Topological Solitons in Doped Zigzag Graphene Nanoribbons.

M. Pilar López-Sancho and Luis Brey
Instituto de Ciencia de Materiales de Madrid-CSIC

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CSIC

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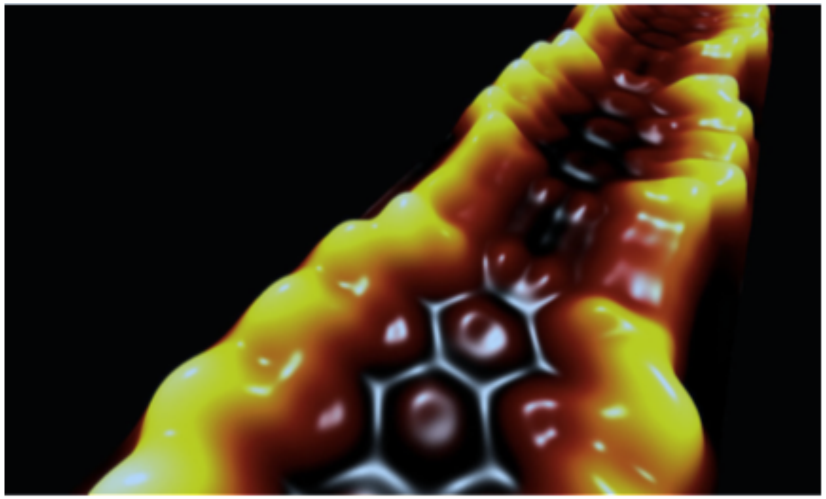
Graphene Nanoribbons

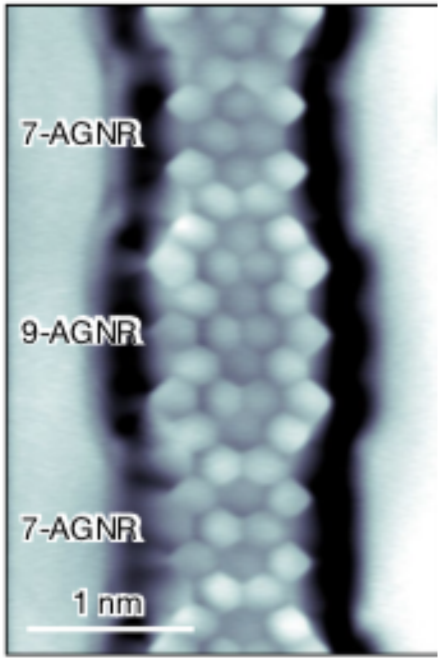
GNRs are narrow strips of graphene of finite width whose electronic behaviour is dominated by quantum confinement and presence of boundaries.
Synthesis tecniques allow atom precision control of their edge and width: tunable electronic properties.
Promising for nanoelectronics and other technologies



STM Image of a GNR superlattice
M. Crommie &F. Fischer

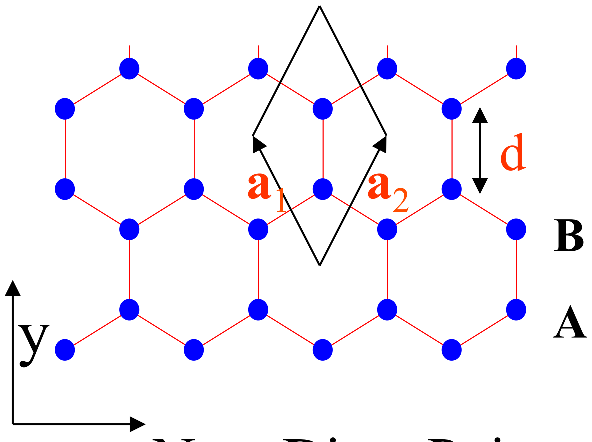
Cao, Zhao, Loui
PRL119,076401 (2017)

Nature (2018)



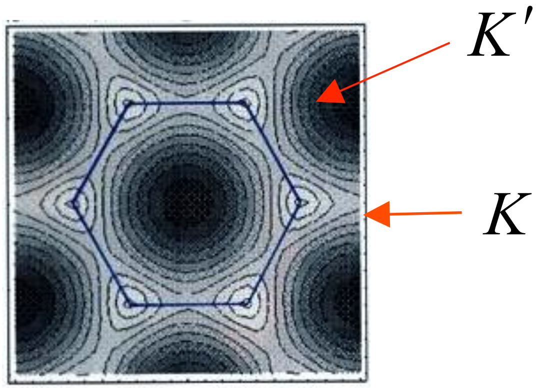
Graphene Band Structure

- For each k there are eigenvalues at $\pm|\varepsilon| \Rightarrow$ particle-hole symmetry
- Conduction and valence bands touch at two points, K and K’, in BZ



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

$$\vec{K} = \frac{2\pi}{a}\left(\frac{2}{3}, 0\right)$$

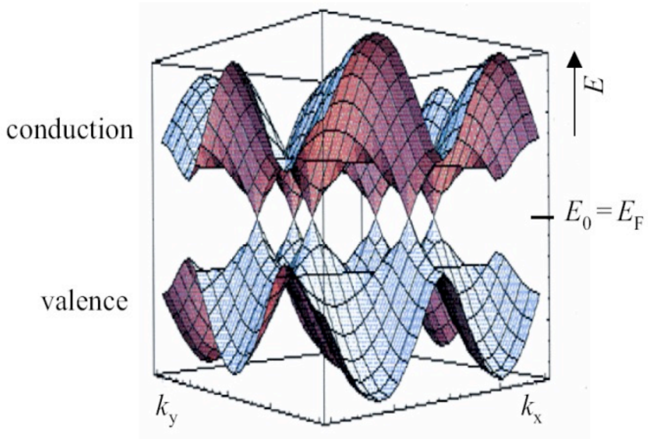


Two inequivalent *Dirac points* in Brillouin zone.

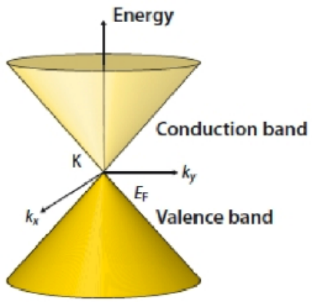
Near Dirac Points

Two valleys $\tau=\pm1$

$$\boxed{H_\tau = \hbar v_F \begin{pmatrix} 0 & k_x - i\tau k_y \\ k_x + i\tau k_y & 0 \end{pmatrix}}$$

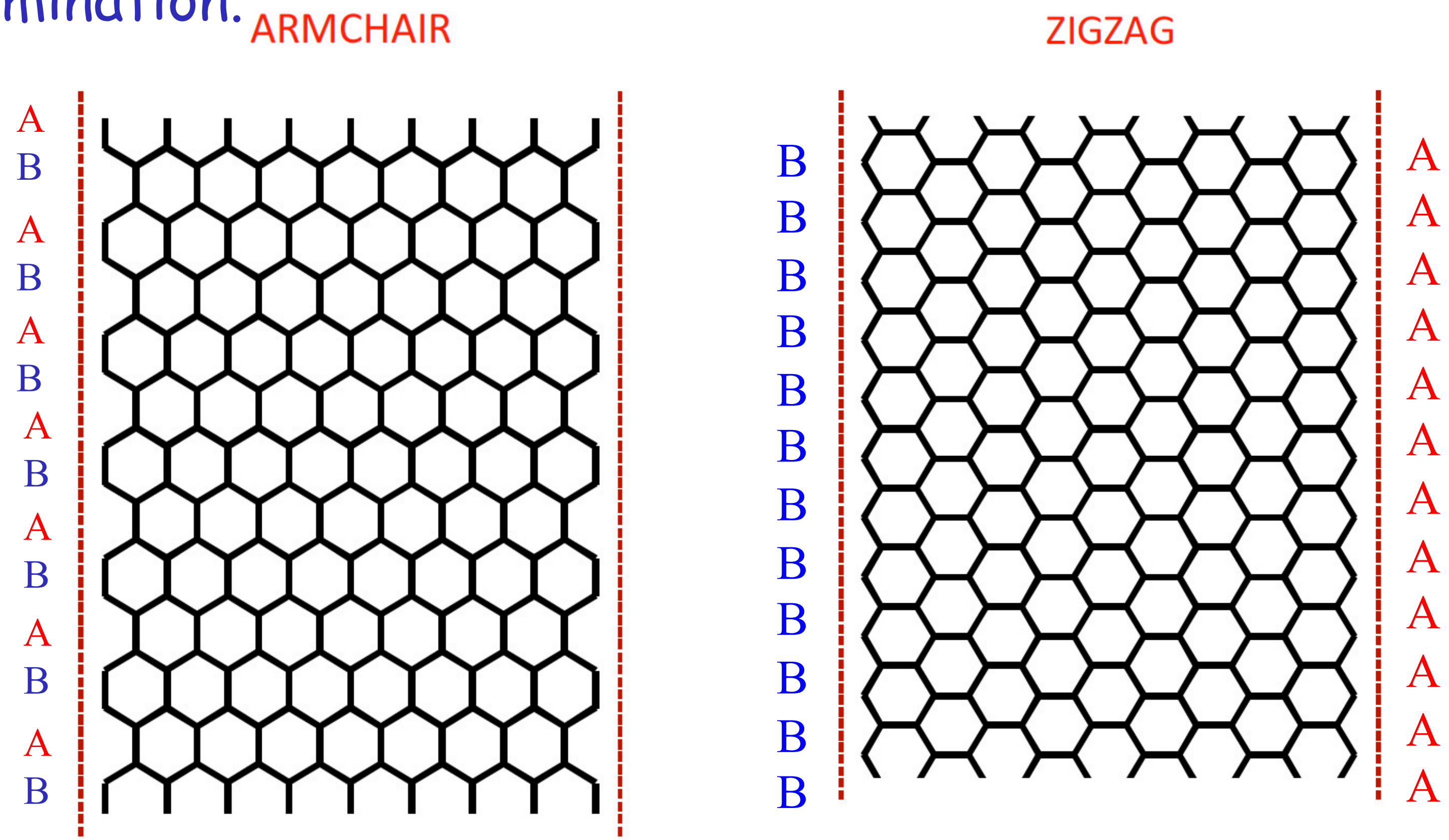


defined with respect the points **K** and **K**



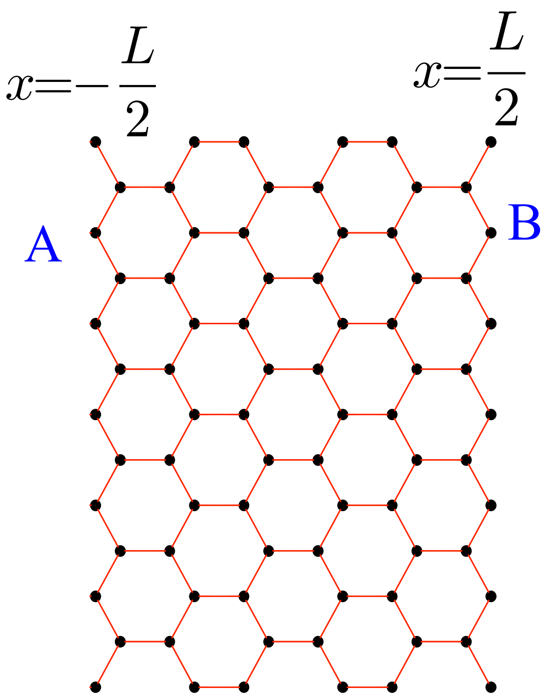
Graphene Nanoribbons. ZZGNR

- Potential connectors in graphene nanoelectronics.
- Fundamental properties.
- Because of the graphene honeycomb lattice, electrical and magnetic properties of GNR depend dramatically on atomic termination.



Electronic Structure ZZGNR

$$\bar{H}_\tau = \hbar v_F \begin{pmatrix} 0 & -i\partial_y + \tau\partial_x \\ -i\partial_y - \tau\partial_x & 0 \end{pmatrix} \qquad \psi(\mathbf{r}) = \begin{pmatrix} \phi_A(\mathbf{r}) \\ \phi_B(\mathbf{r}) \end{pmatrix}$$



Zigzgag termination have zero energy states localized at edges.

$$\phi_A\left(x = \frac{L}{2}\right) = 0$$

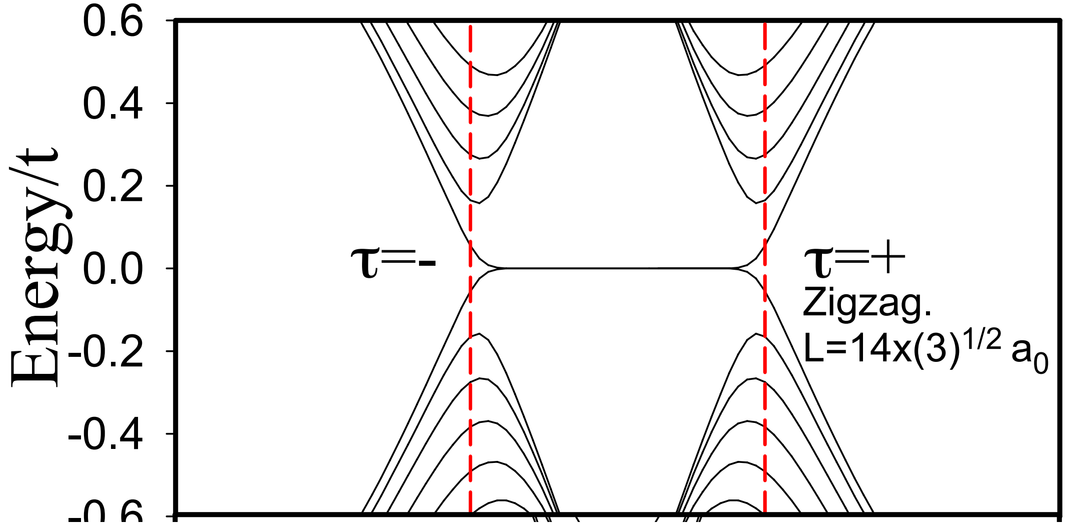
$$\phi_B\left(x = -\frac{L}{2}\right) = 0$$

$$\boxed{\begin{aligned} \psi_{\tau=+}(\mathbf{r}) &= \begin{pmatrix} 0 \\ e^{k_y\left(x-\frac{L}{2}\right)} \end{pmatrix} e^{-ik_y y} \\ \psi_{\tau=-}(\mathbf{r}) &= \begin{pmatrix} e^{-k_y\left(x+\frac{L}{2}\right)} \\ 0 \end{pmatrix} e^{ik_y y} \end{aligned}}$$

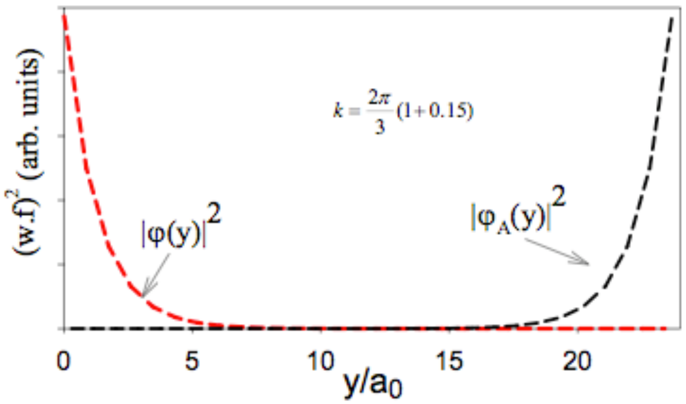
States localized in left edge, atoms A, valley τ=+1, momentum k_y>0
States localized in right edge, atoms B, valley τ =-1, momentum k_y<0
Atoms and valleys are coupled.

Atomistic Calculations

Tight-binding
DFT.



$$H = -t \sum_{<ij>,\sigma} c^{+}_{i,\sigma} c_{j,\sigma}$$



N.Nakada et al PRB (1996)
LB and H.A.Fertig PRB (2006)

Large density of states at the Fermi energy. The system could be unstable against magnetic order. The zero energy states are edge states, the instability will occur at the edges

Electron-Electron Interaction. Hubbard Model

Hubbard model only considers Coulomb repulsion between two electrons at the same atomic site:

$$\hat{H} = -t\sum_{<ij>,\sigma} c^{+}_{i,\sigma} c_{j,\sigma} + U\sum_{i,\sigma} c^{+}_{i,\sigma} c_{i,\sigma} c^{+}_{i,-\sigma} c_{i,-\sigma}$$

Neglecting fluctuations, we get the mean field approximation,

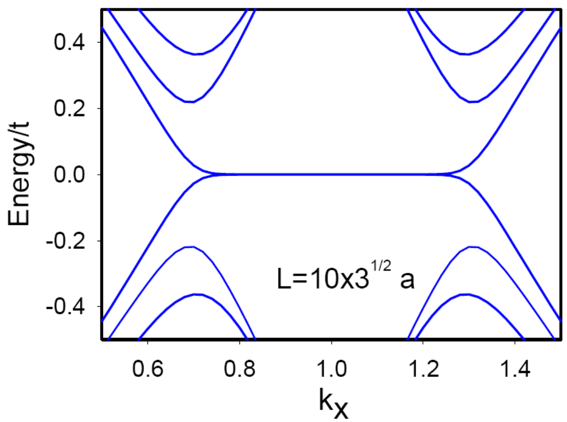
$$\hat{H} = -t\sum_{<ij>,\sigma} c^{+}_{i,\sigma} c_{j,\sigma} + U\sum_{i,\sigma} < c^{+}_{i,\sigma} c_{i,\sigma} > c^{+}_{i,-\sigma} c_{i,-\sigma} - U\sum_{i} < c^{+}_{i,\uparrow} c_{i,\uparrow} >< c^{+}_{i,\downarrow} c_{i,\downarrow} >$$

that should be solved self consistently. We obtain band structure and charge and magnetization at every site.

- *From ab initio calculations U = 2-3eV*
- *Lieb's theorem: A bipartite system at half-filling, with Hubbard interaction, has the ground state characterized by the total spin*

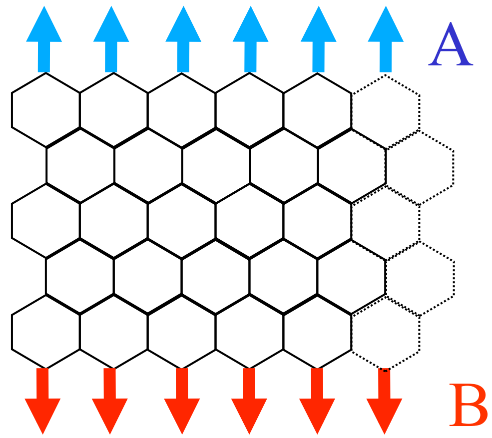
$$S = \frac{1}{2}|N_A - N_B|$$

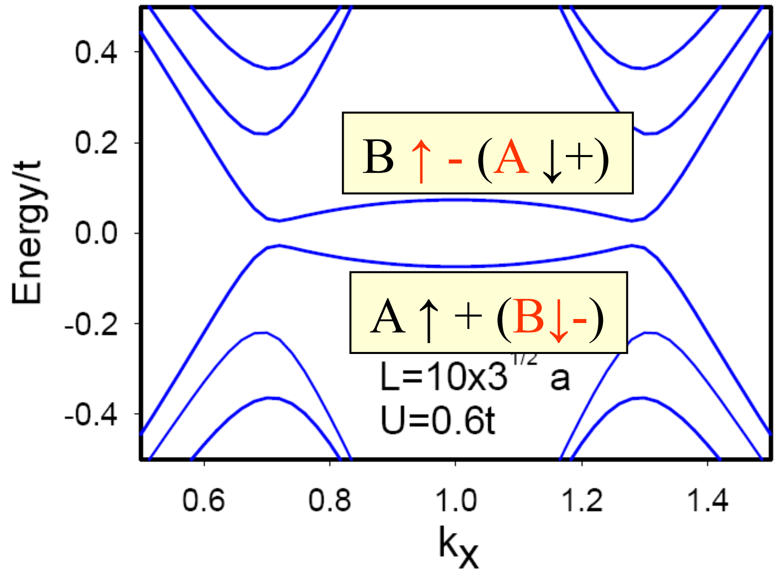
Magnetic Order ZZGNR

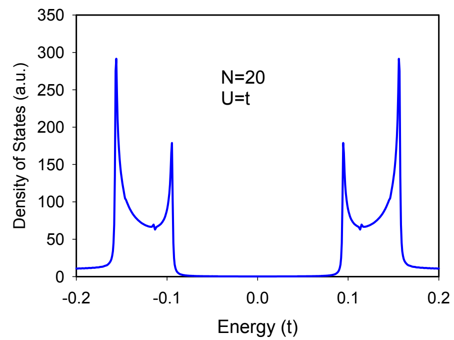


U

The effect of U is basically on the edge. Bulk is paramagnetic.
Atoms B polarize ↓ atoms A polarize ↑



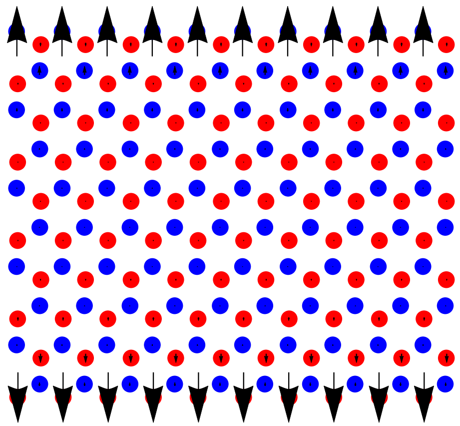


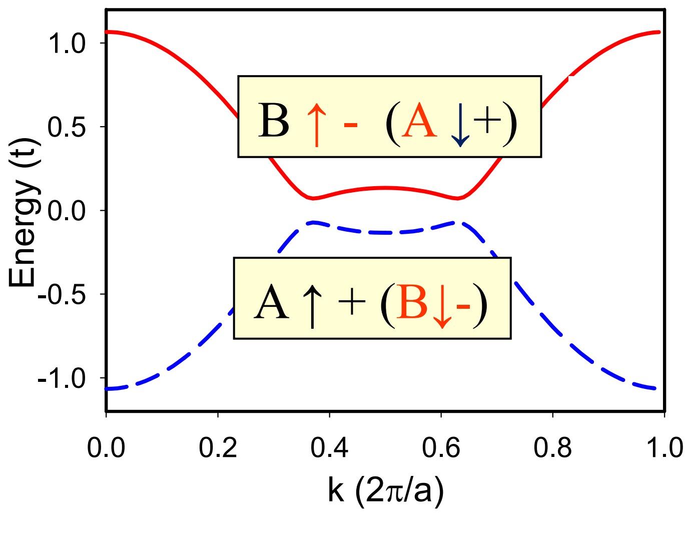


Wakabayashi '98
Y.Son et al '08
Fernández Rossier '08
Brey et al '08

In the localize states spin, valley, edge and atom are coupled.

Two degenerated ground states.





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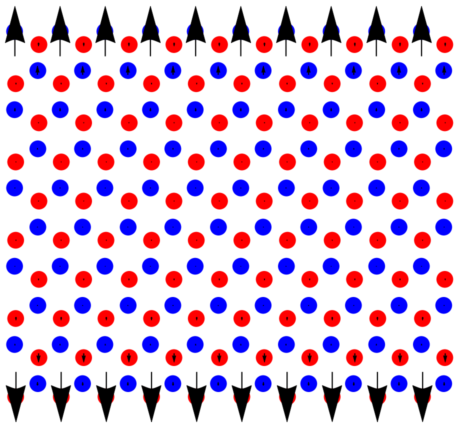

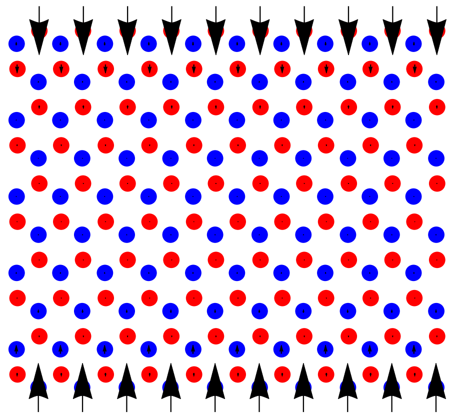

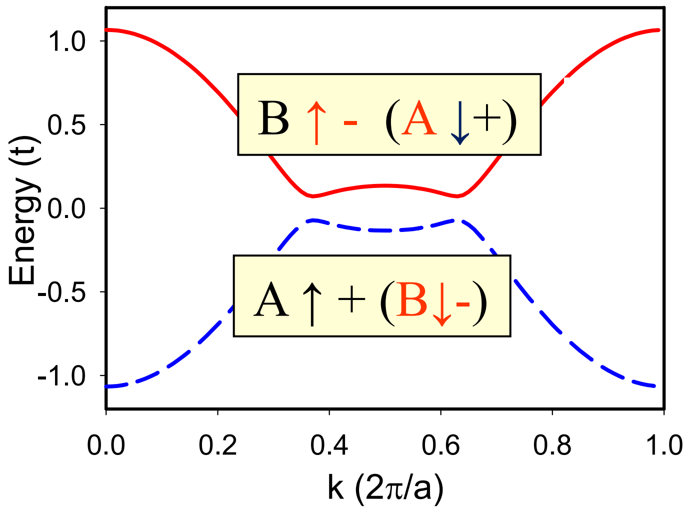

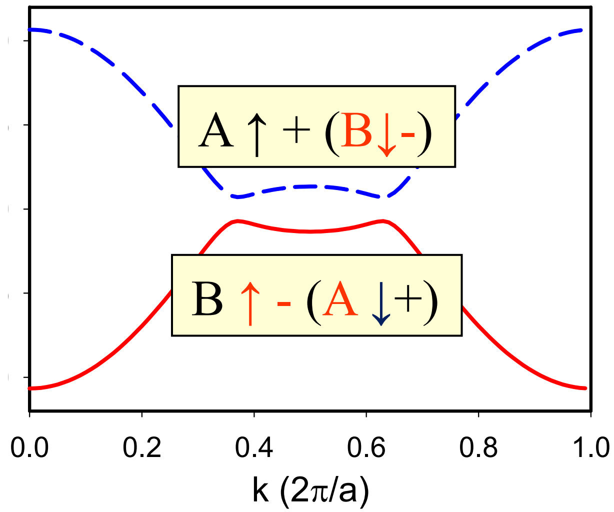

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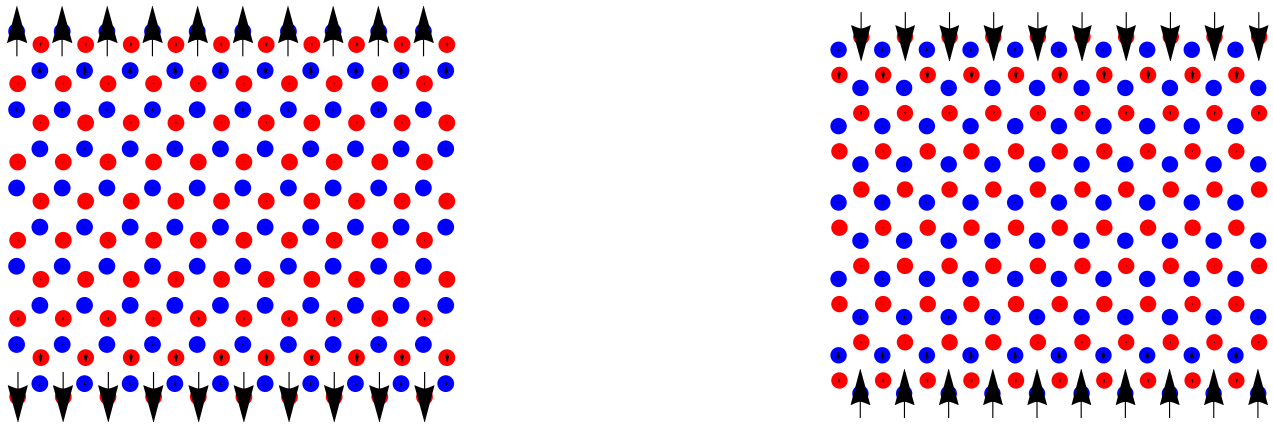
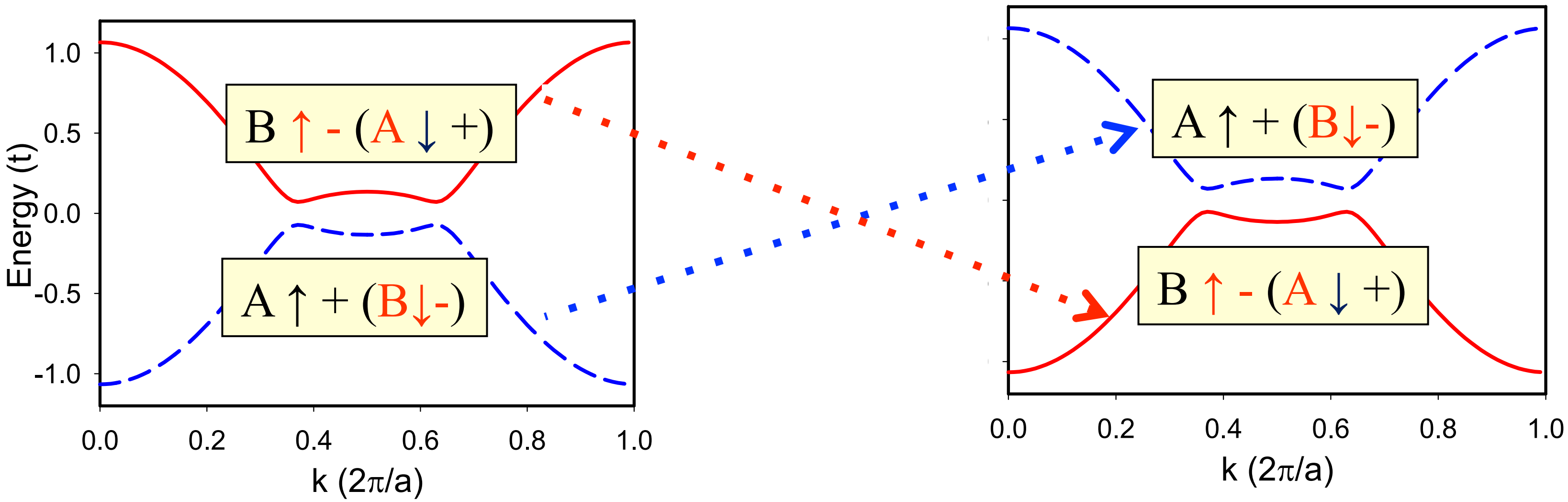
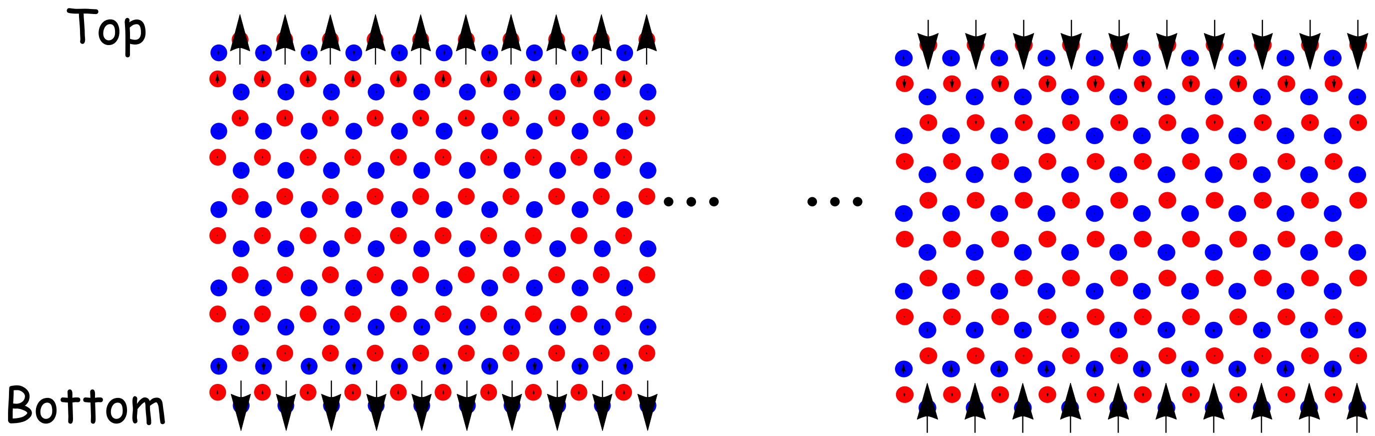


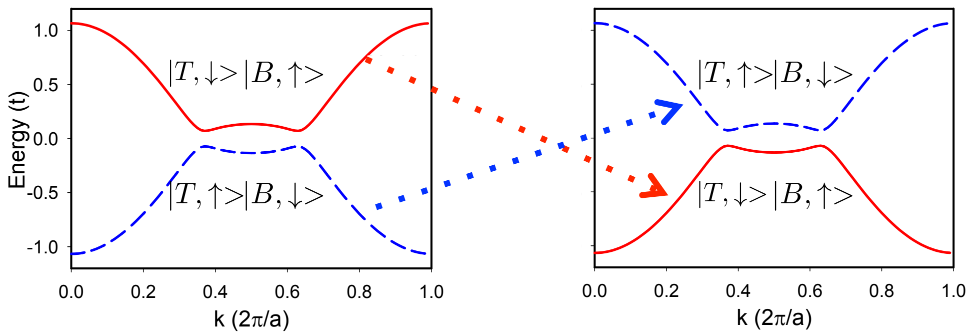
Band Inversion.



Solitons in ZZGNRs



This degeneracy reflects the broken symmetry of the ground state in the spin sector. Associated this degeneracy there exist topological excitations, in this case solitons. At the interface between domains, there will be topological protected states (solitons) one for each spin orientation.



Properties of Solitons in ZZGNRs

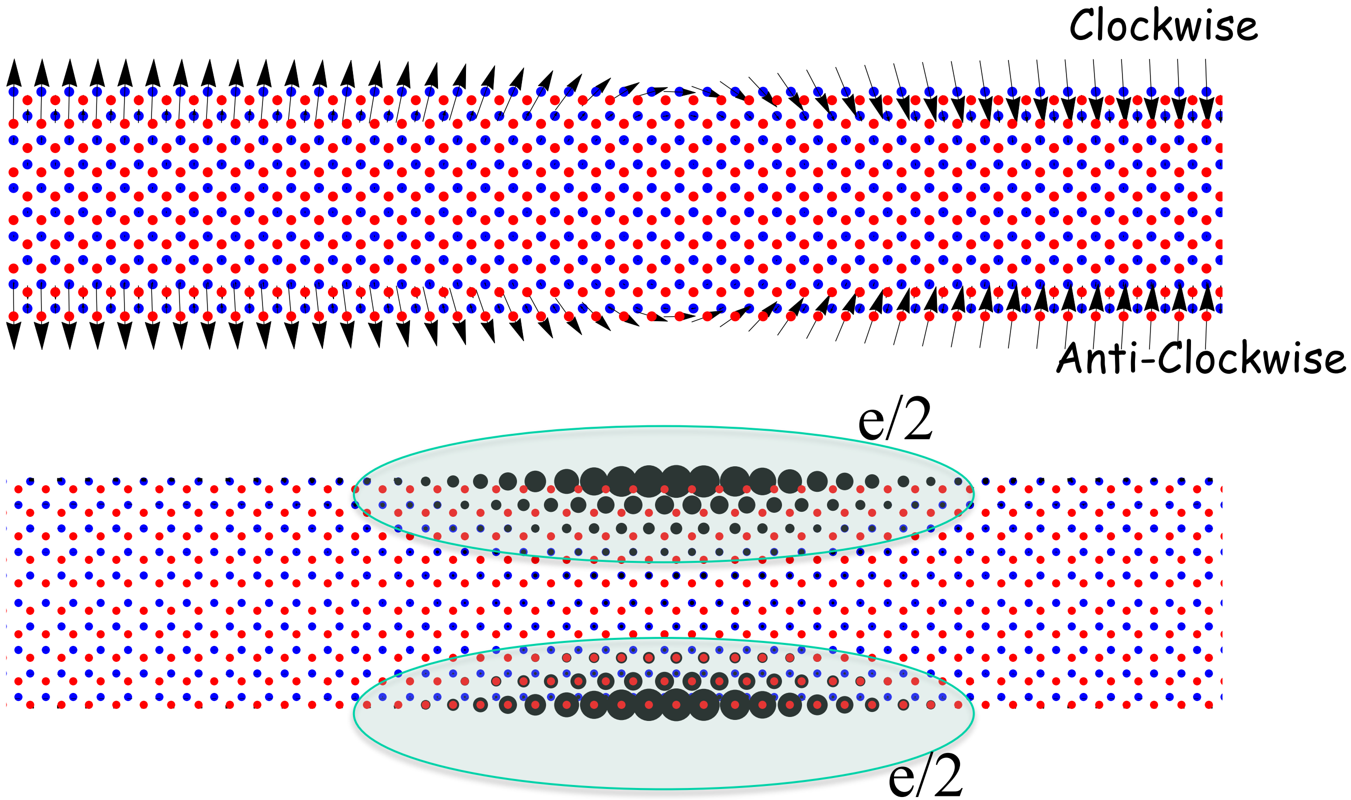
- *Hamiltonian has e-h symmetry, any eigenstate with energy ε has a conjugate state with energy –ε.*
  Therefore, the energy of the topological protected states should be placed at the middle of the gap and have zero energy.
- *Half of the spectral weight of the mid gap state comes from the CB and the other from the VB, Therefore when the Fermi energy is above (below) zero energy, the soliton would carry a charge e/2 (-e/2).*
- *Considering two spin orientations, the topological excitations in ZZGNR's consist of two e/2 charged solitons, with total charge e.*
- *The connection between topological defects and electric charge suggests that solitons can be the relevant charge excitations on ZZGNRs.*

To verify and quantify this proposal,
Tight-Binding + Hubbard numerical calculations.

TB + U self-consistent calculations.

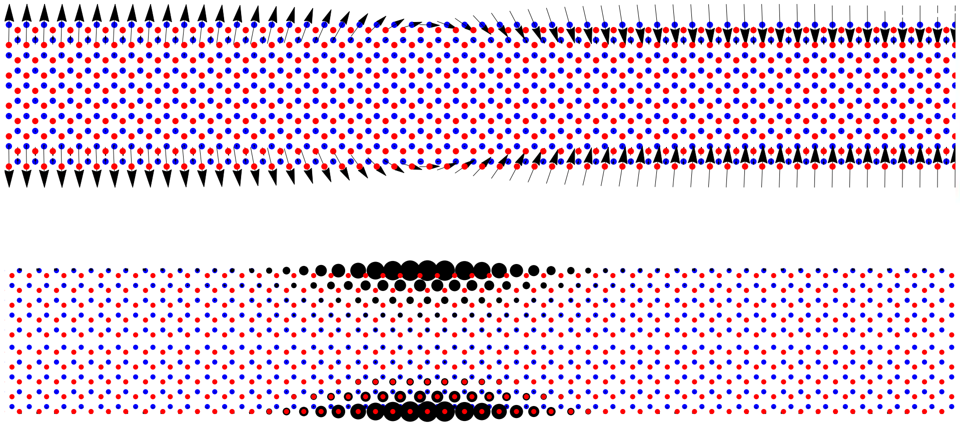
Supercell with appropriated boundary conditions, and an extra electron. Self-consistent solution in the mean field Hubbard model. The solutions converge to the solitonic phase. One electron located at the domain wall.

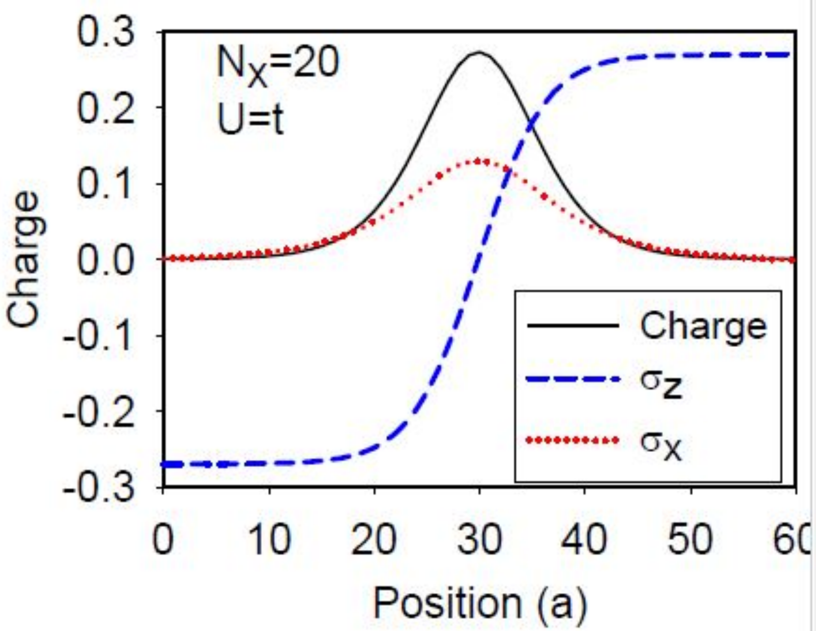
Spins rotate in opposite direction on opposite edges.

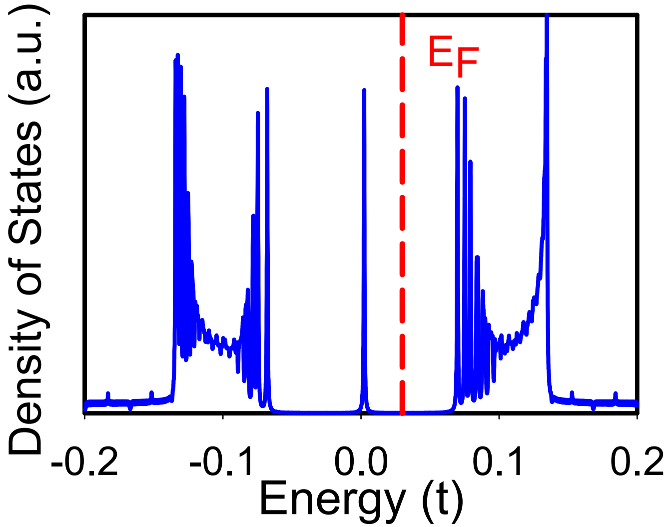


TB + U self-consistent calculations.

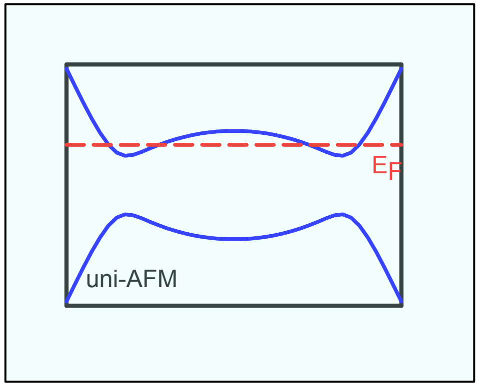
Supercell with appropriated boundary conditions, and an extra electron. The solutions converge to the solitonic phase.

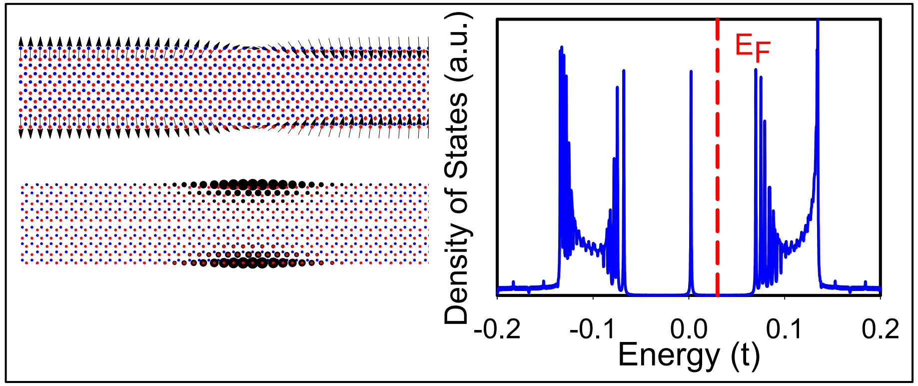


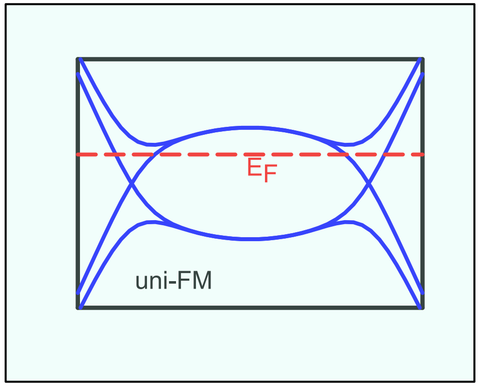


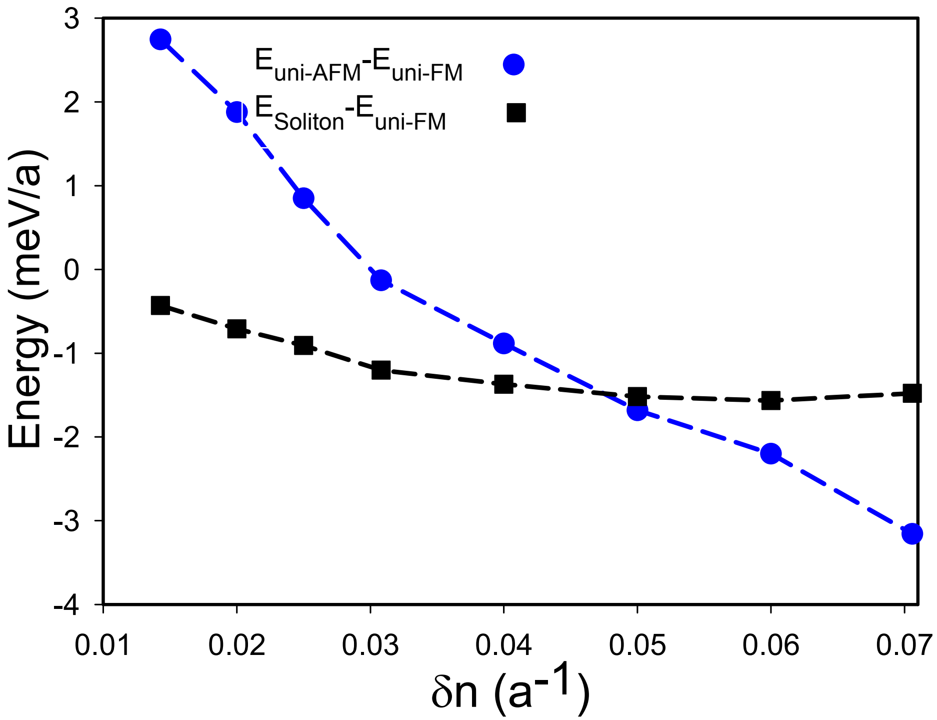


Are solitons the relevant charge excitations?









Yes at low densities!!!

In ZZGNR's a single extra electron can be self trapped in a self induced topological defect.

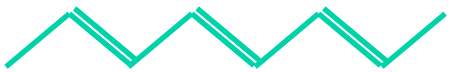
Topological Origin of the Solitons in ZZGNR

In 1D systems the existence of solitons, or interface states, have a topological origin. They are associated with the existence of a Berry phase across the BZ, that is called the Zak phase,

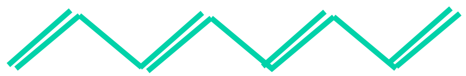
$$\gamma = i \int_{BZ} dk < u(k)|\partial_k|u(k) >$$

The integral is gauge invariant (system with inversion symmetry), but NOT the integrand.

In polyacetylene, two different dimerizations, i.e. two degenerated phases,*



$\gamma = \pi$



$\gamma = 0$

The difference of phases is π, and a soliton appear at the interface between the two dimerizations.

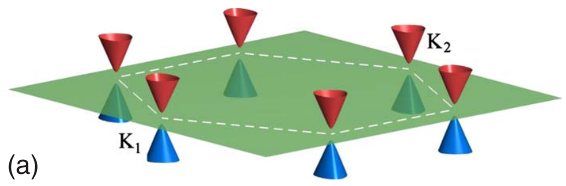
In ZZGNR's the Zak phase is zero!!, It not obvious to relate the existence of solitons with a topological character of the ribbons. Also, there are not edge states.
We propose that the solitons occur because of the existence of two inequivalent valleys each carrying a finite topological charge with opposite sign.

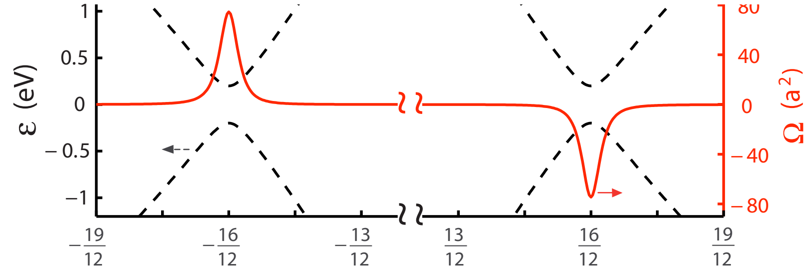
*SSH, PRL (1979)

Topological Aspects of Graphene with Mass

Atoms on sublattice A and B
have opposite onsite energy (mass).
Insulator system.

$$H_\tau = \hbar v_F \begin{pmatrix} -\Delta & k_x - i\tau k_y \\ k_x + i\tau k_y & \Delta \end{pmatrix}$$



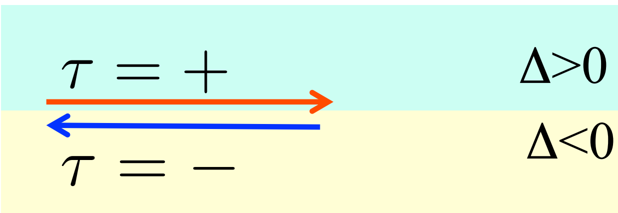


RMP Xiao et al 2010

$$Q = \frac{1}{\Omega}\sum_k \frac{2}{\left(\varepsilon_k^c - \varepsilon_k^v\right)^2} \mathrm{Im}[<\varphi_k^v | v_y | \varphi_k^c><\varphi_k^c | v_x | \varphi_k^v>]$$

$$Q_{\tau=-} = \frac{1}{2} \qquad Q_{\tau=+} = -\frac{1}{2}$$

If there is an interface changing Δ to –Δ, which does not mix valleys, edge states could happen. An edge state for valley K (ΔQ=1) and another edge state, with opposite velocity, for valley K' (ΔQ=-1). Quantum Valley Hall Effect.



Valleys have opposite topological charge,

Yao et al PRL 2009

Topological Aspects of AntiFerromagnetic Graphene

Atoms on sublattice A and B have opposite spin and therefore opposite selfenergy Σ.

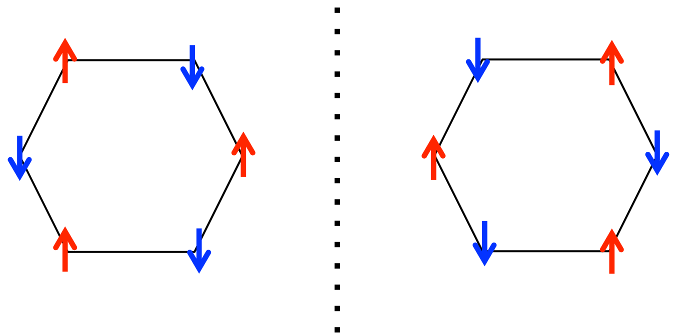
$$H_{\tau}^{s_z}=\begin{pmatrix} -s_z\Sigma & \hbar v_F\left(k_x-i\tau k_y\right) \\ \hbar v_F\left(k_x+i\tau k_y\right) & s_z\Sigma \end{pmatrix}$$

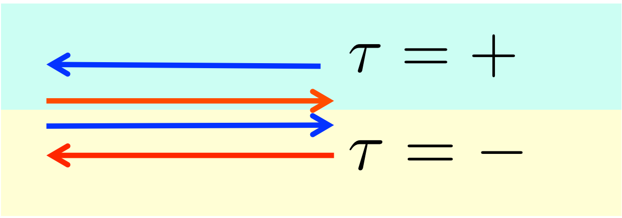
Topological charge depends on valley and spin.

$$\boxed{Q_{\tau=-}^{s_z=\frac{1}{2}}=\frac{1}{2}} \quad \boxed{Q_{\tau=+}^{s_z=\frac{1}{2}}=-\frac{1}{2}} \quad \boxed{Q_{\tau=-}^{s_z=-\frac{1}{2}}=-\frac{1}{2}} \quad \boxed{Q_{\tau=+}^{s_z=\frac{1}{2}}=\frac{1}{2}}$$

At the interface between AF domains, which does not mix valleys and spins , edge states could happen. Four edge states should appear.

Quantum Spin-Valley Hall Effect.





Topological Aspects of AntiFerromagnetic Graphene

Atoms on sublattice A and B
have opposite selfenergy
and opposite spin

$$H_{\tau}^{s_z}=\begin{pmatrix} -s_z\Sigma & \hbar v_F\left(k_x-i\tau k_y\right) \\ \hbar v_F\left(k_x+i\tau k_y\right) & s_z\Sigma \end{pmatrix}$$

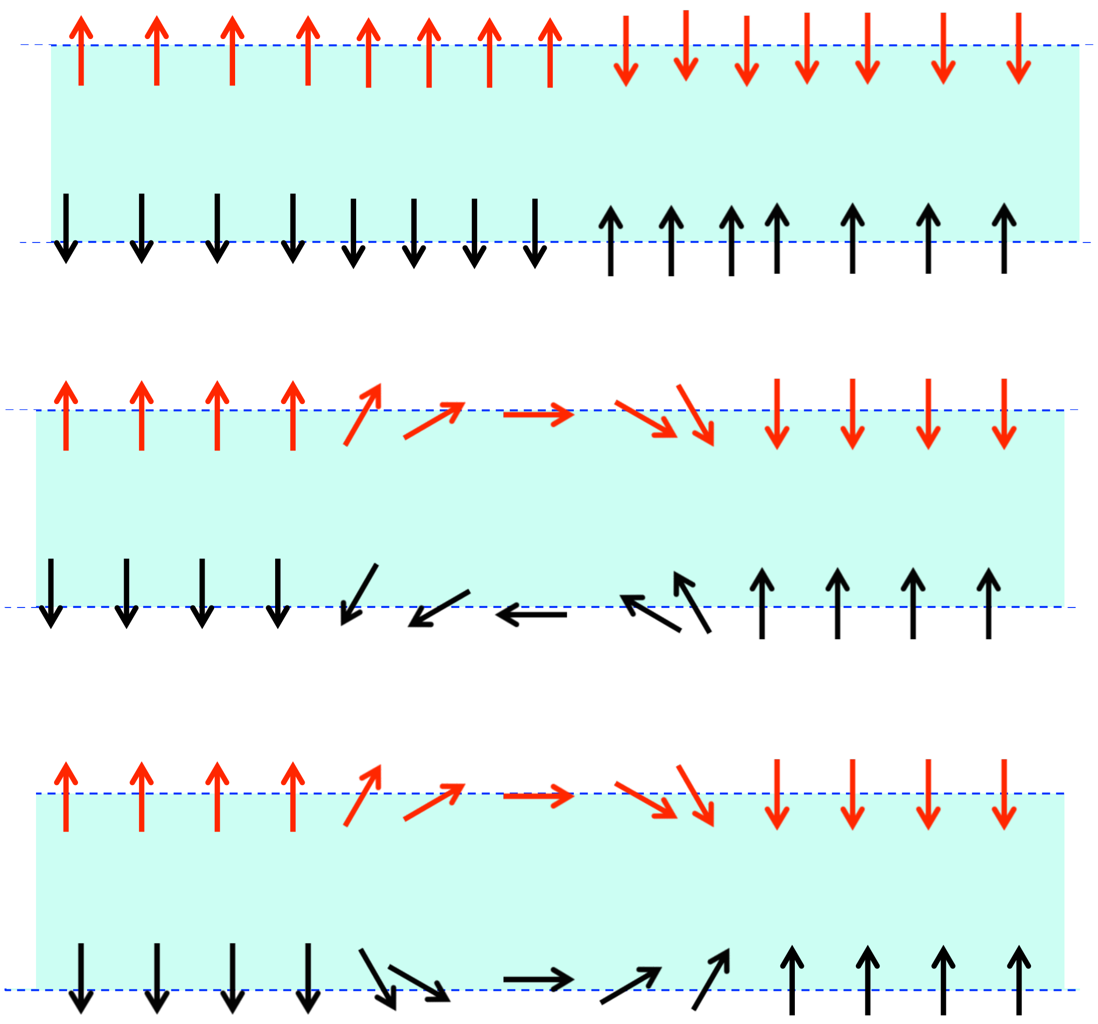
Topological charge depends on valley and spin.

$$\boxed{Q_{\tau=-}^{s_z=\frac{1}{2}}=\frac{1}{2}} \quad \boxed{Q_{\tau=+}^{s_z=\frac{1}{2}}=-\frac{1}{2}} \quad \boxed{Q_{\tau=-}^{s_z=-\frac{1}{2}}=-\frac{1}{2}} \quad \boxed{Q_{\tau=\mp}^{s_z=\frac{1}{2}}=\frac{1}{2}}$$

But, if the spin rotates connecting the two AF domains, the interface mix spins and the interface states disappear.
The system is invariant under rotation. There is not privileged spin orientation. O(3) symmetry.

Gap does not close at the domain wall.

If the spin rotates between the domain walls, no interface states are expected.



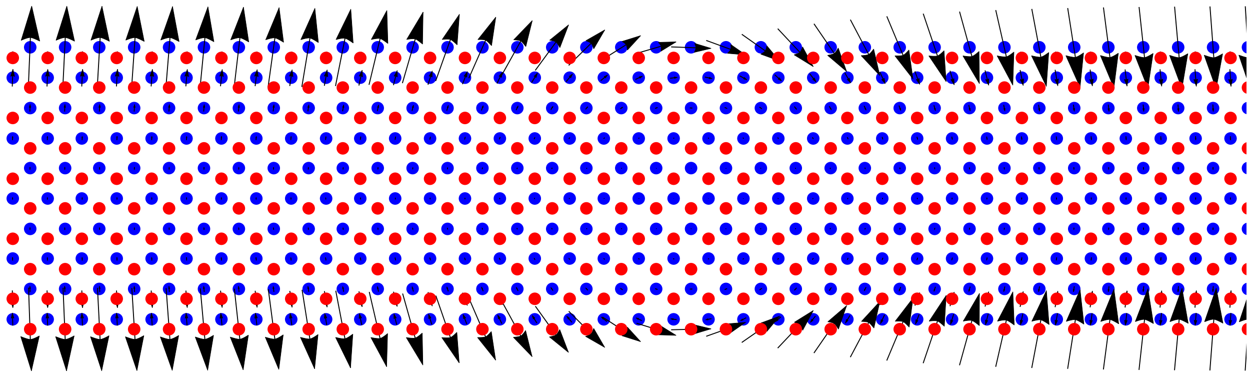
Interface states
in the gap

No interface states.
Spin rotation.

Top and bottom edges
Rotates on opposite
direction.
Interface states.

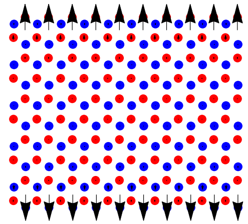
In ZZGNR, in the domain wall, top and bottom edges rotates on opposite direction.

Interface states. Soliton.

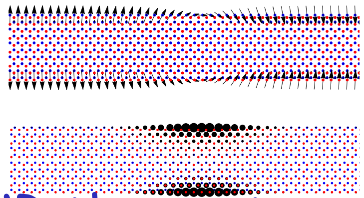


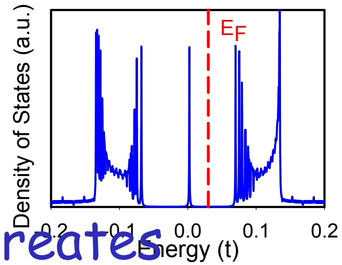
In magnetic ZZGNR, in order to create states in the gap and accommodate an extra electron, top and bottom edges rotate on opposite directions.
In absence of extra charge both edges rotate in same direction and there should be not states in the gap.

Charged Topological Solitons in ZigZag Graphene Nanoribbons.



- ZZGNR's have a broken symmetry state that is degenerated in the spin sector.
- Because of this degeneracy the system has topological excitations solitons which carry an electric charge ±e.





- When adding (subtracting) charge to ZZGNR the system creates a soliton.

In ZZGNR's, at low doping, extra charge creates magnetic domains and becomes localized at the domain wall separating domains with opposite spin polarization.

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