

# A new generation of density-functional methods based on the adiabatic-connection fluctuation-dissipation theorem

Andreas Görling, Patrick Bleiziffer, Daniel Schmidtel, and Andreas Heßelmann

Lehrstuhl für Theoretische Chemie  
Universität Erlangen-Nürnberg

J. Gebhardt, G. Gebhardt, T. Gimon, W. Hieringer, C. Neiß, I. Nikiforidis, H. Schulz,  
E. Trushin, K.-G. Warnick, T. Wölfle

## 1 Introduction

- Orbital-dependent functionals

## 2 Exact-exchange (EXX) Kohn-Sham methods

## 3 Direct RPA and EXXRPA correlation energy

- Adiabatic-connection fluctuation-dissipation theorem for KS correlation energy
- EXXRPA methods
- Direct RPA methods
- Selfconsistent direct RPA
- Correlation potentials
- Total energies, reaction energies
- Bond dissociation, static correlation
- Weak interactions, Van-der-Waals bonds

## 4 Concluding Remarks

## 5 Literature

Orbital- and eigenvalue-dependent exchange-correlation functionals in Kohn-Sham methods in order to

- improve accuracy
- get rid of Coulomb self-interactions and self-interactions in general (qualitatively correct KS spectra, improved input data for TDDFT)
- enable description of static correlation (bond formation and breaking), i.e., multiconfiguration cases
- enable description of Van der Waals interactions and noncovalent, “mean” interactions

## Electronic Schrödinger equation

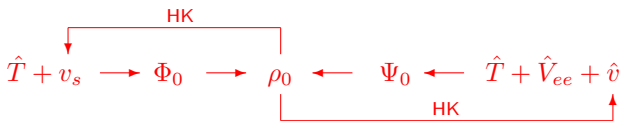
$$[\hat{T} + \hat{V}_{ee} + v]\Psi_0 = E_0\Psi_0$$

## Kohn-Sham equation

$$[\hat{T} + \hat{v}_s]\Phi_0 = E_{0,s}\Phi_0$$

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \quad v_s = v + v_H + v_{xc}$$

## Relation Kohn-Sham to real electronic system



$$E_0 = T_s + U[\rho_0] + E_{xc}[\rho_0] + \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}$$

Ground state energy of an electronic system

$$E_0 = T_s + U + E_x + E_c + \int d\mathbf{r} v_{nuc}(\mathbf{r})\rho(\mathbf{r})$$

Thomas-Fermi-Dirac

$$E_0 = T_s[\rho] + U[\rho] + E_x[\rho] + E_c[\rho] + \int d\mathbf{r} v_{nuc}(\mathbf{r})\rho(\mathbf{r})$$

$$\delta E / \delta \rho(\mathbf{r}) = \mu$$

Conventional Kohn-Sham

$$E_0 = T_s[\{\phi_i\}] + U[\rho] + E_x[\rho] + E_c[\rho] + \int d\mathbf{r} v_{nuc}(\mathbf{r})\rho(\mathbf{r})$$

$$[\hat{T} + \hat{v}_{nuc} + \hat{v}_H + \hat{v}_x + \hat{v}_c]\phi_i = \varepsilon_i \phi_i$$

Kohn-Sham with orbital dependent functionals

$$E_0 = T_s[\{\phi_i\}] + U[\rho] + E_x[\{\phi_i\}] + E_c[\{\phi_i\}] + \int d\mathbf{r} v_{nuc}(\mathbf{r})\rho(\mathbf{r})$$

$$[\hat{T} + \hat{v}_{nuc} + \hat{v}_H + \hat{v}_x + \hat{v}_c]\phi_i = \varepsilon_i \phi_i$$

## Conventional Kohn-Sham methods

$$E_0 = T_s[\{\phi_i\}] + U[\rho_0] + E_x[\rho_0] + E_c[\rho_0] + \int d\mathbf{r} v_{\text{nuc}}(\mathbf{r}) \rho_0(\mathbf{r})$$

$$\left[ \hat{T} + \hat{v}_{\text{nuc}} + \hat{v}_H[\rho_0] + \hat{v}_x[\rho_0] + \hat{v}_c[\rho_0] \right] \phi_i = \varepsilon_i \phi_i$$

## KS methods with orbital- and eigenvalue-dependent xc-functionals

$$E_0 = T_s[\{\phi_i\}] + U[\rho_0] + E_x[\{\phi_i\}] + E_c[\{\varepsilon_s\}, \{\phi_s\}] + \int d\mathbf{r} v_{\text{nuc}}(\mathbf{r}) \rho(\mathbf{r})$$

$$\left[ \hat{T} + \hat{v}_{\text{nuc}} + \hat{v}_H[\rho_0] + \hat{v}_x[\{\phi_i\}] + \hat{v}_c[\{\varepsilon_s\}, \{\phi_s\}] \right] \phi_i = \varepsilon_i \phi_i$$

## Exchange energy

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

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

$$\int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}') v_x(\mathbf{r}') = t_x(\mathbf{r})$$

$$\text{KS response function } \chi_0(\mathbf{r}, \mathbf{r}') = 4 \sum_i^{\text{occ.}} \sum_a^{\text{unocc.}} \frac{\phi_i(\mathbf{r})\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\phi_i(\mathbf{r}')}{\epsilon_i - \epsilon_a}$$

$$t_x(\mathbf{r}) = 4 \sum_i^{\text{occ.}} \sum_a^{\text{unocc.}} \frac{\phi_i(\mathbf{r})\phi_a(\mathbf{r}) \langle a | \hat{v}_x^{\text{NL}} | i \rangle}{\epsilon_i - \epsilon_a}$$

Plane wave methods for solid numerically stable  
 Gaussian basis set methods for molecules numerically demanding

⌘ Auxiliary basis set: Electrostatic potential of Gaussian functions

$$v_x(\mathbf{r}) = \sum_k v_{x,k} f_k(\mathbf{r}) \quad \text{with} \quad f_k(\mathbf{r}) = \int d\mathbf{r}' g_k(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$$

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

$$\int dr \rho_x(\mathbf{r}) = -1 \quad \text{with} \quad \rho_x(\mathbf{r}) = \sum_k v_{x,k} g_k(\mathbf{r})$$

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

⌘ Balancing of auxiliary and orbital basis sets (**uncontracted** orbital basis sets required)

JCP **127**, 054102 (2007)

By preprocessing of auxiliary basis set and regularization techniques, EXX calculations with standard **contracted** orbital basis sets possible (aug-cc-pCVxZ, x = 3, 4, 5)





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



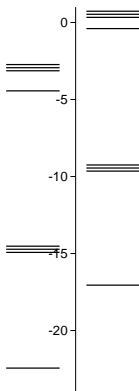
$$3 a_{1g} \quad -4.438 \text{ eV}$$



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



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



$$2 t_{2u} \quad +0.533 \text{ eV}$$



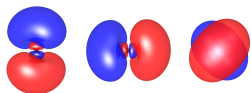
$$3 a_{1g} \quad -0.396 \text{ eV}$$



$$1 t_{2u} \quad -9.448 \text{ eV}$$



$$2 a_{1g} \quad -17.054 \text{ eV}$$



$2 t_{2u}$   $-2.934$  eV



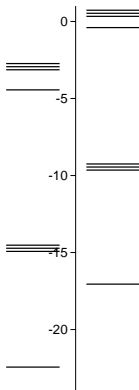
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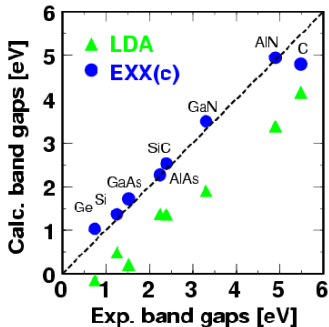


$1 t_{2u}$   $-9.448$  eV



$2 a_{1g}$   $-17.054$  eV

## FLAPW vs. PP EXX band gaps



		EXX+VWNc		Exp.
		FLAPW <sup>a</sup>	PP <sup>b</sup>	
Si	$\Gamma \rightarrow \Gamma$	3.21	3.26	3.4
	$\Gamma \rightarrow L$	2.28	2.35	2.4
SiC	$\Gamma \rightarrow X$	1.44	1.50	
	$\Gamma \rightarrow \Gamma$	7.24	7.37	
	$\Gamma \rightarrow L$	6.21	6.30	
Ge	$\Gamma \rightarrow X$	2.44	2.52	2.42
	$\Gamma \rightarrow \Gamma$	1.21	1.28	1.0
	$\Gamma \rightarrow L$	0.94	1.01	0.7
GeAs	$\Gamma \rightarrow X$	1.28	1.34	1.3
	$\Gamma \rightarrow \Gamma$	1.74	1.82	1.63
	$\Gamma \rightarrow L$	1.86	1.93	
C	$\Gamma \rightarrow X$	2.12	2.15	2.18
	$\Gamma \rightarrow \Gamma$	6.26	6.28	7.3
	$\Gamma \rightarrow L$	9.16	9.18	
	$\Gamma \rightarrow X$	5.33	5.43	

<sup>a</sup>PRB 83, 045105 (2011)

<sup>b</sup>PRB 59, 10031 (1997)

- Problem of Coulomb self-interaction is solved
  - ▶ Physically meaningful orbital and eigenvalue spectra  
 (Improved input data for time-dependent DFT)
  
- Similar total energies of exact-exchange-only Kohn-Sham and HF methods but completely different orbital and eigenvalue spectra

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int_0^\infty d\omega \left[ \chi_\alpha(\mathbf{r}, \mathbf{r}', i\omega) - \chi_0(\mathbf{r}, \mathbf{r}', i\omega) \right]$$

Integration of response functions along complex frequencies

$$\begin{aligned} \frac{-1}{2\pi} \int_0^\infty d\omega \int d\mathbf{r} d\mathbf{r}' g(\mathbf{r}, \mathbf{r}') \chi_\alpha(\mathbf{r}, \mathbf{r}', i\omega) = \\ = \int d\mathbf{r} d\mathbf{r}' g(\mathbf{r}, \mathbf{r}') \left[ \rho_2^\alpha(\mathbf{r}, \mathbf{r}') - \frac{1}{2} \rho(\mathbf{r})\rho(\mathbf{r}') + \rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') \right] \end{aligned}$$

$$\int_0^\infty d\omega \frac{a}{a^2 + \omega^2} = \frac{\pi}{2} \quad \text{later on } g(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

$$\chi_\alpha(\mathbf{r}, \mathbf{r}', i\omega) = -2 \sum_{n \neq 0} \frac{E_n - E_0}{(E_n - E_0)^2 + \omega^2} \langle \Psi_0^\alpha | \hat{\rho}(\mathbf{r}) | \Psi_n^\alpha \rangle \langle \Psi_n^\alpha | \hat{\rho}(\mathbf{r}') | \Psi_0^\alpha \rangle$$

$$V_c(\alpha) = \langle \Psi_0(\alpha) | \hat{V}_{ee} | \Psi_0(\alpha) \rangle - \langle \Phi_0 | \hat{V}_{ee} | \Phi_0 \rangle$$

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int_0^\infty d\omega \left[ \chi_\alpha(\mathbf{r}, \mathbf{r}', i\omega) - \chi_0(\mathbf{r}, \mathbf{r}', i\omega) \right] = \int_0^1 d\alpha V_c(\alpha)$$

Integration along adiabatic connection

$$E_c = \int_0^1 d\alpha V_c(\alpha) \quad \text{with} \quad V_c(\alpha) = \langle \Psi_0(\alpha) | \hat{V}_{ee} | \Psi_0(\alpha) \rangle - \langle \Phi_0 | \hat{V}_{ee} | \Phi_0 \rangle$$

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

$$\Psi_0(\alpha) = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} | \Psi \rangle$$

From Hellmann-Feynman theorem follows

$$\frac{dE_c(\alpha)}{d\alpha} = V_c(\alpha)$$

KS response function  $\chi_0(\mathbf{r}, \mathbf{r}', i\omega)$

$$\chi_0(\mathbf{r}, \mathbf{r}', i\omega) = -4 \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{\epsilon_{ai}}{\epsilon_{ai}^2 + \omega^2} \varphi_i(\mathbf{r}) \varphi_a(\mathbf{r}) \varphi_a(\mathbf{r}') \varphi_i(\mathbf{r}')$$

Basics time-dependent DFT

$$\rho^{(1)} = \mathbf{X}_{\alpha=1} v^{(1)} = \mathbf{X}_0 v_s^{(1)} = \mathbf{X}_0 [v^{(1)} + \mathbf{F}_{\text{Hxc}} \mathbf{X}_{\alpha=1} v^{(1)}]$$

$$v_s = v + v_{\text{H}} + v_{\text{xc}} \quad v_s^{(1)} = v_{\text{pert}}^{(1)} + v_{\text{H}}^{(1)} + v_{\text{xc}}^{(1)}$$

$$v_{\text{Hxc}}^{(1)} = \frac{\delta v_{\text{Hxc}}}{\delta \rho} \rho^{(1)} = \mathbf{F}_{\text{Hxc}} \rho^{(1)} = \mathbf{F}_{\text{Hxc}} \mathbf{X}_{\alpha=1} v^{(1)}$$

Response functions  $\chi_\alpha(\mathbf{r}, \mathbf{r}', i\omega)$  from EXX-TDDFT

$$\mathbf{X}_\alpha = \mathbf{X}_0 + \alpha \mathbf{X}_0 \mathbf{F}_{\text{Hxc}} \mathbf{X}_\alpha \quad \mathbf{X}_\alpha = [\mathbf{1} - \alpha \mathbf{X}_0 \mathbf{F}_{\text{Hxc}}]^{-1} \mathbf{X}_0$$

$$\mathbf{X}_\alpha = \mathbf{X}_0 [\mathbf{X}_0 - \alpha \mathbf{H}_{\text{Hxc}}]^{-1} \mathbf{X}_0 \quad \text{with } \mathbf{X}_0 \mathbf{F}_{\text{Hxc}} \mathbf{X}_0 = \mathbf{H}_{\text{Hxc}}$$

OEP-like equation for sum  $f_{\text{HX}}(\omega, \mathbf{r}, \mathbf{r}')$  of Coulomb and EXX kernel

$$\int d\mathbf{r}'' \int d\mathbf{r}''' \mathbf{X}_0(\mathbf{r}, \mathbf{r}'', \omega) f_{\text{HX}}(\omega, \mathbf{r}'', \mathbf{r}''') \mathbf{X}_0(\mathbf{r}''', \mathbf{r}', \omega) = h_{\text{HX}}(\omega, \mathbf{r}, \mathbf{r}')$$

with

$$\begin{aligned} h_{\text{HX}}(\omega, \mathbf{r}, \mathbf{r}') &= \frac{1}{4} \mathbf{Y}^\top(\mathbf{r}) \boldsymbol{\lambda}(\omega) [\mathbf{A} + \mathbf{B} + \boldsymbol{\Delta}] \boldsymbol{\lambda}(\omega) \mathbf{Y}(\mathbf{r}') \\ &+ \omega^2 \frac{1}{4} \mathbf{Y}^\top(\mathbf{r}) \boldsymbol{\lambda}(\omega) \boldsymbol{\epsilon}^{-1} [\mathbf{A} + \mathbf{B} + \boldsymbol{\Delta}] \boldsymbol{\epsilon}^{-1} \boldsymbol{\lambda}(\omega) \mathbf{Y}(\mathbf{r}) \\ &+ \sum_i \sum_j \sum_a Y_{ia}(\mathbf{r}) \lambda_{ia}(\omega) \frac{\langle a | \hat{v}_x^{\text{NL}} - \hat{v}_x | j \rangle}{\epsilon_a - \epsilon_j} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) + \dots \\ &+ \sum_a \sum_b \sum_i Y_{ia}(\mathbf{r}) \lambda_{ia}(\omega) \frac{\langle b | \hat{v}_x^{\text{NL}} - \hat{v}_x | i \rangle}{\epsilon_b - \epsilon_i} \phi_a(\mathbf{r}) \phi_b(\mathbf{r}) + \dots \end{aligned}$$

$$A_{ia,jb} = 2(ai|jb) - (ab|ji) \quad B_{ia,jb} = 2(ai|bj) - (aj|bi)$$

$$\Delta_{ia,jb} = \delta_{ij} \langle \varphi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \varphi_b \rangle - \delta_{ab} \langle \varphi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \varphi_j \rangle$$

$$\lambda_{ia,jb} = \delta_{ia,jb} \frac{-4\epsilon_{ia}}{\epsilon_{ia}^2 + \omega^2} \quad \epsilon_{ia,jb} = \delta_{ia,jb} \epsilon_{ia} = \delta_{ia,jb} (\epsilon_a - \epsilon_i)$$

$$Y_{ia}(\mathbf{r}) = \phi_i(\mathbf{r}) \phi_a(\mathbf{a})$$

$$\text{RPA: } h_{\text{H}}(\mathbf{r}, \mathbf{r}', \omega) = \mathbf{Y}^\top(\mathbf{r}) \boldsymbol{\lambda}(\omega) \mathbf{C} \boldsymbol{\lambda}(\omega) \mathbf{Y}(\mathbf{r}) \quad \text{with } C_{ia,jb} = (ia|jb)$$



$$E_c = \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left[ \chi_\alpha(\mathbf{r}, \mathbf{r}', i\omega) - \chi_0(\mathbf{r}, \mathbf{r}', i\omega) \right]$$

Representation of  $\chi_\alpha(i\omega)$ ,  $h_x(i\omega)$  in RI basis set with respect to Coulomb norm

$$\mathbf{X}_\alpha = [\mathbf{1} - \alpha \mathbf{X}_0 \mathbf{F}_{\text{Hx}}]^{-1} \mathbf{X}_0 \quad \Rightarrow \quad \mathbf{X}_\alpha = \mathbf{X}_0 [\mathbf{X}_0 - \alpha \mathbf{H}_{\text{Hx}}]^{-1} \mathbf{X}_0$$

(using  $\mathbf{F}_{\text{Hx}} = \mathbf{X}_0^{-1} \mathbf{H}_{\text{Hx}} \mathbf{X}_0^{-1}$ )

$$E_c = \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \text{Tr} \left[ \mathbf{S}^{-1} \mathbf{X}_0 [\mathbf{X}_0 - \alpha \mathbf{H}_{\text{Hx}}]^{-1} \mathbf{X}_0 - \mathbf{S}^{-1} \mathbf{X}_0 \right]$$

with

$$\mathbf{X}_0(i\omega) = \mathbf{D}^T \boldsymbol{\lambda}(i\omega) \mathbf{D} \quad \text{with} \quad D_{ia,h} = (\varphi_i \varphi_a | f_h)_{\text{Coul}} \quad \text{and} \quad \lambda_{ia,jb} = \delta_{ia,jb} \frac{-4\epsilon_{ia}}{\epsilon_{ia}^2 + \omega^2}$$

and

$$\mathbf{H}(i\omega) = \frac{1}{4} \mathbf{D}^T \boldsymbol{\lambda}(i\omega) [\mathbf{A} + \mathbf{B} + \Delta] \boldsymbol{\lambda}(i\omega) \mathbf{D} + (i\omega)^2 \frac{1}{4} \mathbf{D}^T \boldsymbol{\lambda}(i\omega) \boldsymbol{\epsilon}^{-1} [\mathbf{A} + \mathbf{B} + \Delta] \boldsymbol{\epsilon}^{-1} \boldsymbol{\lambda}(i\omega) \mathbf{D} \\ + \mathbf{W}_1(i\omega) + \mathbf{W}_1^T(i\omega) + \mathbf{W}_2(i\omega) + \mathbf{W}_2^T(i\omega)$$

$$E_c = \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \operatorname{Tr} \left[ \mathbf{S}^{-1} \mathbf{X}_0 [\mathbf{X}_0 - \alpha \mathbf{H}_{\text{Hx}}]^{-1} \mathbf{X}_0 - \mathbf{S}^{-1} \mathbf{X}_0 \right]$$

Orthonormalize RI basis set, i.e. make  $\mathbf{S} = \mathbf{E}$ , and use  $\mathbf{X}_0 = -(-\mathbf{X}_0)^{\frac{1}{2}}(-\mathbf{X}_0)^{\frac{1}{2}}$  and carry out analytic integration over coupling constant

$$E_c = \frac{-1}{2\pi} \int_0^\infty d\omega \operatorname{Tr} \left[ (-\mathbf{X}_0(i\omega))^{\frac{1}{2}} \mathbf{U}(i\omega) \left( -\boldsymbol{\tau}^{-1}(i\omega) \ln[|\mathbf{1} + \boldsymbol{\tau}(i\omega)|] + \mathbf{1} \right) \mathbf{U}(i\omega)^T (-\mathbf{X}_0(i\omega))^{\frac{1}{2}} \right]$$

$$\text{with } (-\mathbf{X}_0(i\omega))^{-\frac{1}{2}} \mathbf{H}(i\omega) (-\mathbf{X}_0(i\omega))^{-\frac{1}{2}} = \mathbf{U}(i\omega) \boldsymbol{\tau}(i\omega) \mathbf{U}^\dagger(i\omega)$$

- Complete exchange kernel can be treated (RI-EXXRP+)
- $N^5$  scaling

## RI2-dRPA

$$E_c = \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \operatorname{Tr} \left[ \mathbf{S}^{-1} \mathbf{X}_0 [\mathbf{X}_0 - \alpha \mathbf{H}_H]^{-1} \mathbf{X}_0 - \mathbf{S}^{-1} \mathbf{X}_0 \right]$$

For dRPA, with second RI approximation and  $\mathbf{S} = \mathbf{E}$ ,  $\mathbf{H}_H$  simplifies to

$$\mathbf{H}_H = \mathbf{X}_0 \mathbf{X}_0$$

With spectral representation  $\mathbf{X}_0(i\omega) = -\mathbf{V}(i\omega) \boldsymbol{\sigma}(i\omega) \mathbf{V}^\top(i\omega)$

$$E_c = \frac{1}{2\pi} \int_0^\infty d\omega \operatorname{Tr} [\ln[\mathbf{1} + \boldsymbol{\sigma}(i\omega)] - \boldsymbol{\sigma}(i\omega)]$$

- Only KS response function  $\mathbf{X}_0(i\omega)$  required
- $N^4$  scaling

Optimized-effective-potential equation for  $v_c^{\text{dRPA}}$

$$\int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}') v_c^{\text{dRPA}}(\mathbf{r}') = t_c^{\text{dRPA}}(\mathbf{r})$$

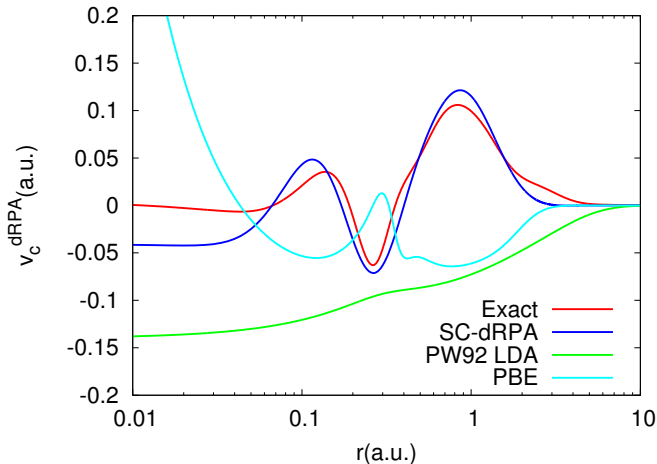
with

$$t_c^{\text{dRPA}}(\mathbf{r}) = \sum_s \int d\mathbf{r}' \frac{\delta E_c^{\text{dRPA}}}{\delta \phi_s(\mathbf{r}')} \frac{\delta \phi_s(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \sum_s \frac{\delta E_c^{\text{dRPA}}}{\delta \epsilon_s} \frac{\delta \epsilon_s}{\delta v_s(\mathbf{r})}$$

$v_c^{\text{dRPA}}$  is represented in auxiliary basis set

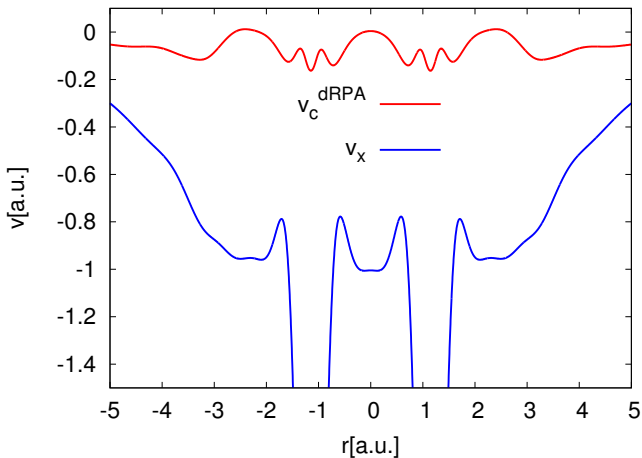
$$\mathbf{X}_0 v_c^{\text{dRPA}} = t_c^{\text{dRPA}}$$

$v_c^{\text{dRPA}}$  for neon atoms



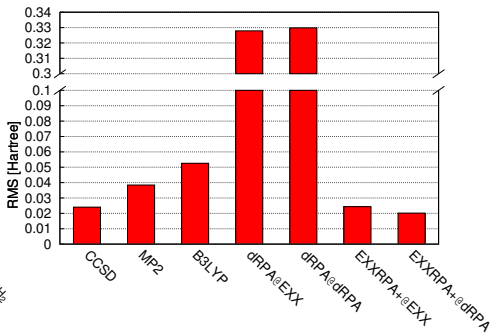
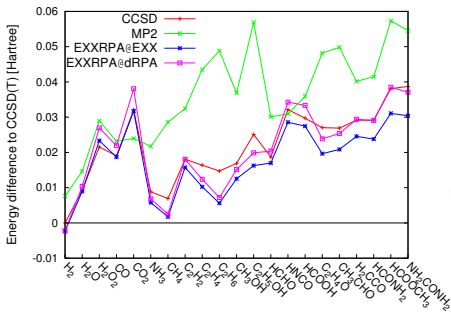
dRPA correlation potential qualitatively correct in contrast to LDA and GGA correlation potential

$v_c^{\text{dRPA}}$  for  $\text{C}_2\text{H}_2$



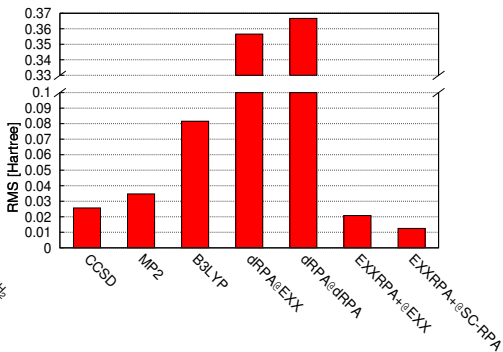
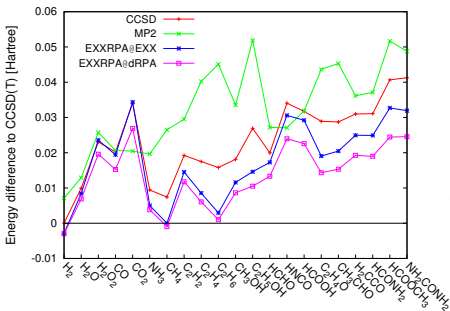
Deviations of total energies from CCSD(T) energies,  $\Delta E = E^{\text{Method}} - E^{\text{CCSD(T)}}$

Orbital basis: aug-cc-pCVTZ RI basis (for  $E_c$  and  $v_{xc}$ ): aug-cc-pVTZ/MP2-fit



Deviations of total energies from CCSD(T) energies,  $\Delta E = E^{\text{Method}} - E^{\text{CCSD(T)}}$

Orbital basis: aug-cc-pCVQZ RI basis (for  $E_c$  and  $v_{xc}$ ): aug-cc-pVQZ/MP2-fit

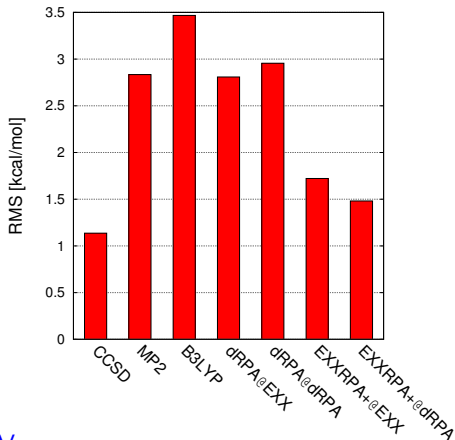




## Deviations of reaction energies from CCSD(T) reaction energies

Orbital basis: aug-cc-pCVTZ

RI basis (for  $E_x$  and  $v_{xc}$ ): aug-cc-pVTZ/MP2-fit

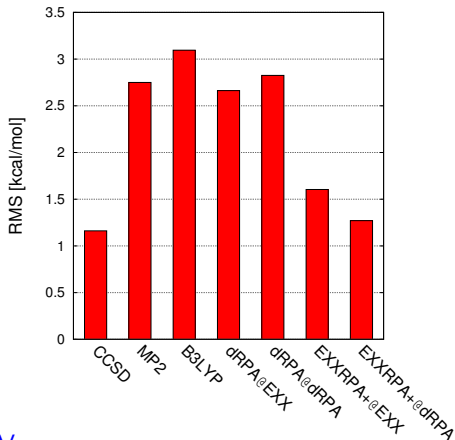


1 kcal/mol = 0.043 eV

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

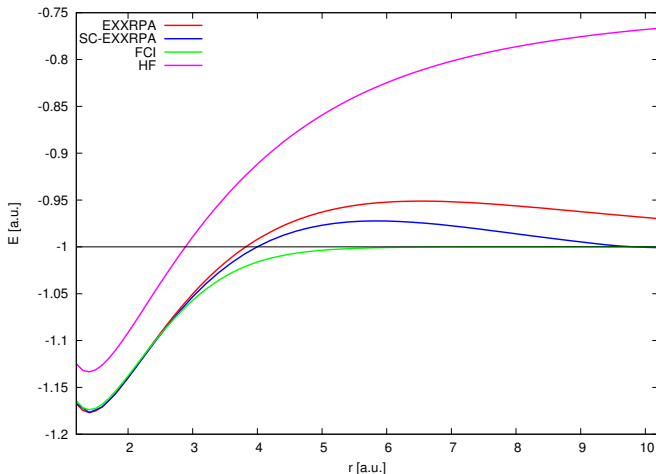
Orbital basis: aug-cc-pCVQZ

RI basis (for  $E_x$  and  $v_{xc}$ ): aug-cc-pVQZ/MP2-fit



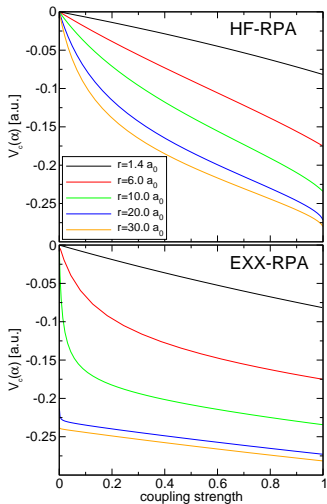
1 kcal/mol = 0.043 eV

Orbital basis: aug-cc-pCVQZ RI basis (for  $E_c$  and  $v_{xc}$ ): aug-cc-pVQZ/MP2-fit

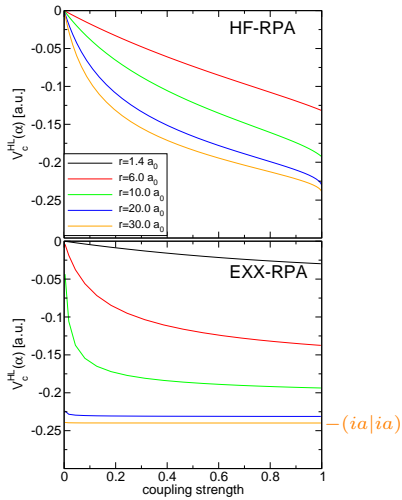


Dissociation limit of other molecules ( $CO$ ,  $N_2$ , etc.) is also treated correctly

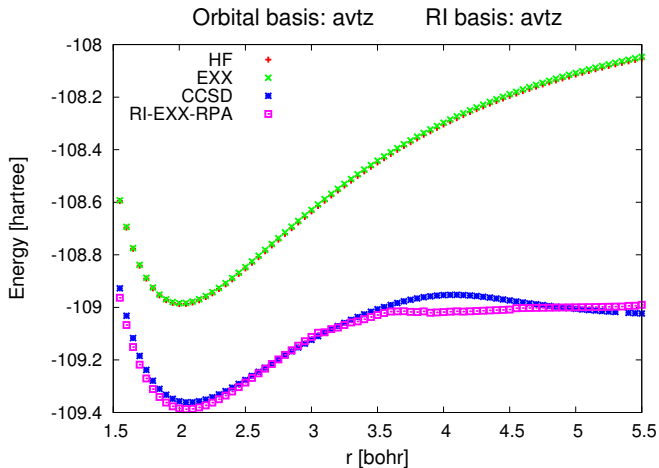
$$E_c = \int_0^1 d\alpha V_c(\alpha)$$



$V_c(\alpha)$



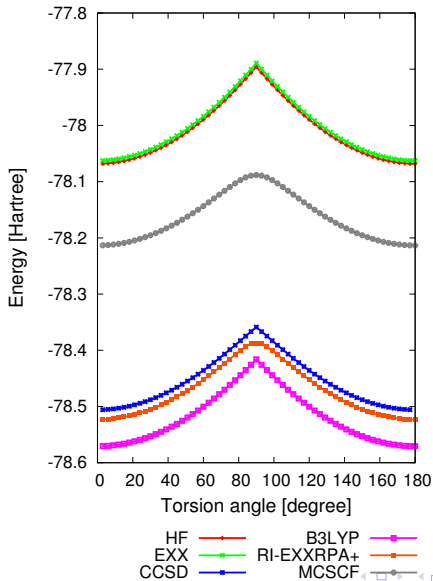
$V_c^{HL}(\alpha)$



Special treatment of singularity in  $\omega$ -Integrand (  $-\tau^{-1} \ln [|1 + \tau(i\omega)|] + 1$  )

# Twisting of ethene

Orbital basis: avqz      RI basis: avqz



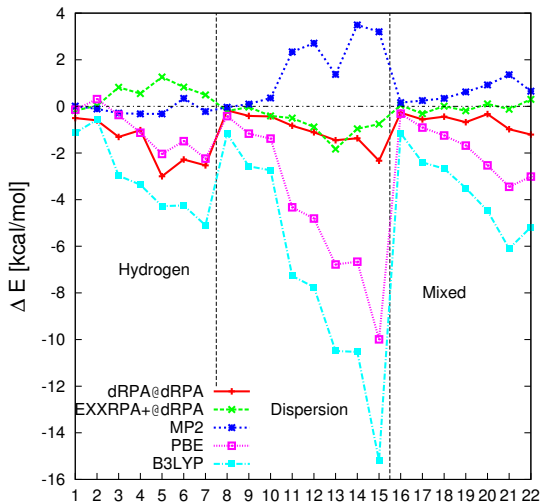
Complex	Basis	CCSD(T)	dRPA @EXX	dRPA @DRPA	EXXRPAs @EXX	EXXRPAs @dRPA	MP2	CCSD <sup>a</sup>
(NH <sub>3</sub> ) <sub>2</sub>	3	3.00	2.36	2.41	2.84	2.89	3.00	2.75
	4		2.52	2.57	2.83	2.99	3.11	
	CBS	3.15	2.62	2.64	2.81	3.02	3.18	2.88
(H <sub>2</sub> O) <sub>2</sub>	3	4.83	3.95	4.03	4.81	4.92	4.72	4.60
	4		4.25	4.33	4.91	5.07	5.02	
	CBS	5.07	4.40	4.46	4.92	5.09	5.21	4.74
(HCONH <sub>2</sub> ) <sub>2</sub>	3	15.37	13.65	13.95	15.56	15.90	15.08	14.65
	4		14.32	14.67	16.01	16.42	15.57	
	CBS	16.11	14.75	15.06	16.28	16.67	15.86	15.28
(HCOOH) <sub>2</sub>	3	17.86	15.51	16.03	18.28	18.73	17.61	17.08
	4		16.41	16.98	18.79	19.34	18.23	
	CBS	18.81	16.97	17.49	19.06	19.60	18.61	17.92
(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	3	1.38	0.99	0.99	1.44	1.33	1.47	1.04
	4		1.08	1.05	1.55	1.42	1.55	
	CBS	1.48	1.16	1.05	1.64	1.44	1.60	1.14
C <sub>2</sub> H <sub>4</sub> ...C <sub>2</sub> H <sub>2</sub>	3	1.44	1.23	1.16	1.34	1.50	1.59	1.26
	4		1.31	1.21	1.42	1.56	1.64	
	CBS	1.50	1.37	1.22	1.49	1.58	1.67	1.31
(CH <sub>4</sub> ) <sub>2</sub>	3	0.50	0.31	0.32	0.41	0.41	0.46	0.38
	4		0.35	0.36	0.44	0.44	0.48	
	CBS	0.53	0.37	0.35	0.44	0.44	0.53	0.41
RMS	3		1.19	0.97	0.19	0.39	0.13	0.45
RMS	CBS		0.93	0.73	0.19	0.37	0.15	0.51

<sup>a</sup> CBS obtained via F12-CCSD

1 kcal/mol = 0.043 eV

## Standard benchmark for non-covalent interactions

$$\Delta E = \Delta E_{\text{Method}}^{\text{Binding}} - \Delta E_{\text{CCSD(T)}}^{\text{Binding}}$$

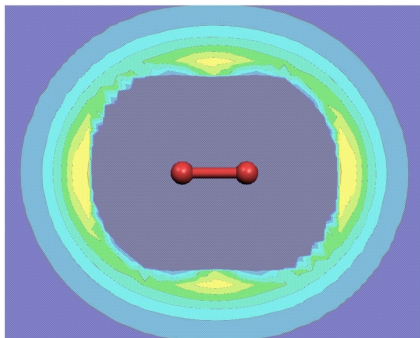
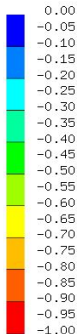
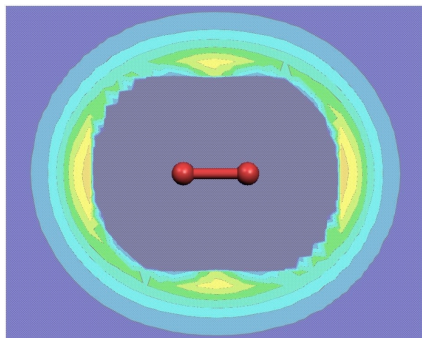


- 1  $\text{NH}_3$  ( $C_{2h}$ )
- 2  $(\text{H}_2\text{O})_2$  ( $C_s$ )
- 3  $(\text{HCOOH})_2$  ( $C_{2h}$ )
- 4  $(\text{CHONH}_2)_2$
- 5 Uracil-Uracil ( $C_{2h}$ )
- 6 2-Pyridoxine-2-Aminopyridine
- 7 AT (WC)
- 8  $(\text{CH}_4)_2$  ( $D_{3d}$ )
- 9  $(\text{C}_2\text{H}_4)_2$  ( $D_{2d}$ )
- 10 Bz- $\text{CH}_4$  ( $C_3$ )
- 11 Bz-Bz ( $C_{2h}$ )
- 12 Pyrazine-Pyrazine ( $C_s$ )
- 13 Uracil-Uracil ( $C_2$ )
- 14 Indole-Bz (stacked)
- 15 AT (stacked)
- 16  $\text{C}_2\text{H}_4 \cdots \text{C}_2\text{H}_2$  ( $C_{2v}$ )
- 17 Bz- $\text{H}_2\text{O}$  ( $C_s$ )
- 18 Bz- $\text{NH}_3$  ( $C_s$ )
- 19 Bz-HCN ( $C_s$ )
- 20 Bz-Bz ( $C_{2v}$ )
- 21 Indole-Bz (T-shaped)
- 22 Phenole-Phenole



CCSD(T)

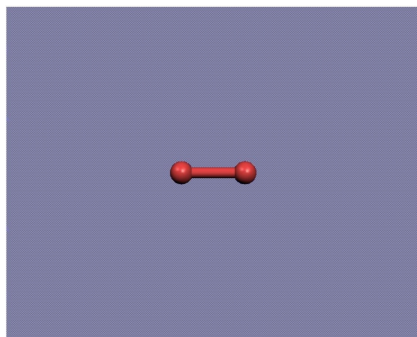
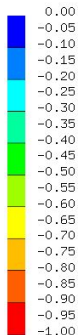
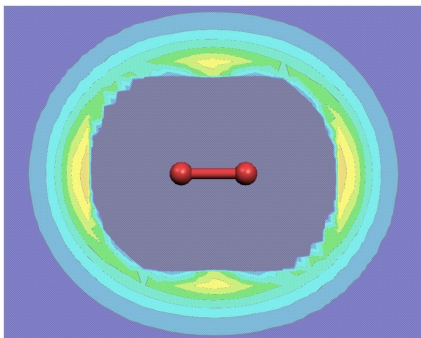
EXXRPA + @dRPA



1 kcal/mol = 0.043 eV

CCSD(T)

B3LYP



1 kcal/mol = 0.043 eV

- EXXRPAs correlation functional combines accuracy at equilibrium geometries with a correct description of dissociation (static correlation) and a highly accurate treatment of VdW interactions
- EXXRPAs correlation functional is self-interaction free
- Self-consistent dRPA yields qualitatively reasonable correlation potentials in contrast to conventional KS methods
- Promising starting point for further developments, e.g., completely self-consistent EXXRPAs method or inclusion of correlation in kernel

Orbital-dependent functionals open up fascinating new possibilities in DFT

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