Electronic structure of monolayer graphene

Graphene seminar 25/04/13

Andor Kormányos

Literature

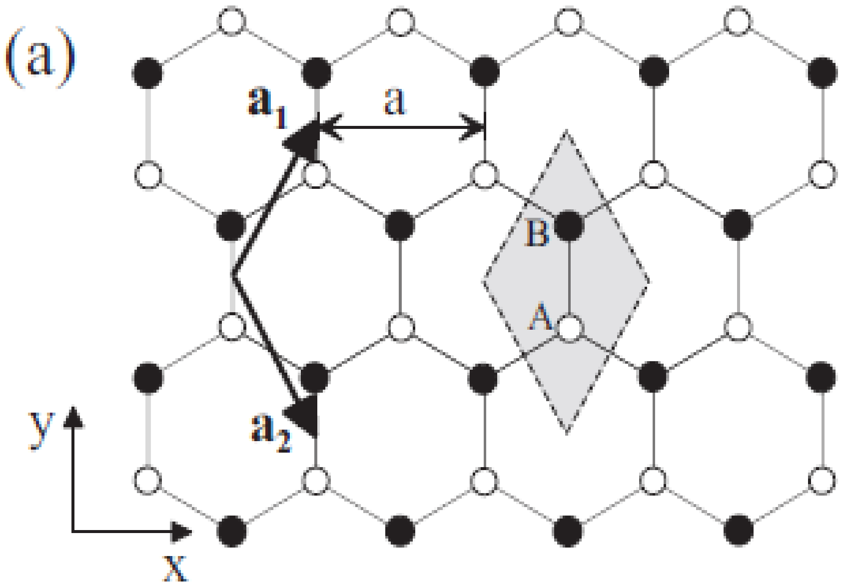
M. I. Katsnelson: Graphene (Cambridge University Press)

Ed McCann: Graphene Nanoelectronics:
Metrology, Synthesis, Properties and
Applications, pages 237-275
(Springer-Verlag Berlin Heidelberg 2012)
ArXiv:1205.4849

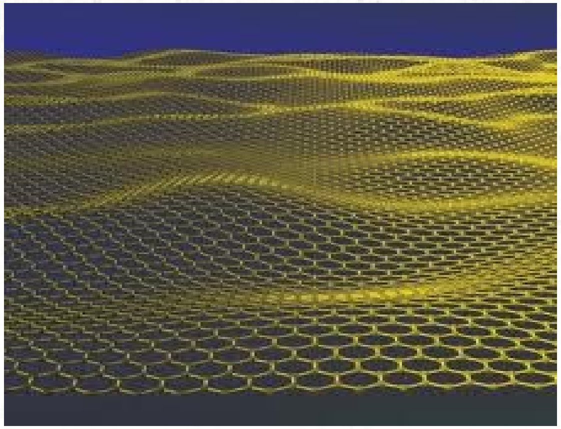
Crystal lattice of monolayer graphene

Hexagonal lattice of carbon atoms

Two atoms in the unit cell:



More realistic view



Electronic structure from DFT calculations

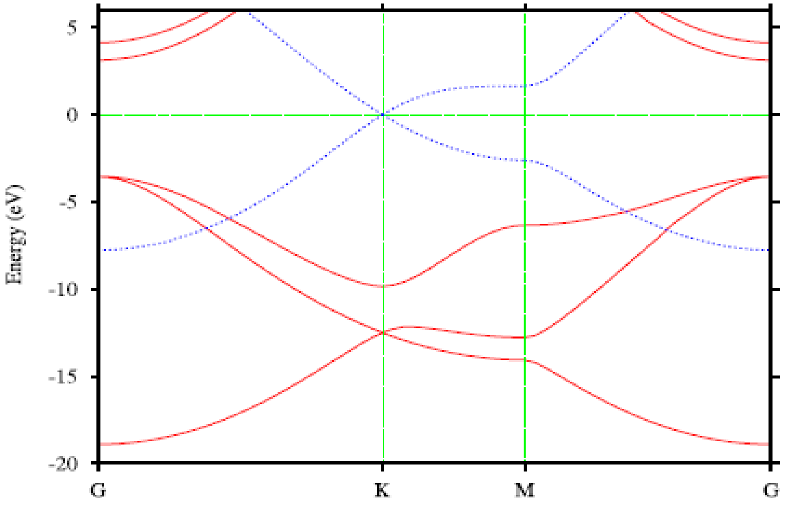
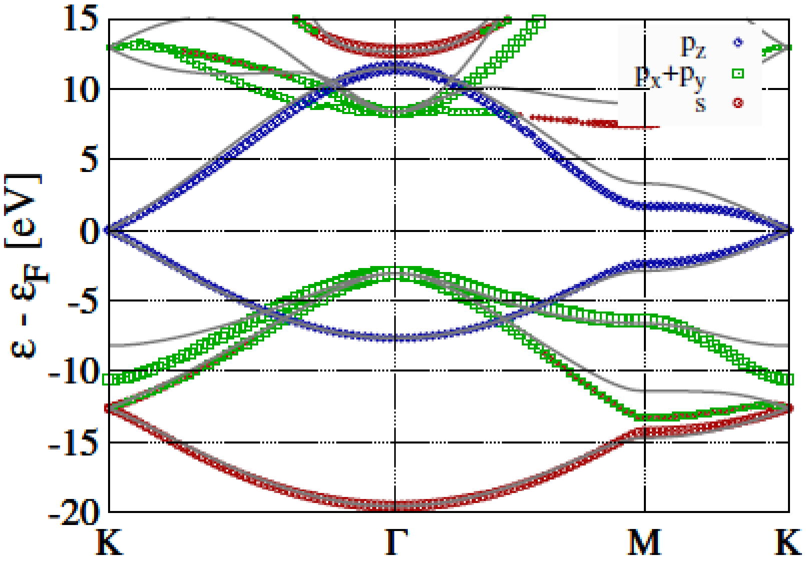


FIG. 1. (Color online) Band structure of a single graphene layer. Solid red lines are σ bands and dotted blue lines are π bands.

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



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

Electronic structure from DFT calculations

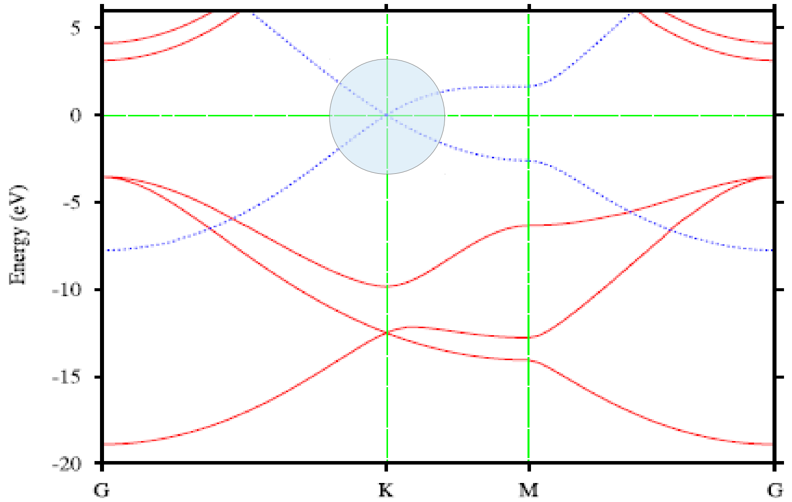


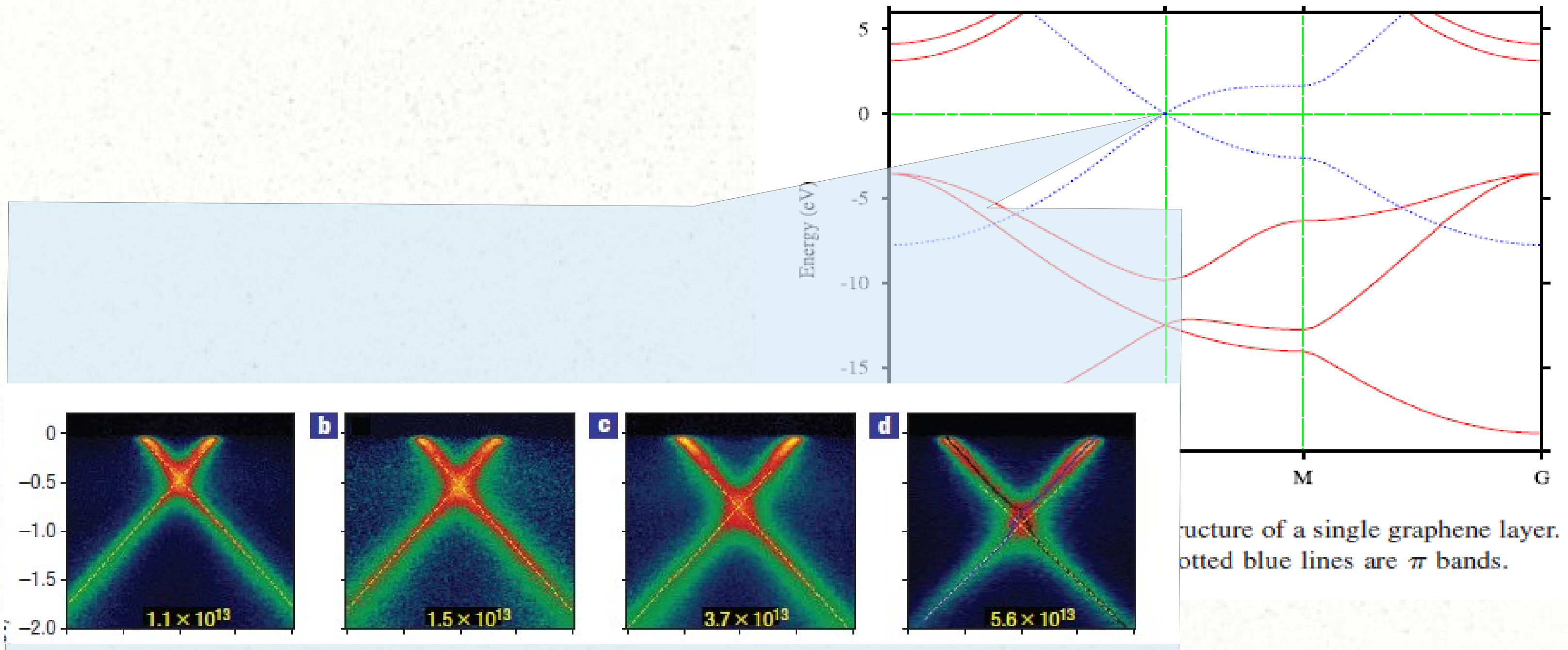
FIG. 1. (Color online) Band structure of a single graphene layer. Solid red lines are σ bands and dotted blue lines are π bands.

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

Crossing of π bands at the K point of the Brillouin zone

Dispersion is linear in Wavenumber close to the K point

Band dispersion from Angle Resolved Photoelectron Spectroscopy (ARPES)



ucture of a single graphene layer.
otted blue lines are π bands.

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 ϕ_j t cell

We can form n Bloch functions

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

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 jth 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} ⇨ $\partial E_j / \partial c^*_{jm} = 0$

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

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: $\det\left(H - E_j S\right) = 0$

Tight-binding model : graphene

There are n=2 orbitals in the unit cell.

Diagonal matrix elements

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

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

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

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

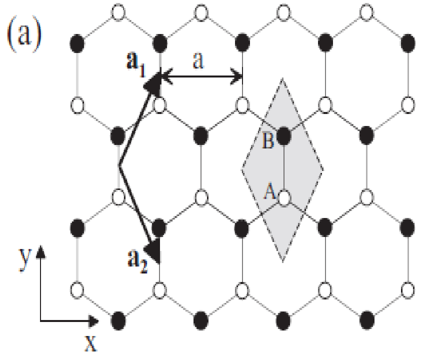
Tight-binding model : graphene

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

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

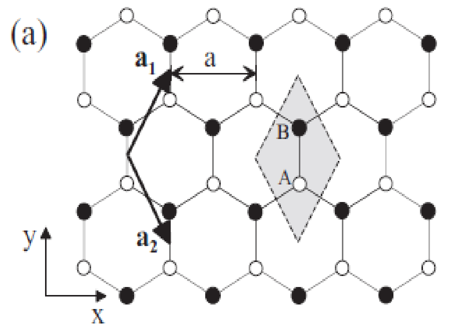
Overlap integrals: assuming again that same site contribution dominate (nearest neighbours are B atoms)

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



Tight-binding model : graphene

Off-diagonal matrix elements



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

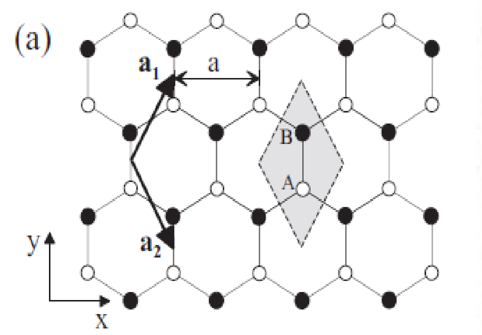
Assumption: dominant contribution comes from nearest-neighbors, other contributions can be neglected. Looking at, e.g., A type atoms, there are 3 nearest-neighbor B atoms

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

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

Tight-binding model : graphene

Off-diagonal matrix elements



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

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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:

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

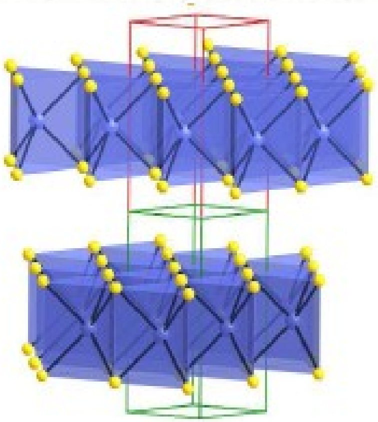
Note, at this step we have made use of the fact that the atomic orbitals ϕ_j are actually p_z orbitals, hence have a rotational symmetry

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 MoS2, arXiv:1304.4831



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

Tight-binding model : graphene

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

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

Note, at this step we have made use of the fact that the atomic orbitals ϕ_j are actually p_z orbitals, hence have a rotational symmetry

Therefore

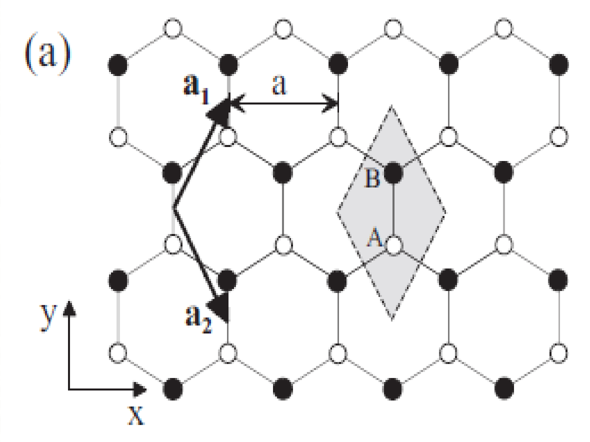
$$H_{AB} \approx -\frac{\gamma_0}{N}\sum_{i=1}^{N}\sum_{l=1}^{3} e^{i\mathbf{k}.\boldsymbol{\delta}_l} \equiv -\gamma_0 f\left(\mathbf{k}\right)$$

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

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

Position of atom B relative to atom A

Tight-binding model : graphene

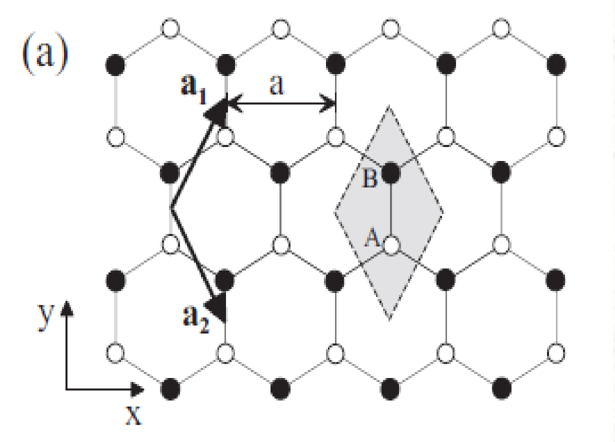


$$\boldsymbol{\delta}_1 = \left(0, \frac{a}{\sqrt{3}}\right) \quad \boldsymbol{\delta}_2 = \left(\frac{a}{2}, -\frac{a}{2\sqrt{3}}\right)$$

$$\boldsymbol{\delta}_3 = \left(-\frac{a}{2}, -\frac{a}{2\sqrt{3}}\right)$$

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

Tight-binding model : graphene



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

Finally

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

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

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

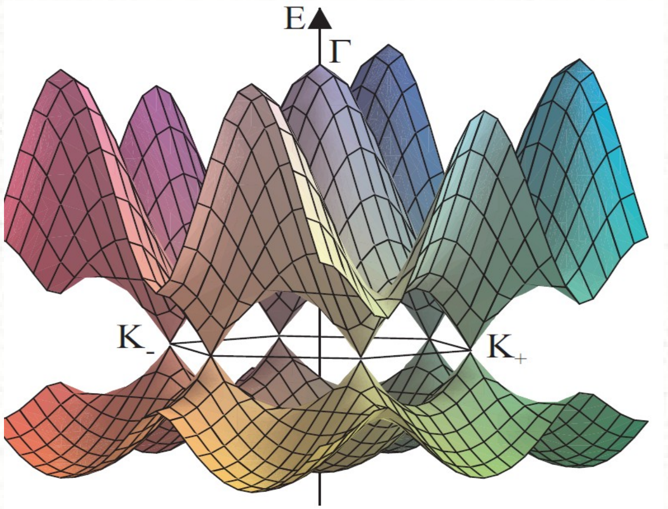
R. Saito, M.S. Dresselhaus, G. Dresselhaus *Physical Properties of Carbon Nanotubes*, (Imperial College Press, London, 1998)

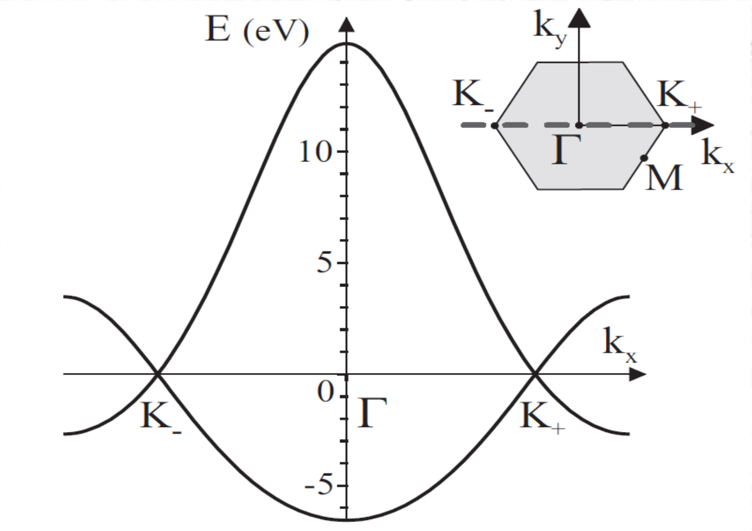
$\gamma_0 = 3.033\,\mathrm{eV}$ $\epsilon_{2p} = 0$ Choice of the origin of the energy axis

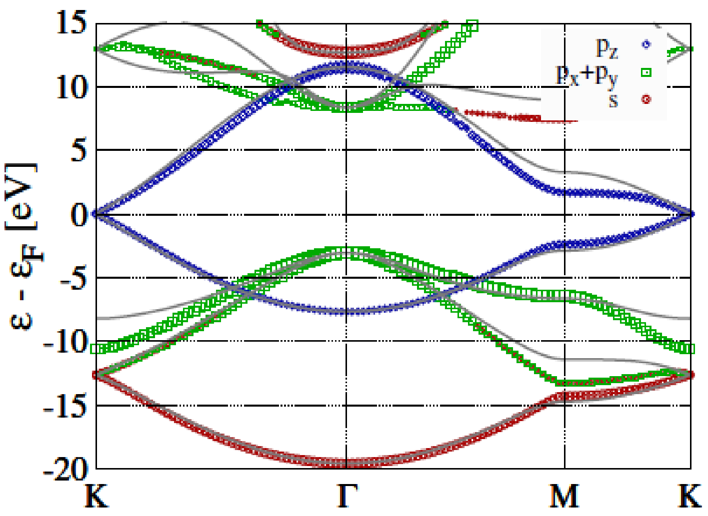
$s_0 = 0.129$ Such parameters can be obtained from DFT or experiments

Tight-binding model : graphene

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







TB

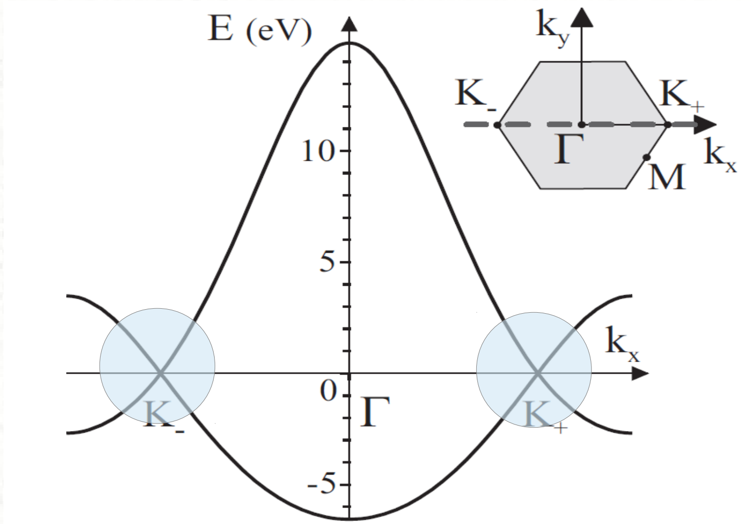
Good qualitative agreement

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(k) up to first order in p

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

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

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

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

Low-energy physics, Dirac-like Hamiltonian

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

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

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

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

What about the overlap matrix S?

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

Finite overlap contributes with ~p^2 terms

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Finite overlap contributes with ~p^2 terms

Higher order terms in momentum in E(**p**) are negligible for energies ≤ 1 eV

Pseudospin and chirality

The eigenstates have two components,
reminiscent of spin ½

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

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 → $(1,0)^T = | \uparrow >$
on B sublattice → $(0,1)^T = | \downarrow >$

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

Some substrates can break this symmetry, though

Pseudospin and chirality

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Note the index ξ: 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 => 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 **p**

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

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

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

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

therefore σ is linked to the direction of n_1

Pseudospin and chirality

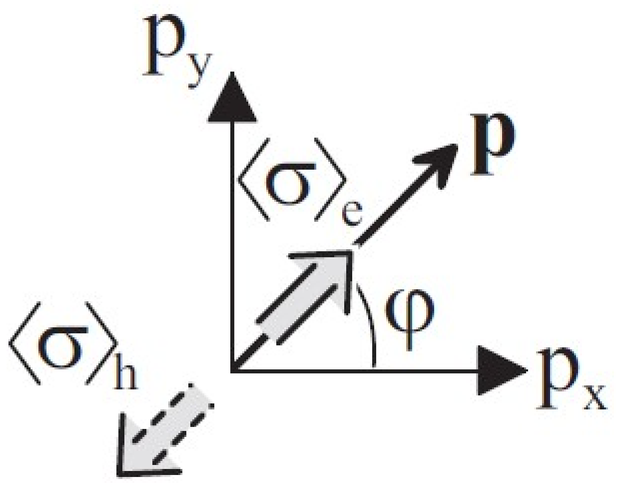
In other words, the eigenstates of the effective Hamiltonian are also eigenstates of the chiral operator $\boldsymbol{\sigma}.\hat{\mathbf{n}}_1$

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

Another way to express this is to calculate $\langle\boldsymbol{\sigma}\rangle = (\langle\sigma_x\rangle, \langle\sigma_y\rangle, \langle\sigma_z\rangle)$ with respect to $\psi_\pm$:

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

In valley K_+



Pseudospin and chirality

Important consequence of the chirality of particles: the probability to scatter into a direction characterized by the angle φ (φ=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!