Vacancies in graphene: Dirac physics and fractional charges

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Yaroslav Don
Omrie Ovdat

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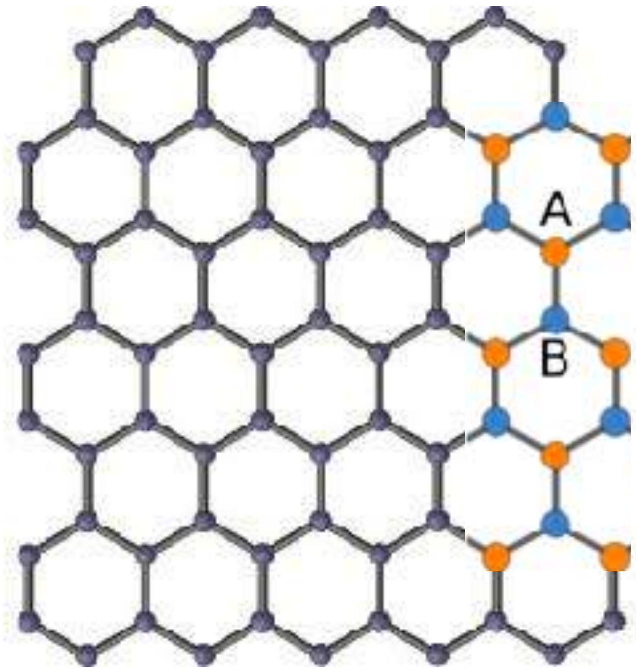
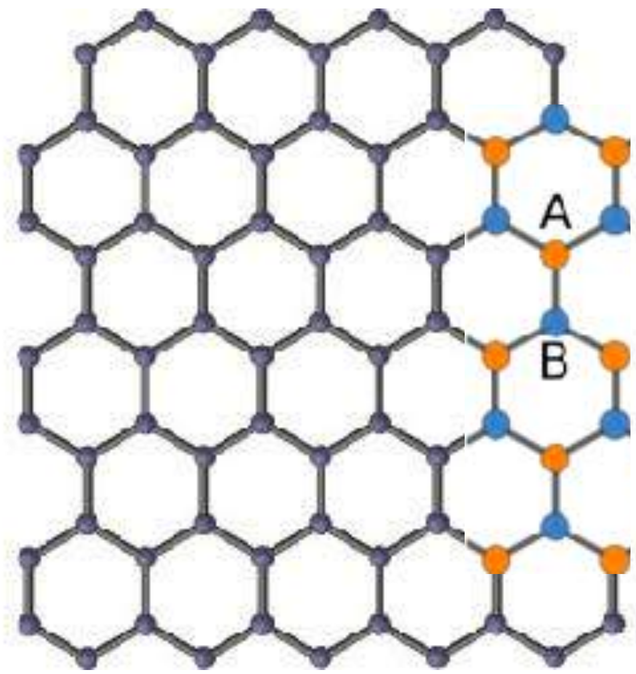
Florent Baboux (LPN, Marcoussis)
Eva Andrei (Rutgers)
Jinhai Mao (Rutgers)
Daniel Brattan (Center for Theoretical Study, Hefei, China)

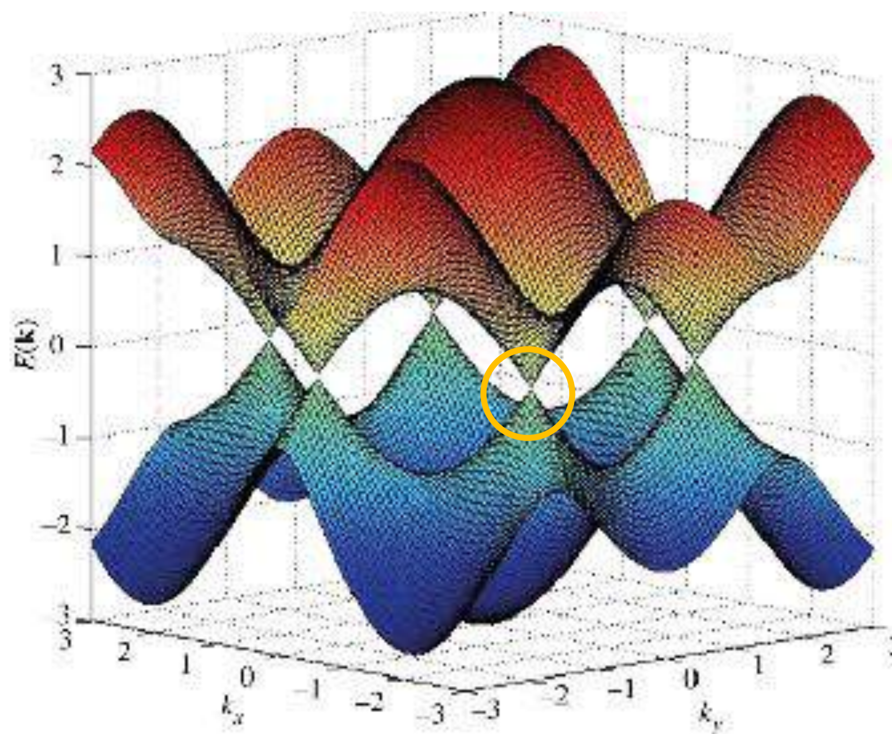
A few words on graphene



- Two-dimensional honeycomb lattice of carbon atoms built out of two triangular sublattices $T_A \ (T_B)$

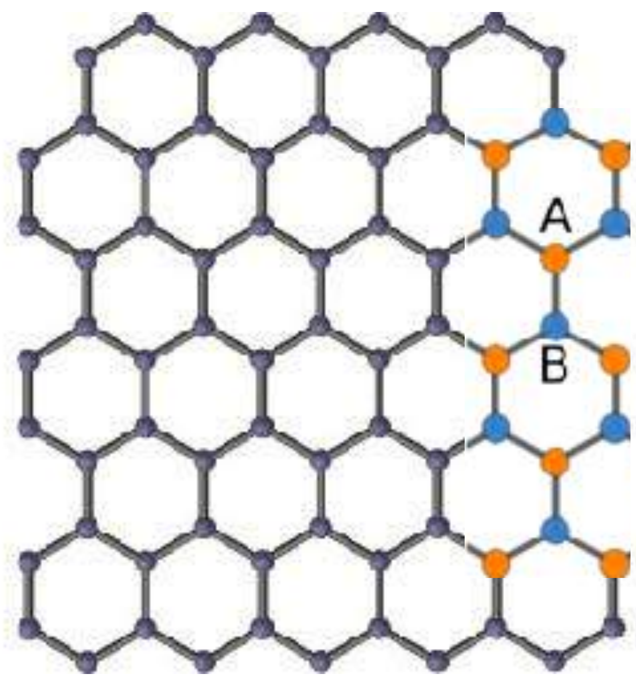
A few words on graphene

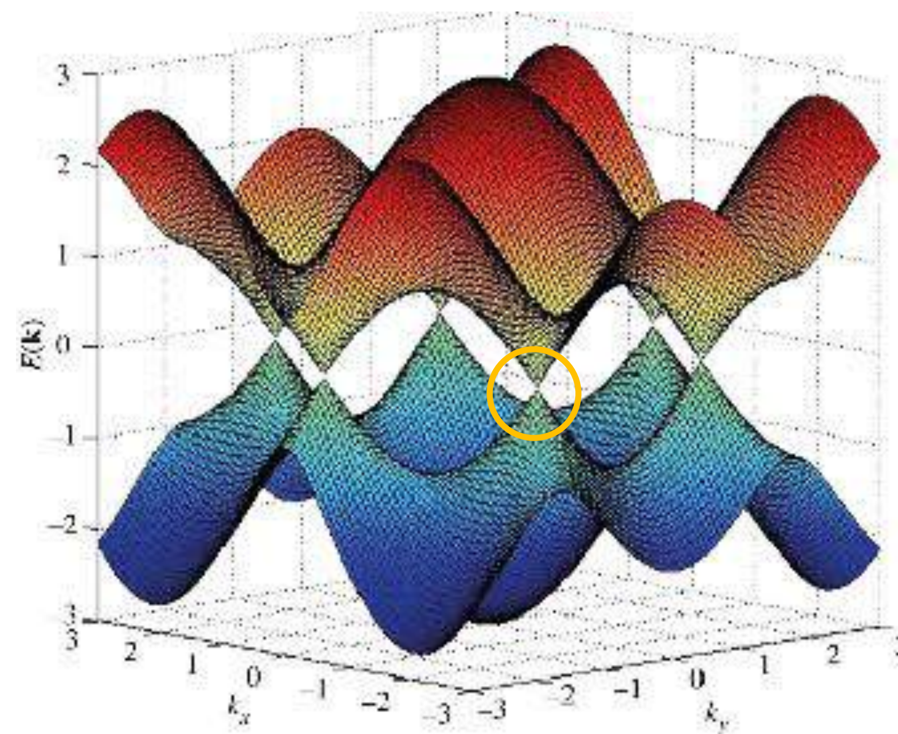


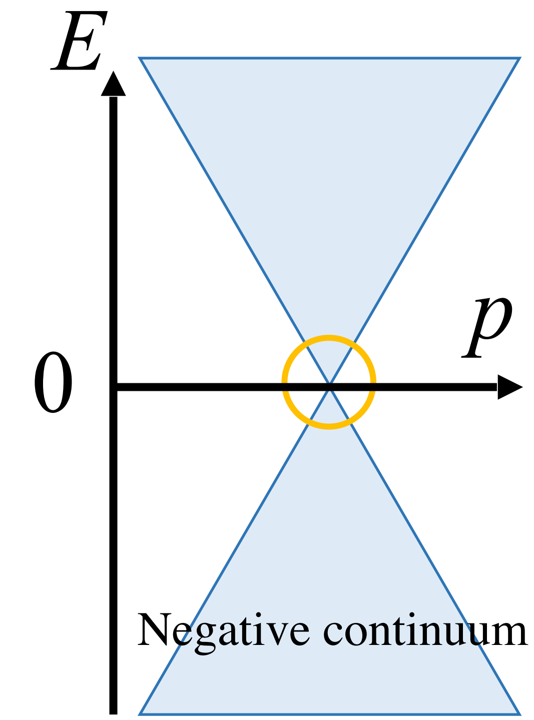


- Two-dimensional honeycomb lattice of carbon atoms built out of two triangular sublattices $T_A \ \ (T_B)$
- Low energy tight binding spectrum : $E = \pm v_F \left|\mathbf{p}\right|$

A few words on graphene





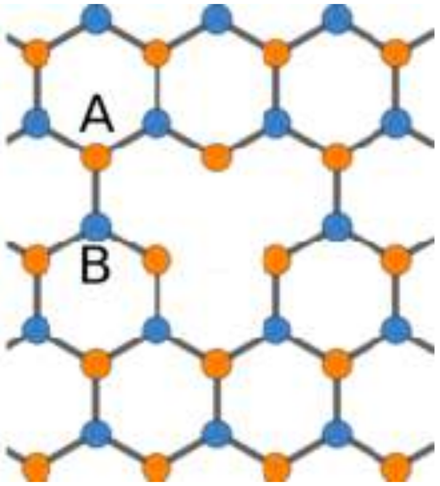


- Two-dimensional honeycomb lattice of carbon atoms built out of two triangular sublattices $T_A \ \ (T_B)$

- Low energy tight binding spectrum : $E = \pm v_F \left|\mathbf{p}\right|$

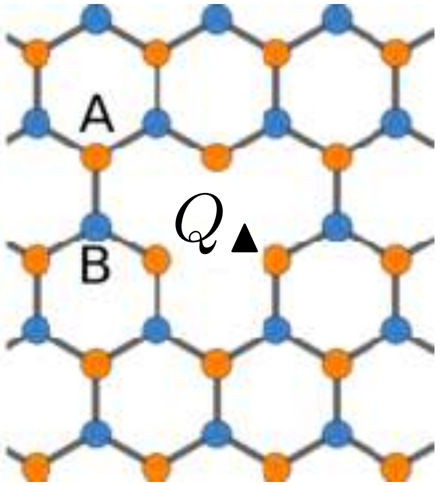
- Admits a continuous description $\Psi = \begin{pmatrix} \psi_A(\mathbf{r}) \\ \psi_B(\mathbf{r}) \end{pmatrix}$ $\qquad H_{\text{Dirac}} = \boldsymbol{\sigma} \cdot \mathbf{p}$

Vacancies in graphene



Created by removing a single carbon atom

Vacancies in graphene



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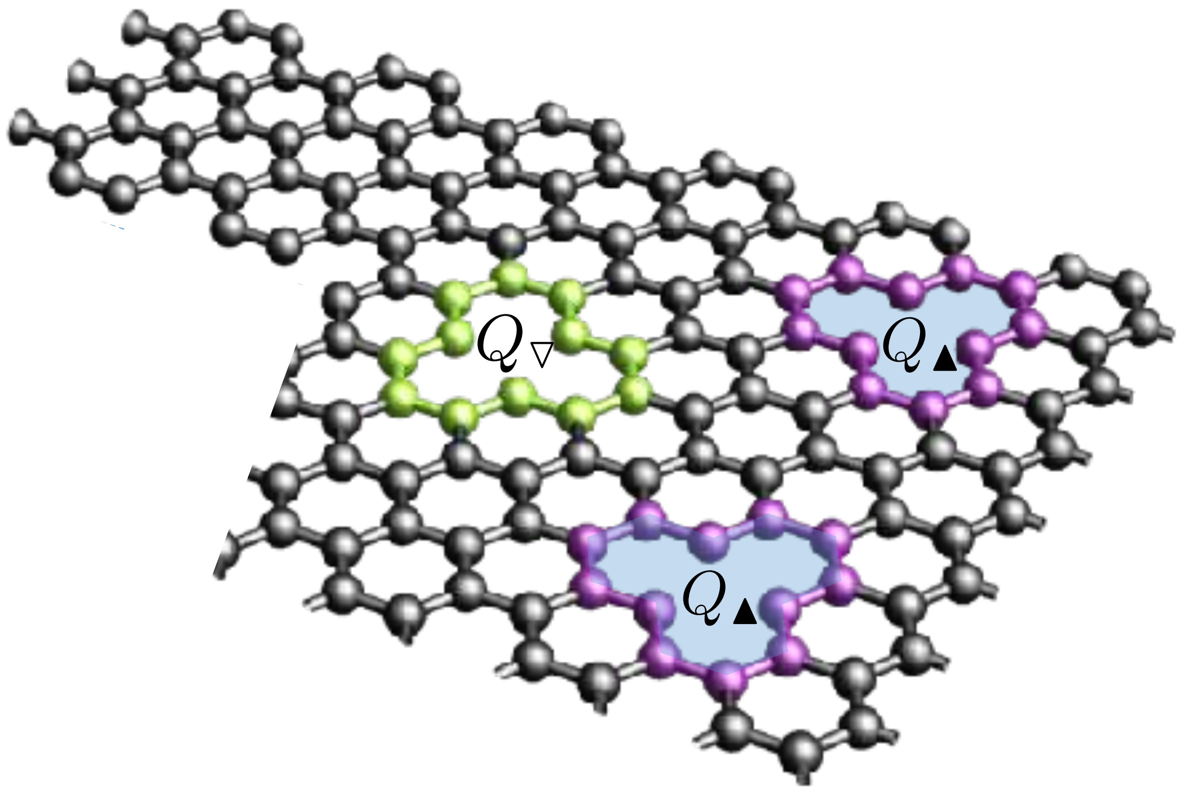
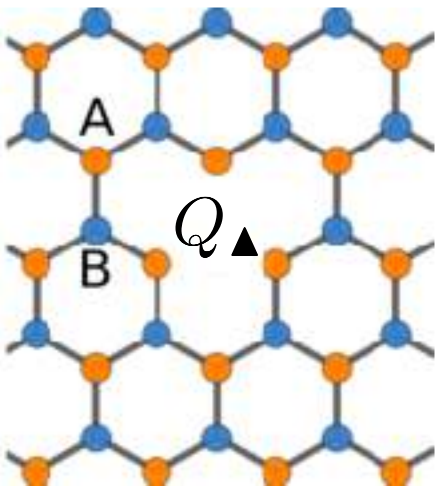
- Induces a stable charge Q at the vacancy site



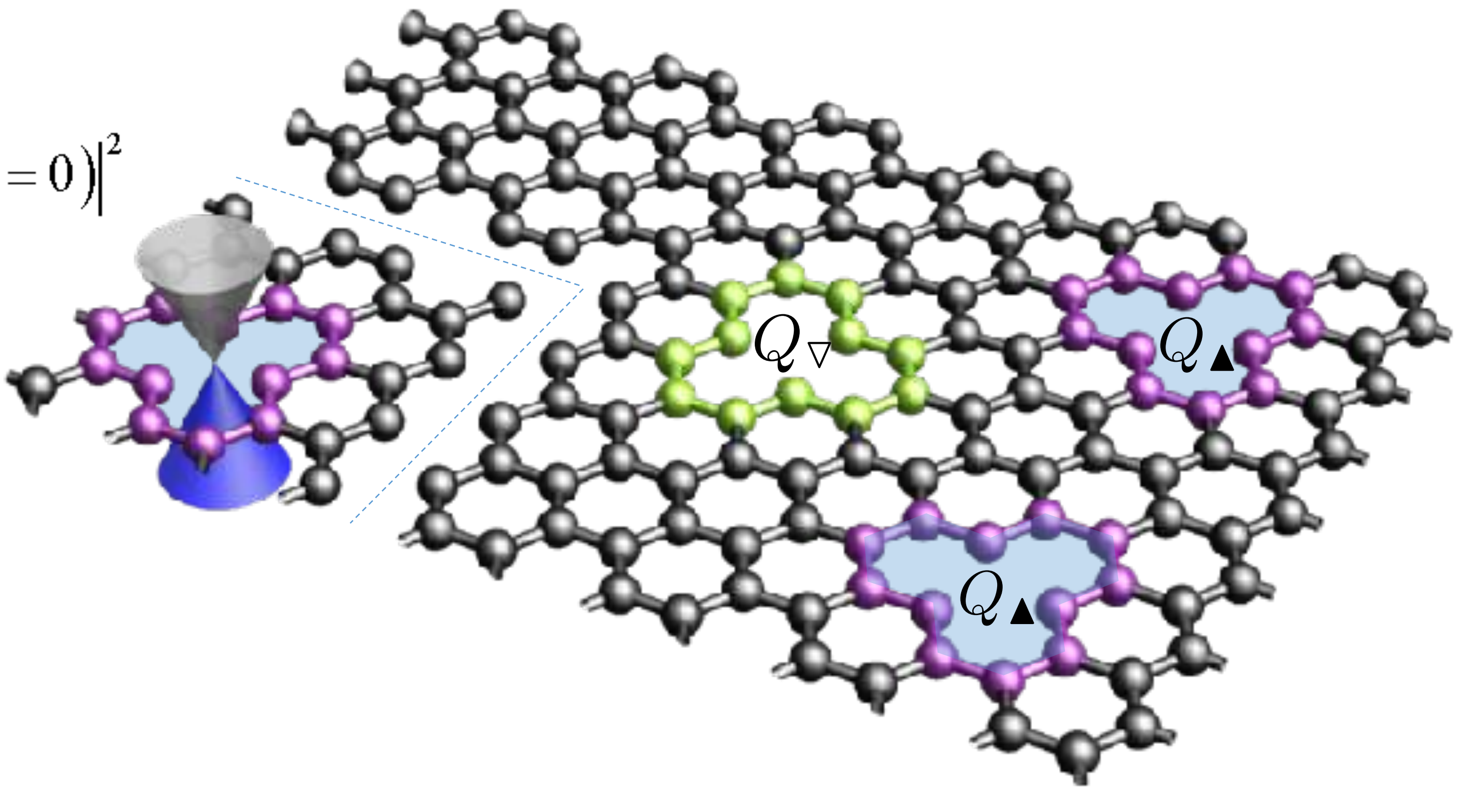
Vacancies in graphene



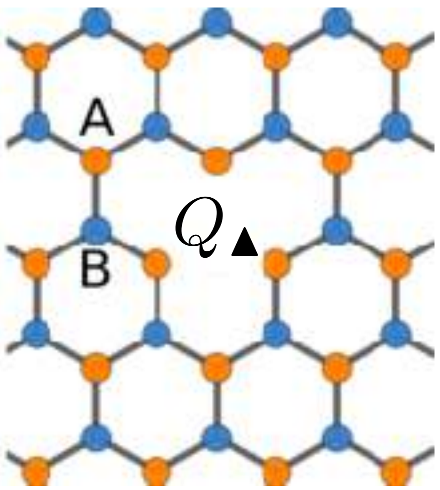
Created by removing a single carbon atom

- Induces a stable charge Q at the vacancy site
- Zero energy modes

$$\rho(\mathbf{r}) = \pm\frac{e}{2}\left|\psi(\mathbf{r}, E=0)\right|^2$$



Vacancies in graphene



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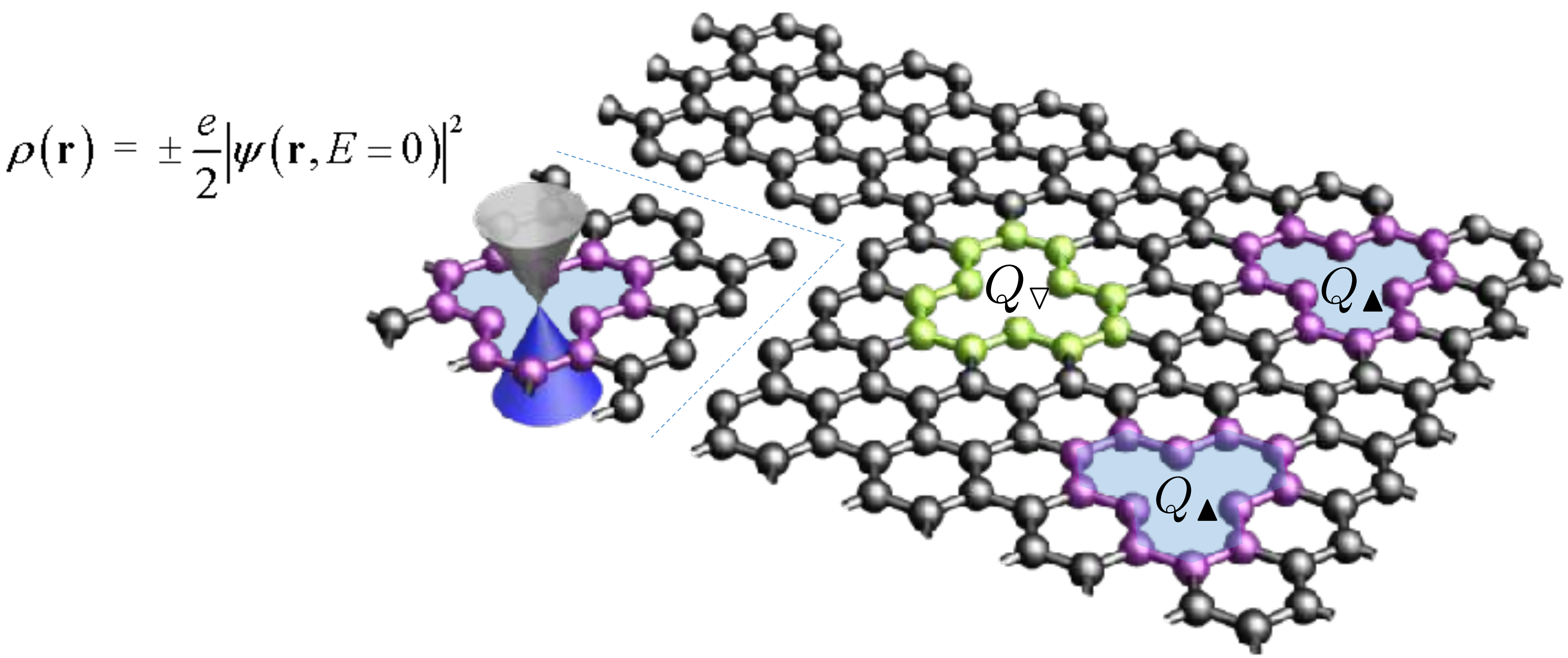
- Induces a stable charge Q at the vacancy site
- Zero energy modes
- Breaks parity (sublattice symmetry)

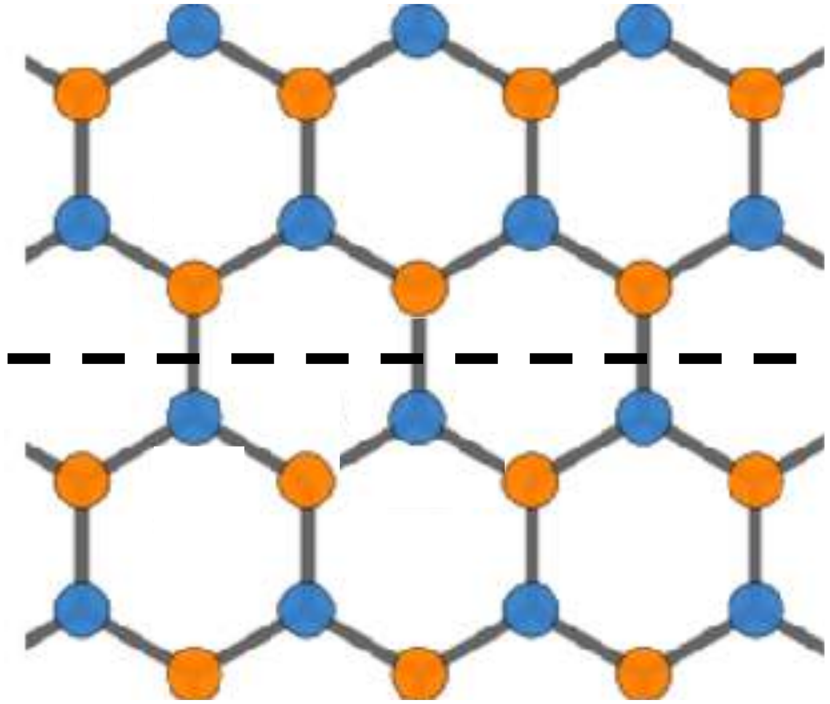


Vacancies in graphene- Parity

- Dirac Hamiltonian $H_{\text{Dirac}} = \boldsymbol{\sigma} \cdot \mathbf{p} = -i\,\boldsymbol{\sigma} \cdot \boldsymbol{\nabla}$ is parity invariant

$$x \mapsto x,\; y \mapsto -y$$

vertical reflection + interchanging sublattices



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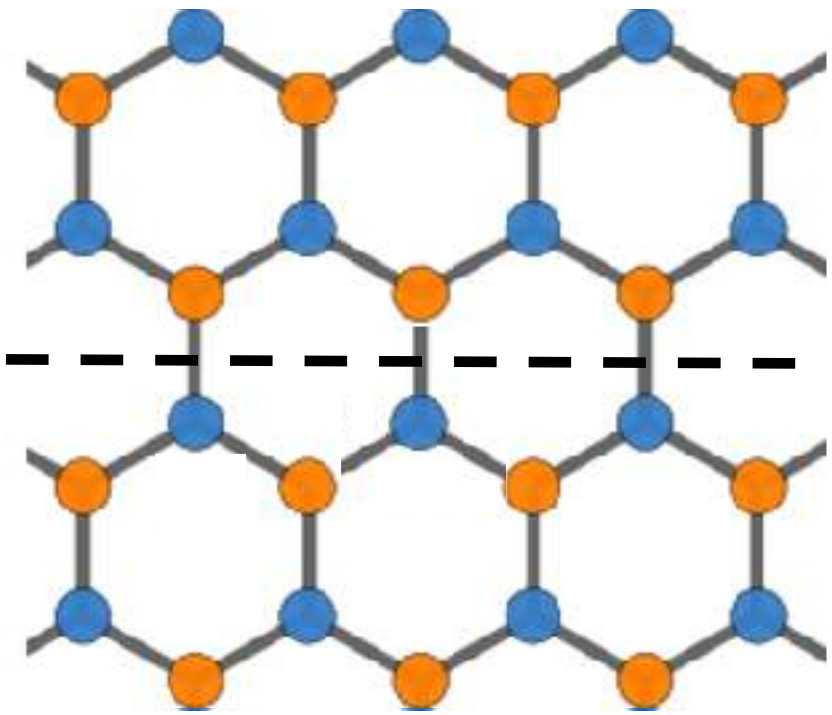

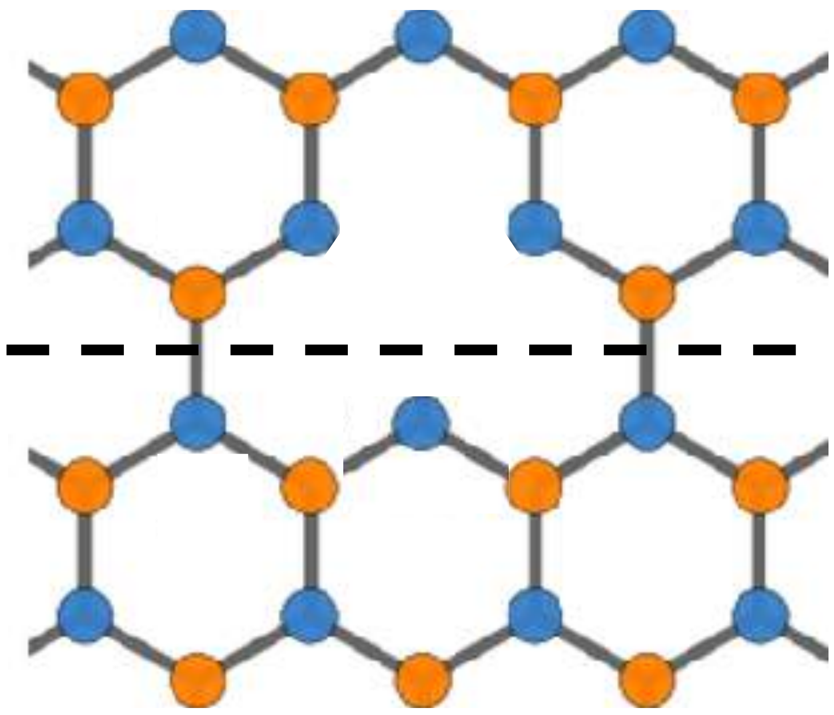

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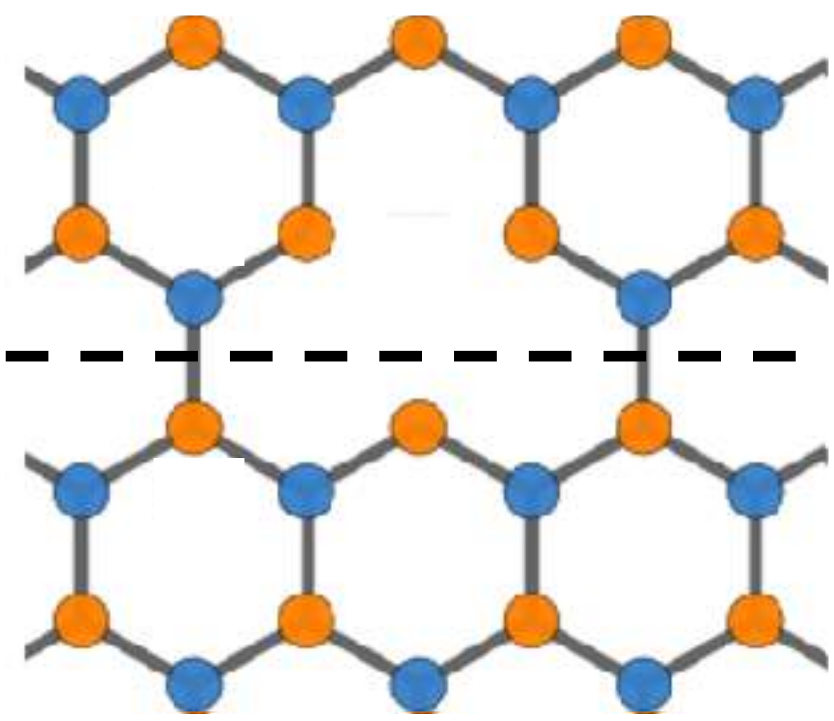
vertical reflection + interchanging sublattices

$$\psi(r,\phi) = e^{im\phi}\begin{pmatrix}\Psi_1(r)\\ i\Psi_2(r)e^{i\phi}\end{pmatrix}$$



$$\Psi_1(r) \to \Psi_2(r), \Psi_2(r) \to -\Psi_1(r)$$

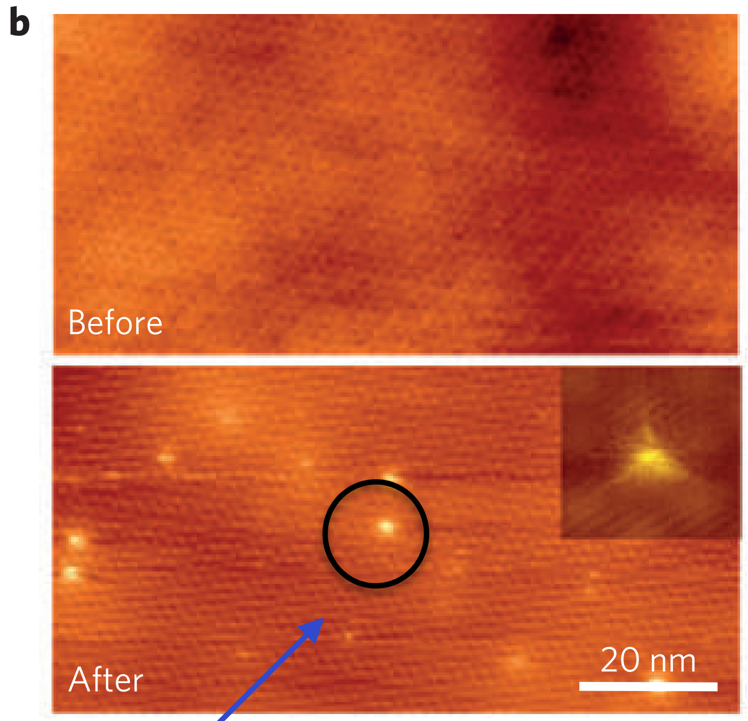
$$m \to -m-1$$

$$j \equiv m + 1/2$$

Degeneracy : $j = \pm 1/2 \leftrightarrow m = -1, 0$

Creating vacancies in graphene

- Sputtering He ions



Local vacancy.

Jinhai Mao, Eva Andrei et al. Nature Physics (2016)

Creating vacancies in graphene

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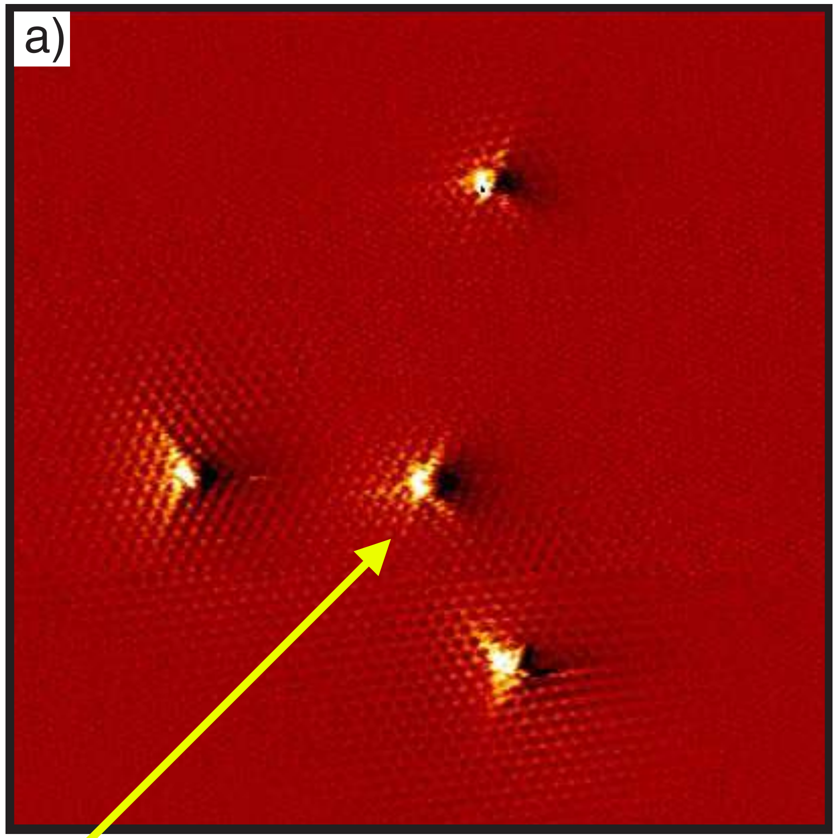
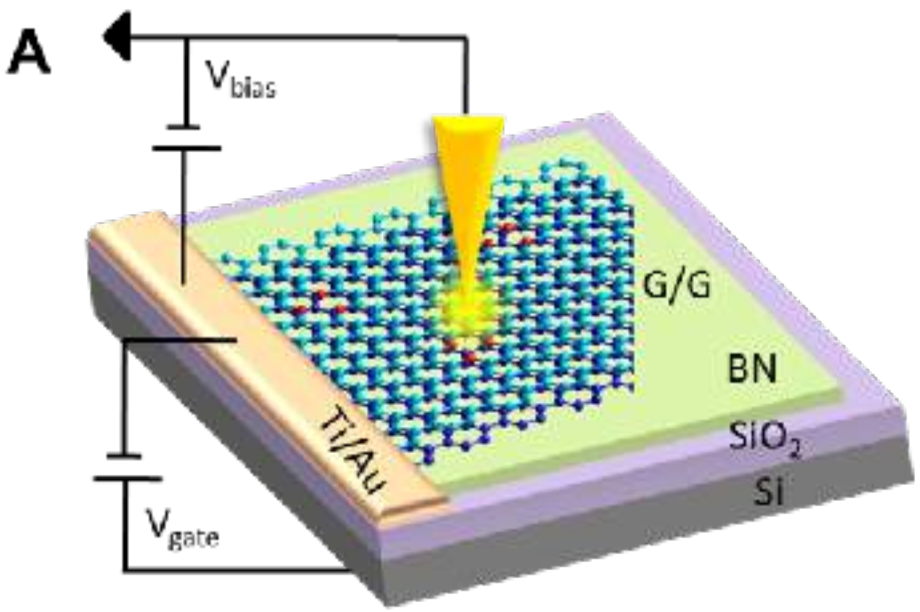


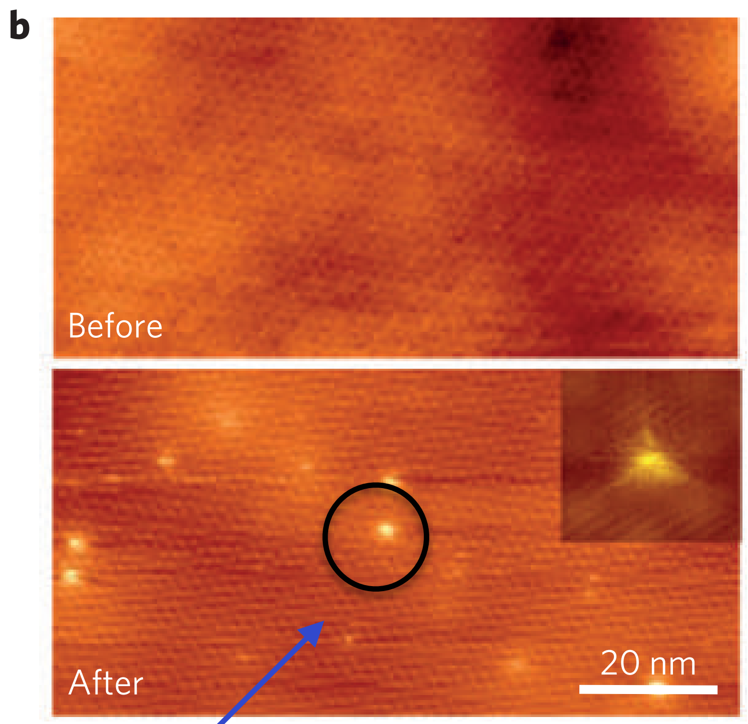
Local vacancy.

M.M. Ugeda et al. Phys. Rev. Lett (2010)

Creating vacancies in graphene

- Sputtering He ions
- Local + Resonance spectrum using STM tip.



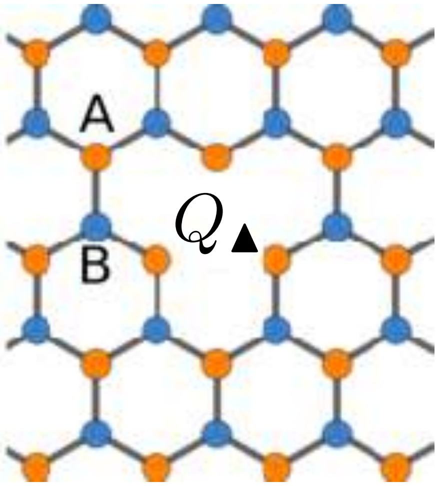


Local vacancy.

Local charge is changed by applying voltage pulses to the STM tip

Jinhai Mao, Eva Andrei et al. Nature Physics (2016)

Vacancies in graphene



Created by removing a single carbon atom

- Induces a stable charge $Q_\blacktriangle$ at the vacancy site
- Zero energy modes
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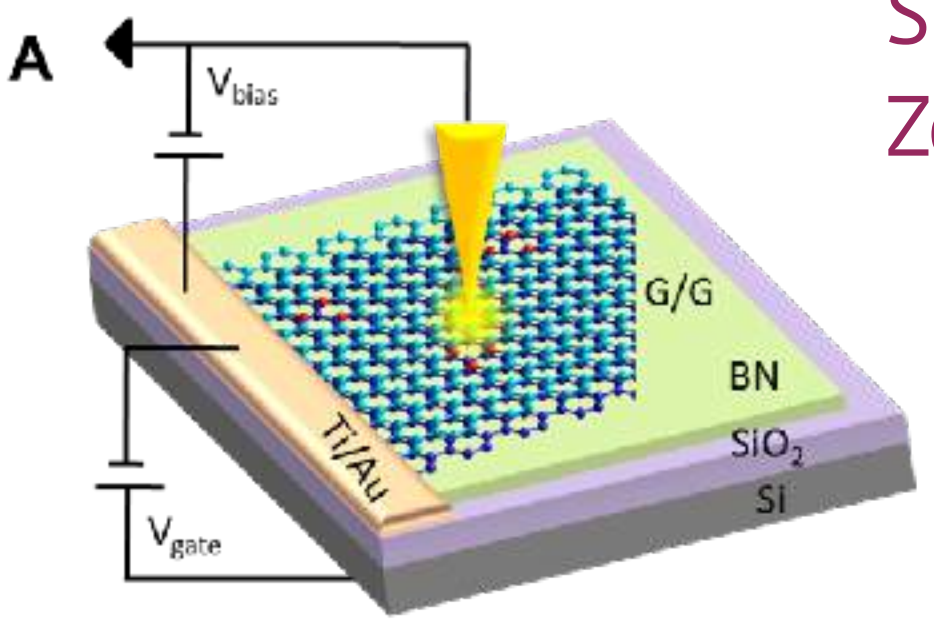
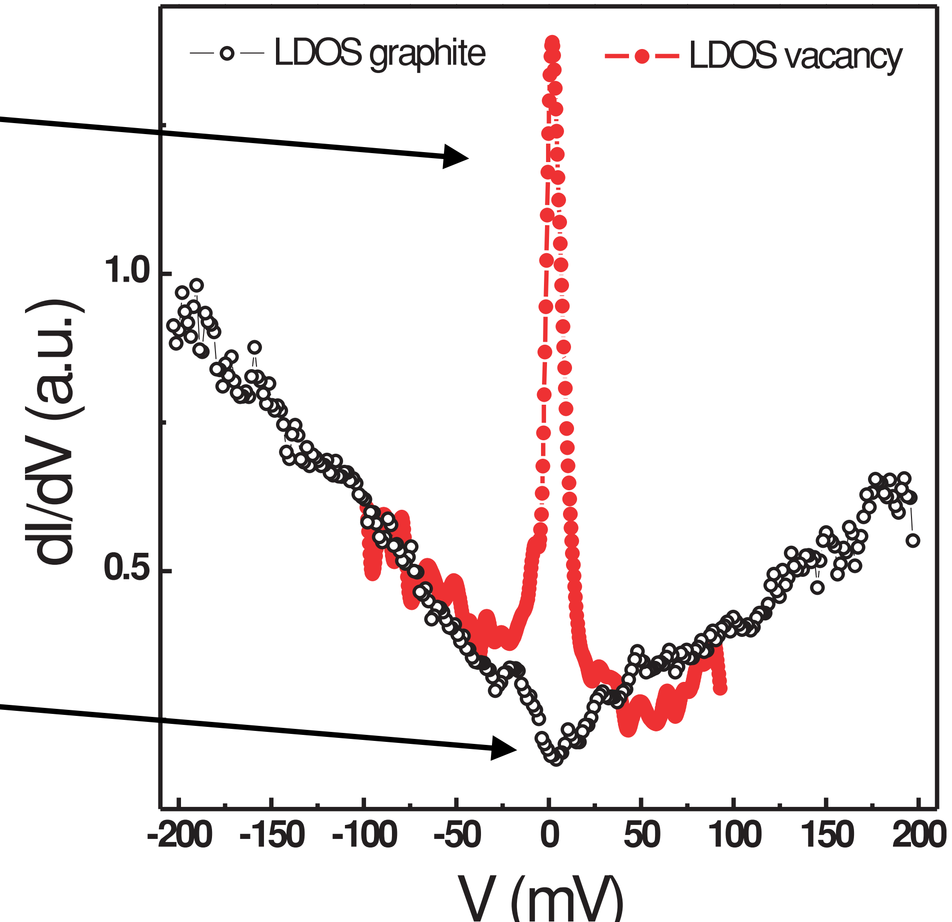
Spectral consequences of vacancies

- Local + Resonance spectrum using STM tip.



Single vacancy
Zero mode

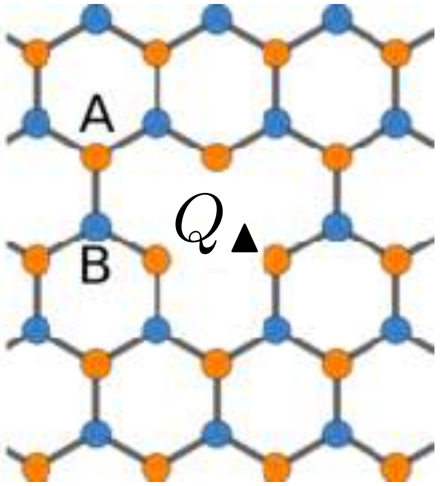
No vacancy



Measure the tunnelling conductance $\frac{\mathrm{d}\delta I}{\mathrm{d}V}$ prop. to the local DOS

M.M. Ugeda et al. Phys. Rev. Lett (2010)

Vacancies in graphene



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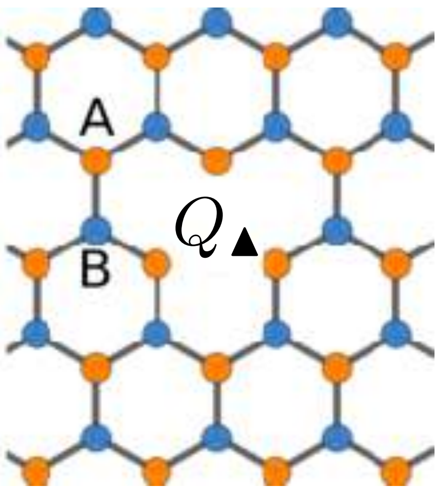
Local charging of vacancies



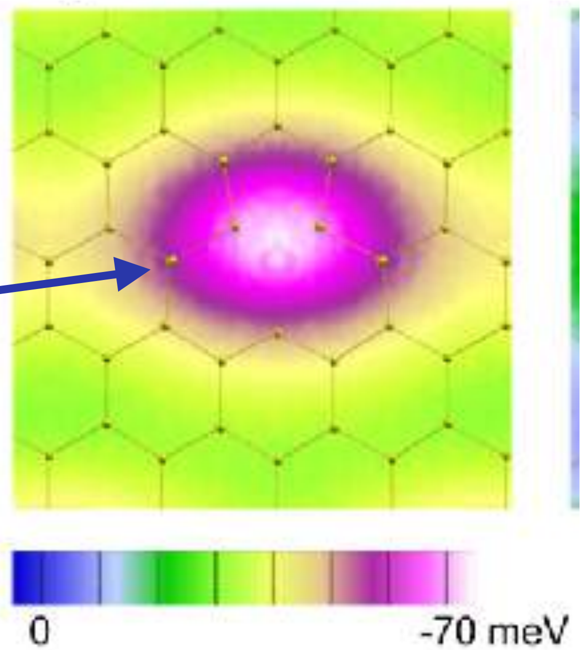
Created by removing a single carbon atom

- Induces a stable charge $Q_\blacktriangle$ at the vacancy site
- Zero energy modes
- Breaks parity (sublattice symmetry)

- Local charge builds up around a vacancy :

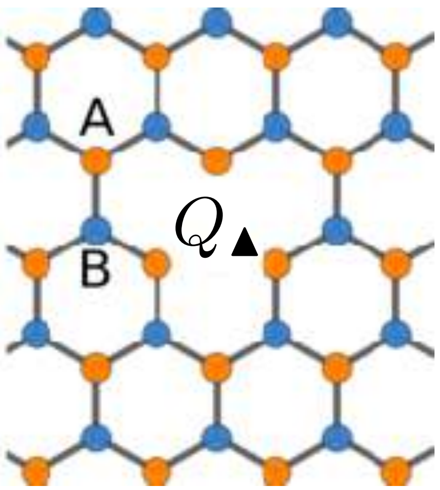
(DFT)

Coulomb potential ~ 1e



Liu, Y., Weinert, M. & Li, L. Nanotechnology 26, 035702 (2015)

Vacancies in graphene



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Before checking that....

Spectral signature of vacancies

- Model the local vacancy charge by a massless Dirac Coulomb model :

$$\boxed{H = -i\boldsymbol{\sigma}\cdot\nabla - \beta / r}$$

$$\beta \equiv Z\alpha$$

fine structure constant

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Scale free problem with continuous scale invariance (CSI)

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The continuous scale invariance (CSI) is broken into a discrete scale invariance (DSI) by any choice of boundary conditions

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Scale free problem with continuous scale invariance (CSI)

The continuous scale invariance (CSI) is broken into a discrete scale invariance (DSI) by any choice of boundary conditions

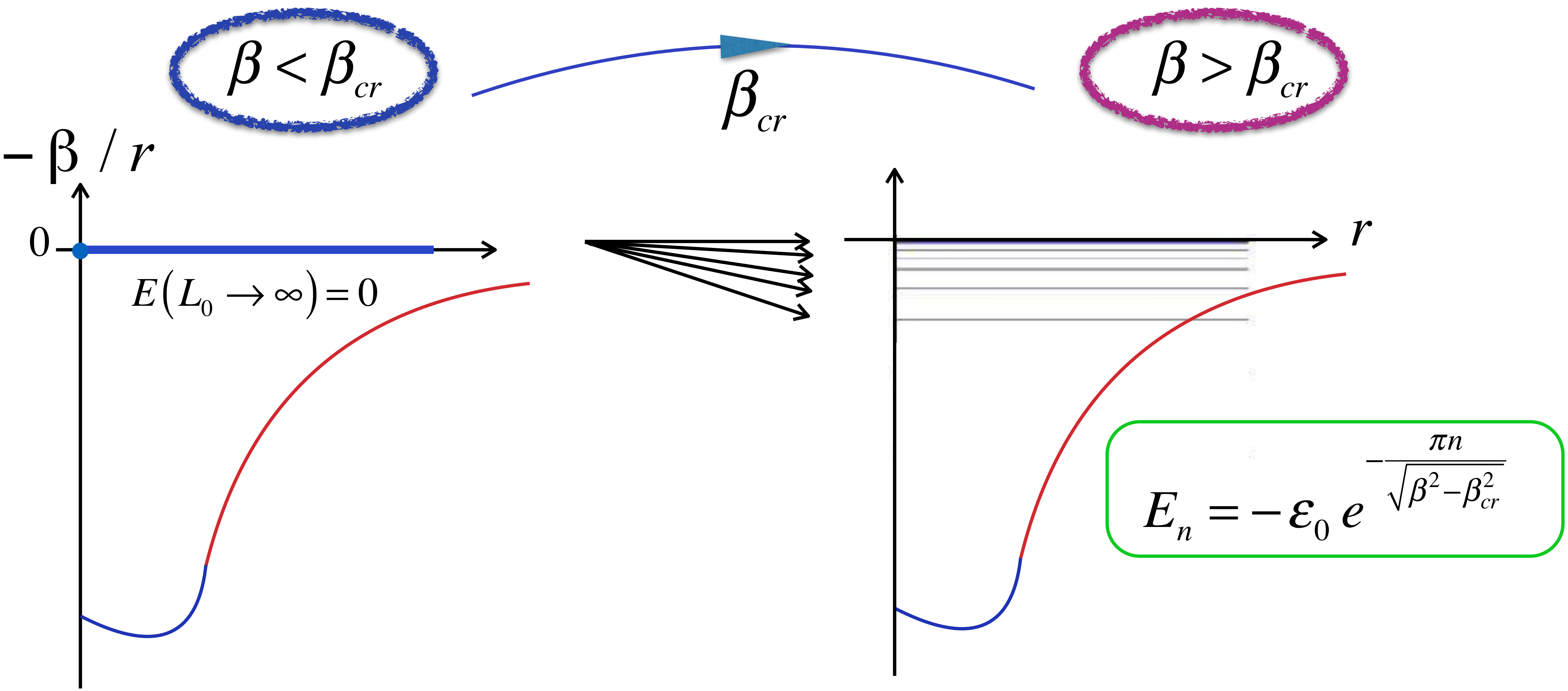
Important and measurable spectral signature (for the zero modes):
quantum phase transition (scale anomaly) !

Omrie Ovdat, J. Mao, Eva Andrei, E.A (2017)

Dirac spectral quantum phase transition

Dimensionless coupling $\beta \equiv Z\alpha$

Singular value $\boxed{\beta_{cr} = \frac{d-1}{2} = \frac{1}{2}}$



Continuous scale invariance (CSI)

Discrete scale invariance (DSI)

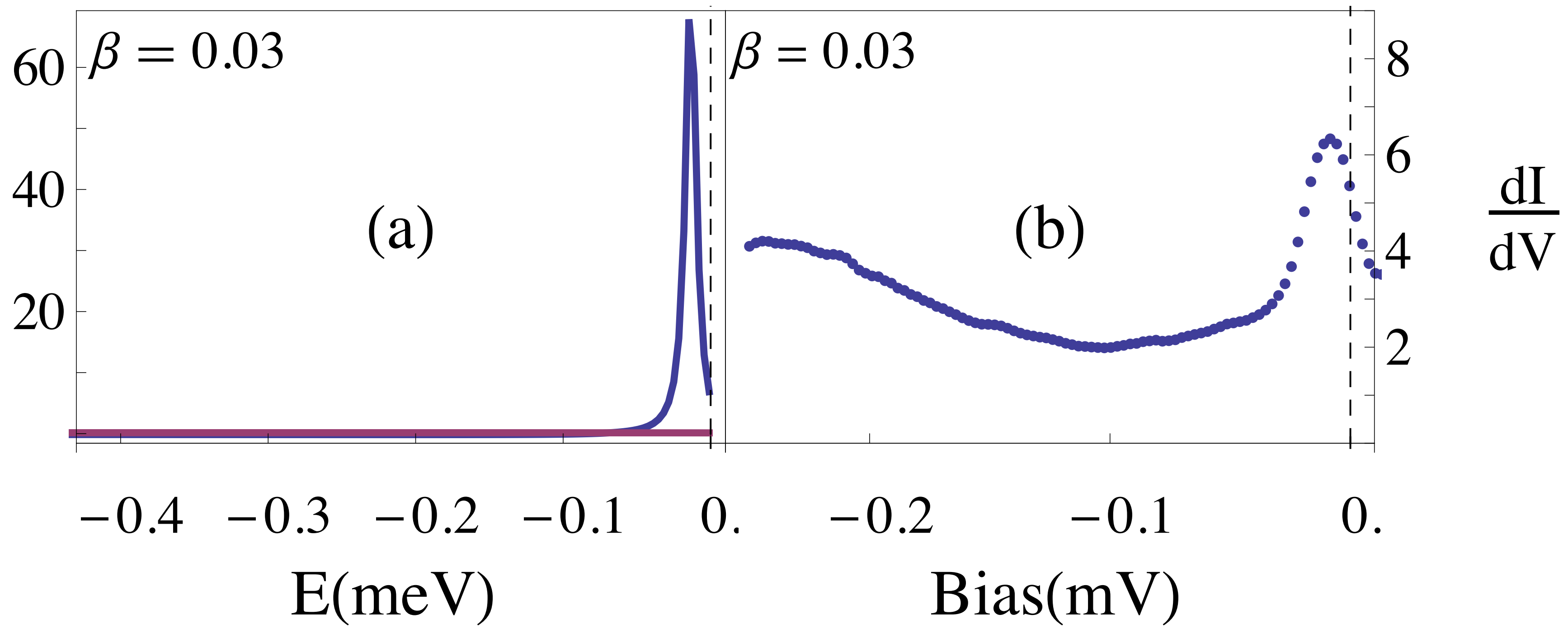
Spectral signature of vacancies

- Massless Dirac Coulomb model :

$$H = -i\boldsymbol{\sigma}\cdot\nabla - \beta / r \qquad \beta \equiv Z\alpha$$

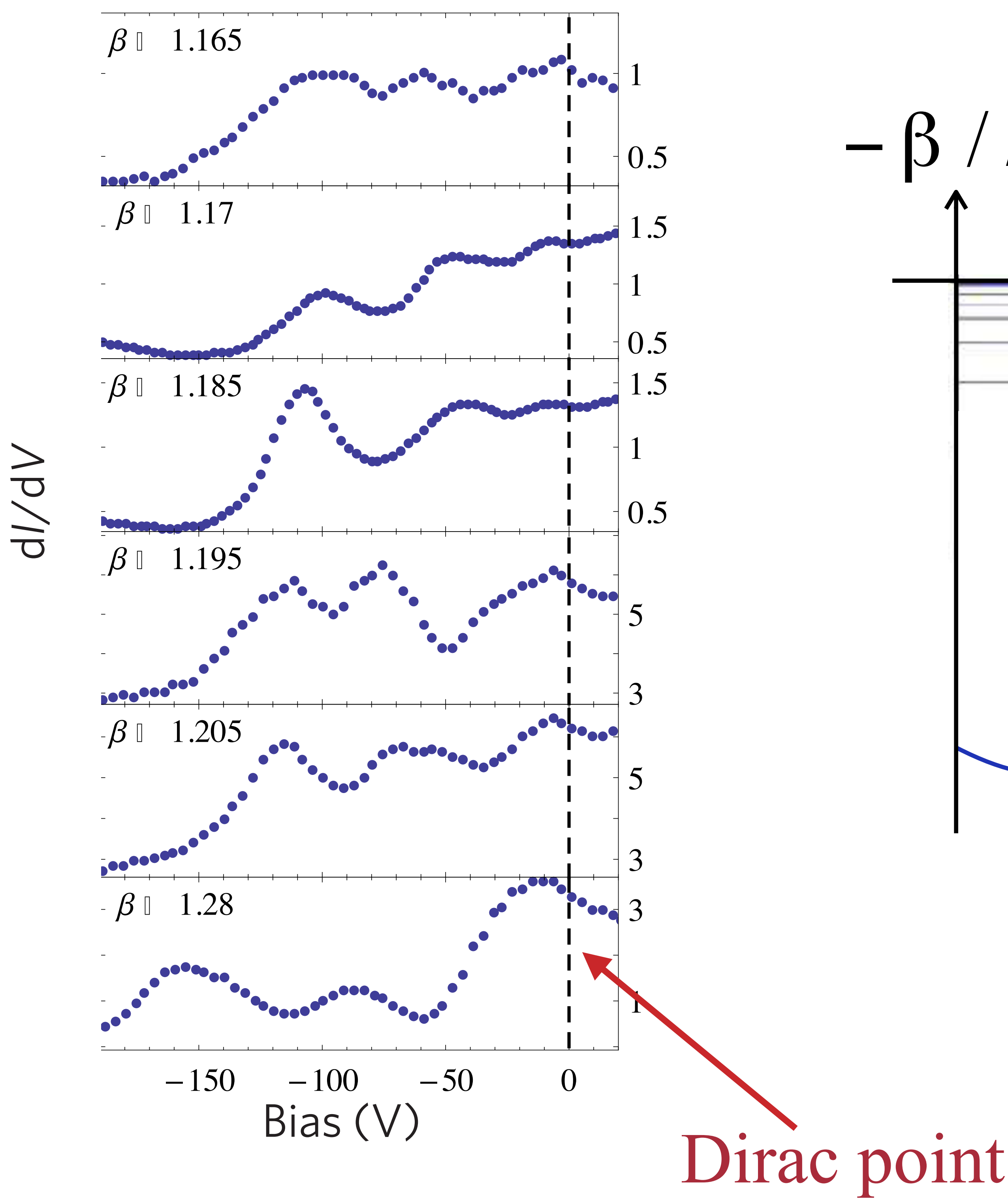
fine structure constant

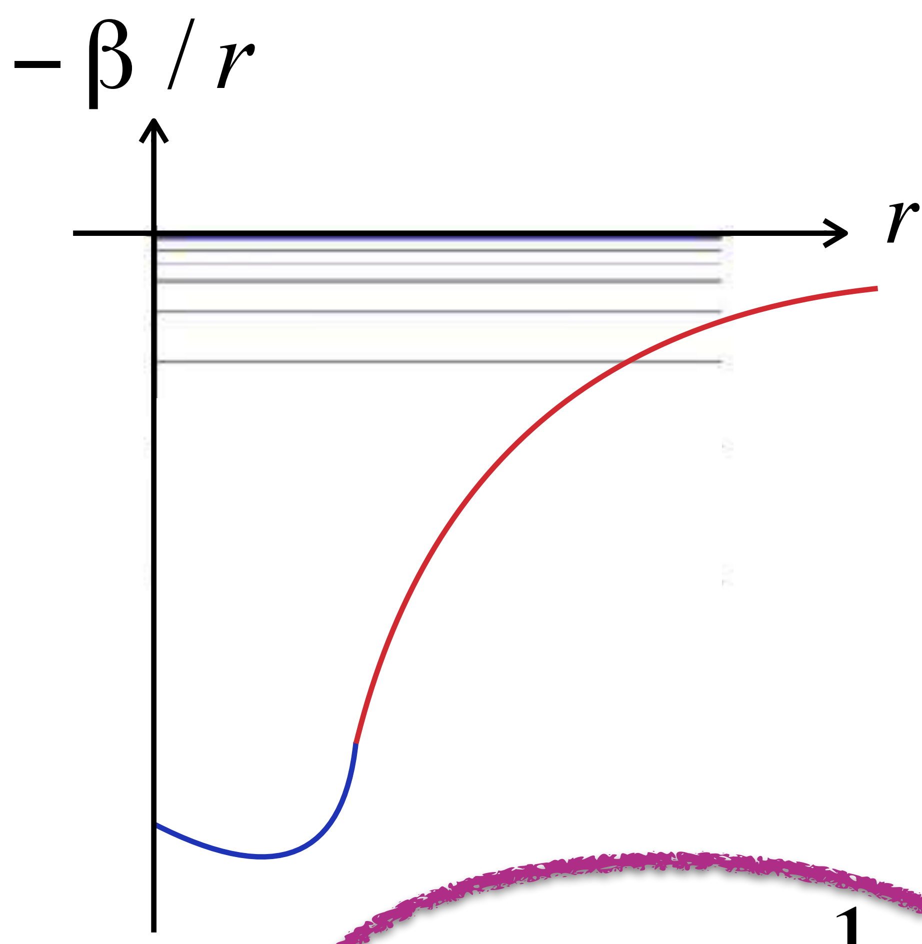
$\beta < 1/2$: Single quasi bound state



Spectral signature of vacancies

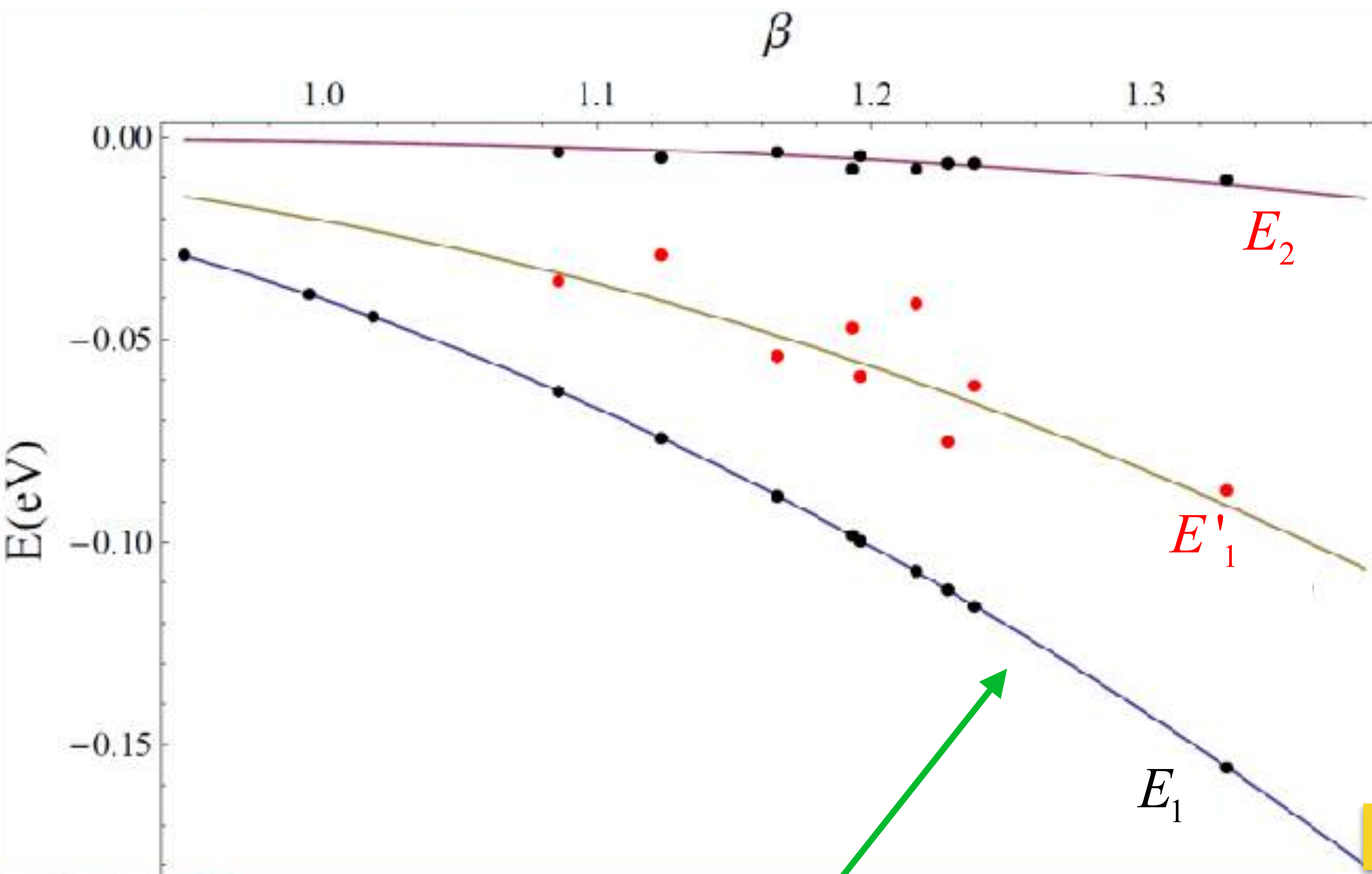
Experiment





$$\beta > \beta_{cr} \equiv \frac{1}{2}$$

Spectral signature of vacancies



$n = 2$

$n = 1$

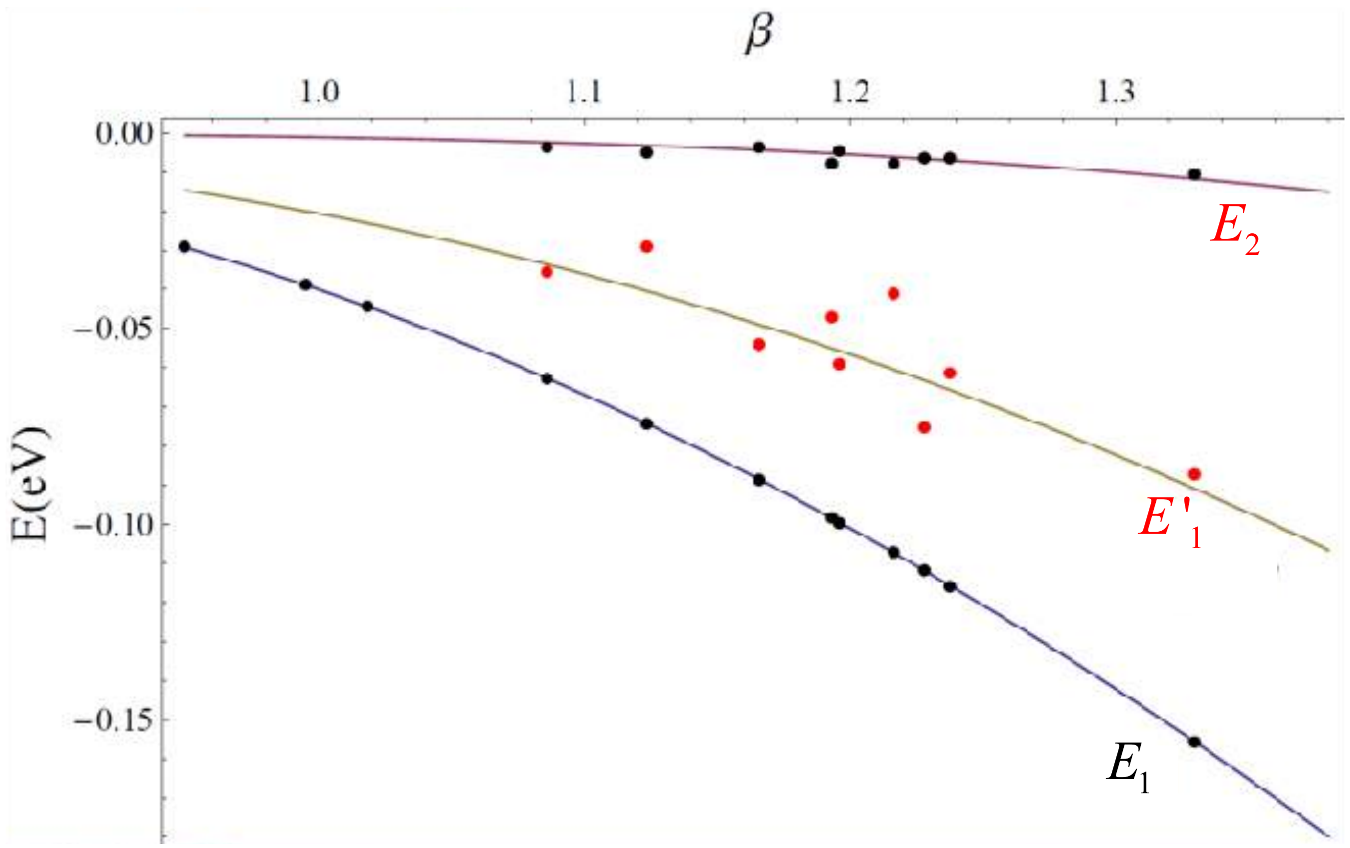
$$\beta > \beta_{cr} \equiv \frac{1}{2}$$

$$E_n = -\varepsilon_0 \, e^{-\frac{\pi n}{\sqrt{\beta^2 - \beta_{cr}^2}}}$$

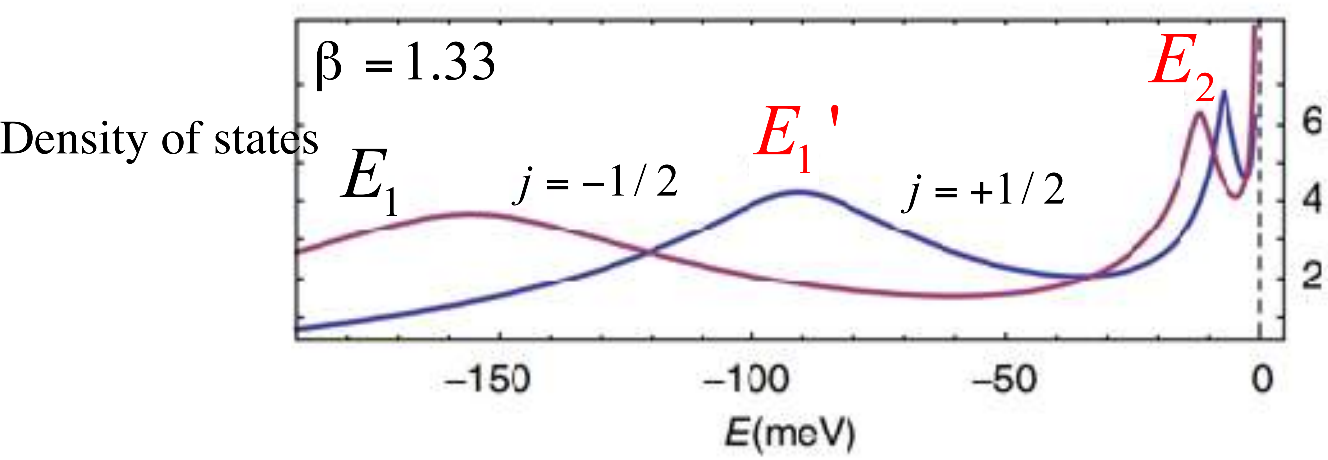
Omrie Ovdat, J. Mao, Eva Andrei, E.A (2017)

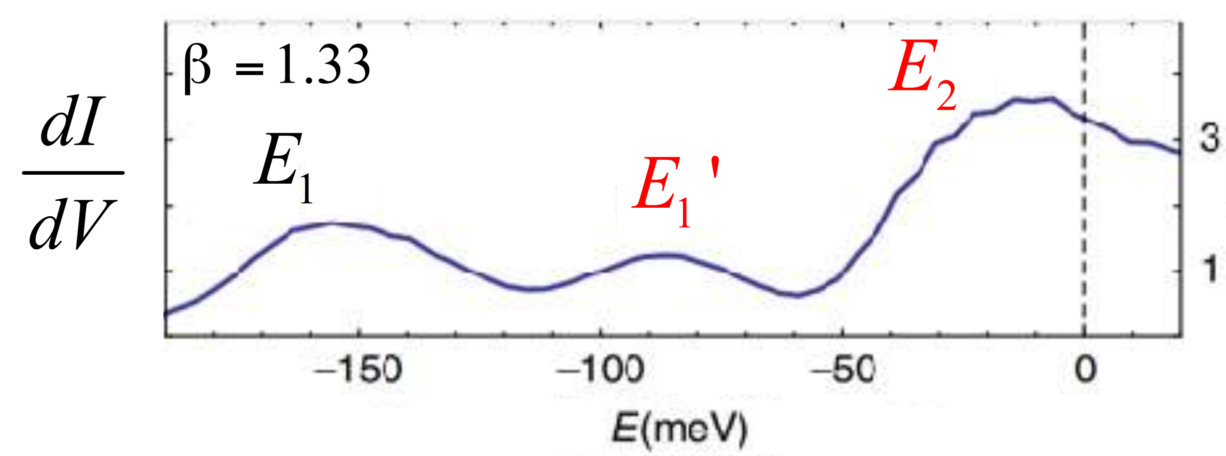
Parity breaking

For s-wave channel m=0,-1, total angular momentum 1/2



Degeneracy lifting for a vacancy between the two lowest angular momentum channels $j = \pm 1/2$

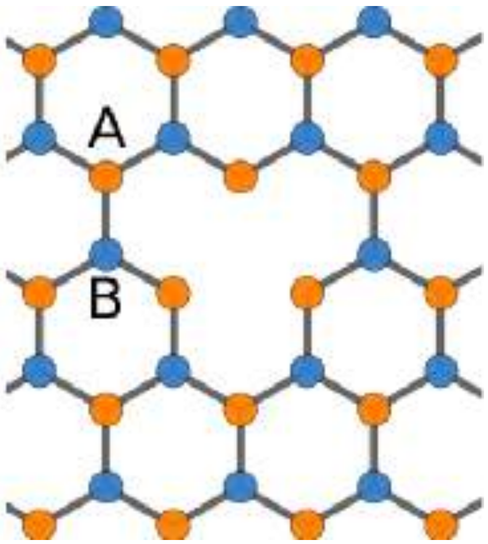




Multiple vacancies : zero modes

N_A A vacancies

N_B B vacancies



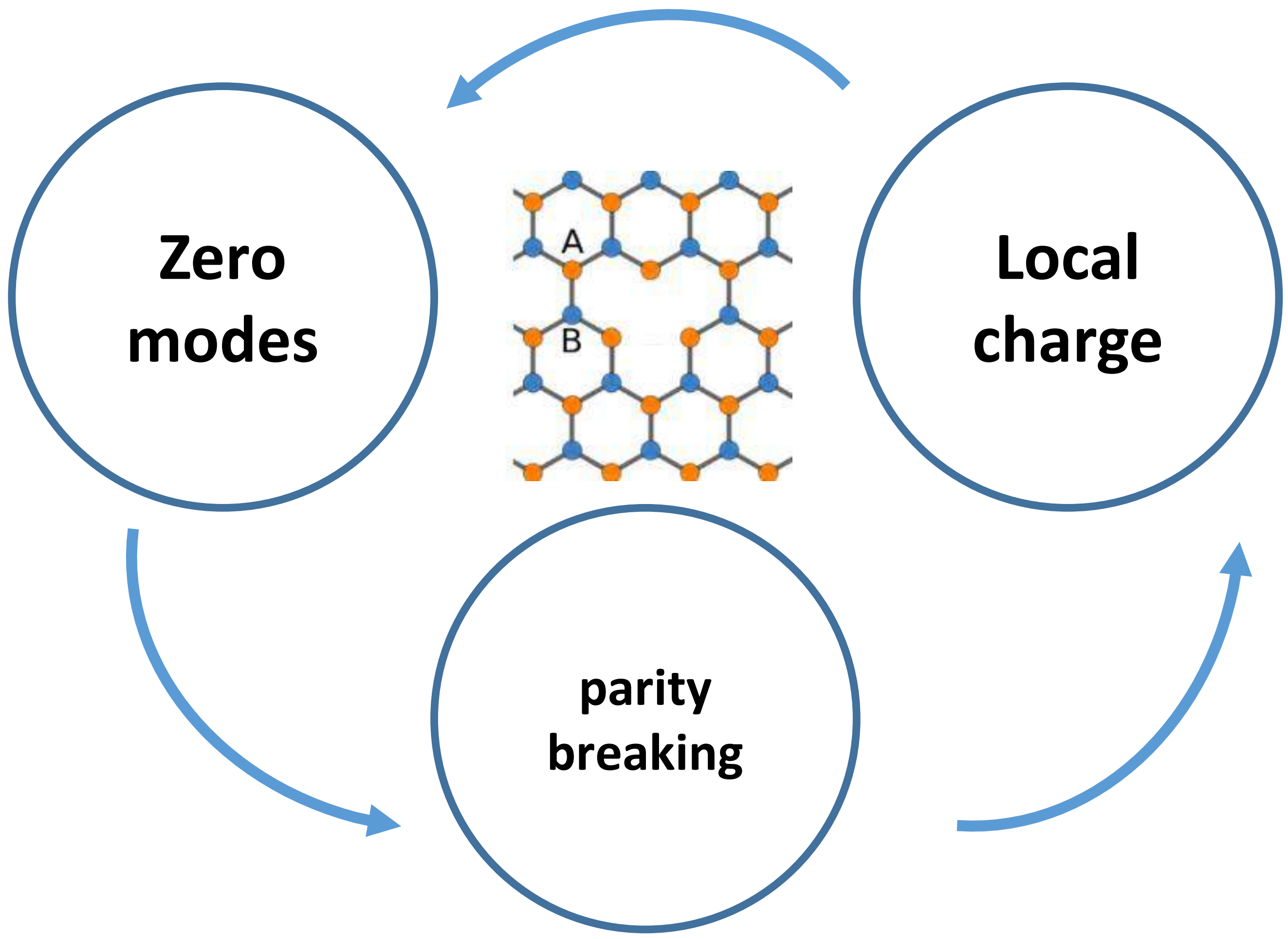
$$H = -t \sum_{\langle i,j \rangle} c_i^{\dagger} c_j + h.\text{c.}$$

$$\# \text{ of zero modes} = |N_A - N_B|$$

Numerical diagonalization
finite lattice

B. Sutherland, Phys. Rev. B 34, 5208–5211 (1986)
E. H. Lieb, Phys. Rev. Lett. 62, 1201 (1989)
V. M. Pereira,et al., Phys. Rev. Lett. 96, 036801 (2006)

Vacancies in graphene



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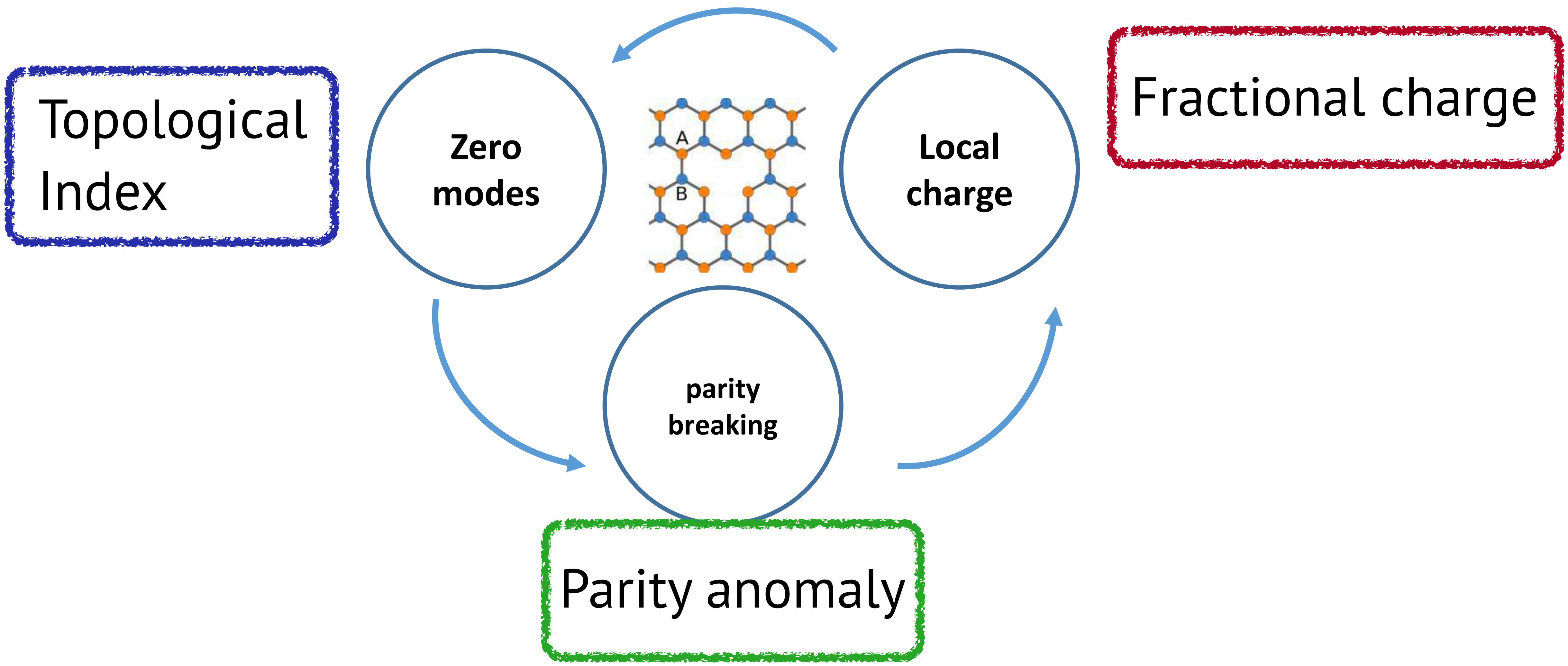
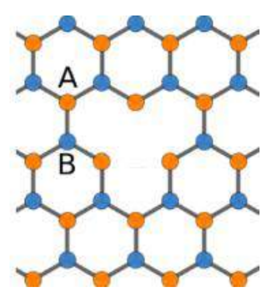


Vacancies in graphene

$$\#\text{ of zero modes} = |N_A - N_B| = |\text{Index } H|$$

Topological Index

Zero modes



Local charge

Fractional charge

parity breaking

Parity anomaly

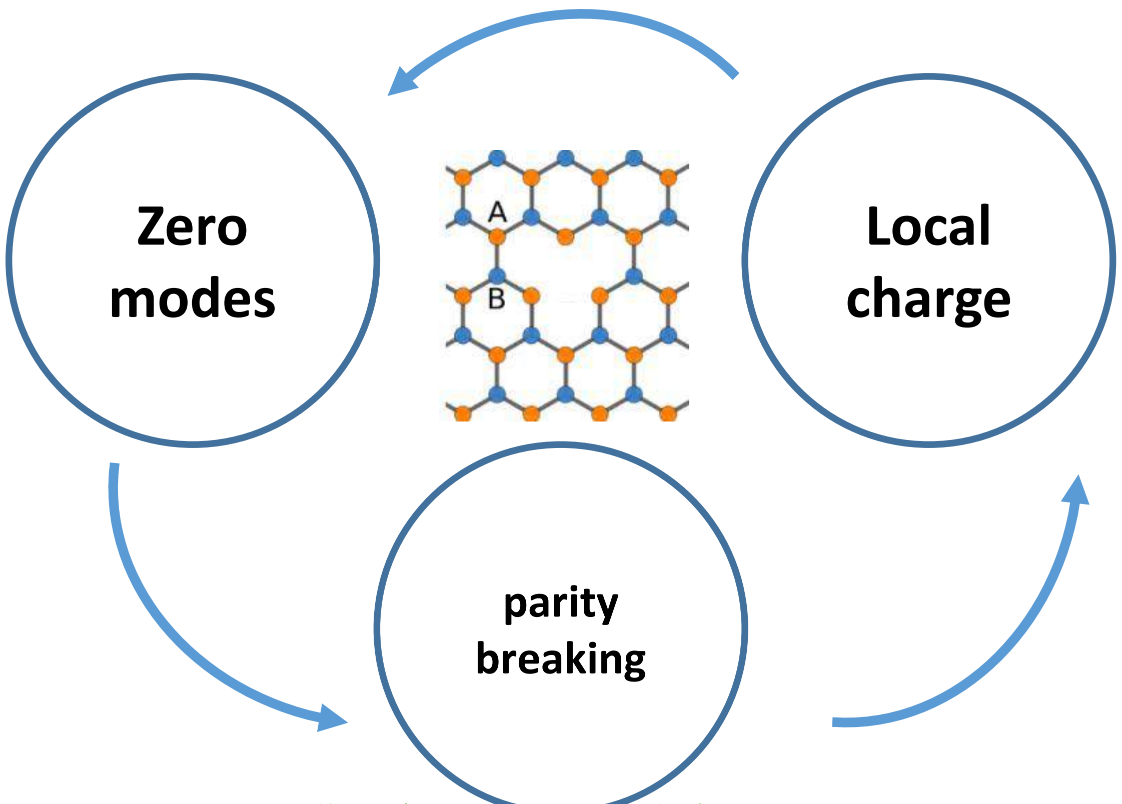
Vacancies in graphene

$$\#\text{ of zero modes} = |N_A - N_B| = |\text{Index } H|$$

$$\text{Index } H \equiv \dim\ker D - \dim\ker D^{\dagger}$$

$$H = -i\,\boldsymbol{\sigma}\cdot\boldsymbol{\nabla} = \begin{pmatrix} 0 & D \\ D^{\dagger} & 0 \end{pmatrix}$$

Topological Index



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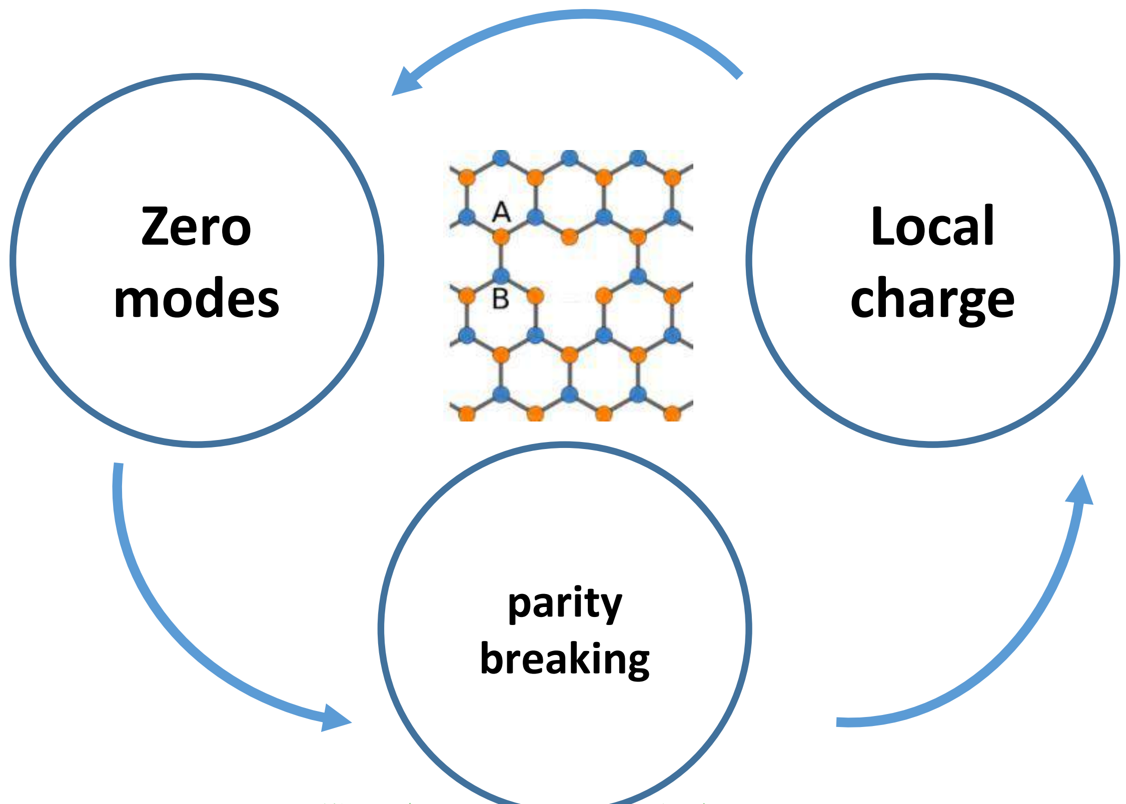

Fractional charge

$$Q = -\frac{e}{2}\operatorname{Index} H$$

Parity anomaly

Vacancies in graphene

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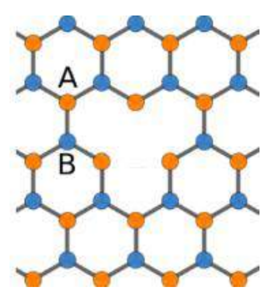
Topological Index

Zero modes



Local charge

Fractional charge

$$Q = -\frac{e}{2}\,\mathrm{Index}\, H$$

parity breaking

Parity anomaly

$$Q \xrightarrow{\text{Parity}} -Q$$

Topological features of vacancies in graphene

- All these features can be explained showing that a vacancy plays the role of a topological edge state.

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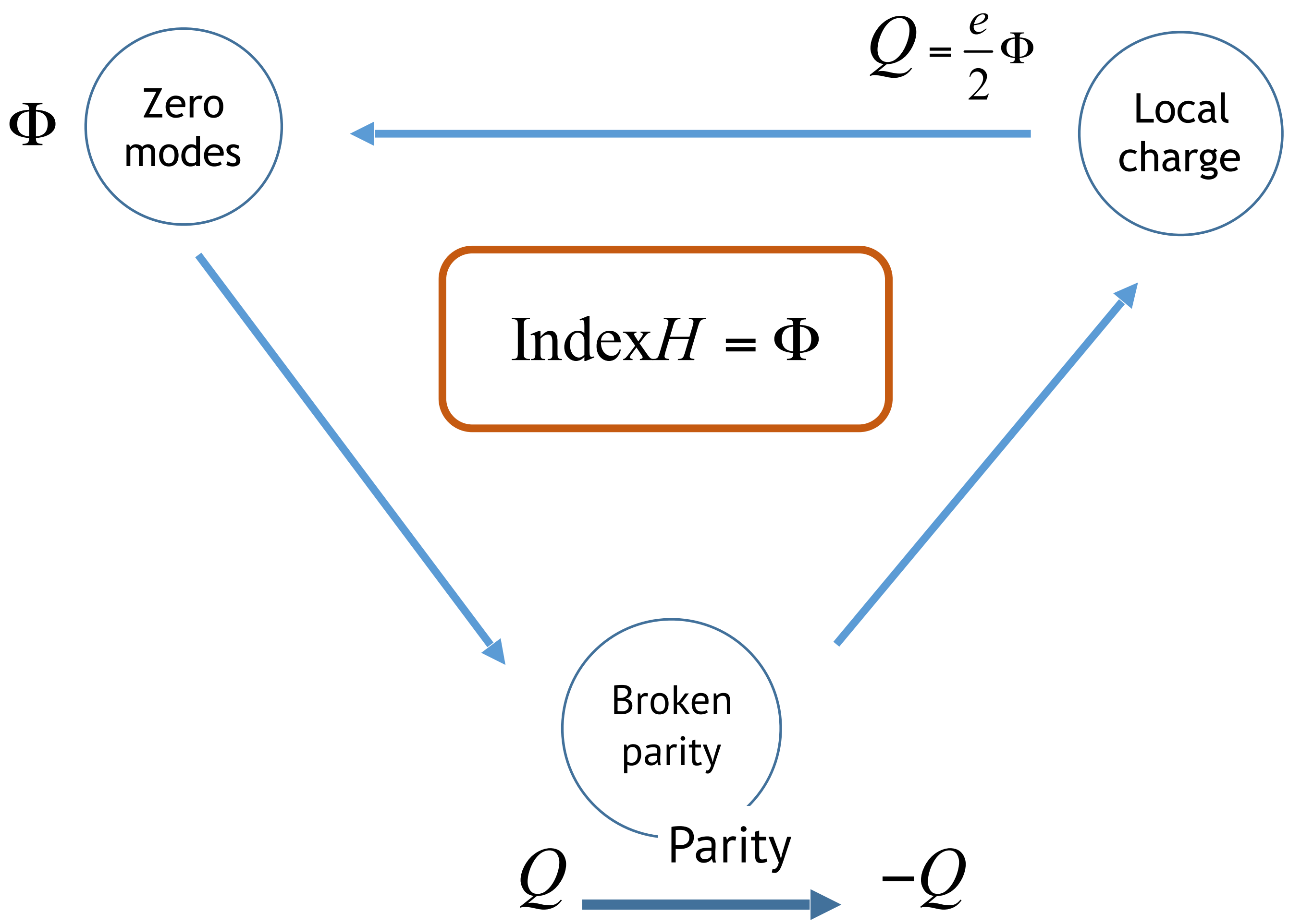
Topological content of magnetic flux is replaced by vacancies



- <u>Massless Dirac model + magnetic flux</u>

Compact space without boundaries :

Atiyah-Singer Index theorem.

- <u>Massless Dirac model + vacancies in graphene :</u>

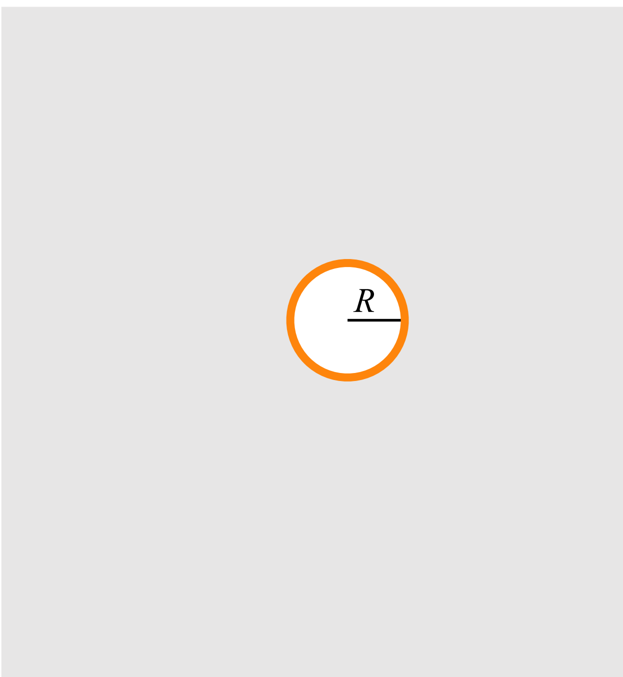
Topological content of the magnetic flux_is replaced by holes in the plane.

$$\boxed{N_B - N_A \Leftrightarrow \Phi}$$

Index theorem in an open space with boundaries and no gauge field

R. Jackiw Phys. Rev. D 29, 2375 (1984)
A. J. Niemi and G. W. Semenoff Phys. Rev. Lett. 51, 2077 (1983)
D. Boyanovsky and R. Blankenbecler Phys. Rev. D 31, 3234 (1985)
M. Ninomiya and C, Tan, Nuclear Physics B 257, 199 (1985)
E. Fradkin, E. Dagotto, and D. Boyanovsky Phys. Rev. Lett. 57, 2967 (1986)
Su, W.-P., J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979)

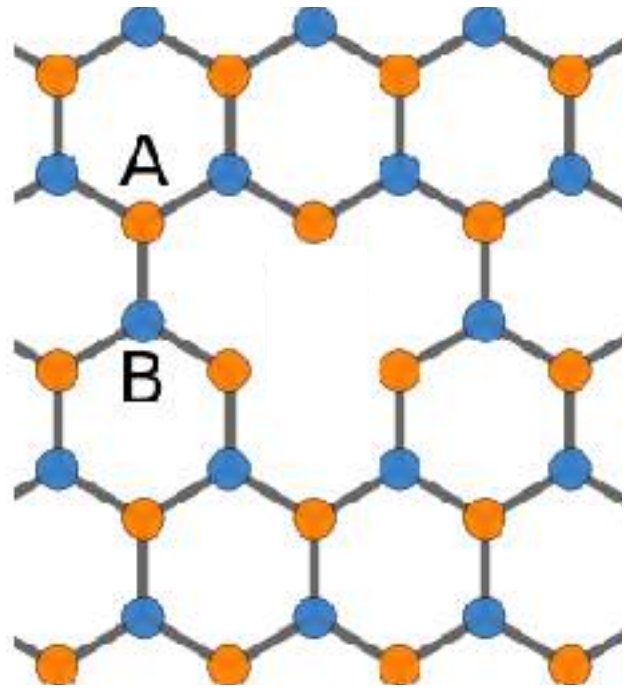
Low energy continuum description



Continuum description

$$\Psi = \begin{pmatrix} \psi_A(\mathbf{r}) \\ \psi_B(\mathbf{r}) \end{pmatrix}$$

$$H_{\text{Dirac}} = \boldsymbol{\sigma} \cdot \mathbf{p}$$

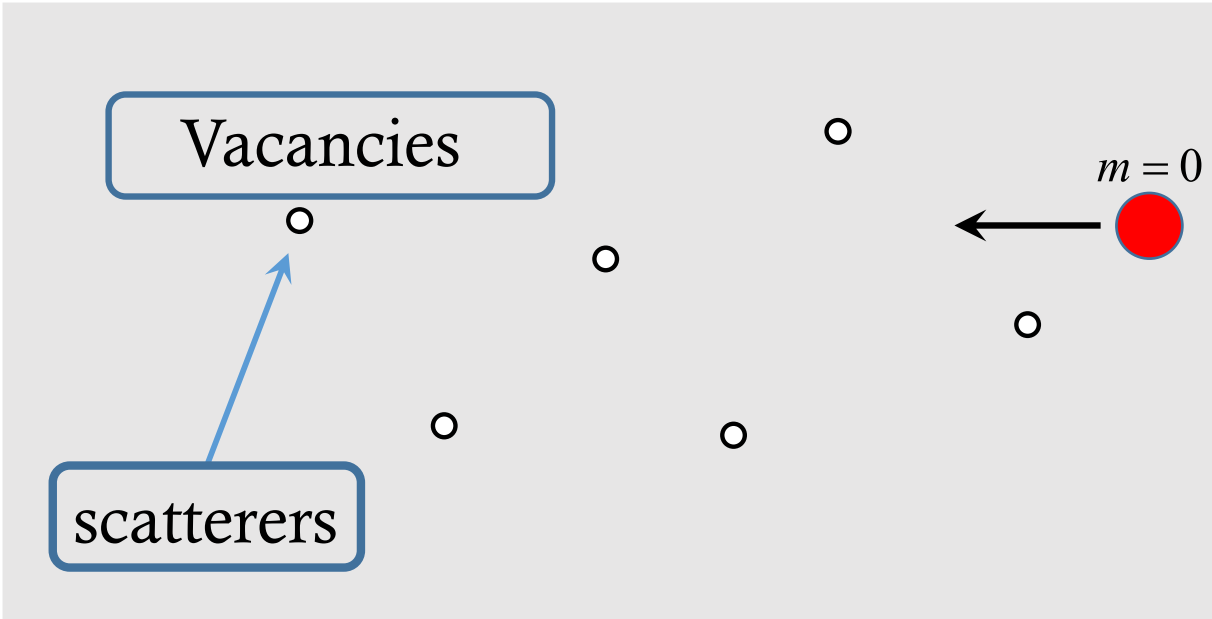


Scattering of a free massless Dirac fermion on a punctured plane

Effective low energy model for graphene:

$$H=\boldsymbol{\sigma}\cdot\mathbf{p}=\begin{pmatrix}0 & -i\partial_x-\partial_y\\ -i\partial_x+\partial_y & 0\end{pmatrix}$$

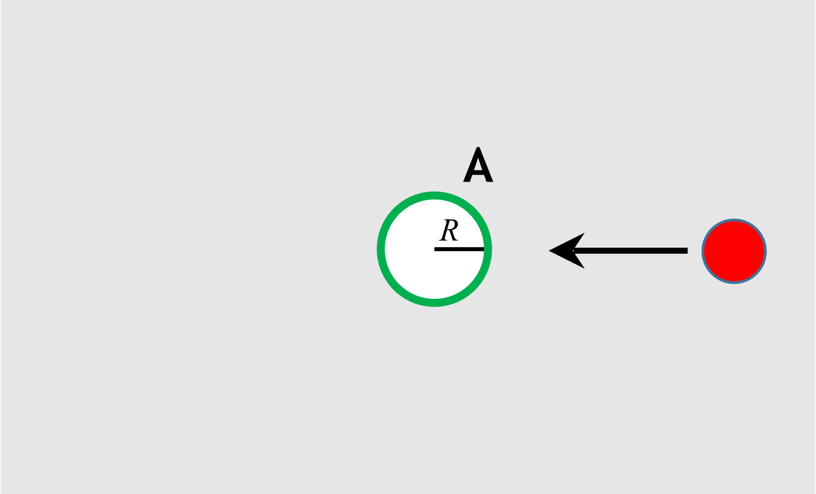
- Single Dirac fermion
- Massless (relativistic) $E=\pm|p|$
- Free (No potential)
- Infinite plane
- Non-trivial topology



Single A-vacancy

Zero energy eigenfunctions : $H\psi(\mathbf{r}) = -i\boldsymbol{\sigma}\cdot\nabla\psi(\mathbf{r}) = 0$

$$\psi(r,\theta,E) = \sum_{m\in\mathbb{Z}} e^{im\theta}\begin{pmatrix}\psi_m^A(r,E)\\ i\psi_m^B(r,E)e^{i\theta}\end{pmatrix}$$



Determined by boundary conditions

$$\psi_m^A|_{r=R} = 0, \quad m \le 0$$
$$\psi_m^B|_{r=R} = 0, \quad m > 0$$

Chiral boundary condition

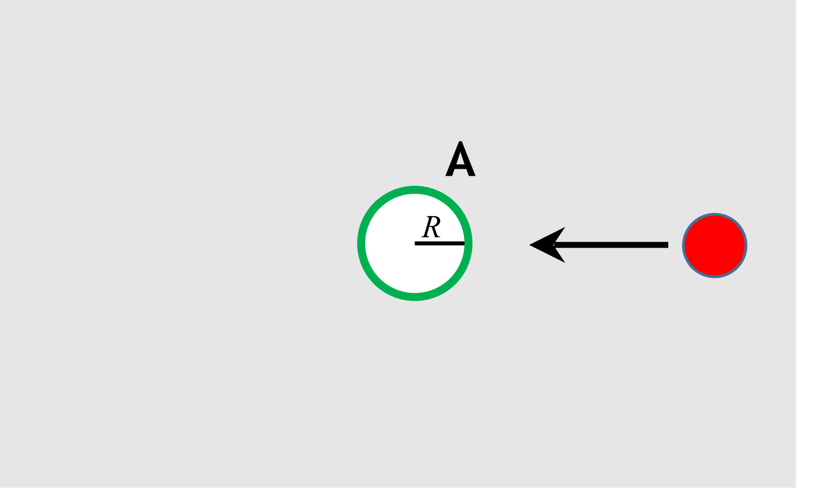
Non standard, *m* dependent, parity breaking

m	$\psi_m^B\|_{r=R}$	$\psi_m^A\|_{r=R}$
$\vdots$	0	
1	0	
0		0
-1		0
-2		0
$\vdots$		0

Single A-vacancy

Zero energy eigenfunctions :

$$\psi(r,\theta) \xrightarrow{\boxed{\text{unique}}} \begin{pmatrix} 0 \\ iB_0 r^{-1} e^{i\theta} \end{pmatrix}$$



All modes, except for :

$$j = \pm 1/2 \leftrightarrow m = -1, 0$$

are projected out.

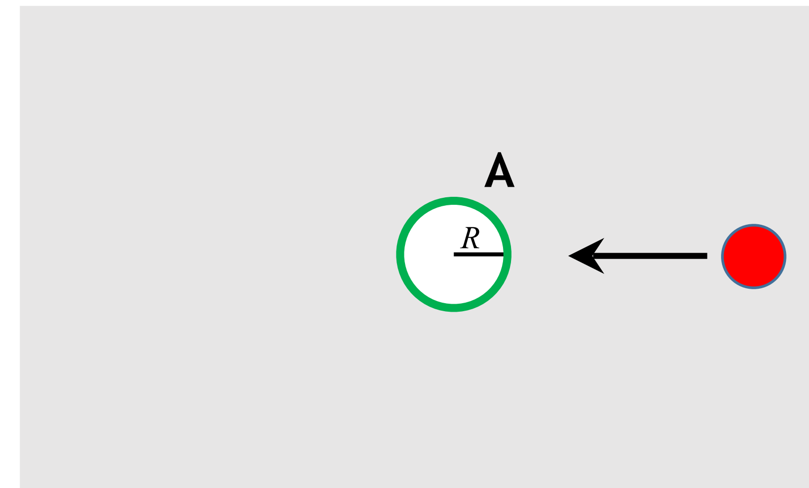
Consistent with the tight-binding model

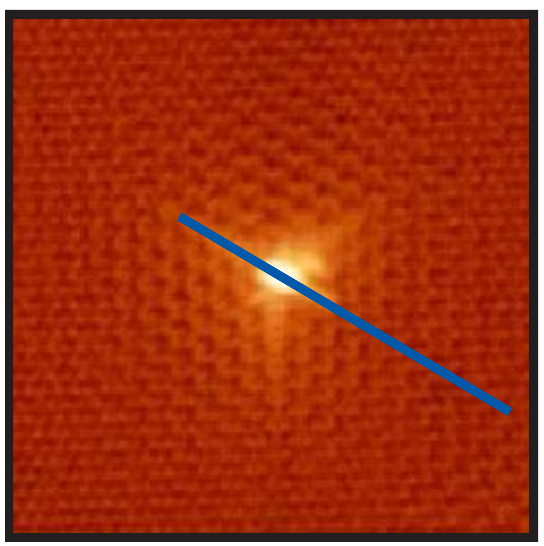
m	$\psi_m^B\|_{r=R}$	$\psi_m^A\|_{r=R}$
$\vdots$	0	
1	0	
0		0
-1		0
-2		0
$\vdots$		0

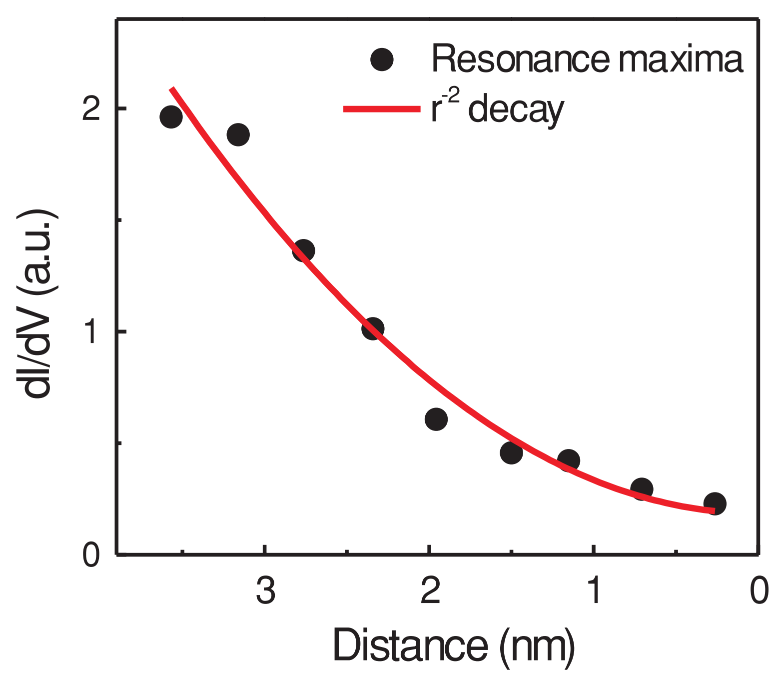
Single A-vacancy

Zero energy eigenfunctions :

$$\psi(r,\theta) \xrightarrow{\boxed{\text{unique}}} \begin{pmatrix} 0 \\ iB_0 r^{-1} e^{i\theta} \end{pmatrix}$$





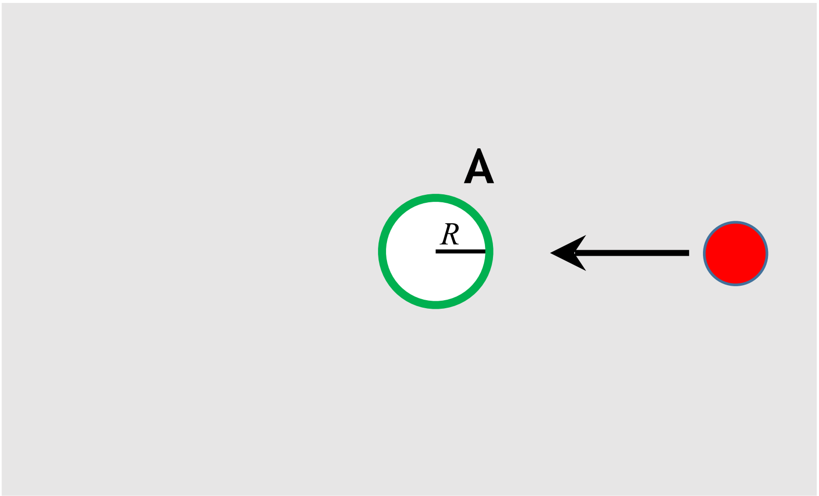


m	$\psi_m^B\vert_{r=R}$	$\psi_m^A\vert_{r=R}$
⋮	0	
1	0	
0		0
-1		0
-2		0
⋮		0

M.M. Ugeda et al. Phys. Rev. Lett (2010)

Chiral boundary conditions break parity but conserve energy reflection

$$H = \begin{pmatrix} 0 & D \\ D^\dagger & 0 \end{pmatrix}$$



- **Energy reflection symmetry**

For every $E > 0$ state
there is a $E < 0$ state

m	$\psi_m^B\|_{r=R}$	$\psi_m^A\|_{r=R}$
⋮	0	
1	0	
0		0
-1		0
-2		0
⋮		0

- **Parity symmetry**

Chiral boundary conditions
do not preserve parity :

$$m \to -m - 1$$

Fractional charge

- Charge density of the Dirac vacuum

$$\rho(\mathbf{r}) = -\frac{e}{2}\sum_n \mathrm{sign}(E_n)\psi_n^\dagger(\mathbf{r})\psi_n(\mathbf{r})$$

With a single vacancy $\rho(\boldsymbol{r}) = -\frac{1}{2\pi}\boldsymbol{\nabla}\cdot\left(\frac{e/2}{r}\hat{\boldsymbol{r}}\right)$

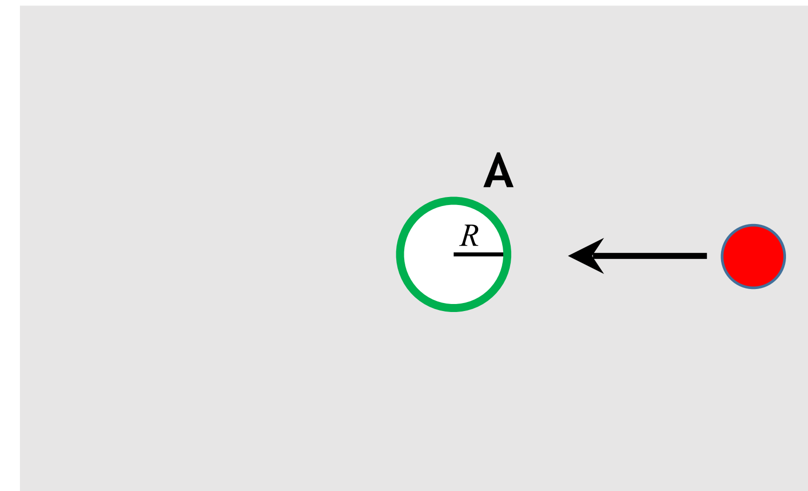
$$Q \equiv \int d\boldsymbol{r}\rho(\boldsymbol{r}) = -\frac{e}{2}\,\mathrm{Index}\,H$$

#of zero modes

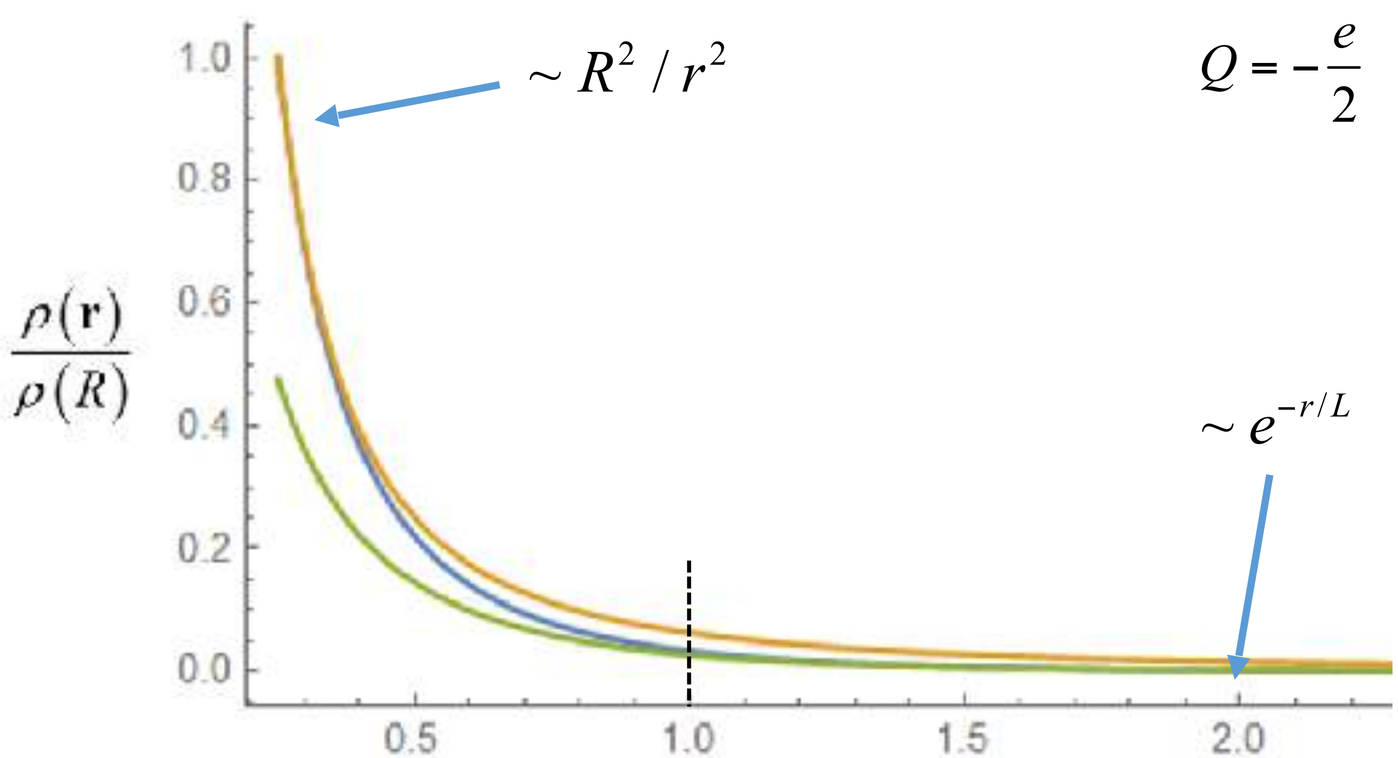
Fractional charge

- Single vacancy charge density

$$\rho\left(\boldsymbol{r}\right) = -\frac{1}{2\pi}\boldsymbol{\nabla}\cdot\left(\frac{e/2}{r}\hat{\boldsymbol{r}}\right) \qquad R \to 0$$



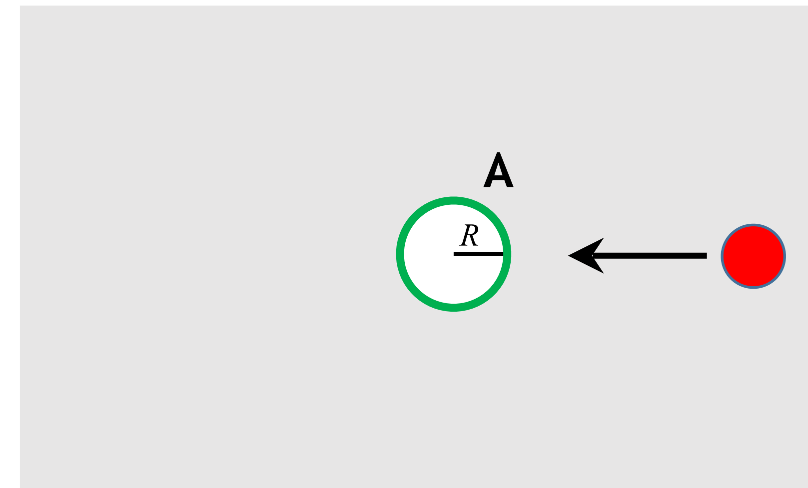
$$\rho(\mathbf{r}) = \pm\frac{e}{2}\left|\psi(\mathbf{r}, E=0)\right|^2$$



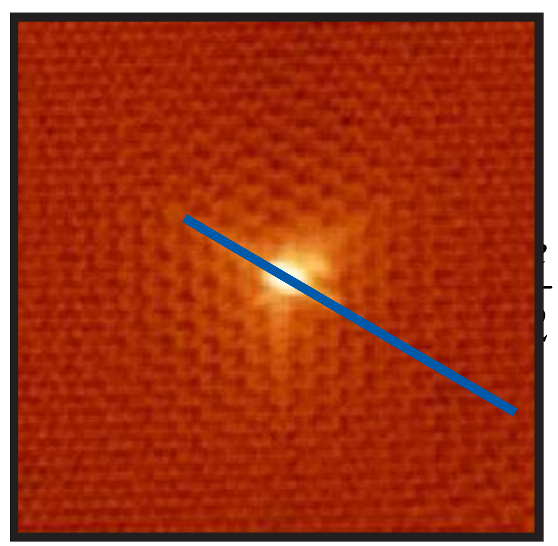
Fractional charge

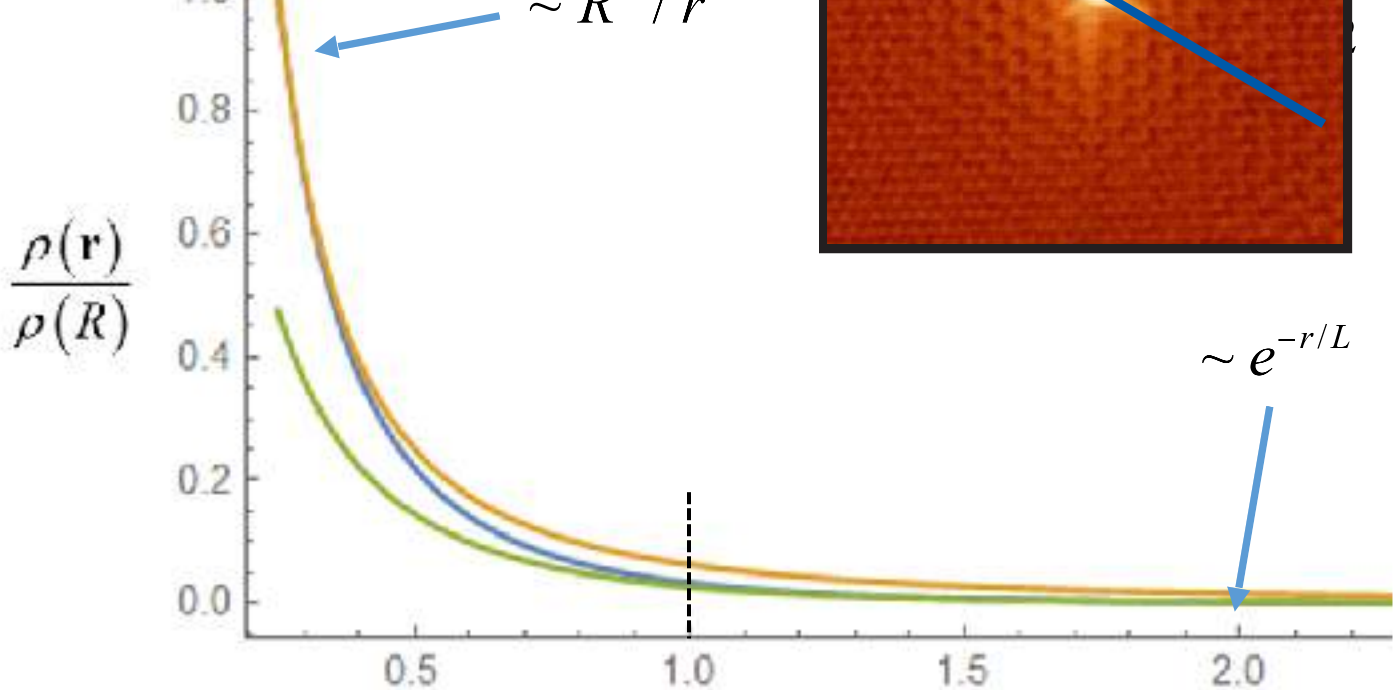
- Single vacancy charge density

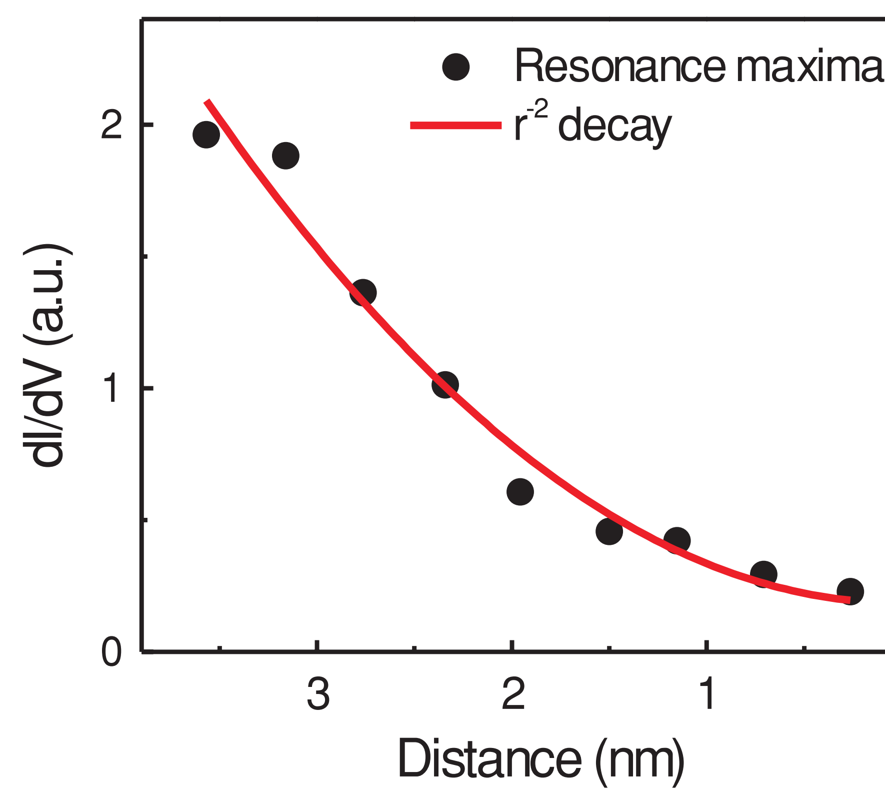
$$\rho(\boldsymbol{r}) = -\frac{1}{2\pi}\boldsymbol{\nabla}\cdot\left(\frac{e/2}{r}\hat{\boldsymbol{r}}\right) \qquad R \to 0$$



$$\rho(\mathbf{r}) = \pm\frac{e}{2}\left|\psi(\mathbf{r}, E=0)\right|^2$$







M.M. Ugeda et al. Phys. Rev. Lett (2010)

Fractional charge

#of zero modes

$$\boxed{Q = \frac{e}{2}\left(\sum_{E_n>0} 1 - \sum_{E_n<0} 1\right) = -\frac{e}{2}\,\mathrm{Index}\,H}$$

Fractional charge

$\boxed{\text{\#of zero modes}}$

$$\boxed{Q = \frac{e}{2}\left(\sum_{E_n>0} 1 - \sum_{E_n<0} 1\right) = -\frac{e}{2}\,\mathrm{Index}\,H}$$

$\boxed{\text{Vanishes without vacancies}}$

$\boxed{\text{Can be fractional}}$

Fractional charge

#of zero modes

$$Q = \frac{e}{2}\left(\sum_{E_n>0} 1 - \sum_{E_n<0} 1\right) = -\frac{e}{2}\,\mathrm{Index}\,H$$

Vanishes without vacancies

Can be fractional

Spectral asymmetry of topological origin

Multiple vacancies- topological switch

$$Q = \int d^2 x \rho(\mathbf{r}) = -\frac{e}{2}(N_A - N_B) = -\frac{e}{2}\,\mathrm{Index}\,H$$

Ansatz wavefunction

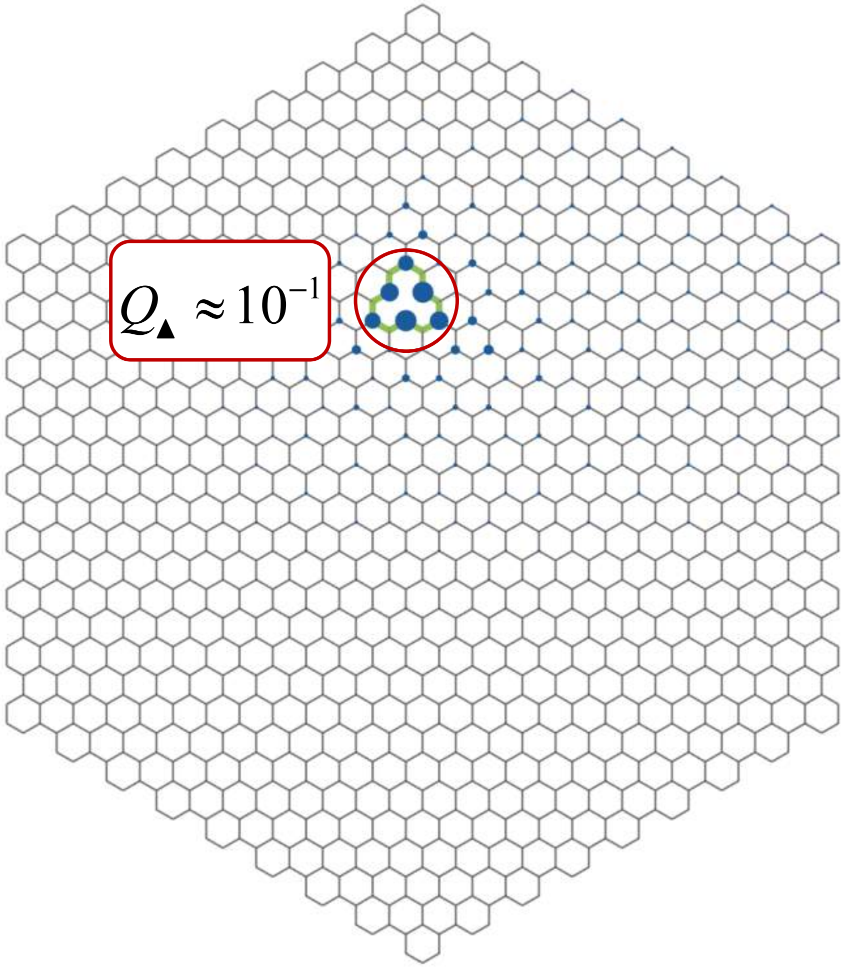
$$\psi_N(z) = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \sum_{k=1}^{N_A} \frac{q_{kA}}{z^* - z^*_{kA}} + \begin{pmatrix} 1 \\ 0 \end{pmatrix} \sum_{k=1}^{N_B} \frac{q_{kB}}{z - z_{kB}}$$

$$\boxed{\#\ \text{of zero modes} = \left| N_A - N_B \right|}$$

Multiple vacancies- topological switch

- Single vacancy

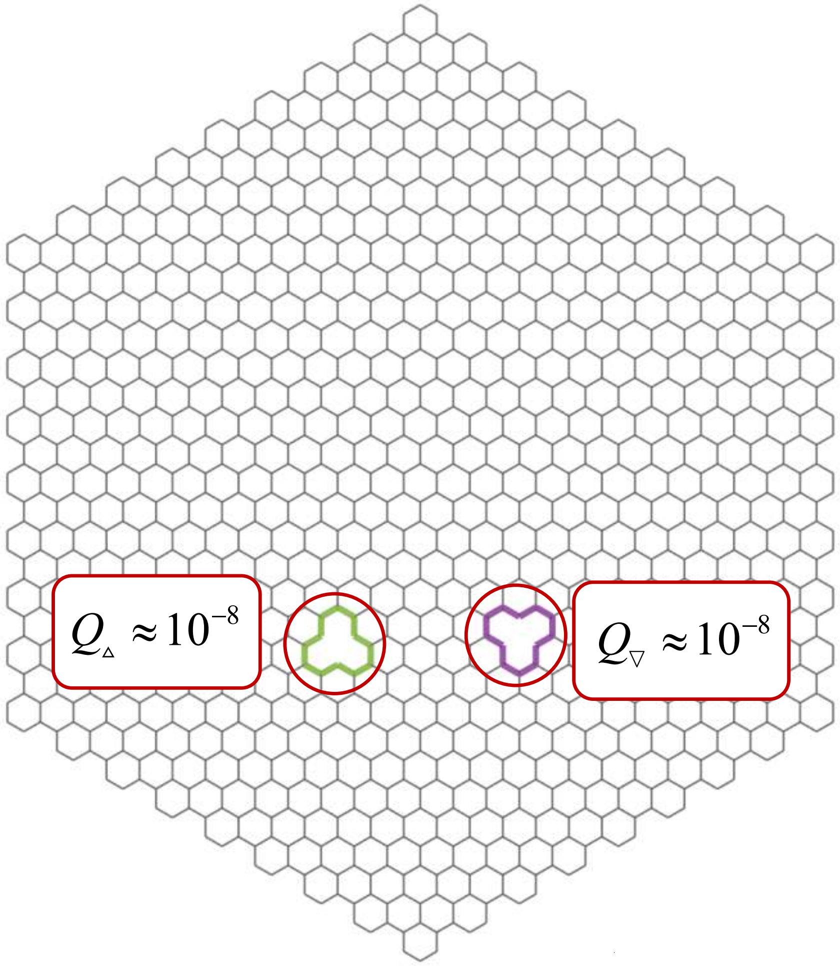
$$Q = -\frac{e}{2}\left|N_A - N_B\right| = -\frac{e}{2}\cdot 1$$



$$\rho(\mathbf{r}) = \pm\frac{e}{2}\left|\psi(\mathbf{r}, E=0)\right|^2$$

- Two vacancies

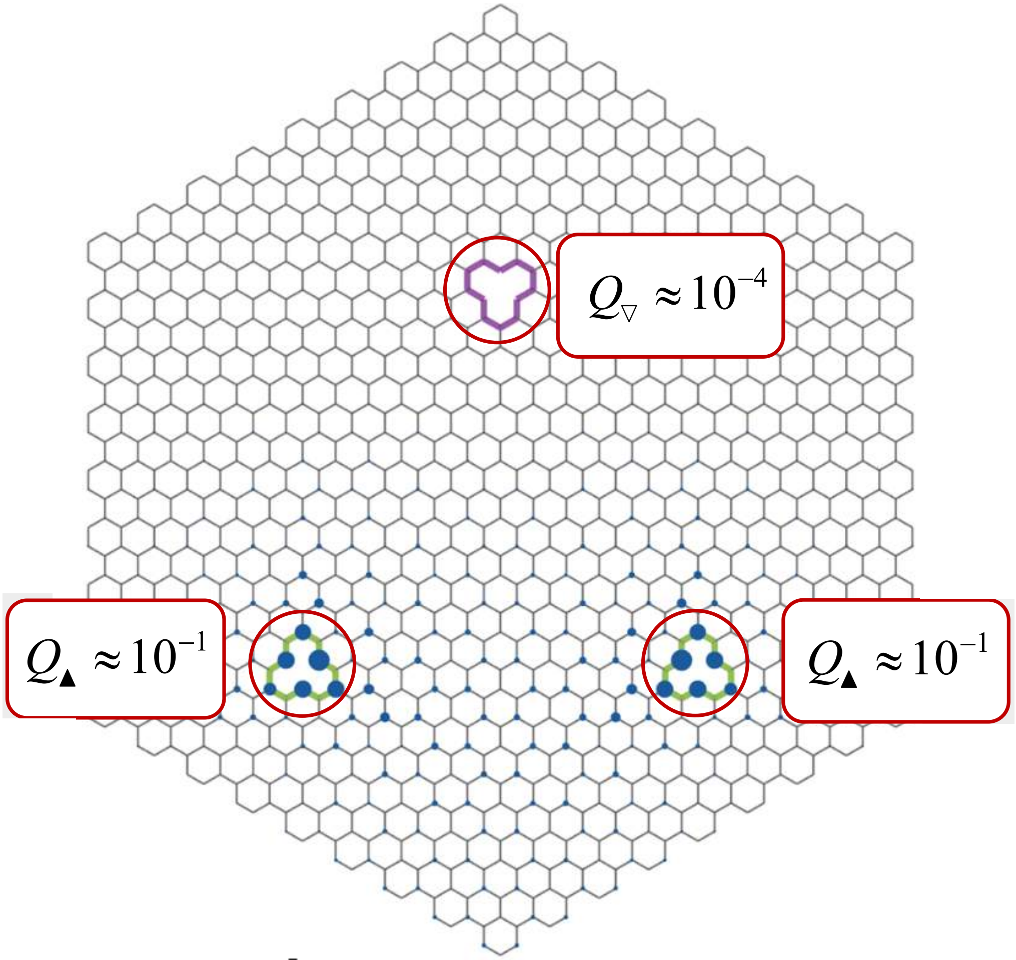
$$Q = -\frac{e}{2}\left|N_A - N_B\right| = -\frac{e}{2}\cdot 0$$



Multiple vacancies- topological switch

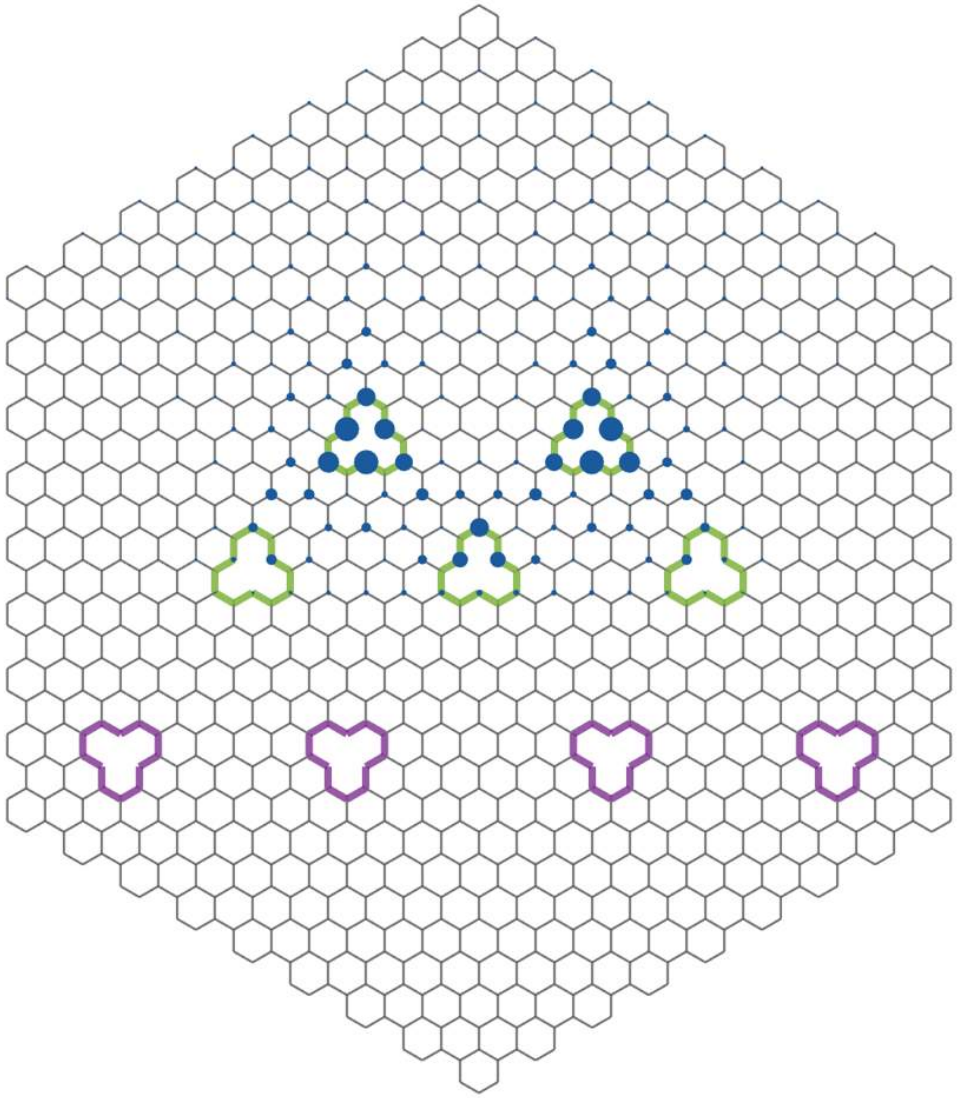
- 3 vacancies : 2 A's and 1 B

$$Q = -\frac{e}{2}\left|N_A - N_B\right| = -\frac{e}{2}\cdot 1$$



$$\rho(\mathbf{r}) = \pm\frac{e}{2}\left|\psi(\mathbf{r}, E=0)\right|^2$$

Multiple vacancies- topological switch

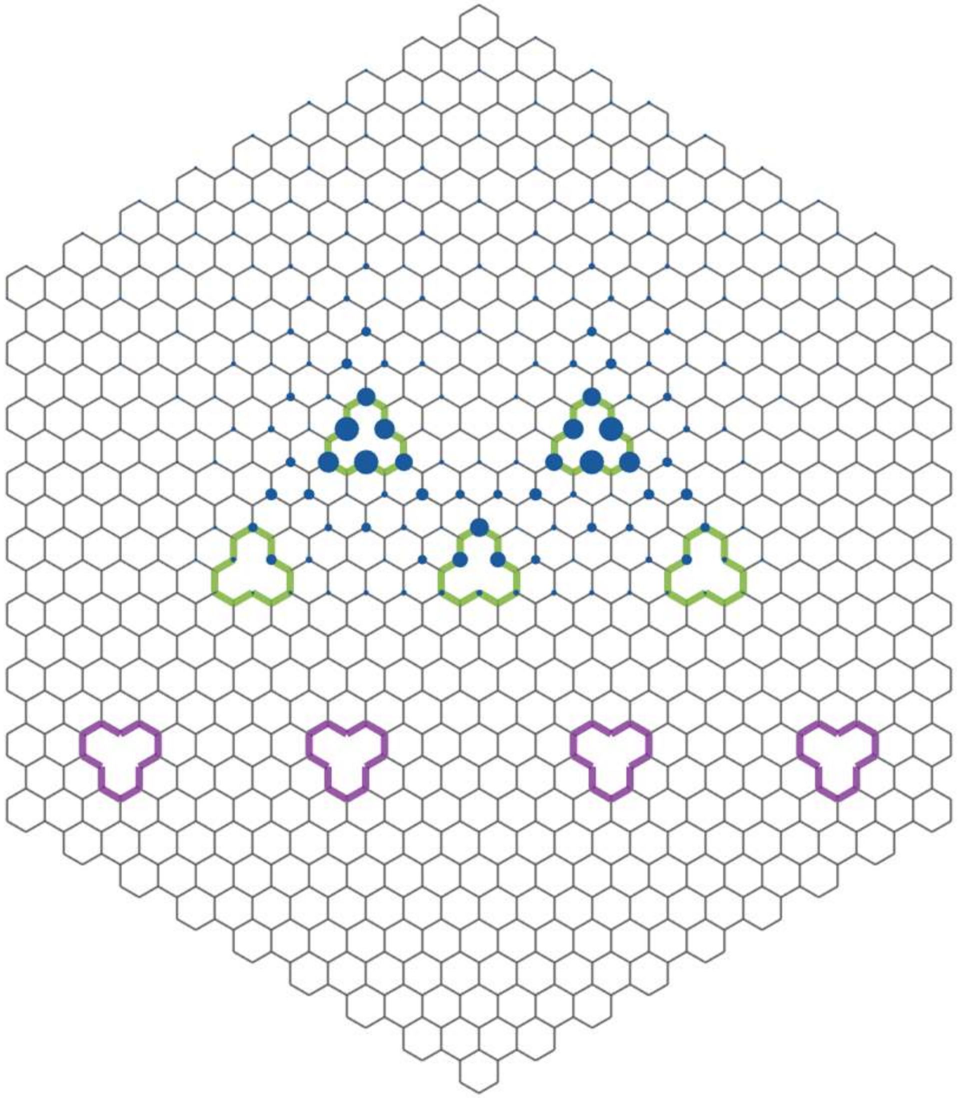


$$N_A = 5,\ N_B = 4$$

$$\mathrm{Index}\, H = |N_A - N_B| = 1$$

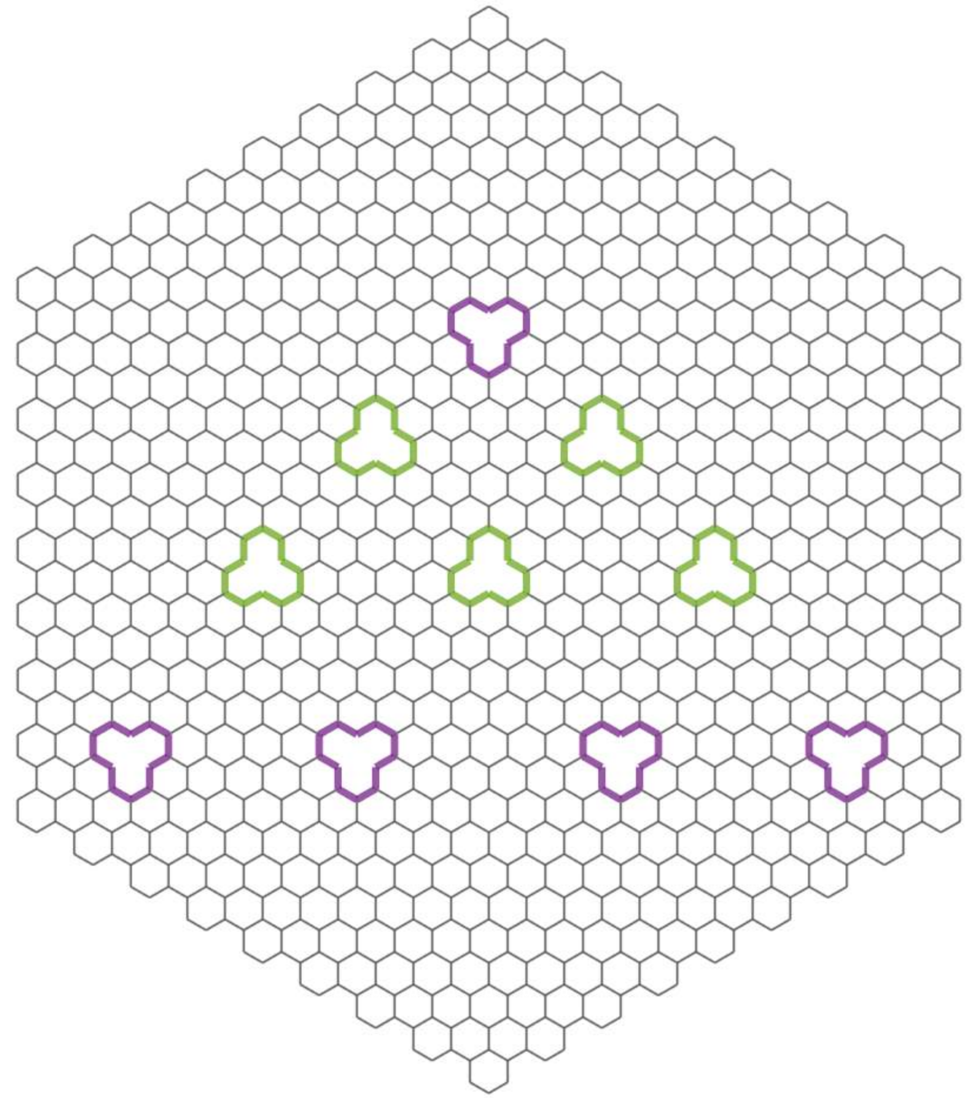
All A vacancies are On and B's Off

Topological switching



$N_A = 5,\ N_B = 4$

$\mathrm{Index}\, H = |N_A - N_B| = 1$



$N_A = 5,\ N_B = 5$

$\mathrm{Index}\, H = |N_A - N_B| = 0$

All A vacancies are On and B's off

All vacancies are Off

Summary-Further directions

- Single atom vacancies in graphene provide realisations of edge state physics of topological origin.

- Graphene vacancies give rise to localised fractional charges, parity symmetry breaking and zero modes.

- Charge fractionalisation result from a new type of chiral boundary conditions without coupling to a gauge field.

- The physics of charged vacancies can be fully described by means of massless free fermions in a Coulomb field.

- This scale free problem leads to a quantum phase transition (scale anomaly) by changing the strength of the local charge.

Summary-Further directions

- Two-dimensional analogous of 1D SSH model.
- Vacancies in graphene allow to realise prominent features of 2+1 QED.
- Existence of zero modes expressed by a topological Index, multi-vacancy modes and related edge state physics have analogs in non electronic graphene. Could be easily observed.
- The Quantum Phase transition (scale anomaly) and parity breaking are specific to (electronic) graphene.
- Magnetism related to vacancies (Lieb Thm. Hubbard + bipartite).

Thank you for your attention.

Some references:

Nature Communications (September 2017)

Phys. Rev. D (RC), March 2018,

J. Phys. A (September 2018)

arXiv:1807.10297 (under review)

Please go to the poster of Omrie and Amit