Coupling of density-functional and wavefunction-based methods

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Outline

- Motivation
- Ansatz
- Related Work
- Implementation
- Functionals
- Results
- Outlook

Motivation

complementarity of methods

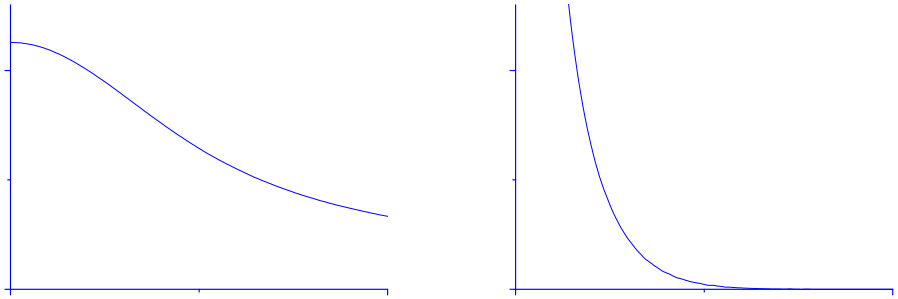
- DFT
  - implicit treatment of dynamic correlation
  - weak basis-set dependence
- ab-initio
  - static correlation, van-der-Waals interactions
  - systematic improvement

$\Longrightarrow$ economy + accuracy ?

Ansatz

- explicit description of inter-electronic cusp:
  large basis sets, long configuration expansions
- basic idea: split r_{ij}^{-1} into *sr* and *lr* parts,
  handle singularity via DFT:

$$\sum_{i<j} \frac{1}{r_{ij}} = \underbrace{\sum_{i<j} \frac{1}{r_{ij}} \operatorname{erf}(\mu r_{ij})}_{V_{ee,lr}} + \underbrace{\sum_{i<j} \frac{1}{r_{ij}} \operatorname{erfc}(\mu r_{ij})}_{V_{ee,sr}}$$



Separation of energy

use constrained-search formalism:

$$E_0 = \min_{\rho \to N} \left(\min_{\Psi \to \rho} \langle \Psi | T + V_{ne} + V_{ee,lr} | \Psi \rangle + E_{sr}[\rho] \right)$$

with

$$\begin{aligned} E_{sr}[\rho] &= \min_{\Psi \to \rho} \langle \Psi | T + V_{ee} | \Psi \rangle - \min_{\Psi \to \rho} \langle \Psi | T + V_{ee,lr} | \Psi \rangle \\ &= U_{H,sr}[\rho] + E_{xc,sr}[\rho] \end{aligned}$$

$$\Longrightarrow E_0 = \min_{\Psi} \left\{ \langle \Psi | T + V_{ne} + V_{ee,lr} | \Psi \rangle + U_{H,sr}[\rho_\Psi] + E_{xc,sr}[\rho_\Psi] \right\}$$

Related work

Savin *et al.*: functionals

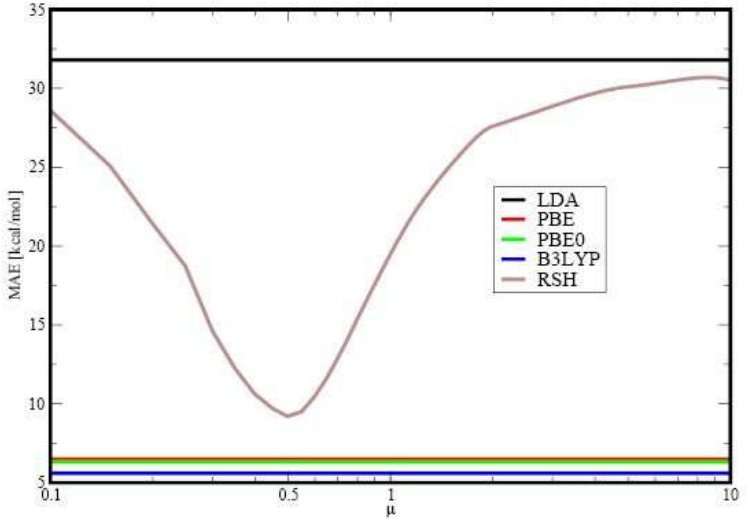
- *sr* LDA/GGA functionals for different $f(\mu)$
- exact *sr* functionals: expansions *vs.* μ and $1/\mu$
- scaling relations

J. Toulouse, A. Savin, H.-J. Flad, Int. J. Quantum Chem. 100 (2004) 1047;
J. Toulouse, F. Colonna, A. Savin, Phys. Rev. A 70 (2004) 062505; J. Chem. Phys. 122 (2005) 014110;
J. Toulouse, Ph. D. thesis, 2005.

Related work (contd.)

Hirao *et al.*, Ángyán *et al.*: *sr*-DFT / *lr*-HF (x-only)

- $4s$-$3d$ excitations in TMA
- polarizabilities of polyenes
- Rydberg, CT exc. with TDDFT



Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, J. Chem. Phys. 120 (2004) 8425;
J. Ángyán, I.C. Gerber, A. Savin, J. Toulouse, Poster at Karlsruhe Nanoscience Workshop, Jan. 2005.

Related work (contd.)

Handy *et al.*: *sr* hybrid DFT / *lr* hybrid DFT

Baer *et al.*: *sr*-DFT / *lr*-HF (xc)

Ángyán *et al.*: *sr*-DFT / *lr*-MP2

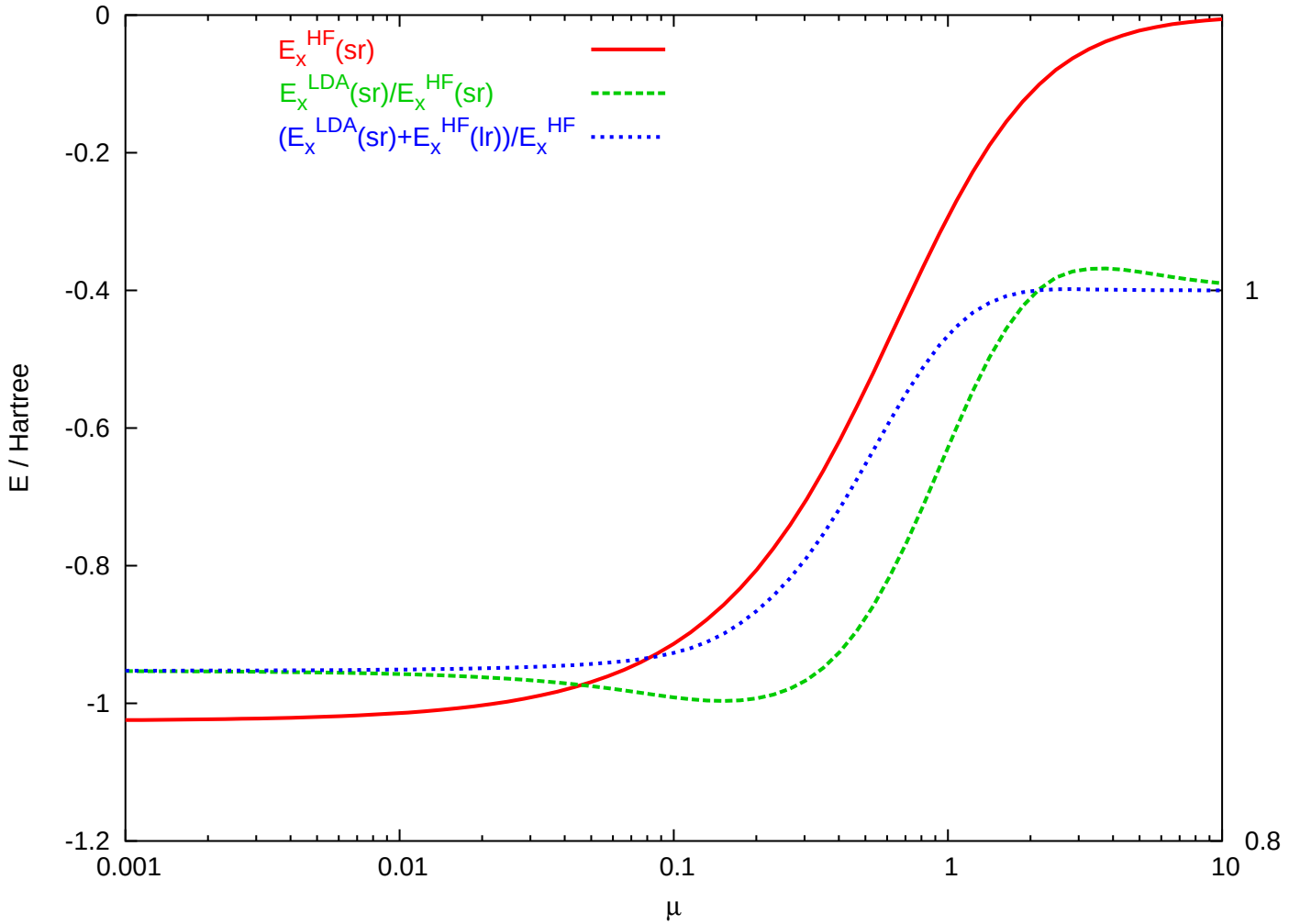
Jensen *et al.*: *sr*-DFT / *lr*-MCSCF

T. Yanai, D.P. Tew, N.C. Handy, Chem. Phys. Lett. 393 (2004) 51;
R. Baer, D. Neuhauser, Phys. Rev. Lett. 94 (2005) 043002;
J. Ángyán, I.C. Gerber, A. Savin, J. Toulouse, Poster at Karlsruhe Nanoscience Workshop, Jan. 2005.
J.K. Pedersen, H.J.Aa. Jensen, J. Chem. Phys., submitted

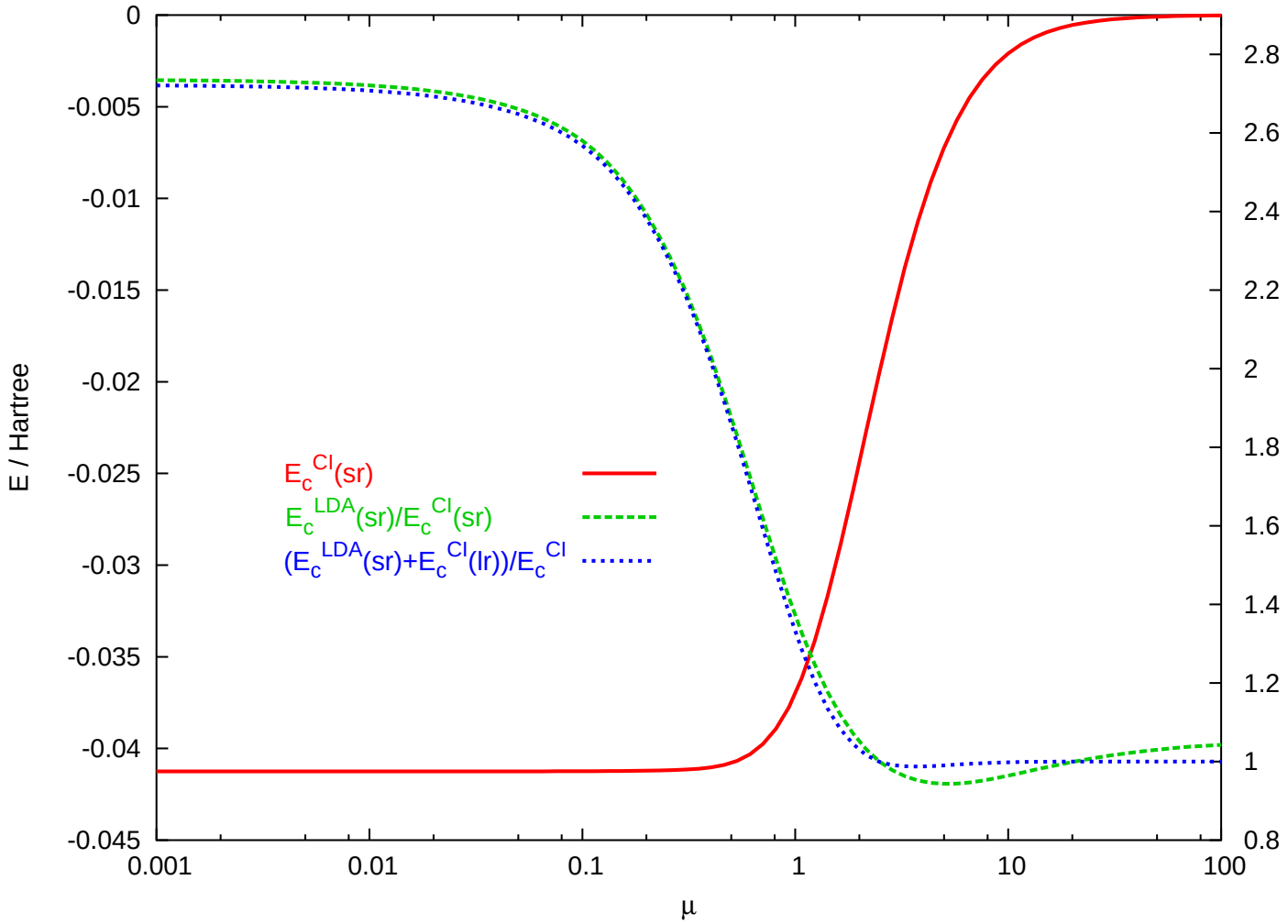
Implementation

- restriction to spin-unpolarized case (closed-shell)
- available *sr*-DFT methods: LDA, GGA
- orbital optimization in hybrid DFT calculation (*sr*-DFT with full *lr*-HF exchange)
- available *lr-post*-HF treatment: MP2, CCSD, CCSD(T), (MR)CISD
- density update at CI level
- program: MOLPRO

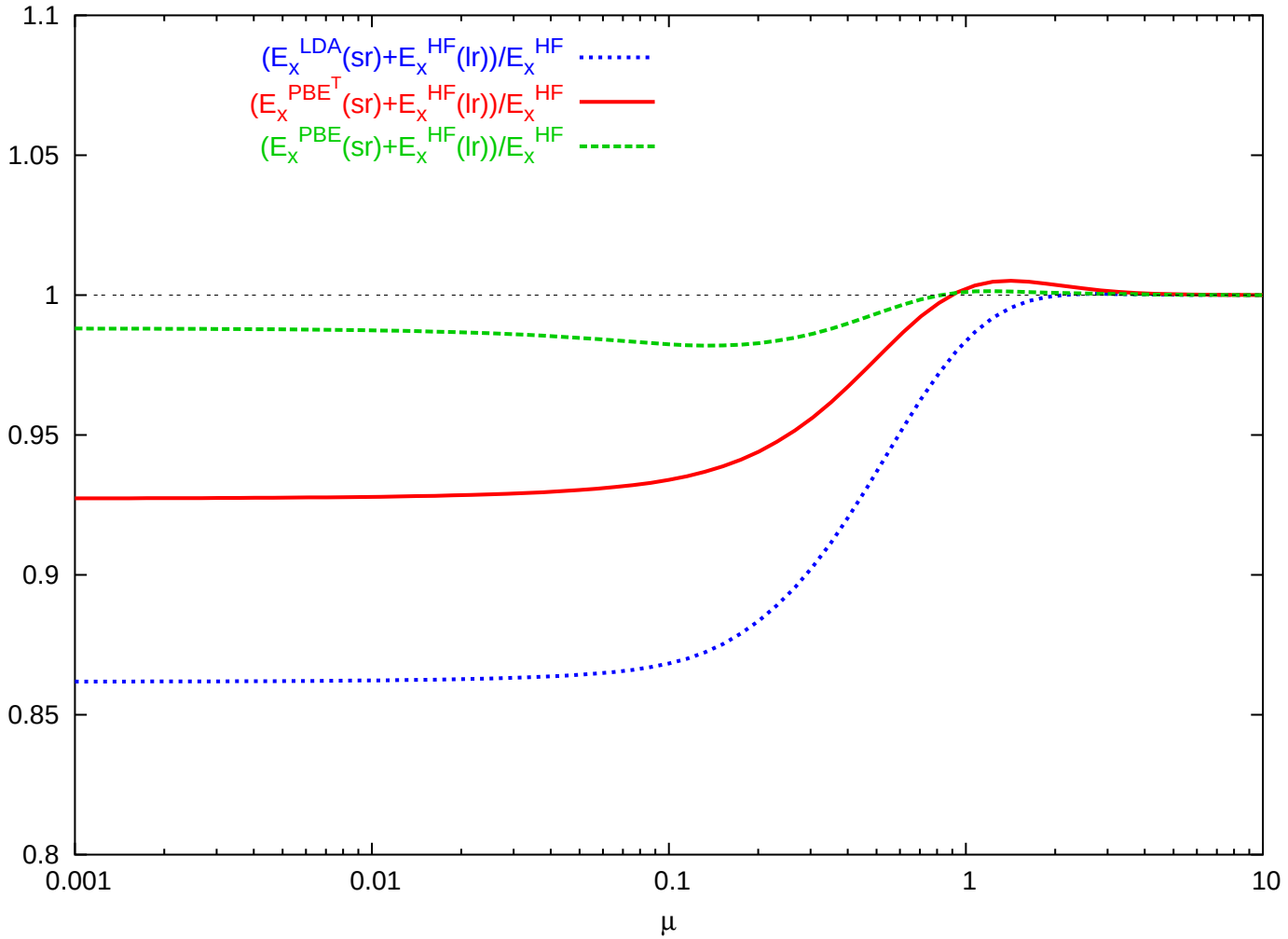
Functionals: *sr* x-LDA, He



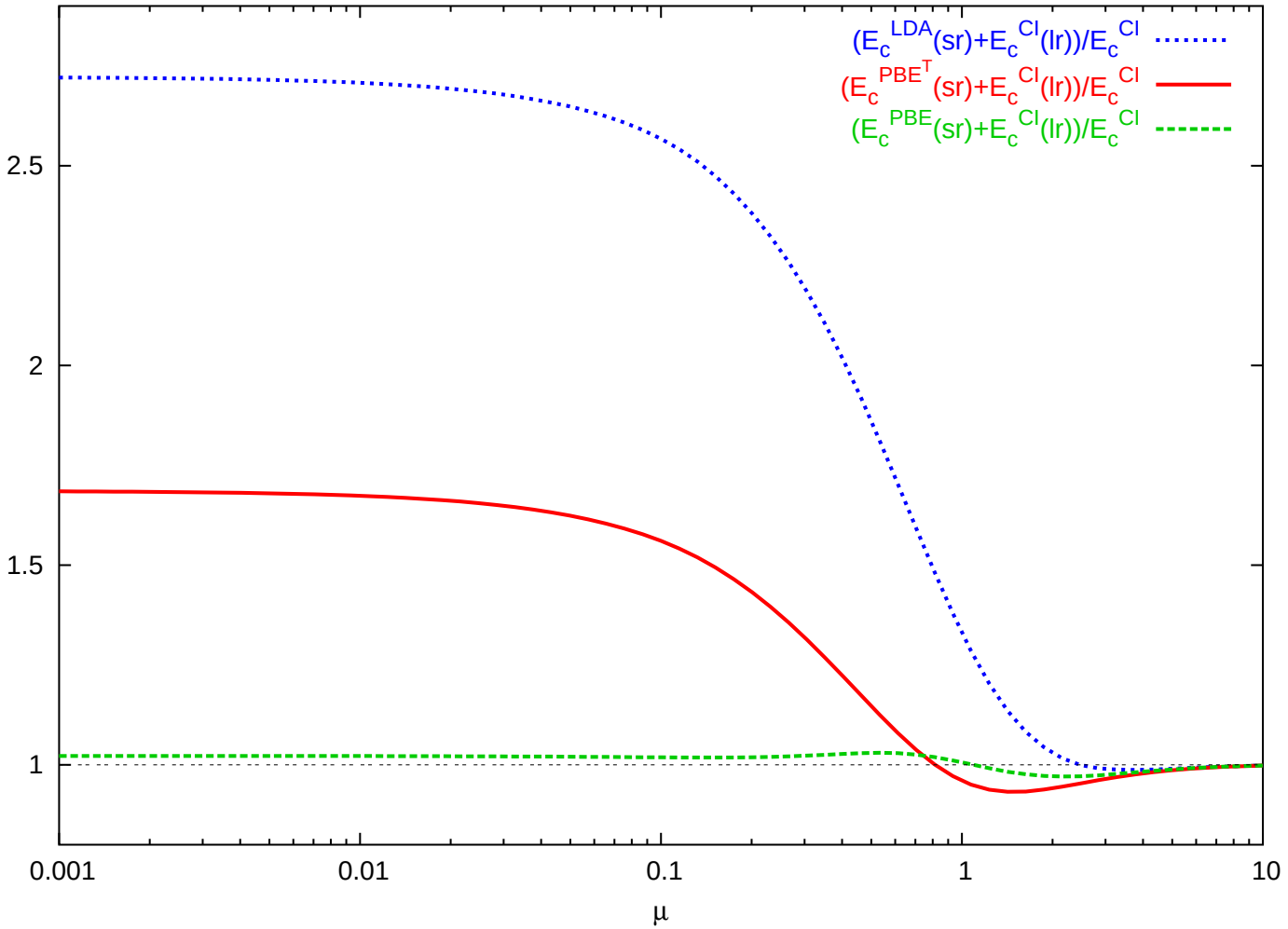
Functionals (contd.): *sr* c-LDA, He



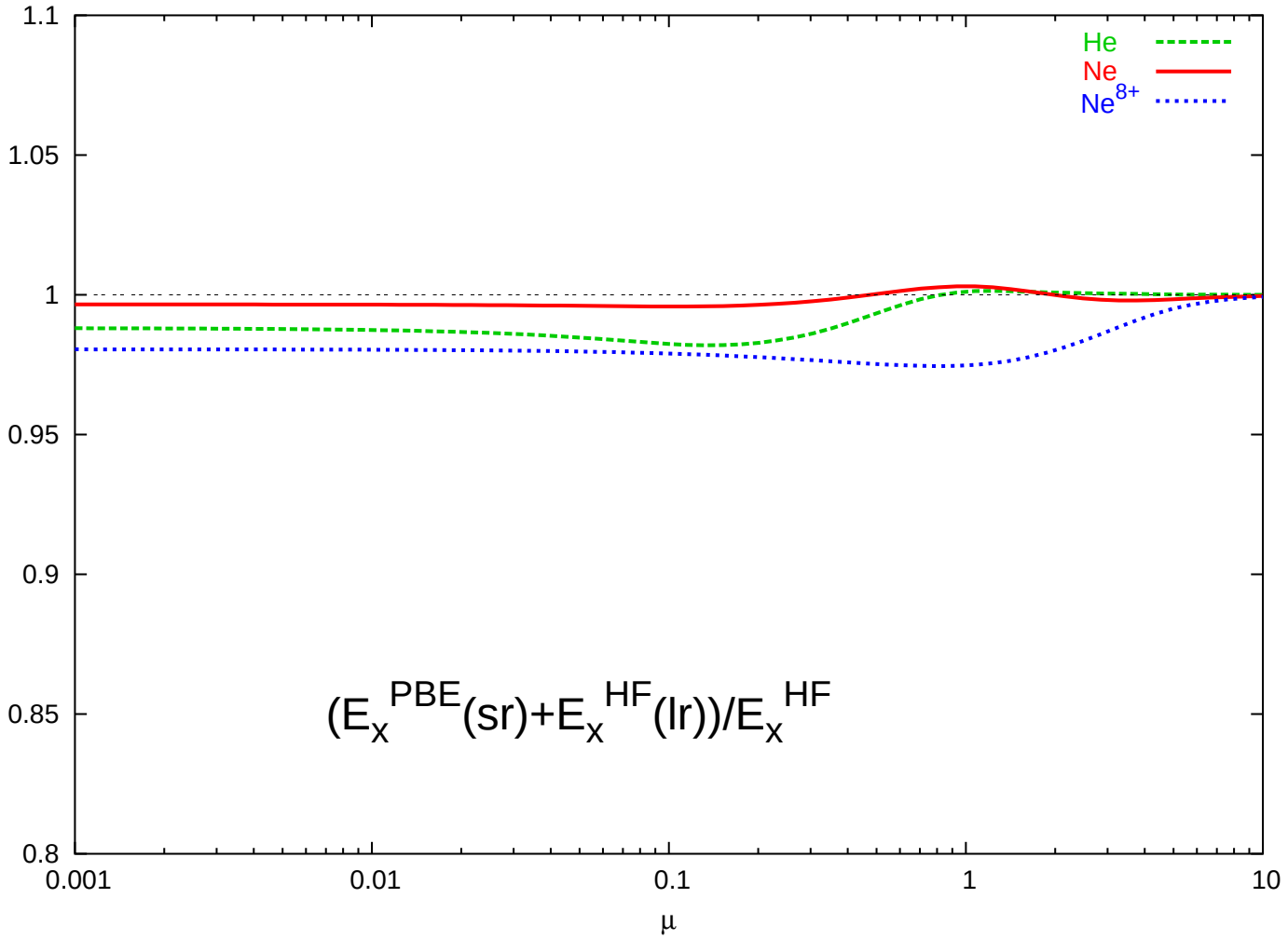
Functionals (contd.): *sr* x-LDA *vs. sr* x-GGA, He



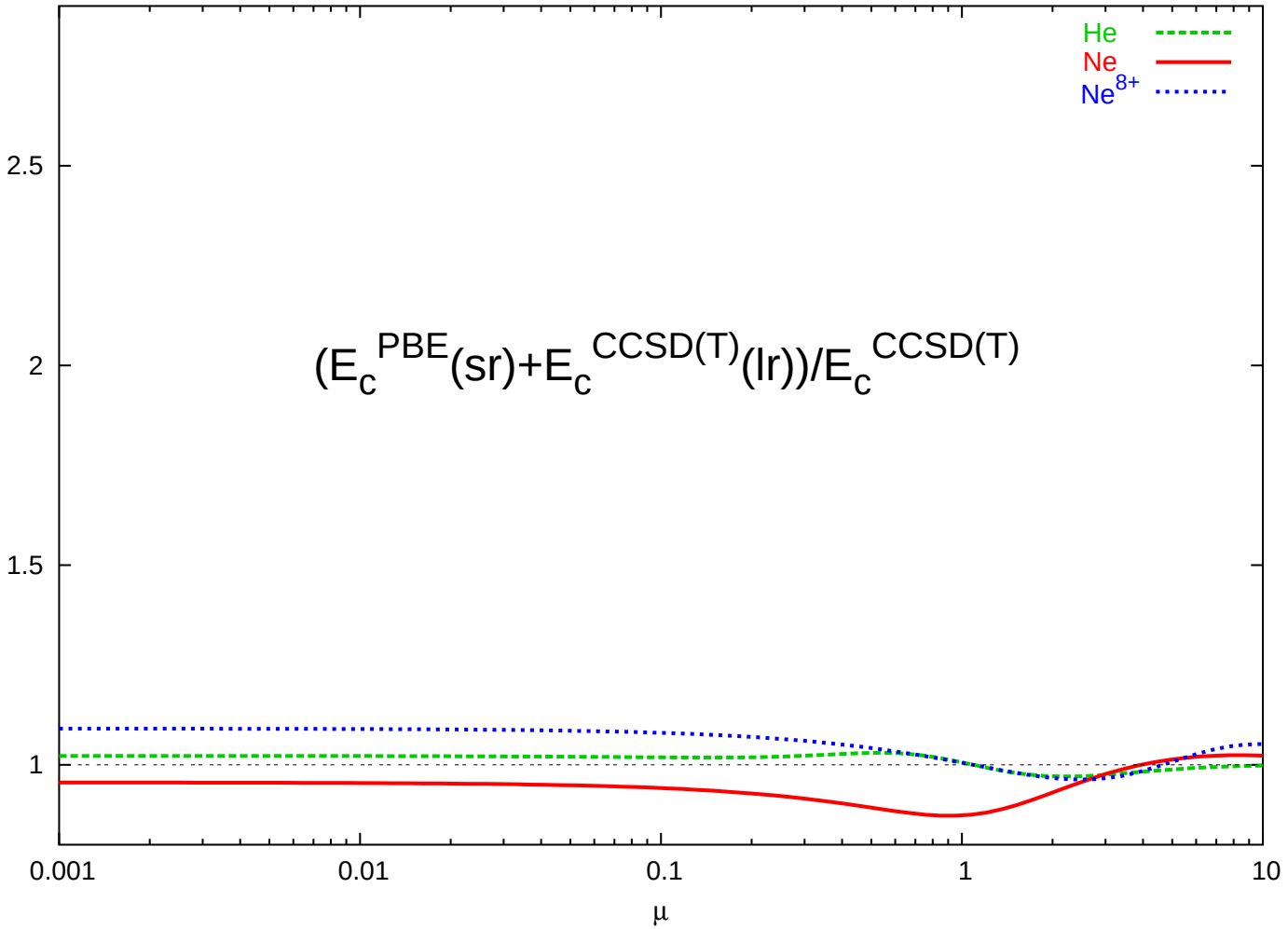
Functionals (contd.): *sr* c-LDA *vs. sr* c-GGA, He



Functionals (contd.): *sr* x-GGA



Functionals (contd.): *sr* c-GGA



Functionals (contd.): x-PBE

$$E_x^{PBE} = \int d^3r\, \rho\, \epsilon_x^{LDA}(\rho)\, F_x(s), \quad s = \frac{|\nabla\rho|}{2k_F\rho}$$

$$F_x = 1 + \kappa - \frac{\kappa}{(1 + \frac{bs^2}{\kappa})}$$

sr modifications:

- $\epsilon_x^{LDA}(\rho) \longrightarrow \epsilon_x^{LDA}(\rho, \frac{\mu}{2k_F})$
- $b \longrightarrow b(\frac{\mu}{2k_F})\, \frac{b}{b(0)}\, \exp(-\alpha(\frac{\mu}{2k_F})^2)$

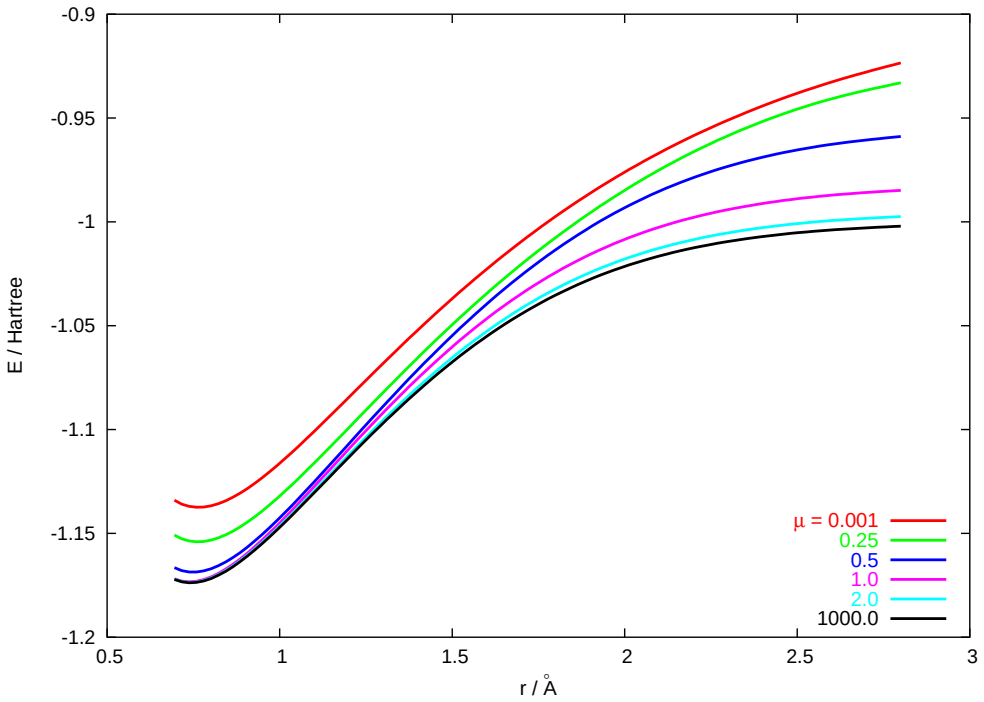
Functionals (contd.): c-PBE

$$
\begin{aligned}
E_c^{PBE} &= \int d^3r\, \rho\, (\epsilon_c^{LDA}(\rho) + H(\rho, t)), \quad t = \frac{|\nabla\rho|}{2k_s\rho} \\
H &= \gamma \ln\left[1 + \frac{\beta t^2}{\gamma}\left(\frac{1 + At^2}{1 + At^2 + A^2t^4}\right)\right] \\
A &= \frac{\beta}{\gamma} \cdot \frac{1}{\exp(-\epsilon_c^{LDA}(\rho)/\gamma) - 1}
\end{aligned}
$$

sr modifications:

- $\epsilon_c^{LDA}(\rho) \longrightarrow \epsilon_c^{LDA}(\rho, \mu)$
- $\beta \longrightarrow \beta\, (\epsilon_c^{LDA}(\rho, \mu)/\epsilon_c^{LDA}(\rho))^{\alpha}$

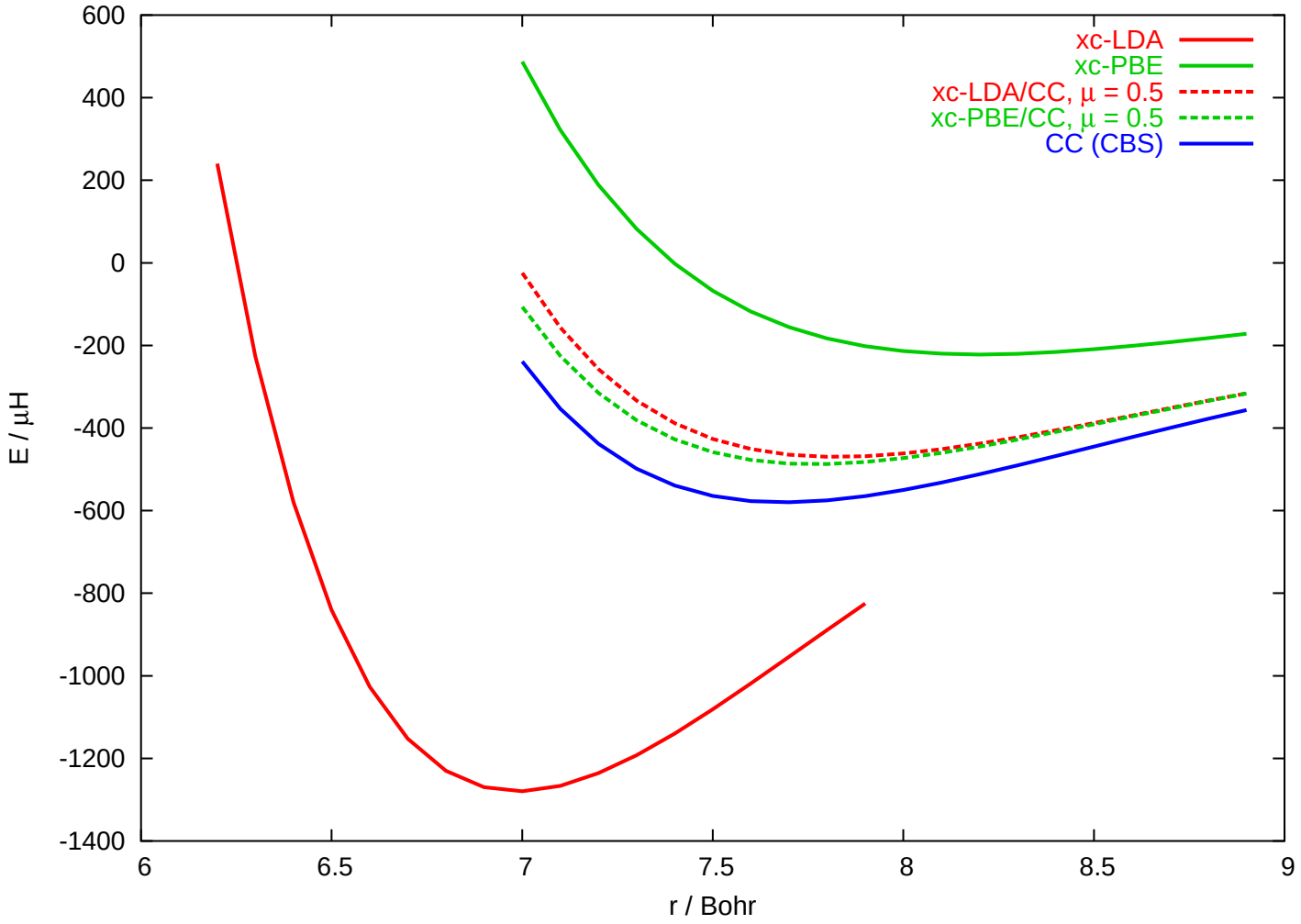
Results: H_2 (xc-LDA/CI)



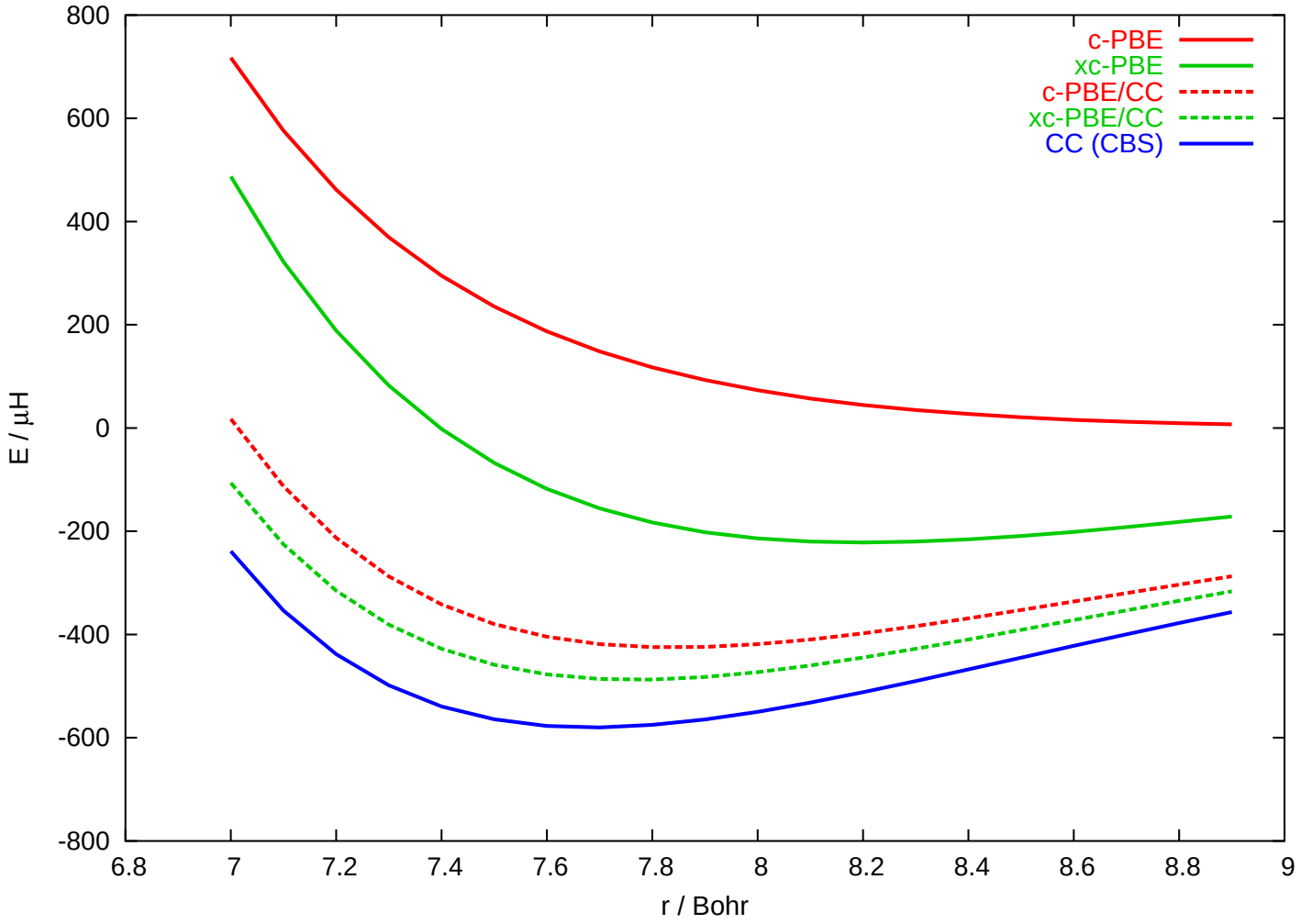
coefficient of the σ_u^2 configuration at $3r_e$

μ	0.001	0.25	0.5	1.0	2.0	100.
C	0.000	-0.184	-0.385	-0.479	-0.509	-0.519

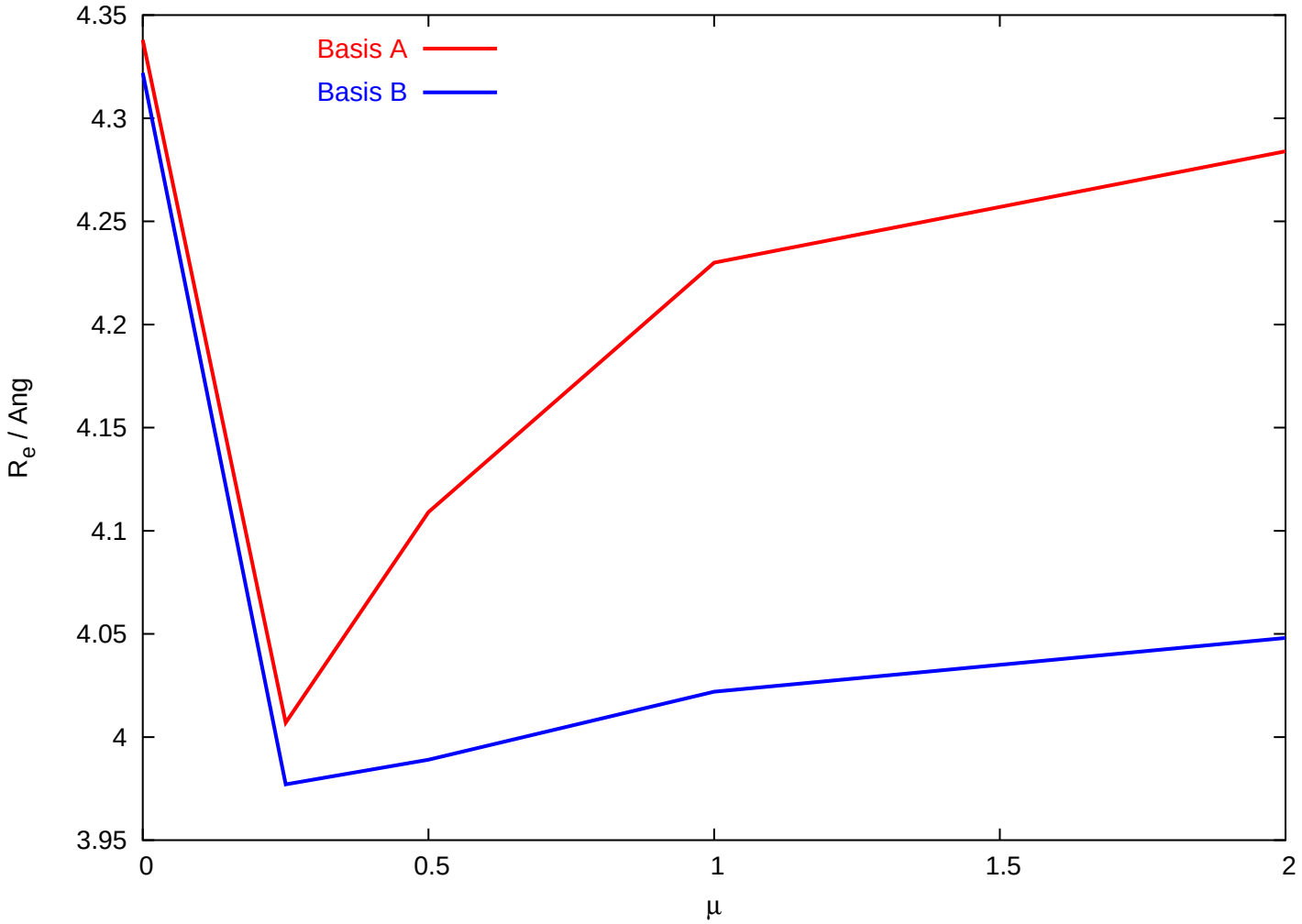
Results (contd.): Kr_2 (xc-DFT/CCSD(T))



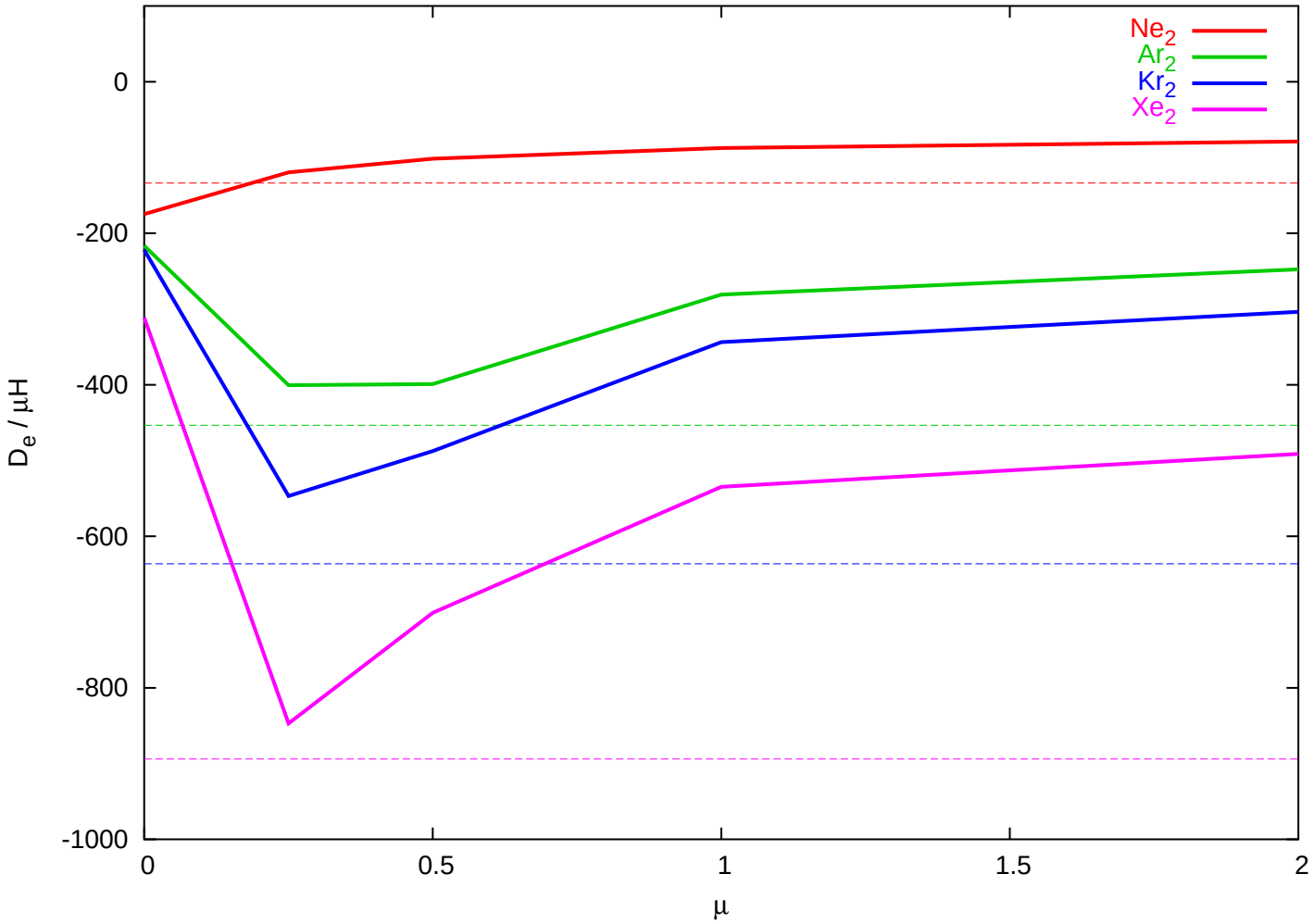
Results (contd.): Kr_2 (xc/c-PBE/CCSD(T))



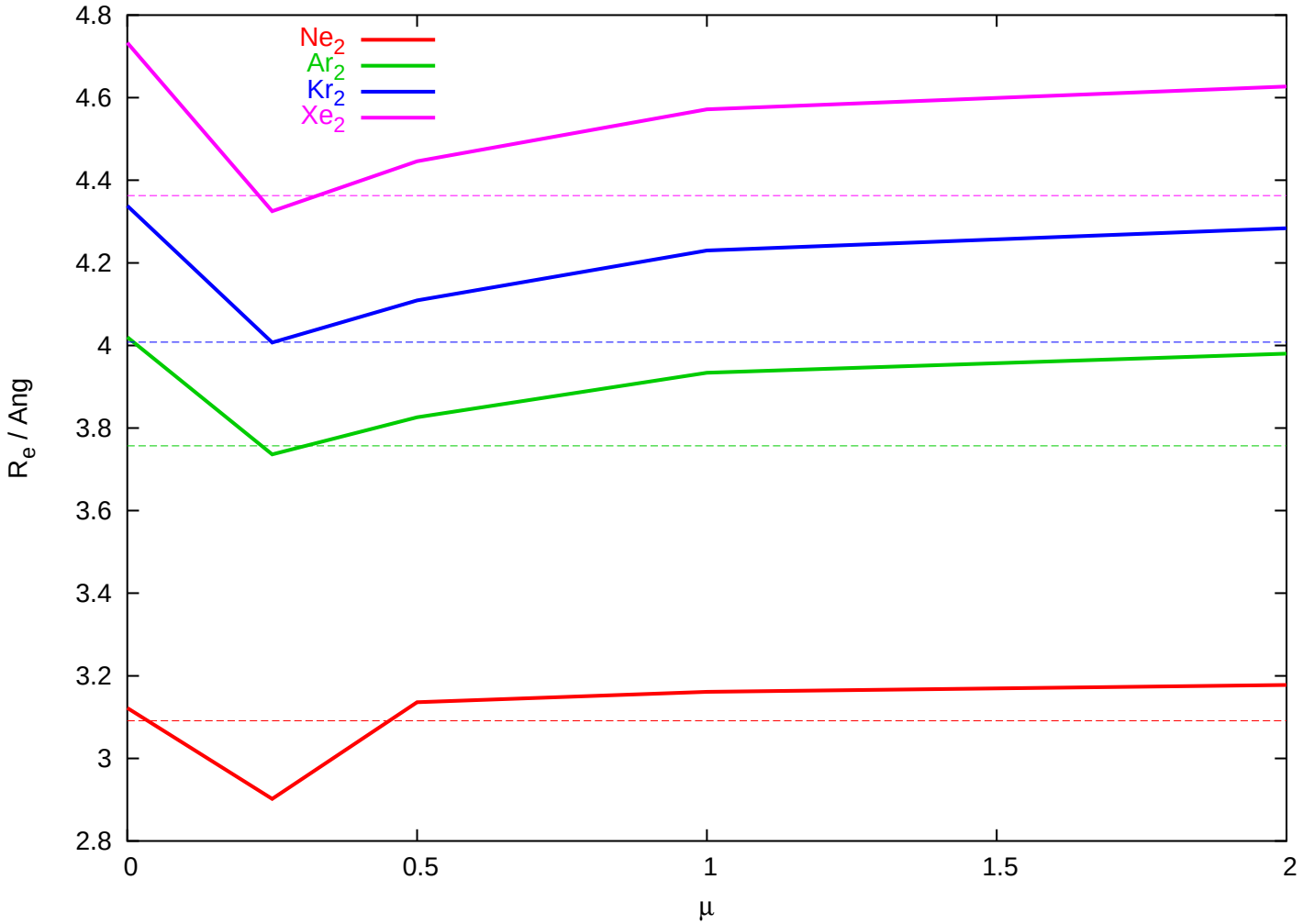
Results (contd.): Kr_2 (xc-PBE/CCSD(T))



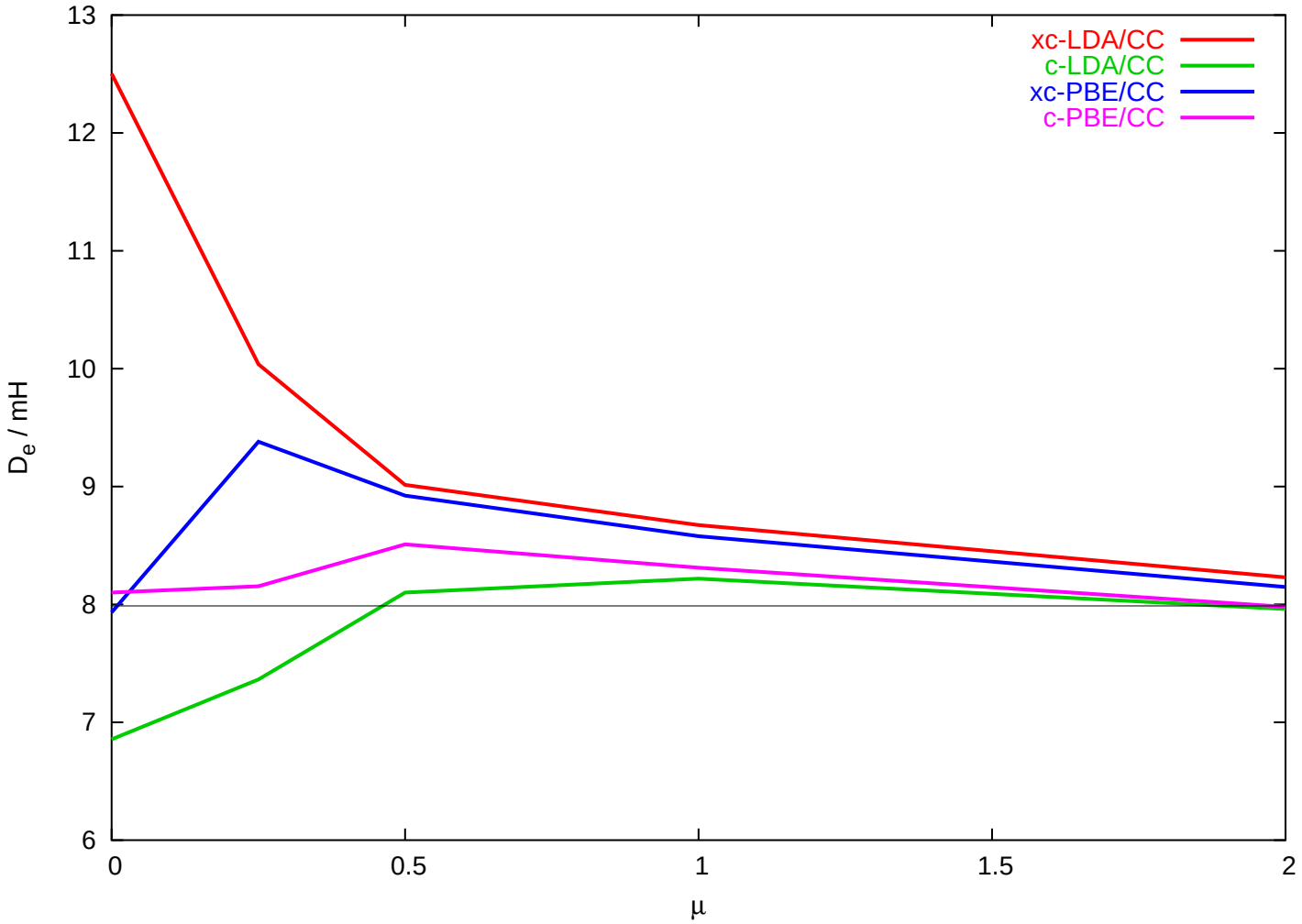
Results (contd.): Rg_2 (xc-PBE/CCSD(T))



Results (contd.): Rg_2 (xc-PBE/CCSD(T))



Results (contd.): $(H_2O)_2$ (xc/c-DFT/CCSD(T))

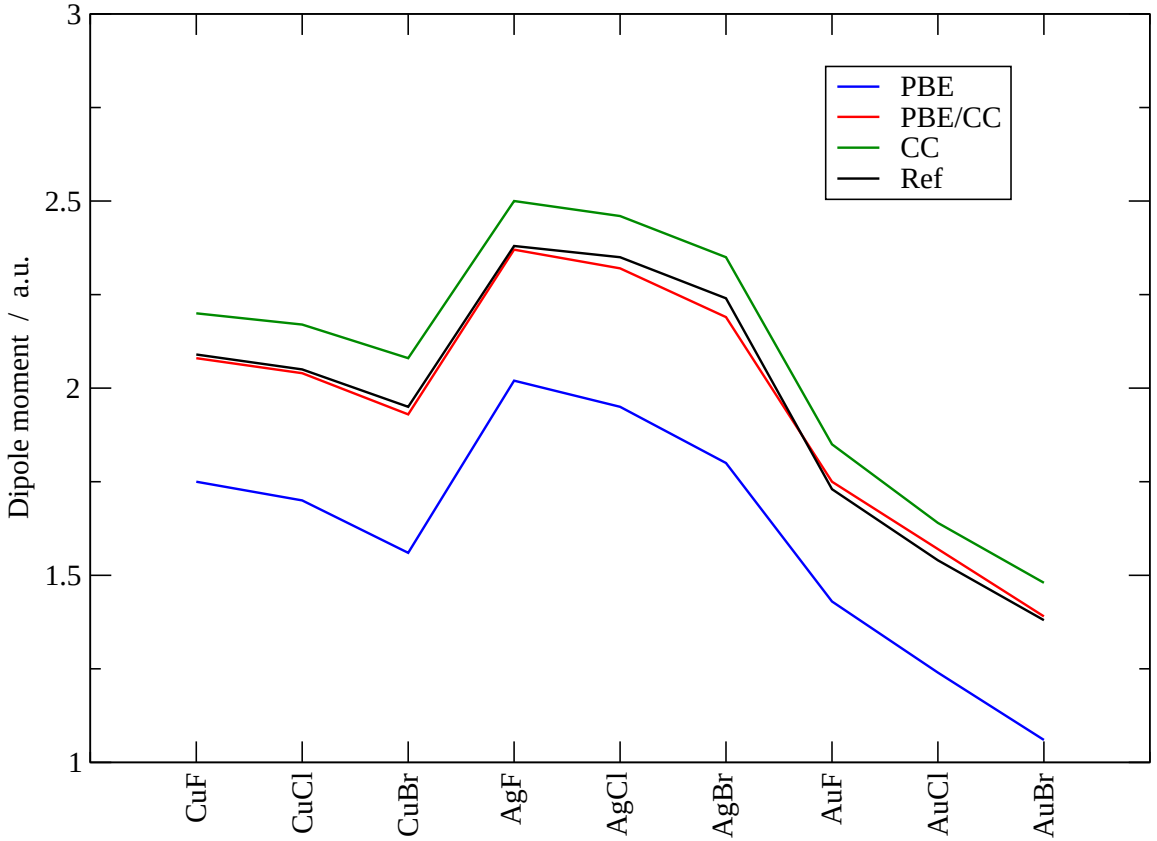


Results (contd.): Reaction energies of closed-shell reactions

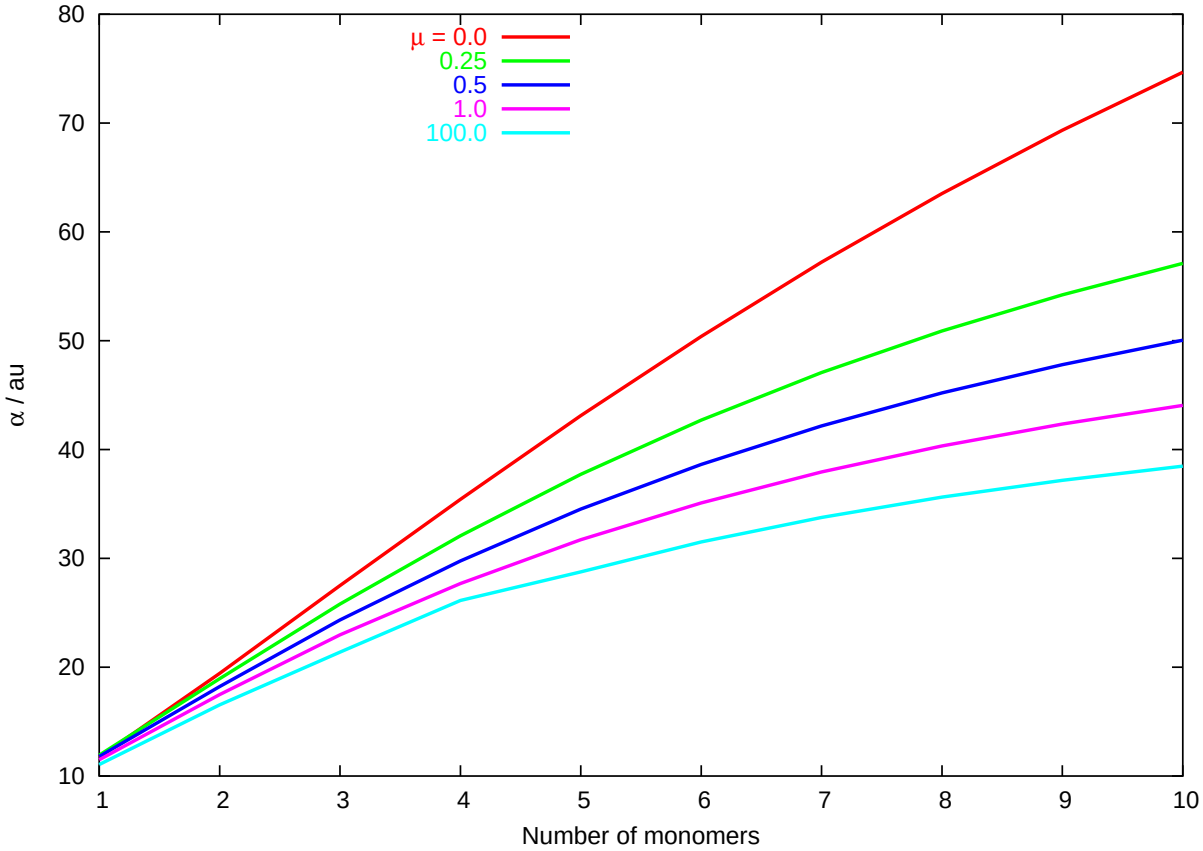
(xc-PBE/CCSD(T), aug-cc-pVTZ)

ΔE (kcal/mol)	μ=0.0	0.5	100.0	exp.
$H_2O_2 + H_2 \rightarrow H_2O + H_2O$	-83.0	-89.6	-87.7	-86.3
$CO + H_2O \rightarrow CO_2 + H_2$	-17.4	-11.2	-5.4	-7.4
$CO + H_2O_2 \rightarrow CO_2 + H_2O$	-100.4	-100.8	-93.1	-93.7
$CH_4 + 4\ H_2O_2 \rightarrow CO_2 + 6\ H_2O$	-277.3	-294.1	-291.3	-288.5
$SO_2 + CO_2 \rightarrow SO_3 + CO$	59.3	55.6	50.8	44.9
$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O$	-41.1	-45.2	-42.3	-48.8
MAE (kcal/mol)	8.9	5.7	3.2	

Results (contd.): Dipole moments of group 11 halides (xc-PBE/CCSD(T))



Results (contd.): Polarizabilities of H_2 chains (xc-PBE/CCSD(T))



Outlook

- coupling with open-shell CCSD(T)
- deriving spin-polarized *sr* functionals

- coupling with local methods (LMP2)
- using multipole/Fourier-transform techniques for *lr* integrals