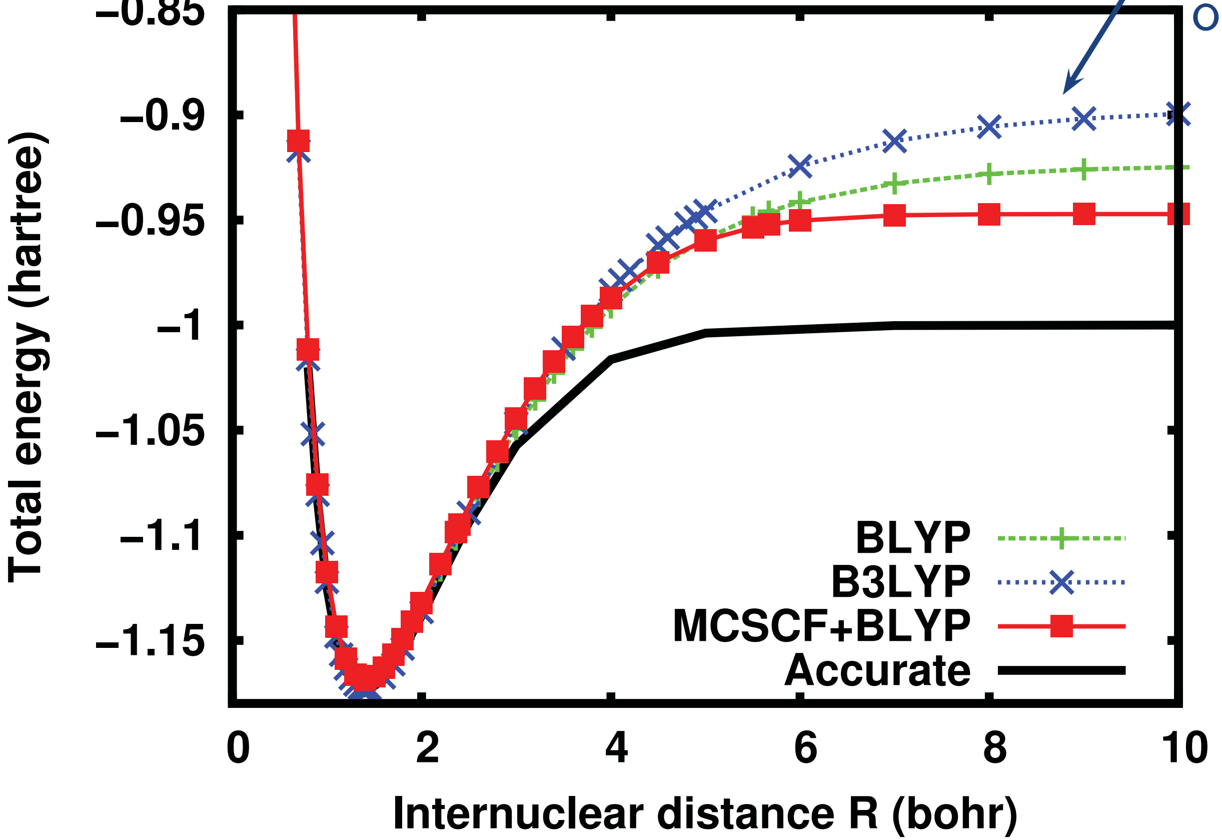


$\Longrightarrow$ **We take λ= 0.25 as for usual hybrid functionals**

Sharkas, Savin, Jensen, Toulouse, JCP 137, 044104 (2012)

Test of MCSCF+DFT on H_2 molecule

$\lambda = 0.25$, cc-pVTZ basis, BLYP functional:



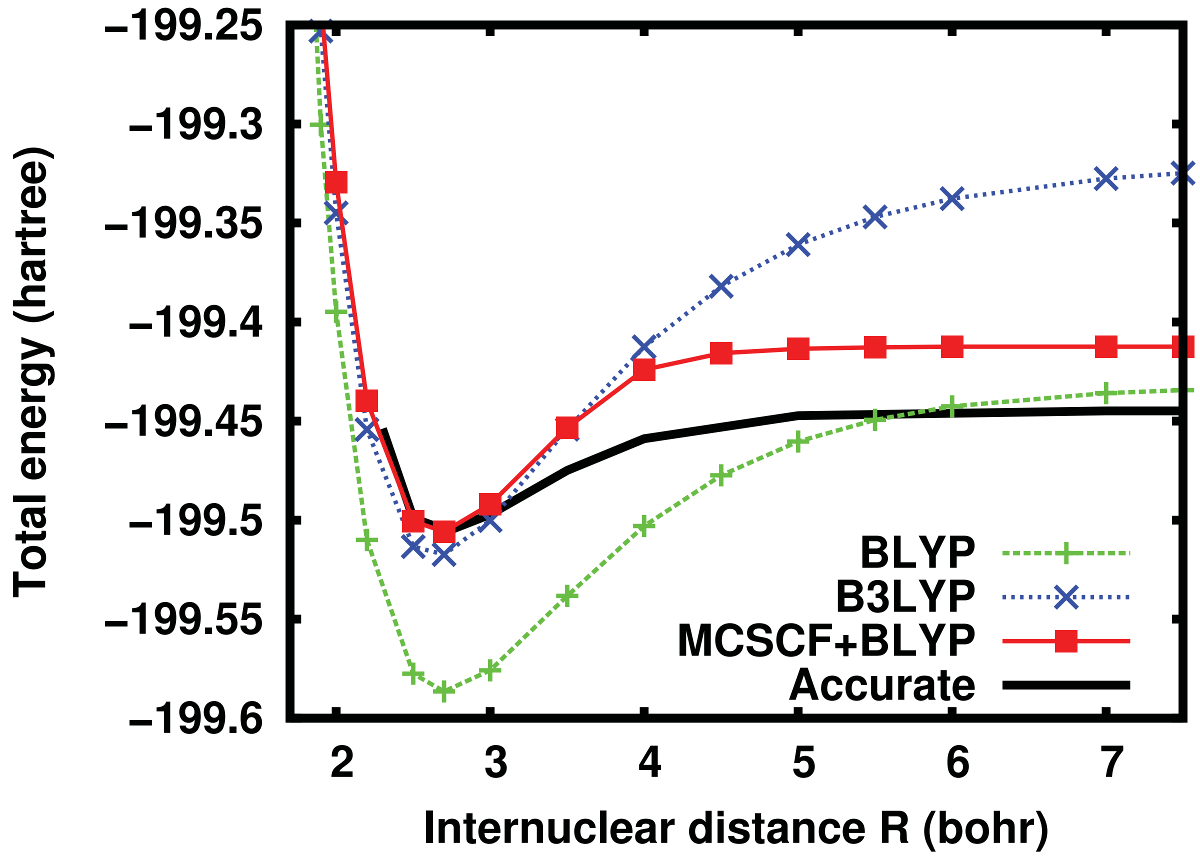
Wrong asymptotics of B3LYP: $-\frac{c}{R}$

$\Longrightarrow$ **MCSCF+BLYP removes the wrong $1/R$ asymptotic term**

Sharkas, Savin, Jensen, Toulouse, JCP 137, 044104 (2012)

Test of MCSCF+DFT on F_2 molecule

$\lambda = 0.25$, cc-pVTZ basis, BLYP functional:

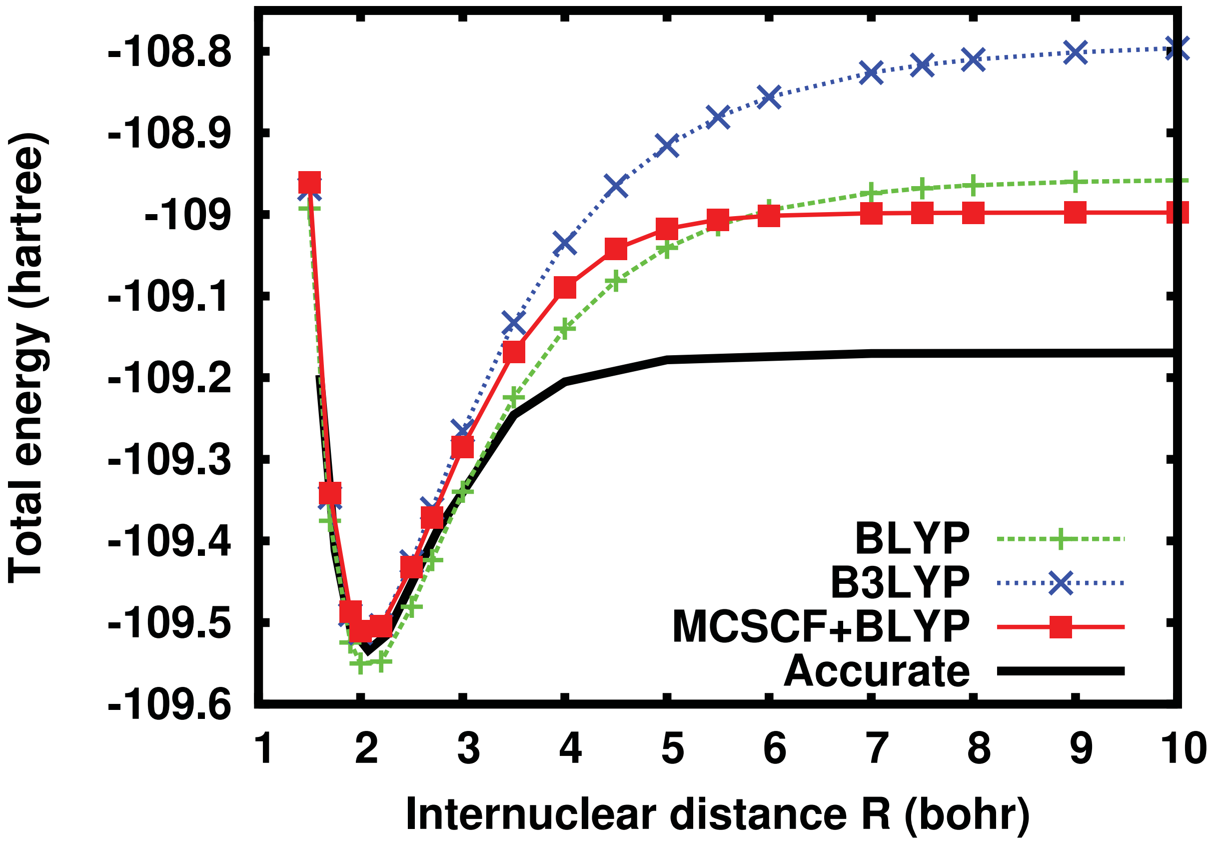


$\Longrightarrow$ MCSCF+BLYP is as good as B3LYP at equilibrium and improves on it at dissociation

Sharkas, Savin, Jensen, Toulouse, JCP 137, 044104 (2012)

Test of MCSCF+DFT on N_2 molecule

$\lambda = 0.25$, cc-pVTZ basis, BLYP functional:



$\Longrightarrow$ **MCSCF+BLYP has still a large error at dissociation**

Sharkas, Savin, Jensen, Toulouse, JCP 137, 044104 (2012)

1. Range-separated hybrids
2. Multiconfigurational hybrids
3. Double hybrids

with K. Sharkas and A. Savin

Double-hybrid approximations (Grimme JCP 2006)

Combination of HF exchange with an exchange functional
and MP2 correlation with a correlation functional:

$$E_{xc}^{\text{DH}} = a_x E_x^{\text{HF}} + (1 - a_x) E_x[n] + (1 - a_c) E_c[n] + a_c E_c^{\text{MP2}}$$

Examples:

- B2-PLYP: $a_x = 0.53$ and $a_c = 0.27$, optimized on heats of formation
- B2GP-PLYP: $a_x = 0.65$ and $a_c = 0.36$, optimized on atomization energies and reaction barrier heights

large fraction of HF exchange $\Longrightarrow$ reduces self-interaction error

$\Longrightarrow$ **reach on average near-chemical accuracy on a variety of systems but empirical**

A theoretical derivation of double hybrids

- Start with linear decomposition of e-e interaction with single-determinant approximation

$$E_0 = \min_{\Phi}\left\{\langle\Phi|\hat{T} + \hat{V}_{ne} + \lambda\hat{W}_{ee}|\Phi\rangle + \bar{E}^{\lambda}_{\mathrm{Hxc}}[n_\Phi]\right\}$$

- Then, define the following perturbation theory:

$$E^{\alpha} = \min_{\Psi}\left\{\langle\Psi|\hat{T} + \hat{V}_{ne} + \lambda\hat{V}^{\mathrm{HF}}_{\mathrm{Hx}} + \alpha\,\lambda\hat{W}|\Psi\rangle + \bar{E}^{\lambda}_{\mathrm{Hxc}}[n_\Psi]\right\}$$

where $\lambda\hat{W} = \lambda\left(\hat{W}_{ee} - \hat{V}^{\mathrm{HF}}_{\mathrm{Hx}}\right)$ is the perturbation.

- At second order, we get a **one-parameter double hybrid**:

$$E_{xc} = \lambda E_x^{\mathrm{HF}} + (1-\lambda)E_x[n] + E_c[n] - \lambda^2 E_c[n_{1/\lambda}] + \lambda^2 E_c^{\mathrm{MP2}}$$

- If density scaling is neglected $E_c[n_{1/\lambda}] \approx E_c[n]$:

$$E_{xc} = \lambda E_x^{\mathrm{HF}} + (1-\lambda)E_x[n] + (1-\lambda^2)E_c[n] + \lambda^2 E_c^{\mathrm{MP2}}$$

This corresponds to Grimme's double hybrids with $a_x = \lambda$ and $a_c = \lambda^2$

Sharkas, Toulouse, Savin, JCP 134, 064113 (2011)

Thermochemistry tests of double hybrids

- set of **49 atomization energies (G2)**
- set of **24 reaction barrier heights (DBH24)**

Mean absolute errors (kcal/mol) :

	G2	DBH24
One-parameter double hybrid with BLYP $a_x = \boldsymbol{\lambda} = 0.65$ and $a_c = \boldsymbol{\lambda}^2 \simeq 0.42$	**1.4**	**1.4**
Two-parameter double hybrid B2-PLYP $a_x = 0.53$ and $a_c = 0.27$	**1.6**	**2.0**

$\Longrightarrow$ **One parameter is enough in double hybrids**

Sharkas, Toulouse, Savin, JCP 134, 064113 (2011)

Summary

Range-separated hybrids: short-range DFT + long-range MBPT

- suited for van der Waals dispersion interactions
- fast basis convergence
- important to include exchange terms in RPA

Multiconfigurational hybrids: MCSCF+DFT

- include explicit static correlation
- extension of usual hybrid functionals
- we still need to improve the functional

Double hybrids: DFT+MP2

- we provided a theoretical derivation of double hybrids
- one parameter is enough
- reach on average near-chemical accuracy for thermochemistry

Web page: www.lct.jussieu.fr/pagesperso/toulouse/