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Radionuclide Sequestration in MOFs: DFT Method Exploration and a Conceptualization of Graph Neural Network

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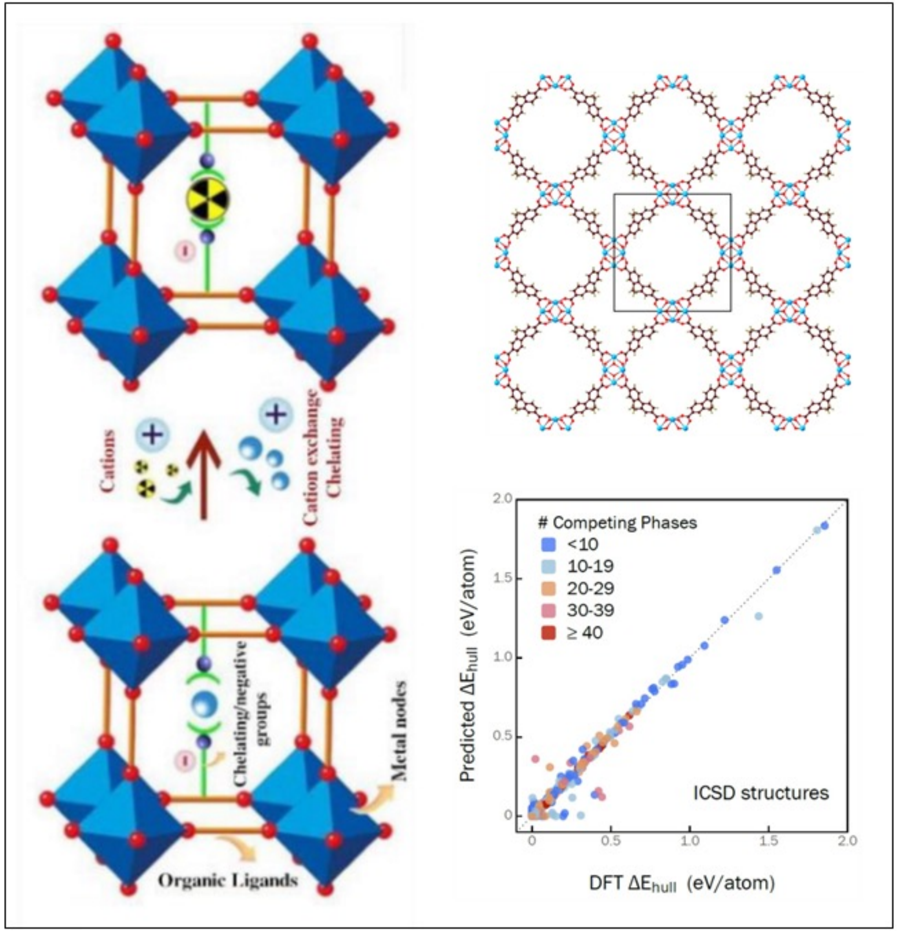
Shubham Pandey, Materials Design, Inc.

20-22 September 2022



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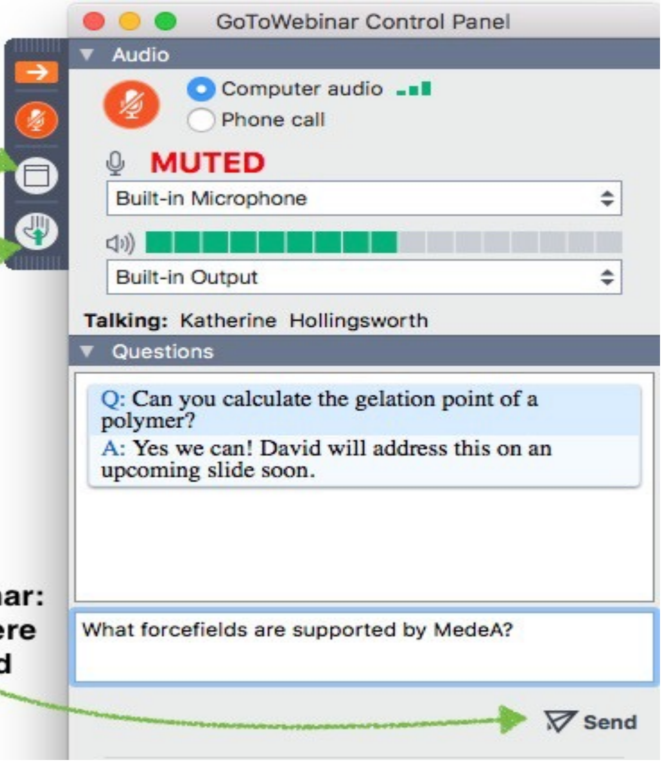
Please Ask Questions!



● Computer audio
○ Phone call

Talking: Katherine Hollingsworth

Q: Can you calculate the gelation point of a polymer?
A: Yes we can! David will address this on an upcoming slide soon.

What forcefields are supported by MedeA?

full screen

during discussion: raise hand to speak

Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

Webinar Speakers

Katherine Hollingsworth

Dr. René Windiks

Dr. Shubham Pandey
Presenter

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Radionuclide Sequestration in MOFs: DFT Method Exploration and a Conceptualization of Graph Neural Network

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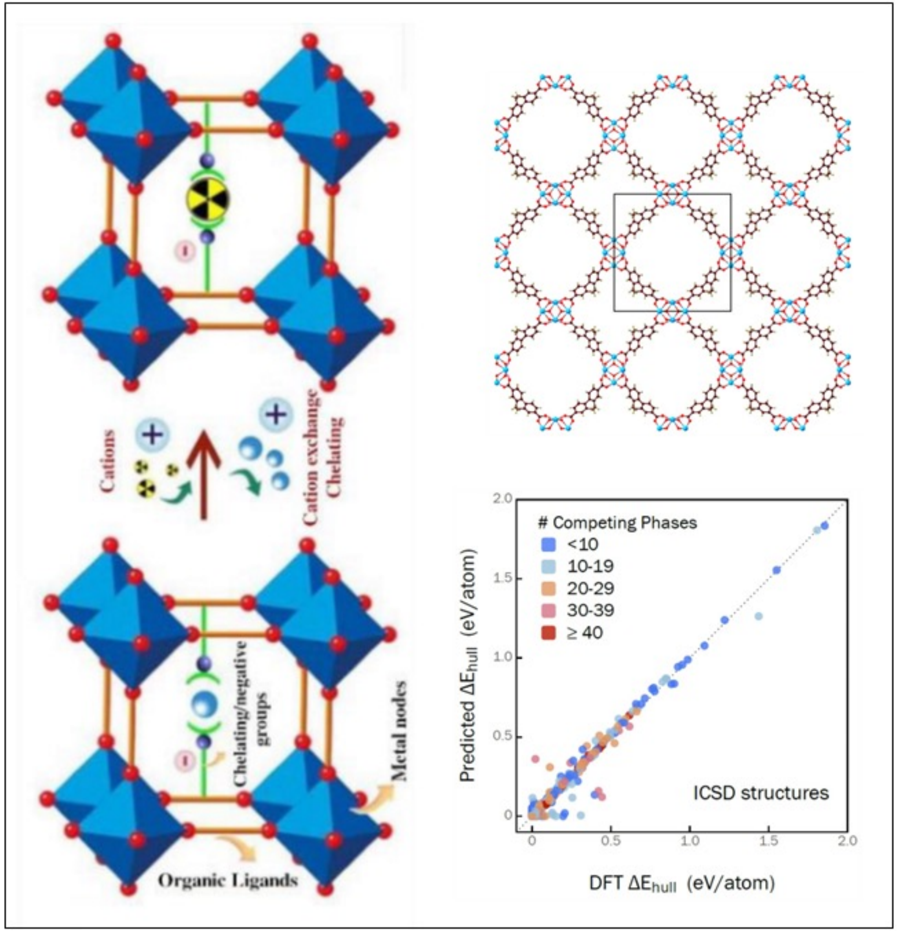
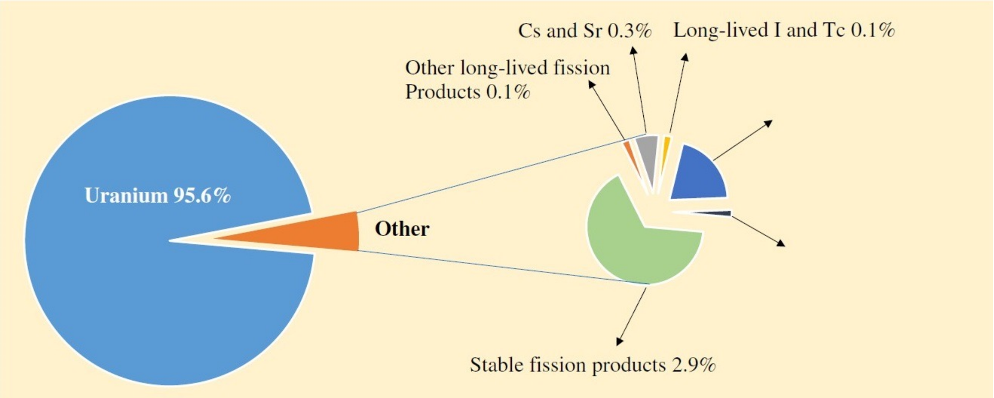


Outline

- Motivation: management of radioactive waste
- Metal-organic Frameworks (MOFs) for sequestration of radionuclides
- Exploration of DFT methods to calculate properties of MOFs
  - Ion-exchange
  - Electronic structures
- Graph Neural Network for predicting phase stability of inorganic materials
  - Total-energy prediction of known and *hypothetical* materials
  - Energy ranking prediction
  - Deriving chemical trends from dimensionality reduction

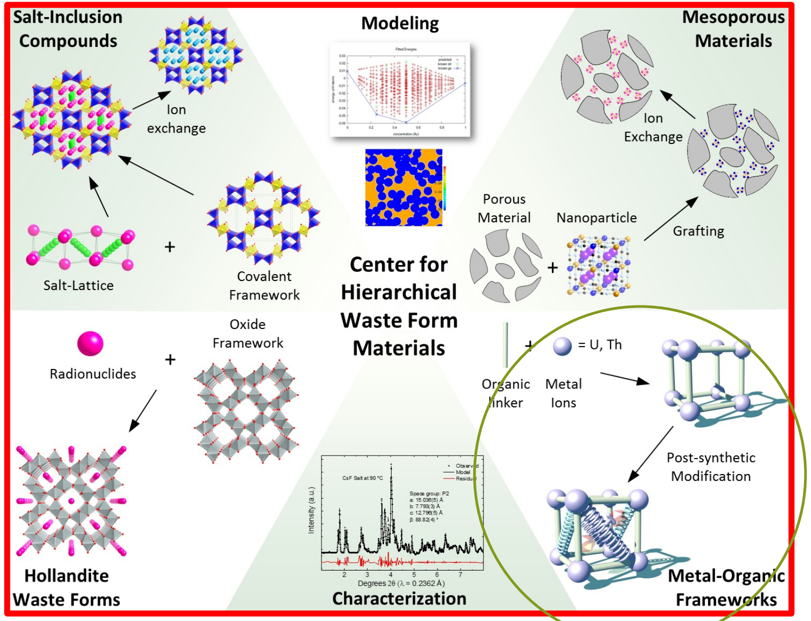
Sequestration Techniques

Radionuclide occurrence in nuclear industries



Sujit K. Ghosh, 2019. Metal-Organic Frameworks for Environmental Applications (page 356, Fig. 11.1)

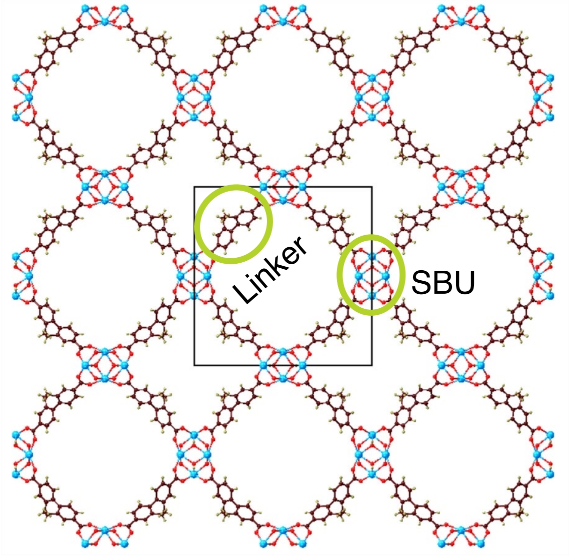
Wasteform Materials



https://science.osti.gov/bes/efrc/Centers/chwm

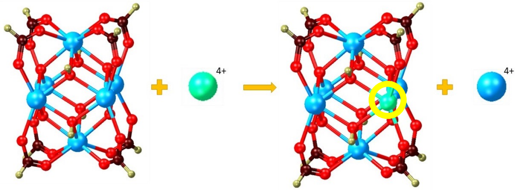
- Glass and cement wasteforms, solvent-extraction process
- Drawbacks: volatility, low uptake capacity, poor stability under radiation field

Why MOFs?

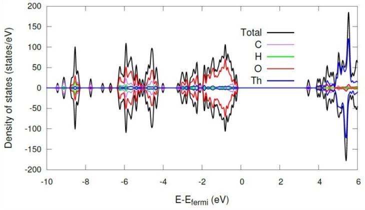


Transition metal and Actinide based MOFs
(Zr, U, Th)

Thermodynamics of Ion-Exchange



Electronic Structures

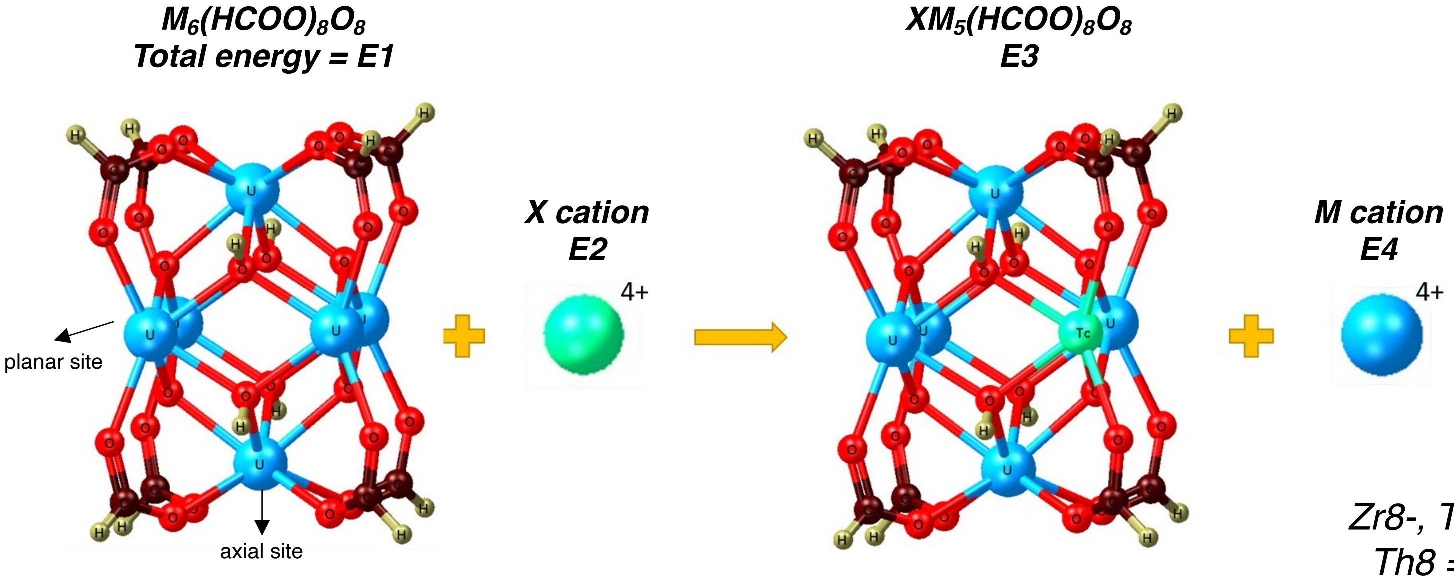


Advantageous MOF properties

- Organometallic: suitable for cation-exchange
- High metal concentration per SBU
- Strong bonding of radionuclide into lattice

Thermodynamics of Ion-Exchange

Ion-Exchange: Substitution of Radionuclides



Parent MOFs

Zr8-, Th8-, Th10-, U8-MOF

Th8 = 8 -(COO)- ligands

Th10 = 10 -(COO)- ligands

Substitution energy ΔE = (E3+E4) – (E1+E2)

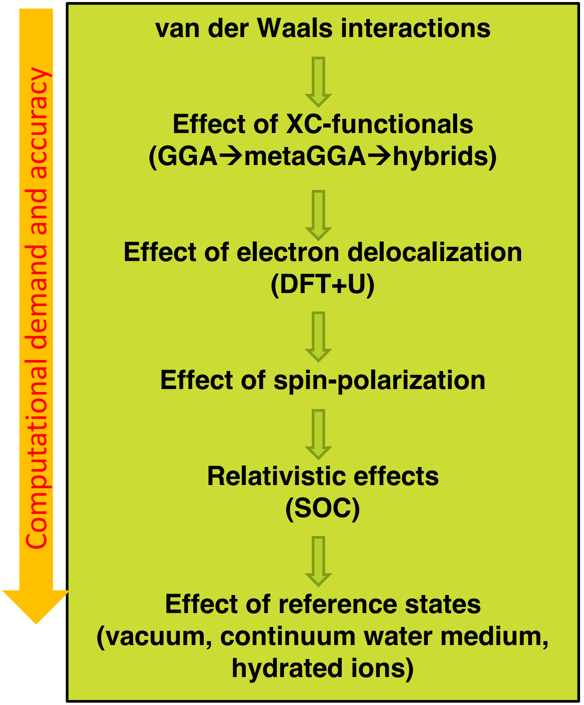
- ***ΔE > 0 : energetically unfavorable substitution***
- ***ΔE < 0 : energetically favorable substitution***

Radionuclides of interest

X = Tc, Th, U, Am, Cm

Finding Reliable DFT Methods for Ion-Exchange

DFT hierarchy



van der Waals interactions

Effect of XC-functionals (GGA→metaGGA→hybrids)

Effect of electron delocalization (DFT+U)

Effect of spin-polarization

Relativistic effects (SOC)

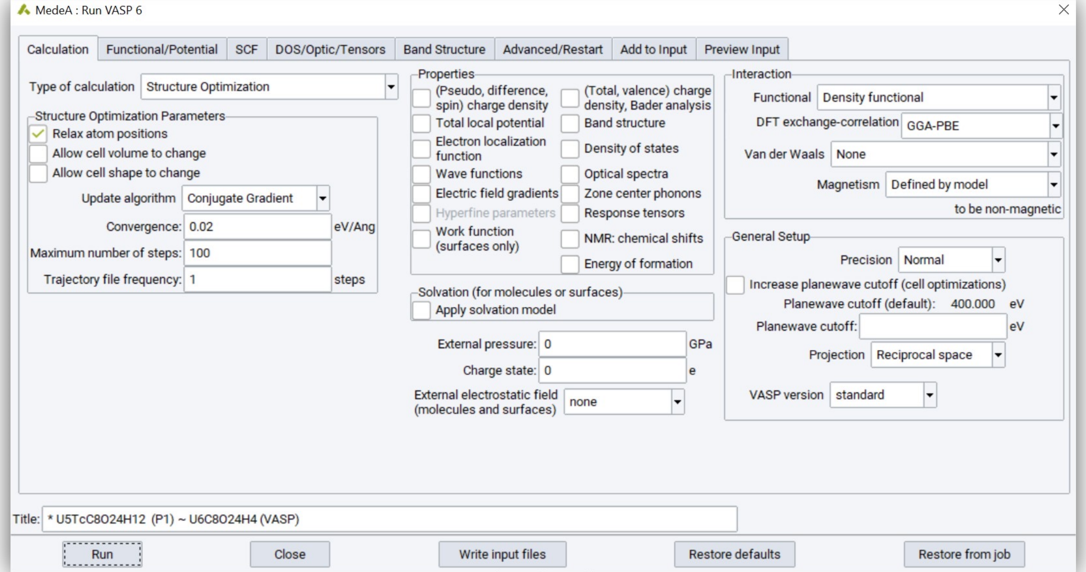
Effect of reference states (vacuum, continuum water medium, hydrated ions)

Calculations performed with bare ions

Calculations performed with hydrated ions

Pandey et al., *J. Phys. Chem. C.*, **123** (2019)

This work can be done with *MedeA VASP 6*



Type of calculation: Structure Optimization

Structure Optimization Parameters
- ☑ Relax atom positions
- ☐ Allow cell volume to change
- ☐ Allow cell shape to change

Update algorithm: Conjugate Gradient
Convergence: 0.02 eV/Ang
Maximum number of steps: 100
Trajectory file frequency: 1 steps

Properties
- ☐ (Pseudo, difference, spin) charge density
- ☐ Total local potential
- ☐ Electron localization function
- ☐ Wave functions
- ☐ Electric field gradients
- ☐ Hyperfine parameters
- ☐ Work function (surfaces only)
- ☐ (Total, valence) charge density, Bader analysis
- ☐ Band structure
- ☐ Density of states
- ☐ Optical spectra
- ☐ Zone center phonons
- ☐ Response tensors
- ☐ NMR: chemical shifts
- ☐ Energy of formation

Solvation (for molecules or surfaces)
- ☐ Apply solvation model

External pressure: 0 GPa
Charge state: 0 e
External electrostatic field (molecules and surfaces): none

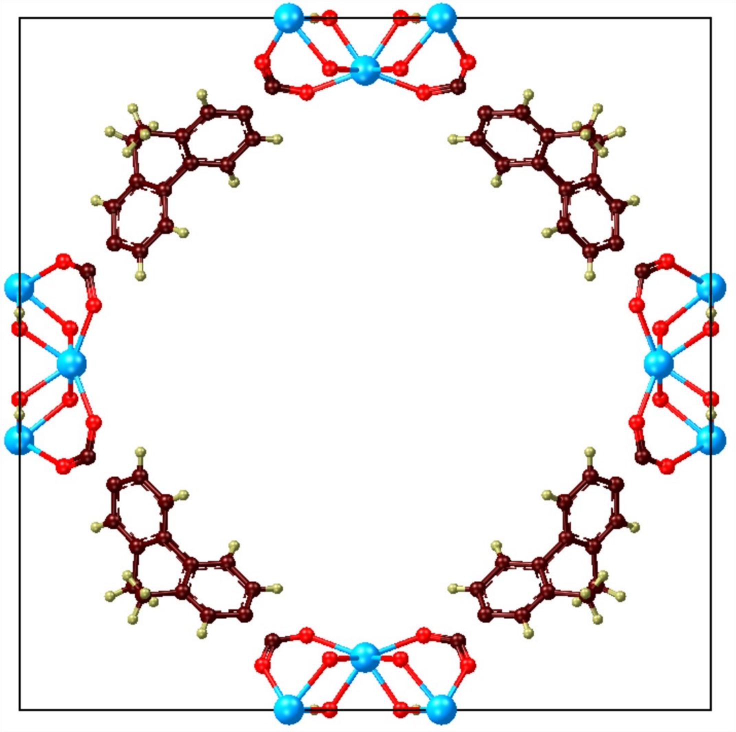
Interaction
Functional: Density functional
DFT exchange-correlation: GGA-PBE
Van der Waals: None
Magnetism: Defined by model
to be non-magnetic

General Setup
Precision: Normal
☐ Increase planewave cutoff (cell optimizations)
Planewave cutoff (default): 400.000 eV
Planewave cutoff: eV
Projection: Reciprocal space
VASP version: standard

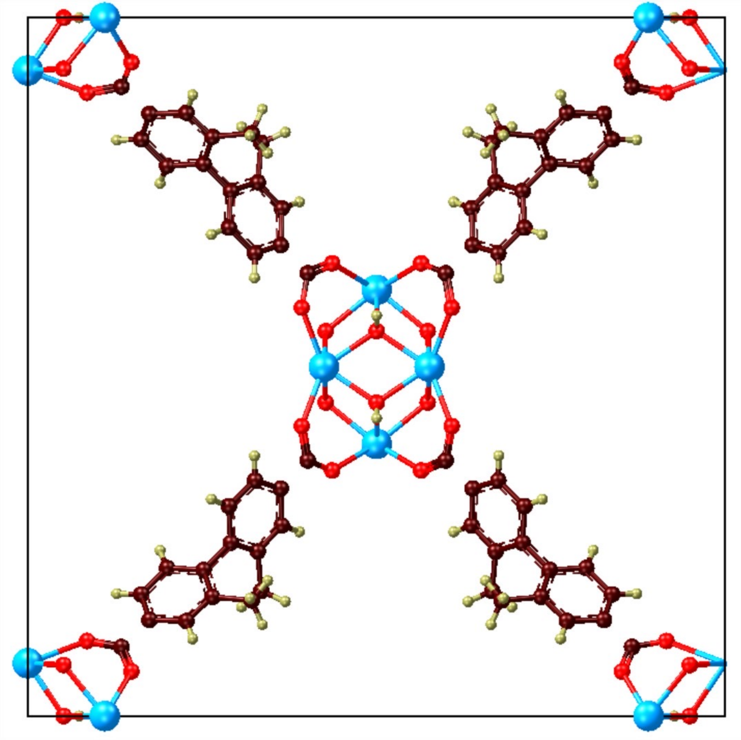
Title: * U5TcC8O24H12 (P1) ~ U6C8O24H4 (VASP)

Convenient MOF Truncation with *MedeA Builders*

Step-1: load crystal structure

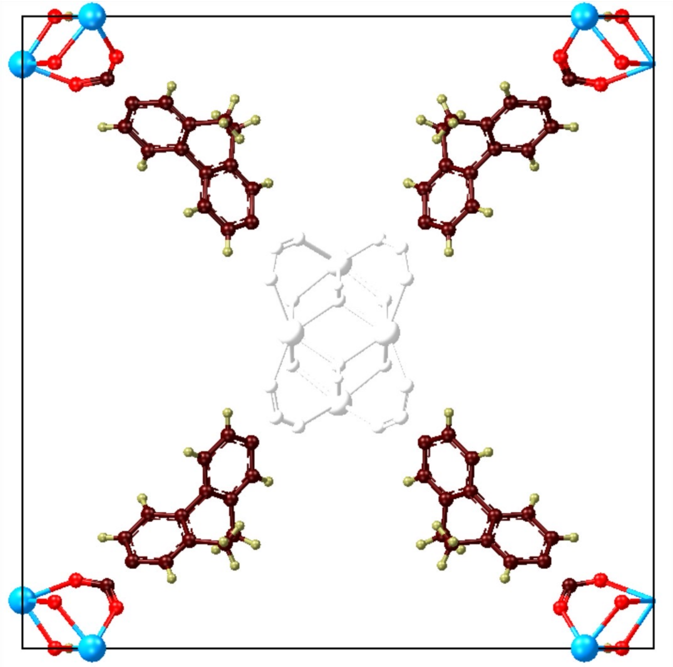


Step-2: center the SBU in the cell

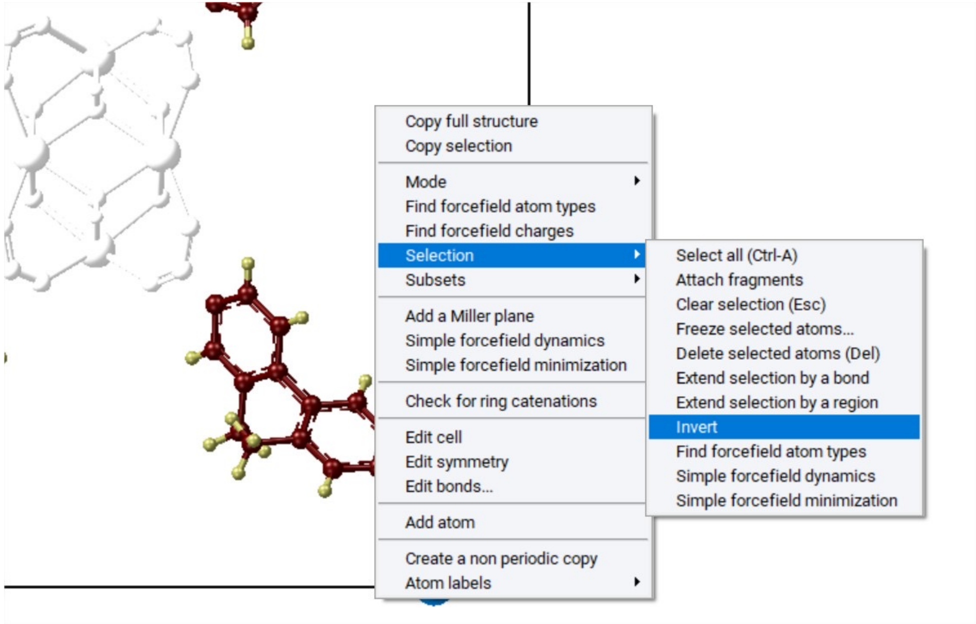


MOF truncation - continued

Step-3: select SBU atoms

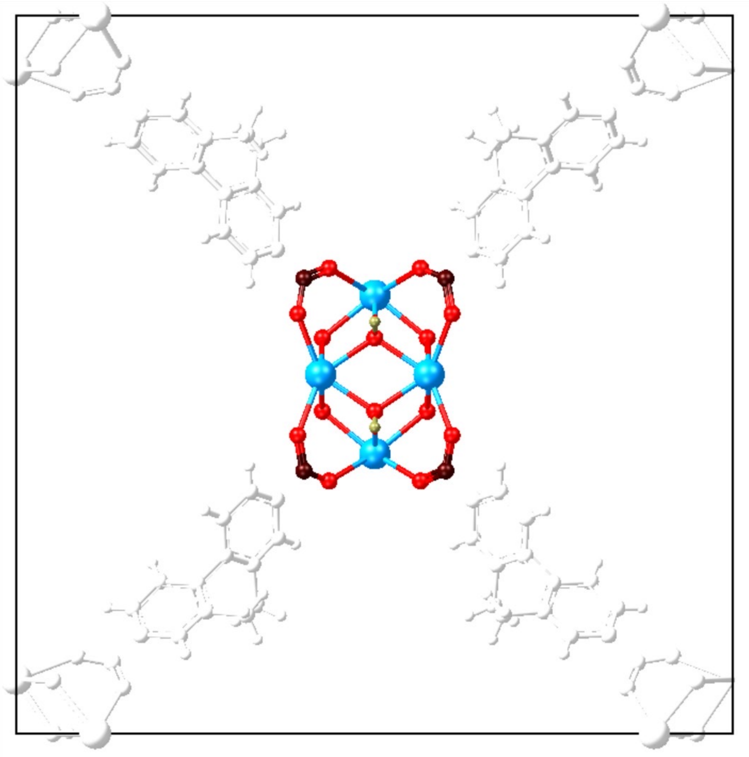


Step-4: invert selection

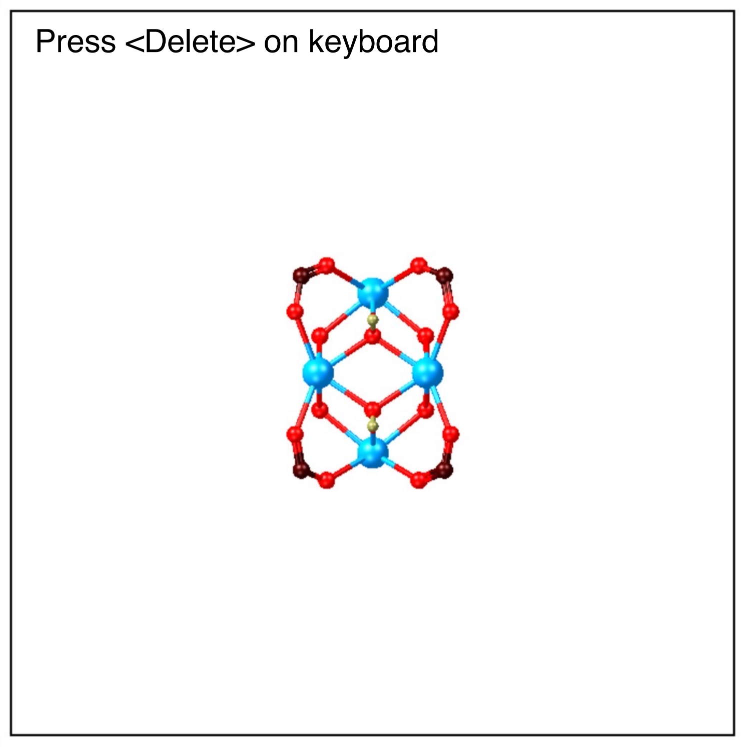


MOF truncation - continued

Step-5: inverted selection
(non SBU atoms are selected)



Step-6: delete selected atoms



Press <Delete> on keyboard

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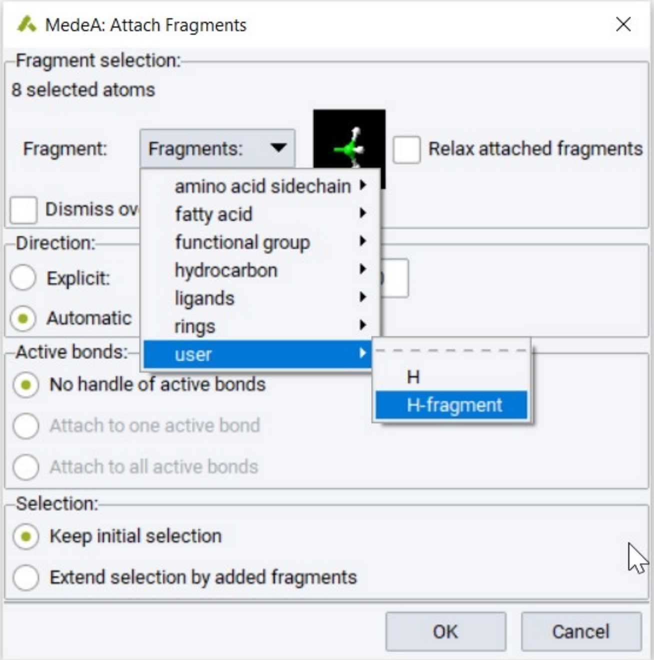
Saturation of –(COO)– ligands in SBU

Step-7: attach H-atoms to C-atoms (selected)



MedeA: Attach Fragments

Fragment selection:

8 selected atoms

Fragment: Fragments:

☐ Relax attached fragments

☐ Dismiss ov

Direction:

○ Explicit:

● Automatic

Active bonds:

● No handle of active bonds

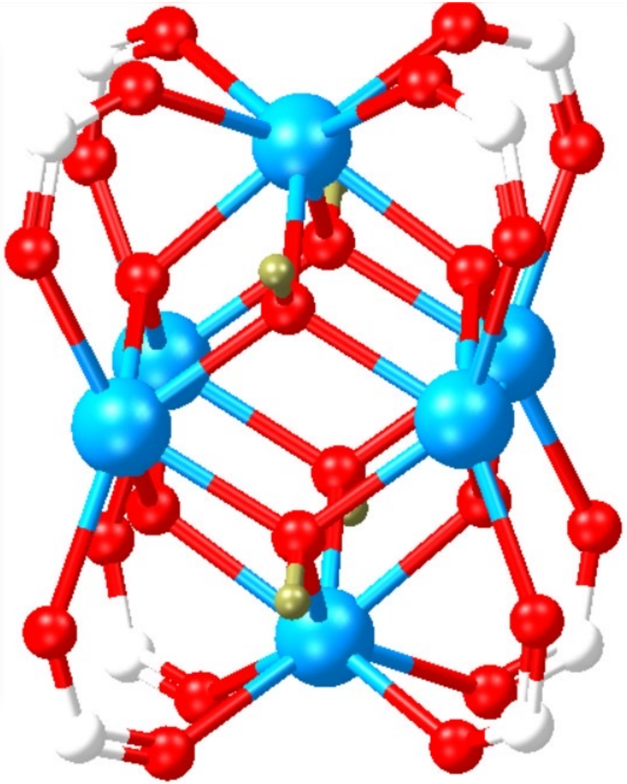
○ Attach to one active bond

○ Attach to all active bonds

Selection:

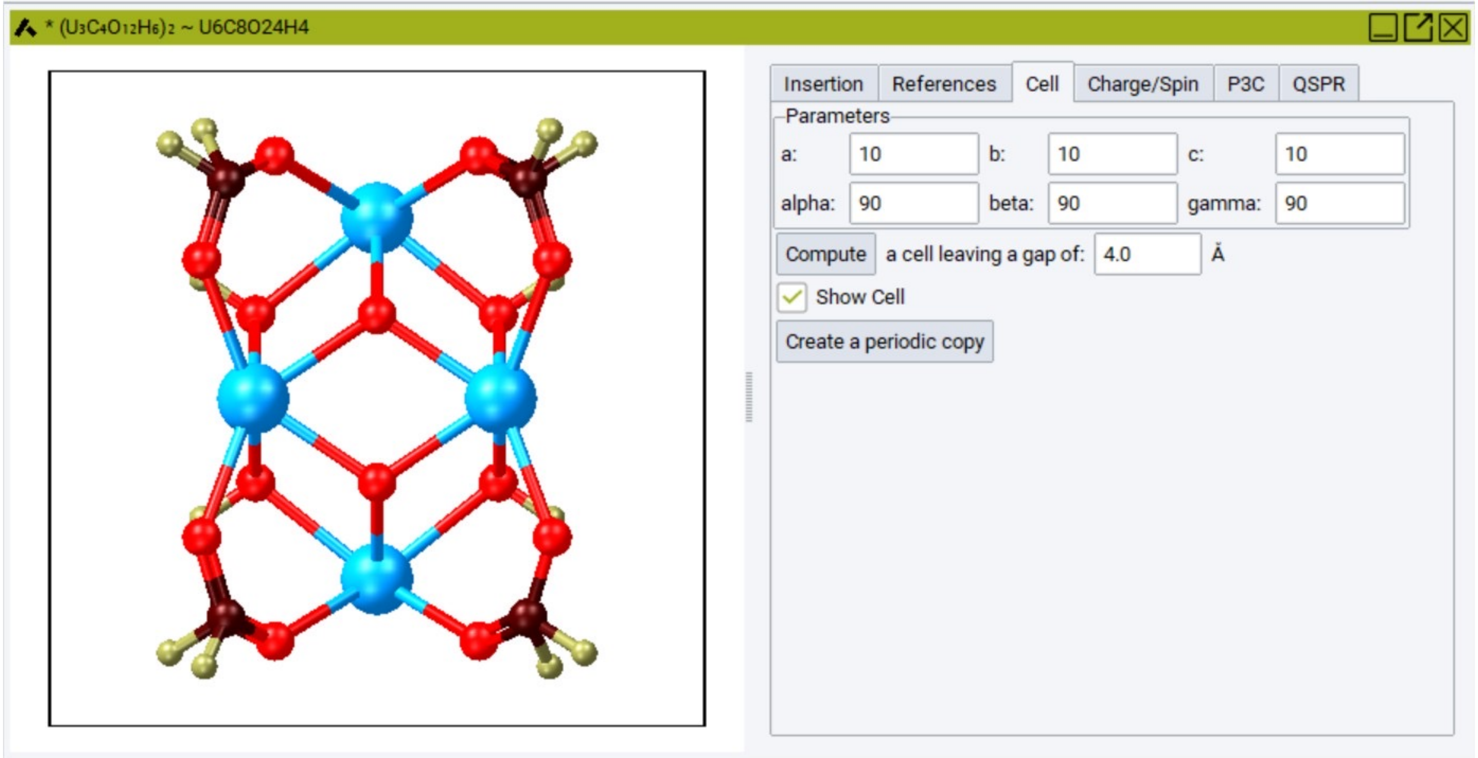
● Keep initial selection

○ Extend selection by added fragments



Final Structure: Saturated SBU

Step-8: position SBU in the center of a cell (isolated SBU)


* $(U_3C_4O_{12}H_6)_2$ ~ U6C8O24H4

Parameters

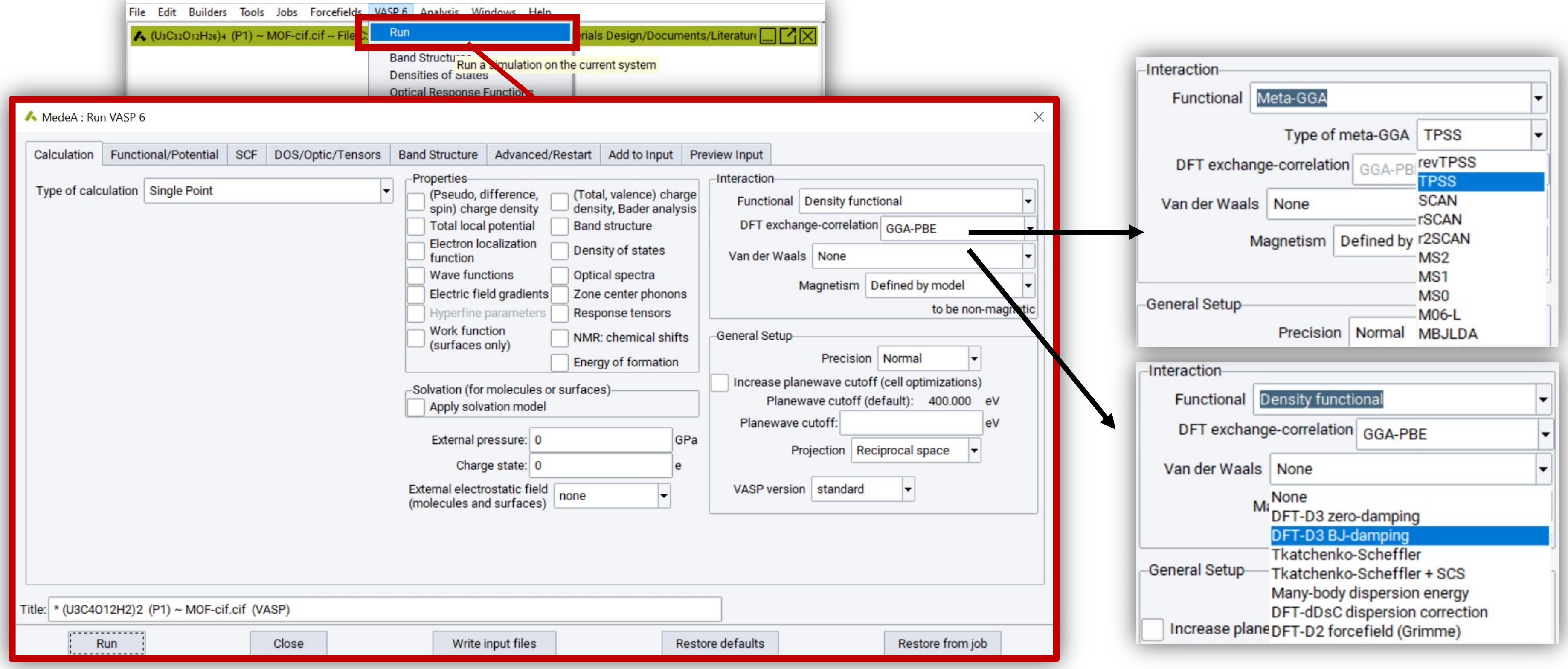
a: 10 b: 10 c: 10

alpha: 90 beta: 90 gamma: 90

Compute a cell leaving a gap of: 4.0 Å

☑ Show Cell

Setting up different DFT methods and vDW corrections in *MedeA VASP*



Type of calculation: Single Point

Properties
- ☐ (Pseudo, difference, spin) charge density
- ☐ Total local potential
- ☐ Electron localization function
- ☐ Wave functions
- ☐ Electric field gradients
- ☐ Hyperfine parameters
- ☐ Work function (surfaces only)
- ☐ (Total, valence) charge density, Bader analysis
- ☐ Band structure
- ☐ Density of states
- ☐ Optical spectra
- ☐ Zone center phonons
- ☐ Response tensors
- ☐ NMR: chemical shifts
- ☐ Energy of formation

Solvation (for molecules or surfaces)
- ☐ Apply solvation model

External pressure: 0 GPa

Charge state: 0 e

External electrostatic field (molecules and surfaces): none

Interaction

Functional: Density functional

DFT exchange-correlation: GGA-PBE

Van der Waals: None

Magnetism: Defined by model

to be non-magnetic

General Setup

Precision: Normal

☐ Increase planewave cutoff (cell optimizations)

Planewave cutoff (default): 400.000 eV

Planewave cutoff: eV

Projection: Reciprocal space

VASP version: standard

Title: * (U3C4O12H2)2 (P1) ~ MOF-cif.cif (VASP)

Interaction

Functional: Meta-GGA

Type of meta-GGA: TPSS

DFT exchange-correlation: GGA-PB

Van der Waals: None

Magnetism: Defined by

General Setup

Precision: Normal

Interaction

Functional: Density functional

DFT exchange-correlation: GGA-PBE

Van der Waals: None

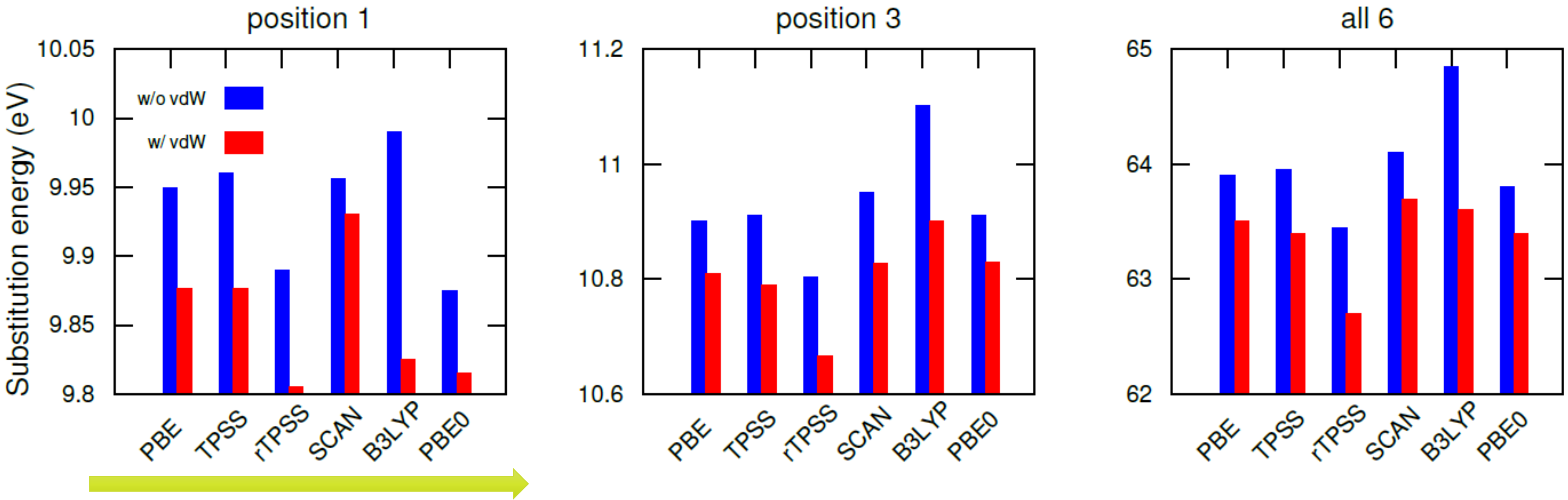
General Setup

☐ Increase plane

Robust Ion-Exchange for Different Exchange-Correlation Functionals

Goal: find most efficient DFT methods to calculate reliable substitution energies

Th substitution in Zr-8 SBU at different metal sites



More sophisticated functionals

GGA-PBE level of theory without vdW corrections sufficient enough to establish favorability of substitution

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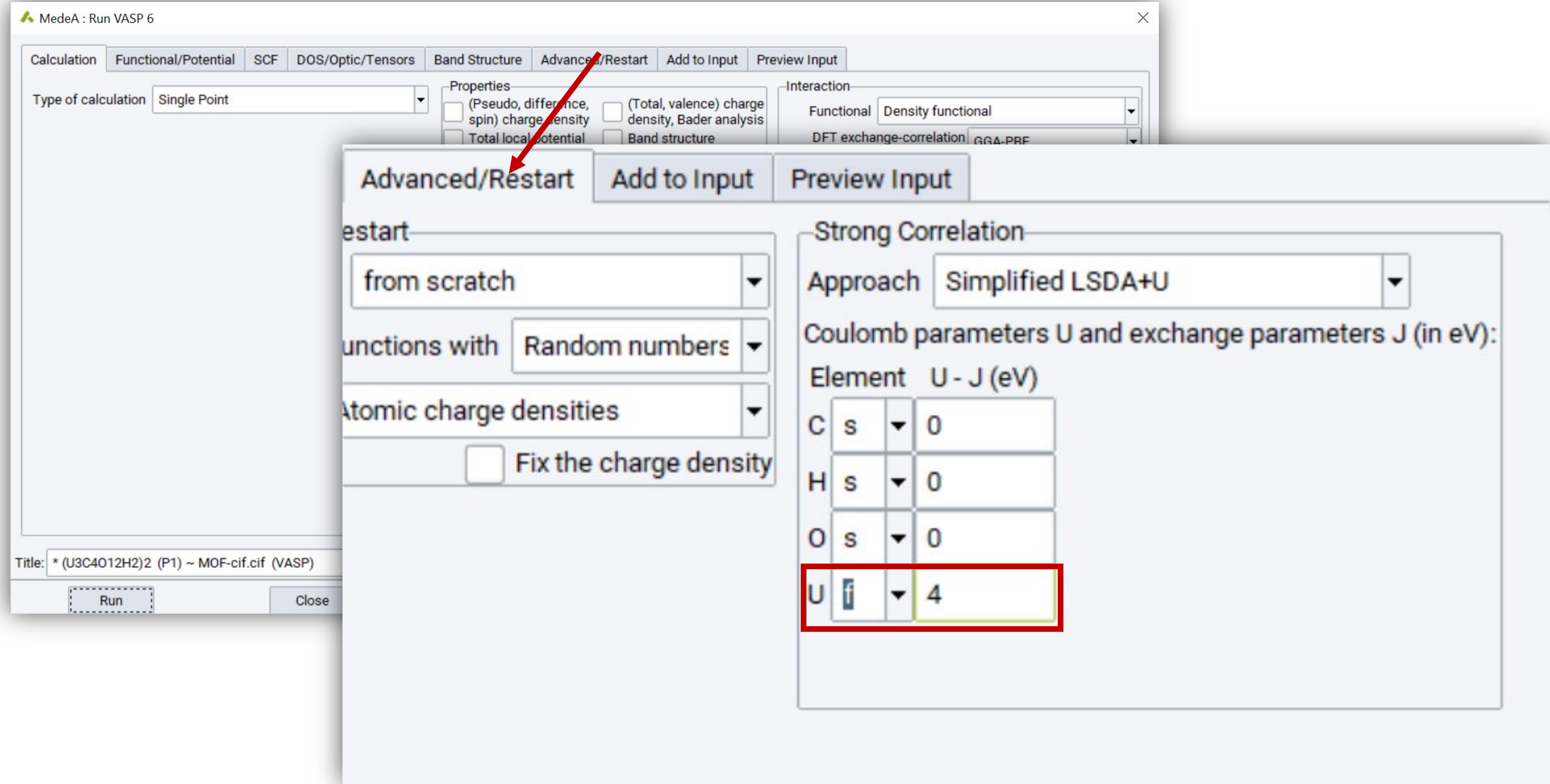
Setting up DFT+U corrections within *MedeA VASP*



Type of calculation: Single Point

Properties
☐ (Pseudo, difference, spin) charge density
☐ (Total, valence) charge density, Bader analysis
☐ Total local potential
☐ Band structure

Interaction
Functional: Density functional
DFT exchange-correlation: GGA-PBE

Title: * (U3C4O12H2)2 (P1) ~ MOF-cif.cif (VASP)

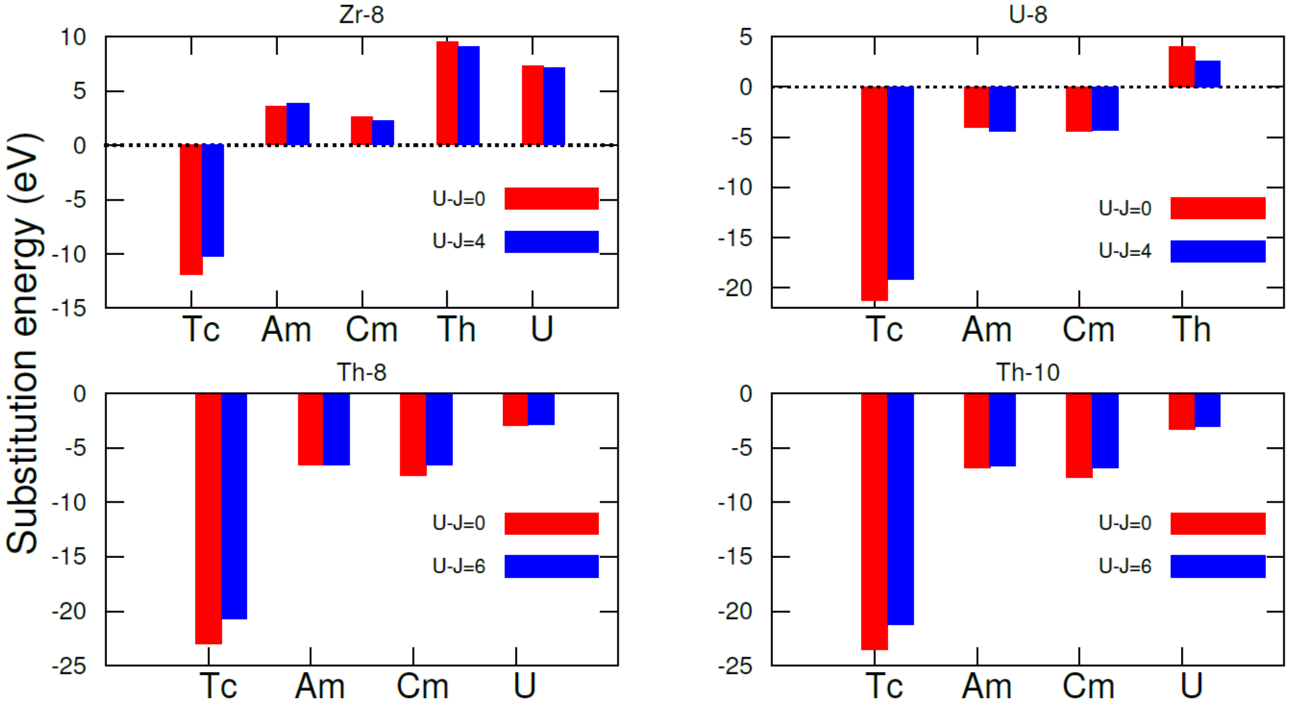
estart: from scratch
unctions with: Random numbers
Atomic charge densities
☐ Fix the charge density

Strong Correlation
Approach: Simplified LSDA+U
Coulomb parameters U and exchange parameters J (in eV):

Element		U - J (eV)
C	s	0
H	s	0
O	s	0
U	f	4

Effect of electron localization on substitution energies

Substitution energies at position 1 in all 4 MOFs



- Magnitude changes by ±40%
- Favorability of substitution is unchanged

DFT+U corrections not required to establish favorability of substitution

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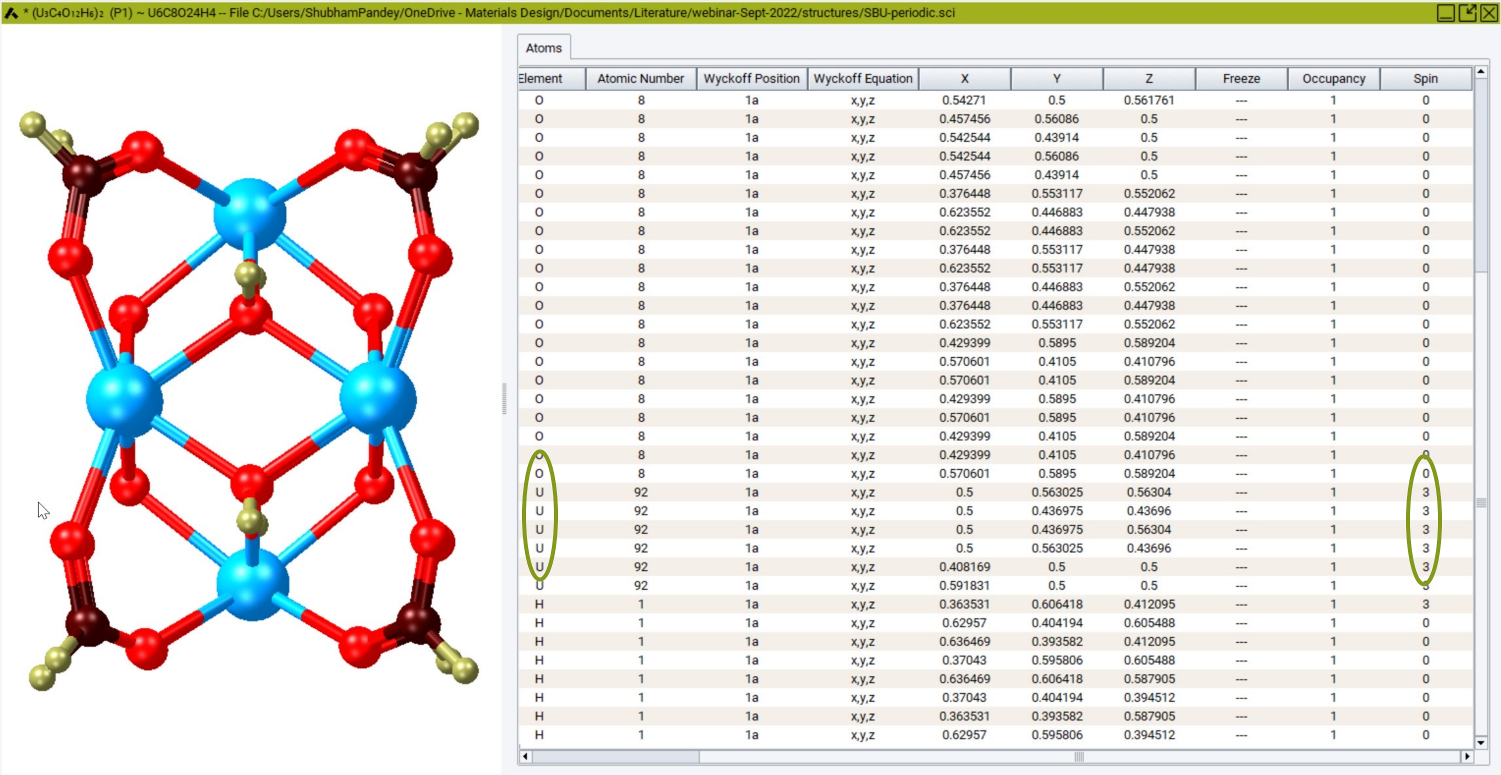
Effect of spin polarization: Initialize magnetic moments with *MedeA Builders*

Atomic spins of cations can be easily defined in the atomic spreadsheet

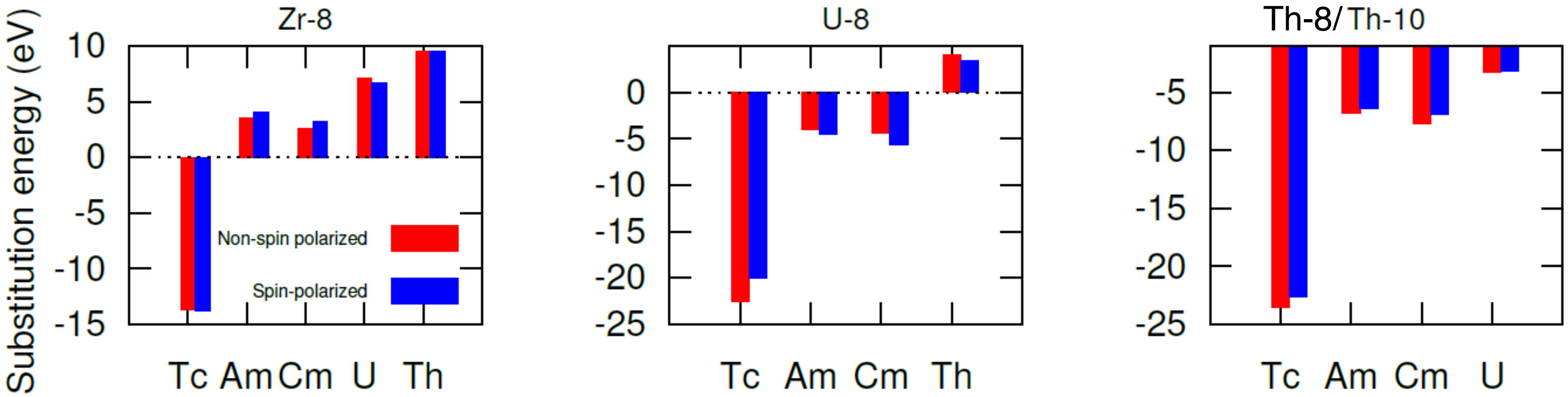


* $(U_3C_4O_{12}H_6)_2$ (P1) ~ U6C8O24H4 -- File C:/Users/ShubhamPandey/OneDrive - Materials Design/Documents/Literature/webinar-Sept-2022/structures/SBU-periodic.sci

Element	Atomic Number	Wyckoff Position	Wyckoff Equation	X	Y	Z	Freeze	Occupancy	Spin
O	8	1a	x,y,z	0.54271	0.5	0.561761	---	1	0
O	8	1a	x,y,z	0.457456	0.56086	0.5	---	1	0
O	8	1a	x,y,z	0.542544	0.43914	0.5	---	1	0
O	8	1a	x,y,z	0.542544	0.56086	0.5	---	1	0
O	8	1a	x,y,z	0.457456	0.43914	0.5	---	1	0
O	8	1a	x,y,z	0.376448	0.553117	0.552062	---	1	0
O	8	1a	x,y,z	0.623552	0.446883	0.447938	---	1	0
O	8	1a	x,y,z	0.623552	0.446883	0.552062	---	1	0
O	8	1a	x,y,z	0.376448	0.553117	0.447938	---	1	0
O	8	1a	x,y,z	0.623552	0.553117	0.447938	---	1	0
O	8	1a	x,y,z	0.376448	0.446883	0.552062	---	1	0
O	8	1a	x,y,z	0.376448	0.446883	0.447938	---	1	0
O	8	1a	x,y,z	0.623552	0.553117	0.552062	---	1	0
O	8	1a	x,y,z	0.429399	0.5895	0.589204	---	1	0
O	8	1a	x,y,z	0.570601	0.4105	0.410796	---	1	0
O	8	1a	x,y,z	0.570601	0.4105	0.589204	---	1	0
O	8	1a	x,y,z	0.429399	0.5895	0.410796	---	1	0
O	8	1a	x,y,z	0.570601	0.5895	0.410796	---	1	0
O	8	1a	x,y,z	0.429399	0.4105	0.589204	---	1	0
O	8	1a	x,y,z	0.429399	0.4105	0.410796	---	1	0
O	8	1a	x,y,z	0.570601	0.5895	0.589204	---	1	0
U	92	1a	x,y,z	0.5	0.563025	0.56304	---	1	3
U	92	1a	x,y,z	0.5	0.436975	0.43696	---	1	3
U	92	1a	x,y,z	0.5	0.436975	0.56304	---	1	3
U	92	1a	x,y,z	0.5	0.563025	0.43696	---	1	3
U	92	1a	x,y,z	0.408169	0.5	0.5	---	1	3
U	92	1a	x,y,z	0.591831	0.5	0.5	---	1	3
H	1	1a	x,y,z	0.363531	0.606418	0.412095	---	1	3
H	1	1a	x,y,z	0.62957	0.404194	0.605488	---	1	0
H	1	1a	x,y,z	0.636469	0.393582	0.412095	---	1	0
H	1	1a	x,y,z	0.37043	0.595806	0.605488	---	1	0
H	1	1a	x,y,z	0.636469	0.606418	0.587905	---	1	0
H	1	1a	x,y,z	0.37043	0.404194	0.394512	---	1	0
H	1	1a	x,y,z	0.363531	0.393582	0.587905	---	1	0
H	1	1a	x,y,z	0.62957	0.595806	0.394512	---	1	0

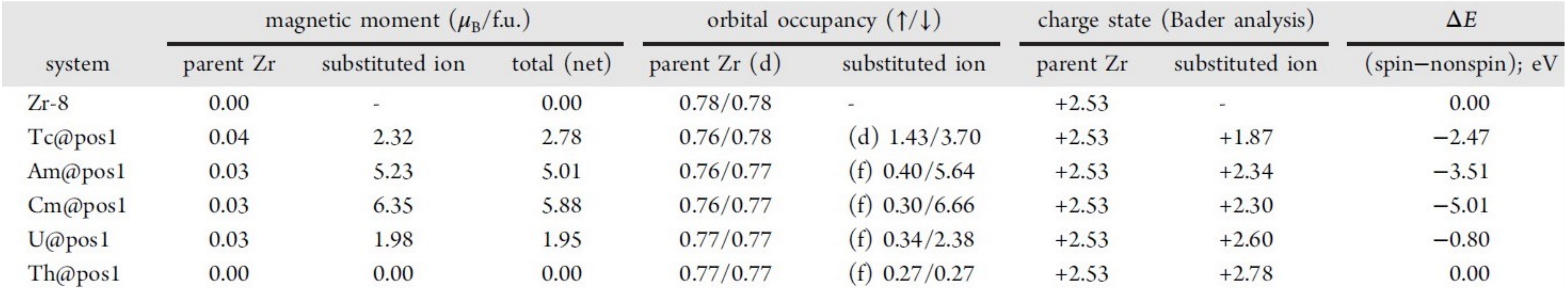
Effect of spin polarization on substitution energies

Substitution energies at position 1 in Zr-, U-, and Th-MOFs



Favorability of substitution independent of spin polarization

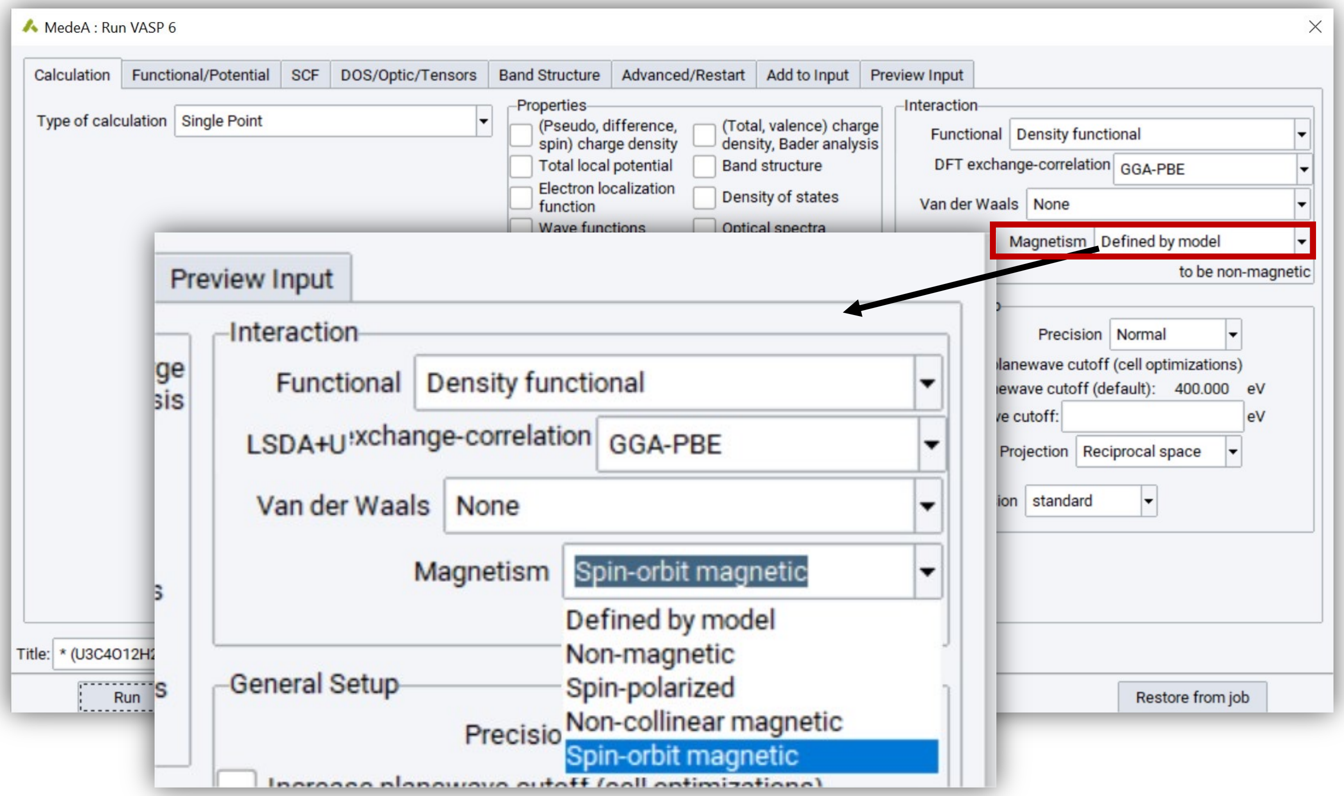
Relate magnetic moments with orbital occupancies



	magnetic moment (μ_B/f.u.)			orbital occupancy (↑/↓)		charge state (Bader analysis)		ΔE
system	parent Zr	substituted ion	total (net)	parent Zr (d)	substituted ion	parent Zr	substituted ion	(spin−nonspin); eV
Zr-8	0.00	-	0.00	0.78/0.78	-	+2.53	-	0.00
Tc@pos1	0.04	2.32	2.78	0.76/0.78	(d) 1.43/3.70	+2.53	+1.87	−2.47
Am@pos1	0.03	5.23	5.01	0.76/0.77	(f) 0.40/5.64	+2.53	+2.34	−3.51
Cm@pos1	0.03	6.35	5.88	0.76/0.77	(f) 0.30/6.66	+2.53	+2.30	−5.01
U@pos1	0.03	1.98	1.95	0.77/0.77	(f) 0.34/2.38	+2.53	+2.60	−0.80
Th@pos1	0.00	0.00	0.00	0.77/0.77	(f) 0.27/0.27	+2.53	+2.78	0.00

- Difference in up- and down-spin orbital occupancies lead to a local magnetic moment
- Magnitude of the difference between up- and down-spin orbital occupancies determine the magnitude of local magnetic moment, and hence the amount by which total energy decreases with spin turned on

Setting up spin-orbit coupling within *MedeA VASP*



MedeA : Run VASP 6

Type of calculation: Single Point

Functional: Density functional

DFT exchange-correlation: GGA-PBE

Van der Waals: None

Magnetism: Defined by model

to be non-magnetic

Precision: Normal

Planewave cutoff (default): 400.000 eV

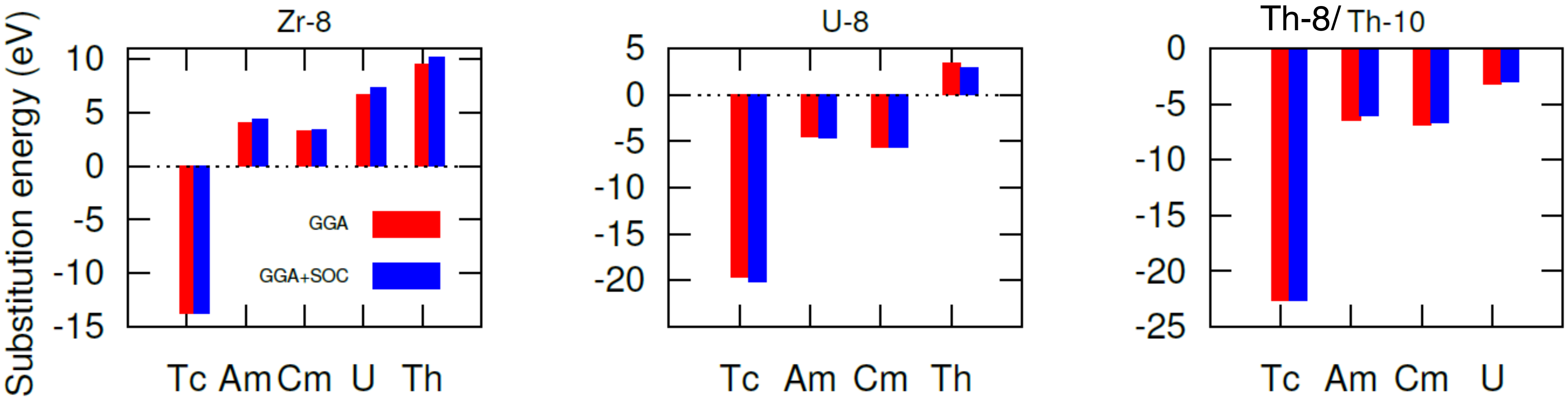
Projection: Reciprocal space

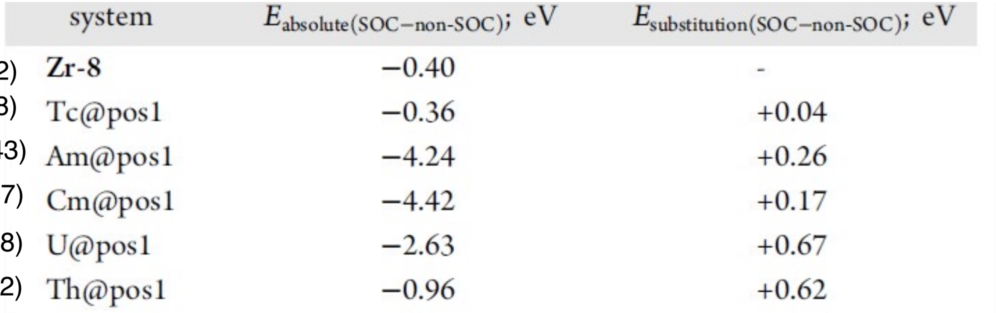
Title: * (U3C4O12H2

Magnetism: Spin-orbit magnetic

Effect of spin-orbit coupling on substitution energies

Substitution energies at position 1 in Zr-, U-, and Th-MOFs



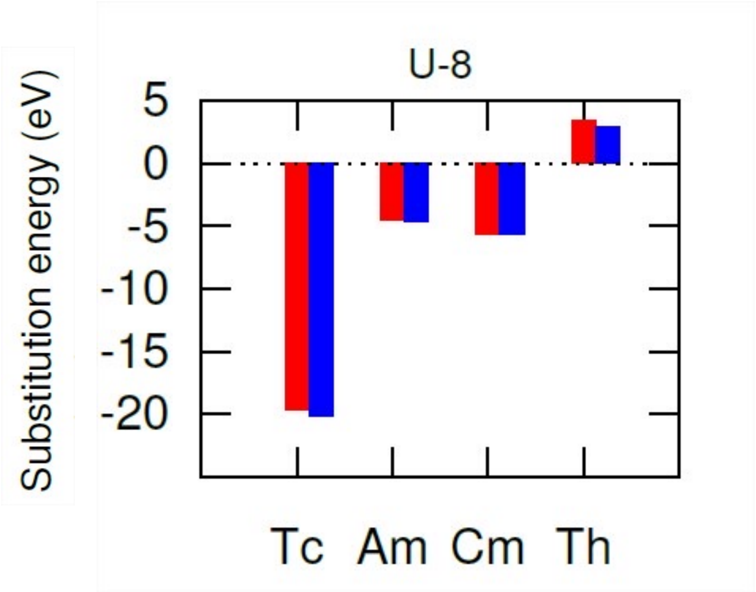


	system	$E_{\text{absolute(SOC−non-SOC)}}$; eV	$E_{\text{substitution(SOC−non-SOC)}}$; eV
(92)	**Zr-8**	−0.40	-
(98)	Tc@pos1	−0.36	+0.04
(243)	Am@pos1	−4.24	+0.26
(247)	Cm@pos1	−4.42	+0.17
(238)	U@pos1	−2.63	+0.67
(232)	Th@pos1	−0.96	+0.62

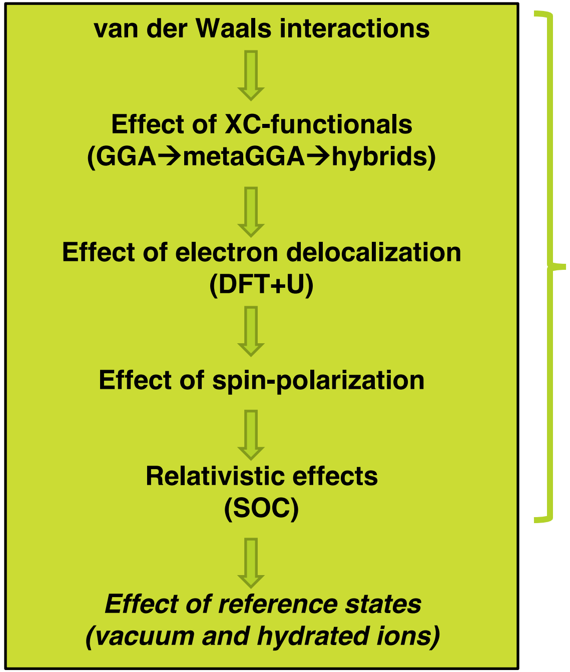
Total energy reduction with SOC depends on atomic mass of the ions

Favorability of substitution independent of SOC

Ion-Exchange Robust with DFT Methods



Abnormally high magnitude of substitution energies



van der Waals interactions

⇩

Effect of XC-functionals (GGA→metaGGA→hybrids)

⇩

Effect of electron delocalization (DFT+U)

⇩

Effect of spin-polarization

⇩

Relativistic effects (SOC)

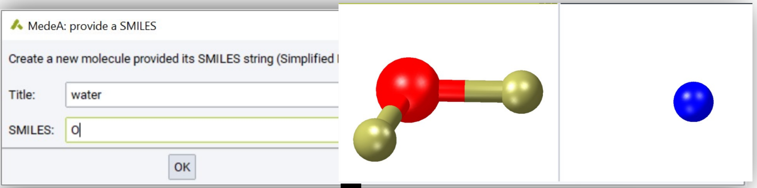
⇩

Effect of reference states (vacuum and hydrated ions)

ions in vacuum

Building ion-water complex

Step-1: build molecule with SMILES

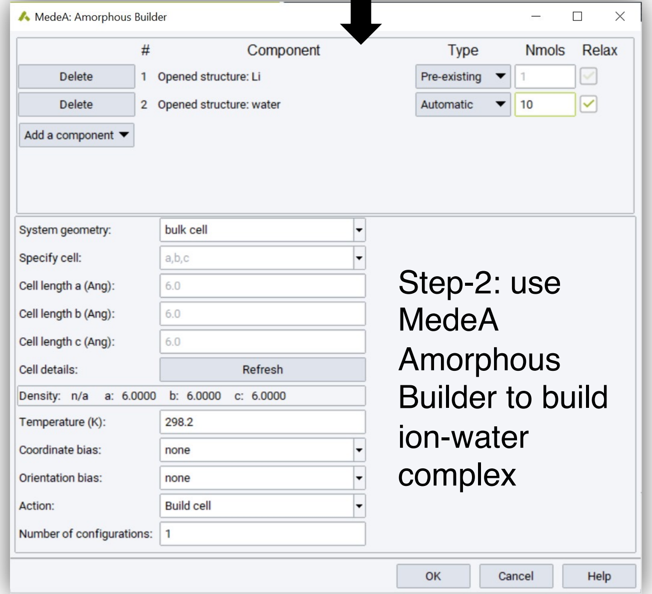


MedeA: provide a SMILES

Create a new molecule provided its SMILES string (Simplified

Title: water

SMILES: O



MedeA: Amorphous Builder

	#	Component	Type	Nmols	Relax
Delete	1	Opened structure: Li	Pre-existing	1	☑
Delete	2	Opened structure: water	Automatic	10	☑

System geometry: bulk cell
Specify cell: a,b,c
Cell length a (Ang): 6.0
Cell length b (Ang): 6.0
Cell length c (Ang): 6.0
Cell details: Refresh
Density: n/a a: 6.0000 b: 6.0000 c: 6.0000
Temperature (K): 298.2
Coordinate bias: none
Orientation bias: none
Action: Build cell
Number of configurations: 1

Step-2: use MedeA Amorphous Builder to build ion-water complex

Cation surrounded by 10 water molecules

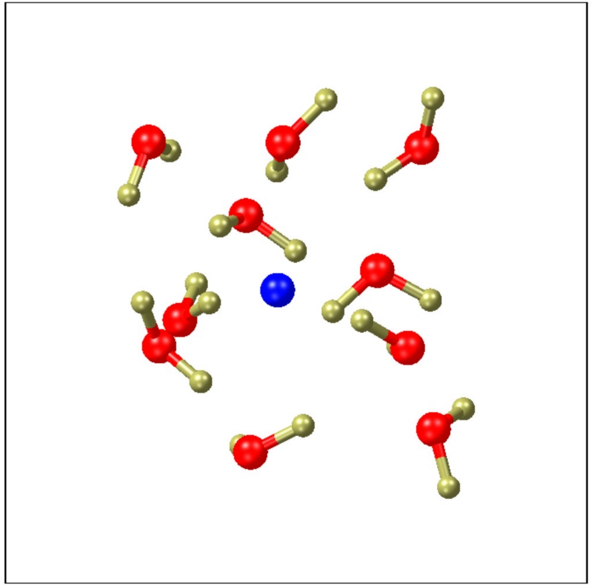
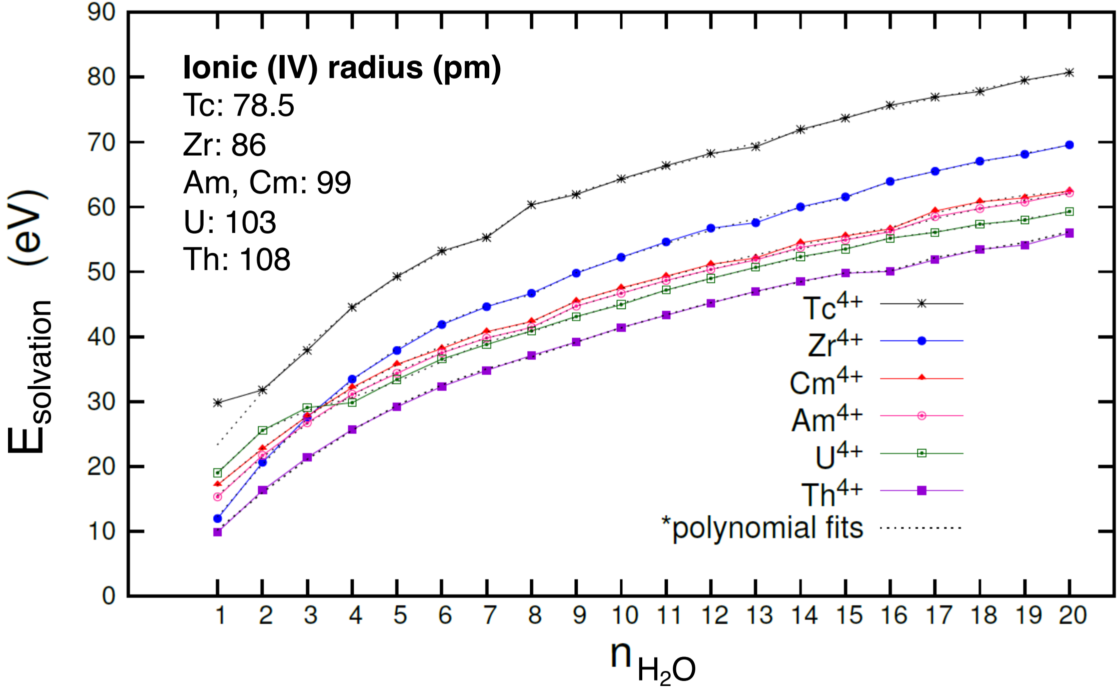


Image-charge correction (dipole correction) taken into account within VASP

Dependence of solvation energies on number of water molecules around the ion

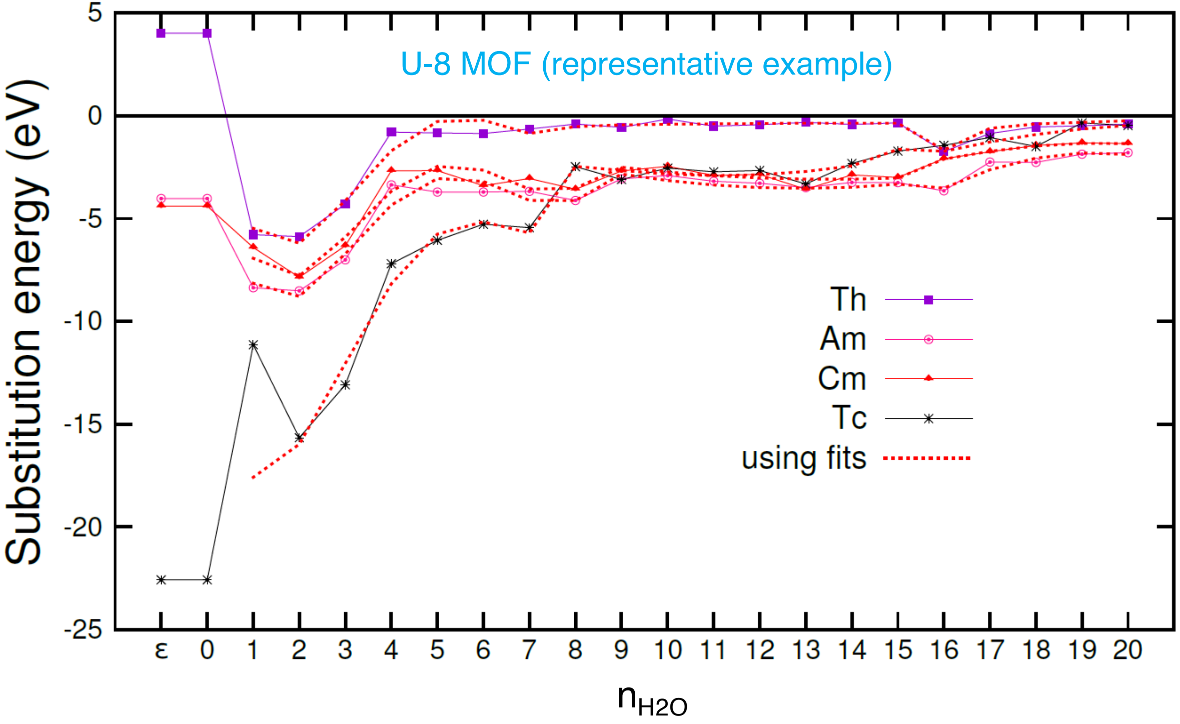
$$E_{\text{solvation}} = E(\mathrm{M}^{4+}) + nE(\mathrm{H_2O}) - E\{\mathrm{M}(\mathrm{H_2O})_n^{4+}\}$$

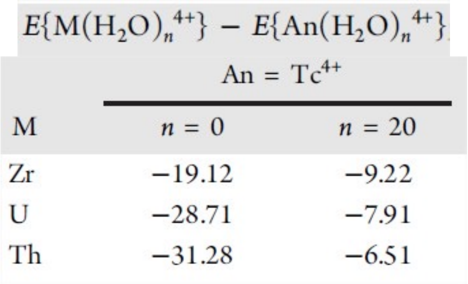


- Solvation energies continuously increase with the number of water molecules
- Total energies of these cation-water complexes will be used for substitution energies

Effect of Cation Reference States on Substitution Energies

Determine most suitable cation-water complex



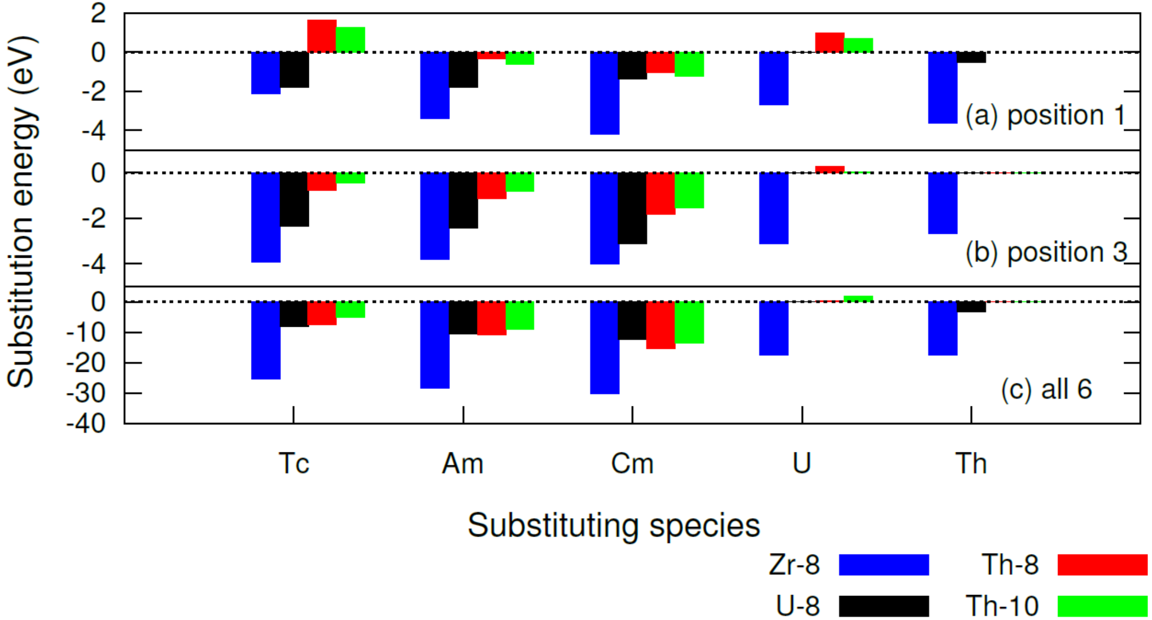


$E\{M(H_2O)_n^{4+}\} - E\{An(H_2O)_n^{4+}\}$

	An = Tc^{4+}	
M	$n = 0$	$n = 20$
Zr	−19.12	−9.22
U	−28.71	−7.91
Th	−31.28	−6.51

Hydrated cations lowers substitution energies significantly

Substitution energies calculated with $\{M(H_2O)_{20}^{4+}\}$



Experimental results[1]

Transmetalation of U-MOF with Th: feasible

Transmetalation of Th-MOF with U: infeasible

All MOFs can sequester Tc, Am, Cm, Th.

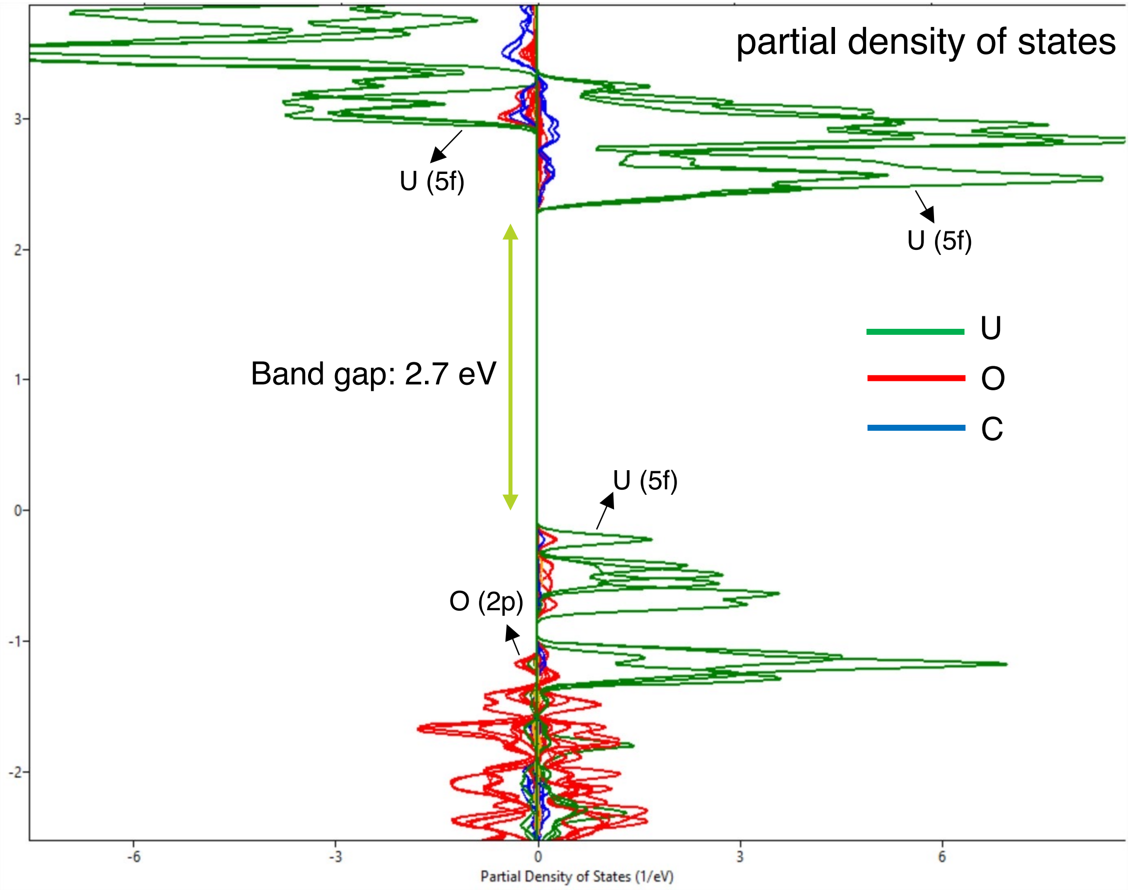
Only Zr-8 MOF can sequester U.

[1] Ejegbavwo et al., J. Am. Chem. Soc. **2019**, 141, 11628-11640

Electronic Structure of MOFs

Pandey et al., *Comp. Mater. Sci.*, **184** (2020)

U-MOF: Mott-Insulator



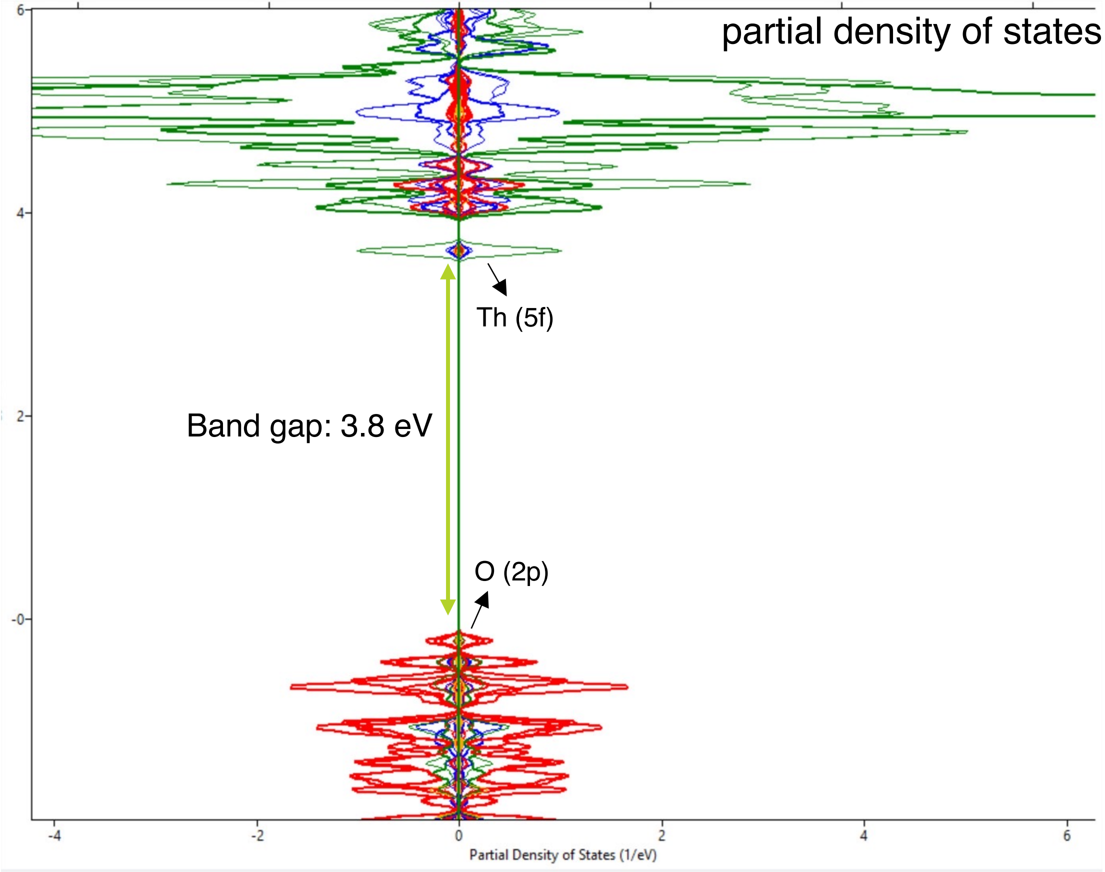
VBM to CBM:
U (5*f*) to U (5*f*) transition

Dependent on

DFT+U
Spin-polarization

materials design

Th-, Zr-MOF: Ligand-to-Metal Charge Transfer Insulator

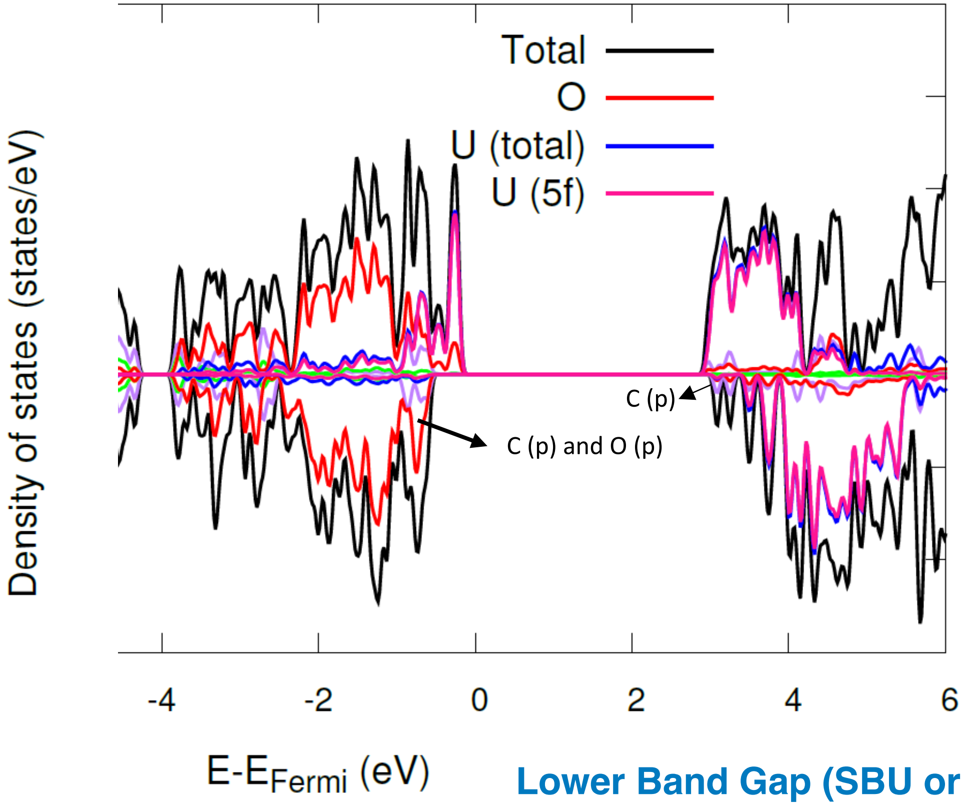


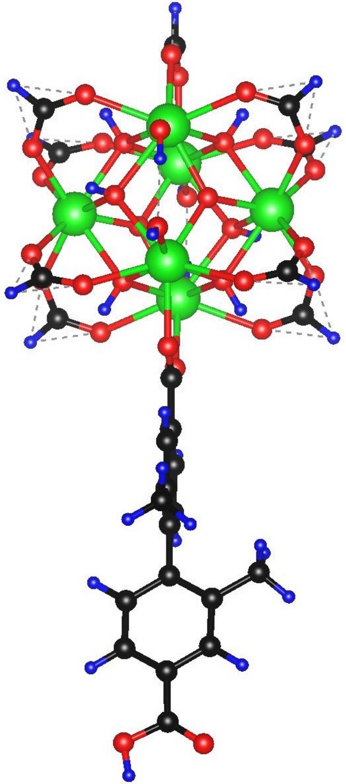
VBM to CBM:
O (2*p*) to Th (5*f*) transition

Independent of

DFT+U
Spin-polarization

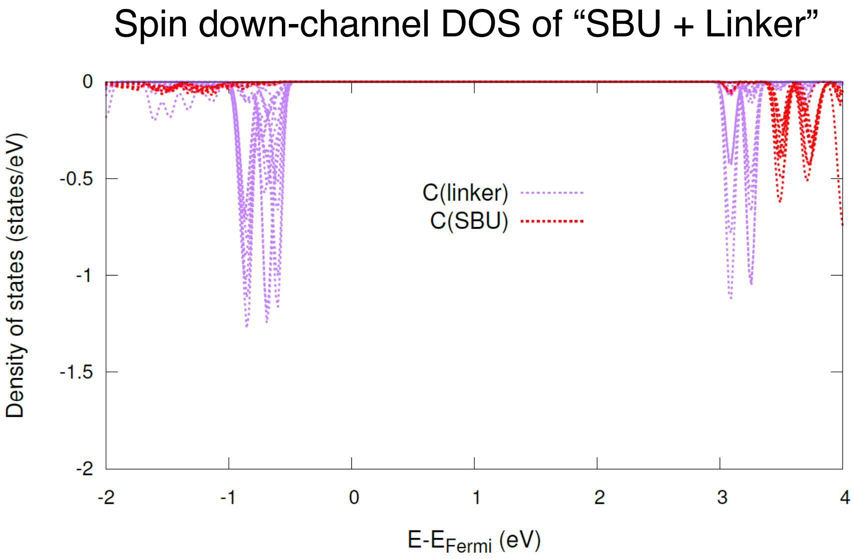
Effect of linker on electronic structure of MOF

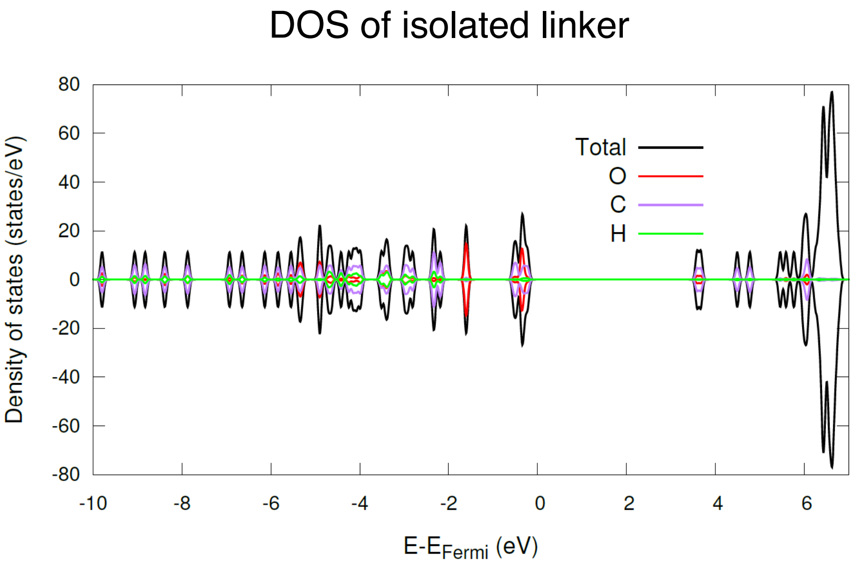




Lower Band Gap (SBU or linker) determines the band gap of MOF

Effect of linker on electronic structure of MOF: closer look on down spin channel





Identical down spin channel of "SBU+linker" and isolated linker

Summary

- Favorability of substitution at metal-nodes robust with DFT methods
- Tc substitution most favorable in all the MOFs

Future work

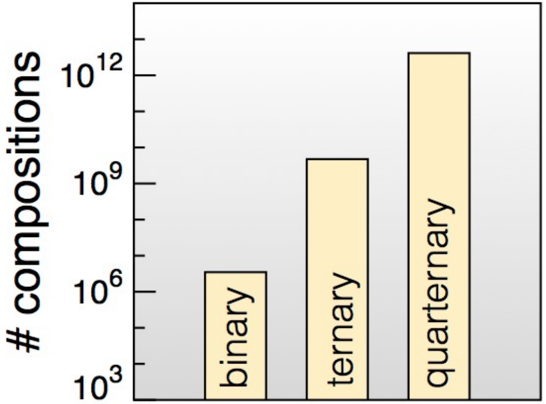
- Solvents such as *N,N*’–dimethylformadide (DMF) can be used as a reference state
- Pores of the MOFs can be investigated to capture the radionuclides

Graph Neural Network (GNN) for Total-Energy and Phase Stability Prediction

Conceptional investigation

Discovering New Compounds in Unexplored Chemical Spaces

Combinatorial phase space

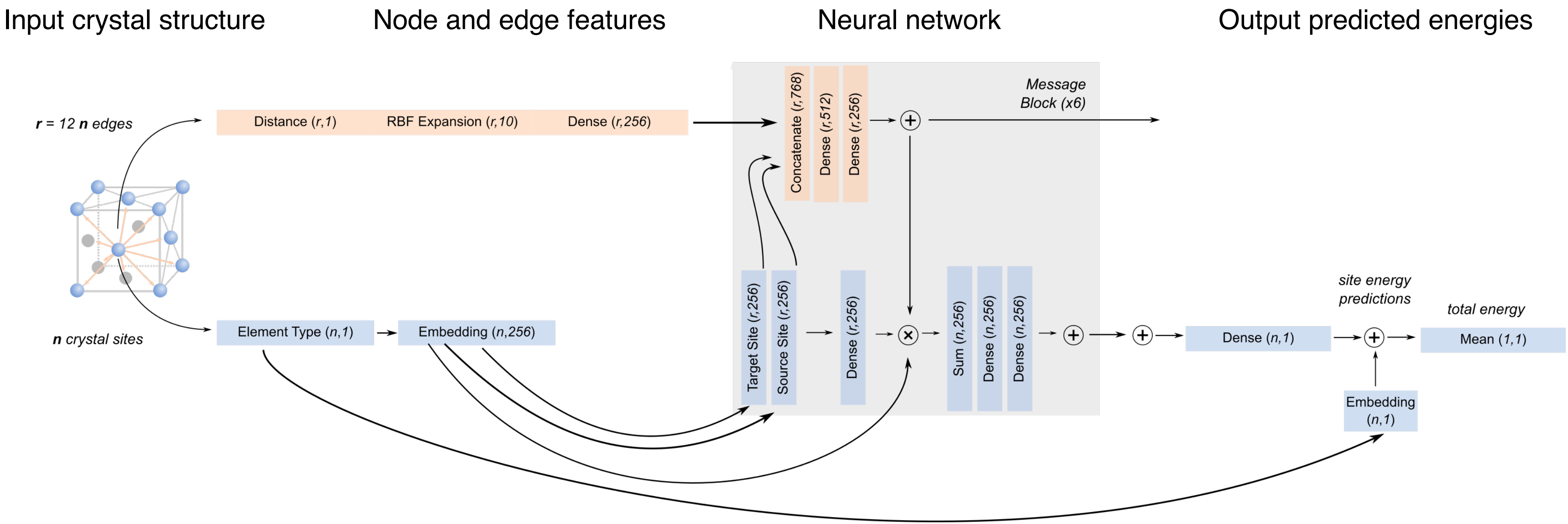


Davies Walsh et al., ***Chem.*** 1 (2018)

- Crystal structure prediction methods use quantum mechanical calculations to evaluate total energy
  - Computationally expensive
  - Ground-state (GS) structure needs to be distinguished from high-energy structures
- Existing crystal graph neural network models to predict total energy trained on GS/near-GS structures[1,2] or energy ranking of structures is unknown[3]

[1]Xie et al., *Phys. Rev. Lett.* **120** (2018), [2]Chen et al., *Chem. Mater.* **31** (2019), [3]Park et al., *Phys. Rev. Mater.* **4** (2020)

Crystal Graph Convolutional Neural Network Architecture



Pandey et. al, *Patterns* **11** (2021)

Training Data: DFT Total Energy of ICSD, Hypothetical Structures

- Total energy of ICSD structures from NREL Materials Database (materials.nrel.gov)
  - 14,000+ ordered, stoichiometric compounds
  - 3,800 mixed-anion compounds
  - Spans 60 elements


NREL

NATIONAL RENEWABLE ENERGY LABORATORY

High Performance Computing Center

Materials Database

NREL MatDB Home

- Hypothetical structures created by ionic substitution in ICSD prototypes[1,2]
  - 11,000+ hypothetical structures
  - 191 compositions spanning 24 elements

Type	**# Compositions**	**Example**
ABX	139	KZnBi
AX_4	18	$CdAs_4$
AX	15	NaSb
ABX_4	13	$NaGaAs_4$
AX_2	6	$CdBi_2$

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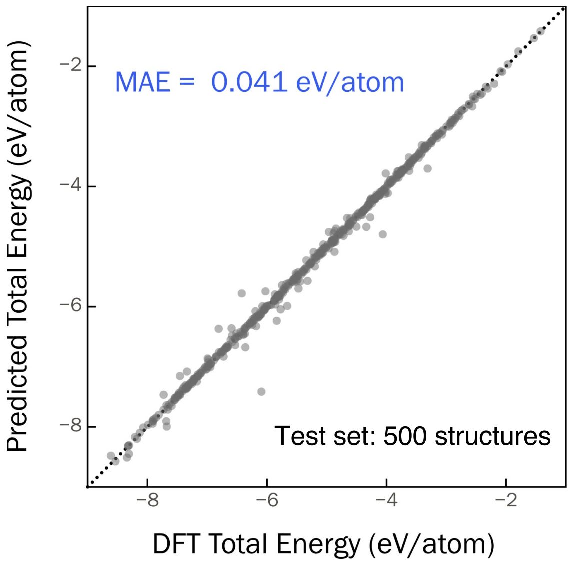
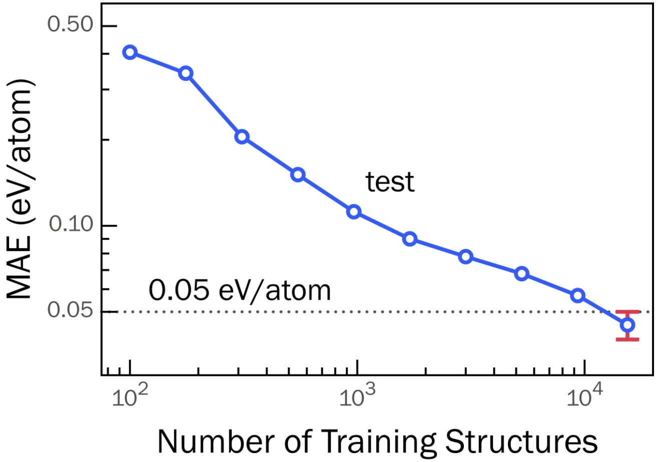
[1] Gorai et al., *Mater. Horizons* **7** (2020), [2] Qu et al., *J. Mater. Chem. A.* **8** (2020)

Model Predicts Energy of ICSD Structures with MAE < 0.05 eV/atom



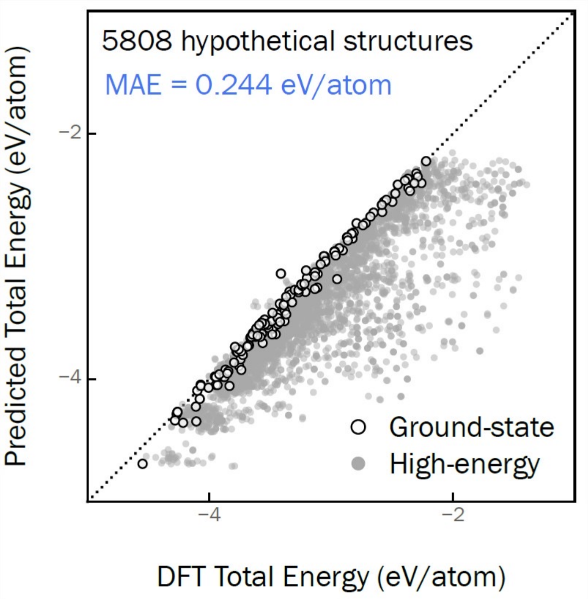


Model performance is comparable to existing models (MAE = 0.03-0.05 eV/atom)[1,2,3]

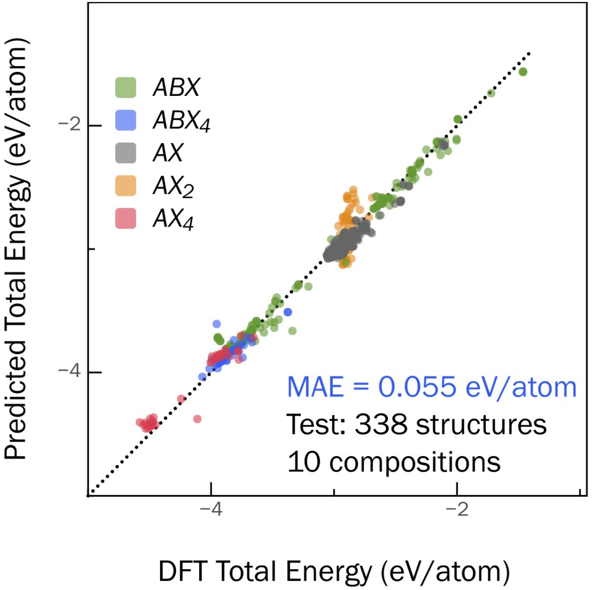
[1] Xie et al., *Phys. Rev. Lett.* **120** (2018), [2] Chen et al., *Chem. Mater.* **31** (2019), [3] Park et al., *Phys. Rev. Mater.* **4** (2020)

Energy of Hypothetical Structures is Severely Underpredicted

Performance of ICSD model on high-energy structures

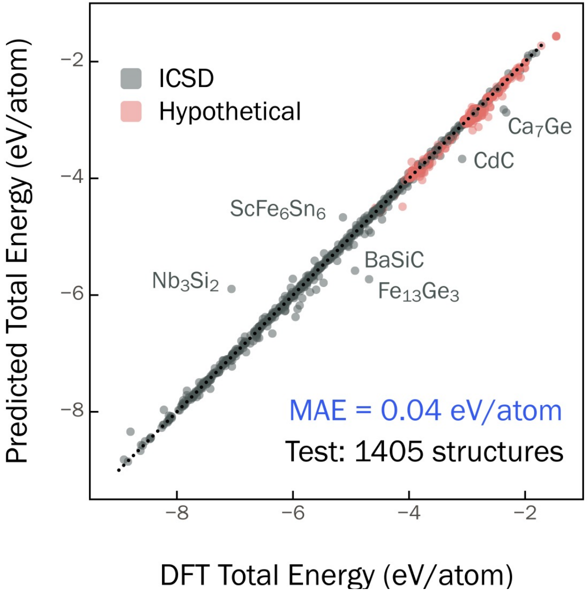


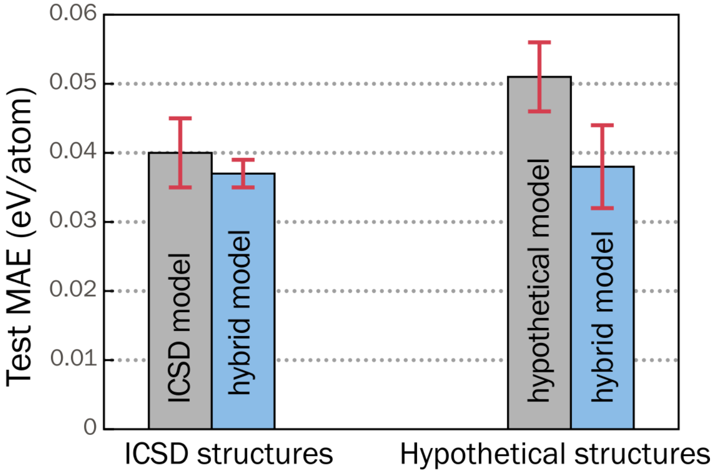
Model trained on hypothetical structures only



Model trained on hypothetical structures only performs poorly for ICSD structures: hybrid model is needed

Hybrid Model to Predict Energy of ICSD *and* Hypothetical Structures

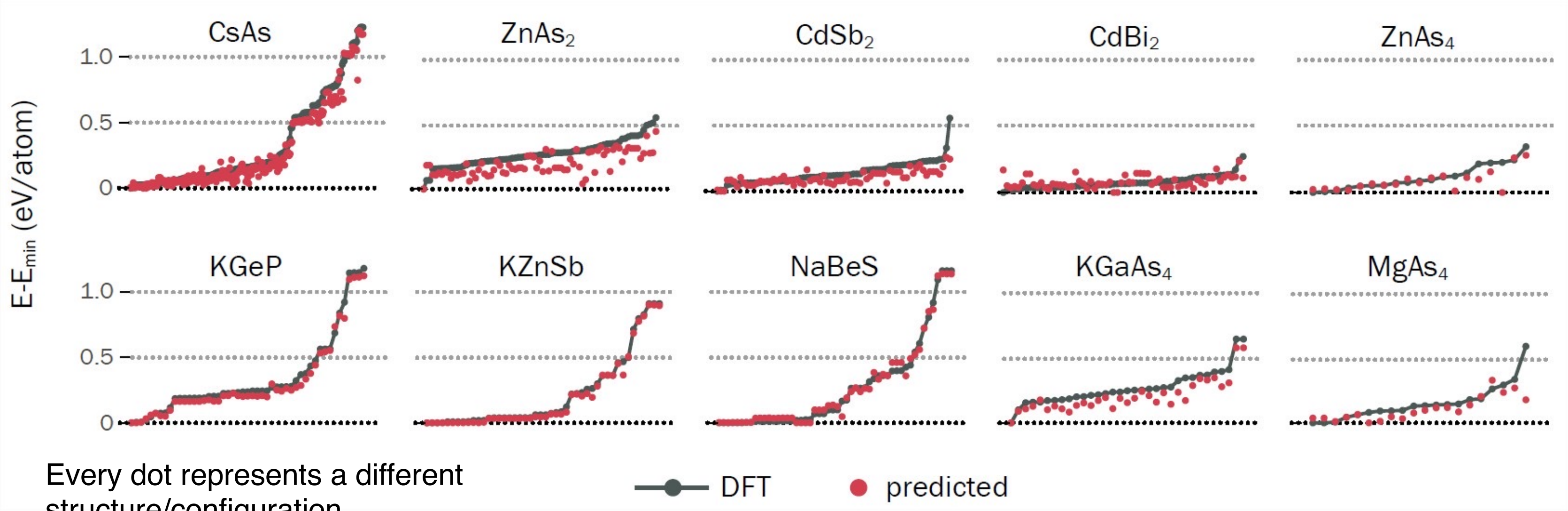




Hybrid model predicts energy of ICSD *and* hypothetical structures with MAE = 0.04 eV/atom

https://github.com/shubhmsme93/hybrid_cgcnn

Hybrid Model: Satisfactory Energetic Ranking of Structures for Given Composition

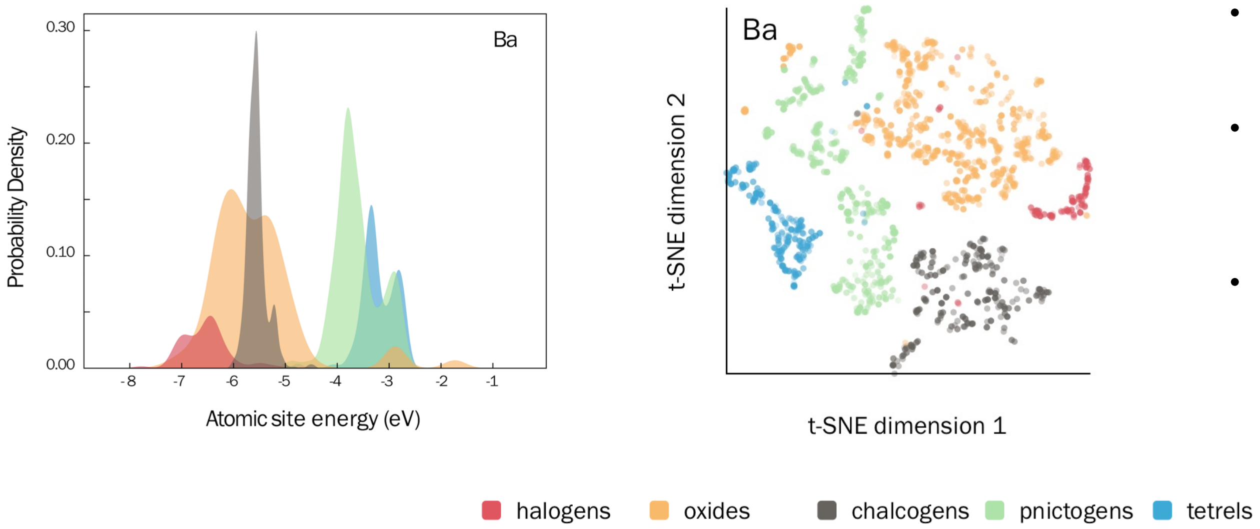


Every dot represents a different structure/configuration

Adding more under-represented compositions can improve their ranking further

Chemical Trends from Analyzing Atomic Site Energies

In GNN, the total energy of a crystal is partitioned into individual atomic site contributions. Aggregate analysis of atomic site energies reveal chemical trends.



- T-distributed stochastic neighbor embedding (tSNE)
- Offers an additional dimension; compared with 1-D site energy distribution
- Lowers the dimensionality (often to 2 dimensions) and preserves the relationship between samples

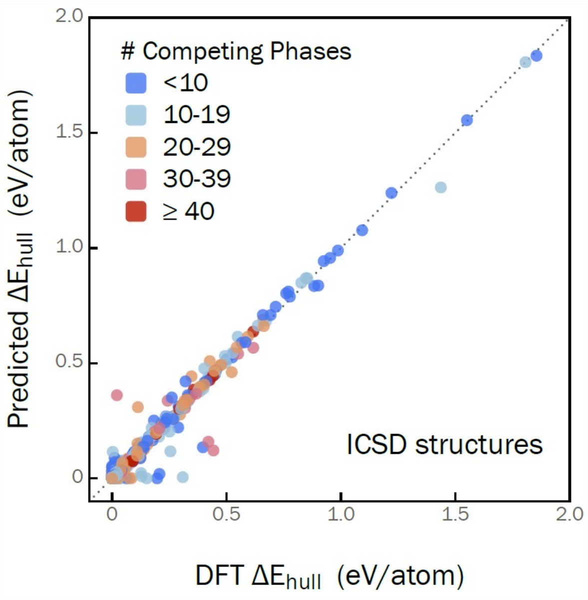
Anions: halides (F, Cl, Br, I), oxides and chalcogenides (O, S, Se, Te), pnictides (N, P, As, Sb, Bi), tetrels (Si, Ge, Sn, Pb)

https://github.com/shubhmsme93/tsne_pca

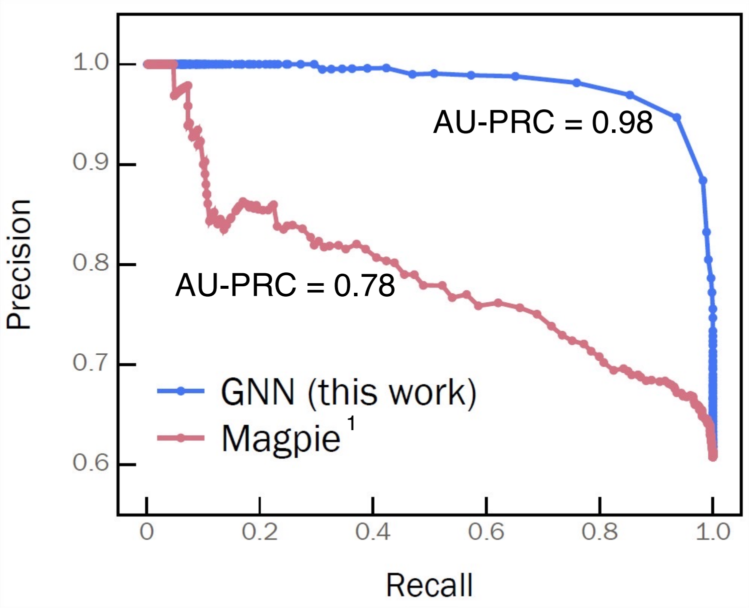
materials design

Model Reliably Predicts Thermodynamic Phase Stability

Energy above hull calculated w.r.t. competing phases in ICSD



Precision-recall curve



[1]Ward et al., npj Comp. Mater. 2, 1-7

- **Convex hull analysis is performed using the formation enthalpy of all competing phases**
- **Composition-only based models biased towards GS structures**

materials design

Summary

- Developed crystal graph neural network to predict total energy of GS and high-energy structures with satisfactory energy ranking of structures.
- Predicted phase-stabilities consistent with DFT.
- Expansion of the dataset of hypothetical structures to include additional elements.
- Future work: evaluate total-energies of unrelaxed hypothetical structures