

**Computational Materials Science Seminar**

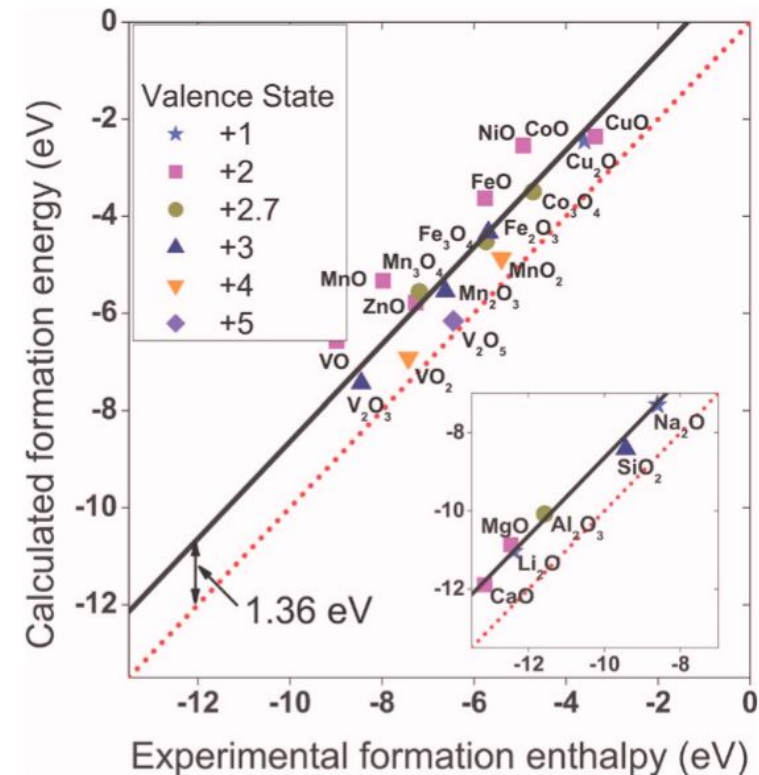
**Energy corrections & Accuracy of phase diagrams  
in the Materials Project**

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1. **Problem statement**
2. **Treating systematic errors**
3. **XC-functionals mixing**
4. **Generalization for more systems**
5. **Adding one more XC-functional**
6. **Practical considerations**

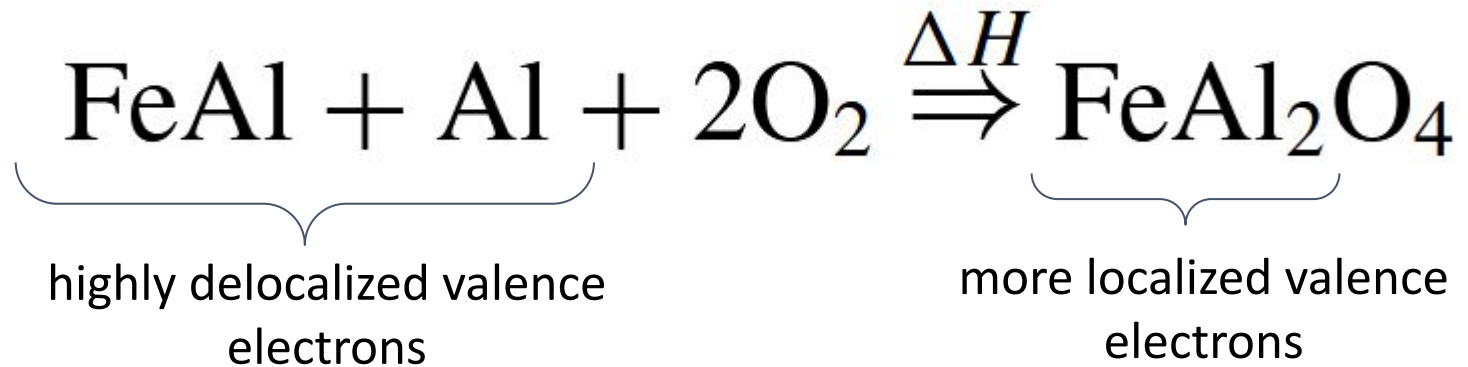
- Going to synthesize → we need to calculate thermodynamic stability
- The target property is energy above hull (needs formation energy  $E_f$ )
- DFT has limited accuracy:
  - we are starting with  $\sim 600$  meV/atom
  - which magnitude is needed?
  - what can be done?





GGA favors delocalization; +U favors localization

→ we do not have accurate energies for reactions where electron structure is changed in this sense



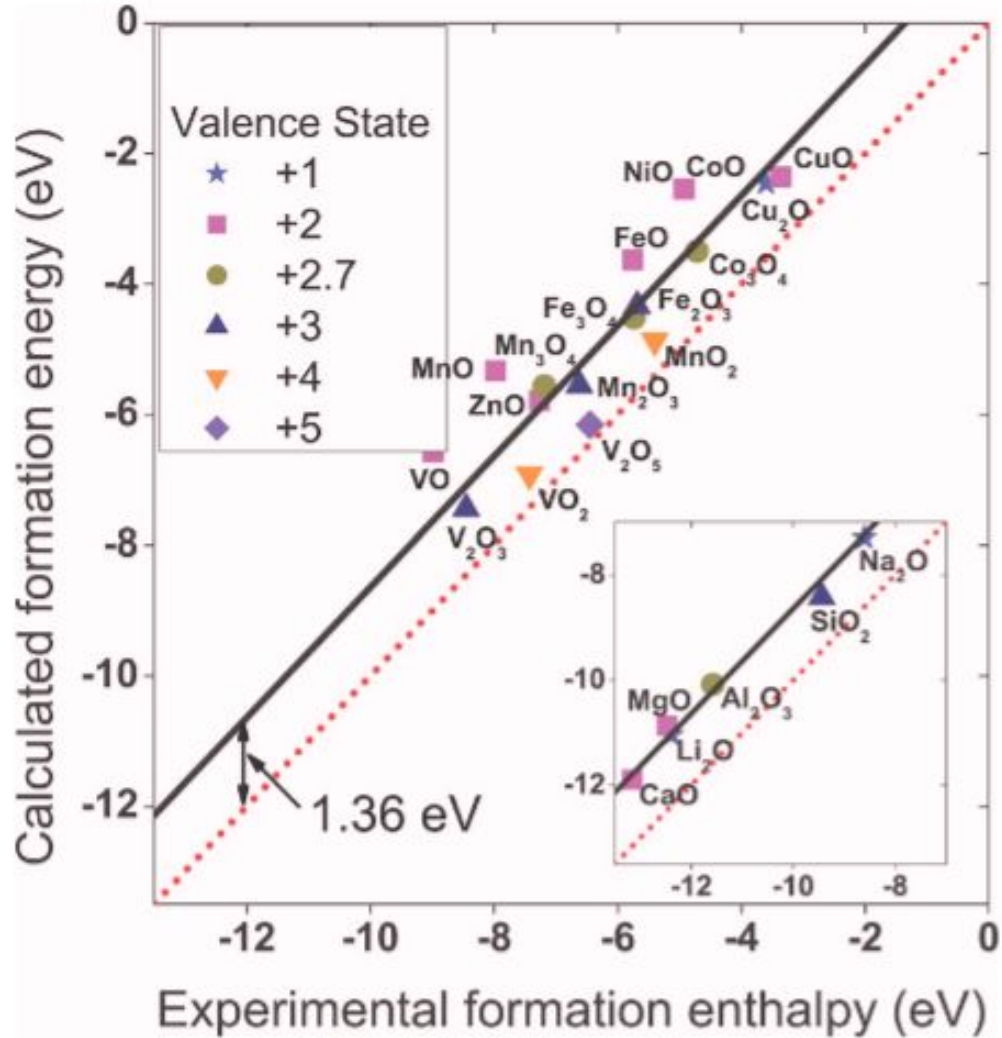
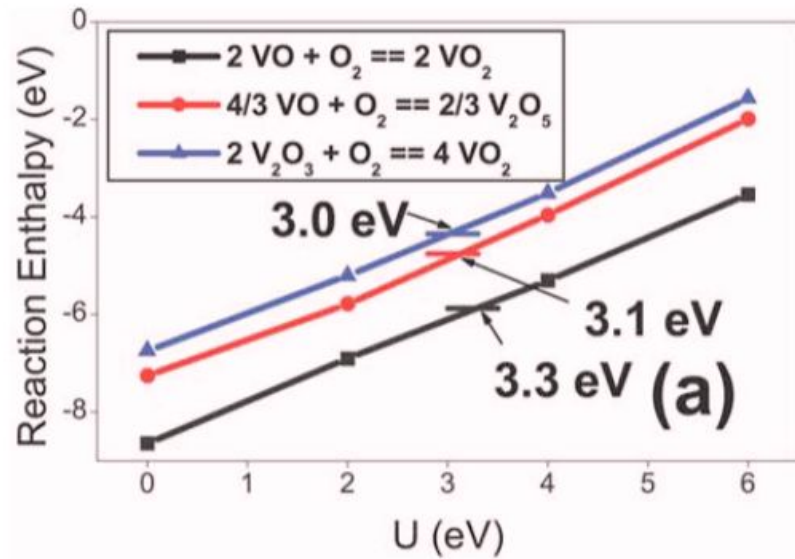
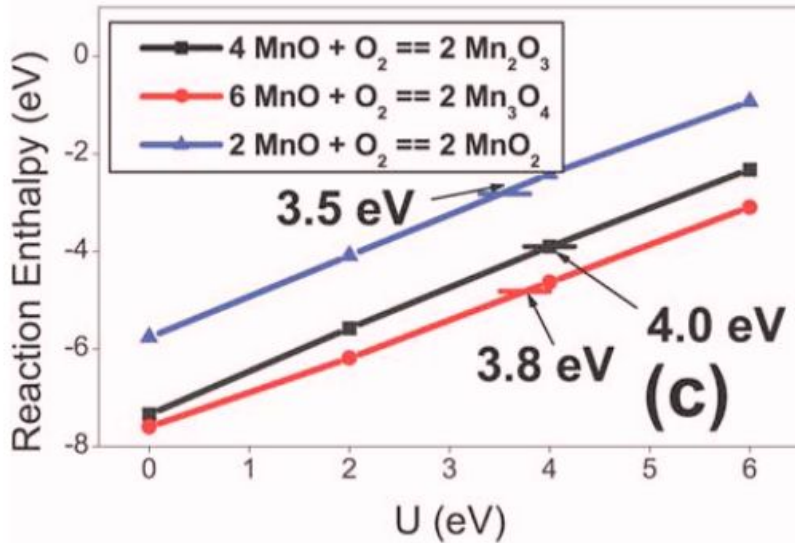


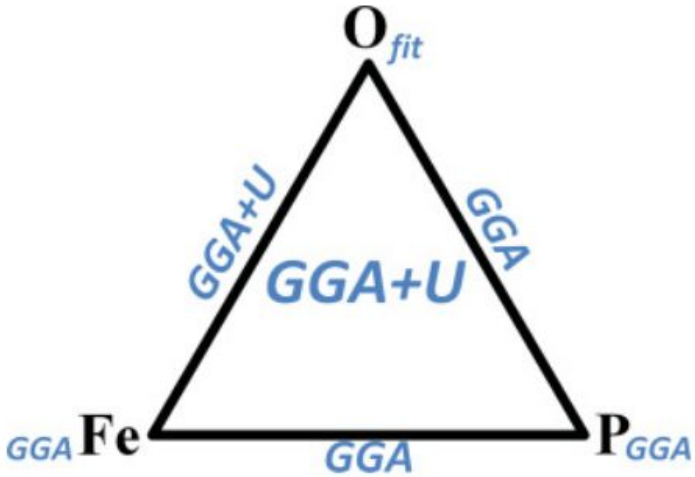
FIG. 1. (Color online) Formation energy of oxides (per O<sub>2</sub> in the reaction) in the GGA approximation as a function of the experimental enthalpy (Refs. 12 and 13). The data symbol indicates the valence of the metal ion. The inset shows nontransition metal oxides. The solid line is the best fit for the nontransition metal data, and a  $-1.36$  eV energy correction for O<sub>2</sub> molecule is obtained from this fit.



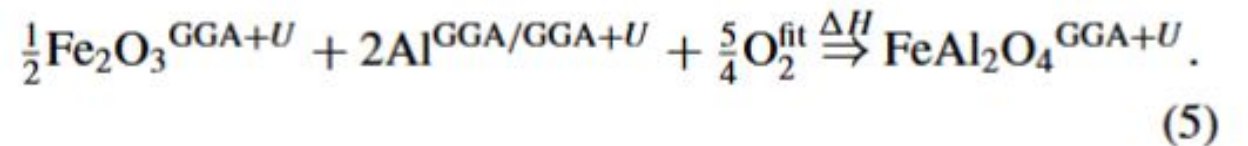
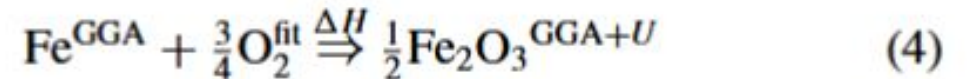
- The U values for different oxidation states are matched  
→ one value can be used

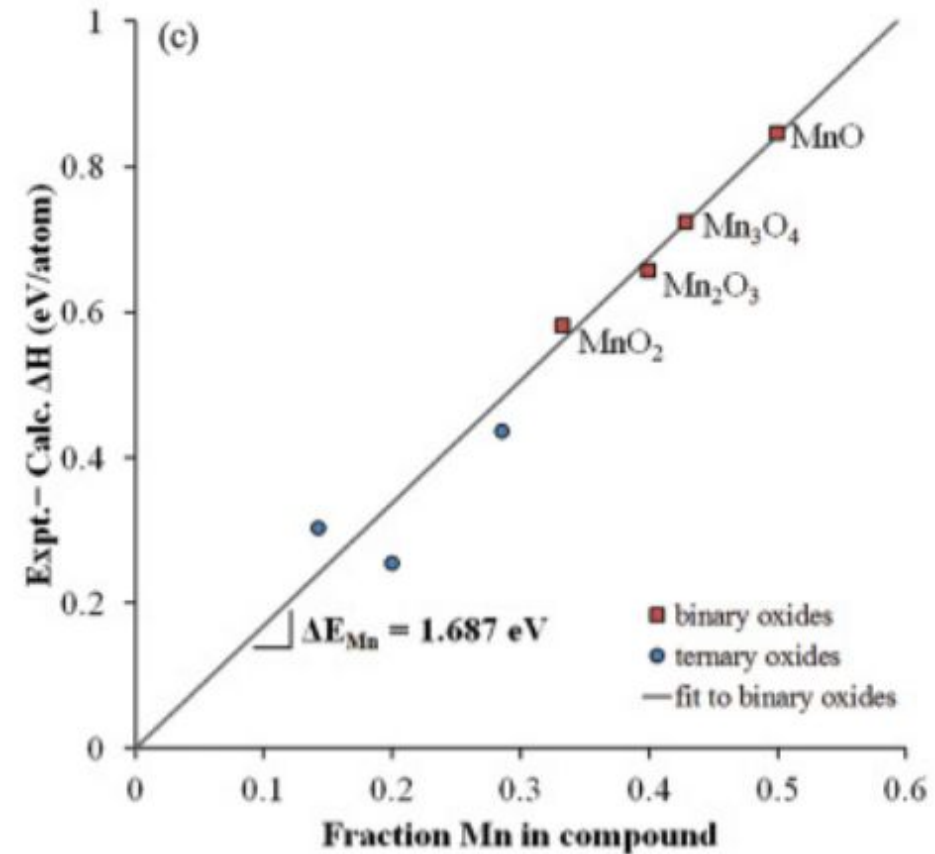
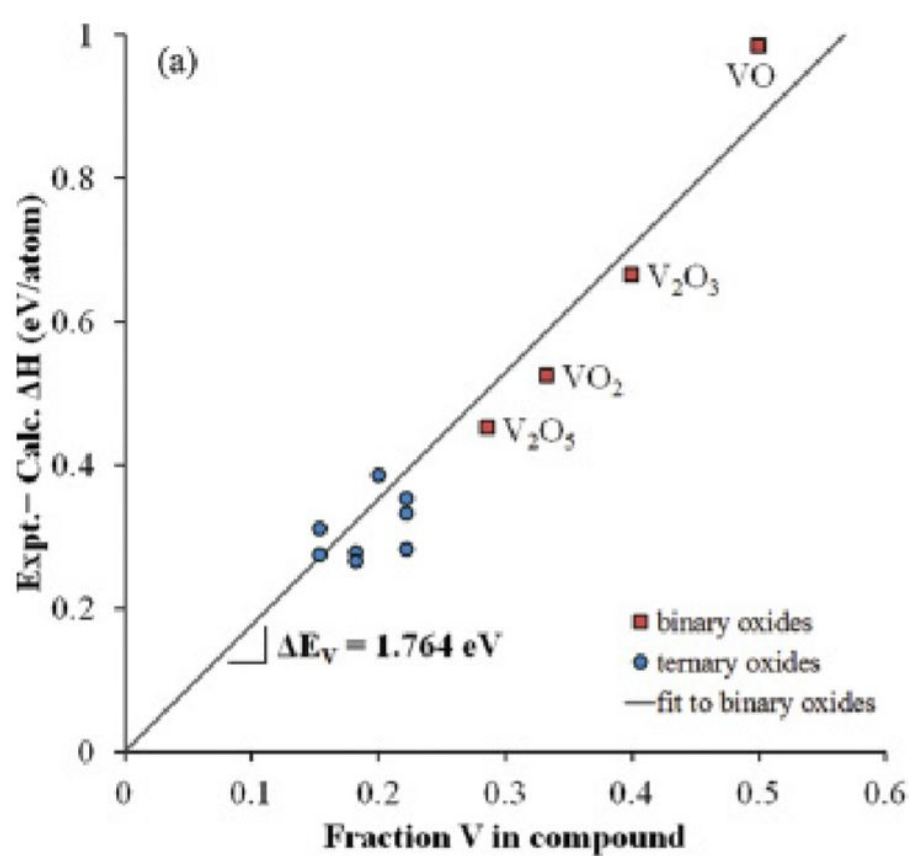


Idea: To decompose general formation reactions as a set of subreactions:

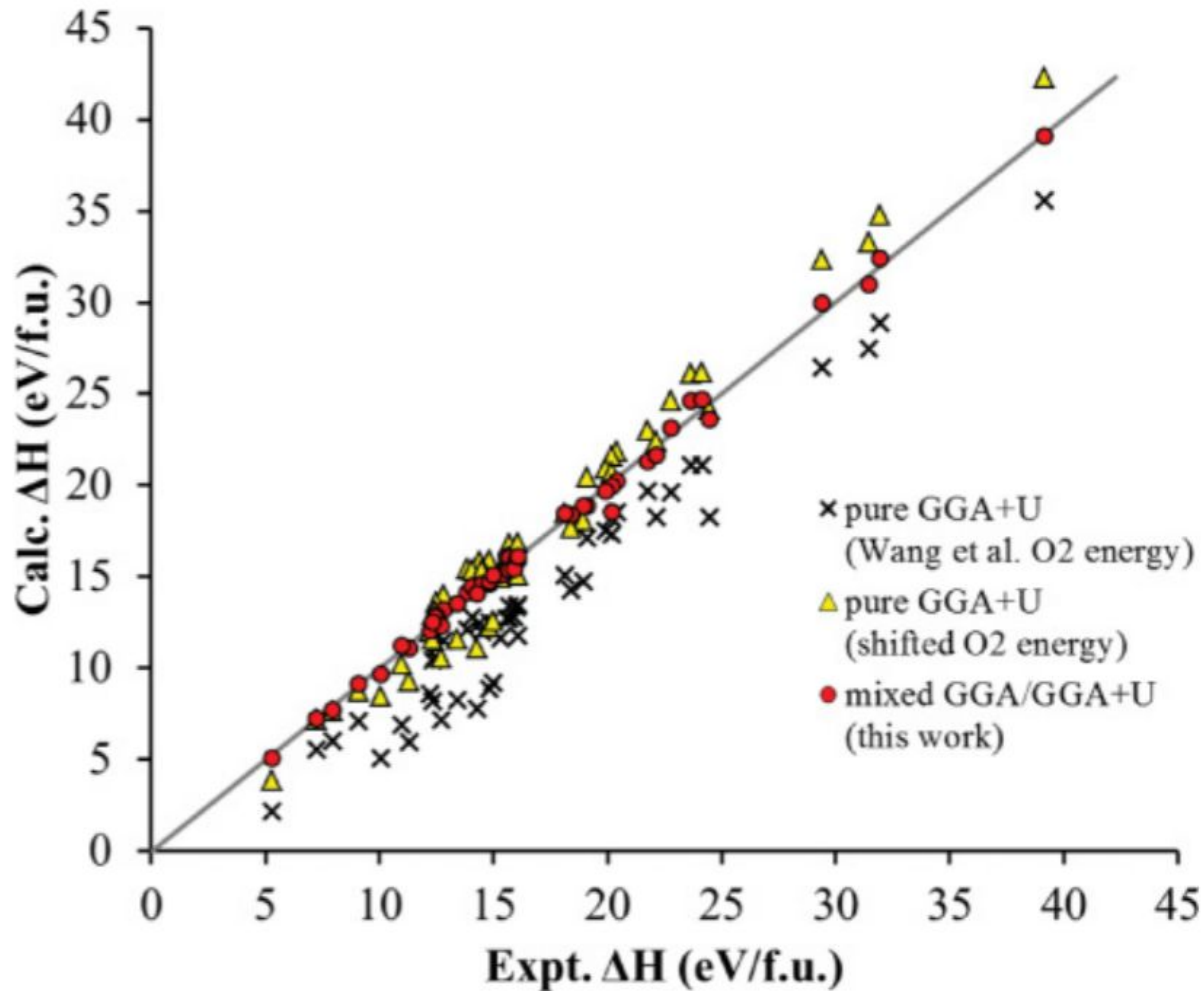


- (a) well represented by GGA alone,
- (b) well represented by GGA + U alone, or
- (c) a formation reaction of a binary compound with localized states with known (e.g., experimentally tabulated) reaction energy





$$E_{\text{compound}}^{\text{GGA+U renorm.}} = E_{\text{compound}}^{\text{GGA+U}} - \sum_M n_M \Delta E_M.$$



MAE(GGA+U) = 464 meV/atom

MAE(GGA\GGA+U)) = 45 meV/atom

Under the carpet: particular fit for GGA bin. oxides (O<sub>2</sub> correction) and U

Many different methods appears later

Not only O<sub>2</sub> energy is a bad reference → correct other too

Wand et al. 2021: repeated for other anions, took more data for fitting (ternary oxides additionally), fitted together

$$\begin{bmatrix} 1 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 1 & \dots \\ 5 & 0 & 0 & 0 & \dots & 2 & \dots \end{bmatrix} \begin{bmatrix} \epsilon_{oxide} \\ \epsilon_{peroxide} \\ \epsilon_{superoxide} \\ \epsilon_F \\ \vdots \\ \epsilon_V \\ \vdots \end{bmatrix} = \begin{bmatrix} \delta E_{Li_2O} \\ \delta E_{KF} \\ \delta E_{V_2O_5} \end{bmatrix}$$

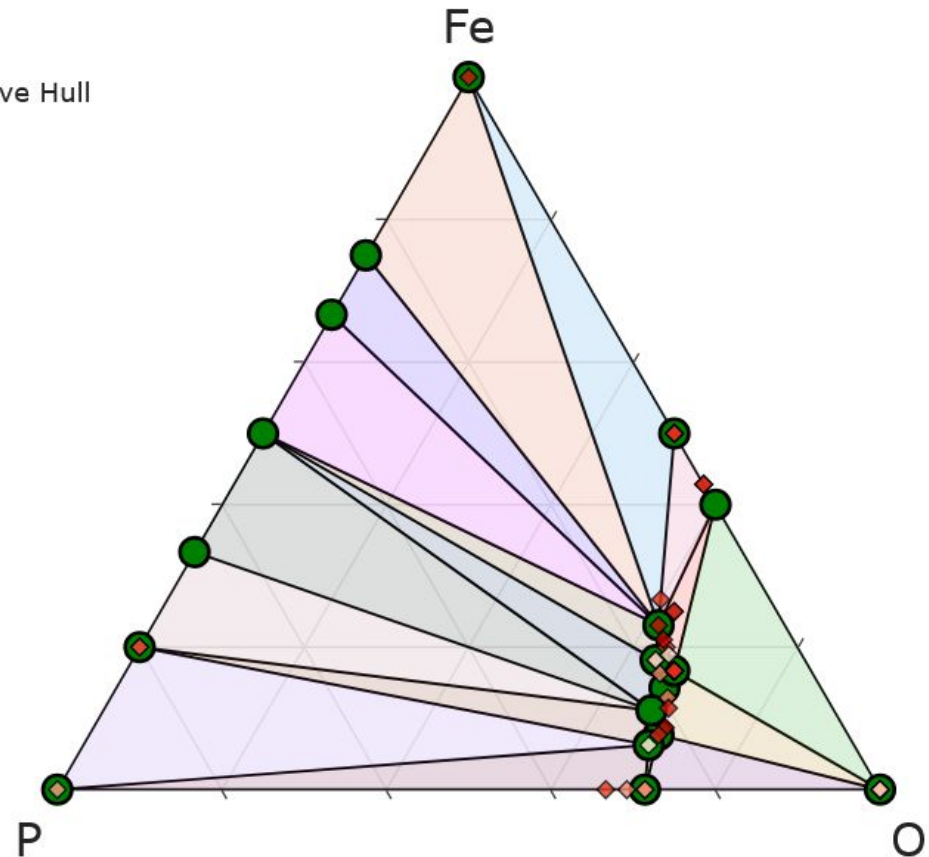
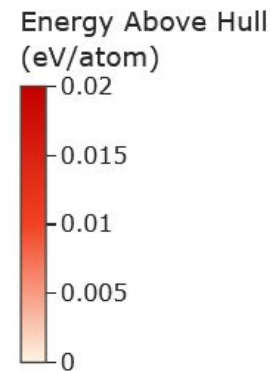
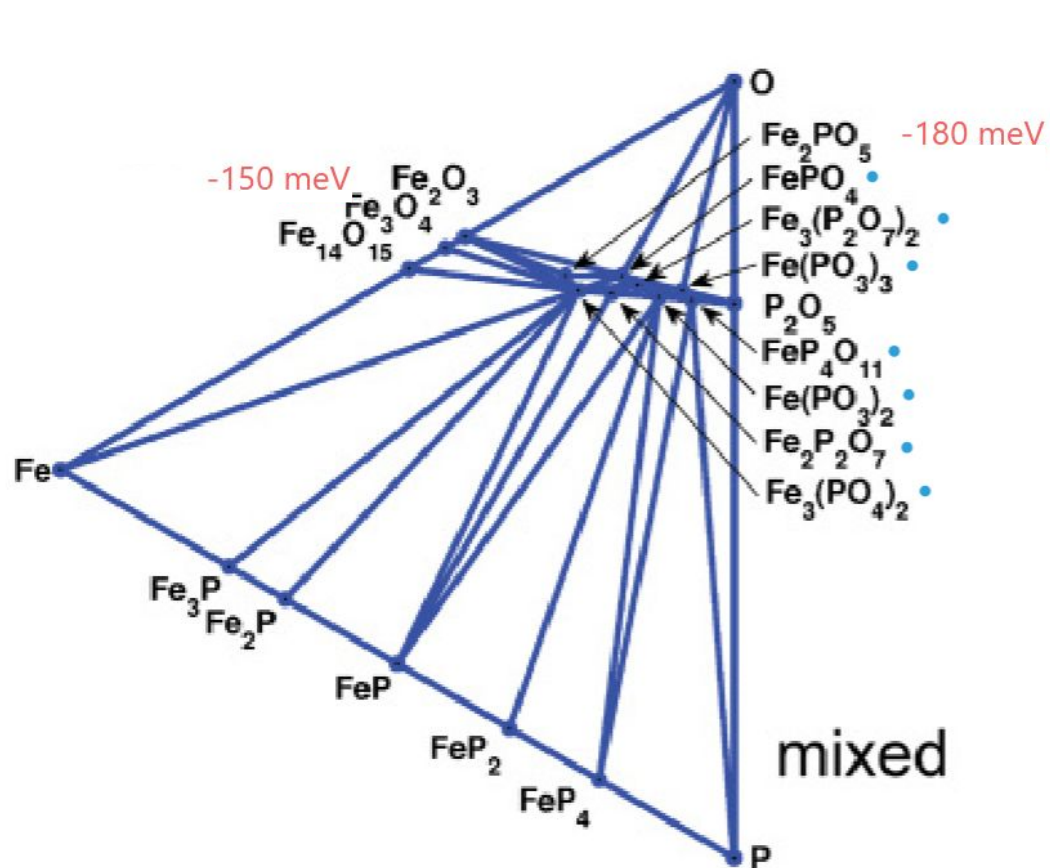
Species	Applies to
Oxide	oxides
Peroxide	peroxides
Superoxide	superoxides
S	anion cpds.
H	anion cpds.
F	anion cpds.
Cl	anion cpds.
Br	anion cpds.
I	anion cpds.
N	anion cpds.
Se	anion cpds.
Si	anion cpds.
Sb	anion cpds.
Te	anion cpds.
V	TM oxides and fluorides
Cr	TM oxides and fluorides
Mn	TM oxides and fluorides
Fe	TM oxides and fluorides
Co	TM oxides and fluorides
Ni	TM oxides and fluorides
W	TM oxides and fluorides
Mo	TM oxides and fluorides

Not only  $O_2$  energy is a bad reference → correct other too

Wand et al. 2021: repeated for other anions,  
took more data for fitting (part of ternary oxides additionally),  
fitted together

lanthanoid, actinoid, or post-transition metal elements (except for Ga and Al) were excluded, as were compounds containing B and As or any of the polyanions  $-SO_3$ ,  $-SO_4$ ,  $-CO_3$ ,  $-OCl_3$ ,  $-ClO_3$ ,  $-ClO_4$ ,  $-NO_2$ ,  $-NO_3$ ,  $-PO_3$ ,  $-PO_4$ ,  $-OH$ ,  $-P_2O_7$ ,  $-SiO_3$ ,  $-SiO_4$ ,  $-Si_2O_5$ ,  $-SeO_3$ ,  $-TiO_3$ ,  $-TiO_4$ , or  $WO_4$ . All these compounds were excluded because they consistently appeared as severe outliers when fitting corrections, indicating that they do not conform well to the model of independent, linear corrections that our scheme assumes.

$MAE_{Wang\_15} = 51 \text{ meV/atom}$ ,  $MAE(TM \text{ oxides})_{Jain\_11} = 45 \text{ meV/atom}$



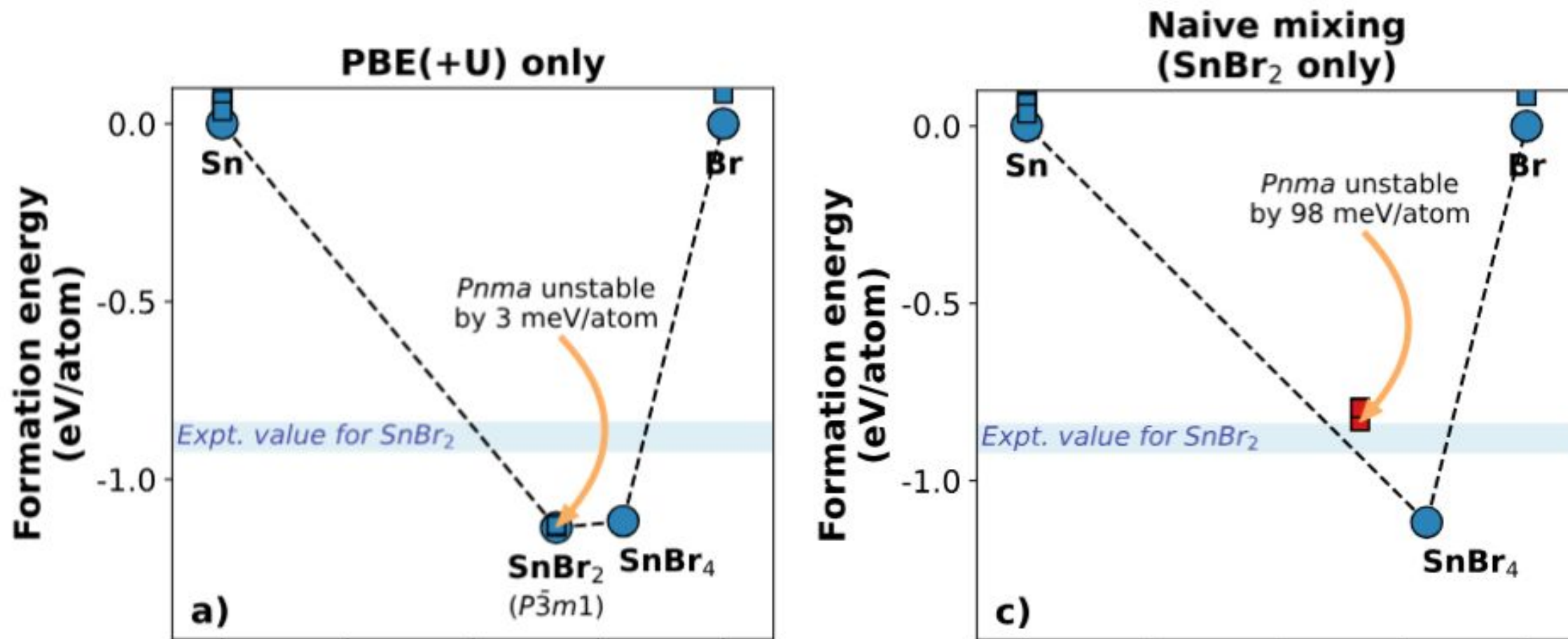
- Corrections were applied within assumption of independence (just summation of several corrections)
- 50 meV/atom at GGA level

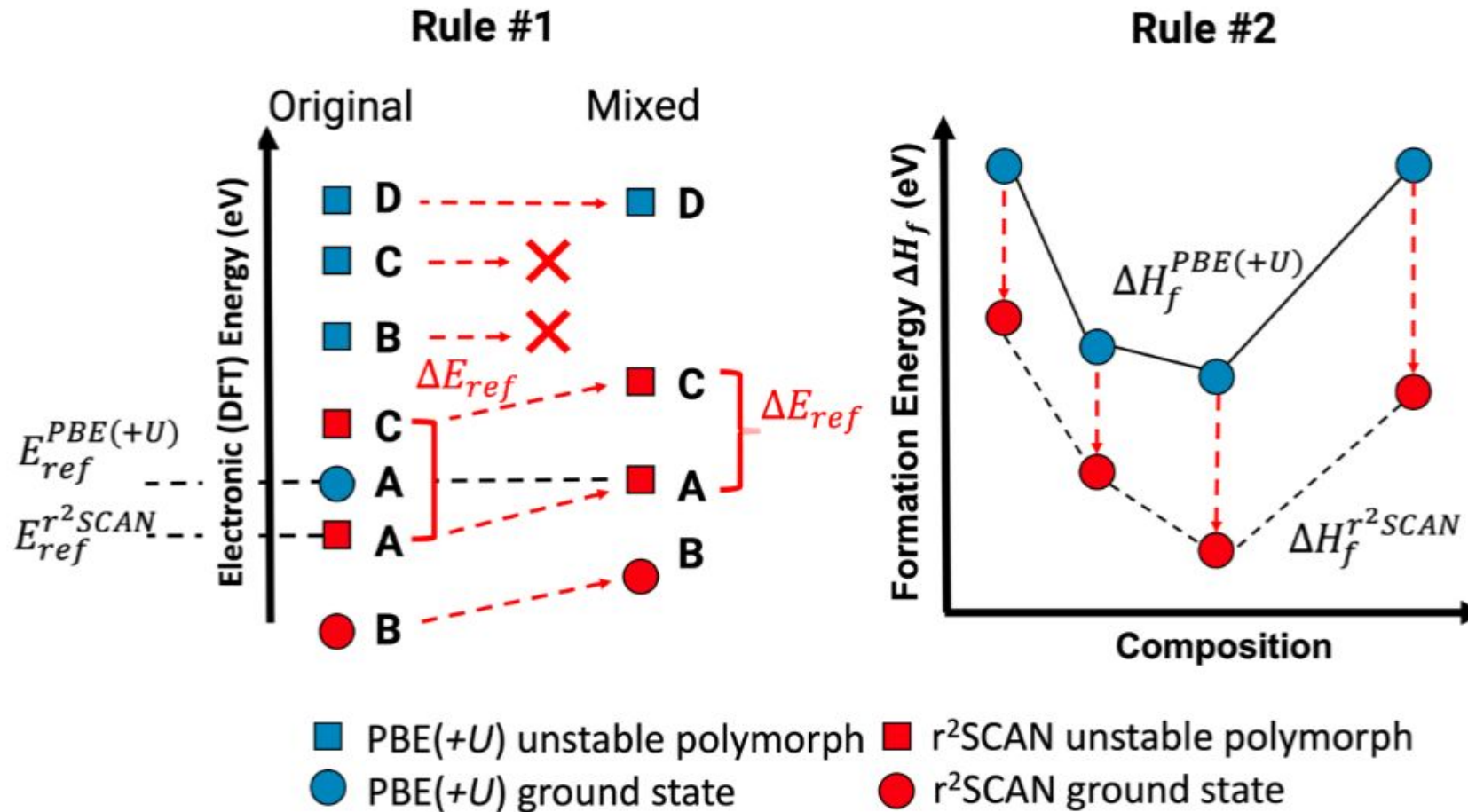
Wang, Amanda, et al. "A framework for quantifying uncertainty in DFT energy corrections." Scientific reports 11.1 (2021): 15496.

- $r^2$ SCAN gives twice more accurate results for  $E_f$  for strongly bonded materials with 4-5x cost

Accuracy: Perdew, John P., et al. "Restoring the density-gradient expansion for exchange in solids and surfaces." Physical review letters 100.13 (2008): 136406.

Comp. cost: Kingsbury, Ryan, et al. "Performance comparison of  $r^2$  SCAN and SCAN metaGGA density functionals for solid materials via an automated, high-throughput computational workflow." Physical Review Materials 6.1 (2022): 013801.



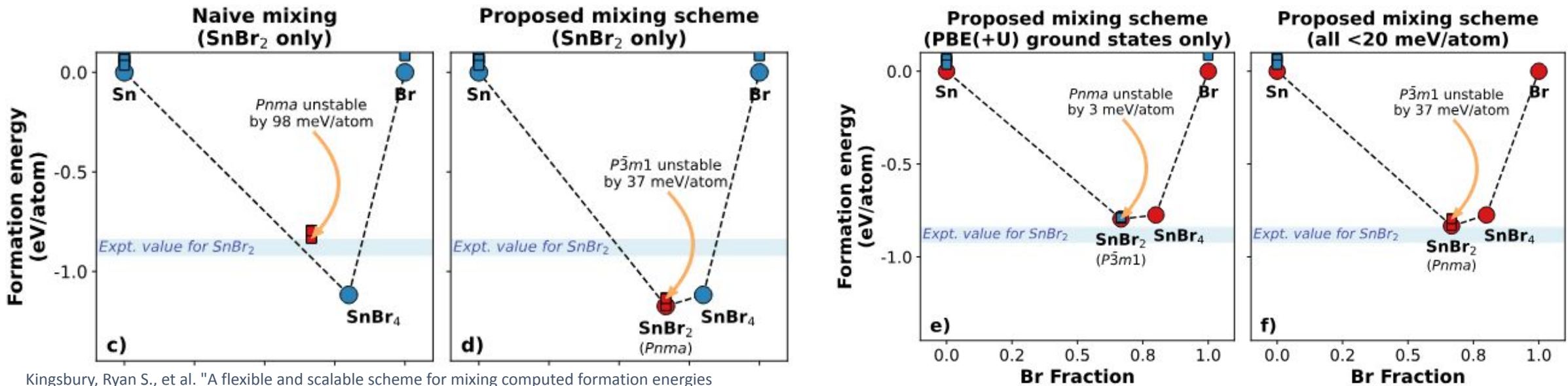
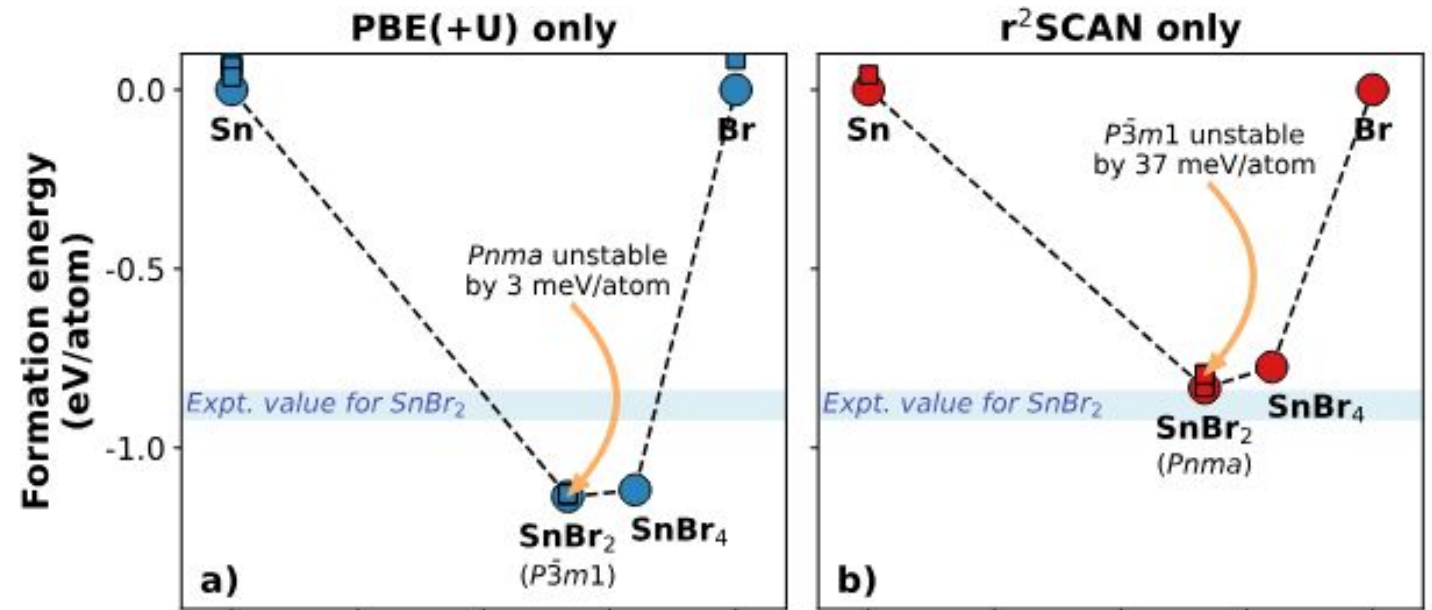


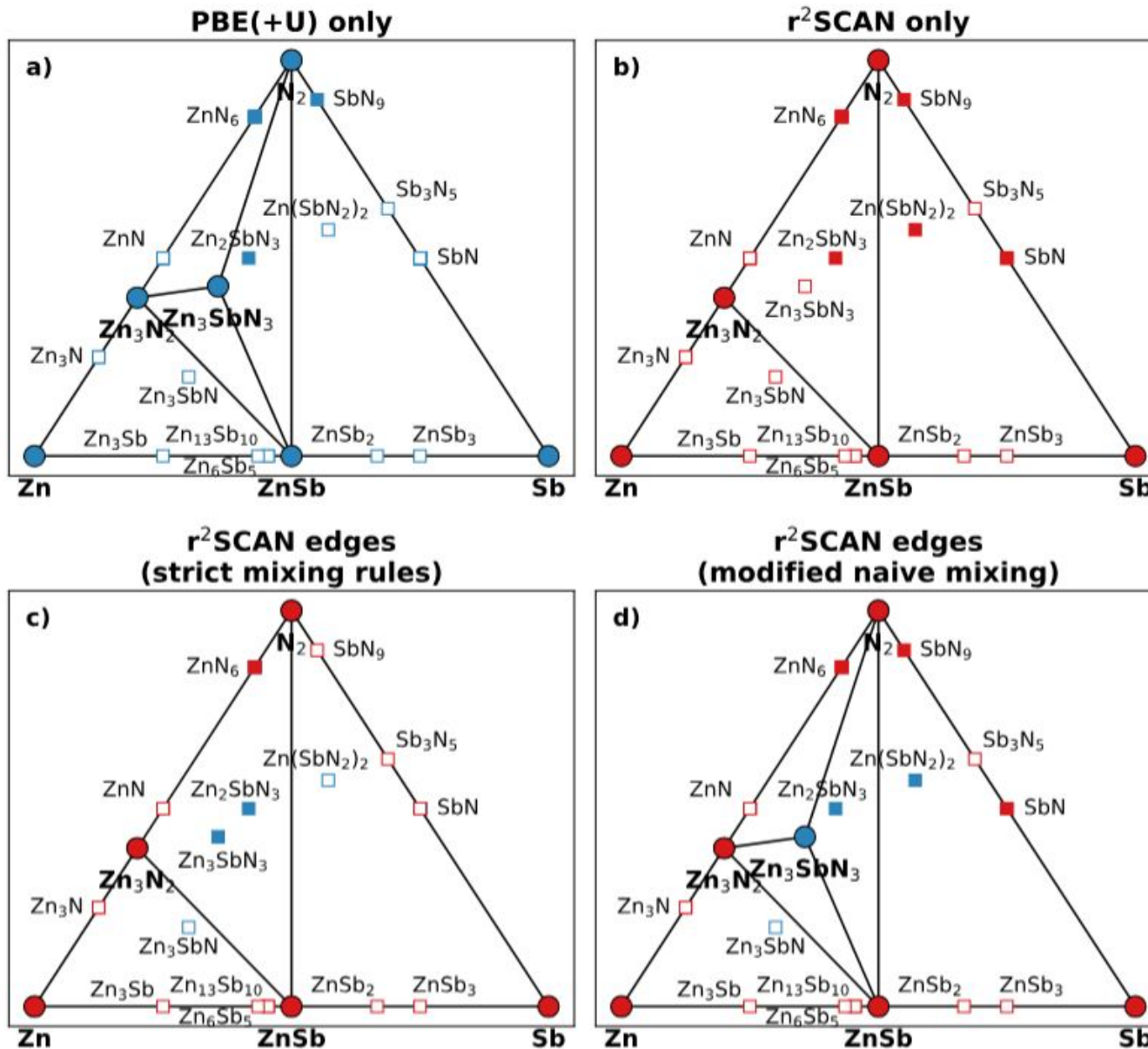


$E_f = -1.136$  eV/atom (PBE(+U))

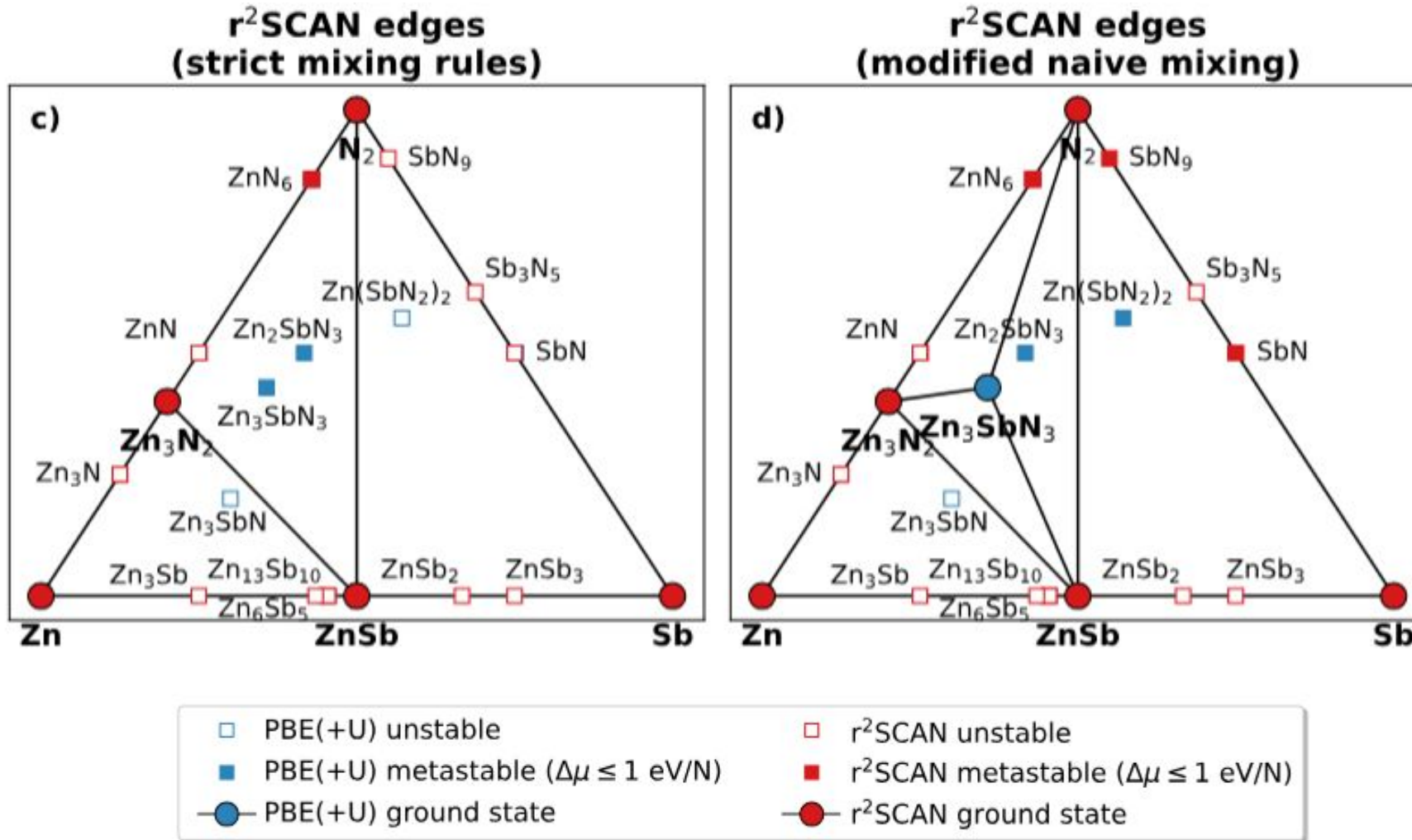
$E_f = -0.833$  eV/atom (R2SCAN)

$E_f = -0.88$  eV/atom (exp. data)





Kingsbury, Ryan S., et al. "A flexible and scalable scheme for mixing computed formation energies from different levels of theory." *npj Computational Materials* 8.1 (2022): 195.



GGA(+U):

elements → bin. oxide      MAE ~200 meV/atom

elements → ternary oxide      MAE ~100 meV/atom

bin. oxide → ternary oxide      MAE ~20 meV/atom

Jain, Anubhav, et al. "Ab initio screening of metal sorbents for elemental mercury capture in syngas streams." *Chemical Engineering Science* 65.10 (2010): 3025-3033.

Hautier, Geoffroy, et al. "Accuracy of density functional theory in predicting formation energies of ternary oxides from binary oxides and its implication on phase stability." *Physical Review B—Condensed Matter and Materials Physics* 85.15 (2012): 155208.

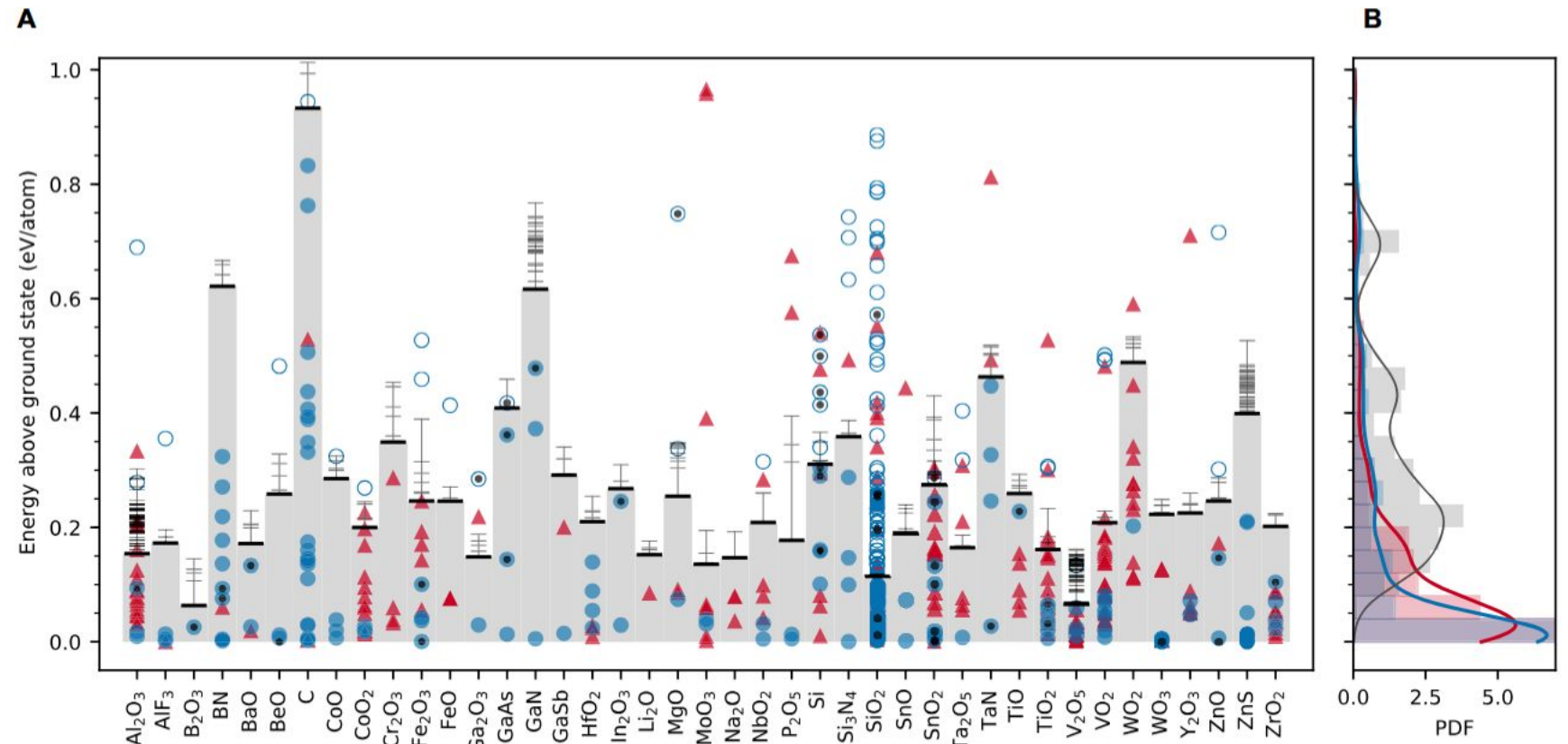
GGA(+U)/r<sup>2</sup>SCAN:

E above hull: similar to GGA(+U)

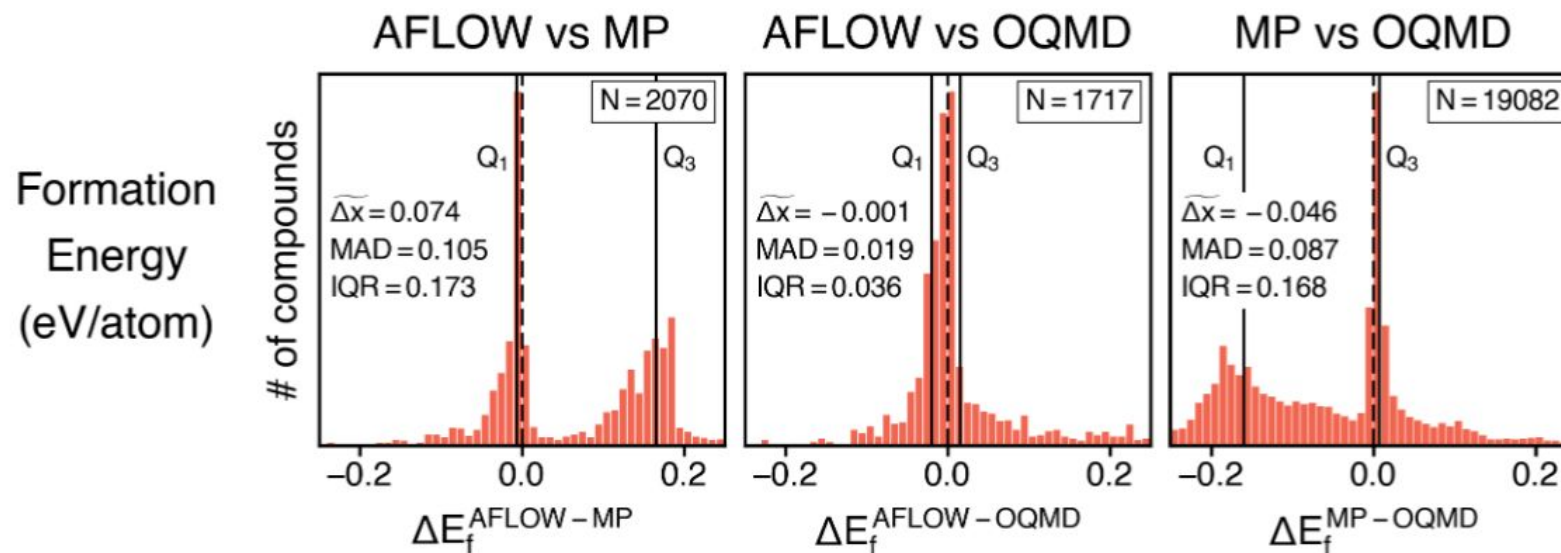
formation energy: roughly averaging, we can expect 30%

accuracy improvement

## Which accuracy do need to correctly predict synthesizability?



**Fig. 2. Assessing the crystalline synthesizability in 41 material systems in the “stability skyline” defined by the amorphous limits. (A)** Energies of inorganic amorphous materials (horizontal bars, amorphous limits in bold) are compared to the crystalline polymorphs available in the Materials Project. Synthesizability ranges defined by the amorphous limits are shaded in gray. Circles and triangles correspond to polymorphs with and without existing ICSD entries, respectively. A circle is open if the ICSD-acquired polymorph is above the amorphous limit and falls under at least one of the exception categories described in the text. **(B)** Corresponding PDFs for ICSD (in blue) and non-ICSD (in red) crystalline polymorphs, compared to amorphous polymorphs (histogram). ICSD structures that have been associated with “high-pressure” synthesis are further tagged with a solid black circle. Units of PDFs are atom per electron volt.



	AFLOW-MP				AFLOW-OQMD				MP-OQMD			
	MAD	IQR	$r$	$\rho$	MAD	IQR	$r$	$\rho$	MAD	IQR	$r$	$\rho$
Formation Energy (eV/atom)	0.105	0.173	0.99	0.99	0.019	0.036	0.99	0.99	0.087	0.168	0.99	0.99

Median absolute difference (MAD), interquartile range (IQR), Pearson’s linear correlation coefficient ( $r$ ), and Spearman’s rank correlation coefficient ( $\rho$ )

MP PDs are accurate enough when approach match the system

Necessary condition: GGA and GGA+U or  $r^2$ SCAN describe the materials in the system well, corresponding calculations are presented in the data for PD  
Sufficient condition: there was analysis\* of the system in the literature (\*for systematic errors)

Cautions:

vdW, antiferromagnetism, incorrect reference states (e.g. elements that are gases or that have a solid-solid phase transition below room temperature)

Further room for improvement: accounting for T and p

e.g. Bartel, Christopher J., et al. "Physical descriptor for the Gibbs energy of inorganic crystalline solids and temperature-dependent materials chemistry." *Nature communications* 9.1 (2018): 4168.