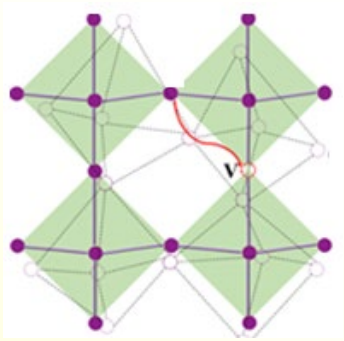
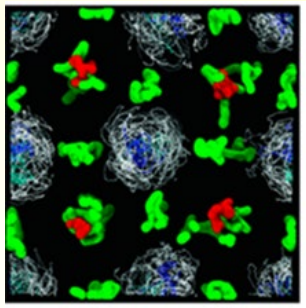
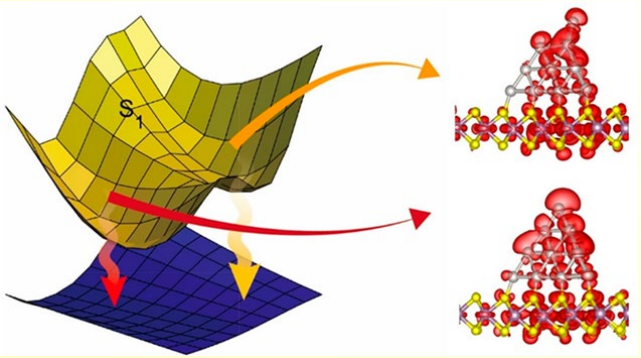
Nonadiabatic Molecular Dynamics with Machine Learning

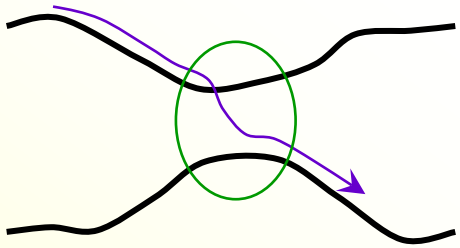
Oleg Prezhdo
U. Southern California

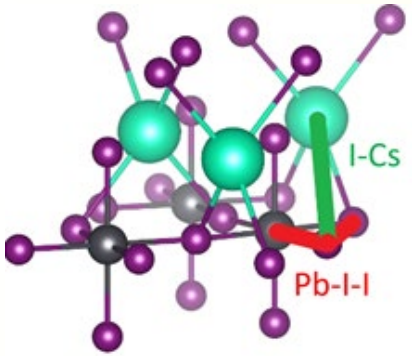




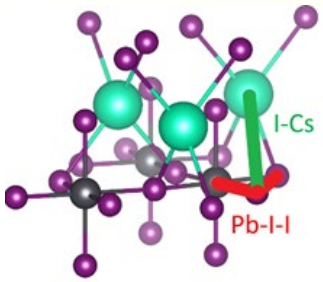
VISTA-61
December 6, 2023







$$\mathrm{I}(\mathrm{X},\mathrm{Y}) = \iint \mathrm{d}x\mathrm{d}y\, p(x,y)\log\left(\frac{p(x,y)}{p(x)p(y)}\right)$$



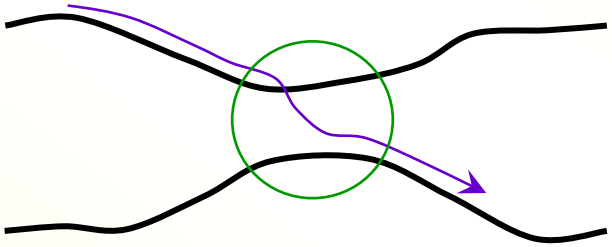
Outline

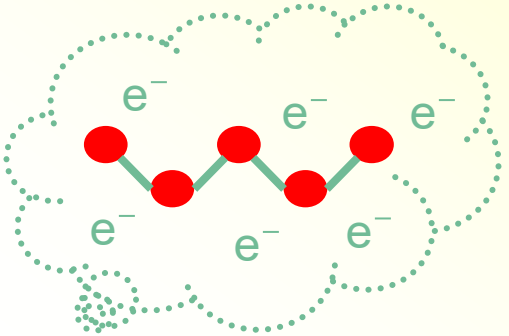
$$i\hbar\left\langle \chi^{\alpha}\left|\vec{\nabla}_{R}\right|\chi^{\beta}\right\rangle \cdot \dot{\vec{R}}$$

- Nonadiabatic Molecular Dynamics for *Nanomaterials*
  - Time-dependent DFT/Classical path approximation
- ML Force Fields to Sample *Rare Events*
  - Plasmonic particles/Defects in halide perovskites
- Interpolating NA-MD Hamiltonians to Extend *Timescale*
  - 1 ns NA-MD including rare events
- Training Atomic Hamiltonians to Extend *System Size*
  - ML models of tight-binding Hamiltonians
- Analyzing NA-MD with *Unsupervised* Learning
  - Making sense of NA-MD data

Non-Adiabatic Molecular Dynamics & Time-Dependent Density Functional Theory

Craig, Duncan, Prezhdo *Phys. Rev. Lett.* **95,** 163001 (2005)
Prezhdo *Acc. Chem. Res.* **54** 4239 (2021)





$$\rho(x) = \sum_p \left|\varphi_p(x)\right|^2 \qquad |\Psi\rangle = \left|\varphi_p(x_1,t)\varphi_q(x_2,t)\ldots\varphi_v(x_N,t)\right\rangle_{SD}$$

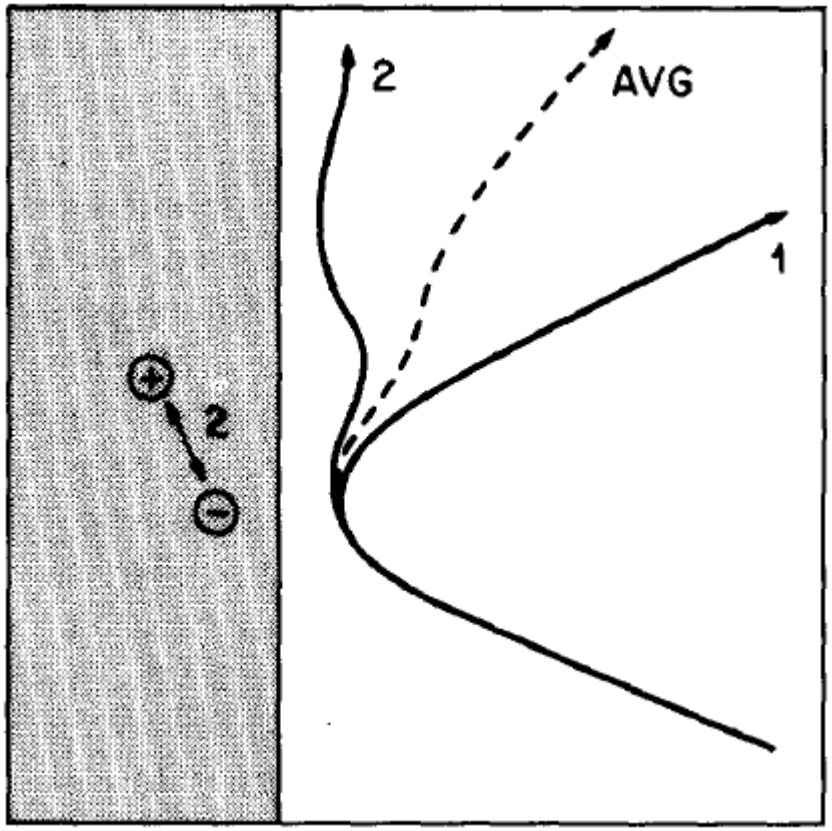
$$i\hbar\frac{\partial\varphi_p(x,t)}{\partial t} = H\varphi_p(x,t) \quad p = 1,2\ldots$$

time-dependent Kohn-Sham eq.

$$i\hbar\dot{c}^{\alpha} = \sum_{\beta} c^{\beta}\left(\varepsilon^{\beta}\delta_{\alpha\beta} - \boxed{i\hbar\left\langle\chi^{\alpha}\left|\vec{\nabla}_R\right|\chi^{\beta}\right\rangle\cdot\dot{\vec{R}}}\right)$$

non-adiabatic coupling

Why Ehrenfest is not Enough and Surface Hopping (Master Equation) is Needed?



1. Branching – average surface is not physical
2. Equilibrium – Ehrenfest cannot properly transfer energy from quantum to classical
3. Decoherence – phonons should induce electronic decoherence, e.g. quantum Zeno effect

Surface Hopping in Many-Body Kohn-Sham Basis

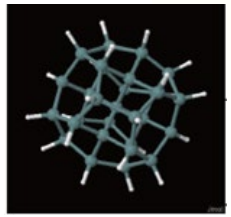
Craig, Duncan, Prezhdo *Phys. Rev. Lett.* **95,** 163001 (2005)
Akimov, Prezhdo, *J. Theor. Comp. Chem.* **9**, 4959 (2013)

$$|\varphi_a \varphi_b \cdots \varphi_p\rangle = \sum_{j\neq k\neq \cdots \neq l}^{N_e} C_{j\cdots l}(t)|\tilde{\varphi}_j \tilde{\varphi}_k \cdots \tilde{\varphi}_l\rangle$$

$$i\hbar \frac{\partial}{\partial t} C_{q\cdots v}(t) = \sum_{a\cdots p}^{N_e} C_{a\cdots p}(t)[E_{q\cdots v}\delta_{aq}\cdots\delta_{pv} + \mathbf{D}_{a\cdots p;q\cdots r}\cdot\dot{\mathbf{R}}].$$

$$\mathbf{D}_{a\cdots p;q\cdots r}\cdot\dot{\mathbf{R}} = -i\hbar\langle\tilde{\varphi}_a\tilde{\varphi}_b\cdots\tilde{\varphi}_p|\frac{\partial}{\partial t}|\tilde{\varphi}_q\tilde{\varphi}_r\cdots\tilde{\varphi}_v\rangle$$

D is non-zero only if different in one orbital, very sparse
Multiple excitons in $Si_{29}H_{24}$: 25 VB and 24 CB orbitals
98,101 states = ground+600SE+97,500DE



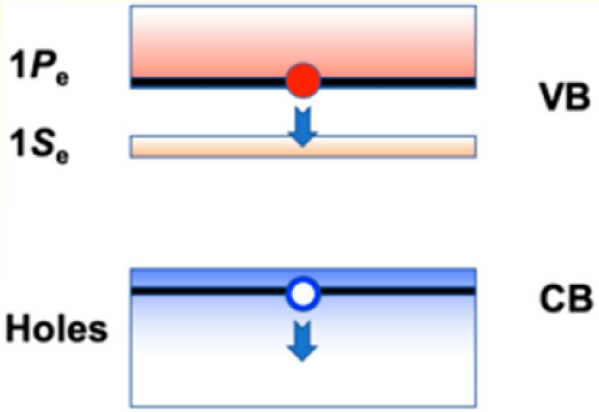
Hyeon-Deuk, Prezhdo *Nano Lett.* **11**, 1845 (2011); *ACS Nano* **6**, 1239 (2012)

Auger Processes via Coulomb

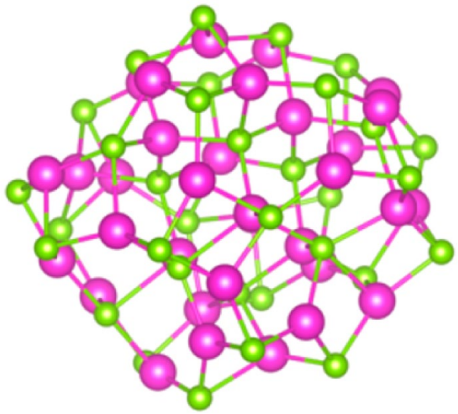
G. Zhou, G. Lu, O. V. Prezhdo, *Nano Lett.* **21** 756 (2021)

$$V_{ij} = \langle \Phi_m^n | \hat{V} | \Phi_p^q \rangle = \langle mn|pq\rangle - \langle mn|qp\rangle$$

$$\langle mn|pq\rangle = \frac{e^2}{2} \int d\mathbf{r}_1\, d\mathbf{r}_2 \varphi_m^*(\mathbf{r}_1)\, \varphi_n^*(\mathbf{r}_2) r_{12}^{-1} \varphi_p(\mathbf{r}_1)\, \varphi_q(\mathbf{r}_2)$$



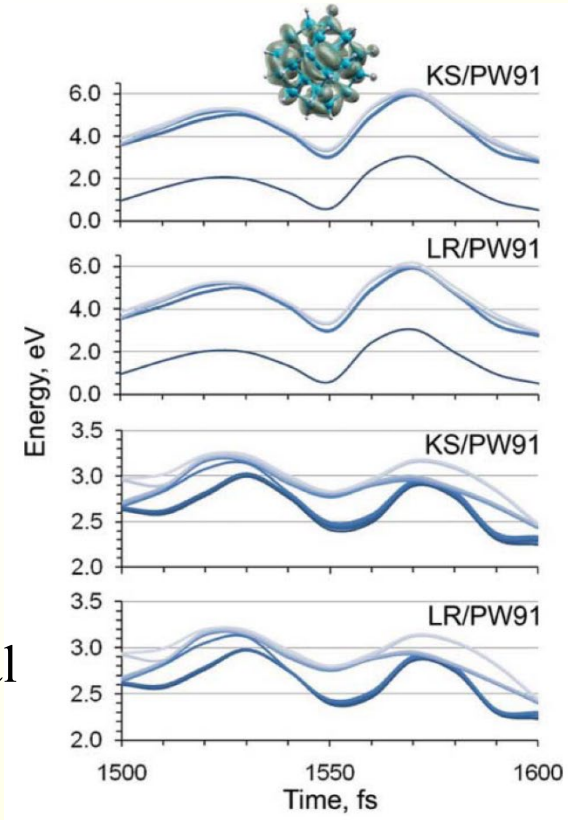
- Use both NA coupling and Coulomb matrix elements (from linear response TD-DFT)
- Off-diagonal, do not solve Cassida eqs.

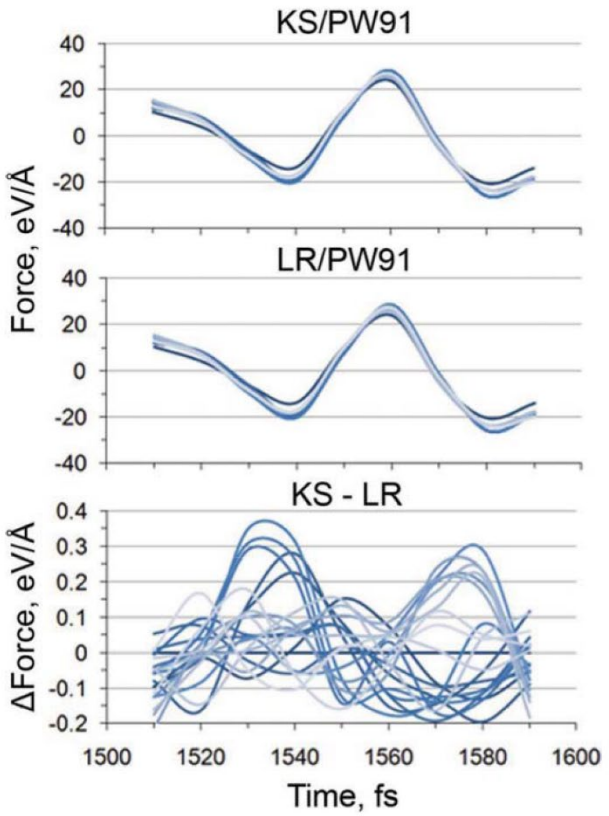


Why Surface Hopping in Kohn-Sham Representation Works

S. Fischer, B. Habenicht, A. Madrid, W. Duncan,
O. V. Prezhdo, *J. Chem. Phys.* **134**, 024102 (2011)

- KS close to LR/TDDFT
- No bond-breaking, conformational changes.
- Many-electrons, single excitation is a small perturbation
- Averaging over many initial conditions and pathways





Classical Path Approximation

Useful for Nanoscale Systems

Prezhdo, Duncan, *Prog. Surf. Sci.* **84**, 30 (2009)

Akimov, Prezhdo, *J. Theor. Comp. Chem.* **9**, 4959 (2013)

1. DFT functional (Hamiltonian) depends on ground state density, even though the true density does evolve
2. Ground and excited state trajectories are similar

Justification:

1. Excitation of 1 or 2 electrons out of hundreds does not change density and forces much
2. Thermal fluctuations are larger than differences in equilibrium geometries of ground and excited electronic states

Key Advantages – allows use of ground state trajectory, while still evolving electronic state populations – electronic and atomic timestep separation (1*as* & 1*fs*)

PYXAID: PYthon eXtension of Ab Initio Dynamics

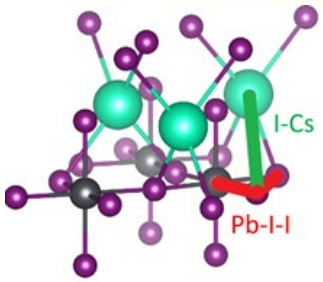
Akimov, Prezhdo *J. Theor. Comp. Chem.* **9**, 4959 (2013)
ibid. **10**, 789 (2014)

- Electron-vibrational, electron-electron, spin-orbit interactions
- Non-perturbative, all degrees of freedom, configuration dependent

Python interfaced with Quantum Espresso, VASP

DFTB+: Pal, Trivedi, Akimov, Aradi, Frauenheim, Prezhdo
J. Theor. Comp. Chem. **12** 1436 (2016)
Auger processes: Zhou, Lu, Prezhdo, *Nano Lett.* **21**, 756 (2021)

Wang, Akimov, Prezhdo
JPC Lett. **7** 2100 (2016)
Prezhdo
Acc. Chem. Res. **54** 4239 (2021)



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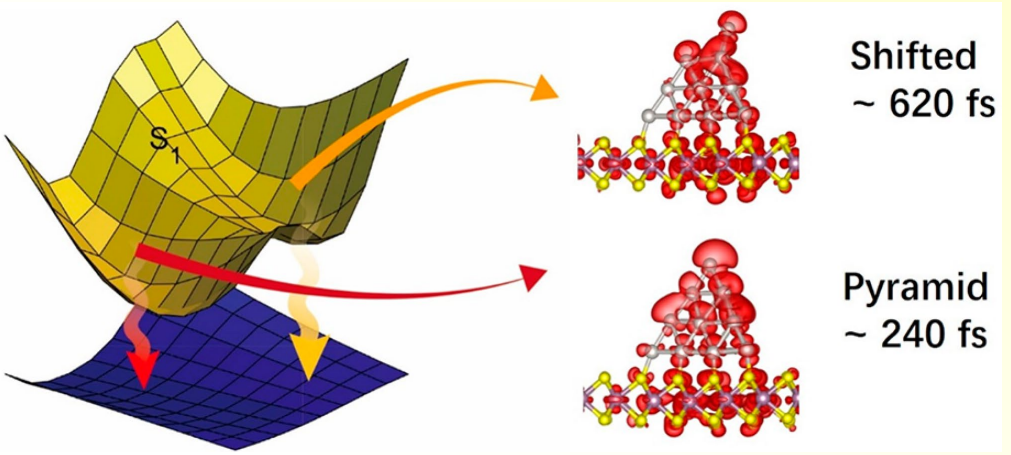
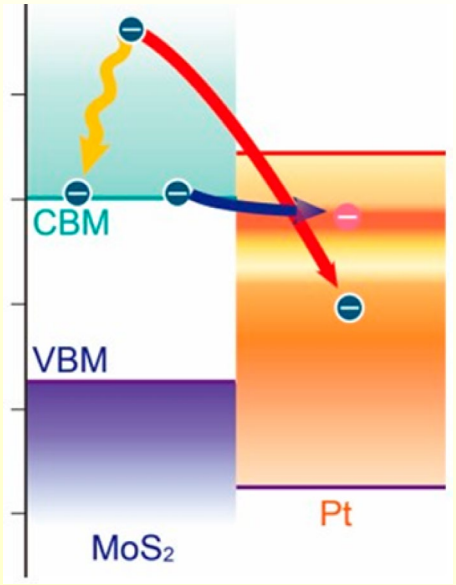
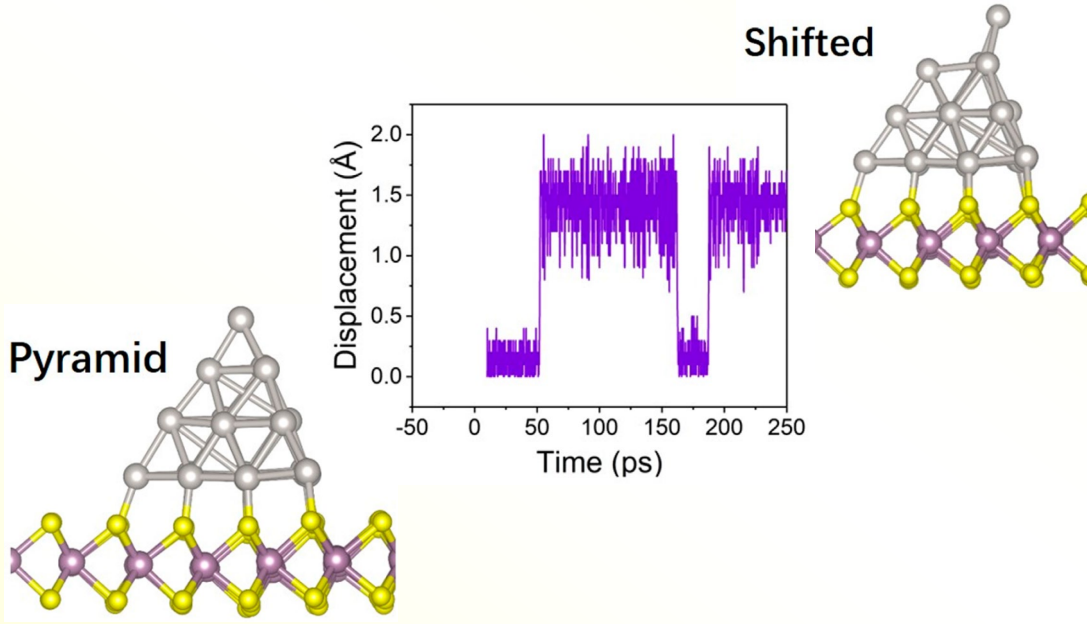
Hot Electrons in Metallic Particles

W. Chu, W. A. Saidi, O. V. Prezhdo, *ACS Nano* **14** 10608 (2020)

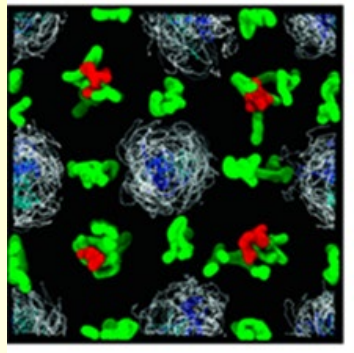
- Plasmon driven catalysis from heating or via excited states?
- 50 ps fluctuation of top atom
- Hot electron lifetime grows
- Injection energy important

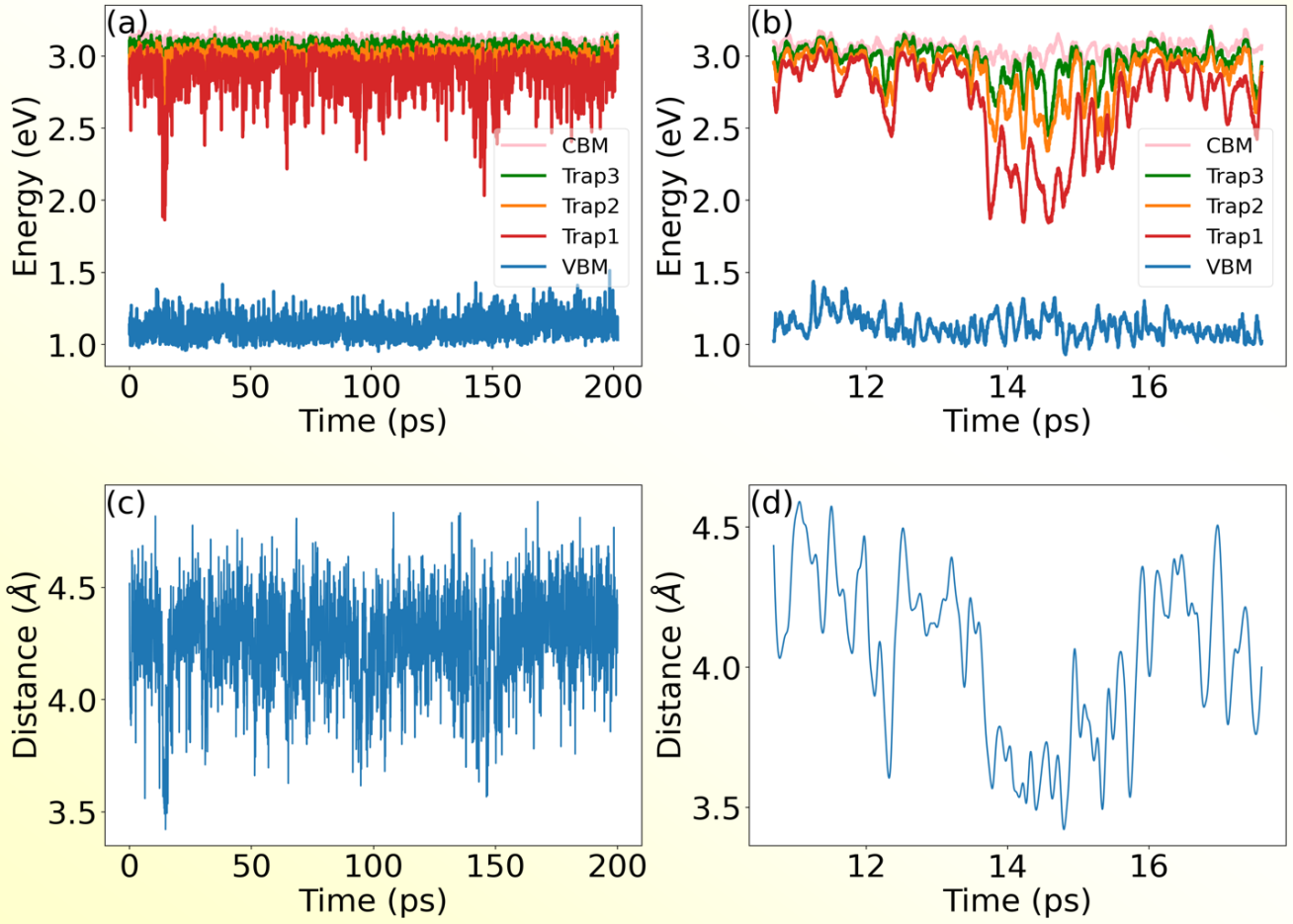






Trap States in $MAPbI_3$

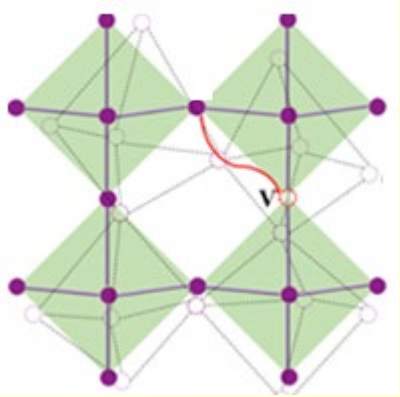




- 100 ps fluctuations create **deep traps**
- Charges are trapped and lost
- We interpolate nonadiabatic coupling with ML using 2% of data

Charge and Ion Synergy in $MAPbI_3$ Perovskite

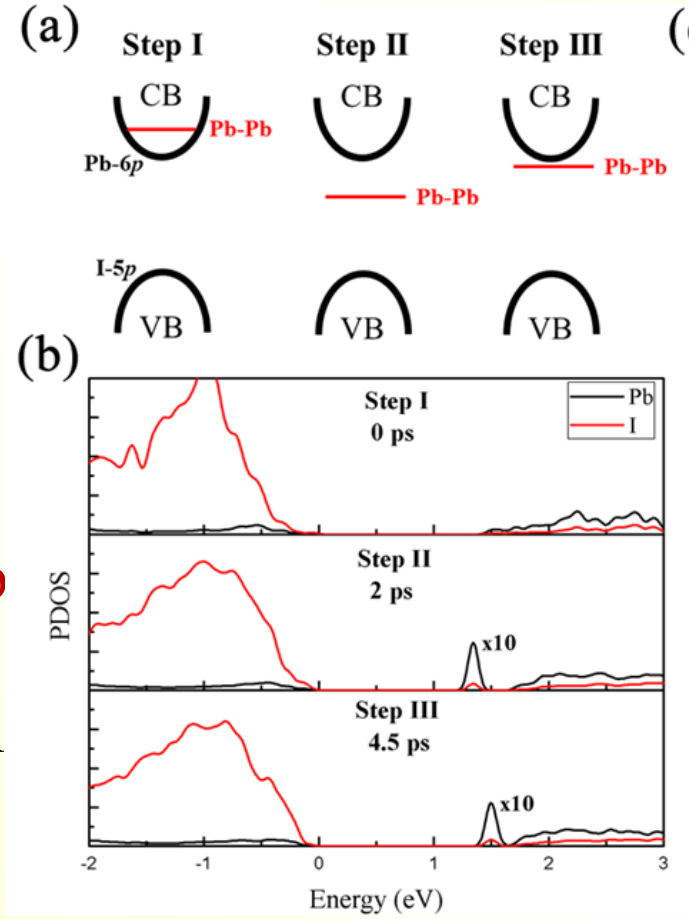
Tong … Prezhdo, *JACS* **142** 3060 (2020); *JACS* **144** 6604 (2022)

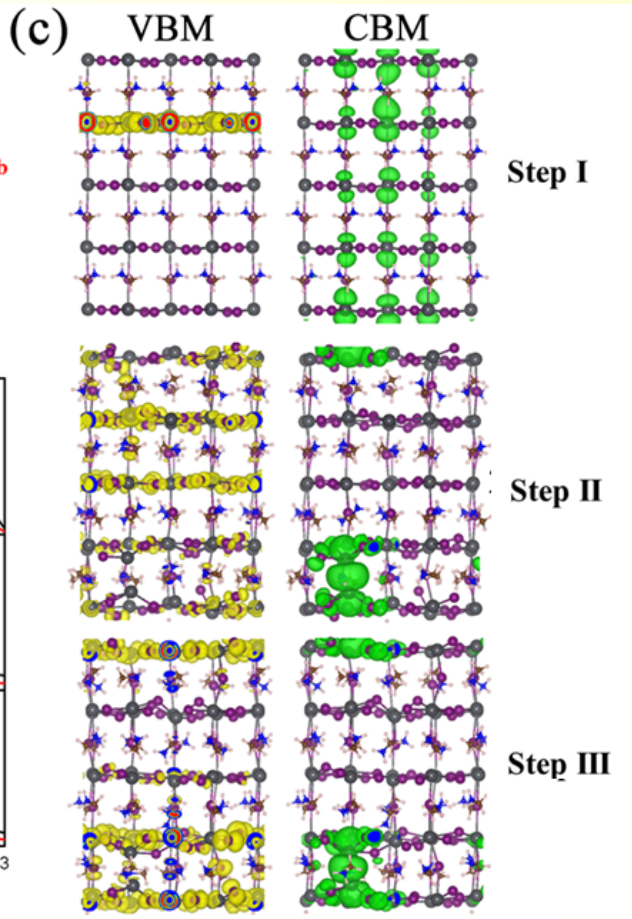


Step	relaxation time (ns)
I	0.12
II	0.013
III	0.035

Halide vacancy migration moves trap from CB into bandgap

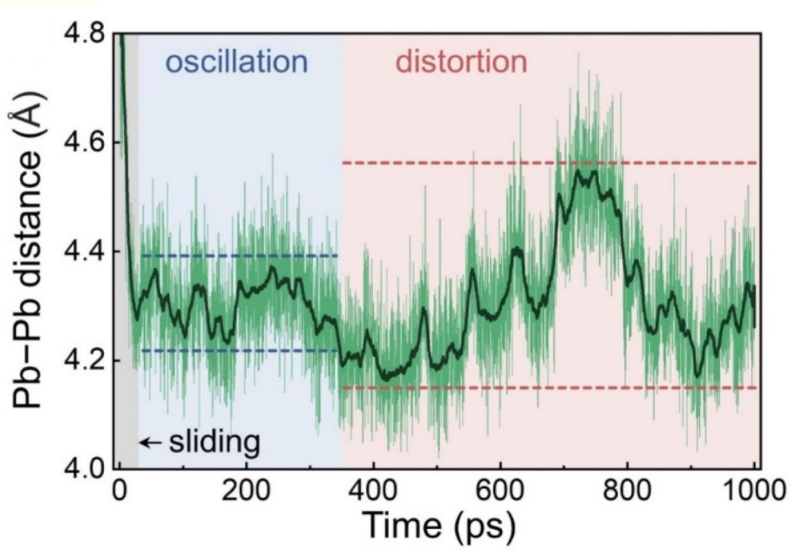
Charge recombination accelerates 10-fold

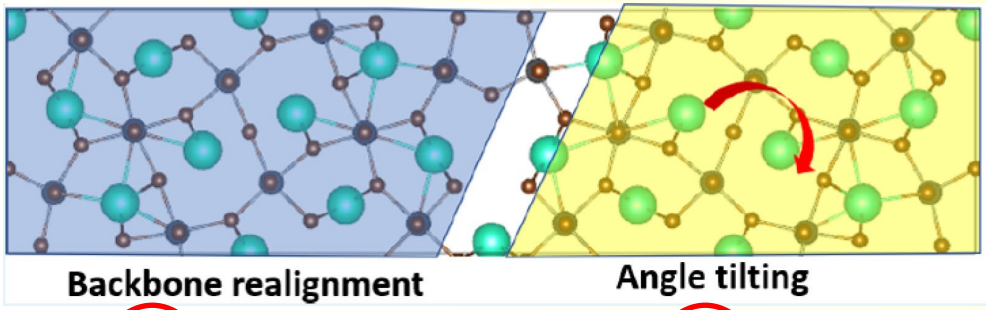


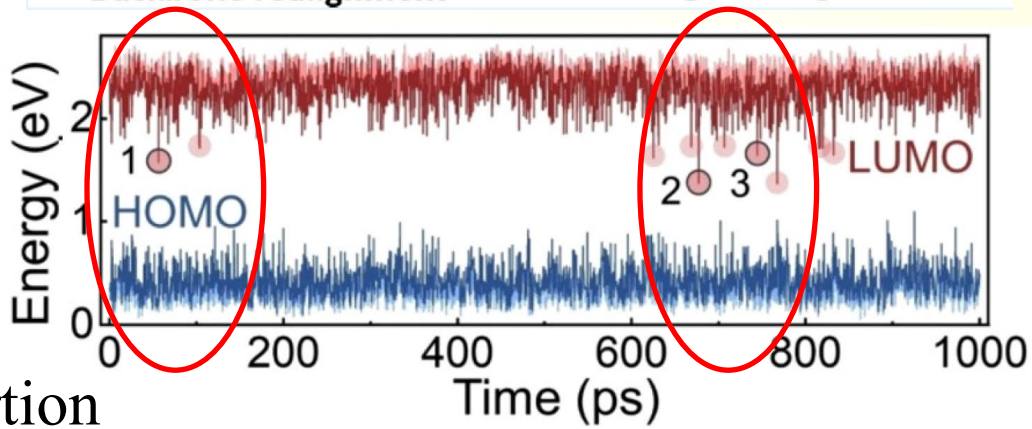


Evolution of $CsPbBr_3$ Grain Boundary

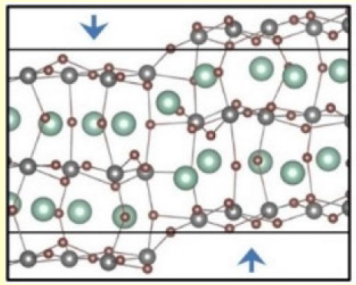
Wu. Liu, Chu, Wang, Vasenko, Prezhdo *ACS AMI* **14** 55753 (2022)
Liu, Wu, Vasenko, Prezhdo, *Nanoscale* **15** 285 (2023)







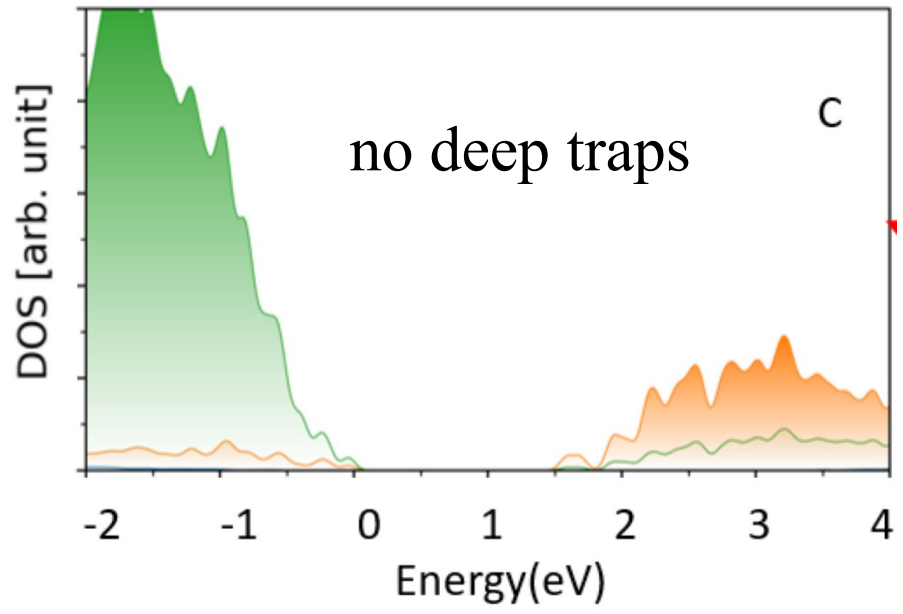
- few traps during oscillation
- traps during sliding and distortion



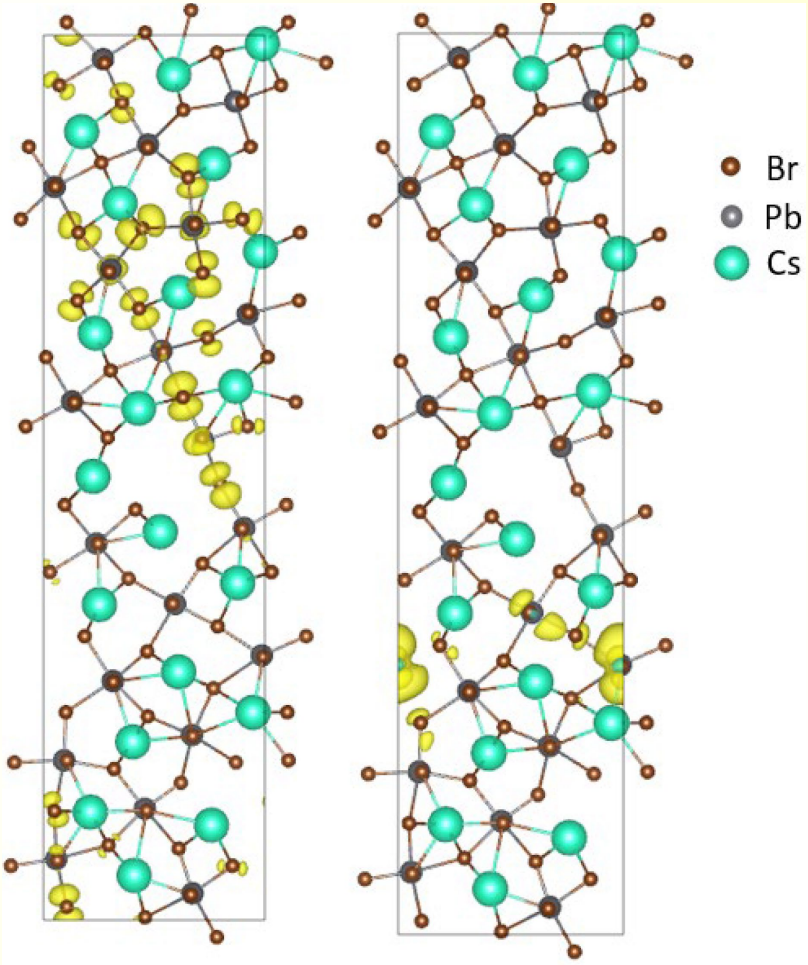
3 ps sliding ⇒ 400 ps oscillation ⇒ 600 ps distortion

Evolution of $CsPbBr_3$ Grain Boundary

Wu. Liu, Chu, Wang, Vasenko, Prezhdo *ACS AMI* **14** 55753 (2022)
Liu, Wu, Vasenko, Prezhdo, *Nanoscale* **15** 285 (2023)



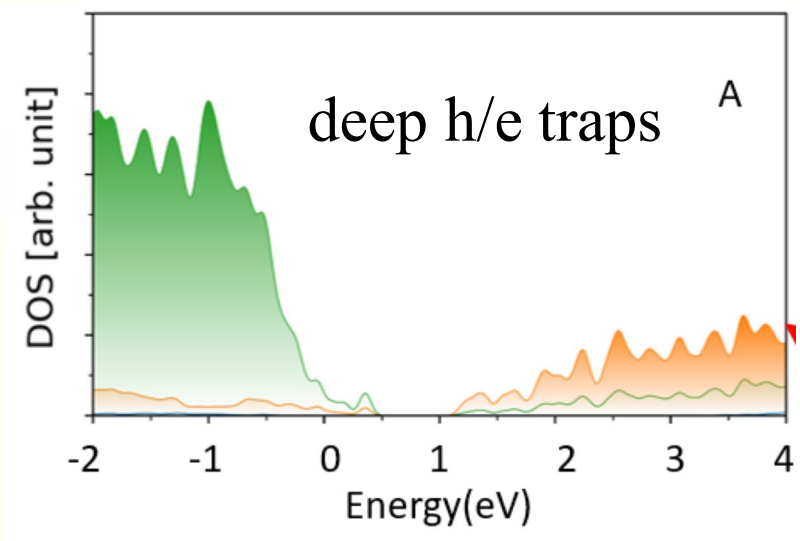
HOMO LUMO



- HOMO has localization at grain boundary but not a trap
- Charges are separated

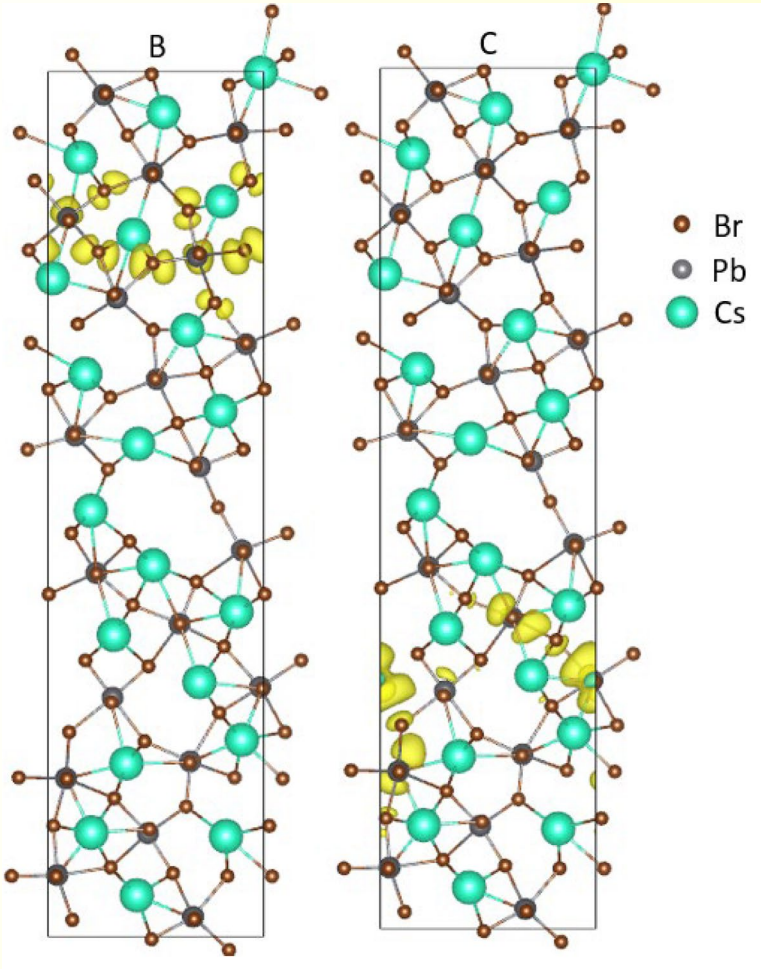
Evolution of $CsPbBr_3$ Grain Boundary

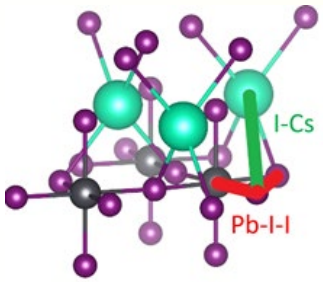
Wu. Liu, Chu, Wang, Vasenko, Prezhdo *ACS AMI* **14** 55753 (2022)
Liu, Wu, Vasenko, Prezhdo, *Nanoscale* **15** 285 (2023)



- Deep traps are localized in sub-boundary layers
- Charges are separated

HOMO LUMO





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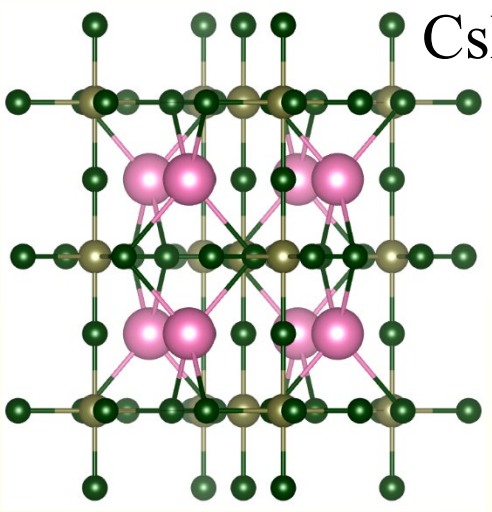
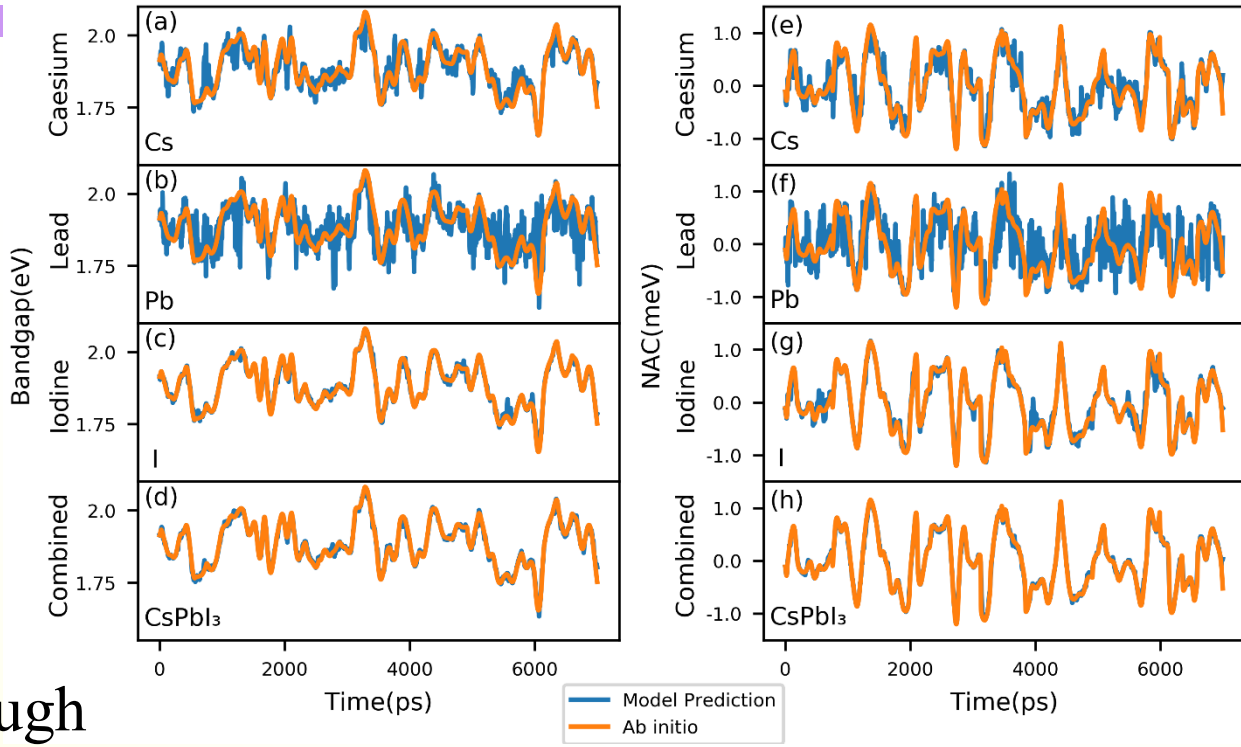
ML Models of NA-MD Hamiltonian

How, Wang, Chu, Tkatchenko, Prezhdo, *J. Phys. Chem. Lett.* **12** 12026 (2021); *J. Chem. Phys.* **156** 054110 (2022)





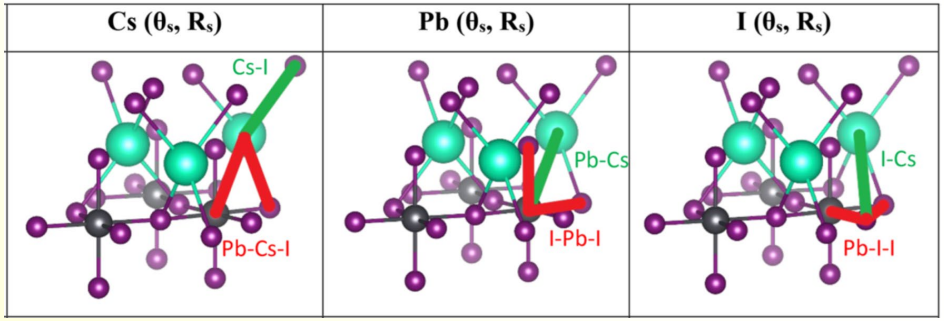
- Every 3rd iodine is enough
- Cs performs better than Pb though Cs does not contribute to wavefunctions, while Pb determines HOMO and LUMO

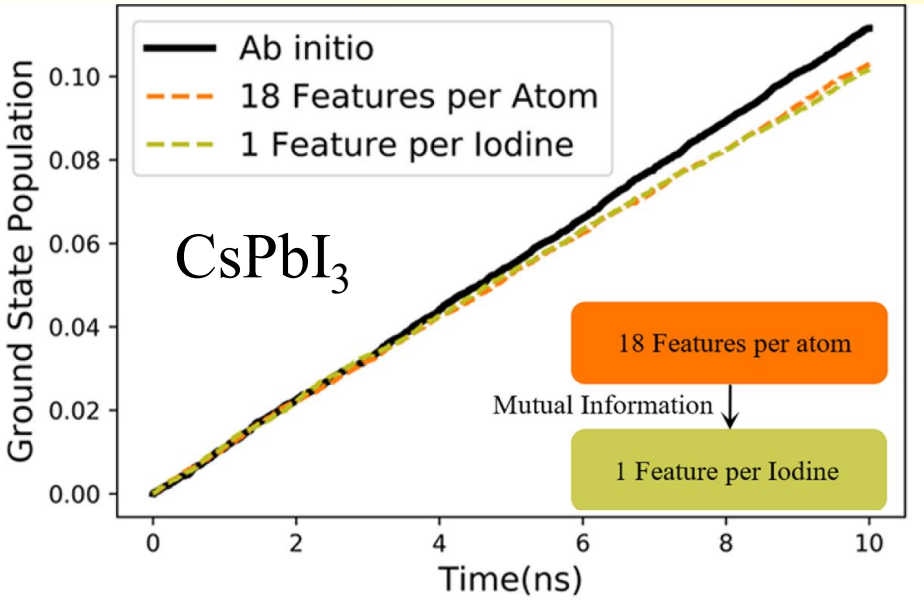
$$G_i^{mod} = 2^{1-\zeta} \sum_{j,k\neq i}^{atoms} \left(1+\cos\left(\theta_{ijk}-\theta_s\right)\right)^{\zeta} \times e^{\left[-\eta\left(\frac{R_{ij}+R_{ik}}{2}-R_s\right)^2\right]} f_C\left(R_{ij}\right) f_C\left(R_{ik}\right)$$

ML Models of NA-MD Hamiltonian

How, Wang, Chu, Tkatchenko, Prezhdo, *J. Phys. Chem. Lett.* **12** 12026 (2021)
J. Chem. Phys. **156** 054110 (2022)

1 feature per iodine sufficient





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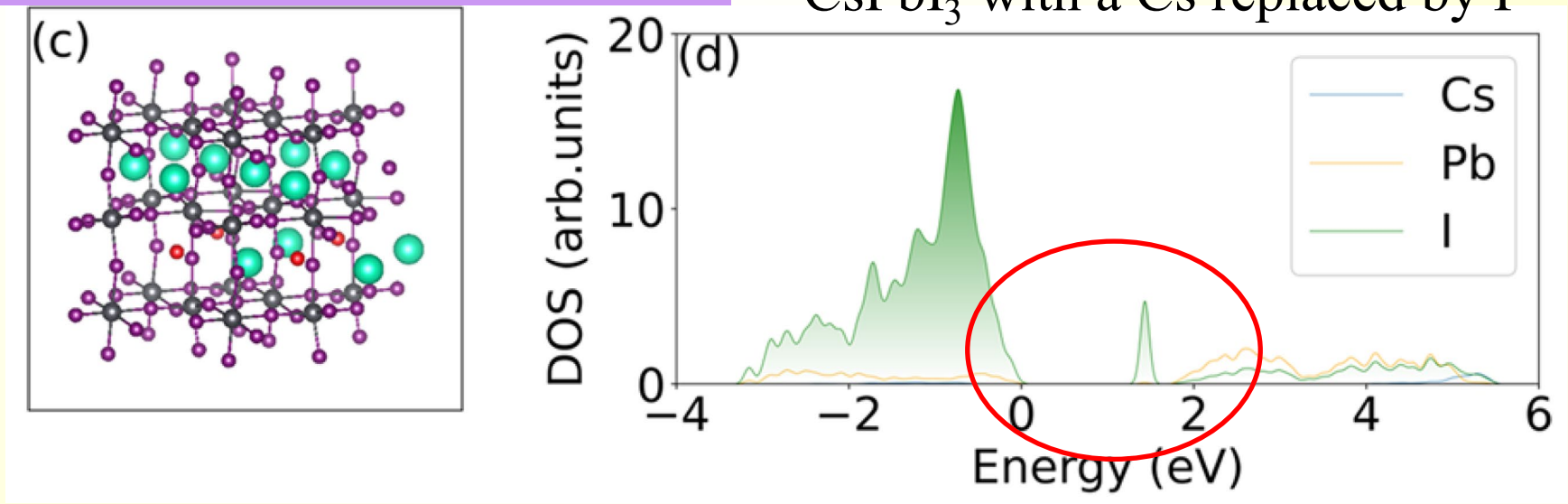
$$I(X,Y) = \iint dxdy\, p(x,y)\log\left(\frac{p(x,y)}{p(x)p(y)}\right)$$ - mutual information

Interpolating NA-MD Hamiltonian

JPC Lett. **12** 6070 (2021); *ibid.***13** 331 (2022); *ibid.* **14** 7092 (2023)

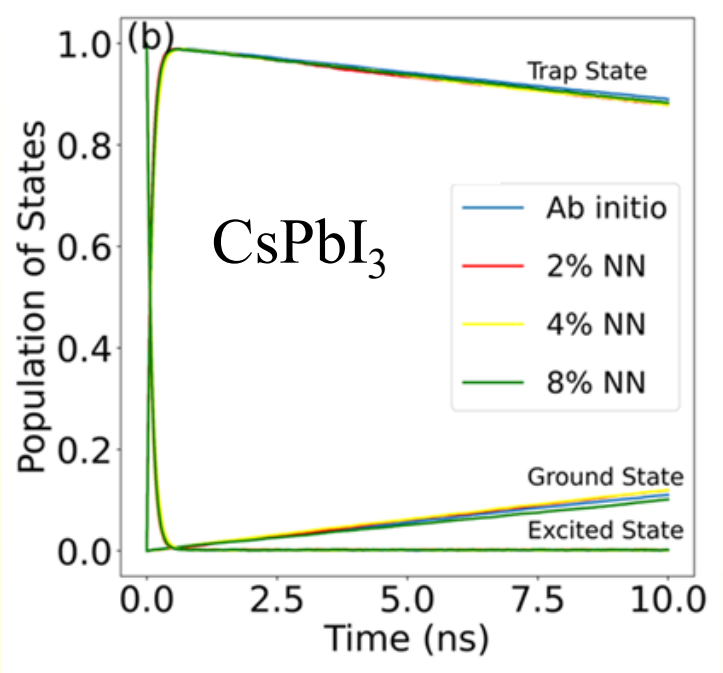
$CsPbI_3$ with a Cs replaced by I

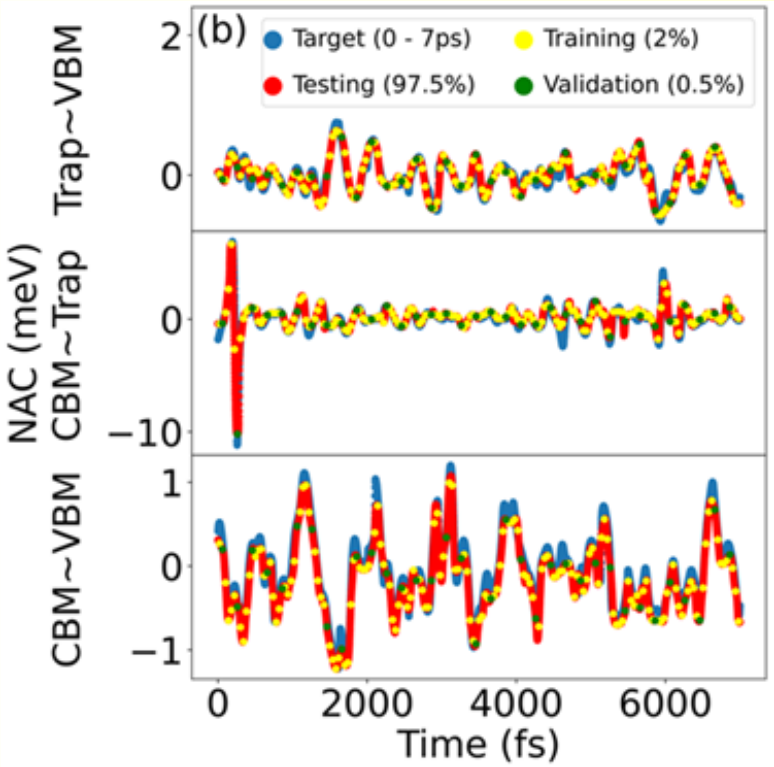


- Training NA-MD Hamiltonian similarly to force-field is complicated
- Under classical path approximation, train force-field, generate trajectory, and interpolate NA-MD Hamiltonian along trajectory

Interpolating NA-MD Hamiltonian

JPC Lett. **12** 6070 (2021); *ibid.***13** 331 (2022); *ibid.* **14** 7092 (2023)

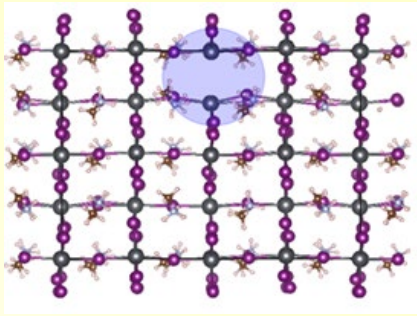


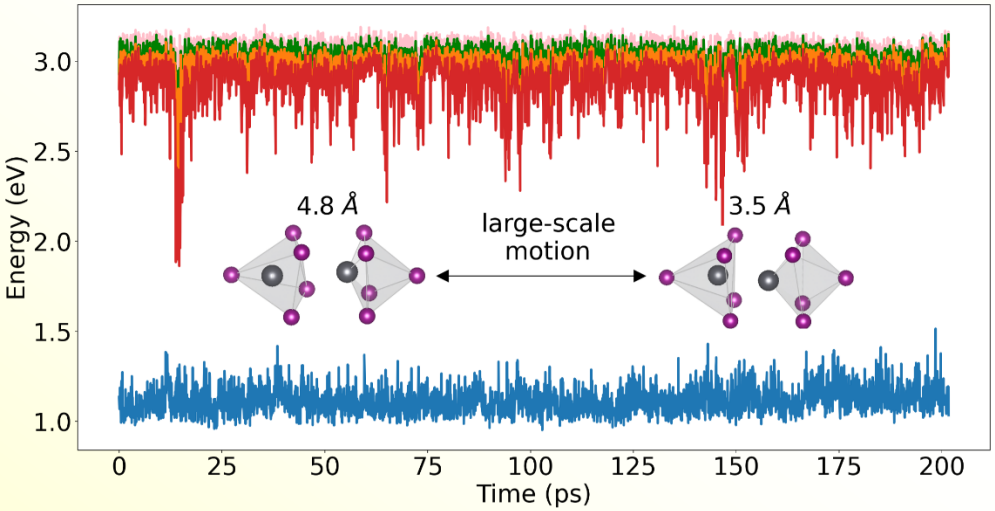


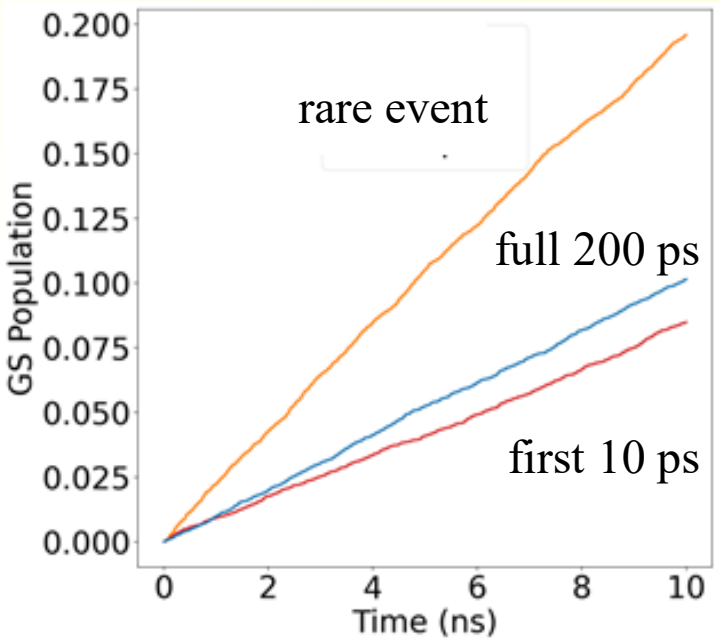
- **2%** of ab initio data enough for training
- Energy gaps easier than nonadiabatic coupling
- Peaks in nonadiabatic coupling are important
- CNN, KRR, iFFT give similar results; LSTM allows longer steps

$$i\hbar\left\langle \chi^{\alpha}\left|\vec{\nabla}_{R}\right|\chi^{\beta}\right\rangle\cdot\dot{\vec{R}}$$

Nanosecond Quantum Dynamics in $MAPbI_3$

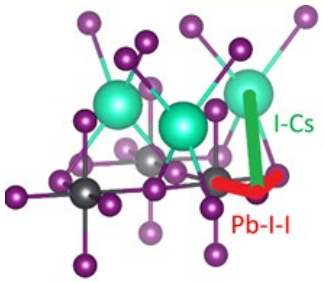






- Machine learning force field
- Interpolated nonadiabatic Hamiltonian

- Standard ab initio result (10ps) is slower than true dynamics because it misses rare events

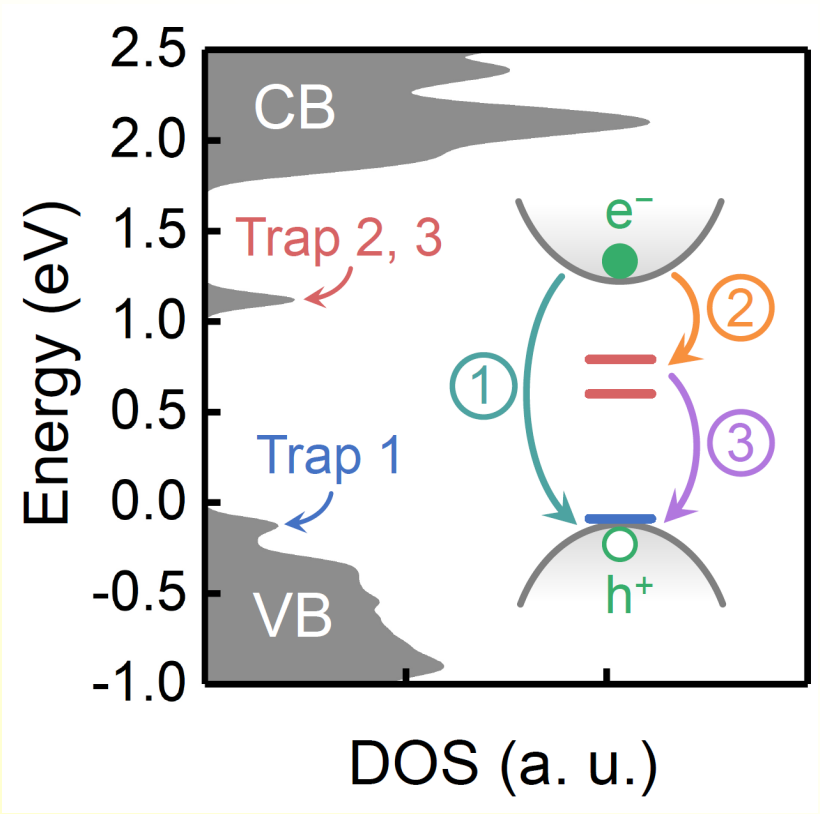


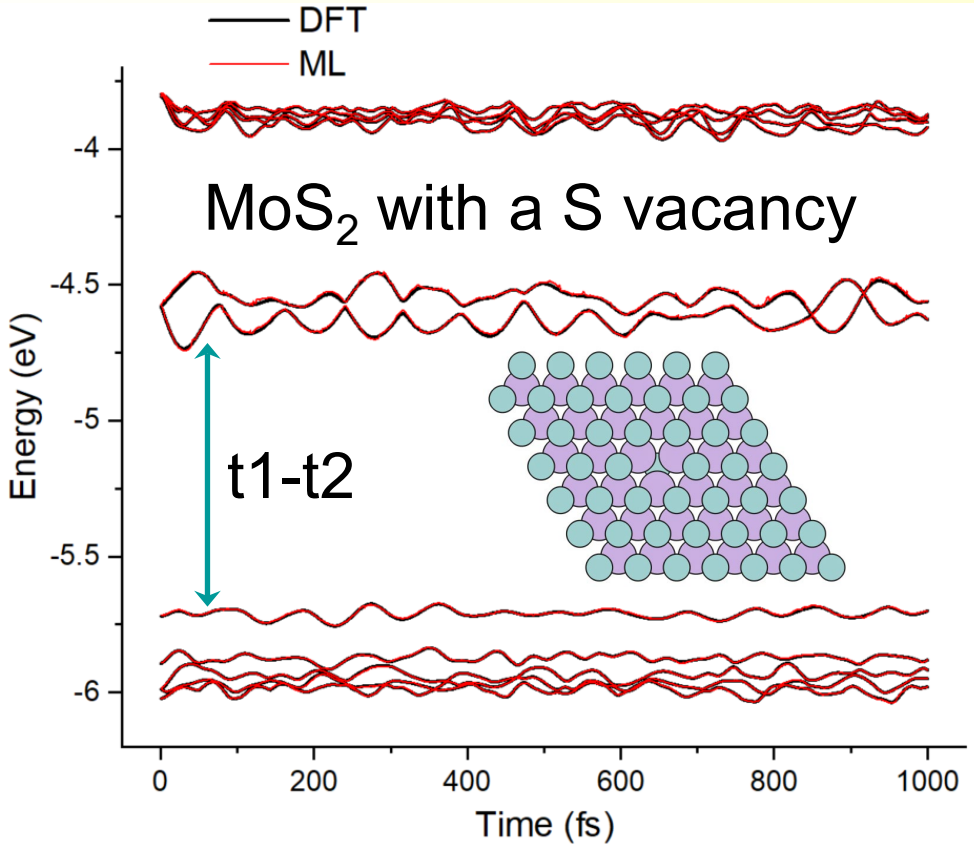
Outline

$$i\hbar\left\langle \chi^{\alpha}\left|\vec{\nabla}_{R}\right|\chi^{\beta}\right\rangle \cdot \dot{\vec{R}}$$

- Nonadiabatic Molecular Dynamics for *Nanomaterials*
  - Time-dependent DFT/Classical path approximation
- ML Force Fields to Sample *Rare Events*
  - Plasmonic particles/Defects in halide perovskites
- Interpolating NA-MD Hamiltonians to Extend *Timescale*
  - 1 ns NA-MD including rare events
- Training Atomic Hamiltonians to Extend *System Size*
  - ML models of tight-binding Hamiltonians
- Analyzing NA-MD with *Unsupervised* Learning
  - Making sense of NA-MD data

ML Models of Electronic Hamiltonian
(Increasing System Size)

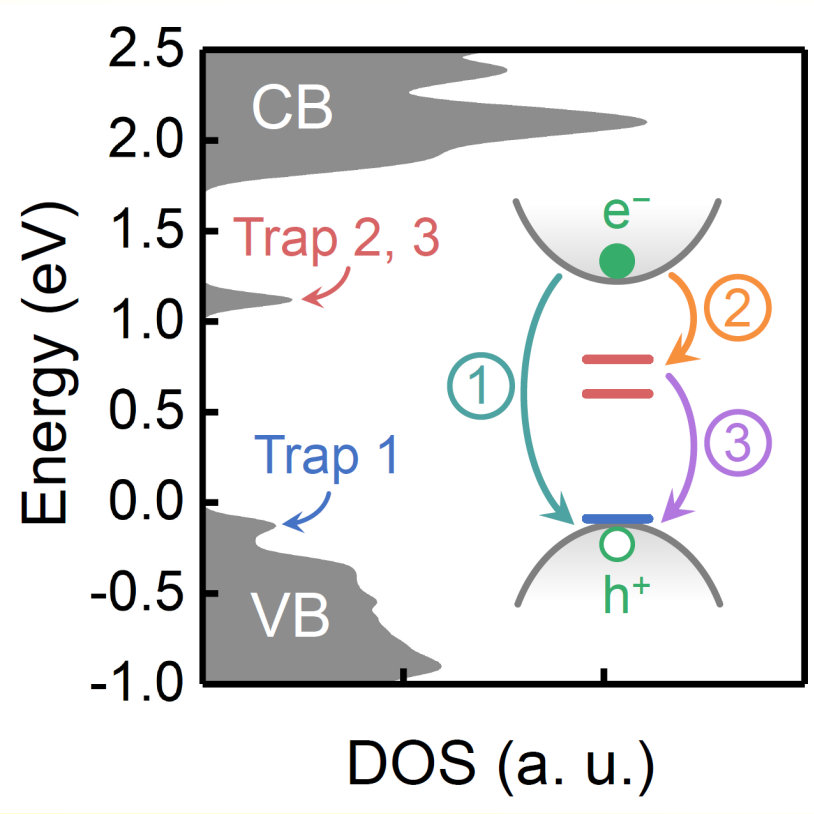




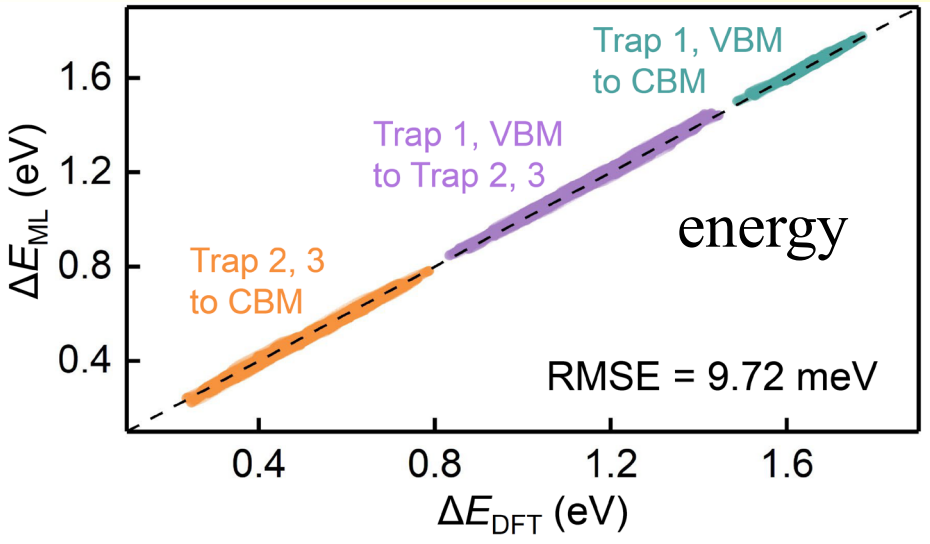
Thermal fluctuations of energy levels reproduced well

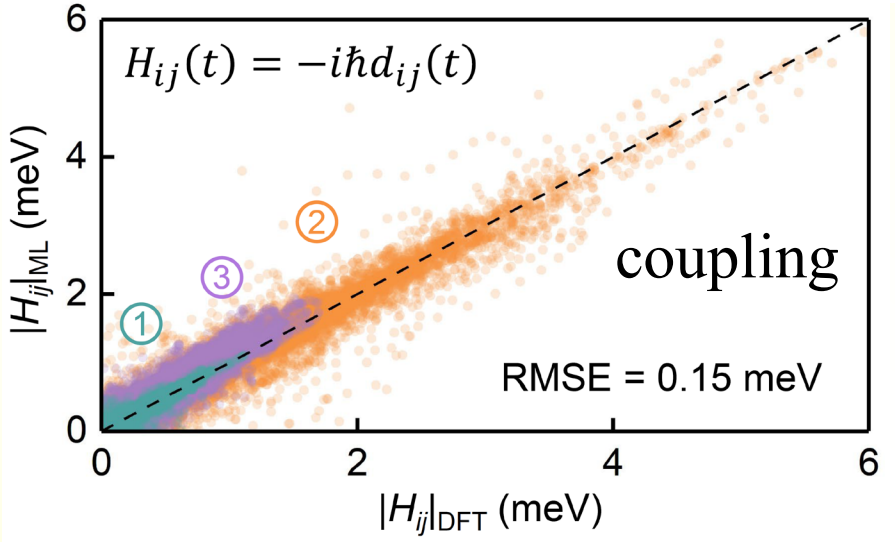
Li et al. Nature Comp. Sci. **2** 367 (2022)

ML Models of Electronic Hamiltonian
(Increasing System Size)



Nonadiabatic coupling
within 0.1 meV accuracy





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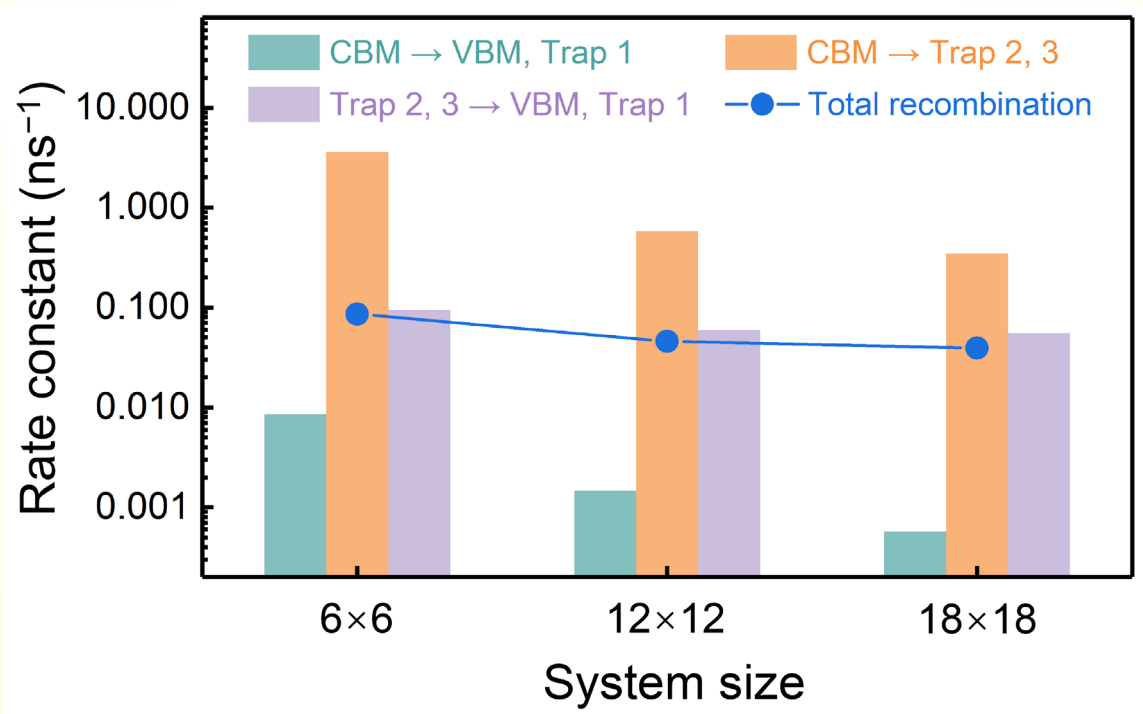
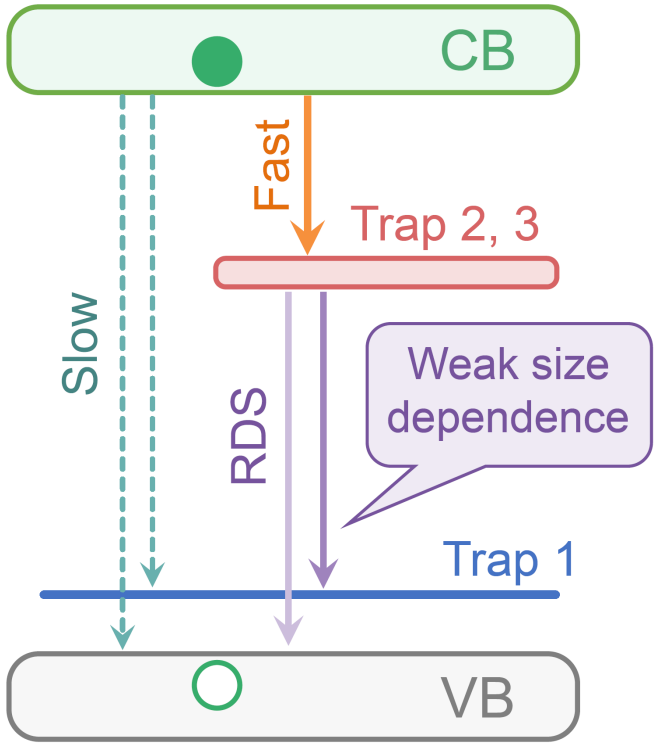
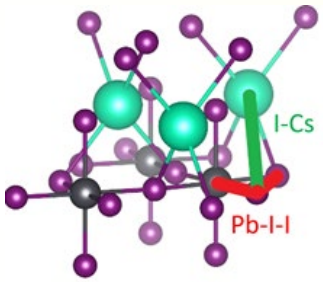




Total recombination shows size dependence, but trap-trap does not



Outline

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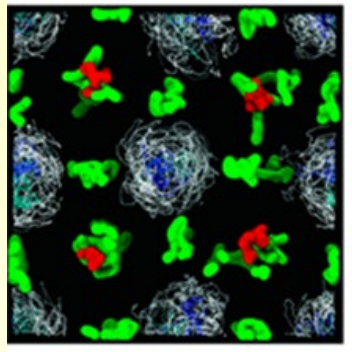
Longer Lifetime at Higher T

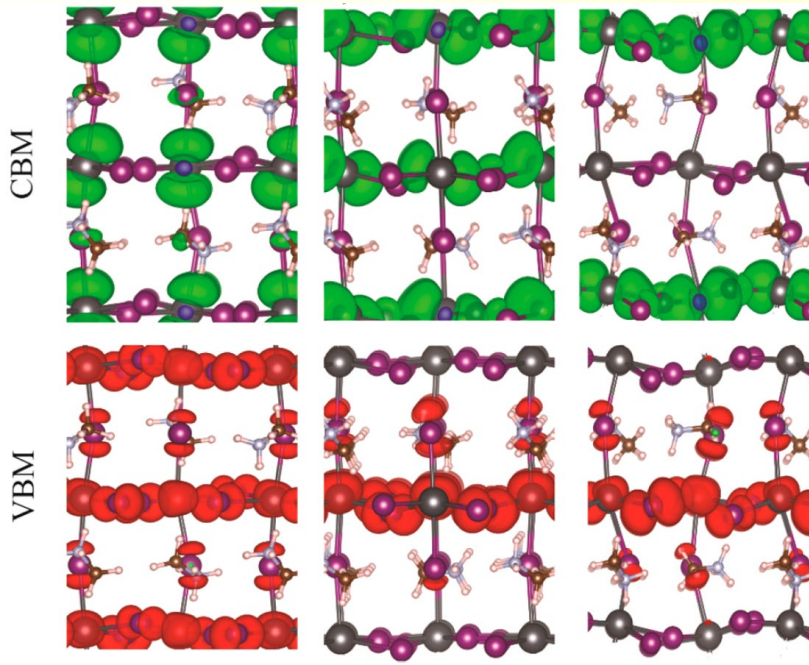


Li, Tang, Casanova, Prezhdo, *ACS Energy Lett.* **3** 2713 (2018)

$$i\hbar\left\langle \chi^{\alpha}\left|\vec{\nabla}_{R}\right|\chi^{\beta}\right\rangle \cdot \dot{\vec{R}}$$

- Nonadiabatic coupling is proportional to orbital overlap and atomic velocity
- Disorder at higher T localizes orbitals

$MAPbI_3$ 0K 200K 300K



$$\mathrm{I(X,Y)} = \iint \mathrm{d}x\mathrm{d}y\, p(x,y)\log\left(\frac{p(x,y)}{p(x)p(y)}\right)$$

Mutual Information Analysis

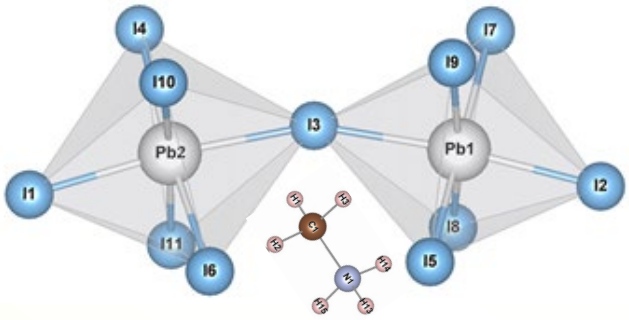
- Geometry more important than motion
- $CH_3NH_3^+$ also contribute, though do not participate in transport

Machine Learning Analysis

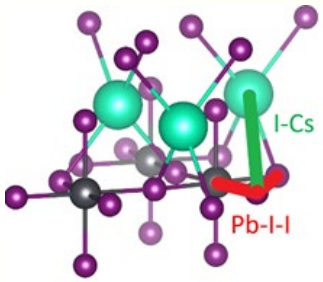
Zhou, Chu, Prezhdo, *ACS Energy Lett.* **5** 1930 (2020)
Mangan, Zhou, Chu, Prezhdo, *J. Phys. Chem. Lett.* **12**, 8672 (2021)

$i\hbar\langle\chi^{\alpha}\lvert\vec{\nabla}_R\rvert\chi^{\beta}\rangle\cdot\dot{\vec{R}}$	I-I-I angle	I-Pb-I (90°) angle	Pb-I-Pb angle	I-Pb-I (180°) angle	Pb-I-Pb motion
Mutual Information	0.87	0.73	0.71	0.63	0.62
	MA-axis *c* angle	I-Pb-I (90°) motion	MA-MA angle	MA-MA distance	MA-axis *a* angle
Mutual Information	0.61	0.60	0.60	0.59	0.59

Mutual information between nonadiabatic coupling and coordinate or motion



- Geometry more important than motion
- I-I-I most important (octahedral tilt)
- MA ($CH_3NH_3^+$) also contribute, though do not participate in transport



In Lieu of Conclusions

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