2. Van der Waals materials

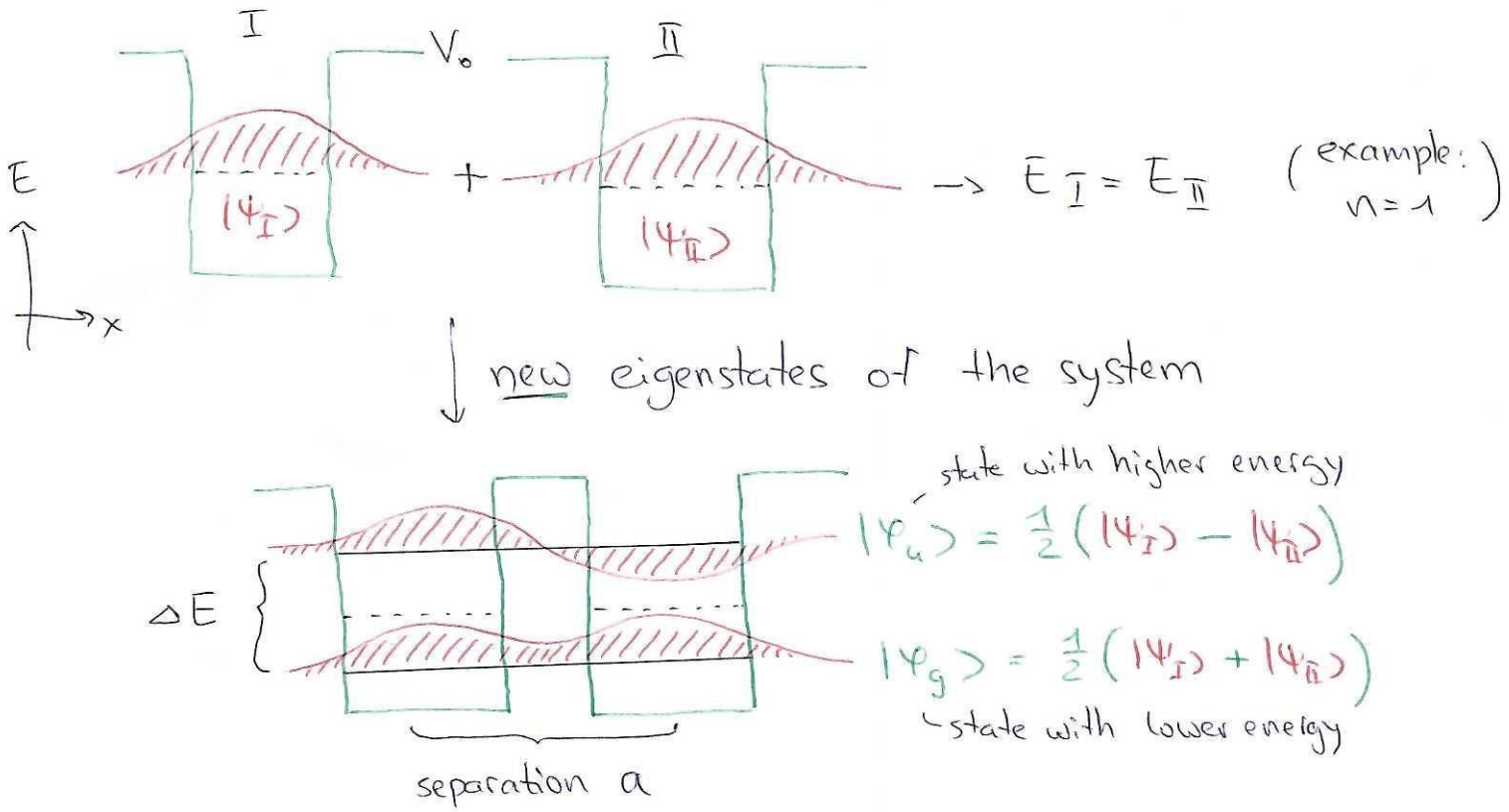
- Naturally layered structures, ideally suited to provide <u>two-dimensional</u> systems

↳ Nature of <u>vdW</u>-bonding vs. <u>covalent</u>* bonds

---

* basic model for <u>covalent</u> bonding:

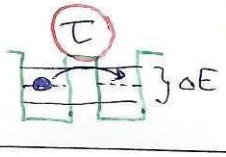
<u>Double/coupled potential wells</u>



↳ Electrons are „delocalized" / „spread" over both wells

↳ Strength of the coupling <u>ΔE</u> scales with the <u>spatial overlapping of the wavefunctions</u> (<u>typically 1-10 eV</u> for real covalent bonds)

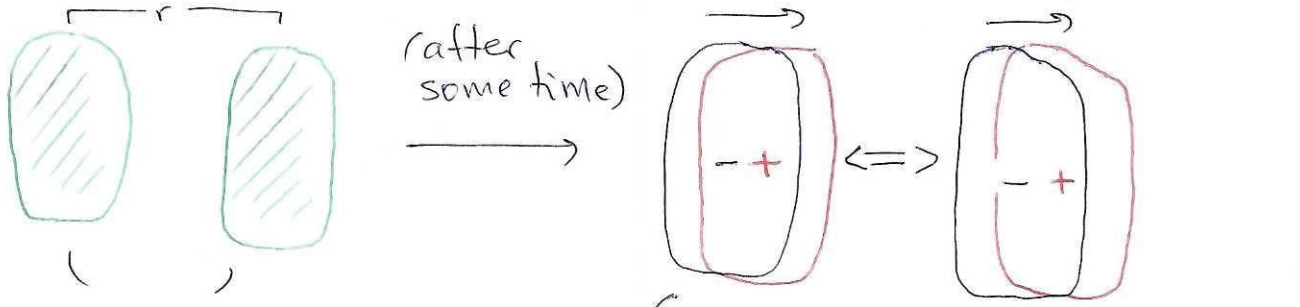
↳ Coupling can be expressed as tunnel-rate <u>$\tau \sim \frac{\hbar}{E}$</u> between wells:



2.1. Van der Waals interaction

Q: „How can atoms or molecules interact when there is no substantial electronic wavefunction overlap?"

(schematic A:)



two neutral molecules, no „dangling bonds" (all bonds are saturated in each molecule)

1. spontaneous fluctuation of e^- distribution → 2. induced change in e^- distribution in the other molecule

3. electrostatic attraction

↳ Van der Waals interaction = Dipole-dipole attraction

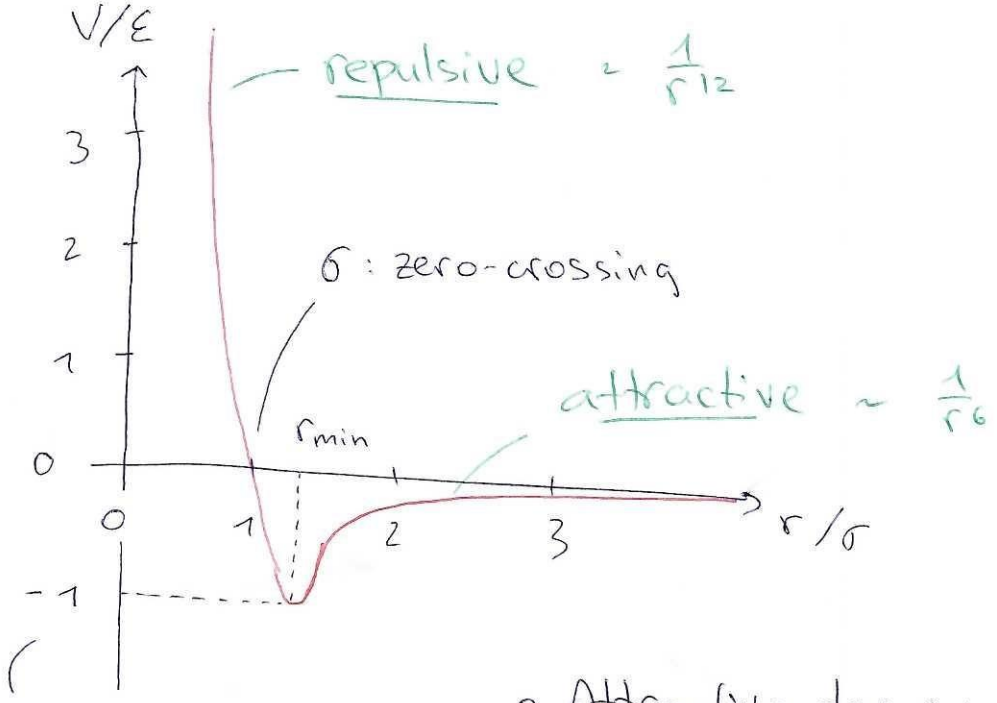
↳ Typical binding strength: ~ 100's of meV

- much weaker than covalent or ionic (1-10 eV!)
- still sufficient to hold matter together (also $\gg k_B T$ at $T \sim 290K$, ~ 25 meV)

Commonly used expression to describe van der Waals interaction:

$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

: Lennard-Jones potential



ε: potential depth

- Attractive term: $-\left(\frac{\sigma}{r}\right)^{6}$
  - ↳ motivated by dipole ($\sim \frac{1}{r^3}$) - dipole ($\sim \frac{1}{r^3}$) interaction [3+3=6 :)]
- Repulsive term: $\left(\frac{\sigma}{r}\right)^{12}$ — why 12 ?!
  - ↳ phenomenologically describes short-range repulsion due to Pauli-blocking
  - ↳ exponent „12" is chosen for mathematical convenience

finding extremum:

$\frac{d}{dr} V_{LJ}(r) \stackrel{!}{=} 0$ at r_m = ?

$\frac{dV}{dr} = 4\varepsilon\left(-\frac{12\sigma^{12}}{r_m^{13}} + \frac{6\sigma^6}{r_m^7}\right) \stackrel{!}{=} 0$

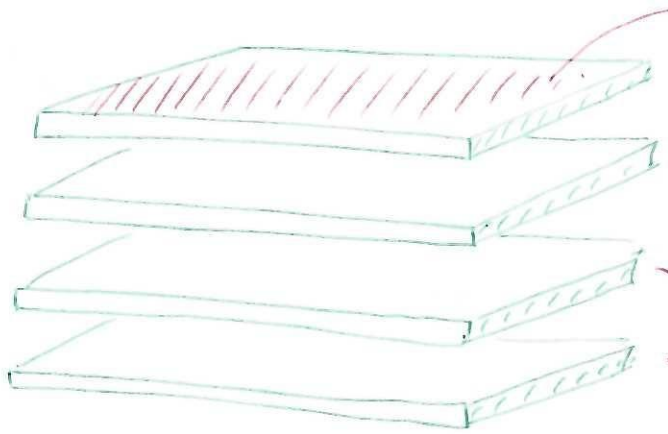
$-\frac{2\sigma^6}{r_m^6} + 1 = 0$

$r_m = \sqrt[6]{2}\,\sigma \approx 1.12\sigma$

$V_{LJ}(r_m) = -\varepsilon$

2.2. Graphene & friends

Generic van der Waals crystal:

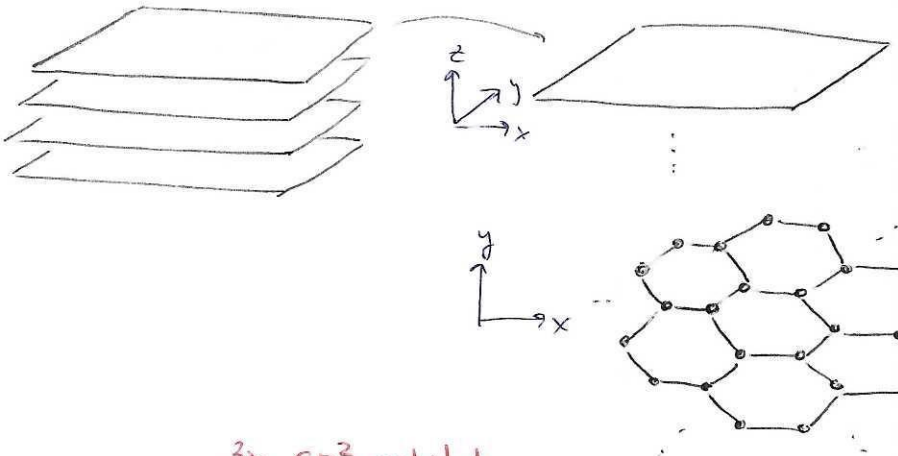


- strong binding of atoms in the plane (covalent / ionic)
- weak van der Waals forces between the layers

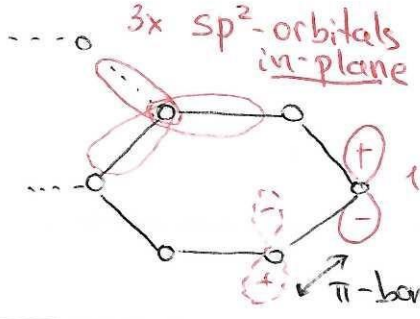
↳ separation of layers is relatively easy and often „clean" (~ no dangling bonds)

(↳ family of vdW crystals is vast, thus focusing on several prominent examples:)

Graphite → Graphene



hexagonal lattice of carbon atoms



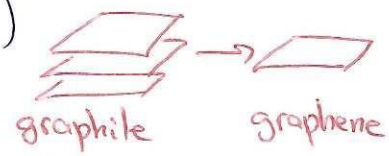
- sigma-bonds via sp^2
- π-bonds via p_z

all within one layer

↳ forces between graphene layers are purely van der Waals

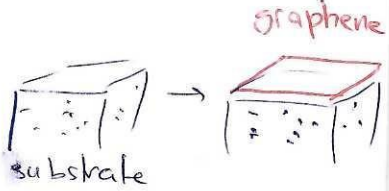
↳ separation of individual graphene layers via:

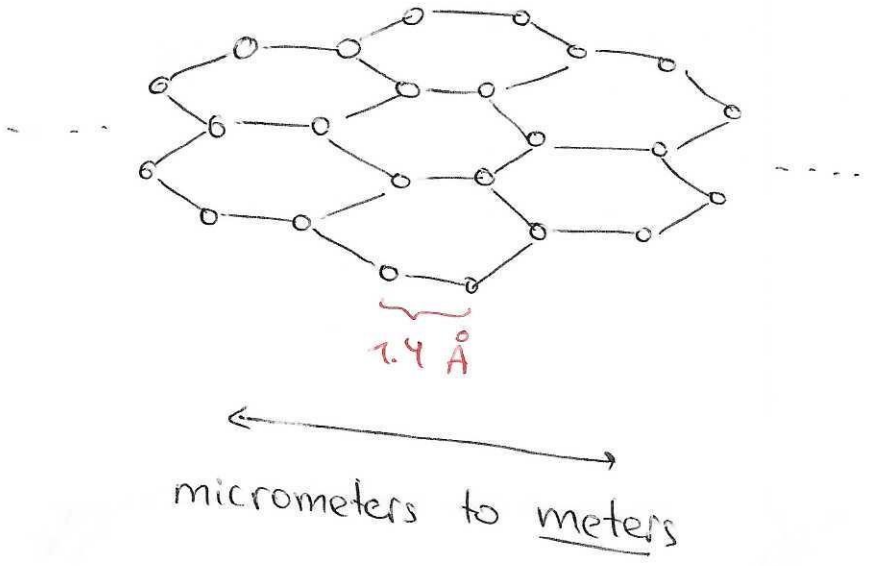
top-down
- mechanical exfoliation („scotch tape technique")
- liquid exfoliation („shaking" with ultrasound)
- photoexfoliation (heating and delamination via intense radiation)



↳ (alteratively) growth of single layers:

bottom-up
- chemical vapour deposition (CVD)
- molecular beam epitaxy (MBE)
- chemical synthesis





thinnest possible material

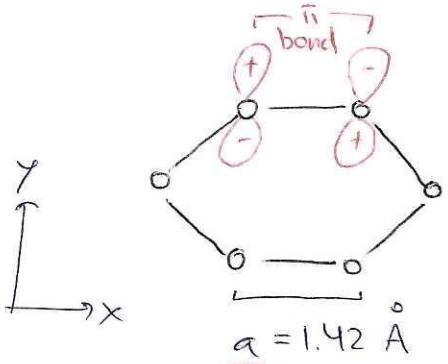
~ one-atom thin

Q: „Ok, it's very thin but so what?"

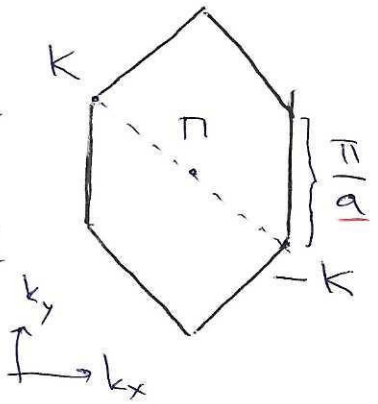
Properties of graphene

Electronic structure: (changes substantially at critical symmetry points in reciprocal space in comparison to (3D) graphite)

most relevant for e^- properties



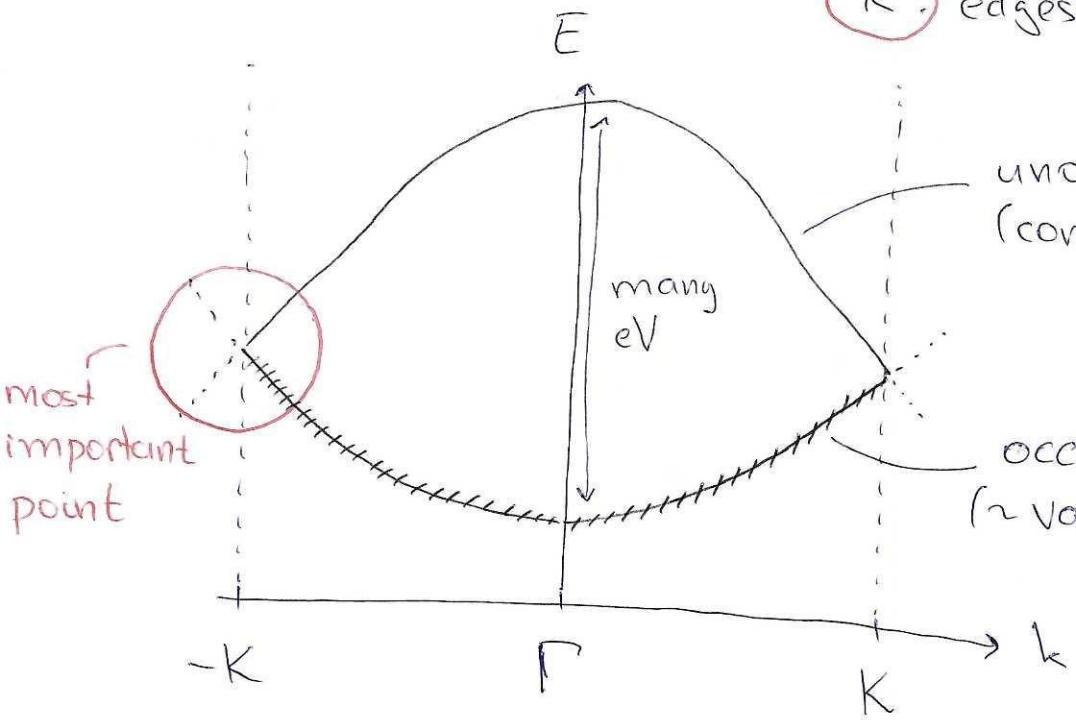
hexagonal crystal structure in real space → hexagonal Brillouin zone in reciprocal space



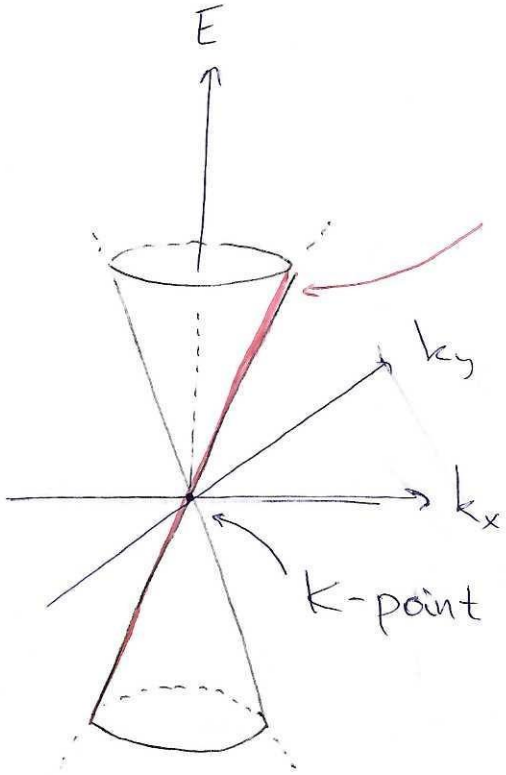
[important points of high symmetry:

Γ: center of Brillouin zone

K: edges of the hexagon in Brillouin zone]



↳ zoom-in on e^- structure around k-point:



Linear Dispersion for electrons:

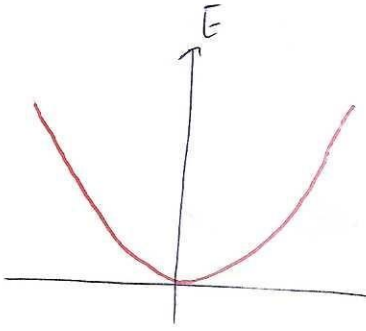
$E(k) \sim k$!

- this is very unusual
- electrons usually behave ~~as~~ similar to free-space particles with a quadratic dispersion* $E(k) \sim k^2$

---

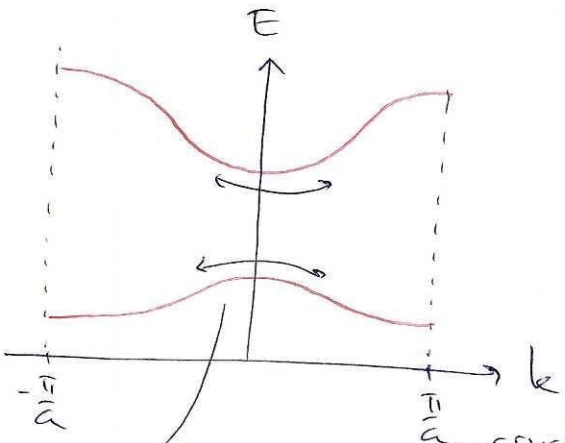
* effective mass & electron dispersion in matter:

e^- dispersion in free space



$E = \frac{\hbar^2 k^2}{2m_0}$

e^- dispersion in a solid



↳ crystal with lattice constant a

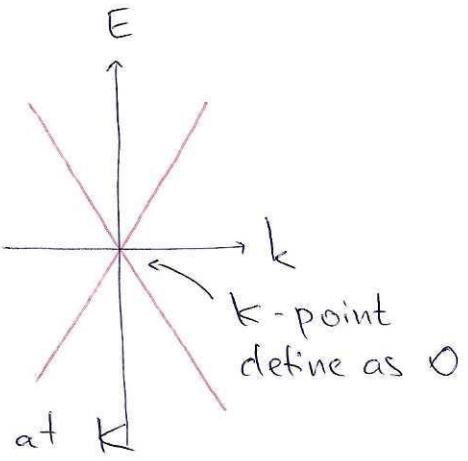
regions of parabolic dispersion

One can define an effective mass of e^-

e.g. via $E(k) = \frac{\hbar^2 k^2}{2m^*} \rightarrow$ $m^* := \hbar^2 \left(\frac{d^2E}{d^2k}\right)^{-1}$

8

↳ effective mass in graphene:



(1) let's use:

$$m^* := \hbar^2 \left(\frac{d^2E}{d^2k}\right)^{-1} = \begin{cases} 0 & \text{for } k = 0 \text{ at } K \\ \infty & \text{for } k > 0 \end{cases}$$

?! infinite mass

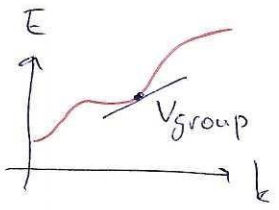
issue: non-relativistic description does not work

(2) better use:

- define effective mass via momentum & group velocity:

$$p = m^* v_{group}$$

$$\hbar k = \frac{1}{\hbar} \frac{\partial E}{\partial k}$$



↳ $\hbar k = \frac{1}{\hbar} \frac{\partial E}{\partial k} \cdot m^*$

↳ $\boxed{m^* := \hbar^2 k \left(\frac{\partial E}{\partial k}\right)^{-1}}$

in graphene: $E \sim k$, define $E = c_g \cdot \hbar k$

↳ $m^* = \hbar^2 k \cdot \frac{1}{c_g \hbar} = \frac{\hbar}{c_g} \cdot \hbar k$ (relativistic mass)

→ at $k = 0 \rightarrow m^* = 0$ ✓ mass at rest = zero

at $k > 0 \rightarrow m^* = \frac{\hbar}{c_g} \cdot k$ relativistic mass ✓

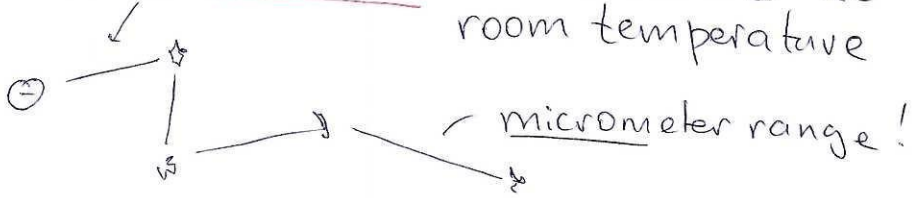
[consider $E = c_g \cdot \hbar k = c_g \cdot m^* c_g = m^* c_g^2$ ✓]

→ Electrons in graphene behave as mass-less relativistic particles in graphene, similar to photons

- note that:
  - ↳ only for small k
  - ↳ c_g is about 100x smaller than speed of light

↳ key graphene properties:

- extremely high electron mobility
- very long mean free path for electrons at room temperature



- high mechanical stability
- supports up to 20% strain

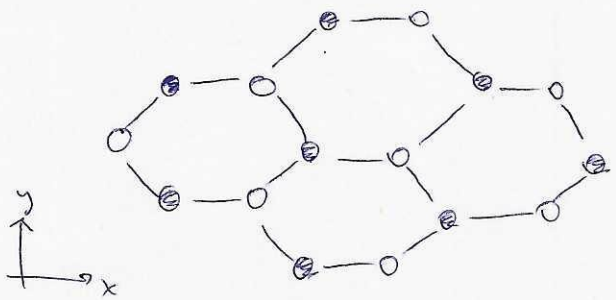
+ used as e^--conductor in heterostructures
+ interesting for infra-red / THz-photonics
+ host correlated electron phases in heterostructures (e.g. superconductivity in twisted bilayer graphene)

Van der Waals 2D materials beyond graphene

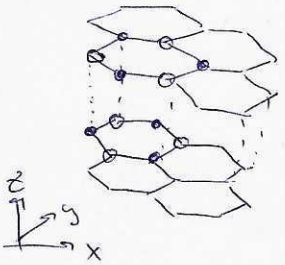
↳ 100's of chemically & structurally distinct vdW crystals that can be produced as very thin layers or monolayers

→ Exemplary, broadly studied materials & material families:

(1) Boron nitride (hexagonal hBN)



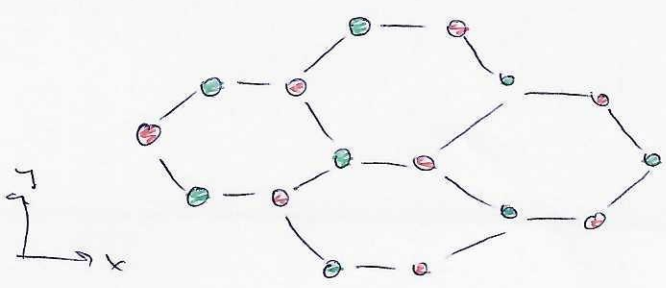
○ nitrogen
● boron



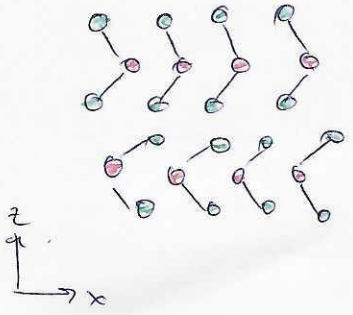
- insulator, bangap ~ 6eV (larger in 1L)
- used as dielectric & encapsulating / protecting material in heterostructures
- can host localized emitters

(2) Transition-metal dichalcogenides (TMDs or TMDCs)

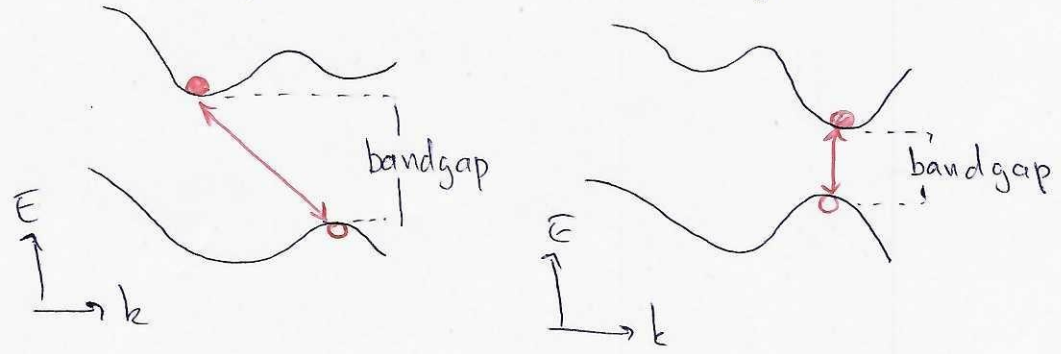
(often: MoS_2, $MoSe_2$, WS_2, WSe_2, WTe_2..)



● transition-metal (Mo, W)
● 2x chalcogen (S, Se, Te)



- large part of TMDCs are semiconductors
- bandgaps ~ 1 - 2 eV
- indirect in 3D, direct semiconductors in 2D



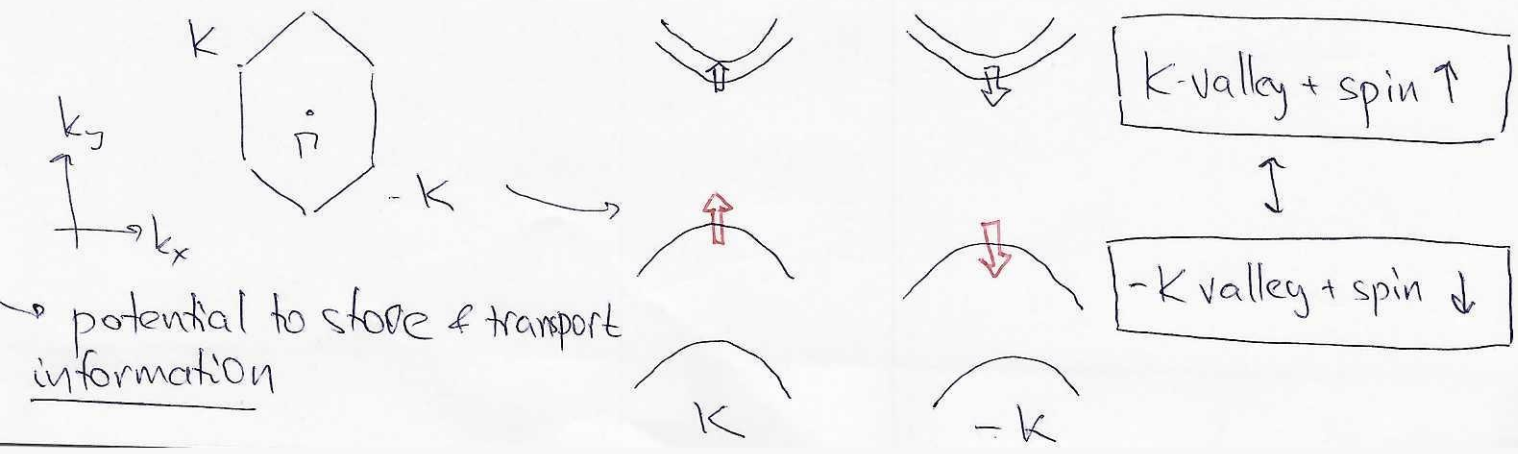
↳ lowest energy transition of e^- does not require finite momentum

↳ couples strongly to light (since photon momentum ≈ 0)

↳ interesting material for opto-electronics & photonics

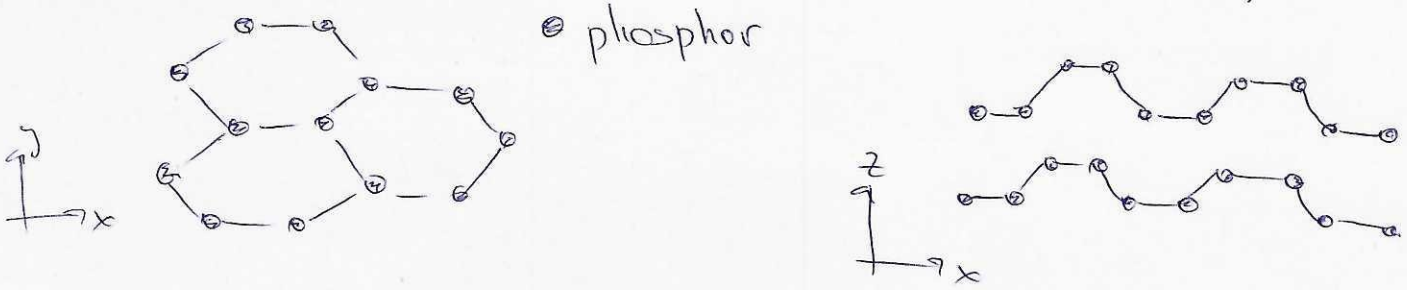
↳ strong e^--e^- interactions give rise to a host of many-particle states
→ platform to study many-body physics

- coupling of spin & valley degrees of freedom



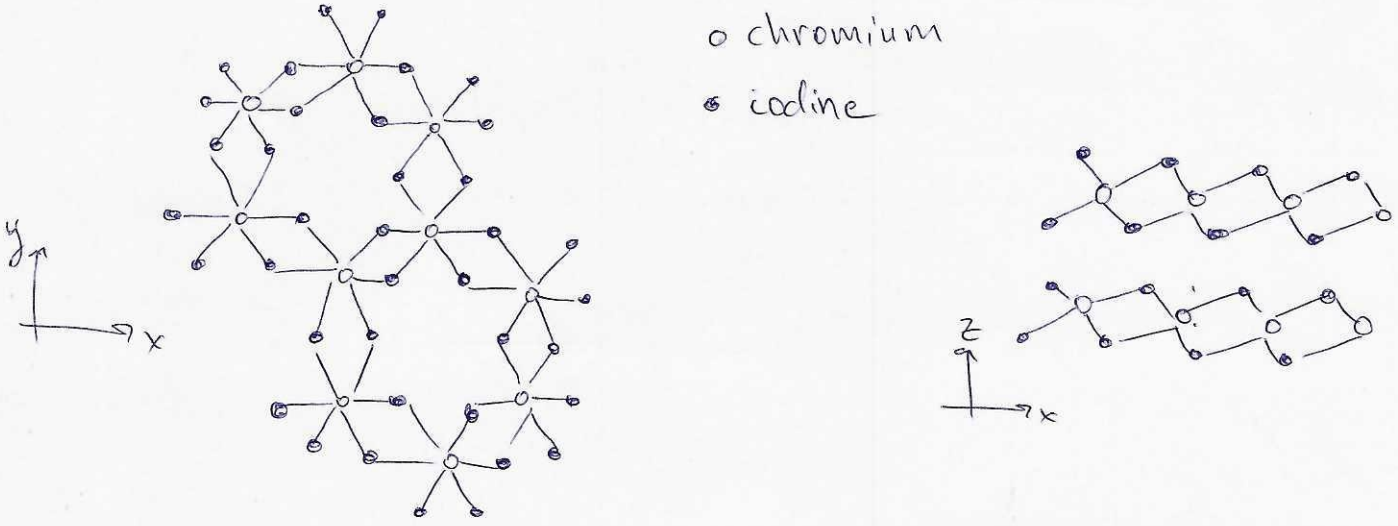
↳ potential to store & transport information

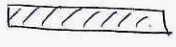
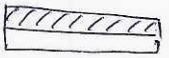
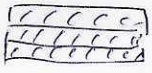
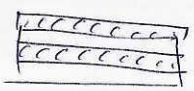
(3) Black phosphorus („BP", 1L = phosphorene)



- narrow-gap semiconductor
- bandgap ~ 0.3eV in 3D, → 1.5eV in 2D
  - ↳ high layer-dependent tunability
  - ↳ interesting for both optics & transport
- high mobility ~ 1000's of cm^2/Vs even at elevated temperatures (similar to Si)

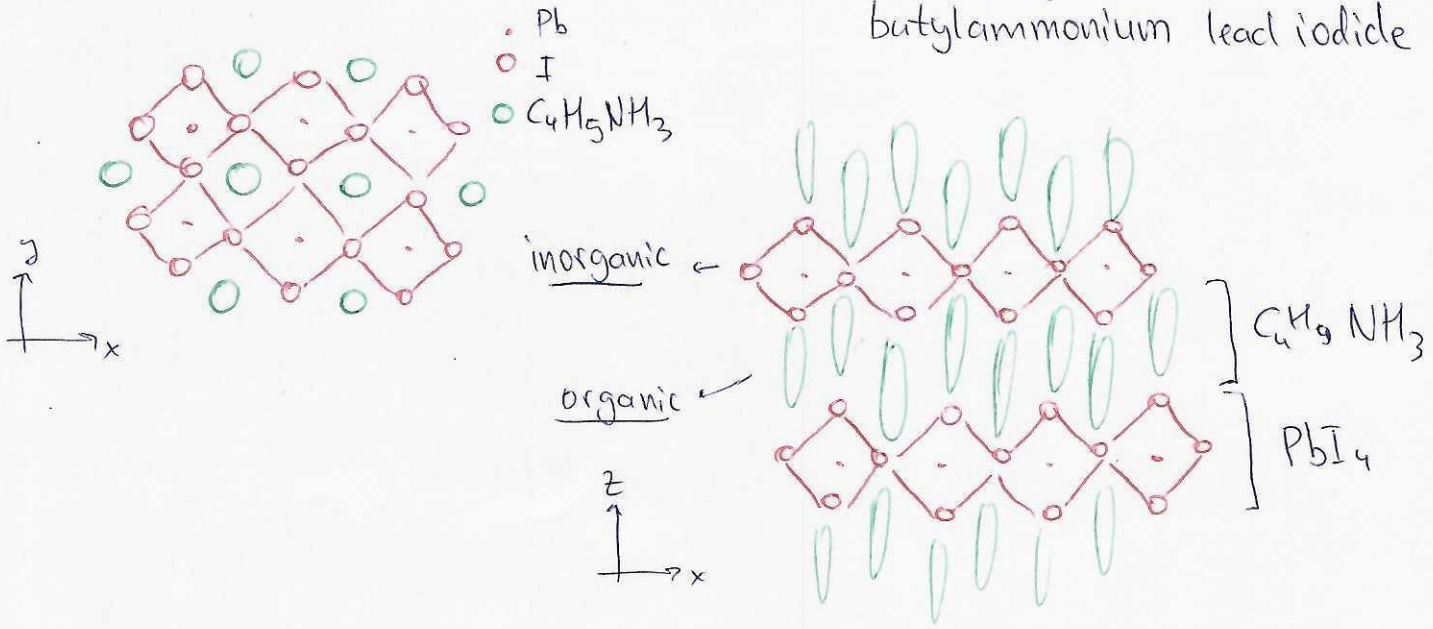
(4) vdW magnets – e.g. Chromium triiodide (CrI_3)



- layer-dependent magnetism
- 1L  - ferromagnet, 2L  - anti-ferromagnet,
  3L  - ferromagnet, 4L  - anti-ferromagnet

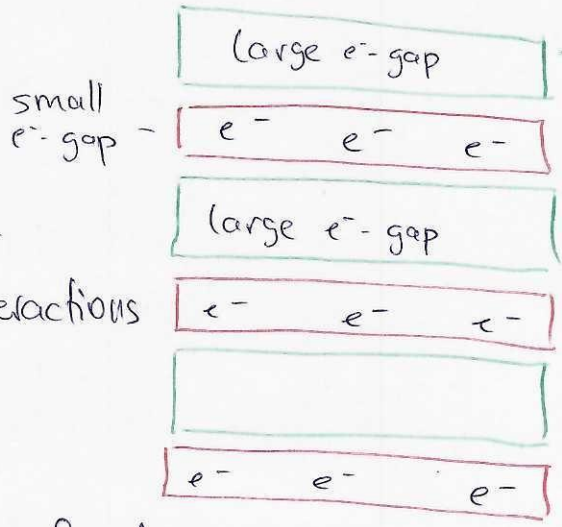
(5) Metal-halide 2D perovskites (e.g. $(C_4H_9NH_3)_2PbI_4$)

butylammonium lead iodide



- organic-inorganic hybrids
- semiconductors with layer-number & composition-dependent bandgaps ~ 1 – 3 eV
- „natural" multi-quantum well systems

formed by self-assembly



- strong light-matter coupling & e⁻-e⁻ interactions
- soft materials

↳ interesting for fundamental physics of interacting electronic & vibrational system

+ potential applications as light-emitters & solarcells