Manipulating Graphene at the Atomic-scale

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(I) Atomic-scale Gating
   -- Tunable charge centers

(II) Nanoribbon Edge States
   -- Controllable edge functionalization
(I) Atomic-scale Gating

Macroscopic: 
Electrode

Microscopic:
Charged Impurity

Klein Tunneling

Coulomb Impurity
Physics of a Coulomb Impurity

Non-relativistic Case (Hydrogen)

$E = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} - \frac{Ze^2}{r}$

$V_{\text{eff}} = -\frac{Ze^2}{r}$

Ultra-relativistic Case for Graphene

$E = v_F p - \frac{Ze^2}{\varepsilon r}$

Critical Charge: $Z_c = \frac{\varepsilon g}{2\alpha_g}$
Physics of a Coulomb Impurity

Non-relativistic Case (Hydrogen)

\[ E = \frac{P_r^2}{2m} + \frac{L^2}{2mr^2} - \frac{Ze^2}{r} \]

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Ultra-relativistic Case for Graphene

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Critical Charge: \( Z_c = \frac{\varepsilon_g}{2\alpha_g} \)
Predicted Behavior for Dirac Fermions Near Coulomb Potential

\( Q = + Z |e| > 0 \)

(Subcritical (\( Z < Z_c \))

Predicted quasi-bound-states (atomic collapse states)

(Solution to Dirac Equation using a Continuum Model)

Supercritical (\( Z > Z_c \))

Charge asymmetry

Pereira et al., PRL 99, 166802 (2007)
Shytov et al., PRL 99, 246802 (2007)
Deposit Cobalt Atoms onto Graphene / SiO$_2$ Device

Spectroscopy at Site of Cobalt Atom on Graphene

Atomic Resonances, Gate-induced Charging

Gated Cobalt Atom Spectroscopy

Off-atom Problems: Bi-stability and Inhomogeneity

Charge bi-stability: Co on Graphene

Previous Impurities in Semiconductors

Graph. / SiO₂ Rough Topography

Graph. / SiO₂ Charge Inhomogeneity
A New Substrate Solves these Problems (BN)

BN substrate in new STM geometry

BN flake
CVD Graphene
Doped Si bottom gate

Crommie, Zettl

Less Inhomogeneity for Graphene on BN


Moiré Patterns

\[ \theta = 21^\circ \pm 1^\circ \]

\[ \theta = 7^\circ \pm 1^\circ \]

(a) Graph./BN

(b) 4 nm

(c) 4 nm

(d) 4 nm

(e) \( k_{BN} \)

(f) \( k_{gr} = 2.95 \text{ Å}^{-1} \)

Gate-dependent STM Spect.


Atomic Manipulation on Graphene/BN: Co Trimers

Trimers: no charge bi-stability
Trimers Are Stable, Tunable Charge Centers

Q = 0 State (uncharged)

$Q = +1 \ |e| \ \text{State (charged)}$

Co Trimer Provides a Stable Charged State
**dI/dV Spectra on Graphene around Charged Co Trimer**

Distance dependent spectra around charged Co trimer

- LDOS Asymmetry
- No Bound-state
Comparing Experiment to Predictions for Dirac Fermions

**EXPERIMENT**

Graphene around Co trimer
(Q = +1|e|)

- 1.6nm
- 2.2nm
- 3.5nm
- 6.4nm

**THEORY**

LDOS (a.u.)

**Interband Dielectric Constant:** $\varepsilon_g = 3.0 \pm 1.0$

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**Previous Theory for $\varepsilon_g$:**
- T. Ando, *J. of the Phys. Soc. of Japan* 75, 074716 (2006): $\varepsilon_g \approx 2$
- E. H. Hwang and S. Das Sarma, *PRB* 75, 205418 (2007): $\varepsilon_g \approx 2$

**Previous Experiment for $\varepsilon_g$:**
- D. A. Siegel, et al., *PNAS* 108, 11365 (2011): $\varepsilon_g < 6$
- J. P. Reed, et al., *Science* 330, 805 (2010): $\varepsilon_g = 15$
Spatial Dependence Reflects Charge Asymmetry

Cobalt Trimer: Sub-critical Impurity

$\epsilon_g = 3.0 \pm 1.0$

Y. Wang, et al., submitted for publication
Nanoribbons: Controlling the Edge

**GNRs**
- Tunable Gaps
- Edge-states
- Spin

**Graphene**

**Armchair**

**Zigzag**

Tunable Gaps

Spin-polarized


Some Previous Nanoribbon Investigations

**Lithography: Transport**

- **Graphene platelet on Si(100)**
  
  ![Graphene platelet on Si(100)](image)
  

- **Armchair GNRs grown on Au**
  
  Jinming Cao et al., *Nature* **466**, 470 (2010)

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Some Previous Edge Investigations

**Graphite Step edge**

- **Y. Kobayash et al., PRB 71**, 193406 (2005)

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**Graphene Edges on SiC & Cu**

GNRs from Unzipped Nanotubes


Different Chiralities Observed

Width = 19.8 nm

$48 \text{ Å} \times 48 \text{ Å}$

$\theta = 5.8^\circ$

$(8, 1) \text{ GNR}$

STM Spectroscopy of Nanoribbon Edge State

(8, 1) GNR
width = 19.8 nm

Gap Width Dependence

Control GNR Edge Through H$_2$ Plasma Etch

Room temperature STM

Crommie, Dai, Louie, Zettl (unpublished)
Nano-scale Structure of Edge

Can Find Edge Symmetry, But What is H-Composition?

- Zigzag edge
- (2, 1) Chiral edge
- Armchair edge
What is Hydrogen Edge Structure?

Calculate Thermodynamic Stability of Different Edge Structures

Previous Work:
Wassman, Seitsonen, Marco Saitta, Lazzeri, Mauri,
*PRL* 101, 096402 (2008)

O. Yazyev, S. G. Louie & co-workers
Comparing Exp. Edge to Theory w/ Proper H-structure

EXPERIMENT

THEORY

Averaged Linescans

Armchair GNR

Experiment
Theory

Zigzag GNR

Experiment
Theory

Edge
Conclusion

I) Dirac Fermion Screening of Tunable Charge Impurities
II) Controlling GNR Edges through Chemical Functionalization

Future:

Atomic Collapse

SPSTM of GNRs

Pseudo-field and Spin
Collaborators:

**Co-PI’s**

**Students + Postdocs + Visitors**

**Tunable Charge Centers**
Victor Brar, Regis Decker, Yang Wang, Q. Wu, H. Tsai, Will Regan, A. Shytov

**Nanoribbon Edges**
Chenggang Tao, Yen-Chia Chen, Liying Jiao, Juanjuan Feng, Xiaowei Zhang, R. Capaz, Oleg Yazyev
The End