Development and applications of ensemble error-estimation xc functionals in computational surface science

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SUNCAT Center for Interface Science and Catalysis
SLAC National Accelerator Laboratory

Electronic structure calculations with the GPAW code: Users and developers meeting
Technical University of Denmark, May 21-23, 2013

Computational materials design

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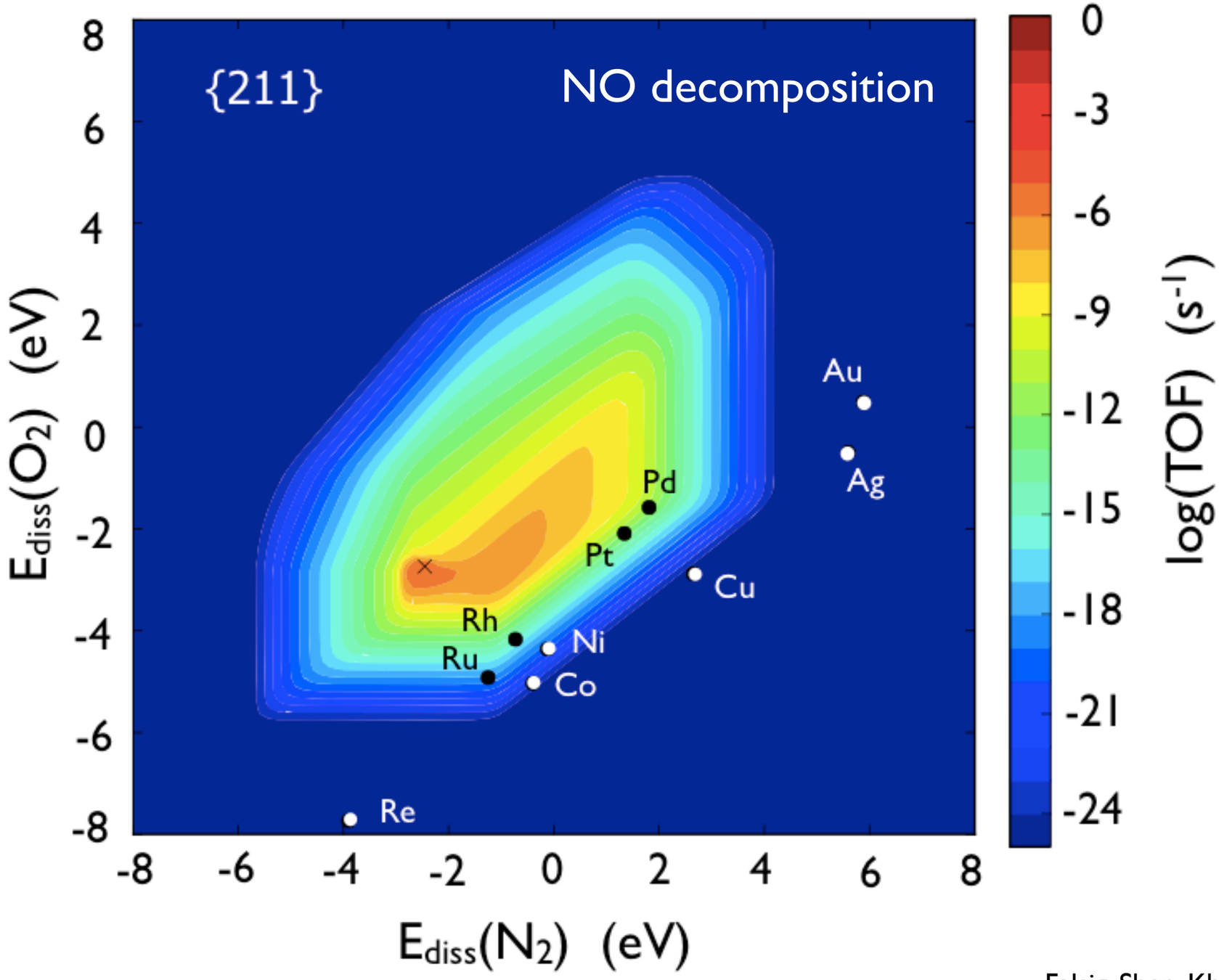

Falsig, Shen, Khan, Guo, Jones, Dahl, Bligaard, *Topics in Catalysis* (2013)

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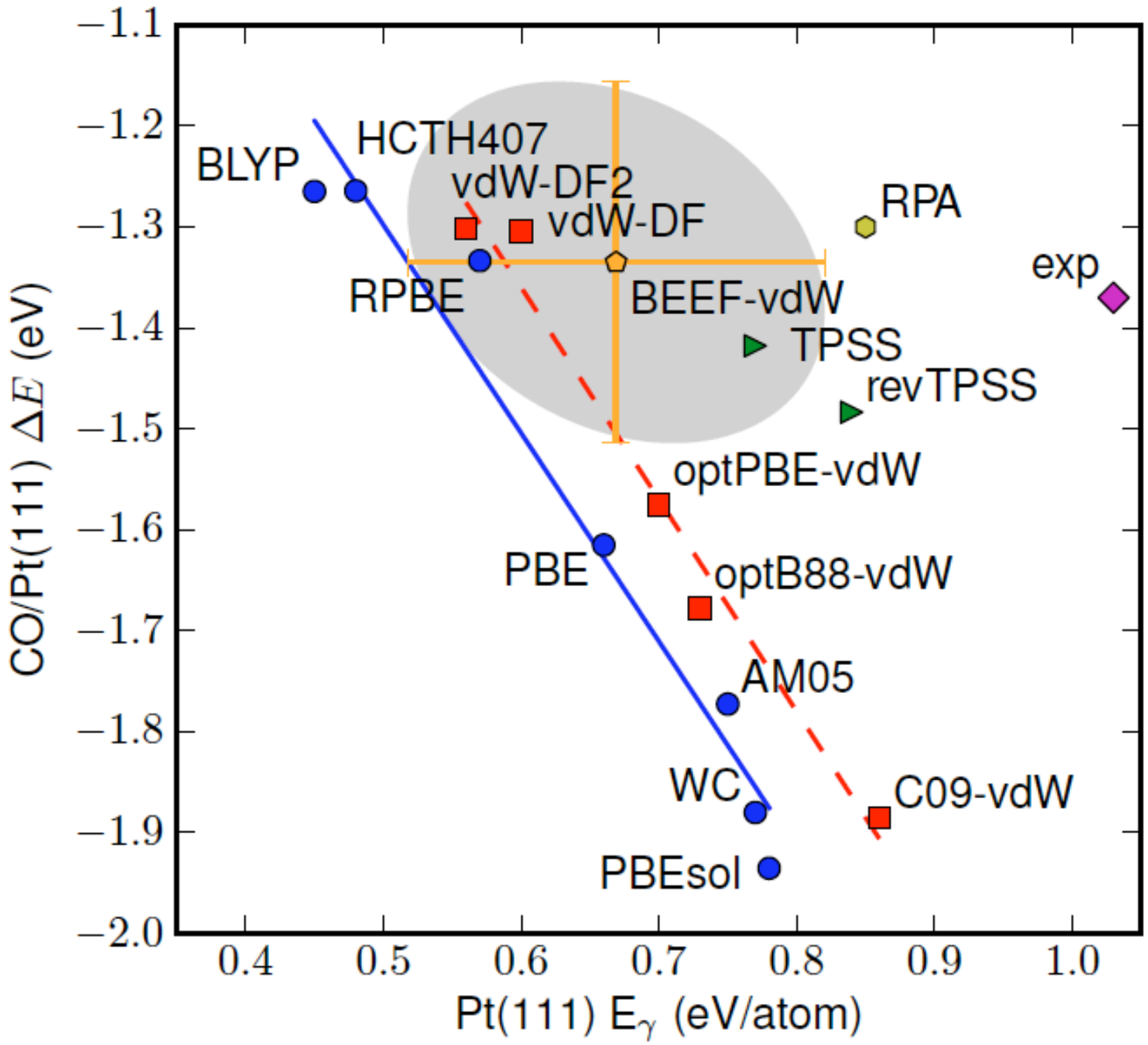
XC model compromise



Wellendorff, Lundgaard, Møgelhøj, Petzold, Landis, Nørskov, Bligaard, Jacobsen,
Phys. Rev. B **85**, 235149 (2012)

Ammonia synthesis on Ru

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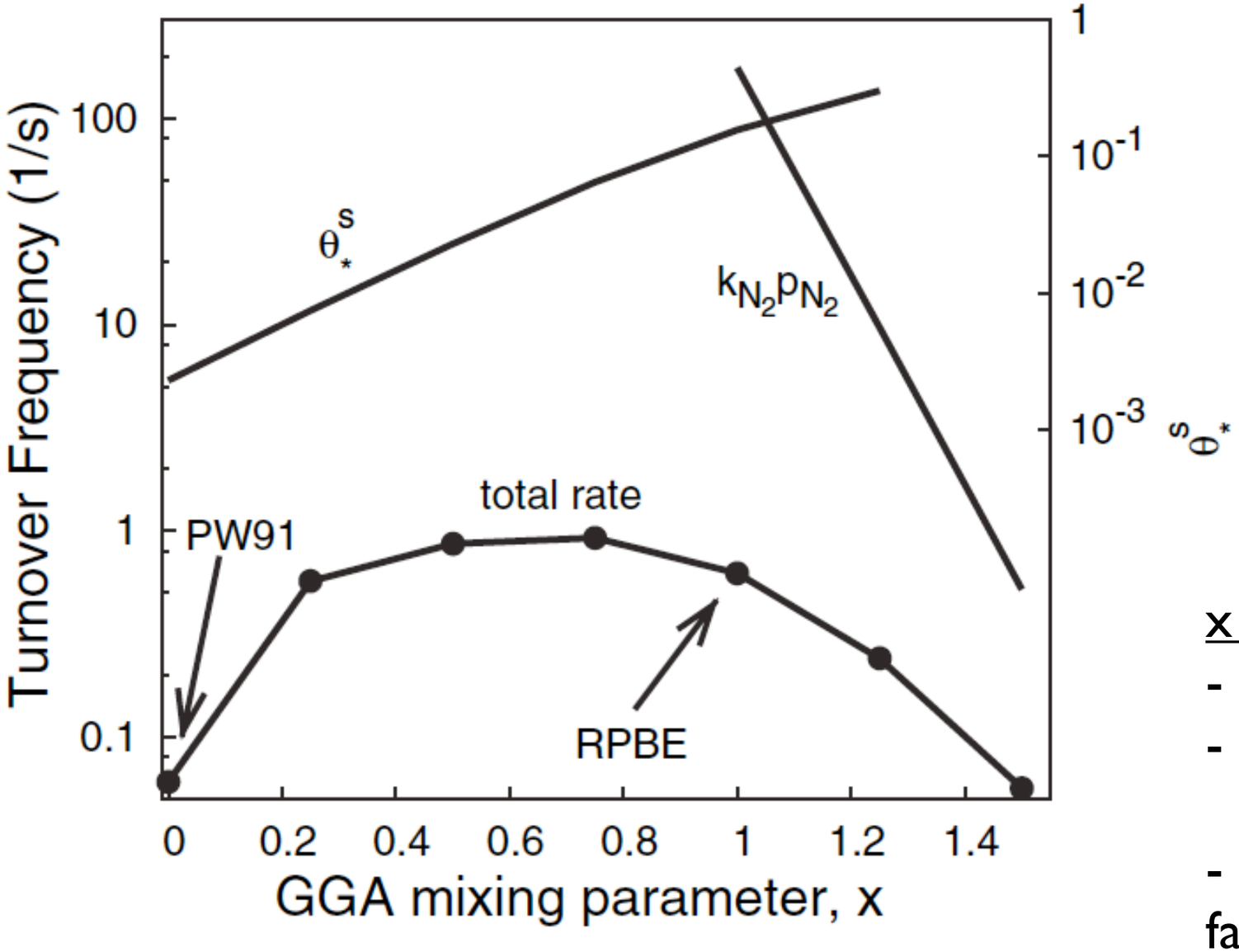
$XC = x \cdot RPBE + (1 - x) \cdot PW91$



Honkala *et al.*, *Science* **307**, 555 (2005)

x → 0:

- barriers decrease.
- adsorption energies increase.

- N_2 dissociation becomes much faster, but the coverage of free sites also decrease.
- total rate is rather insensitive.

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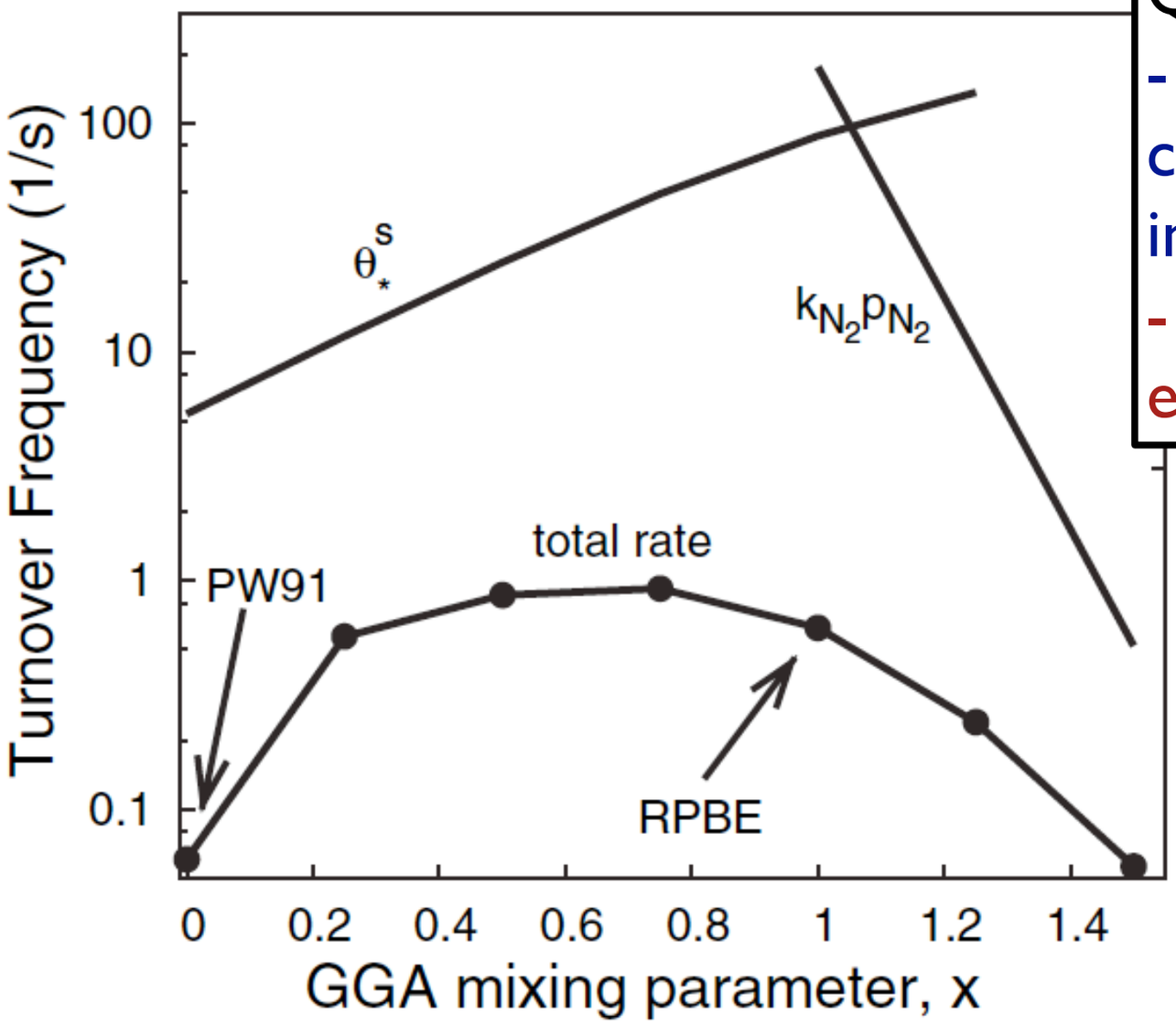

Honkala *et al.*, *Science* **307**, 555 (2005)

Questions:

- What is the influence on scientific conclusions of inherent variations in DFT predictions?
- How can we reliably estimate the errors of GGA-DFT?

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- barriers decrease.
- adsorption energies increase.

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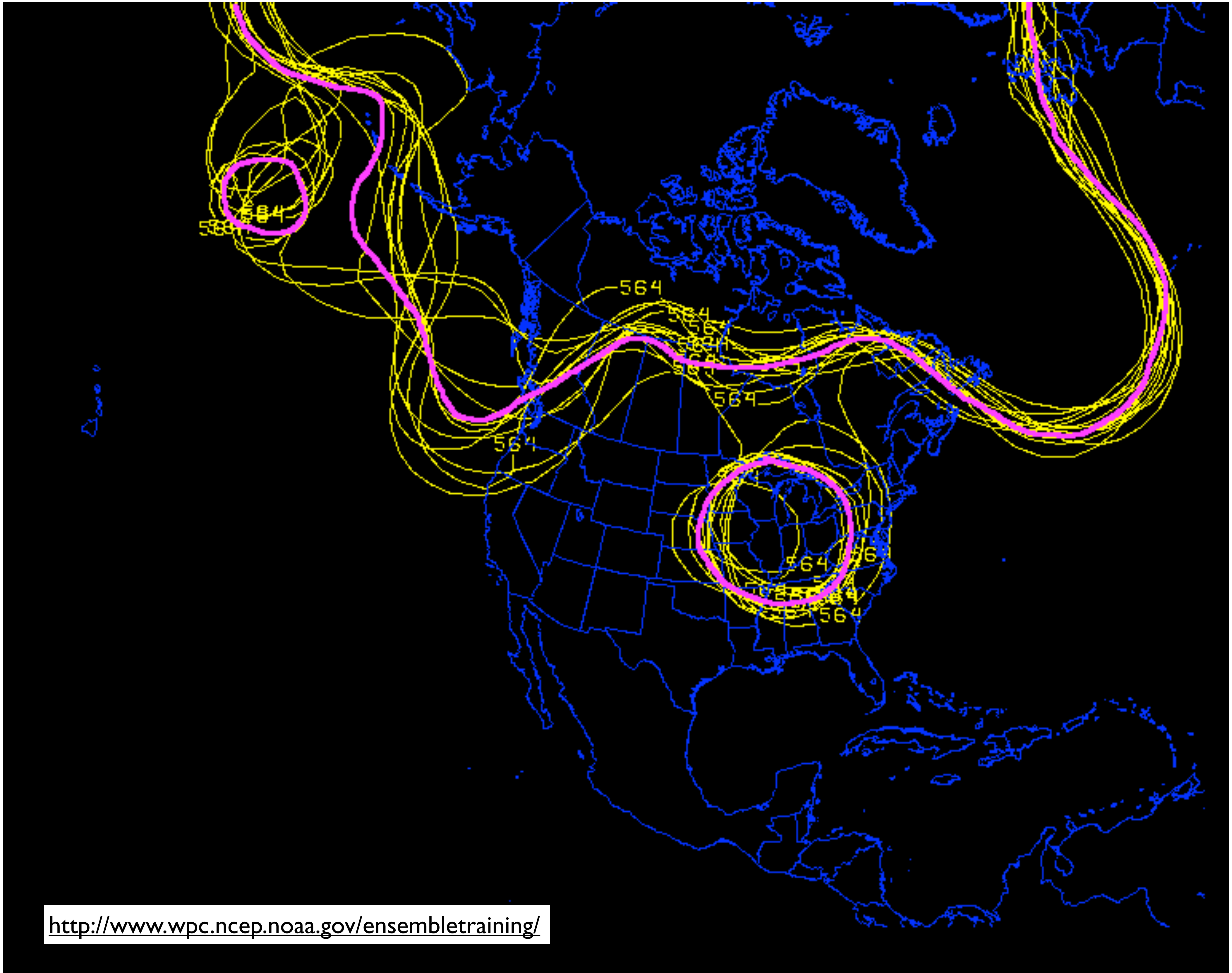
Ensemble prediction in weather forecasting



Ensemble XC functionals

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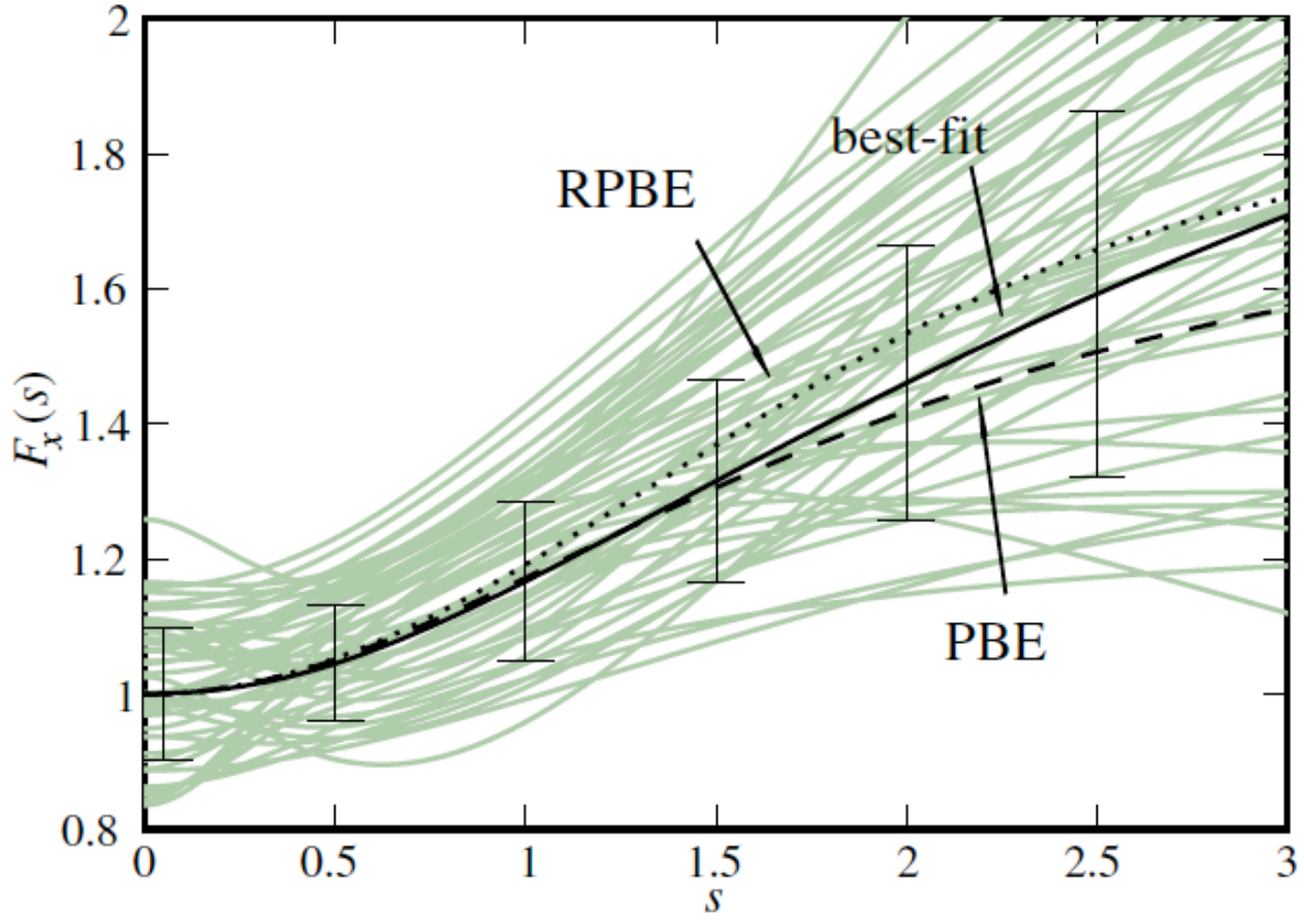
GGA XC model space

$$E = E_0 + E_{\mathrm{xc}}^{\mathrm{GGA}}$$

$$E_{\mathrm{x}}^{\mathrm{GGA}} = \int n(\mathbf{r})\varepsilon^{\mathrm{LDA}}(n(\mathbf{r}))F_{\mathrm{x}}(s)d\mathbf{r}$$



Probability distribution for the model parameters

$$P(\theta|MD) \sim \exp(-C(\theta)/T)$$

Quadratic cost function to be minimized

$$C(\theta) = \frac{1}{2}\sum_k \left(E_k(\theta) - E_k^{\mathrm{exp}}\right)^2$$

Mortensen, Kaasbjerg, Frederiksen, Nørskov, Sethna, Jacobsen, *PRL* **95**, 216401 (2005)

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Error-estimation ensemble

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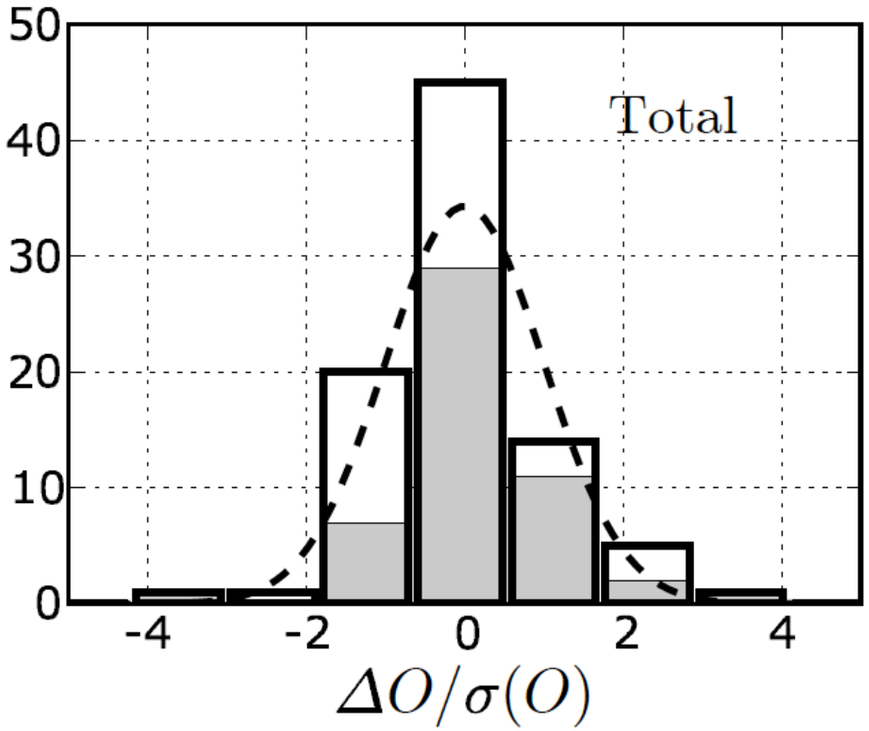
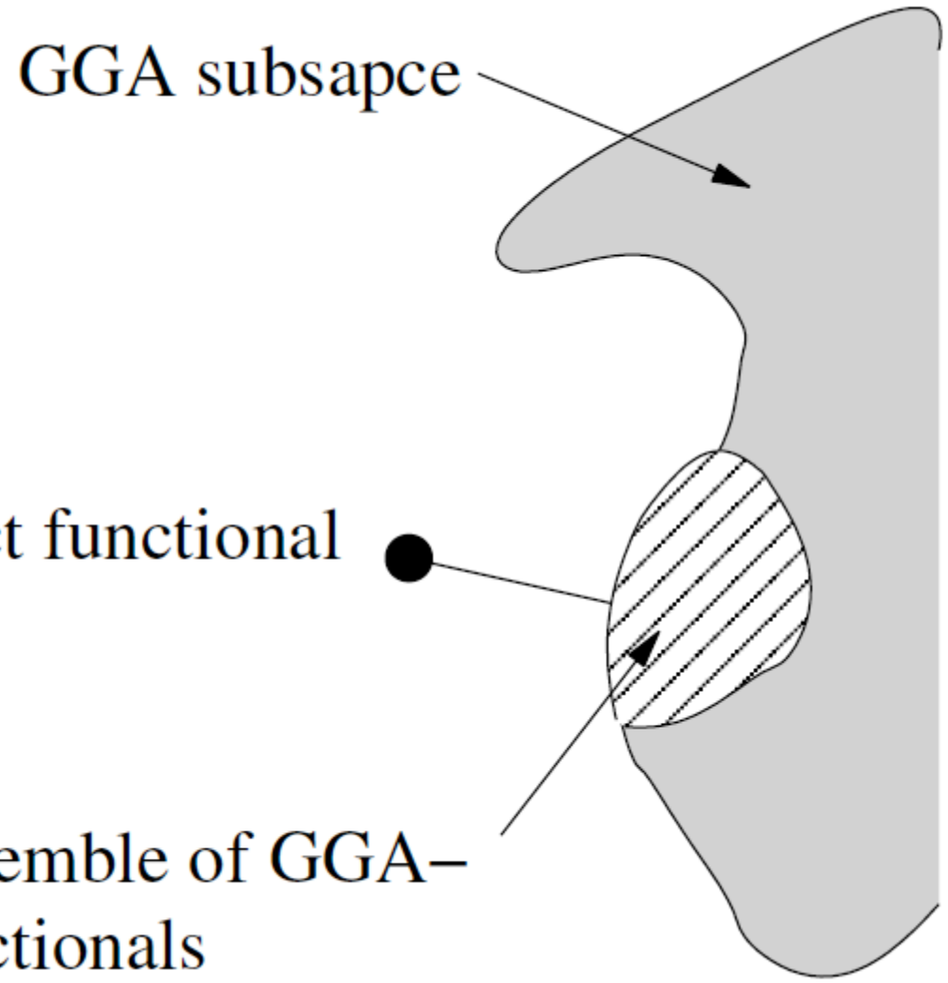
$$\sigma_{\mathrm{BEE}}(O) = \sqrt{\frac{1}{N}\sum_{\mu=1}^{N}(O(\theta^{\mu}) - O_{\mathrm{bf}})^2}$$





K. Kaasbjerg, Master Thesis, DTU (June 2005)

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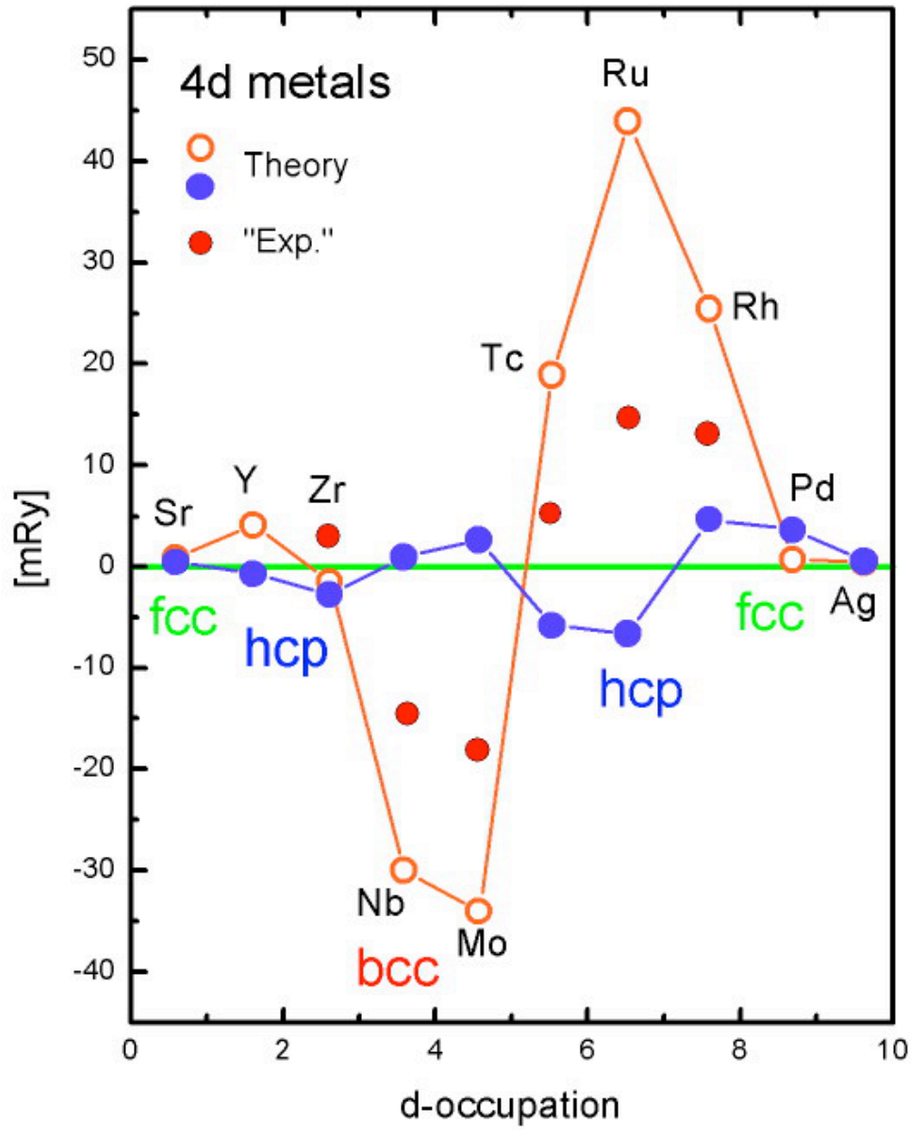
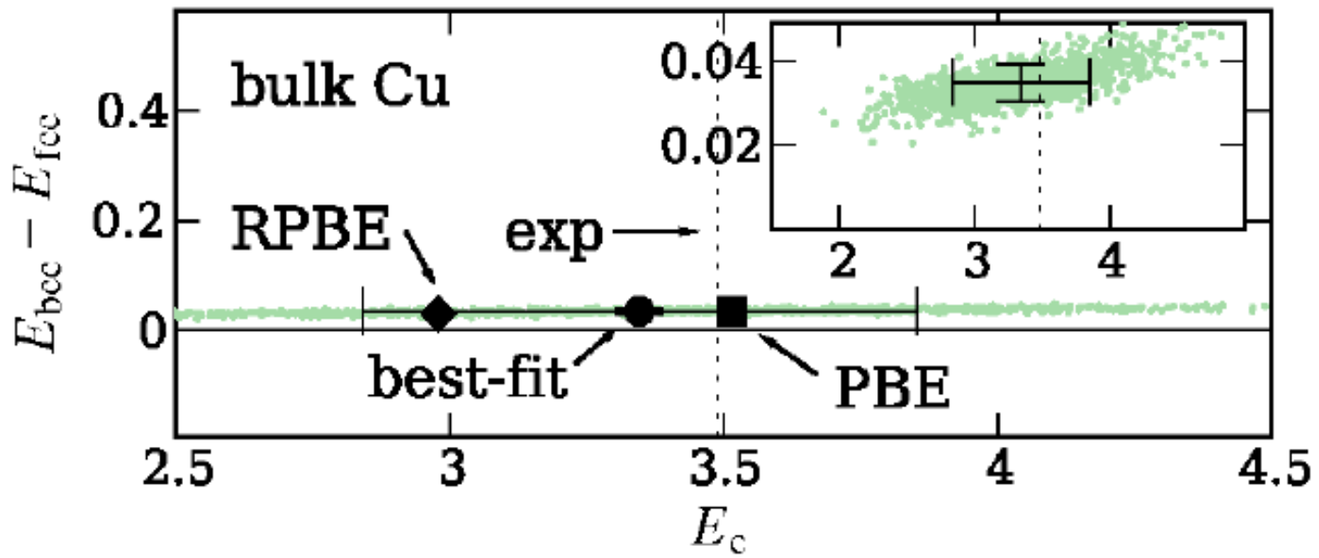
Bulk Cu cohesive energy and structural energy difference



Skriver, *PRB* **31**, 1909 (1985)



Mortensen, Kaasbjerg, Frederiksen, Nørskov, Sethna, Jacobsen,
PRL **95**, 216401 (2005)

BEEF-vdW density functional

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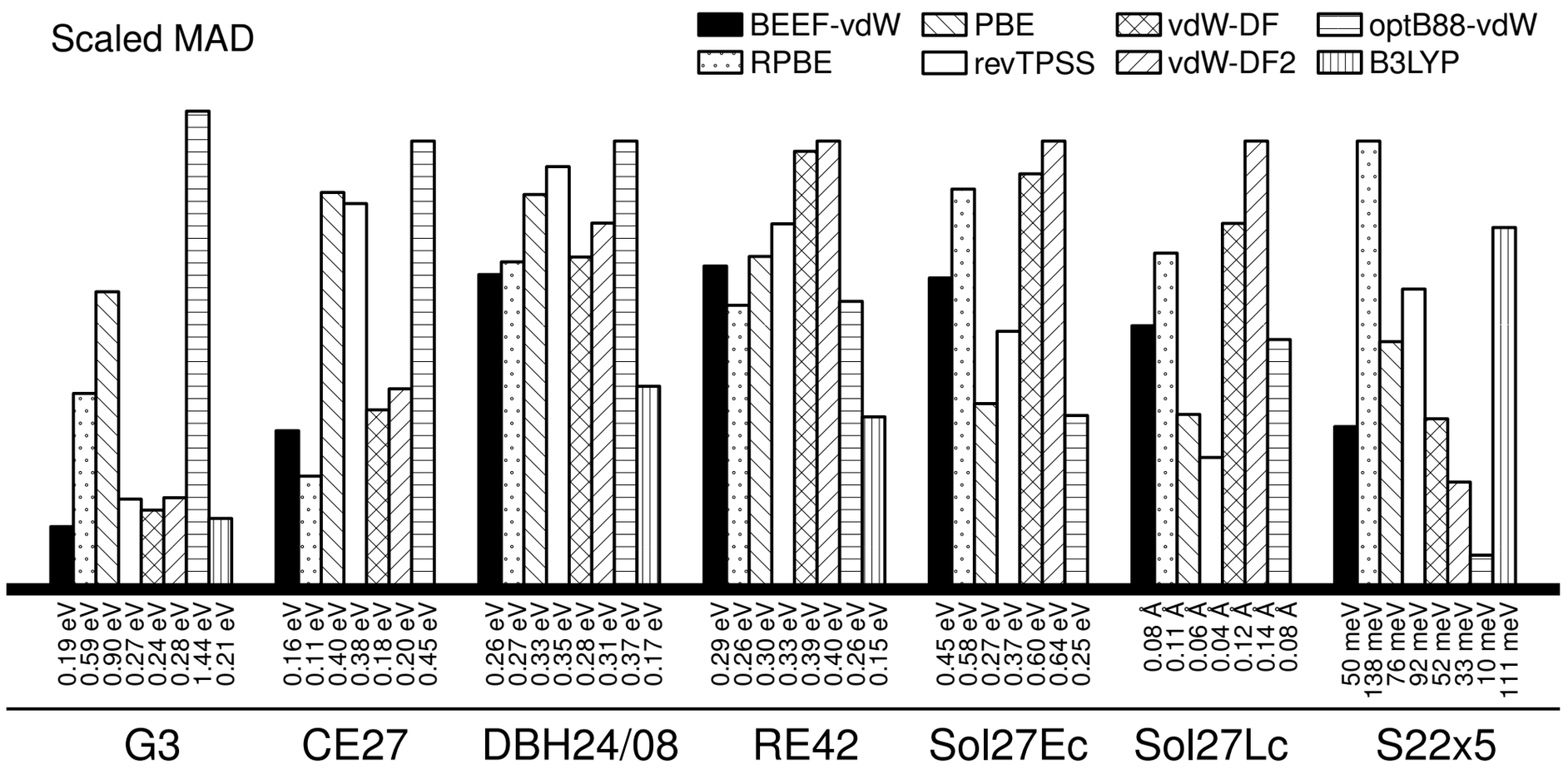
GGA+vdW model space

$$F_x(s) = \sum_{m=0}^{29} a_m B_m(t(s))$$

$$E_c = \alpha_c E_c^{\mathrm{LDA}} + (1-\alpha_c) E_c^{\mathrm{PBE}} + E_c^{\mathrm{nl}}$$



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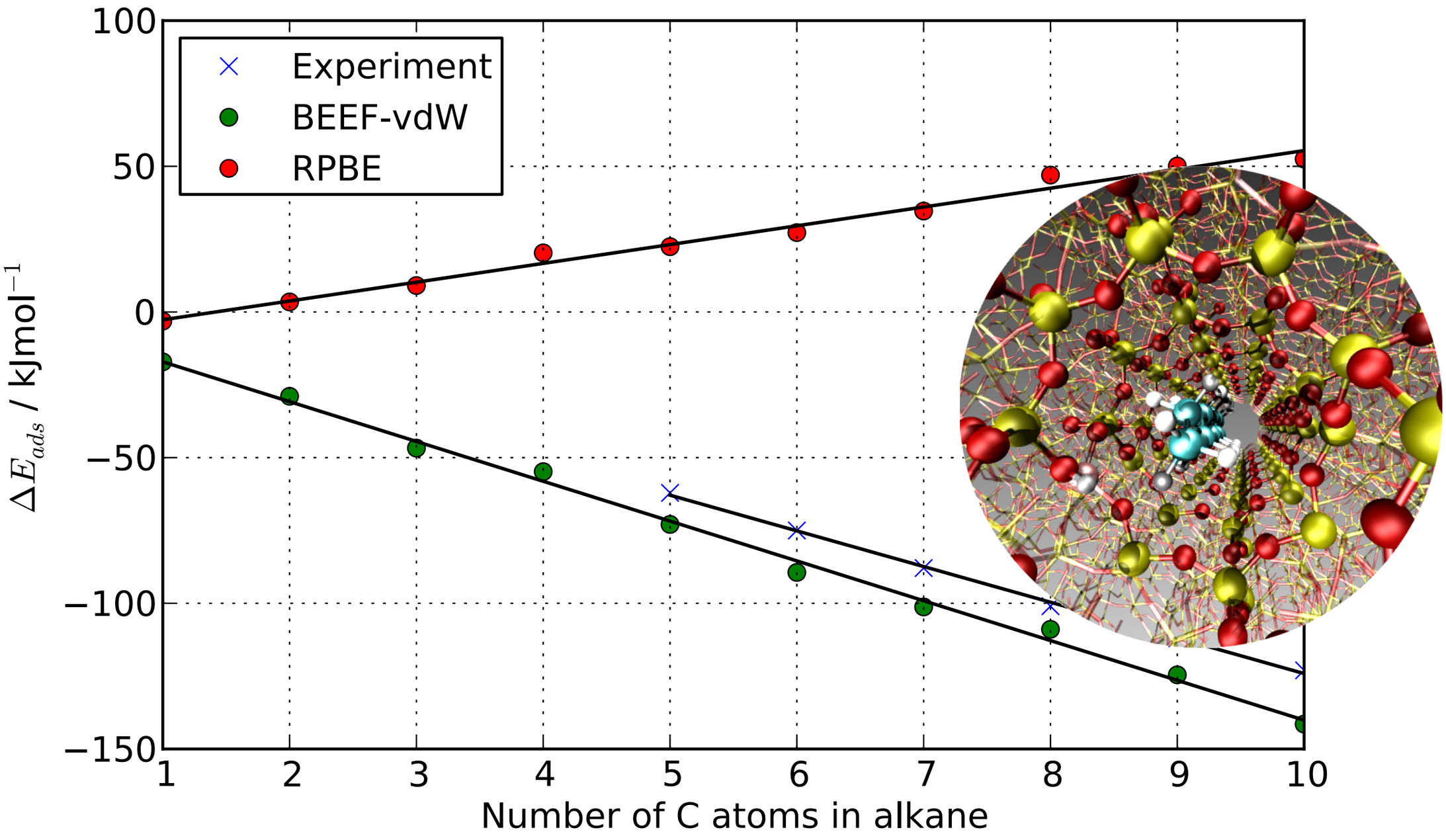
Physisorption of n-Alkanes in ZSM-22



Brogaard, Moses, Nørskov, Catalysis Letters 142, 1057 (2012)

BEEF-vdW error-estimation ensemble

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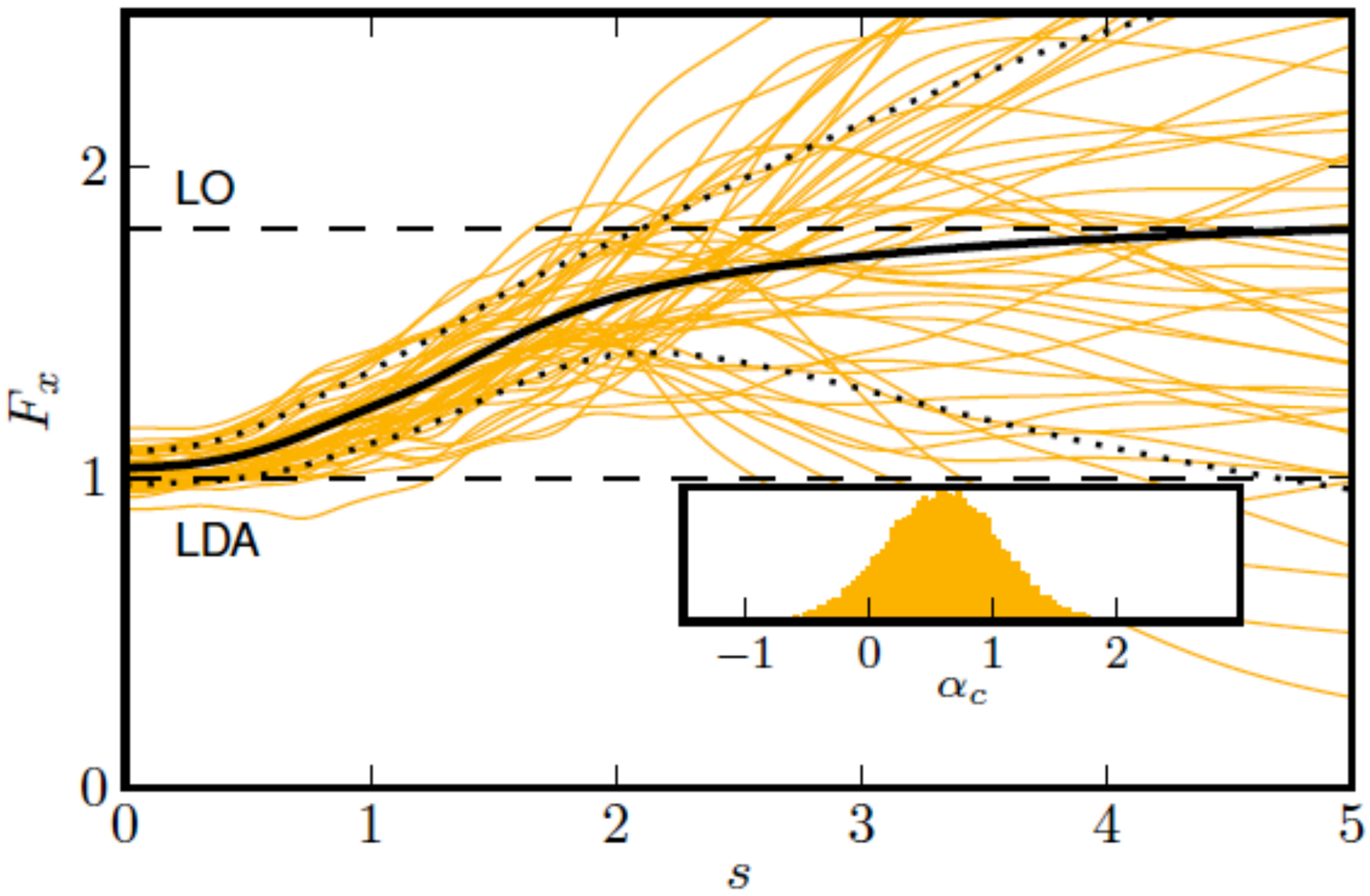

$$\sigma_{\mathrm{BEE}}(O) = \sqrt{\frac{1}{N}\sum_{\mu=1}^{N}\left(O(\theta^{\mu}) - O_{\mathrm{bf}}\right)^2}$$

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It's really fast and simple!

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```
>>> from gpaw import GPAW
>>> from ase.dft.bee import BEEF_Ensemble

>>> calc = GPAW(gpw)
>>> ens  = BEEF_Ensemble(calc)
>>> de   = ens.get_ensemble_energies()
```

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GPAW:

non-self-consistent xc contributions $\left[\delta E_x^0, \delta E_x^1, \ldots, \delta E_x^{29}, \delta E_c^\alpha\right]$

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GPAW:

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VASP, Quantum Espresso:
Johannes Voss @ SUNCAT

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CO adsorption on Rh(111)

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3. ssh

```
from ase import *
from gpaw import GPAW
from ase.dft.bee import BEEF_Ensemble
import numpy as np

names = ['CO_Rh111', 'Rh111', 'CO']
# generating data
for i, name in enumerate(names):
    calc = GPAW(name+'.gpw')
    e    = calc.get_potential_energy()
    ens  = BEEF_Ensemble(calc)
    de   = ens.get_ensemble_energies()
    ens.write(name+'.bee')
    if i == 0:
        E  = e
        dE = de
    else:
        E  = np.append(E, e)
        dE = np.vstack((dE, de))
    del calc, ens
# evaluating
E_ads  = E[0] - E[1] - E[2]
de_ads = de[0,:] - de[1,:] - de[2,:]
dE_ads = np.std(de_ads)
E_exp  = -1.45
err    = E_ads - E_exp
print "-------------------------"
print "E_ads DFT  : %.2f eV" % E_ads
print "E_ads exp. : %.2f eV" % E_exp
print "E_ads error: %.2f eV" % err
print "error est. :  %.2f eV" % dE_ads
print "-------------------------"
                              32,1          Top
```

3. ssh

```
-------------------------
E_ads DFT  : -1.60 eV
E_ads exp. : -1.45 eV
E_ads error: -0.15 eV
error est. :  0.17 eV
-------------------------
[jewe@suncatls1 ~/]:: 
```

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Sensitivity of reactivity volcanos: NO decomposition

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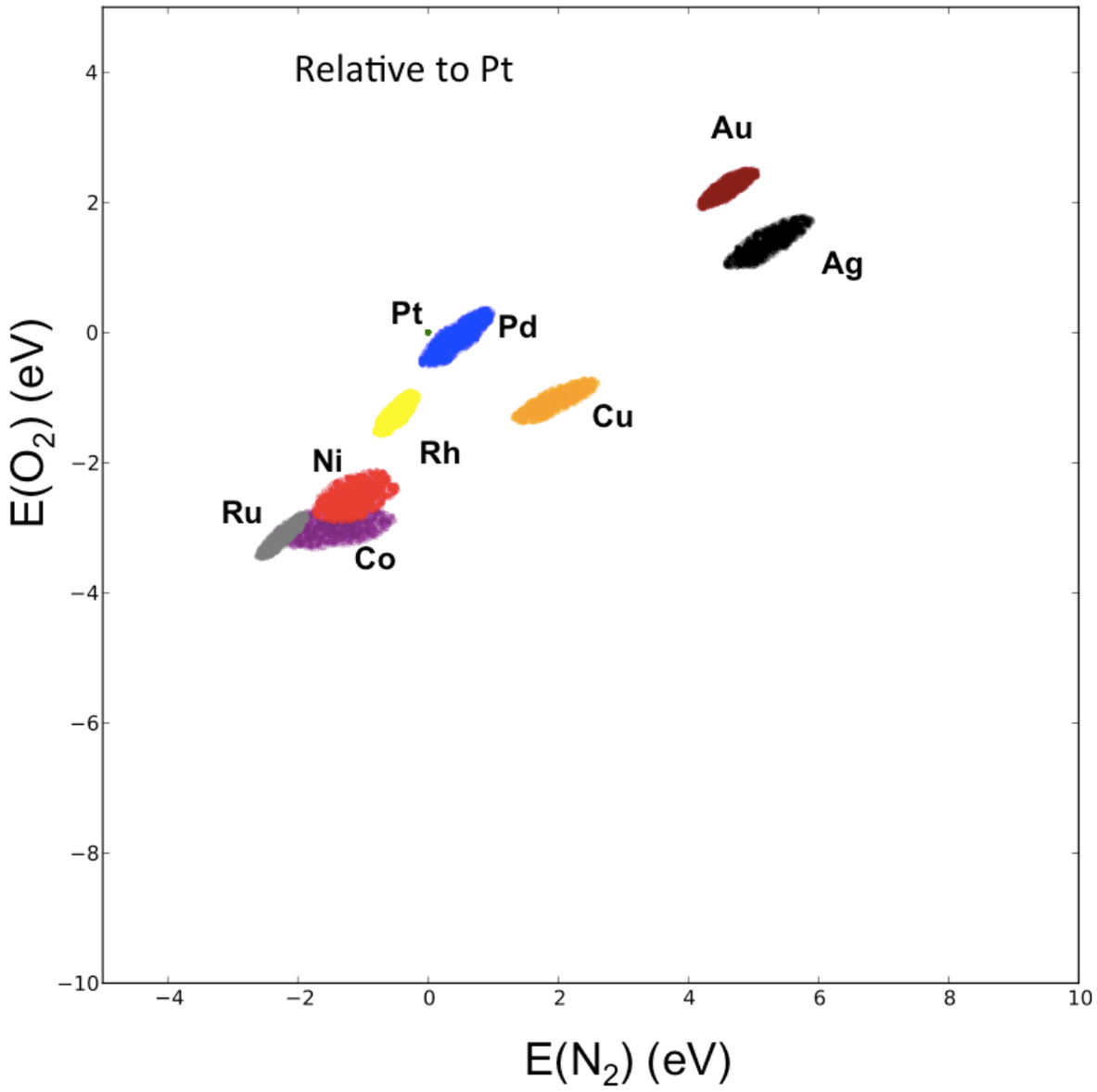
What is the probability that a certain metal/alloy will be more active than Pt for direct NO decomposition?

Distributions of ensemble predictions relative to Pt(111)



Khan, Lundgaard, Wellendorff, Nørskov, Jacobsen, Bligaard (2013)

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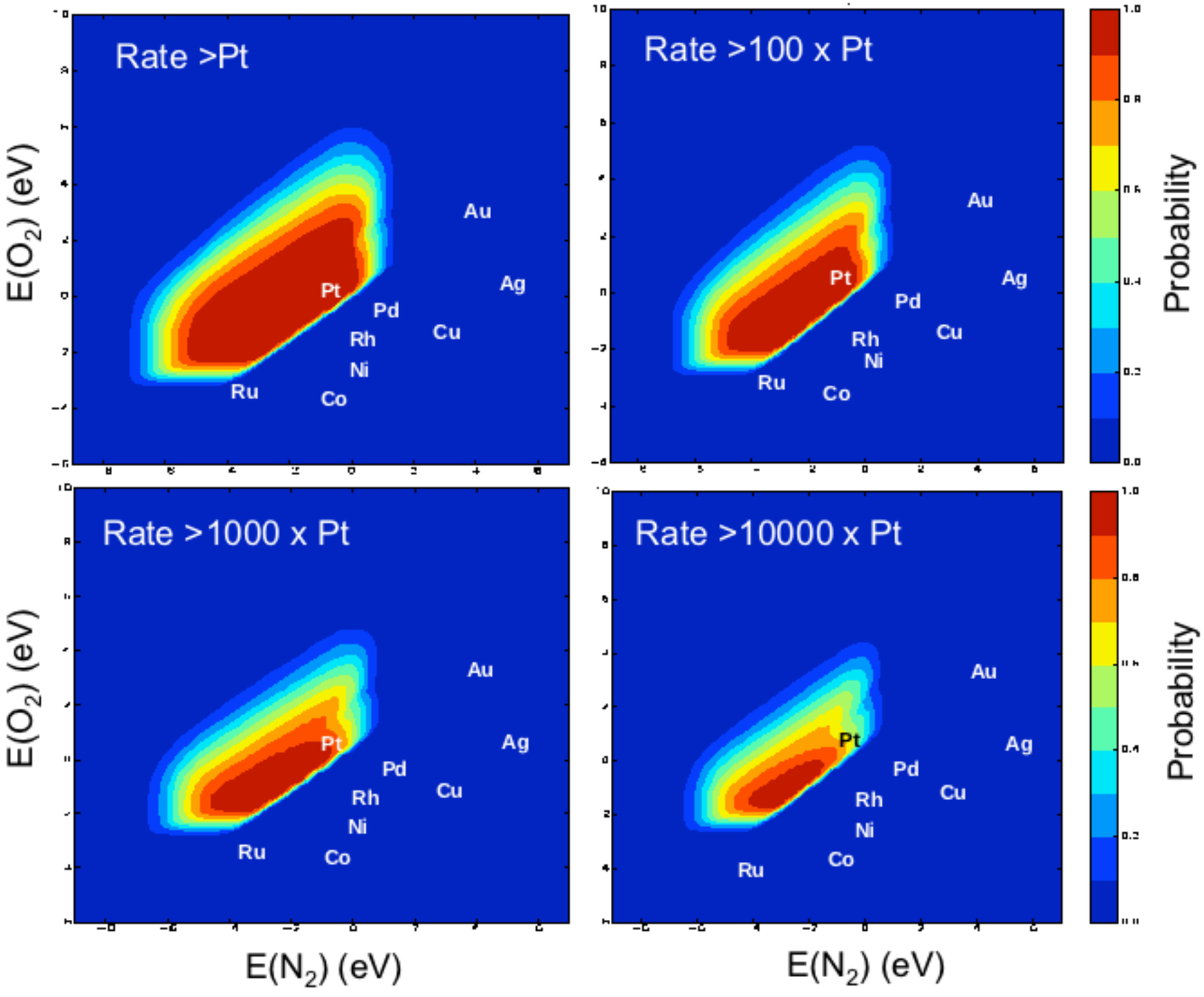
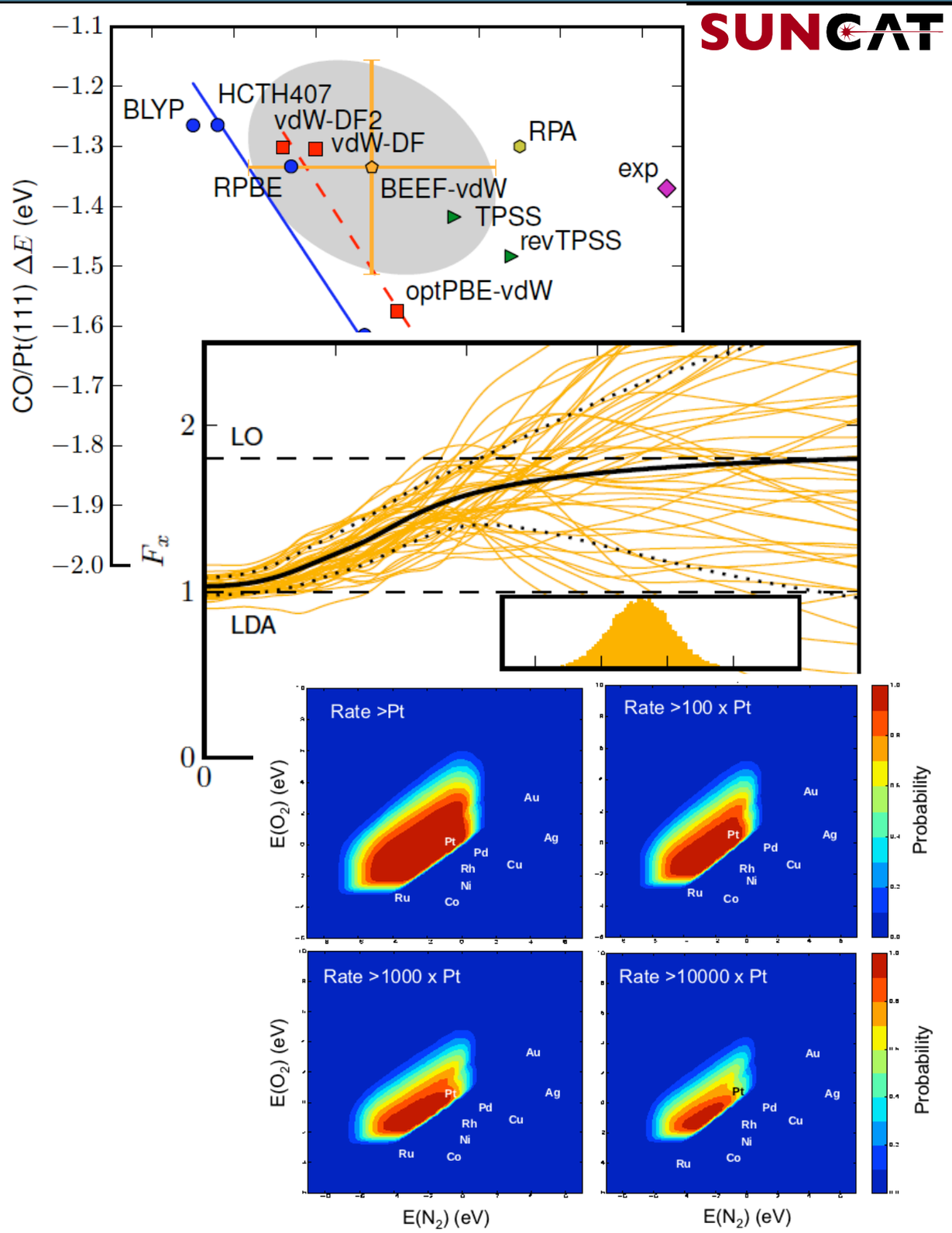


Summary and outlook

- A BEEF ensemble of xc functionals offers a systematic and quantitative framework for **assessing the sensitivity of scientific conclusions** within the chosen XC model space, e.g., GGA+vdW.

- **Probabilistic volcano plots** should be particularly useful in computational catalysis.

- Work continues in the SUNCAT theory group towards ensemble functionals for surface science that include **metaGGA exchange**, **non-local correlation**, and **screened exact exchange**.



Thanks!

Collaborators
Keld Lundgaard
Karsten W. Jacobsen
Jens K. Nørskov
Thomas Bligaard

Organizations
CAMD
SUNCAT

U.S. Department of Energy
Office of Basic Energy Sciences

A meta-GGA functional: mBEEF

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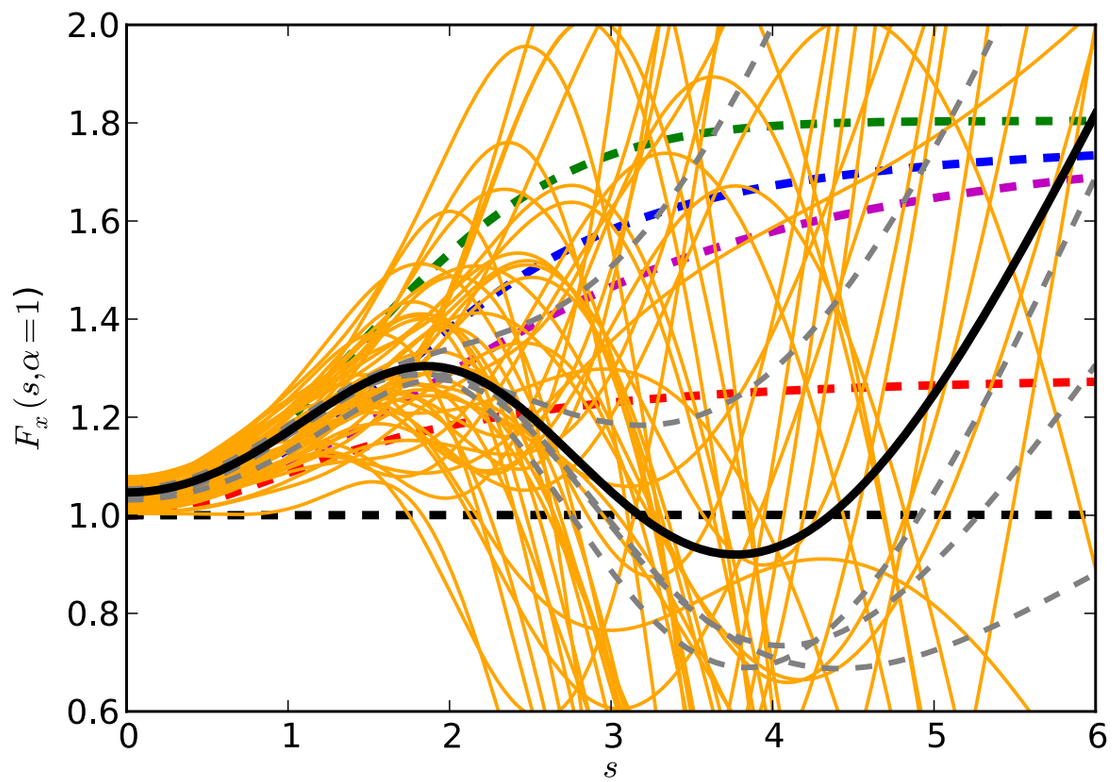
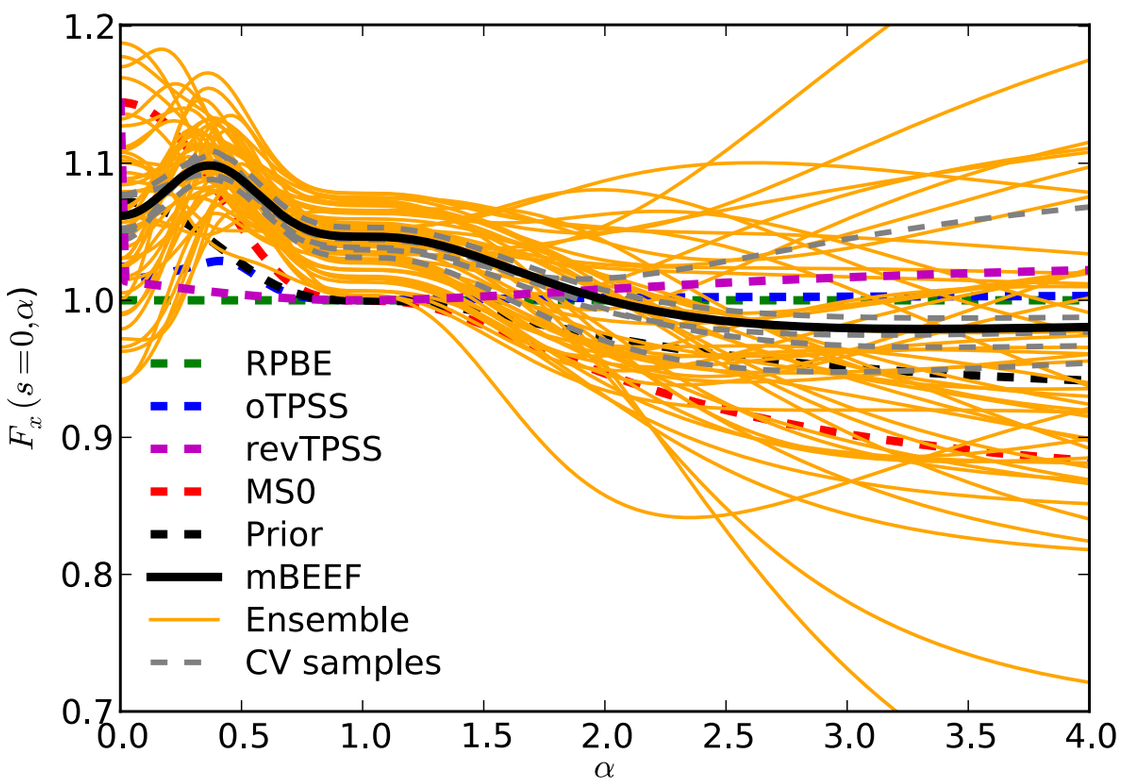
$$F_x(n, \nabla n, \tau) = F_x(s, \alpha)$$

$$\tau_\sigma(\boldsymbol{r}) = \frac{1}{2}\sum_i^{\text{occ.}} |\nabla \phi_{i\sigma}(\boldsymbol{r})|^2$$

$$\alpha = \left(\tau - \tau^{\text{W}}\right)/\tau^{\text{HEG}} \in [0, \infty]$$





Wellendorff, Lundgaard, Jacobsen, Bligaard (2013)

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Non-covalent interactions: electrostatics vs. dispersion

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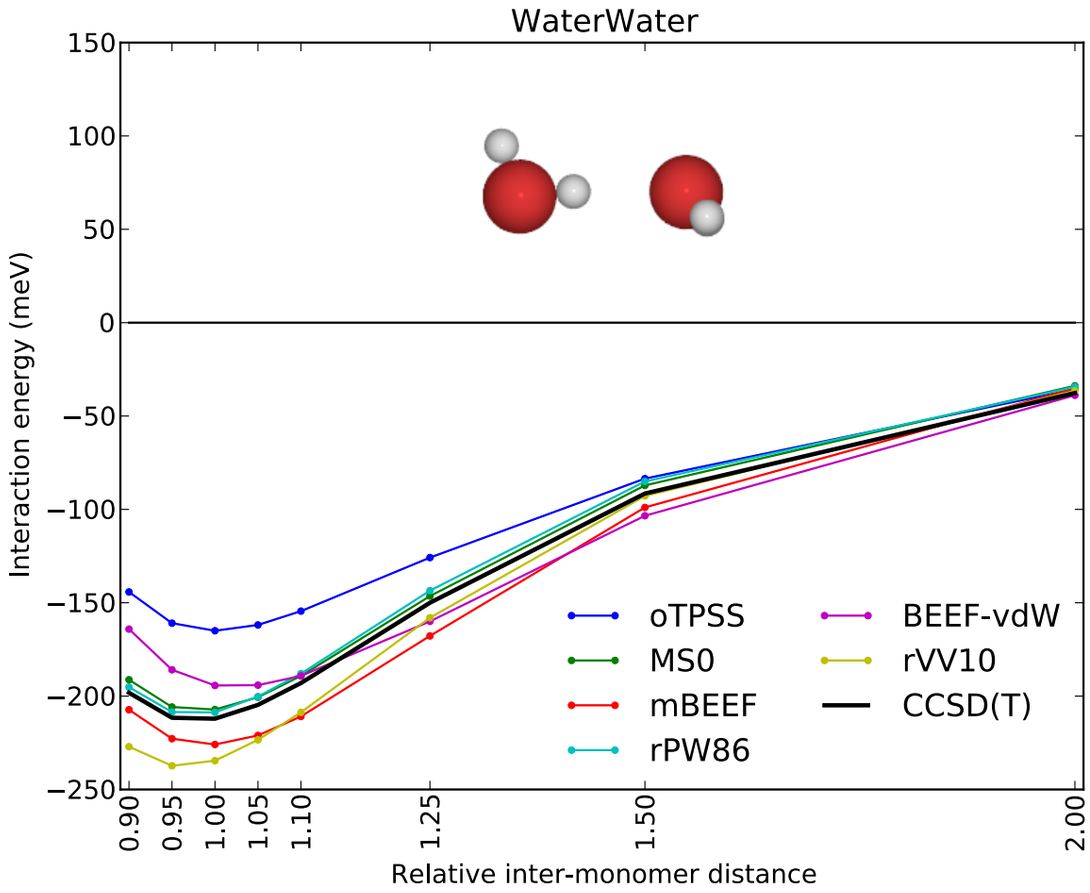
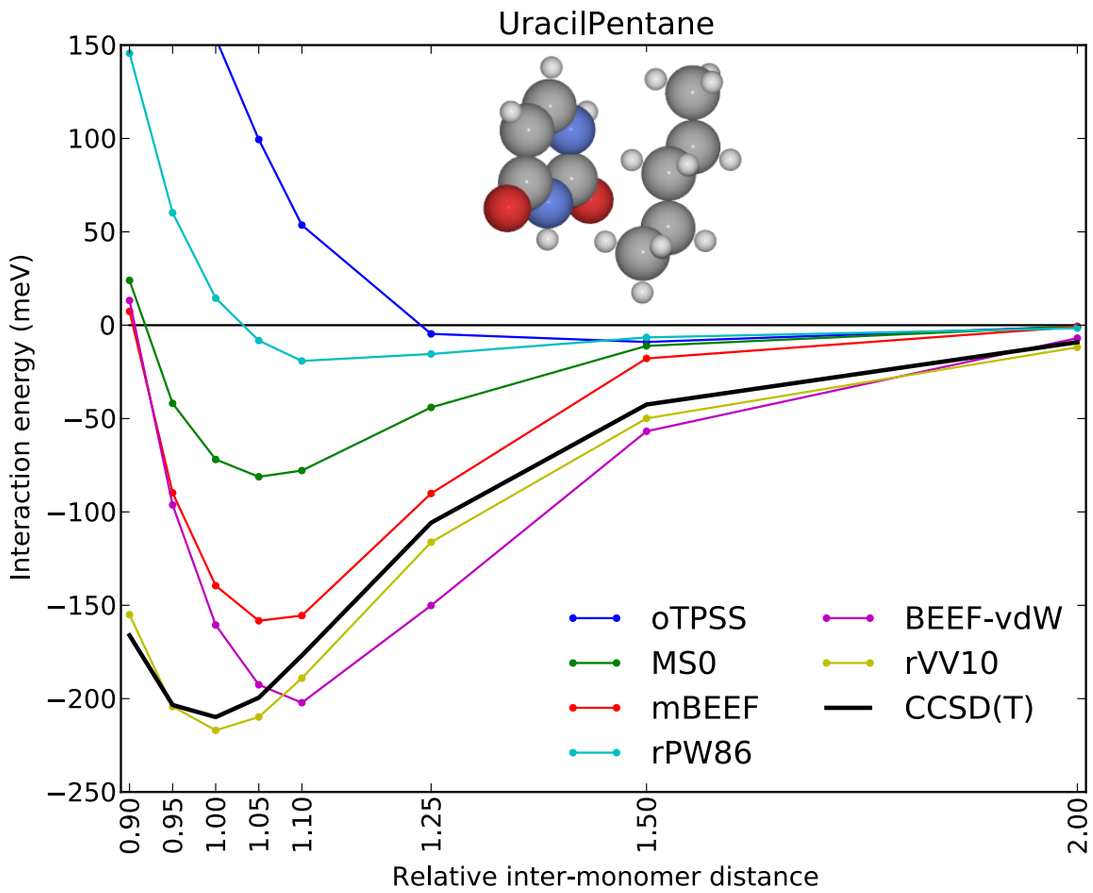
GGAs and MGGAs can capture hydrogen bonding quite well, but higher-level theory is needed for long-range dispersion, e.g. non-local correlation functionals or RPA.

Disp/Elec = 0.29



Disp/Elec = 3.44



S66x8 data set: Rezac Riley, Hobza, *J. Chem. Theory Comput.* **7**, 2427 (2011)

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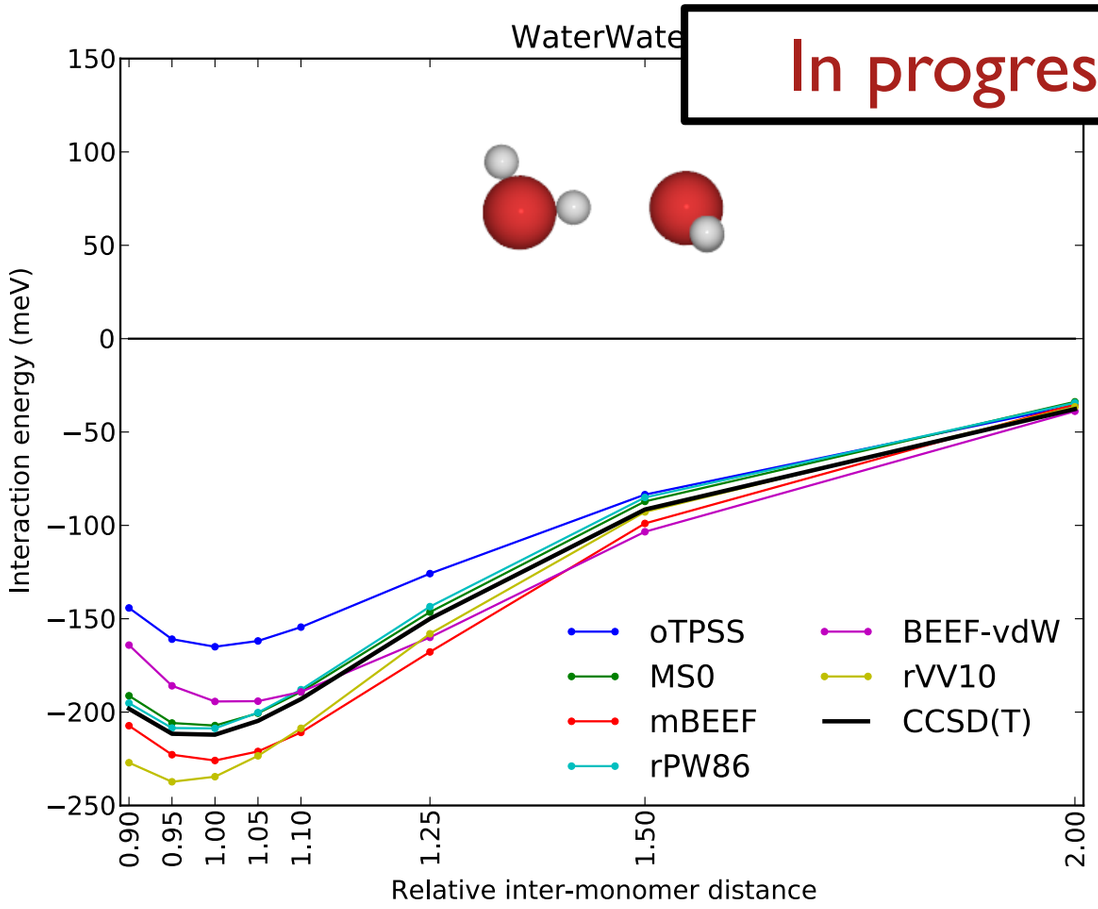
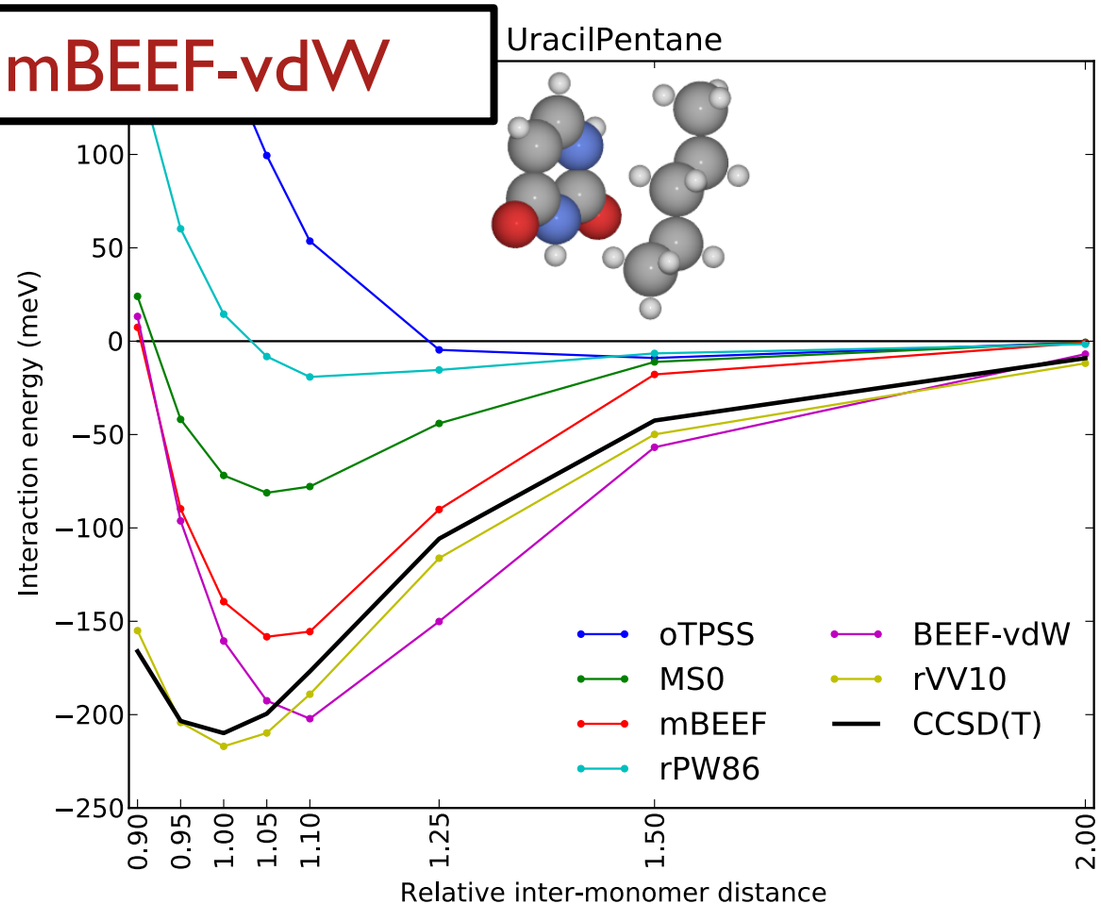


In progress: mBEEF-vdW

Disp/Elec = 3.44



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