

# Accuracy of meta-generalized gradient approximation functionals in describing correlated transition metal-based systems

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Group picture in June 2023



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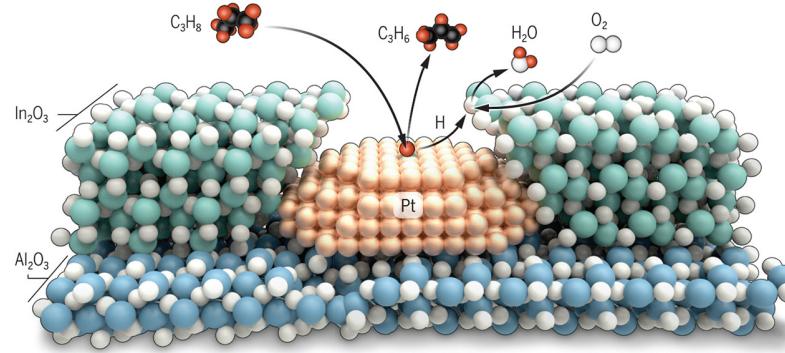
Swathilakshmi



Reshma



# Describing correlated electrons: important for several applications



Energy storage (batteries), energy harvesting (catalysis), safety (gas sensors), memory/compute devices (magnetic): utilize transition metal (TM) oxides (TMOs) or TM fluorides (TMFs)

- Electrons are highly correlated in TMOs and TMFs
- Often require redox-behavior (i.e., exchange of  $d$  electrons to  $s/p$  and vice-versa)

To understand or identify new materials theoretically/computationally: need to describe electronic structure of TMOs and TMFs accurately

- Key properties: redox/formation enthalpies (thermodynamic), lattice parameters (structural), band gaps (electronic), on-site magnetic moments (magnetic)

# Jacob's ladder and metaGGA



SCAN and r<sup>2</sup>SCAN represent the state-of-the-art in XC functionals

**Do these functionals also suffer from SIEs in correlated systems?**

**If so, can we use a Hubbard  $U$  correction effectively to mitigate SIEs?**

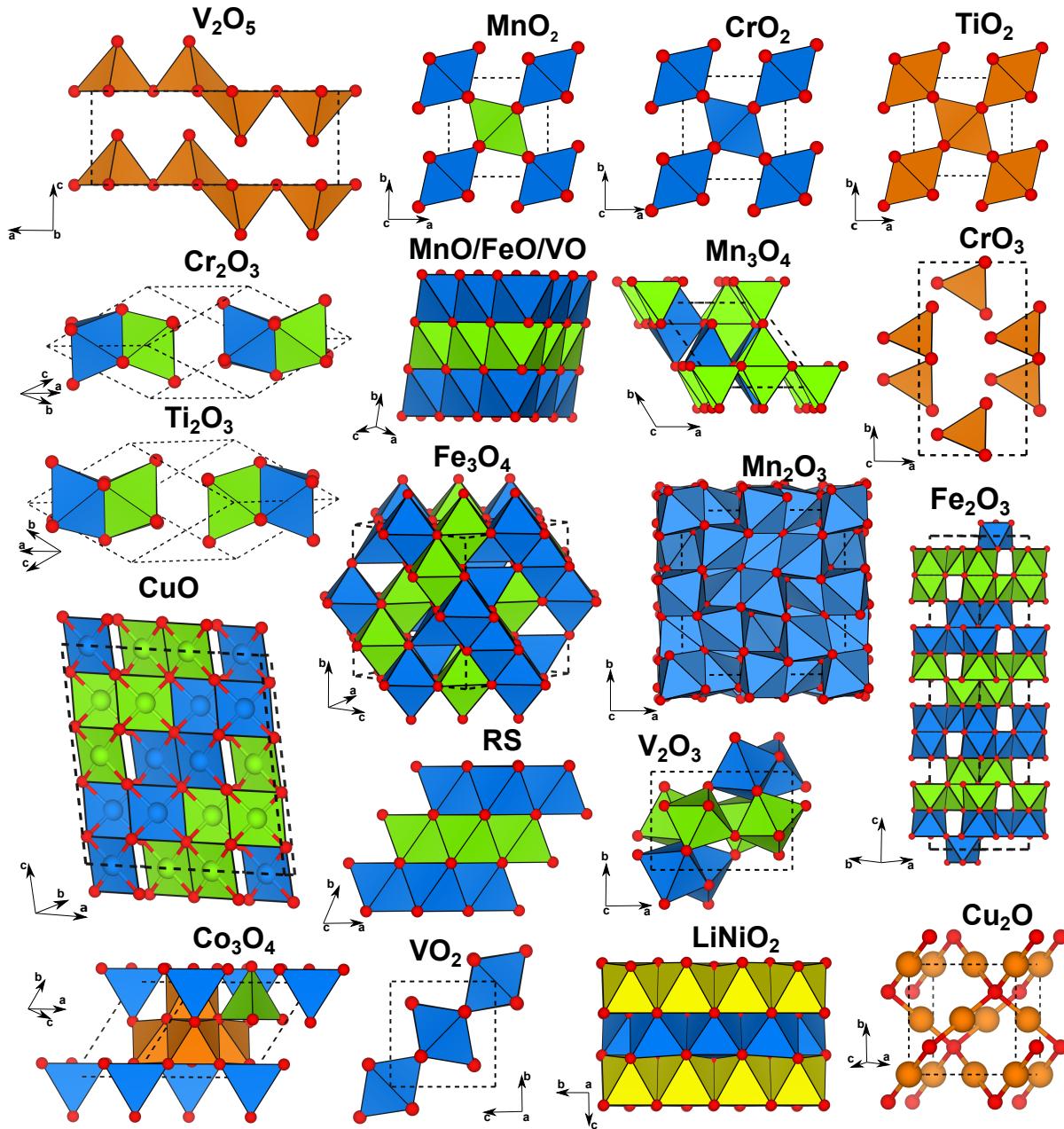
Generalized gradient approximation (GGA): well-established

- Suffers from self-interaction errors (SIEs) in correlated systems
- Mitigated by Hubbard  $U$  correction (*unknown a priori*)

MetaGGA: higher on Jacob's ladder

- Strongly constrained and appropriately normed (SCAN): satisfies all 17 known XC constraints
  - More accurate than GGA, convergence difficulties
- Restored regularized SCAN (r<sup>2</sup>SCAN): satisfies 16 constraints
  - More accurate than GGA, lower convergence difficulties

# Systems considered: TMOs



3d binary metal oxides known experimentally

Magnetic configurations: known antiferromagnetic (AFM), else ferromagnetic (FM)

Rocksalt (RS)

- $VO$ ,  $MnO$ ,  $FeO$ ,  $CoO$ ,  $NiO$

Rutile

- $TiO_2$ ,  $VO_2$ ,  $CrO_2$ ,  $MnO_2$

Spinel

- $Mn_3O_4$ ,  $Fe_3O_4$ ,  $Co_3O_4$

Hexagonal

- $Ti_2O_3$ ,  $Cr_2O_3$ ,  $Fe_2O_3$

Cubic

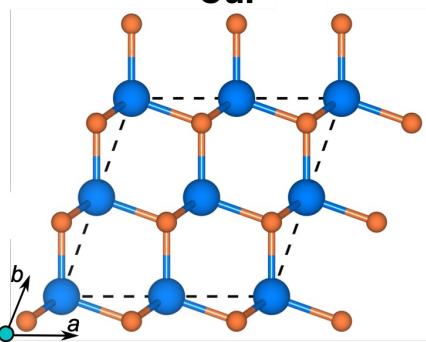
- $Mn_2O_3$

Others:

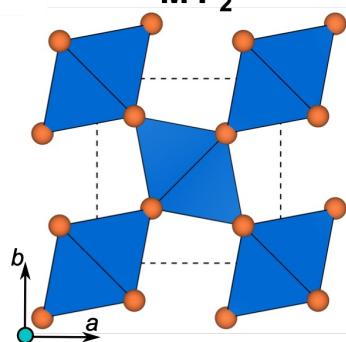
- $V_2O_3$ ,  $V_2O_5$ ,  $CrO_3$ ,  $LiNiO_2$ ,  $Cu_2O$ ,  $CuO$

# Systems considered: TMFs

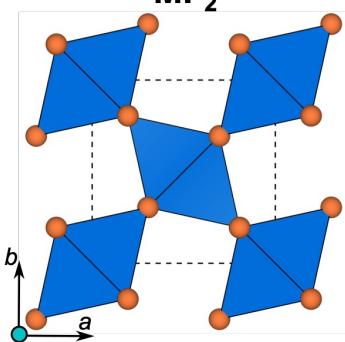
$\text{CuF}$



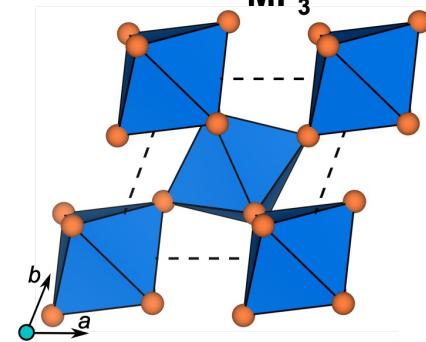
$\text{M}'\text{F}_2$



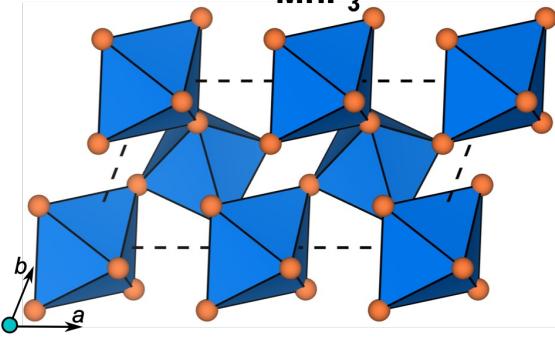
$\text{MF}_2$



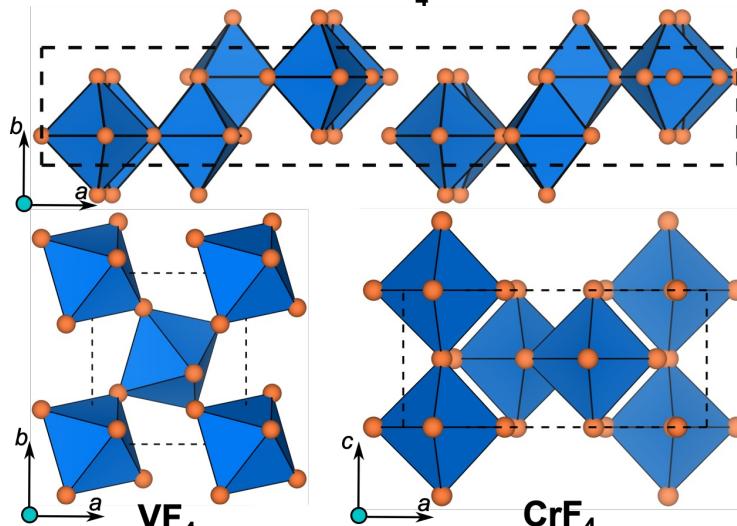
$\text{MF}_3$



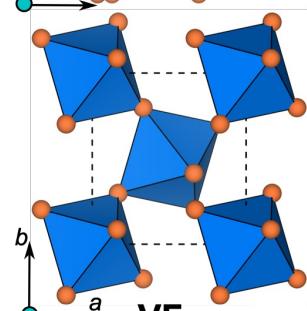
$\text{MnF}_3$



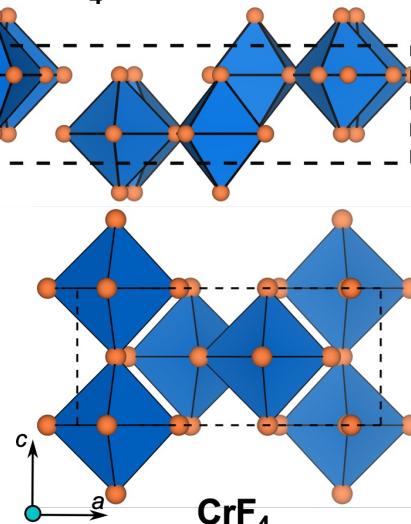
$\text{TiF}_4$



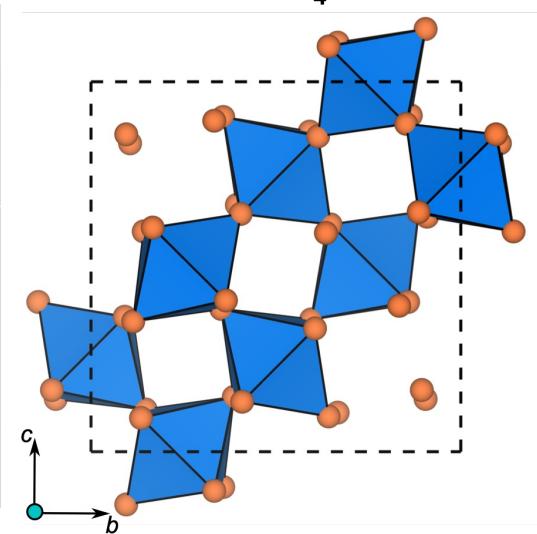
$\text{VF}_4$



$\text{CrF}_4$



$\text{MnF}_4$



3d binary metal fluorides

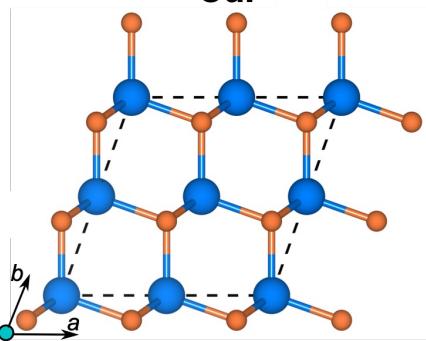
Hexagonal ( $\text{MF}_3$ ):  $\text{TiF}_3$ ,  $\text{VF}_3$ ,  $\text{CrF}_3$ ,  $\text{FeF}_3$ ,  $\text{CoF}_3$ ,  $\text{NiF}_3$

Rutile-like ( $\text{MF}_2/\text{M}'\text{F}_2$ ):  $\text{CrF}_2$ ,  $\text{MnF}_2$ ,  $\text{FeF}_2$ ,  $\text{CoF}_2$ ,  $\text{NiF}_2$ ,  $\text{CuF}_2$

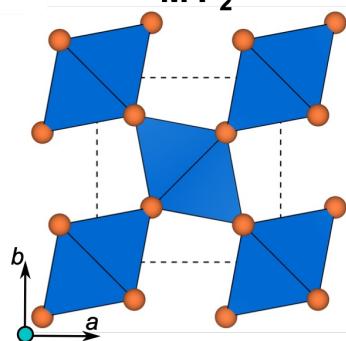
Others:  $\text{MnF}_3$ ,  $\text{TiF}_4$ ,  $\text{VF}_4$ ,  $\text{CrF}_4$ ,  $\text{MnF}_4$ ,  $\text{CuF}$

# Systems considered: TMFs

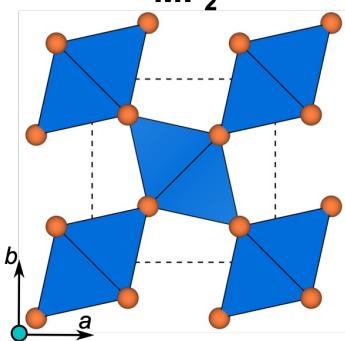
$\text{CuF}$



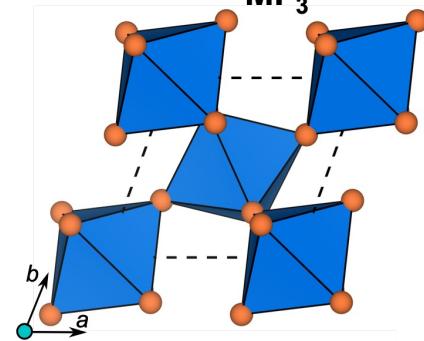
$\text{M}'\text{F}_2$



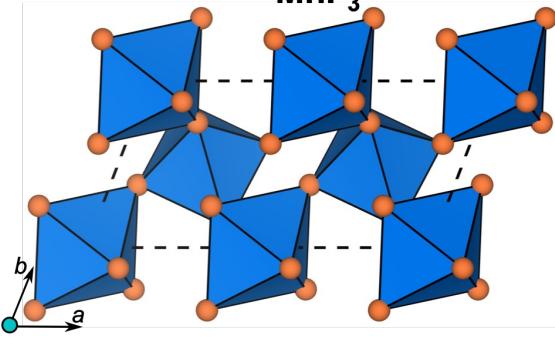
$\text{MF}_2$



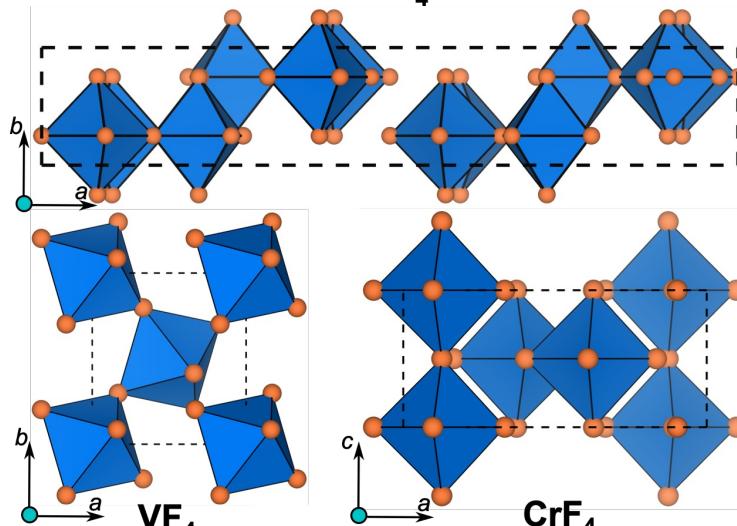
$\text{MF}_3$



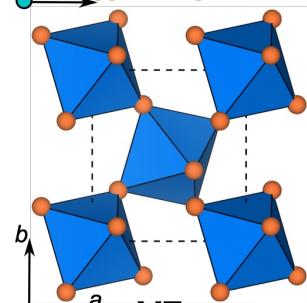
$\text{MnF}_3$



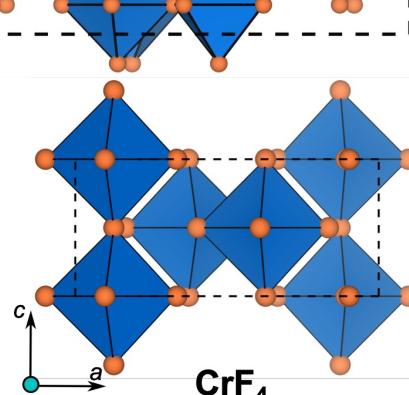
$\text{TiF}_4$



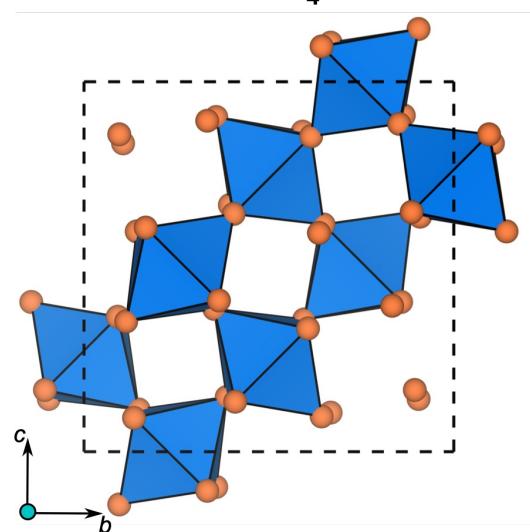
$\text{VF}_4$



$\text{CrF}_4$



$\text{MnF}_4$



3d binary metal fluorides

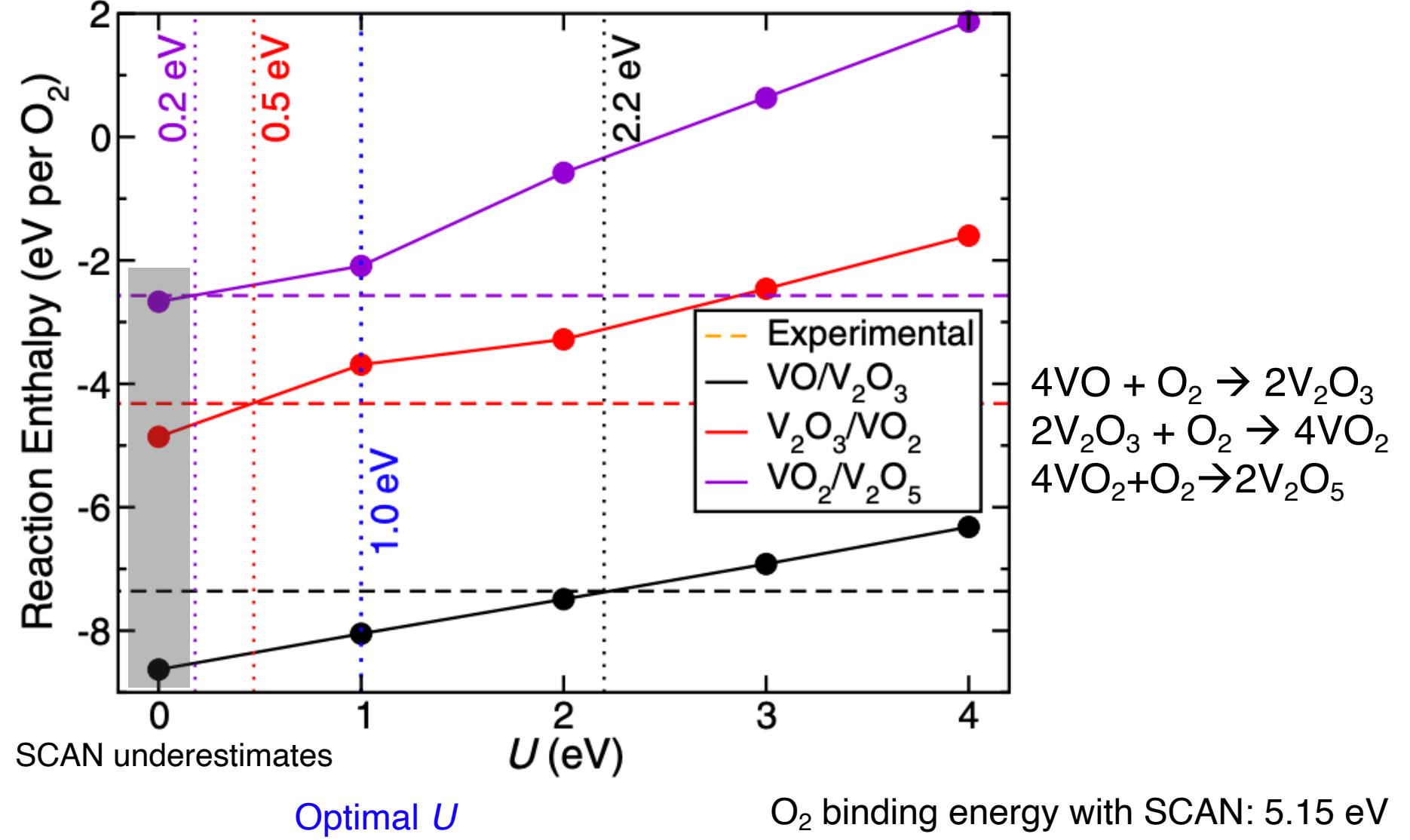
Within the TMOs and TMFs considered, examine whether SIEs are present

- Explore oxidation/fluorination enthalpies
- Followed by structural, electronic, and magnetic properties

# SCAN overestimates oxidation enthalpies

Errors reduced by  $U$  correction

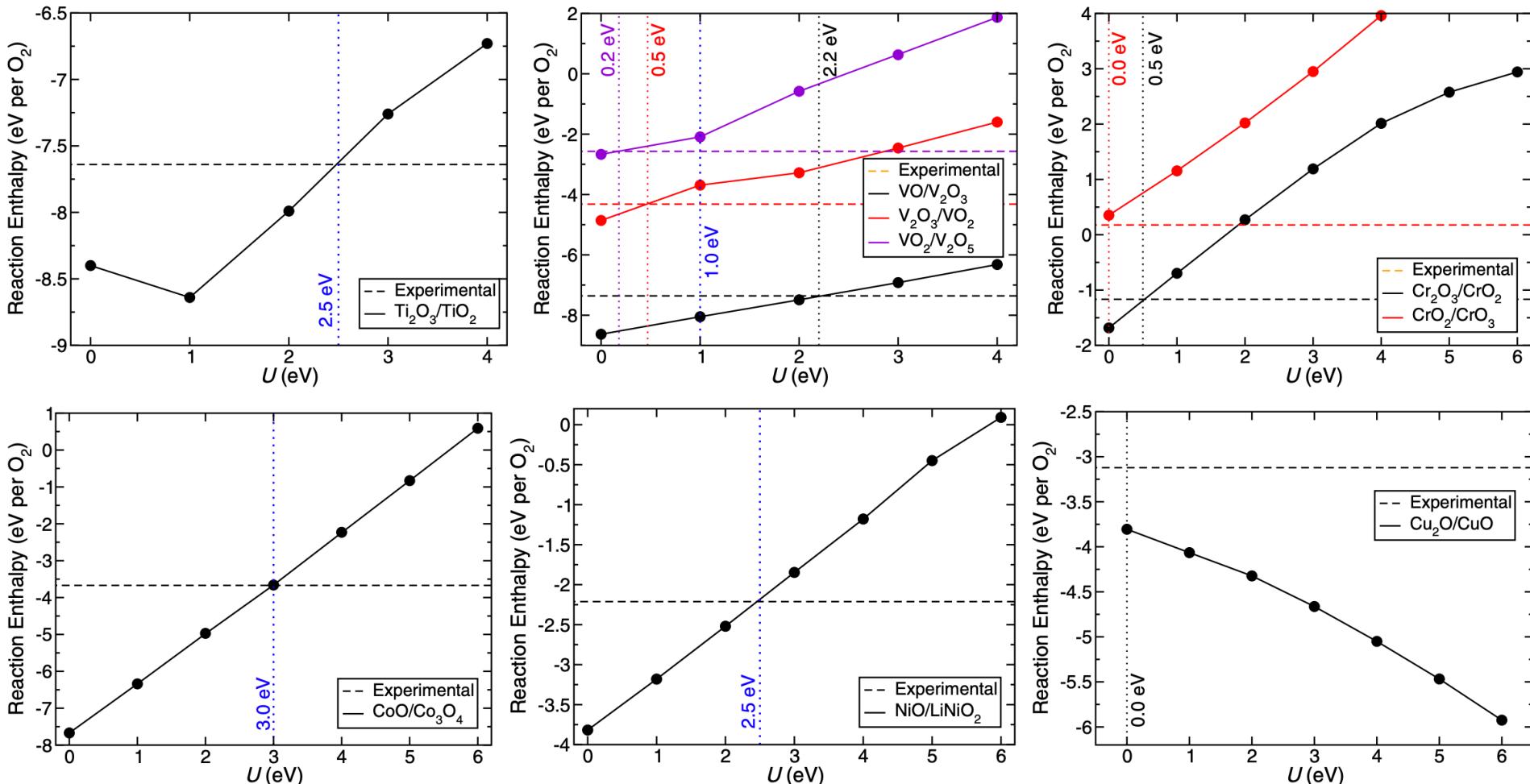
Similar trends on all TMs, except Cr and Cu



# SCAN overestimates oxidation enthalpies

Errors reduced by  $U$  correction

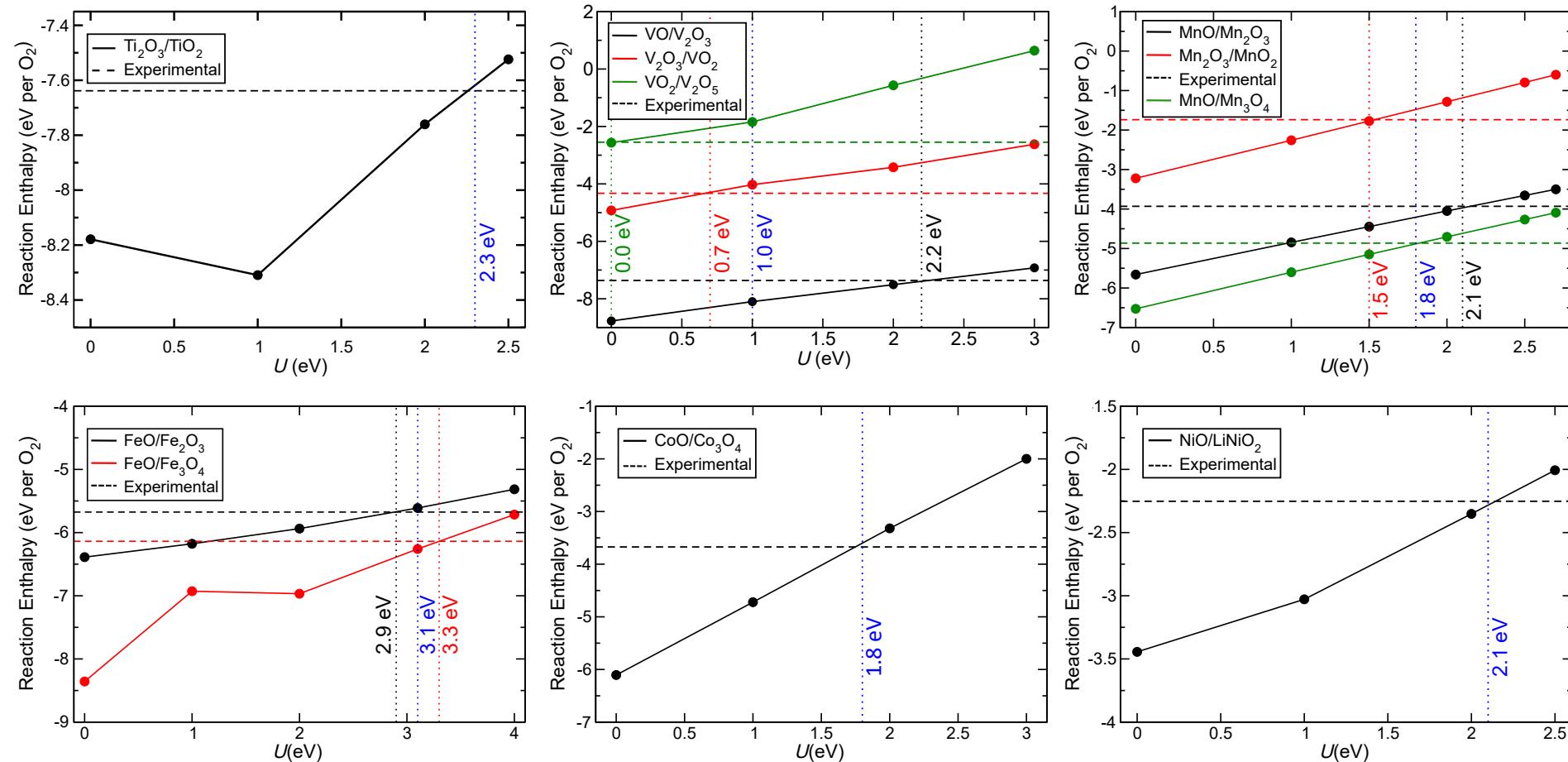
Similar trends on all TMs, except Cr and Cu



$\text{O}_2$  binding energy with SCAN: 5.15 eV

# $r^2$ SCAN: similar trends as SCAN in TMOs

O<sub>2</sub> binding energy with  $r^2$ SCAN: 5.43 eV

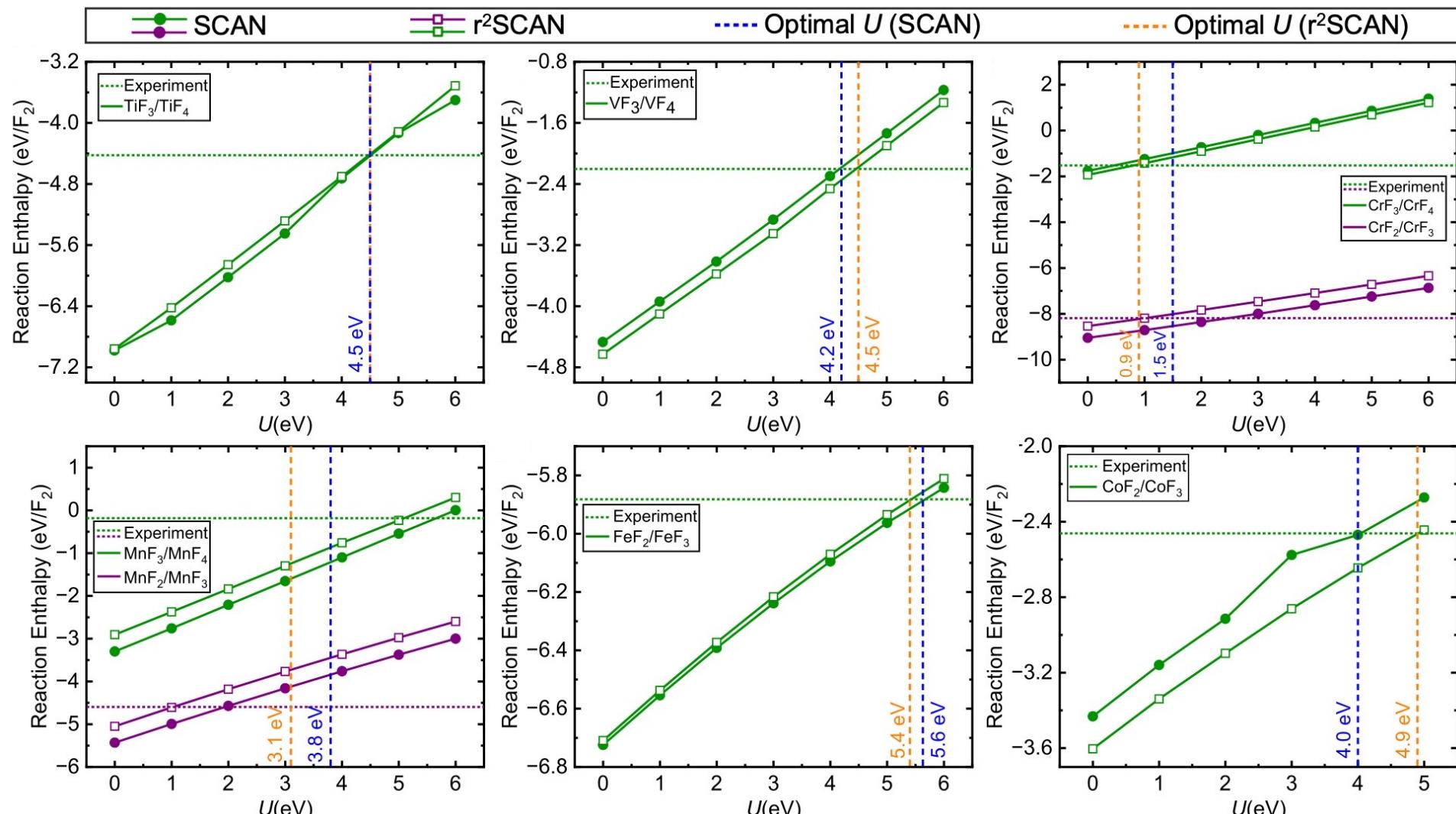


- Underestimation of oxidation enthalpies by  $r^2$ SCAN: similar to SCAN
- Optimal *U* values: similar in Ti, V, Fe, and Ni
- No *U* required in Cr and Cu: identical to SCAN
- Significantly lower *U* with  $r^2$ SCAN in Mn and Co than SCAN

# Both functionals need $U$ in TMFs

Optimal  $U$  values in TMFs different from TMOs

$F_2$  binding: SCAN (1.57 eV),  $r^2$ SCAN (1.63 eV)



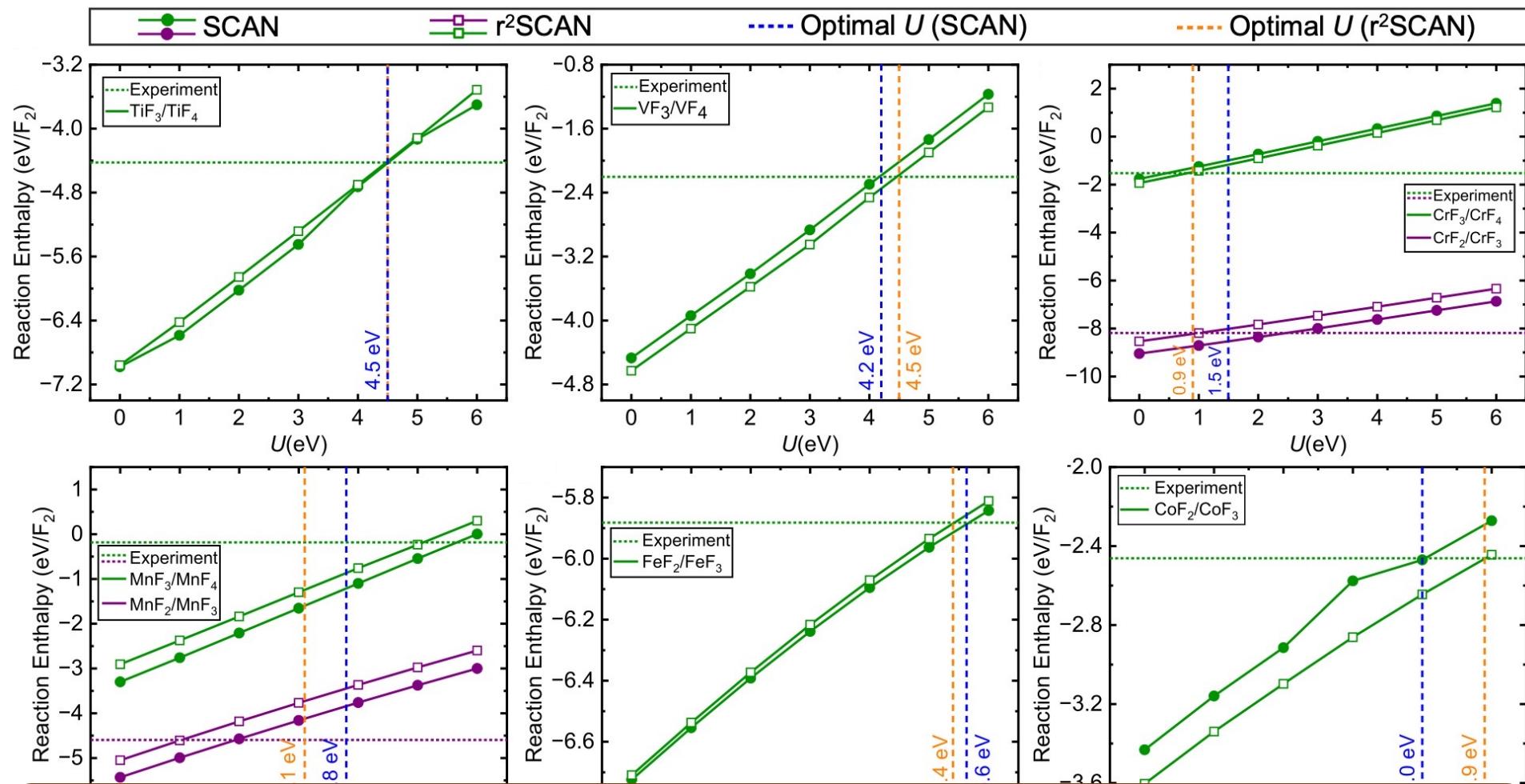
Optimal  $U$  in fluorides > oxides: more ionic bonds, more localization

Surprisingly, no  $U$  needed in Ni (besides Cu)

# Both functionals need $U$ in TMFs

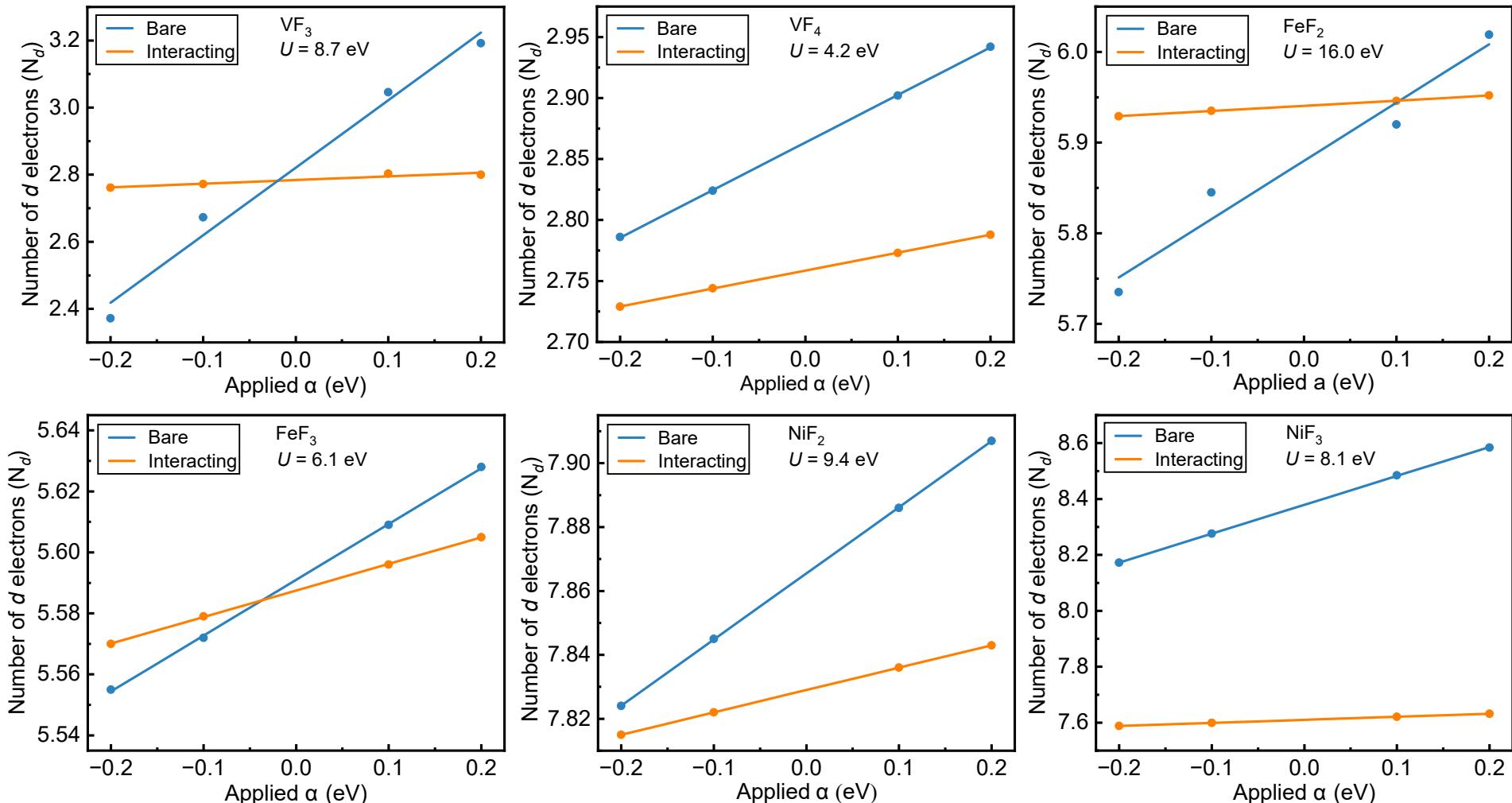
Optimal  $U$  values in TMFs different from TMOs

$F_2$  binding: SCAN (1.57 eV),  $r^2$ SCAN (1.63 eV)



Any other techniques to evaluate optimal  $U$ ?

# Linear response theory yields unphysical $U$ values in TMFs



Using experimental oxidation/fluorination enthalpies yields physical  $U$  corrections

- Can be used across all oxidation states of a TM

# Optimal $U$ values: summary

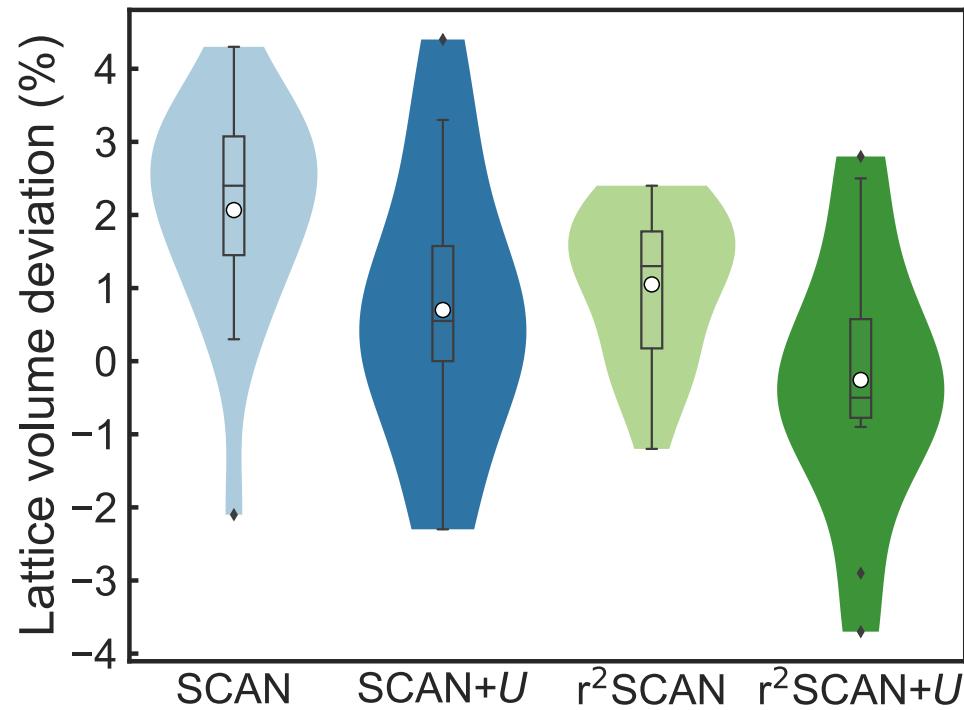
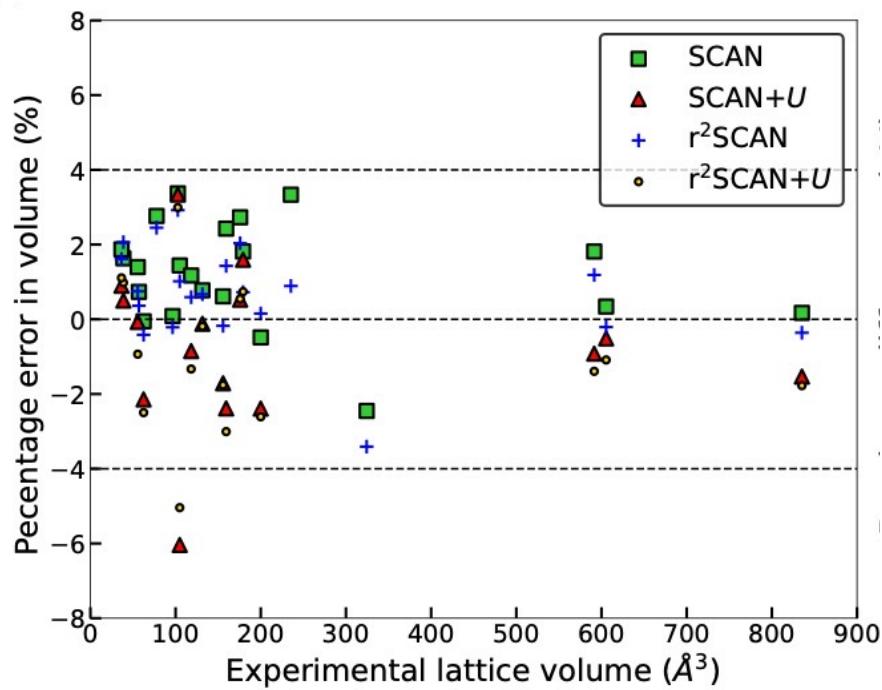
Transition Metal	Oxides		Fluorides	
	SCAN+ $U$	$r^2$ SCAN+ $U$	SCAN+ $U$	$r^2$ SCAN+ $U$
Ti	2.5	2.3	4.5	4.5
V	1.0	1.0	4.2	4.5
Cr	0.0	0.0	1.5	0.9
Mn	2.7	1.8	3.1	3.8
Fe	3.1	3.1	5.4	5.6
Co	3.0	1.8	4.0	4.9
Ni	2.5	2.1	0.0	0.0
Cu	0.0	0.0	0.0	0.0

# Optimal $U$ values: summary

Transition Metal	Oxides		Fluorides	
	SCAN+ $U$	$r^2$ SCAN+ $U$	SCAN+ $U$	$r^2$ SCAN+ $U$
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Co	3.0	1.8	4.0	4.9
Ni	2.5	2.1	0.0	0.0

What about other properties? Are improvements 'significant enough' to warrant  $U$  addition?

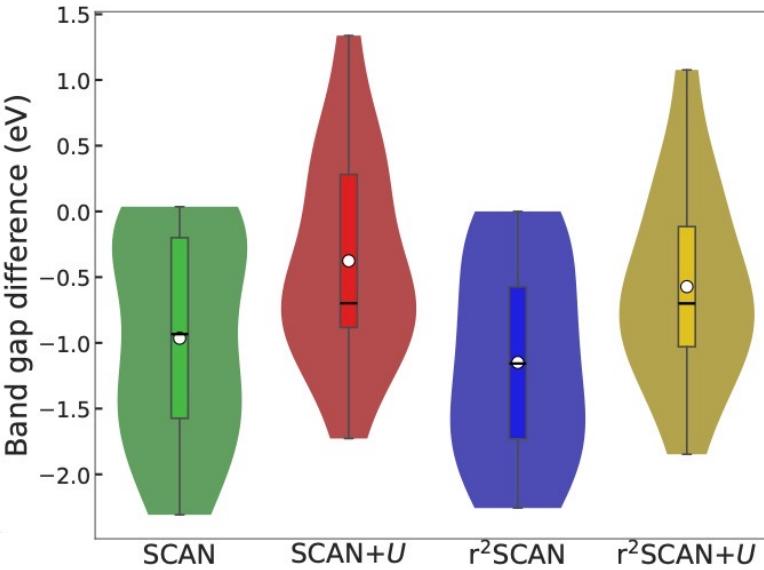
# Lattice parameters: similar with or without $U$



Distribution of errors in lattice parameter predictions: similar with/without  $U$  in TMOs

Average errors in lattice parameter predictions in TMFs: slightly better in  $U$  corrected functionals

# Band gaps: $U$ makes a qualitative difference



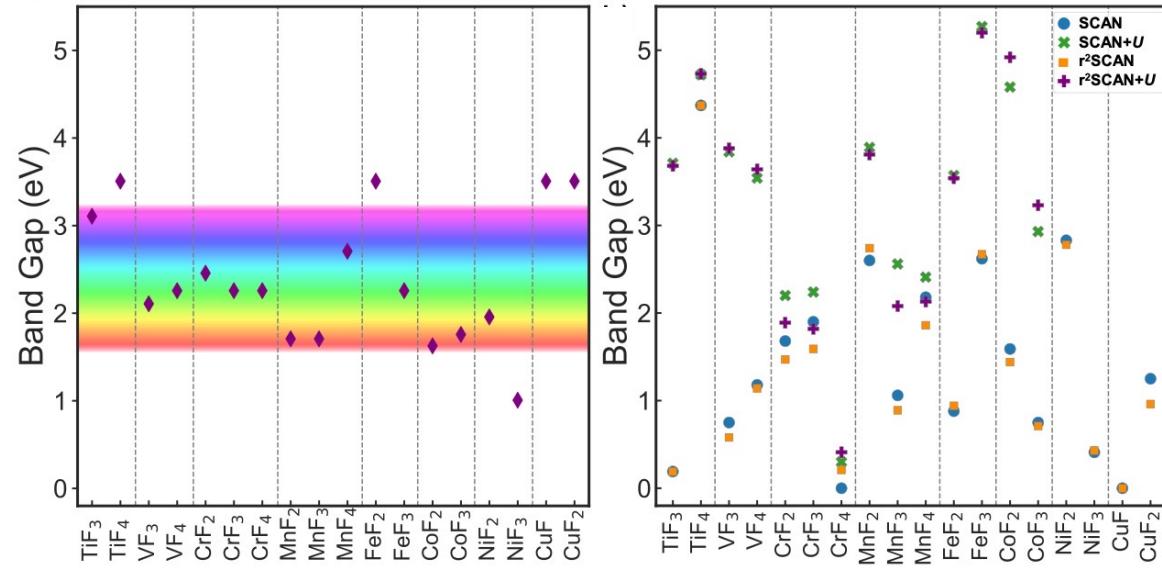
TMOs:  $U$  addition increases band gap

Reduces error on average across all TMOs compared to 'bare' functionals

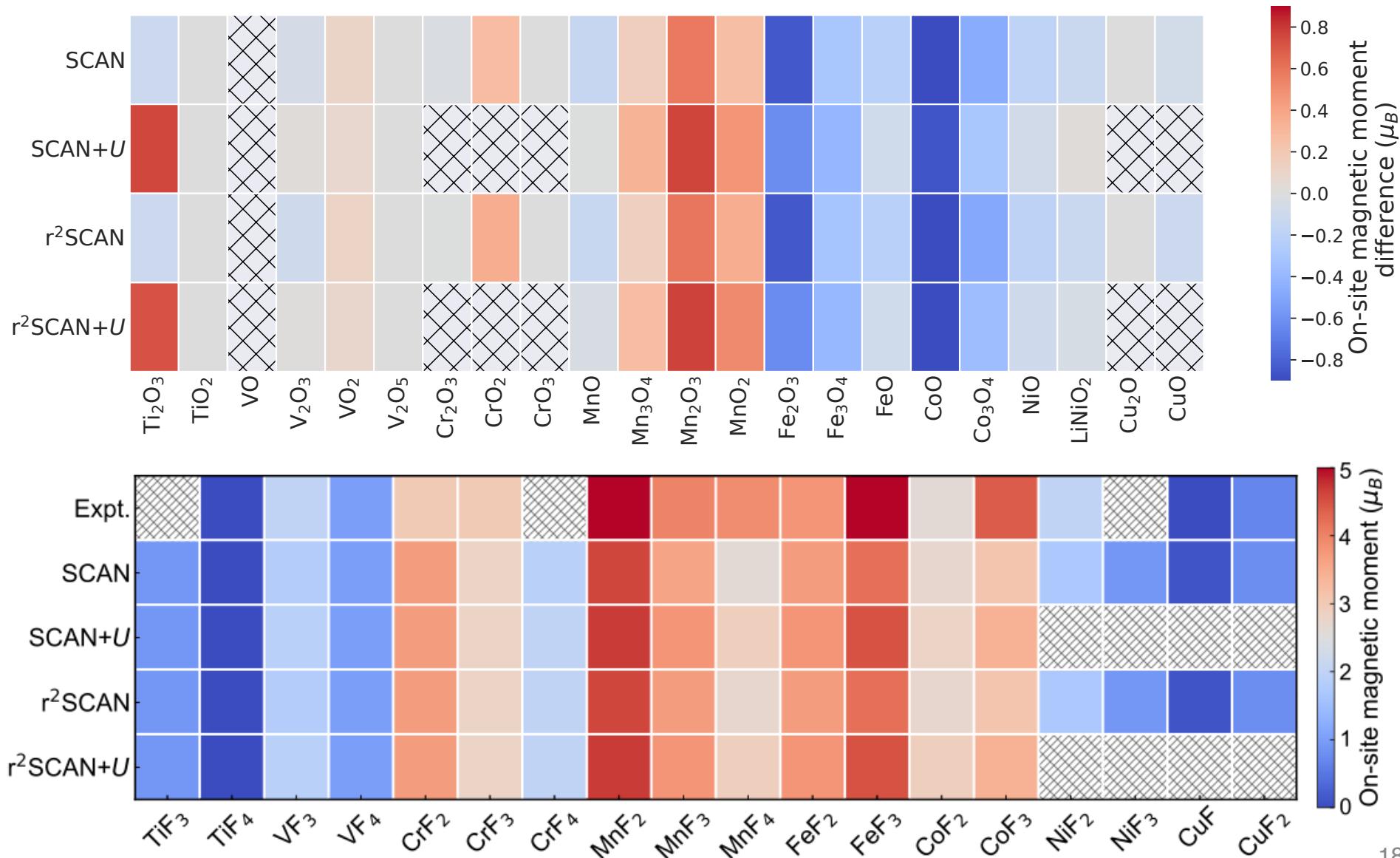
TMFs:  $U$  addition increases band gap

Experimental band gaps: only powder color samples available; qualitative band gap trends

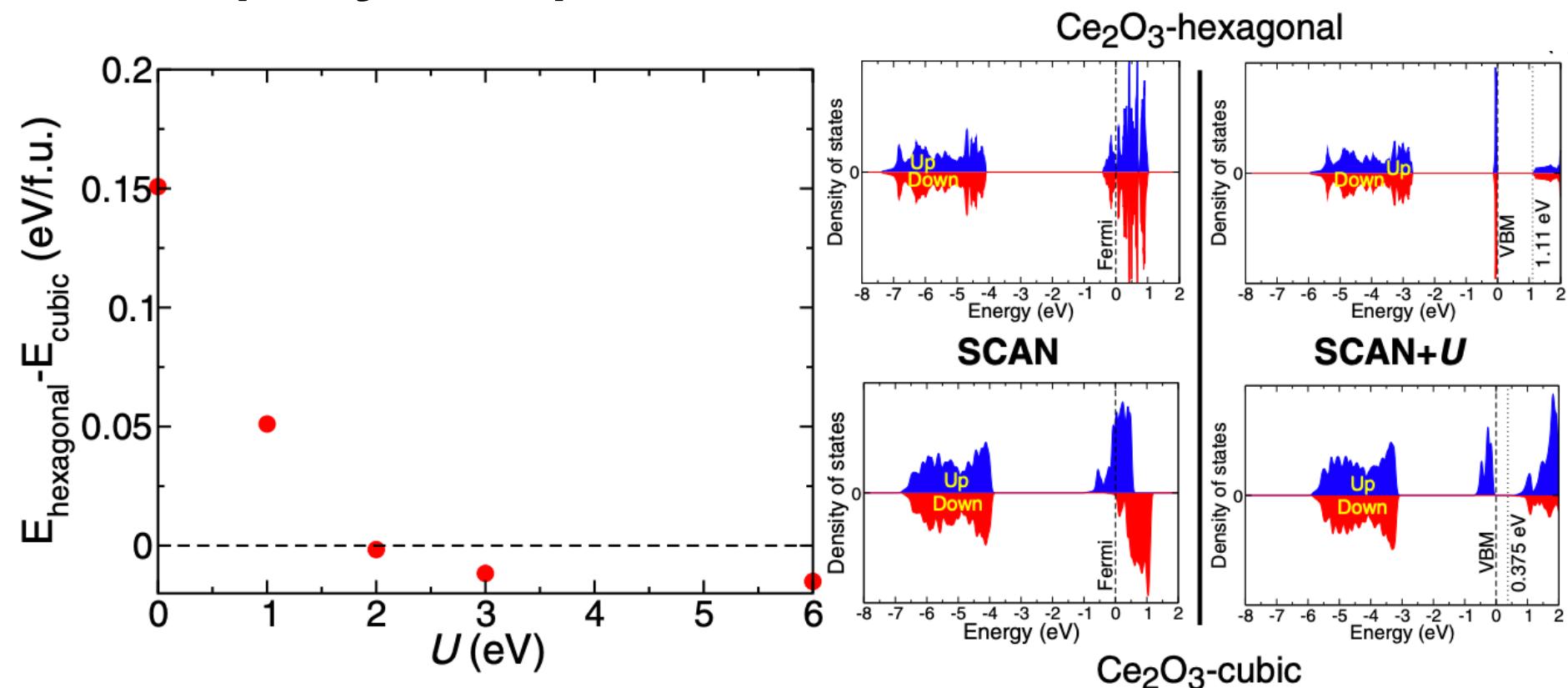
$U$  band gaps closer to hybrid functional values



# Magnetic moments: $U$ makes a difference in TMOs



# $U$ correction: identifies right ground state polymorph



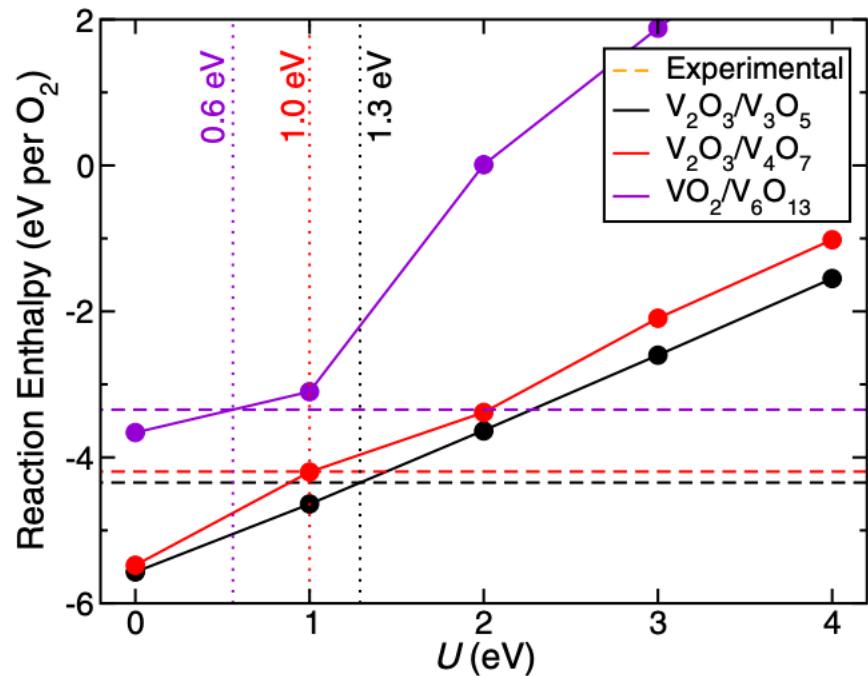
Case of  $\text{Ce}_2\text{O}_3$

Known ground state is hexagonal; cubic is competing structure

SCAN predicts wrong ground state polymorph due to wrong electronic structure

- $\text{Ce}_2\text{O}_3$  known to be a semiconductor (~2.4 eV optical gap)

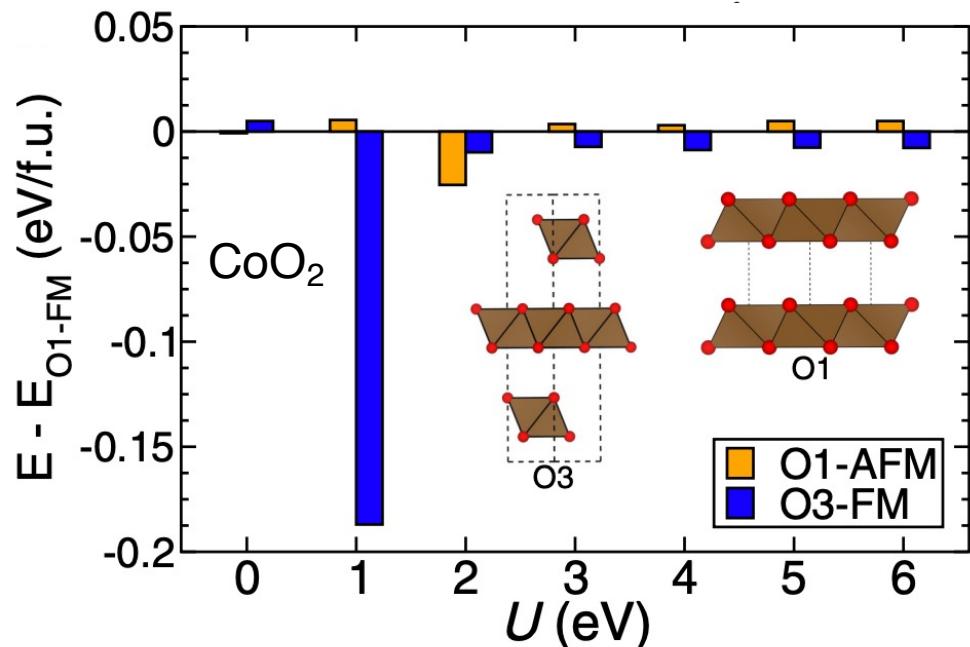
# Transferability checks



$U$  values derived with both SCAN and  $r^2$ SCAN are transferable to systems not used in determining optimal  $U$

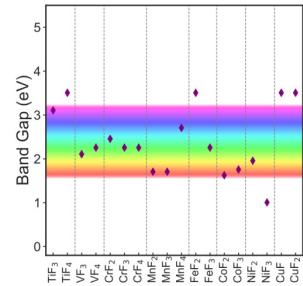
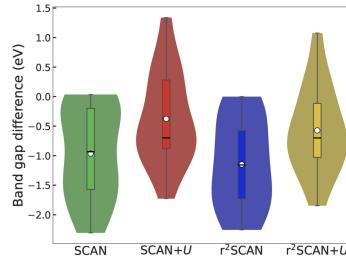
Transferability checks with fluorides: non-trivial due to lack of data

Composition (space group)	Source	Voltage (V)	Magnetic moment ( $\mu_B$ )
$LiCoO_2$ – $CoO_2$ ( $R\bar{3}m$ )	Expt.	4.05	-
	$r^2$ SCAN	4.12	-
	$r^2$ SCAN+ $U$	4.23	-
$LiNiO_2$ – $NiO_2$ ( $P1m1$ )	Expt.	3.85	-
	$r^2$ SCAN	3.54	-
	$r^2$ SCAN+ $U$	3.92	-
$SrFeO_3$ ( $Pm\bar{3}m$ )	Expt.	-	$2.7 \pm 0.4$
	$r^2$ SCAN	-	3.375
	$r^2$ SCAN+ $U$	-	3.819



# Conclusions

- Systems with correlated electrons: highly useful for several applications
  - Need computations to describe ground state well
- State-of-the-art SCAN and r<sup>2</sup>SCAN suffer from SIEs in TMOs and TMFs
  - Can be corrected using  $U$ , based on experimental oxidation enthalpies
- Adding  $U$  improves electronic and magnetic properties
  - Ground state polymorph prediction is better



“Accuracy of metaGGA functionals in describing transition metal fluorides”, D.B. Tekliye, and G. Sai Gautam, [arXiv 2401.10832](#) (2024) [under review].

“Performance of the r<sup>2</sup>SCAN functional in transition metal oxides”, S. Swathilakshmi, R. Devi, and G. Sai Gautam, [J. Chem. Theory Comput. 19](#), 4202-4215 (2023).

“Evaluating optimal  $U$  for 3d transition-metal oxides within the SCAN+ $U$  framework”, O.Long, G. Sai Gautam, and E.A. Carter, [Phys. Rev. Mater. 4](#), 045401 (2020).

“Evaluating transition metal oxides within DFT-SCAN and SCAN+ $U$  frameworks for solar thermochemical applications”, G. Sai Gautam, and E.A. Carter, [Phys. Rev. Mater. 2](#), 095401 (2018).