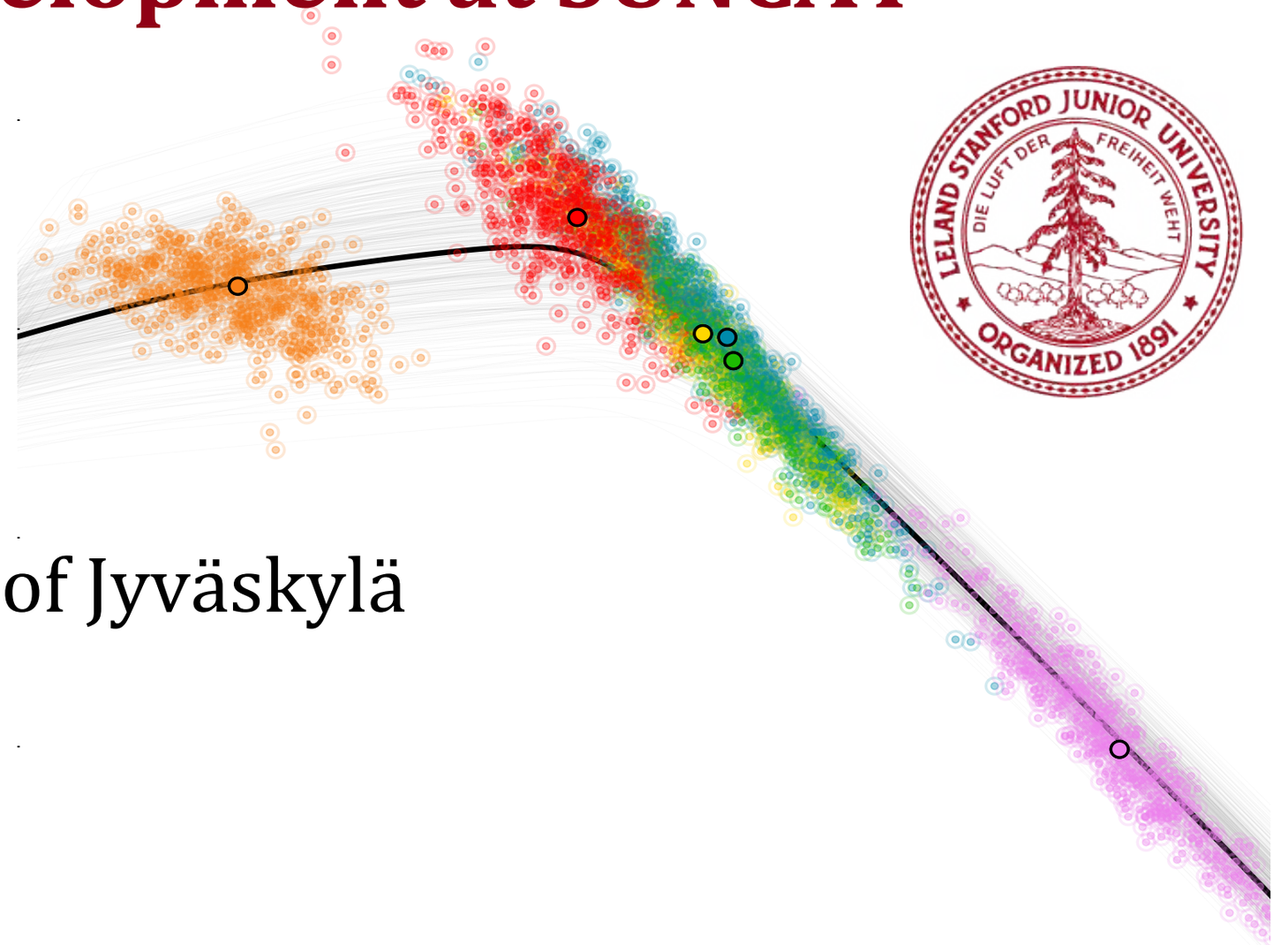
Bayesian error estimation functionals and further method development at SUNCAT



GPAW 2016 – University of Jyväskylä
June 8th, 2016

Johannes Voss

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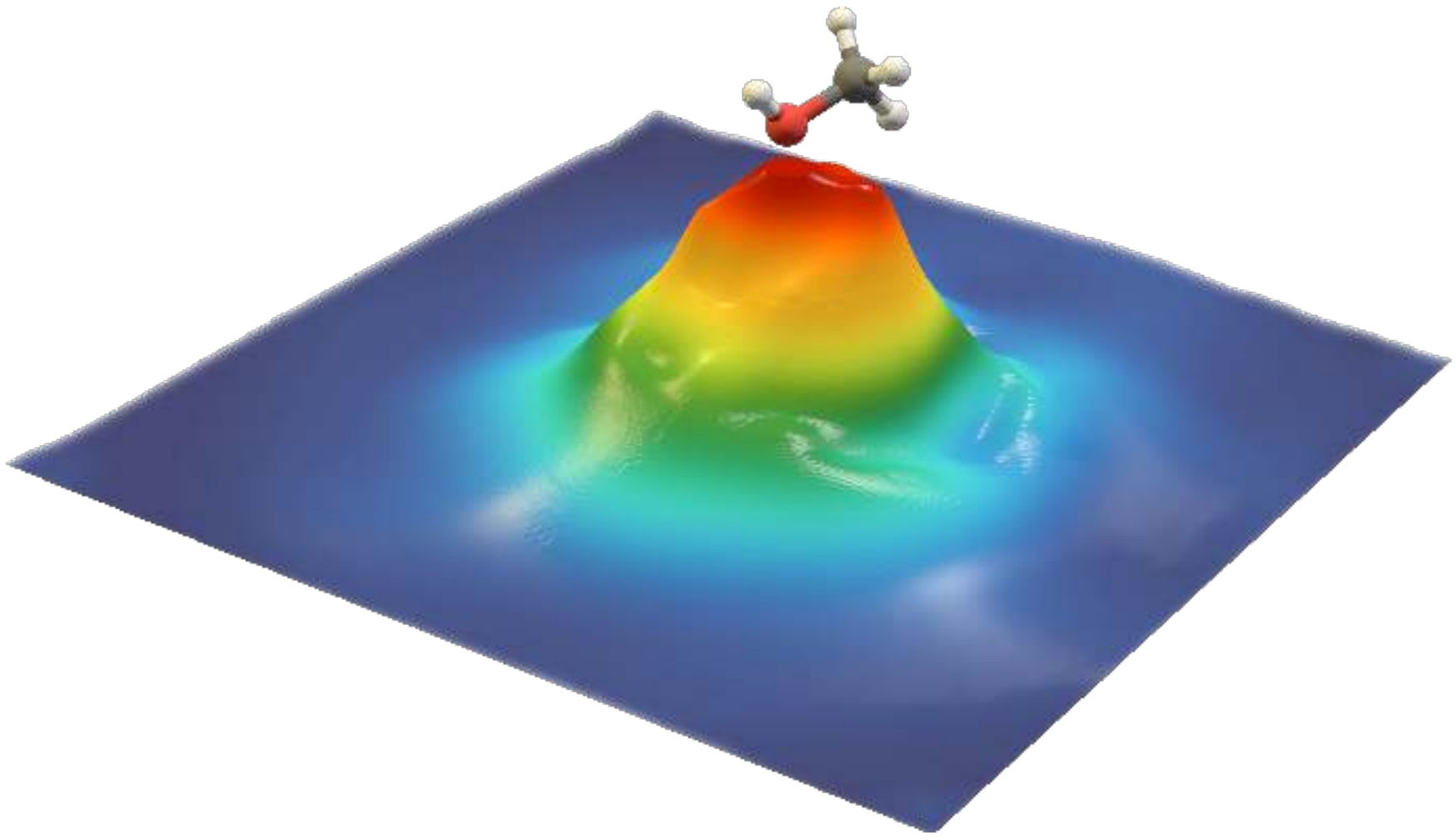
SUNCAT
CENTER FOR INTERFACE SCIENCE AND CATALYSIS

U.S. DEPARTMENT OF ENERGY | Office of Science

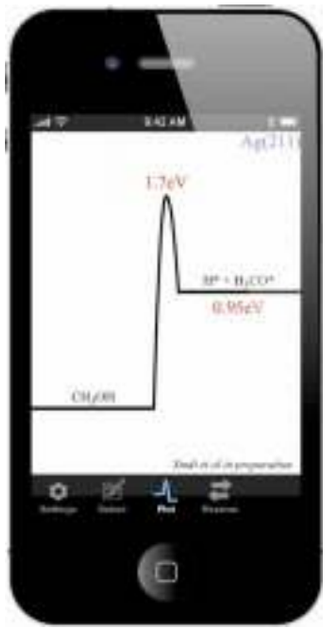
SLAC NATIONAL ACCELERATOR LABORATORY

Method development at SUNCAT in general

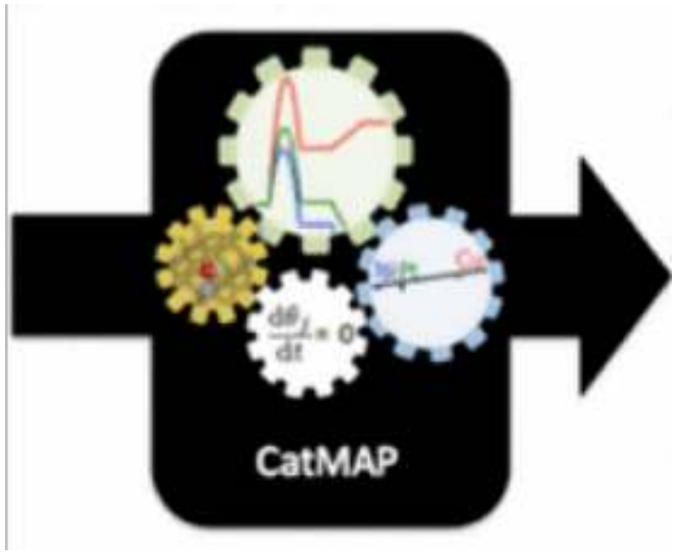


Methods for the design of catalysts for chemical transformations of interest for energy conversion and storage

Software developed at SUNCAT

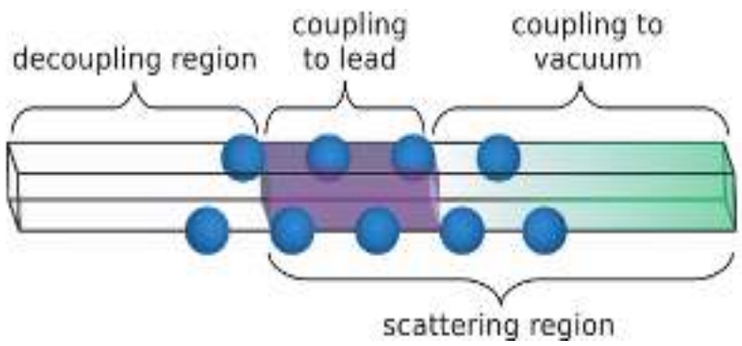


CatApp



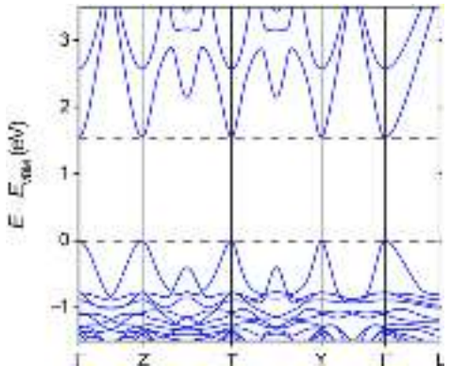
CatMAP

GPU-acceleration of RPA calculations in GPAW



Transport code for electronic emission from surfaces

ASE interface for Quantum Espresso

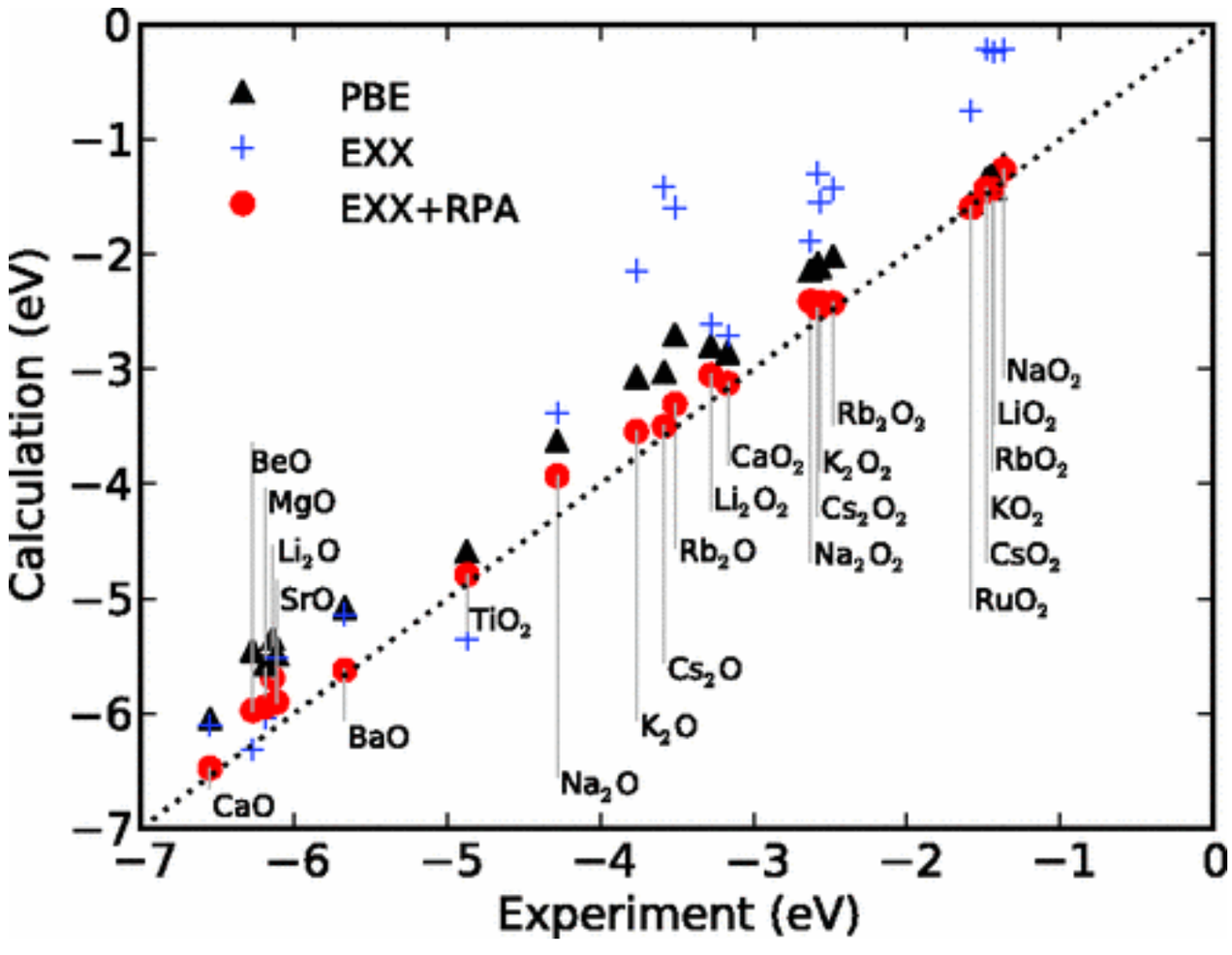


GLLBsc for Quantum Espresso

Software developed at SUNCAT: GPU-accelerated RPA in GPAW

Yan *et al.*, Comp. Phys. Commun. 184, 2728 (2013)

Total energy method taking advantage of GPUs for large matrix multiplications for response function calculation

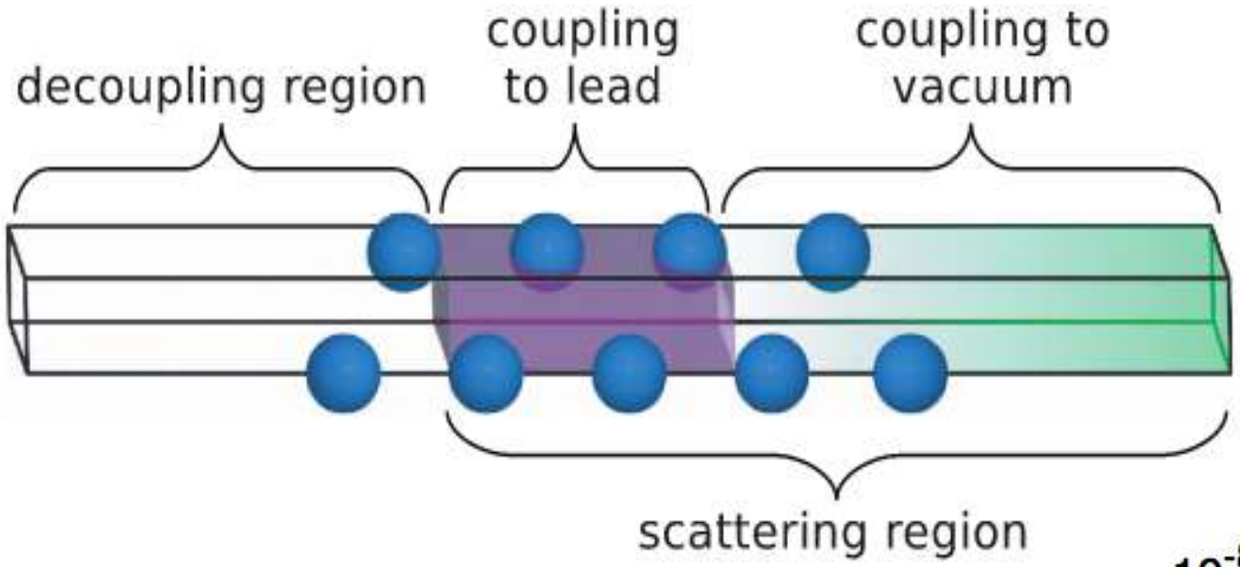


Yan *et al.*, PRB 87, 075207 (2013)

(not currently developed anymore)

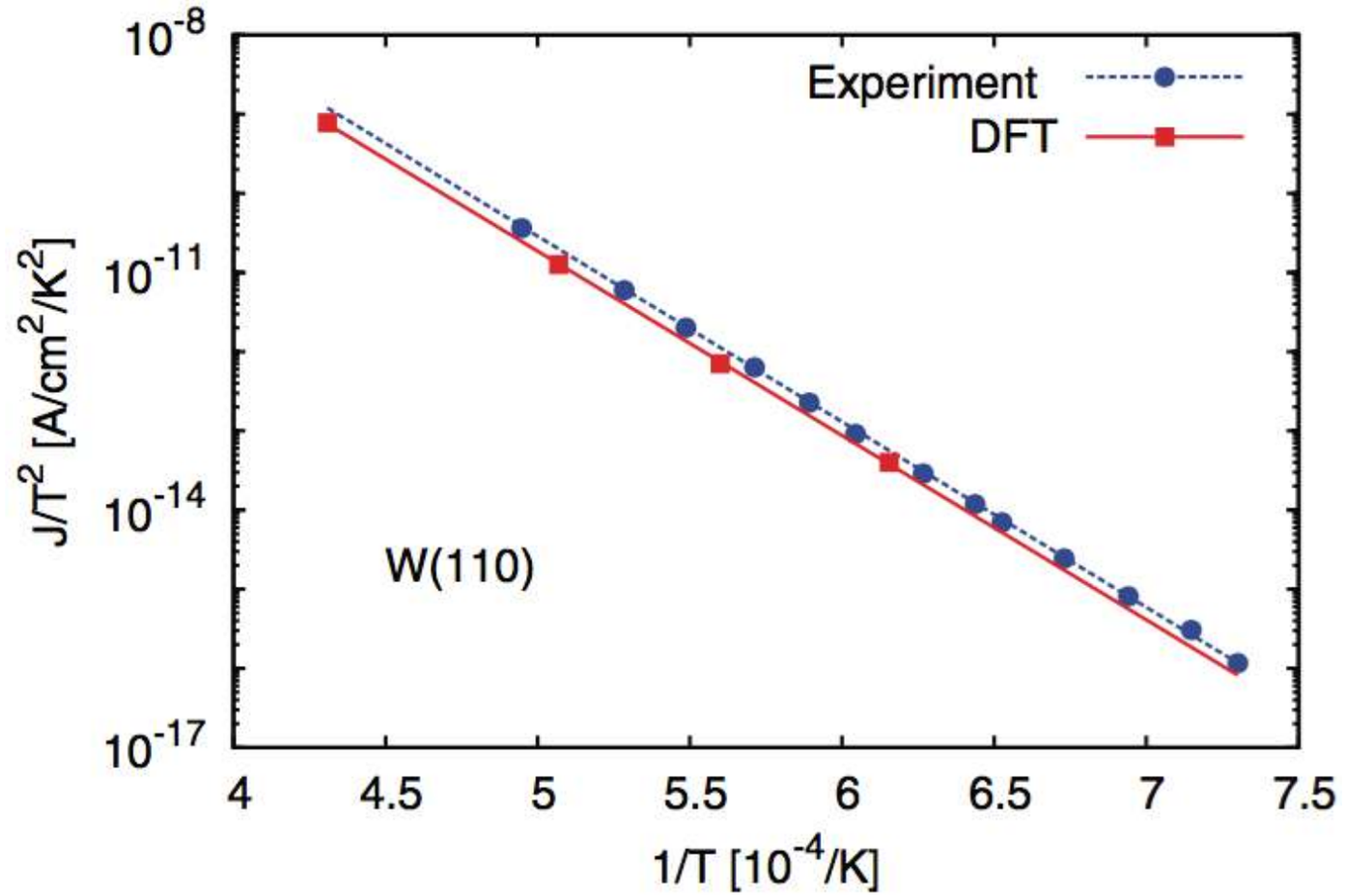
Software developed at SUNCAT:

Transport code for electronic emission from surfaces



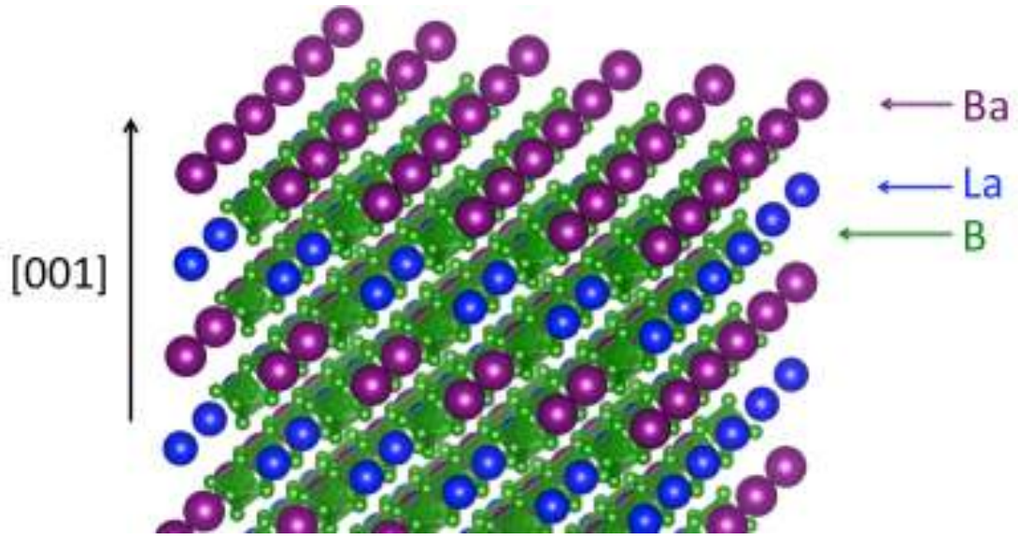
Voss *et al.*, J. Chem. Phys. 138, 204701 (2013)

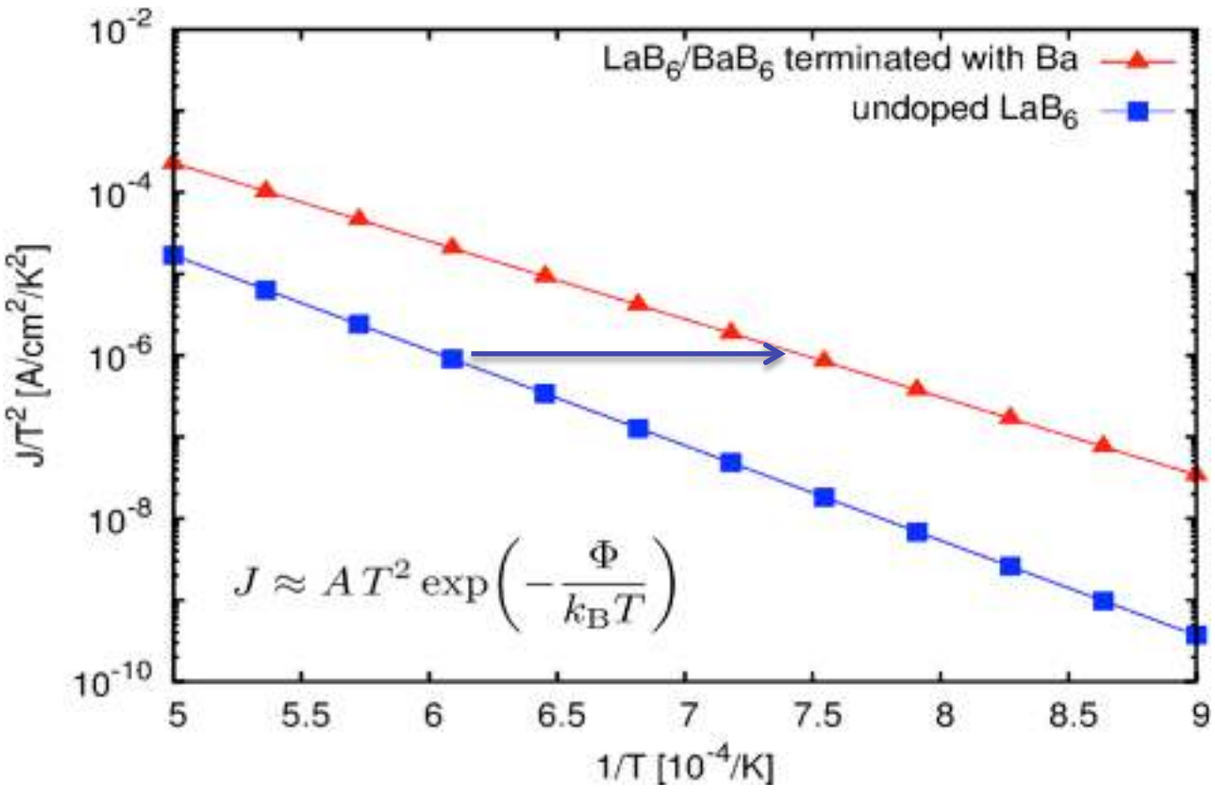
Localized basis set for atoms, mixed plane wave + realspace basis for vacuum region

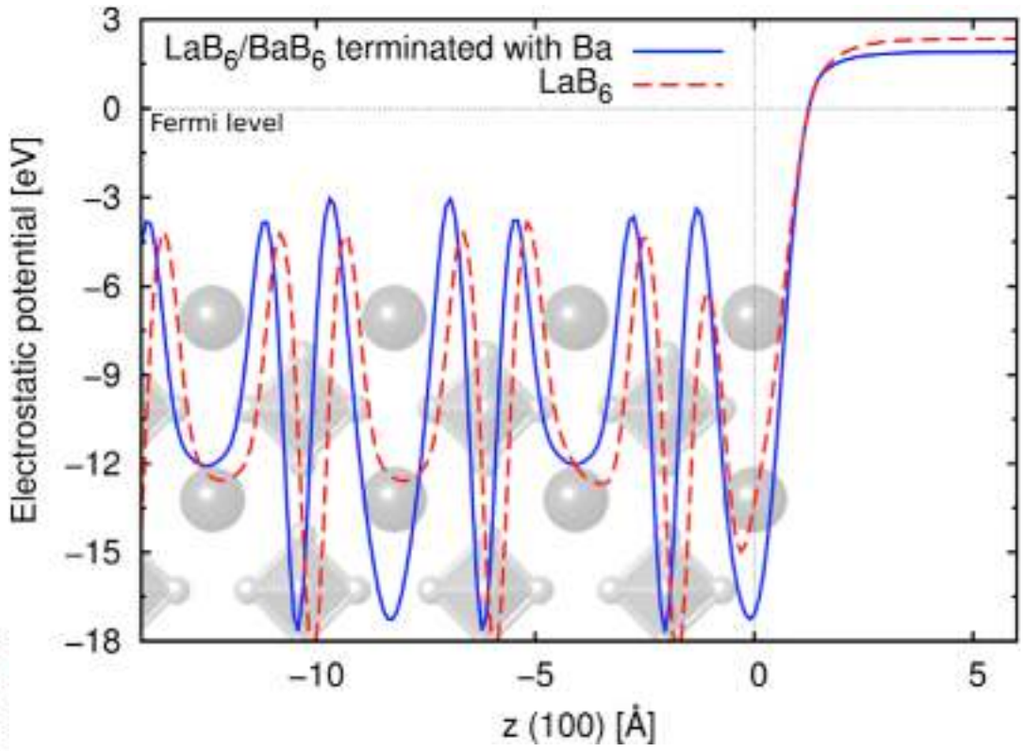


Software developed at SUNCAT:

Transport code for electronic emission from surfaces



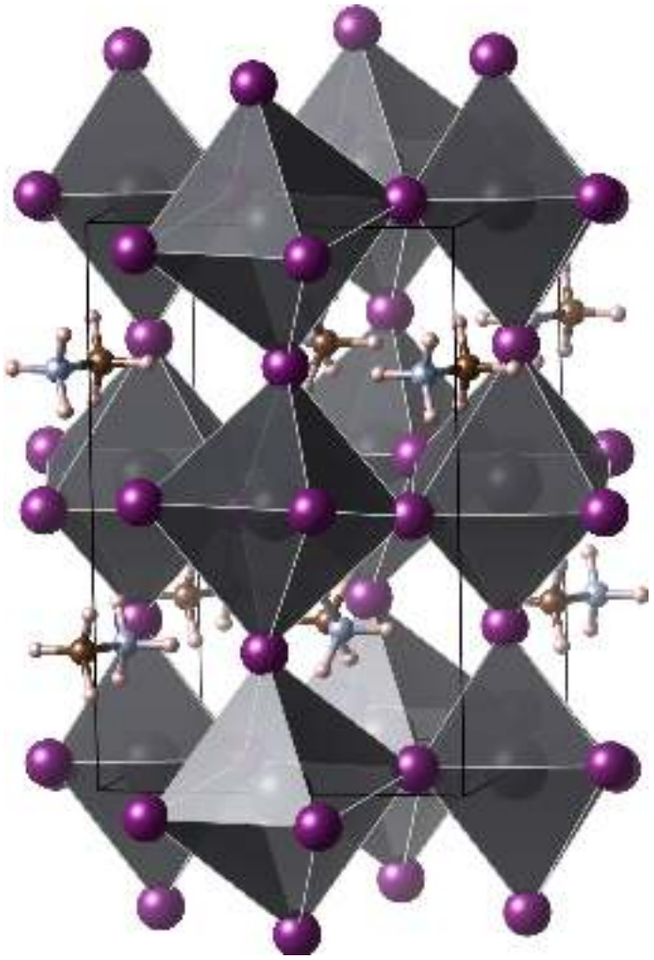


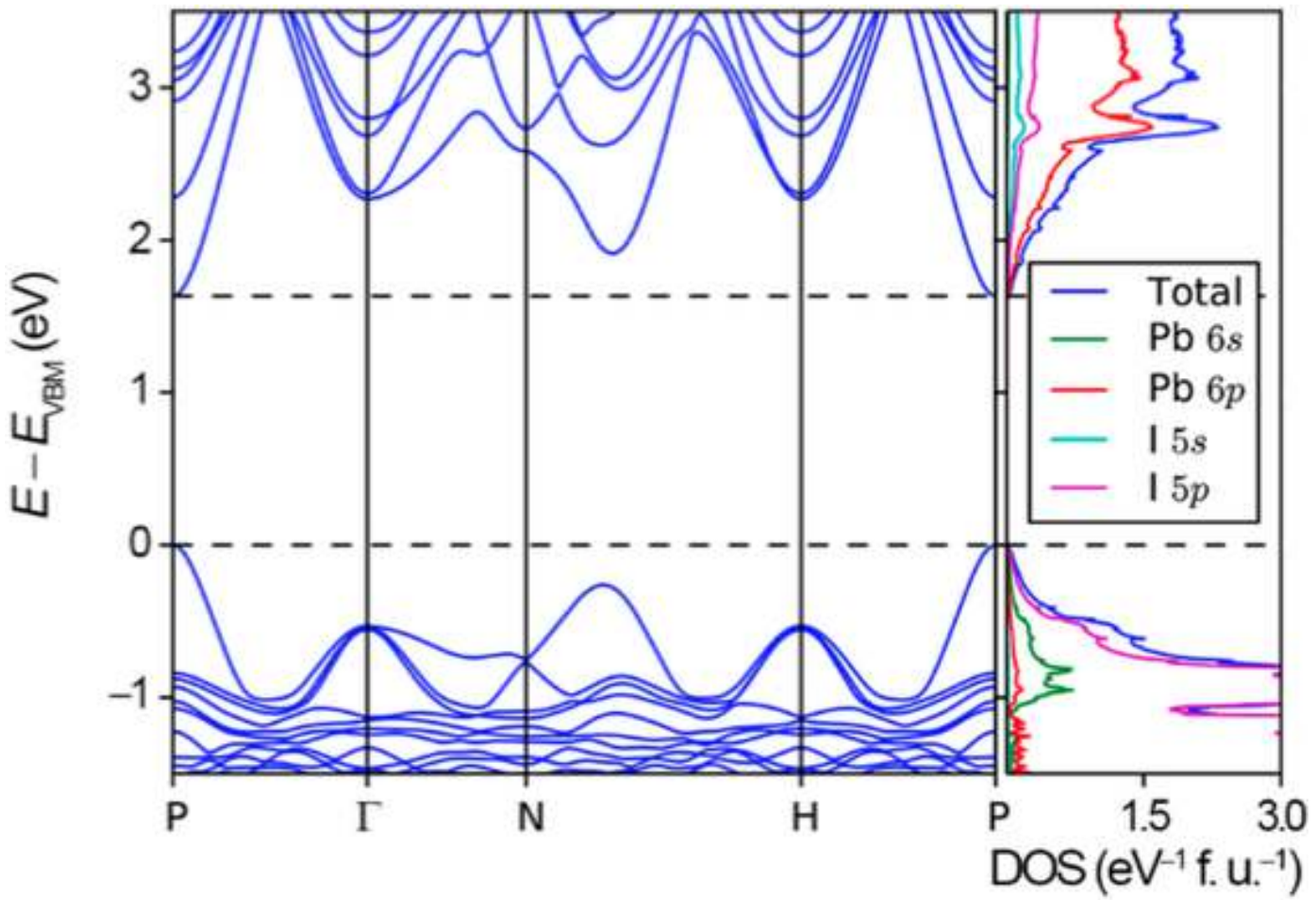


Enhanced emission without sacrificing stability

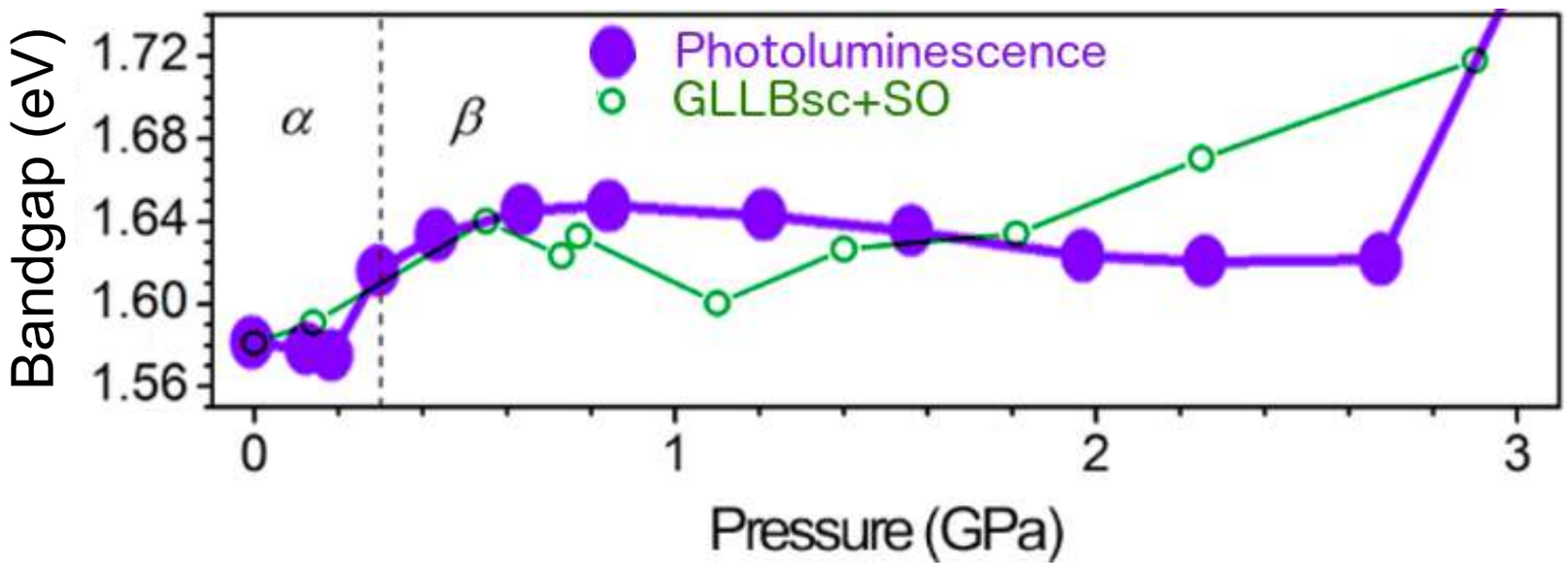
Voss *et al.*, Phys. Rev. Appl. 2, 024004 (2014)

GLLBsc in Quantum Espresso: Hybrid Pb-perovskites





Jaffe, Lin, Beavers, Voss et al. ACS Central Science (April 2016)
10.1021/acscentsci.6b00055



BEE functional development

Motivation:

- Quantification of uncertainties on DFT (total energy) results

- Fitting of functional of increasing complexity to improve description of reaction energetics

GGA➔meta-GGA➔Hybrid functionals etc.

Bayes' theorem

- Conditional probability:

$$P(A \mid B) = \frac{P(A \cap B)}{P(B)}$$

- Hence:

$$P(A \cap B) = P(A \mid B)P(B) = P(B \mid A)P(A)$$

- Bayes' theorem:

$$P(A \mid B) = \frac{P(B \mid A)P(A)}{P(B)}$$

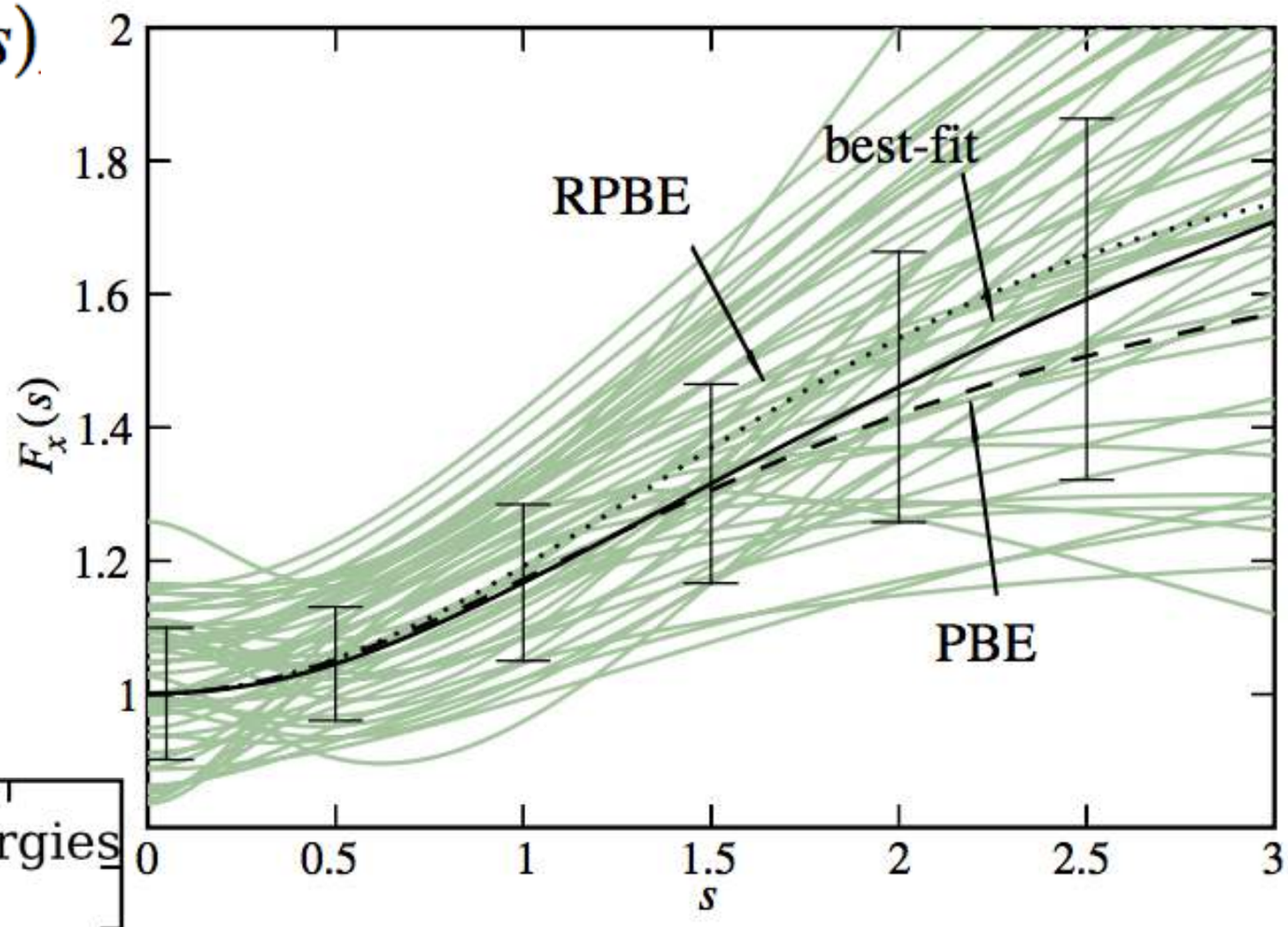
First BEE xc functional

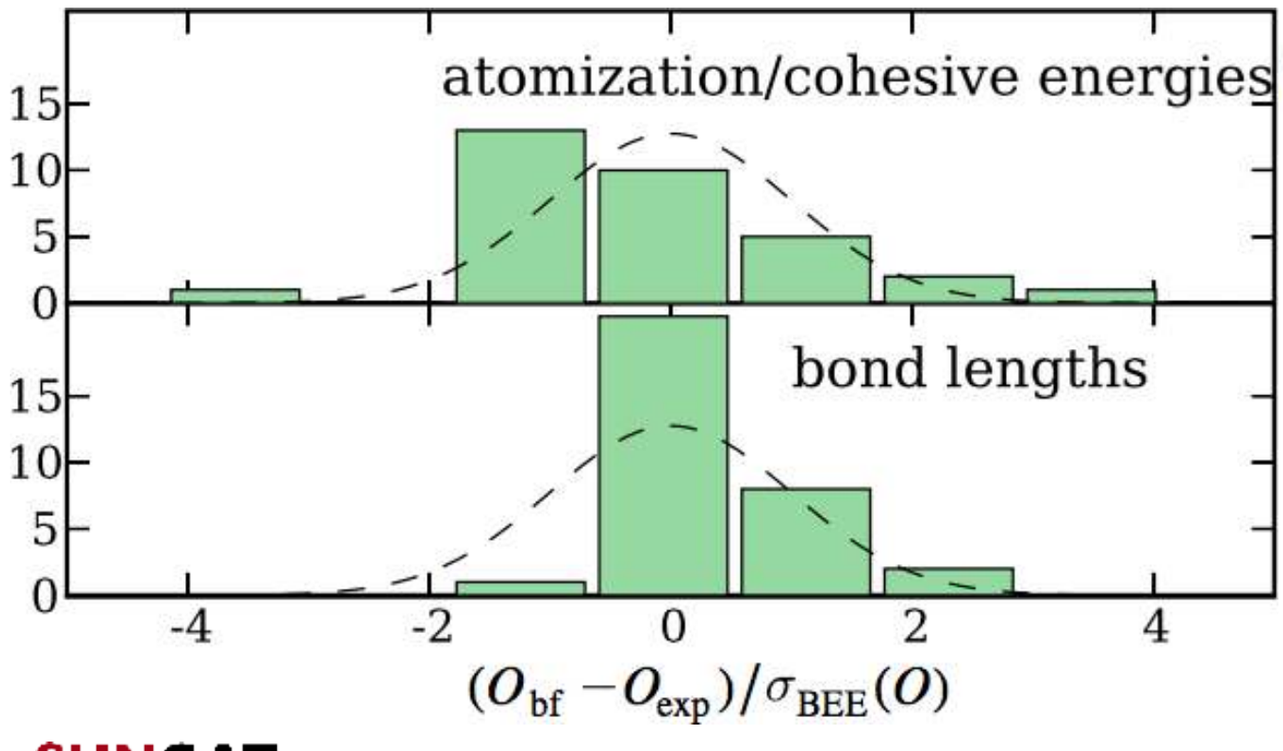
$$E_{\mathrm{x}}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{\mathrm{x}}^{\mathrm{LDA}}(n(\mathbf{r})) F_{\mathrm{x}}(s)$$

$$F_{\mathrm{x}}(s) = \sum_{i=1}^{N_{\mathrm{p}}} \theta_i \left(\frac{s}{1+s} \right)^{2i-2}$$

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

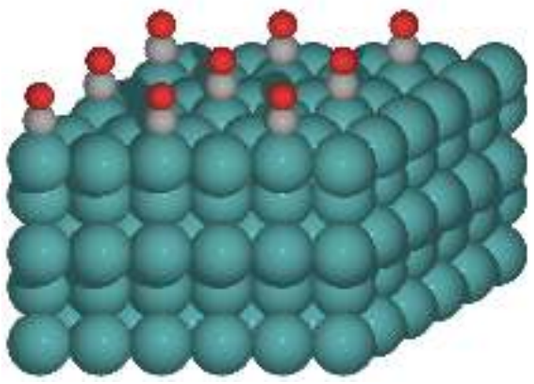
Mortensen *et al.*, PRL 95, 216401 (2005)



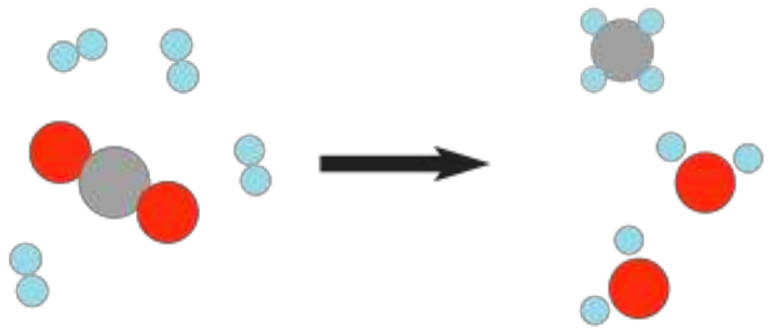


BEEF-(vdW) training sets

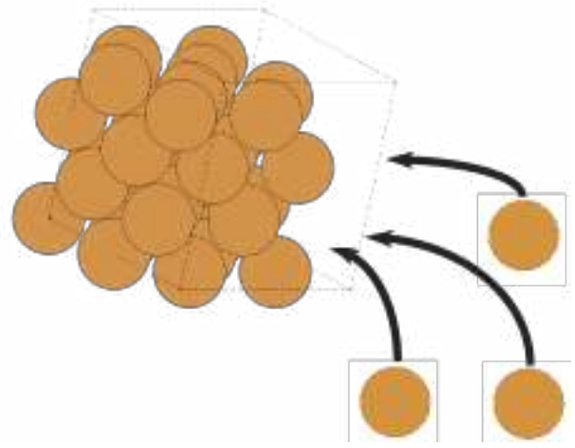
Chemisorption energies



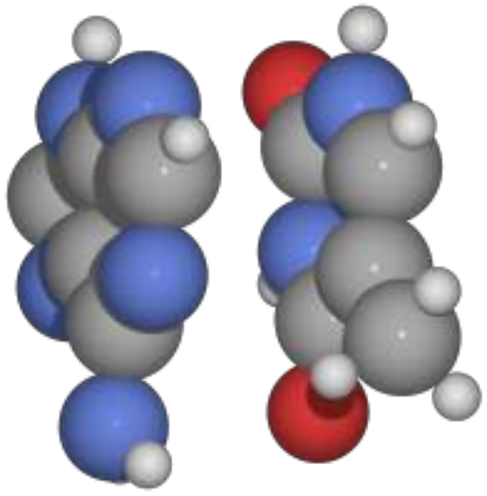
Reaction energies



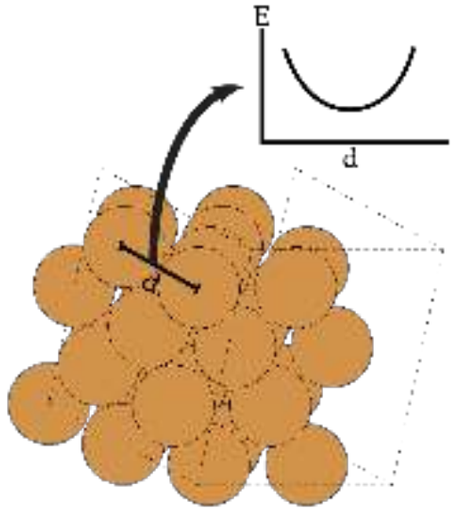
Cohesive energetics



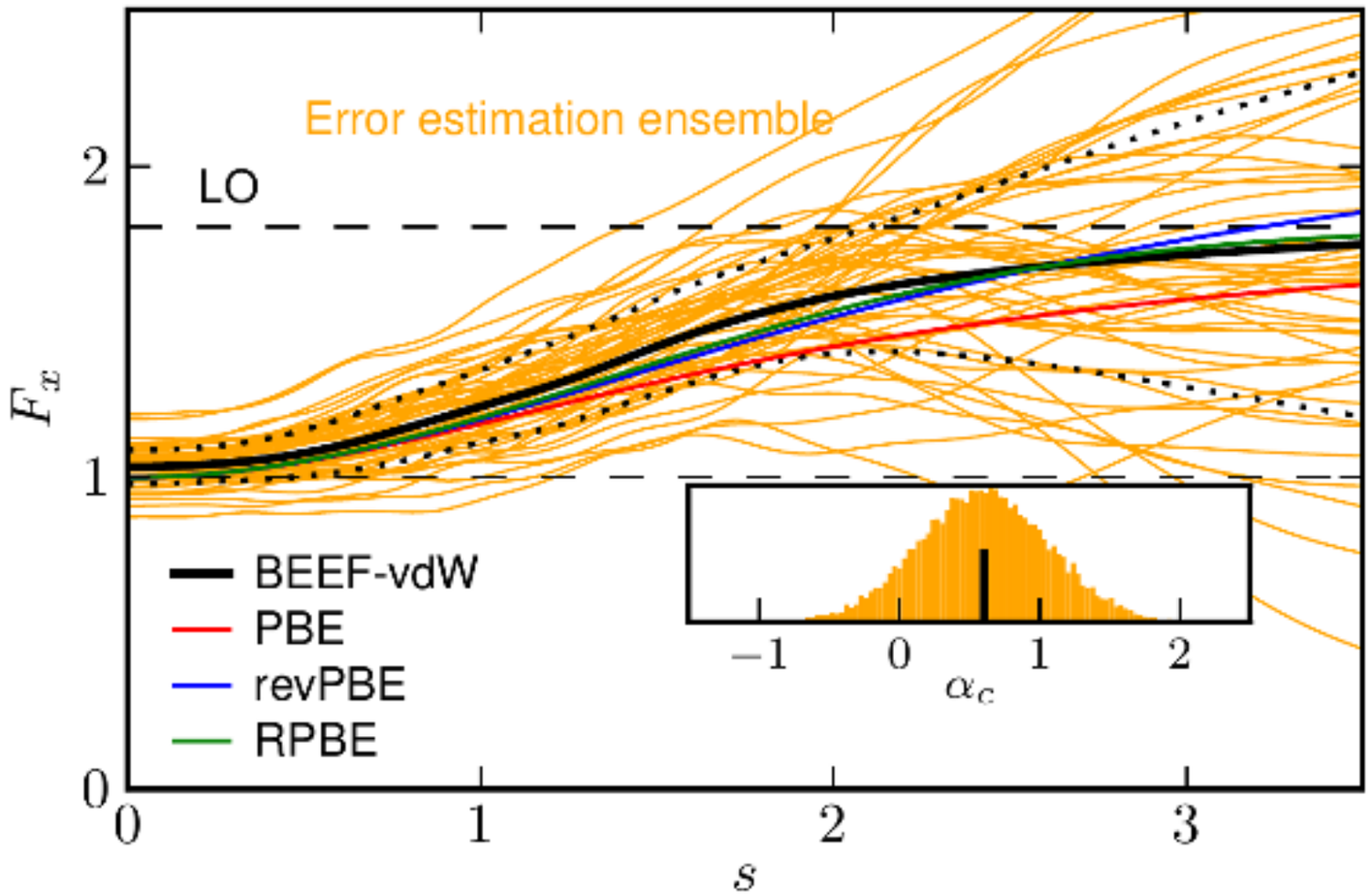
Dispersion energetics



Lattice constants

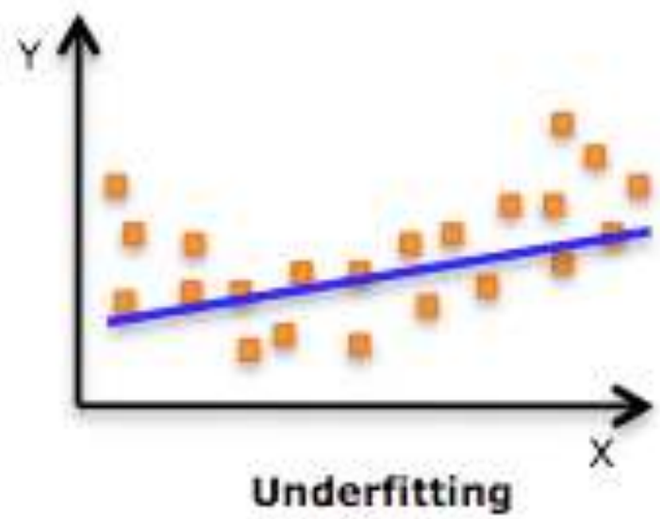


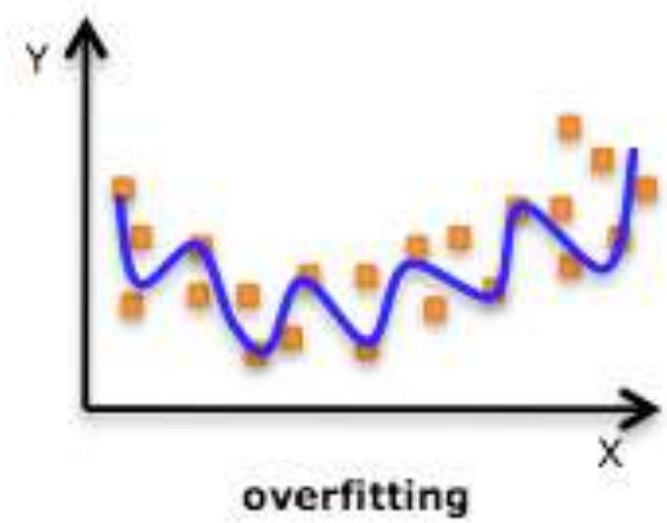
BEEF-vdW



Wellendorff *et al.*, PRB 85, 235149 (2012)

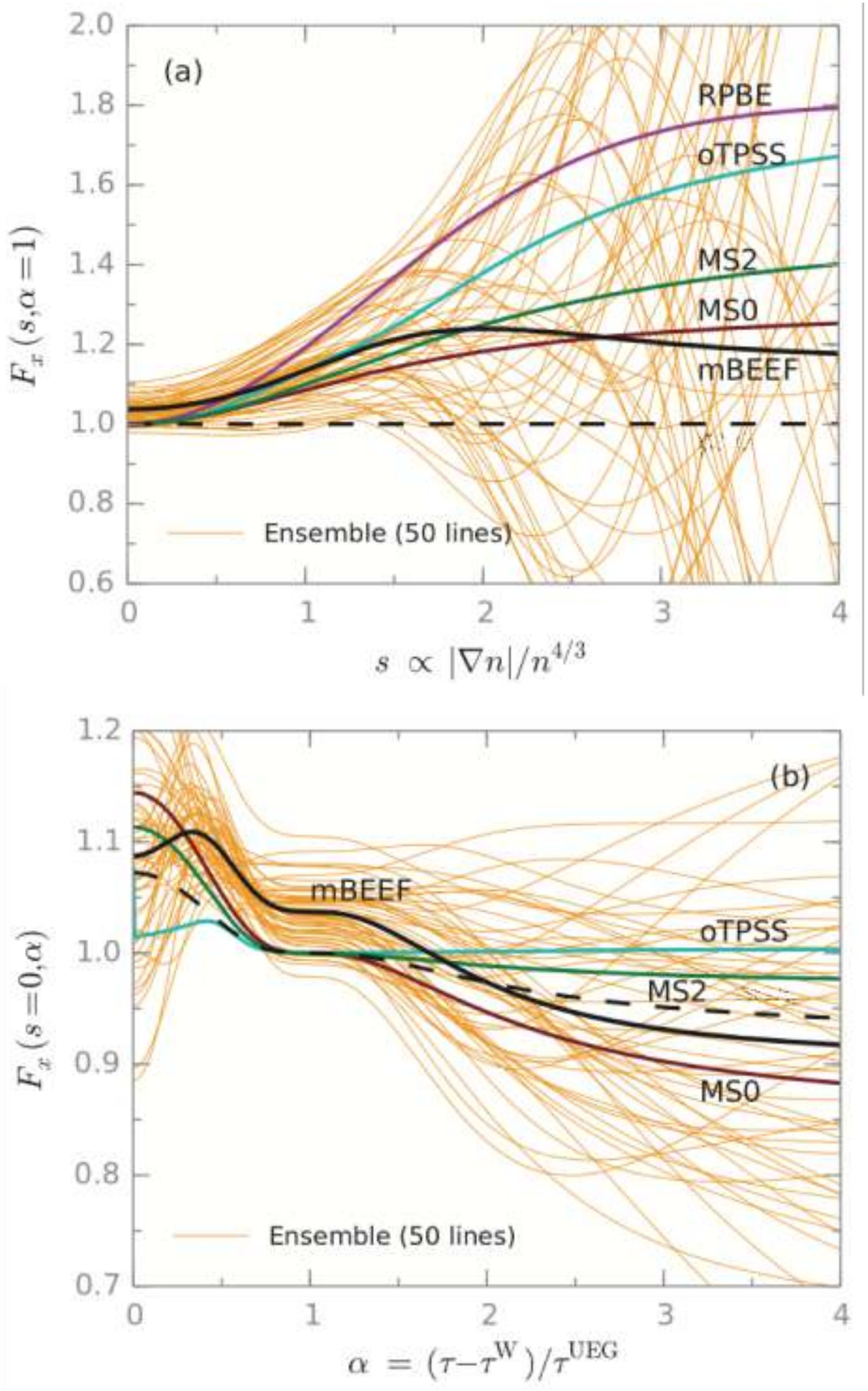
- Exchange enhancement expanded in Legendre polynomials
- Strength of PBE gradient correction to correlation fitted
- vdW-(DF2)-functional yielding good lattice constants
- Regularized fit



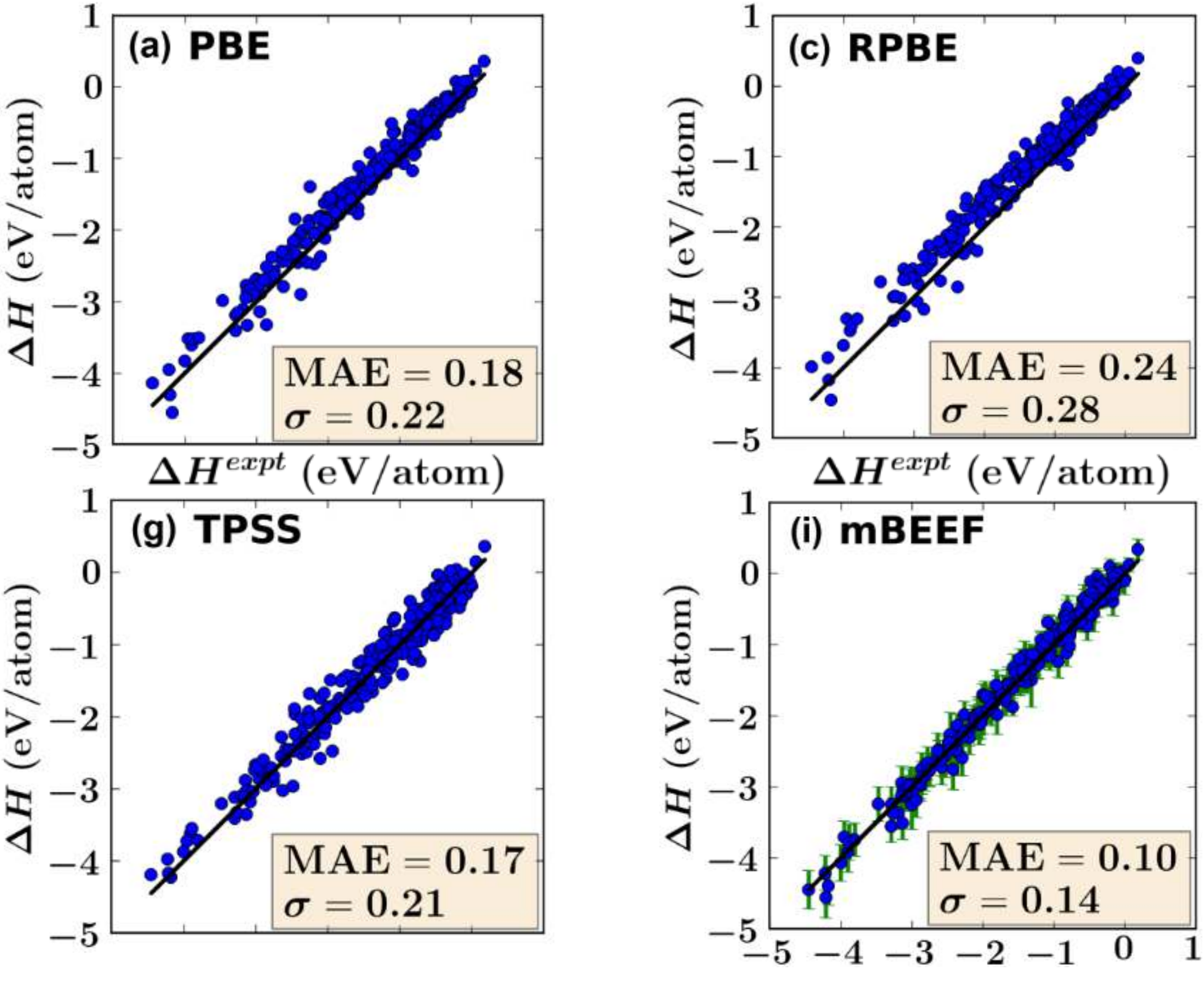


m(eta)BEEF

- x-enhancement factor now also depends on Kohn-Sham kinetic energy density
- Switch to PBEsol for semi-local correlation
- Robust fitting reducing the influence of outliers



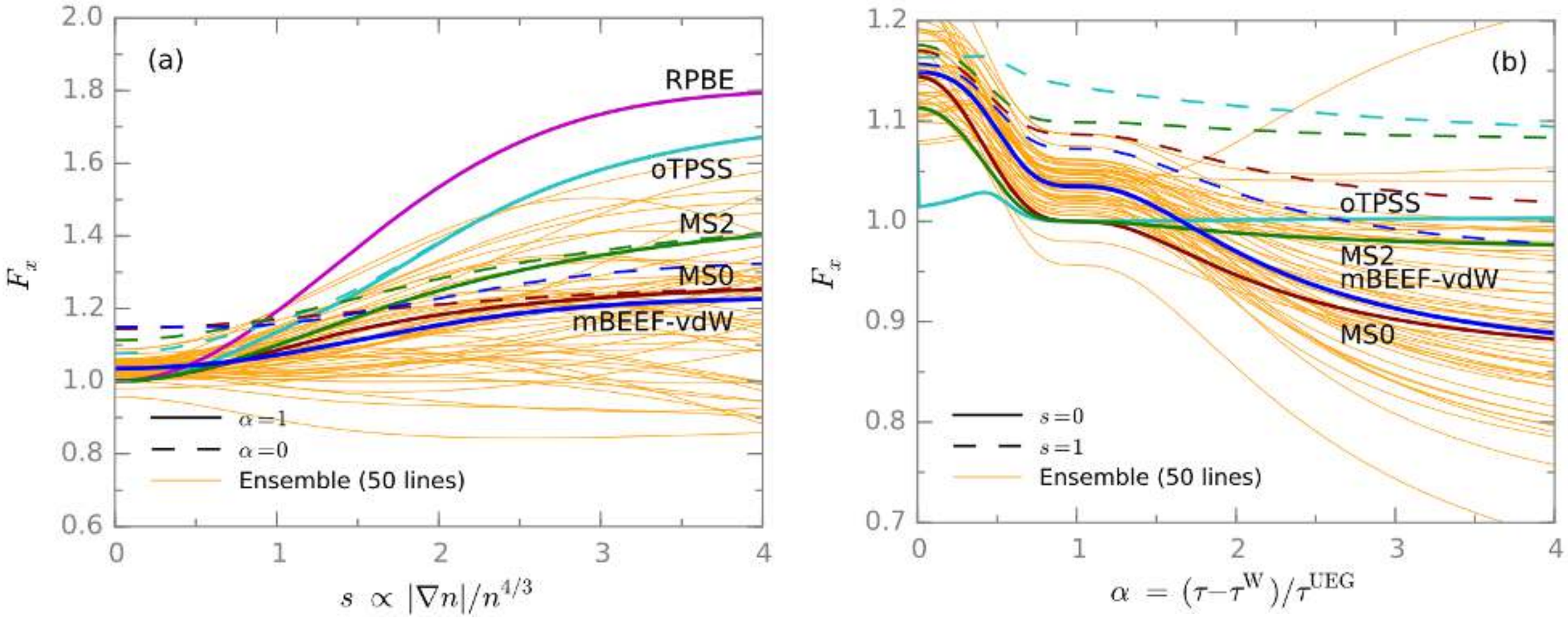
mBEEF – improved cohesive energies



Pandey & Jacobsen, PRB 91, 235201 (2015)

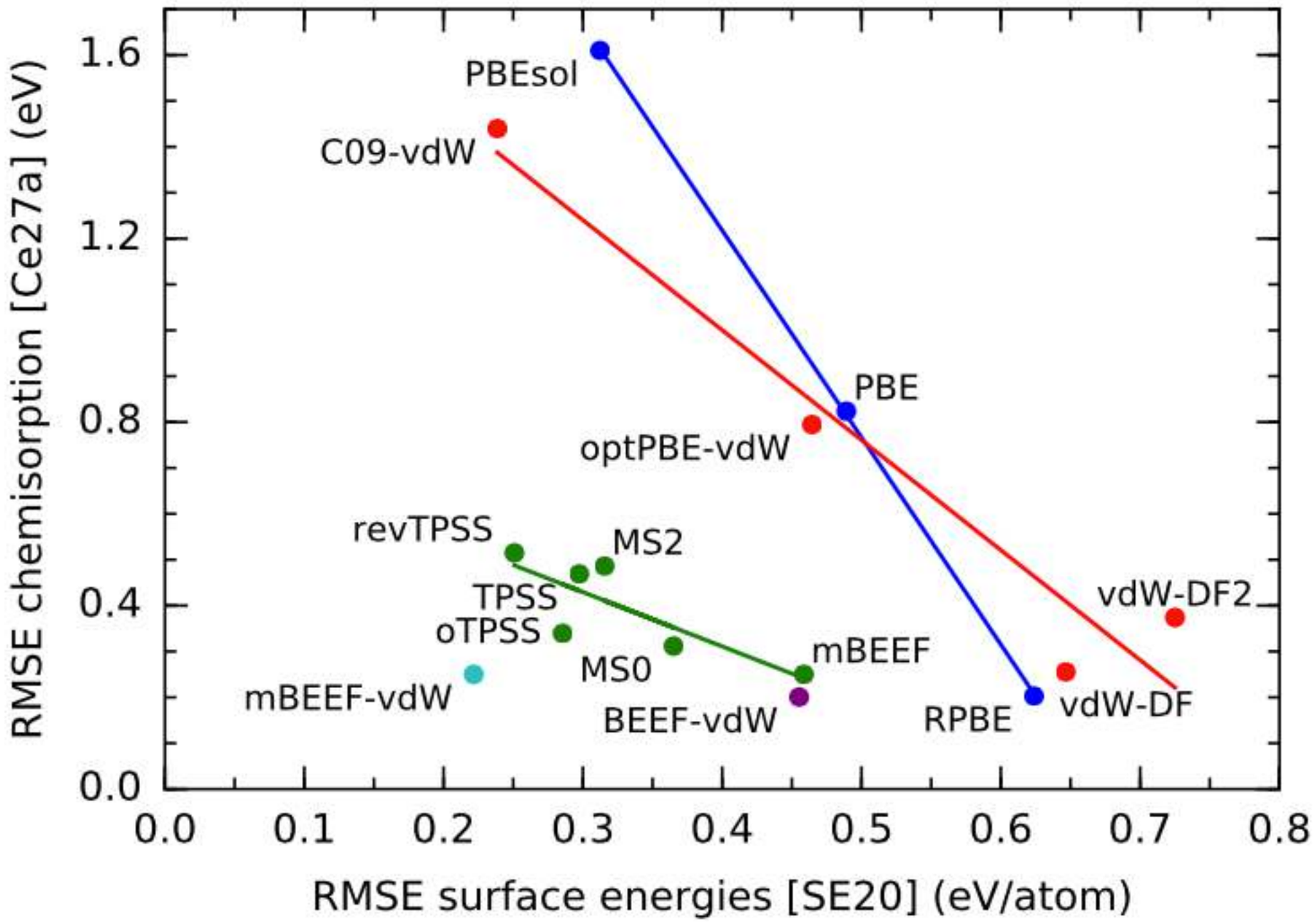
mBEEF-vdW

- In addition to exchange enhancement fitting, weighting of LDA and PBEsol semi-local correlation and vdW-DF2 nonlocal correlation



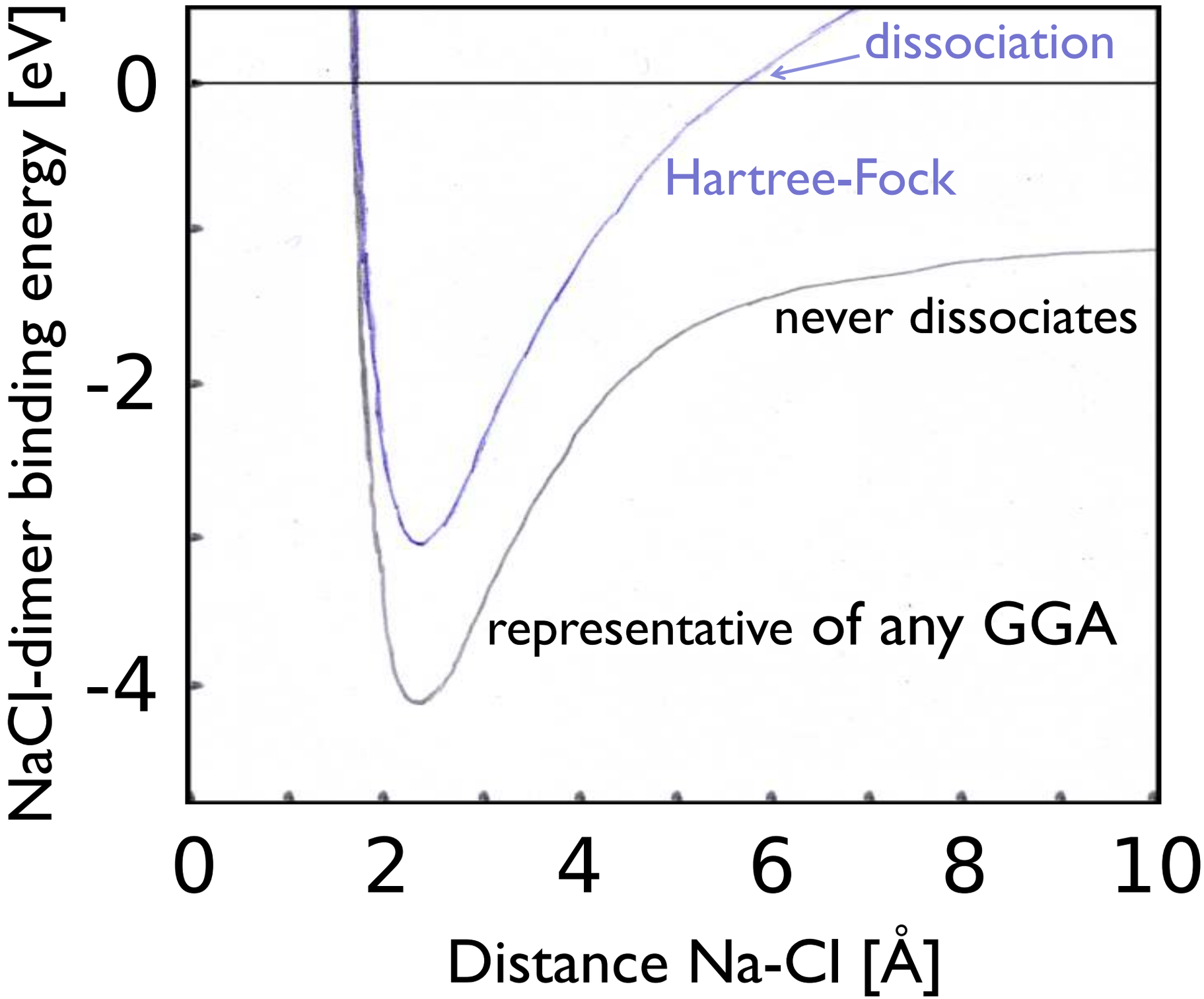
Lundgaard *et al.* (2016)

BEEF-class Functional Performance



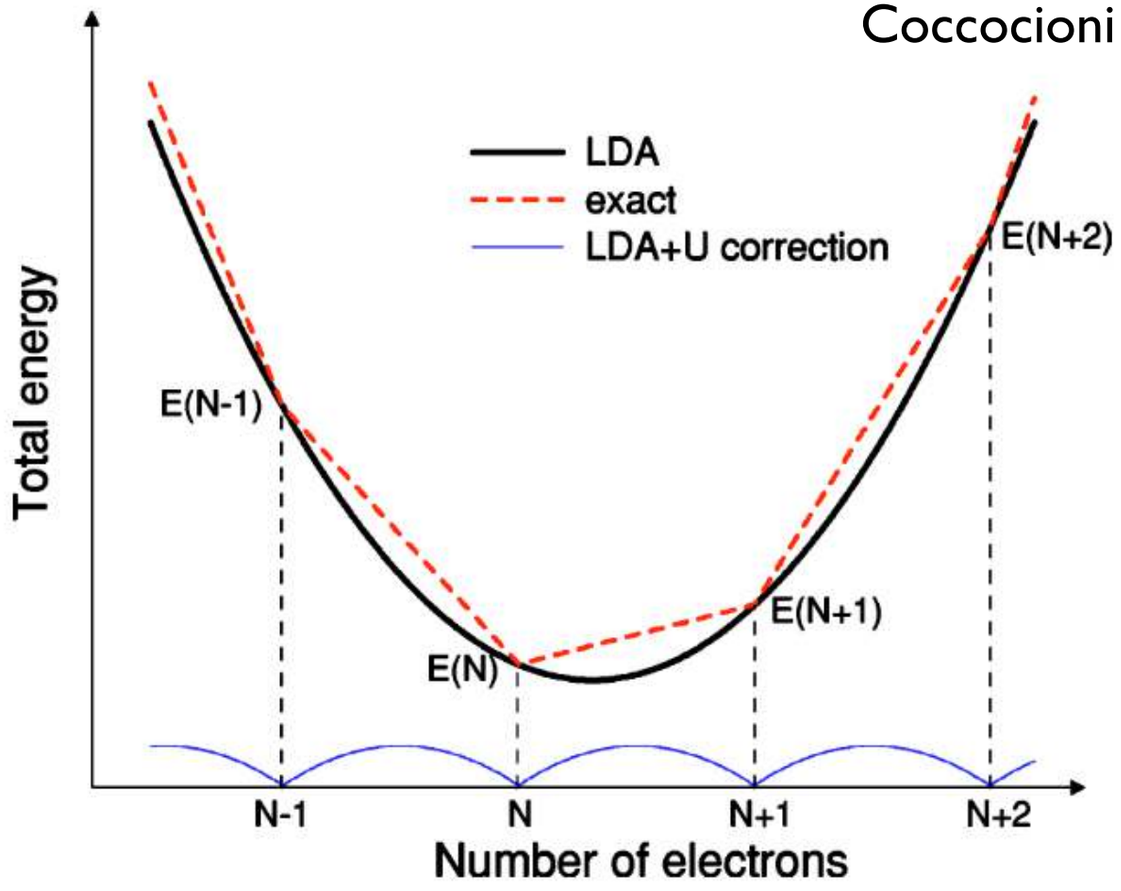
Lundgaard *et al.* (2016)

Motivation: Spurious charge transfer from self-interaction errors



Suppression of SI errors

Coccocioni & Gironcoli PRB 71, 035105 (2005)



- GGA+U: different U-values for product/reactants and for bulk and surface atoms

→ hybrid functionals

Conclusion & outlook

- Each fitted rung of BEE functional has improved the accuracy of the functionals

- Next step is including Fock exchange

- Are more/larger training data sets needed?

From more expensive wave function methods?

Include spectral properties in training (spectroscopy on surface or adsorbate states) ?

Acknowledgments

Jens K. Nørskov
Karsten Wedel Jacobsen
Thomas Bligaard

Keld Lundgaard
Shaama Mallikarjun Sharada

Former students and postdocs:
Jess Wellendorff
Andreas Møgelhøj
Jun Yan

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