Sicherheit in Technik und Chemie

BAM
Bundesanstalt für
Materialforschung
und -prüfung

NEW CHEMICAL UNDERSTANDING WITH AUTOMATION AND HIGH-THROUGHPUT COMPUTATIONS

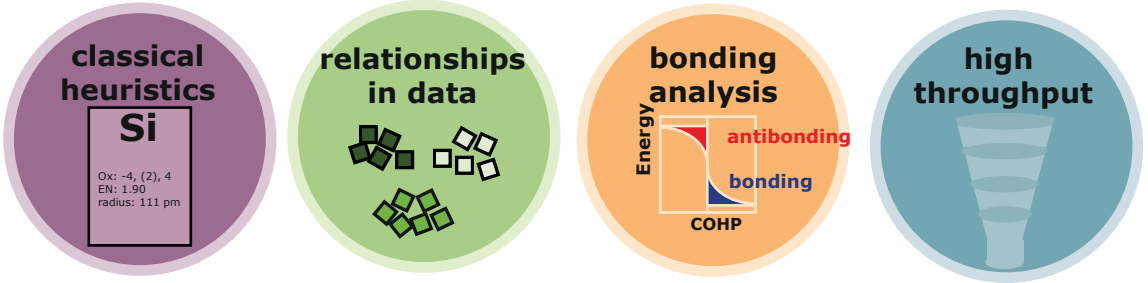
Dr. Janine George

About me

2008-2017: Doctorate (RWTH Aachen)
- Computational Chemistry

2018-April 2021: Marie Curie Fellow (UCLouvain)
- Materials Informatics
- Data Analysis
- Materials Project

May 2021: Junior Group (BAM, University of Jena)
"Computational Materials Design"



Website:

https://jageo.github.io/

BAM: Bundesanstalt für Materialforschung und -prüfung

Federal Institute for Materials Research and Testing

scientific-technical federal institute in Berlin

Tasks:

- Safety in technology and chemistry
- Physical and chemical tests of substances and equipment
- Development of legal regulations
- Consulting (German government, Industry, ...)

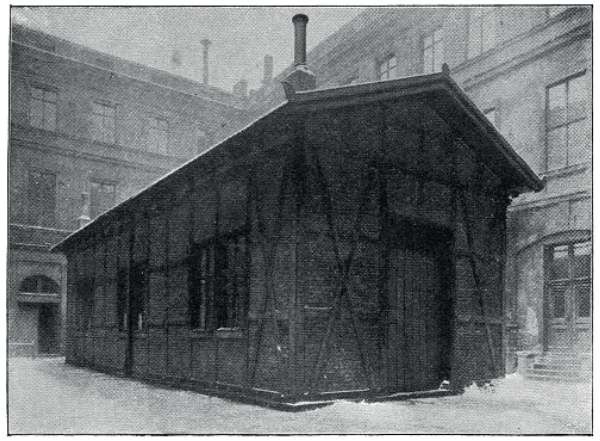
1500 people work at BAM

150 years of BAM

How it started:

- „strength tests“ for iron and steel after collapsing bridges, breaking wheel axles and derailing trains

- in a backyard

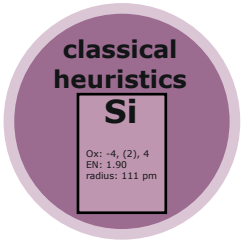


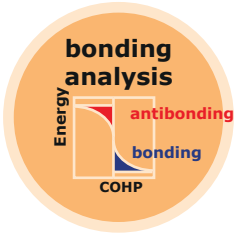
Since 1990:

- Laboratory under the open sky

Agenda

Automation to Test
Chemical Heuristics





Automation
for Materials Design
and Understanding

Chemical Heuristics?

Chemists have always been excellent at finding patterns and rules based on data

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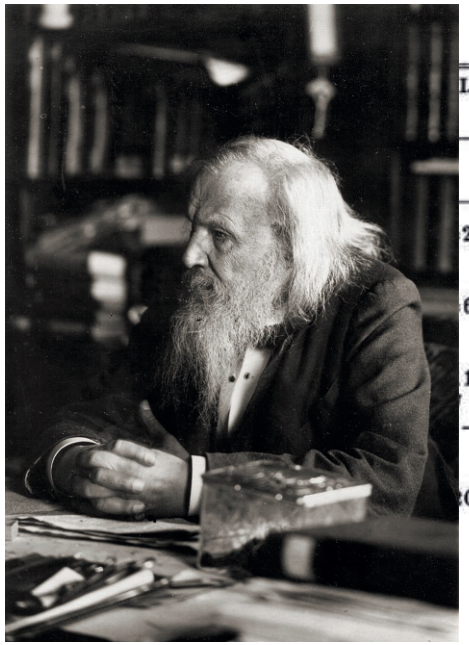
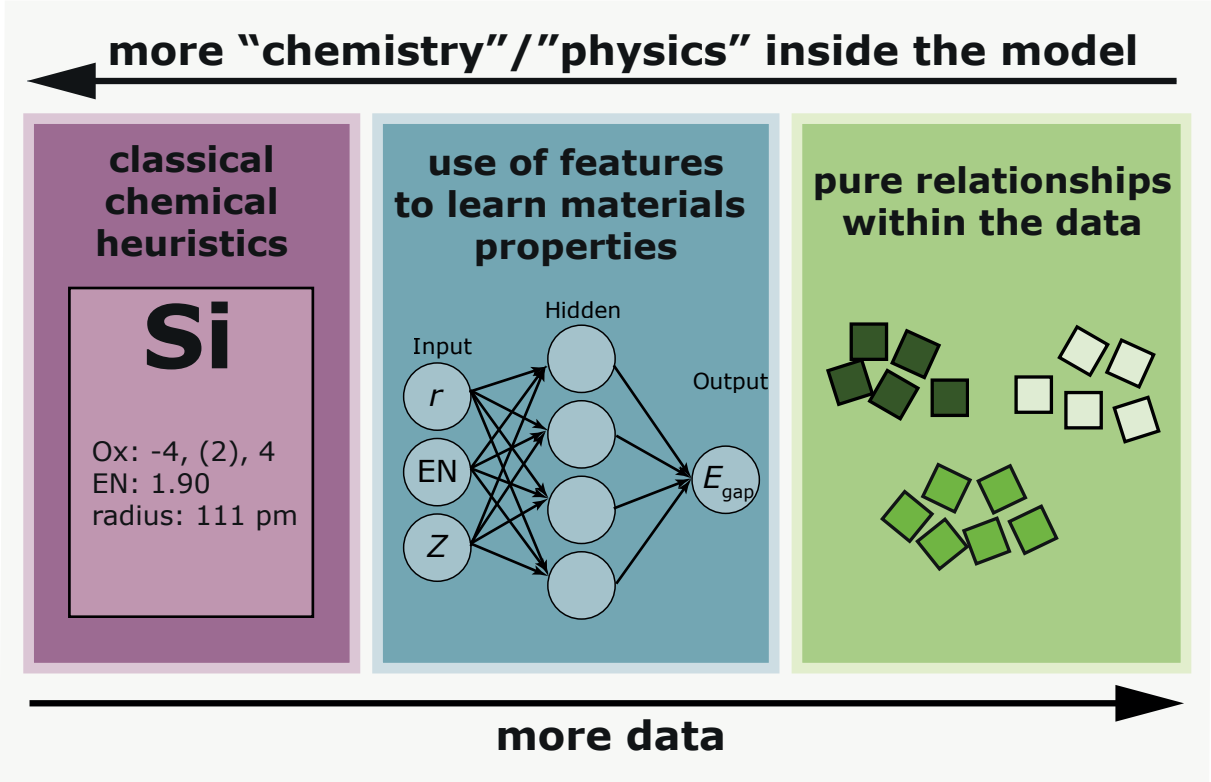


I.	Gruppe III. $\frac{}{R^2O^3}$	Gruppe IV. $\frac{RH^4}{RO^2}$	Gruppe V. $\frac{RH^3}{R^2O^5}$	Gruppe VI. $\frac{RH^2}{RO^3}$	Gruppe VII. $\frac{RH}{R^2O^7}$	Gruppe VIII. $\frac{}{RO^4}$
	B=11	C=12	N=14	O=16	F=19	
24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
65	—=68	—=72	As=75	Se=78	Br=80	
	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108
12	In=113	Sn=118	Sb=122	Te=125	J=127	
	?Di=138	?Ce=140	—	—	—	— — — —
—	—	—	—	—	—	
	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
00	Tl=204	Pb=207	Bi=208	—	—	
	—	Th=231	—	U=240	—	— — — —

Periodic Table of Elements

Pattern/Rule before understanding underlying physics/chemistry

New opportunities: More data, AI, Python tools



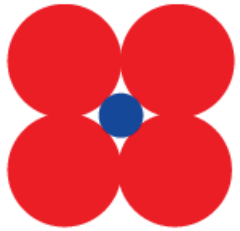
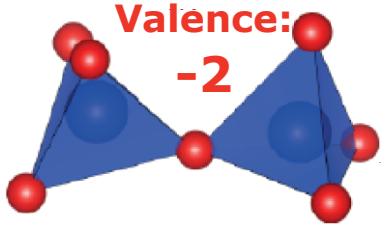
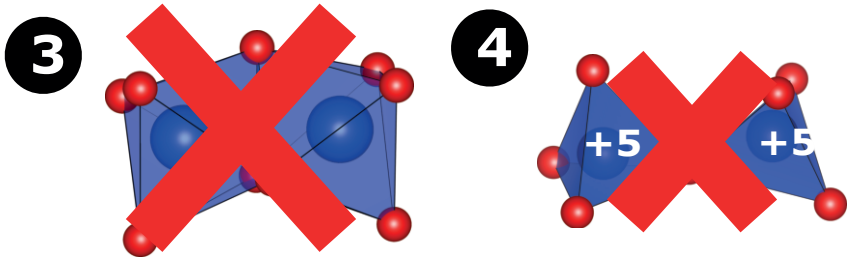
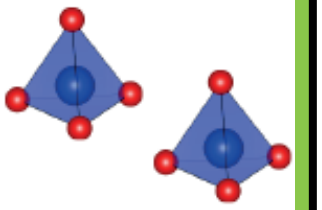
Test of classical heuristics

Development of data-driven heuristics

Figure from: **J. George**, G. Hautier, *Trends in Chemistry*, **2021**, *3*, 86-95.

Why the 5 Pauling Rules?

"A set of principles governing the structure of complex ionic crystals" (L. Pauling, *J. Am. Chem. Soc.* **1929**, *51*, 1010.)

1 Radius Ratio	2 Local Charge Balance	Environment Connections	5 Parsimony
			

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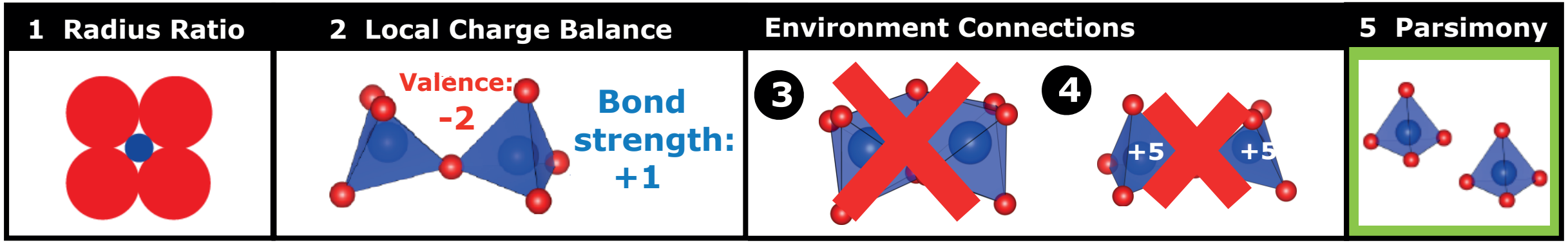


Can we use these rules for a fast prediction of stable materials?
Environments can be determined very fast

Still in use today!

Method

Experimentally-Known Oxides from the Materials Project

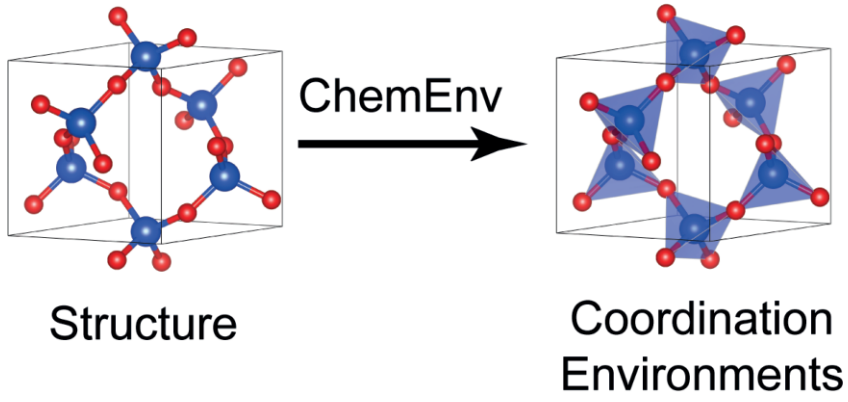
- 5000 Oxides from the Materials Project (www.materialsproject.org)
- Also in Inorganic Crystal Structure Database

Method

Experimentally-Known Oxides from the Materials Project

↓

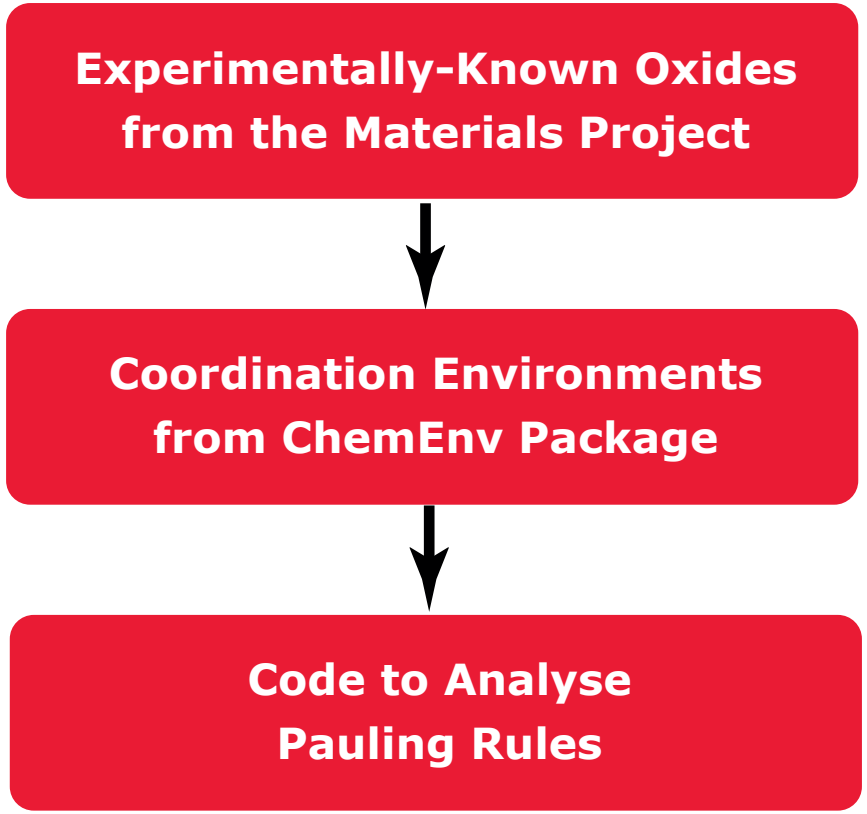
Coordination Environments from ChemEnv Package



- ChemEnv: Implemented in Python Package *pymatgen*
- Web application (https://crystaltoolkit.org/)

ChemEnv: D. Waroquiers, **J. George**, M. Horton, S. Schenk, K. Persson, G.-M. Rignanese, X. Gonze, G. Hautier *Acta Cryst. B*, **2020**, 76, 683.

Method

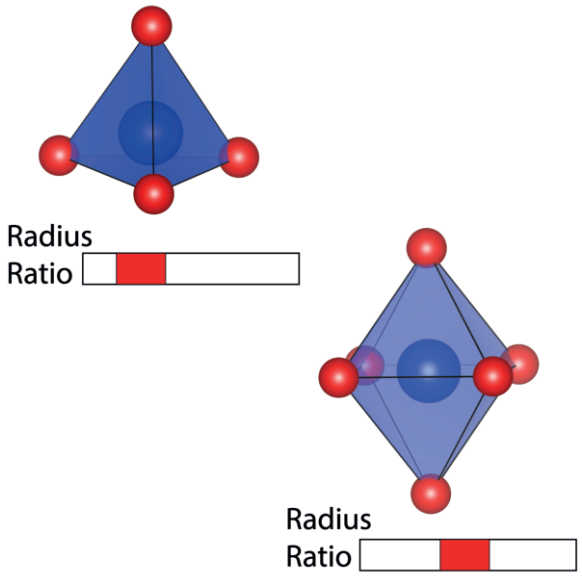


- Source code: https://github.com/JaGeo/PaulingPublication
- All details in our publication:

J. George, et al.
Angew. Chem. Int. Ed. **2020**, *59*, 7569.

1. Radius Ratio Rule

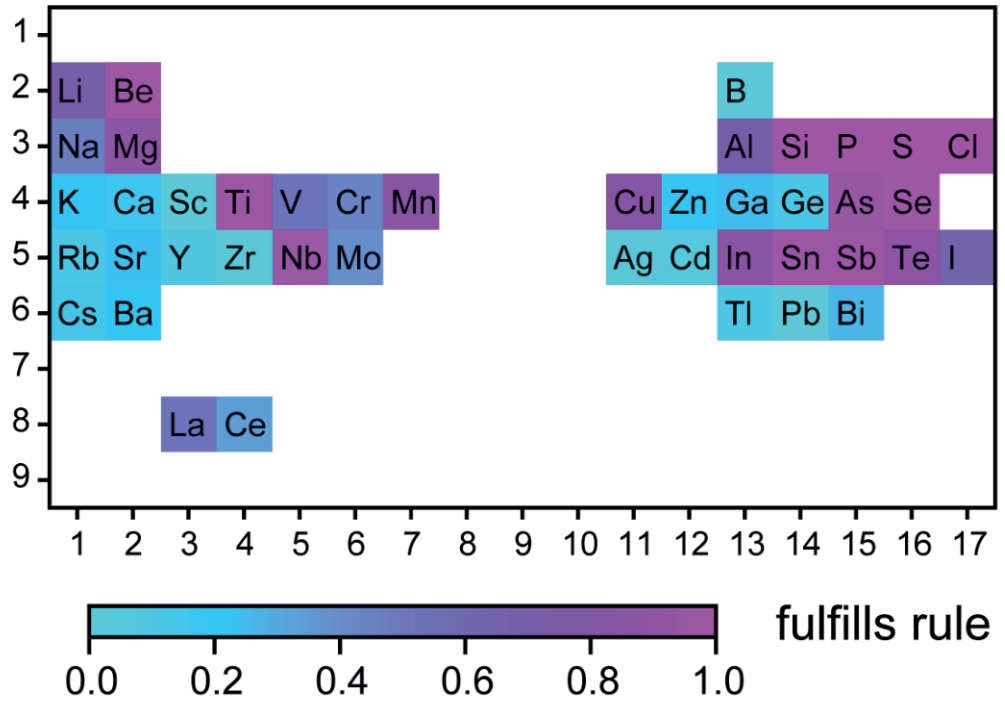
"[...] The coordination number of the cation [is determined] by the radius ratio [of cation and anion radius]."



- Comparison of Prediction by Rule to Geometric Determination via ChemEnv
- Univalent radii by Pauling

1. Radius Ratio Rule

Rule is only fulfilled for 66% of all tested environments!



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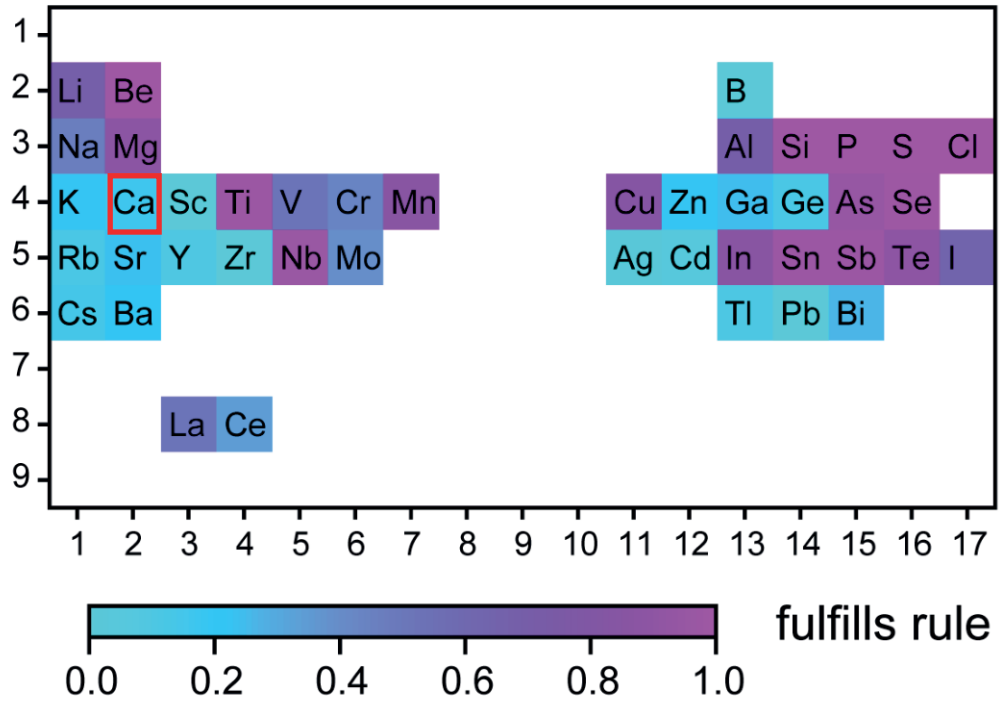
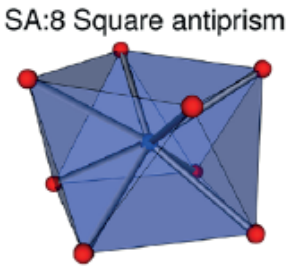


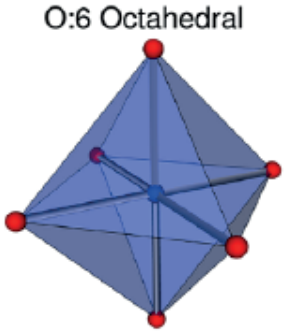
J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.

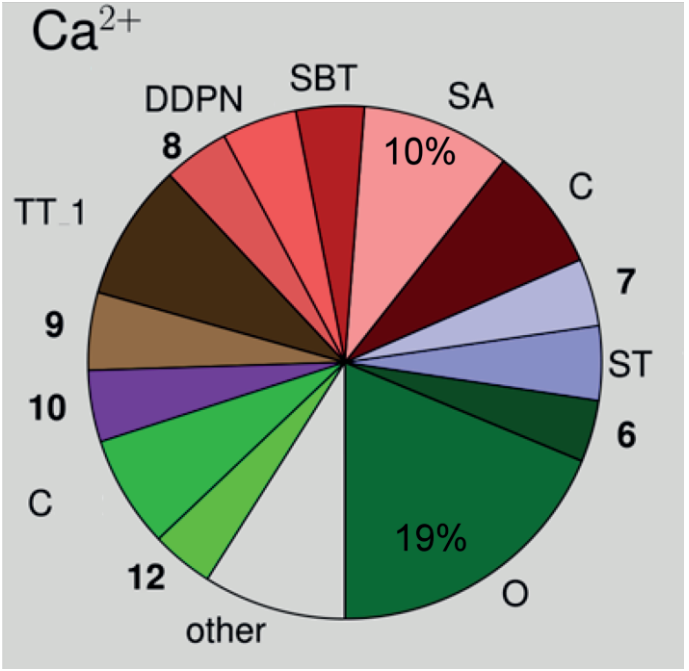
1. Radius Ratio Rule

- Radius ratio predicts square antiprism (SA)



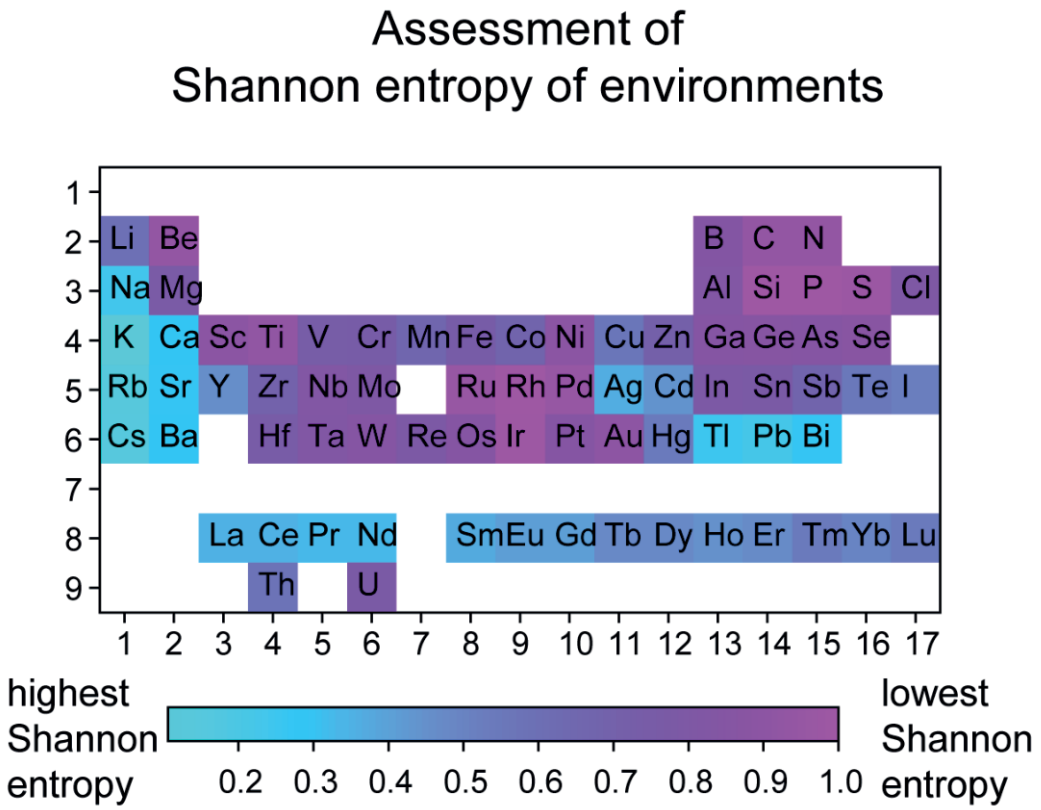
- Not even the most frequent environment





Figures from: D. Waroquiers, et al. *Chem. Mater.* **2017**, *29*, 8346.

1. Radius Ratio Rule

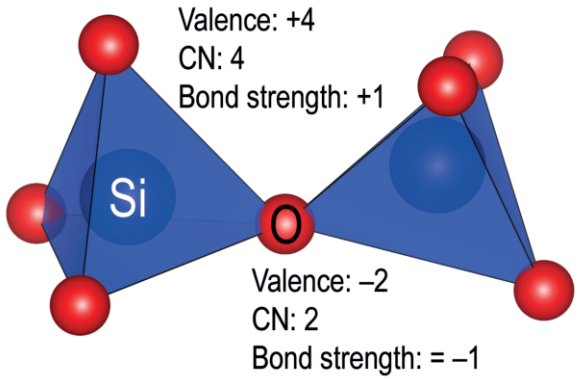


- High Shannon entropy:
  many different environments with low frequencies
- Limits of 1st rule:
  one radius ratio cannot be enough

J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.

2. Electrostatic Valence Principle

"In a stable coordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it [...] ."



- O:

  - valence: -2
  - neighbors: 2 Si neighbors
    both neighbors:
    +1 bond strength

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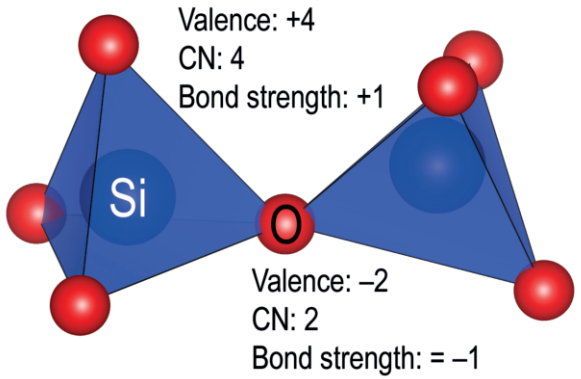

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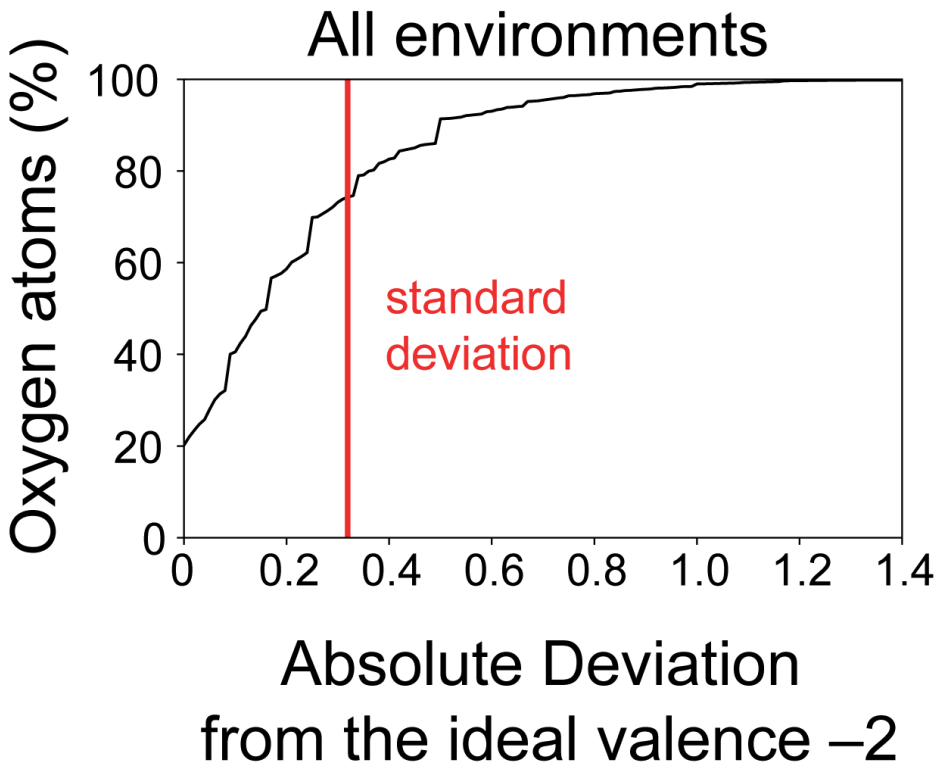
  - valence: -2
  - neighbors: 2 Si neighbors
    both neighbors:
    +1 bond strength

Test for every O in 5000 oxides

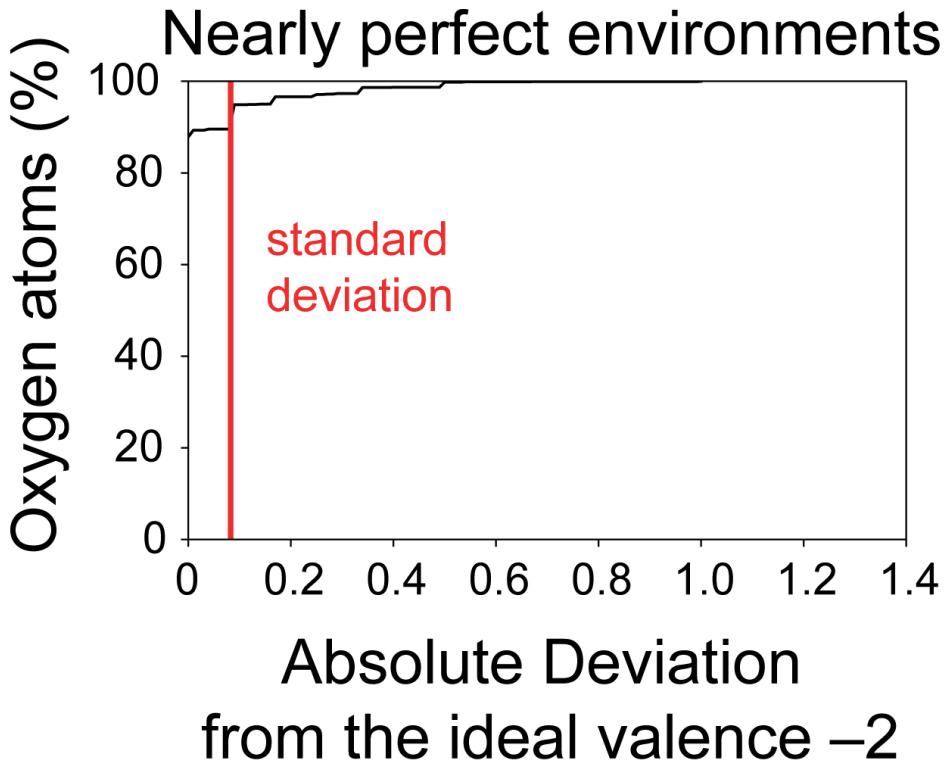
2. Electrostatic Valence Principle



- Only 20% fulfill rule

J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.

2. Electrostatic Valence Principle

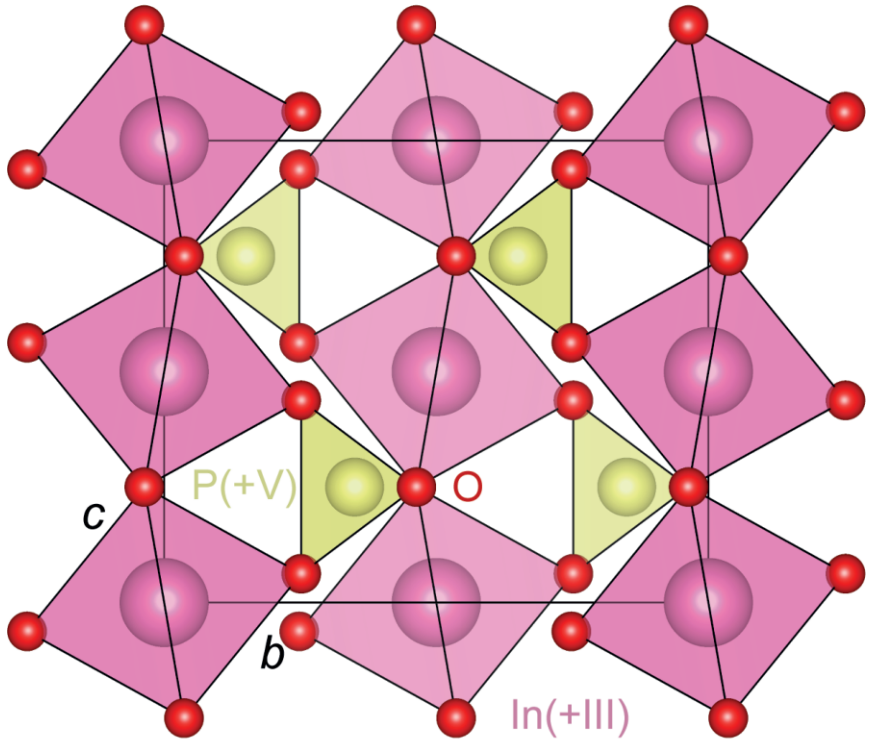


- Situation changes:
  only nearly perfect environments
- Distortion as local charge
  compensation [1]

J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.
[1] W. H. Baur, *Trans. Am. Crystallogr. Assoc.*, **1970**, *6*, 129.

2. Electrostatic Valence Principle

$InPO_4$



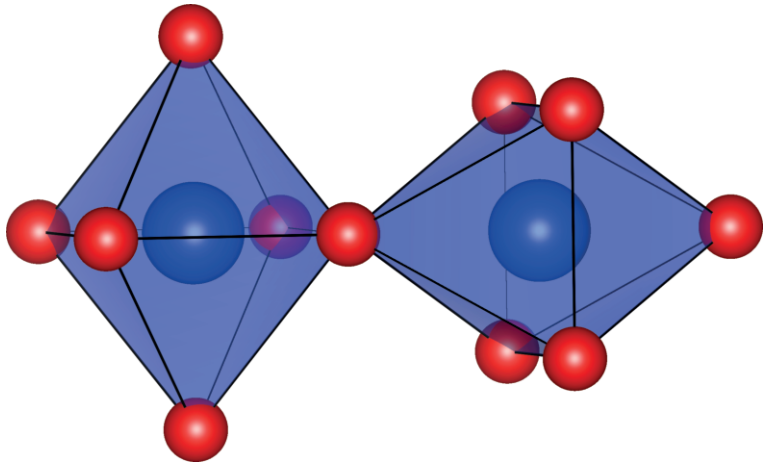
- In (+III): octahedral coordination
- P (+V): tetrahedral coordination

Bond strengths:
2 1/4 and 1 3/4 instead of 2

Crystal structure from: R. Mooney, *Acta Cryst.* **1956**, *9*, 113-117.

3. The Sharing of Edges and Faces

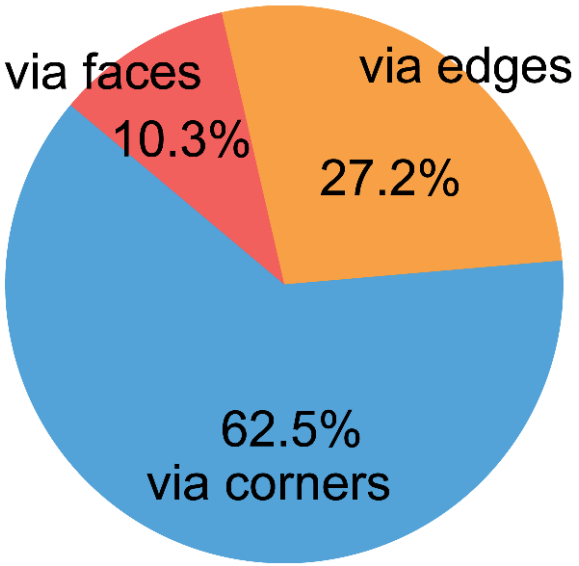
"The presence of shared edges, and particularly of shared faces, in a coordinated structure decreases its stability; [...]."



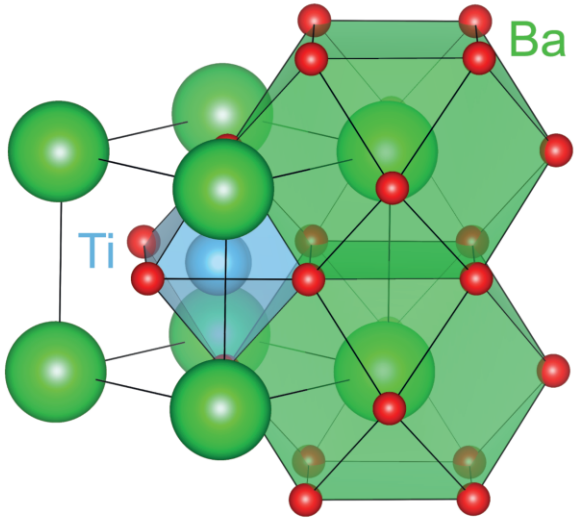
- Connected pairs of polyhedra

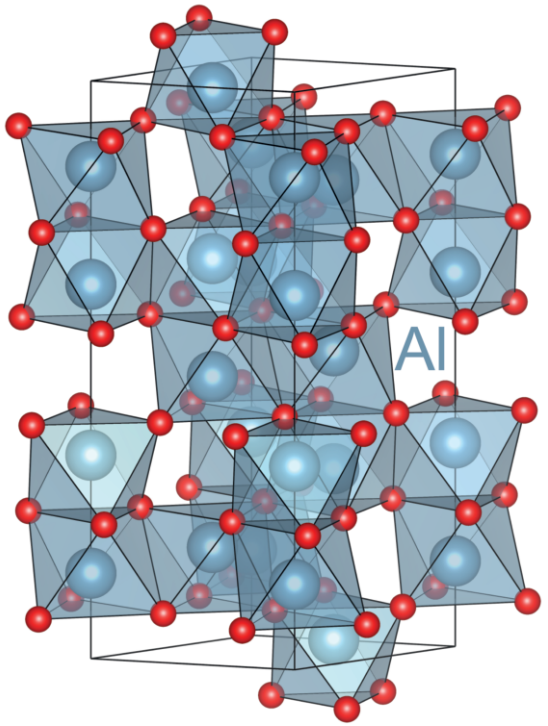
J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.

3. The Sharing of Edges and Faces



Polyhedra are mostly connected via corners





- Connections of the polyhedra

J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.

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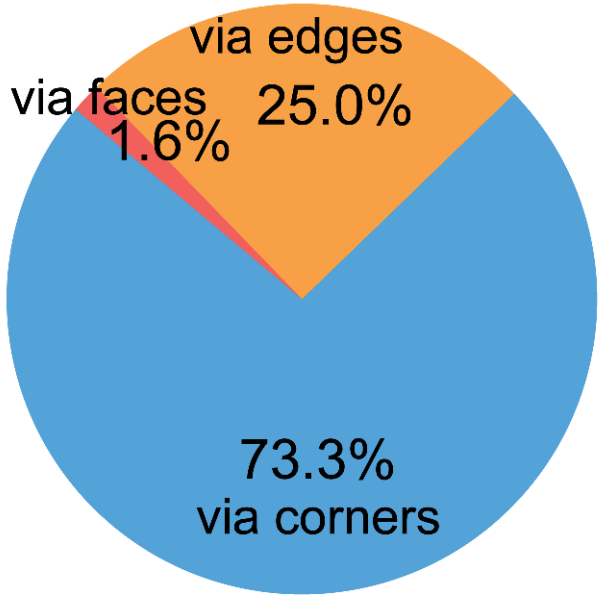


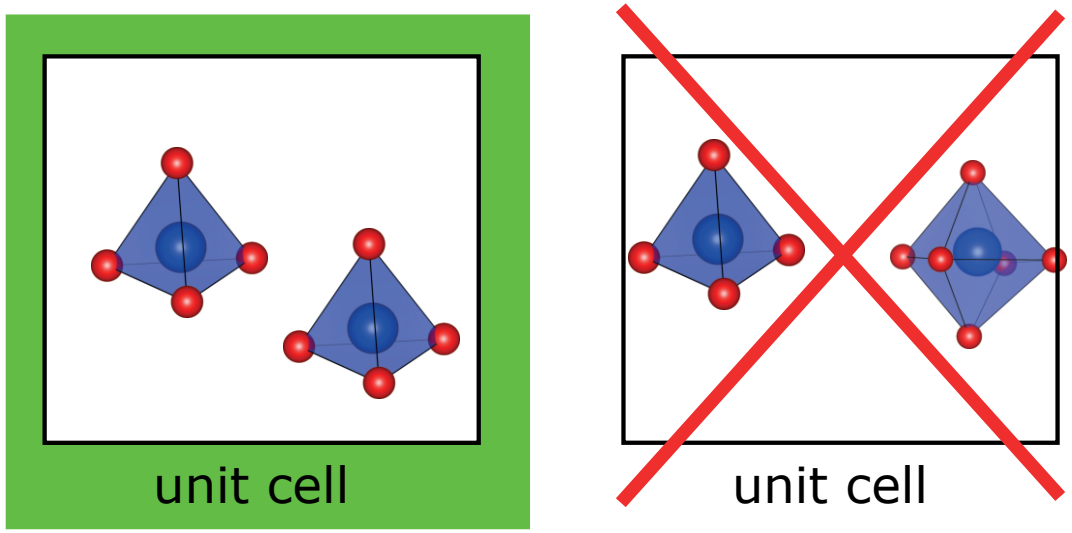
- Only coordination numbers ≤ 8
- Strong influence of the coordination numbers

- Connections of the polyhedra

J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.

5. Rule of Parsimony

"The number of essentially different kinds of constituents in a crystal tends to be small."



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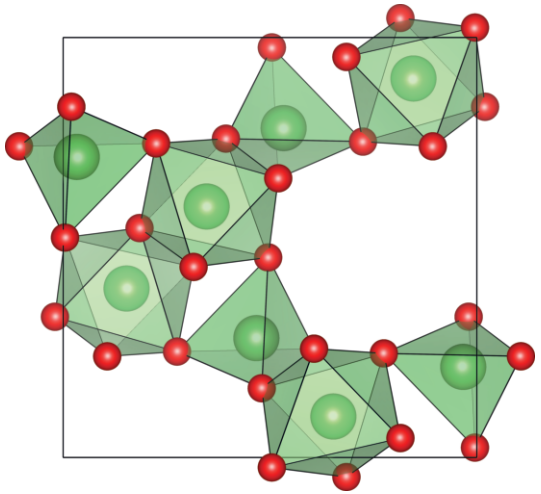


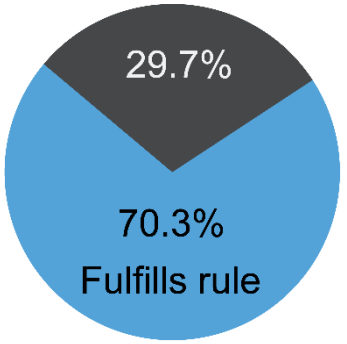
As_2O_5:
As (V) has tetrahedral and octahedral coordination environments

J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.
Crystal structure from: M. Jansen, *Angew. Chem. Int. Ed.*, **1977**, *16*, 314.

5. Rule of Parsimony

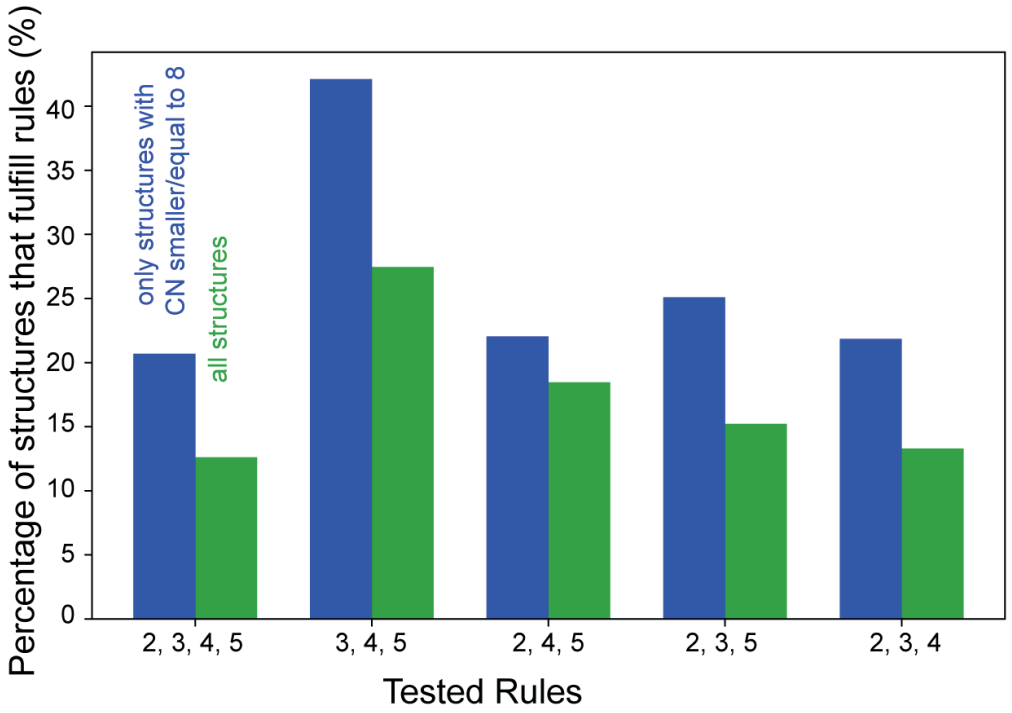
“The number of essentially different kinds of constituents in a crystal tends to be small.”

How large is the percentage of structures in which all cations of the same element and the same valence have the same coordination number?



J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.

Combined Assessment



- **First analysis of all 5 Rules**

- **Combined Assessment of Rules 2 to 5**
  - **2-5: fulfilled by 13% of all structures**

J. George, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7569.

Other studies on chemical heuristics including pymatgen

BAM

Materials discovery by chemical analogy: role of oxidation states in structure prediction†

Daniel W. Davies, [a] Keith T. Butler, [a] Olexandr Isayev [b] and Aron Walsh *[cd]

Structure-Based Synthesizability Prediction of Crystals Using Partially Supervised Learning

Jidon Jang,† Geun Ho Gu,† Juhwan Noh, Juhwan Kim, and Yousung Jung*

Cite This: *J. Am. Chem. Soc.* 2020, 142, 18836–18843 Read Online

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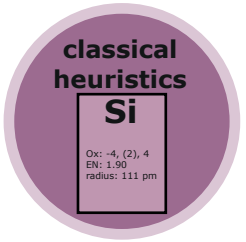
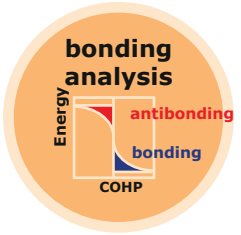
Testing passing | downloads 287k total | coverage 84%

Agenda

Automation to Test
Chemical Heuristics



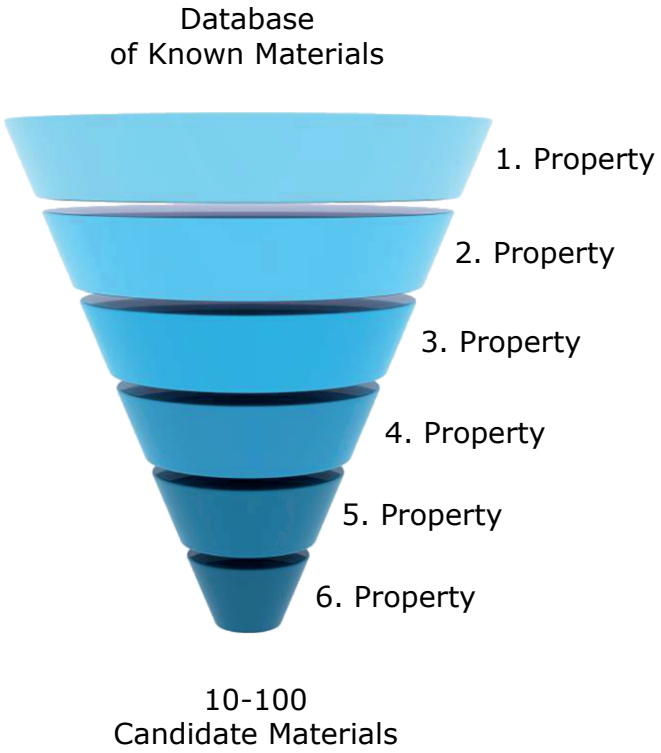


Automation
for Materials Design
and Understanding

THE DISCOVERY OF NEW MATERIALS WITH COMPUTED PROPERTIES

MATERIALS PROJECT

High-Throughput Studies



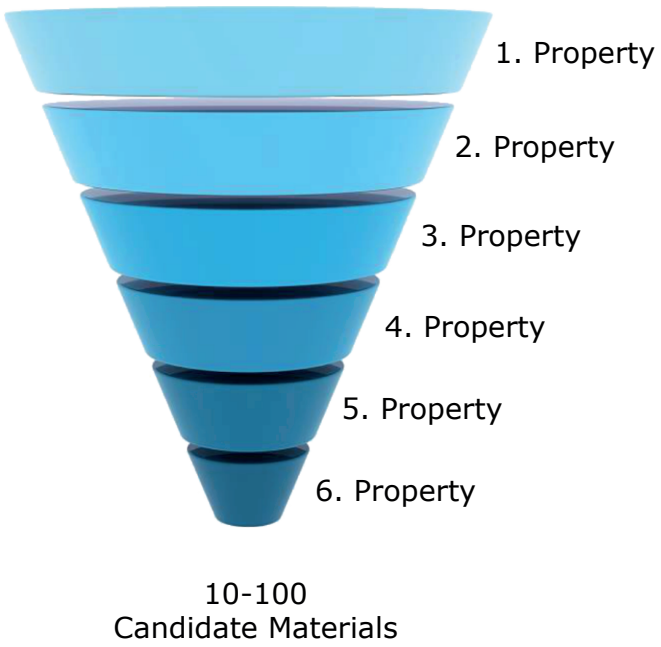
- Only very few compounds are characterized well

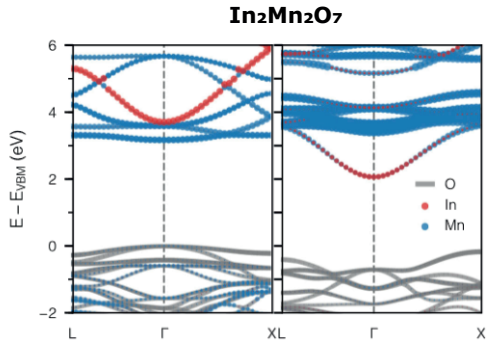
- Computed materials properties can help!

MATERIALS PROJECT

- Reduced number of materials need to be synthesized and characterized

High-Throughput Studies



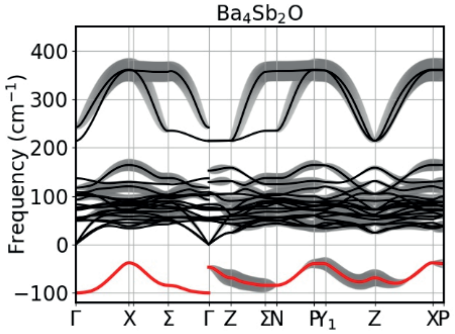


- materials for spintronic applications

W. Chen, J. George, et al.
npj Comput Mater, 2019, 5, 72.

- new ferroelectric materials

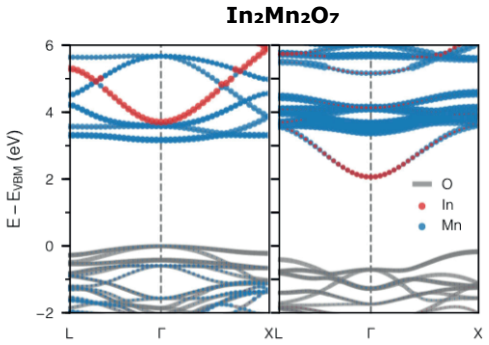
M. Markov, L. Alaerts, H. P. C. Miranda, G. Petretto, W. Chen, J. George, et al.
PNAS, 2021, 118, e2026020118.



- photovoltaic materials

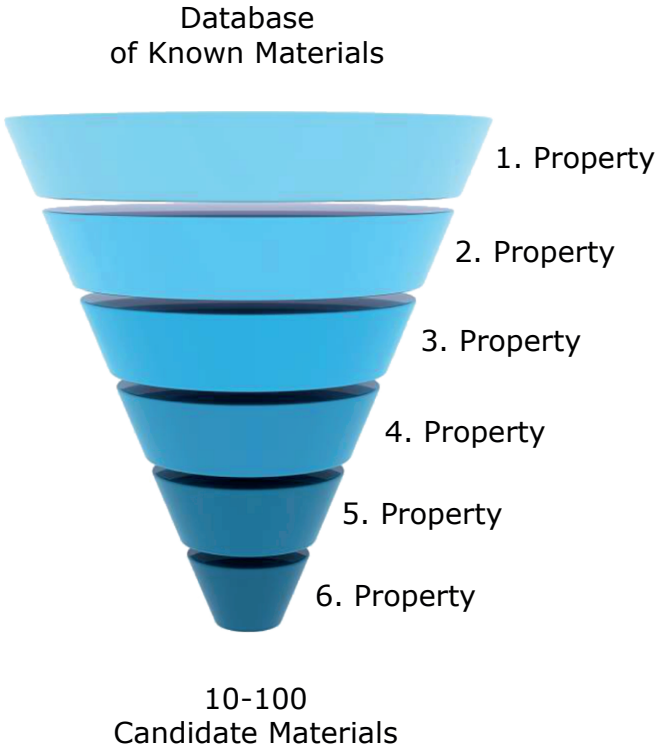
D. Dahliah, G. Brunin, J. George, et al.
Energy & Environmental Science
2021, DOI 10.1039/D1EE00801C.

High-Throughput Studies



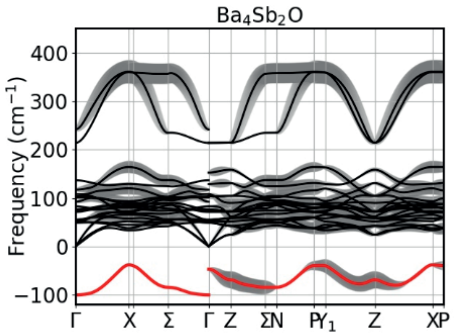
- materials for spintronic applications

W. Chen, J. George, et al.
npj Comput Mater, 2019, 5, 72.



- new ferroelectric materials

M. Markov, L. Alaerts, H. P. C. Miranda, G. Petretto, W. Chen, J. George, et al.
PNAS, 2021, 118, e2026020118.

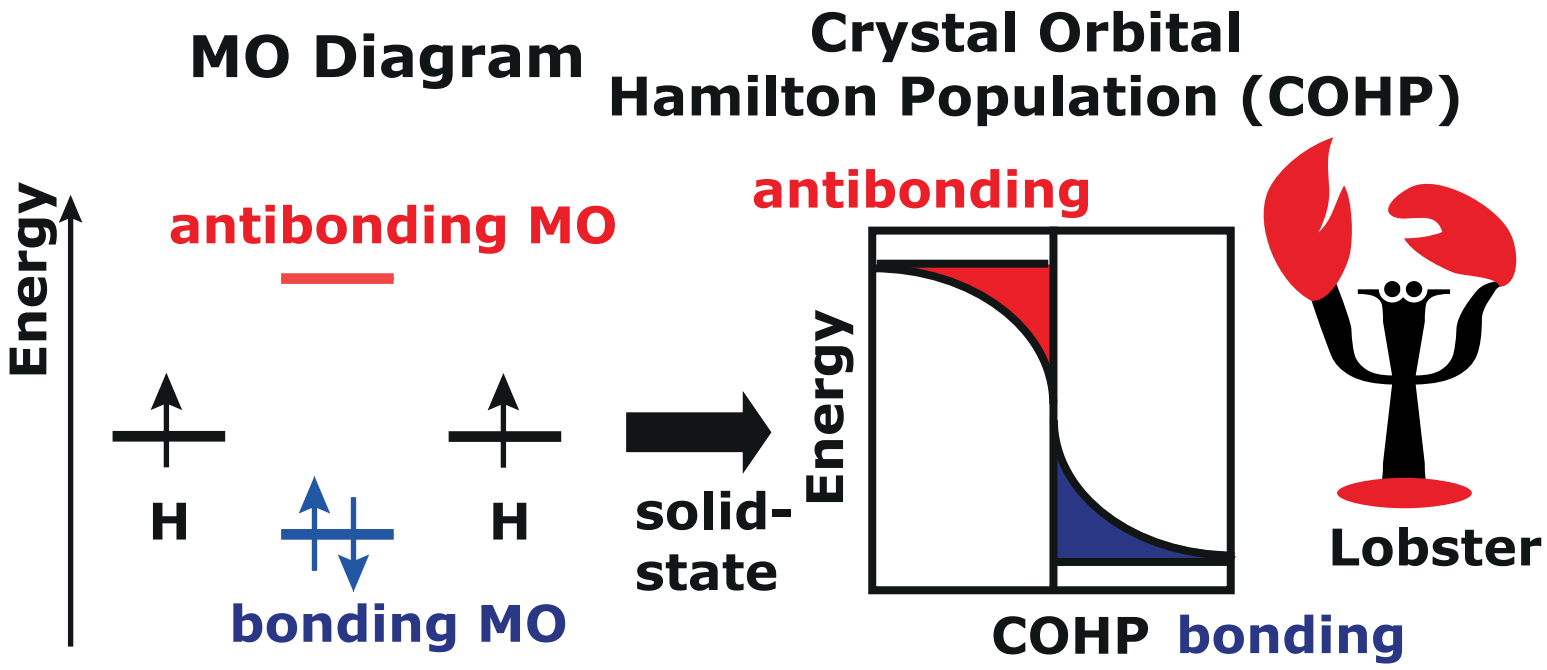


- photovoltaic materials

D. Dahliah, G. Brunin, J. George, et al.
Energy & Environmental Science
2021, DOI 10.1039/D1EE00801C.

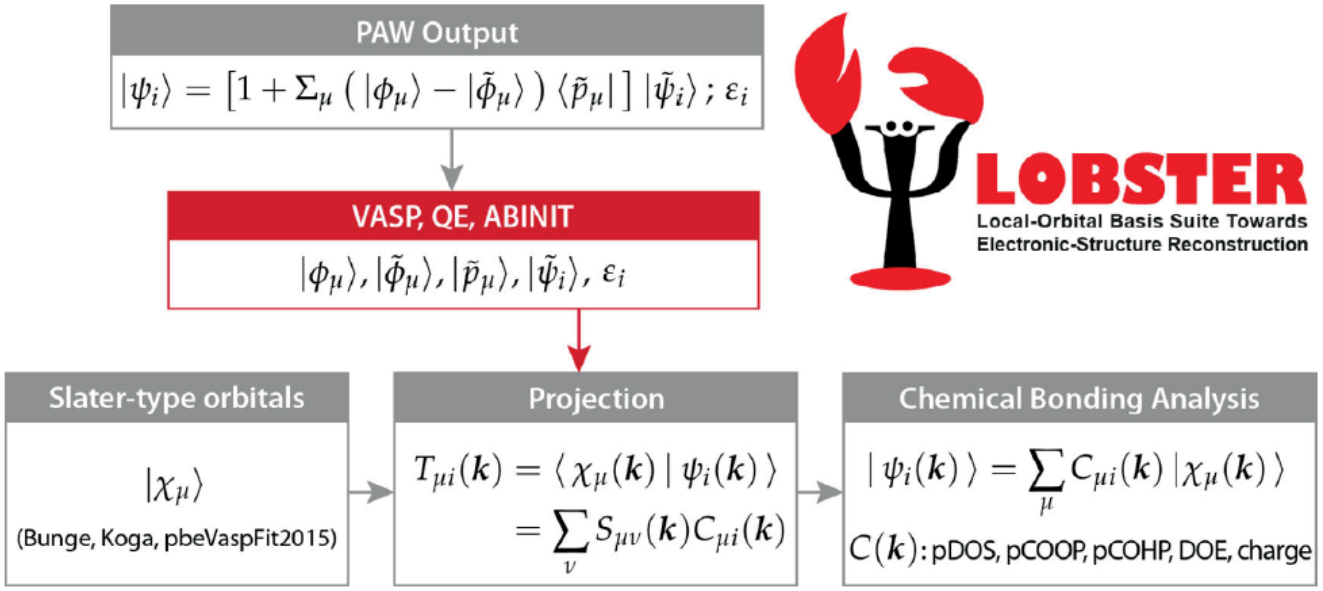
CHEMICAL UNDERSTANDING!

Chemical understanding: Bonding Analysis



R. Nelson, C. Ertural, **J. George,** V. L. Deringer, G. Hautier, R. Dronskowski, "LOBSTER : Local orbital projections, atomic charges, and chemical-bonding analysis from projector-augmented-wave-based density-functional theory" J. Comput Chem., 2020, 41, 1931– 1940.

Chemical understanding: Lobster



see www.cohp.de for more info (Dronskowski group)

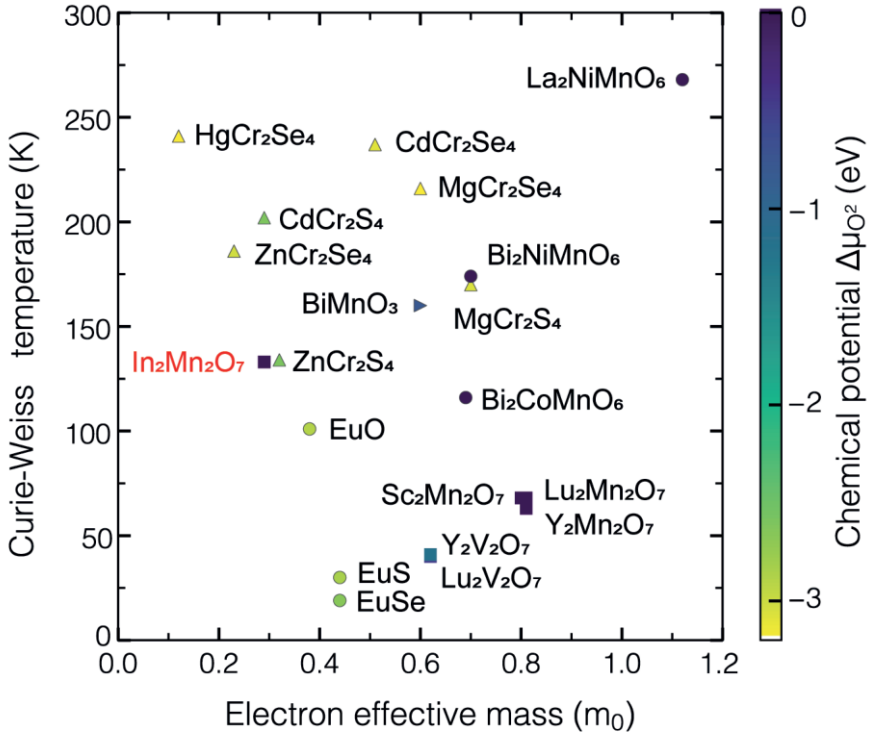
VASP/QE/Abinit

PAW method

R. Nelson, C. Ertural, **J. George,** V. L. Deringer, G. Hautier, R. Dronskowski, "LOBSTER : Local orbital projections, atomic charges, and chemical-bonding analysis from projector-augmented-wave-based density-functional theory" J. Comput Chem., 2020, 41, 1931– 1940.

Lobster in High-Throughput Studies

materials for spintronic applications (electronic devices):



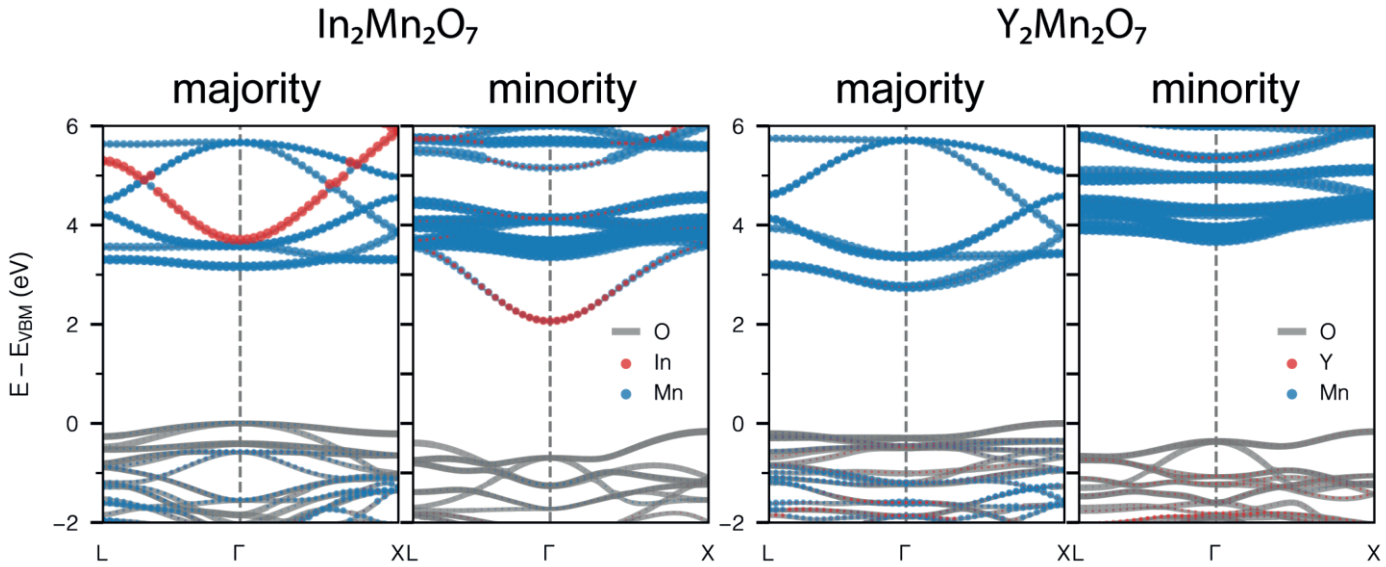
Properties:

- ferromagnetic compound
- good semiconductor
- high Curie temperature
- stable against oxidation

Start from Materials Project

W. Chen, J. George, et al. *npj Comput Mater*, **2019, *5*, 72.**

Lobster in High-Throughput Studies

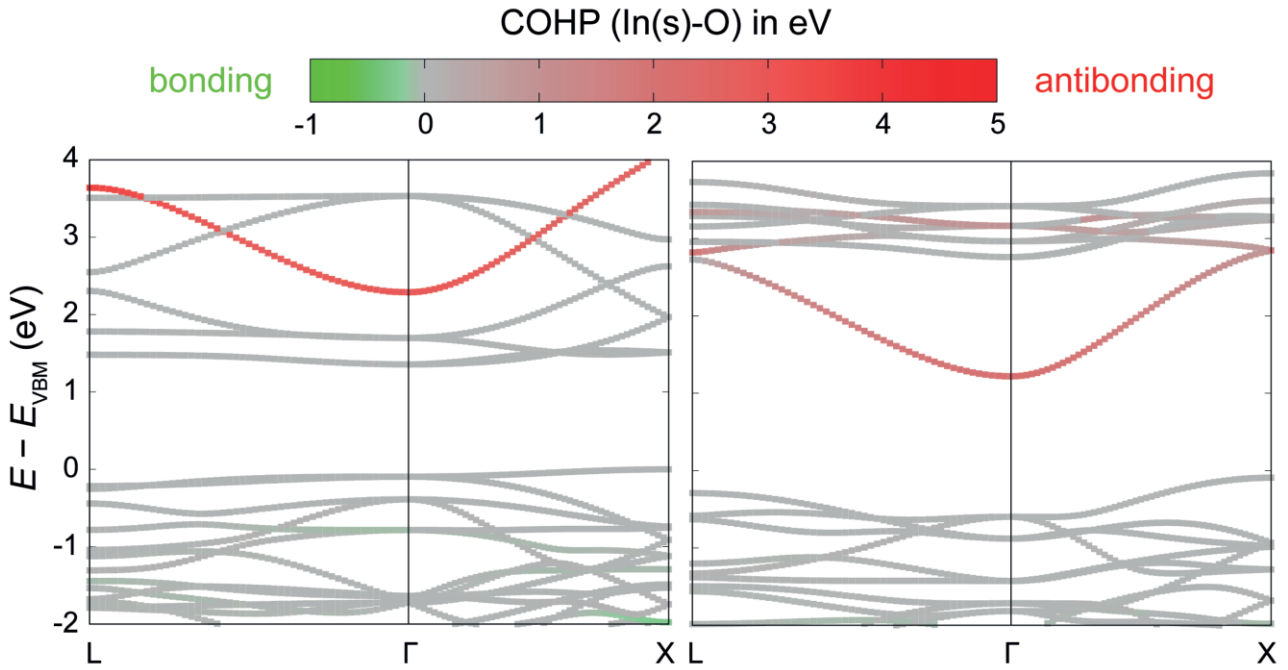


Understanding of the results:

- Difference to other pyrochlore compounds
- In 5s contribution

W. Chen, J. George, et al. *npj Comput Mater*, **2019**, *5*, 72.

Lobster in High-Throughput Studies

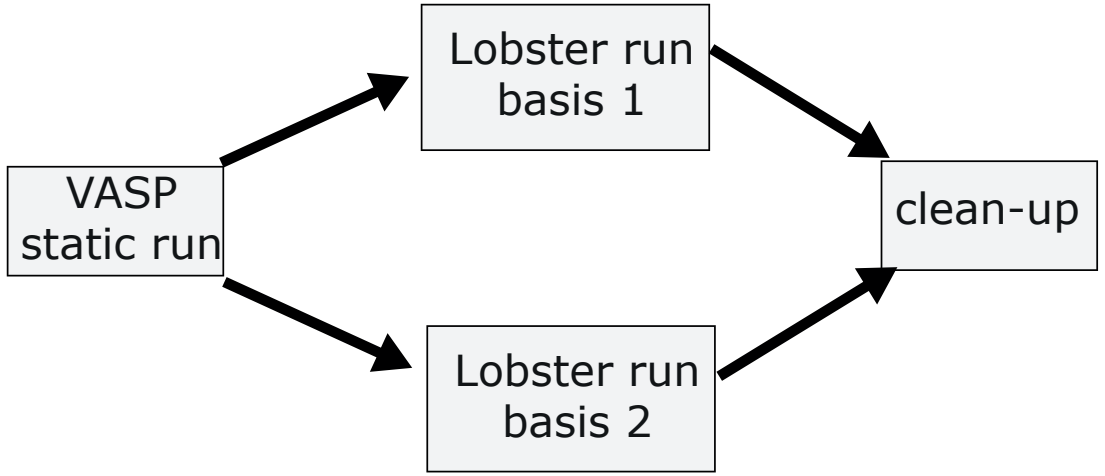


Understanding of the results:
Antibonding In (5s) - O interaction

W. Chen, J. George, et al. *npj Comput Mater*, **2019**, *5*, 72.

High-Throughput Bonding Analysis

Simplify Understanding of Stability and Properties Based on Chemical Bonds



-calculates DFT wave function

- calculates number of bands

-projects plane wave-based basis on atomic orbitals

-analyses bonding situation

-deletes wave function (large files)

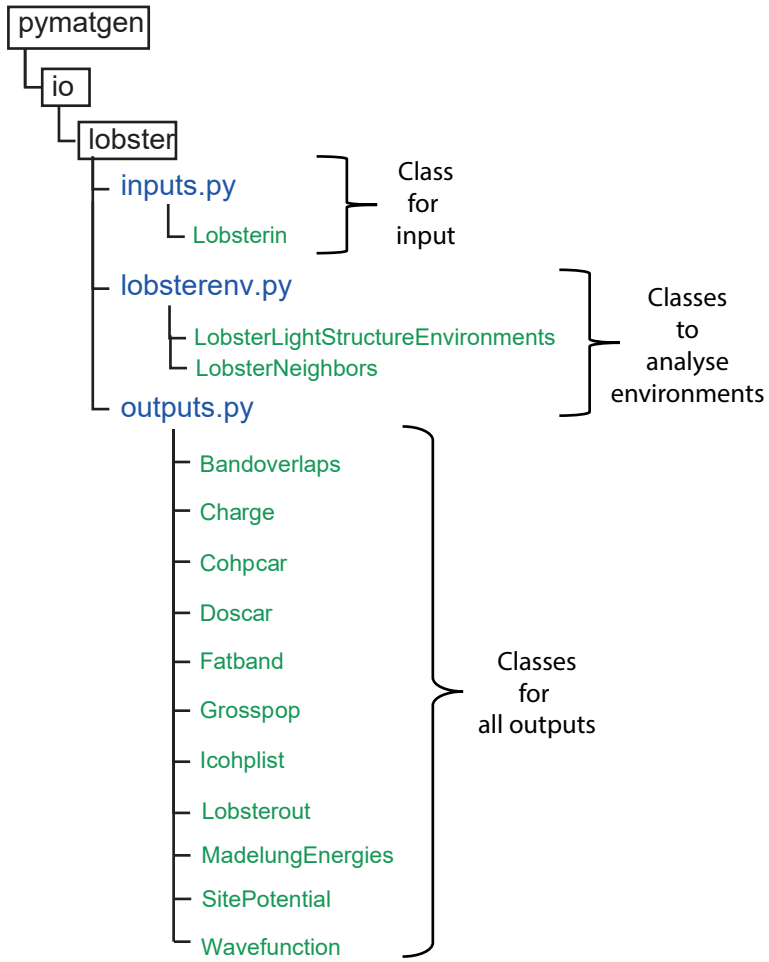
- few lines of code to start fully automated workflow

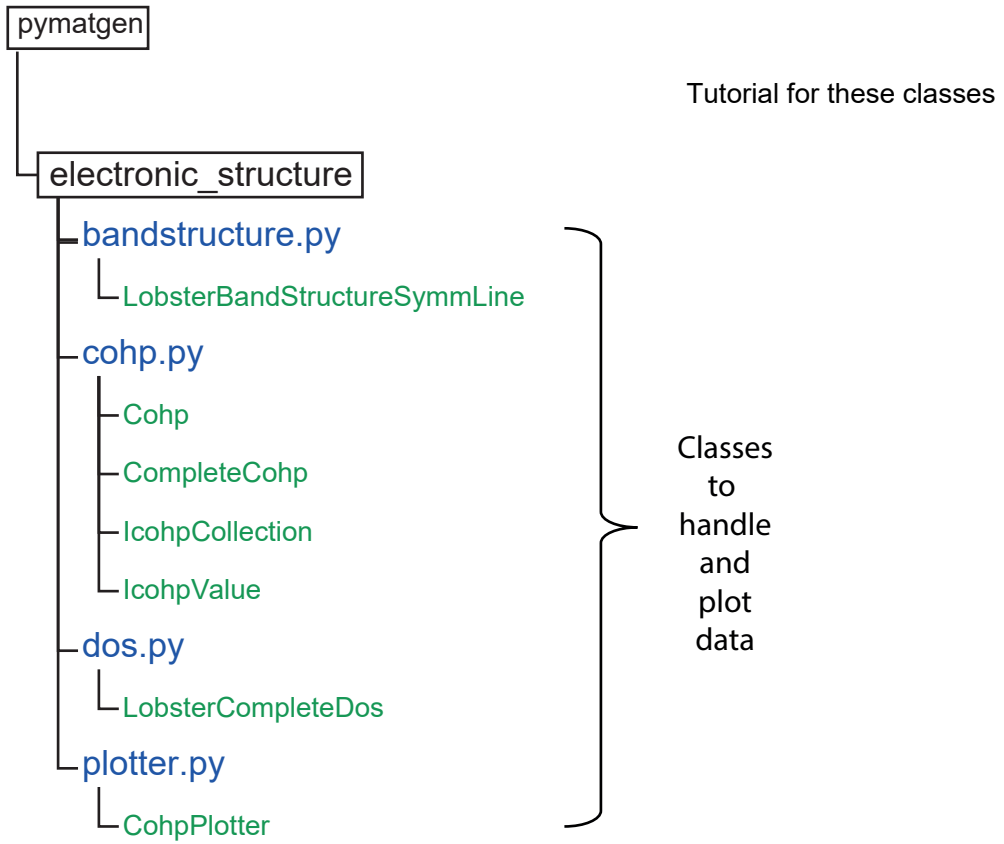
- implemented in pymatgen atomate

- tutorial is available

- similar workflows for many properties available!

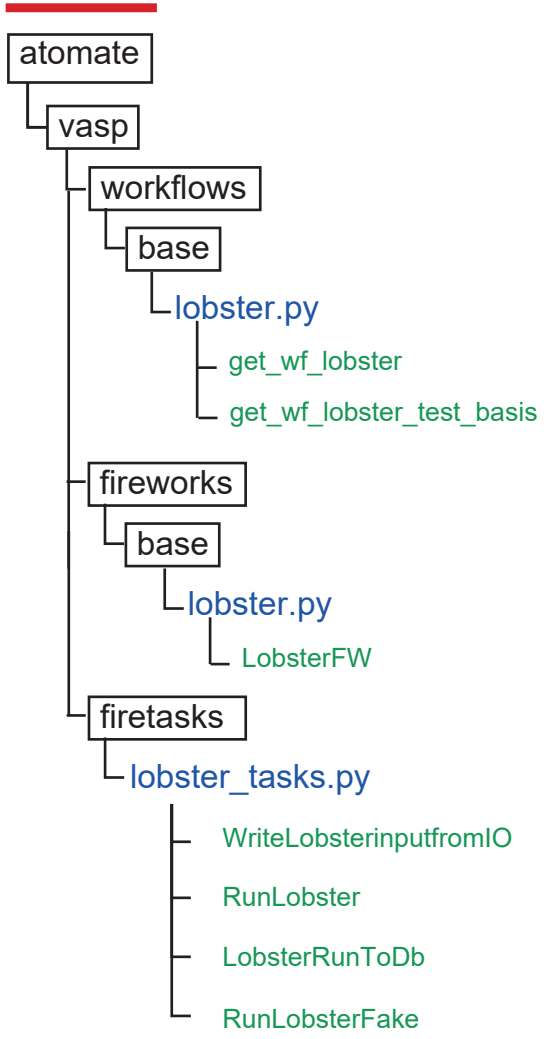
New classes for pymatgen



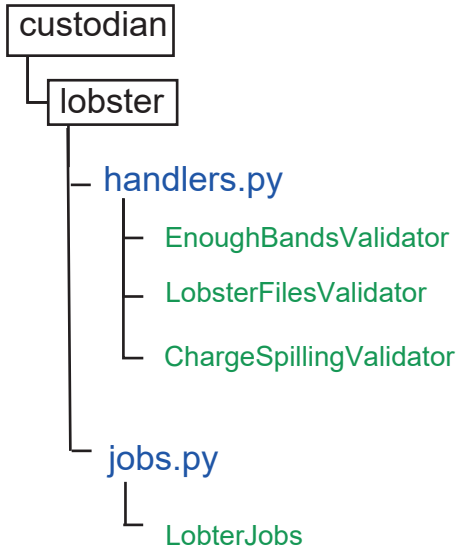


Implementations were started by Marco Esters (now: Duke University)
Code review and suggestions: Guido Petretto, UCLouvain

New classes for atomate (and +custodian)

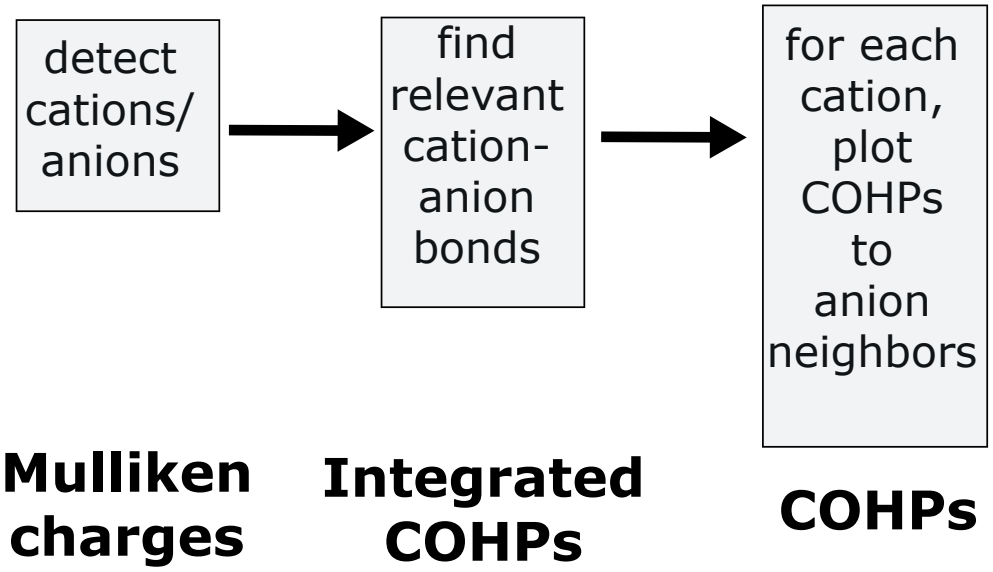


Two different Lobster workflow
- one will search for the best projection
- the other one will use a pre-defined basis set



Code review and suggestions: Guido Petretto, UCLouvain
Alex Ganose (now: Imperial College London)

High-Throughput Bonding Analysis



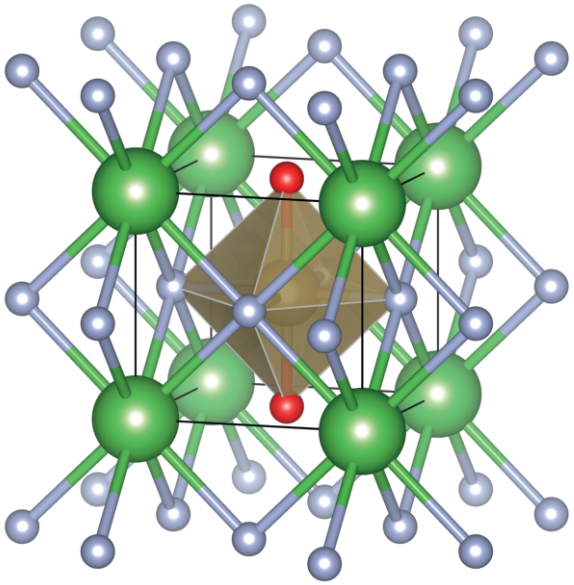
- Automatic analysis of the results
- Analyses most important bonds automatically
- Work in progress!
- Will simplify correlation with other materials properties

Mulliken Charges in Lobster: C. Ertural, S. Steinberg, R. Dronskowski, *RSC Advances* **2019**, 9, 29821–29830.

High-Throughput Bonding Analysis

Example: $LaTaN_2O$

anion order?



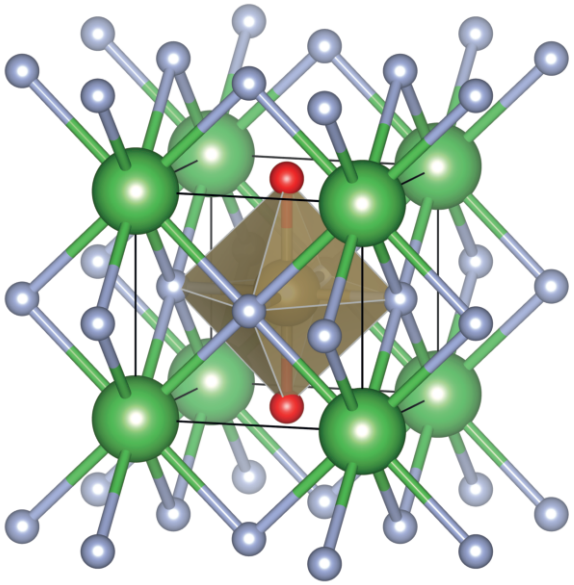
The compound $LaTaN_2O$ has 2 symmetry-independent cations with relevant cation-anion interactions: La0, Ta1. La0 has a Cuboctahedral (CN=12) coordination environment. It has 8 La-N (mean ICOHP: -1.52 eV), and 4 La-O (mean ICOHP: -0.98 eV bonds. Ta1 has an octahedral (CN=6) coordination environment. It has 4 Ta-N (mean ICOHP: -4.87 eV), and 2 Ta-O (mean ICOHP: -4.9 eV bonds.

Example from: J. George, et al. „Automated Bonding Analysis with Crystal Orbital Hamilton Populations“, In Preperation.

High-Throughput Bonding Analysis

Example: $LaTaN_2O$

anion order?

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```


Example from: J. George, et al. „Automated Bonding Analysis with Crystal Orbital Hamilton Populations“, In Preperation.

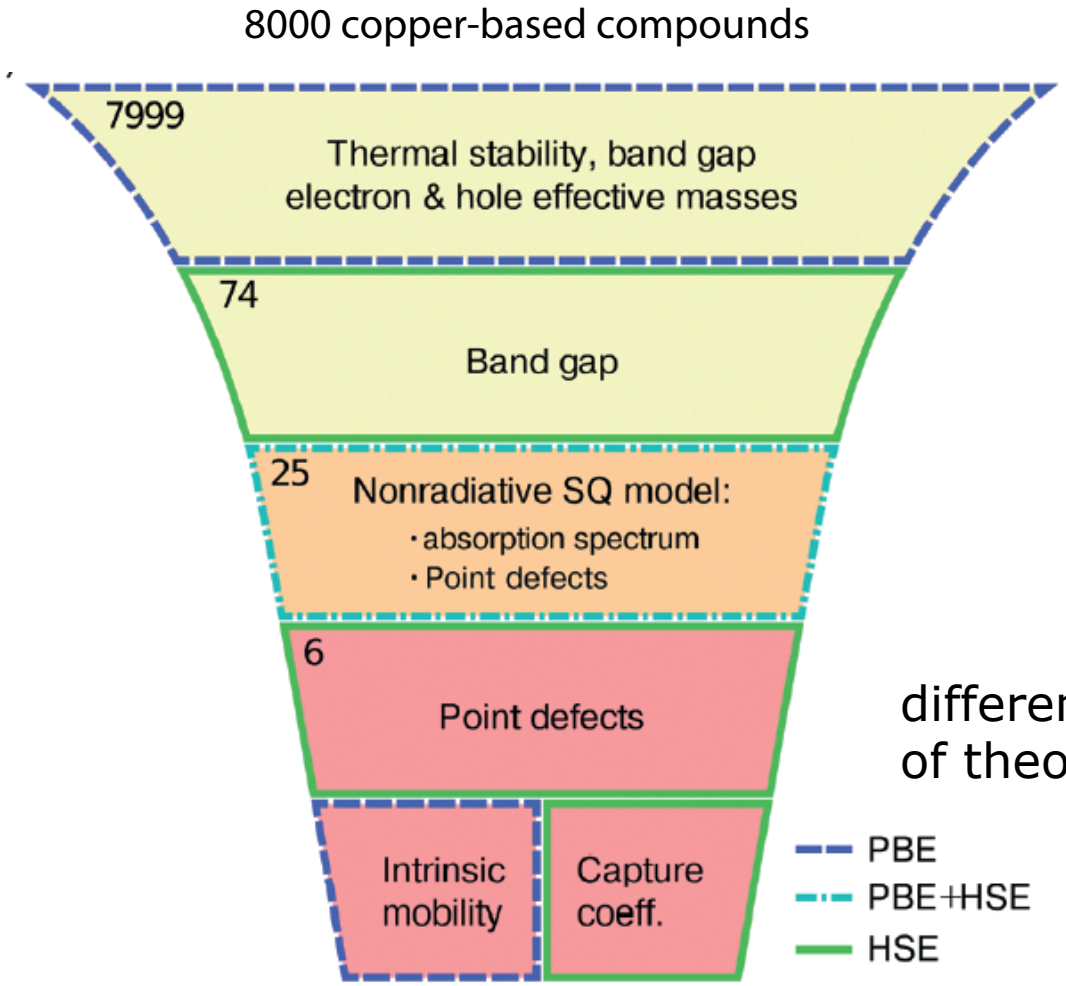
High-throughput search photovoltaics:

Our recent search for photovoltaics

- high-throughput studies become more complex

- search for good photovoltaics = search for „defect-tolerant" materials

- including carrier lifetime estimates (point defects are important!)

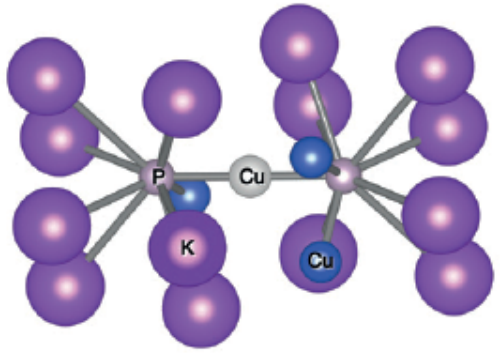


Picture from :
D. Dahliah, G. Brunin, J. George, et al.
Energy & Environmental Science
2021, DOI 10.1039/D1EE00801C.

High-throughput search photovoltaics:

Our recent search for photovoltaics

Analysis of Bonding Cu-Anion Bonds
To Understand Formation Energy
of Cu Vacancies



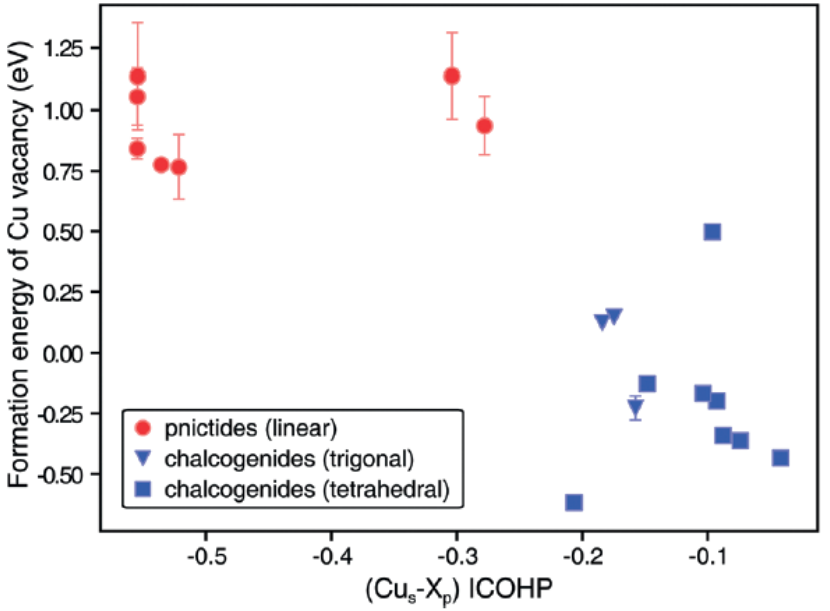
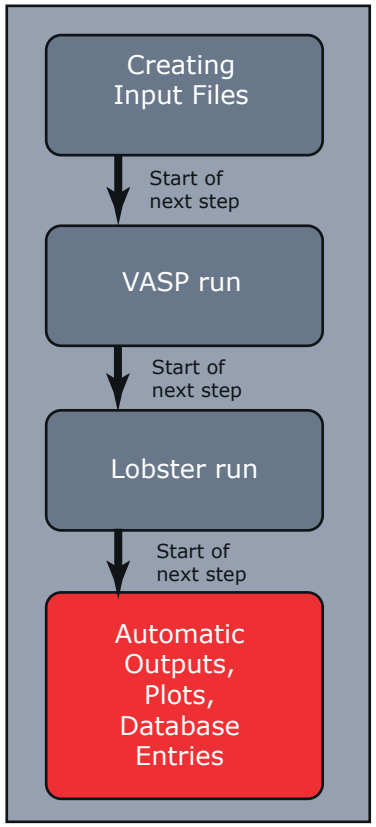


Fig. 10 Formation energy of the neutral Cu-vacancy *versus* integrated COHP (ICOHP) in the range of [−2,0] eV from VBM for alkali-Cu based candidates (structures without defect). The vertical lines correspond to the range of formation energy at different growth conditions.

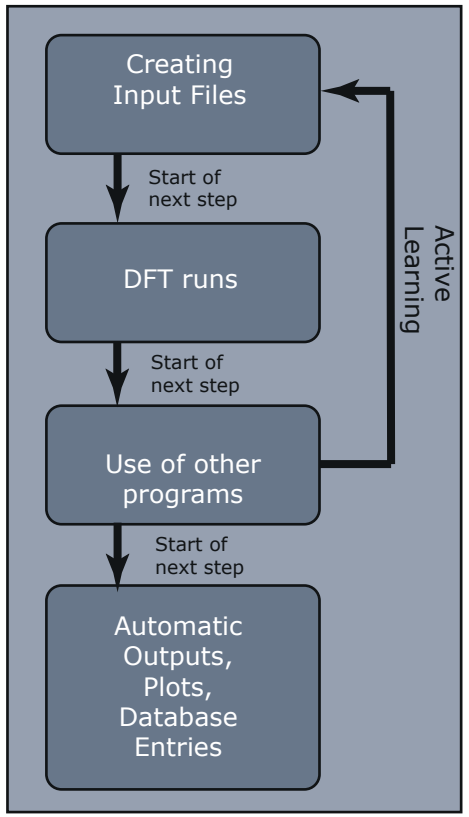
Picture from :
D. Dahliah, G. Brunin, J. George, et al.
Energy & Environmental Science
2021, DOI 10.1039/D1EE00801C.

Vision for Automation

Bonding Analysis



General Vision



Several processes have been automated in a similar way

- band structure calculations
- point defects

Forum: J. George, "Automation in Computational Materials Science", Trends in Chemistry 2021, 3, 697–699.

High-Throughput Studies

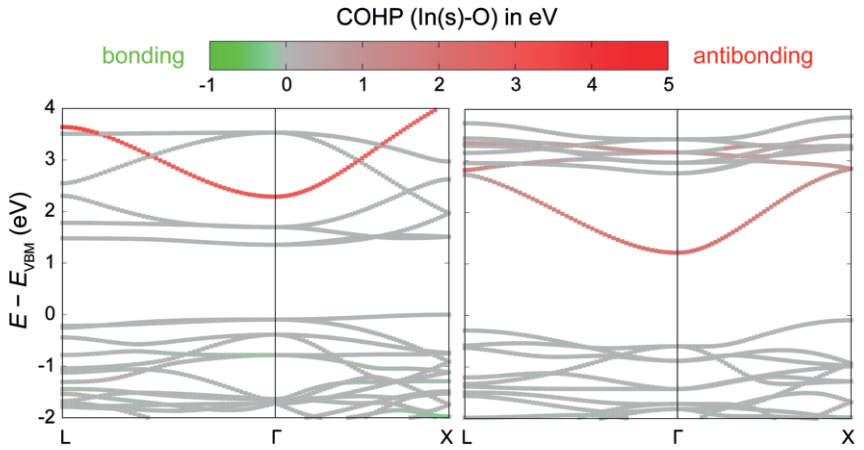
- Discover new materials (spintronic applications, ferroelectrics)

- New opportunities due to automation:

  - answers to complex questions can be automated

  - reproducibility

- (High-throughput) bonding analysis to understand stabilities/properties

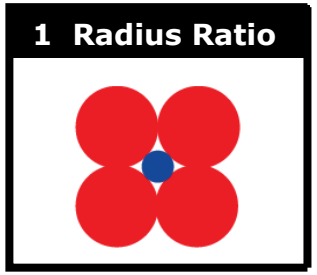


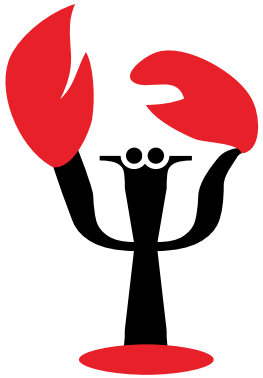
Summary

- Chemical heuristics rules can be tested!

- New chemical insights based on bonding analysis!

- Automation and Python tools play an important role!





Lobster

Acknowledgements

Prof. Geoffroy Hautier, UCLouvain
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Dr. Matthew Horton
Dr. Wei Chen
Dr. Maksim Markov
Diana Dahliah

Dr. Ryky Nelson
Christina Ertural

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