

Machine learning electrochemistry: when quantum mechanics gets wet, briny, and oxidizing

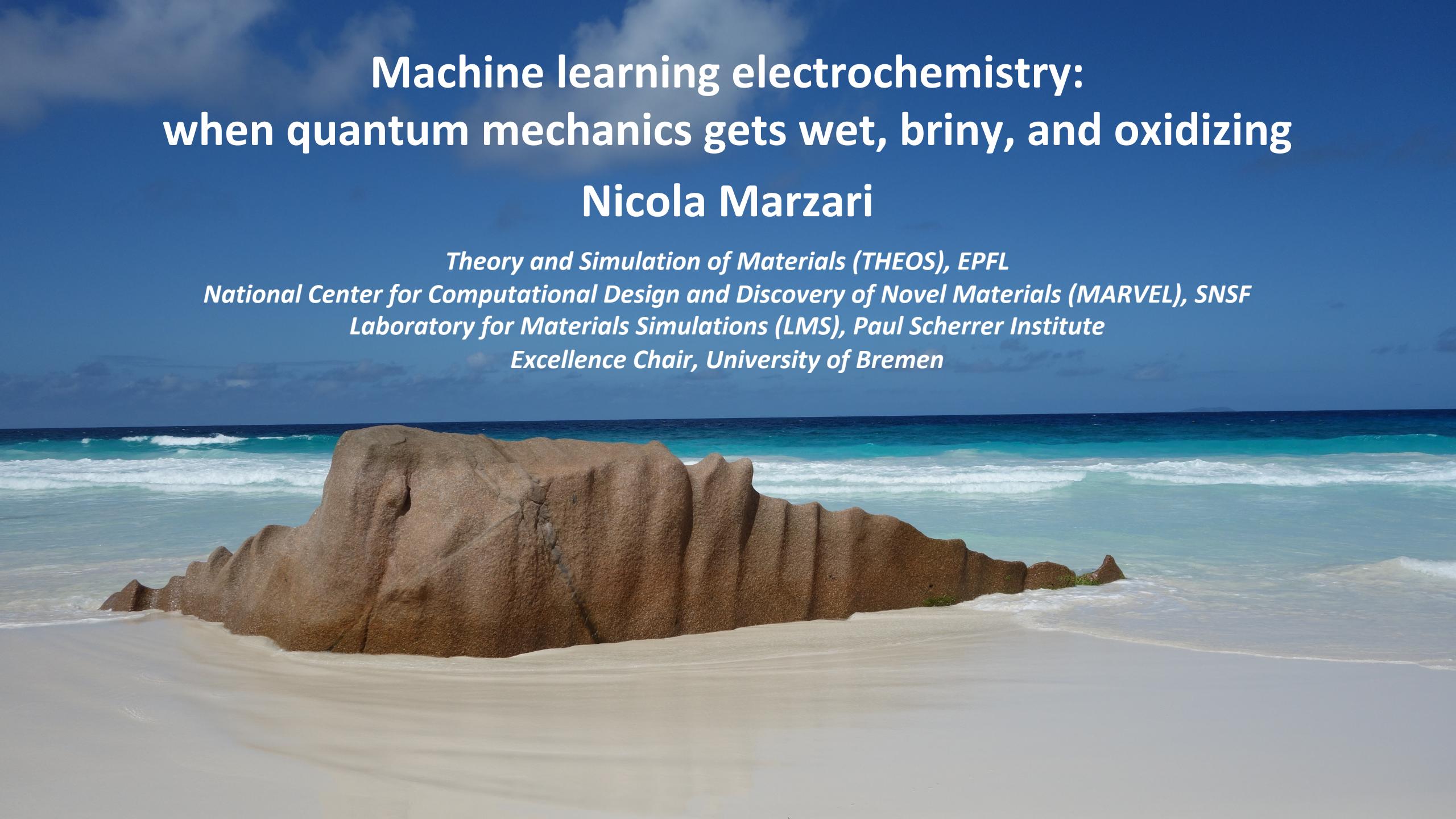
Nicola Marzari

Theory and Simulation of Materials (THEOS), EPFL

National Center for Computational Design and Discovery of Novel Materials (MARVEL), SNSF

Laboratory for Materials Simulations (LMS), Paul Scherrer Institute

Excellence Chair, University of Bremen



WHERE IT ALL STARTED

Interatomic Potentials from First-Principles Calculations: The Force-Matching Method

To cite this article: F. Ercolessi and J. B. Adams 1994 *EPL* 2

A NOVEL SCHEME FOR ACCURATE MD SIMULATIONS OF LARGE SYSTEMS

Alessandro De Vita† and Roberto Car

*Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), PPH-Ecublens,
CH-1015 Lausanne, Switzerland*

De Vita, A., Car, R. A Novel Scheme for Accurate Md Simulations of Large Systems. *MRS Online Proceedings Library* **491**, 473–480 (1997). <https://doi.org/10.1557/PROC-491-473>

Neural network models of potential energy surfaces

Thomas B. Blank, Steven D. Brown, August W. Calhoun,^{a)} and Douglas J. Doren
Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

(Received 6 February 1995; accepted 7 June 1995)

Neural networks provide an efficient, general interpolation method for nonlinear functions of several variables. This paper describes the use of feed-forward neural networks to model global properties of potential energy surfaces from information available at a limited number of configurations. As an

J. Chem. Phys. **103**, 4129–4137 (1995)



WHERE IT ALL STARTED

Neural networks provide an efficient, general interpolation method for nonlinear functions of several variables. This paper describes the use of feed-forward neural networks to model global properties of potential energy surfaces from information available at a limited number of configurations. As an

J. Chem. Phys. 103, 4129–4137 (1995)



First-principles simulations in realistic electrochemical environments

Energy: Electrified solid-liquid interfaces are key to harvesting, storing, and converting energy:

- Photocatalysis in a dye-sensitized solar cell
- Electrolyte chemistry in a lithium-ion battery
- Fuel-into-electricity in a fuel cell

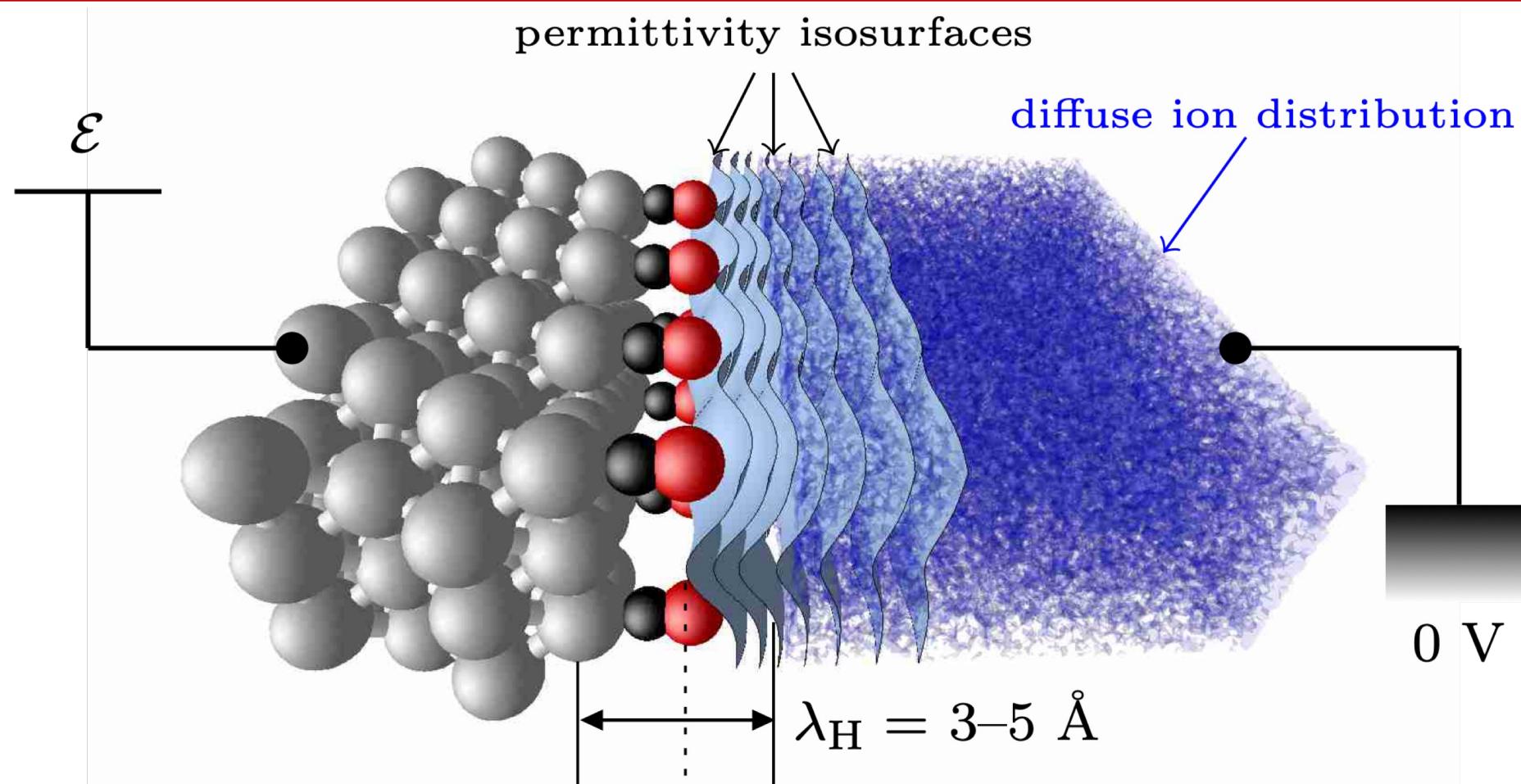
Technology: Key industrial reactions take place in aqueous solutions or solvents

Synthesis: Growth of nanoparticles and crystals by wet chemistry is strongly influenced by the solvent

Biology: Many processes take place in salty, watery environments



First-principles simulations in realistic electrochemical environments



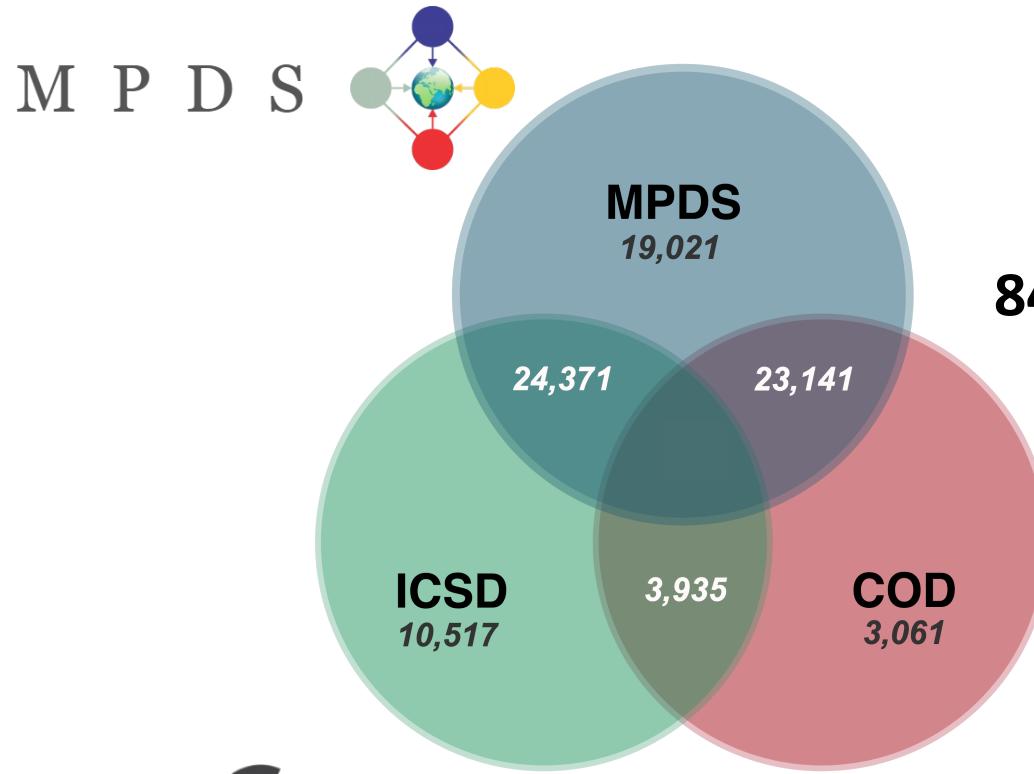
- I. Dabo, B. Kozinsky, N. E. Singh-Miller, and N. Marzari, Phys. Rev. B. 77, 115139 (2008)
- I. Dabo, E. Cancès, Y. L. Li, and N. Marzari, arXiv:0901.0096v2 (2009), and in *Fuel Cell Science: Theory, Fundamentals, and Biocatalysis* (Wiley, New York, 2010).
- O. Andreussi, I. Dabo, and N. Marzari, JCP 136, 064102 (2012)



1. NNs FOR MATERIALS DISCOVERY AND DESIGN (ALL-SOLID-STATE BATTERIES)

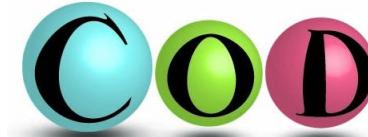


MC3D: EXPERIMENTALLY KNOWN STOICHIOMETRIC INORGANICS

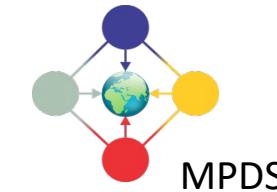
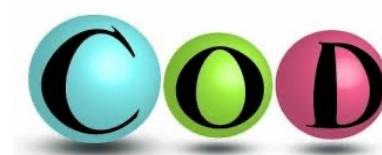
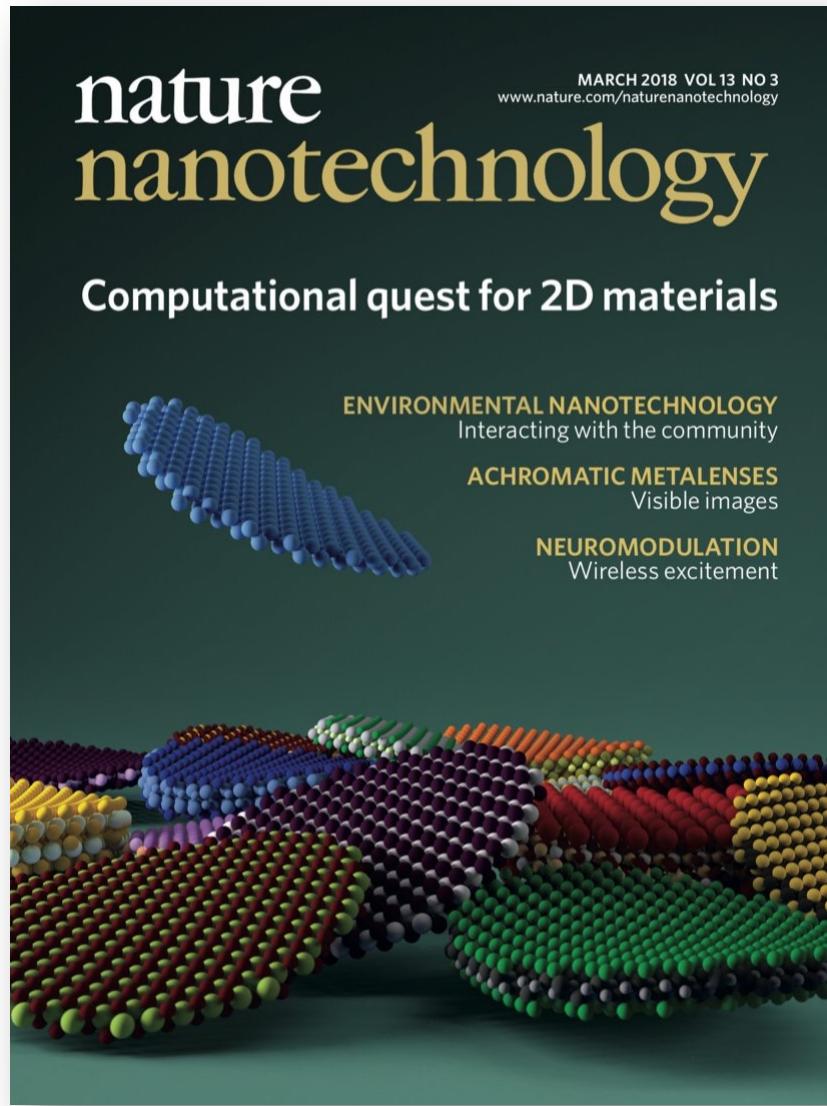


900,000 ENTRIES: RAW EXPERIMENTAL DATA
84,000: UNIQUE STOICHIOMETRIC COMPOUNDS

<https://mc3d.materialscloud.org/>



MC2D: EXFOLIABLE INORGANICS (2000+ “EASILY”)



[RETURN TO ISSUE](#)

[< PREV](#)

ARTICLE

[NEXT >](#)

Expansion of the Materials Cloud 2D Database

Davide Campi*, Nicolas Mounet, Marco Gibertini, Giovanni Pizzi, and Nicola Marzari*

Cite this: ACS Nano 2023, 17, 12, 11268–11278

Publication Date: June 13, 2023 ▾

<https://doi.org/10.1021/acsnano.2c11510>

Copyright © 2023 American Chemical Society. This publication is licensed under [CC-BY 4.0](#).

[Open Access](#)

Article Views

1711

Altmetric

1

Citations

2

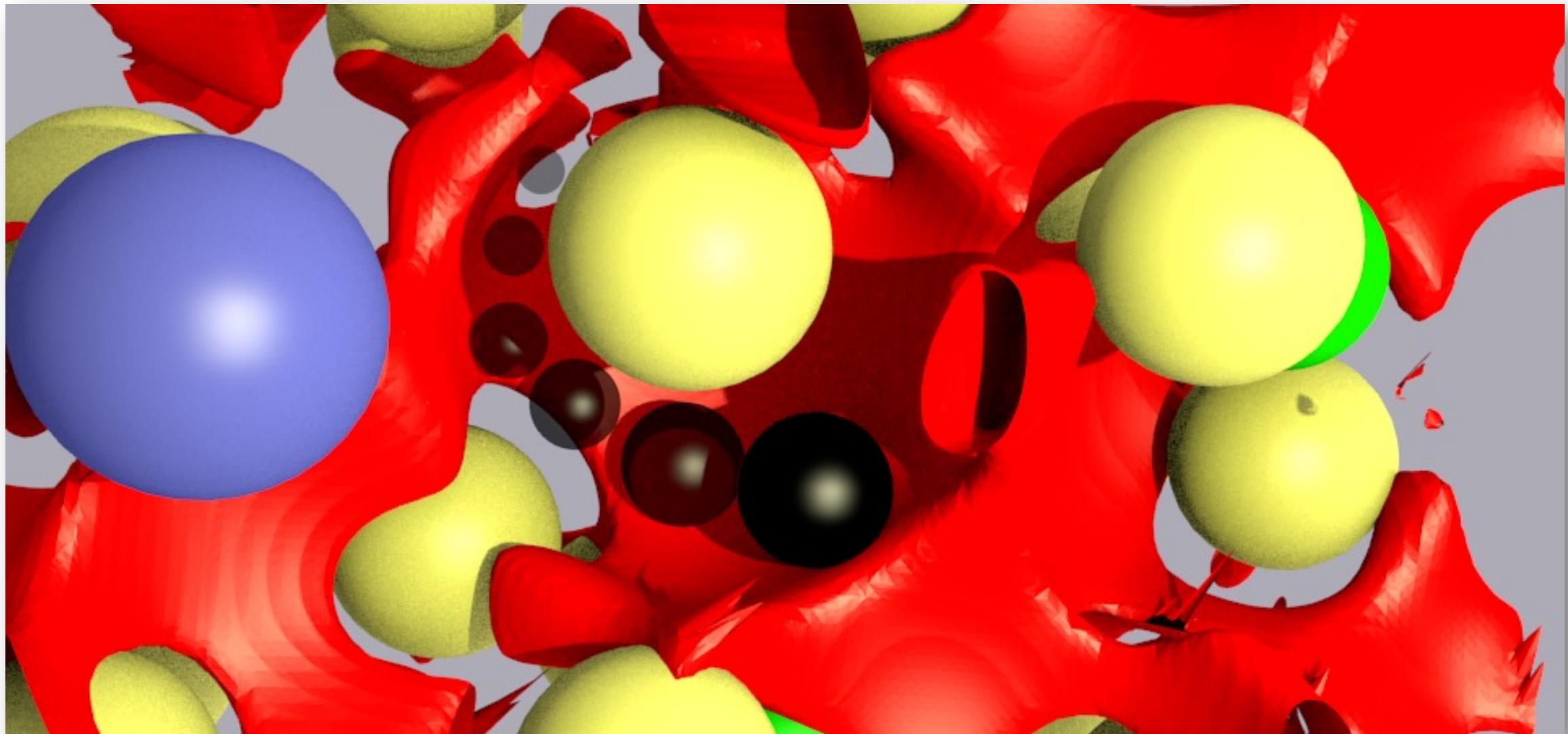
[LEARN ABOUT THESE METRICS](#)

D. Campi *et al.*, ACS Nano 17, 11268 (2023)

<https://mc2d.materialscloud.org/>



A PHYSICAL MODEL: PINBALL MD



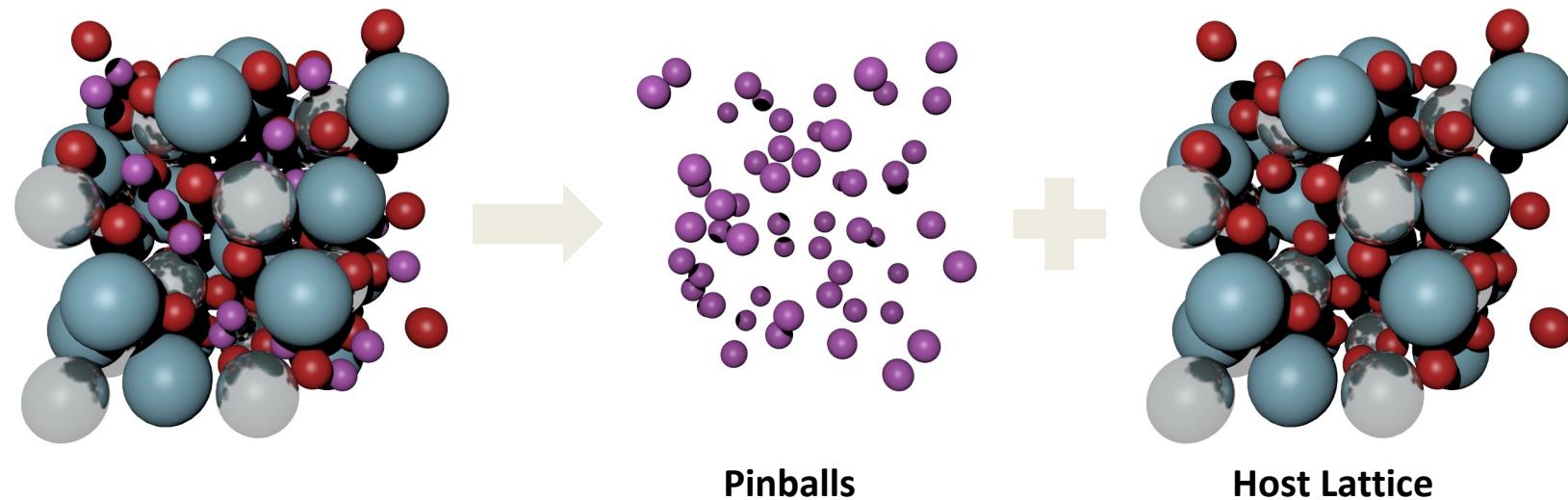
L. Kahle, A. Marcolongo, and N. Marzari, Physical Review Materials 2, 065405 (2018)



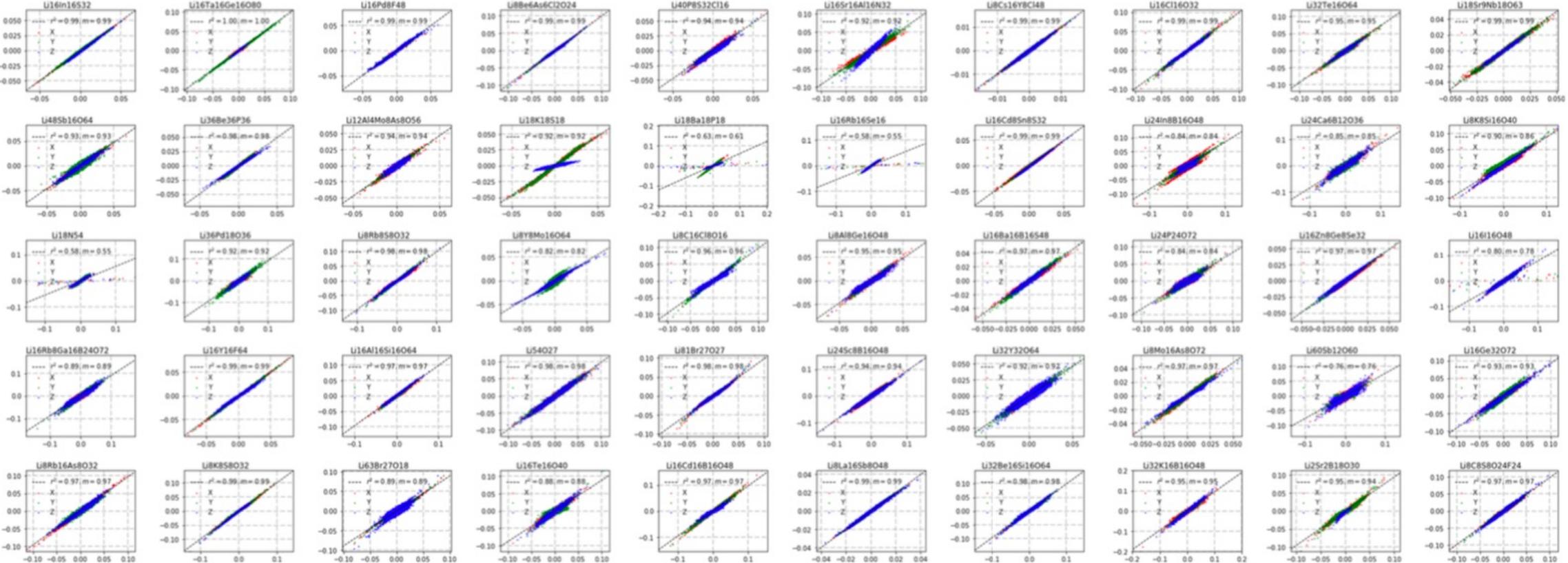
A PHYSICAL MODEL: PINBALL MD

- Frozen host lattice plus fully ionized and mobile cations; 4 fitting parameters
- Similar accuracy of DFT, and \sim 1000 times faster

$$\mathcal{H}_1^P = \frac{1}{2} \sum_p^P M_p \dot{R}_p^2 + \alpha_{1,2} \int n_{H_0}(\mathbf{r}) V_{\text{ext}}^P(\mathbf{r}) d\mathbf{r} + \beta_{1,2} \sum_{I,J}^{H_0-P, P-P} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$



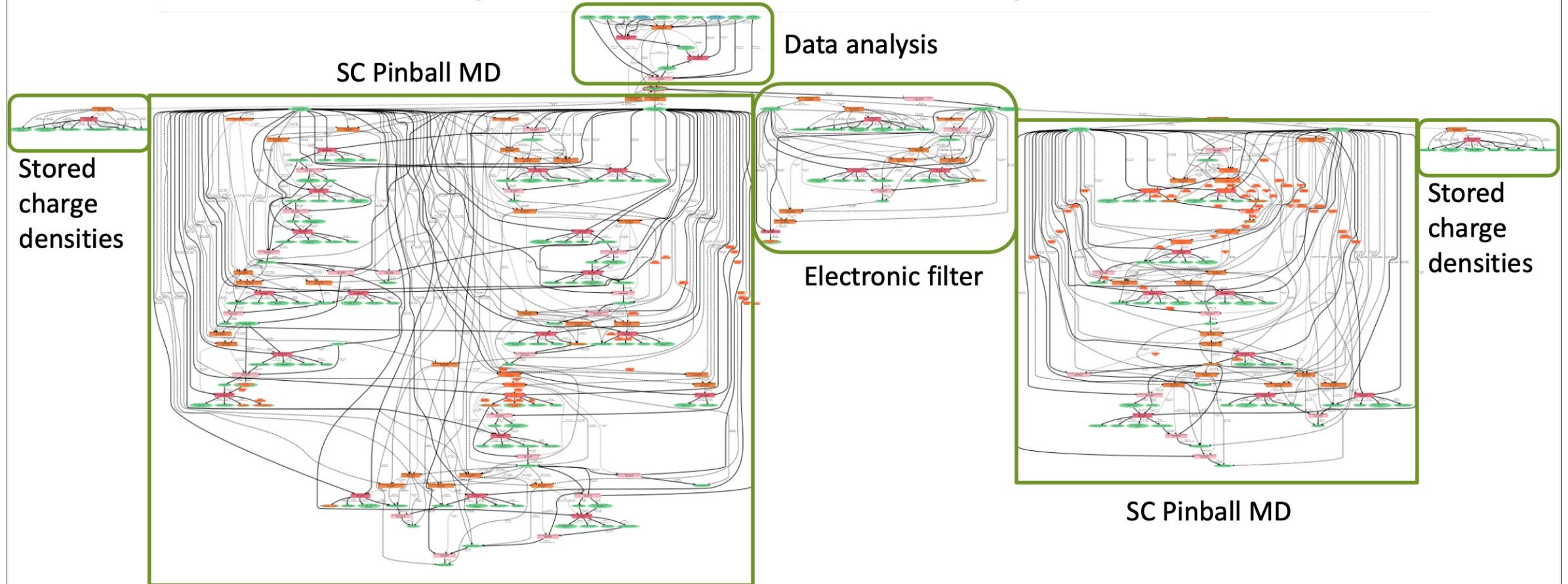
BROADLY APPLICABLE



Self-consistent vs pinball forces in randomly selected ionic compounds from the screening.



AUTOMATED AiiDA WORKFLOWS



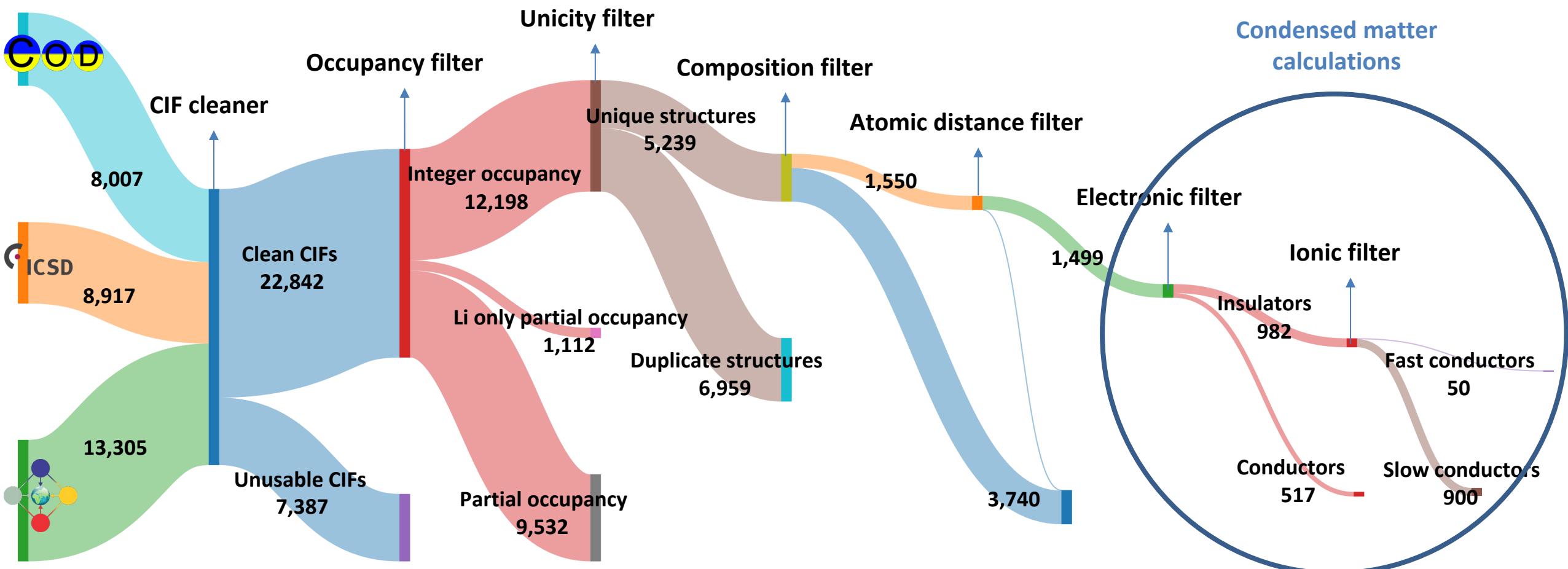
G. Pizzi, A. Cepellotti, R. Sabatini, N. Marzari, B. Kozinsky, Comp. Mat. Sci. 111, 218 (2016)

S.P. Huber et al., Nature Scientific Data 7, 300 (2020)

S.P. Huber, Nature Reviews Physics 4, 431 (2022)

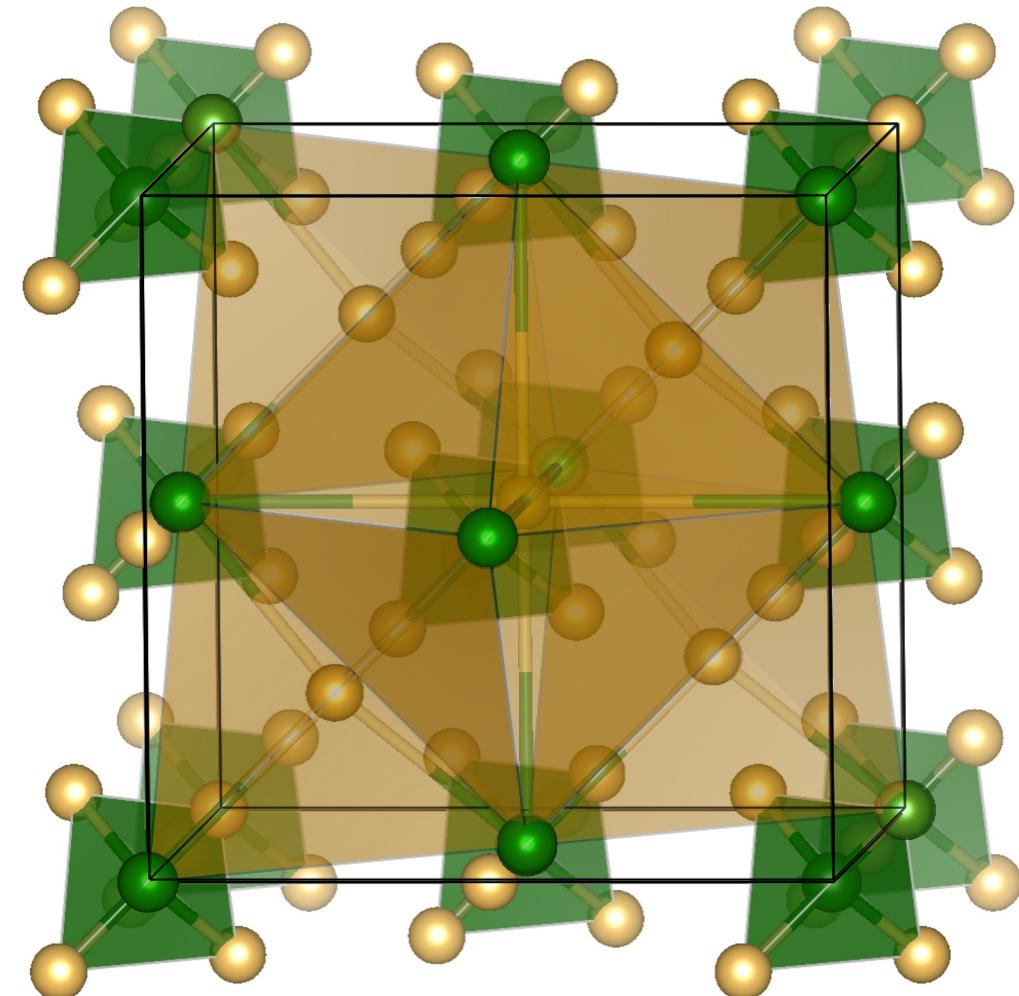


DISCOVERY: HIGH-THROUGHPUT SCREENING

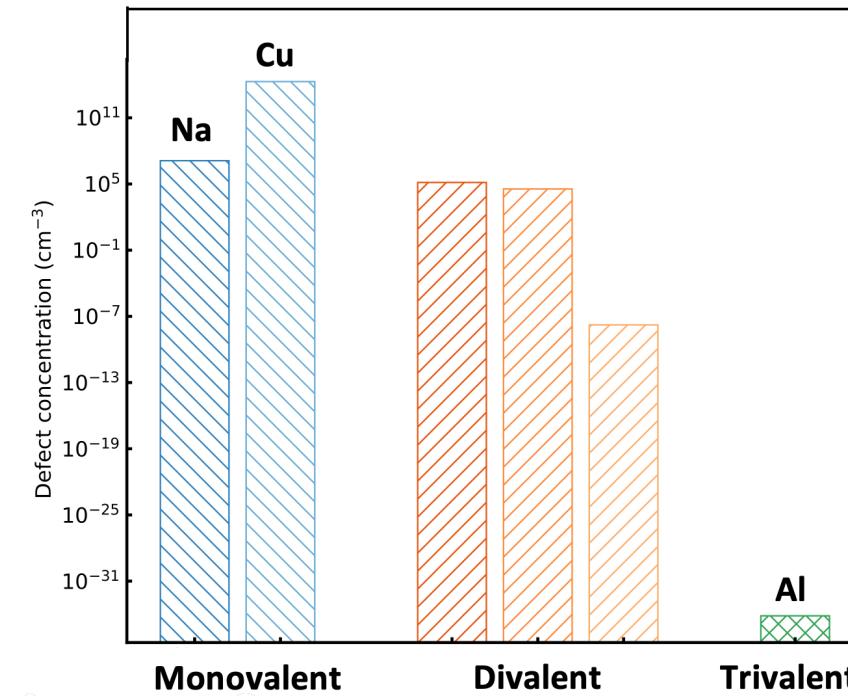
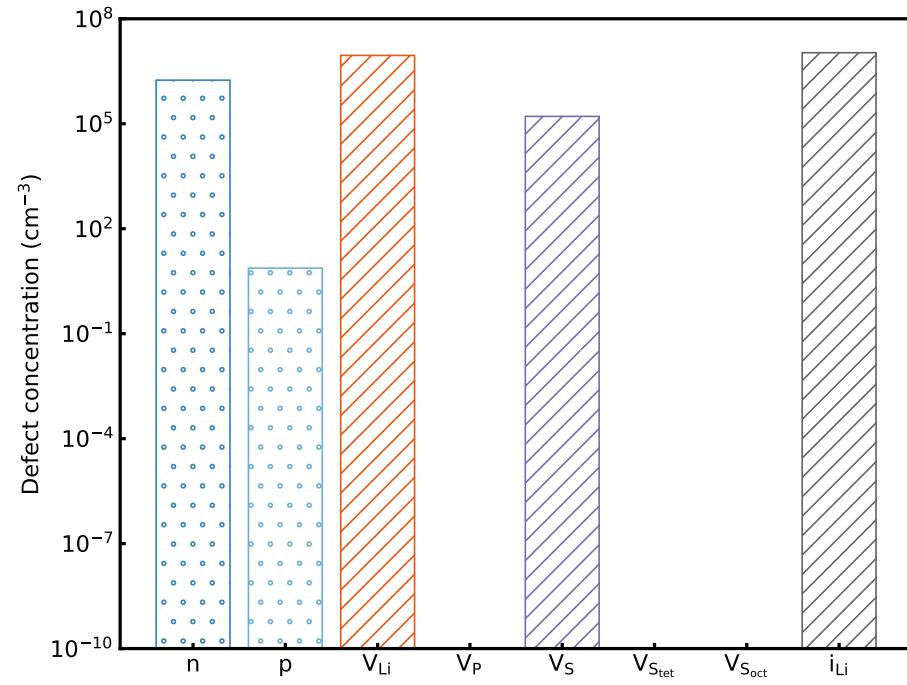


DESIGN: ARGYRODITE Li_7PS_6

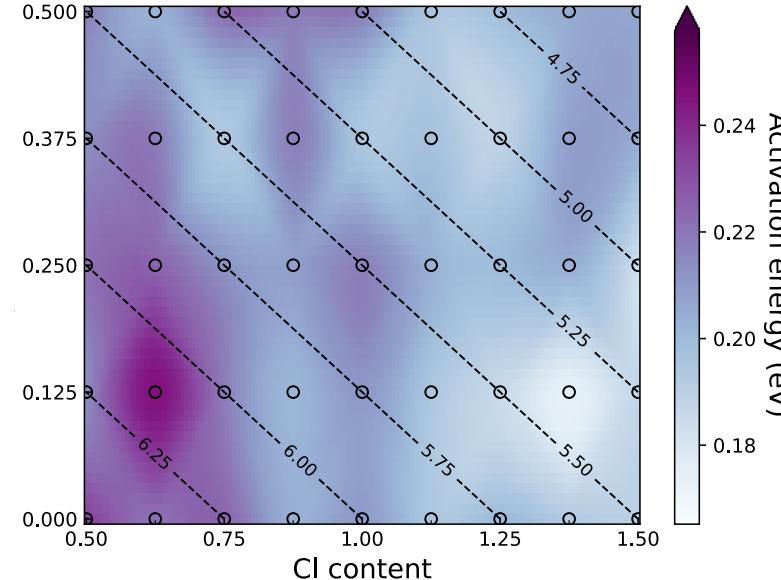
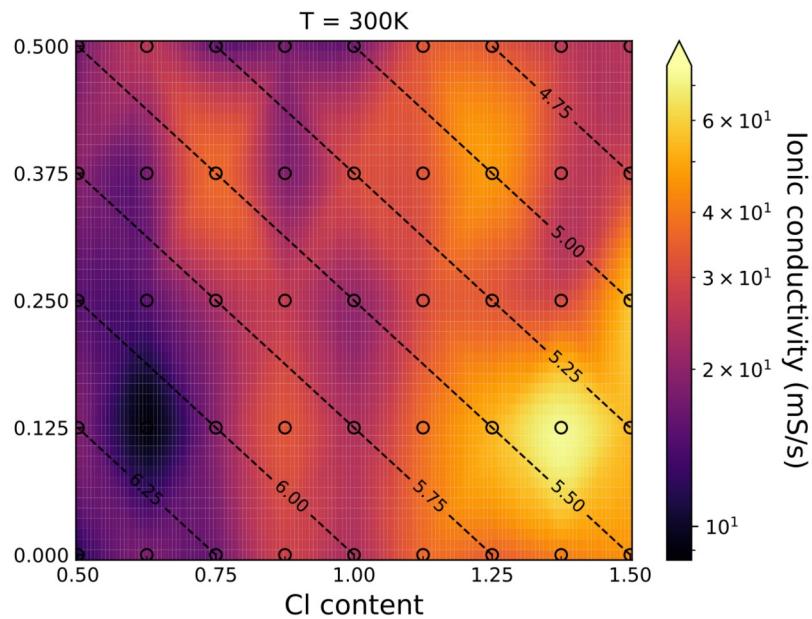
- $\text{Li}_7(\text{PS}_4)\text{S}_2$
- Face-centered cubic lattice of PS_4 tetrahedra
- The remaining 2 sulfurs are distributed over the octahedral and tetrahedral voids of the FCC lattice (S_{oct} and S_{tet})



AiiDA-DEFECTS: NATIVE DEFECTS AND DOPANTS



ACTIVATION ENERGY MAP $\text{Li}_{7-2x-y}\text{Mg}_x\text{PS}_{6-y}\text{Cl}_y$

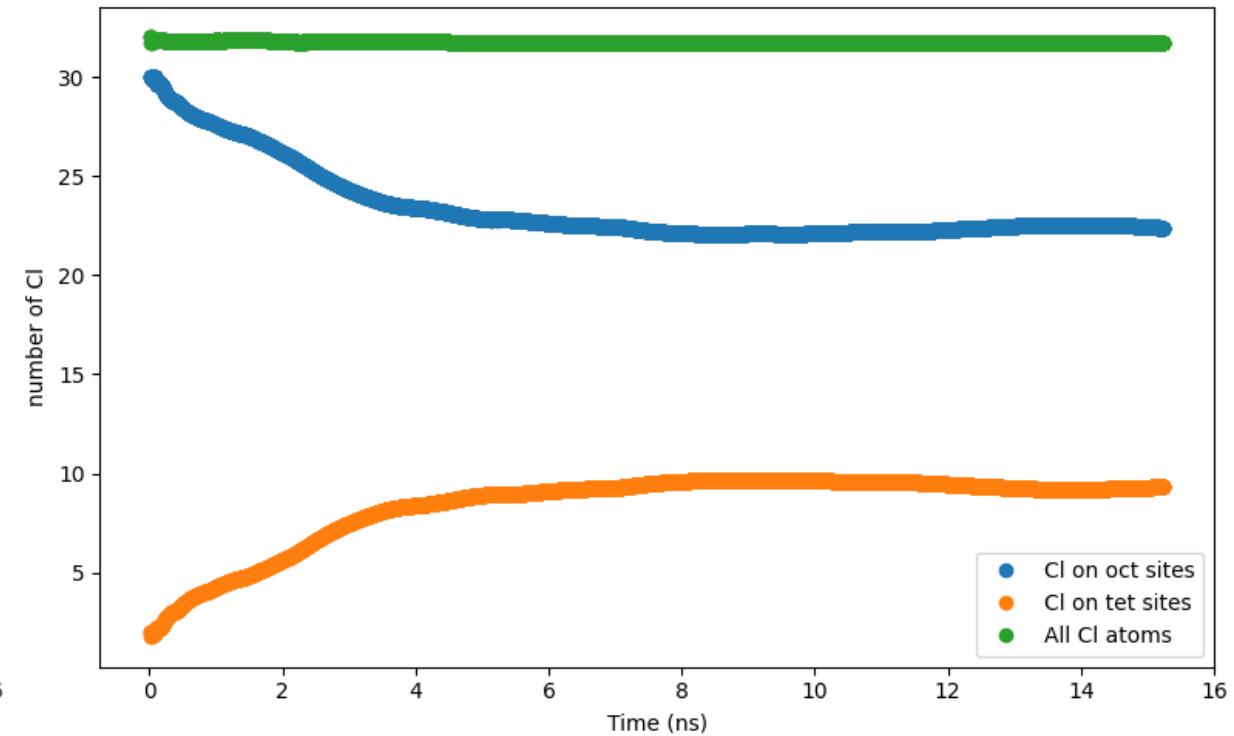
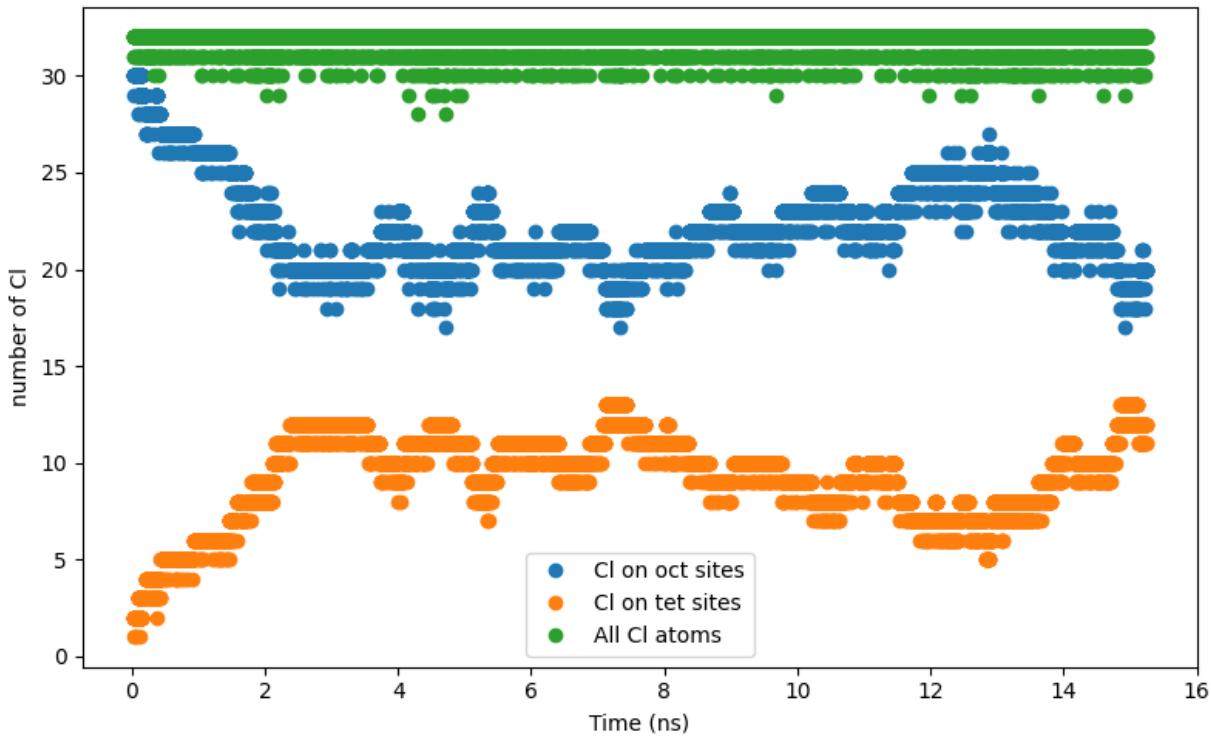


- The region with the highest ionic conductivity corresponds to high Cl and low Mg content.
- These results were confirmed by experiments, and two patents granted.

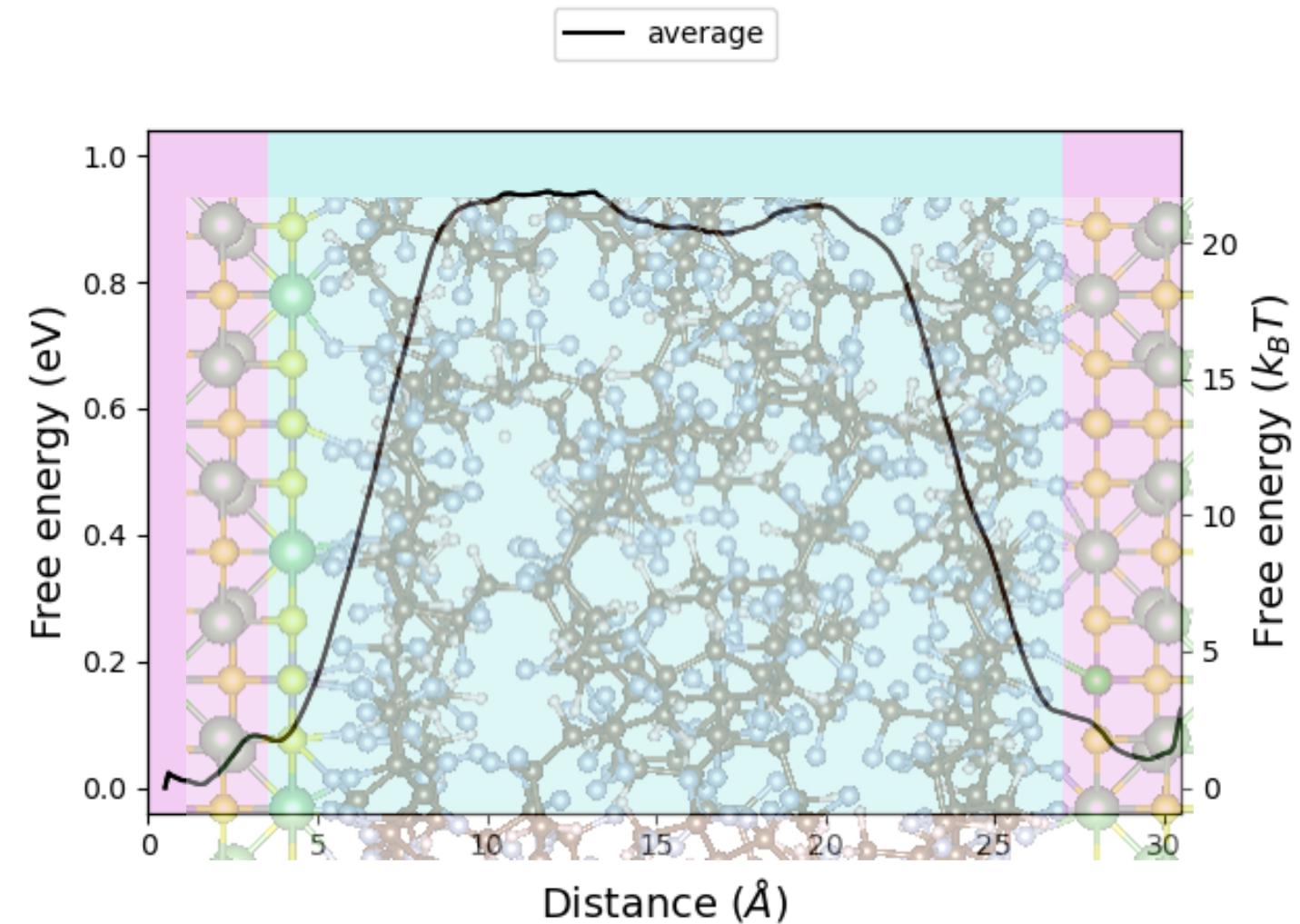
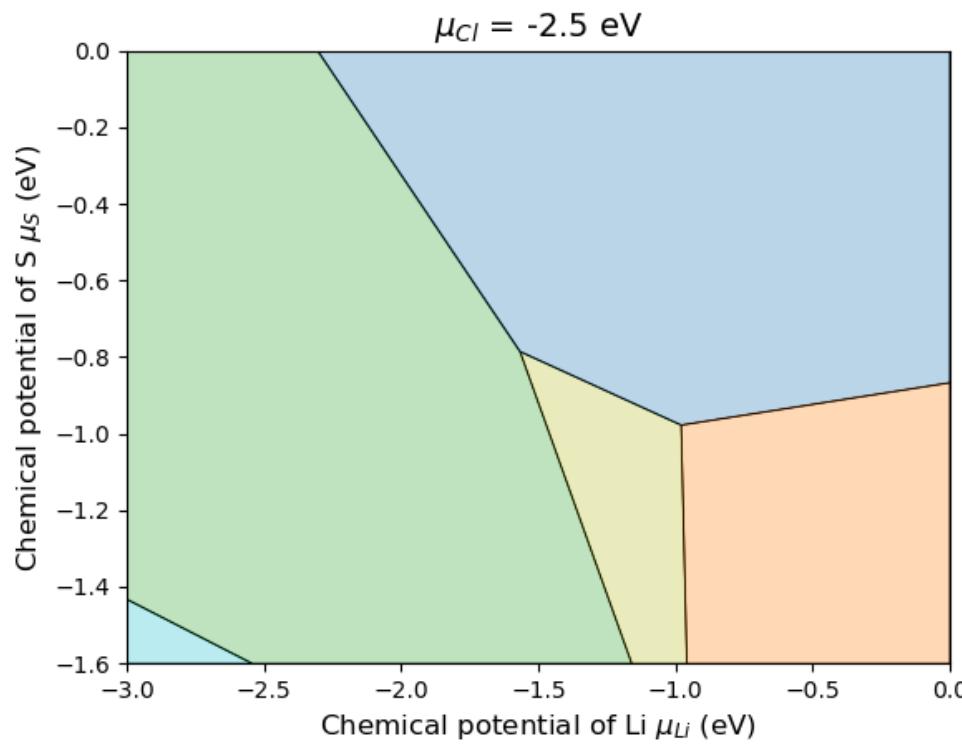


EQUILIBRATING THE IMMOBILE IONS

Experimentally at 300K, Cl have a 35% occupancy on tet sites, and 65% on oct sites. Computationally at 0K, all Cl on the oct site



POLYMER/ ARGYRODITE INTERFACES



2. NNs FOR SOLVATION

Solvation Free Energies from Machine Learning Molecular Dynamics

Nicéphore Bonnet* and Nicola Marzari



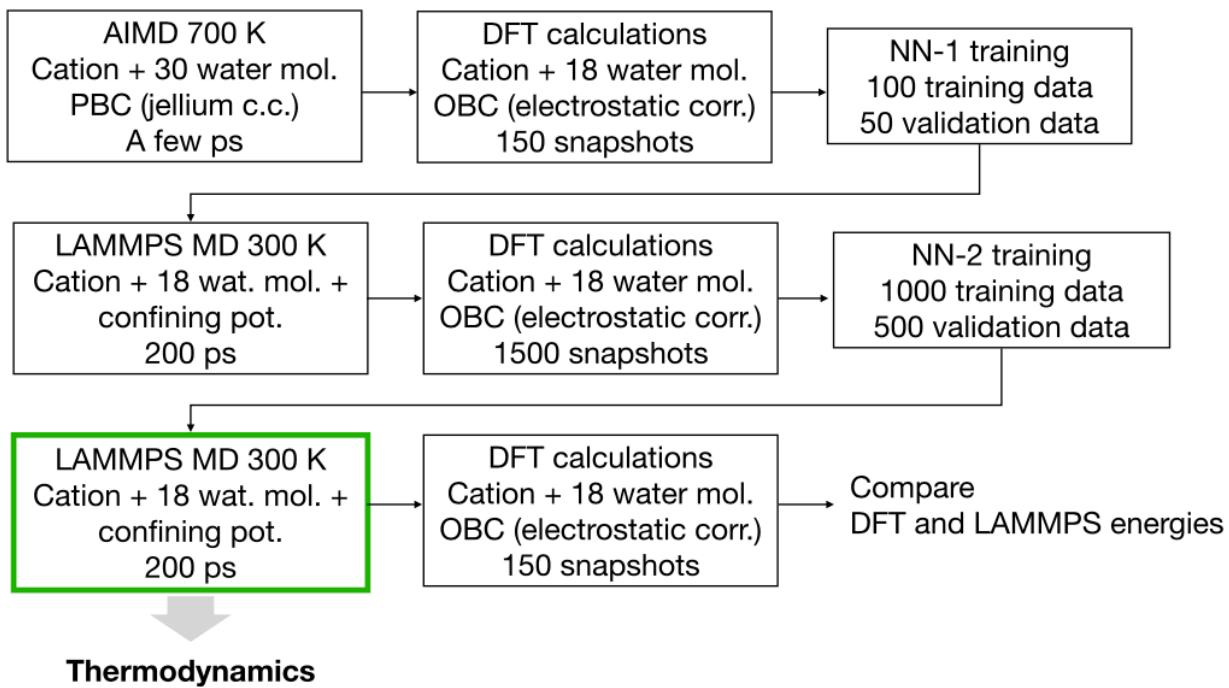
Cite This: *J. Chem. Theory Comput.* 2024, 20, 4820–4823



Read Online



SOLVATION FREE ENERGIES



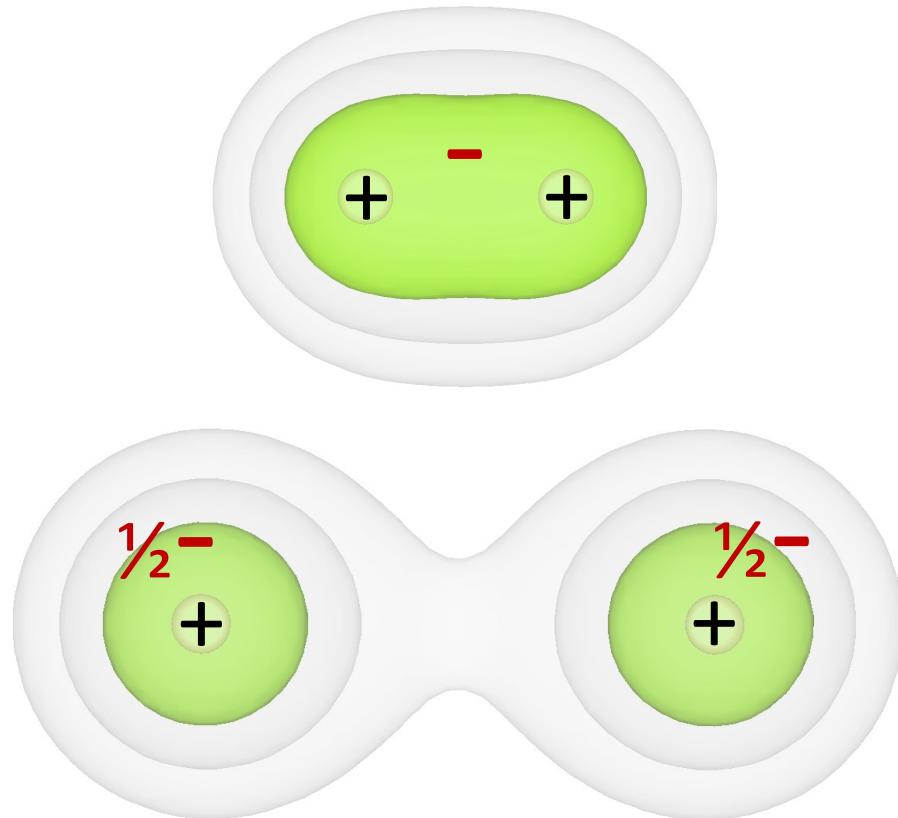
cation	calc. (this work)	exp.
Li^+	5.05	4.92–5.57
Na^+	4.10	3.78–4.47
K^+	3.31	3.06–3.73
Rb^+	3.15	2.85–3.49
Cs^+	2.86	2.59–3.26
Be^{2+}	25.71	24.82–25.07
Mg^{2+}	19.60	18.97–19.21
Ca^{2+}	16.34	15.60–16.59
Sr^{2+}	14.80	14.30–15.08
Ba^{2+}	13.40	12.95–13.74
MRE	1.8%	



3. GRAND-CANONICAL NNs



STANDARD DFT GETS LOST ON REDOX

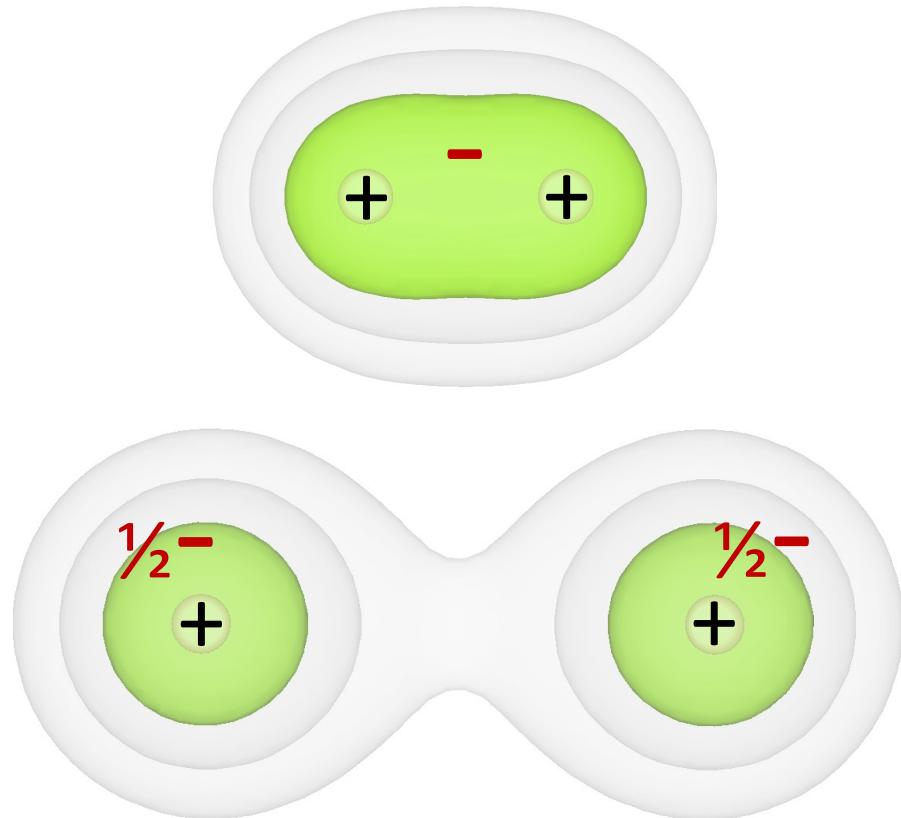


Schrödinger
$$H = -\frac{1}{2}\nabla^2 + V_{ext}(\vec{r})$$

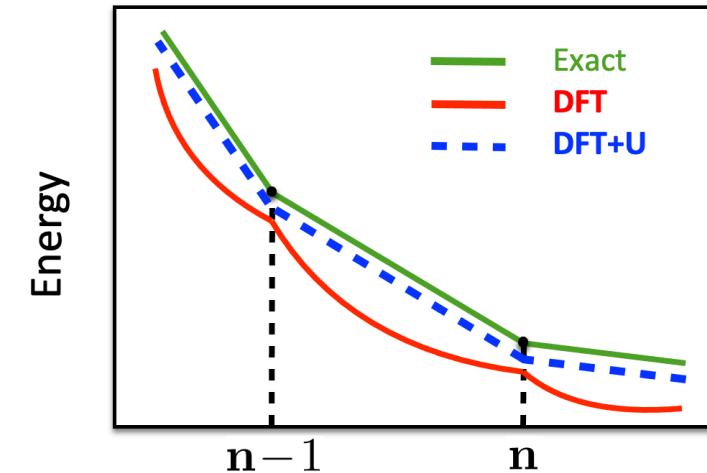
Kohn-Sham
$$H = -\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_H(n(\vec{r})) + V_{xc}(n(\vec{r}))$$



STANDARD DFT GETS LOST ON REDOX



$$E = E_{\text{DFT}} + \frac{1}{2} \sum_{I,\sigma} \textcolor{blue}{U^I} \text{Tr} [(1 - \mathbf{n}^{I\sigma}) \mathbf{n}^{I\sigma}]$$



V.I. Anisimov and coworkers PRB (1991), PRB (1995)

S. Dudarev, A. P. Sutton and coworkers PRB (1995)

M. Cococcioni and S. de Gironcoli. PRB (2005)

H.J. Kulik, M. Cococcioni, D.A. Scherlis, and N. Marzari, PRL (2006)

Schrödinger

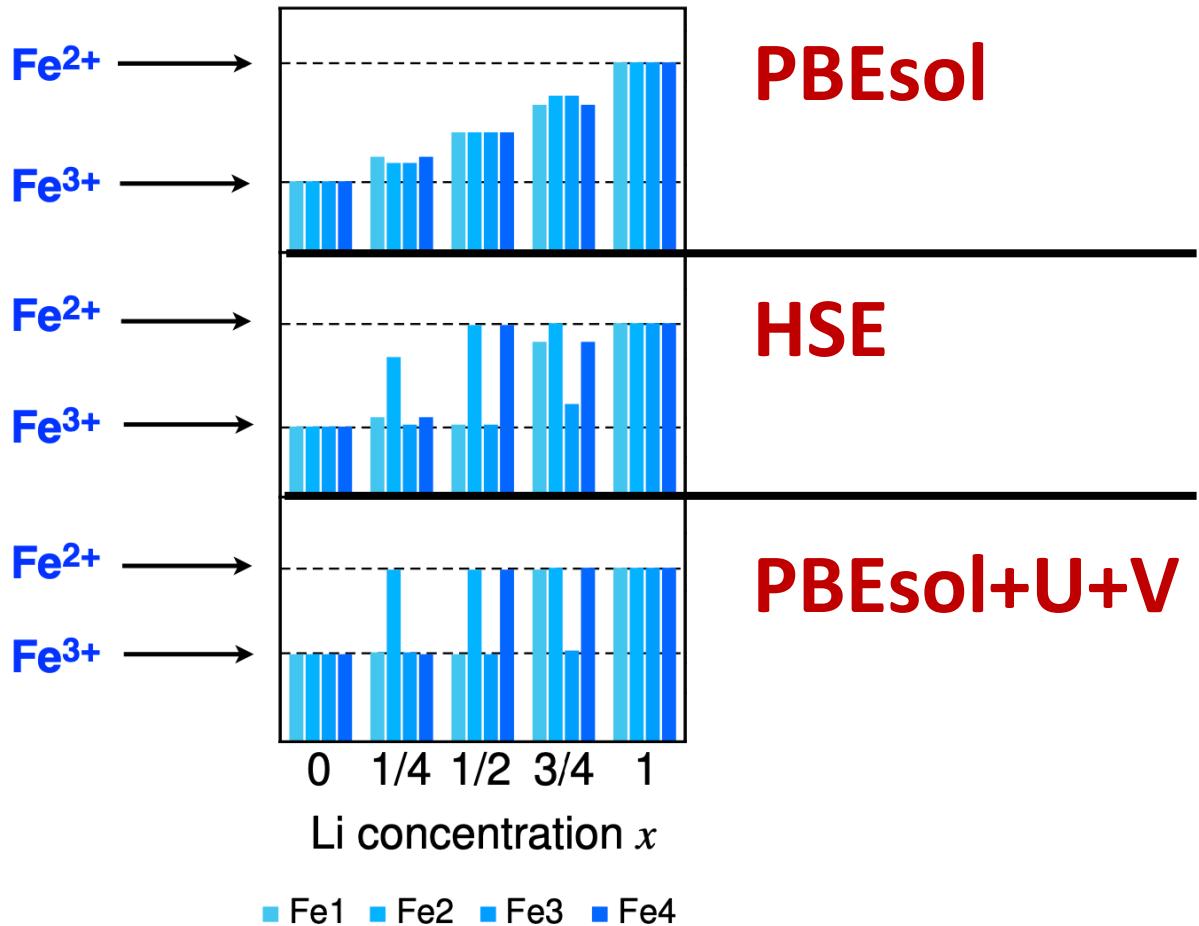
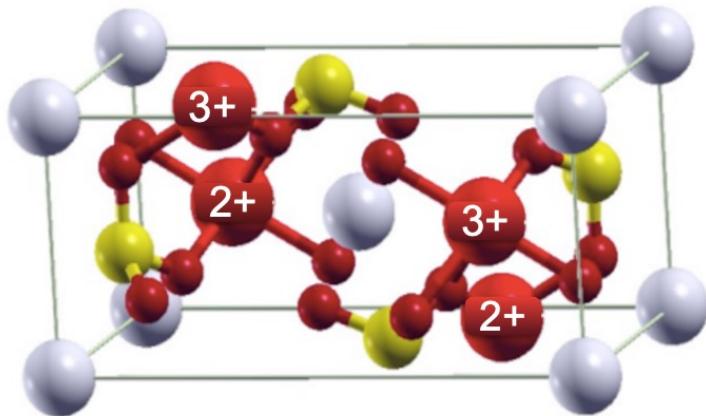
$$H = -\frac{1}{2} \nabla^2 + V_{ext}(\vec{r})$$

Kohn-Sham

$$H = -\frac{1}{2} \nabla^2 + V_{ext}(\vec{r}) + V_H(\mathbf{n}(\vec{r})) + V_{xc}(\mathbf{n}(\vec{r}))$$



CORRECT DESCRIPTION OF MIXED VALENCE



M. Cococcioni and N. Marzari, Phys. Rev. Materials 3, 033801 (2019)
I. Timrov, F. Aquilante, M. Cococcioni, and N. Marzari, Phys. Rev. X Energy 1, 033003 (2022)

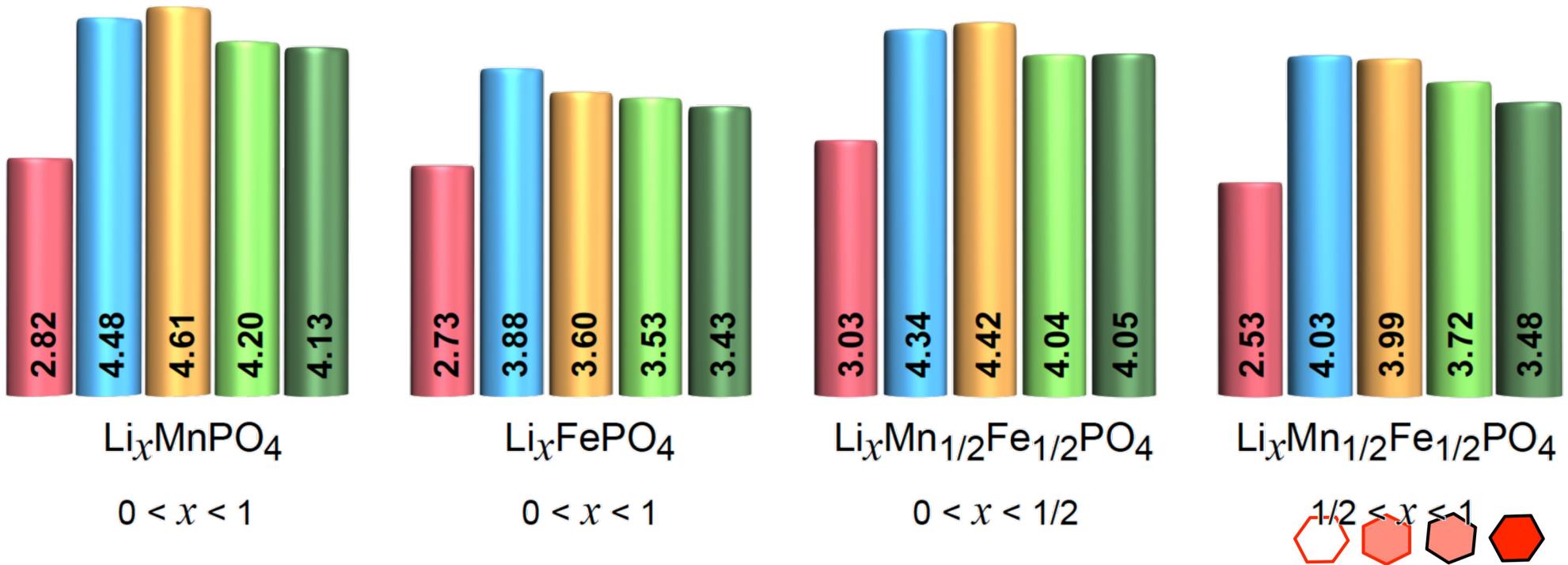


Li-ION CATHODE VOLTAGES

I. Timrov, F.
Aquilante, M.
Cococcioni and
N. Marzari,
Phys. Rev. X
Energy (2022)

$$\Phi = -\frac{E(\text{Li}_{x_2}\text{S}) - E(\text{Li}_{x_1}\text{S}) - (x_2 - x_1)E(\text{Li})}{(x_2 - x_1)e}$$

- DFT
- HSE06
- DFT+ U
- DFT+ $U+V$
- Expt.



4. SPECTRAL OPERATOR REPRESENTATIONS (SOREPs)



USE ELECTRONIC, NOT IONIC, FEATURES

Materials Cartography: Representing and Mining Materials Space Using Structural and Electronic Fingerprints

Oleksandr Isayev,[†] Denis Fourches,[†] Eugene N. Muratov,[†] Corey Oses,[‡] Kevin Rasch,[‡] Alexander Tropsha,^{*,†} and Stefano Curtarolo^{*,‡,†}

SPA^HM: the spectrum of approximated Hamiltonian matrices representations†

Alberto Fabrizio, ^{ID} ^{‡,ab} Ksenia R. Briling, ^{ID} ^{‡,a} and Clemence Corminboeuf ^{ID} ^{*ab}

nature chemistry

ARTICLES

<https://doi.org/10.1038/s41557-020-0527-z>

Quantum machine learning using atom-in-molecule-based fragments selected on the fly

Bing Huang ^{ID} and O. Anatole von Lilienfeld ^{ID}

Representing individual electronic states for machine learning GW band structures of 2D materials

Nikolaj Rørbaek Knøsgaard ^{1,✉} & Kristian Sommer Thygesen ¹

Choosing optimal representation methods of atomic and electronic structures is essential when machine learning properties of materials. We address the problem of representing quantum states of electrons in a solid for the purpose of machine learning state-specific

Generate electronic structure

Define theoretical framework

Apply operator

Overlap, kinetic energy, Hamiltonian, ...

Compute operator spectrum

Basis independence and physical mixing

Map to ML features

Construct and shape feature space

$$f: \{\mathbf{R}_I, Z_I, \dots\} \rightarrow \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N)$$

$$f: \{\mathbf{R}_I, Z_I, \dots\} \rightarrow \{|\phi_i\rangle\}$$

$$A_{ij} = \langle \phi_i | \hat{A} | \phi_j \rangle$$

$$A |\phi_i\rangle = \lambda_i S |\phi_i\rangle$$

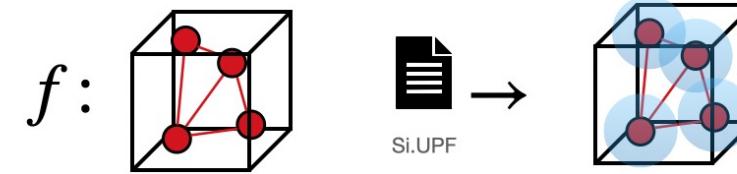
$$g : \{\lambda_i\} \rightarrow \mathbf{x}$$



SINGLE-SHOT DFT AS AN EASY AND ACCURATE STARTING POINT

Generate electronic structure

Decorate with pseudo-atomic charges



Apply operator

Single-shot Kohn-Sham DFT Hamiltonian

$$V_{\text{KS}} [\tilde{\rho}(\mathbf{r})]$$

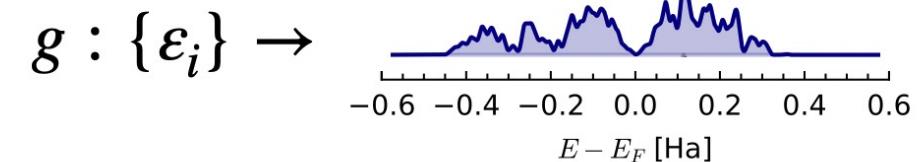
Compute operator spectrum

Generalized diagonalization

$$H |\phi_i\rangle = \varepsilon_i S |\phi_i\rangle$$

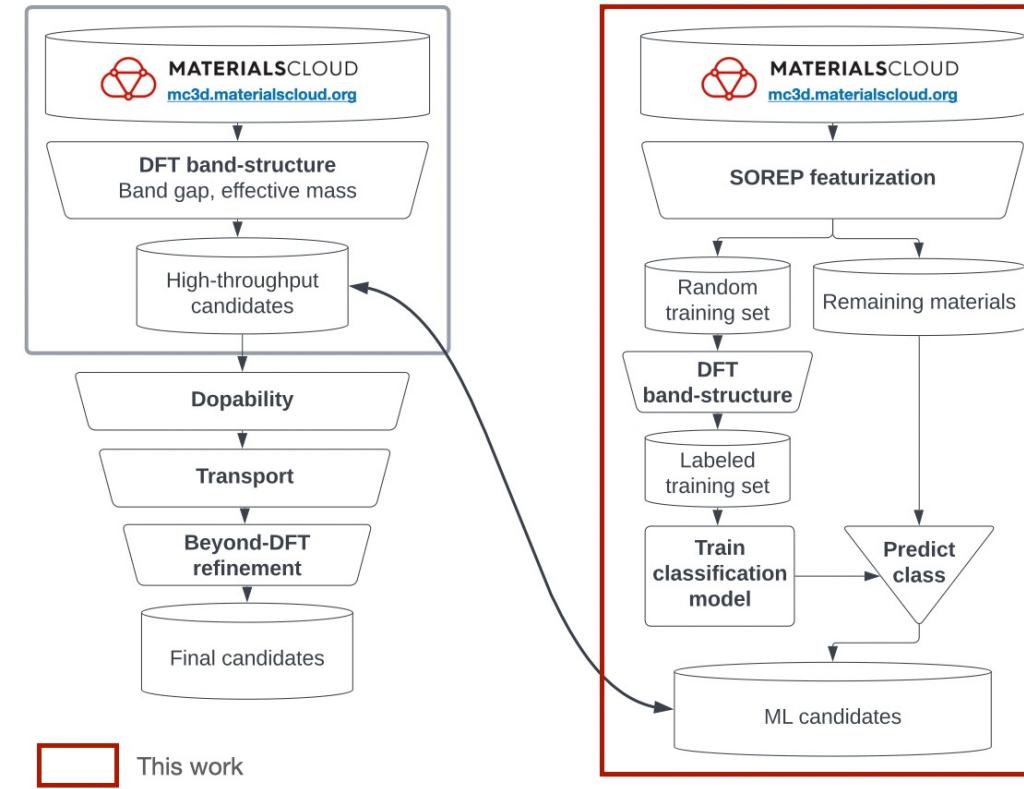
Map to ML features

Density of states



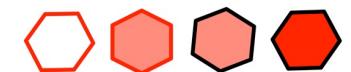
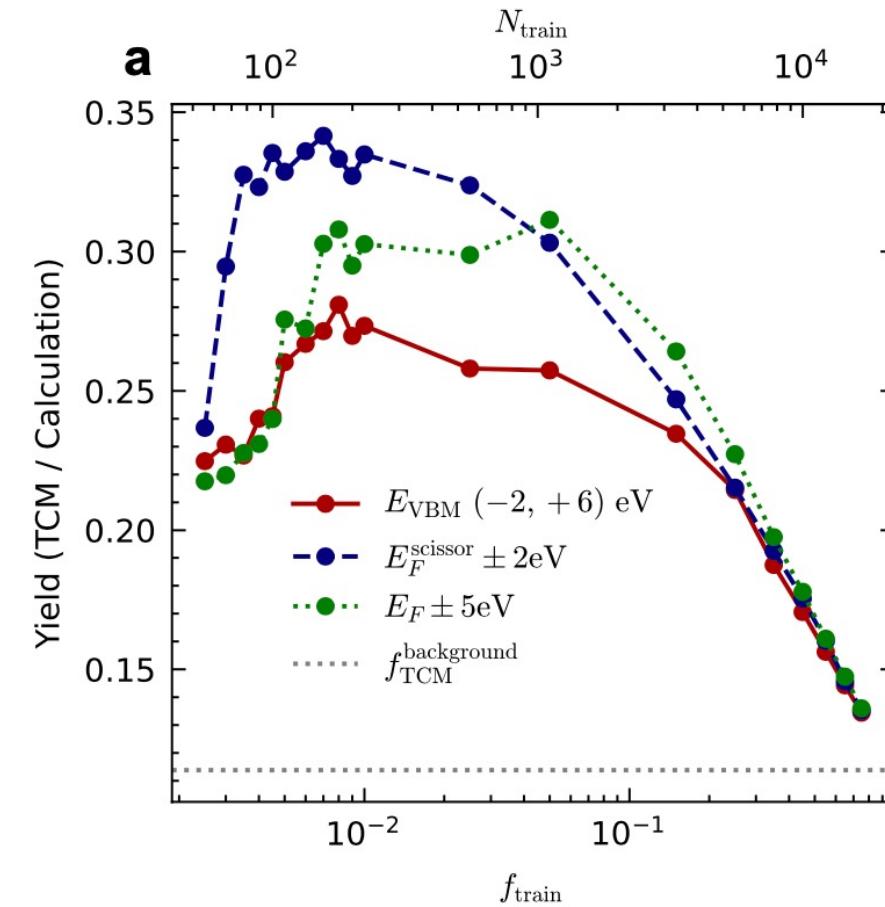
SEARCH FOR TRANSPARENT CONDUCTORS

- **Predict TCM screening classification**
 - Cost-constrained (< scf + bands)
- **Diverse materials (MC3D)**
 - 85 elements, 30'000 materials
- **Electronic properties**
 - $E_{\text{gap}} > 0.5 \text{ eV}$
 - $m_e^* \leq 0.5 m_e$ and/or $m_h^* \leq 1.0 m_e$



SEARCH FOR TRANSPARENT CONDUCTORS

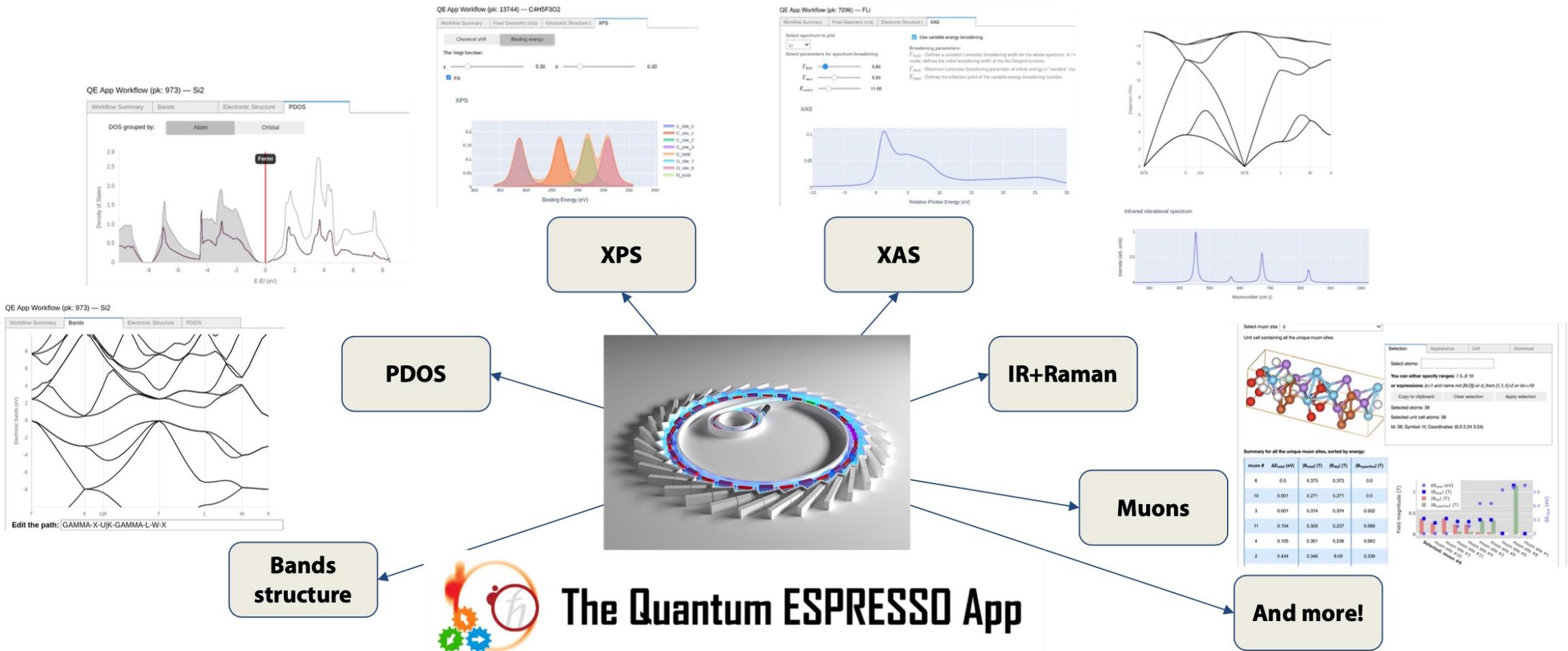
- **Data-efficient**
 - Find 76% (1920) of TCMs w/ 1% (220) training data
- **Strong acceleration**
 - Peak 3.9x, practical ~2.5x
 - (trade-off b/w no. found and accel.)
- **Physically interpretable features**



5. DIGITAL INFRASTRUCTURES



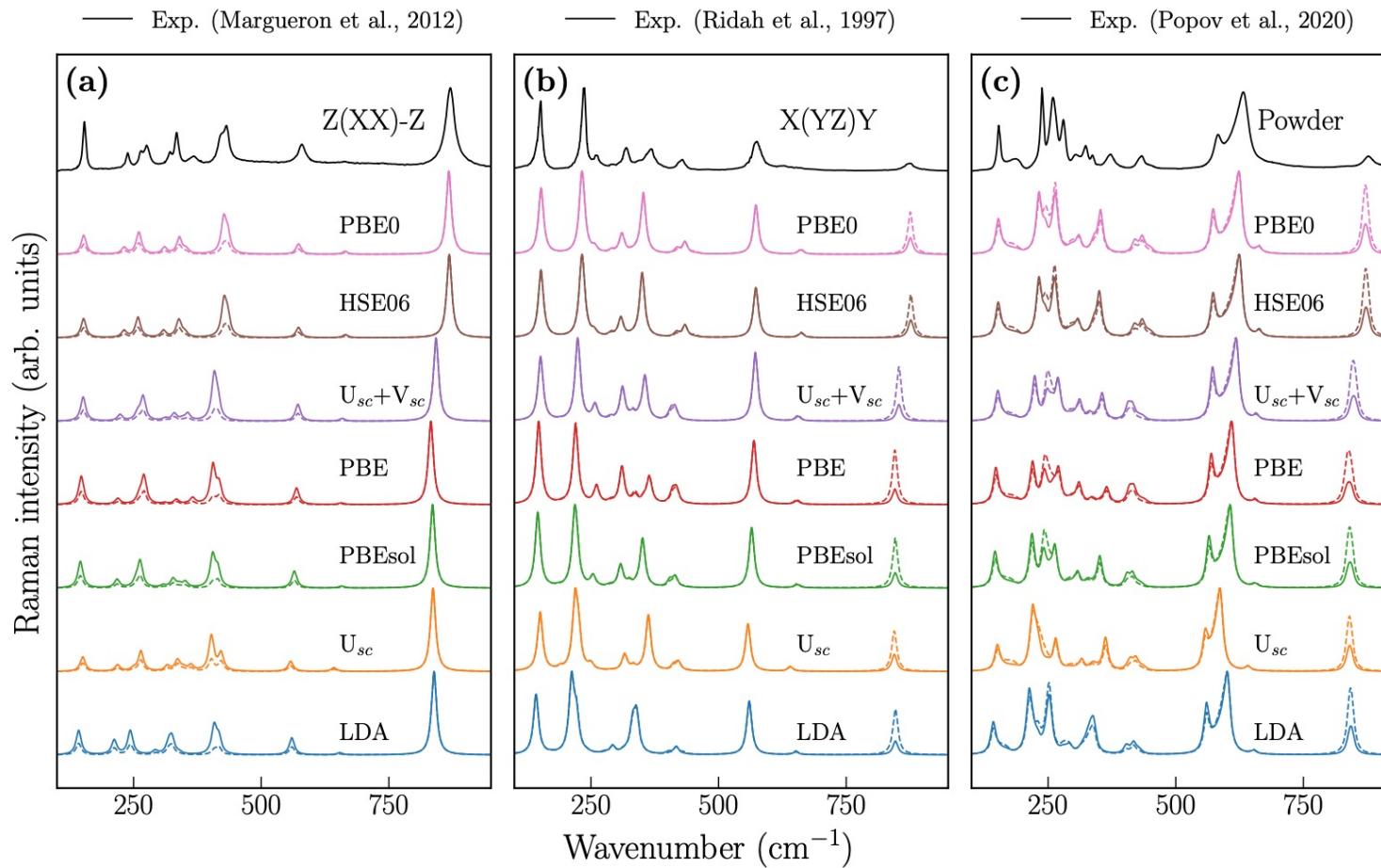
ACCESSIBLE SIMULATIONS



Contributors: E. Bainglass (PSI), M. Bercx (PSI), M. Bonacci (PSI), D. Dou (EPFL), P. Gillespie (CNR-NANO Modena), M. A. Hernández-Bertrán (CNR-NANO Modena), D. Hollas (Bristol), N. Marzari (EPFL, PSI), A. Ortega-Guerrero (Empa), C. Pignedoli (Empa), D. Prezzi (CNR-NANO Modena), G. Pizzi (PSI), I. Timrov (EPFL, PSI), J. Yu (PSI), A. Yakutovich (Empa)



AUTOMATED ALL-FUNCTIONALS IR/RAMAN (LiNbO_3)

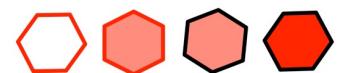
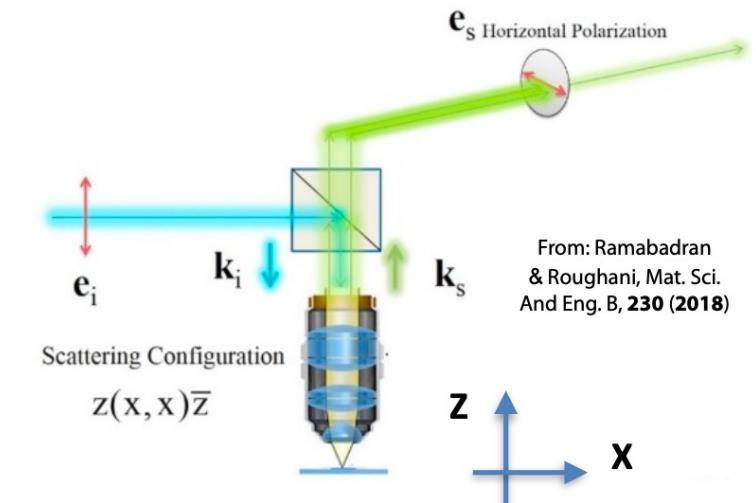


POLARIZED SINGLE-CRYSTAL RAMAN

$$I_{\text{Raman}} \propto |e_i \cdot \alpha(\mathbf{q}) \cdot e_s|^2$$

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s (\approx \mathbf{0})$$

$$\frac{\partial \chi_{ij}}{\partial \tau_{I,k}}(\mathbf{q}) = \frac{\partial \chi_{ij}}{\partial \tau_{I,k}} - \frac{8\pi}{\Omega} \frac{\sum_l q_l Z_{I,lk}^*}{\sum_{s,s'} q_s \epsilon_{ss}^\infty q_{s'}} \sum_{l'} \chi_{ijl'}^{(2)} q_{l'}$$



Welcome to the AiiDAlab Quantum ESPRESSO app! 🙌

The [Quantum ESPRESSO](#) app (or QE app for short) is a graphical front end for calculating materials properties using Quantum ESPRESSO (QE). Each property is calculated by workflows powered by the [AiiDA engine](#), and maintained in the [Quantum ESPRESSO plugin](#) for AiiDA.

The QE app allows you to calculate properties in a simple 4-step process:

- 🔍 **Step 1:** Select the structure you want to run.
- ⚙️ **Step 2:** Select the properties you are interested in.
- 💻 **Step 3:** Choose the computational resources you want to run on.
- 🚀 **Step 4:** Submit your workflow.

New users can go straight to the first step and select their structure. Once you've already run some calculations, you can select the corresponding workflow using the dropdown below.

Happy computing! 🎉

Select computed workflow or start a new one: ▼ + New ⟳ Refresh

◀ Previous step ⟲ Reset ▶ Next step

▼ ○ **Step 1: Select structure**

Select a structure from one of the following sources and then click "Confirm" to go to the next step.

ⓘ Currently only three-dimensional structures are supported.

[Supported structure formats](#)

AUTOMATED CELL ASSEMBLY AND TESTING

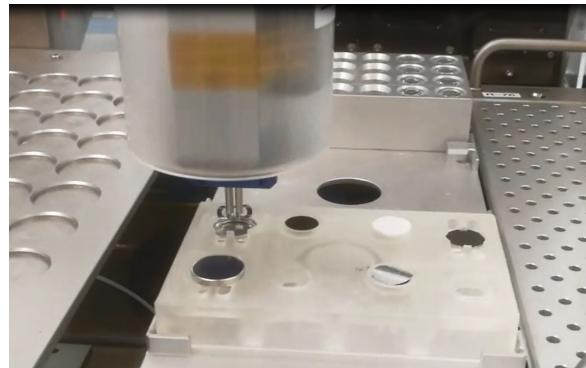
Features accessible via AiiDAlab GUI:

Cell selection

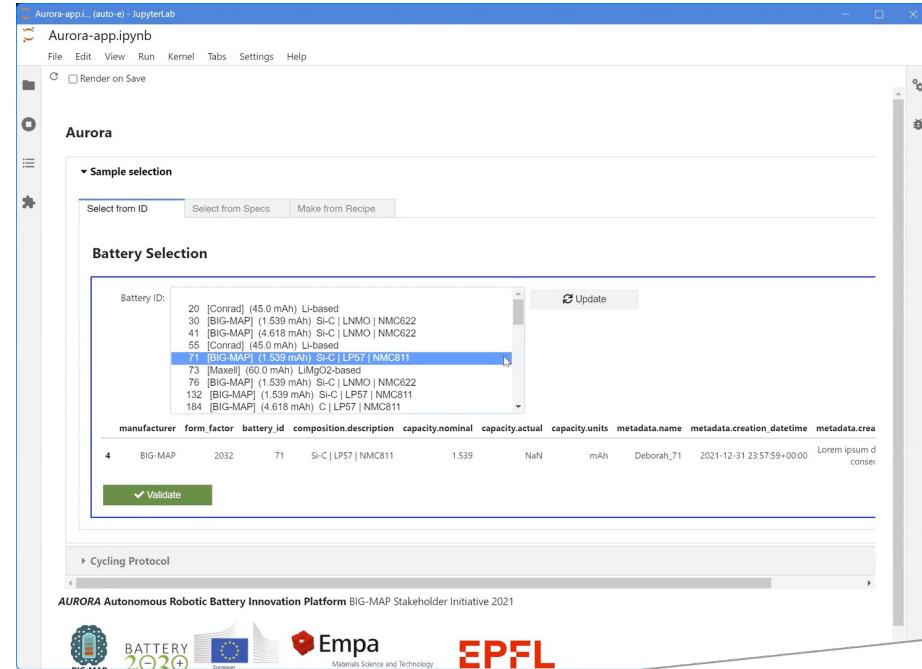
- Select specific battery (list from Lab's Catalogue)
- Search battery by ID or specification
- Create battery with desired specs from "recipe":
 - request user to load battery into the cycler
 - synthesis & assembling recipe, to be sent to the robot

Battery testing protocol

Experiment monitoring

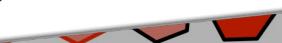


P. Kraus et al., J. Mater. Chem. A, 2024, Advance Article



A bridge between trust and control: computational workflows meet automated battery cycling†

Peter Kraus, ^{af} Edan Bainglass, ^b Francisco F. Ramirez, ^c Enea Svaluto-Ferro, ^a Loris Ercole, ^c Benjamin Kunz, ^a Sebastiaan P. Huber, ^c Nukorn Plainpan, ^a Nicola Marzari, ^{bc} Corsin Battaglia ^{*ade} and Giovanni Pizzi ^{*bc}



REVIEW ARTICLE | INSIGHT

<https://doi.org/10.1038/s41563-021-01013-3>

nature
materials



Electronic-structure methods for materials design

Nicola Marzari¹✉, Andrea Ferretti² and Chris Wolverton³

The accuracy and efficiency of electronic-structure methods to understand, predict and design the properties of materials has driven a new paradigm in research. Simulations can greatly accelerate the identification, characterization and optimization of materials, with this acceleration driven by continuous progress in theory, algorithms and hardware, and by adaptation of concepts and tools from computer science. Nevertheless, the capability to identify and characterize materials relies on the predictive accuracy of the underlying physical descriptions, and on the ability to capture the complexity of realistic systems. We provide here an overview of electronic-structure methods, of their application to the prediction of materials properties, and of the different strategies employed towards the broader goals of materials design and discovery.



ACKNOWLEDGEMENTS



FUNDING



PAUL SCHERRER INSTITUT



<http://theosrv1.epfl.ch>

**Theory and Simulation of Materials
(2011 onwards)**

<http://nccr-marvel.ch>

**Swiss National Centre for Computational
Design and Discovery of Novel Materials
(2014-26)**

<http://max-centre.eu>

**H2020 Centre of Excellence MaX:
Materials Design at the Exascale
(2015-26)**

<https://www.psi.ch/en/lms>

**Laboratory for Materials Simulations
(2021 onwards)**

<https://www.big-map.eu>

**H2020 Battery Interface Genome – Materials
Acceleration Platform (Battery 2030+, 2020-23, ...)**

<https://www.uni-bremen.de/mapex>

U Bremen Excellence Chair (2018-25)

**H2020 Nanoscience Foundries and Fine Analysis
H2020 European Materials Modelling Council**

H2020 Marketplace

H2020 Intersect

H2020 DOME 4.0

H2020 OpenModel

H2020 NEP

H2020 EPFL Fellows

H2020 EPFL Innovators

H2020 Marie Curie

EPFL Open Science

NCCR Catalysis

PASC

PRACE

Constellium

IBM

Innosuisse

Richemont Varinor

Robert Bosch Stiftung

Samsung

Solvay

nfffa.eu

PRACE



RICHEMONT

Robert Bosch Stiftung

