4. Atomically-thin semiconductors

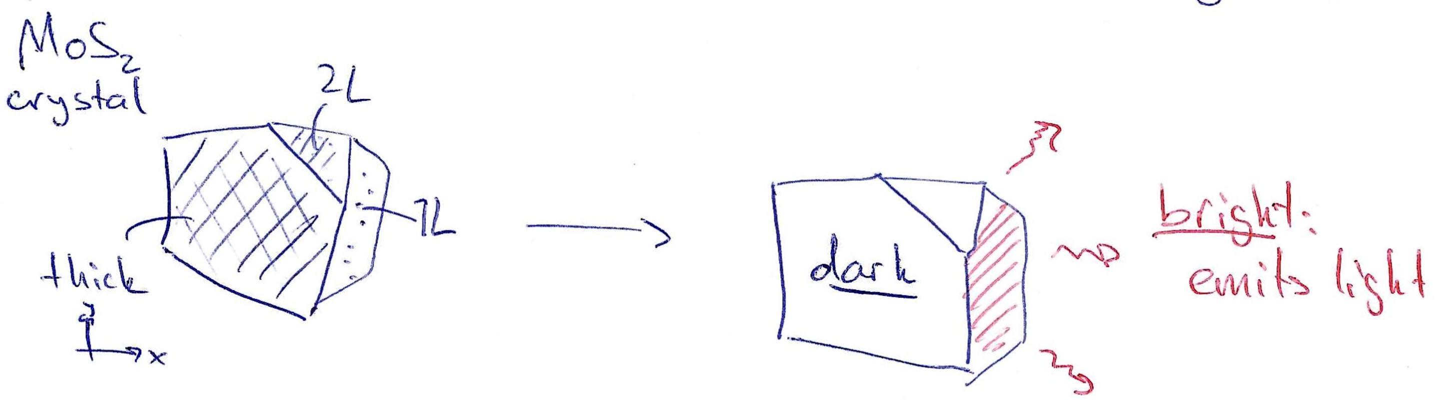
- materials for opto-electronics, photonics, valleytronics* (valley-index as information carrier), and twistronics* (rotation angle to tune material properties)

- strong electronic interations & light-matter coupling (=> fundamental solid state physics)

main representatives: transition metal dichalcogenides (TMDCs: MoS_2, WSe_2, ...)

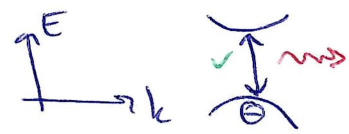
① Initial observation:

|| Only monolayers are efficient light emitters



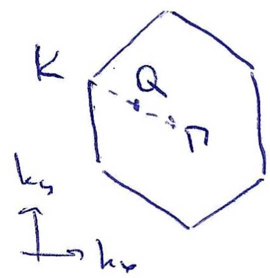
- reason: → Bulk, 4L, 3L, 2L .. are indirect semiconductors

→ 1L are directs semiconductors

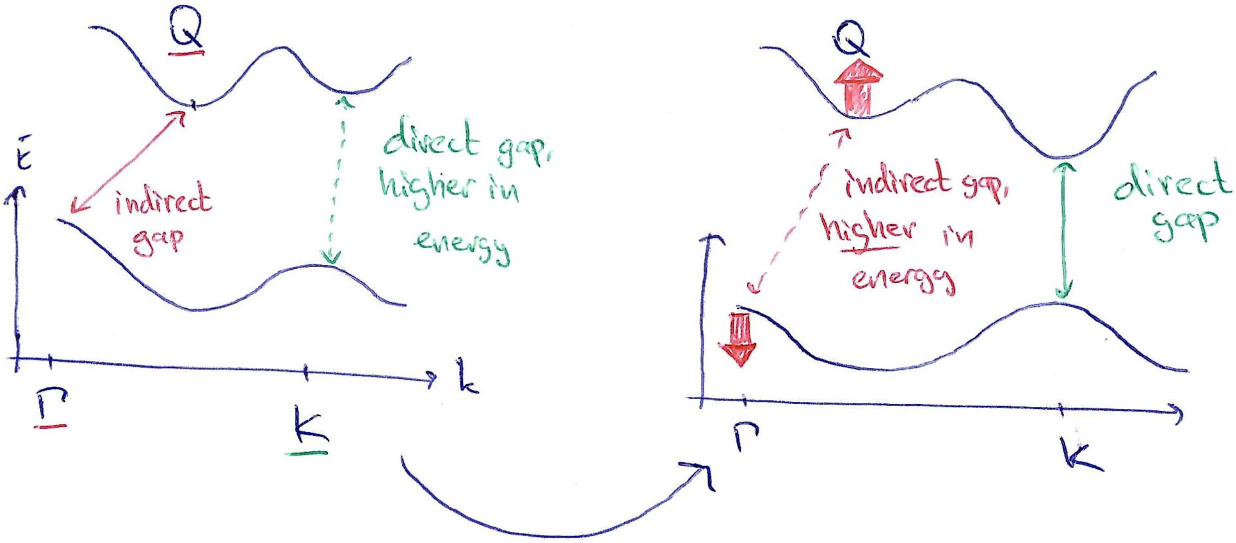


② Indirect-to-direct transition

Q: „Why does it happen?"



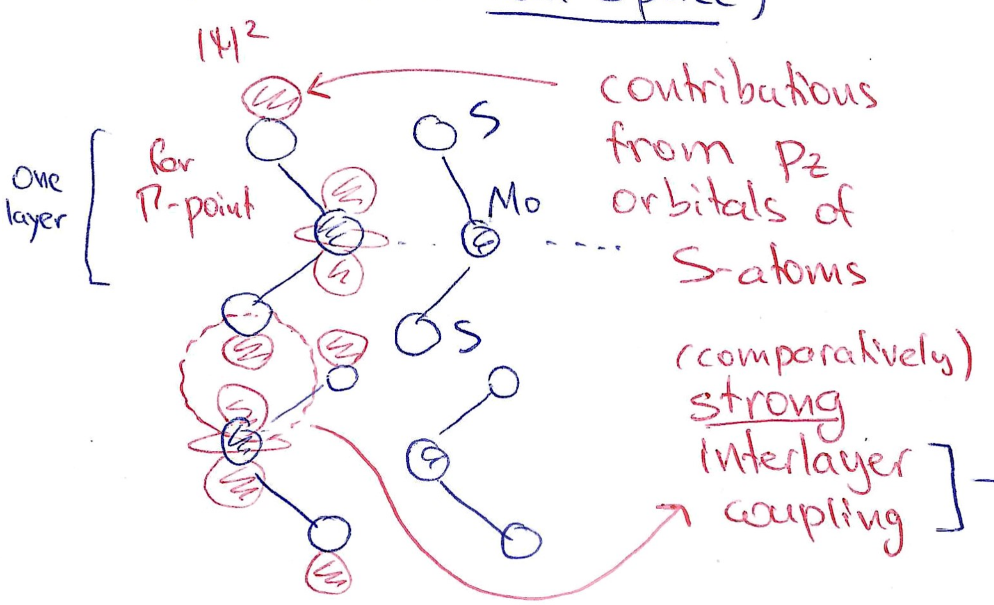
Bulk, ..., 2L — 1L

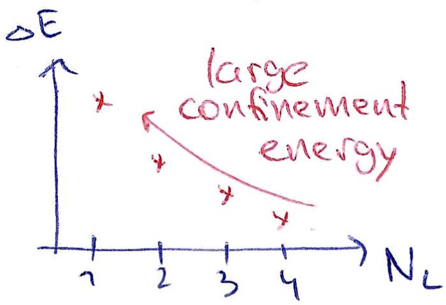


- indirect gap increases
- direct gap remains unaffected

Why?

↳ indirect gap: electron states at Γ and Q points:
(wavefct. in real space)

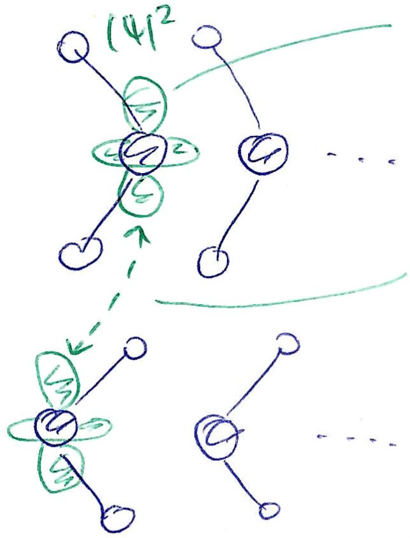




$\Delta E \sim \frac{n}{m L^2}$

(comparatively) strong interlayer coupling → small effective mass in z-direction

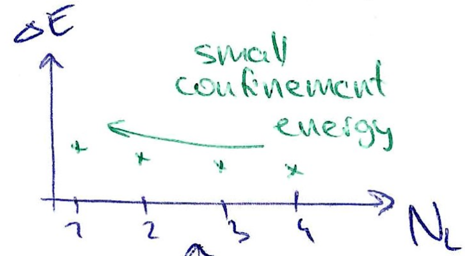
↳ **direct gap** : electron states at $\underline{K}$ points



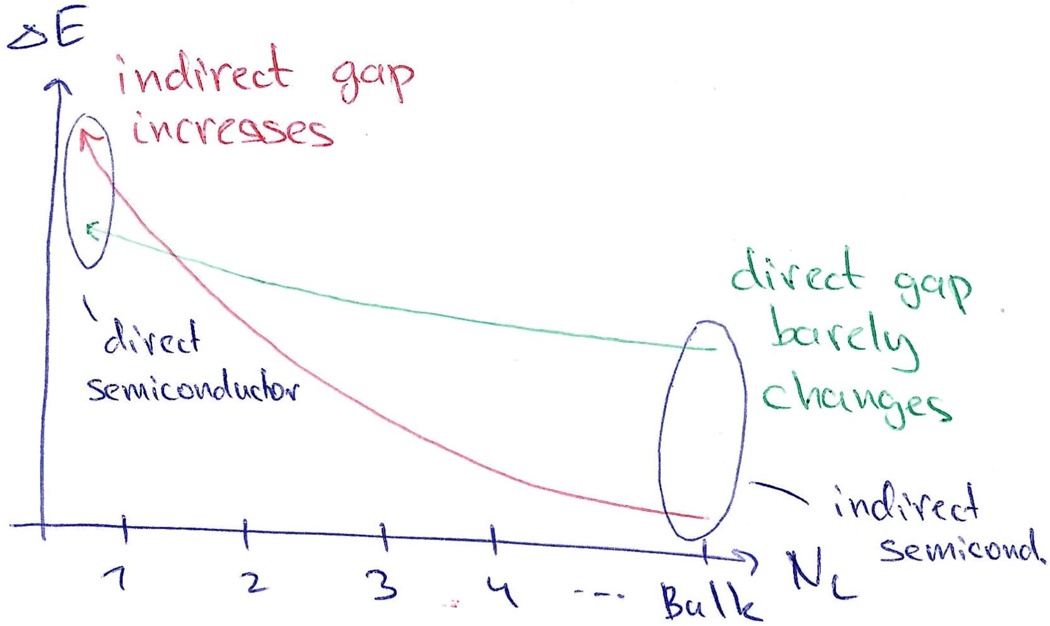
d-orbitals of Mo-atoms

no spatial overlap, *weak* interlayer coupling] → large effective mass in z-direction

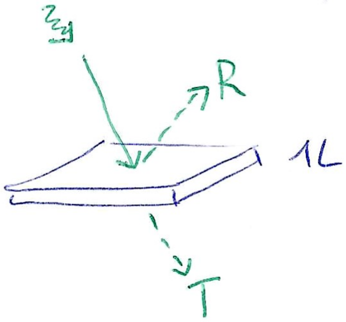
$\Delta E \approx \frac{h}{mL^2}$



→ to summarize

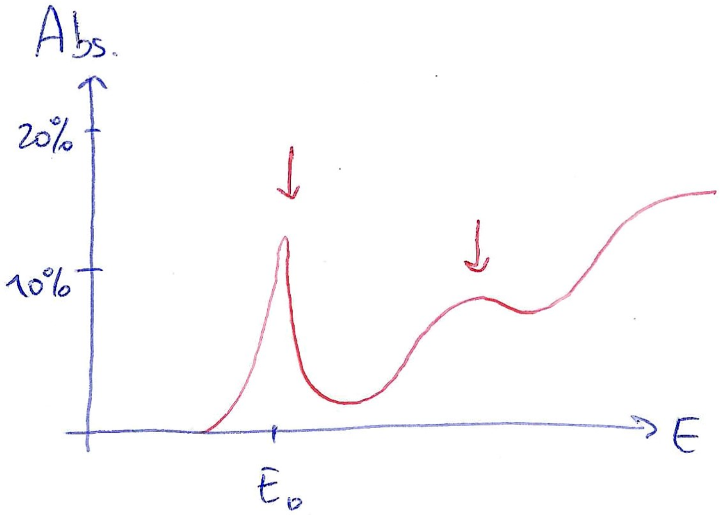


③ Optical absorption of TMDC monolayers

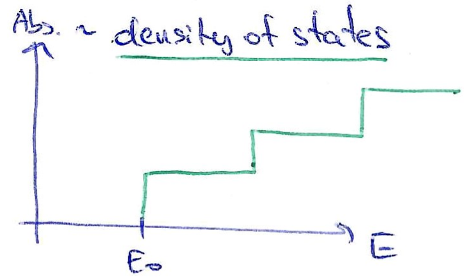


$$\underset{\text{absorption}}{A} = 1 - R - T$$

→ typical spectrum at room temperature

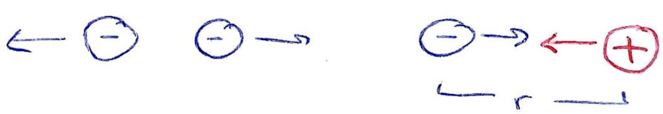


vs. expectation from non-interacting 2D electrons:



→ interactions between electrons (and holes) are strong:

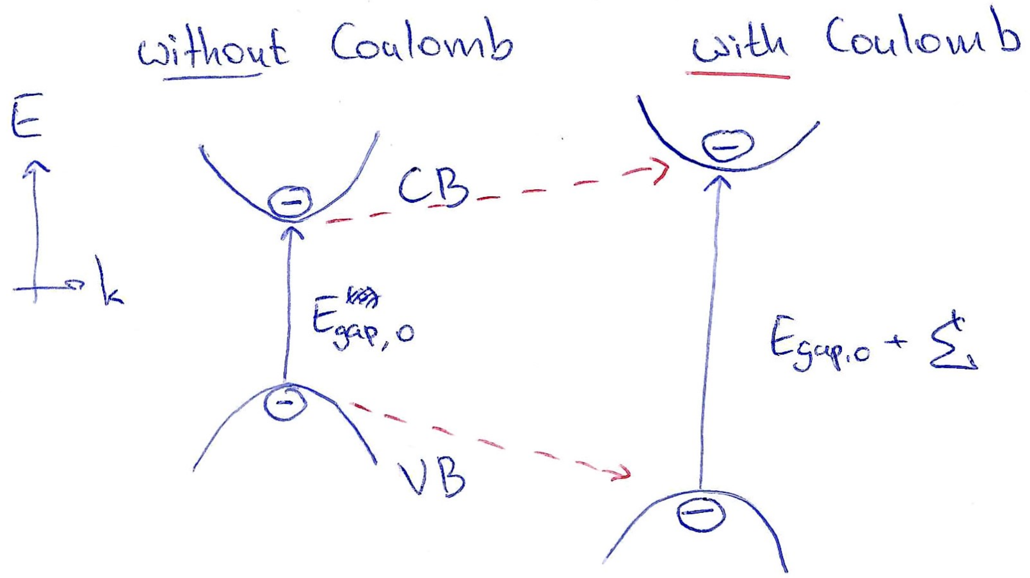
Coulomb forces:



$$\left[\vec{F} \sim \frac{e^2}{r^2} \quad (\text{in 3D}) \right]$$

→ Strong Coulomb interactions lead to renormalization (= change) of energies & formation of new quasiparticles

Bandgap renormalization

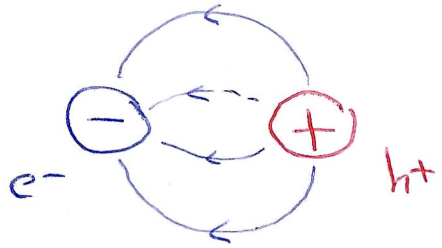


↳ energy required to excite an e^- from valence to conduction band increases due to e^--e^--interactions (contribution Σ, typically $\Sigma < E_{gap,0}$)

↳ effective size of the bandgap depends on the strength of Coulomb interaction

New quasiparticles: Excitons

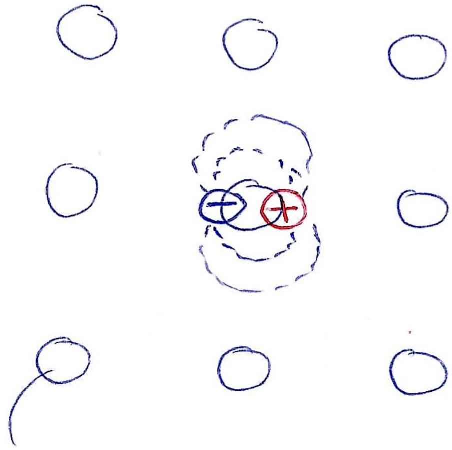
Excitons := Coulomb-bound electron-hole pairs (from attractive interaction)



↳ often determine optical properties of semiconductors

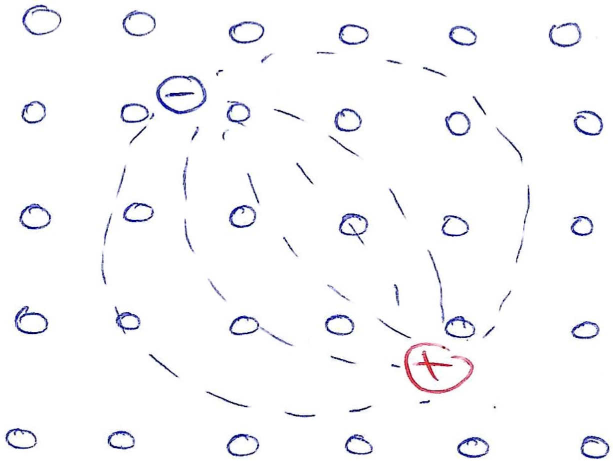
- generally two main types of excitons:

Frenkel exciton vs. **Wannier-Mott exciton**



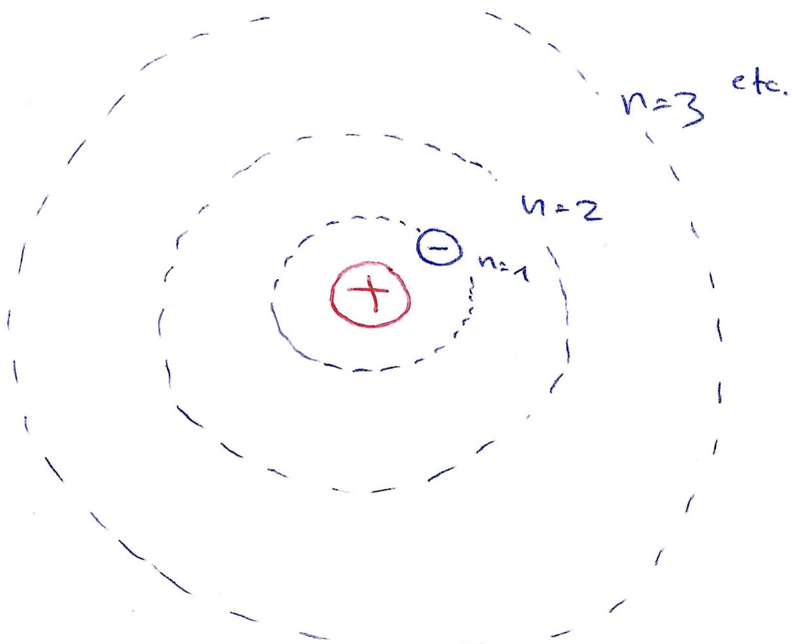
molecule / unit cell in a crystal

vs.



- localized on one unit cell
- delocalized over many unit cells

→ in 2D materials excitons can share both Frenkel & Wannier properties, yet can be often described accurately in Wannier picture:



≙ hydrogenic model = similar to proton+electron problem

→ However in contrast to H-atom, exciton are composed of e^- and h^+ quasiparticles with effective masses m^* that are located in a solid state environment with increased dielectric screening ε

↳ Binding energies* in 2D can be approximated as:

* how strong e^- and h^+ are bound

$$E_{bind} = \frac{R_y}{(n-\frac{1}{2})^2} \times \frac{\mu}{\varepsilon^2} \qquad (R_y \approx 13.6\,eV)$$

- $\frac{1}{(n-\frac{1}{2})^2}$ from 2D dimensionality
- $\mu = \left(\frac{1}{m_e} + \frac{1}{m_h}\right)^{-1}$ reduced effective mass
- ε: dielectric screening constant of the environment

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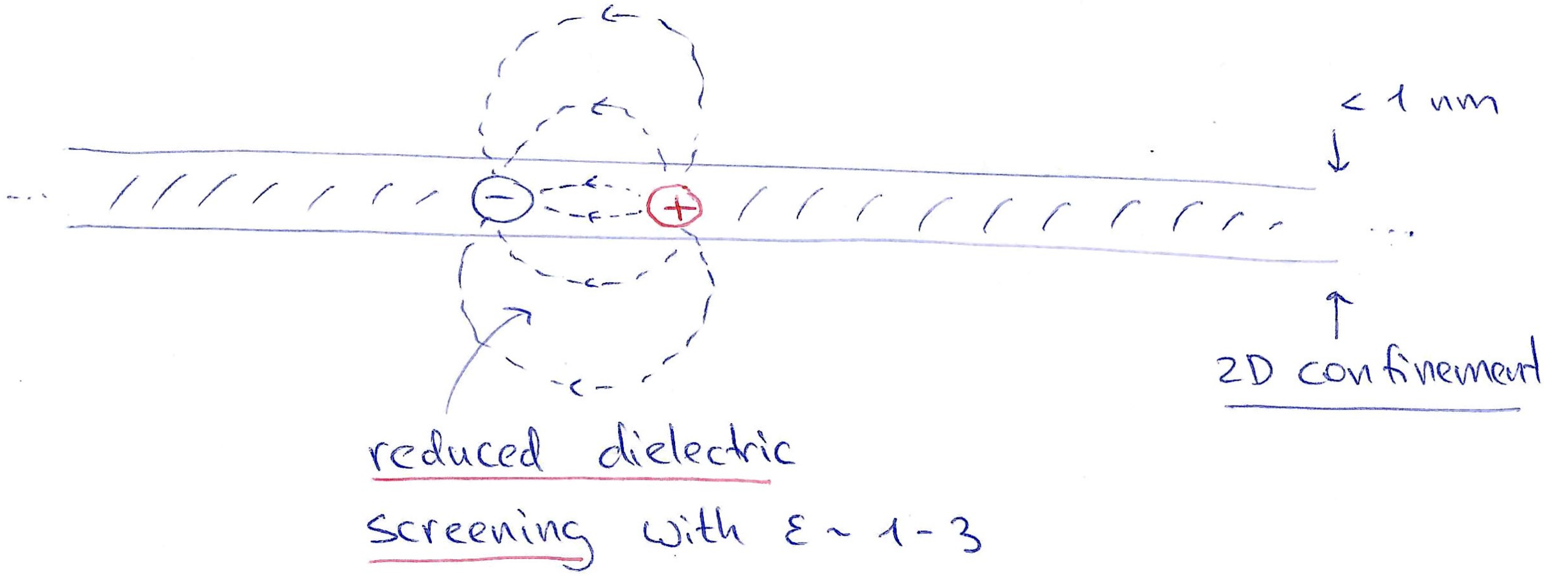
*typical values for quantum wells (e.g. GaAs): $\mu \sim 0.1\, m_0$, $\varepsilon \sim 10$ → $E_{bind} \sim$ 10's of meV $\ll E_{gap}$, $\leq k_B T$

→ excitons in monolayer materials

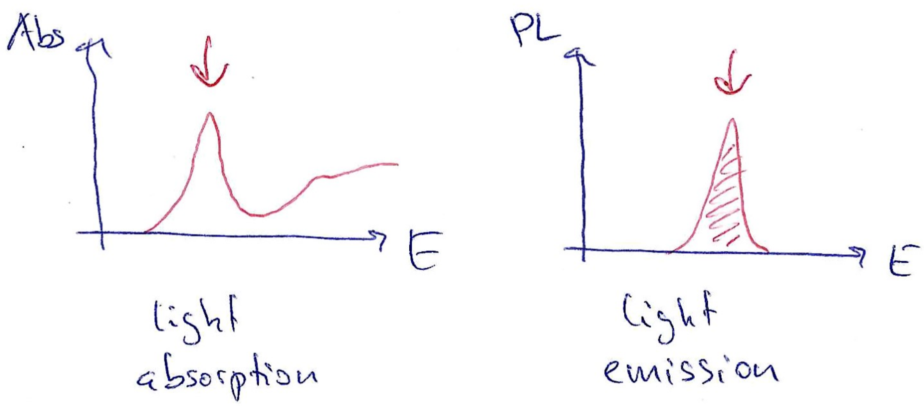


→ binding energies are very large, 0.2 - 0.5 eV ($\gg k_B T$)

④ Measuring Coulomb effects

Option 1: Combine optics & electron transport

↳ Exciton ground state from optical spectra

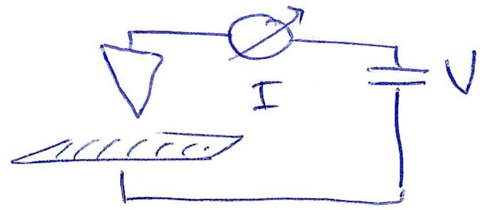


✓

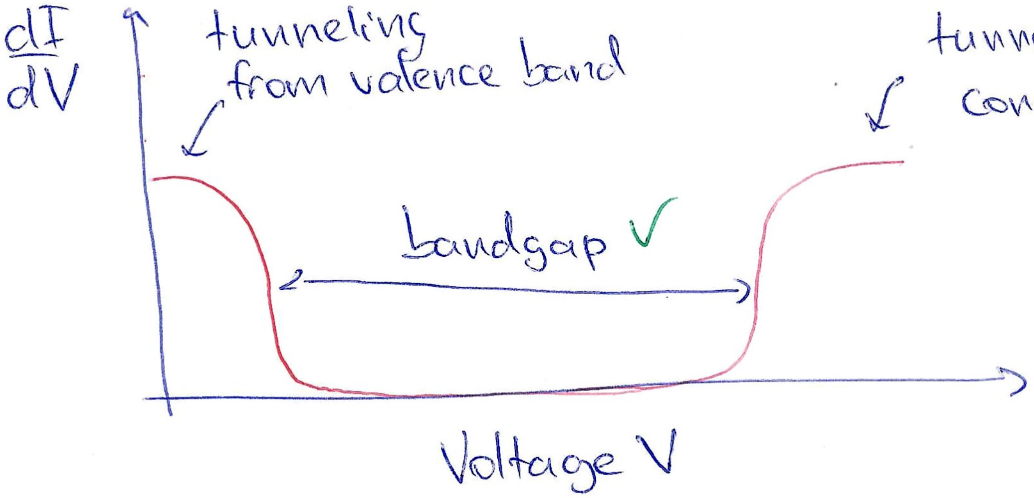
9/

↪ electronic bandap from <u>scanning tunneling spectroscopy</u>* ✓

tunes the possibility to tunnel through possible transitions ~~into~~ from occupied into unoccupied states

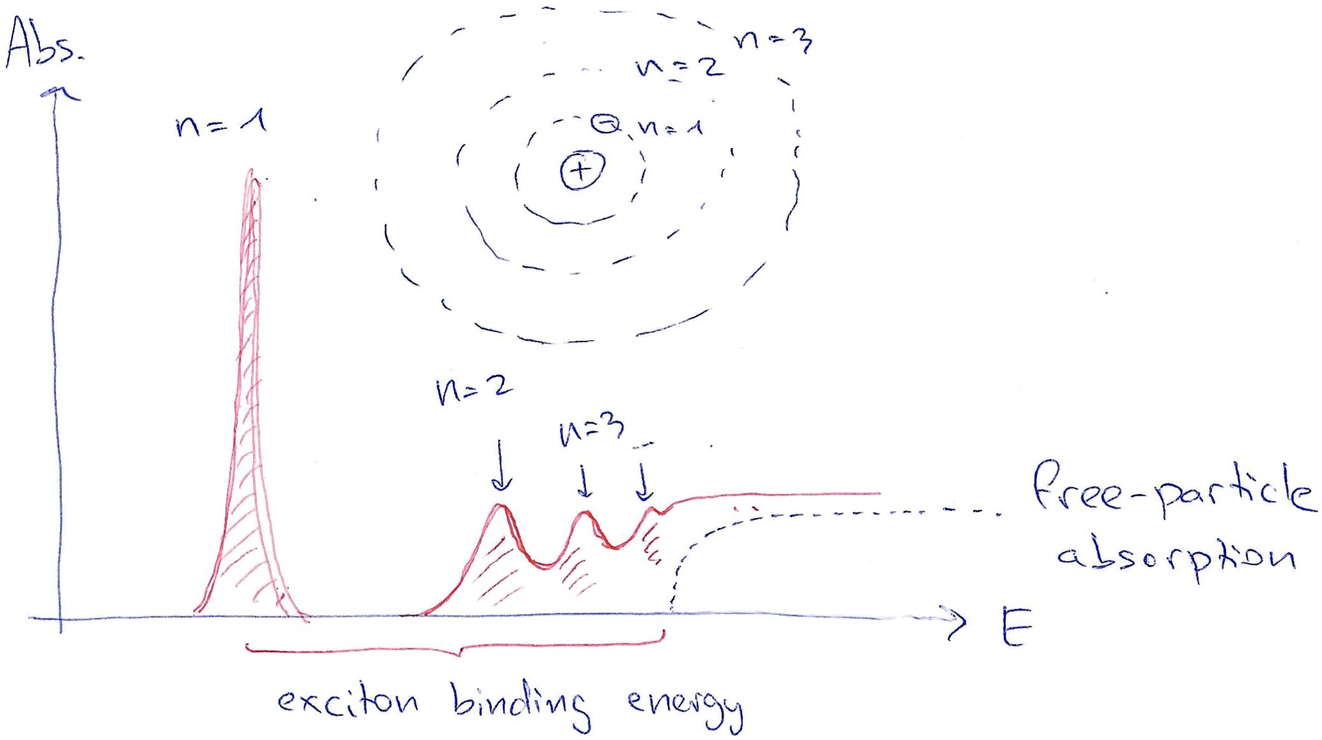


* := I(V) one one position



$E_{binding} = E_{bandgap} - E_{exciton}$

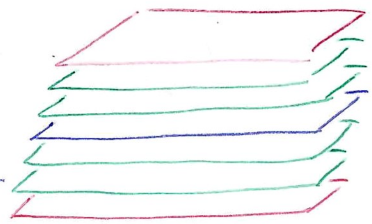
Option 2: Measure <u>excited</u> exciton states



(4) Heterostructures

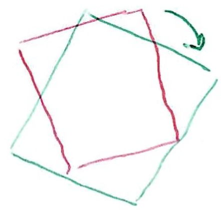
↝ artificial combinations of different materials (including layered systems) has a rich history of research (e.g. quantum wells, organic blends, etc..)

↝ Van der Waals crystalls offer an excellent platform to combine different materials due to <u>relaxed lattice matching requirements</u>

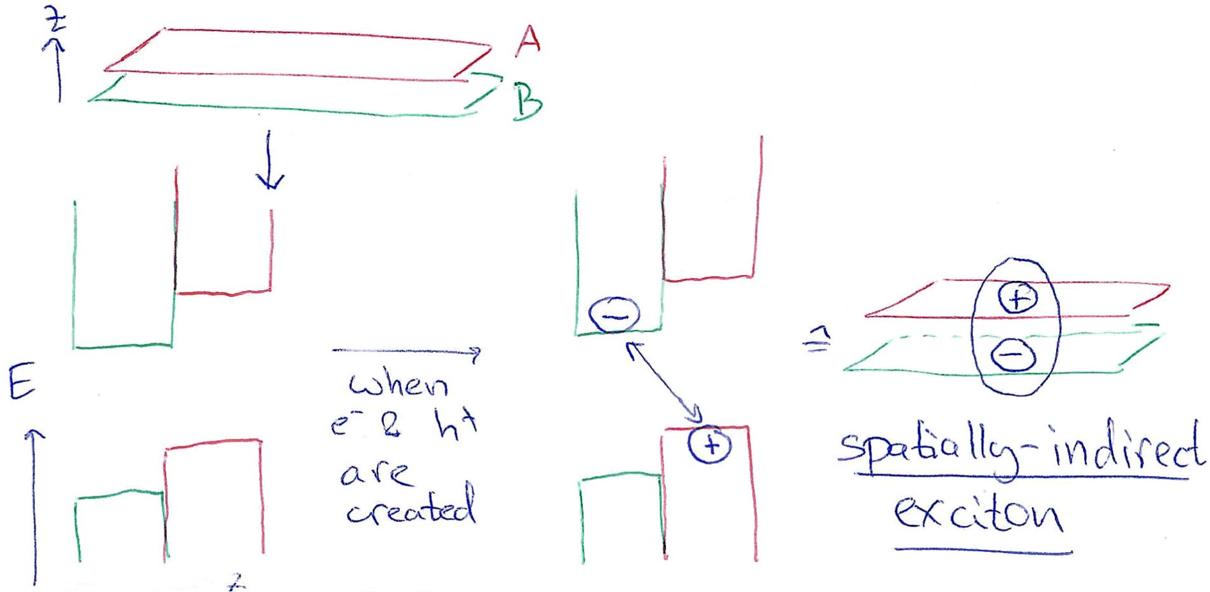


} restacking into artificial heterostructure held together by van der Waals forces

(interfaces can be <u>atomically sharp</u> + layers can be <u>twisted</u>



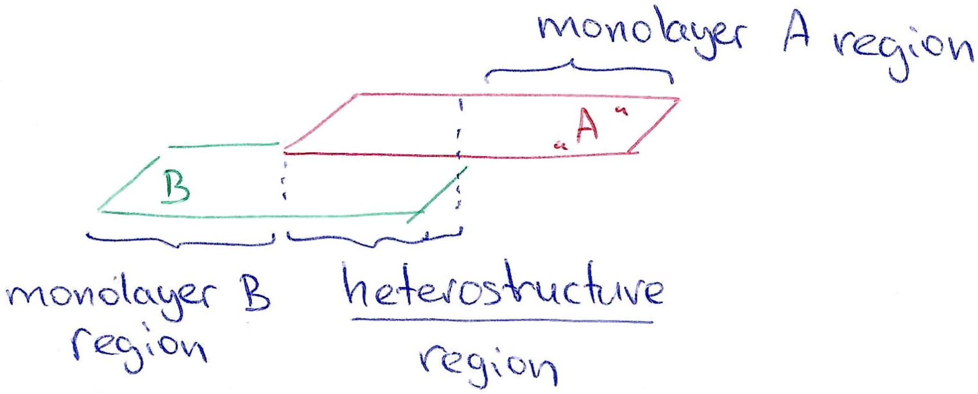
↝ e.g. combining two semiconducting layers:

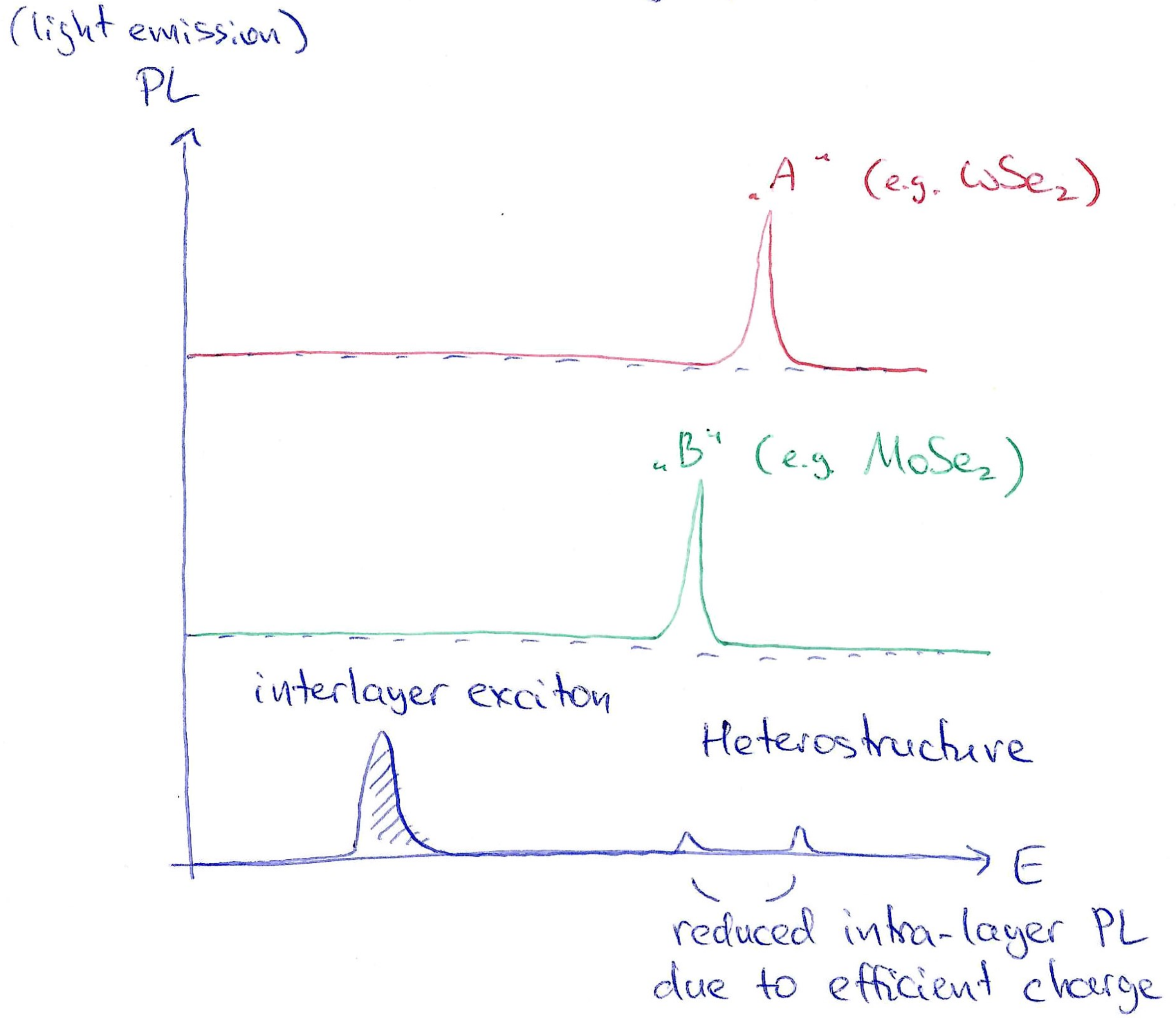


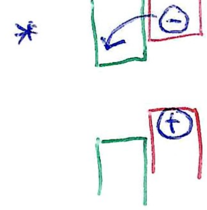
↳ indirect excitons are:

- (often) long-lived
- externally highly tunable
- can store spin- or valley „information" for a long time

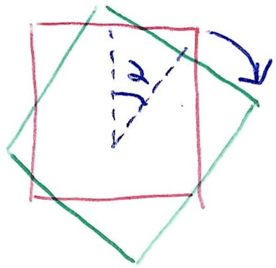
Q: „How to detect interlayer excitations?"





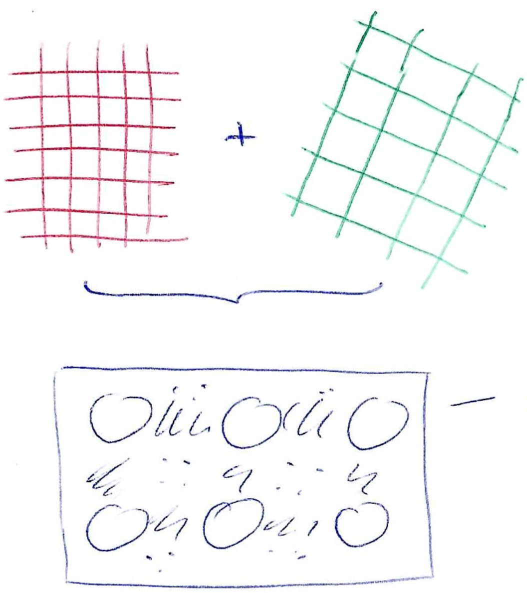


↳ electronic, optical, and vibrational properties can be tuned by the relative <u>twist angle</u> between the layers



↳ important phenomenon: **Moiré effect**

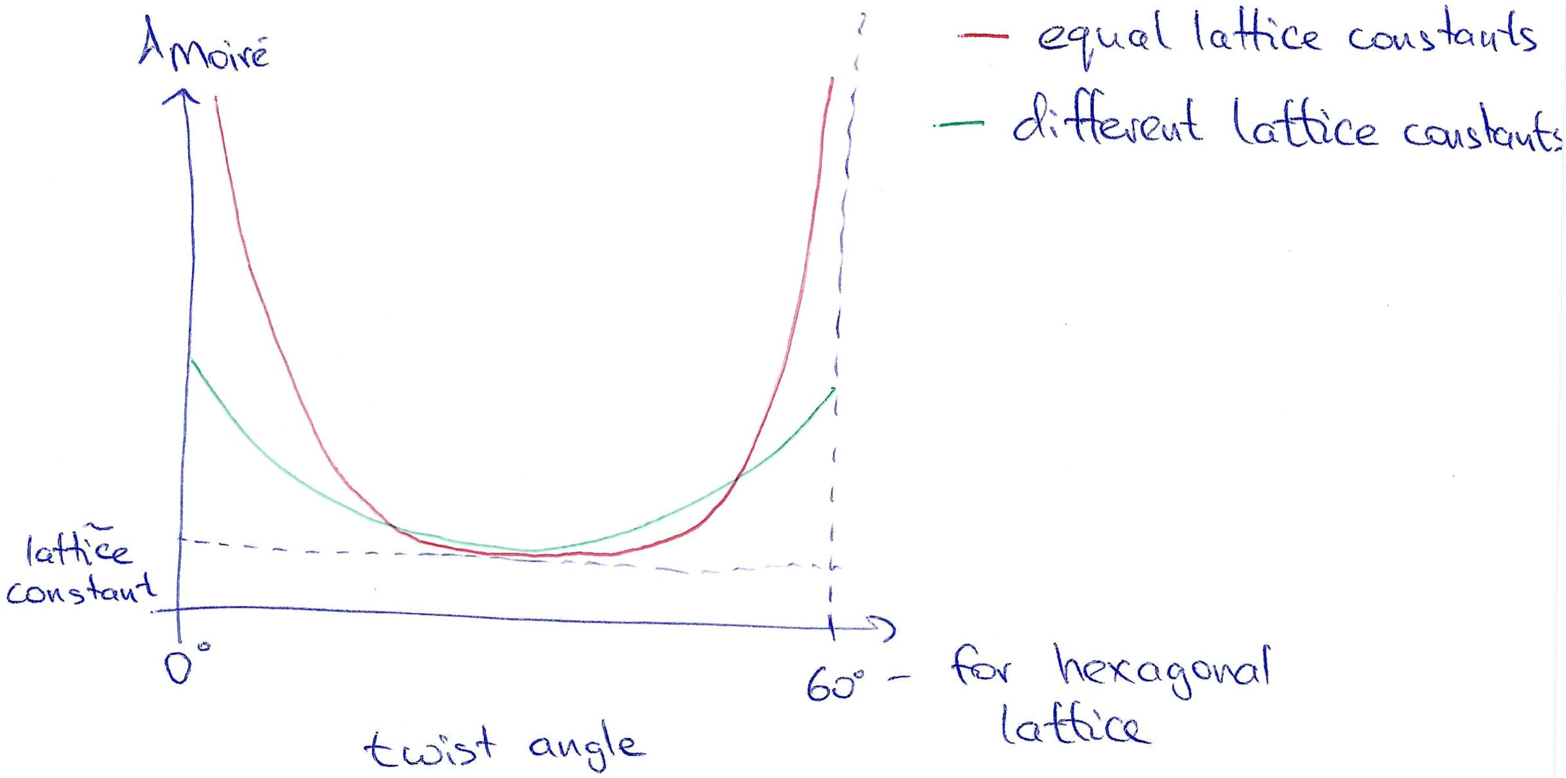
↳ appears when two inequivalent lattices are overlaid



- lattice constant mismatch
- angle mismatch

— Moiré superlattice

↳ Moiré superlattice period:



[→ however, at very small angles atomic reconstruction can occur (atoms shift slightly into energetically more favorable positions)
↳ different patterns & domains emerge]

⇒ rich, contemporary field of 2D materials physics studying electronic, optical & vibrational excitations in <u>artificial lattices</u>