Utrecht University

ETSF

# Light-matter interaction in 2D from first-principles

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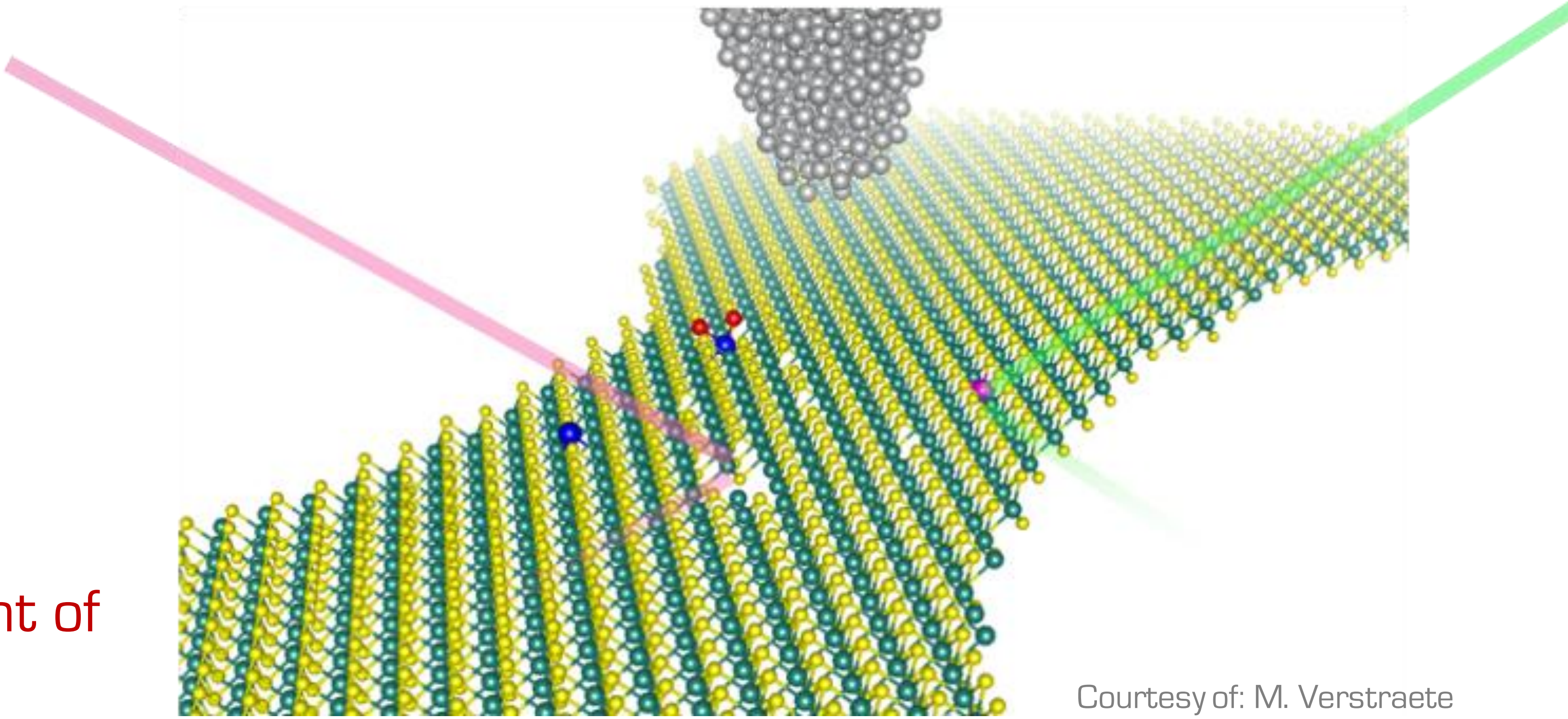
# Controlling Quantum Materials

To develop quantum technology it is necessary to control/tune QM properties

Light allows easy access to the core material properties

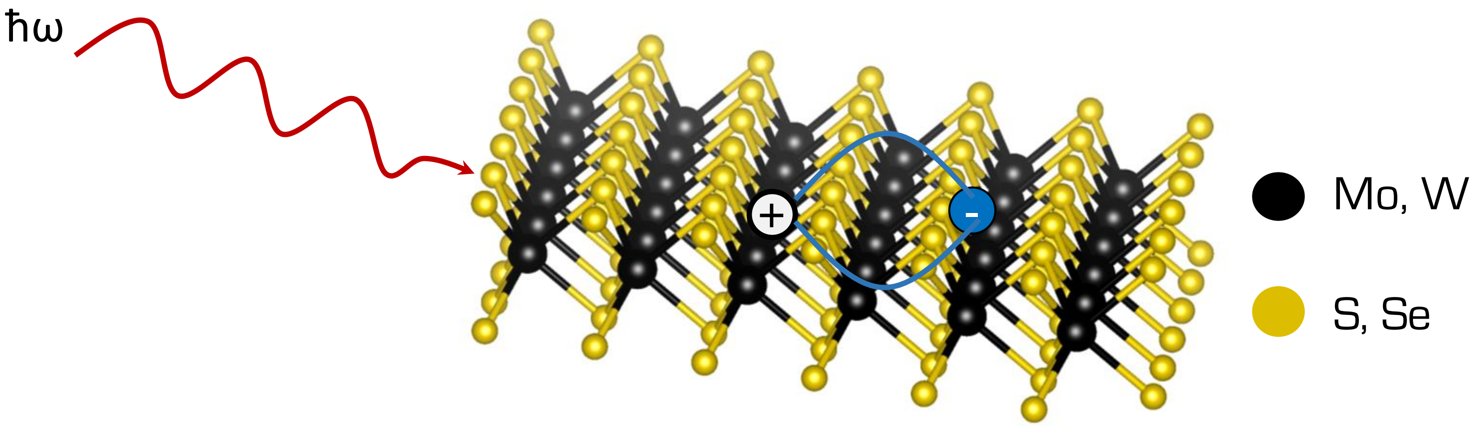
Light
- Generates
- Probes
- Controls
- Interacts with
  - excited states in matter

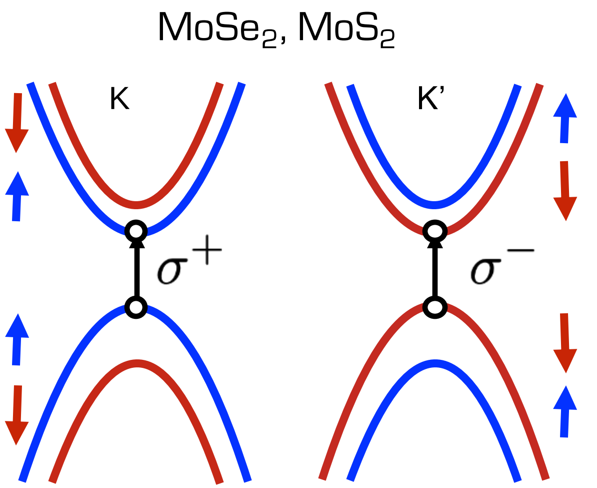
Theory & Simulations for a **simultaneous quantum** treatment of **light, lattice vibrations & electron-hole bound pairs**



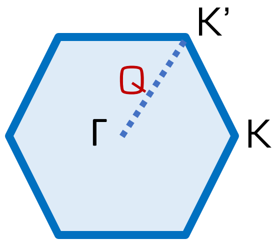
Courtesy of: M. Verstraete

# Exciton Physics in 2D: light-matter interaction



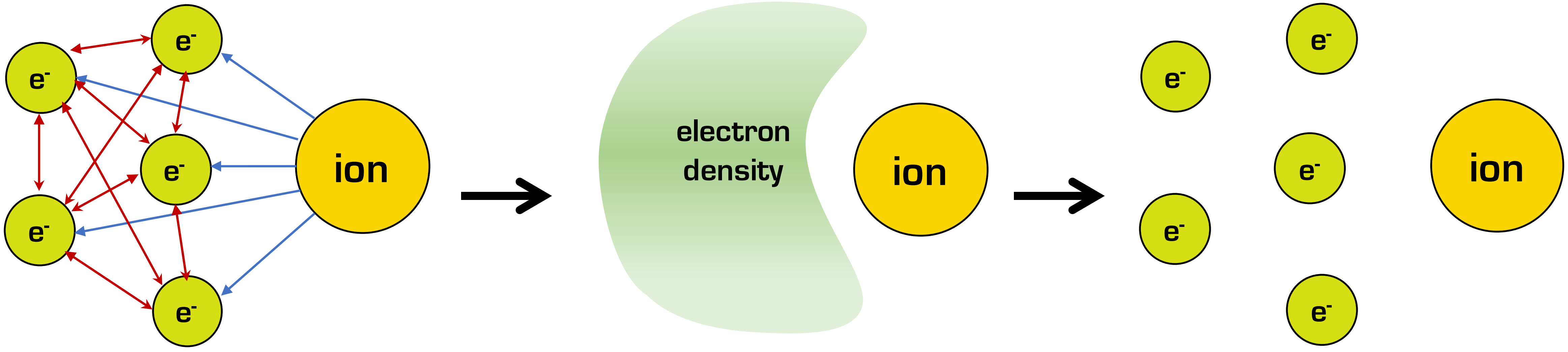

- 2D: Direct gap
- High Spin-Orbit Coupling
- Valley selective optical spin pumping




Applications in
- Spintronics/Valleytronics
- Optoelectronics
- Photovoltaics
- Quantum information

Tune their properties with
- Strain
- Alignment/Twisting of HS

# The Density Functional Theory perspective




**Many-Body**

N Interacting particles

$$\psi(r_1, s_1; r_2, s_2; \ldots; rN, sN)$$

$$\hat{H}\,\psi = (\hat{T} + \hat{V} + \hat{U})\psi = E\psi$$

**Hohenberg-Kohn**

Energy is a unique functional of eletron density n

$$E = E[n(r)]$$

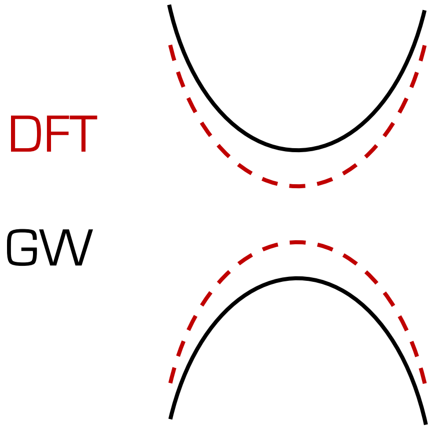
**Kohn-Sham**

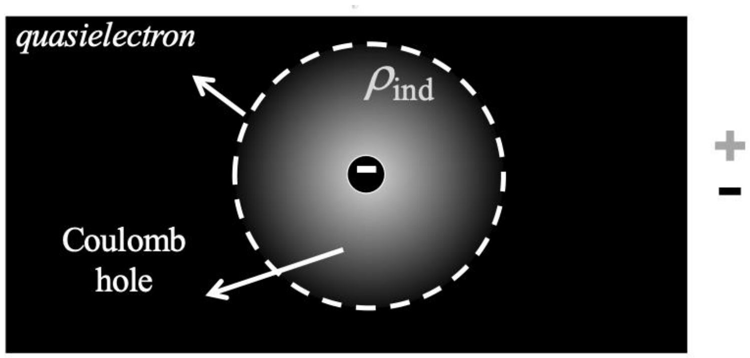
N Independent particles auxiliary potential and same electronic density

$$\sim\varphi_i(x, s)$$

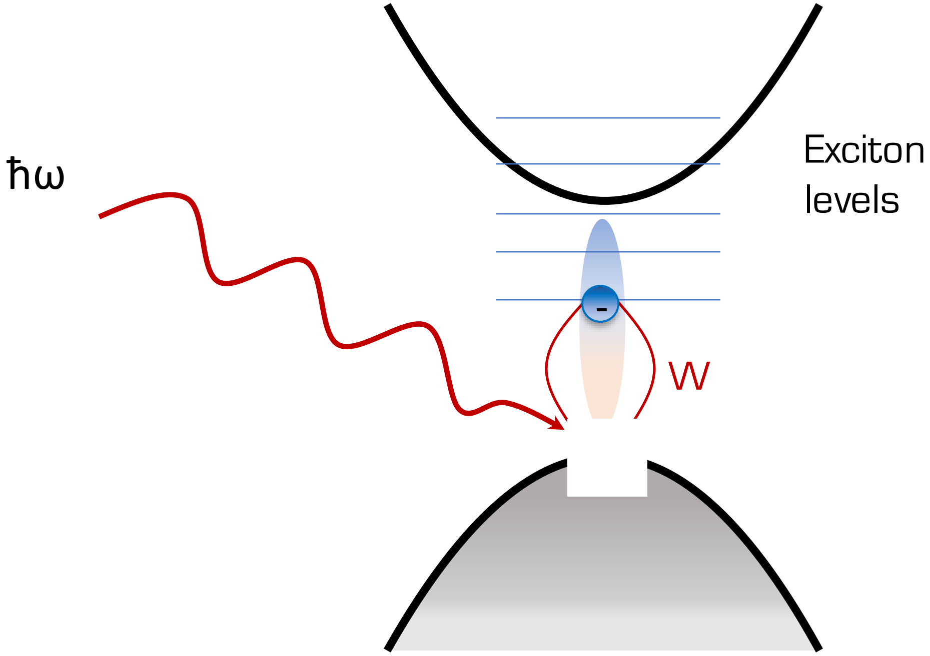
$$\hat{H}\,\varphi = (\hat{T} + \hat{V}_{KS})\varphi = E\varphi$$

# Quantum Many-Body Problem




Courtesy: I. Aguilera




**DFT**: approximation on $e^-$-$e^-$ interaction
=> band gap underestimation

**GW**: interacting electrons via
dynamical screened Coulomb interaction W(r, r', $\omega$)

Experiments: ARPES, STS, …

**Bethe–Salpeter Eq.** on top of GW
=> calculate neutral excitations

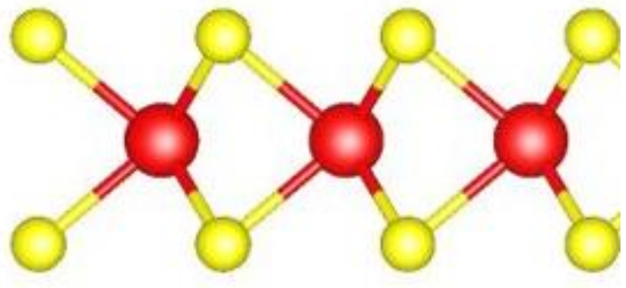
$$E_{binding} = \Delta E_{cv} - E_{exc}$$

Yambo©

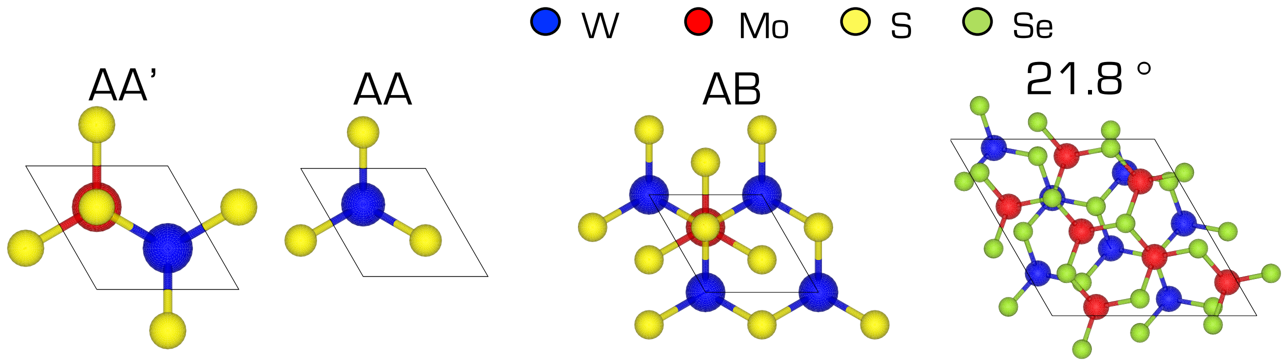
Experiment: Light Absorption

# Outline: Exciton physics in

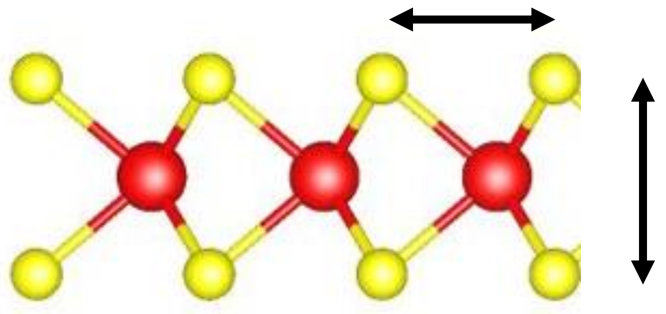
## TMDs MLs



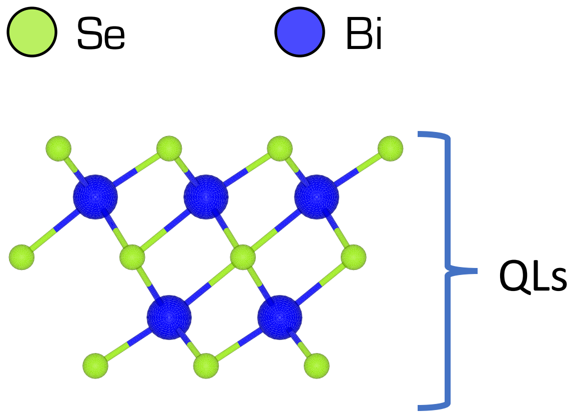
## vdW HS: $MoS_2/WS_2$ $MoSe_2/WSe_2$




## Strain effect on optical absorption



## High energy excitations in 6QL $Bi_2Se_3$

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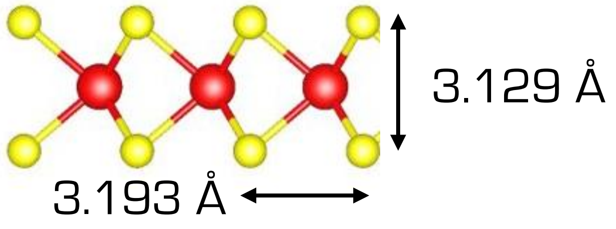
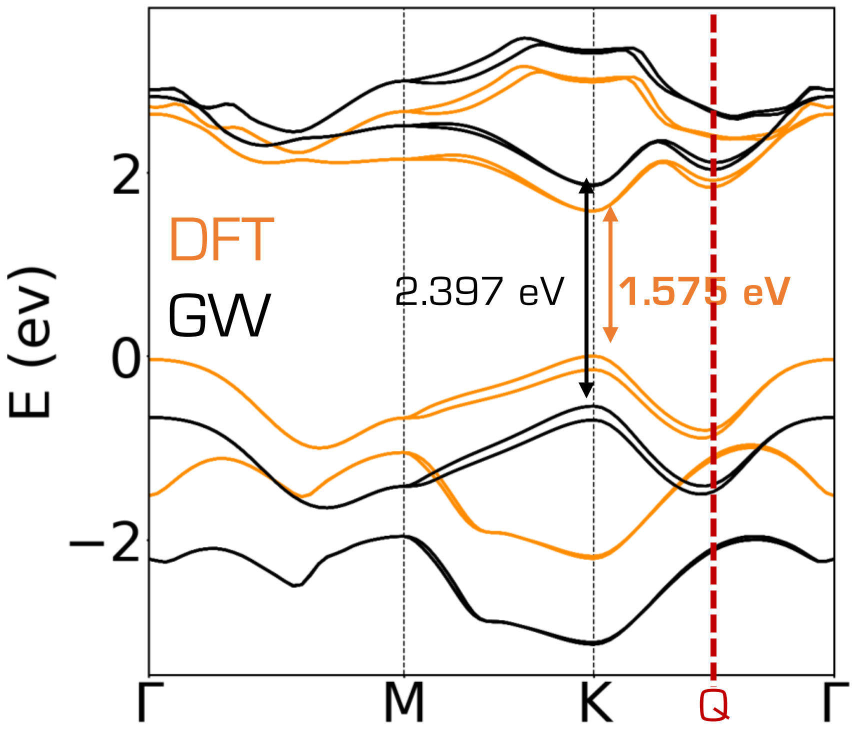
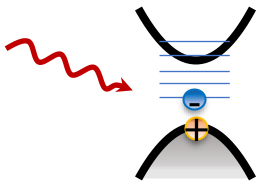
# $MoS_2$

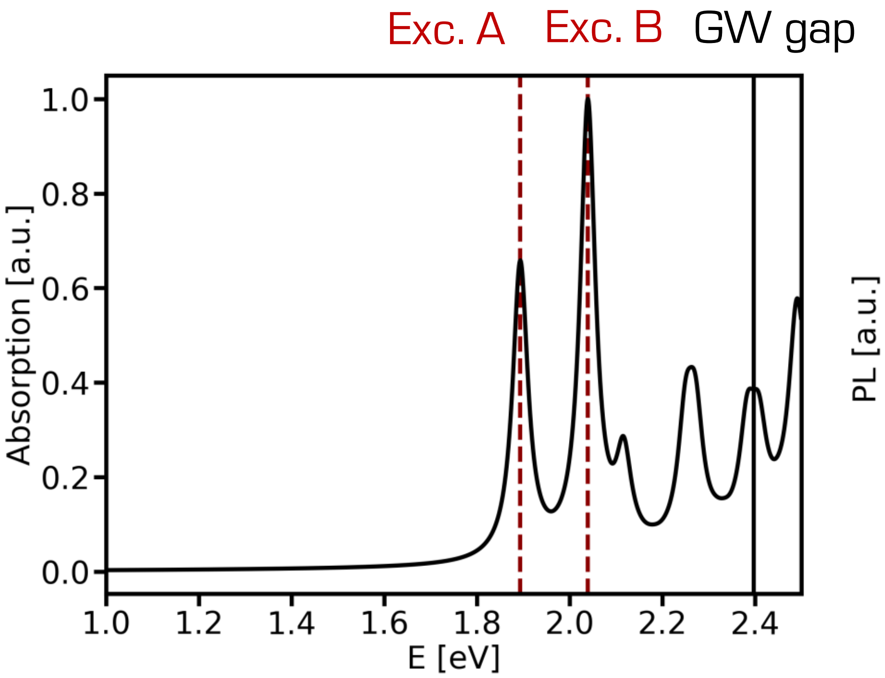


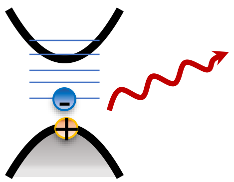

Strong quantum confinement
Low dielectric screening

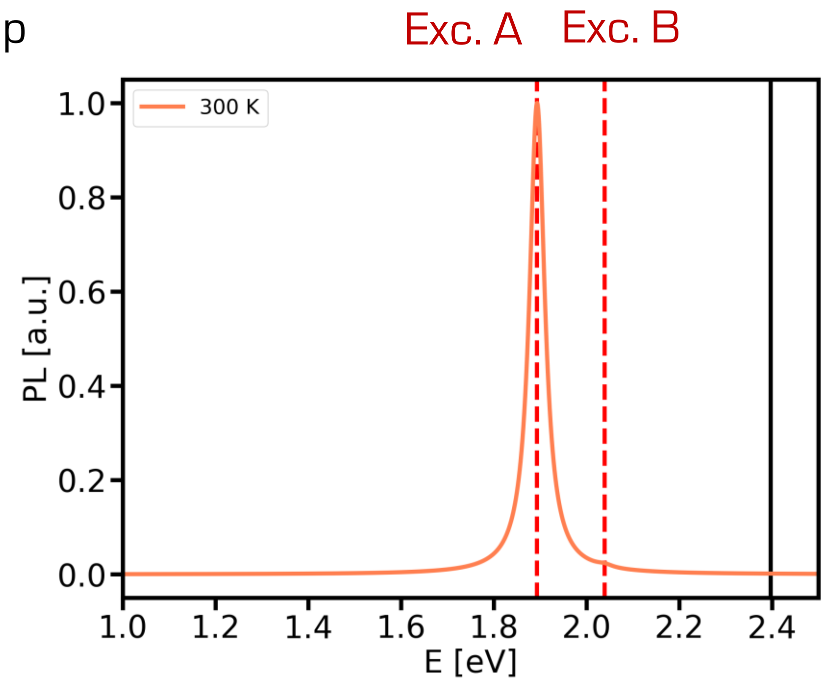
→ High exciton binding energy



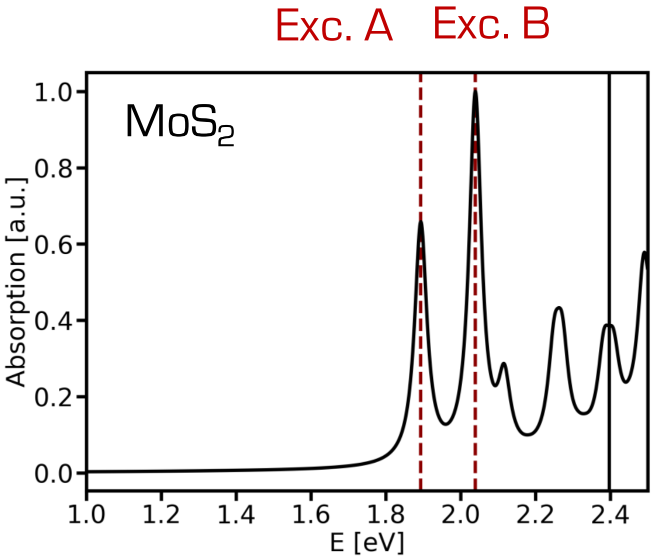



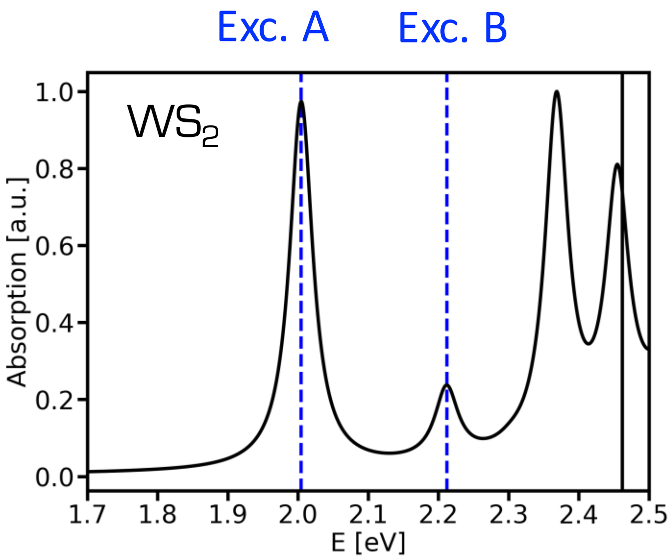


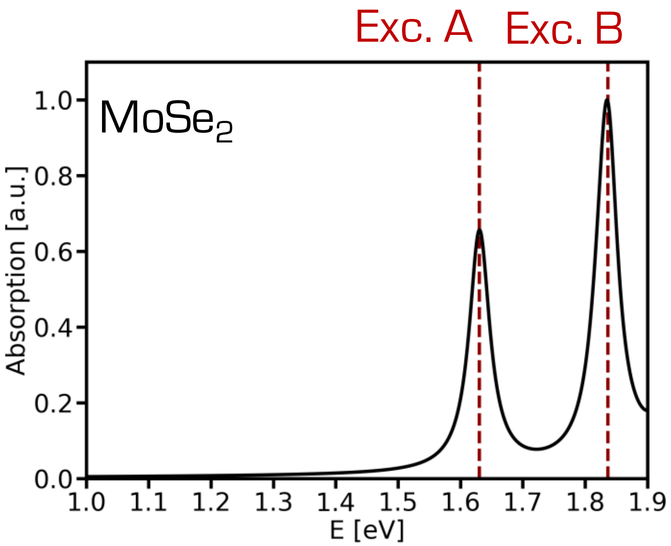



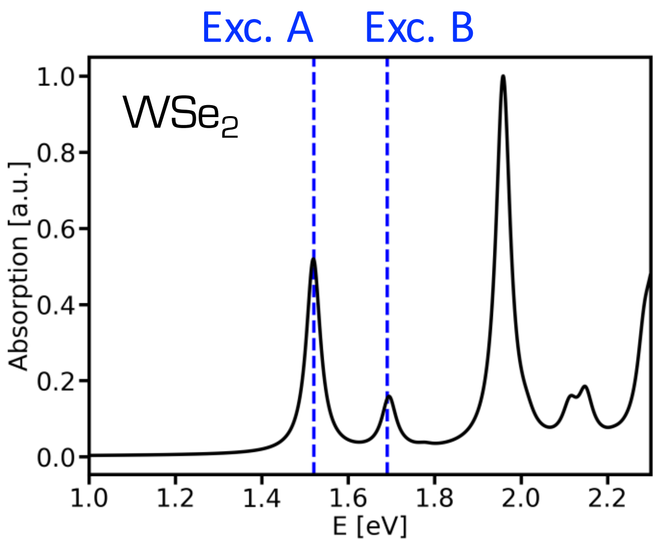


# Absorption spectra: monolayers




Dependence of exciton energy on :

- Structrural relaxation

- Pseudpototentials:
  full semi-core states (s, p, d)

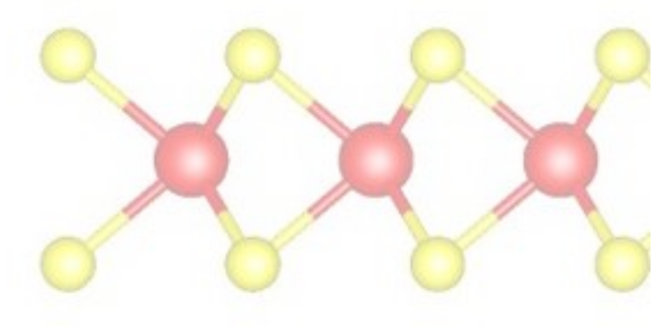
- Exchange correlation functional

→ Necessary accurate convergence:

Otherwise one gets unphysical results:
- indirect gap MLs
- wrong exciton energy

# Outline: Exciton physics in

TMDs MLs



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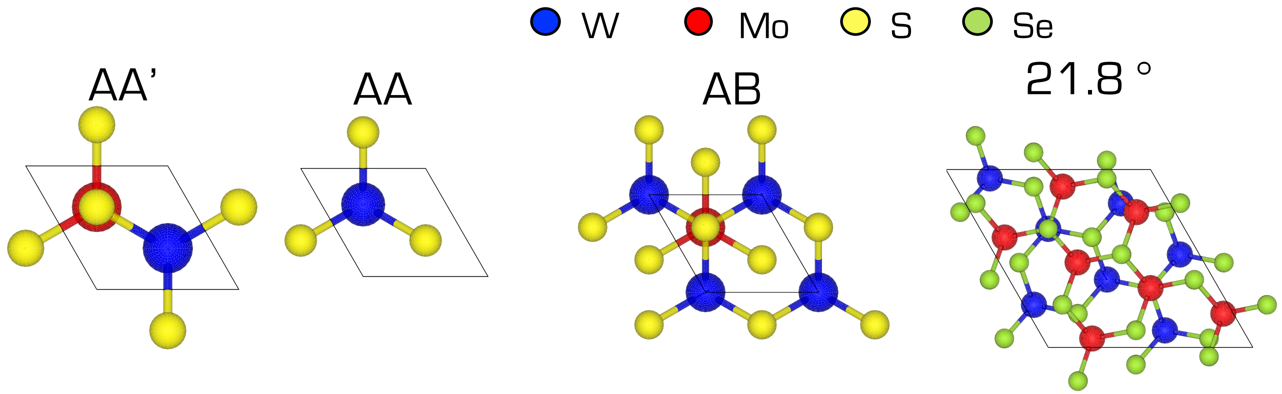


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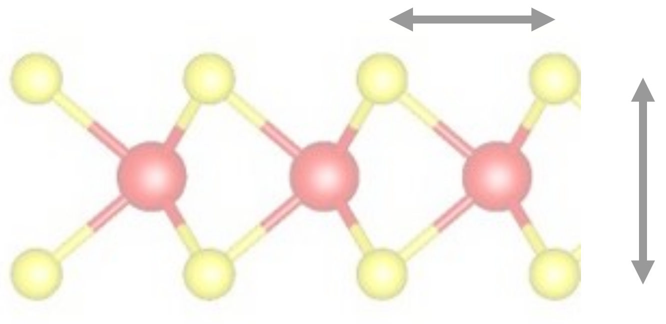

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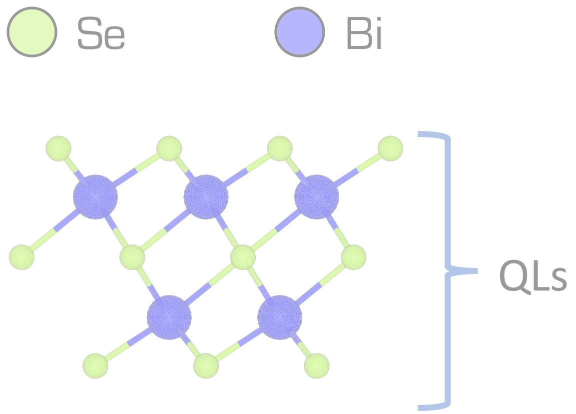
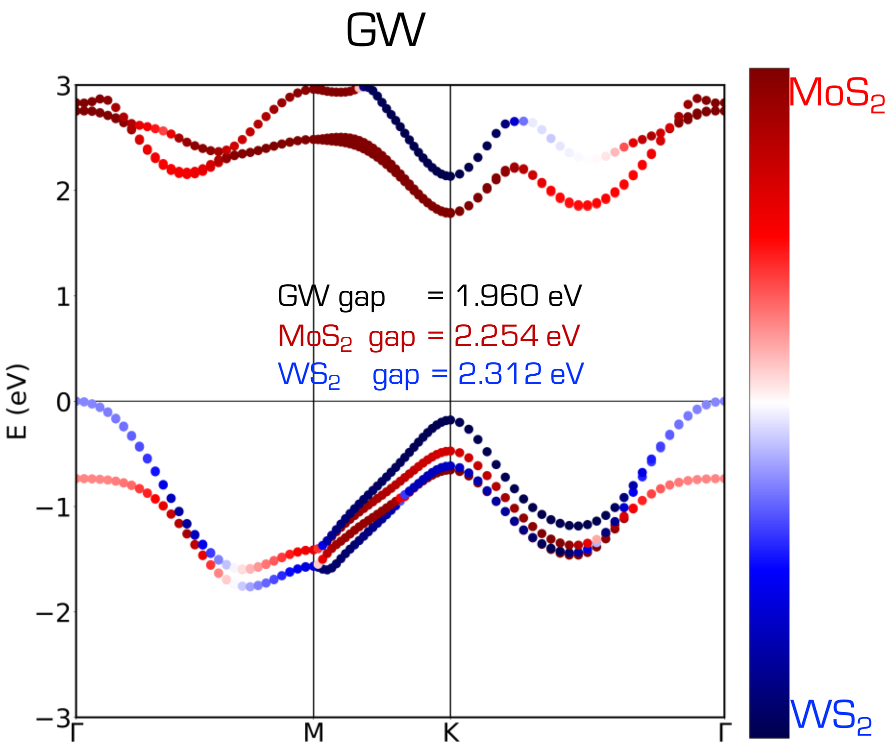
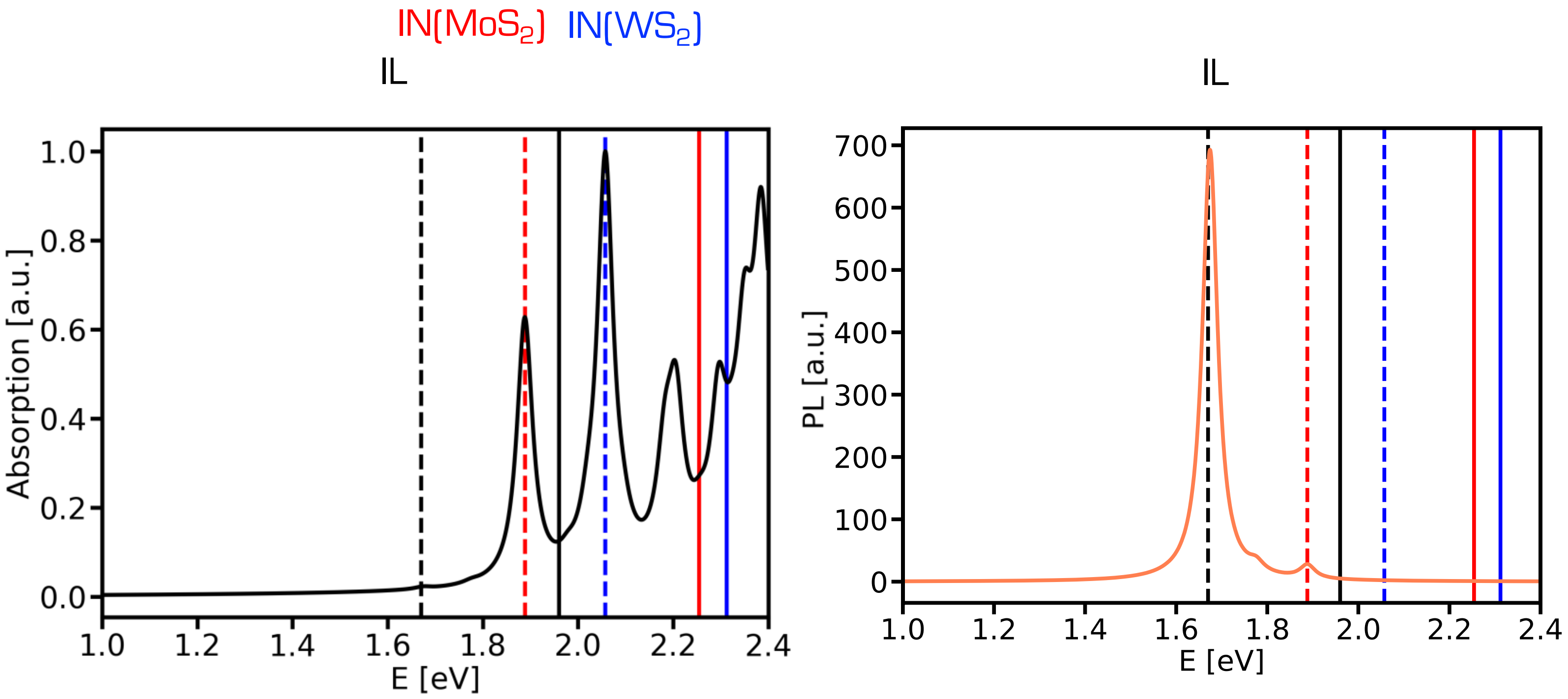
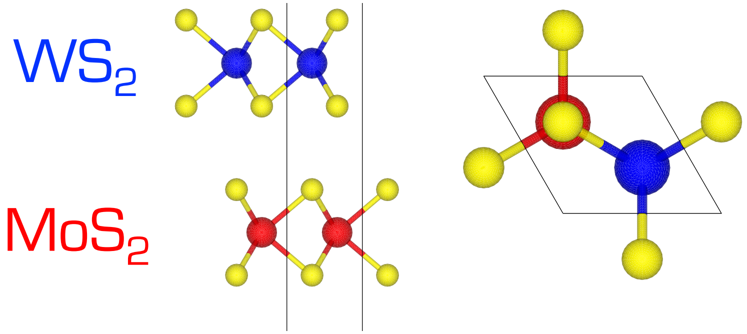


# $MoS_2/WS_2$ AA' stacking



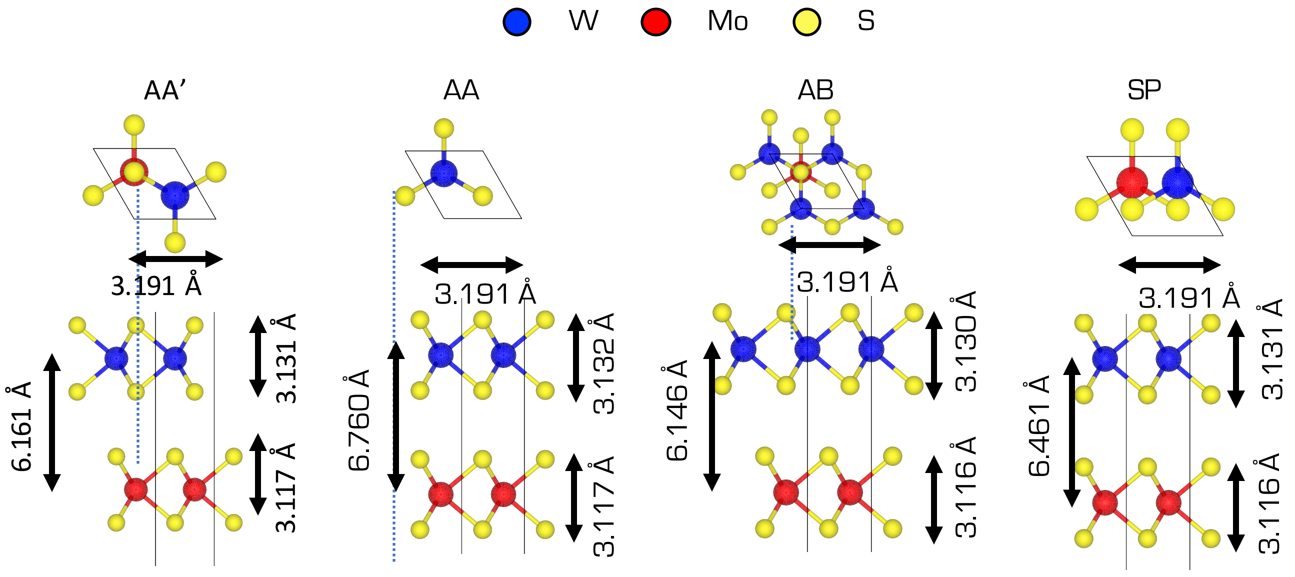



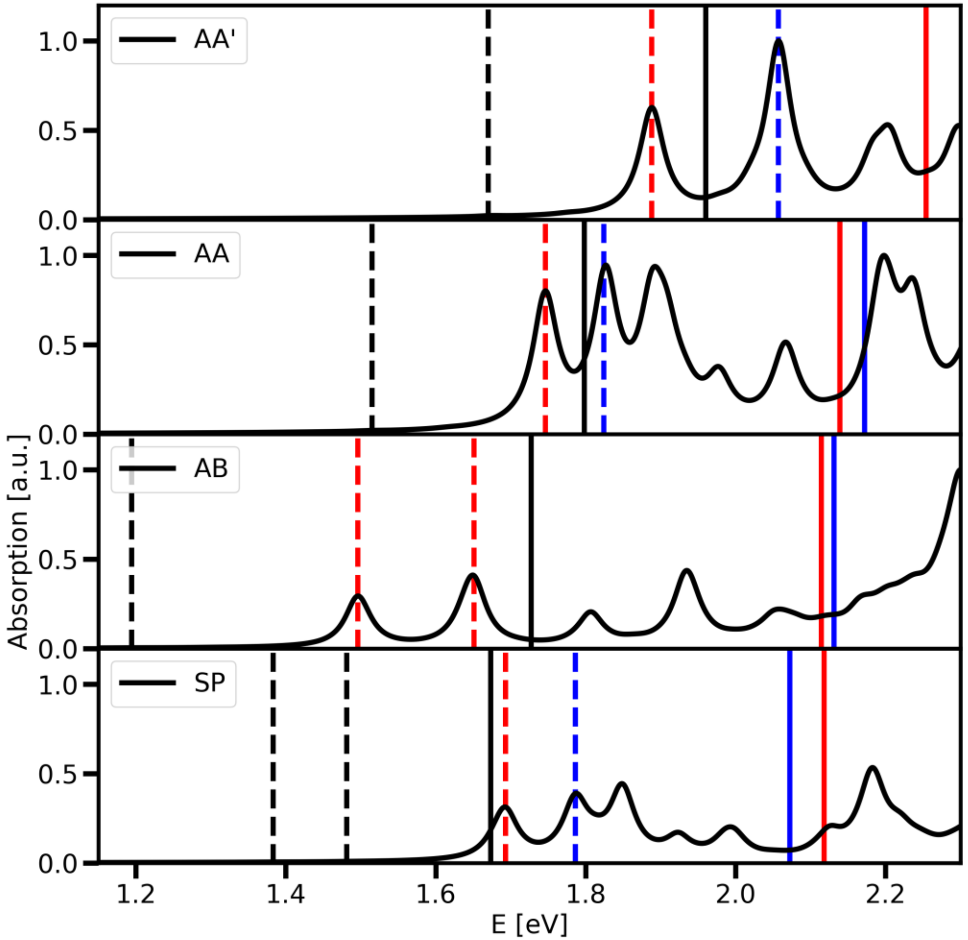

Energy shift INtralayer exciton w.r.t to the isolated case




New emerging features: InterLayer exciton
- electron and hole spatially separated
- visible in PL

# $MoS_2/WS_2$ different stacking

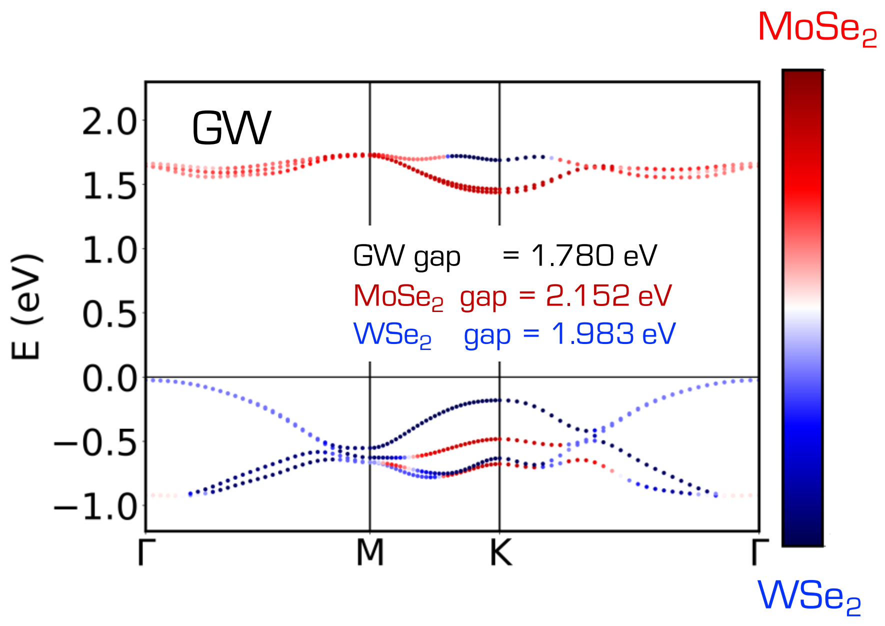


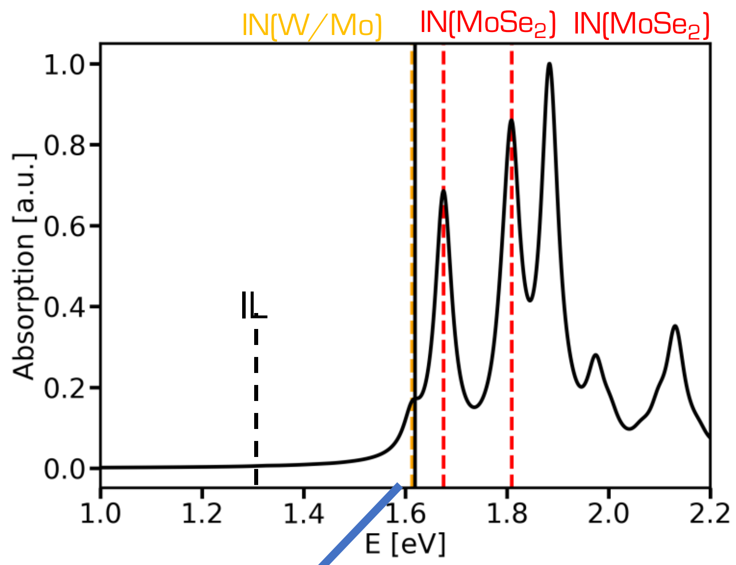



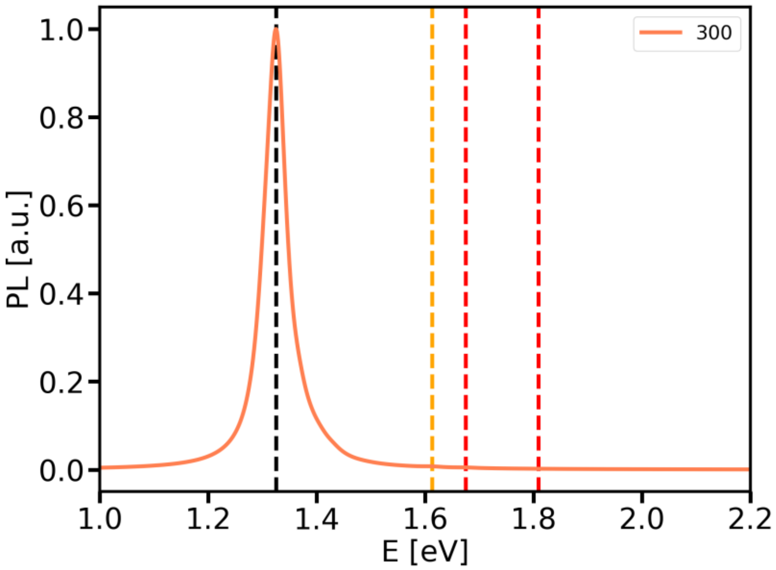

**Intralayer and Interlayer exciton energy increases**

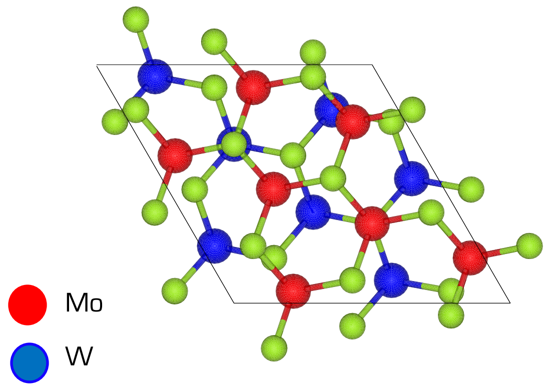
- Suppression of IN($WS_2$) exciton for AB
- Characterization of HS stacking

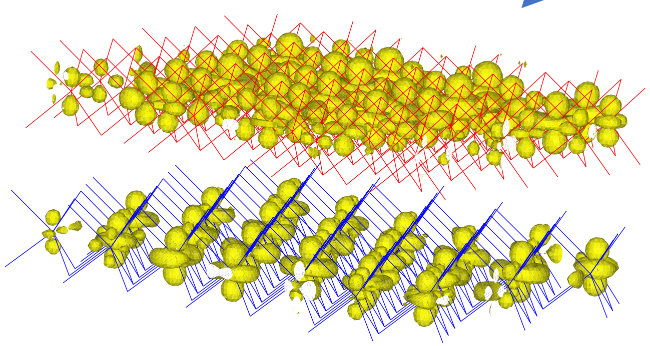
# $MoSe_2/WSe_2$ AA Twisted



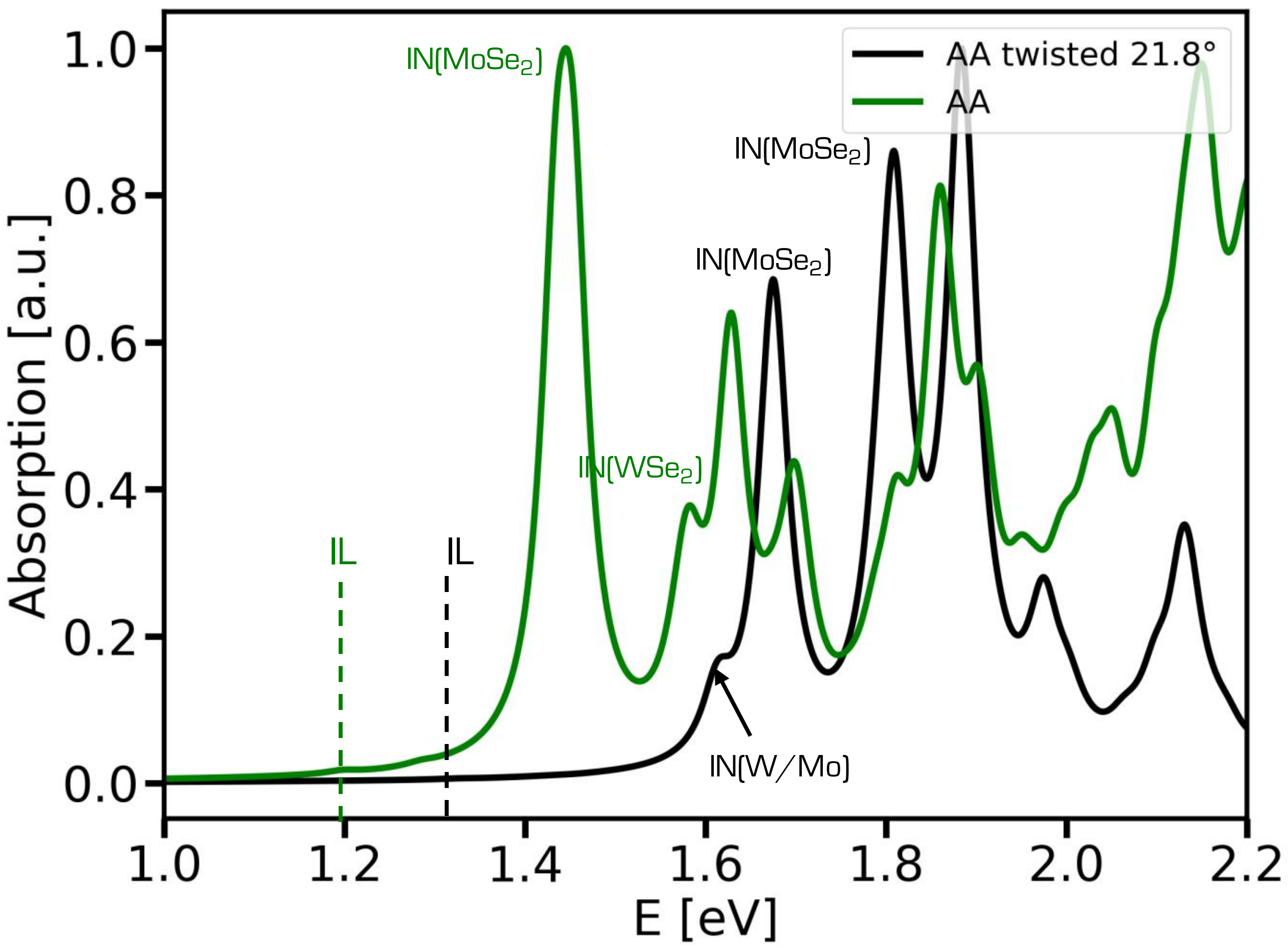



New emerging features:

- flat bands
- InterLayer exciton barely visible
- two degenerate INtralayer excitons IN(W/Mo)
- inhibition of intralayer $WSe_2$ exciton

# Excitonic features in twisted HS

$MoSe_2/WSe_2$




Complex excitonic features in twisted HS:

- Moiré significantly alters the optical properties of the material
- InterLayer exciton (~1.3 eV) disappears
- IN-Plane 'mixed' from $MoSe_2$ & $WSe_2$ layers
- Two IN-Plane excitons in $MoSe_2$ layers

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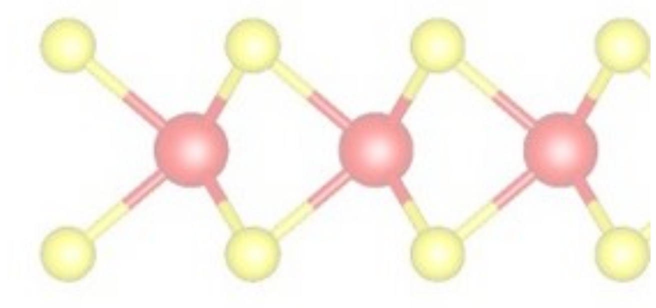

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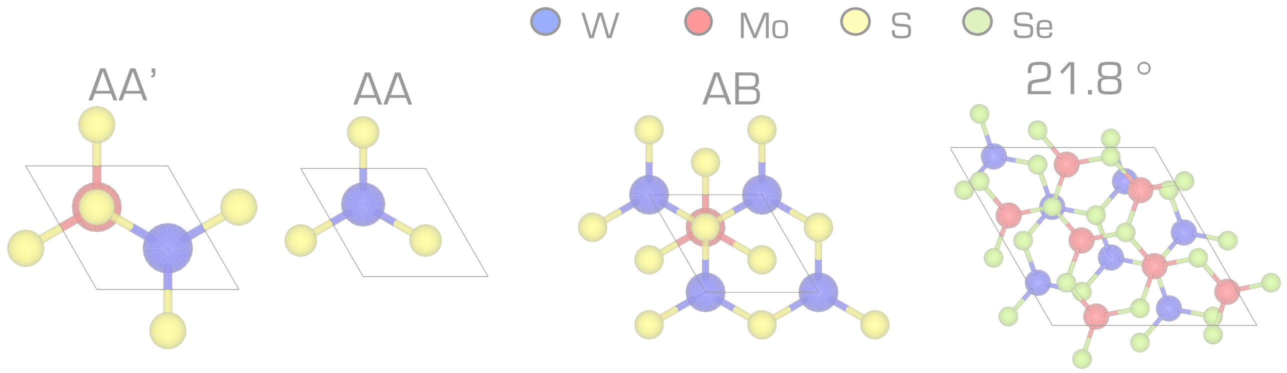


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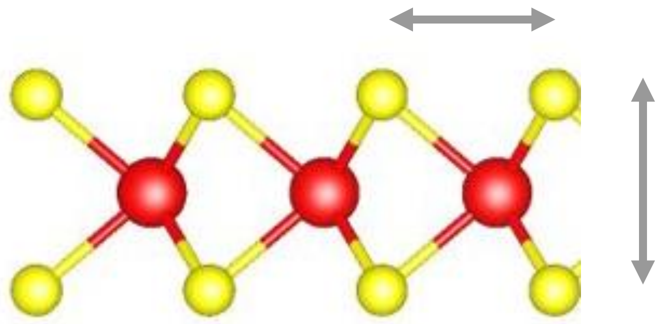

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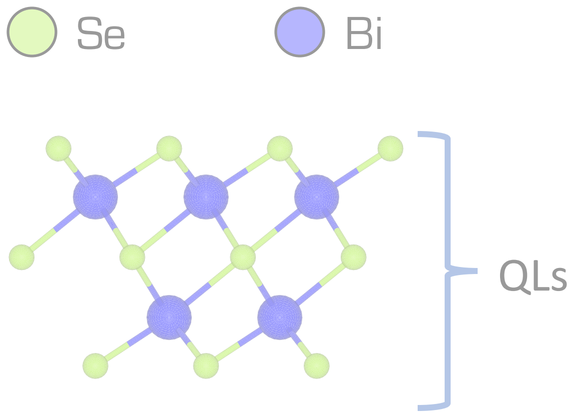


# Wannier-TB

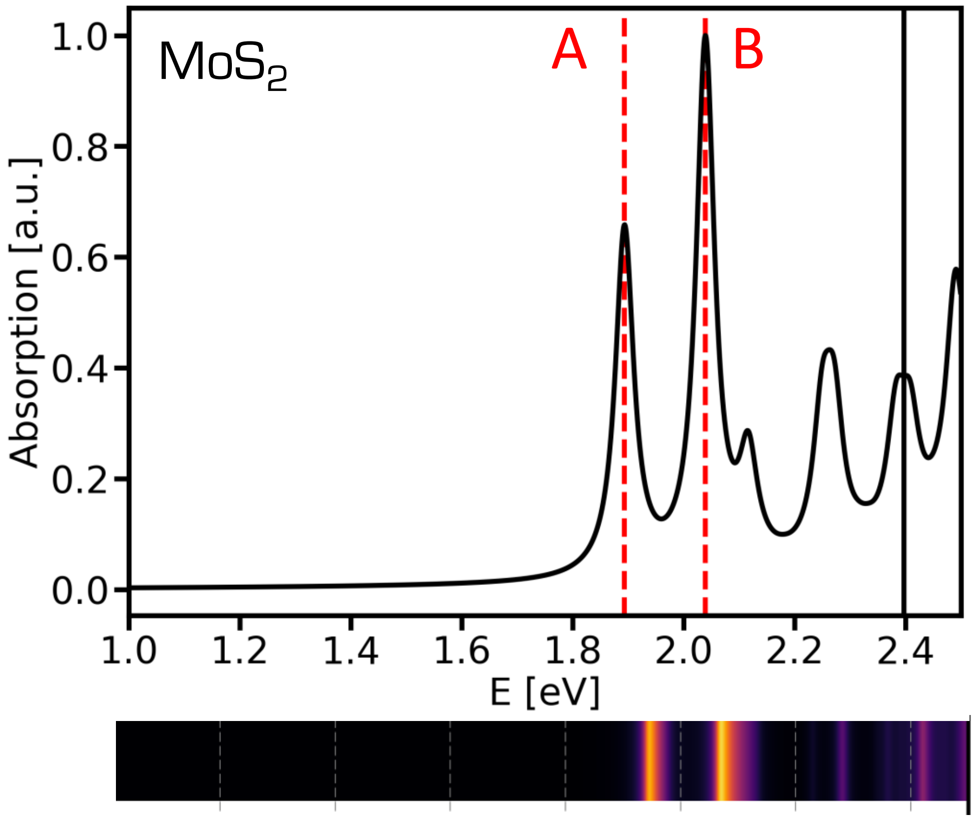
☹ DFT+GW+BSE for large systems is computationally expensive

QUANTUMESPRESSO DFT

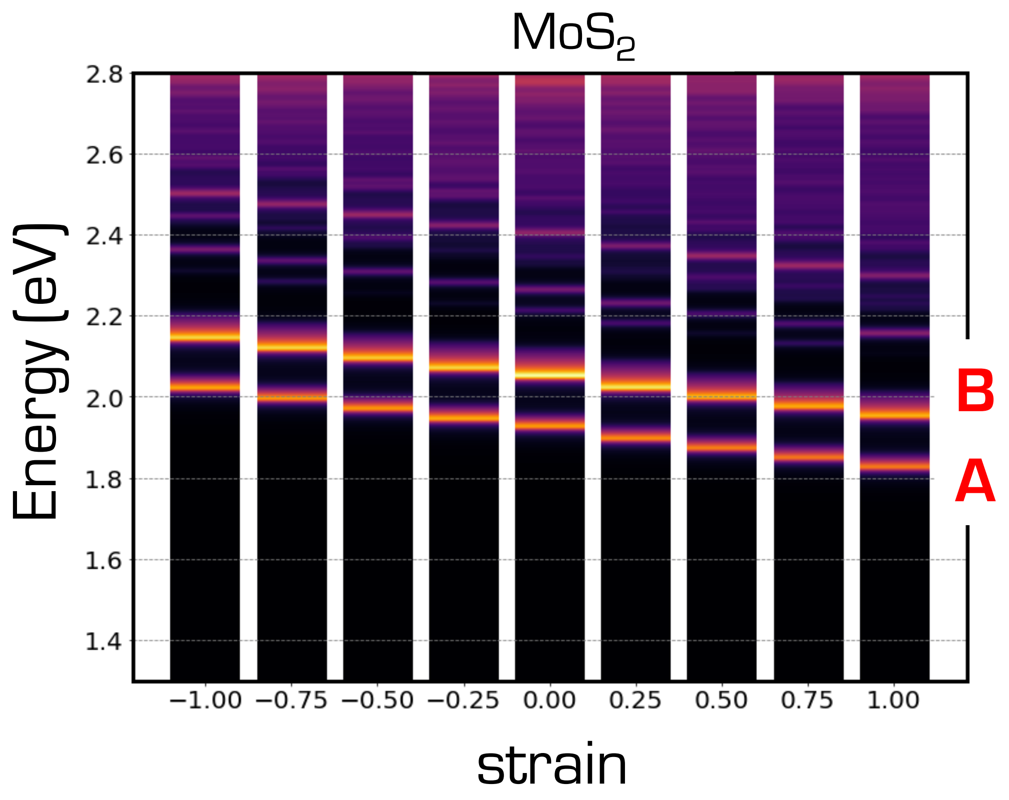
Yambo GW

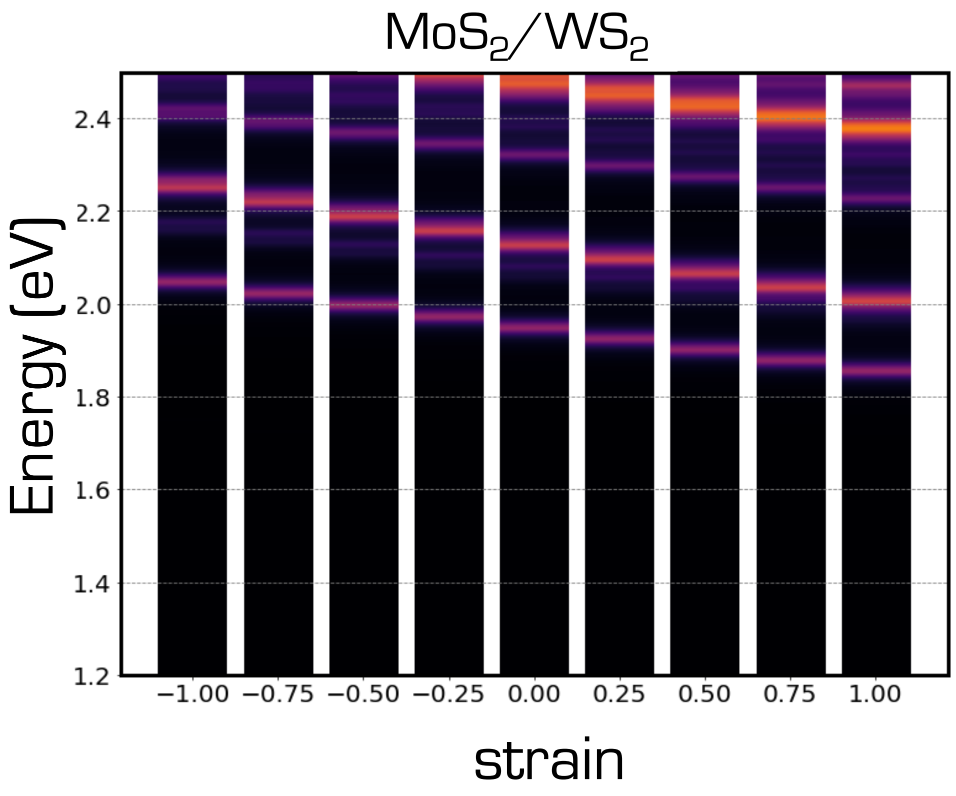
WANNIER90 Maximally Localized Wannier Functions

Solve Wannier-TB model Hamiltonian + BSE using a semi-empirical Coulomb potential (eg. Rytova-Keldysh)



# Tuning exciton energy by strain




A and B Exciton energies

- decrease for positive strain
- increase for negative strain

Same behaviour

- for TMDs ML: **$WS_2$, $MoSe_2$, $WSe_2$**
- for TMD heterostructures: **$MoS_2/WS_2$ - $MoSe_2/WSe_2$**

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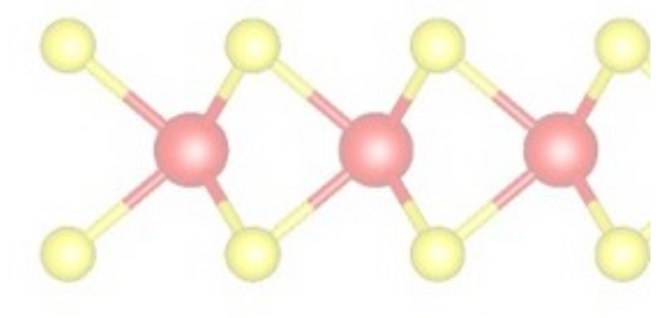

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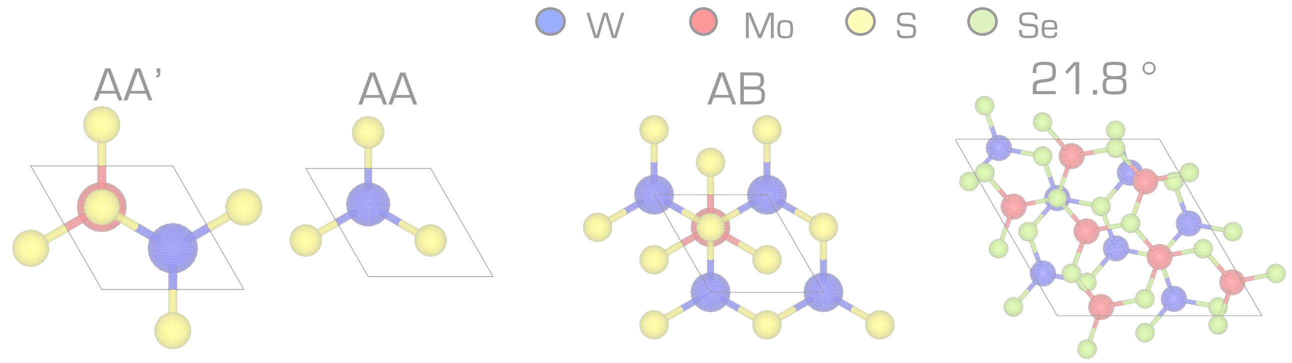


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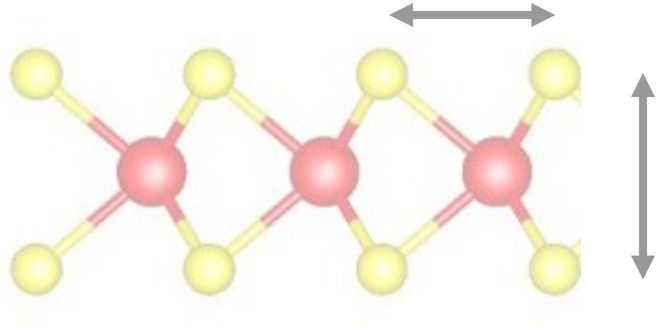

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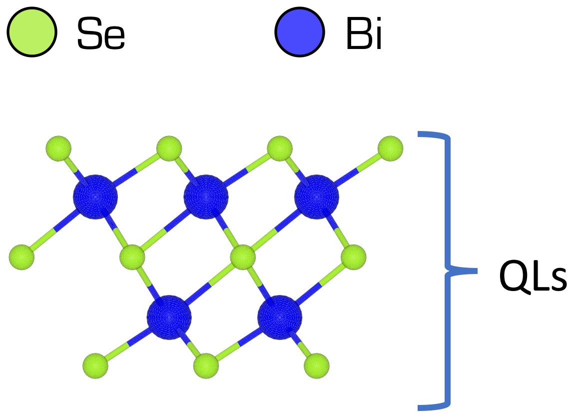


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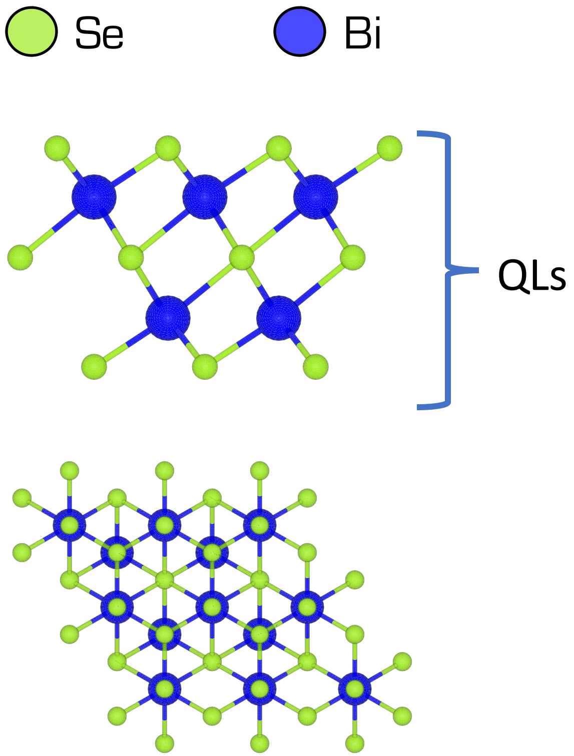
# $Bi_2Se_3$: exotic optical properties

## Effect of 3D → 2D transition

### Crystal structure

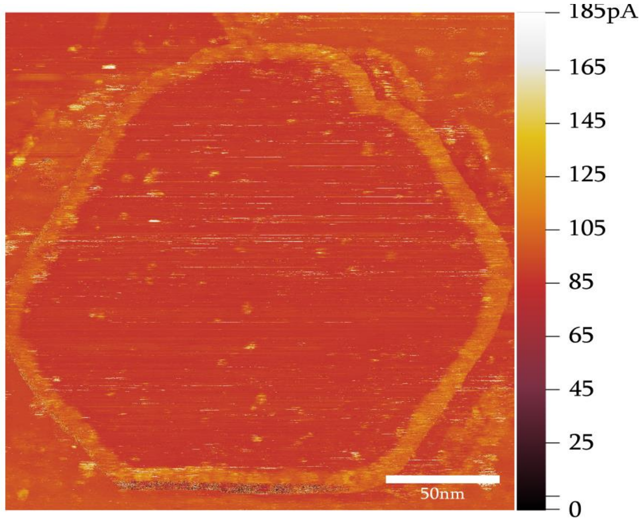



Rhombohedral ($R\bar{3}m$)
vdW stacking

### Topology

Bulk $Bi_2Se_3$ : topological gap ~300 meV

2D : Topological ≥ 4 QLs
STM, GW-TB, 8-bands **k·p**



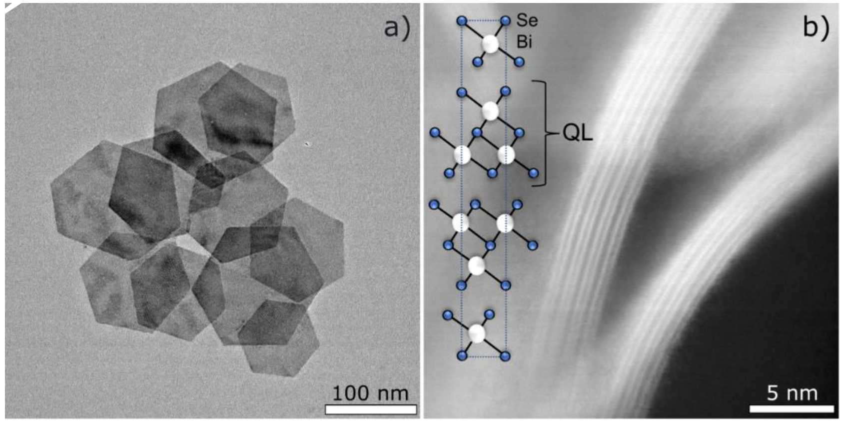

J. R. Moes et al. (2023)

Talk pillar 1 updates & L. Licéran

### Optics

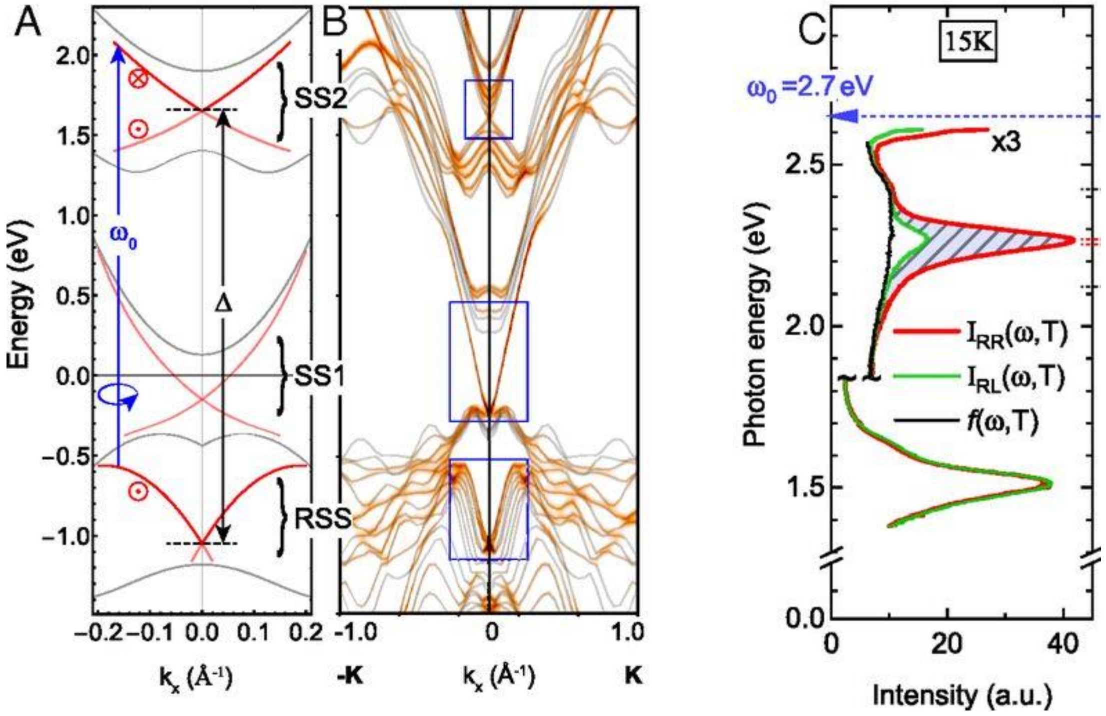
High energy excitations:

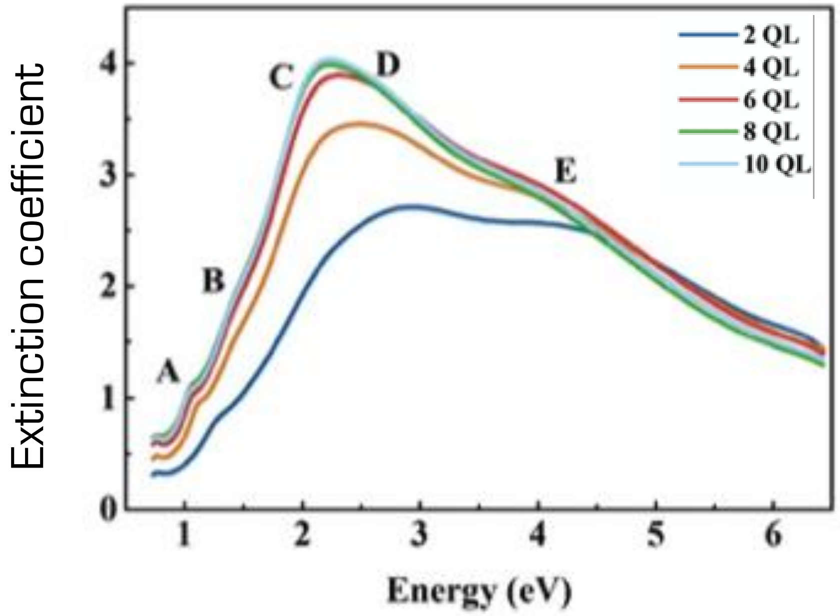
- Preserved circular polarization
- Surface-to-surface transition
- e-h dissociation in BZ by $e^-$-cooling
- Fast e-h recombination




J. Vliem , R. Reho et al. in preparation (2024)

# High-energy excitations in bulk $Bi_2Se_3$




chiral excitons

- surface e$^-$ and hole
- Strong SOC
- Locking spin-momentum

Conservation of incident polarization!

SS = Surface State
RSS = Rashba Surface State

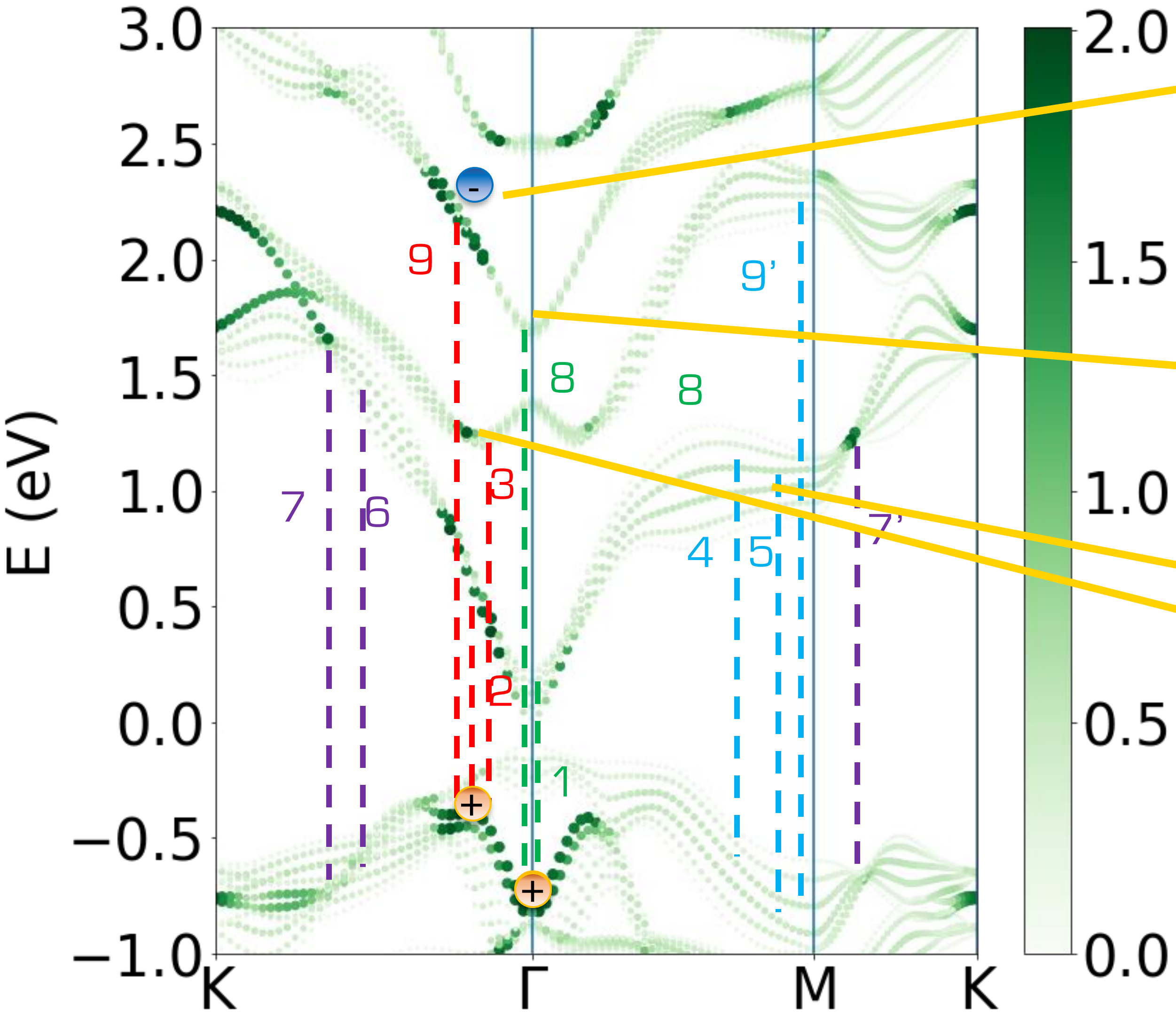
H. –H. Kung et al. PNAS, vol. **116** (2019)

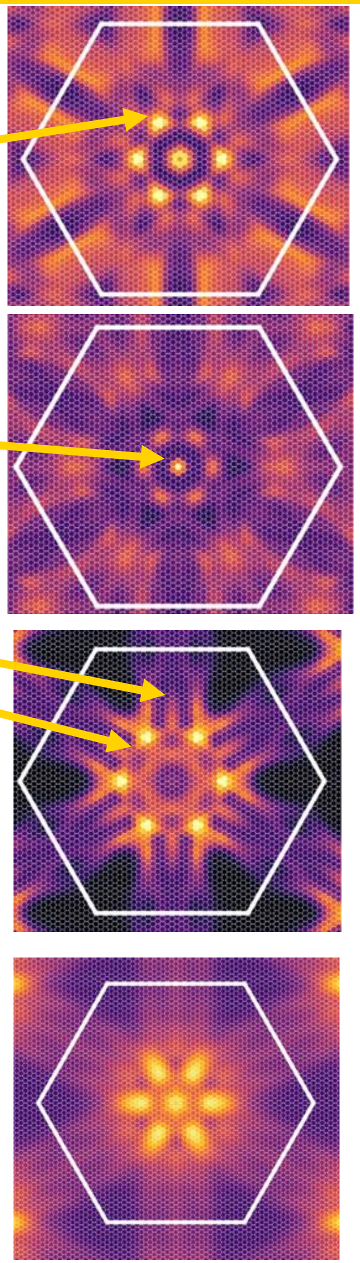
Blueshift of the D peak

Surface to surface transition

M. Fang et al. Appl. Phys. Lett. **118** (2021)

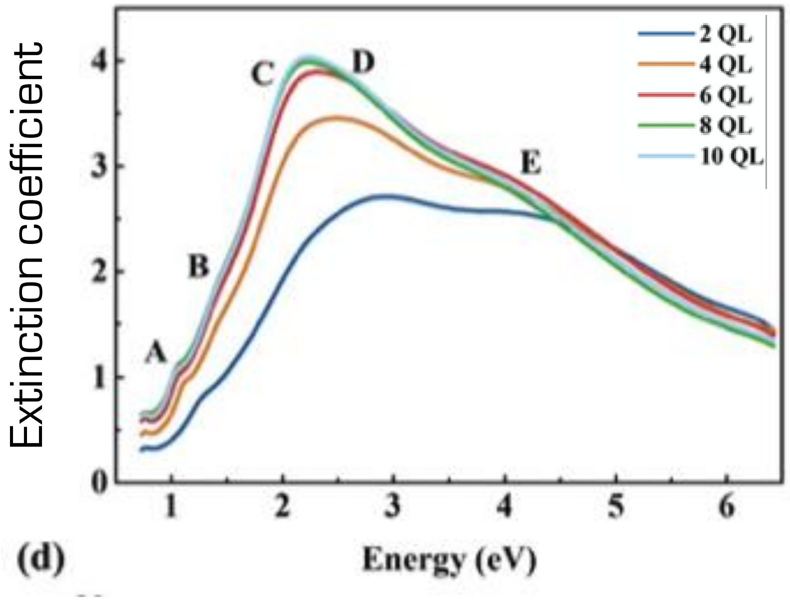
# 6QL $Bi_2Se_3$: electronic and optical properties

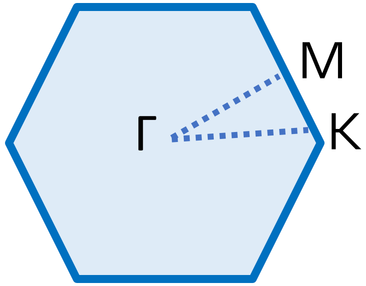


2.6-2.9 eV

1.0-3.25 eV

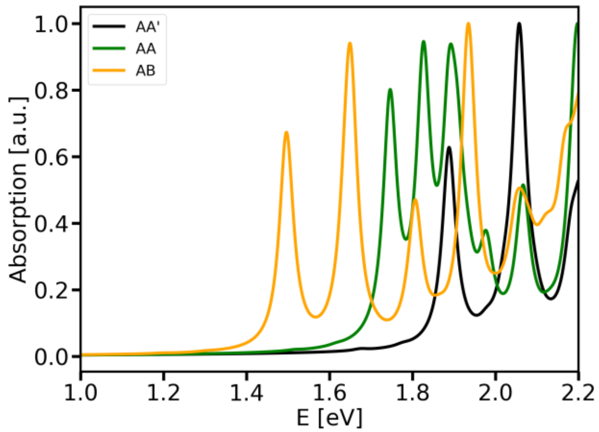


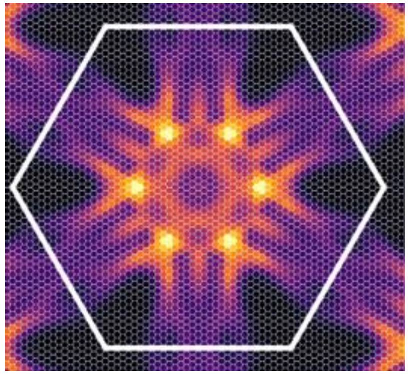



# Conclusions

Controlling **TMDs** properties via:
- Vertical and Lateral straining
- HeteroStructure alignement & twisting

**$Bi_2Se_3$**
- composite chiral exciton
- interesting and non-trivial light-matter conversion excitations
  → microscopic description of the system
- Control cooling, lifetimes of transitions with the number of layers



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QUANTUMESPRESSO

Yambo

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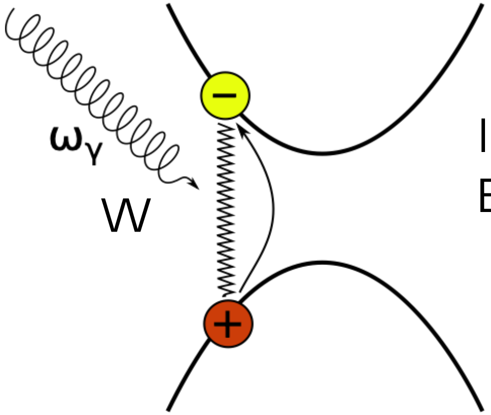
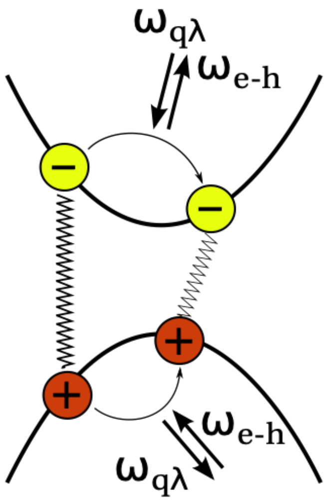
# First-principles Real Time Dynamics

## Excitation



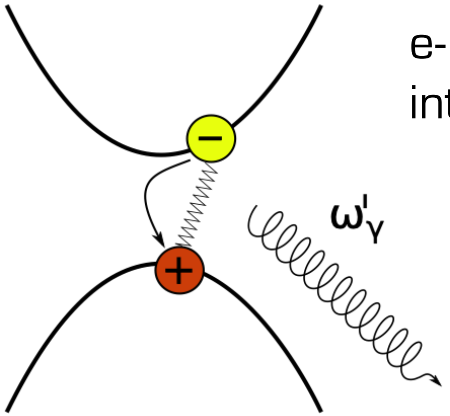

light absorption & Exciton formation

## Relaxation




e- e-
e- h+
e- phonon
e- photon
interactions

## Emission




e- photon interaction

- Beyond ground state to catch many-body physics (GW)
- BSE to describe excitons/absorption
- Electron & Hole **real time dynamics** driven by electron-phonon interaction to describe emission (PL)

→ PL, pump & probe exp., non-linear optics, with Time & Temperature dependence

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D. Sangalli *et al.* J Phys. Condens. Matter 2019
Melo & Marini, PRB 2016; EPL 2017
Marini *et al* Comput. Phys. Comm. 2009

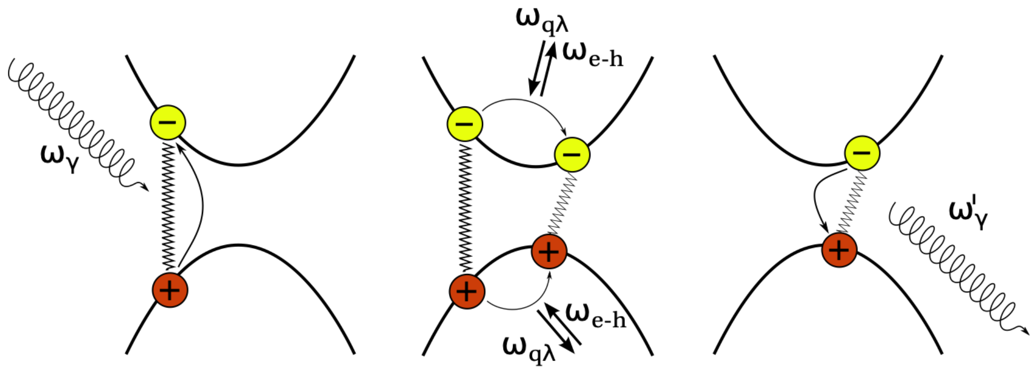
# Time-Dependent Dynamics

BKE for the single time Green's function

$$\frac{\partial}{\partial \tau}\rho(\tau) + \mathrm{i}[h_{\mathrm{ext}}(\tau), \rho(\tau)] = -S[\{G\},\{\Sigma\}](\tau)$$

DFT + external fields

NEQ collision integral




$S[\{G\},\{\Sigma\}](\tau)$

$\Sigma^{\lessgtr} = \mathrm{i}G^{\lessgtr}W^{\gtrless}$

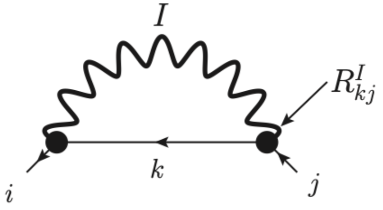
$S[\{G\}](\tau)$

$S[\rho](\tau)$ Markovian chain (no memory)

No vertex corrections

GBKA

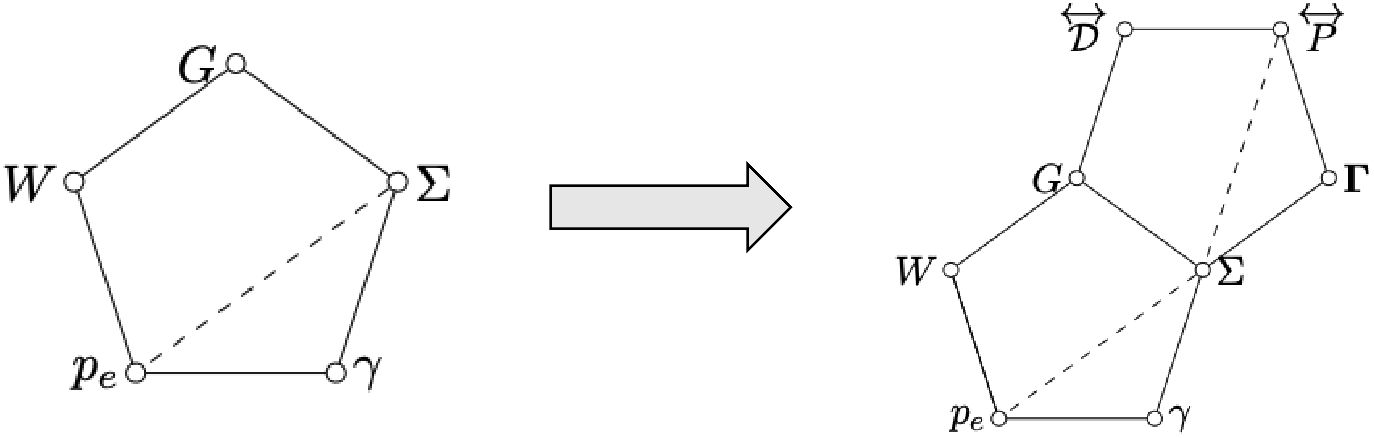
+ completed collision




- Low intensity pump
- $\tau_{collision} < \tau_{quasi-particle}$
- Quasi-stationary state

# Beyond exciton physics at equal times: Coupling with EM field

Hedin's eq.




**D**: Photon propagator

**P**: Transverse photon polarization

$\mathbf{p_e}$: Longitudinal polarization

Equation of motion for $L^<$ :

$$\mathcal{L}^<_T(\omega) = [1-L^{o,r}(\omega)K]^{-1} L^{o<}_{T'}(\omega)[1- K L^{0,a}(\omega)]^{-1}_{T'T''} \Pi_{T''}$$

propagation filtering excitation

**K** : $e^-$-$e^-$ collisions: common ingredient in real time simulations.
$e^-$-phonon: Renormalization of the energies and introduces a decay channel. Optional: exciton-phonon term
$e^-$-photon: interaction with light gives absorption (GW+BSE)

$\mathbf{L^{0<}}$ : Independent-particle response function, Residuals

$\mathbf{\Pi}$ : Dipoles matrix elements

# Photoluminescence Workflow