Density-functional methods for electronic systems at finite temperatures

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Overview

Finite-temperature density-functional theory
DFT for grand canonical ensembles

Problem: μ- and T-dependent exchange-correlation functionals required

Approach: Orbital-dependent, finite-temperature exchange-correlation functionals

First step: Temperature-dependent exact-exchange formalism,
i.e., exchange energy and Kohn-Sham exchange potential are treated exactly

Orbital-dependent functionals
Historic development of DFT

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 OEP equation

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

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

Plane wave methods for solid numerically stable

Gaussian basis set methods for molecules numerically demanding

- Auxiliary basis set: Electrostatic potential of Gaussian functions

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

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

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

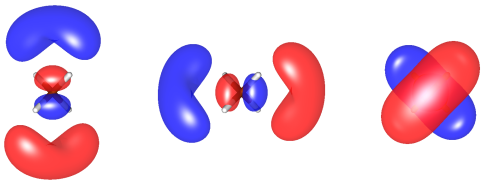
$$\langle \phi_{HOMO}|v_x|\phi_{HOMO}\rangle = \langle \phi_{HOMO}|\hat{v}_x^{\mathrm{NL}}|\phi_{HOMO}\rangle$$

- 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

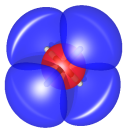
JCP **127**, 054102 (2007)

By preprocessing of auxiliary basis set and singular value decomposition of response function, EXX calculations with standard **contracted** orbital basis sets (aug-cc-pCVQZ) possible

EXX vs. GGA (PBE) orbitals of methane



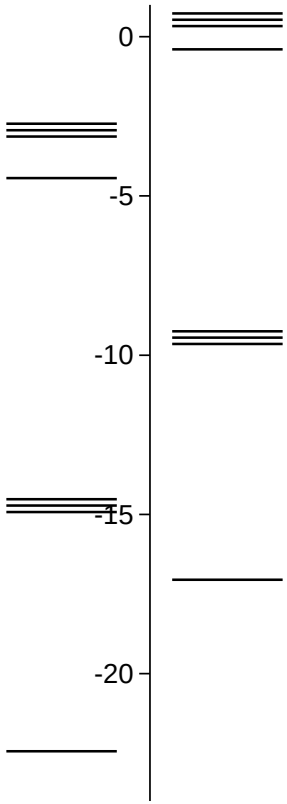
$2\,t_{2u}$ $-2.934\,\mathrm{eV}$



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

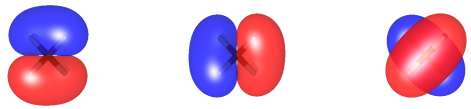
$1\,t_{2u}$ $-14.724\,\mathrm{eV}$

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



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

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

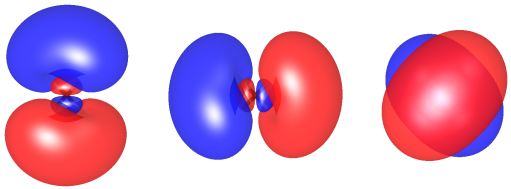


$1\,t_{2u}$ $-9.448\,\mathrm{eV}$

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

contour value 0.032

EXX vs. GGA (PBE) orbitals of methane



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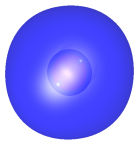

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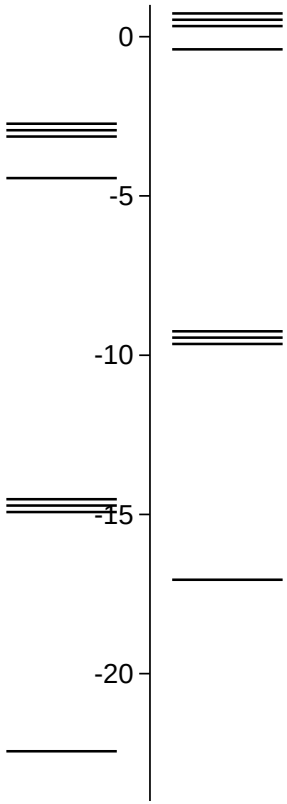

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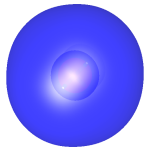


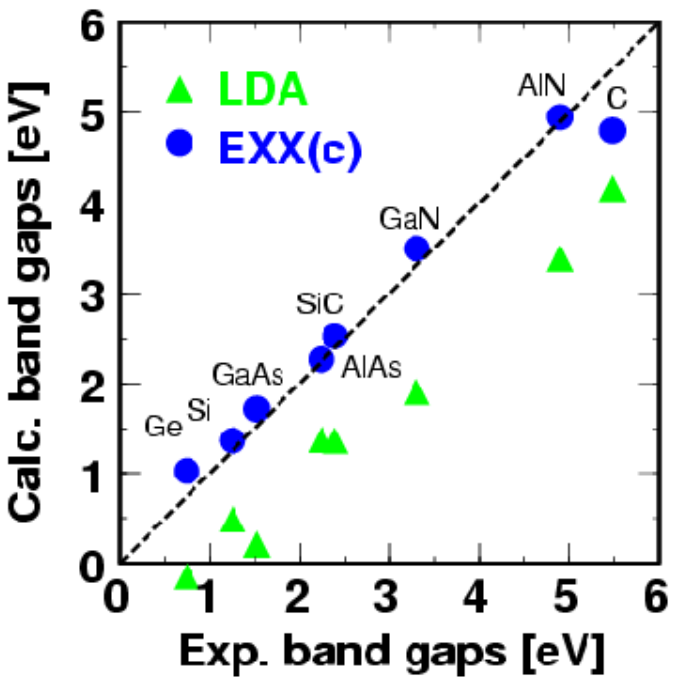
$3\,a_{1g}$ $-0.396\,eV$

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

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

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

Electronic structure methods for grand canonical ensembles

Electronic Schrödinger equation: $[\hat{T} + \hat{V}_{ee} + \hat{v}]\Psi_{N,n} = E_{N,n}\Psi_{N,n}$

$T = 0$	finite T
$E_{N,0} = \min_{\Psi \to N} E[\Psi]$	$\Omega_{v,T,\mu} = \min_{\hat{\Gamma}} \Omega[\hat{\Gamma}]$
$E[\Psi] = \langle \Psi \vert \hat{H} \vert \Psi \rangle$	$\Omega[\hat{\Gamma}] = \mathrm{Tr}\ \hat{\Gamma}\left[\hat{H} + kT \ln \hat{\Gamma} - \mu \hat{N}\right]$
$E_{N,0} = E[\Psi_0]$	$\Omega_{v,T,\mu} = \Omega[\hat{\Gamma}_{v,T,\mu}]$
$\hat{H}\Psi_0 = E_{N,0}\Psi_0$	$\hat{\Gamma}_{v,T,\mu} = \sum_N \sum_n \frac{\exp[(-1/kT)(E_{N,n} - \mu N)]}{Z_{v,T,\mu}} \vert \Psi_{N,n} \rangle \langle \Psi_{N,n} \vert$
	$Z_{v,T,\mu} = \sum_N \sum_n \exp[(-1/kT)(E_{N,n} - \mu N)]$

$$T = 0$$

$$\Phi_0 \longleftrightarrow \hat{T} + \hat{v}_s \longleftrightarrow \rho_0 \longleftrightarrow \hat{T} + \hat{V}_{ee} + \hat{v} \longleftrightarrow \Psi_0$$

$$v_S(\boldsymbol{r}) = v(\boldsymbol{r}) + v_{\mathsf{H}}\left([\rho_0];\boldsymbol{r}\right) + v_{xc}\left([\rho_0];\boldsymbol{r}\right)$$

finite T

$$\hat{\Gamma}^{\mathsf{KS}}_{v_S,T,\mu} \longleftrightarrow \hat{T} + \hat{v}_s \longleftrightarrow \rho_{v,T,\mu} \longleftrightarrow \hat{T} + \hat{V}_{ee} + \hat{v} \longleftrightarrow \hat{\Gamma}_{v,T,\mu}$$

$$v_s(\boldsymbol{r}) = v(\boldsymbol{r}) + v_{\mathsf{H}}\left([\rho_{v,T,\mu}];\boldsymbol{r}\right) + v_{xc}\left([\rho_{v,T,\mu}],T,\boldsymbol{r}\right)$$

Basic density-functionals for grand canonical ensembles

$T = 0$	finite T

$$F[\rho] = \min_{\Psi \to \rho} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\mathsf{ee}} | \Psi \rangle \right\} \to \Psi[\rho]$$

$$F[\rho, T] = \min_{\Gamma \to \rho} \left\{ \mathsf{Tr}\, \hat{\Gamma} \left[\hat{T} + \hat{V}_{\mathsf{ee}} + kT \ln \hat{\Gamma} \right] \right\} \to \Gamma[\rho, T]$$

$$T_s[\rho] = \min_{\Psi \to \rho} \left\{ \langle \Psi | \hat{T} | \Psi \rangle \right\} \to \Phi[\rho]$$

$$T_s[\rho, T] = \min_{\Gamma \to \rho} \left\{ \mathsf{Tr}\, \hat{\Gamma} \left[\hat{T} + kT \ln \hat{\Gamma} \right] \right\} \to \Gamma^{\mathsf{KS}}[\rho, T]$$

$$U[\rho] + E_x[\rho] = \langle \Phi | \hat{V}_{\mathsf{ee}} | \Phi \rangle$$

$$U[\rho] + E_x[\rho, T] = \mathsf{Tr}\, \Gamma^{\mathsf{KS}}[\rho, T] \hat{V}_{\mathsf{ee}}$$

$$E_c[\rho] = F[\rho] - T_s[\rho] - U[\rho] - E_x[\rho]$$

$$E_c[\rho, T] = F[\rho, T] - T_s[\rho, T] - U[\rho] - E_x[\rho, T]$$

Temperature-dependent exact-exchange energy

$$[\hat{T} + v_s]\Phi_{N,n} = E^{\mathsf{KS}}_{N,n}\Phi_{N,n}$$

$$\hat{\Gamma}^{\mathsf{KS}}_{v_s,T,\mu} = \sum_N \sum_n \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}} \, |\Phi_{N,n}\rangle\langle\Phi_{N,n}|$$

$$T_s = \mathsf{Tr}\,\Gamma^{\mathsf{KS}}_{v_s,T,\mu}[T + kT\ln\Gamma^{\mathsf{KS}}_{v_s,T,\mu}] = \sum_i \left[f_i\langle i|-\tfrac{1}{2}\vec{\nabla}^2|i\rangle + kT\,[f_i \ln f_i + (1-f_i)\ln(1-f_i)]\right]$$

$$U + E_x = \mathsf{Tr}\,\Gamma^{\mathsf{KS}}_{v_s,T,\mu}\hat{V}_{\mathsf{ee}} = \frac{1}{2}\sum_i \sum_j g_{ij}\,[\langle ij|ij\rangle - \langle ij|ji\rangle]$$

$$g_{ij} = f_i\, f_j \qquad\qquad f_i = \frac{1}{1 + e^{(1/kT)(\varepsilon_i - \mu)}}$$

$$\int d\boldsymbol{r}'\; X_s(T,N,\boldsymbol{r},\boldsymbol{r}')\; v_x(T,N,\boldsymbol{r},\boldsymbol{r}') = t_x(T,N,\boldsymbol{r})$$

KS response function

$$X_s(T,N,\boldsymbol{r},\boldsymbol{r}') = \frac{\delta\rho(\boldsymbol{r})}{\delta v_s(\boldsymbol{r}')}$$

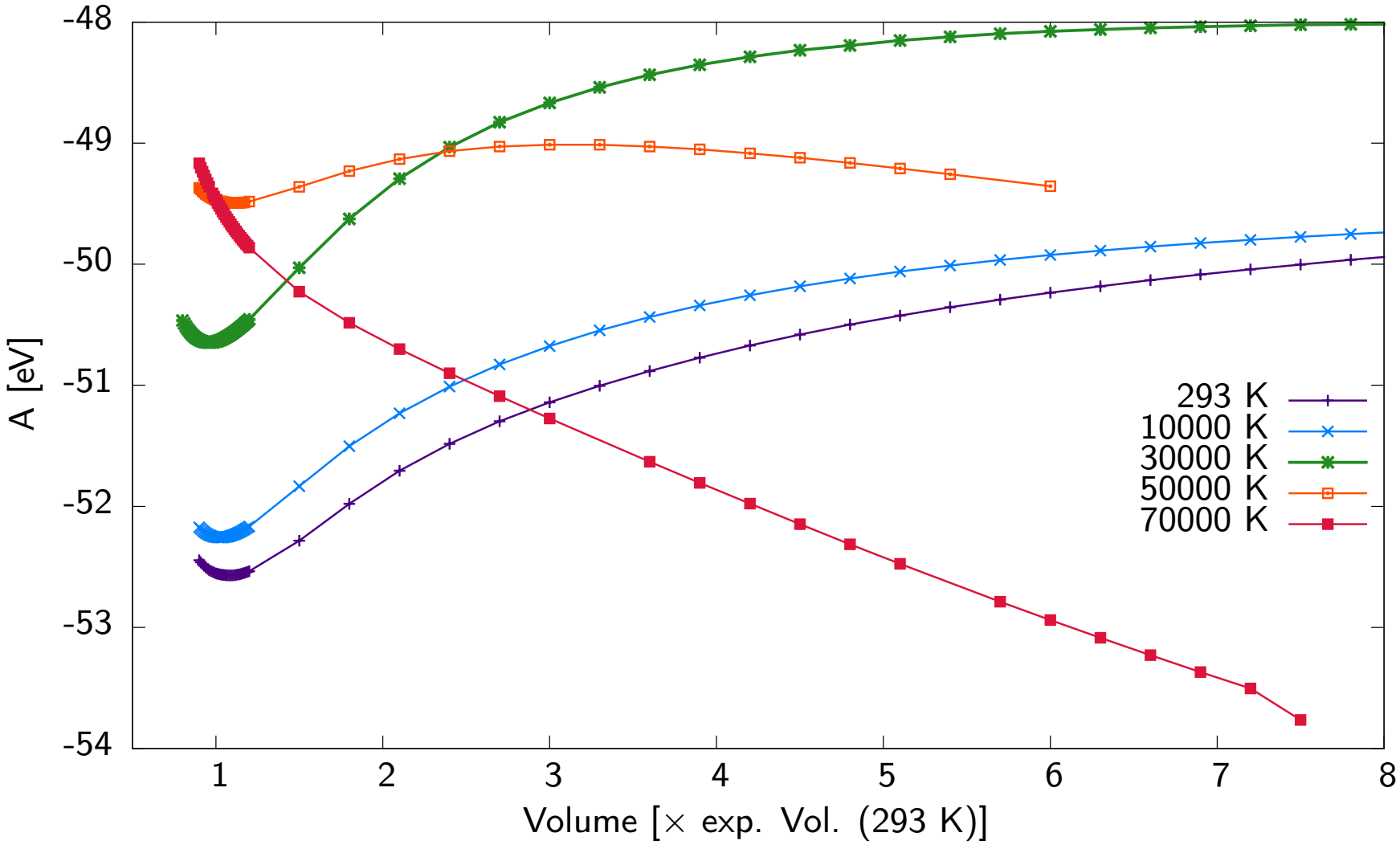
$$= \sum_i f_i \sum_{j\neq i}\left[\frac{\phi_i^\dagger(\mathbf{r})\,\phi_j(\mathbf{r})\,\phi_j^\dagger(\mathbf{r}')\,\phi_i(\mathbf{r}')}{\varepsilon_i-\varepsilon_j} + \text{c.c.}\right] + \sum_i \phi_i^\dagger(\mathbf{r})\,\phi_i(\mathbf{r})\,\frac{\delta f_i}{\delta v_s(\mathbf{r}')}$$

Right-hand side

$$t_x(T,N,\mathbf{r}) = \sum_i f_i \sum_{j\neq i}\left[\frac{\langle\phi_i|\hat{v}_x^{\mathrm{NL}}|\phi_j\rangle\phi_j^\dagger(\mathbf{r})\,\phi_i(\mathbf{r})}{\varepsilon_i-\varepsilon_j} + \text{c.c.}\right] + \sum_i \langle\phi_i|\,\hat{v}_x^{\mathrm{NL}}\,|\phi_i\rangle\,\frac{\delta f_i}{\delta v_s(\mathbf{r})}$$

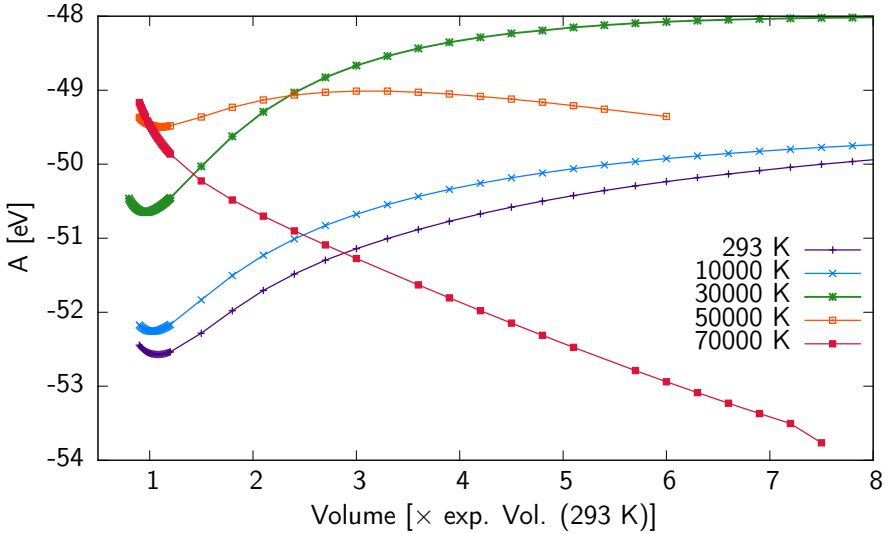
Test application bulk aluminum I

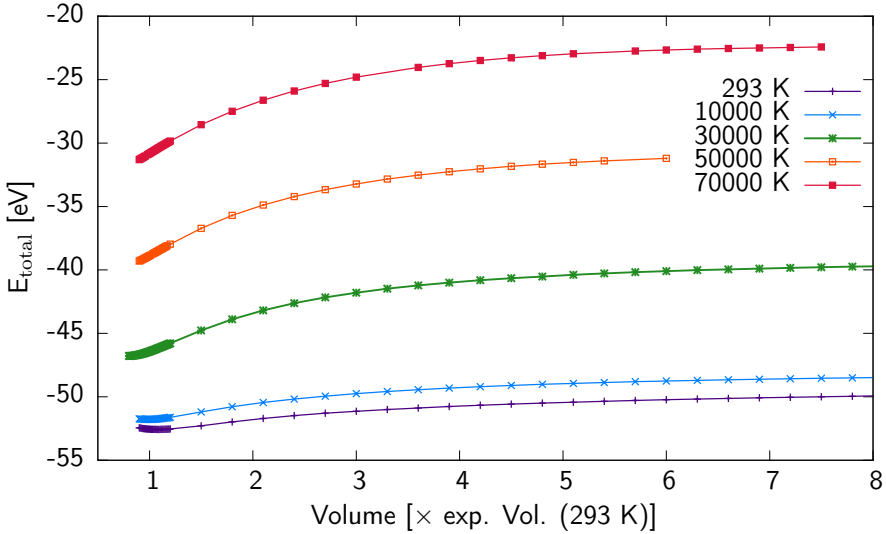
Free energy $A = E - TS$ for bulk Al (fcc lattice, 6×6×6 k-points)

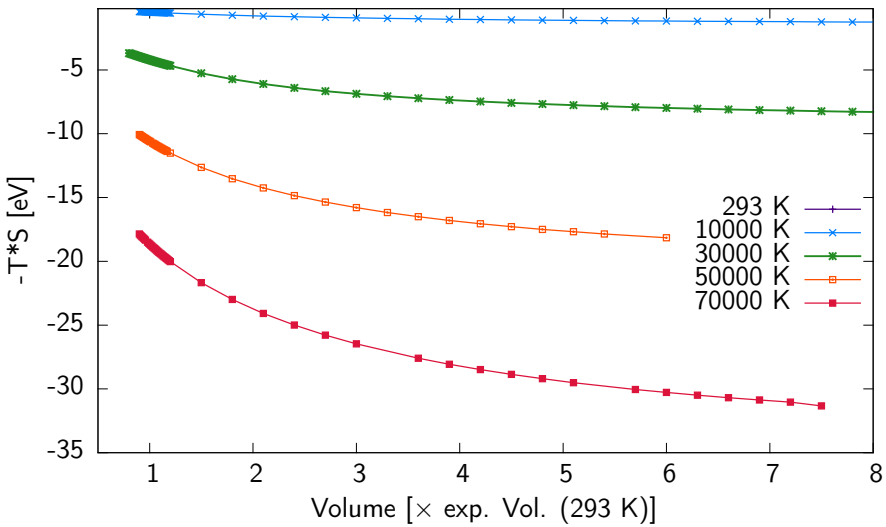


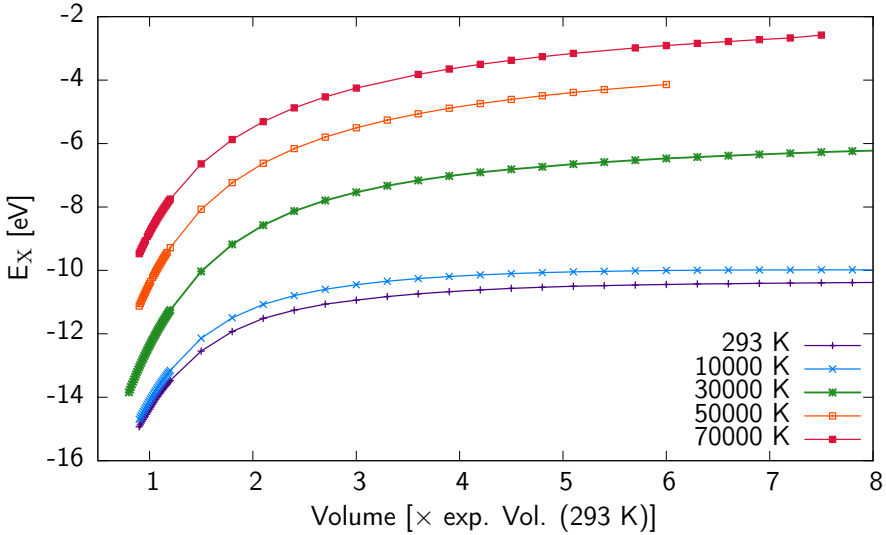
Test application bulk aluminum II

Contributions to free energy $A = E - TS$





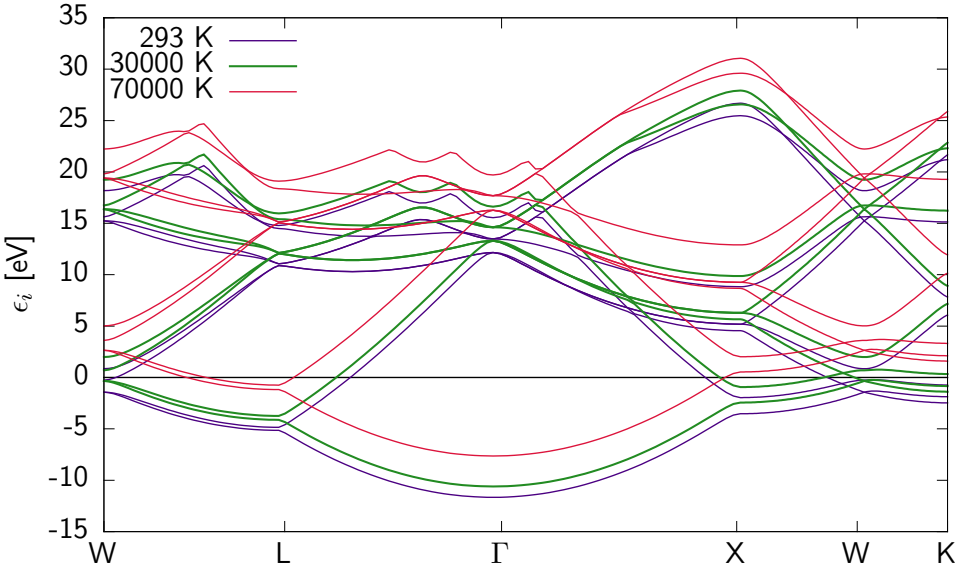




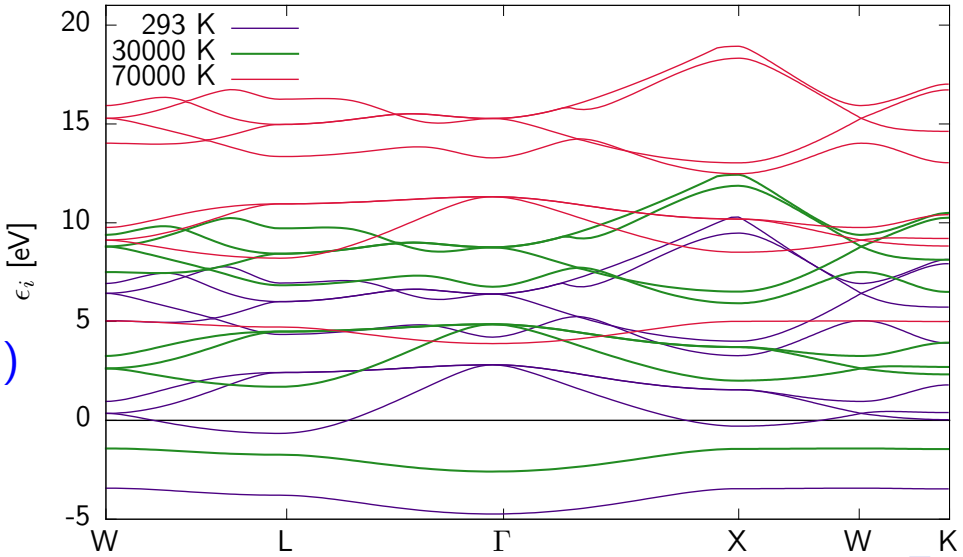
Test application bulk aluminum III

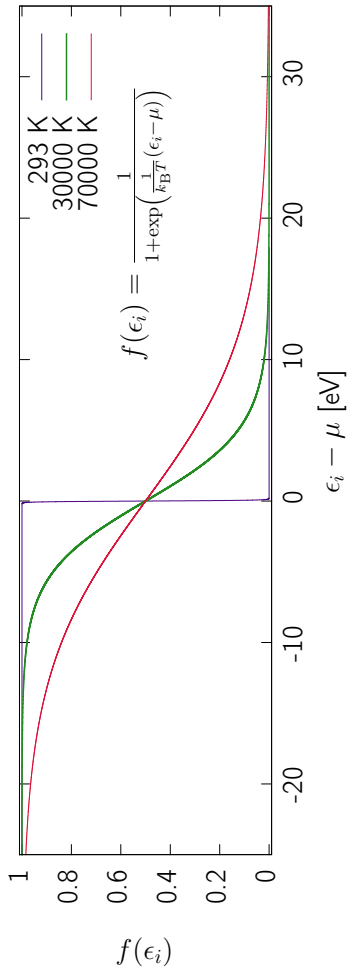
Band structures of aluminum

exp. Vol. (293 K)



5.1 × exp. Vol. (293 K)





Summary
temperature-dependent EXX method

- Enables exact treatment of temperature in electronic structure calculations at exchange level
- Correlation functional supplementing exact treatment of exchange required
- What can we learn from electronic structure calculations at high temperatures? (Would inclusion of noncollinear spin, spin-orbit interactions, or magnetic fields be of interest?)

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

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

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

with

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

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

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

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

$$\mathrm{Y}_{ia}(\boldsymbol{r}) = \phi_i(\boldsymbol{r})\phi_a(\boldsymbol{a})$$

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

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

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

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

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

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

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

with

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

and

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

RI-EXXRPA method II

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

Analytic integration over coupling constant

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

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 (RI-EXXRPA+)
- 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 $\mathbf{X}_0(i\omega) = -\mathbf{V}(i\omega)\,\boldsymbol{\sigma}(i\omega)\,\mathbf{V}^\top(i\omega)$

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

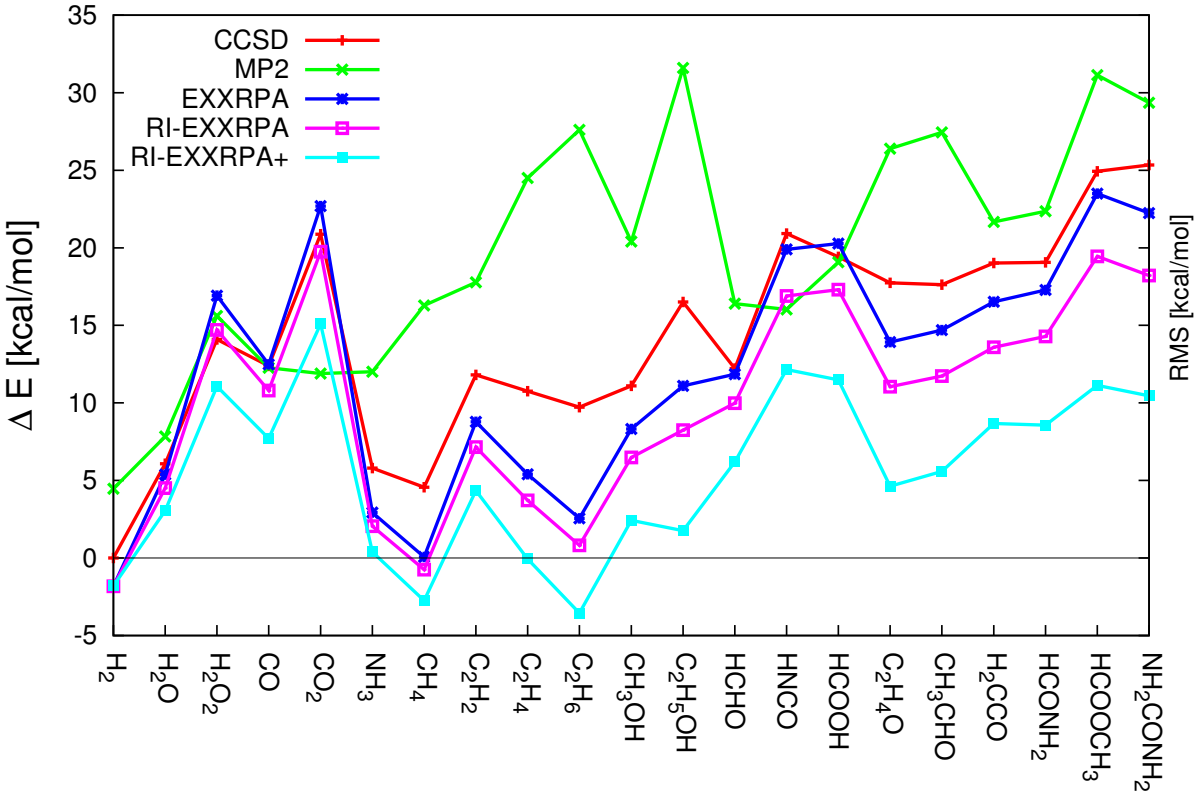
- Only KS response function $\mathbf{X}_0(i\omega)$ required
- N^4 scaling

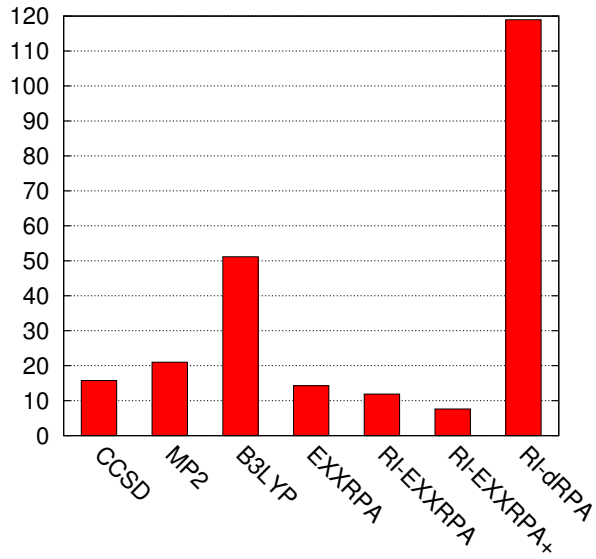
Results EXXRPA correlation methods I

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

Orbital basis: aug-cc-pVQZ RI basis: aug-cc-pVQZ

OEP (EXX) balanced uncontracted basis sets



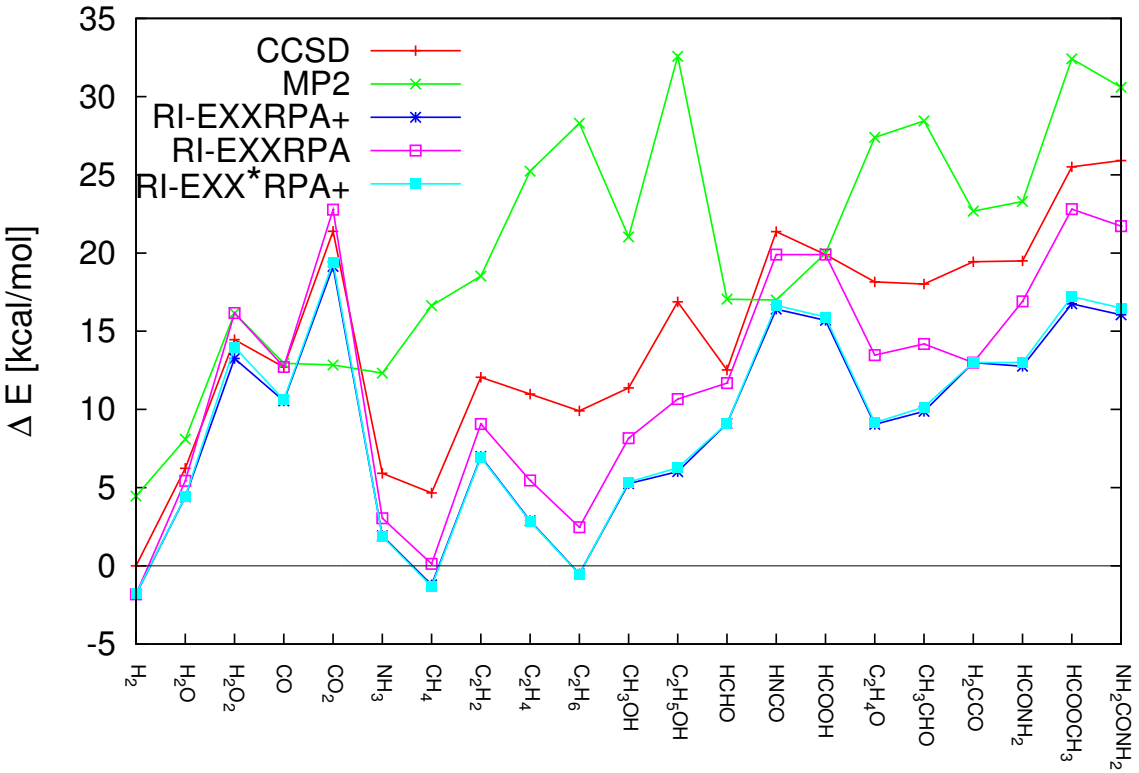


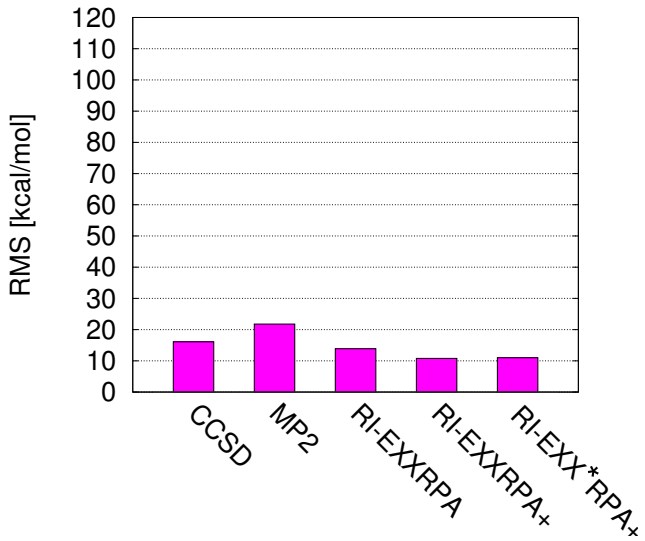
Results EXXRPA correlation methods II

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

Orbital basis: aug-cc-pCVQZ RI basis: aug-cc-pV5Z

OEP (EXX) basis sets equal to RPA basis sets



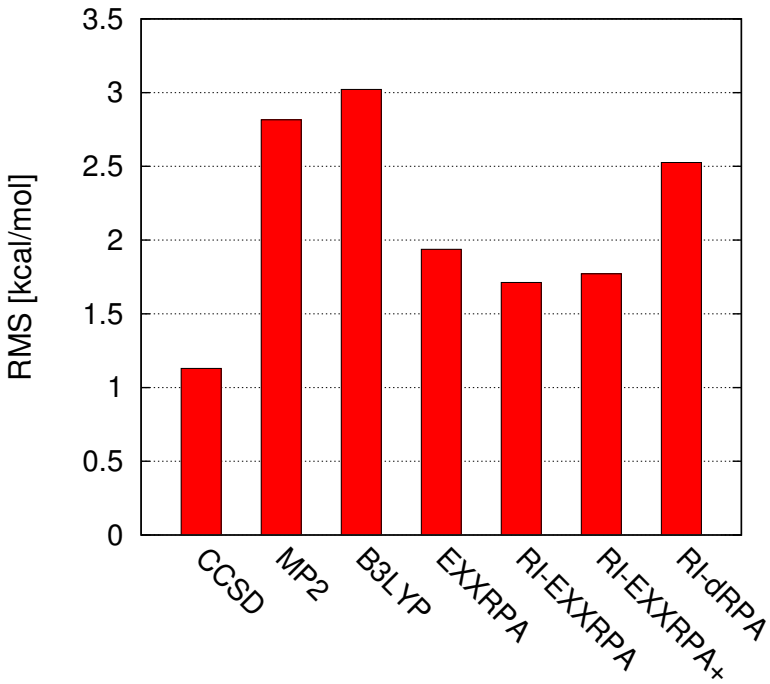


* OEP (EXX) balanced uncontracted basis sets

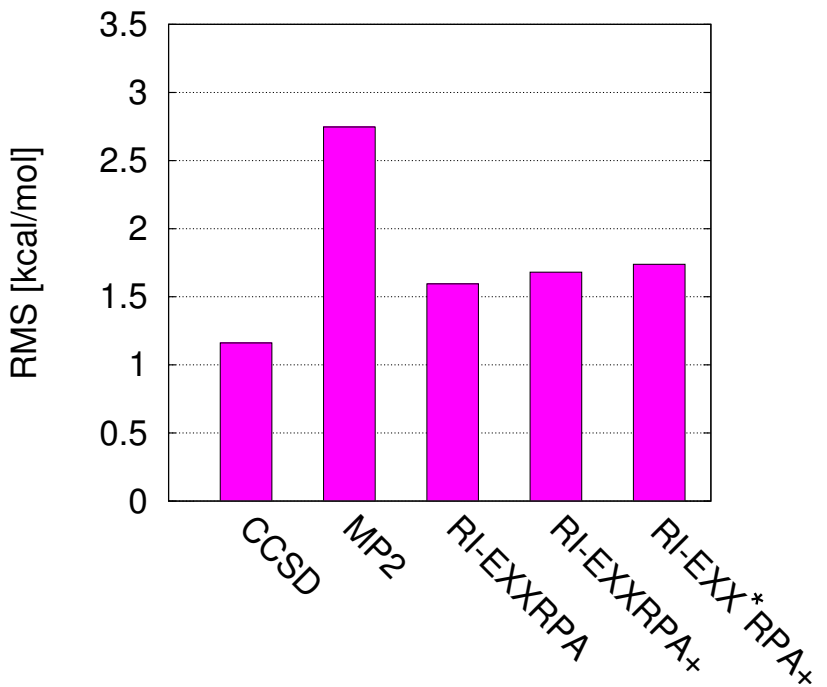
Results EXXRPA correlation methods III

Deviations of reaction energies from CCSD(T) reaction energies

Orbital basis: aug-cc-pVQZ
RI basis: aug-cc-pVQZ
OEP (EXX) balanced uncontracted basis sets



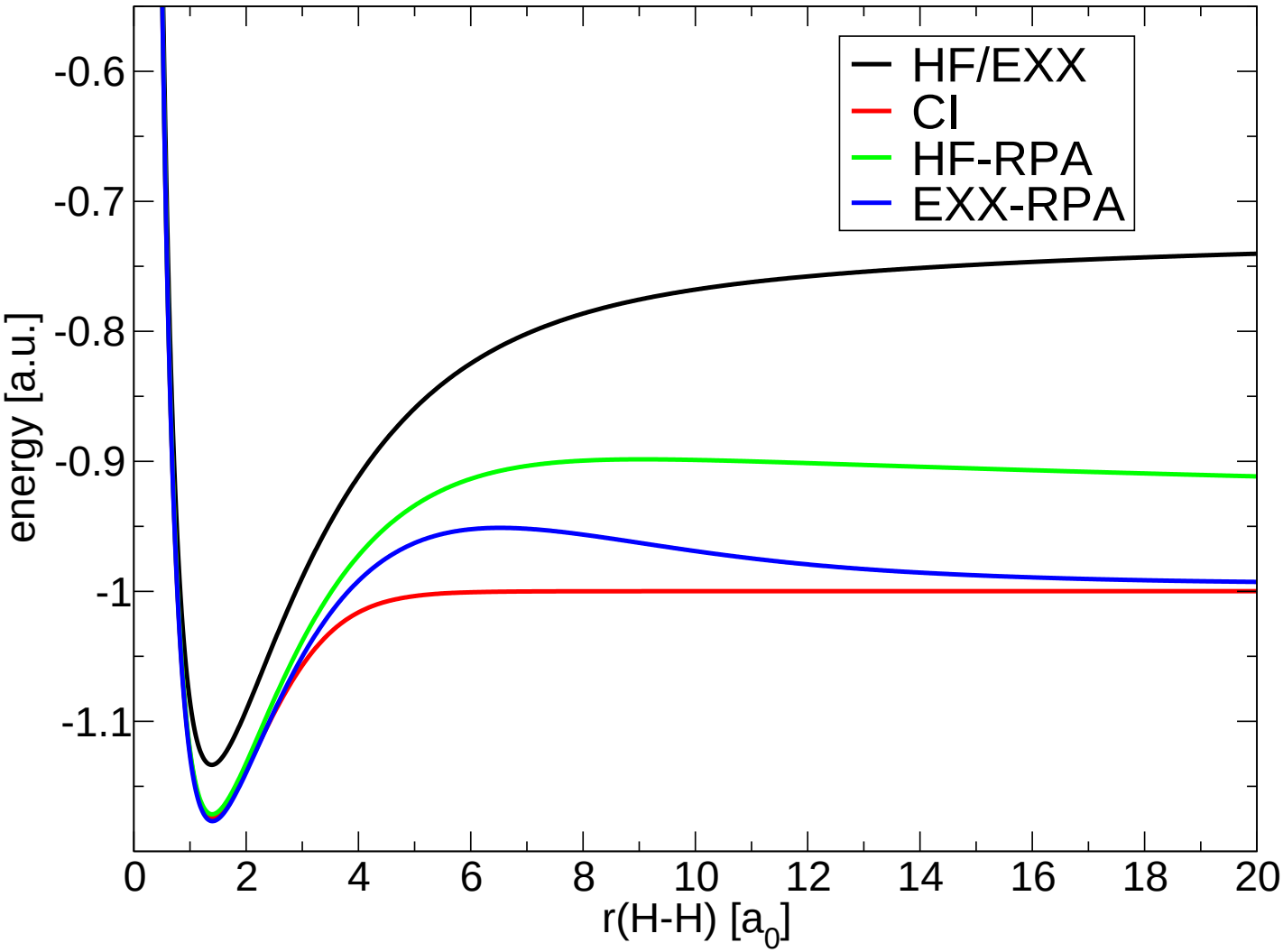
Orbital basis: aug-cc-pCVQZ
RI basis: aug-cc-pV5Z
OEP (EXX) basis sets equal to RPA basis sets



* OEP (EXX) balanced uncontracted basis sets

Dissociation of H_2

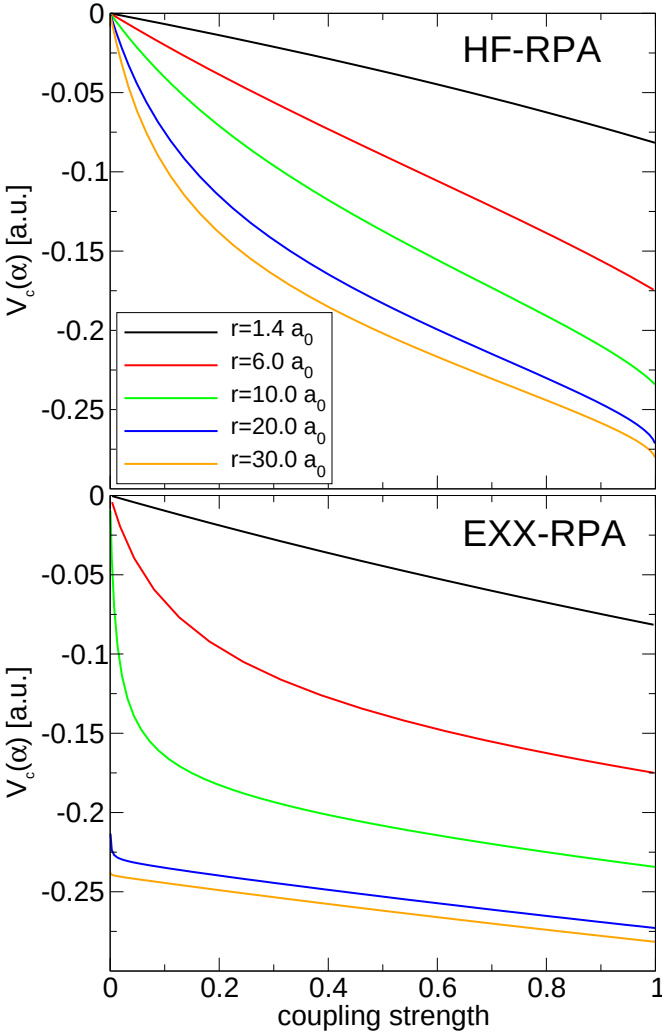
basis set: aug-cc-pVQZ



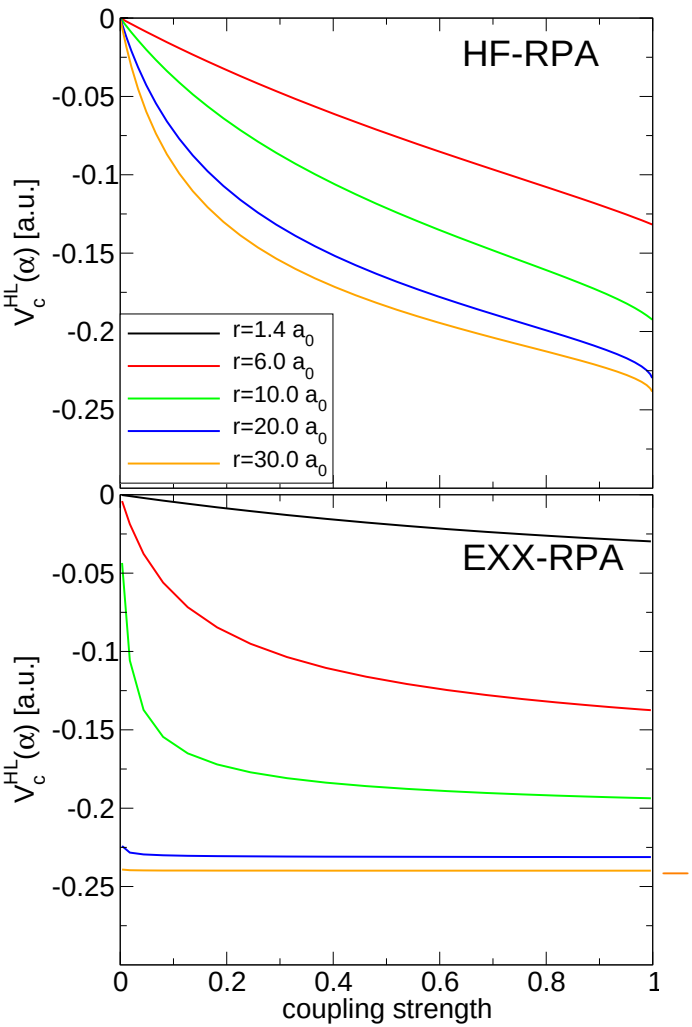
Dissociation limit of other molecules (CO, N_2, etc.) is also treated correctly

Coupling constant integrand

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



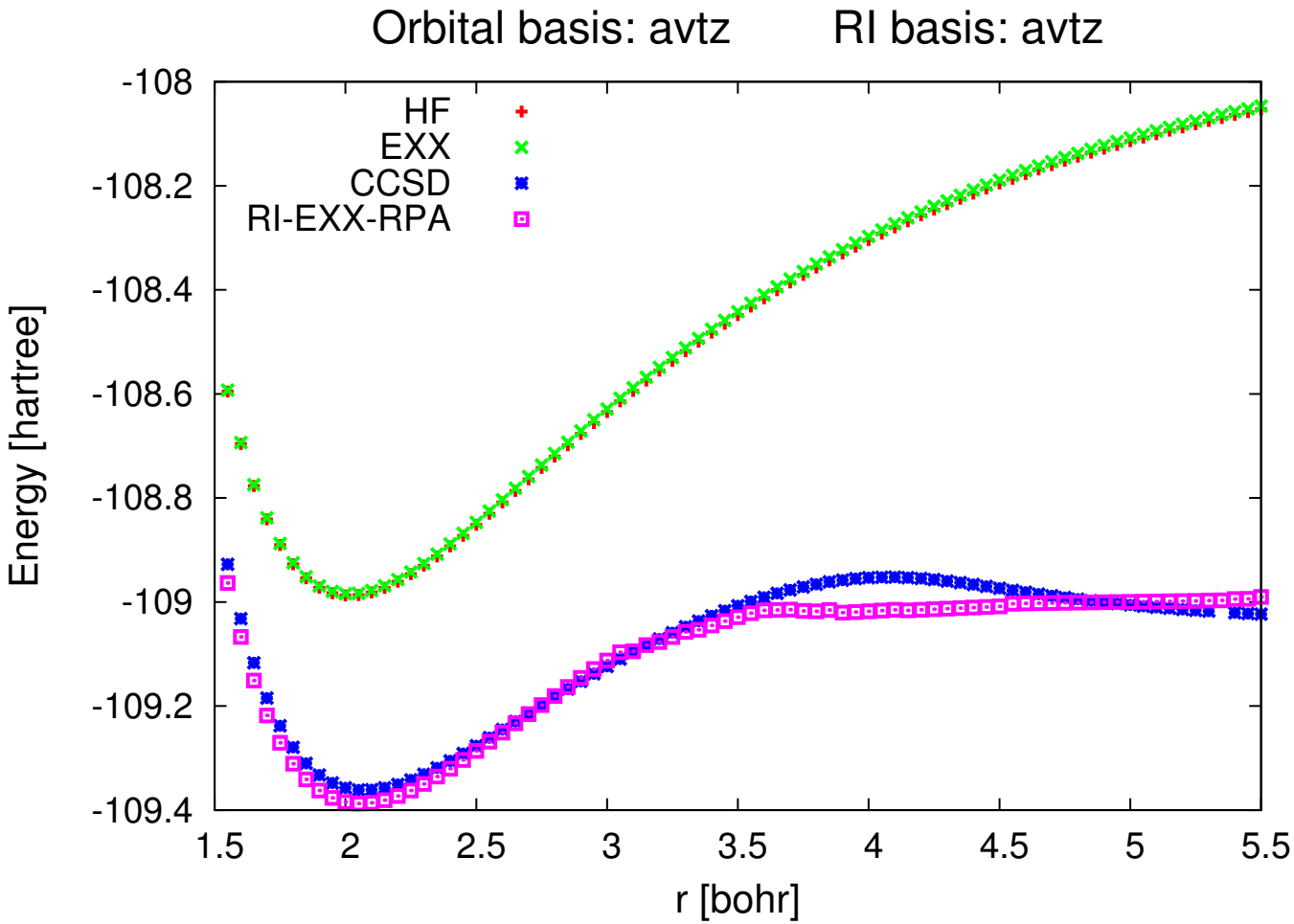
$V_c(\alpha)$



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

$-(ia|ia)$

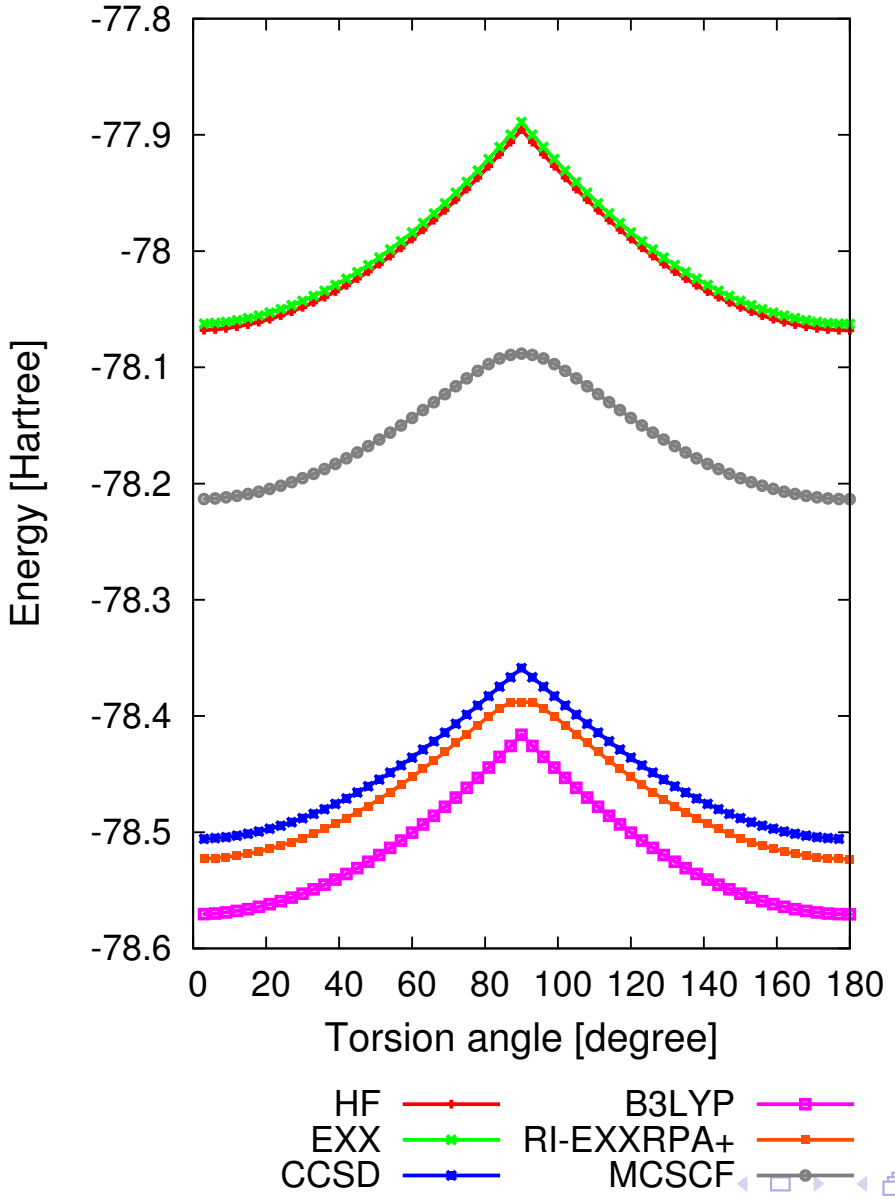
Dissociation of N_2



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

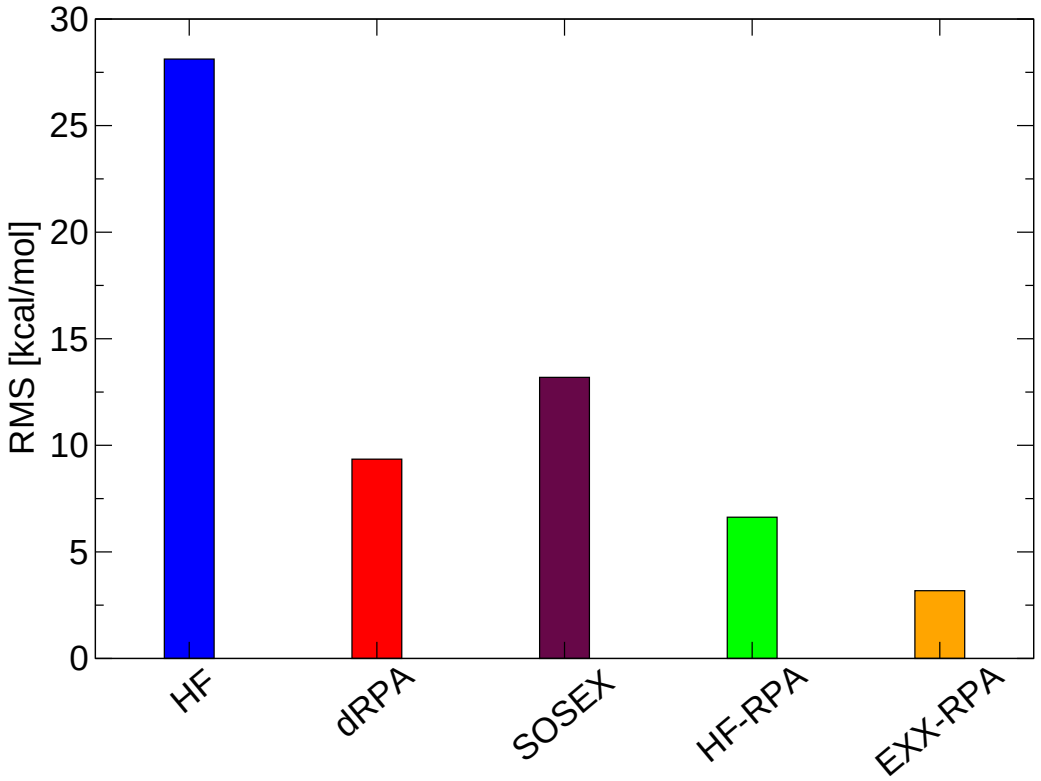
Binding energies in kcal/mol

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

EXX-RPA vs. HF based RPA

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
- Generalization to finite temperatures

Orbital-dependent functionals open up fascinating new possibilities in DFT

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TDEXX

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Mol. Phys. **109**, 2473 (2011) Review

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