Chair of Experimental Solid State Physics, LMU Munich

"Introduction to Graphene and 2D Materials"

SS24 Lecture 2, 22/4/2024

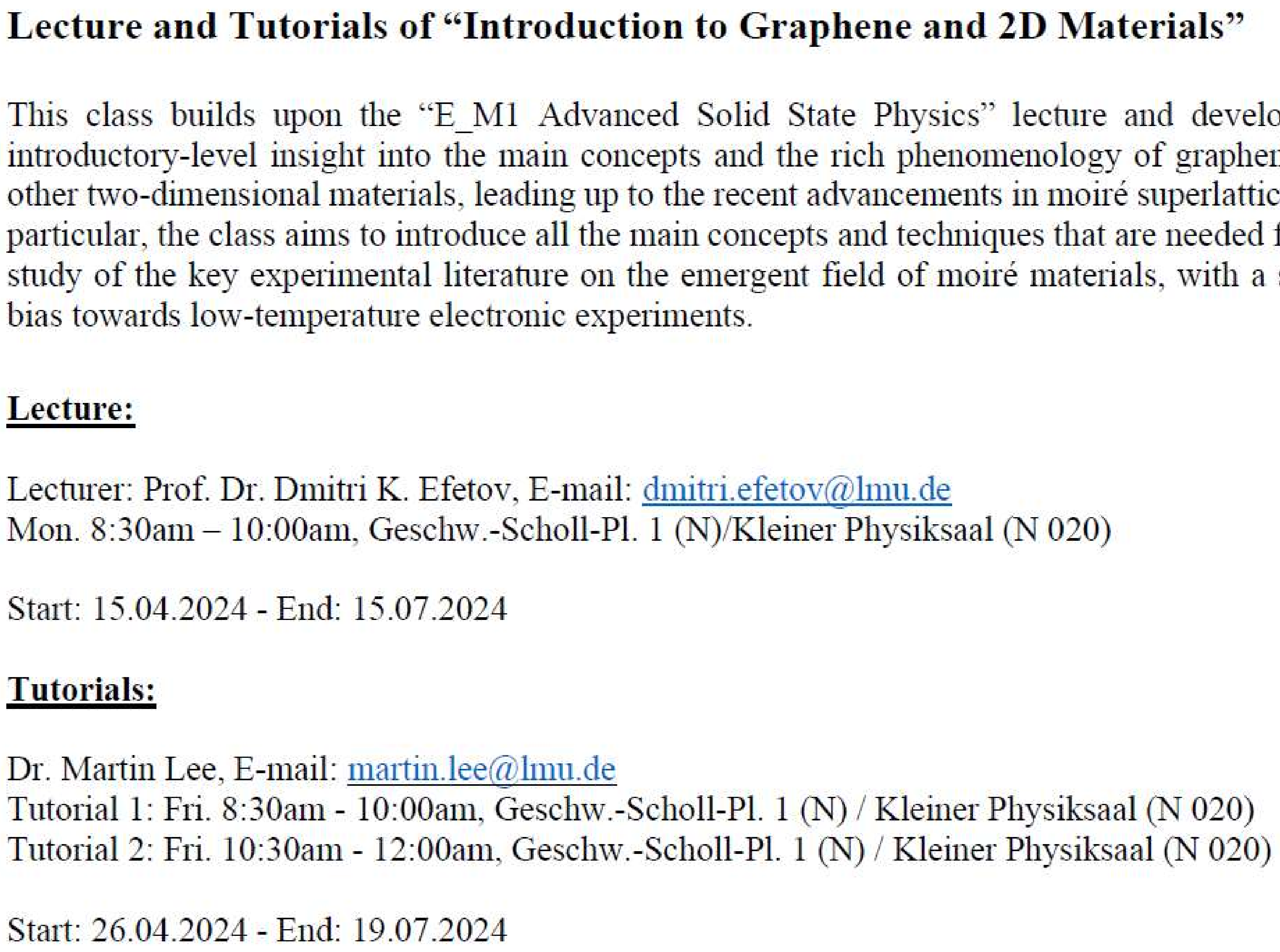
Lecture Structure

Summer term SS 2024

Event	Room	Time	Lecturer
Lecture "Introduction to Graphene and 2D Materials" Lecture Materials: Lecture outline Lecture 1	Geschw.-Scholl-Pl. 1 (N)/Kleiner Physiksaal (N 020)	Mon. 8:30am – 10:00am Begin: 15.04.24 End: 15.07.24	Prof. Dr. D.K.Efetov
Tutorials "Introduction to Graphene and 2D Materials" Exercises:	Geschw.-Scholl-Pl. 1 (N)/Kleiner Physiksaal (N 020)	Fri. 08:30am – 10:00am Fri. 10:30am – 12:00pm Begin: 19.04.24 End: 19.07.24	Dr.M.Lee

→ More info on https://www.quantummatter.physik.lmu.de/

Lecture Structure



Lecture and Tutorials of "Introduction to Graphene and 2D Materials"

This class builds upon the "E_M1 Advanced Solid State Physics" lecture and develops an introductory-level insight into the main concepts and the rich phenomenology of graphene and other two-dimensional materials, leading up to the recent advancements in moiré superlattices. In particular, the class aims to introduce all the main concepts and techniques that are needed for the study of the key experimental literature on the emergent field of moiré materials, with a strong bias towards low-temperature electronic experiments.

Lecture:

Lecturer: Prof. Dr. Dmitri K. Efetov, E-mail: dmitri.efetov@lmu.de
Mon. 8:30am – 10:00am, Geschw.-Scholl-Pl. 1 (N)/Kleiner Physiksaal (N 020)

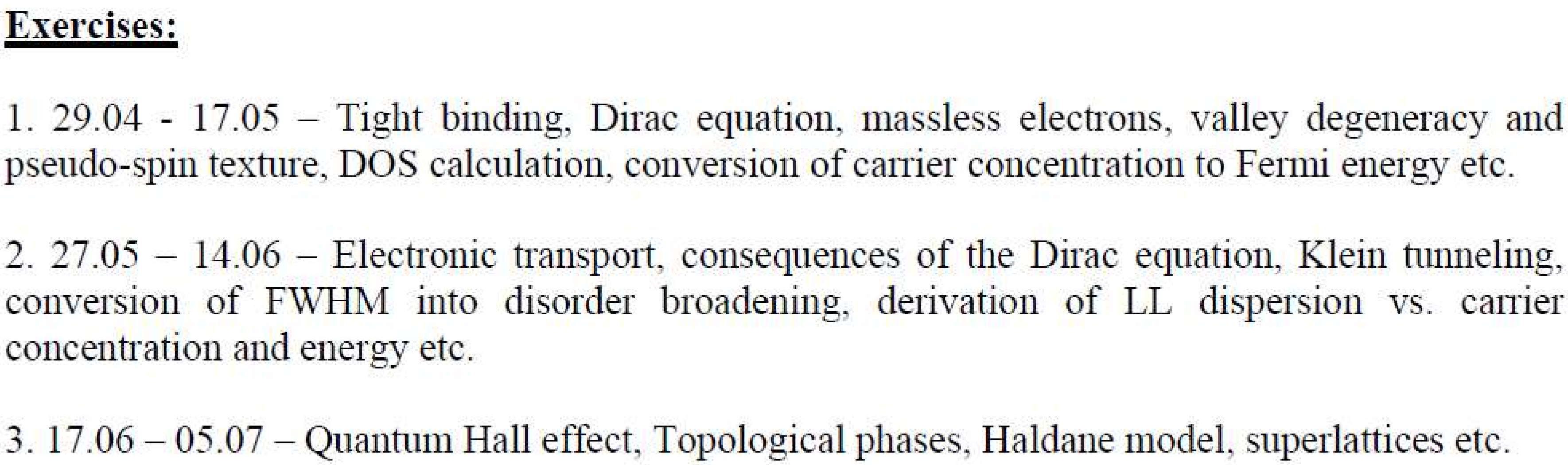
Start: 15.04.2024 - End: 15.07.2024

Tutorials:

Dr. Martin Lee, E-mail: martin.lee@lmu.de
Tutorial 1: Fri. 8:30am - 10:00am, Geschw.-Scholl-Pl. 1 (N) / Kleiner Physiksaal (N 020)
Tutorial 2: Fri. 10:30am - 12:00am, Geschw.-Scholl-Pl. 1 (N) / Kleiner Physiksaal (N 020)

Start: 26.04.2024 - End: 19.07.2024

Lecture Structure



Exercises:

1. 29.04 - 17.05 – Tight binding, Dirac equation, massless electrons, valley degeneracy and pseudo-spin texture, DOS calculation, conversion of carrier concentration to Fermi energy etc.

2. 27.05 – 14.06 – Electronic transport, consequences of the Dirac equation, Klein tunneling, conversion of FWHM into disorder broadening, derivation of LL dispersion vs. carrier concentration and energy etc.

3. 17.06 – 05.07 – Quantum Hall effect, Topological phases, Haldane model, superlattices etc.

Outline - Lecture 2

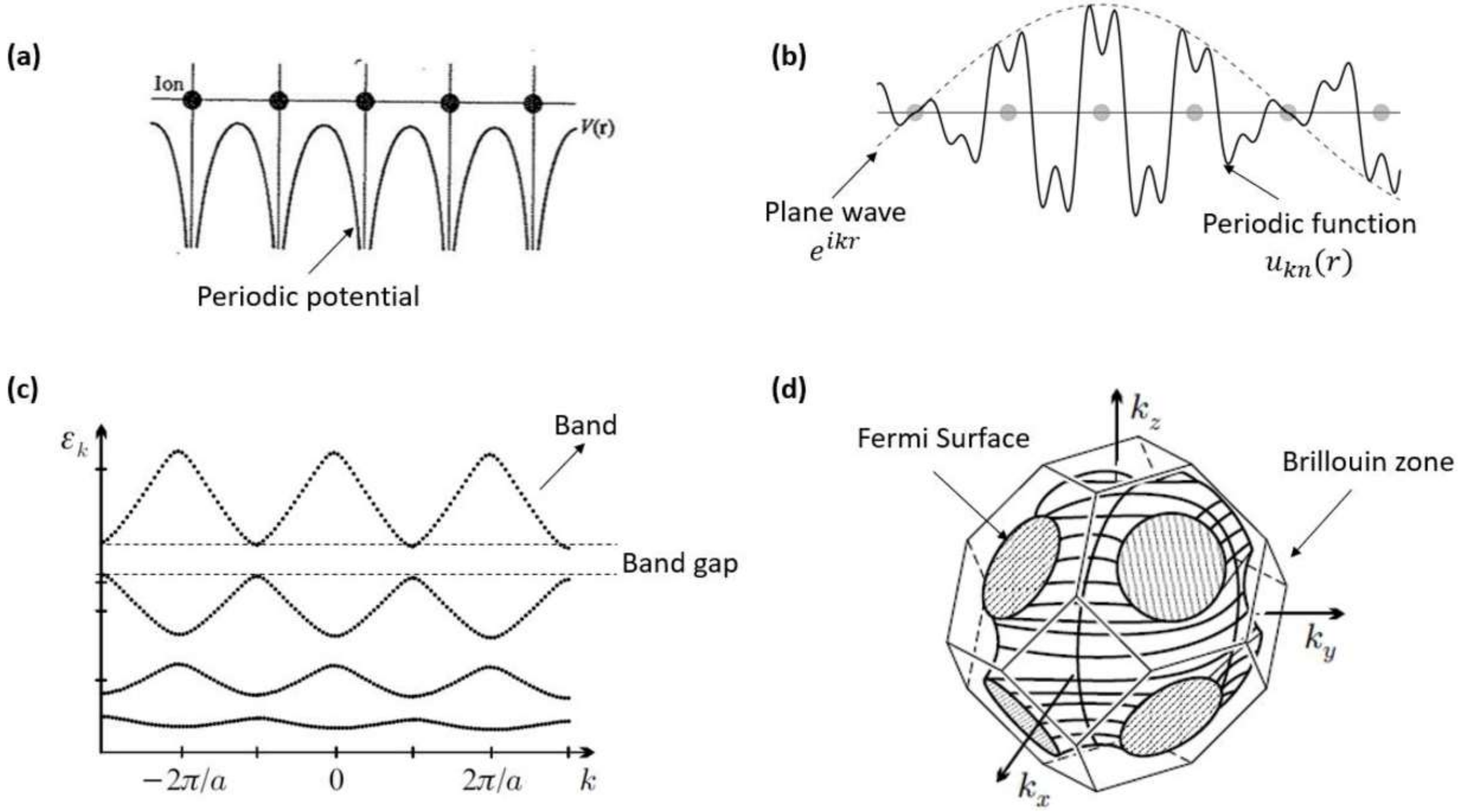
- Short reminders on basic 3D concepts of crystals and band-structure theory – Bloch’s band theory, Bravais lattice, reciprocal lattice, tight binding model.

- Applying the above concepts to the tight binding calculations of single-layer graphene, hBN and AB bilayer graphene.

Bloch waves and band structure

- Blochs theorem states that the solutions od the Schrödingers equation in a periodic potential takes the form of plane waves that are modulated by a periodic function, and are the basis for the states in crystals.

- Bloch waves lead to the formation of electronic bands and Fermi surfaces.



Tight binding model definition

- The tight-binding model (or TB model) is an approach for the calculation of electronic band structures using an approximate set of wave functions based upon superposition of wave functions for isolated atoms located at each atomic site.

- When the atom is placed in a crystal, this atomic wave function overlaps adjacent atomic sites, and so are not true eigenfunctions of the crystal Hamiltonian. The overlap is less when electrons are tightly bound, which is the source of the descriptor "tight-binding". Any corrections to the atomic potential required to obtain the true Hamiltonian H of the system, are assumed small.

Recipe to calculate band structure from tight binding

1. Use Bloch's method to define wavefunctions, which reflect the lattice symmetry (are invariant under any lattice vector translation R_n), and include orbital wavefunctions $\varphi_m(\mathbf{r})$ of the atoms of a single atom Hamiltonian H_{at} in the crystal. Use a linear combination of these as trial wave-functions which are defined as:

$$\psi_m(\mathbf{r}) \approx \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n} e^{i\mathbf{k}\cdot\mathbf{R}_n} \, \varphi_m(\mathbf{r}-\mathbf{R}_n) \, .$$

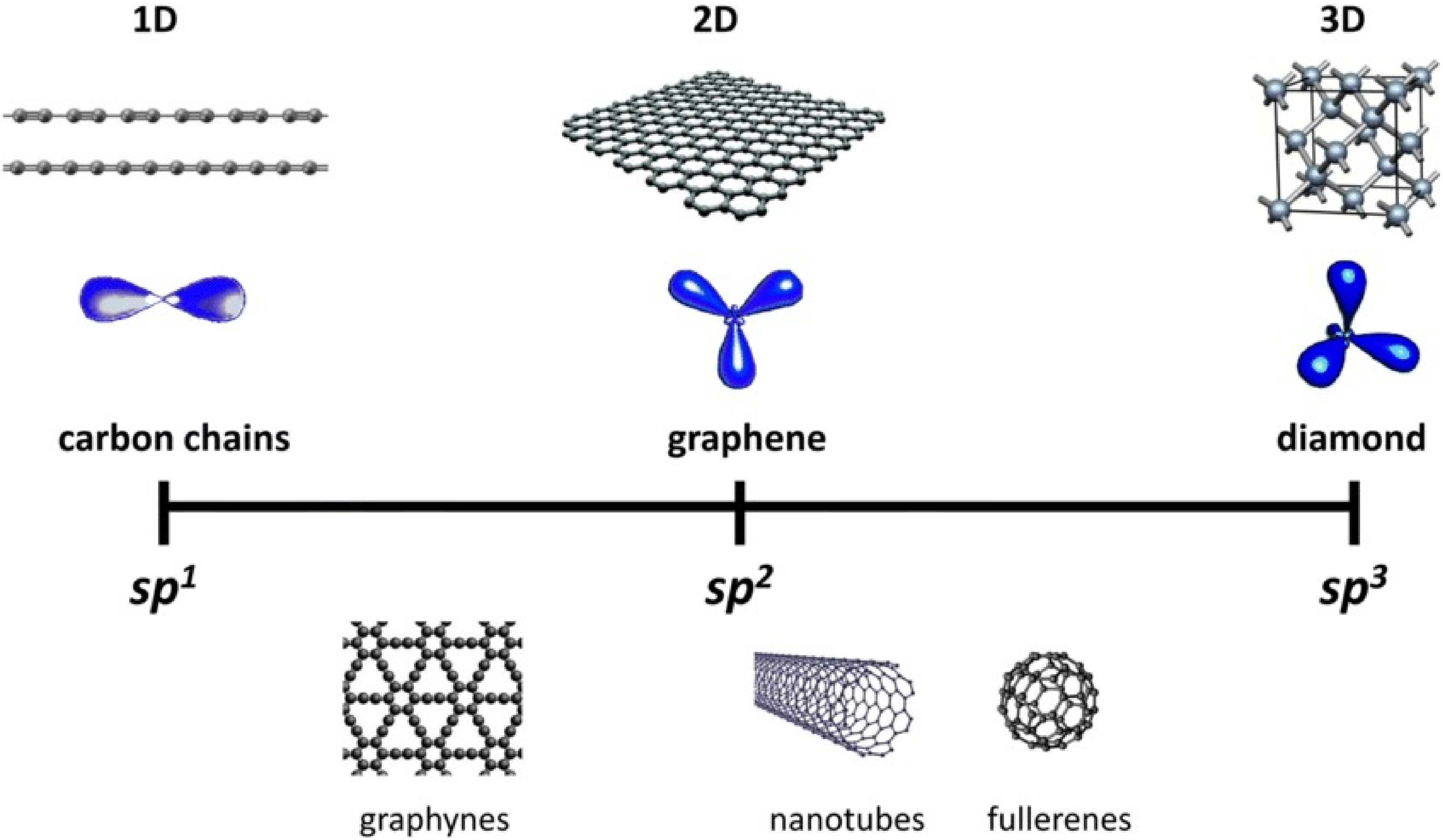
2. Define Hamiltonian, is based on the potentials of the atoms in the crystals, where $V(\mathbf{r}-\mathbf{R}_n)$ is the atomic potential of a site R_n in the crystal. In the tight-binding limit these can be assumed to be small corrections ΔU :

$$H(\mathbf{r}) = H_{\mathrm{at}}(\mathbf{r}) + \sum_{\mathbf{R}_n \neq \mathbf{0}} V(\mathbf{r}-\mathbf{R}_n) = H_{\mathrm{at}}(\mathbf{r}) + \Delta U(\mathbf{r}) \, ,$$

3. Solve Schroedingers equation to get Energy Eigenstates:

$$\varepsilon_m = \int d^3r \, \psi_m^*(\mathbf{r}) H(\mathbf{r}) \psi_m(\mathbf{r})$$

Hybridized $sp^{1,2,3}$ orbitals in carbon systems

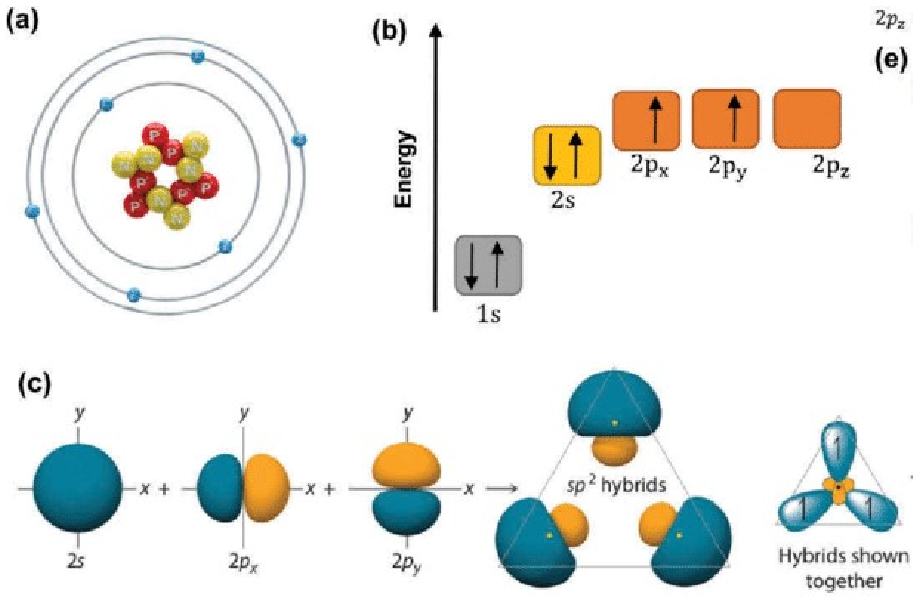


Hybridized bonds in carbon molecules - sp^2 bonds

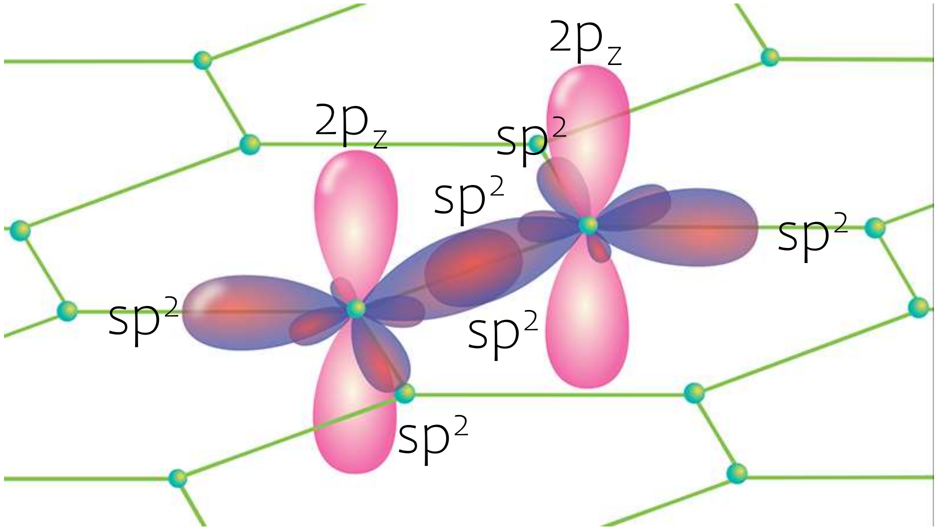
- In molecules or crystals atomic orbitals can hybridize and form bonds with nearest neighbors → the s and p orbitals can hybridize into sp^2 orbitals.

- In graphene each carbon atom has an arrangement of $2(1s)3(sp^2)1(2p_z)$ orbitals, instead of a typical atomic arrangement of $2(1s)2(2s)1(2p_x)1(2p_y)$.

Carbon orbitals:



Carbon orbitals in a graphene lattice:

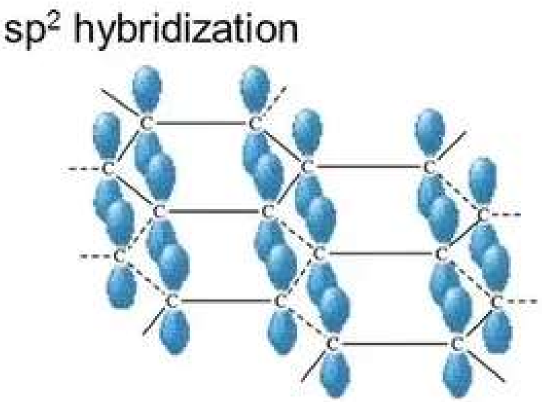


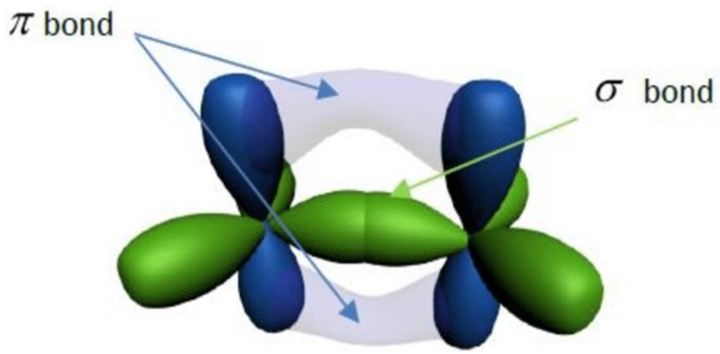
Graphene π-bands

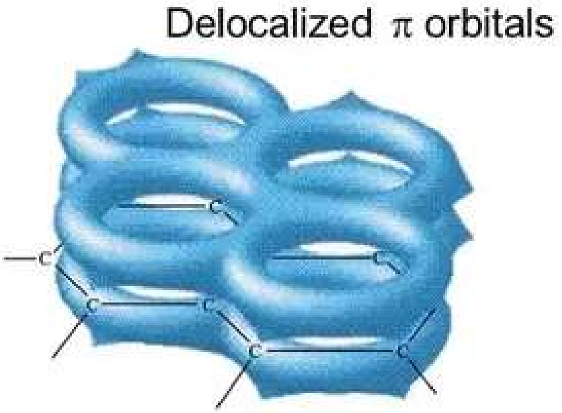
- Bands formed from the sp^2 orbitals, the σ-bands, lie at high energy and do not contribute to the electronic properties. They are very strongly bound and give rise to the ultra-strong mechanical properties of the graphene lattice.

- Bands formed by the p_z orbitals, the π-bands, lie at low energy and define the electronic properties → even though they not very tightly bound to the carbon atoms, the tight binding approximation works very well.

- Each tightly bound electron contributed to one band → each unit cell contains two A and B sublattices, and hence two p_z orbitals form 2 electronic bands.



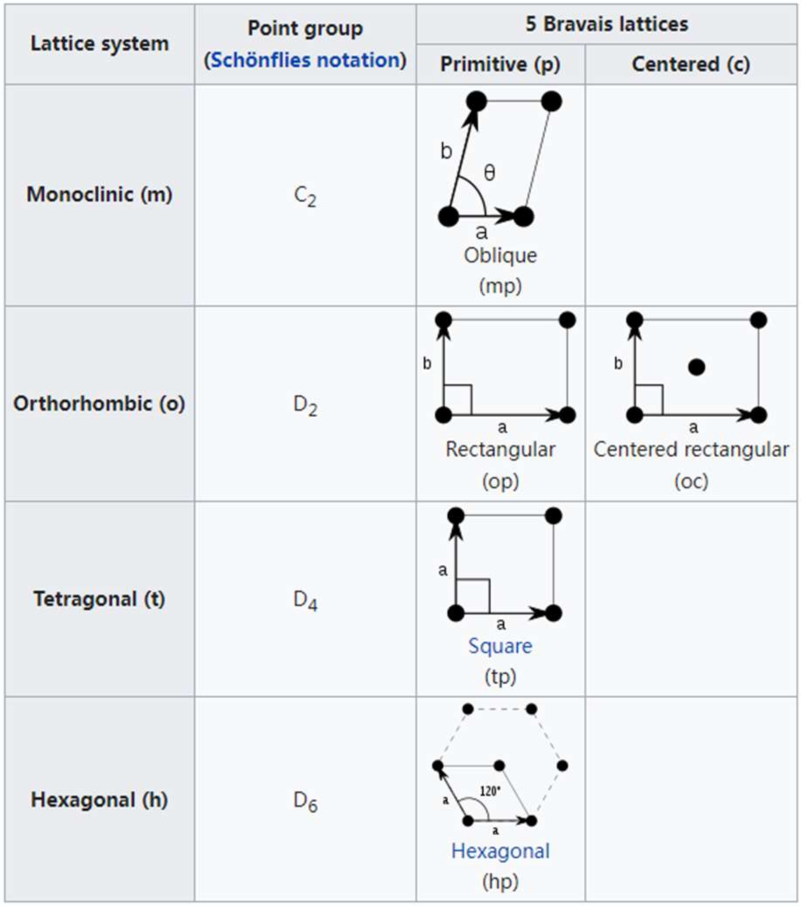




Bravais lattice in 2D

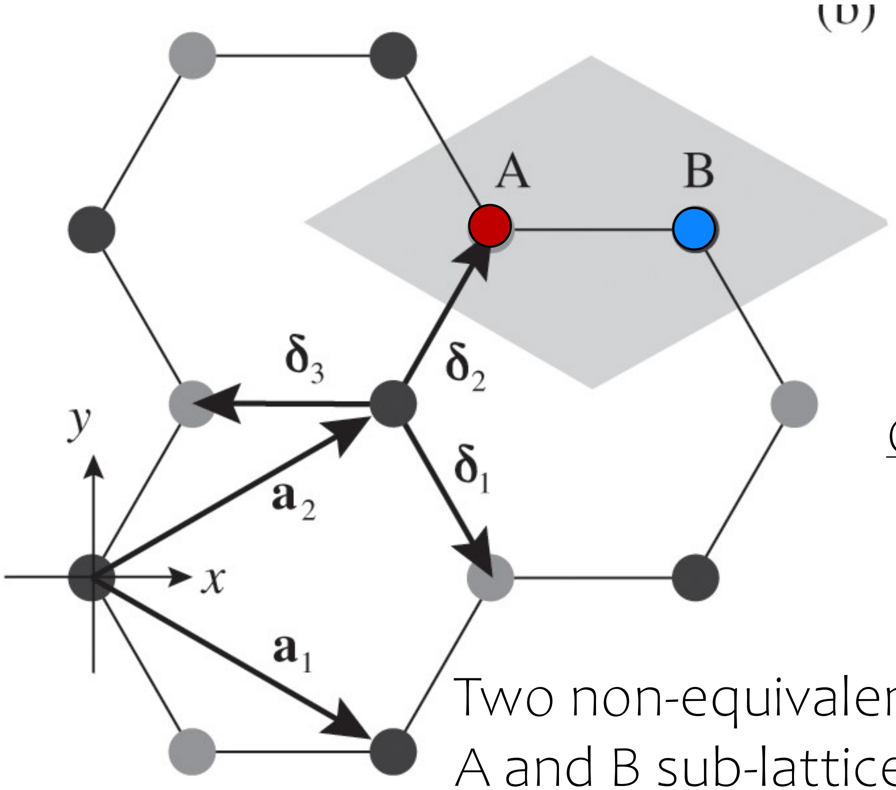
- Any crystal lattice can be described by giving a set of two base vectors $\vec{a}_1$, $\vec{a}_2$, where a lattice can be formed by generating an infinity of translations vectors $\vec{R} = u\vec{a}_1 + v\vec{a}_2$ with u, v = integers.

- The end points of all possible translations vectors define the lattice as a periodic sequence of points in space - crystal lattices show a translation symmetry.



Lattice system	Point group (Schönflies notation)	5 Bravais lattices	
		Primitive (p)	Centered (c)
Monoclinic (m)	C_2	Oblique (mp)	
Orthorhombic (o)	D_2	Rectangular (op)	Centered rectangular (oc)
Tetragonal (t)	D_4	Square (tp)	
Hexagonal (h)	D_6	Hexagonal (hp)	

Graphene hexagonal lattice

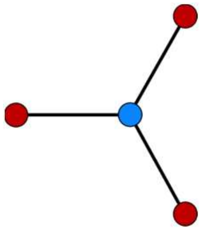


Two non-equivalent A and B sub-lattices

<u>Unit cell vectors:</u>

$$\overrightarrow{a_1} = \frac{\sqrt{3}a_0}{2}(\sqrt{3}, -1)$$
$$\overrightarrow{a_2} = \frac{\sqrt{3}a_0}{2}(\sqrt{3}, +1)$$

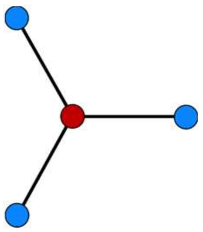
<u>B neighbors:</u>



<u>Carbon translation vectors:</u>

$$\overrightarrow{\delta_1} = \frac{a_0}{2}(1, -\sqrt{3})$$
$$\overrightarrow{\delta_2} = \frac{a_0}{2}(1, \sqrt{3})$$
$$\overrightarrow{\delta_3} = a_0(-1,0)$$

<u>A neighbors:</u>



- Graphene lattice consists of carbon atoms arranged on a 2D Honeycomb lattice → <u>not a Bravais lattice</u>.

- Graphene unit cell, has 2 equivalent hexagonal sub-lattices, called A and B – which form a non-primitive unit cell with A and B carbon atoms on a hexagonal lattice → bipartite lattice, which contains 2 hexagonal sublattices A and B.

Reciprocal lattice

- Fourier transform of the Bravais lattice → from real space into momentum space (k-space). Set of all wavevectors $\overrightarrow{b_1}$, $\overrightarrow{b_2}$ of plane waves in the Fourier series of a spatial function whose periodicity is the same as that of a direct lattice.

- Has fundamental role in most analytic studies of in the theory of diffraction and electron wave functions.

- The Brillouin zone is a Wigner-Seitz cell of the reciprocal lattice (basically unit cell of the reciprocal lattice).

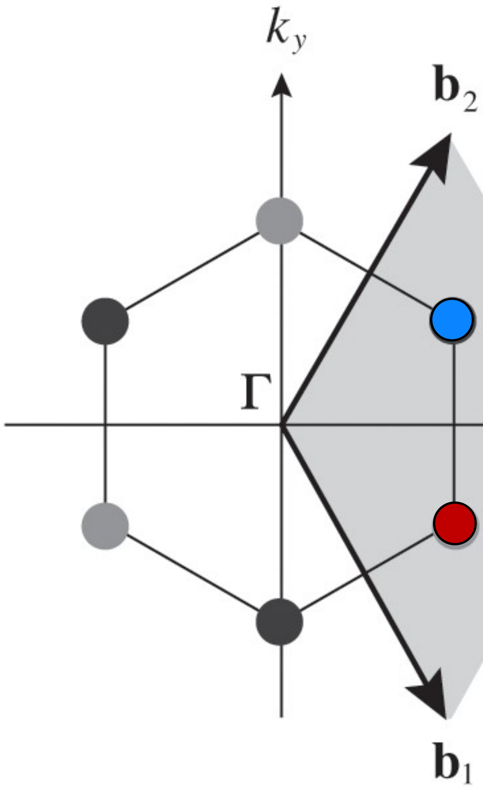
$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\,\delta_{ij}$$

Graphene reciprocal lattice

Reciprocal vectors:

$$\overrightarrow{b_1} = \frac{2\pi}{3a_0}(1, -\sqrt{3})$$

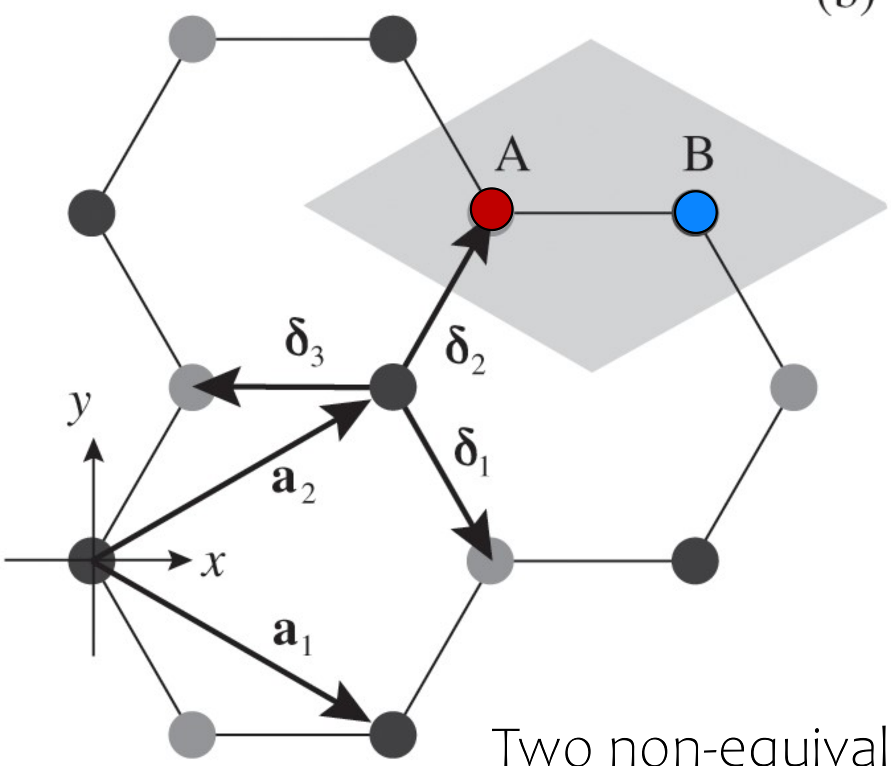
$$\overrightarrow{b_2} = \frac{2\pi}{3a_0}(1, \sqrt{3})$$



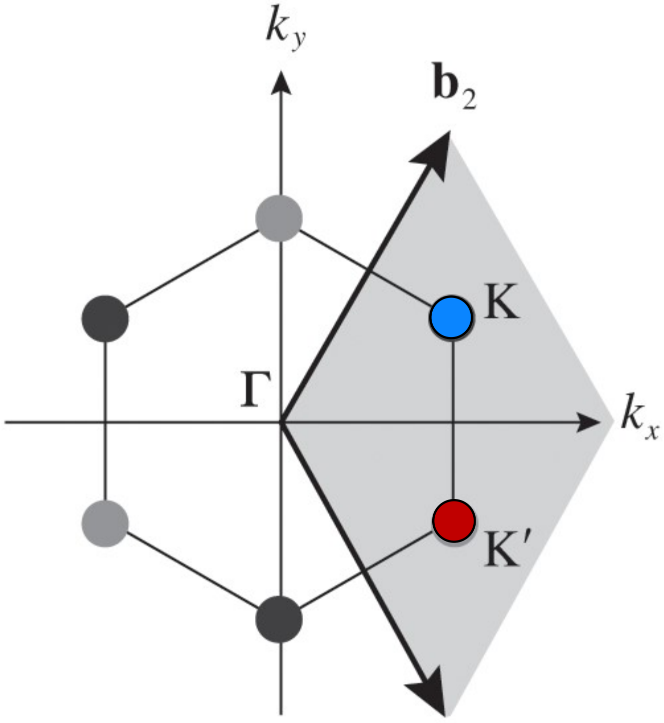
Two non-equivalent
K and K’ points

- High symmetry points in the BZ – Γ, M, K, K’
- A and B sub-lattices translate in the K and K’ points in the BZ

Graphene lattice and reciprocal lattice



Two non-equivalent
A and B sub-lattices



Two non-equivalent
K and K’ points

- A and B sub-lattices translate into the K and K’ points in the BZ.
- Symmetries of the real and reciprocal space protect the Dirac points:

  - inversion symmetry (C_2 or A → B)
  - time reversal symmetry (T or k → -k)
  - 120° rotation symmetry (C_3 or 0° → 120°)

Graphene band structure via tight binding derivation

- Hamiltonian:

$$\hat{H}\psi_k(\vec{r}) = [-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})]\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\psi_k(\vec{r})$$

- Since the two sub-lattices A and B only commute separately with the Hamiltonian, we need to treat these separately and define also separate wave-functions for these, resulting in a set of two orthogonal wave-functions:

$$\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}A}(\vec{r}) + \psi_{\vec{k}B}(\vec{r})$$

$$= \frac{1}{\sqrt{N}} A\left(\vec{k}\right) \sum_n e^{i\vec{k}\overrightarrow{R_n}} u_A(\vec{r} - \overrightarrow{R_n}) + \frac{1}{\sqrt{N}} B\left(\vec{k}\right) \sum_n e^{i\vec{k}\overrightarrow{R_n}} u_B\left(\vec{r} - \overrightarrow{R_n}\right)$$

- Solution of the Hamiltonian then become (with lattice vectors $\vec{R} = u\vec{a}_1 + v\vec{a}_2$):

$$H_{AB} = \sum_n \int e^{i\vec{k}\overrightarrow{R_n}} u_A^*(\vec{r} - \overrightarrow{R_n}) H(\vec{r}) u_B\left(\vec{r} - \overrightarrow{R_n}\right) d\vec{r}$$

- The anti-commutation relations are:

$$\left\{A\left(\vec{k}\right), A^\dagger\left(\vec{k}'\right)\right\} = \left\{B\left(\vec{k}\right), B^\dagger\left(\vec{k}'\right)\right\} = \delta_{\vec{k},\vec{k}'}$$

A and B basis representation

- One can also rewrite this in a matrix form in the basis of the A and B wave-functions:

$$\psi_{\vec{k}}(\vec{r}) = \begin{pmatrix} \psi_{\vec{k}A}(\vec{r}) \\ \psi_{\vec{k}B}(\vec{r}) \end{pmatrix} \rightarrow \begin{pmatrix} \psi_{\uparrow} \\ \psi_{\downarrow} \end{pmatrix}$$

spinor representation

- Here the A and B sublattice sites act as two orthogonal wave-functions, and one can make the same analogy as for the spinor of the 2 states of the spin. We will show that this description can be explained as the isospin.

$$H(\vec{k}) = \begin{bmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{bmatrix}$$

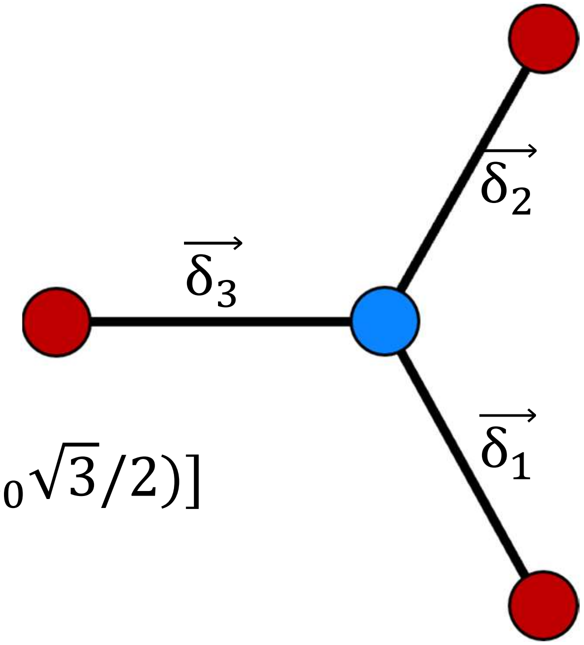
- Solving the Hamiltonian for the AA and BB combination leads only to the self energies, which by symmetry are just zero:

$$H_{AA} = H_{BB} = 0$$

Graphene band structure via tight binding derivation

- For the H_{AB} and H_{BA} only translation vectors to the nearest neighbor sites give finite values. For the A lattice sites (3 adjacent B sites) these vectors are just the nearest neighbor vectors. And for B analogously:

$$\overrightarrow{\delta_1} = \frac{a_0}{2}(1,-\sqrt{3}),\ \overrightarrow{\delta_2} = \frac{a_0}{2}(1,\sqrt{3}),\ \overrightarrow{\delta_3} = a_0(-1,0)$$



- Leading to:

$$H_{AB} = \gamma_0 \sum_n e^{-i\vec{k}\overrightarrow{\delta_n}} = \gamma_0[e^{-ik_x a_0} + 2e^{ik_x a_0/2}\cos(k_y a_0\sqrt{3}/2)]$$

$$H_{BA} = \gamma_0 \sum_n e^{i\vec{k}\overrightarrow{\delta_n}} = \gamma_0[e^{ik_x a_0} + 2e^{-ik_x a_0/2}\cos(k_y a_0\sqrt{3}/2)]$$

- With γ_0:

$$\gamma_0 = \int u_A^*(\vec{r})H(\vec{r})u_B\left(\vec{r} + \overrightarrow{\delta_3}\right) \sim 2.8eV$$

A and B basis representation

- One can also rewrite this in a matrix form in the basis of the A and B wave-functions:

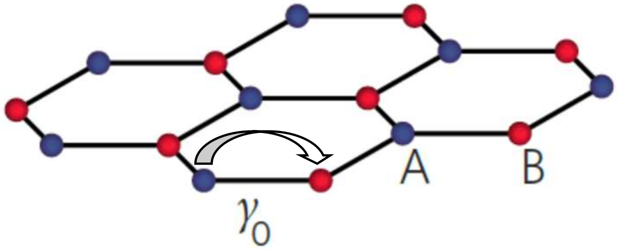
$$\psi_{\vec{k}}(\vec{r}) = \begin{pmatrix} \psi_{\vec{k}A}(\vec{r}) \\ \psi_{\vec{k}B}(\vec{r}) \end{pmatrix} \rightarrow \begin{pmatrix} \psi_{\uparrow} \\ \psi_{\downarrow} \end{pmatrix}$$

spinor
representation

$$H(\vec{k}) = \gamma_0 \begin{bmatrix} 0 & [e^{-ik_x a_0} + 2e^{ik_x a_0/2}\cos(k_y a_0\sqrt{3}/2)] \\ [e^{ik_x a_0} + 2e^{-ik_x a_0/2}\cos(k_y a_0\sqrt{3}/2)] & 0 \end{bmatrix}$$

$$\gamma_0 = \int u_A^*(\vec{r})H(\vec{r})u_B\left(\vec{r} + \overrightarrow{\delta_3}\right) \sim 2.8eV$$

$\gamma = \gamma_0$ can be interpreted as the hopping parameter of an electron tunneling from A to B lattice sites.



Graphene band-structure – Dirac cones

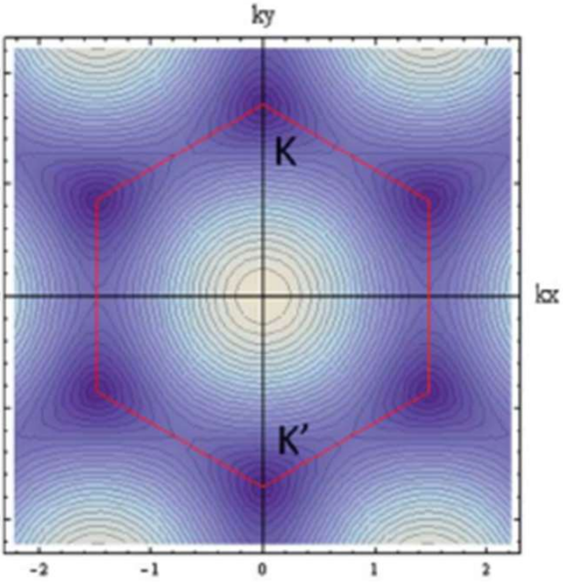
- Solve Schroedingers equation to get Energy Eigenstates:

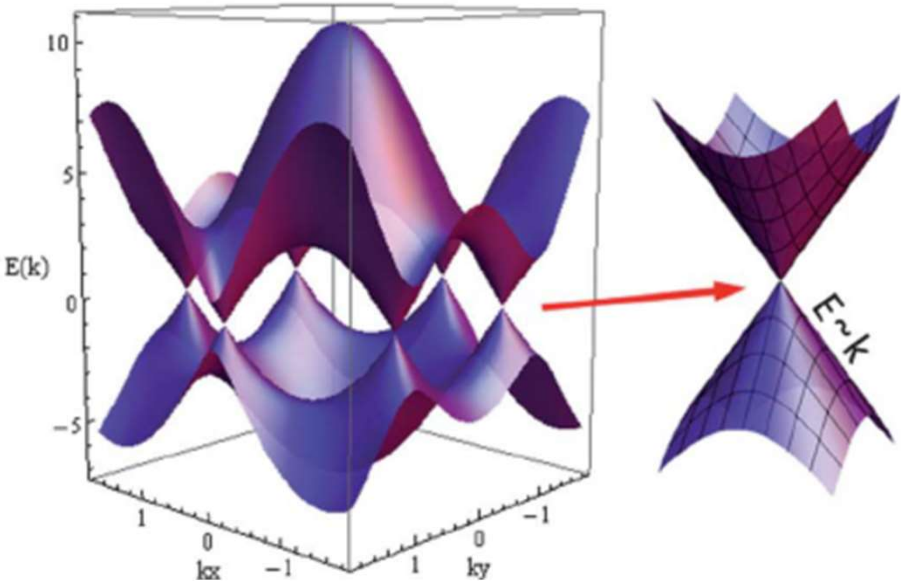
$$\varepsilon_m = \int d^3r\, \psi_m^*(\mathbf{r}) H(\mathbf{r}) \psi_m(\mathbf{r})$$

- The final solution of the Eigen-energies of the Hamiltonian have the form:

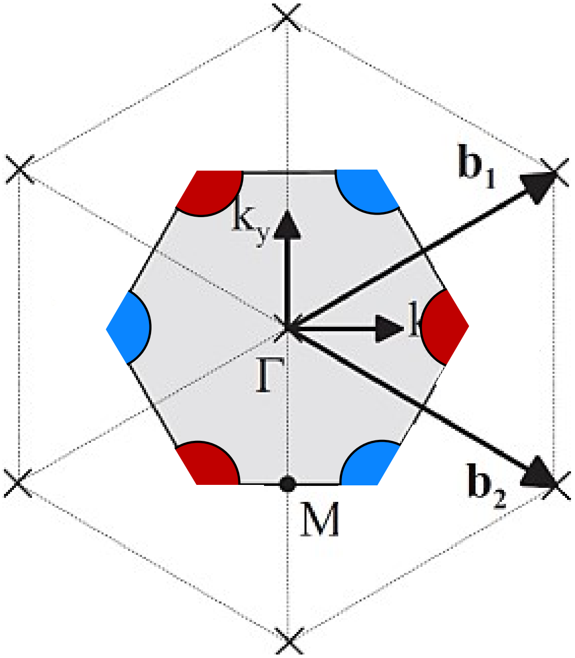
$$E(\vec{k}) = \pm\gamma_0 \sqrt{3 + 2\cos(\sqrt{3}k_y a_0) + 4\cos(3k_x a_0/2)\cos(\sqrt{3}k_y a_0/2)}$$

- Dirac cones are formed in the K and K' points. Here the electrons can be shown to be massless and the dispersion relation described by the Dirac equation.





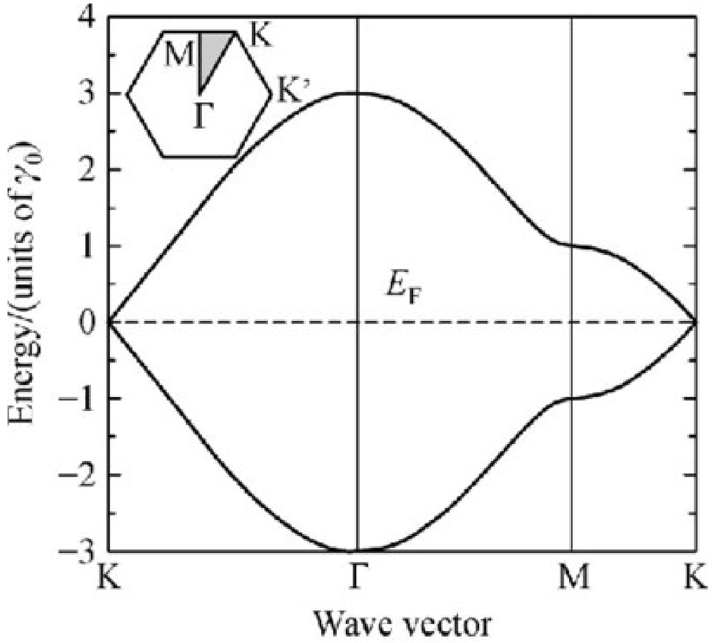
Dirac cones in the K and K’ points

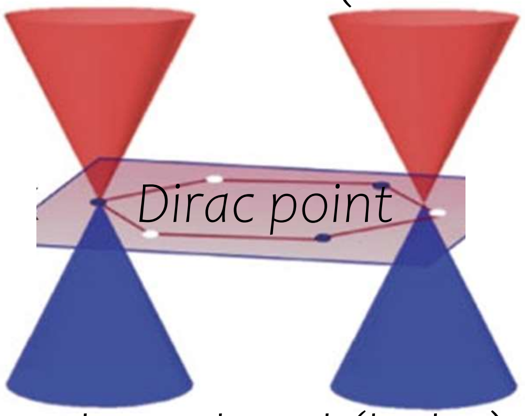


- Linear dispersion relation → Effective mass of the electrons is zero $m^* = 0$.

$$m^* = \pm\hbar\left(\frac{d^2E_k}{dk^2}\right)^{-1} \sim 0 \qquad v_F = \frac{\sqrt{3}a_0\gamma}{2\hbar} \sim \frac{c}{300} \sim 10^6\, m/s$$

- Dirac cones are formed in the K and K’ points → 2 valleys → no band-gaps.





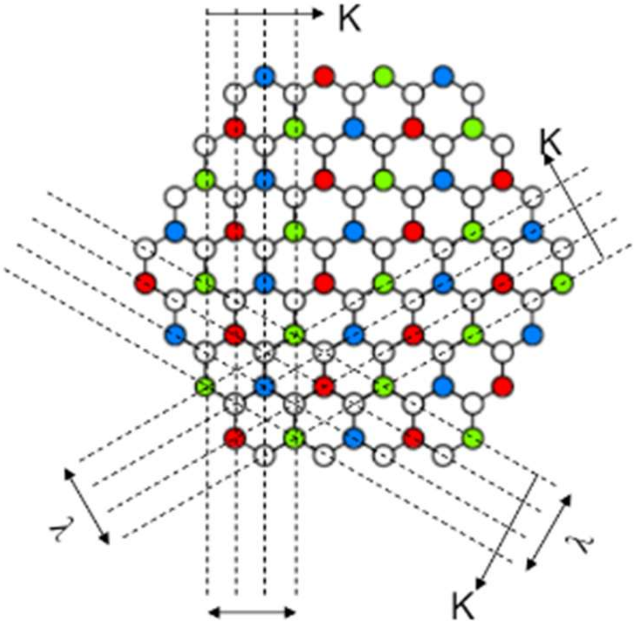
Valley K’ *Valley K*

conduction band (electrons)

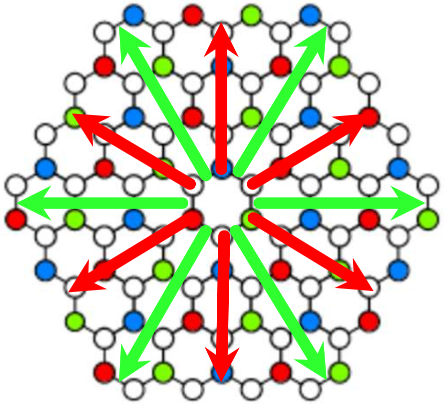
valence band (holes)

Phase changes under hopping from A to B

Propagation directions:



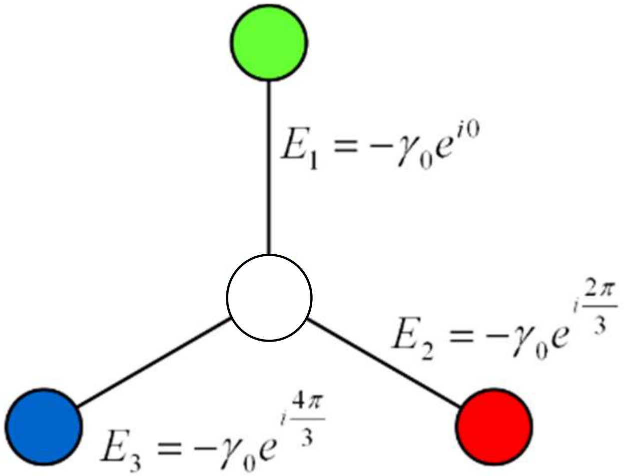
Allowed k-vectors:



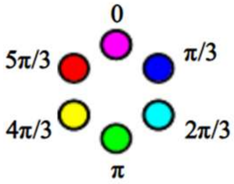
→ metallic

→ gapped

Phase changes under hopping:



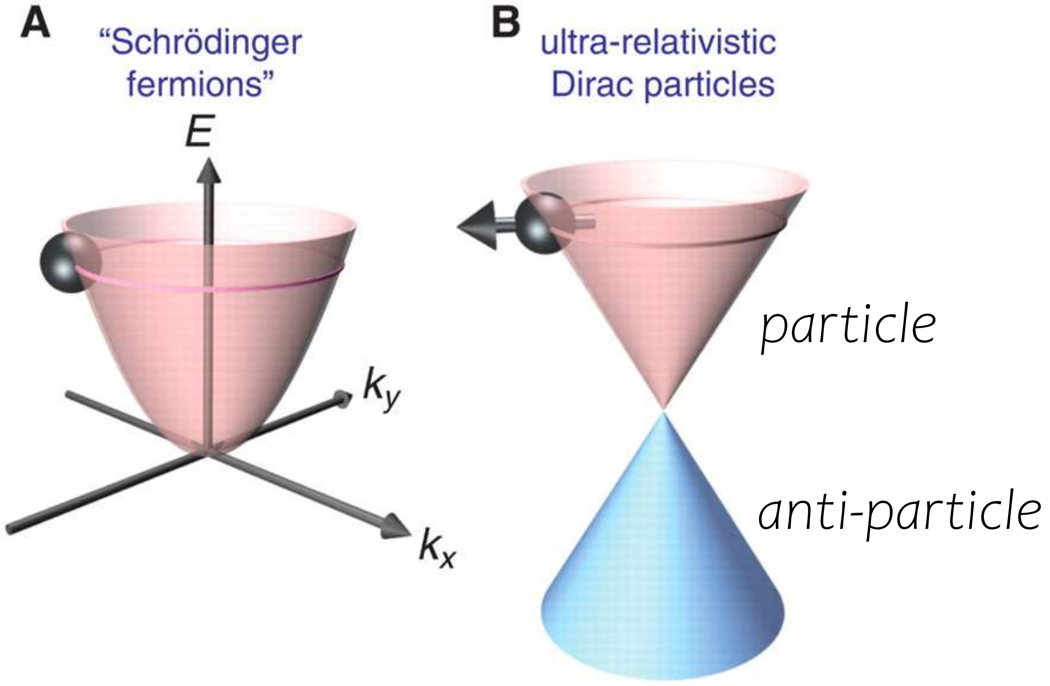
Phase:



Analogy to Dirac equation

- Non-relativistic particles – Schroedinger equation – no spin vs. momentum locking.

- Relativistic particles – Dirac equation – spin and momentum are locked.



$\hat{H} = \hat{p}^2 / 2m^*$ $\hat{H} = c\,\vec{\sigma} \cdot \hat{p}$

- $(i\hbar\gamma^{\mu}\partial^{\mu} - mc)\psi = 0$

- $H(\vec{p}) = c\vec{\sigma}\vec{p}$
  ($\vec{\sigma}$ *Pauli matrizes)*

- *v = c , m = 0*

- *spin // momentum*

→ *"Helicity" (or "chirality" for particles with mass)*

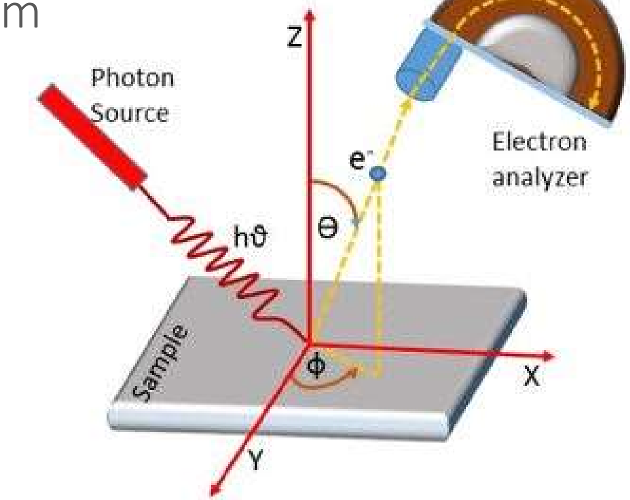
Angle-resolved photo emission maps band-structure

ARPES measurement schematic:

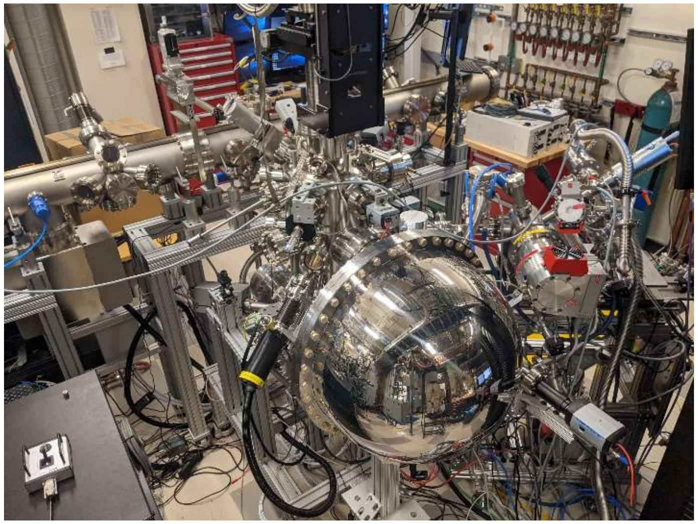
Energy and momentum conserving photo-emission process

$$E_{\text{kin}} = h\nu - \phi - E_B,$$

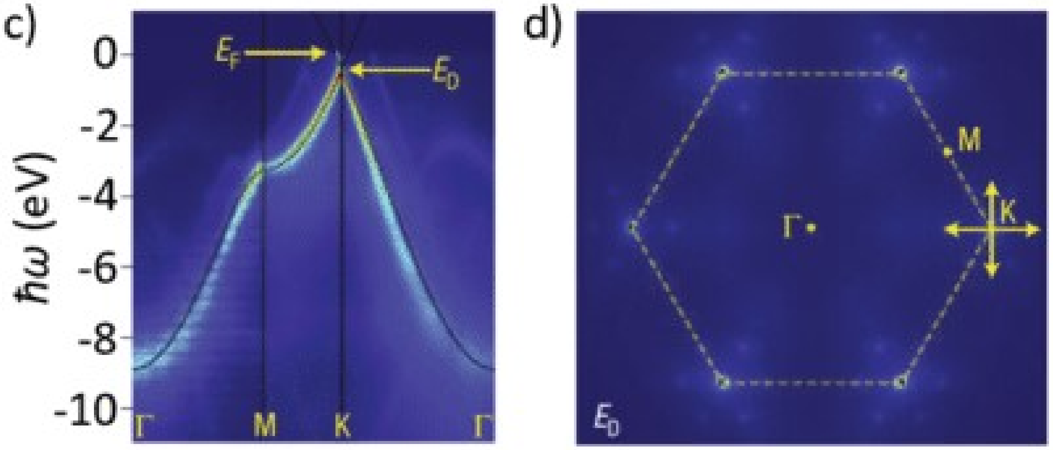
$$\hbar \mathbf{k}_{||} = \sqrt{2mE_{\text{kin}}}\,\sin(\vartheta),$$

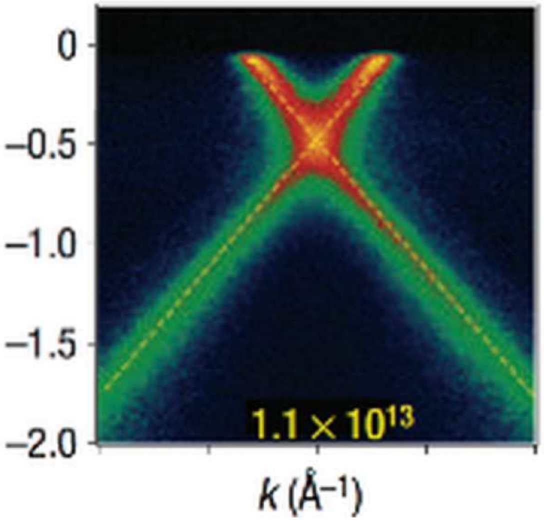


ARPES tool:



ARPES measurements of single-layer graphene:





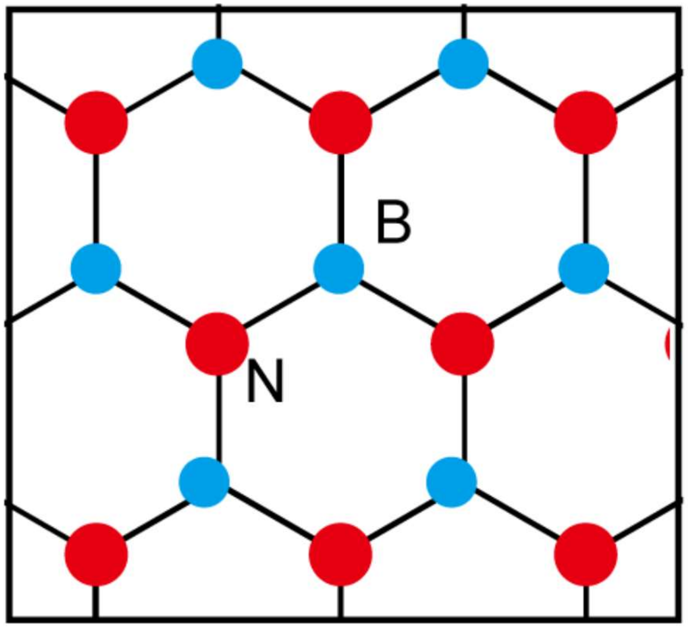
hBN tight binding

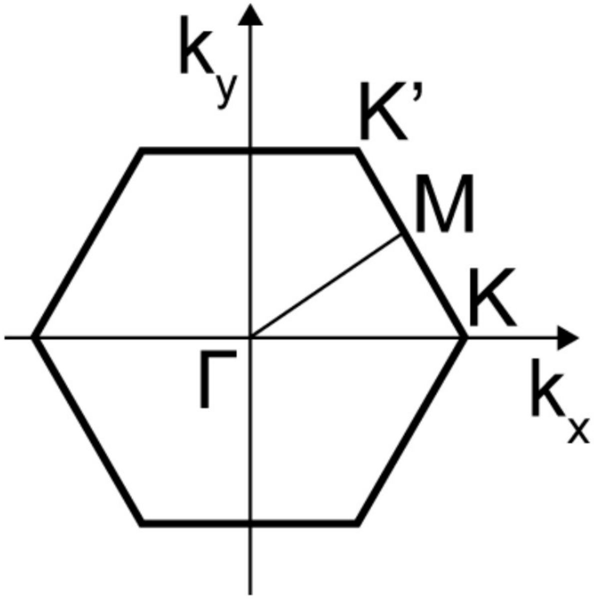
- We use a Hamiltonian that considers only the pz orbitals (or hybridized orbital) from the boron B and nitrogen N atoms.

- We consider only nearest neighbor hopping. Onsite energy on the B atom is E_B and onsite energy of the N atom is E_N.

- γ_0 is the hopping parameter between N and B.

- $\overrightarrow{\delta_n}$ are the translation vectors between the B and N atoms.





hBN tight binding

- We use a Hamiltonian that considers only the p_z orbitals (or hybridized orbital) from the boron B and nitrogen N atoms.

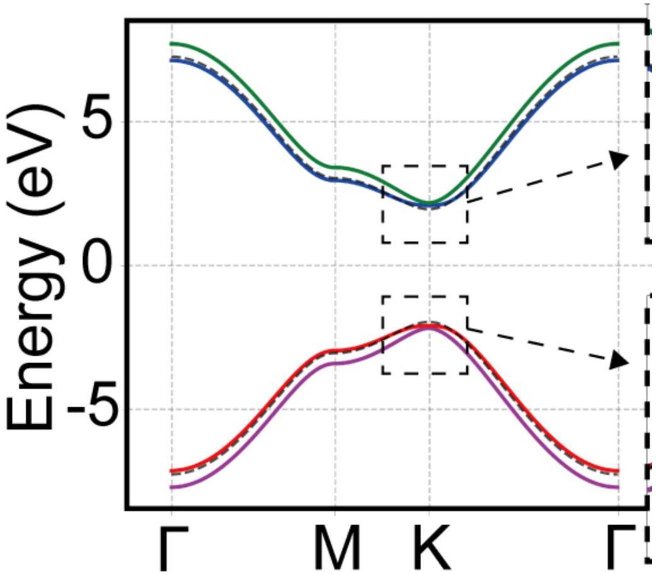
- We consider only nearest neighbor hopping. Onsite energy on the B atom is E_B and onsite energy of the N atom is E_N.

- γ_0 is the hopping parameter between N and B.

- $\overrightarrow{\delta_n}$ are the translation vectors between the B and N atoms.

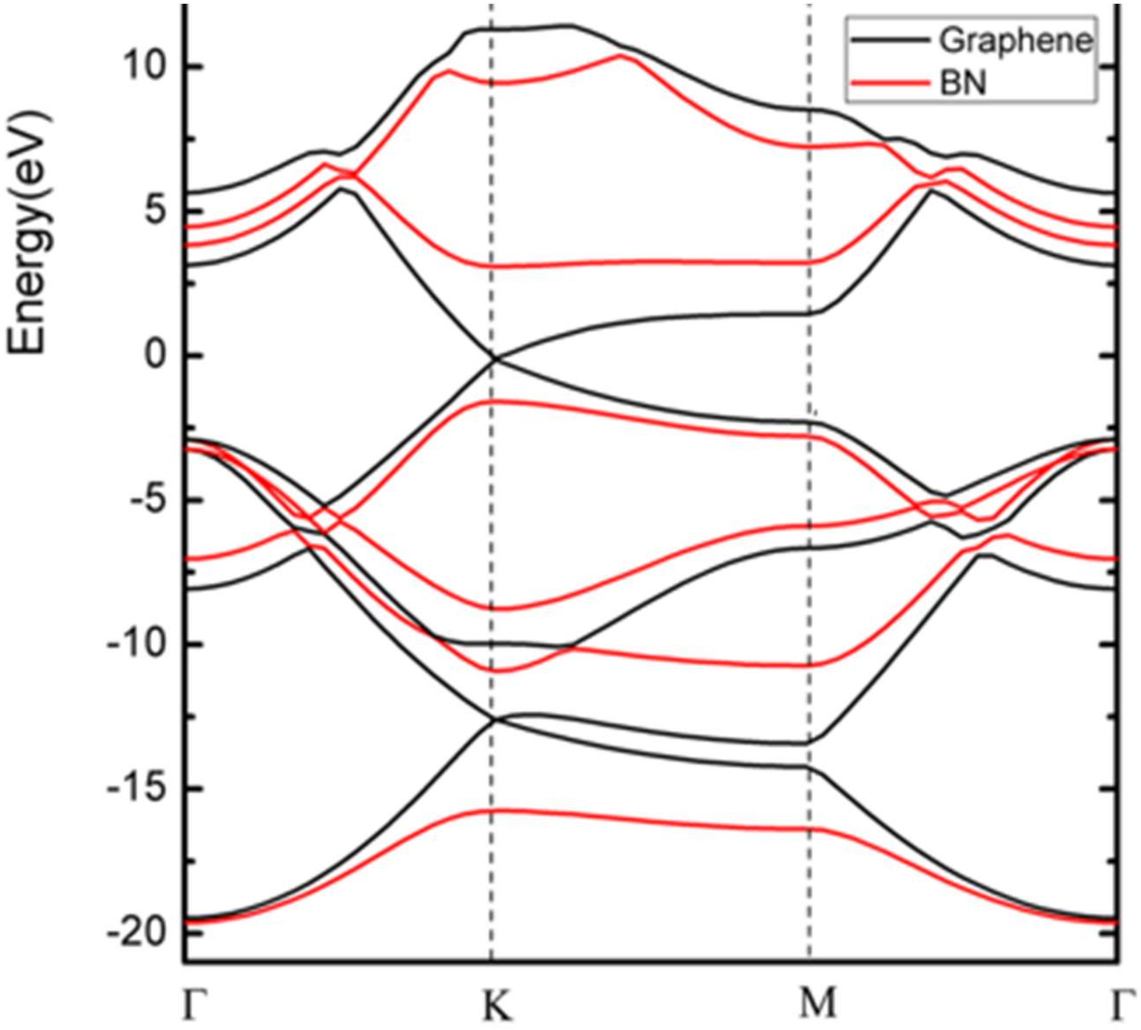
$$H(\vec{k})=\begin{bmatrix} M_0 & \gamma_0 \sum_n e^{-i\vec{k}\overrightarrow{\delta_n}} \\ \gamma_0 \sum_n e^{i\vec{k}\overrightarrow{\delta_n}} & -M_0 \end{bmatrix}$$

$$M_0 = (E_B - E_N)/2$$

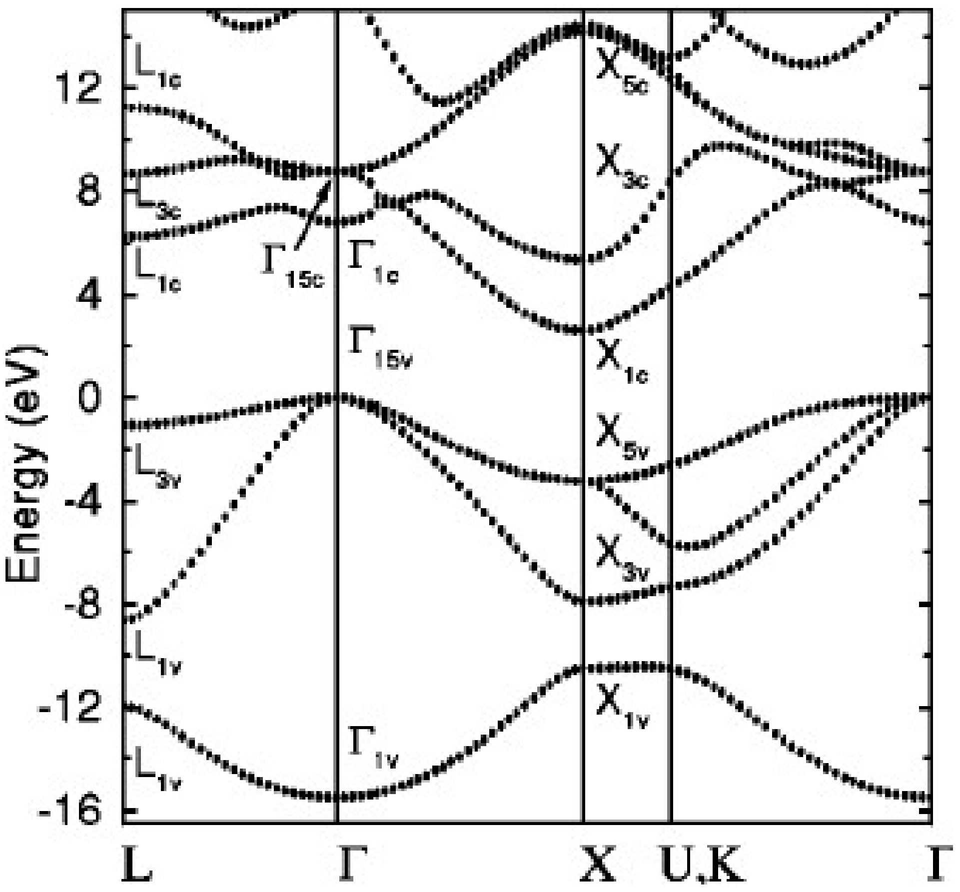


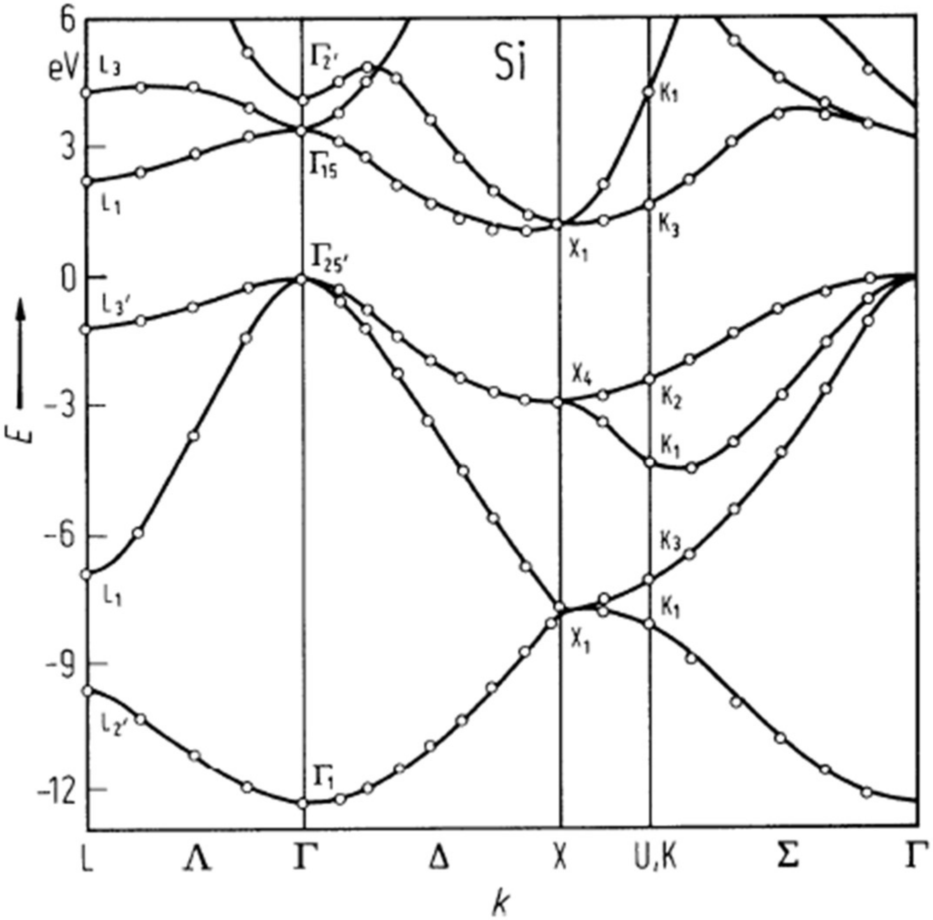
Comparison hBN and graphene band-structure

- Band-structures between hBN and graphene are similar, but the inequivalence of the A and B carbon sub-lattices, which are now replaced by N and B sub-lattices, have no C_2T symmetry, and the Dirac point are lifted and replaced by large band gaps.

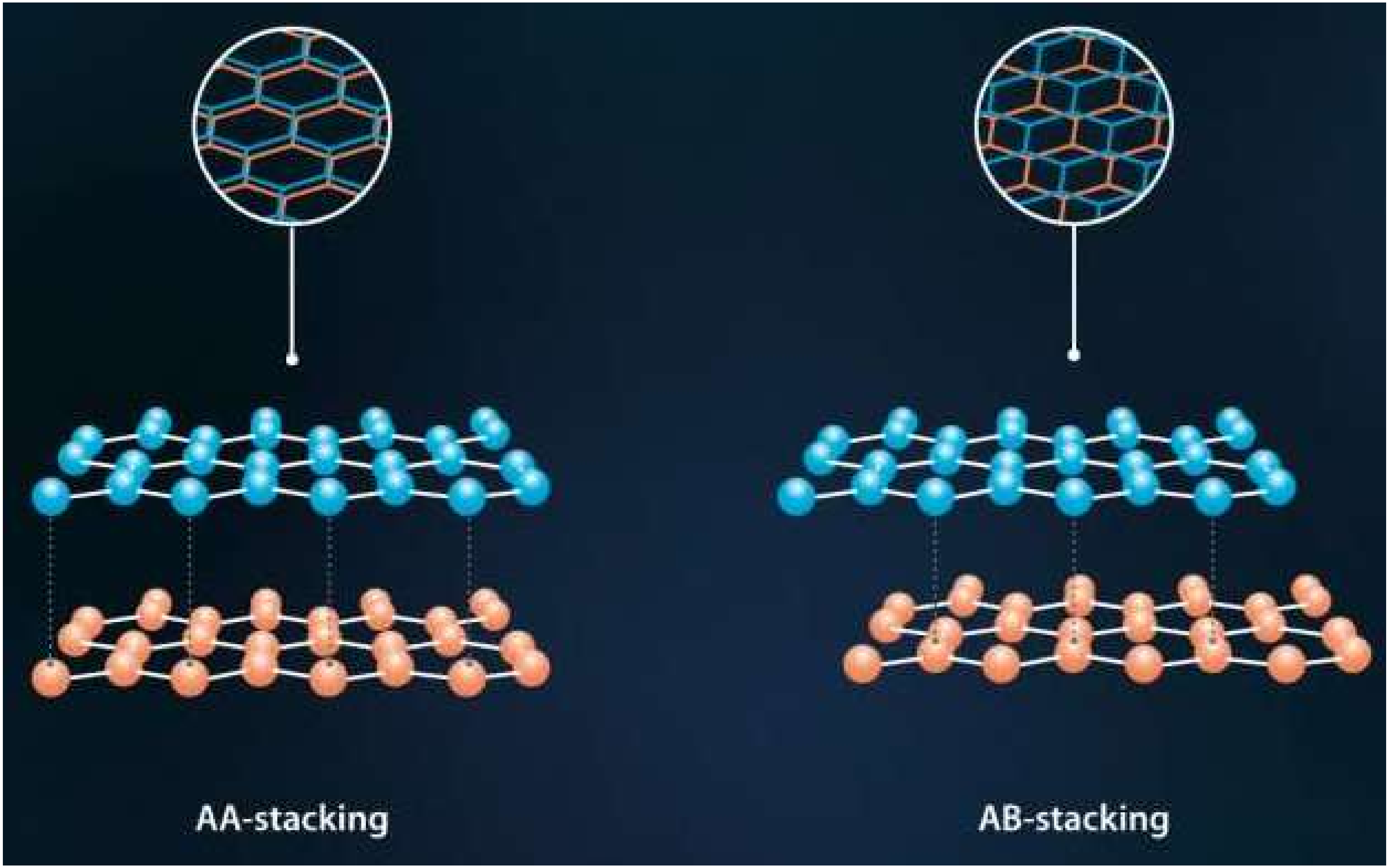


Similar gap closing in SiC vs. Si

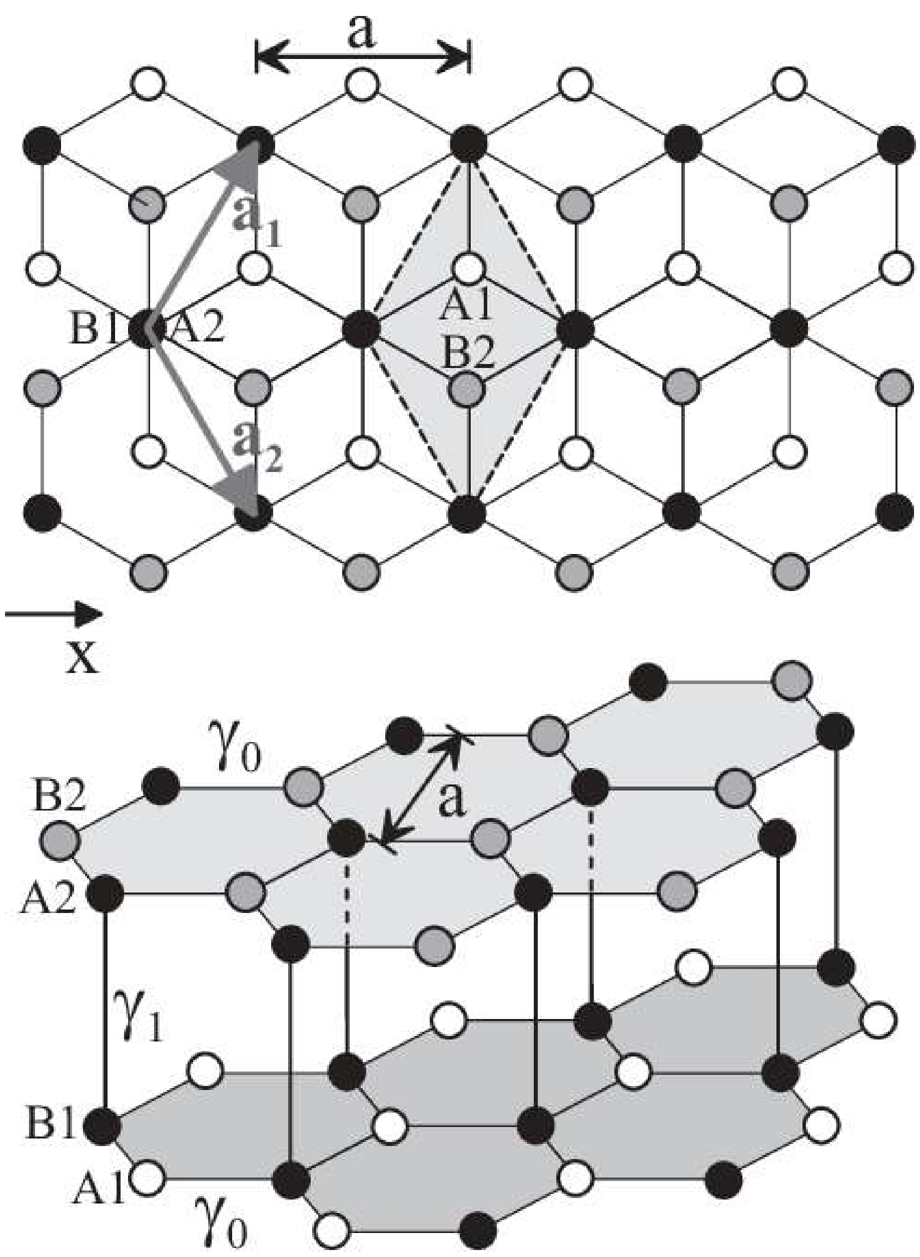




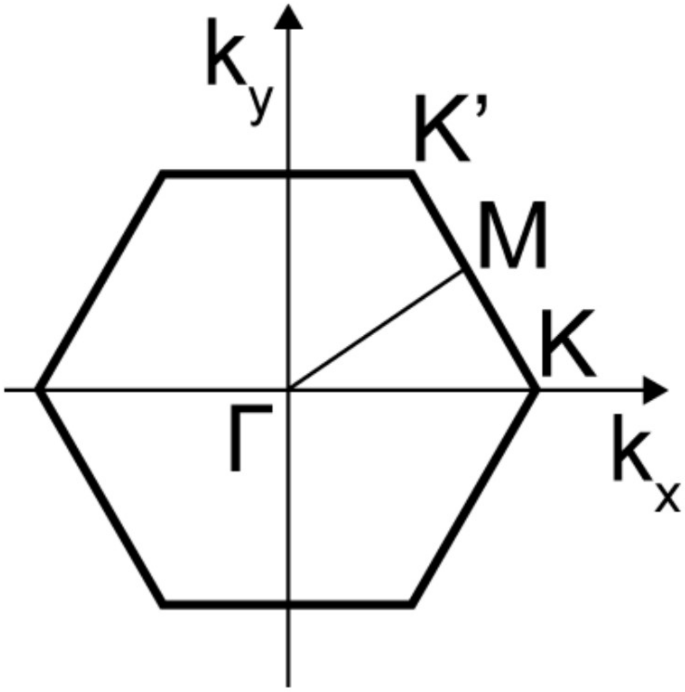
Bilayer graphene



AB bilayer graphene unit cell and BZ

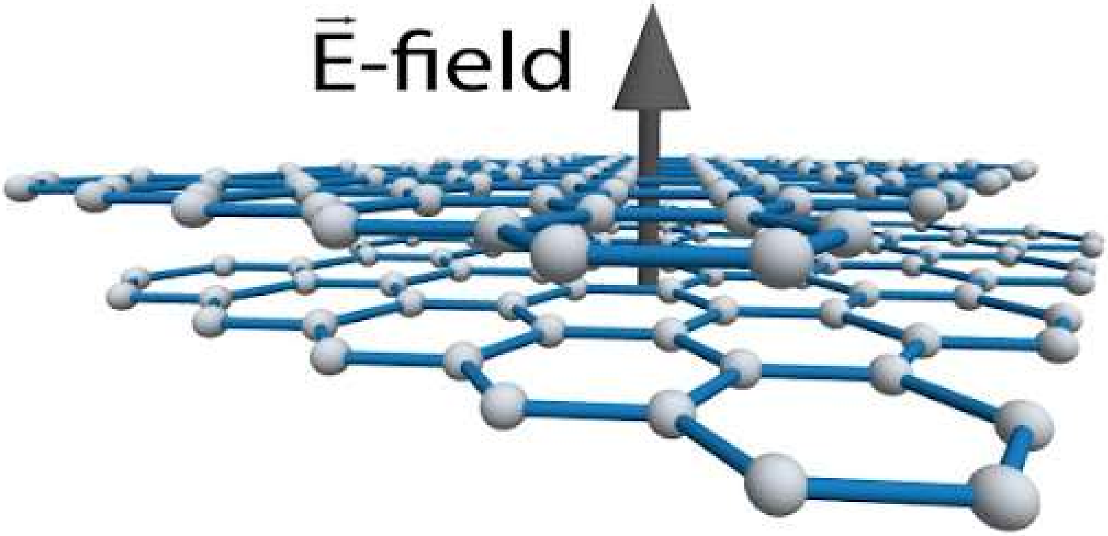


- AB bilayer graphene consists of two AB stacked graphene layers. The unit cell can be spanned by the same unit cell vectors like in single-layer graphene, with now 4 atoms in the unit cell. This results in A and B (A’ and B’) sub-lattices in each layer, and therefore 4 equivalent sub-lattices.



Potential difference between the layers

- One big difference to single graphene, is that one can put the two graphene layers onto different potentials, which define a potential difference between the layers Δ. This can f.e. be induced by a perpendicular electric field E.



- Solving the Hamiltonian for the self energies of the A1A1, B1B1, A2A2, B2B2 combination leads only to the self energies, which by symmetry should be just zero, but now can be raised or lowered by Δ :

$$-H_{A1A1} = -H_{B1B1} = H_{A2A2} = H_{B2B2} = \Delta/2$$

Isospin in AB bilayer graphene

- One can also rewrite this in a matrix form in the basis of the A1 and B1, and A2 and B2 wave-functions:

$$\psi_{\vec{k}}(\vec{r}) = \begin{pmatrix} \psi_{\vec{k}A1}(\vec{r}) \\ \psi_{\vec{k}B1}(\vec{r}) \\ \psi_{\vec{k}A2}(\vec{r}) \\ \psi_{\vec{k}B2}(\vec{r}) \end{pmatrix}$$

- Similar to single-layer graphene we can define the isospin properties in AB bilayer graphene, where we now have 4 orthogonal wave-functions.

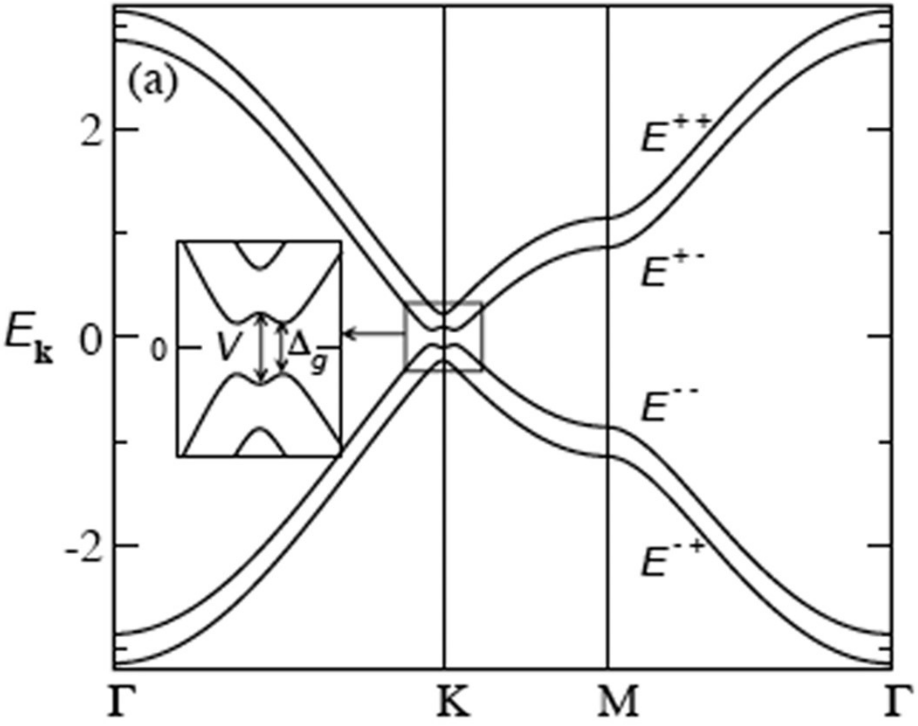
$$\mathcal{H} = \begin{pmatrix} -\Delta/2 & \gamma_0 \sum_i e^{-i\vec{k}\vec{\delta}_i} & 0 & 0 \\ \gamma_0 \sum_i e^{-i\vec{k}\vec{\delta}_i} & -\Delta/2 & \gamma_1 & 0 \\ 0 & \gamma_1 & \Delta/2 & \gamma_0 \sum_i e^{-i\vec{k}\vec{\delta}_i} \\ 0 & 0 & \gamma_0 \sum_i e^{-i\vec{k}\vec{\delta}_i} & \Delta/2 \end{pmatrix}$$

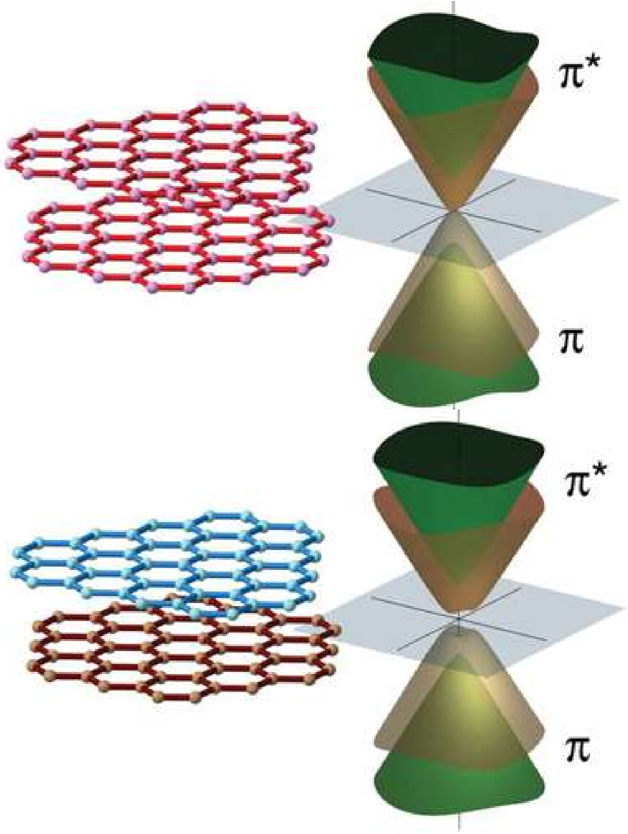
- Solving the Hamiltonian gets us the following band-structure:

$$\epsilon^{\pm}_{1,2}(\vec{\kappa}) = \pm\sqrt{\frac{\gamma_1^2}{2} + \frac{\Delta^2}{4} + \hbar^2 v_F^2 \kappa^2 \pm \sqrt{\frac{\gamma_1^4}{4} + \hbar^2 v_F^2 \kappa^2 (\gamma_1^2 + \Delta^2)}}$$

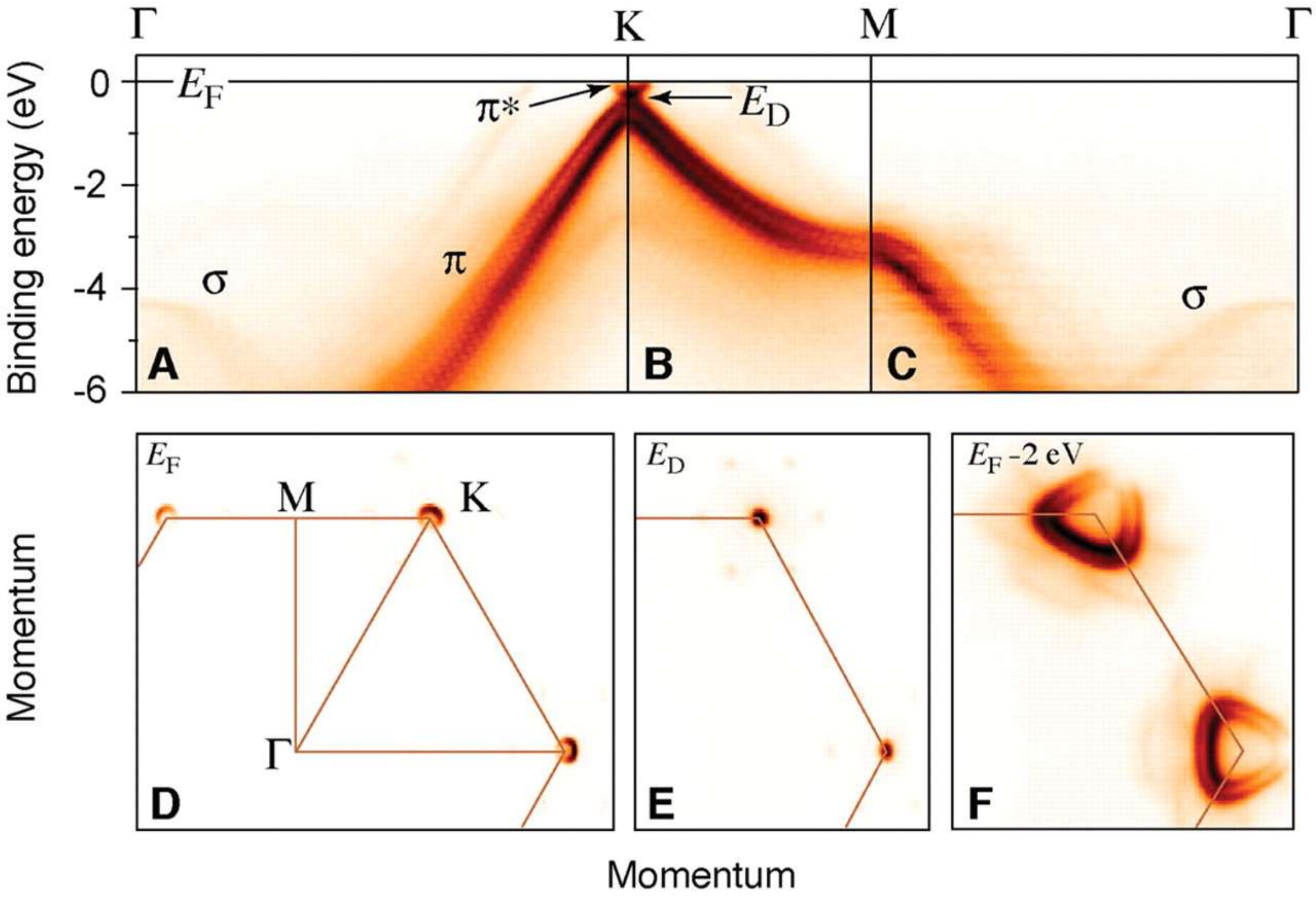
AB bilayer graphene band structure

- Unlike single layer graphene, that has 2 bands (2 electrons per unit cell), AB bilayer graphene has 4 bands (4 electrons per unit cell).
- The K-point are connected by one point, but can be gapped out, when a potential difference is applied between the layers.
- AB bilayer graphene has isospin properties, defined by 4 spinor like wave-functions.





ARPES on AB bilayer graphene



Exotic new band structures