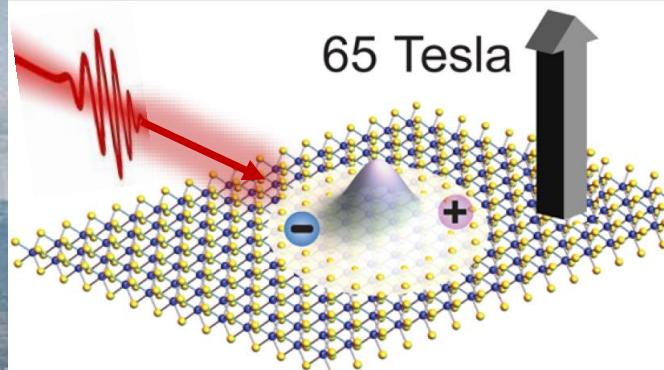


Monolayer Semiconductors:

Optical properties, excitons, & (the importance of) dielectric screening



Scott Crooker

National High Magnetic Field Laboratory
Los Alamos National Lab

Quantum Science Summer School
Penn State University

NATIONAL HIGH
MAGNETIC
FIELD LABORATORY

Useful / interesting review-type papers on monolayer TMDs (with an emphasis on optics and/or valleytronics):

Valleytronics in 2D materials

JR Schaibley, H. Yu, G. Clark, P. Rivera, J. S. Ross, K. Seyler, W. Yao, X. Xu
Nature Reviews Materials **1**, 16055 (2016)

Light-valley interactions in 2D semiconductors

KF Mak, D. Xiao, J. Shan
Nature Photonics **12**, 451 (2018)

Why all the fuss about 2D semiconductors?

Andres Castellanos-Gomez
Nature Photonics **10**, 202 (2016)

Photonics and optoelectronics of 2D semiconductor TMDs

K. F. Mak and J. Shan
Nature Photonics **10**, 216 (2016)

Spins and pseudo-spins in layered TMDs

Xiaodong Xu, Wang Yao, Di Xiao, Tony F. Heinz
Nature Physics **10**, 343 (2014)

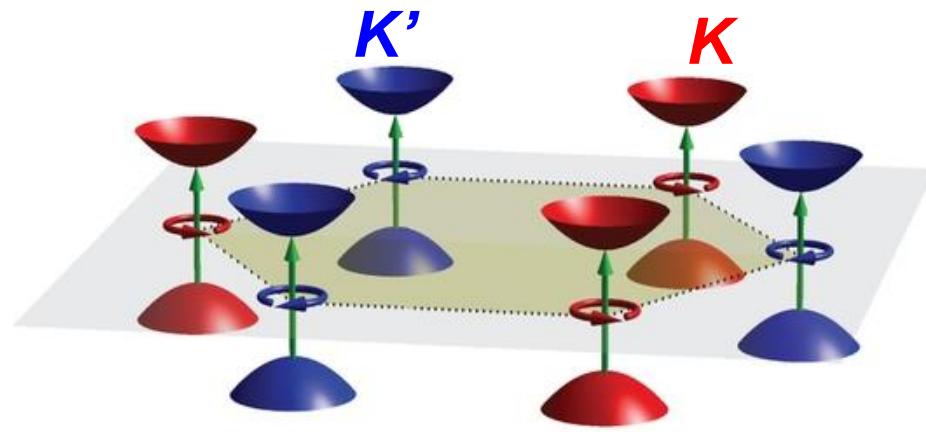
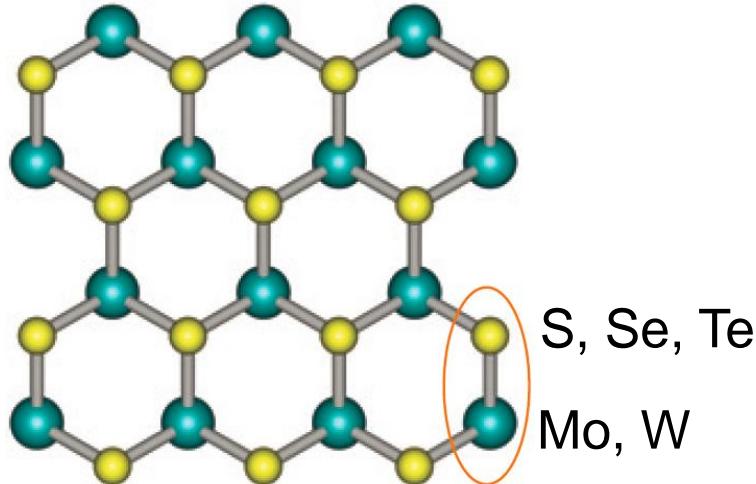
Van der Waals heterostructures

A. K. Geim and I. V. Grigorieva
Nature **499**, 419 (2013)

Today: Monolayer “TMD” semiconductors

Optical properties, excitons, & dielectric screening

Monolayer "transition-metal dichalcogenides" (MoS_2 , WSe_2 , etc)



-from X. Xu *et al.*, *Nat. Phys.* **10**, 343 (2014)

Direct-gap semiconductors!
 $E_{gap} \sim 1.5 - 2 \text{ eV}$ (*infrared – red*)

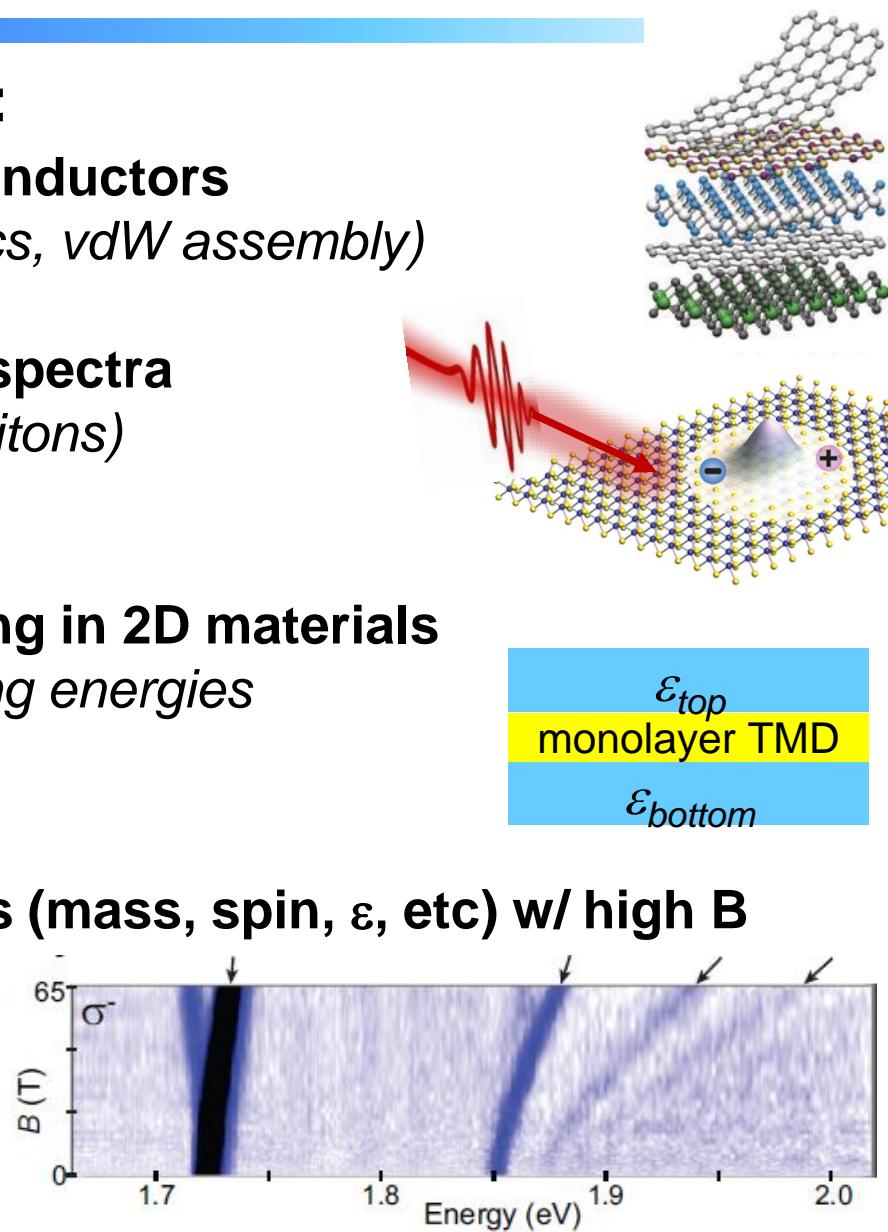
*(like graphene... but ^ useful for optoelectronics
& future quantum devices)*

Today: Monolayer “TMD” semiconductors

Optical properties, excitons, & dielectric screening

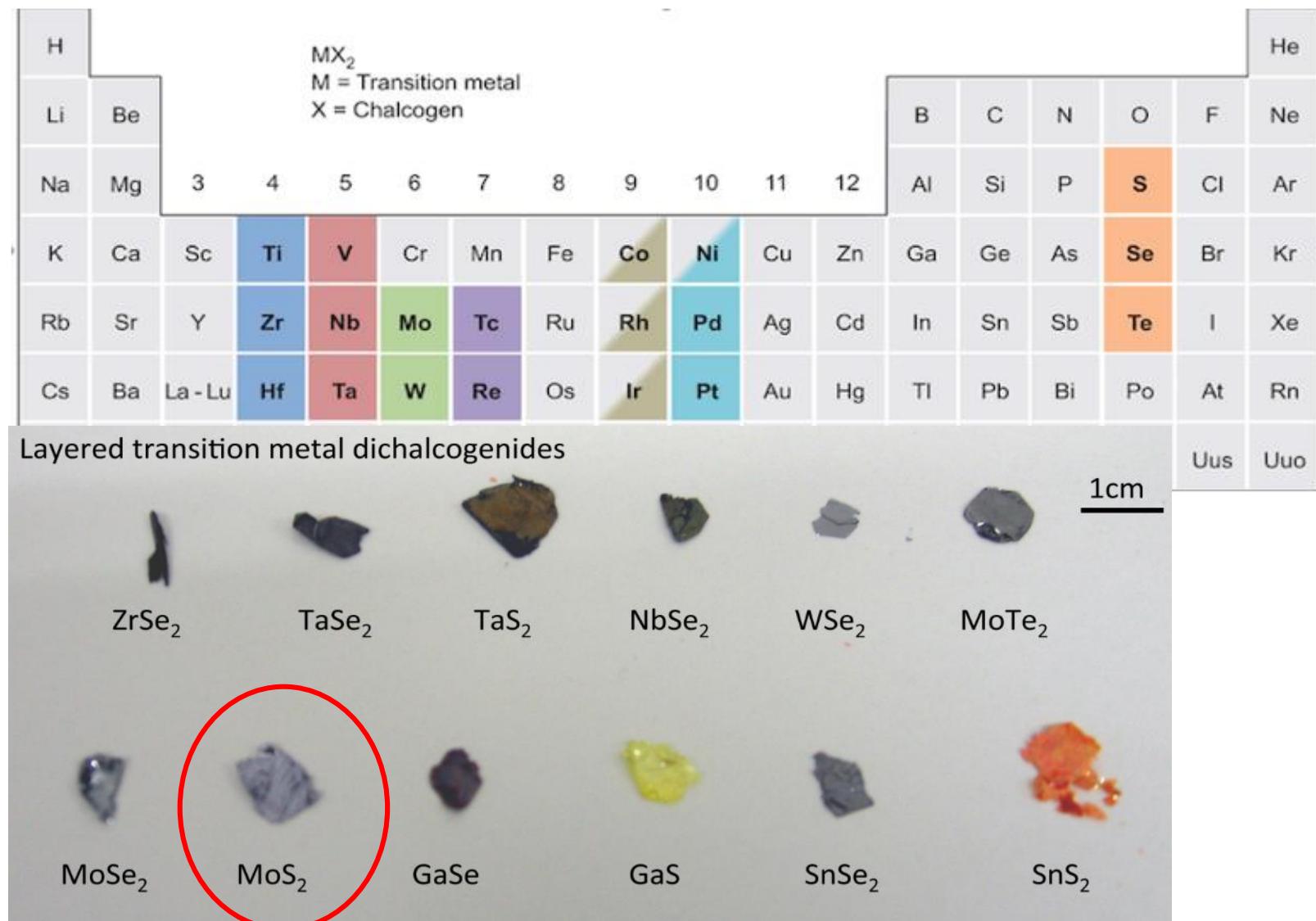
Outline:

- **Brief intro to monolayer TMD semiconductors**
 - *why all the recent fuss? (valleytronics, vdW assembly)*
- **Basic optical properties and optical spectra**
 - *tightly-bound electron-hole pairs (excitons)*
 - *Rydberg excitons*
- **The importance of dielectric screening in 2D materials**
 - *environment affects bandgaps, binding energies*
 - *“Coulomb Engineering”*
- **Determining fundamental parameters (mass, spin, ϵ , etc) w/ high B**



ε_{top}
monolayer TMD
 ε_{bottom}

“Transition-Metal Dichalcogenide” (TMD) materials



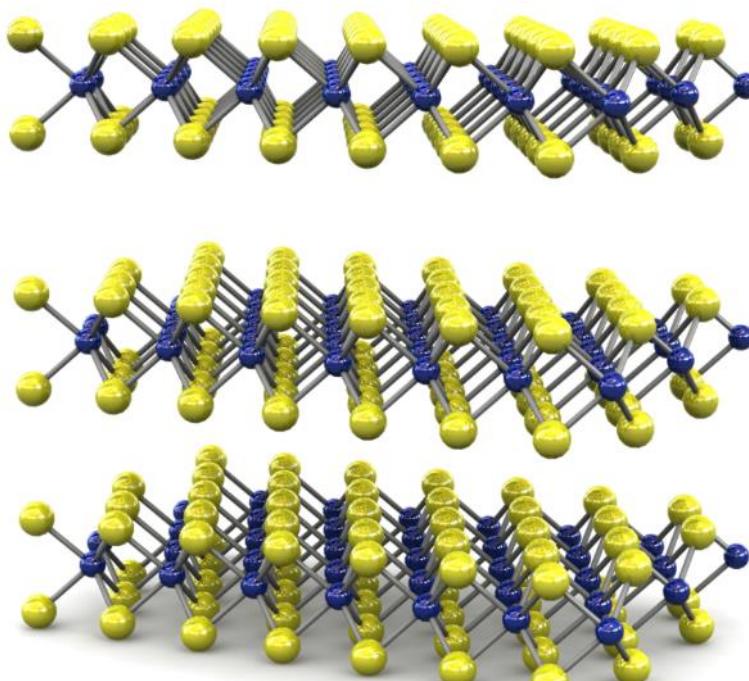
M. Chhowalla et. al. Nature Chemistry 5, 263–275 (2013).

Bulk TMD semiconductors: MoS_2 , MoSe_2 , WS_2 , WSe_2

Molybdenite (MoS_2)



Bulk: layered, *indirect*-gap semiconductors

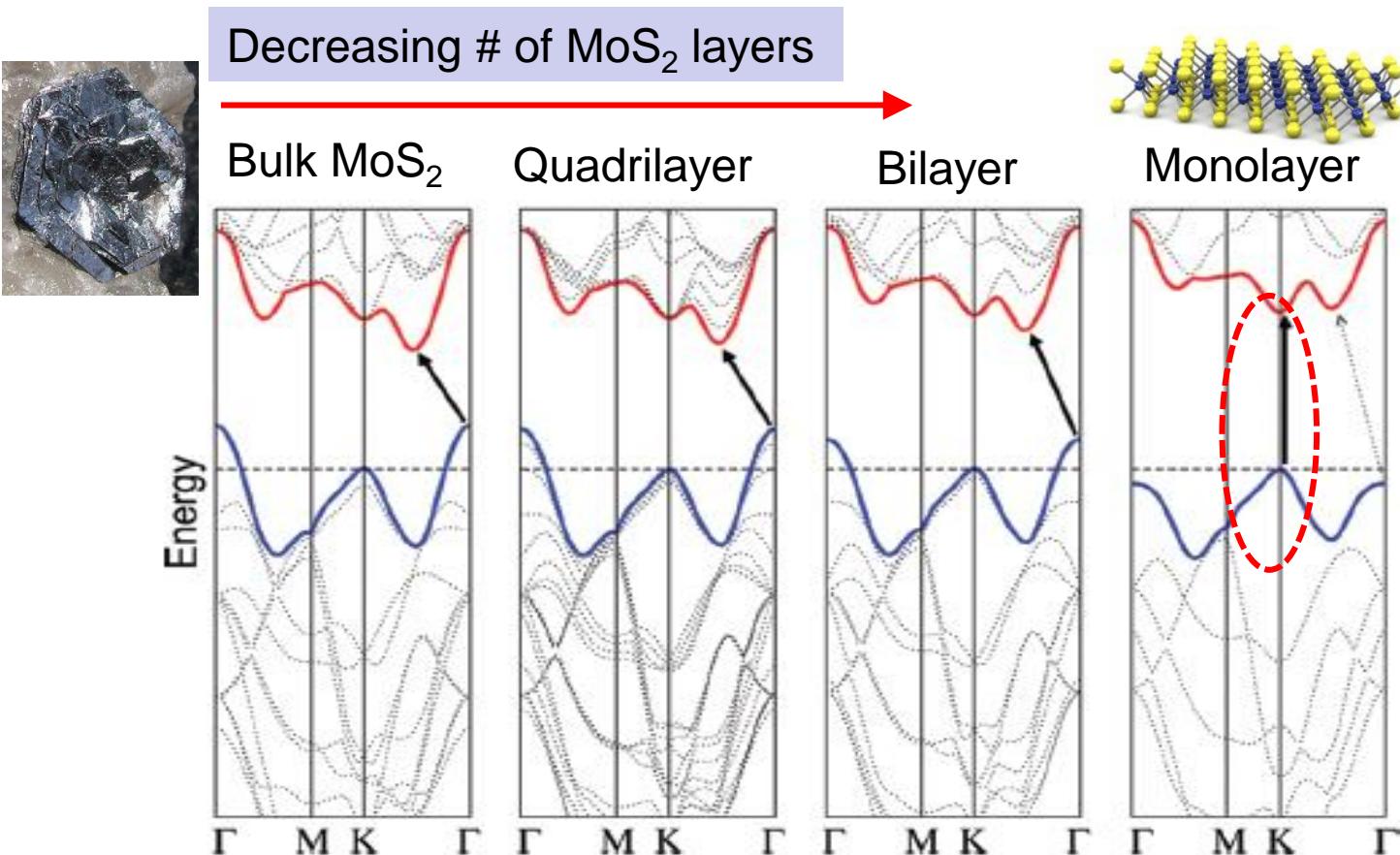


So... why all the recent attention?

3D to 2D: Indirect- to direct-gap semiconductor

A. Splendiani, F. Wang *et al.*, Nano Letters **10**, 1271 (2010)

K. F. Mak, J. Hone, J. Shan, T. F. Heinz *et al.*, PRL **105**, 136805 (2010)



So... why all the recent attention?

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A. Splendiani, F. Wang *et al.*, Nano Letters **10**, 1271 (2010)
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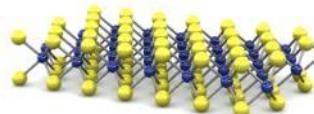
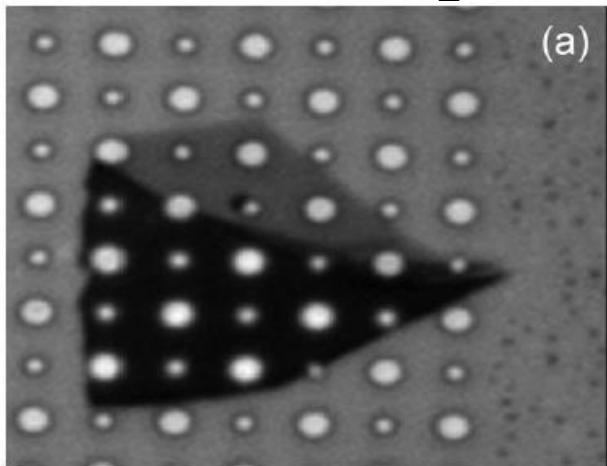
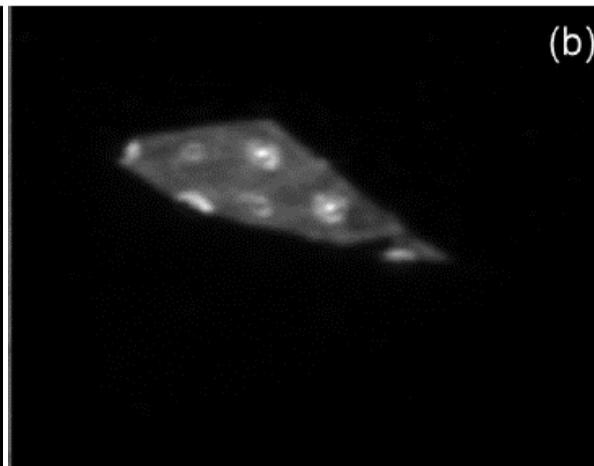


Image (MoS_2)

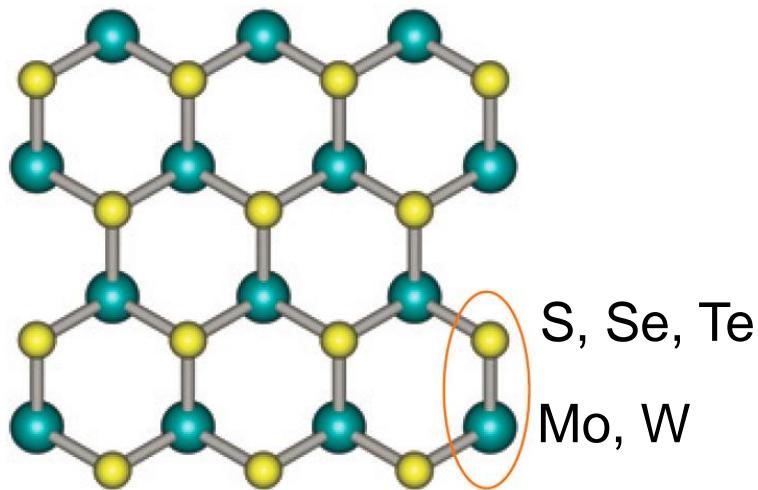


Photoluminescence

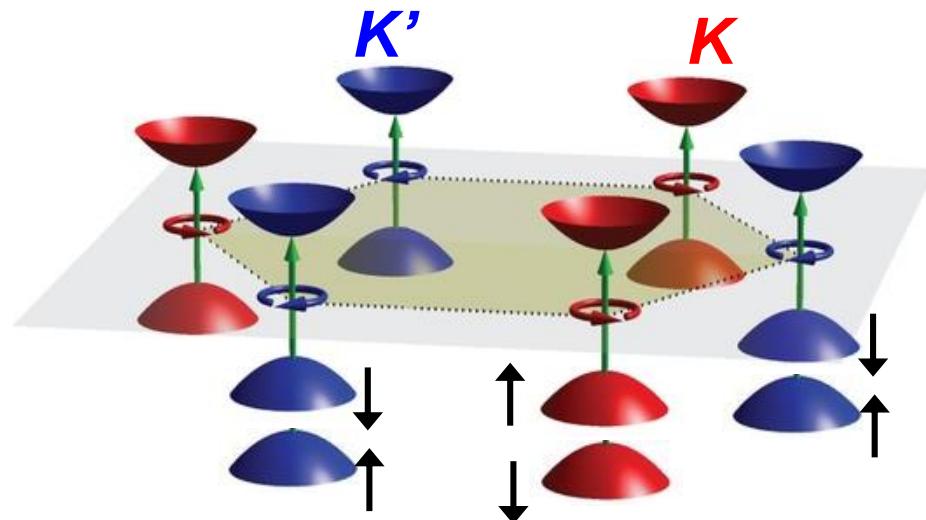


**Direct bandgap
~ 1.5 – 2 eV**

Motivation II: “Valley pseudospin” & valleytronics



-from X. Xu et al., *Nat. Phys.* **10**, 343 (2014)



Key point:

lack of inversion + spin-orbit coupling: *spin-valley locking*
Valley-specific optical selection rules

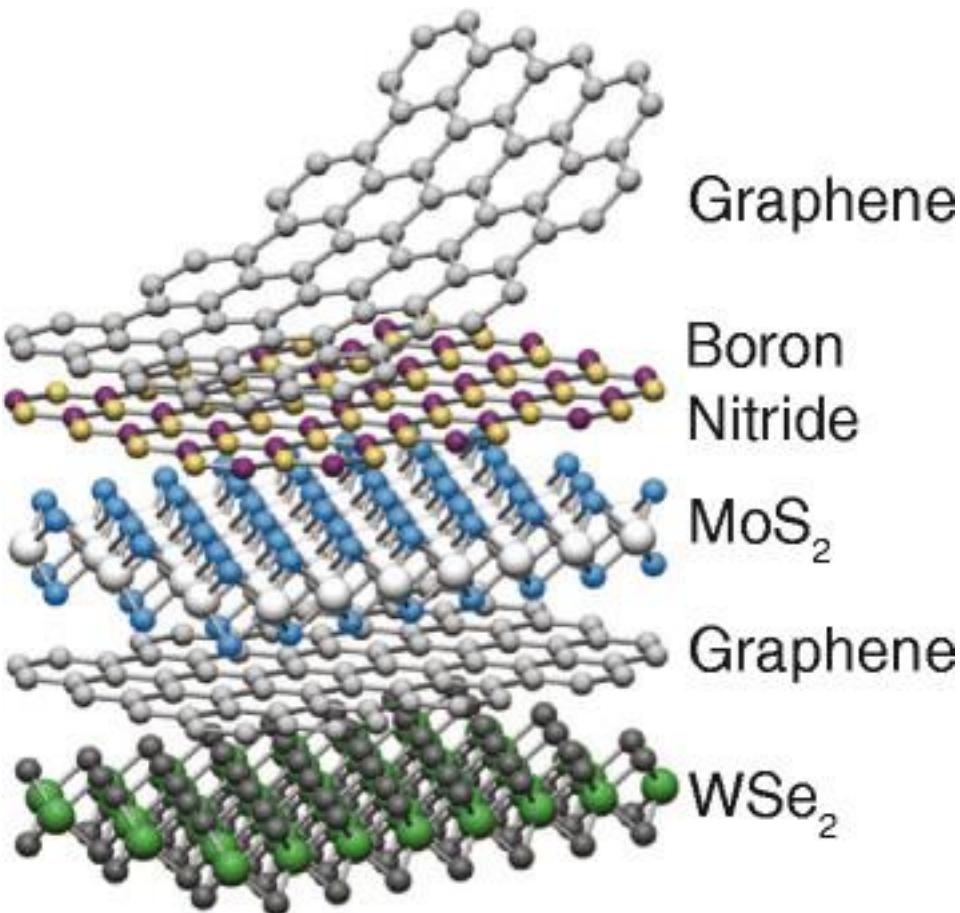
RCP & LCP light couple *selectively* to K & K' valleys

Easy access to valley degrees of freedom

Excellent reviews: X. Xu, D. Xiao, W. Yao, & T. Heinz, *Nature Physics* **10**, 343 (2014)
K. F. Mak, D. Xiao, & J. Shan, *Nature Photonics* **12**, 451 (2018)

Motivation III: van der Waals heterostructures

Opto-electronic ('spin/valleytronic'?) quantum devices
via van der Waals assembly of 2D layers



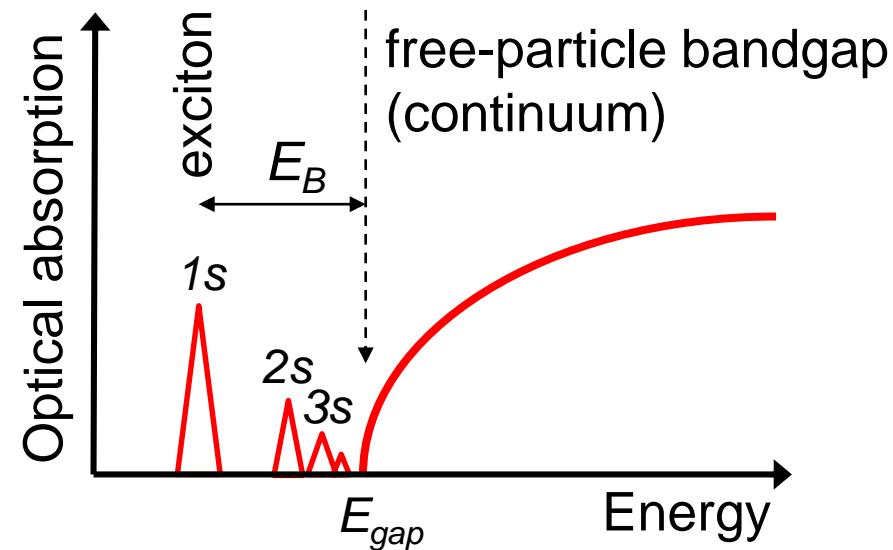
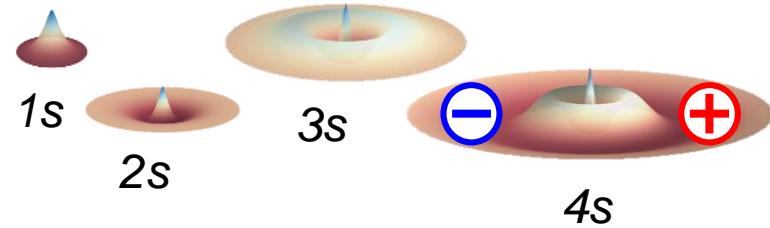
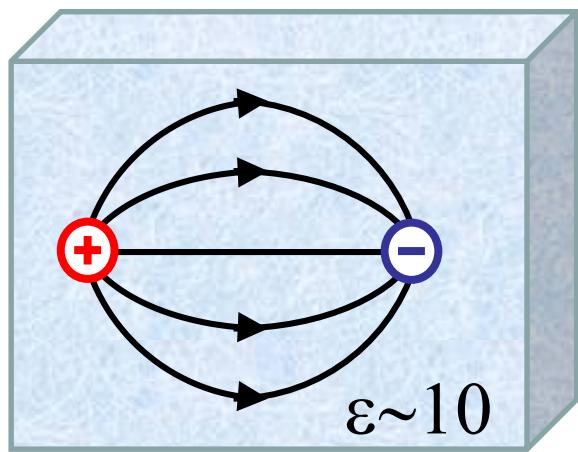
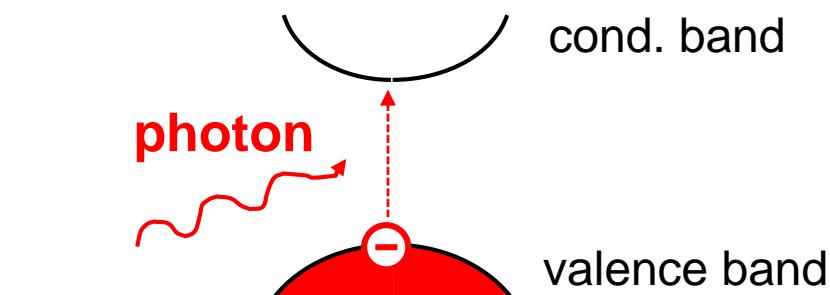
Geim & Grigorieva, Nature 499, 419 (2013)

As-yet-unknown

(but essential for rational design of real quantum devices)

- 1) Role of dielectric screening?
- E_{gap} ? exciton binding?
- 2) Fundamental parameters?
- e , h , exciton masses?
- form of potential $V(r)$?
- 3) Spin & valley dynamics of electrons & holes?
etc...

Fundamental optical excitation in a semiconductor: electron-hole pair (exciton)

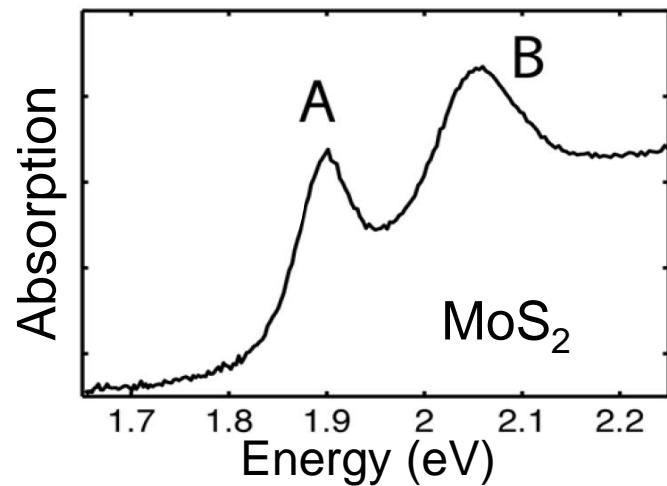
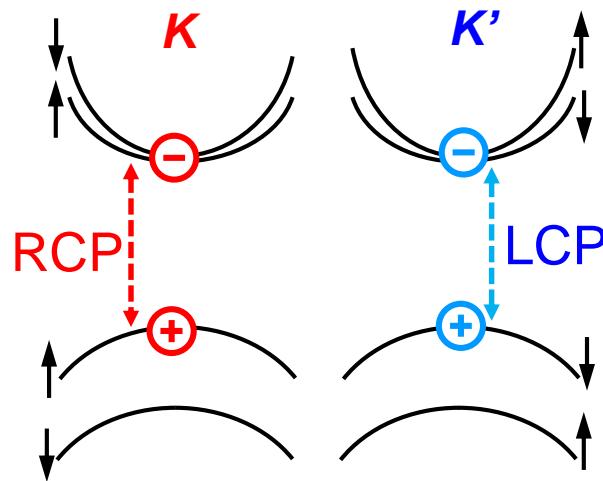
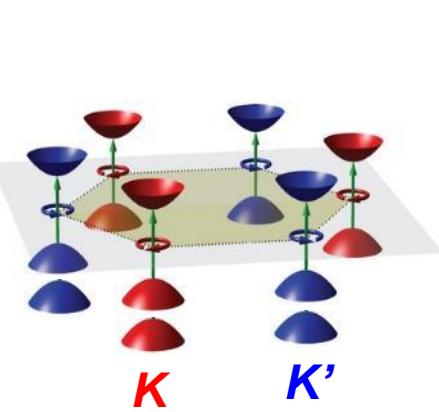


Coulomb-bound state: the exciton
hydrogen-like; $1/\epsilon r$ potential (in bulk)

Binding energy: $\frac{13.6\text{eV}}{\epsilon^2} \frac{m^*}{m_e}$ **~5 meV** (small)

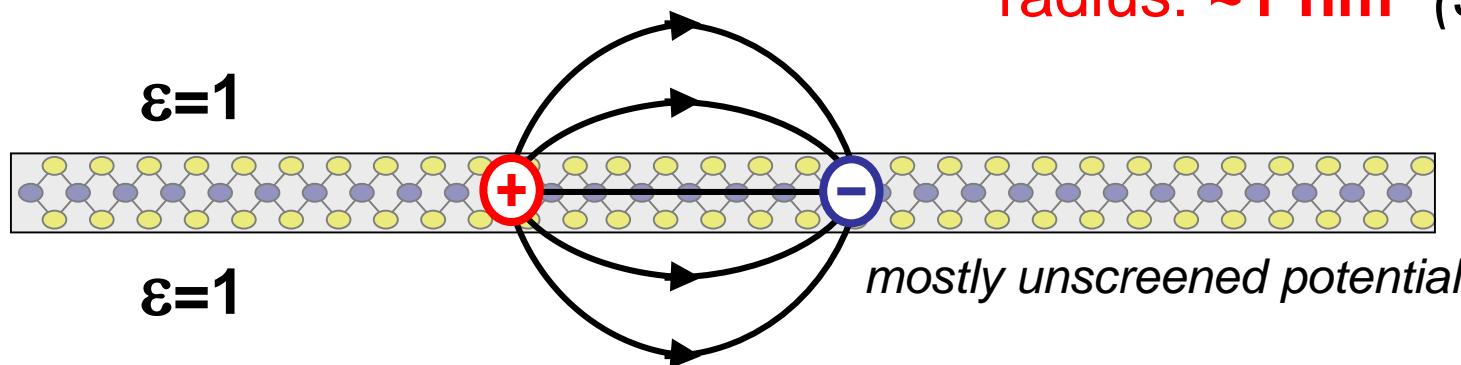
Radius: $a_B \epsilon \frac{m_e}{m^*}$ **~10 nm** (big)
(for GaAs)

Excitons in 2D semicond.: *Small & tightly bound*

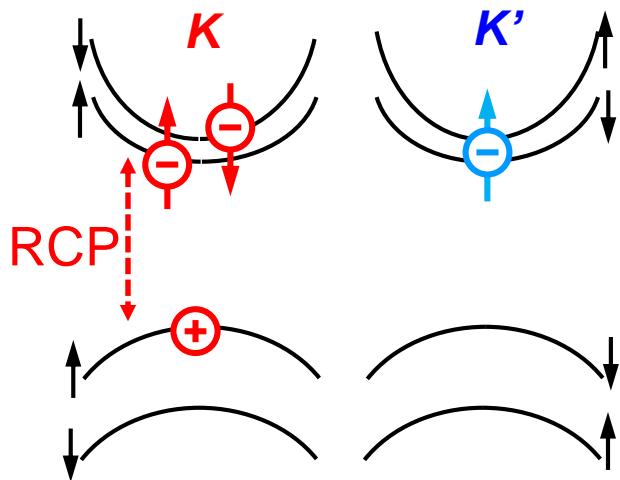


Strong light-matter coupling: Excitons dominate the absorption spectrum

Fundamental exciton parameters: binding energy: **~500 meV (huge!)**
radius: **~1 nm (small!)**

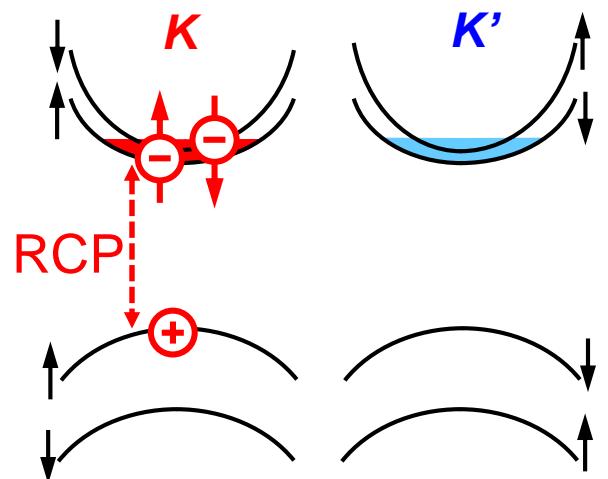


Other states: “dark” excitons, charged excitons (trions)



“Bright” neutral excitons: optically allowed
-both PL and absorption

“Dark” neutral excitons: spin- and/or valley-forbidden
-no absorption. Maybe PL



If monolayer is electron or hole-doped:

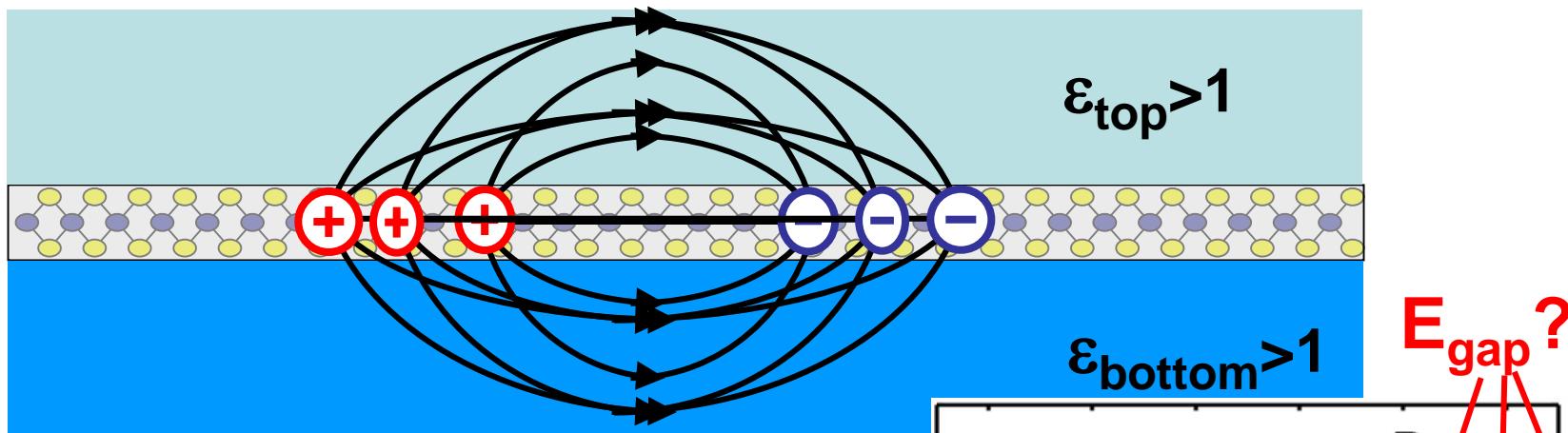
Negatively-charged exciton (trion): optically allowed
1 hole + 2 electrons
-both PL and absorption

trion

exciton

Positively-charged exciton (trion): allowed
1 electron + 2 holes
- both PL and absorption

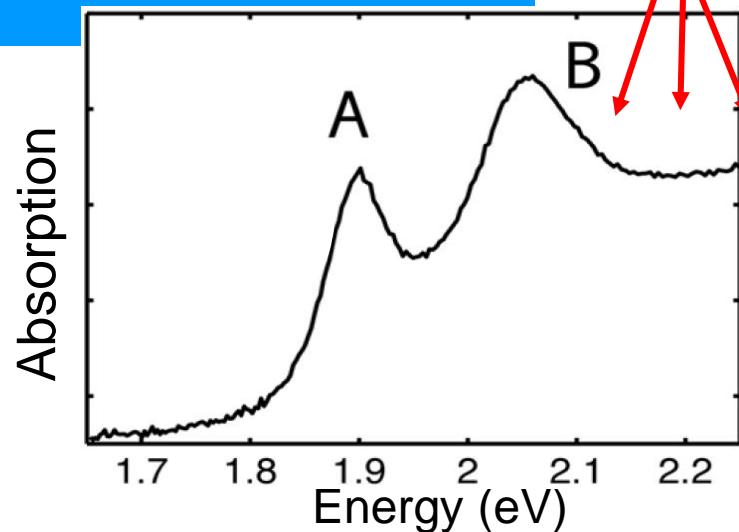
Expectation: Extreme sensitivity to dielectric environment



- Exciton radius increases
- Binding energy decreases (a lot!)
...but how to measure?

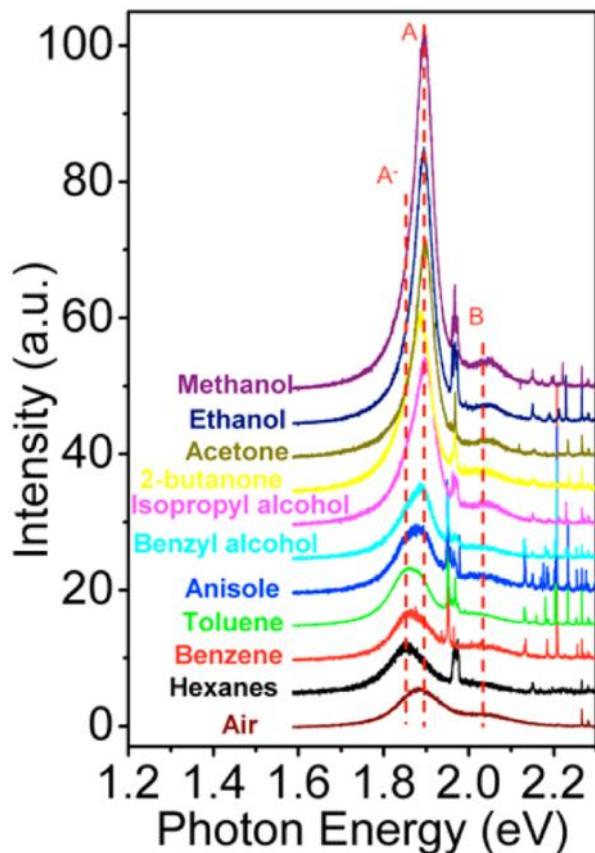
Unfortunately....

Exciton's transition energy is not a good indicator of dielectric environ.
...need some other measurable



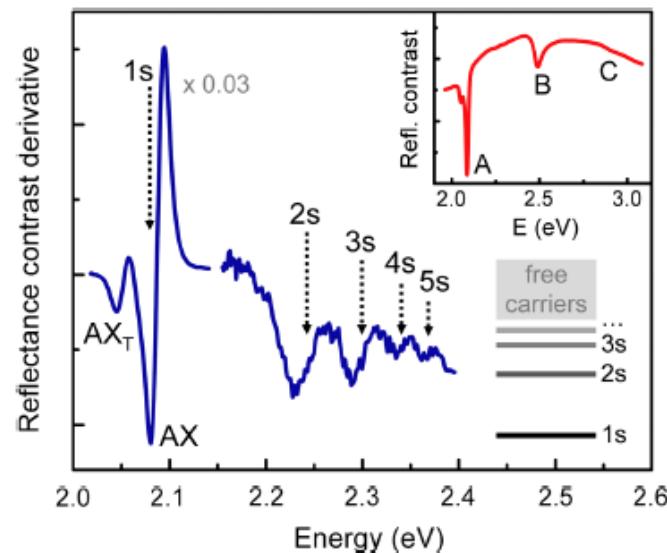
Exciton's energy *alone* is not a good indicator

Very little shift in exciton transition energy with dielectric screening!
because *reduction of binding energy compensated by reduction of bandgap*



Need some other measurable...

Other approaches:
Identification of 2S, 2P, etc excitons



Y. Lin et al., Nano Lett. 14, 5569 (2014)

A. Chernikov, PRL 113, 076802 (2014)

Z. Ye, Nature 513, 214 (2014)

K. He, PRL 113, 026803 (2014)

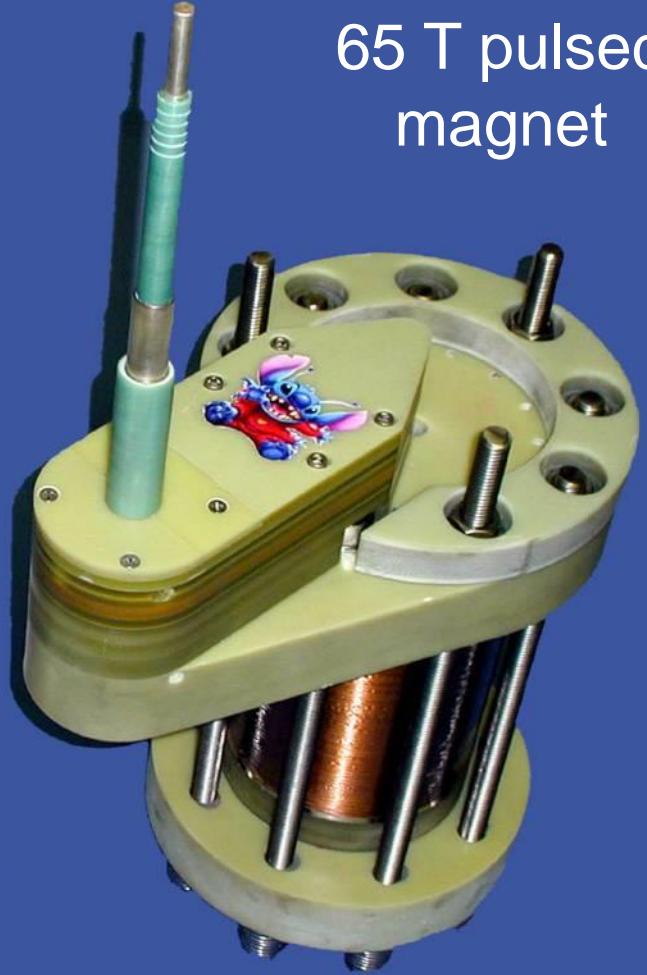
G. Wang, PRL 114, 097403 (2015)

etc

High magnetic fields (to the rescue!)

Diamagnetic shift is a *direct probe* of exciton's size

65 T pulsed magnet



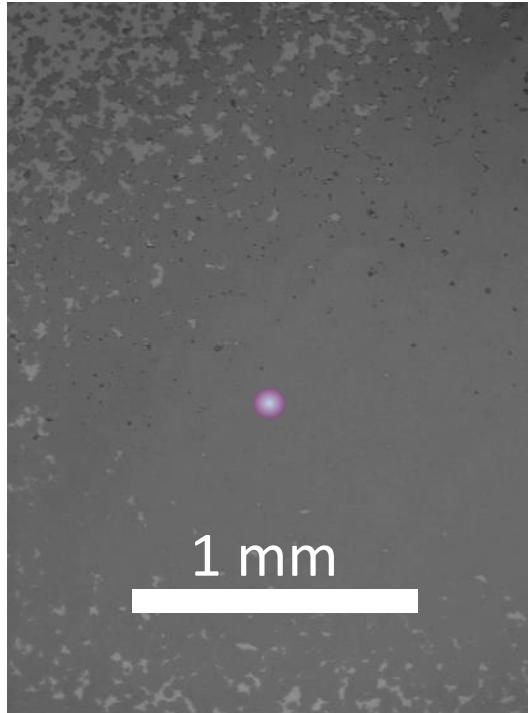
$$\Delta E_{\text{dia}} = \frac{e^2}{8m_r} \langle r^2 \rangle \mathbf{B}^2 = \sigma \mathbf{B}^2$$

Why high magnetic fields for monolayer TMD semiconductors?

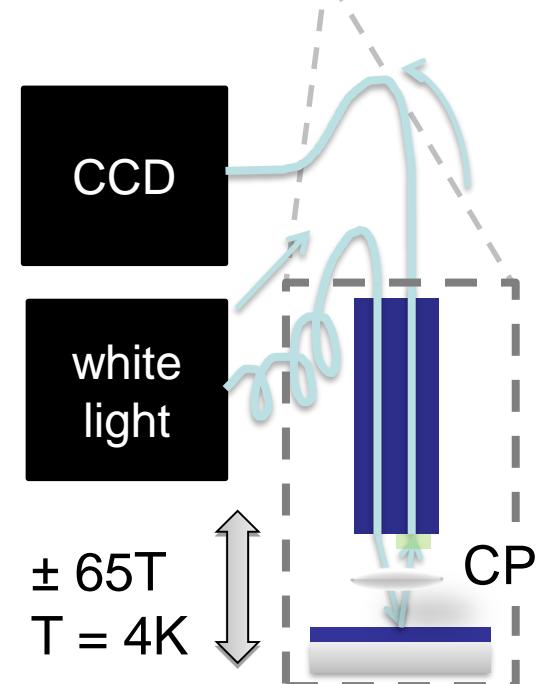
- Large e^- , h^+ masses ($\sim 0.4 m_0$)
small cyclotron energy ($\hbar\omega \sim 0.3 \text{ meV/T}$)
- Huge exciton binding energy (200-500meV)
- 100 T *still* ‘weak-field limit’ for $1s$ exciton
(i.e., cyclotron energy \ll binding energy)

First studies: Circularly-polarized magneto-reflection of large-area TMD monolayers

Large-area CVD WS₂ & MoS₂ to
avoid vibrations & misalignment

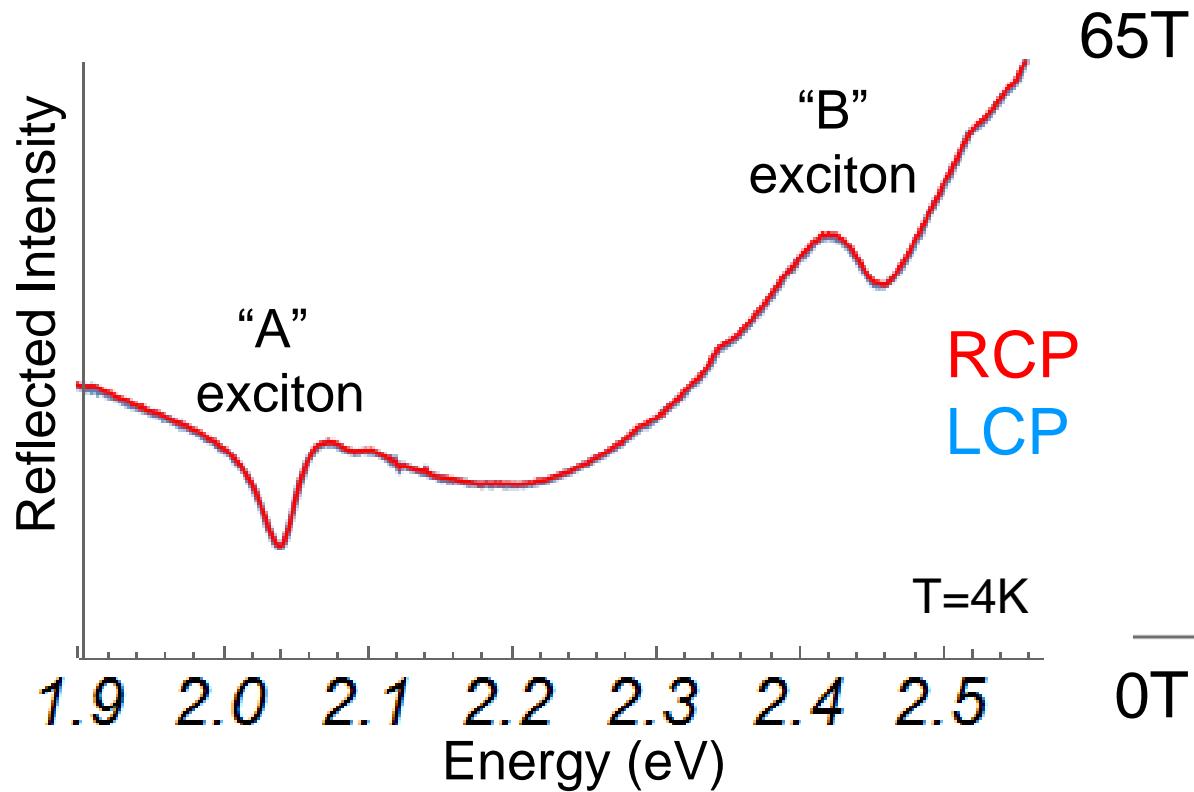
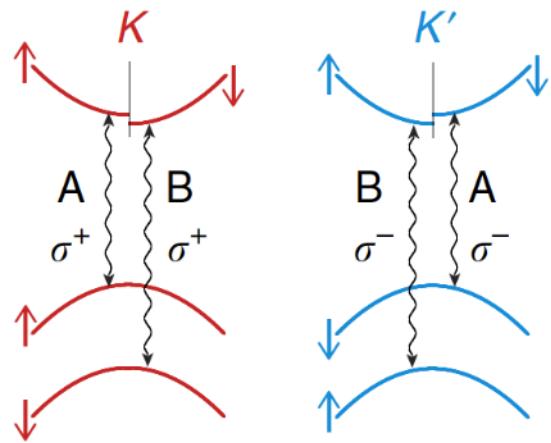


Kathy McCreary
(NRL)

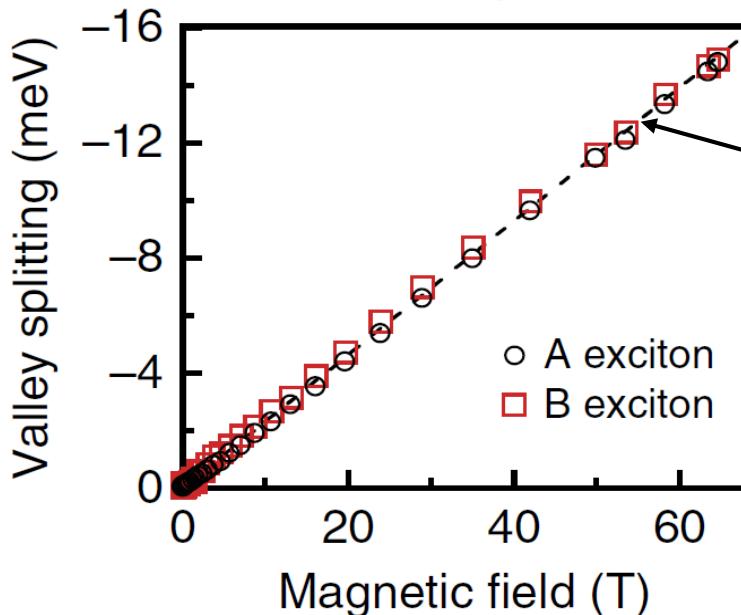
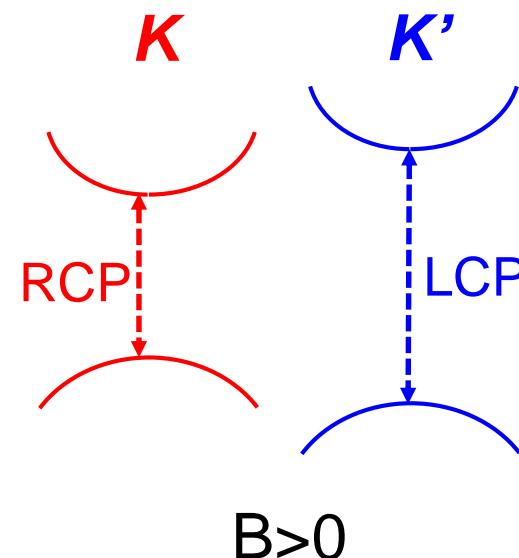
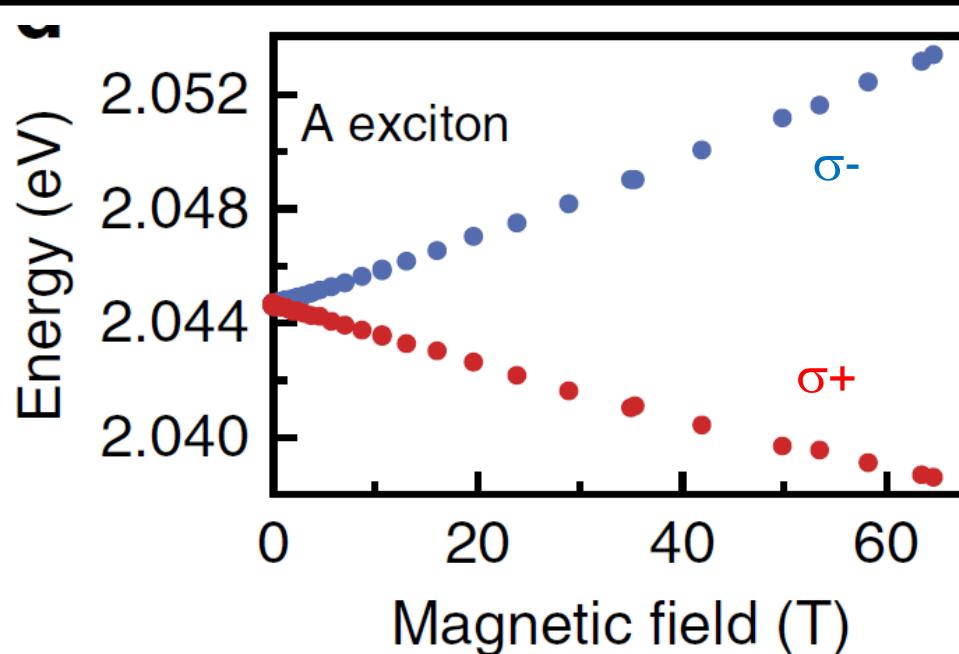


Circularly-polarized optical spectroscopy to 65 T

Single 65T magnet pulse, all data taken in ~50ms. CVD monolayer WS₂



Exciton splitting: Valley Zeeman Effect

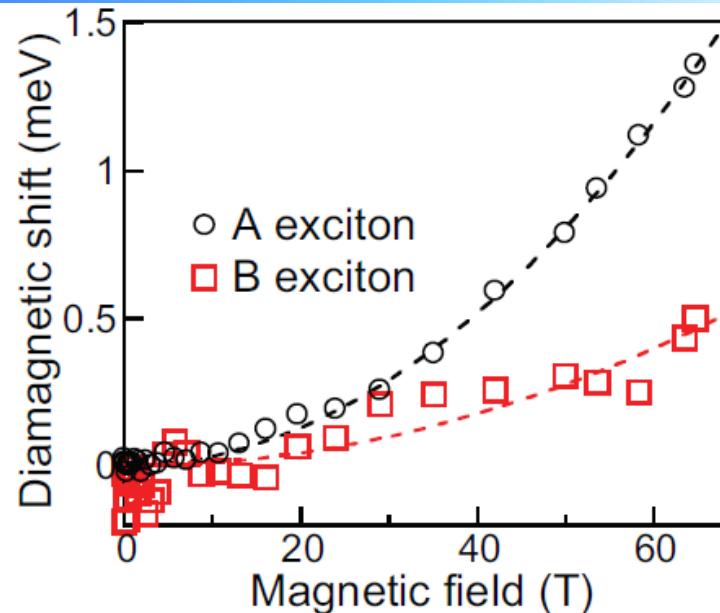
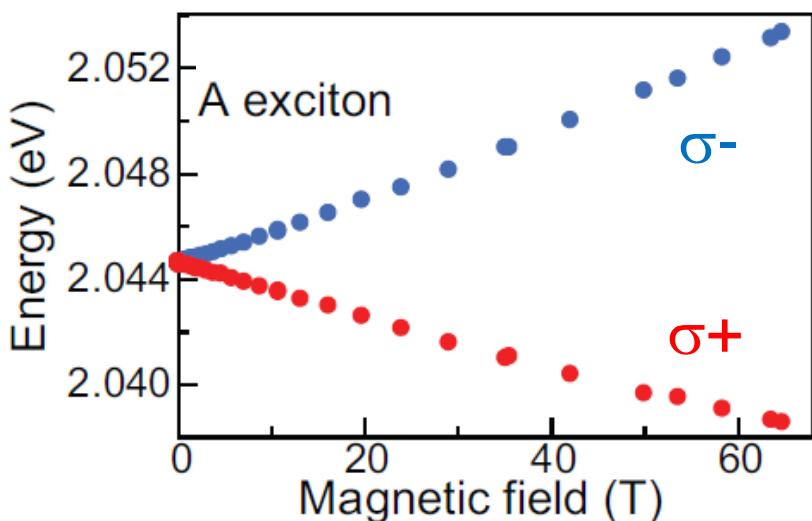


Splitting gives the Valley Zeeman Effect

$g_v = -4.0$ For both A... and B excitons
(unexpected b/c masses are different?)

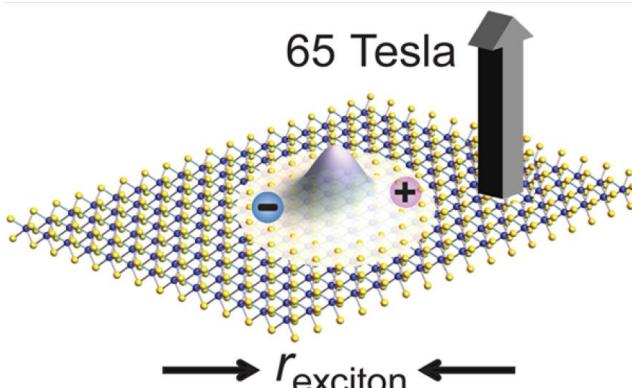
Consistent with atomic orbital moment only
(ie, Berry curvature effects play little role?)

Average exciton energy: Diamagnetic shift



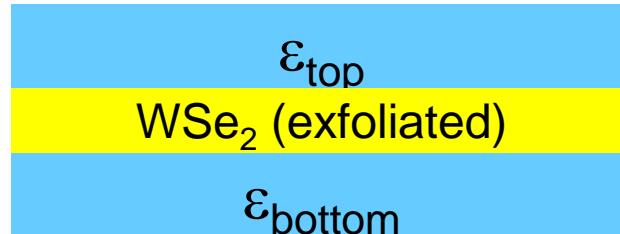
$$\Delta E_{\text{dia}} = \frac{e^2}{8m_r} \langle r^2 \rangle \mathbf{B}^2 = \sigma \mathbf{B}^2$$

- A exciton *radius*: **1.53 nm** (*if $m_r = 0.16m_0$*)
- A exciton *binding energy*: **~410 meV** (*with some modeling*)

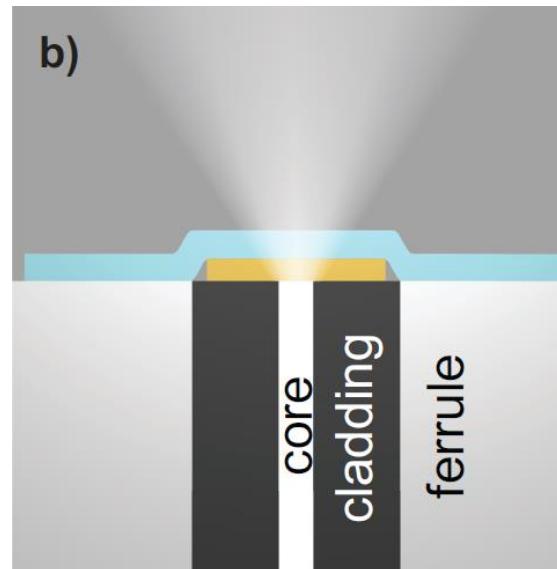
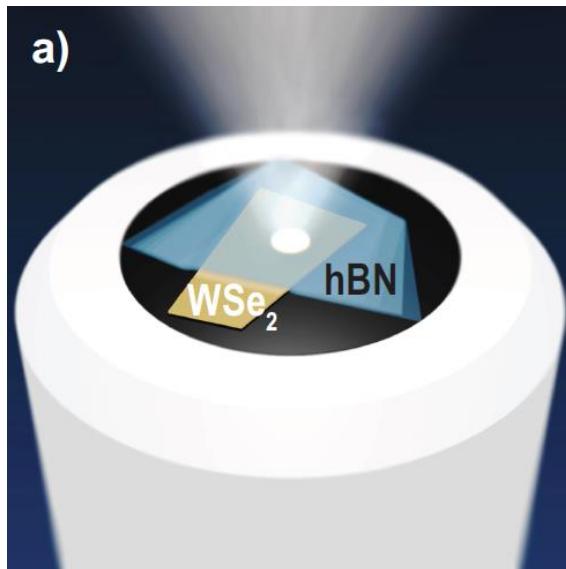


Next: Vary dielectric environment, measure exciton size (& binding energy)

- Circularly-polarized absorption spectroscopy of **exfoliated/encapsulated** WSe₂ flakes



- Transfer WSe₂ flakes over the core of a singlemode optical fiber
(for mechanical stability – no drifts or vibrations)

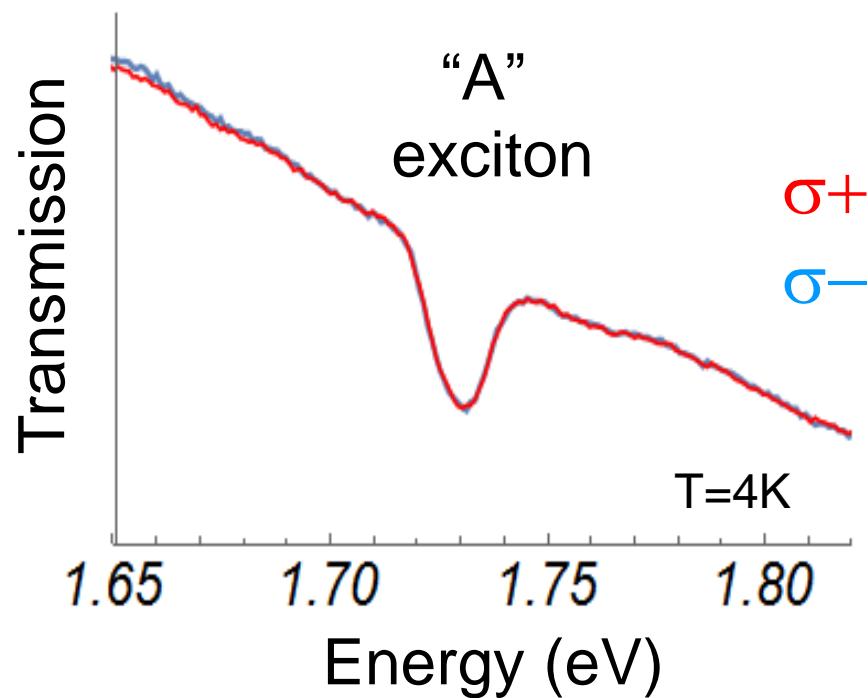
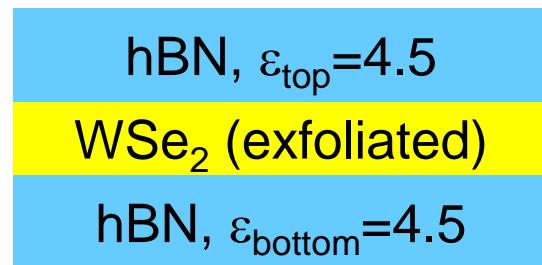
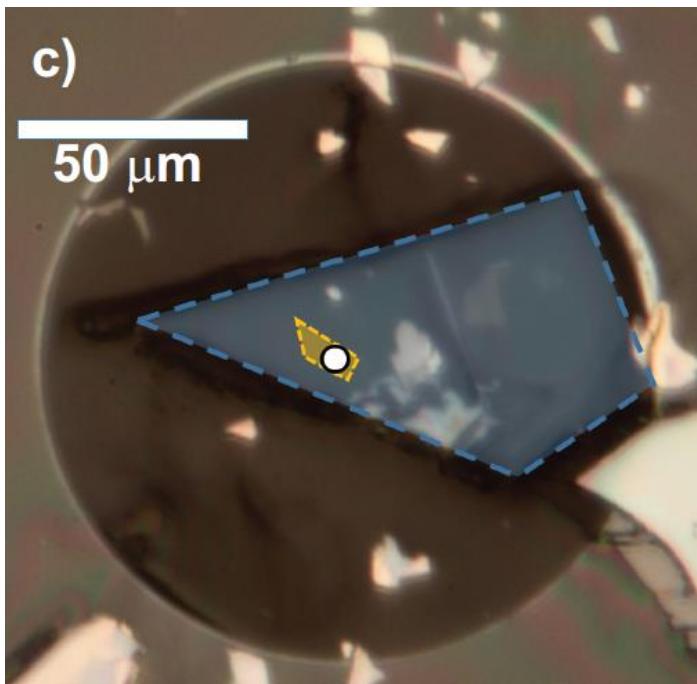


Nathan Wilson
U. Washington

Magneto-transmission of encapsulated WSe₂ to 65 T

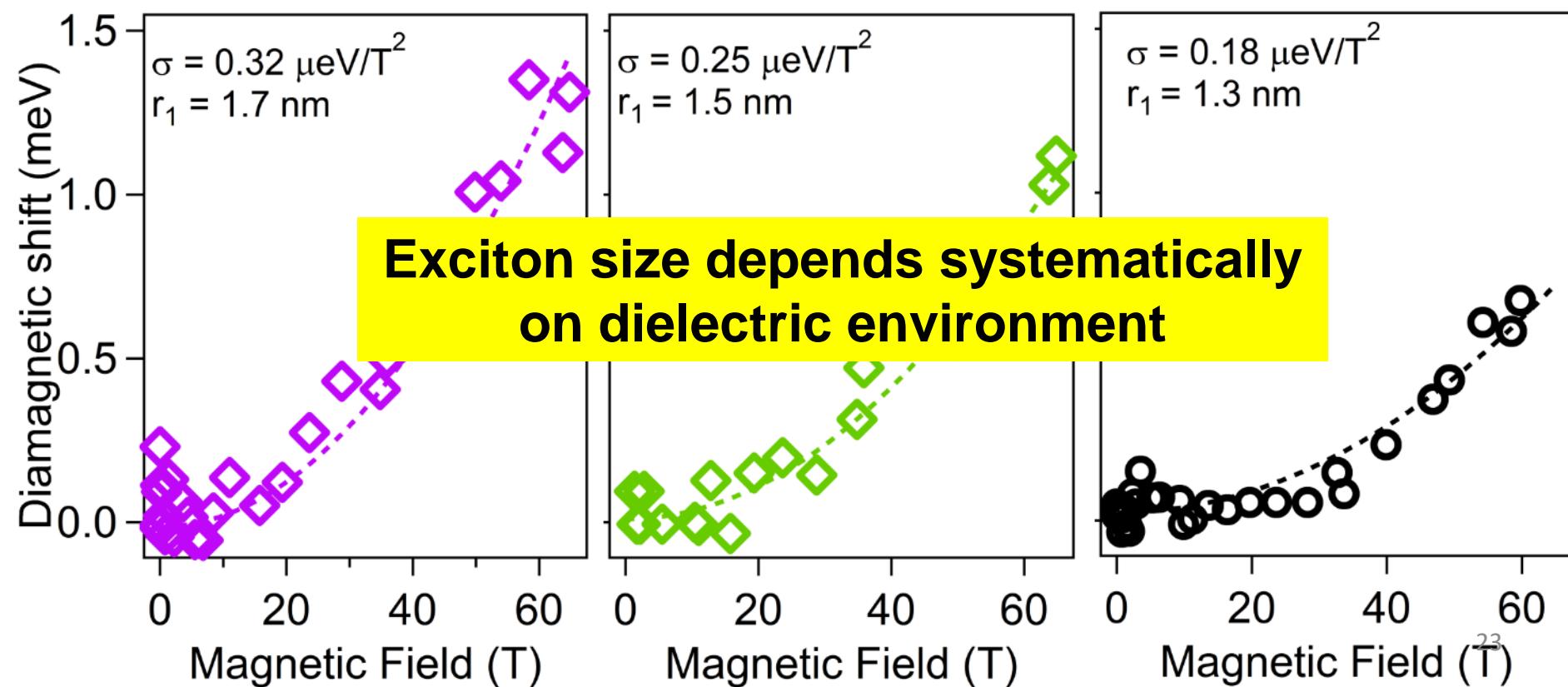
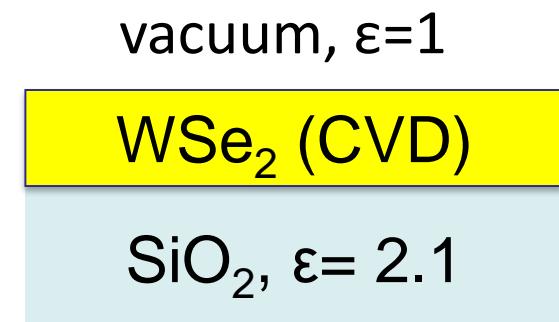
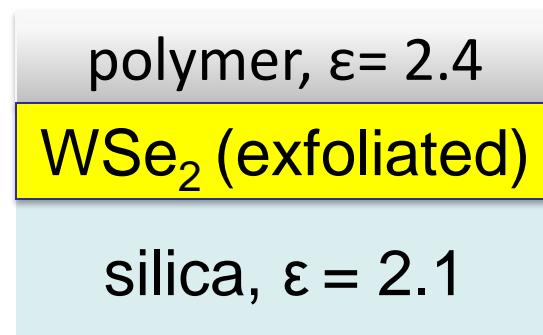
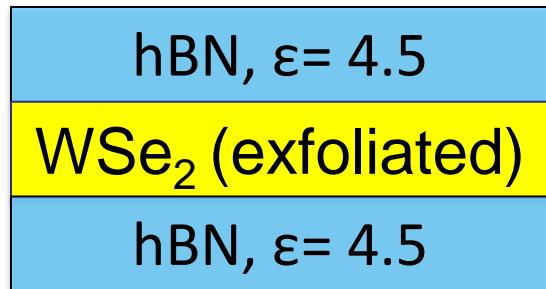
Stier *et al.*, Nano Letters **16**, 7054 (2016)

WSe₂ encapsulated in hBN

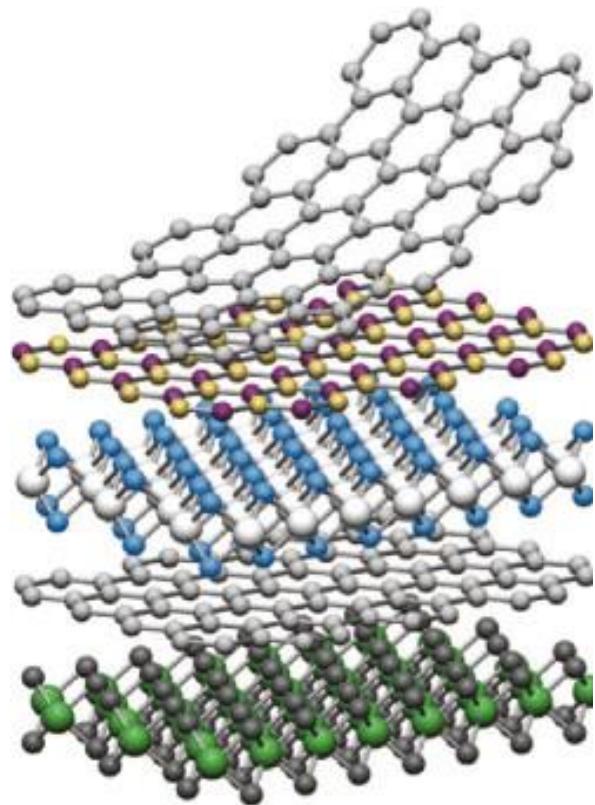
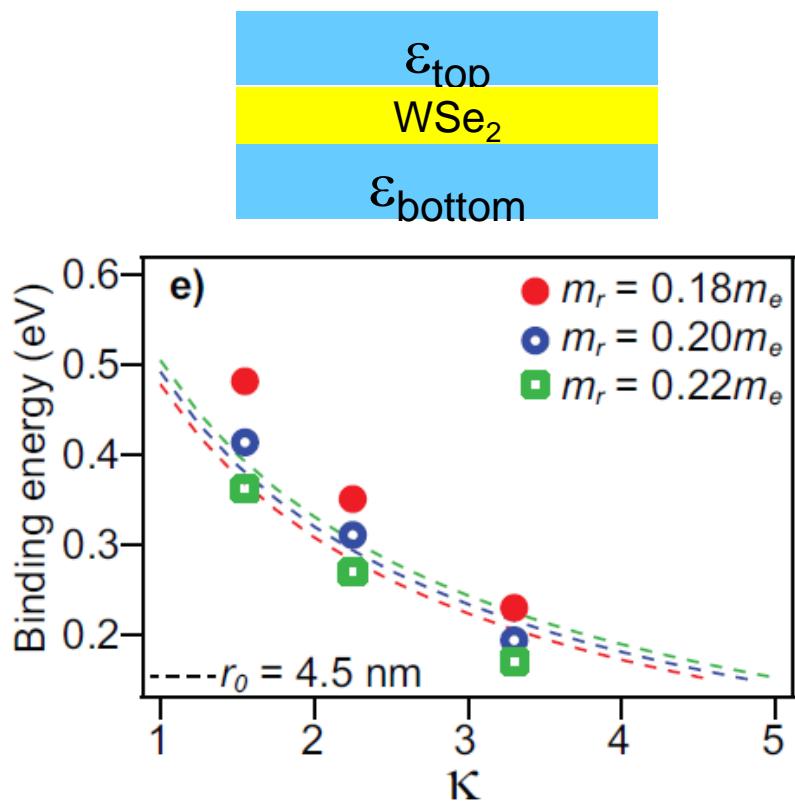


Diamagnetic shift: a direct probe of exciton size

Stier et al., Nano Letters 16, 7054 (2016)



Binding energy (& bandgap!) depend on dielectric environ.



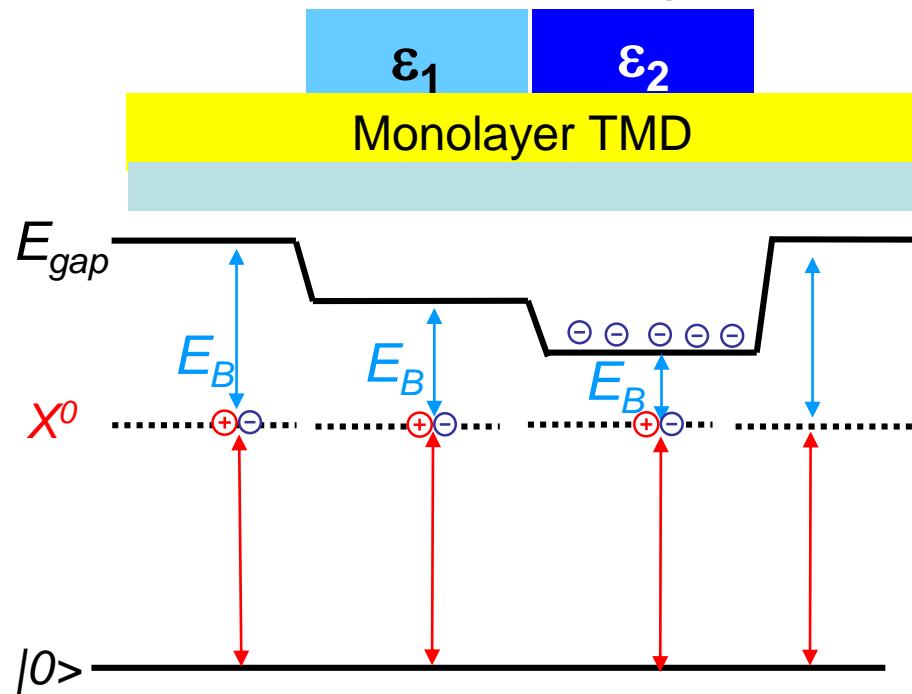
Main message

Integration of 2D semiconductors in real quantum devices:

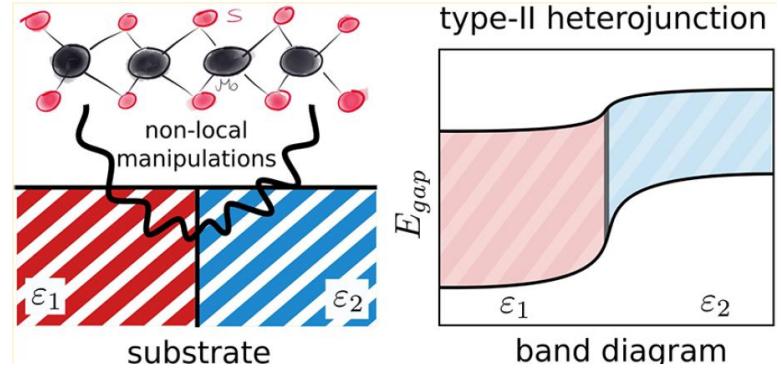
- Dielectric environment plays an unavoidable (and very significant) role
- 100s of meV variation in bandgap, exciton binding energy

Opportunity: “Coulomb engineering” of monolayer devices

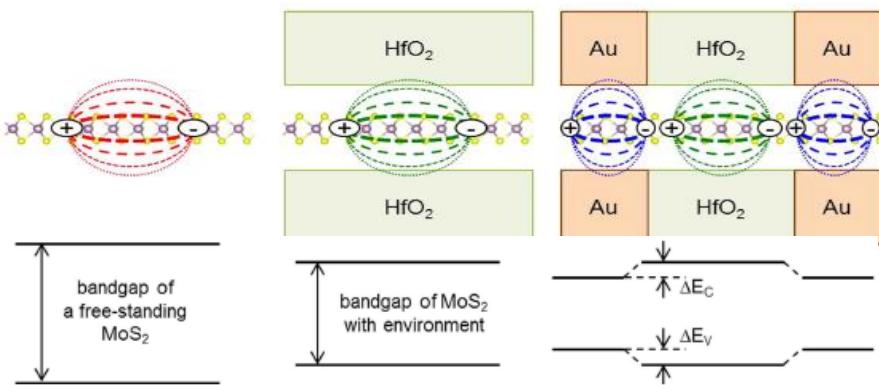
(Lateral) modulation of E_{gap} w/ dielectrics!



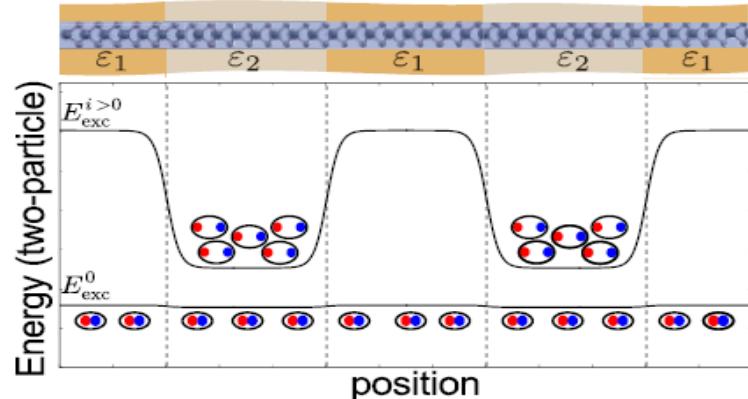
“Coulomb engineering” of monolayer TMDs: theory



Rosner *et al*, Nano Lett. **16**, 2232 (2016)



Ryou *et al*, Sci. Rep. **6**, 29184 (2016)



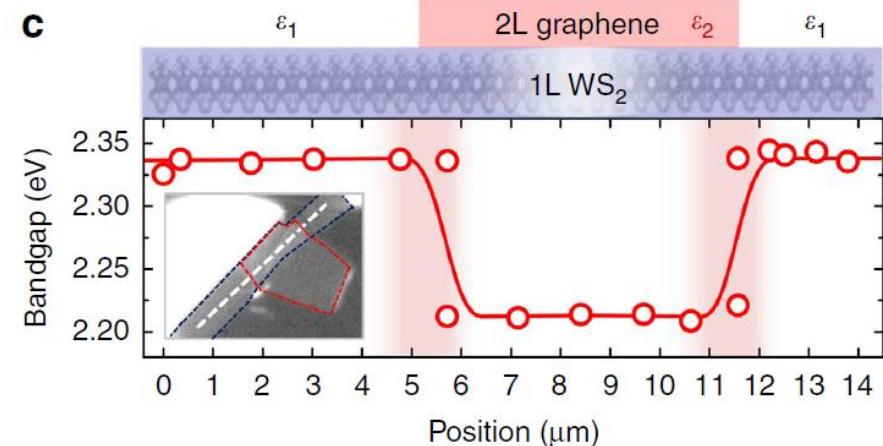
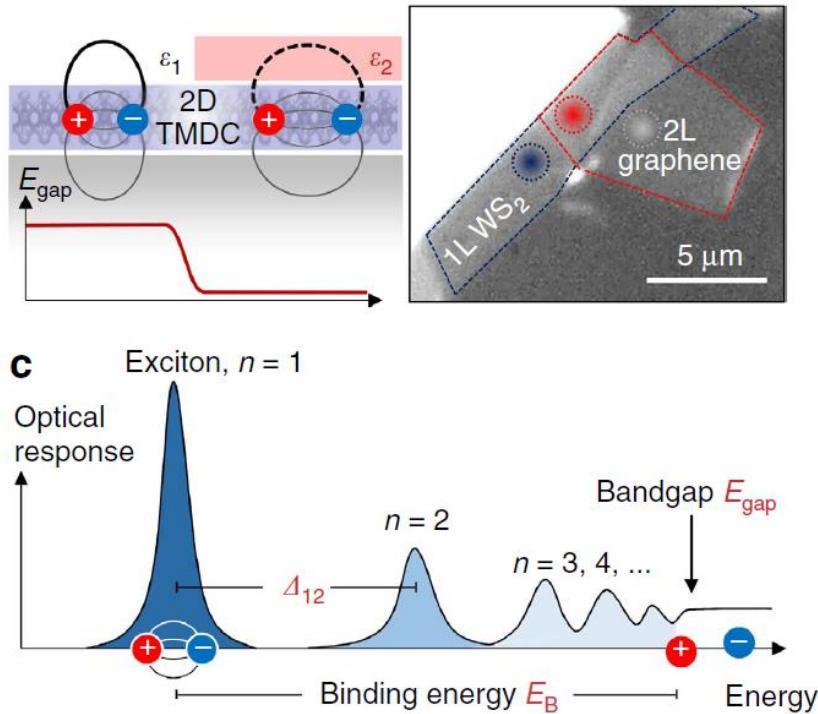
Steinke *et al*, PRB **96**, 045431 (2017)

also...

- Andersen *et al*, Nano Lett. **15**, 4616 (2015)
Latini *et al*, PRB **92**, 245123 (2015)
Kylanpaa & Komsa, PRB **92**, 205418 (2015)

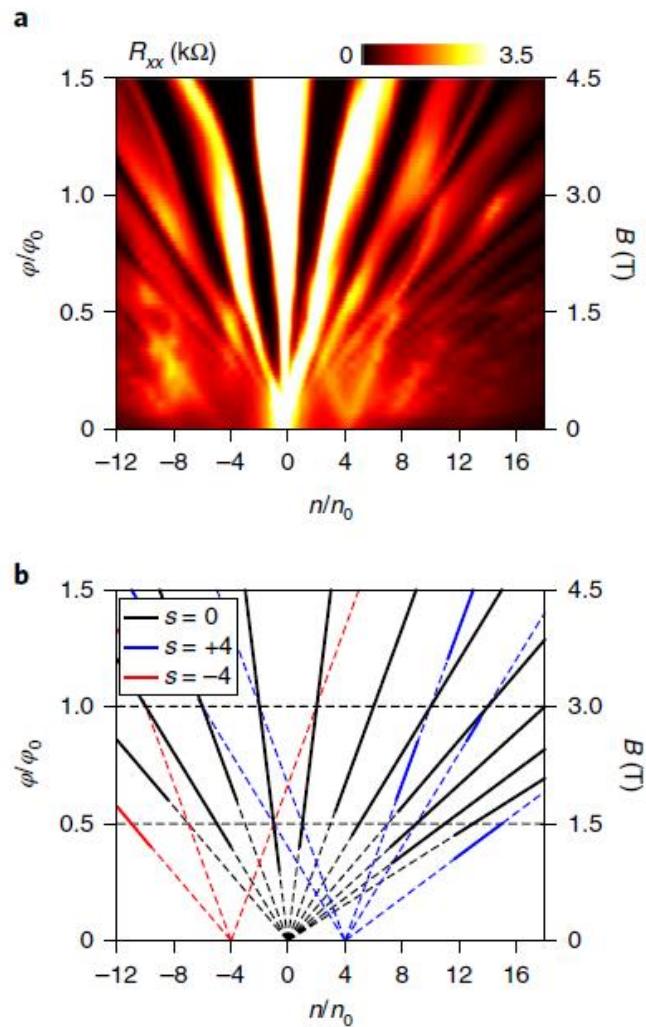
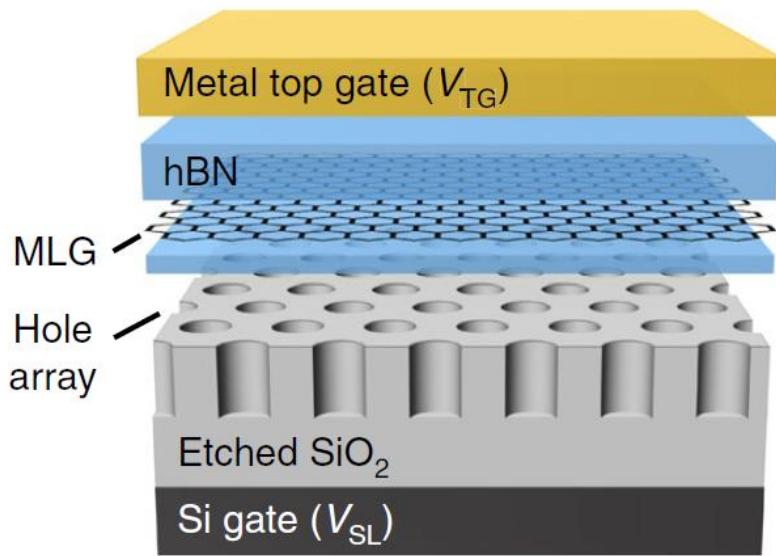
“Coulomb engineering” of monolayer TMDs: experiments

Raja et al, Nature Comm. 8, 15251 (2017)



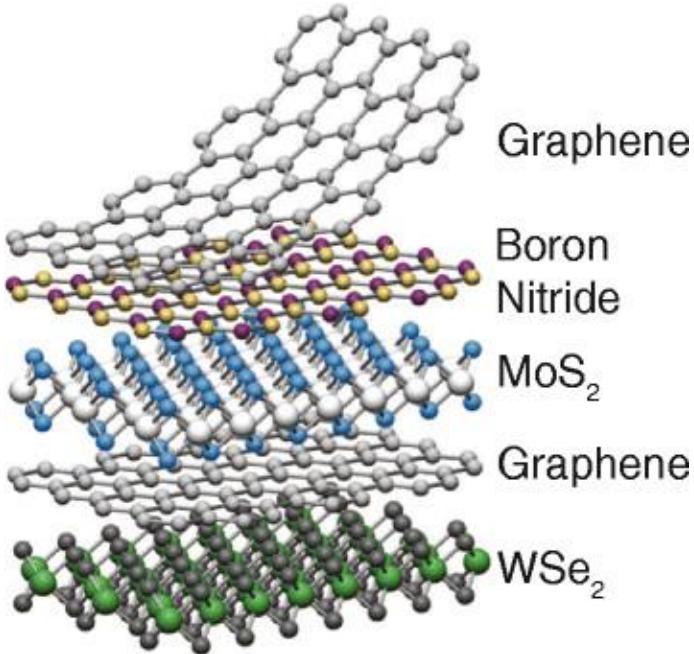
“Coulomb engineering” of monolayer graphene

Forsythe *et al*, Nature Nanotech. 13, 566 (2018)



...and surely more to come...

Monolayer TMDs: *Many fundamental material parameters haven't been experimentally measured/confirmed*

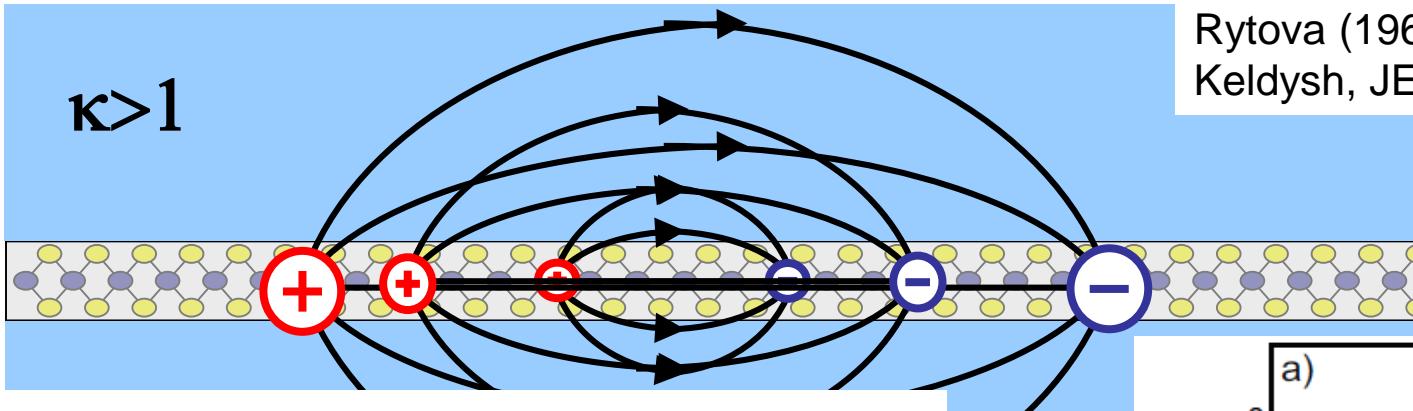


- Electron/hole/exciton mass?
- values come from DFT theory
- e-h electrostatic potential $V(r)$?
- Dielectric screening parameters of a single monolayer?
- mostly from DFT theory

Key point:

All of these material parameters can be experimentally measured by spectroscopy of Rydberg excitons in high magnetic field

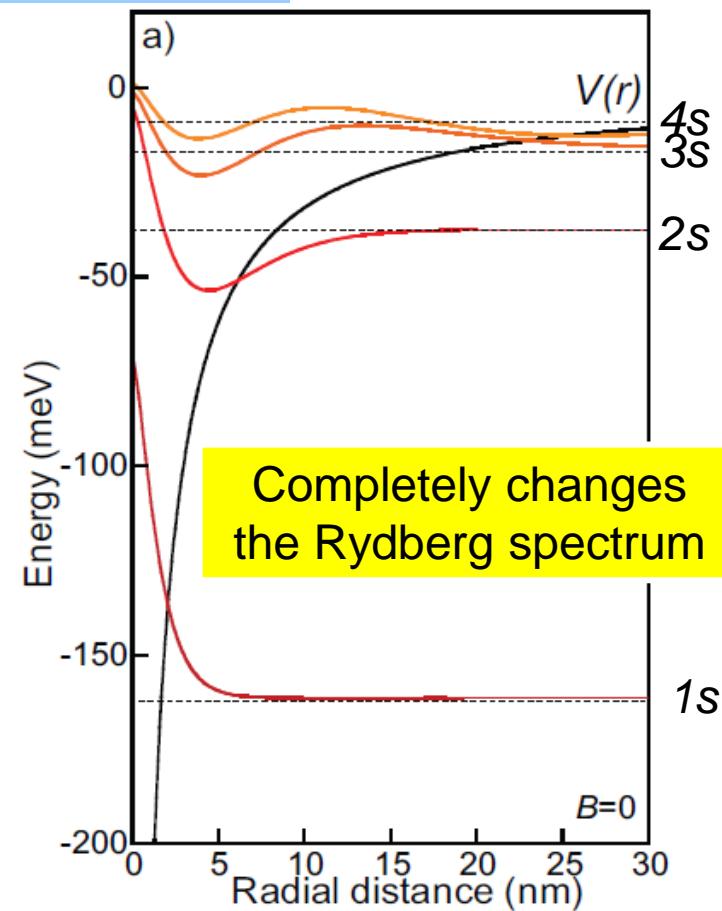
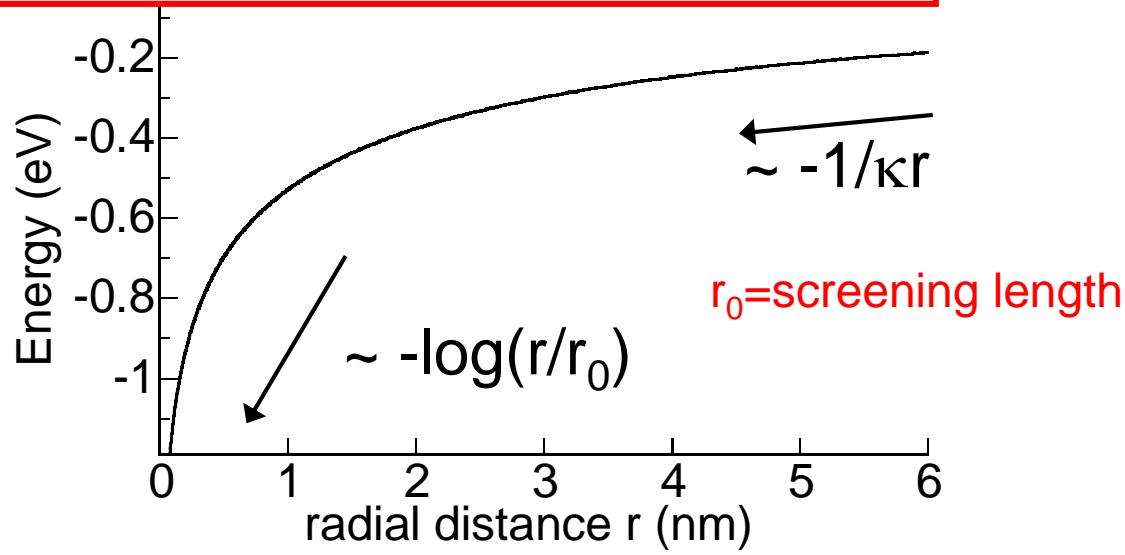
Electrostatic potential $V(r)$ in a 2D semiconductor: not $\sim 1/r$



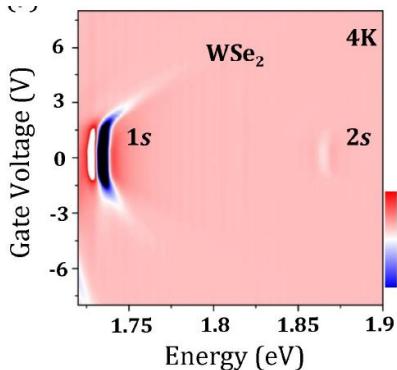
Rytova (1967), arXiv:1806.00976
Keldysh, JETP Lett. **29**, 658 (1979)

Rytova-Keldysh potential:

$$V_K(r) = -\frac{e^2}{8\epsilon_0 r_0} \left[H_0 \left(\frac{\kappa r}{r_0} \right) - Y_0 \left(\frac{\kappa r}{r_0} \right) \right]$$

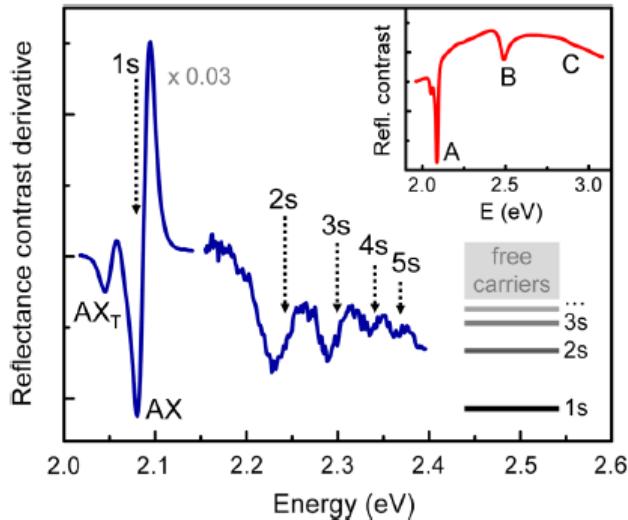


Rydberg (2s, 3s, 4s,...) excitons in monolayer TMDs

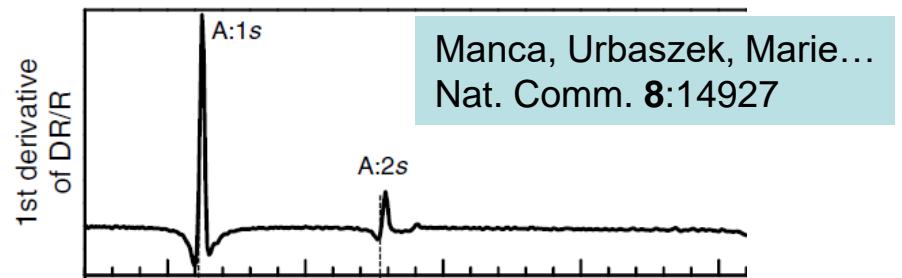


Scharf, Shan, Mak, Dery
arXiv:1606.07101

He, Mak, Shan,...
PRL 113, 026803

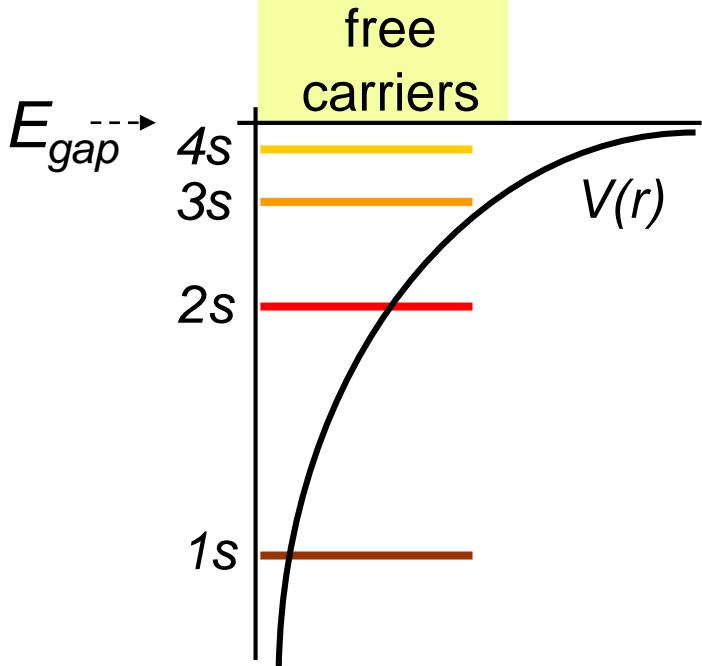
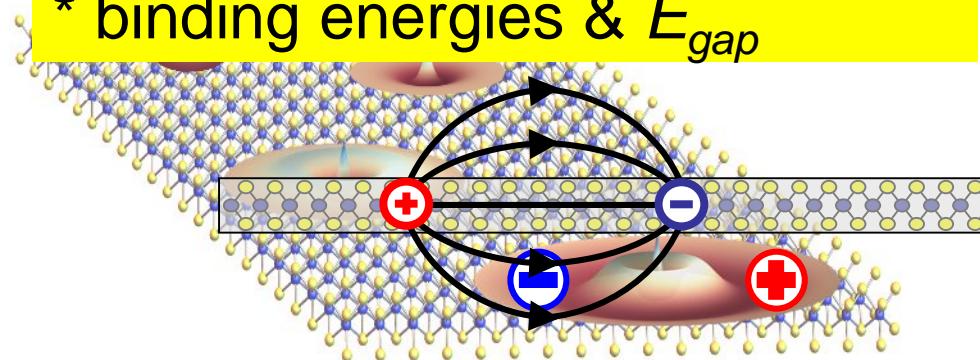


Chernikov, Heinz...
PRL 113, 076802



Rydberg series informs about

- * non-hydrogenic potential $V(r)$
- * binding energies & E_{gap}



Magnetic fields uniquely identify Rydberg excitons

Each Rydberg state has a very distinct diamagnetic shift

“Weak-B regime”
($h\omega_c^* \ll E_B$)

$$\Delta E_{\text{dia}} = \frac{e^2}{8m_r} \langle r^2 \rangle B^2 = \sigma B^2$$

ns excitons uniquely identified by size

2D hydrogenic model:

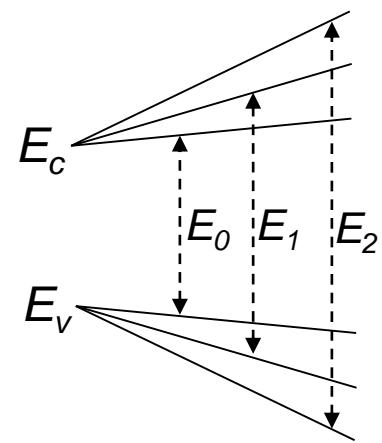
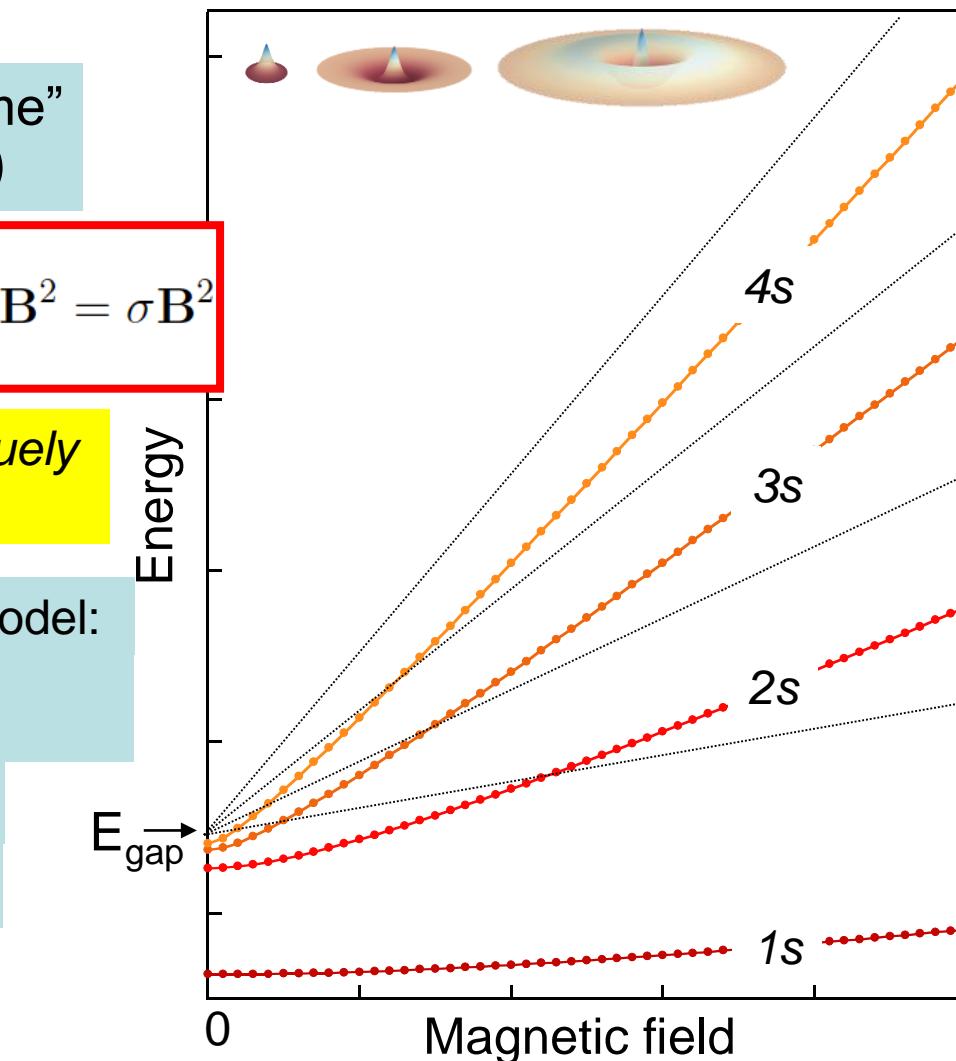
[MacDonald & Ritchie
PRB 33, 8336 (1986)]

$$\sigma_{2s} = 39 \times \sigma_{1s}$$

$$\sigma_{3s} = 245 \times \sigma_{1s}$$

“Strong-B regime”
($h\omega_c^* \gg E_B$)

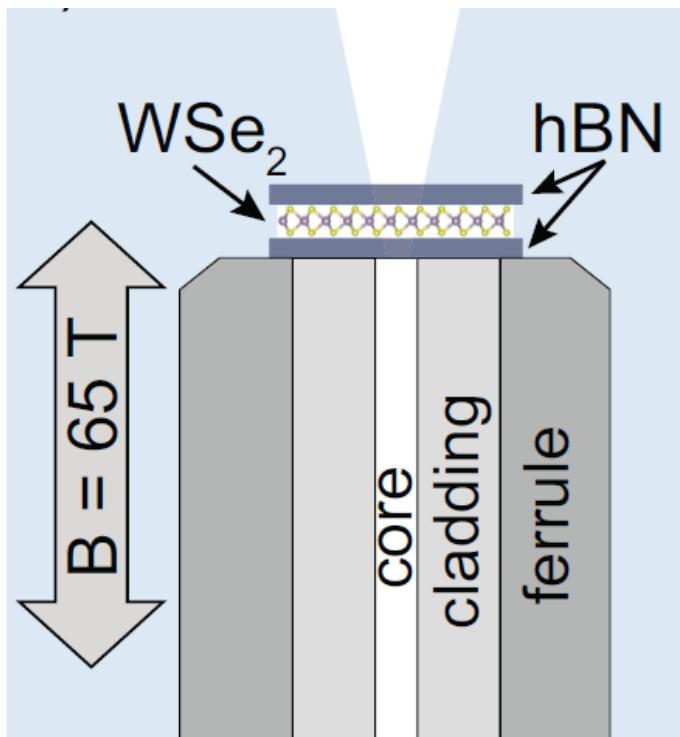
$$\Delta E \sim (N + \frac{1}{2}) h\omega_c^*$$



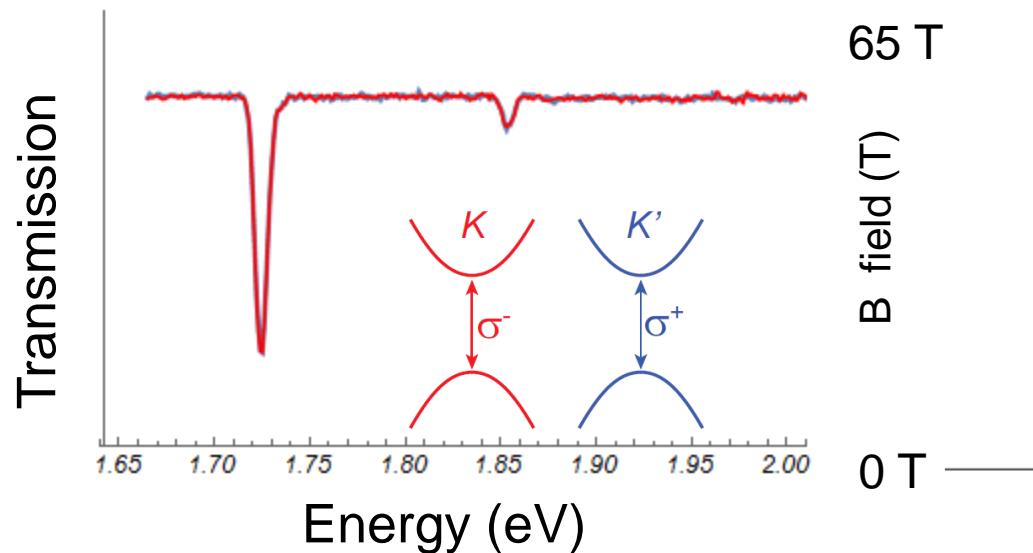
Key point:
Allows to measure reduced mass, m_r

65T magneto-absorption of hBN-encapsulated WSe₂

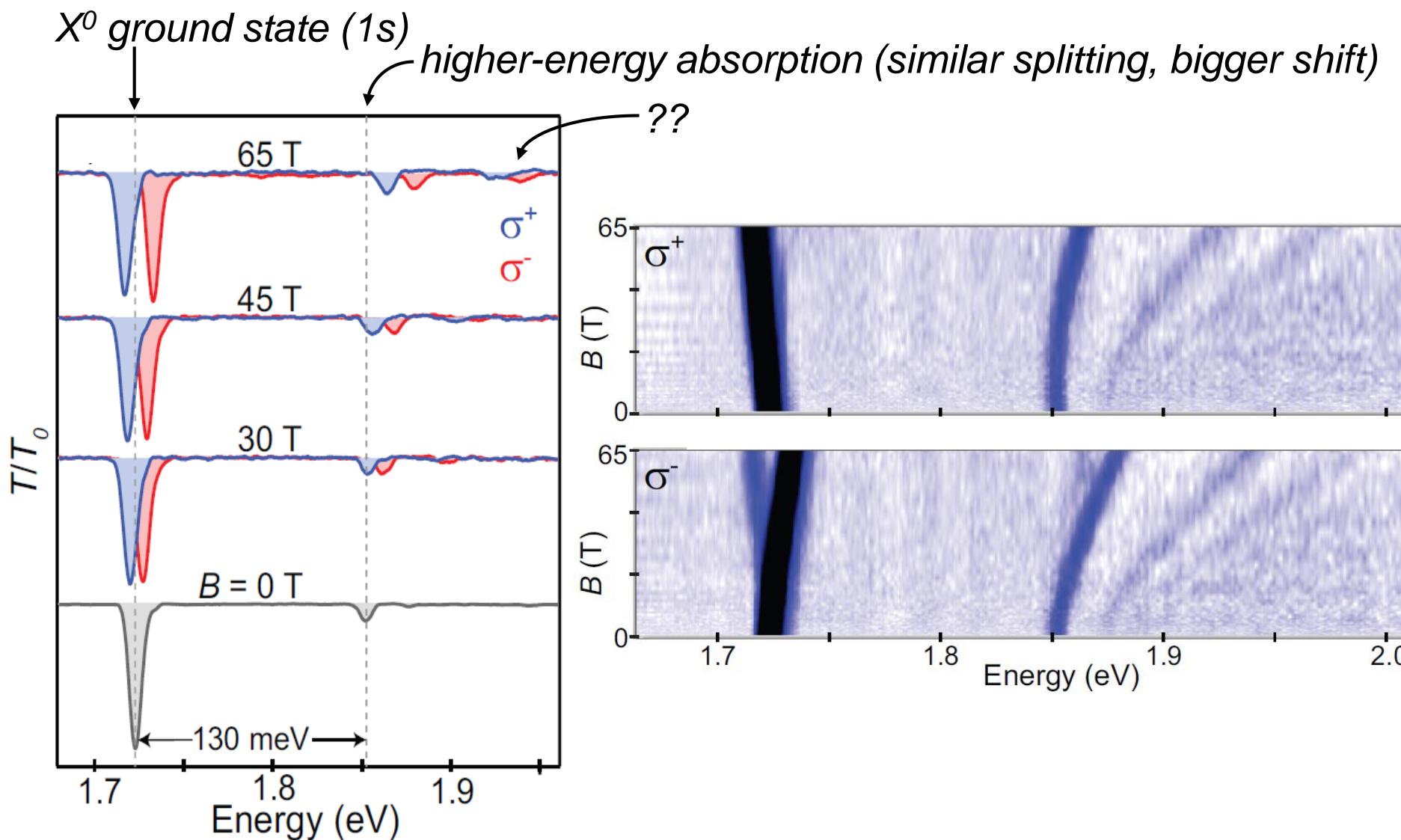
Transfer hBN/WSe₂/hBN over a singlemode optical fiber
(for mechanical stability – no drifts or vibrations)



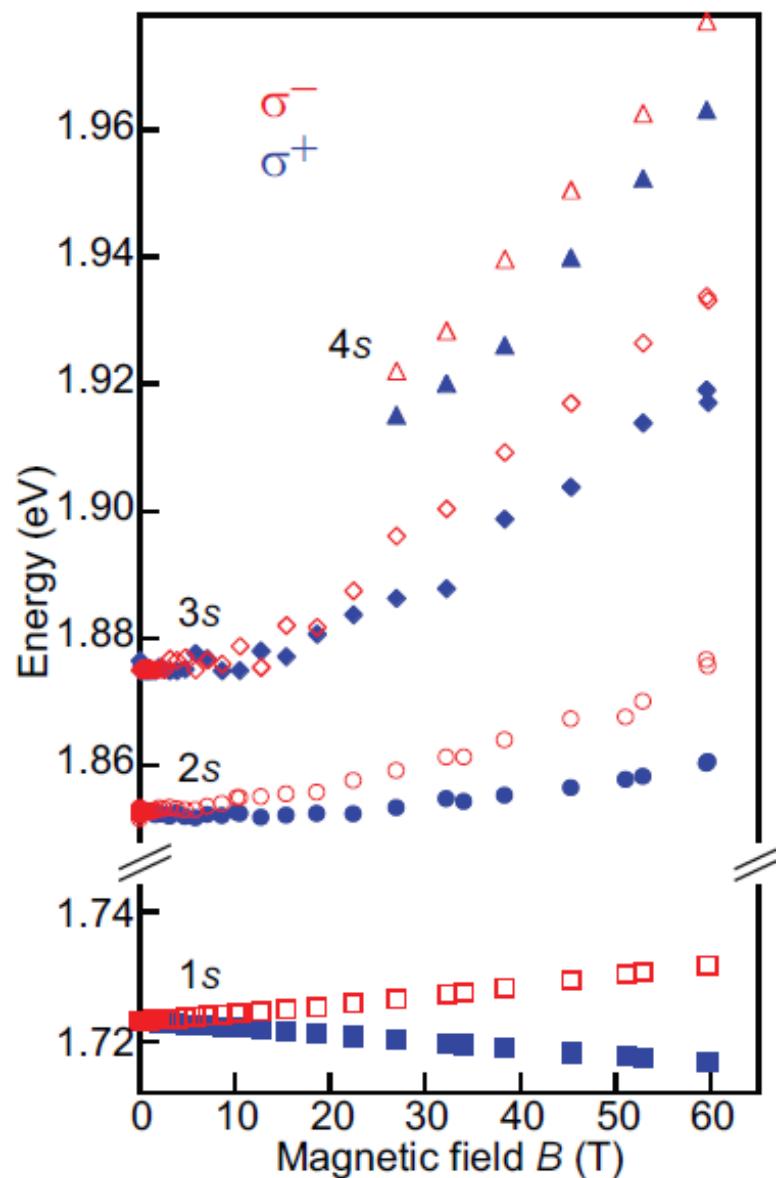
Nathan Wilson (UW), Andreas Stier



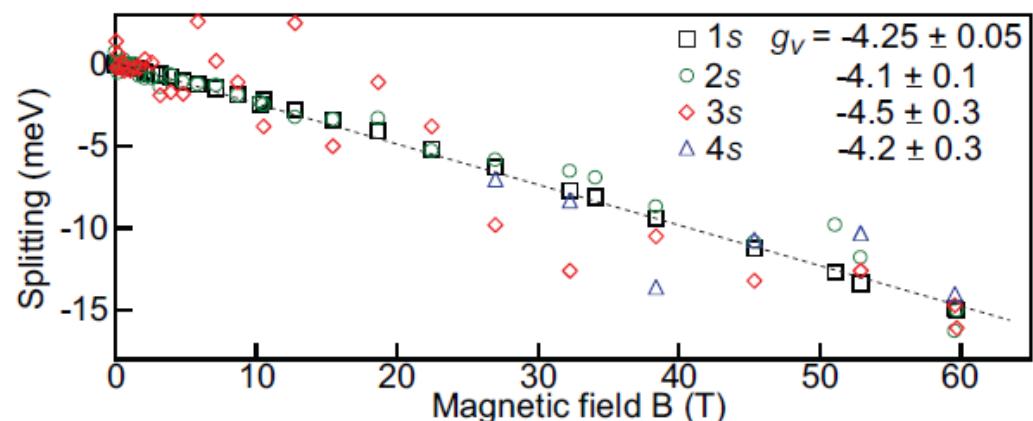
Rydberg states of neutral excitons in WSe₂



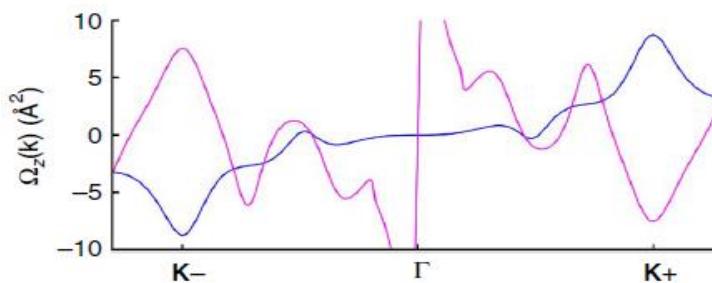
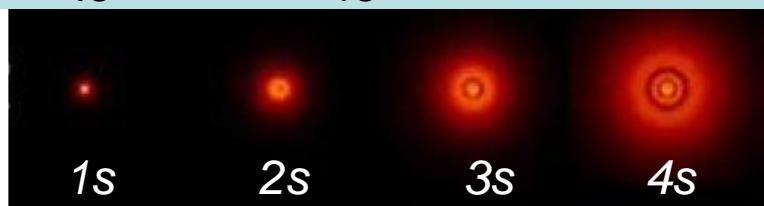
ns Rydberg excitons in WSe₂ – valley Zeeman effects



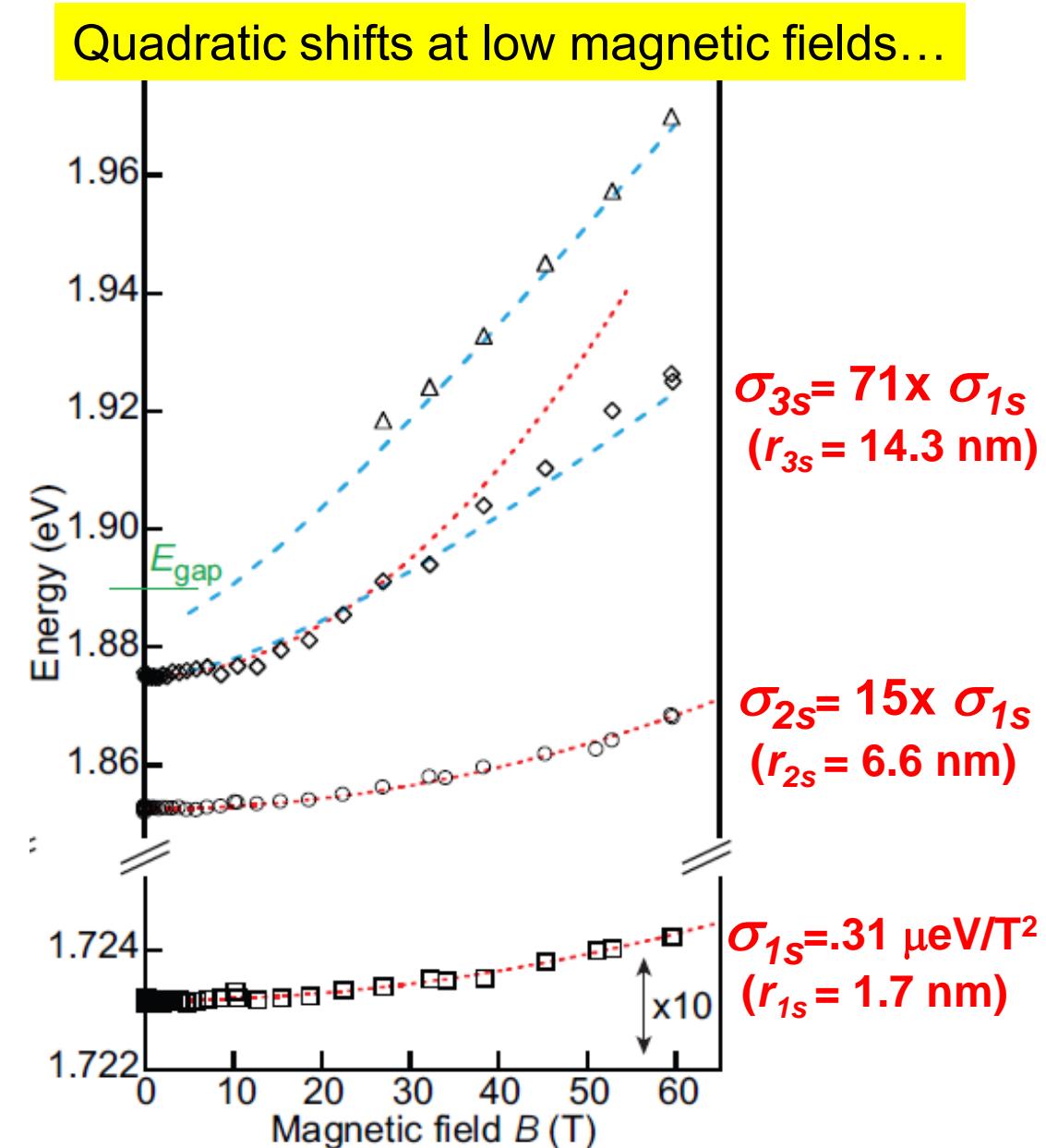
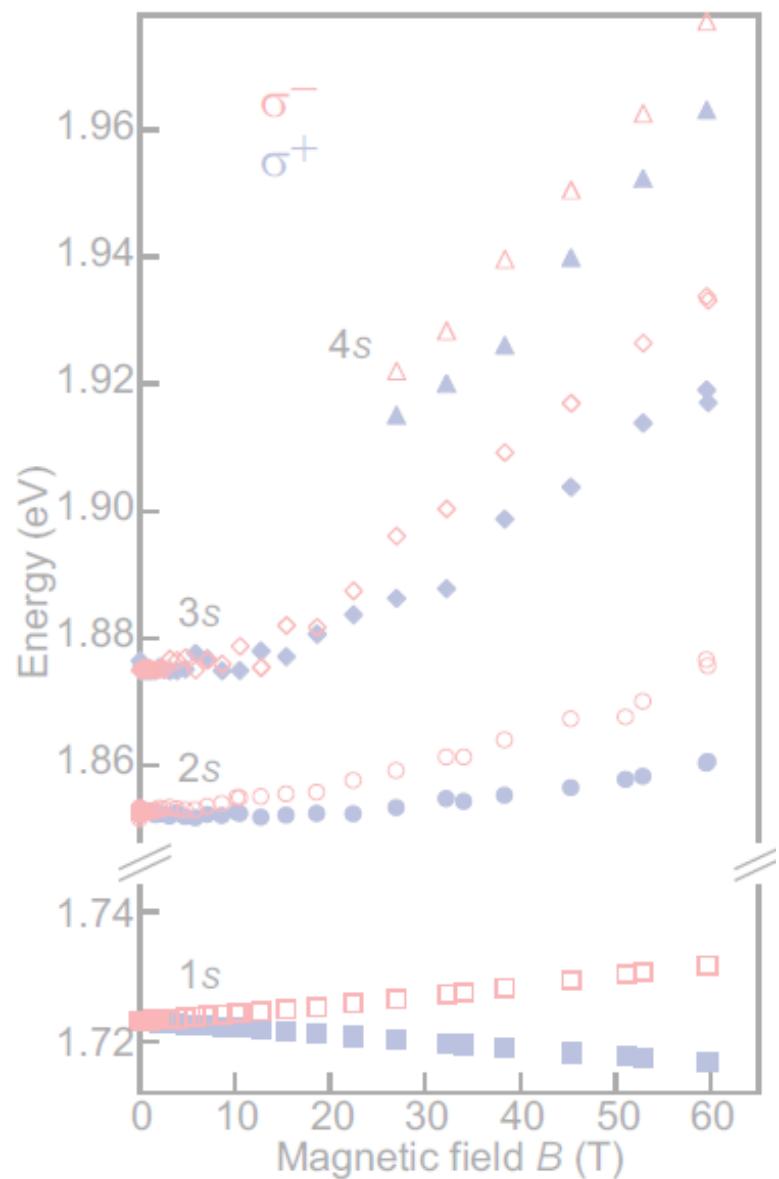
Similar valley Zeeman effect for 1s, 2s, 3s, 4s



...but r_{4s} is $>10 \times r_{1s}$ (& $>100 \times$ area)!

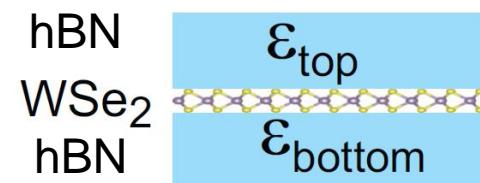


Diamagnetic shifts of ns Rydberg excitons in WSe₂



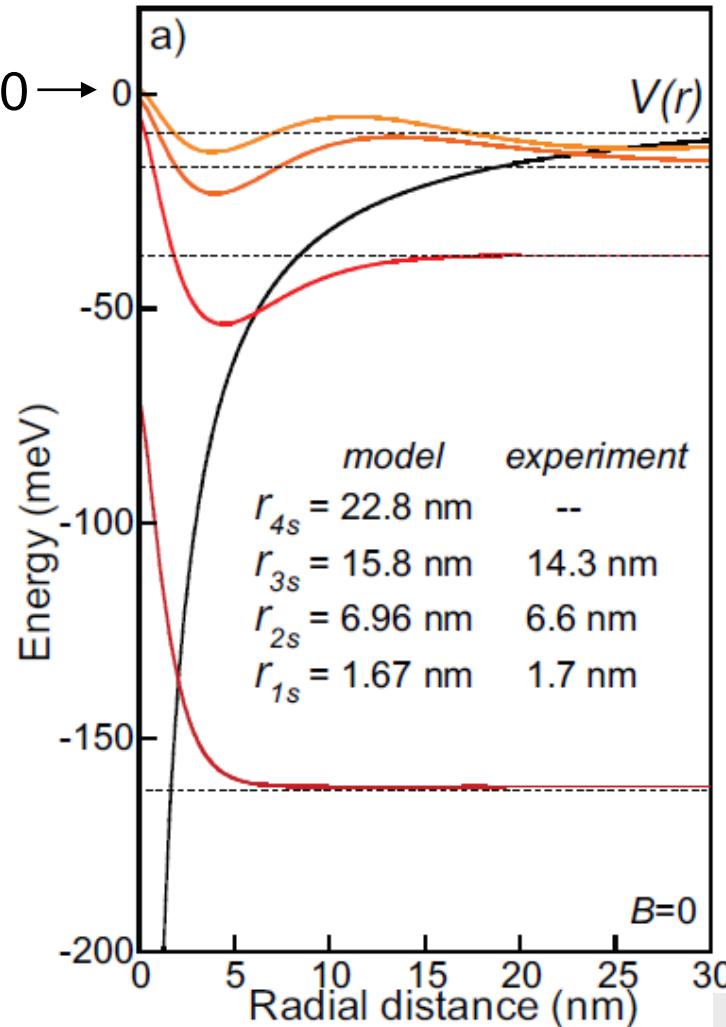
(Surprisingly) good agreement w/ ‘Rytova-Keldysh’ potential

$$V_K(r) = -\frac{e^2}{8\varepsilon_0 r_0} \left[H_0 \left(\frac{\kappa r}{r_0} \right) - Y_0 \left(\frac{\kappa r}{r_0} \right) \right]$$



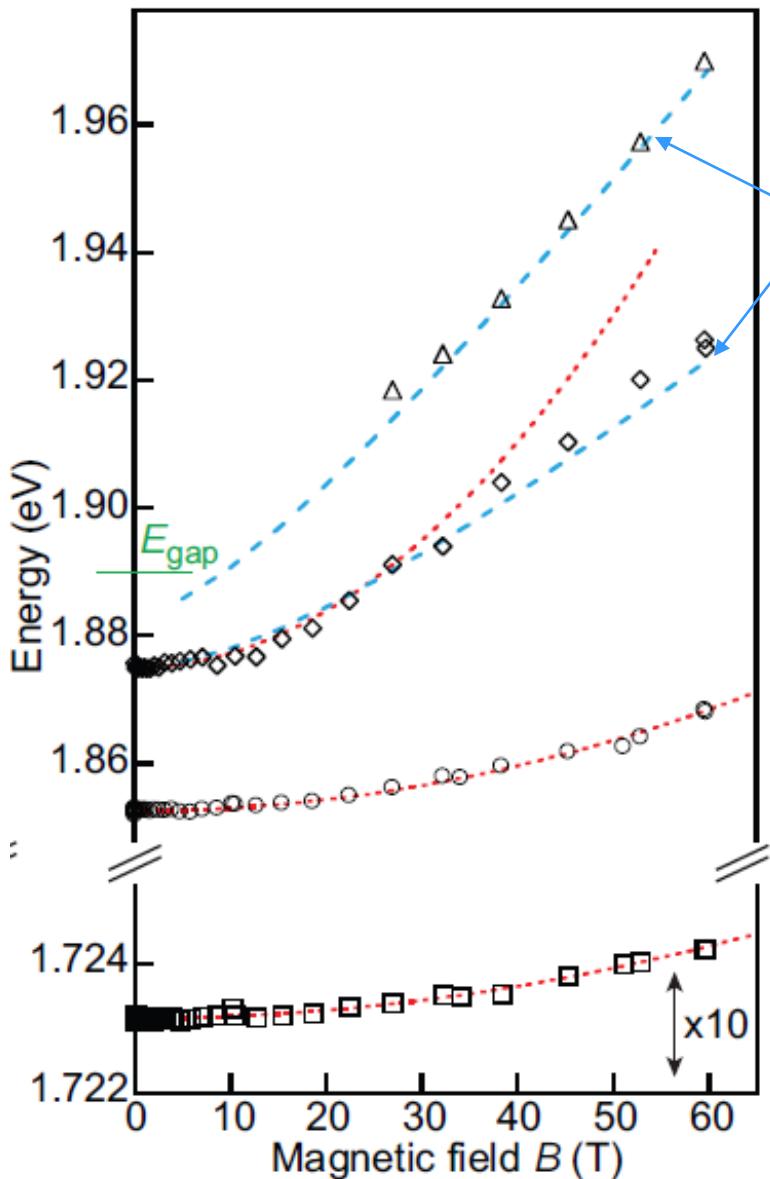
$$\kappa = (\varepsilon_t + \varepsilon_b)/2$$

$$E_{\text{gap}} = 1.890 \rightarrow 0$$



- ✓ Radii
- ✓ Energies
- ✓ E_{gap}

High-field shifts of 3s & 4s : Exciton reduced mass



$$H^{(s)} = -\frac{\hbar^2}{2m_r} \left(\partial_r^2 + \frac{1}{r} \partial_r \right) + \frac{e^2 B^2}{8m_r} r^2 + V_K(r)$$

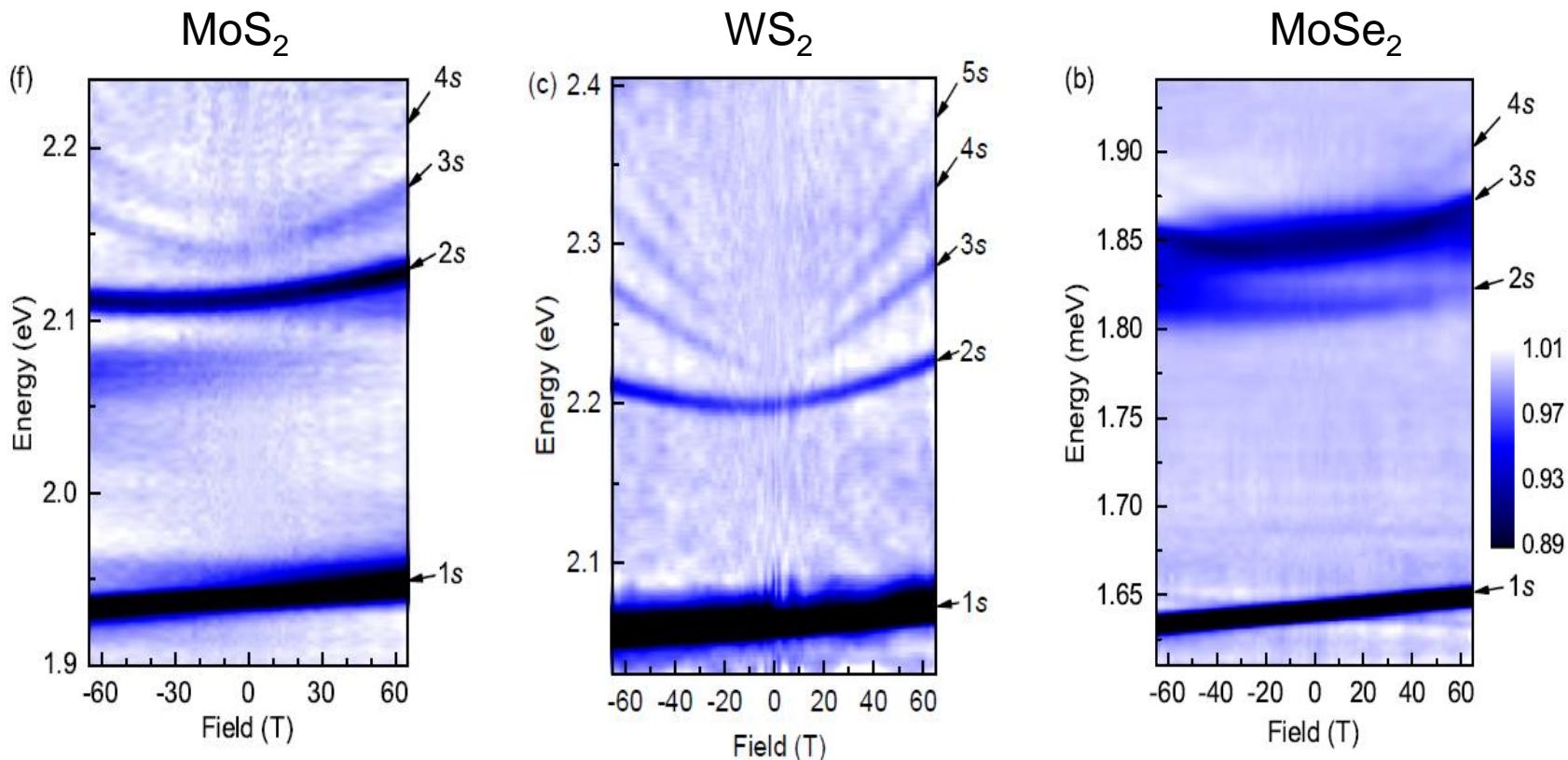
$$m_r = 0.20 \pm 0.01 m_0$$

Direct experimental measure of
reduced mass of X^0 in WSe_2
[DFT theory: $\sim 0.18 m_0$]

Very recent measurements of MoS₂, MoSe₂, WS₂

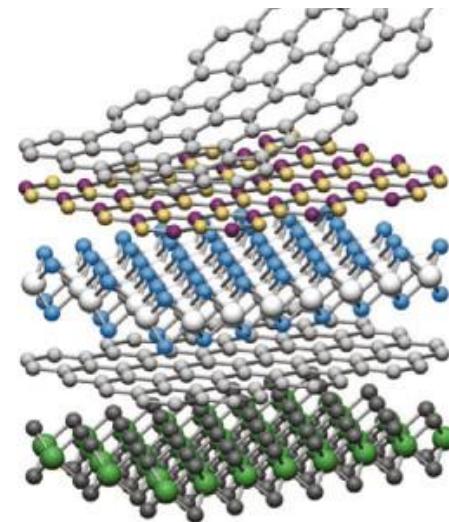
Goryca et al, arXiv:1904.03238

Material	m_r (m_0)	E_b (meV)	E_{gap} (eV)	κ	r_0 (nm)	r_{1s} (nm)
hBN MoS ₂ hBN	0.275 ± 0.015	221	2.160	4.45	3.4	1.2
hBN MoSe ₂ hBN	0.350 ± 0.015	231	1.874	4.4	3.9	1.1
hBN WS ₂ hBN	0.175 ± 0.007	180	2.238	4.35	3.4	1.8
hBN WSe ₂ hBN*	0.20 ± 0.01	167	1.890	4.5	4.5	1.7



Summary

- **Opto-electronics in monolayer TMD semiconductors**
 - *Excitons are small and tightly bound (200-500 meV)*
 - *E_B and free-particle gap always depend on dielectric environment*
 - *“Coulomb Engineering” in monolayer TMDs via (patterned) dielectrics*
- **High B fields: an important tool for 2D semiconductors**
 - *Quantify role of dielectric environment*
 - *identify & quantify excited Rydberg states*
 - *direct measure of mass, screening length, free-particle gap, test models of $V(r)$*



Stier et al, Nano Lett. (2018)

Stier et al, PRL 120, 057405 (2018)

Goryca et al, arXiv:1904.03238