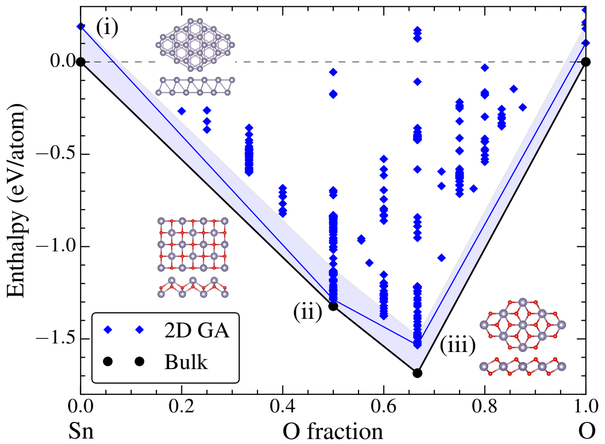
Search of Energy Landscapes by Evolutionary Algorithms and Data Mining

Richard G. Hennig, University of Florida

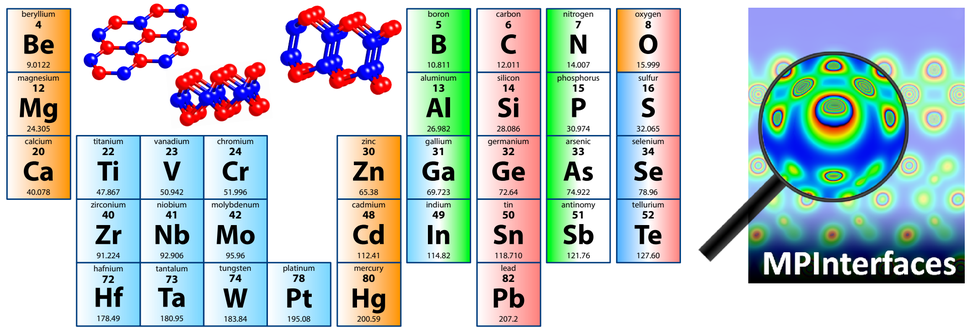
Structure and Energy Landscapes

- Structure representation
- Features of energy landscapes
- Structure searches for 2D materials by datamining, chemical substitution, and evolutionary algorithms

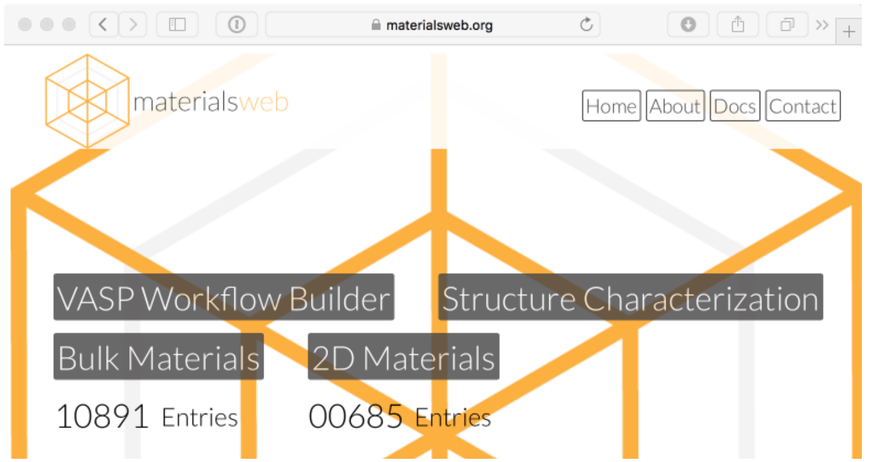


GASP - Genetic algorithm and machine learning for structure predictions

MPInterfaces - High throughput framework for 2D materials



Data available at http://materialsweb.org



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Open source available at https://github.com/henniggroup

Acknowledgment

- MPInterfaces for novel 2D materials: **K. Mathew**, **A. Singh**, **M. Ashton**, **J. Paul**, **D. Gluhovic**, **H. Zhuang**, J. Gabriel, M. Blonsky, M. Johannes, R. Ramanathan, R. Duan, Z. Ziyu
- VASPsol solvation model and nanocrystals: K. Mathew, J. Gabriel, C. Bealing
- GASP genetic algorithm and machine learning: **B. Revard**, **W. Tipton**, **A. Yesupenko**, B. Antonio, S. Honrao
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- Computational resources provided by HiPerGator@UF and NSF XSEDE

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Part I: The Energy Landscape

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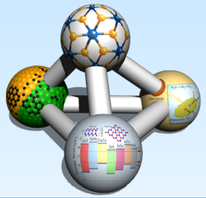
Materials Structure Space



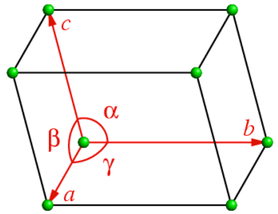
Mixed representation of materials structure space (real space representation)

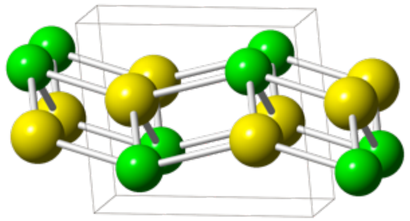
Real variables:

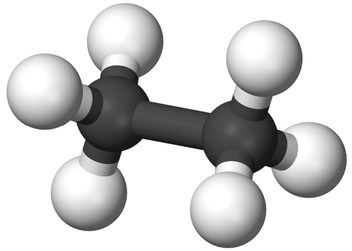
- Atom positions
- Lattice parameters (for crystalline structures)

Integer variables:

- Number of atoms
- Atomic species







Dimensionality of materials structure space

- Determined by number of atoms: $3N_{atom} + 3$ for crystals, $3N_{atom}$ for molecules and clusters

Complexity of materials structure space

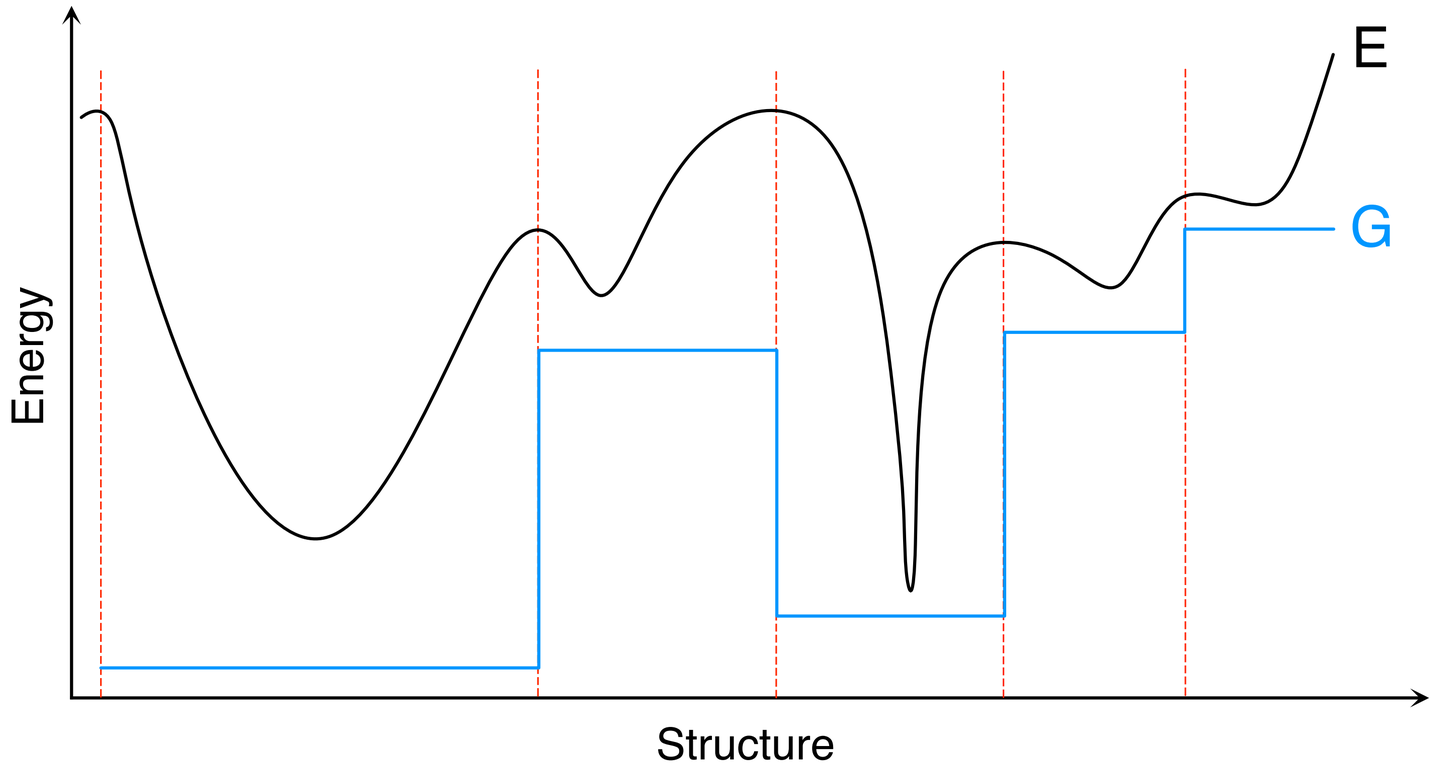
- Exponential increases with number of atoms and number of species
- Reduced by space and point group symmetries

Energy landscape space has continues and integer variables

Minimum Gibbs Free Energy Principle

Computational structure prediction based on optimization

- Stable structure at (p, T) ⇒ Lowest Gibbs free energy, $G(p, T) = E(V, S) - TS + pV$
- Gibbs free energy of a structure is an integral over the basin of the local minimum
  - Expensive to calculate
  - Difficult to explore due to discontinuities
  - Can contain minima not present in the energy landscape

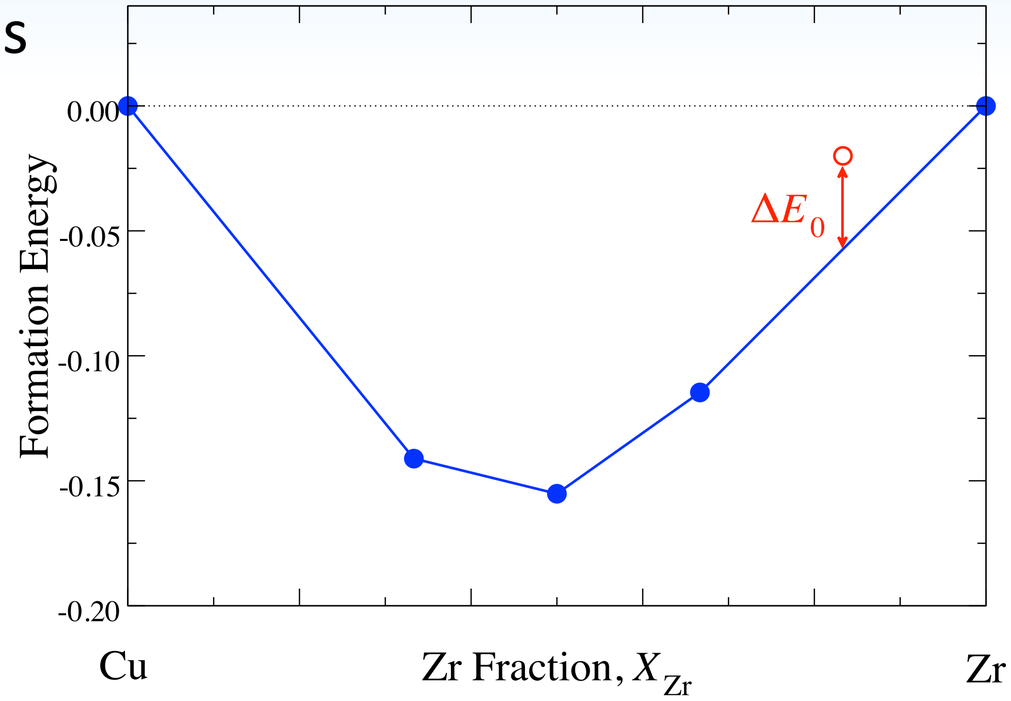


Free energy landscape space is discontinuous and difficult to search

Minimum Energy Principle

Computational structure prediction based on energy minimization

- Combined optimization over real and integer variables
- For multi-component materials, we need to consider stability against competing phases
  - ➡ Concept of convex hull



Energy methods

Interpolative
(Semi-)empirical methods

Extrapolative and predictive
First-principles or *ab-initio* methods

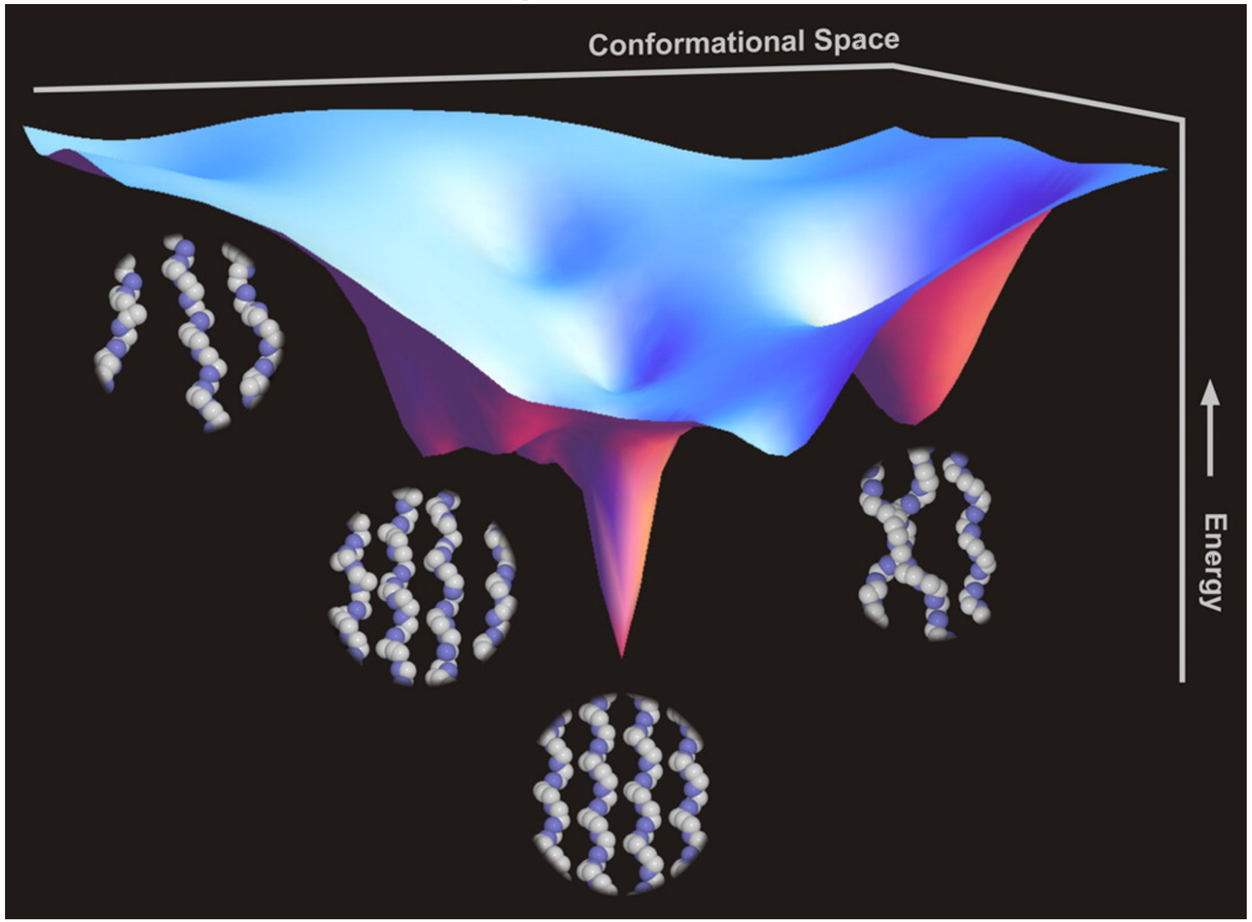
- Density-functional theory offers balance of speed and accuracy
- Pseudopotentials and plane-wave basis (VASP)

Structure for multi-component materials requires knowledge of competing phases

General Features of the Energy Landscape

Bell–Evans–Polanyi principle

- Highly exothermic chemical reactions have low activation energies
- Low-energy basins are expected to occur near other low-energy basins
- These regions are referred to as **‘funnels’**



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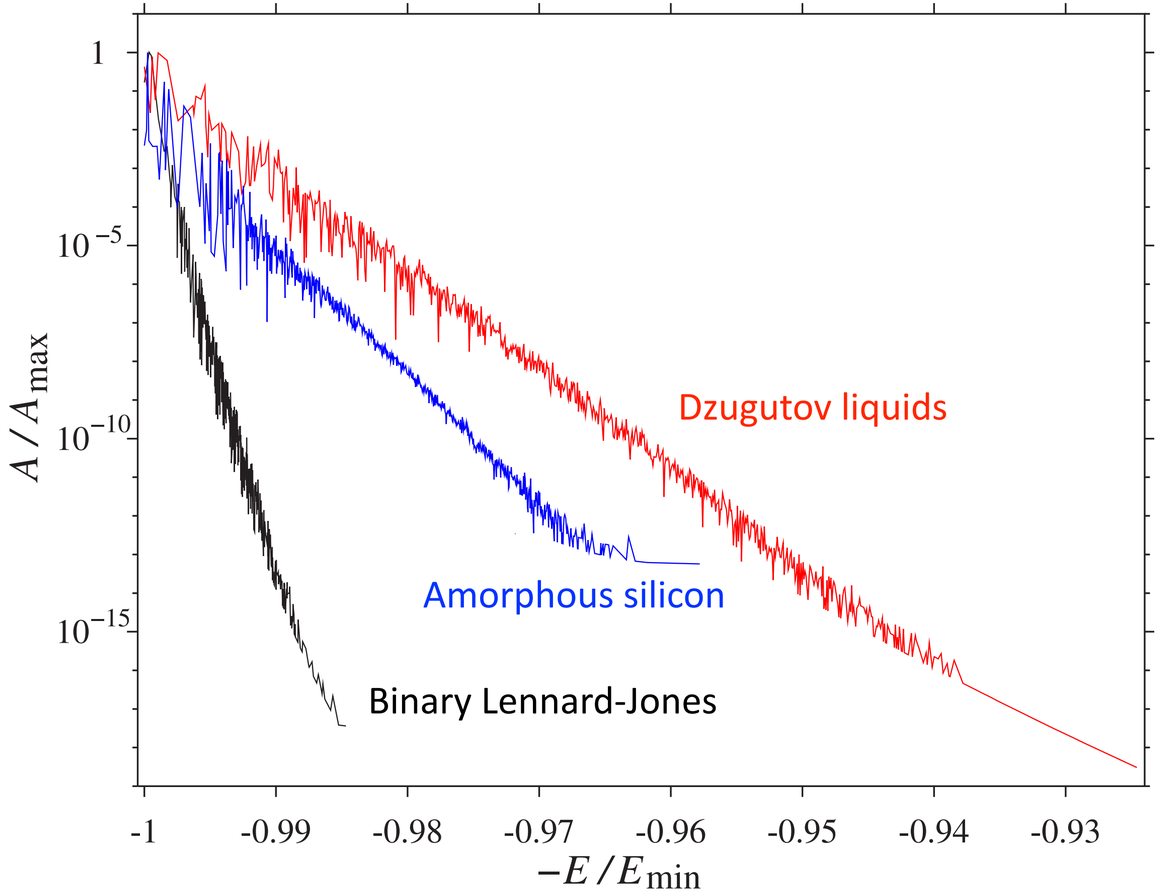
General Features of the Energy Landscape

Probability distribution of energies of local minima

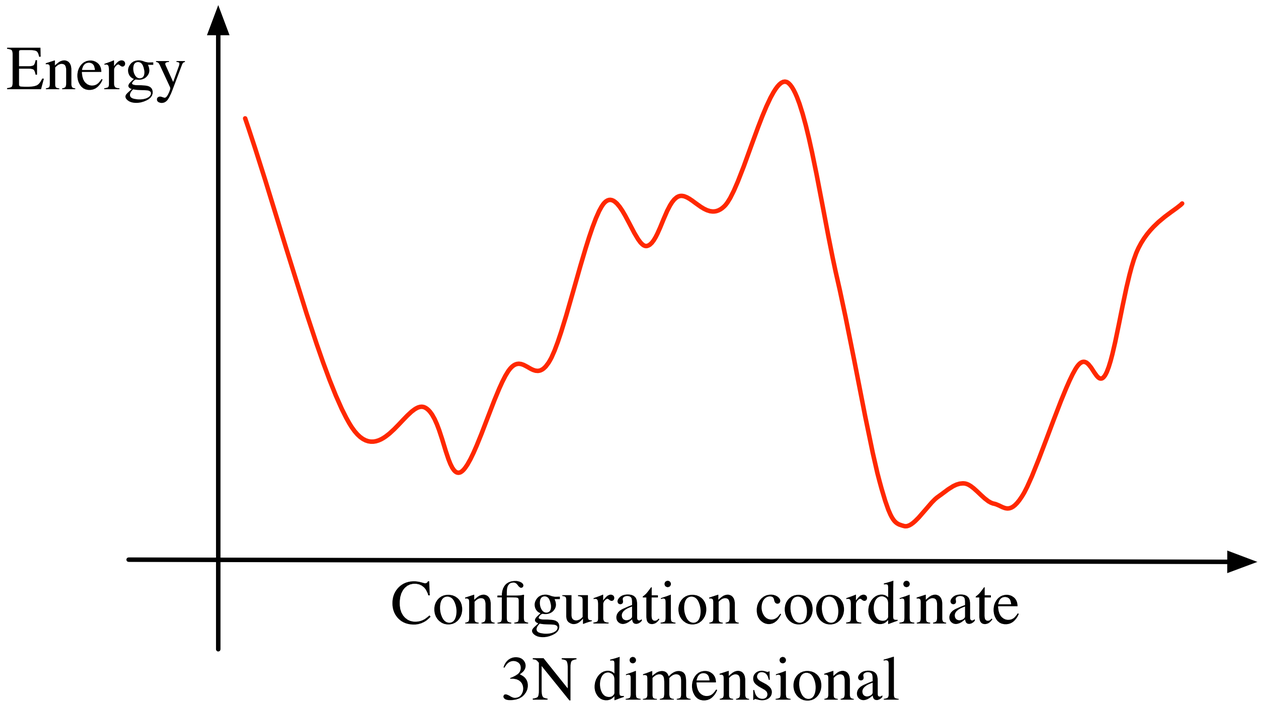
- Basins with lower-energy minima have larger hyper-volumes
- Related to similar elastic constants and vibrational frequencies for different structures
- Power law probability distribution of these hyper-volumes
- Order in the arrangement of basins of different sizes
- Smaller basins filling gaps between larger ones



Massen & Doye, Phys. Rev. E **75**, 037101 (2007)

Illustration of Energy Landscape

- 1D and 2D cuts through 3*N*-dimensional configuration space
- Not a good representation of the distribution of basins in 3*N* dimensions



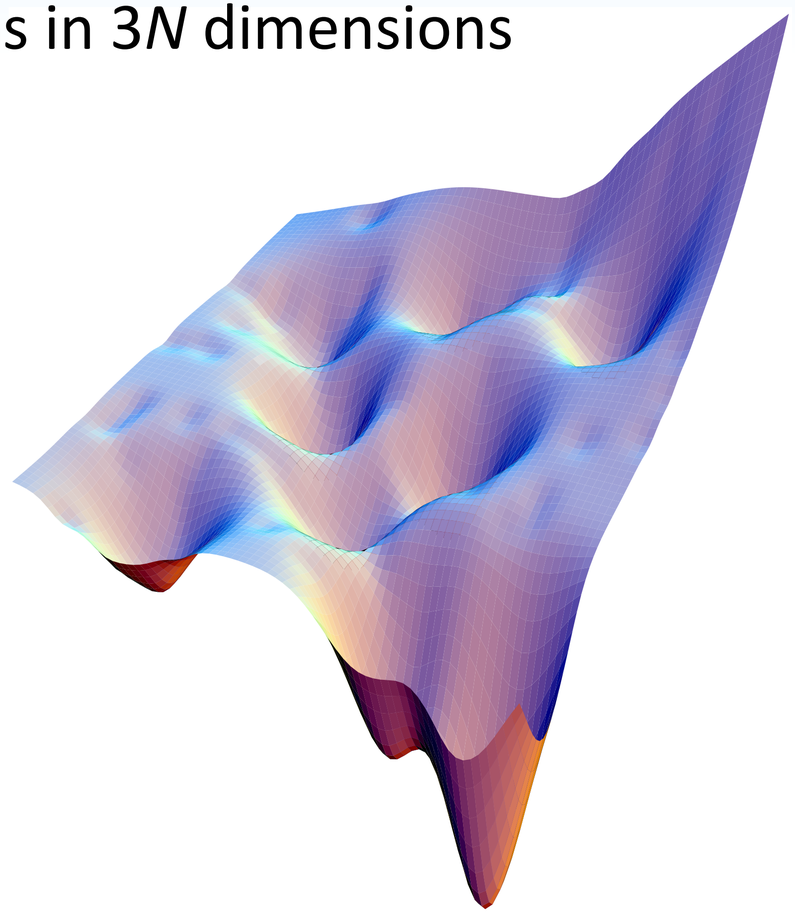


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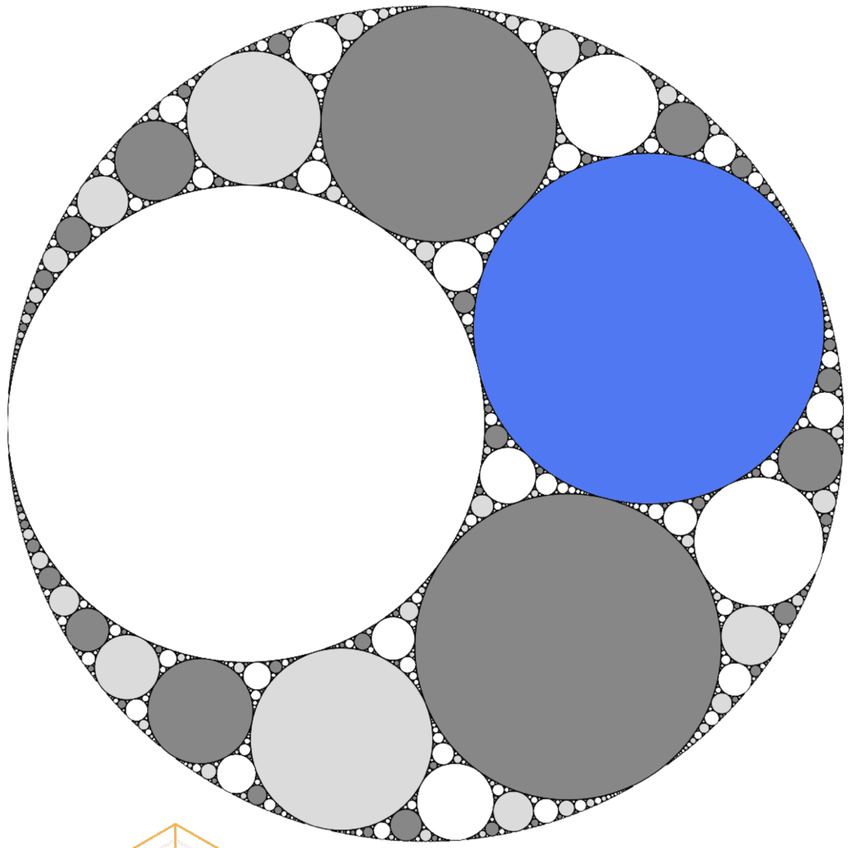
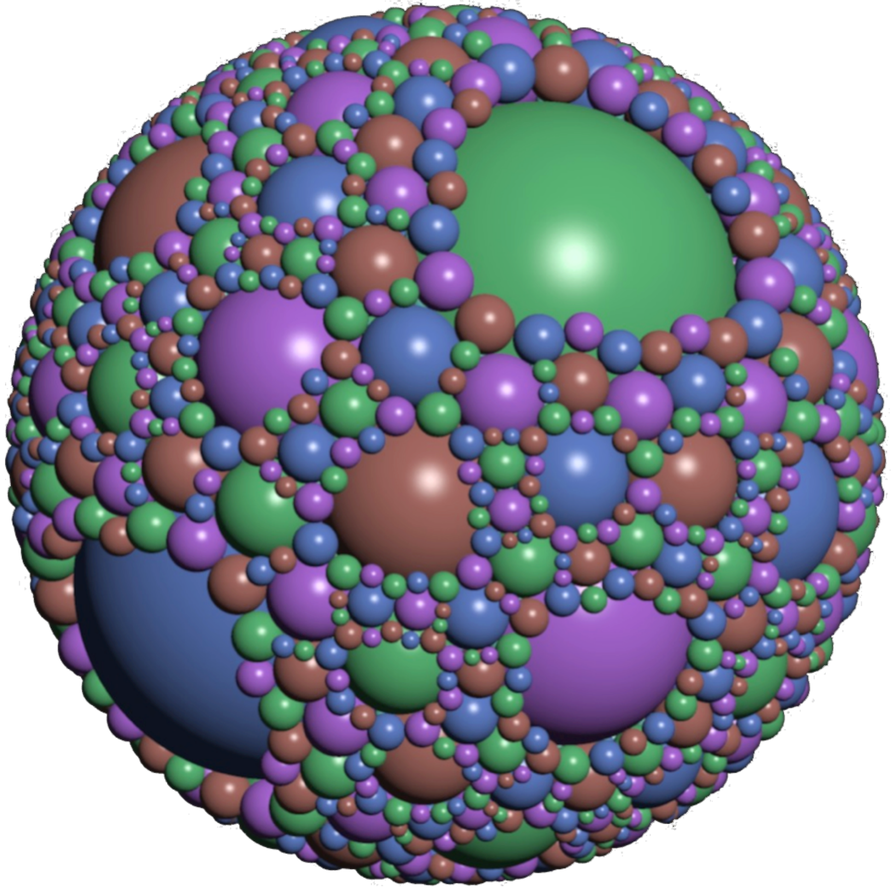
Illustration of Energy Landscape

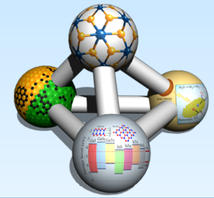
- 1D and 2D cuts through 3*N*-dimensional configuration space
- Not a good representation of the distribution of basins in 3*N* dimensions
- Similarities between Apollonian sphere packings and energy landscapes



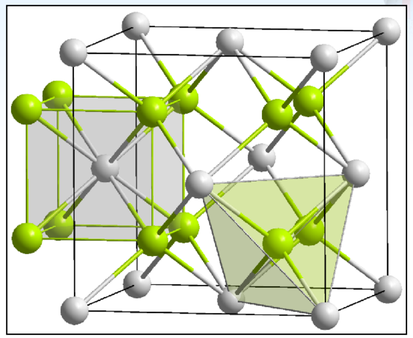


Doye & Massen Phys. Rev. E **71**, 016128 (2005)

Symmetry and Structural Motifs



The Rule of Parsimony: *"The Number of essentially different kinds of constituents in a crystal tends to be small."* (Linus Pauling 1929)

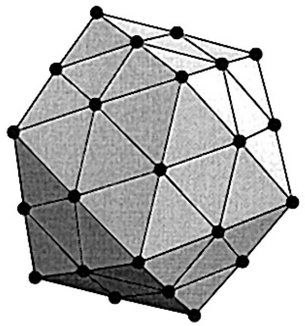


Correlation between energy and symmetry

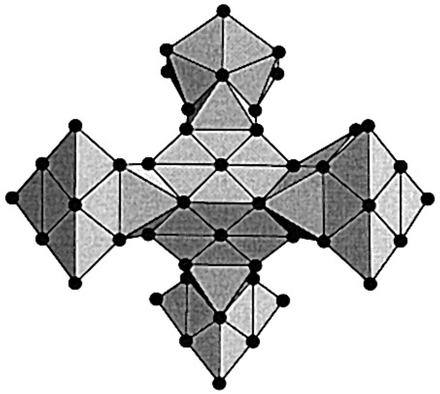
- Low (and high) energy minima tend to correspond to symmetrical structures
- High symmetry of low-energy minima supported by the ubiquity of crystals

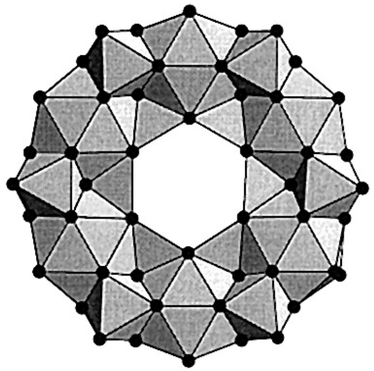
Example: 55-atom Lennard-Jones clusters (D. Wales '98)

Lowest energy



Two highest energy





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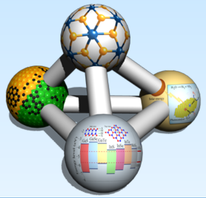
Frequency of Space Groups



For crystals of small organic molecules

- 75% of about 30,000 compounds occur in only five space groups
- 29 space groups only have one entry and 35 space groups none at all

Space Group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1$	$C2/c$
Frequency	36%	14%	12%	7%	7%

Inorganic systems show different space group frequencies

- 67% of about 100,000 compounds occur in only 24 space groups

Space Group	*Pnma*	$P2_1/c$	$Fm\bar{3}m$	$Fd\bar{3}m$
Frequency	7.4%	7.2%	5.6%	5.1%
Examples	Fe_3C, $CaTiO_3$	ZrO_2	Cu	C, Cu_2Mg

- Note: bcc is not among one of the top 24 space groups

Some space groups are much more common than others in crystals

Specific Features of Energy Landscapes

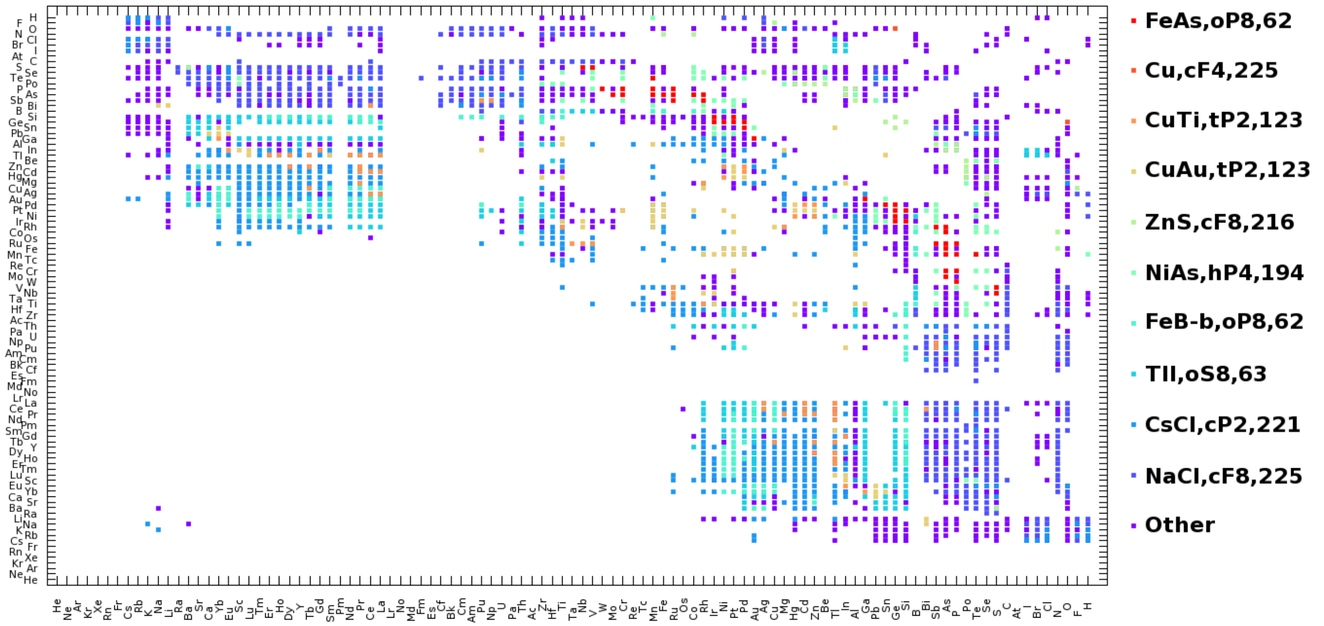
Chemical considerations

- Know a great deal about the chemistry of the systems we study
- Know which atomic types prefer to bond to one another
- Approximate bond lengths
- Likely coordination numbers of the atoms

Resulting empirical rules

- Hume-Rothery rules
- Laves rules for intermetallics
- Pauling rules for ionic materials
- Pettifor structure maps

...



How can we utilize this information to accelerate structure searches?

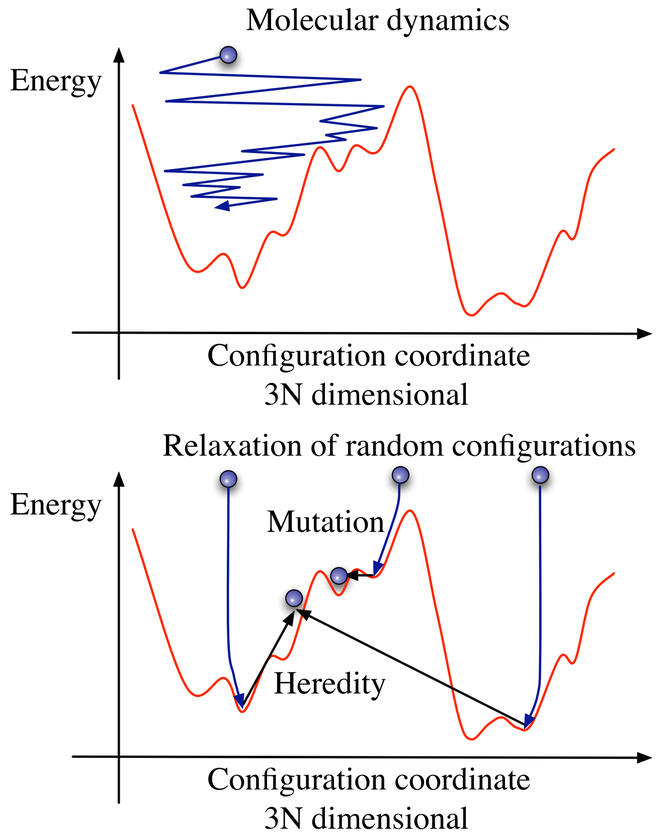
Structure Prediction Methods

Limited success of conventional optimization methods

- Guess of structures based on symmetry and chemistry (trial-and-error)
- Simulated annealing (molecular dynamics, cooling from high temperature)

Advances in optimization methods:

- **Accelerated molecular dynamics**, Voter *et al.* ’97
- **Metadynamics**, Parinello *et al*. ’02
- **Minima hopping**, search for neighboring minima, Goedecker ’04
- **Random search**, randomly sampling phase space, Pickard & Needs ’06
- **Evolutionary algorithms**
  Generation of structures, Bush *et al*. ’95, Woodley *et al*. ’99, Oganov ’06
- **Particle Swarm Optimization**, Ma *et al.* ’10
- **Datamining of structure databases**, Ceder *et al*.



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Part I: Discovery of 2D Materials

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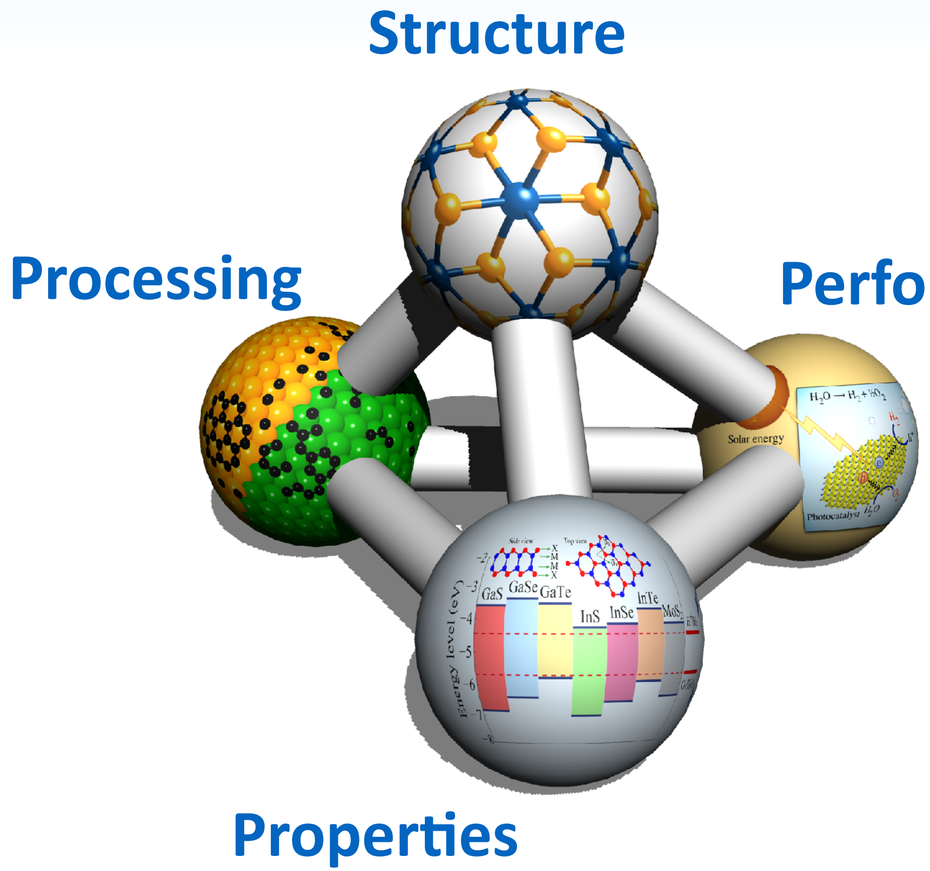
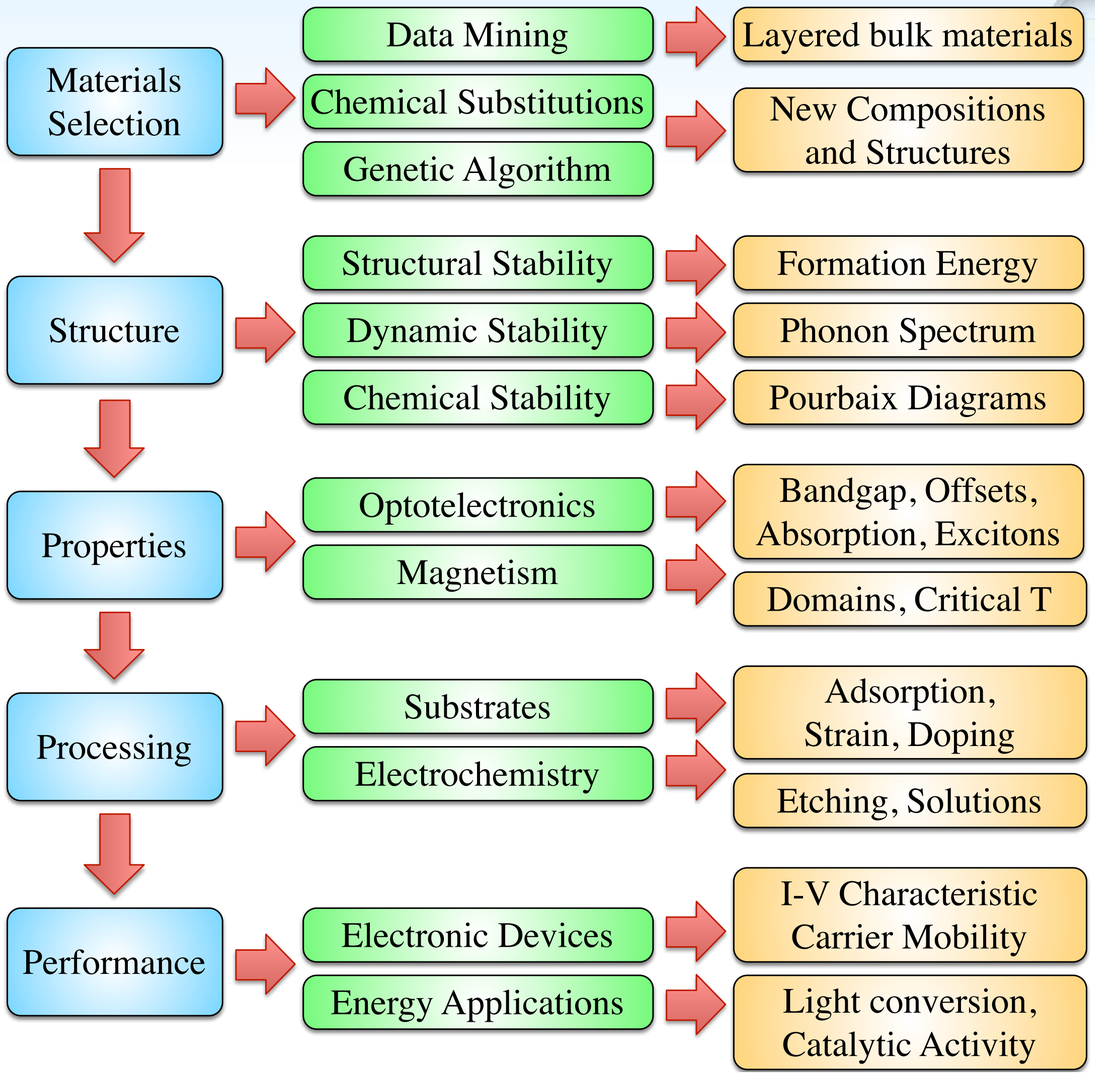
Materials Informatics of 2D Materials





H. L. Zhuang and RGH, JOM 66, 366 (2014)

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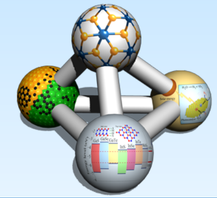

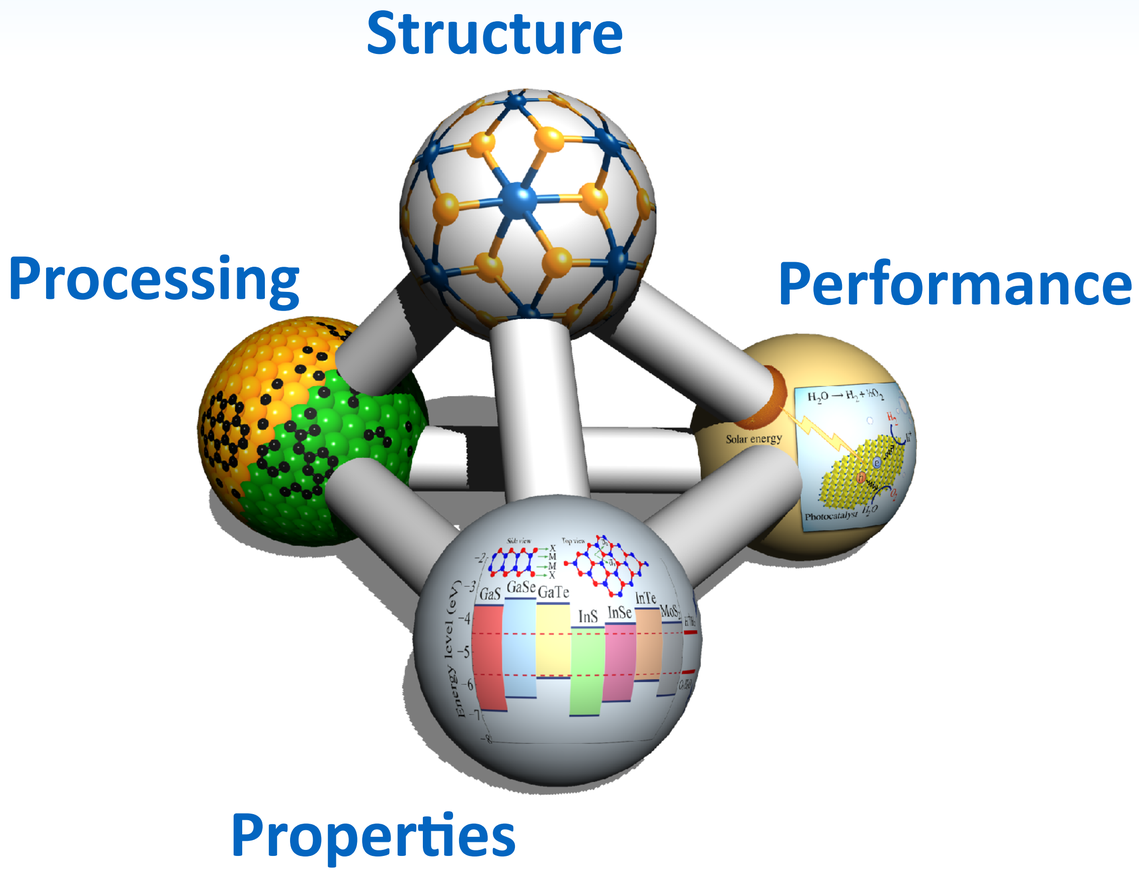

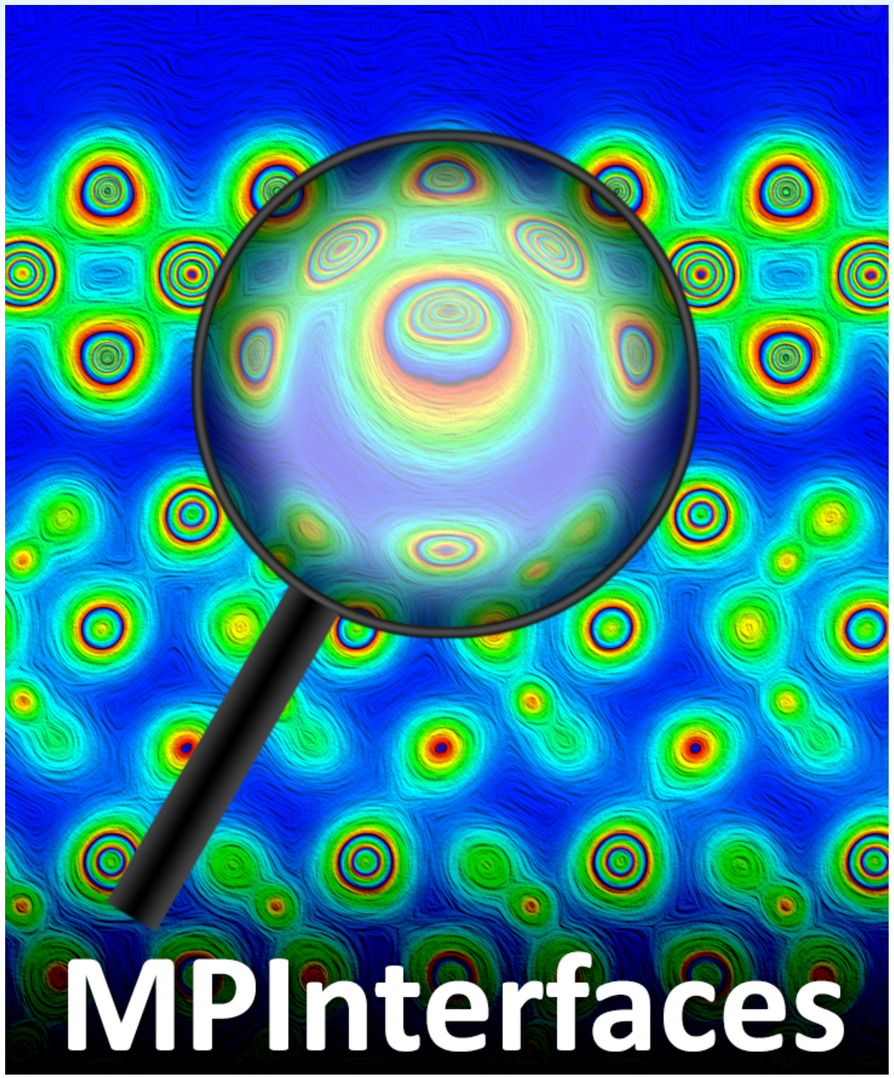

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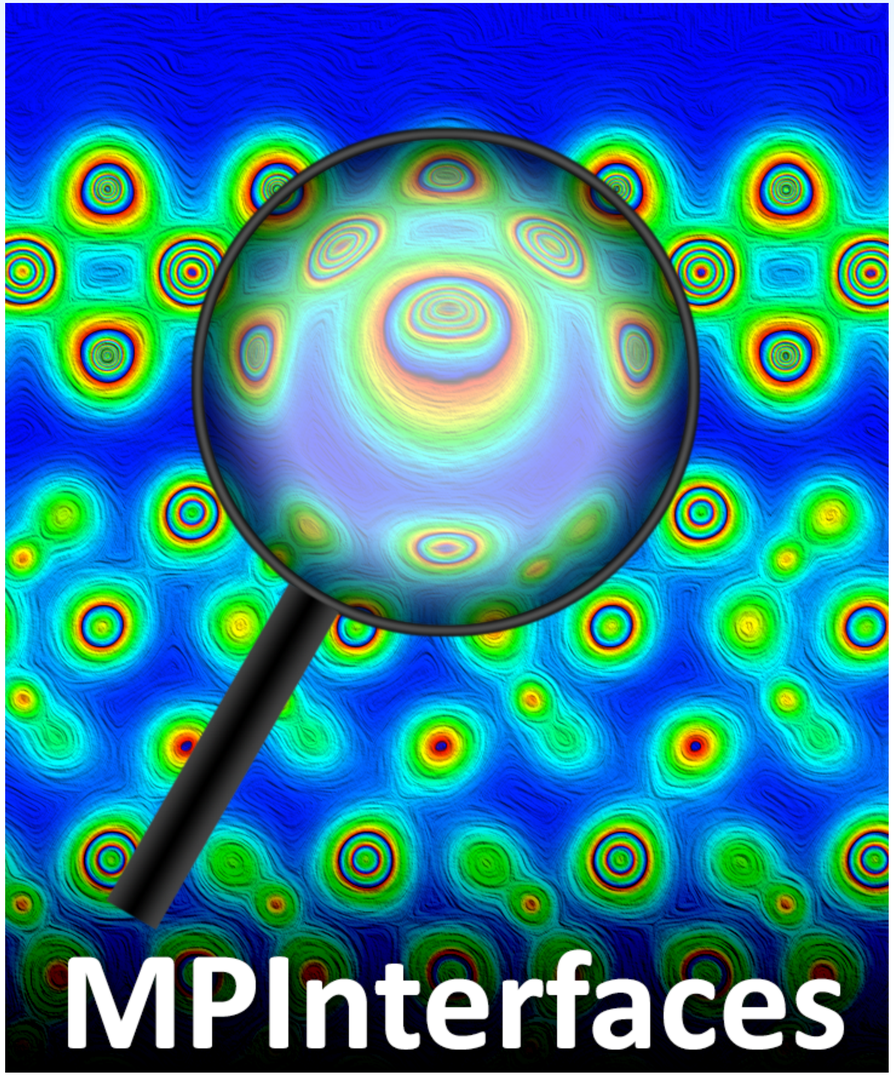
Structure and Stability of 2D Materials

- Classification of 2D materials
- Criteria for stability $\Delta E_f < 200$ meV/atom
- Methods for 2D materials discovery
  - Datamining for exfoliation
  - Chemical substitutions and etching
  - Evolutionary algorithm searches



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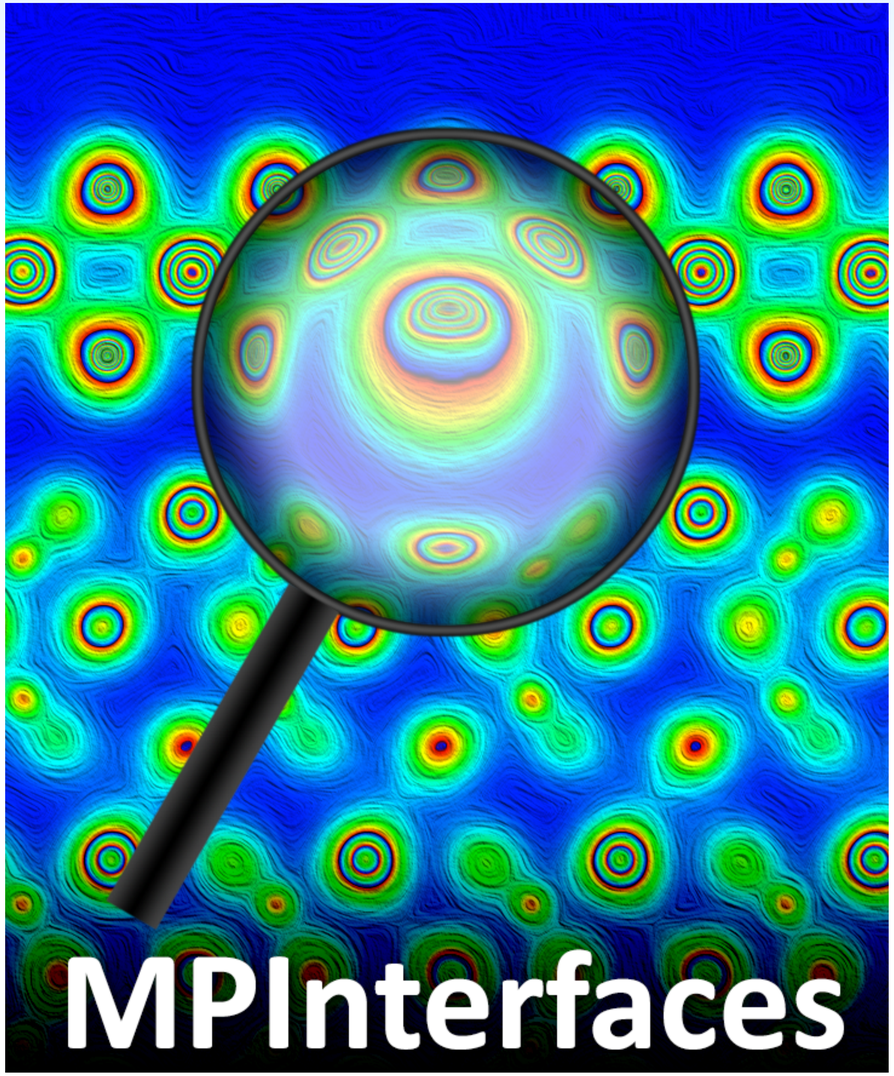

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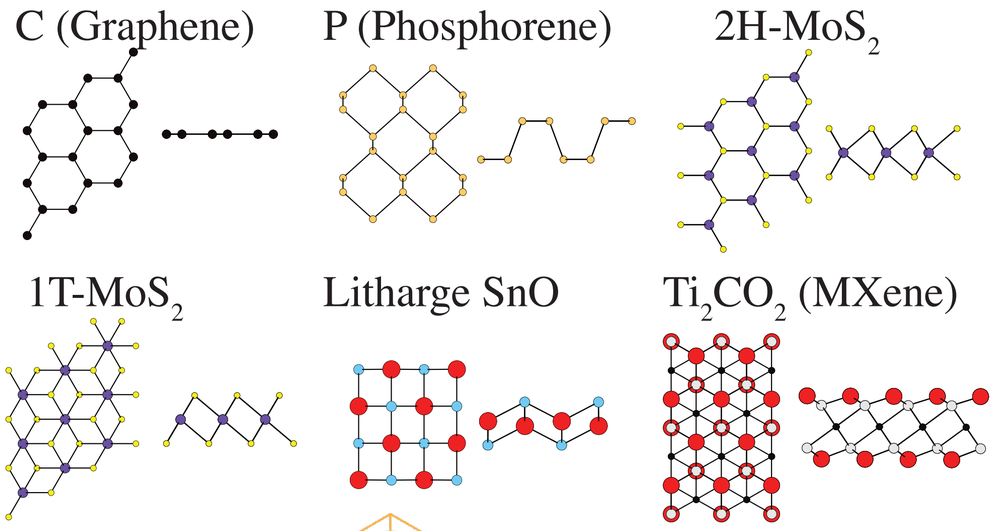
Classification of 2D Materials

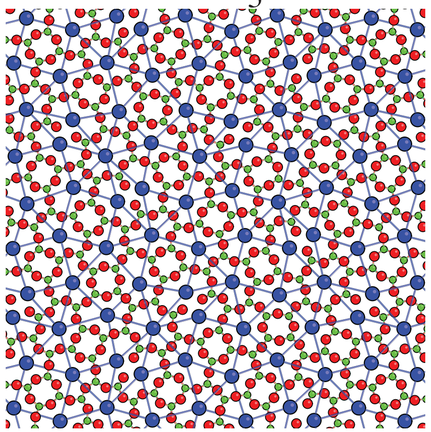
Definition: A 2D material is a material with finite thickness in one dimension and essentially infinite extent in the other two dimensions.

- Classification into crystalline and amorphous materials
- 2D crystals include **periodic** and **aperiodic** crystals based on point group
- Aperiodic 2D crystals include **incommensurate crystals** and **quasicrystals**

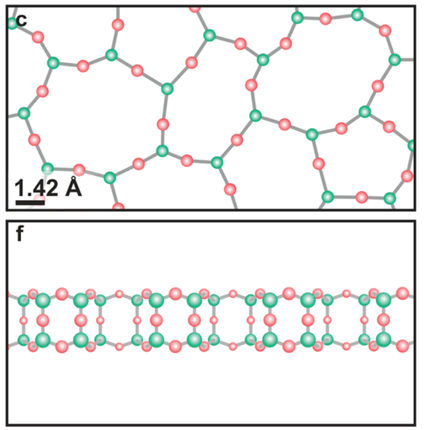
a) Crystalline 2D Materials



b) Quasicrystalline 2D $BaTiO_3$



c) Amorphous 2D SiO_2



Paul, Hennig, *et al*. submitted 2017

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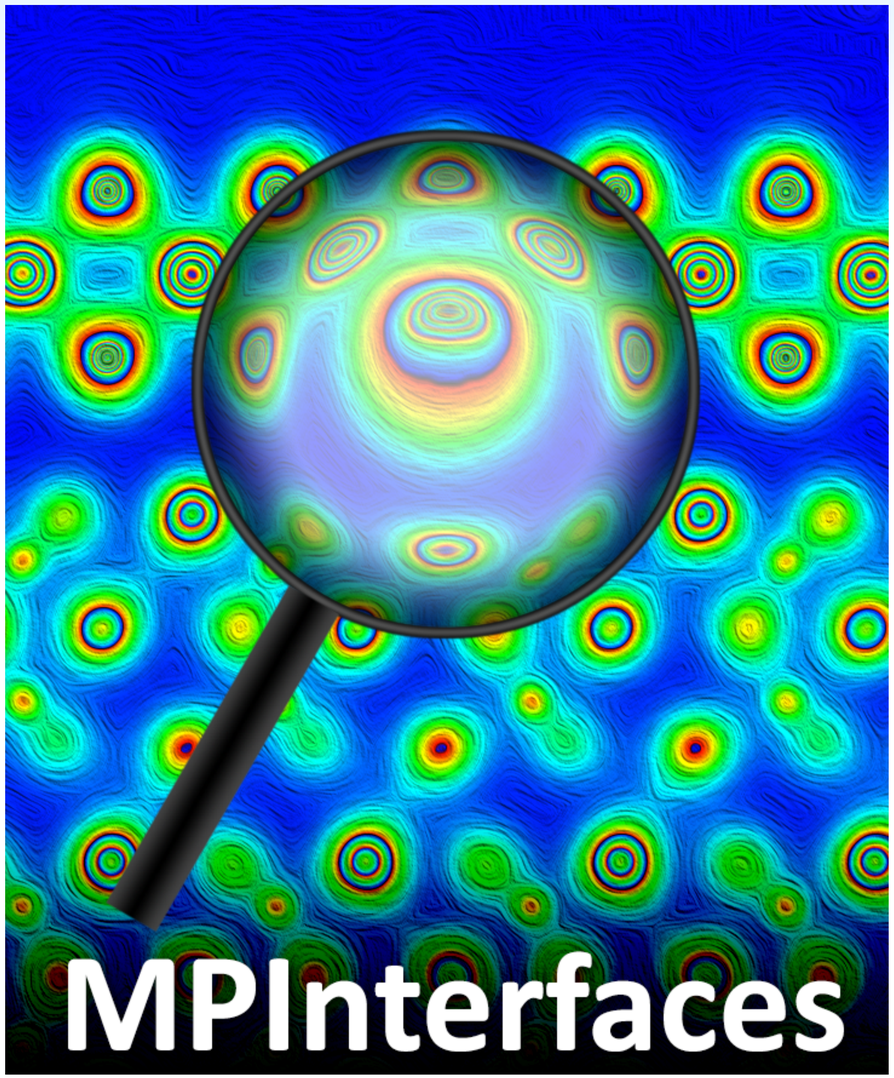


Thermodynamic Stability of 2D Materials

Formation energy

$$\Delta G_\mathrm{f} = G_\mathrm{2D} - \min_\mathrm{phases} G_\mathrm{3D}$$

$$\text{approximated by } \Delta E_\mathrm{f} = E_\mathrm{2D} - \min_\mathrm{phases} E_\mathrm{3D}$$

min over single or mixture of phases

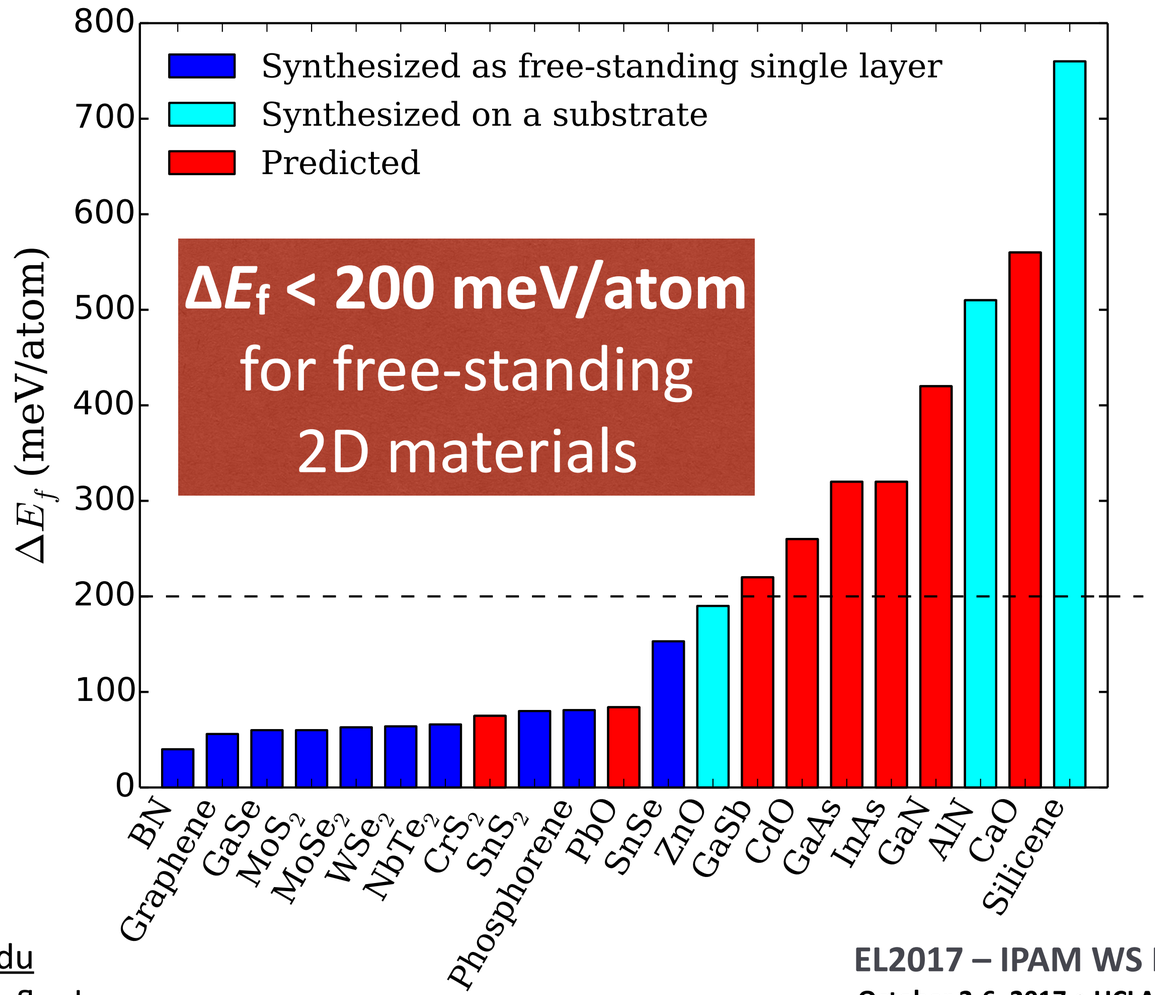
- Comparison of VASP PAW using vdW-DF optB88 with QMC and RPA shows accuracy of ΔE_f of 30 meV/atom

2D materials are metastable

- Energy can always be lowered by van der Waals interactions for multi-layers

Stabilization by substrates

- Substrates used to nucleate and grow 2D materials
- Stabilization through physi- and chemisorption



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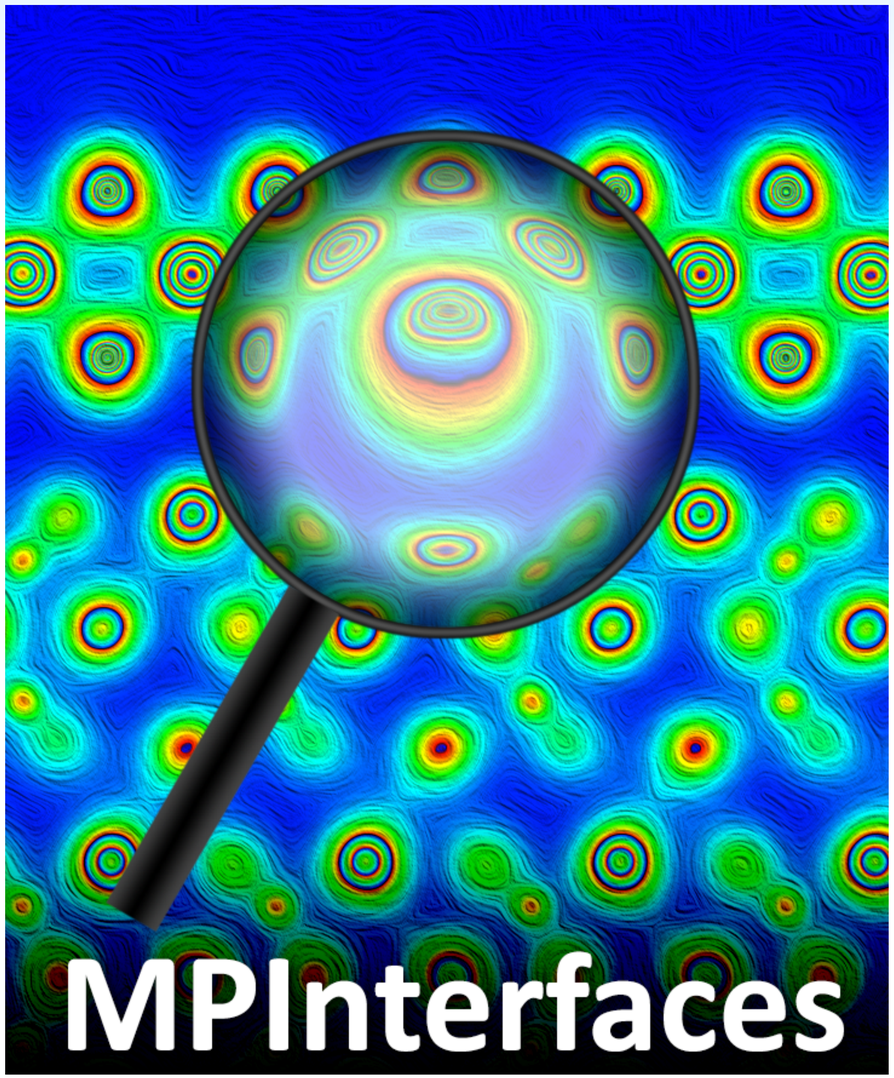
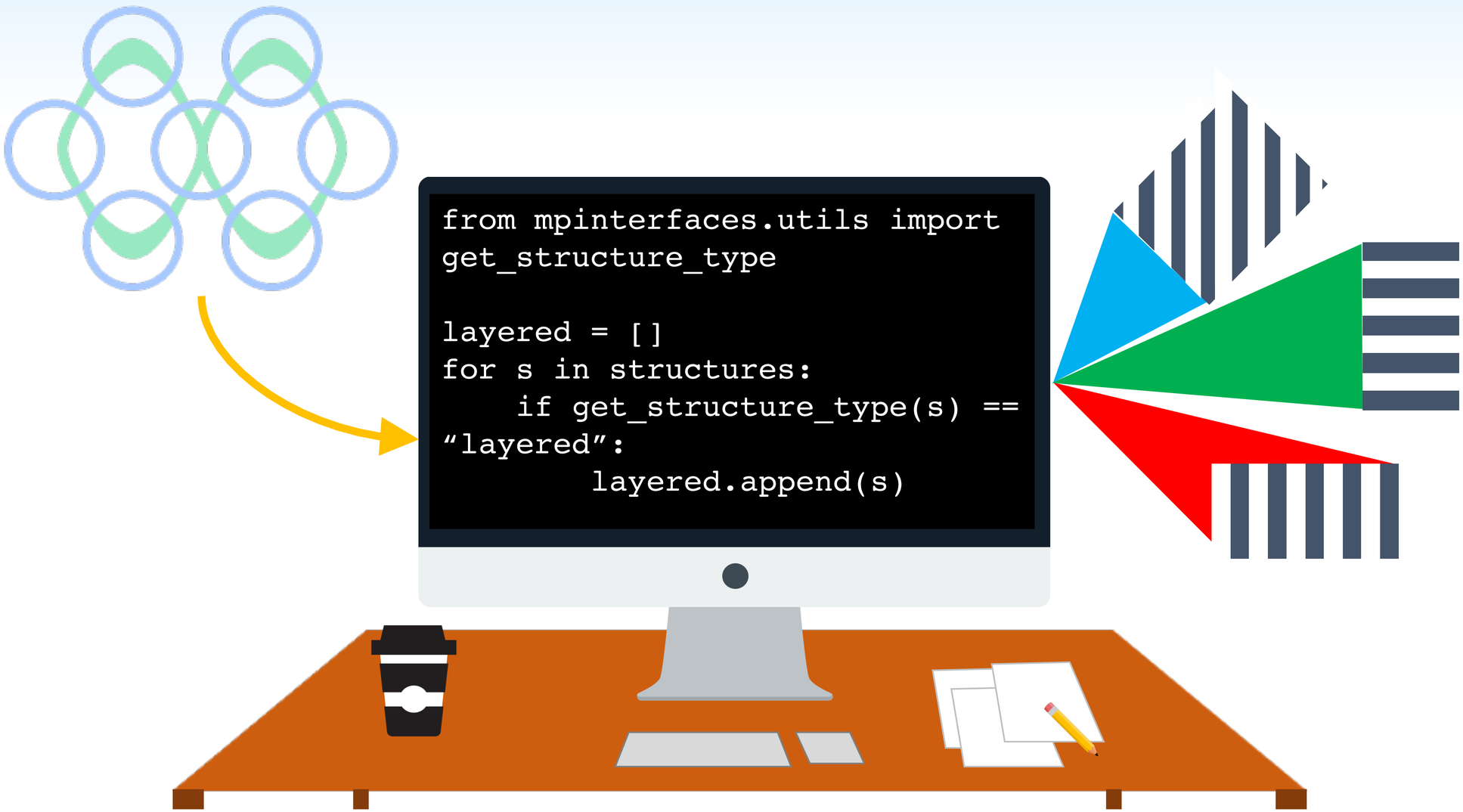


Datamining to Discover 2D Materials



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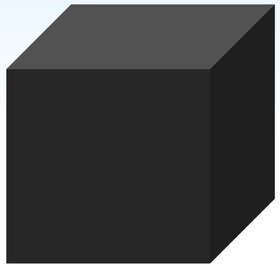
Dimensionality of Structural Motifs

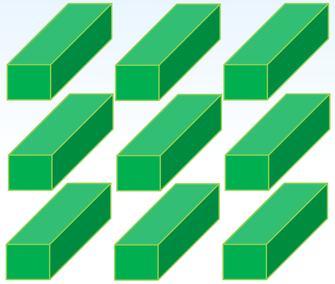


3D

Conventional & intercalated crystals

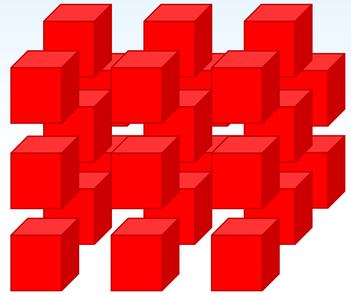
2D

Layered crystals



1D

Chain-like crystals



0D

Molecular & atomic crystals

Large numbers of crystals with each dimensionality exist in most major crystal structure databases. How can we classify them?

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Searching for Layered Compounds

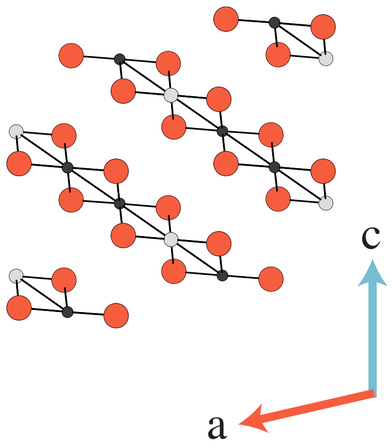
The ideal case

Search for materials with:
- low packing fractions
- gaps along c-axis

You'll find about 100 layered materials in the ICSD[1,2]

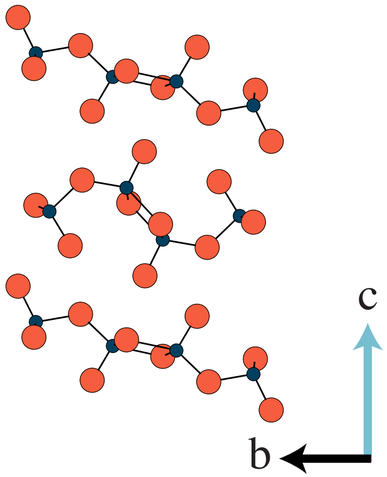
Reality

Co_2NiO_6
mp-765906



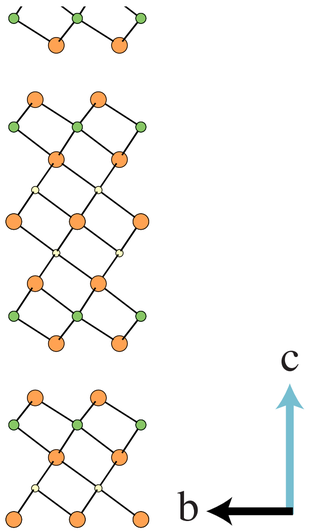
Gaps along other axes

V_2O_5
mp-25643



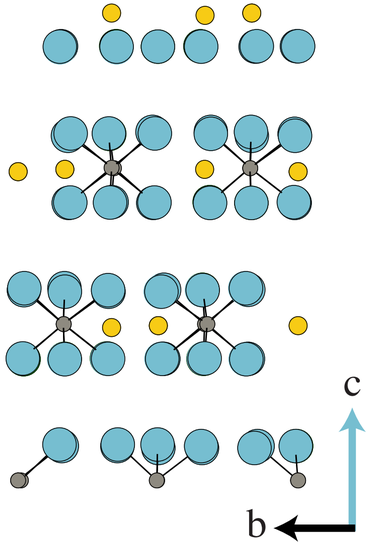
No planar gaps at all

$Ge_2Te_5As_2$
mp-14791



High packing fractions

Li-WCl_6
mp-570512



Gaps along multiple axis

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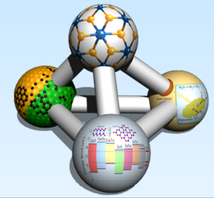
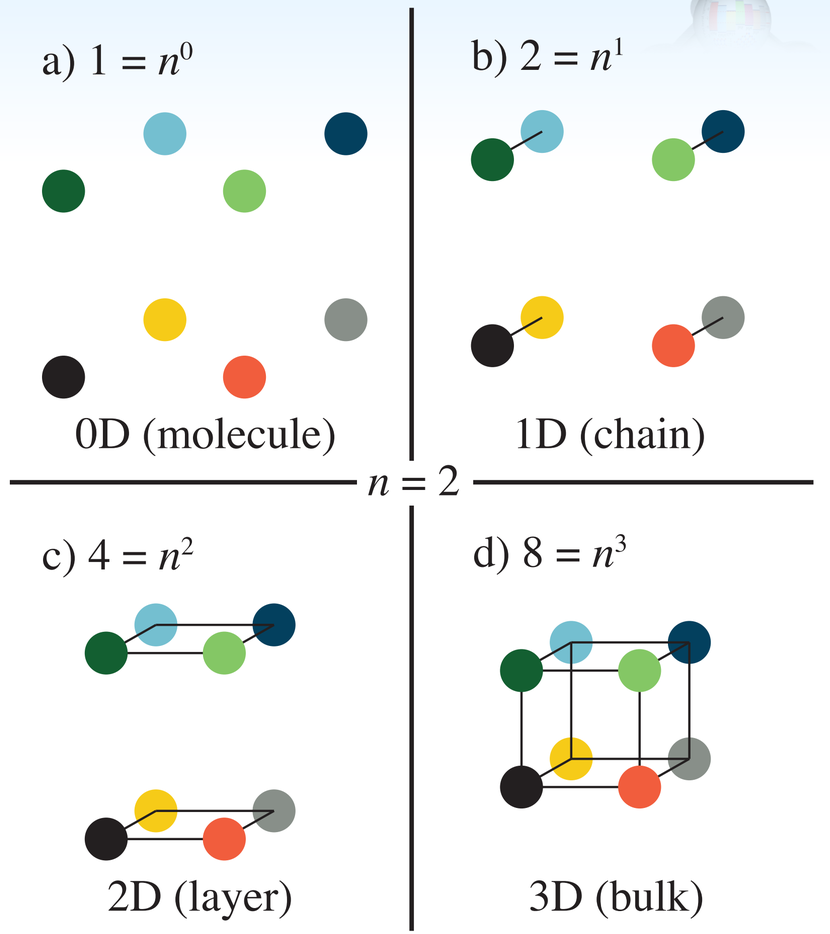
MPInterfaces & materialsweb

[1] Björkman, et al. *Phys. Rev. Lett.* 2012
[2] Lebègue, et al. *Phys. Rev. X* 2013

The Topology Scaling Algorithm



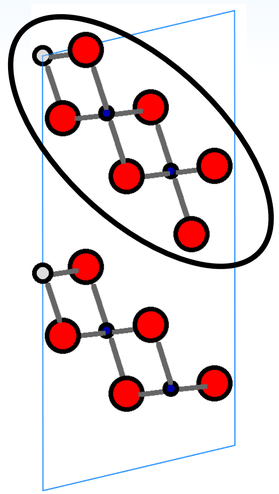
1. Identify bonded atomic clusters in the structure based on covalent radius overlap
2. Make a $n \times n \times n$ supercell of the structure
3. Re-identify bonded atomic clusters, and compare sizes with original cluster sizes



The Topology Scaling Algorithm

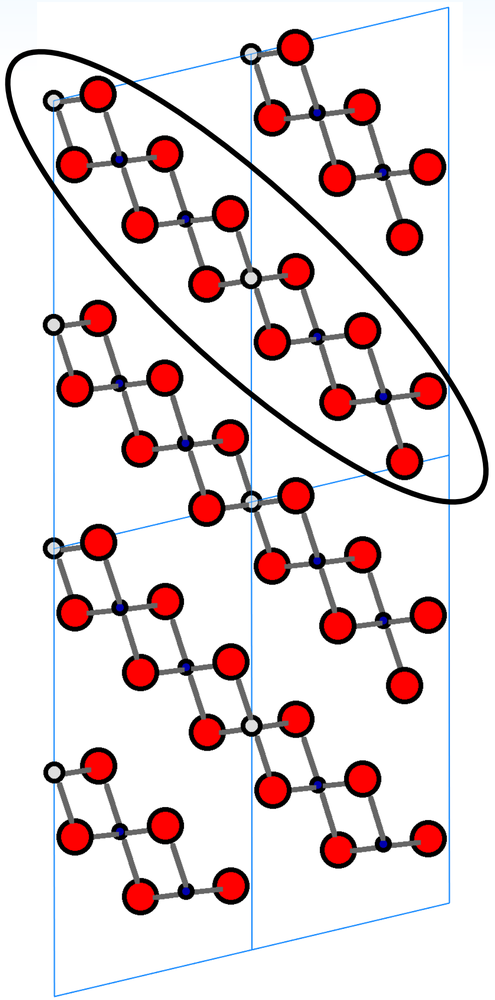
Co_2NiO_6
mp-765906

1×1×1 cell



Cluster of 9 atoms

2×2×2 cell



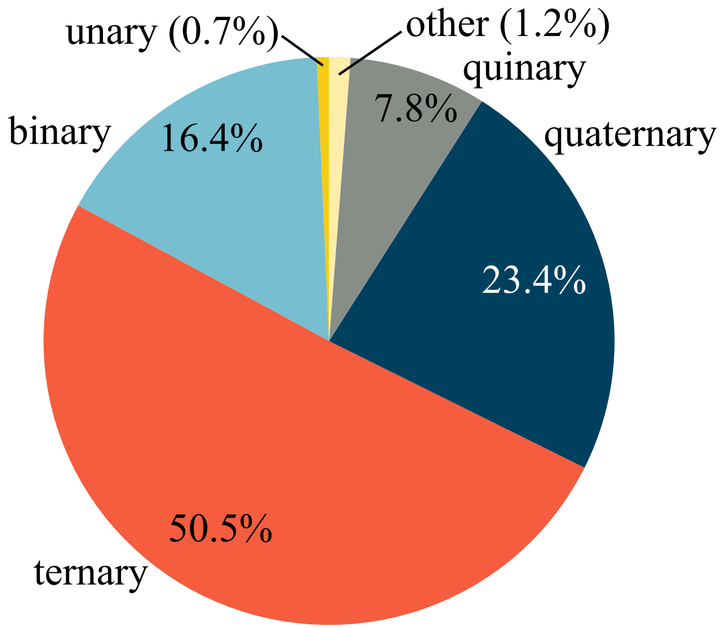
Cluster of 36 atoms

N^2 scaling ⇒ Layered Material

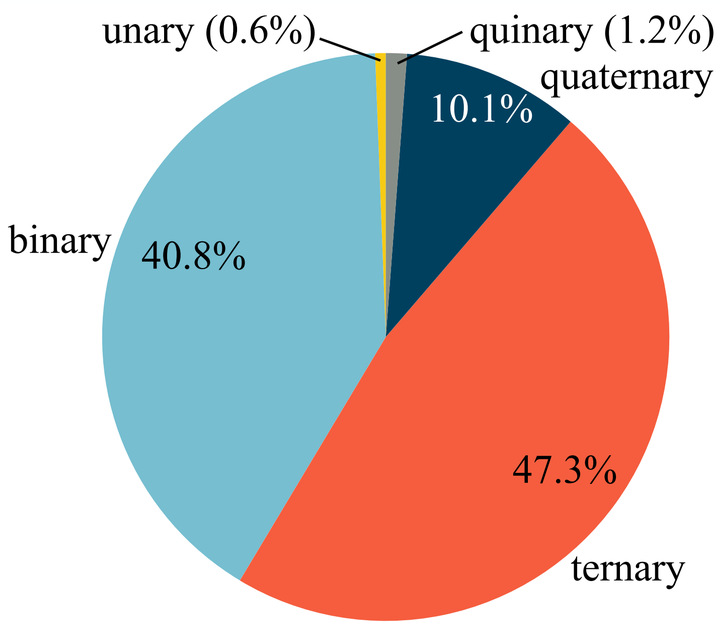
Ashton, Paul, Sinnott & Hennig. *Phys. Rev. Lett.* 2017

Layered Materials in MaterialsProject

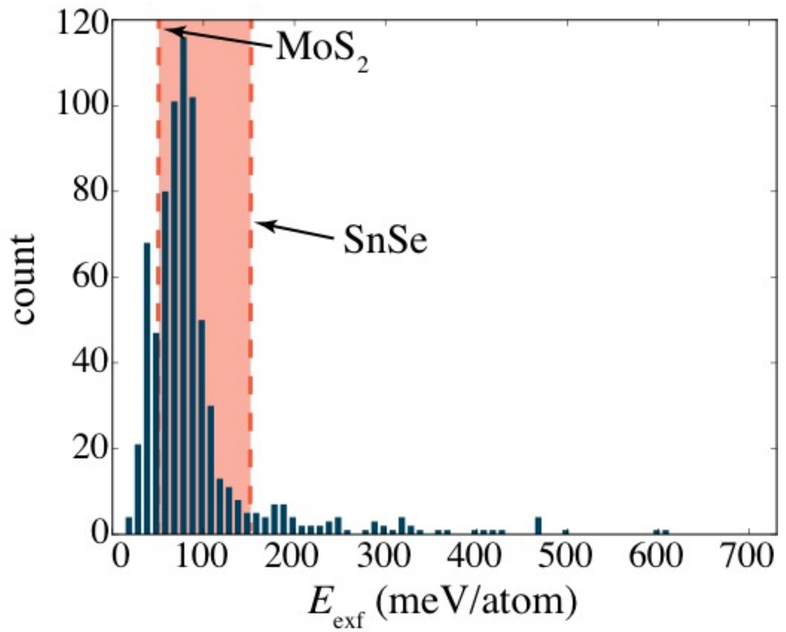
All materials: about 65,000



Layered materials: 1,560 (2%)



Exfoliation energy



826/1560 have unique monolayers and are nearly stable with E_{hull} < 50 meV/atom.
Identified 625 2D materials with energy below 150 meV/atom
Binary and ternary compounds more likely to be layered.

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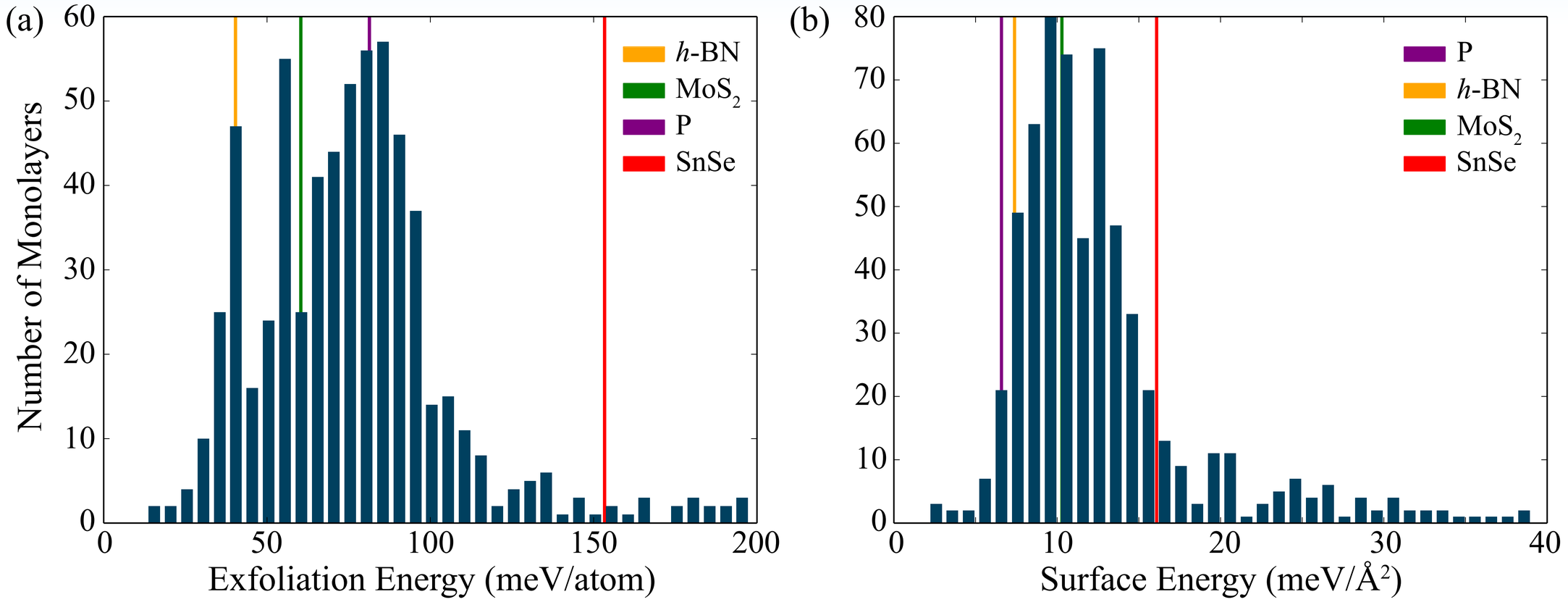
MPInterfaces & materialsweb

Ashton, Paul, Sinnott & Hennig. *Phys. Rev. Lett.* 2017

Stability Criteria for 2D Materials

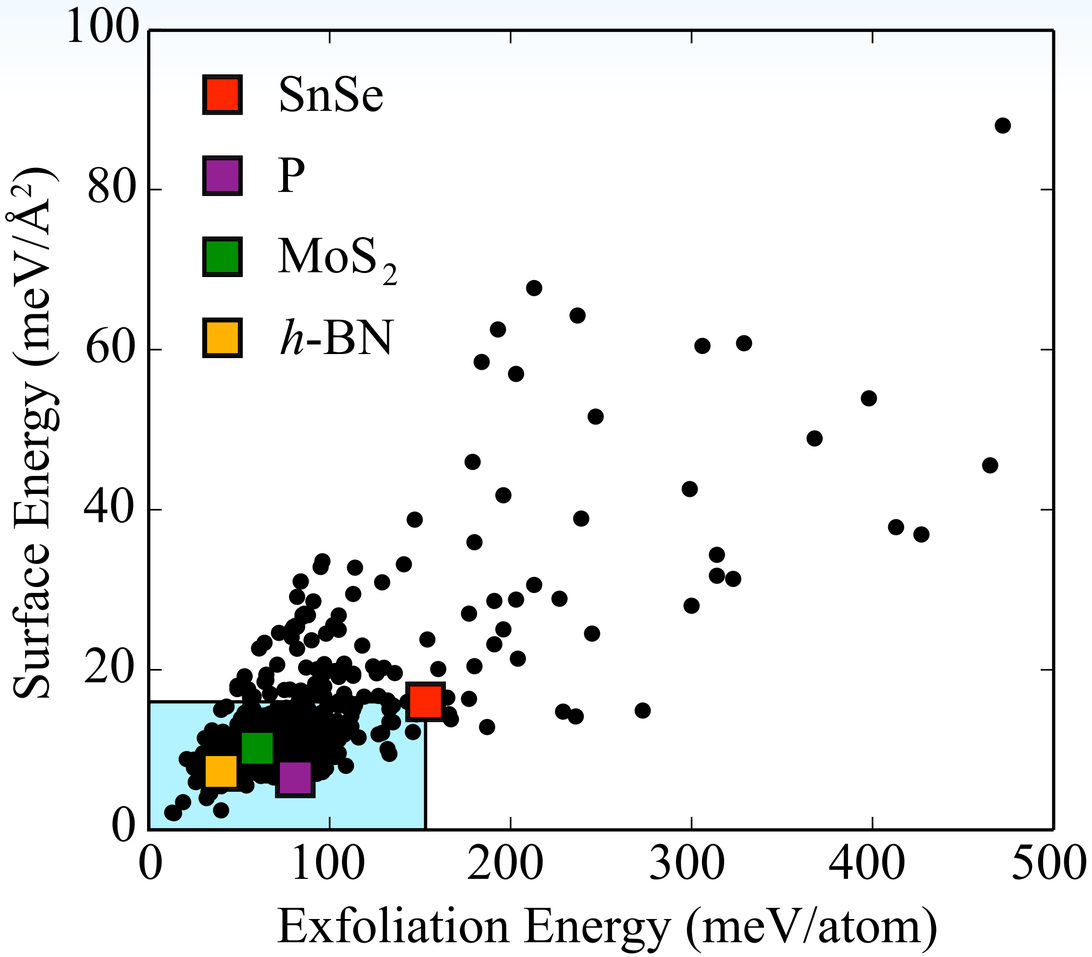
Exfoliation Energy vs. Surface Energy



Ashton, Paul, Sinnott & Hennig. *Phys. Rev. Lett.* 2017

Stability Criteria for 2D Materials

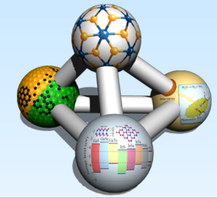
Exfoliation Energy vs. Surface Energy



Alternative empirical measures of stability with similar results.

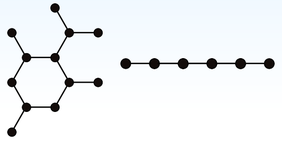
Ashton, Paul, Sinnott & Hennig. *Phys. Rev. Lett.* 2017

Structure Prototypes

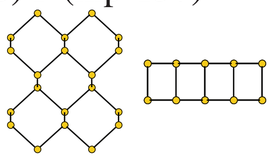


Elementary 2D Materials

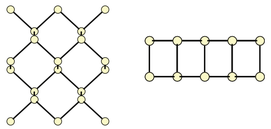
a) C (mp-48)



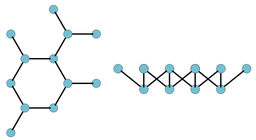
b) P (mp-157)



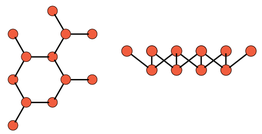
c) As (mp-158)



d) Sb (mp-104)

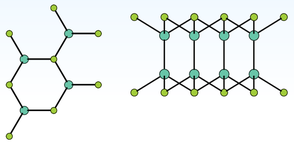


e) Bi (mp-23152)

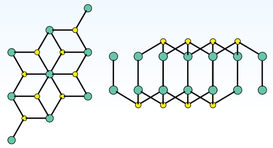


Binary A-B 2D Materials

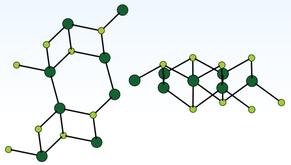
a) GaSe (mp-568263)



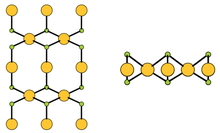
b) GaS (mp-9889)



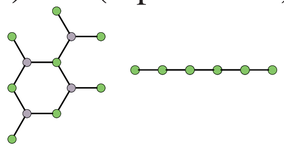
c) InSe (mp-21405)



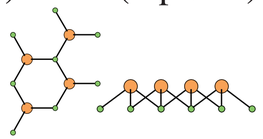
d) AuSe (mp-2793)



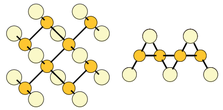
e) BN (mp-604884)



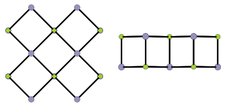
f) GeTe (mp-938)



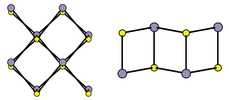
g) AuBr (mp-505366)



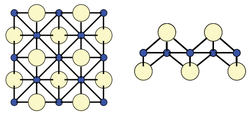
h) SnSe (mp-8936)



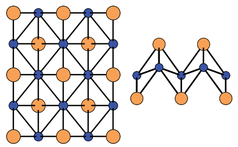
i) SnS (mp-2231)



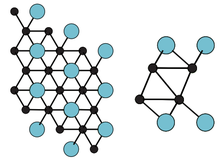
j) CuBr (mp-22917)



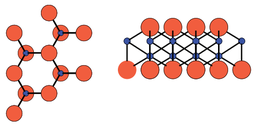
k) CuTe (mp-20826)



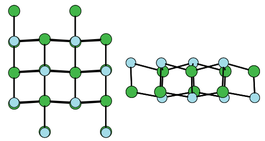
l) ZrCl (mp-27440)



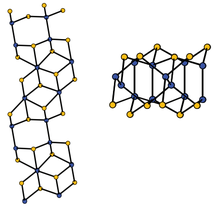
m) CuI (mp-570136)



n) TlF (mp-720)



o) SiP (mp-2798)



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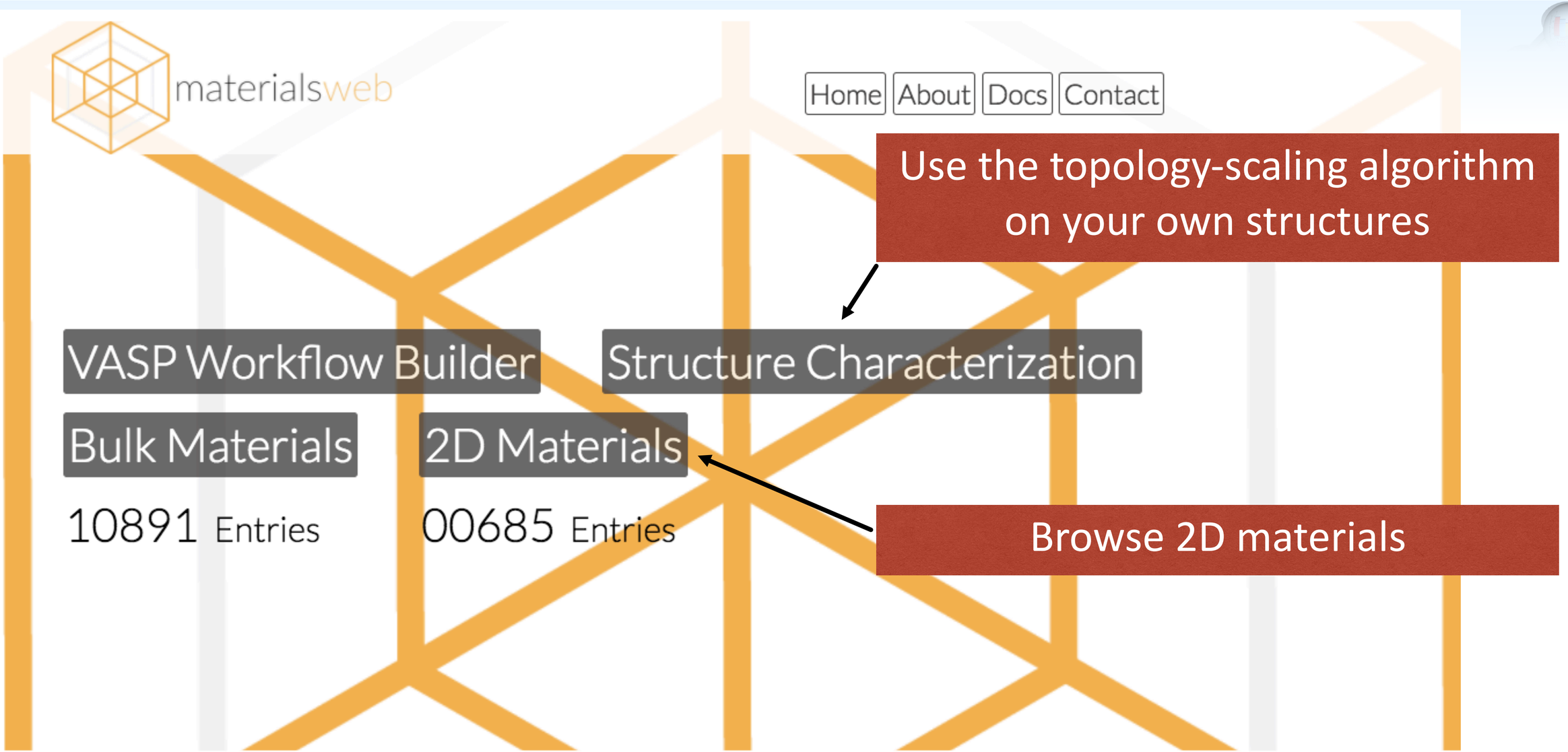
Ashton, Paul, Sinnott & Hennig. *Phys. Rev. Lett.* 2017

Online Database: https://materialsweb.org



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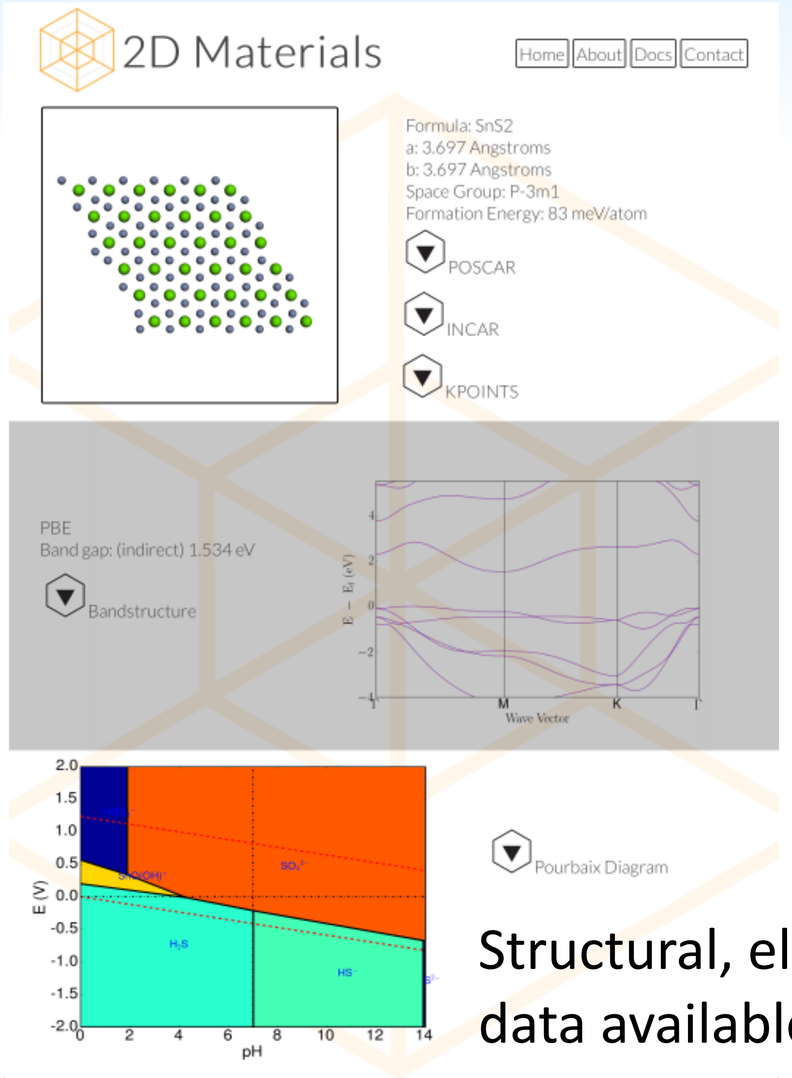
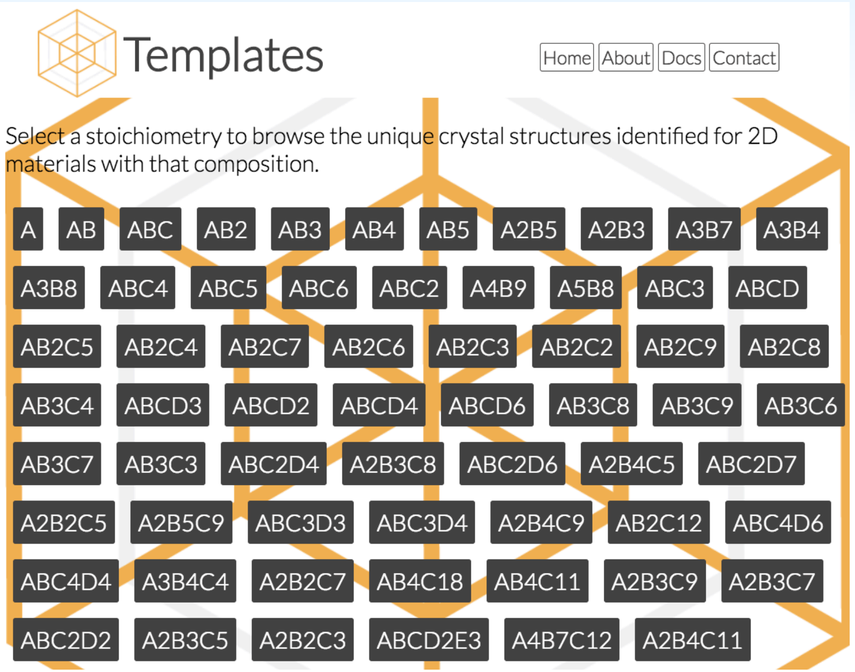
Online Database: https://materialsweb.org





Unique crystal structures for each 2D material stoichiometry in the DB

Structural, electronic and thermodynamic data available for all materials

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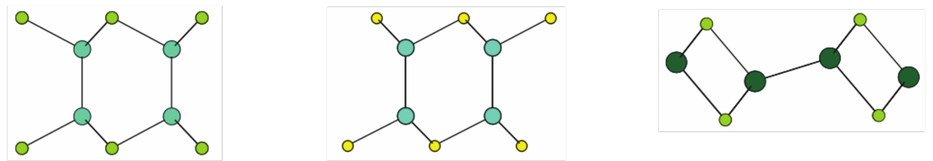
Ashton, Paul, Sinnott & Hennig. *Phys. Rev. Lett.* 2017

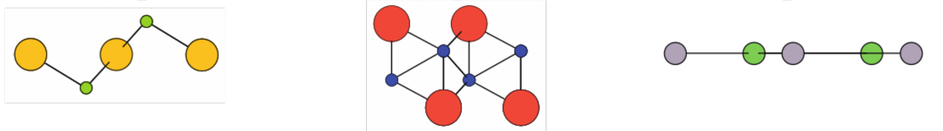
Using Crystal Structure Templates

Unique AB crystal structures

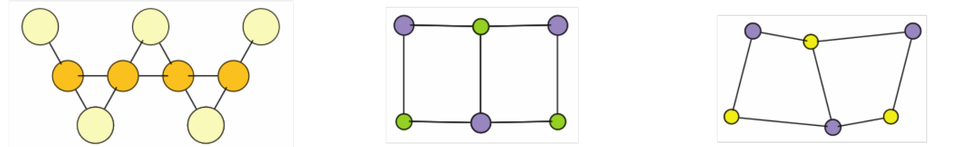
a) GaSe (mp-568263) b) GaS (mp-9889)* c) InSe (mp-21405)*



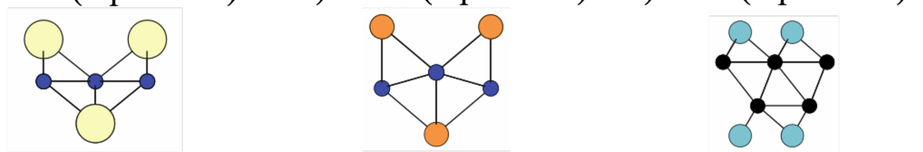
d) AuSe (mp-2793) e) CuI (mp-570136) f) BN (mp-604884)



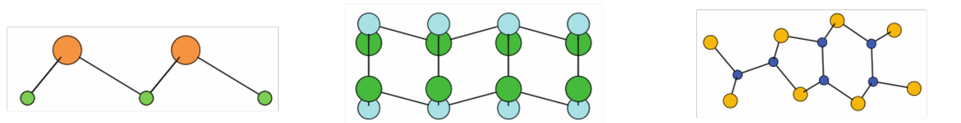
g) AuBr (mp-505366) h) SnSe (mp-8936) i) SnS (mp-2231)



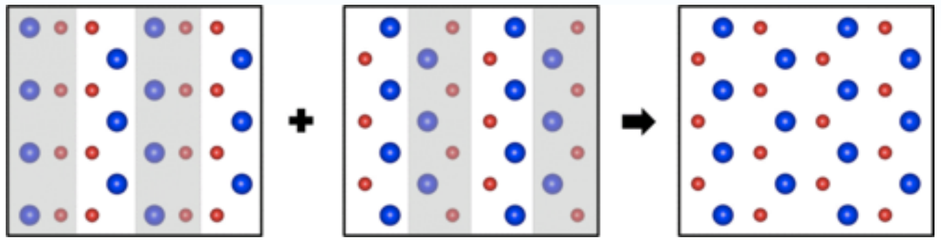
j) CuBr (mp-22917) k) CuTe (mp-20826) l) ZrCl (mp-27440)



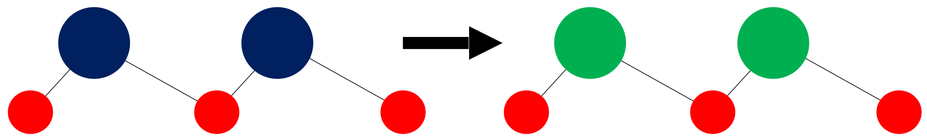
m) GeTe (mp-938)† n) TlF (mp-720) o) SiP (mp-2798)



Genetic algorithms



Element substitution



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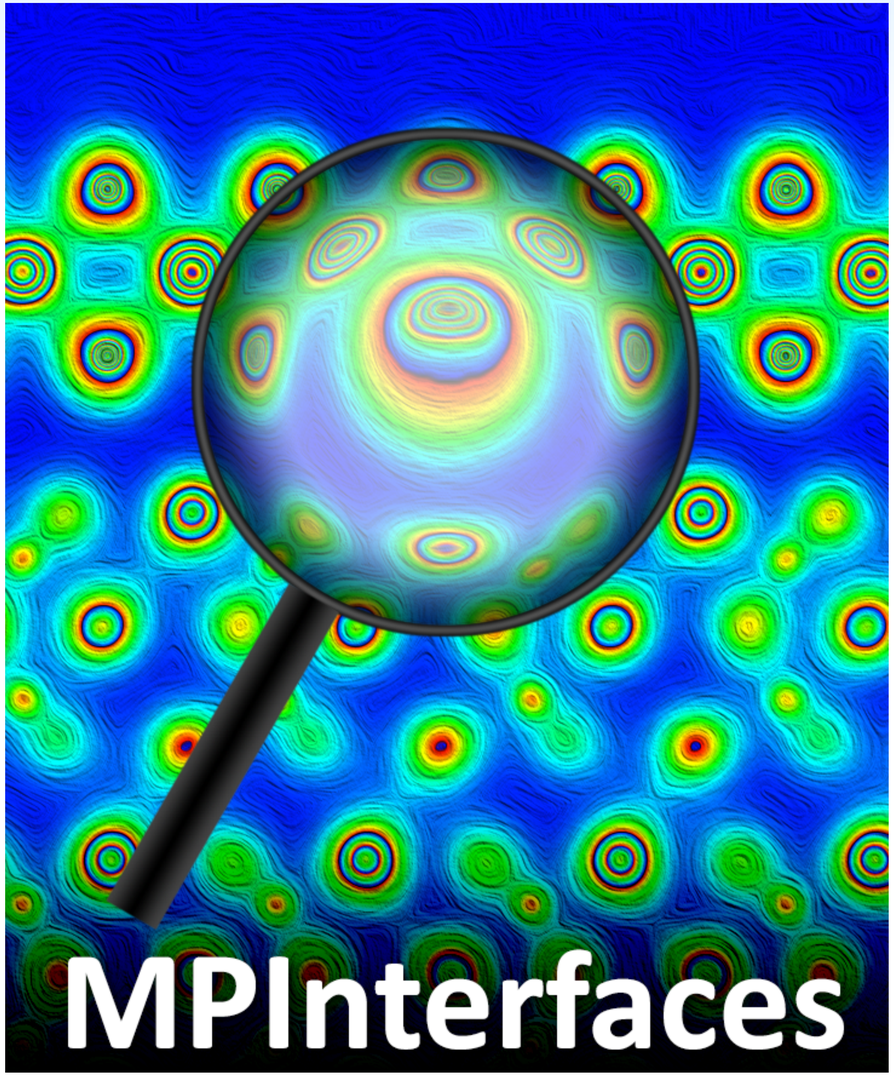
Ashton, Paul, Sinnott & Hennig. *Phys. Rev. Lett.* 2017

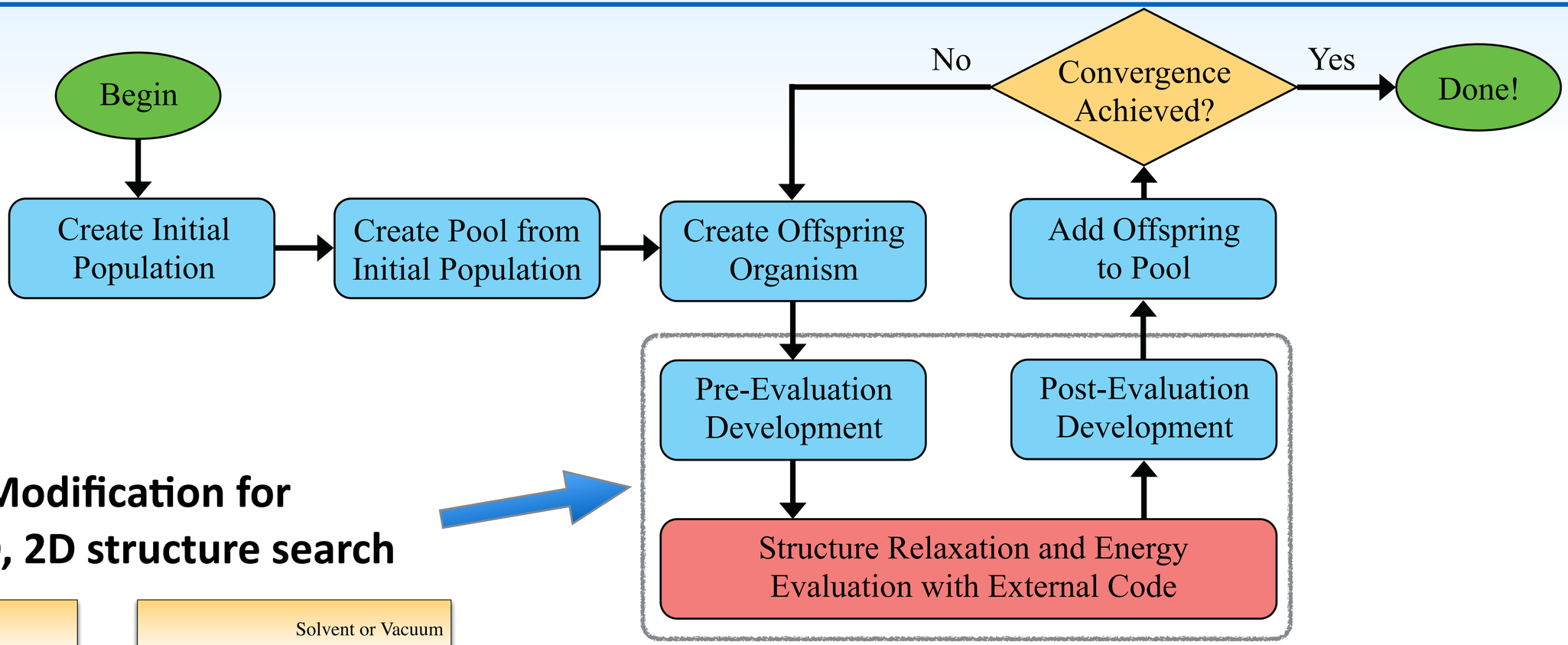
Structure and Stability of 2D Materials

- Classification of 2D materials
- Criteria for stability $\Delta E_f < 200$ meV/atom
- **Methods for 2D materials discovery**
  - Datamining for exfoliation
  - Chemical substitutions and etching
  - **Evolutionary algorithm searches**

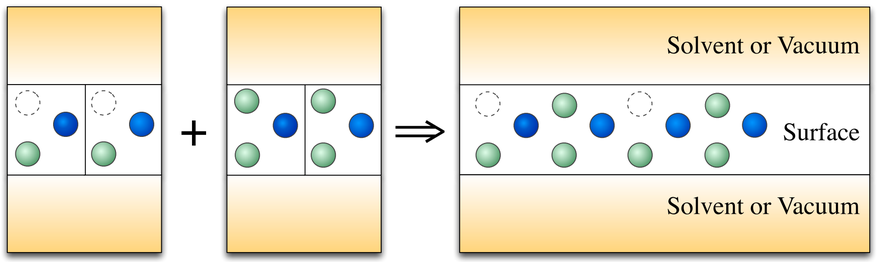


rhennig@ufl.edu
http://hennig.mse.ufl.edu

Genetic Algorithm Search for 2D Materials



Modification for
0D, 1D, 2D structure search



Grand canonical genetic algorithm
Variable number of atoms and composition

https://github.com/henniggroup/gasp-python

W. W. Tipton, RGH, J. Phys.: Cond. Matter 25, 495401 (2013)

B. C. Revard, W. W. Tipton, A. Yesypenko, R. G. Hennig, PRB 93, 054117 (2016)

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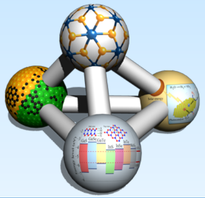
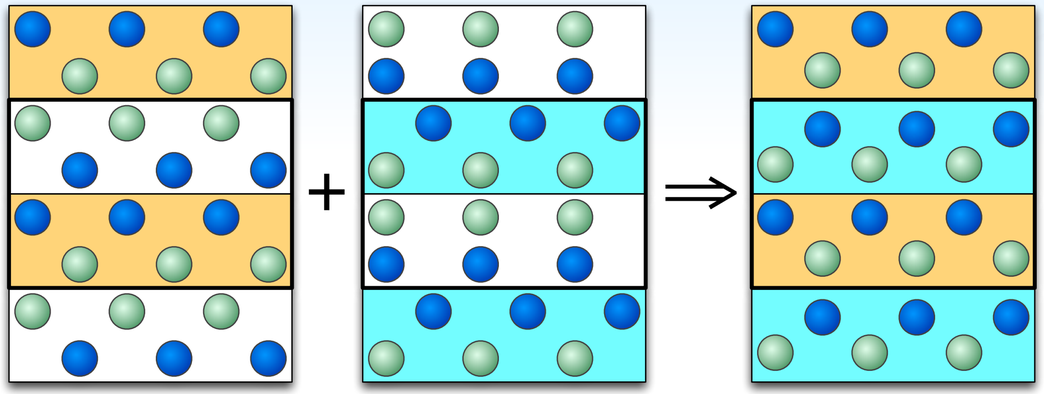
Genetic Operations



Mating:

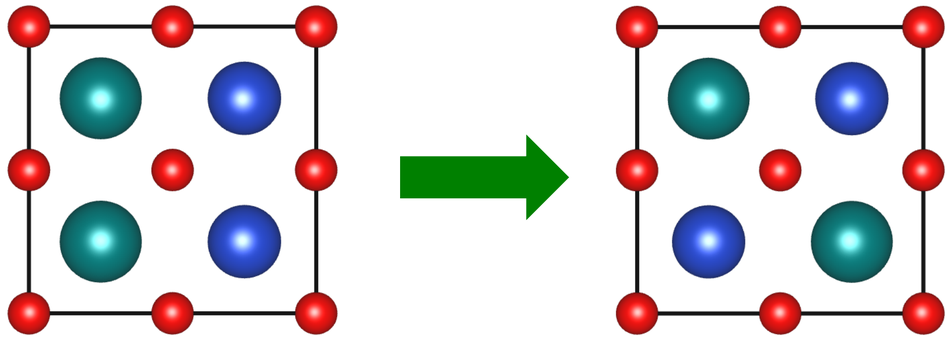
- combines two structures
- preserves local structural motifs
- handles different lattices



Mutation:

1. Structural Mutation
   - lattice strain
   - atomic coordinate displacement
2. Permutation
   - swap atomic locations
3. Number of atoms mutation
   - add or remove atoms

$$\vec{a}' = (\mathbb{I} + \epsilon_{ij})\vec{a}$$



https://github.com/henniggroup/gasp-python

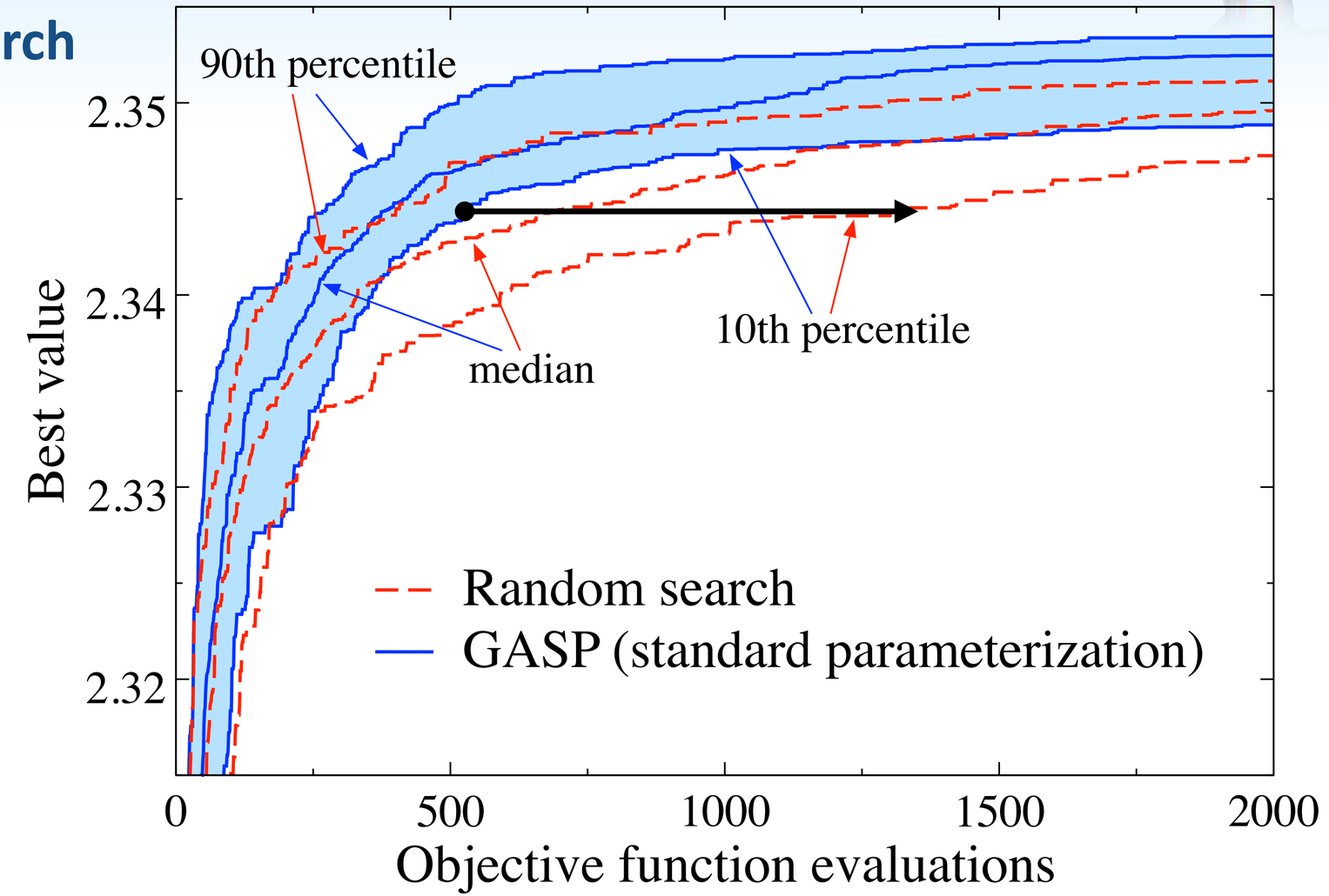
W. W. Tipton, RGH, J. Phys.: Cond. Matter 25, 495401 (2013)

B. C. Revard, W. W. Tipton, A. Yesypenko, R. G. Hennig, PRB 93, 054117 (2016)

Efficiency of Genetic Algorithm

Efficiency compared to random search

- Random search requires 2-3x more structure relaxations
- Genetic algorithm learns from previous structures



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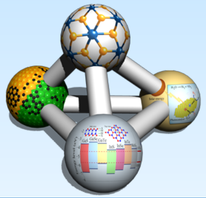
Phase Diagram Searching

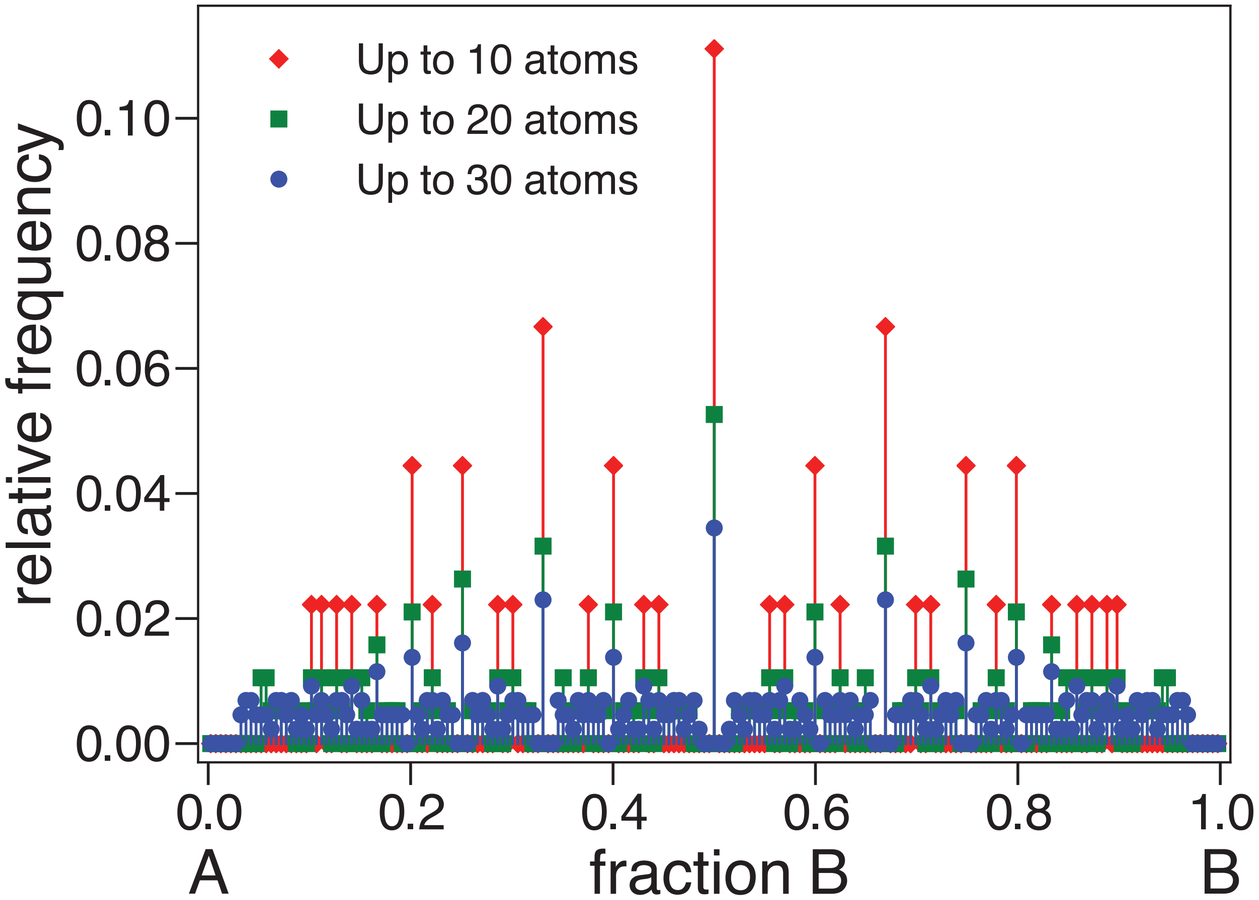


Problem:

- Naïve algorithm oversamples average compositions

Solutions

1. Use larger endpoint structures
   - Works but expensive
2. Preferentially select parents with similar compositions
   - Needs metric for distance of structures in composition space



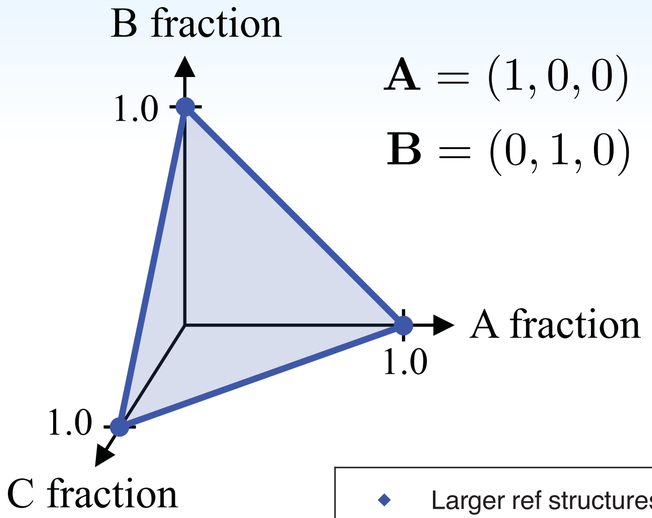
Phase Diagram Searching

Metric for distance in composition space

- Express composition as a vector
- Use L_1 Norm to define distance:

$$d_{XY} = \frac{1}{2}\left|\left|\mathbf{X} - \mathbf{Y}\right|\right|_1$$

$$\left|\left|\mathbf{A} - \mathbf{B}\right|\right|_1 = \left|\left|(1, -1, 0)\right|\right|_1 = |1| + |-1| + |0| = 2$$

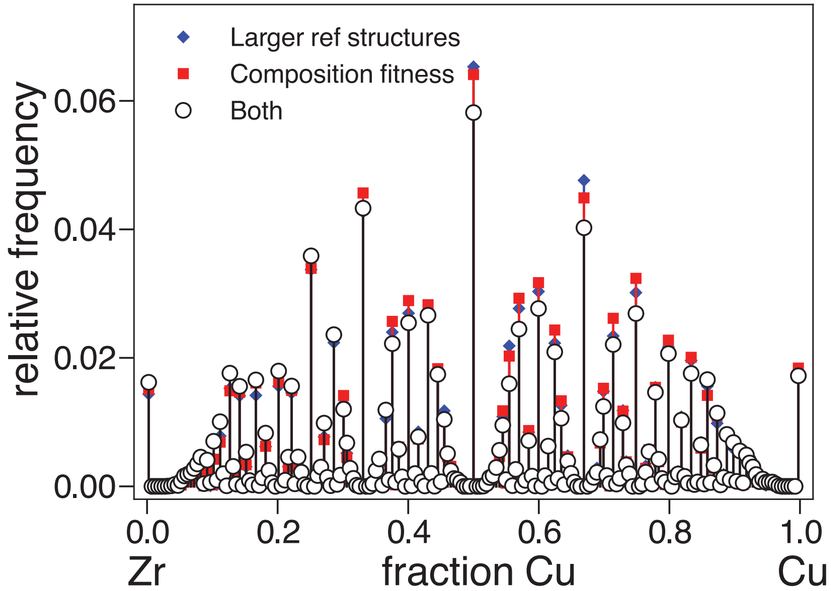


Fitness for structures

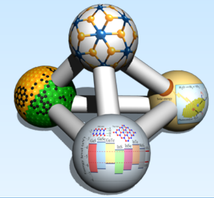
- Composition fitness $f_{comp} = 1 - d$
- Relative fitness $f_{rel} = w_{comp} f_{comp} + (1 - w_{comp}) f_{reg}$

Fitness for structures

- Sampling distribution improved but not uniform
- Use partial phase diagram searches if needed

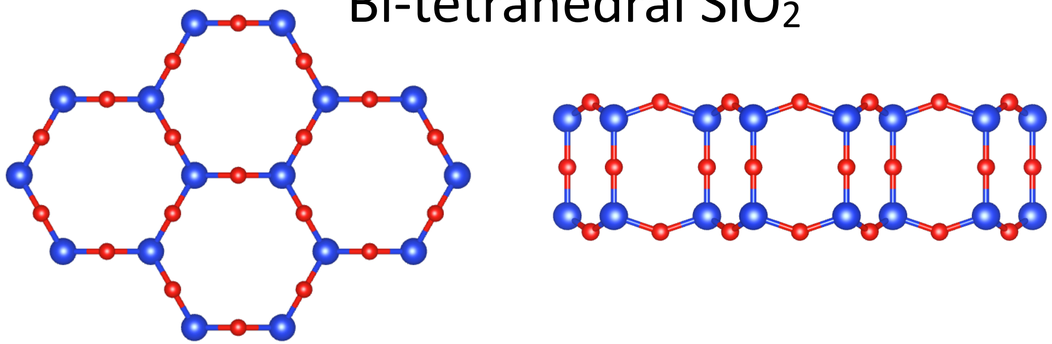


Genetic Algorithm – 2D Group-IV Dioxides



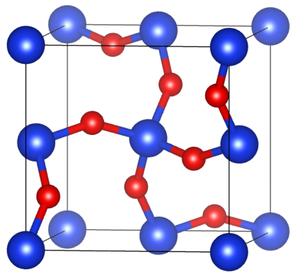
- SiO_2 recently synthesized in 2D form

Bi-tetrahedral SiO_2

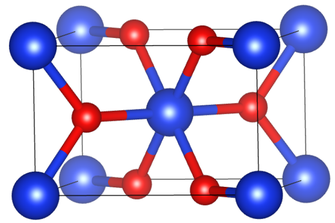


- Bulk structures not layered

α-Quartz (SiO_2)

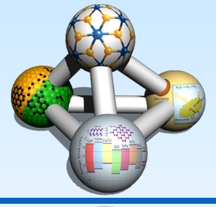


Rutile (GeO_2, SnO_2, PbO_2)



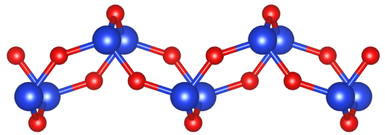
- Cations are
  - 4-fold coordinated in α-quartz structure
  - 6-fold coordinated in rutile structure

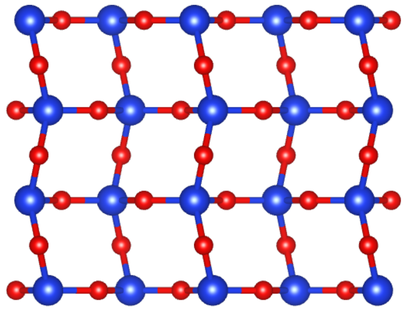
Genetic Algorithm – 2D Group-IV Dioxides



- For 2D SiO_2, the algorithm predicted an orthorhombic structure

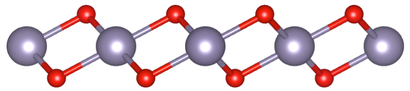
Orthorhombic SiO_2

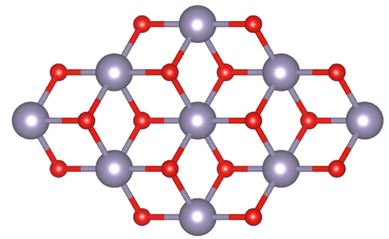




- For GeO_2, the algorithm found the 1*T* structure

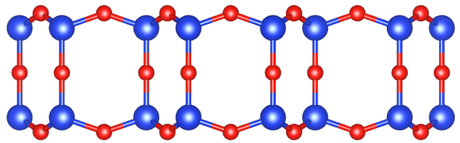
1*T* GeO_2

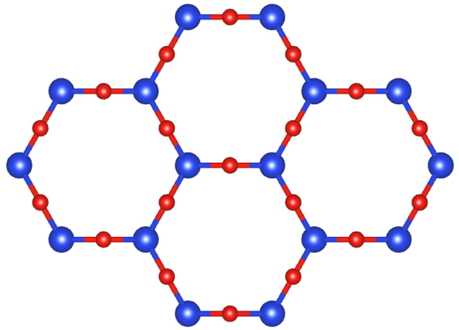




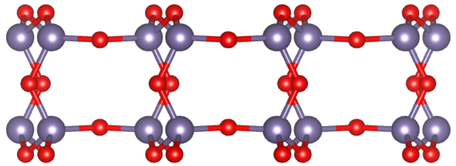
- Seeded both searches with the bi-tetrahedral structure
- Found lower energy monoclinic structure of 2D GeO_2

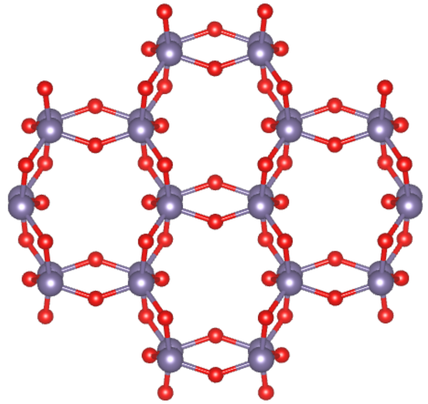
Bi-tetrahedral SiO_2





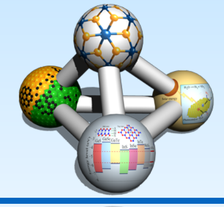
Monoclinic GeO_2



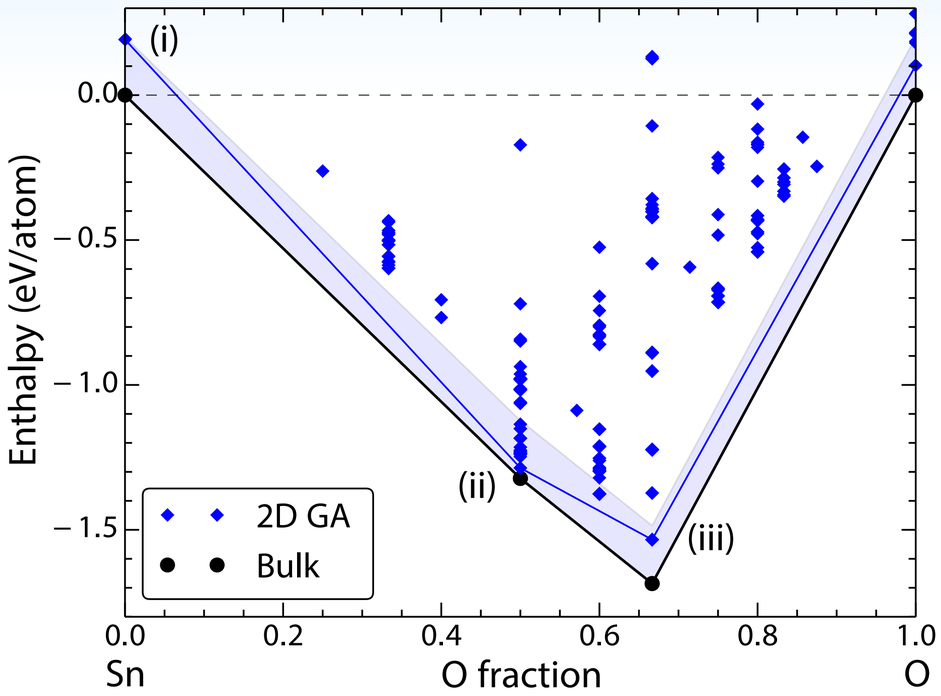


Seeding search with known structures improves performance

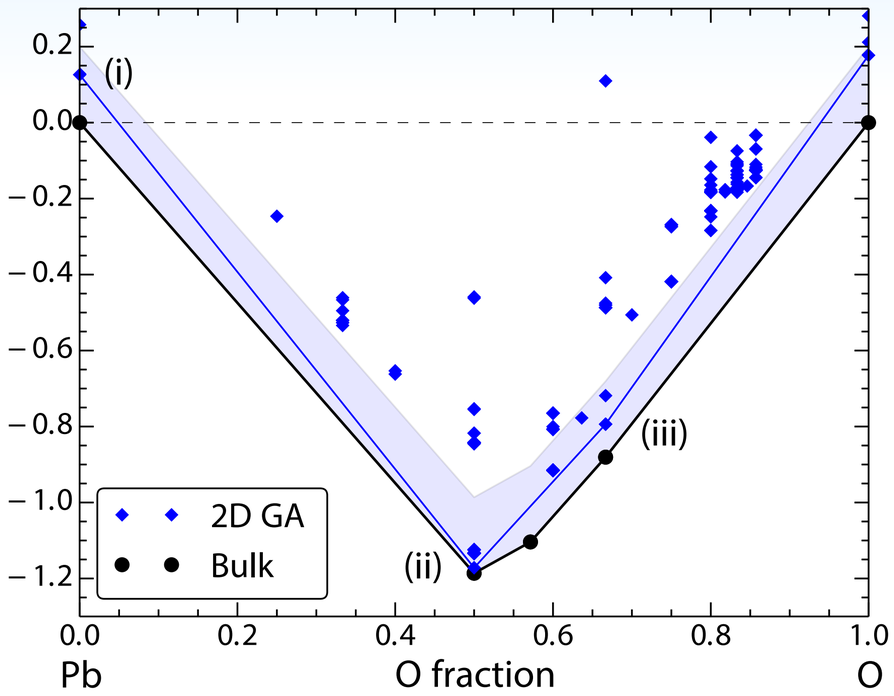
Genetic Algorithm – 2D Tin and Lead Oxides

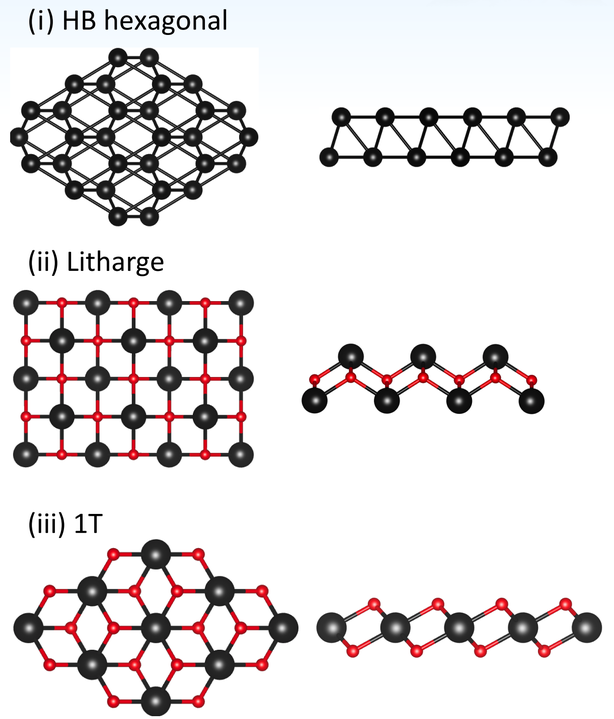


2D Sn-O Phases



2D Pb-O Phases





Confirmation of our previous prediction of litharge structure for 2D SnO and PbO

New prediction of 1*T* structure for 2D SnO_2 and PbO_2

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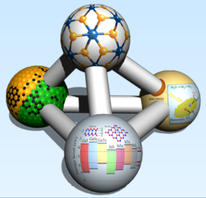
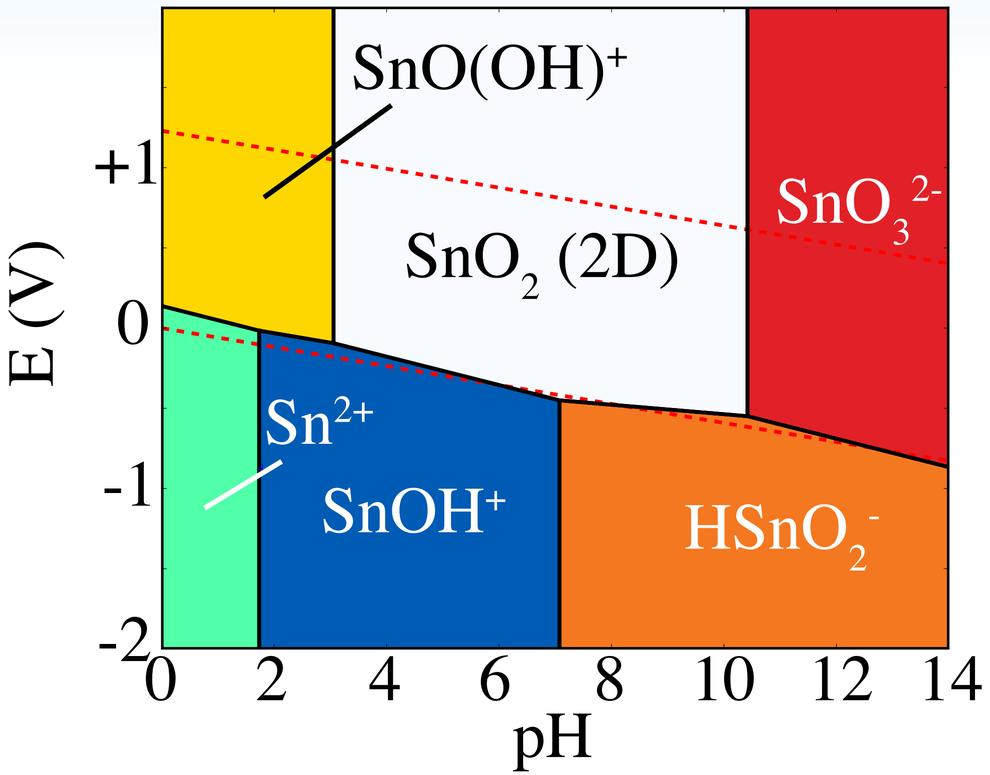
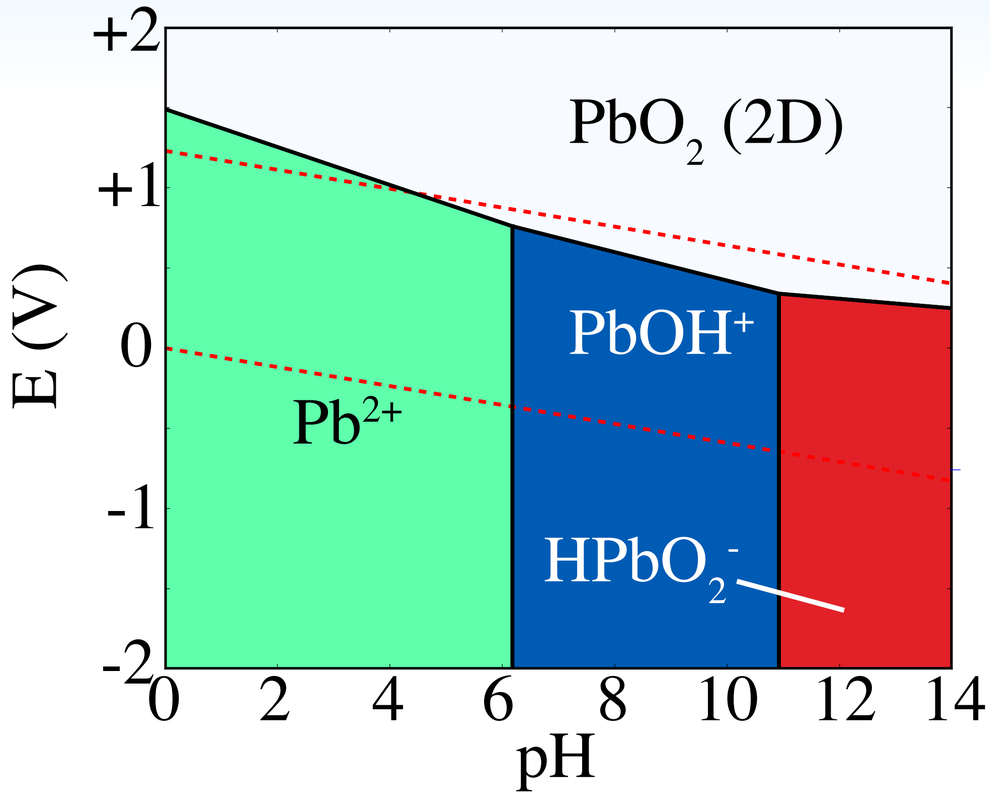
Genetic Algorithm – 2D Tin and Lead Oxides



2D Sn-O Phases



2D Pb-O Phases



The 2D SnO_2 and PbO_2 1T phases are stable in water for ionic concentrations of 10^{-6}!

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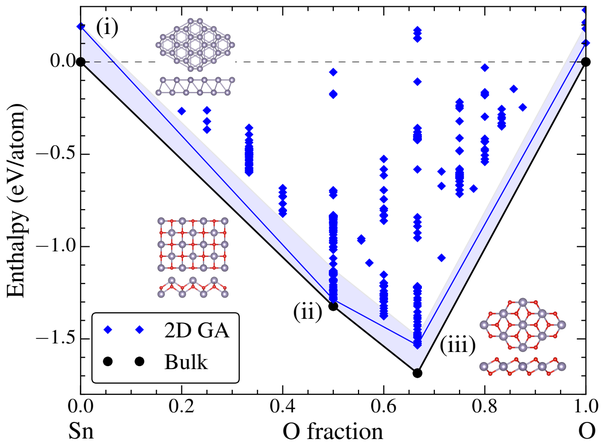
Search of Energy Landscapes by Evolutionary Algorithms and Data Mining

Richard G. Hennig, University of Florida

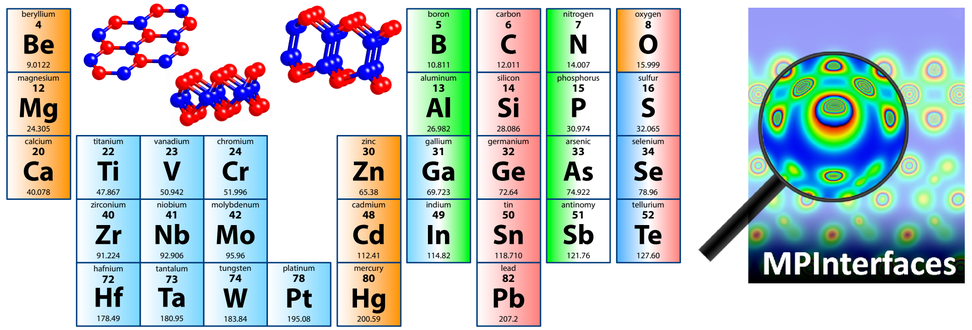
Structure and Energy Landscapes

- Structure representation
- Features of energy landscapes
- Structure searches for 2D materials by datamining, chemical substitution, and evolutionary algorithms

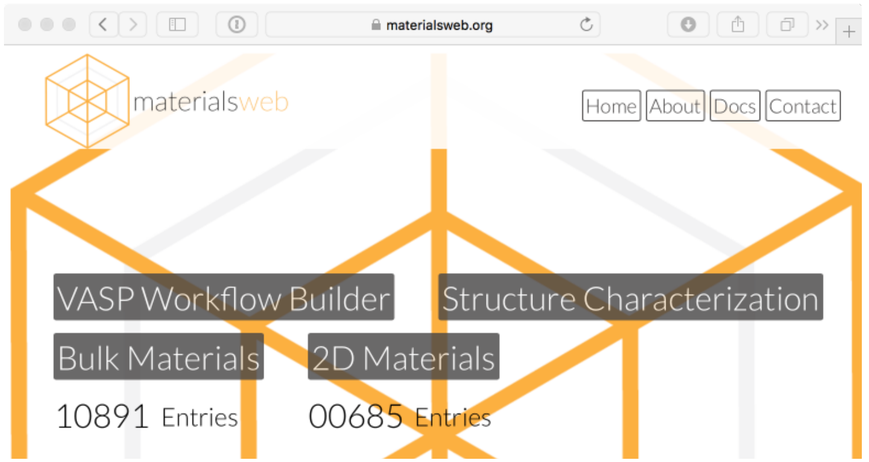


GASP - Genetic algorithm and machine learning for structure predictions

MPInterfaces - High throughput framework for 2D materials



Data available at http://materialsweb.org



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Open source available at https://github.com/henniggroup