Physics of Graphene: Possibility of relativistic electronics and spintronics

> Chung-Yu Mou National Center for Theoretical Sciences National Tsing Hua University Taiwan

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**Collaborators:** 

Hsiu-Hau Lin (National Tsing Hua U, Taiwan) Toshiya Hikihara (Hokkaido U, Japan) Xiao Hu (NIMS, Tsukuba, Japan) Horng-Tay Jeng (Academic Sinica, Taiwan) Bor-Luen Huang (Naitonal Tsing Hua U, Taiwan) Shin-Tza Wu (National Chung-Cheng U, Taiwan)

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• Background and Introduction: Transport and magnetic properties

 Novel magnetism associated with edge states and flat-band in nanoribbon

Impurity band due to point defects in graphene

囊括凝體物理重要 平臺的兩個現代電 子科技之基礎元件

### 電子科技之基礎--MOSFET

#### (metal-oxide-semiconductor field-effect transistor)





# Fundamental unit of logical gates (AND, OR, addition, ...)

### 電子科技之基礎--磁記錄



### **Basis : Nonrelativistic Quantum Mechanics**

$$E = \frac{\hbar^2 k^2}{2m^*} (\sqrt{p^2 + m^{*2} c^4} = m^{*2} c^4 + \frac{p^2}{2m^*} + ...) \quad m^* = \text{Effective mass}$$

Transport:	Mater
Speed determined by mobility	<u>Si</u> (4.
$m^* \vec{\upsilon} = e \vec{E} \cdot \tau \Rightarrow \vec{\upsilon} = \mu \vec{E}$	Ge
$\mu = \frac{e\tau}{m^*} = \text{mobility}$	<u>Ga</u> InS
$\sigma = \frac{1}{\rho} = e \left( n_e \mu_e + n_h \mu_h \right)$	Zn( ZnS

	Electron	Hole
aterial	effective	effective
	mass	mass
	Group IV	
(4.2K)	1.08 m <sub>e</sub>	$0.56 \ m_{e}$
<u>Ge</u>	$0.55 m_{e}$	$0.37 \ m_{e}$
	III-V	
<u>GaAs</u>	$0.067 \ m_{e}$	$0.45  m_{e}$
<u>InSb</u>	$0.013 \ m_{e}$	$0.6 m_e$
	II-VI	
<u>ZnO</u>	$0.19  m_{e}$	1.21 m <sub>e</sub>
<u>ZnSe</u>	$0.17m_e$	$1.44 \ m_{e}$

### d-orbit (more localized) magnetism

### Local moment: Pauli versus Coulomb



 $(\uparrow \downarrow - \downarrow \uparrow) \cdot \phi_a(r_1) \phi_a(r_2) \qquad \uparrow \uparrow \cdot \left[ \phi_a(r_1) \phi_b(r_2) - \phi_b(r_1) \phi_a(r_2) \right]$ 

**Exchange interactions:**  $J\vec{S}_i \cdot \vec{S}_i$ 



### **Background for search new platform**



### **Element of Carbon Network**



# Carbon $1S^2 2S^2 2P^2$ 4 electrons in $\sigma$ bonds $(SP^2) + \pi$ bond or $SP^3$

# **Diversity of carbon forms**



### Unexpected realization of graphene sheet (⇔ Mermin-Wagner theorem)



mechanically exfoliated graphene sheets

AFM image of single-layer graphene on SiO<sub>2</sub> K.S. Novoselove et al., Science 306, 666 (2004)

#### **Spontaneous ripples in free-standing graphene**



Ripples are of order 2–20 Å high and 20–200 Å wide; Meyer et al., Nature 446, 60, (2007); Fasolinao et al., Nature Materials 6, 858 (2007)

### **Epitaxial growth of graphene**



### **CVD graphene on metal substrates**



• Etching and transfer



Floating graphene after Ni being etched Ni: Kim et al., Nature 457, 706 (2009)



Cu: Li et al., Science 324, 1312 (2009)

### Parent spectrum Two dimensional Dirac Fermions



### **Quasi-Dirac Fermions**



### **Expectation**

$$m^*\vec{\upsilon} = e \,\vec{E}\cdot\tau \Rightarrow \vec{\upsilon} = \mu \,\vec{E}$$

•  $m^* = 0$ 

• Berry phase & absence of back scattering

T. Ando et al., J. Phys. Soc. Jap. 67, 2857 (1998)

 $\Rightarrow$  huge  $\mu$  and high speed

+

### **Potential complication: Klein Paradox**



$$T \rightarrow 1 \text{ as } V_0 >> m_0 c^2$$

V<sub>0</sub>: repulsive for electrons, attractive for positrons

### No confinement for electrons On/off ratio is reduced in graphene FET

### **Super-Qualities**

•  $m^* = 0$  expect huge mobility Carrier mobility: 200000 cm<sup>2</sup>/V.s (Geim, 2008, 300K,  $n \approx 10^{13} cm^{-2}$ ) **Ballistic transport at micronscale** Epitaxial graphene: 2000 cm<sup>2</sup>/V.s (27K)  $\lambda_{\phi} \ge 1 \mu m$ **CVD graphene: 4050** cm<sup>2</sup>/V.s (room temp) Si 1500 cm<sup>2</sup>/V.s high speed GaAs 8500 cm<sup>2</sup>/V.s **InSb (undoped) 77000** cm<sup>2</sup>/V.s

• Thermal conductivity (room temp)

 $\approx 5 \times 10^3 Wm^{-1} K^{-1} \sim 10 \times \text{Cu or Al}$ 

### Room temperature Graphene FET



Nanoribbon, Hongjie Dai's group, Science 319, 1229 (2008) ; Nature 458, 872(2009)



X. Liang et al., Nano Letters 7, 3840 (2007); Y.Q. Wu, APL 92, 092102 (2008) Kedzierski, IEEE Electron Dev. 55, 2078 (2008)

# **RF** performance

Technology	f <sub>T</sub> (GHz)
InP	22 (GHz-µm)
ITRS Bulk NMOS	9 (GHz-µm)
SOI (90nm)	11 (GHz-µm)
Graphene made from SiC <sup>1</sup>	10 (GHz-μm)
Mechanically exfoliated Graphene (500nm) <sup>2</sup>	14.7 (GHz)
Carbon nanotube transistor <sup>3</sup> ( $3\mu$ m)	50 (GHz)

- 1. J.S. Moon et al., ECS Transactions 19, 35 (2009)
- 2. I. Meric et al., IEEE Electron Device Meeting (2008)
- 3. S. Rosenblatt et al., Appl. Phys. Lett. 87, 1531111 (2005) Theoretical value: THz (L=20nm W=0.69Nm) , L.C. Castro et al, IEEE Trans. Nanotech. 4, 699 (2005)



# d0 magnetism ?

#### Magnetic levitation at room temperature Graphite: two of the strongest diamagnetic materials (the other one is bismuth)



#### Pyrolytic Graphite http://cgi.ebay.com.hk/ws/eBayISAPI.dll?ViewItem&item=180186727424

### Why magnetism?

#### Evidences of Magnetic Caron?



Shibayama et al. Phys. Rev. Lett. 84, 1744(2000)

### Weak ferromagnetism



#### **Mechanism:**

Magnetic impurity? Defects?

Triplet excitons condensate?

Esquizani et al. Phys. Rev. B 66, 024429 (2002)

#### **Defects induced weak ferromagnetism**



Magnetism persists to the case when only 0.1% carbon atoms gets shifted

Esquinazi et al Phys. Rev. Lett. 91, 227201, 2001

#### **Unequivocal linear temperature behavior**



Barzola-Quiquia et al Phys. Rev. B 76, 161403, 2007

#### $\pi$ electrons ferromagnetism: spectroscopic evidence

#### X-ray circular dichroism (XMCD)



Ohldag et al., PRL 98, 187204 (2007).

### **Extreme form: Carbon foam**



Attractive. One of the lightest substances ever made, nanoscale froth condensed from superheated carbon atoms is also magnetic at room temperature for a few hours.

# Extensive tests show that magnetic impurity can only account for 20% of magnetism, Science 304, 42 (2004).

#### **Other evidences for roles of defects**



#### **Absence of strong localization!** Novoselov et al. Nature 438, 197 (2005)

### **Universal** ?



Geim and Novoselov, Nature Mater. 6, 183 (2007)

Tan et al., PRL 99, 246803 (2007)

### Weak localization and weak antilocalizaion



In some samples: Morozov et al., PRL 97, 016801 (2006)



Wu et al., PRL 98, 136801 (2007)

### **Inverse compressibility**



Martin et al., Nature Phys. 4, 144 (2008)



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## Peculiar density of states in edges of graphene

#### **STM measurement**







#### **Typical SIS for armchair edge**



**Typical SIS for zig-zag edge** 

# How do we understand it?

# **Fourier transform along the interface**



#### **SUSY Quantum Mechanics and zero-energy state**



Huang et al. Phys. Rev. B 70, 205408 (2004)

#### Localization of the zero-energy state

$$\psi = \left(-\frac{t_1}{t_2}\right)^n$$



## Interacting electrons in zigzag ribbons

$$\mathbf{M=1} \qquad H = -t \sum_{\langle i,j \rangle \sigma} C_{i,\sigma}^{+} C_{j,\sigma} + H.c. + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$



Hikihara, Hu, Lin, and Mou, PRB 68, 035432 (2003)

## Paramagnetism as a result of bi-partite nature



#### **Calculation by Local Spin Density Approximation**



#### H. Lee et al., PRB 72, 174431 (2005)

# Possible origin of Curie-like behavior



Shibayama et al. Phys. Rev. Lett. 84, 1744(2000)

# **Proposed half-metallic application for spintronics**



Son et al., Nature 444, 347 (2006)



## Nanostructure confinement and ferromagnetism in armchair nanoribbon





HH Lin et al., Phys. Rev. B 79, 035405 (2009)

## **Outline:**

- •Background and Introduction: Transport and Magnetic properties
- Novel magnetism associated with
- edge states and flat-band in nanoribbons
- Impurity band due to point defects in graphene

#### Many possible defects on graphene

Vanacies, Pentagon-heptagon pair, adatoms, cracks...





#### Stone and Wales, Nature 430, 870, 2004

What is the best candidate for ferromagnetism?

#### **Ferromagentism of Dirac band**



Peres, Guinea, and Neto, Phys. Rev. B 72, 174406 (2005)

Large nonspherical-defects (cracks..., real localized states in zig-zag edges) -- carrier mediated ferromagnetism

**RKKY on graphene: AB antiferromagnetic**AA ferromagneticAA ferromagneticA



Brey at al., Phys. Rev. Lett. 99, 116802 (2007); Saremi, Phys. Rev. B 76, 184430 (2007)

# Plausible candidates: disk-like or point defects



The zero-energy state was known for Dirac Hamiltonian

$$G(r,r') = G_0(r,r') + G_0(r,0)uG_0(0,r') + G_0(r,0)uG_0(0,0)uG_0(0,r') + \cdots$$
  
=  $G_0(r,r') + G_0(r,0)\frac{1}{1/u - G_0(0,0)}G_0(0,r')$ 

**Perturbative approach**: Balatsky et al., Phys. Rev. B 51, 15547 (1995); Pereira et al. Phys. Rev. Lett 96, 036801 (2006) .....

#### **Continuum limit: point defect** $\Rightarrow$ **disk like potential**

$$E = 0, \ \psi \approx \frac{1}{\sqrt{r}}$$

Dong et al., Phys. Rev. A 58, 2160 (1998)



## **Reflection of anomalous behaviors at zero energy**



## Strong diamagnetism

$$\chi = -\frac{a^2 t^2 e^2}{2\pi\hbar^2} \delta(\varepsilon_F)$$



## **Investigations on magnetism of point-like defects**

•Local moments are established near point defects

### •Conflicting reports on long-range order (ferromagnetism or antiferromagentism ? ) Semimetal

Herbut, Phys. Rev. Lett 97, 146401 (2006) (RG + Hubbard model)

Antiferromagnetism (Hubbard U + LDA) Yazyev and Helm, Phys. Rev. B 75, 125408 (2007)

(1st principle); Brey et al. Phys. Rev. Lett. 99, 116802 (2007)

#### Ferromagnetism

Vozmediano et al. Phys. Rev. B 72, 155121 (2005); Yazyev, Phys. Rev. Lett. 101, 037203 (2008) (Stacking

along c-axis is responsible for ferromagnetism)

#### **Our approach: constructing exact wavefunction**

$$(H_0 + u\delta_{r,0})\psi = E_0\psi$$

**Huygens' principle:** 



 $\psi = A \operatorname{Re} G_0(r, 0, E_0) (\operatorname{BC}: \psi \to 0)$ 

Check: Using  $(E - H_0)G_0(r, r', E) = \delta_{r,r'}$  $(E - H_0) \operatorname{Re} G_0(r, 0, E) = \delta_{r,0} = u\delta_{r,0} \operatorname{Re} G_0(r, 0, E)$ Self-consistent condition:  $\frac{1}{u} = \operatorname{Re} G_0(0, 0, E_0) \equiv g_0(0, 0, E_0)$ 



# **Semi-localization**

 $\Psi = A \operatorname{Re} G_0(r, 0, E_0)$   $G_0(\vec{r}, 0, 0) \propto \operatorname{Re} \sum_{D} \int \frac{d\theta}{2\pi} \int_{\lambda} k dk e^{ikr\cos\theta} \frac{e^{i\phi_{\vec{k}}}}{-\nu k} e^{i\vec{k}_D \cdot \vec{r}} = \frac{1}{r} \frac{2}{\nu} \left[ 1 - J_0(k_D r) \right] \sin \frac{4\pi x}{3a}$ 



**Defects are strongly coupled** -- direct exchange dominates



## overlapping is strong!

#### sensitive to boundary and size!

## **Multi-defects state of our construction**

$$\psi = \sum_{i} A_{i} \operatorname{Re} G_{0}(r, r_{i}, E)$$

#### **Self-consistent condition:**

$$(E - H_0)\psi = \sum_i A_i \delta_{r,r_i} = u \sum_i \delta_{r,r_i} \psi = u \sum_i \delta_{r,r_i} \sum_j A_j \operatorname{Re} G_0(r_i, r_j, E)$$

$$\det \begin{pmatrix} 1/u - g_{11} & -g_{12} & \cdot & -g_{1N} \\ -g_{21} & 1/u - g_{22} & \cdot & -g_{2N} \\ \cdot & \cdot & \cdot & \cdot \\ -g_{N1} & -g_{NN-1} & \cdot & 1/u - g_{NN} \end{pmatrix} = 0$$

#### **Random matrix and Impurity band**

 $u \to \infty$  and  $\operatorname{Re} G(0, 0, E) \approx -\gamma E$  and for  $E \approx 0$ 

$$\det(\alpha E1-h) = \det\begin{pmatrix} \gamma E & -g_{12}^{0} & \cdots & -g_{1N}^{0} \\ -g_{21}^{0} & \gamma E & \cdots & -g_{2N}^{0} \\ \vdots & \vdots & \ddots & \vdots \\ -g_{N1}^{0} & -g_{NN-1}^{0} & \cdots & \gamma E \end{pmatrix} = 0$$

∴  $r_i$  positions are random,  $g_{ij}^0$  are random Mapping ⇒ eigenvalues of random matrix

#### **Generalized Central Limit Theorem and Wigner Semi-Circle Law**



## **Reconstruction of Dirac band in self-consistent Born approximation**



Peres et al., Phys. Rev. B 73, 125411 (2006)



#### **Dirac band must be reconstructed**



### **Does defects support ferromagnetism?**



$$C_{ab} = e^{2} \int dr_{1} \int dr_{2} \frac{\left|\Psi_{a}(r_{1})\right|^{2} \left|\Psi_{b}(r_{2})\right|^{2}}{\left|r_{1}-r_{2}\right|}, \ J_{ab} = e^{2} \int dr_{1} \int dr_{2} \frac{\Psi_{a}^{*}(r_{1})\Psi_{b}(r_{1})\Psi_{b}^{*}(r_{2})\Psi_{a}(r_{2})}{\left|r_{1}-r_{2}\right|}$$

(expressible in q space)

#### **Magnetism of two-defects**



**Triplet for AA** Agree with LDA bandwidth  $\rightarrow 0$ , triplet is favored

#### What about finite density of defects ?



**Exchange Energy (gain)** 

$$H = \frac{e^{2}}{8\pi\varepsilon_{0}} \sum_{ij\sigma_{i}} C_{i\sigma}^{+} C_{i\sigma} \frac{1}{|r_{i} - r_{j}|} C_{j\sigma'}^{+} C_{j\sigma'}$$
$$= \frac{e^{2}}{8\pi\varepsilon_{0}} \left[ \sum_{ij} \frac{n_{i}n_{j}}{|r_{i} - r_{j}|} - \sum_{ij\sigma_{i}} C_{i\sigma}^{+} C_{j\sigma'} \frac{1}{|r_{i} - r_{j}|} C_{j\sigma'}^{+} C_{i\sigma} \right]$$

# **Flat-band ferromagnetism**

# Mielke-Tasaki mechanism:

Non-vanishing overlaps between Wannier orbitals Prog. Theor. Phys. 99, 498, (1998) (for Hubbard model) Essentially, exchange energy wins.

Example: Arita et al, PRL88, 127202 (2002)  $\int_{a}^{2} \int_{b}^{a} \int$ 

FIG. 2. The band structure (left panel) and the optimized atomic configuration (right) of the (undoped) polyaminotriazole obtained by the GGA-DFT. The solid (dotted) lines represent bands having  $\pi$  ( $\sigma$ ) character.


# Linear-like temperature dependence of M



Barzola-Quiquia et al Phys. Rev. B 76, 161403, 2007

 $\delta \propto T$ 

## **Does the impurity band conduct?**

Conductivity

$$\vec{J} = rac{iet}{\hbar} \sum_{i\vec{\delta}} \vec{\delta} C^{+}_{i+\delta,\sigma} C^{-}_{i,\sigma}$$

$$\frac{\sigma}{4e^2/h} = \frac{w^2}{4\pi\delta^2}$$

Intrinsic  $\lambda = 30$ nm [Martin et al., Nature Phys. 4, 144 (2008)]  $n_I \approx 10^{-5} - 10^{-6}$ 

$$\delta/t \approx 10^{-3} \qquad \qquad \frac{\sigma}{4e^2/h} = O(1)$$

# **Summary**

- •Graphene is a promising material both for spintronics and electronics. It is relativistic!
- Defects and edges in graphene have anomalous contributions to transport and magnetism
- Edge states in zig-zag edges of nanoribbons or cracks are origin of paramagnetism in graphene ribbons
- Point defects on graphene are correlated and form an impurity band with a universal density of state characterized by Wigner's semi-circle law.

#### **Integer and Fractional Quantum Hall effect**





von Klitzing





# Anderson localization, metal-insulator transition, ...



V(x)



Χ

### **Giant Magnetoresistance**



A. Fret P.Grünberg





Spin bottleneck magnetoresistance



# Making Carbon Nanoribbon from Carbon Nanotube



## Berry phase, diamagnetism, and Quantum Hall effect



n (10<sup>12</sup> cm<sup>-2</sup>)



Brey at al., Phys. Rev. Lett. 99, 116802 (2007); Saremi, Phys. Rev. B 76, 184430 (2007)