Nanoribbons, edges and quantum dots

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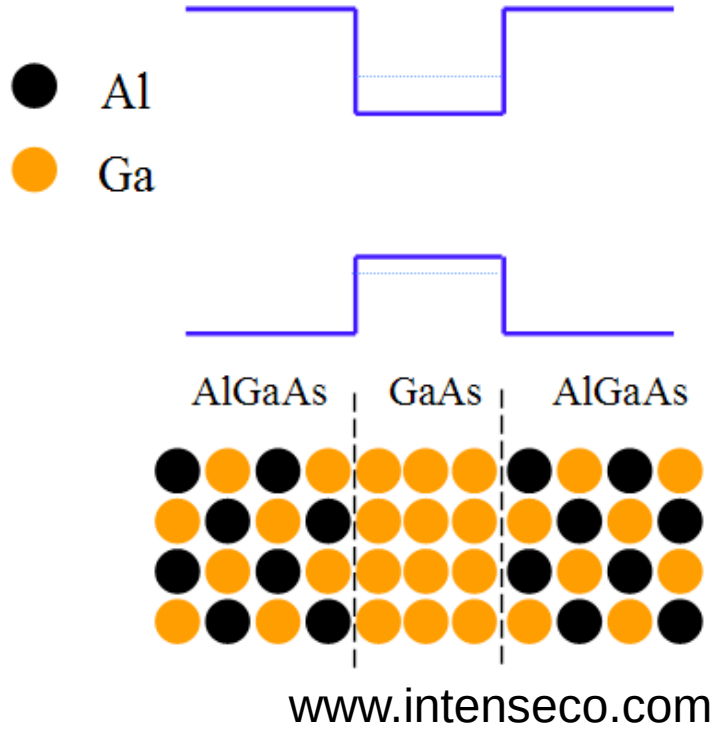
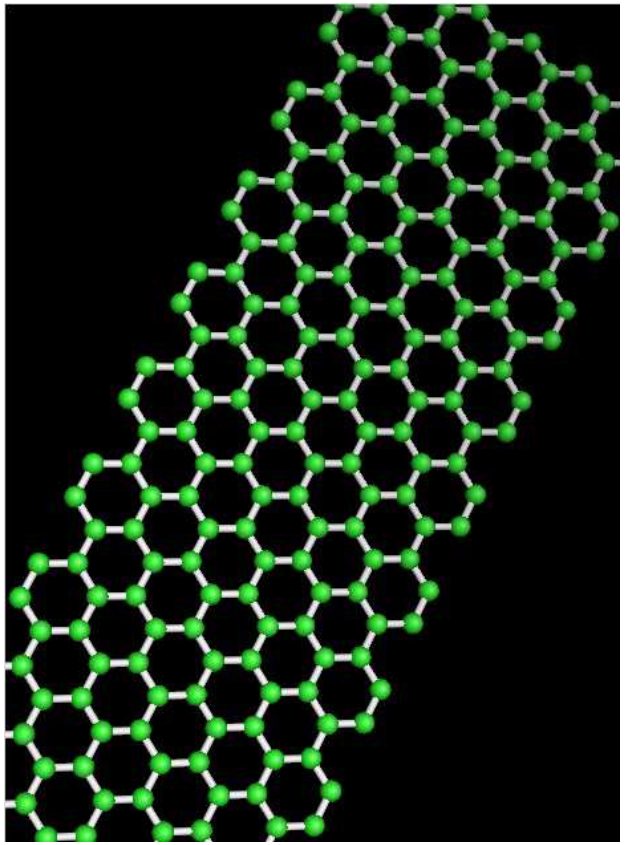
13/06/13

Introduction

- Building quantum wells like in semiconductors is impossible in bulk graphene because of KLEIN tunneling



www.intenseco.com



- Solution: cut graphene into ribbons / nanostructures
- Vacuum as infinite high potential barrier

Overview

- Summary of electronic properties of graphene
- Nanoribbons
  - Calculation of electronic structure with Dirac equation
  - Calculation of electronic structure with Tight Binding method
- Spin polarization at zigzag edges
- Conductance quantization
- Graphene quantum dots

Summary: Graphene properties

- TB Hamiltonian and Ansatz $\psi = c_A \Phi_A^k(\vec{r}) + c_B \Phi_B^k(\vec{r})$

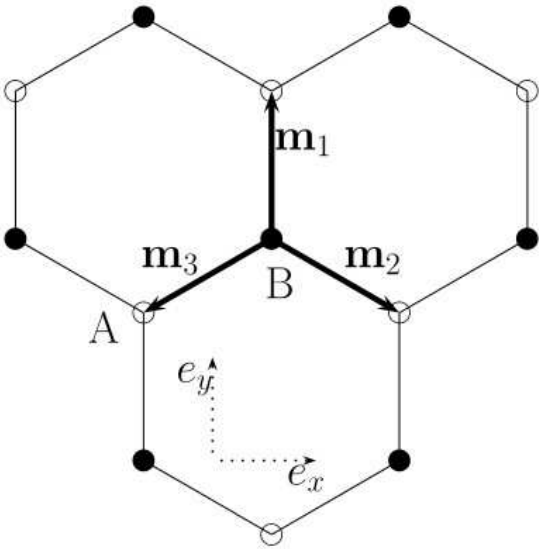
  where: $\Phi_{A/B}^k = \frac{1}{\sqrt{N}} \sum_{\vec{R}_{A/B}}^{N} e^{i\vec{k}\vec{R}_{A/B}} \chi(\vec{r} - \vec{R}_{A/B})$

- leads to (if overlap integrals are neglected):

$$\begin{pmatrix} E_0 & -t\, f(k) \\ -t\, f^*(k) & E_0 \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = \mathrm{E} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

- with the geometrical factor

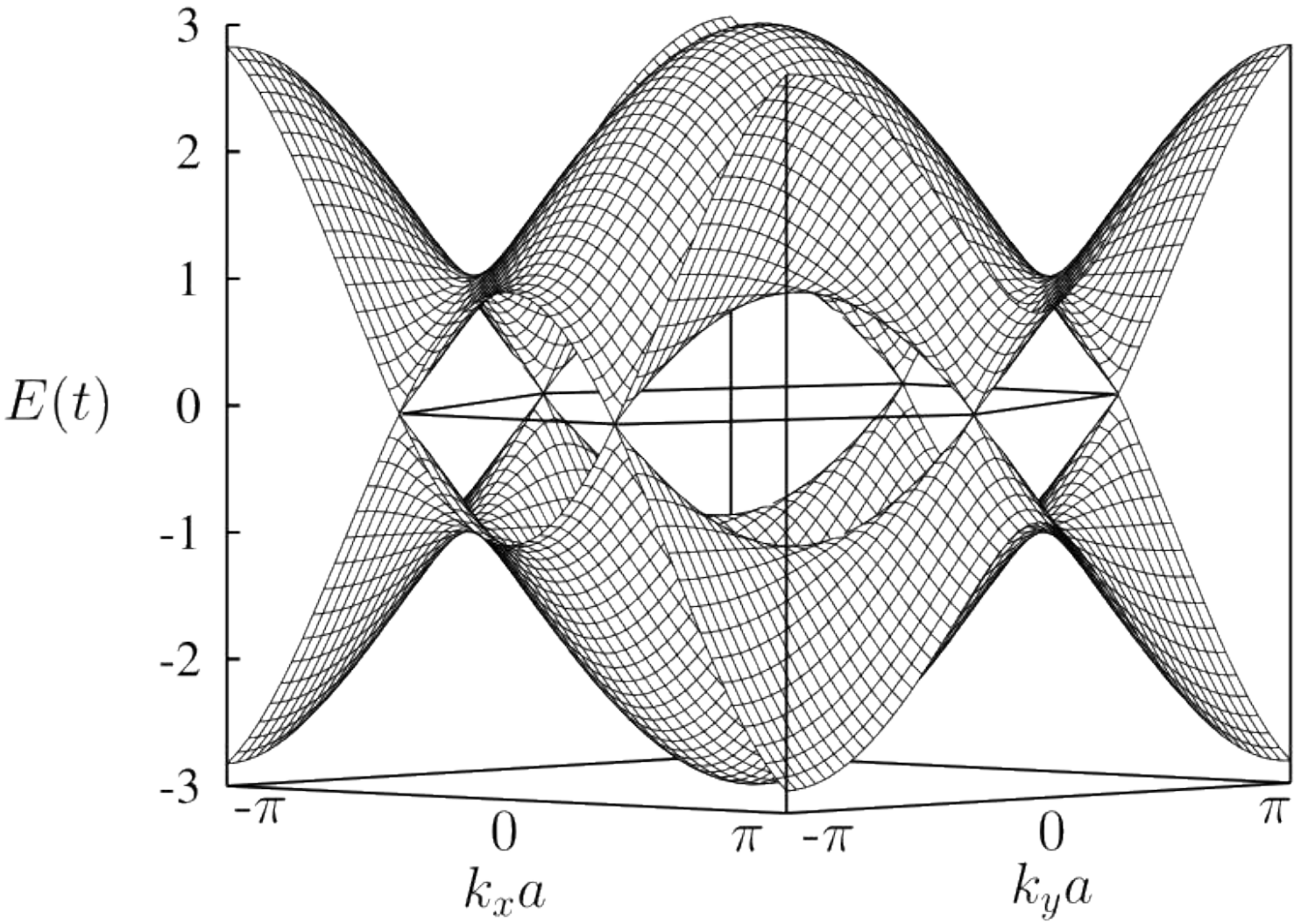
$$f(\vec{k}) = \sum_{\vec{m}_l} e^{-i\vec{k}\vec{m}_l}$$



P. Dietl, Diplomarbeit, KIT, 2009

Summary: electronic structure

- Eigenvalues are $E(\vec{k}) = E_0 \pm t|f(\vec{k})|$



P. Dietl, Diplomarbeit, KIT 2009

Summary: low energy limit

- Expansion of $f(k)$ around K and K' points

$$\vec{k} = \vec{K}^{(\prime)} + \vec{q}$$

- due to low energies the wave function is a LC of 4 terms leading to a 4 dimensional space

$$(\vec{K}A, \vec{K}B, \vec{K}'A, \vec{K}'B)$$

- Dirac-like Hamiltonian

$$-\hbar\, v_f \begin{pmatrix} 0 & -q_x + iq_y & 0 & 0 \\ -q_x - iq_y & 0 & 0 & 0 \\ 0 & 0 & 0 & q_x + iq_y \\ 0 & 0 & q_x - iq_y & 0 \end{pmatrix} \begin{pmatrix} c_A \\ c_B \\ c'_A \\ c'_B \end{pmatrix} = E \begin{pmatrix} c_A \\ c_B \\ c'_A \\ c'_B \end{pmatrix}$$

where $v_F = \frac{\sqrt{3}\, t\, a}{2\hbar} \approx 10^6\, \mathrm{m/s}$

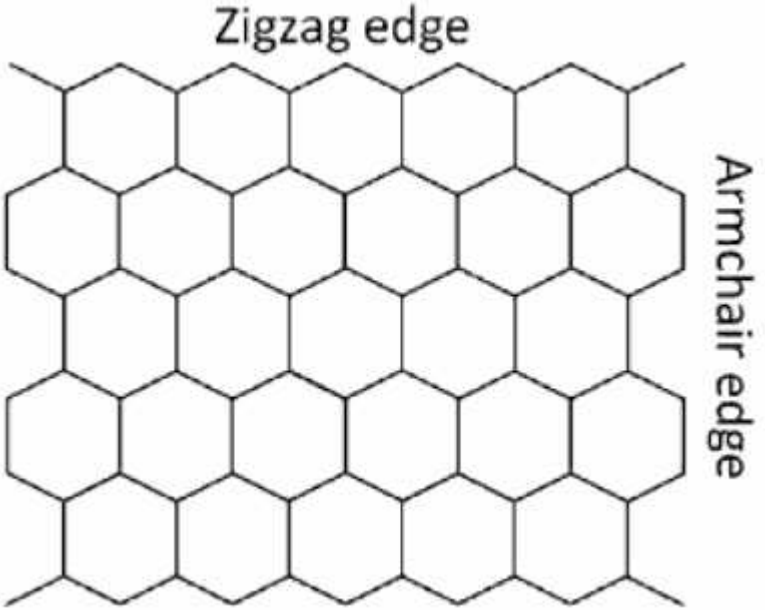
Summary: low energy limit

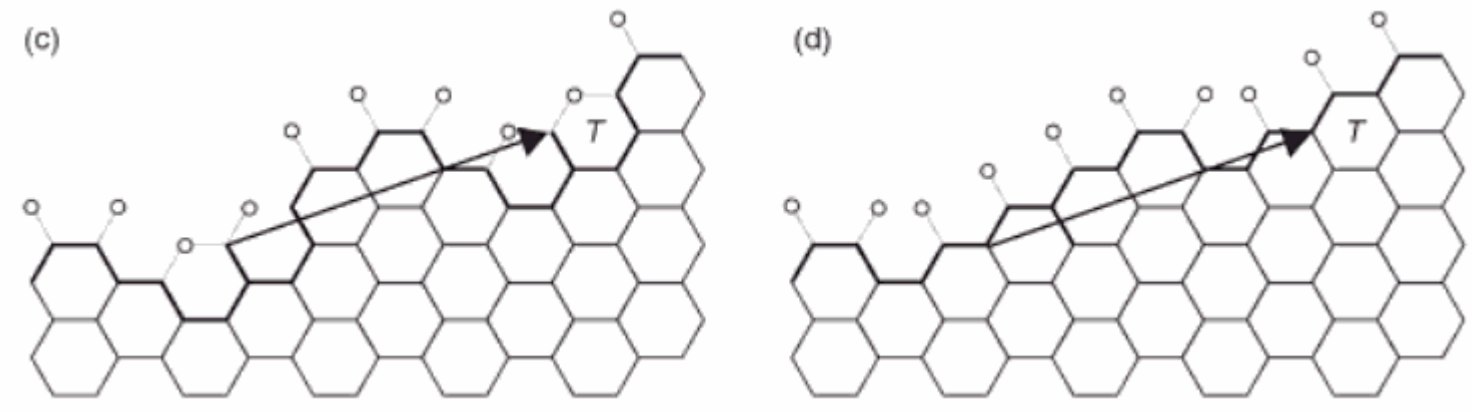
- General solution for wave function consists of 4 terms

$$\psi_{K,K'}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R_A}}^{N} c_A \, e^{i\vec{K}\vec{R_A}} \chi(\vec{r} - \vec{R_A}) - \frac{1}{\sqrt{N}} \sum_{\vec{R_A}}^{N} c'_A \, e^{i\vec{K'}\vec{R_A}} \chi(\vec{r} - \vec{R_A})$$
$$+ \frac{1}{\sqrt{N}} \sum_{\vec{R_B}}^{N} c_B \, e^{i\vec{K}\vec{R_B}} \chi(\vec{r} - \vec{R_B}) - \frac{1}{\sqrt{N}} \sum_{\vec{R_B}}^{N} c'_B \, e^{i\vec{K'}\vec{R_B}} \chi(\vec{r} - \vec{R_B})$$

Graphene nanoribbons

- different shape of ribbons:
  - armchair
  - zigzag
  - arbitrary

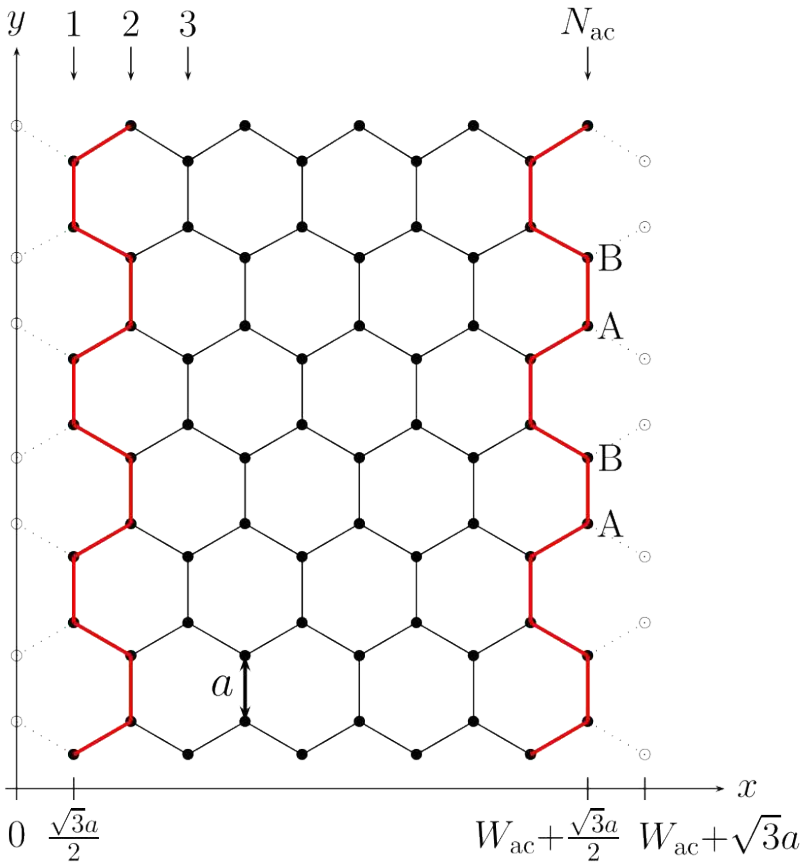


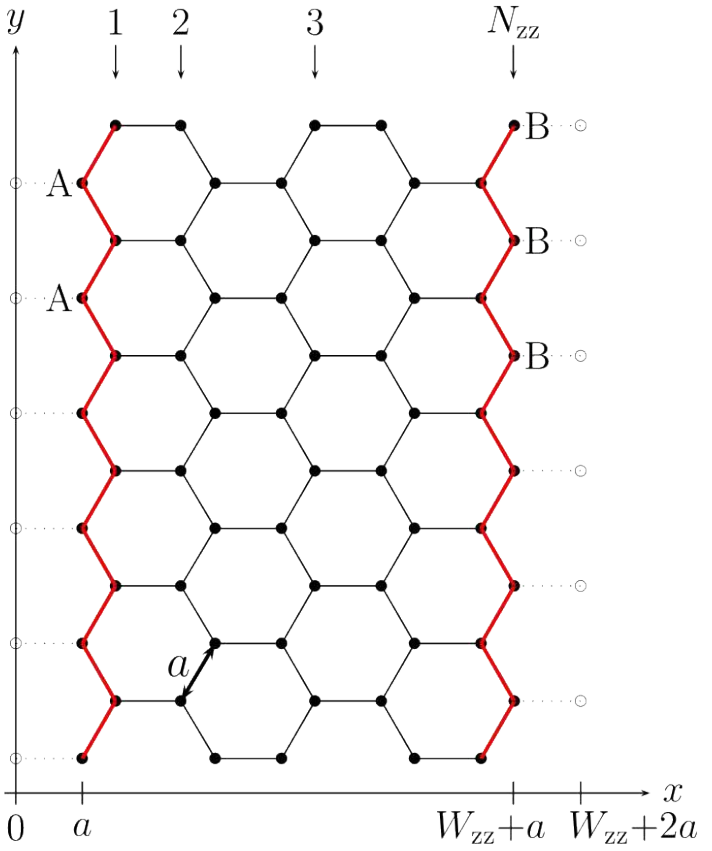


M.I. Katnelson, Graphene Carbon in Two Dimensions, 2012

Armchair & ZigZag boundary conditions

- infinite dimension in y, but finite in x-direction
- Wavefunction must vanish at the atom sites next to the edges

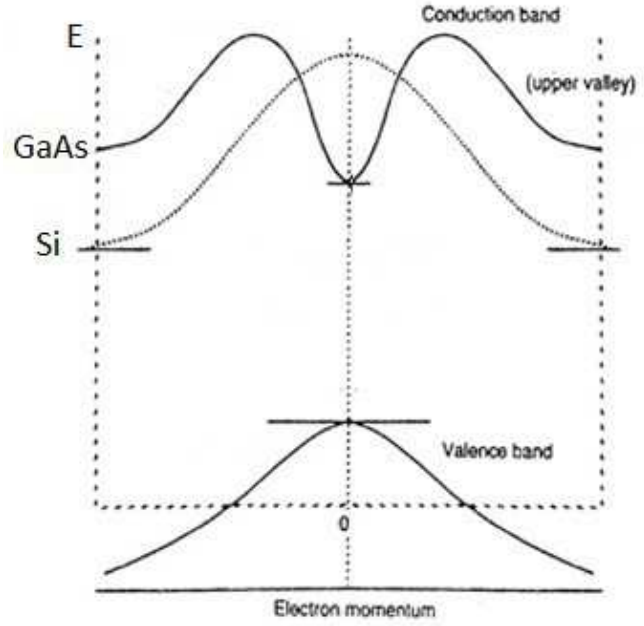


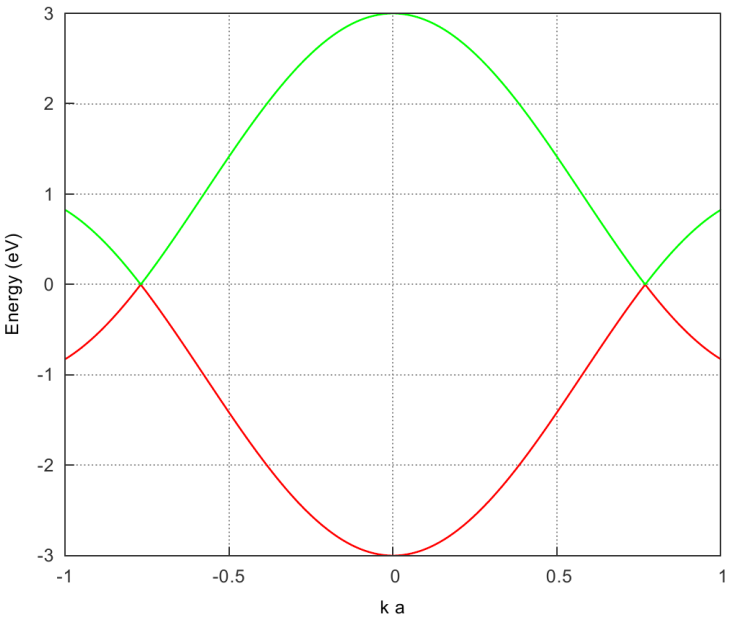


P. Dietl, Diplomarbeit, KIT, 2009

Valley mixing

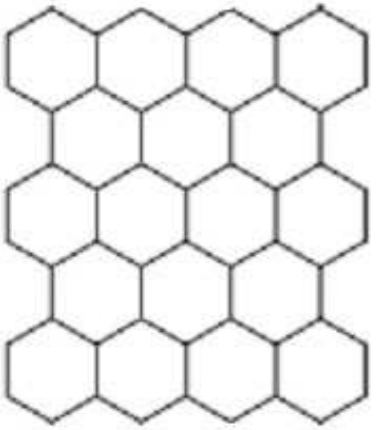
- If you have a potential well and a band structure, you need to combine 2 states of the same energies with different k-vectors $e^{-ik_x x} \pm e^{ik_x x}$ to create $\sin$ or $\cos$ - functions, that fulfill the boundary conditions
- These 2 states can be in a single valley – like in the case of GaAs with a direct band gap or in different valleys like in Si or graphene $\Rightarrow$ valley mixing

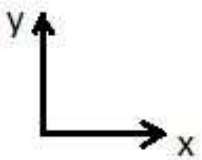


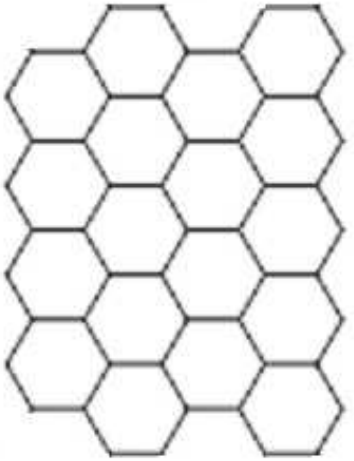


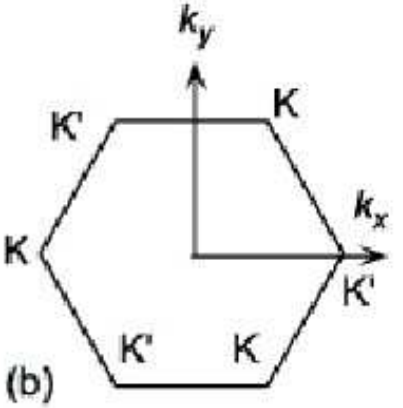
Valley mixing in GNRs

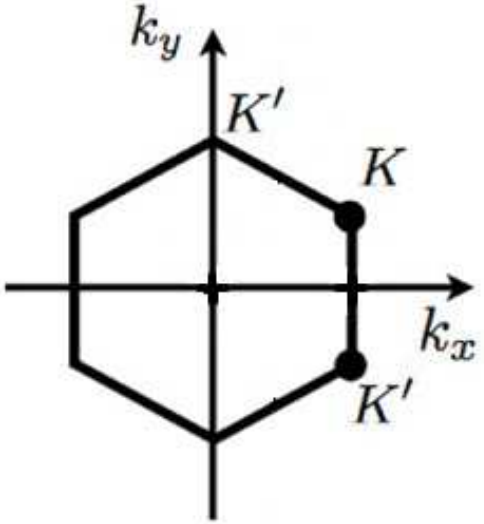
- Valley mixing is different in armchair and zigzag
- The structure is rotated by 30° and so the Brillouin zone
- Armchair: to create a sin(x) or cos(x), both valleys are needed. They are coupled
- Zigzag: a cone lies symmetric around $k_x = 0$. 2 states from same valley $\Rightarrow$ no coupling between K & K'











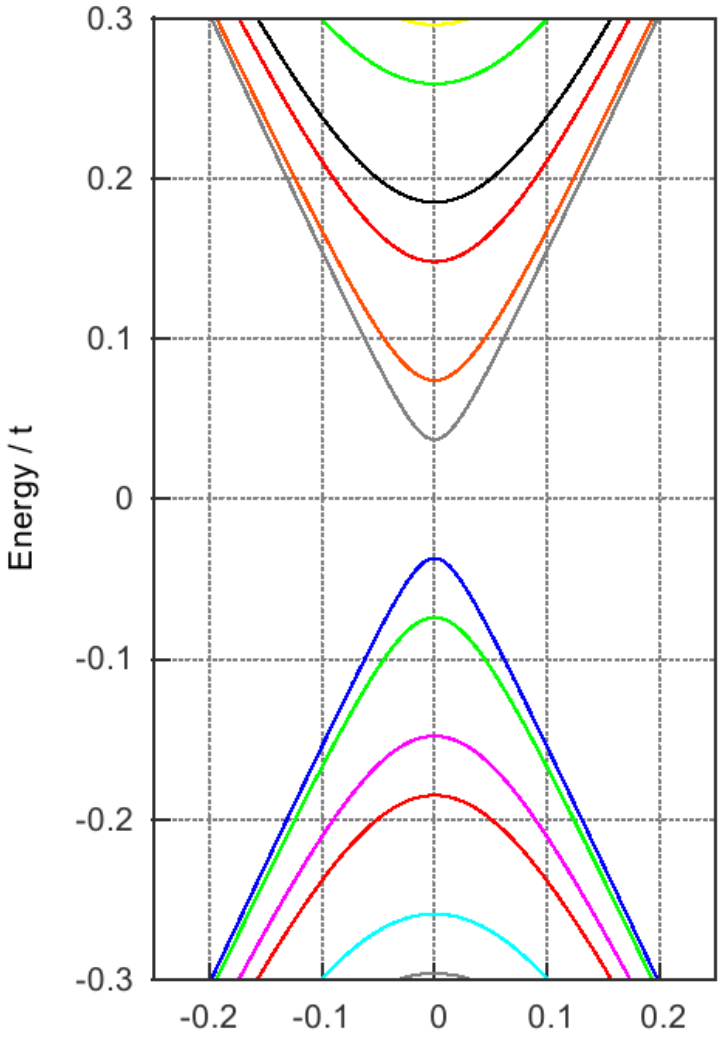
Armchair ribbon

- Calculation of dispersion relation by Dirac-Hamiltonian in low energy limit
- … blackboard …

$$E = \pm\sqrt{\left(\frac{\pi n}{N_{ac}/2+1} + \frac{2\pi}{3}\right)^2 + \left(k_y\sqrt{3}a\right)^2}\,\frac{\sqrt{3}}{2}t$$

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

- if $N_{ac} = 3\,m - 1$: no bandgap

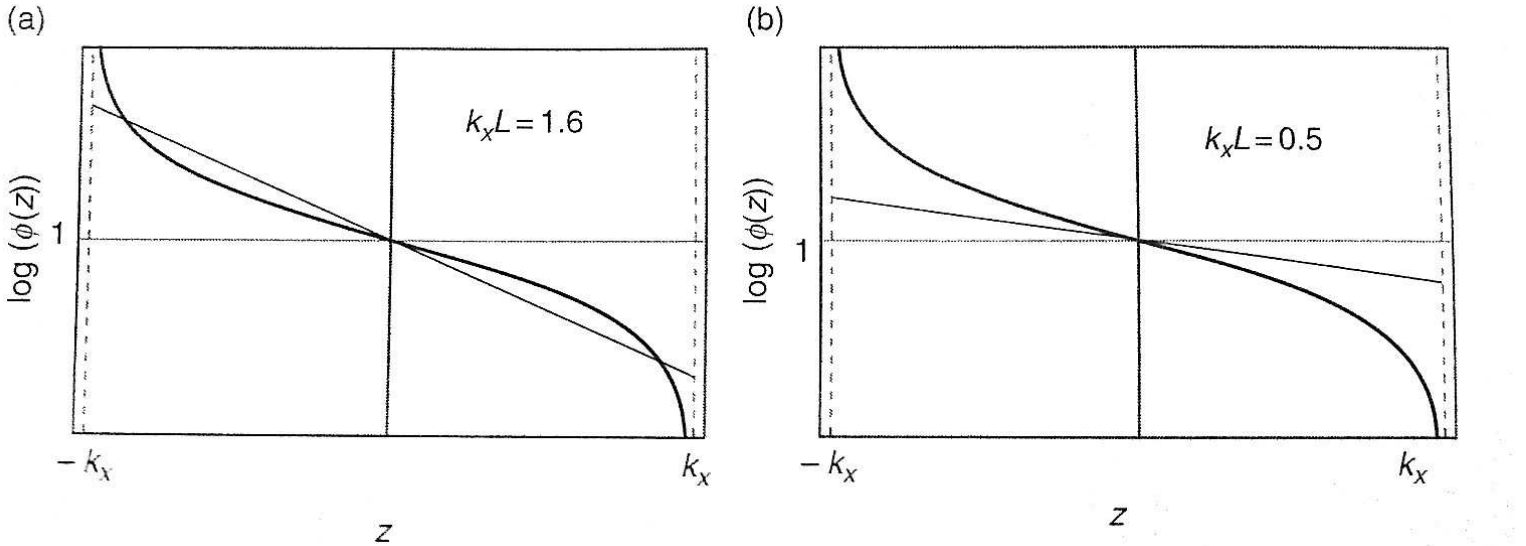


Zigzag ribbon

- Dirac Hamiltonian changes because of the rotation of the Brillouin zone, $q_x \to -q_y$ and $q_y \to q_x$.

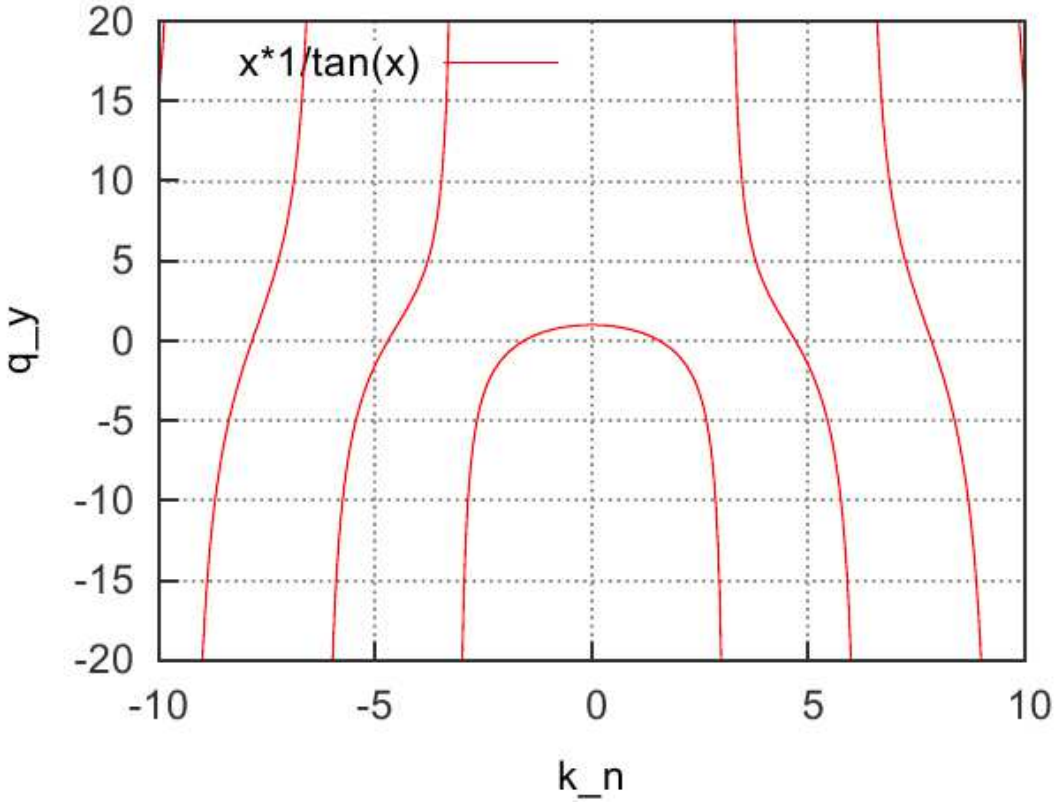
$$-\hbar v_f \begin{pmatrix} 0 & q_y + \partial_x & 0 & 0 \\ q_y - \partial_x & 0 & 0 & 0 \\ 0 & 0 & 0 & -q_y + \partial_x \\ 0 & 0 & -q_y - \partial_x & 0 \end{pmatrix} \begin{pmatrix} c_A \\ c_B \\ c'_A \\ c'_B \end{pmatrix} = E \begin{pmatrix} c_A \\ c_B \\ c'_A \\ c'_B \end{pmatrix}$$

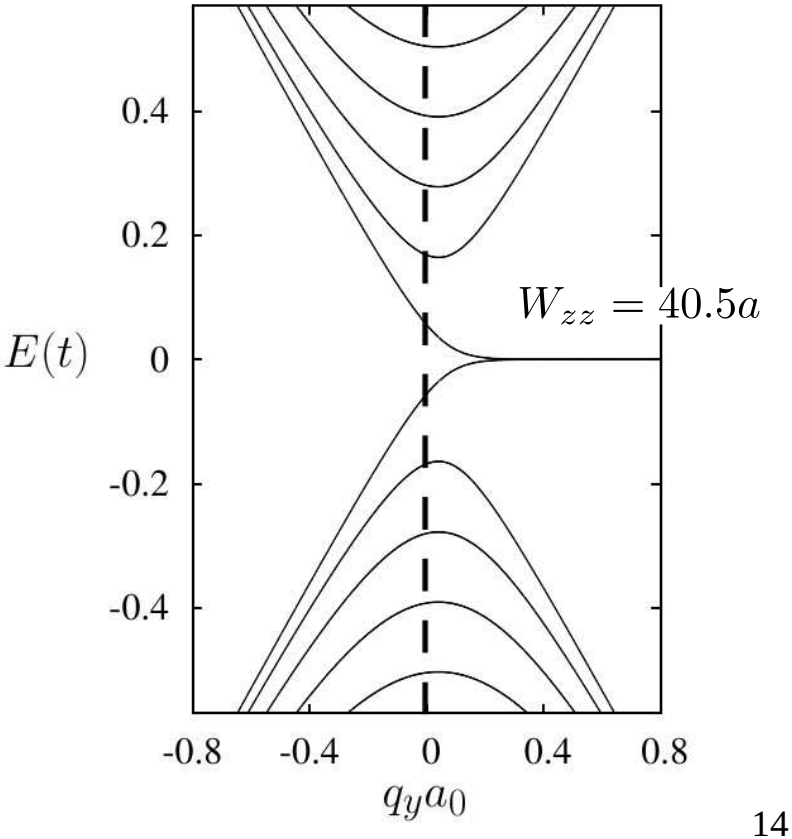
- Graphical solution of $\frac{q_y - z}{q_y + z} = e^{-2z(W_{zz}+2a)}$



Zigzag ribbon

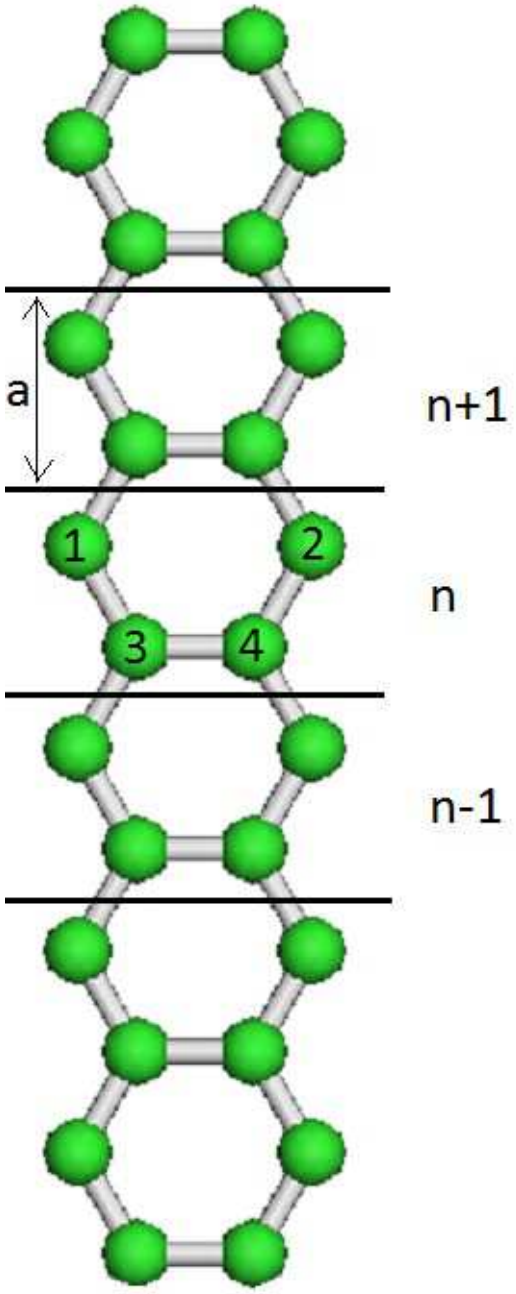
- Solving the expression $q_y = \frac{k_n}{\tan(k_n(W_{zz}+2a)}$
- “choose” a value for q_y , find discrete values for k_n
- Plot the energy: $\epsilon = \pm\sqrt{q_y^2 + k_n^2}$





P. Dietl, Diplomarbeit, KIT, 2009

Zigzag – full electronic structure



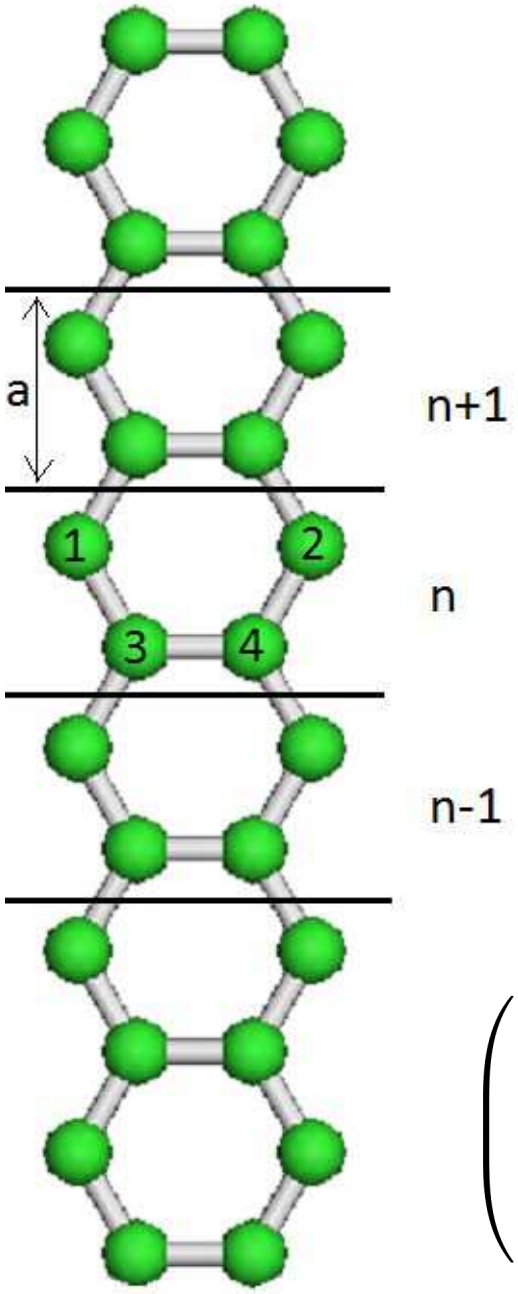
- Treat ribbon as a 1D chain
- Unit cells are repeated
- Tight binding model for a chain:

$$H_{n,n}\Phi_n + H_{n,n-1}\Phi_{n-1} + H_{n,n+1}\Phi_{n+1} = E\Phi_n$$

- Using Bloch's Theorem $\Phi_n = e^{i\,k\,n\,a}\,\Phi_0$

$$(e^{-ika}H_{n,n-1} + H_{n,n} + e^{ika}H_{n,n+1})\Phi_0 = E\Phi_0$$

Zigzag – full electronic structure



- Nearest neighbor coupling with hopping parameter t

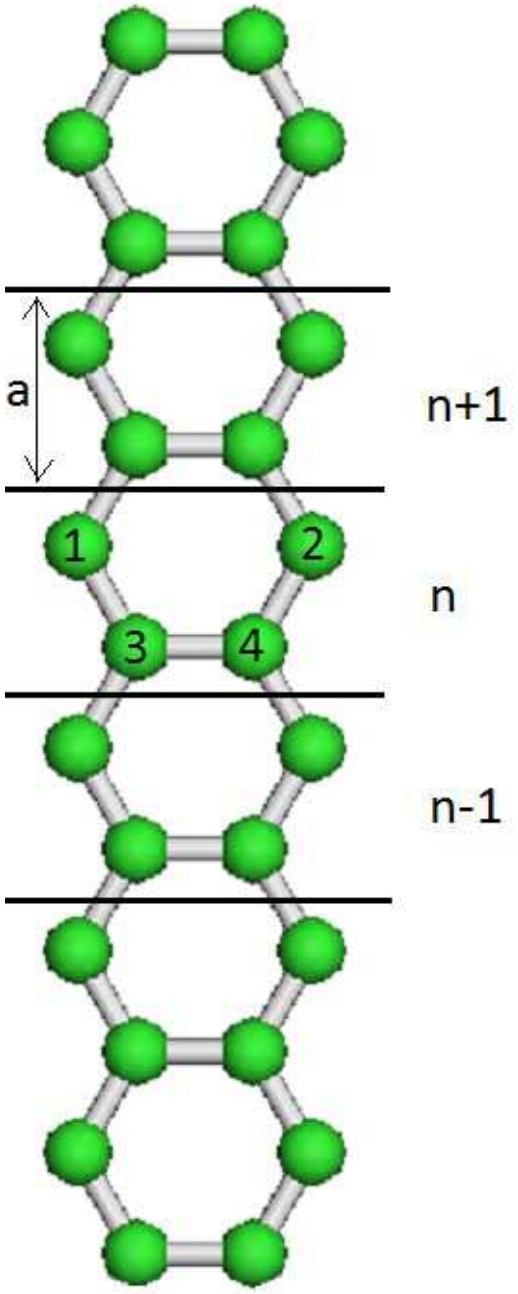
$$H_{n,n} = \begin{pmatrix} 0 & 0 & t & 0 \\ 0 & 0 & 0 & t \\ t & 0 & 0 & t \\ 0 & t & t & 0 \end{pmatrix}, \quad H_{n,n+1} = \begin{pmatrix} 0 & 0 & t & 0 \\ 0 & 0 & 0 & t \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

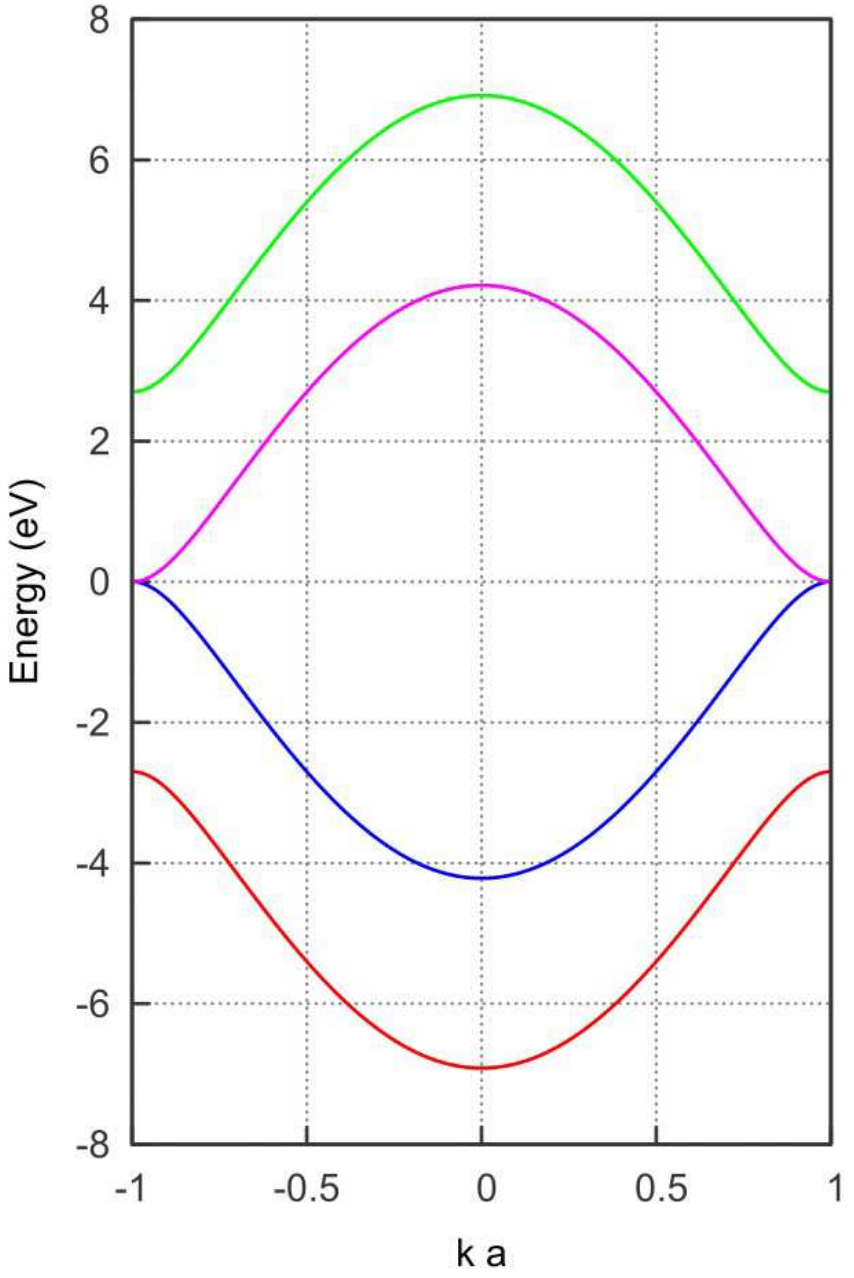
$$H_{n,n-1} = (H_{n,n+1})^{\dagger}$$

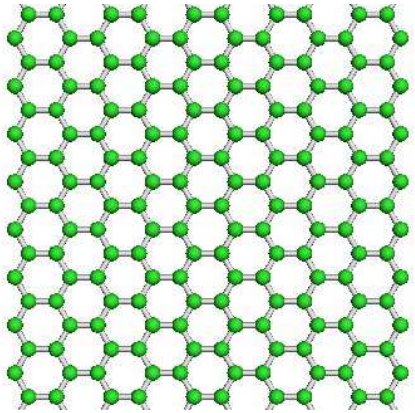
- Obtain energies by Eigenvalues of

$$\begin{pmatrix} 0 & 0 & -t\left(1+e^{i\,a\,k}\right) & 0 \\ 0 & 0 & 0 & -t\left(1+e^{i\,a\,k}\right) \\ -t\left(1+e^{-i\,a\,k}\right) & 0 & 0 & -t \\ 0 & -t\left(1+e^{-i\,a\,k}\right) & -t & 0 \end{pmatrix}$$

Zigzag – full electronic structure

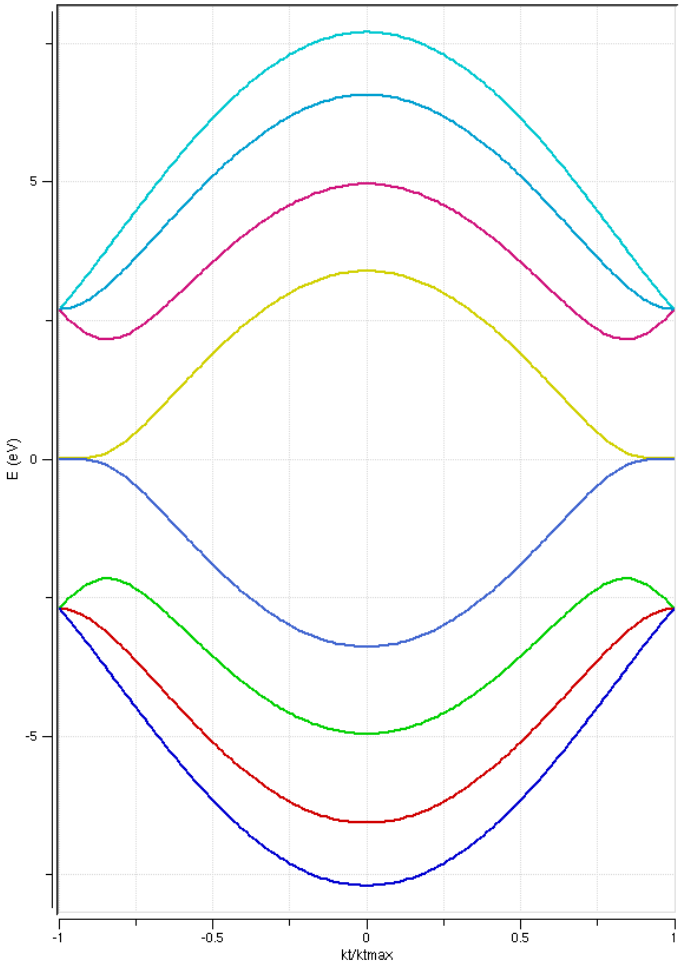




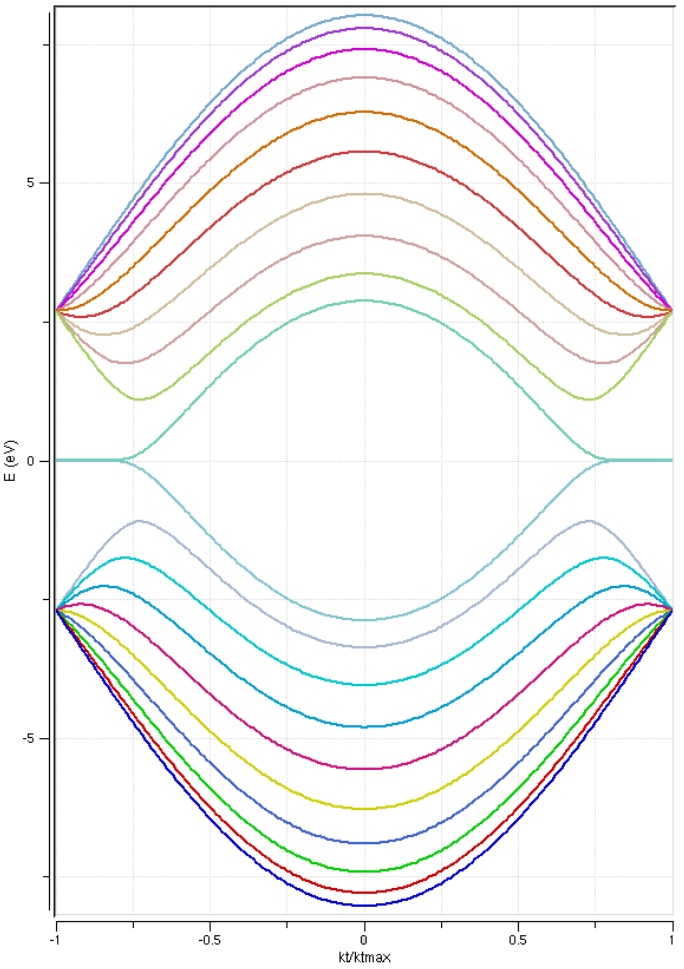


Zigzag – full electronic structure

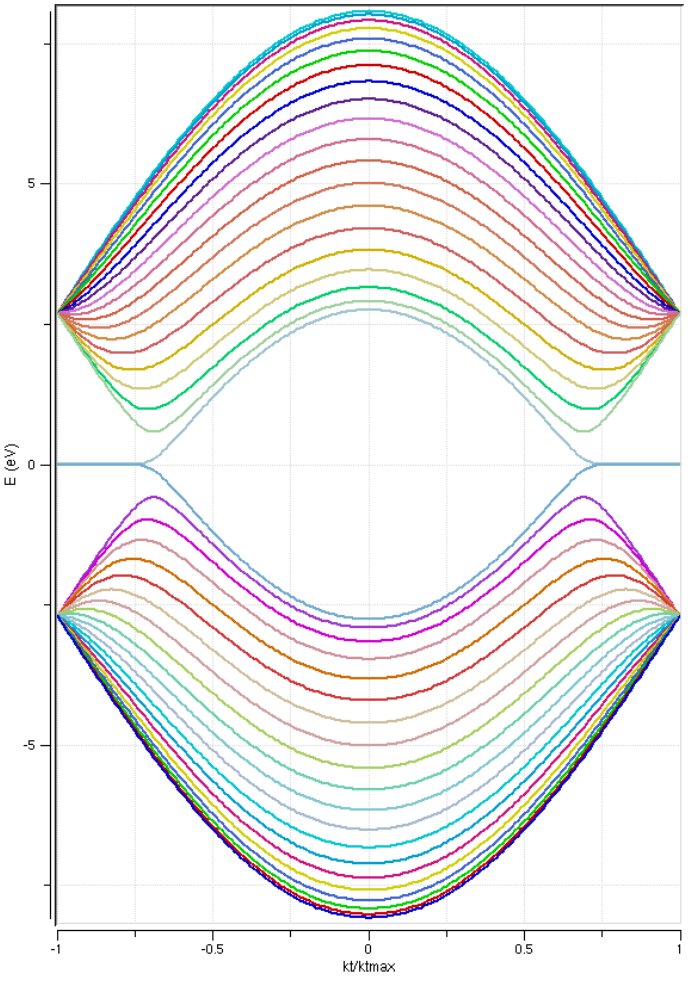
- For wider ribbons the dispersionless states appear



$N = 8$

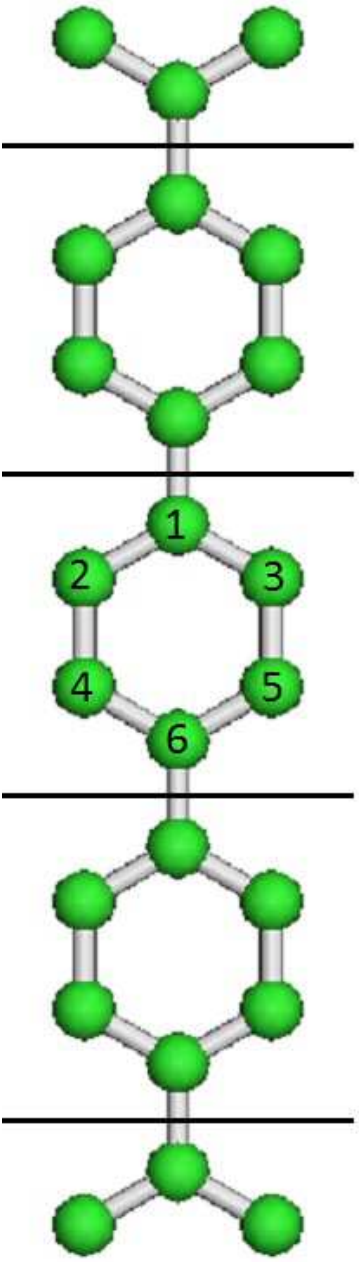


$N = 20$

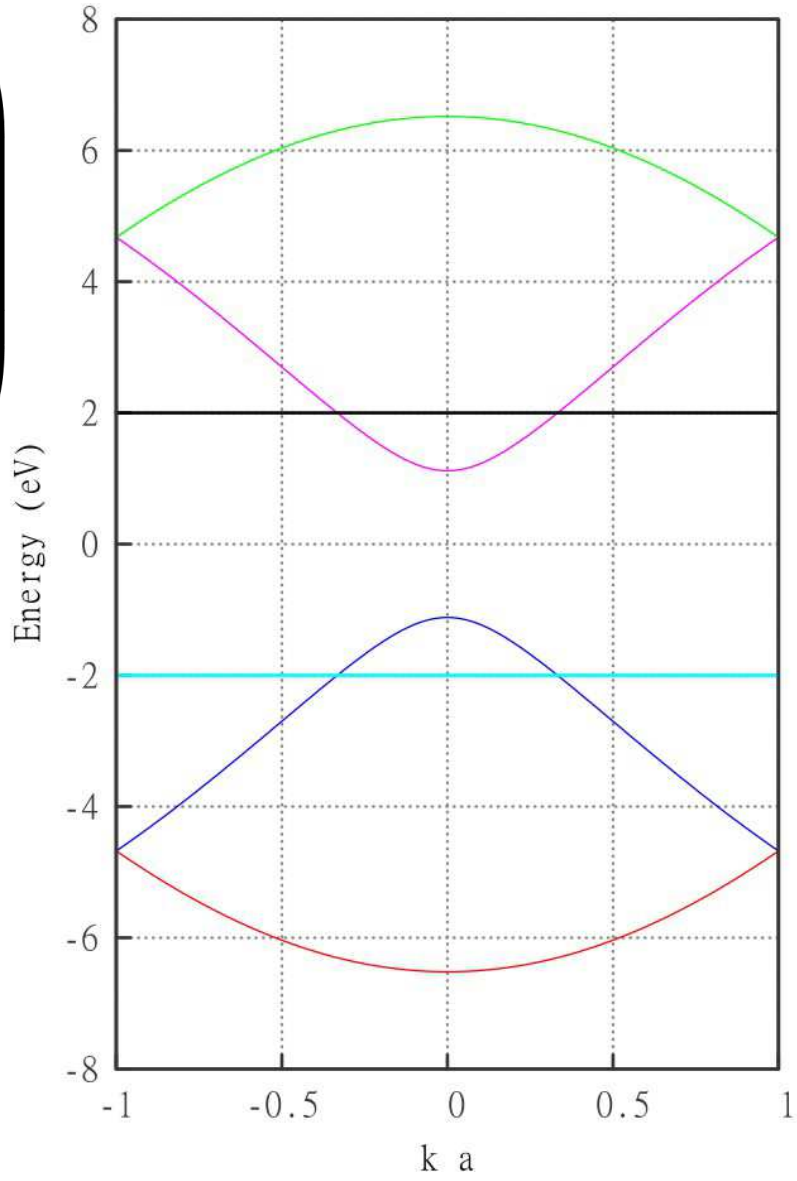


$N = 40$

Armchair – full electronic structure

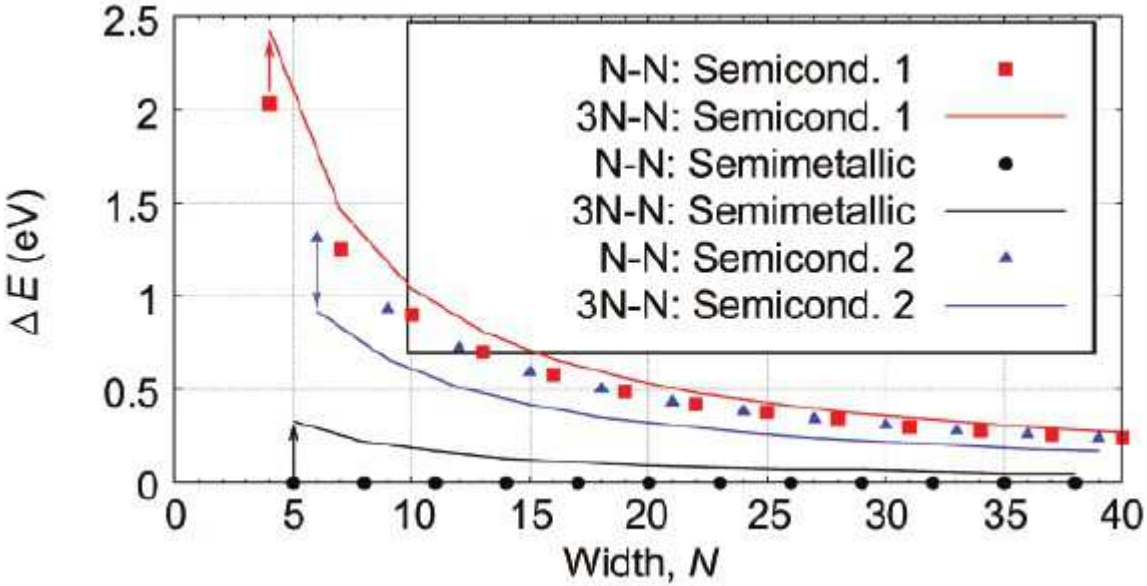


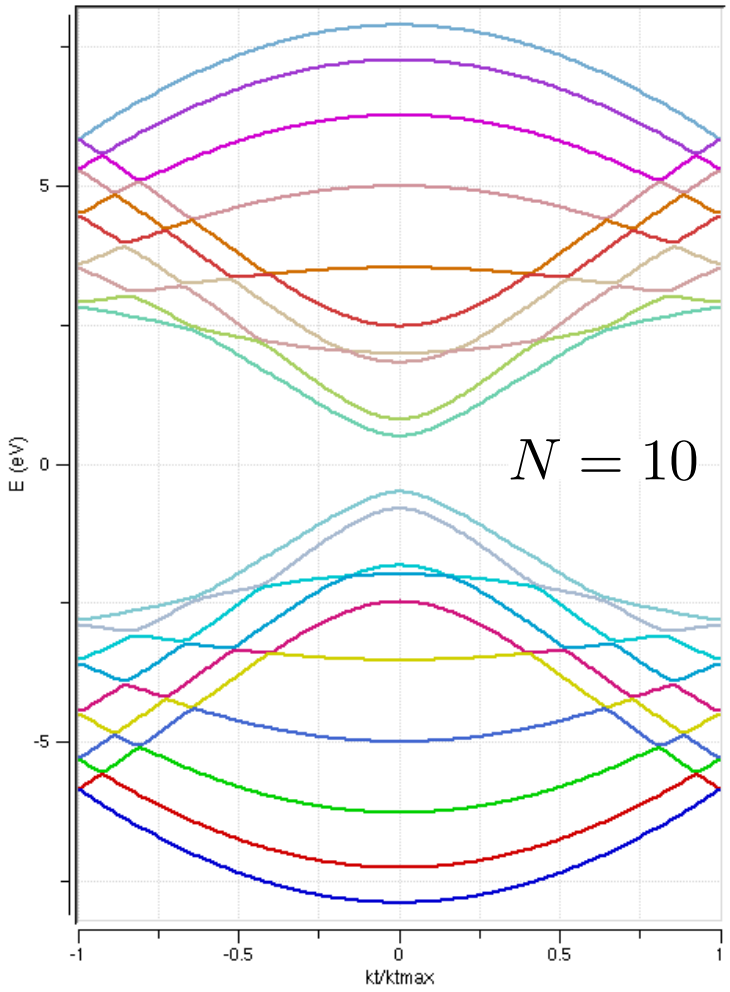
$$-\begin{pmatrix} 0 & t & t & 0 & 0 & t\,e^{ika} \\ t & 0 & 0 & t & 0 & 0 \\ t & 0 & 0 & 0 & t & 0 \\ 0 & t & 0 & 0 & 0 & t \\ 0 & 0 & t & 0 & 0 & t \\ t\,e^{-ika} & 0 & 0 & t & t & 0 \end{pmatrix}$$

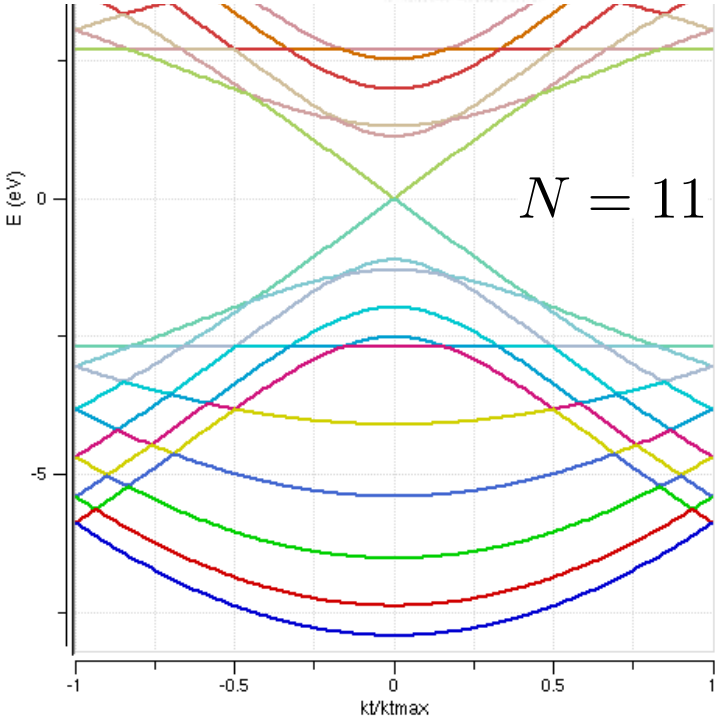


Armchair – full electronic structure

A. Cresit et. al., Nano Res (2008)







- Low energy approximation just reasonable for wide ribbons

Zigzag – edge states

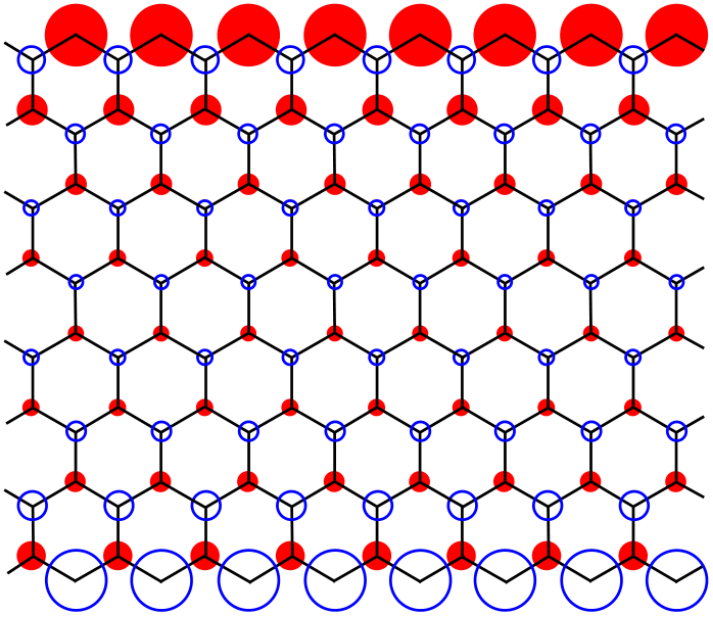
- TB model does not include spins / magnetism

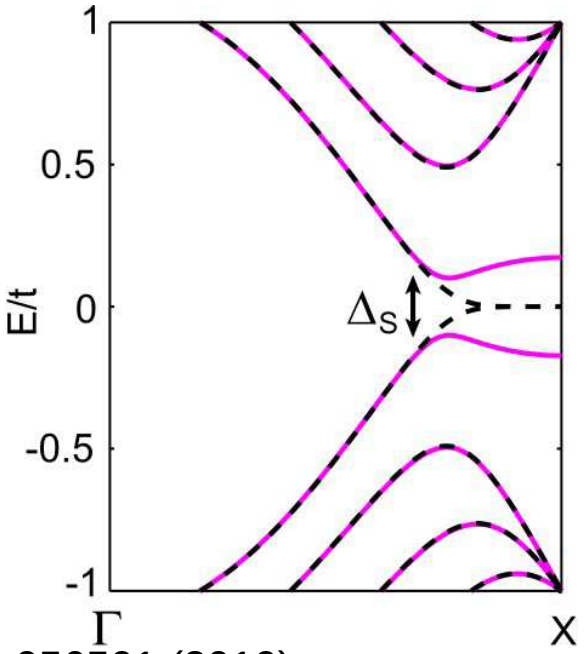
$\Rightarrow$ adding a electron-electron interaction term to the Hamiltonian

Hubbard-model: $H = H_{TB} + H', \quad H' = U \sum_i n_{i\uparrow} n_{i\downarrow}$

- Mean field approximation:

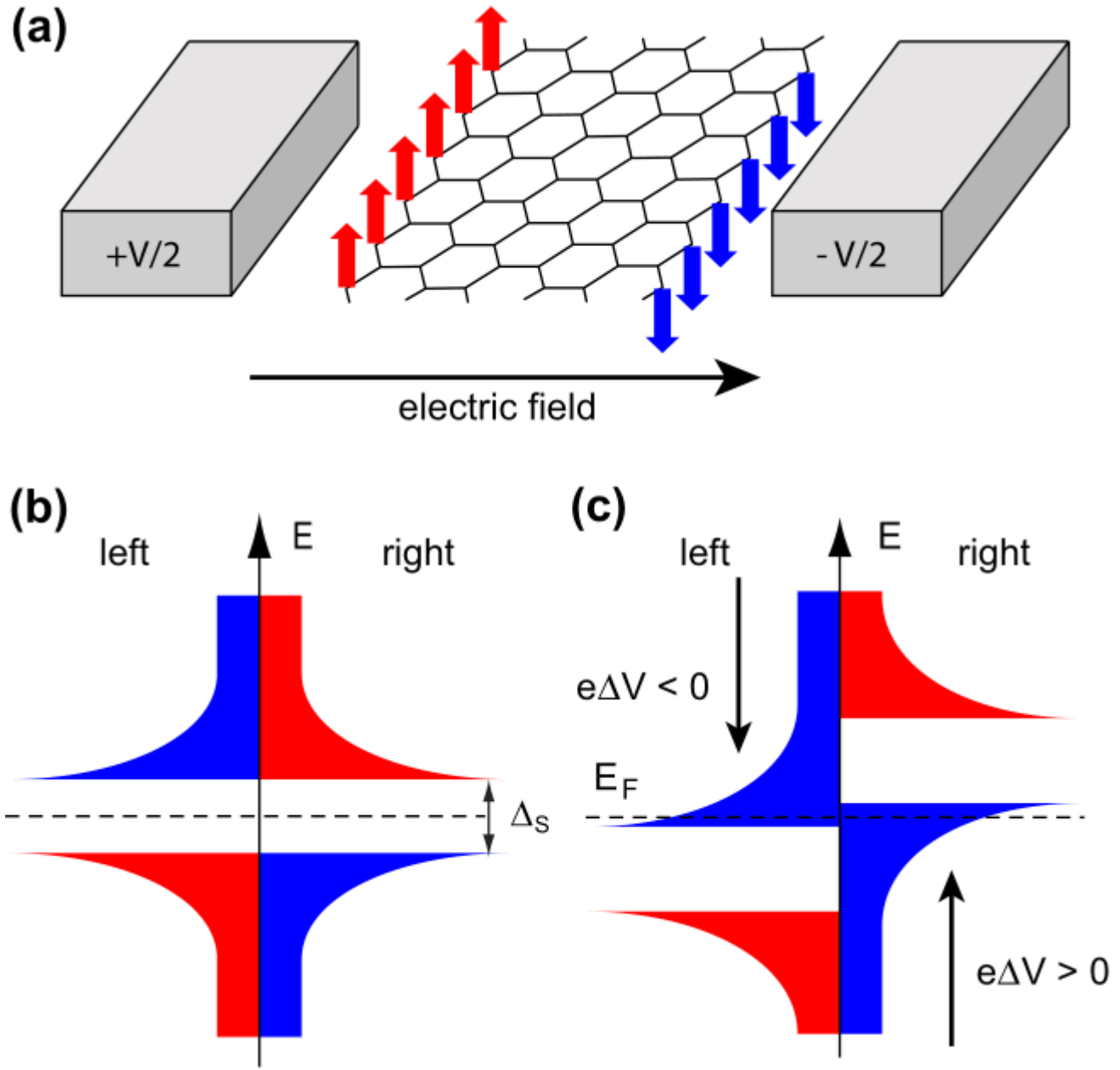
$$H'_{\mathrm{mf}} = U \sum_i \left(n_{i\uparrow} \langle n_{i\downarrow} \rangle + \langle n_{i\uparrow} \rangle n_{i\downarrow} + \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \right)$$





O. Yazyev, Rep. Prog. Phys. 73, 056501 (2010)

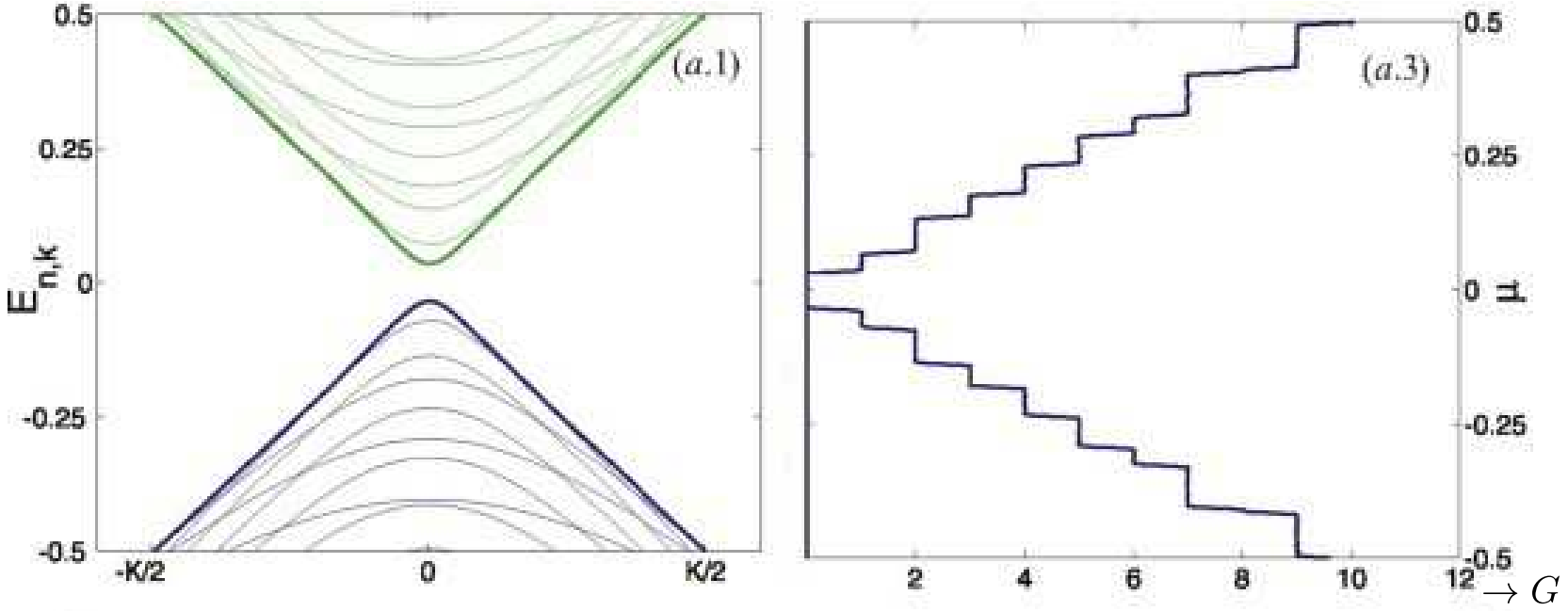
Zigzag – edge effects



O. Yazyev, Rep. Prog. Phys. 73, 056501 (2010)

Conductance quantization

- Landauer formula $G = \frac{2e^2}{h} \sum_n T_n$
- Assume ballistic transport, $T_n \approx 1$
  (holds for ribbons with smoothly varying $W(y)$)
- Conductance increases of additional $\frac{2e^2}{h}$ as soon as the energy reaches a new band



O. Roslyak et. al., Phys. Lett. A 374, 4061–4064 (2010)

Graphene quantum dots

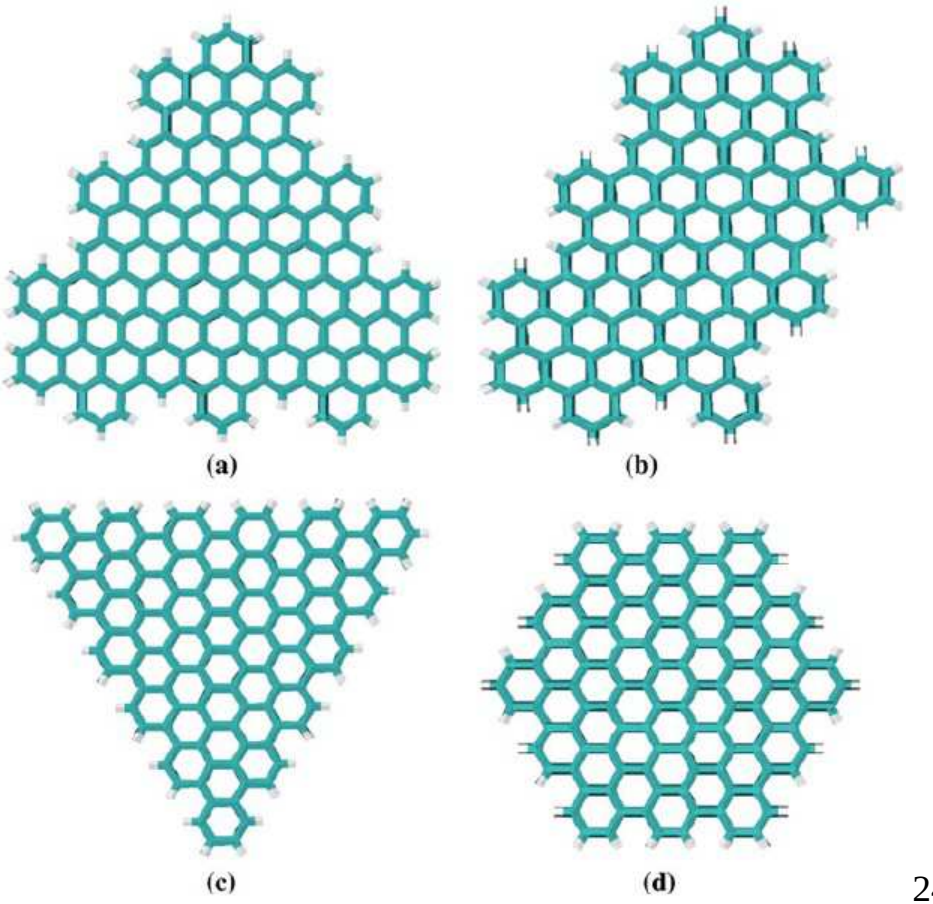
- Energy states can be calculated with TB method (Hückel method)

$\Rightarrow$ Hamiltonian $H_{n,n}$ of the chain before - without the neighbor unit cells

- Electrostatic effects lead to the Coulomb blockade

$$E_C(Q) = \frac{Q^2}{2C}$$

if e tunnels into the dot or vice versa Q is changed by $\pm e$



B. Mandal et. al., J Nanopart Res 14, 1317 (2012)

Conclusion

- There are armchair and zigzag ribbons showing a different behavior due to different BCs and corresponding valley mixing
- If the ribbons width is not too narrow, Dirac equation gives a good band structure (for low energies)
- Zigzag edges show a spin polarization which could be used for spin polarized transport
- The transmission probability for each channel is ≈ 1
  Each band adds a G_0 once its energy is reached
- Quantum dots show coulomb blockade
  single electron transistor possible

References

- Petra Dietl, *Numerical Studies of Electronic Transport through Graphene Nanoribbons with Disorder,* Diploma Thesis, KIT, 2009
- Branislav K. Nikolić, *Graphene Nanoribbons And Carbon Nanotubes,* University of Delaware, 2012
- Mikhail I. Katsnelson, *Graphene Carbon in two Dimensions,* University Press Cambridge, 2012
- Oleg V. Yazyev, *Emergence of magnetism in graphene materials and nanostructures,* Rep. Prog. Phys. 73, 056501 (2010)
- B. Mandal, *Exploring the electronic structure of graphene quantum dots,* J Nanopart Res. 14, 1317 (2012)

1 Band structure calculation of GNRs with Dirac equation

1.1 Armchair ribbon

We start with Dirac equation obtained by low energy approximation of the band structure of infinite expanded graphene.
As q_y is not restricted we can use plane waves as a solution. This part of the solution can be seperated $c^{(')}_{A,B} = e^{iq_y y}\varphi^{(')}_{A,B}$ For the solution in real space we therefore just need to replace $q_x = -i\partial_x$. Applying this to the Dirac equation one yields
Applying the Dirac Equation on yields

$$\begin{aligned}(-i\partial_x + iq_y)\,\varphi_A &= \epsilon\varphi_B \\ -(i\partial_x + iq_y)\,\varphi_B &= \epsilon\varphi_A\end{aligned} \tag{1}$$

where $\epsilon = \frac{E}{\hbar v_F}$
Putting the second in the first equation (or vice versa) the following differential equation of second order is obtained

$$\left(-\partial_x^2 + q_y^2\right)\varphi^{(')}_{A,B} = \epsilon^2\varphi^{(')}_{A,B} \tag{2}$$

We try to solve it with the Ansatz:

$$\varphi_B(x) = e^{ik_n x}, \qquad \varphi_B^{'}(x) = e^{-ik_n x} \tag{3}$$

And we find the energy to be $\epsilon = \pm\sqrt{k_n^2 + q_y^2}$ as one would expect. But what are the allowed values for k_n ?
We need to consider the boundary conditions, which are - according to the figure on slide 9 - the following:

$$\Psi_{K,K'}(R_A)|_{x=0} = 0 \qquad \Psi_{K,K'}(R_B)|_{x=0} = 0 \tag{4}$$

$$\Psi_{K,K'}(R_A)|_{x=W_{ac}+\sqrt{3}a} = 0 \qquad \Psi_{K,K'}(R_B)|_{x=W_{ac}+\sqrt{3}a} = 0 \tag{5}$$

where Ψ is the most general solution consisting of four terms, as mentioned before.
By using the propertiers of the Wannier function that $\chi(R_A - R_A) = 1$ and $\chi(R_A - R_B) = 0$, we obtain

$$\varphi_{A,B}(x=0) = \varphi^{'}_{A,B}(x=0) \tag{6}$$

$$\varphi_{A,B}(x = W_{ac} + \sqrt{3}a) = e^{-\Delta K(W_{ac}+\sqrt{3}a)}\varphi^{'}_{A,B}(x = W_{ac} + \sqrt{3}a) \tag{7}$$

with ΔK the distance between K and $K^{'}$. By insert the Ansatz (Eq.(12)) we find the possible values of k_n

$$k_n = \frac{\pi n}{W_{ac} + \sqrt{3}a} + \frac{2\pi}{3\sqrt{3}a} \tag{8}$$

Now we can find an expression for the energy depending on q_y and therefore the band structure of the armchair ribbon:

$$E = \pm\sqrt{\left(\frac{\pi n}{N_{ac}/2 + 1} + \frac{2\pi}{3}\right)^2 + \left(k_y\sqrt{3}a\right)^2}\frac{\sqrt{3}}{2}t \tag{9}$$

where W_{ac} was replaced by $W_{ac} = (N_{ac} - 1)\frac{\sqrt{3}a}{2}$. As q_y is 0 in the case of the armchair ribbon it can be replaced by k_y to make it clear that it starts from the middle of the Brillouin zone.

1.2 Zigzag ribbon

As the Brillouin zone is rotated in this case we need to replace q_x by $-q_y$ and q_y by q_x. The infinite direction still remains in y-direction, where we again use plane waves.

$$-\hbar\, v_f \begin{pmatrix} 0 & q_y + \partial_x & 0 & 0 \\ q_y - \partial_x & 0 & 0 & 0 \\ 0 & 0 & 0 & -q_y + \partial_x \\ 0 & 0 & -q_y - \partial_x & 0 \end{pmatrix} \begin{pmatrix} c_A \\ c_B \\ c'_A \\ c'_B \end{pmatrix} = E \begin{pmatrix} c_A \\ c_B \\ c'_A \\ c'_B \end{pmatrix} \tag{10}$$

We get the equations

$$(-\partial_x + q_y)\varphi_A = \epsilon\varphi_B \tag{11}$$
$$(\partial_x - q_y)\varphi_B = \epsilon\varphi_A \tag{12}$$

we obtain the same differential as before in Eq. (2). As we have no valley mixing we need to make a more general Ansatz. For sublattice A and the K valley it is of the form

$$\varphi_A = \alpha e^{zx} + \beta e^{-zx} \tag{13}$$

and $z = \sqrt{q_y^2 - \epsilon^2}$ can be real or imaginary.
For the B sublattice we find

$$\varphi_B(x) = \frac{\alpha}{\epsilon}(z - q_y)e^{zx} - \frac{\beta}{\epsilon}(z + q_y)e^{-zx} \tag{14}$$

With the boundary conditions

$$\Psi(R_A)|_{x=0} = 0 \qquad \Psi(R_B)|_{x=W_{zz}+2a} = 0 \tag{15}$$

we get

$$\varphi_A(x = 0) = \varphi_A^{'}(x = 0) = 0 \tag{16}$$
$$\varphi_B(x = W_{zz} + 2a) = \varphi_B^{'}(x = W_{zz} + 2a) = 0 \tag{17}$$

By inserting the Ansatz (24) & (25) into (27) & (28) we obtain a transcendental equation

$$\frac{q_y - z}{q_y + z} = e^{-2z(W_{zz}+2a)} \tag{18}$$

Graphical solution yield that there are nontrivial real solution just for $q_y > \frac{1}{W_{zz}+2a}$. For these values a almost flat band is obtained - the so called dispersionless states which corresponds to the edge states. If $q_y < \frac{1}{W_{zz}+2a}$ a solution can be found for imaginary $z = ik_n$. In this case equation (18) can be transformed into

$$q_y = \frac{k_n}{\tan(k_n(W_{zz} + 2a)} \qquad \text{with } \epsilon = \pm\sqrt{q_y^2 + k_n^2} \tag{19}$$