Combining many-body methods and density-functional theory

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Hybrids combining many-body methods and DFT

Goal: improve the accuracy of present-day DFT

1. **Multiconfigurational hybrids** (MCSCF+DFT)
   and **double hybrids** (MP2+DFT)
   with B. Civalleri, H. J. Jensen, L. Maschio, A. Savin, K. Sharkas

   $\longrightarrow$ static (or strong) correlation or self-interaction error

2. **Range-separated hybrids** (lrRPA+srDFT)
   with J. Ángyán, O. Franck, G. Jansen, E. Luppi, B. Mussard, P. Reinhardt, A. Savin, W. Zhu

   $\longrightarrow$ van der Waals dispersion interactions

3. **Time-dependent range-separated hybrids** (lrBSE+srTDDFT)
   with T. Helgaker, E. Rebolini, A. Savin, A. Teale

   $\longrightarrow$ Rydberg, charge-transfer, double excitations

Multiconfigurational hybrids (MCSCF+DFT)

Multideterminant 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 $\bar{E}^{\lambda}_{\text{Hxc}}[n]$

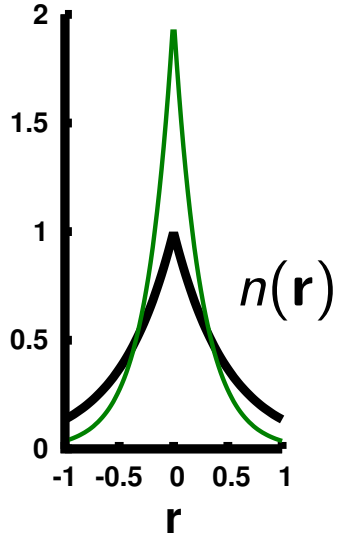
- Hartree and exchange contributions:

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

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

- Correlation contribution:

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



- Approximations for Ψ and $E_{xc}[n]$

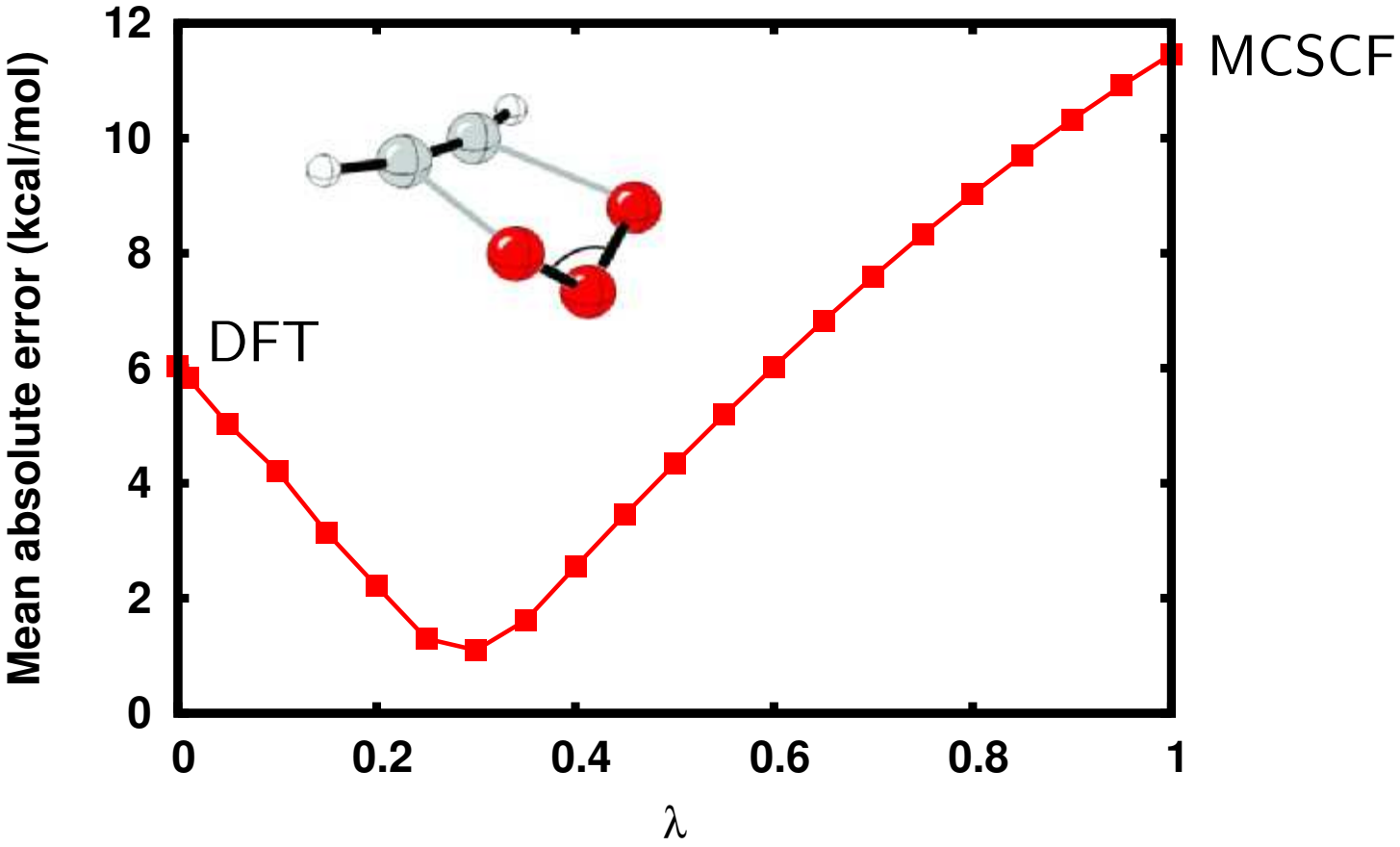
MCSCF: $\Psi = \sum_n c_n \Phi_n$

BLYP, PBE, etc...

Sharkas, Savin, Jensen, Toulouse, JCP, 2012

What value for the empirical parameter λ?

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

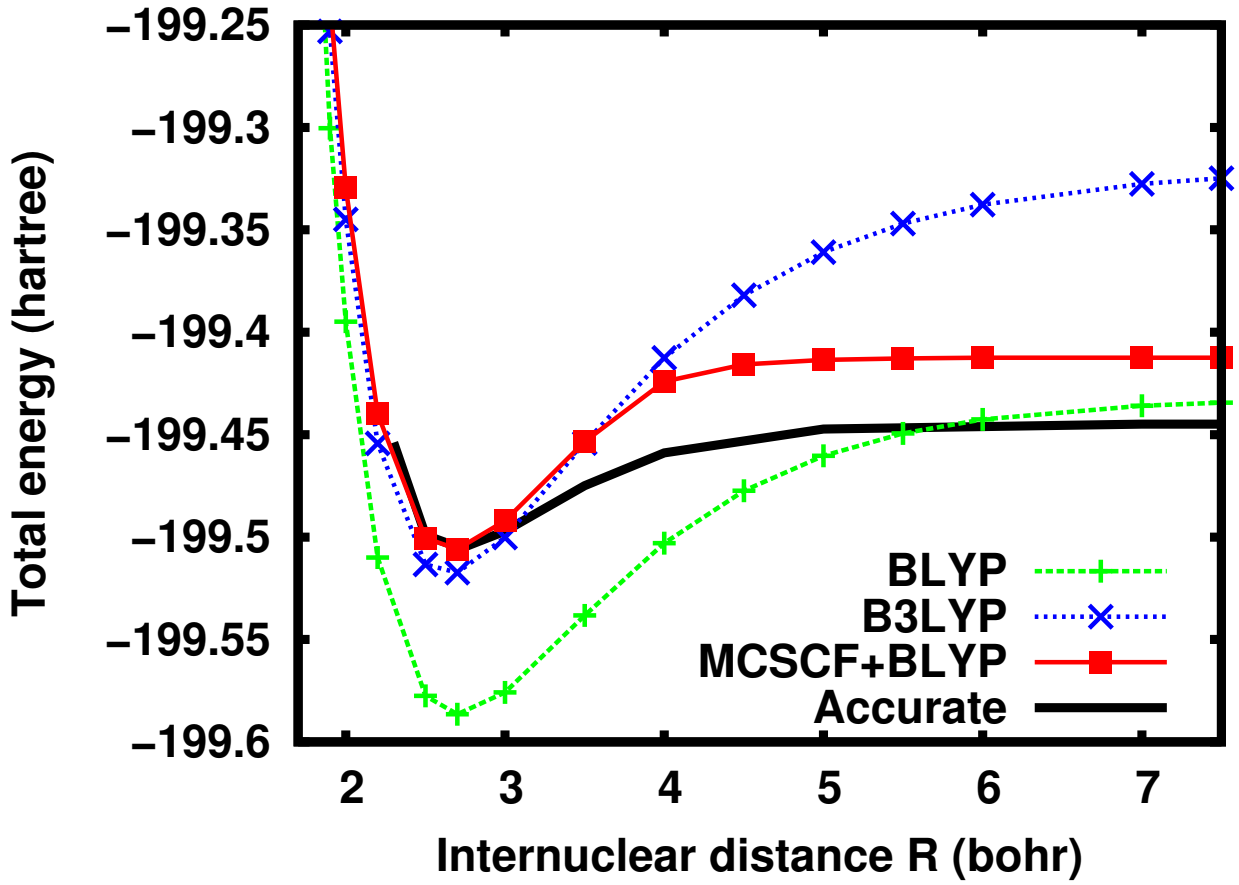


$\Longrightarrow$ **We take λ= 0.25 as for usual hybrid functionals**

Sharkas, Savin, Jensen, Toulouse, JCP, 2012

Test of MCSCF+DFT on F_2 molecule

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



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

Sharkas, Savin, Jensen, Toulouse, JCP, 2012

Double hybrids (MP2+DFT)

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

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

- Then, define the following perturbation theory:

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

where $\boldsymbol{\lambda} \hat{W} = \boldsymbol{\lambda} \left(\hat{W}_{ee} - \hat{V}^{\mathrm{HF}}_{\mathrm{H}x} \right)$ is a Møller-Plesset-type perturbation.

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

$$E^{\mathrm{MP2+DFT}}_{xc} = \boldsymbol{\lambda} E^{\mathrm{HF}}_{x} + (1 - \boldsymbol{\lambda}) E_x[n] + (1 - \boldsymbol{\lambda}^2) E_c[n] + \boldsymbol{\lambda}^2 E^{\mathrm{MP2}}_{c}$$

$\Longrightarrow$ **This provides a theoretical derivation of Grimme's double hybrids with only one parameter $\boldsymbol{\lambda}$**

Sharkas, Toulouse, Savin, JCP, 2011

Performance of one-parameter double hybrids

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

- For MP2+BLYP, optimization of $\boldsymbol{\lambda}$ on sets of molecular atomization energies and reaction barrier heights leads to $\boldsymbol{\lambda} \approx \mathbf{0.65}$, corresponding to a fraction $\boldsymbol{\lambda}^2 \approx 0.42$ of MP2 correlation.
- Inclusion of MP2 correlation allows one to use a **larger fraction of HF exchange**, which reduces the self-interaction error.
- Like the two-parameter double hybrids, the one-parameter double hybrids **reach near chemical accuracy (1-2 kcal/mol)** on thermochemistry properties for **systems without important static correlation effects**.
- For molecular crystals, double hybrids do not improve over MP2.

Sharkas, Toulouse, Savin, JCP, 2011

Sharkas, Toulouse, Maschio, Civalleri, JCP, submitted

Range-separated hybrids (lrRPA+srDFT)

Based on a **range separation** of e-e interaction

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

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

short-range density functional

Savin, in *Recent developments and applications of modern DFT*, 1996

Toulouse, Colonna, Savin, PRA, 2004

- Single-determinant approximation:

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

  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

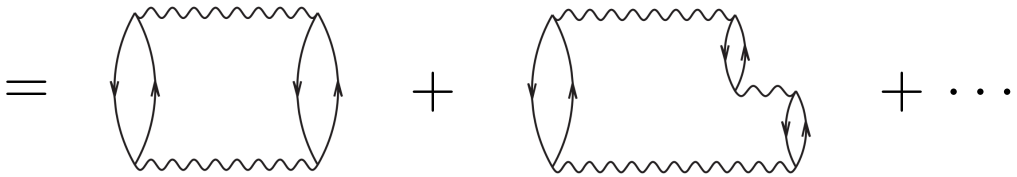
Ángyán, Gerber, Savin, Toulouse, PRA, 2005

Toulouse, Gerber, Jansen, Savin, Ángyán, PRL, 2009

lrRPA variants from ring coupled cluster doubles

- **dRPA** = direct ring CCD (without exchange):

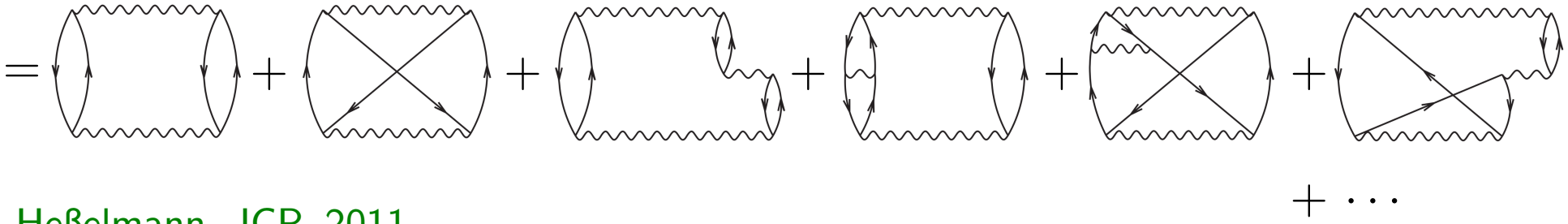
$$E^{\mathrm{lr}}_{c,\mathrm{dRPA}} = \frac{1}{2}\,\mathrm{tr}\left[\mathbf{w}^{\mathrm{lr}}_{ee}\mathbf{T}^{\mathrm{lr}}_{\mathrm{drCCD}}\right]$$



Scuseria, Henderson, Sorensen, JCP, 2008

- **RPAx-SO2** = ring CCD with exchange (Szabo-Ostlund's variant)

$$E^{\mathrm{lr}}_{c,\mathrm{RPAx\text{-}SO2}} = \frac{1}{2}\,\mathrm{tr}\left[\mathbf{w}^{\mathrm{lr}}_{ee}\mathbf{T}^{\mathrm{lr}}_{\mathrm{rCCDx}}\right]$$

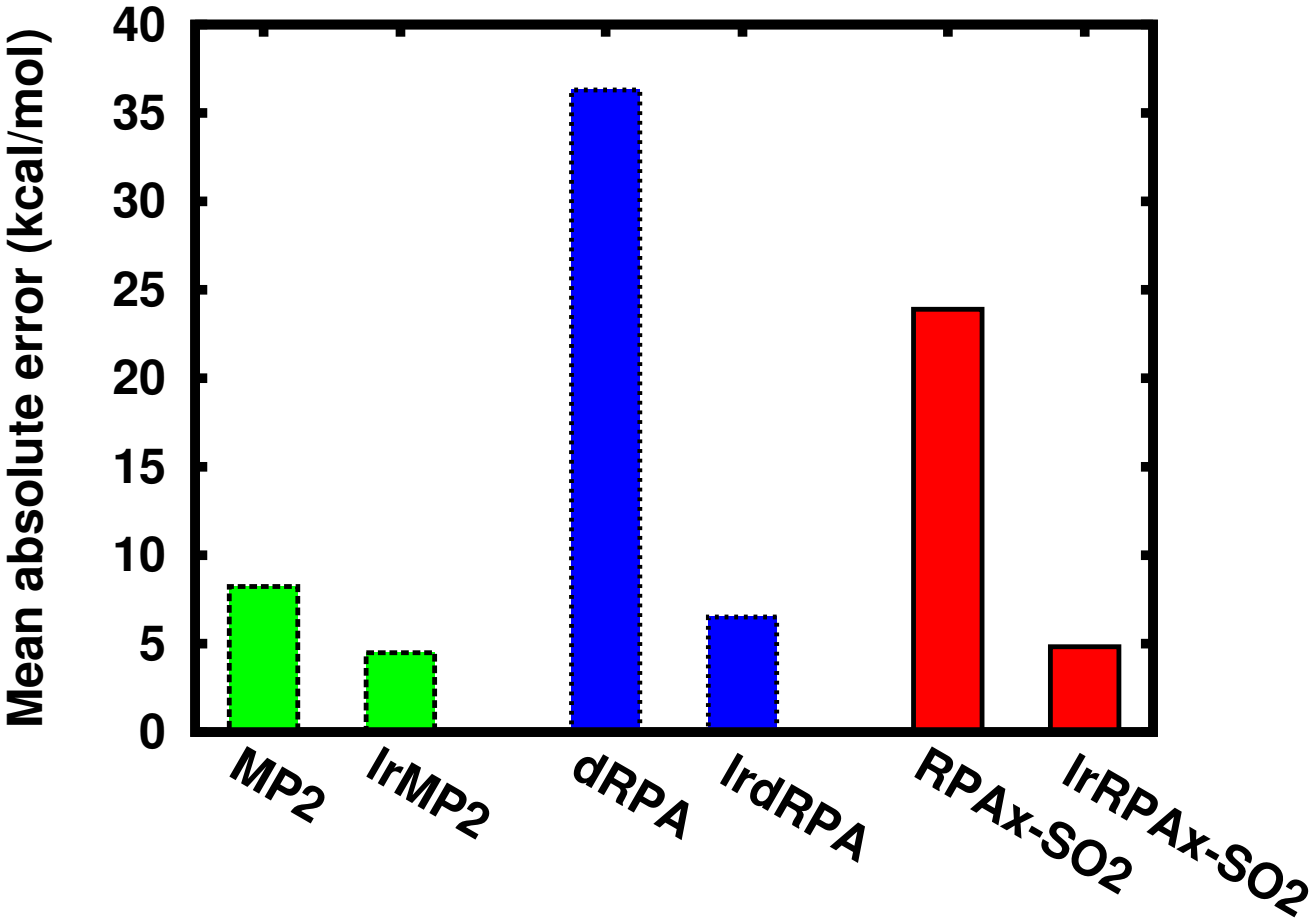


Heßelmann, JCP, 2011

Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011

Test of lrRPA+srDFT on atomization energies

AE6 set: 6 atomization energies of small molecules
($\mu = 0.5$ bohr^{-1}, srPBE functional, cc-pVQZ, spin unrestricted):



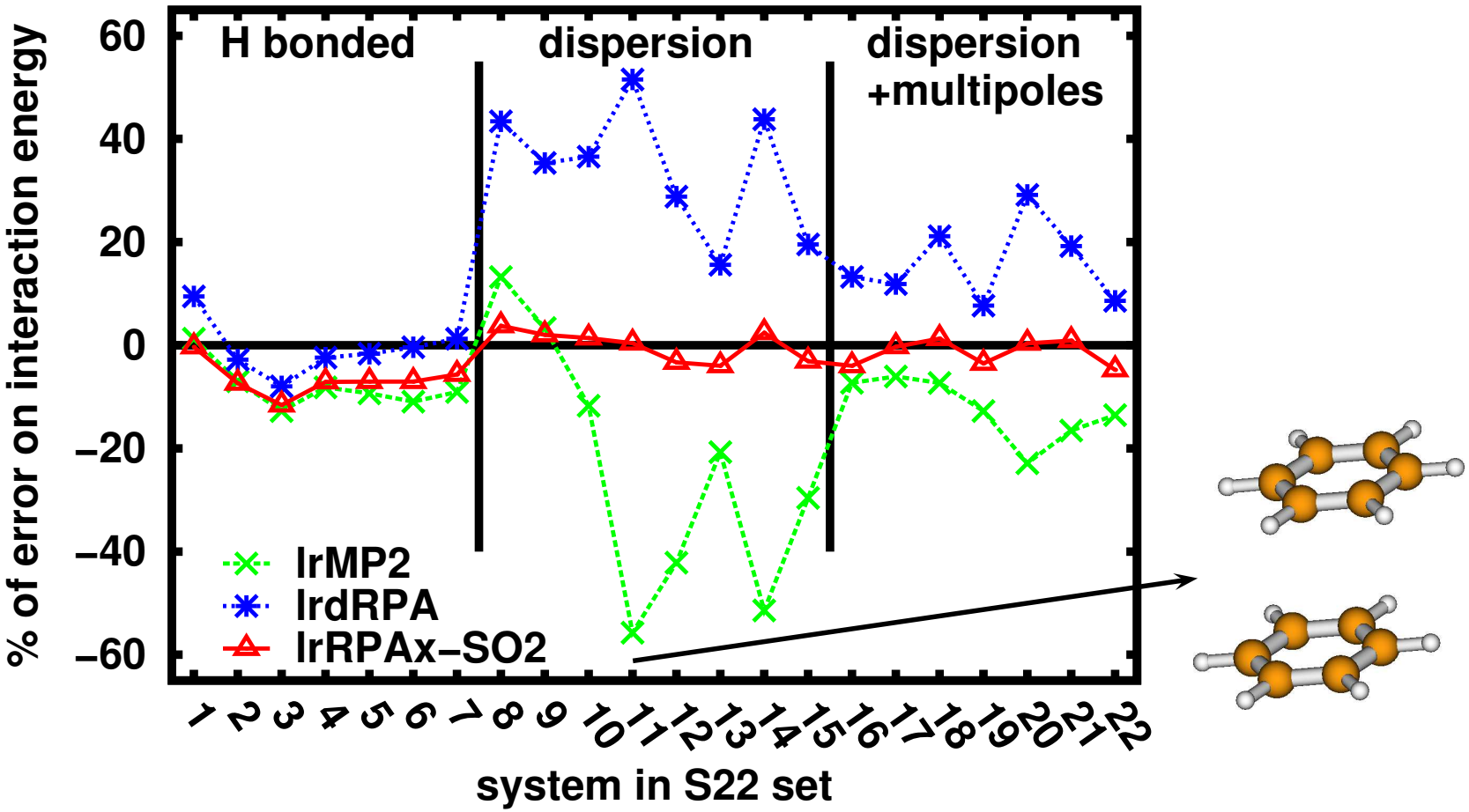
$\Longrightarrow$ **Range separation improves the accuracy for all methods**

$\Longrightarrow$ **All range-separated methods give a MAE of about 5 kcal/mol**

Mussard, Reinhardt, Luppi, Ángyán, Toulouse, in prep.

Test of lrRPA+srDFT on weak intermolecular interactions

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



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

Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011

Time-dependent range-separated hybrids

Linear-response TDDFT equation

$$\chi^{-1}(\omega) = \chi_0^{-1}(\omega) - f_{\mathrm{H}xc}(\omega)$$

$\Longrightarrow$ excitation energies, linear-response properties

- Range separation for exchange kernel is now standard:

$$f_{xc} = f_x^{\mathrm{lr,HF}} + f_x^{\mathrm{sr,DFT}} + f_c^{\mathrm{DFT}}$$

Tawada, Tsuneda, Yanagisawa, Yanai, Hirao, JCP, 2004

- Here, **range separation for both exchange and correlation kernels**: Start with lrMP2+srDFT scheme for ground state:

$$E_{xc} = E_x^{\mathrm{lr,HF}} + E_x^{\mathrm{sr,DFT}} + E_c^{\mathrm{lr,MP2}}$$

linear response

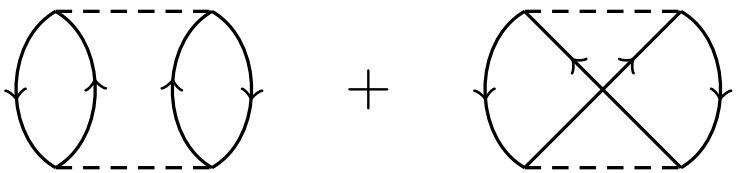
$$f_{xc} = f_x^{\mathrm{lr,HF}} + f_{xc}^{\mathrm{sr,DFT}} + f_c^{\mathrm{lr,(2)}}(\omega)$$

Rebolini, Savin, Toulouse, MP, 2013; Rebolini, Savin, Toulouse, in prep.

Other similar schemes: Pernal, JCP, 2012; Fromager, Knecht, Jensen, JCP, 2013; Hedegård, Heiden, Knecht, Fromager, Jensen, JCP, 2013

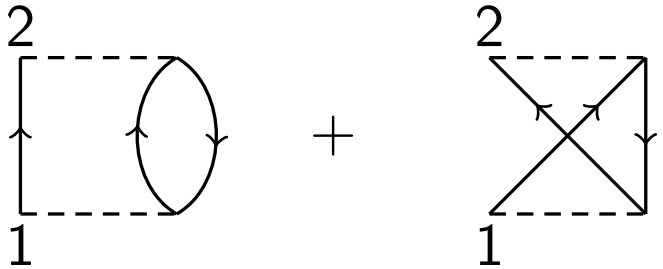
Second-order correlation self-energy and kernel

$$E_c^{\mathrm{MP2}} =$$



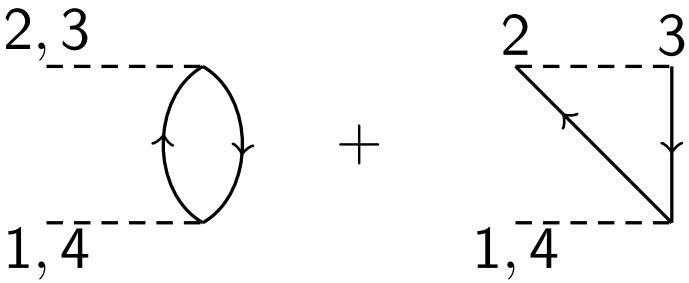
$$\frac{\delta}{\delta G_0(1,2)}$$

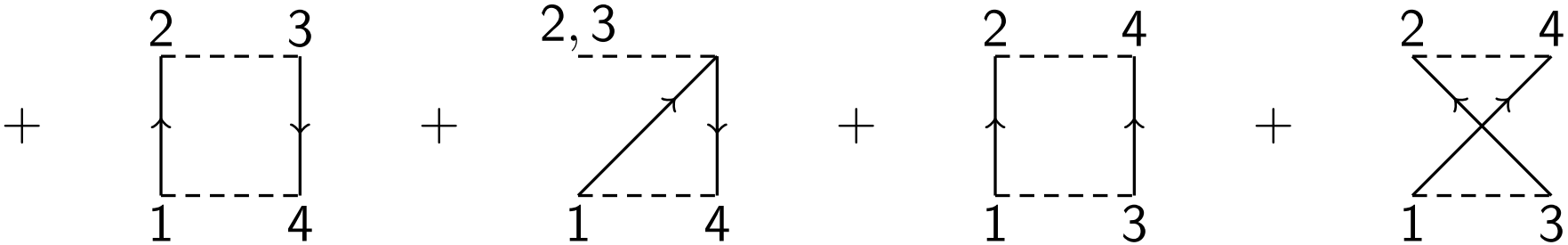
$$\Sigma_c^{(2)}(2,1) =$$



$$\frac{\delta}{\delta G_0(3,4)}$$

$$\Xi_c^{(2)}(2,4;1,3) =$$





In an orbital basis

- Long-range second-order correlation kernel (lrBSE2):

$$f^{\mathrm{lr},(2)}_{c,ia,jb}(\omega) = -\sum_{k,c} \frac{\langle jk||ic\rangle^{\mathrm{lr}}\langle ca||kb\rangle^{\mathrm{lr}}}{\omega - (\varepsilon_a + \varepsilon_c - \varepsilon_k - \varepsilon_j)} - \sum_{k,c} \frac{\langle jc||ik\rangle^{\mathrm{lr}}\langle ka||cb\rangle^{\mathrm{lr}}}{\omega - (\varepsilon_b + \varepsilon_c - \varepsilon_i - \varepsilon_k)}$$
$$+ \frac{1}{2}\sum_{c,d} \frac{\langle cd||ib\rangle^{\mathrm{lr}}\langle ja||dc\rangle^{\mathrm{lr}}}{\omega - (\varepsilon_c + \varepsilon_d - \varepsilon_j - \varepsilon_i)} + \frac{1}{2}\sum_{k,l} \frac{\langle kl||ib\rangle^{\mathrm{lr}}\langle ja||lk\rangle^{\mathrm{lr}}}{\omega - (\varepsilon_b + \varepsilon_a - \varepsilon_k - \varepsilon_l)}$$

$\Longrightarrow$ The correlation kernel can be large when ω is close to a double excitation energy.

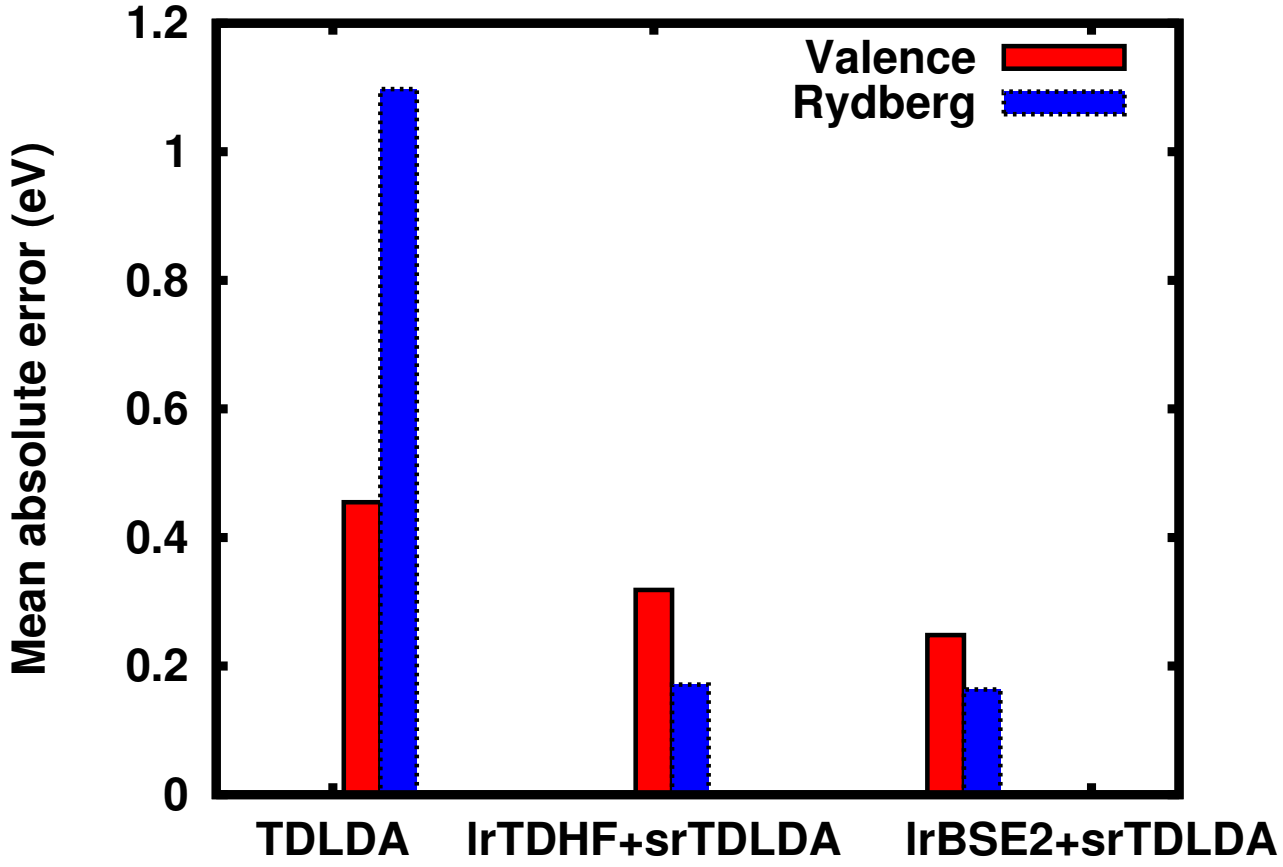
- Calculation of excitation energies in two steps:
  1. lrTDHF+srTDLDA calculation in the TDA: $\mathbf{A}\,\mathbf{X}_0 = \omega_0\,\mathbf{X}_0$
  2. perturbative addition of lrBSE2 kernel: $\omega = \omega_0 + \mathbf{X}_0^\dagger\,\mathbf{f}_c^{\mathrm{lr},(2)}(\omega_0)\,\mathbf{X}_0$

Zhang, Steinmann, Yang, JCP, 2013

Rebolini, Savin, Toulouse, in prep.

Test of lrBSE2+srTDDFT on excitation energies

56 singlet and triplet excitation energies of 4 small molecules N_2, CO, H_2CO, C_2H_4 ($\mu = 0.35$ bohr^{-1}, srLDA functional, TDA, Sadlej+ basis):



$\Longrightarrow$ **For these systems, lrBSE2+srTDLDA does not improve much over lrTDHF+srTDLDA**

Rebolini, Savin, Toulouse, in prep.

Summary

Multiconfigurational hybrids (MCSCF+DFT)

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

Double hybrids (MP2+DFT)

- we provided a theoretical derivation of one-parameter double hybrids
- reach near-chemical accuracy when static correlation not important

Range-separated hybrids (lrRPA+srDFT)

- fast basis convergence
- important to include exchange terms for dispersion interactions

Time-dependent range-separated hybrids (lrBSE2+srTDDFT)

- frequency-dependent second-order long-range correlation kernel
- more tests needed, in particular for effect of double excitations