Hot Electron Cooling in Silicon Nanoclusters via Landau–Zener Nonadiabatic Molecular Dynamics

Brendan Smith
SUNY Buffalo
Akimov Research Group

University at Buffalo The State University of New York

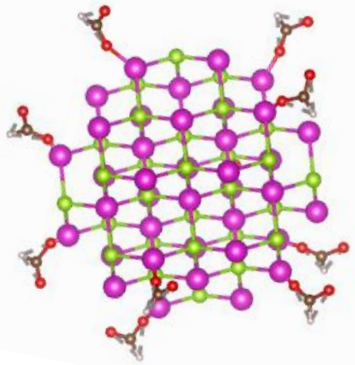
Motivation / Background

Goal: **Simulate Non-Adiabatic dynamics in nanoscale / periodic systems**

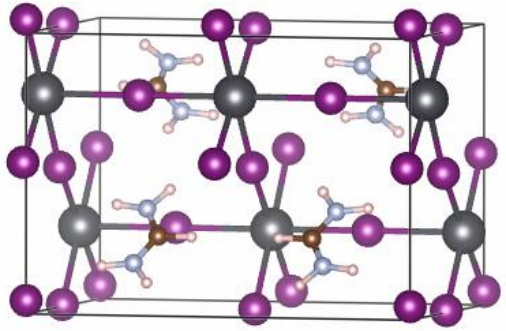
High demand for clean energy sources
One way to meet this demand is though photovoltaic cells

Nanoscale and periodic systems are common sensitizers in photovoltaic devices

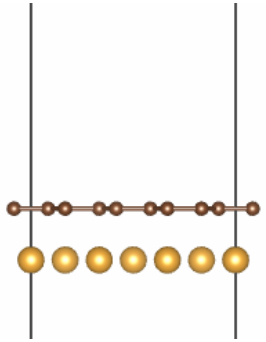
Nanoclusters



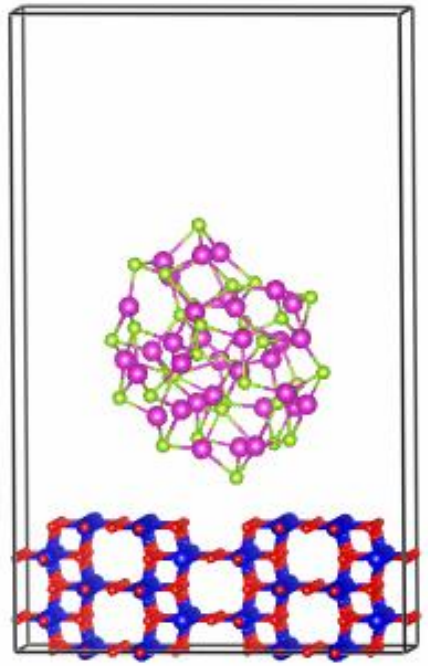
Periodic Solids



Monolayer Interface



Cluster / Slab Interface



Nonadiabatic dynamics is ***very*** expensive for nanoscale and periodic systems

Why?

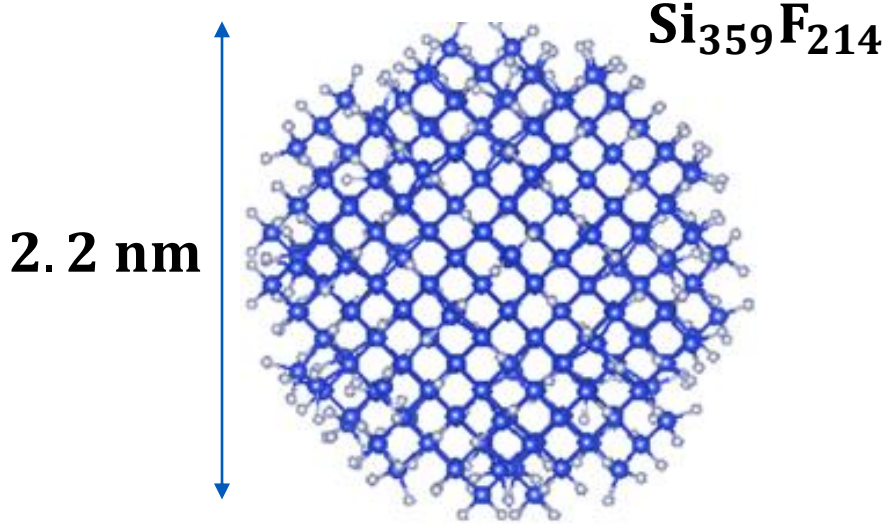
- Computational expense scales with system size
- Simulations require many molecular dynamics trajectories (initial conditions).
- Trajectories need to be sufficiently long enough to capture the dynamical process.

Affordable NAMD for Large Systems

Classical Path Approximation (CPA)

Prezhdo, O. V.; Duncan, W. R.; Prezhdo, V. V. *Progress in Surface Science* 2009, *84* (1), 30–68

aka Neglect-of-Back-Reaction Approximation (NBRA)



Si atoms

4 x 359 = 1,436 electrons

F atoms

7 x 214 = 1,498 electrons

1,436 + 1,498 = 2,934 electrons

- Changes to a single electron make only a small change to the density
- Allows for the use of precomputed nuclear trajectories for NAMD

Makes NAMD for large systems possible

Can still be expensive

NBRA workflow

Smith, B.; Akimov, A. V. *JPCL.* 2020, *11* (4), 1456–1465.

1. **Perform a sampling of a certain electronic state**
   ETA: days - weeks

2. **Compute H_{vib} for all trajectories for all times**
   ETA: days - weeks

3. **Compute nonadiabatic dynamics**
   ETA: day(s)

WFC-based NBRA

NAC-Free NBRA

Obtain nuclear coordinates and state energies for all trajectories for all times

$$D_{ij} \approx \frac{\langle \Phi_i(t) | \Phi_j(t-dt) \rangle - \langle \Phi_j(t) | \Phi_i(t-dt) \rangle}{2dt}$$

$$P_{ij} = -2dt \frac{Re\left(c_i c_j^* D_{ij}\right)}{c_i c_i^*}$$

$$P_{ij} = \exp\left(-\frac{\pi}{2\hbar} \sqrt{\frac{Z_{ij}^3(t_{min})}{\ddot{Z}_{ij}(t_{min})}} \right)$$

Belyaev, A. K.; Lebedev, O. V. *Phys. Rev. A* 2011, *84* (1), 014701

Landau-Zener within NBRA

Belyaev, A. K.; Lebedev, O. V. *Phys. Rev. A* 2011, *84* (1), 014701

In 2011, Belyaev and Lebedev (BL) reformulate original LZ formula in terms of only adiabatic properties:

- Energy gaps
- Time-derivatives

$$P_{ij}^{LZ,diabatic} \quad \Leftrightarrow \quad P_{ij}^{LZ,adiabatic}$$

$$\exp\left(-\frac{2\pi H_{ij}^2}{\hbar v\left|H'_{ii}+H'_{jj}\right|}\right) \qquad \exp\left(-\frac{\pi}{2\hbar}\sqrt{\frac{Z_{ij}^3(t_{min})}{\ddot{Z}_{ij}(t_{min})}}\right)$$

Electronic coupling

2nd derivative

Diabatic energy

Adiabatic energy

Such properties are easily obtainable with Popular electronic structure software packages

Energy Gaps as N-point Lagrange Interpolants

$$Z_{ij}(t) = \sum_{n=1}^{N} Z_{ij}(t_n) \prod_{m=1,m\neq n}^{N} \left(\frac{t-t_m}{t_n-t_m}\right)$$

Computed derivatives with standard differentiation

$$\frac{\partial^2 Z_{ij}}{\partial t^2}(t) = \frac{1}{dt^2}\left[Z_{ij}(t_{n-1}) - 2Z_{ij}(t_n) + Z_{ij}(t_{n+1})\right]$$

$$t_{min} = \frac{\left(Z_{ij}(t_{n-1}) - Z_{ij}(t_{n+1})\right)dt}{2\left(Z_{ij}(t_{n-1}) - 2Z_{ij}(t_n) + Z_{ij}(t_{n+1})\right)} \qquad \frac{\partial^2 Z_{ij}}{\partial t^2}(t) > 0$$

Energy gaps and derivatives used to compute P_{ij}

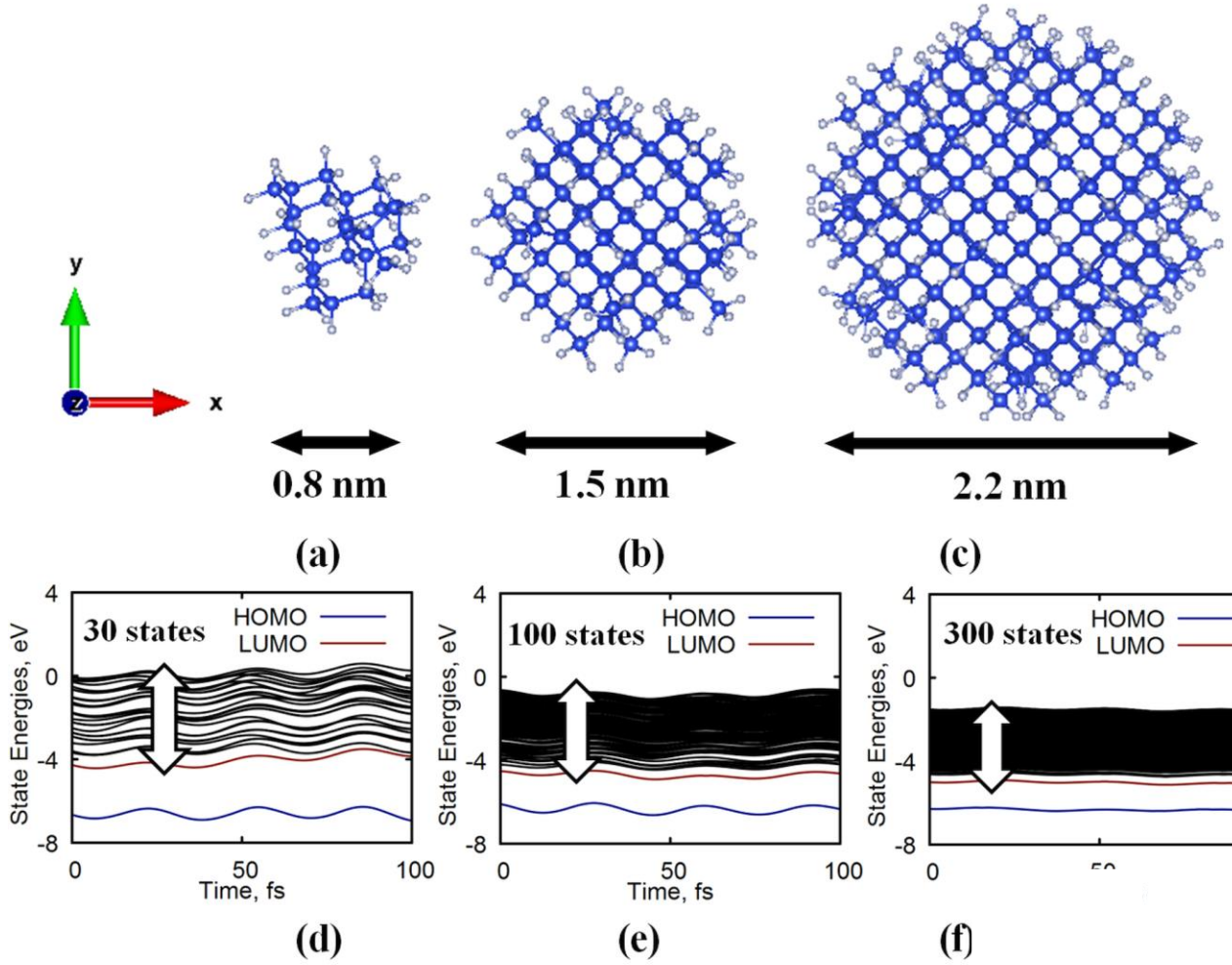
NAC-Free NAMD in Silicon Nanoclusters

- Computations are carried out using the Libra software package interfaced with the DFTB+ program

Akimov, A. V. *J. Comput. Chem.* 2016, *37* (17), 1626–1649
Aradi, B et al. *J. Phys. Chem. A* 2007, *111* (26), 5678–5684.

https://github.com/Quantum-Dynamics-Hub/libra-code

- Studied hot electron relaxation in H- and F-terminated silicon nanocrystals
- Effect capping atom mass and electronegativity on the NAMD is investigated
- Effect of nanocrystal size on NAMD is also considered

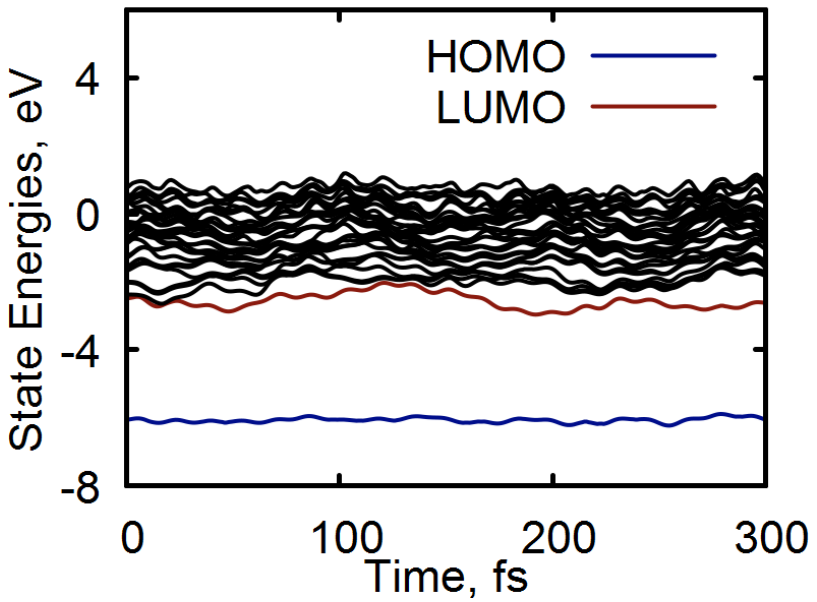


Effect of Capping Atom

Central question: How does the choice of capping atom affect NA transition probability?

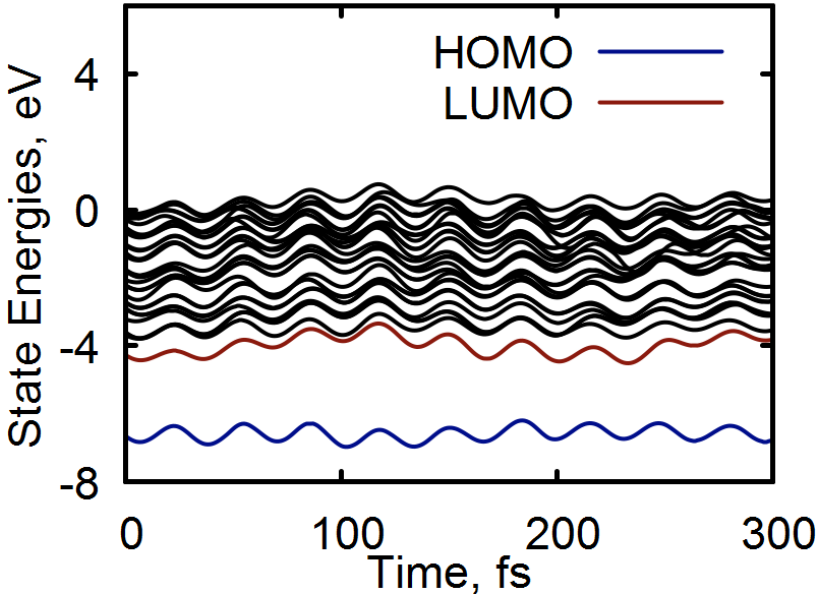
Silicon Nanocrystal termination options

Hydrogen termination



Smaller energy gaps
Faster energy fluctuation

Fluorine termination



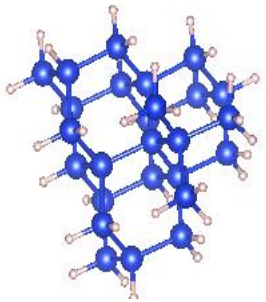
Larger energy gaps
Slower energy fluctuation

Chemical identity strongly effects energy gaps / density of states

$$P_{ij} = \exp\left(-\frac{\pi}{2\hbar}\sqrt{\frac{Z_{ij}^3(t_{min})}{\ddot{Z}_{ij}(t_{min})}}\right)$$

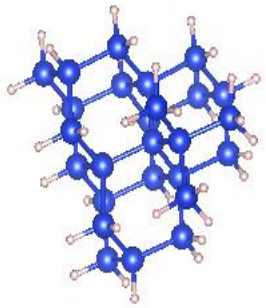
Mass primarily effects the energy gap fluctuations

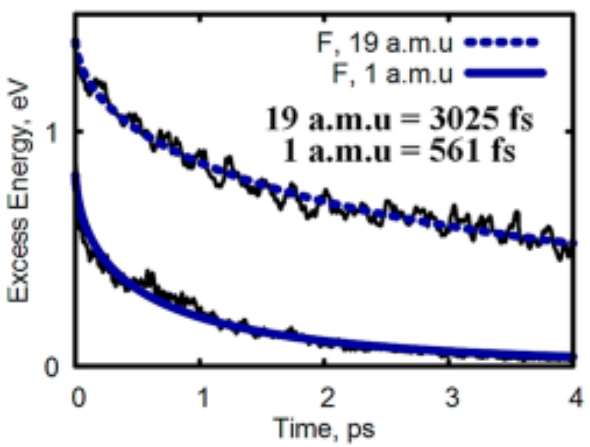
Mass vs. Chemical Identity

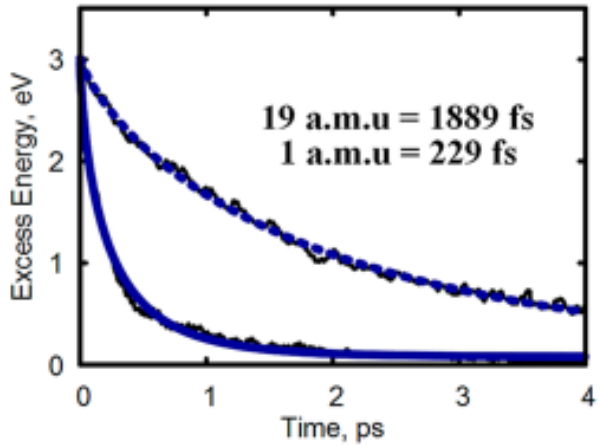


Swap atomic masses

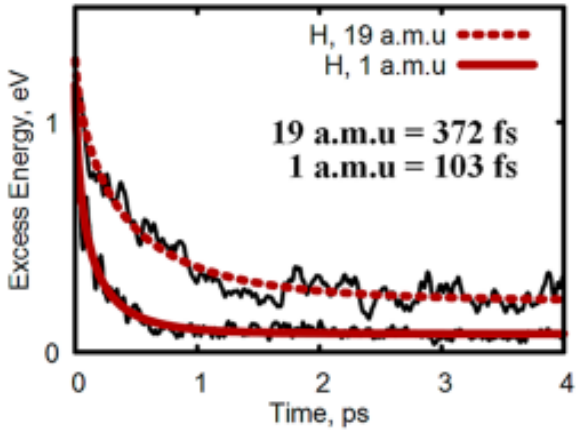
Keep identity fixed

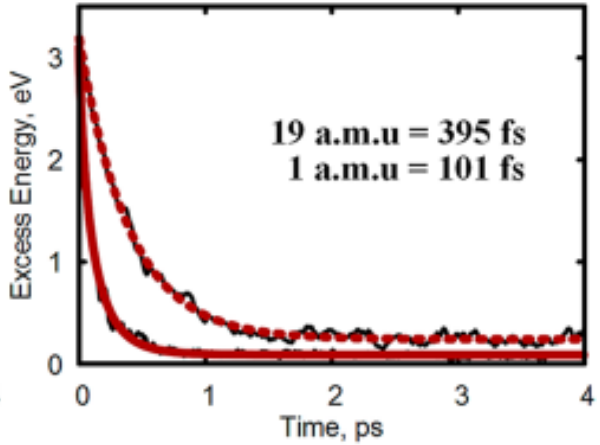




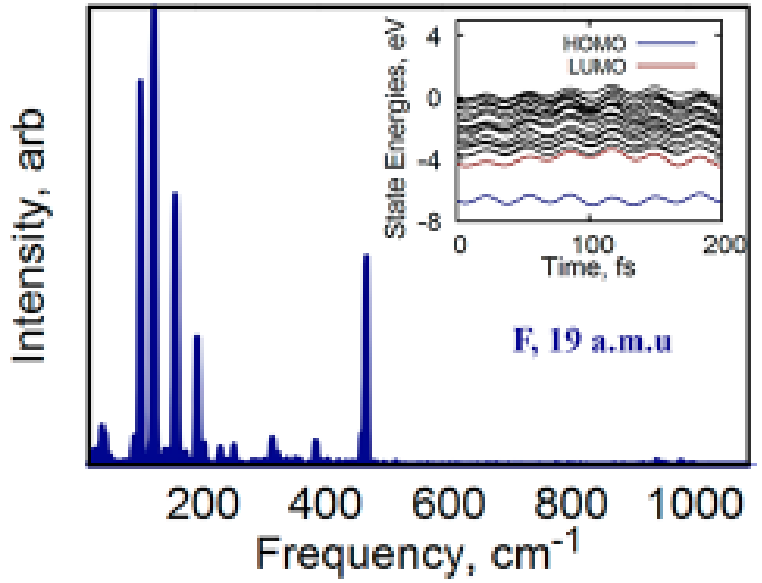


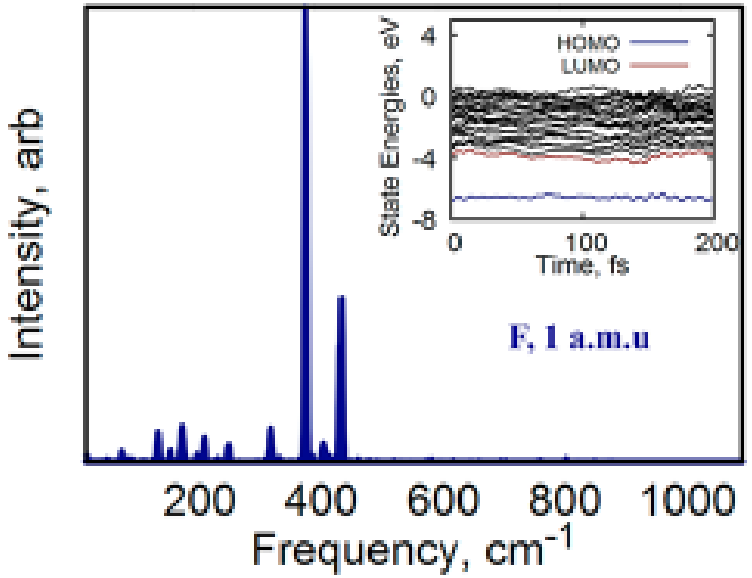
6-7x slow down





4x slow down





Size Effect

Hydrogen Termination

(fs)	1 eV	2 eV	3 eV
$Si_{26}H_{36}$ (0.8 nm)	103	126	101
$Si_{66}H_{40}$ (1.5 nm)*	115 - 150	52 (1.3 eV)	-
$Si_{105}H_{94}$ (1.5 nm)	182	95	82
$Si_{359}H_{214}$ (2.2 nm)	59	64	72

Fluorine Termination

(fs)	1 eV	2 eV	3 eV
$Si_{26}F_{36}$ (0.8 nm)	3025	1998	1889
$Si_{66}F_{40}$ (1.5 nm)**	444 / 493	472 / 704	528 / 1136
$Si_{105}F_{94}$ (1.5 nm)	199	270	280
$Si_{220}F_{120}$ (2.2 nm)**	268 / 290	277 / 442	263 / 623
$Si_{359}F_{214}$ (2.2 nm)	118	150	142

* Reeves, K. G. et al. *Nano Lett.* 2015, *15* (10), 6429–6433

** Wong, J. C.; Li, L.; Kanai, Y. JPCC 2018, 122, 29526−29536.

Summary

- A cost-effective algorithm is developed for computing nonadiabatic dynamics in large chemical systems
- The cost of nonadiabatic dynamics is only slightly greater than the cost of a molecular dynamics trajectory
- A key advantage is that the new method naturally incorporates decoherence
- We find that hot electron cooling becomes faster as silicon quantum dots becomes larger. Hot electron cooling is slower when fluorine is used as the capping atom
- Slower dynamics fluorine termination options is rationalized by larger energy gaps and slower gap fluctuations

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Acknowledgements

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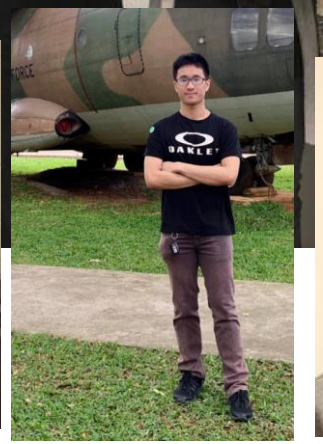
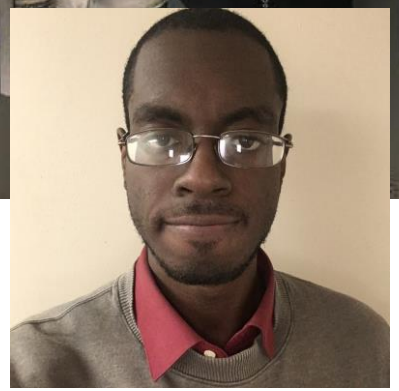
https://akimovlab.github.io/group.html





Advisor

Dr. Alexey Akimov

Group Members

Mahsa Jabbar
Story Temen
Achira Boonrath
Yating Yang
Mahsa Mofidi
Austin Cadore
Mohammad Shakiba

SUNY Buffalo Center for Computational Research

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