Accurate density-functional methods based on correlation energy functionals within the exact-exchange random phase approximation

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Overview

Shortcomings of conventional DFT methods

- Coulomb self-interactions
  - qualitatively wrong orbital and eigenvalue spectra
    no Rydberg orbitals
    metallic instead of semiconducting band structures
  - inaccurate response properties with time-dependent DFT
- Insufficient description of static correlation
- Van der Waals interactions not described

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

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

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

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

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

KS response function $\chi_s(\mathbf{r},\mathbf{r}') = 4\sum_{i}^{\text{occ.}}\sum_{a}^{\text{unocc.}} \dfrac{\phi_i(\mathbf{r})\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_a}$

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

Plane wave methods for solid numerically stable

Gaussian basis set methods for molecules numerically demanding

- Auxiliary basis set: Electrostatic potential of Gaussian functions

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

$$v_x(\mathbf{r}) = \sum_k v_{x,k} \; f_k(\mathbf{r}) \qquad \rho_x(\mathbf{r}) = \sum_k v_{x,k} \; g_k(\mathbf{r})$$

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

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

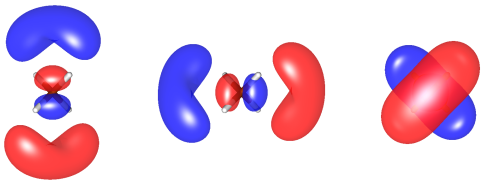
$$\langle \phi_{HOMO} | v_x | \phi_{HOMO} \rangle = \langle \phi_{HOMO} | \hat{v}_x^{\mathrm{NL}} | \phi_{HOMO} \rangle$$

- 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

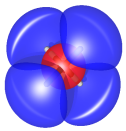
JCP **127**, 054102 (2007)

Purely analytical, numerical stable method that can easily be implemented.

EXX vs. GGA (PBE) orbitals of methane



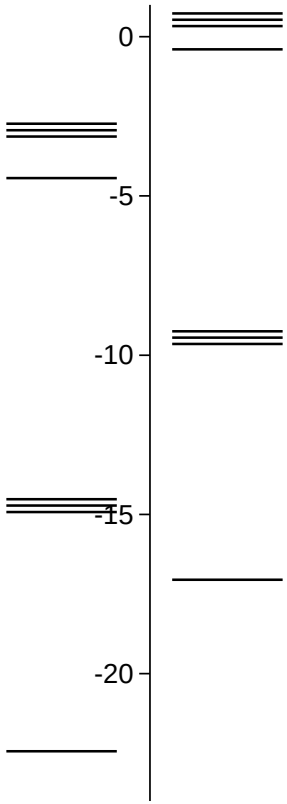
$2\,t_{2u}$ $-2.934\,\mathrm{eV}$



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

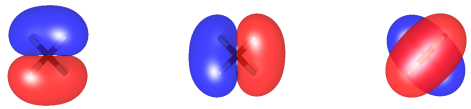
$1\,t_{2u}$ $-14.724\,\mathrm{eV}$

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



$2\,t_{2u}$ $+0.533\,\mathrm{eV}$

$3\,a_{1g}$ $-0.396\,\mathrm{eV}$

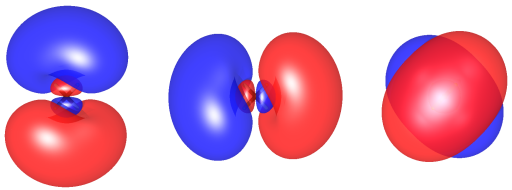


$1\,t_{2u}$ $-9.448\,\mathrm{eV}$

$2\,a_{1g}$ $-17.054\,\mathrm{eV}$

contour value 0.032

EXX vs. GGA (PBE) orbitals of methane



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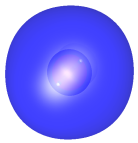

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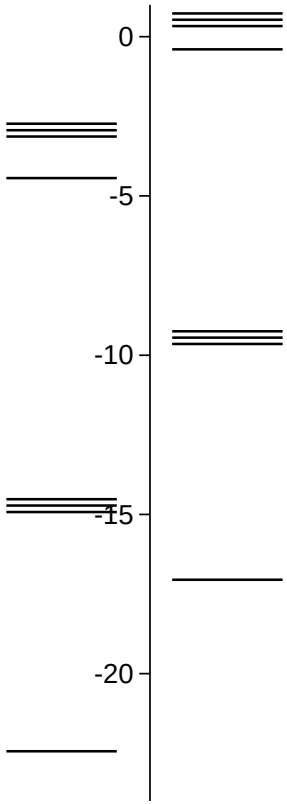

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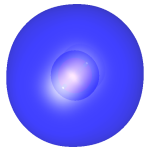


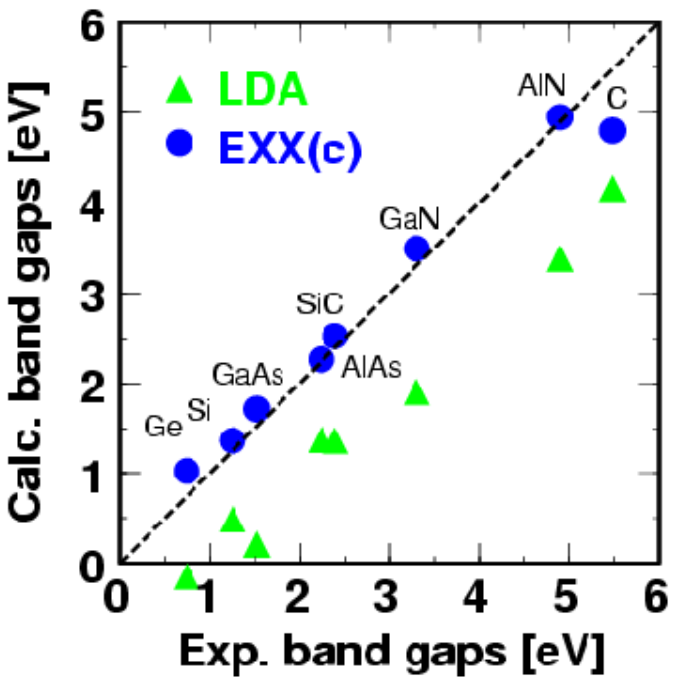
$3\,a_{1g}$ $-0.396\,\mathrm{eV}$

$1\,t_{2u}$ $-9.448\,\mathrm{eV}$

$2\,a_{1g}$ $-17.054\,\mathrm{eV}$

contour value 0.013

Band gaps of semiconductors



FLAPW vs. PP EXX band gaps

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

[a] PRB **83**, 045105 (2011)
[b] PRB **59**, 10031 (1997)

Summary EXX-KS method

EXX-KS methods solve the problem of Coulomb self-interactions and, in contrast to GGA-KS methods, yield qualitatively correct KS orbital and eigenvalue spectra.

EXX orbitals and eigenvalues are well-suited as input for TDDFT methods. Problem of treating excitations with Rydberg character is solved.

Correlation functional supplementing exact treatment of exchange required

Adiabatic-connection fluctuation-dissipation theorem for DFT correlation energy I

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

Integration of response functions along complex frequencies

$$\frac{-1}{2\pi}\int_0^\infty d\omega \int d\mathbf{r}\, d\mathbf{r}' g(\mathbf{r},\mathbf{r}')\, \chi_\alpha(\mathbf{r},\mathbf{r}',i\omega) =$$

$$= \int d\mathbf{r}\, d\mathbf{r}'\; g(\mathbf{r},\mathbf{r}') \left[\rho_2^\alpha(\mathbf{r},\mathbf{r}') - \frac{1}{2}\rho(\mathbf{r})\rho(\mathbf{r}') + \rho(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right]$$

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

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

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

Adiabatic-connection fluctuation-dissipation theorem for DFT correlation energy II

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

Integration along adiabatic connection

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

Required input quantities are $\chi_0(\boldsymbol{r},\boldsymbol{r}',\mathrm{i}\omega)$ and $\chi_\alpha(\boldsymbol{r},\boldsymbol{r}',\mathrm{i}\omega)$

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

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

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

Exact frequency-dependent exchange kernel

OEP-like equation for sum $f_{\mathsf{Hx}}(\omega, \boldsymbol{r}, \boldsymbol{r}')$ of Coulomb and EXX kernel

$$\int d\boldsymbol{r}'' \int d\boldsymbol{r}''' \; \mathbf{X}_0(\boldsymbol{r}, \boldsymbol{r}'', \omega) \; f_{\mathsf{Hx}}(\omega, \boldsymbol{r}'', \boldsymbol{r}''') \; \mathbf{X}_0(\boldsymbol{r}''', \boldsymbol{r}', \omega) = h_{\mathsf{Hx}}(\omega, \boldsymbol{r}, \boldsymbol{r}')$$

with

$$\begin{aligned} h_{\mathsf{Hx}}(\omega, \boldsymbol{r}, \boldsymbol{r}') = {} & \tfrac{1}{4} \mathbf{Y}^{\intercal}(\boldsymbol{r}) \boldsymbol{\lambda}(\omega) \left[\mathbf{A} + \mathbf{B} + \boldsymbol{\Delta} \right] \boldsymbol{\lambda}(\omega) \mathbf{Y}(\boldsymbol{r}') \\ & + \omega^2 \tfrac{1}{4} \mathbf{Y}^{\intercal}(\boldsymbol{r}) \boldsymbol{\lambda}(\omega) \boldsymbol{\epsilon}^{-1} \left[\mathbf{A} + \mathbf{B} + \boldsymbol{\Delta} \right] \boldsymbol{\epsilon}^{-1} \boldsymbol{\lambda}(\omega) \mathbf{Y}(\boldsymbol{r}) \\ & + \sum_i \sum_j \sum_a Y_{ia}(\boldsymbol{r}) \lambda_{ia}(\omega) \frac{\left\langle a \middle| \hat{v}_{\mathsf{x}}^{\mathsf{NL}} - \hat{v}_{\mathsf{x}} \middle| j \right\rangle}{\epsilon_a - \epsilon_j} \phi_i(\boldsymbol{r}) \phi_j(\boldsymbol{r}) + \cdots \\ & + \sum_a \sum_b \sum_i Y_{ia}(\boldsymbol{r}) \lambda_{ia}(\omega) \frac{\left\langle b \middle| \hat{v}_{\mathsf{x}}^{\mathsf{NL}} - \hat{v}_{\mathsf{x}} \middle| i \right\rangle}{\epsilon_b - \epsilon_i} \phi_a(\boldsymbol{r}) \phi_b(\boldsymbol{r}) + \cdots \end{aligned}$$

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

$$\Delta_{ia,jb} = \delta_{ij} \left\langle \varphi_a \middle| \hat{v}_{\mathsf{x}}^{\mathrm{NL}} - \hat{v}_{\mathsf{x}} \middle| \varphi_b \right\rangle - \delta_{ab} \left\langle \varphi_i \middle| \hat{v}_{\mathsf{x}}^{\mathrm{NL}} - \hat{v}_{\mathsf{x}} \middle| \varphi_j \right\rangle$$

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

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

$$h_{\mathsf{H}}(\boldsymbol{r}, \boldsymbol{r}', \omega) = \mathbf{Y}^{\intercal}(\boldsymbol{r}) \boldsymbol{\lambda}(\omega) \, \boldsymbol{C} \, \boldsymbol{\lambda}(\omega) \mathbf{Y}(\boldsymbol{r}) \qquad \text{with} \qquad C_{ia,jb} = (ia|jb)$$

EXXRPA method

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

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

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

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

$$\left[\epsilon^2 + \alpha\,\epsilon^{1/2}\,[\mathbf{A}+\mathbf{B}+\mathbf{\Delta}]\epsilon^{1/2}\right]\mathbf{z}_n(\alpha) = \Omega_n^2(\alpha)\left[\mathbf{1} - \alpha\,\epsilon^{-1/2}[\mathbf{A}-\mathbf{B}+\mathbf{\Delta}]\epsilon^{-1/2}\right]\mathbf{z}_n(\alpha)$$

EXX-RPA correlation energy

$$E_c = \int_0^1 d\alpha\, V_c(\alpha) \quad \text{with} \quad V_c(\alpha) = \left[\sum_n \left[\mathbf{z}_n^T(\alpha)\,\epsilon^{1/2}\,\mathbf{C}\,\epsilon^{1/2}\,\mathbf{z}_n(\alpha)\right]/\Omega_n(\alpha)\right] - \text{Tr}[\mathbf{C}]$$

- Some terms of exchange kernel neglected
- Products $\phi_i(\boldsymbol{r})\phi_a(\boldsymbol{r})$ treated as if linearly independent
- N^6 scaling

RI-EXXRPA method I

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

Representation of $\chi_0(i\omega)$, $h_x(i\omega)$ in RI basis set with respect to Coulomb norm

$$E_c = \frac{-1}{2\pi}\int_0^\infty d\omega \int_0^1 d\alpha \; Tr\Big[\mathbf{S}^{-1}\,\mathbf{X}_0\,[\mathbf{X}_0 - \alpha\,\mathbf{H}]^{-1}\mathbf{X}_0 - \mathbf{S}^{-1}\mathbf{X}_0\Big]$$

Representation of $\chi_\alpha(i\omega)$ (using $\mathbf{F}_{\mathsf{Hx}} = \mathbf{X}_0^{-1}\mathbf{H}_{\mathsf{Hc}}\mathbf{X}_0^{-1}$)

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

Orthonormalize RI basis set, i.e. make $\mathbf{S} = \mathbf{E}$, and use $\mathbf{X}_\alpha = -(-\mathbf{X}_\alpha)^{\frac{1}{2}}(-\mathbf{X}_\alpha)^{\frac{1}{2}}$

$$E_c = \frac{-1}{2\pi}\int_0^\infty d\omega \int_0^1 d\alpha \; Tr\Big[(-\mathbf{X}_0)^{\frac{1}{2}}\,\Big[-\mathbf{1} - \alpha(-\mathbf{X}_0)^{-\frac{1}{2}}\mathbf{H}(-\mathbf{X}_0)^{-\frac{1}{2}}\Big]^{-1}(-\mathbf{X}_0)^{\frac{1}{2}} - \mathbf{X}_0\Big]$$

with

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

and

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

RI-EXXRPA method II

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

Analytic integration over coupling constant

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

with

$$(-\mathbf{X}_0(\mathrm{i}\omega))^{\frac{1}{2}}\mathbf{H}(\mathrm{i}\omega)(-\boldsymbol{X}_0(\mathrm{i}\omega))^{\frac{1}{2}} = \mathbf{U}(\mathrm{i}\omega)\,\boldsymbol{\tau}(\mathrm{i}\omega)\,\mathbf{U}^{\intercal}(\mathrm{i}\omega)$$

- Complete exchange kernel can be treated
- Products $\phi_i(\boldsymbol{r})\phi_a(\boldsymbol{r})$ no longer treated as linearly independent
- N^5 scaling

RI2-dRPA method

RI-EXXRPA

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

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

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

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

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

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

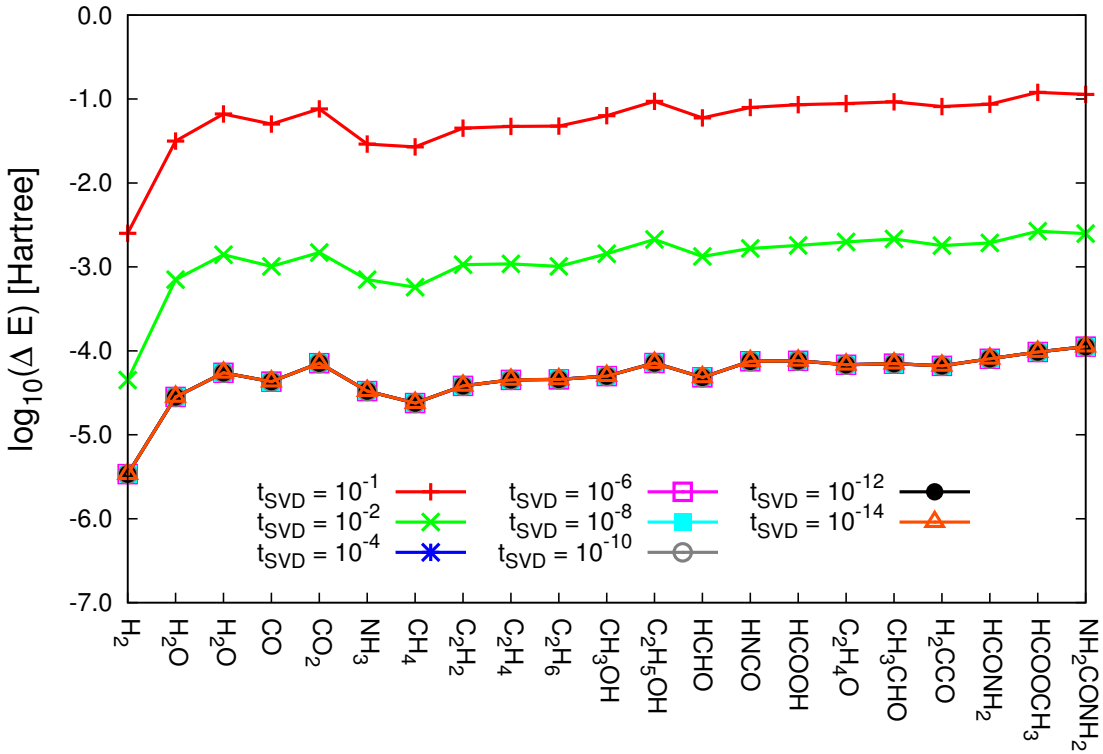
Numerical accuracy of RI-RPA methods I

Dependence on cutoff in singular value decomposition of $\mathbf{X}_0(i\omega)$

$$-\mathbf{X}_0(i\omega) = \mathbf{V}(i\omega)\,\boldsymbol{\sigma}(i\omega)\,\mathbf{V}(i\omega) \qquad [-\mathbf{X}_0(i\omega)]^{-\frac{1}{2}} = \mathbf{V}(i\omega)\,\boldsymbol{\sigma}(i\omega)^{-\frac{1}{2}}\,\mathbf{V}(i\omega)$$

$$\Delta E = E^{\text{RI-dRPA}} - E^{\text{dRPA}}$$

aug-cc-pVQZ RI and orbital basis

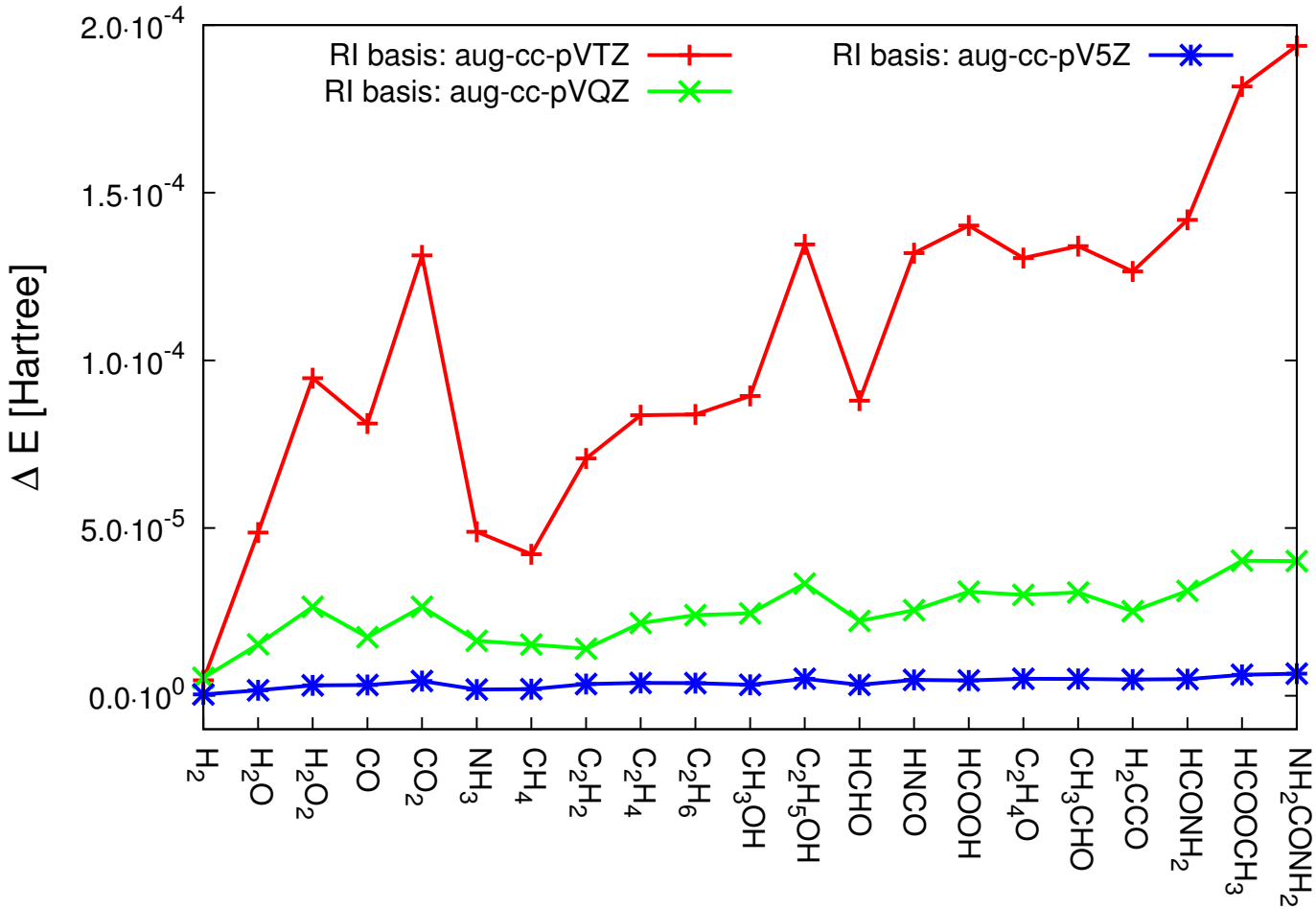


Numerical accuracy of RI-RPA methods II

Dependence on RI basis set

$$\Delta E = E^{\text{RI-dRPA}} - E^{\text{dRPA}}$$

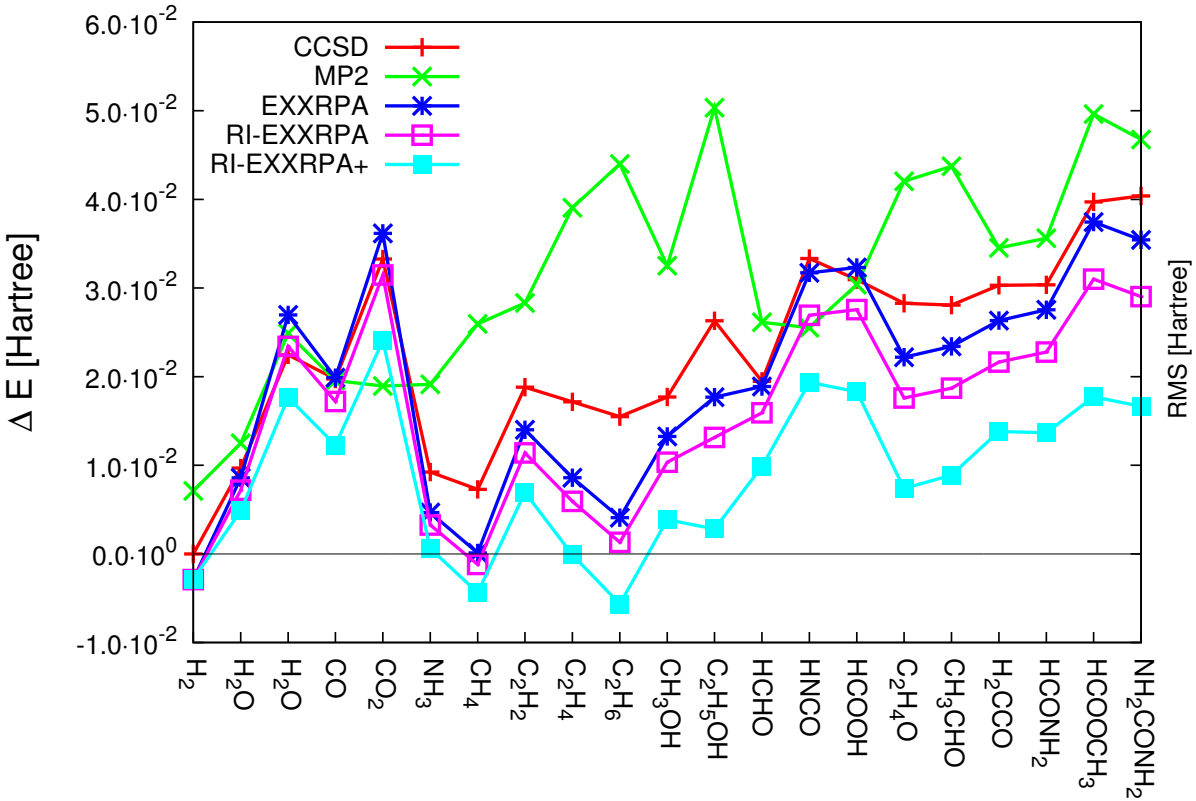
aug-cc-pVTZ orbital basis set

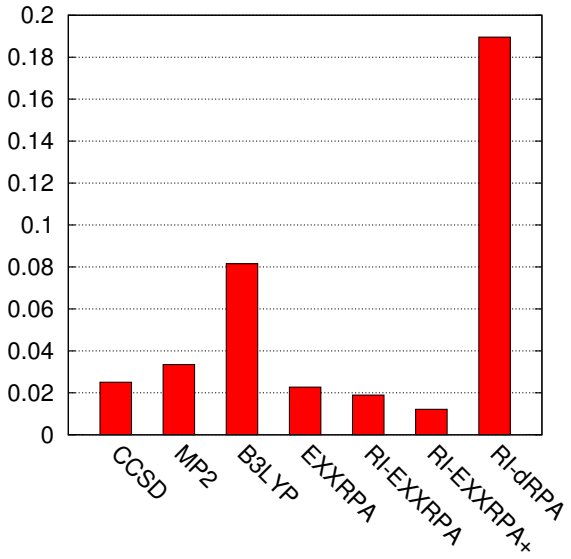


Results EXXRPA correlation methods I

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

Orbital basis: avqz RI basis:avqz

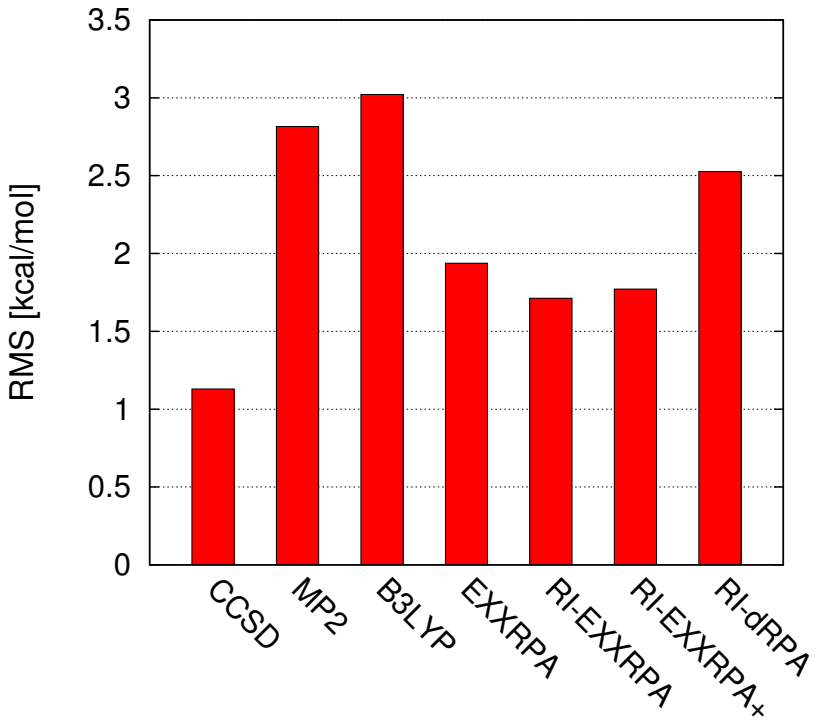




Results EXXRPA correlation methods II

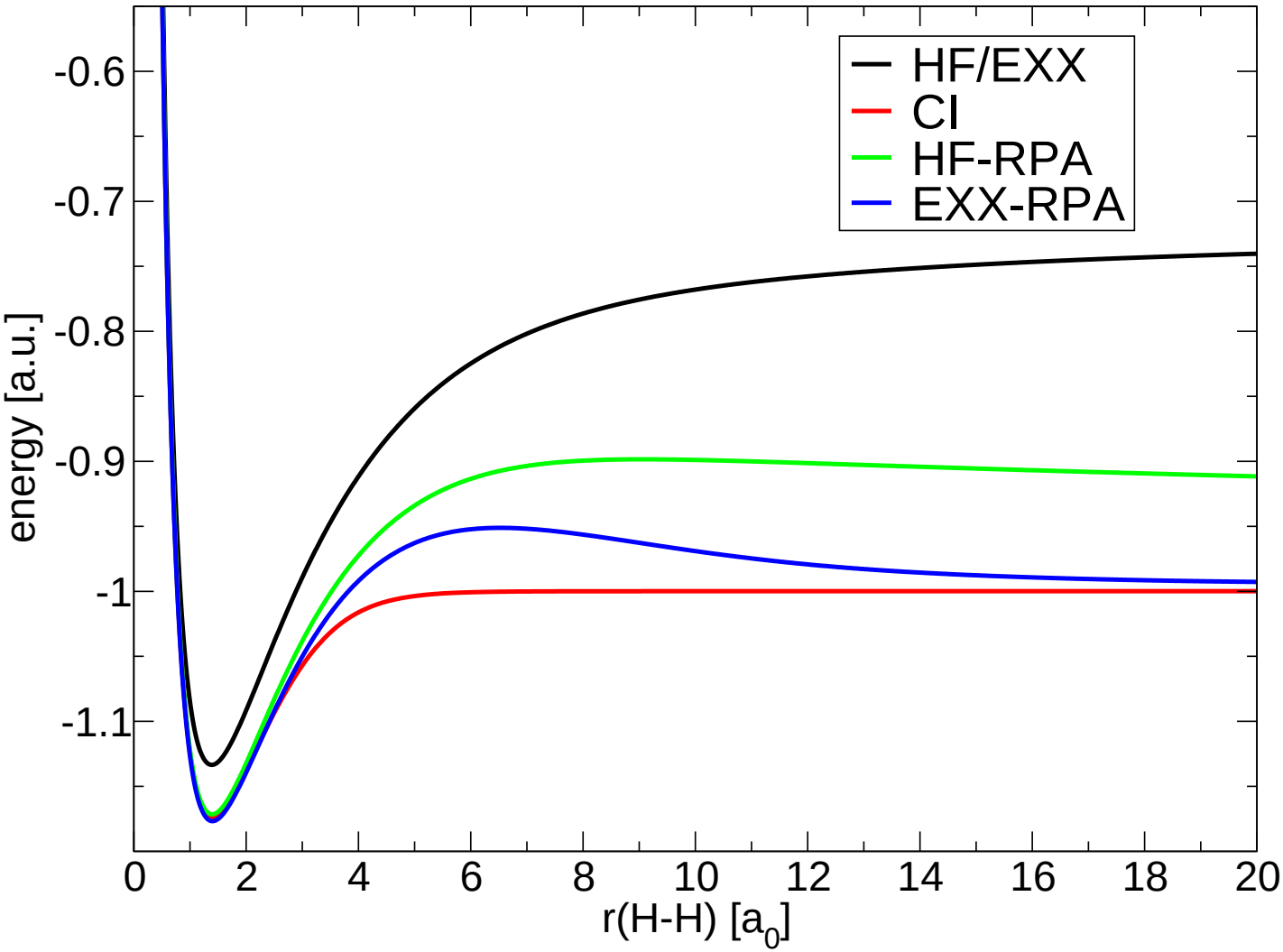
Deviations of reaction energies from CCSD(T) reaction energies

Orbital basis: avqz RI basis: avqz



Dissociation of H_2

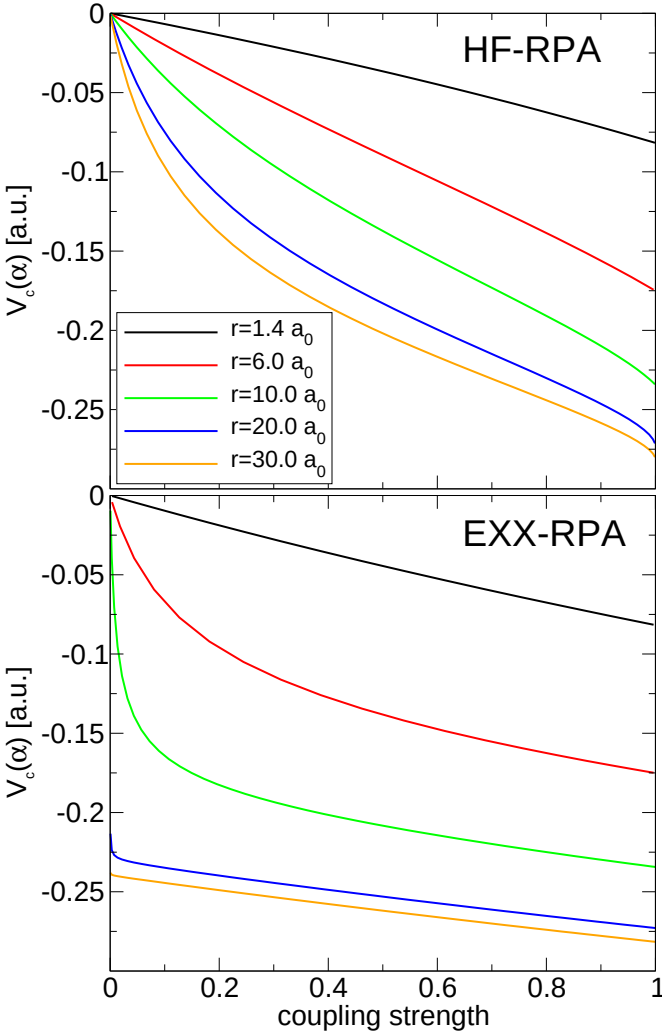
basis set: aug-cc-pVQZ



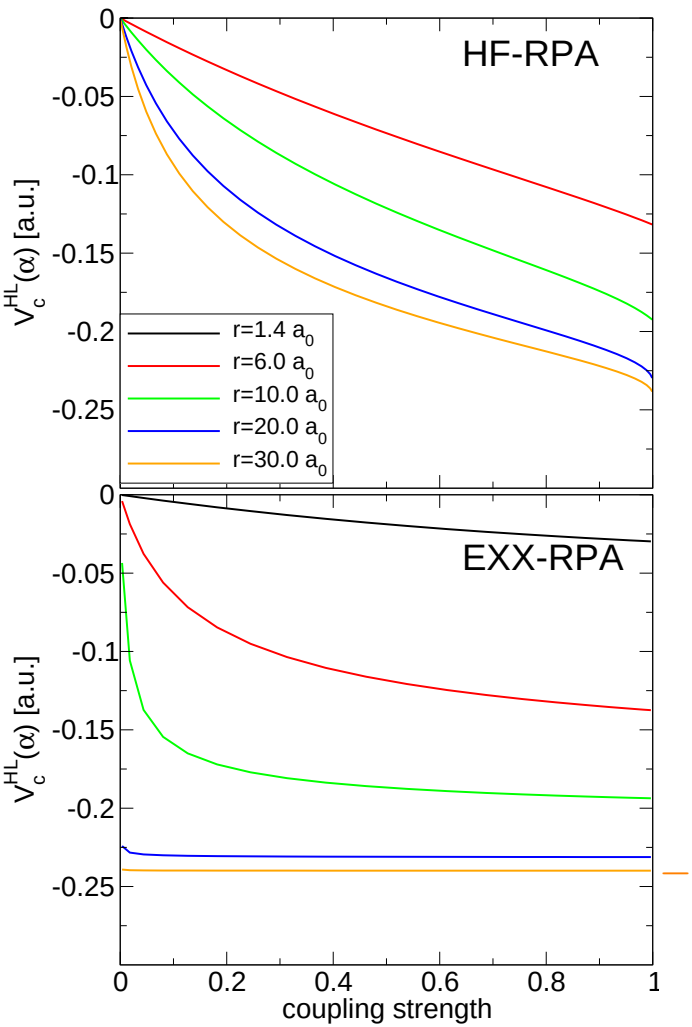
Dissociation limit of other molecules (CO, N_2, etc.) is also treated correctly

Coupling constant integrand

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



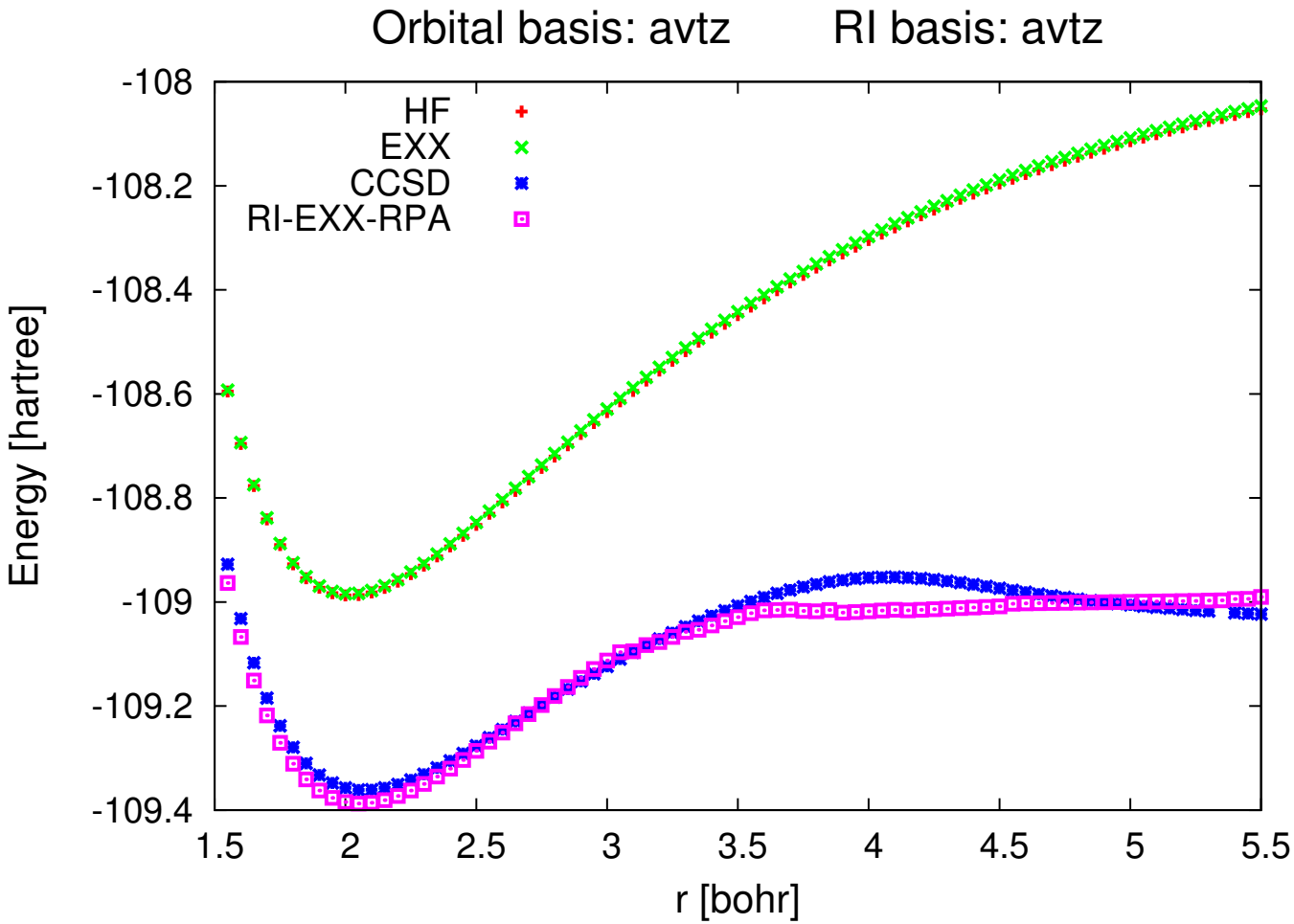
$V_c(\alpha)$



$V_c^{\mathrm{HL}}(\alpha)$

$-(ia|ia)$

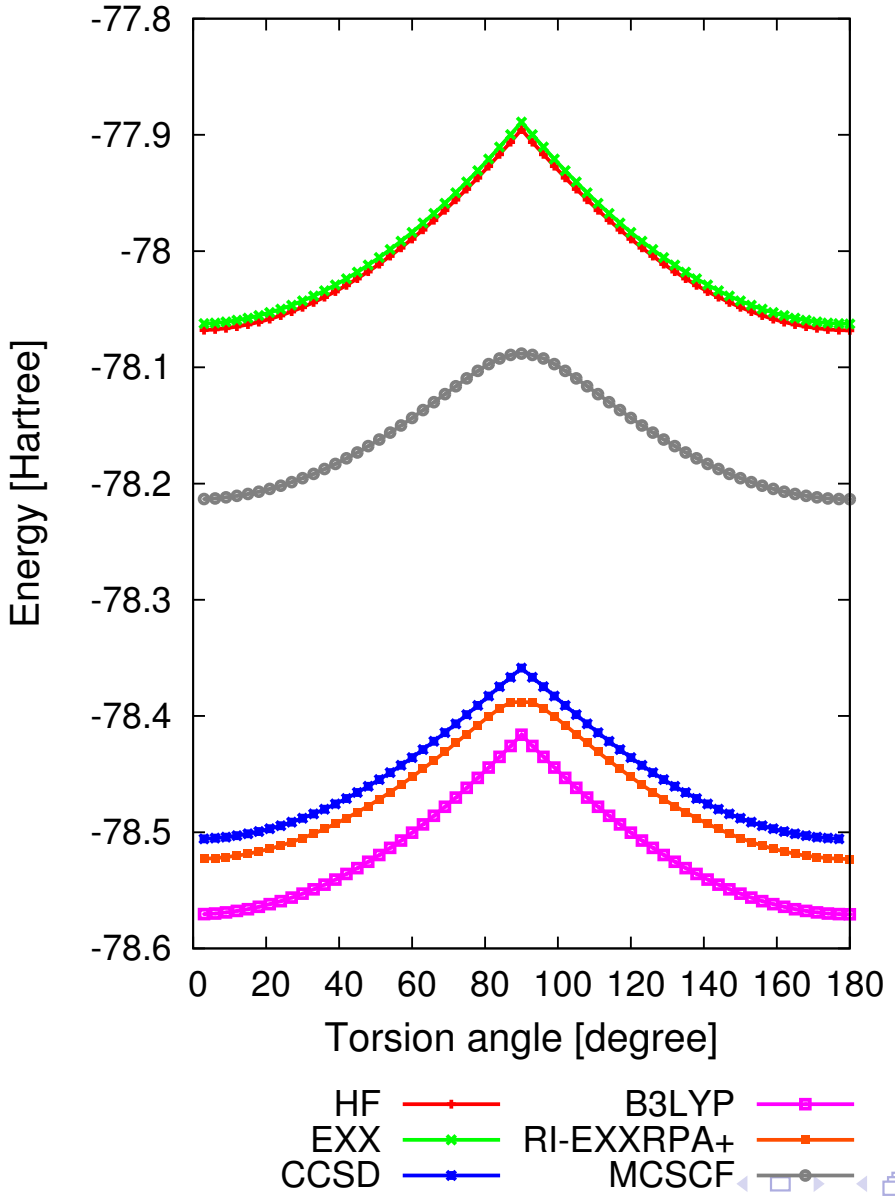
Dissociation of N_2



Special treatment of singularity in ω-Integrand ($-\boldsymbol{\tau}^{-1} \ln\left[\,|\mathbf{1} + \boldsymbol{\tau}(\mathrm{i}\omega)|\,\right] + 1$)

Twisting of ethene

Orbital basis: avqz RI basis: avqz



RI-EXXRPA for noncovalent bonds

Binding energies in kcal/mol

Complex	Basis	Reference	RI-EXXRPA	RI-EXXRPA+	RI-dRPA	TPSS-RI-dRPA	MP2	F12-CCSD
$(NH_3)_2$	3		2.54	2.76	2.33		3.00	
	4		2.61	2.83	2.46		3.11	
	CBS	3.15	2.70	2.92	2.58	2.74	3.18	2.88
$(H_2O)_2$	3		4.29	4.55	3.73		4.72	
	4		4.60	4.86	4.24		5.02	
	CBS	5.07	4.81	5.06	4.59	4.52	5.21	4.74
$(HCONH_2)_2$	3		14.87	15.27	13.43		15.08	
	4		15.42	15.84	14.23		15.57	
	CBS	16.11	15.77	16.21	15.28	15.42	15.86	15.28
$(HCOOH)_2$	3		17.40	17.90	15.25		17.61	
	4		18.06	18.46	16.24		18.23	
	CBS	18.81	18.50	18.81	16.91	17.91	18.61	17.92
$(C_2H_4)_2$	3		1.04	1.14	0.93		1.47	
	4		1.13	1.24	1.04		1.55	
	CBS	1.48	1.19	1.33	1.13	1.20	1.60	1.14
$C_2H_4\cdots C_2H_2$	3		1.34	1.45	1.21		1.59	
	4		1.37	1.46	1.26		1.64	
	CBS	1.50	1.41	1.49	1.31	1.27	1.67	1.31
$(CH_4)_2$	3		0.30	0.37	0.29		0.46	
	4		0.34	0.36	0.33		0.48	
	CBS	0.53	0.36	0.34	0.35	0.40	0.49	0.41
RMS	3		0.83	0.55	1.80		0.61	
RMS	4		0.50	0.25	1.29		0.31	
RMS	CBS		0.29	0.13	0.94	0.52	0.15	0.51

– Geometries from test set of Jurečka, P.; Šponer, J.; Černý, J.; Hobza, P.; *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985
– Reference: CBS CCSD(T) values from Takatani, T.; Hohenstein, E. G.; Malagoli, M.; Marshall, M. S.; Sherrill, C. D.; *J. Chem. Phys.* **2010**, *132*, 144104

Hartree-Fock based RPA

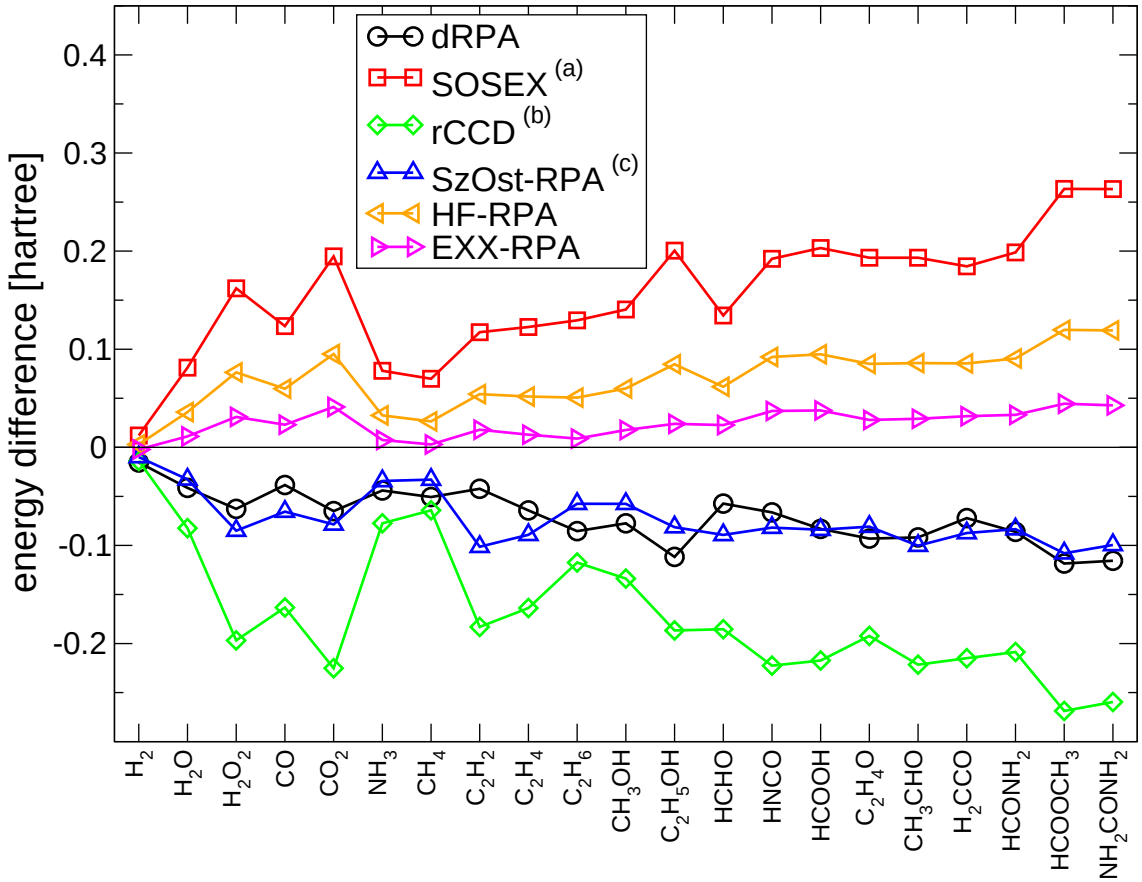
$$-\frac{1}{4\pi}\sum_{pqrs}\langle pr||qs\rangle\int_0^\infty d\omega\left[\chi_{pq,rs}(i\omega)-\chi^{\mathrm{HF}}_{pq,rs}(i\omega)\right]$$

$$\begin{aligned}
&= V_{ee}-V_{ee}^{\mathrm{HF}} - \frac{1}{4}\int d\mathbf{r}d\mathbf{r}'\left[\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{\rho^{\mathrm{HF}}(\mathbf{r})\rho^{\mathrm{HF}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\\
&+\frac{1}{4}\int d\mathbf{r}d\mathbf{r}'\left[\frac{\rho(\mathbf{r}',\mathbf{r})\rho(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{\rho^{\mathrm{HF}}(\mathbf{r}',\mathbf{r})\rho^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\\
&+\frac{1}{4}\int d\mathbf{r}d\mathbf{r}'\frac{\delta(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{4}\int d\mathbf{r}d\mathbf{r}'\frac{\delta(\mathbf{r}-\mathbf{r}')\rho^{\mathrm{HF}}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\\
&-\frac{1}{4}\int d\mathbf{r}d\mathbf{r}'\sum_q\frac{\phi_q^\dagger(\mathbf{r}')\phi_q(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{4}\int d\mathbf{r}d\mathbf{r}'\sum_q\frac{\phi_q^\dagger(\mathbf{r}')\phi_q(\mathbf{r}')\rho^{\mathrm{HF}}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}$$

Starting formula of HF based RPA, i.e., expression of HF based correlation energy via fluctuation-dissipation formula, is approximate

EXX-RPA vs. HF based RPA I

Deviations of total energies from CCSD(T) correlation energies (aug-cc-pVTZ basis set)



(a) A. Grüneis, M. Marsman, J. Harl, L. Schimka, and G. Kresse, J. Chem. Phys. **131**, 154115 (2009).
(b) A. D. MacLachlan and M. A. Ball, Rev. Mod. Phys. **36**, 844 (1964).
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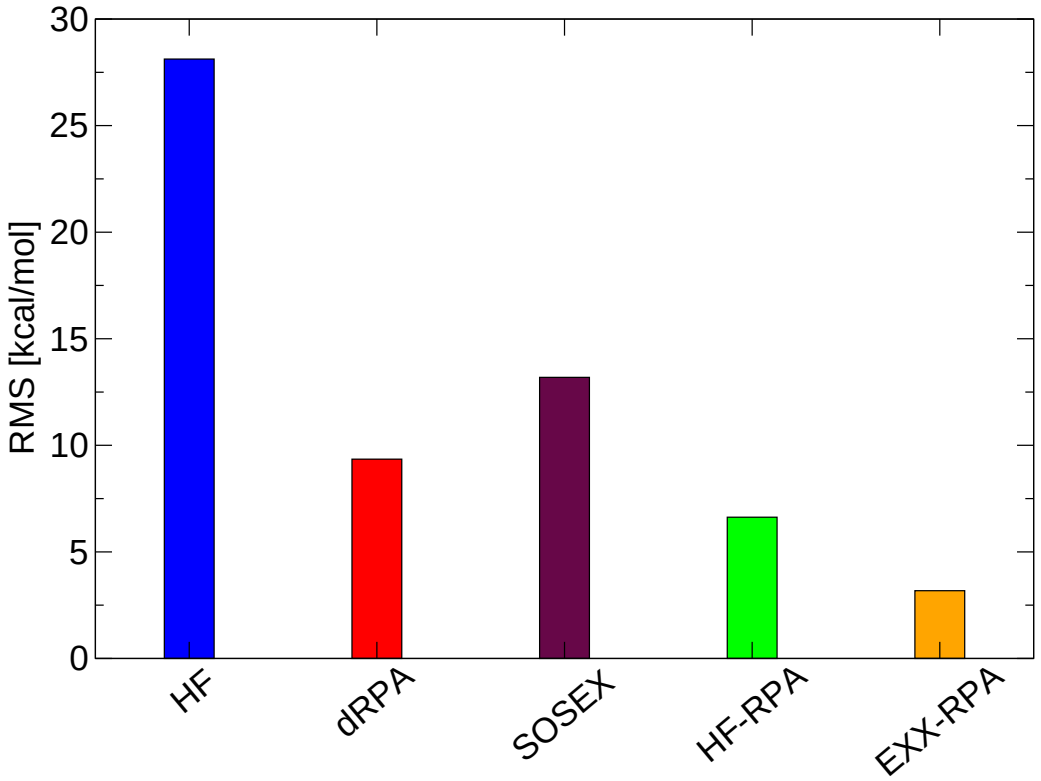
EXX-RPA vs. HF based RPA II

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

rCCD and SzOst-RPA yield distinctively larger deviations
(larger deviations than HF)

Summary EXX-RPA

- EXX-RPA correlation functional combines accuracy at equilibrium geometries with a correct description of dissociation (static correlation) and a highly accurate treatment of VdW interactions

- Promising starting point for further developments, e.g. inclusion of correlation in KS potential or in kernel

Orbital-dependent functionals open up fascinating new possibilities in DFT

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