How Molecular Dynamics Simulations Provide New Insights to Energy Materials

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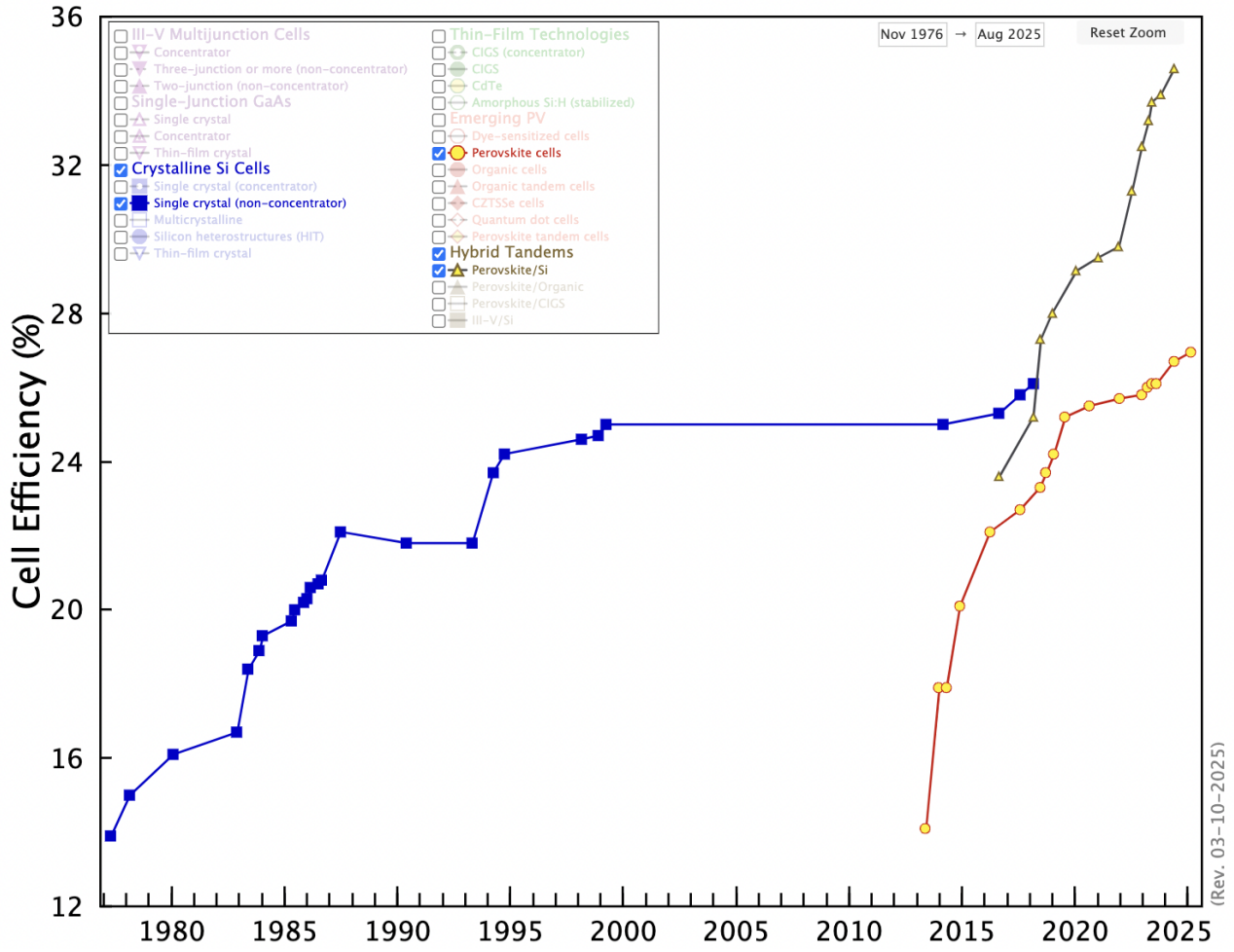
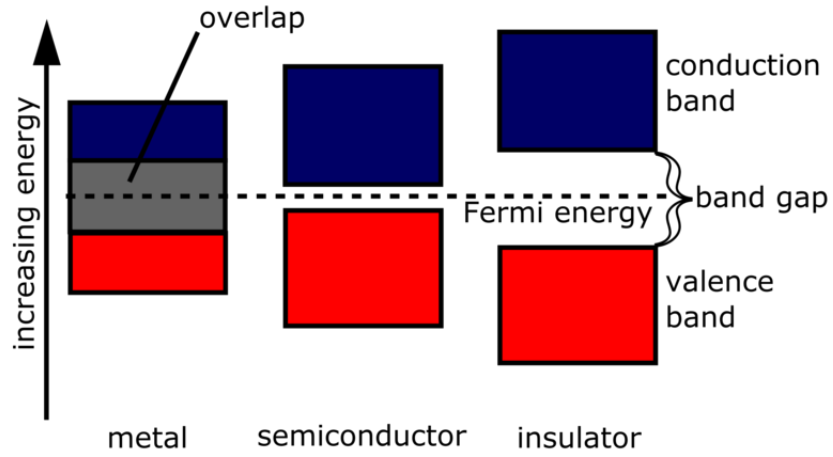
The pursuit of new energy materials



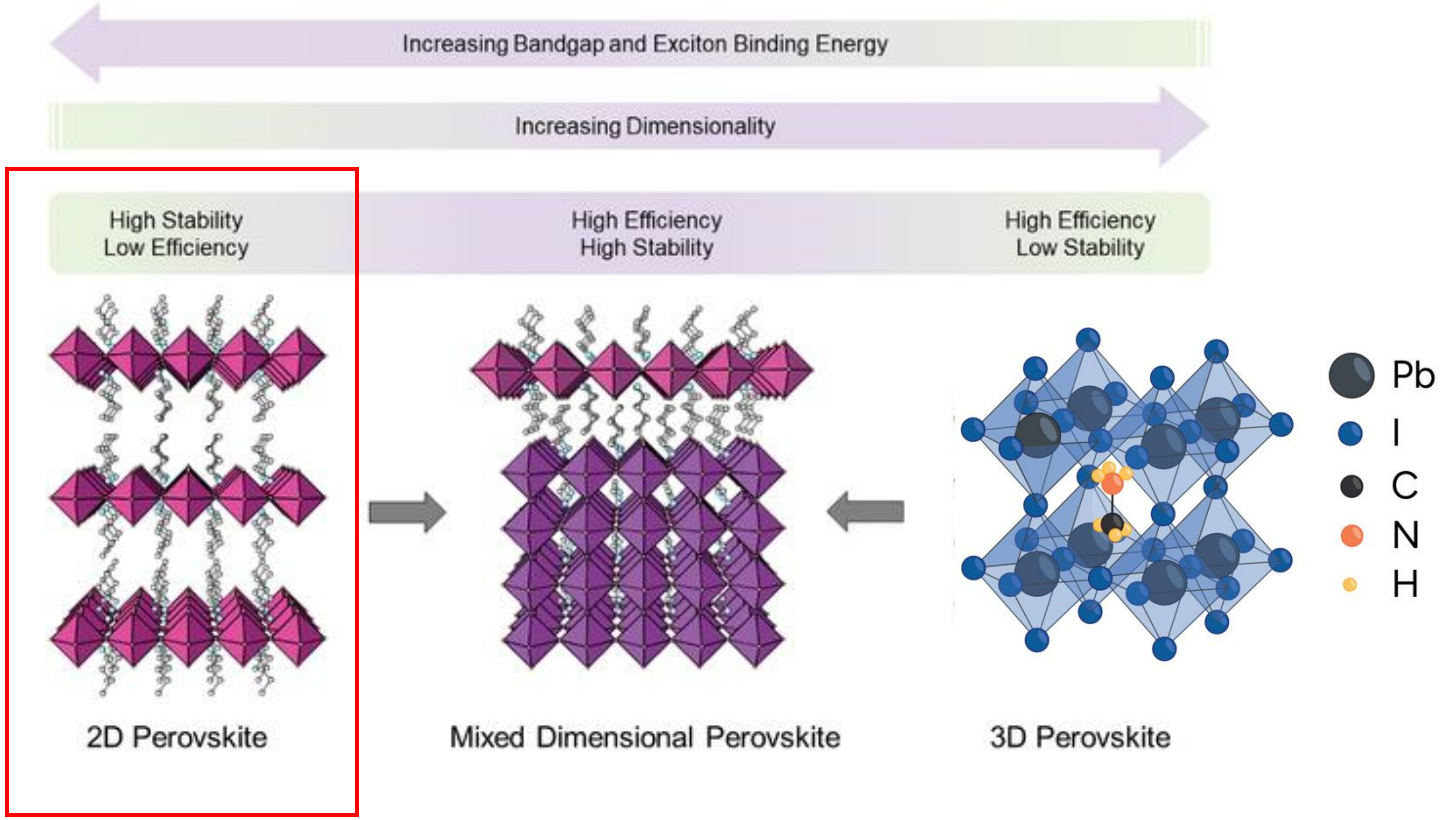
National Renewable Energy Lab



Question

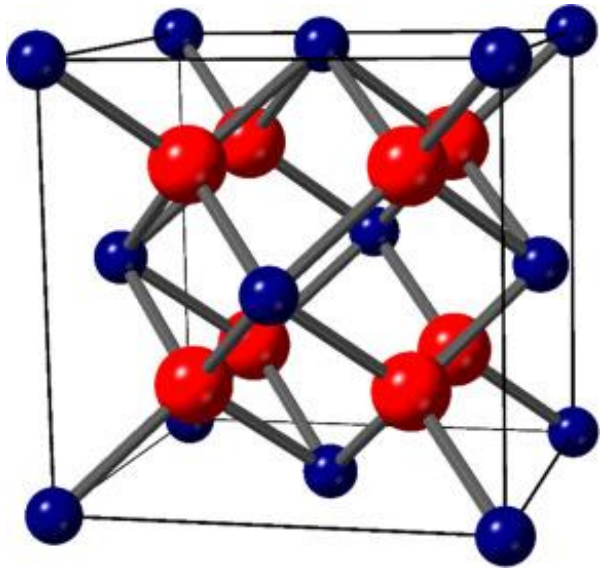
From a first principles/theory perspective, what makes a material an efficient energy material?

Proposed energy materials



Perovskite (“Solar” Cell)

Uranium
Oxygen



Uranium Dioxide (“Nuclear” Cell)

Wu, G. et al. *Advanced Materials* **2022**, *34* (8), 2105635.

Methods and Theories Overview

How using innovative methods can lead to more accurate simulations and new discoveries

Why we use molecular dynamics (MD) simulations

Atoms are basically always “moving” to some degree

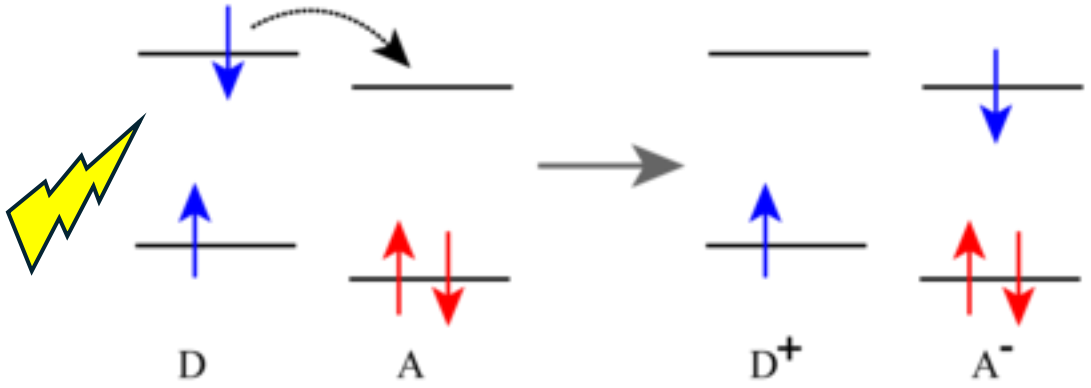
Use MD simulations to model *dynamic* interactions and events such as:

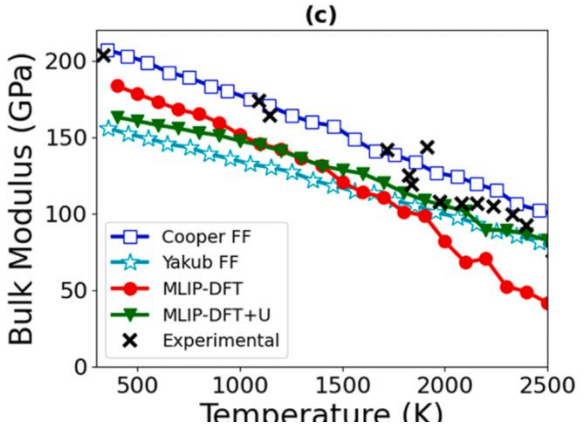
Reactions
Protein folding
Charge transfer
Molecular parameters

Molecular Parameters

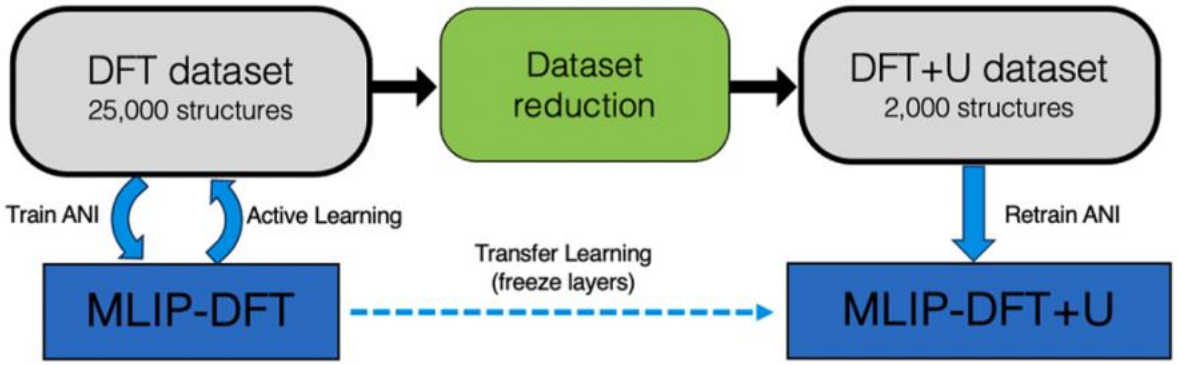
Specific heat
Bulk modulus
Phase changes

Charge Transfer





Using machine learning (ML) for nuclear fuels



DFT *Density Functional Theory*
MLIP *Machine Learning Interatomic Potential*
DFT+U *DFT plus Hubbard Parameter*

Active Learning ML

An iterative method that automatically trains the MLIP

1. Sampling
   - Atomic coordinates are generated and added to training dataset
2. Labeling
   - Energies and forces for each atom (in each system) assigned
3. Training
   - Fit the MLIP to the training dataset, described by steps 1 and 2

Question: Why did we add DFT+U structures?

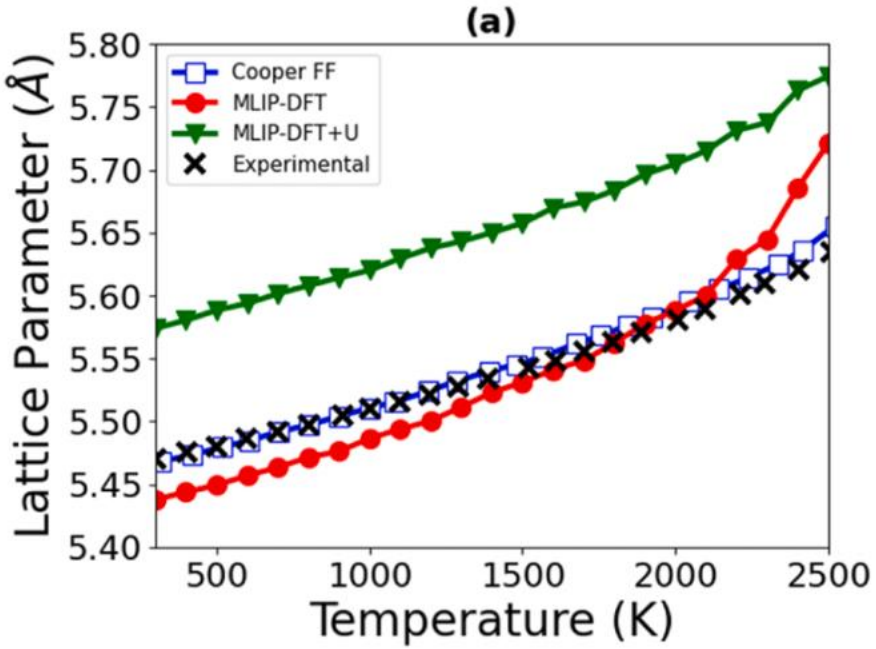
Answer: More accurate! Some structures had **high energy/force deviations** that required a more robust computation

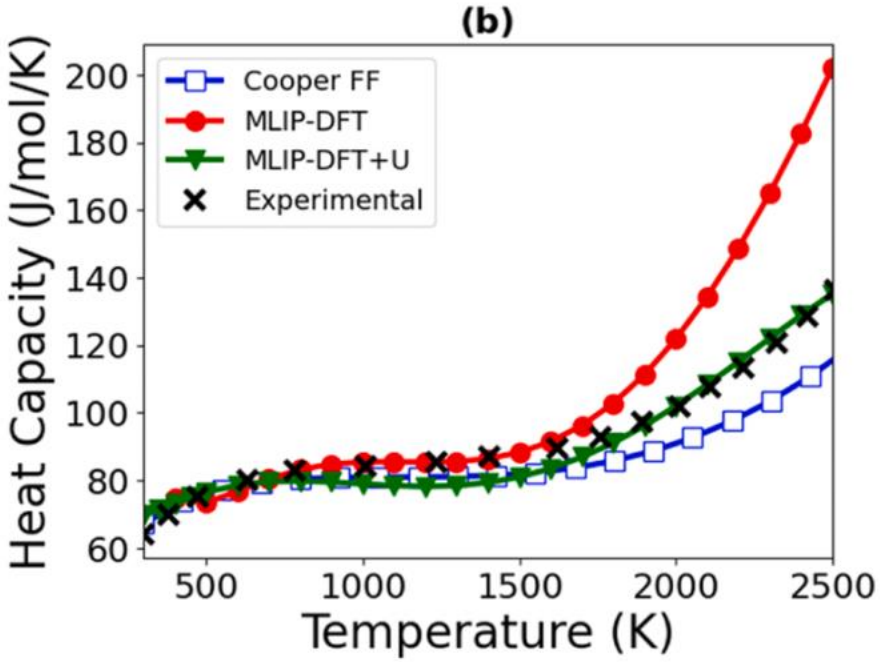
Tradeoff: High cost for high accuracy

Results: ML development for uranium dioxide

Methods development project:

Can we create a MLIP that can accurately predict values within reasonable error to experimental values?



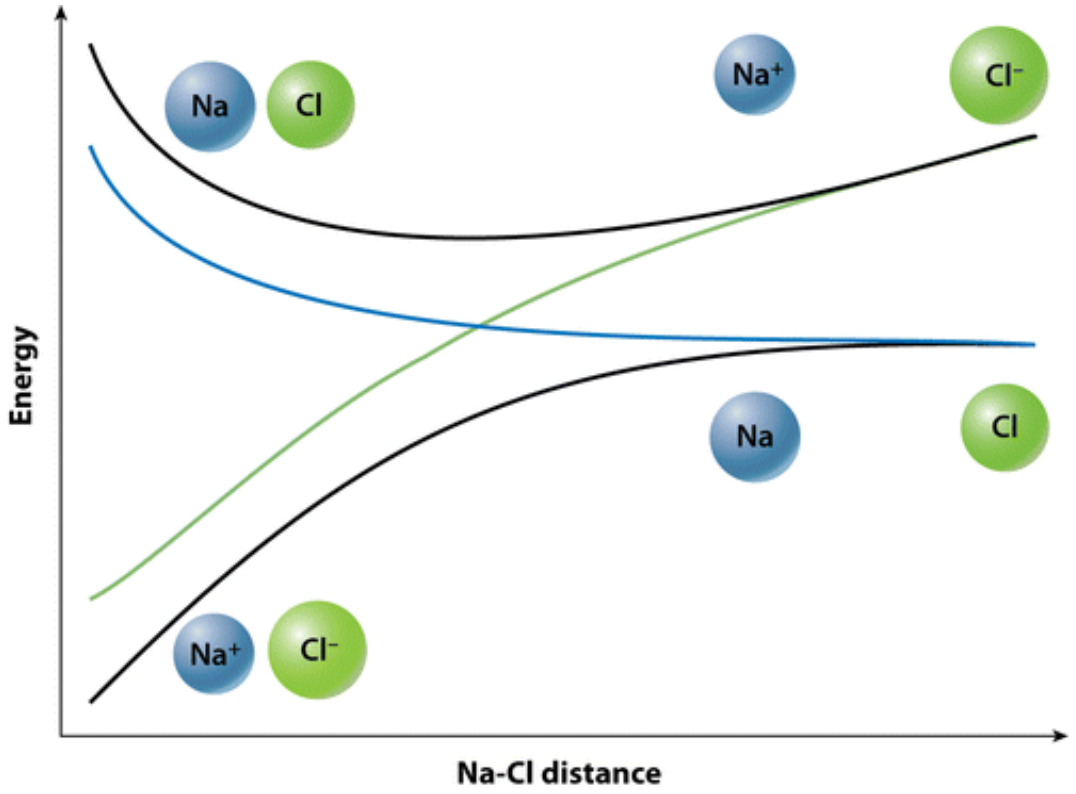


DFT+U overestimates lattice parameters by ~0.10Å

MLIP with DFT+U data provides great accuracy compared to experiment

Nonadiabatic coupling

Voorhis, T. V. et al. *Annual Review of Physical Chemistry* 2010, *61* (Volume 61, 2010), 149–170.



Born-Oppenheimer approximation: Nuclei move slow compared to electrons

Adiabatic vs. Diabatic

Adiabatic

Based on the Born-Oppenheimer Approximation

Changes its physical character to remain an eigenstate of the electronic Hamiltonian

Diabatic

Does not change its physical character as one moves along a reaction coordinate/path

Charge transfer

Marcus rate ∝ coupling (V_{kl})

Marcus rate ∝ site energies^{-1} $\left(\frac{1}{\lambda}\right)$

$$k_{Marcus} = \left(\frac{V_{kl}{}^2}{\hbar}\right)\sqrt{\frac{\pi}{\lambda k_B T}}\, exp\left(-\frac{(\Delta A + \lambda)^2}{4\lambda \mathrm{k}_B T}\right)$$

$$\lambda = \frac{\sigma^2}{2\mathrm{k_B T}} \qquad \sigma = \langle (dE - \langle dE \rangle)^2 \rangle$$

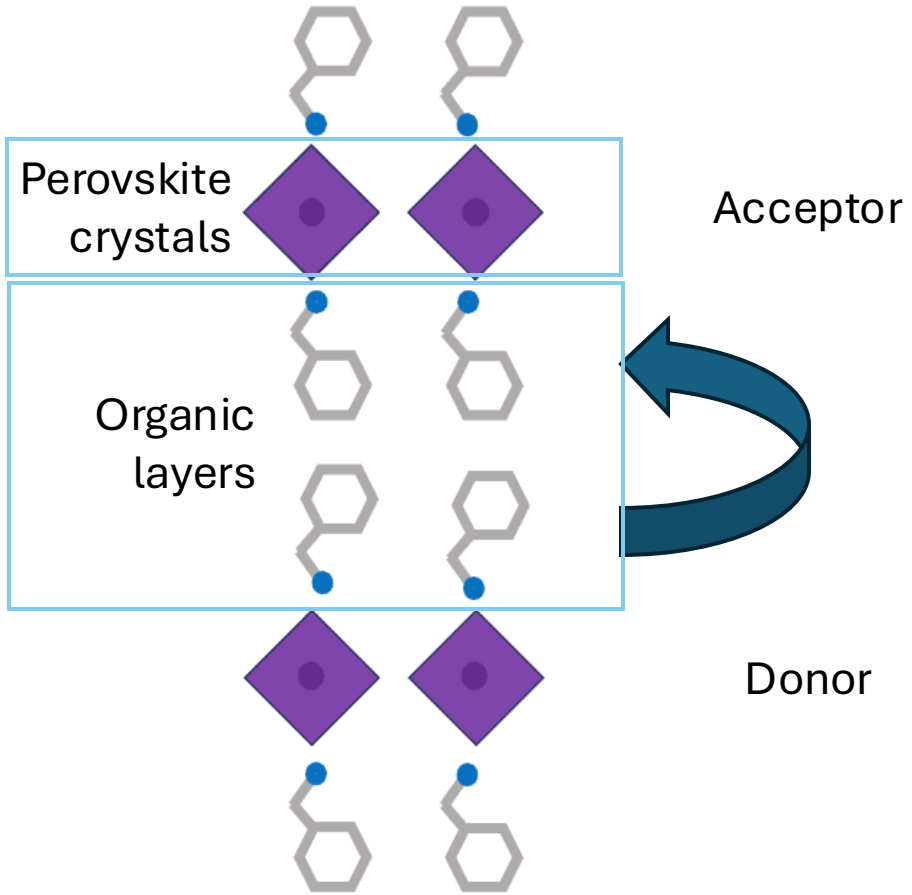
Energy fluctuations

$$\mu_{hopping} = \frac{eD}{k_B T} = \frac{e k_{Marcus} L^2}{k_B T}$$

Charge Carrier Hopping Mobility

Marcus, R. A. The Journal of Chemical Physics 1965, 43 (8), 2654-2657.

Computing Nonadiabatic coupling



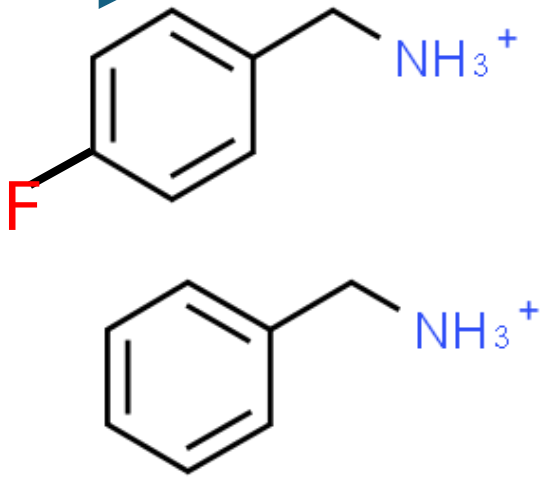
Fragment-based diabatization method

Create donor and acceptor blocks

$$\tilde{H} = \begin{bmatrix} \tilde{H}_{DD} & \tilde{H}_{DA} \\ \tilde{H}_{AD} & \tilde{H}_{AA} \end{bmatrix}$$

Diagonalize each block separately

$$H' = \begin{bmatrix} \varepsilon_{1,D} & 0 & & V_{DA} \\ 0 & \varepsilon_{2,D} & & \\ \vdots & & \ddots & \\ & V_{AD} & & \varepsilon_{1,A} & 0 \\ & & & 0 & \varepsilon_{2,A} \\ & & & \vdots & & \ddots \end{bmatrix}$$



Donor Energies

Acceptor Energies

Donor-Acceptor Couplings

Kondov, I. The Journal of Physical Chemistry C 2007, 111 (32), 11970-11981.

Results: Perovskite solar cells

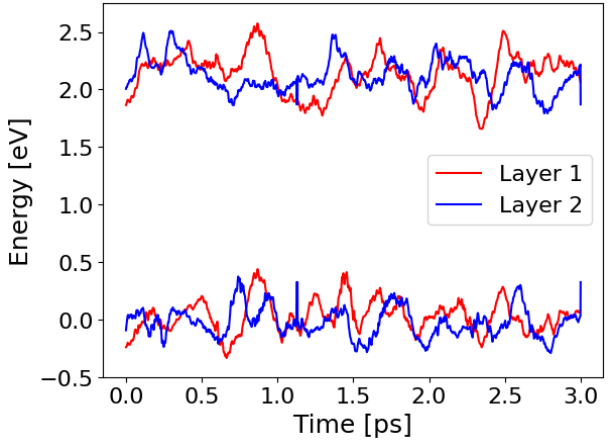
Methods application project:

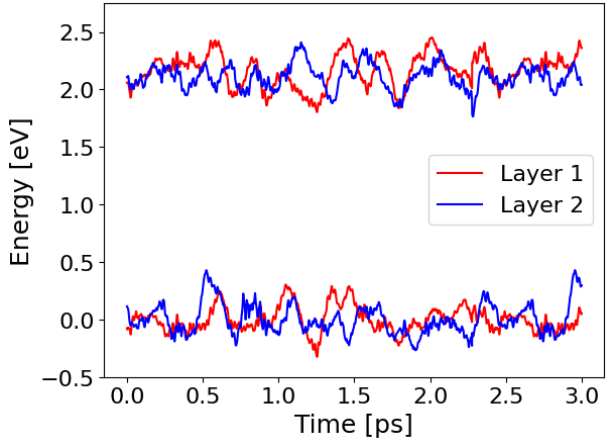
Why does adding fluorine to 2D perovskite crystals enhance efficiencies?

		Organic Spacers	Inorganic Crystals
Average displacement (Å)	BZA	1.25	0.81
	F-BZA	1.02	0.72

Fluorine substitution enhances the PCE of the 2D perovskite **not** through coupling effects but through **reorganization energy and structural stabilization**.

More energy fluctuations





Less energy fluctuations

Published papers based on this work

Contents lists available at ScienceDirect

Artificial Intelligence Chemistry

journal homepage: www.journals.elsevier.com/artificial-intelligence-chemistry

Building a DFT+U machine learning interatomic potential for uranium dioxide

Elizabeth Stippell [a,b], Lorena Alzate-Vargas [a], Kashi N. Subedi [a], Roxanne M. Tutchton [a], Michael W.D. Cooper [c], Sergei Tretiak [a,d], Tammie Gibson [a], Richard A. Messerly [a,*]

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[b] University of Southern California, Los Angeles, CA 90007, USA
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[d] Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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Research Article

Enhancing Interlayer Charge Transport of Two-Dimensional Perovskites by Structural Stabilization via Fluorine Substitution

Elizabeth Stippell, Wei Li, Claudio Quarti, David Beljonne, and Oleg V. Prezhdo*

Cite This: ACS Appl. Mater. Interfaces 2025, 17, 2032–2040

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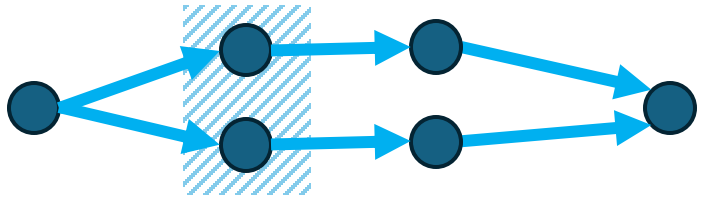
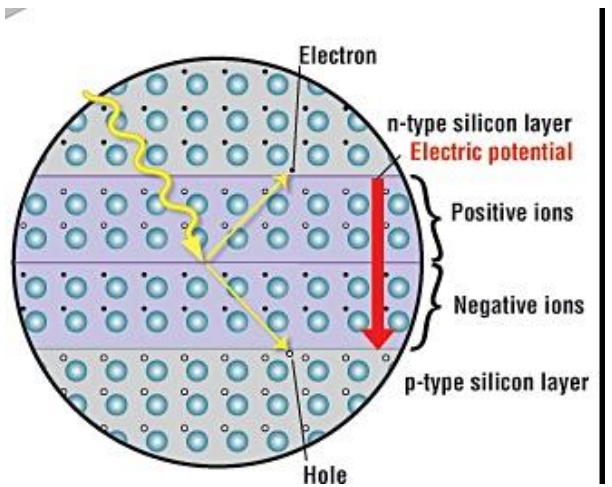
Extra Slides




Electron
n-type silicon layer
Electric potential
Positive ions
Negative ions
p-type silicon layer
Hole