

Kohn-Sham methods based on the adiabatic-connection fluctuation-dissipation theorem combining accuracy, wide applicability, and computational efficiency

Andreas Görling, Patrick Bleiziffer, Jannis Erhard,
Simon Kalaß, Egor Trushin

Lehrstuhl für Theoretische Chemie
Universität Erlangen-Nürnberg

S. Bönisch, T. Döpper, A. Heßelmann, W. Hieringer, L. Fromm, S. Frühwald,
S. Maisel, C. Neiß, D. Schmidt, H. Soni, A. Thierbach,

1 Introduction

2 Correlation energy via the adiabatic-connection fluctuation-dissipation theorem (ACFD)

- Kohn-Sham methods with orbital-dependent functionals
- ACFD theorem
- Approximations for the exchange-correlation kernel
- Power series approximation (PSA) for correlation kernel
- Parametrization and performance of PSA

3 Concluding Remarks

4 Literature

	DFT (GGA, B3LYP)	MP2	CCSD(T)	CASSCF/PT2
accuracy	low	medium	high	high
applicability				
multireference	no	no	no	yes
Van-der-Waals	no	yes	yes	yes
handling				
'black-box'-like	yes	yes	yes	no
formal scaling	$N^3 - N^4$	N^5	N^7	factorial

Aim: Development of more powerful DFT methods

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

Correlation from adiabatic-connection fluctuation-dissipation (ACFD) theorem

Orbitals and eigenvalues from Kohn-Sham equations

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

$$\hat{v}_c = 0$$

EXX

$$\hat{v}_c = \hat{v}^{\text{ACFD[H]}}$$

dRPA or ACFD[H]

$$\hat{v}_c = \hat{v}^{\text{ACFD[Hx+}\tilde{c}]}$$

self-consistent \hat{v}_c

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

Integration of response functions along complex frequencies

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

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

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

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

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

Integration along adiabatic connection

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

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

From Hellmann-Feynman theorem follows

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

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

Mol. Phys. **109**,2473 (2010)

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

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

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

Introduction of RI basis set orthonormalized with respect to Coulomb norm

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr} \left[\mathbf{X}_\alpha(i\omega) - \mathbf{X}_0(i\omega) \right] \mathbf{F}_H$$

Response matrix $\mathbf{X}_\alpha(i\omega)$ from TDDFT

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

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

(I) ACFD[H]: direct Random Phase Approximation (dRPA)

$$\mathbf{F}_{Hxc}^\alpha \approx \alpha \mathbf{F}_H \qquad f_H(\mathbf{r} - \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

$$\begin{aligned} \mathbf{X}_\alpha &= [\mathbf{1} - \mathbf{X}_0 \alpha \mathbf{F}_H]^{-1} \mathbf{X}_0 \\ &= (-\mathbf{X}_0)^{\frac{1}{2}} \left[-\mathbf{1} - \alpha (-\mathbf{X}_0)^{\frac{1}{2}} \mathbf{F}_H (-\mathbf{X}_0)^{\frac{1}{2}} \right]^{-1} (-\mathbf{X}_0)^{\frac{1}{2}} \end{aligned}$$

(II) ACFD[Hx]: Hartree plus exact exchange kernel (EXXRPA)

$$\mathbf{X}_0 \mathbf{F}_{Hx} \mathbf{X}_0 = \mathbf{H}_{Hx}$$

$$\begin{aligned} \mathbf{X}_\alpha &= \mathbf{X}_0 [\mathbf{X}_0 - \alpha \mathbf{H}_{Hx}]^{-1} \mathbf{X}_0 \\ &= (-\mathbf{X}_0)^{\frac{1}{2}} \left[-\mathbf{1} - \alpha (-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{Hx} (-\mathbf{X}_0)^{-\frac{1}{2}} \right]^{-1} (-\mathbf{X}_0)^{\frac{1}{2}} \end{aligned}$$

$$\begin{aligned}
 h_{\text{HX}}(\omega, \mathbf{r}, \mathbf{r}') &= \frac{1}{4} \sum_{ia} \sum_{jb} \varphi_i(\mathbf{r}) \varphi_a(\mathbf{r}) \lambda_{ia}(\omega) \mathbf{M}_{ia,jb}^{\text{I}} \lambda_{jb}(\omega) \varphi_j(\mathbf{r}') \varphi_b(\mathbf{r}') \\
 &+ \frac{\omega^2}{4} \sum_{ia} \sum_{jb} \varphi_i(\mathbf{r}) \varphi_a(\mathbf{r}) \lambda_{ia}(\omega) \epsilon_{ia}^{-1} \mathbf{M}_{ia,jb}^{\text{II}} \epsilon_{jb}^{-1} \lambda_{jb}(\omega) \varphi_j(\mathbf{r}') \varphi_b(\mathbf{r}') \\
 &+ \sum_{ia} \sum_j \varphi_i(\mathbf{r}) \varphi_a(\mathbf{r}) \lambda_{ia}(\omega) \frac{\langle a | \hat{v}_x^{\text{NL}} - \hat{v}_x | j \rangle}{\epsilon_a - \epsilon_j} \varphi_i(\mathbf{r}') \varphi_j(\mathbf{r}') + \dots \\
 &+ \sum_{ia} \sum_b \varphi_i(\mathbf{r}) \varphi_a(\mathbf{r}) \lambda_{ia}(\omega) \frac{\langle b | \hat{v}_x^{\text{NL}} - \hat{v}_x | i \rangle}{\epsilon_b - \epsilon_i} \varphi_a(\mathbf{r}') \varphi_b(\mathbf{r}') + \dots
 \end{aligned}$$

$$\mathbf{M}_{ia,jb}^{\text{I}} = 4(ai|jb) - (ab|ji) - (aj|bi) + \delta_{ij} \langle \varphi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \varphi_b \rangle - \delta_{ab} \langle \varphi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \varphi_j \rangle$$

$$\mathbf{M}_{ia,jb}^{\text{II}} = -(ab|ji) + (aj|bi) + \delta_{ij} \langle \varphi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \varphi_b \rangle - \delta_{ab} \langle \varphi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \varphi_j \rangle$$

$$\lambda_{ia}(\omega) = -4\epsilon_{ia} / (\epsilon_{ia}^2 + \omega^2) \quad \epsilon_{ia} = \epsilon_a - \epsilon_i$$

dRPA:
$$h_{\text{H}}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{ia} \sum_{jb} \varphi_i(\mathbf{r}) \varphi_a(\mathbf{r}) \lambda_{ia}(\omega) (ia|jb) \lambda_{jb}(\omega) \varphi_j(\mathbf{r}') \varphi_b(\mathbf{r}')$$

$$\mathbf{F}_{\text{Hxc}}^\alpha = \alpha \mathbf{F}_{\text{Hx}} + \alpha^2 \mathbf{F}_{\text{c}}^{(2)} + \alpha^3 \mathbf{F}_{\text{c}}^{(3)} + \dots$$

$$\mathbf{X}_0 \mathbf{F}_{\text{Hxc}}^\alpha \mathbf{X}_0 = \mathbf{H}_{\text{Hxc}}^\alpha, \quad \mathbf{X}_0 \mathbf{F}_{\text{Hx}} \mathbf{X}_0 = \mathbf{H}_{\text{Hx}}, \quad \mathbf{X}_0 \mathbf{F}_{\text{c}}^{(n)} \mathbf{X}_0 = \mathbf{H}_{\text{c}}^{(n)}$$

$$\mathbf{H}_{\text{Hxc}}^\alpha = \alpha \mathbf{H}_{\text{Hx}} + \alpha^2 \mathbf{H}_{\text{c}}^{(2)} + \alpha^3 \mathbf{H}_{\text{c}}^{(3)} + \dots$$

Higher order terms: Power series approximation

$$\begin{aligned} (-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{\text{Hxc}}^\alpha (-\mathbf{X}_0)^{-\frac{1}{2}} &= \alpha (-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{\text{Hx}} (-\mathbf{X}_0)^{-\frac{1}{2}} + \alpha^2 (-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{\text{c}}^{(2)} (-\mathbf{X}_0)^{-\frac{1}{2}} + \dots \\ &= \alpha (-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{\text{Hx}} (-\mathbf{X}_0)^{-\frac{1}{2}} + \alpha^2 \beta_2 \left[(-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{\text{Hx}} (-\mathbf{X}_0)^{-\frac{1}{2}} \right]^2 + \dots \end{aligned}$$

$$(-\mathbf{X}_0)^{\frac{1}{2}} \mathbf{F}_{\text{c}}^{(n)} (-\mathbf{X}_0)^{\frac{1}{2}} = \beta_n \left[(-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{\text{Hx}} (-\mathbf{X}_0)^{-\frac{1}{2}} \right]^n$$

$$\begin{aligned} \mathbf{X}_\alpha &= (-\mathbf{X}_0)^{\frac{1}{2}} \left\{ -1 - \alpha (-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{\text{Hx}} (-\mathbf{X}_0)^{-\frac{1}{2}} \right. \\ &\quad \left. - \alpha^2 \beta_2 \left[(-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{\text{Hx}} (-\mathbf{X}_0)^{-\frac{1}{2}} \right]^2 - \dots \right\}^{-1} (-\mathbf{X}_0)^{\frac{1}{2}} \end{aligned}$$

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

Hartree plus exchange kernel for $\mathbf{X}_\alpha = (-\mathbf{X}_0)^{\frac{1}{2}} \left[-\mathbf{1} - \alpha (-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{Hx} (-\mathbf{X}_0)^{-\frac{1}{2}} \right] (-\mathbf{X}_0)^{\frac{1}{2}}$

$$= (-\mathbf{X}_0)^{\frac{1}{2}} \mathbf{U} [-\mathbf{1} - \alpha \boldsymbol{\tau}]^{-1} \mathbf{U}^T (-\mathbf{X}_0)^{\frac{1}{2}}$$

with $(-\mathbf{X}_0)^{-\frac{1}{2}} \mathbf{H}_{Hx} (-\mathbf{X}_0)^{-\frac{1}{2}} = \mathbf{U} \boldsymbol{\tau} \mathbf{U}^T$

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

Analytic coupling-constant integration

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

- Complete frequency-dependent exchange kernel can be treated
- N^5 scaling (N^4 scaling for ACFD[H])

J. Chem. Phys. **136**, 134102 (2012)

$$E_c = \frac{-1}{2\pi} \int_0^{\infty} d\omega \int_0^1 d\alpha \operatorname{Tr} \left\{ \left[(-\mathbf{X}_0)^{\frac{1}{2}} \mathbf{U} \left([-\mathbf{1} - \alpha\tau - \beta_2(\alpha\tau)^2 - \dots]^{-1} + \mathbf{1} \right) \mathbf{U}^T (-\mathbf{X}_0)^{\frac{1}{2}} \right] \mathbf{F}_H \right\}$$

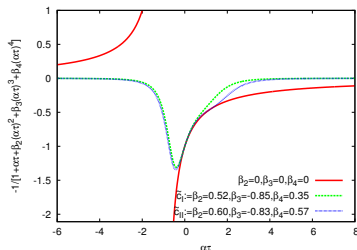
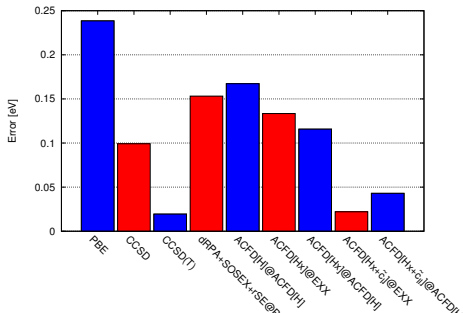
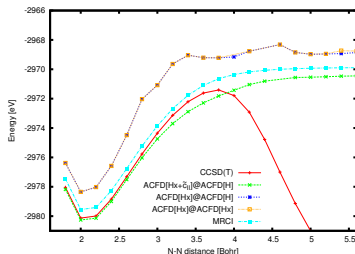
- Parameters β_n
- Numerical coupling-constant integration
- N^5 scaling
- Additional computational cost with respect to ACFD[Hx] method is negligible

Phys. Rev. Lett. **117**, 143002 (2016)

Training set with reaction energies

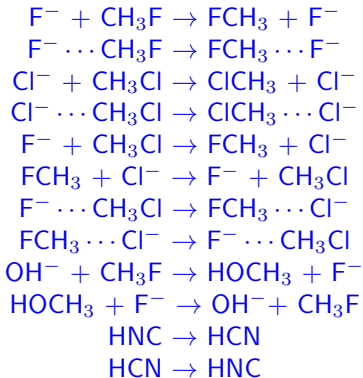
t-HONO	→	c-HONO	HCN	→	HNC
HNCO	→	HOCN	HNCO	→	HONC
HNCO	→	HCNO	HOCN	→	HONC
HOCN	→	HCNO	HCNO	→	HONC
H ₂ CO	→	t-HCOH	HCCH	→	H ₂ CC
t-N ₂ H ₂	→	c-N ₂ H ₂	CO+H ₂	→	H ₂ CO
H ₂ O+F ₂	→	HOF+FH	N ₂ +3H ₂	→	2NH ₃
t-N ₂ H ₂	→	N ₂ +H ₂	HCCH+H ₂	→	C ₂ H ₄
CO ₂ +4H ₂	→	CH ₄ +2H ₂ O	H ₂ CO+2H ₂	→	CH ₄ +H ₂ O
CO+3H ₂	→	CH ₄ +H ₂ O	CO+H ₂ O ₂	→	H ₂ O+CO ₂
HCN+3H ₂	→	CH ₄ +NH ₃	H ₂ O ₂ +H ₂	→	2H ₂ O
HCCH+3H ₂	→	2CH ₄	F ₂ +H ₂	→	2FH

N₂ dissociation

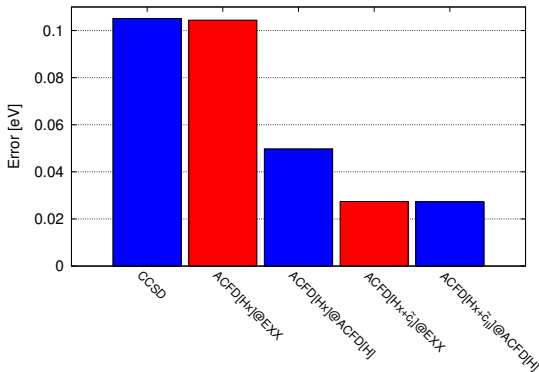


$$1 / \left[-1 - (\alpha\tau) - \beta_2(\alpha\tau)^2 - \beta_3(\alpha\tau)^3 - \dots \right]$$

Test set with reaction barriers

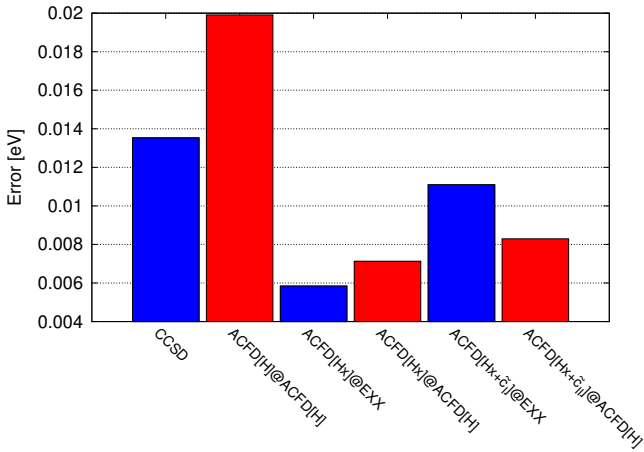


RMS of test set for reaction barriers



0.1 eV = 2.30 kcal/mol

Dimerization energies from A24 test set of non-covalent bound dimers



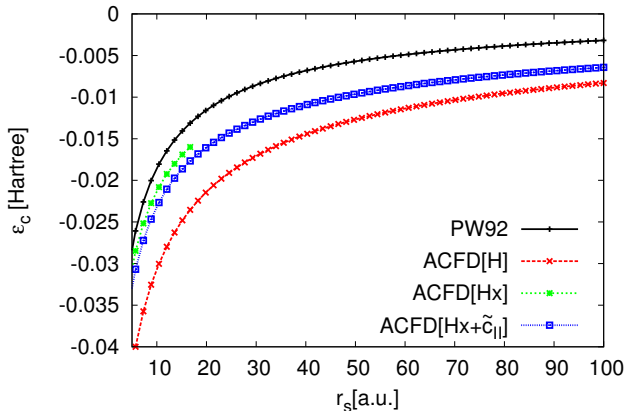
0.01 eV = 0.23 kcal/mol

$$E_c = \frac{-1}{2\pi} \int_0^{\infty} d\omega \int_0^1 d\alpha \operatorname{Tr} \left\{ \left[(-\mathbf{X}_0)^{\frac{1}{2}} \mathbf{U} ([g(\alpha\tau)]^{-1} + \mathbf{1}) \mathbf{U}^T (-\mathbf{X}_0)^{\frac{1}{2}} \right] \mathbf{F}_H \right\}$$

$$g(\alpha\tau) = -\mathbf{1} - \alpha\tau - \beta_2(\alpha\tau)^2 - \beta_3(\alpha\tau)^3 - \beta_4(\alpha\tau)^4 \dots$$

Disadvantages of fitting parameters $\beta_2, \beta_3, \beta_4$ of truncated PSA with training set of molecular reactions

- reliable only if $|\tau|$ not too large
- choice of training set somewhat arbitrary
- error cancellations because non-self-consistent v_{xc}
- influence of technical issues (e.g. basis sets)



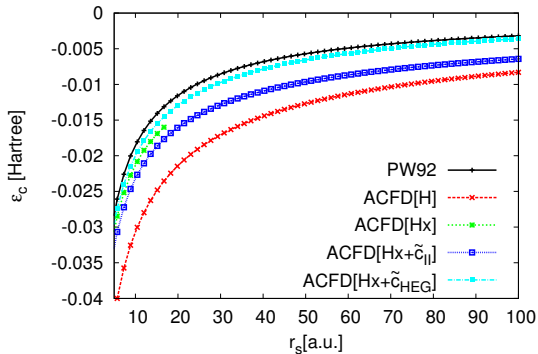
For molecules in ground state geometries typically $-0.3 < \tau < 3$

For HEG at $r_s = 100$: $-10 < \tau < 1.4 \cdot 10^7$, at $r_s = 2000$: $-200 < \tau < 2.8 \cdot 10^8$

Taylor series $-1 - \alpha\tau - \beta_2(\alpha\tau)^2 - \beta_3(\alpha\tau)^3 - \beta_4(\alpha\tau)^4$ up to fourth order cannot work for HEG

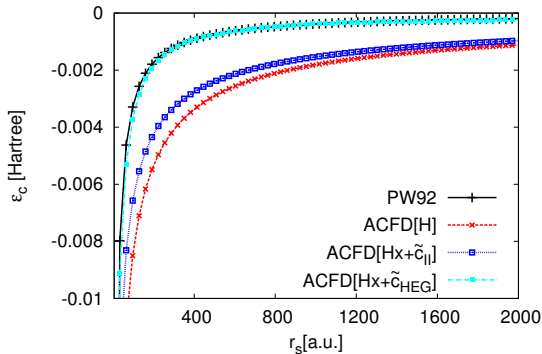
$$g(\alpha\tau) = -1 - \alpha\tau - \beta_2(\alpha\tau)^2 - \beta_3(\alpha\tau)^3 - \beta_4(\alpha\tau)^4 \dots$$

$g(\alpha\tau)$ as linear combination of Gaussian functions,
optimized for H₂ and HEG with $200 \leq r_s \leq 1000$

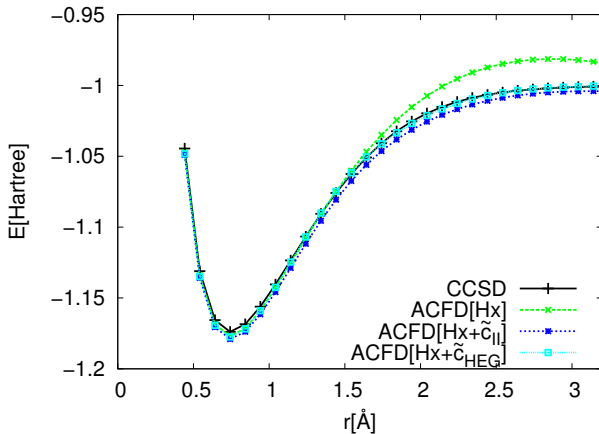


$$g(\alpha\tau) = -1 - \alpha\tau - \beta_2(\alpha\tau)^2 - \beta_3(\alpha\tau)^3 - \beta_4(\alpha\tau)^4 \dots$$

$g(\alpha\tau)$ as linear combination of Gaussian functions,
optimized for H₂ and HEG with $200 \leq r_s \leq 1000$

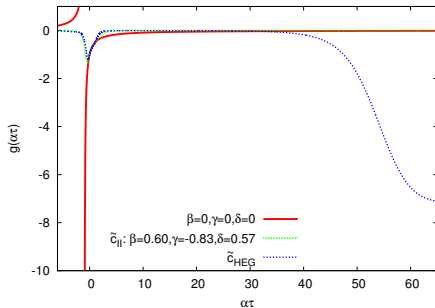
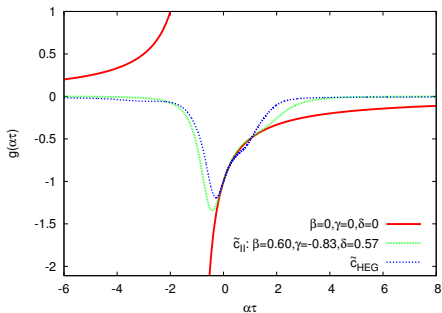


$$g(\alpha\tau) = -1 - \alpha\tau - \beta_2(\alpha\tau)^2 - \beta_3(\alpha\tau)^3 - \beta_4(\alpha\tau)^4 \dots$$



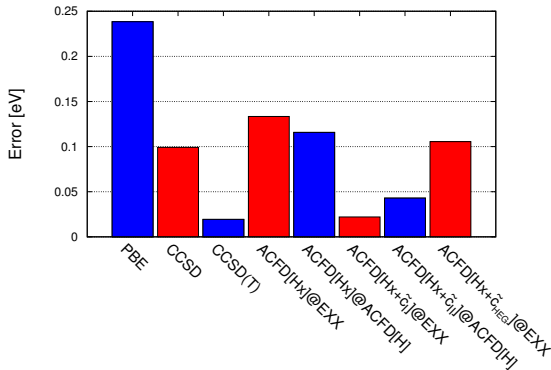
H₂ dissociation

$$g(\alpha\tau) = -1 - \alpha\tau - \beta_2(\alpha\tau)^2 - \beta_3(\alpha\tau)^3 - \beta_4(\alpha\tau)^4 \dots$$



Training/test set with reaction energies

t-HONO	→	c-HONO
HCN	→	HNC
HNCO	→	HOCN
HNCO	→	HONC
HNCO	→	HCNO
HOCN	→	HONC
HOCN	→	HCNO
HCNO	→	HONC
H ₂ CO	→	t-HCOH
HCCH	→	H ₂ CC
t-N ₂ H ₂	→	c-N ₂ H ₂
CO+H ₂	→	H ₂ CO
H ₂ O+F ₂	→	HOF+FH
N ₂ +3H ₂	→	2NH ₃
t-N ₂ H ₂	→	N ₂ +H ₂
HCCH+H ₂	→	C ₂ H ₄
CO ₂ +4H ₂	→	CH ₄ +2H ₂ O
H ₂ CO+2H ₂	→	CH ₄ +H ₂ O
CO+3H ₂	→	CH ₄ +H ₂ O
CO+H ₂ O ₂	→	H ₂ O+CO ₂
HCN+3H ₂	→	CH ₄ +NH ₃
H ₂ O ₂ +H ₂	→	2H ₂ O
HCCH+3H ₂	→	2CH ₄
F ₂ +H ₂	→	2FH



- ⌘ ACFD[$H_x + \tilde{c}$] methods combine accuracy at equilibrium geometries with a correct description of dissociation (static correlation) and a highly accurate treatment of VdW interactions
- ⌘ ACFD[H_x] and ACFD[$H_x + \tilde{c}$] methods are self-interaction free
- ⌘ Power series approximation for correlation kernel in ACFD[$H_x + \tilde{c}$] methods removes singularities in ACFD frequency integration

New areas of application for DFT: highly accurate electronic structure calculations which so far were the realm of CC and multi-reference methods

ACFD methods

- Mol. Phys. **108**, 359 (2010) J. Chem. Phys. **139**, 084113 (2013)
Phys. Rev. Lett. **106**, 093001 (2011) Phys. Rev. A **88**, 042513 (2013)
Mol. Phys. **109**, 2473 (2011) Review J. Chem. Phys. **141**, 204107 (2014)
J. Chem. Phys. **136**, 134102 (2012) J. Chem. Phys. **142**, 244108 (2015)
J. Chem. Comput. **9**, 2264 (2013)

PSA

- Phys. Rev. Lett. **117**, 143002 (2016)
Viewpoint in Physics **9**, 108 (2016) by Kieron Burke