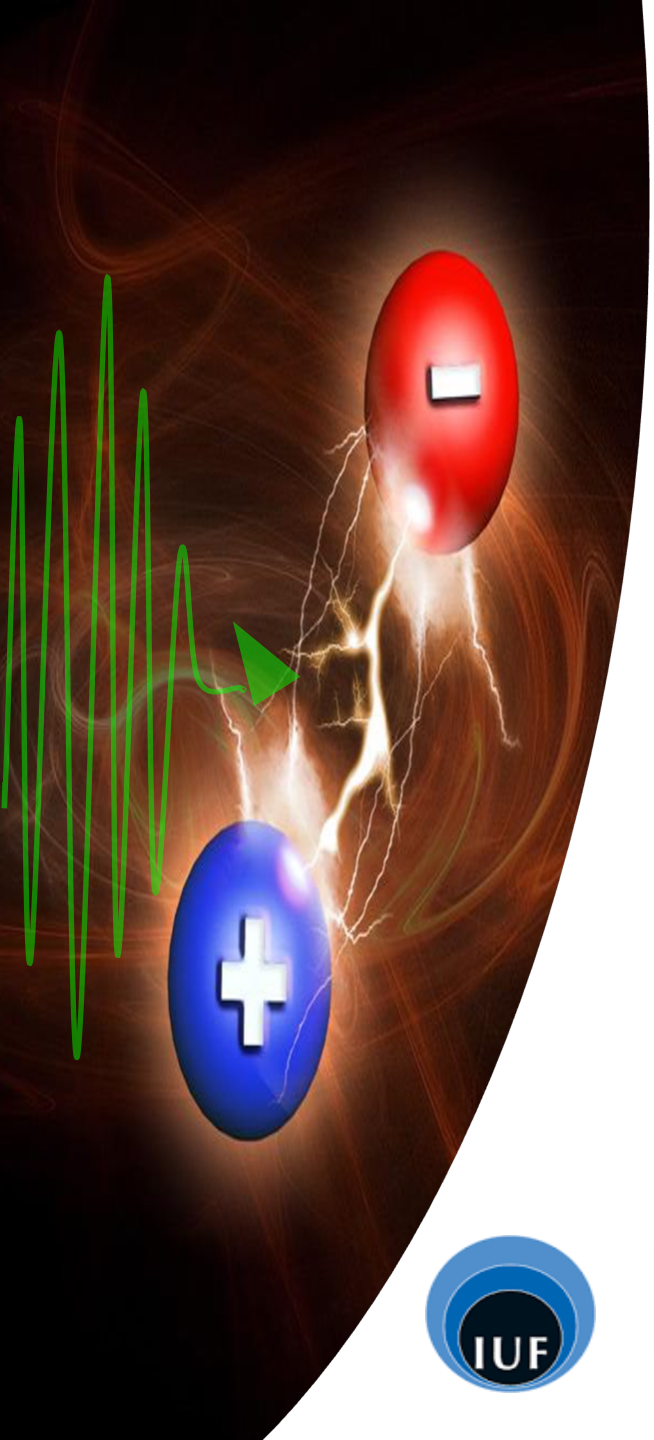

Optical Control of the Exciton Properties in Atomically Thin Semiconductors

Xavier MARIE

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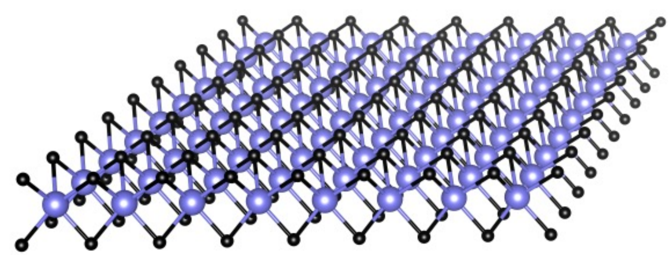
Institut National des Sciences Appliquées (CNRS-UT), Toulouse

&

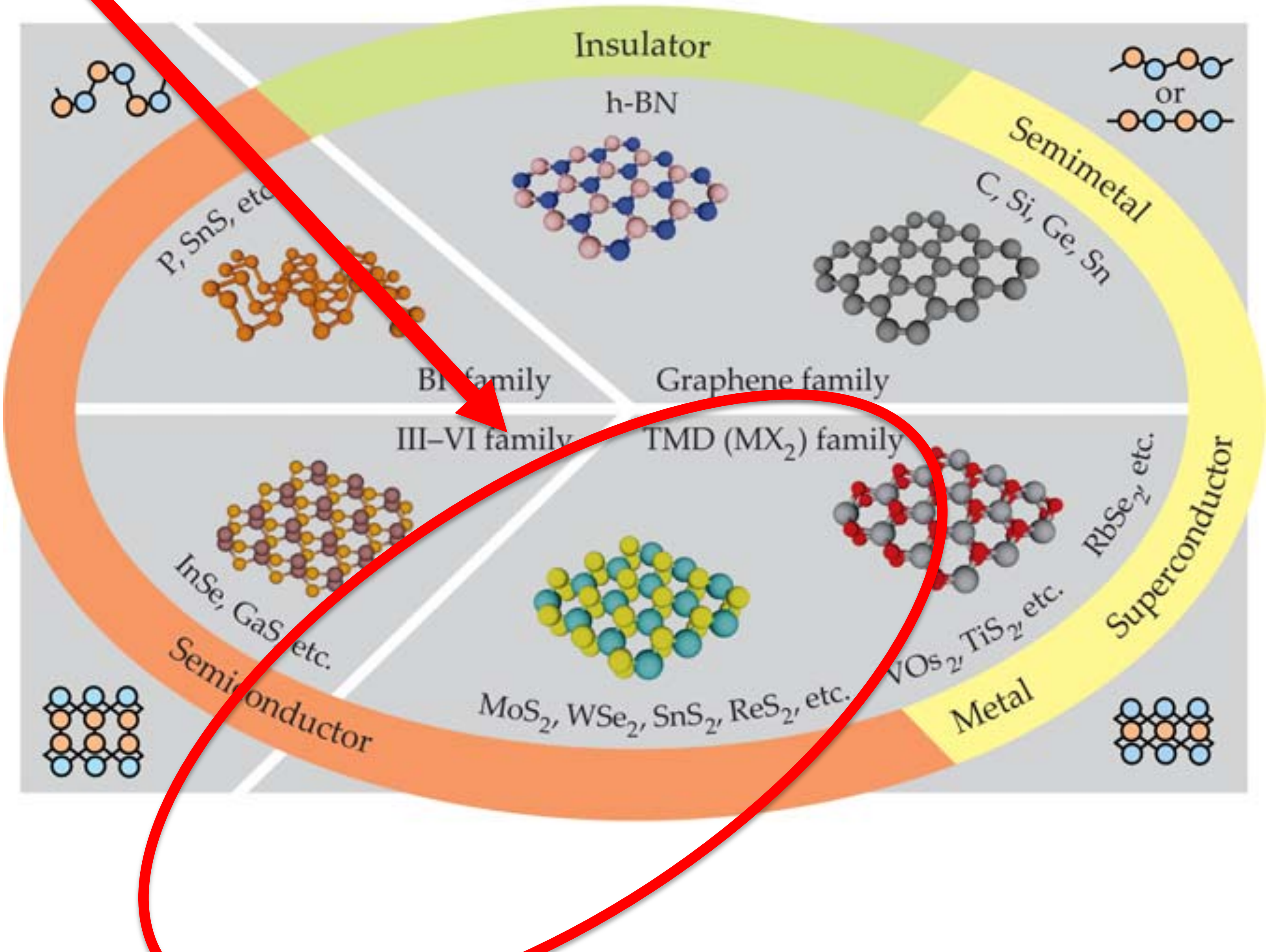
Institut Universitaire de France, Paris



ICISE, Vietnam, October 2025

Laboratoire de Physique & Chimie des Nano-Objets

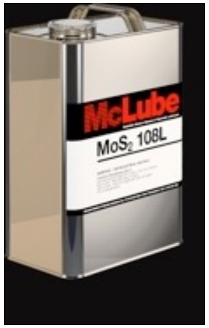
2D Materials...



Transition Metal Dichalcogenides (TMD) : MoS_2, $MoSe_2$, WS_2, WSe_2…

MoS_2 **Molybdenum disulfide :**

Natural occurance as mineral Molybdenite

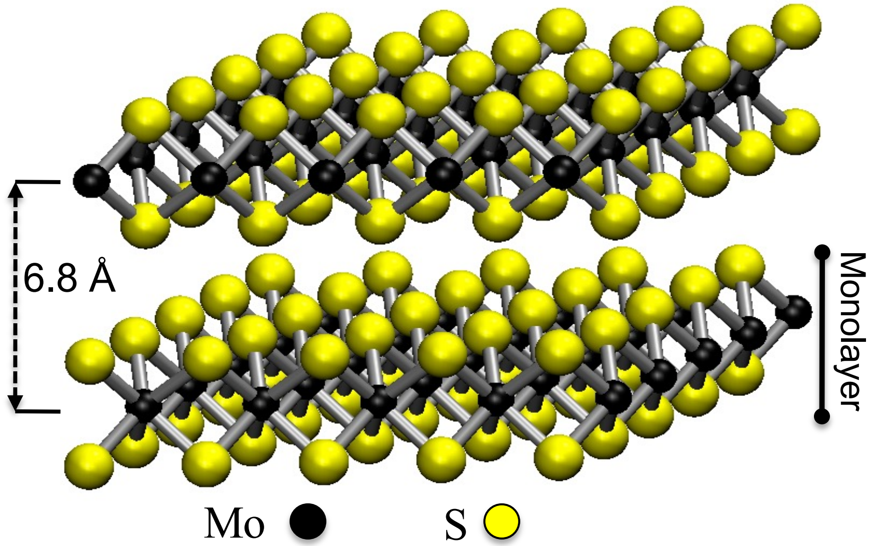


current Applications

- lubricant up to 350 °C
- Nylon, Teflon, ski wax
- catalyst in petroleum refineries

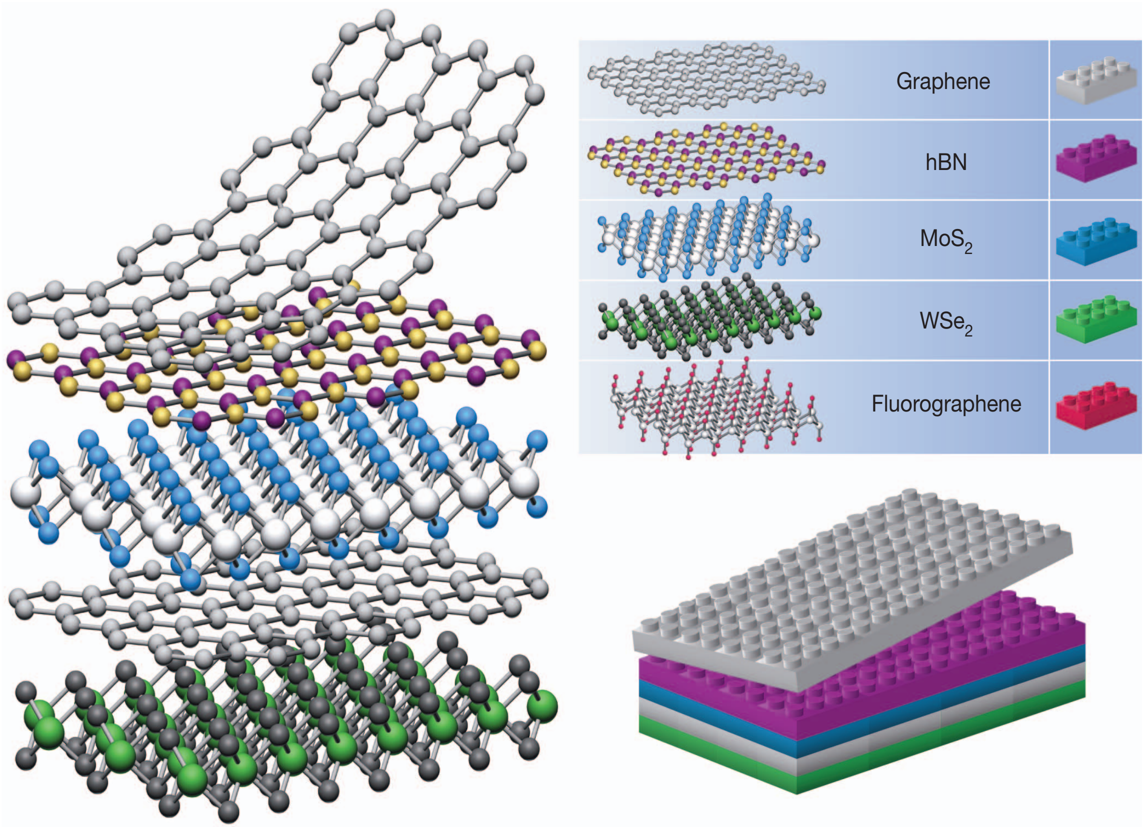
similar to graphite:

multilayers connected by van der Waals bonding



Two Two-Dimensional Materials are better than one...

Van der Waals Heterostructures



Multilayers of weakly coupled two-dimensional crystals

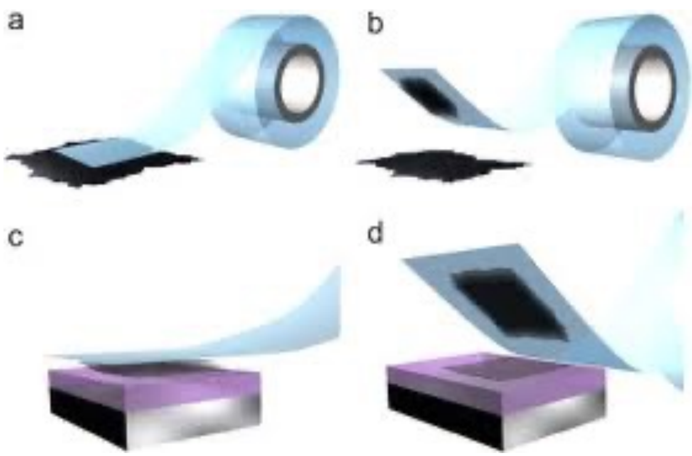
Nature **499,** 419 (2013)
Manchester

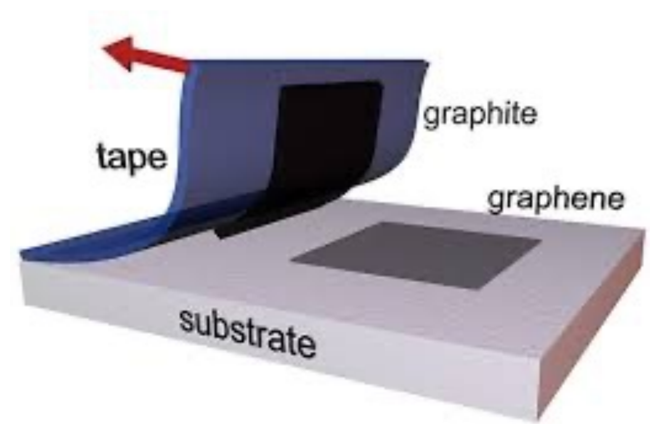
→ ***Original properties of these heterostructures with optical and electronic properties distinct from its components***

→ ***Band structure engineering***

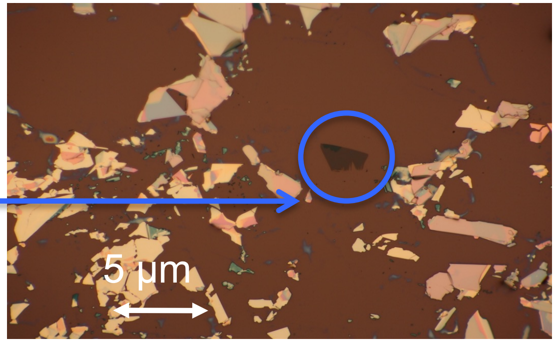
How to isolate a monolayer: *exfoliation...*

Same Procedure as Graphene
Novoselov/Geim : Nobel Prize 2010
Proc. Natl.Acad. Sci. U.S.A **102**, 1045 (2005).



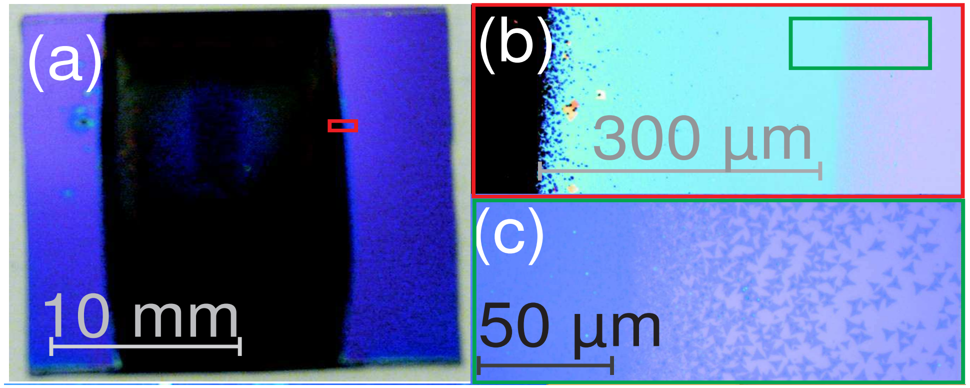


'*scotch tape method*' works for:
- Graphene
- MoS_2 monolayers
- ….



Growth of TMD monolayers

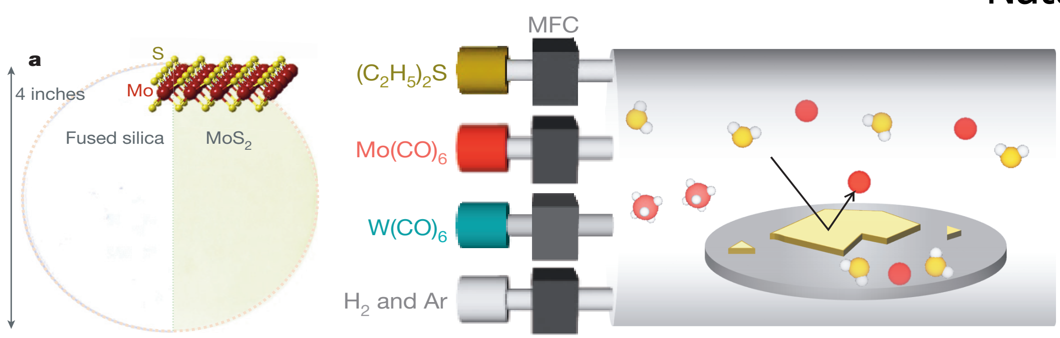
CVD



Nanolett. **14**, 3185 (2014); Berkeley
SST **29** 064008 (2014);
Riverside&Regensburg

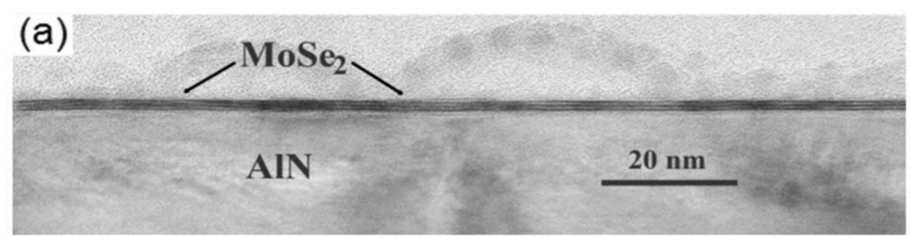
MOCVD

Nature **656,** 14417 (2015)
Cornell

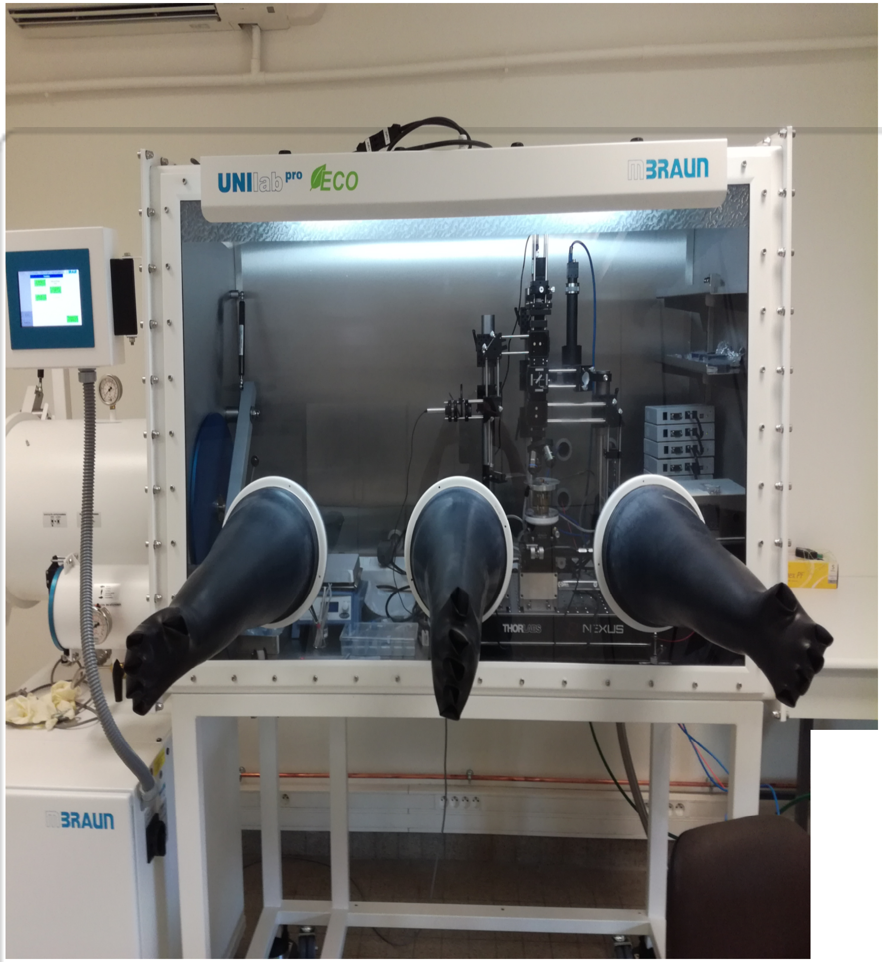


MBE

Nanoscale **7**, 7896 (2015) ; Athens&Leuven
ACS Nano **12**, 2319 (2018) ; Grenoble
APL **125**, 053102 (2024); Grenoble&Toulouse

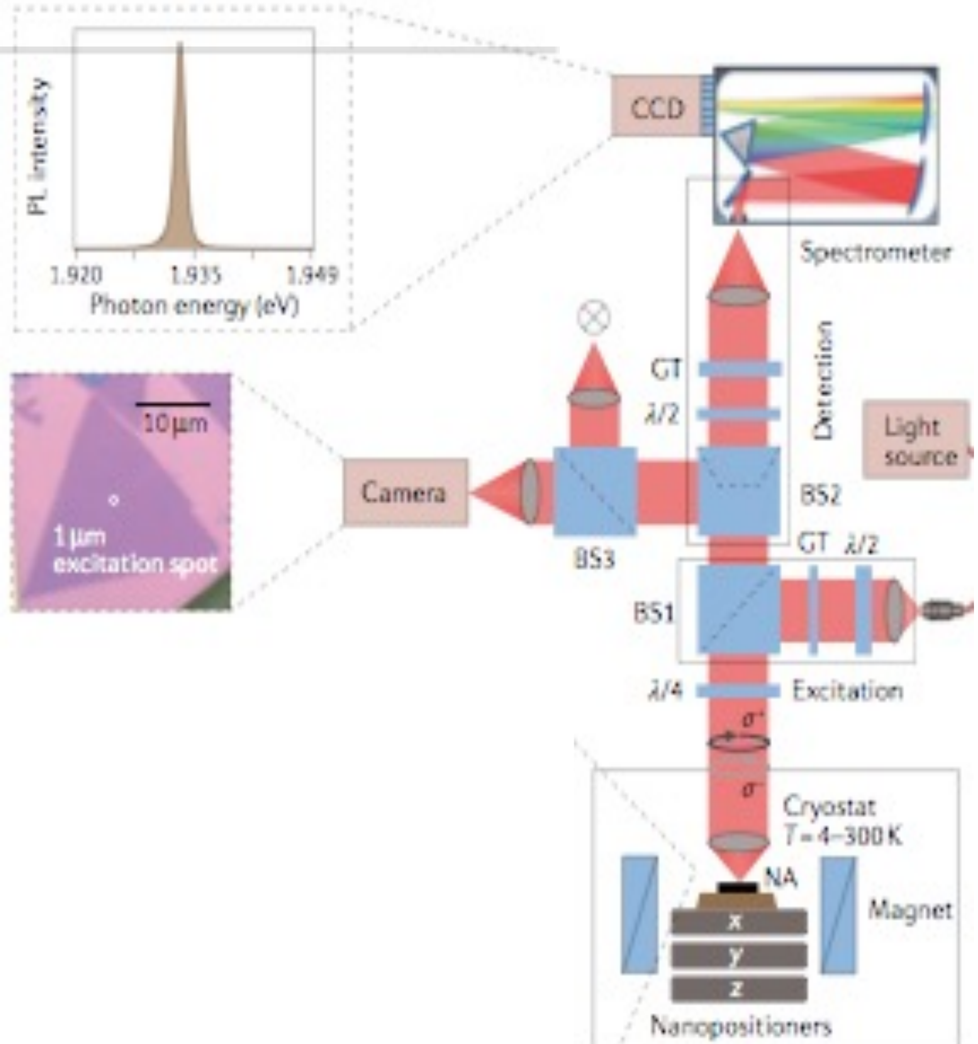


Fabrication and Micro-Photoluminescence Spectroscopy



Exfoliation and transfer

2D Materials **1**, 011002 (2014);
Delft

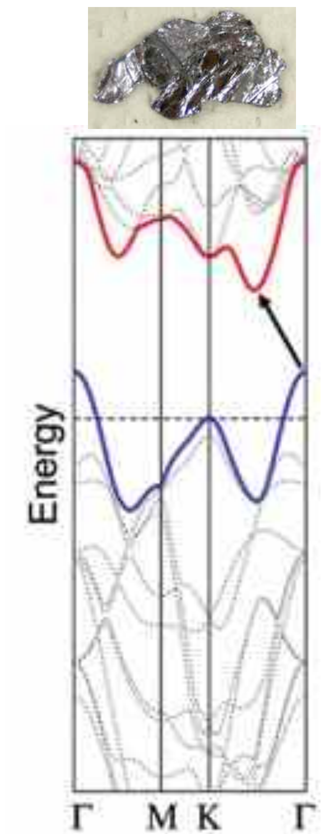


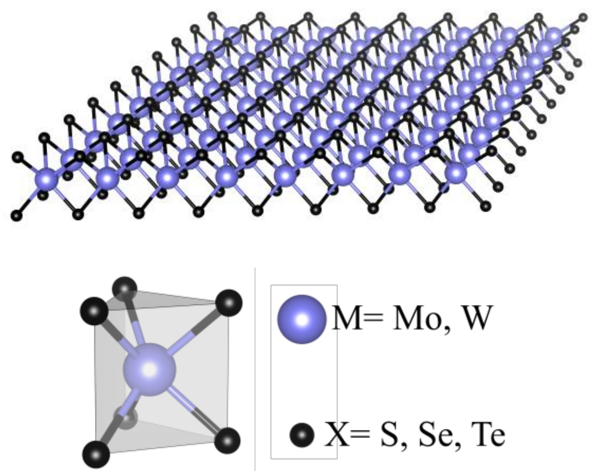
Nature Reviews Physics **3**, 39 (2021);
Toulouse

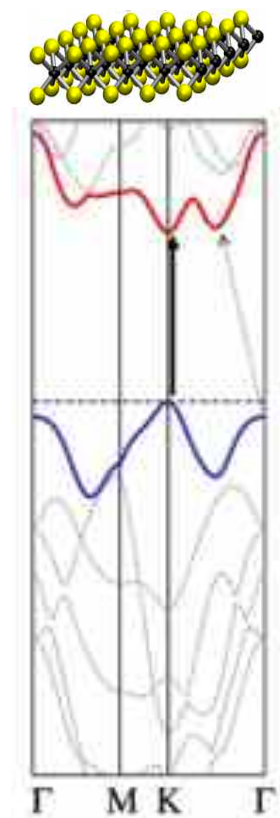
MX_2 monolayers : strong interaction with light

~15% absorption of light for a monolayer

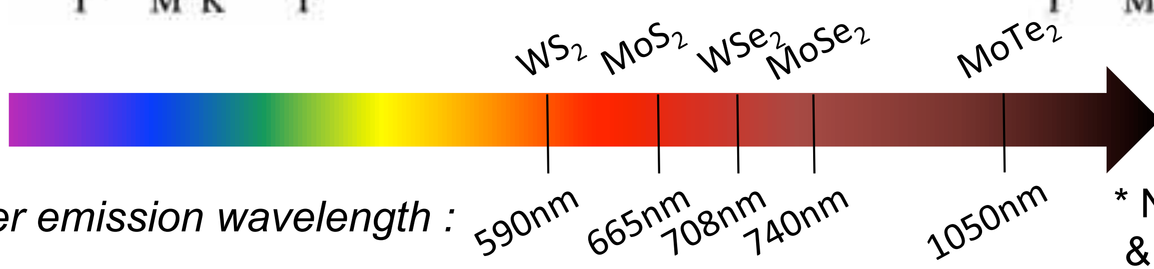
bulk **indirect** band gap → monolayer : **direct** band gap at K points*







Monolayer emission wavelength :

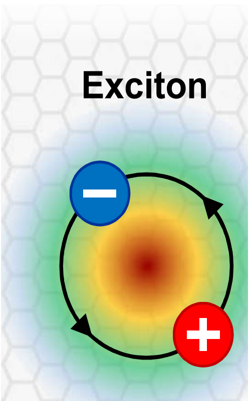


* Nano Lett.**10**, (2010); **Berkeley**
& PRL **105**, (2010); **Columbia**

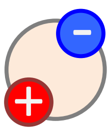
Optical properties governed by robust 2D excitons

MX_2 monolayers – common properties : strong interaction with light

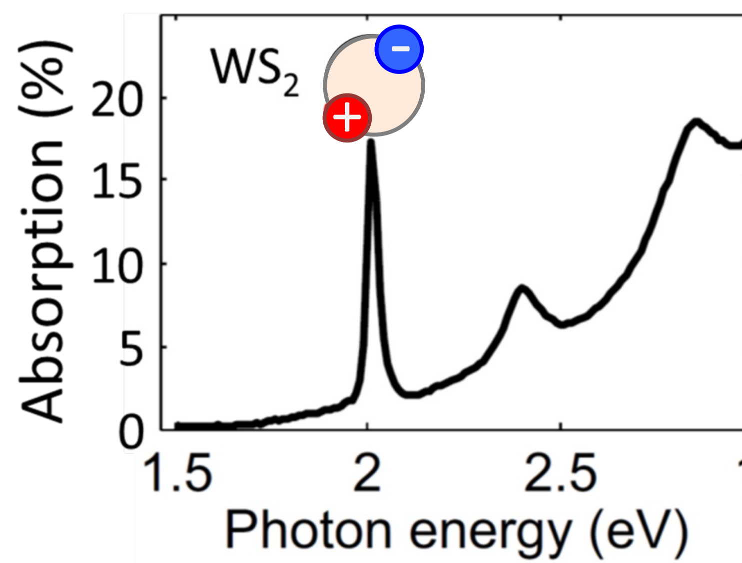
~15% absorption of light for a monolayer !



Material	Binding energy **E_B**
1 ML WSe_2	~ 200-500 meV*
ZnO	60 meV
GaAs QW	~10 meV

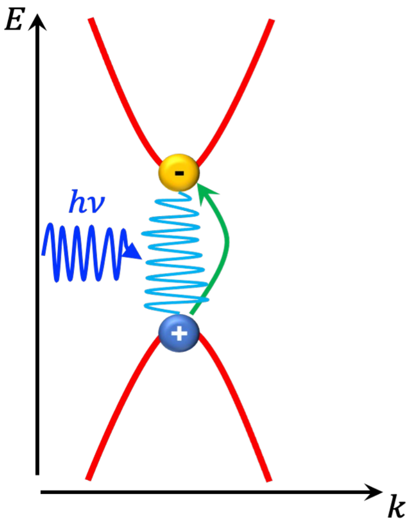


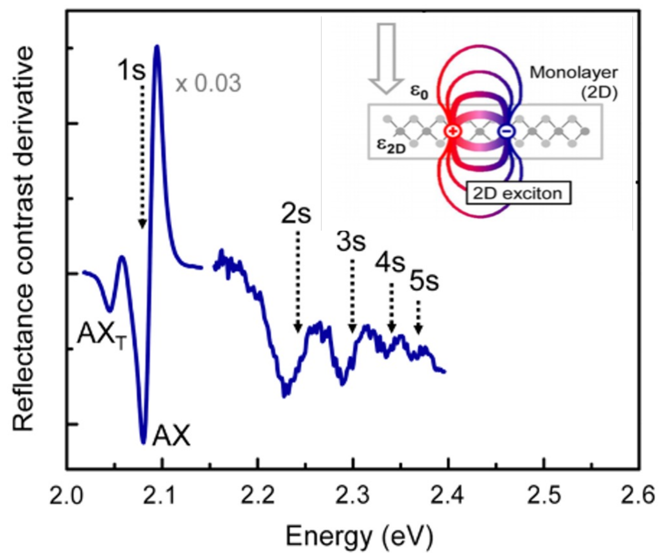
Exciton = bound electron-hole pair



* PRL 120, 057405 (2018) ;Nature Com. **10**, 4172 (2019) ;
Los Alamos - Toulouse

Exciton binding energy and Rydberg states





Strong Coulomb Interaction :

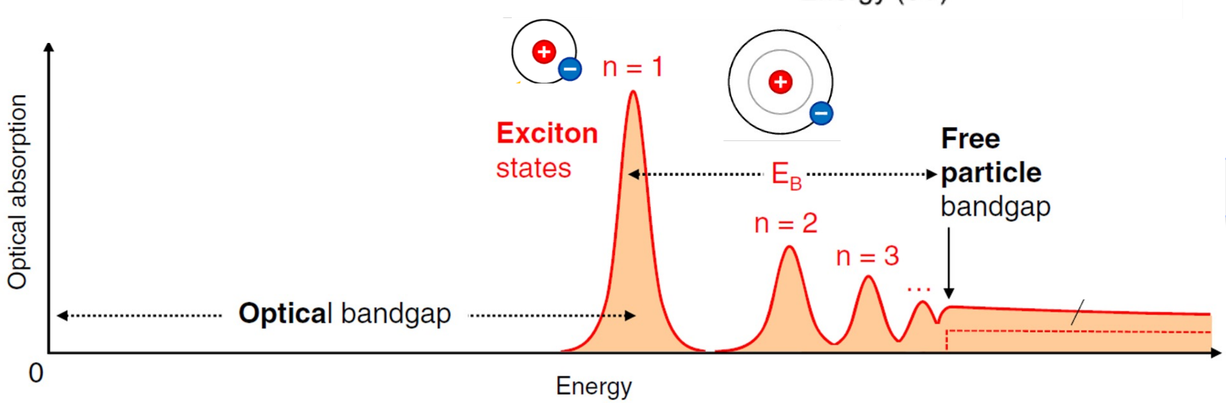
Exciton binding energy

$$E_B = 500\,meV$$

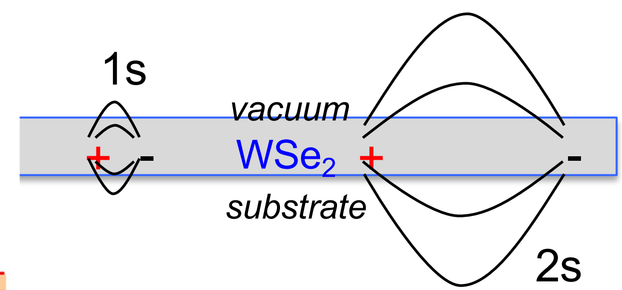
2D confinement

weak dielectric screening

large effective mass



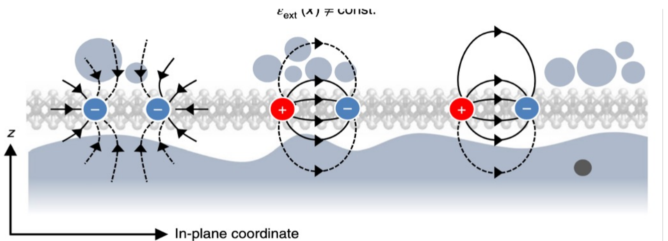
dielectric (anti-) screening



Review of Modern Physics **90**, 021001 (2018)

Toulouse-Regensburg-St Petersburg-Stanford

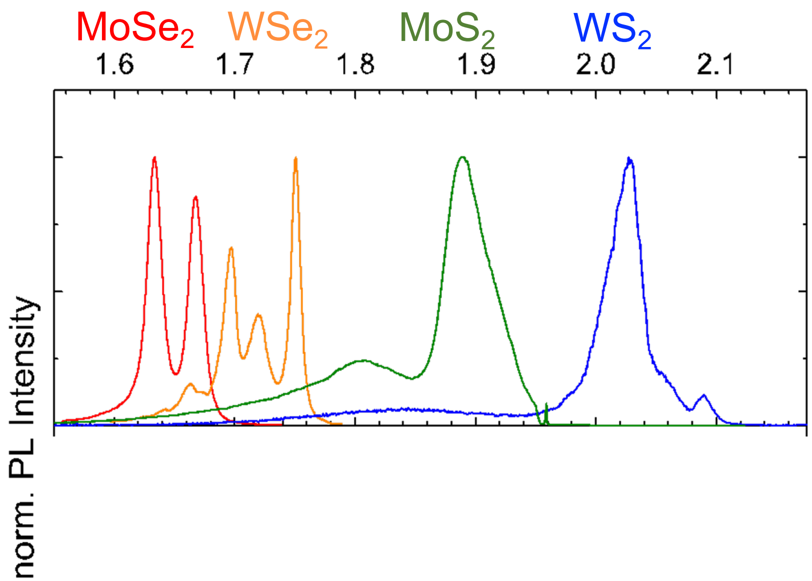
Dielectric disorder and effect of hBN encapsulation

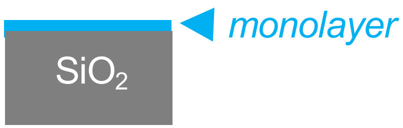


Nature Nano **14**, 832 (2019), Regensburg

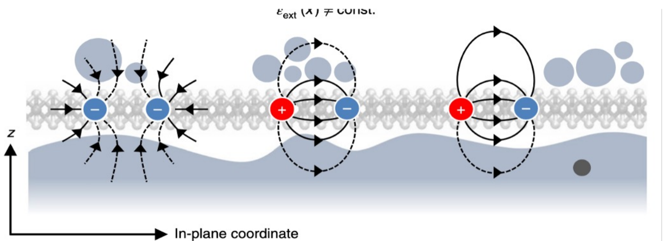
- Substrate roughness
- Charged traps
- Adsorbed molecules…

Photoluminescence



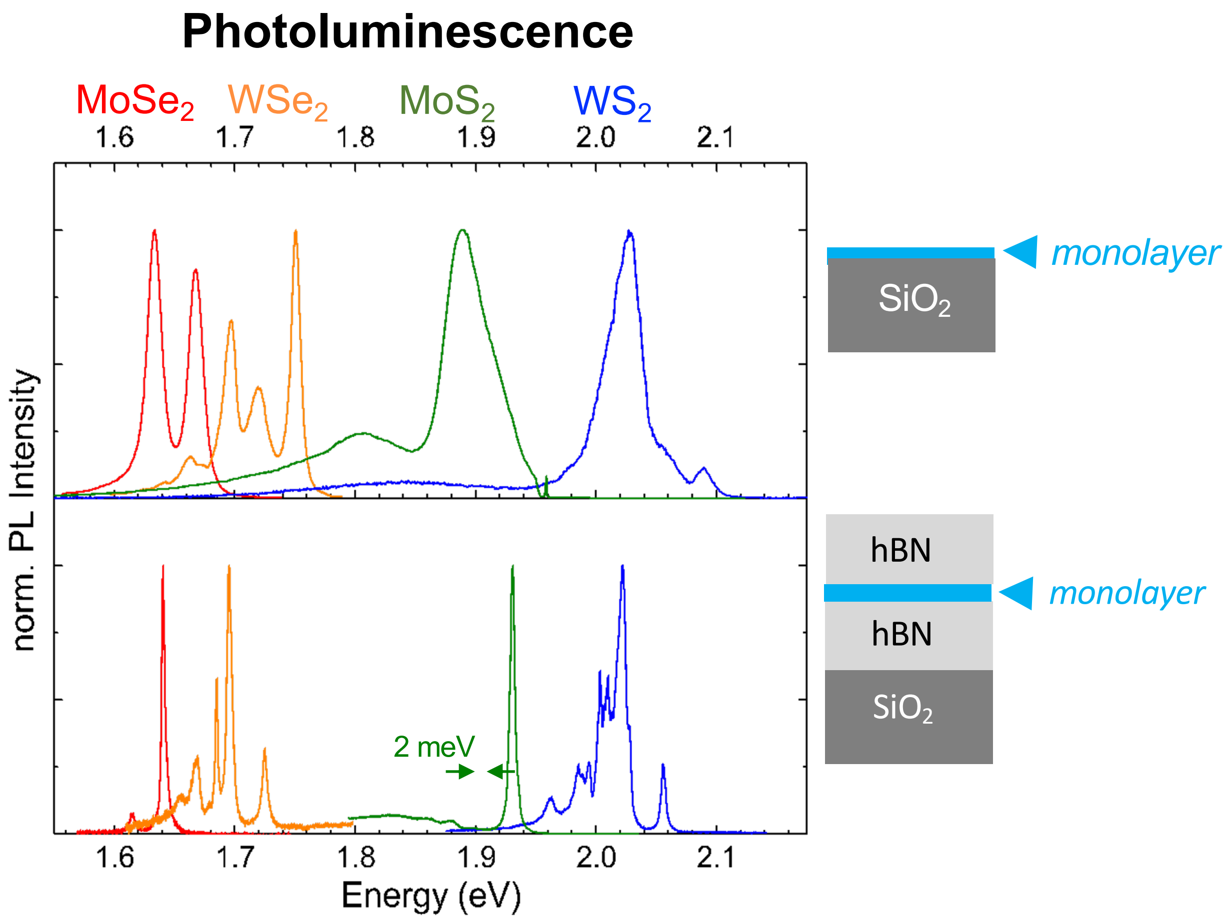


Dielectric disorder and effect of hBN encapsulation



Nature Nano **14**, 832 (2019), Regensburg

- Substrate roughness
- Charged traps
- Adsorbed molecules…

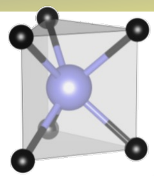


PRX **7,** 021026 (2017); Toulouse
Nature Com. **8**, 14927 (2017)
Toulouse-St-Petersburg
Nature Nano **15**, 283 (2020) ;
Strasbourg - Toulouse

Linewidth: 1- 4 meV
→ close to homogeneous broadening

See also: Berkeley, Columbia, Regensburg, Seatle, ETH, Dresden, Stanford, Grenoble, Barcelona…

Spin and valley degrees of freedom



- Broken inversion symmetry
- Strong Spin-Orbit coupling

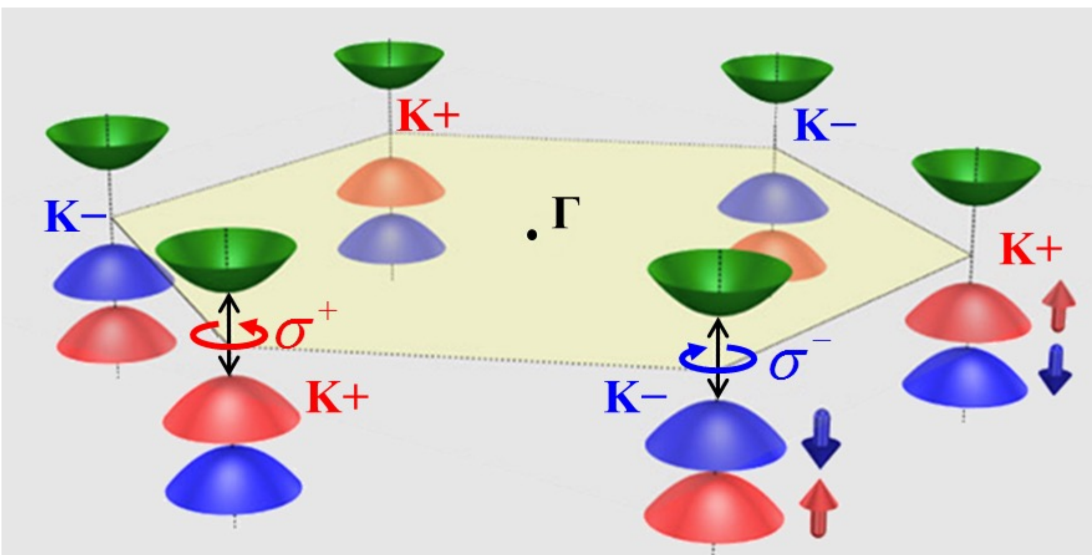
→

Chiral Interband Selection Rules σ^+/σ^-

→

Initializing and detecting ***valley index*** ***& spin*** with polarized light

2D hexagonal Brillouin zone



Time reversal symmetry
→ ***Spin splitting at different K valleys is opposite***

Theory: Phys. Rev. Lett. (2012) **Seattle**

Experiments: Nature Nano. (2012) **Columbia**
Nature Com. (2012) **Beijing**
Phys. Rev. B (2012) **Toulouse**

Outline…

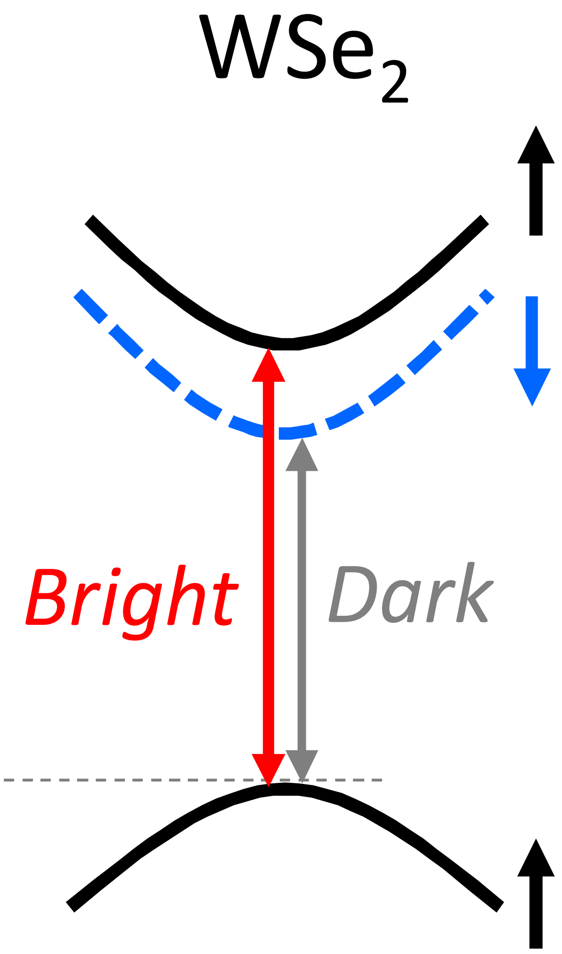
- ***Bright and Dark excitons***
- ***Control of the Excitons radiative lifetime***
- ***Control of the Bright-Dark splitting***

Bright and dark excitons…

	Δ_{SO}^{VB}	Δ_{SO}^{CB}
MoS_2	147meV	3meV
$MoSe_2$	186meV	21meV
$MoTe_2$	214meV	27meV
WS_2	433meV	-27meV
WSe_2	463meV	-38meV

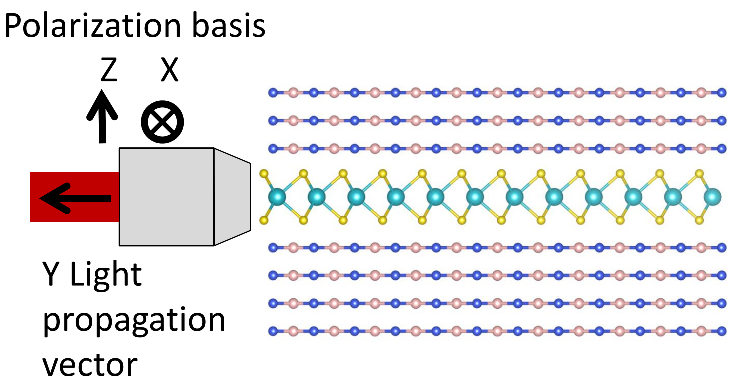
DFT calculation
ARPES measureme

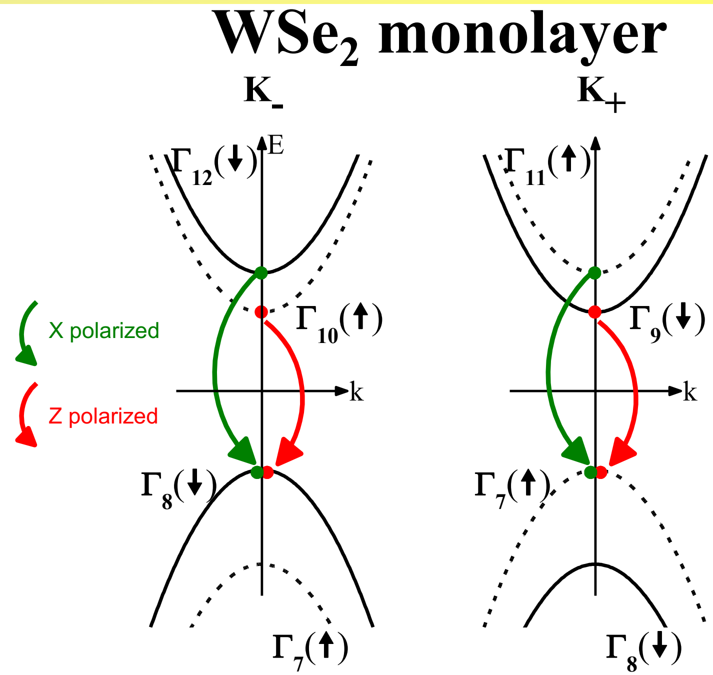
PRB **88**, 245436 (2013)

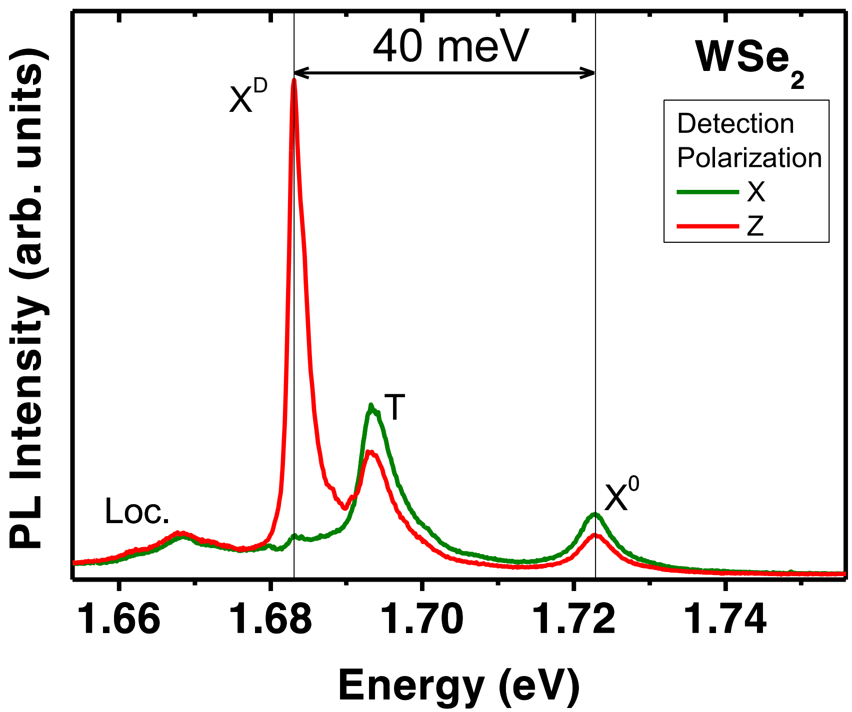


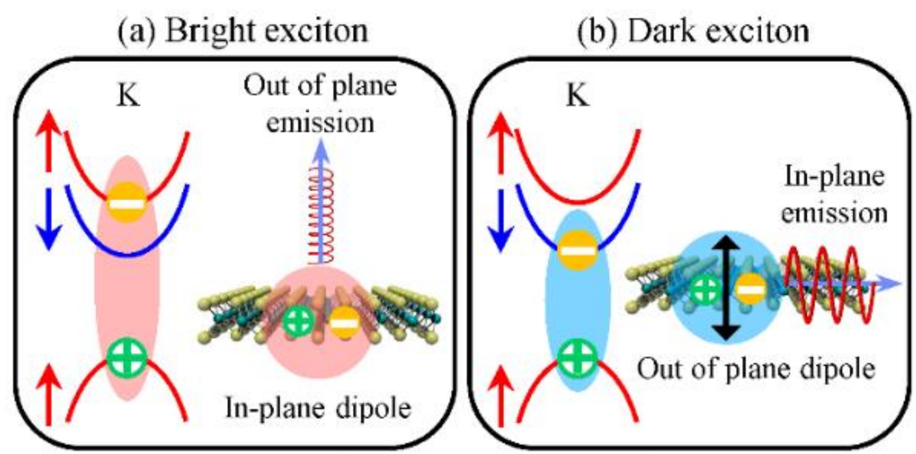
→ **Bright and dark (spin-forbidden) excitons**

Optical selection rules : in-plane propagation of light



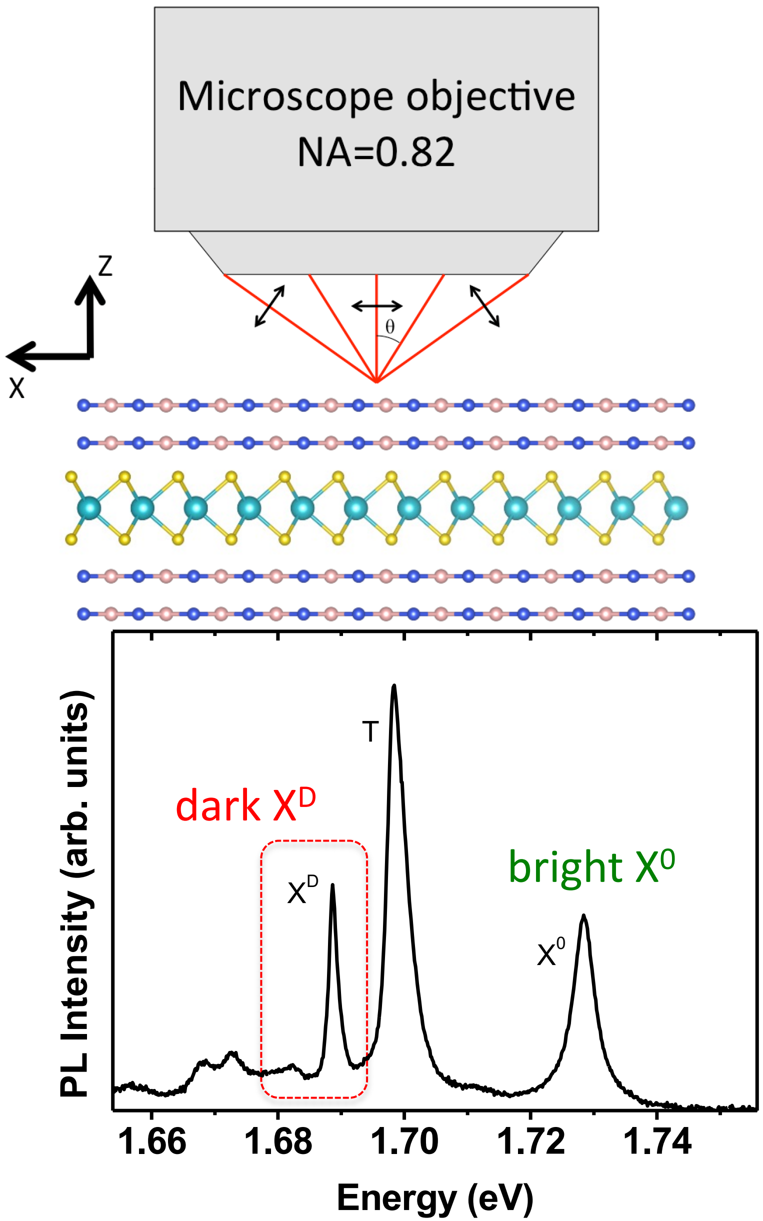


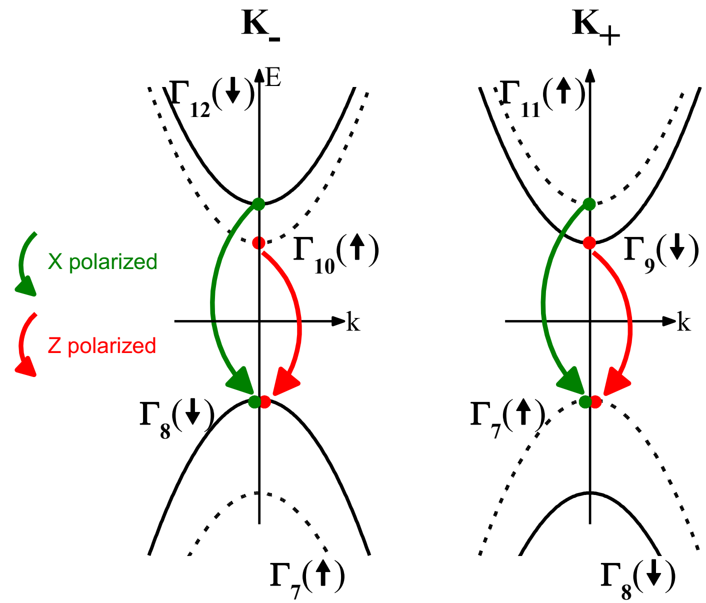




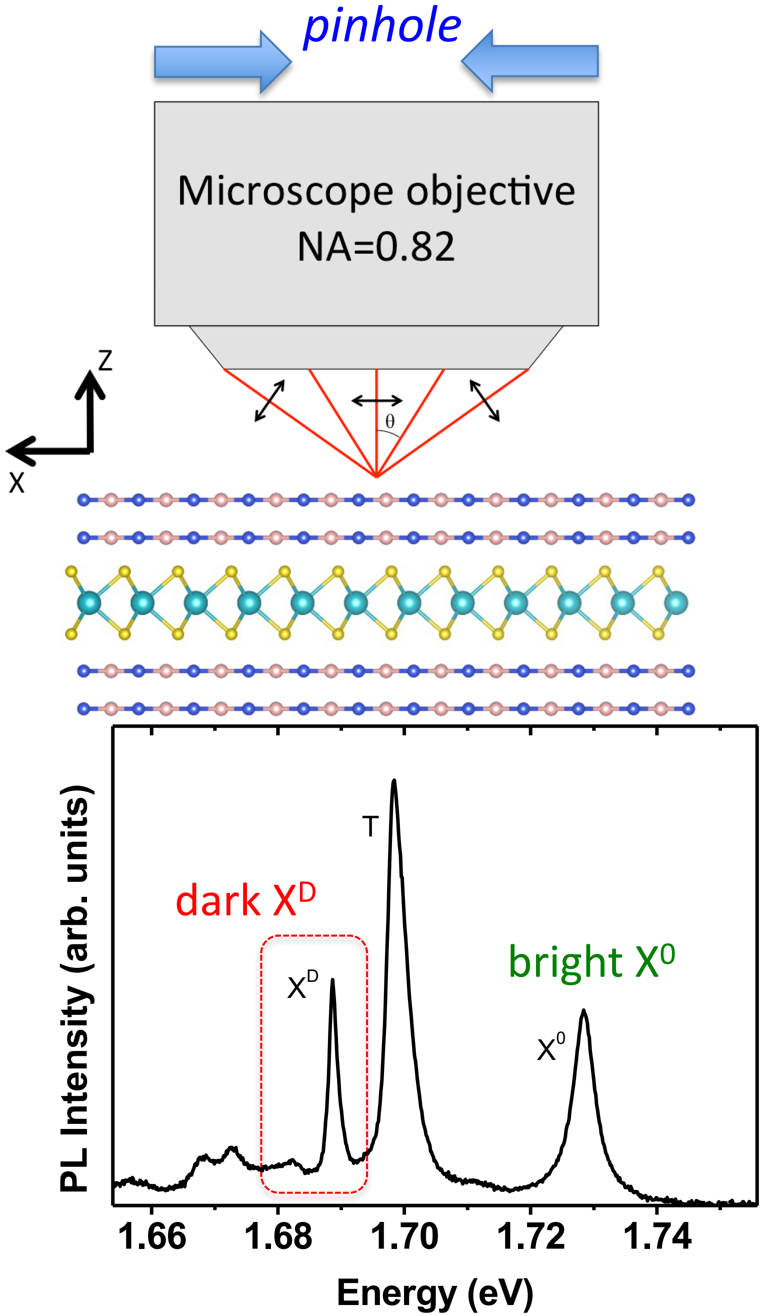
PRL **119**, 047401 (2017); Toulouse- St Petersburg

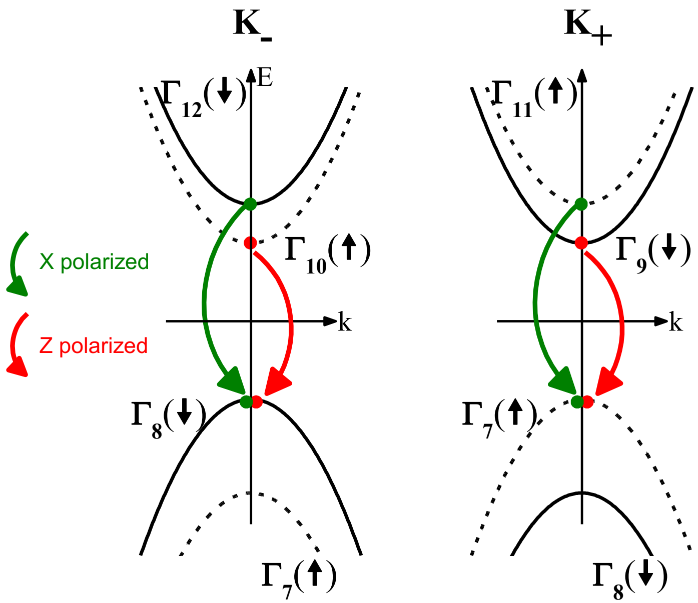
« Dark » exciton transition in classical geometry



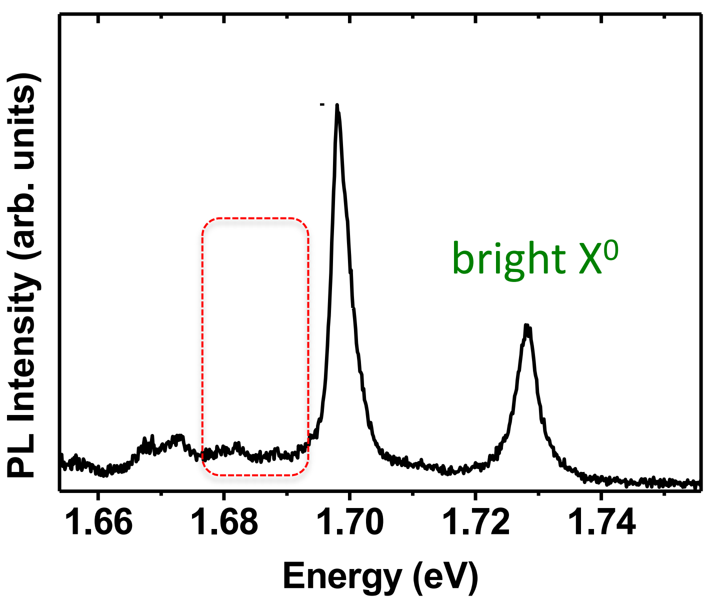


« Dark » exciton transition in classical geometry



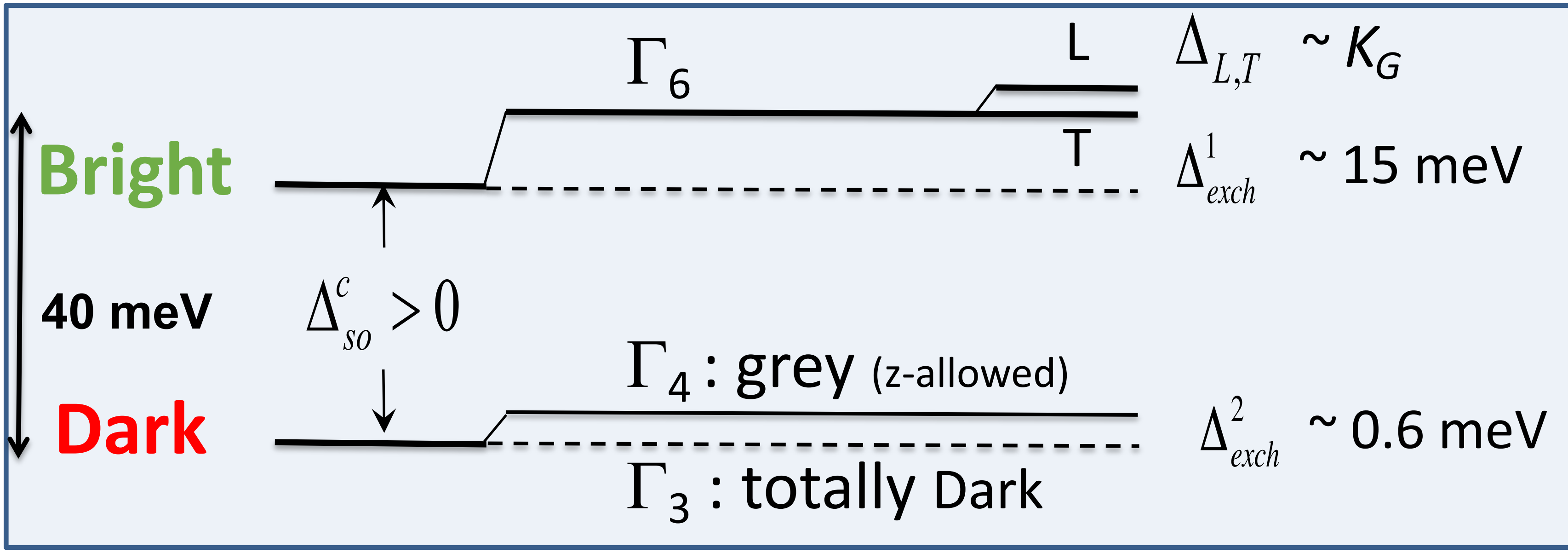


Pinhole almost CLOSED



Exciton fine structure in WSe_2 monolayer

D_{3h} point symmetry group



→ **Bright-dark exciton splitting governed by CB spin-orbit splitting and exchange interaction**

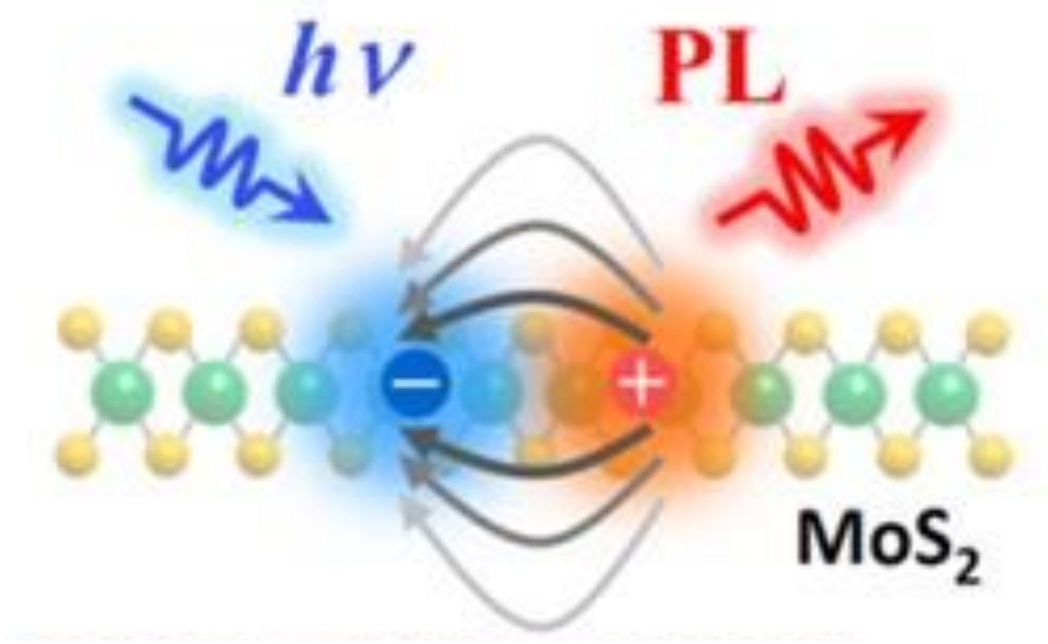
Outline…

- ***Bright and Dark excitons***
- ***Control of the exciton radiative lifetime***
- ***Control of the Bright-Dark splitting***

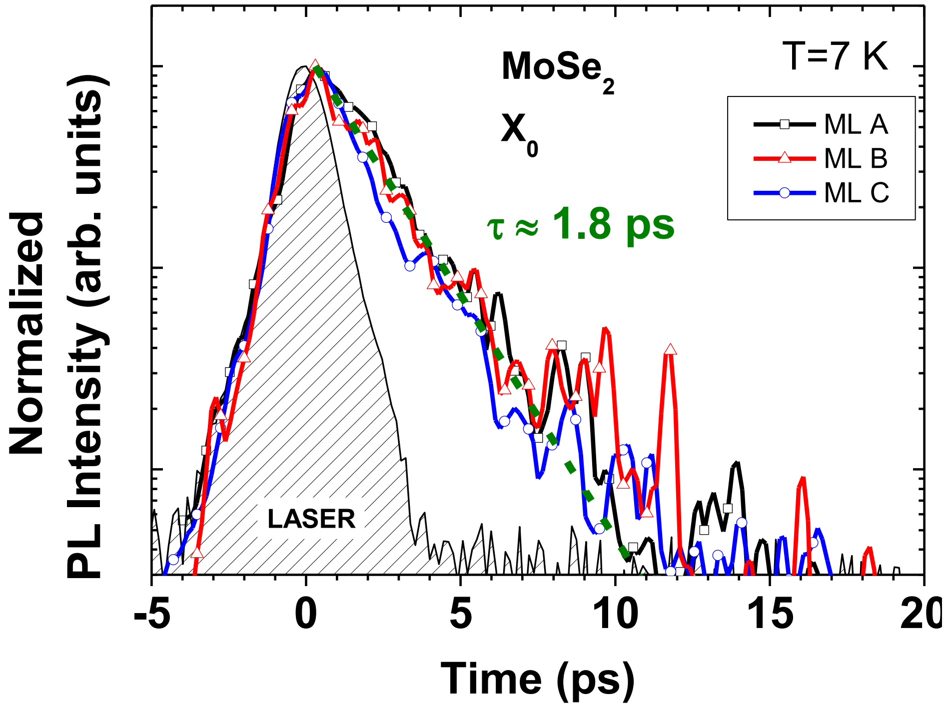
Exciton lifetime probed by time-resolved photoluminescence

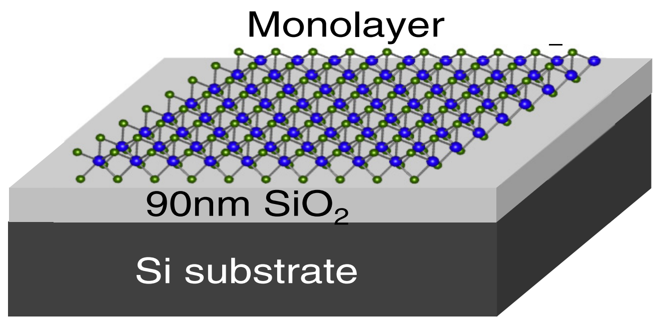
Laser: 1 ps pulse

Detection: Synchro-scan streak camera
Time-resolution : ~1 ps



Short exciton radiative lifetime





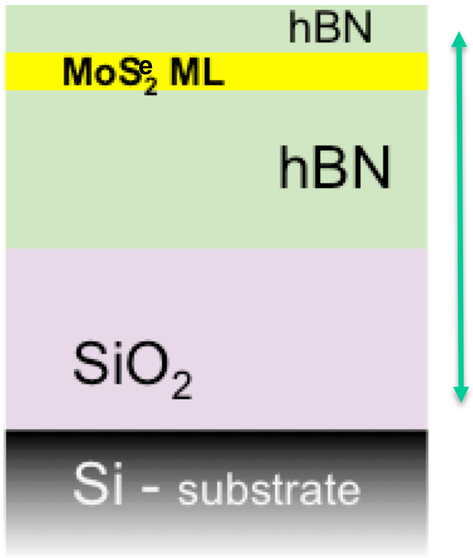
APL 99, 102109 (2011), Regensburg
PRL 112, 047401 (2014), Toulouse – Beijing
PRB 93, 205423 (2016) ; Toulouse

→ Exciton radiative lifetime : $\tau_{rad}^{0} \sim 2$ ps

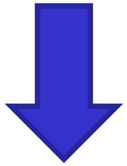
Calculations :
PRB **93**, 045407 (2016); Cornell
Nano Lett. **15**, 2794 (2015); MIT-Berkeley-Roma
τ_{rad} **~ ps**

→ *MoS2 atomically thin mirror*, PRL **120**, 037401 (2018); ETH Zurich

Exciton radiative lifetime, influence of hBN and cavity



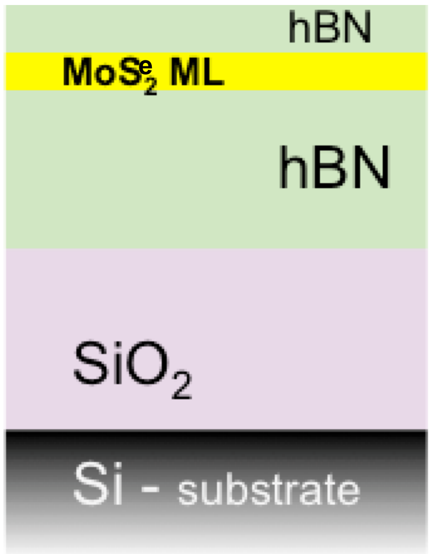
Cavity



Enhancement or inhibition of spontaneous emission (**Purcell effect**)

PR. **69**, 681 (1946) - Purcell
J. Lum. **1,** 693 (1970) ; Drexhage
PRL **58**, 666 (1987) - Haroche

Exciton radiative lifetime, influence of hBN and cavity

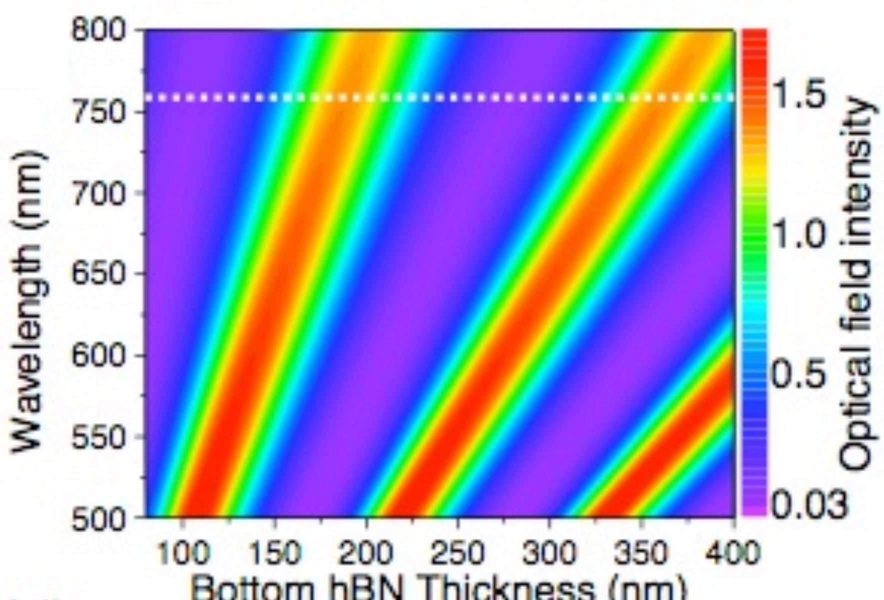


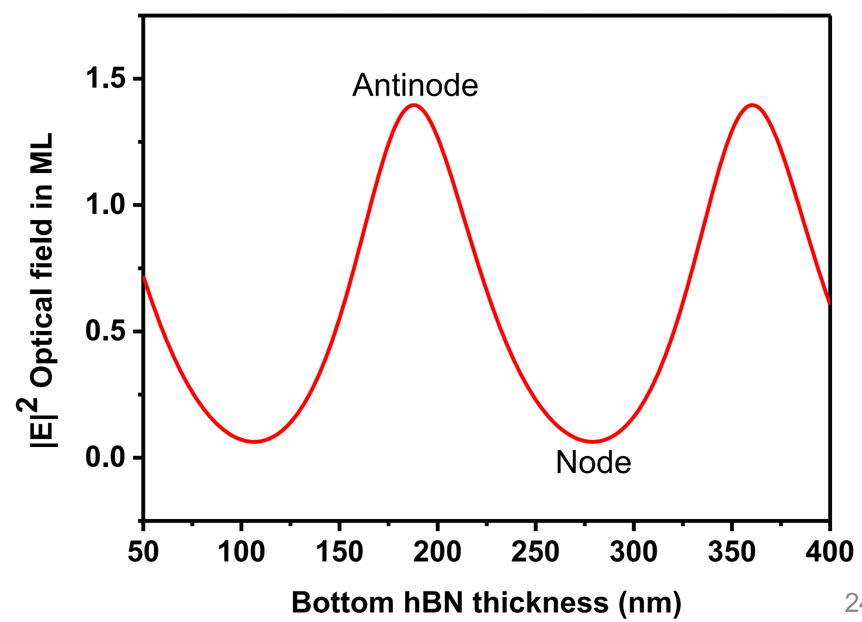
Cavity

PR. **69**, 681 (1946) - Purcell
J. Lum. **1,** 693 (1970) ; Drexhage
PRL **58**, 666 (1987) - Haroche

Enhancement or inhibition of spontaneous emission (**Purcell effect**)

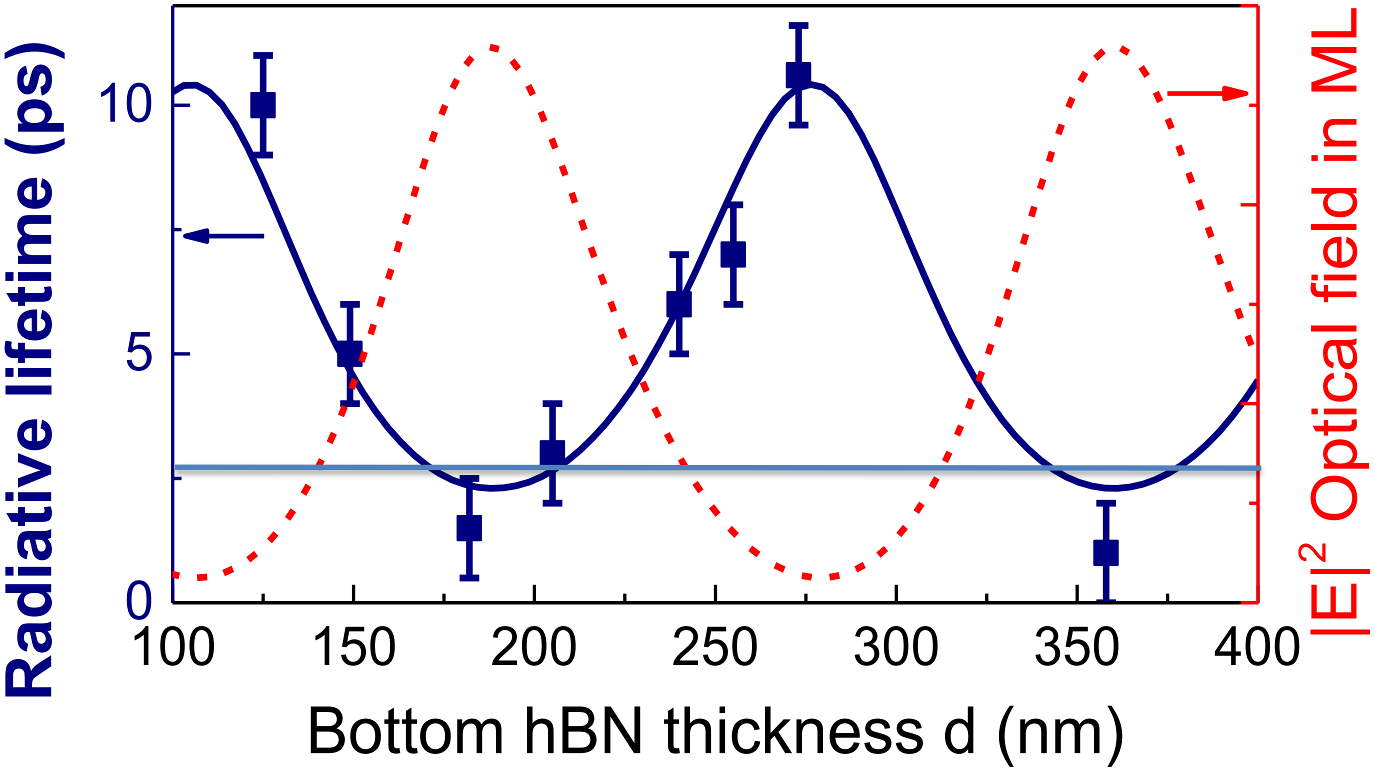
Transfer matrix simulation

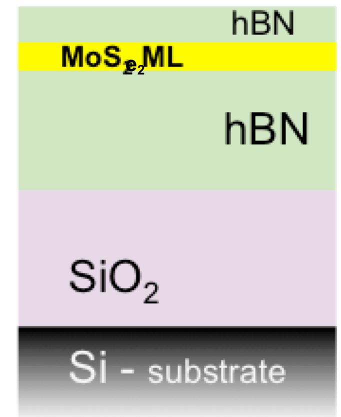




Control of the 2D exciton radiative lifetime

Purcell effect





Fitting parameter :
Vacuum radiative lifetime : 2.7 ps

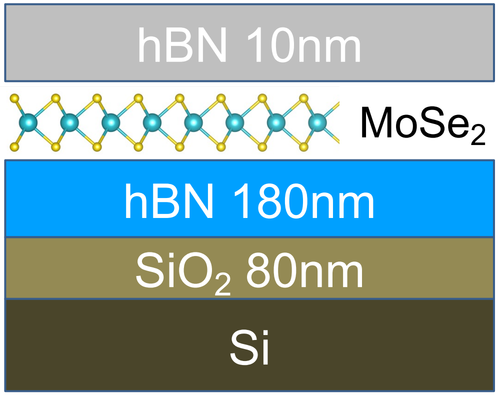
PRL **123**, 067401 (2019) ;
Toulouse/St-Petersburg

Similar results :
PRL **124**, 027401 (2020); Harvard
Phys. Rev. Res. **2**, 012029(R) (2020); Stanford

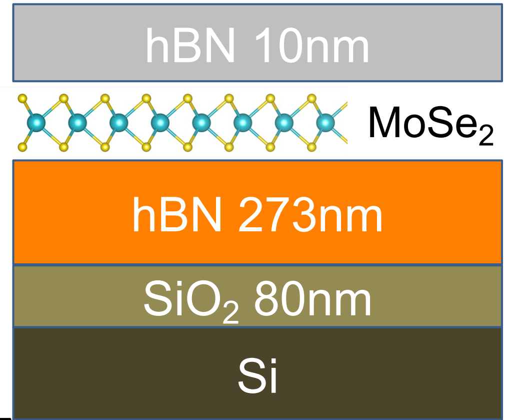
Control of the exciton radiative lifetime : ~ 1 – 10 ps

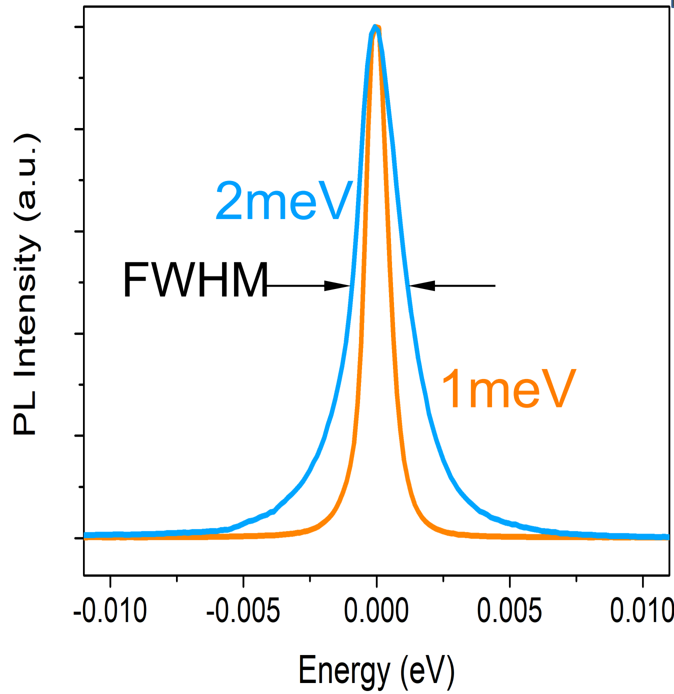
Control of the 2D exciton linewidth

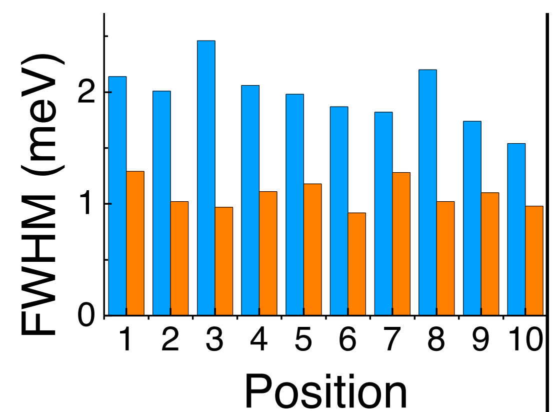
Sample I: ML at antinode



Sample II: ML at node







Cw Photoluminescence spectra

$$\Gamma_{exp} = \Gamma_r + \Gamma_{nr} = \Gamma_r^{vac}\left(1 + r\cos(2qd')\right) + \Gamma_{nr}$$

$$q = \frac{\omega}{c}$$

Outline…

- ***Bright and Dark excitons***
- ***Control of the Excitons radiative lifetime***
- ***Control of the Bright-Dark splitting***

Exciton Lamb shift ?

Lamb shift:

Lamb, Retherford, Phys. Rev. **72**, 241 (1947); Columbia

Virtual emission and re-absorption of a photon ⇒ Transition energy shift δE ($\delta E \propto$ oscillator strength)

Ivchenko, *Optical Spectroscopy of Semiconductor Nanostructures (2005)*
Combescot, Dubin, Shiau, EPL **138**, 36002 (2022)

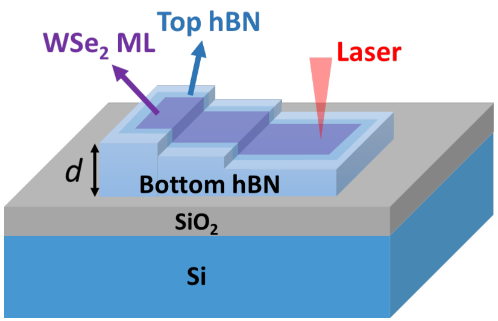
Exciton Lamb shift ?

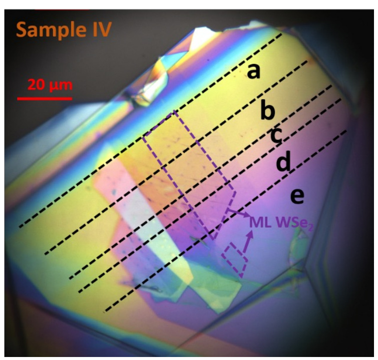
Lamb shift:

Lamb, Retherford, Phys. Rev. **72**, 241 (1947); Columbia

Virtual emission and re-absorption of a photon → Transition energy shift δE ($\delta E \propto$ oscillator strength)

Ivchenko, *Optical Spectroscopy of Semiconductor Nanostructures (2005); St Petersburg*
Combescot, Dubin, Shiau, EPL **138**, 36002 (2022); Paris

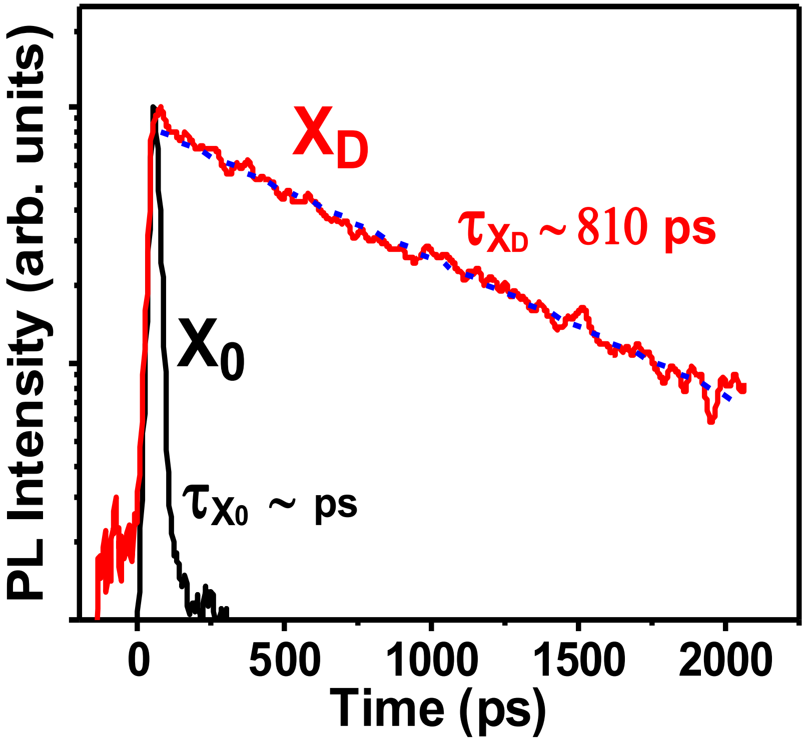




What about the Lamb shift on dark and bright excitons ?

Dark exciton : z-polarized and small oscillator strength

Time Resolved Photoluminescence of WSe_2 ML

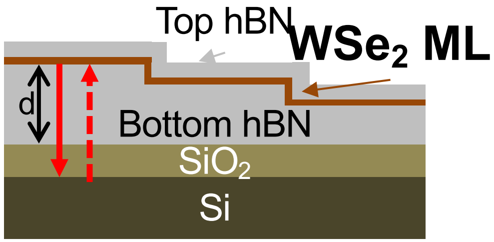


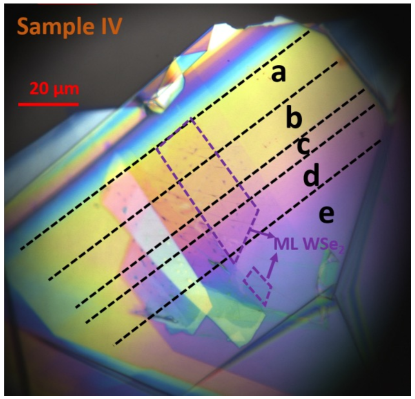
→ Dark exciton z-polarized

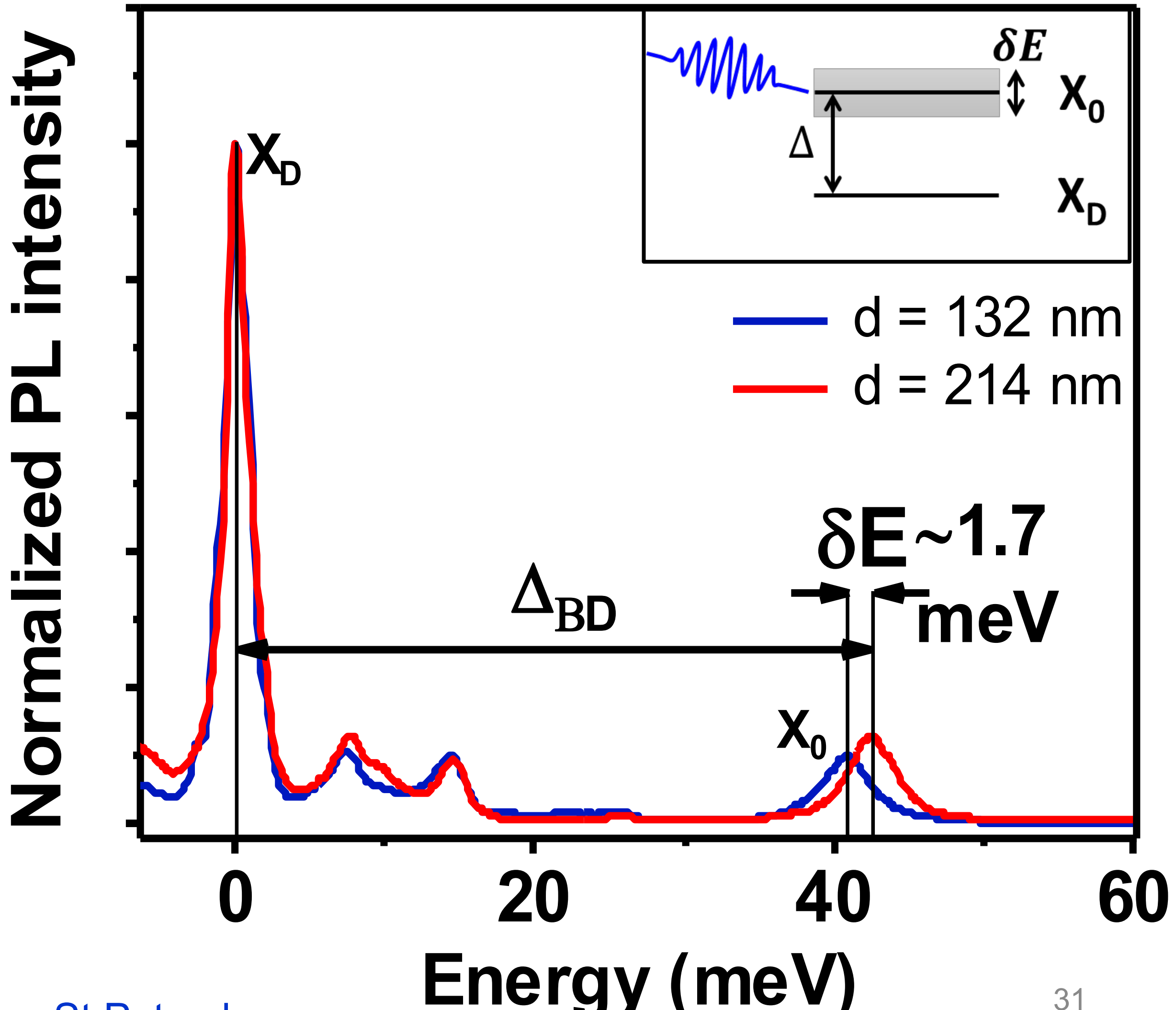
→ Oscillator strength 1000x smaller than the bright one

Dark exciton:
negligible Lamb shift

Lamb shift in WSe_2 monolayer ?





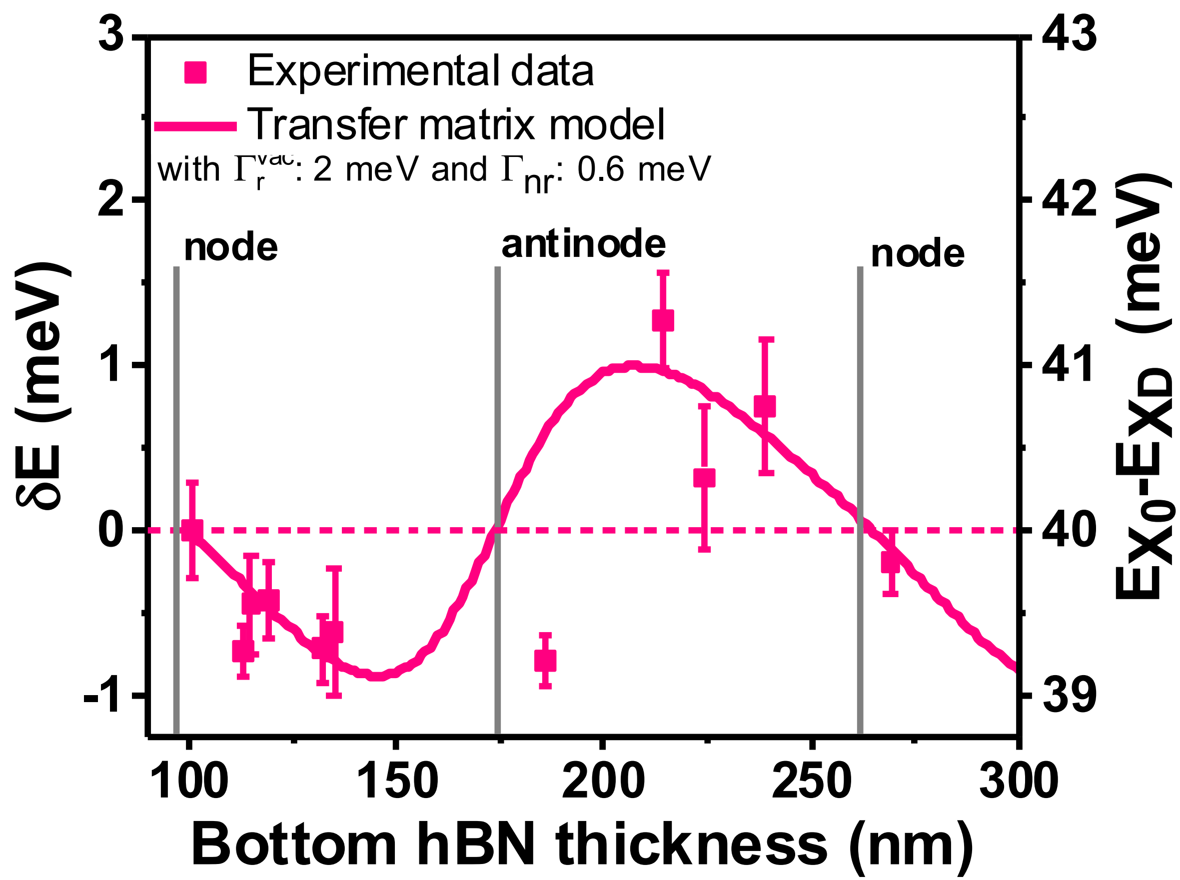


PRL **131**, 116901 (2023) ; Toulouse- St Petersburg

Control of the bright-dark splitting using Lamb shift

X_0 - X_D splitting shift

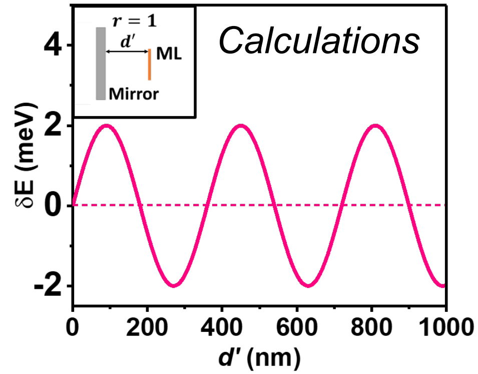
PRL **131**, 116901 (2023) ; Toulouse- St Petersburg

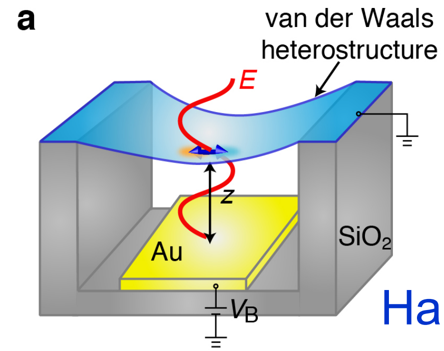


Variation of the exciton bright- dark splitting

→ **2D excitons : sensitive probes of vacuum fluctuations of electromagnetic field**

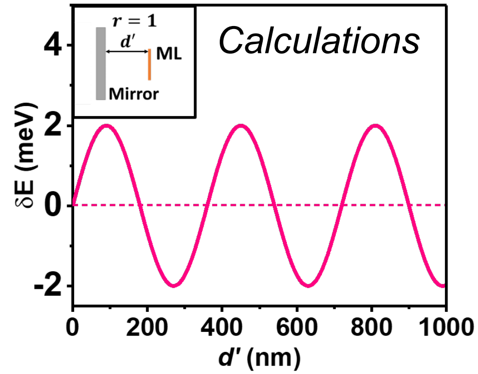
- Control of the bright-dark exciton splitting in TMDs **with an external mirror (r=1)**

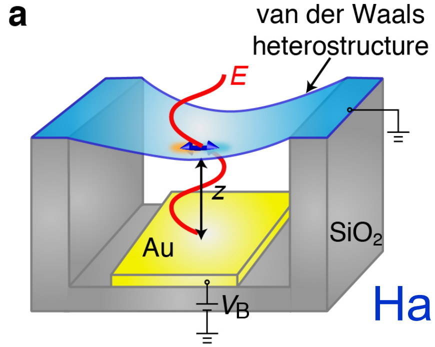




Harvard

- Control of the bright-dark exciton splitting in TMDs **with an external mirror (r=1)**





Harvard

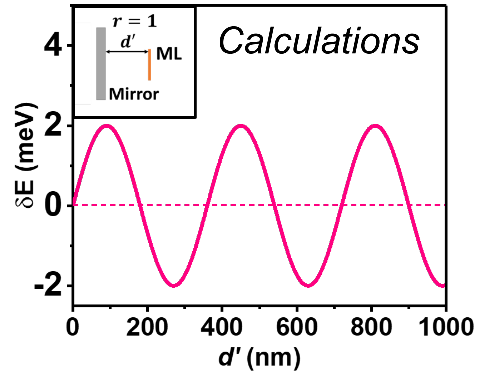
- **In other semiconductors ?**

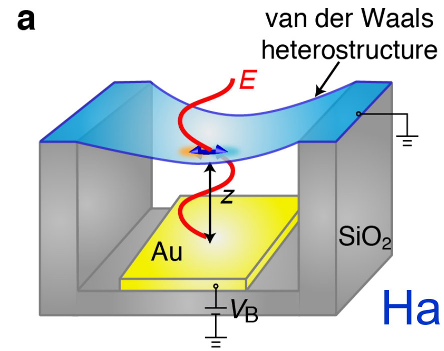
Bright dark exciton splitting in GaAs quantum wells :
~100 μeV (short range exchange interaction) ; PRB **50**, 14246 (1994) Southampton
PRL **78**, 1355 (1997) Toulouse

→ similar amplitude as the predicted Lamb shift

Perspectives

- Control of the bright-dark exciton splitting in TMDs **with an external mirror (r=1)**





Harvard

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PRL **78**, 1355 (1997) Toulouse

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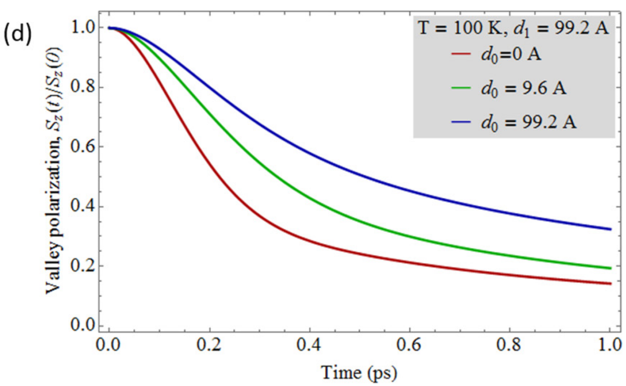
- **Control of the exciton spin dynamics** by the environment (long-range exchange)

PRB **103**, 085302 (2021); St Petersburg-Toulouse

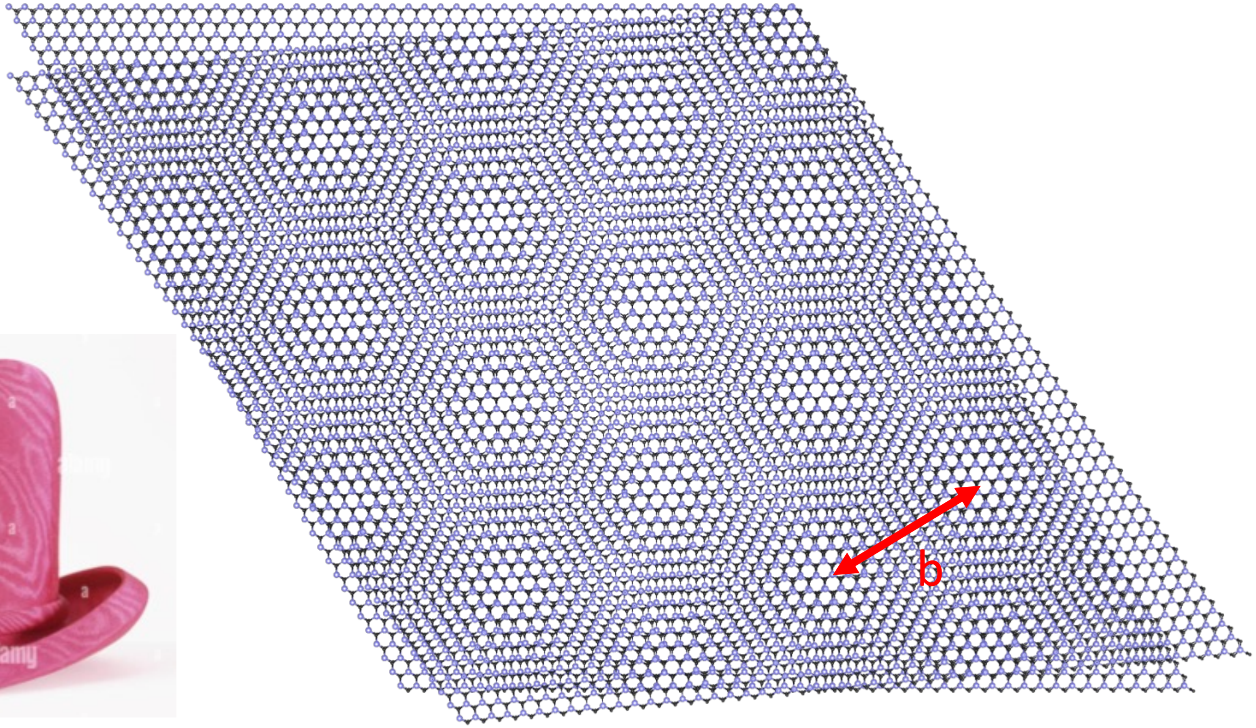


New degree of freedom : twist angle bewteen the monolayers ?

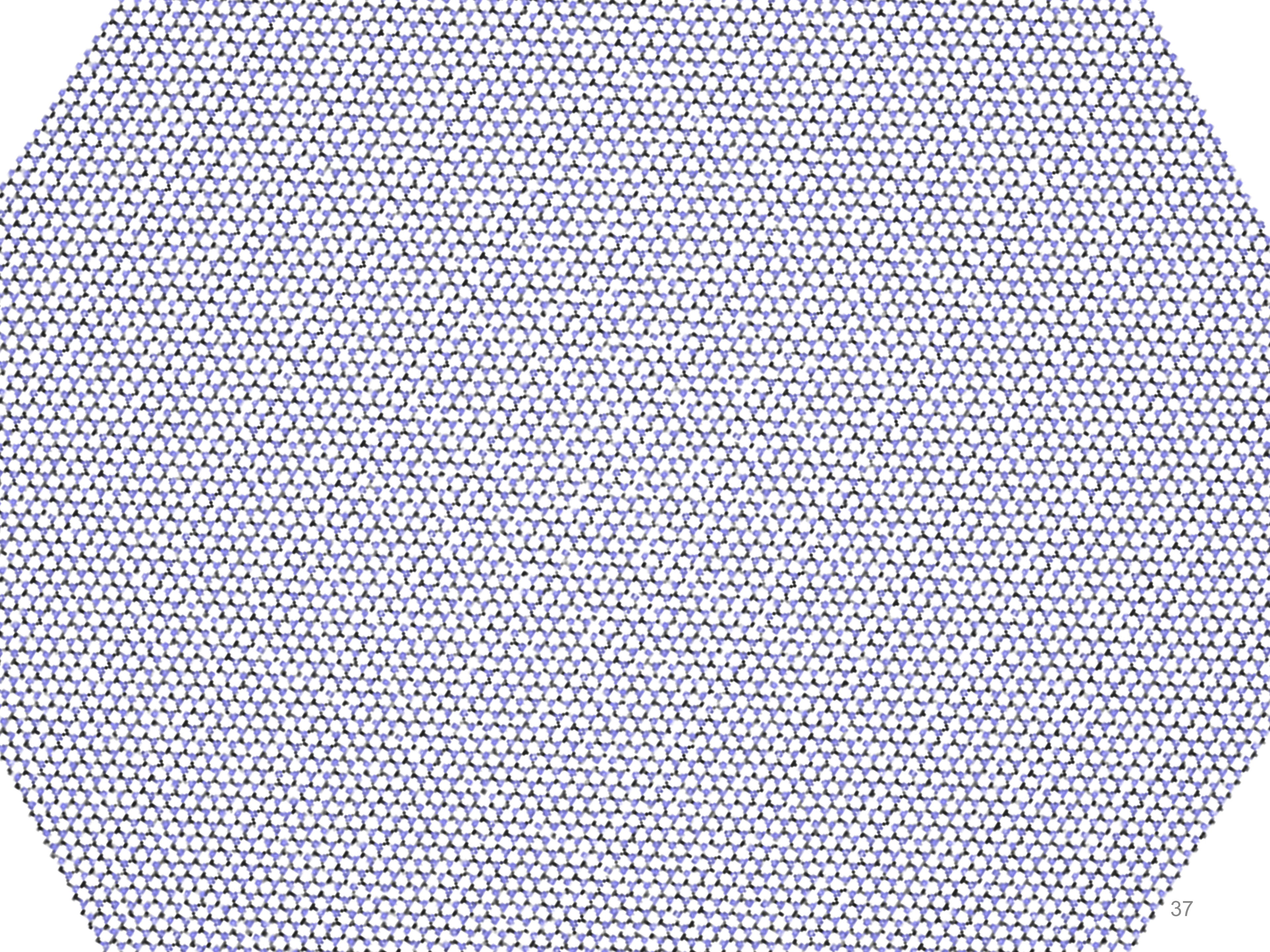
Moiré pattern appears for small lattice mismatch δ and/or small twist angle $\delta\theta$

$$b \approx a/\sqrt{\delta^2 + \delta\theta^2}$$

	MoS2	MoSe2	WS2	WSe2
a_0 (Å)	3.1604	3.299	3.154	3.286



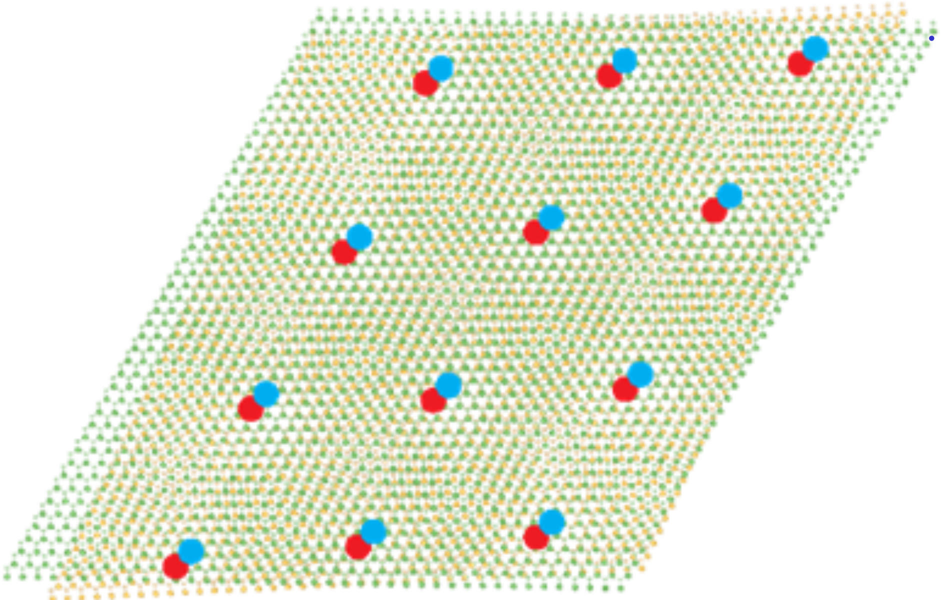
Silk Moiré hat

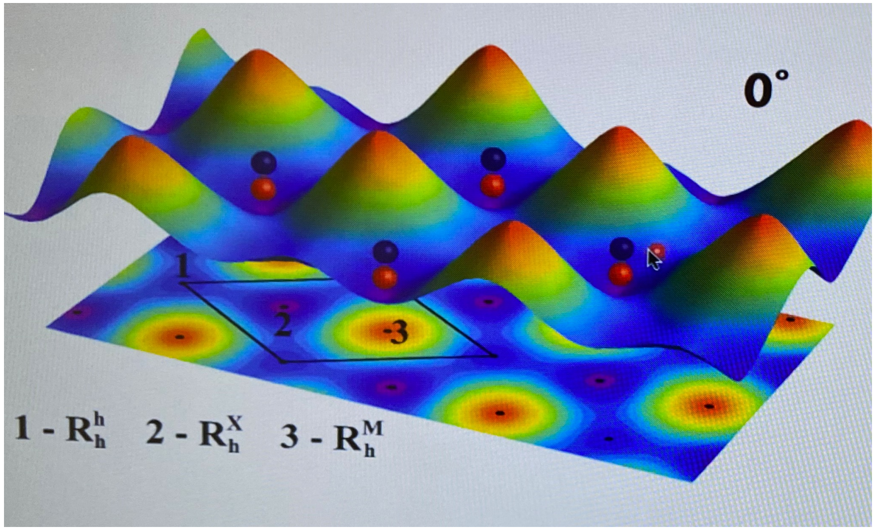


Moiré excitons

$MoSe_2/WSe_2$

Nature 579, 353 (2020); Cornell
Nature **580**, 472 (2020) ; ETH Zurich
Science **379**, eadg0014(2023) ; Berkeley, Beijing….
Nature Rev. Mat. **9**, 460 (2024); Princeton
…





- **Formation of a Moiré superlattice, where excitons can be localized at specific positions in the superlattice unit cell.**
- **Analogy with cold atoms trapped in optical lattices**
  → Different quantum phases : condensate, Mott insulator, superfluidity…

Collaboration

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