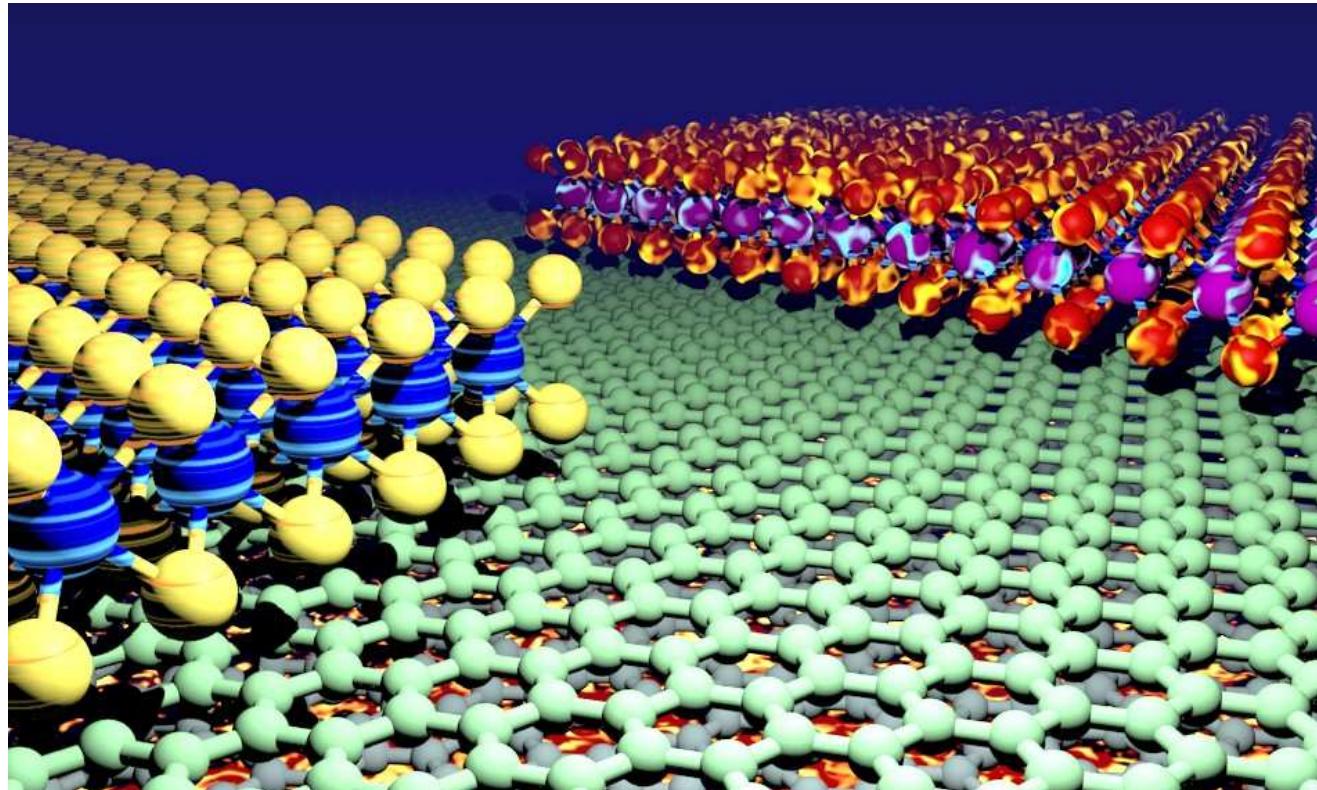


Lecture 1: An introduction to 2D materials



Pedagogical School “Emergent phenomena in van der Waals heterostructures”

January 7th 2023, Tata Institute of Fundamental Research (TIFR), India



Today's plan

- Families of 2D materials
- An introduction to the theory tools: electronic structure, second quantization and mean-field theory
- The tunability of 2D materials
- An introduction to computational tools

Schedule for the lecture

- 30 min lecture
- 5 min break
- 30 min lecture

You can download the slides and software from

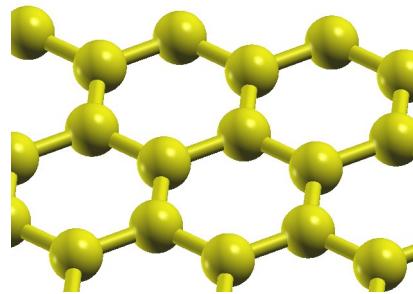
https://github.com/joselado/emergent_phenomena_in_van_der_Waals_school_tifr_2023



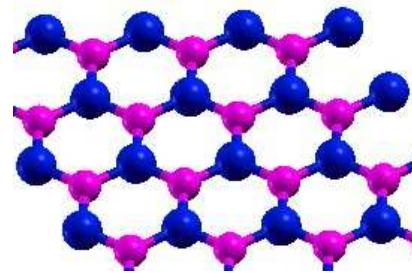
The world of 2D materials

The two-dimensional materials world

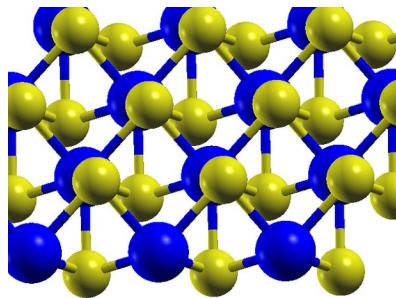
Semimetal
Graphene



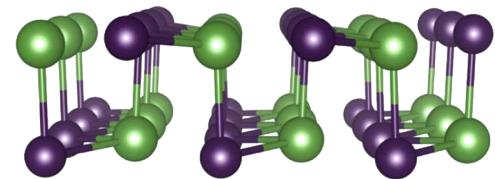
Insulator
BN



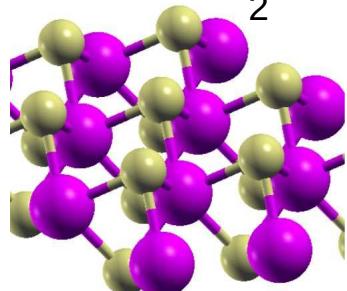
Superconductor
 NbSe_2



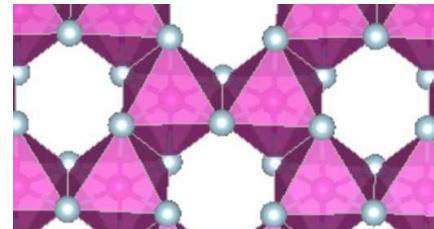
Ferroelectric
 SnTe



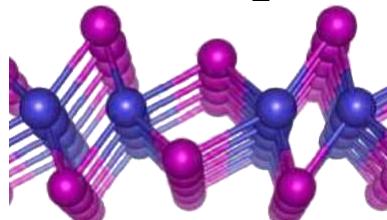
Semiconductor
 WSe_2



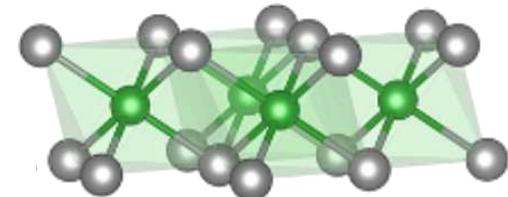
Ferromagnet
 CrI_3



Quantum spin
Hall insulator
 WTe_2

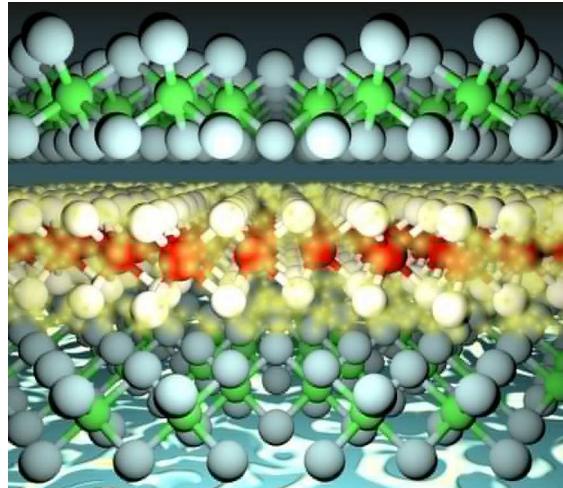


Multiferroic
 NiI_2

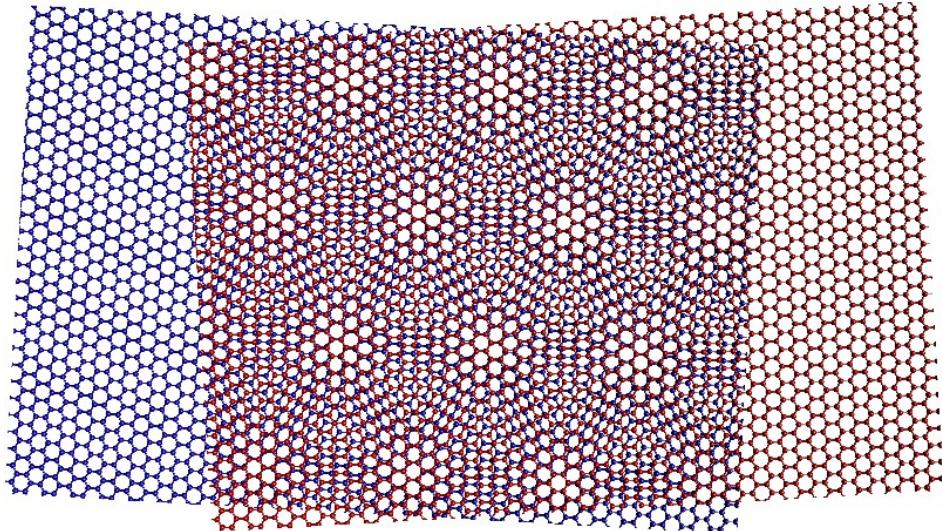


The flexibility of two-dimensional materials

They can be stacked



They can be rotated

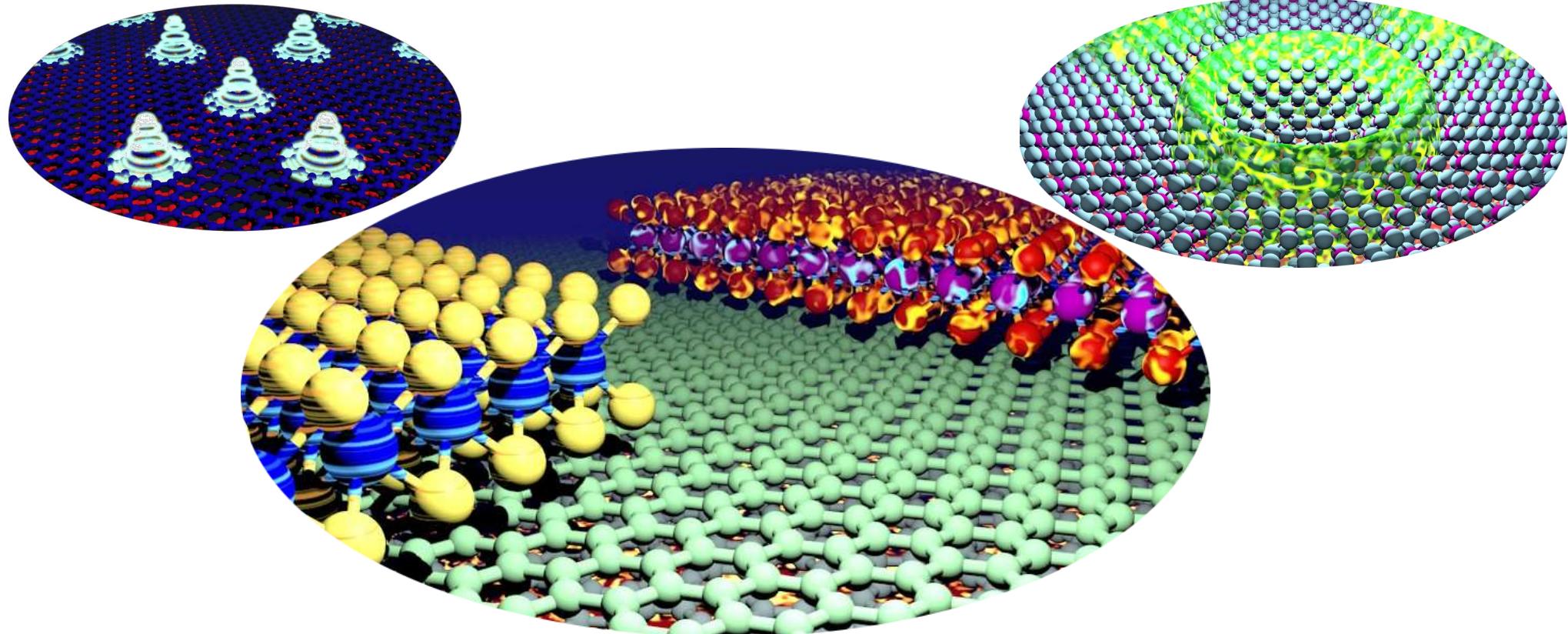


Nature 499.7459 419. (2013)

Science 361.6403 690-693. (2018)

These are unique features of two-dimensional materials

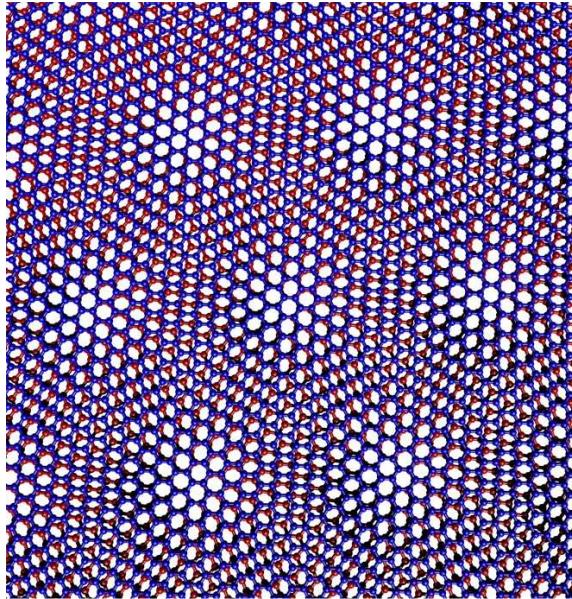
A new universe in each van der Waals heterostructure



Each van der Waals heterostructure allows creating a whole new universe for electrons

One material, a zoo of electronic phases

Twisted bilayer graphene

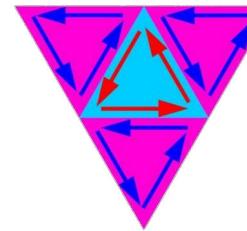


Superconductivity



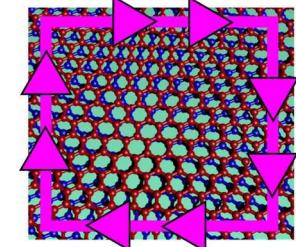
Nature 556, 43–50 (2018)

Topological networks



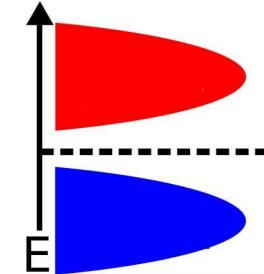
Nano Lett. 18, 11,
6725-6730 (2018)

Chern insulators



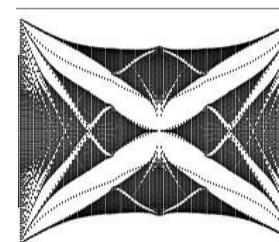
Science 365, 605-608
(2019)

Correlated insulators



Nature 556, 80–84
(2018)

Quasicrystalline physics



Science 361, 782-786 (2018)

Fractional Chern insulators



Nature 600, 439–443
(2021)

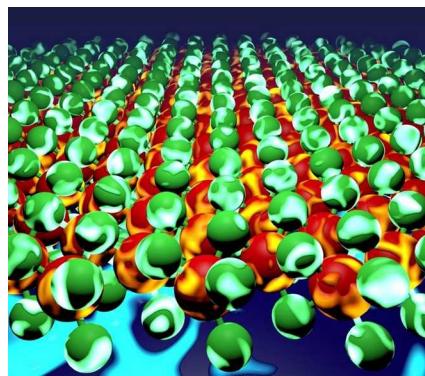
A bilayer of a van der Waals material realizes a variety of widely different electronic states

Controlling electronic states in van der Waals materials

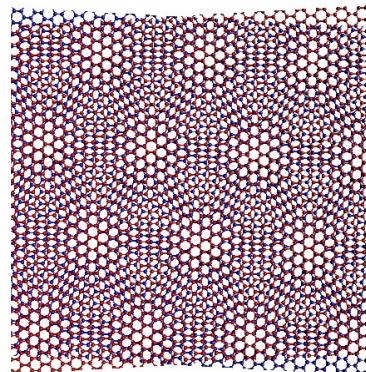
*Of course, we can use the typical knobs of bulk compounds
(pressure, chemical doping, etc)*

Most importantly, we can exploit the full tunability of van der Waals materials

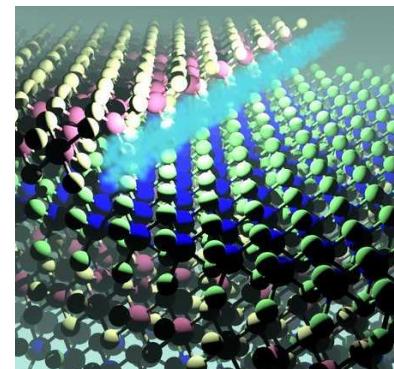
Gating



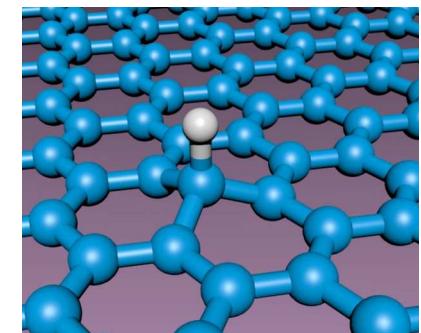
Twist engineering



Materials engineering



Atomic engineering



Science 306, 5696, 666-669 (2004)

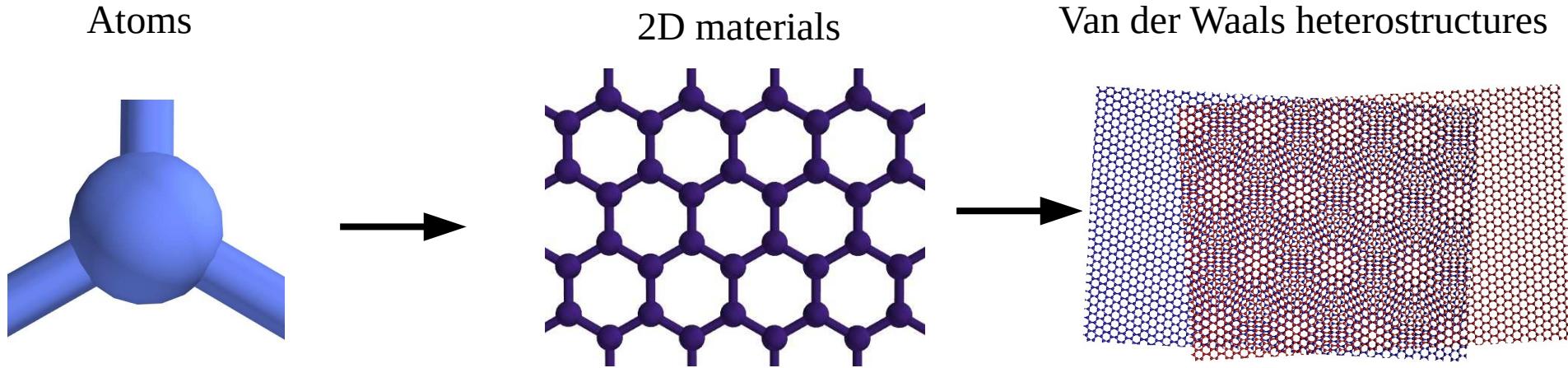
Nat, Rev, Mat, 6, 201–206 (2021)

Nature 499, 419–425 (2013)

Science, 352(6284), 437-441 (2016)

Allowing to independently control different features of the electronic structure

From atoms to quantum matter



***How do we understand and predict properties
as we put more and more atoms together?***

A reminder about theory tools:
second quantization,
electronic structure
and mean-field theory

How do we describe quantum matter?

We use quantum mechanics to understand electrons in materials

$$H|\Psi\rangle = -i\partial_t|\Psi\rangle$$

Hamiltonian Wavefunction of the system

Two main kinds of phenomena can emerge

Single particle phenomena

Many-body phenomena

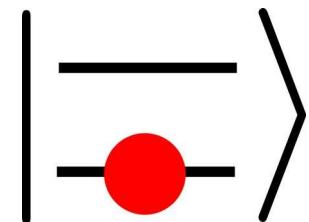
Two different kinds of quantum mechanical formalism

Systems where our number of particles is constant

First quantization, description based on a Hilbert space

Describes metals, semiconductors, insulators

Highly successful and easy formalism

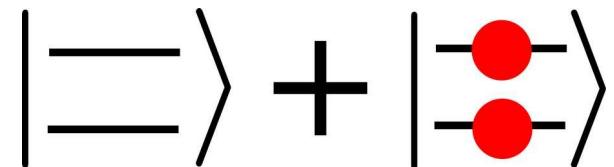


Systems where the number of particles fluctuates

Second quantization, description based on a Fock space

Describes superconductors, superfluids, correlated matter

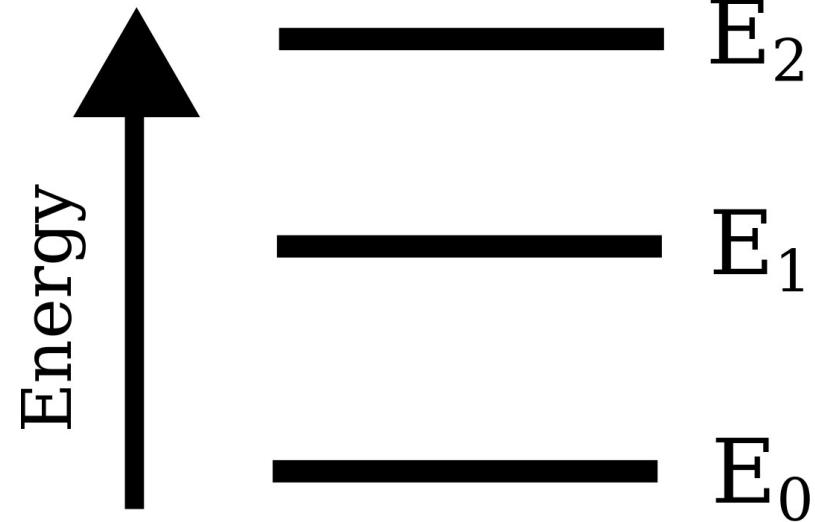
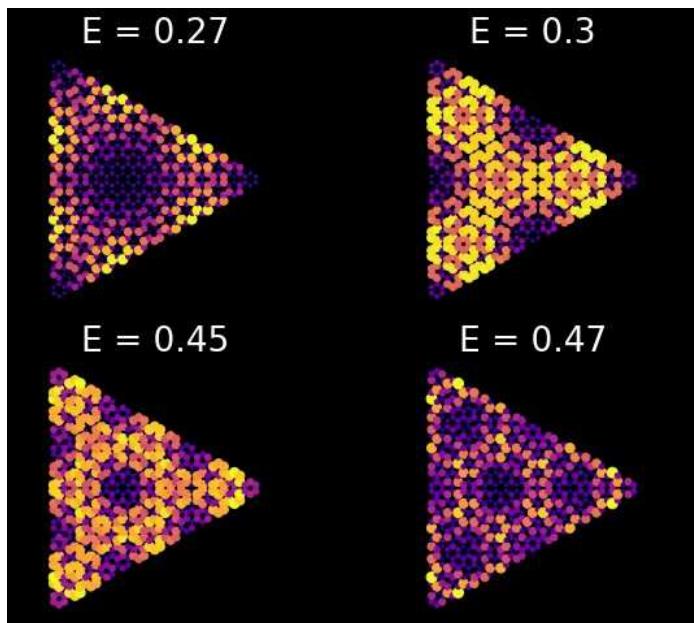
Leads to much exotic phenomena, yet also more challenging



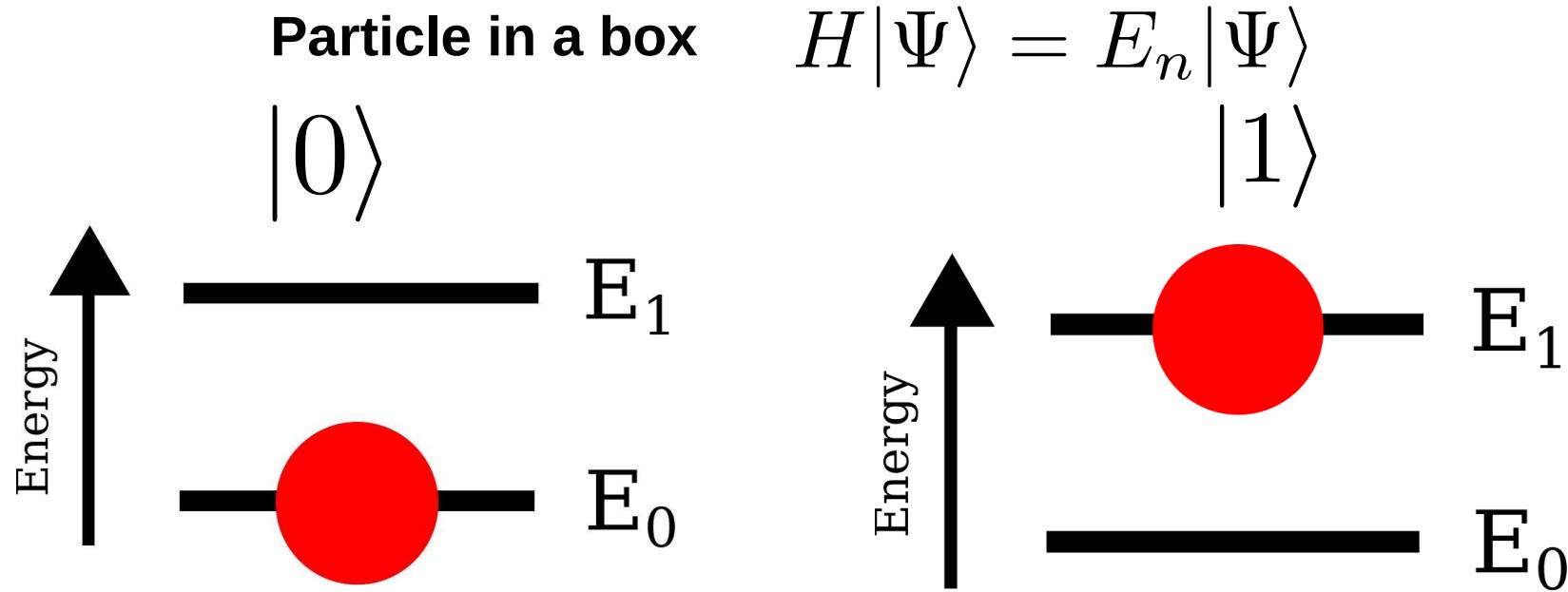
A reminder of a simple single particle state

Particle in a box

$$H|\Psi\rangle = E_n|\Psi\rangle$$



A reminder of a simple single particle state

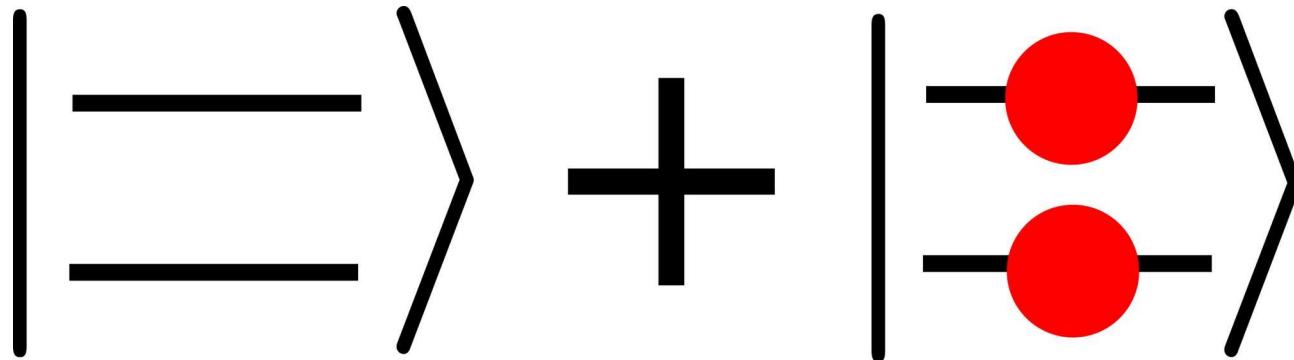


These two states describe having one particle, in one of the possible energy level

From single particle to many body

But what if our state is a combination of states with different numbers of particles?

A state having both 0 particles and 2 particles



How do we describe states like these?

The idea of second quantization

Define operators that can create or destroy particles

c_i Annihilation operator, destroys a particle in site i

c_i^\dagger Creation operator, creates a particle in site i

The empty vacuum state $|\Omega\rangle$ is defined as $c_i |\Omega\rangle = 0$

The Hamiltonian is written in terms of creation and annihilation operators

$$H = c_0^\dagger c_1 + h.c.$$

The idea of second quantization

Lets see some examples using the two-levels presented before

$$|\Omega\rangle = \left| \begin{array}{c} \text{---} \\ \text{---} \end{array} \right\rangle$$

The “vacuum” state

$$c_0^\dagger |\Omega\rangle = \left| \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \right\rangle$$

One particle in level #0

$$c_1^\dagger |\Omega\rangle = \left| \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \right\rangle$$

One particle in level #1

$$c_0^\dagger c_1^\dagger |\Omega\rangle = \left| \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \right\rangle$$

Two particles in level #0 & #1

Fermionic quantum statistics in second quantization

Fermi-Dirac statistics for electrons

- Wavefunctions are antisymmetric with respect to interchanging labels
- There can only be 0 or 1 fermion per level

$$\{c_i^\dagger, c_j\} = c_i^\dagger c_j + c_j c_i^\dagger = \delta_{ij} \quad \{c_i, c_j\} = 0$$

Anti-symmetric wavefunction

$$c_0^\dagger c_1^\dagger |\Omega\rangle = -c_1^\dagger c_0^\dagger |\Omega\rangle$$

At most one fermion per site

$$c_0^\dagger c_0^\dagger |\Omega\rangle = 0$$

Different kinds of Hamiltonians

Single particle Hamiltonians

$$H = \sum_{ij} t_{ij} c_i^\dagger c_j$$

Insulators, semiconductors, metals

Many-body Hamiltonian

$$H = \sum_{ijkl} V_{ijkl} c_i^\dagger c_j c_k^\dagger c_l$$

Fractional quantum Hall states, superconductors, quantum magnets

With second quantization, both cases can be treated on the same footing



What about interactions?

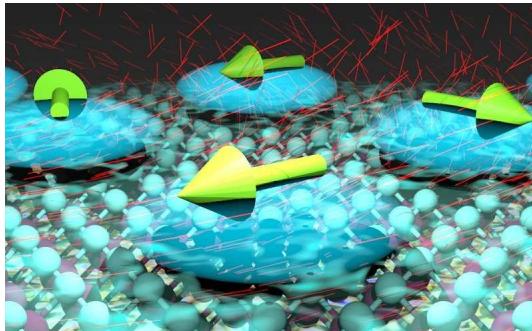
What happens when we put interactions?

$$H = \sum_{ij} t_{ij} c_i^\dagger c_j + \sum_{ijkl} V_{ijkl} c_i^\dagger c_j c_k^\dagger c_l$$

The role of electronic interactions

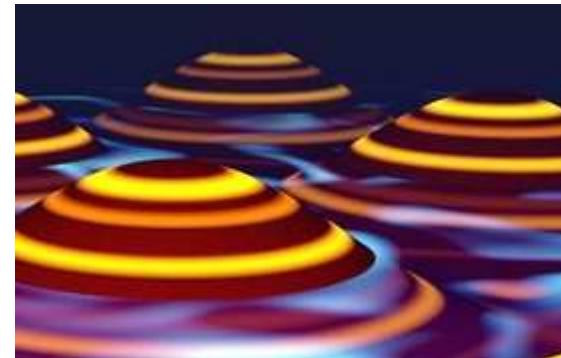
Electronic interactions are responsible for symmetry breaking

**Broken
time-reversal symmetry**
Classical magnets



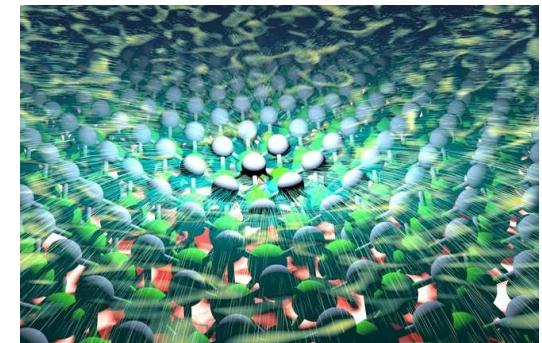
$$\mathbf{M} \rightarrow -\mathbf{M}$$

**Broken
crystal symmetry**
Charge density wave



$$\mathbf{r} \rightarrow \mathbf{r} + \mathbf{R}$$

**Broken
gauge symmetry**
Superconductors



$$\langle c_{\uparrow} c_{\downarrow} \rangle \rightarrow e^{i\phi} \langle c_{\uparrow} c_{\downarrow} \rangle$$

A simple interacting Hamiltonian

Free Hamiltonian

*Interactions
(Hubbard term)*

$$H = \sum_{ij} t_{ij} [c_{i\uparrow}^\dagger c_{j\uparrow} + c_{i\downarrow}^\dagger c_{j\downarrow}] + \sum_i U c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow}$$

From now on lets consider we have a spin degree of freedom \uparrow, \downarrow

What is the ground state of this Hamiltonian?

$U < 0$ Superconductivity

$U > 0$ Magnetism

The mean-field approximation, superconductivity

Mean field: Approximate four fermions by two fermions times expectation values

*Four fermions
(not exactly solvable)*

$$U c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow} \approx U \langle c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger \rangle c_{i\uparrow} c_{i\downarrow} + h.c.$$

$$U c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow} \approx \Delta c_{i\uparrow} c_{i\downarrow} + h.c.$$

For $U < 0$
i.e. attractive interactions

$\Delta \sim \langle c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger \rangle$ is the superconducting order

The mean-field approximation, magnetism

Mean field: Approximate four fermions by two fermions times expectation values

**Four fermions
(not exactly solvable)**

$$U c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow} \approx U \langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle c_{i\downarrow}^\dagger c_{i\downarrow} + \dots + h.c.$$

**Two fermions
(exactly solvable)**

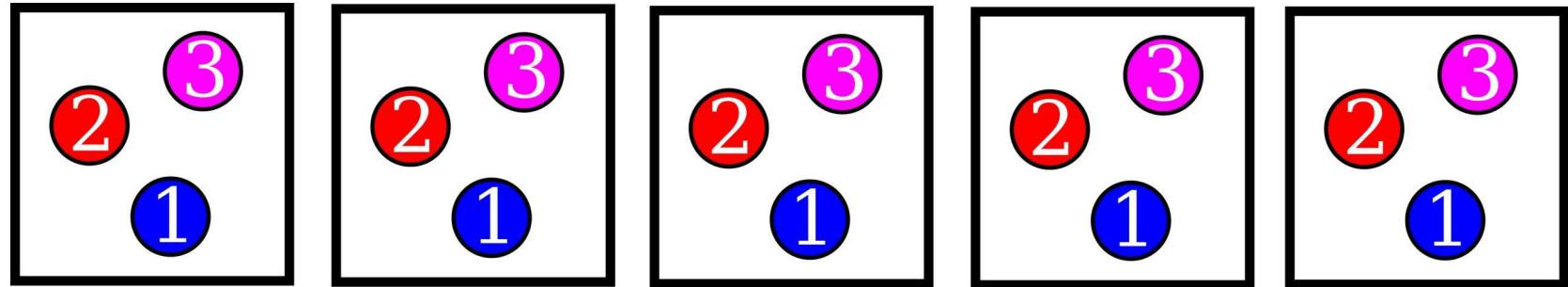
$$U c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow} \approx M \sigma_{ss'}^z c_{i,s}^\dagger c_{i,s'} + h.c.$$

For $U > 0$
i.e. repulsive interactions

Magnetic order

$$M \sim \langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle - \langle c_{i\downarrow}^\dagger c_{i\downarrow} \rangle$$

Electronic band-structures

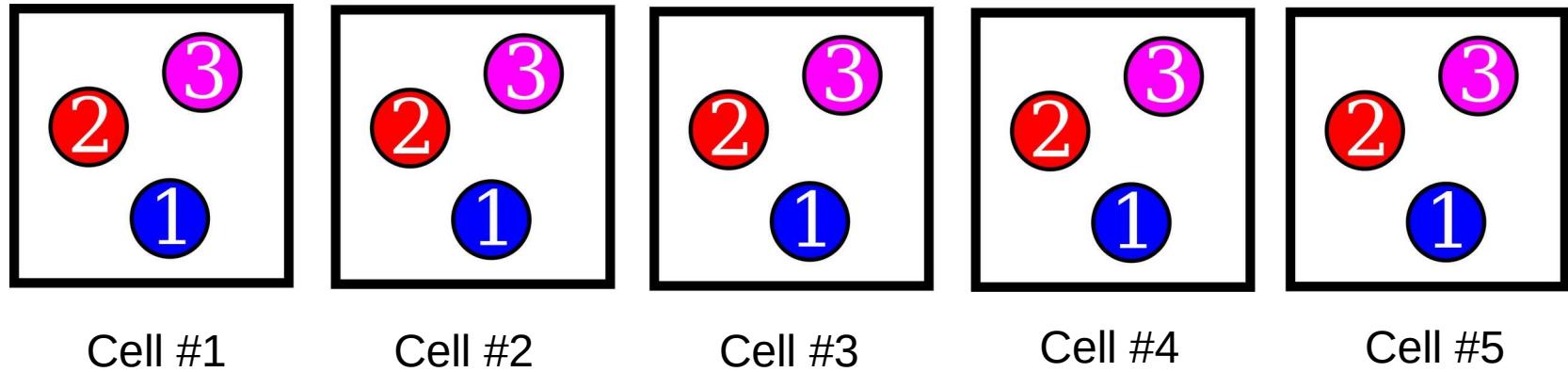


$$c_{\alpha,n}^\dagger$$

index of the orbital in the unit cell

Index of the unit cell

Electronic band-structures



$$H = \sum_{n,\alpha,\beta} t_{\alpha\beta} c_{\alpha,n}^\dagger c_{\beta,n} + \sum_{n,\alpha,\beta} \gamma_{\alpha\beta} c_{\alpha,n}^\dagger c_{\beta,n+1} + h.c.$$

Intra-cell hoppings Inter-cell hoppings

Electronic band-structures

$$H = \sum_{n,\alpha,\beta} t_{\alpha\beta} c_{\alpha,n}^\dagger c_{\beta,n} + \sum_{n,\alpha,\beta} \gamma_{\alpha\beta} c_{\alpha,n}^\dagger c_{\beta,n+1} + h.c.$$

Unitary transformation

$$\Psi_{\phi,\alpha}^\dagger \sim \sum_{n,\beta} e^{i\phi n} U_{\alpha\beta} c_{n,\beta}^\dagger \quad H = \sum_{\phi,\alpha} \epsilon_{\phi,\alpha} \Psi_{\phi,\alpha}^\dagger \Psi_{\phi,\alpha}$$

$\epsilon_{\phi,\alpha}$ are the eigenvalues of the matrix

$$h(\phi) = t_{\mu\nu} + \gamma_{\mu\nu} e^{i\phi} + h.c.$$

Properties of the electronic dispersion

From now on, lets work with a specific electronic dispersion $\epsilon_{\vec{k}}$

Density of states

$$D(\omega) \sim \int \delta(\omega - \epsilon_{\vec{k}}) d^N \vec{k}$$

Group velocity

$$v_F = \frac{\partial \epsilon_{\vec{k}}}{\partial k_\alpha}$$

Effective mass

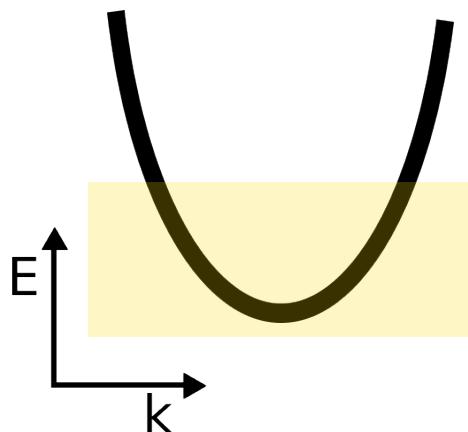
$$\frac{1}{m_{\alpha\beta}} = \frac{\partial^2 \epsilon_{\vec{k}}}{\partial k_\alpha \partial k_\beta}$$

Fermi surface

$$\{\vec{k}\} \text{ with } \epsilon_{\vec{k}} = \epsilon_F$$

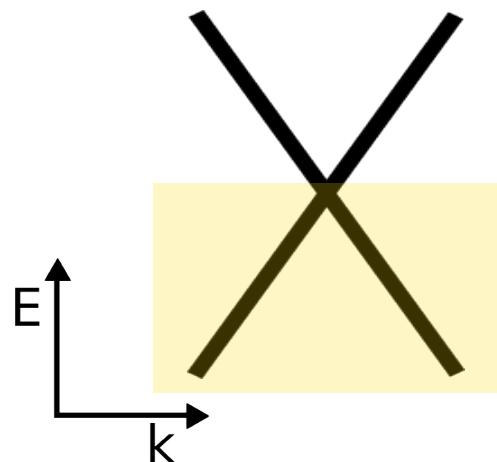
Three important electronic dispersions

Parabolic bands



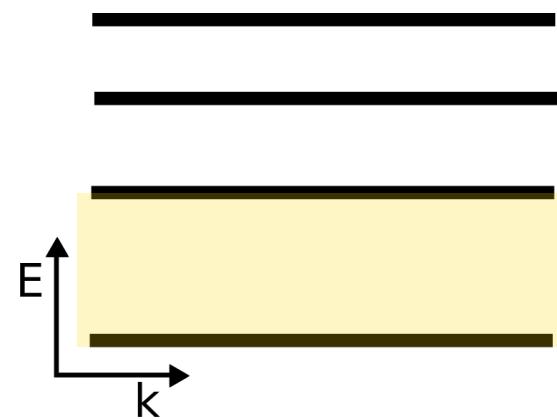
TMDCs
Effective free-electrons

Dirac dispersion



graphene
Topology & relativistic physics

Flat bands



Quantum Hall, moire
Topology & correlations



Break

5 min break

(optional) to discuss during the break

What is the physical meaning of these terms in the Hamiltonian?

$$c_{n,\uparrow}^\dagger c_{n,\downarrow}$$

$$c_{n,\uparrow}^\dagger c_{n+1,\downarrow}$$

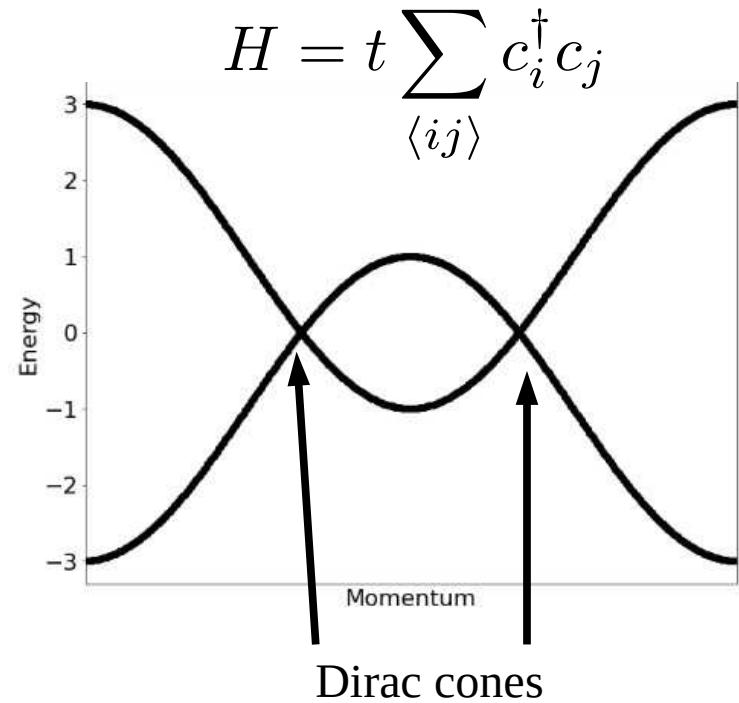
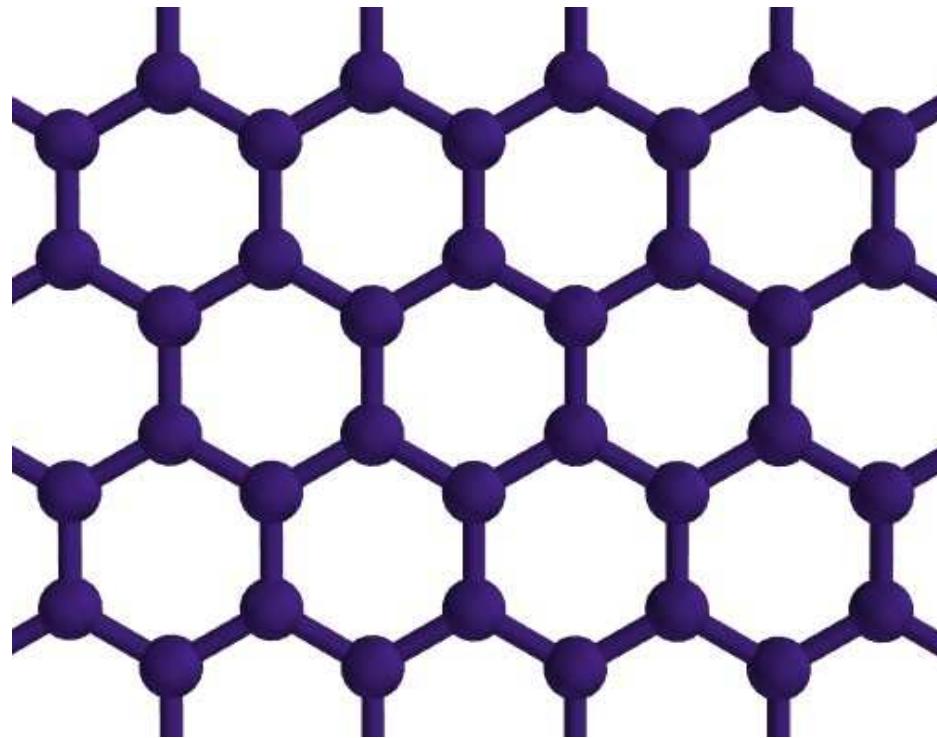
$$c_{n,\uparrow}^\dagger c_{n+1,\uparrow}^\dagger$$

and which symmetries do they break?

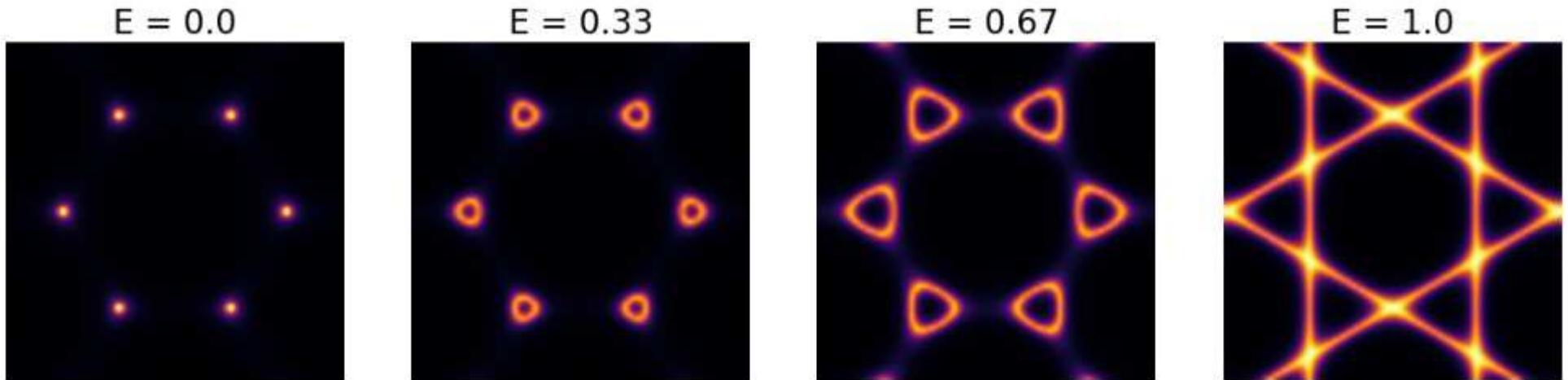
Graphene and its electronic structure

Electronic structure of monolayer graphene

The electronic structure of graphene is captured by a single orbital model in the honeycomb lattice

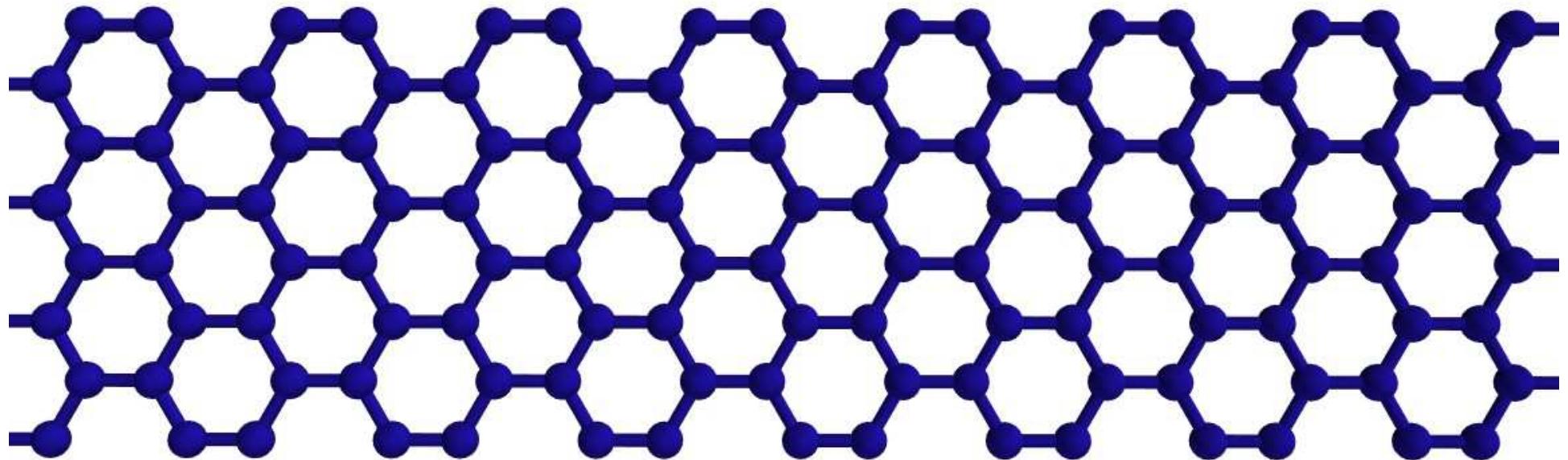


Fermi surface of graphene



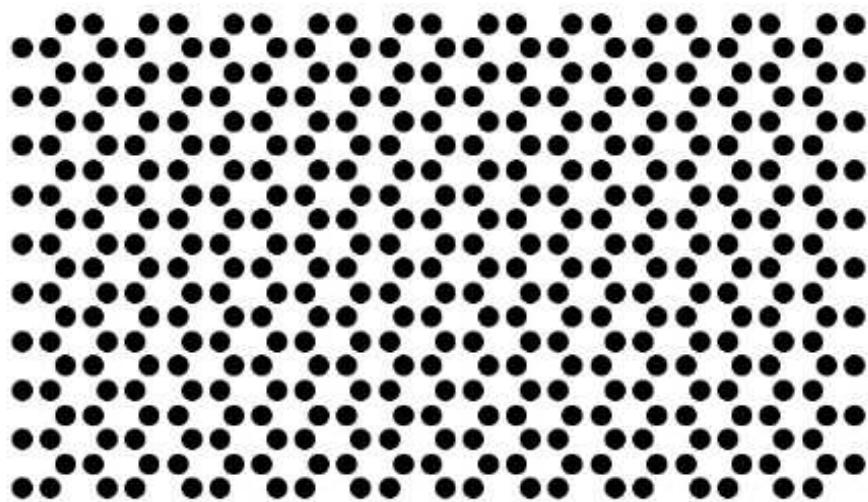
Confining two-dimensional materials, graphene nanoribbons

Let us see what happens to the electronic structure when we reduce the dimensionality



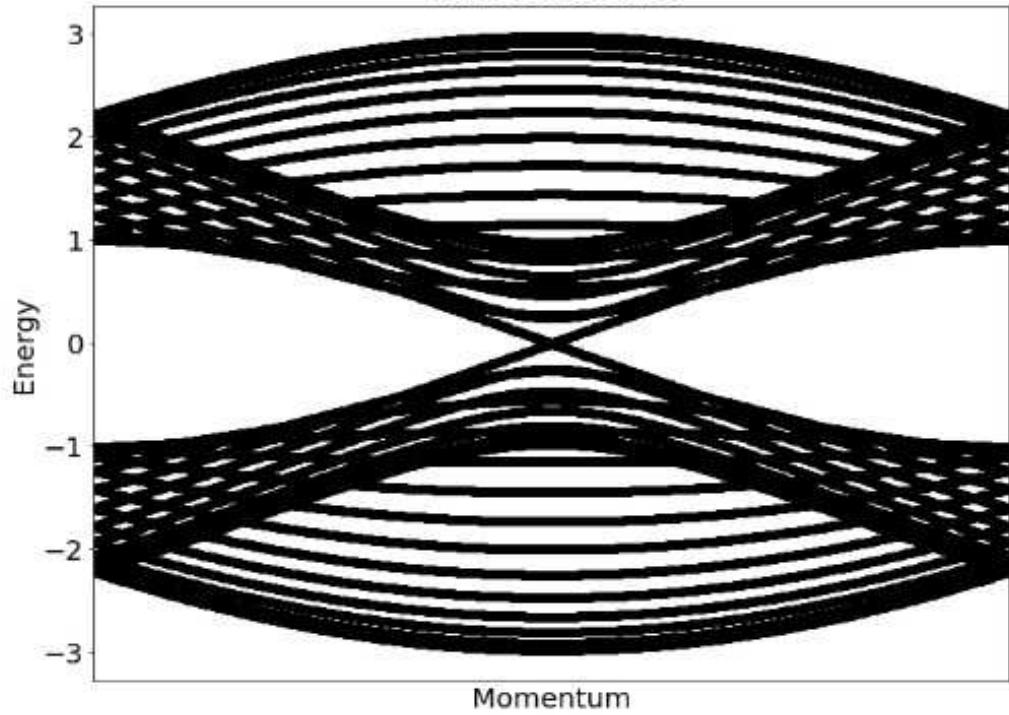
Graphene nanoribbons

Structure



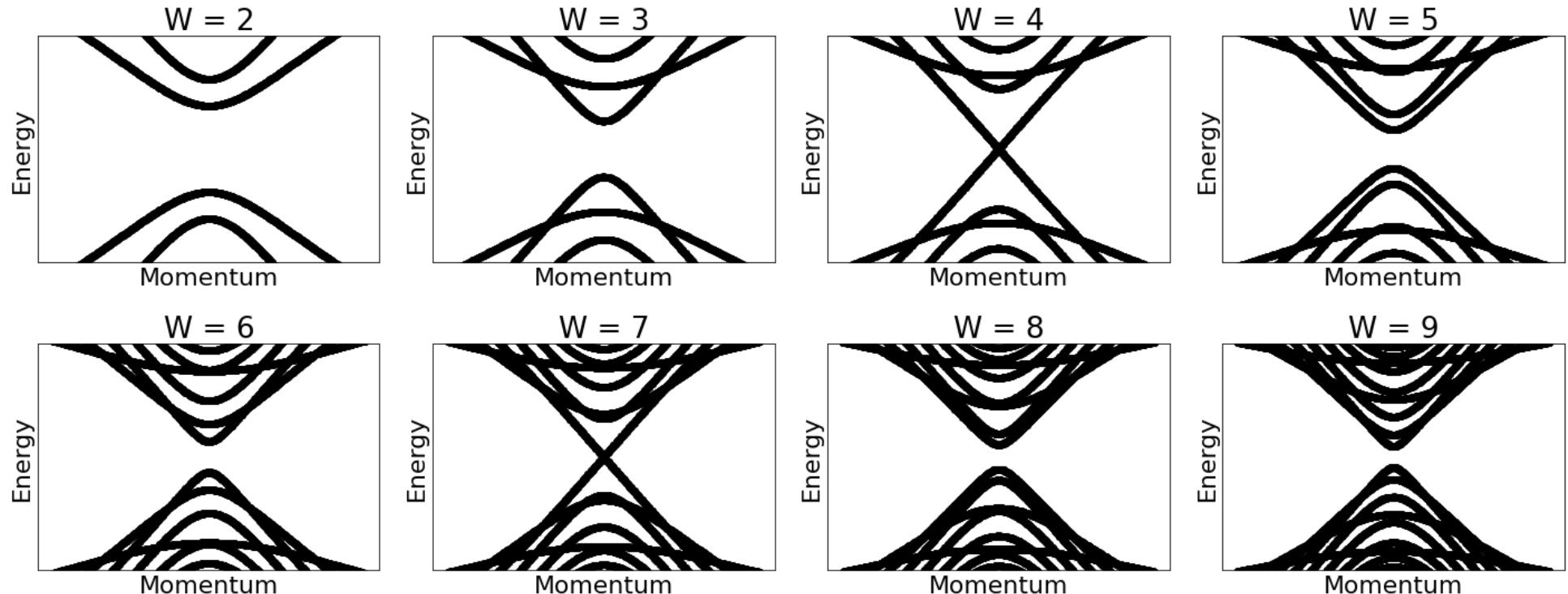
$$H = t \sum_{\langle ij \rangle} c_i^\dagger c_j$$

Band structure



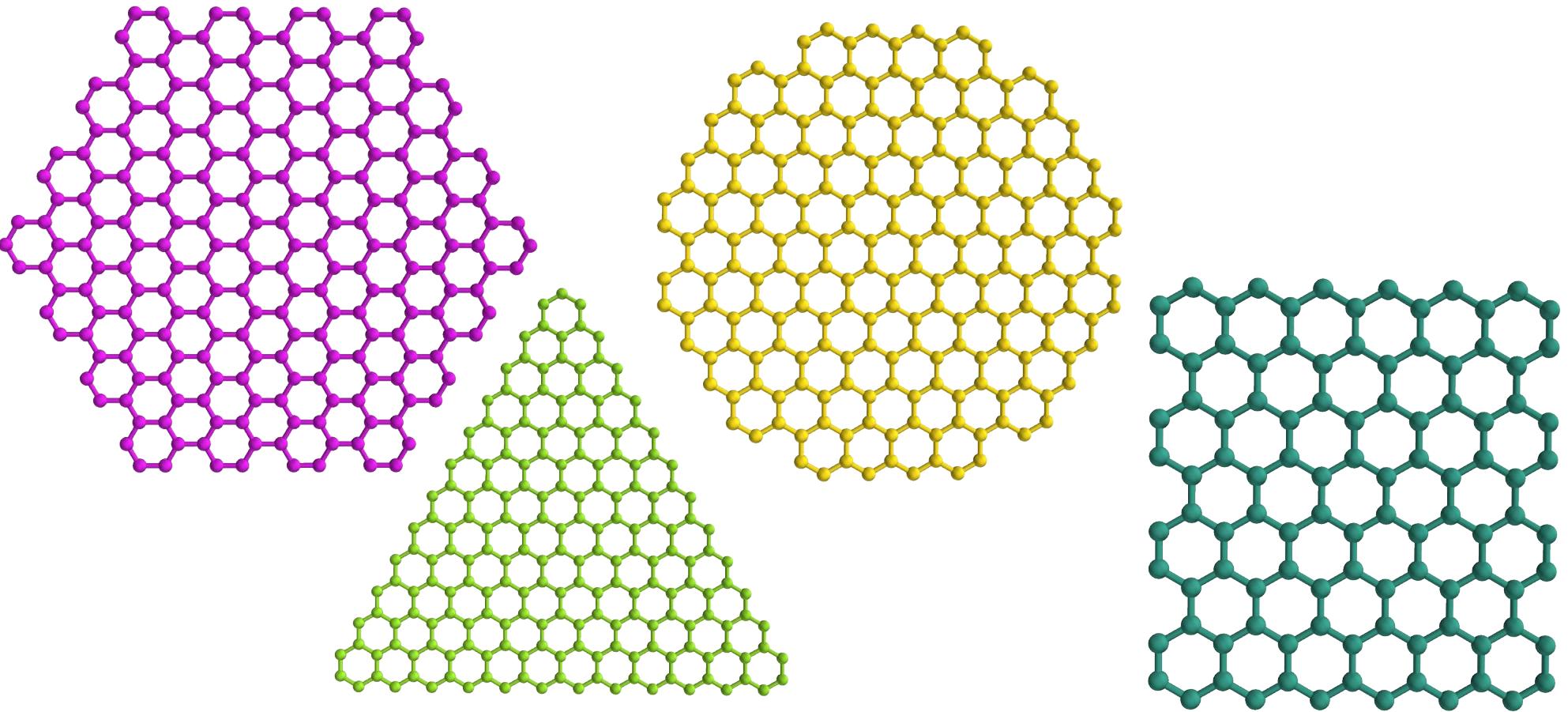
Electronic structure of graphene armchair nanoribbons

The width of a graphene nanoribbon drastically controls its electronic properties

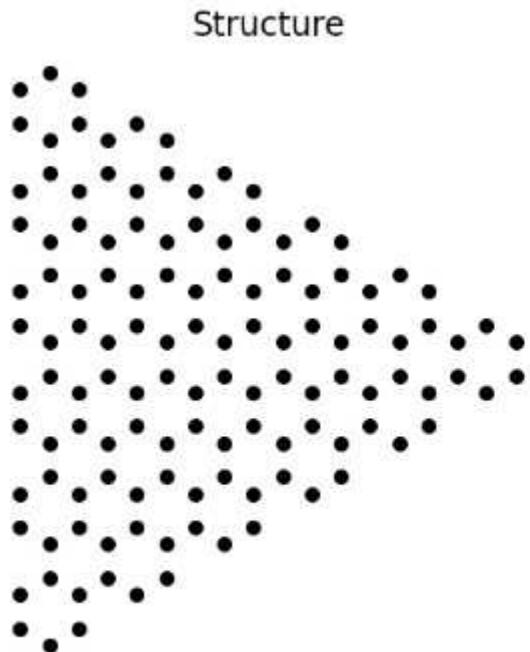


Quantum dots of 2D materials

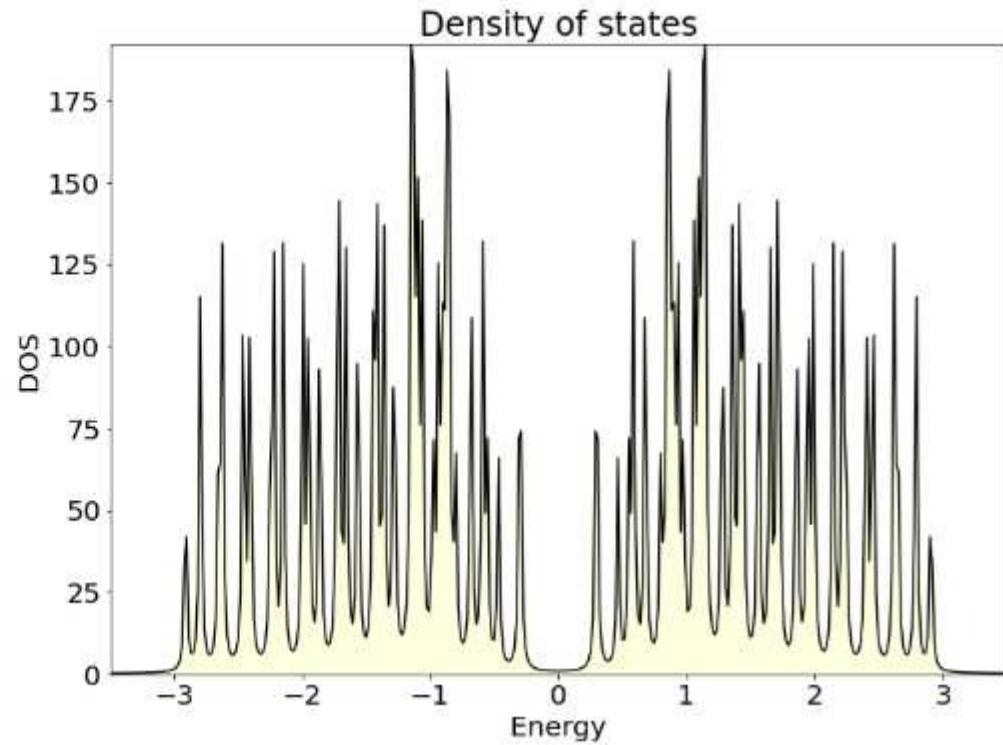
Graphene quantum dots



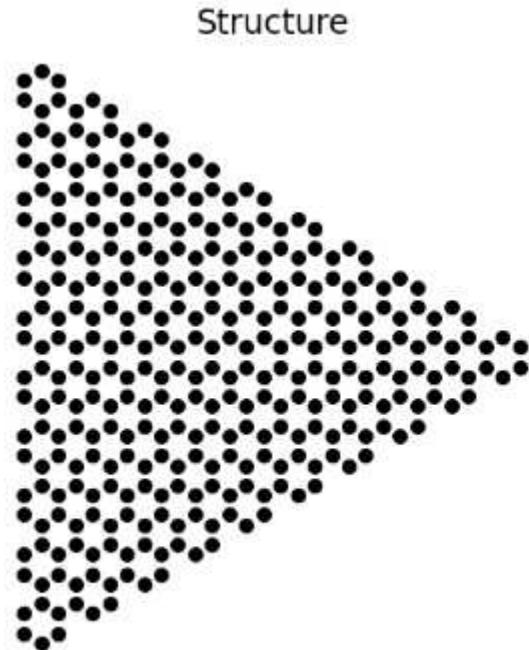
Electronic structure of graphene armchair nanoislands



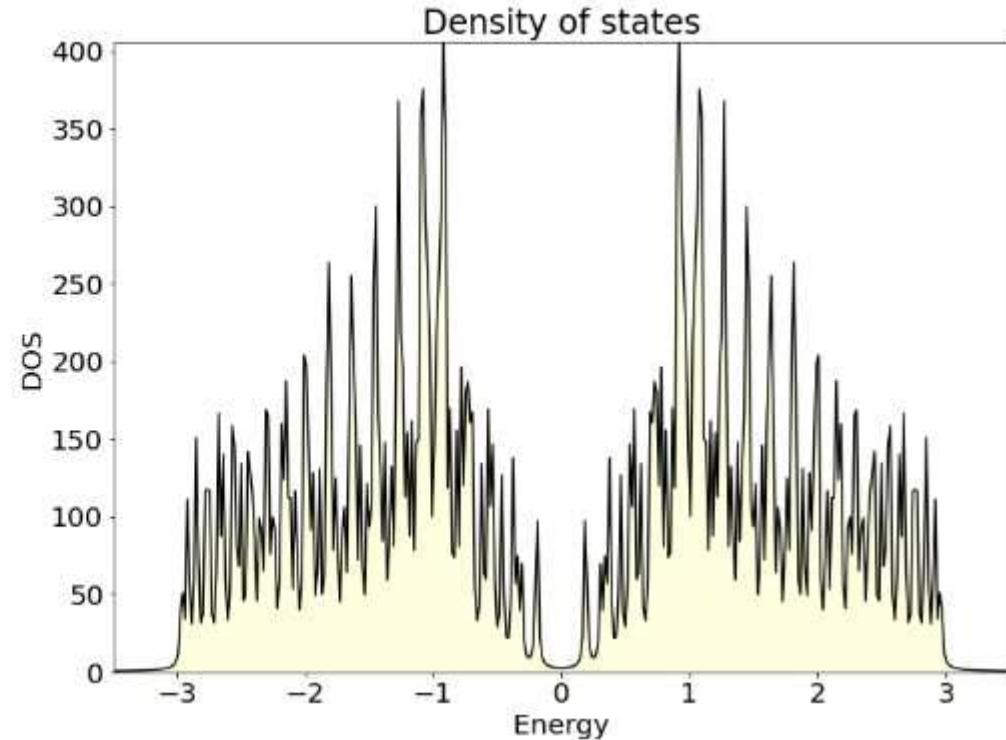
$$H = t \sum_{\langle ij \rangle} c_i^\dagger c_j$$



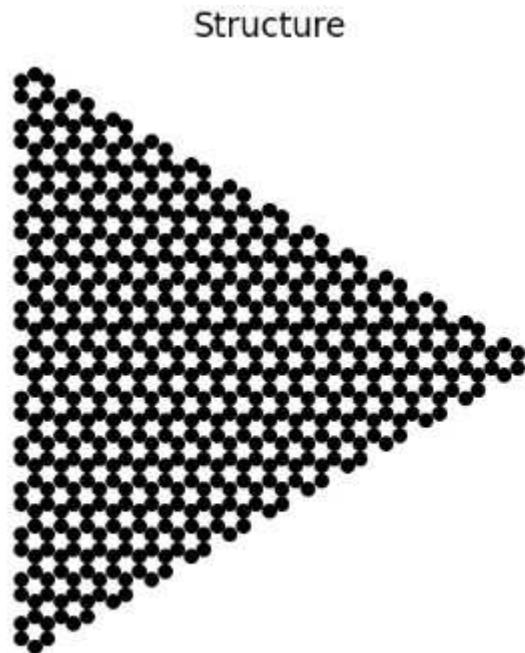
Electronic structure of graphene armchair nanoislands



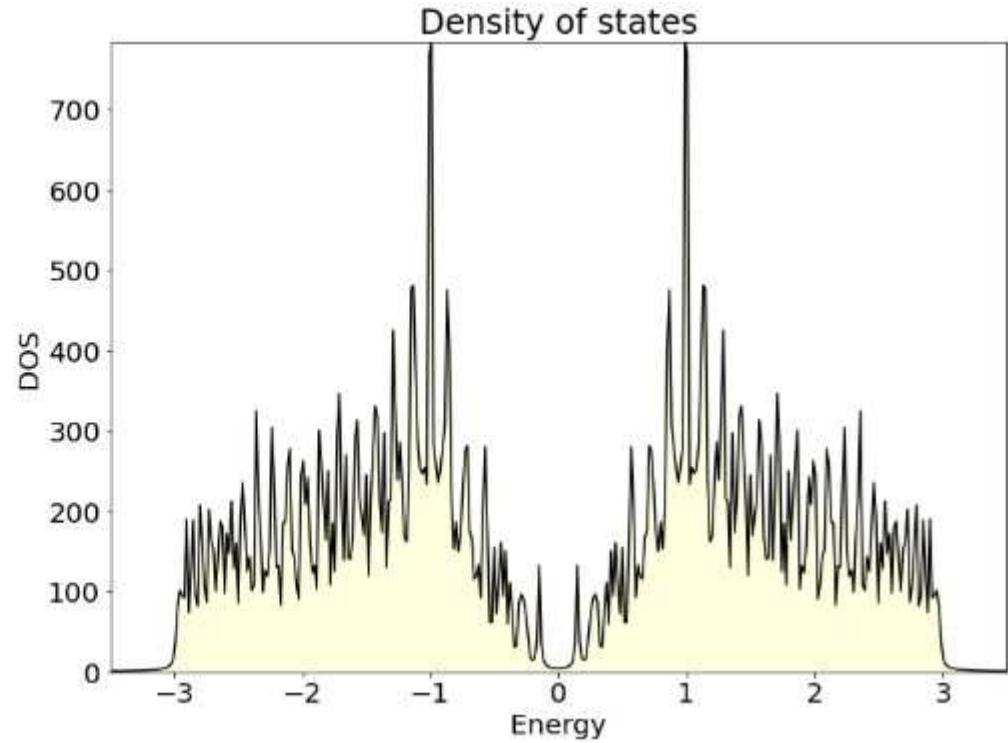
$$H = t \sum_{\langle ij \rangle} c_i^\dagger c_j$$



Electronic structure of graphene armchair nanoislands

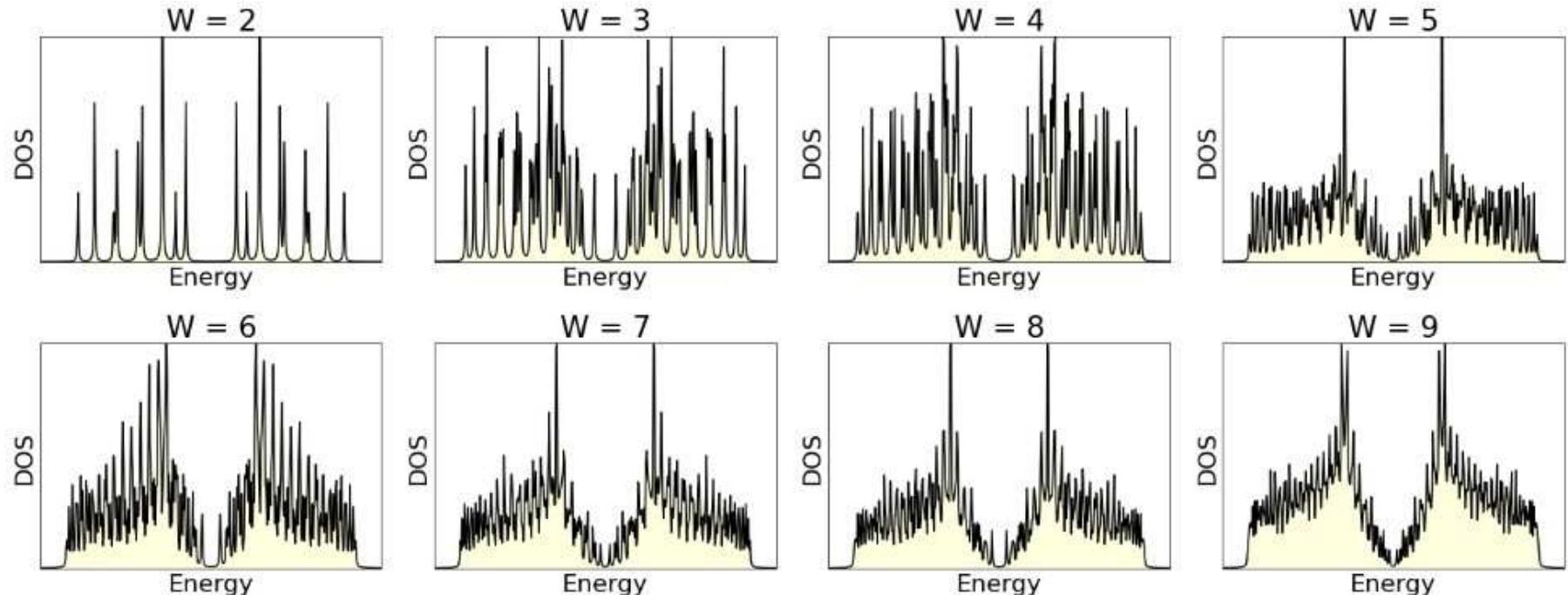


$$H = t \sum_{\langle ij \rangle} c_i^\dagger c_j$$

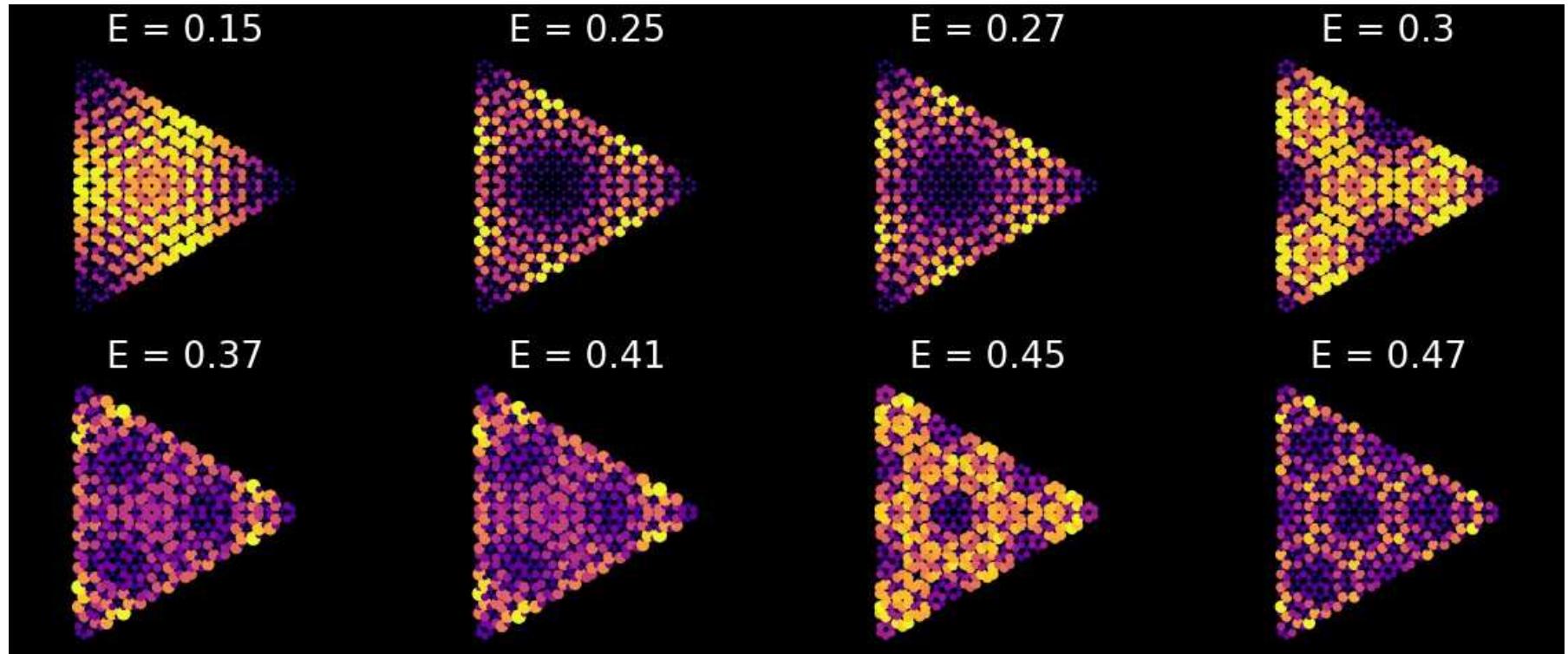


Graphene islands of different widths

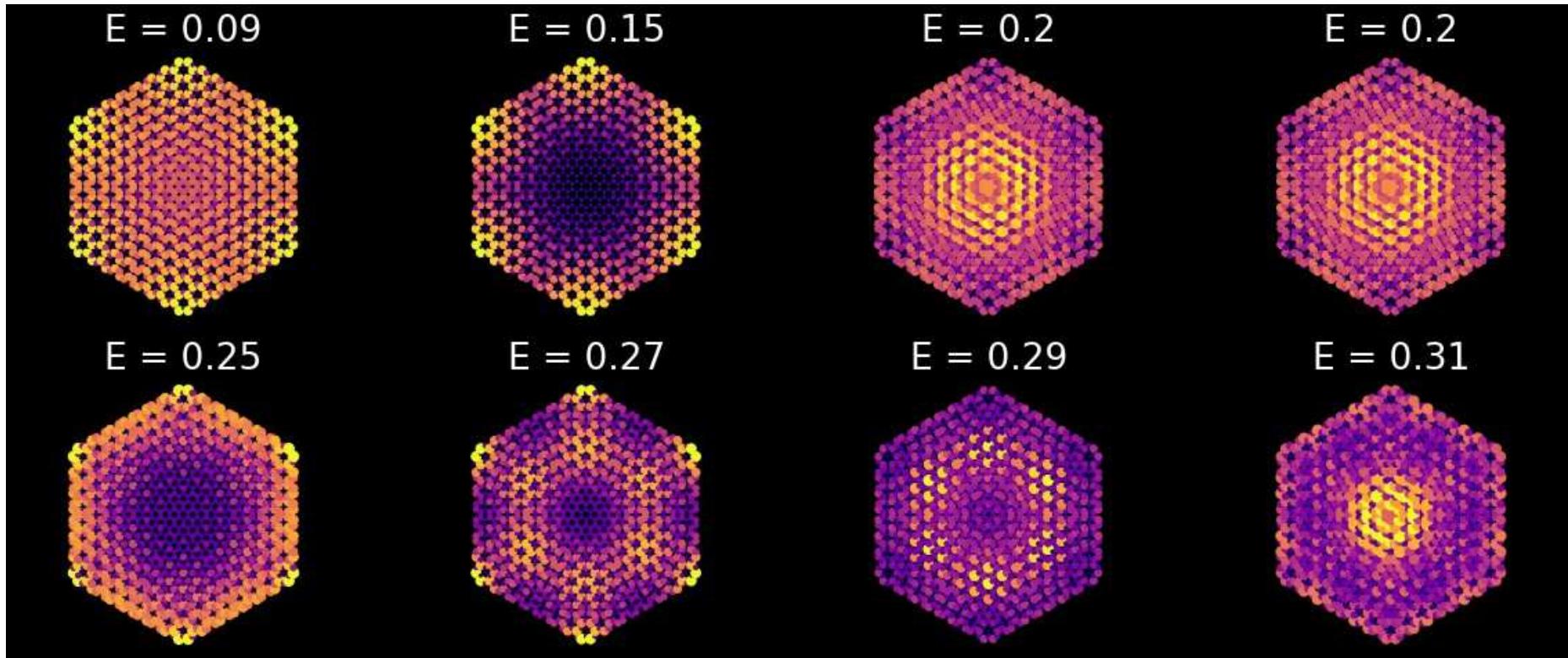
As the island becomes bigger, the spectrum of graphene is recovered



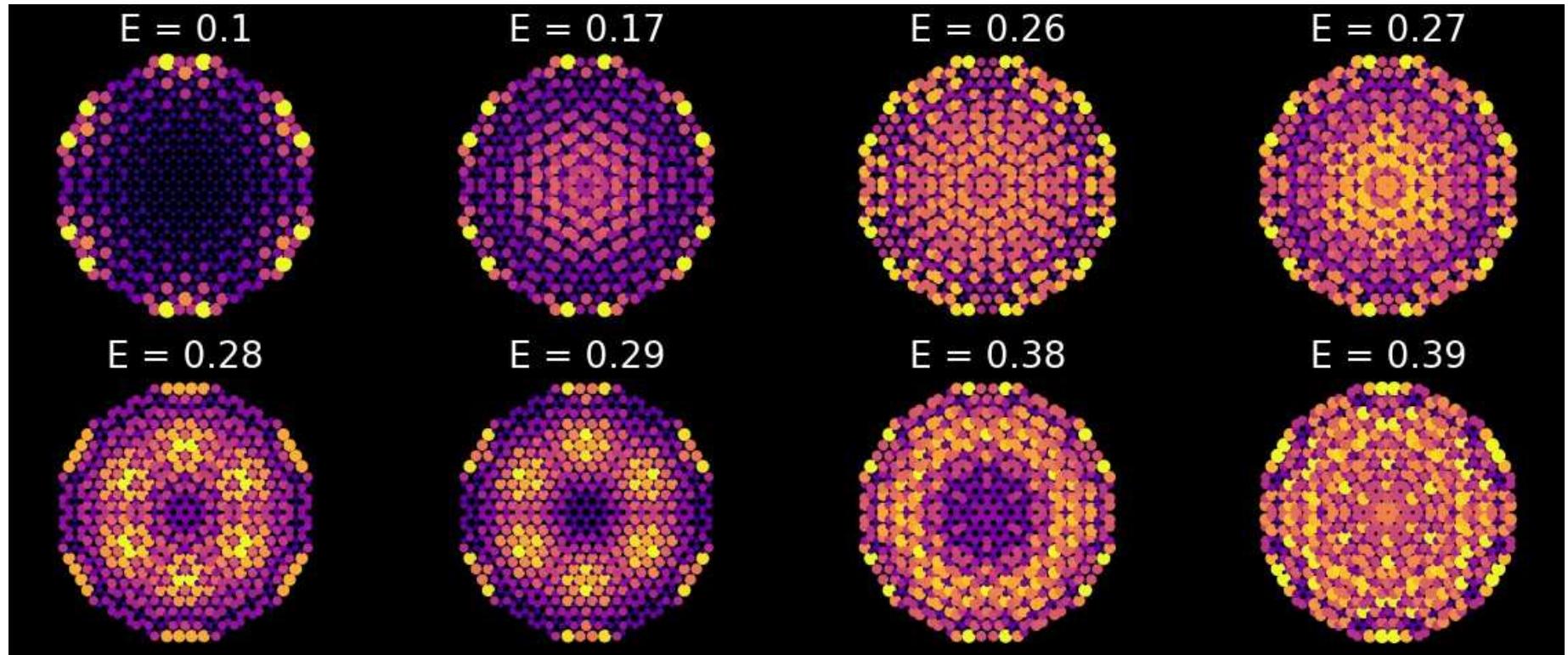
Confined modes in graphene islands



Confined modes in graphene islands



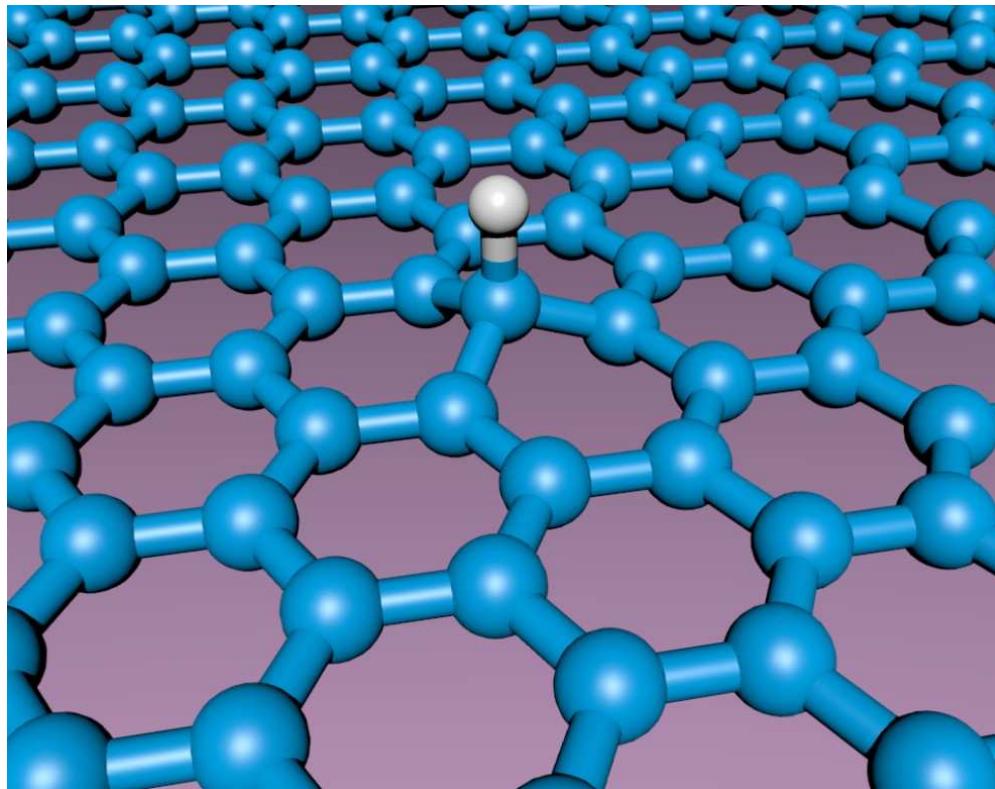
Confined modes in graphene islands



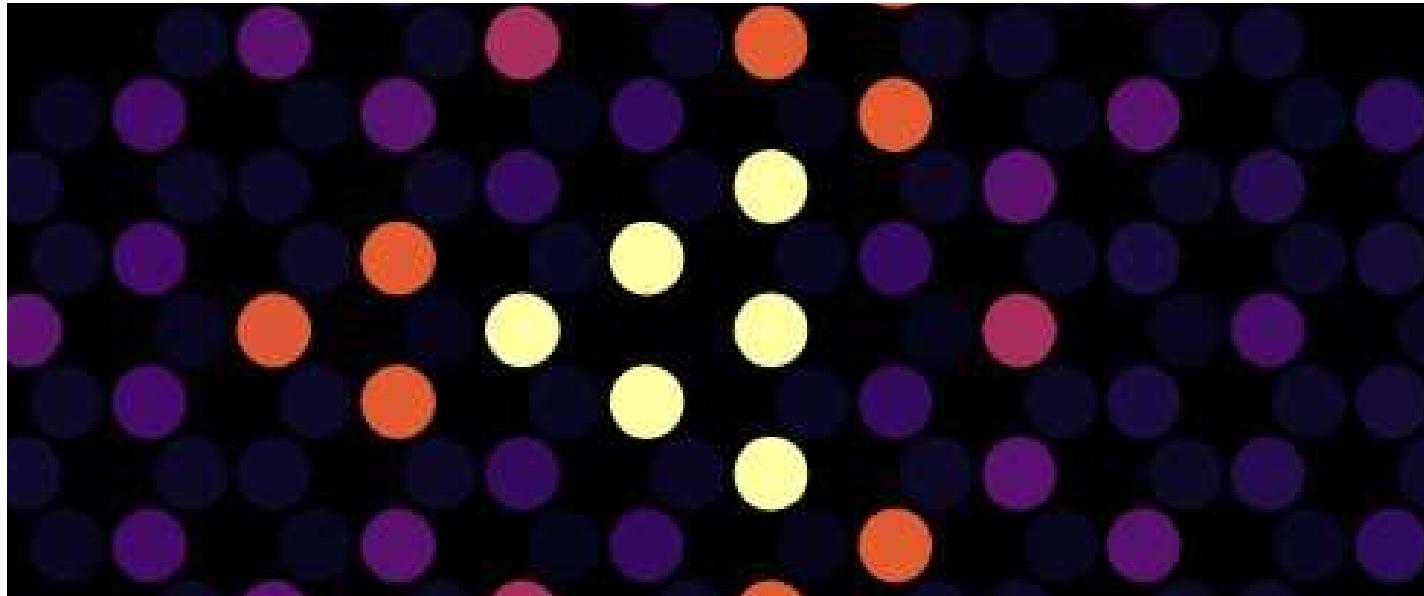
Defects in 2D materials

Impurities in monolayer graphene

Hydrogen adsorption in graphene



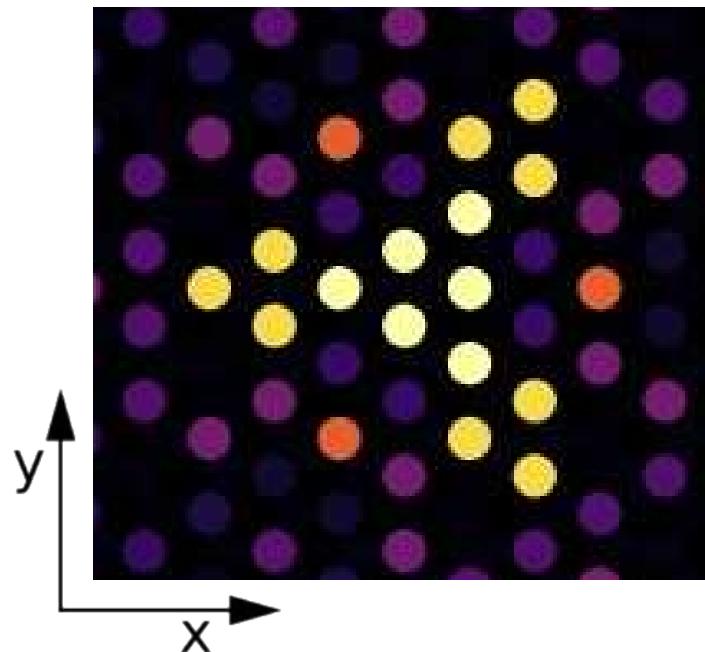
Individual hydrogen atoms in graphene



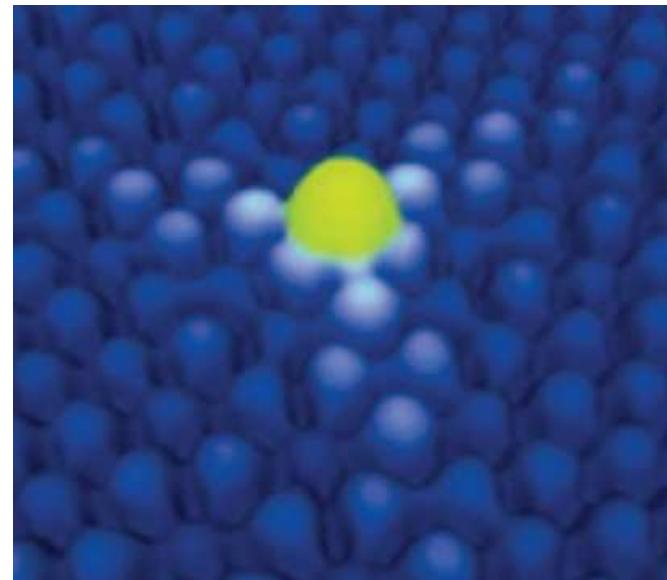
$$H = t \sum_{\langle ij \rangle} c_i^\dagger c_j$$

Single impurity in monolayer graphene

Local density of states



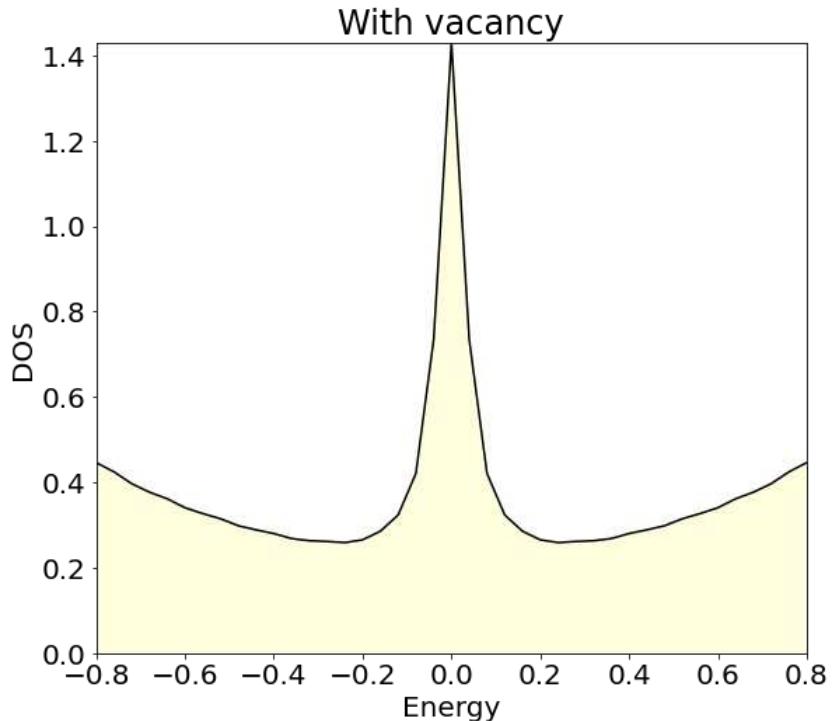
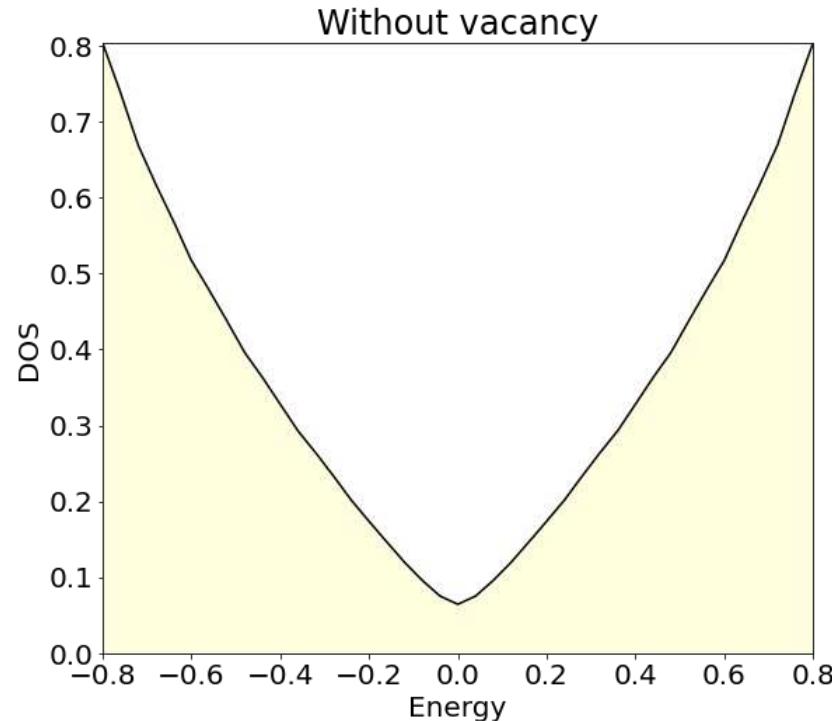
Experimental local density of states



Science, 352(6284), 437-441 (2016)

Hydrogen atoms create zero modes in graphene

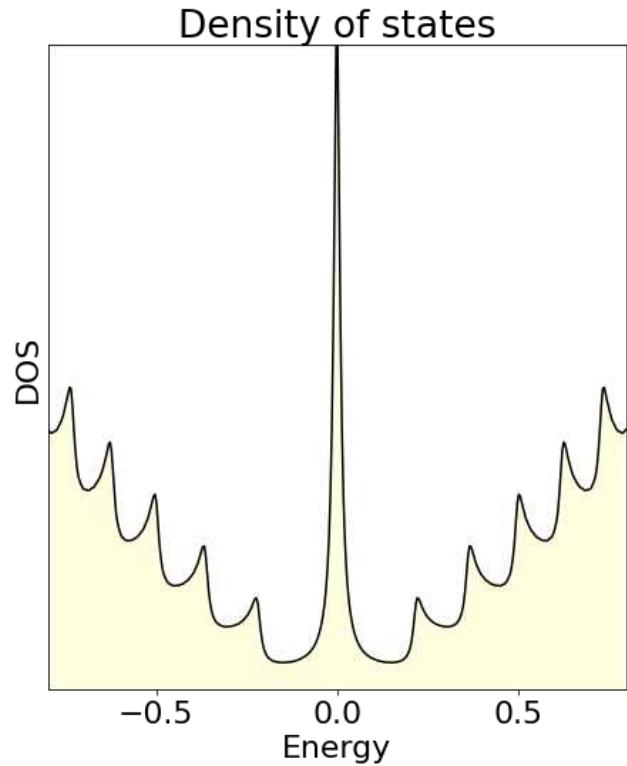
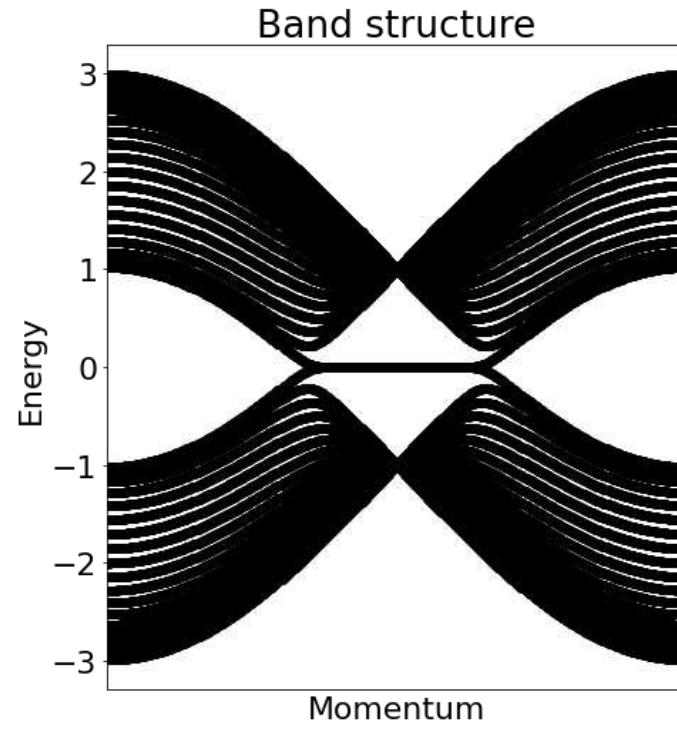
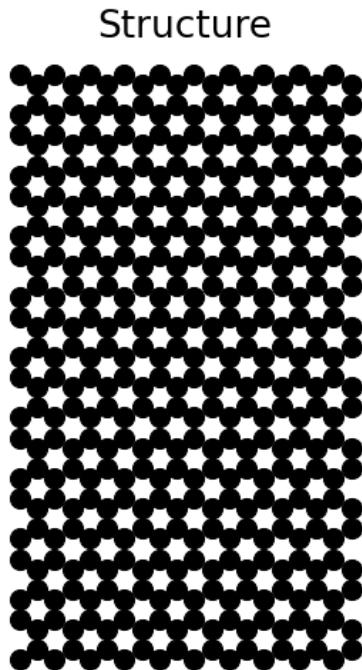
Individual hydrogen atoms in graphene



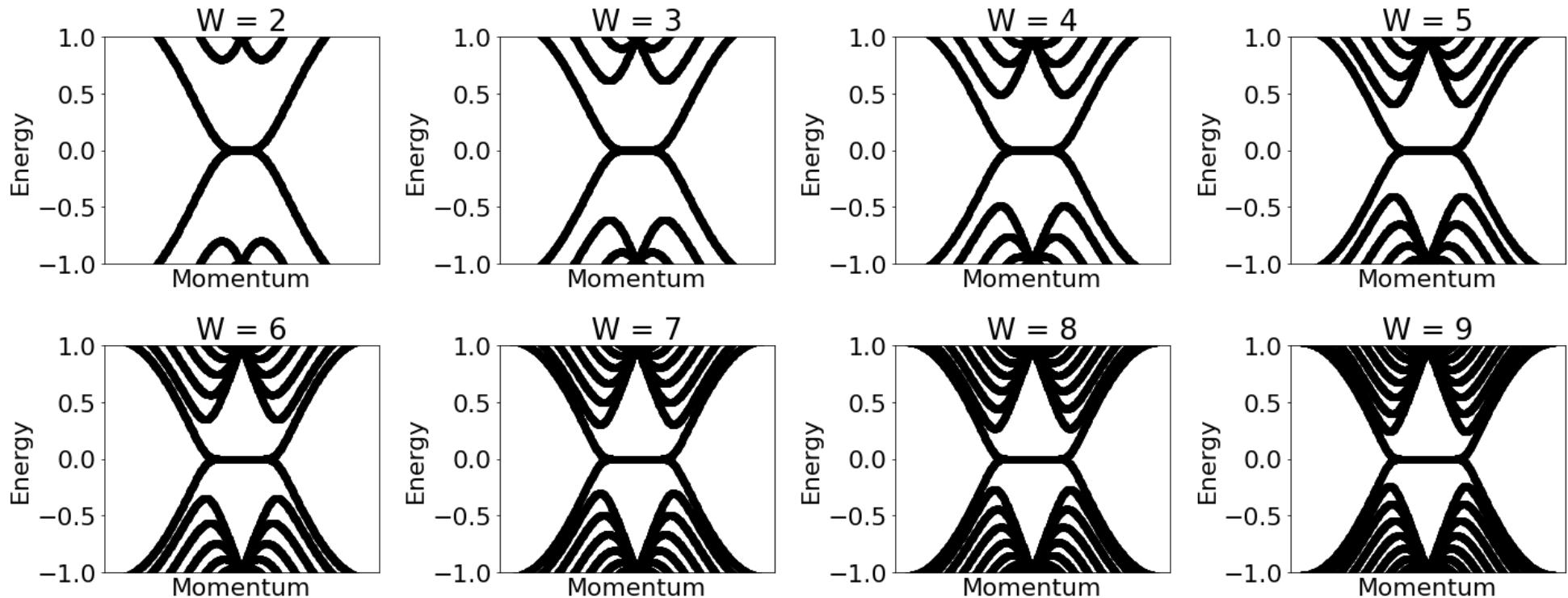
A vacancy in graphene gives rise to resonant zero modes

Electronic instabilities in 2D materials

Flat bands in graphene nanoribbons

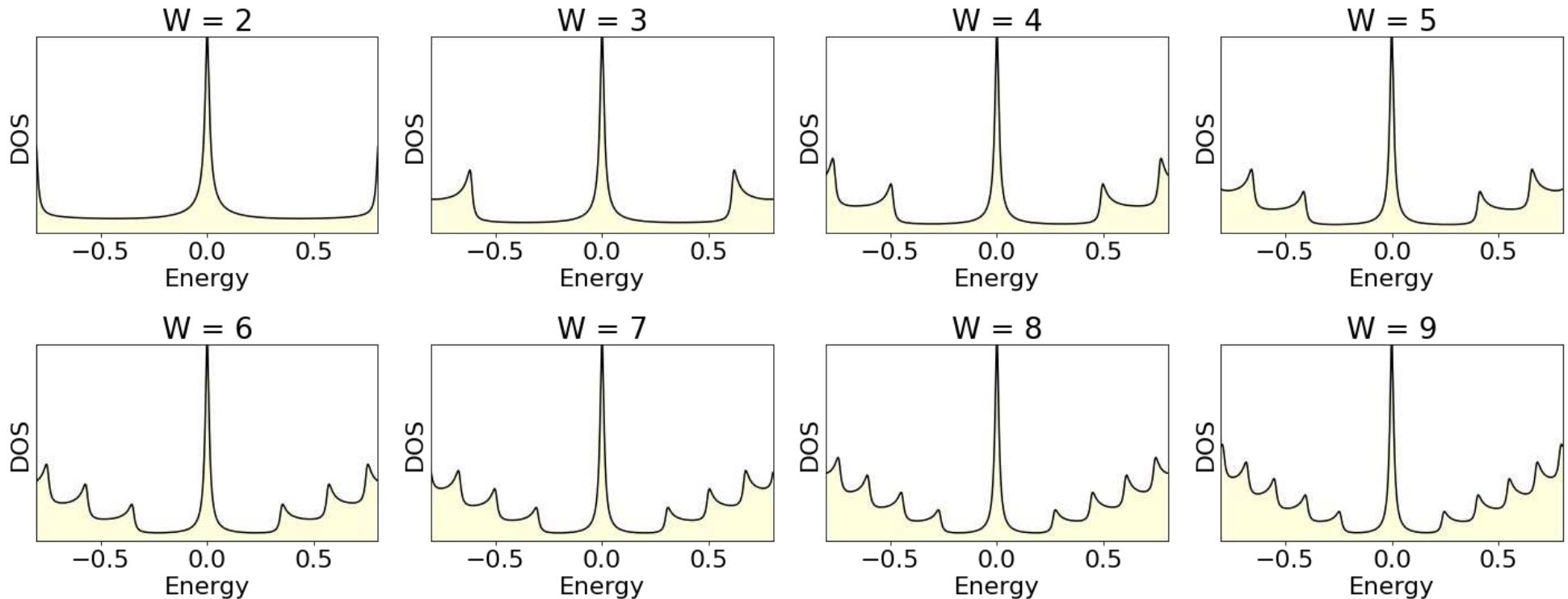


Electronic structure of zigzag graphene nanoribbons



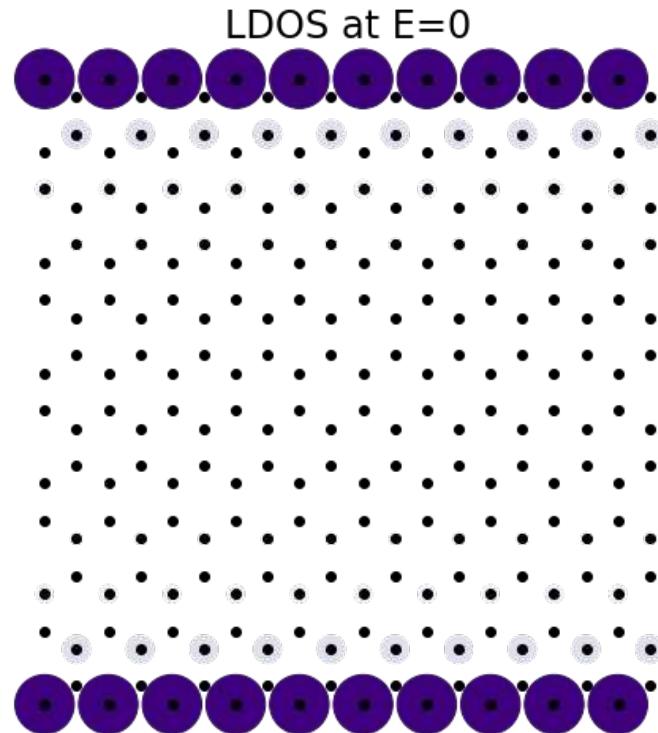
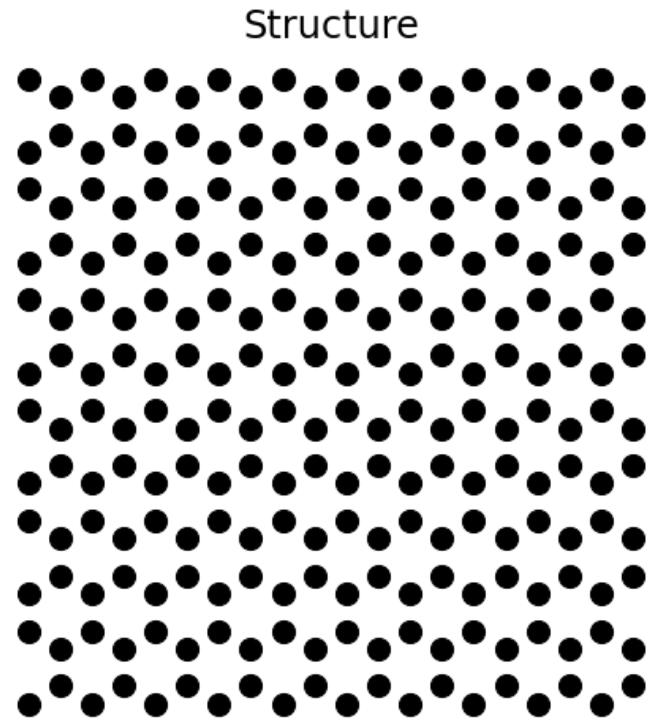
Flat bands appear in graphene zigzag nanoribbon of any width

Electronic structure of zigzag graphene nanoribbons



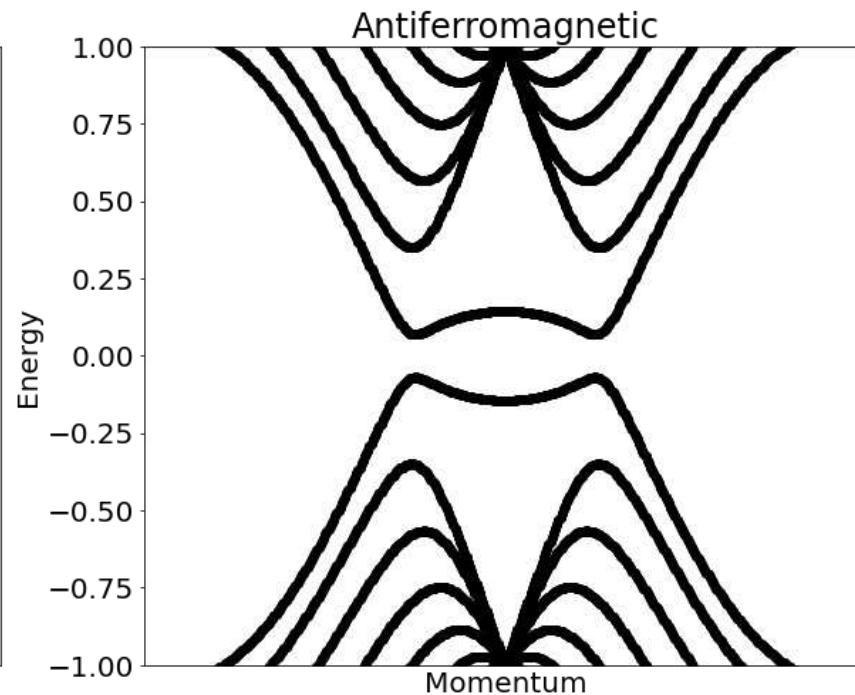
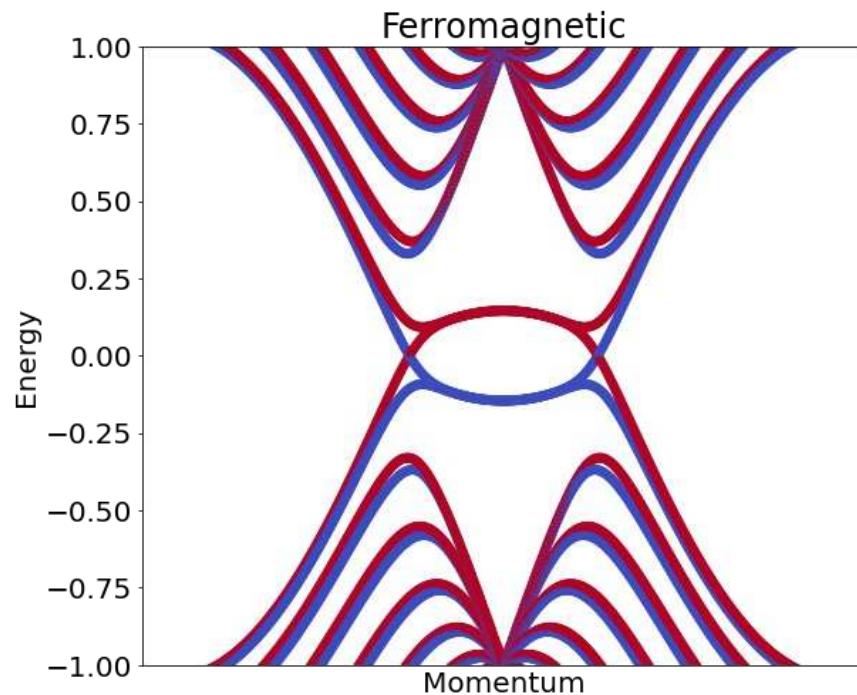
A divergent density of states appears in zigzag nanoribbon of any width

Electronic structure of graphene zigzag ribbons



Electronic interactions in graphene nanoribbons

Depending on the selfconsistent solution, the electronic structure can radically change



$$H = \sum_{ij,s} t_{ij} c_{is}^\dagger c_{js} + \sum_i U c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow}$$

Hands-on

Pyqula for the exercise sessions

- High level user friendly library for Python to solve tight-binding models
- Focus on:
 - Easy to use
 - Performing complex calculations with minimal effort
 - Full compatibility of different calculation modes

About the library

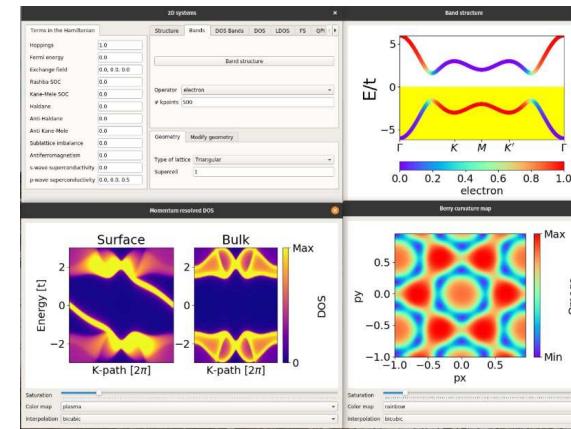
pyqula (library based)

```
from pyqula import geometry
g = geometry.honeycomb_lattice()
h = g.get_hamiltonian()
h.add_rashba(0.2) # Rashba spin-orbit coupling
h.add_zeeman([0.,0.,0.6]) # Zeeman field
from pyqula import topology
(kx,ky,omega) = h.get_berry_curvature() # compute Berry curvature
c = h.get_chern() # compute the Chern number
```

- Python library
- Ideal for complex models/calculations
- For writing in Python

<https://github.com/joselado/pyqula>

Quantum-lattice (built on top of pyqula)



- User-friendly interface for tight binding models
- Ideal for simple models and quick checks
- Fully interface-based, no scripting

<https://github.com/joselado/quantum-lattice>

Hamiltonians

Real-space tight binding Hamiltonians

$$H_0 = \sum_{i,j,s,s'} t_{i,j}^{s,s'} c_{i,s}^\dagger c_{j,s'} + \sum_{i,j,s,s'} \Delta_{i,j}^{s,s'} c_{i,s}^\dagger c_{j,s'}^\dagger + h.c.$$

With electronic interactions

$$H_{int} = \sum_{i,j,s,s'} V_{i,j} \sum_s c_{i,s}^\dagger c_{i,s} \sum_{s'} c_{j,s'}^\dagger c_{j,s'}$$

Workflow of the library

Create the geometry of the model

Dimensionality, supercell, vacancies, etc...

```
from pyqula import geometry
g = geometry.kagome_lattice() # get the geometry object
h = g.get_hamiltonian() # get the Hamiltonian object
(k,e) = h.get_bands() # compute the band structure
```

Include the different terms in the Hamiltonian

Kinetic energy, spin-orbit coupling, magnetism, superconductivity, interactions, etc..

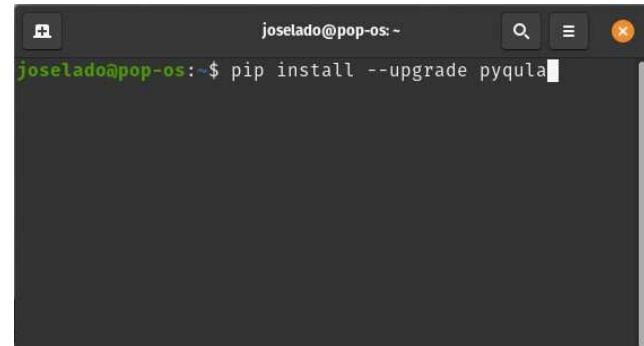
Compute the different observables of the system

Band structure, spectral functions, local DOS, topological invariants, expectation values, etc...

Installation

With pip (from the command line)

pip install --upgrade pyqula



A screenshot of a terminal window titled 'joselado@pop-os: ~'. The command 'pip install --upgrade pyqula' is visible in the terminal window.

*You can also download the whole source from

<https://github.com/joselado/pyqula>

Capabilities

Single particle Hamiltonians

- Spinless, spinful and Nambu basis for orbitals
- Full non-collinear electron and Nambu formalism
- Include magnetism, spin-orbit coupling and superconductivity
- Band structures with state-resolved expectation values
- Momentum-resolved spectral functions
- Local and full operator-resolved density of states
- 0d, 1d, 2d and 3d tight binding models
- Electronic structure unfolding in supercells

Capabilities

Interacting mean-field Hamiltonians

- Selfconsistent mean-field calculations with local/non-local interactions
- Both collinear and non-collinear formalism
- Anomalous mean-field for non-collinear superconductors
- Full selfconsistency with all Wick terms for non-collinear superconductors
- Constrained and unconstrained mean-field calculations
- Automatic identification of order parameters for symmetry broken states
- Hermitian and non-Hermitian mean-field calculations

Capabilities

Topological characterization

- Berry phases, Berry curvatures, Chern numbers and Z2 invariants
- Operator-resolved Chern numbers and Berry density
- Frequency resolved topological density
- Spatially resolved topological flux
- Real-space Chern density for amorphous systems
- Wilson loop and Green's function formalism

Capabilities

Spectral functions

- Spectral functions in infinite geometries
- Surface spectral functions for semi-infinite systems
- Interfacial spectral function in semi-infinite junctions
- Single impurities in infinite systems
- Operator-resolved spectral functions
- Green's function renormalization algorithm

Capabilities

Chebyshev kernel polynomial based-algorithms

- Local and full spectral functions
- Non-local correlators and Green's functions
- Locally resolved expectation values
- Operator resolved spectral functions
- Reaching system sizes up to 10000000 atoms on a single-core laptop

Capabilities

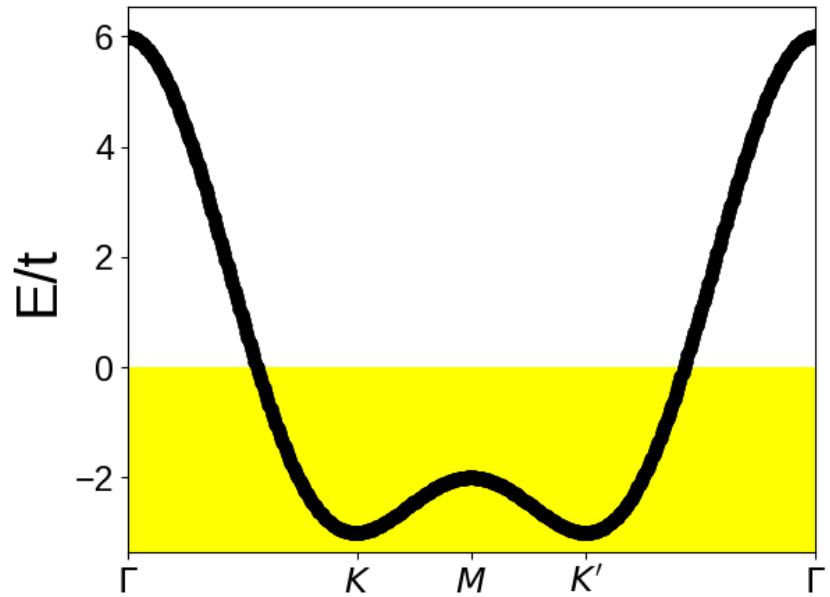
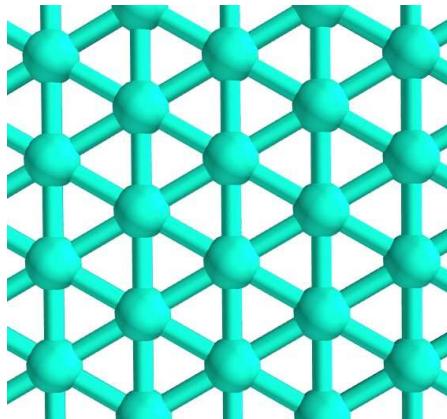
Quantum transport

- Metal-metal transport
- Metal-superconductor transport
- Fully non-collinear Nambu basis
- Non-equilibrium Green's function formalism
- Operator-resolved transport
- Differential decay rate
- Tunneling and contact scanning probe spectroscopy

First neighbor Hamiltonian in a triangular lattice

$$H = t \sum_{\langle ij \rangle} c_i^\dagger c_j$$

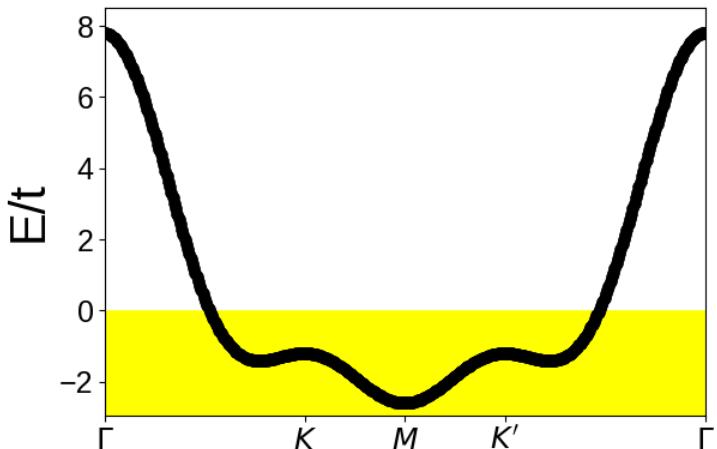
```
from pyqula import geometry
g = geometry.triangular_lattice() # get the geometry object
h = g.get_hamiltonian() # get the Hamiltonian object
(k,e) = h.get_bands() # compute the band structure
```



First and second neighbor Hamiltonian in a triangular lattice

$$H = t_1 \sum_{\langle ij \rangle} c_i^\dagger c_j + t_2 \sum_{\langle\langle ij \rangle\rangle} c_i^\dagger c_j$$

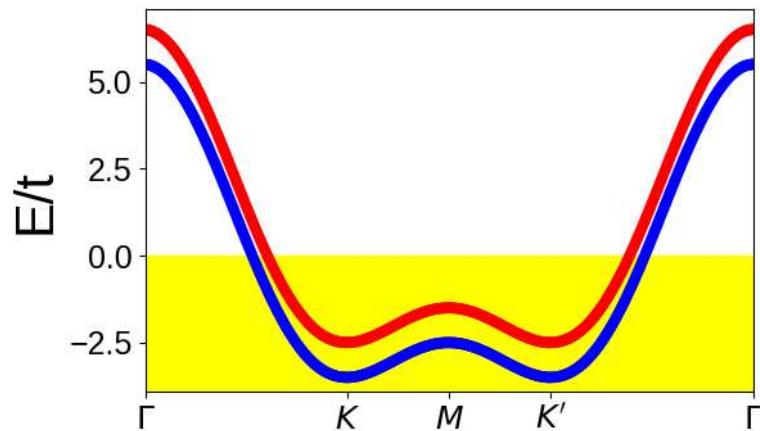
```
from pyqula import geometry
g = geometry.triangular_lattice() # get the geometry object
h = g.get_hamiltonian(tij=[1.0,0.3]) # get the Hamiltonian object
(k,e) = h.get_bands() # compute the band structure
```



Triangular lattice with an exchange field

$$H = t \sum_{\langle ij \rangle} c_{i,s}^\dagger c_{j,s} + B_z \sum_i \sigma_z^{s,s'} c_{i,s}^\dagger c_{j,s}$$

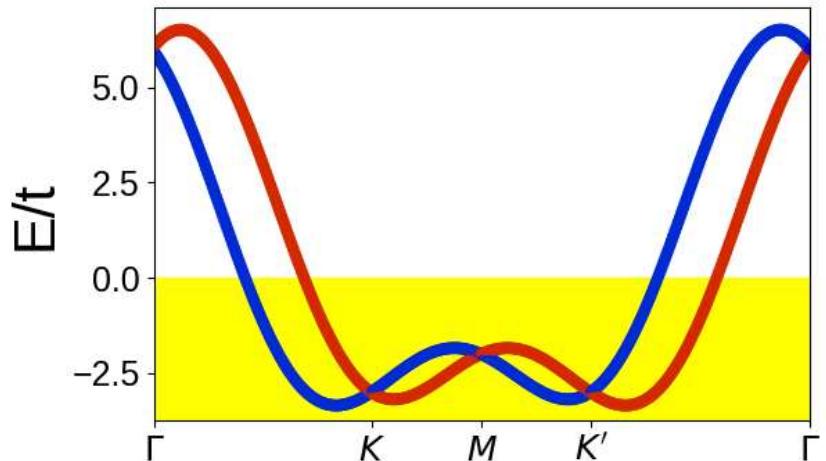
```
from pyqula import geometry
g = geometry.triangular_lattice() # get the geometry object
h = g.get_hamiltonian() # get the Hamiltonian object
h.add_exchange([0.,0.,0.5]) # add exchange field
(k,e,c) = h.get_bands(operator="sz") # compute the band structure
```



Triangular lattice with Rashba spin-orbit coupling

$$H = t \sum_{\langle ij \rangle} c_{i,s}^\dagger c_{j,s} + i\lambda_R \sum_{\langle ij \rangle} [(\mathbf{r}_i - \mathbf{r}_j) \times \boldsymbol{\sigma}^{s,s'}] \cdot \hat{z} c_{i,s}^\dagger c_{j,s}$$

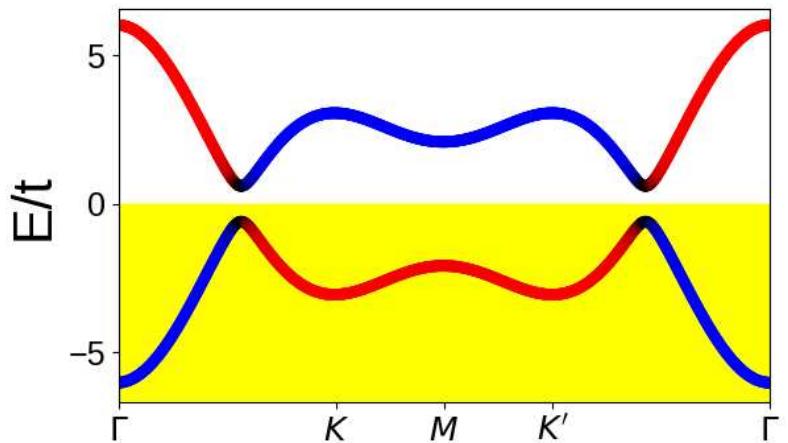
```
from pyqula import geometry
g = geometry.triangular_lattice() # get the geometry object
h = g.get_hamiltonian() # get the Hamiltonian object
h.add_rashba(0.6) # add Rashba SOC
(k,e,c) = h.get_bands(operator="sx") # compute the band structure
```



Triangular lattice with superconductivity

$$H = t \sum_{\langle ij \rangle} c_{i,s}^\dagger c_{j,s} + \Delta \sum_i c_{i,\uparrow}^\dagger c_{i,\downarrow}^\dagger + h.c.$$

```
from pyqula import geometry
g = geometry.triangular_lattice() # get the geometry object
h = g.get_hamiltonian() # get the Hamiltonian object
h.add_swave(0.6) # add superconductivity
(k,e,c) = h.get_bands(operator="electron") # compute the band structure
```



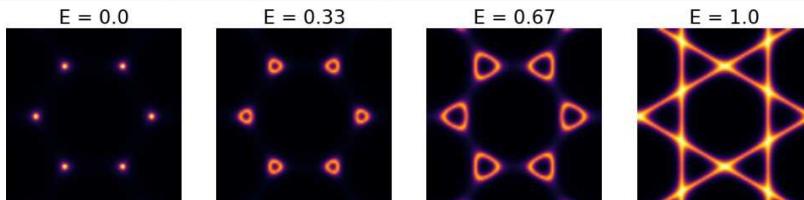
(Optional) exercise sessions

Download Jupyter-notebook from

https://github.com/joselado/emergent_phenomena_in_van_der_Waals_school_tifr_2023

You will see examples with the code

```
from pyqula import geometry
g = geometry.honeycomb_lattice() # generate a honeycomb lattice
h = g.get_hamiltonian() # generate the Hamiltonian
delta = 0.1 ; nk = 80 # smearing and knet
energies = np.linspace(0.,1.,4) # energies
ip = 1 # counter for the plot
for e in energies:
    (x,y,d) = h.get_fermi_surface(e=e,delta=delta,nk=nk) # compute Fermi surface
    plt.subplot(1,len(energies),ip) ; ip += 1 # set subplot
    d2d = d.reshape((nk,nk)) ; plt.imshow(d2d,vmin=0.,vmax=2./delta,cmap="inferno",interpolation="bicubic")
    plt.title("E = "+*str(np.round(e,2))) ; plt.axis("off")
```



You have to modify them, and answer questions

Exercise

- Identify at which energy the van Hove singularity appears
- Compute the Fermi surface at higher energies. How many pockets do you have after you pass the van Hove singularity?

