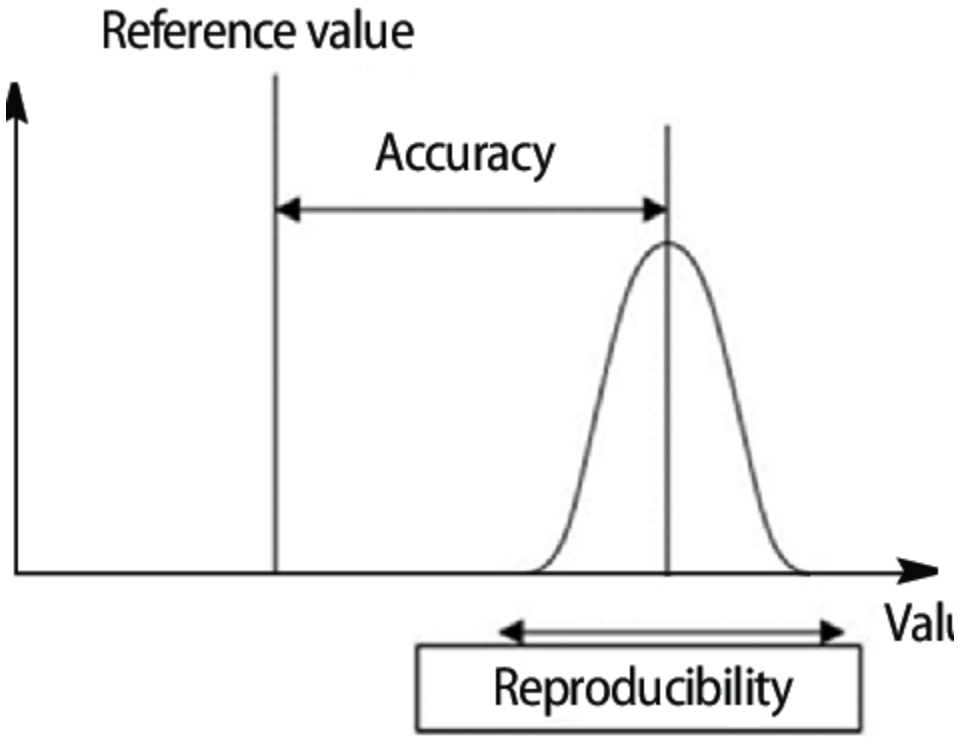
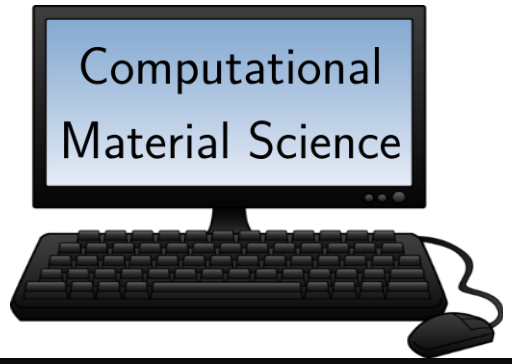
Reproducibility in DFT



Oliver T. Hofmann

Graz University of Technology

Institute of Solid State Physics



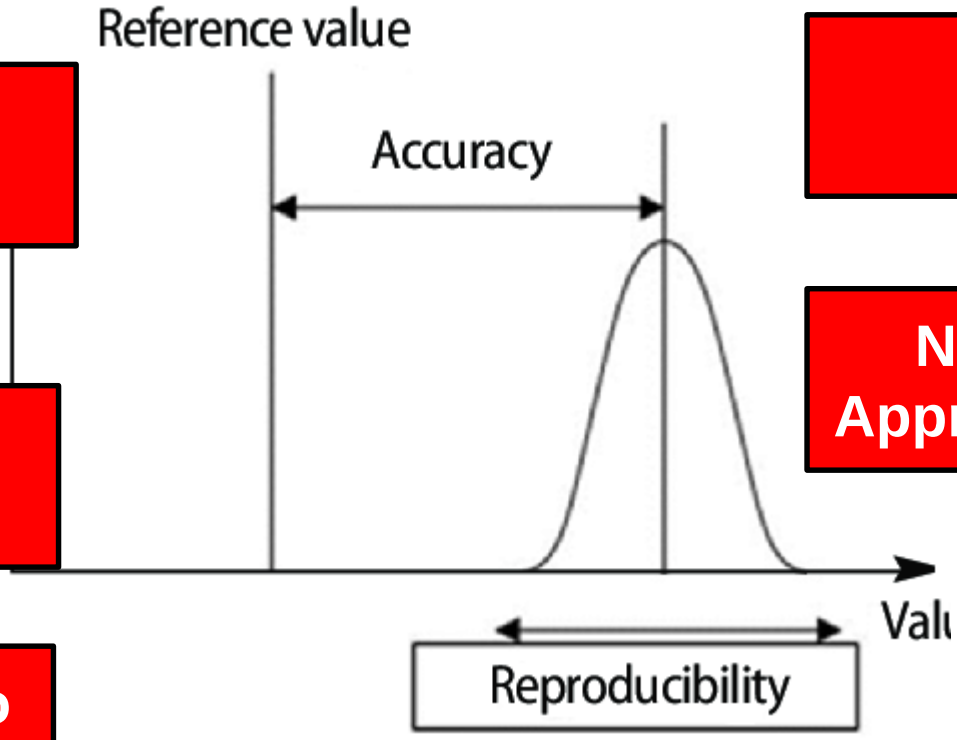

```
Self-consistency cycle converged.

Writing energy levels:
| Potential vacuum level, "upper" slab surface:     1.05183443 eV
| Potential vacuum level, "lower" slab surface:    -0.99735438 eV
| Work function ("upper" slab surface)        :     6.28672777 eV
| Work function ("lower" slab surface)        :     4.23753896 eV
| VBM (reference: upper_vacuum level)         :     6.29221153 eV
| CBM (reference: upper vacuum level)         :     6.27296902 eV
------------------------------------------------------------

Energy and forces in a compact form:
| Total energy uncorrected      :         -0.352548462337739E+07 eV
| Total energy corrected        :         -0.352548464211578E+07 eV  <-- do not rely on this value for anything but (periodic) metals
| Electronic free energy        :         -0.352548466085418E+07 eV

-----------------------------------
```

How far can we trust these values?

Physics

Functional

Comparison to Experiment



Code

Numerical Approximations

How far can we trust these values?

Slides and discussion partly based on work of S. Cottenier

Why is this relevant?

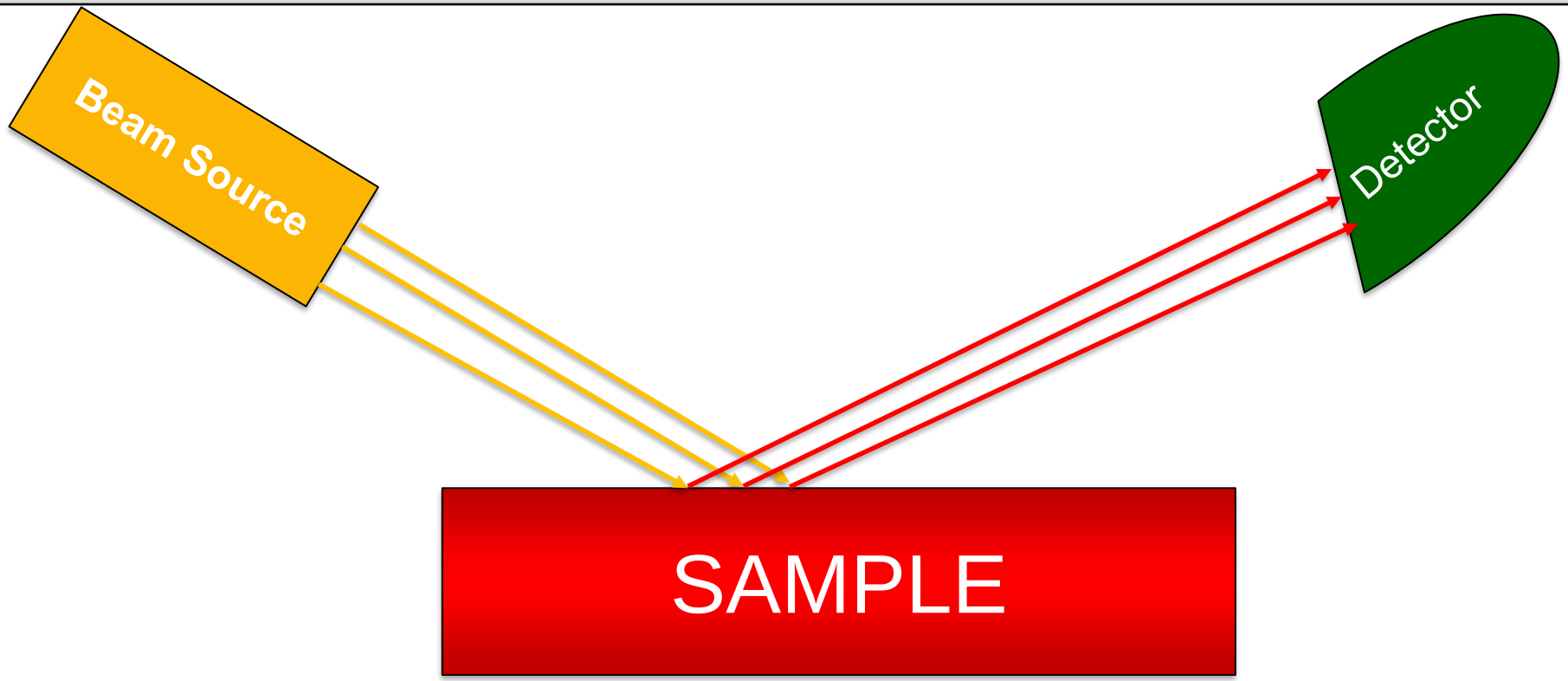
- **Accounting for systematic errors increases quantitative predictions**
- **Non-systematic approximations → error bars**

Material Design

Consistency with literature

Validation of Experiments

A practical problem

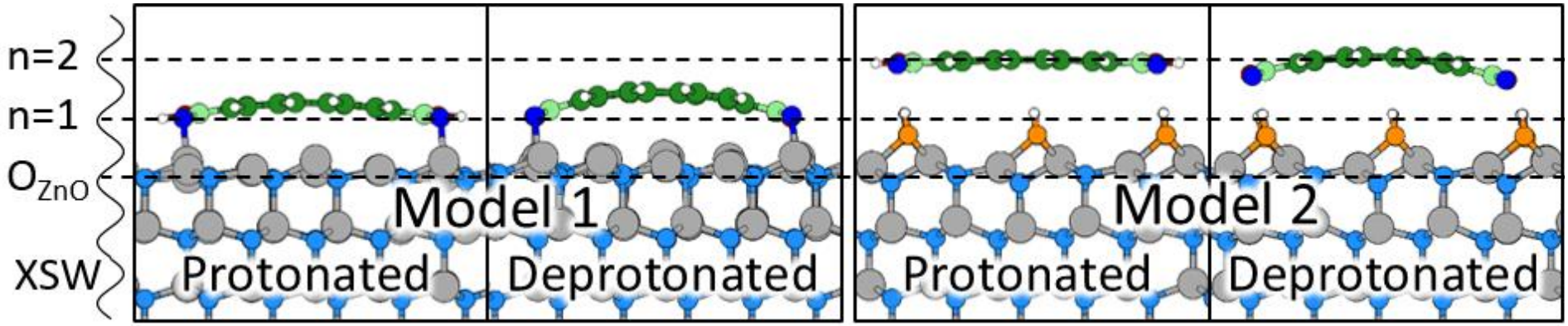


Measurement ≠ **Interpretation**

Additional knowledge and assumptions

A practical problem

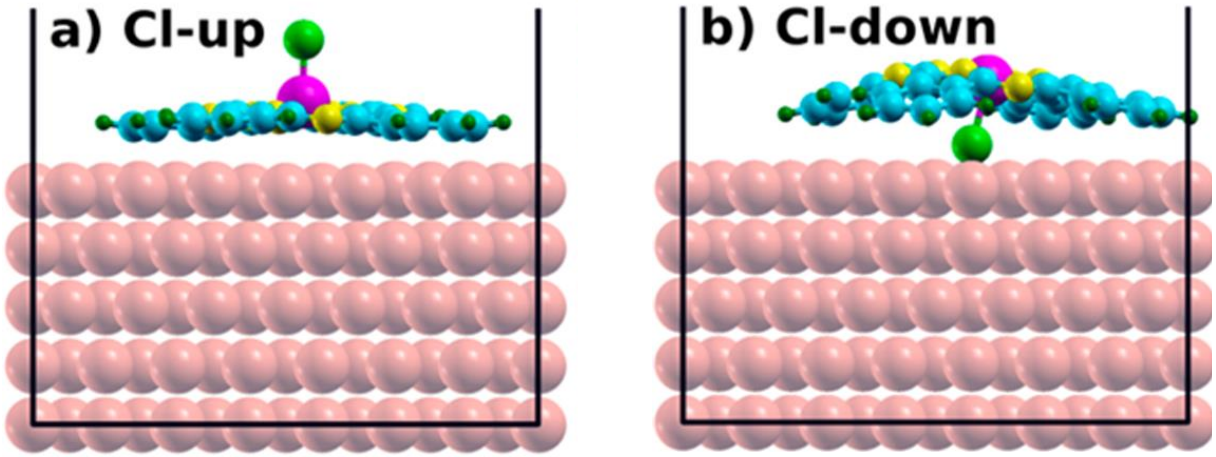
X-Ray Standing Wave Technique



Measurement ≠ **Interpretation**

Additional knowledge and assumptions

A practical problem

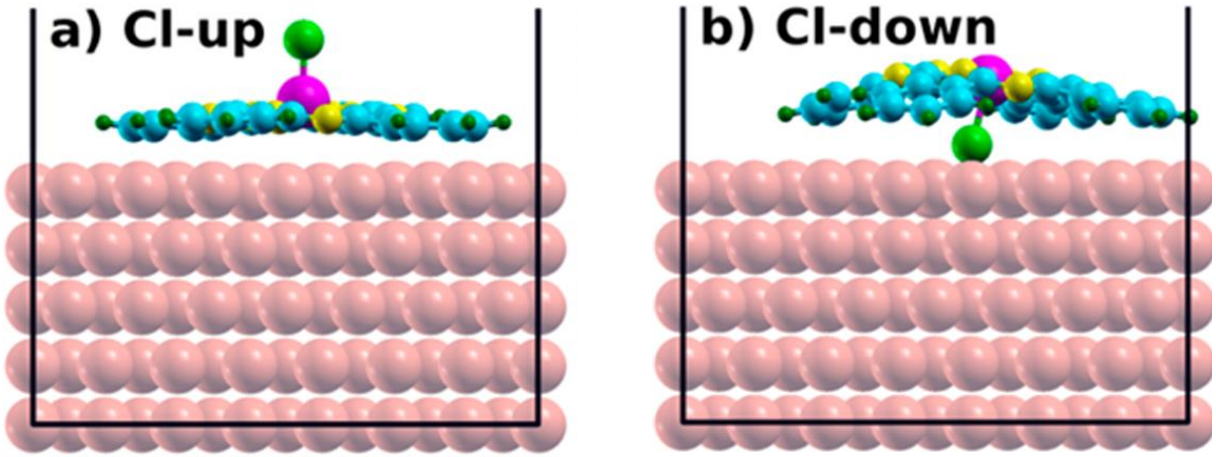


	(a) Cl-up		(b) Cl-down	
atom	XSW	DFT	XSW	DFT
C	2.36(7)	2.45	4.44(7)	3.18
N	2.63(3)	2.58	4.71(3)	3.72
Ga	2.13(5)	3.14	4.21(5)	3.79
Cl	3.96(3)	5.36	1.88(3)	1.51

Which structure is correct?

Wruss et al., The Journal of Physical Chemistry C, 120 (12), 6869, 2016

A practical problem



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Cl	3.96(3)	5.36	1.88(3)	1.51

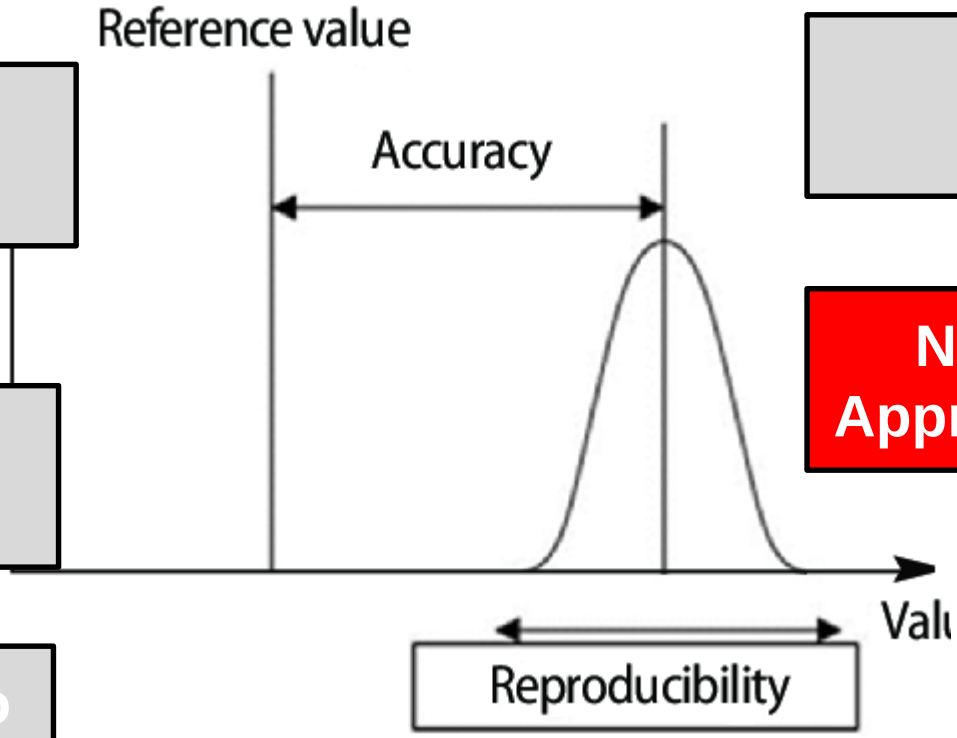
What accuracy / reproducibility do we expect?

Wruss et al., The Journal of Physical Chemistry C, 120 (12), 6869, 2016

Physics

Functional

Comparison to Experiment

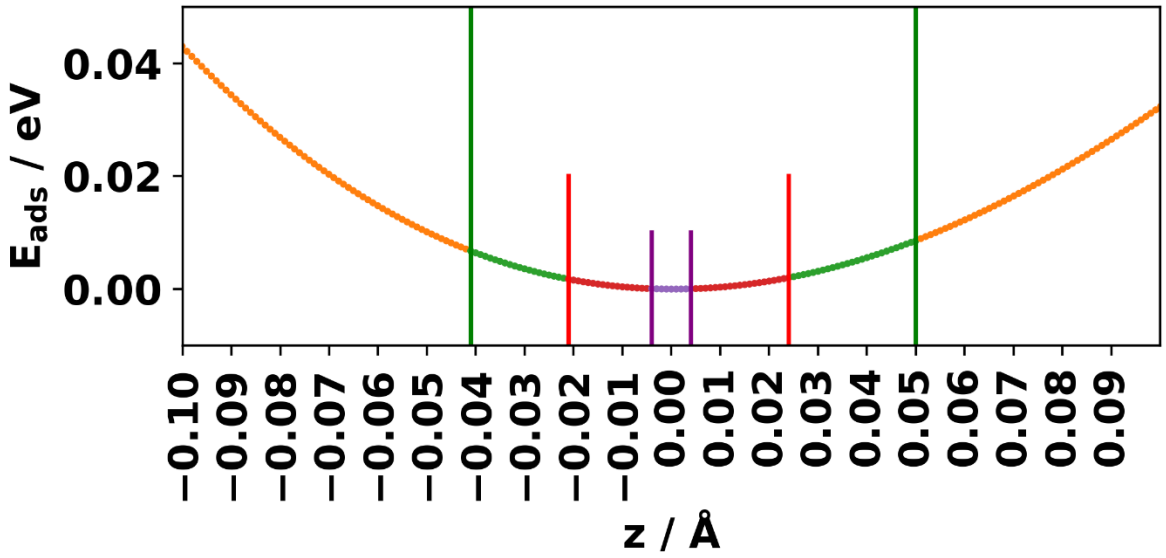


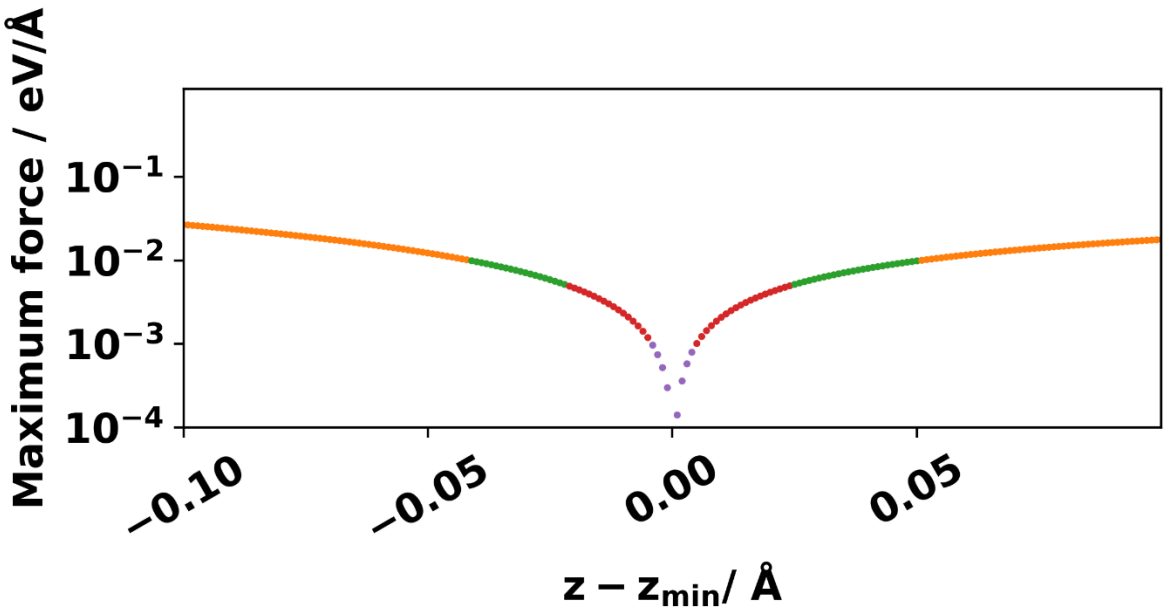
Code

Numerical Approximations

How far can we trust these values?

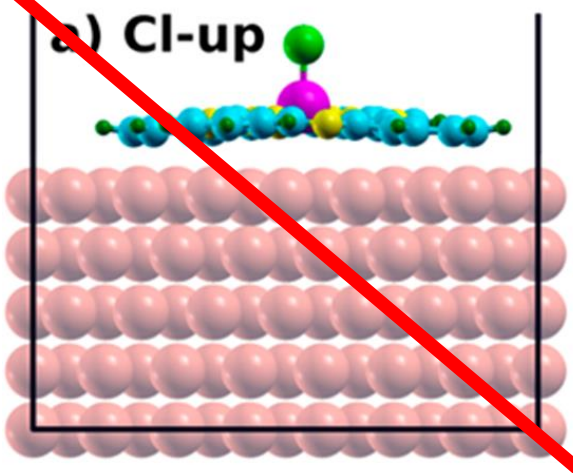
Reproducability of adsorption heights

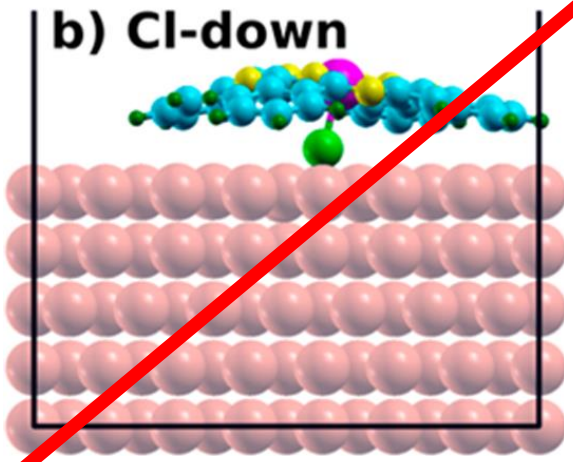


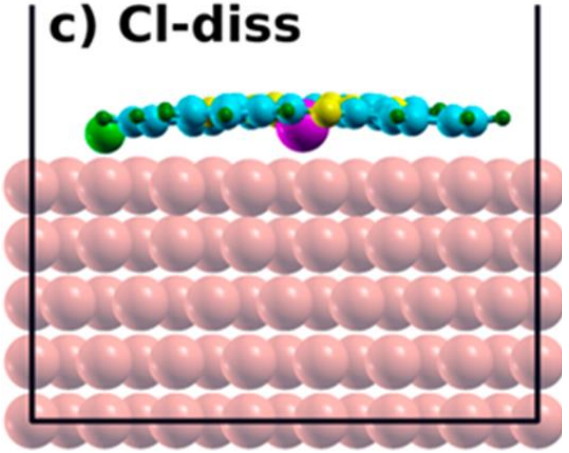


Threshold (eV/Å)	Δz (Å)
0.1	n/a
0.01	~ 0.1
0.005	~0.05
0.001	0.01

A practical problem







	(a) Cl-up		(b) Cl-down		(c) Cl-diss	
atom	XSW	DFT	XSW	DFT	XSW	DFT
C	2.36(7)	2.45	4.44(7)	3.18	2.36(7)	2.51
N	2.63(3)	2.58	4.71(3)	3.72	2.63(3)	2.68
Ga	2.13(5)	3.14	4.21(5)	3.79	2.13(5)	2.14
Cl	3.96(3)	5.36	1.88(3)	1.51	1.88(3)	1.86

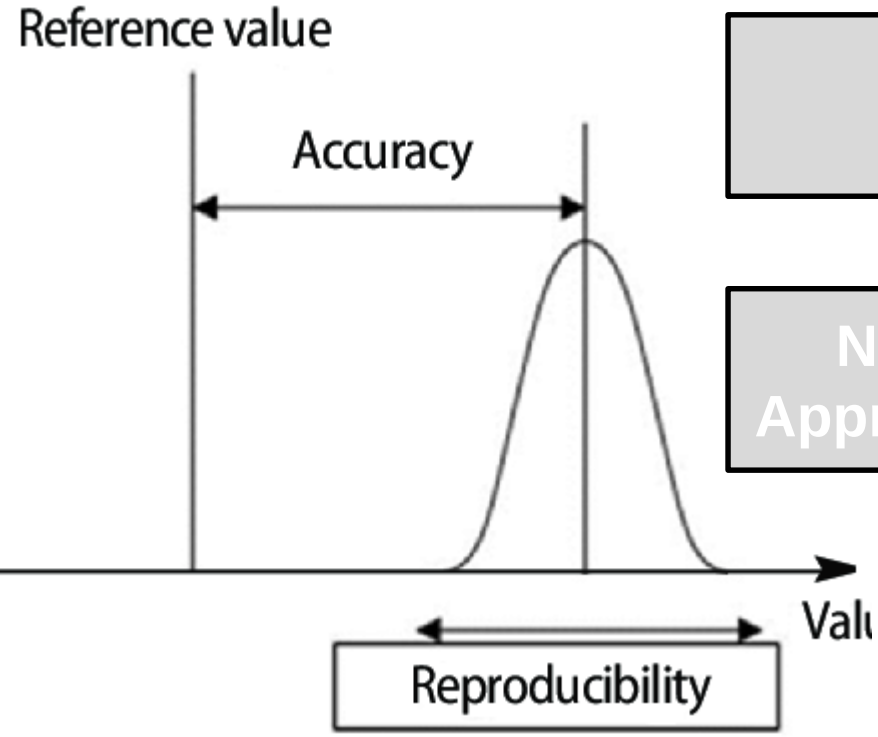
Which structure is correct?

Wruss et al., The Journal of Physical Chemistry C, 120 (12), 6869, 2016

Physics

Functional

Comparison to Experiment

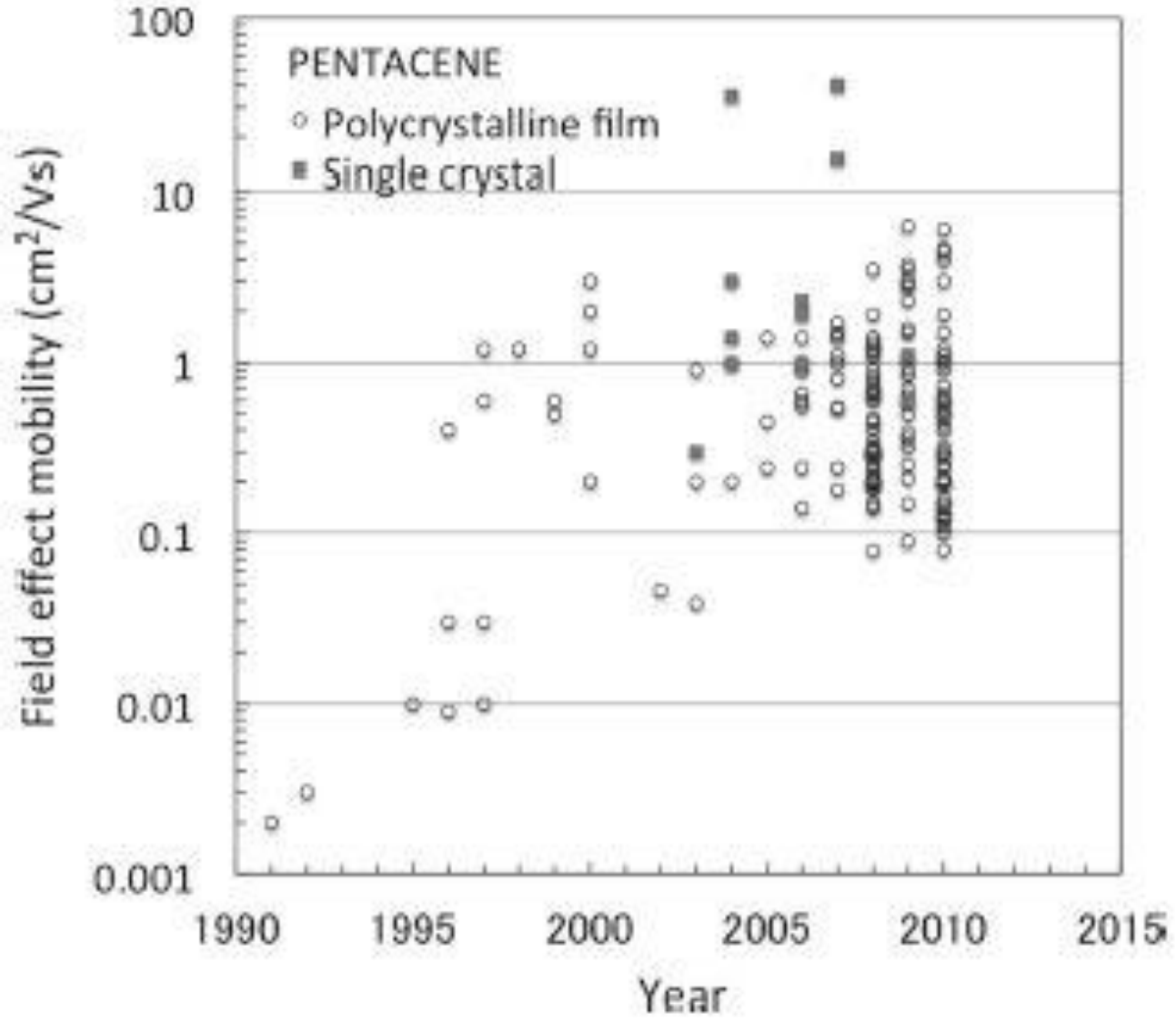


Code

Numerical Approximations

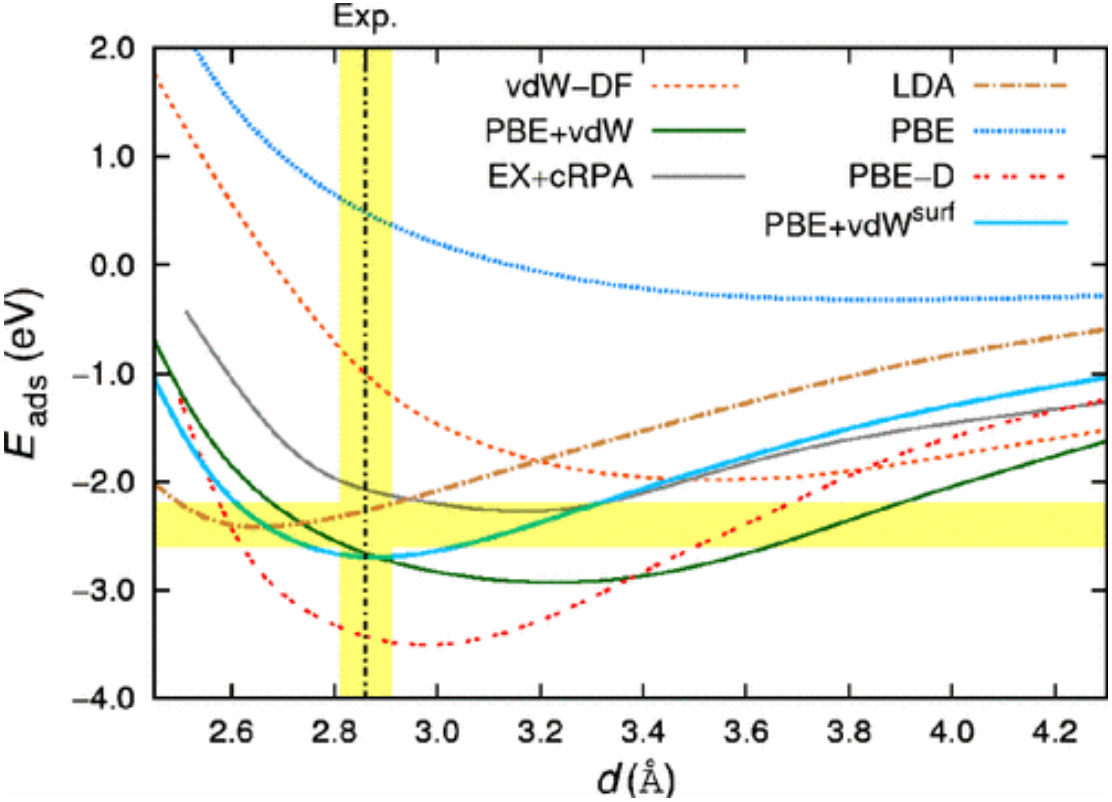
How far can we trust these values?

Experimental values for FET-mobilities of pentacene



https://download.e-bookshelf.de/download/0000/7577/19/L-X-0000757719-0002284395.XHTML/index.xhtml

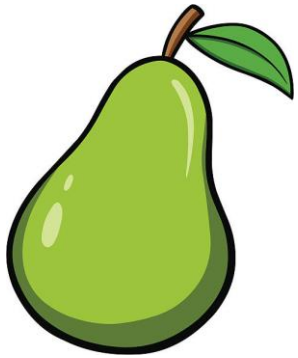
The benchmark problem: PTCDA/Ag(111)



Challenge: Reliability of benchmark (especially experimental)

Ruiz et al., Phys. Rev. Lett. 108, 146103, 2012

Theory	Experiment
• Structural model • Zero Temperature • Clamped Nucleii • Relativistics on/off	• Interpretation • Finite Temperature • Zero-point motion • Fully relativistic

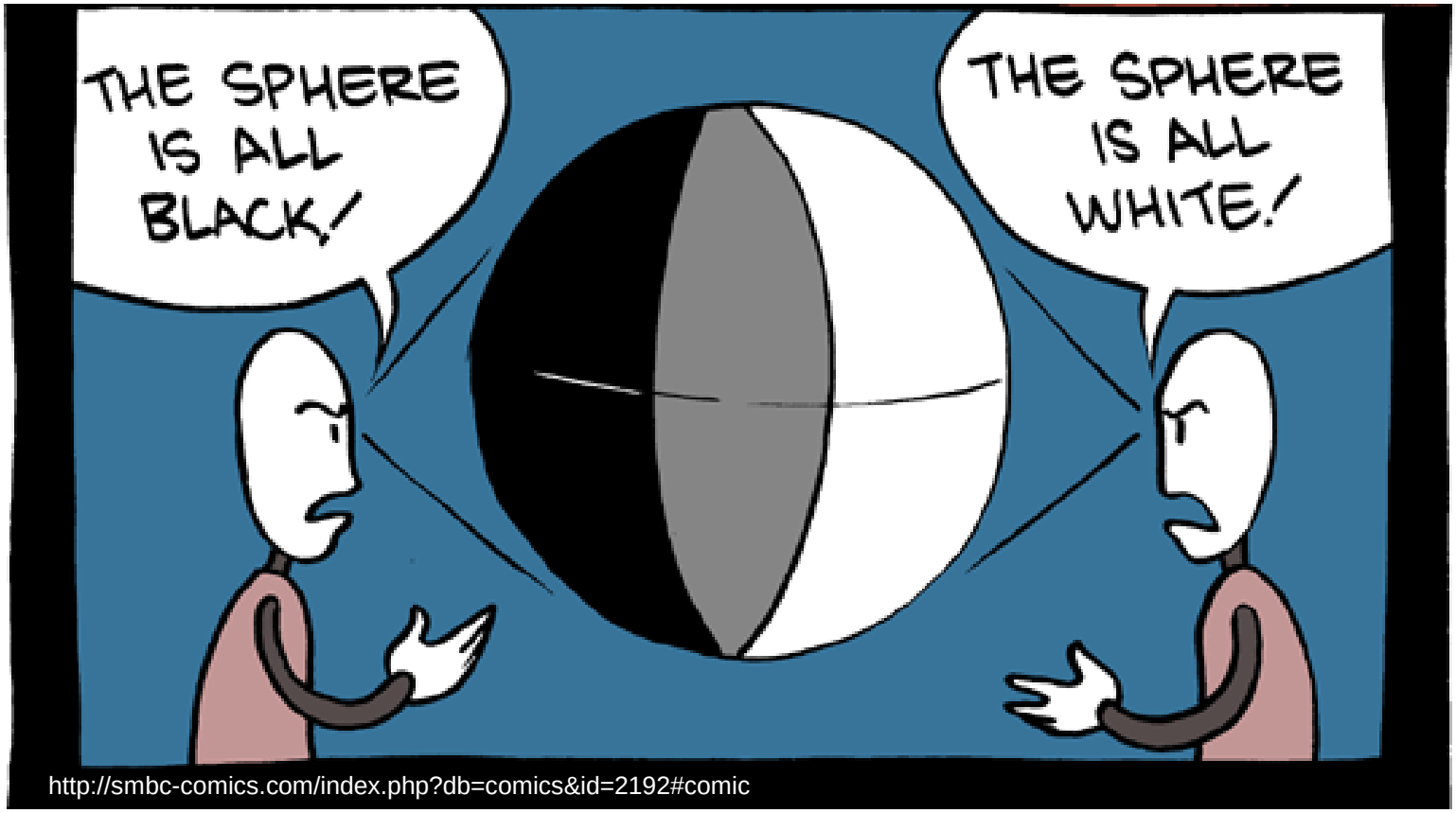


Extrapolate to 0 K / estimate ZPE / switch on relativistics

Do not take experimental results at face value

Comparing to higher-level theory preferred, but:

- **Observation bias / confirmation bias**



http://smbc-comics.com/index.php?db=comics&id=2192#comic

Comparing to higher-level theory preferred, but:

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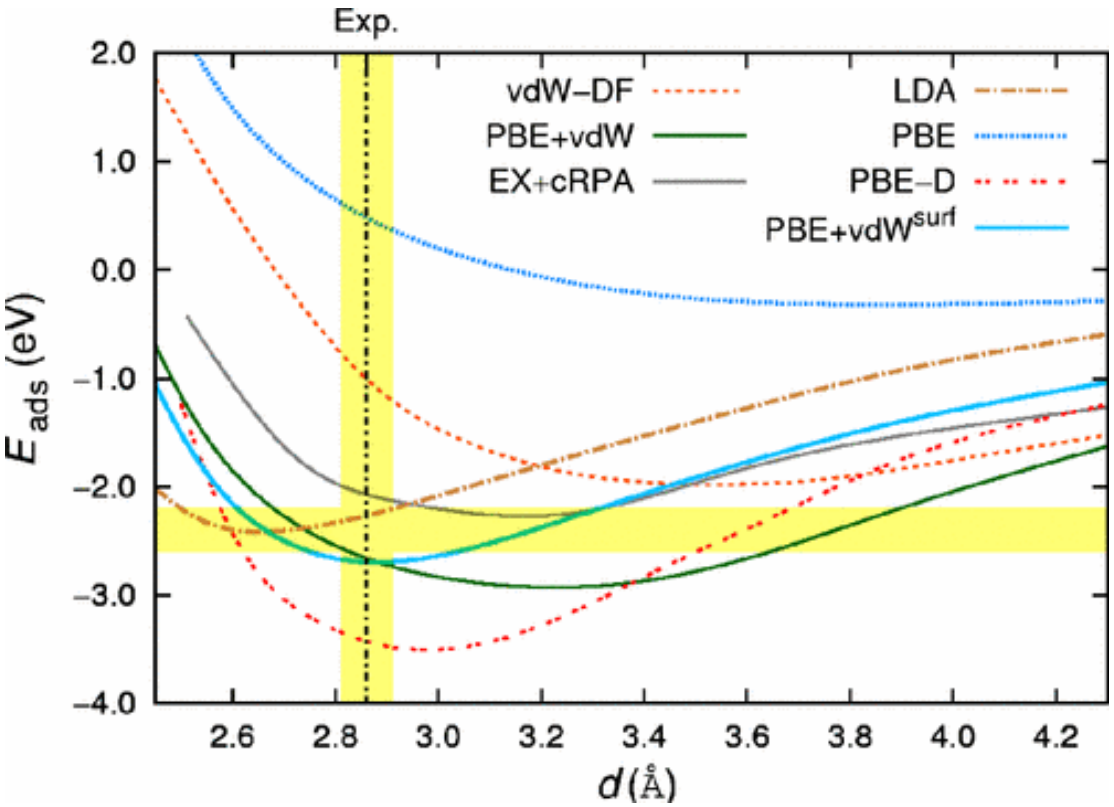
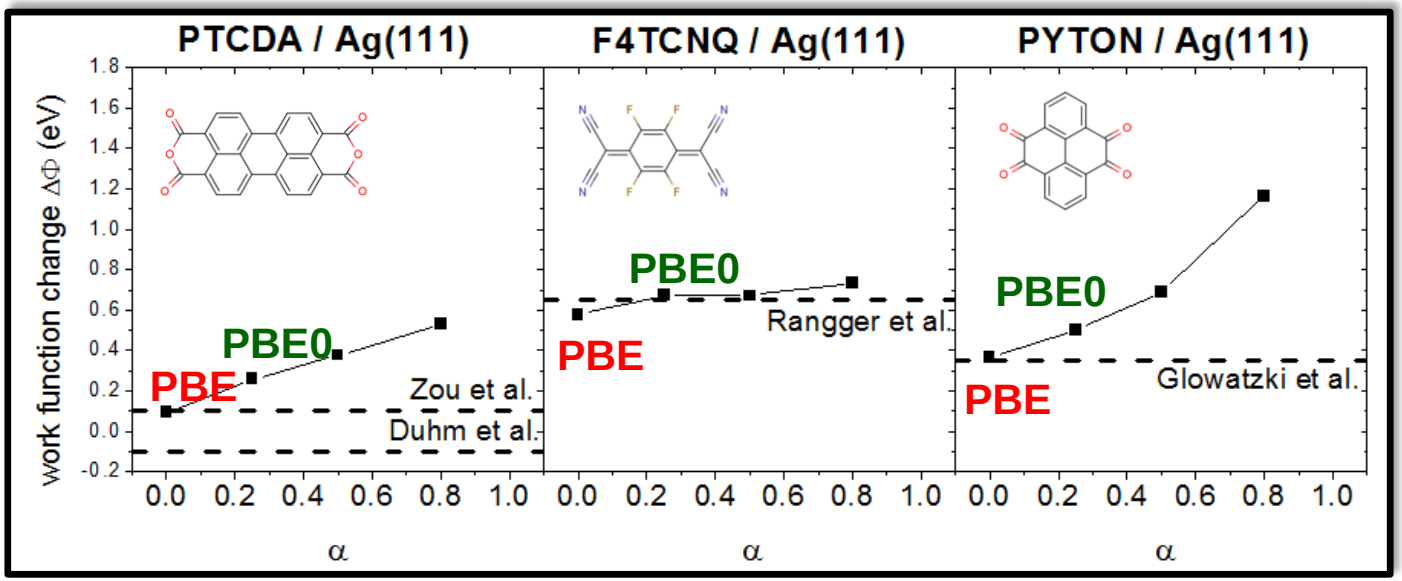


Ruiz et al., Phys. Rev. Lett. 108, 146103, 2012

Comparing to higher-level theory preferred, but:

- **Observation bias**
- **Higher Level not always more accurate**

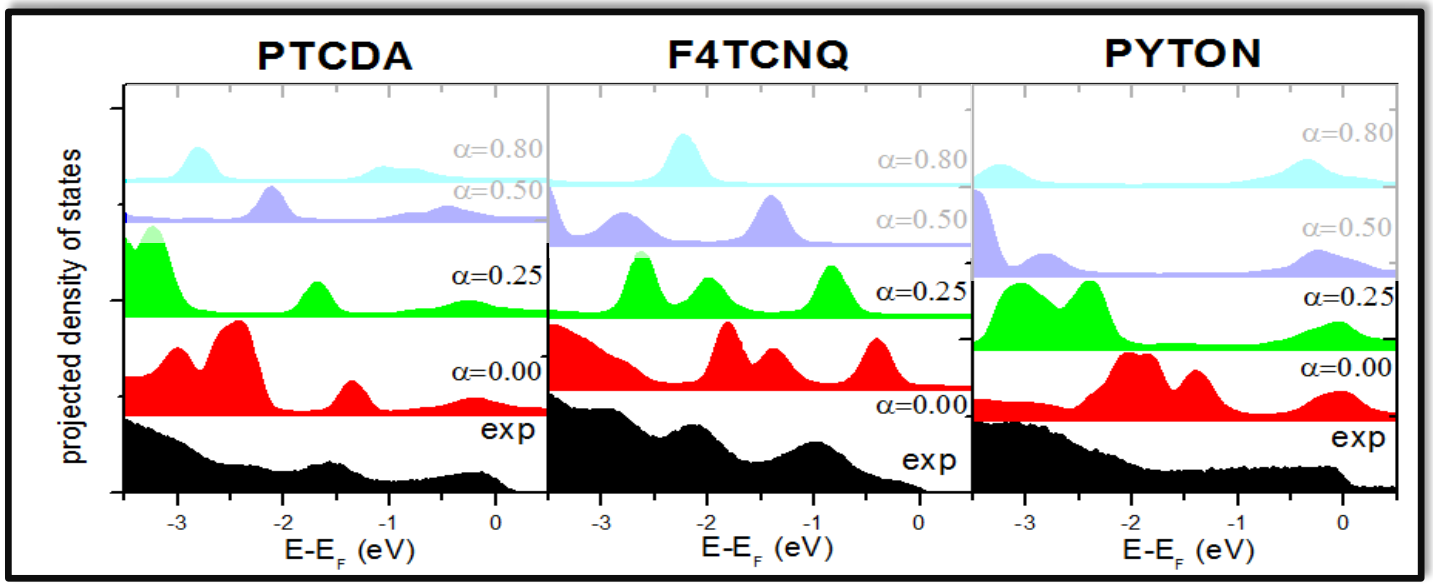


Directly related to piecewise linearity

Hofmann et al., New Journal of Physics, 15 (12), 123028, 2013

Comparing to higher-level theory preferred, but:

- **Observation bias**
- **Higher Level not always more accurate**

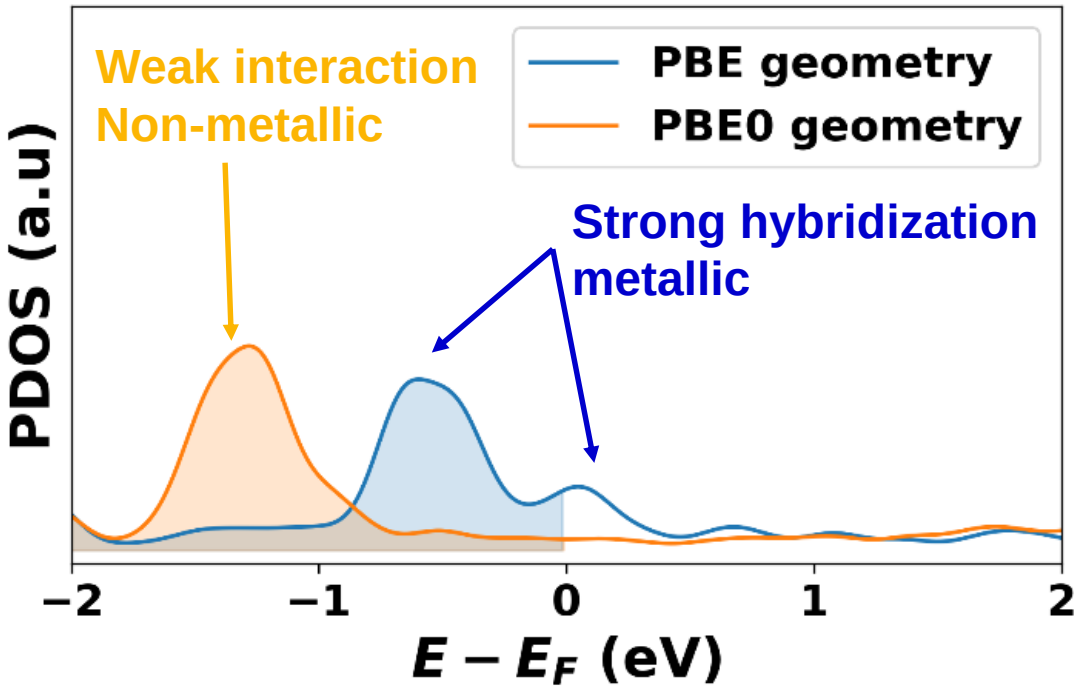


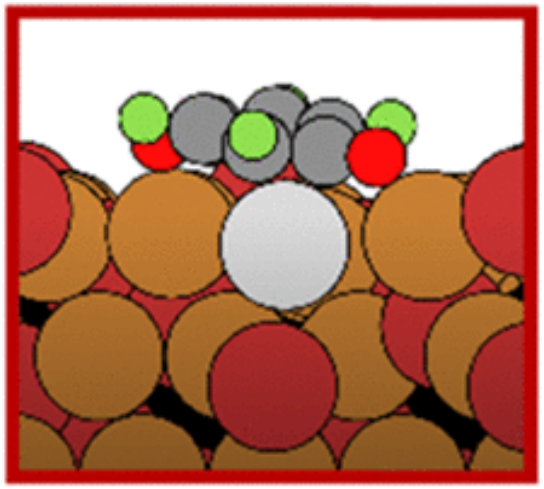
Directly related to piecewise linearity

Hofmann et al., New Journal of Physics, 15 (12), 123028, **2013**

Comparing to higher-level theory preferred, but:

- Observation bias
- Higher level not always more accurate
- Consistency (geometry / electronic structure)





Difference has physical background

Wruss et al., The Journal of Physical Chemistry C, 123 (12), 7118, 2019

Comparing to higher-level theory preferred, but:

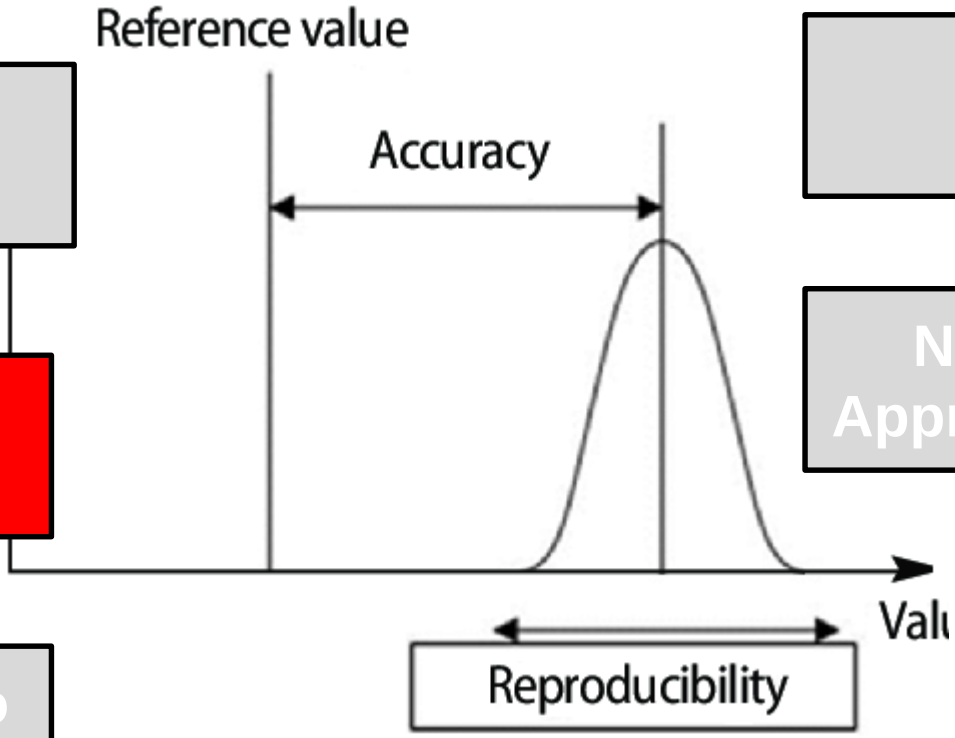
- **Observation bias**
- **Higher level not always more accurate**
- **Consistency (geometry / electronic structure)**
- **Often impossible**

Understanding of numerics / physics imperative!

Physics

Functional

Comparison to Experiment

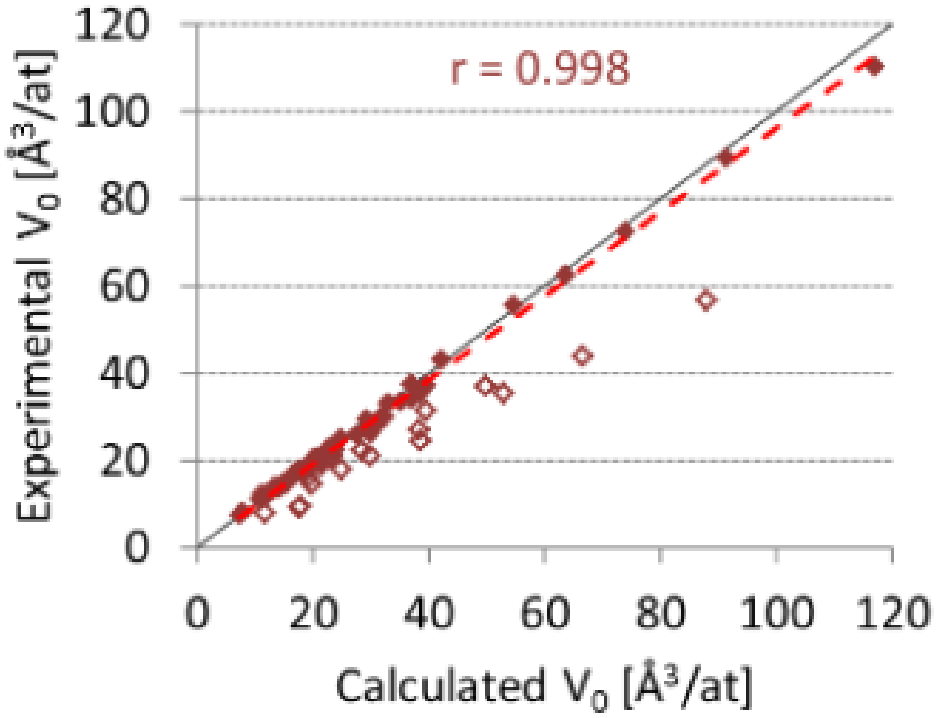


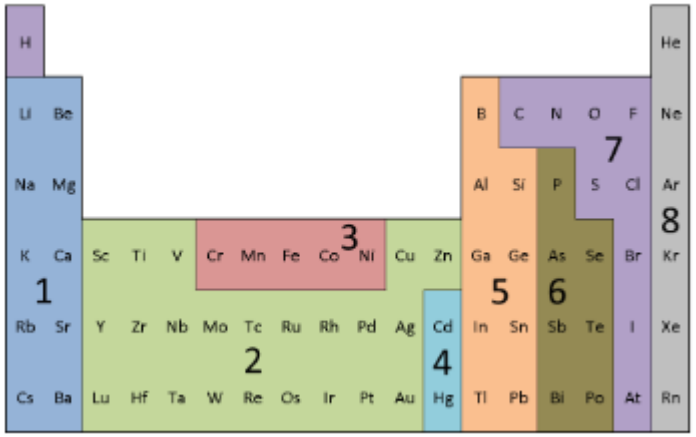
Code

Numerical Approximations

How far can we trust these values?

Systematic evaluation against experiment



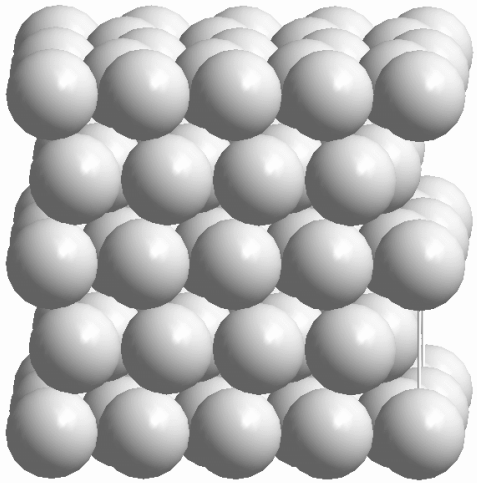


- **Small systematic error for PBE (slope)**
- **Residual scatter (r)**
- **Some classes excluded (physics!)**

Lejaeghere, K, CRITICAL REVIEWS IN SOLID STATE AND MATERIALS SCIENCES, 39 (1), 1

Practical application: Volume of β-Sn

Not an excluded class	**28.37 Å³/atom**
Bare PBE result:	**27.29 Å³/atom**
Systematic error (3.8%):	**27.38 Å³/atom**
Zero-point correction:	**27.38 Å³/atom**
Non-systematic error (1.1):	**27.38 ± 1.1 Å³/atom**
Experiment:	**26.46 Å³/atom (extrapolated to 0 K)**

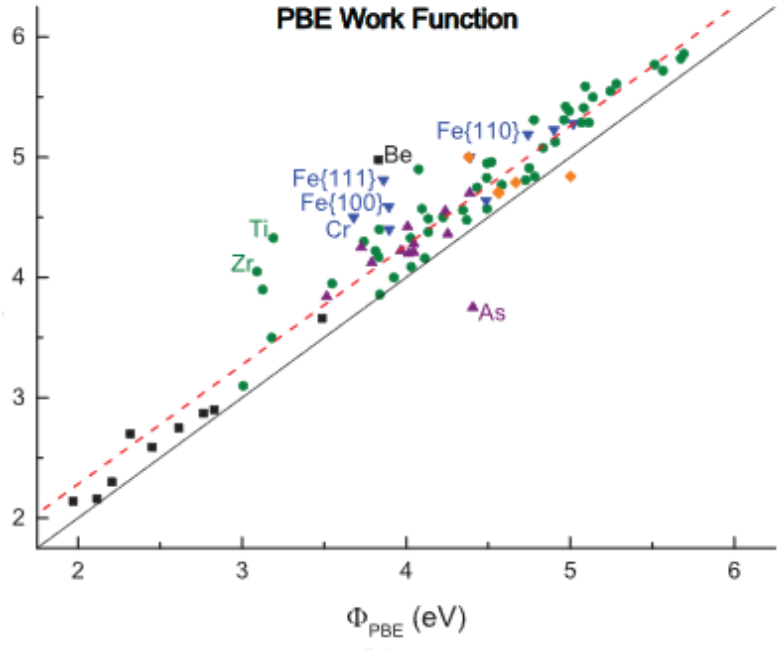


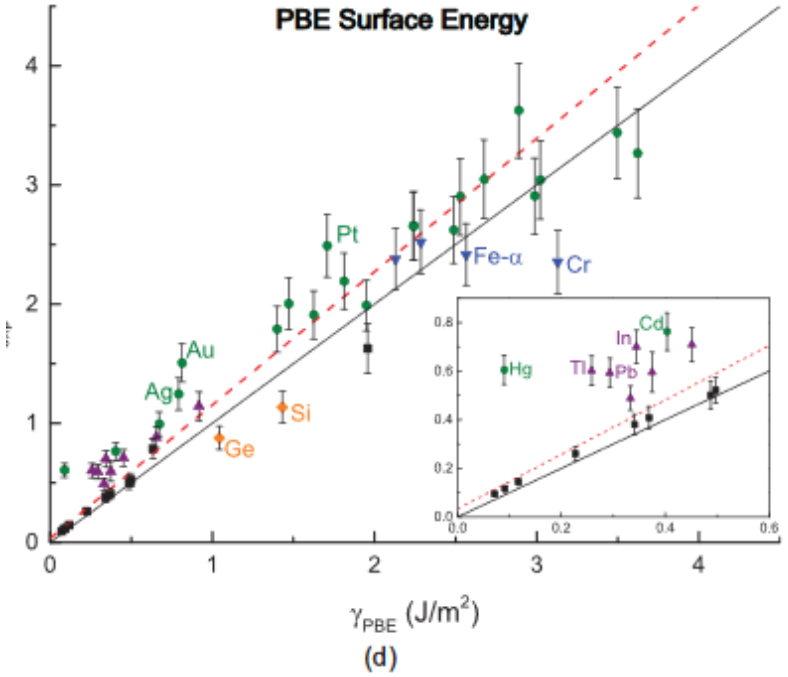
Slide taken from S. Cottenier

Lejaeghere, K, CRITICAL REVIEWS IN SOLID STATE AND MATERIALS SCIENCES, 39 (1), 1

Systematic evaluation against experiment

	β_0 (eV)	β_1	SER
Φ_{LDA}	0.22 ± 0.09	0.94 ± 0.02	$1.22^{1.47}_{1.05}$
Φ_{PBE}	0.30 ± 0.09	0.99 ± 0.02	$1.29^{1.55}_{1.11}$
	β_0 (J/m^2)	β_1	SER
γ_{LDA}	0.00 ± 0.01	0.93 ± 0.02	$1.36^{1.74}_{1.12}$
γ_{PBE}	0.03 ± 0.01	1.12 ± 0.02	$2.34^{2.98}_{1.92}$





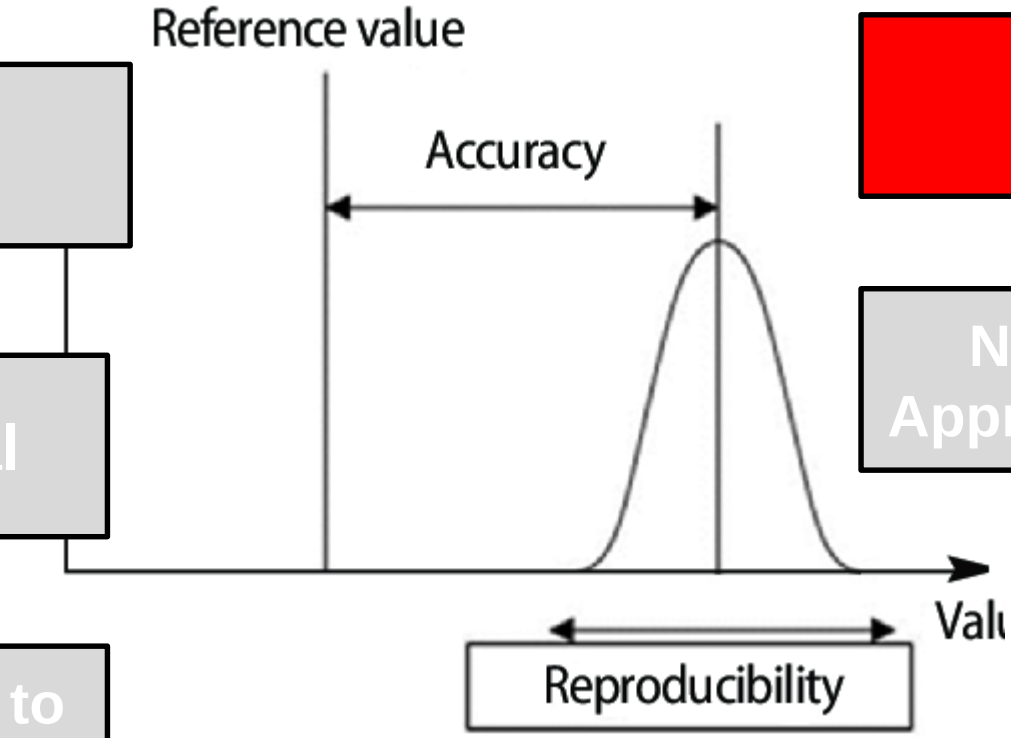
Several more properties have been investigated

De Waele et al, PRB 94, (2016)

Physics

Functional

Comparison to Experiment



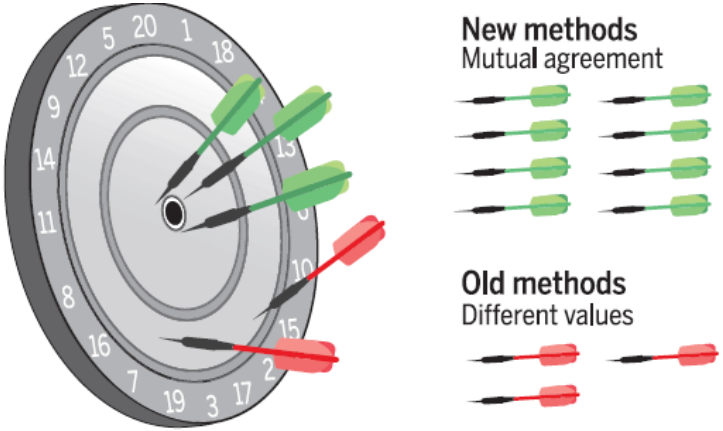
Code

Numerical Approximations

How far can we trust these values?

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere,* Gustav Bihlmayer, Torbjörn Björkman, Peter Blaha, Stefan Blügel, Volker Blum, Damien Caliste, Ivano E. Castelli, Stewart J. Clark, Andrea Dal Corso, Stefano de Gironcoli, Thierry Deutsch, John Kay Dewhurst, Igor Di Marco, Claudia Draxl, Marcin Dułak, Olle Eriksson, José A. Flores-Livas, Kevin F. Garrity, Luigi Genovese, Paolo Giannozzi, Matteo Giantomassi, Stefan Goedecker, Xavier Gonze, Oscar Grånäs, E. K. U. Gross, Andris Gulans, François Gygi, D. R. Hamann, Phil J. Hasnip, N. A. W. Holzwarth, Diana Iuşan, Dominik B. Jochym, François Jollet, Daniel Jones, Georg Kresse, Klaus Koepernik, Emine Küçükbenli, Yaroslav O. Kvashnin, Inka L. M. Locht, Sven Lubeck, Martijn Marsman, Nicola Marzari, Ulrike Nitzsche, Lars Nordström, Taisuke Ozaki, Lorenzo Paulatto, Chris J. Pickard, Ward Poelmans, Matt I. J. Probert, Keith Refson, Manuel Richter, Gian-Marco Rignanese, Santanu Saha, Matthias Scheffler, Martin Schlipf, Karlheinz Schwarz, Sangeeta Sharma, Francesca Tavazza, Patrik Thunström, Alexandre Tkatchenko, Marc Torrent, David Vanderbilt, Michiel J. van Setten, Veronique Van Speybroeck, John M. Wills, Jonathan R. Yates, Guo-Xu Zhang, Stefaan Cottenier*

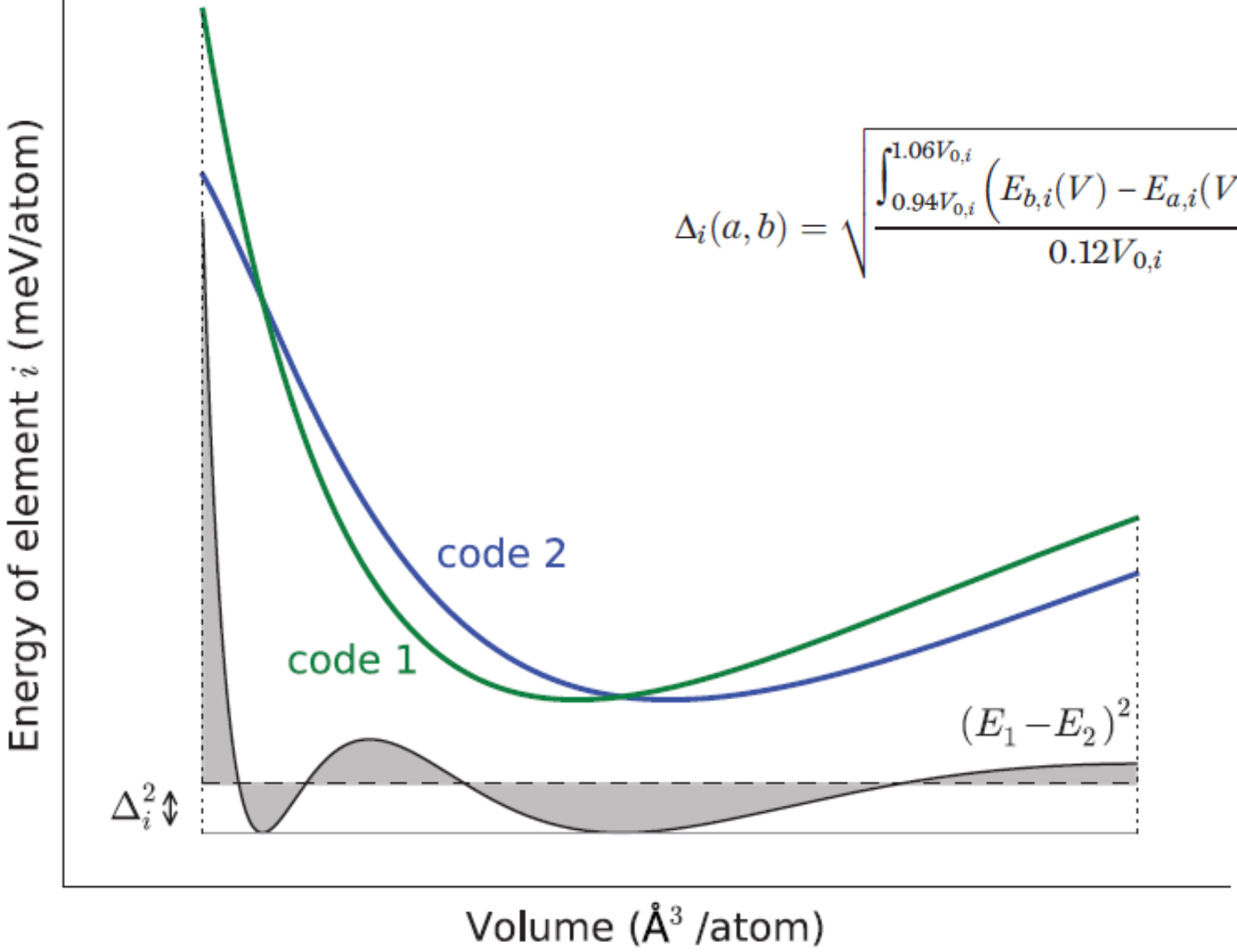


Many modern materials codes tested

Kurt Lejaeghere et al., Science, 351 6280

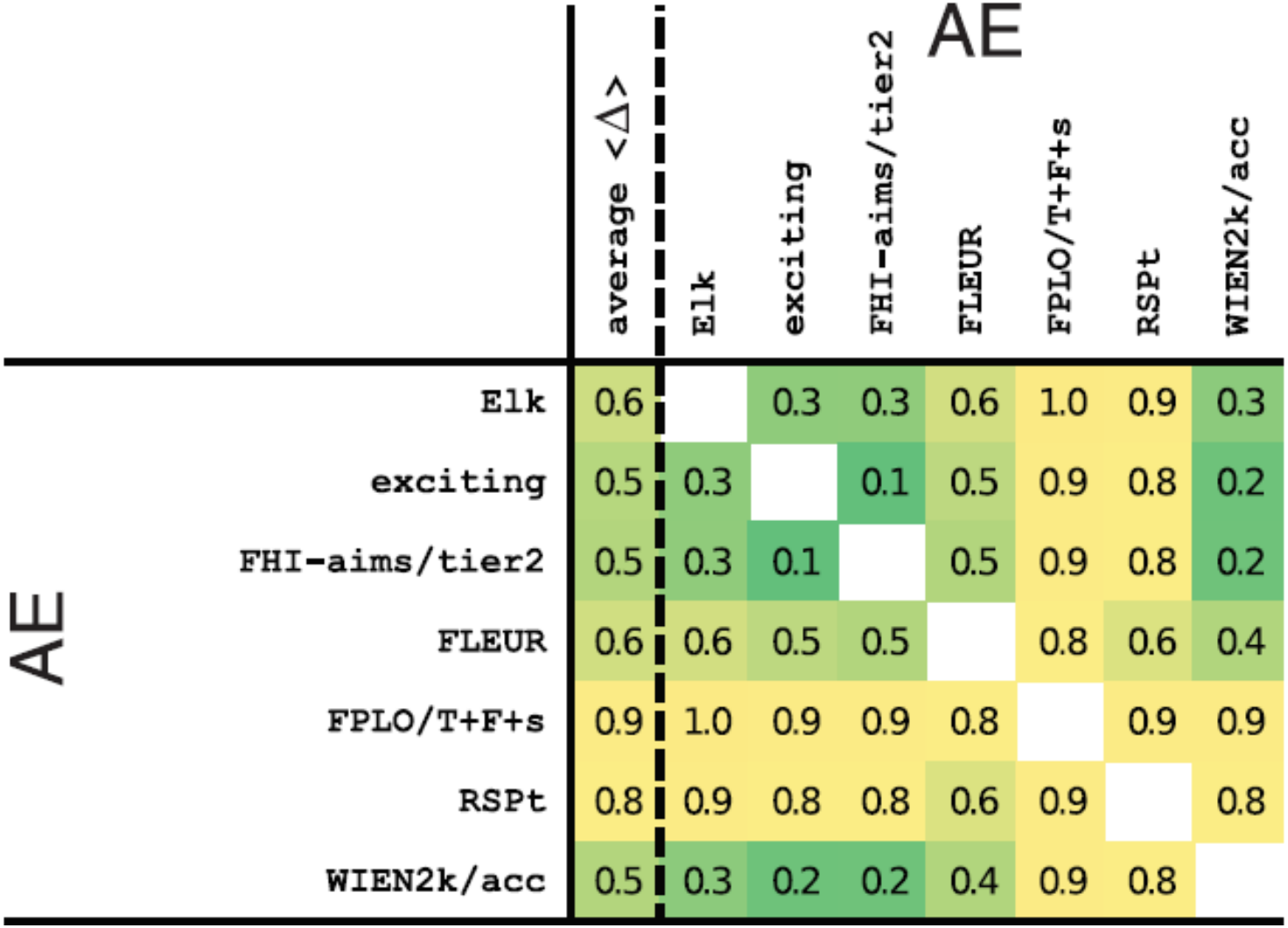
How well do two codes agree?

$$\Delta_i(a,b) = \sqrt{\frac{\int_{0.94V_{0,i}}^{1.06V_{0,i}} \left(E_{b,i}(V) - E_{a,i}(V)\right)^2 dV}{0.12V_{0,i}}} \quad (1)$$



Kurt Lejaeghere et al., Science, 351 6280

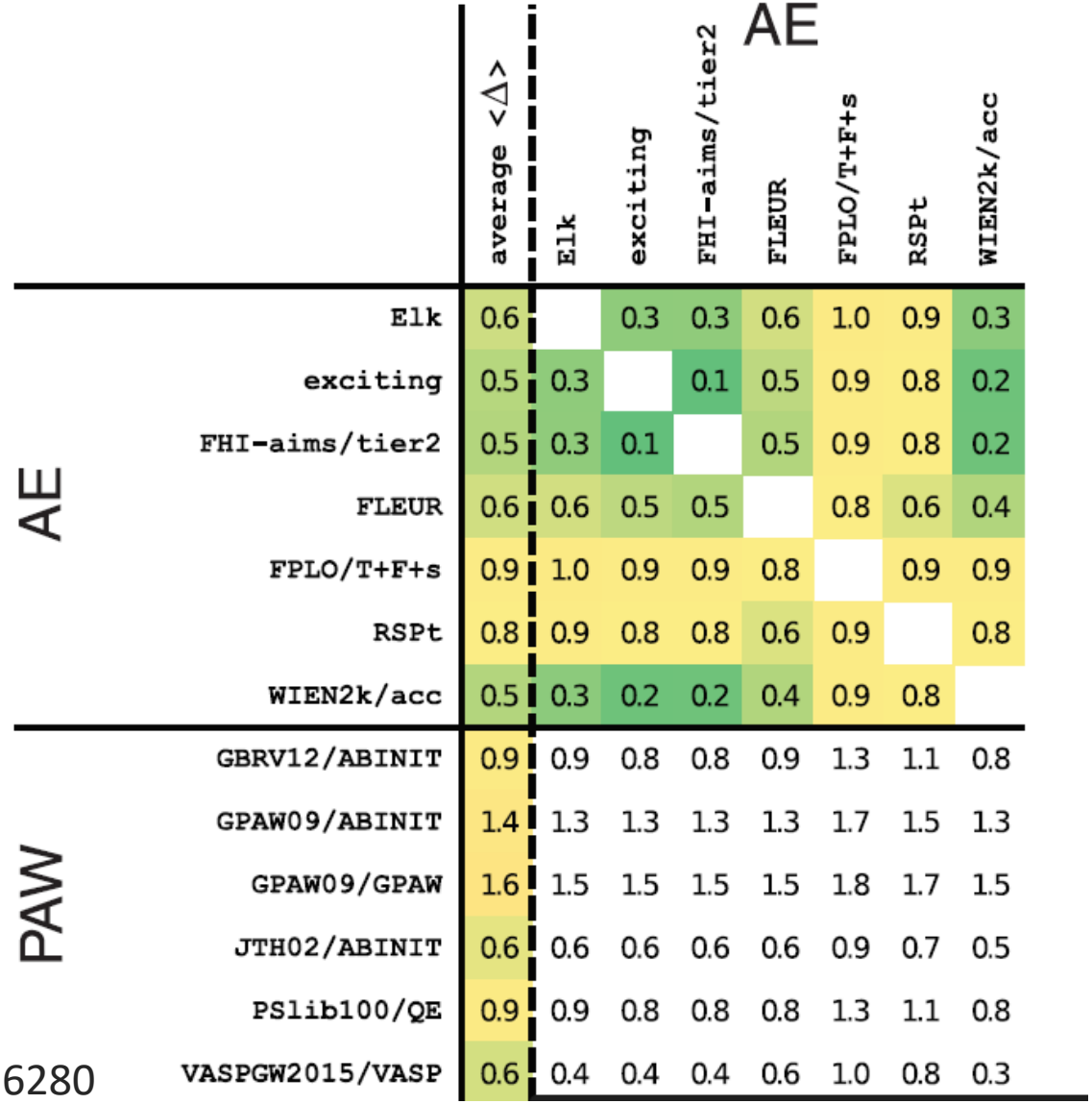
Comparison of all-electron codes



AE	average <Δ>	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	

Kurt Lejaeghere et al., Science, 351 6280

All Electron (AE) versus Plan Waves



		average <Δ>	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
	PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
	VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3

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Time heals old wounds

Table 2. Precision evolution of PAW and pseudopotential sets over time. The Δ values are expressed as an average over the all-electron methods (in millielectron volts per atom) and are listed chronologically per code. The corresponding code settings and the DFT-predicted EOS parameters are listed in tables S17, S19 to S26, S30, S31, and S33. The most recent potentials are the ones used to generate the data shown in Fig. 4.

	Year	⟨Δ⟩versus AE
JTH01/ABINIT	2013	1.1
JTH02/ABINIT	2014	0.6
Vdb/CASTEP	1998	6.5
OTFG7/CASTEP	2013	2.6
OTFG9/CASTEP	2015	0.7
GPAW06/GPAW	2010	3.6
GPAW09/GPAW	2012	1.6
PSlib031/QE	2013	1.7
PSlib100/QE	2013	1.0
VASP2007/VASP	2007	2.0
VASP2012/VASP	2012	0.8
VASPGW2015/VASP	2015	0.6

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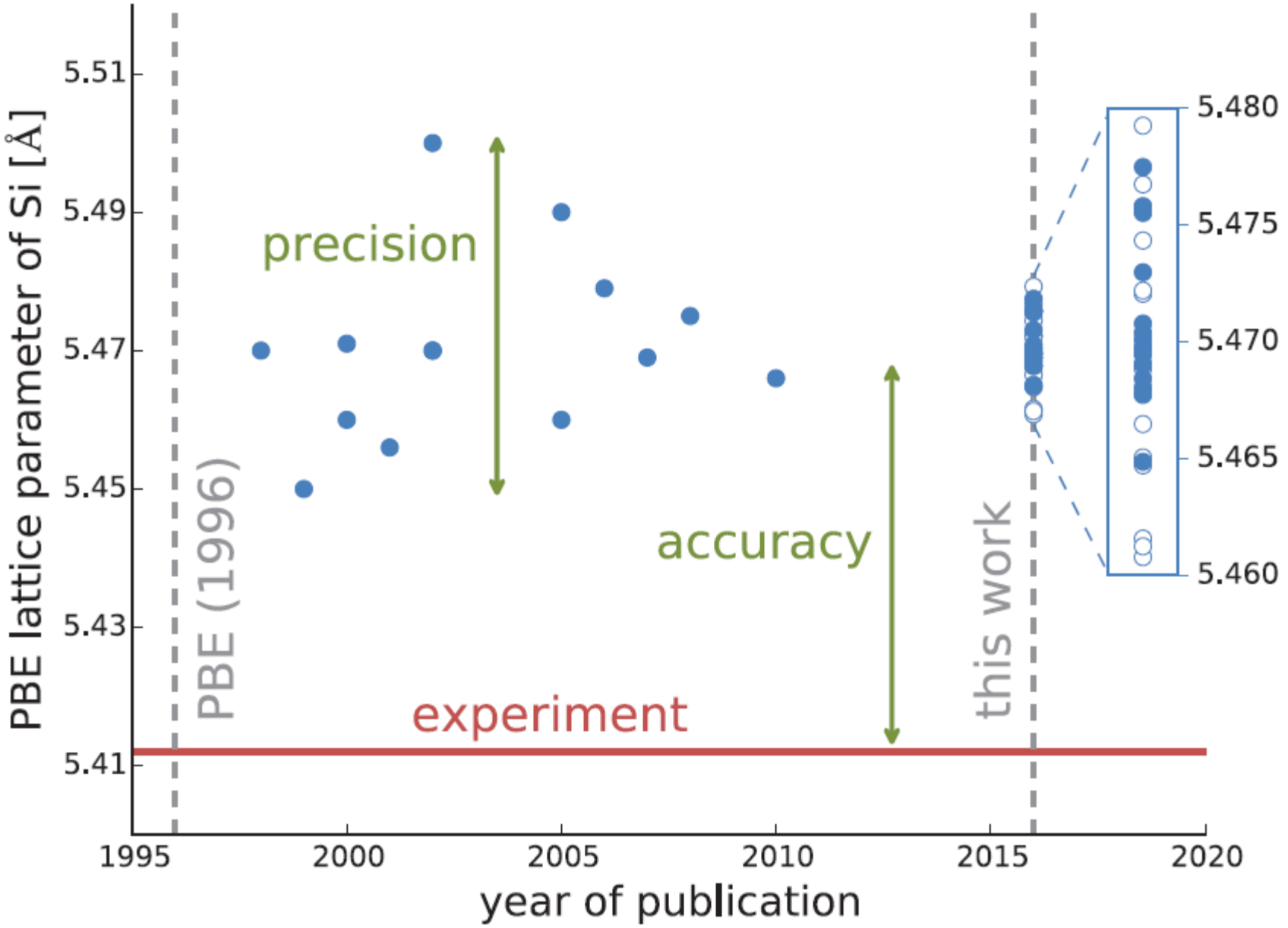

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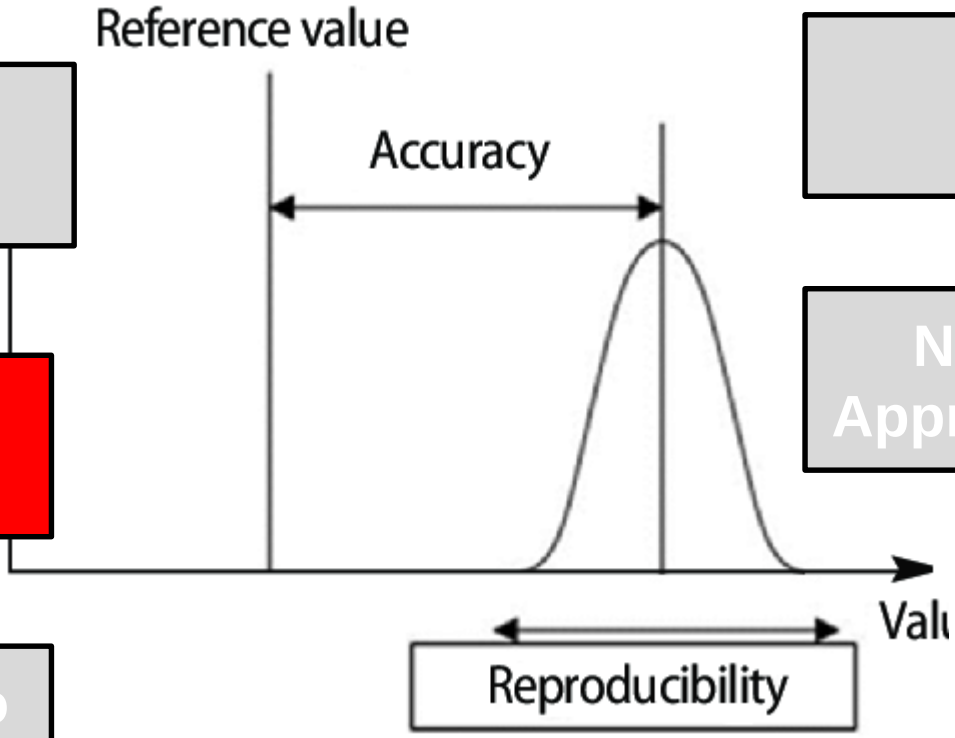
Physics

Functional

Comparison to Experiment



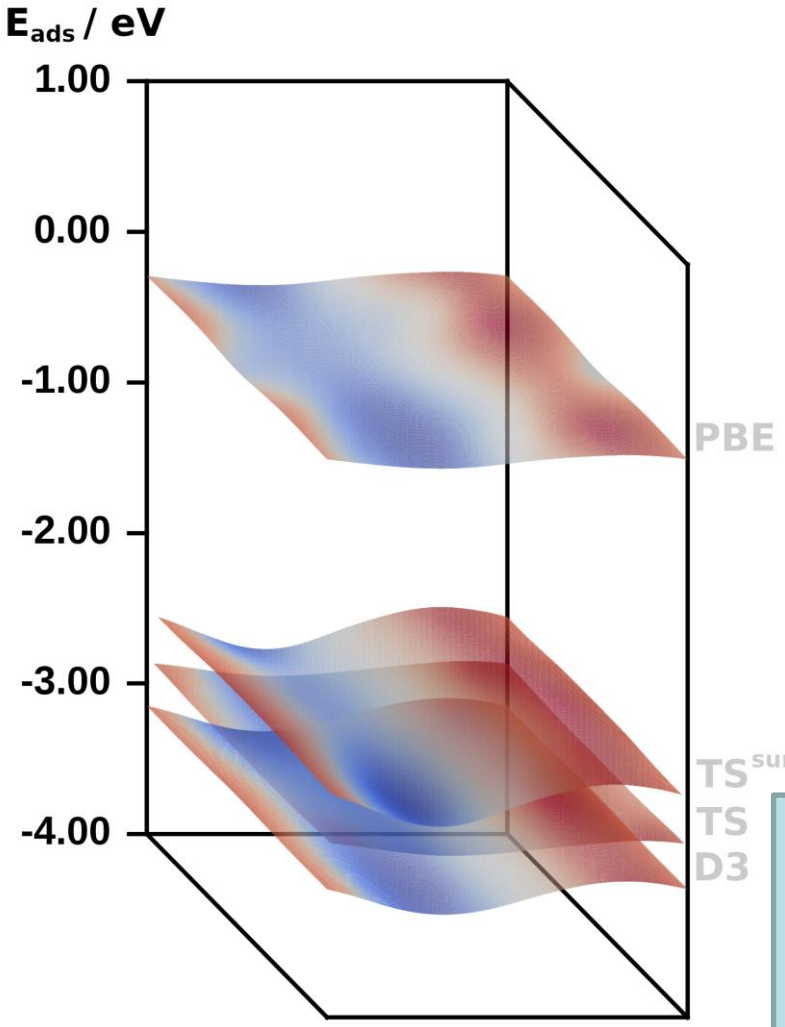
Code

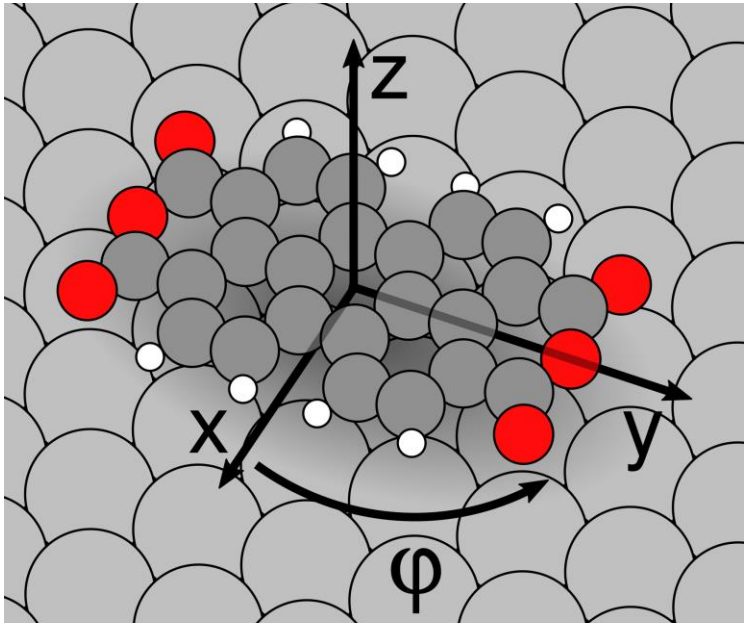
Numerical Approximations

How far can we trust these values?

Lukas Hörmann

Will results at least be consistent?

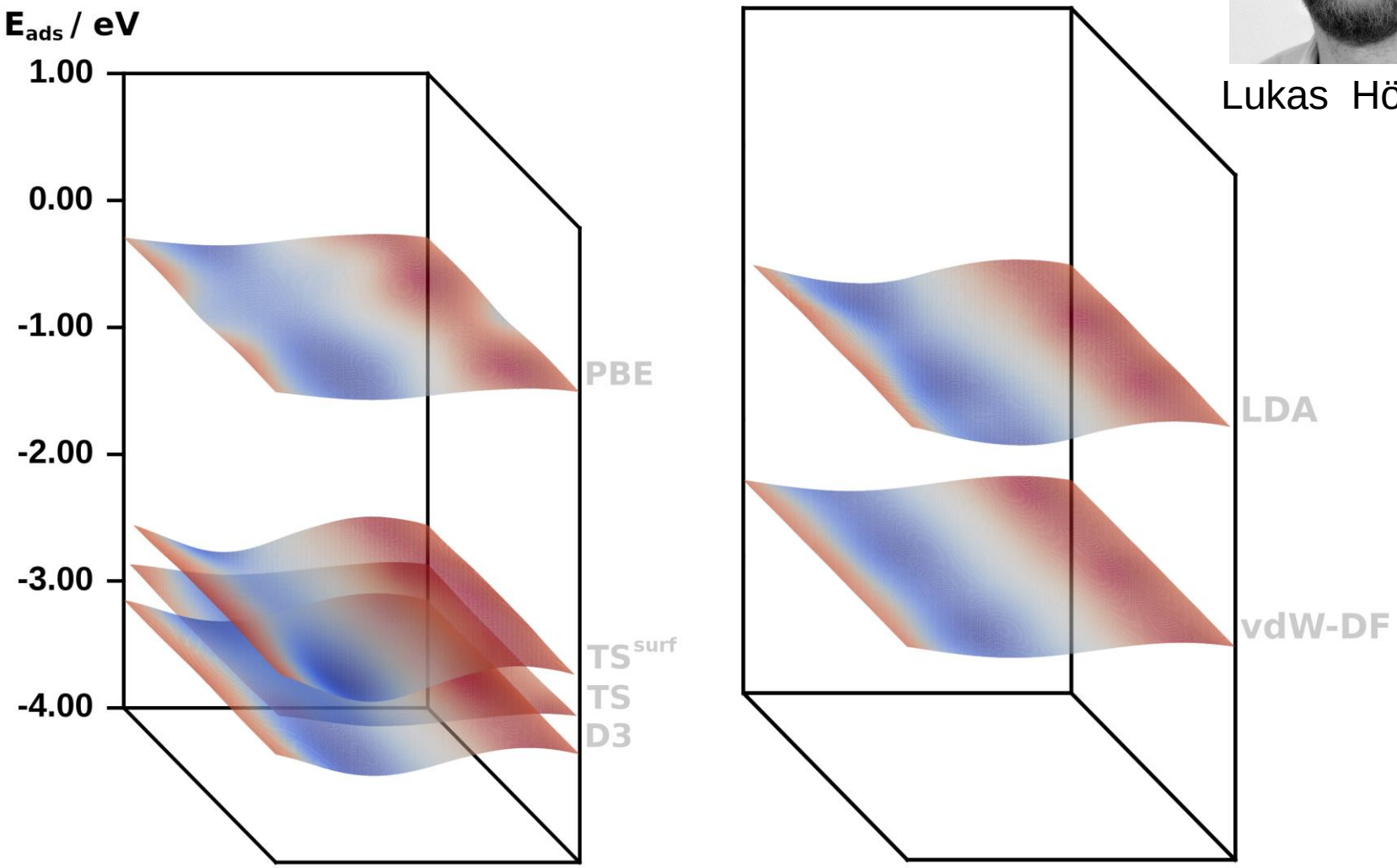




Overall shape of PES (mostly) independent of vdW treatment

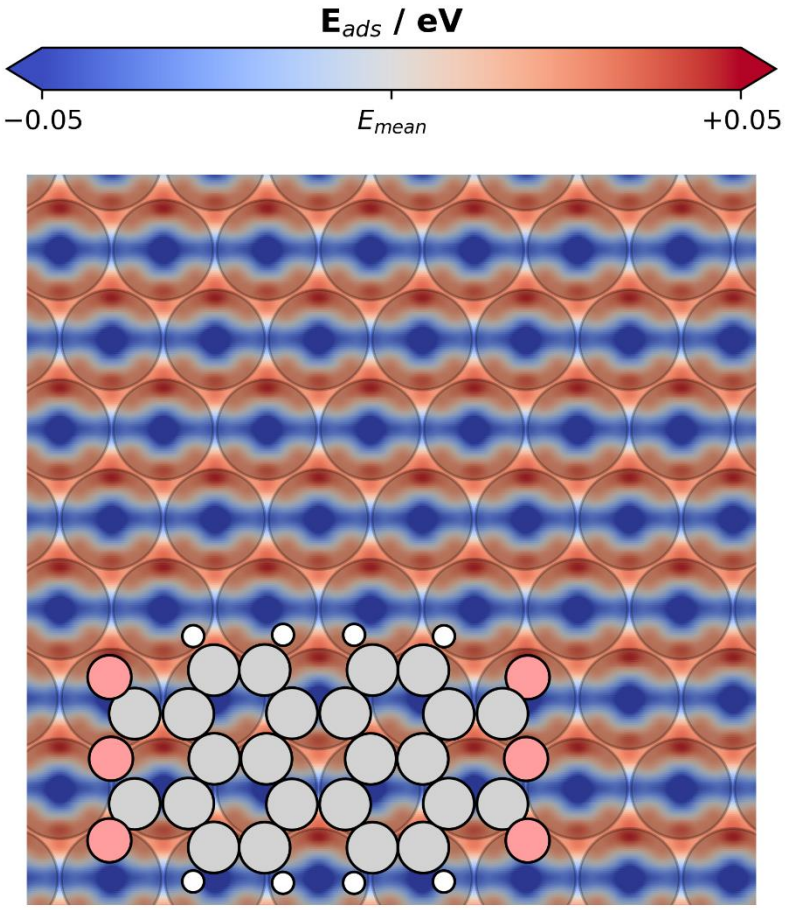
Lukas Hörmann

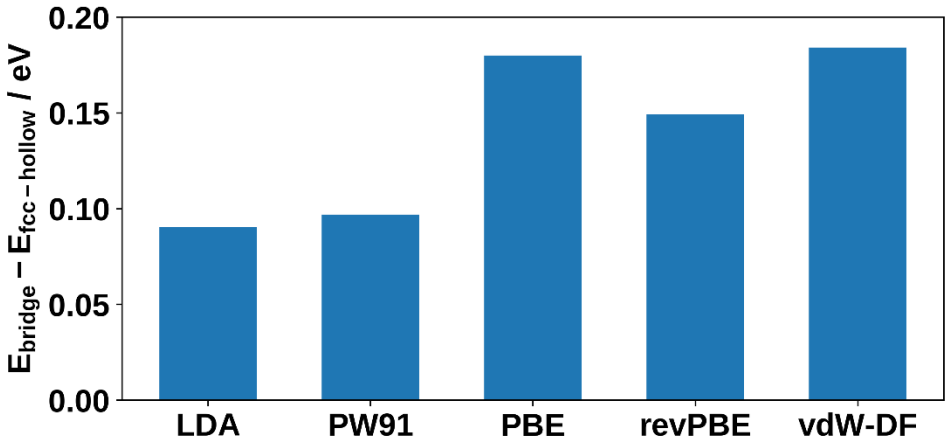
Will results at least be consistent?



Will results at least be consistent?

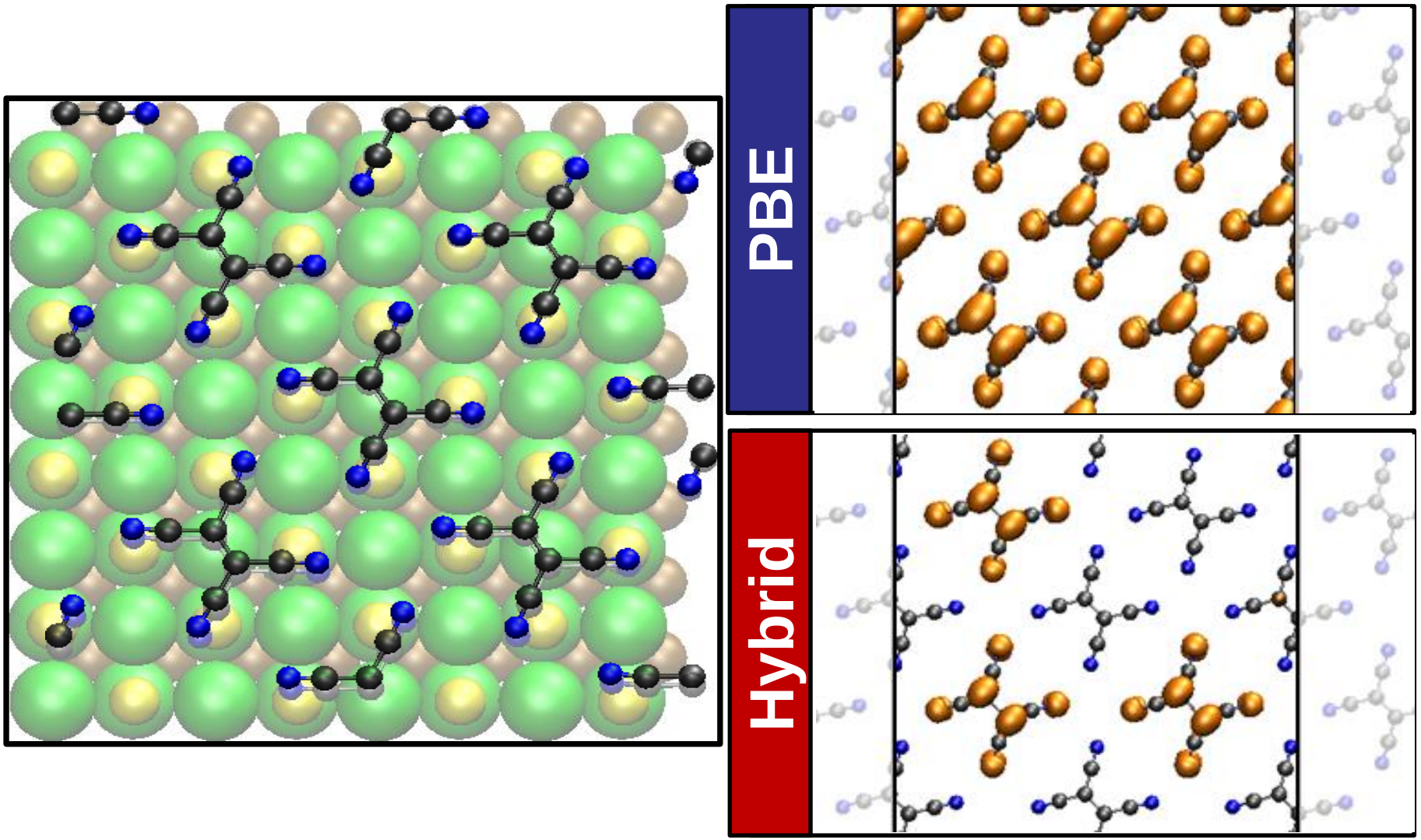
PBE – vdW-DF





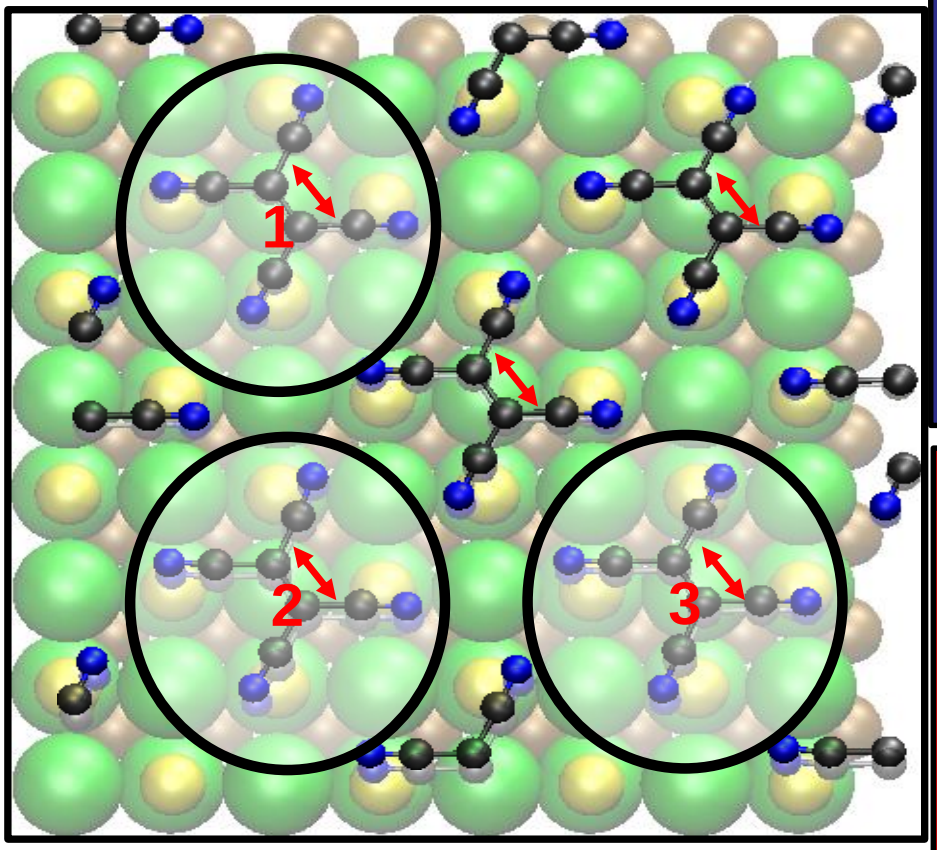
specific adsorption sites
Systematically favored

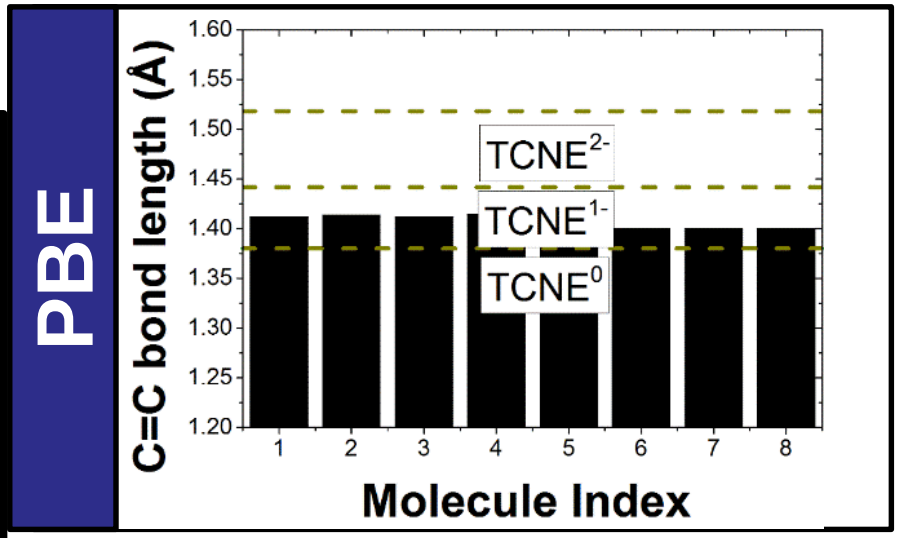
Will results at least be consistent?

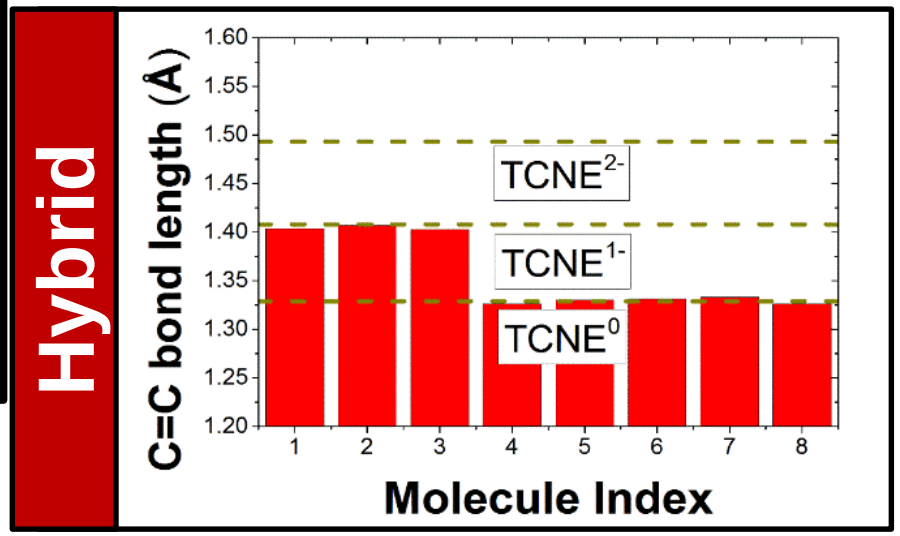


Hofmann et al., ACS Nano, 9 (5) 5391, 2015

Will results at least be consistent?



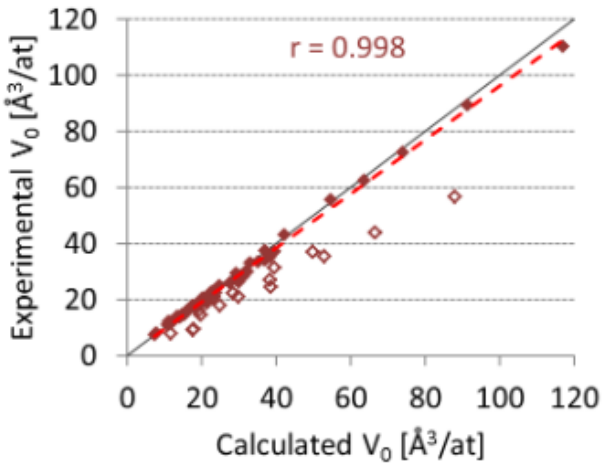


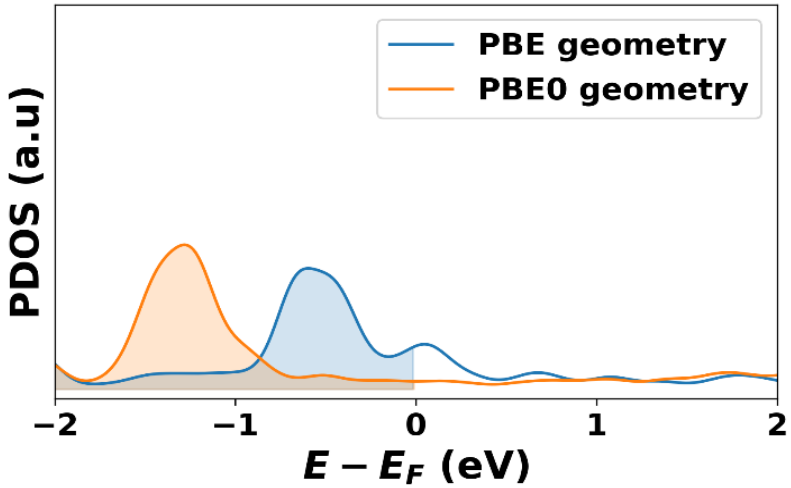


Hofmann et al., ACS Nano, 9 (5) 5391, 2015

Summary

- Results essentially independent of used code
- Ab-initio calculations have systematic and non-systematic errors
- Careful comparison to experiments (interpretation, physical)
- More sophisticated methods not always better (geometry, numerics)





Summary

- **Different functionals often qualitatively similar, sometimes quantative differences (physics!)**

Be aware of functional-inherent errors