Structure / Phase Search with DFT

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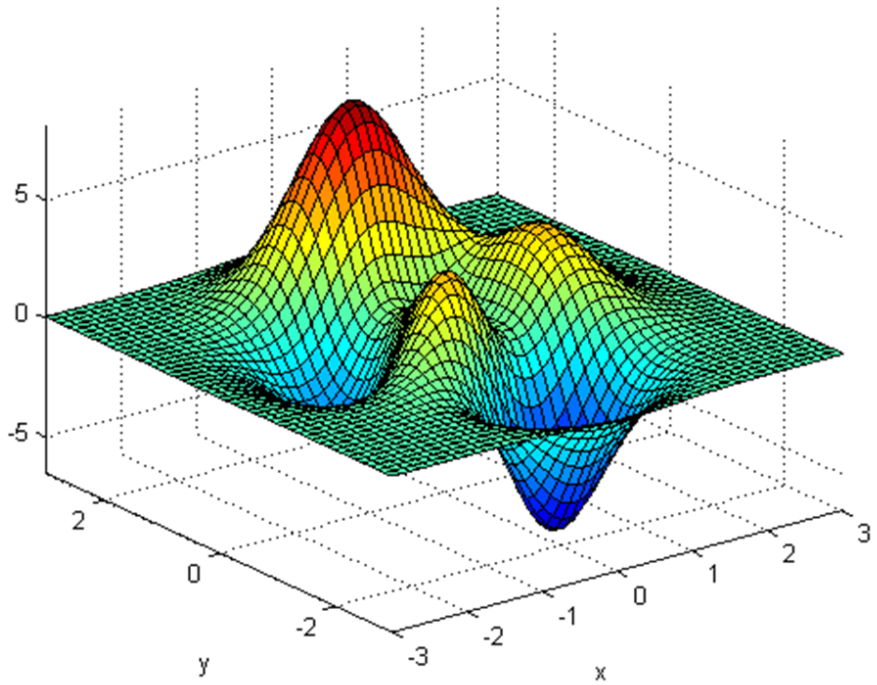
Take-Home Message 1

30 years ago, John Maddox declared that our inability to predict new crystal structure from its chemical composition is a "scandal in the physical sciences" ...[Nature 335 (1988), p. 201]

... who knows the Potential Energy Surface (PES) of a material ?



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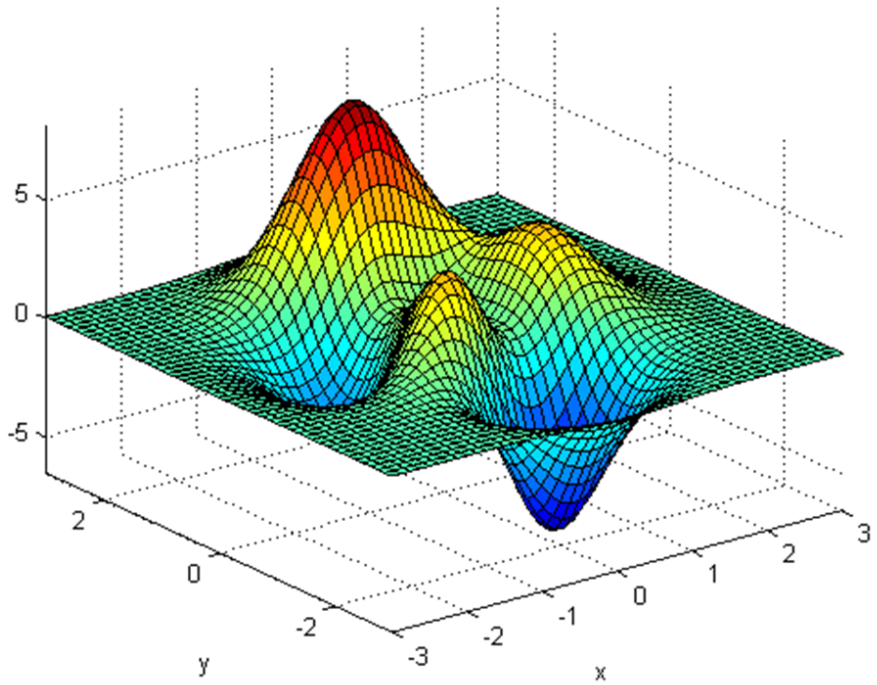


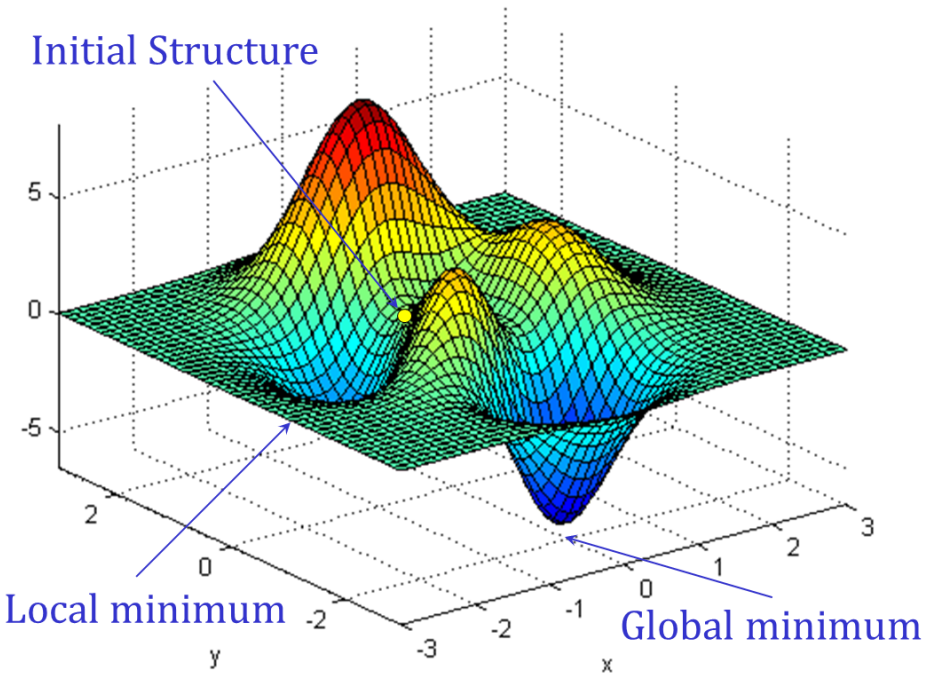
... no one !

Exploration of the PES

- Structural relaxations in perdiodic DFT codes

$$\hat{H}(r_i\ , R_\alpha) \equiv \hat{H}^{el}_{R_\alpha}(r_i) \qquad \text{Choice of the DFT XC functional}$$

$$E^{DFT}_{GS}[\rho] \longrightarrow \frac{\partial E}{\partial R_\alpha} \qquad \text{Hellmann-Feynman forces}$$



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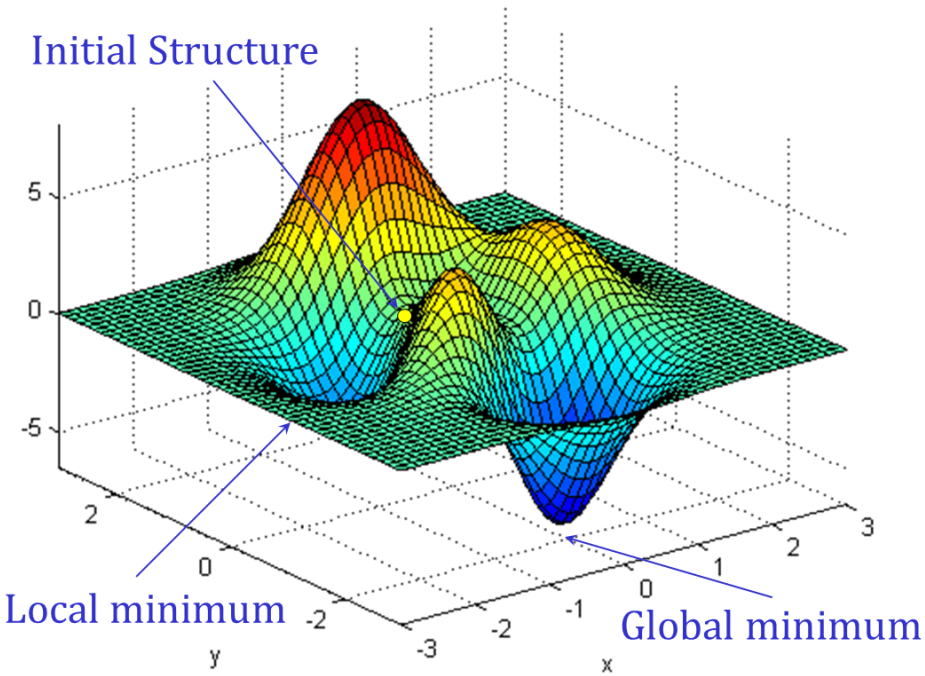


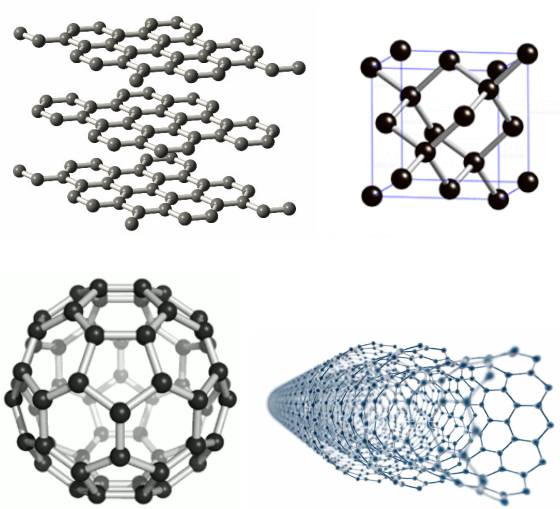
LOCAL energy minimization procedures !

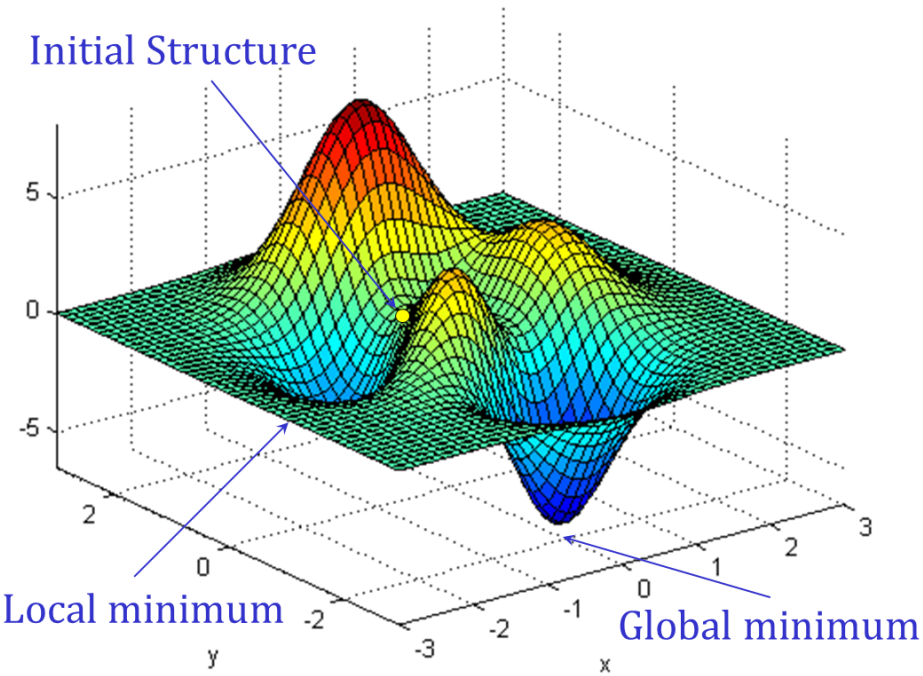
Exploration of the PES

- Structural relaxations in perdiodic DFT codes

Constrained simulation boxes → Impact on Polymorphism

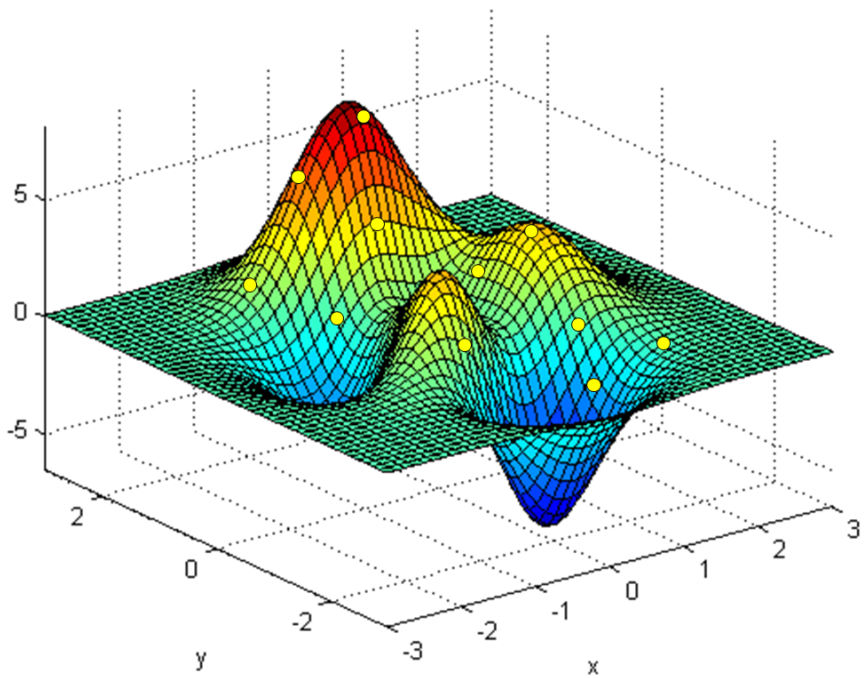
Fully ordered structures → No statistical distribution





Exploration of the PES

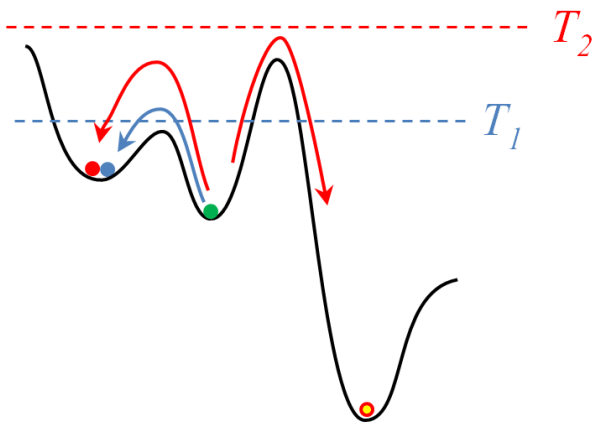
- Sampling Methods → Global minimization procedures
  - Stochastic algorithms
    - Simulated annealing (Thermostat)
    - Random displacements / perm.
  - Genetic algorithm
    - Crystallographic populations
    - Darwin principle
  - Bayesian algorithm
    - Occurrence probability
    - Neuronal networks



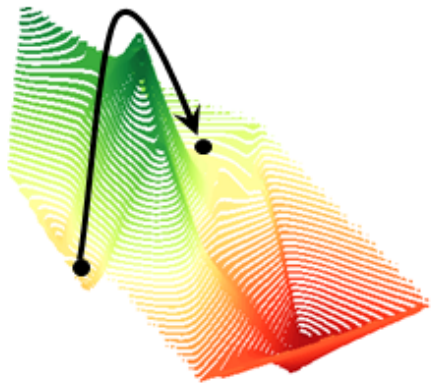
Growing interest in the past 15 years (high-throughput calculations)

Stochastic Methods

- How to get around energy barriers of PES?



- Use temperature + quenching
- Less and less used in condensed matter



- Random atomic distributions / permutations
- More and more used in condensed matter

The more you check, the more confident you are on the results ... no limits !
You can afford "coarse" calculations to screen / identify more interesting areas

Bayesian / Genomic Methods

Material Project

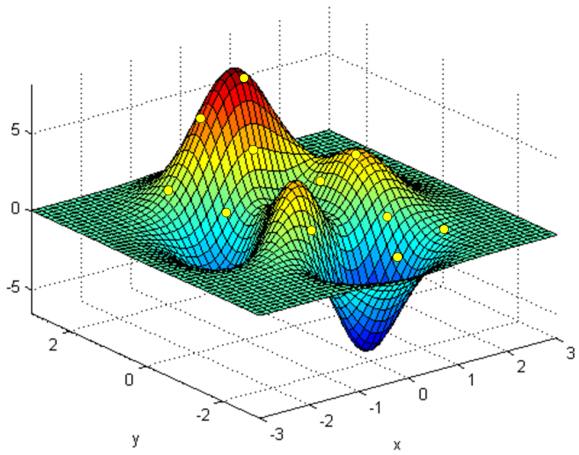
G. Ceder - MIT

(2006)

BAYESIAN ALGORITHM

Probabilistic

Neuronal networks



USPEX

A. Oganov - NYU

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GENETIC ALGORITHM

Evolutionary

Darwin principle

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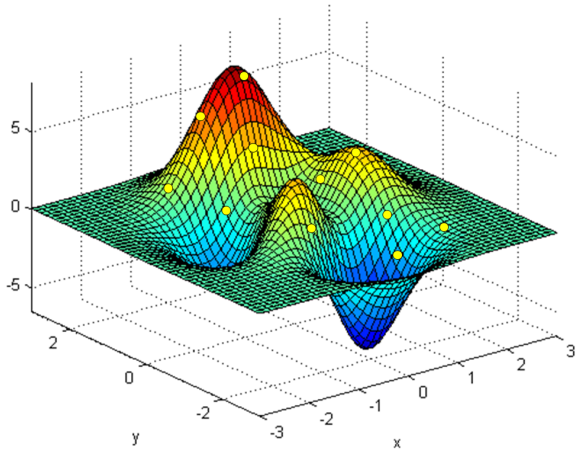

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Hematite Fe_2O_3
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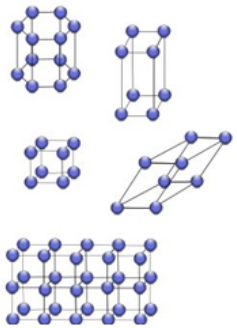
Karelianite V_2O_3
Tistarite Ti_2O_3



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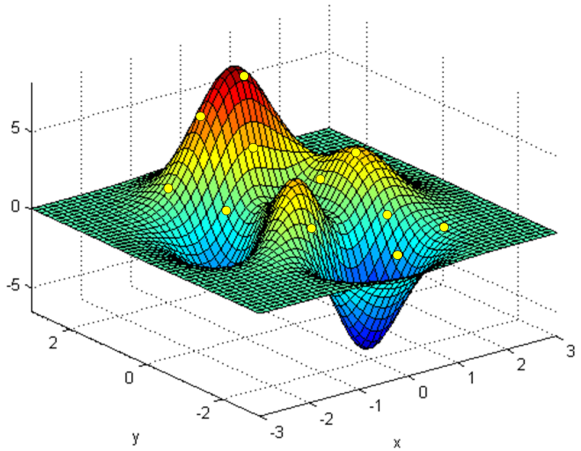

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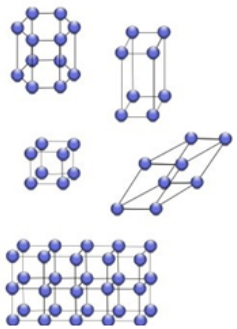

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Structure populations injected in periodic codes to perform Local Energy Minimizations

Bayesian / Genomic Methods

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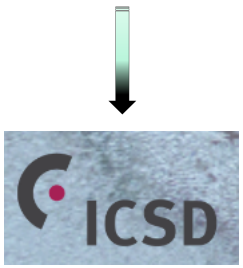

Bayesian Algorithm
Probabilistic
Neuronal networks

Performances

✓	PES sampling	✓
✓	Numerical cost	✓
✓	Exotic structures	✓

USPEX
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Genetic Algorithm
Evolutionary
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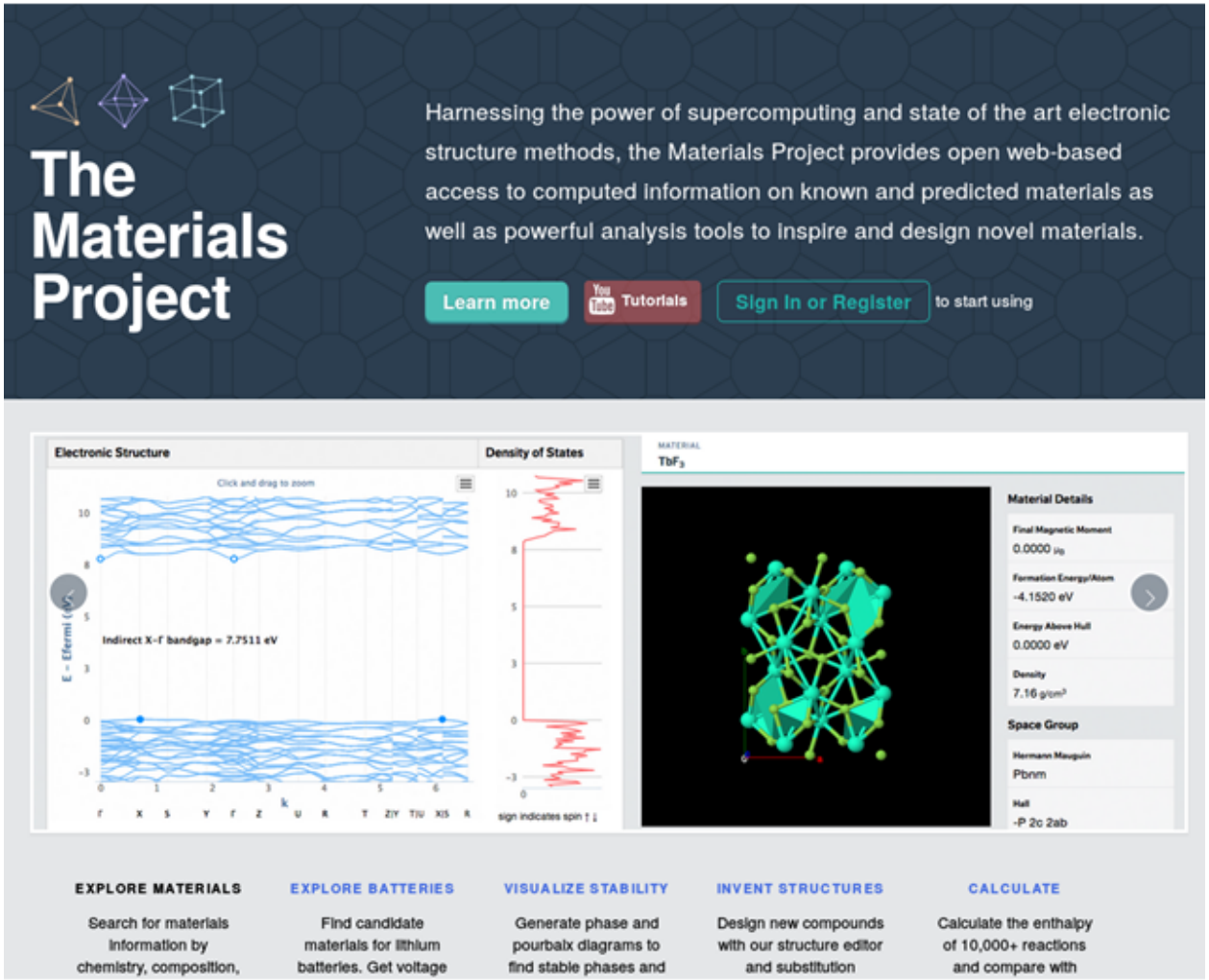
The Material Project Initiative (MIT / Berkeley)



Huge open source database - Just play with it !

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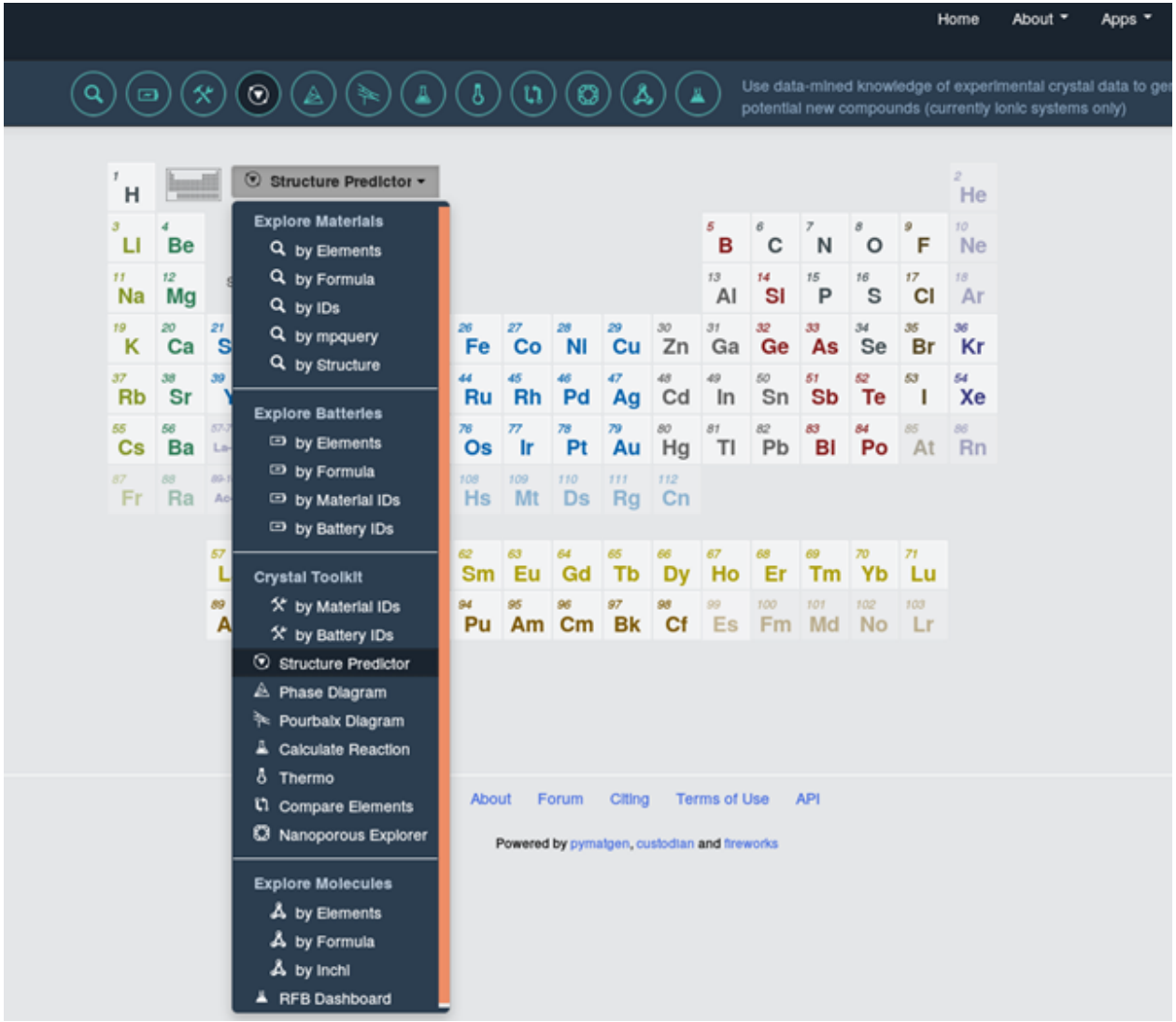

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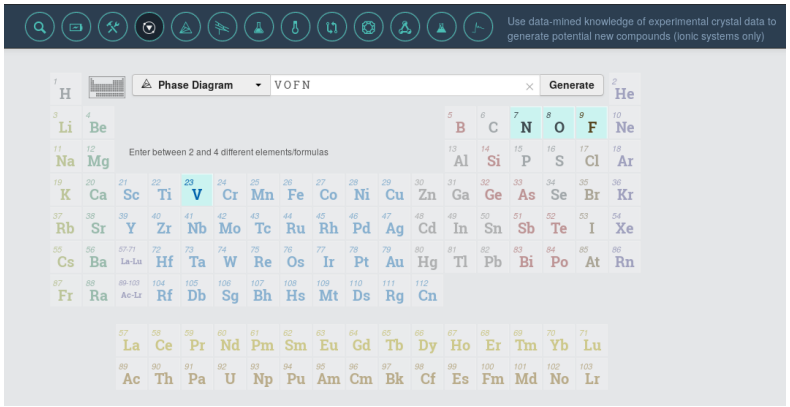
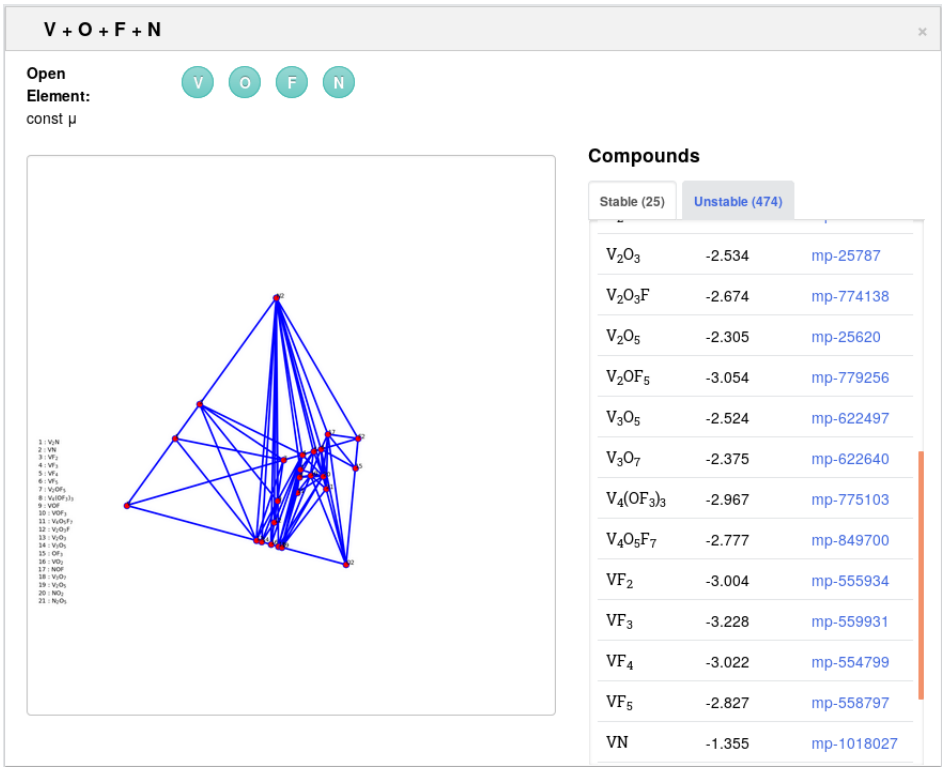
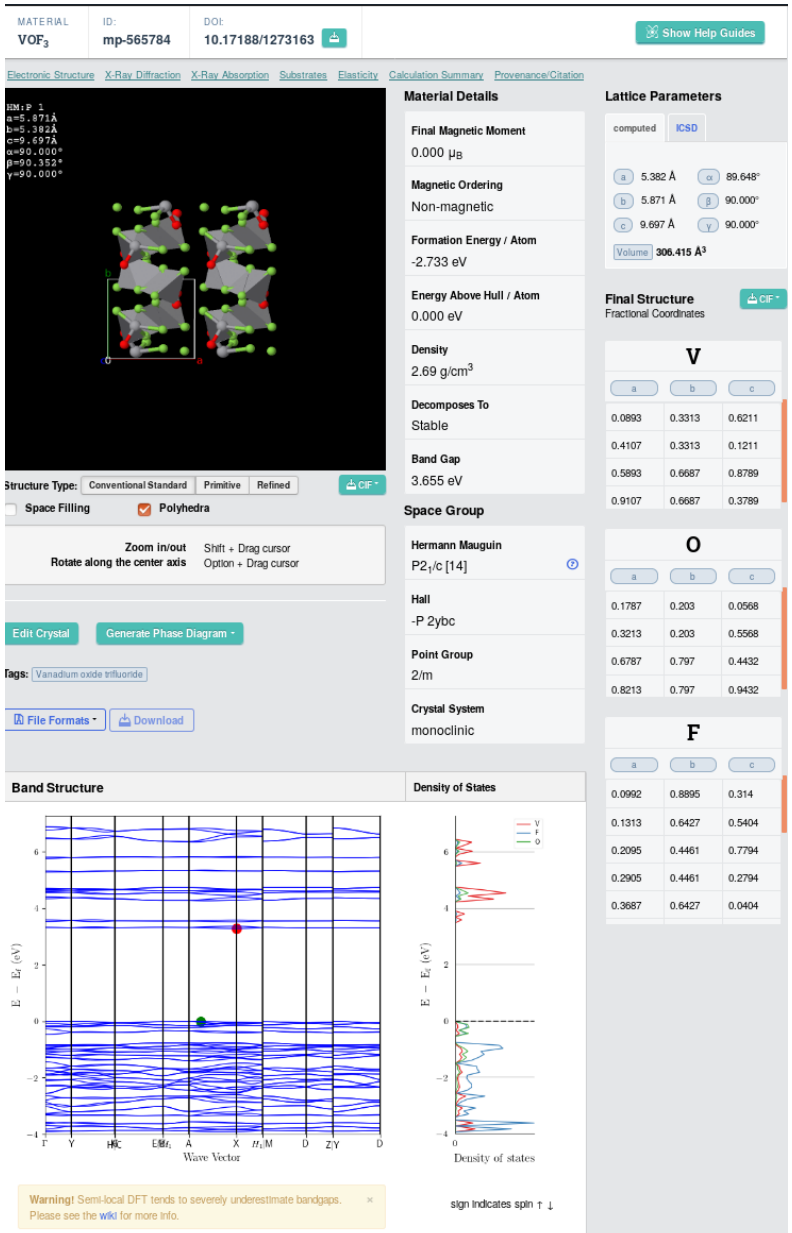
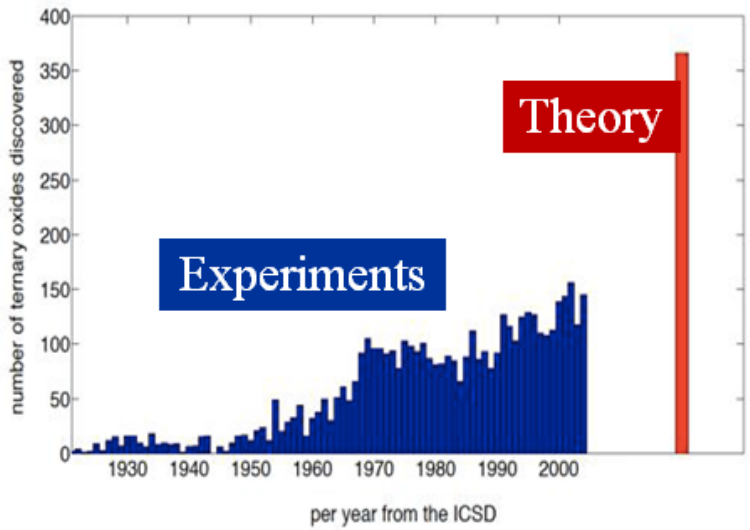
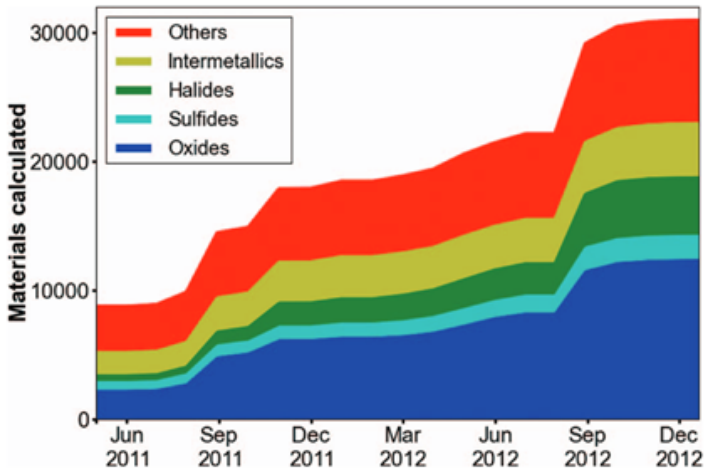






Combinatorial Approaches (Bayesian or Genetic)





Very powerful to discover new structures but ...

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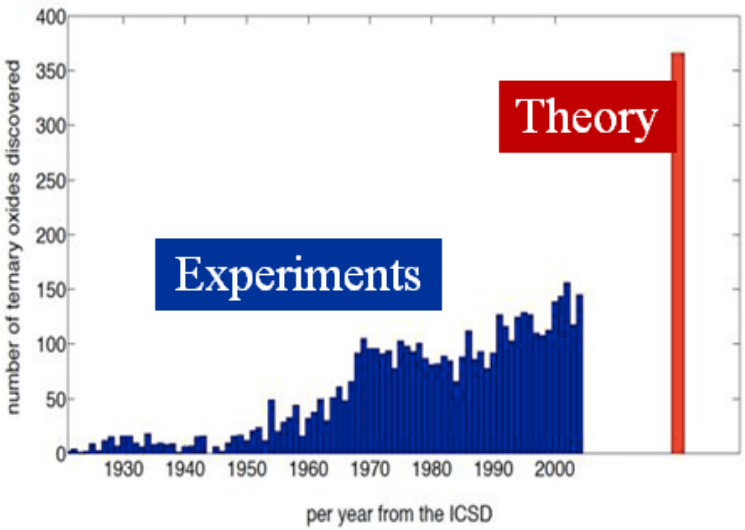

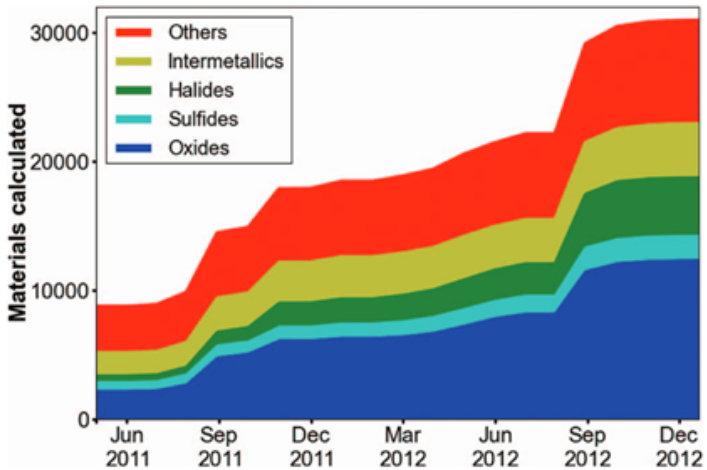

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- Thermal contributions not accounted (DFT enthalpies rather than Gibbs energies)
- Perfectly ordered phases
- What about interpretations ?

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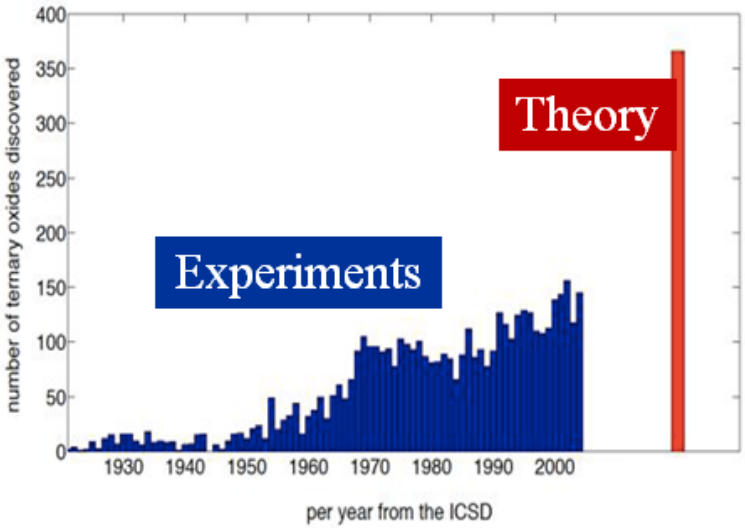

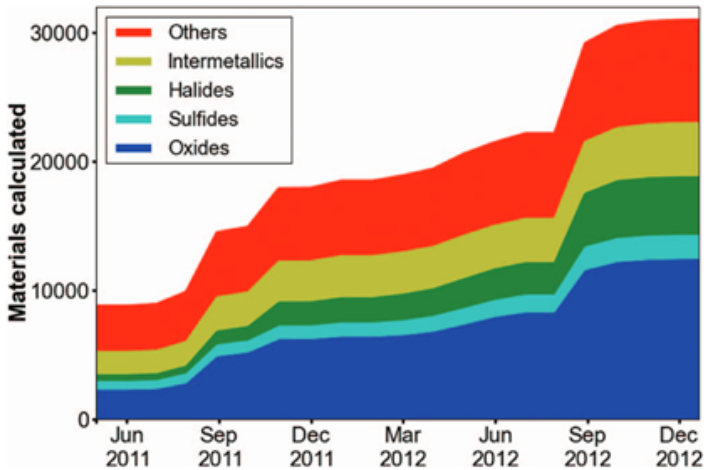

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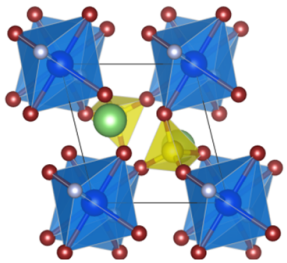
... how many of them will be synthesized?
... how many of them will have the targeted properties?

Example 1

- The *tavorite* $LiFeSO_4F$ electrode



Tavorite Structure	V (volt)
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Mueller et al. Chem. Mater. 23 (2011) 3854

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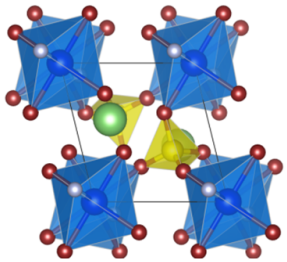

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Poor or no electrochemical activity

Mueller et al. Chem. Mater. 23 (2011) 3854

Take-Home Message 2

Computational (high-throughput) Approaches can be very powerful but need to be combined with Conceptual Approaches to perform better

Mix Algorithms & Computations

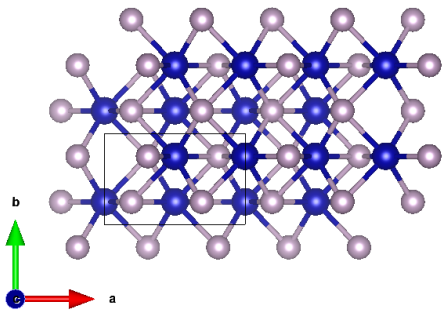
with Concepts & Chemical Knowledge

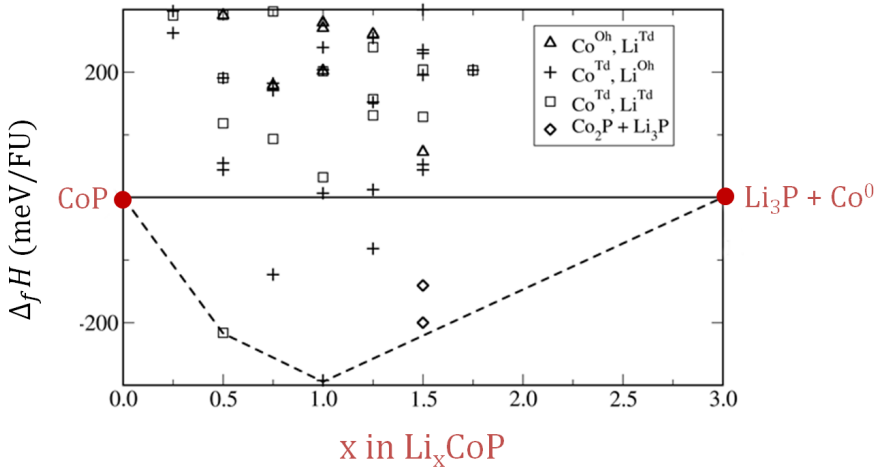
Mixing Algorithms with Chemical Knowledge

Electrochemical Reaction : $CoP + 3Li \rightleftarrows Co^0 + Li_3P$

1. Use what you know about metal environment, chemical bonding, crystallography to built hypothetical but realistic initial populations
2. Use stochastic procedures to make random displacements and/or permutations
3. Compute "Phase Stability Diagrams"

$$\Delta_f H(x) = E^{DFT}_{Li_xCoP} - \left\{ \frac{x}{3} \left(E^{DFT}_{Co^0} + E^{DFT}_{Li_3P} \right) + \frac{2x}{3} E^{DFT}_{CoP} \right\}$$



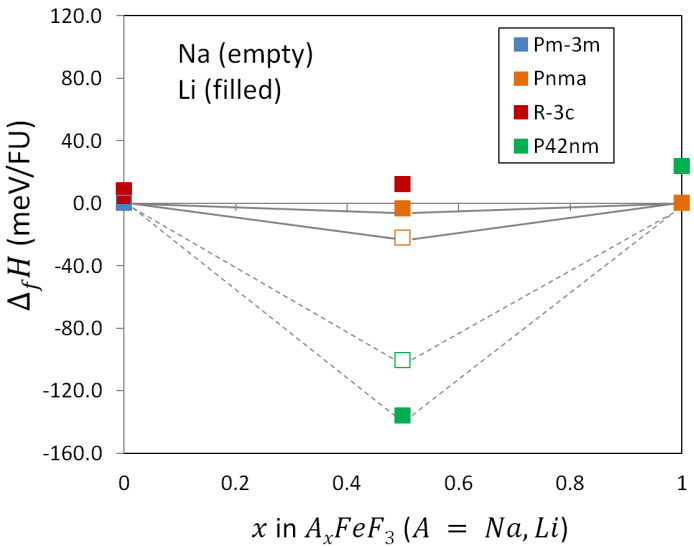


Check the dynamic stability with phonons or experiments

Mixing Computations with Crystal Structures Analysis

(2006) Electrochemical Reaction : $FeF_3(R\bar{3}c) + 0.5Li \longrightarrow Li_{0.5}FeF_3(P4_2nm)$

(2017) New Mechanism : $NaFeF_3 - 1Na \longrightarrow FeF_3(Pm\bar{3}m)$ $\quad FeF_3 + Li(Na) \rightleftarrows Li(Na)FeF_3$



Kinetic vs. **Thermodynamic** control

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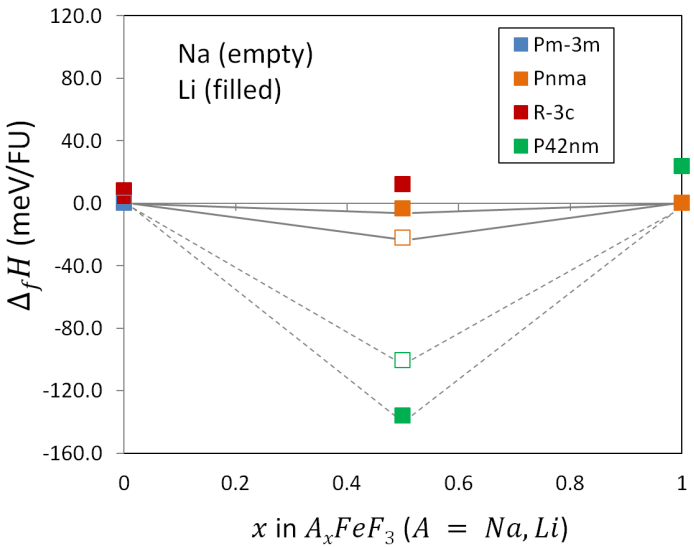

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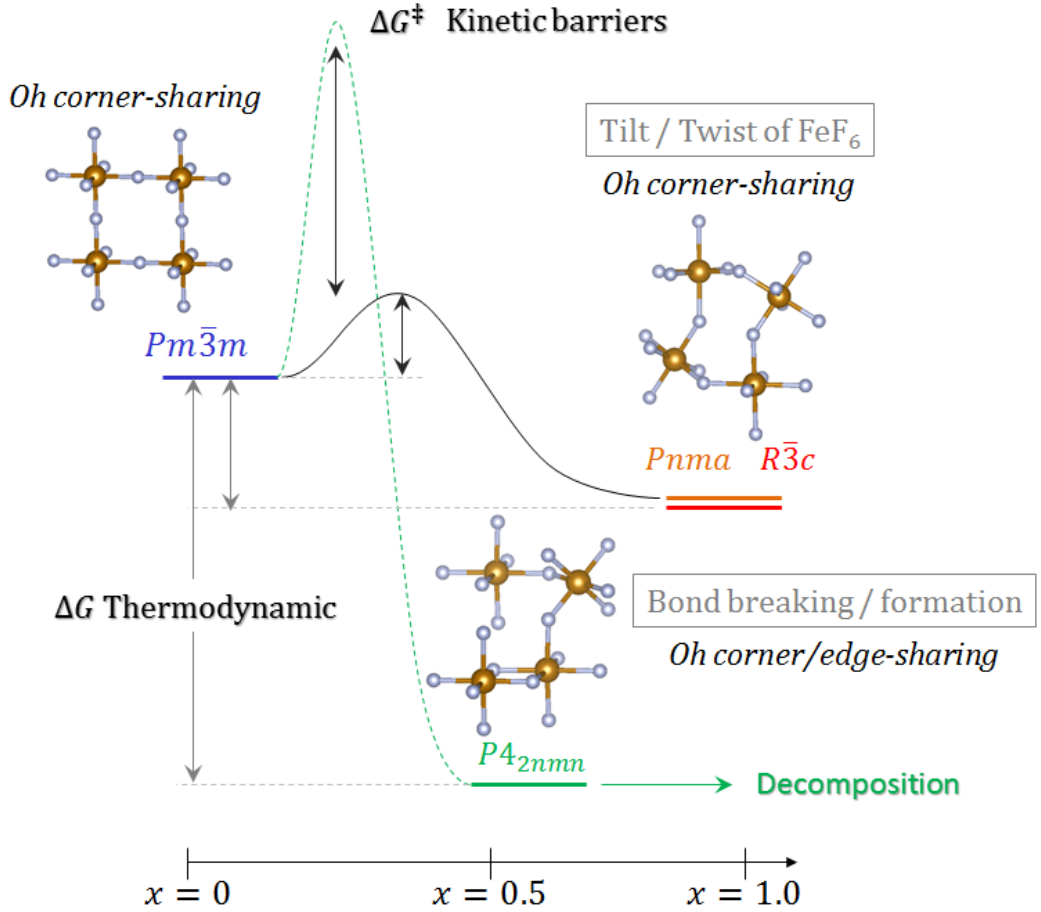
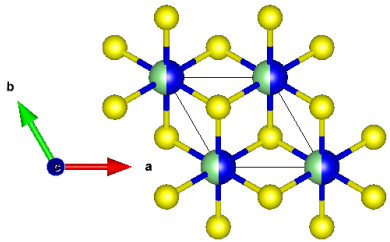


Statistical Distribution / Disorder

- How to account for fractional site occupations with PERIODIC DFT CALCULATIONS?



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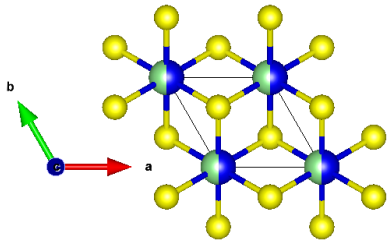

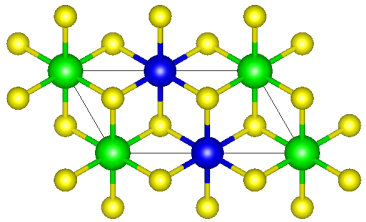

$2 \times 1 \times 1$ supercell

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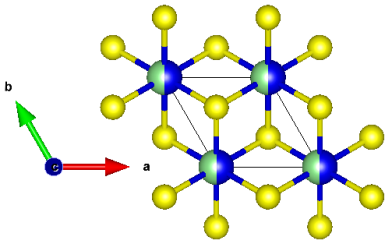

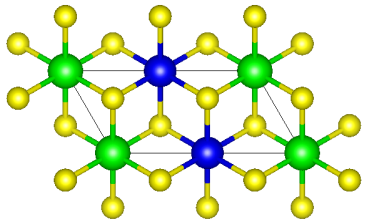

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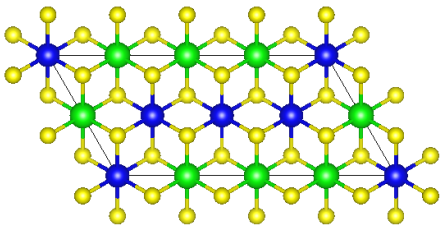
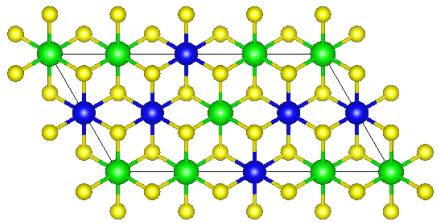
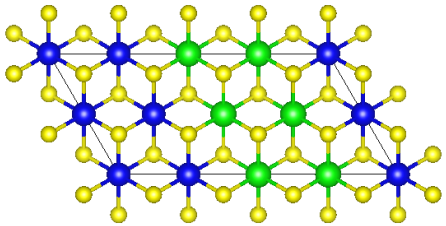






...

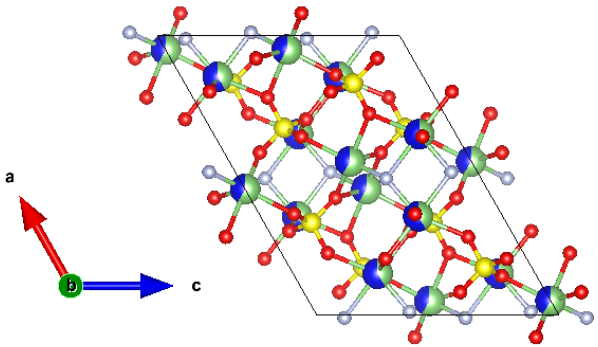
$2 \times 2 \times 1$ supercells

1) Use Lattice Model to build Cluster Expansion of Energy

$$E(\sigma) = E_0 + \sum_i V_i \sigma_i + \sum_{<i,j>} V_{i,j} \sigma_{i,j} + \dots$$

Statistical Distribution / Disorder

2) Sometimes cheaper to look at Local Chemical Bonds



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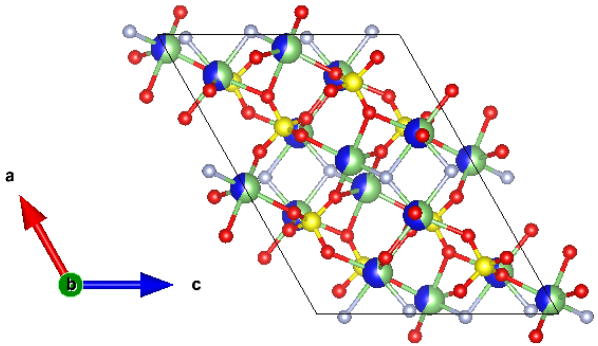
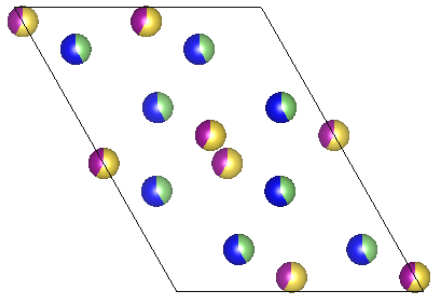


$LiFe^{2+}SO_4F$



4900 configurations !

$2 \neq$ sites M1 and M2

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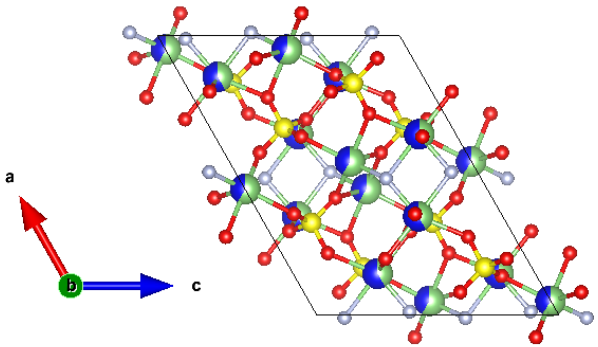

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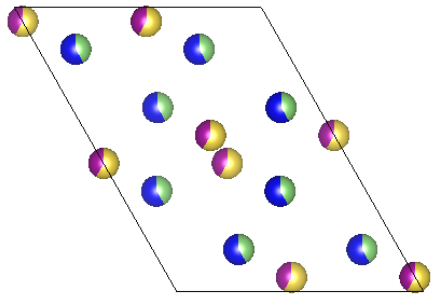

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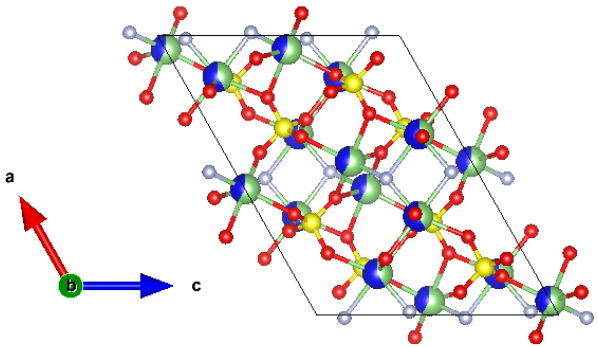

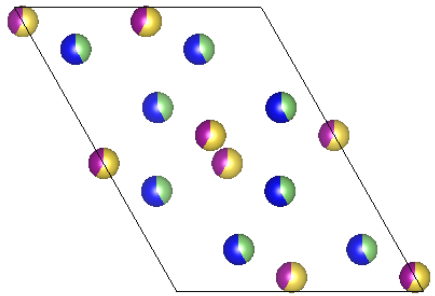

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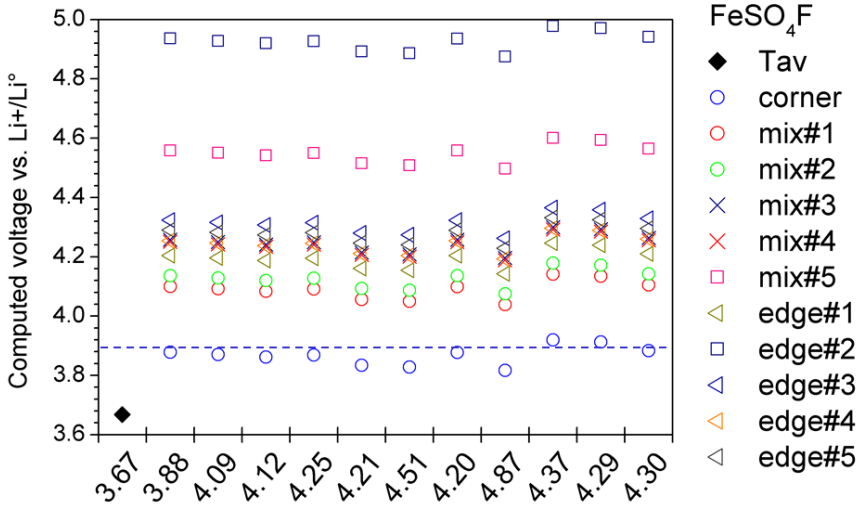

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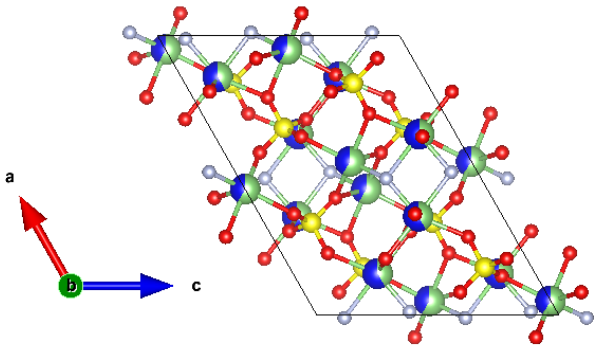

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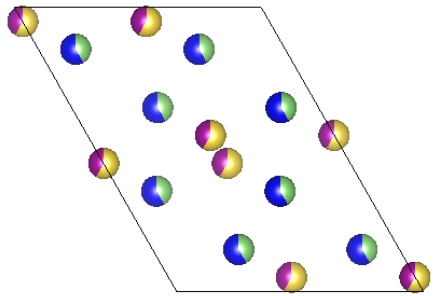

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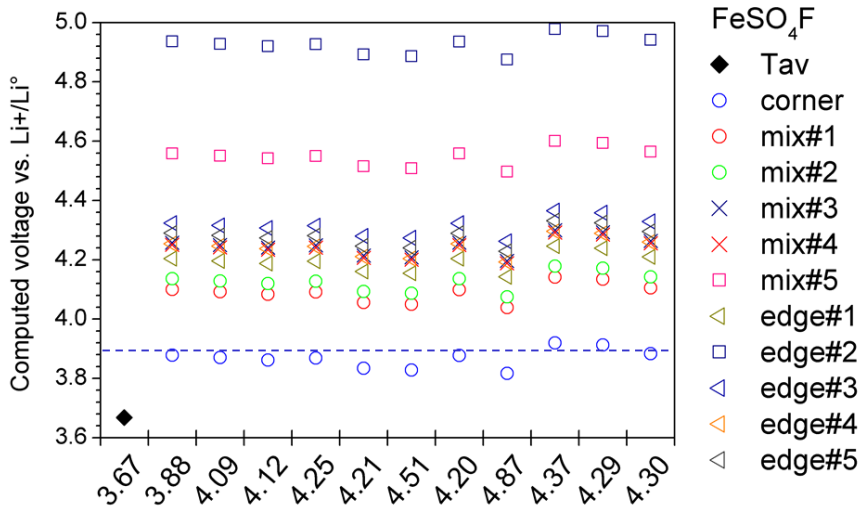

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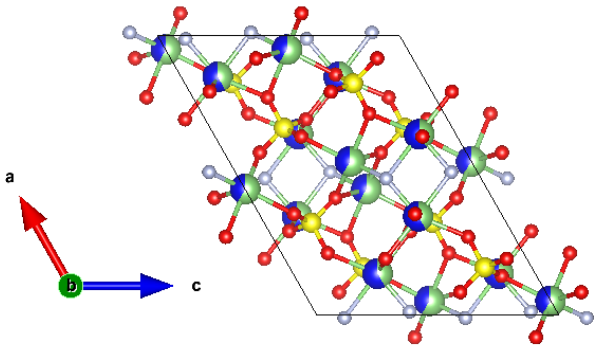

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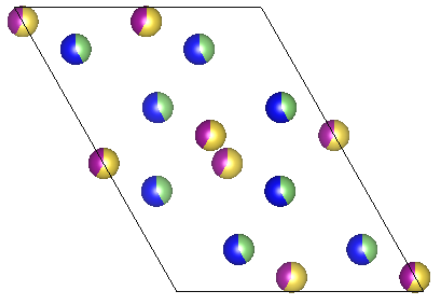

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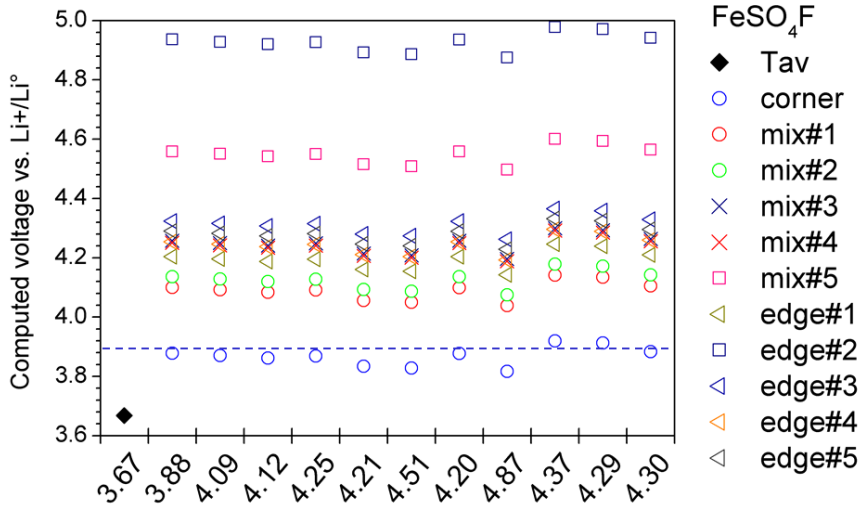

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$Fe^{3+} - Fe^{3+}$

- corner-sharing (d=3.6Å)

$\oplus$ Still consistent with M1/M2 disorder

$\oplus$ Equivalent results whatever U_{Fe} (2-6 eV)

Take-Home Message 3

Sometimes computations are less required than chemical intuitions, basic rules of chemical bonding, electronegativity, polarisability ... to make rational design of new materials

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Sometimes computations are less required than chemical intuitions, basic rules of chemical bonding, electronegativity, polarisability ... to make rational design of new materials

Most often, the "ideal structure / phase" you are looking for to improve one given target property / application already exists in the crystallographic databases.

Take-Home Message 3

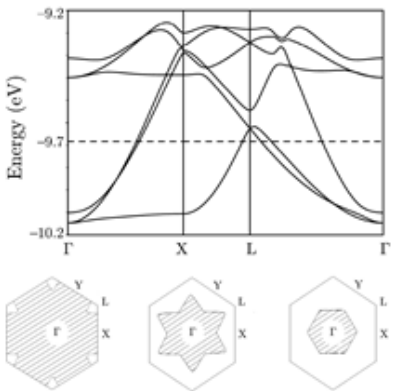
Sometimes computations are less required than chemical intuitions, basic rules of chemical bonding, electronegativity, polarisability ... to make rational design of new materials

Most often, the "ideal structure / phase" you are looking for to improve one given target property / application already exists in the crystallographic databases.

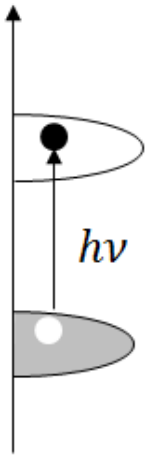
You just don't know where to search it ...

Tuning a Property through Material Functionalization

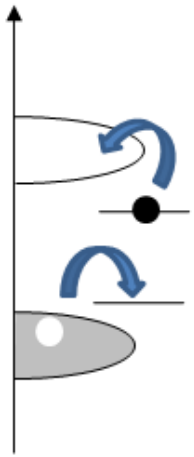
Transport



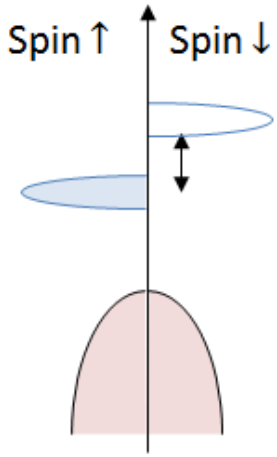
Optical



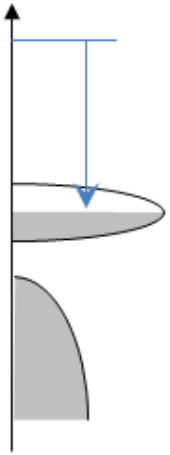
Doping



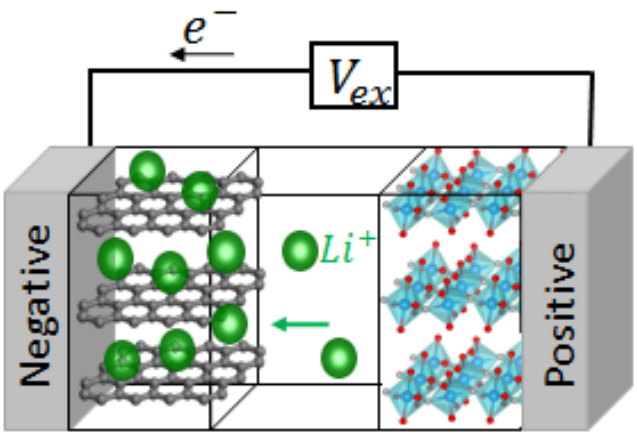
Magnetism

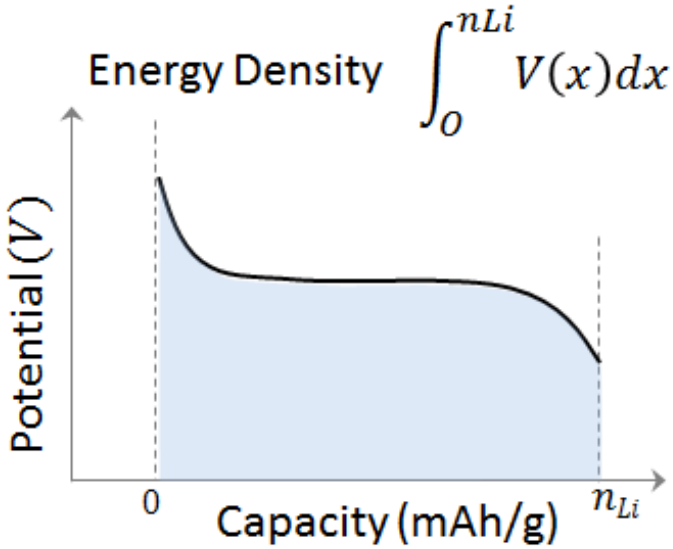


Redox



Design of Redox Materials





Discharge / Charge

$$Li_nA \rightleftarrows A + nLi^+ + ne^-$$
$$C + nLi^+ + ne^- \leftrightarrows Li_nC$$

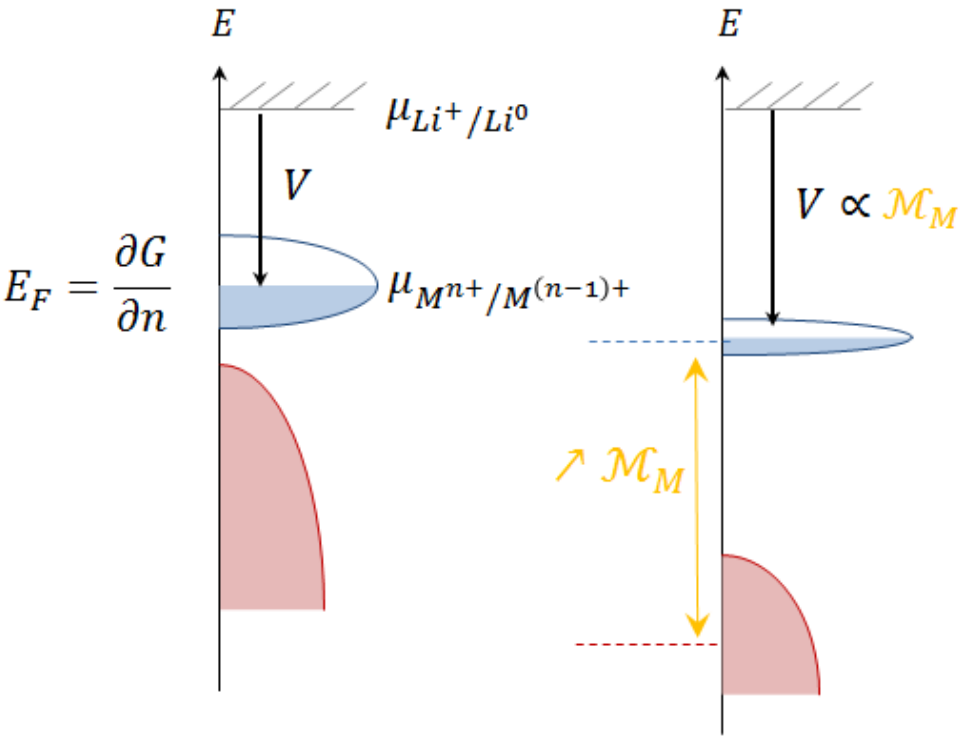
$$C + Li_nA \rightleftarrows Li_nC + A$$

Potential $$V(Volt) = -\frac{1}{nF}\Delta_r G$$

Capacity $$C(mAh/g) = \frac{\Delta x_{Li}.F}{\mathcal{M}}$$

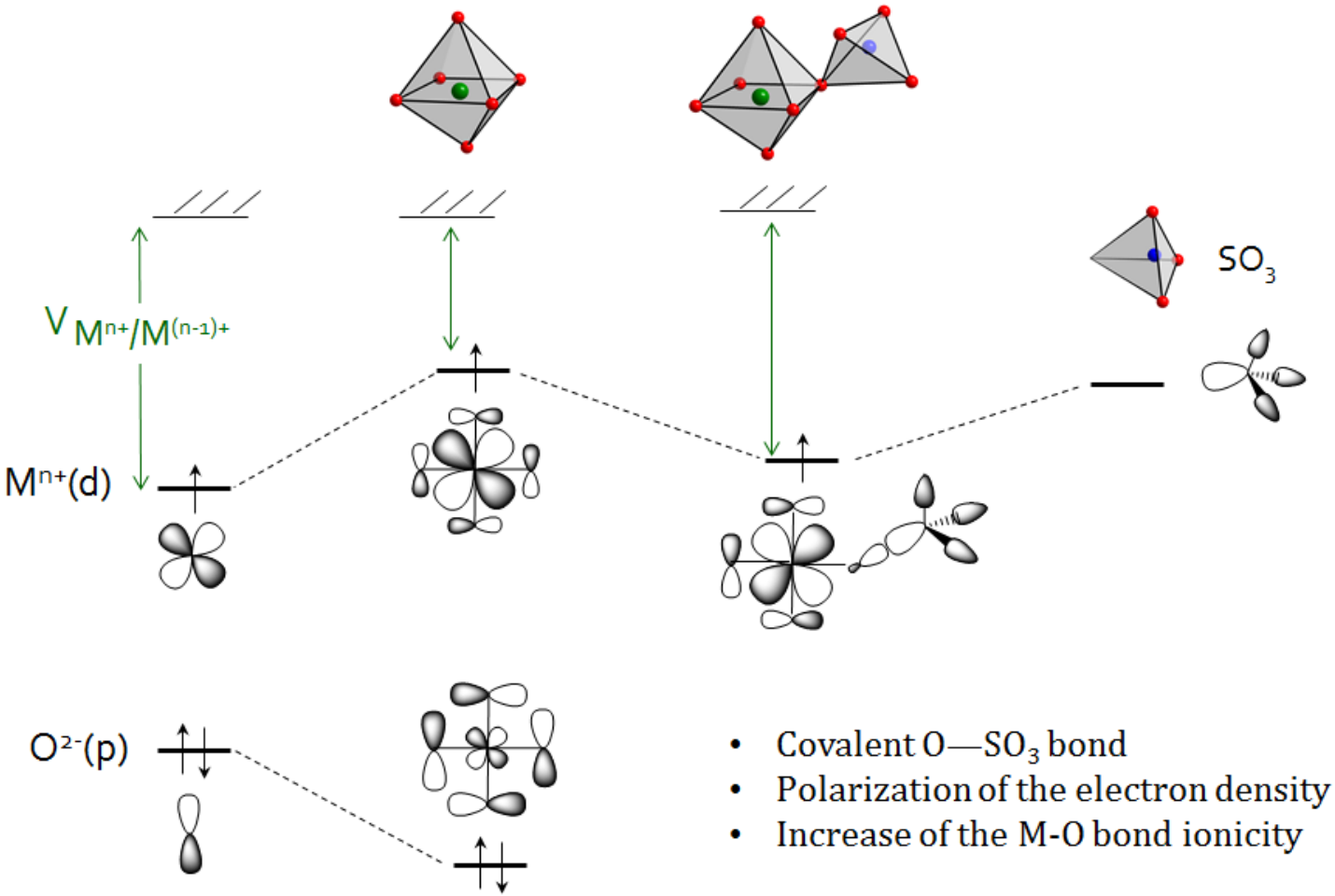
Design of Redox Materials

- Conceptual Approach to the Potential
  Goodenough (1997)



Design of Redox Materials

- Conceptual Approach to the Potential Molecular Orbital Picture (local)

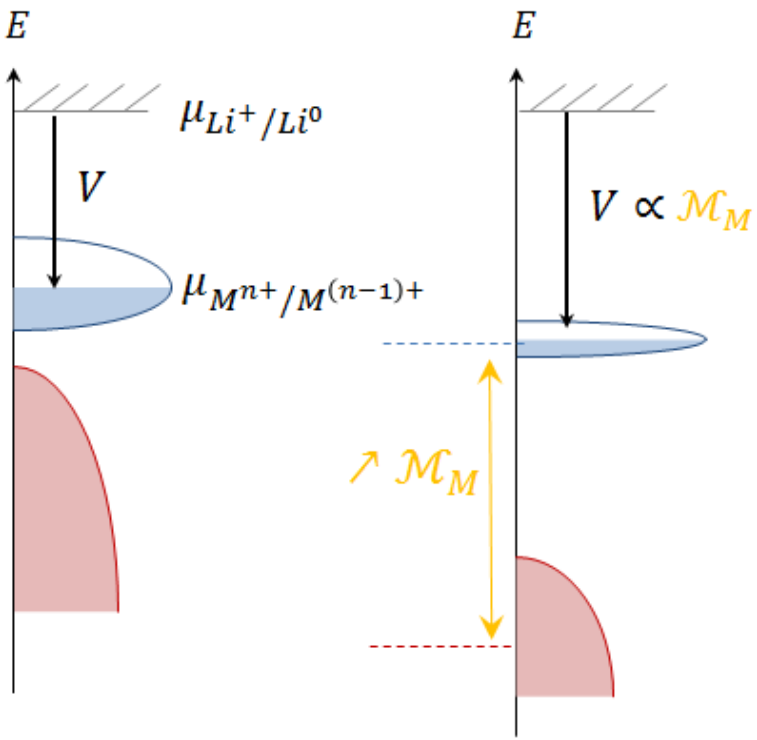


- Covalent O—SO_3 bond
- Polarization of the electron density
- Increase of the M-O bond ionicity

Design of Redox Materials

- Conceptual Approach to the Potential
  Goodenough (1997)

$$E_F = \frac{\partial G}{\partial n}$$



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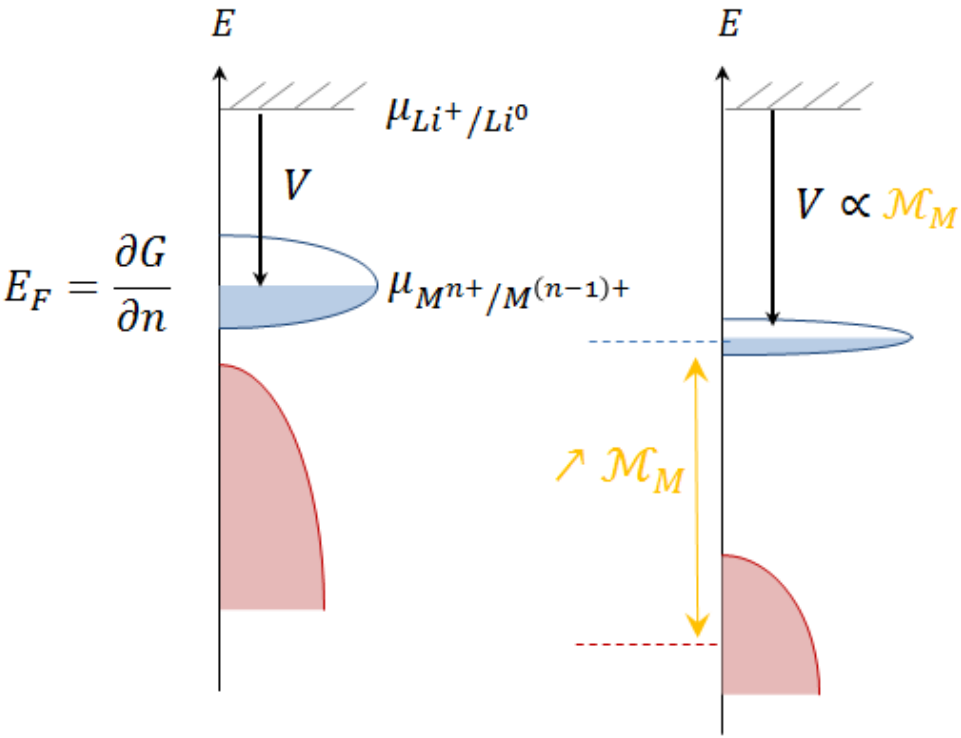
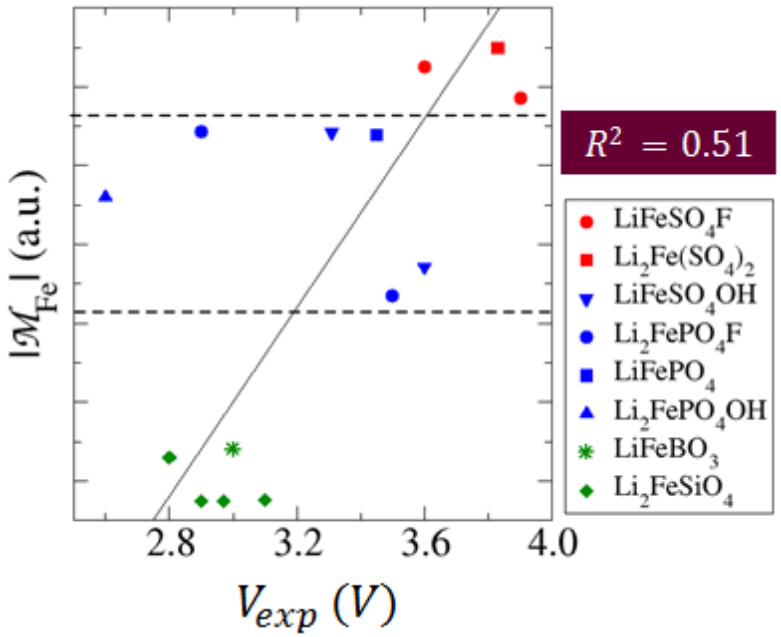




Design of Redox Materials

- Conceptual / Perturbative Approach to the Potential

$$V \propto \Delta E_{H/\ominus} + \Delta E_{H/\oplus} = \mu^0 + 2\eta + q_\ominus V_H(r_M) + q_\oplus V_H(r_{Li})$$

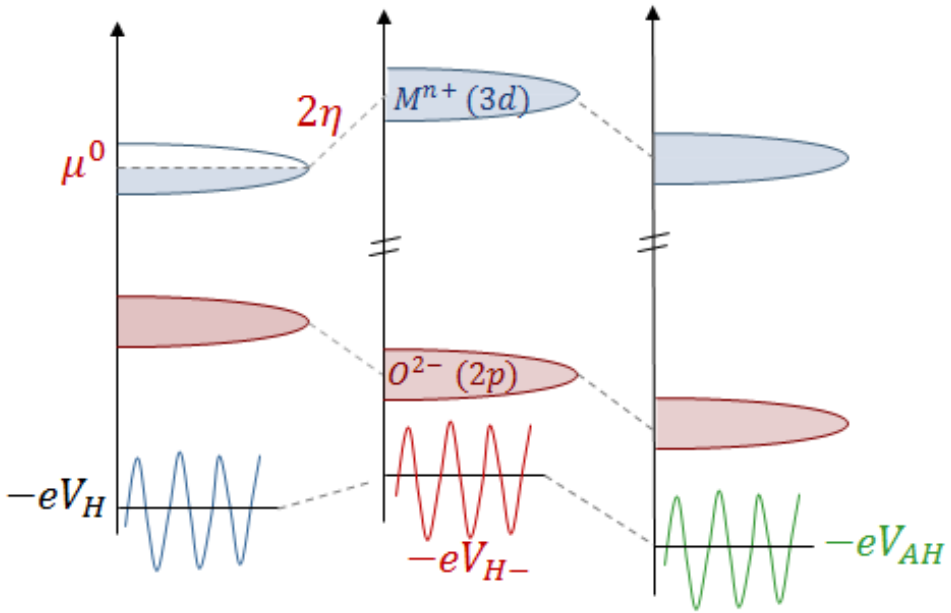
Electronic

Ionic

Chemical Potential

Chemical Hardness $\eta = \frac{\delta\mu}{\delta n}$

Electrostatic terms



Design of Redox Materials

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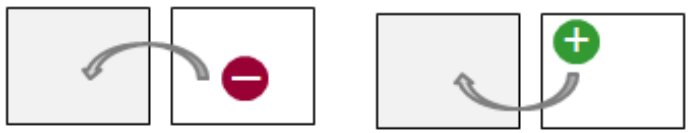
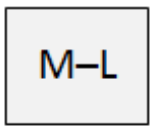
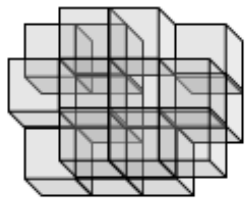
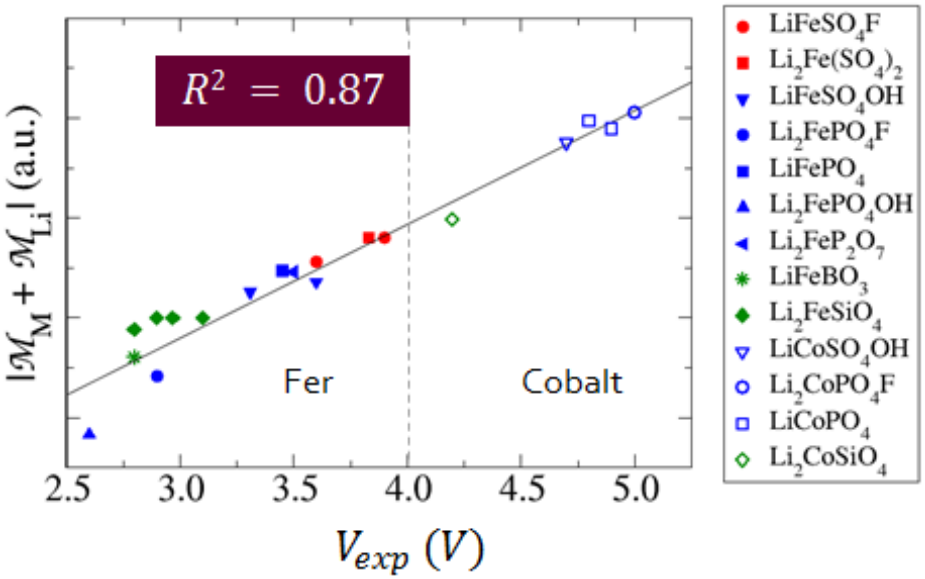
$$V \propto \Delta E_{H/\ominus} + \Delta E_{H/\oplus} = \mu^0 + 2\eta + q_\ominus V_H(r_M) + q_\oplus V_H(r_{Li})$$

Electronic — Ionic — Short-Range — Long-Range







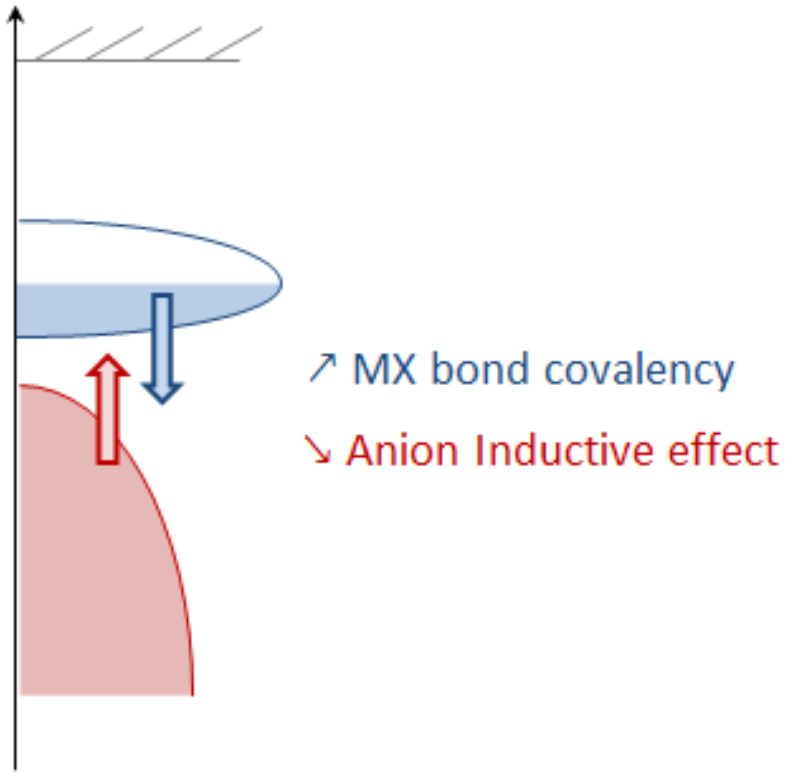


- Works pretty well
- New SR and LR Descriptors
- We know where to search in the database ...

Design of Redox Materials

- Conceptual Approach to the Capacity

  J. Rouxel (1996) "Anion-cation redox competition and the formation of new compounds in highly covalent systems"

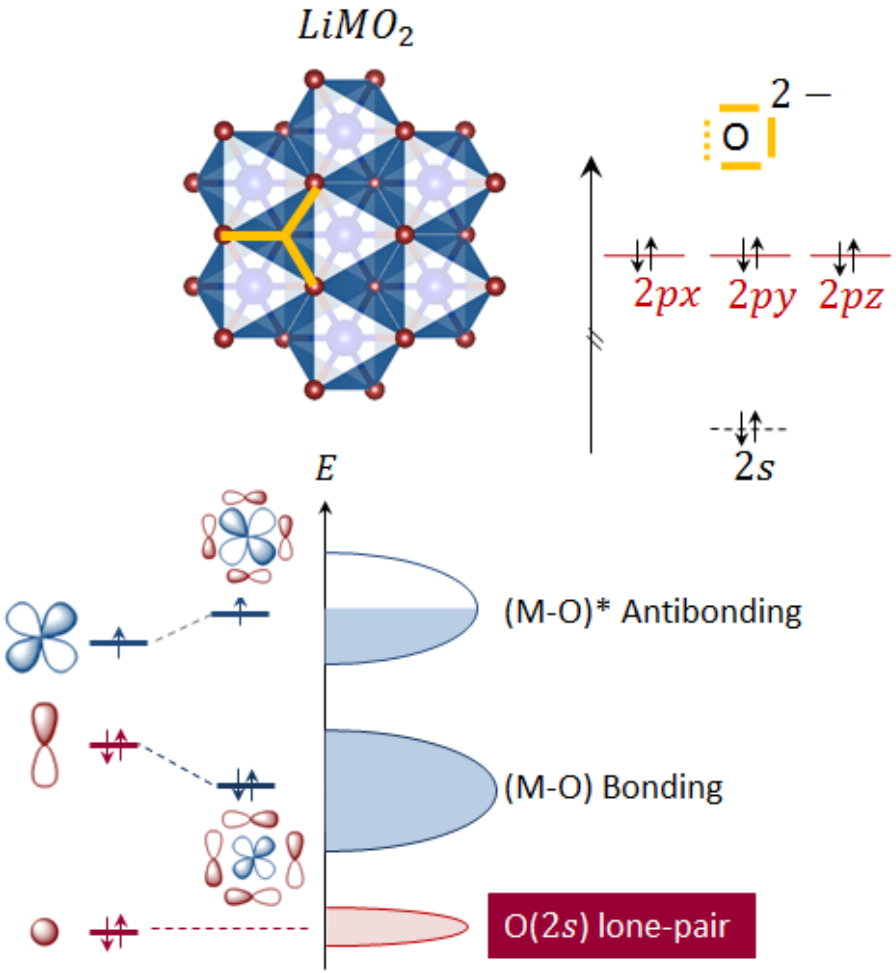


1 Redox Band
↓
2 Redox Band

Cationic & Anionic Redox

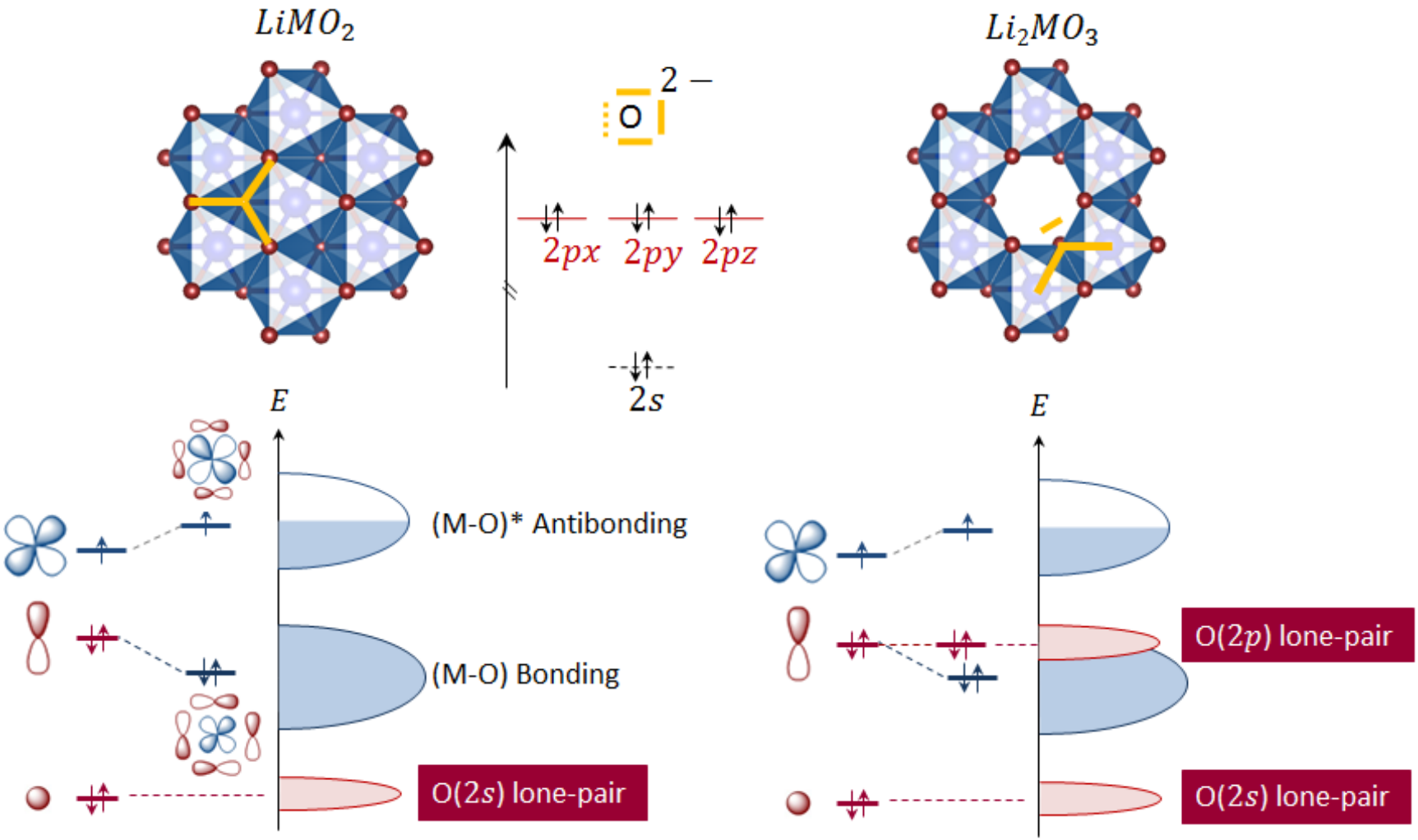
PARADOX
High Potential = ↗ $\Delta\chi$
High Capacity = ↘ $\Delta\chi$

Design of Redox Materials



know to be instable when removing Li

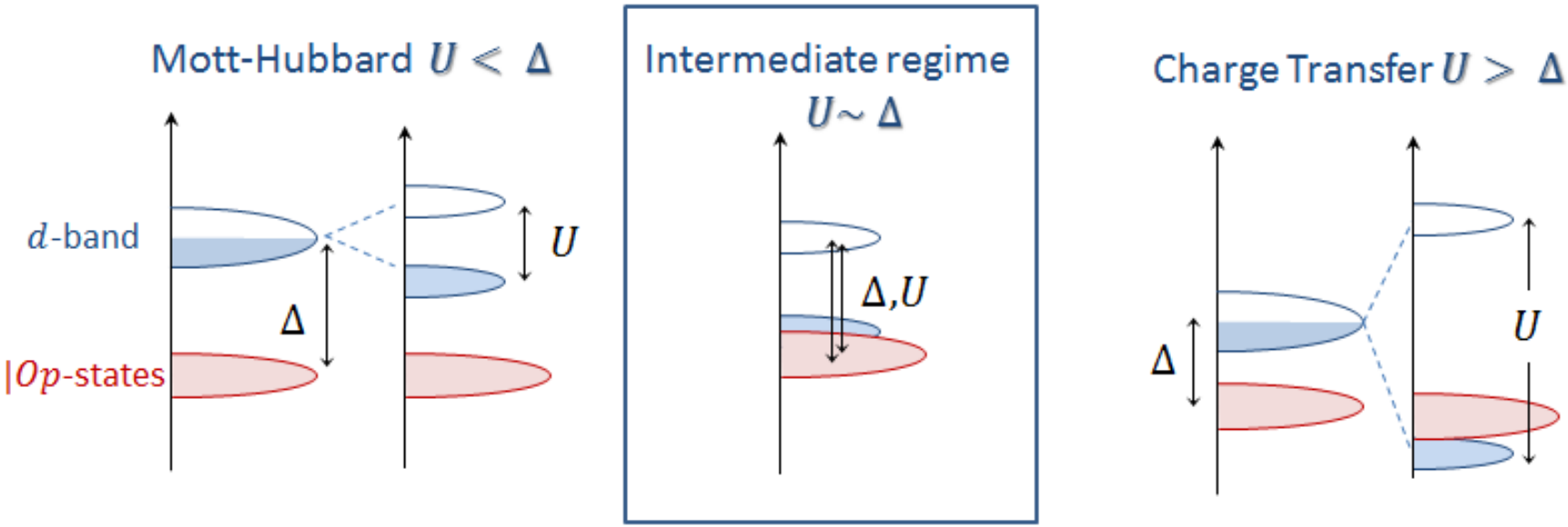
Design of Redox Materials



Known to be instable when removing Li

Work much better but not for all TMs

Design of Redox Materials



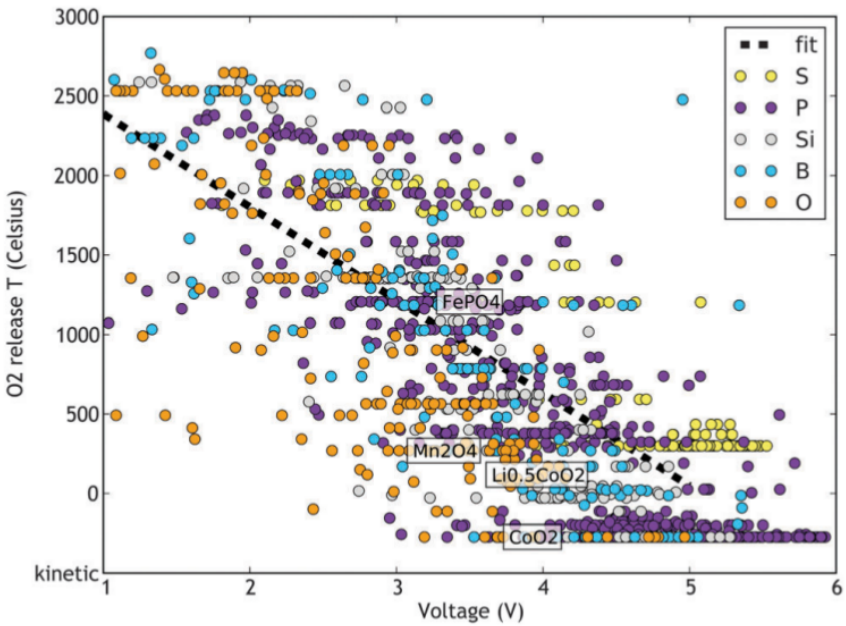
M(4d), M(5d) High Energy Density

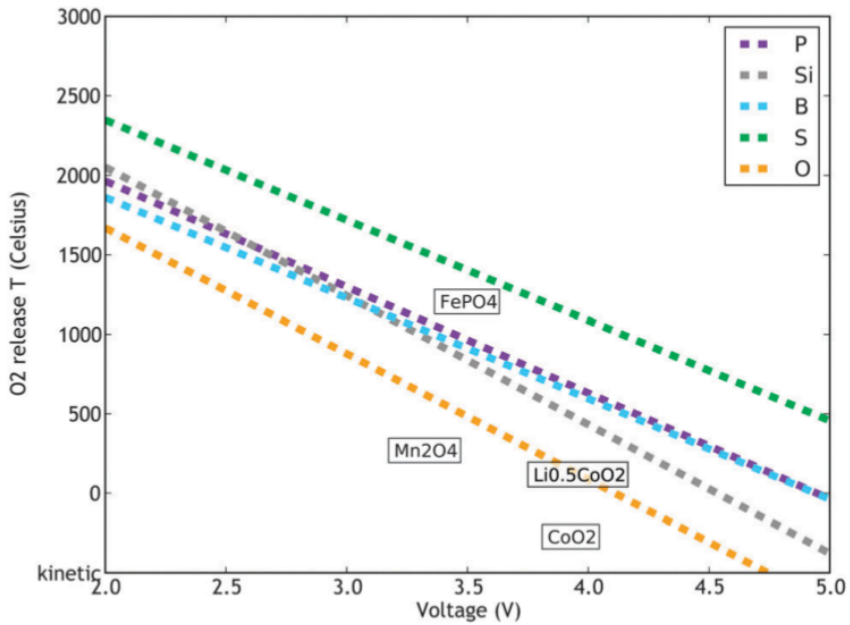
M(3d) Structure Instability

Energy & Envir. Sci. 17, 5942-5953 (2017)

Design of Redox Materials

- Voltage vs. O_2 release





PCCP 17, 5942-5953 (2015)

Do you really need so many calculations were needed ?

Conclusions

Never forget that low-energy properties of materials are mainly governed / dictated by crystal structures and local chemical bonding !

- Global exploration of PES are very tough procedures that sometimes work, sometimes not. Not necessarily related to DFT weakness when it fails !
- Computational (high-throughput) calculations must be combined with more Conceptual approaches to accelerate the discovery of new materials
- Almost all physical / chemical properties can be rationalized with meaningful descriptors that help guiding experimentalists towards new directions

Never forget that the "ideal structure" of the property you target for the next Nobel Price is most likely already in ICSD ! Think more about meta-stability for breakthrough...