## Carbon Nanostructures

## I. Graphene

## Outline:

Introduction (Making graphene, Applications, etc.)
Band structure
Physics of Dirac electrons (Barry phase, Klein tunneling)
Half-Integer Quantum Hall Effect
Mobility in Graphene

## References:

E. McCann Graphene monolayers Lancaster University, UK Tight-binding model, QHE
C. Beenakker, Reviews of Modern Physics, 80, 1337 (2008)
L. Tapaszto \& J. Cserti talks, MAFIHE Teli Iskola a Grafenrol 2011, ELTE
A. Geim talk, TNT Conference 2010
http://www.tntconf.org/2010/Presentaciones/TNT2010 Geim.pdf

## Carbon nanostructures



## Graphene - Nobel Prize in Physics 2010



Andre Geim


Kostya Novoselov

Electric Field Effect in Atomically Thin Carbon Films
K. s. Novoselov, ${ }^{1}$ A. K. Geim, ${ }^{1+}$ S. V. Morozov, ${ }^{2}$ D. Jiang, ${ }^{1}$
Y. Zhang, ' S. V. Dubonos, ${ }^{2}$ I. V. Grigorieva, ${ }^{1}$ A. A. Firsov ${ }^{2}$

We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiry overlap between valence and conduutance bands, and they exhibit a strong ambipols
electric field effect such that electrons and holes in concentrations up to 10 pis electric fied effect such that electrons and holes in concentrotions up to 10 P" per
square centimeter and with room-temperature moblities of $\sim 10,000$ square squatimeters per volt-second can be induced by applying gate voltage.

Surprising, since growth of macroscopic 2D objects is strictly forbidden due to phonons
 (Mermin Wagner)

## GOING DUTCH <br> associate professor in Nijmegen: 1994-2000


micron-sized Hall probes to investigate superconductors, ferromagnetics, etc

structures from Nottingham lithography in Russia: Sergey Dubonos measurements in Nijmegen

fractional flux vortices \& vortex shells

writing up with Irina Grigorieva:
Nature 390, 259 (1997); Nature 396, 144 (1998); Nature 407, 55 (2000); PRL 79, 4653 (1997); PRL 85, 1528 (2000)

## PERCEPTION CHANGE

## everything (and everybody) is magnetic;

 ever present diamagnetism is NOT negligible"FRIDAY NIGHTS" in MANCHESTER
sticky feet: geckos climb due to their hairy toes

submicron size (!) - standard spatial scale in our work

## GECKO TAPE

proof of concept: biomimetic dry adhesive based on "gecko principle"


PLACING EMPHASIS


Geim, Sergey Dubonos,
Irina Grigorieva, Kostya Novoselov et al
Nature Materials 2003



## THE LEGEND OF SCOTCH TAPE

2002 PhD project of Da Jiang: make graphite films as thin as possible and study
their "mesoscopic" properties including electric field effect \& metallic transistor


Oleg Shklyarevskii's idea


## BEYOND OBSERVATION


hand-made devices (Novoselov)
first on glass slides,
then on oxidized Si wafer

## EUREKA MOMENT



## Graphene - Nobel Prize in Physics 2010



Andre Geim Kostya Novoselov

Electric Field Effect in Atomically Thin Carbon Films
K. S. Novoselov, ${ }^{1}$ A. K. Geim, ${ }^{1+}$ S. V. Morozov, ${ }^{2}$ D. Jiang. ${ }^{1}$
Y. Zhang,' S. V. Dubonos, ${ }^{2}$ I. V. Grigorieva, ${ }^{1}$ A. A. Firsov ${ }^{2}$

We describe monocystalline gaphitic films, which are a few atoms thick but are nonetheless stable under a mbient conditions, metallic, and of remarkably high quality. The fllms are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolse electric field effect such that electrons and holes in concentrations up to $10{ }^{13}$ per centimeters per volt-second can be induced by applying gate voltage.
"for groundbreaking experiments regarding the two dimensional material graphene"

Surprising, since growth of macroscopic 2D objects is strictly forbidden due to phonons
 (Mermin Wagner)

## How to make graphene?


a) Mechanical exfoliation


For proper SiO2 thickness interference makes it visible by optical microscope

+ Even size of 1mm, + high quality, - low yield


## b) Mechanical or Chemical extraction

sonication + centrifugation, often intercalation
$\rightarrow$ Submicrometer crystallites

+ Mass production, industrial scale
- Small falke size
-Remaining attached chemicals (oxide)
$\rightarrow$ Good for polycrystalline films and composite materials. Suspension can be printed resulting highly conductive bendable film
Ruoff, Nature 2006, Manchester, Nanolett '08,Coleman et al, Nature Nano '08

Intercalation



## b) Epitaxial growth of a monolayer

Grow a monolayer of $C$ and chemically remove the substrate
1)SiC substrate: (upper figs.)

SiC is insulator, Graphene layers grow as a carpet on the surface. Layers are electrically
 well isolated (different stacking). Possible to grow 1,2 layers.

- Difficult growth process

2) CVD on $\mathrm{Cu}, \mathrm{Ni}$ (Lower figs.) "Easy" to do: $\mathrm{T}+$ gas flow. Self terminating process. Result: single layer, - polycrystalline, it follows the crystallites of the metal surface, Use HCl to remove substrate. (commercial available)


## Identification



## Properties, applications

## Electronic properties:

- Truly 2D electron gas on the surface. New possibilities: SC, Ferro, high dielectrics, use local probes.
- Massless Dirac electrons
-Good electronic quality: submicrons without scattering @RT although adsorbates etc. Due to weak e-ph coupling mobility > $200000 \mathrm{~cm}^{2} / \mathrm{Vs}$ @ RT (Si: <1500 cm²/Vs)
- Quantum effect at RT

transistor @ 300 GHz
Applications:

1) Ultra High Frequency Transistors

- Ballistic transport
- high velocity
- great electrostatics
- scales to nm size

2009: 100 GHz (IBM \& HRL)
2010: 300 GHz (UCLA \& Samsung)
scaling $>1 \mathrm{THz}$
Nature 467, 305 (2010)

## Properties, applications

## Electronic properties:

- Truly 2D electron gas on the surface. New possibilities: SC, Ferro, high dielectrics, use local probes.
- Massless Dirac electrons
-Good electronic quality: submicrons without scattering @RT although adsorbates etc. Due to weak e-ph coupling mobility $>200000 \mathrm{~cm}^{2} /$ Vs @ RT (Si: <1500 cm²/Vs)
- Quantum effect at RT


Flexible transparent electronics
Nature 457, 706 (2009) Hong, Nature Nano 2010

## Applications:

2) Electrode for liquid crystals

- transparent ~97\%
- conductive $\rho<100 \Omega / \square$ -flexible: strain >15\% -chemically inert - reasonable chip 50\$/m² -Bendable, wearable Samsung's Graphene Road Map: first products in 2012



## Properties, applications

## Thermal, mechanical properties

Heat conductivity $5000 \mathrm{Wm}^{-1} \mathrm{~K}^{-1}$
(Cu $400 \mathrm{Wm}^{-1} \mathrm{~K}^{-1}$ )


Nano Lett. 8, 902 (2008)

Impermeable to gases (also He)
$\rightarrow$ When wafers will be available It will be ideal for biomolecular and ion transport membranes

Science 321, 385 (2008)


Strongest material, Due to strong $\mathrm{sp}^{2}$ bonds up to $20 \%$ $\rho=0.77 \mathrm{mg} / \mathrm{m}^{2}$
Other possible applications: Ultrafast photo detectors, Strain sensor, TEM membranes, high sensitive sensors, DNA sequencing etc.

## BANDSTRUCTURE OF GRAPHENE



Three dimensional layered material with hexagonal 2D layers [shown here with Bernal (AB) stacking]


Two dimensional material; zero gap semiconductor; Dirac spectrum of electrons

> Bilayer


## 1 Tight binding model of monolayer graphene

 $1.1 \mathrm{sp}^{2}$ hybridisationCarbon has 6 electrons: $\mathbf{2}$ are core electrons, 4 are valence electrons - one 2 s and three 2 p orbitals
$\mathbf{s p}^{2}$ hybridisation

- single 2s and two 2 p orbitals hybridise forming three " $\sigma$ bonds" in the x-y plane

- remaining $2 p_{z}$ orbital [" $\pi$ " orbital] exists perpendicular to the $x-y$ plane
only $\pi$ orbital relevant for energies of interest for transport measurements - so keep only this one orbital per site in the
 tight binding model


## 1 Tight binding model of monolayer graphene <br> 1.2 lattice of graphene


$\mathbf{2}$ different atomic sites - $\mathbf{2}$ triangular sub-lattices

## 1 Tight binding model of monolayer graphene <br> 1.3 reciprocal lattice


triangular reciprocal lattice

- hexagonal Brillouin zone


## 1 Tight binding model of monolayer graphene <br> 1.4 Bloch functions

We take into account one $\pi$ orbital per site, so there are two orbitals per unit cell.

Bloch functions $\quad \Phi_{A}(\vec{k}, \vec{r})=\frac{1}{\sqrt{N}} \sum_{\vec{R}_{A}}^{N} e^{i \vec{k} \cdot \vec{R}_{A}} \varphi_{A}\left(\vec{r}-\vec{R}_{A}\right)$

$$
\begin{array}{cc}
\Phi_{B}(\vec{k}, \vec{r})=\frac{1}{\sqrt{N}} \sum_{\vec{R}_{B}}^{N} e^{i \vec{k} \cdot \vec{R}_{B}} \varphi_{B}\left(\vec{r}-\vec{R}_{B}\right) \\
\text { sum over all type } \\
\text { B atomic sites } \\
\text { in } \mathbf{N} \text { unit cells } & \text { wavefunction }
\end{array}
$$

## 1 Tight binding model of monolayer graphene

1.4 Bloch functions

We take into account one $\pi$ orbital per site, so there are two orbitals per unit cell.

Bloch functions : label with $\mathbf{j}=\mathbf{1}$ [A sites] or $\mathbf{2}$ [ B sites]


## 1 Tight binding model of monolayer graphene

1.5 Secular equation

Eigenfunction $\Psi_{j}(f o r j=1$ or 2 ) is written as a linear combination of Bloch functions:

$$
\Psi_{j}(\vec{k}, \vec{r})=\sum_{j^{\prime}=1}^{2} C_{i j^{\prime}}(\vec{k}) \Phi_{j^{\prime}}(\vec{k}, \vec{r})
$$

Eigenvalue $\mathbf{E}_{\mathrm{j}}(\mathrm{for} \mathbf{j}=1$ or 2 ) is written as:

$$
E_{j}(\vec{k})=\frac{\left\langle\Psi_{j}\right| H\left|\Psi_{j}\right\rangle}{\left\langle\Psi_{j} \mid \Psi_{j}\right\rangle}
$$

substitute expression in terms of Bloch functions

$$
E_{j}(\vec{k})=\frac{\sum_{i, l}^{2} C_{j i}^{*} C_{j l}\left\langle\Phi_{i}\right| H\left|\Phi_{l}\right\rangle}{\sum_{i, l}^{2} C_{j i}^{*} C_{j l}\left\langle\Phi_{i} \mid \Phi_{l}\right\rangle} \equiv \frac{\sum_{i, l}^{2} H_{i l} C_{j i}^{*} C_{j l}}{\sum_{i, l}^{2} S_{i l} C_{j i}^{*} C_{j l}}
$$

$$
\begin{gathered}
\text { defining transfer } \\
\text { integral matrix }
\end{gathered} H_{i l}=\left\langle\Phi_{i}\right| H\left|\Phi_{l}\right\rangle ; \quad \begin{gathered}
\text { and overlap } \\
\text { integral matrix }
\end{gathered} \quad S_{i l}=\left\langle\Phi_{i} \mid \Phi_{l}\right\rangle
$$ elements elements

## 1 Tight binding model of monolayer graphene

1.5 Secular equation

$$
E_{j}(\vec{k})=\frac{\sum_{i, l}^{2} H_{i l} C_{j i}^{*} C_{j l}}{\sum_{i, l}^{2} S_{i i} C_{j i}^{*} C_{j l}}
$$

If the $H_{i l}$ and $S_{i l}$ are known, we can find the energy by minimising with respect to $C_{j m}^{*}$ :

$$
\begin{aligned}
& \frac{\partial E_{j}}{\partial C_{j m}^{*}}=\frac{\sum_{l}^{2} H_{m l} C_{j l}}{\sum_{i, l}^{2} S_{i l} C_{j i}^{*} C_{j l}}-\frac{\sum_{i, l}^{2} H_{i l} C_{j i}^{*} C_{j l} \sum_{l}^{2} S_{m l} C_{j l}}{\left(\sum_{i, l}^{2} S_{i l} C_{j i}^{*} C_{j l}\right)^{2}} \\
& \frac{\partial E_{j}}{\partial C_{j m}^{*}}=0 \Rightarrow \sum_{l=1}^{2} H_{m l} C_{j l}=E_{j} \sum_{l=1}^{2} S_{m l} C_{j l}
\end{aligned}
$$

## 1 Tight binding model of monolayer graphene

1.5 Secular equation

$$
\sum_{l=1}^{2} H_{m l} C_{j l}=E_{j} \sum_{l=1}^{2} S_{m l} C_{j l}
$$

Explicitly write out sums:

$$
\begin{aligned}
m=1 & \Rightarrow H_{11} C_{j 1}+H_{12} C_{j 2}=E_{j}\left(S_{11} C_{j 1}+S_{12} C_{j 2}\right) \\
m=2 & \Rightarrow H_{21} C_{j 1}+H_{22} C_{j 2}=E_{j}\left(S_{21} C_{j 1}+S_{22} C_{j 2}\right)
\end{aligned}
$$

Write as a matrix equation:

$$
\begin{gathered}
\left(\begin{array}{ll}
H_{11} & H_{12} \\
H_{21} & H_{22}
\end{array}\right)\binom{C_{j 1}}{C_{j 2}} \\
=E_{j}\left(\begin{array}{ll}
S_{11} & S_{12} \\
S_{21} & S_{22}
\end{array}\right)\binom{C_{j 1}}{C_{j 2}} \\
H C_{j}=E_{j} S C_{j}
\end{gathered}
$$

Secular equation gives the eigenvalues:

$$
\operatorname{det}(H-E S)=0
$$

## 1 Tight binding model of monolayer graphene

1.6 Calculation of transfer and overlap integrals

$$
H_{i j}=\left\langle\Phi_{i}\right| H\left|\Phi_{j}\right\rangle ; \quad S_{i j}=\left\langle\Phi_{i} \mid \Phi_{j}\right\rangle \quad \Phi_{j}(\vec{k}, \vec{r})=\frac{1}{\sqrt{N}} \sum_{\vec{R}_{j}}^{N} e^{i \vec{k} \cdot \vec{R}_{j}} \varphi_{j}\left(\vec{r}-\vec{R}_{j}\right)
$$

## Diagonal matrix element

$$
H_{A A}=\left\langle\Phi_{A}\right| H\left|\Phi_{A}\right\rangle=\frac{1}{N} \sum_{\vec{R}_{A i}}^{N} \sum_{R_{A j}}^{N} e^{i \vec{k}\left(\vec{R}_{A j}-\vec{R}_{A}\right)}\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right| H\left|\varphi_{A}\left(\vec{r}-\vec{R}_{A j}\right)\right\rangle
$$

Same site only:

$$
\begin{aligned}
H_{A A} & =\frac{1}{N} \sum_{R_{A i}}^{N}\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right| H\left|\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right\rangle & S_{A A} & =\frac{1}{N} \sum_{\vec{R}_{A, i}}^{N}\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right) \mid \varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right\rangle \\
& =\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right| H\left|\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right\rangle & & =\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right) \mid \varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right\rangle \\
& \equiv \varepsilon_{0} & & \equiv 1
\end{aligned}
$$

A and B sites are chemically identical:

$$
H_{A A}=H_{B B}=\varepsilon_{0} \quad S_{A A}=S_{B B}=1
$$

## 1 Tight binding model of monolayer graphene

1.6 Calculation of transfer and overlap integrals

## Off-diagonal matrix element

$$
H_{A B}=\left\langle\Phi_{A}\right| H\left|\Phi_{B}\right\rangle=\frac{1}{N} \sum_{R_{R_{i}}}^{N} \sum_{R_{B j}}^{N} e^{i \vec{k} \cdot\left(\vec{R}_{B j}-\vec{R}_{A}\right)}\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right| H\left|\varphi_{B}\left(\vec{r}-\vec{R}_{B j}\right)\right\rangle
$$

Every A site has 3 B nearest neighbours:


$$
\begin{aligned}
& \vec{\delta}_{1}=R_{B 1}-R_{A i}=\left(0, \frac{a}{\sqrt{3}}\right) ; \quad \vec{\delta}_{2}=R_{B 2}-R_{A i}=\left(\frac{a}{2},-\frac{a}{2 \sqrt{3}}\right) ; \\
& \vec{\delta}_{3}=R_{B 3}-R_{A i}=\left(-\frac{a}{2},-\frac{a}{2 \sqrt{3}}\right)
\end{aligned}
$$

$H_{A B}=\frac{1}{N} \sum_{R_{A i}}^{N}\left[\sum_{\delta_{j}=1}^{3} e^{i \vec{k} \hat{\delta}_{j}}\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right| H\left|\varphi_{B}\left(\vec{r}-\vec{R}_{B j}\right)\right\rangle\right]=\sum_{\delta_{j}=1}^{3} e^{i \vec{k} . \vec{\delta}_{j}}\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right| H\left|\varphi_{B}\left(\vec{r}-\vec{R}_{B j}\right)\right\rangle$
Parameterise nearest neighbour transfer integral:

$$
\begin{array}{rlrl}
\gamma_{0} & =-\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right)\right| H\left|\varphi_{B}\left(\vec{r}-\vec{R}_{B j}\right)\right\rangle & s & =\left\langle\varphi_{A}\left(\vec{r}-\vec{R}_{A i}\right) \mid \varphi_{B}\left(\vec{r}-\vec{R}_{B j}\right)\right\rangle \\
\Rightarrow \quad H_{A B} & =-\gamma_{0} f(\vec{k}) ; \quad f(\vec{k})=\sum_{\delta_{j}=1}^{3} e^{i \vec{k} \bar{\delta}_{j}} & \Rightarrow \quad S_{A B}=s f(\vec{k})
\end{array}
$$

## 1 Tight binding model of monolayer graphene <br> 1.6 Calculation of transfer and overlap integrals

## Off-diagonal matrix element

$$
\begin{gathered}
\xrightarrow[\mathrm{A}^{2}]{\mathrm{B}_{1} \vec{\delta}_{1}} \vec{\delta}_{1}=R_{B 1}-R_{A i}=\left(0, \frac{a}{\sqrt{3}}\right) ; \quad \vec{\delta}_{2}=R_{B 2}-R_{A i}=\left(\frac{a}{2},-\frac{a}{2 \sqrt{3}}\right) ; \\
\vec{\delta}_{3}=R_{B 3}-R_{A i}=\left(-\frac{a}{2},-\frac{a}{2 \sqrt{3}}\right) \\
f(\vec{k})=\sum_{\delta_{j}=1}^{3} e^{i \vec{k} . \vec{\delta}_{j}}=e^{i k_{y} a / \sqrt{3}}+2 e^{-i k_{y} a / 2 \sqrt{3}} \cos \left(\frac{k_{x} a}{2}\right)
\end{gathered}
$$

## 1 Tight binding model of monolayer graphene

1.7 Calculation of energy

$$
H=\left(\begin{array}{cc}
\varepsilon_{0} & -\gamma_{0} f(\vec{k}) \\
-\gamma_{0} f^{*}(\vec{k}) & \varepsilon_{0}
\end{array}\right) ; \quad S=\left(\begin{array}{cc}
1 & s f(\vec{k}) \\
s f^{*}(\vec{k}) & 1
\end{array}\right)
$$

Secular equation gives the eigenvalues:

$$
\begin{gathered}
\operatorname{det}(H-E S)=0 \\
\operatorname{det}\left(\begin{array}{c}
\varepsilon_{0}-E \quad-\left(\gamma_{0}+E s\right) f(\vec{k}) \\
-\left(\gamma_{0}+E s\right) f^{*}(\vec{k}) \\
\varepsilon_{0}-E
\end{array}\right)=0 \\
\left(E-\varepsilon_{0}\right)^{2}-\left(\gamma_{0}+E s\right)^{2} \mid f(\vec{k})^{2}=0 \\
E=\frac{\varepsilon_{0} \pm \gamma_{0}|f(\vec{k})|}{1 \mp s|f(\vec{k})|}
\end{gathered}
$$

## 1 Tight binding model of monolayer graphene

### 1.7 Calculation of energy

$$
E=\frac{\varepsilon_{0} \pm \gamma_{0} \mid f(\vec{k})}{1 \mp s \mid f(\vec{k})} \quad \text { Typical parameter values [quoted in Saito et al]: }
$$

$$
f(\vec{k})=e^{i k_{,}, a / \sqrt{3}}+2 e^{-i, k_{k}, a \sqrt{3}} \cos \left(\frac{k_{, ~}, a}{2}\right)
$$



Two non-equivalent K-points


## $\underline{2}$ Expansion near the $K$ points

2.1 Exactly at the K point


Two non-equivalent K-points

$$
\begin{array}{ll}
\vec{\delta}_{1}=\left(0, \frac{a}{\sqrt{3}}\right) ; & \Rightarrow K \cdot \vec{\delta}_{1}=0 \\
\vec{\delta}_{2}=\left(\frac{a}{2},-\frac{a}{2 \sqrt{3}}\right) ; & \Rightarrow K \cdot \vec{\delta}_{2}=\frac{2 \pi}{3} \\
\vec{\delta}_{3}=\left(-\frac{a}{2},-\frac{a}{2 \sqrt{3}}\right) ; & \Rightarrow K \cdot \vec{\delta}_{3}=-\frac{2 \pi}{3}
\end{array}
$$

$$
\vec{K}=\left(\frac{4 \pi}{3 a}, 0\right) \quad \vec{\delta}_{2}=\left(\frac{a}{2},-\frac{a}{2 \sqrt{3}}\right) ; \quad \Rightarrow \quad K . \vec{\delta}_{2}=\frac{2 \pi}{3}
$$

$f(\vec{K})=\sum_{\vec{\delta}_{j}=1}^{3} e^{i \vec{K} \cdot \vec{\delta}_{j}}=e^{0}+e^{2 \pi i / 3}+e^{-2 \pi i / 3}=0$

At the corners of the Brillouin zone (K points), electron states on the $A$ and $B$ sub-lattices decouple and have exactly the same energy

K points also referred to as "valleys"

## 2 Expansion near the K points

 2.1 Exactly at the K point6 corners of the Brillouin zone ( $K$ points), but only two are non-equivalent


Two non-equivalent K-points

We consider two $K$ points with the following wave vectors:

$$
\vec{K}=\left(\frac{4 \pi}{3 a}, 0\right) ; \quad \vec{K}^{\prime}=\left(-\frac{4 \pi}{3 a}, 0\right)
$$

## KomplexNano

## 2 Expansion near the K points

2.2 Linear expansion


Two non-equivalent K-points

Consider two non-equivalent $K$ points:

$$
\vec{K}, \vec{K}^{\prime}=\xi\left(\frac{4 \pi}{3 a}, 0\right) ; \quad \xi= \pm 1
$$

and small momentum near them:

$$
\vec{k}=\xi\left(\frac{4 \pi}{3 a}, 0\right)+\frac{\vec{p}}{\hbar}
$$

## 2 Expansion near the K points

### 2.2 Linear expansion

Consider two non-equivalent $K$ points:

$$
\vec{K}, \vec{K}^{\prime}=\xi\left(\frac{4 \pi}{3 a}, 0\right) ; \quad \xi= \pm 1
$$

and small momentum near them:

$$
\vec{k}=\xi\left(\frac{4 \pi}{3 a}, 0\right)+\frac{\vec{p}}{\hbar}
$$

Two non-equivalent
K-points
Linear expansion in small momentum: $f(\vec{k})=-\frac{\sqrt{3} a}{2 \hbar}\left(\xi p_{x}-i p_{y}\right)+O(p a / \hbar)^{2}$

$$
H=\left(\begin{array}{cc}
0 & -\gamma_{0} f(\vec{k}) \\
-\gamma_{0} f^{*}(\vec{k}) & 0
\end{array}\right) \approx v\left(\begin{array}{cc}
0 & \xi p_{x}-i p_{y} \\
\xi p_{x}+i p_{y} & 0
\end{array}\right)
$$

$$
S=\left(\begin{array}{cc}
1 & s f(\vec{k}) \\
s f^{*}(\vec{k}) & 1
\end{array}\right) \approx\left(\begin{array}{ll}
1 & 0 \\
0 & 1
\end{array}\right)+O\left(\frac{s p a}{\hbar}\right) \quad v=\frac{\sqrt{3} a \gamma_{0}}{2 \hbar} \approx 10^{6} \mathrm{~m} / \mathrm{s}
$$

## 2 Expansion near the K points

### 2.2 Linear expansion

$$
\begin{aligned}
& H=\left(\begin{array}{cc}
0 & -\gamma_{0} f(\vec{k}) \\
-\gamma_{0} f^{*}(\vec{k}) & 0
\end{array}\right) \approx v\left(\begin{array}{cc}
0 & \xi p_{x}-i p_{y} \\
\xi p_{x}+i p_{y} & 0
\end{array}\right) \\
& S=\left(\begin{array}{cc}
1 & s f(\vec{k}) \\
s f^{*}(\vec{k}) & 1
\end{array}\right) \approx\left(\begin{array}{ll}
1 & 0 \\
0 & 1
\end{array}\right)+O\left(\frac{s p a}{\hbar}\right) \quad v=\frac{\sqrt{3} a \gamma_{0}}{2 \hbar} \approx 10^{6} \mathrm{~m} / \mathrm{s}
\end{aligned}
$$

New notation for components on $\mathbf{A}$ and $B$ sites

$$
C_{j}=\binom{C_{j 1}}{C_{j 2}} \Leftrightarrow \psi=\binom{\psi_{A}}{\psi_{B}}
$$

$$
S^{-1} H C_{j}=E_{j} C_{j} \Rightarrow v\left(\begin{array}{cc}
0 & \xi p_{x}-i p_{y} \\
\xi p_{x}+i p_{y} & 0
\end{array}\right)\binom{\psi_{A}}{\psi_{B}}=E\binom{\psi_{A}}{\psi_{B}}
$$

## $\underline{2}$ Expansion near the K points

### 2.3 Dirac-like equation

For one K point (e.g. $\xi=+1$ ) we have a 2 component wave function,

$$
\psi=\binom{\psi_{A}}{\psi_{B}}
$$

with the following effective Hamiltonian:

$$
\begin{array}{r}
H=v\left(\begin{array}{cc}
0 & p_{x}-i p_{y} \\
p_{x}+i p_{y} & 0
\end{array}\right)=v\left(\begin{array}{cc}
0 & \pi^{+} \\
\pi & 0
\end{array}\right)=v\left(\sigma_{x} p_{x}+\sigma_{y} p_{y}\right)=v \vec{\sigma} \cdot \vec{p} \\
\pi=\mathrm{p}_{\mathrm{x}}+\mathrm{i} \mathrm{p}_{\mathrm{y}}=\mathrm{pe}^{\mathrm{i} \varphi}
\end{array} \begin{aligned}
& \text { Bloch function amplitudes on } \\
& \text { the AB sites ('pseudospin') } \\
& \pi^{+}=\mathrm{p}_{\mathrm{x}}-\mathrm{ip} \mathrm{p}_{\mathrm{y}}=\mathrm{pe}^{-\mathrm{i} \varphi}
\end{aligned} \quad \begin{aligned}
& \text { mimic spin components of } \\
& \text { a relativistic Dirac fermion }
\end{aligned}
$$

Pseudospin is an index that indicates on which of the two sublattices a quasi-particle is located

## $\underline{2 \text { Expansion near the } \mathrm{K} \text { points }}$

### 2.3 Dirac-like equation

To take into account both $K$ points $(\xi=+1$ and $\xi=-1)$ we can use a 4 component wave function,

$$
\psi=\left(\begin{array}{l}
\psi_{A K} \\
\psi_{B K} \\
\psi_{A K^{\prime}} \\
\psi_{B K^{\prime}}
\end{array}\right)
$$

with the following effective Hamiltonian:

$$
H=v\left(\begin{array}{cccc}
0 & p_{x}-i p_{y} & 0 & 0 \\
p_{x}+i p_{y} & 0 & 0 & 0 \\
0 & 0 & 0 & -p_{x}-i p_{y} \\
0 & 0 & -p_{x}+i p_{y} & 0
\end{array}\right)
$$

Isospin K and K' valleys are also called isospin.

## 2 Expansion near the K points

2.3 Dirac-like equation
$H=v\left(\begin{array}{cc}0 & \pi^{+} \\ \pi & 0\end{array}\right)=v \vec{\sigma} \cdot \vec{p}=v p \vec{\sigma} \cdot \vec{n}$

massless

$$
\begin{aligned}
& \text { Dirac fermions } \\
& \hat{H}=v_{F} \vec{\sigma} \cdot \hat{p}
\end{aligned}
$$


monolayer graphene

$$
v_{F}=c / 300=10^{6} \mathrm{~m} / \mathrm{s}
$$

## Basic transport characteristics

## Measurement:

Graphene (blue) is etched to a Hall bar shape and contacted by metal leads (yellow). Si layer is doped, used as a backgate ( $G$ ). By applying voltage on $G$ the chemical potential of graphene can be varied.

Effect of gate voltage, $\mathrm{V}_{\mathrm{g}}$ ?

$$
N=C_{g} V_{g} / e \quad \rightarrow \quad n \sim V_{g} \rightarrow k_{F} \sim \sqrt{V_{g}}
$$

## Drude model:

$$
\begin{aligned}
& v_{d} \equiv \mu E, j \equiv e n v_{d}=e n \mu E=\sigma E, \sigma=e n \mu \\
& \qquad \sigma=1 / \rho=\frac{e^{2} n \tau}{m}, \quad \mu=\frac{e \tau}{m}, \quad R_{H}=\frac{V_{y}}{I}=\frac{E_{y}}{j_{x}}=-\frac{B}{n e}
\end{aligned}
$$

Measurement of Hall resistance allows to determine $n$.
Combining it with $\rho, \mu$ can be derived.
Fig. a: longitudinal resistance vs. Vg, $\Delta R \approx 100$ times!
Fig. b: mobility and charge carrier density vs. Vg

- At $V_{g}=0, R_{H}$ (and $n$ ) changes sign $\rightarrow$ boarder between $e$ and $h$ bands
- If $\mathrm{V}_{\mathrm{g}} \rightarrow 0 \mathrm{R} \lambda$, however R is finite ( $\approx 4 \mathrm{kOhm}$ ) at Dirac point although $\mathrm{n}=0$. (No real OFF state.)

- mobility largest at Dirac point ( $\mathrm{V}_{\mathrm{s}}=0$ ).

Nature 438, 201(2005)

## 3 Consequences of Dirac like spectrum 3.1 Berry's phase $\pi$

Massless Dirac fermions with Berry's phase $\pi$

$$
\begin{aligned}
& H=v\left(\begin{array}{cc}
0 & \pi^{+} \\
\pi & 0
\end{array}\right)=v p\left(\begin{array}{cc}
0 & e^{-i \varphi} \\
e^{i \varphi} & 0
\end{array}\right) ; \\
& E=v p \quad \Leftrightarrow \quad \psi(\varphi)=\frac{1}{\sqrt{2}}\binom{e^{-i \varphi / 2}}{e^{i \varphi / 2}}
\end{aligned}
$$



Making a loop around $\mathrm{k}=0$ induces a phase shift of $\pi$.
Similar to the $360^{\circ}$ rotation of an $1 / 2$ e spin.

### 3.2 Massless Dirac Fermions?

Consider Quasi Classical Dynamics of Dirac electrons
$\vec{v} \equiv \frac{1}{\hbar} \frac{\partial E}{\partial \vec{k}}=\frac{1}{\hbar} \hbar v_{F} \frac{\vec{k}}{|k|}=v_{F} \stackrel{\rightharpoonup}{e_{k}}=v_{F}^{2} \frac{\vec{k}}{E^{\prime}}$
$E(\vec{k})= \pm \hbar v_{F}|\vec{k}|$
thus $|v|=v_{F}, \vec{v} \| \vec{k}$
$\rightarrow$ Speed of e is constant independent of
momentum, like photons ( $\mathrm{V}_{\mathrm{F}} \leftrightarrow \mathrm{C}$ )
What is $m$, effective mass?
$\frac{1}{m}=\frac{1}{m_{x x}}=\frac{1}{\hbar^{2}} \frac{\partial^{2} E}{\partial k_{x}^{2}}$
For quadratic dispersion: $E=\frac{\hbar^{2} k^{2}}{2 m_{e f f}}, m=m_{e f f}$
For Dirac electrons, where $E(\vec{k})=\hbar v_{F}|\vec{k}|$ ?
Naively $1 / m=0$, but NOT. To calculate $1 / m$ :

$\frac{\partial^{2}|k|}{\partial k_{x}^{2}}=\cdots=\frac{k_{y}^{2}}{|k|^{3}} \rightarrow \frac{1}{m_{x x}}=\frac{1}{\hbar} v_{F} \frac{k_{y}^{2}}{k^{3}}$
$\frac{\partial|k|}{\partial k_{x}}=\frac{1}{2} \frac{2 k_{x}}{|k|} \rightarrow$ Effective mass depends on $k$

### 3.3 Klein tunneling and backscattering

$$
\frac{1}{m_{x x}}=\frac{v_{F}}{\hbar} \frac{k_{y}^{2}}{|k|^{3}}
$$

N-P junction:
Potential profile with a step of Uo at a distance d


Klein scattering: perfect transmission at normal incident

Evolution of group velocity:

$$
\begin{equation*}
\frac{d v_{x}}{d t} \equiv \frac{1}{m_{x x}} F_{x}=\frac{1}{m_{x x}}(-e) E_{0} \tag{*}
\end{equation*}
$$

In linear electrostatic potential (e.g. slope in Figure) :

$$
V=E_{0} x, \quad E_{x}=E_{0}, \quad F_{x}=-e E_{0}
$$

At normal incident: $k_{y}=0 \rightarrow \frac{d v_{x}}{d t}=0 \rightarrow$ backscattering is avoided. Electron can propagate through an infinite high potential barrier.

$$
\hbar \dot{\vec{k}} \equiv \vec{F}=-e E_{0} \stackrel{\rightharpoonup}{e_{x}}(* *)
$$

Effect of the potential profile, $U$ (see figure):

- k decreases and changes sign (**)
- based on $\left(^{*}\right), \vec{v}$ stays constant, i.e. $\vec{v}=v_{F} \overrightarrow{e_{x}}$.
$\rightarrow$ e ends up in the valence band


### 3.3 Klein tunneling and backscattering

1 CLASSICAL PHYSICS

2. QUANTUM MECHANICS


3 QUANTUM ELECTRODYNAMICS


Beenakker, Reviews of Modern Physics, 80, 1337 (2008)

## Klein tunneling and backscattering

Result of proper calculation
Wave function matching


Transmission probability vs. D of normally incident electrons

- in single- and bi-layer graphene (red and blue curves, respectively) and in a non-chiral zero-gap semiconductor (green curve)


Transmission probability T through a 100 -nm-wide barrier as a function of the incident angle, two different barrier height
Katsnelson et al Nature Physics, 2, 620 (2006)

$\rightarrow$ Difficult to measure whether it is $100 \%$, since e-s out of normal incident also arrive

## Klein backscattering \& Fabry-Perot Interferences



Interferences on P-N-P junction
When incident angle, $\alpha$ is varied from positive to negative, phase of the reflection amplitude ( R ) jumps $\pi$. Its sign changes. (At $\alpha=0, R=0$ ).

If $\alpha<>0 \rightarrow \mathrm{R}>0$, several scatterings in $\mathrm{P}-\mathrm{N}-\mathrm{P} \rightarrow$ interference pattern
Accumulated phase in one circle:
$\Delta \theta=2 \theta_{\text {wвк }}+\Delta \theta_{1}+\Delta \theta_{2}$
where $\theta_{\text {wвк }}$ phase from travelling in N $\Delta \theta_{1}, \Delta \theta_{2}$ Klein back reflection phase of the
At $B=0$ (see Fig. a) the incident angles interfaces
$\Delta \theta_{1(2)}$ at $P-N$ and $N$-P have opposite signs $\rightarrow$ jumps in $\Delta \theta_{1}, \Delta \theta_{2}$ cancels
At $\mathrm{B}>0$ (see Fig. b), trajectories are curved, $\rightarrow$ incident angles at $\mathrm{P}-\mathrm{N}$ and $\mathrm{N}-\mathrm{P}$ can be equal In this case one can show that $\Delta \theta_{1}+\Delta \theta_{2}=\pi$ (It is the Barry phase previously derived!) Thus for $\mathrm{B}=0 \pi$ and trajectories with small $p_{y} \pi$ shift is expected (i.e. sign change) transmission amplitude
(Fig.c) one can show, it is robust against barrier roughness Shytov et al. PRL 101, 156804 (2008)

## Klein backscattering \& Fabry-Perot Interferences



## Klein backscattering \& Fabry-Perot Interferences

## N-P-N device

Separate gating by backgate and topgate
Topgate width $=20 \mathrm{~nm}!\rightarrow$ ballistic


## G vs. VTG vs. VBG

- Conductance is lower when N -$\mathrm{P}-\mathrm{N}$ setting instead of $\mathrm{N}-\mathrm{N}-\mathrm{N}$ -Oscillations at N-P-N configuration:
- $\mathrm{V}_{\text {TG }}$ varies pot. barrier $\rightarrow$ $\delta \theta_{\text {wвк }} \rightarrow$ oscillations -Oscillatory G is induced by trajectories with incident angle where neither $T$, nor $R$ is large (i.e. $\alpha$ not too small)


Young et al. Nature Physics 5, 222 (2009)

## Klein backscattering \& Fabry-Perot Interferences

N-P-N device
Separate gating by backgate and topgate
Topgate width $=20 \mathrm{~nm}!\rightarrow$ ballistic

b

roung et al. Ivature rnysics $ヶ, \angle<\angle$ ( LUUUY)

G oscillations vs. $\mathbf{B}$ (Dots experiment, line theory) At different B fields ( $B=0,200,400,600,800 \mathrm{mT}$ from bottom to top) the oscillations of $G$.
In this $B$ range $\approx \pi$ shift is induced in the interference pattern.

$n_{2}\left(10^{12} \mathrm{~cm}^{-2}\right)^{\sim} V_{\text {TG }}$

## KomplexNano

## Integer Quantum Hall effect in a $2 d$ semiconductor



## 3 Integer quantum Hall effect

## Graphene monolayer




In graphene the electron density can be easily varied. QHE investigated as a function of n , not only B .

Novoselov et al, Nature 438, 197 (2005);
Zhang et al, Nature 438, 201 (2005).

## KomplexNano

## Landau levels and QHE

## Monolayer:

$$
\mathrm{H}=\mathrm{v} \xi\left(\begin{array}{cc}
0 & \pi^{+} \\
\pi & 0
\end{array}\right)
$$

| In a perpendicular magnetic field $\mathrm{B}:$ | $\left.\left.\begin{array}{c}\vec{p}=-i \hbar \nabla-\frac{e}{c} \vec{A}, \operatorname{rot} \vec{A}=B \vec{l}_{z} \\ \pi=p_{x}+i p_{y} ; \pi^{+}=p_{x}-i p_{y} \\ \pi \rightarrow \text { lowering operator } \\ \pi^{+} \longrightarrow \text { raising operator }\end{array}\right\} \begin{array}{c}\text { of magnetic oscillator } \\ \text { eigenstates } \phi_{\mathrm{n}}\end{array}\right\}$ |
| :---: | :---: |

We are able to determine the spectrum of discrete Landau levels

States at zero energy are determined by

$$
\text { monolayer: } \pi \phi_{0}=0
$$

2D Landau levels of chiral electrons
$J=1$ monolayer $\mathrm{J}=2$ bilayer

$$
\pi \varphi_{0}=0
$$

$$
\mathrm{g}\left(\begin{array}{cc}
0 & \left(\pi^{+}\right)^{\mathrm{J}} \\
\pi^{\mathrm{J}} & 0
\end{array}\right) \psi=\varepsilon \psi
$$

$$
\binom{\varphi_{0}}{0} \Rightarrow \varepsilon=0
$$

valley
index

$$
\left(\begin{array}{cccc}
0 & \left(\pi^{+}\right) & & \\
\pi & 0 & & \\
& & 0 & \left(-\pi^{+}\right) \\
& & (-\pi) & 0
\end{array}\right)\left(\begin{array}{l}
A+ \\
\widetilde{B}+ \\
\widetilde{B}- \\
A-
\end{array}\right)
$$

## KomplexNano

monolayer:
$H=v \xi\left(\begin{array}{cc}0 & \pi^{+} \\ \pi & 0\end{array}\right)$
state at zero energy:

$$
\pi \phi_{0}=0
$$



4-fold degenerate zero-energy
Landau level for electrons with Berry's phase $\pi$
J.McClure, Phys. Rev. 104, 666 (1956)
F.Haldane, PRL 61, 2015 (1988)
Y.Zheng and T.Ando,

Phys. Rev. B 65, 245420 (2002)
V.P. Gusynin and S.G. Sharapov,

Phys. Rev. Lett 95, 146801 (2005)
N.M.R. Peres, F. Guinea and A.H. Castro Neto, PRB 73, 125411 (2006)

## QHE in graphene

monolayer

bilayer


## KomplexNano



Unconventional Quantum Hall Effect and Berry's Phase of $2 \pi$ in Bilayer Graphene
K.Novoselov, E.McCann, S.Morozov, V.Fal'ko, M.Katsnelson, U.Zeitler, D.Jiang, F.Schedin, A.Geim Nature Physics 2, 177-180 (2006)

## Carbon Nanostructures - Part II

## I. Graphene

## Outline:

Introduction (Making graphene, Applications, etc.)
Band structure
Physics of Dirac electrons (Barry phase, Klein tunneling)
Half-Integer Quantum Hall Effect
Mobility in Graphene (ways to improve...)

## References:

E. McCann Graphene monolayers Lancaster University, UK Tight-binding model, QHE
C. Beenakker, Reviews of Modern Physics, 80, 1337 (2008)
L. Tapaszto \& J. Cserti talks, MAFIHE Teli Iskola a Grafenrol 2011, ELTE
A. Geim talk, TNT Conference 2010
http://www.tntconf.org/2010/Presentaciones/TNT2010 Geim.pdf
N.Peres, F. Guinea and A.H. Castro Neto, PRB 73, 125411 (2006)

## Half Integer Quantum Hall effect in graphene

Novoselov et al, Nature 438, 197 (2005)


Graphene in Hall geometry
Sample width of 200 nm

- Sample: Hall geometry is etched from graphene flakes by oxigen plasma (a)


QHE vs. density (gate voltage)


Conventional way of QHE measurement
-In magnetic field Shubnikov-de Haas oscillations are presented. (b) At large B field, $\rho_{x x}$ gets zero as for QHE. Great advantage of graphene, that the charge density ( n can be varied by gate voltage. QHE effect can be studied as
a function of $n$.
Figure c: QHE measurement at $14 \mathrm{~T}, 4 \mathrm{~K}$.
Half-Integer Quantum Hall effect
Properties:
Height of the Hall plateaus is $4 \mathrm{e}^{2} / \mathrm{h}$

- First e (h) plateau is at $2 e^{2} / h$
- $\rho_{x x}$ is zero at the place of the plateaus.

$$
\sigma_{x y}=4 e^{2} / h(n+1 / 2)
$$

(Inset: same for multilayer graphite. The first plateau has the same height as the rest)
$\rho_{\mathrm{xx}}$ has maximum at $\mathrm{n}=0 \rightarrow$ There is Landau level at zero energy. Electrons or holes contribute?

## Half Integer Quantum Hall effect in graphene

## Solution of the graphene Hamiltonian in B field

Let us start with the effective Dirac Hamiltonian at the K point
$H=v\left(\begin{array}{ll}\pi & \pi^{+}\end{array}\right), \quad \pi=p_{x}+i p_{y}, \quad \pi^{+}=p_{x}-i p_{y}$.
Hint: Besides a constant $\pi$ and $\pi^{+}$are the same operators as the raising and lowering operators of the harmonic oscillator Hamiltonian of the normal 2DEG in B field, i.e.
$\hat{H}=\hbar \omega_{c}\left(\hat{a}^{+} \hat{a}+\frac{1}{2}\right)$.
In case of magnetic field: $\vec{p}=\frac{\hbar}{i} \vec{\nabla}-\frac{\mathrm{e}}{\mathrm{c}} \vec{A}, \quad \vec{\nabla} \times \vec{A}=B \overrightarrow{e_{z}}$
Let us use a gauge of $\vec{A}=(-B y, 0,0)$ :
$\pi=\frac{\hbar}{i} \partial_{x}+{ }_{c}^{e} B y+\hbar \partial_{y}$,
$\pi^{+}=\frac{\hbar}{i} \partial_{x}+\frac{e}{c} B y-\hbar \partial_{y}$.
Take the wave function ansatz, $\Psi(\vec{r})=\binom{c_{1} \phi_{n}}{c_{2} \phi_{n+1}} \frac{e^{i k_{x} x}}{\sqrt{L}}: \quad \pi=\hbar k_{x}+{ }_{c}^{e} B y+\hbar \partial_{y}$,
$\pi^{+}=\hbar k_{x}+\frac{{ }_{c}^{e}}{} B y-\hbar \partial_{y}$.
Replacing $y$ by $y^{\prime}$, where

$$
\hbar k_{x}+{ }_{c}^{e} B y={ }_{c}^{e} B y^{\prime}: \quad \pi={ }_{c}^{e} B y^{\prime}+\hbar \partial_{y^{\prime \prime}}
$$

$\pi^{+}={ }_{c}^{e} B y^{\prime}-\hbar \partial_{y}{ }^{\prime}$.

## Half Integer Quantum Hall effect in graphene

## Solution of the graphene Hamiltonian in B field

Let us introduce $a^{+}, a$ which fulfills the algebra of the raising and lowering operators of the harmonic oscillator: $a=\pi^{+} \frac{c}{e B} \frac{1}{\sqrt{2} r_{c}}, a^{+}=\pi \frac{c}{e B} \frac{1}{\sqrt{2} r_{c}}$, where $r_{c}$ is the cyclotron radius $r_{c}{ }^{2}=\frac{\hbar c}{e B}$.

It gives

$$
\begin{aligned}
& a=\frac{1}{\sqrt{2} r_{c}}\left(y^{\prime}+r_{c}^{2} \partial_{y^{\prime}}\right) \\
& a^{+}=\frac{1}{\sqrt{2} r_{c}}\left(y^{\prime}-r_{c}^{2} \partial_{y^{\prime}}\right)
\end{aligned}
$$

These two operators fulfill: $\left[a, a^{+}\right]=1$.
$\phi_{n}$ is the eigenfunction of the $a$ related harmonic oscillator, i.e.

$$
a\left|\phi_{n}\right\rangle=\sqrt{n}\left|\phi_{n-1}\right\rangle, \quad a^{+}\left|\phi_{n}\right\rangle=\sqrt{n+1}\left|\phi_{n+1}\right\rangle .
$$

Returning to the Dirac Hamiltonian:

$$
H=v\left(\begin{array}{ll}
\pi & \pi^{+} \\
\pi & =-v\left(\frac{c}{e B} \frac{1}{\sqrt{2} r_{c}}\right)^{-1}\left(a_{a^{+}}\right.
\end{array}\right)=-v \frac{\sqrt{2} \hbar}{r_{c}}\left(a_{a^{+}} \quad a\right)
$$

## Half Integer Quantum Hall effect in graphene

## Solution of the Hamiltonian of Dirac electrons in B field

Let us start with the wavefunction $\Psi_{n}(\vec{r})=\binom{\phi_{n}}{\alpha \phi_{n+1}} \frac{i^{i k_{x} x}}{\sqrt{L}}$ where $\alpha= \pm 1$.

$$
\begin{gathered}
H \Psi_{n} \rightarrow\left(\begin{array}{cc} 
& a \\
a^{+} &
\end{array}\right)\binom{\phi_{n}}{\alpha \phi_{n+1}}=\binom{\sqrt{n+1} \alpha \phi_{n}}{\sqrt{n+1} \phi_{n+1}}=\sqrt{n+1} \alpha\binom{\phi_{n}}{\alpha \phi_{n+1}} \\
H \Psi_{n}=-v \frac{\sqrt{2} \hbar}{r_{c}} \sqrt{n+1} \alpha \Psi_{n}
\end{gathered}
$$

$$
\text { Landau levels in graphene: } E_{n}= \pm v \frac{\sqrt{2} \hbar}{r_{c}} \sqrt{n+1}, \quad n=0,1,2, \ldots
$$

There is an extra solution as well: $\Psi_{0}=\binom{0}{\phi_{0}} \frac{e^{i k_{x} x}}{\sqrt{L}} . \quad H \Psi_{0}=\binom{0}{0}=E \Psi_{0} \rightarrow \boldsymbol{E}_{0}=\mathbf{0}$.

## Degeneracy of the levels:

Similar to normal Landau Levels. $L>y>0 \rightarrow L>\frac{\hbar c}{e B} k_{x}>0$ and $k_{x}=\frac{2 \pi}{L} n$ where $n$ is integer. $\rightarrow$ The degeneracy: $N=\frac{L^{2} B / c}{h / e}$ i.e. number of flux quantum penetrating the sample.

Solving the problem for the $K^{\prime}$ effective Hamiltonian gives the same spectrum as the one for $K$. Therefore each $E_{n}$ energy level has a degeneracy of $N * 2 * 2$. 2 from the two valleys, 2 from the real spin of the electrons.



## Half Integer Quantum Hall effect in graphene

## Solution of the Hamiltonian of Dirac electrons in B field

## Remark:

The edge states behave similar to the ones of QHE of normal 2DEGs.

$$
v_{x}=\frac{1}{\hbar} \frac{\partial E}{\partial k_{x}}=\frac{1}{\hbar} \frac{\partial E}{\partial y} \frac{\partial y}{\partial k_{x}}=\frac{1}{\hbar} \frac{\partial E}{\partial y} \frac{1}{e B / c}
$$

On the two sides of the sample they propagate to opposite direction.

Half-integer quantum Hall-effect:
Due to the 2 spin and 2 valley, there are 4 -fold degenerate Landau levels. Each degeneracy provides a conductance channel with $G=\frac{e^{2}}{h}$. Therefore each filled LL enhance the Hall conductance by $G=\frac{2 \cdot 2 \cdot e^{2}}{h}$. When $E_{F}$ is placed on a LL, the Hall conductance changes from a quantized plateau to the next one. Since there is a LL at ZERO ENERGY the first electron like Hall plateau is at $G=\frac{2 \cdot e^{2}}{h}$ and the rest are at $G=\frac{2 \cdot 2 \cdot e^{2}}{h}\left(n+\frac{1}{2}\right)$.
The zero energy LL makes the QHE of graphene special. It consist e and hole states as well.
N.Peres et al., PRB 73, 125411 (2006)


## Quantum Hall effect at room temperature

## Landau-levels

## Comparing to GaAs based 2DEGs

$\mathrm{E}_{\mathrm{n}}= \pm \sqrt{2 e \hbar v^{2}|n| B} \quad$ 2D Dirac fermions ( $\mathrm{m}=0$ )
$\mathrm{E}_{\mathrm{n}}=\hbar \omega_{C}(n+1 / 2) \quad 2 \mathrm{D}$ free electrons

Experiment
$\mathrm{E}_{1}(29 \mathrm{~T}) \approx 1800 \mathrm{~K} \gg \mathrm{kT}$ $\mu \approx 10^{4} \mathrm{~cm}^{2} / V s$ @RT (weak $T$ dependence)

Limitation of $B$, that $\omega_{c} \uparrow \gg 1$ ( $\tau$ elastic mean free path).
If the amount of scattering can be further decreased, QHE gets visible at lower B fields. $\rightarrow$ New possibilities for current standard, quantum circuits at room temperature

## Mobility and scattering mechanisms

Conductance in simple Drude picture:

$$
\sigma=e^{2} \tau \frac{n}{m}
$$

However the effective mass depends on $k$, thus one has to average $1 / \mathrm{m}$ for all filled states.

Accurate calculation of $\sigma$, from Boltzmann equation (see Solyom 24.3.39.):
$\sigma=e^{2} \tau \frac{n}{m}=e^{2} \tau \cdot 2 \cdot 2 \cdot \int_{\text {filled } k \text { states }} \frac{d^{2} k}{(2 \pi)^{2}} \frac{1}{m_{x x}}$
Result:

$$
\sigma=e^{2} \tau \frac{v_{F}}{\hbar \pi} k_{F}
$$

with relaxation length $l \equiv v_{F} \tau$

$$
\sigma=\frac{2 e^{2}}{h} l k_{F}
$$

Mean free path: $\quad l=\frac{\hbar}{e} \mu \sqrt{n \pi}$
E.g. for mobility $=600.000, \mathrm{l}$ is $\approx 3 \mu \mathrm{~m}$

$E(\vec{k})=\hbar v_{F}|\vec{k}|$
R vs. $\boldsymbol{V}_{g}$ Transport characteristics


## Mobility and scattering mechanisms

## What limits the mobility at room $T$ ?

Source of $1 / \tau$ ?
Scattering mechanisms resulting resistivity:

- potential scattering: impurities, defects, vacancies
- Electron - phonon scattering
- Etc.

Usual terms: (see Solyom II.)

- Residual resistivity ( $\rho_{0}$ ): $T$ independent
- Longitudinal acoustic phonons $\left(\rho_{A}\right)$ : linear in $T$

$$
\rho\left(V_{\mathrm{g}}, T\right)=\rho_{0}\left(V_{\mathrm{g}}\right)+\rho_{\mathrm{A}}(T) ; \quad \rho_{\mathrm{A}}(T)=\left(\frac{h}{e^{2}}\right) \frac{\pi^{2} D_{\mathrm{A}}^{2} k_{\mathrm{B}} T}{2 h^{2} \rho_{\mathrm{s}} v_{\mathrm{s}}^{2} V_{\mathrm{F}}^{2}}
$$

Measurements (see Fig. a,b)

- At higher $T$, strong deviation from linear $T$ dependence - Dependence also on Vg
$\rightarrow$ It suggests scattering on high energy phonon modes



## Mobility and scattering mechanisms

$$
\begin{aligned}
\rho\left(V_{\mathrm{g}}, T\right) & =\rho_{0}\left(V_{\mathrm{g}}\right)+\rho_{\mathrm{A}}(T)+\rho_{\mathrm{g}}\left(V_{\mathrm{g}}, T\right) ; \\
\rho_{\mathrm{g}}\left(V_{\mathrm{g}}, T\right) & =B_{1} V_{\mathrm{g}}^{-\alpha_{\mathrm{g}}}\left(\frac{1}{e^{(59 \mathrm{meV}) / k_{\mathrm{g}} T}-1}+\frac{6.5}{e^{\left(15 S m e V / k_{\mathrm{k}} T\right.}-1}\right)
\end{aligned}
$$

$\boldsymbol{\rho}_{\mathrm{B}}$ : additional term to fit the measurements (see Fig. $\mathrm{c}, \mathrm{d}$ ) Bose-Einstein distribution ~ population of high energy phonon modes, e.g. optical phonons
Very good fit of the measured curves with alfa=1.04
Optical phonons of graphene?

- Strong Vg dependence is not expected
- Mainly out of plane phonons at this energy. It is not expected to give strong contribution

Interfacial phonon scattering: Surface optical phonon modes in $\mathrm{SiO}_{2}$ couples to e-s in graphene
The expected phonon energies and coupling strength (1:6.5) are inserted into $\rho_{B}$
Strong Vg dependence is also expected


## Mobility and scattering mechanisms

## What limits the mobility at room $T$ ?

Different $T$ dependence of $\rho_{0}, \rho_{A}, \rho_{B}$ allows to separate the three contributions. $\left(\rho_{B}=\rho-\rho_{0}-\rho_{A}\right)$

Fig. a
$\rho_{\mathrm{A}} \mathrm{V}_{\mathrm{g}}$ independent
$\rho_{B} \sim V_{g}{ }^{-1.04}$ relation confirmed
$\rightarrow$ Residual resistivity dominates
Fig. b
Derive the mobility related to two e-p processes :
$\mu=1 /$ ne $\rho=1 / \mathrm{c}_{\mathrm{g}} \mathrm{V}_{\mathrm{g}} \mathrm{e} \rho$
$\rightarrow \mathrm{SiO}_{2}$ contribution (c) dominates
$\rightarrow$ The intrinsic, LA phonon scattering mobility at $\mathrm{n}=10^{12} \mathrm{~cm}^{-2}$ (technologically relevant) : $\mu \approx 200000$ (see blue dot) Higher than any known semiconductor! (E.g. InSb $\approx 77000$ and carbon nanotubes $\approx 100000$ ).

## Contributions at Room T



Residual resistivity $p_{0}$ Residual resistivity $P_{0}$

| - |
| :--- |
| Sample 1 |
| - |
| Sample 2 |
| Sample 3 |


| Sample 2 |
| :--- |
| - Sample 3 | LA phonon resistivity $\rho_{k}$

$\because$ Sample 1
Equation (1)
$T=306 \mathrm{~K}$

| $\mathrm{SiO}_{2}$ phonon resistivity |
| :--- |
| Sample |

Sample 1
Sample 2
Sample 1
Sample 2
Sample 3

| Sample 3 |
| :--- |
| Equation (za). |

Equation (20)
$T=306 \mathrm{~K}$
D


LA phonon limited mobi Giobal fat to Samp $1+2$
$\mathrm{SiO}_{2}$ phonon limited mo
1
$\quad$ Sample 1
$\cdots$
Sample 2 Sample 2
Sample 3 - - Sample 3

Total phonon limited mo
Sample 1 Sample 2
Sample 3 - Sample 3

## Mobility and scattering mechanisms

## What limits the mobility at room $T$ ?

Different $T$ dependence of $\rho_{0}, \rho_{A}, \rho_{B}$ allows to separate the three contributions. $\left(\rho_{B}=\rho-\rho_{0}-\rho_{A}\right)$

T dependence
Fig. a
$\rho_{\mathrm{A}} \mathrm{V}_{\mathrm{g}}$ independent
$\rho_{B} \sim \vee_{g}{ }^{i-1.04}$ relation confirmed
$\rightarrow$ Residual resistivity dominates
Fig. $b$
Derive the mobility related to two e-p processes :
$\mu=1 /$ ne $\rho=1 / c_{g} V_{g} \mathrm{e} \rho$
$\rightarrow \mathrm{SiO}_{2}$ contribution (c) dominates
$\rightarrow$ The intrinsic, LA phonon scattering mobility at $\mathrm{n}=10^{12} \mathrm{~cm}^{-2}$ (technologically relevant) : $\mu \approx 200000$
(see blue line) Higher than any known semiconductor!
(E.g. InSb $\approx 77000$ and carbon nanotubes $\approx 100000$ ).


Fig. c
Comparision with graphites, sources of exfoliated graphene
Mobility is much smaller than for graphites. It is impurity dominated.
$\rightarrow$ Residual res. not due to point defects but due to charge impurities in $\mathrm{SiO}_{2 \text { substrate }}$

## Suspended flakes

To improve mobility eliminate the substrate. $\rightarrow$ Suspended graphene samples Two techniques:

- Etched SiO by BHF

low-T mobilities: few million $\mathrm{cm}^{2} / \mathrm{V}$ •s This high quality samples allowed to demonstrate Fractional QHE in graphene

At room T the mobility is $10 \mathrm{k}-100 \mathrm{~km}^{2} / \mathrm{V} \cdot \mathrm{s}$ ? New flexural phonons appears in suspended samples, low energy out of plane vibrations $\rightarrow$ Try to apply tension

Andrei, Kim \& Yacoby also Manchester

- Use an organic polimer bellow, expose and desolve


PMGI based organic polymer Possible with any metal contacts! $\rightarrow$ spin physics, superconductivity $600.000 \mathrm{~cm} 2 / \mathrm{Vs} @ 5.0 \mathrm{E} 9 \mathrm{~cm}^{-2}, 77 \mathrm{~K} . \mathrm{L}^{\sim} 3 \mu \mathrm{~m}$ $\rightarrow$ Observation of condcutance quantization, 0.7 anomaly N. Tombros arXiv:1009.4213

## Suspended flakes

## Conductance quantization in graphene

- PMGI based organic polimer
- short and wide channels, reduce the role of edge roughness
- K-K' valley degeneracy is lifted.





## Better substrate - Boronnitride


room-T mobility
close to $100,000 \mathrm{~cm} 2 / \mathrm{V} \cdot \mathrm{s}$
Advantages:

- Atomically smooth surface that is relatively free of dangling bonds and charge traps.
- Lattice constant similar to that of graphite, and has large optical phonon modes and a large electrical bandgap.



Dean et. al., NatureNanotech 5, 722 (2010)

## Carbon nanostructures



1985
H.W.Kroto

Mass spectrometer


1991
S lijima
Electron microscope

Graphene
2D


2004
K. S. Novoselov Optical microscope

## Carbon Nanostructures

## II. Carbon Nanotubes (CNT)

Outline:
Single walled carbon nanotubes (wrapping)
Synthesis
Electronic properties (metallic vs. semiconducting CNT)
Quantum transport (Ballistic conductance, Fabry-Perot interference)
CNT Quantum dots (spin, orbital degeneracy, Orbital and SU(4) Kondo effect)

## References:

S Ilani and P. L. McEuen Annu. Rev. Condens. Matter Phys 1, 1-25 2010. and references within.
P. Jarillo-Herrero, Quantum transport in carbon nanotubes, phd thesis 2005. Wikipedia: en.wikipedia.org/wiki/Carbon_nanotubes

## Carbon Nanotubes (CNT)

CNT = Big carbon molecule, Rolled
up graphene with half buckyballs at
the ends.
Diameter ~nm, length up to 15 cm
Single-walled CNT
Multi-walled CNT

## Synthesis of CNT

|  | - Arc discharge (original method) <br> graphite electrode + voltage, <br> $30 \%$ of weight could generate CNT |
| :--- | :--- |
| Nanotube | - Laser ablation <br> pulzed laser on graphite target in inert gas. |
| CNT are forming on cold surface yield of 70\%, mainly |  |
| single wall |  |

## Electronic properties of CNT

Band structure

## Metallic or semiconducting?

Starting point is the band structure of graphene (a). Rolling up $\rightarrow$ periodic boundary condition i.e. quantization of the e wavenumber in the circumferencial direction, $\mathrm{k}_{\perp}$ :

$$
\Delta \mathrm{k}_{\perp} \pi \mathrm{d}=2 \pi,
$$

where $d$ is the diameter of the tube.
$\rightarrow$ 1D bands form from discrete slices of the graphene spectrum

If a slice passes through the Dirac point (see Fig. c) $\rightarrow$ Metallic CNT If not $\rightarrow$ Semiconducting CNT (see Fig.b)


## Electronic properties of CNT

Fig. d: phase of $K$ point wavefunction of graphene. Due to 3 -fold symmetry A atoms have three possible phases: $0,120^{\circ}, 240^{\circ}$, color coded by red, green, blue.

There are two ways of rolling up:

d - Red atom rolled to an other red one (Fig. c).
$\rightarrow$ Wave function satisfies the boundary condition i.e. wave function in K is a legitimate solution on the cylinder. $\rightarrow$ There is slice pass through $\mathrm{K} \rightarrow$ metallic CNT (Fig. c) (MCNT)
-Red atom rolled to blue or green (Fig. b)
There is a phase mismatch of $2 / 3 \pi$ at the boundaries. This can be solved by changing K to $\mathrm{K}+\mathrm{k}^{0}{ }_{1}$, where $\mathrm{k}^{0}{ }_{\perp} \pi \mathrm{d}=-2 / 3 \pi$

$\rightarrow$ lowest quantized wavefunction is away from $K \rightarrow$ semiconducting CNT (Fig. b) (SCNT Consequences: $-2 / 3$ of CNTs are semiconducting

$$
\text { - with energy gap of } E_{g}=2 \cdot \hbar v_{F} k_{\perp}^{0}=4 \hbar \nu_{F} / 3 d \approx 0.7 \mathrm{eV} / \mathrm{d}[\mathrm{~nm}]
$$

## Electronic properties of CNT

In reality usual metallic tubes also shows small bandgap. Since the metallic band structure is instable against perturbation like e.g. mechanical deformation. Everything what destroys $A \Leftrightarrow B$ symmetry (i.e. pseudospin) generates gap. Taken into account the curvature of small diameter CNTs also generates gap.

Figures: measured transport characteristics @RT. Gate electrode is used to change the e filling.

## Maximal conductance:

In Landauer picture each ballistic subband gives a maximal conductance of $\mathrm{e}^{2} / \mathrm{h}$. In CNT there are 4 subbands, due to 2 spin and 2 isospin (valley $K, K^{\prime}$ ) degeneracies. I.e. $G_{\max }=4 e^{2} / h$.
The conductance is also limited by contact resistances.


It has to be a clear transparent barrier. For semiconductor
tubes palladium gives Schottky-barrier free contacts for p-type CNTs. While Al with low work function gives good contact to n-type CNTs.

## Electronic properties of CNT

Typical numbers of mean free path and mobility: $\mathrm{I}_{\mathrm{e}}^{\sim 100 \mathrm{~nm}}$ (SCNT) $\sim 1 \mu \mathrm{~m}$ (MCNT) @RoomT and $\mu>100.000 \mathrm{~cm}^{2} / \mathrm{Vs}(S C N T), \mathrm{I}_{\mathrm{e}} \sim 10 \mu \mathrm{~m}$ (MCNT) @<50K

The large mean free path has the same origin as for graphene. C has light mass, $\mathrm{sp}^{2}$ is a strong bonds $\rightarrow$ high energy phonons, which are only populated at high $T$.


## Quantum transport of CNT

Ballistic and coherent transport at low T (T<5K)

## Fabry-Perot cavity

Due to coherent scattering on the imperfect contacts interferences occur: periodic oscillations as a function of gate and bias. $\mathrm{V}_{\mathrm{g}}$ or bias changes k and thereby the accumulated phase on one loop. Periodicity $\left(\mathrm{V}_{\mathrm{c}}\right)$ is proportional to $L^{-1}$, where $L$ is the length of CNT segment.

Sample geometry with electron path scattered on the contact interfaces'


Corresponding scattering matrix problem


Periodicity of the oscillations vs. Length of the CNT segment periodicity determined by arrow position in right figure



## CNT Quantum dots

## Quantum dots:

If the barrier resistance $\mathrm{R}^{\sim} \mathrm{h} / \mathrm{e}^{2}$, e -s are localized between the contacts.
$\rightarrow$ Qdot physics.
Typical charging energy:

$$
U \approx 5-20 \mathrm{meV} / L[\mu m]
$$

For short segments also large level spacing, transport through individual quantum levels.

## Shell structure:

Level spectrum and symmetries
Graphene has three 2-fold symmetries:
Pseudo spin $A \Leftrightarrow B$, Isospin ( $K, K^{\prime}$ ), electron spin
First generates the Dirac spectrum (e-h symmetry)
Second two induce 4-fold degenerate levels of Qdot with SU(4)
The $\mathrm{K}^{\prime} / \mathrm{K}$ isospin corresponds to solution encircle clockwise /anticlockwise around the tube. From valley degeneracy of graphene $\rightarrow$ orbital degeneracy of Qdot levels.
In a Qdot longitudinal momentum is also quantized: $\Delta k_{\|}=\pi / L$ resulting a level spacing of: $\Delta=\hbar v_{F} \Delta k_{\|}$

## CNT Quantum dots

## Experiments:

Qdot levels demonstrating the shells with 4 levels
The 4-fold degenerate shells were observed in experiments. Every $4^{\text {th }}$ Coulomb diamond is wider. Level spacing has to be paid when a new shell opens. If there is disorder the isospin degeneracy is lifted. (see right lowest Fig.) Mostly this is the case, only newest
 ultraclean CNT devices show 4 -fold degeneracy.

The 4 states in the shell can be split by applying $B$ field parallel to tube axis:

$$
E_{C W / C C W}^{\dagger / 1}=-\left(\mu_{\text {orb }}+\mu_{\text {spin }}\right) \cdot B_{\|}=\left( \pm \frac{d e v_{F}}{4} \pm \frac{1}{2} g \mu_{B}\right) B_{\|}
$$


$B$ field dependence of the 4 levels


## CNT Quantum dots

In semiconducting CNTs one can access the single electron and single hole filling of the quantum dot (see right figs). Large diamond corresponds to the empty quantum dot.

In ultraclean CNTs (grown on top of the electrodes) shell structure was studied at single e filling (see bottom left fig.).

Evolution of the 4 states in B field $V_{s d}=-2 m V$
$1 e$ and 1 hole state of semiconducting CNTs



As $B \|$ | increased $E$ of $K$ states are decreasing while one of $K^{\prime}$ increasing, similar to figure on previous slide.
Surprising that at $\mathrm{B}=0$ the four states are split in two 2-fold degenerate levels. See also inset for zoom in. Reason: spin orbit coupling. $\mathrm{E}-\mathrm{s}$ on K and $\mathrm{K}^{\prime}$ orbitals induce $B$ field, which effects the e spin

$$
\mathbf{B}_{\mathrm{SO}}=-(\overline{\mathbf{v}} \times \overline{\mathbf{E}}) / c^{2}
$$

$\rightarrow K \downarrow$ and $\mathrm{K} \uparrow$ get lower energy. $\mathrm{SU}(4)$ symmetry is lifted.

Nature 429, 389 (2004).

## SU(4) and orbital Kondo effect in CNT

## Kondo situations in CNT Qdot:

a)Normal Kondo: Two degenerated spin states
b) Orbital Kondo: Two orbitals have the same energ'
c)Two orbitals $x$ two spin states are degenerate

Kondo situations in CNT


Yellow region: at finite $B$ field two states with same spin get degenerate, inducing a situation of orbital Kondo effect Green region: 4-fould degeneracy, spin and orbital induces a SU(2)xSU(2)=SU(4)


## SU(4) and orbital Kondo effect in CNT

## Orbital Kondo effect

Fig. a) At $B=5.8 \mathrm{~T}$ for 1 e occupation of the last shell (I) there is a conductance increase due to Kondo effect, see yellow dotted line. (Orange numbers are the spin of the dot, green lines are boarder between charge states) Fig. b) Bias slice at the Orbital Kondo situation ( $\mathrm{B}=5.9 \mathrm{~T}, \mathrm{~V}_{\mathrm{g}}=937 \mathrm{mV}$ ). Inset: Peak height follows Kondo scaling.

Yellow region: at finite $B$ field two states with same spin get degenerate, inducing a situation of orbital Kondo effect Green region: 4-fould degeneracy, spin and orbital induces a $\operatorname{SU}(2) \times S U(2)=S U(4)$ Kondo situation ${ }^{\text {Kanillo-Herrero Mature } 434,484(2005)}$


## SU(4) and orbital Kondo effect in CNT

## SU(4) Kondo effect signatures

Fig. a) Decreasing T, G increases in the valley of state I and III.
Fig. b) $\mathrm{B}=0$ zero bias resonance appears in state I and III. (There is no orbital splitting as in previous slide due to higher Kondo temperature $\delta_{B}<T_{K}$ )
Fig. c) At $B=1.5 T$ the Kondo resonance splits into 4 branches for state I
Fig. d) The splitting of the 4 states vs. B field for state I.
Outer lines are cotunneling from |-> to |+> orbitals, while the inner lines are cotunneling process from $\mid-, \uparrow>$
tol-, $\downarrow>$. $\left(\mu_{\text {spin }}=\mu_{\mathrm{B}}, \mu_{\text {orbital }}=13 \mu_{\mathrm{B}}\right)$ The multiple splitting provides direct evidence of the SU(4) Kondo resonance.
(For $\mathrm{B}=1.5 \mathrm{~T}$ \& III the inner two states are not split.


