Real-Time GW-BSE Investigation on Spin-Valley Exciton Dynamics

Jin Zhao

University of Science and Technology, China (USTC)

VISTA Seminor

Seminor 25

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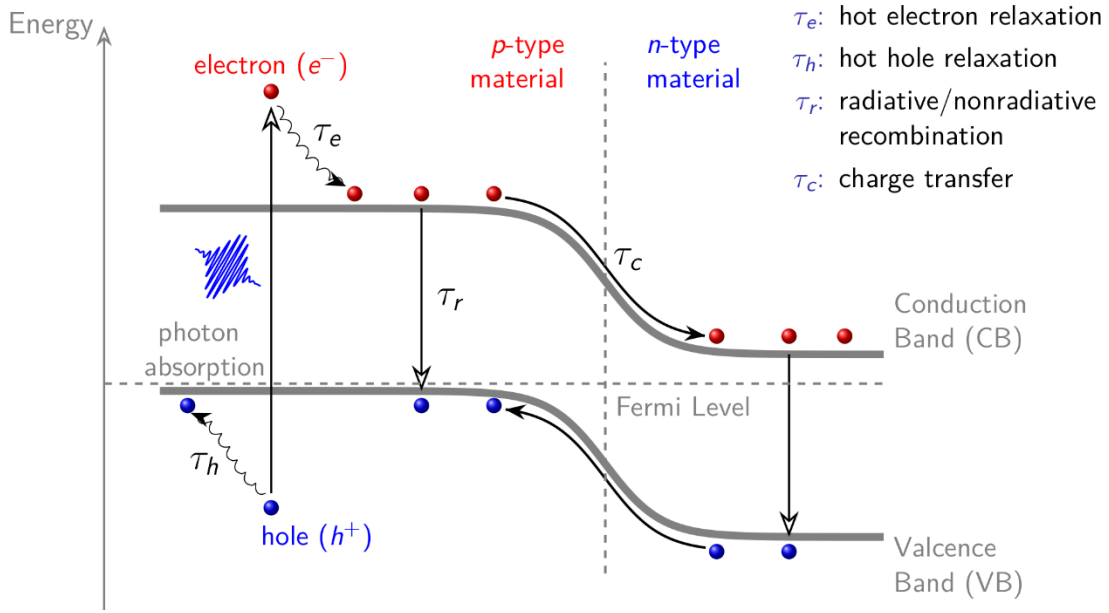
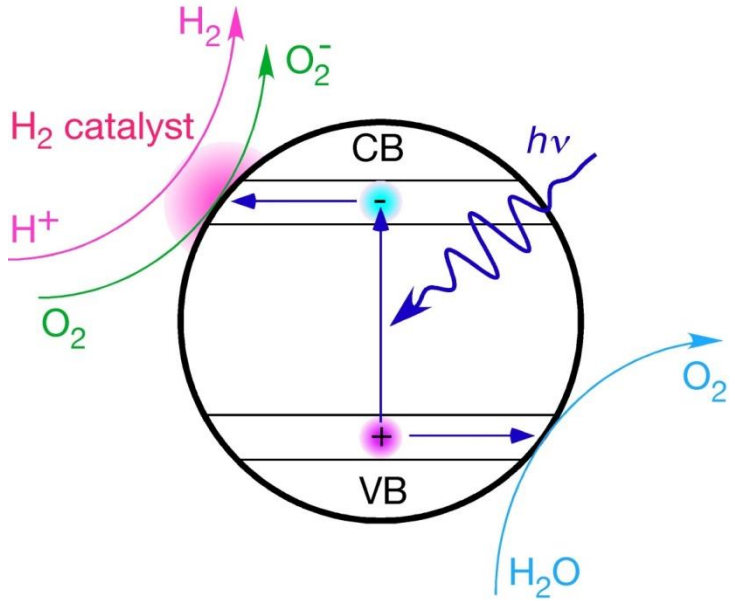
Excited Carrier Dynamics in Solar Energy Conversion



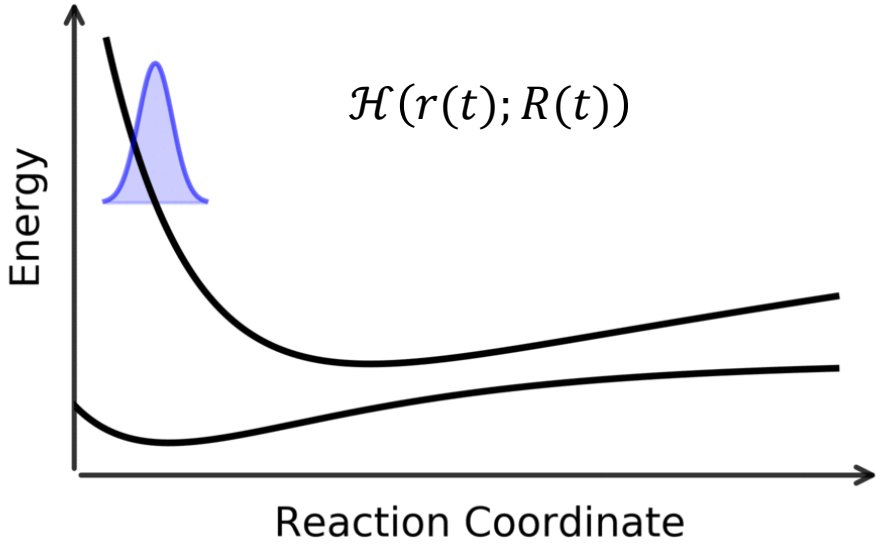


Photovoltaics

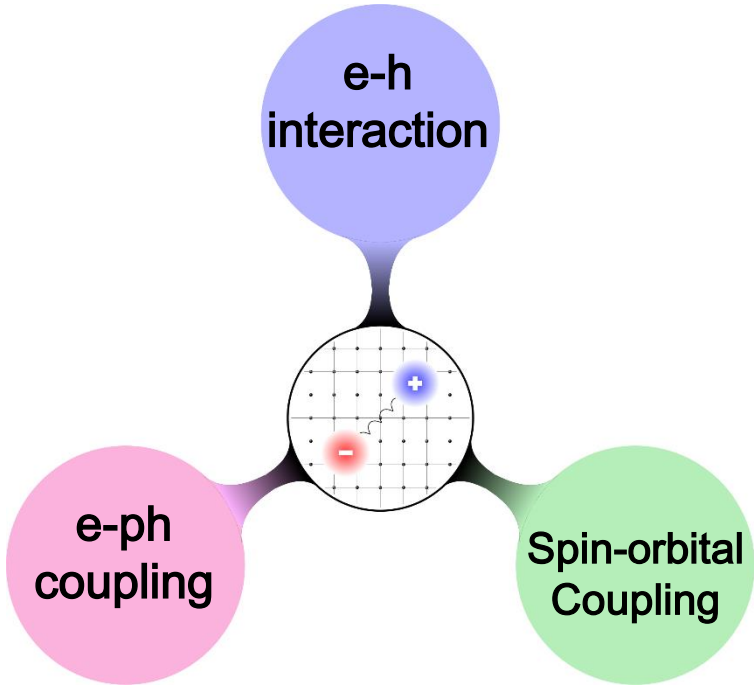
Photocatalysis

- **hot carrier relaxation**
- **electron-hole recombination**
- **interfacial charge transfer**

Challenges for *Ab Initio* Calculations

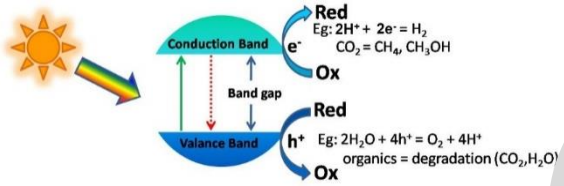


Time-dependent dynamics
Nonadiabatic effects

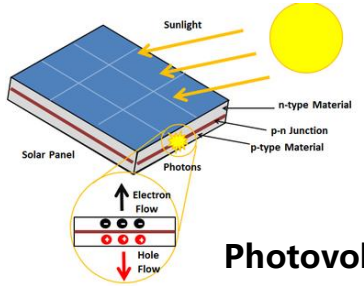


Different interactions

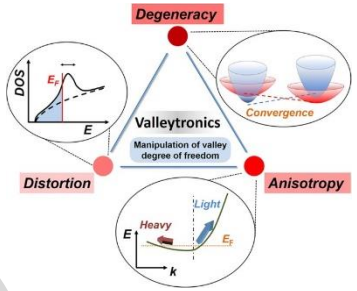
Hefei – Nonadiabatic Molecular Dynamics (Hefei-NAMD)



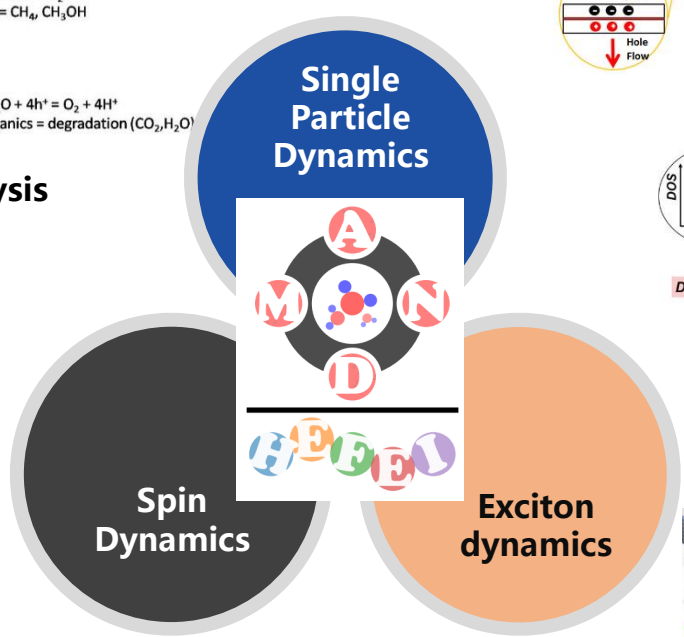
Photocatalysis

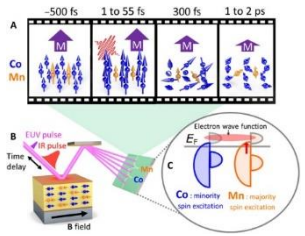


Photovoltaics

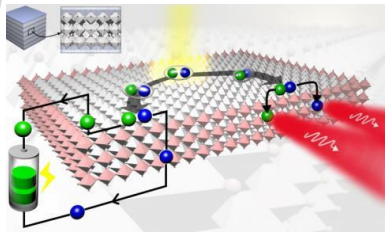


valleytronics





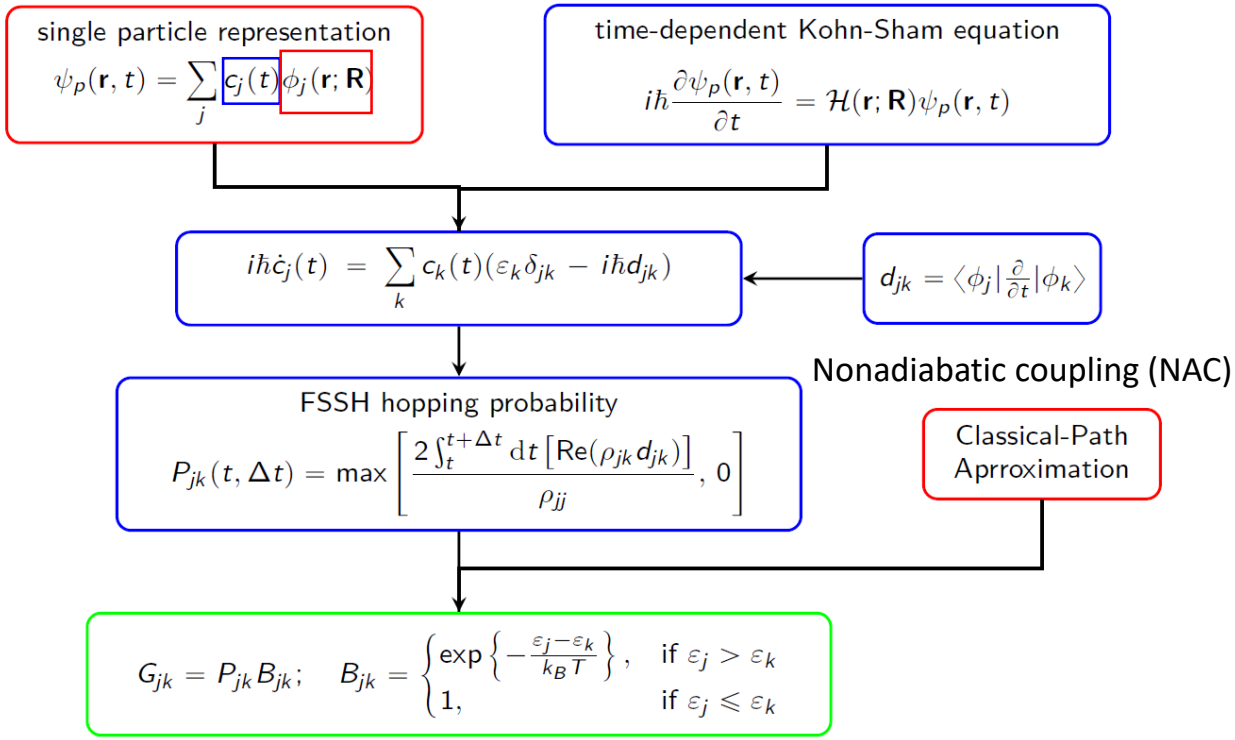
Spintronics



optoelectronics

http://staff.ustc.edu.cn/~zhaojin/code.html

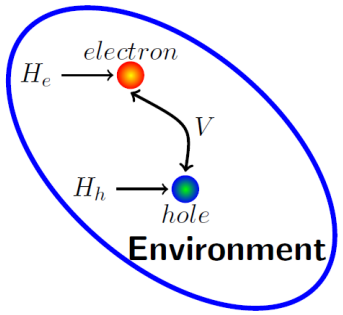
Surface Hopping Combined with TDKS



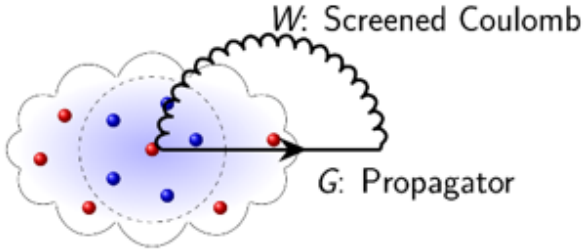
A. Akimov and O. Prezhdo: Pyxaid

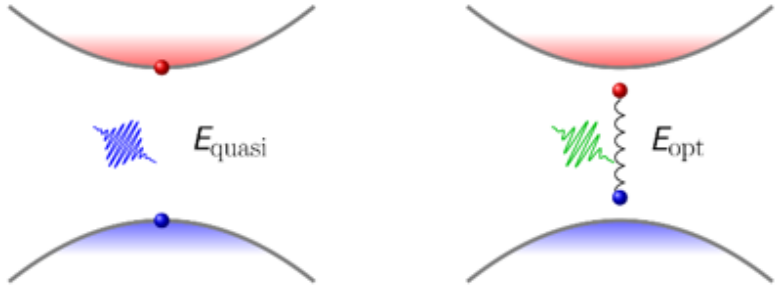
Q. Zheng, X. Jiang, et. al. J. Zhao: Hefei-NAMD

GW + BSE to Describe the Exciton



$\Sigma = GW$:





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

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

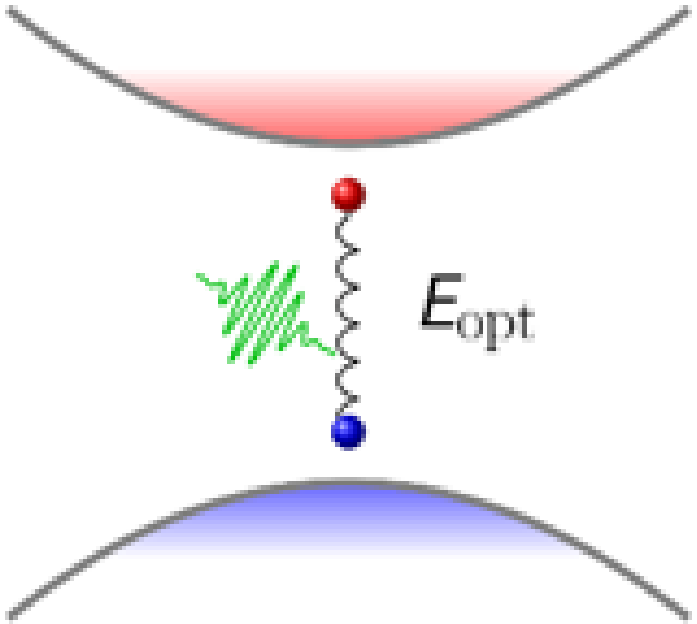
GW: self-energy take place of exchange correlation potential

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:

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

Coulomb Interaction:

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

Exchange Interaction:

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

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

Diabatic Representation

Single-particle

TDDFT

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

Real-time - BSE

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

two-particle

Diabatic:

$$H^{cvk}_{c'v'k'}=\left(E^{QP}_{ck}-E^{QP}_{vk}\right)\delta_{cc'}\delta_{vv'}\delta_{kk'}-W^{cvk}_{c'v'k'}+2v^{cvk}_{c'v'k'}$$
$$-i\hbar\left(\langle ck|\frac{\partial}{\partial t}|c'k\rangle\,\delta_{vv'}+\langle vk|\frac{\partial}{\partial t}|v'k\rangle^{*}\delta_{cc'}\right)\delta_{kk'}$$

Adiabatic Representation

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

Diagonalize the BSE Hamiltonian to get the exciton basis sets

Adiabatic:

Expand the state ket $|\Psi\rangle$ in time-dependent two-particle Schrödinger equation

$$i\hbar\frac{\partial\left|\Psi\left(r_e, r_h, t\right)\right\rangle}{\partial t} = H\left|\Psi\left(r_e, r_h, t\right)\right\rangle$$

using the following basis:

$$\left|x_I\right\rangle = \sum_{cvk} f^I_{cvk}\left|cvk\right\rangle$$

where $|x_I\rangle$ is the eigenstate of exciton:

$$H\left|x_I\right\rangle = E^x_I\left|x_I\right\rangle$$

Adiabatic:

$$|\Psi\rangle = \sum_I A_I |x_I\rangle$$

$$i\hbar \dot{A}_K = \sum_I H_{KI} A_I$$

$$H_{KI} = E_K^x \delta_{KI} - i\hbar \langle x_K | \frac{\partial}{\partial t} | x_I \rangle$$

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

Single particle

Exciton-phonon interaction
Non-adiabatic coupling for exciton

$$\langle x_K | \frac{\partial}{\partial t} | x_I \rangle$$

$$= \sum_{\substack{cvk \\ c'v'k'}} f^I_{c'v'k'} f^{*K}_{cvk} \langle cvk | \frac{\partial}{\partial t} | c'v'k' \rangle + \sum_{cvk} \dot{f}^I_{cvk} f^{*K}_{cvk}$$

$$= \sum_{\substack{cvk \\ c'v'}} f^I_{c'v'k} f^{*K}_{cvk} \left(\langle ck | \frac{\partial}{\partial t} | c'k \rangle \, \delta_{vv'} + \langle vk | \frac{\partial}{\partial t} | v'k \rangle^* \delta_{cc'} \right)$$

$$+ \sum_{cvk} \langle f^K_{cvk} | \frac{d}{dt} | f^I_{cvk} \rangle$$

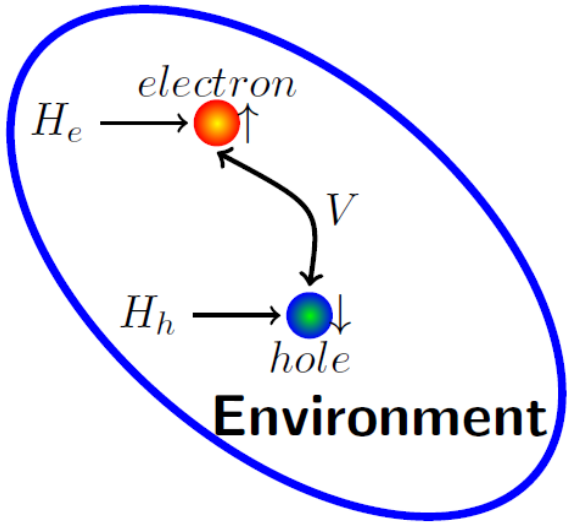
$$= \sum_{cc'vk} f^{*K}_{cvk} \langle ck | \frac{\partial}{\partial t} | c'k \rangle \, f^I_{c'vk} + \sum_{vv'ck} f^{*K}_{cvk} \langle vk | \frac{\partial}{\partial t} | v'k \rangle^* f^I_{cv'k}$$

$$+ \frac{1}{2dt} \sum_{cvk} \left(\langle f^K_{cvk}(t) | f^I_{cvk}(t+dt) \rangle - \langle f^K_{cvk}(t+dt) | f^I_{cvk}(t) \rangle \right)$$

Exciton with Spin

Hamiltonian:

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



Exciton dynamics with SOC

$$
\begin{aligned}
&\langle c\sigma_c v\sigma_v k|H|c'\sigma_{c'}v'\sigma_{v'}k'\rangle \\
= &\left(E^{QP}_{c\sigma_c k}\delta_{cc'}\delta_{\sigma_c\sigma_{c'}} + \langle c\sigma_c k|H^{SO}|c'\sigma_{c'}k\rangle\right)\delta_{vv'}\delta_{\sigma_v\sigma_{v'}}\delta_{kk'} \\
&-\left(E^{QP}_{v\sigma_v k}\delta_{vv'}\delta_{\sigma_v\sigma_{v'}} - \langle v'\sigma_{v'}k|H^{SO}|v\sigma_v k\rangle\right)\delta_{cc'}\delta_{\sigma_c\sigma_{c'}}\delta_{kk'} \\
&-W^{c\sigma_c v\sigma_v k}_{c'\sigma_c v'\sigma_v k'}\delta_{\sigma_c\sigma_{c'}}\delta_{\sigma_v\sigma_{v'}} + v^{c\sigma_c v\sigma_c k}_{c'\sigma_{c'}v'\sigma_{c'}k'}\delta_{\sigma_c\sigma_v}\delta_{\sigma_{c'}\sigma_{v'}}
\end{aligned}
$$

Screened coulomb interaciton

$$
W^{c\sigma_c v\sigma_v k}_{c'\sigma_c v'\sigma_v k'} = \frac{1}{\Omega}\sum_{GG'}\frac{4\pi\epsilon^{-1}_{GG'}(k-k')}{|k-k'+G||k-k'+G'|}B^{c\sigma_c k}_{c'\sigma_{c'}k'}(G)B^{v\sigma_v k*}_{v'\sigma_v k'}(G')
$$

Exchange interaction

$$
v^{c\sigma_c v\sigma_c k}_{c'\sigma_{c'}v'\sigma_{c'}k'} = \frac{1}{\Omega}\sum_{G\neq 0}\frac{4\pi}{|G|^2}B^{c\sigma_c k}_{v\sigma_c k}(G)B^{c'\sigma_{c'}k'*}_{v'\sigma_{c'}k'}(G)
$$

$$
\langle n\sigma k|H^{SO}|n'\sigma' k\rangle = \sum_{\alpha,i,j}\langle\tilde{\psi}_{n\sigma k}|\tilde{p}^{\alpha}_{i\sigma k}\rangle\langle\phi^{\alpha}_{i\sigma k}|H^{SO}|\phi^{\alpha}_{j\sigma' k'}\rangle\langle\tilde{p}^{\alpha}_{j\sigma' k'}|\tilde{\psi}_{n'\sigma' k'}\rangle
$$

Realization of *GW* + Real-Time BSE

Single-particle

TDDFT

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

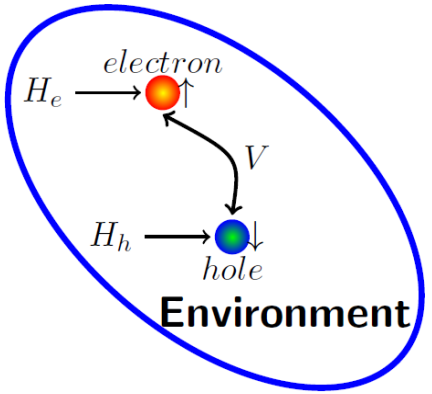
Real-time - BSE

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

two-particle

Hamiltonian:

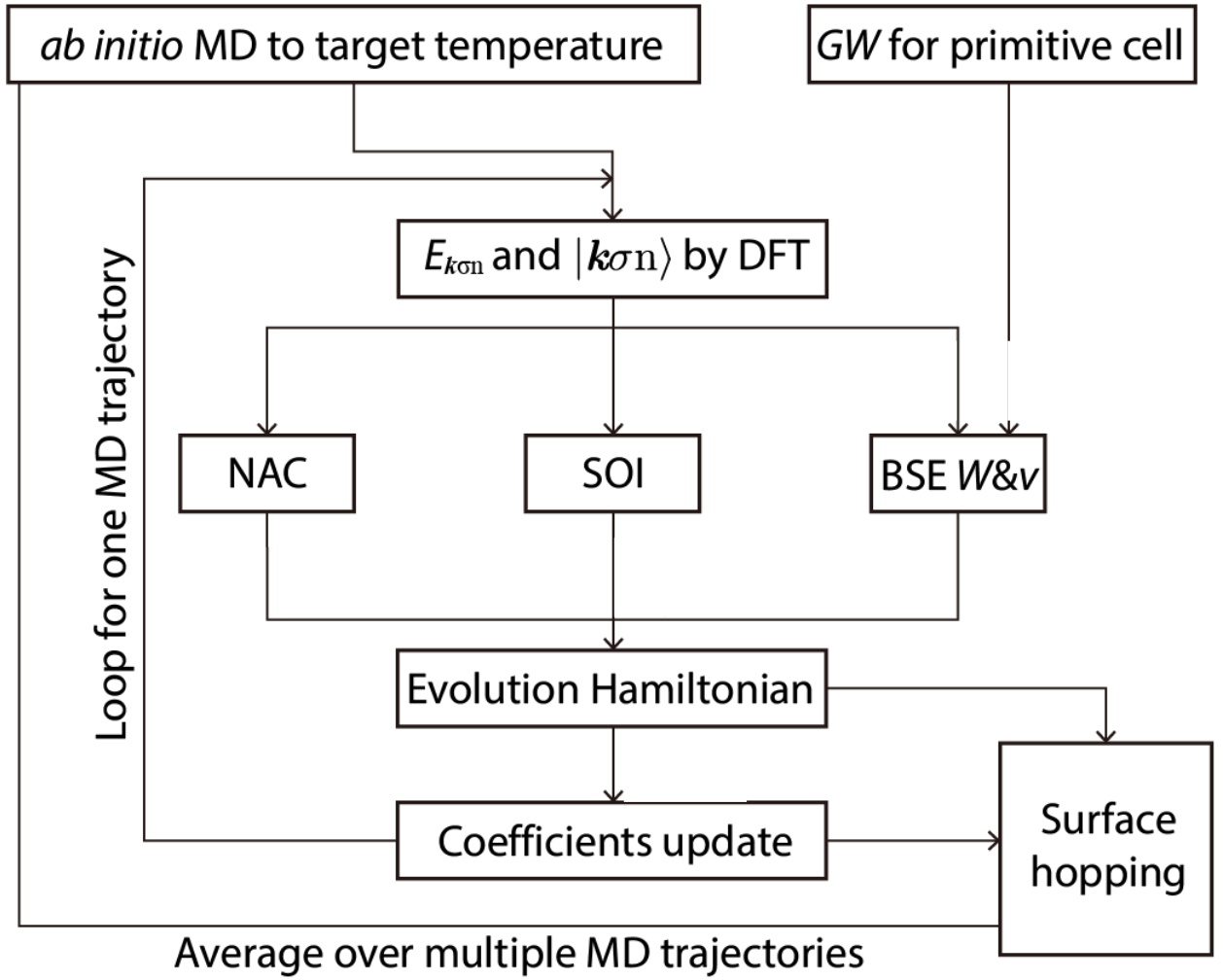
$$H=H_e+H_h+V_{e-h}+H^{SO}$$



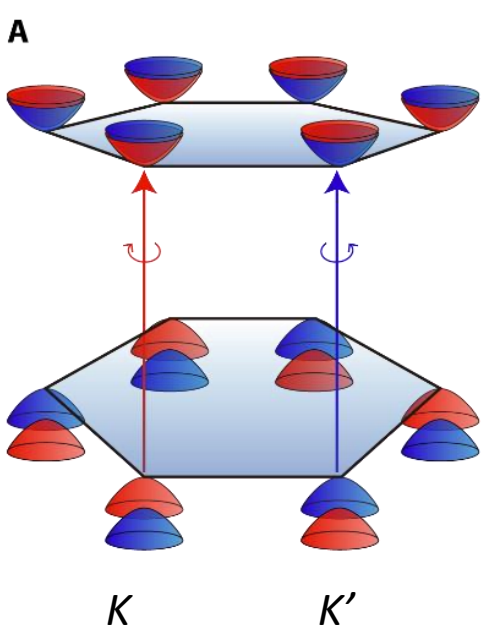
Spin orbital coupling

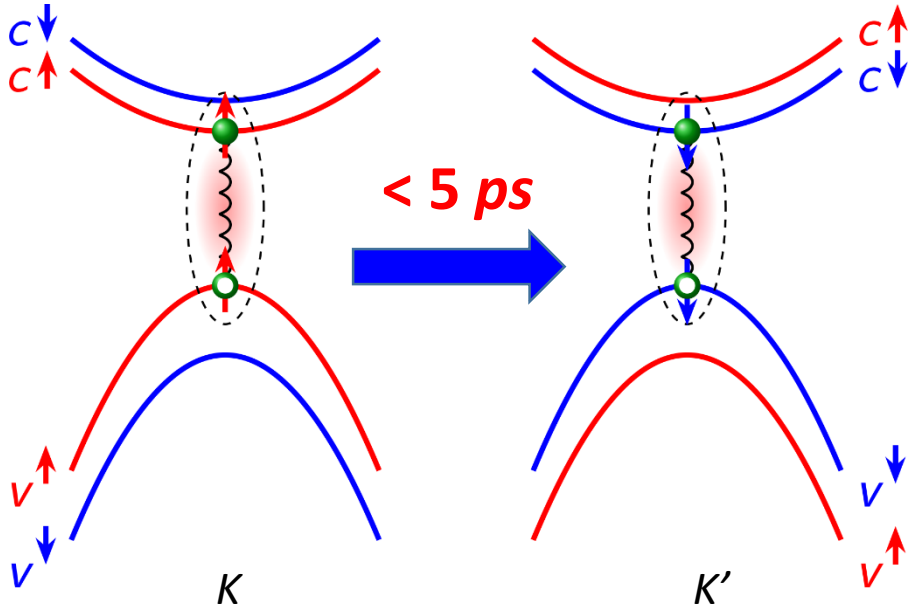
- ✓ **Many-body interaction:** Coulomb and exchange
- ✓ **Exciton-phonon interaction:** real-time BSE + molecular dynamics
- ✓ **Spin orbital coupling:** adiabatic and diabatic representation
- ✓ **Nonadiabatic:** surface hopping

Workflow of Real-Time GW-BSE NAMD



Fast Intervalley Bright Exciton Scattering in Transition Metal Dichalcogenide

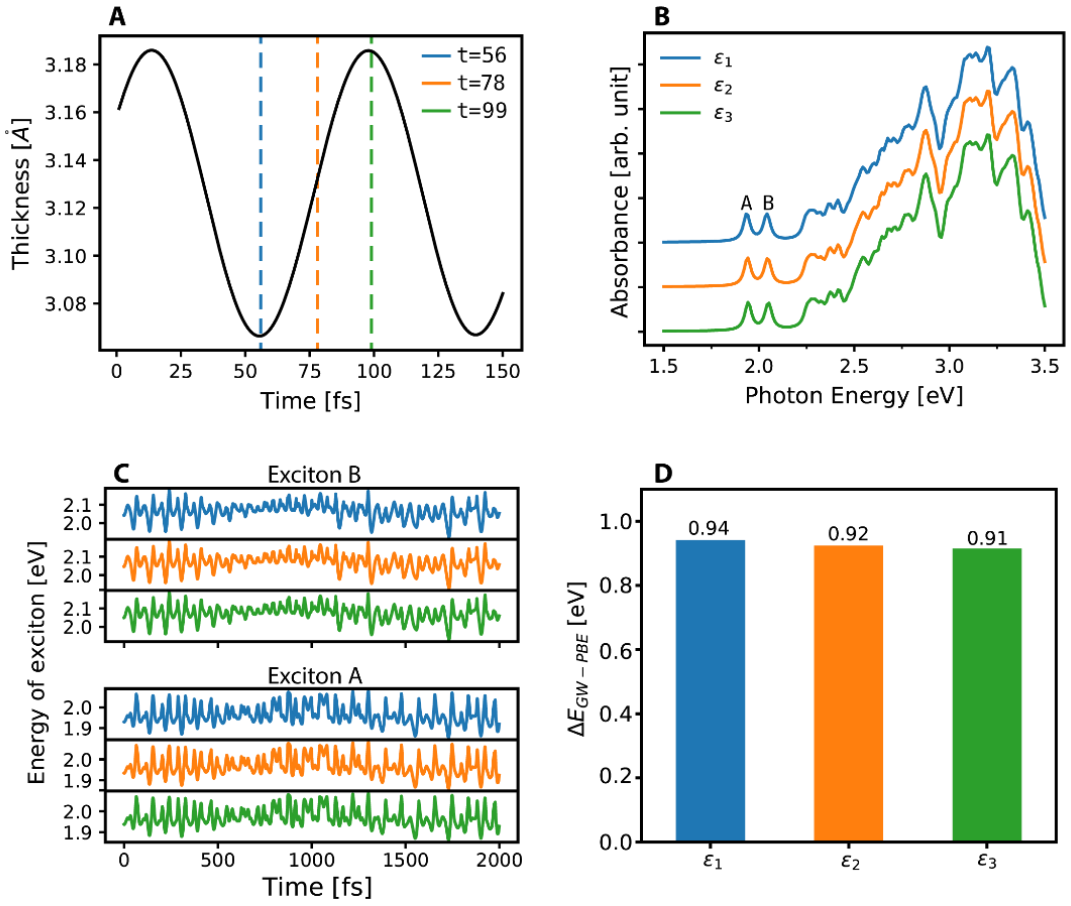




Intervalley bright exciton scattering requires the spin flip and momentum transition of both electron and hole

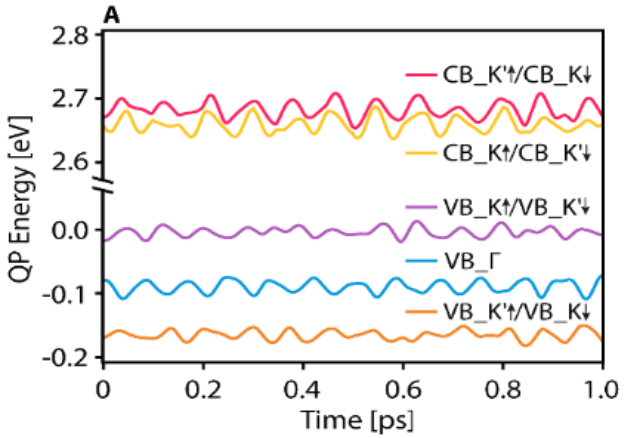
Puzzle: how can such intervalley bright exciton happen within several picoseconds?

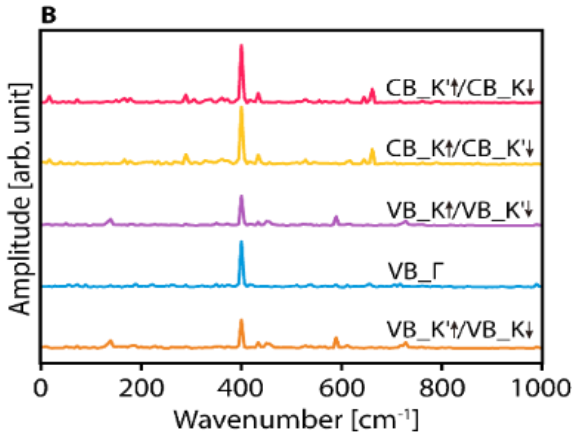
Test of the Dielectric Function Approximation

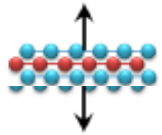


The dielectric function and *GW* QP correction almost does not change with the structure

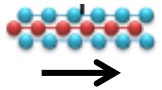
Time Dependent Quasi-Particle Energies and Optical Band Gap of MoS_2



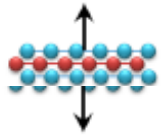




A_1 mode ~400 cm^{-1}



LA mode ~180 cm^{-1}



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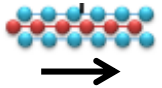
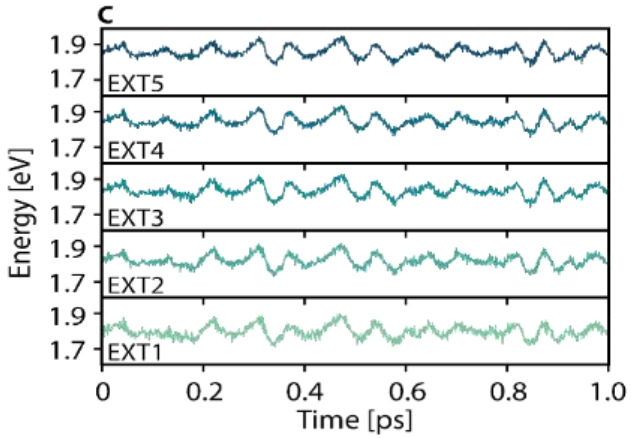
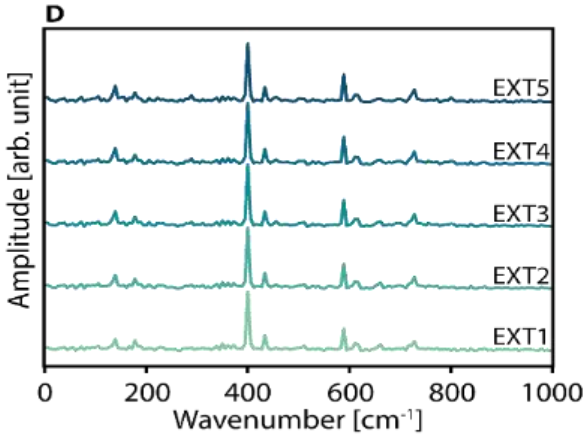
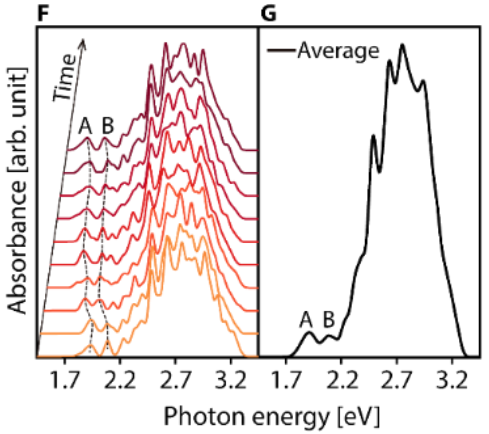


A_1 mode ~400 cm^{-1} LA mode ~180 cm^{-1}

Electron-phonon interaction



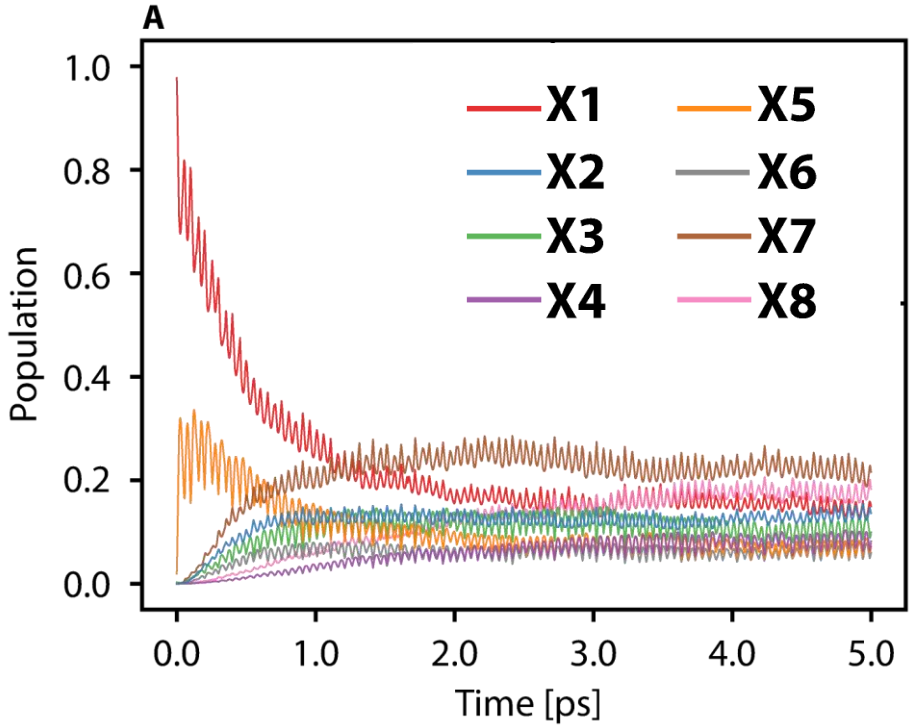


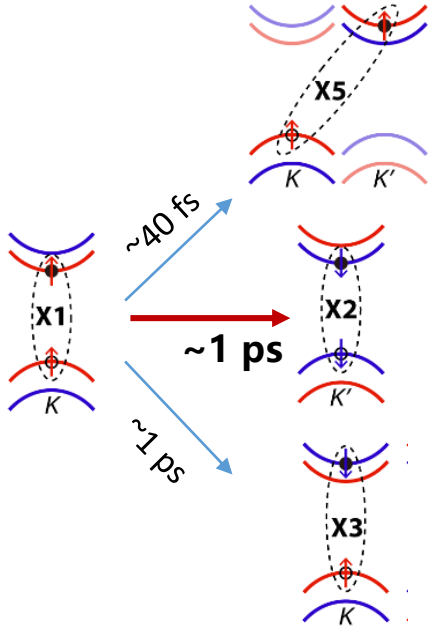


Time-dependent absorption spectrum

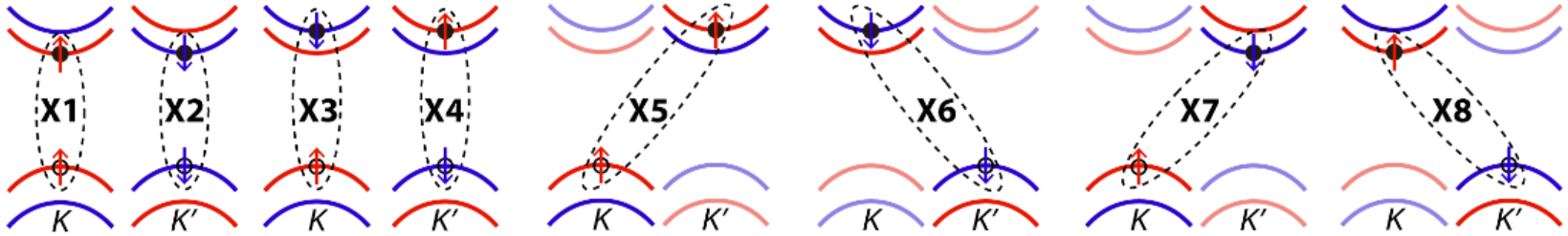
Exciton-phonon interaction

Exciton Dynamics in MoS_2





Bright Exciton transition happens in several ps

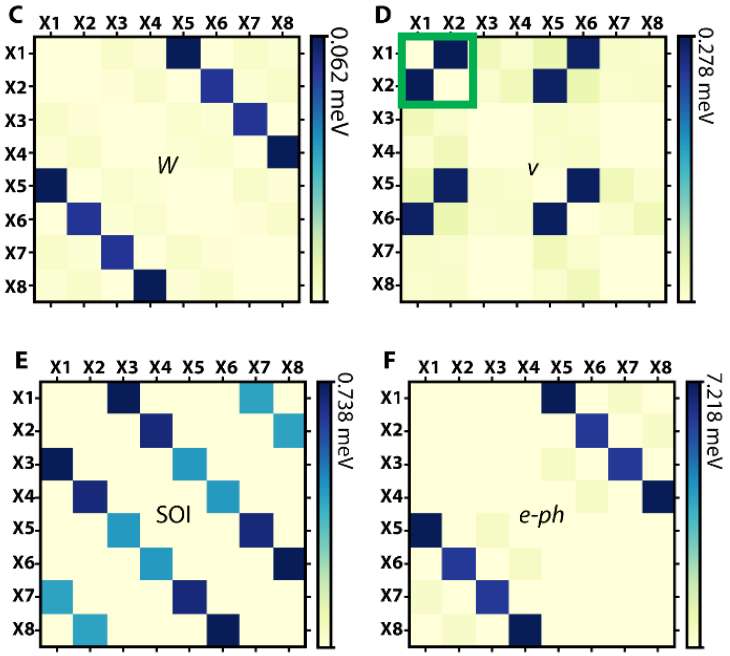


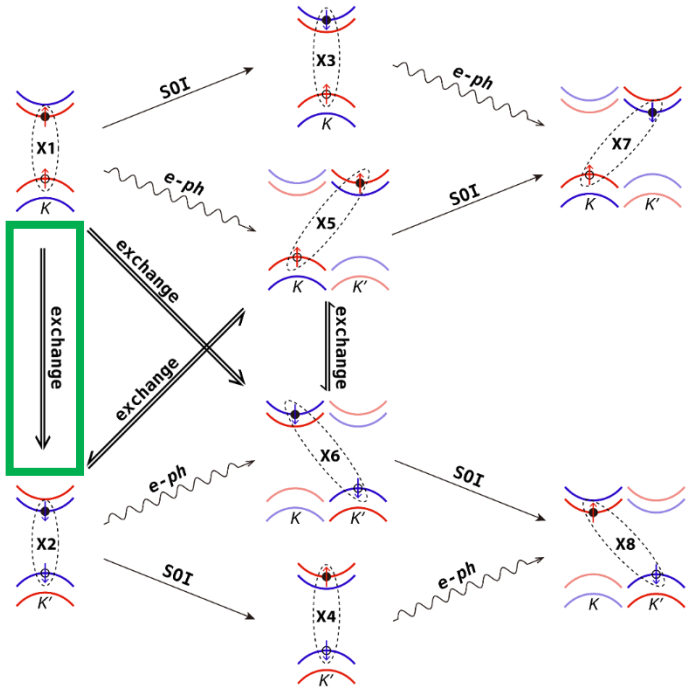
Exchange Interaction Induced Bright Exciton Scattering

Nonadiabatic Coupling Elements:

Single particle dynamics: *e-ph*

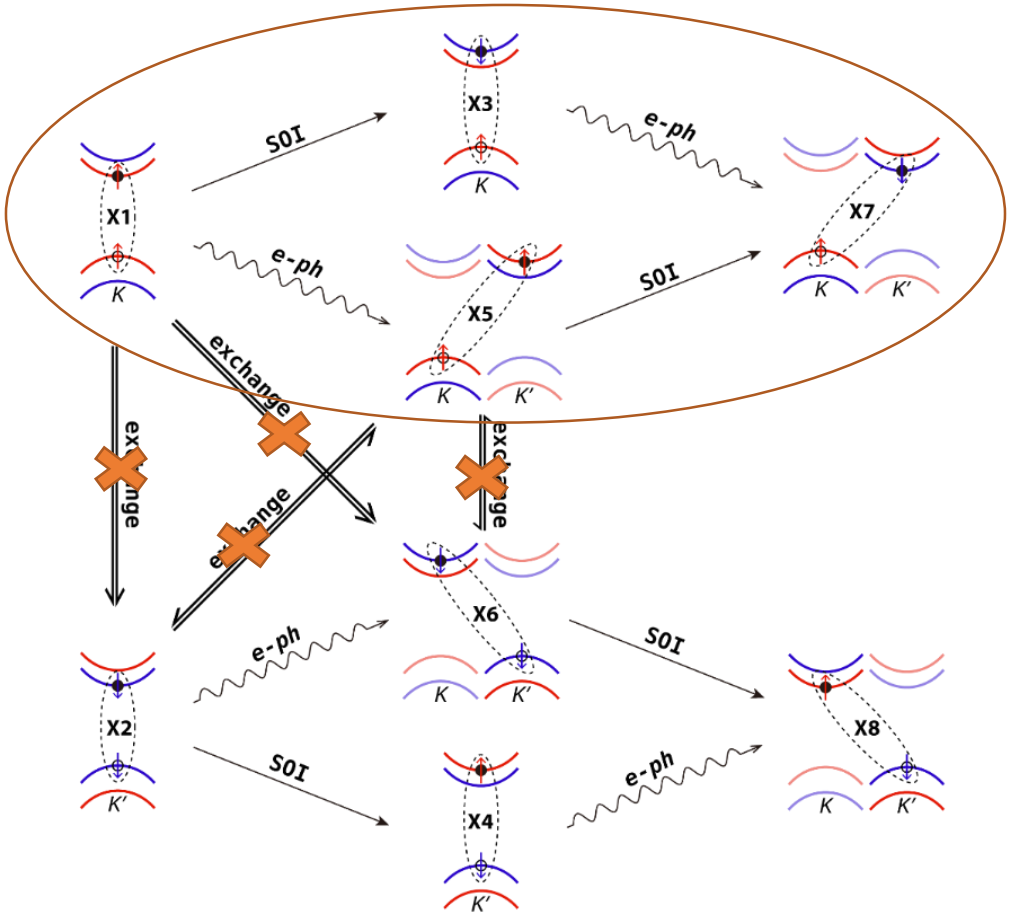
Exciton dynamics: *e-ph* + *W* (*e-h* Coulomb) + *v* (*e-h* exchange) + SOC

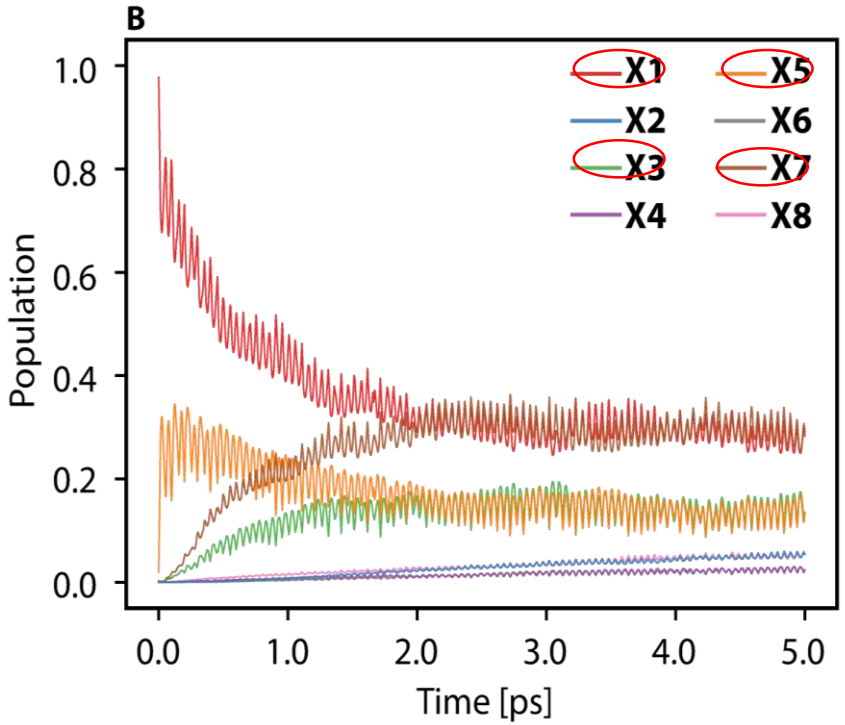




Bright Exciton transition is induced by *e-h* exchange interaction

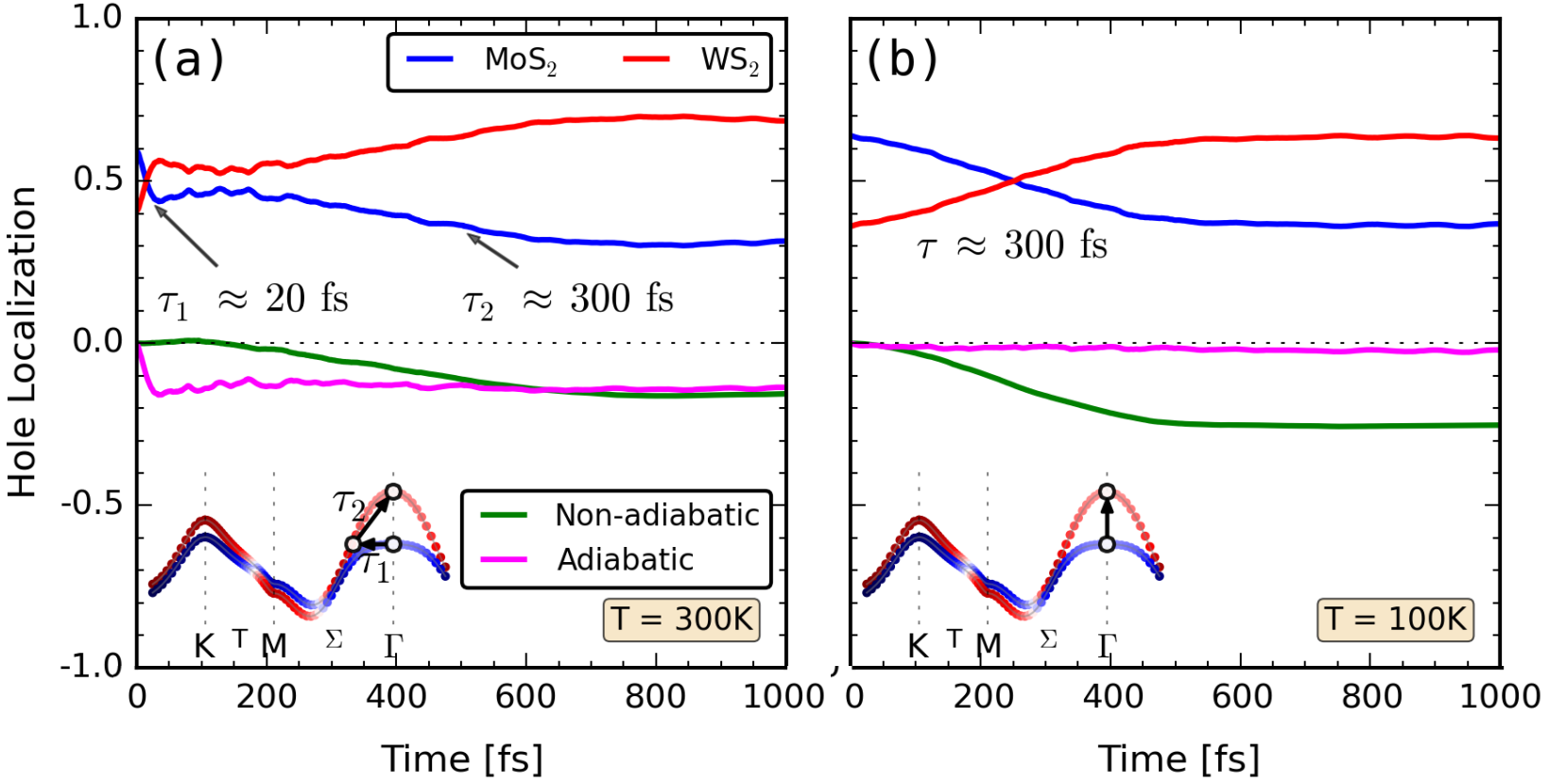
Single Particle Picture

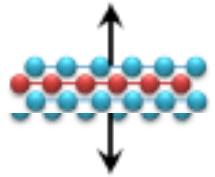




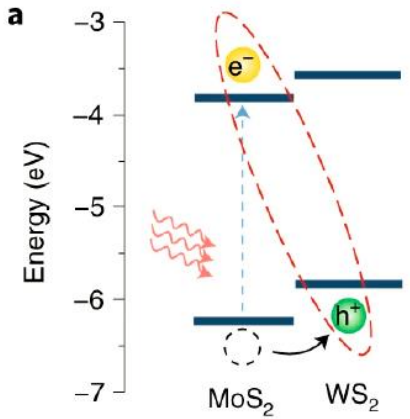
Spin particle picture: photoexcited hole keeps in K valley

Ultrafast Charge Transfer at TMD Heterostructure



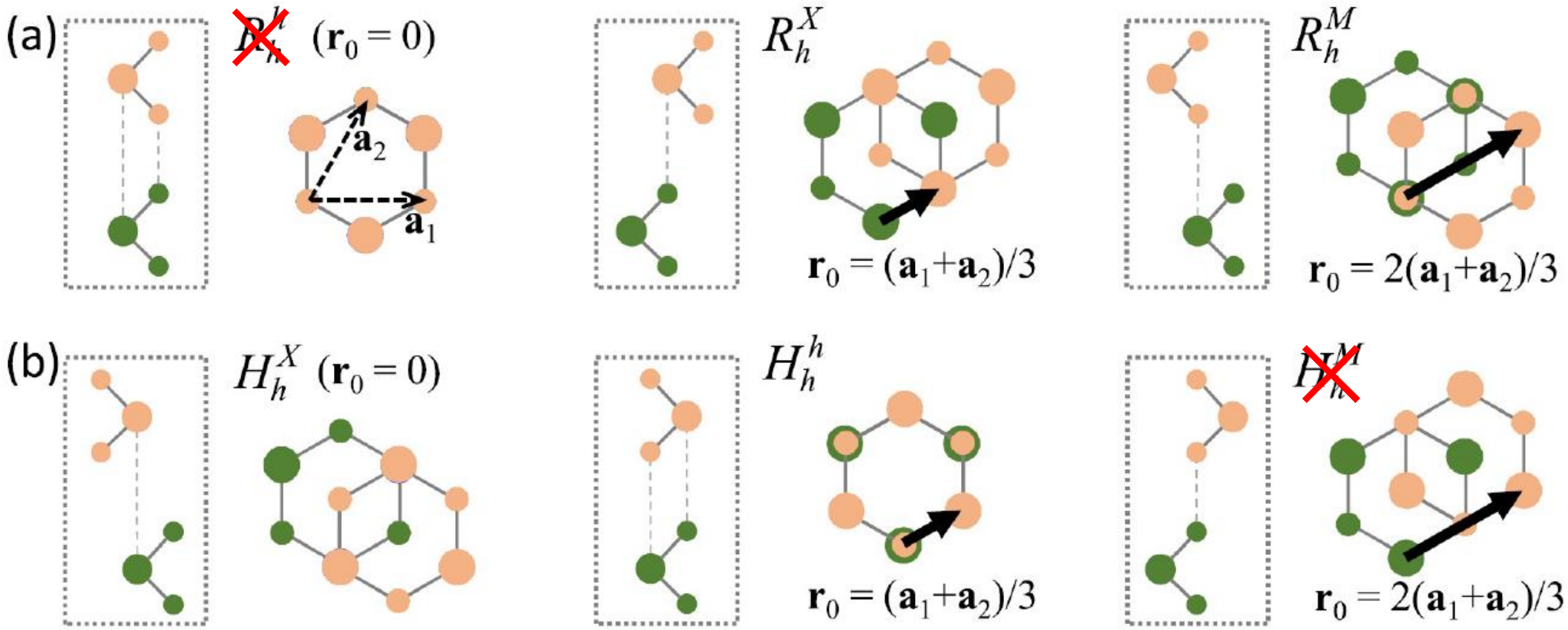


A_1 mode
~400 cm^{-1}
T=83 fs

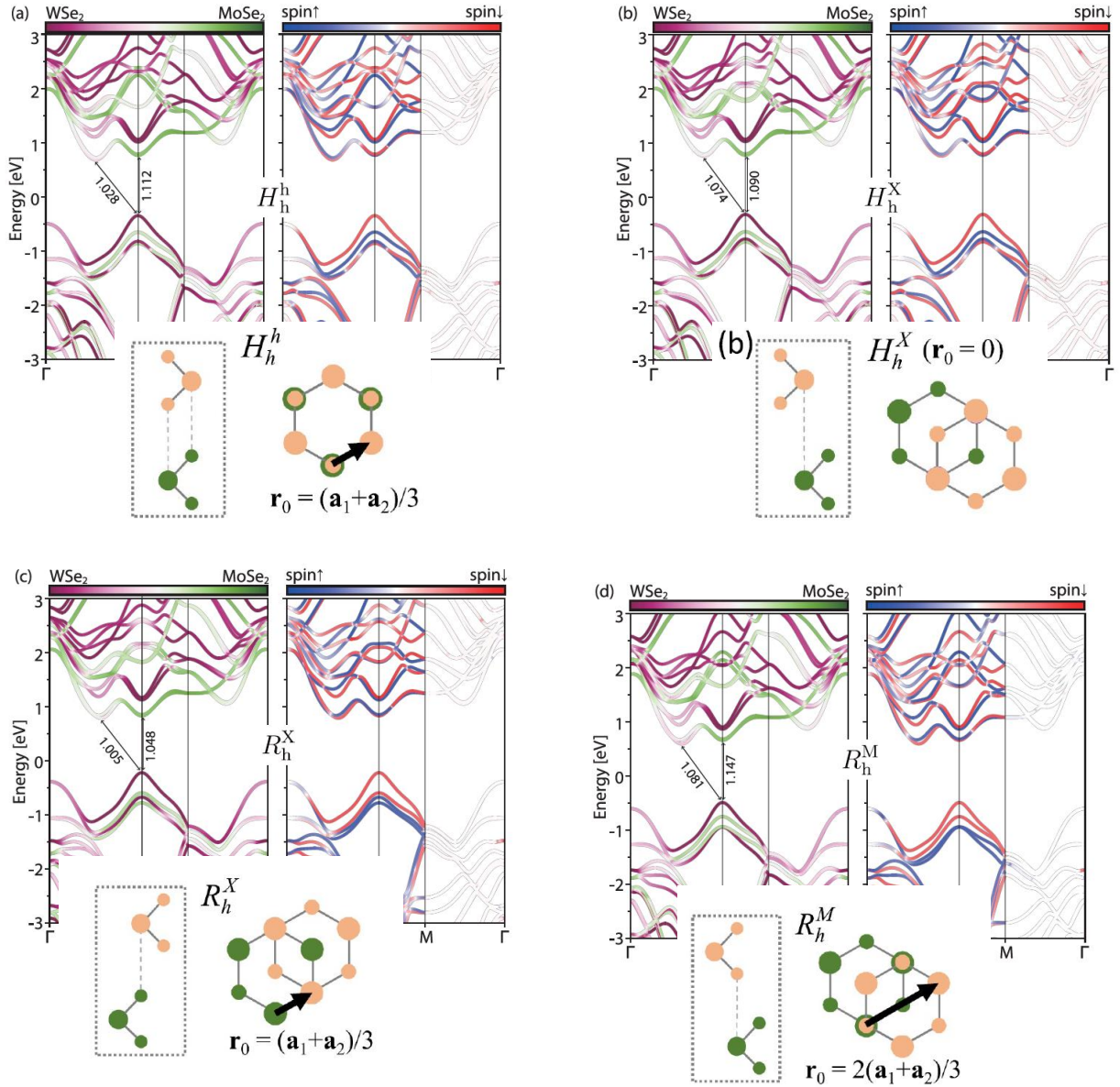


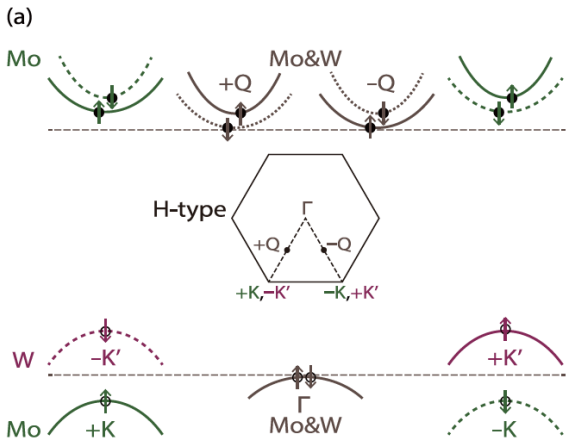
Q. Zheng, et.al. *Nano Lett.* **17**, 6435-6442 (2017)

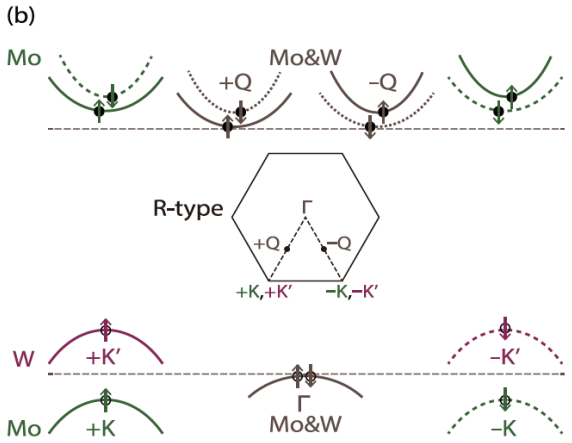
Different Stacking of $MoSe_2/WSe_2$



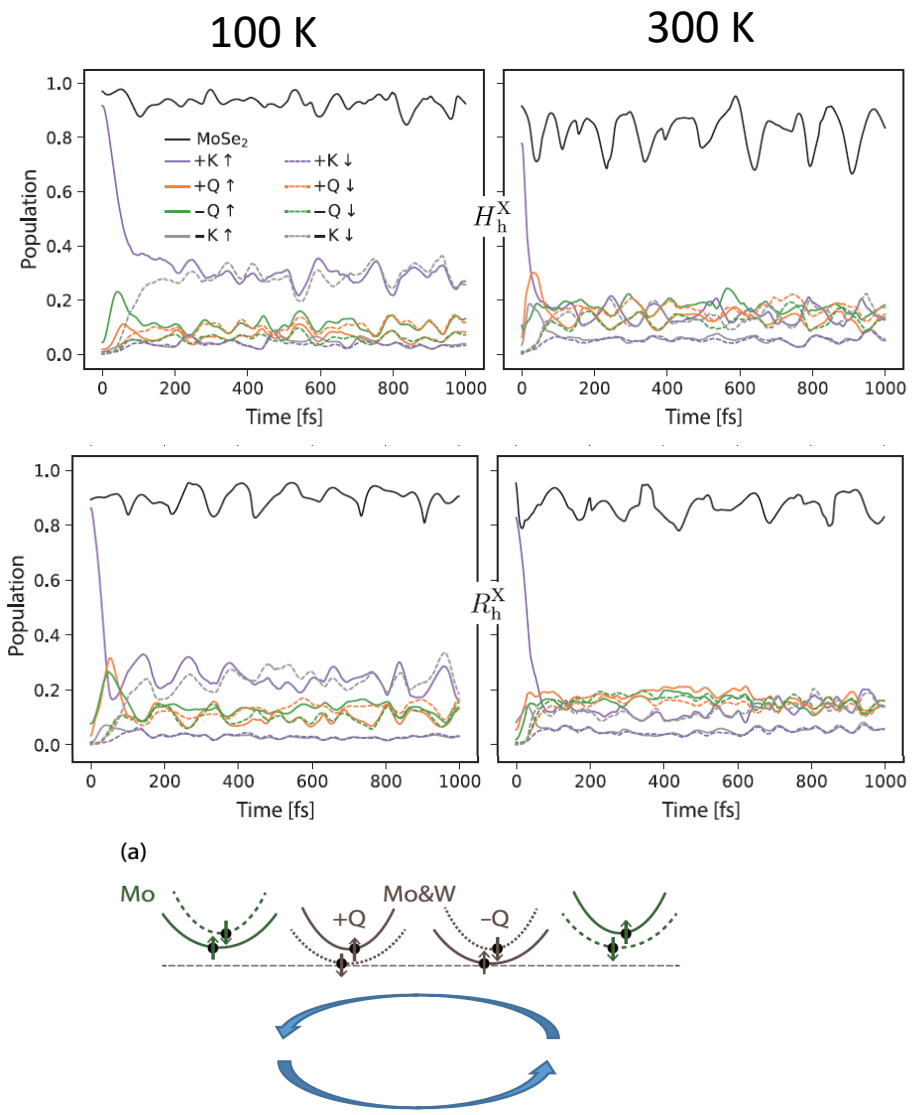
Band Structure of $MoSe_2/WSe_2$



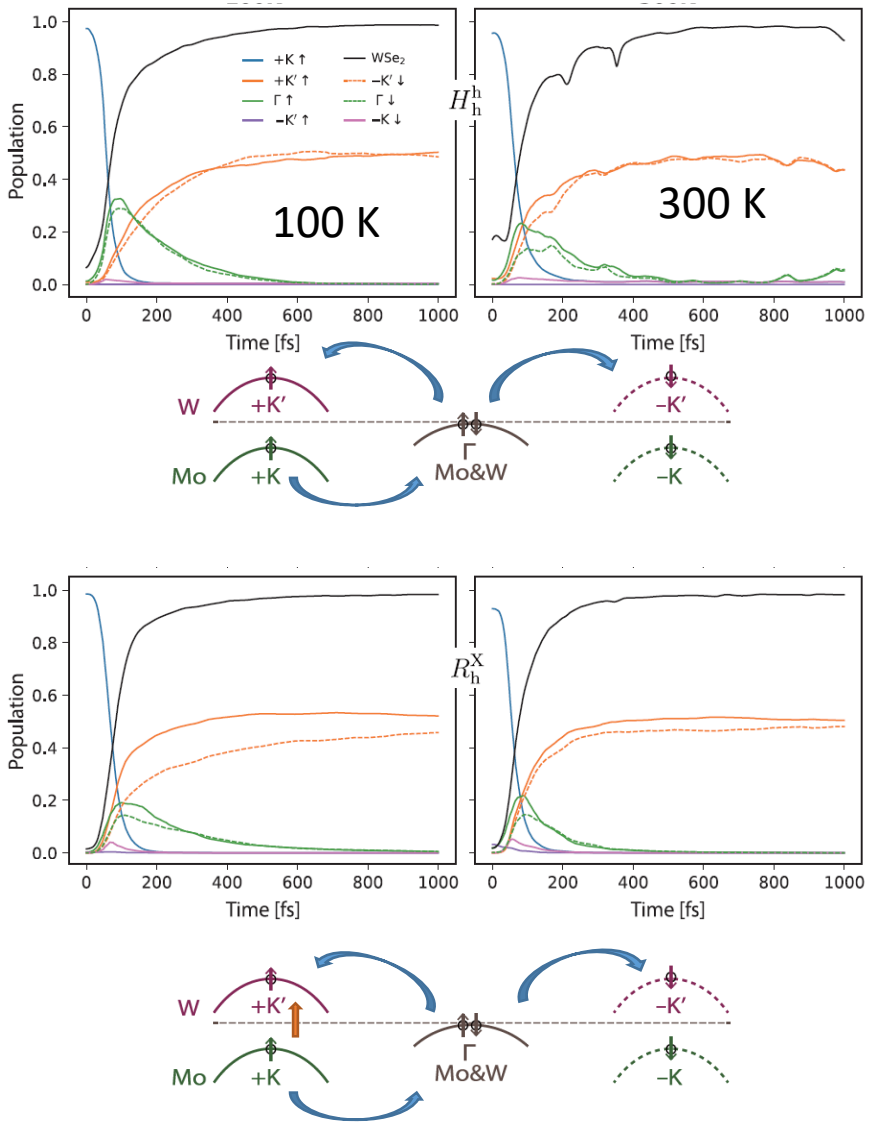




Exciton Dynamics at $MoSe_2/WSe_2$

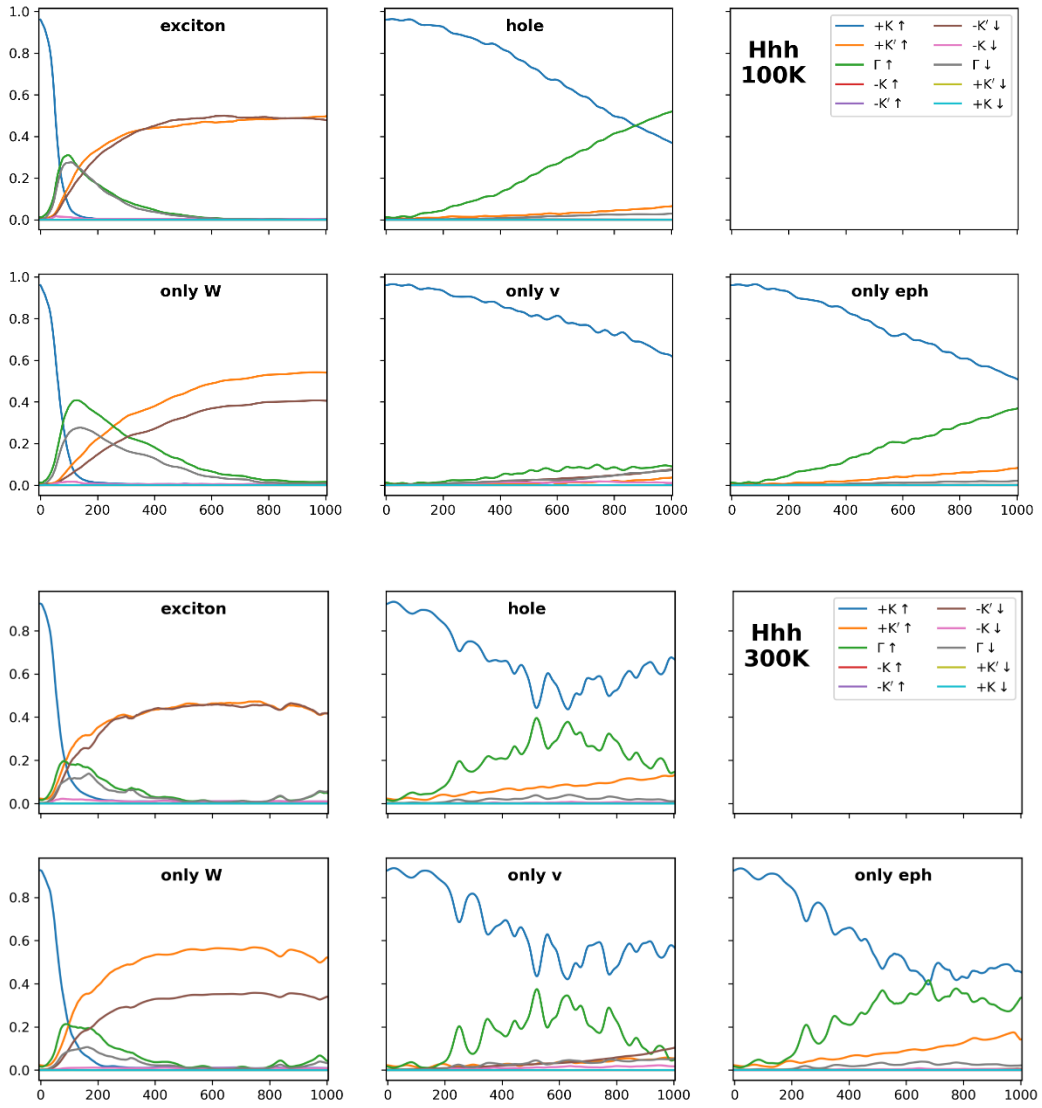


Electron



Hole

Mechanism of Exciton Dynamics at $MoSe_2/WSe_2$



E-ph and SOC

Coulomb Interaction (W)

Exchange Interaction (v)

Summary

Single-particle

TDDFT

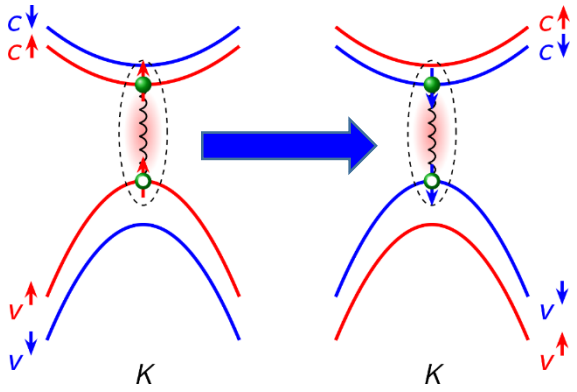
$$i\hbar\frac{\partial\psi(r,t)}{\partial t}=\mathcal{H}(r;R)\psi(r,t)$$

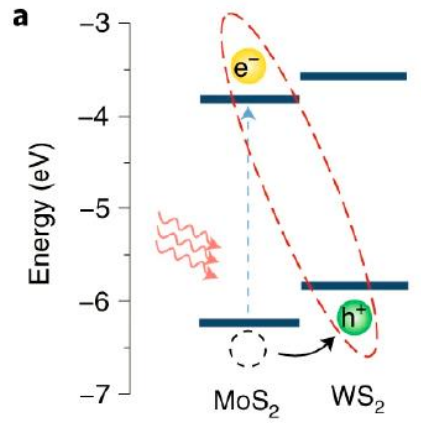
Real-time - BSE

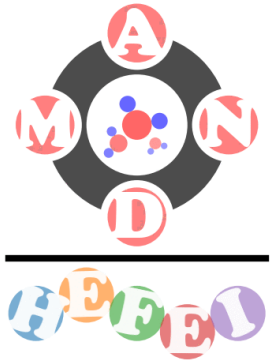
$$i\hbar\frac{\partial\psi(r_e,r_h,t)}{\partial t}=\mathcal{H}(r;R)\psi(r_e,r_h,t)$$

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

Future work based on *GW* + rt-BSE NAMD Simulation

✓Exciton Lifetime

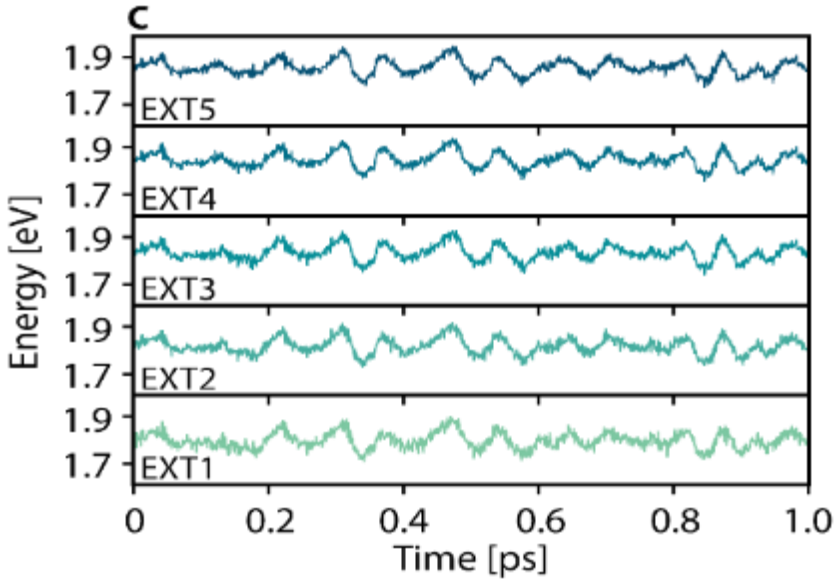
✓Hot exciton Relaxation

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

✓Exciton-Phonon Interaction

✓Exciton-Polaron interaction

…



Several thousands of exciton energies
from *GW* + rt-BSE NAMD

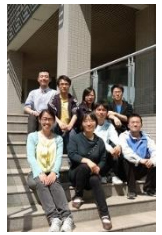
⬇

Machine learning for excited state
potential energy surface

⬇

Photocatalysis

Acknowledgement



2011

2013

2015

2016

2017

2019

2020

My Group

Zhenggang Lan
兰峥岗
South China Normal University
Surface hopping

Wissam A. Saidi
U. Pitt
DFT calculations

Xingguo Ren
任新国
USTC
GW+BSE

Hrvoje Petek
U. Pitt
Experiments

Jinlong Yang
杨金龙
USTC
Ph.D advisor
Discussion & support

Collaborators