MESA+
INSTITUTE FOR NANOTECHNOLOGY

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Two-dimensional (2D) materials

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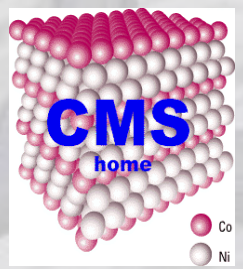
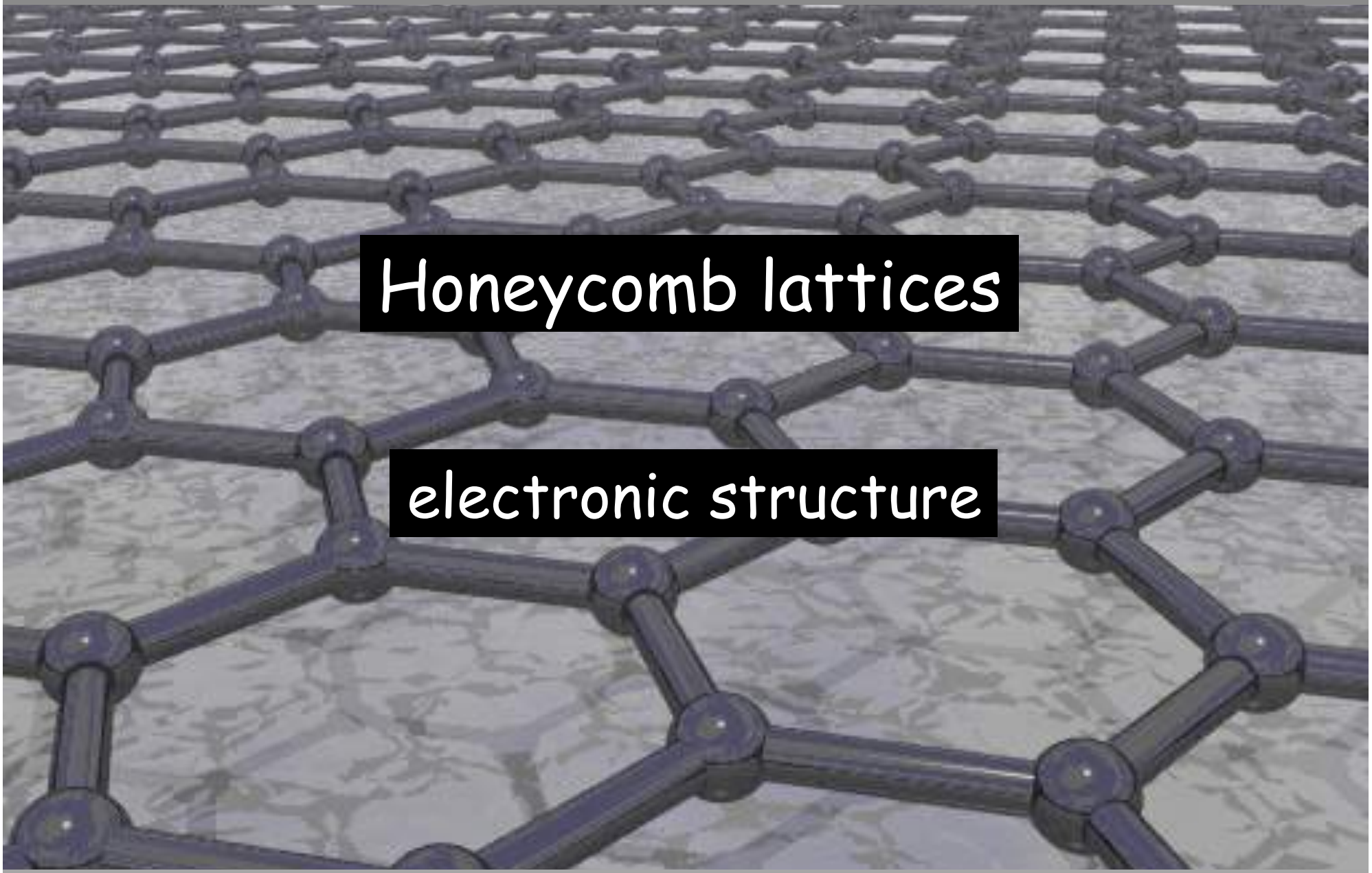


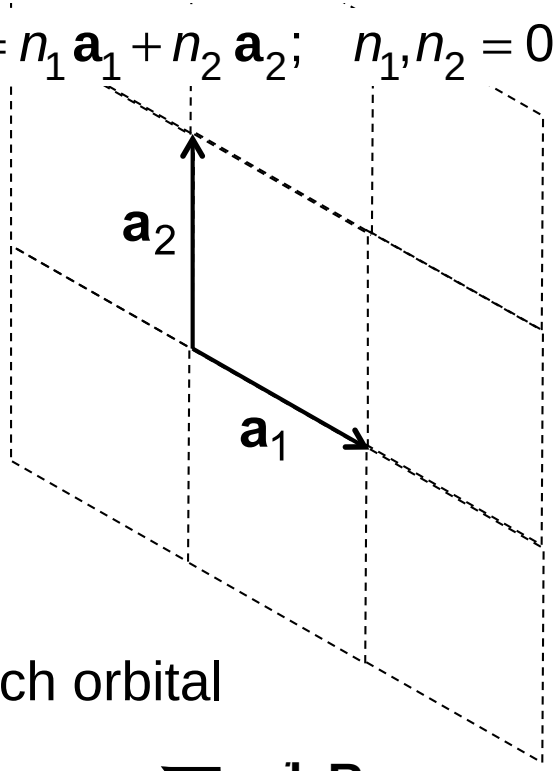
FOM


Honeycomb lattices
electronic structure

Real space lattice and Reciprocal lattice

real space lattice

$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2; \quad n_1, n_2 = 0, \pm 1, \pm 2, \ldots$



Bloch orbital

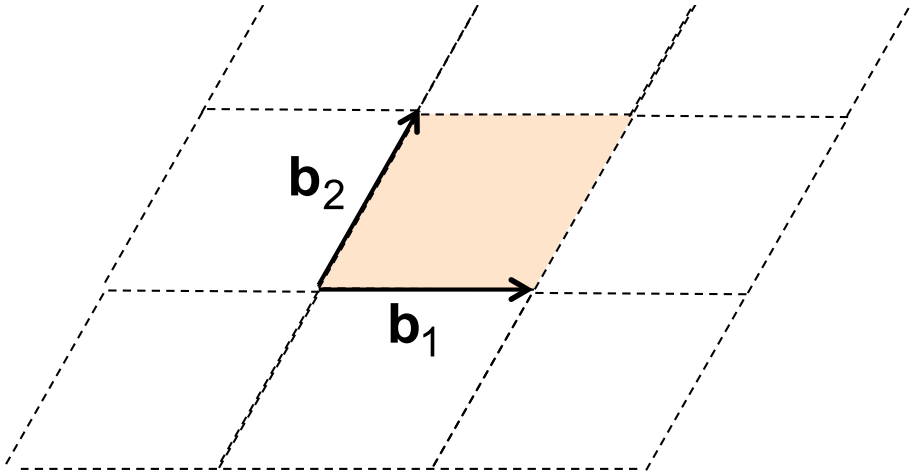
$$\chi_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_i(\mathbf{r} - \mathbf{R})$$

tedious to calculate

in non-rectangular lattice

reciprocal lattice

$\mathbf{K} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2; \quad m_1, m_2 = 0, \pm 1, \pm 2, \ldots.$



where $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{i,j}$

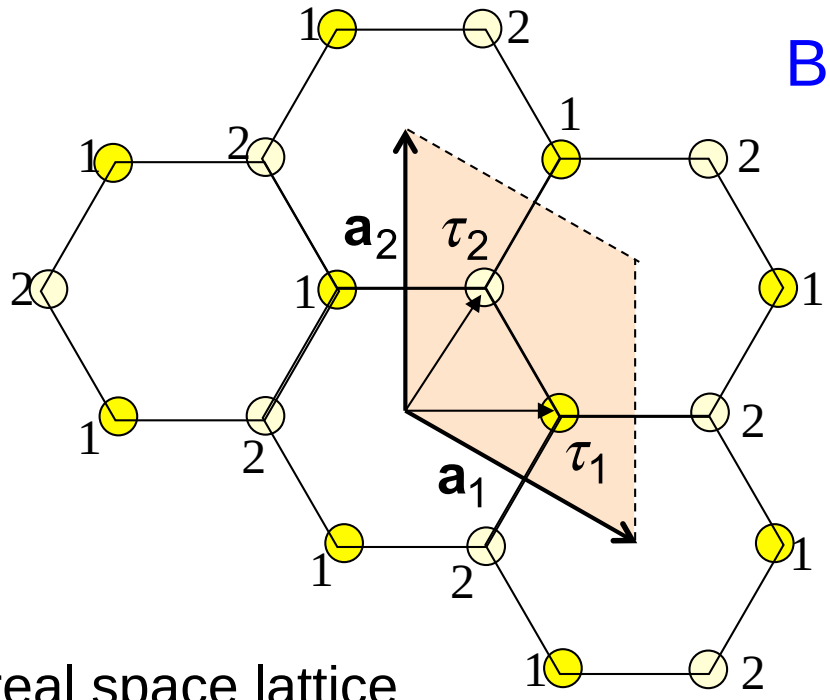
we need $\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2$

then $\mathbf{k} \cdot \mathbf{R} = 2\pi \left(k_1 n_1 + k_2 n_2 \right)$

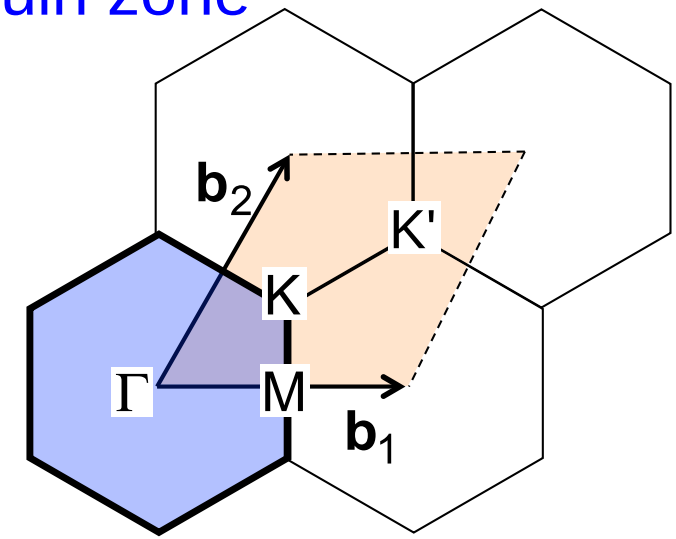
becomes easy

reciprocal lattice is observed in diffraction experiments

Graphene lattice



Brillouin zone



real space lattice

$$\mathbf{a}_1 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right) \qquad \mathbf{a}_2 = a\,(0,1)$$

reciprocal lattice

$$\mathbf{b}_1 = \frac{2\pi}{a}\left(\frac{2}{\sqrt{3}}, 0\right) \qquad \mathbf{b}_2 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, 1\right)$$

carbon atoms in two sublattices

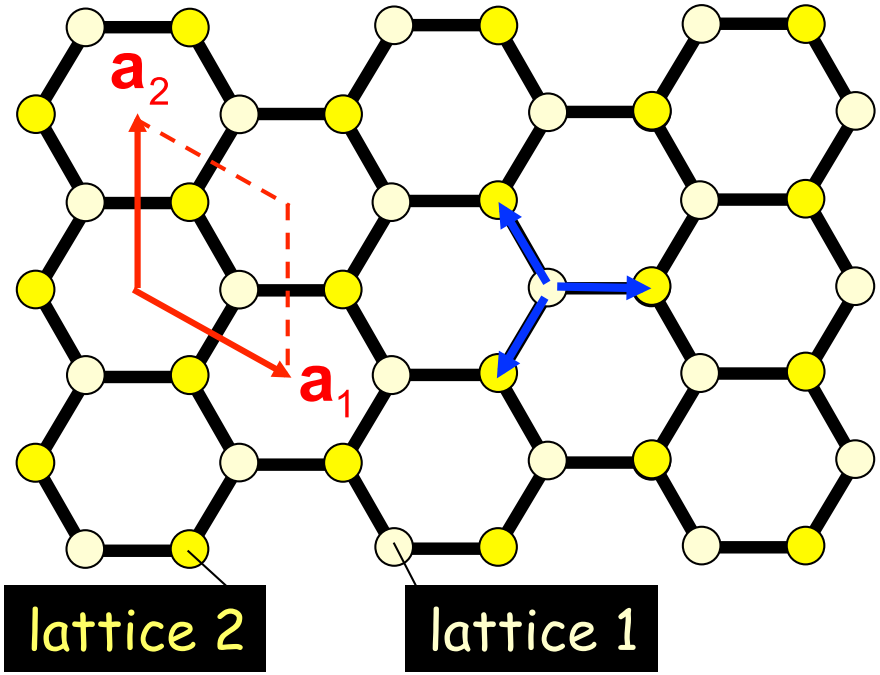
$$\tau_1 = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 \qquad \tau_2 = \frac{1}{3}\mathbf{a}_1 + \frac{2}{3}\mathbf{a}_2$$

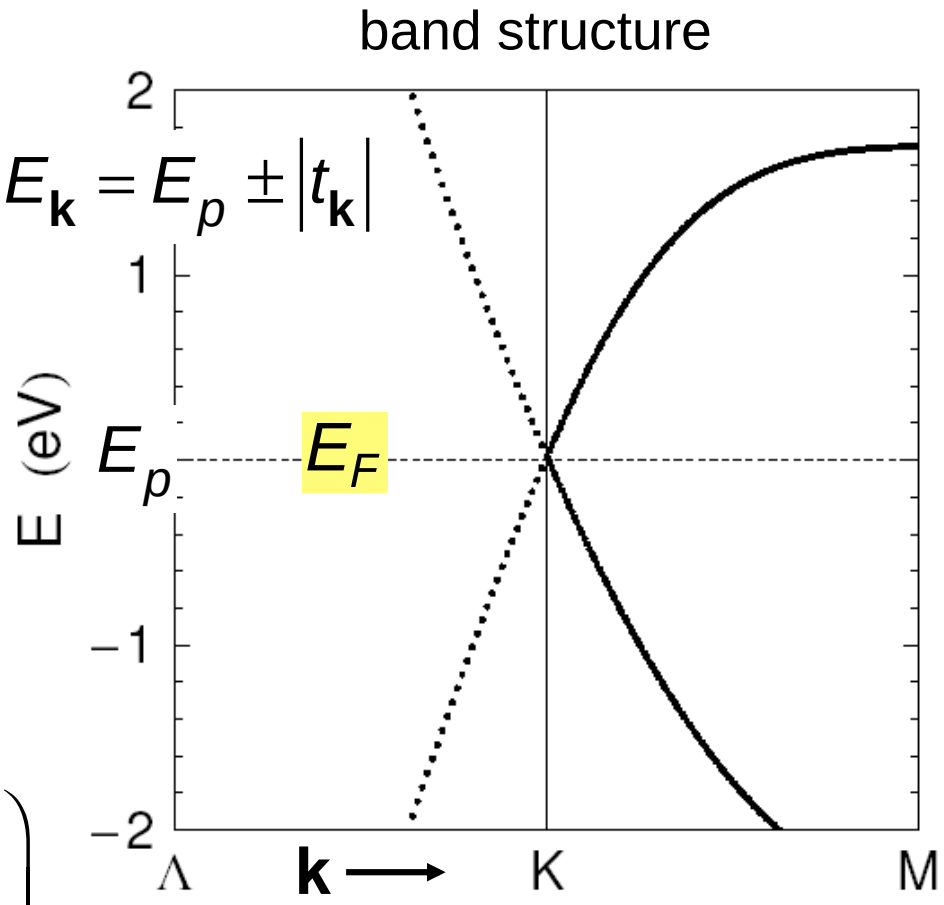
special points

$$\mathrm{K} = \frac{1}{3}\mathbf{b}_1 + \frac{1}{3}\mathbf{b}_2 \qquad \mathrm{K'} = \frac{2}{3}\mathbf{b}_1 + \frac{2}{3}\mathbf{b}_2$$

$$\mathrm{M} = \frac{1}{2}\mathbf{b}_1 \qquad \Gamma = (0,0)$$

Graphene, a textbook toy model





nearest neighbor tight-binding

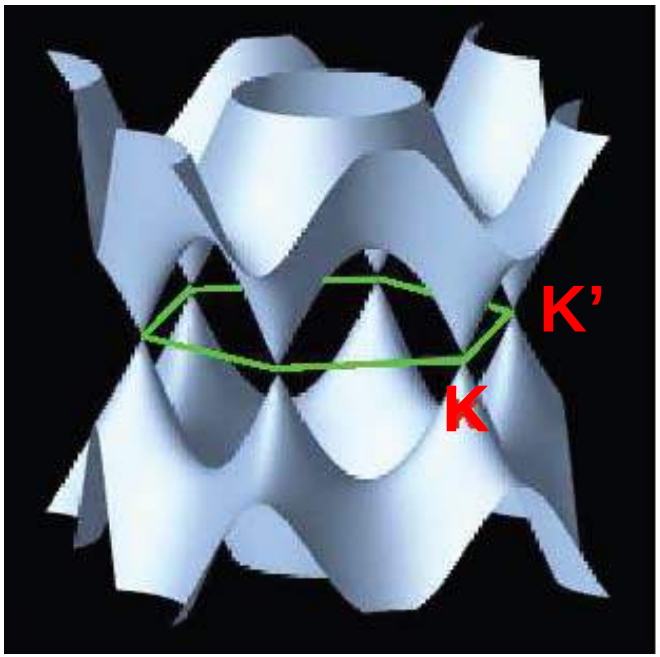
$$\begin{pmatrix} E_p & t_{\mathbf{k}} \\ t_{\mathbf{k}}^* & E_p \end{pmatrix} \begin{pmatrix} c_{1,\mathbf{k}} \\ c_{2,\mathbf{k}} \end{pmatrix} = E_{\mathbf{k}} \begin{pmatrix} c_{1,\mathbf{k}} \\ c_{2,\mathbf{k}} \end{pmatrix}$$

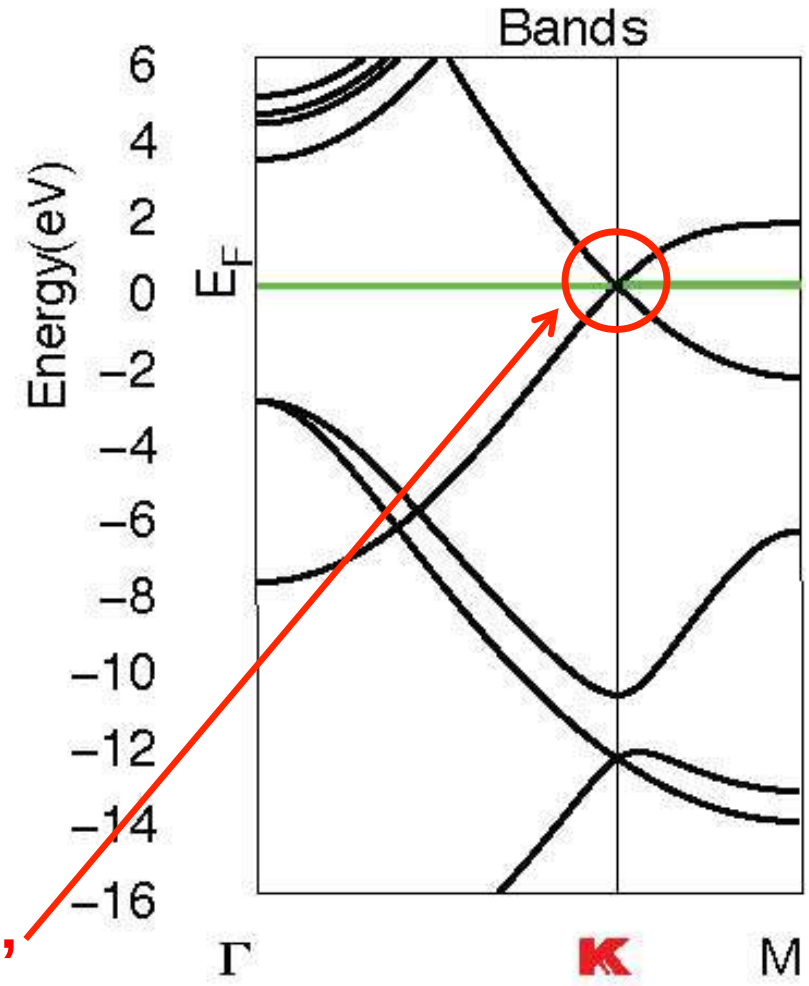
$$t_{\mathbf{k}} = t\left(1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2}\right)$$

- band gap zero at E_F

Graphene full band structure, DFT (LDA)

band structure



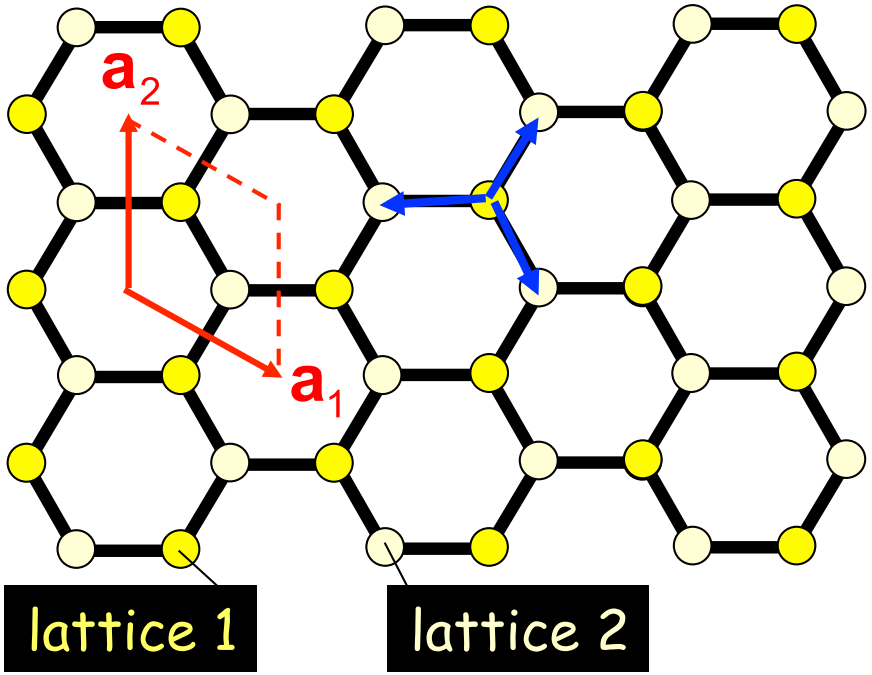


Fermi energy E_F at **K, K'**

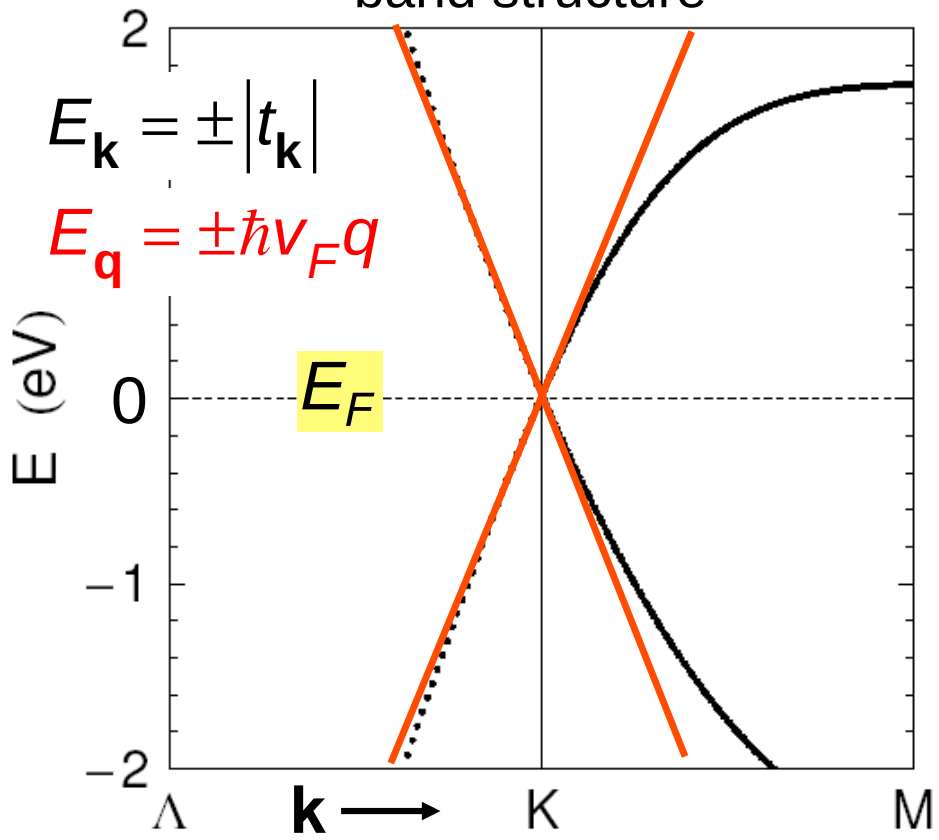
all the "action" is around **K, K'**

graphene is a "zero band gap" semiconductor

Graphene long wave length approximation



band structure



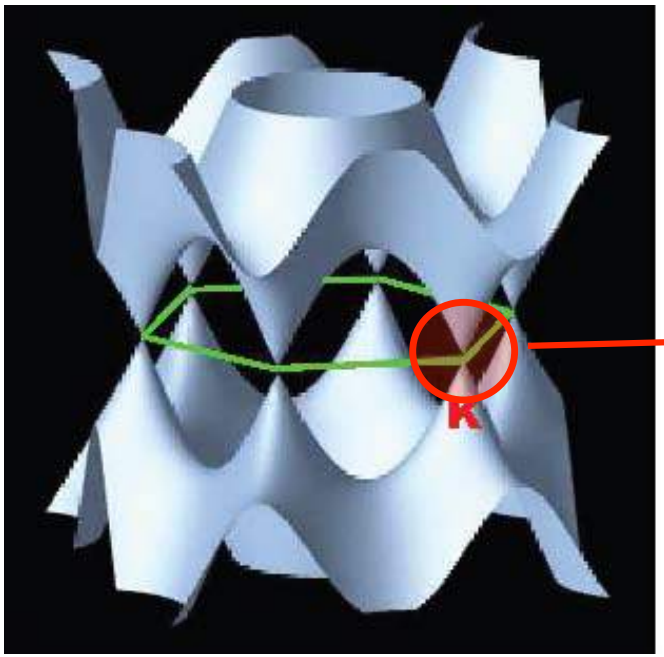
nearest neighbor tight-binding

$$\begin{pmatrix} 0 & t_{\mathbf{k}} \\ t_{\mathbf{k}}^{*} & 0 \end{pmatrix} \begin{pmatrix} c_{1,\mathbf{k}} \\ c_{2,\mathbf{k}} \end{pmatrix} = E_{\mathbf{k}} \begin{pmatrix} c_{1,\mathbf{k}} \\ c_{2,\mathbf{k}} \end{pmatrix}$$

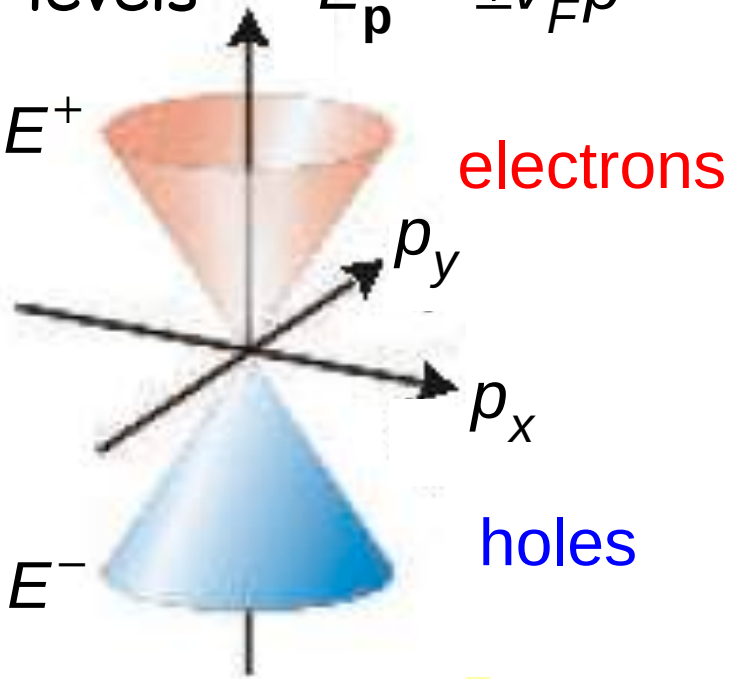
- linear dispersion close to E_F
- dispersion of ultra-relativistic particle

$$t_{\mathbf{k}} = t\left(1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2}\right) \approx \hbar v_F \left(q_x - iq_y\right)$$

Graphene long wave length approximation



energy levels $E^{\pm}_{\mathbf{p}} = \pm v_F p$



Fermi energy E_F at **K, K'**

"Dirac cones"

all the "action" is around **K, K'**

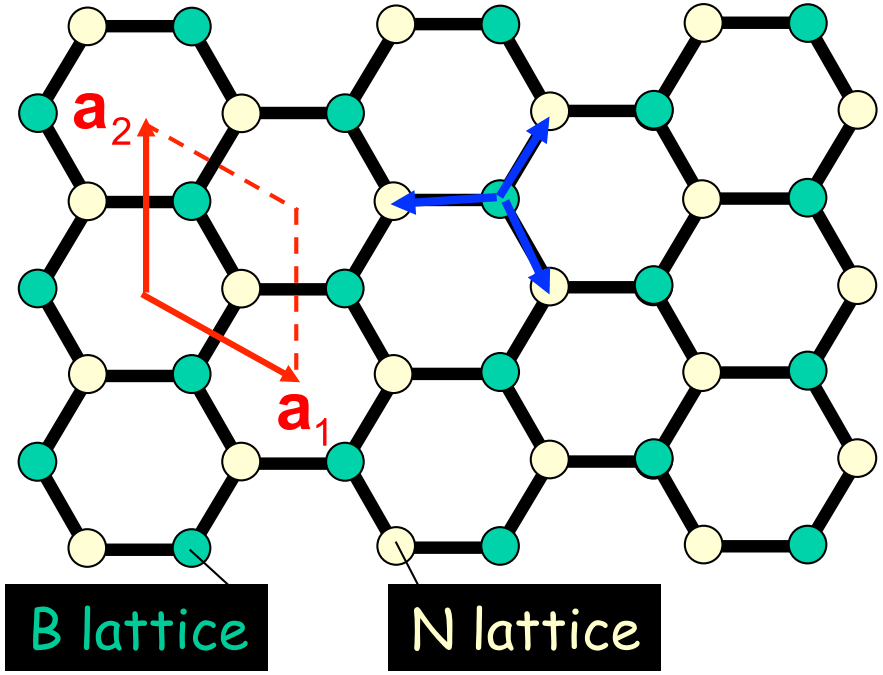
define "momenta"

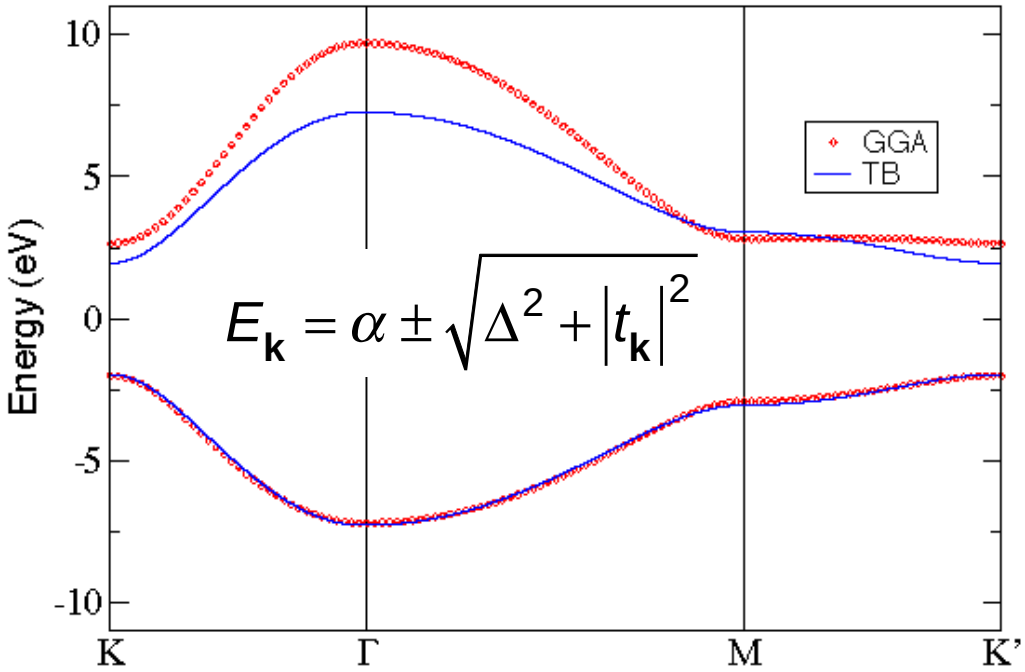
$\mathbf{k} = \mathbf{K} + \mathbf{q}$ $\quad \mathbf{k}' = \mathbf{K}' + \mathbf{q}'$

$\mathbf{p} = \hbar\mathbf{q}$ $\quad \mathbf{p}' = \hbar\mathbf{q}'$

with $qa \ll 1, \quad q'a \ll 1$

Hexagonal boron nitride, another textbook material





nearest neighbor tight-binding (Hueckel)

$$\begin{pmatrix} \alpha+\Delta & t_{\mathbf{k}} \\ t_{\mathbf{k}}^* & \alpha-\Delta \end{pmatrix} \begin{pmatrix} c_{B,\mathbf{k}} \\ c_{N,\mathbf{k}} \end{pmatrix} = E_{\mathbf{k}} \begin{pmatrix} c_{B,\mathbf{k}} \\ c_{N,\mathbf{k}} \end{pmatrix}$$

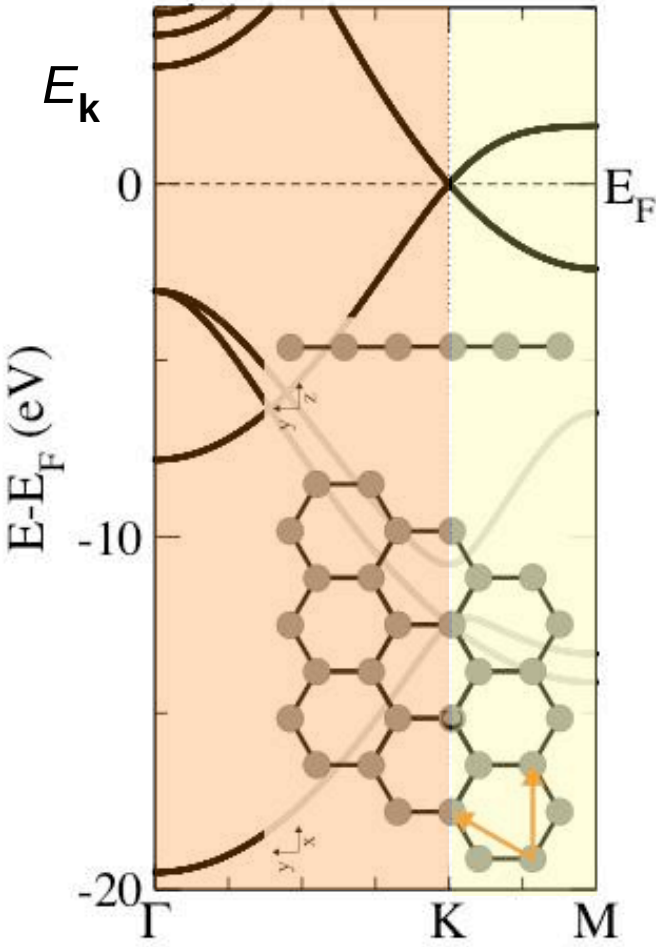
$$t_{\mathbf{k}} = t\left(1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2}\right)$$

$$E_g = 2\Delta \approx 6 \text{ eV}$$

➢ h-BN is an insulator

Honeycomb lattices: DFT(GGA) calculations

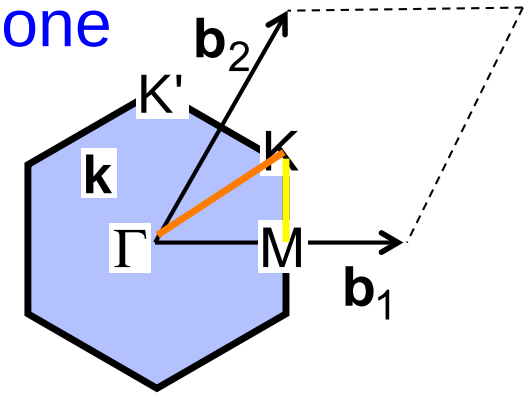
graphene



(semi)metal

How to plot a band structure?

Brillouin zone



$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2$$

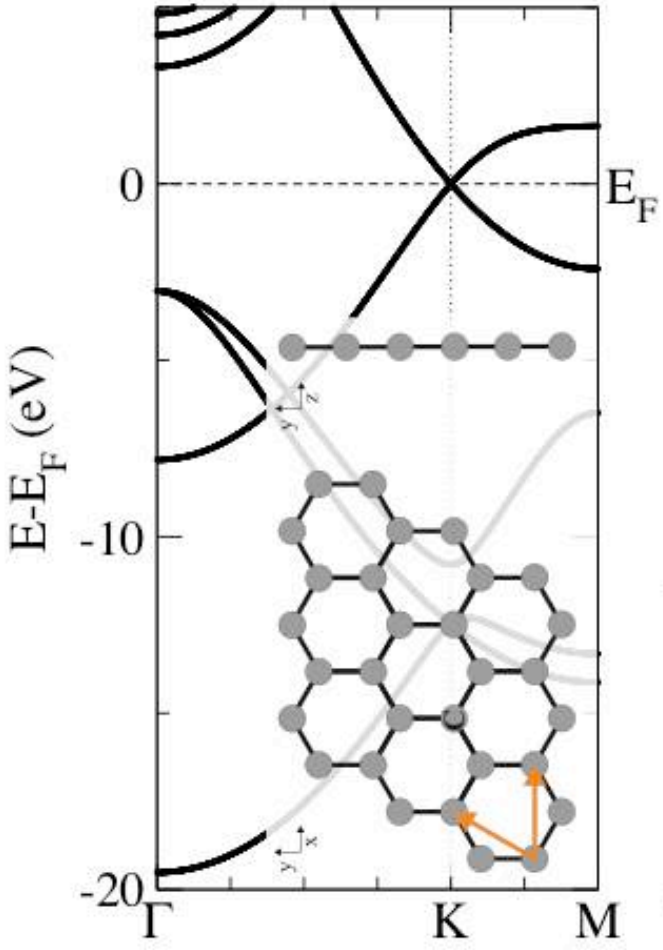
$$\Gamma\mathrm{K}: \mathbf{k} = k\,\mathbf{b}_1 + k\,\mathbf{b}_2; \quad 0 \le k \le \tfrac{1}{3}$$

$$\mathrm{KM}: \mathbf{k} = \left(\tfrac{1}{3} + k\right)\mathbf{b}_1 + \left(\tfrac{1}{3} - 2k\right)\mathbf{b}_2; \quad 0 \le k \le \tfrac{1}{6}$$

M. Bokdam, thesis, U Twente (2013); M. Bokdam, GB, NTvN, 282 (2014)

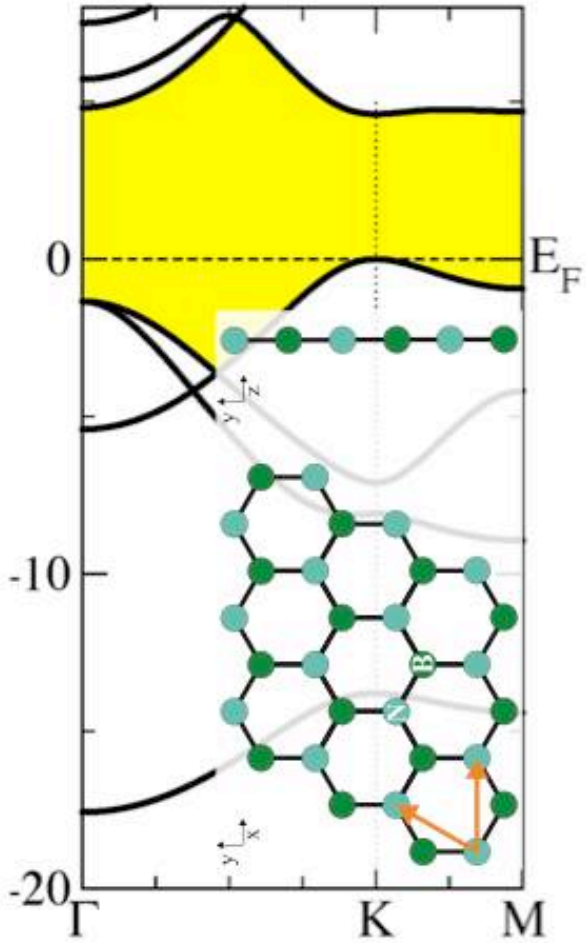
Honeycomb lattices: DFT(GGA) calculations

graphene



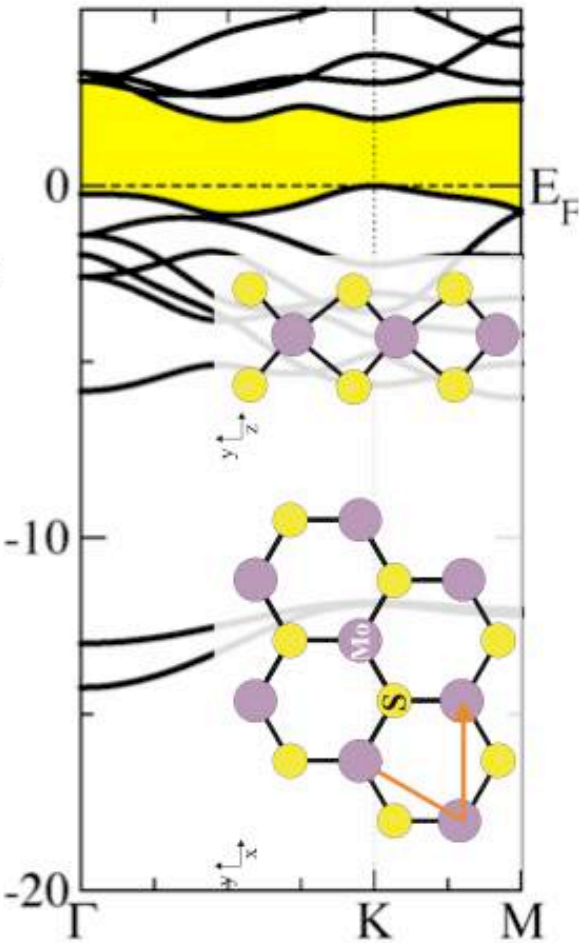
(semi)metal

boron nitride



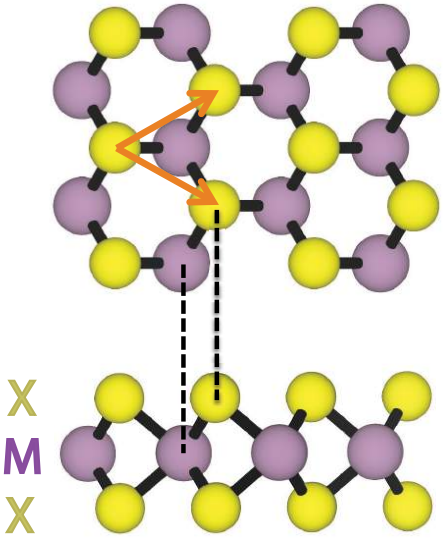
insulator

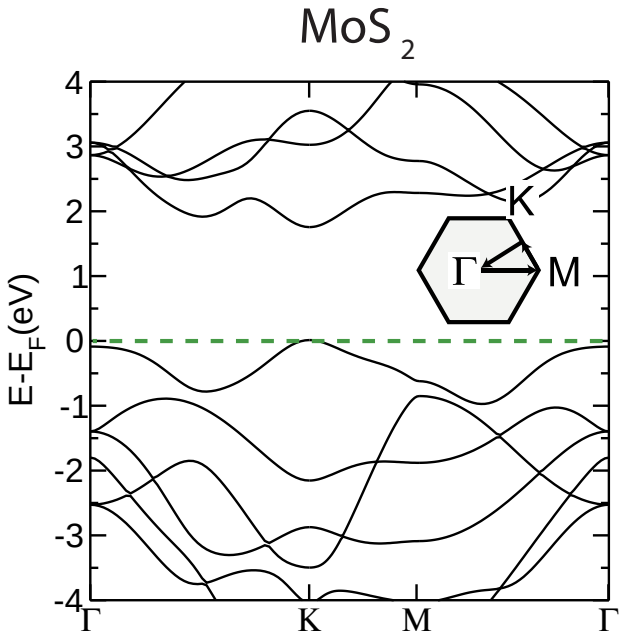
MoS_2

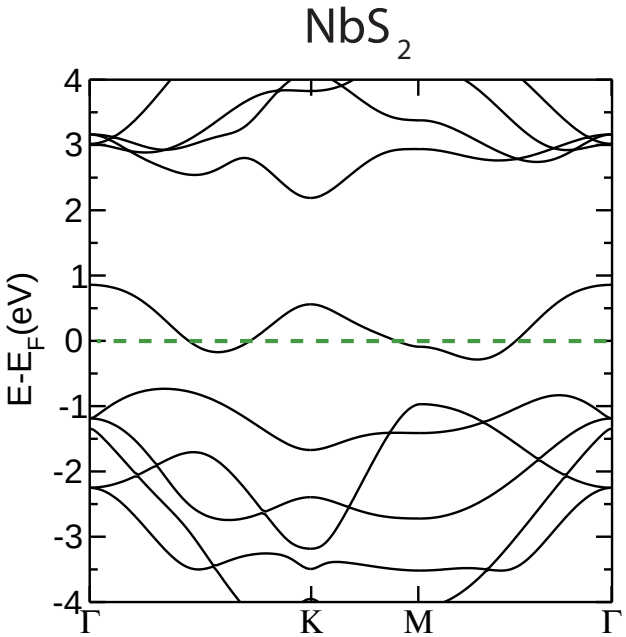


semiconductor

MX_2 lattices: DFT(GGA) calculations





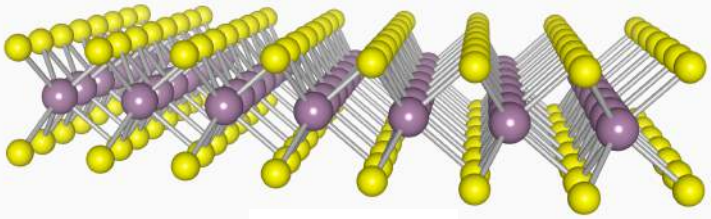


semiconductor

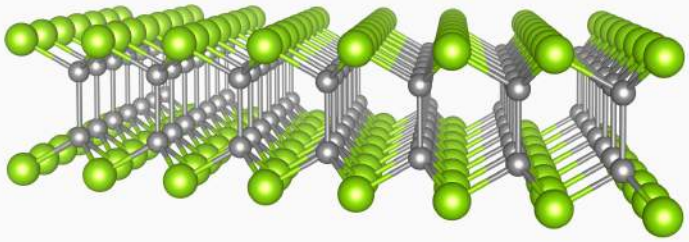
metal

hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.798
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.96	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33		hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]

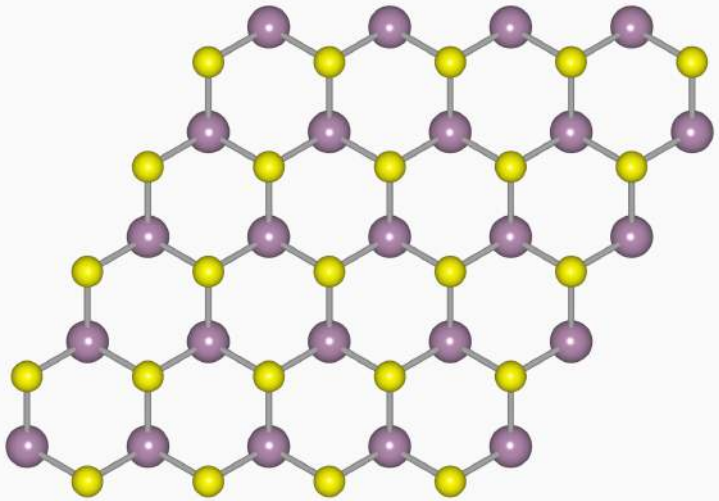
MoS_2 versus GaSe

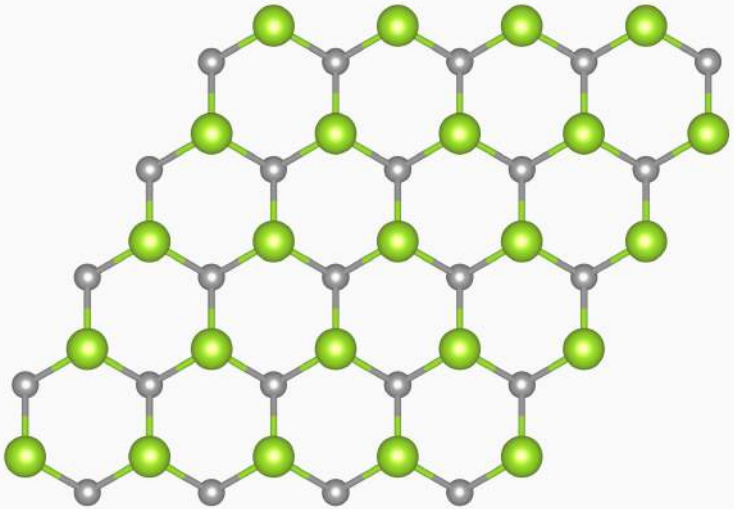


MoS_2

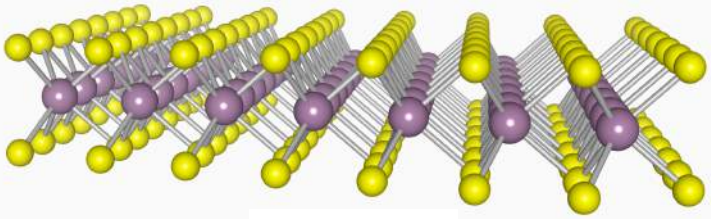


GaSe

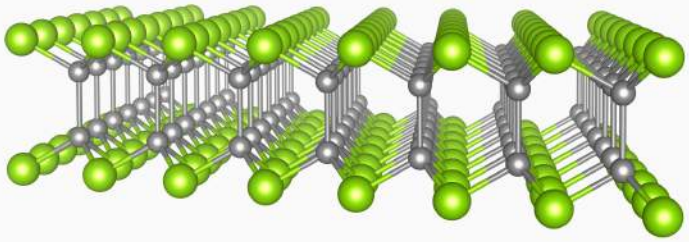




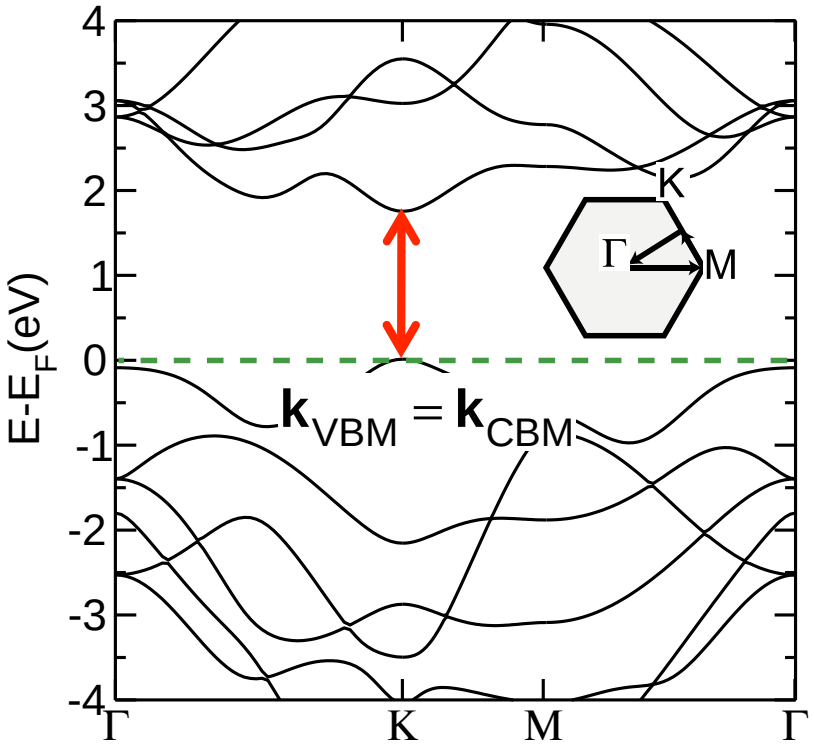
MoS_2 versus GaSe

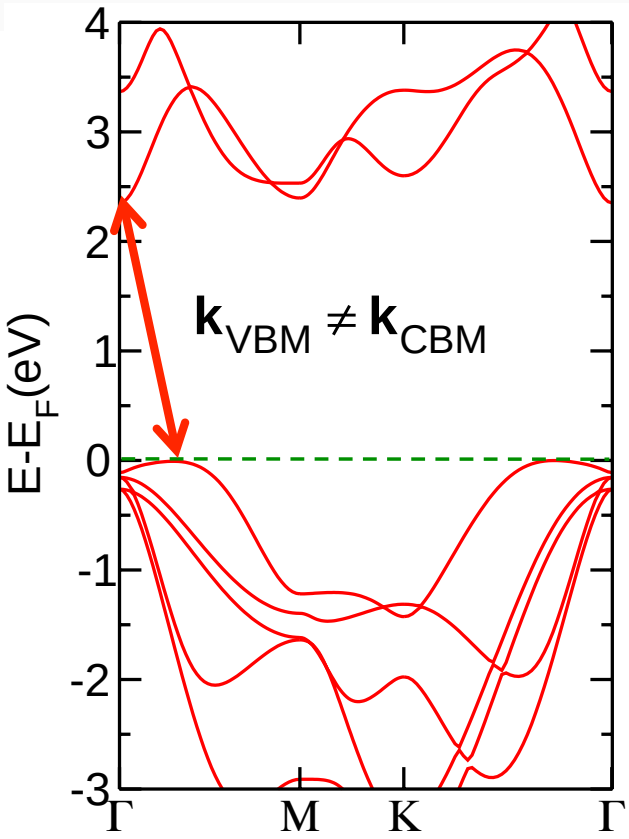


MoS_2



GaSe

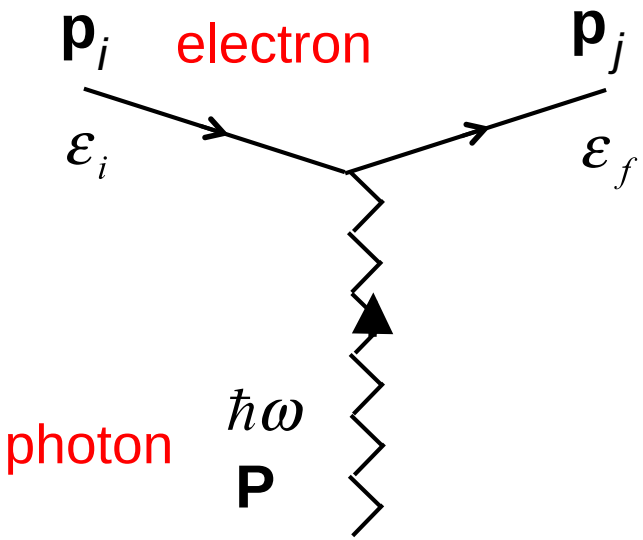




direct semiconductor

indirect semiconductor

optical absorption: first order perturbation



selection rules optical absorption

$\varepsilon_i + \hbar\omega = \varepsilon_f$ conservation of energy

with translation symmetry

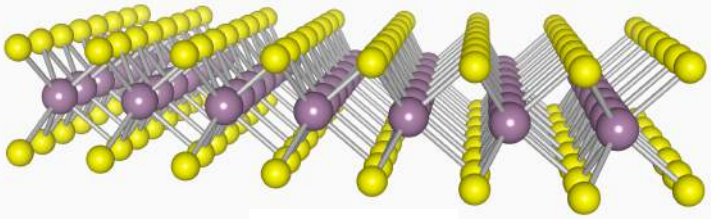
$\mathbf{p}_i + \mathbf{P} = \mathbf{p}_f$ conservation of momentum

photon momentum is negligible

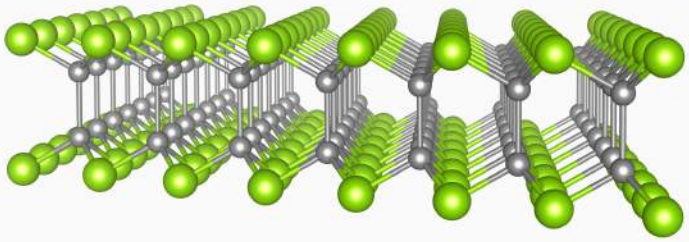
$\hbar\mathbf{k}_i + \hbar\mathbf{K} = \hbar\mathbf{k}_f \Rightarrow \mathbf{k}_i \approx \mathbf{k}_f$

only direct transitions (**k**-conserving) are allowed

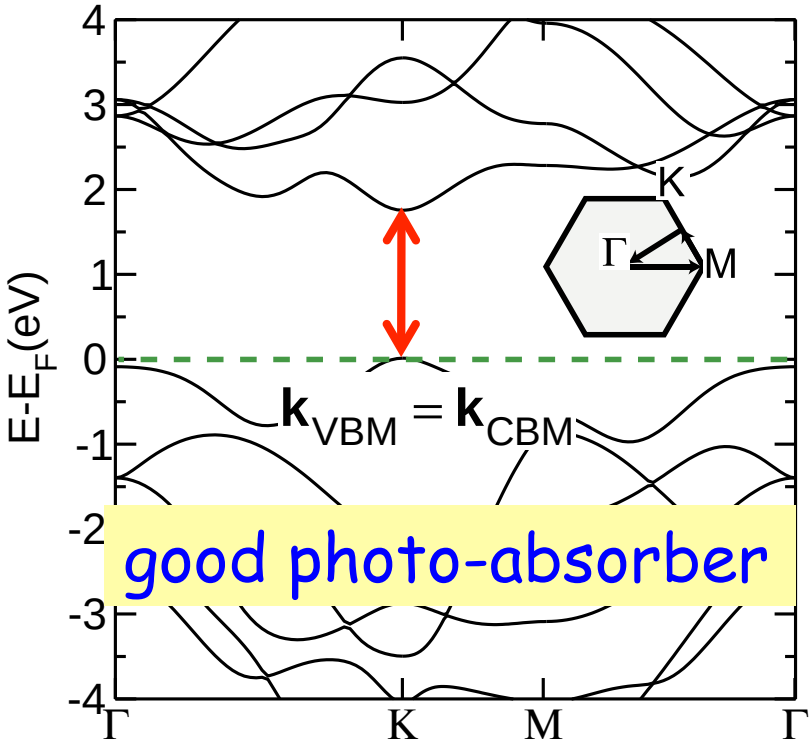
MoS_2 versus GaSe



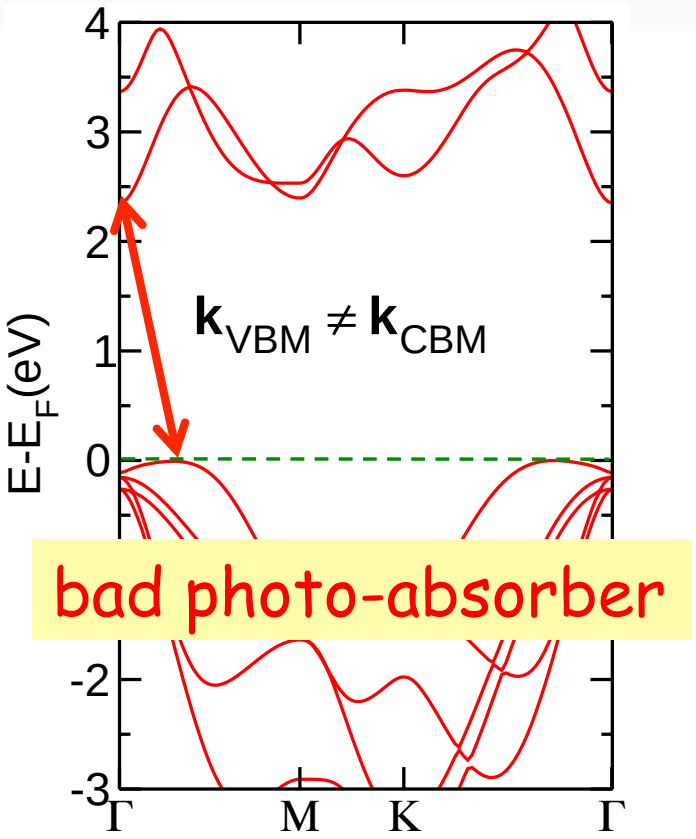
MoS_2



GaSe



good photo-absorber



bad photo-absorber

direct semiconductor

indirect semiconductor