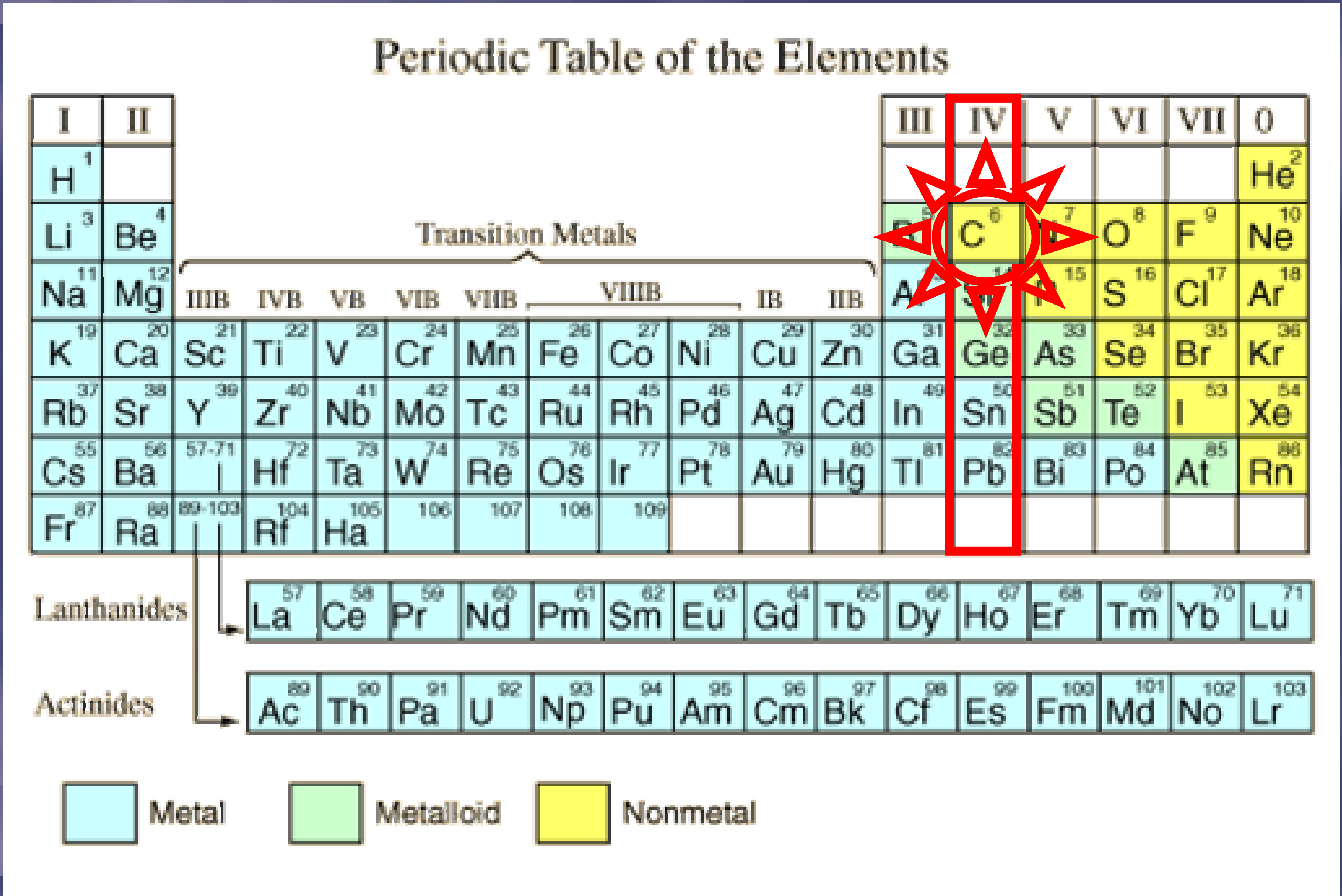
Graphite, graphene and relativistic electrons

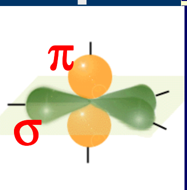
- Introduction
- Physics of graphene
- Experiments
  - Transport – electric field effect
  - Quantum Hall Effect – chiral fermions
  - STM – Landau levels of Dirac fermions
  - Induced superconductivity

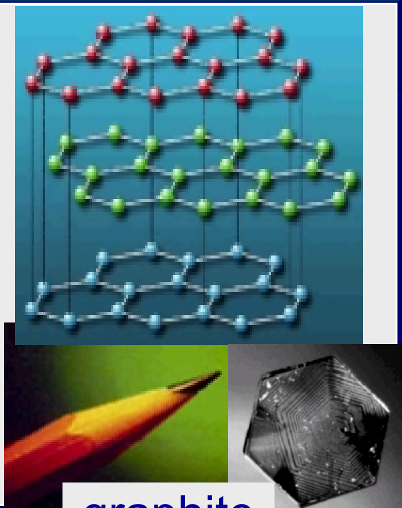

Periodic Table of the Elements
I II III IV V VI VII 0
H 1
He 2
Li 3 Be 4
C 6 O 8 F 9 Ne 10
Transition Metals
Na 11 Mg 12
IIIB IVB VB VIB VIIB VIIIB IB IIB
S 16 Cl 17 Ar 18
K 19 Ca 20 Sc 21 Ti 22 V 23 Cr 24 Mn 25 Fe 26 Co 27 Ni 28 Cu 29 Zn 30 Ga 31 Ge 32 As 33 Se 34 Br 35 Kr 36
Rb 37 Sr 38 Y 39 Zr 40 Nb 41 Mo 42 Tc 43 Ru 44 Rh 45 Pd 46 Ag 47 Cd 48 In 49 Sn 50 Sb 51 Te 52 I 53 Xe 54
Cs 55 Ba 56 57-71 Hf 72 Ta 73 W 74 Re 75 Os 76 Ir 77 Pt 78 Au 79 Hg 80 Tl 81 Pb 82 Bi 83 Po 84 At 85 Rn 86
Fr 87 Ra 88 89-103 Rf 104 Ha 105 106 107 108 109
Lanthanides
La 57 Ce 58 Pr 59 Nd 60 Pm 61 Sm 62 Eu 63 Gd 64 Tb 65 Dy 66 Ho 67 Er 68 Tm 69 Yb 70 Lu 71
Actinides
Ac 89 Th 90 Pa 91 U 92 Np 93 Pu 94 Am 95 Cm 96 Bk 97 Cf 98 Es 99 Fm 100 Md 101 No 102 Lr 103
Metal
Metalloid
Nonmetal

Carbon allotropes

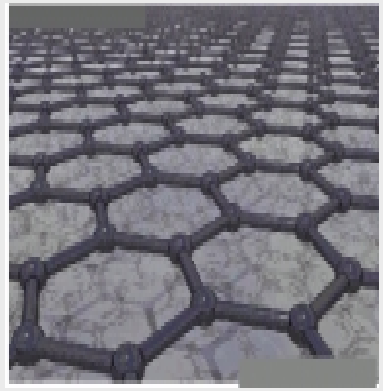
	3D	2D	1D	0D
sp^2	graphite	Graphene 2005	Carbon nanotube Multi-wall1991 Single wall 1993	Buckyball 1985
sp^3	diamond			

sp^2

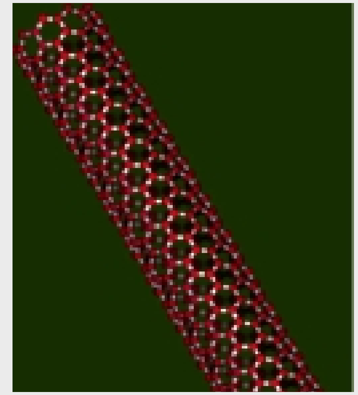




graphite



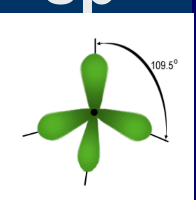
Graphene
2005

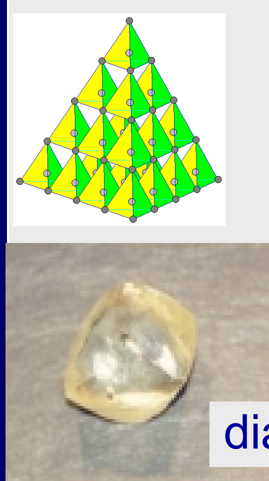


Carbon nanotube
Multi-wall1991
Single wall 1993

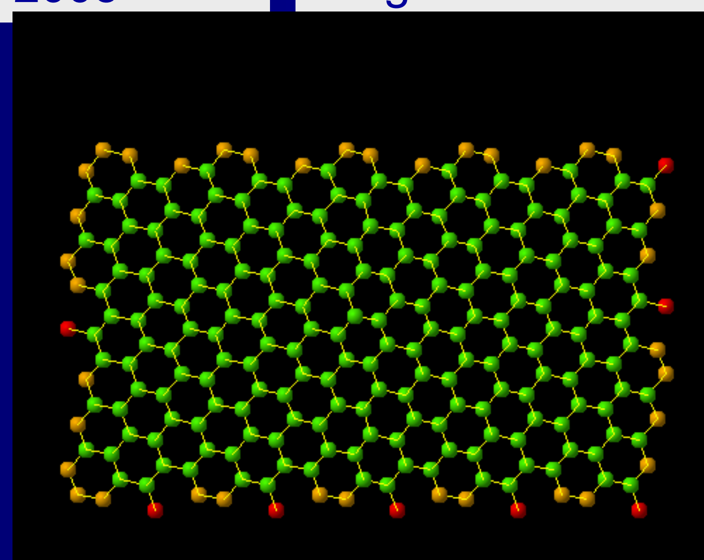
Buckyball
1985

sp^3





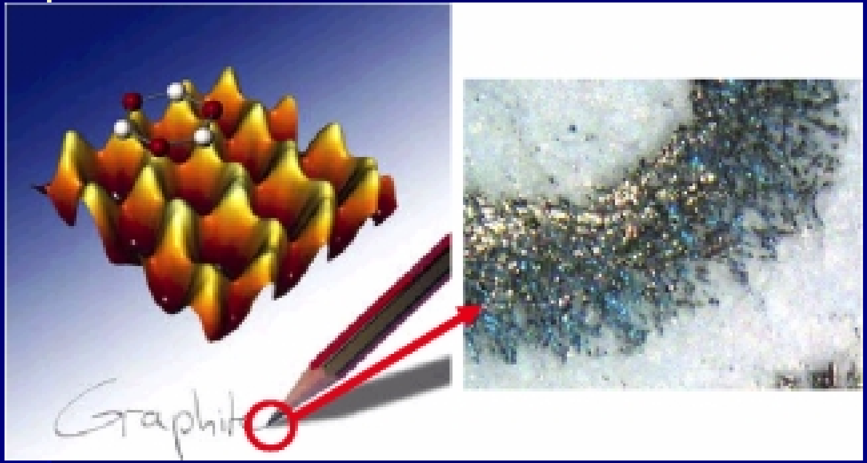
diamond



Sample Fabrication

Novoselev et al (2005)

- Micromechanical cleavage by “drawing”

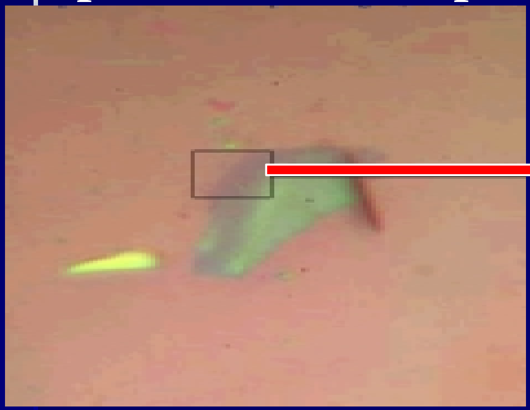


- Properties:
  - Large contiguous samples (10 μm)
  - Stable, Inert
  - Strong
  - High conductivity
  - Large field effect

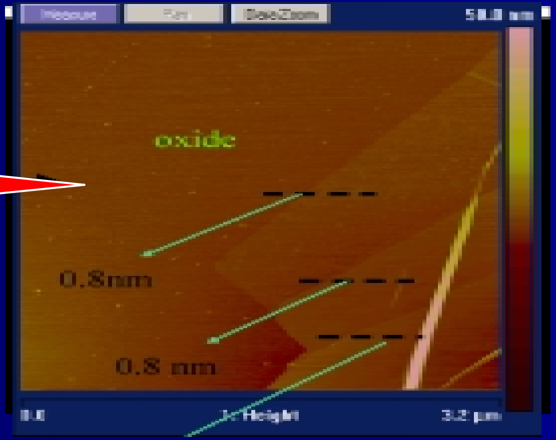
Rutgers

Sample Processing

Optical microscope

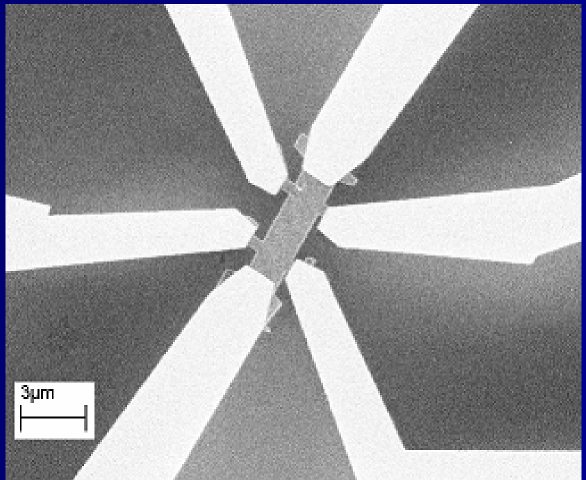


AFM



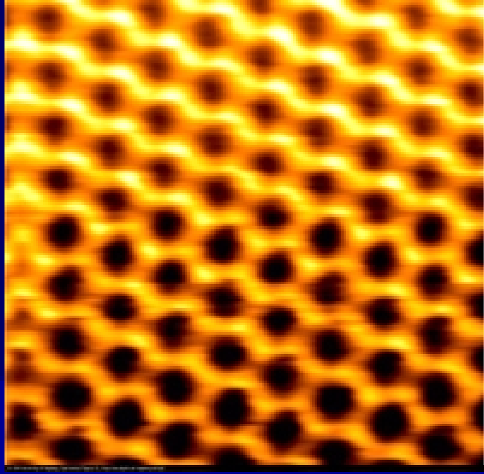
Electron diffraction

Electron beam lithography



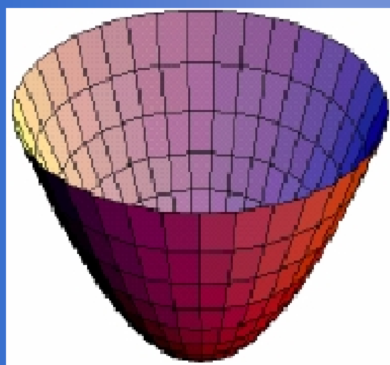
Graphene device

Why graphene

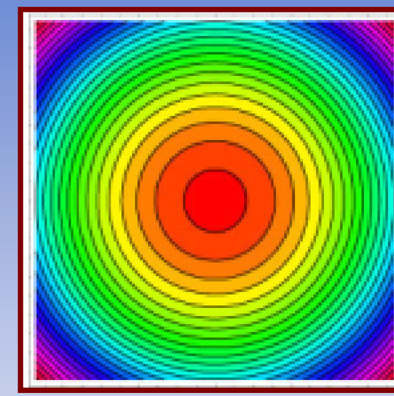


- New Physics:
  - Electrons behave as massless Dirac Fermions (neutrinos with zero mass)
- Novel devices
  - Strong Field effect (metallic FET)
  - Intrinsically long mean-free-path – high conductivity
  - Unusual transport (negative dielectric constant -lensing)
  - Naturally inert
  - High-strength composites
  - nanometer-sized molecular electronic devices

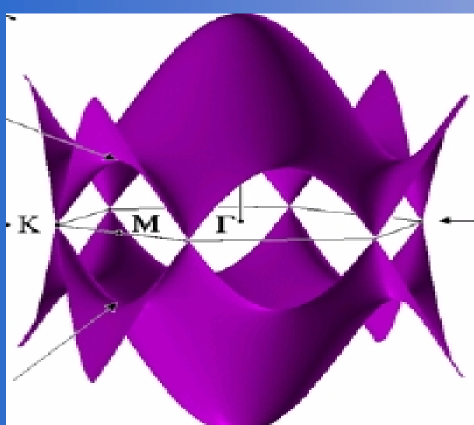
Electron Energy Dispersion



Electron energy depends on momentum (wavelength).
In normal metal dispersion is parabolic



How is graphene different?

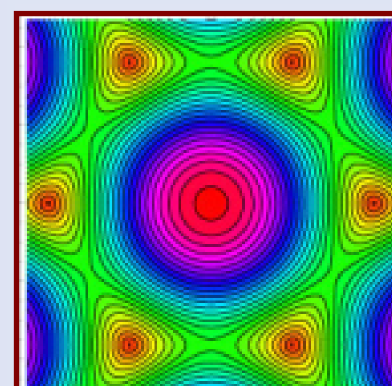


$$K.E. = mv^2/2$$

$$P = mv$$

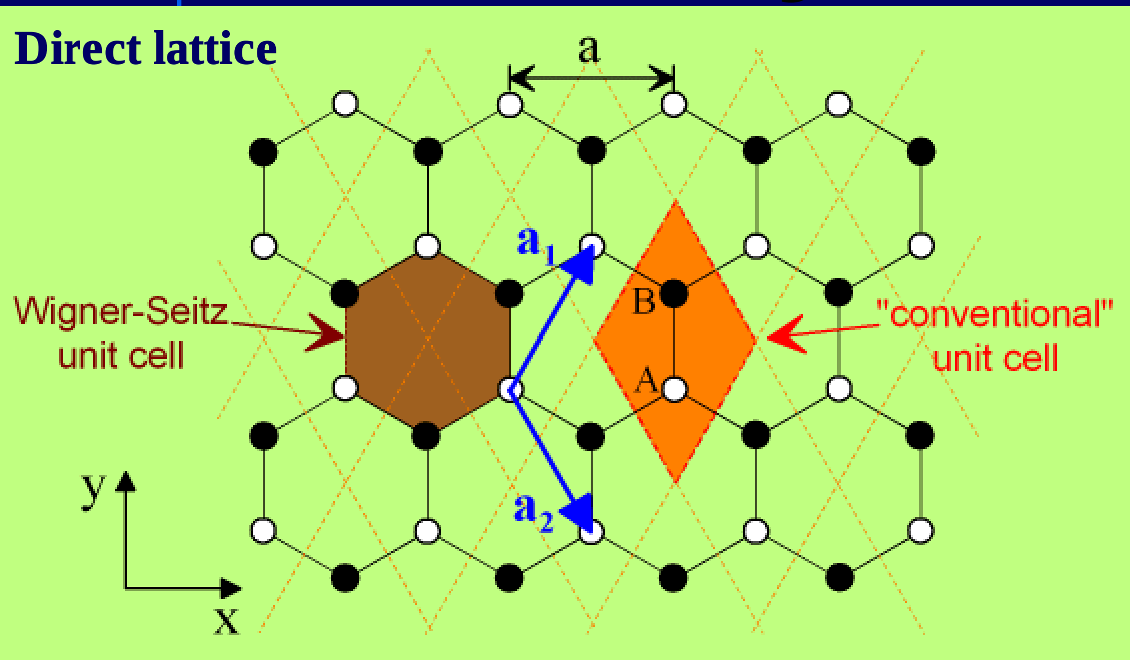
$$K.E. = P^2/(2m)$$

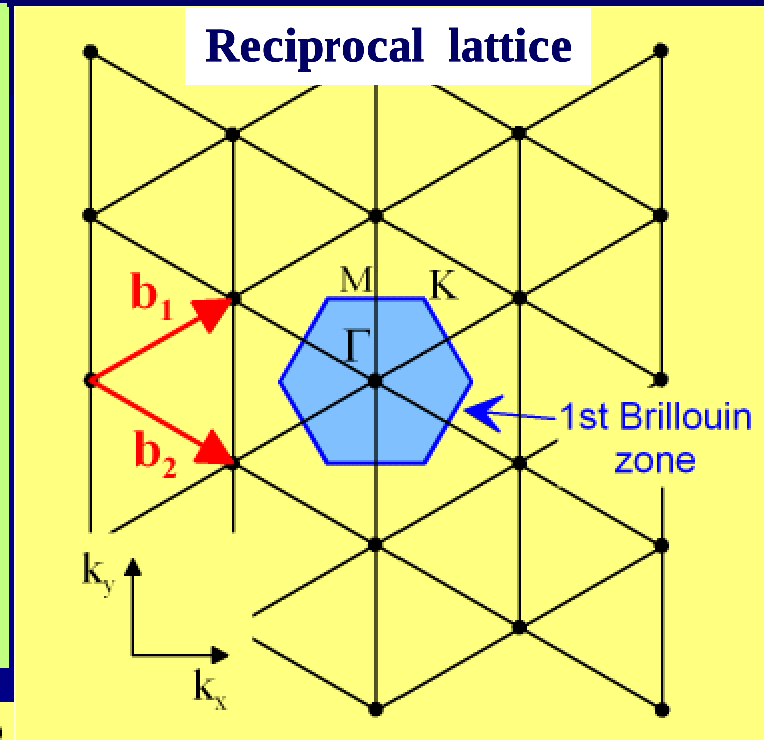
… the electrons are strongly diffracted by the graphene lattice-- the E(p) relation is unconventional

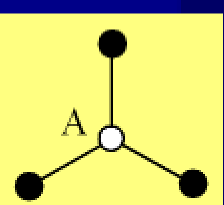


Rutgers

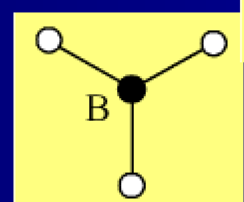
The Honeycomb Lattice





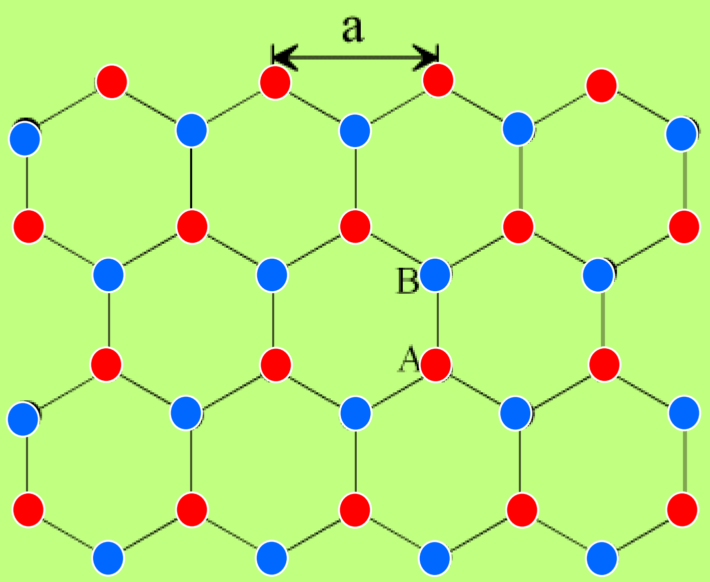


➔ 2 different types of atomic sites (chemicaly identical)



triangular reciprocal lattice – hexagonal Brillouin zone

Electronic Wavefunctions

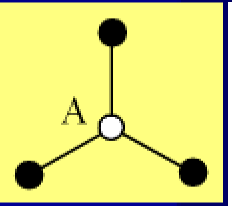


sum over all A sites

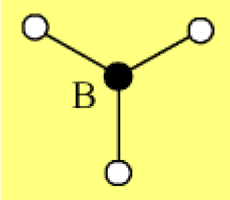
atomic wavefunction

$$\Phi_A(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_A}^{N} e^{i\vec{k}.\vec{R}_A} \varphi_A(\vec{r}-\vec{R}_A)$$

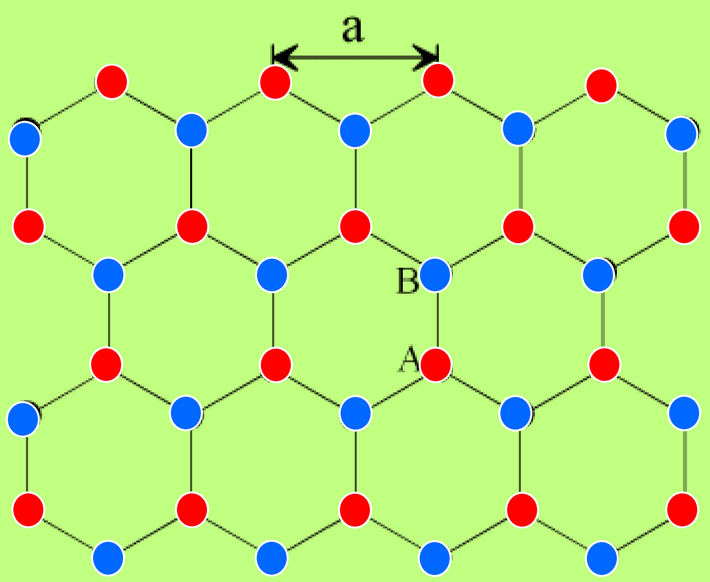
$$\Phi_B(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_B}^{N} e^{i\vec{k}.\vec{R}_B} \varphi_B(\vec{r}-\vec{R}_B)$$



- → 2 different types of atomic sites
- → 2 Bravais sub-lattices
- → 2 sets of Bloch functions



Electronic Wavefunctions



sum over all A sites

atomic wavefunction

$$\Phi_A(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_A}^{N} e^{i\vec{k}.\vec{R}_A} \varphi_A(\vec{r}-\vec{R}_A)$$

$$\Phi_B(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_B}^{N} e^{i\vec{k}.\vec{R}_B} \varphi_B(\vec{r}-\vec{R}_B)$$

$$\Psi(\vec{k},\vec{r}) = C_A \Phi_A(\vec{k},\vec{r}) + C_B \Phi_B(\vec{k},\vec{r})$$

Linear combination of two sets of Bloch functions

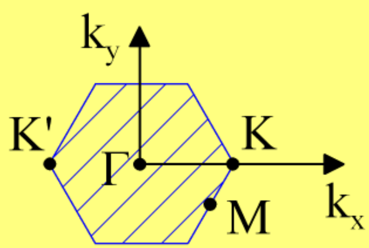
Tight binding model

Wallace, 1947

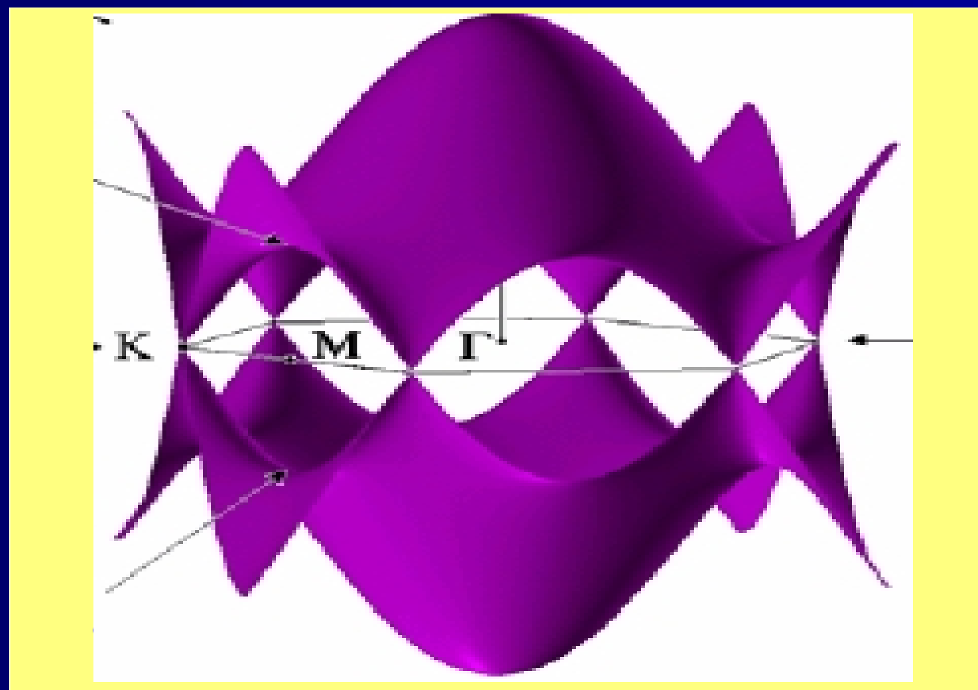
Energy: $$E_k = \pm\gamma_o \sqrt{1 \pm 4\cos\frac{k_y a}{2}\cos\frac{\sqrt{3}k_x a}{2} + 4\cos^2\frac{k_y a}{2}}$$

$\gamma_0 \approx 3.033eV$ π bond overlap, (Saito *et al*)

Brillouin zone



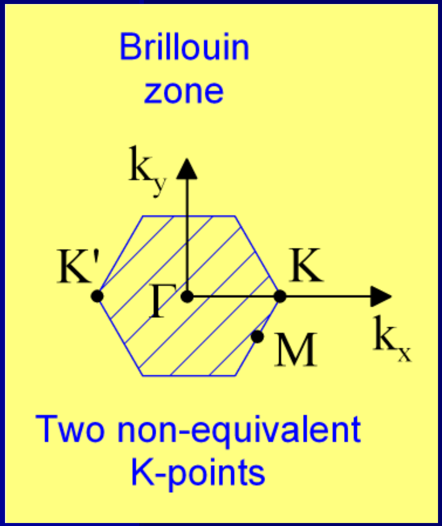
Two non-equivalent K-points

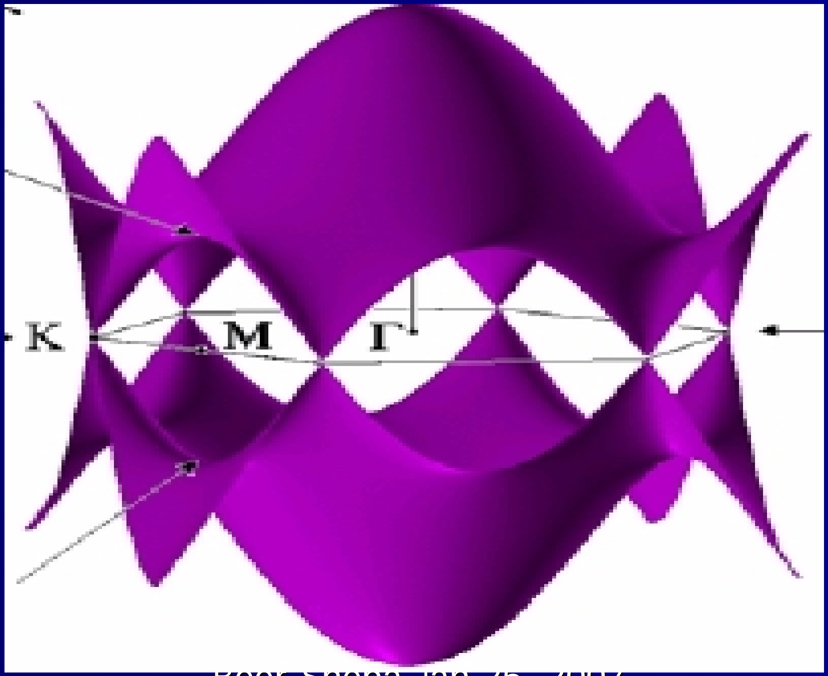


Tight binding model

For neutral sample:

- *particle-hole symmetry*
- *valence and conduction bands touch at E=0*
- *No Fermi surface: six "Dirac" points, only two inequivalent*





Electrons in graphene :
Dirac fermions

Semenoff, 1984
Haldane, 1988

- Near K point:
  - *Effective Hamiltonian* $H = v_F \vec{\sigma} . \vec{p}$ (Pauli)
  - *linear dispersion*

$$E(\vec{q}) = \pm v_F \hbar |\vec{q}|,$$

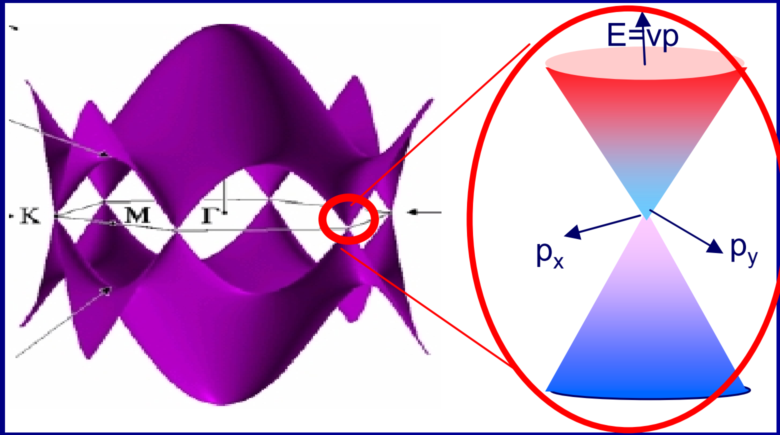
$$\vec{q} = \vec{k} - \vec{K}_F, \quad v_F \approx 10^6 \,\mathrm{m/s} \sim c/300$$

  - *Zero band mass*
  - *Wavefunction*

$$\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = \frac{1}{\sqrt{2}} e^{i\vec{k}\vec{r}} \begin{pmatrix} e^{-i\varphi/2} \\ e^{i\varphi/2} \end{pmatrix} \qquad \varphi = tan^{-1}(k_x / k_y)$$

  - *Bloch function amplitudes on the AB sites ('pseudospin') mimic spin components of a relativistic Dirac fermion.*

Dirac-Weyl equation: relativistic massless particle - Dirac fermions ("old" neutrino)



Electrons in graphene :
Dirac fermions

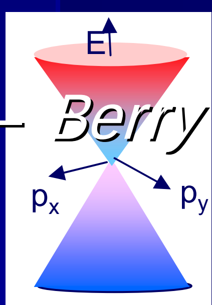
Semenoff, 1984
Haldane, 1988

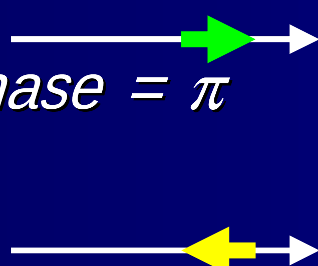
- Near K point:
  - *Effective Hamiltonian* $H = v_F \vec{\sigma}.\vec{p}$

helicity

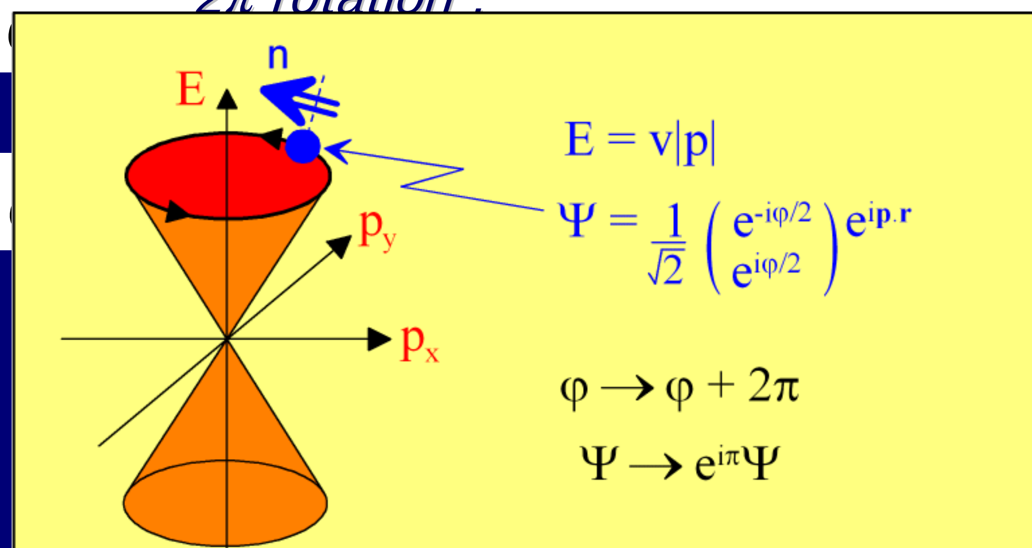
Dirac-Weyl equation: relativistic massless particle - Dirac fermions ("old" neutrino)

  - *Helical particles: pseudospin projection on momentum axis conserved.*
  - *Berry phase = π*





Wavefunction transformation under 2π rotation :



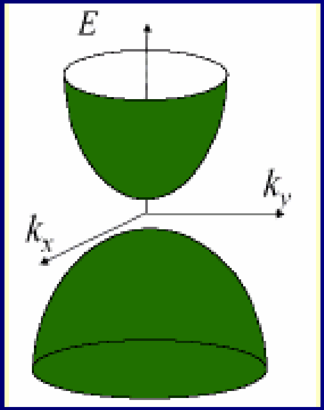
Graphene and conventional electron systems

Low energy excitations

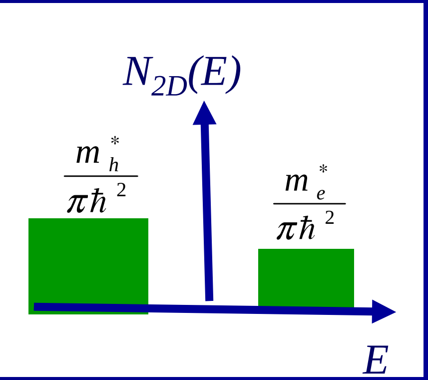
Conventional semiconductor

$$E = \frac{p^2}{2m_e^*}$$

$$E = \frac{p^2}{2|m_h^*|}$$

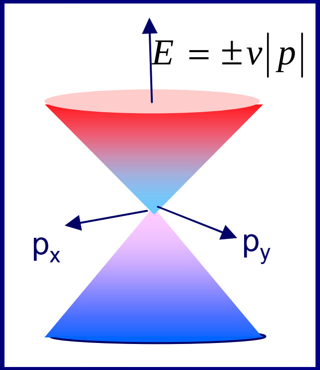


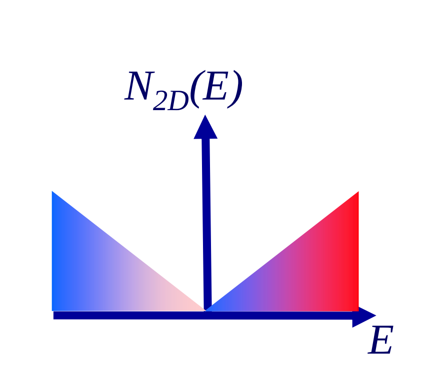
Density of states

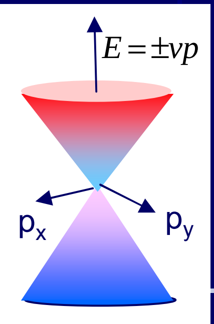


Graphene

- Zero band mass
- Gapless
- Electron-hole symmetry
- Pair creation
- Chiral (Pseudospin ½)
- Berry phase π



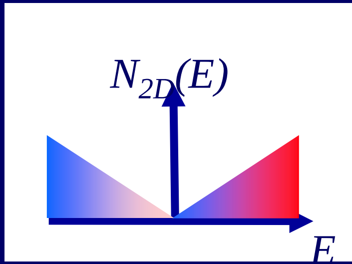




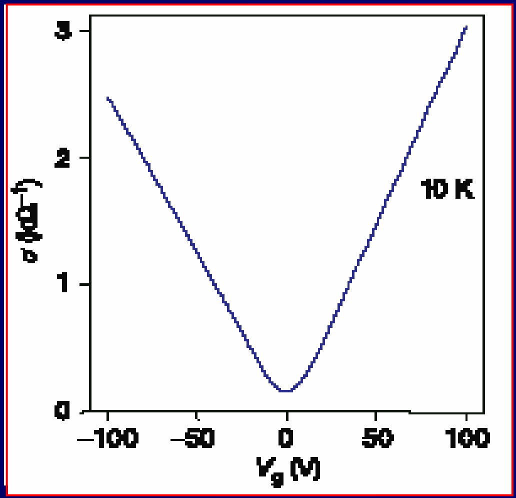
Relativistic electrons in graphene – experimental implications

- Vanishing DOS at Dirac point **q** *Electric field effect*
- *Berry phase π (no backscatering)* **q** *Large conductivity*
- *Chiral particles* **q** *Landau level at E=0*
- *Chiral particles* **q** *Anomalous QHE*
- *pair creation* **q** *Penetration through electrostatic barriers (Klein paradox)*

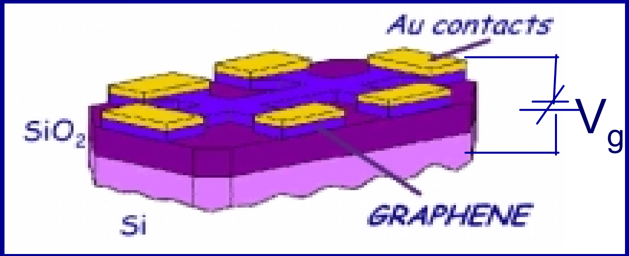
Electric field effect in graphene



conductivity



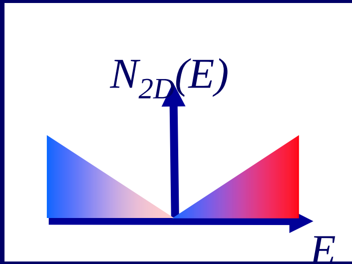
Novoselov et al, Nature 2005



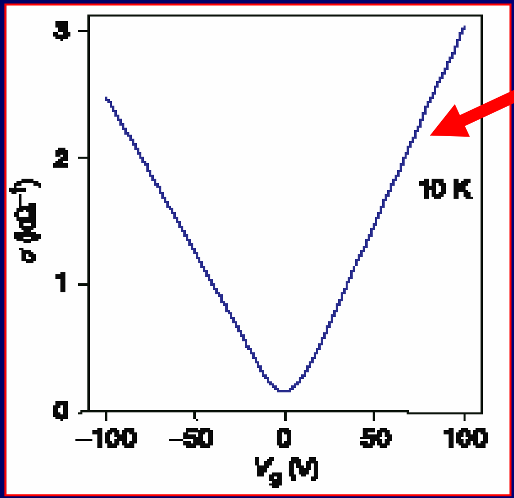
peak around zero
can be shifted by
chemical doping
(exposure to NO_2, NH_3, CO, etc)

Rutgers

Electric field effect in graphene

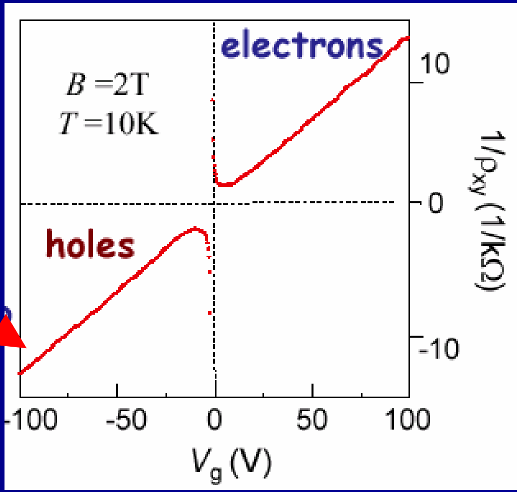


conductivity



$$\sigma = ne\mu = \frac{\varepsilon\varepsilon_0 \mu V_g}{d}$$

Hall effect



$$\frac{1}{\rho_{xy}} = \frac{ne}{B}$$

Novoselov et al, Nature 2005

mobilities up to 6,000 cm²/V·s at 300K

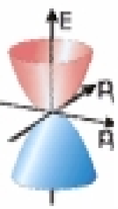
ballistic transport already on submicron scale !

~50,000 cm²/V·s (below 30K)

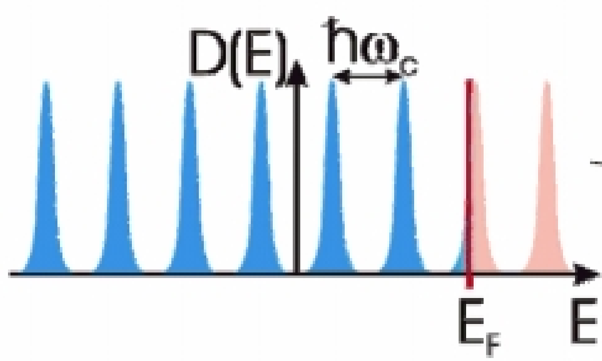
DOS – in magnetic field

2DEG

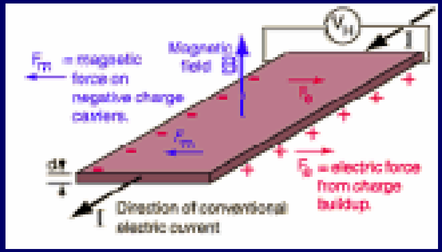
$$\omega_c = eB/(mc) = \hbar/(ml_B^2)$$



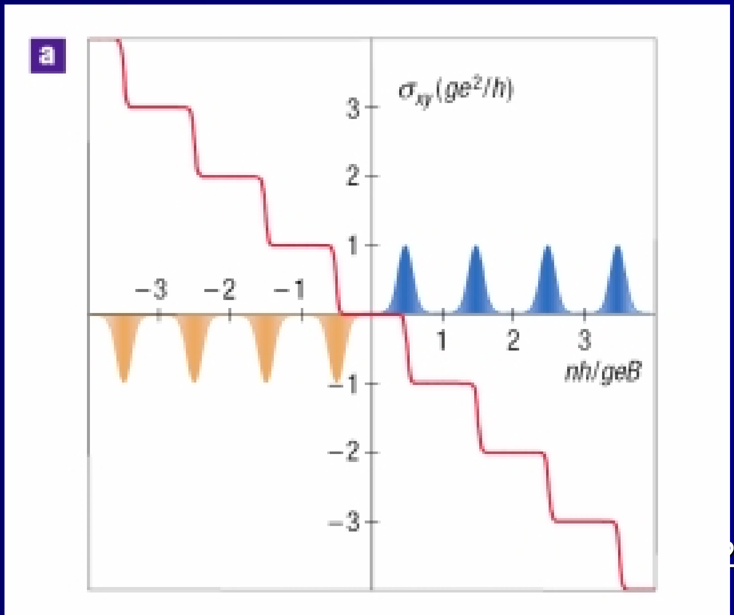
$$E_n = \hbar\omega_c(j+1/2)$$

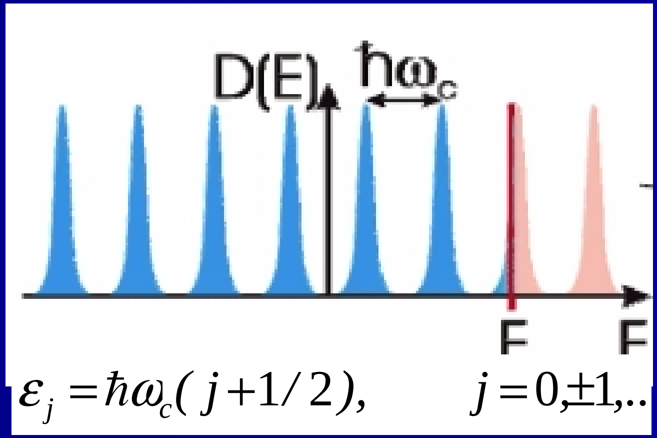


IQHE



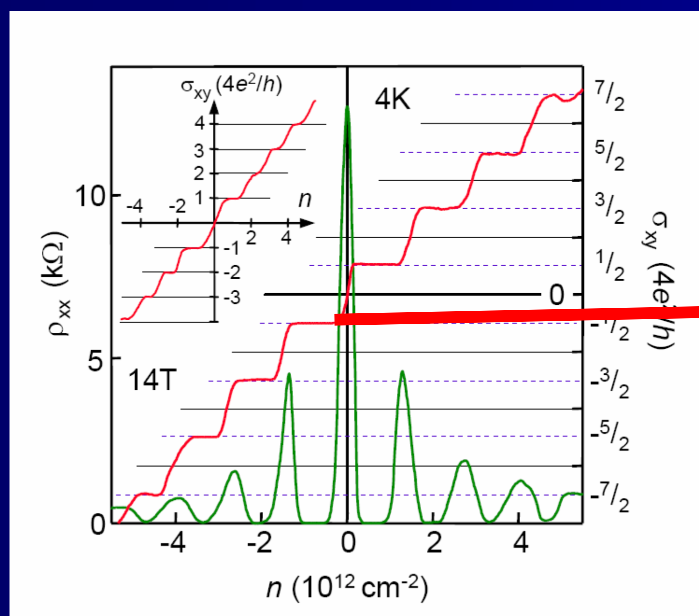
- Each filled Landau level contributes an additional quantum of conductance ge^2/h to the Hall conductivity (degeneracy = g).
- Quantum Hall plateaux when $nh/geB = n/n_\phi$ = integer – QHE
  - measures commensurability of electrons with flux lattice
  - Quantum Hall plateaux - ***independent of LL energy*** !!



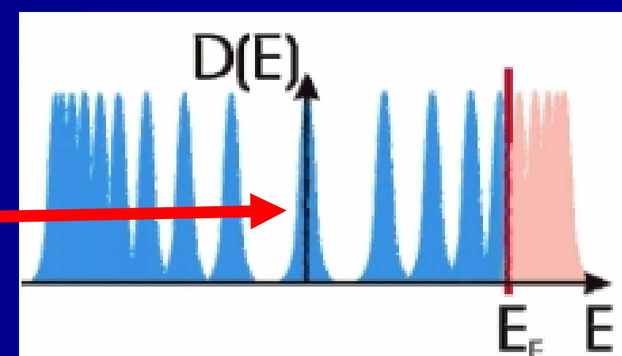


IQHE in graphene

- LL energy – not seen in QHE
- Need direct probe



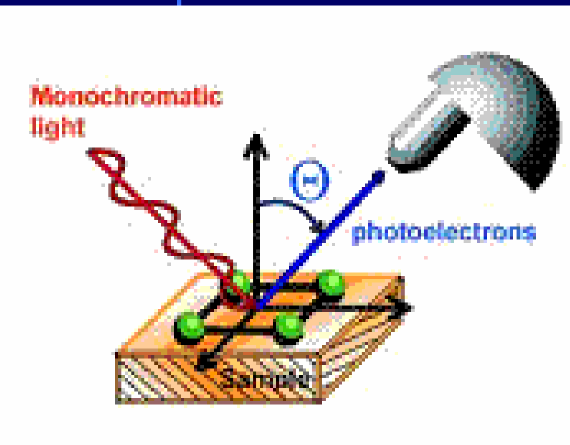
Novoselev et al Nature 2005
Zhang et al Nature 2005

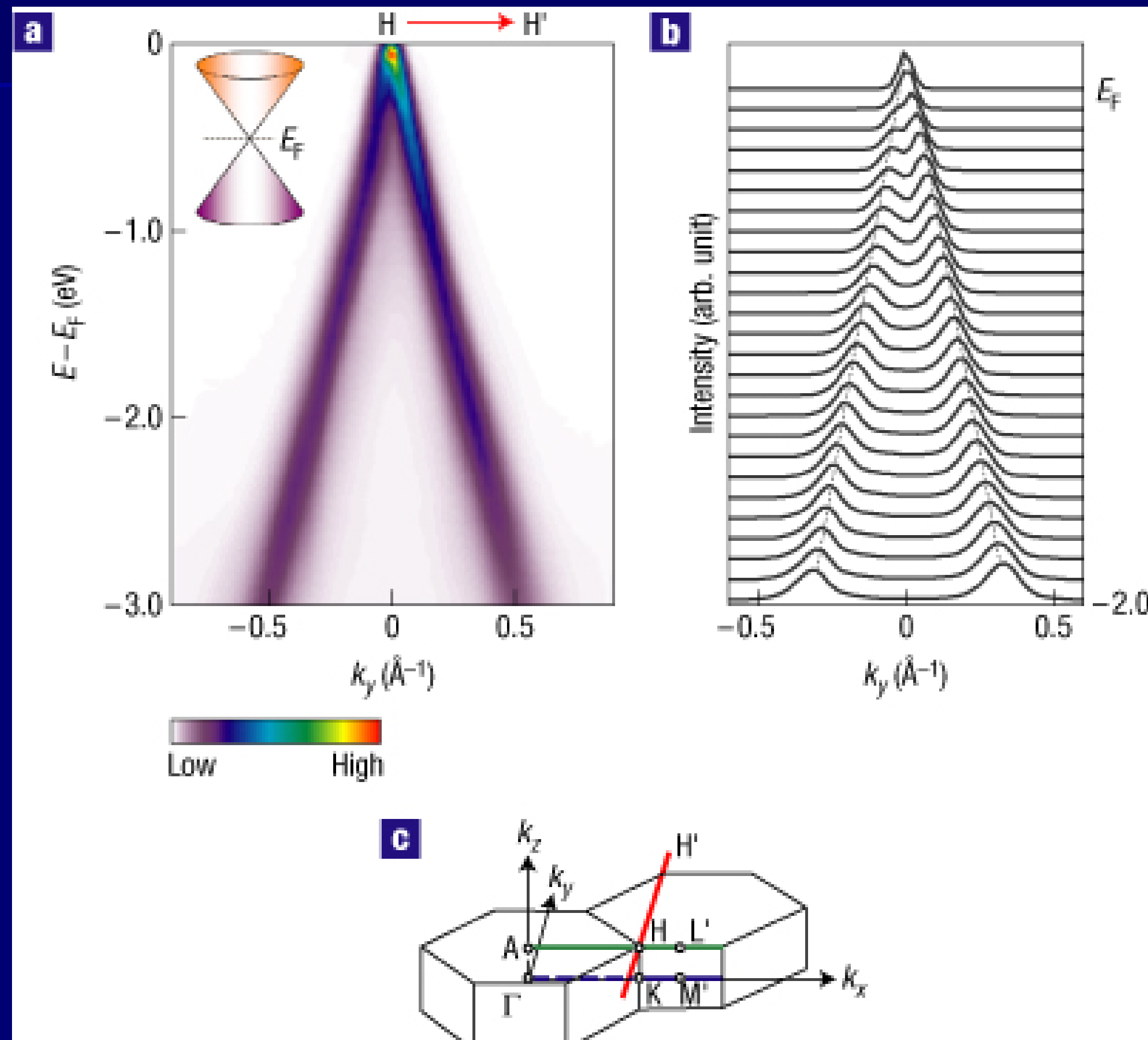


Landau level at E=0 –
no QHE plateau at 0.

ARPES on graphite

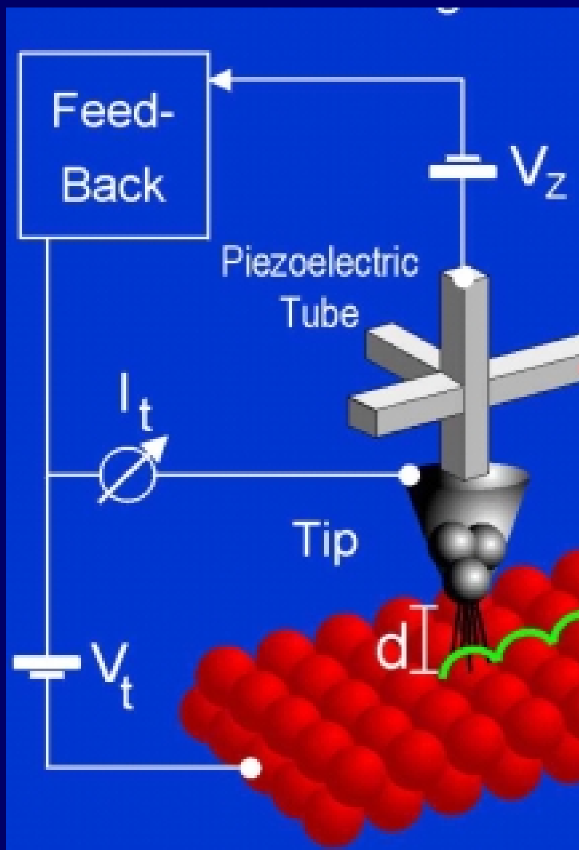
Zhou et al Nature 2006

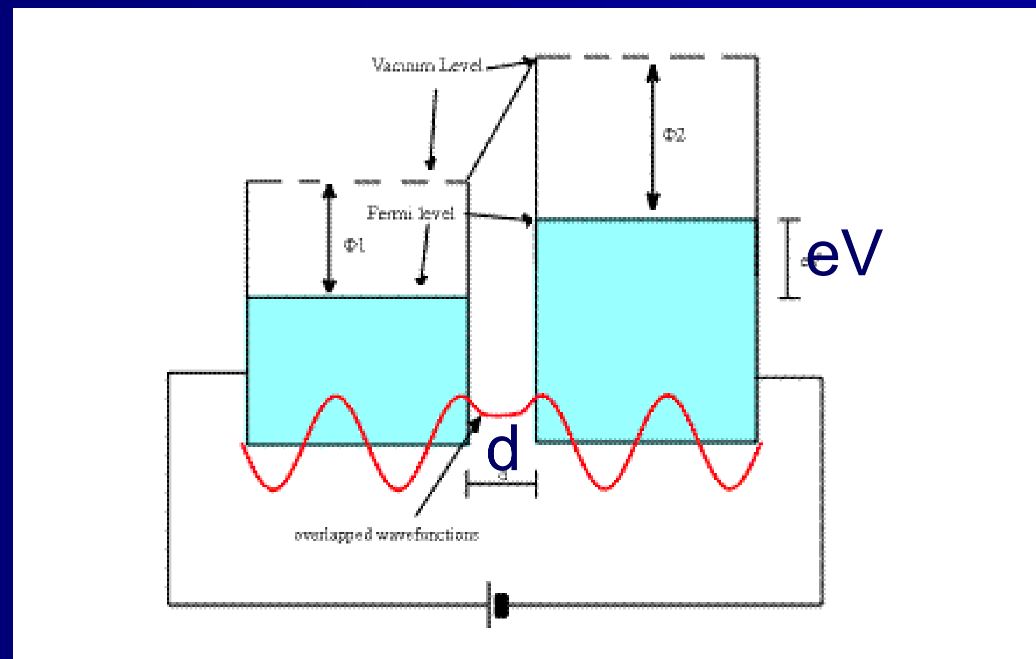




- ➢ Momentum resolution
- X No empty states
- X No magnetic field

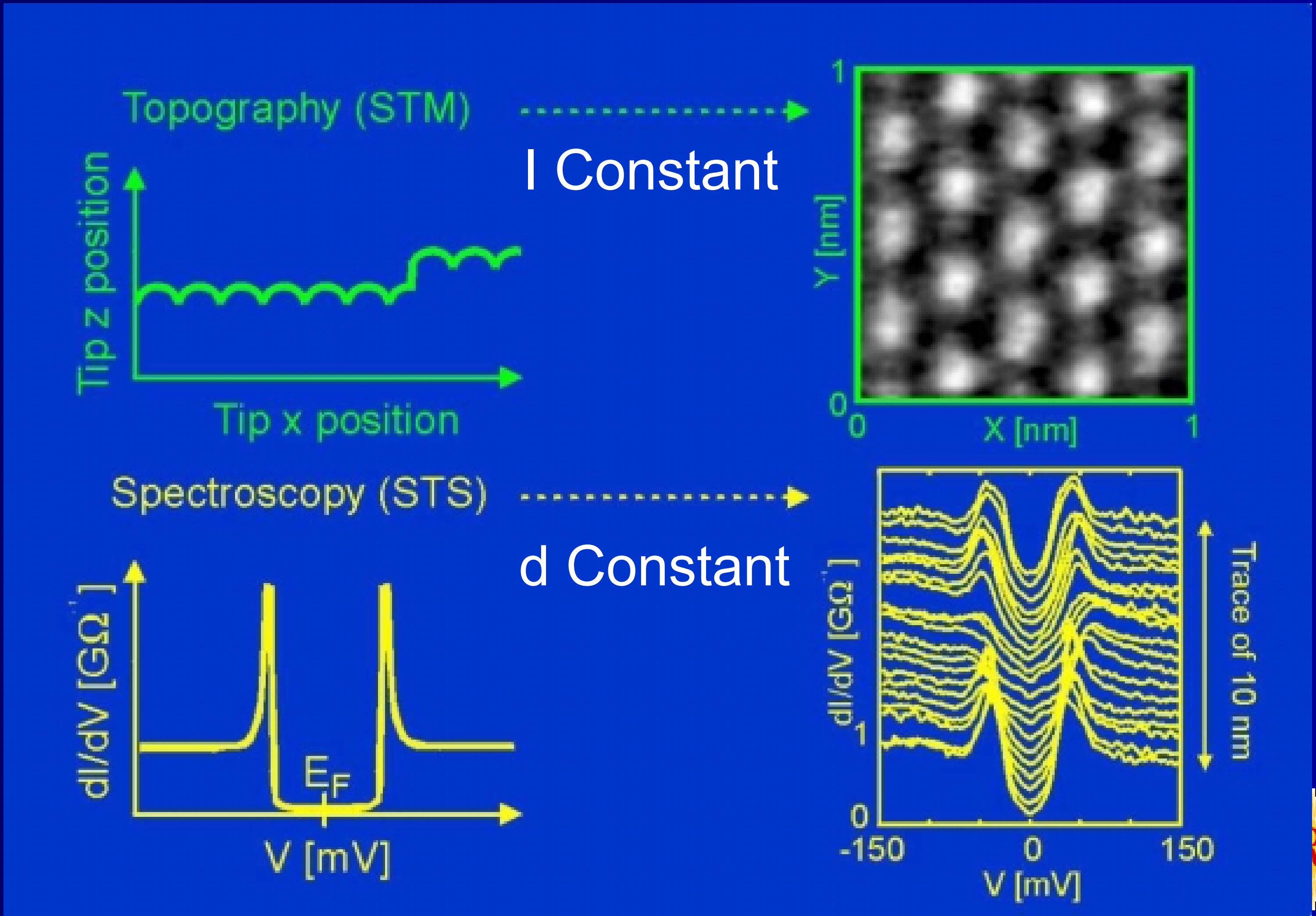
STM





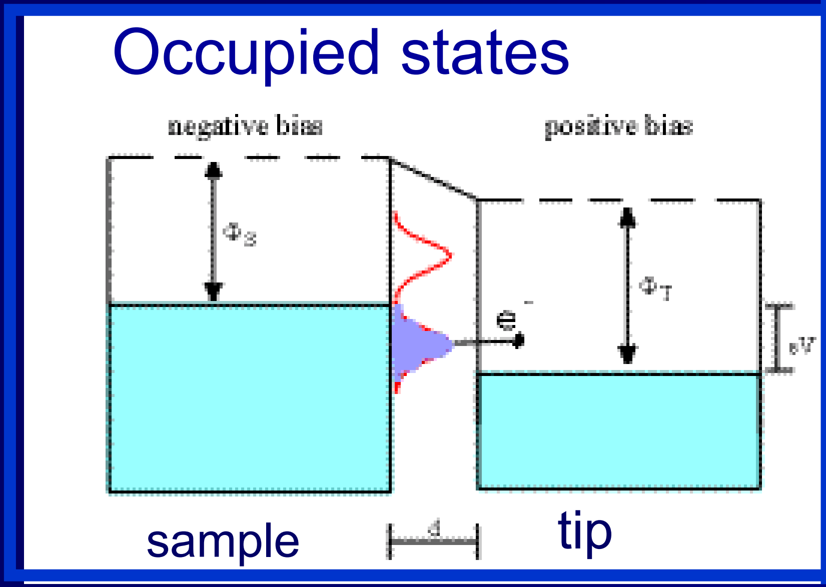
$$I \propto V\rho_s(0,E_F)\,exp(-2\kappa d); \quad \kappa = \frac{\sqrt{2m\Phi}}{\hbar}$$

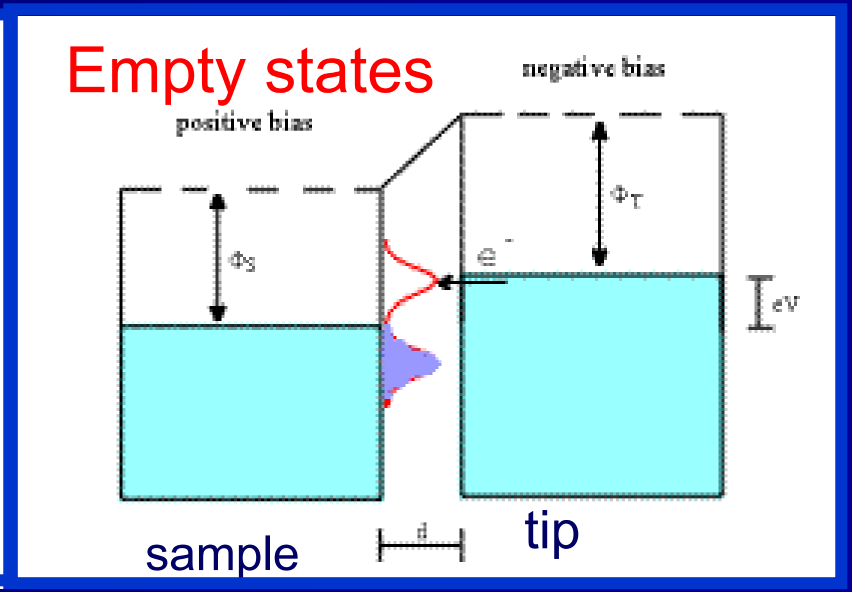
STM



Topography (STM)
I Constant
Tip z position
Tip x position
Y [nm]
X [nm]
0
1
Spectroscopy (STS)
d Constant
dI/dV [GΩ⁻¹]
E_F
V [mV]
-150
0
150
Trace of 10 nm

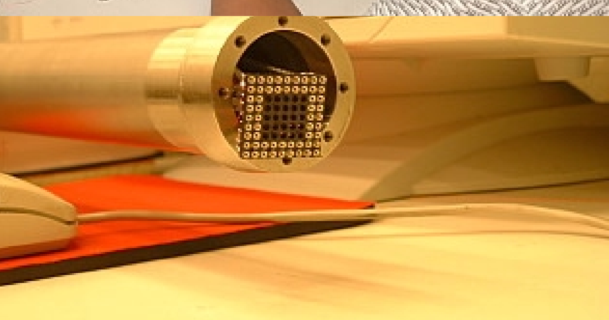
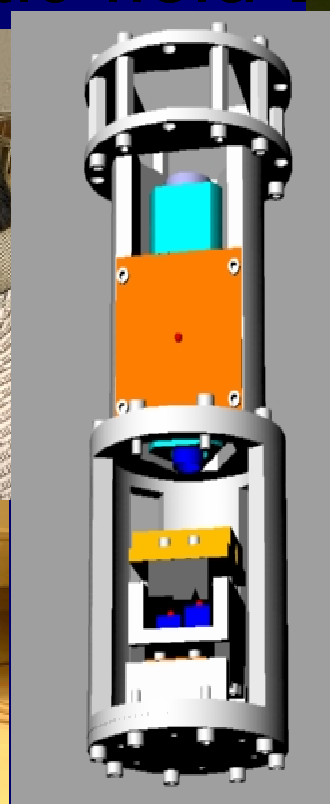
STM


Occupied states
negative bias
positive bias
Φ_S
Φ_T
e⁻
eV
sample
d
tip


Empty states
negative bias
positive bias
Φ_T
Φ_S
e⁻
eV
sample
d
tip

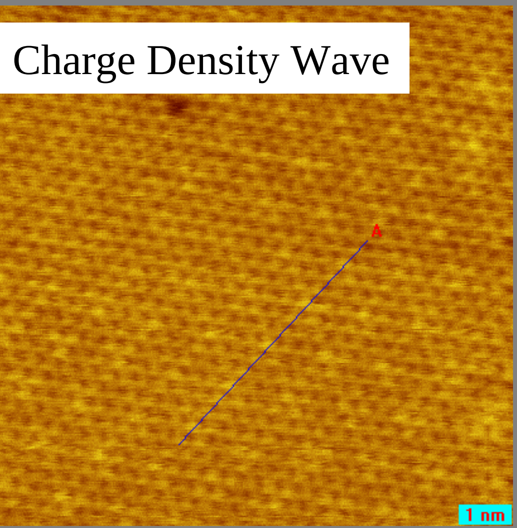
STM – direct observation of Landau levels

- Low temperatures -2K
- Magnetic field 15T

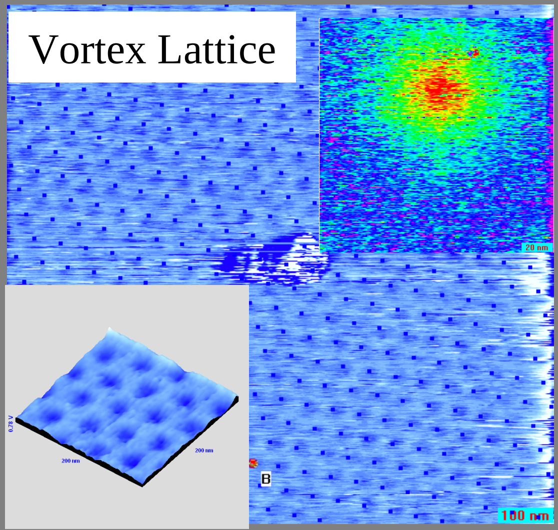





LT –HF- STM

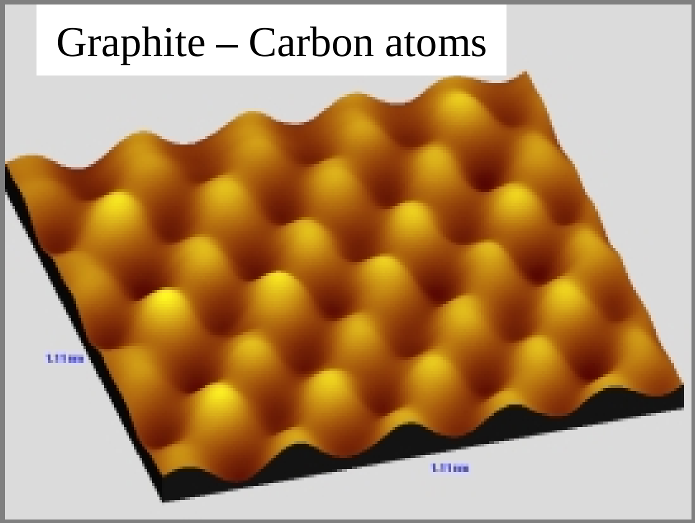
Low Temperature High Field Scanning Tunneling Microscope



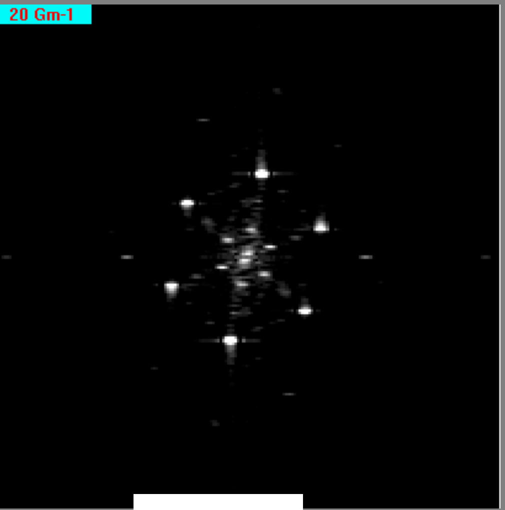
Charge Density Wave



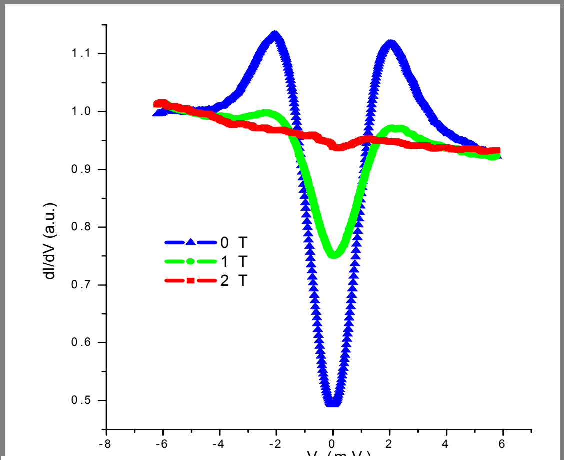
Vortex Lattice



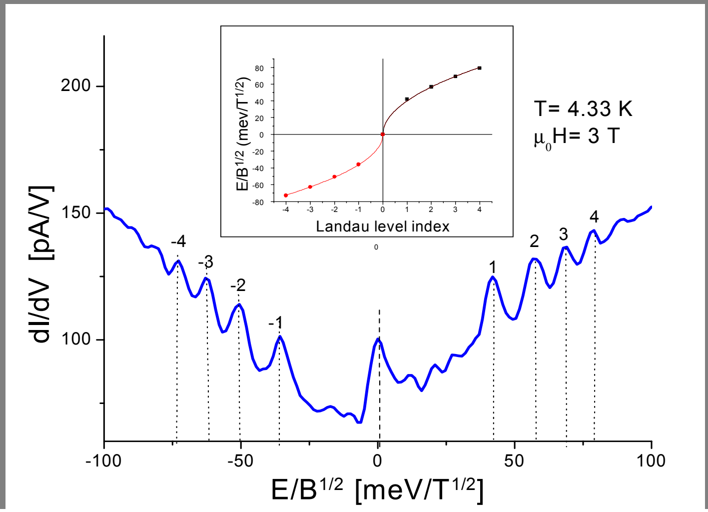
Graphite – Carbon atoms



NbSe2



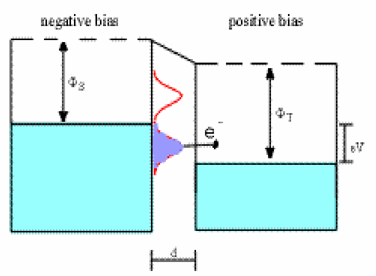
Superconducting Gap

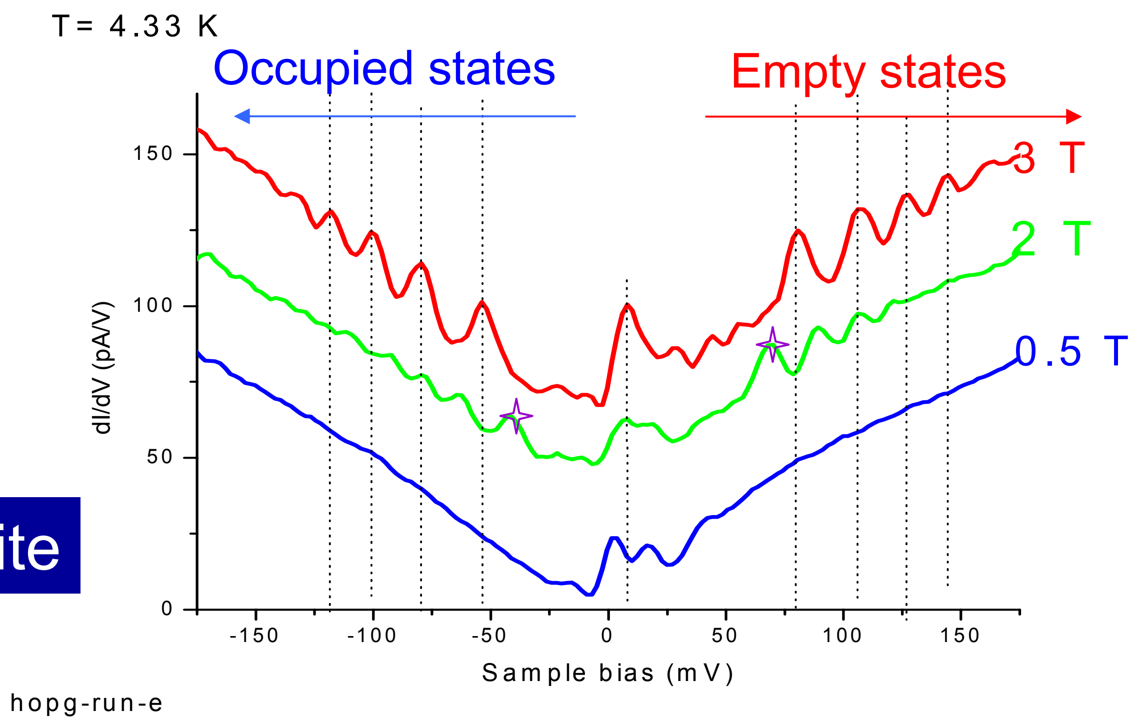


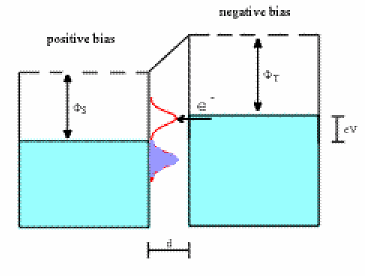
Relativistic Electrons – Quantum Hall Effec

STM on graphite

- Landau level spectroscopy - HOPG





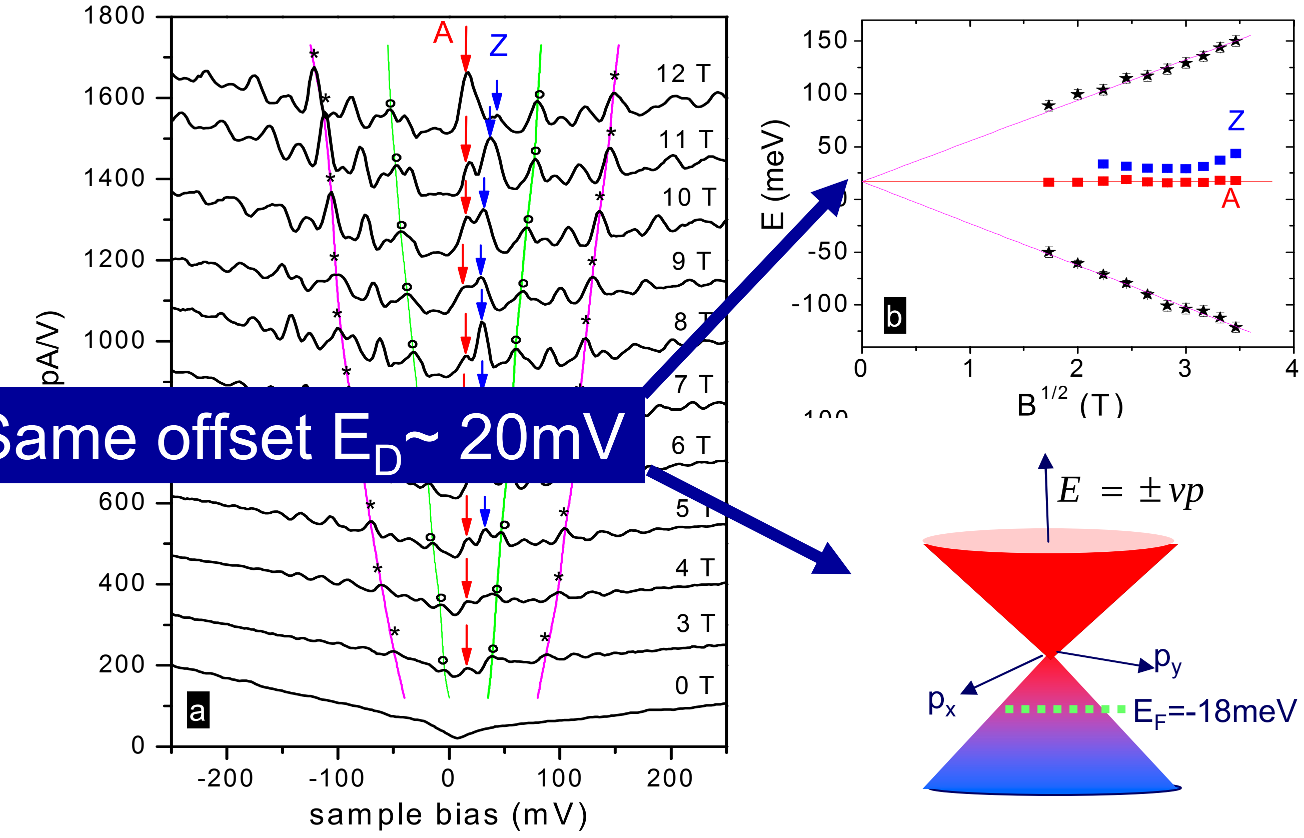


HOPG graphite

- Direct measure of energy levels
- Both electron and hole states

Rutgers

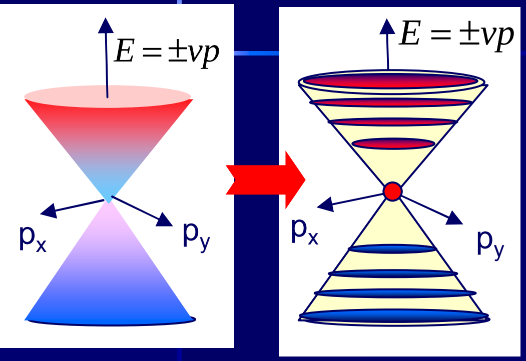
Landau level spectroscopy

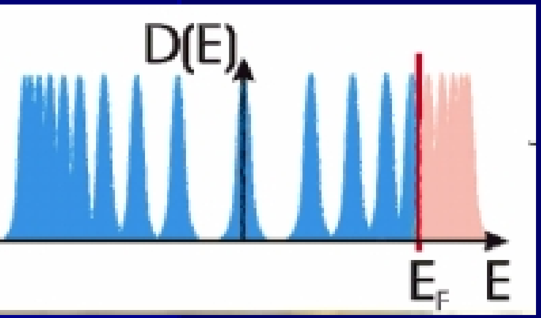


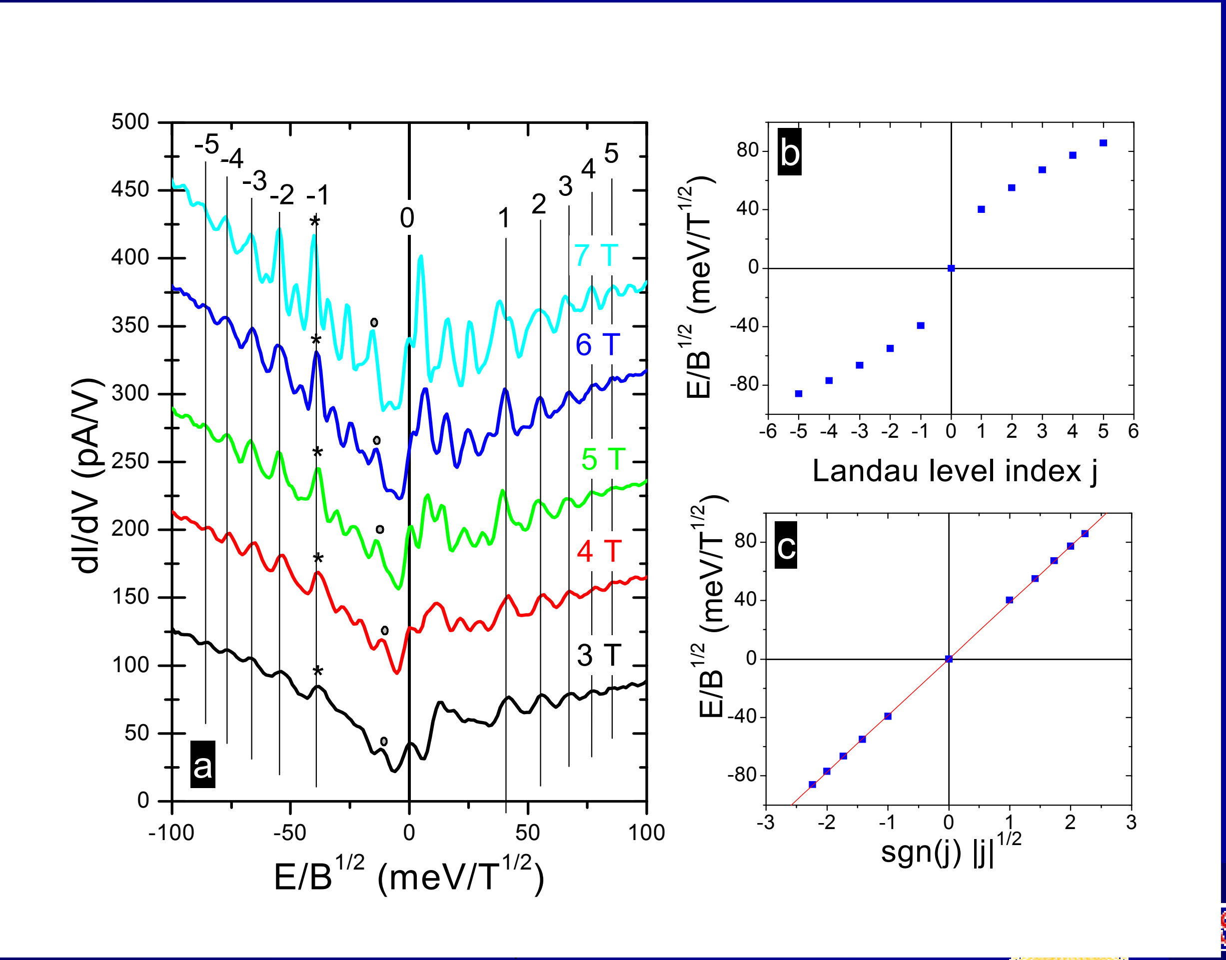
Same offset E_D~ 20mV

Landau levels of Dirac fermions

$$E_n = sgn(j)\sqrt{2e\hbar v_F^2 \,|j|\, B}, \quad j = 0, \pm 1, \dots$$







$v_F = 1.07 \times 10^6$ m/s

The linear sequence

- Two choices:
  - Standard 2d Electrons
    - Linear in *B, j*
    - No state at E=0

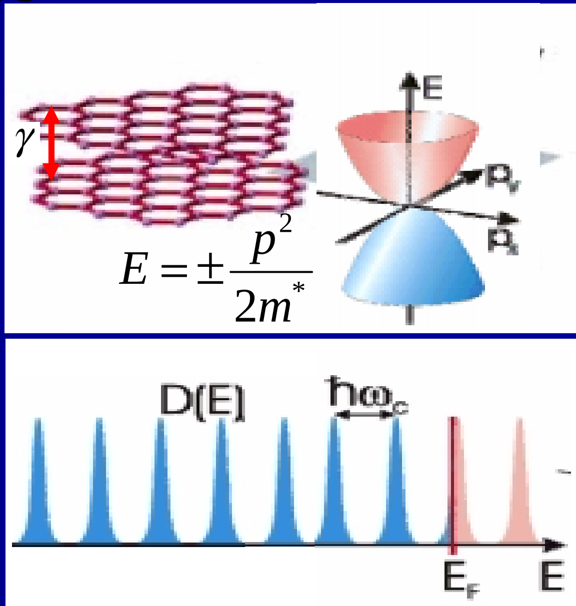
$$E_n = \hbar\omega_c(j+1/2), \quad j = 0,\pm1,\ldots$$

  - 2 layer graphene – massive chiral particles
    - Coupling between layers γ → m* = γ / v_F^2
    - Cyclotron frequency

$$\omega_c = eB / m^* c$$

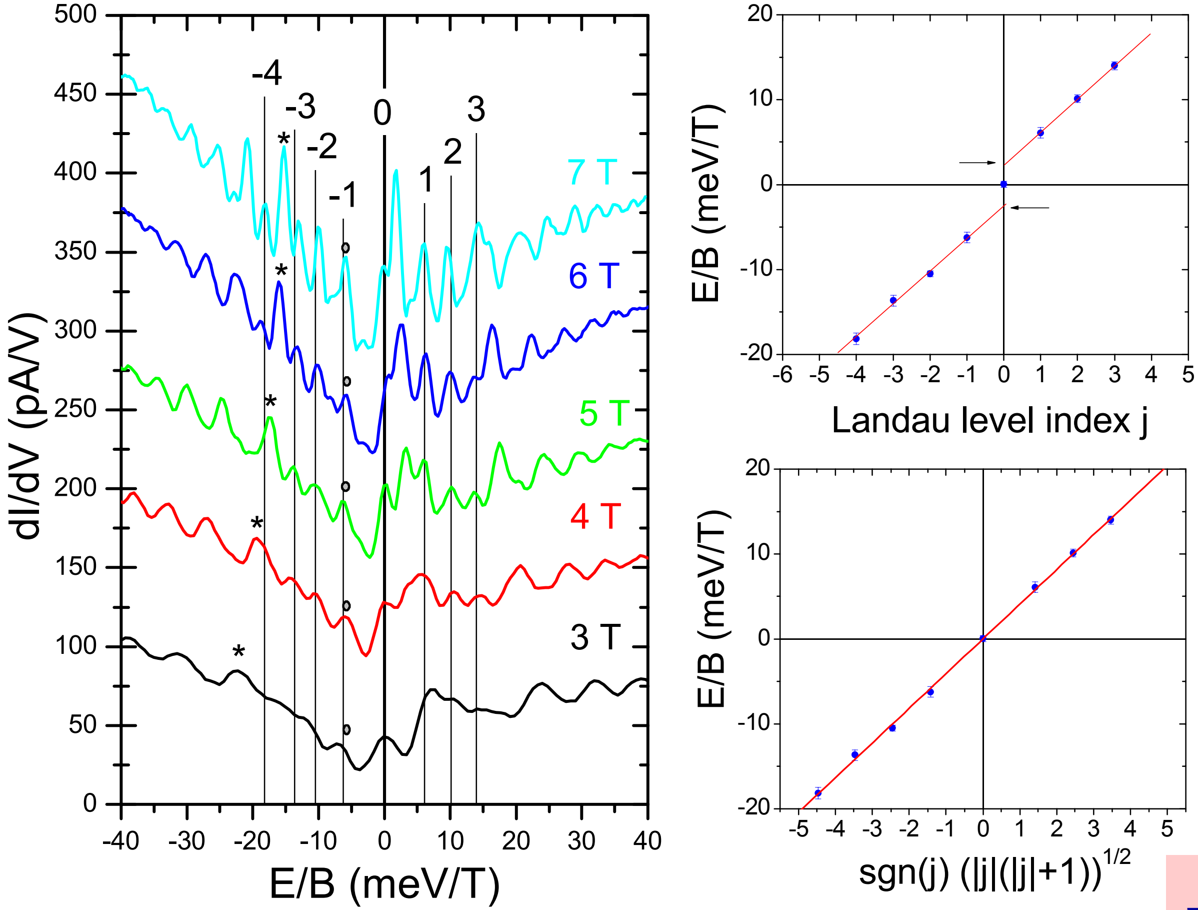
    - Linear in *B*
    - State at E=0

$$E_n = sgn(n)\hbar\omega_c\sqrt{(| j |(| j |+1))}, \quad j = 0,\pm1,\ldots$$



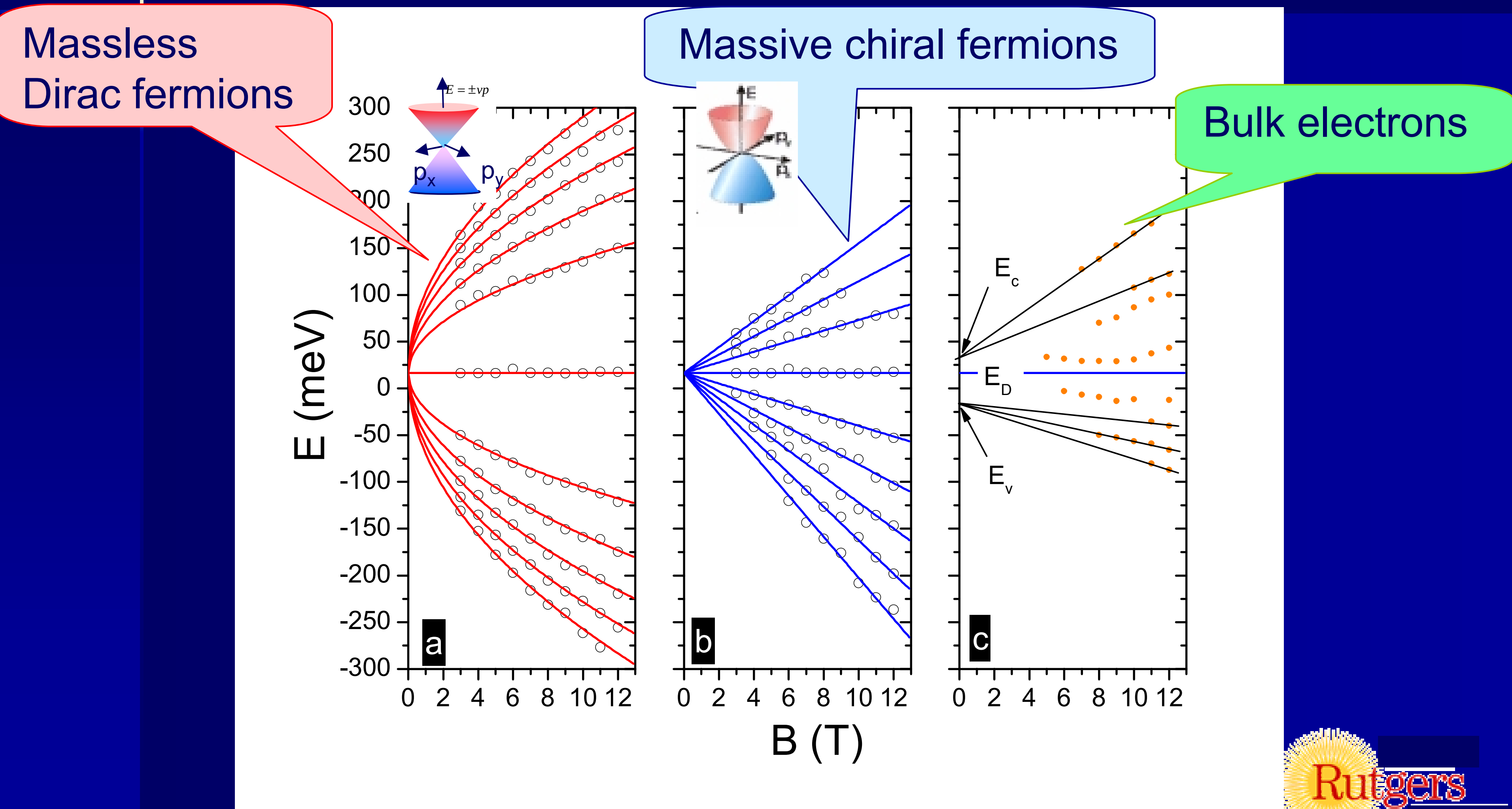
Massive chiral particles

$$E_n = sgn(j)\hbar\omega_c\sqrt{(|j|(|j|+1))}, \quad j = 0, \pm 1, \ldots$$



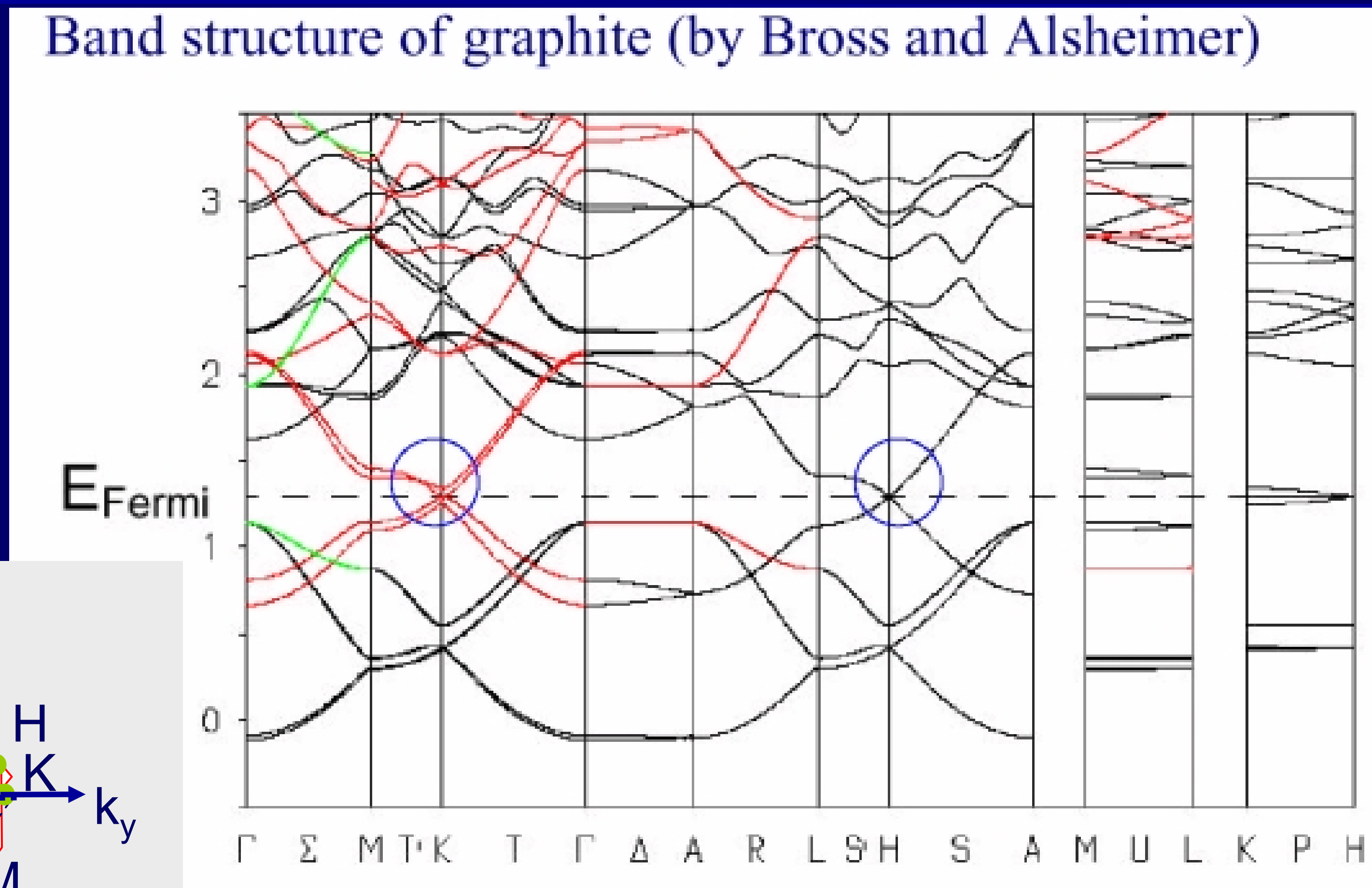
$m^* = 0.03\ m_e$

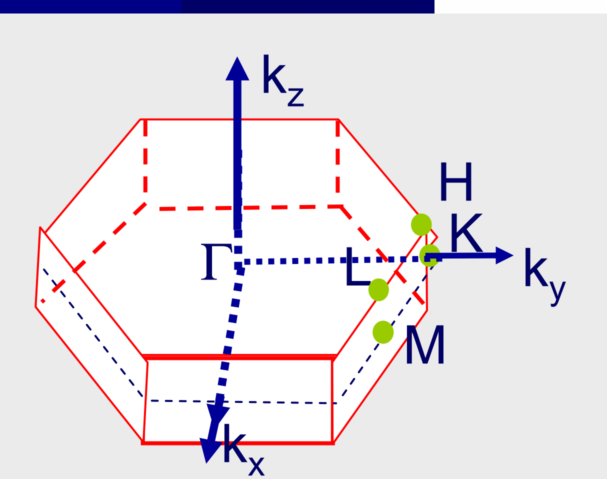
Classification of spectra



Rutgers

Graphite – band structure

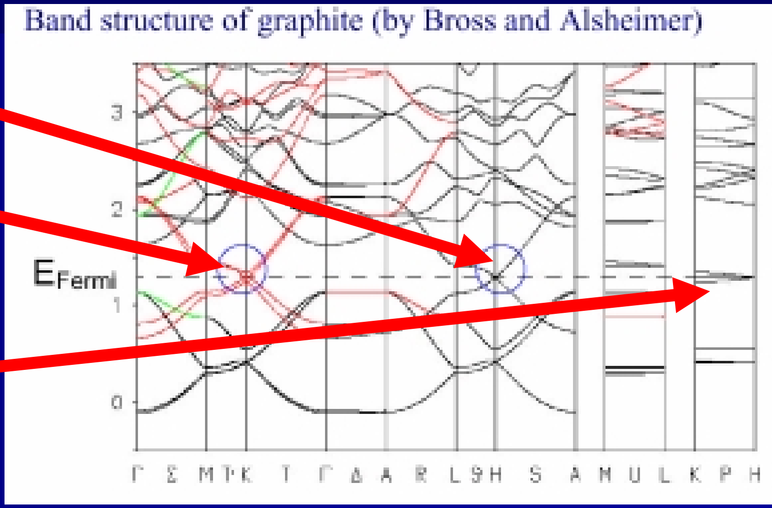


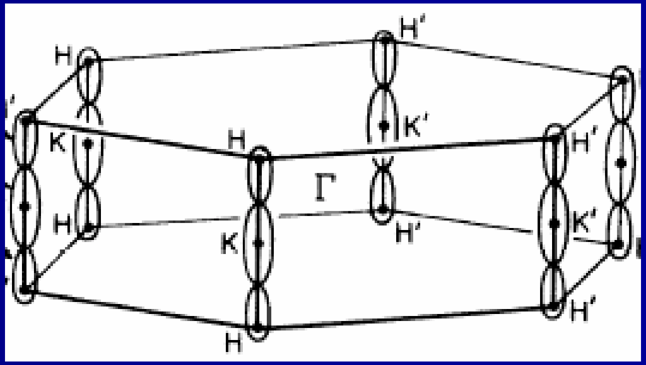


Graphite – band structure

- H – Dirac cone (E$_F$ below DP)
- K – quadratic (minimum at DP)
- L-M small gap
- K-H – continuous band
  - interlayer coupling dominates all non-k selective measurements:

Transport, STM ..



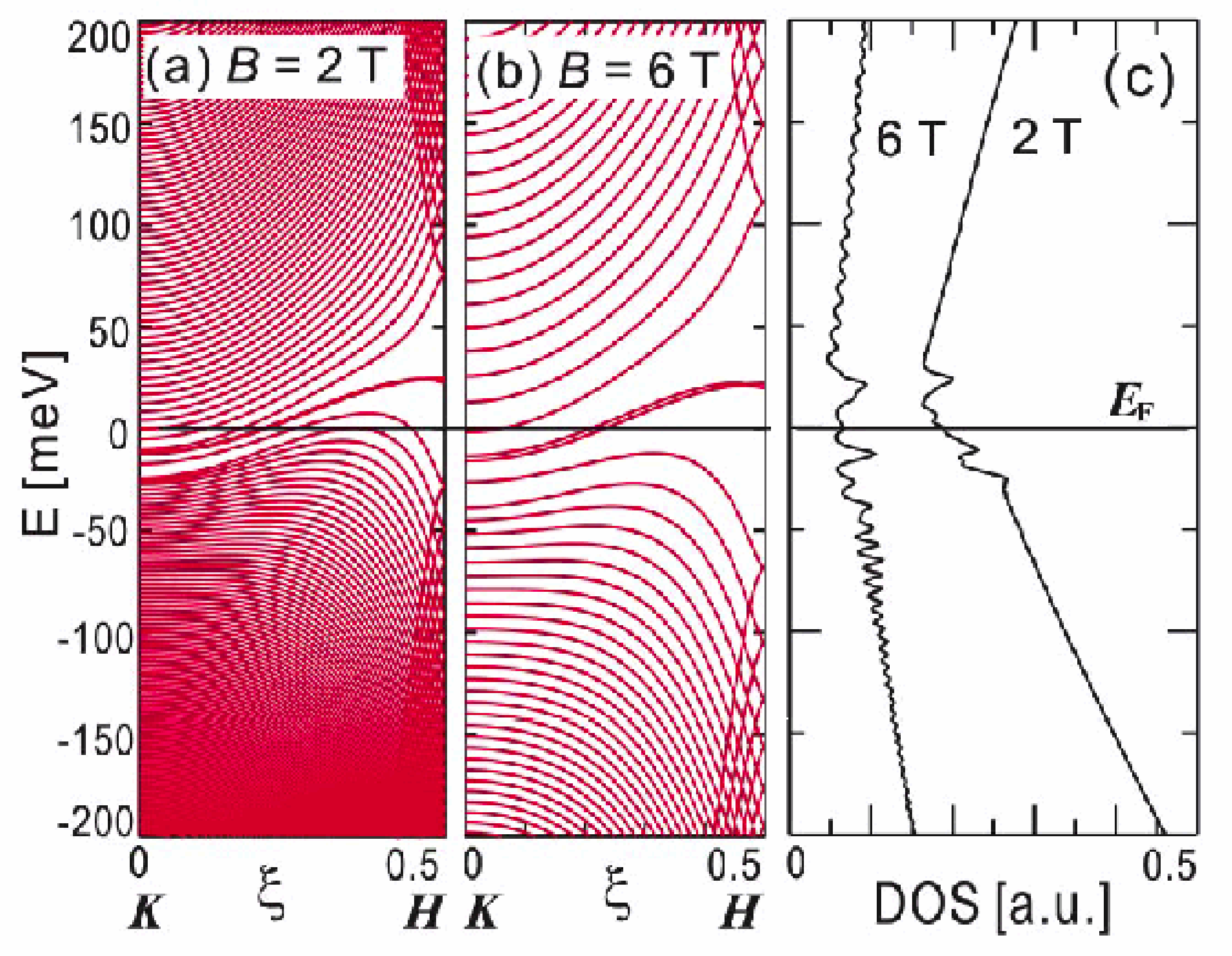


Rutgers

Graphite – Landau levels

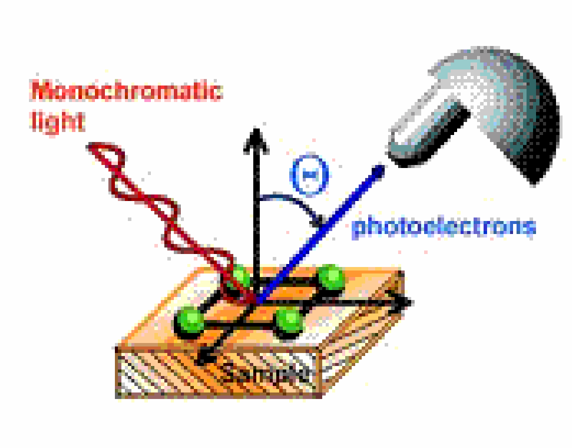
STM on Kish graphite -Matsui et al PRL 05

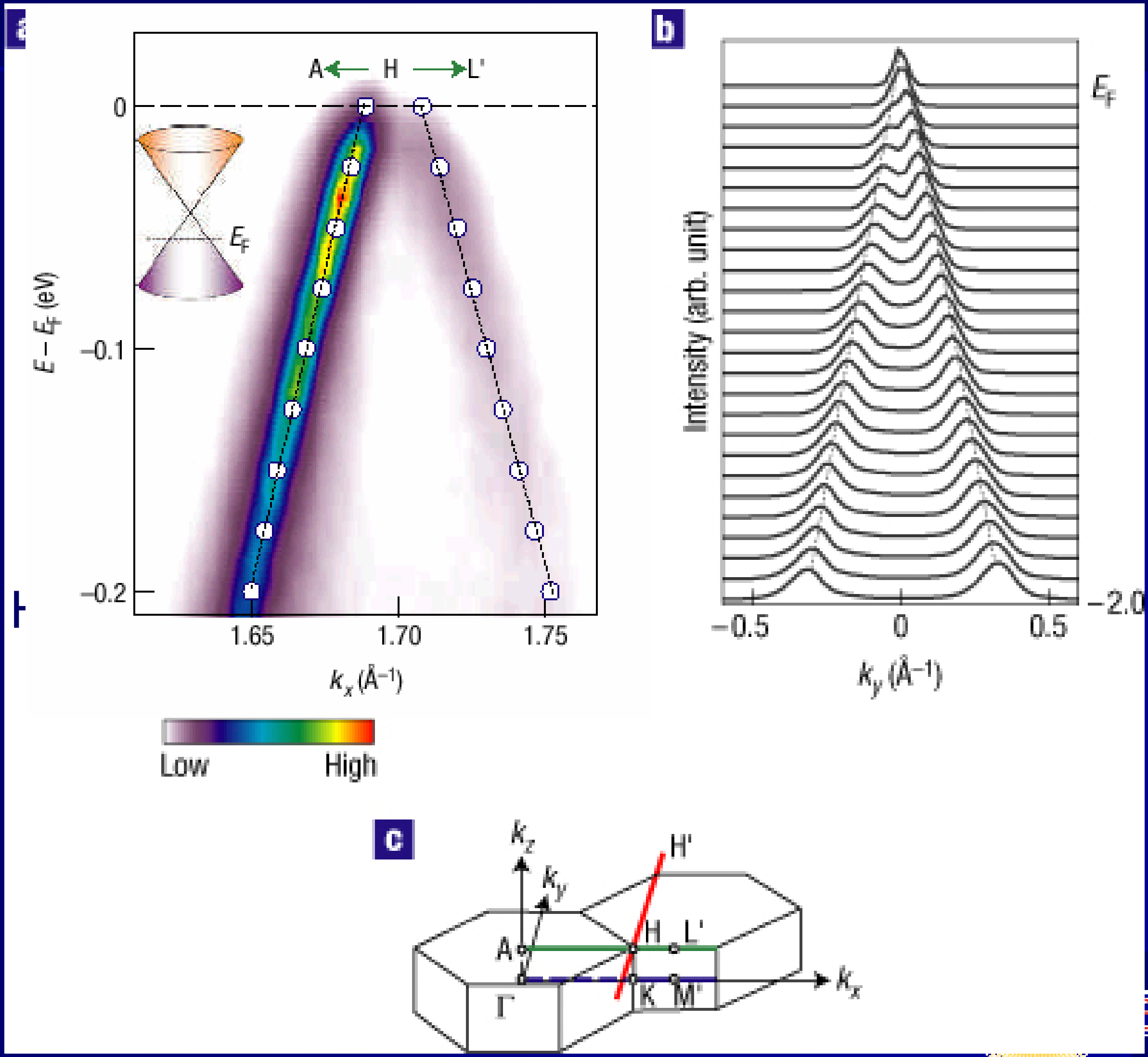
- Spectrum dominated by K-H states
- LL due to H and K points are "buried"



ARPES on graphite

Zhou et al Nature 2006



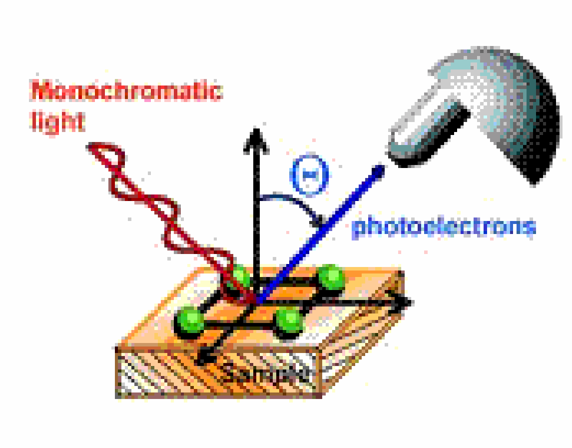


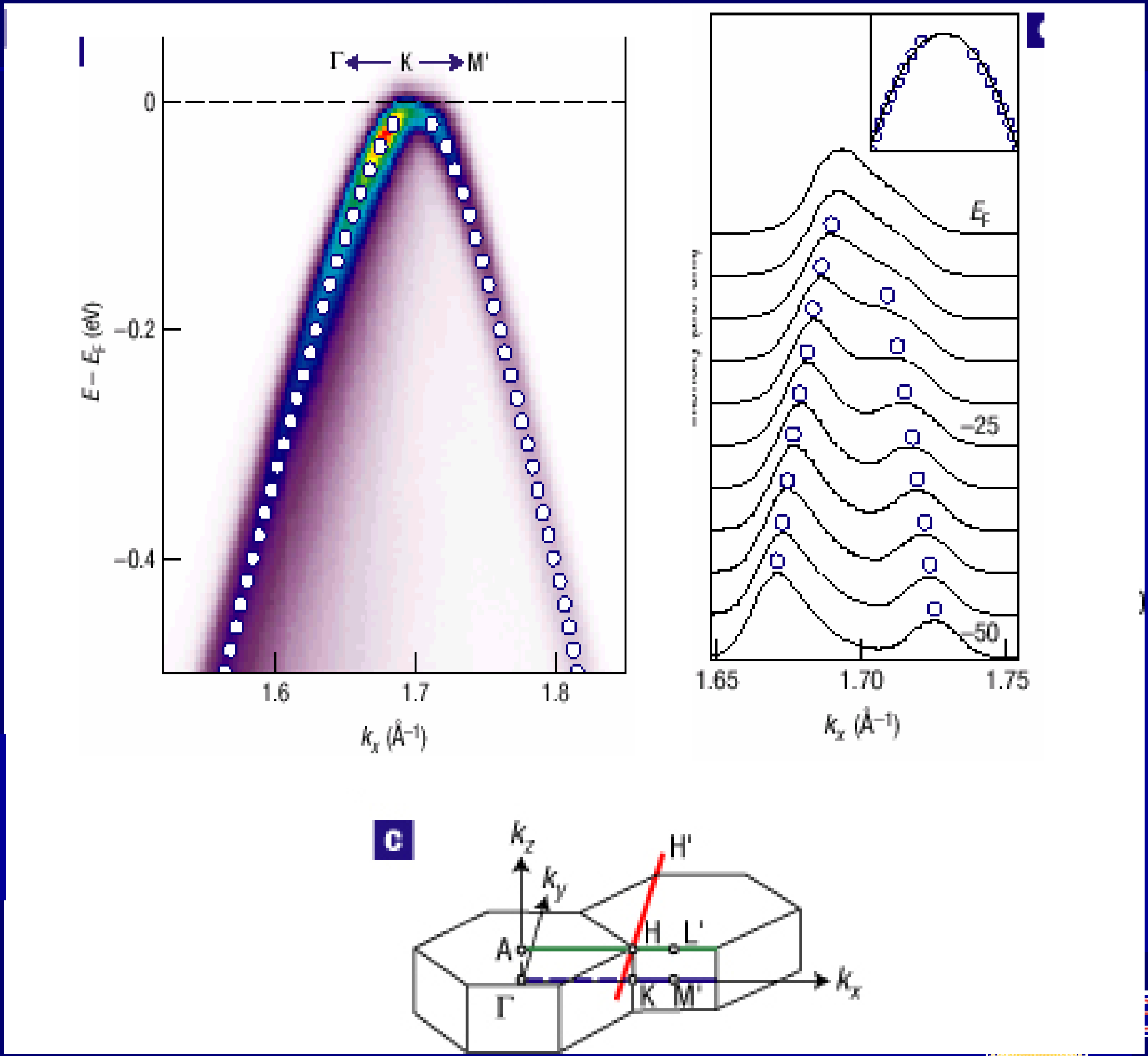
H point

Dirac point at H: 50mV above E_f

ARPES on graphite

Zhou et al Nature 2006





K point

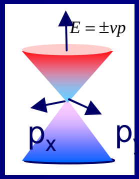
Parabolic dispersion –maximum at K.

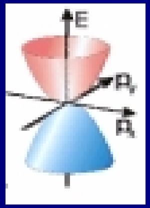
Compare to ARPES

- ARPES
  - H point :

  E_F-E_D= -50 mV

  - K point E_F=E_D





- STM
  - E_F-E_D= -20 mV
  - E_F-E_D= -20 mV
  - No energy offset between spectra.
  - No contribution from states with finite k_z

- STM Spectra inconsistent with bulk

☛ Surface layers of graphene

Summary

- Electrons on the surface of graphite
  - Massles Dirac fermions
    - Linear energy dispersion
    - Zero band mass
    - Landau level sequence follows $E_j \propto (B\, j)^{1/2}$
    - Zero energy Landau level
  - Massive chiral fermions
    - Quadreatic dispersion
    - Finite band mass
    - Landau level sequence follows $E_j \propto B\, (j(j+1))^{1/2}$
    - Zero energy Landau level
- SNS junction
    - Multiple Andreev Reflections observed.
    - Thin graphite - evidence of cooper pair current.
    - Graphene - proximity effect and MAR are suppressed near the Dirac po
- What next
  - STM near Impurities, defects
  - Many-body effects – FQHE, WC
  - Confinement: electrical, magnetic ?
  - ...