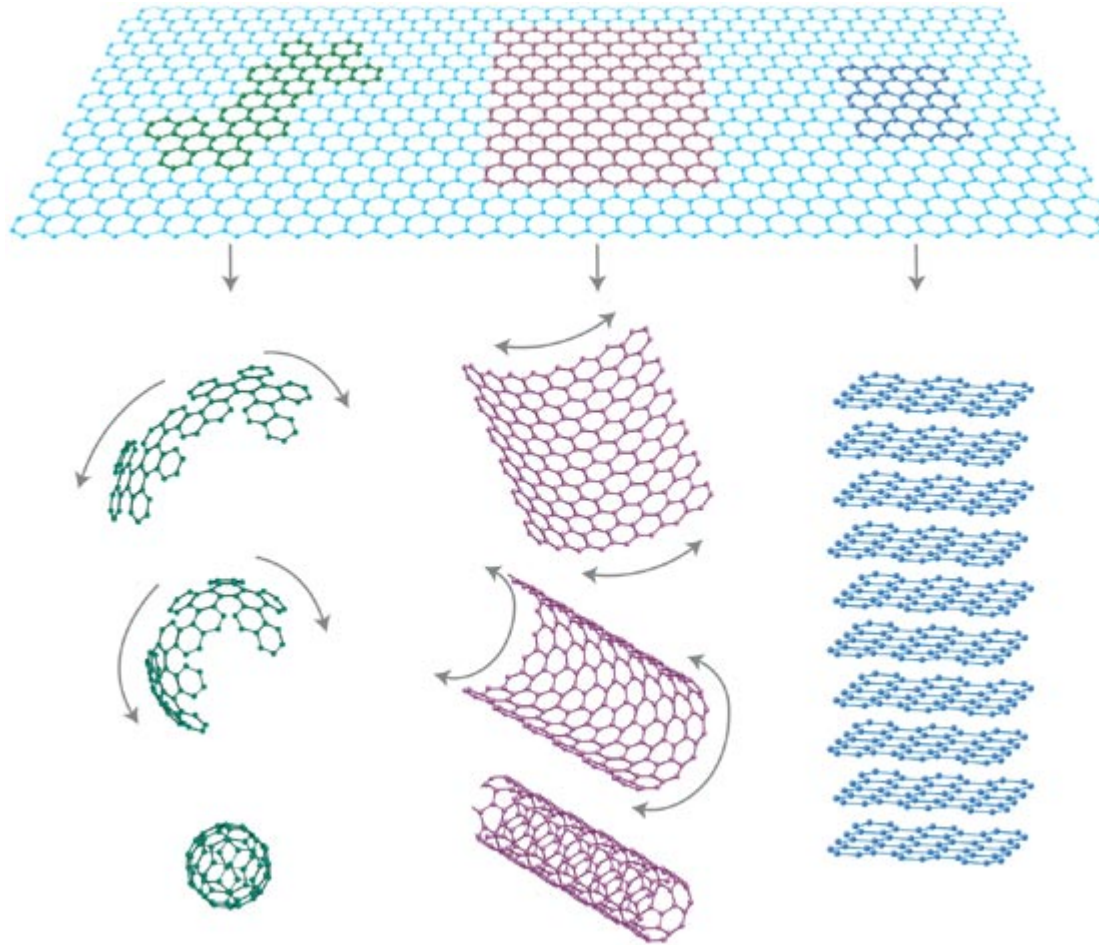# 15. Carbon-based electronics: Carbon nanotubes and graphene
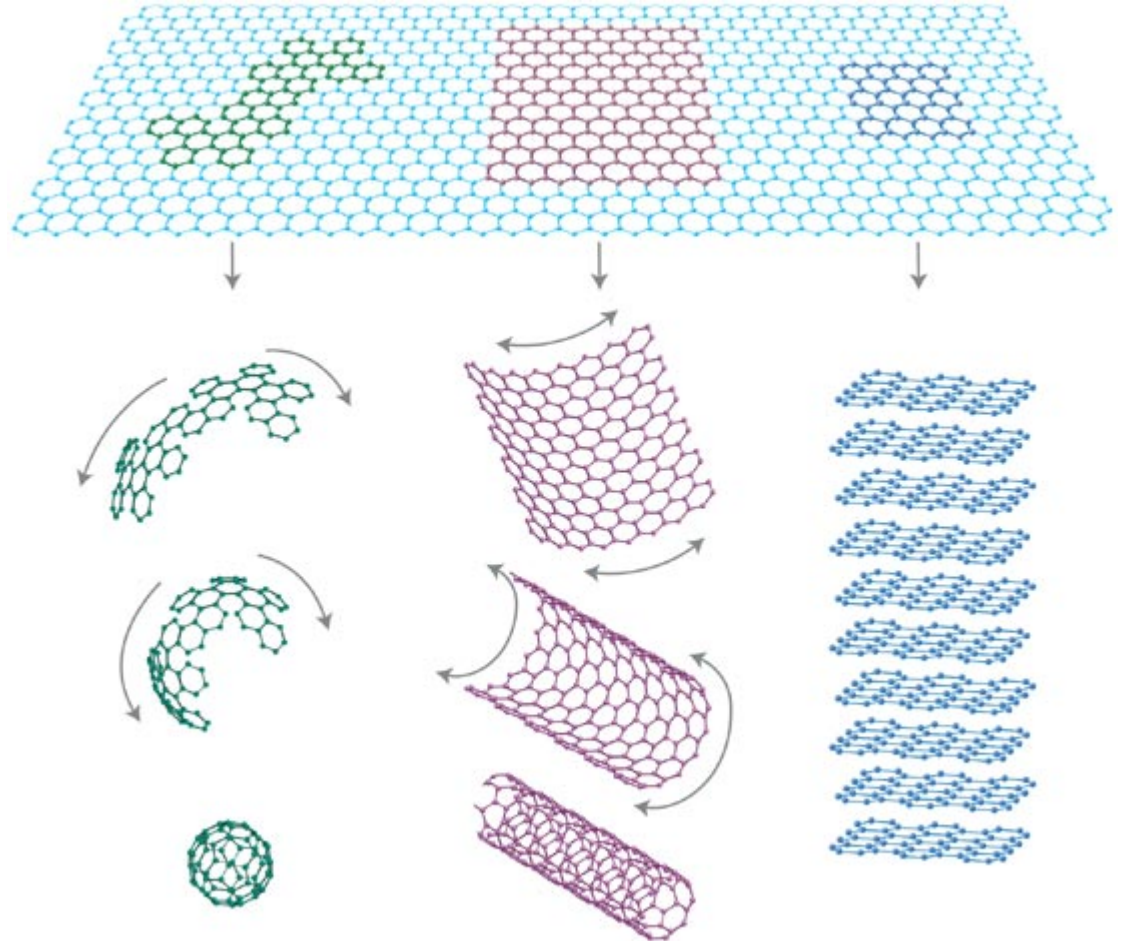
15.1 Graphene – A two-dimensional material

Graphene: 2D layer of carbon atoms in a honeycomb lattice (trigonal lattice with two-dimensional basis)

2D crystal should not exist

Mermin-Wagner-Theorem: 2D structures unstable due to long wavelength thermal phonons

2004 fabricated on a substrate by the groups of K. S. Novoselov and A. K. Geim

→ Nobel prize 2010

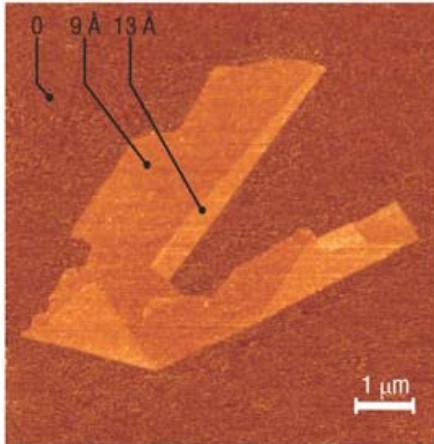A. K. Geim et al., Nature Materials **6**, 183 (2007)

Graphene is a basic 2D structure for building carbon materials of all other dimensionalities. It can be wrapped up into 0D *buckyballs*, rolled into 1D *nanotubes* or stacked into 3D *graphite*.
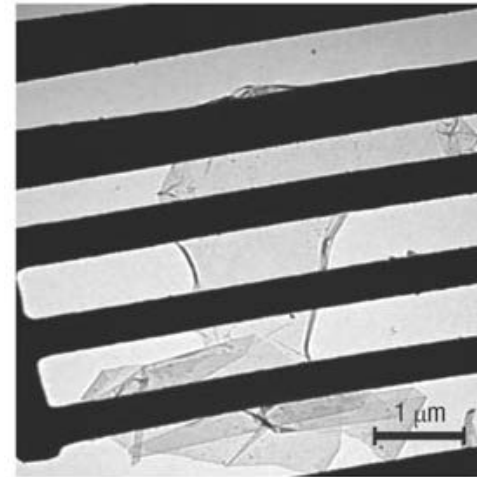
15.1 Graphene – A two-dimensional material

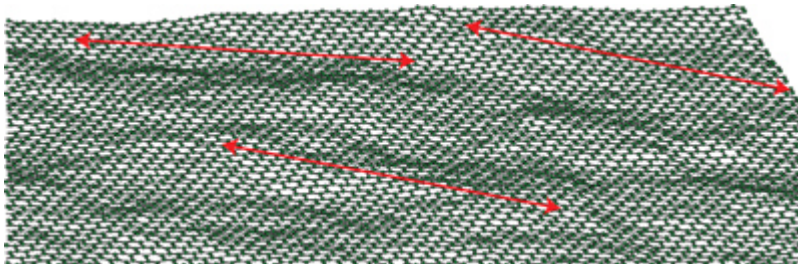**Graphene on a substrate optical detection**

A. K. Geim et al., Nature Materials **6**, 183 (2007)

Free-standing (better free-hanging) graphene

A. K. Geim et al., Nature Materials **6**, 183 (2007)

Formation of ripples

A. Fasolino *et al.*, Nature Materials **6**, 858 (2007)

- Anharmonic interactions stabilize graphene
- Height variations ~1 Å
- Length of fluctuations ~80 Å

15.1 Graphene – Properties of carbon

- Carbon has 4 valence electrons
- 2s, $2p_x$ and $2p_y$ orbitals form bonding sp^2 hybrid orbitals in a plane
- $2p_z$ orbital is perpendicular to the plane and contains 1 free electron per C atom
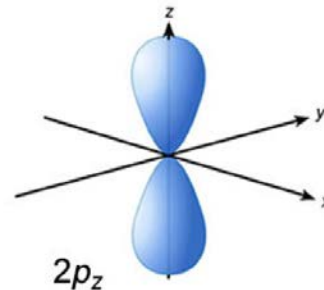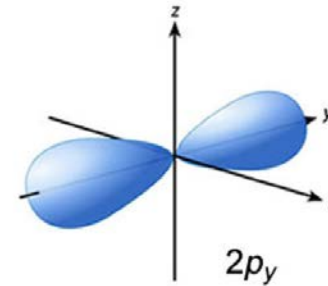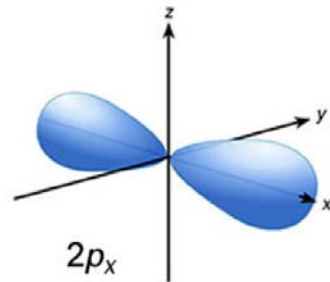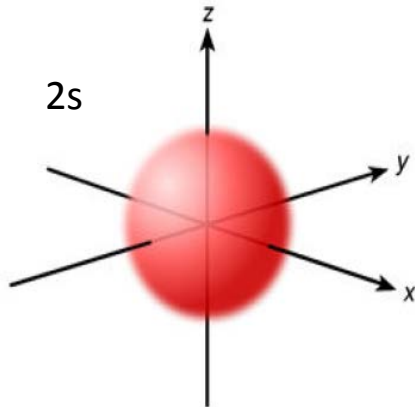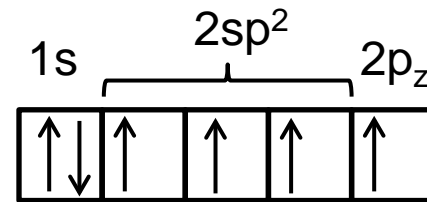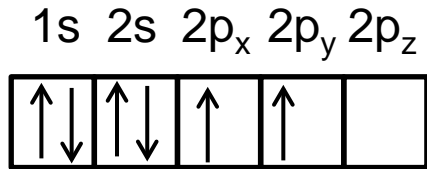
2s $2p_x$ $2p_y$ $2p_z$ $2sp^2$ sp^2 hybrid orbitals
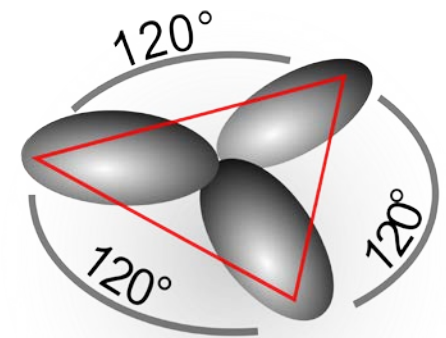
15.1 Graphene – Crystal lattice

Triangular lattice with basis of two atoms.

Lattice vectors

$$\vec{a}_1 = \frac{a}{2}(3,\sqrt{3}), \ \vec{a}_2 = \frac{a}{2}(3,-\sqrt{3})$$

Carbon-carbon distance
a≈1.42 Å.

Reciprocal lattice vectors

$$\vec{b}_1 = \frac{2\pi}{3a}(1,\sqrt{3}), \ \vec{b}_2 = \frac{2\pi}{3a}(1,-\sqrt{3})$$

Dirac points

$$\vec{K} = \frac{2\pi}{3a}(1,\frac{1}{\sqrt{3}}), \ \vec{K}' = \frac{2\pi}{3a}(1,-\frac{1}{\sqrt{3}})$$
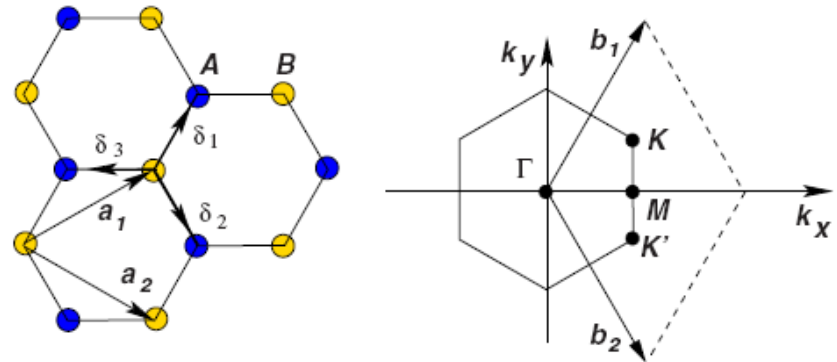

FIG. 2. (Color online) Honeycomb lattice and its Brillouin zone. Left: lattice structure of graphene, made out of two interpenetrating triangular lattices (a_1 and a_2 are the lattice unit vectors, and δ_i, $i=1,2,3$ are the nearest-neighbor vectors). Right: corresponding Brillouin zone. The Dirac cones are located at the K and K' points.

Nearest-neighbor vectors

$$\vec{\delta}_1 = \frac{a}{2}(1,\sqrt{3}), \ \vec{\delta}_2 = \frac{a}{2}(1,-\frac{1}{\sqrt{3}}), \ \vec{\delta}_3 = -a(1,0)$$
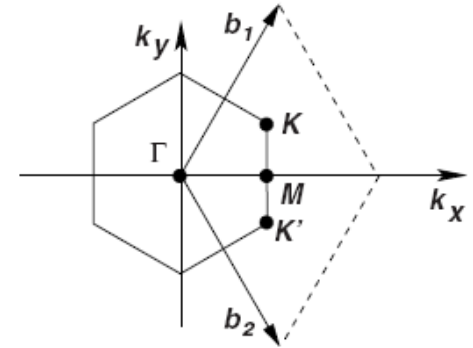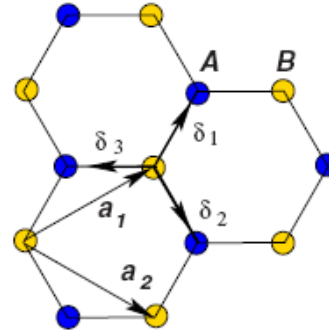
A. H. Castro Neto *et al.*, Rev. Mod. Phys. 81, 109 (2009)

15.1 Graphene – Electronic structure

Nearest-neighbor tight-binding Hamiltonian

$$H = -t \sum_{\langle i,j \rangle, \sigma} (a^\dagger_{\sigma,i} b_{\sigma,j} + h.c.)$$

$a^\dagger_{\sigma,i} \ (a_{\sigma,i})$ creation (annihilation) of electron with spin σ on lattice site A in unit cell i

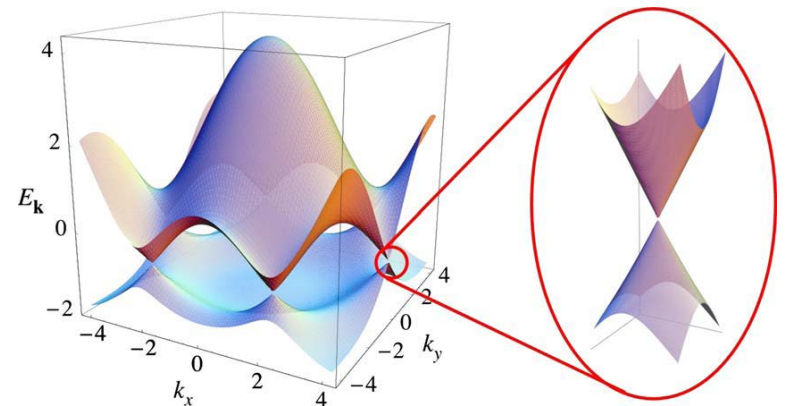$b^\dagger_{\sigma,i} \ (b_{\sigma,i})$ creation (annihilation) of electron with spin σ on lattice site B in unit cell i

$t \approx 2.8 \ \text{eV}$ nearest neighbor hopping

Energy bands

$$E_\pm(k) = \pm t \sqrt{3 + f(\vec{k})}$$

$$f(\vec{k}) = 2\cos(\sqrt{3} k_y a) + 4\cos(\frac{\sqrt{3}}{2} k_y a)\cos(\frac{3}{2} k_x a)$$

15.1 Graphene – Electronic structure
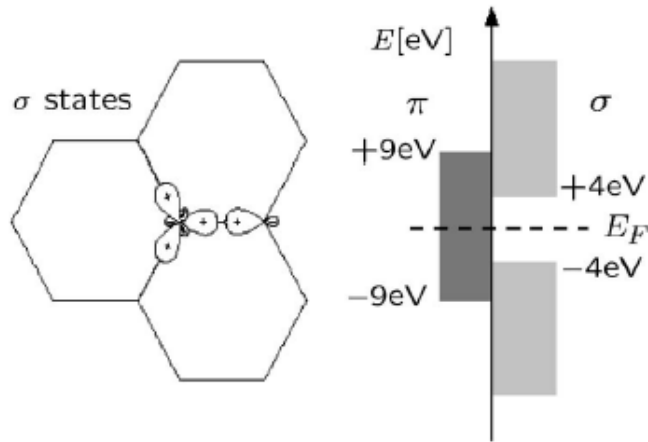
Consideration of all energy bands

FIG. 4. The σ bonds in the carbon hexagonal network connect the carbon atoms and are responsible for the binding energy and the elastic properties of the graphene sheet (left). The π bonds are perpendicular to the surface of the sheet. The corresponding bonding and antibonding σ bands are separated by a large energy gap (right), while the bonding and antibonding π states lie in the vicinity of the Fermi level (E_F). Adapted from Loiseau et al., 2006.
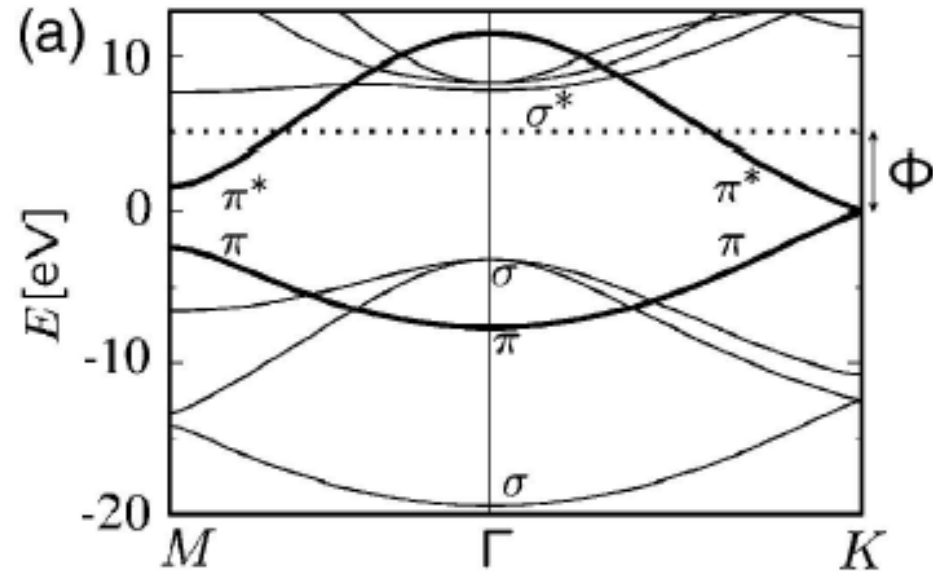
J.-C. Charlier, X. Blase, and S. Roche, Rev. Mod. Phys. 79, 677 (2007)

15.1 Graphene – Electronic structure

Expansion around Dirac points

$$\vec{k} = \vec{K} + \vec{q} \text{ with } \left|\vec{q}\right| \square \left|\vec{K}\right|$$
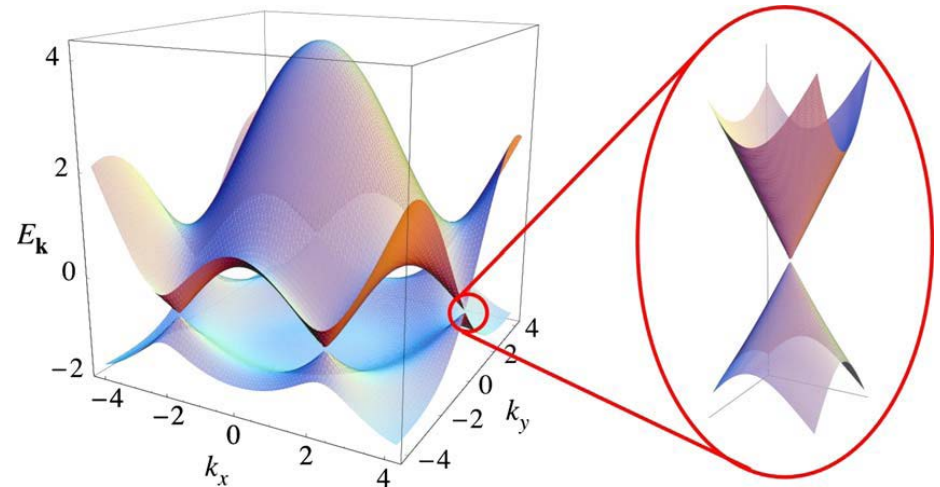
$$E_{\pm}(\vec{q}) = \pm v_F \left|\vec{q}\right|$$

$$v_F = 3ta/2 \approx 10^6 \text{ m/s}$$

$$H = -t\begin{pmatrix} 0 & f(\vec{k}) \\ f(\vec{k})^* & 0 \end{pmatrix}$$

$$H \approx \hbar v_F \begin{pmatrix} 0 & \pm q_x - iq_y \\ \pm q_x + iq_y & 0 \end{pmatrix} = \hbar v_F (\pm q_x \sigma_x + q_y \sigma_y)$$

Low-energy Hamiltonian from expansion around *K* (upper sign) and *K'* (lower sign)

- Linear dispersion at two inequivalent K points or „valleys", called K and K'
- Charge carriers behave like massless Dirac particles
- Two sublattices lead to „pseudospin" (spinor structure of the wave function)

A. H. Castro Neto *et al.*, Rev. Mod. Phys. 81, 109 (2009)
M. I. Katsnelson, Graphene: Carbon in Two Dimensions, Cambridge University Press (2012)

15.1 Graphene – Electronic structure

Density of states

$$\rho(E) = \frac{2A_c}{\pi} \frac{|E|}{v_F^2} \text{ with } A_c = \frac{3\sqrt{3}a^2}{2}$$
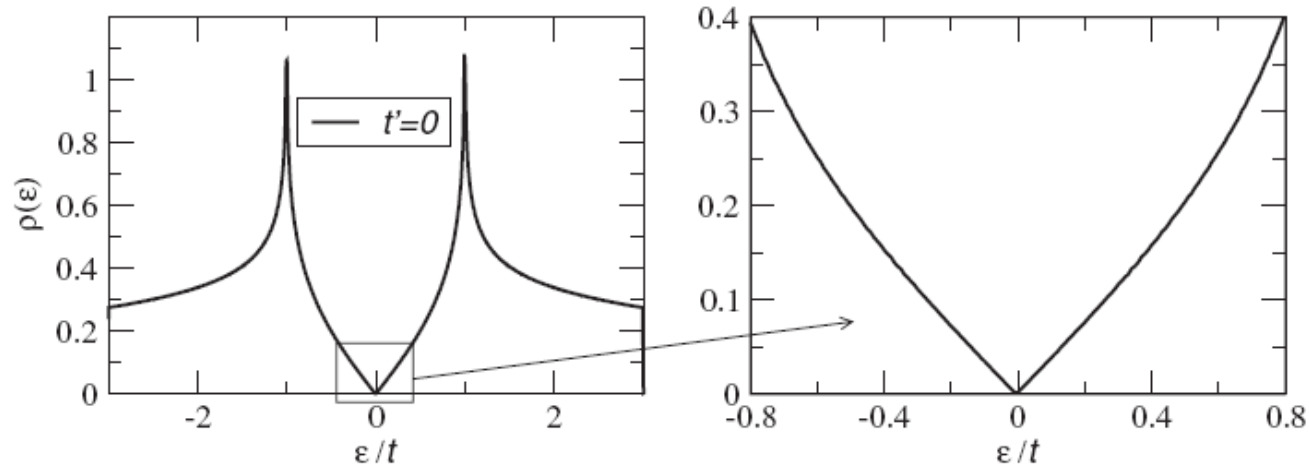

FIG. 5. Density of states per unit cell as a function of energy (in units of t) computed from the energy dispersion (5), t' =0.2t (top) and t' =0 (bottom). Also shown is a zoom-in of the density of states close to the neutrality point of one electron per site. For the case t' =0, the electron-hole nature of the spectrum is apparent and the density of states close to the neutrality point can be approximated by $\rho(\epsilon) \propto |\epsilon|$.

A. H. Castro Neto et al., Rev. Mod. Phys. 81, 109 (2009)

15.1 Graphene – Electronic structure

Low-energy Hamiltonian from expansion around *K* (upper sign) and *K'* (lower sign) in real space

$$\hbar v_F \begin{pmatrix} 0 & \pm i\partial_x + \partial_y \\ \pm i\partial_x - \partial_y & 0 \end{pmatrix} \begin{pmatrix} \psi_A(x,y) \\ \psi_B(x,y) \end{pmatrix} = E \begin{pmatrix} \psi_A(x,y) \\ \psi_B(x,y) \end{pmatrix}$$

Solution

$$\psi(x,y) = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(\mp i\phi/2) \\ s\exp(\pm i\phi/2) \end{pmatrix} e^{i(\pm q_x x + q_y y)} \qquad \begin{array}{l} \phi = \arctan(q_x/q_y) \\ s = \mathrm{sgn}(E) \end{array}$$

Energy eigenstates are eigenstates of the helicity operator
("spin" in direction of motion or opposite)

$$\hat{h} = \frac{1}{2}\sigma \cdot \frac{\vec{q}}{q} \qquad \hat{h}\psi(x,y) = \frac{s}{2}\psi(x,y)$$

Valley K (K'):
Electrons have positive (negative),
holes negative (positive) helicity

T. T. Heikkila, The Physics of Nanoelectronics, Oxford University Press (2013)

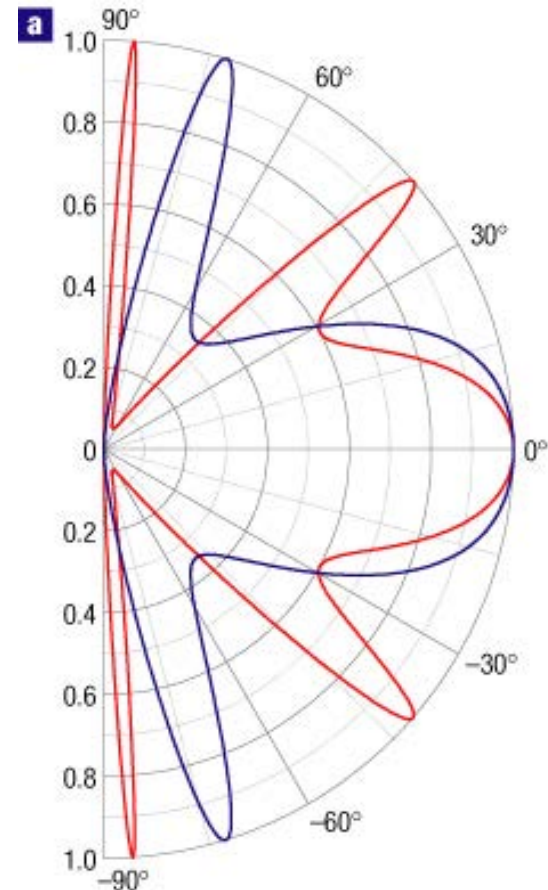# 15.1 Graphene – Klein tunneling (or paradox)

Chirality prevents backscattering
- Perfect transmission through a square barrier (for edges sharp compared to Fermi wavelength)

Disadvantage: No "gap" for carriers as needed for a transistor.
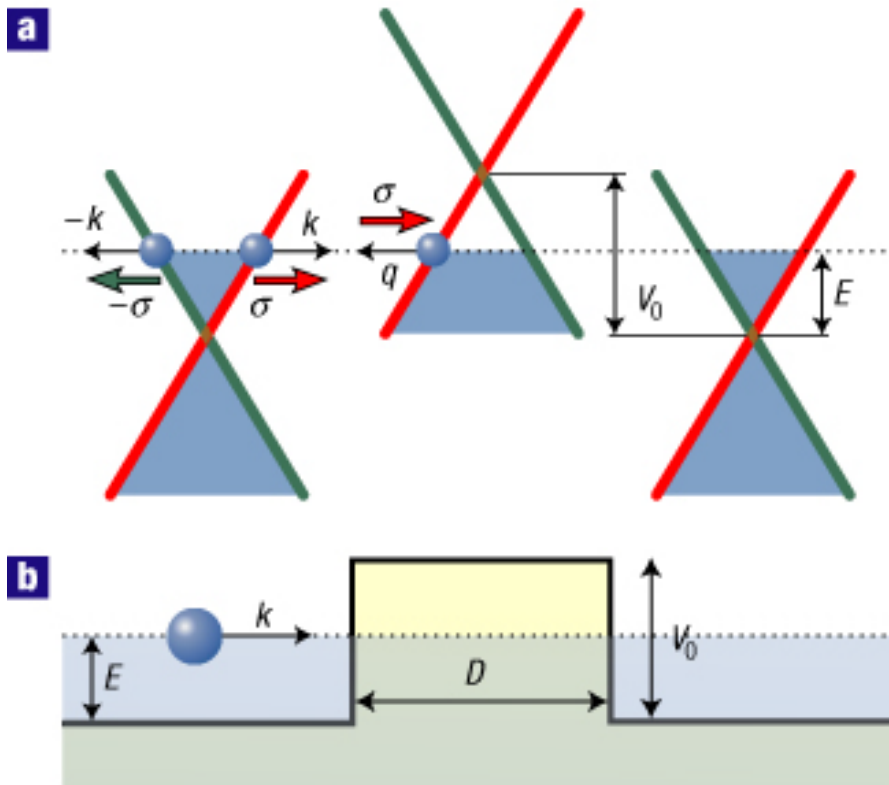
Transmission probability T through a 100-nm-wide barrier as a function of the incident angle for graphene.

M. I. Katsnelson, K. S. Novoselov, and A. K. Geim, Nature Physics 2, 620 (2006)
T. T. Heikkila, The Physics of Nanoelectronics, Oxford University Press (2013)
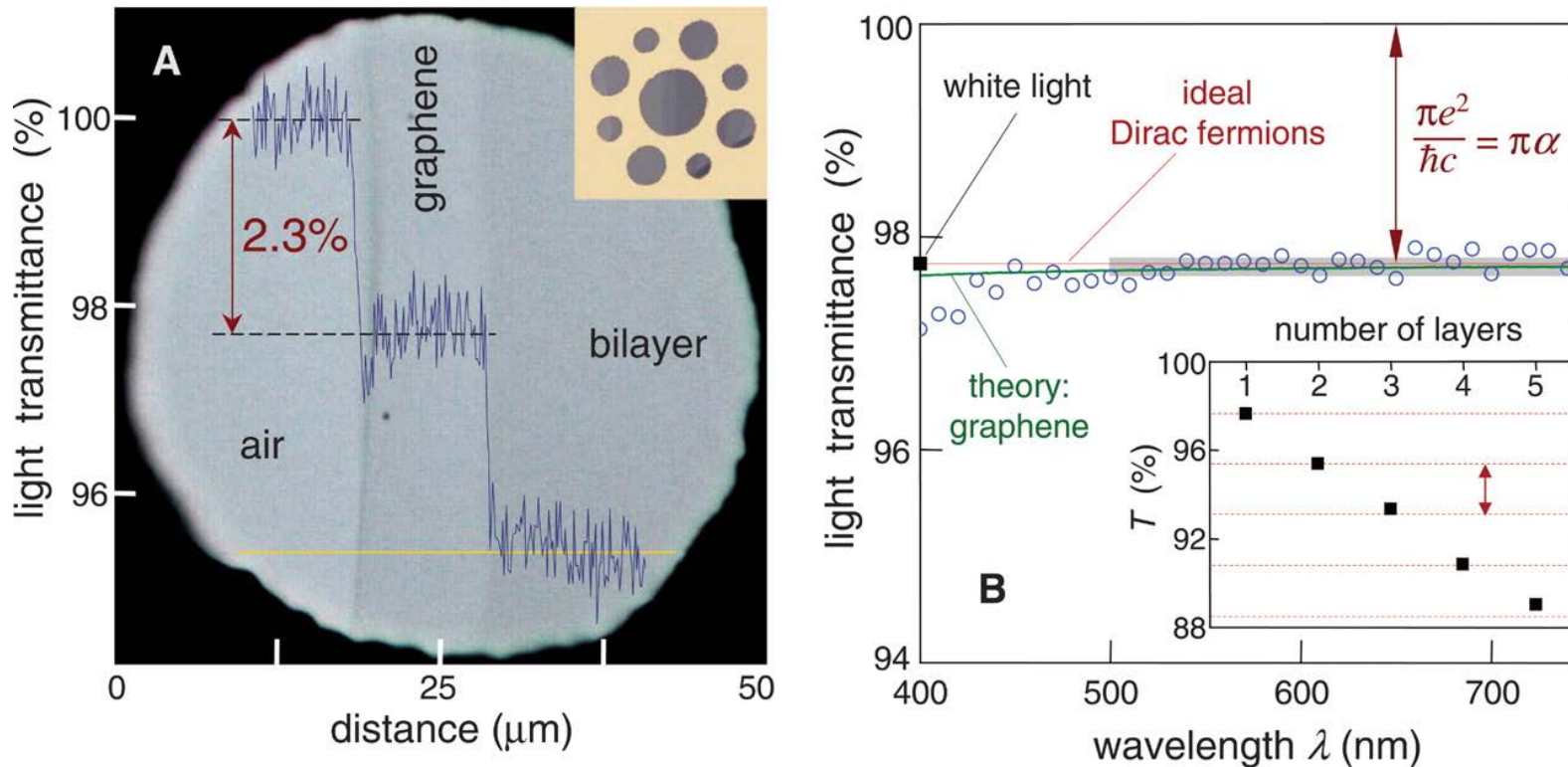
15.1 Graphene – Optical properties (just for fun)

Fig. 1. Looking through one-atom-thick crystals. (A) Photograph of a 50-µm aperture partially covered by graphene and its bilayer. The line scan profile shows the intensity of transmitted white light along the yellow line. (B) Transmittance spectrum of single-layer graphene (open circles). Slightly lower transmittance for < 500 nm is probably due to hydrocarbon contamination. (Inset) Transmittance of white light as a function of the number of graphene layers (squares). The dashed lines correspond to an intensity reduction by $\pi\alpha$ with each added layer.

Graphene: Relativistic electrons (except for v_F instead of the speed of light c).
The interaction of light with relativistic particles is described by the fine structure constant α. The Fermi velocity is only a prefactor for the Hamiltonian of graphene and the interaction with light, and, accordingly, the coefficient may not change the strength of the interaction.

R. R. Nair *et al.*, Science 320, 1308 (2008)

15.2 Bilayer graphene – Electronic structure

$$H = -\gamma_0 \sum_{\substack{\langle i,j \rangle \\ m,\sigma}} (a^\dagger_{m,i,\sigma} b_{m,j,\sigma} + h.c.)$$

$$-\gamma_1 \sum_{j,\sigma} (a^\dagger_{1,j,\sigma} a_{2,j,\sigma} + h.c.)$$

$$-\gamma_4 \sum_{j,\sigma} (a^\dagger_{1,j,\sigma} b_{2,j,\sigma} + a^\dagger_{2,j,\sigma} b_{1,j,\sigma} + h.c.)$$

$$-\gamma_3 \sum_{j,\sigma} (b^\dagger_{1,j,\sigma} b_{2,j,\sigma} + h.c.)$$
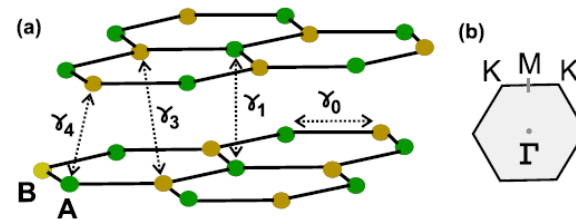
FIG. 9. (Color online) Lattice structure of bilayer graphene, its respective electronic hopping energies, and Brillouin zone. (a) Lattice structure of the bilayer with the various hopping parameters according to the SWM model. The A sublattices are indicated by darker spheres. (b) Brillouin zone. Adapted from Malard *et al.*, 2007.

Plane *m*, unit cell *i*, spin *σ*, sublattices *A,B*

$$\gamma_0 = t \approx 2.8 \text{ eV}, \ \gamma_1 \approx 0.4 \text{ eV}, \ \gamma_4 \approx 0.04 \text{ eV}, \ \gamma_3 \approx 0.3 \text{ eV} \qquad \text{(taken from graphite)}$$

$$H_k = \begin{pmatrix} -V & v_F q & 0 & 3\gamma_3 a q^* \\ v_F q^* & -V & \gamma_1 & 0 \\ 0 & \gamma_1 & V & v_F q \\ 3\gamma_3 a q & 0 & v_F q^* & V \end{pmatrix}$$

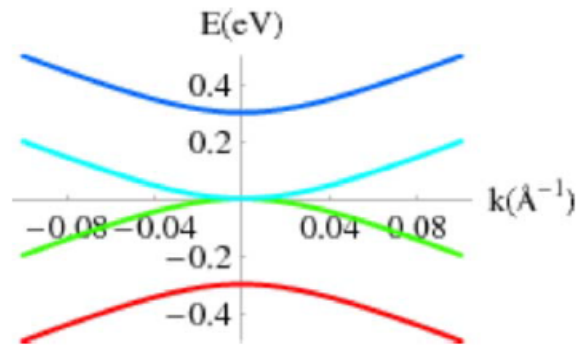$$\vec{k} = \vec{K} + \vec{q} \text{ with } \left|\vec{q}\right| \Box \left|\vec{K}\right|$$

$$q = q_x + i q_y \qquad \gamma_4 \text{ neglected}$$
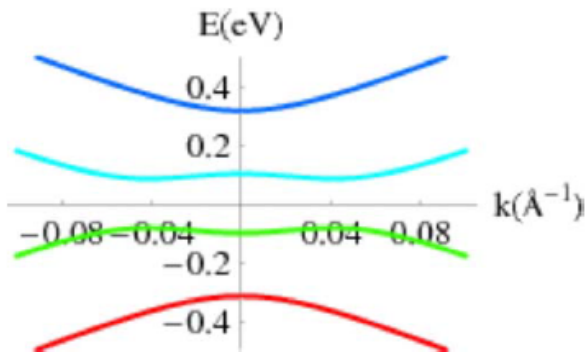
2*V*: potential difference between the two layers

15.2 Bilayer graphene – Electronic structure

Dispersion relation
$$E_\pm^2 = V^2 + v_F^2 |q|^2 + \frac{\gamma_1^2}{2} \pm \sqrt{v_F^2 |q|^2 \gamma_1^2 + \frac{\gamma_1^2}{4} + 4V^2 v_F^2 |q|^2}$$

FIG. 10. (Color online) Band structure of bilayer graphene of $V=0$ and $\gamma_3=0$.
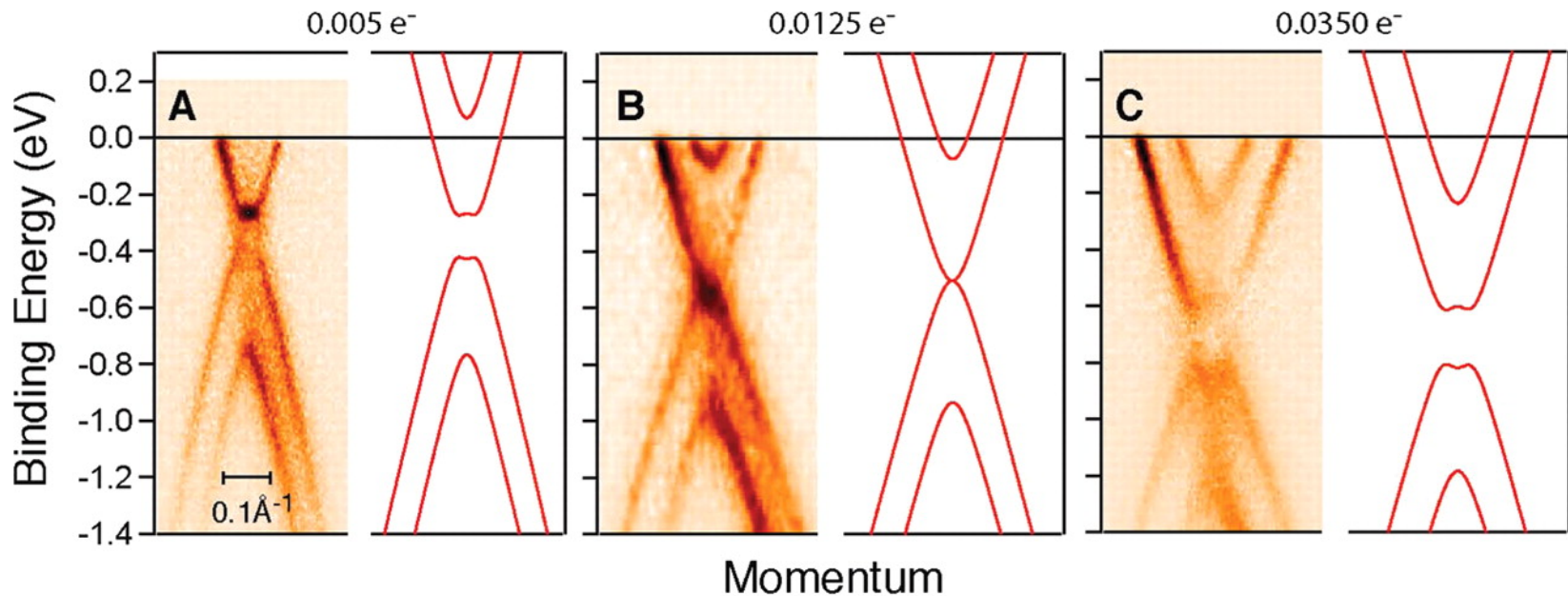
- Quadratic dispersion for V=0

FIG. 11. (Color online) Band structure of bilayer graphene for $V \neq 0$ and $\gamma_3=0$.

- Voltage difference between the layers allows to open a gap

15.2 Bilayer graphene – Electronic structure

Evolution of gap closing and reopening by changing the doping level by potassium adsorption. Experimental and theoretical bands (solid lines) (**A**) for an as-prepared graphene bilayer and (**B** and **C**) with progressive adsorption of potassium are shown. The number of doping electrons per unit cell, estimated from the relative size of the Fermi surface, is indicated at the top of each panel.

T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, Science 313, 951 (2006)

→ Further graphene stacks with more layers are possible.

15.3 Graphene nanoribbons

Why boundaries?

Experimentally: Finite structures
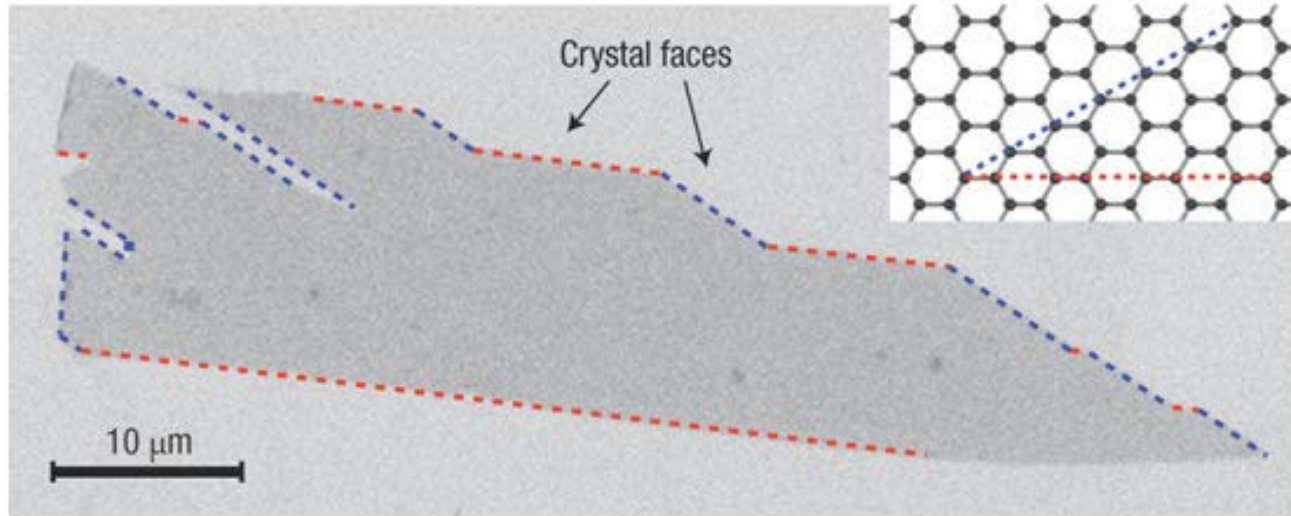
A. K. Geim and K. S. Novoselov, Nature Materials 6, 183 - 191 (2007)
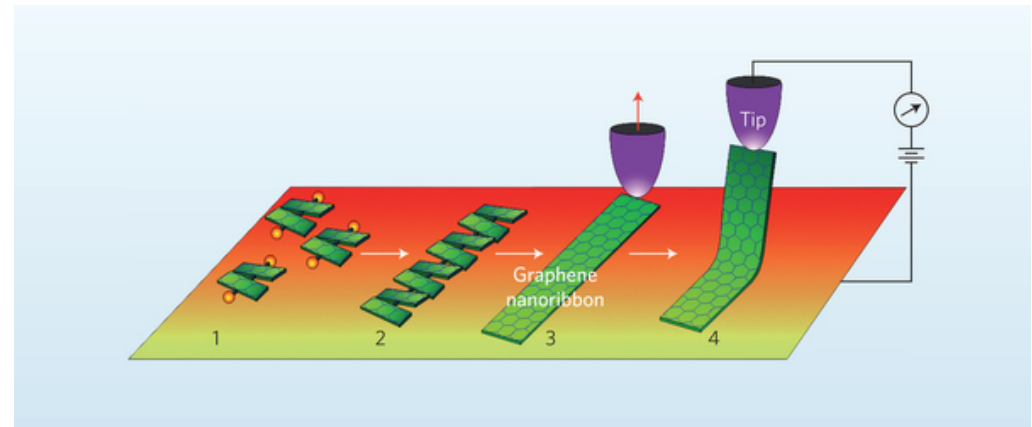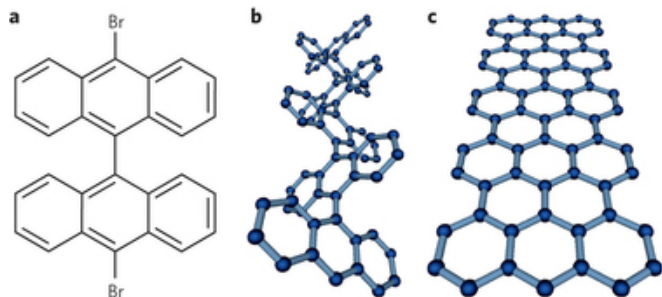
M. Koch et al., Nat. Nanotechnol. 7, 713 (2012)

15.3 Graphene nanoribbons

Edges – Armchair vs. zigzag
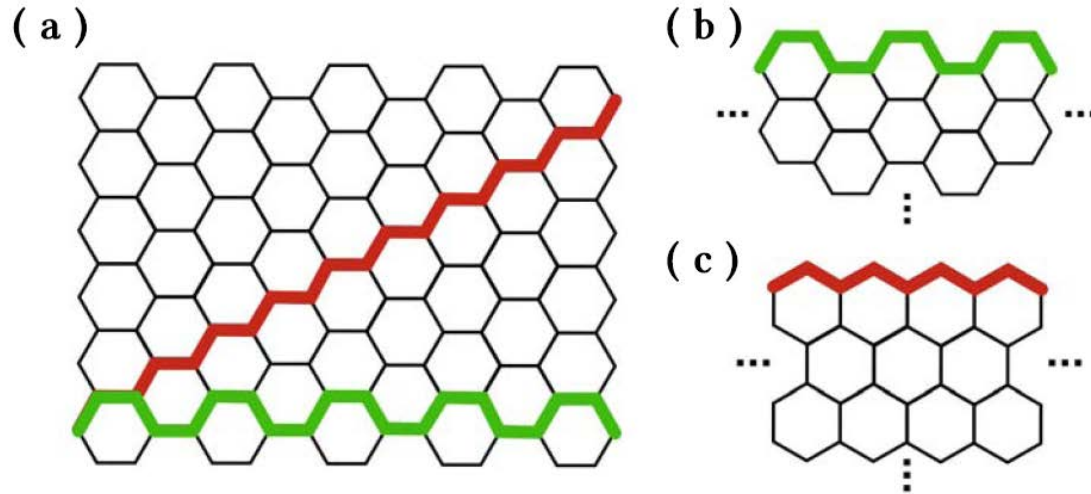
(a)   Graphene with indicated cuts
(b)   Armchair edge
(c)   Zigzag edge

GNR: Graphene Nanoribbon

S.M.-M. Dubois, Z. Zanolli, X. Declerck and J.-C. Charlier, Eur. Phys. J. B 72, 1 (2009)

15.3 Graphene nanoribbons

Armchair
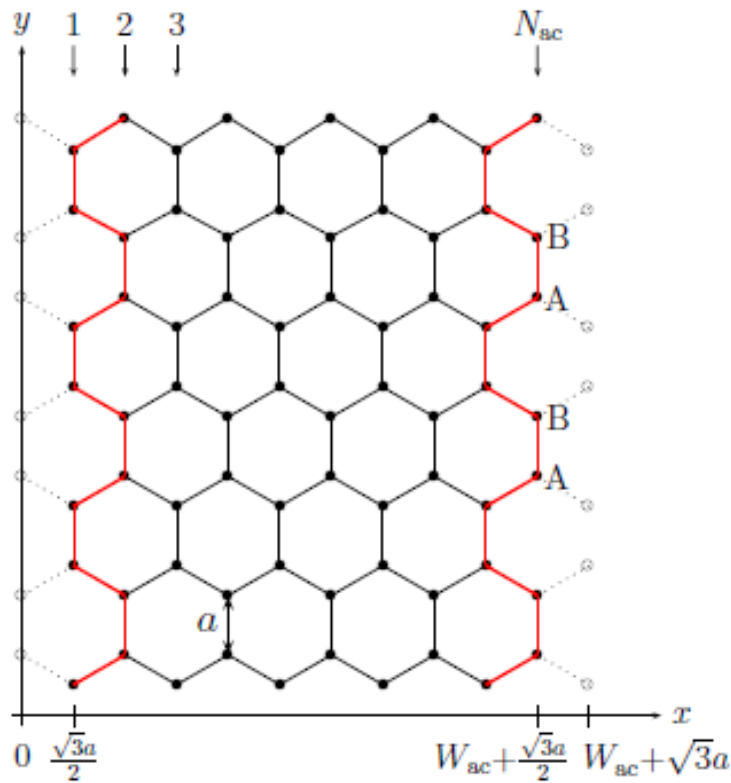
Zigzag

$$W_{ac} = (N_{ac} - 1)\frac{\sqrt{3}}{2}a$$

$$W_{zz} = (N_{zz} - 1)\frac{3}{2}a$$

C-C distance   a=1.42 Å

lattice constant $a_0 = \sqrt{3}a$

P. Dietl, Diploma thesis, KIT 2009
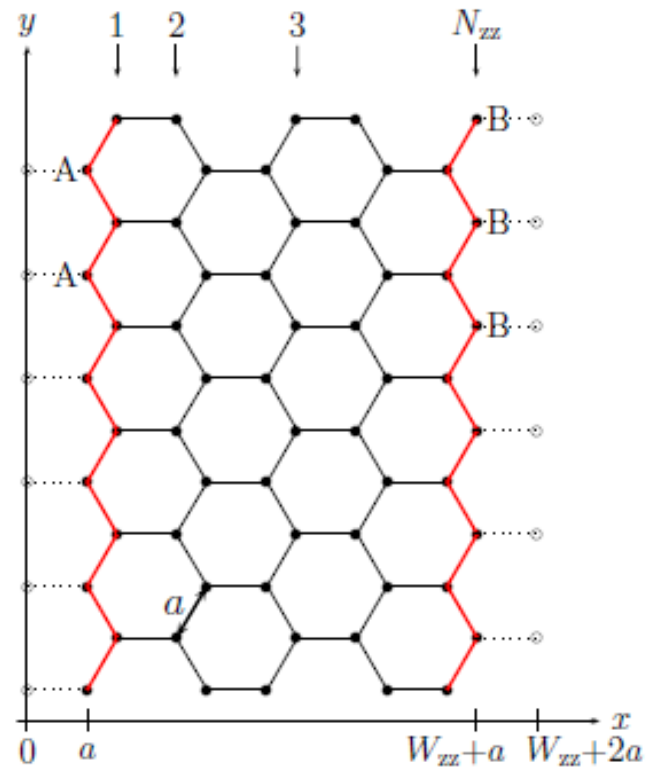
15.3 Graphene nanoribbons – Band structure

Armchair nanoribbon

$$E = \pm \frac{3at}{2}\sqrt{k_n^2 + q_y^2}$$

$$k_n = \frac{\pi n}{W_{ac} + \sqrt{3}a} + \frac{4\pi}{3\sqrt{3}a}$$

There is no gap
for every third
ribbon

Metallic for:

$$N_{ac} = 3m - 1$$

Dirac equation — Tight Binding band structure plots.
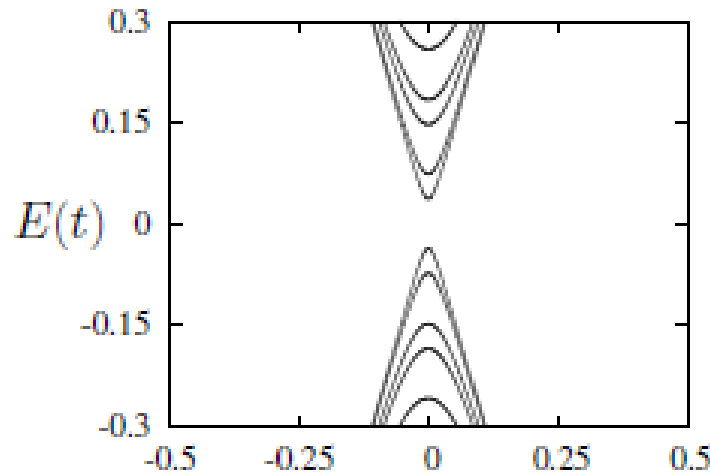
$W_{ac} = 47\frac{\sqrt{3}}{2}a$

$W_{ac} = 49\frac{\sqrt{3}}{2}a$

P. Dietl, Diploma thesis, KIT 2009

15.3 Graphene nanoribbons – Band structure

Armchair nanoribbon

Dirac equation

Tight Binding
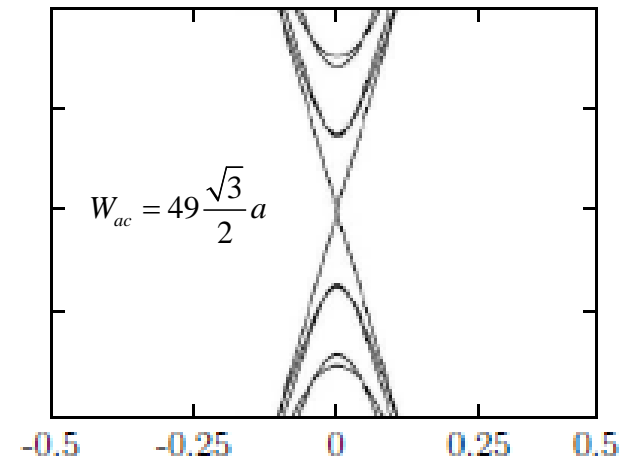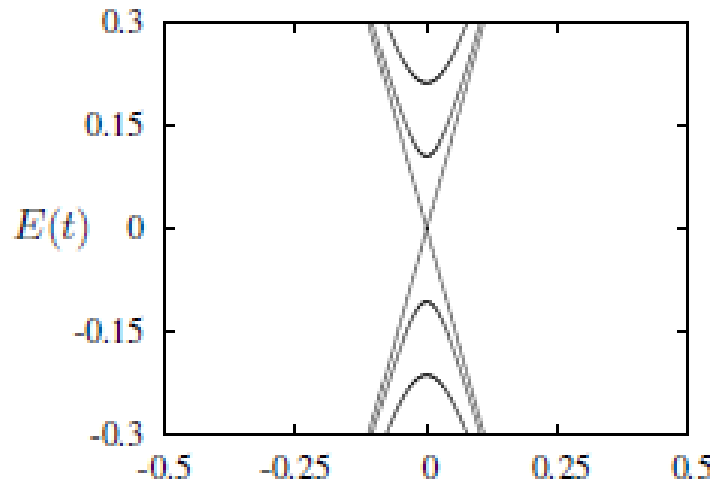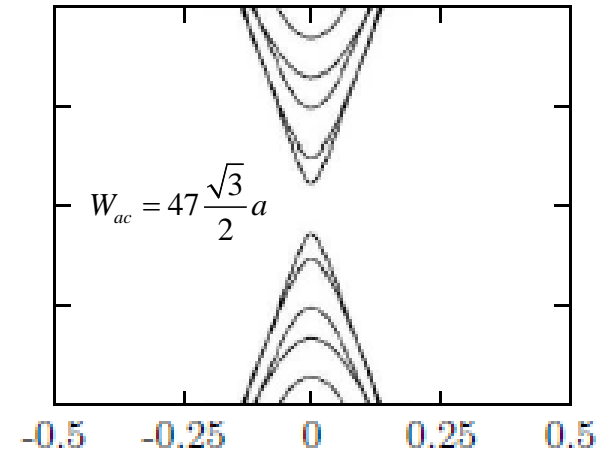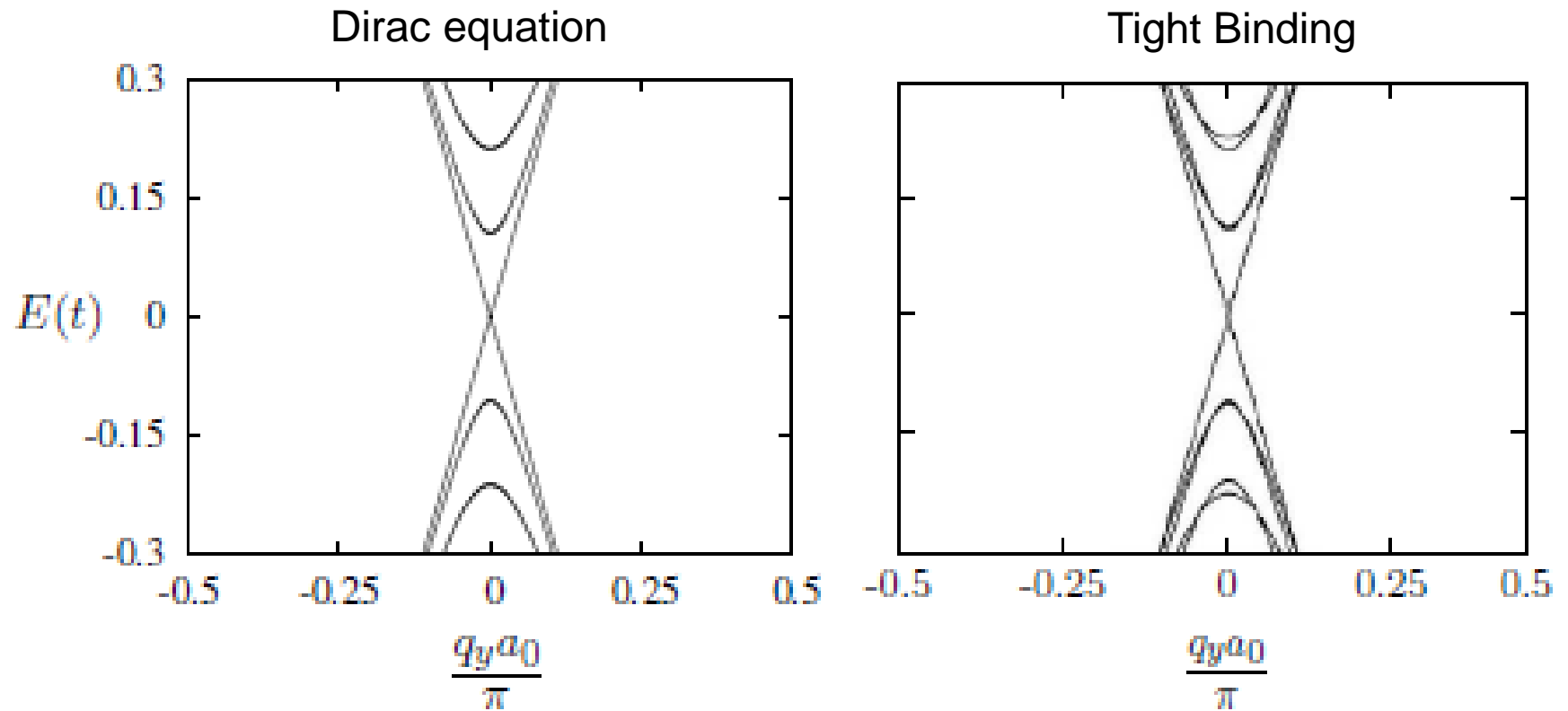
Deviations in the degeneracy of bands
→ continuous limit not completely justified

15.3 Graphene nanoribbons – Band structure

Zigzag nanoribbon

$$\frac{q_y - z}{q_y + z} = e^{-2z(W_{zz} + 2a)}$$

$$E = \pm \frac{3at}{2}\sqrt{q_y^2 - z^2}$$

(1) $z \in \square$ for $q_y > \dfrac{1}{W_{zz} + 2a}$
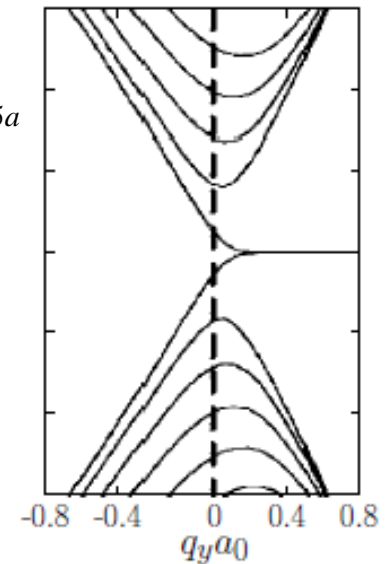
(2) $z = ik_n \in \square$ for $q_y < \dfrac{1}{W_{zz} + 2a}$

$$q_y = \frac{k_n}{\tan(k_n(W_{zz} + 2a))}$$

$$E = \pm \frac{3at}{2}\sqrt{q_y^2 + k_n^2}$$

P. Dietl, Diploma thesis, KIT 2009

Dirac equation

Tight Binding

$W_{zz} = 40.5a$
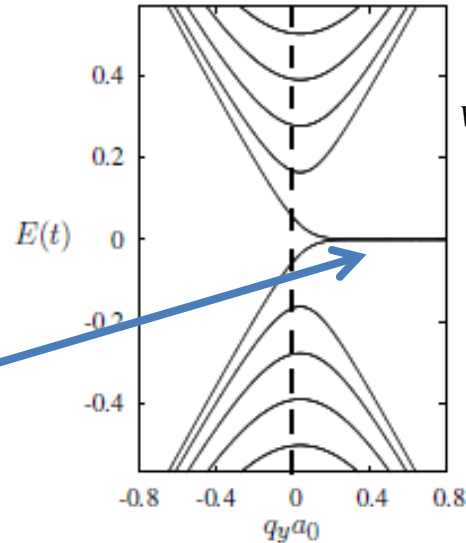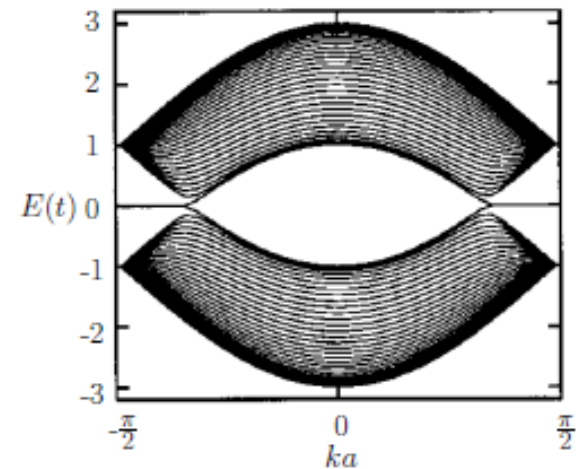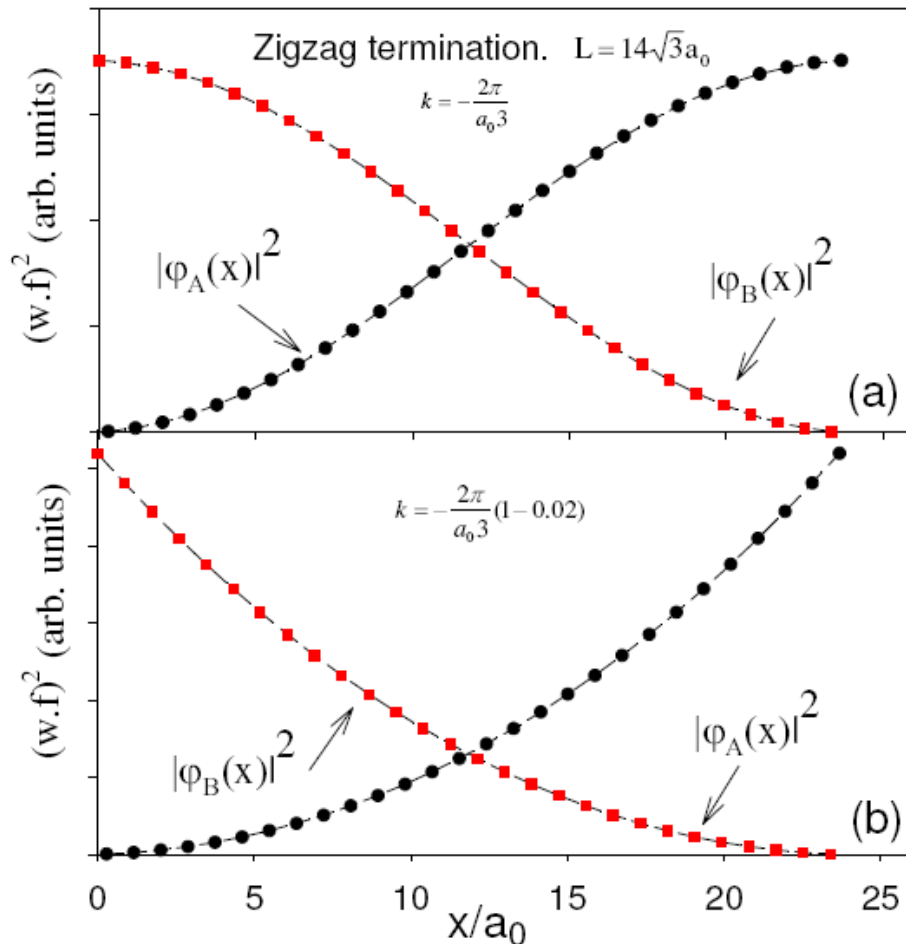
FIG. 4: (*Color online*) Squared wavefunction for the state closest to zero energy for a zigzag nanoribbon, as obtained from tight binding calculations. The width of the ribbon is $L = 14\sqrt{3}a_0$. (a) $k = -2\pi/3a_0$, and (b) $k = (-2\pi/3a_0)(1 - 0.02)$. Both are measured from the center of the Brillouin zone.
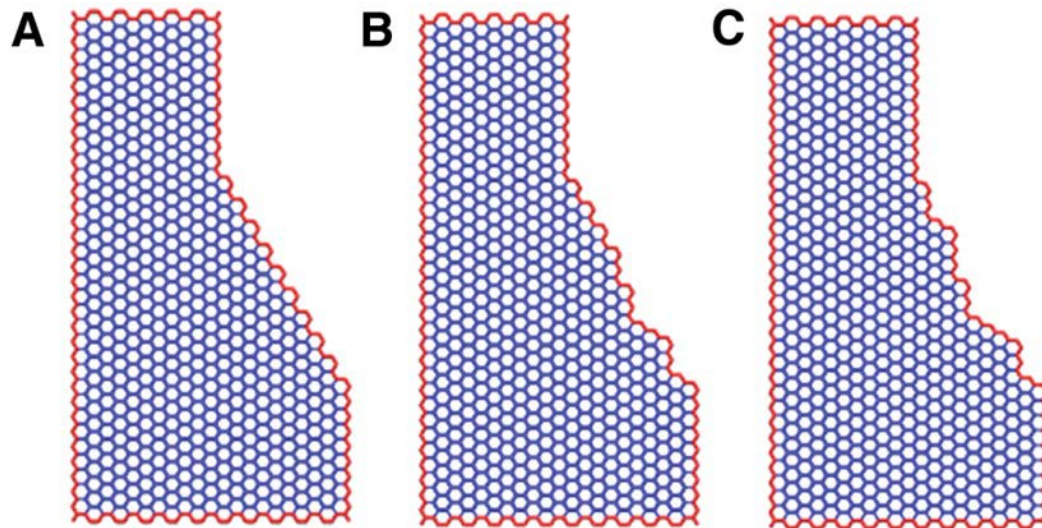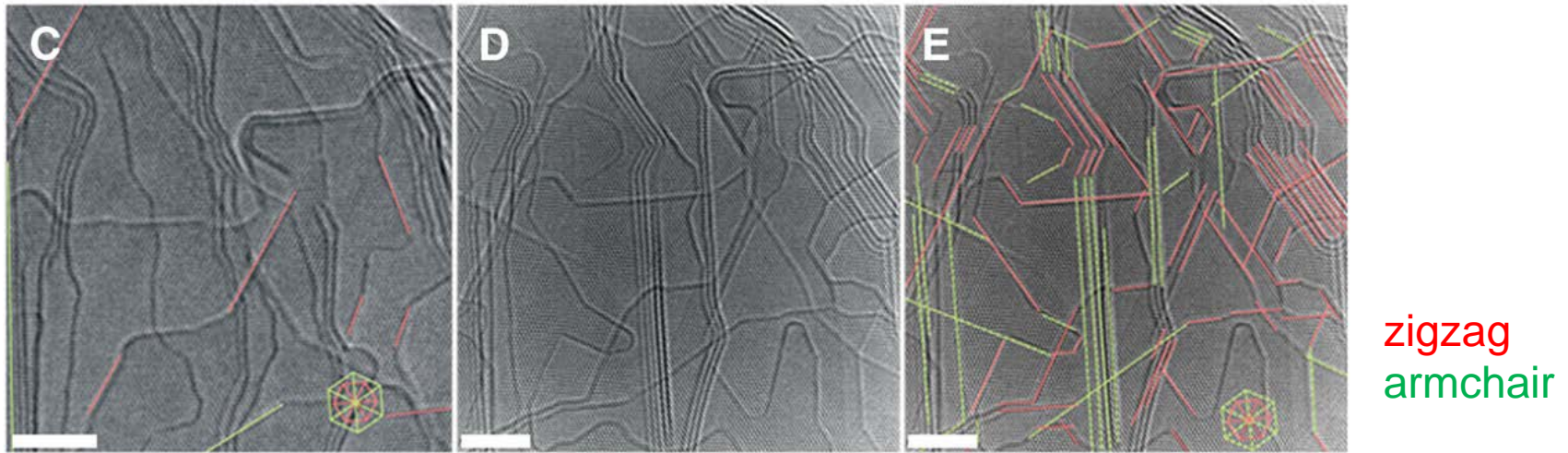
Zigzag nanoribbon

The dispersion-free state is located at the edge and decays exponentially towards the middle.

L. Brey und H. A. Fertig,
Phys. Rev. B 73, 235411 (2006)

15.3 Graphene nanoribbons – Controlling edges

Controlled Formation of Sharp Zigzag and Armchair Edges

zigzag
armchair

Armchair edges rearrange to zigzag edges when a bias voltage is applied

X. Jia *et al.*, Science **323**, 1701 (2009)

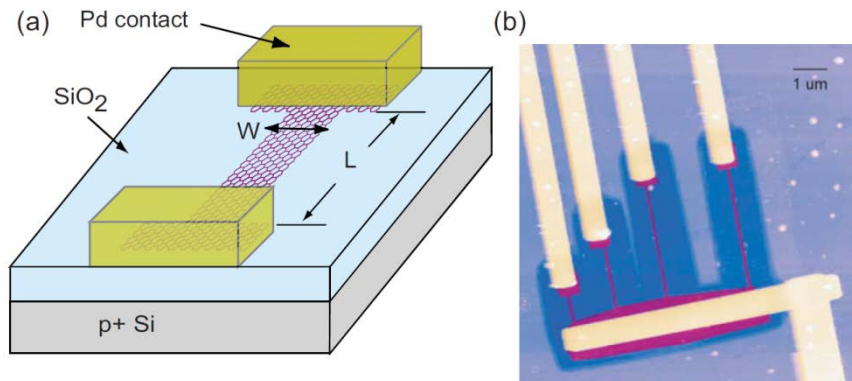# 15.3 Graphene nanoribbons – Charge transport

Conductance of ribbons

$$G = G_0 \tau(E_F) = G_0 \sum_n \tau_n(E_F)$$
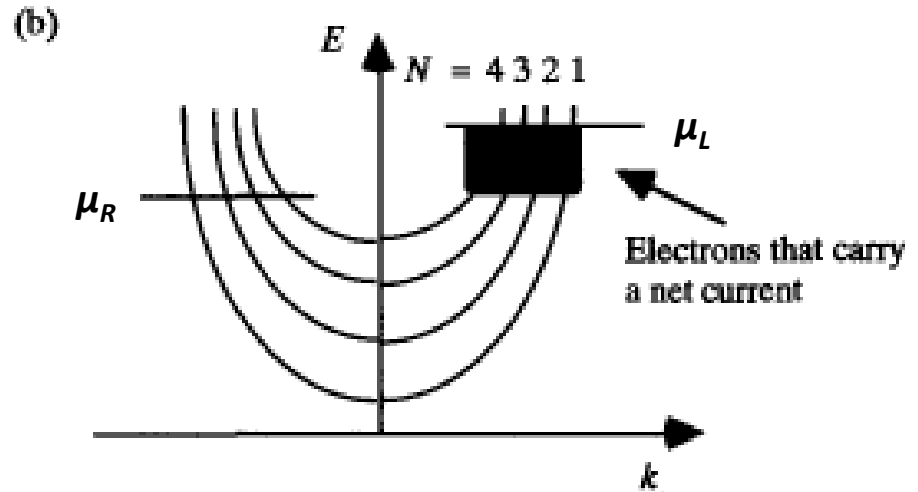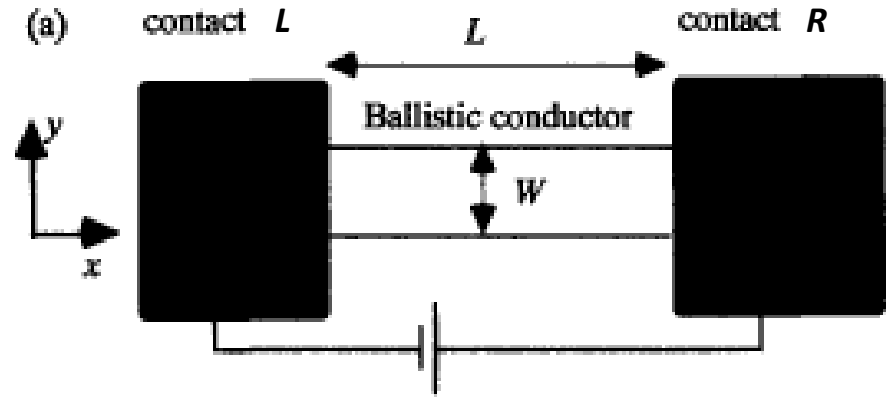
with $G_0 = \dfrac{2e^2}{h} \approx 77.5 \ \mu S$

Transmission probability: $\tau_n = 0,1$

Conductance quantization: $\sum_n \tau_n(E_F) = M$

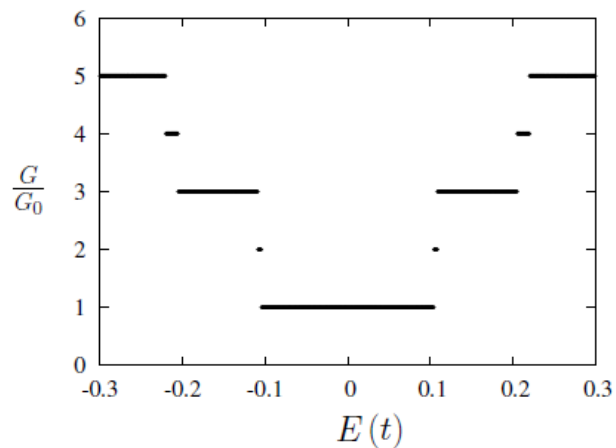determined by number of modes
below the Fermi energy.

S. Datta, Electronic Transport in Mesoscopic Systems,
Cambridge University Press (1997)

Y.-M. Lin et al., Phys. Rev. B **78**, 161409(R) (2008)

15.3 Graphene nanoribbons – Charge transport
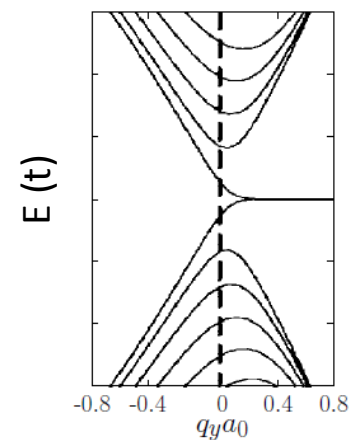
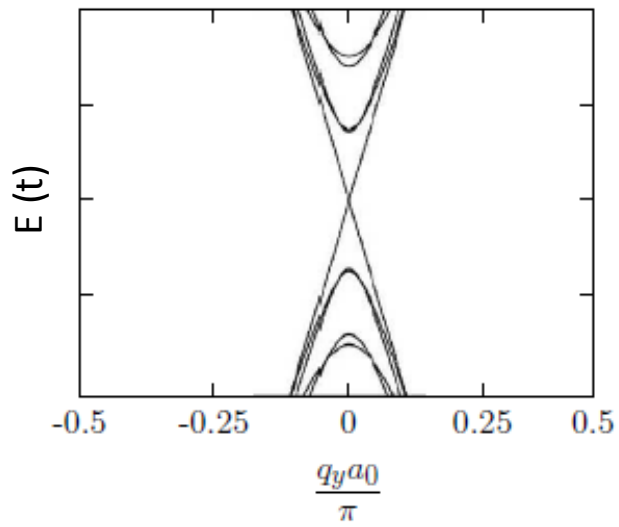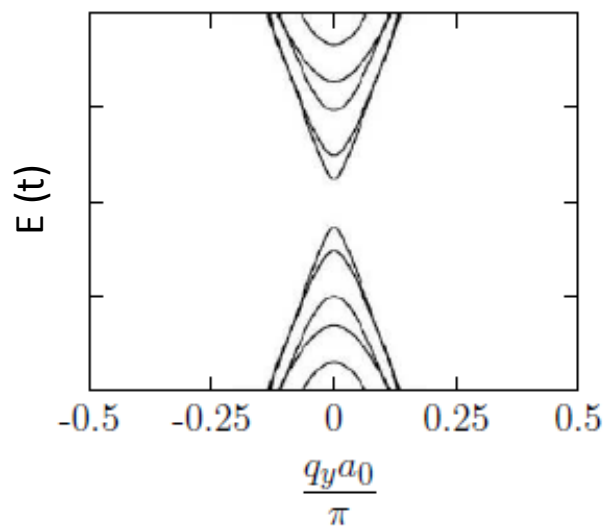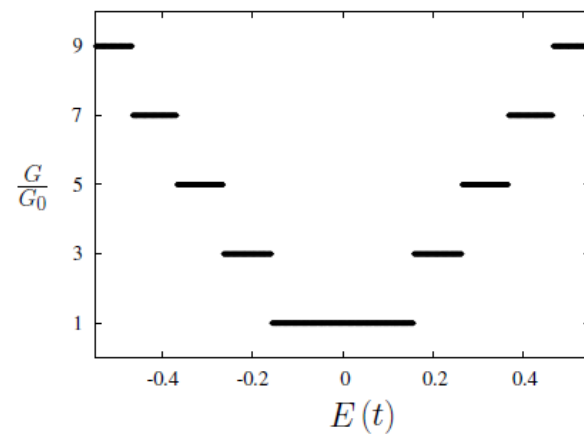**Conductance of ribbons – ideal case**

| Armchair – semiconducting | Armchair – metallic | Zigzag |
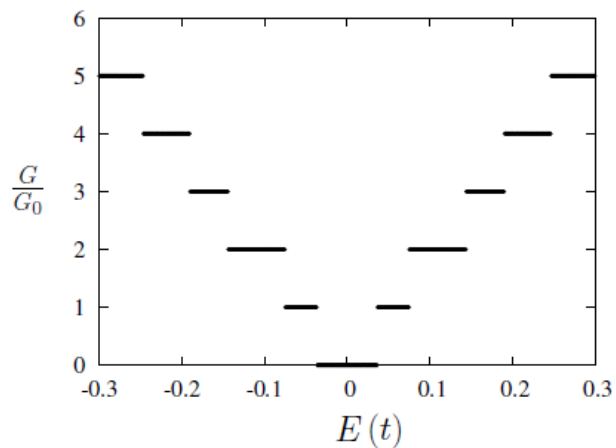
15.3 Graphene nanoribbons – Charge transport

Experimental results

"Subband formation in graphene nanoribbons"

W = 30 nm
(a) L= 900 nm
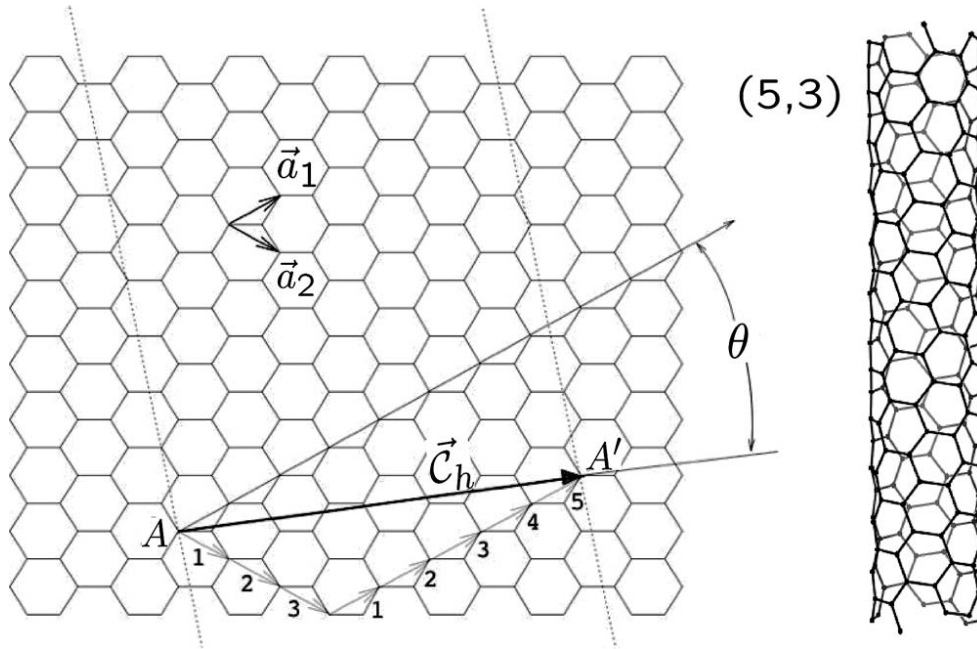(b) L= 1.7 µm
Voltage 10 mV

(a) ΔG=1.7 µS
(b) ΔG=0.6 µS

Compare

$$G_0 = \frac{2e^2}{h} \approx 77.5 \; \mu S$$

→ Low total transmission

15.4 Carbon nanotubes

(5,3)
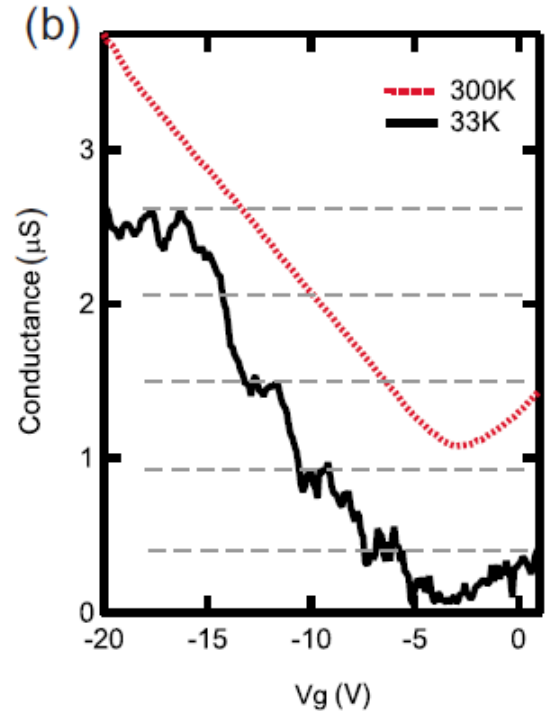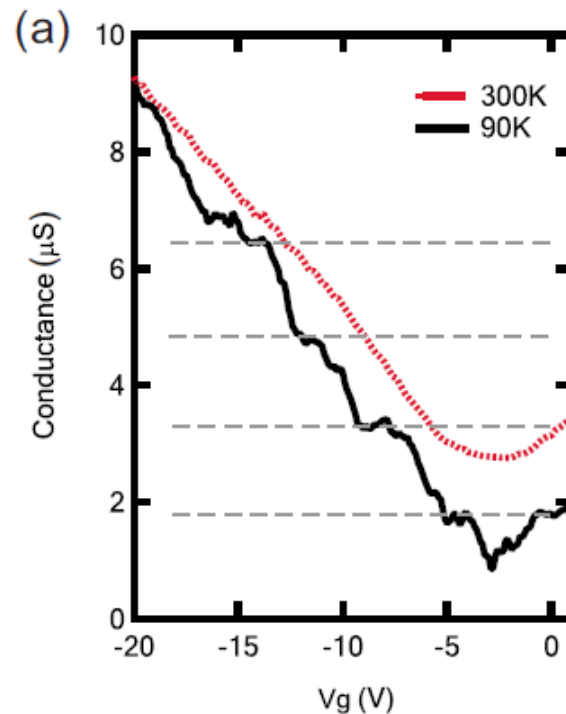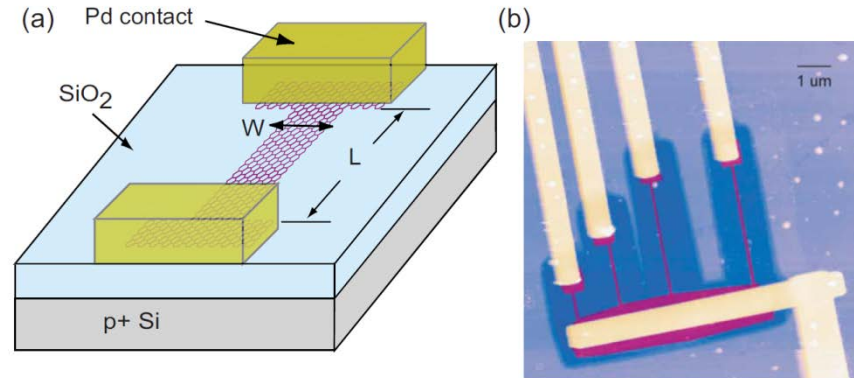
Two-atom basis

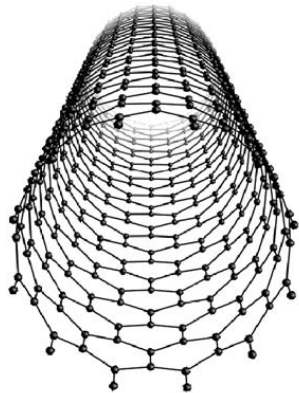$$\vec{a}_1 = a(\frac{\sqrt{3}}{2}, \frac{1}{2}) \qquad a = \sqrt{3}a_{CC}$$

$$\vec{a}_2 = a(\frac{\sqrt{3}}{2}, -\frac{1}{2}) \qquad a_{CC} \approx 0.14 \text{ nm}$$

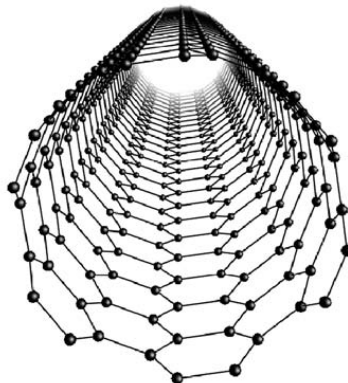Chiral vector   Circumference

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \qquad U = \left| \vec{C}_h \right|$$
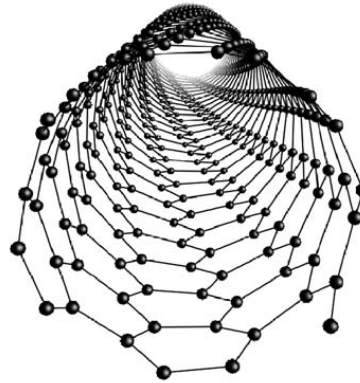
Translational vector

$$\vec{T} = t_1 \vec{a}_1 + t_2 \vec{a}_2$$

(12,0)   (6,6)   (6,4)

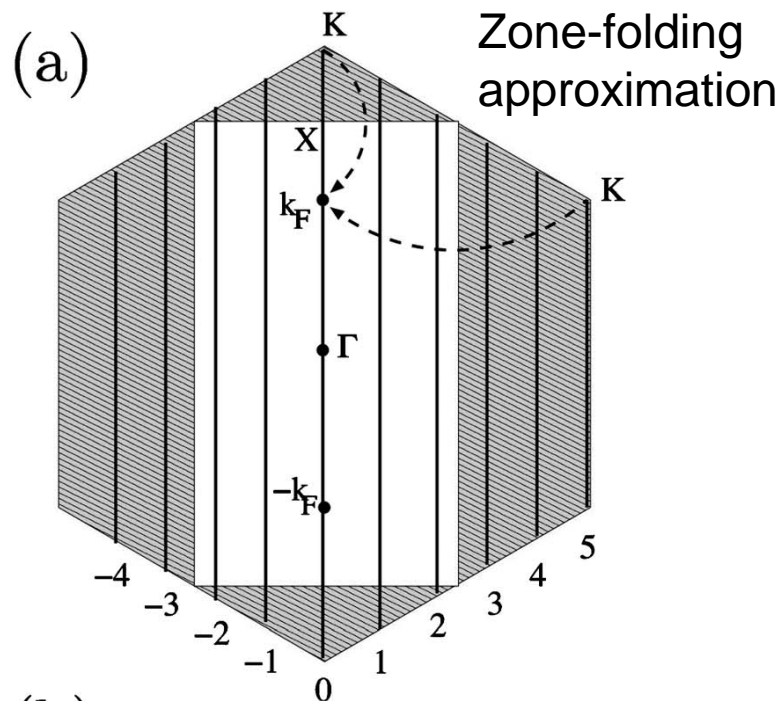Three types of nanotubes: zigzag, armchair, chiral

J.-C. Charlier et al., Rev. Mod. Phys. 79, 677 (2007)

15.4 Carbon nanotubes – Electronic structure

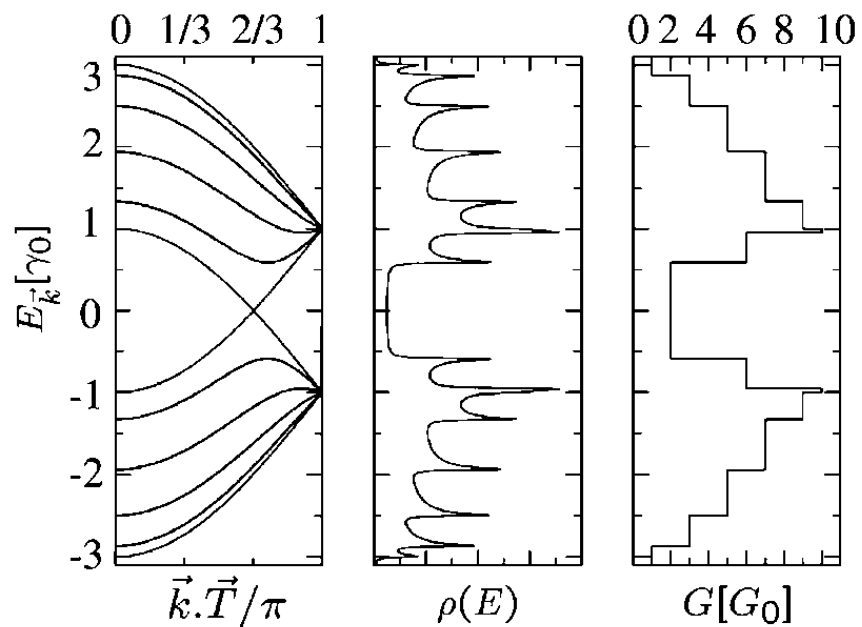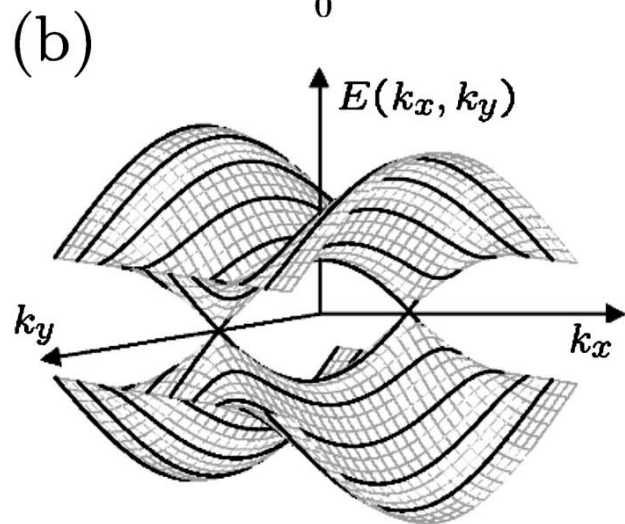Zone-folding approximation

Metallic tube for

$$n - m = 3l \quad l = 1, 2, 3, \ldots$$

FIG. 33. Band structure (left), density of states (middle), and conductance (right) for the (5,5) armchair nanotube.

J.-C. Charlier et al., Rev. Mod. Phys. 79, 677 (2007)

15.4 Carbon nanotubes – Electronic structure

Condition for phase of wave function $\quad \psi_k(\vec{r} + \vec{C}_h) = \exp(i\vec{k} \cdot \vec{C}_h)\psi_k(\vec{r}) = \psi_k(\vec{r})$

$$\longrightarrow \quad \exp(i\vec{k} \cdot \vec{C}_h) = 1$$

$$\vec{k} = \vec{K} + \vec{q} \qquad \vec{C}_h = n\vec{a}_1 + m\vec{a}_2 = (n,m) \qquad \vec{K} \cdot \vec{C}_h = \frac{2\pi}{3}(n-m)$$

Metallic tube

$$\exp(i\vec{K} \cdot \vec{C}_h) = 1$$

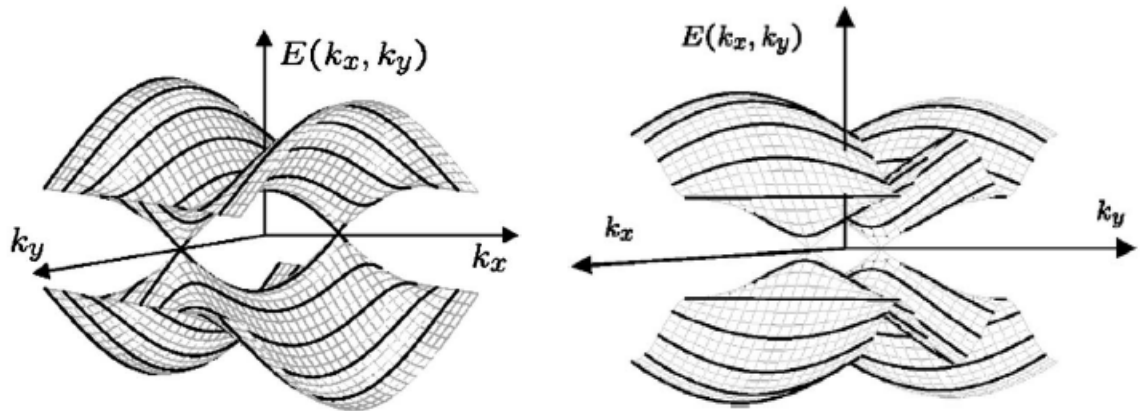$$\vec{q} \cdot \vec{C}_h = 2\pi l$$

$$n - m = 3l$$

Semiconducting tube

$$\exp(i\vec{K} \cdot \vec{C}_h) = \pm\exp(2i\pi / 3)$$

$$\vec{q} \cdot \vec{C}_h = \frac{2}{3}\pi(3l \pm 1)$$

$$n - m = 3l \pm 1$$

Condition fulfilled for
- (n,n) tube: armchair
- $(n,0)$ tube: zigzag, if $n=3l$

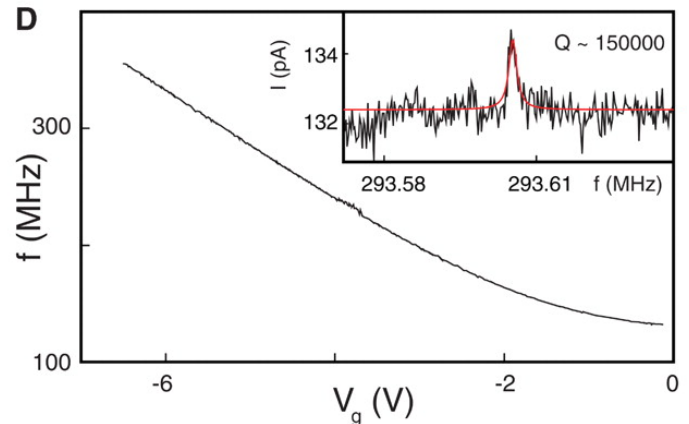J.-C. Charlier et al., Rev. Mod. Phys. 79, 677 (2007)
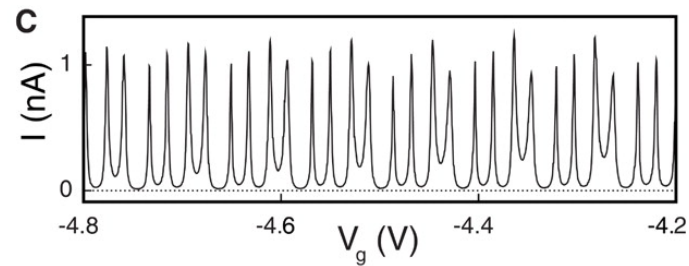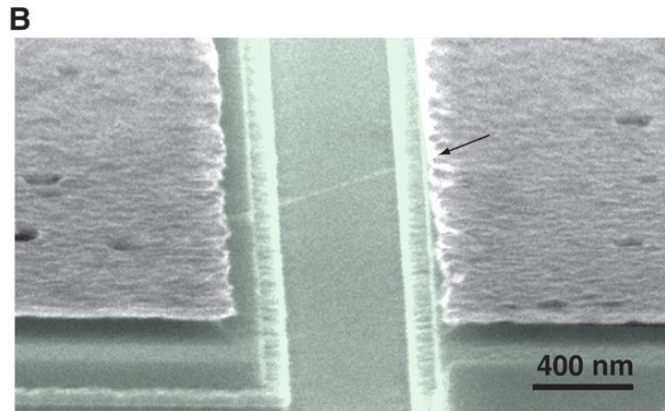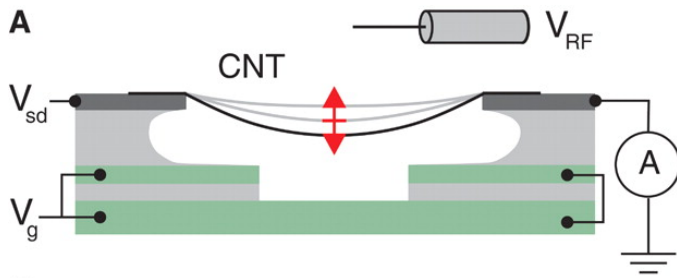
15.4 Carbon nanotubes

Beyond the zone-folding approximation

Curvature effects
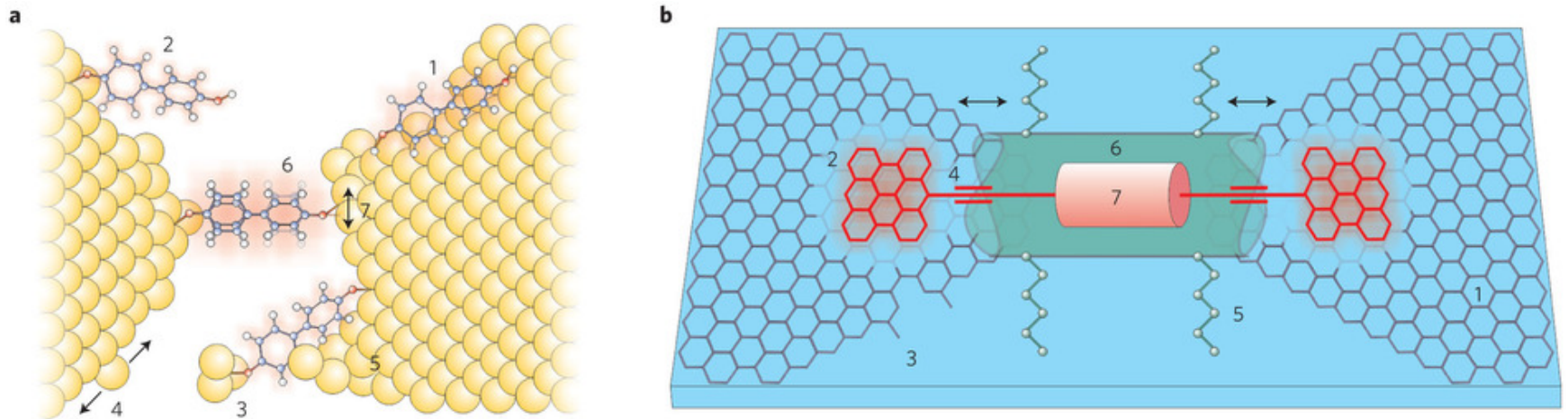a) C-C Bond normal and parallel to axis are different (different lengths)
b) no planar symmetry (p_z orbitals not exactly parallel)
     → Mixing of σ and π states

Strong coupling between single-electron tunneling and nanomechanical motion

G. A. Steele et al., Science 325, 1103 (2009)

a, Typical three-dimensional structure of a metal-based junction with unbound (1), bound (2) and cluster-bound (3) molecules. Drifting gold surface atoms (4) limit the stability and render the potential landscape of the junction undefined because of remote protrusions (5). Stochastic sulphur-gold switching in the anchor group affects (7) the conductance of the molecule under test (6). **b**, A graphene-based junction constrains the structure to two dimensions. It consists of hydrophobic single-layer graphene (1) on a hydrophilic substrate. Large-area anchor groups (2) provide low-contact resistances. Fault-tolerant design to compensate edge defects (3) is achieved by spacers (4) and cages (6). Self-alignment (indicated by the arrows) of the functional unit (7) is attained by hydrophilic side groups (5).

15.5 Graphene nanostructures in molecular electronics

F. Prins et al., Nano Lett. 11, 4607 (2011)

15. Summary

Graphene: Two-dimensional carbon
- Symmetry of the lattice leads to bandstructure that causes unique electronic properties: Low energy excitations close to Dirac points behave like massless, relativistic fermions.

Graphene nanoribbons (GNRs)
Two kinds of (main) edges in GNRs: **armchair** and **zigzag**.
- Armchair GNRs: Some with, some without band gap (semiconducting vs. metallic).
- Zigzag GNRs are metallic, exhibit dispersionless states at high momenta.
- Quantized conductance at low temperatures.

Carbon nanotubes
- (n,n) tubes are of type armchair; ($n,0$) tubes are of type zigzag.
- Tubes can be semiconducting or metallic.
- Armchair tubes are always metallic.
- Used as quantum dots (see chapter 8).