Libra Workshop and Summer School on Excited States and Nonadiabatic Dynamics 2024

Nonadiabatic Dynamics in Metal Halide Perovskites

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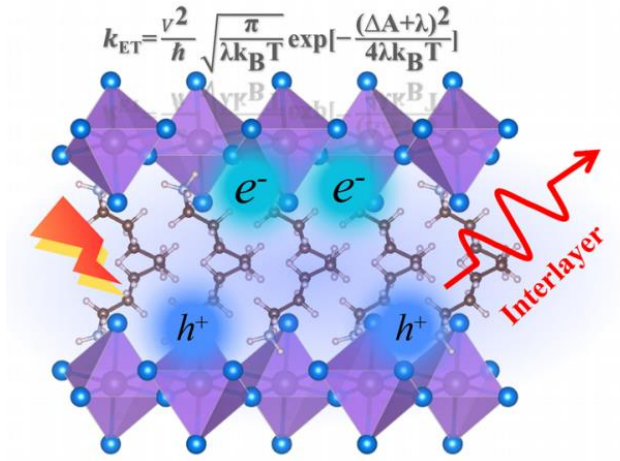
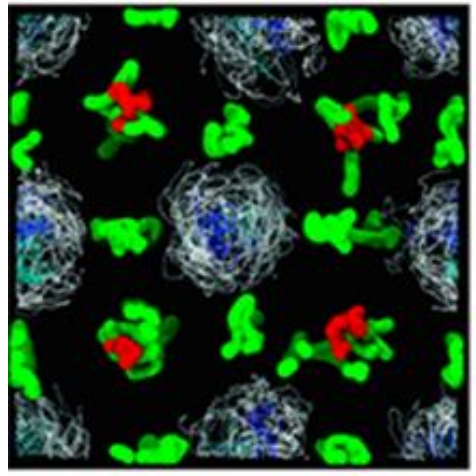
Outline

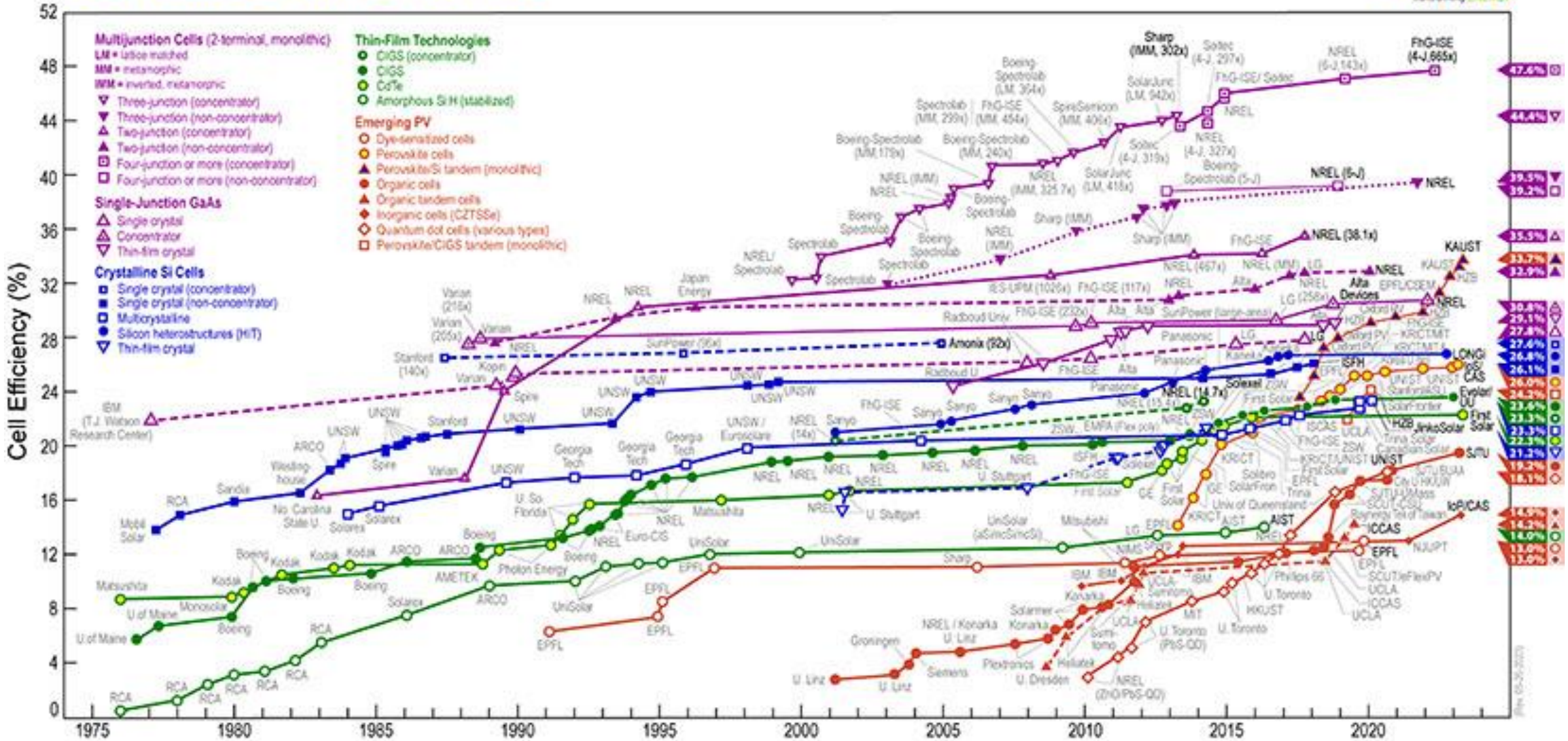
1. **Theoretical methodologies**:
   a. Interlayer carrier dynamics in 2D perovskites.
   b. Spin-orbital coupling in nonadiabatic dynamics.
   c. Hamiltonian repetition method for long-time nonadiabatic dynamics.



2. **Why can quantum dynamics teach about perovskites**:
   a. Why many defects are benign?
   b. Mechanisms of defect passivation.
   c. Unusual T and P dependence.

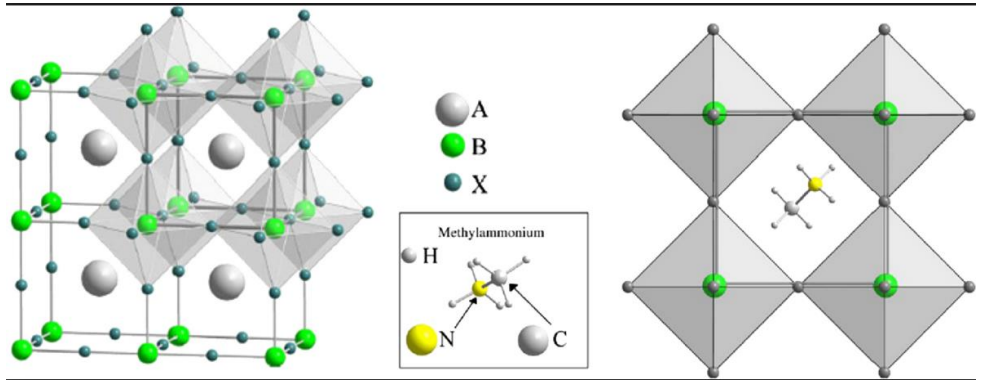


Best Research-Cell Efficiencies



3D/2D Perovskites

Generic formula: ABX_3, BX_6 octahedral
$CH_3NH_3PbI_3$

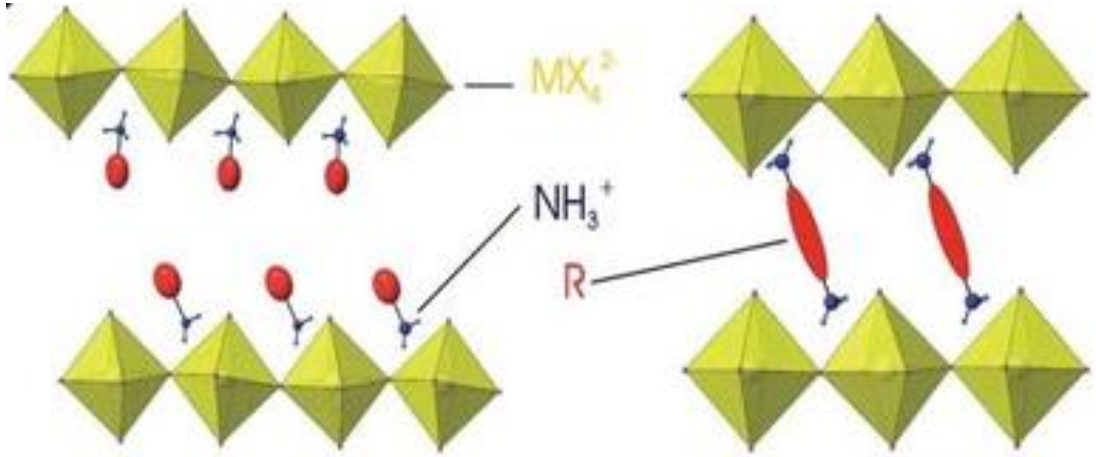


☑ Low exciton binding energy, ~19 meV
☑ Long carrier diffusion length
☑ High absorption coefficients
☑ Low recombination rate

× stability issue （Humidity, Light, Thermal）

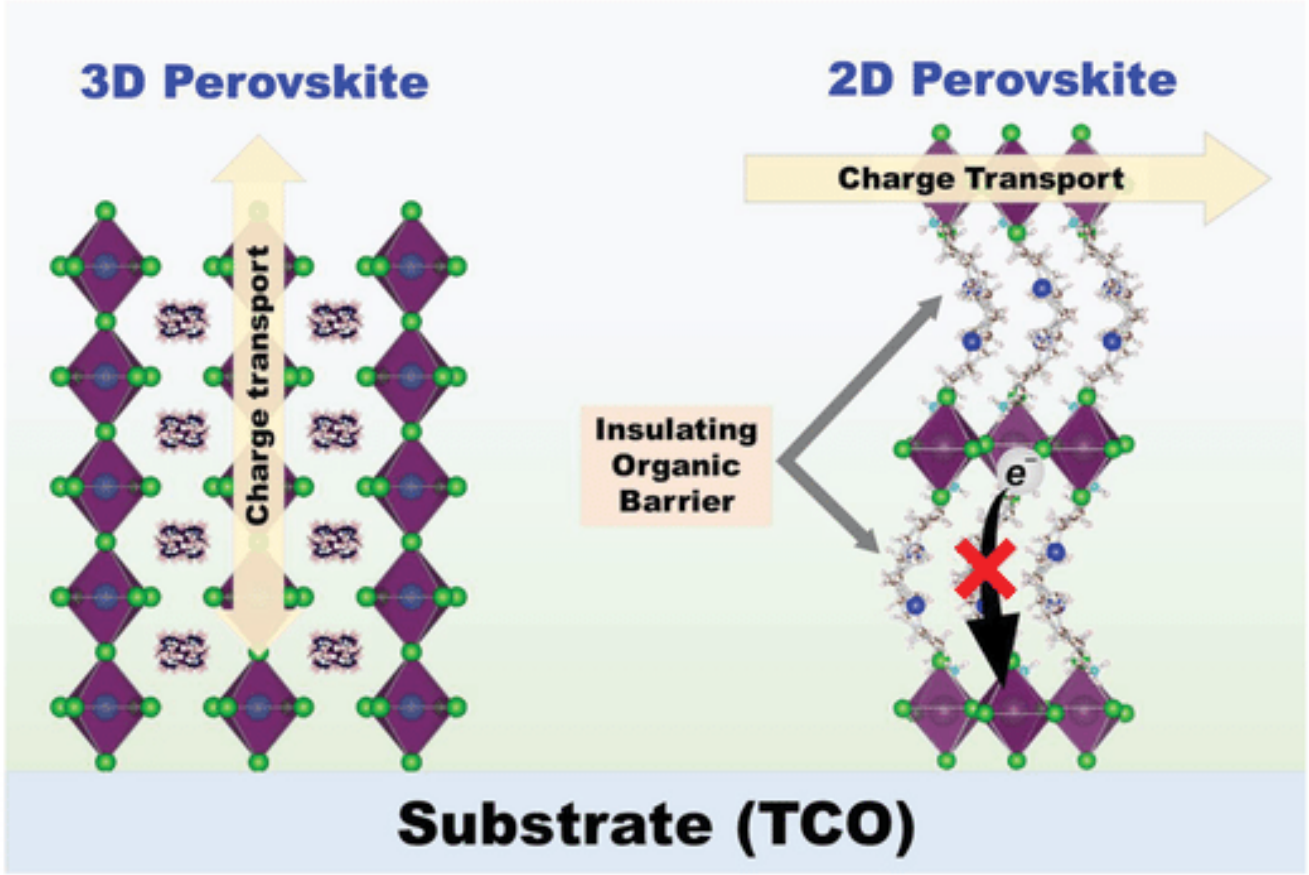
Ruddlesden-Popper
$(RNH_3)_2A_{n-1}B_nX_{3n+1}$

Dion-Jacobson
$R(NH_3)_2A_{n-1}B_nX_{3n+1}$

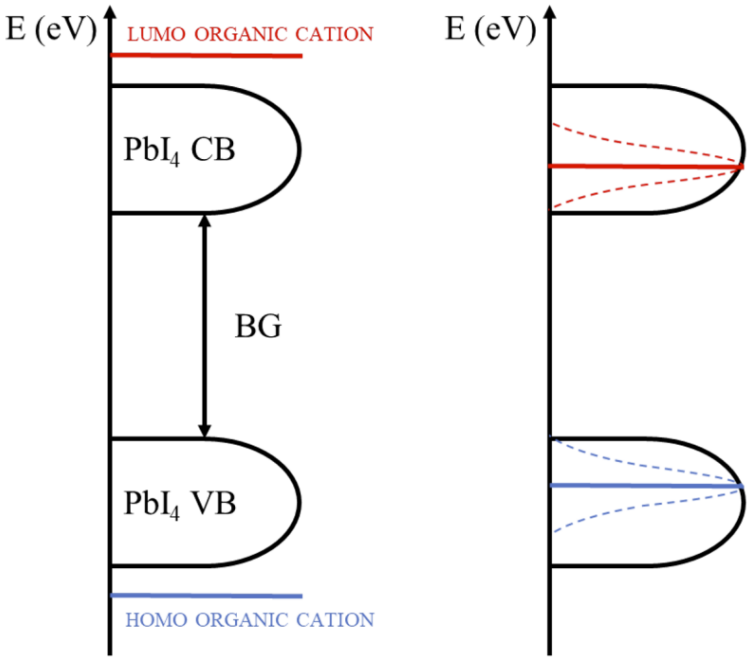


☑ High stability (Hydrophobicity of spacer cations)
☑ Structural tunability

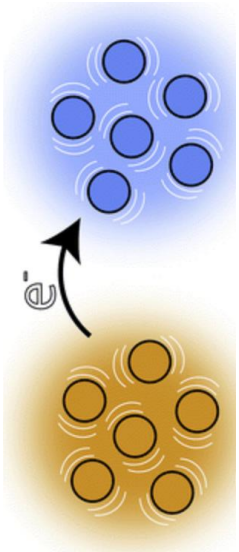
Interlayer Charge Transport in 2D Perovskites

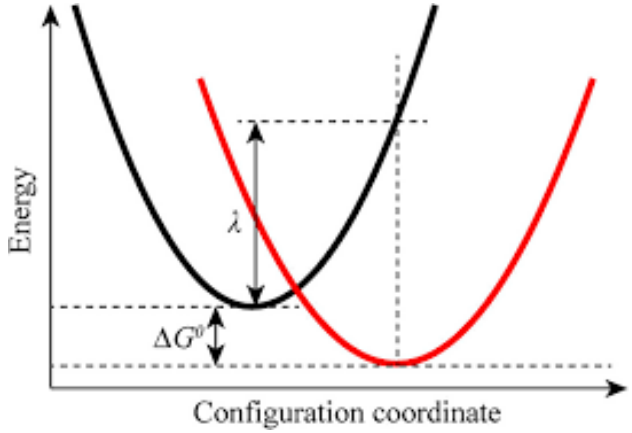


The interlayer charge transfer is limited by the insulating nature of spacer cations!



Marcus Electron Transfer





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

$$\frac{J(\omega)}{\omega} = \frac{1}{2k_B T}\int_0^{\infty} \langle \delta\Delta E(0)\delta\Delta E(t)\rangle_M \cos\omega t$$

$$\lambda = \frac{2}{\pi}\int_0^{\infty}\frac{J(\omega)}{\omega}d\omega$$

$\boldsymbol{V_{kl}}$: diabatic coupling between localized states (non-local electron-phonon coupling)

$\boldsymbol{\lambda}$: reorganization energy (local electron-phonon coupling)

$\boldsymbol{\Delta G}$: barrier height, zero for equivalent layer

Methods for diabatization:

- block diagonalization
- generalized Mulliken-Hush method
- fragment charge difference
- fragment energy difference
- projection methods
- fragment orbital density functional theory
- constrained density functional theory
- block-localized wavefunction theory

Projection-operator Diabatization (POD) Approach

- **Kohn-Sham Hamiltonian** expressed in terms of **orthogonalized atomic orbital** basis set is partitioned in **donor** and **acceptor** blocks
- **coupling matrix** between donor and acceptor states are identified **transformed** matrix elements of the **off-diagonal block**

$$\psi^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\mathbf{k}\mathbf{R_n}} \sum_i C_i^{\mathbf{k}} \phi_i^{\mathbf{k}} (\mathbf{r} - \mathbf{R_n})$$

The Bloch function can be expressed as linear combination of atomic orbital basis

$$H^{\mathbf{k}} = \sum_n e^{\mathbf{i}\mathbf{k}\mathbf{R}_n} \langle \phi_i(\mathbf{r}) | H | \phi_j(\mathbf{r} - \mathbf{R}_n) \rangle$$

$$S^{\mathbf{k}} = \sum_n e^{\mathbf{i}\mathbf{k}\mathbf{R}_n} \langle \phi_i(\mathbf{r}) | S | \phi_j(\mathbf{r} - \mathbf{R}_n) \rangle$$

Löwdin symmetric procedure:

$$|\tilde{\phi}_i\rangle = \sum_j S_{ji}^{1/2} |\phi_j\rangle \qquad \tilde{H} = S^{-1/2} H S^{-1/2}$$

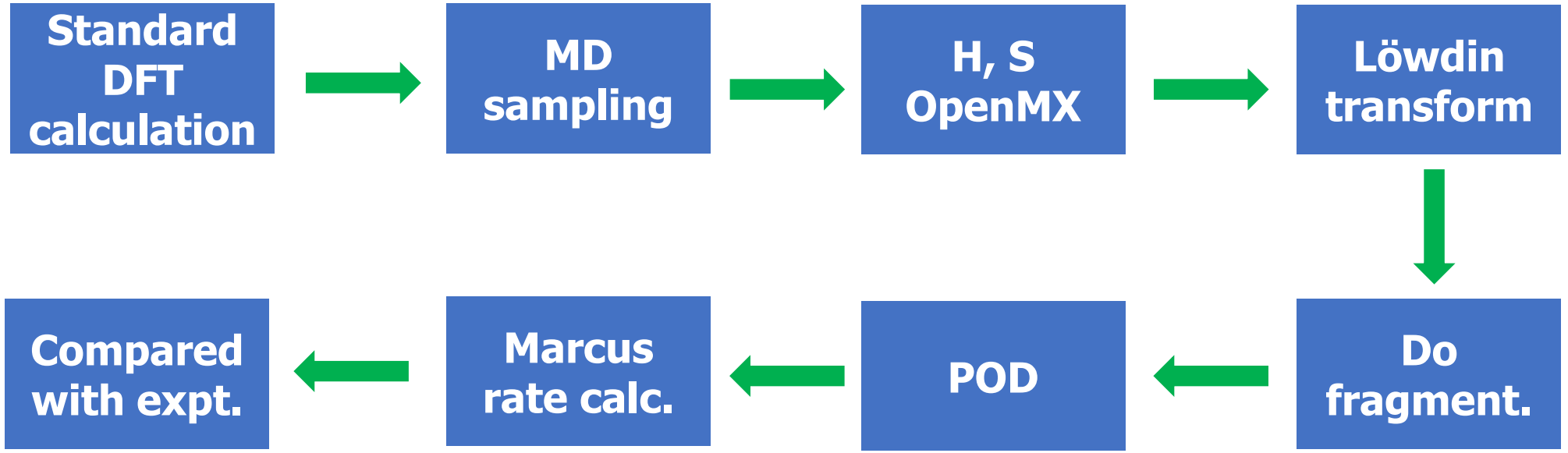
Diabatic energy:

$$\varepsilon_{DD} = T_D^+ \tilde{H}_{DD} T_D;\ \varepsilon_{AA} = T_A^+ \tilde{H}_{AA} T_A$$

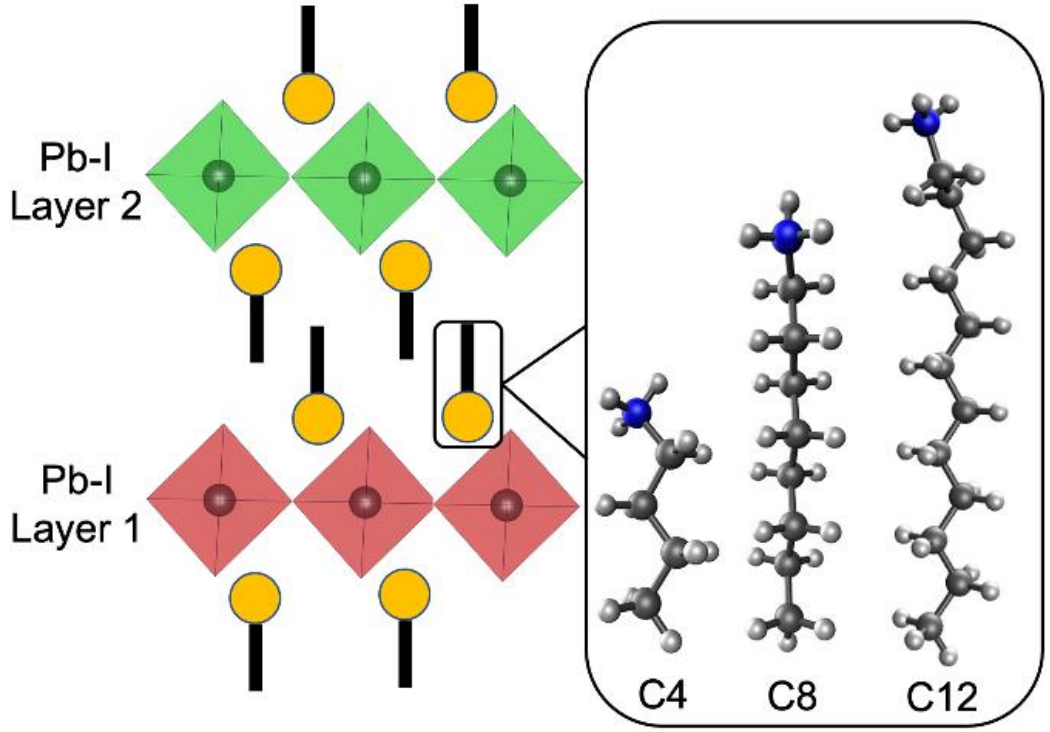
$$T_A^+ \begin{bmatrix} \tilde{H}_D & \tilde{H}_{DA} \\ \tilde{H}_{AD} & \tilde{H}_A \end{bmatrix} T_D = \begin{bmatrix} \varepsilon_D & V_{DA} \\ V_{AD} & \varepsilon_A \end{bmatrix}$$

J. Comput. Theory Chem., 2023, **19**, 9403

Workflow: interfacing with OpenMX



Alkyl Length-dependent Interlayer Charge Transfer



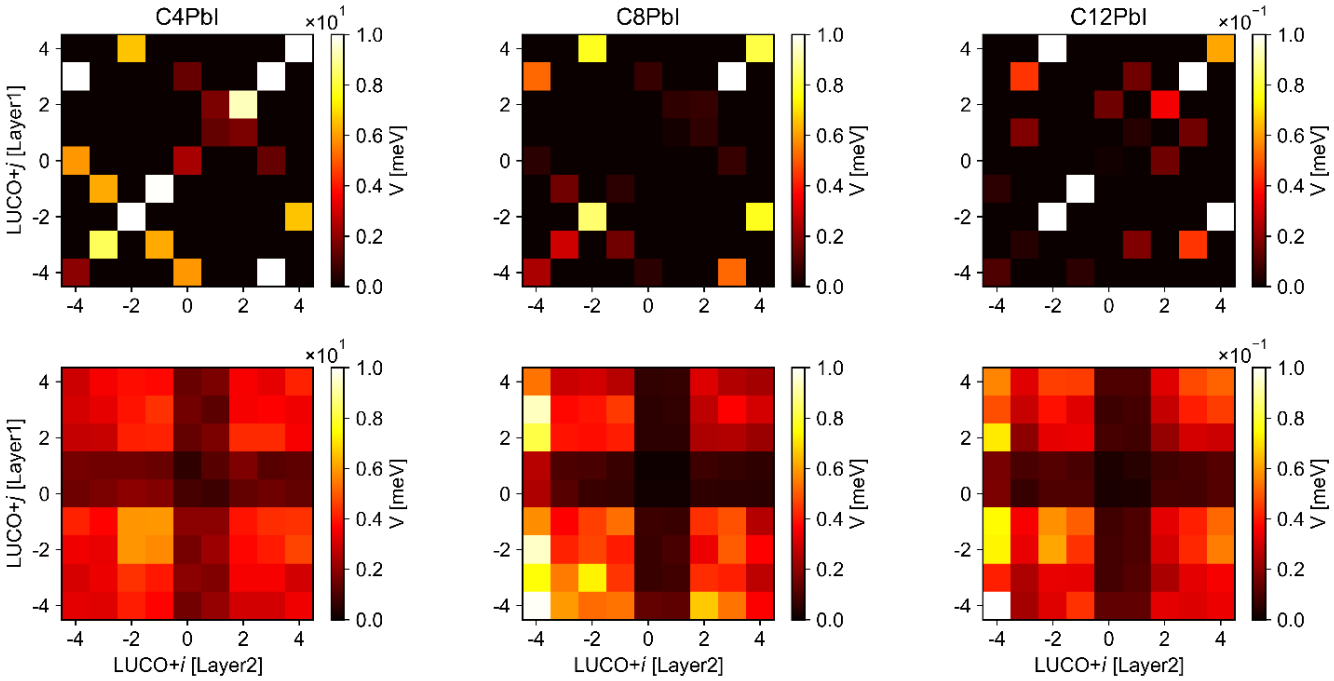
Ye et al., Nature Comm., 2020, **11**, 5481
Boeije et al. J. Am. Chem. Soc. 2023, **145**, 21330

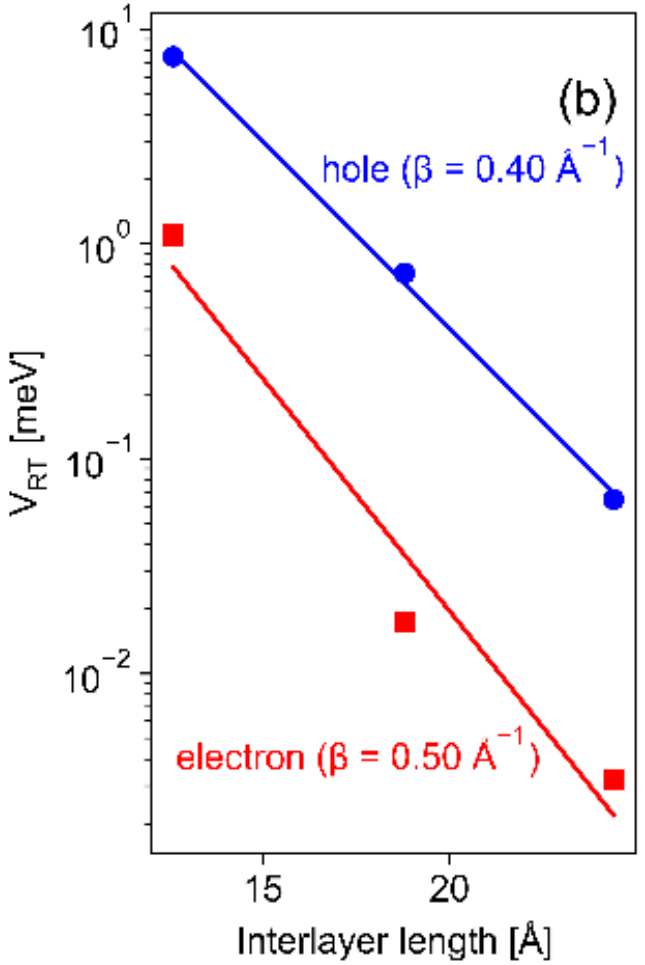
J. Comput. Theory Chem., 2023, **19**, 9403

Charge Transfer Couplings

0K

300K





- Hole transfer coupling is larger than electron transfer coupling
- Thermal fluctuation enhances the electronic coupling
- Longer organic cations decrease the electronic coupling

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Electron and Hole Hopping Time

Table 1. Parameters for Interlayer Charge Transfer Computed for the Investigated 2D Layered Perovskites and Corresponding Transition Rates and Mobilities[a]

		V_{kl} (meV)	$\langle V_{kl}^2\rangle^{1/2}$ (meV)	σ_V (meV)	λ (eV)	τ_{Marcus}	μ_{hop} ($cm^2\ V^{-1}\ s^{-1}$)
C4PbI	L	8.7×10^{-2}	1.10	1.08	0.83	137.6 ns	4.46×10^{-6}
	H	0.36	7.44	7.41	1.08	38.5 ns	1.59×10^{-5}
C8PbI	L	1.38×10^{-4}	1.73×10^{-2}	1.72×10^{-2}	0.97	2.3 ms	6×10^{-10}
	H	1.98×10^{-3}	0.73	0.65	0.54	18.8 ns	7.35×10^{-5}
C12PbI	L	4.34×10^{-5}	3.2×10^{-3}	3×10^{-3}	1.18	572.0 ms	3.99×10^{-12}
	H	3.95×10^{-3}	6.46×10^{-2}	6.43×10^{-2}	1.11	690.2 μs	3.31×10^{-9}

[a]HOCO–HOCO (H) and LUCO–LUCO (L) electronic couplings for the 0 K structures (V_{kl}) and canonically averaged electronic couplings from the MD simulations ($\langle V_{kl}^2\rangle^{1/2}$), along with its standard deviation (σ_V); the averaged reorganization energy (λ); the hole and electron hopping time obtained from Marcus theory (τ_{Marcus}); and the carrier mobility calculated based on the Marcus hopping rate (μ_{hop}).

CPA for NA-MD based on constrained DFT

$$i\hbar \frac{\partial \psi(\mathbf{r}, t; \mathbf{R})}{\partial t} = H_e(\mathbf{r}, t; \mathbf{R}) \psi(\mathbf{r}, t; \mathbf{R})$$

$$\psi(\mathbf{r}, t; \mathbf{R}) = \sum_l c_l(t) \phi_l(\mathbf{r}; \mathbf{R}(t))$$

Expanding adiabatic wavefunction in fragment orbital basis

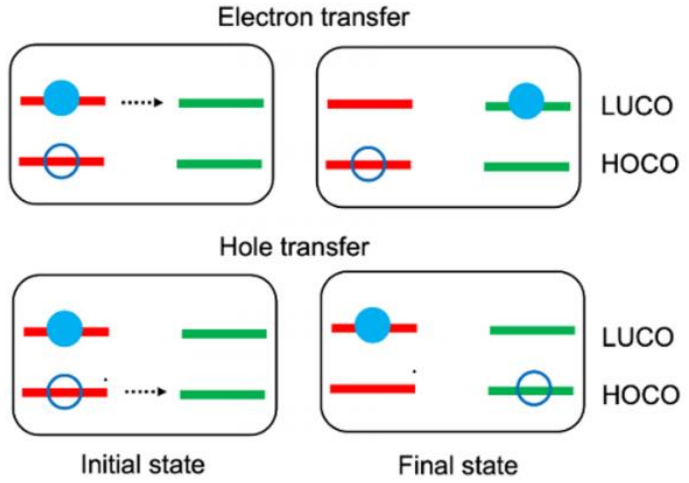
$$i\hbar \sum_l \frac{\partial c_k(t)}{dt} = \sum_l H_{vib,kl}(t) c_l(t)$$

$$H_{vib,kl} = H_{kl} - i\hbar \mathbf{d}_{kl}$$

If we consider H->H; L->L transitions

$$H_{kl} = \langle \phi_k | H | \phi_l \rangle$$

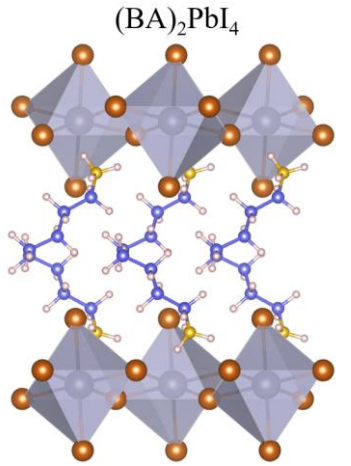
The key is to obtain the donor-acceptor energy splitting

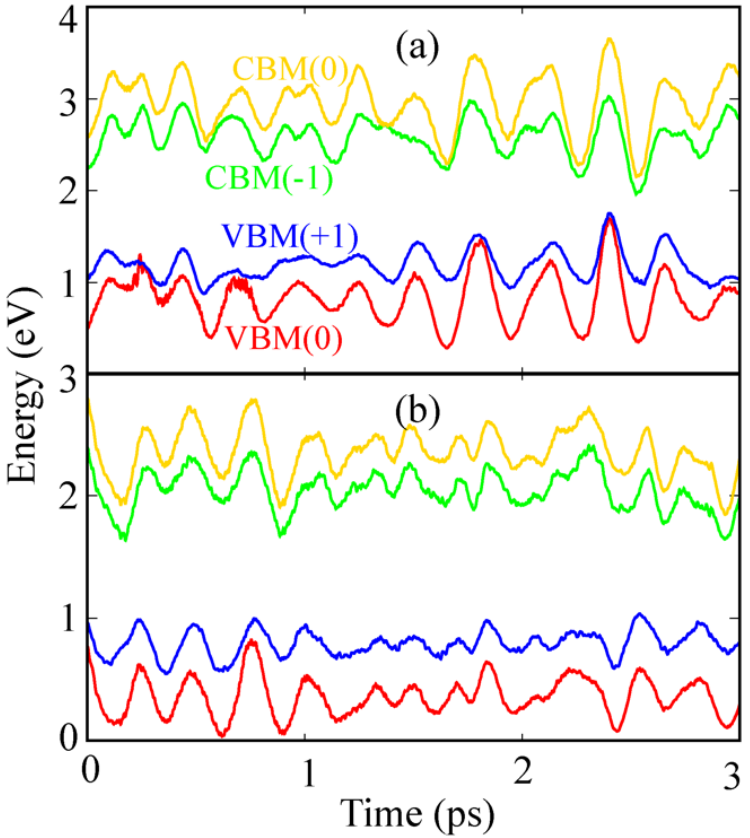


- **Insider layer**, electronic coupling is zero, basis is orthogonal; but NAC is non-zero
- **Between layers**, electronic coupling is non-zero; but NAC vanishes

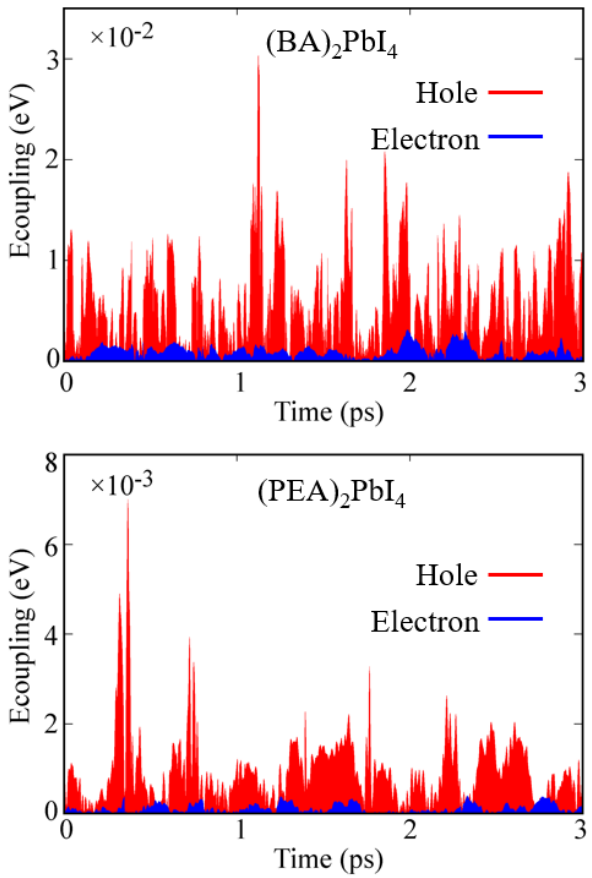
CPA for NA-MD based on constrained DFT

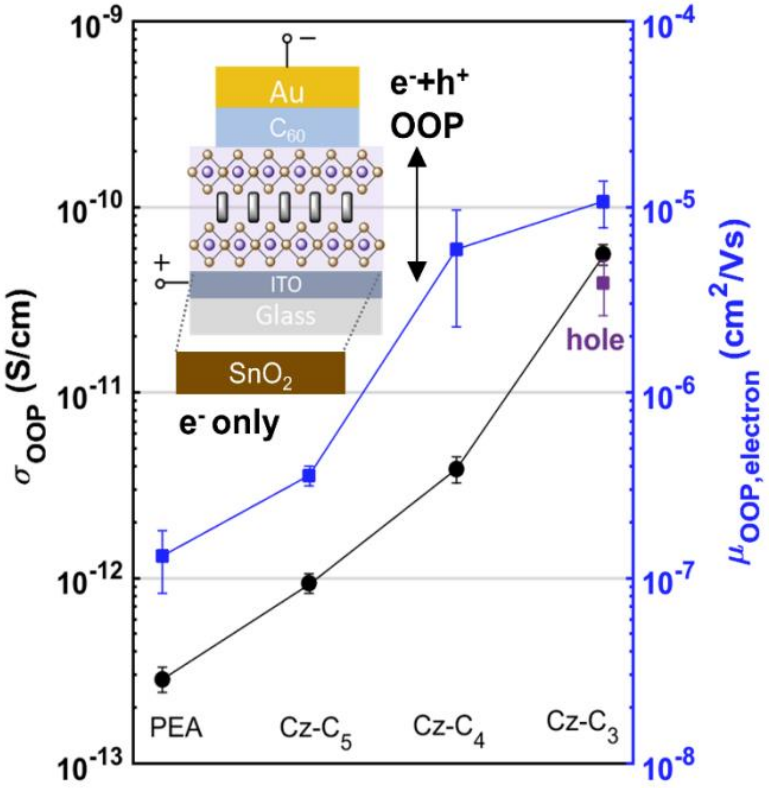
- The excited state is approximately by perturbation of ground state charge density.
- The charge is constrained at one layer through adding/removing electrons and then hop to another layer.
- The splitting between donor and acceptor site energies characterizes the ET process within the two state picture.





CPA for NA-MD based on constrained DFT





PEA has 10^{-6} - 10^{-7} $cm^2/V/s$ out-of-plane carrier mobility, this gives 100 ns – 1 us hopping time

$$\mu_{\mathrm{hop}} = \frac{eD}{k_{\mathrm{B}}T} = \frac{ek_{\mathrm{Marcus}}L^2}{k_{\mathrm{B}}T}$$

Boeije et al. J. Am. Chem. Soc. 2023, 145, 21330

CPA for NA-MD based on constrained DFT

		$< V^2 >^{1/2}$ (meV)	λ (eV)	τ_{Marcus}	τ_{DISH}	D_{COM} (Å)	μ_{Marcus} ($cm^2/V/s$)	μ_{DISH} ($cm^2/V/s$)
BAPbI	L	1.10	0.83	137.6 ns	24.0ns	12.6	$4.46\ 10^{-6}$	$2.6\ 10^{-5}$
	H	7.44	1.08	38.5 ns	5.2ns		$1.59\ 10^{-5}$	$1.2\ 10^{-4}$
PEAPbI	L	0.13	0.66	1.7 us	17.9µs	15.94	$5.8\ 10^{-7}$	$5.5\ 10^{-8}$
	H	0.27	0.60	210 ns	5.3µs		$4.7\ 10^{-6}$	$1.8\ 10^{-7}$

Spin-orbit Interactions in Nonadiabatic Dynamics

$$(\hat{h}^{\mathrm{KS}} + \hat{h}^{\mathrm{SOC}})\psi_i^{\mathrm{adi}} = \epsilon_i^{\mathrm{adi}}\psi_i^{\mathrm{adi}}$$

$$\psi_i = \phi_i^{\alpha}\alpha + \phi_i^{\beta}\beta = \begin{pmatrix} \phi_i^{\alpha} \\ \phi_i^{\beta} \end{pmatrix}, \quad i = 1, \ldots, N$$

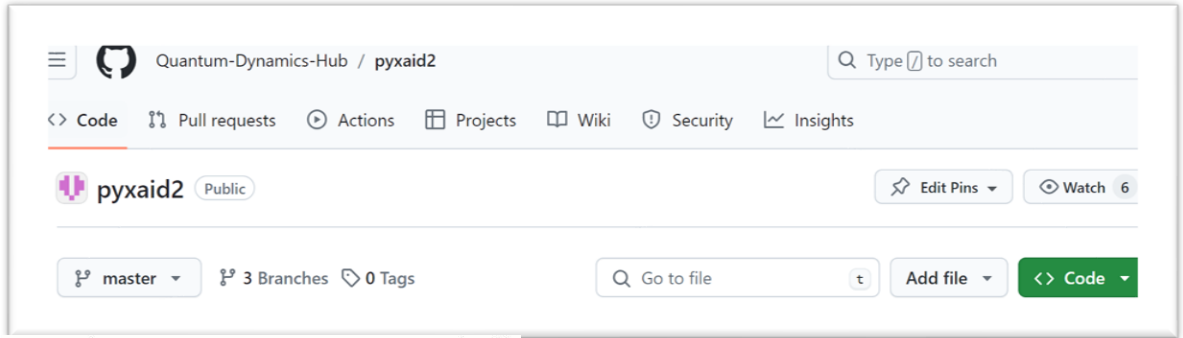
$$d_{ij}\left(t + \frac{\mathrm{d}t}{2}\right) \equiv \frac{\langle \Phi_i(t)|\Phi_j(t + \mathrm{d}t)\rangle - \langle \Phi_i(t + \mathrm{d}t)|\Phi_j(t)\rangle}{2\mathrm{d}t}$$

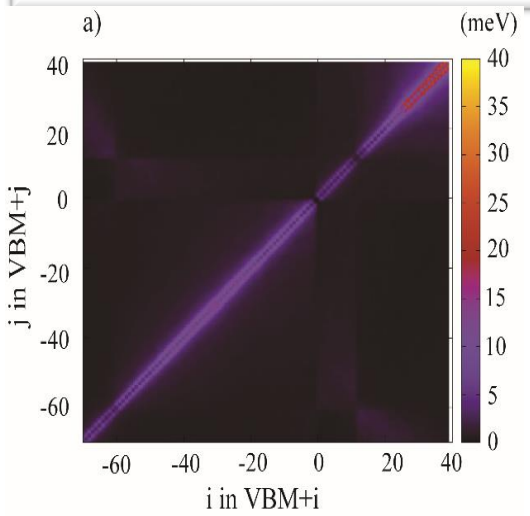
$$\langle \psi_i(t)|\psi_j(t')\rangle = (\phi_i^{\alpha}(t)\phi_j^{\beta}(t))\begin{pmatrix} \phi_j^{\alpha}(t') \\ \phi_j^{\beta}(t') \end{pmatrix}$$

$$= \langle \phi_i^{\alpha}(t)|\phi_j^{\alpha}(t')\rangle + \langle \phi_i^{\beta}(t)|\phi_j^{\beta}(t')\rangle$$

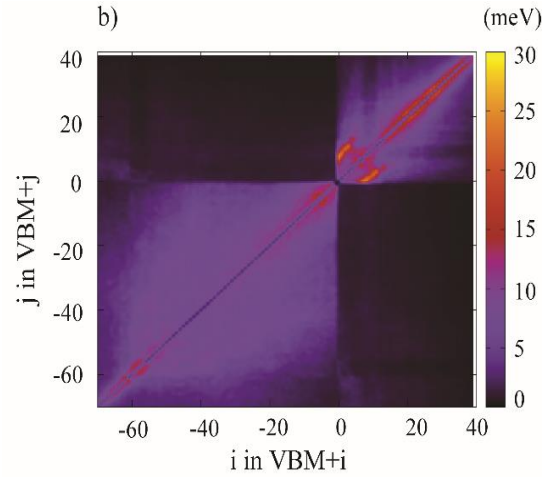
ACS Energy Lett., 2018, **3**, 2159

Wavefunctions are expressed as two-component spinors





Without SOC

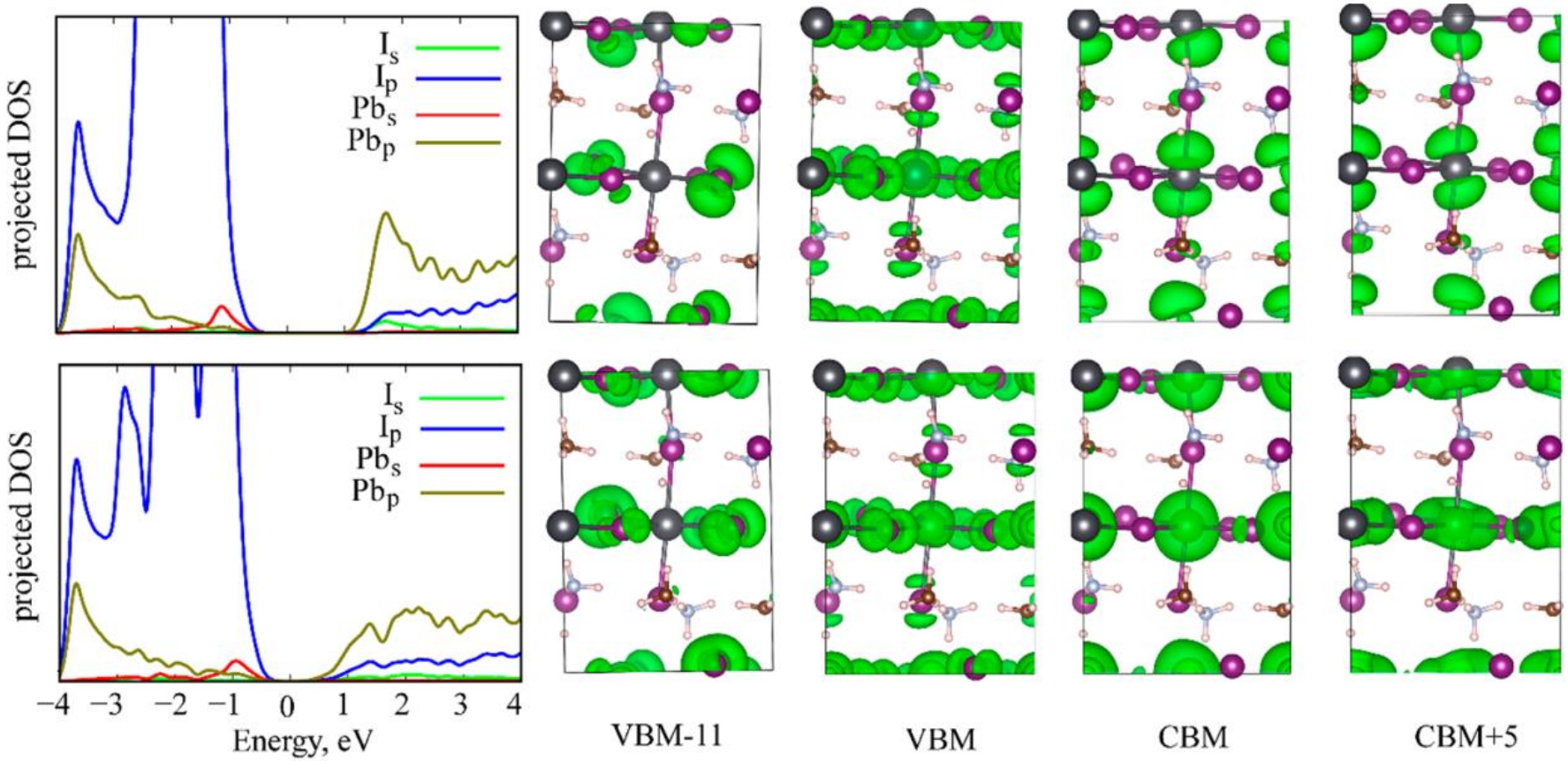


With SOC

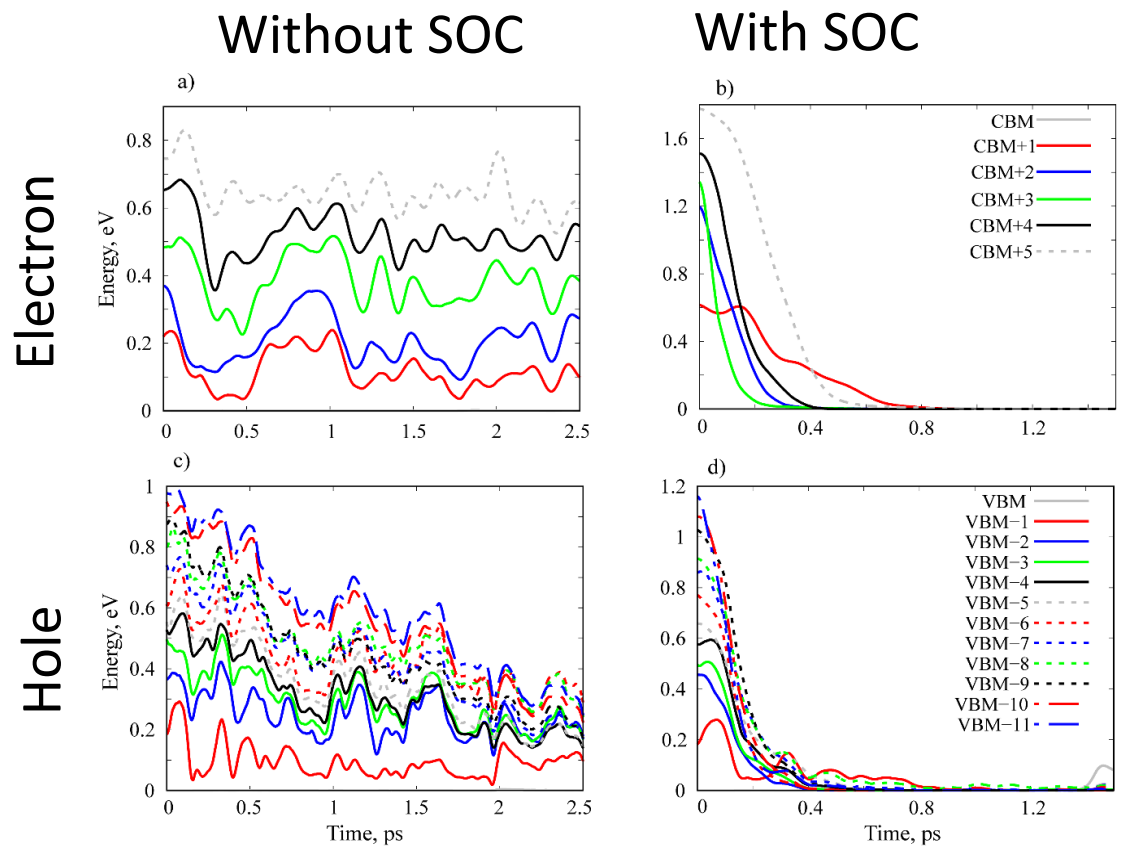
Spin-orbit Interactions in Nonadiabatic Dynamics

Without SOC

With SOC



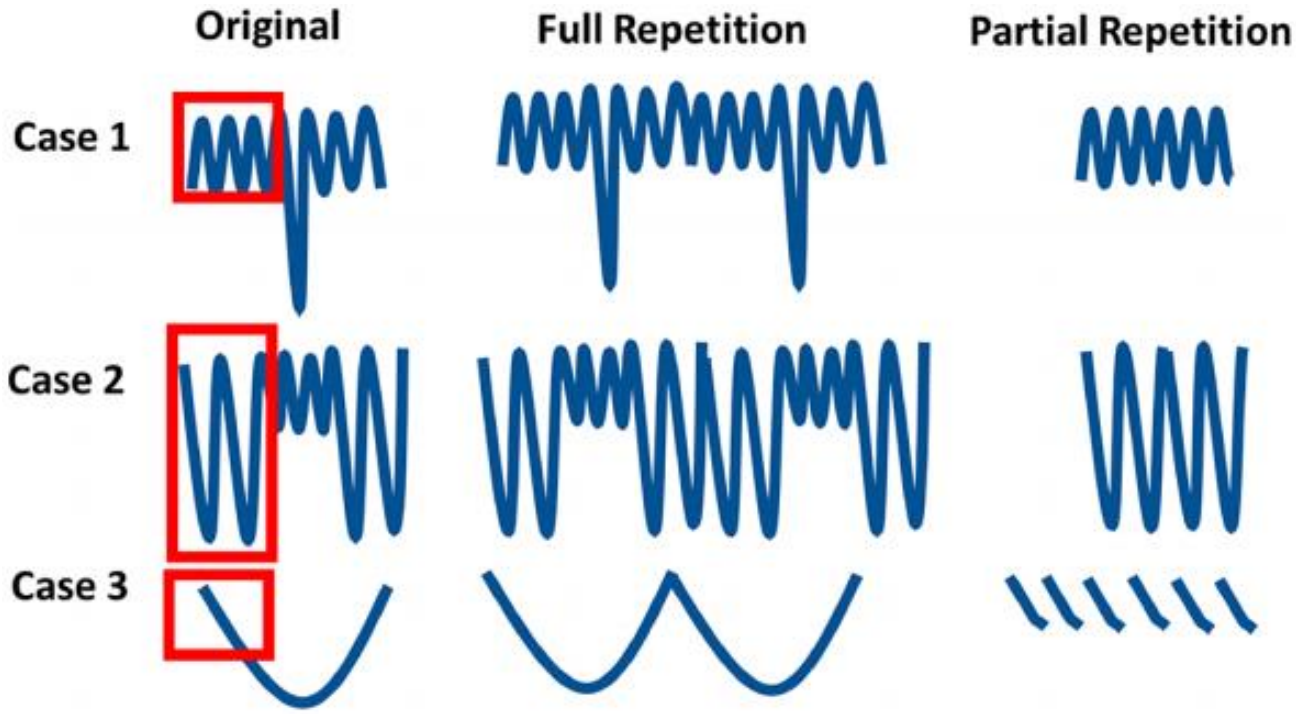
Spin-orbit Interactions in Nonadiabatic Dynamics



- Hole relaxation faster than electron relaxation - denser DOS for holes
- Spin-orbit interaction greatly speeds up relaxation - larger NA coupling

Hamiltonian Repetition in Nonadiabatic Dynamics

Repetition should capture the essential feature of the Hamiltonian

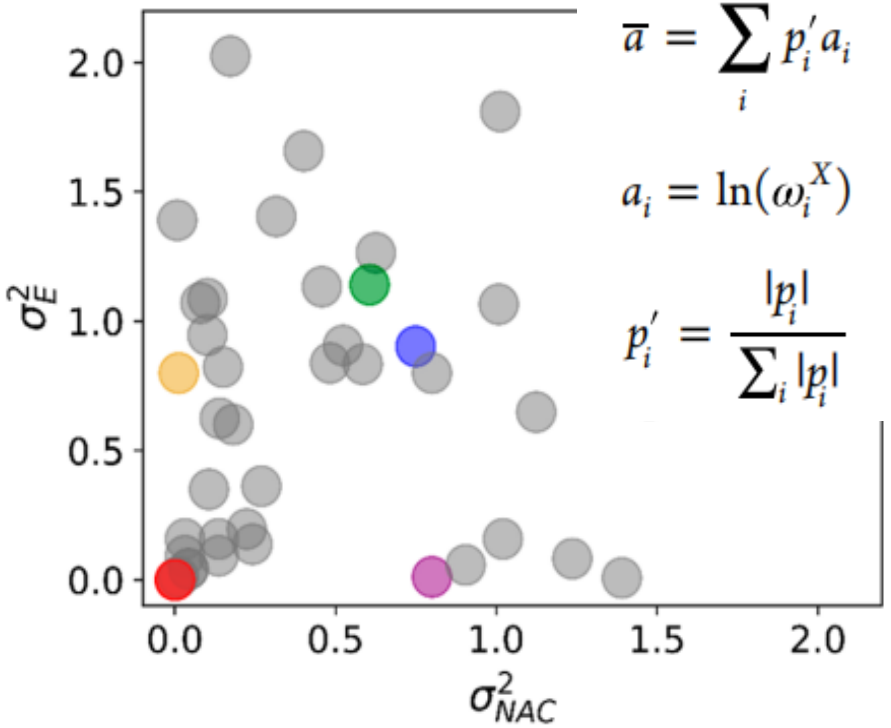


$$\sigma_X^{\,2} = \sum_i p_i'(a_i - \overline{a})^2$$

$$\overline{a} = \sum_i p_i' a_i$$

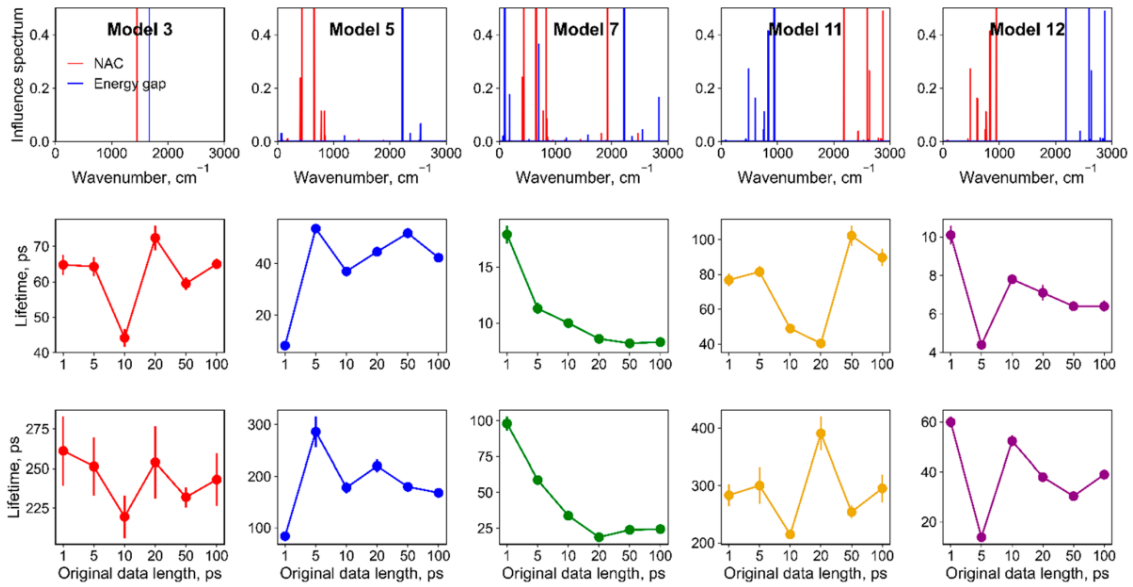
$$a_i = \ln(\omega_i^X)$$

$$p_i' = \frac{|p_i|}{\sum_i |p_i|}$$



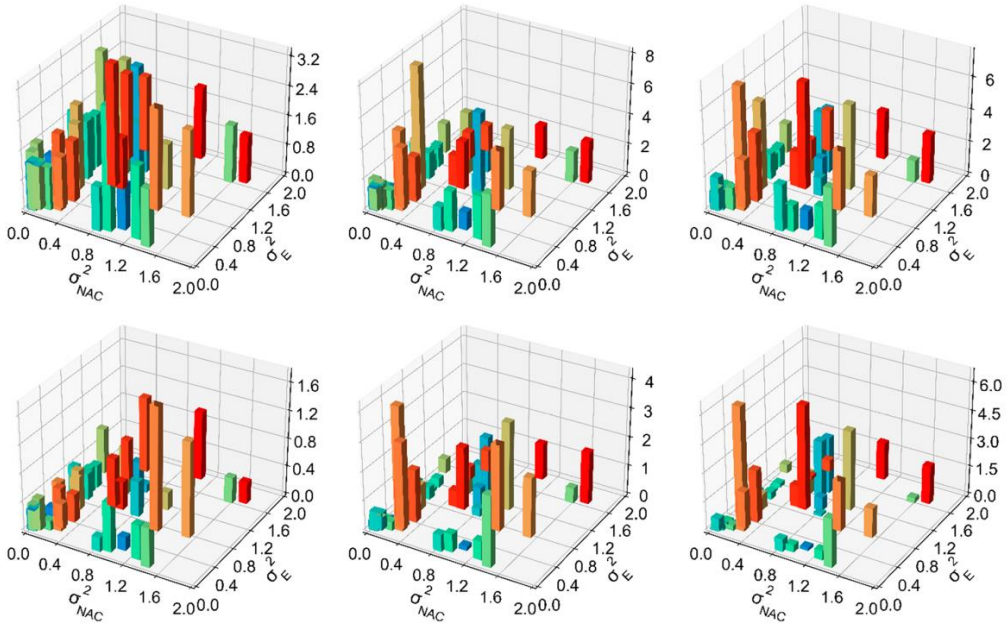
J. Phys. Chem. Lett., 2022, **13**, 9688

Hamiltonian Repetition in Nonadiabatic Dynamics



Convergence hard to achieve for the data sets involving low-frequency modes

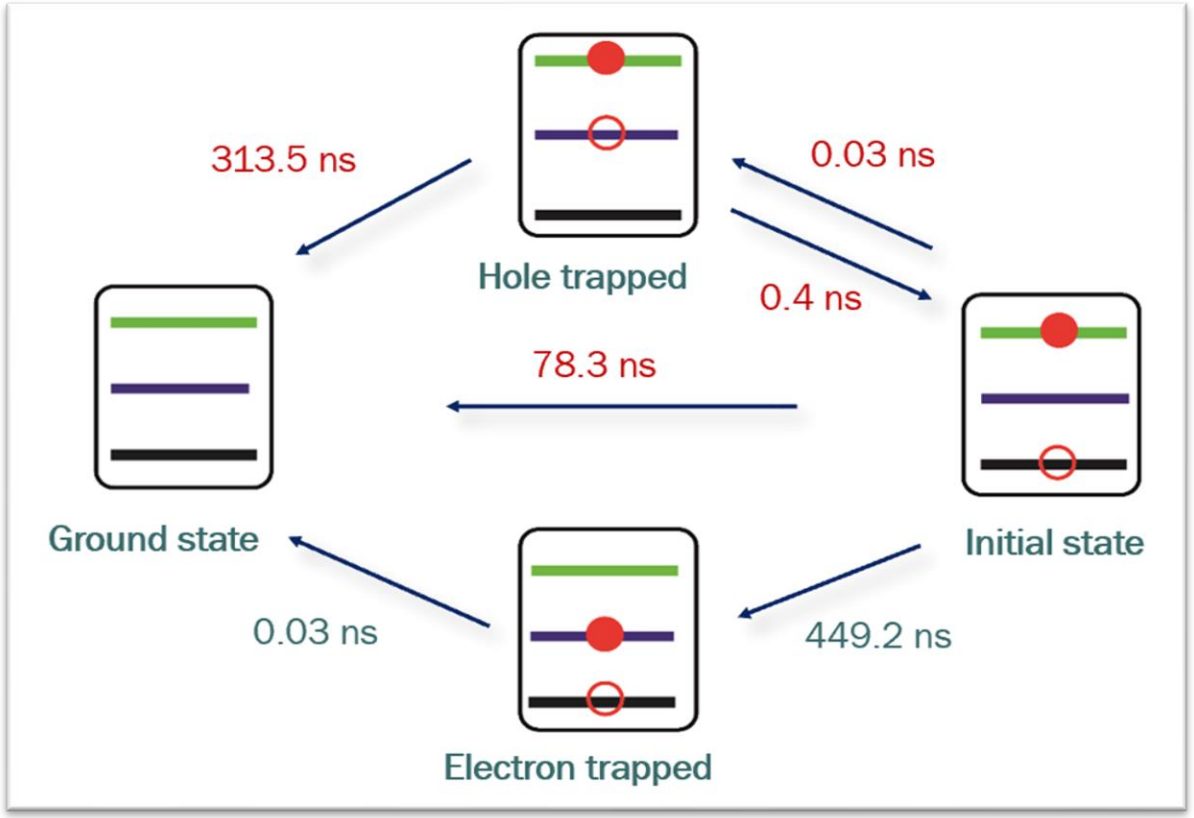
The repetition approach becomes inaccurate in simulations with very small NACs



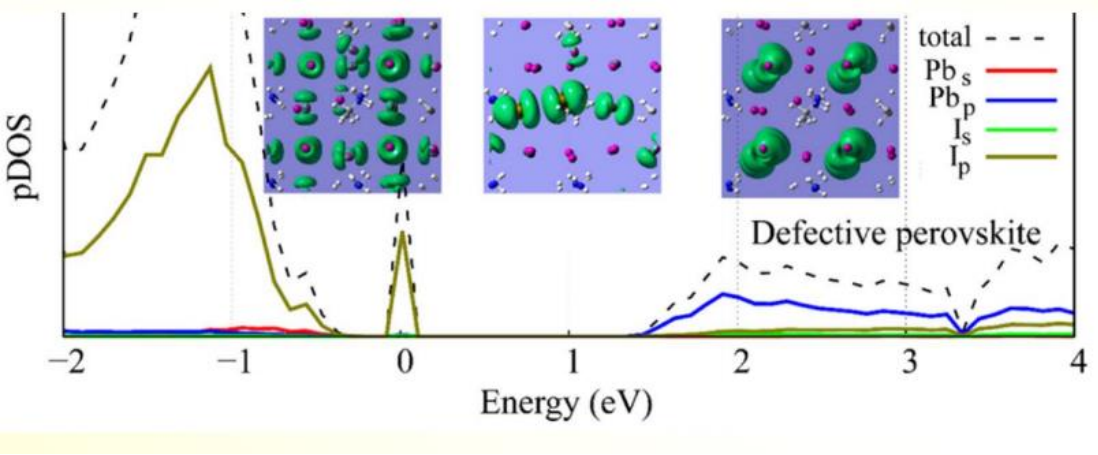
The overestimation or underestimation does not directly depend on the dispersion of frequencies

J. Phys. Chem. Lett., 2022, **13**, 9688

Iodine Interstitials Suppress Recombination

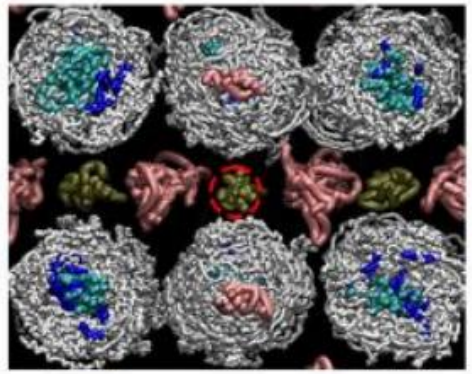


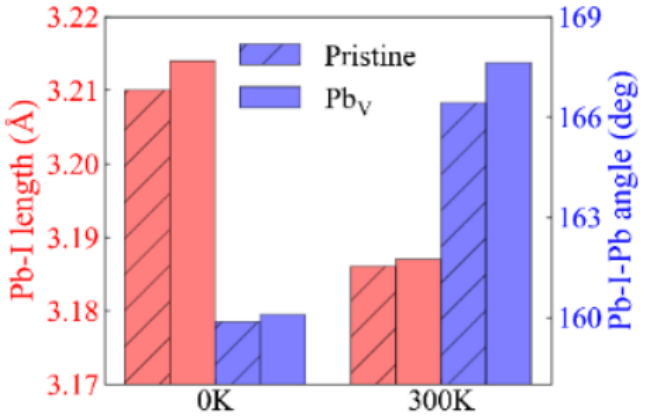
- Hole trapping is fast, but recombination of trapped hole with free electron is slow because wavefunction overlap is small
- Hole can be trapped and de-trapped multiple times before recombining, increasing free carrier lifetimes

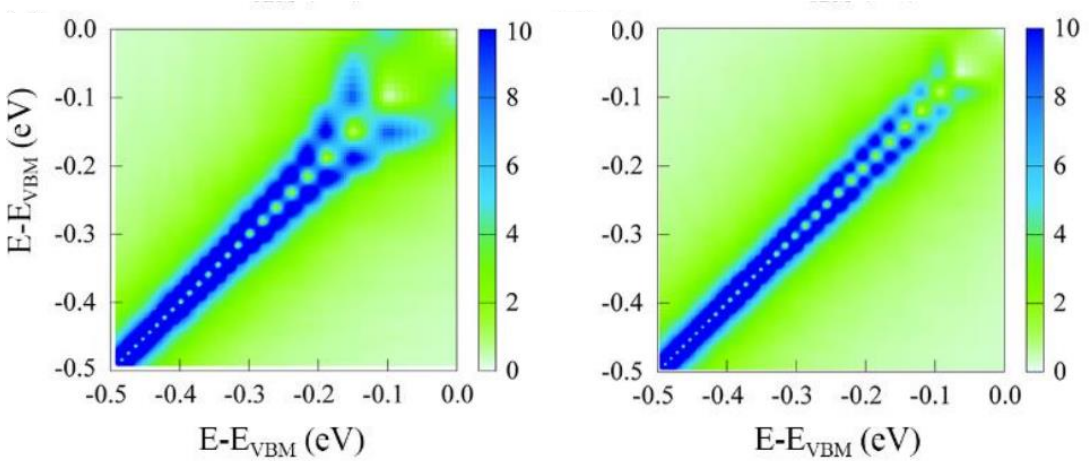


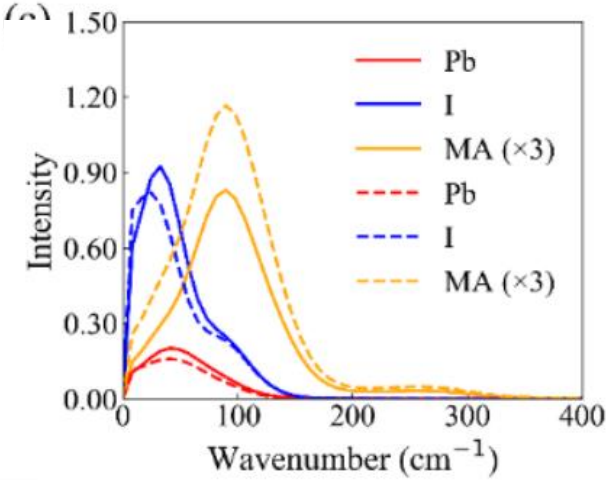
ACS Energy Lett., 2017, **2**, 1270

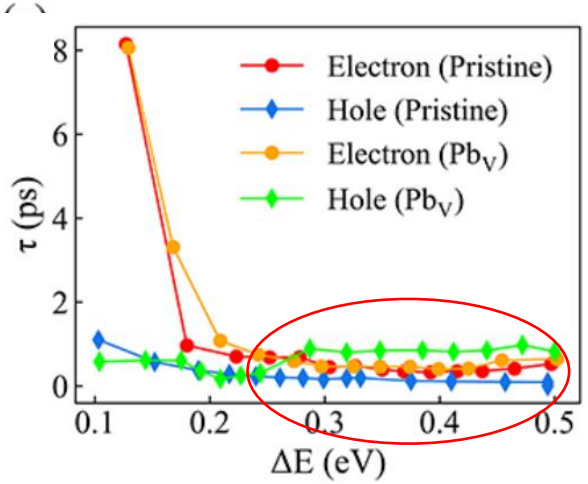
Pb Vacancy Slows Down Carrier Cooling







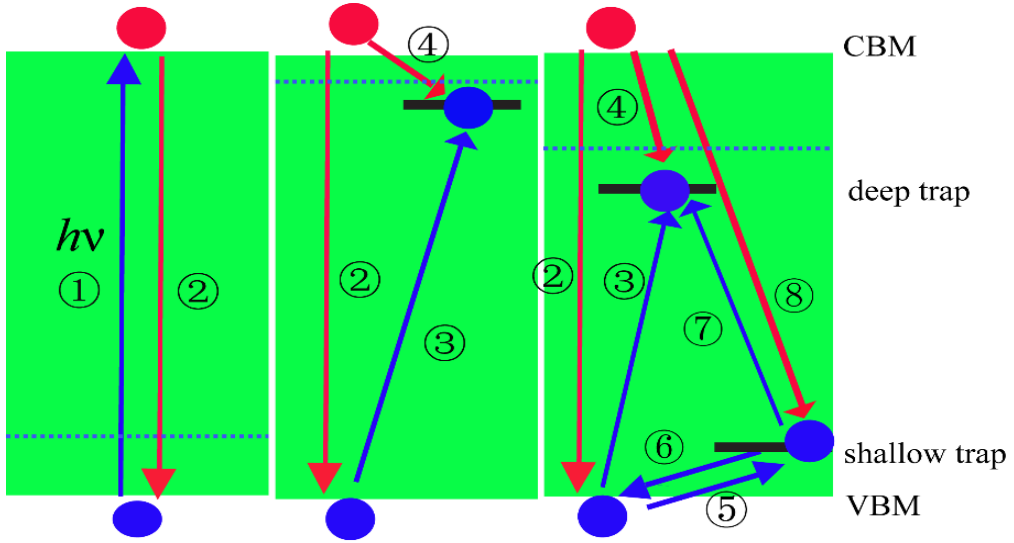




- Pb vacancy increase the structural ordering, decreases fluctuations of Pb and I atoms, and reduces NA couplings
- Pb vacancy introduces intraband states capable of trapping hot holes, slowing down its cooling further

Inorgan. Chem. Front., 2024, **9**, 5549

Oxidization States of Iodine Vacancy

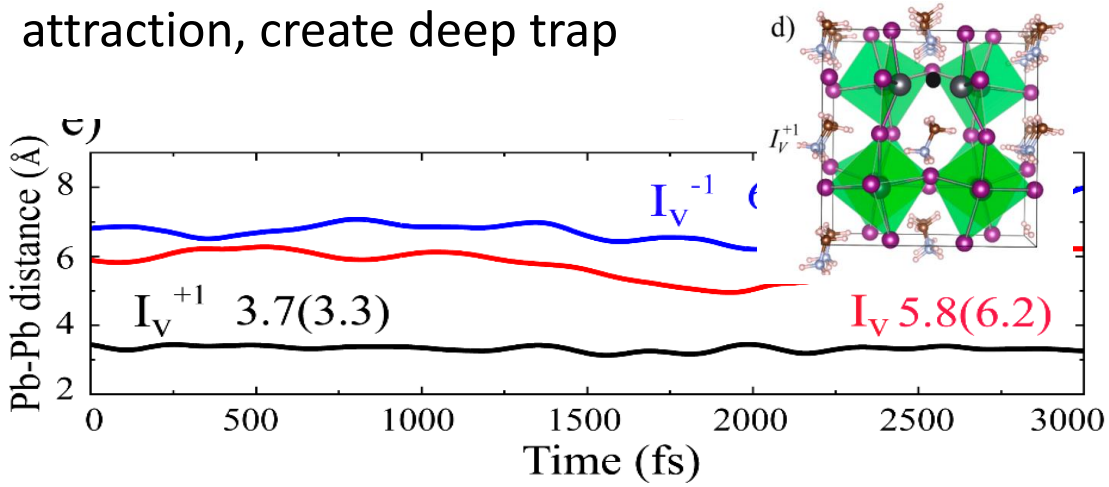


	Recomb. time	Mechanism
Pristine	152ns	CBM->VBM
Missing I^-	136ns	CBM->VBM
Missing I	27ns	CBM->VBM, via trap
Missing I^+	3ns	Sequential (via trap)

Missing I^-: Lose an electron enlarges the Pb-Pb distance due to Coulomb repulsion, and creates no trap states

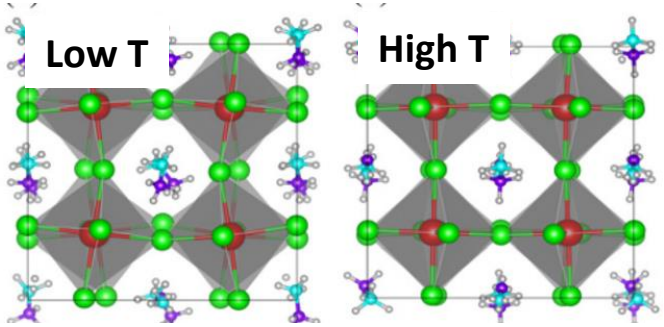
Missing I: create shallow trap

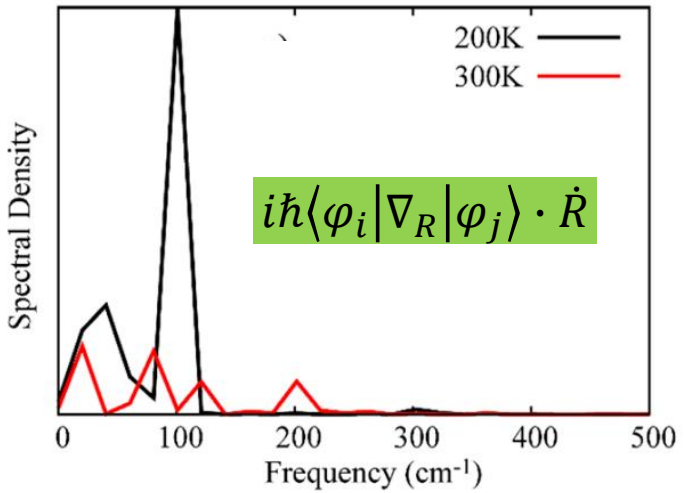
Missing I^+: Capture of an electron shortens the Pb-Pb distance and form Pb-Pb dimer due to Coulomb attraction, create deep trap

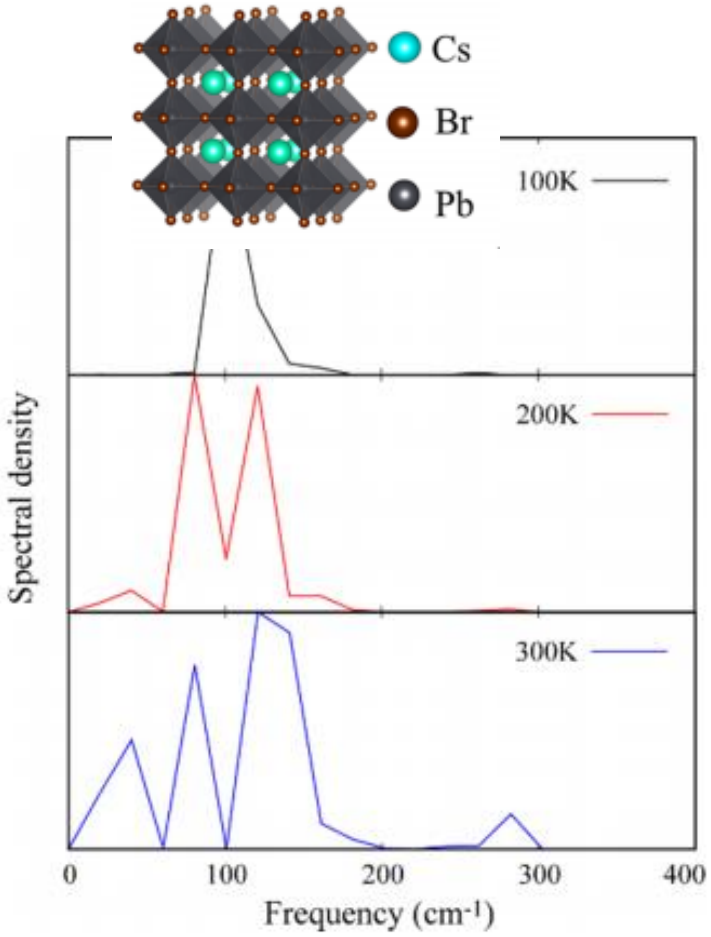


J Am. Chem. Soc. 2018, **140**, 15753

Temperature-dependent Carrier Lifetime





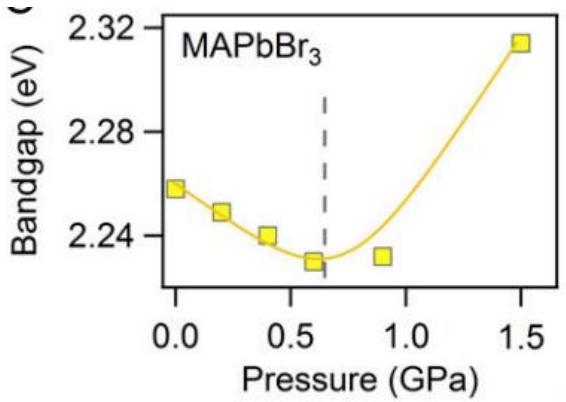


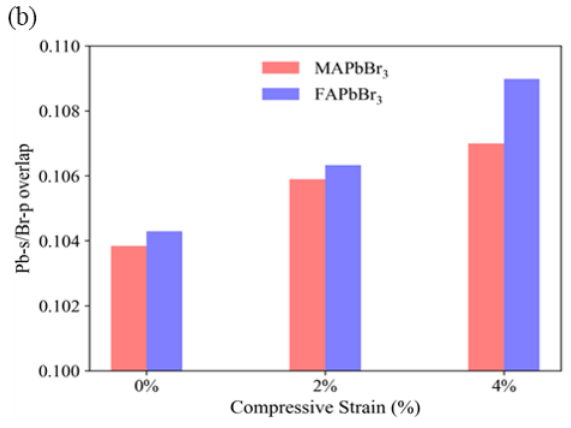
	d (Å)	θ (deg)	E_g (eV)	σ_E (eV)	NAC (meV)	T_2^* (fs)	T_1 (ns)
100 K	2.975	170.5	1.48	0.088	1.14	7.9	0.89
200 K	2.971	168.7	1.60	0.12	1.34	5.9	1.22
300 K	2.970	165.8	1.75	0.15	1.80	4.7	1.45

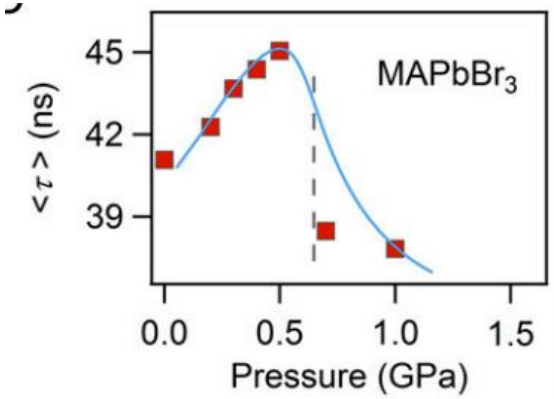
- Higher T increases **rotational disorder of organic cations** which suppresses fluctuation of Pb-I lattice in **hybrid organic-inorganic perovskite**
- Higher T activates **broad range of phonon modes**, accelerating pure-dephasing in **all-inorganic perovskite**

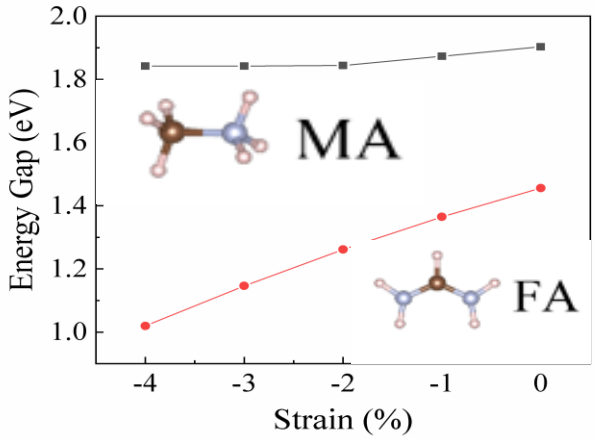
Inorgan. Chem. Front., 2022, **9**, 5549
J. Phys. Chem. Lett. 2019, **10**, 6219
ACS Energy Lett., 2018, **3**, 2713

Anti-correlation between Carrier Lifetime and Eg









		Energy Gap (eV)	|NAC| (meV)	Dephasing Time (fs)	Lifetime (ns)
$MAPbBr_3$	0	1.90	0.52	6.05	10.32
	-2%	1.85	0.53	5.32	12.49
	-4%	1.84	0.55	4.90	12.63
$FAPbBr_3$	0	1.46	0.58	4.93	0.38
	-2%	1.26	0.63	4.34	0.35
	-4%	1.02	0.66	3.39	0.30

- The larger band gap variations is induced by stronger Pb-s/Br-p overlap, facilitated by the larger Pb-Br-Pb angle
- Compression suppresses the fluctuations of organic cations, unlocks the Pb-Br vibration and enhance the electron-phonon interactions

Kong et al, PNAS, 2016, 113, 8910

Chem. Mater. 2020, **32**, 4707

Chem. Mater., to be submitted

Summary

- Longer alkyl chain slows down interlayer CT
- SOC accelerates nonradiative dynamics
- Simple Hamiltonian repetition extends the NA-MD time scale
- Defects trap/de-trap free charges (softness)
- Breaking the hybridization of dangling states passivate defect states
- Disorder (unusual T and P dependence)

Acknowledgements

Collaborators

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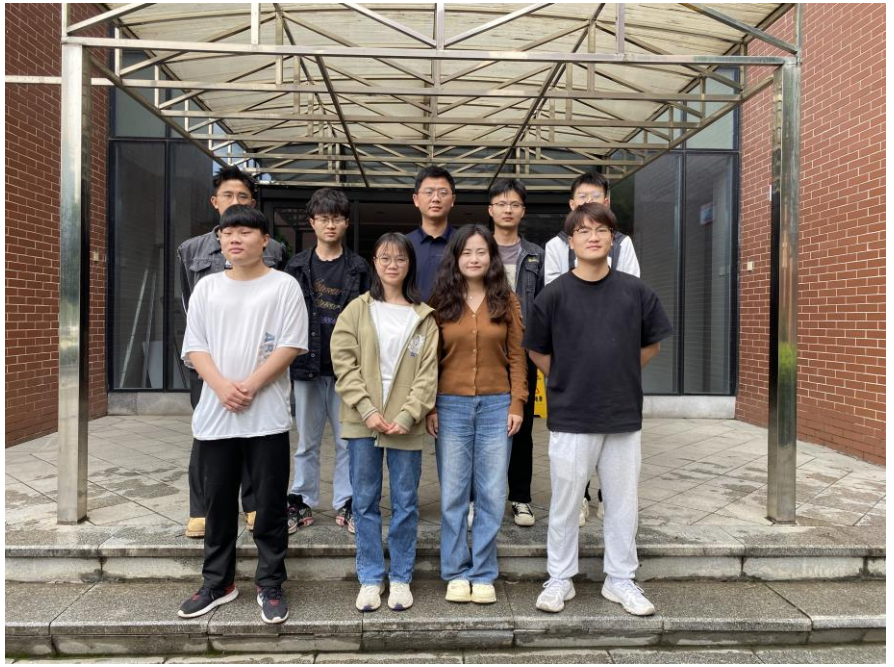
- Alexey V. Akimov (U Buffalo, U.S.)
- David Beljonne (UMONS, Belgium)
- Zhufeng Hou (CAS, China)



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Jiayi, Ting, Xueying, Ning

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