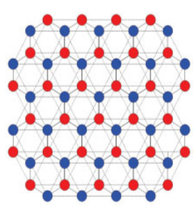
Graphene: Electronic structure

Universiteit Antwerpen

Bravais lattice



Two equivalent carbon sublattices A and B

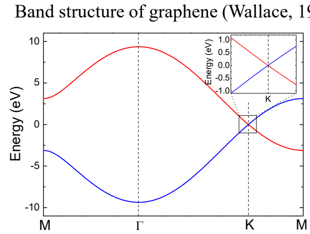
Relative amplitude of sublattice wavefunctions

$\psi_z^{\mathbf{A}}(r) + e^{i\theta}\,\psi_z^{\mathbf{B}}(r)$ θ=0: bonding θ = π: antibonding

$$|k_{\perp}\rangle = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\frac{1}{\sqrt{2}}\begin{pmatrix}\pm 1\\ e^{i\theta_k}\end{pmatrix}$$

$$\theta_k = \tan^{-1}(k_y/k_x)$$

Band structure of graphene (Wallace, 1947)



Massless, relativistic particles

$E=c(p^2+m^2c^2)^{1/2}$

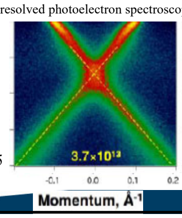
↓ Dirac equation

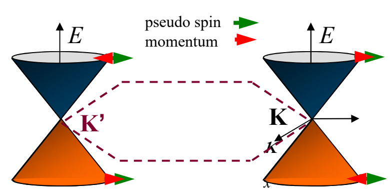
$E=v|p|$

$c/v \cong 375$

$v\sim 10^6\ ms^{-1}$

ARPES:
angle resolved photoelectron spectroscopy





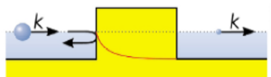
$H_{eff} = \hbar v_F \overleftrightarrow{\sigma}\cdot\vec{k}$

A. Bostwick et al., New. J. Phys. **9** (2007) 385

Universiteit Antwerpen

Klein paradox

Quantum tunneling



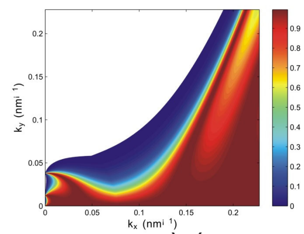
Tunneling probability ↓ when
width and/or height of barrier ↑

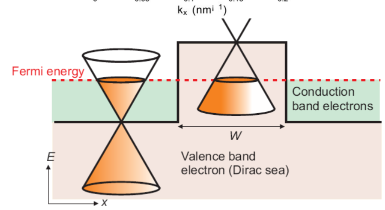
Non-relativisitic ↔ relativistic tunneling

$$E = \frac{\hbar^2}{2m^*}\left(k_x^2 + k_y^2\right) \rightarrow T(k_y)$$

$$E = \hbar v_F \, |\vec{k}| \qquad \rightarrow T(k_x, k_y)$$

O. Klein (1929) → paradoxical implication of Dirac equation:
if an electron with low velocity encounters a barrier $V > 2m_o c^2$
the tunnel probability → 1





Consequence:
- conduction cannot be closed by an external gate
- electrostatic confinement is not possible

M.I. Katsnelson *et al,* Nature Phys. **2**, 620 (2006)

M. Barbier, *et al*, Phys. Rev. B **77**, 115446 (2008)

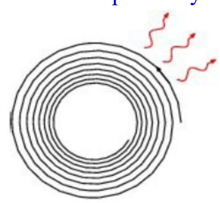
Universiteit Antwerpen

Atomic collapse

Universiteit Antwerpen

Atoms (Kepler problem)

Classical physics
→ unstable planetary atoms



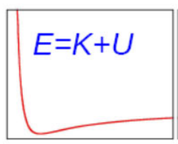
Quantum theory (Bohr, 1913)
→ stable orbits (wave nature of electrons)

Rydberg formula:

$$E_n = -\frac{me^4 Z^2}{2\hbar^2 n^2}$$

Lower bound: $E_1 = -\frac{me^4 Z^2}{2\hbar^2}$

Heisenberg (1926) : *uncertainty principle* $\Delta p \Delta x \geq \hbar/2$



$$K_{\rm nr} = \frac{p^2}{2m} \sim \frac{\hbar^2}{2mr^2} \gg U = -\frac{Ze^2}{r}$$

Planetary atom stabilized by QM (zero point motion)

Universiteit Antwerpen

Quantum mechanics

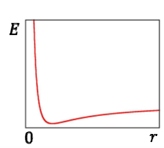
Usually:

$$U = -\frac{Ze^2}{r} \qquad U \propto -\frac{1}{r}$$

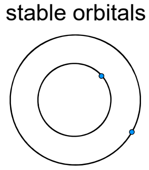
$$K = \frac{p^2}{2m} \sim \frac{\hbar^2}{2mr^2} \qquad K \propto \frac{1}{r^2}$$

$\boldsymbol{r} \to \mathbf{0}$:

- $|K| \gg |U|$
- $\mathrm{E} = K + U \to \infty$



stable orbitals



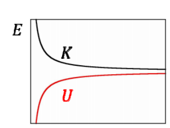
With relativity:

$$U = -\frac{Ze^2}{r} \qquad U \propto -\frac{1}{r}$$

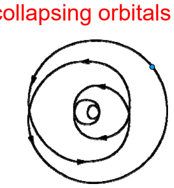
$$K = cp \sim \frac{c\hbar}{r} \qquad K \propto \frac{1}{r}$$

$\boldsymbol{r} \to \mathbf{0}$:

- $|K|$?? $|U|$
- $K + U =$??



collapsing orbitals ?



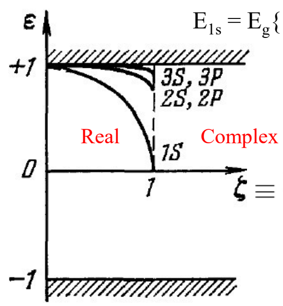
$$\frac{Ze^2}{\hbar c} = Z\alpha = 1$$

Universiteit Antwerpen

Dirac atoms can implode

Dirac (1929)

$E_{1s} = E_g\{1-(Z\alpha)^2\}^{1/2}$



$\zeta \equiv \frac{Ze^2}{\hbar c} = Z\alpha$

$\alpha = 1/137$

Subcritical (Z < 137)

Complex energies when $\zeta > 1$

What happens for Z > 137 ?

Pomeranchuk & Smorodinskii (1945)
Werner and Wheeler (1957)

Finite size of nucleus
Pomeranchuk nuclear form factor
$r_0 = 1.2\ 10^{-12}$ cm

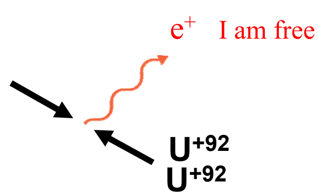
⇒ $Z \to 170$

Universiteit Antwerpen

Experiment

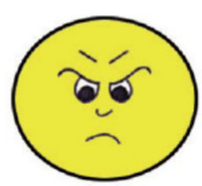
Collision of heavy ions

- Darmstadt experiments (1980s & 1990s)
- Uranium (Z = 92)
- 3-6 MeV collisions



Signature of atomic collapse: **positron emission**

>> No signature of supercritical emission <<



Universiteit Antwerpen

Graphene

Klein tunneling: Coulomb potential → no bound states

$\frac{Ze^2}{\hbar c} = Z\alpha = 1$

Graphene: $c \rightarrow v_F$ $\alpha \rightarrow \alpha_{eff} = \alpha(c/v_F) \approx 2.5$ *Large effective fine structure constant*

$\varepsilon_0 \rightarrow \varepsilon$ (graphene + environment) $e^2 \rightarrow e^2/\varepsilon$

Scaling of effective charge

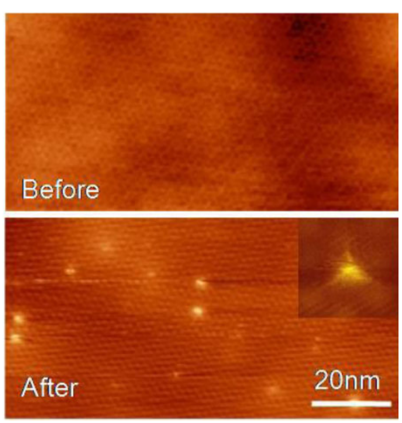
$\beta = \alpha_{eff}\,(Z/\varepsilon)$ → critical value $\beta_c \approx 1/2 \rightarrow Z_c \approx \varepsilon/2\alpha_{eff} \sim 1$

Manifestion of collapse: formation of resonances (quasi-localized spatial structure)

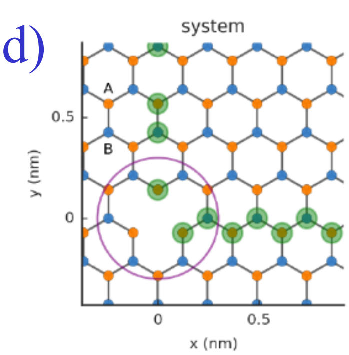
Universiteit Antwerpen

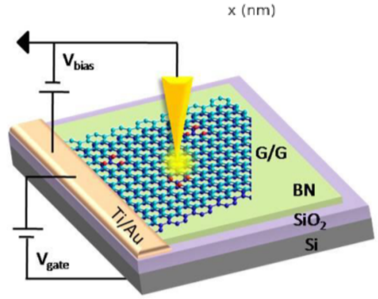
A.V. Shytov et al, PRL **99**, 246802 (2007)

Vacancy (charged)



Rutgers University
(Andrei-group)



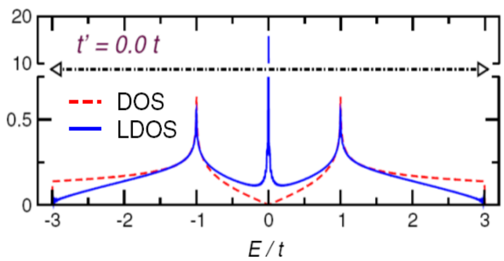


Universiteit Antwerpen

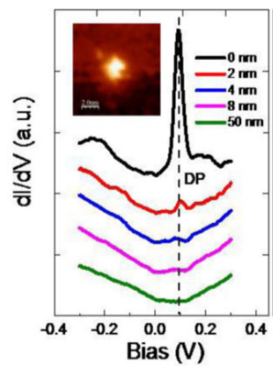
PRL **96**, 036801 (2006) PHYSICAL REVIEW LETTERS week ending 27 JANUARY 2006

Disorder Induced Localized States in Graphene

Vitor M. Pereira,[1,2] F. Guinea,[1,3] J. M. B. Lopes dos Santos,[2] N. M. R. Peres,[1,4] and A. H. Castro Neto[1]

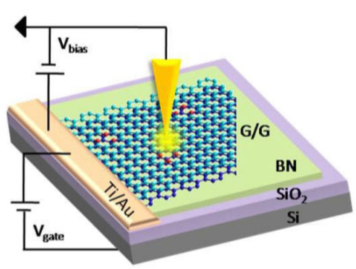


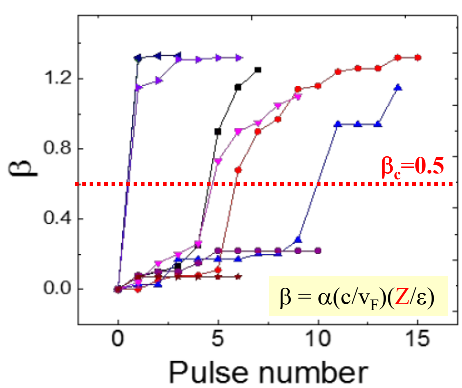
Spatial dependence



Vacancy → resonance close to the Fermi level (half filled case)

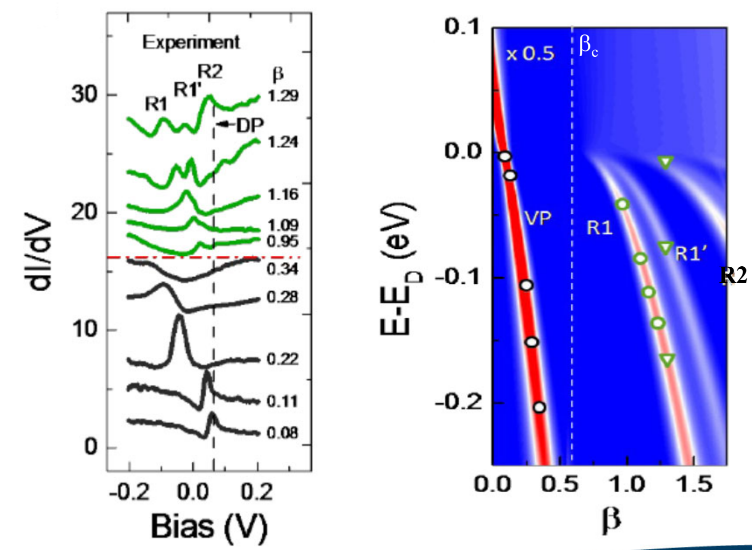
Charging vacancy in graphene





Spectrum

$$\beta = \frac{Z}{\kappa}\alpha_g = \frac{Z}{\kappa}\frac{1}{137}\frac{c}{v_F}$$



Universiteit Antwerpen

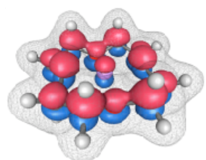
Modelling electronic properties

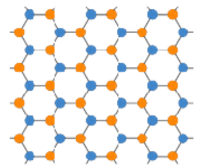
Universiteit Antwerpen

ab initio
(first principals)

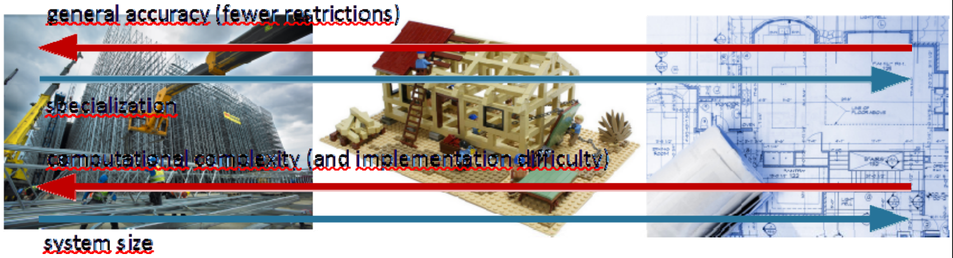
tight-binding
(approximate numeric)

continuum
(approximate analytical)





$-i\hbar v_F \vec{\sigma}\cdot\vec{\nabla}\psi(\vec{r}) = E\psi(\vec{r})$



general accuracy (fewer restrictions)

specialization

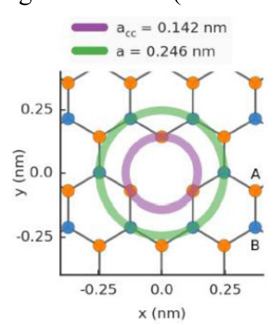
computational complexity (and implementation difficulty)

system size

Theory

$$H = t\sum_i (a_i^\dagger b_i + H.c.) + \sum_i (V(r_i^A)a_i^\dagger a_i + V(r_i^B)b_i^\dagger b_i)$$

Tight-binding hamiltonian (including next nearest neighbor interactions)



$$V(r) = \begin{cases} -\hbar v_F \frac{\beta}{r_0}, \text{ if } r \le r_0 \\ -\hbar v_F \frac{\beta}{r}, \text{ if } r > r_0 \end{cases}$$

$r_0 = 0.5$ nm

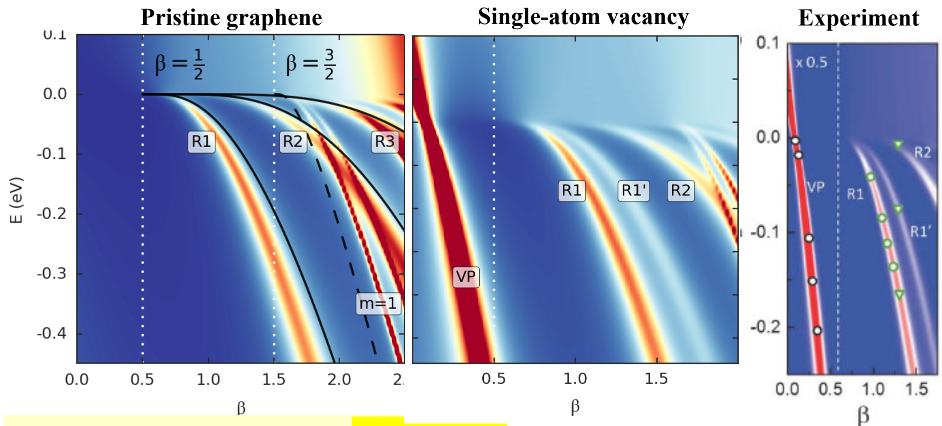
→ Exact numerical solution for a hexagonal sample

Pybinding (Python + tight-binding)

> Open source software project:
https://github.com/dean0x7d/pybinding

Universiteit Antwerpen

Dirac versus TB approach



r → 0: $\varphi_j \sim r^\gamma$

$\gamma = (j^2 - \beta^2)^{1/2}$

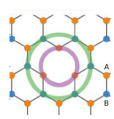
$j = m + ½ = \pm½, \pm3/2, \ldots$

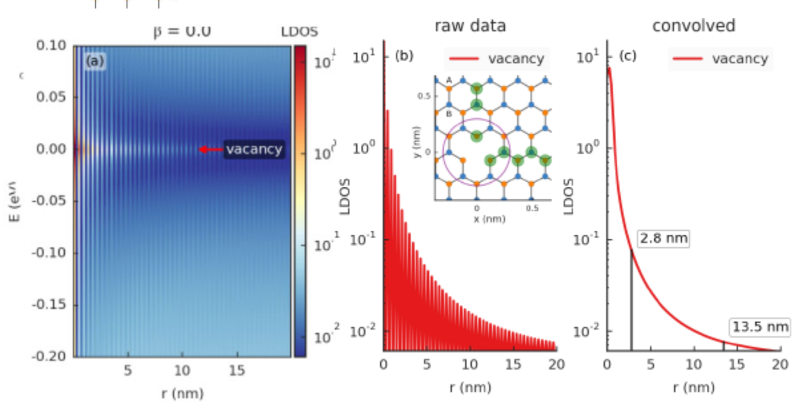
$J_z = L_z + \sigma_z/2$

m=0: R1: n=1
R2: n=2
R3: n=3

Qualitative differences: - VP-state
- R1' - state

Vacancy peak (β < 0.5)

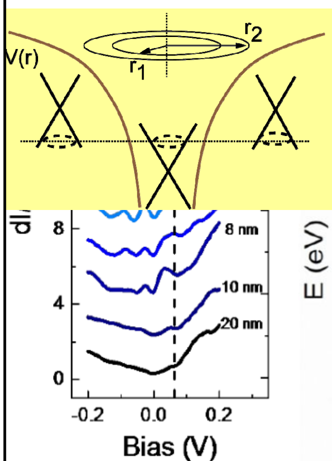


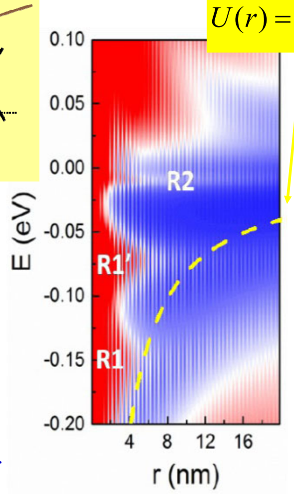


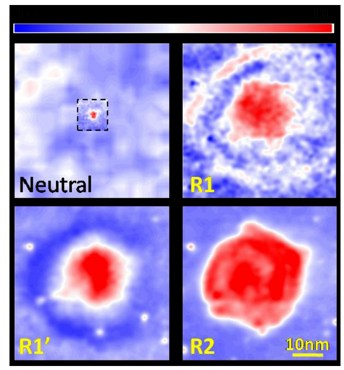
Vacancy: atom from sublattice B is removed → sublattice symmetry is broken
VP-state is localized on sublattice A (and LDOS is zero on sublattice B)

Spatial dependence (β > 0.5)

$$U(r) = \beta \frac{h v_F}{r}$$ ➔ Local Dirac point



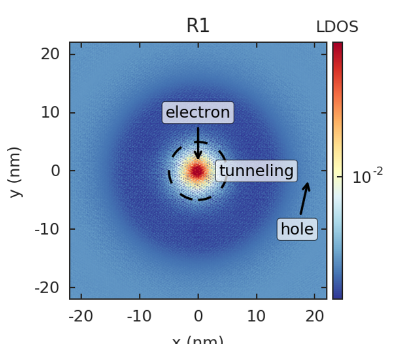




Collapsed states extend far beyond the vacancy site

Vacuum polarization

LDOS for collapse resonance R1

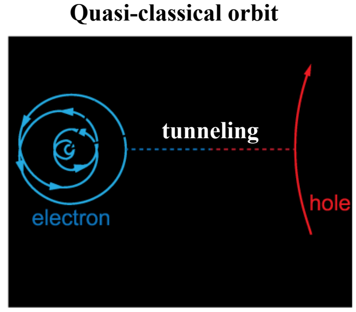


hole continuum

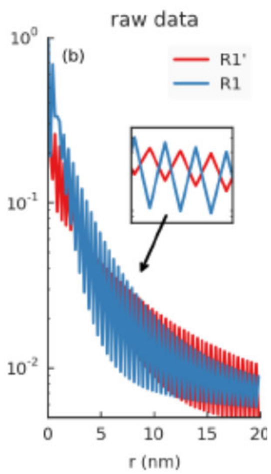
quasi-bound electron inside Coulomb pot.

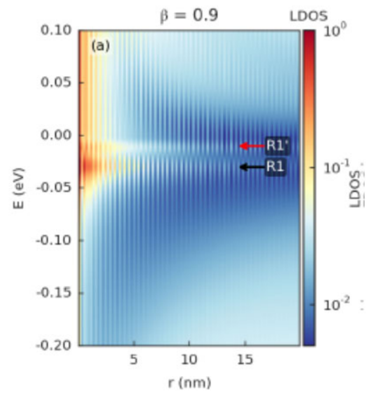
low intensity ring

Quasi-classical orbit



R1 ←→ R1′

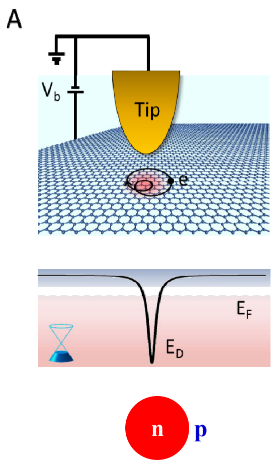


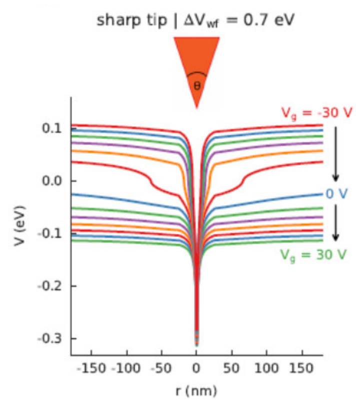


- R1 is more localized than R1'
- R1 has higher probability to be on sublattice B (= vacancy)
- R1' is more localized on sublattice A

STM-tip induced collapse state

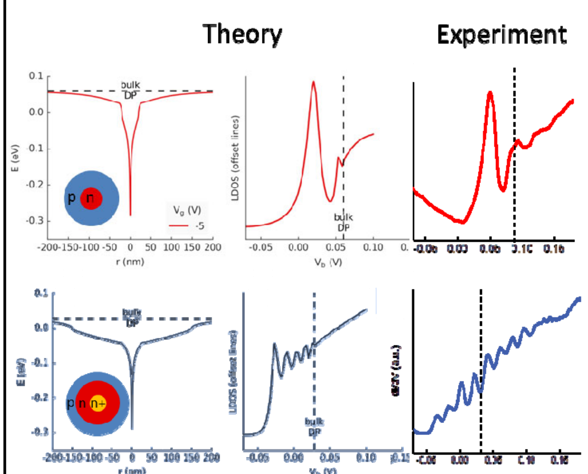
STM-tip induced potential

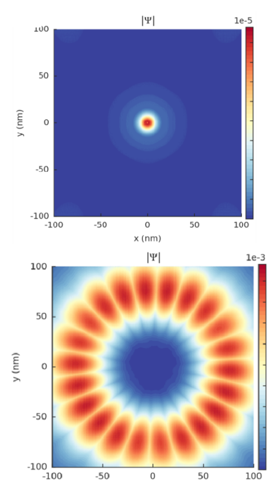




Universiteit Antwerpen

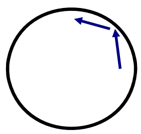
LDOS

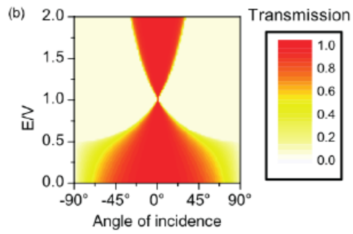


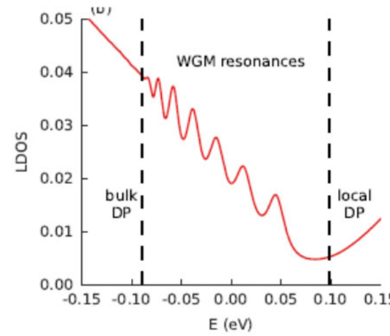


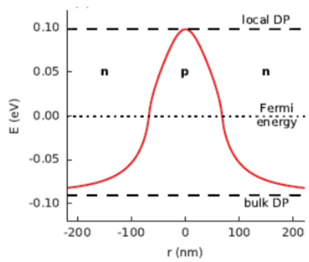
Universiteit Antwerpen

Whispering gallery modes









- Radius pn-dot changes with E_F (from nm to μm)
- m-large: electron hits pn-boundary under large angle θ → T(θ) << 1
- Length of closed loop = nλ → resonance
- quasi-confinement closer to the circumference of the junction → WGM

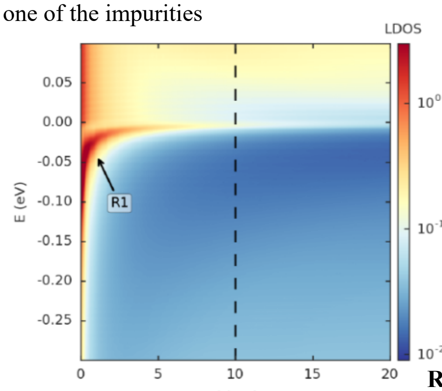
Universiteit Antwerpen

Y. Zhao et al, Science **348,** 672 (2015)

Molecular collapse

β_1=β_2=0.4 → two subcritical impurities

LDOS in center of one of the impurities



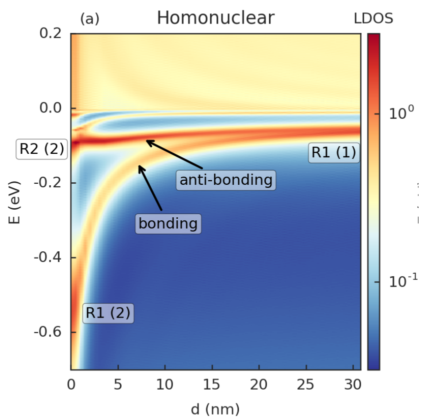
collapse ←

Recent exp. confirmation:
M. Crommie group, Berkeley
Nature Commun. (2019)

Universiteit Antwerpen

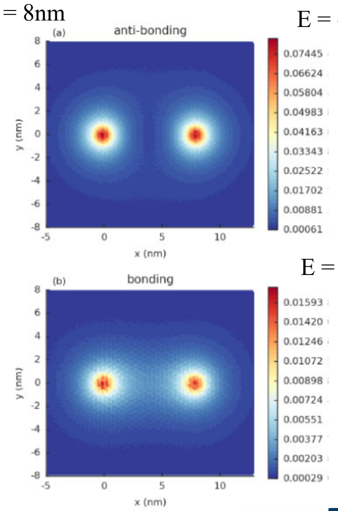
Molecular collapse

2 impurities with $\beta_1=\beta_2=0.9$



d = 8nm

E = -77meV



E = -135 meV

Universiteit Antwerpen

Buckling induced *flat bands*:

Giant nanoscale periodic strain

Universiteit Antwerpen

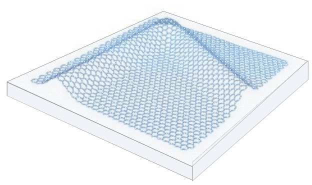
Morphological effect in graphene buckling

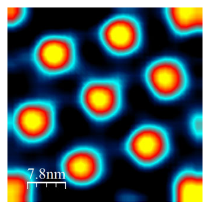
Periodic potential → reshape band structure → exotic physics (e.g. Hofstadter butterfly)

Flat band → quenching of kinetic energy → interaction driven quantum phases
e.g. magic angle twisted bilayer graphene (SC, Mott insulator, …)

Moiré pattern, e.g. h-BN/graphene, twisted bilayer graphene → hexagonal symmetry

Periodic buckling structure → buckling mode: - different SL symmetry
- periodic strain → periodic pseudo-magnetic field



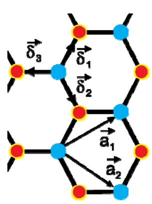


Time reversal symmetry

Symmetry of SL ≠ underlying lattice

Graphene: a = 0.14nm
SL: a = 14 nm

Strain



$$H = -\sum_{i,j} t_0 a_i^\dagger b_j + h.c.$$

$$t_n = t_0 e^{-\beta(d_n/a-1)}$$

$$d_n = a + \delta_n$$

$$t_n = t_0\, e^{-\beta\delta_n/a} = t_0\,(1 - \beta\delta_n/a + \dots) = t_0 + \delta t$$

strain ↓

To first order: $\delta t = -\frac{\beta}{a^2}\delta_n \cdot \bar{u} \cdot \delta_n$

$H = v_F \sigma\cdot(p + eA)$

$$A_x = \pm\beta/a(u_{xx} - u_{yy})$$
$$A_y = \pm\beta/a(-2u_{xy})$$
$$B = \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}$$

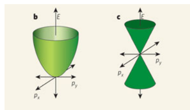
Opposite sign in K and K' → no broken time reversal symmetry

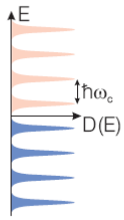
F. Guinea *et al*, Nat. Phys. 6, 30 (2010)

Magnetic field effects

Landau levels

Normal 2DEG





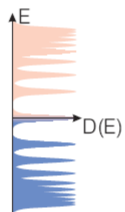
$$E_n = \hbar\omega_c (n + 1/2)$$

$$\omega_c = \frac{eB}{m^* c}$$

Graphene

$$H = \hbar v_F \vec{\sigma} \cdot \vec{k} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix}$$

$$\vec{k} \rightarrow \vec{k} + \frac{e}{\hbar c}\vec{A}$$



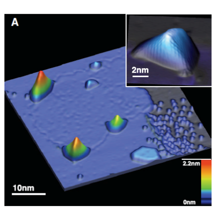
← **Zero energy state**
Is shared by electrons and hol

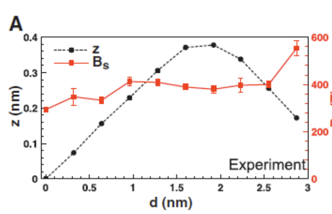
$$E_n = \pm\sqrt{2eB\hbar v_F^2 \left(n + 1/2 \pm 1/2\right)}$$

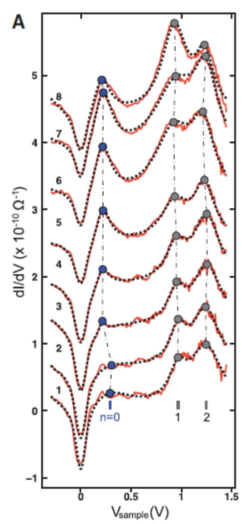
↑ **chirality**

Strained graphene: pseudo-magnetic fields

- ✦ **experimental observation (STM):** **N. Levy et al., Science 329 (2010)**
- ✦ **graphene grown on Pt (111) forms highly strained nanobubbles**
- ✦ **pseudo-magnetic fields of order 400T**



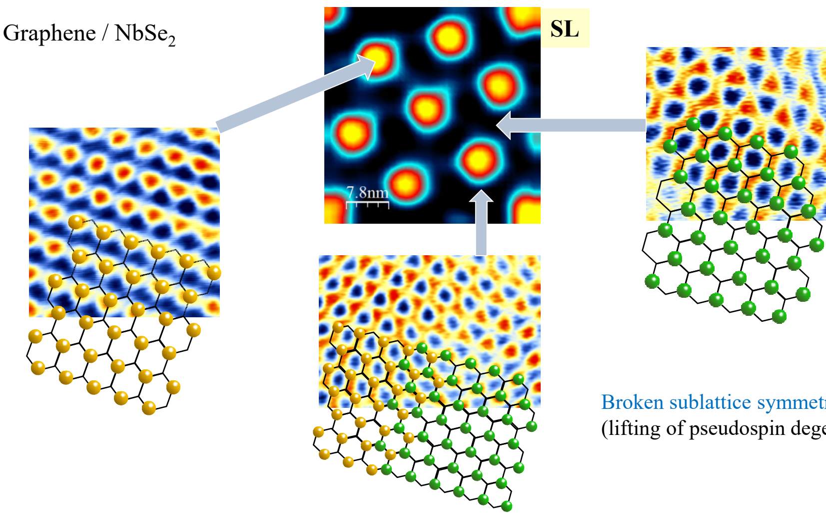




Pseudospin polarization of graphene lattice

Spatial resolution

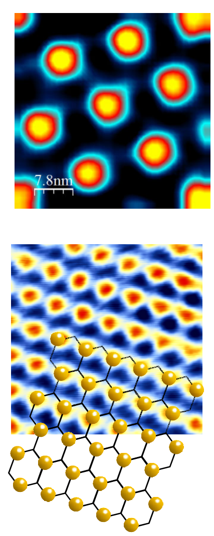
Graphene / $NbSe_2$

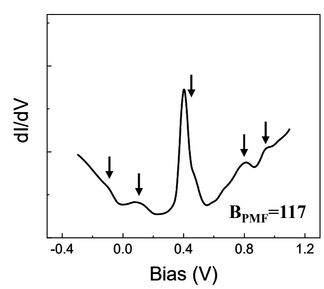


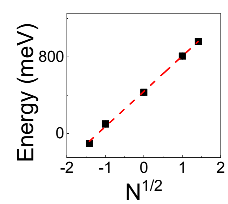
Broken sublattice symmetry
(lifting of pseudospin degeneracy)

Universiteit Antwerpen

LDOS in bright region





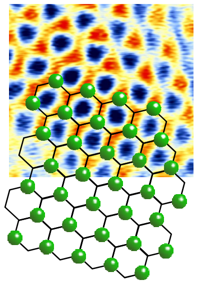


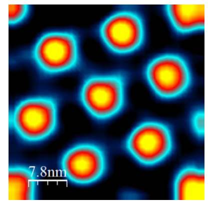
$$E_N = sgn(N) v_F \sqrt{2e\hbar|N|B}$$

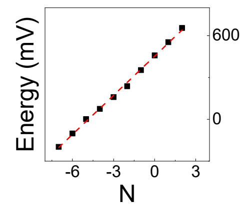
B_{PMF} = 117 T

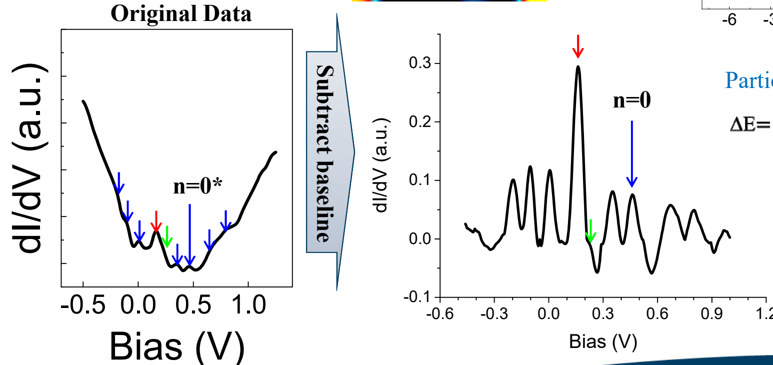
Universiteit Antwerpen

LDOS in dark region









Particle in a box

$\Delta E = \frac{\hbar v_F \pi}{W} = 94$ meV

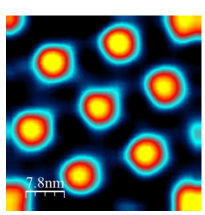
W = 16 nm

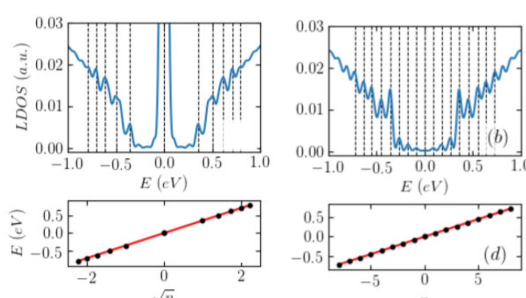
Theoretical simulation

$$B_{PMF}(x,y) = B[\cos(a_b \boldsymbol{b_1 r}) + \cos(a_b \boldsymbol{b_2 r}) + \cos(a_b \boldsymbol{b_3 r})]$$

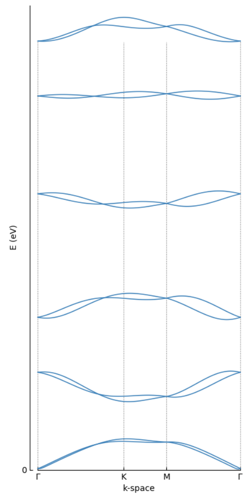
$$\boldsymbol{b_1} = (1, -\tfrac{1}{\sqrt{3}}), \boldsymbol{b_2} = (0, \tfrac{2}{\sqrt{3}}), \boldsymbol{b_3} = \boldsymbol{b_1} + \boldsymbol{b_2}$$

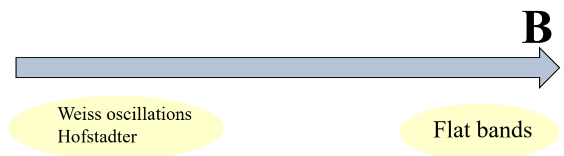
$B_{PMF}^{max} = 3B$, $B_{PMF}^{min} = -1.5B.$





Towards flat band





Conclusions

⇒ Graphene as a lab. for investigating ***relativistic quantum mechanical*** effects
(which have not been observed with 'real' particles):
- Klein paradox
- Atomic collapse

Kepler problem:

⇒ Graphene: effects due to A/B sublattices are observable (R1/R1' collapsed states)

Nature Nanotechnology **12**, 1045 (2017) Nature Physics **12**, 545 (2016)

⇒ STM-tip: transition from quantum (AC-states) to classical (WGM)

⇒ Outlook: - molecular collapsed states: bonding / anti-bonding states
- magnetic fields: non-scaling of Landau levels when in collapsed state
critical charge independent of magnetic field

Buckling problem:

SL with arbitrary symmetry
Alternative way to create flat bands → *Strongly correlated states*

experiment

Rutgers University (group of Eva Andrei)

Jinhai Mao
Yuhang Jiang
Guohong Li
Takashi Taniguchi
Eva Andrei

Advanced Materials Laboratory, Tsukuba

Kenji Watanabe

University of Manchester

Andre Geim

theory

University of Antwerp

Dean Moldovan
Massoud Ramezani Masir → Leiden, The Netherlands
Lucian Covaci → University of Texas, Austin
Slaviša Milovanovic
Miša Andelkovic
François Peeters

Universiteit Antwerpen

THE END

Universiteit Antwerpen