Promising first results with an RPA correlation functional based on the frequency-dependent Kohn-Sham exchange-kernel

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Overview

Correlation energy of electronic systems within the Kohn-Sham formulation of DFT

Real electronic system and its ground state energy

$$E_0 = \langle \Psi_0 | \hat{T} + \hat{V}_{ee} + \hat{v}_{ext} | \Psi_0 \rangle$$

Kohn-Sham model system of "non-interacting electrons" with same ground state electron density ρ_0 as real system

$$E_s = \langle \Phi_0 | \hat{T} + \hat{v}_s | \Phi_0 \rangle = T_s + \int v_s(\mathbf{r}) \rho_0(\mathbf{r}) d\mathbf{r}$$

Energy contributions

$$E_0 = T_s + U + E_x + E_c + \int v_{ext}(\mathbf{r})\, \rho_0(\mathbf{r})\, d\mathbf{r}$$

$$T_s = \langle \Phi_0 | \hat{T} | \Phi_0 \rangle \qquad U + E_x = \langle \Phi_0 | \hat{V}_{ee} | \Phi_0 \rangle$$

$$E_c = \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle - \langle \Phi_0 | \hat{T} + \hat{V}_{ee} | \Phi_0 \rangle$$

KS potential

$$v_s = v_{ext} + v_H + v_x + v_c$$

Exact-exchange (EXX) – KS calculations with post-SCF RPA correlation

1. Step: Self-consistent calculation of KS orbitals

$$[\hat{T} + \hat{v}_{ext} + \hat{v}_H + \hat{v}_x]\,\varphi_i = \epsilon_i\,\varphi_i$$

$$v_H(\mathbf{r}) = \frac{\delta U}{\delta \rho(\mathbf{r})} = \int d\mathbf{r}\,\frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

$$\int d\mathbf{r}'\,\chi_s(\mathbf{r},\mathbf{r}')\,v_x(\mathbf{r}') \;=\; t(\mathbf{r})$$

2. Step: Calculation of groundstate energy

$$E_0 = T_s[\{\varphi_i\}] + U[\rho_0] + E_x[\{\varphi_i\}] + E_c^{\text{RPA-EXX}}[\{\varphi_i\}] + \int d\mathbf{r}\,v_{ext}(\mathbf{r})\,\rho_0(\mathbf{r})$$

Exact treatment of KS exchange

Exchange energy

$$E_x = -\frac{1}{2}\sum_{i,j}^{\text{occ.}} \int d\mathbf{r} d\mathbf{r}' \; \frac{\phi_i(\mathbf{r}')\phi_j(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}$$

Exchange potential $v_x(\vec{r}) = \dfrac{\delta E_x[\{\phi_i\}]}{\delta\rho(\vec{r})}$

Integral equation for v_x by taking derivative $\frac{\delta E_x}{\delta v_s(\mathbf{r})}$ in two ways

$$\int d\mathbf{r}' \frac{\delta E_x}{\delta\rho(\mathbf{r}')} \; \frac{\delta\rho(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \int d\mathbf{r}' \sum_i^{\text{occ.}} \frac{\delta E_x}{\delta\phi_i(\mathbf{r}')} \; \frac{\delta\phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})}$$

$$\int d\mathbf{r}' \; \chi_s(\mathbf{r},\mathbf{r}') \; v_x(\mathbf{r}') \; = \; t(\mathbf{r})$$

KS response function $\chi_s(\mathbf{r},\mathbf{r}') = 4 \sum_i^{occ.} \sum_a^{unocc.} \frac{\phi_i(\mathbf{r})\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_a}$

Perturbation theory yields $\frac{\delta\phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \sum_{s\neq i} \phi_s(\mathbf{r}') \; \frac{\phi_s(\mathbf{r})\phi_i(\mathbf{r})}{\varepsilon_i - \varepsilon_s}$

- Auxiliary basis set: Electrostatic potential of Gaussian functions

$$f_k(\mathbf{r}) = \int d\mathbf{r}' g_k(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$$

$$\rho_x(\mathbf{r}) = \sum_h \rho_{x,h}\, g_k(\mathbf{r})$$

- Incorporation of exact conditions to treat asymptotic of $v_x(\mathbf{r})$

$$\int dr \rho_x(\mathbf{r}) = -1$$

$$\langle \phi_{HOMO}|v_x|\phi_{HOMO}\rangle = \langle \phi_{HOMO}|\hat{v}_x^{NL}|\phi_{HOMO}\rangle$$

- Construction and balancing scheme for auxiliary and orbital basis sets, orbital basis set needs to be converged for given auxiliary basis set, uncontracted orbital basis sets required

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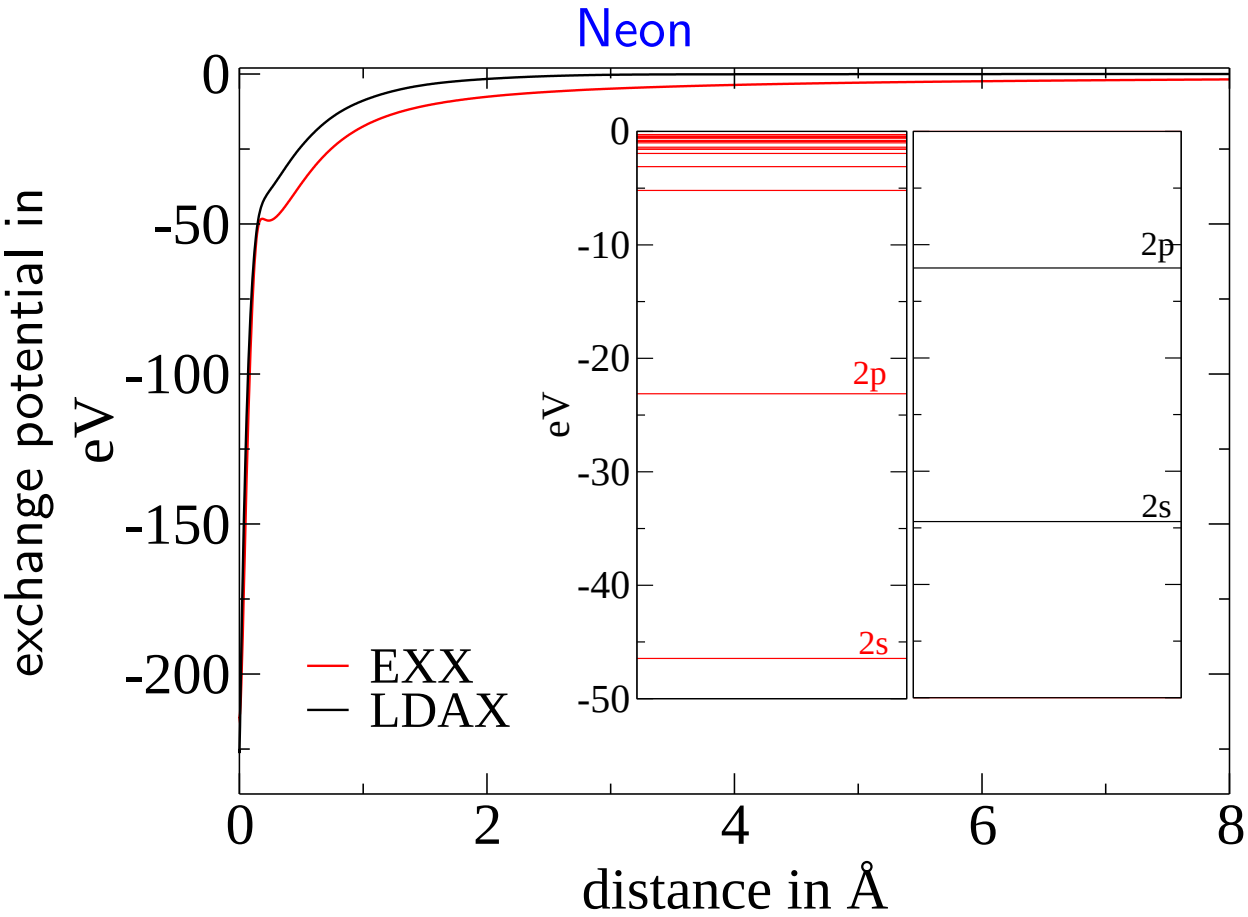
Efficient, purely analytical, numerical stable method that can easily be implemented.

EXX vs. LDA/GGA in finite systems



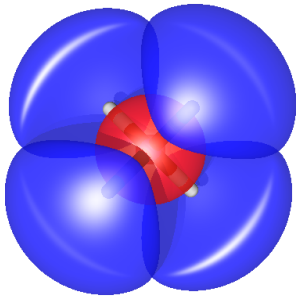
LDA/GGA exchange potential exhibits wrong asymptotic behavior

LDA/GGA (as well as HF) one-particle spectrum qualitatively wrong

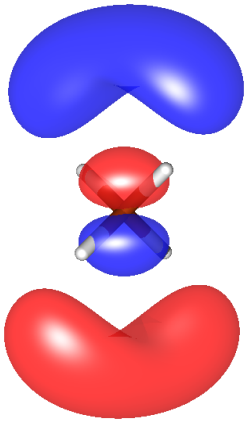
No error cancellation between v_x and v_c

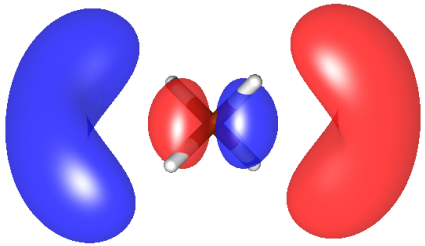
EXX (LHF) valence orbitals of methane

unoccupied orbitals

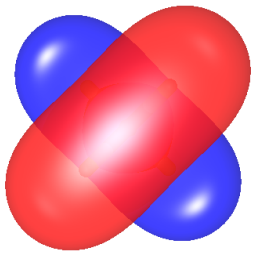


$3\,a_{1g}$ $-4.438\,\text{eV}$



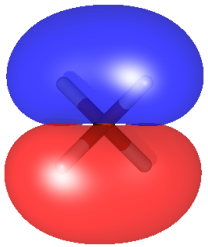


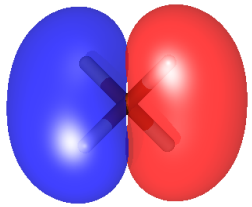
$2\,t_{2u}$ $-2.934\,\text{eV}$



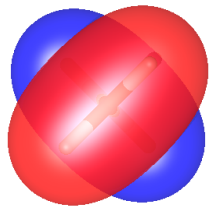
occupied orbitals

$2\,a_{1g}$ $-22.437\,\text{eV}$





$1\,t_{2u}$ $-14.724\,\text{eV}$



Basic TDDFT response equations

$$\delta\rho = \chi_s\,\delta v_s = \chi_s\,\delta v_{ext} + \chi_s f_{uxc}\,\delta\rho$$

$$v_s = v_{ext} + v_H + v_x + v_c$$

$$\delta v_s = \delta v_{ext} + f_{uxc}\,\delta\rho$$

$$[1 - \chi_s f_{uxc}]\,\delta\rho = \chi_s\,\delta v_{ext} \quad \Rightarrow \quad \delta\rho = [1 - \chi_s f_{uxc}]^{-1}\,\chi_s\,\delta v_{ext}$$

Search for poles of response function leads to Casida equation

$$\left[\boldsymbol{\varepsilon}^2 - 4\,\boldsymbol{\varepsilon}^{1/2}\mathbf{K}(\omega_n)\boldsymbol{\varepsilon}^{1/2}\right]\,\mathbf{z}_n = \omega_n^2\,\mathbf{z}_n$$

with $K_{ia,jb} = \int d\mathbf{r}d\mathbf{r}'\;\varphi_i(\mathbf{r})\,\varphi_a(\mathbf{r})\,f_{uxc}(\omega,\mathbf{r},\mathbf{r}')\,\varphi_j(\mathbf{r}')\,\varphi_b(\mathbf{r}')$

XC-kernel is frequency-dependent derivative of v_{xc} with respect to ρ

Orbital-dependent exchange kernel

OEP-like equation for exact exchange kernel

$$f_x(\omega, \mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' d\mathbf{r}''' \, \chi_s^{-1}(\omega, \mathbf{r}, \mathbf{r}'') \, h_x(\omega, \mathbf{r}'', \mathbf{r}''') \, \chi_s^{-1}(\omega, \mathbf{r}''', \mathbf{r}')$$

$$f_x = \chi_s^{-1} \, h_x \, \chi_s^{-1}$$

Numerically highly unstable equation

Solving this equation not advisable

Alternative form of the TDDFT response equation

$$[1 - \chi_s\, f_u - \chi_s\, f_x]\, \delta\rho = \chi_s\, \delta\, v_{ext}$$

with $\delta\rho = \chi_s \delta v_s$ and $f_x = \chi_s^{-1} h_x \chi_s^{-1}$

$$[\chi_s - \chi_s\, F_u\, \chi_s - h_x]\, \delta v_s = \chi_s\, \delta v_{ext}$$

Search for frequencies ω with singular δv_s leads to

$$\left[\boldsymbol{\varepsilon}^2 + 4\,\boldsymbol{\varepsilon}^{1/2}\,[\mathbf{C} + \mathbf{X}(\omega_n)]\boldsymbol{\varepsilon}^{1/2}\right]\, \mathbf{z}_n = \omega_n^2\, \mathbf{z}_n$$

with

$$C_{ia,jb} = \langle ia|jb\rangle \qquad \boldsymbol{\varepsilon}_{ia,jb} = (\boldsymbol{\varepsilon}_i - \boldsymbol{\varepsilon}_a)\delta_{ia,jb}$$

$$X_{ia,jb}(\omega) = X^{(1)}_{ia,jb}(\omega) + X^{(2)}_{ia,jb}(\omega)$$

Approximation: products $\varphi_i(\mathbf{r})\varphi_a(\mathbf{r})$ treated as linear independent
Strictly, projection on space spanned by products $\{\varphi_i\, \varphi_a\}$ required

Form of $h_x(\omega, \mathbf{r}, \mathbf{r}')$

$$h_x(\omega, \mathbf{r}, \mathbf{r}') = \sum_{ia} \sum_{jb} \varphi_i(\mathbf{r})\, \varphi_a(\mathbf{r})\, \lambda_{ia}(\omega) \left[X^{(1)}_{ia,jb}(\omega) + X^{(2)}_{ia,jb}(\omega) \right] \lambda_{jb}(\omega)\, \varphi_j(\mathbf{r}')\, \varphi_b(\mathbf{r}') + h^{(3)}(\omega, \mathbf{r}, \mathbf{r}')$$

with

$$\lambda_{ia} = \frac{4\varepsilon_{ia}}{\omega^2 - \varepsilon_{ia}^2}$$

and

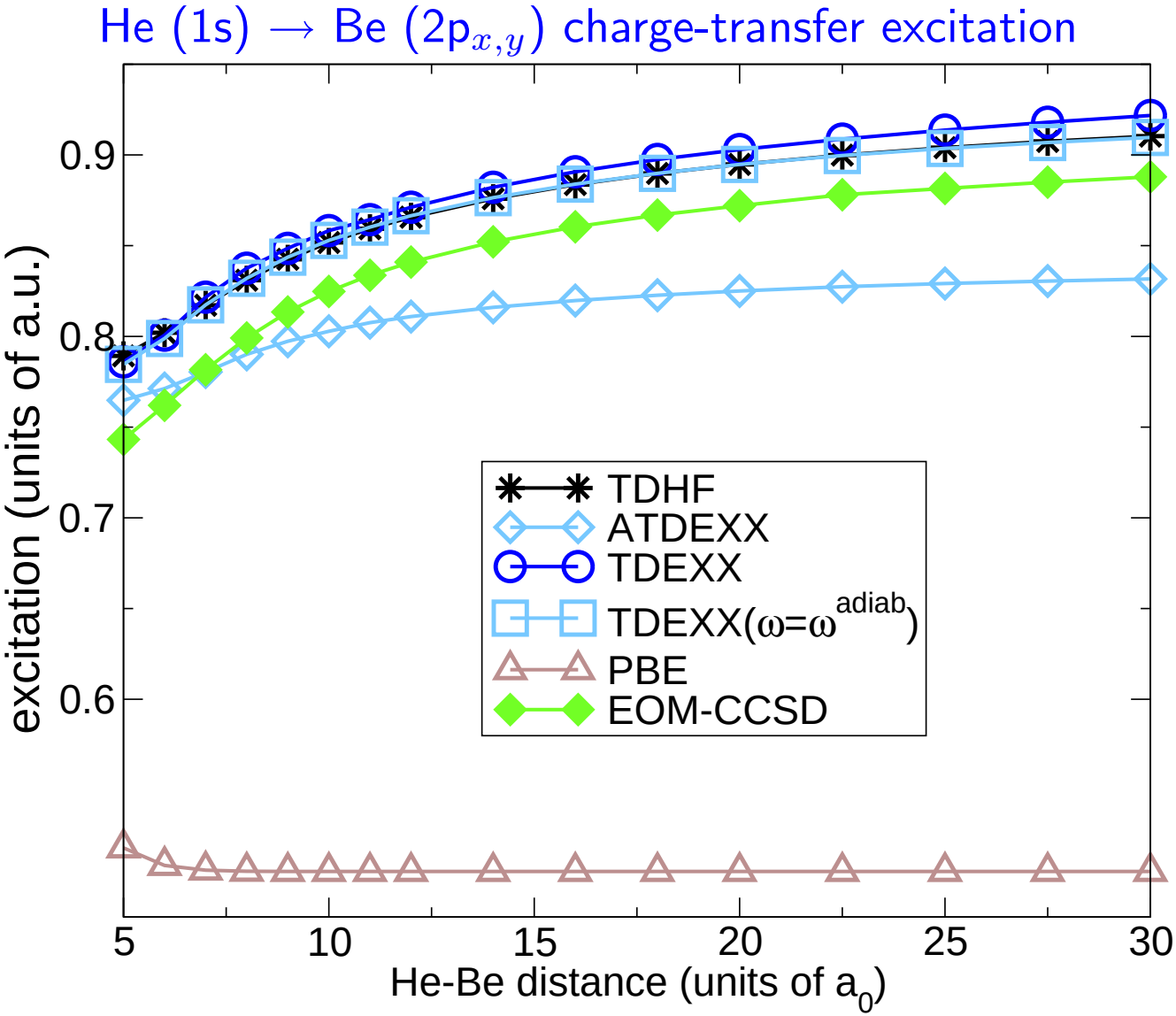
$$X^{(1)}_{ia,jb}(\omega) = -\frac{1}{4} \left(\left[1 + \frac{\omega^2}{\varepsilon_{ia}\varepsilon_{jb}} \right] \langle ia|jb\rangle + \left[1 - \frac{\omega^2}{\varepsilon_{ia}\varepsilon_{jb}} \right] \langle ia|bj\rangle \right)$$

$$X^{(2)}_{ia,jb}(\omega) = \frac{1}{4} \left[1 + \frac{\omega^2}{\varepsilon_{ia}\varepsilon_{jb}} \right] \left(\delta_{ij} \Delta V^{\text{unocc}}_{\text{x},ab} - \delta_{ab} \Delta V^{\text{occ}}_{\text{x},ij} \right)$$

$$\Delta V^{\text{unocc}}_{\text{x},ab} = \langle \varphi_a \,|\, \hat{v}^{\text{NL}}_{\text{x}} - \hat{v}_{\text{x}} \,|\, \varphi_b \rangle \qquad \Delta V^{\text{occ}}_{\text{x},ij} = \langle \varphi_i \,|\, \hat{v}^{\text{NL}}_{\text{x}} - \hat{v}_{\text{x}} \,|\, \varphi_j \rangle$$

Term $h^{(3)}$ shall be neglected

TDEXX results I



TDEXX results II
Excitations of ethene

method	basis	B_{3u}	B_{1u}	B_{1g}	B_{2g}	A_g
TDHF	1[1]	7.13	7.38	7.73	7.90	8.50
	3[2]	7.12	7.37	7.71	7.87	8.07
EXX(unc)	1	7.13	6.03	7.95	7.89	8.33
	3	7.11	6.03	7.92	7.86	7.97
ATDEXX	1	7.13	7.04	7.83	7.89	8.28
	3	7.16	7.06	7.83	7.89	8.04
TDEXX	1	7.14	7.39	7.74	7.91	8.49
	3	7.13	7.38	7.72	7.87	8.08
TDEXX(ω_{adiab})	1	7.13	7.35	7.74	7.91	8.48
	3	7.13	7.36	7.72	7.87	8.08
EXX/ALDA	1	7.12	7.78	7.88	7.91	8.40
	3	7.09	7.76	7.85	7.88	7.99
TDPBE	1	7.39	6.45	8.30	6.99	8.02
	3	6.83	6.42	6.98	6.78	6.80
TDLDA	4[3]	6.66	7.45	7.22	7.21	8.24
Expt. [4]		7.15	7.66	7.83	8.00	8.29

[1] aug-cc-pVTZ basis set
[2] uncontracted C[14s9p5d3f],H[8s5p3d] basis set from Heßelmann *et al.* + two diffuse s,p-functions
[3] Sadlej basis set, C(10s6p4d)/[5s3p2d], H(6s4p)/[3s2p]
[4] Foresman *et al.*

Correlation energy from the fluctuation-dissipation theorem with EXX-RPA response function

$$E_c = -\frac{1}{2\pi} Im \int_0^1 d\alpha \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \int_0^\infty d\omega \Big(\chi_\alpha(\mathbf{r}_1, \mathbf{r}_2, \omega + i\eta) - \chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega + i\eta) \Big)$$

χ_α from TDEXX, i.e., $\chi_\alpha = (1 - \alpha \chi_0 f_{ux})^{-1} \chi_0$

$$\chi_\alpha = \chi_0 + \alpha \chi_0 f_{ux} \chi_0 + \alpha^2 \chi_0 f_{ux} \chi_0 f_{ux} \chi_0 + \cdots$$

$$\int_0^1 d\alpha \, \chi_\alpha = \chi_0 + \frac{1}{2} \chi_0 f_{ux} \chi_0 + \frac{1}{3} \chi_0 f_{ux} \chi_0 f_{ux} \chi_0 + \cdots$$

$$= \sum_{ia,jb} \varphi_i(\mathbf{r}_1) \varphi_a(\mathbf{r}_2) \left[-\boldsymbol{\lambda} + \frac{1}{2} \boldsymbol{\lambda} [\mathbf{C}+\mathbf{X}] \boldsymbol{\lambda} - \frac{1}{3} \boldsymbol{\lambda} [\mathbf{C}+\mathbf{X}] \boldsymbol{\lambda} [\mathbf{C}+\mathbf{X}] \boldsymbol{\lambda} + \cdots \right]_{ia,jb} \varphi_j(\mathbf{r}_1) \varphi_b(\mathbf{r}_2)$$

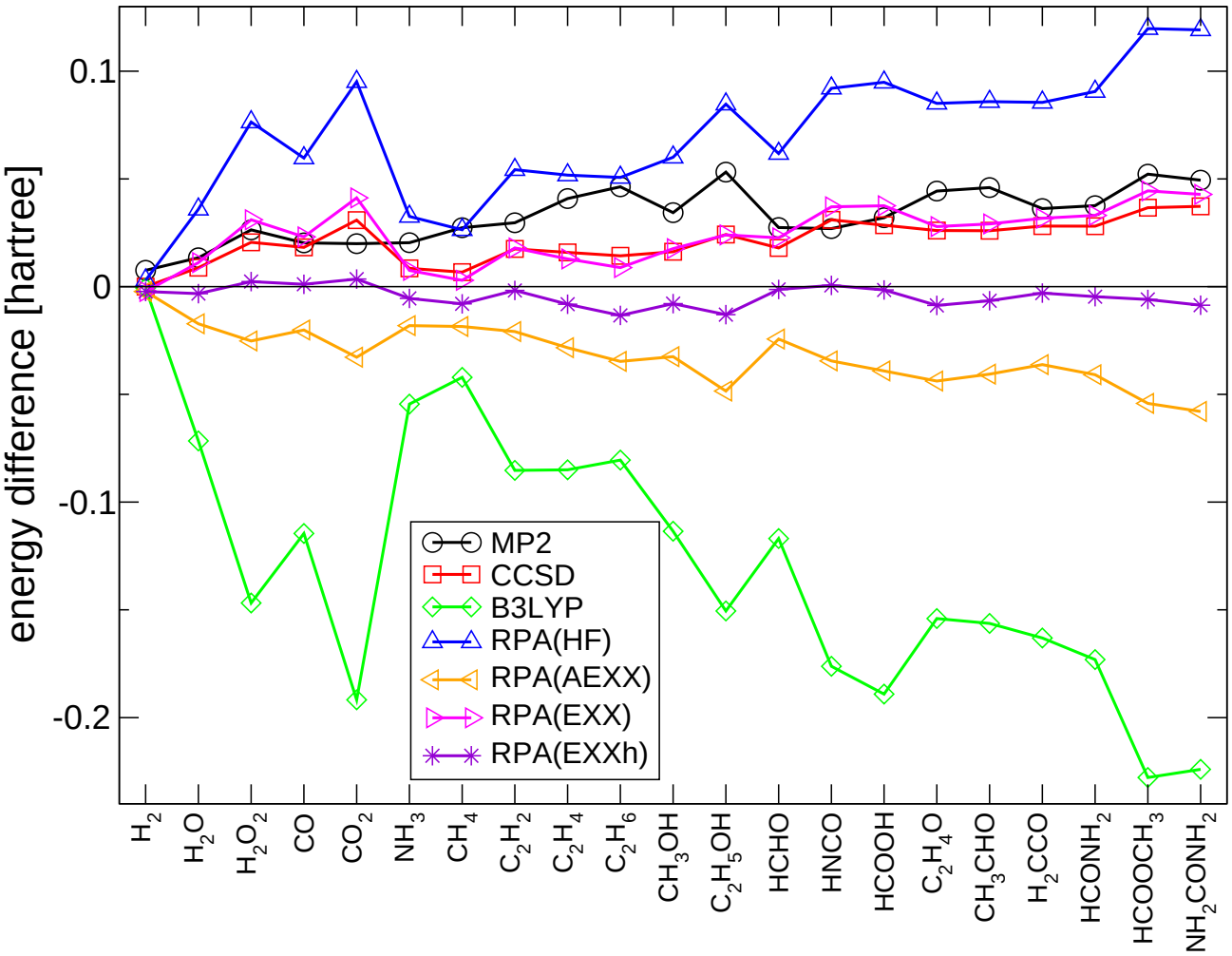
Orbital-dependent correlation energy

$$E_c = -\frac{1}{2\pi} \int_0^\infty d\eta \sum_{ia,jb} \left[\boldsymbol{\lambda}^{\frac{1}{2}} \left(-ln \left[1 + \boldsymbol{\lambda}^{\frac{1}{2}} (\mathbf{C}+\mathbf{X}) \boldsymbol{\lambda}^{\frac{1}{2}} \right] \left[\boldsymbol{\lambda}^{\frac{1}{2}} (\mathbf{C}+\mathbf{X}) \boldsymbol{\lambda}^{\frac{1}{2}} \right]^{-1} + 1 \right) \boldsymbol{\lambda}^{\frac{1}{2}} \right]_{ia,jb} \langle ib | aj \rangle$$

with $\lambda_{ia,jb} = \delta_{ia,jb} \frac{4\varepsilon_{ai}}{\varepsilon_{ai}^2 - (i\eta)^2}$ and $X_{ia,jb}(i\eta)$

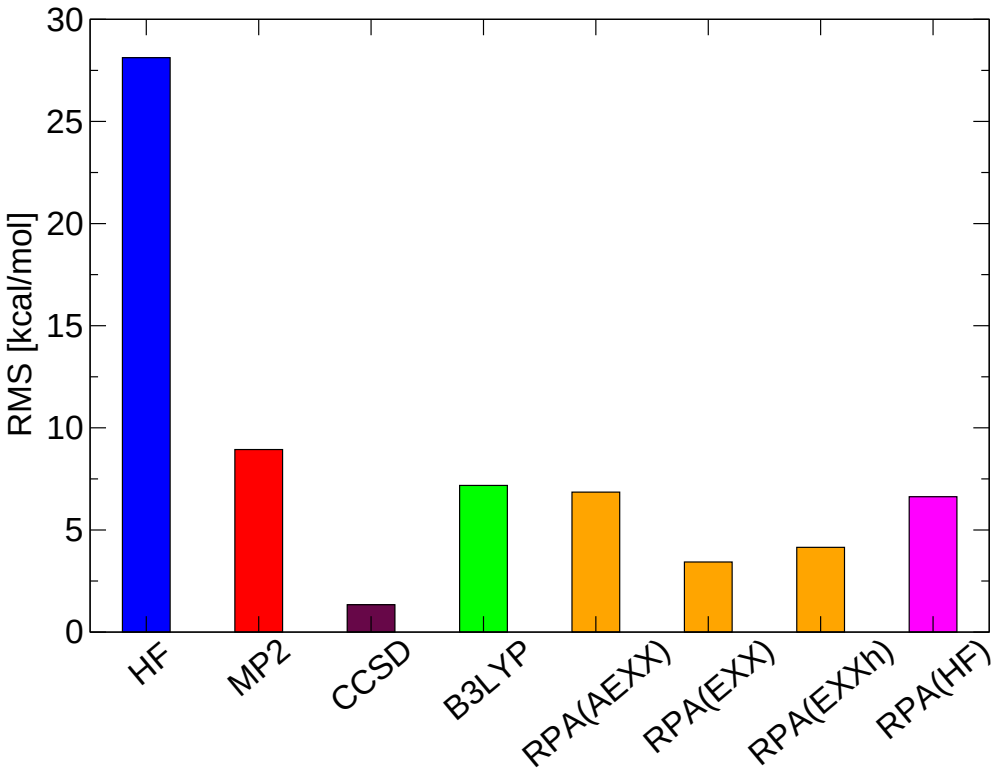
Results EXX-RPA correlation functional I

Deviations of correlation energies from CCSD(T) correlation energies (Always correlation energies with respect to HF, aug-cc-pVTZ basis set)



Results EXX-RPA correlation functional II

Deviations of reaction energies (RMS) from CCSD(T)



$C_2H_2+H_2$	$\rightarrow$	C_2H_4
$C_2H_4+H_2$	$\rightarrow$	C_2H_6
$C_2H_6+H_2$	$\rightarrow$	$2CH_4$
$CO+H_2$	$\rightarrow$	H_2CO
H_2CO+H_2	$\rightarrow$	CH_3OH
$H_2O_2+H_2$	$\rightarrow$	$2H_2O$
$C_2H_2+H_2O$	$\rightarrow$	CH_3CHO
$C_2H_4+H_2O$	$\rightarrow$	C_2H_5OH
CH_3CHO+H_2	$\rightarrow$	C_2H_5OH
$CO+NH_3$	$\rightarrow$	$HCONH_2$
$CO+H_2O$	$\rightarrow$	CO_2+H_2
$HNCO+NH_3$	$\rightarrow$	NH_2CONH_2
CH_3OH+CO	$\rightarrow$	$HCOOCH_3$
$CO+H_2O_2$	$\rightarrow$	CO_2+H_2O

Concluding Remarks

- Reformulation of basic TDDFT response equations enables use of orbital-dependent kernels, e.g., EXX kernel
  PRA **80**, 012507 (2009)

- Charge-Transfer can be described by TDDFT if frequency-dependent EXX kernel is used, adiabatic EXX kernel yields distance behavior of charge-transfer excitations too small by factor $\frac{1}{2}$
  PRA **80**, 012507 (2009), Z. Phys., in press,
  Int. J. Quantum Chem., in press

- Promising orbital-dependent correlation functional from fluctuation-dissipation theorem with response function from RPA including KS exchange-kernel
  Mol. Phys., in press