

# *Electronic structure of monolayer graphene*

Graphene seminar 25/04/13

Andor Kormányos

# *Literature*

M. I. Katsnelson: Graphene (Cambridge University Press)

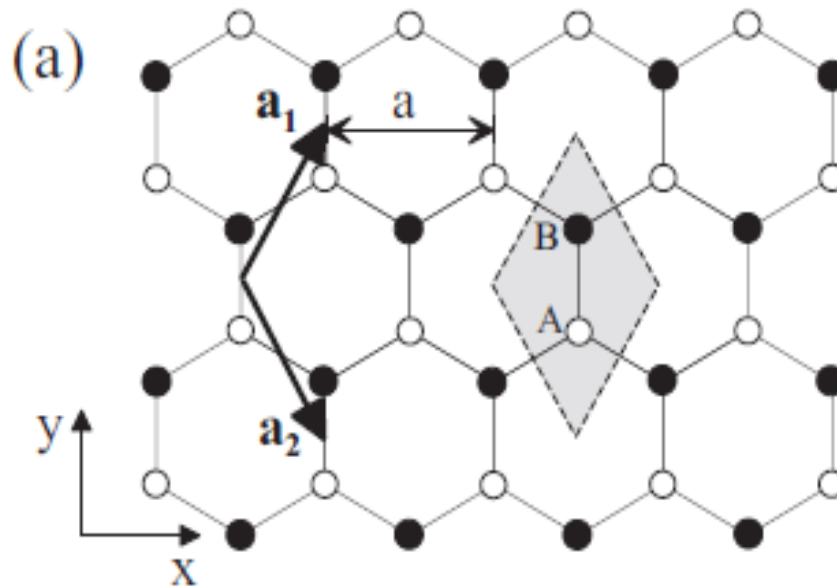
Ed McCann: Graphene Nanoelectronics:  
Metrology, Synthesis, Properties and  
Applications, pages 237-275  
(Springer-Verlag Berlin Heidelberg 2012)  
[ArXiv:1205.4849](https://arxiv.org/abs/1205.4849)



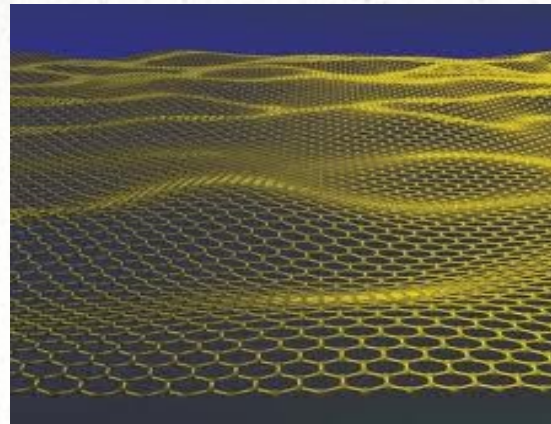
# *Crystal lattice of monolayer graphene*

Hexagonal lattice of carbon atoms

Two atoms in the unit cell:



More realistic view



# Electronic structure from DFT calculations

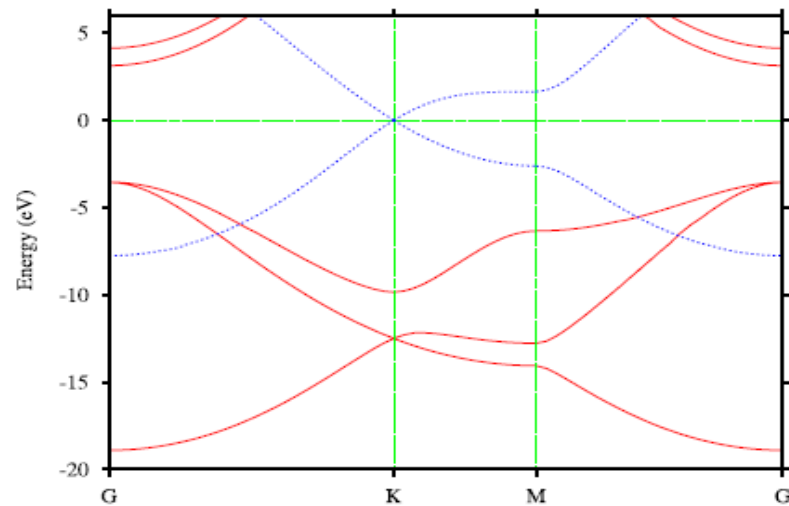
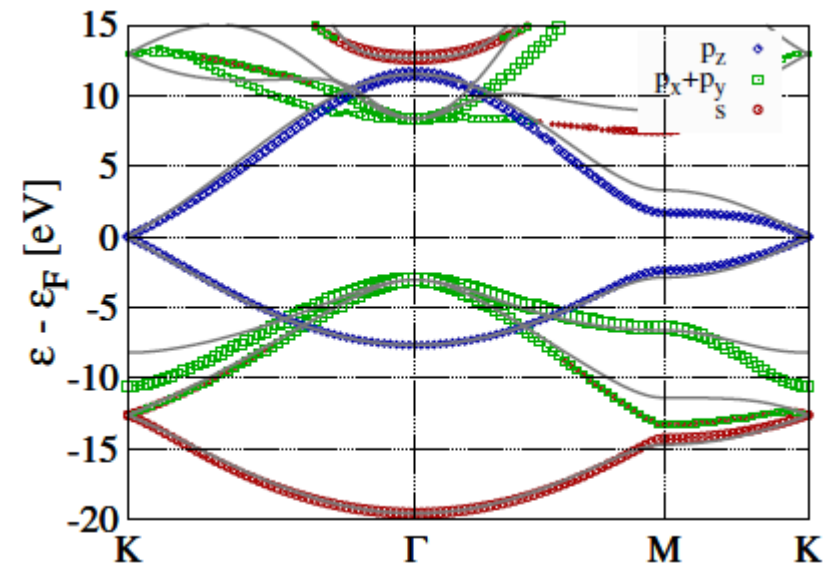


FIG. 1. (Color online) Band structure of a single graphene layer. Solid red lines are  $\sigma$  bands and dotted blue lines are  $\pi$  bands.

Phys Rev B **77**, 035427 (2008)



Phys Rev B **82**, 245412 (2010)

# *Electronic structure from DFT calculations*

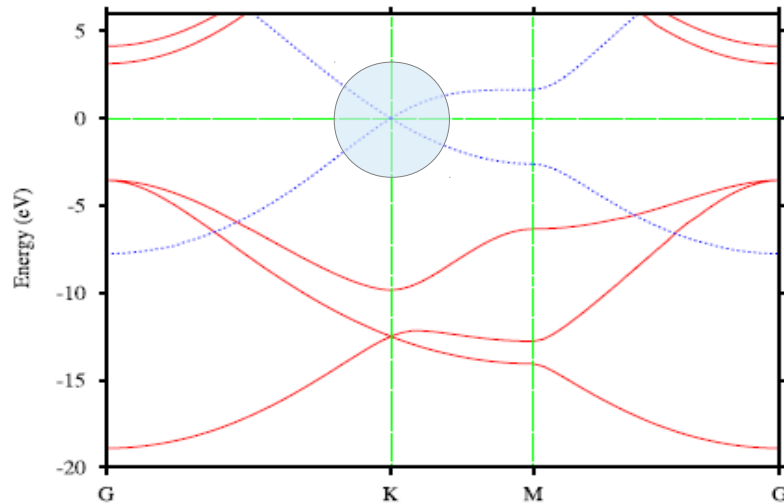


FIG. 1. (Color online) Band structure of a single graphene layer. Solid red lines are  $\sigma$  bands and dotted blue lines are  $\pi$  bands.

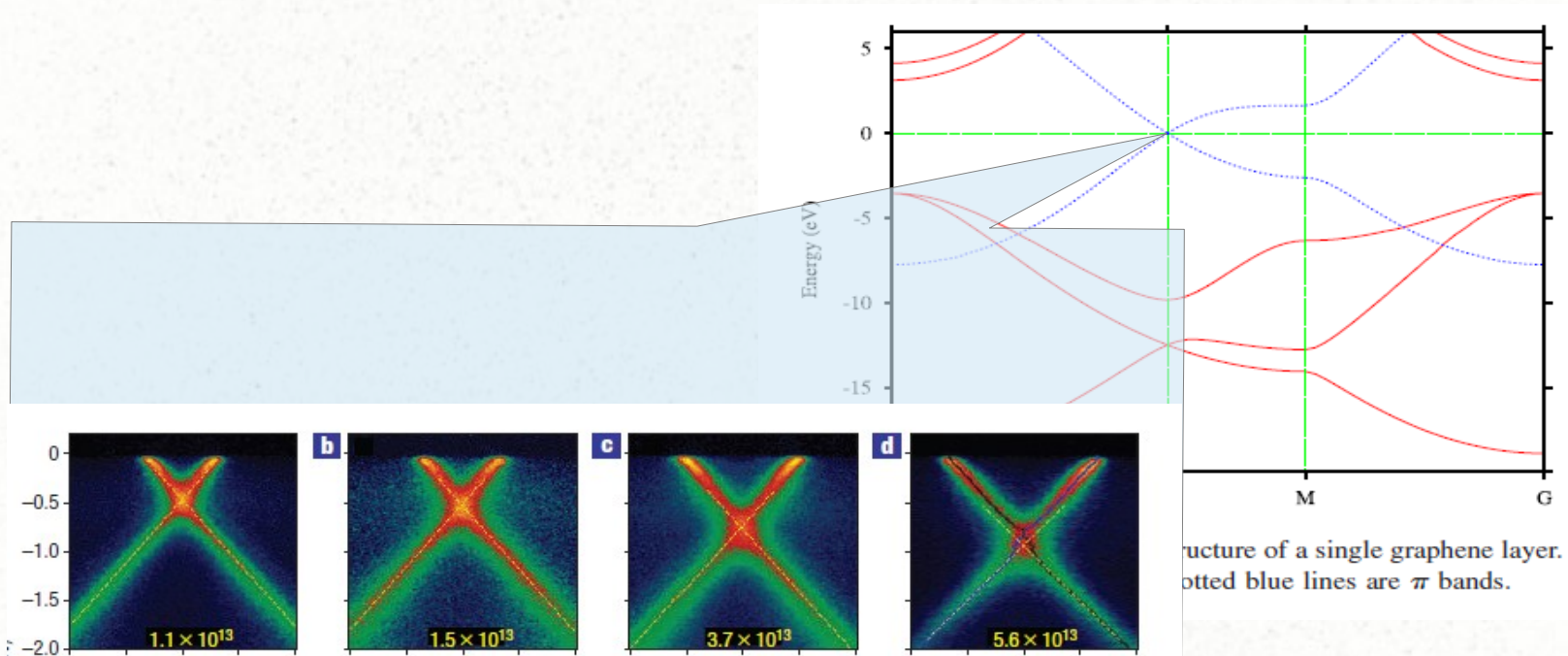
Crossing of  $\pi$  bands at the K point of the Brillouin zone

Dispersion is linear in Wavenumber close to the K point

Phys Rev B 77, 035427 (2008)



# *Band dispersion from Angle Resolved Photoelectron Spectroscopy (ARPES)*



Nature Physics **3**, 36 (2007)

## *Tight-binding model: general theory*

It is assumed that the system has translational invariance => we consider an infinite graphene sheet

In general, there are  $n$  atomic orbitals in the  $\phi_j$  cell

We can form  $n$  Bloch functions

$$\Phi_j(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{i=1}^N e^{i\mathbf{k} \cdot \mathbf{R}_{j,i}} \phi_j(\mathbf{r} - \mathbf{R}_{j,i})$$

An electronic function is a linear combination of these Bloch functions

$$\Psi_j(\mathbf{k}, \mathbf{r}) = \sum_{l=1}^n c_{j,l}(\mathbf{k}) \Phi_l(\mathbf{k}, \mathbf{r})$$



## *Tight-binding model: general theory*

The energy of the  $j$ th band:

$$E_j(\mathbf{k}) = \frac{\langle \Psi_j | \mathcal{H} | \Psi_j \rangle}{\langle \Psi_j | \Psi_j \rangle},$$

Substituting the expansion

$$E_j(\mathbf{k}) = \frac{\sum_{i,l}^n c_{ji}^* c_{jl} \langle \Phi_i | \mathcal{H} | \Phi_l \rangle}{\sum_{i,l}^n c_{ji}^* c_{jl} \langle \Phi_i | \Phi_l \rangle} = \frac{\sum_{i,l}^n H_{il} c_{ji}^* c_{jl}}{\sum_{i,l}^n S_{il} c_{ji}^* c_{jl}}$$

$$H_{il} = \langle \Phi_i | \mathcal{H} | \Phi_l \rangle$$

$$S_{il} = \langle \Phi_i | \Phi_l \rangle$$



## *Tight-binding model: general theory*

Minimizing the energy with respect to the coefficients  $c_{jm}^* \Rightarrow \partial E_j / \partial c_{jm}^* = 0$

$$\sum_{l=1}^n H_{ml} c_{jl} = E_j \sum_{l=1}^n S_{ml} c_{jl}$$

For the special case of two orbitals per unit cell:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_{j1} \\ c_{j2} \end{pmatrix} = E_j \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_{j1} \\ c_{j2} \end{pmatrix}$$

In short

$$H\psi_j = E_j S\psi_j$$

Eigenenergies:

$$\det(H - E_j S) = 0$$

## *Tight-binding model : graphene*

There are  $n=2$  orbitals in the unit cell.

Diagonal matrix elements

$$H_{AA} = \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N e^{i\mathbf{k} \cdot (\mathbf{R}_{A,j} - \mathbf{R}_{A,i})} \langle \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) | \mathcal{H} | \phi_A(\mathbf{r} - \mathbf{R}_{A,j}) \rangle$$

$$\mathbf{k} = (k_x, k_y)$$

**Assumption:** dominant contribution comes from  $i=j$ , others can be neglected

$$H_{AA} \approx \frac{1}{N} \sum_{i=1}^N \langle \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) | \mathcal{H} | \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) \rangle$$

$\langle \phi_A | \mathcal{H} | \phi_A \rangle$  Within the summation this expectation value is the same for every value of  $i$

$$H_{AA} \approx \frac{1}{N} \sum_{i=1}^N \epsilon_{2p} = \epsilon_{2p}$$

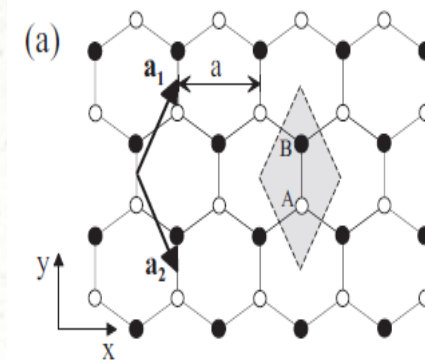
# *Tight-binding model : graphene*

Carbon atoms on sublattice B are chemically identical to atoms on sublattice A:

$$H_{BB} = H_{AA} \approx \epsilon_{2p}$$

**Overlap integrals:** assuming again that same site contribution dominate (nearest neighbours are B atoms)

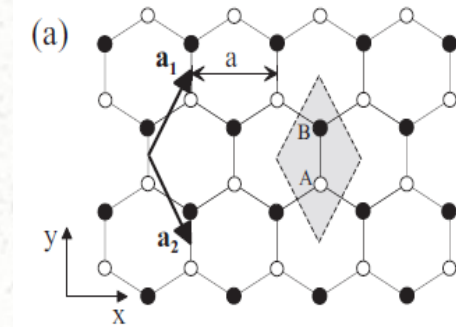
$$S_{AA} \approx \frac{1}{N} \sum_{i=1}^N \langle \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) | \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) \rangle = 1$$





# *Tight-binding model : graphene*

Off-diagonal matrix elements



$$H_{AB} = \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N e^{i\mathbf{k} \cdot (\mathbf{R}_{B,j} - \mathbf{R}_{A,i})} \langle \phi_A (\mathbf{r} - \mathbf{R}_{A,i}) | \mathcal{H} | \phi_B (\mathbf{r} - \mathbf{R}_{B,j}) \rangle$$

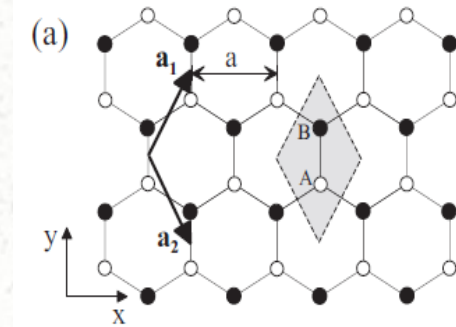
**Assumption:** dominant contribution comes from nearest-neighbors, other contributions can be neglected. Looking at, e.g., A type atoms, there are 3 nearest-neighbor B atoms

$$H_{AB} \approx \frac{1}{N} \sum_{i=1}^N \sum_{l=1}^3 e^{i\mathbf{k} \cdot (\mathbf{R}_{B,l} - \mathbf{R}_{A,i})} \langle \phi_A (\mathbf{r} - \mathbf{R}_{A,i}) | \mathcal{H} | \phi_B (\mathbf{r} - \mathbf{R}_{B,l}) \rangle$$

The index “l” depends on the index “i”

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The index “l” depends on the index “i”

## *Tight-binding model : graphene*

The matrix element between nearest-neighbor A and B atoms has the same value for each neighboring pair:

$$\gamma_0 = -\langle \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) | \mathcal{H} | \phi_B(\mathbf{r} - \mathbf{R}_{B,l}) \rangle$$

Note, at this step we have made use of the fact that the atomic orbitals  $\phi_j$  are actually p<sub>z</sub> orbitals, hence have a **rotational symmetry**

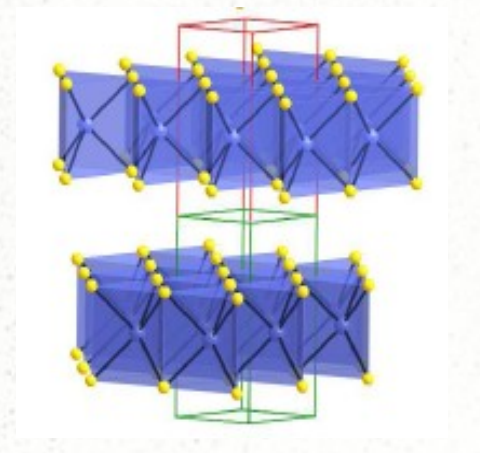


# *Footnote: general method to obtain tight-binding Hamiltonians*

**General method:** Slater-Koster parametrization of hopping integrals  
Physical Review **94**, 1498 (1954)  
For recent introduction see, e.g., Sergej Konschuh PhD thesis

Slater-Koster parametrization is still useful, especially in connection with first principles methods and group theory.

**Recent examples:** Bilayer MoS<sub>2</sub>, arXiv:1304.4831



Spin-orbit coupling in trilayer graphene:  
Phys Rev B **87**, 045419 (2013)

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Note, at this step we have made use of the fact that the atomic orbitals  $\phi_j$  are actually p<sub>z</sub> orbitals, hence have a **rotational symmetry**

Therefore

$$H_{AB} \approx -\frac{\gamma_0}{N} \sum_{i=1}^N \sum_{l=1}^3 e^{i\mathbf{k} \cdot \boldsymbol{\delta}_l} \equiv -\gamma_0 f(\mathbf{k})$$

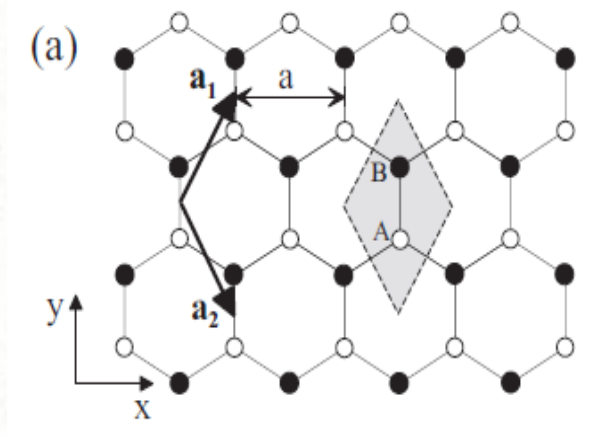
$$f(\mathbf{k}) = \sum_{l=1}^3 e^{i\mathbf{k} \cdot \boldsymbol{\delta}_l}$$

$$\boldsymbol{\delta}_l = \mathbf{R}_{B,l} - \mathbf{R}_{A,i}$$

Position of atom B relative to atom A



## *Tight-binding model : graphene*



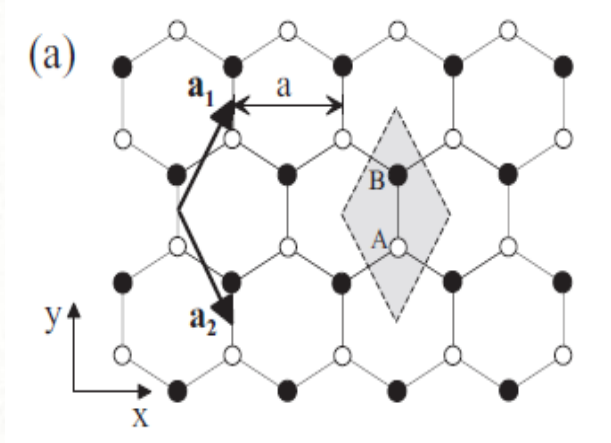
$$\delta_1 = \left( 0, \frac{a}{\sqrt{3}} \right) \quad \delta_2 = \left( \frac{a}{2}, -\frac{a}{2\sqrt{3}} \right)$$

$$\delta_3 = \left( -\frac{a}{2}, -\frac{a}{2\sqrt{3}} \right)$$

$$f(\mathbf{k}) = e^{ik_y a / \sqrt{3}} + 2e^{-ik_y a / 2\sqrt{3}} \cos(k_x a / 2)$$



## *Tight-binding model : graphene*



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Finally

$$H_{AB} \approx -\gamma_0 f(\mathbf{k}) \quad H_{BA} \approx -\gamma_0 f^*(\mathbf{k})$$

In a similar fashion:  $S_{AB} = s_0 f(\mathbf{k})$

## *Tight-binding model : graphene*

In summary:

$$H_1 = \begin{pmatrix} \epsilon_{2p} & -\gamma_0 f(\mathbf{k}) \\ -\gamma_0 f^*(\mathbf{k}) & \epsilon_{2p} \end{pmatrix}$$

$$S_1 = \begin{pmatrix} 1 & s_0 f(\mathbf{k}) \\ s_0 f^*(\mathbf{k}) & 1 \end{pmatrix}$$

The corresponding eigenenergies:

$$\det \begin{pmatrix} \epsilon_{2p} - E & -(\gamma_0 + E s_0) f(\mathbf{k}) \\ -(\gamma_0 + E s_0) f^*(\mathbf{k}) & \epsilon_{2p} - E \end{pmatrix} = 0$$

From

R. Saito, M.S. Dresselhaus, G. Dresselhaus *Physical Properties of Carbon Nanotubes*, (Imperial College Press, London, 1998)

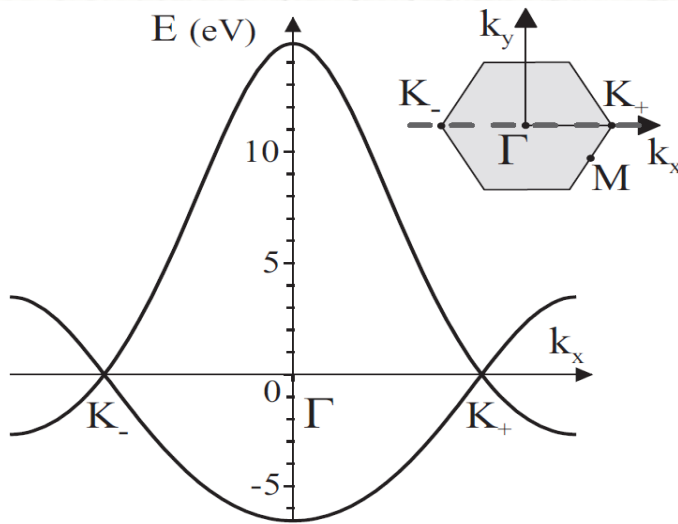
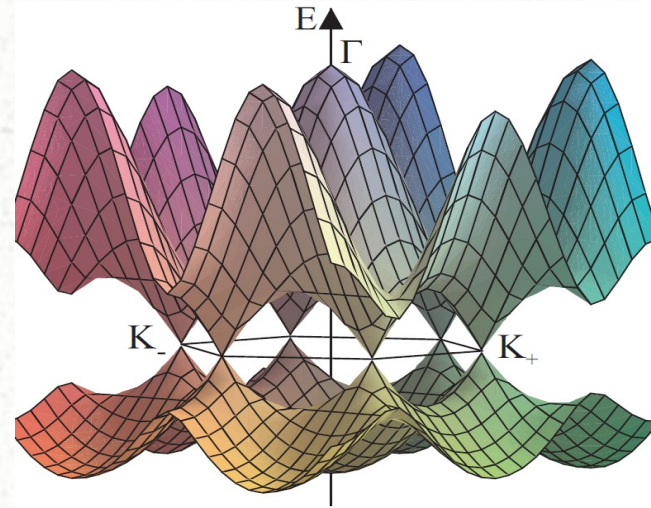
$$\gamma_0 = 3.033 \text{ eV}, \quad \epsilon_{2p} = 0 \quad \text{Choice of the origin of the energy axis}$$

$$s_0 = 0.129, \quad \text{Such parameters can be obtained from DFT or experiments}$$



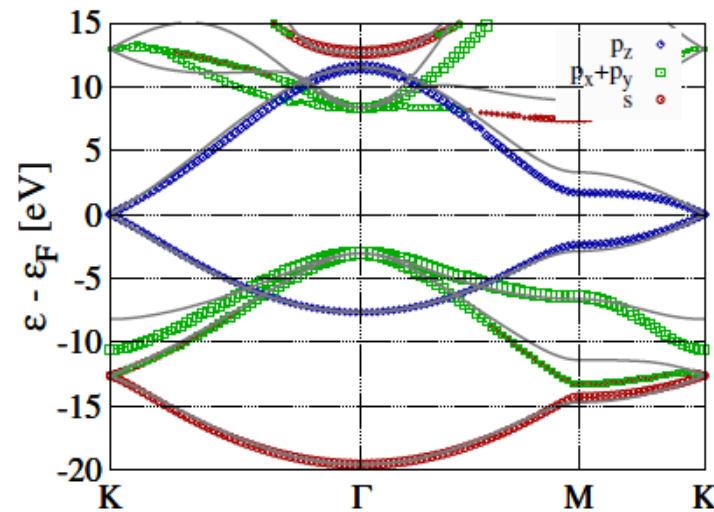
# Tight-binding model : graphene

$$E_{\pm} = \frac{\epsilon_{2p} \pm \gamma_0 |f(\mathbf{k})|}{1 \mp s_0 |f(\mathbf{k})|}$$



TB

Good qualitative agreement



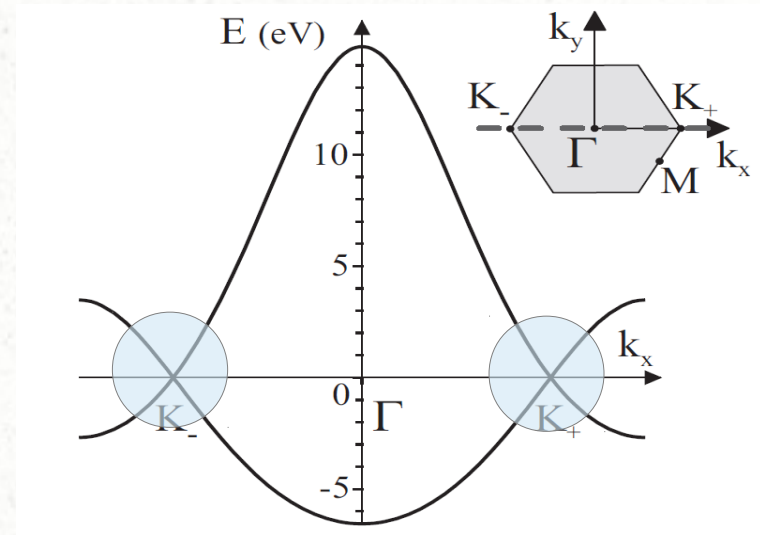
DFT



# Low-energy physics, Dirac-like Hamiltonian

Fermi energy lies at  $E=0$

Only two K points are inequivalent, the others are connected by reciprocal vector, or see the original Brillouin zone



$$\mathbf{K}_\xi = \xi \left( \frac{4\pi}{3a}, 0 \right)$$

$K_-$ ,  $K_+$  points often called “valleys”

$$E_\pm = \frac{\epsilon_{2p} \pm \gamma_0 |f(\mathbf{k})|}{1 \mp s_0 |f(\mathbf{k})|}$$

$$f(\mathbf{K}_\xi) = e^0 + e^{i\xi 2\pi/3} + e^{-i\xi 2\pi/3} = 0$$

Gaples band structure

## *Low-energy physics, Dirac-like Hamiltonian*

Introducing the momentum measured from the K point(s)

$$\mathbf{p} = \hbar\mathbf{k} - \hbar\mathbf{K}_\xi$$

and expanding  $f(\mathbf{k})$  up to first order in  $\mathbf{p}$

$$f(\mathbf{k}) \approx -\frac{\sqrt{3}a}{2\hbar} (\xi p_x - i p_y)$$

and we obtain the famous 2D massless Dirac Hamiltonian of graphene

$$H_{1,\xi} = v \begin{pmatrix} 0 & \xi p_x - i p_y \\ \xi p_x + i p_y & 0 \end{pmatrix} \quad v = \sqrt{3}a\gamma_0/(2\hbar)$$



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The actual value of the velocity  $v$  is  $10^6$  m/s  $\approx c/300$



## *Low-energy physics, Dirac-like Hamiltonian*

$$H_{1,\xi} = v \begin{pmatrix} 0 & \xi p_x - ip_y \\ \xi p_x + ip_y & 0 \end{pmatrix}$$

If we now consider  $H_1$  to be an effective Hamiltonian and solve the corresponding Schrödinger equation:

$$E_{\pm} = \pm vp \quad \psi_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm \xi e^{i\xi\varphi} \end{pmatrix} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$$

$$\mathbf{p} = (p_x, p_y) = p (\cos \varphi, \sin \varphi)$$

What about the overlap matrix S?

$$E_{\pm} = \frac{\epsilon_{2p} \pm \gamma_0 |f(\mathbf{k})|}{1 \mp s_0 |f(\mathbf{k})|} \quad \text{Finite overlap contributes with } \sim p^2 \text{ terms}$$

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Higher order terms in momentum in  $E(\mathbf{p})$  are negligible for energies  $\leq 1$  eV

## *Pseudospin and chirality*

The eigenstates have two components, reminiscent of spin  $\frac{1}{2}$

$$\psi_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm \xi e^{i\xi\varphi} \end{pmatrix} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$$

Looking back to the original definitions, the two components correspond to the relative amplitude of the Bloch function on the A and B sublattice.

This degree of freedom is called **pseudospin**.

If the wavefunction was finite only on A sublattice  $\rightarrow (1,0)^T = |\uparrow\rangle$   
on B sublattice  $\rightarrow (0,1)^T = |\downarrow\rangle$

In graphene, the density is usually shared equally between A and B sublattice.

Some substrates can break this symmetry, though



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**Note the index  $\xi$** : in addition to pseudospin, there is another degree of freedom: **valley**

The valleys are usually not coupled, except in the case of atomic scale scatterers and certain boundaries  $\Rightarrow$  two independent Hamiltonians

## *Pseudospin and chirality*

The particles described by the Dirac Hamiltonian of monolayer graphene have yet another property: they are **chiral**

This means that the orientation of pseudospin depends on the direction of the electronic momentum  $\mathbf{p}$

To see this more clearly, let's write the effective Hamiltonian as

$$H_{1,\xi} = v (\xi \sigma_x p_x + \sigma_y p_y)$$

and define a pseudospin vector as  $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ .

and a unit vector as  $\hat{\mathbf{n}}_1 = (\xi \cos \varphi, \sin \varphi, 0)$



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$$\text{Then } H_{1,\xi} = vp \boldsymbol{\sigma} \cdot \hat{\mathbf{n}}_1$$

therefore  $\boldsymbol{\sigma}$  is linked to the direction of  $\mathbf{n}_1$

## *Pseudospin and chirality*

In other words, the eigenstates of the effective Hamiltonian are also eigenstates of the chiral operator  $\sigma \cdot \hat{n}_1$

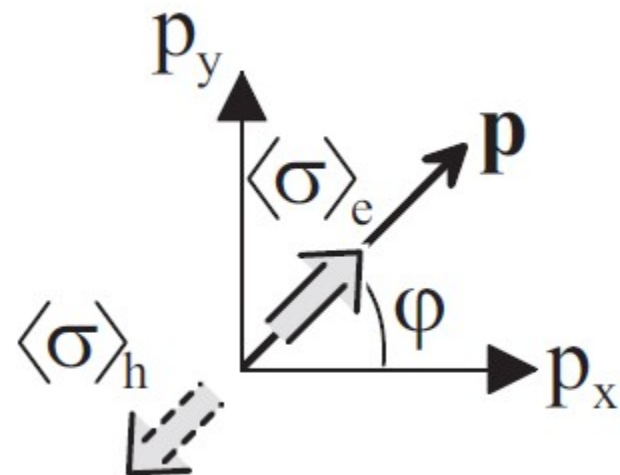
$$\sigma \cdot \hat{n}_1 \psi_{\pm} = \pm \psi_{\pm}.$$

Another way to express this is to calculate with respect to  $\psi_{\pm}$ ,

$$\langle \sigma \rangle_{e/h} = \pm (\xi \cos \varphi, \sin \varphi, 0).$$

In valley  $K_+$

$$\langle \sigma \rangle = (\langle \sigma_x \rangle, \langle \sigma_y \rangle, \langle \sigma_z \rangle)$$





## *Pseudospin and chirality*

Important consequence of the chirality of particles: the probability to scatter into a direction characterized by the angle  $\varphi$  ( $\varphi=0$  corresponds to forward Scattering) is proportional to

$$w(\varphi) = |\langle \psi_{\pm}(\varphi) | \psi_{\pm}(0) \rangle|^2$$

For monolayer graphene

$$w(\varphi) = \cos^2(\varphi/2)$$

**No backscattering!**

