Charge transport in electrochemical reactions: ab initio simulations

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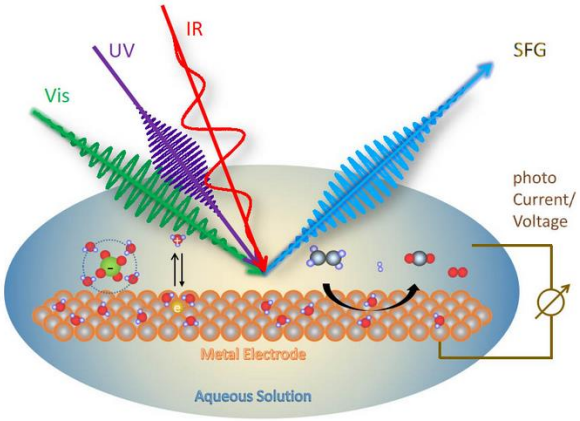
Half of electrochemical reaction is charge transport !

The critical charge transport questions in electrochemical reactions:



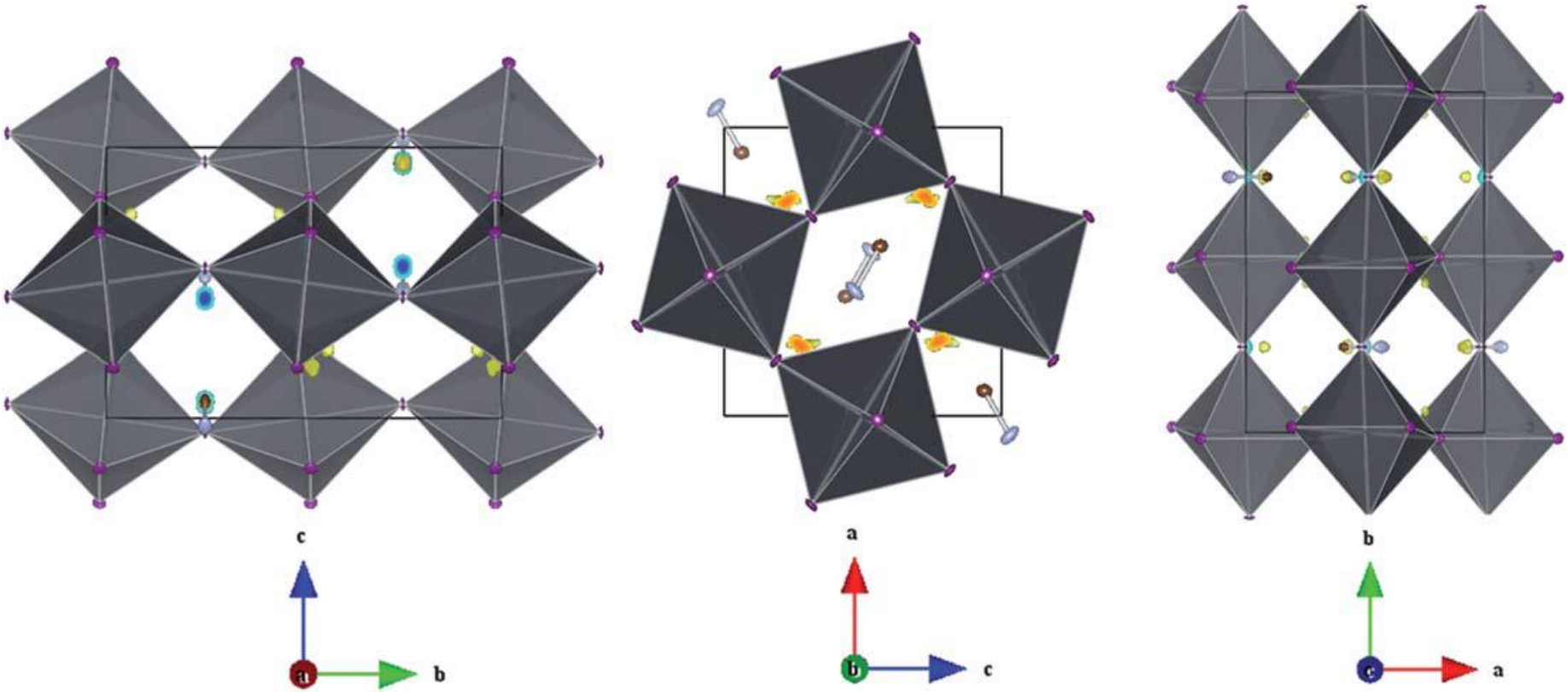
- **Bulk transport in electrodes, like oxides**
- **The charge transport through protection layers**
- **Where the electron will be stored before reactions?**
- **Hot carrier cooling and transport (hot carrier induced chemical reaction?)**
- **Is electrochemical reaction always an adiabatic process? Can charge transport become the bottleneck?**

Outline

- ❖ Carrier mobility in hybrid perovskite (an unconventional picture)
- ❖ Charge transfer in c-Si/a-SiO2 interface (protection layer)
- ❖ Hot carrier cooling and charge transfer
- ❖ Direct rt-TDDFT simulation of nonadiabatic process and reaction

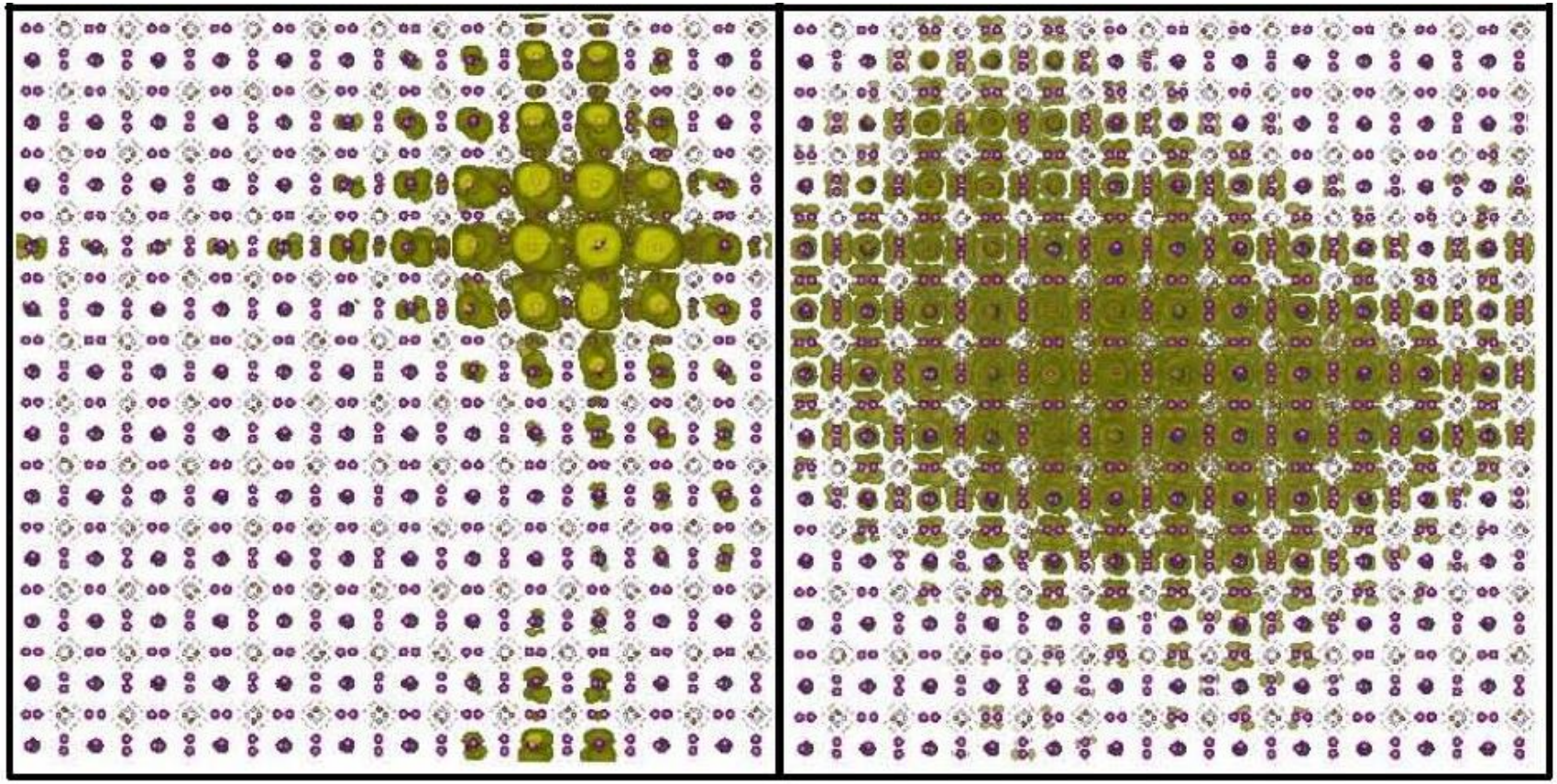
The random orientation of the CH_3NH_3 molecule

- There is no experimental evidence for the ferroelectricity
- The CH_3NH_3 has random orientation (8 possible directions)
- What is the electronic effects of this random orientation?



Baikie, et.al. J. Mater. Chem. A. 2013, 1, 5628

Hybrid (CH3NH3)PbI_3 perovskite: electron localization



CBM **VBM**

~20,000 atoms
Using 60,000 processors, takes < 1 hour

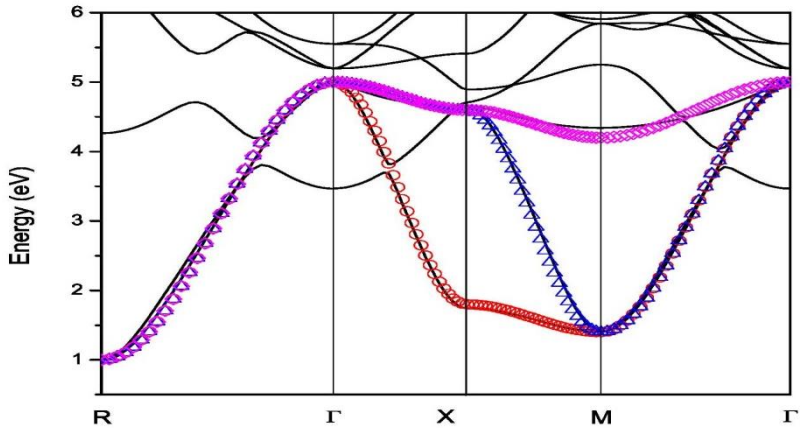
Some experimental observations about MAPbI3

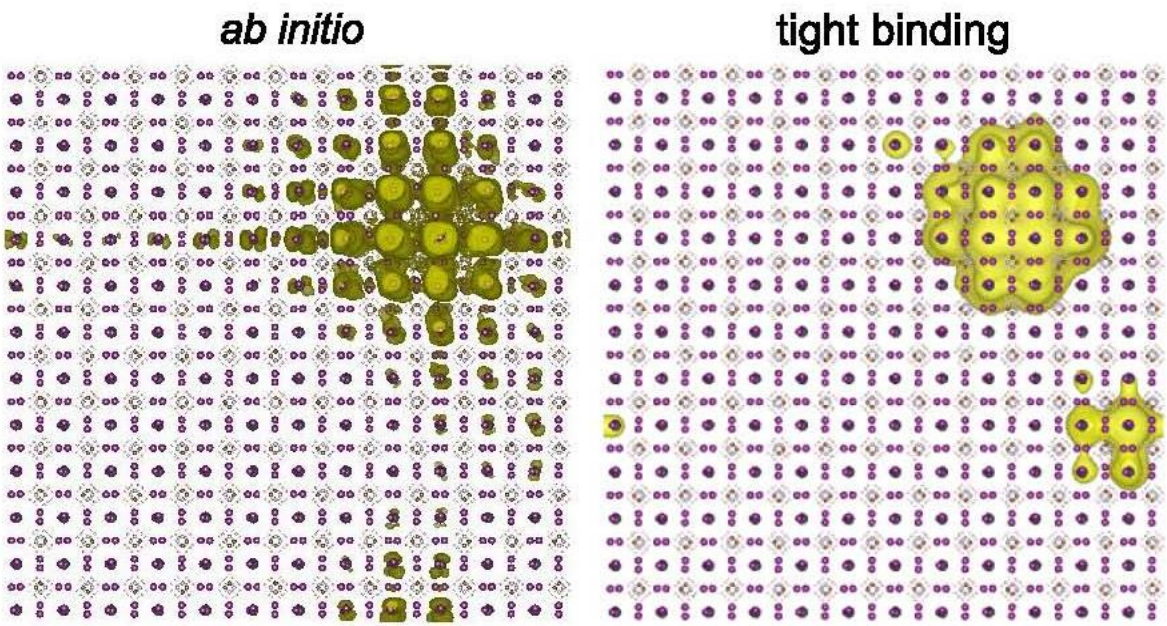
- Mean free path very long (μm?)
- Activated electron-hole recombination
- Large Auger effects at high concentration
- I-V curve increases after some initial period
- Large hysteresis
- I mobility

Many of these agree with electron-hole separation

How about mobility ?

Tight-binding fitting of the MAPbI3 Hamiltonian





Non-adiabatic molecular dynamics to simulate the wave function propagation

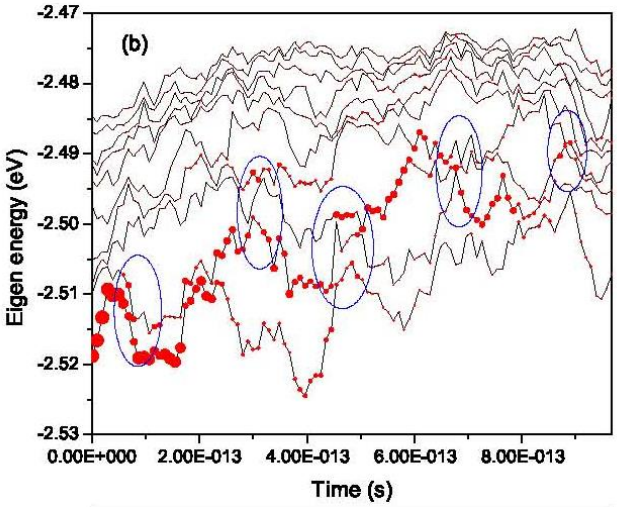
$$i\frac{\partial\varphi}{\partial t}=H(t)\varphi$$

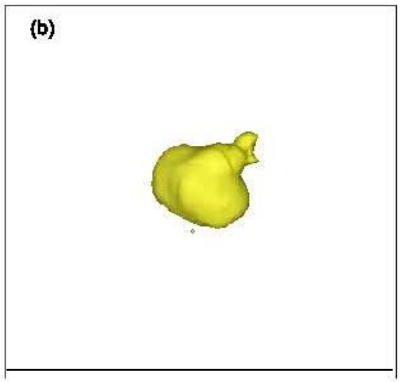
$$\psi(t+\Delta t)=\exp[-iH(t)\Delta t]\psi(t)$$

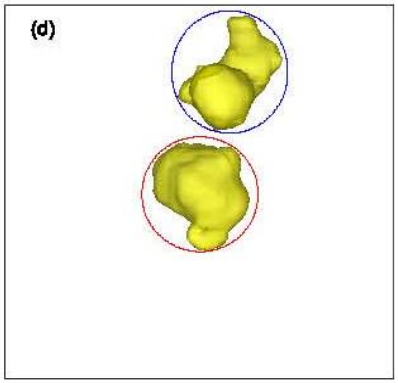
$$R^2(t)=\langle\psi(t)|(r-r0)^2|\psi(t)\rangle$$

H(t) is determined by CH_3NH_3 random flopping

What causes the electron diffusion?

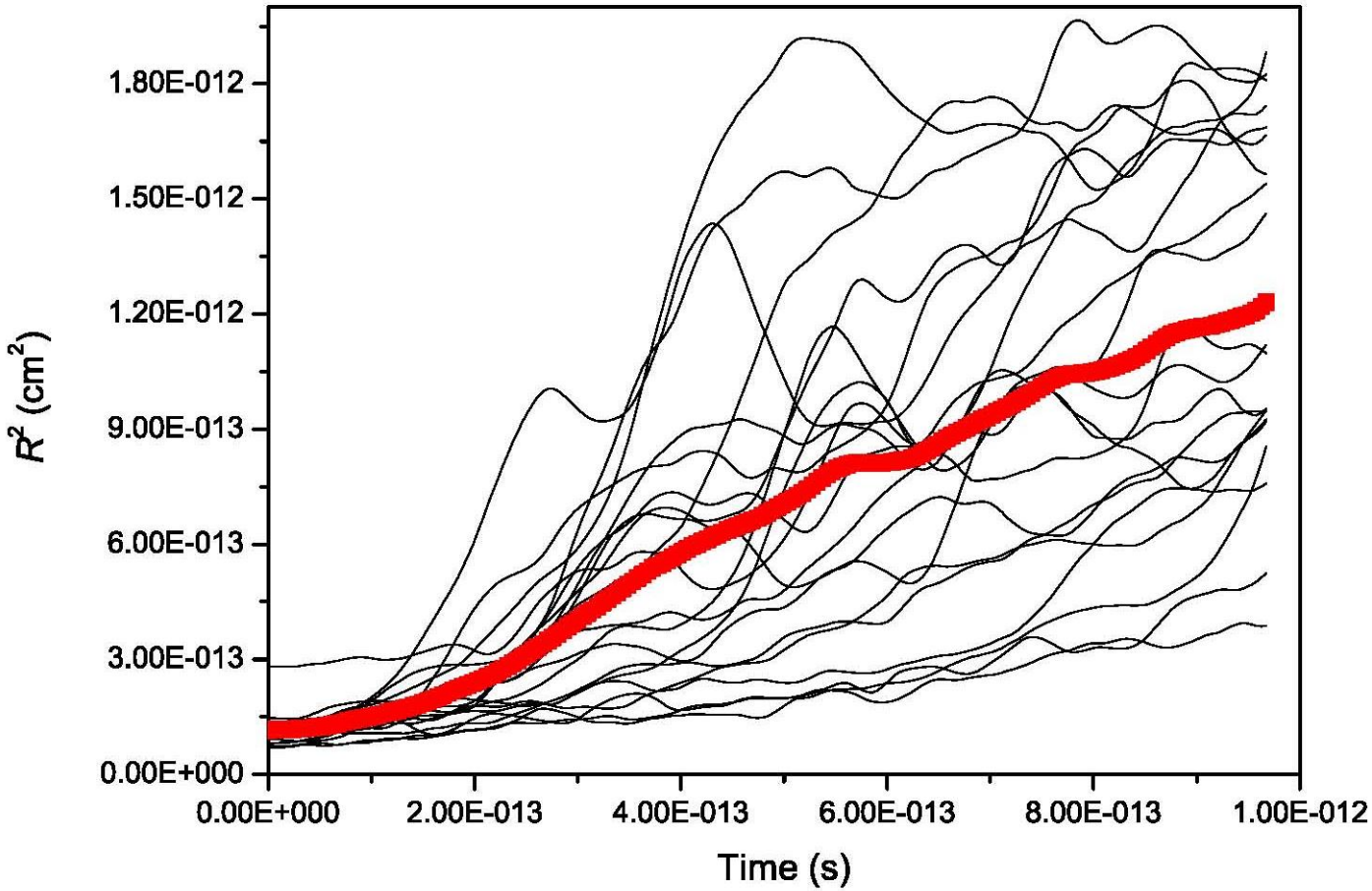




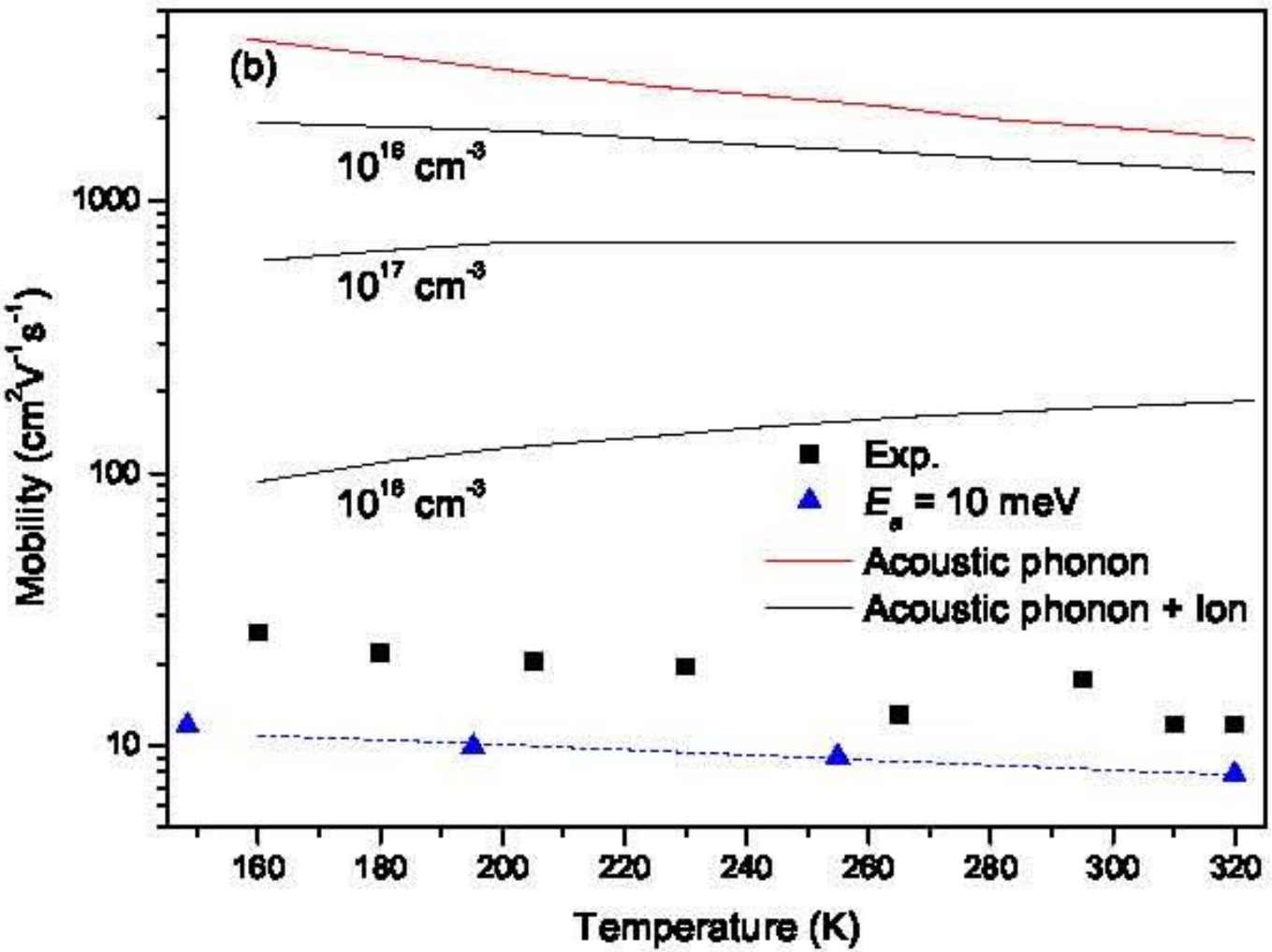


- ❖ **Each adiabatic state does not drift quickly, but their energy fluctuates**
- ❖ **When the energies of two nearby states crossing each other, the electron makes a hop.**

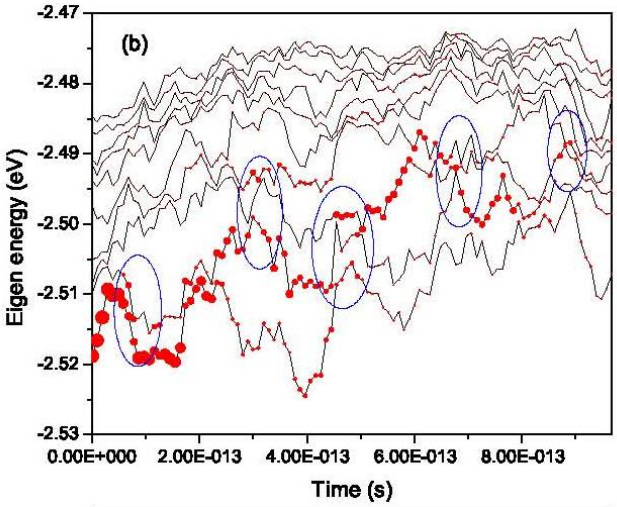
The calculation of diffusion constant from: R^2 (t)

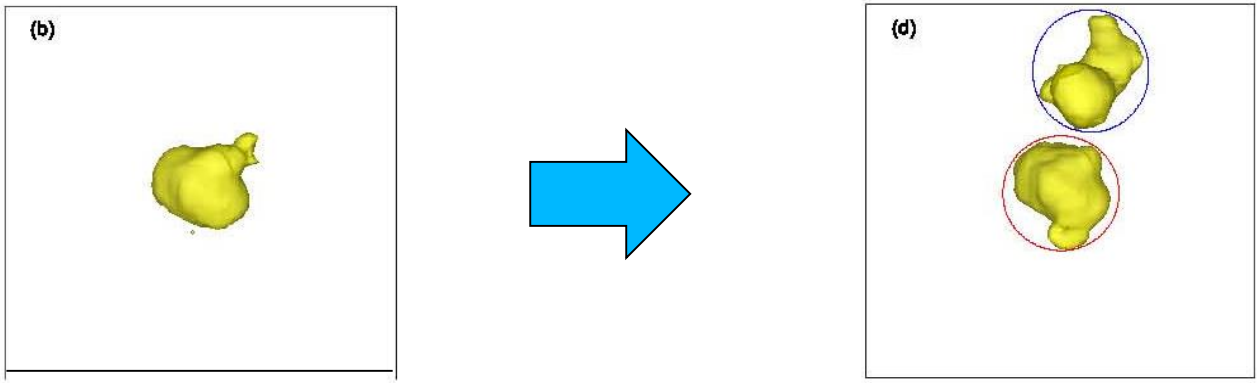


Comparison with experiments



What causes the electron diffusion?





- ❖ Each adiabatic state does not drift quickly, but their energy fluct
- ❖ When the energies of two nearby states crossing each other, the electron makes a hop.

Large polaron effects due to PbI3 lattice polarization

$$E = \langle\psi| H_0 |\psi\rangle - E^{\mathrm{P}}$$

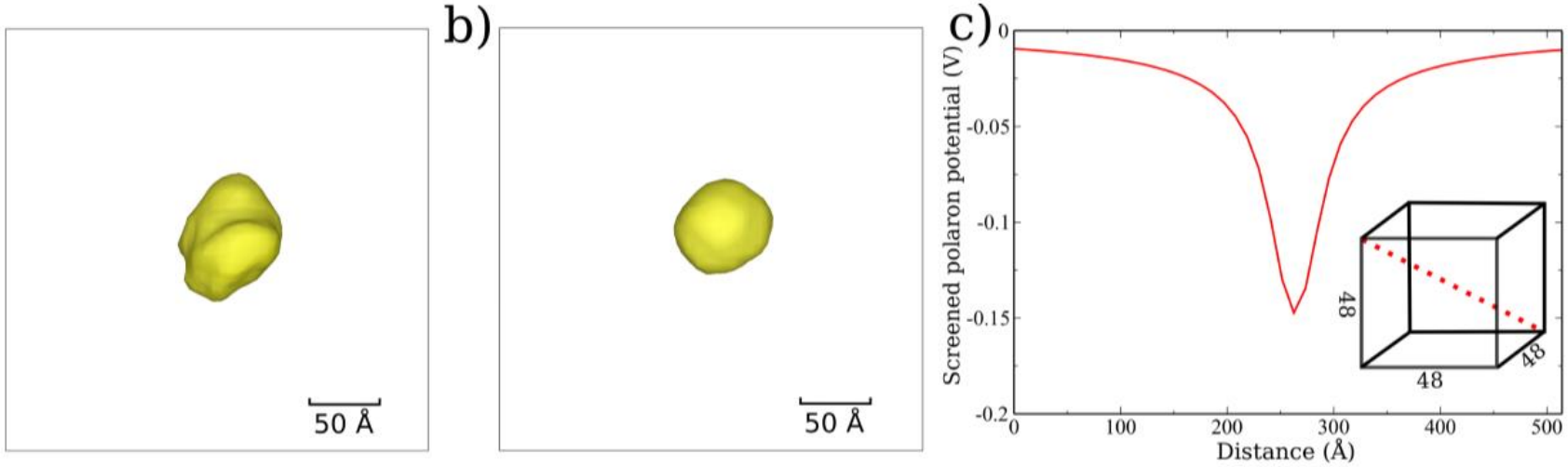
$$E^{\mathrm{P}} = \frac{1}{2\bar{\epsilon}} \int d\mathbf{r} V^{\mathrm{P}}(\mathbf{r})\rho(\mathbf{r})$$

$$H |\psi\rangle = (H_0 - \frac{1}{\bar{\epsilon}} V^{\mathrm{P}}[\rho]) |\psi\rangle = \epsilon |\psi\rangle$$

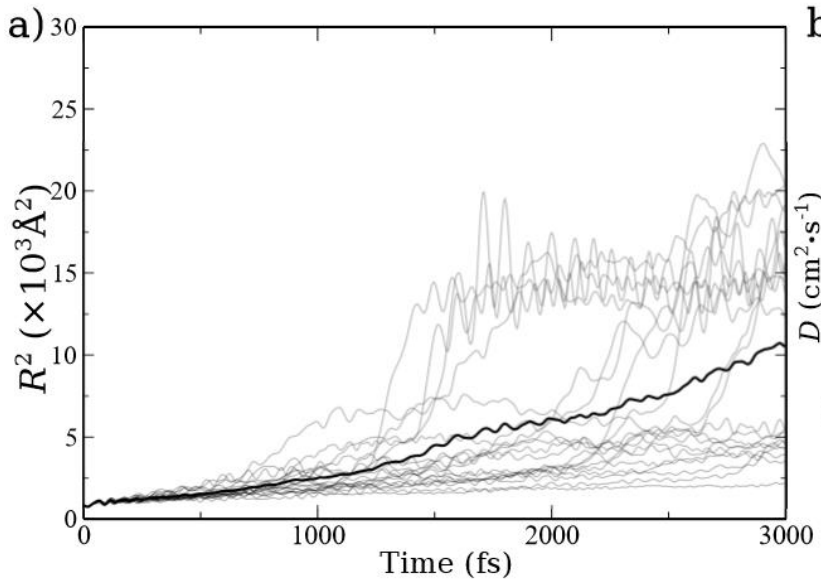
$$\psi(t+dt) = \mathrm{e}^{-iH(t)dt}\psi(t)$$

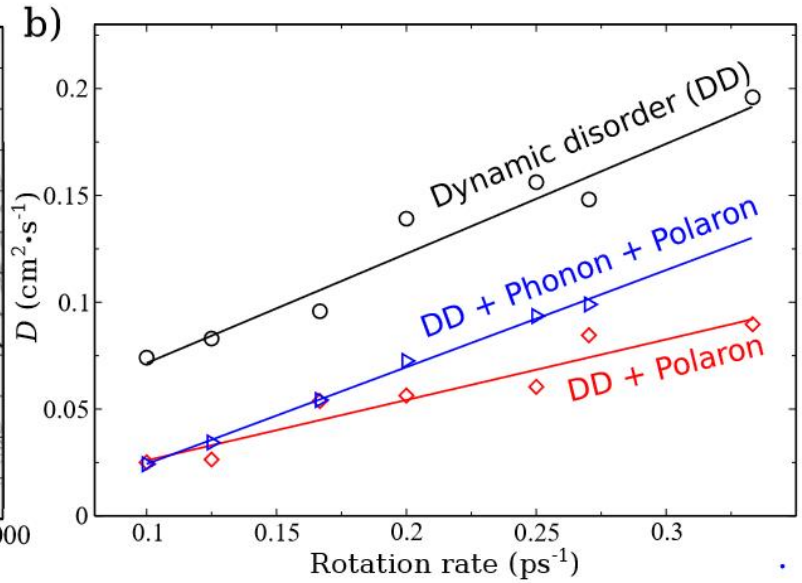
$$\approx \left[1 - iH(t)dt - \frac{1}{2}H^2(t)dt^2 + \frac{i}{6}H^3(t)dt^3 + \frac{1}{24}H^4(t)dt^4\right]\psi(t)$$

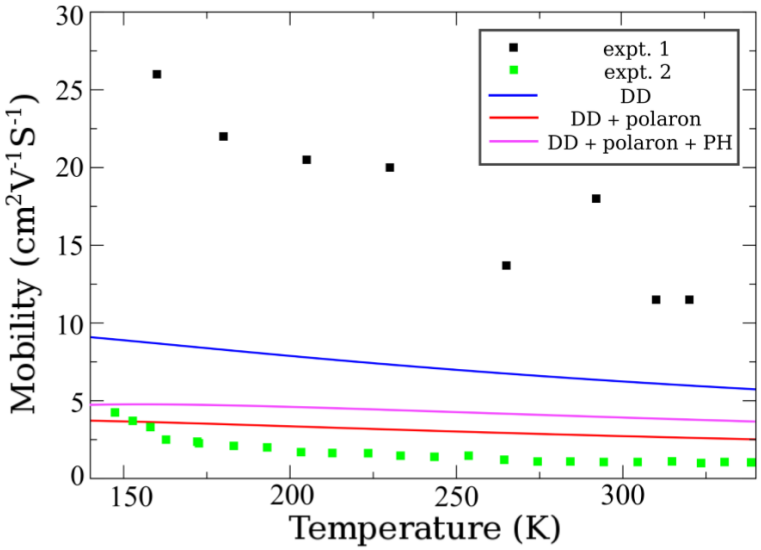
The effect of PbI3 lattice polarization



The effect of PbI3 lattice polarization







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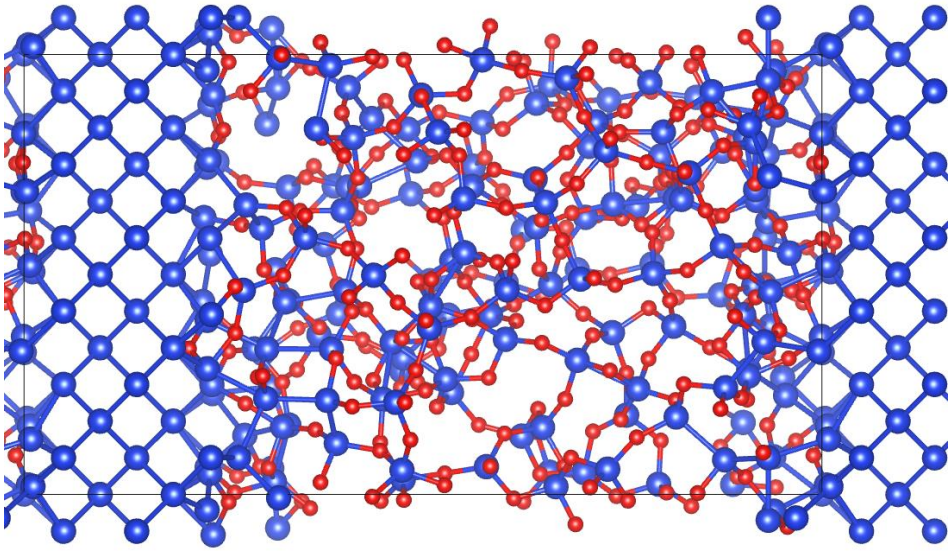
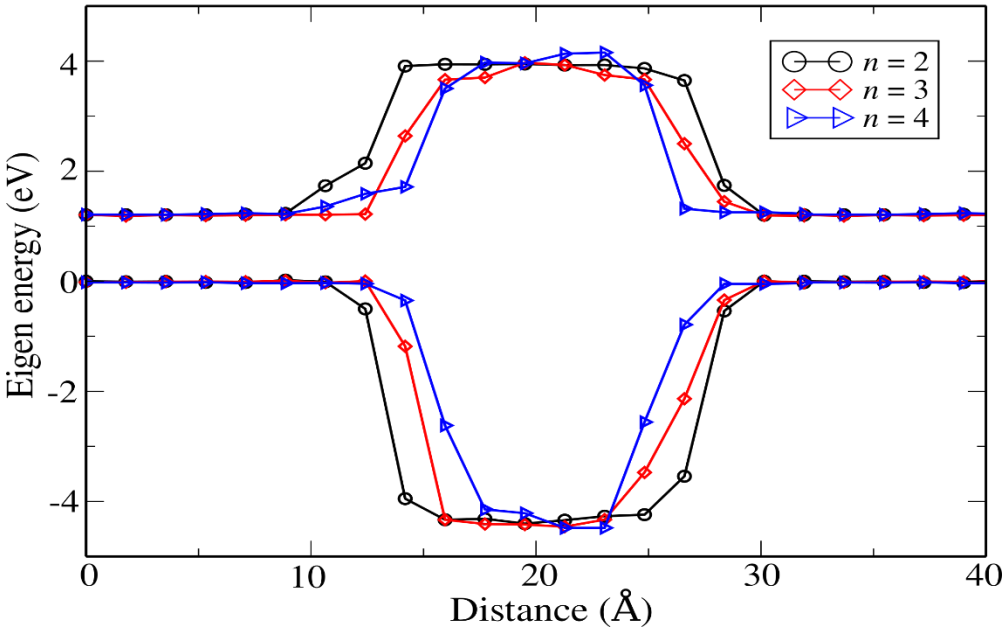
c-Si/a-SiO2 model interfaces (with different interfacial thickness)



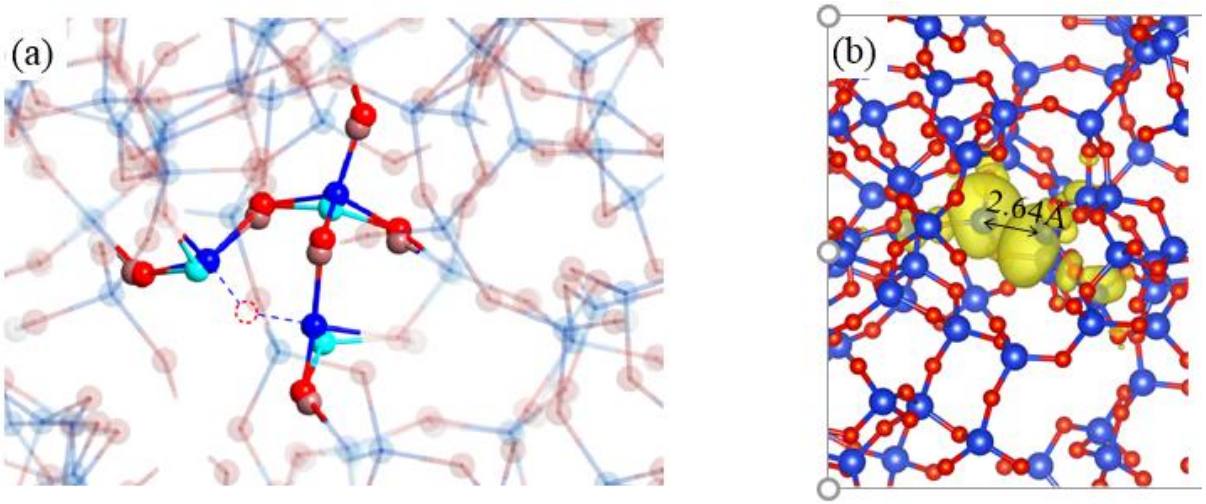


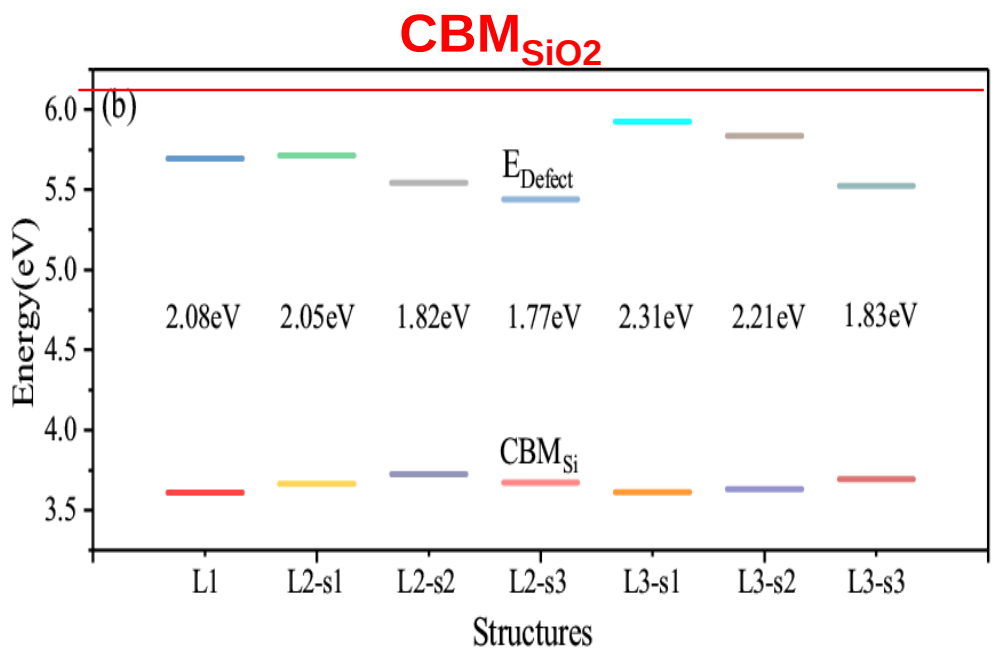
HSE calculations (to get the correct band gaps for Si and SiO2)

Band offset:

	calc.	exp.
CBM:	2.9,	3.0 (eV)
VBM:	4.4,	4.3 (eV)

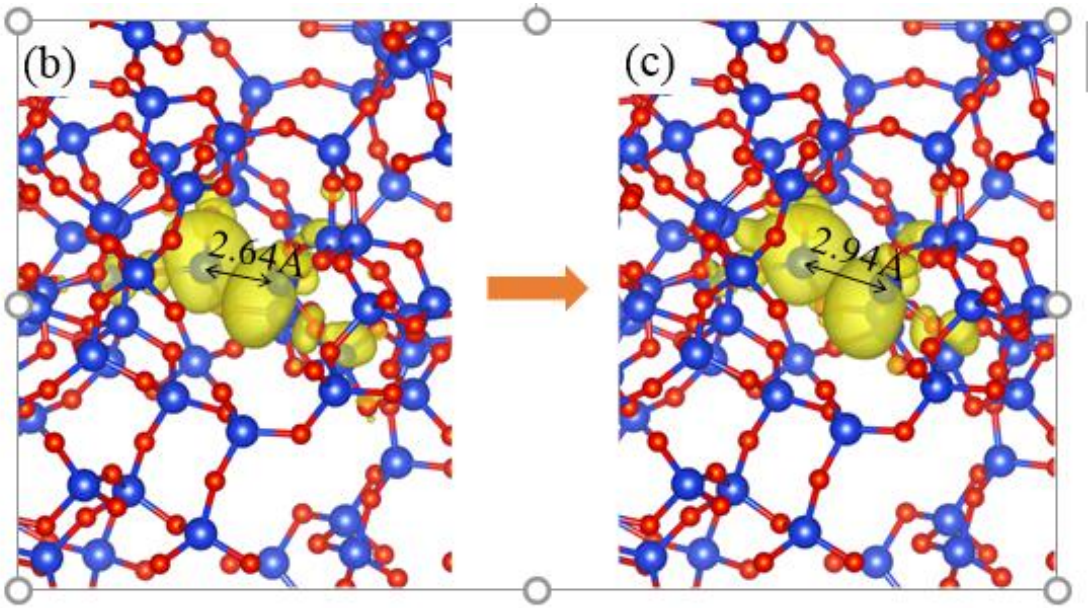
O vacancy in a-SiO2





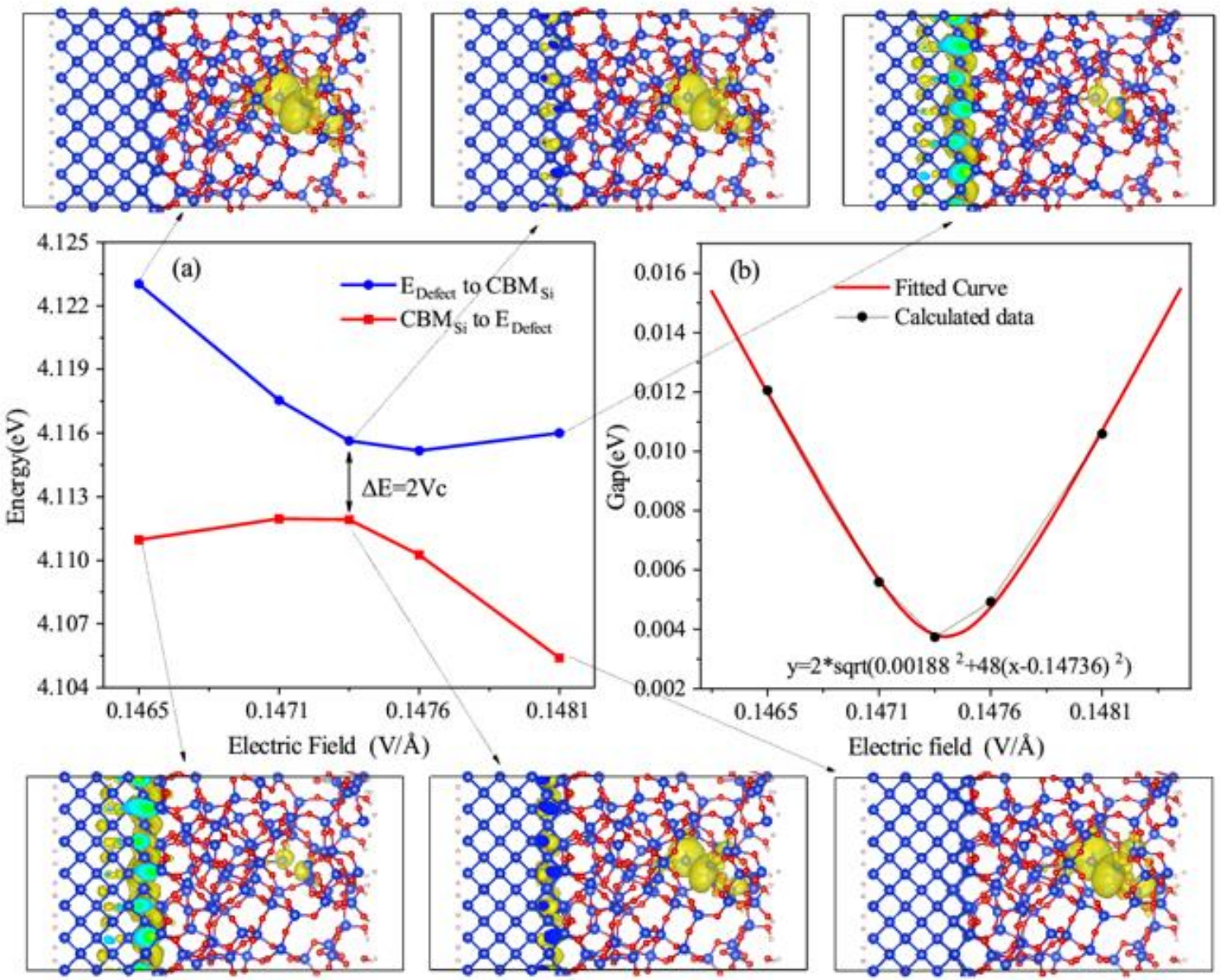
Reorganization energy and Marcus theory

$$\nu_{trapping} = \frac{2\pi}{\hbar}\left|V_C\right|^2 \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp\left[-\frac{(\Delta G+\lambda)^2}{4\lambda k_B T}\right]$$



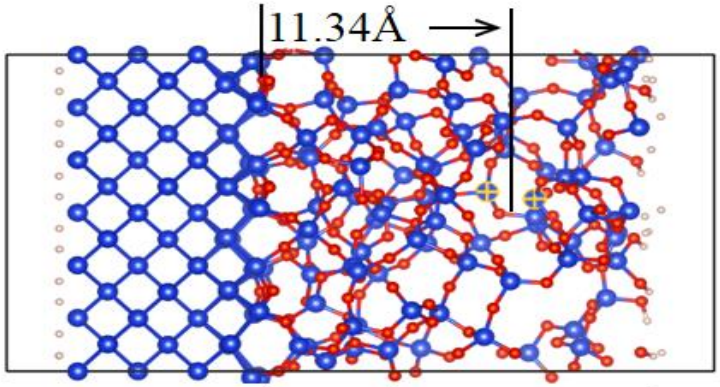
Re-organization energy: ~ 0.6 eV
(the Si-Si moves away after obtain the electron)

Electron state coupling

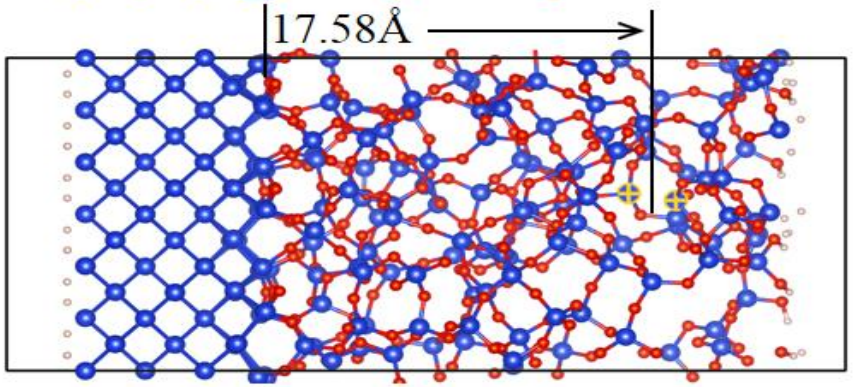


Changing the distance between defect and Si (while keeping the defect geometry the same)

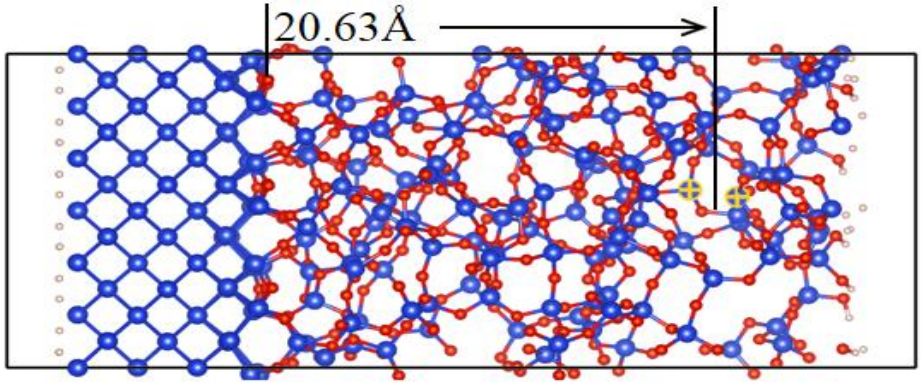
(a) L1

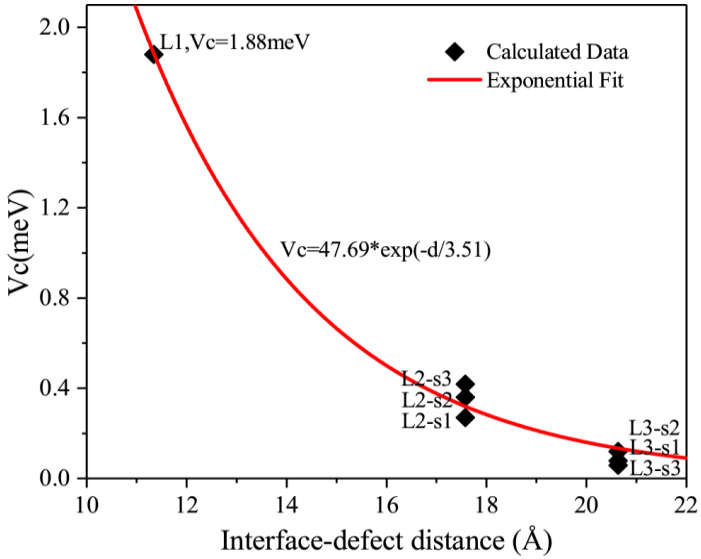


(b) L2-s1

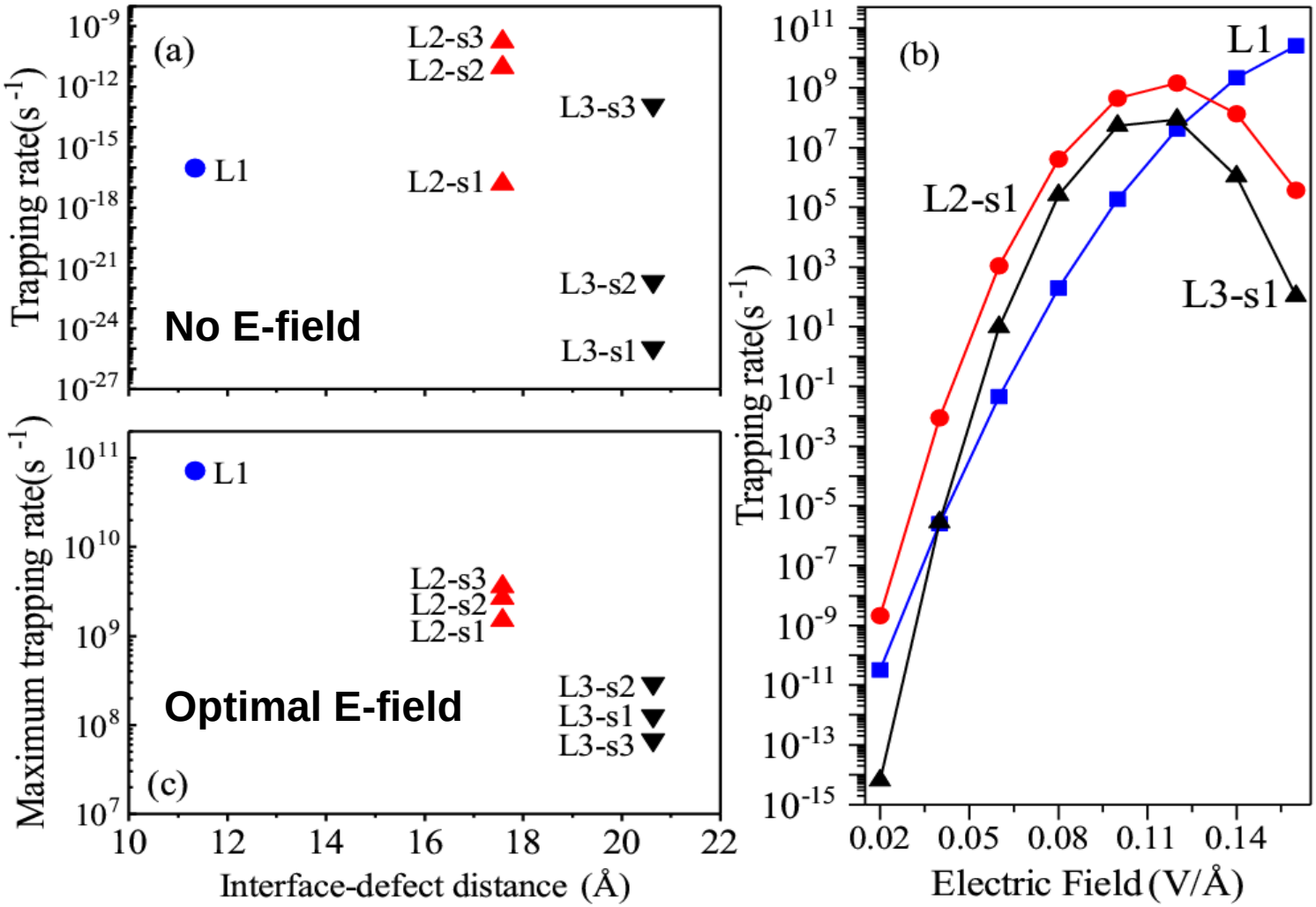


(c) L3-s1





Charge hopping rate as a function of electric field and distance



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NAMD based on adiabatic states

time-dependent Schrodinger equation

$$i\frac{\partial \psi}{\partial t} = H(t)\psi.$$

use adiabatic eigen states as basis function

$$\psi(t) = \sum_i C_i(t)\varphi_i(t).$$

$$H(t)\varphi_i(t) = \varepsilon_i(t)\varphi_i(t).$$

Ehrenfest dynamic

$$\dot{C}_i(t) = -i\varepsilon_i(t)C_i(t) - \sum_k C_k(t)V_{ik}(t)$$

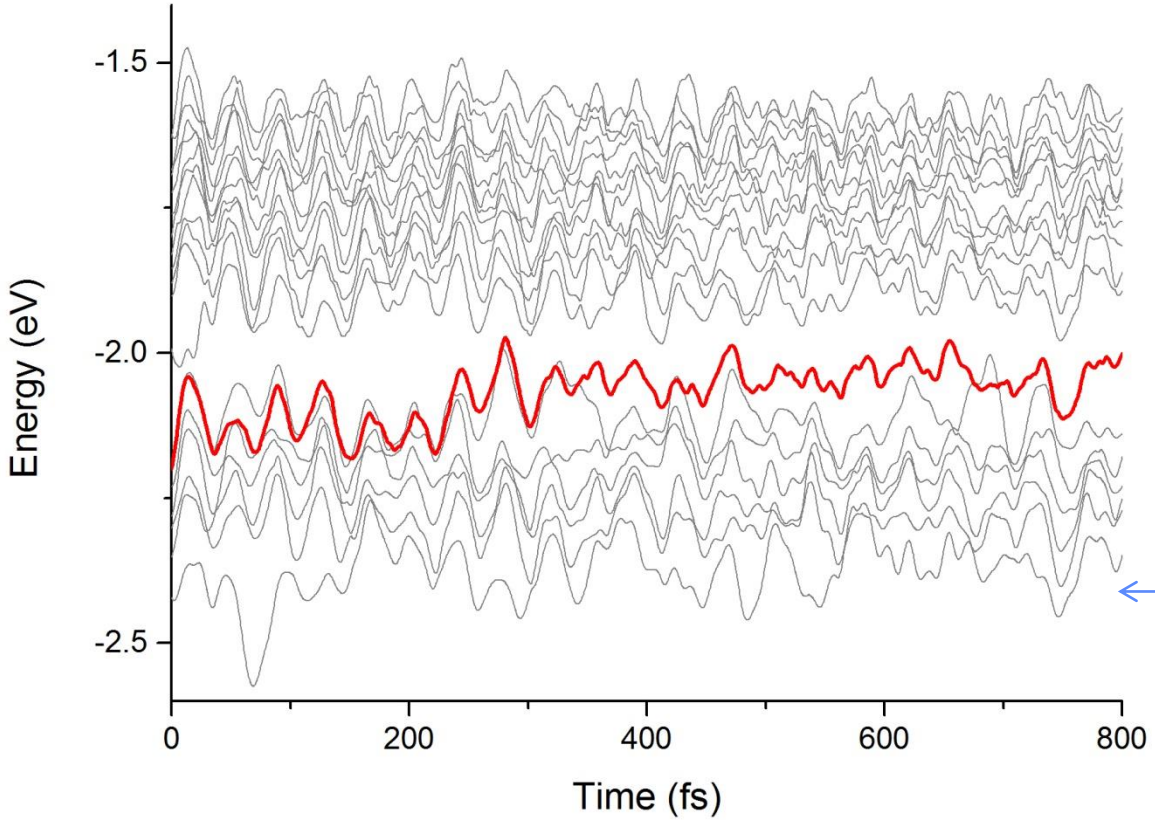
$$V_{ik}(t) = [\langle\varphi_i(t)|\varphi_k(t+\delta t)\rangle - \delta_{i,k}]/\delta t$$

Over heating of Ehrenfest dynamics

Ehrenfest dynamic in the presentation of density matrix

$$\dot{D}_{ij} = i(\varepsilon_j - \varepsilon_i)D_{ij} + \sum_k (D_{ik}V_{kj} - D_{kj}V_{ik})$$

Ehrenfest dynamic does not include zero-phonon effect, so electron is over heated.



Hot electron in a Si QD

CBM

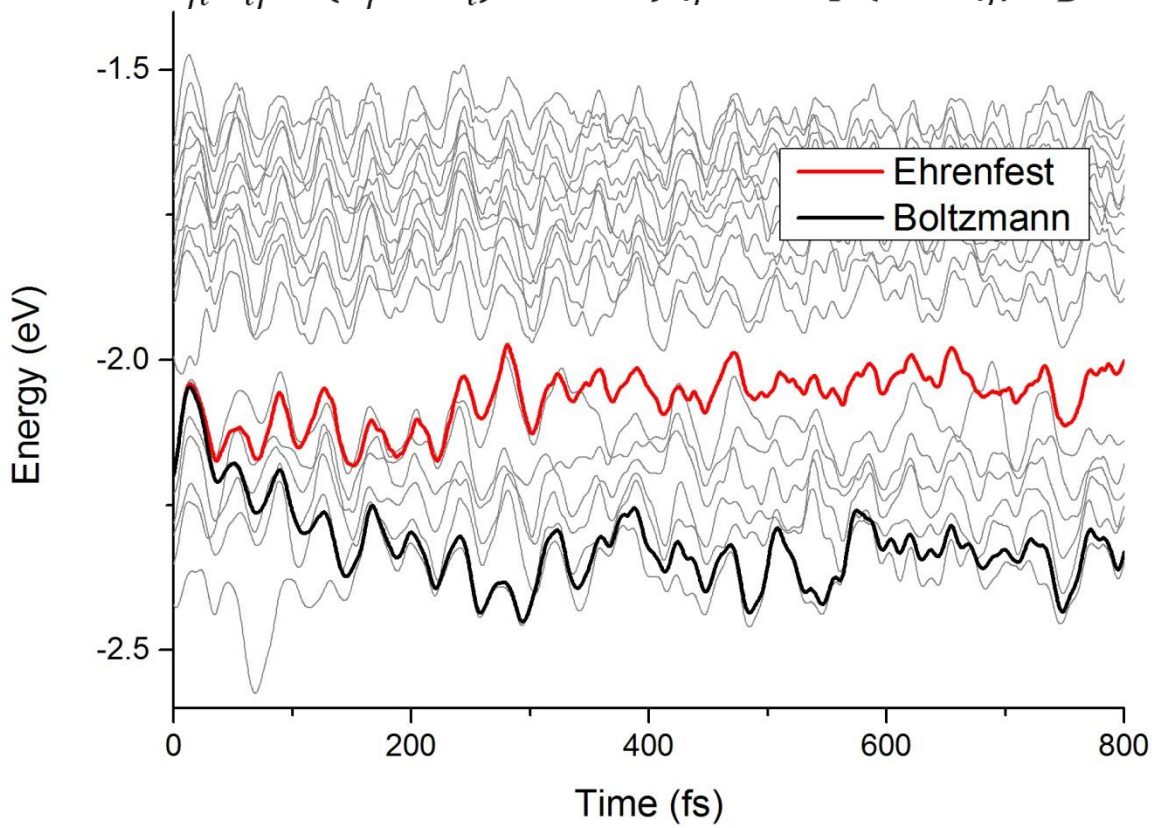
Introduce a Boltzmann factor in NAMD

Include a Boltzmann factor to introduce zero-phonon effect

$$\dot{D}_{ij} = i(\varepsilon_j - \varepsilon_i)D_{ij} + \sum_k (D_{ik}V_{kj}f_{jk} - D_{kj}V_{ik}f_{ik})$$

if $D_{ji}V_{ij} * (\varepsilon_j - \varepsilon_i) < 0 \quad f_{ij} = 1$

if $D_{ji}V_{ij} * (\varepsilon_j - \varepsilon_i) > 0 \quad f_{ij} = \exp(-\Delta\varepsilon_{ij}/k_B T$



Decoherence

Boltzmann algorithm does not consider decoherence.

For each eigen state φ_i, there is a corresponding wavefunction Ψ_i for atoms. Ψ_i describes how the atoms

A transition from i to j at t_0:

$$\varphi_i \Psi_i \rightarrow \varphi_j \Psi_j$$

$$\Psi_i(t_0) = \Psi_j(t_0)$$

$$\Psi_i(t_0 + t) \neq \Psi_j(t_0 + t)$$

$$< \Psi_i(t_0 + t) | \Psi_j(t_0 + t) > = \exp(-t/\tau_{ij})$$

τ_{ij} **is the decoherence time**

Off-diagonal terms in the density matrix decay exponentially. This is not included in the Boltzmann

A new formalism

It includes both: Boltzmann factor (detailed balance) and dephasing time tau

$$D_{ij} = P_{ij} + P_{ji}{}^{*} \ (i \neq j)$$

$$\dot{P}_{ij} = i(\varepsilon_j - \varepsilon_i)P_{ij} + \sum_k \left(D_{ik}V_{kj} - D_{kj}V_{ik}\right) - \frac{P_{ij}}{\tau_{ij}} - D_{ii}V_{ij}$$

$$\dot{D}_{ii} = \sum_j (D_{ik}V_{ki} - D_{ki}V_{ik}) + \sum_j 2Re(P_{ij}V_{ji})f_{ij}(\exp\left(-\frac{\Delta\varepsilon_{ij}}{k_B T}\right) - 1) - \sum_j 2Re(P_{ji}V_{ij})(1 - f_{ij})(\exp\left(-\frac{\Delta\varepsilon_{ij}}{k_B T}\right) - 1)$$

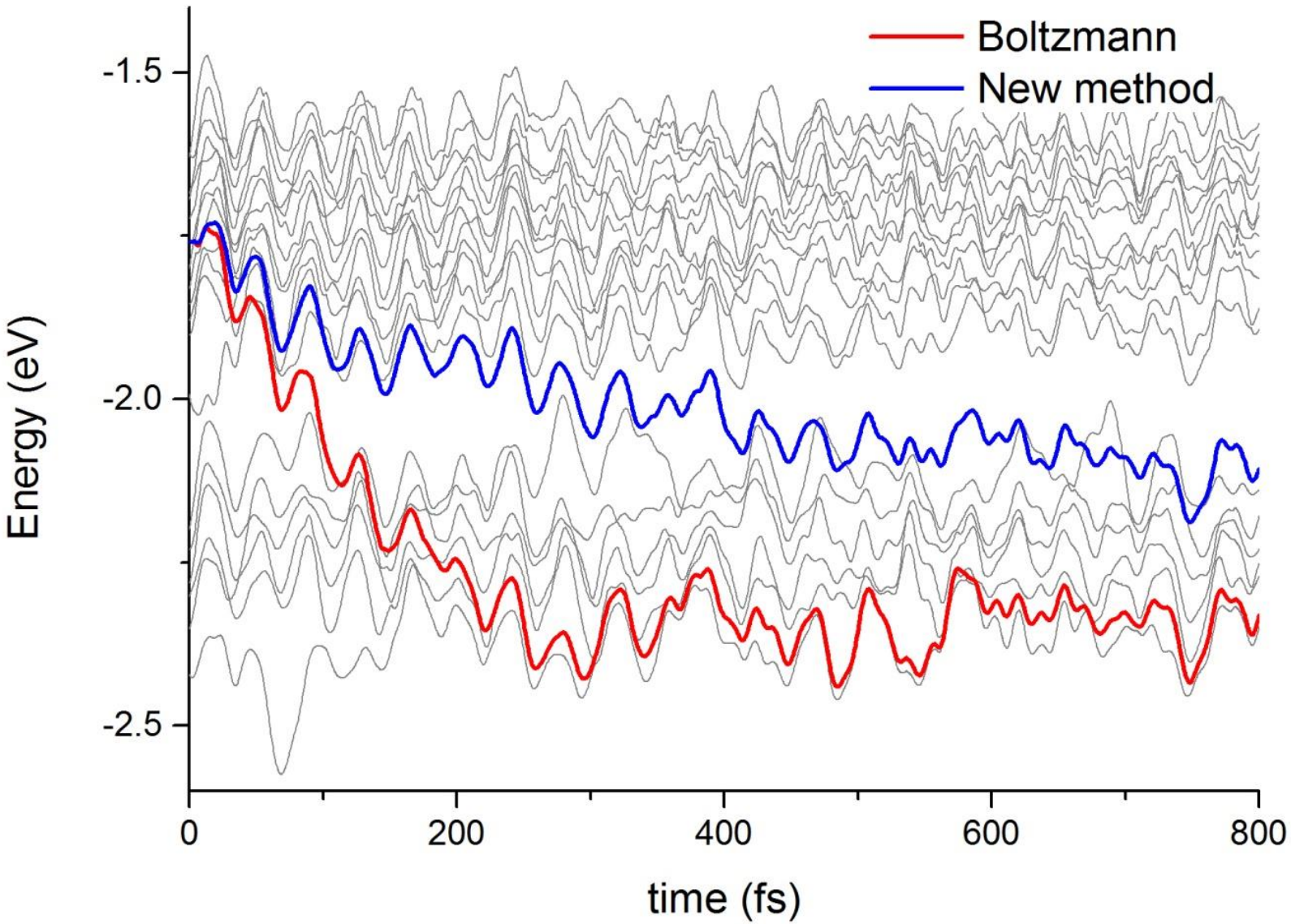
f_{ij}=1 ($\varepsilon_i > \varepsilon_j$) or 0 ($\varepsilon_i < \varepsilon_j$)

Here τ_{ij} is treated explicitly.

$$\tau_{ij}(t_0) = \sqrt{\frac{2(k_B T)^2}{S_{ij}(t_0)}} \qquad S_{ij}(t_0) = < |\frac{d}{dt}\left(\tilde{E}_i(t_0, t) - \tilde{E}_j(t_0, t)\right)|^2 >_t$$

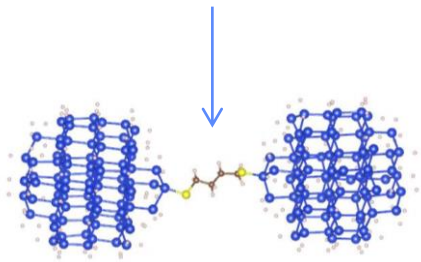
$$\tilde{E}_i(t_0, t) = \langle \varphi_i(t_0)|H(t)|\varphi_i(t_0)\rangle$$

Boltzmann algorithm leads to too fast decay

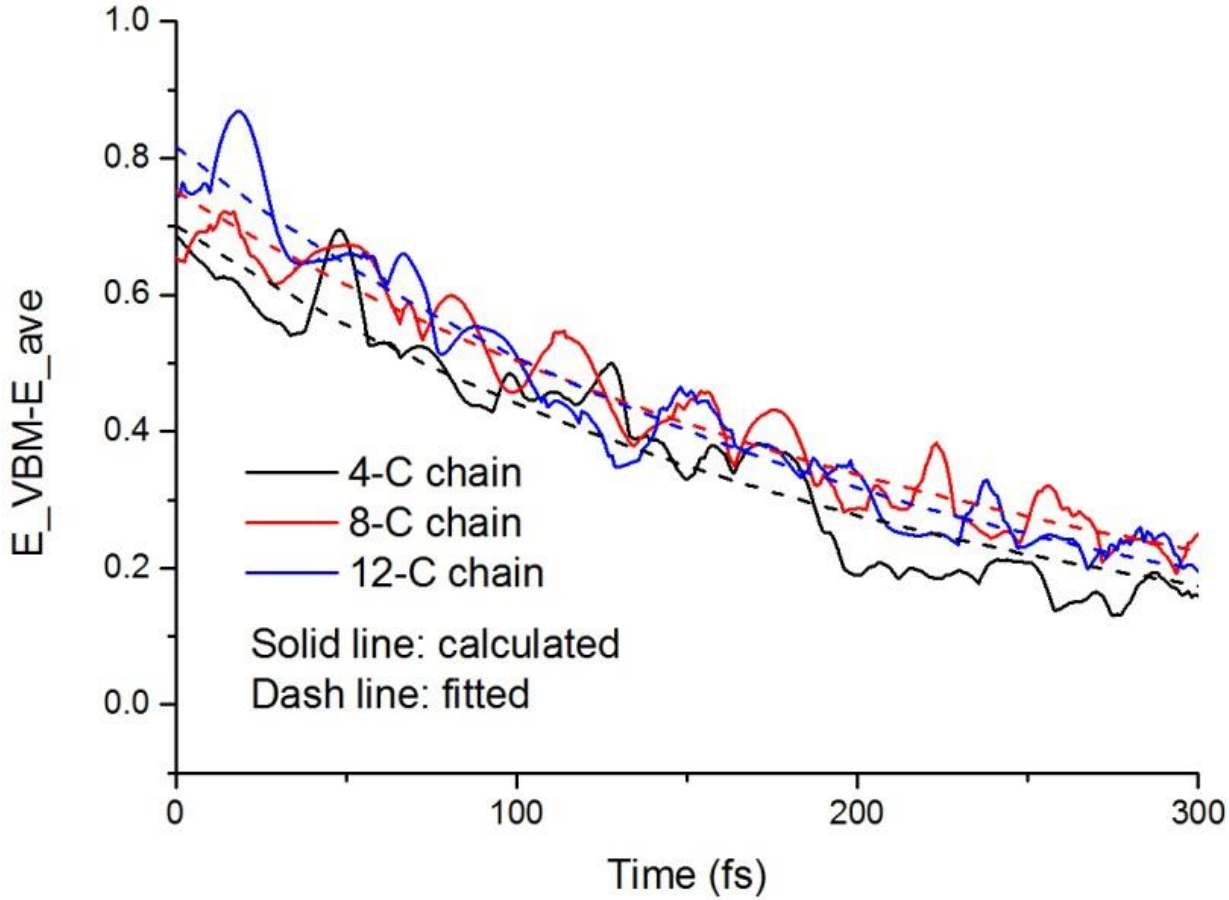


The effect of QD distance on hot hole cooling

n-C chain



The hot hole cooling time is not sensitive to the QD distance.

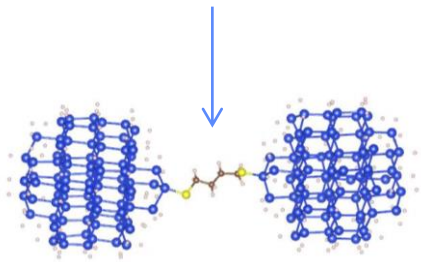


Using A*exp(-t/tau) to fit the calculated curve

The fitted tau is:
4-C: 215 fs
8-C: 250 fs
12-C: 211 fs

The effect of QD distance on charge transfer rate

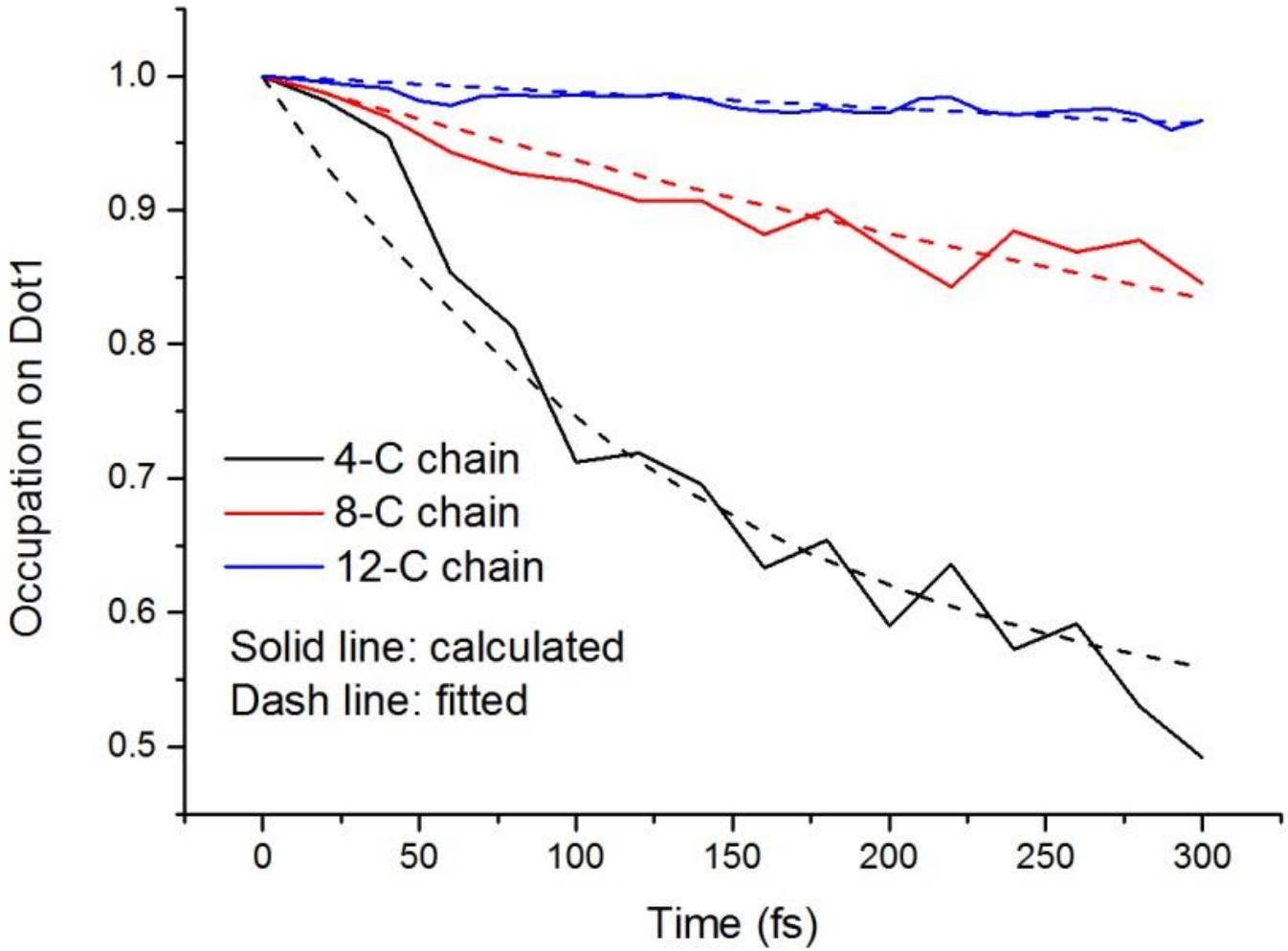
n-C chain



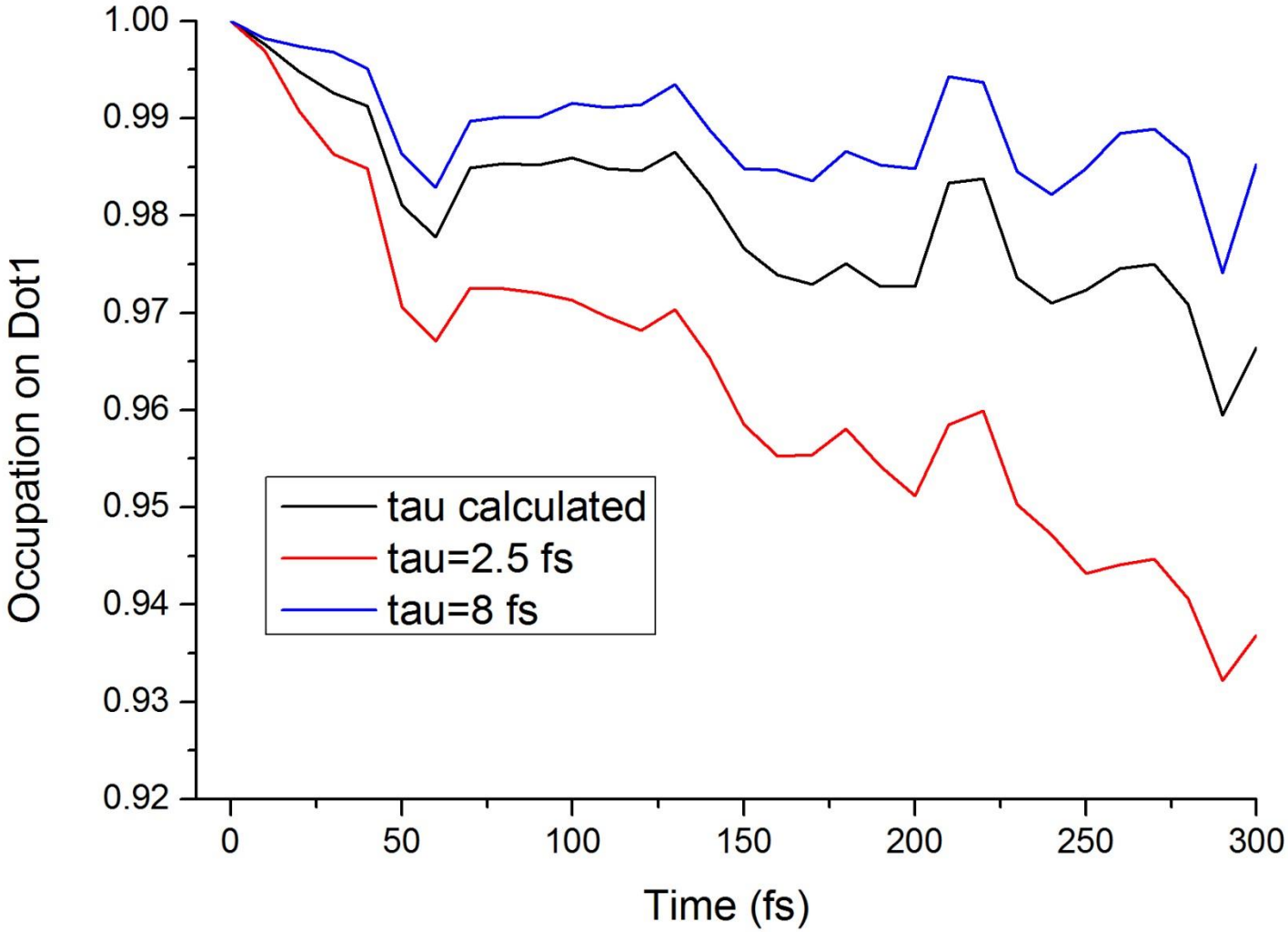
Longer chain leads to slower charge transfer.

Using 0.5exp(-t/tau)+0.5 to fit the calculated curve

The fitted tau is:
4-C: 140 fs
8-C: 747 fs
12-C: 4041 fs



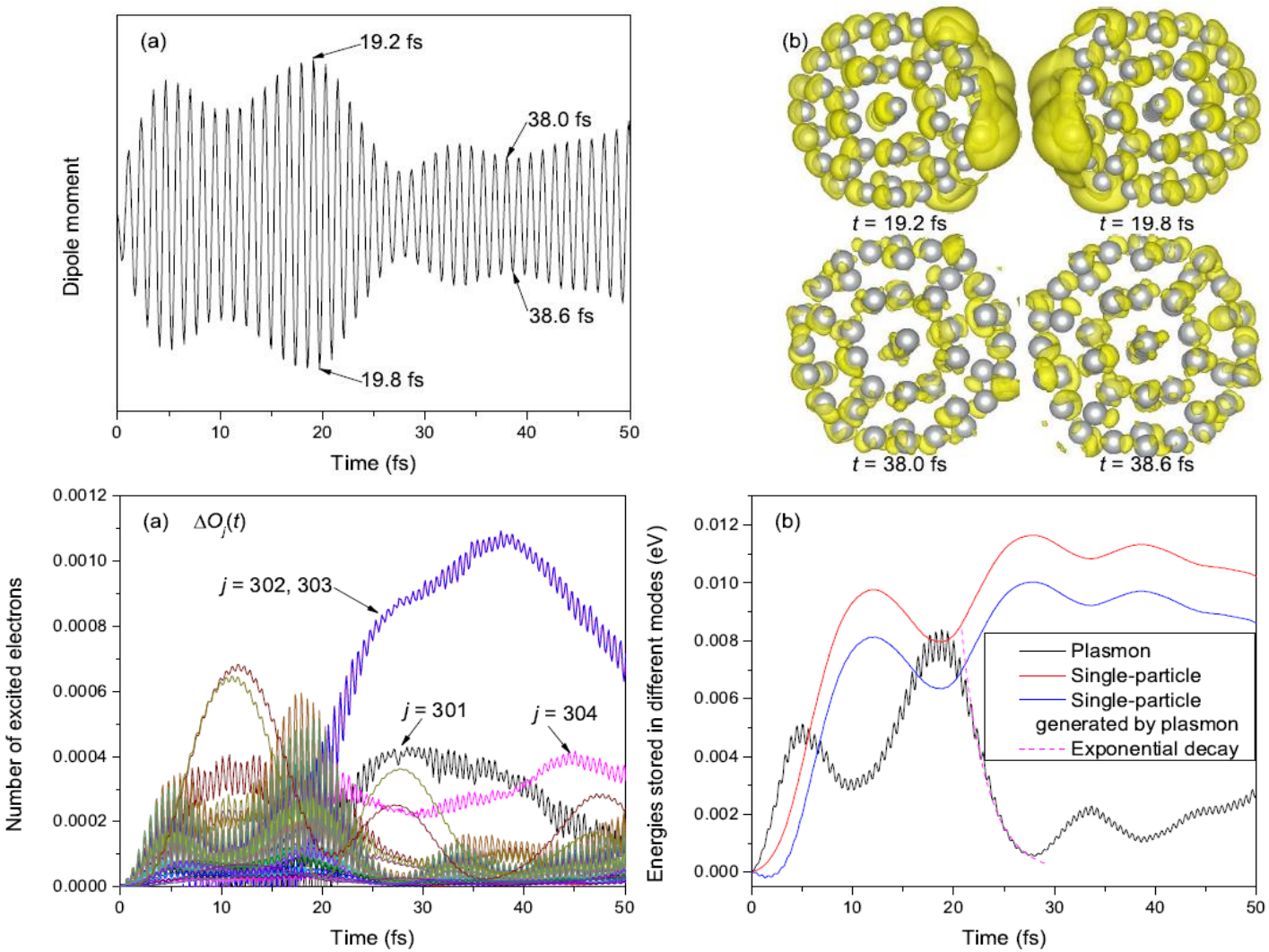
Explicit treatment of τ_{ij} is important



Charge transfer in the 12-C chain case using

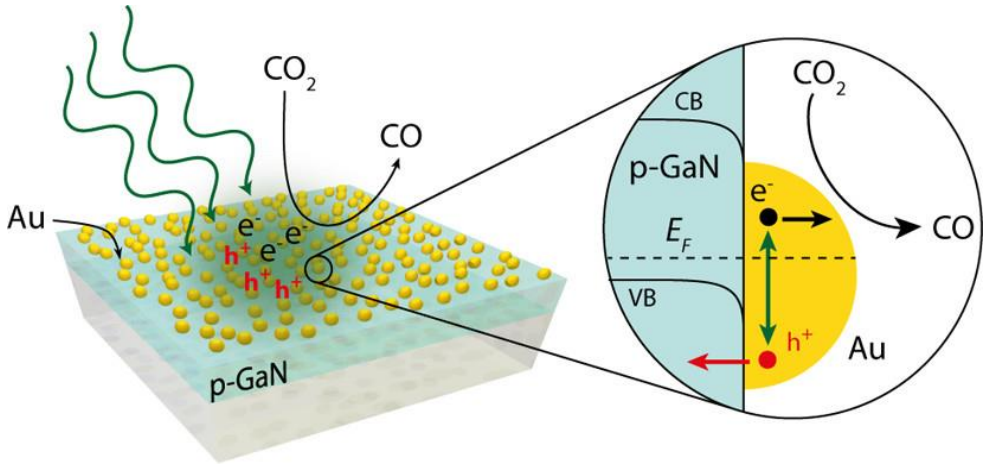
Rt-TDDFT simulation of plasmon in Ag55

More than 80% of the plasmon energy can be converted into single particle excitation as a hole (in Ag d-state)



Charge Transfer from Au to GaN

Inspired by the work done by Dr. DuChene, Professor Atwater, et al, we want to directly simulate the carrier (hole) cooling process from Au to GaN.



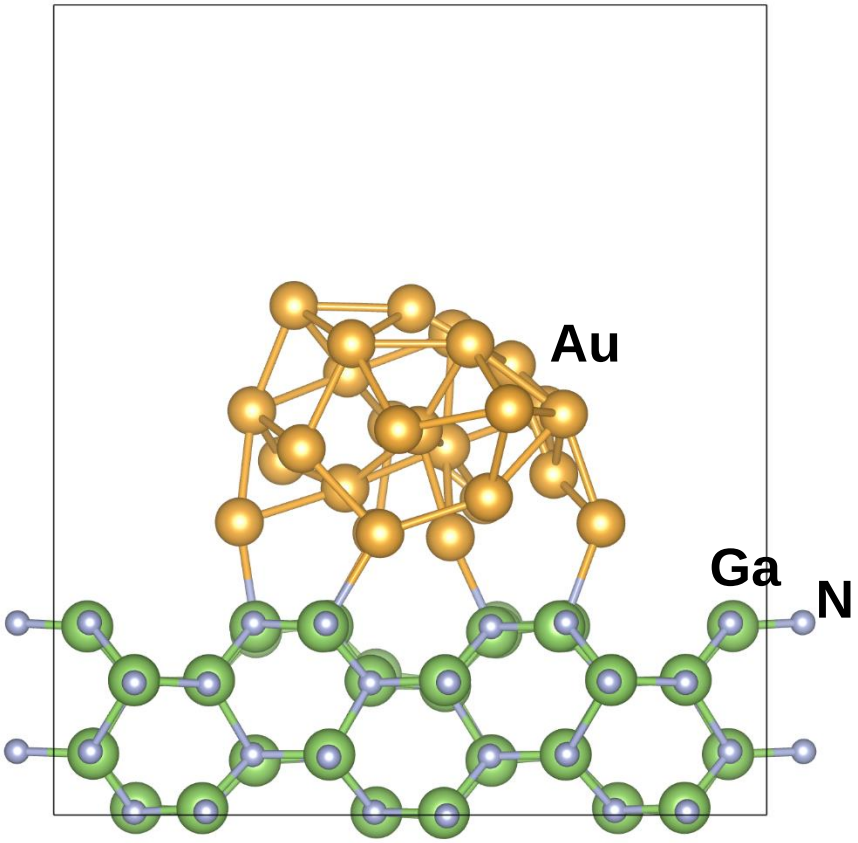
Published in: Joseph S. DuChene; Giulia Tagliabue; Alex J. Welch; Wen-Hui Cheng; Harry A. Atwater; *Nano Lett.* 18, 2545-2550.
DOI: 10.1021/acs.nanolett.8b00241

GaN[1-100] / Au model system

- In the expt., the polar [0001] surface is used.
  We limit our self to non-polar GaN surface[1-100], in order to simplify the model for the simulation for now.
  The polar potential can be added by applying E field later on.

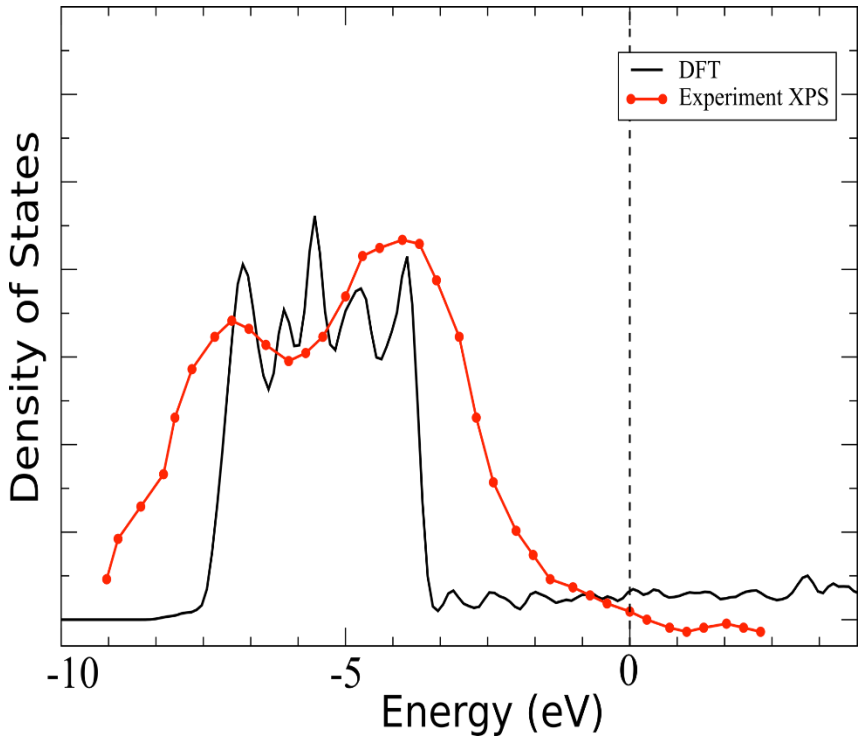
- A 26 Au atom cluster is attached to the surface of GaN.

- The system is fully relaxed with GGA functional.

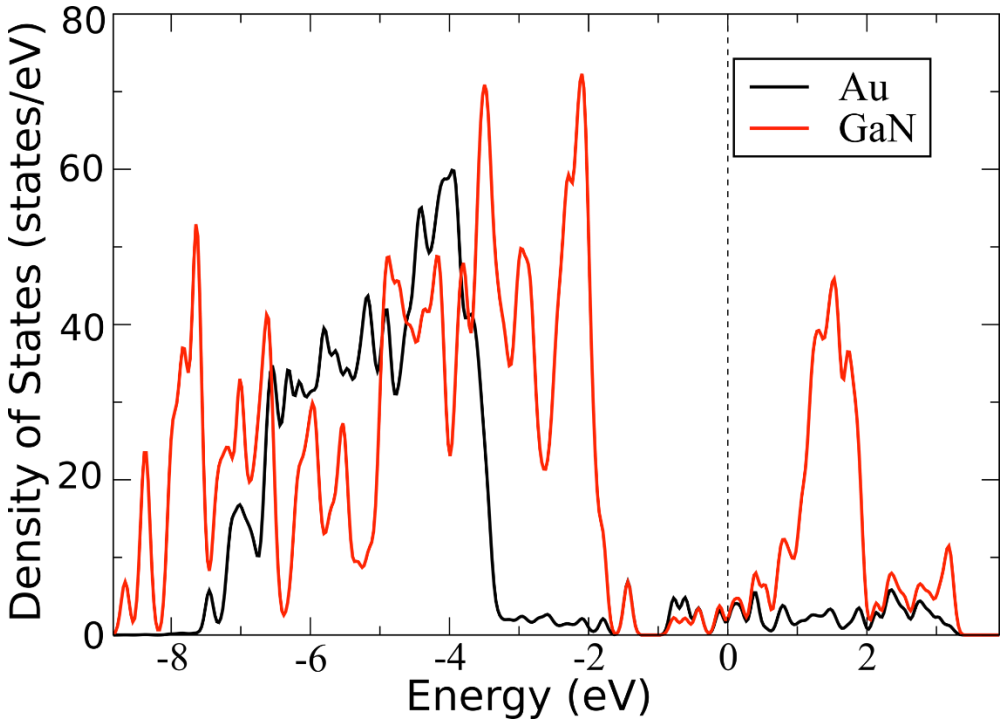


The DOS and alignment between Au and GaN

Pure Au system

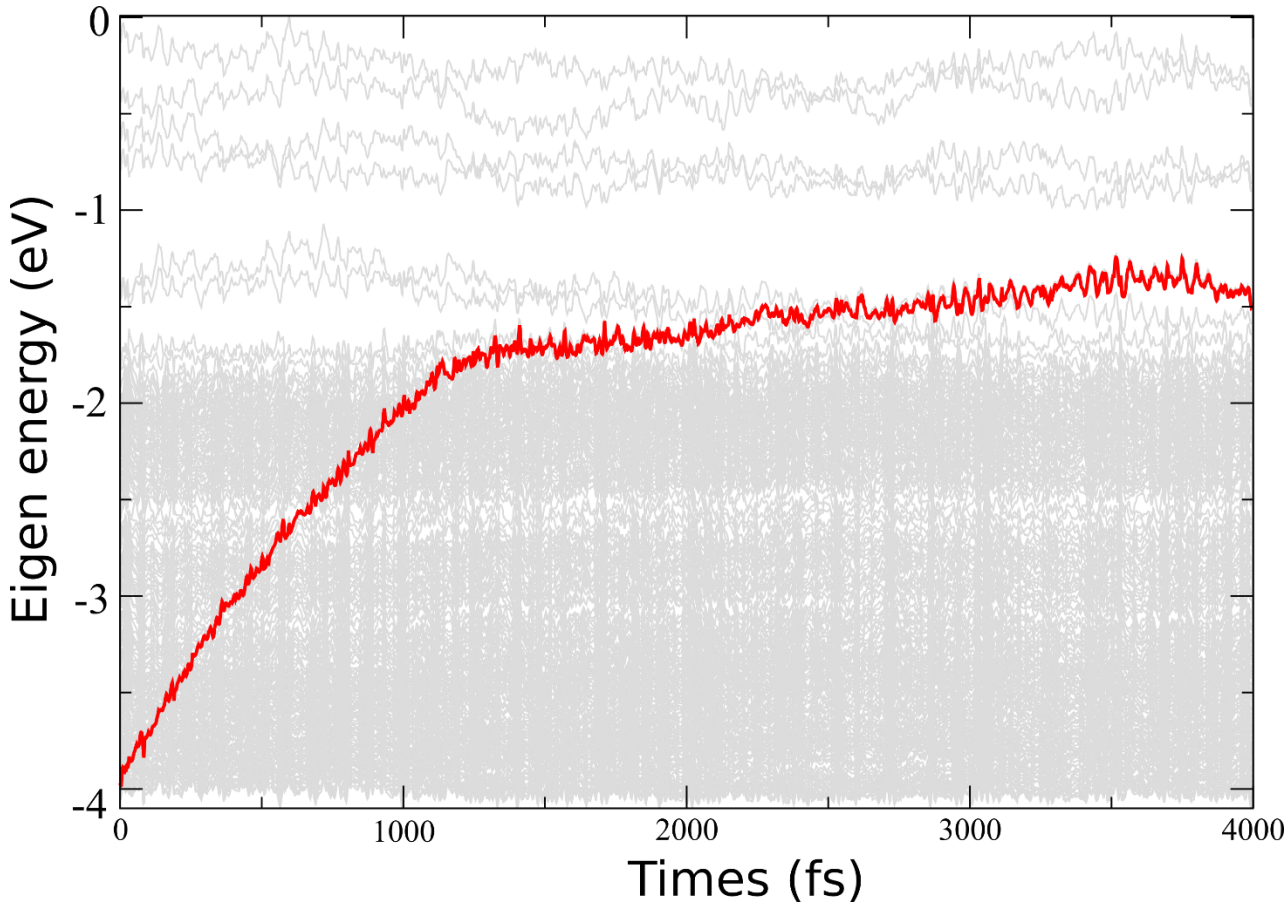


Au on GaN (nonpolar surface)



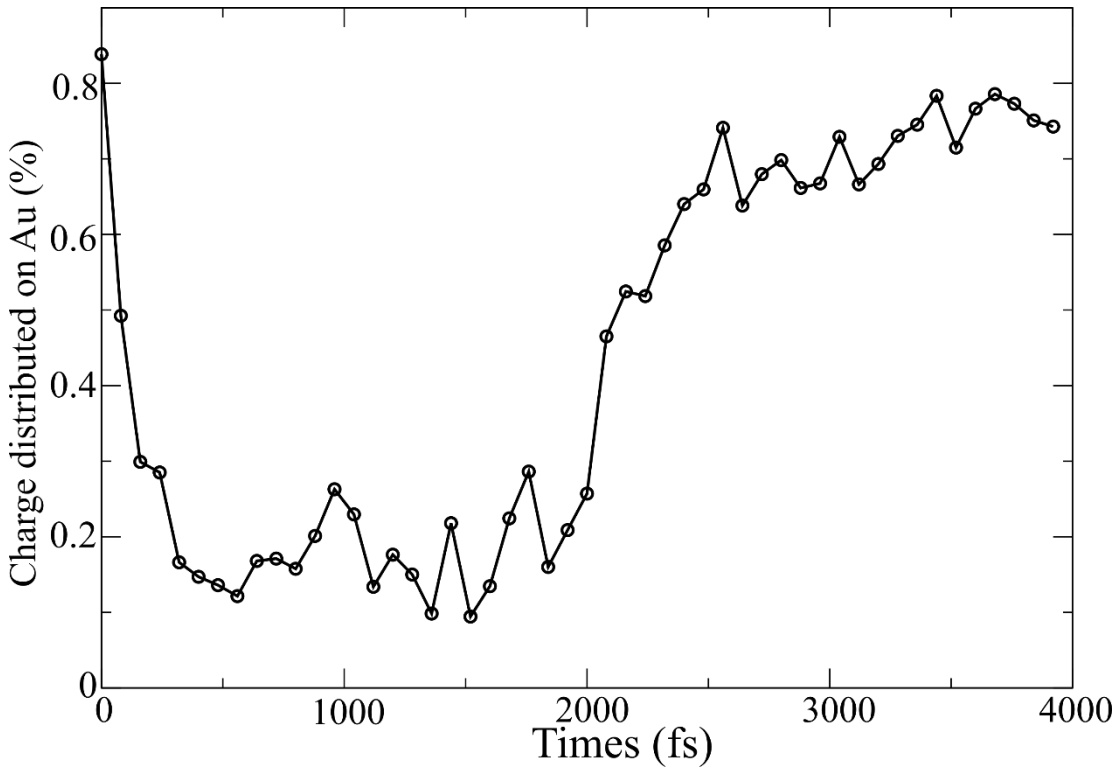
NAMD Energy Evolution

- The hole can quickly cools down to the edge of GaN around **1ps**.
- Owing to the relatively small size of Au cluster, the density of states of Au s orbitals within the gap of GaN is low → **phonon bottle neck**.
  It will take a long time for the hole to cool to the Fermi level.

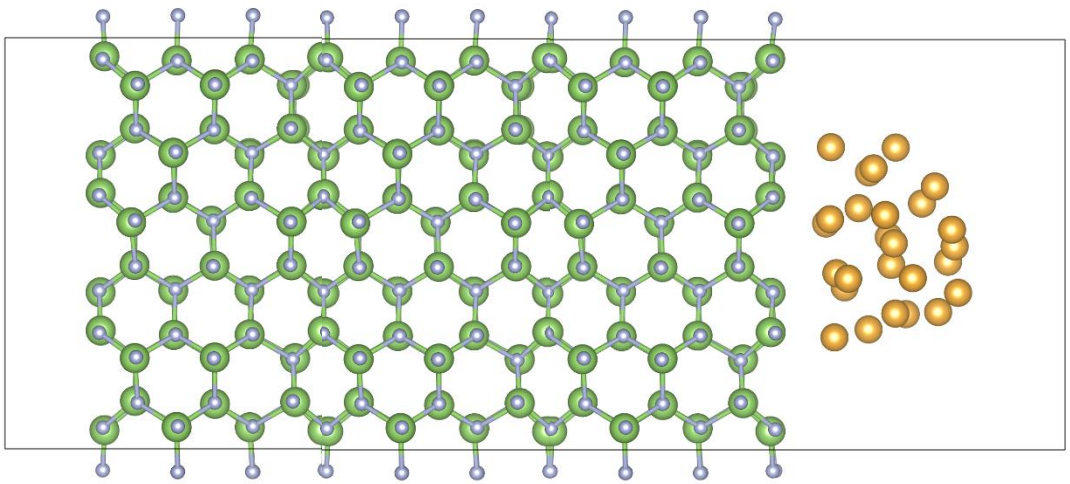


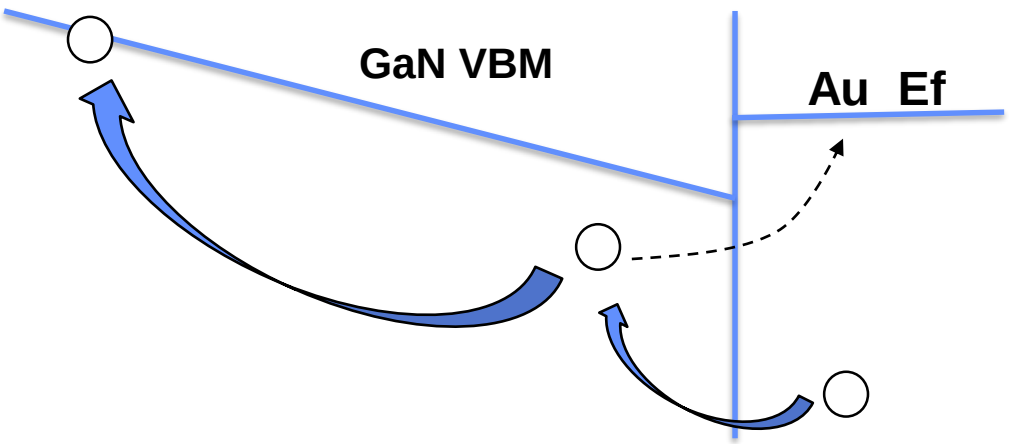
Adiabatic eigen energy — Averaged energy of the excited hole

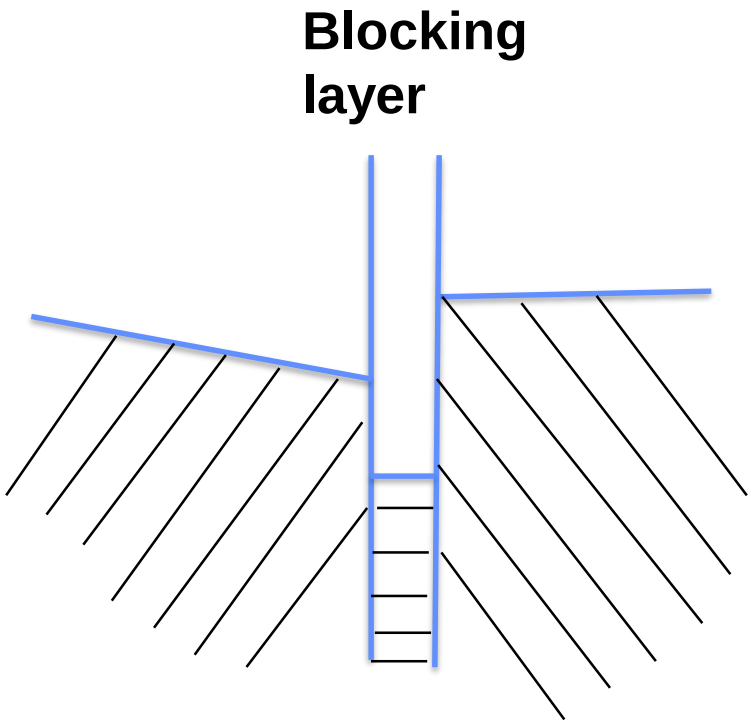
Charge transfer from Au to GaN (then back!)



Some ideas to help the charge transfer





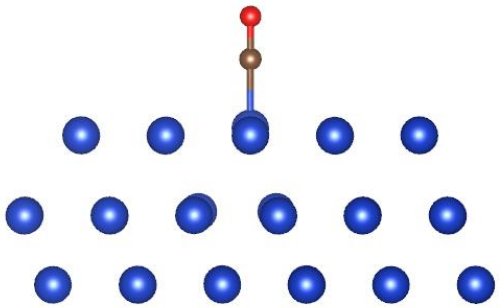


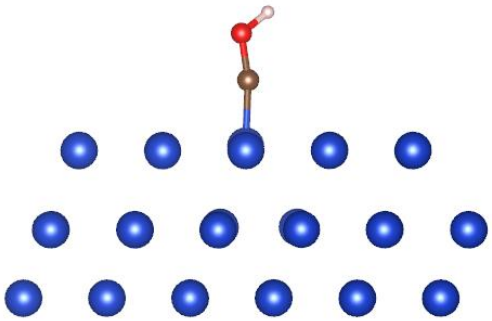
Outline

- Carrier mobility in hybrid perovskite (an unconventional picture)
- Charge transfer in c-Si/a-SiO2 interface (protection layer)
- Hot carrier cooling and charge transfer (NAMD simulation)
- Direct rt-TDDFT simulation of nonadiabatic process and reaction

CO reduction

$$Cu\text{-}CO + H^+ + e^- \rightarrow Cu\text{-}COH$$





We want to understand the details of the electron transfer process

- **How does such electron transfer couple to the proton transfer?**
  ⇒ Is this an adiabatic or non-adiabatic process?

- **Which factors can affect the electron transfer process?**
  ⇒ Can we enhance the electron transfer to increase the reaction rate?

Implicit Solvent Model

$$Cu\text{-}CO + H^+ + e^- \rightarrow Cu\text{-}COH$$

The solvent model is tuned so that it can reproduce the correct H^+ free energy in water

H^+: $H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$, (SHE)

$$G(H^+(aq)) = \frac{1}{2} G(H_2(g)) + |e|U^{abs},\ U^{abs} = U^{SHE} + 4.4\ V$$

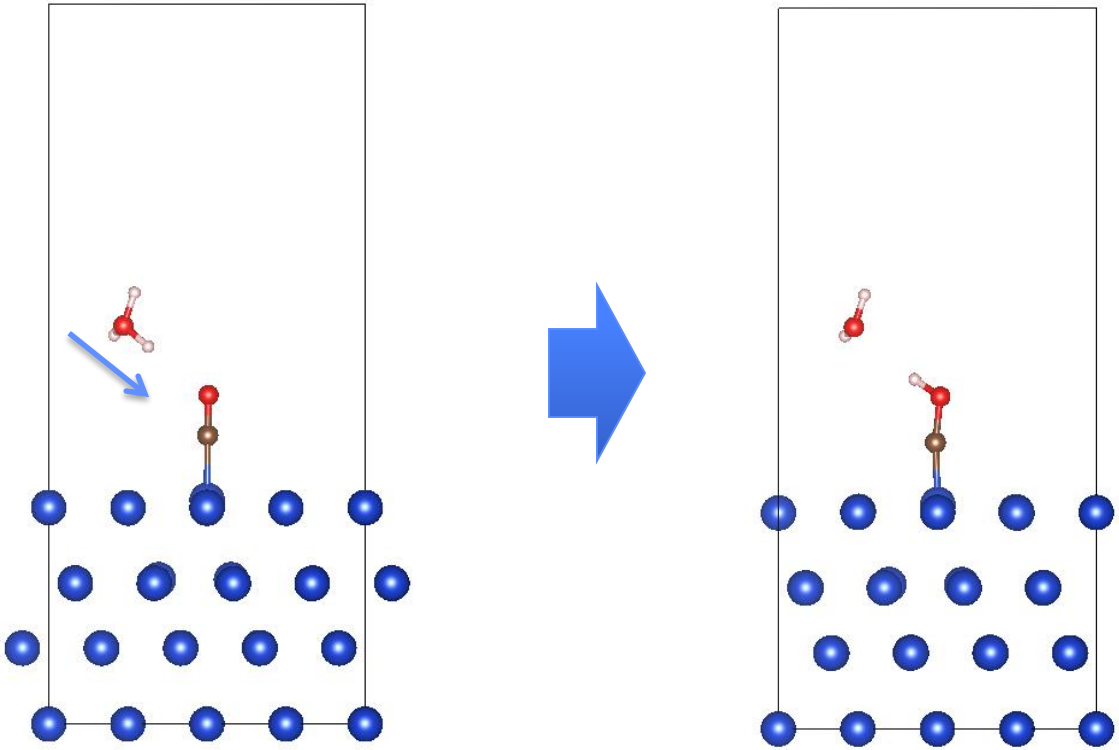
$$G(H_2(g)) = E_{Tot}(H2(g)) + ZPE + H_{vib} - TS$$

Tune the H^+ solvent model so that the DFT calculated free energy equals to the "experimental" free energy

We do similar fitting for other ions: C, O and Cu

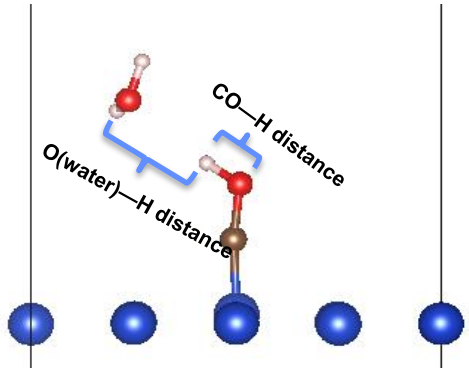
Perform Dynamics Simulation

Initialize H_3O^+ with velocity towards *CO
Compared MD and TDDFT, to see the effects of nonadiabatic process

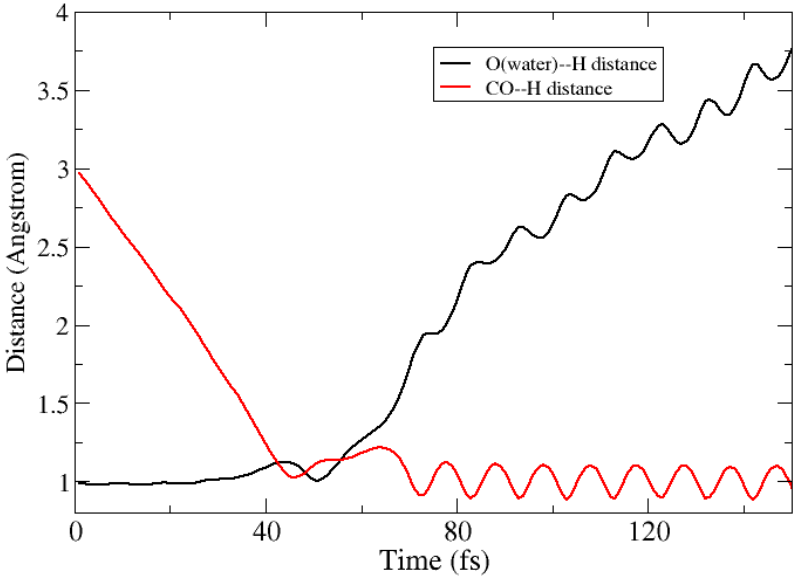


Proton transfer: nonadiabatic process ?

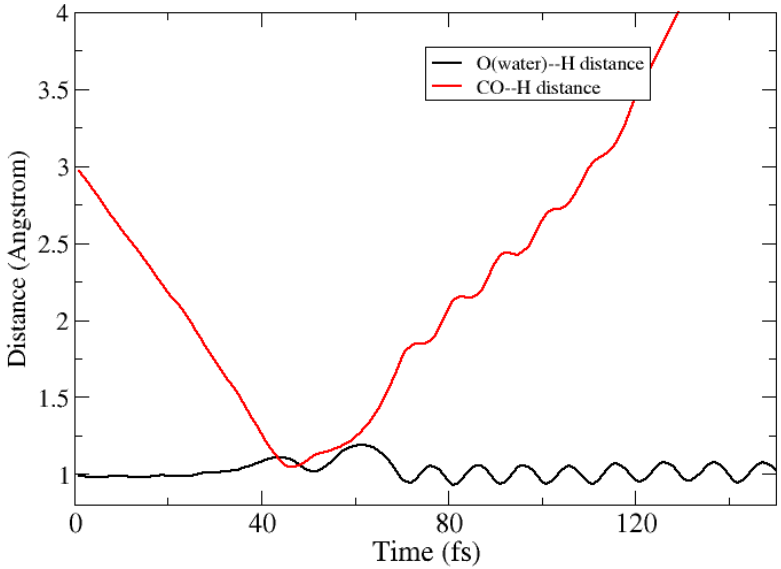
Same initial velocity



MD simulation:
Proton transfer happens

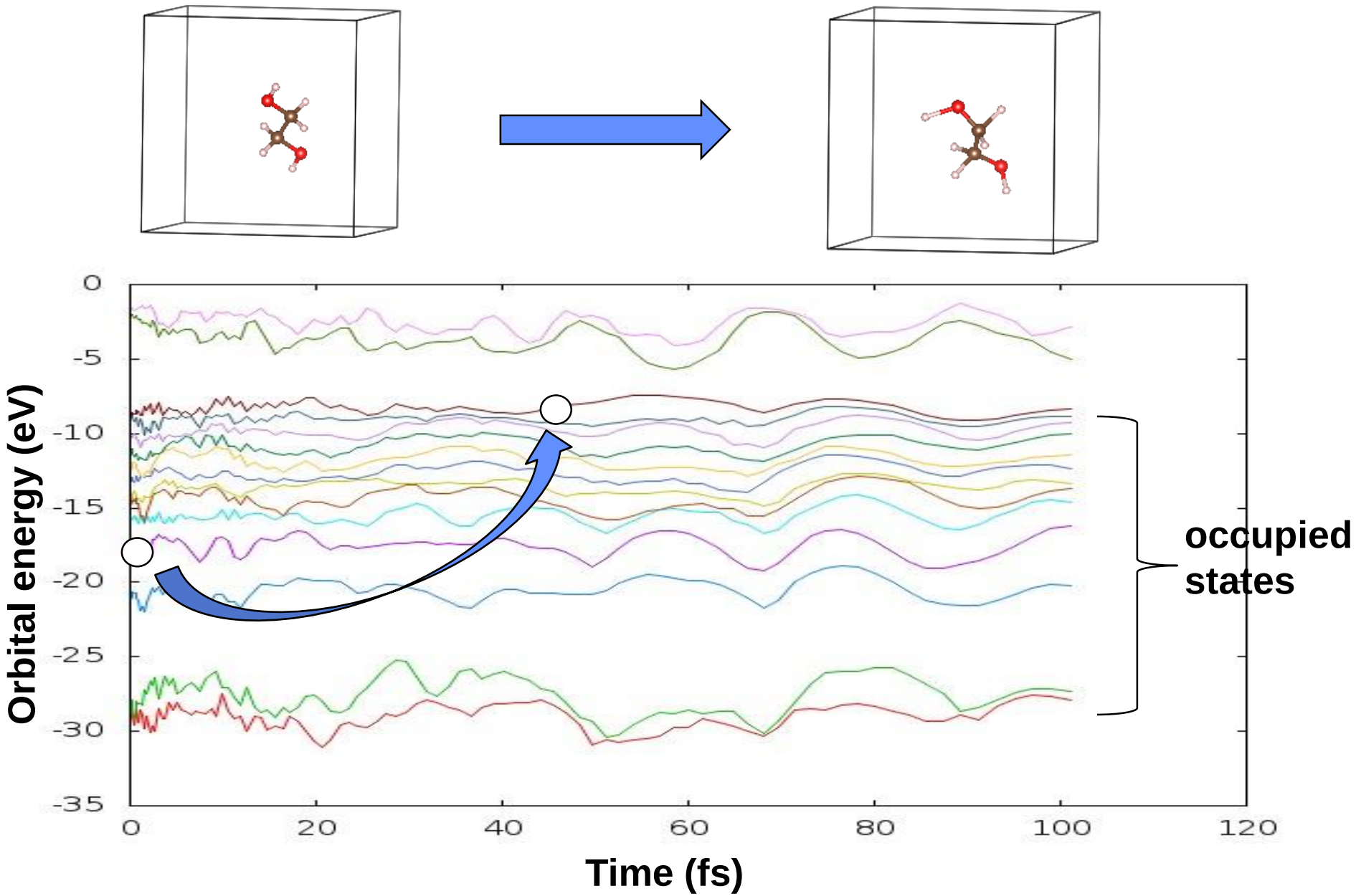


TDDFT simulation:
Proton transfer NOT happens

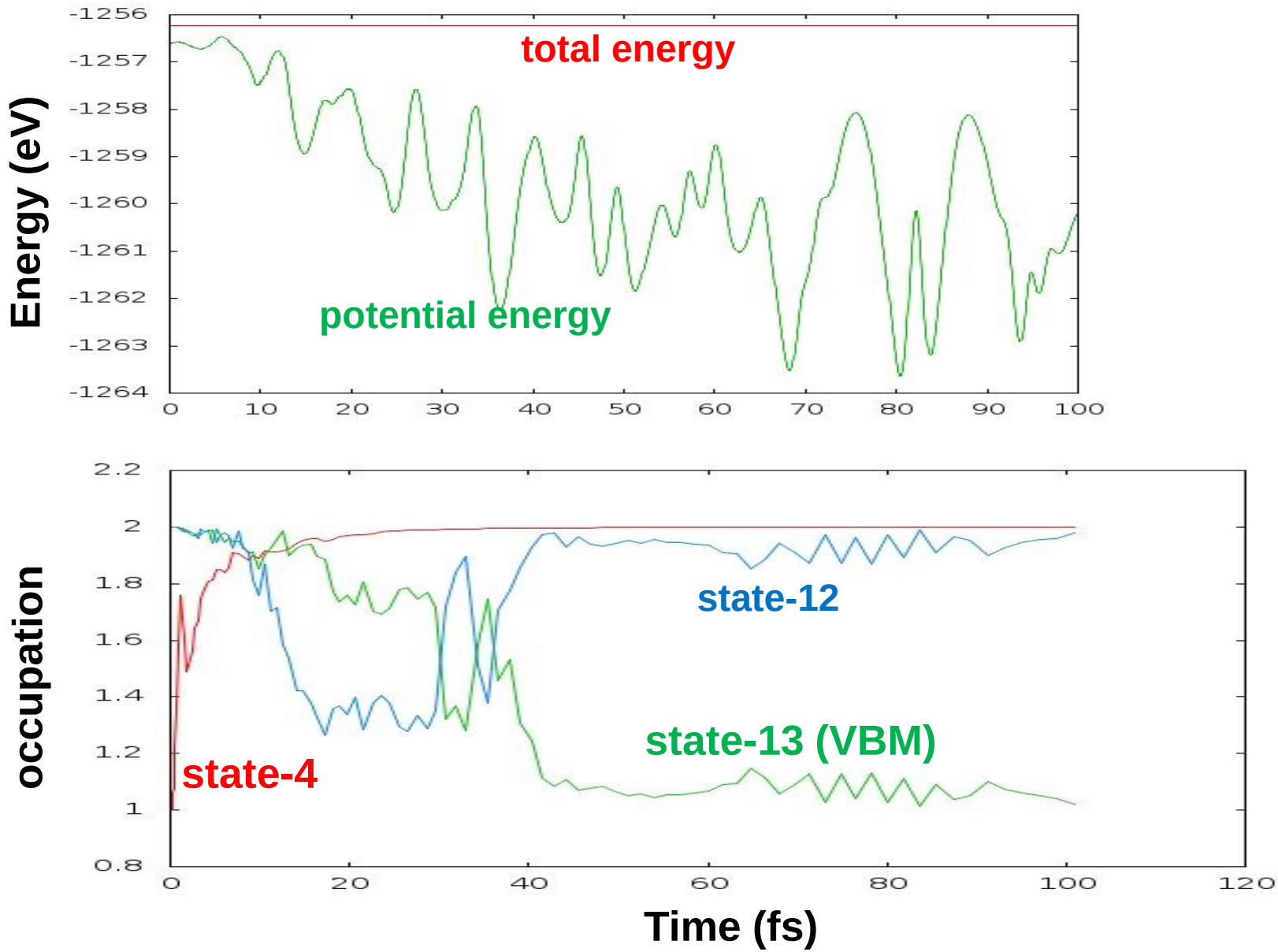


The Born-Oppenheimer MD and TDDFT get different results, nonadiabatic process?

$C_2O_2H_6$ excitation (rt-TDDFT simulations)



Energy change and hot carrier cooling



Thank you!