Emergence of Quantum Phases in Novel Materials

Ramón Aguado

Mª José Calderón

Leni Bascones

Alberto Cortijo

Teoría y Simulación de Materiales
Instituto de Ciencia de Materiales de Madrid

More is different

"The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe."

"The behavior of large and complex aggregates of elementary particles, it turns out, is not to be understood in terms of a simple extrapolation of the properties of a few particles. Instead, at each level of complexity entirely new properties appear."

1972, Anderson

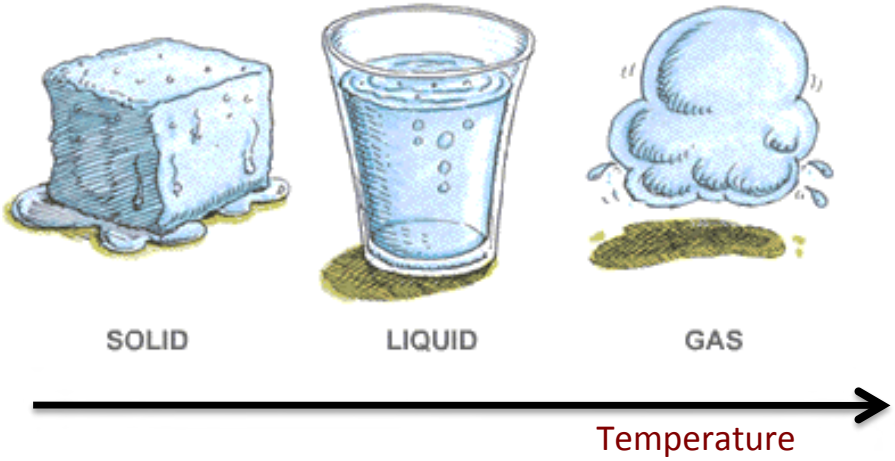
Emergence

Emergence

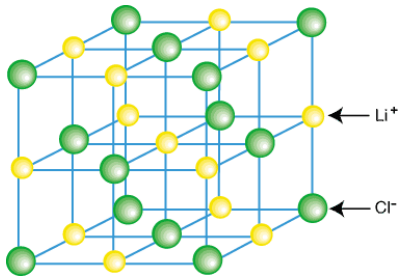
The arising of novel and coherent structures, patterns and properties during the process of self-organization in complex systems

Goldstein, Economist (1999)

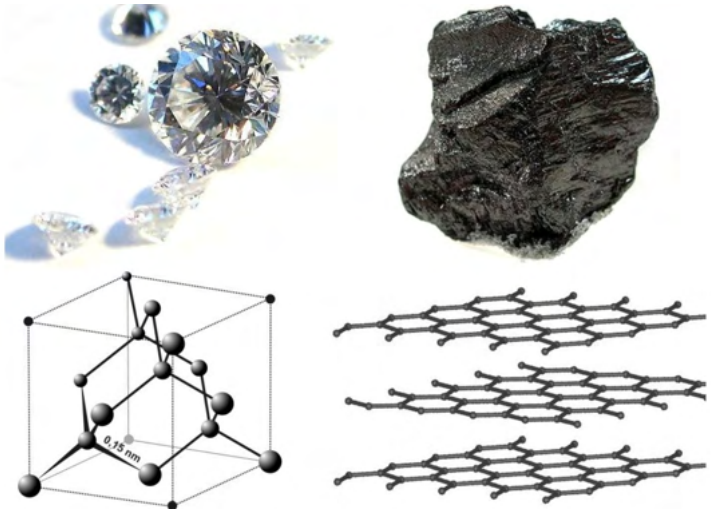
Emergence in condensed matter physics



Solids: broken translational symmetry

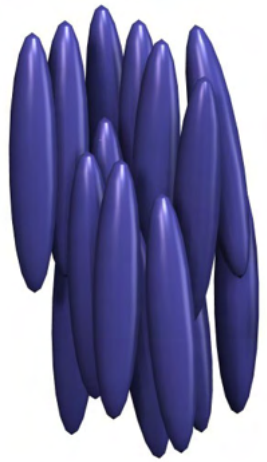


©askiitians



©Itub

Nematic liquid crystal:
Broken rotational symmetry



©kebes

Emergence in condensed matter

Electrons interact with each other and with the environment

Collective many-body behavior
(strongly correlated materials & mesoscopic systems)

To understand the complex behavior
Isolate the fundamental processes

More than 35 years of intensive research effort and
continuously new surprises appear

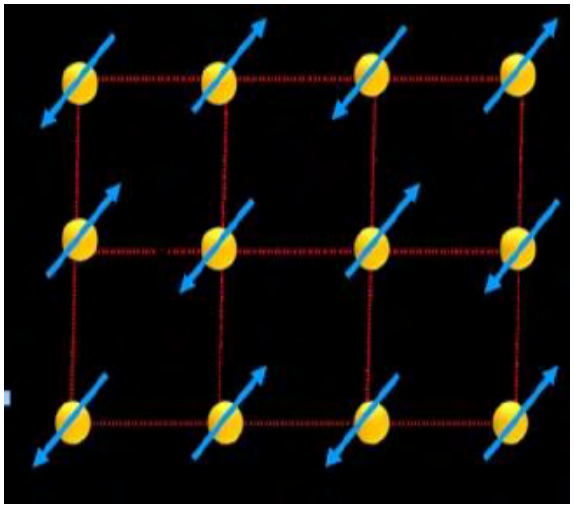
Emergence in condensed matter

Pauli exclusion principle

Quantum states: Magnetism: Ferromagnetism, Antiferromagnetism
Charge density waves, Superconductivity, Nematicity, and other

Electrons:
itinerant or localized

- Origin of magnetism
- Scattering processes
- Metallicity



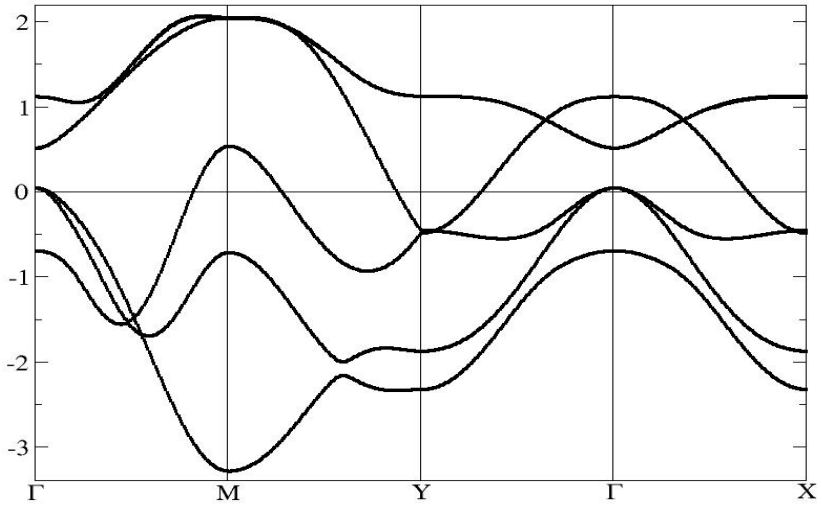
Lattice: Symmetries, Frustrated, Bipartite …

Dimension: Influence in ordered states but also in “normal state”

Topology: A new way to classify condensed matter systems with novel effects

And many other issues: interplay with disorder …

Band theory & DFT: Our basic description of solids



Bloch states: electronic bands

The electron moves in the average periodic potential of the solid

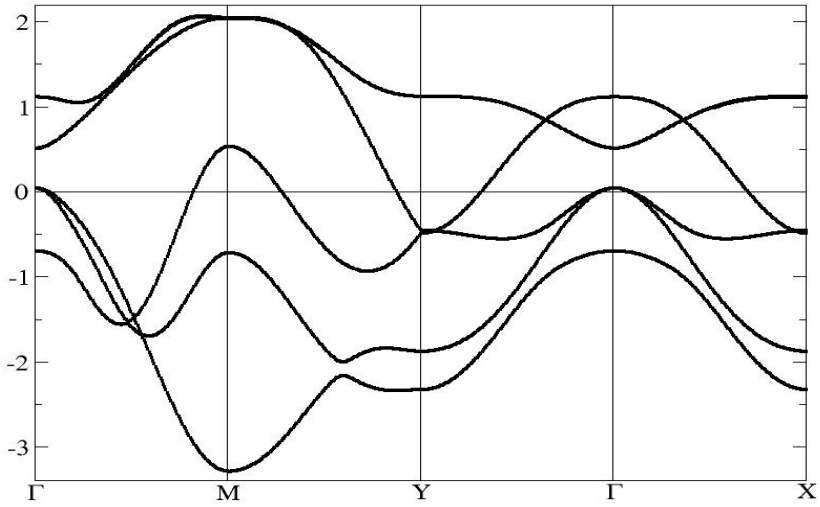
Band theory: Basis of our understanding of solids

- Metals and insulators

- Dependence on temperature of measurable quantities (Cv, χ, ..)

- Density Functional Theory: Ability to calculate the bands

Emergence in condensed matter



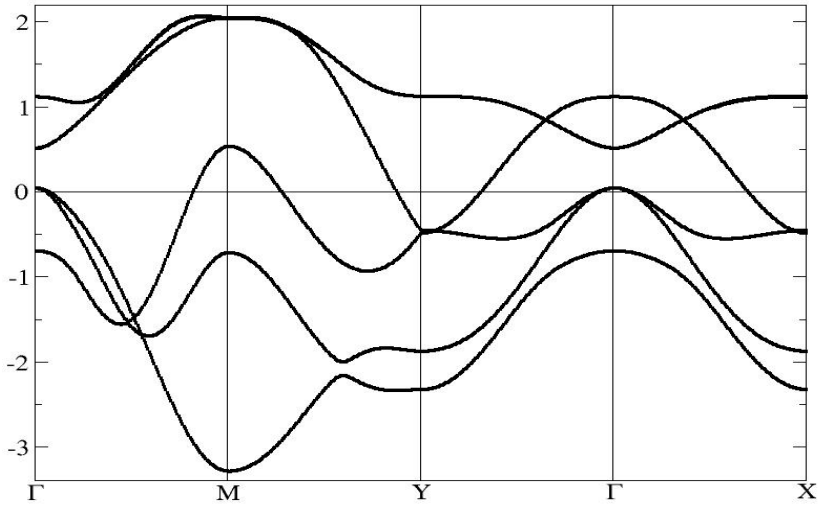
Bands generally calculated using DFT

Band theory is basically a description based on single particle states

Interactions are not small and the electrons should react to the presence of other electrons

Why does band theory work?

Emergence in condensed matter



Bands generally calculated using DFT

Band theory is basically a description based on single particle states

↓

Fermi liquid theory

Perturbative versus non-perturbative effect of interactions

↘

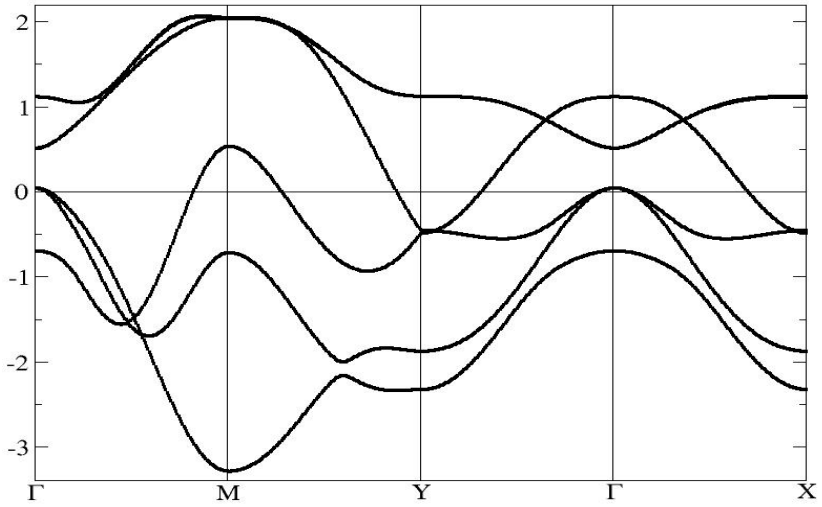
Same behavior but with renormalized parameters

{

Metals and insulators

Dependence on temperature of measurable quantities (Cv, χ, ..)

Emergence in condensed matter



Bands generally calculated using DFT

Band theory is basically a description based on single particle states

↓

Fermi liquid theory

Perturbative versus non-perturbative effect of interactions

↙

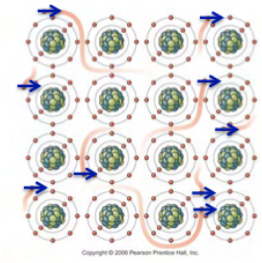
Phase transitions & symmetry breaking

Examples of electronic ordered phases

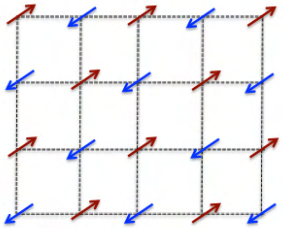
Spin order

Charge order

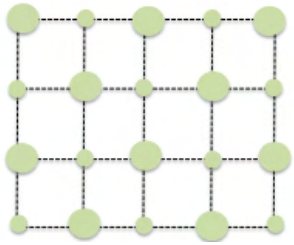
The symmetry of the atomic lattice is preserved



Neel antiferromagnet

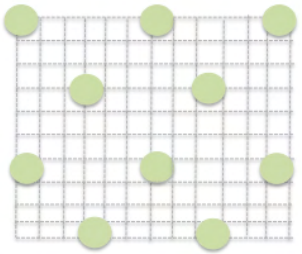


Charge density wave

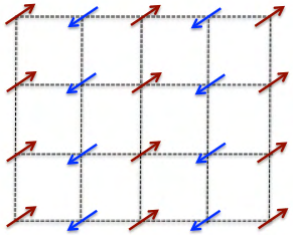


Lattice translational symmetry broken

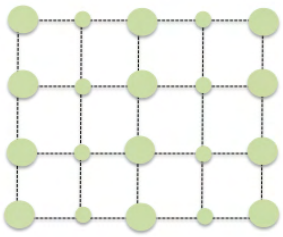
Wigner crystal



Stripe antiferromagnet



Charge stripes



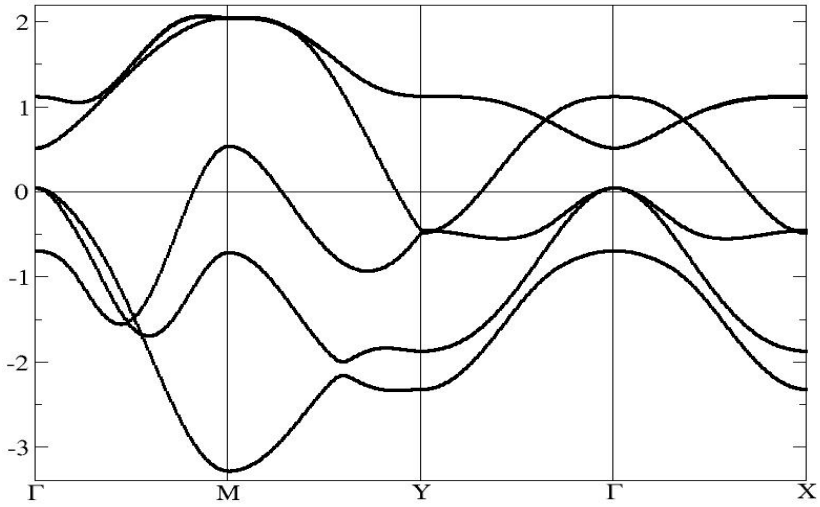
Lattice translational and rotational symmetry broken

Latice rotational symmetry broken

Spin nematic

Charge nematic

Emergence in condensed matter



Bands generally calculated using DFT

Band theory is basically a description based on single particle states

↓

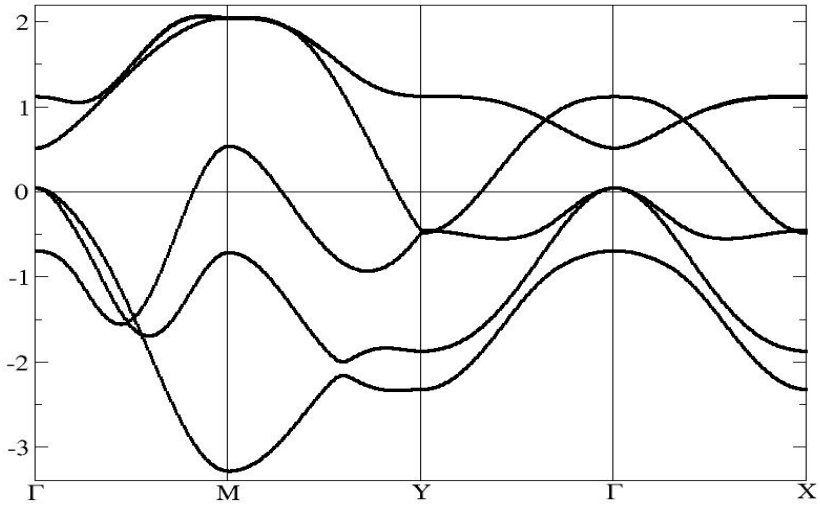
Fermi liquid theory

Perturbative versus non-perturbative effect of interactions

Phase transitions & symmetry breaking

- Fermi surface instabilities (itinerant electrons)
- Localization (electronic bands are lost)
- Itinerant + local electrons

Emergence in condensed matter



Bands generally calculated using DFT

Band theory is basically a description based on single particle states

↓

Fermi liquid theory

Perturbative versus non-perturbative effect of interactions

Given a particular system,
should we expect that band theory works?

What kind of instabilities may the system show?

Interactions: localization and superconductivity

Mott transition:

a material predicted by band theory to be metallic becomes **an insulator due to electronic interactions**
even without symmetry breaking

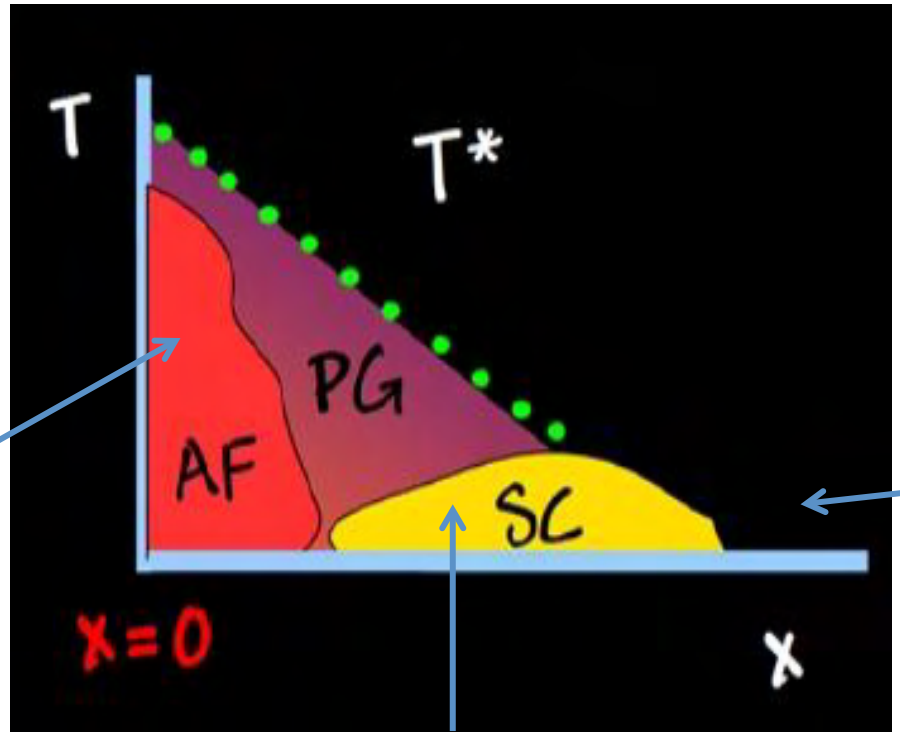
Superconductivity:

Below a critical temperature **resistivity goes to zero**.
(due to phonons we know, but probably also
due to magnetic fluctuations or Mott physics)

Interactions: localization and superconductivity

Cuprates: high temperature superconductors

From an antiferromagnetic Mott insulator to a superconductor and then a metal



Antiferromagnetic Mott insulator

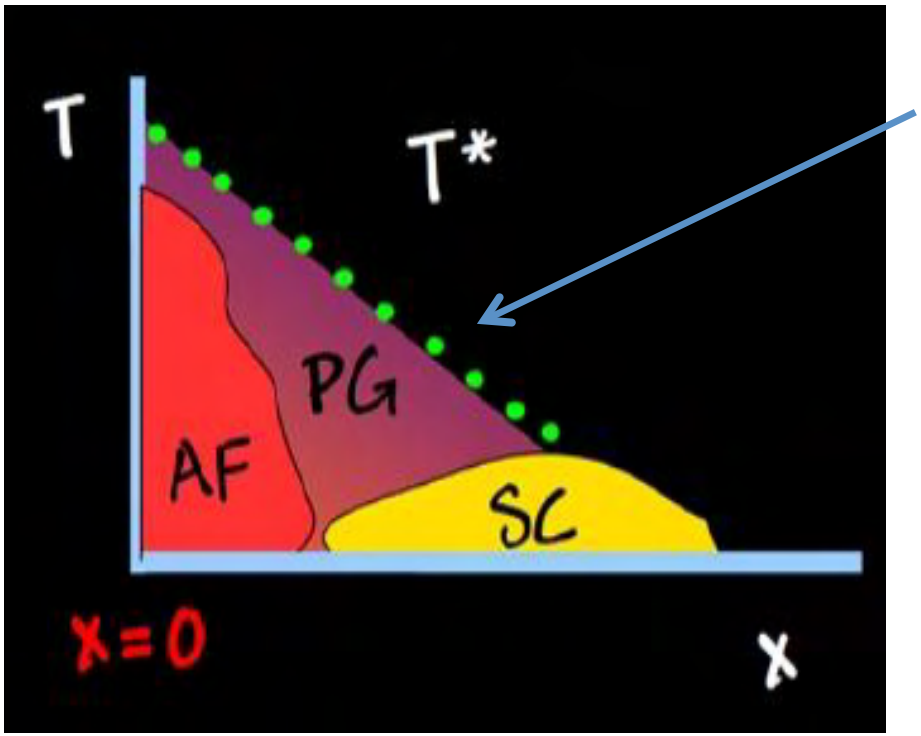
Metal

High-temperature superconductor

Interactions: localization and superconductivity

Cuprates: high temperature superconductors

From an antiferromagnetic Mott insulator to a superconductor and then a metal

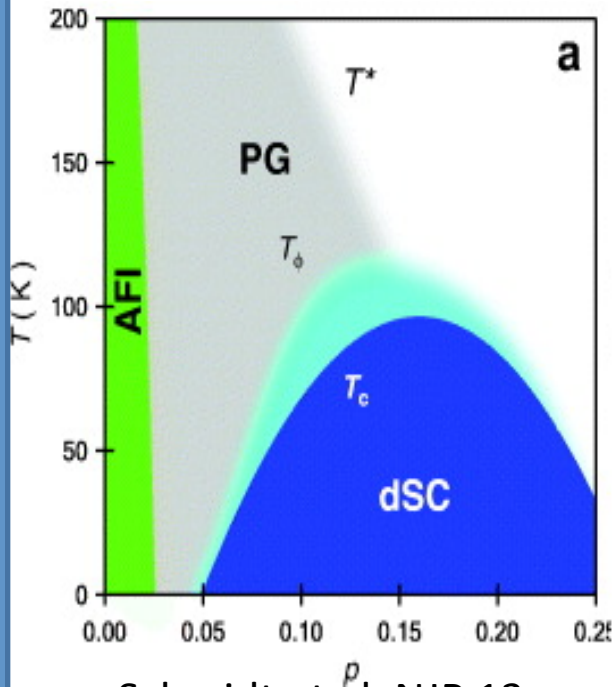


Pseudogap: Is it a new state of matter? A remanent of the Mott insulator or another broken symmetry phase?

Interactions: localization and superconductivity

Hole doped cuprates: high temperature superconductors

Huge developments in ideas and in theoretical and experimental techniques



Schmidt et al, NJP 13, 065014 (2011)

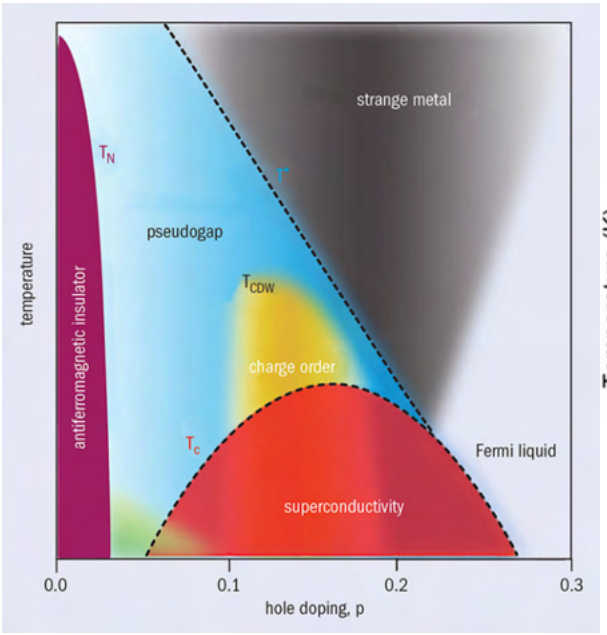
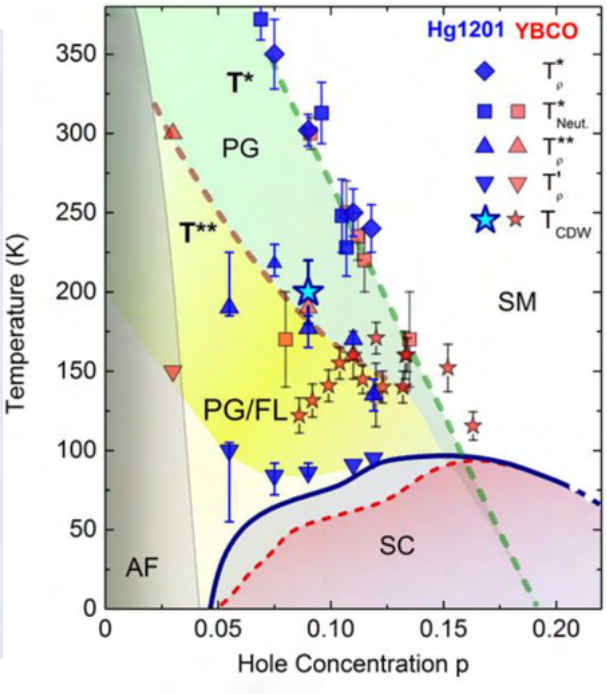
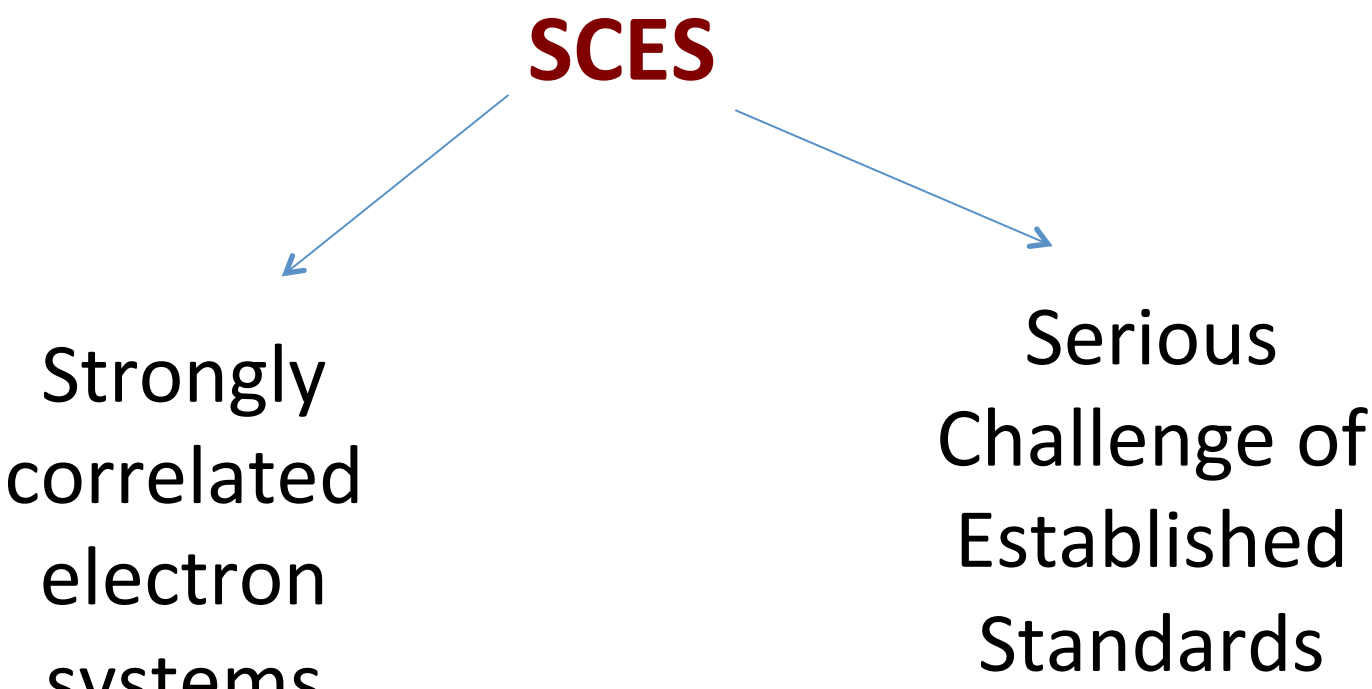


Fig: Inna Vishik



Nature Comms 5, 5875 (2014)

Emergence in condensed matter



Emergence in condensed matter

SCES

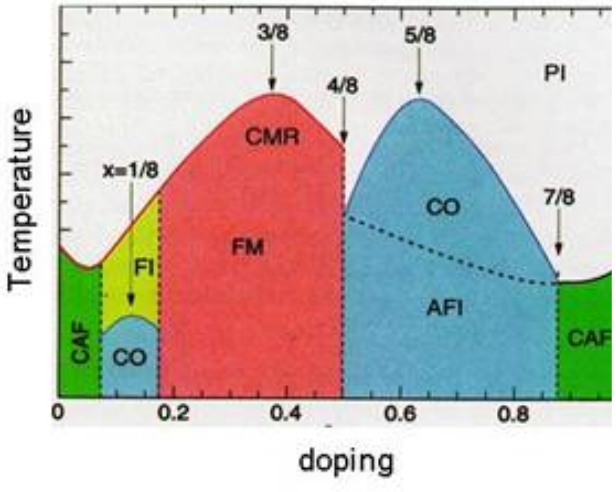
Strongly correlated electron systems

Difficulty to unveil the fundamental properties both theoretically & experimentally (away from controlled theoretical limits, competing states, not always possible to do many experiments…)

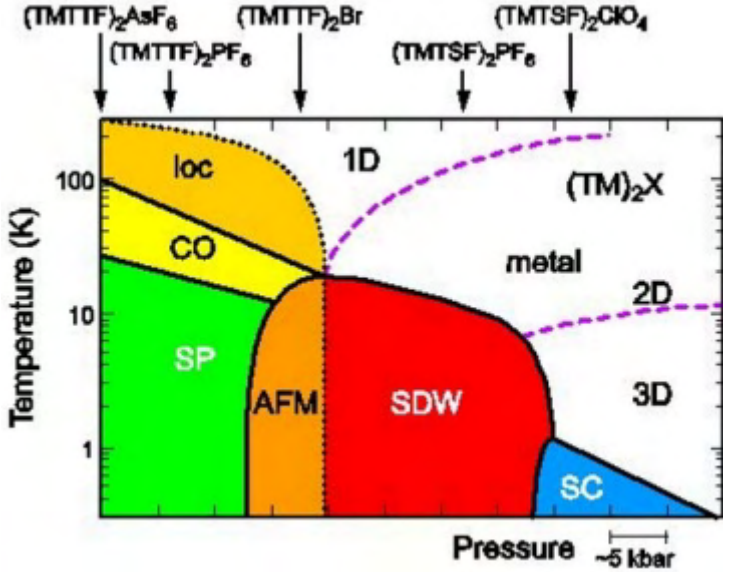
Emergence in condensed matter from electronic interactions

Strongly correlated electron systems:

very sensitive to changes(Pressure, Magnetic Field, doping…)



Typical phase diagram of manganites

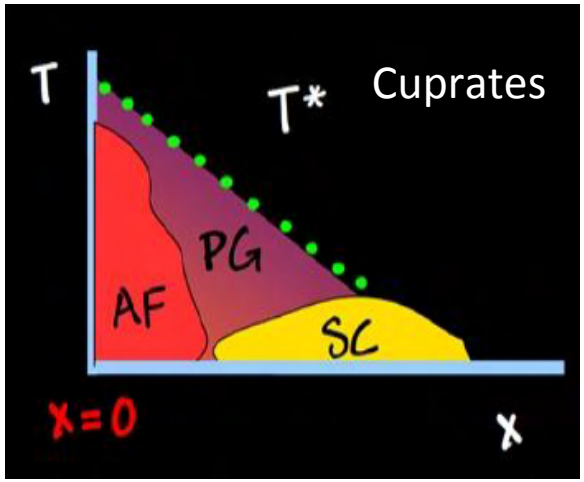


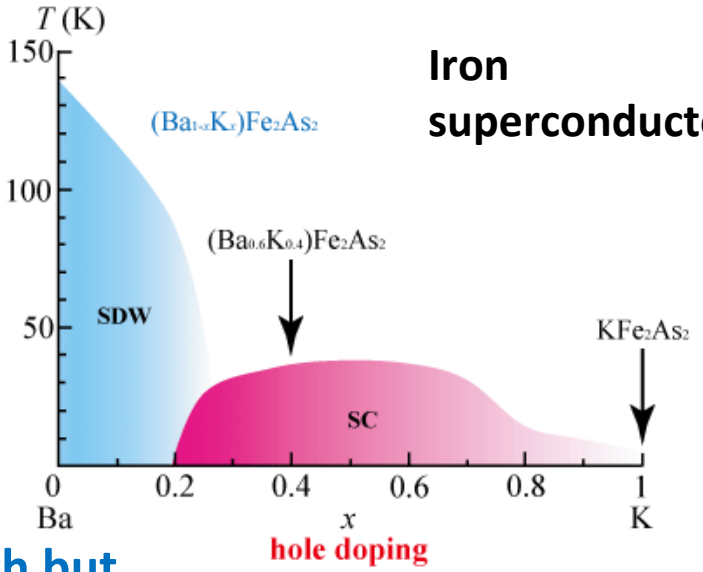
Organic material

Fig: www.physics.berkeley.edu

Magnetism and superconductivity often appear close to each other

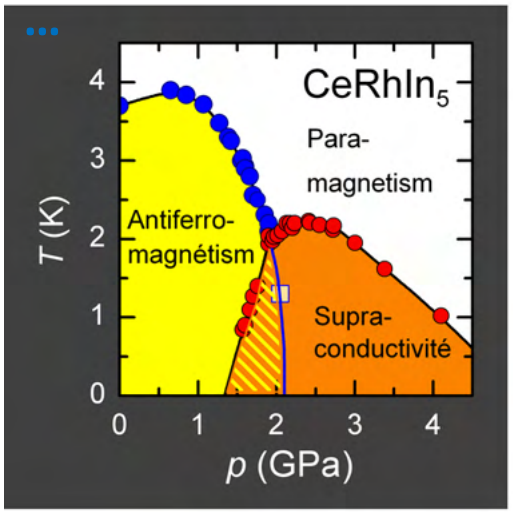
High temperature superconductors





Iron superconductors

Their critical temperatures do not look high but



Heavy fermion

Fig:www.supraconductivite.fr

Organic salt

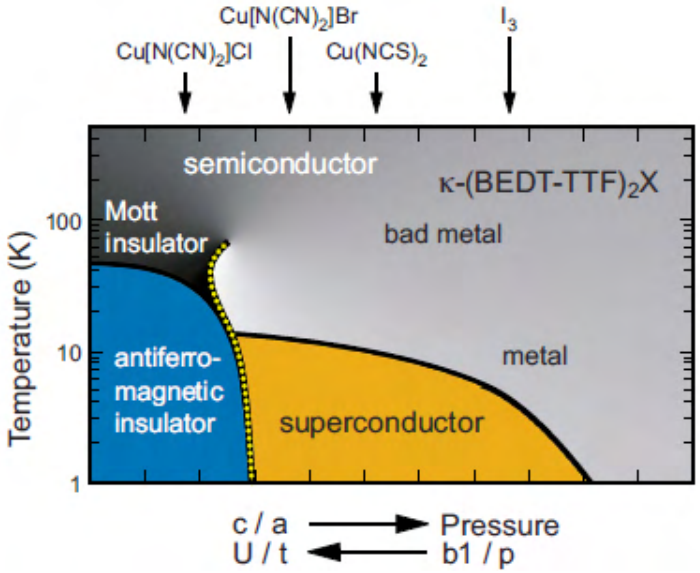


Fig: Faltelmeier, PRB (2007)

Do other phases compete or cooperate with superconductivity? Description in terms or local or itinerant spins?

Parent compound: Insulator

Parent compound: Metal

Hole doped cuprates (charge order)

Iron superconductor FeSe (nematic state)

Iron superconductor Ba-122 (quantum criticality)

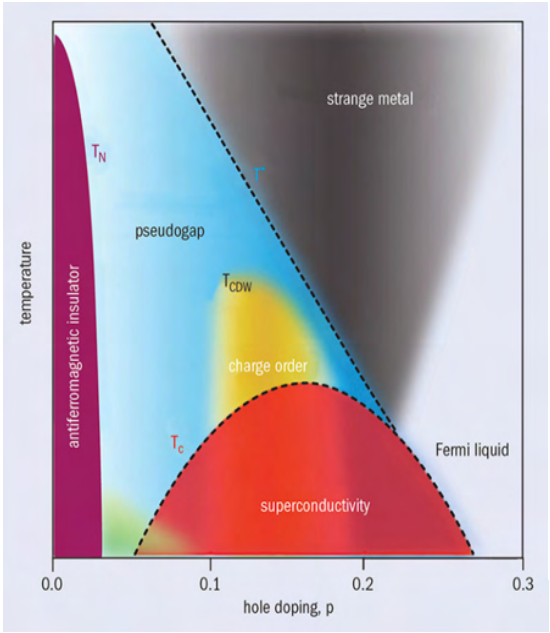
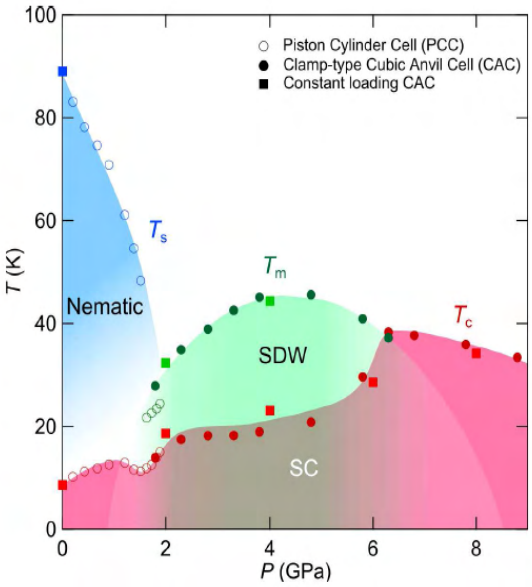
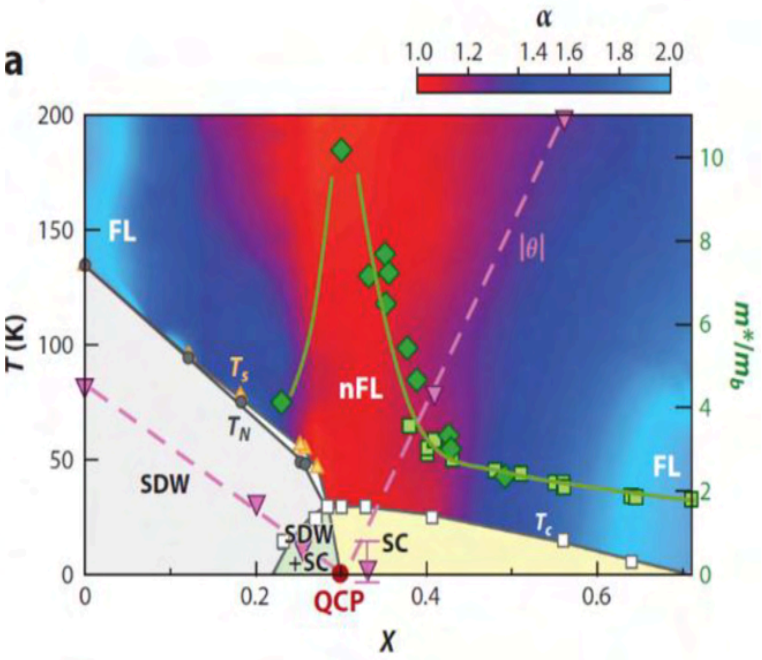


Fig: Inna Vishik



Sun et al, Nat. Comm. 12146 (2016)



Emergence in condensed matter

Kondo effect:

A minimum in the resistivity of metals with magnetic impurities with a lot of physics behind

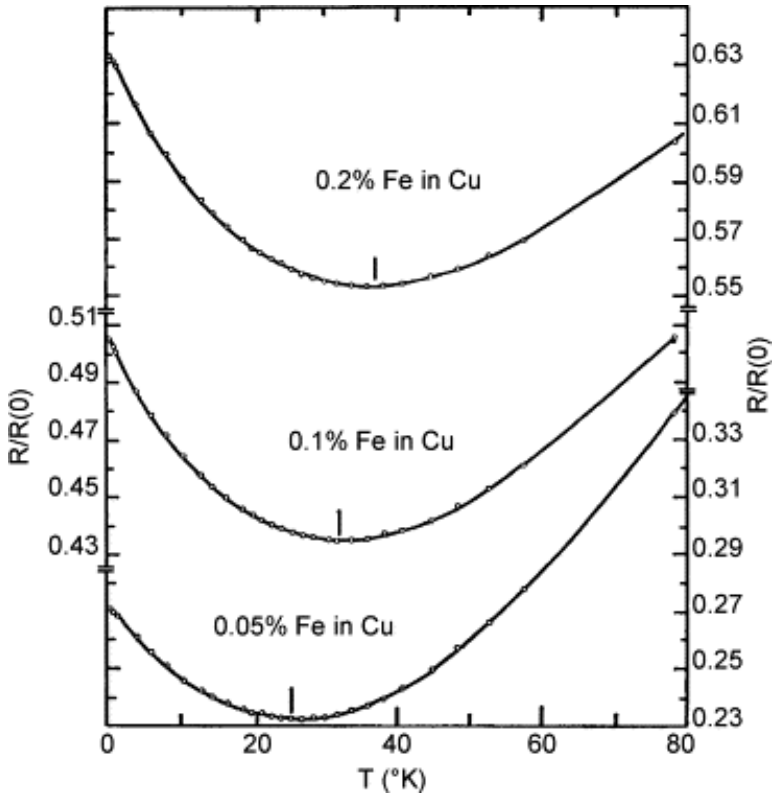
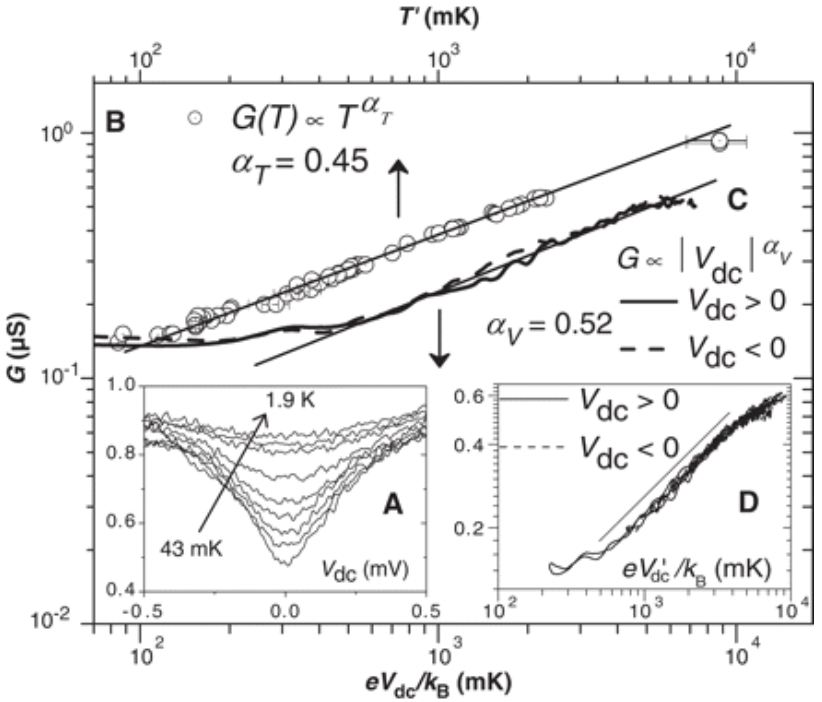


Fig: Kasai et al, (2001)



One dimension:

Dramatic effect of interactions: Luttinger liquids

Fig: Jonpol et al, Science (2009)

Emergence in mesoscopic systems

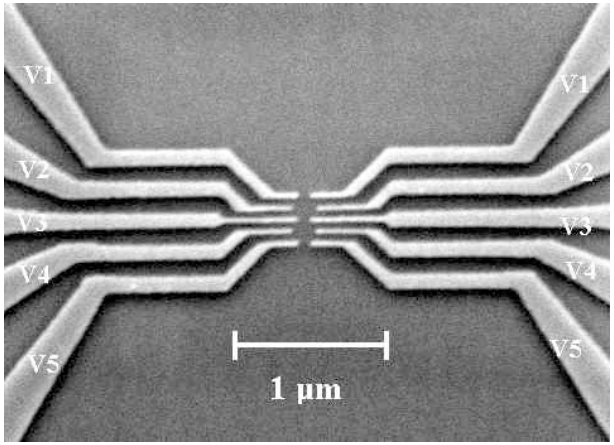


Fig: www.gaia3d.co.uk

Kondo effect in
Quantum Dots

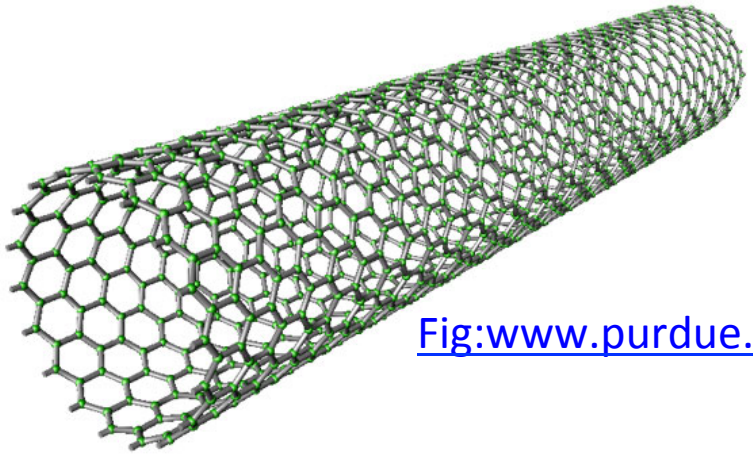


Fig:www.purdue.edu

Luttinger liquid behavior
in carbon nanotubes

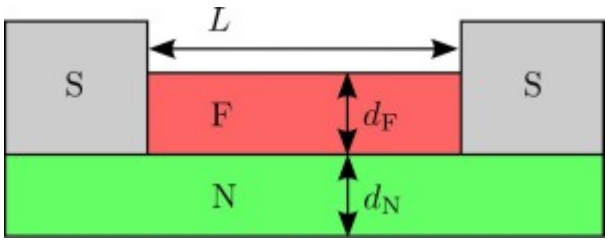


Fig:iopscience.iop.org

Different phases put in contact
(superconducting & ferromagnetic)

Topological and 2D systems

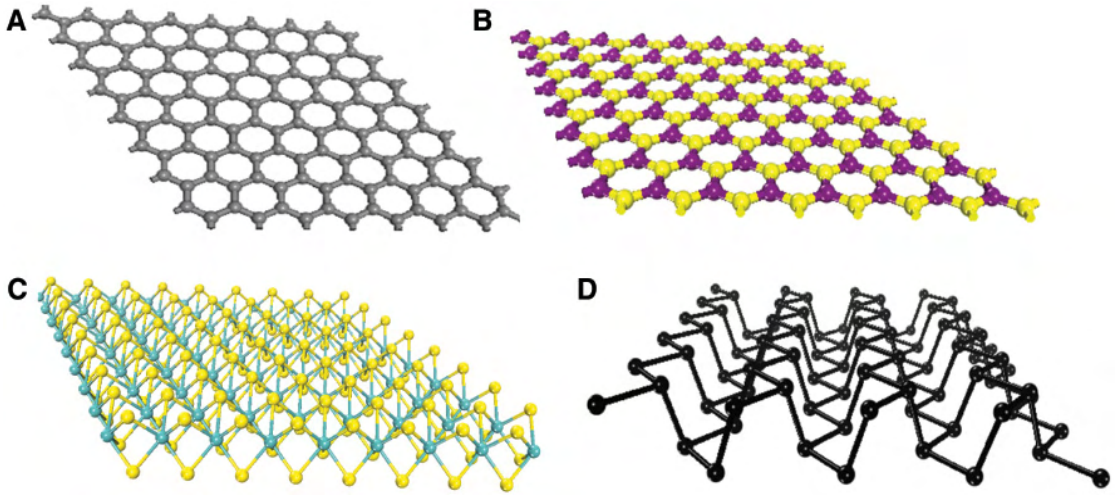
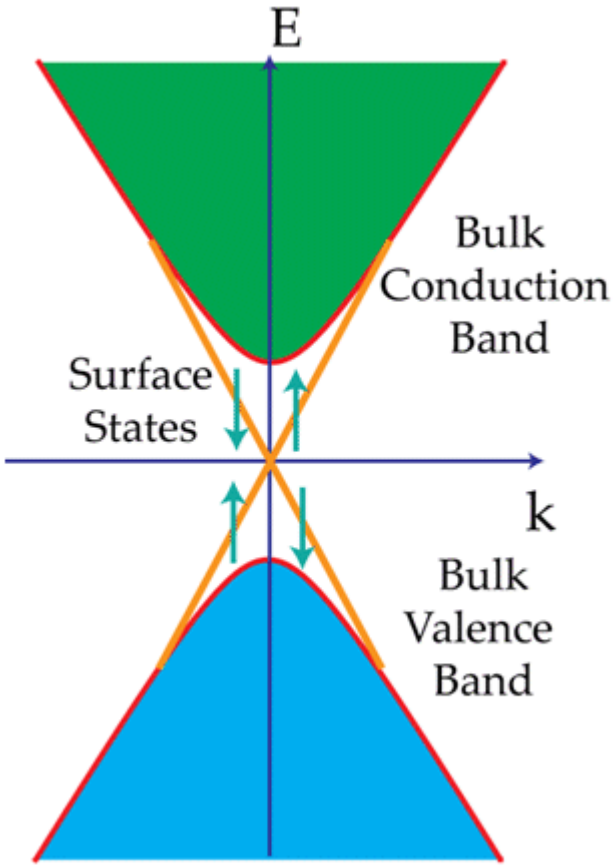


Fig:Nanophotonics 4, 128 (2015)

New properties in atomic layers.
Even at the single particle level!



Topological insulators,
Weyl semimetals

Fig: Hoffman's lab

Engineering new materials and heterostructures

2D LEGO

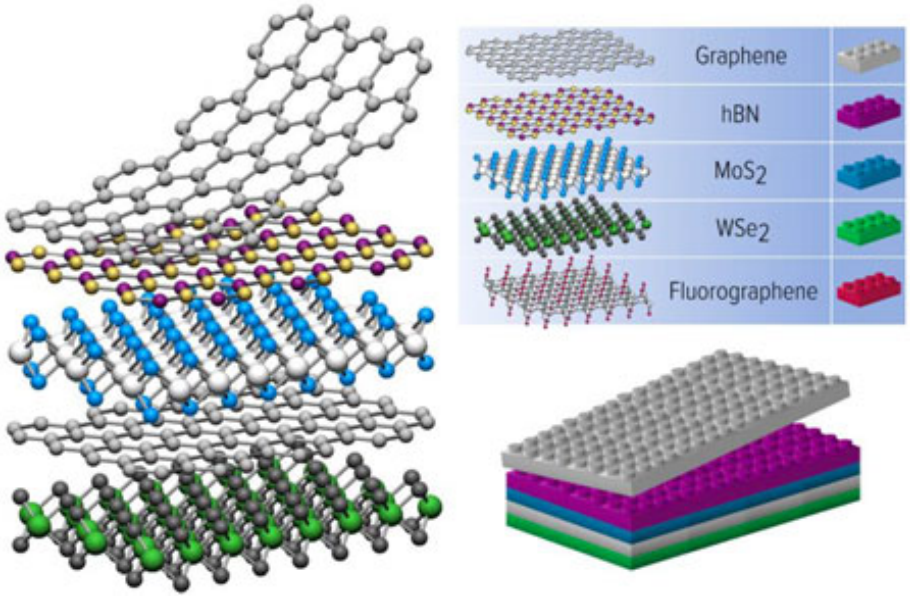
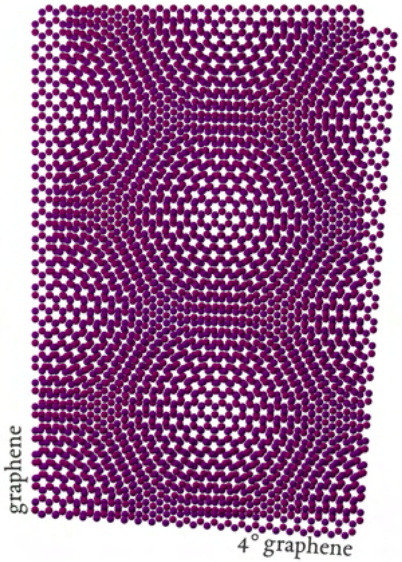


Fig: Geim & Grigorieva, Nature 499, 419 (2013)

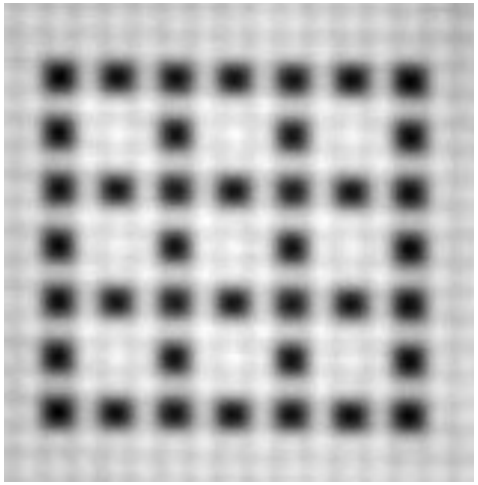


©Ponor

Moiré heterostructures (huge unit cells)

Possibility to engineer band structures or alternate materials with different funcionalities (ferromagnetic, superconductor …)

Atomic lattices on surfaces

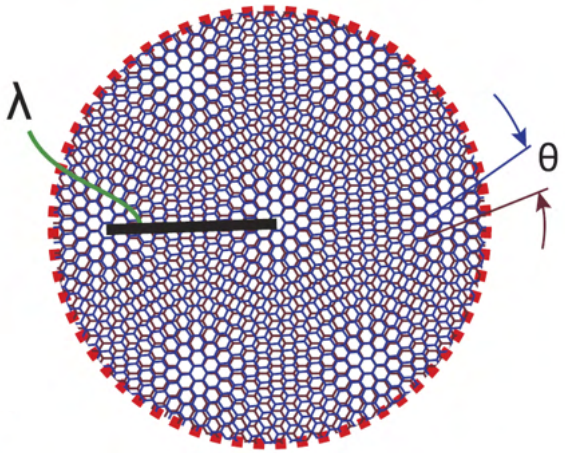


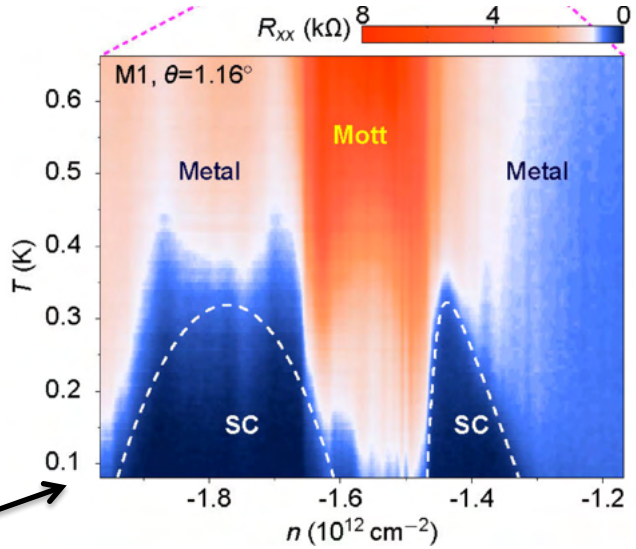
Yan & Liljeroth, Advances in Physics X, 4, 2019

Moiré flat bands: a new platform to study the effects of correlations

March 2018

Magic angle twisted bilayer graphene (1.1º)

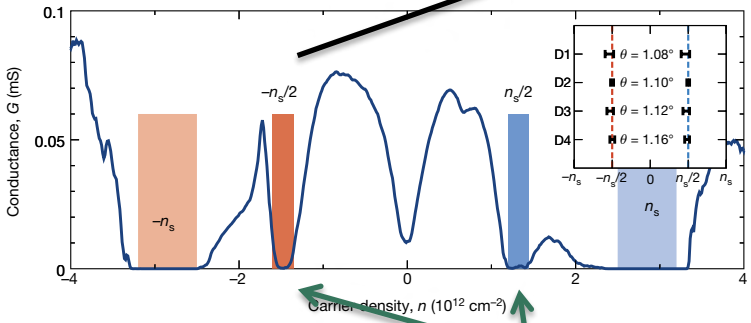




Cao et al, Nature 556, 43 (2018)

Moiré unit cell > 10.000 atoms
Highly tunable system (doping, angle …)

Correlated insulating state

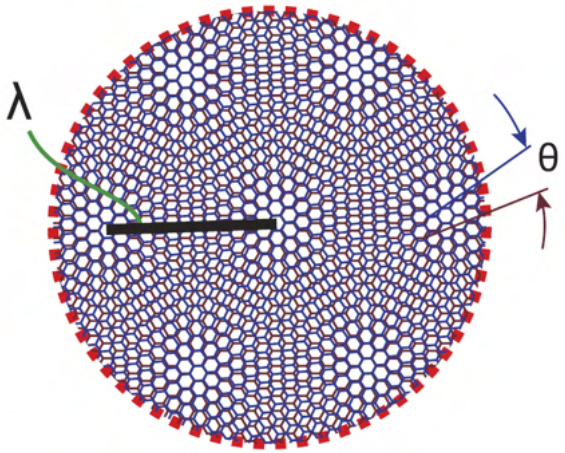


Two correlated insulating states
(half-filling electron & hole bands)

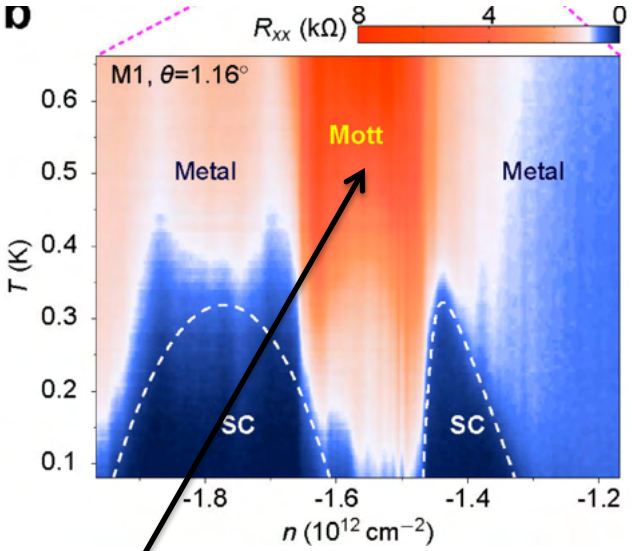
Cao et al, Nature 556, 80 (2018), Nature 556, 43 (2018)

Moiré flat bands: a new platform to study the effects of correlations

Magic angle twisted bilayer graphene (1.1º)

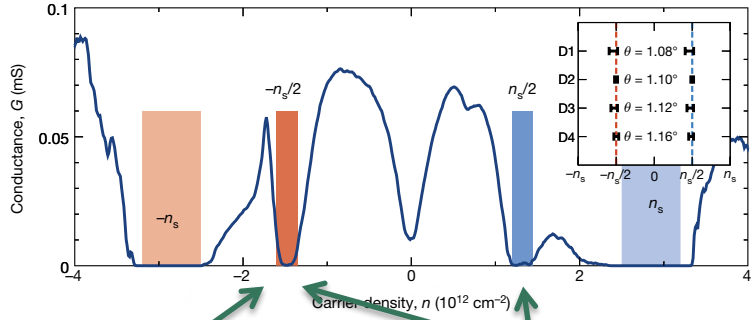


Moiré unit cell > 10.000 atoms
Highly tunable system (doping, angle …)



Cao et al, Nature 556, 43 (2018)

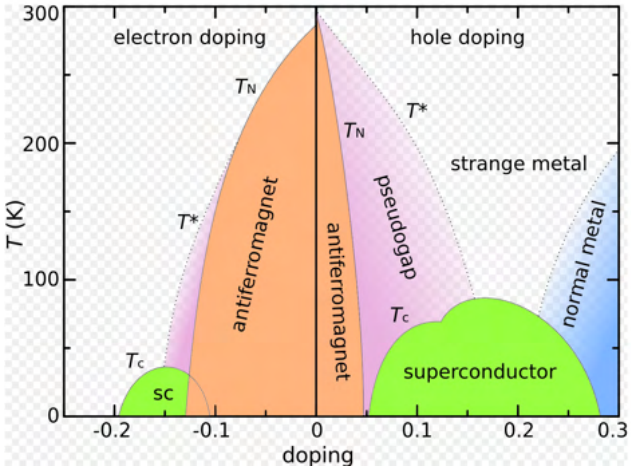
Correlated insulating state



Superconductivity

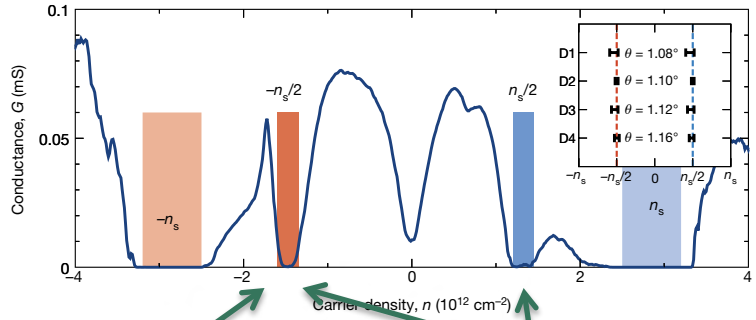
Two correlated insulating states
(half-filling electron & hole bands)

Cao et al, Nature 556, 80 (2018), Nature 556, 43 (2018)



Moiré flat bands where 2D materials, correlations and topology meet

March 2018

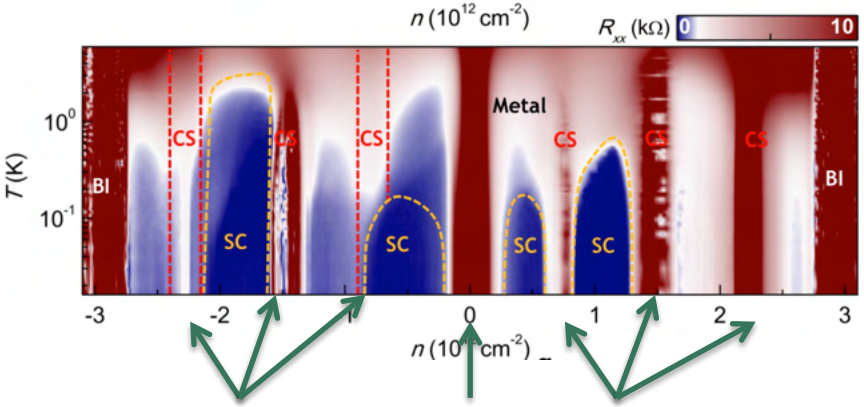


Superconductivity

Two correlated insulating states (half-filling electron & hole bands)

Cao et al, Nature 556, 80 (2018), Nature 556, 43 (2018)

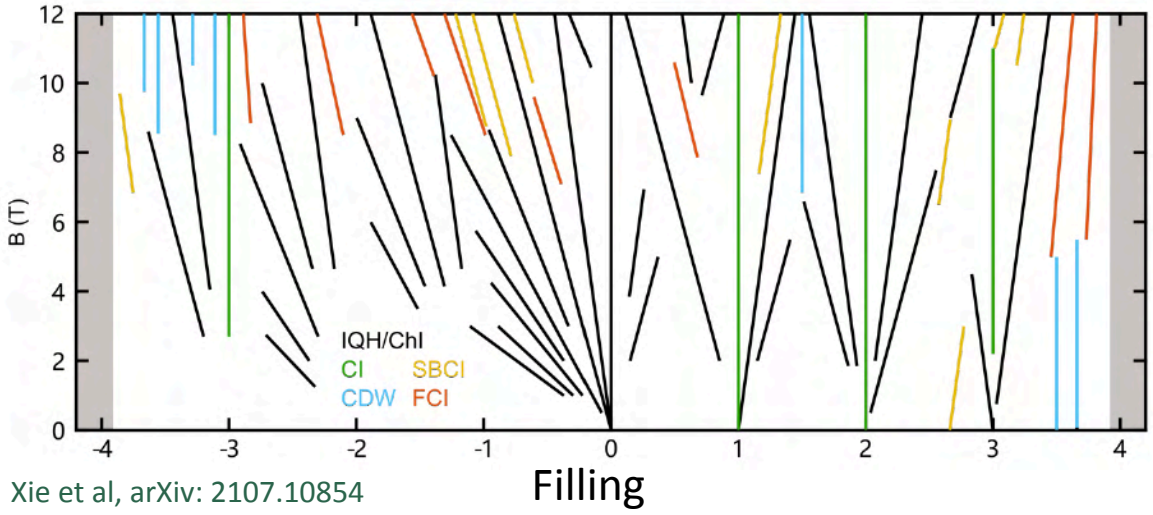
January 2019



Correlated states at all integer fillings

Lu et al Nature 574, 653 (2019)

July 2021 (compressibility measurements)



Xie et al, arXiv: 2107.10854

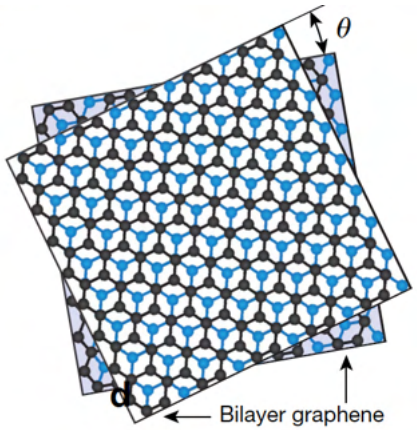
- Correlated insulators (integer filling)
- Charge Density Wave
- Chern Insulators/IQH
- Symmetry broken Chern insulators
- Fractional Chern insulators

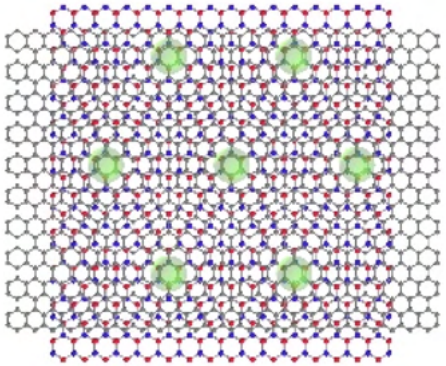
Moiré flat bands where 2D materials, correlations and topology meet

Other graphene based twisted heterostructures

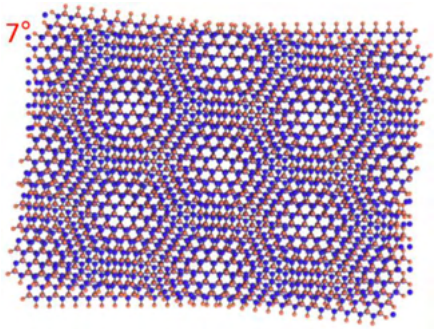
Twisting other 2D materials (semiconductors, magnetic …)

Twisted double bilayer graphene

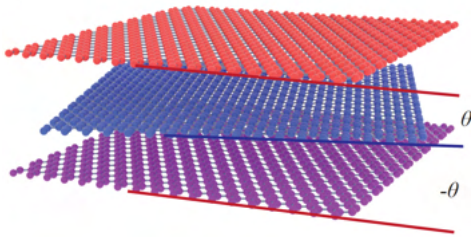




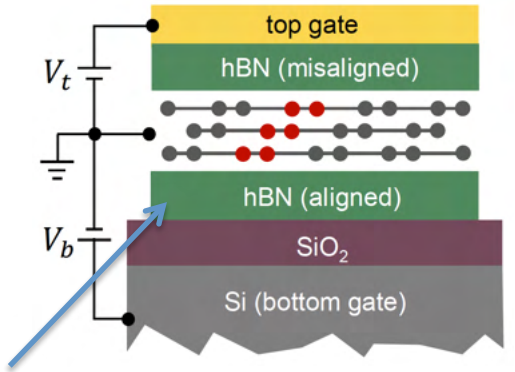
Twisted bilayer WSe_2



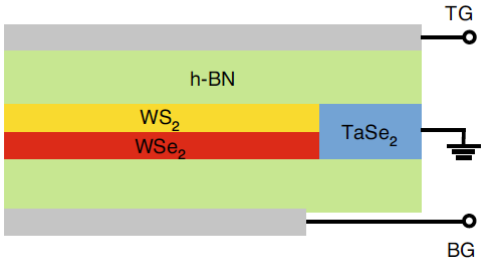
Twisted graphene trilayer (Moiré 3.0)



Trilayer ABC graphene/hBN



Twisted bilayer WSe_2/WS_2



Play with the substrate also in twisted heterostructures

Liu et al, Nature 583, 221 (2020), Park et al, Nature 590, 249 (2021), Chen et al, Nature 572, 215 (2019), An et al, Nanoscale Horizons 9,(2020), Jin et al Nature Materials 20, 940 (2021)

Quantum Phases in Novel Materials

Basic ideas & generic concepts

Different kinds of phenomena & why they happen

Theoretical description

Many different analytical & numerical methods and approaches

Experimental signatures of the quantum states

Materials and platforms

where these quantum phases appear

Emergence of Quantum Phases in Novel States: Outline

- ❑ Introduction: Emergence and Basic Concepts (L. Bascones)
- ❑ Fermi liquid theory (L. Bascones)
- ❑ Electronic correlations: Mott, Hund and Luttinger Physics (L. Bascones)
- ❑ Magnetism (M.J. Calderón)
- ❑ Superconductivity (M.J. Calderón)
- ❑ Dirac Materials (A. Cortijo)
- ❑ Topological Insulators and topological semimetals (A. Cortijo)
- ❑ Kondo effect in metals and nanostructures (R. Aguado)
- ❑ Topological superconductivity (R. Aguado)

Basic concepts: the Fermi gas

- Focus on electrons. Work at fixed μ
- Electrons are fermions: **Fermi-Dirac Statistics**

energy

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/K_B T}+1}$$

chemical potential

Zero temperature

Step function

States filled up to the Fermi Energy ε_F which defines a **Fermi surface**

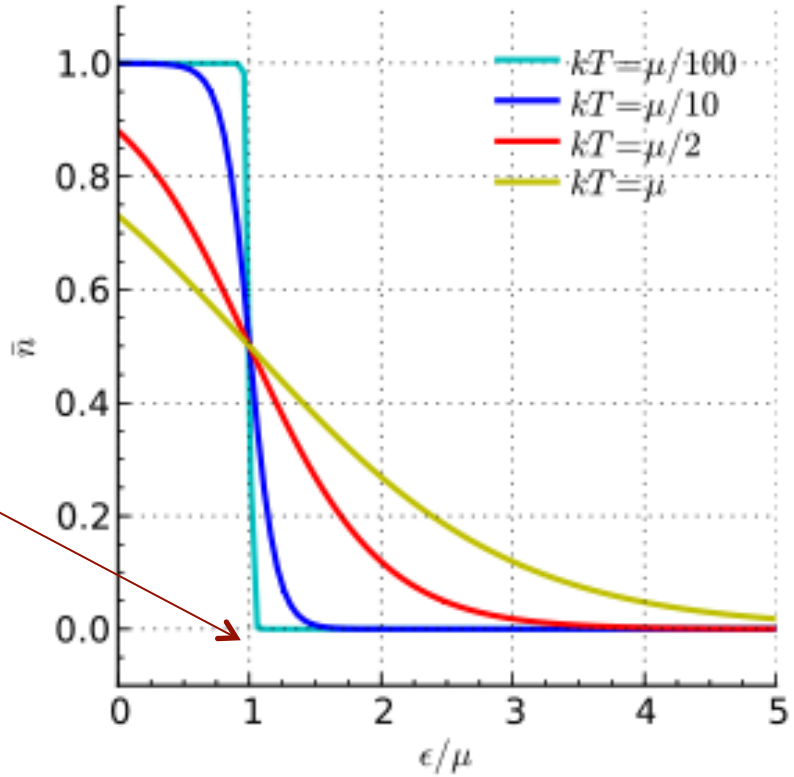


Fig: Wikipedia

High temperatures (classical gas)

$K_B T \gg \mu$

$f(\varepsilon) \propto e^{-\varepsilon/K_B T}$

Maxwell-Boltzmann distribution function

Basic concepts: the Fermi gas

- **Low temperatures**

(quantum gas, Fermi-Dirac)

$K_B T << \mu$

Free energy

- **Specific heat** $C_v = \left.\frac{\partial F}{\partial T}\right|_{\mu}$

$C_v = \gamma T$ **Linear in temperature**

Magnetization

- **Spin susceptibility** $\chi_s = \frac{\partial M}{\partial H}$

Magnetic field

$\chi_s = \mu_B^2 N(\varepsilon_F)$ **independent of T**

Bohr magneton

Density of states at Fermi level

Pauli susceptibility

- **High temperatures**

(classical gas, Maxwell-Boltzmann)

$K_B T >> \mu$

- **Specific heat**

$C_v =$ **independent of T**

- **Spin susceptibility**

$\chi_s \propto \frac{1}{T}$ **Curie law**

Basic concepts: the Fermi gas

Different temperature dependence of measurable quantities in the degenerate (quantum) and classical limits

- **Low temperatures** (quantum gas) $K_B T \ll \mu$
- **High temperatures** (classical gas) $K_B T \gg \mu$

o **Specific heat**

$C_v = \gamma T$ **Linear in temperature**

$C_v =$ **independent of T**

o **Spin susceptibility**

$\chi_s = \mu_B^2 N(\varepsilon_F)$ **independent of T**

Pauli susceptibility

$\chi_s \propto \frac{1}{T}$ **Curie law**

Consequence of Pauli exclusion principle

Non-interacting fermions are correlated due to Fermi statistics & Pauli principle

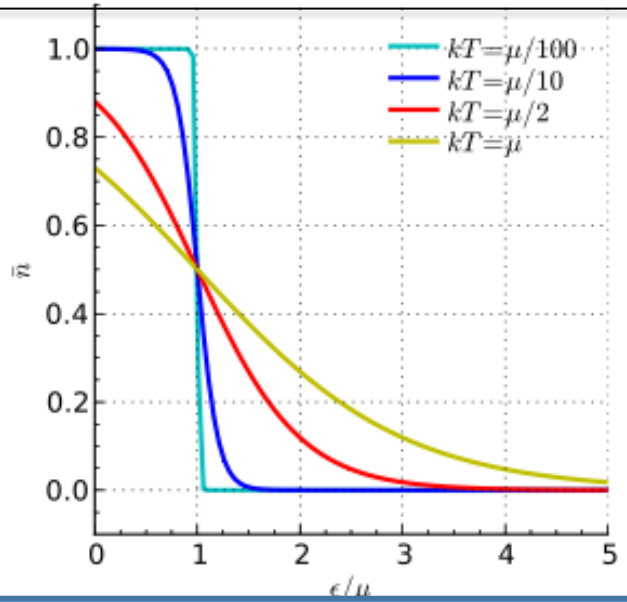
Basic concepts: the Fermi gas

Different temperature dependence of measurable quantities in the degenerate (quantum) and classical limits

- **Low temperatures** (quantum gas) $K_B T << \mu$
- **High temperatures** (classical gas) $K_B T >> \mu$

Fermi temperature $T_F = \varepsilon_F / K_B$

Temperature below which quantum effects are important



Basic concepts: the Fermi gas

Different temperature dependence of measurable quantities in the degenerate (quantum) and classical limits

- **Low temperatures** (quantum gas) $K_B T << \mu$
- **High temperatures** (classical gas) $K_B T >> \mu$

Fermi temperature $T_F = \varepsilon_F / K_B$

Temperature below which quantum effects are important

In metals

$\varepsilon_F \sim 3$ eV

$T_F \sim 2400$ K

Metals generically have to be treated as degenerate gases

In TBG & doped semiconductors

$\varepsilon_F \sim$ few meV

$T_F \sim 50$ K

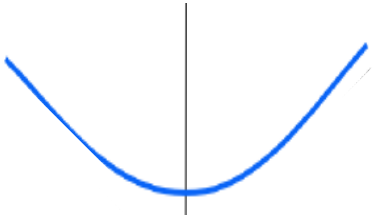
TBG & SMC behave as degenerate gases ONLY at very low T

Basic concepts: lattice and energy bands vs the continuum

In free space: Parabolic band

Kinetic energy $= \frac{k^2}{2m}$

- Isotropic
- No length scale
- Momentum conserved



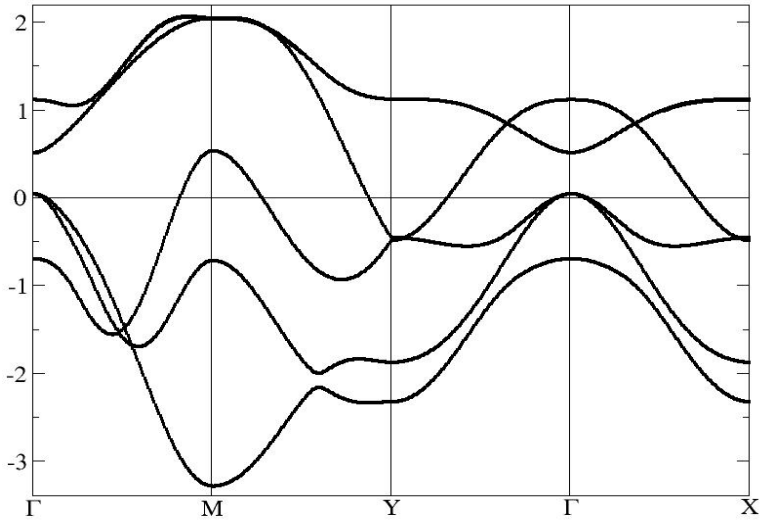


Fig: Calderón et al, PRB, 80, 094531 (2009)

In a solid:

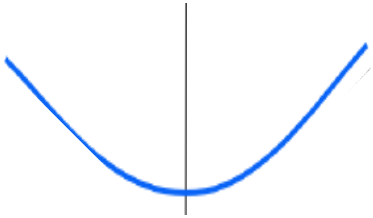
- periodic potential of the ionic lattice
- Length scale: the lattice constant **a**
- Momentum conserved modulus **$2\pi/a$**
- In general, anisotropic potential
- Energy bands filled up to $\varepsilon_{F.}$ **Fermi surface**
- Effective mass (band mass)

$$m^{-1} = |\partial^2\varepsilon/\partial k^2|$$

Basic concepts: lattice and energy bands vs the continuum

In free space: Parabolic band

$$\text{Kinetic energy} = \frac{k^2}{2m}$$



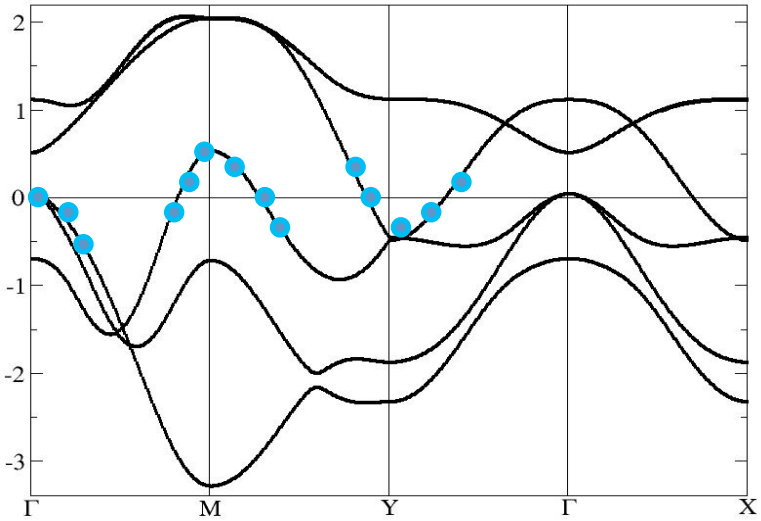


Fig: Calderón et al, PRB, 80, 094531 (2009)

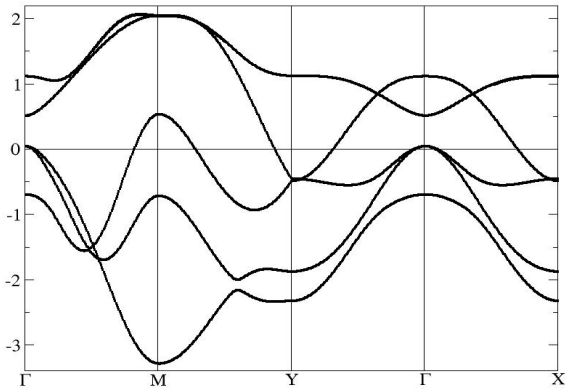
Some phenomena can be described in terms of **parabolic bands** which substitute the energy bands close to the Fermi surface

Careful!

This is not always possible

Some effects are intrinsic to the lattice

Basic concepts: massless fermions in graphene



Parabolic bands:

Continuum approximation

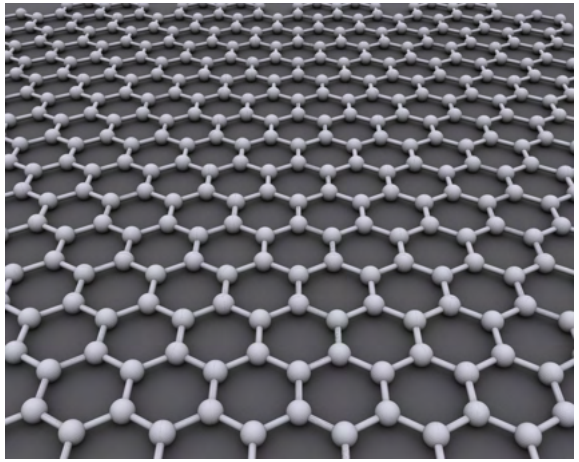
$$\frac{k^2}{2m}$$

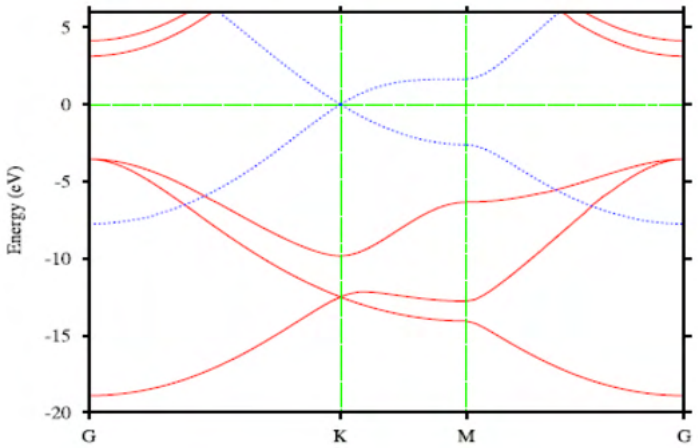
Effective mass (band mass)

$$m^{-1} = |\partial^2\varepsilon/\partial k^2|$$

Fig: Calderón et al, PRB, 80, 094531 (2009)

Graphene:





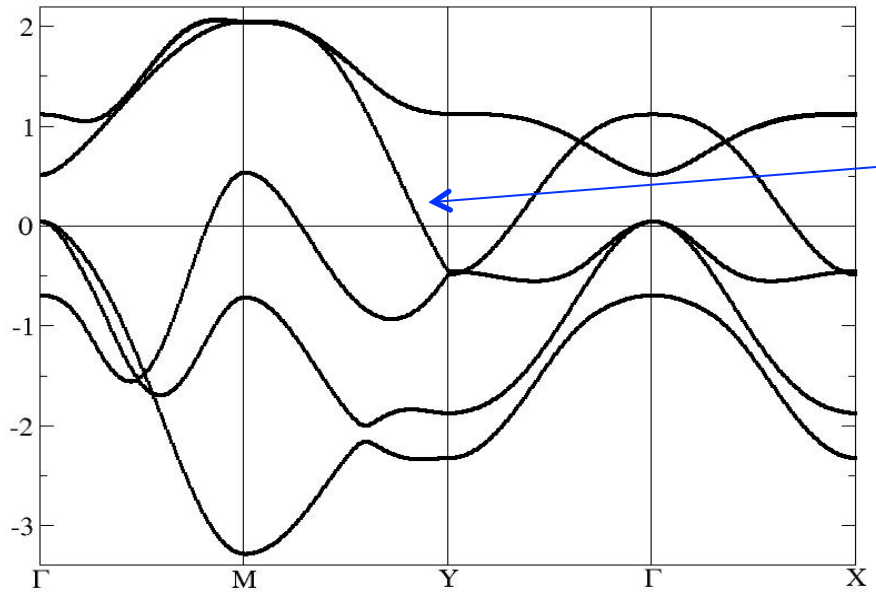
Linear bands close to Fermi level

Continuum approximation

$$E \sim v_F k$$

Effective mass (band mass) is zero!

Basic concepts: metals and insulators



Metallicity
in clean systems
Bands crossing
the Fermi level
(finite DOS)

Fig: Calderón et al, PRB, 80, 094531 (2009)

Insulating behaviour
in clean systems
Bands below
Fermi level filled

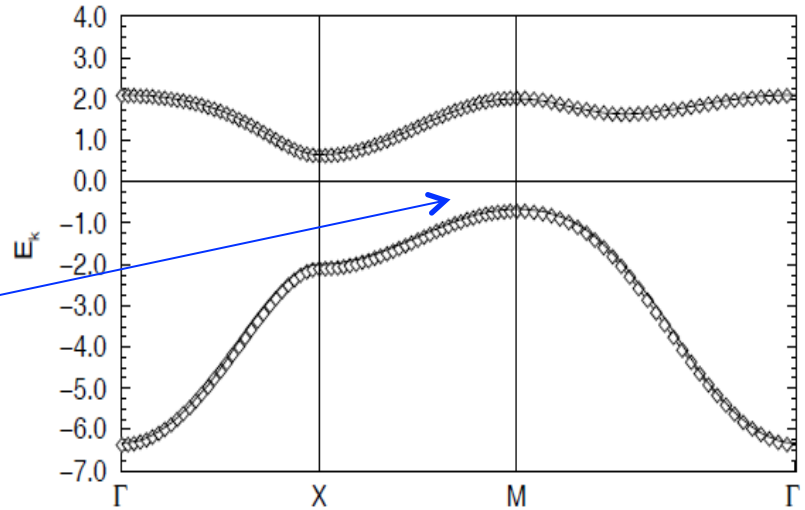
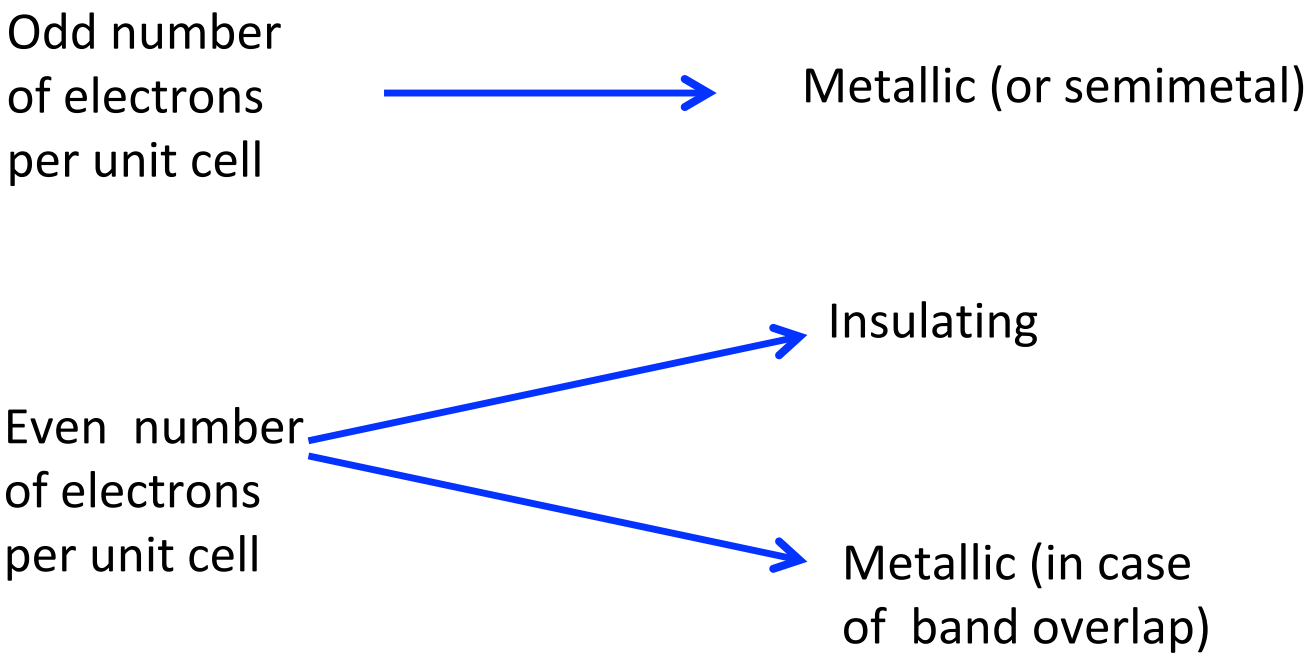


Fig: Hess & Serene, PRB 59, 15167 (1999)

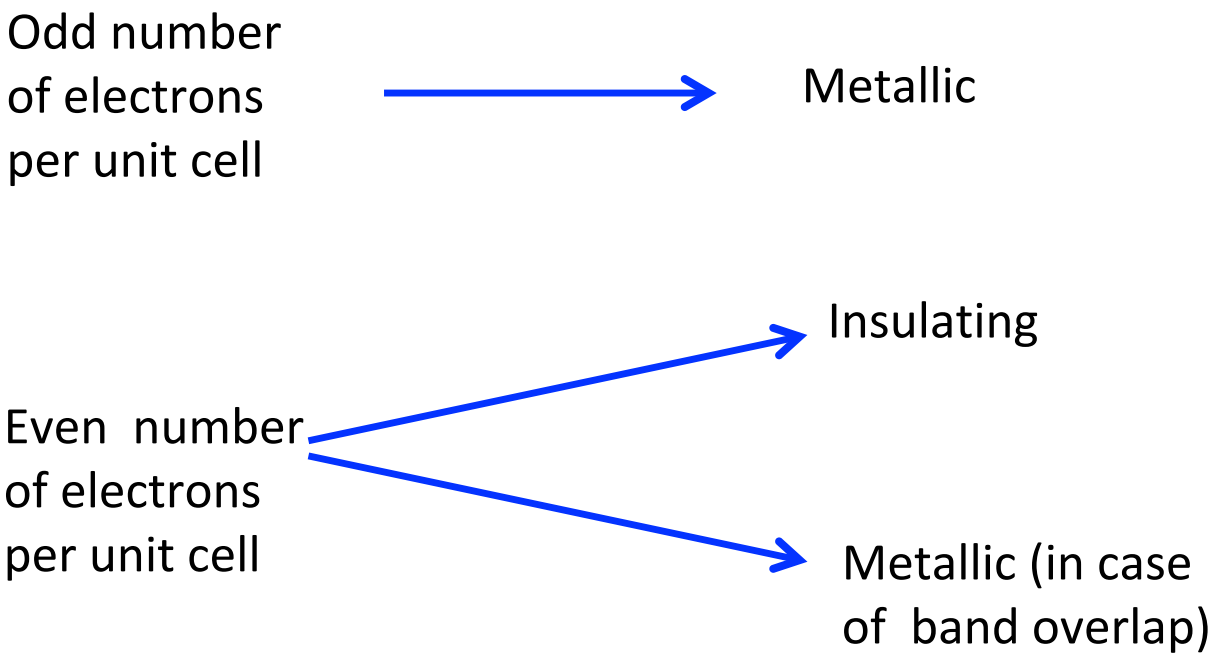
Basic concepts: metals and insulators

Spin degeneracy (no symmetry breaking):
Each band can hold 2 electrons per unit cell



Basic concepts: metals and insulators

Spin degeneracy:
Each band can hold 2 electrons per unit cell



Stops being valid in a Mott insulator!

Basic concepts: strength of interactions

Strength of interactions: **U**

Kinetic energy: W bandwidth

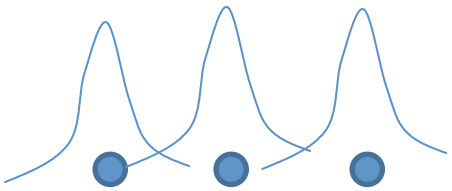
U/W

Narrow bands
more sensitive to interactions

Interactions are not small compared to kinetic energy

- Focus on electrons close to the Fermi surface.
- Core electrons + nucleus form the ion

Kinetic energy: tight binding model using atomic orbitals as a basis



Larger spread of wave function (less localized orbitals)

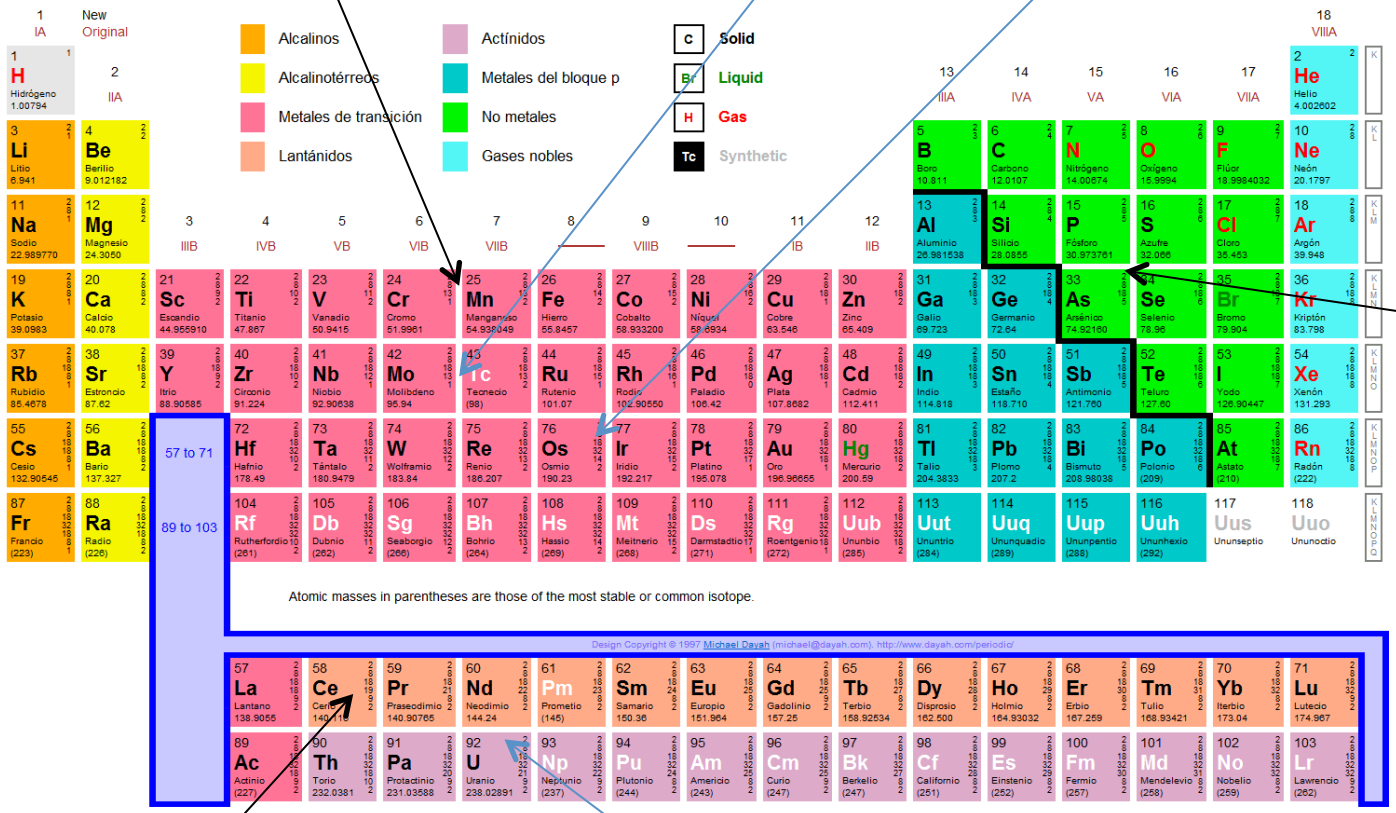
Larger overlap between orbitals
in neighbouring sites
(larger kinetic energy)

Two electrons are
less likely to be found
very close
(smaller effective interaction)

Basic concepts: strength of interactions

3d: competition between kinetic energy & interaction

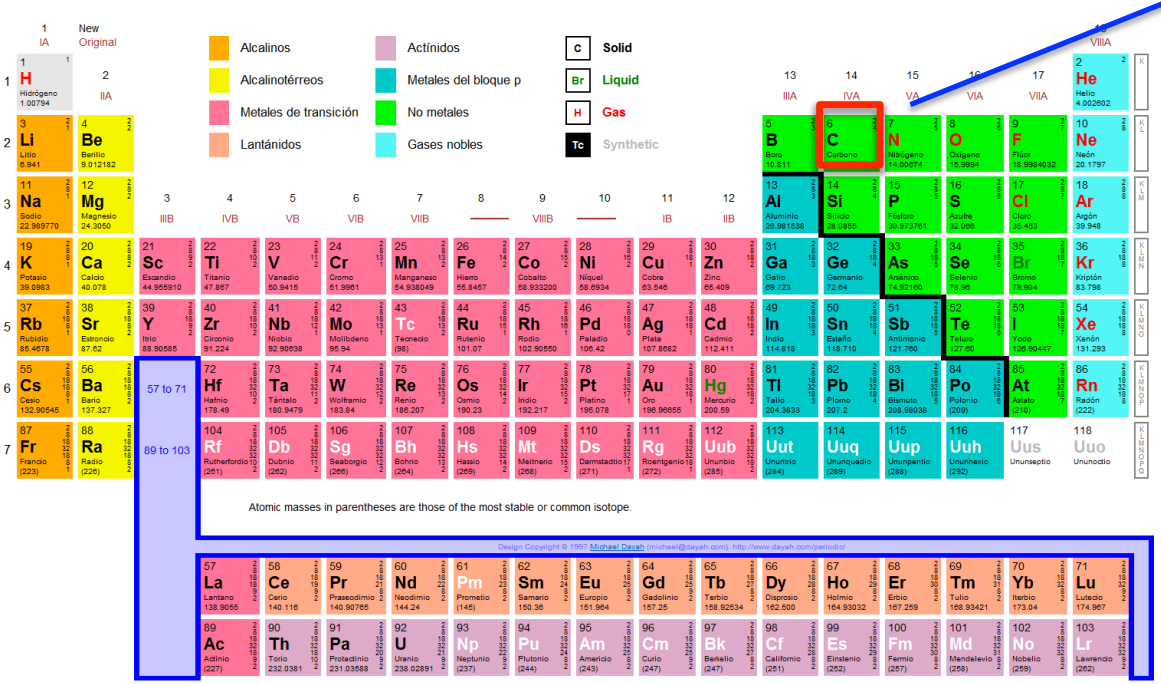
Interaction strength decreases in 4d & overall in 5d due to larger extension of the orbital



s & p electrons kinetic energy more important

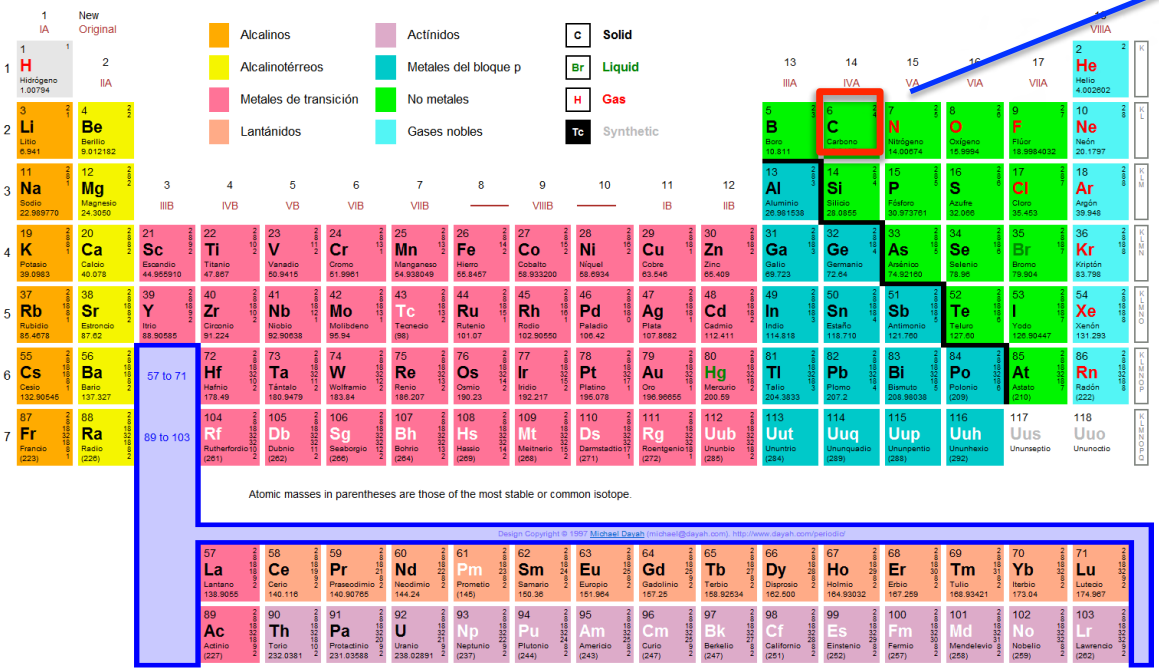
4f overall and 5f orbitals are quite localized on a site. Very small kinetic energy. Interactions win

Basic concepts: strength of interactions

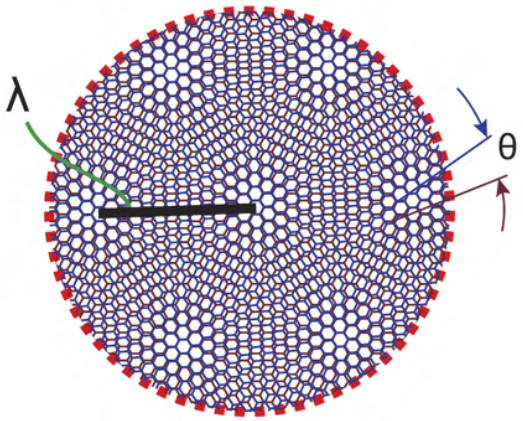


p-orbitals,
extended wave functions
(interactions in graphene
not expected to be very
relevant)

Basic concepts: strength of interactions

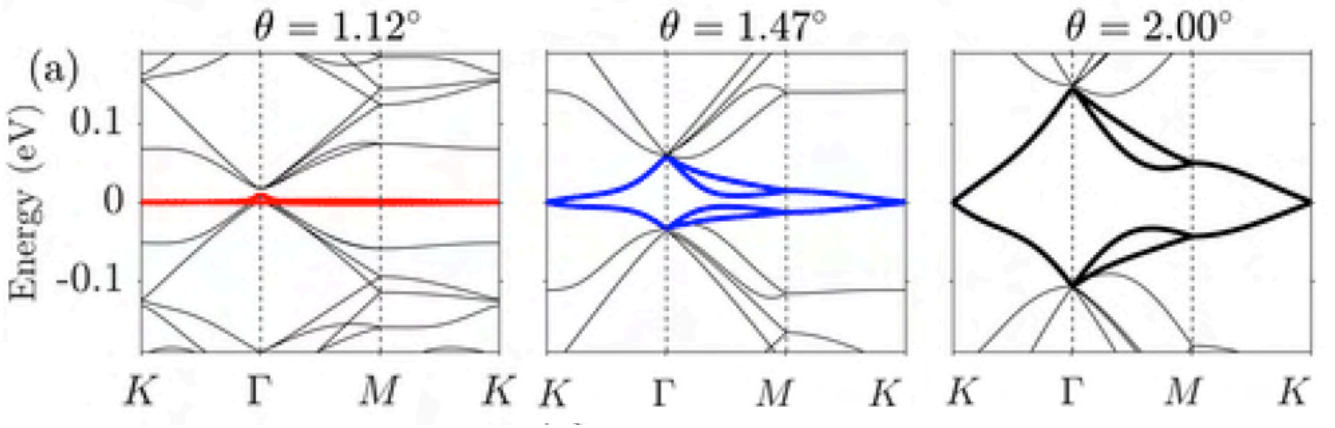


p-orbitals,
extended wave functions (interactions in graphene not expected to be very relevant)

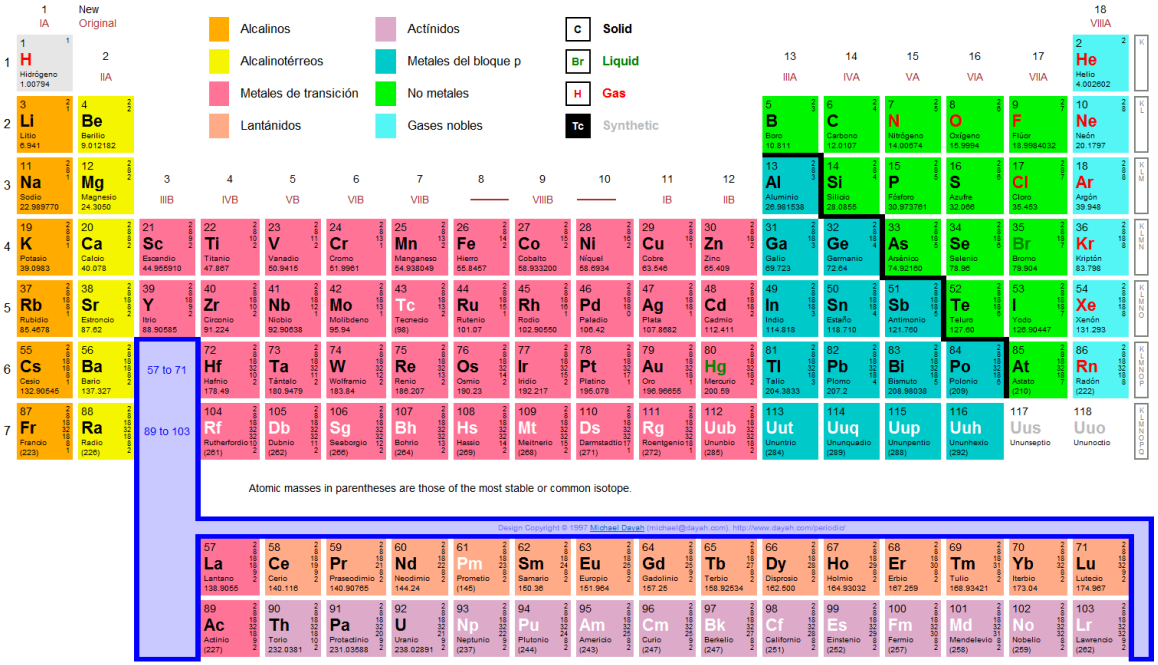


Flat bands close to the magic angle ~1.1º

Very small W

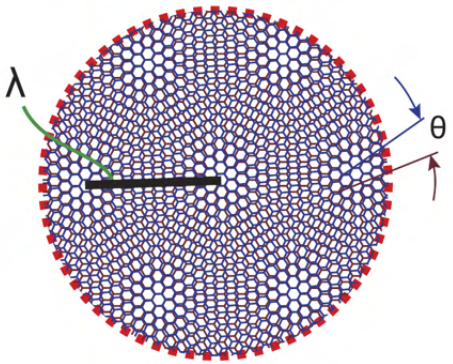


Basic concepts: strength of interactions



Cuprates, manganites, iron superconductors

U, W ~ 2-3 eV



Twisted bilayer graphene and other moiré heterostructures

U, W ~ 1- 50 meV

Basic concepts: strength of interactions

Assume 3D, free space (continuum), let $n = N_e / V$ (**n electronic density**)

N_e: Number of electrons

V: Volume

Kinetic energy $\int_{-\infty}^{\varepsilon_F} \varepsilon \, g(\varepsilon) \, d\varepsilon \propto n^{2/3}$

$g(\varepsilon)$: density of states

Interaction energy $\propto \langle 1/r \rangle \cong n^{1/3}$

Coulomb interaction: $\frac{e^2}{r}$

Valid for 1/r interaction

$$\frac{\textbf{Interaction energy}}{\textbf{Kinetic energy}} \propto n^{-1/3}$$

Important in semiconductors

Careful in metals !

Due to Pauli principle the importance of interactions decreases with increasing density

Basic concepts: Screening and Hubbard model

Coulomb interaction: $\frac{e^2}{r}$

Interaction is larger when electrons are closer

Long range character

Hamiltonian on the lattice (kinetic energy + interactions)

$$\sum_{ij\sigma} t_{ij}\, c^{\dagger}_{i\sigma} c_{j\sigma} + h.c. + U \sum_{j} n_{j\uparrow} n_{j\downarrow} + \sum_{i \neq j \sigma\sigma'} U_{ij} n_{i\sigma} n_{j\sigma'}$$

I,j lattice sites
σ spin

Kinetic Energy
(Tight binding)

Interaction (repulsion between electrons in the same site, only different spin)

Interaction (repulsion between electrons in different sites)

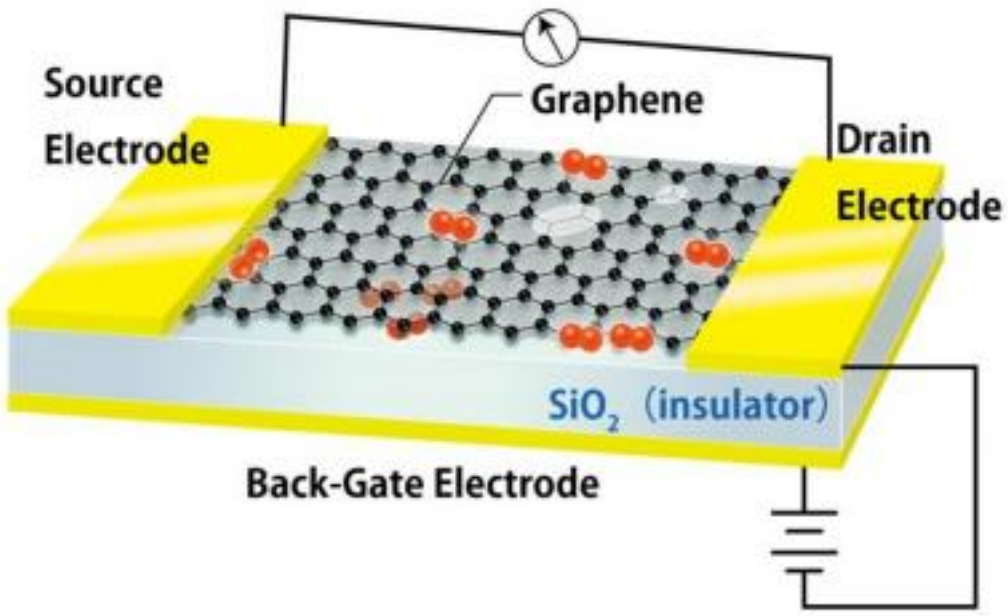
Basic concepts: Screening and Hubbard model

Coulomb interaction: $\frac{e^2}{\varepsilon r}$

Interaction is larger when electrons are closer

Long range character

Other electrons in the solid (metal) or gate screen the Coulomb interaction. The interaction decays faster than 1/r



Screening also enters

increases ε

Basic concepts: Screening and Hubbard model

Hubbard model : lattice model, 1 orbital per site . Approximation

$$\sum_{ij\sigma} t_{ij}\, c^{\dagger}_{i\sigma} c_{j\sigma} + \text{h.c.} + U \sum_{j} n_{j\uparrow} n_{j\downarrow}$$

Interactions restricted to electrons in the same site

I,j lattice sites
σ spin

Kinetic Energy
(Tight binding)

Interaction Energy

Works better for localized electrons

It looks simple but it is not well understood. Basic in the study of correlated electrons

Basic concepts: Summary

- Electrons in a solid follow Fermi-Dirac statistics. In a typical metal the degeneracy temperature is much higher than room temperature (in MATBG no).

- $C_v = \gamma T$ Linear in temperature $\chi_s = \mu_B^2 N(\varepsilon_F)$ independent of T

- Parabolic bands (continuum) versus lattice models. Linear bands (no mass)

- Band theory: metallic or insulating character on the basis of the number of electrons per unit cell.

- U/W controls strength of interactions

- s and p orbitals less sensitive to interactions, f orbitals are the most correlated. d-electrons interplay between kinetic energy & interactions.
In TBG & other correlated moirés interactions are important due to very small W

- In 3 D and with 1/r in the continuum limit the importance of interactions decreases with increasing density

- Screening and Hubbard model