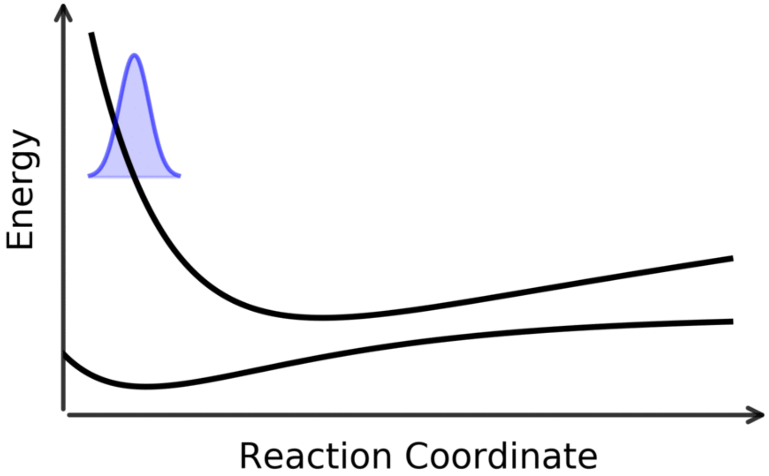
Excited Carrier Dynamics in Condensed Matter System

From ab initio simulation

Jin Zhao
University of Science and Technology of China

- **Back ground**
- **Single particle dynamics**
- **Spin dynamics**
- **Exciton Dynamics**
- **Outlook**

Carrier Dynamics in Condensed Matter Systems



Condensed matter physics: Charge, spin and orbital

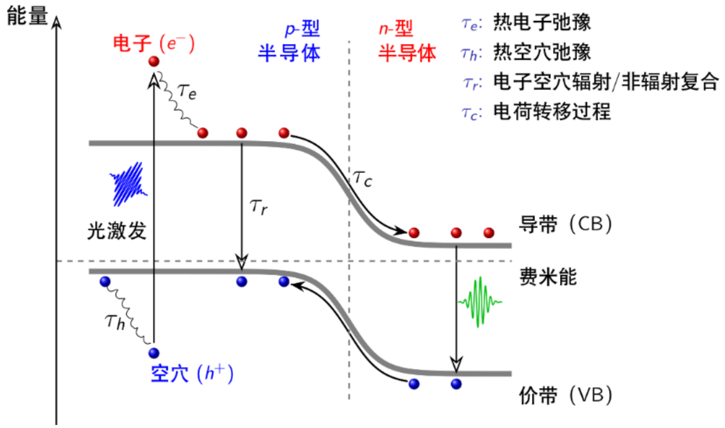
Important tool: First principles calculations

$$\mathcal{H}\psi = E\psi$$

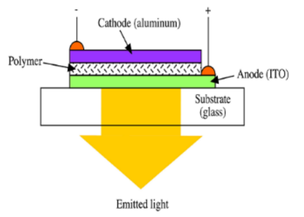
$$i\hbar\frac{\partial}{\partial t}\psi = \mathcal{H}\psi$$

Multi-dimension: energy, momentum, real space, spin, time

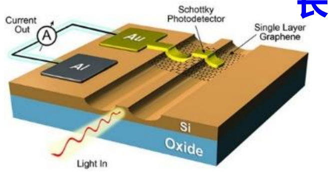
Applications of Photoexcited Carrier Dynamics



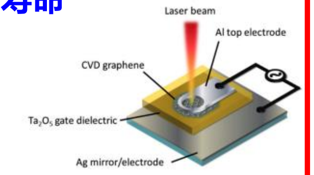
太阳能电池各种载流子动力学
行为共同决定效率



发光器件
长寿命



光探测器
中等寿命



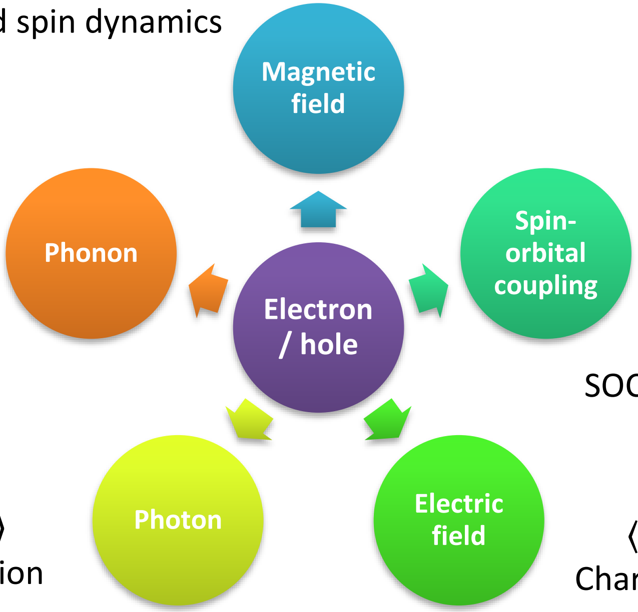
光调制器
短寿命

不同光电器件对材料载
流子寿命有不同要求

Determining Factors of Carrier Dynamics

No perturbation, no relaxation : $\langle \boldsymbol{\psi_i} | \boldsymbol{\psi_j} \rangle = \mathbf{0}$

With perturbation:



$\langle \psi_i | B | \psi_i \rangle$
SOC induced spin dynamics

$\left\langle \psi_i \middle| \frac{\partial}{\partial t} \middle| \psi_i \right\rangle$
$\langle \psi_{nk} | \Delta V | \psi_{n'k'} \rangle$
Nonradiative relaxation

$\langle \psi_i | H_{SOC} | \psi_i \rangle$
SOC induced spin dynamics

$\langle \psi_i | E e^{i\omega t} | \psi_i \rangle$
Radiative relaxation

$\langle \psi_i | E | \psi_i \rangle$
Charge transport

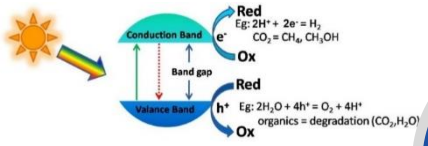
Many-body effects:

- e-e interaction
- e-h interaction (exciton effects)
- spin-spin interaction

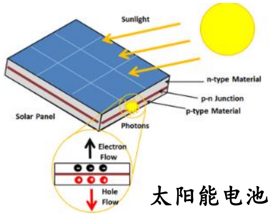
Other effects:

- Nuclear quantum effects
- Potential energy surface of the excited state

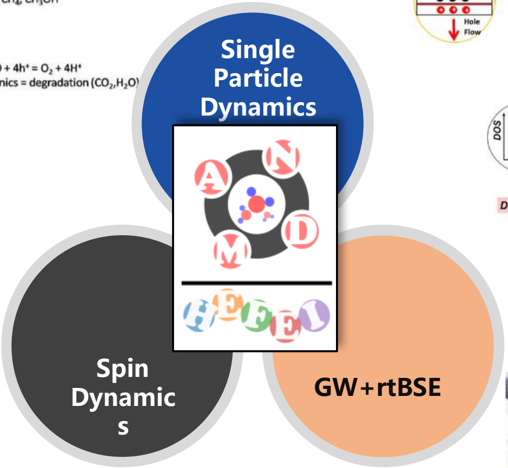
Ab initio Code for Excited Carrier Dynamics



光催化



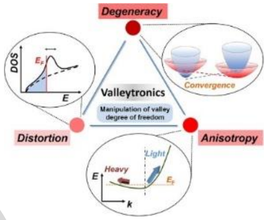
太阳能电池



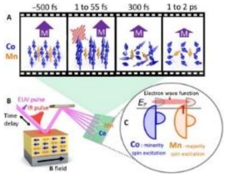
Single Particle Dynamics

Spin Dynamics

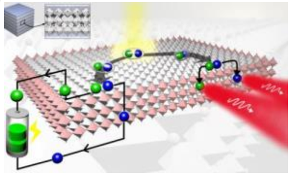
GW+rtBSE



谷电子学



光调控自旋动力学



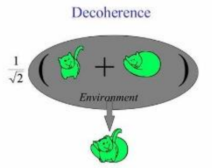
光电器件

Hefei-NAMD

2016

郑奇靖

Quantum decoherence

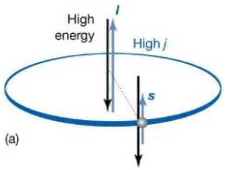


2018

褚维斌

赵传寓

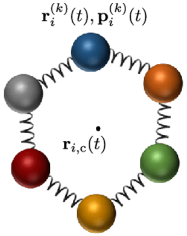
Spin-orbital Coupling



2018

郑奇靖

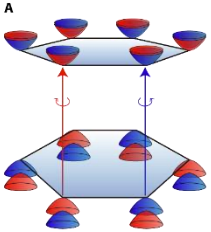
Nuclear Quantum effects



2018

褚维斌

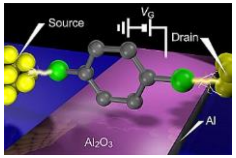
GW + real-time BSE



2021

蒋翔

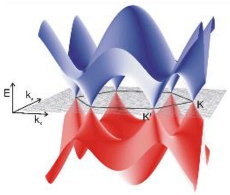
Charge transport



now

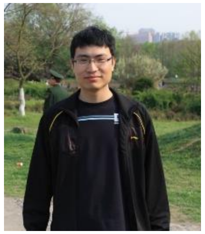
田韫哲

Dynamics in momentum space



now

郑镇法



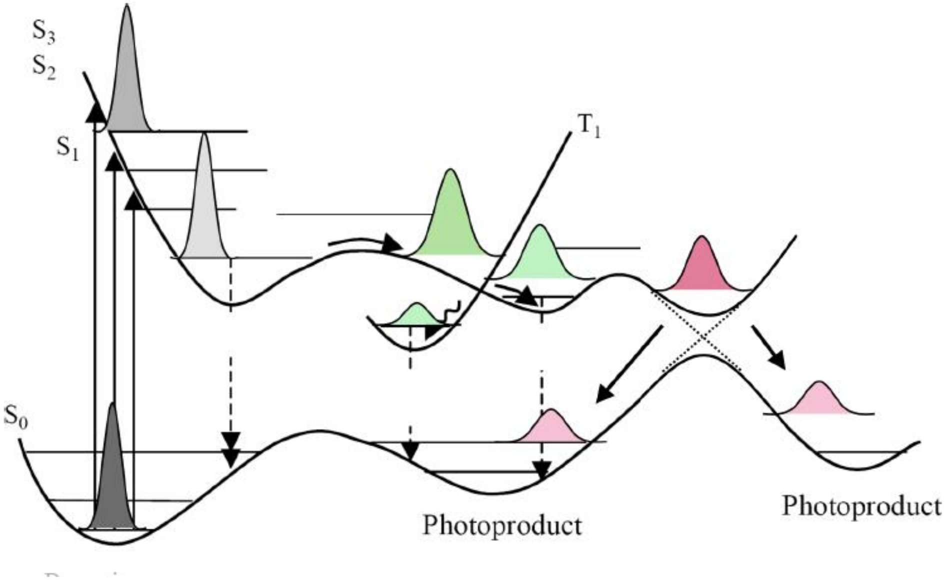
史永亮

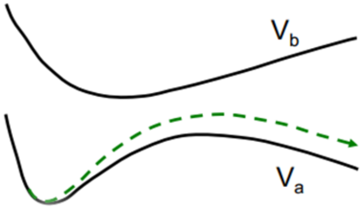
- Back ground
- **Single particle dynamics**
- Spin dynamics
- Exciton Dynamics
- Outlook

Beyond Born-Oppenheimer Approximation

Mixed Quantum-Classical approximation

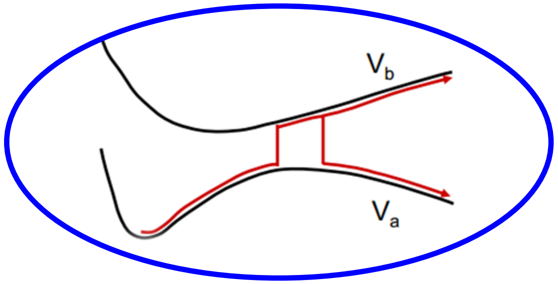
$$\Psi(\mathbf{r},\mathbf{R},t) = \Omega_j(\mathbf{R},t)\Phi_j(\mathbf{r};\mathbf{R}); \qquad \hat{\mathcal{H}}_{el}(\mathbf{r};\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R}) = E_j(\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R})$$





Ehrenfest Dynamics

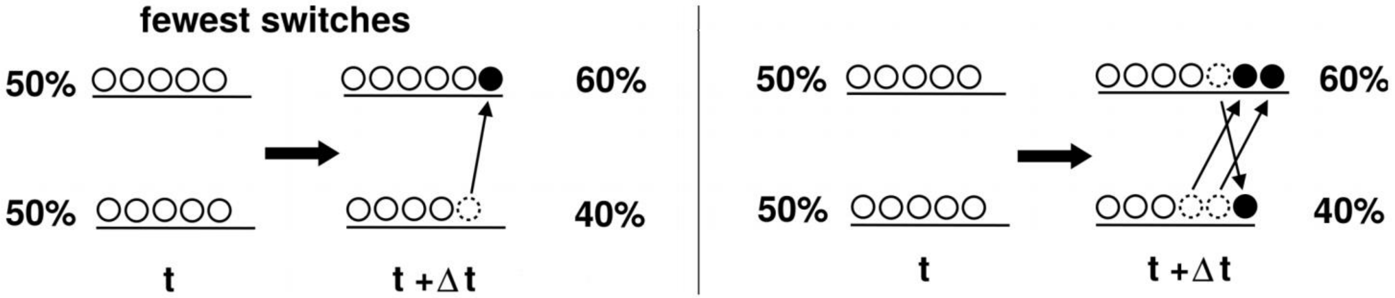
$$M_\alpha \ddot{\mathbf{R}}_\alpha = -\nabla_\alpha \langle \hat{\mathcal{H}}_{el}(\mathbf{r},\mathbf{R}) \rangle$$



Surface Hopping

$$M_\alpha \ddot{\mathbf{R}}_\alpha = -\nabla_\alpha E_k^{el}(\mathbf{R})$$

Fewest surface hopping



Assumptions

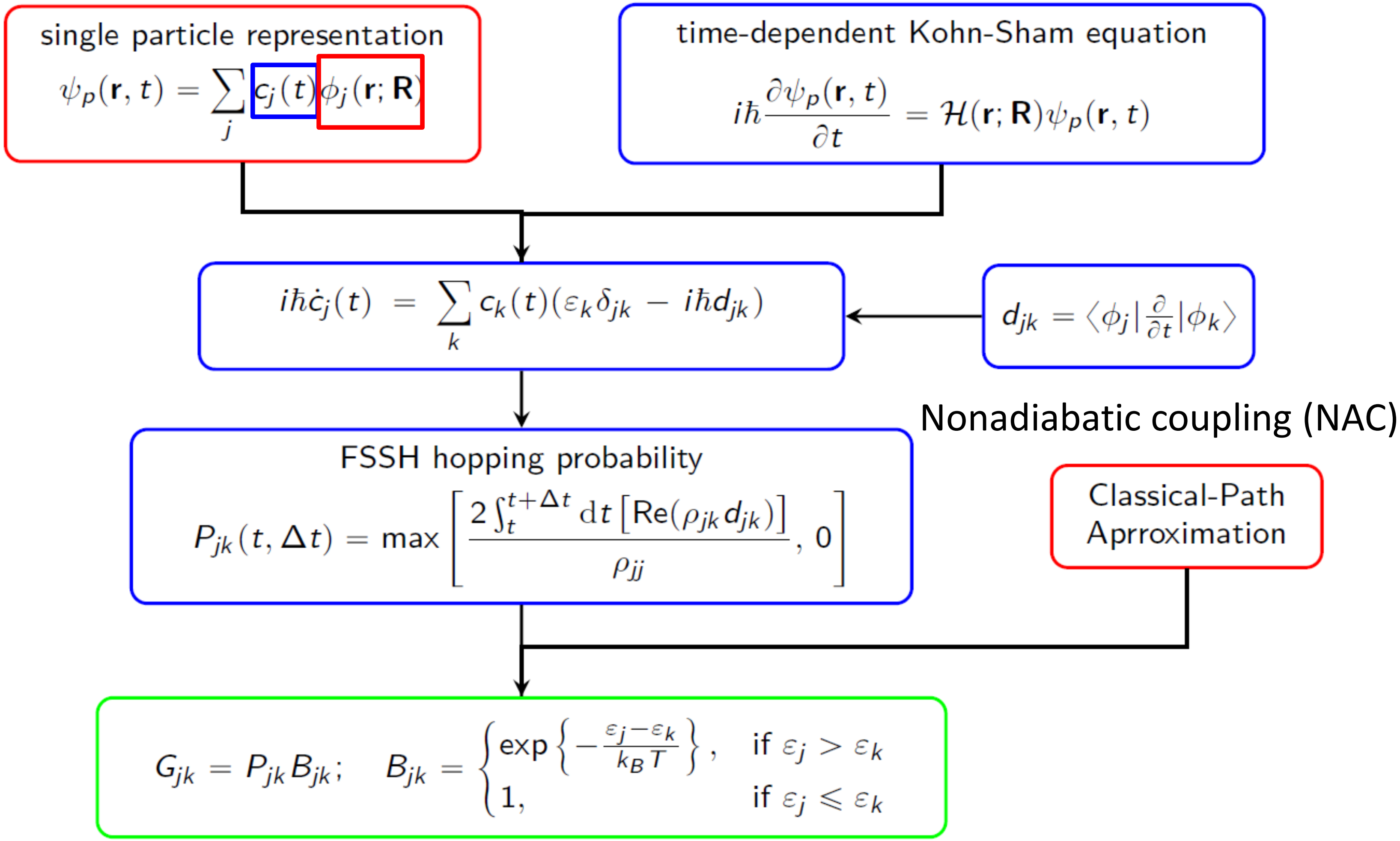
- Ensemble of independent trajectories have same coefficients $C_j(t)$.
- Internal consistency condition $N_j(t) \propto C_j^*(t)C_j(t) = \rho_{jj}(t)$.
- Hops from j to different $k \neq j$ are independent.
- Overall trajectory hops should be minimum.

Fewest-Switches: Hopping Probability

Transition from current state j to state $k \neq j$ is allowed only if population of state j is decreasing.

$$P_{jk}(t, \Delta t) = \max\left(-\frac{2\int_t^{t+\Delta t} \mathrm{d}t \left[\hbar^{-1}\,\mathrm{Im}(\rho_{jk}H_{jk}) - \mathrm{Re}(\rho_{jk}\mathbf{d}_{jk}\cdot\dot{\mathbf{R}})\right]}{\rho_{jj}}, 0 \right)$$

Surface Hopping Combined with TDKS



single particle representation

$$\psi_p(\mathbf{r},t) = \sum_j \boxed{c_j(t)}\boxed{\phi_j(\mathbf{r};\mathbf{R})}$$

time-dependent Kohn-Sham equation

$$i\hbar\frac{\partial\psi_p(\mathbf{r},t)}{\partial t} = \mathcal{H}(\mathbf{r};\mathbf{R})\psi_p(\mathbf{r},t)$$

$$i\hbar\dot{c}_j(t) = \sum_k c_k(t)(\varepsilon_k\delta_{jk} - i\hbar d_{jk})$$

$$d_{jk} = \langle\phi_j|\tfrac{\partial}{\partial t}|\phi_k\rangle$$

Nonadiabatic coupling (NAC)

FSSH hopping probability

$$P_{jk}(t,\Delta t) = \max\left[\frac{2\int_t^{t+\Delta t}\mathrm{d}t\,\left[\mathrm{Re}(\rho_{jk}d_{jk})\right]}{\rho_{jj}},\ 0\right]$$

Classical-Path Aprroximation

$$G_{jk} = P_{jk}B_{jk};\quad B_{jk} = \begin{cases}\exp\left\{-\frac{\varepsilon_j-\varepsilon_k}{k_BT}\right\}, & \text{if } \varepsilon_j > \varepsilon_k\\ 1, & \text{if } \varepsilon_j \leqslant \varepsilon_k\end{cases}$$

A. Akimov and O. Prezhdo: Pyxaid
Q. Zheng, X. Jiang, et. al. J. Zhao: Hefei-NAMD

Electron-phonon interaction – Nonadiabatic coupling

$$H_{ki} = \epsilon_k \delta_{ik} - i\hbar \left\langle k \middle| \frac{\partial}{\partial t} \middle| i \right\rangle$$

Nonadiabatic coupling

$$d_{jk} = \left\langle \varphi_j \middle| \frac{\partial}{\partial t} \middle| \varphi_k \right\rangle = \frac{\boxed{\langle \varphi_j | \nabla_R H | \varphi_k \rangle}}{\epsilon_k - \epsilon_j} \dot{R}$$

Electron-phonon matrix elements

$$\mathbf{d}_{jk} = \langle \phi_j | \frac{\partial}{\partial t} | \phi_k \rangle = \frac{\langle \phi_j(t) | \phi_k(t + \Delta t) \rangle - \langle \phi_j(t + \Delta t) | \phi_k(t) \rangle}{2\Delta t}$$

- ✓ charge transfer dynamics
- ✓ Electron-hole recombination

Electron-phonon interaction - Decoherence Correction

退相干时间

纯退相干时间（根据光响应理论）

$$D(t) = \exp(i\omega t)\left\langle -\frac{i}{\hbar}\int_0^t \Delta E d(\tau) t\right\rangle$$

能级差 （右图一）

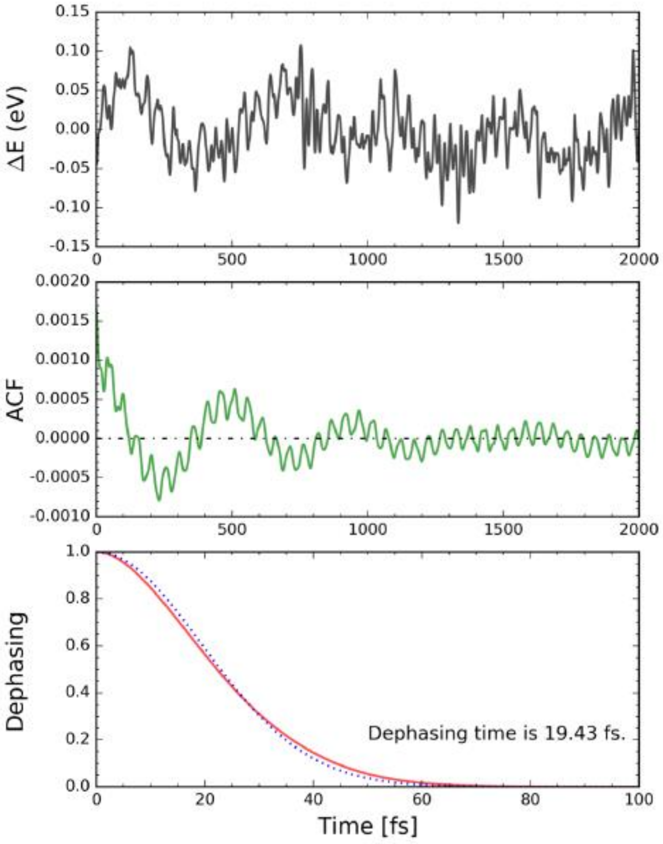
$$\Delta E \; = \; \Delta E_{ij} - < \Delta E_{ij} >_T$$

自关联函数 （右图二）

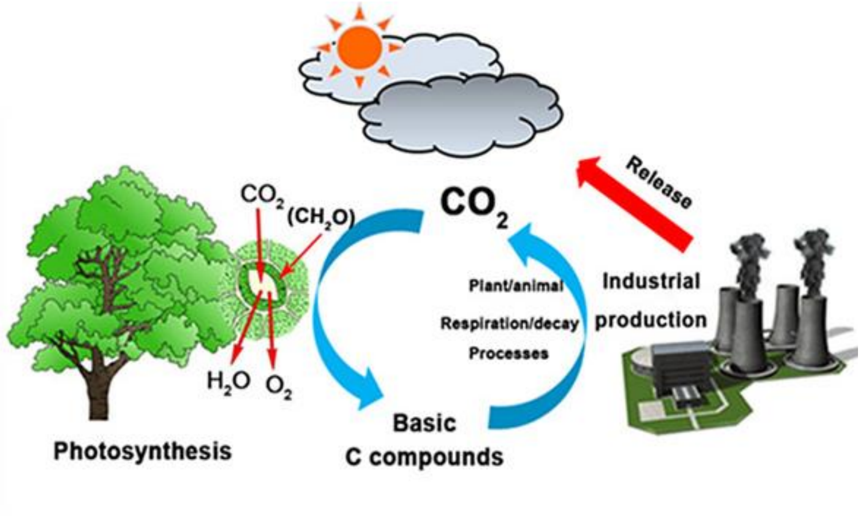
$$C(t) = < \Delta E(\tau)\Delta E(0) >$$

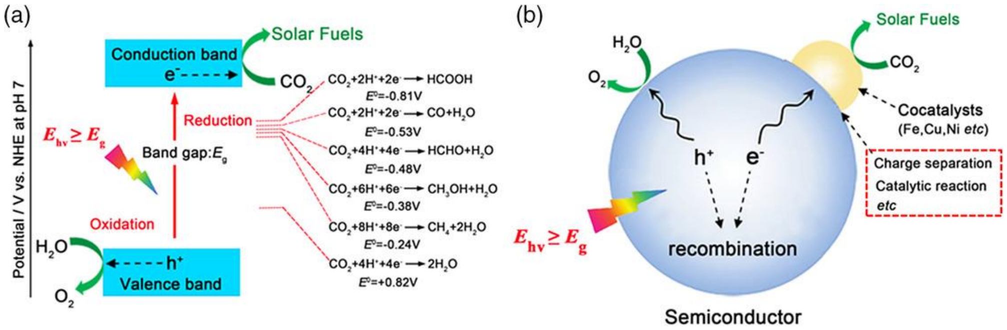
退相干函数（二次卷积形式，右图三）

$$D(t) = \exp\left(-\frac{1}{\hbar^2}\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \Delta E(t)\cdot\Delta E(0)\rangle\right)$$



What is Photocatalysis



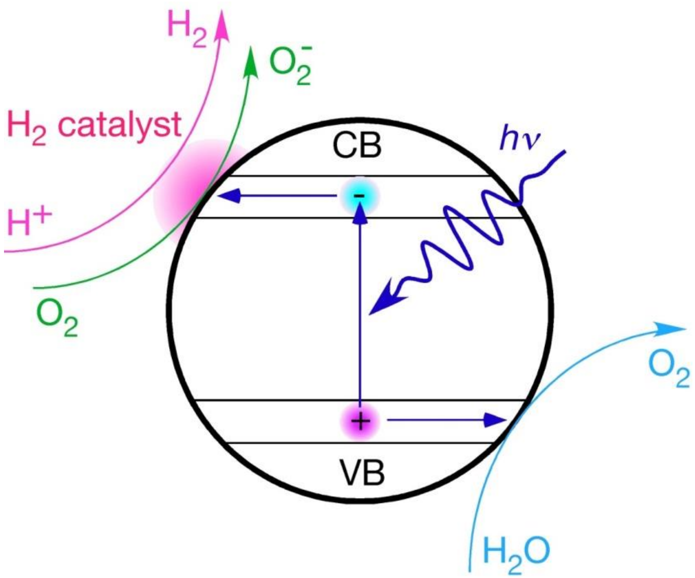


- ✓ 光解水
- ✓ 光还原CO_2
- ✓ 降解污染物

…

目标：通过第一性原理计算理解光催化反应机制，提出理论设计提升反应效率

Crucial Processes in Photocatalysis on Surfaces



- ✓ **Photo-absorption**
  - **absorption spectra (DFT, GW+BSE)**
- ✓ **Photoexcited carrier trapping**
  - **Lifetime of photoexcited carriers**
  - **Carrier migration to surface**
  - **Carrier trapping by molecules**
- ✓ **Photochemical reaction on the surface**
  - **Excited state reaction barrier**

Crucial Processes in Photocatalysis on Surfaces

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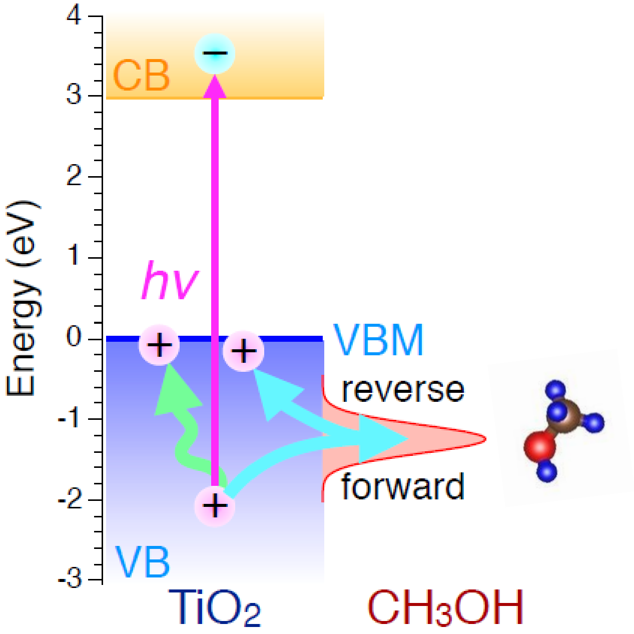
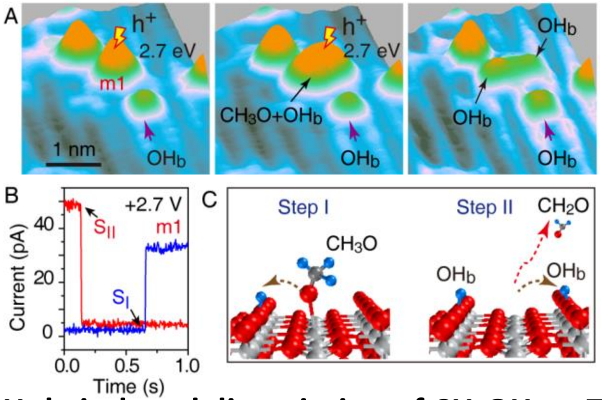
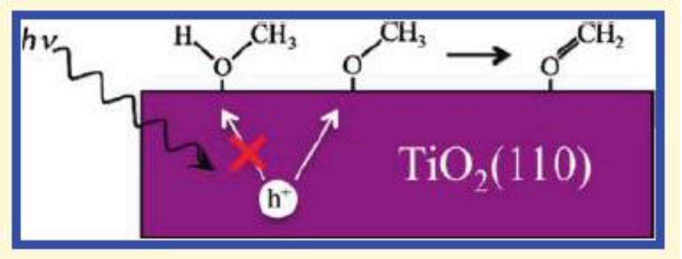
Excited Carrier Dynamics

CH_3OH behaves as a hole scavenger on TiO_2





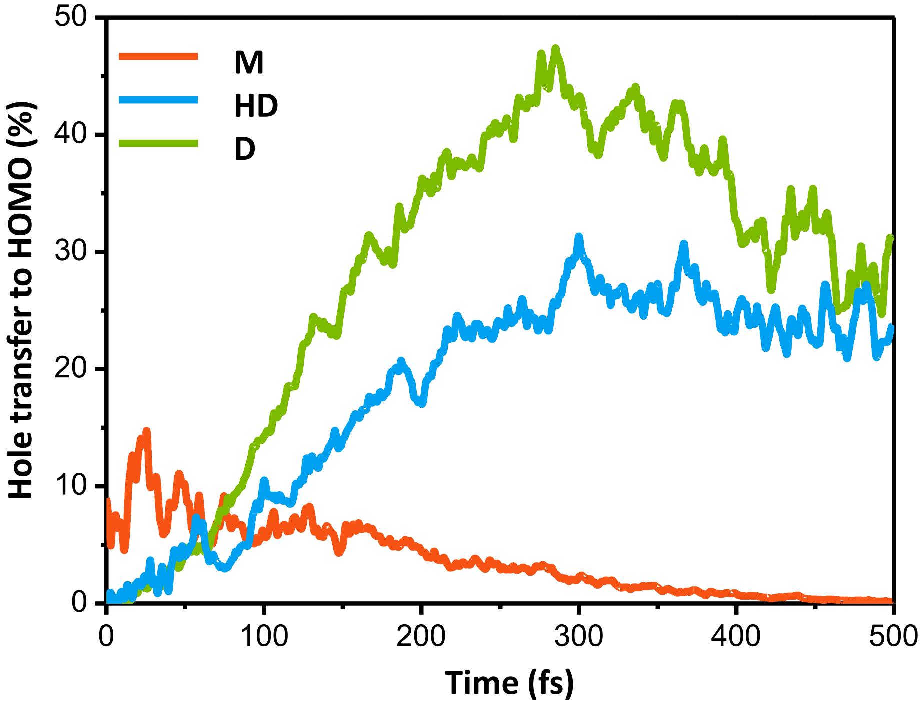
Hole induced dissociation of CH_3OH on TiO_2 observed by Bing Wang et.al.

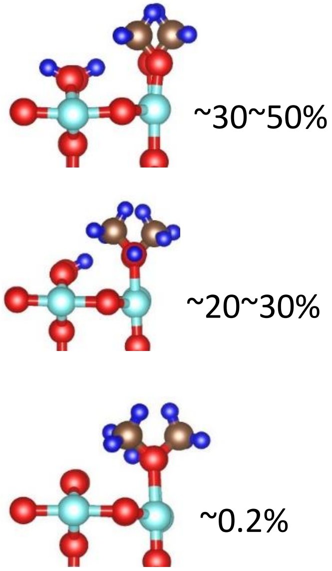


Henderson et.al. believes that CH_3O is the hole trapper in stead of CH_3OH

M. Shen and M. A. Henderson, *J. Phys. Chem. Lett.* ***2****, 2707-2710* (2011)

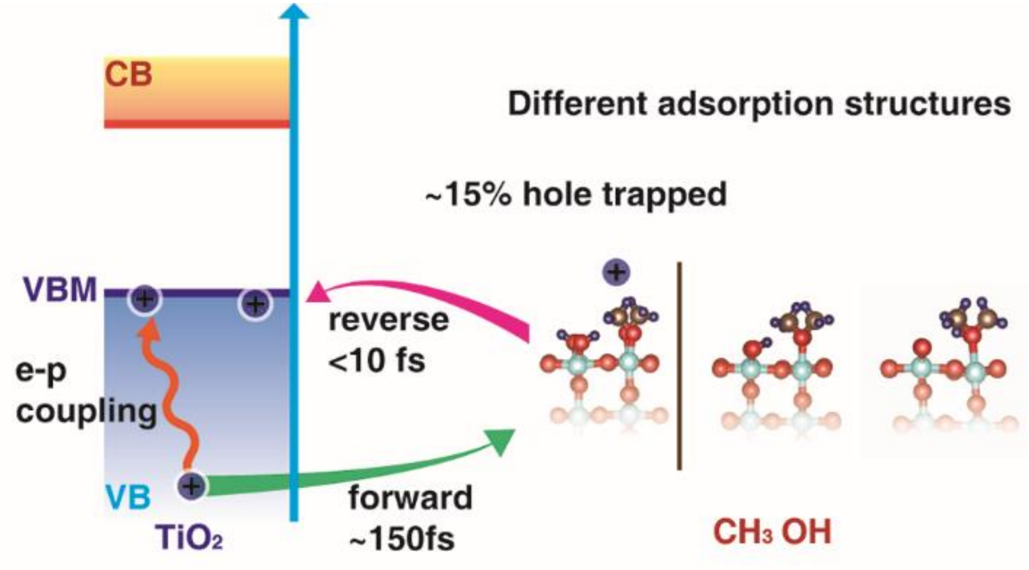
Hole trapping sites





Average from 10^5 trajectories

CH_3OH as a Hole Scavenger on TiO_2 Surface

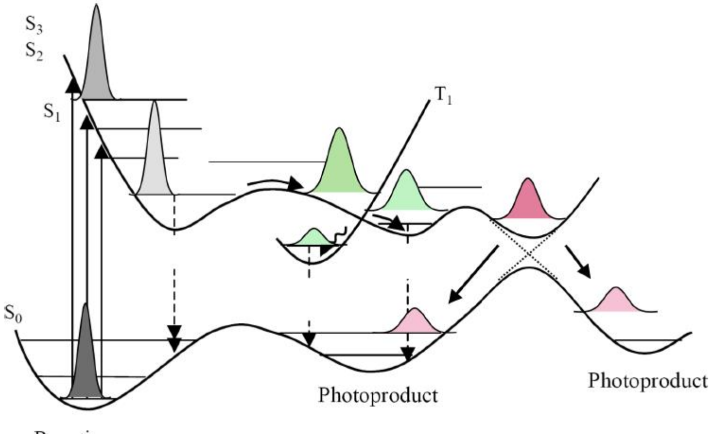


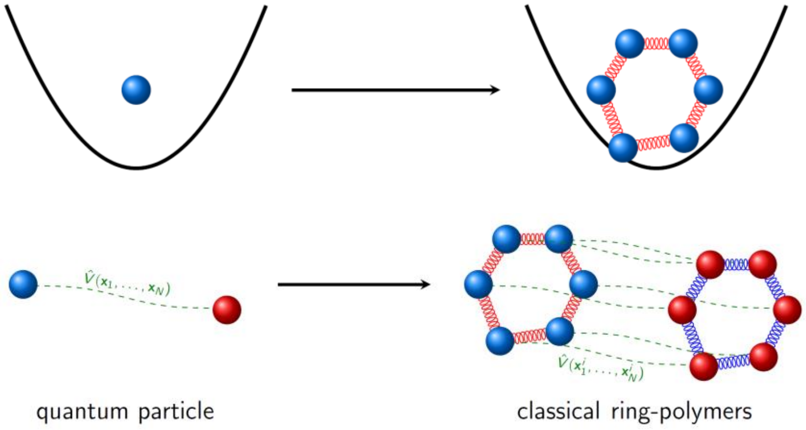
W. Chu, W. A. Saidi, Q. Zheng*, Y. Xie, Z. Lan, O. V. Prezhdo, H. Petek and **J. Zhao*** *J. Am. Chem. Soc*, 138, 13740, **(2016)**

Nuclear Quantum Effects in NAMD

Mixed Quantum-Classical approximation

$\Psi(\mathbf{r},\mathbf{R},t) = \Omega_j(\mathbf{R},t)\Phi_j(\mathbf{r};\mathbf{R})$; $\hat{\mathcal{H}}_{el}(\mathbf{r};\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R}) = E_j(\mathbf{R})\Phi_j$

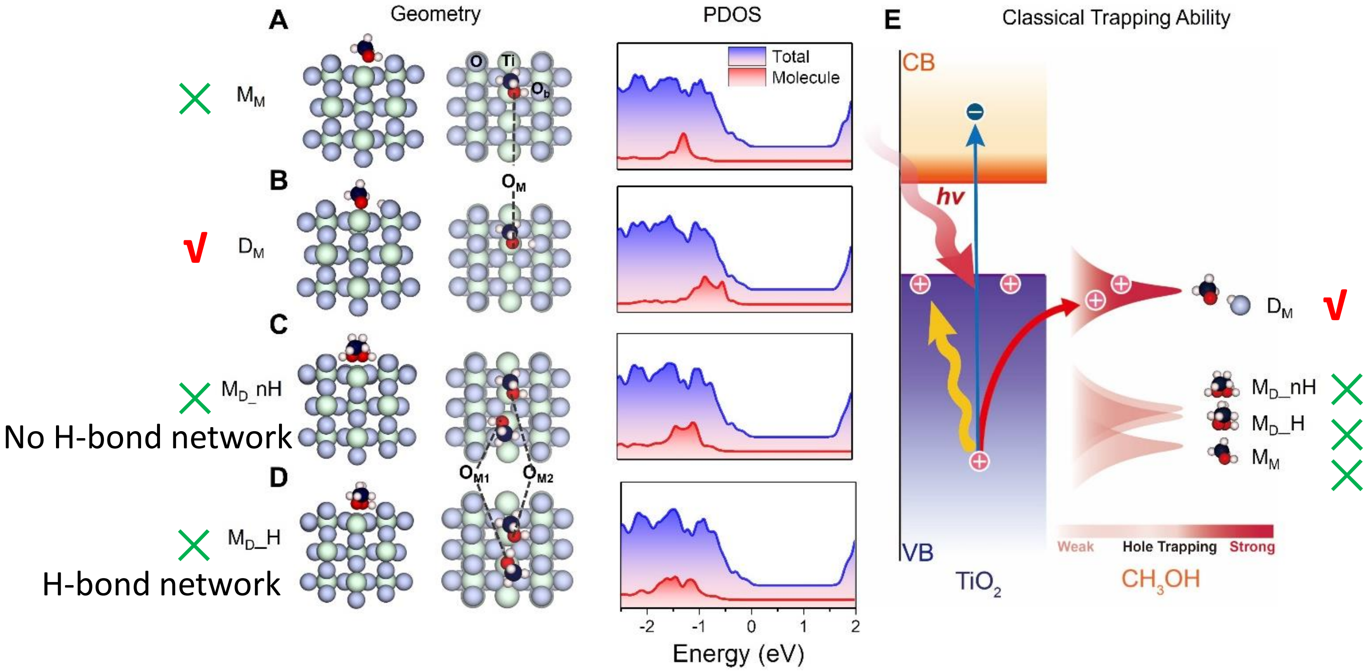




Ring-polymer molecular dynamics (RPMD)

Q: 如何在mixed quantum-classical approximation中考虑核量子效应
A: RPMD + NAMD

Different Adsorption Structures of CH_3OH on TiO_2



No H-bond network

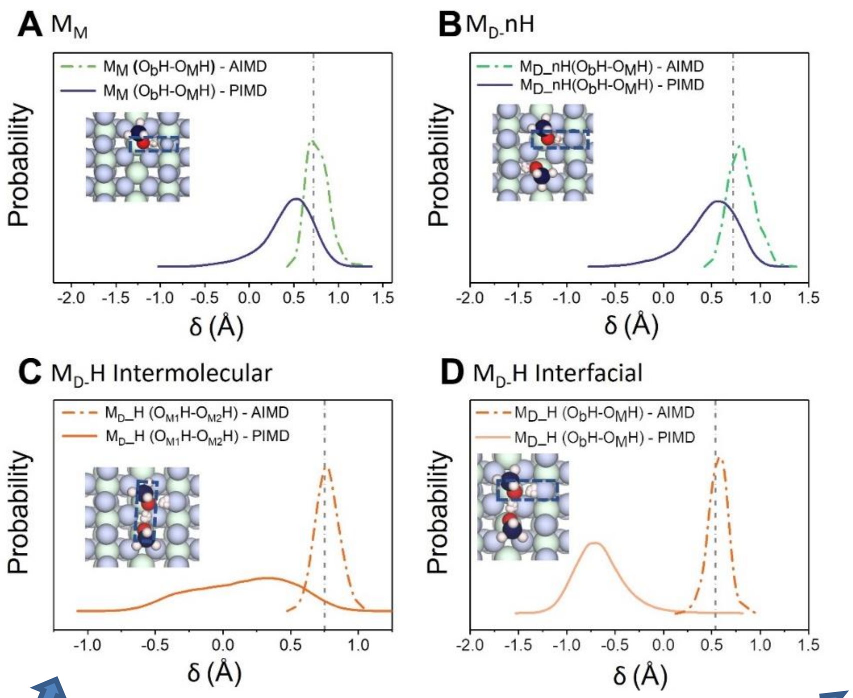
H-bond network

Dissociated CH_3O (D_M) behaves as hole scavenger

Nuclear Quantum effects (NQEs) on the Adsorption Structures

No H-bond network

H-bond network



$$\delta = R_{\mathrm{O_aH}} - R_{\mathrm{O_dH}}$$

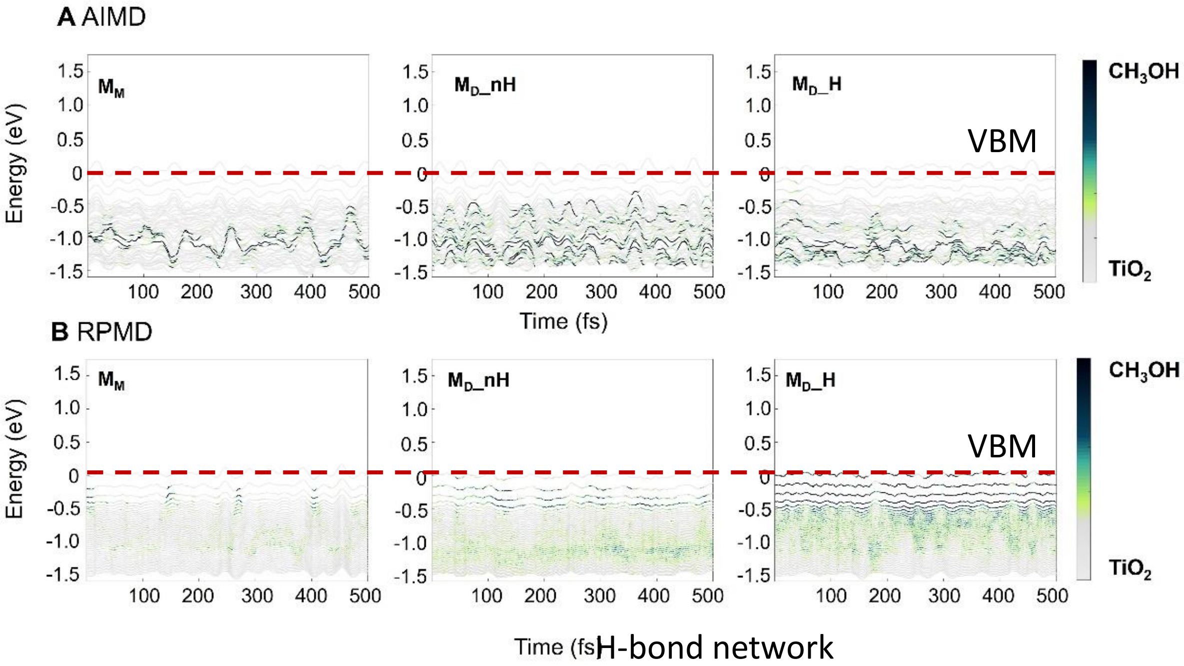
$\delta > 0$ no proton transfer

$\delta < 0$ proton tranfer

Quantum proton delocalization

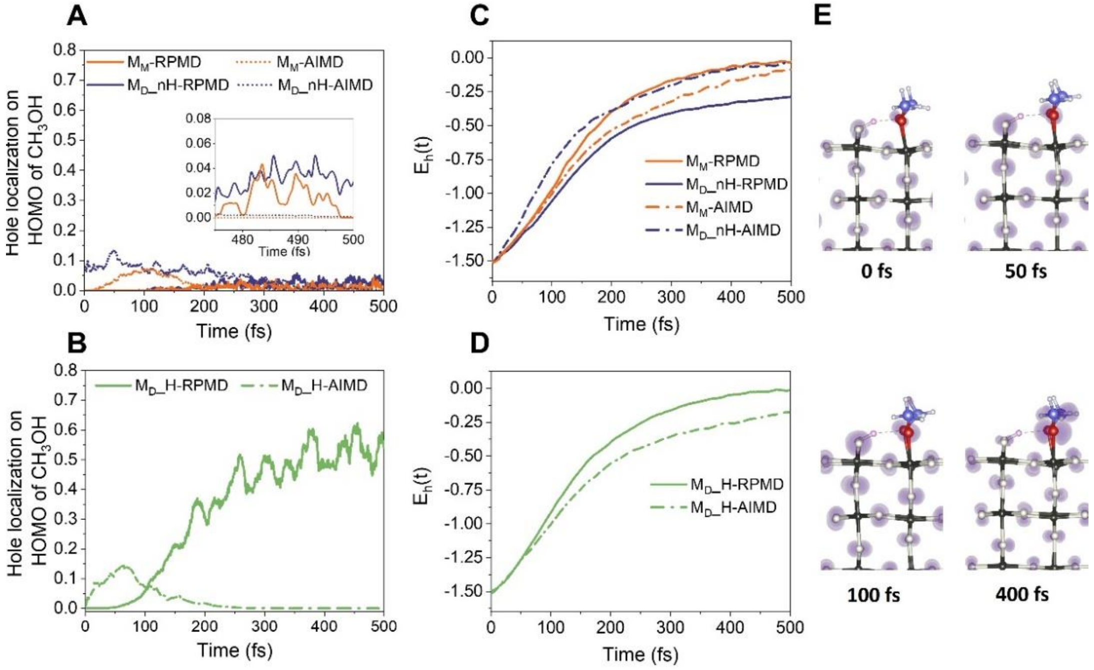
NQEs induced proton transfer

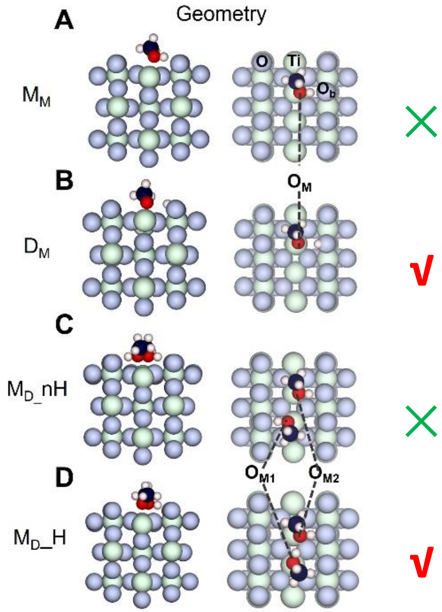
Nuclear Quantum effects on the Energy Level Alignment



NQEs change the band alignment of M_D_H system, where a H-bond network is formed.

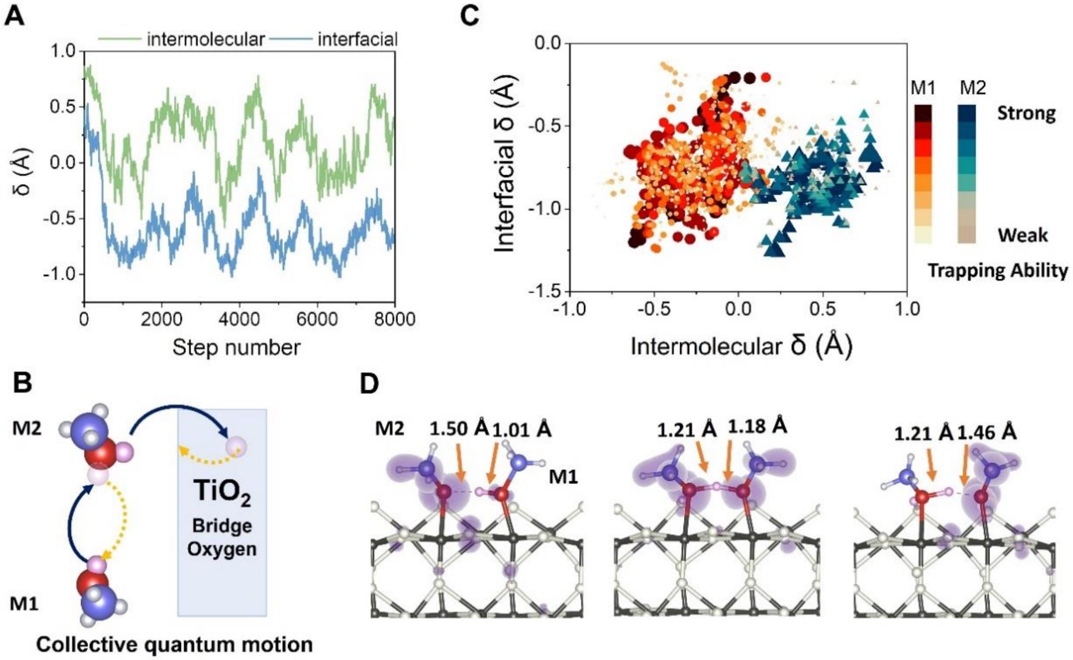
Nuclear Quantum Effects on Hole Trapping





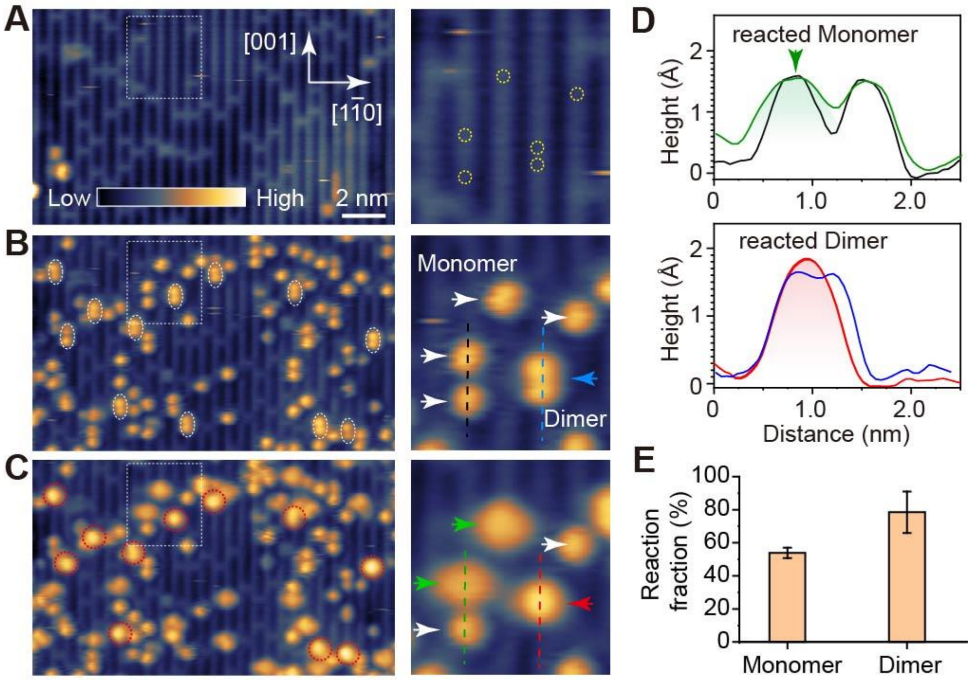
NQEs makes M$_D$_H behave as a hole scavenger.

Collective Nuclear Quantum Motion Coupled Hole Transfer



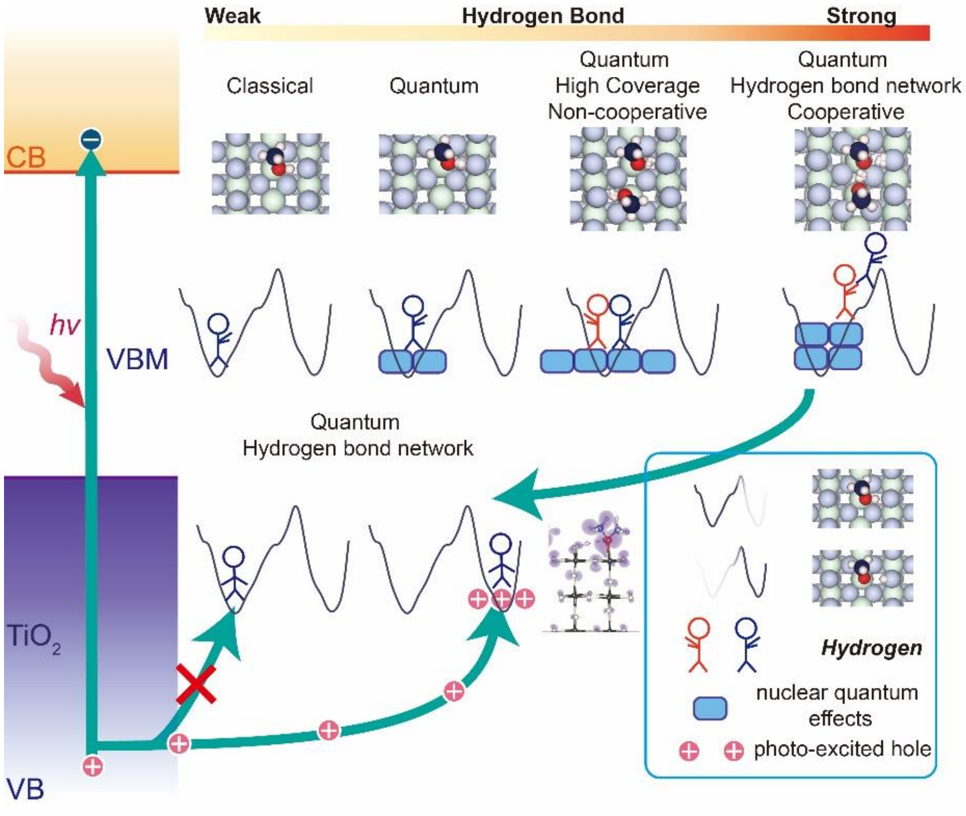
In the H-bond network, the quantum proton motion is collective, which couples with hole trapping dynamics.

Experimental Evidence by STM



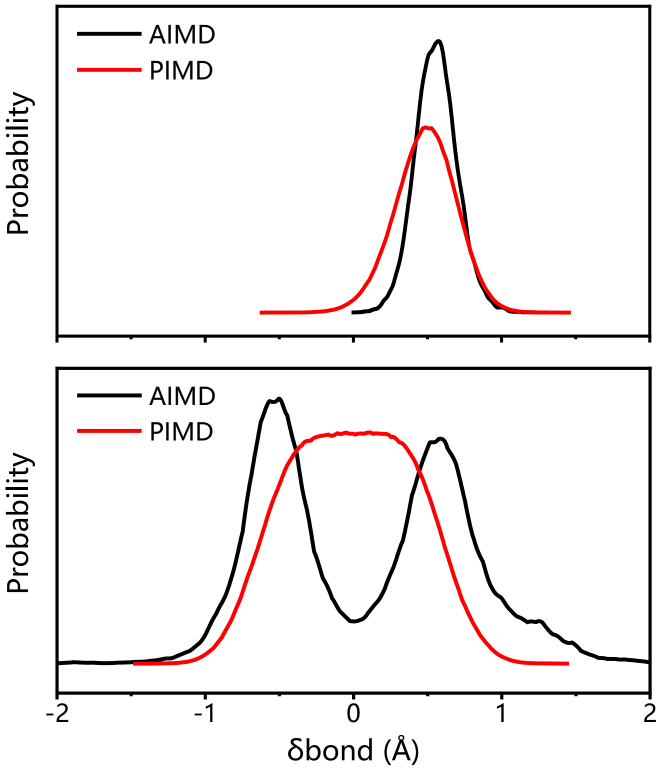
Dimer formation (H-bond network) improves the photochemical reaction rate.

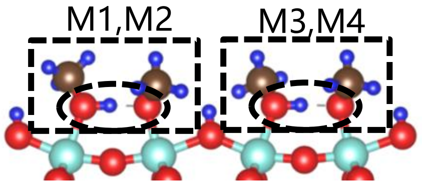
Summary - Example I

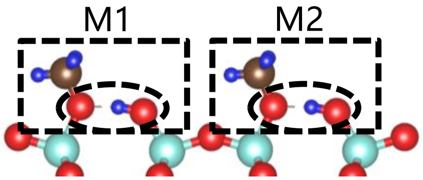


W. Chu *et al.* X. Li*, J. Zhao* *Sci. Adv.* **8**, eabo2675 (2022)

Outlook - Example I



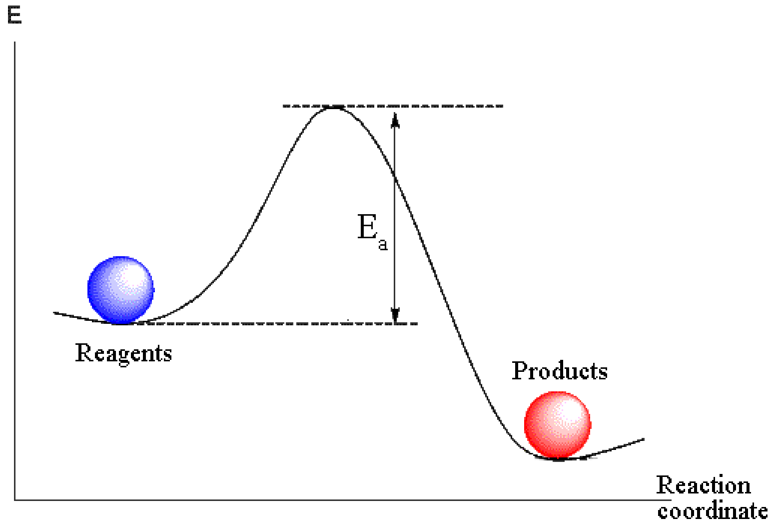


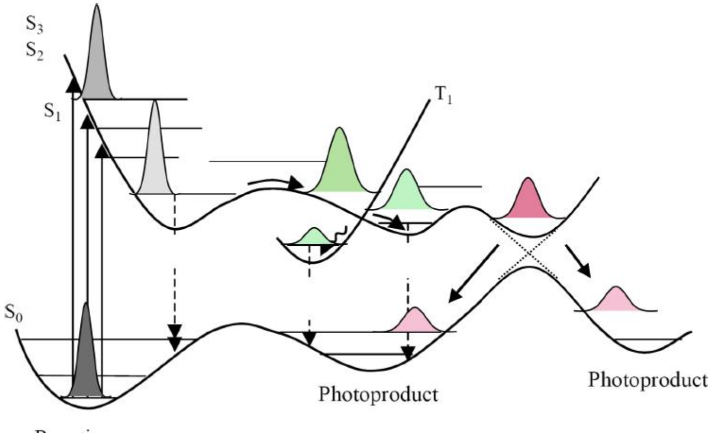


RPMD/PIMD is very expensive!

Machine Learning + PIMD/RPMD

Outlook - Part II





基态催化：

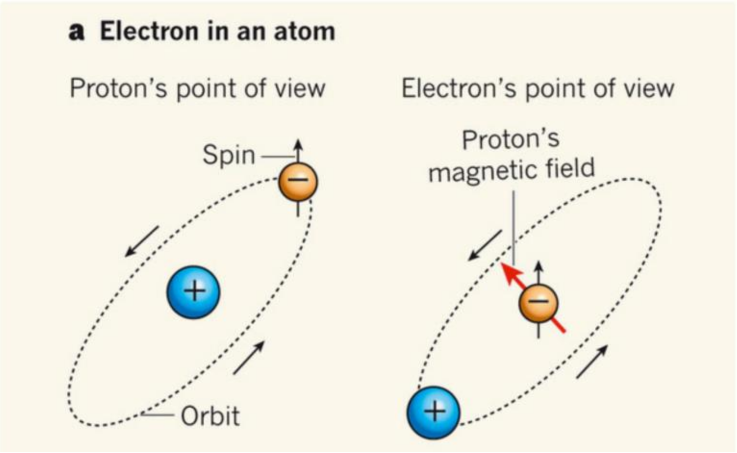
计算反应势垒，方法非常成熟

光催化：

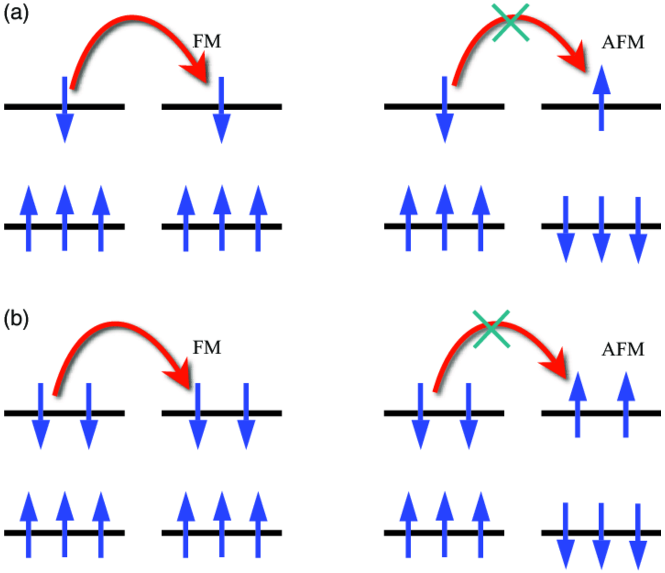
- ✓ **激发态势能面**
- ✓ **势能面交叉**
- ✓ **激发态载流子寿命**

- Back ground
- Single particle dynamics
- **Spin dynamics**
- Exciton Dynamics
- Outlook

Spin Dynamics

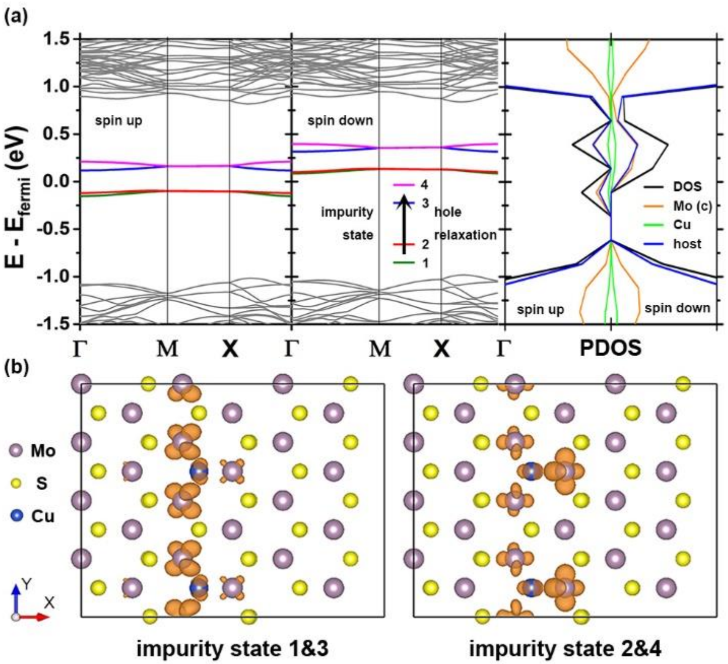


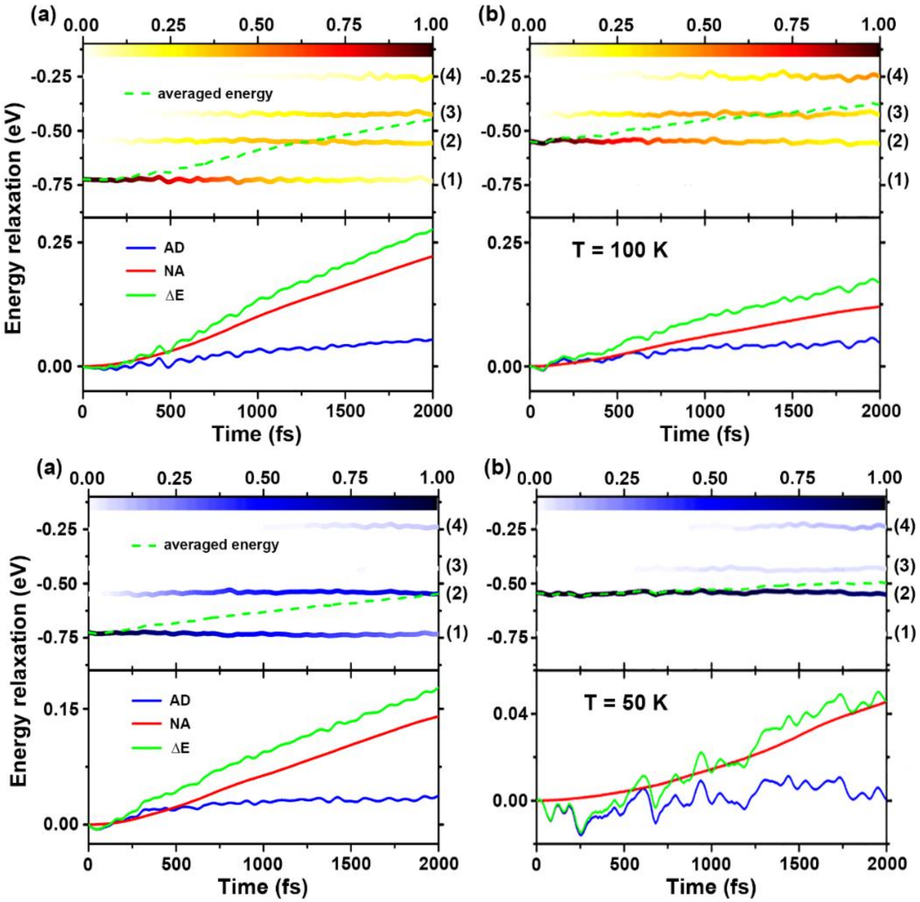
Spin-Orbital Interaction



Spin-Spin Interaction

Dynamics of Photogenerated Spin Hole Current





赵传寓

C. Zhao, et al. and J. Zhao*, *Phys. Rev. B* **96**, 134308 (2017)

NAMD with SOC

The time-dependent Schrödinger equation

$$i\hbar\frac{\partial|\Psi(\mathbf{r},\mathbf{R}(t),\mathbf{s},t)\rangle}{\partial t}=\hat{\mathcal{H}}^{tot}(\mathbf{r},\mathbf{R}(t),\mathbf{s})|\Psi(\mathbf{r},\mathbf{R}(t),\mathbf{s},t)\rangle \tag{1}$$

where the total Hamiltonian is given by

$$\hat{\mathcal{H}}^{tot}(\mathbf{r},\mathbf{R}(t),\mathbf{s})=\hat{\mathcal{H}}^{0}(\mathbf{r},\mathbf{R}(t))+\hat{\mathcal{H}}^{soc}(\mathbf{r},\mathbf{R}(t),\mathbf{s}) \tag{2}$$

by expanding the wavefunction with a basis set $\{|\psi_i\rangle\}$ or different representations

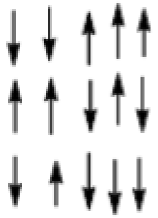
$$|\Psi\rangle=\sum_i|\psi_i\rangle\langle\psi_i|\Psi\rangle=\sum_i c_i|\psi_i\rangle \tag{3}$$

and substituting eq (3) into eq (1), we have

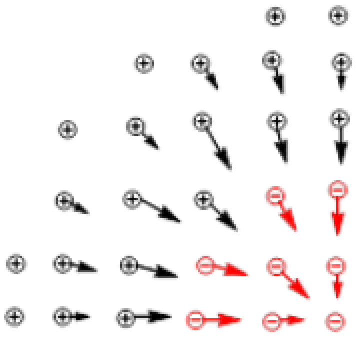
$$\begin{aligned}\frac{\partial c_j(t)}{\partial t}&=-\sum_i\left[i\hbar^{-1}\langle\psi_j|\hat{\mathcal{H}}^{tot}|\psi_i\rangle+\langle\psi_j|\frac{\mathrm{d}}{\mathrm{d}t}|\psi_i\rangle\right]c_i(t)\\&=-\sum_i\left[i\hbar^{-1}\langle\psi_j|\hat{\mathcal{H}}^{0}|\psi_i\rangle+i\hbar^{-1}\langle\psi_j|\hat{\mathcal{H}}^{soc}|\psi_i\rangle+\langle\psi_j|\frac{\mathrm{d}}{\mathrm{d}t}|\psi_i\rangle\right]c_i(t)\\&=-\sum_i\left(i\hbar^{-1}H^{0}_{ji}+i\hbar^{-1}H^{soc}_{ji}+T_{ji}\right)c_i(t)\end{aligned} \tag{4}$$

Choices of Representations

Ising Model –
vectors point
UP OR DOWN
***ONLY* → simplest**



Heisenberg Model –
vectors point in
any direction
IN SPACE



- "Spin-diabatic" representation
  - $H^{0}_{ji} = E_j \delta_{ji}$, i.e. $\{|\psi_i\rangle\} \Rightarrow$ eigenstates of $\hat{\mathcal{H}}^{0}$.
  - $H^{soc}_{ji} = 0$ for same spin multiplicity.
  - $T_{ji} = 0$ for different spin multiplicity.
  - Used with *weak* SOC.
- "Spin-adiabatic" representation
  - $H^{0}_{ji} + H^{soc}_{ji} = \Lambda_{ji}\delta_{ji}$, i.e. $\{|\psi_i\rangle\} \Rightarrow$ eigenstates of $\hat{\mathcal{H}}^{tot}$.
  - Hopping solely determined by T_{ji}.
  - *Strong* SOC.

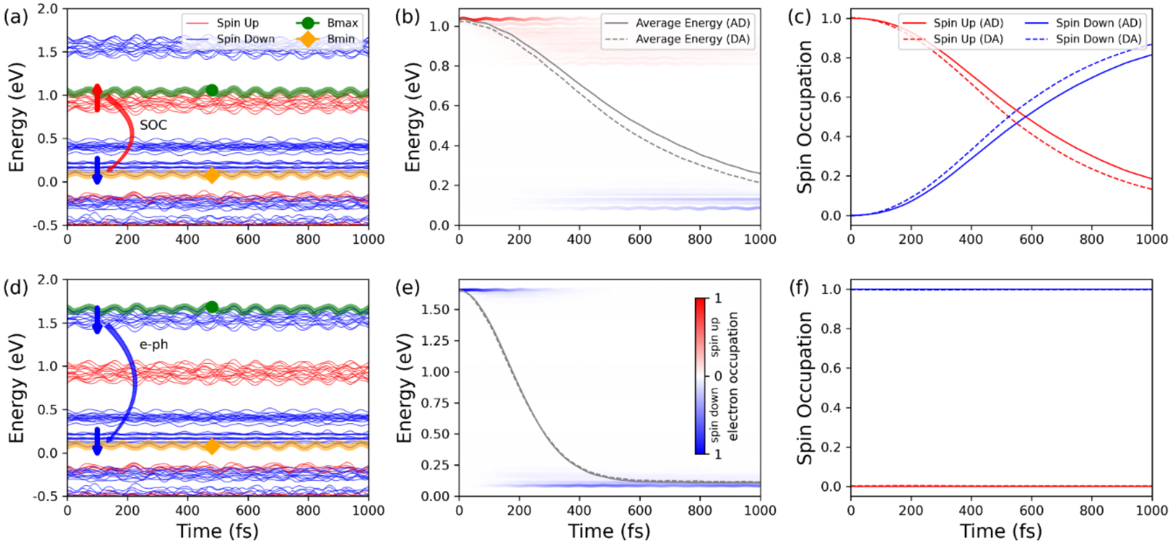
The hopping probility within FSSH

$$P_{j\to k}(t,\Delta t) = \max\left(-\frac{2\Delta t\left[\hbar^{-1}\,\mathrm{Im}(c_j^{*}c_k(H^{0}_{jk}+H^{soc}_{jk})) - \mathrm{Re}(c_j^{*}c_k T_{jk})\right]}{c_j^{*}c_j},\ 0\right)$$

郑奇靖

Ni金属自旋轨道耦合引发超快退磁过程

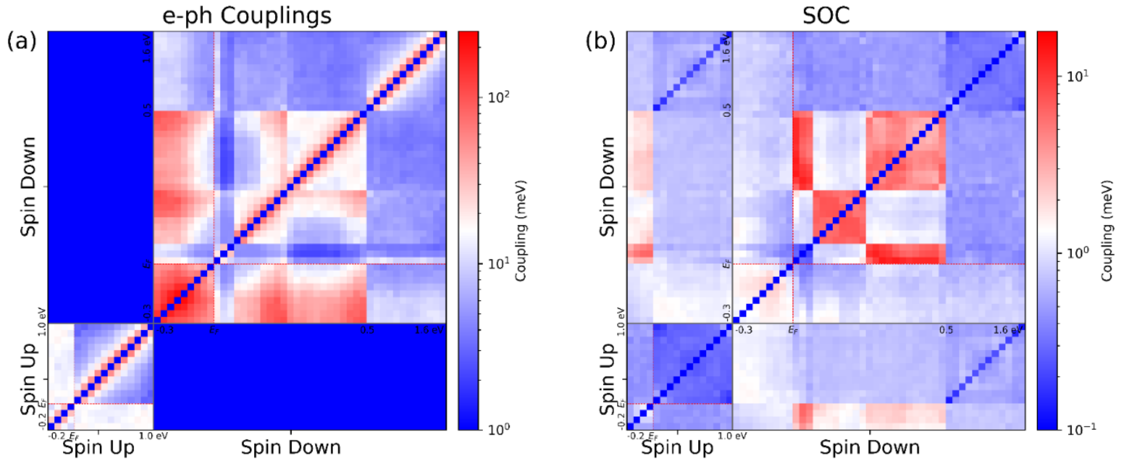
Spin up electrons **will** flip to Spin down electrons due to SOC



Spin down electrons **will NOT** flip to Spin up electrons due to SOC
They will decay to spin down electrons with lower energies.

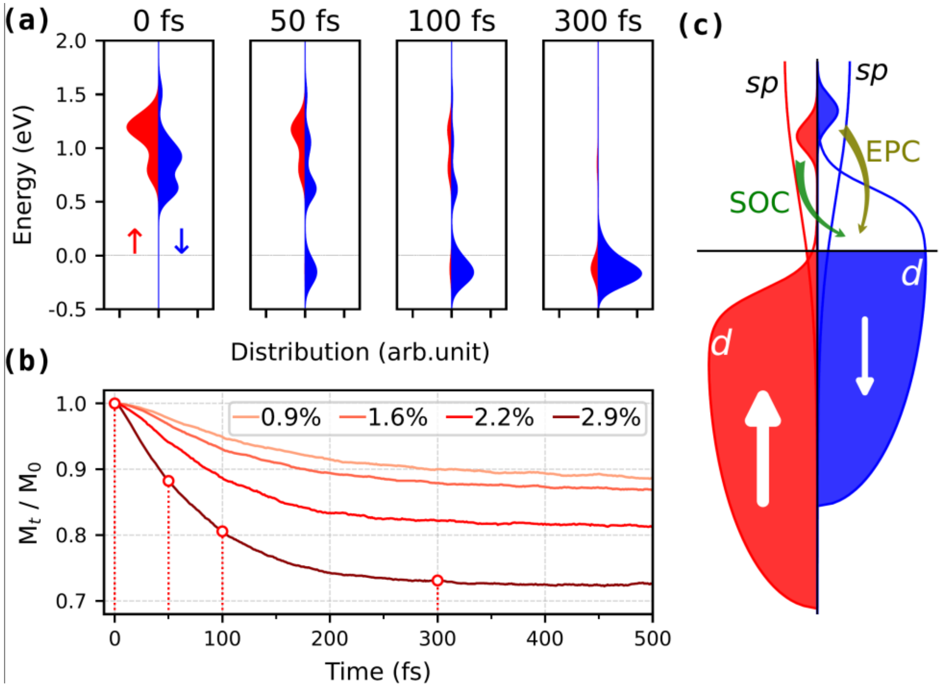
自旋轨道耦合与电声耦合

$$H_{ki} = \epsilon_k \delta_{ik} - i\hbar \left\langle k \middle| \frac{\partial}{\partial t} \middle| i \right\rangle + i\hbar \langle k | \mathcal{H}^{SOC} | i \rangle$$



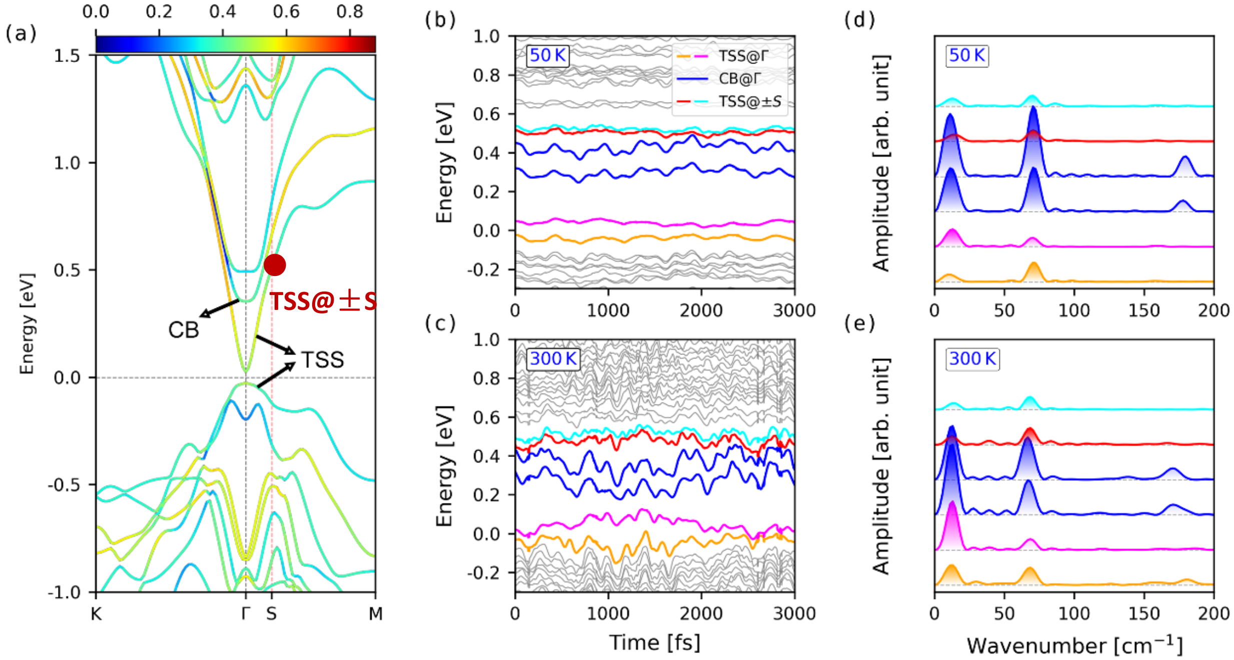
In Ni, e-ph coupling > SOC. The electron tends to decay through the orbitals with the same spin.

Ni体系超快退磁



Z. Zheng, Q. Zheng*, J. Zhao*, *Phys. Rev. B* **105**, 085142 (2022)

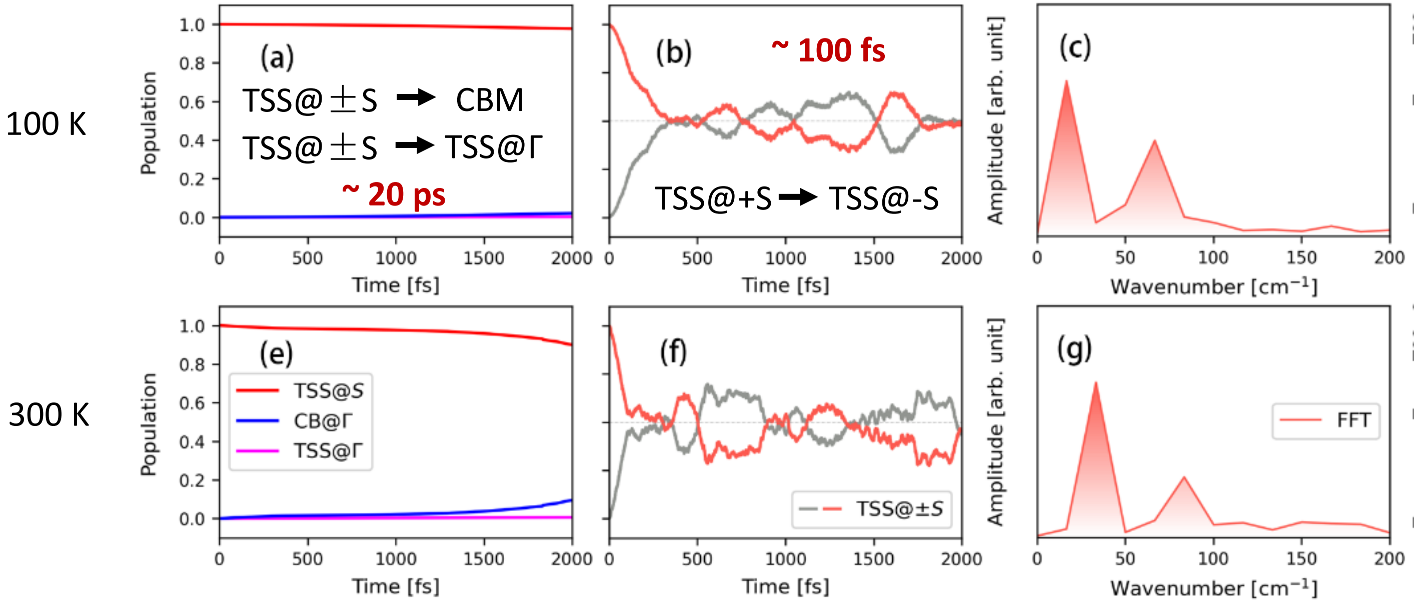
Excited Electron Dynamics in Bi_2Se_3



Back scattering between TSS@+S and TSS@-S is forbidden

$$|+> = \mathcal{T}|-> \quad \langle +|U|-\rangle = 0$$

Backscattering Between two TSS@±S Time-Reversal Partners



$$d_{jk} = -i\hbar \left\langle \varphi_j \middle| \frac{\partial}{\partial t} \middle| \varphi_k \right\rangle = -i\hbar \frac{\left\langle \varphi_j(t) \middle| \varphi_k(t+\Delta t) \right\rangle - \left\langle \varphi_j(t+\Delta t) \middle| \varphi_k(t) \right\rangle}{2\Delta t}$$

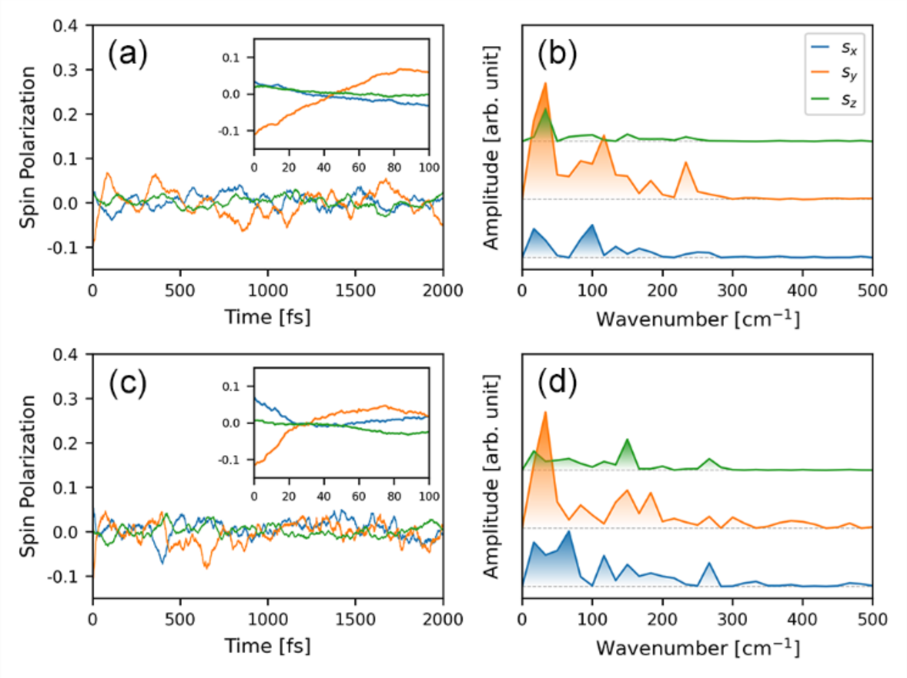
$|+> = \mathcal{T}|->$ $\quad \langle + | U | - \rangle = 0$

Without phonon excitation

$|+,(t+\Delta t) > \neq \mathcal{T}|-,t>$ $\quad \langle +,t | -,(t+\Delta t) \rangle \neq 0$

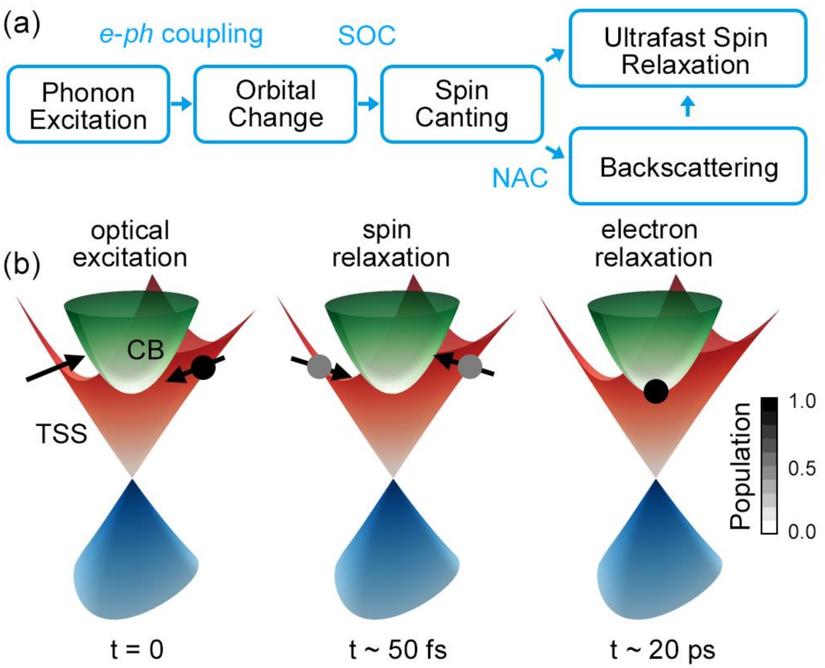
With phonon excitation

Excited State Spin Dynamics in Bi_2Se_3

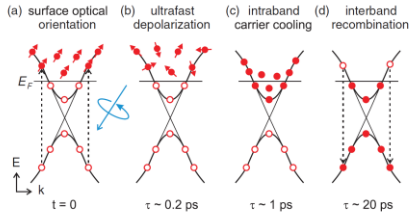


Spin canting occurs in ~ 50 fs

Ultrafast Spin Relaxation of the Excited TSS Electron



C. Zhao, Q. Zheng*, J. Zhao*, *Fundamental Research* in press



N. Gedik* et al. *Phys. Rev. Lett.* 107, 077401 (2011)

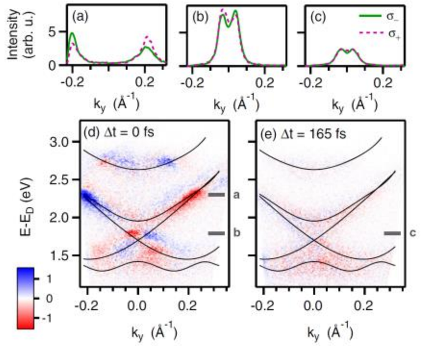
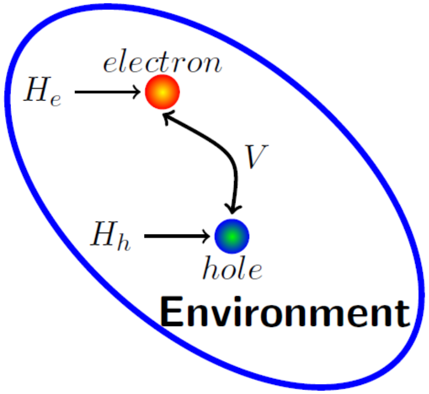


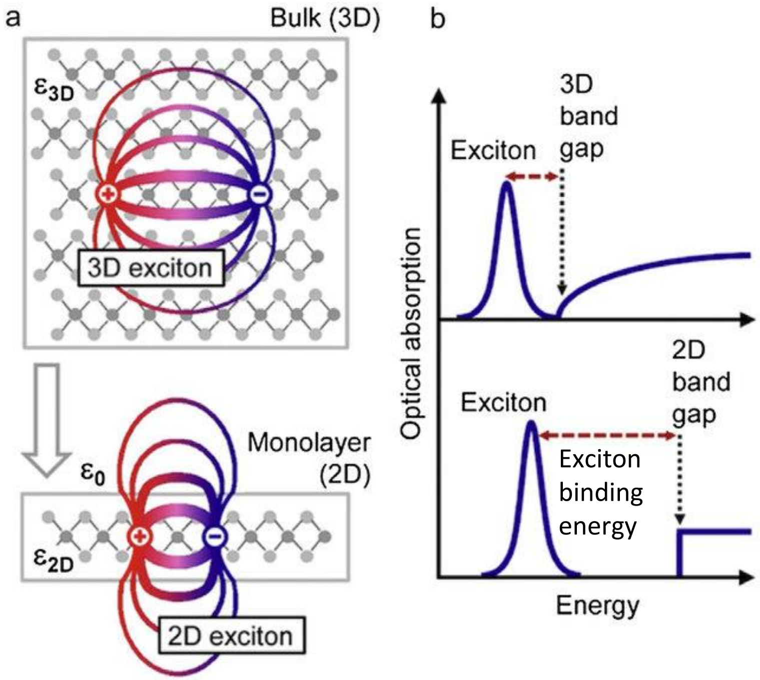
FIG. 2. Helicity-dependent population asymmetry. (a)–(c) Momentum distribution curves (MDCs) of the unoccupied band structure, excited with σ_+ (dashed purple line) and σ_- (solid green line) polarized pulses. (a) and (b) were taken at $\Delta t = 0$, and (c) at $\Delta t = 165$ fs, at the energies marked by the short gray lines in (d) and (e). (d),(e) Asymmetry image: Difference between the populations of the unoccupied bands when excited by σ_- and σ_+ polarized pulses, taken at $\Delta t = 0$ and 165 fs respectively. Black lines are guides to the eye that follow the dispersions of the unoccupied bands.

Z. X. Shen* et al. *Phys. Rev. Lett.* 122, 167401 (2019)

- Back ground
- Single particle dynamics
- Spin dynamics
- **Exciton Dynamics**
- Outlook

Excitons in 2D Materials

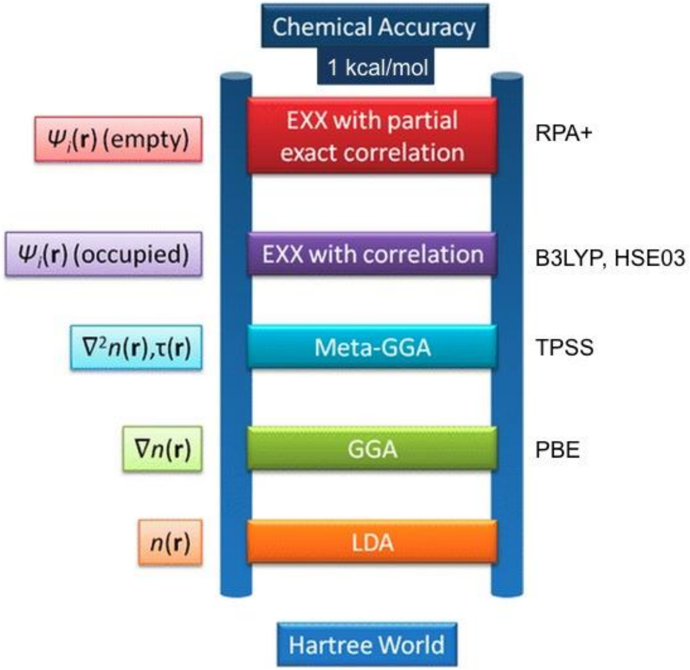


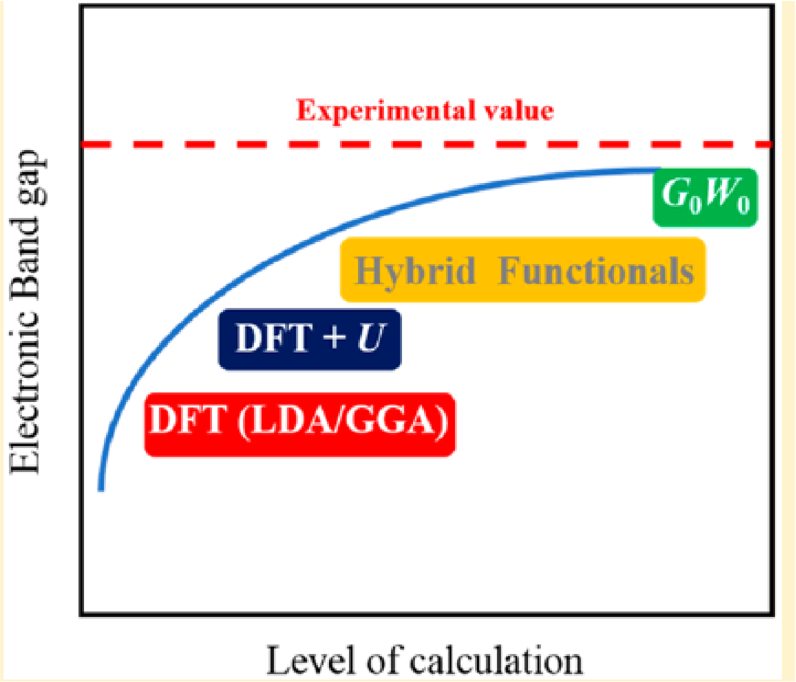


A. Chernikov et al. *Phys. Rev. Lett.* **113** 076802 (2014)

2D materials: quantum confinement significantly reduce the dielectric screening and increase the exciton binding energy

Failure of DFT

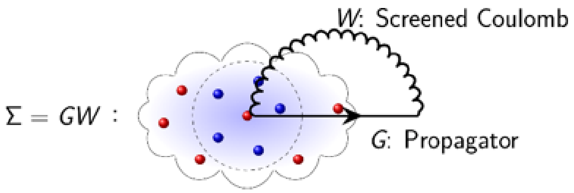


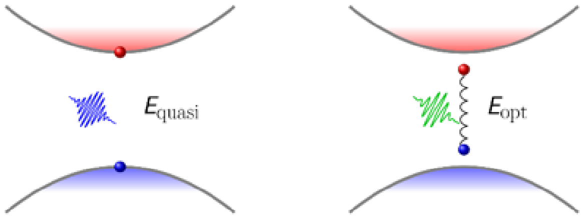


https://www.sas.upenn.edu/~jianmint/Research/

A. Morales-Garcia et al. J. Phys. Chem. C, 121, 18862 (2017)

GW + BSE to Describe the Exciton





$$\Sigma^{\mathrm{GW}}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\frac{i}{2\pi}\int \mathrm{d}\omega\, e^{i\omega\eta} G(\boldsymbol{r},\boldsymbol{r}',\omega+\omega')W(\boldsymbol{r},\boldsymbol{r}',\omega')$$

$$H^{cvk}_{c'v'k'} = \left[E^{\mathrm{QP}}_{ck} - E^{\mathrm{QP}}_{vk}\right]\delta_{cc'}\delta_{vv'}\delta_{kk'} - W^{cvk}_{c'v'k'} + 2v^{cvk}_{c'v'}$$

GW: self-energy take place of exchange correlation potential

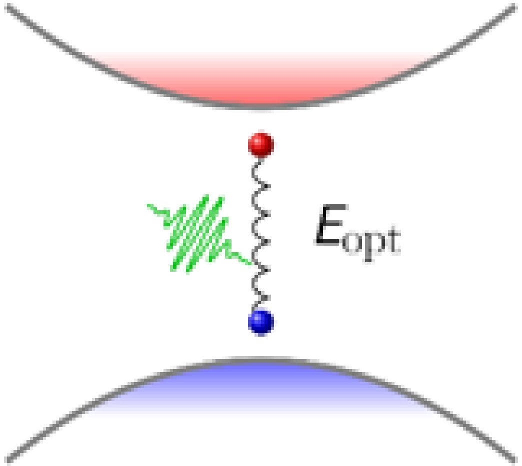
Accurate Quasi-particle energies

✚

Bethe-Salpeter Equation (BSE): Screened Coulomb (*W*) and exchange (*v*) interaction of electron and hole

Exciton binding energy and wave function

Exciton Dynamics is Important



Exciton dynamics:

Exciton relaxation

Bright-to-dark transition

Single-to-multi transition

Singlet fission

Exciton annihilation (radiative and nonradiative)

…

10,000 times of GW+BSE calculations are too expensive!

Realization of *GW* + Real-Time BSE

From GW

BSE Hamiltonian:

$$\langle \mathbf{k}cv | H | \mathbf{k}'c'v' \rangle = \boxed{\left(E^{QP}_{\mathbf{k}c} - E^{QP}_{\mathbf{k}v} \right)} \delta_{\mathbf{k}\mathbf{k}'} \delta_{cc'} \delta_{vv'} - W^{\mathbf{k}cv}_{\mathbf{k}'c'v'} + v^{\mathbf{k}cv}_{\mathbf{k}'c'v'} .$$

Coulomb Interaction:

$$W^{\mathbf{k}cv}_{\mathbf{k}'c'v'} = \frac{1}{\Omega} \sum_{\mathbf{G}\mathbf{G}'} \frac{4\pi \boxed{\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{k}-\mathbf{k}')}}{|\mathbf{k}-\mathbf{k}'+\mathbf{G}||\mathbf{k}-\mathbf{k}'+\mathbf{G}'|} \boxed{\left(B^{\uparrow\mathbf{k}c}_{\uparrow\mathbf{k}'c'}(\mathbf{G}) + B^{\downarrow\mathbf{k}c}_{\downarrow\mathbf{k}'c'}(\mathbf{G}) \right) \left(B^{\uparrow\mathbf{k}v*}_{\uparrow\mathbf{k}'v'}(\mathbf{G}') + B^{\downarrow\mathbf{k}v*}_{\downarrow\mathbf{k}'v'}(\mathbf{G}') \right)}$$

Exchange Interaction:

$$v^{\mathbf{k}cv}_{\mathbf{k}'c'v'} = \frac{1}{\Omega} \sum_{\mathbf{G}\neq 0} \frac{4\pi}{|\mathbf{G}|^2} \boxed{\left(B^{\uparrow\mathbf{k}c}_{\uparrow\mathbf{k}v}(\mathbf{G}) + B^{\downarrow\mathbf{k}c}_{\downarrow\mathbf{k}v}(\mathbf{G}) \right) \left(B^{\uparrow\mathbf{k}'c'*}_{\uparrow\mathbf{k}'v'}(\mathbf{G}) + B^{\downarrow\mathbf{k}'c'*}_{\downarrow\mathbf{k}'v'}(\mathbf{G}) \right)},$$

from time-dependent Kohn-Sham basis sets

Rigid dielectric function during MD

QP energy: Rigid shift from KS energy

10,000 real-time *GW* + BSE
– 1 *GW* + real-time BSE

Realization of *GW* + Real-Time BSE

Single-particle

TDDFT

$$i\hbar\frac{\partial\psi(\boldsymbol{r},\boldsymbol{t})}{\partial\boldsymbol{t}}=\mathcal{H}(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r},\boldsymbol{t})$$

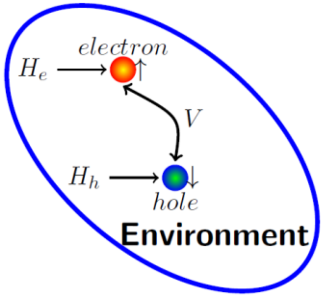
Real-time - BSE

$$i\hbar\frac{\partial\psi(\boldsymbol{r}_e,\boldsymbol{r}_h,\boldsymbol{t})}{\partial\boldsymbol{t}}=\mathcal{H}(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r}_e,\boldsymbol{r}_h,\boldsymbol{t})$$

two-particle

Hamiltonian:

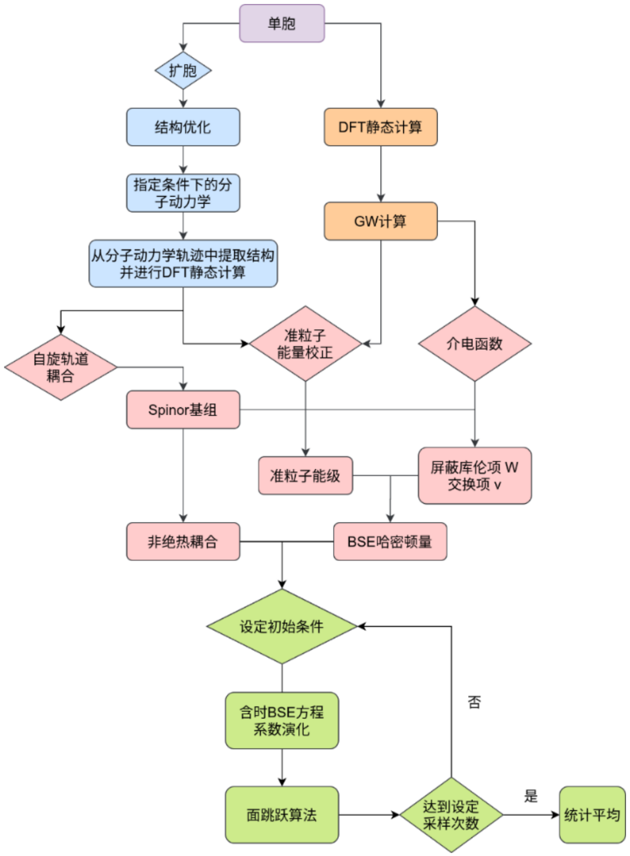
$$H = H_e + H_h + V_{e-h} + H^{SO}$$



Spin orbital coupling

- ✓ **Many-body interaction:** Coulomb and exchange
- ✓ **Exciton-phonon interaction:** real-time BSE + molecular dynamics
- ✓ **Spin orbital coupling:** adiabatic and diabatic representation
- ✓ **Nonadiabatic:** surface hopping

含时激子动力学方法实现



单胞

扩胞

结构优化

指定条件下的分子动力学

从分子动力学轨迹中提取结构并进行DFT静态计算

DFT静态计算

GW计算

自旋轨道耦合

准粒子能量校正

介电函数

Spinor基组

准粒子能级

屏蔽库伦项 W
交换项 v

非绝热耦合

BSE哈密顿量

设定初始条件

含时BSE方程系数演化

面跳跃算法

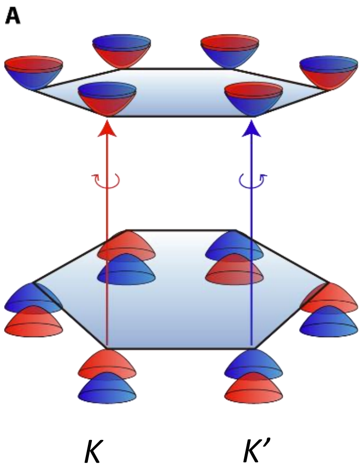
达到设定采样次数

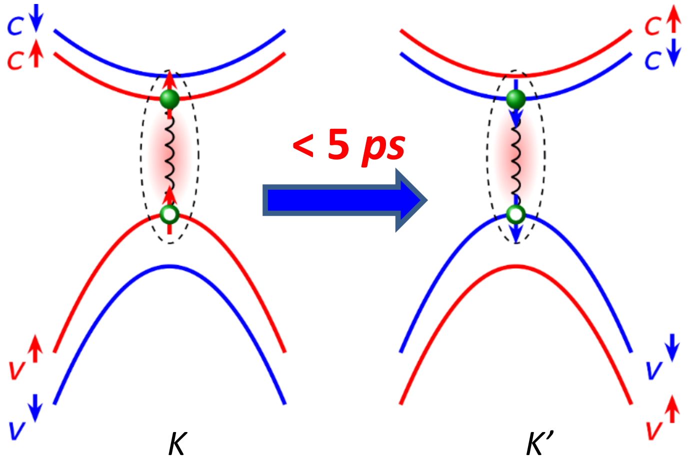
否

是

统计平均

Fast Intervalley Bright Exciton Scattering in Transition Metal Dichalcogenide

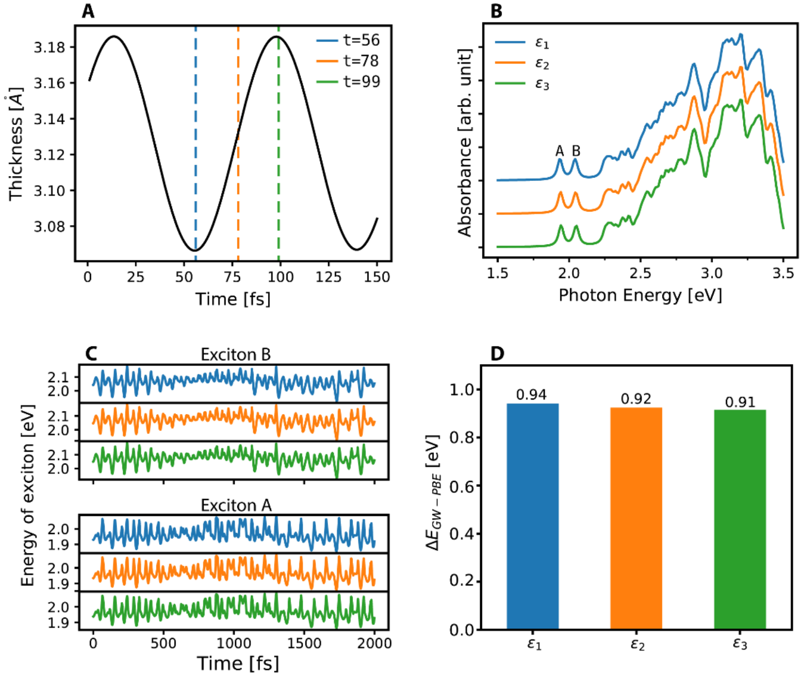




Intervalley bright exciton scattering requires the spin flip and momentum transition of both electron and hole

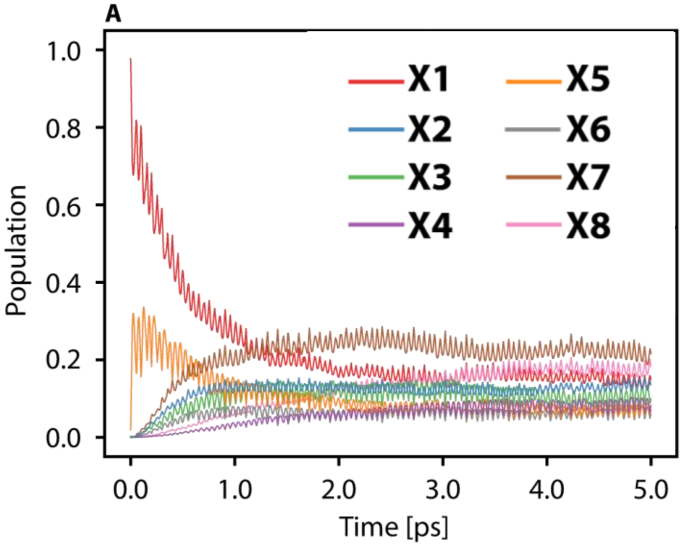
Puzzle: how can such intervalley bright exciton happen within several picoseconds?

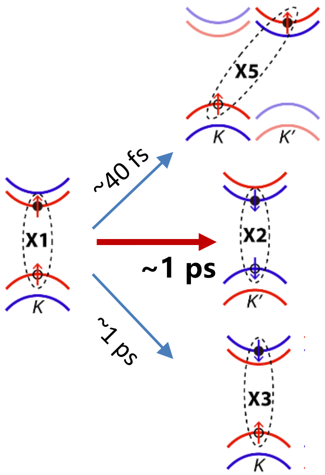
Test of the Dielectric Function Approximation



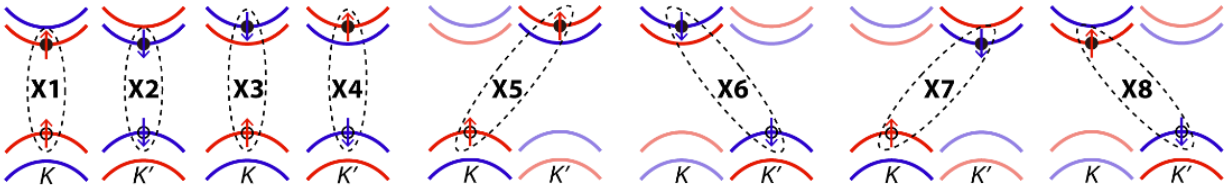
The dielectric function and *GW* QP correction almost does not change with the structure

Exciton Dynamics in MoS_2





Bright Exciton transition happens in several ps

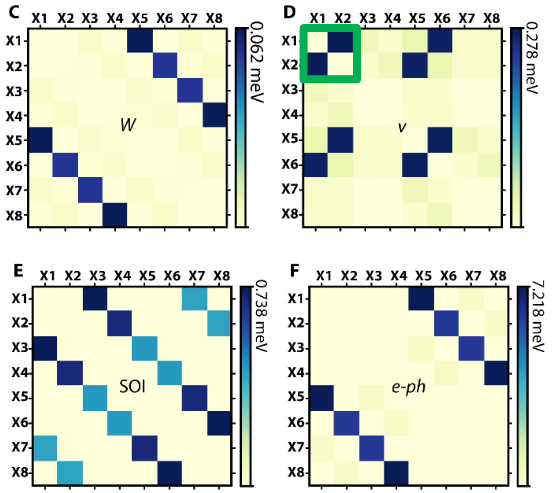


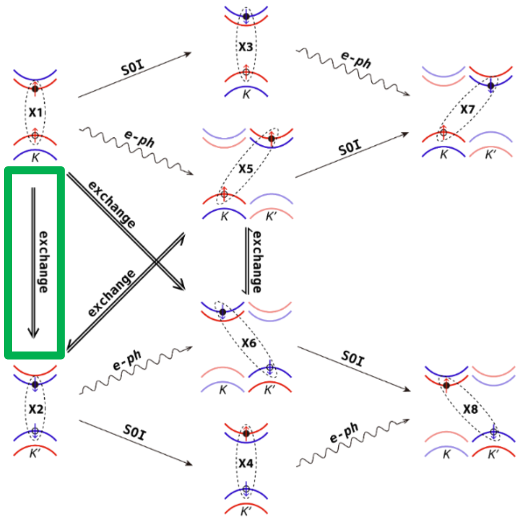
Exchange Interaction Induced Bright Exciton Scattering

Nonadiabatic Coupling Elements：

Single particle dynamics： *e-ph*

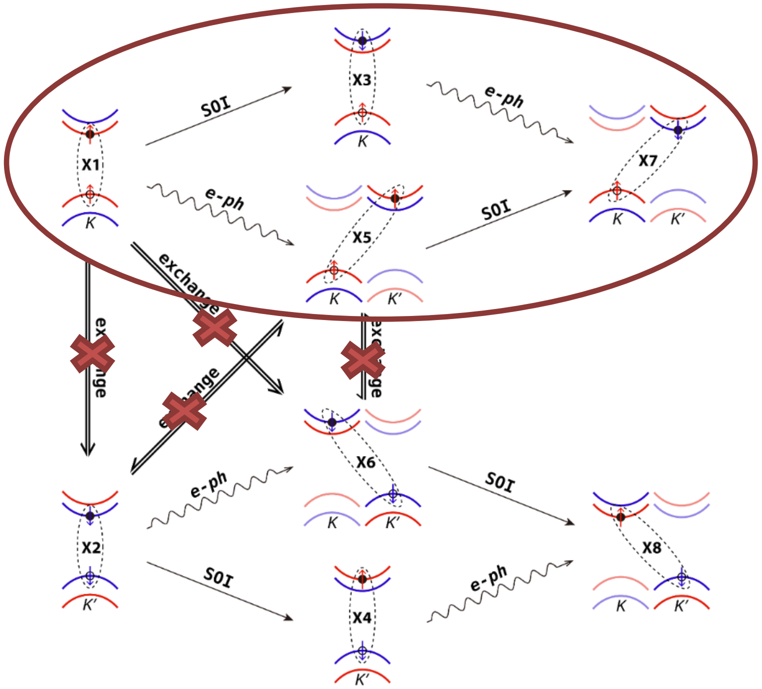
Exciton dynamics: *e-ph* + *W* (*e-h* Coulomb) + *v* (*e-h* exchange) + SOC

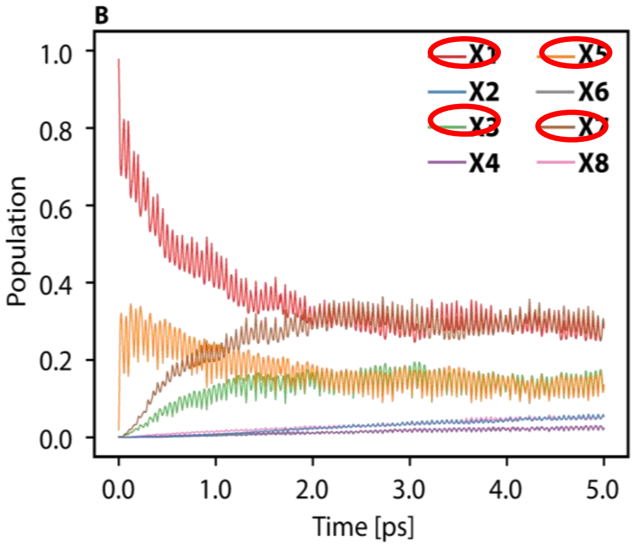




Bright Exciton transition is induced by *e-h* exchange interaction

Single Particle Picture





Spin particle picture: photoexcited hole keeps in K valley

Summary

Single-particle

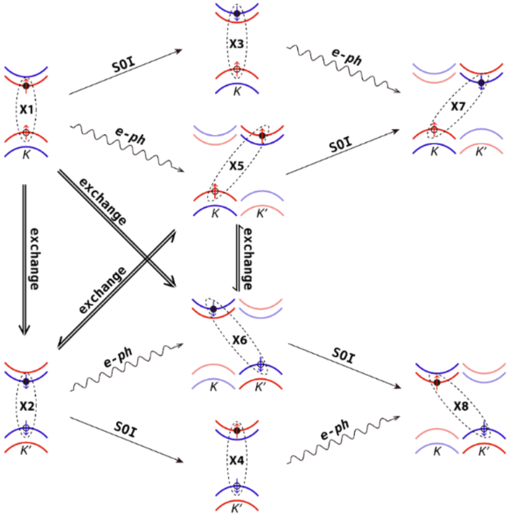
TDDFT

$$i\hbar\frac{\partial\psi(\boldsymbol{r},\boldsymbol{t})}{\partial\boldsymbol{t}}=\mathcal{H}(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r},\boldsymbol{t})$$

Real-time - BSE

$$i\hbar\frac{\partial\psi(\boldsymbol{r}_e,\boldsymbol{r}_{h,}\boldsymbol{t})}{\partial\boldsymbol{t}}=\mathcal{H}(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r}_e,\boldsymbol{r}_{h,}\boldsymbol{t})$$

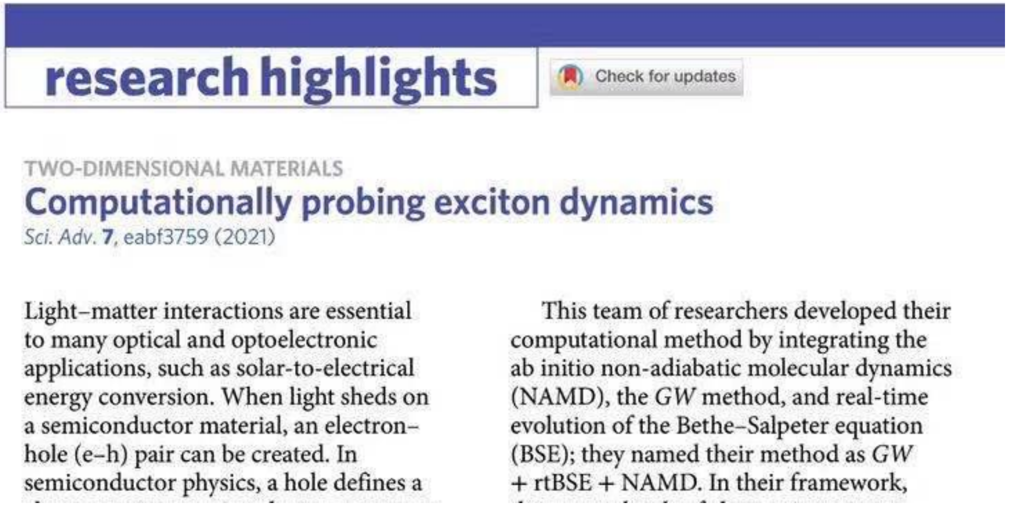
two-particle



- ✓ **Many-body interaction**
- ✓ **Exciton-phonon interaction**
- ✓ **Spin orbital coupling**
- ✓ **Nonadiabatic effects**

X. Jiang, Q. Zheng, Z. Lan, W. A. Saidi, X. Ren and J. Zhao* *Sci. Adv.*, **7**, eabf3759, (2021)

Xiang Jiang
蒋翔



research highlights

Check for updates

TWO-DIMENSIONAL MATERIALS

Computationally probing exciton dynamics

Sci. Adv. **7**, eabf3759 (2021)

Light–matter interactions are essential to many optical and optoelectronic applications, such as solar-to-electrical energy conversion. When light sheds on a semiconductor material, an electron–hole (e–h) pair can be created. In semiconductor physics, a hole defines a

This team of researchers developed their computational method by integrating the ab initio non-adiabatic molecular dynamics (NAMD), the *GW* method, and real-time evolution of the Bethe–Salpeter equation (BSE); they named their method as *GW* + rtBSE + NAMD. In their framework,

- Back ground
- Single particle dynamics
- Spin dynamics
- Exciton Dynamics
- **Outlook**

What can be Done Using the GW-rtBSE NAMD Simulation

✓Exciton Lifetime

✓Hot exciton Relaxation

✓Exciton transition
  at interface
  via spin valley
  bright-to-dark
  …

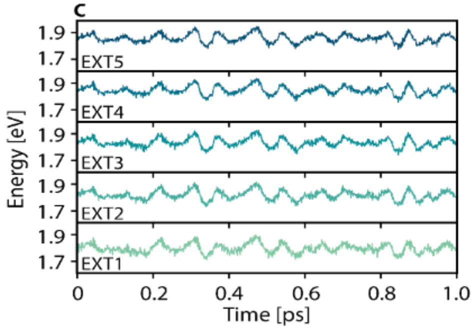
✓Exciton-Phonon Interaction

✓Exciton-Polaron interaction

✓Excited state potential surface from machine learning

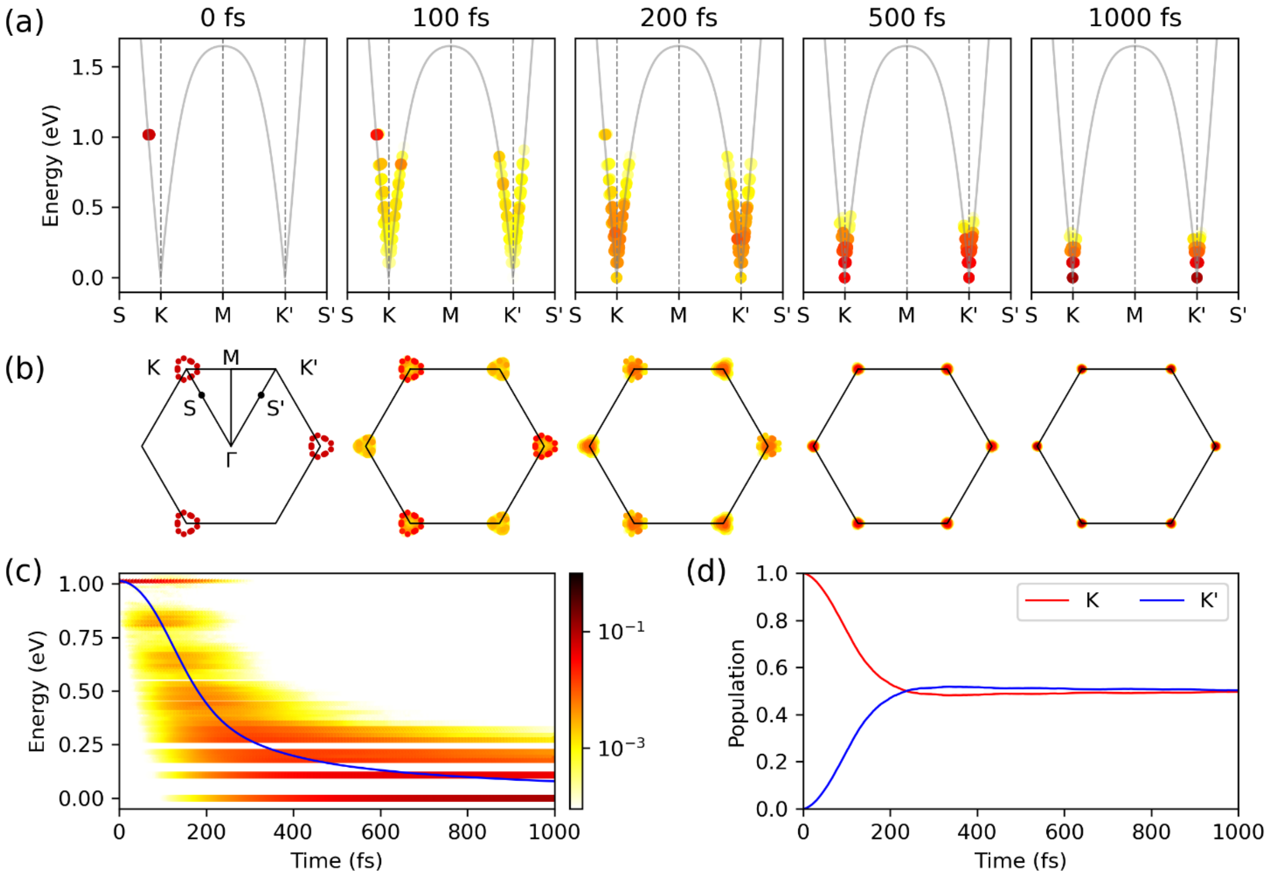
Photo-induced phase transition

Photocatalysis

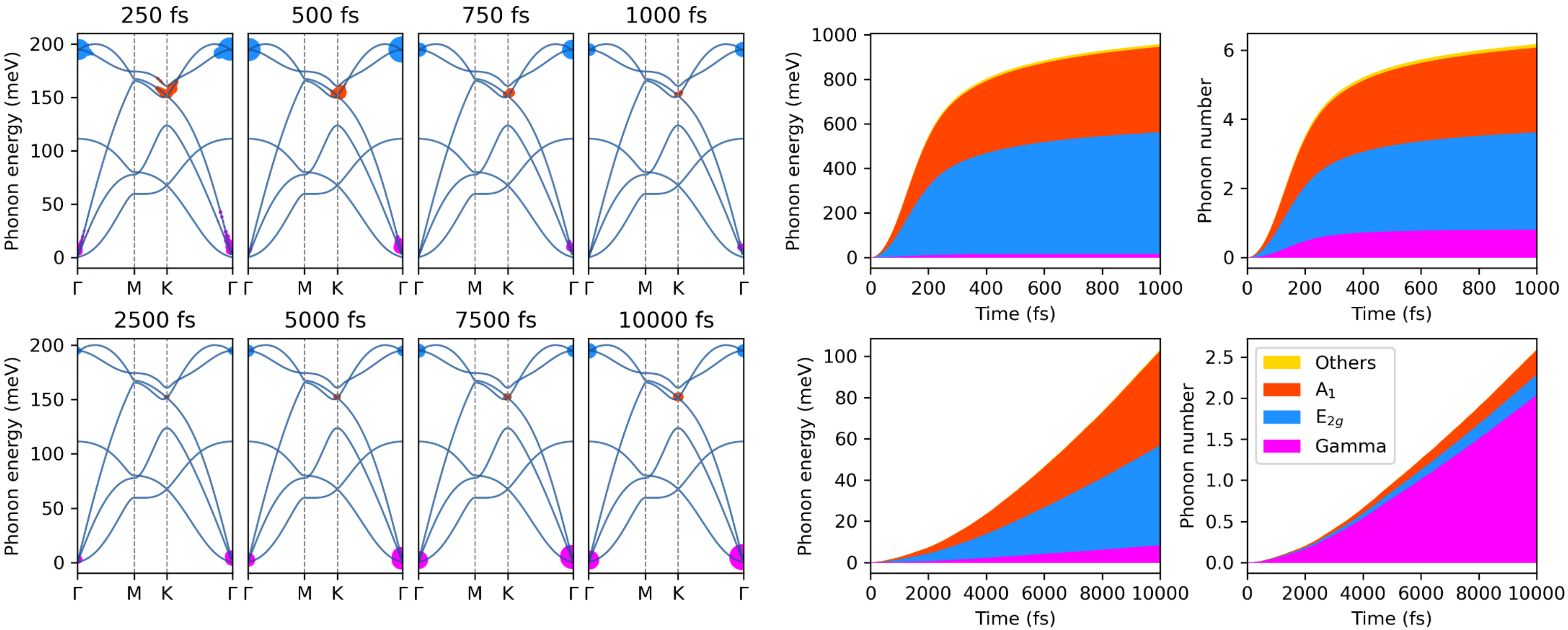


Several thousands of exciton energies can be used for machine learning

NAMD Simulation in Momentum Space

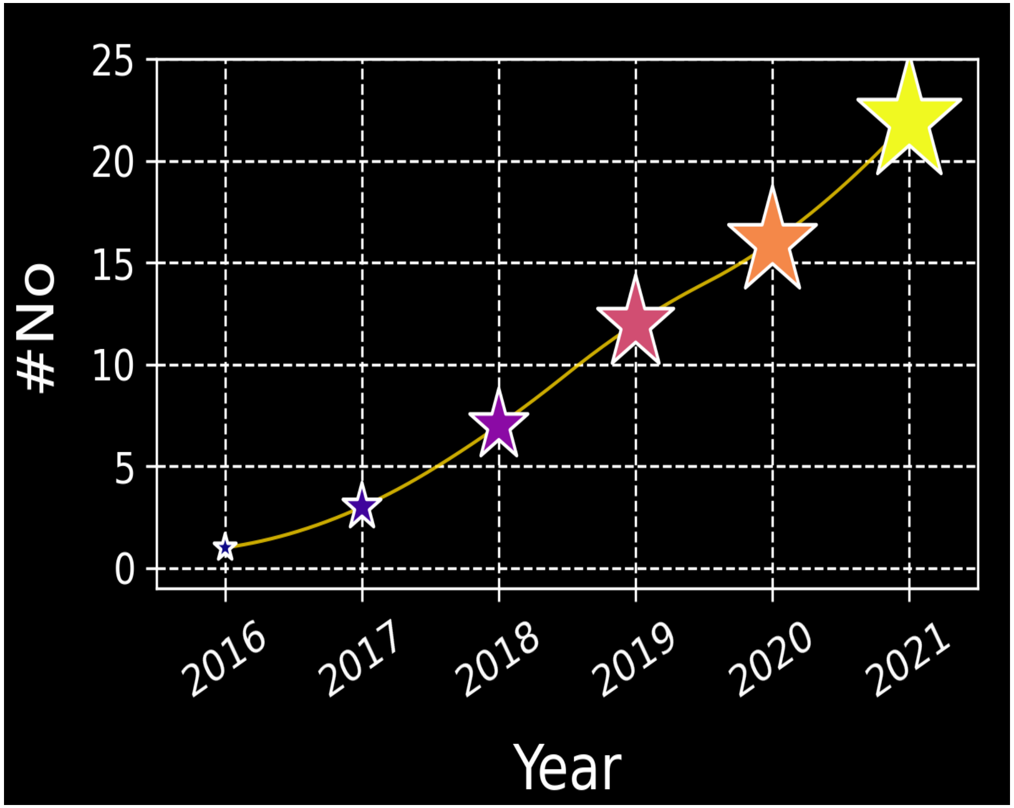


Phonon Excitation



Hefei-NAMD的应用与推广

Publications by Hefei-NAMD （over 80)



Journal	Number of Publications
Sci. Adv.	3
Nat. Commun.	1
Phys. Rev. Lett.	3
JACS	2
Adv. Mater.	1
Nano Lett.	4
ACS NANO	1
J. Phys. Chem. Lett.	18
Chem. Sci.	1
Angew Chem.	1

RESEARCH ARTICLE

ADVANCED MATERIALS
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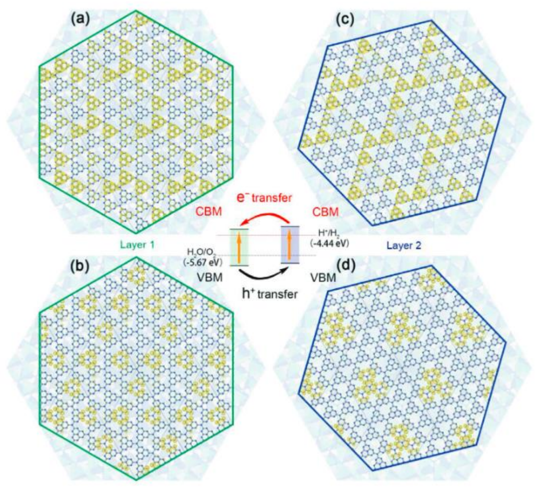
Ultrafast Interlayer Charge Separation, Enhanced Visible-Light Absorption, and Tunable Overpotential in Twisted Graphitic Carbon Nitride Bilayers for Water Splitting

*Xirui Zhang, Tong Wu, Chao Yu, and Ruifeng Lu**



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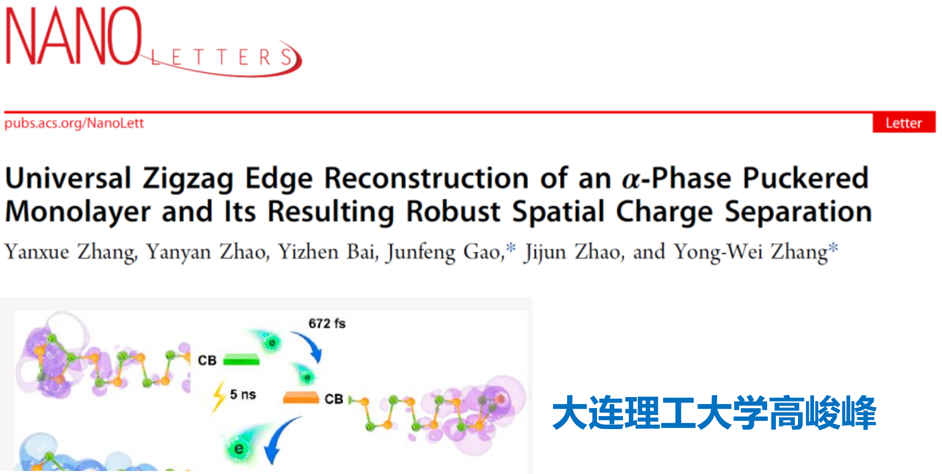

NANO LETTERS

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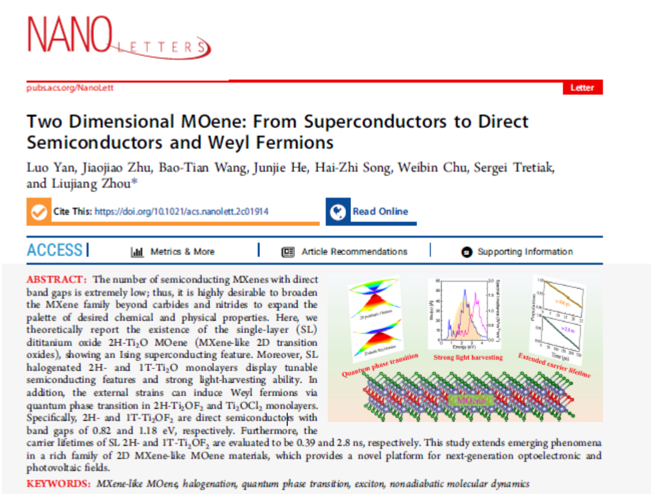
Letter

Universal Zigzag Edge Reconstruction of an α-Phase Puckered Monolayer and Its Resulting Robust Spatial Charge Separation

Yanxue Zhang, Yanyan Zhao, Yizhen Bai, Junfeng Gao,* Jijun Zhao, and Yong-Wei Zhang*

大连理工大学高峻峰



NANO LETTERS

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Letter

Two Dimensional MOene: From Superconductors to Direct Semiconductors and Weyl Fermions

Luo Yan, Jiaojiao Zhu, Bao-Tian Wang, Junjie He, Hai-Zhi Song, Weibin Chu, Sergei Tretiak, and Liujiang Zhou*

Cite This: https://doi.org/10.1021/acs.nanolett.2c01914

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ABSTRACT: The number of semiconducting MXenes with direct band gaps is extremely low; thus, it is highly desirable to broaden the MXene family beyond carbides and nitrides to expand the palette of desired chemical and physical properties. Here, we theoretically report the existence of the single-layer (SL) dititanium oxide 2H-Ti_2O MOene (MXene-like 2D transition oxides), showing an Ising superconducting feature. Moreover, SL halogenated 2H- and 1T-Ti_2O monolayers display tunable semiconducting features and strong light-harvesting ability. In addition, the external strains can induce Weyl fermions via quantum phase transition in 2H-Ti_2OF_2 and Ti_2OCl_2 monolayers. Specifically, 2H- and 1T-Ti_2OF_2 are direct semiconductors with band gaps of 0.82 and 1.18 eV, respectively. Furthermore, the carrier lifetimes of SL 2H- and 1T-Ti_2OF_2 are evaluated to be 0.39 and 2.8 ns, respectively. This study extends emerging phenomena in a rich family of 2D MXene-like MOene materials, which provides a novel platform for next-generation optoelectronic and photovoltaic fields.

KEYWORDS: *MXene-like MOene, halogenation, quantum phase transition, exciton, nonadiabatic molecular dynamics*

电子科大周柳江

Reference & Developers

Video
Hefei-NAMD使用的一些经验
https://www.koushare.com/video/videodetail/11720

Hefei-NAMD基本流程介绍
https://www.bilibili.com/video/BV1p5411c7RS

Hefei-NAMD培训
https://www.koushare.com/lives/room/341102

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http://staff.ustc.edu.cn/~zqj
http://staff.ustc.edu.cn/~zhaojin
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Determining Factors of Carrier Dynamics

No perturbation, no relaxation : $\boldsymbol{\langle \psi_i | \psi_j \rangle = 0}$

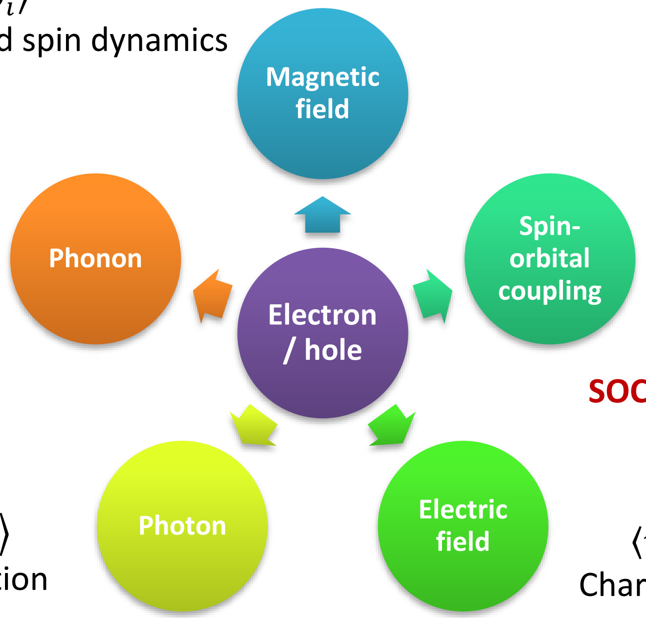
Many-body effects:

- e-e interaction
- **e-h interaction (exciton effects)**
- spin-spin interaction

With perturbation:

$\langle \psi_i | B | \psi_i \rangle$
Magnetic field induced spin dynamics

$\boldsymbol{\left\langle \psi_i \middle| \frac{\partial}{\partial t} \middle| \psi_i \right\rangle}$
$\boldsymbol{\langle \psi_{nk} | \Delta V | \psi_{n'k'} \rangle}$
Nonradiative relaxation



$\boldsymbol{\langle \psi_i | H_{SOC} | \psi_i \rangle}$
SOC induced spin dynamics

$\langle \psi_i | E e^{i\omega t} | \psi_i \rangle$
Radiative relaxation

$\langle \psi_i | E | \psi_i \rangle$
Charge transport

Other effects:

- **Nuclear quantum effects**
- Potential energy surface of the excited state

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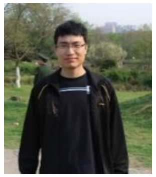

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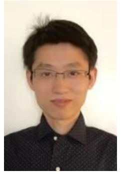

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