Manipulating Graphene at the Atomic-scale

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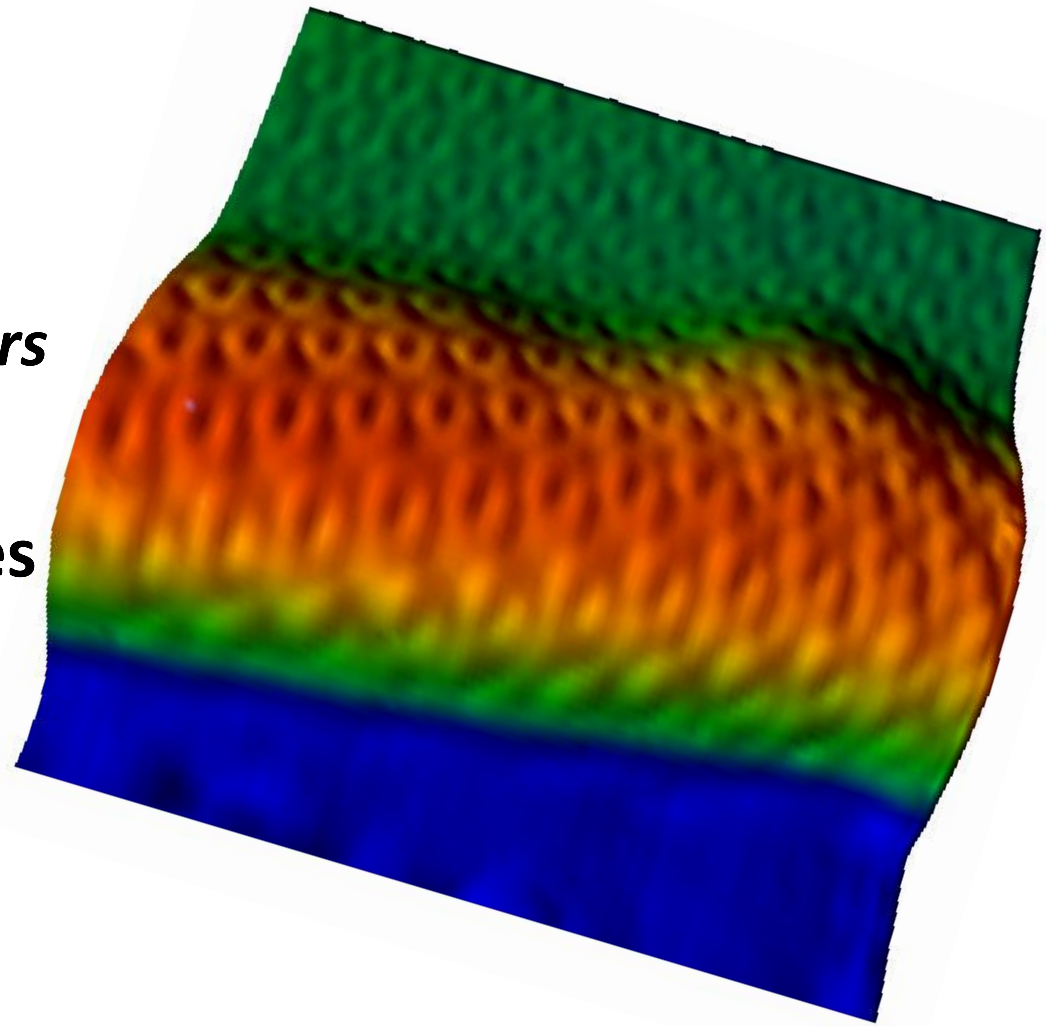
Materials Science Division, LBNL

(I) Atomic-scale Gating

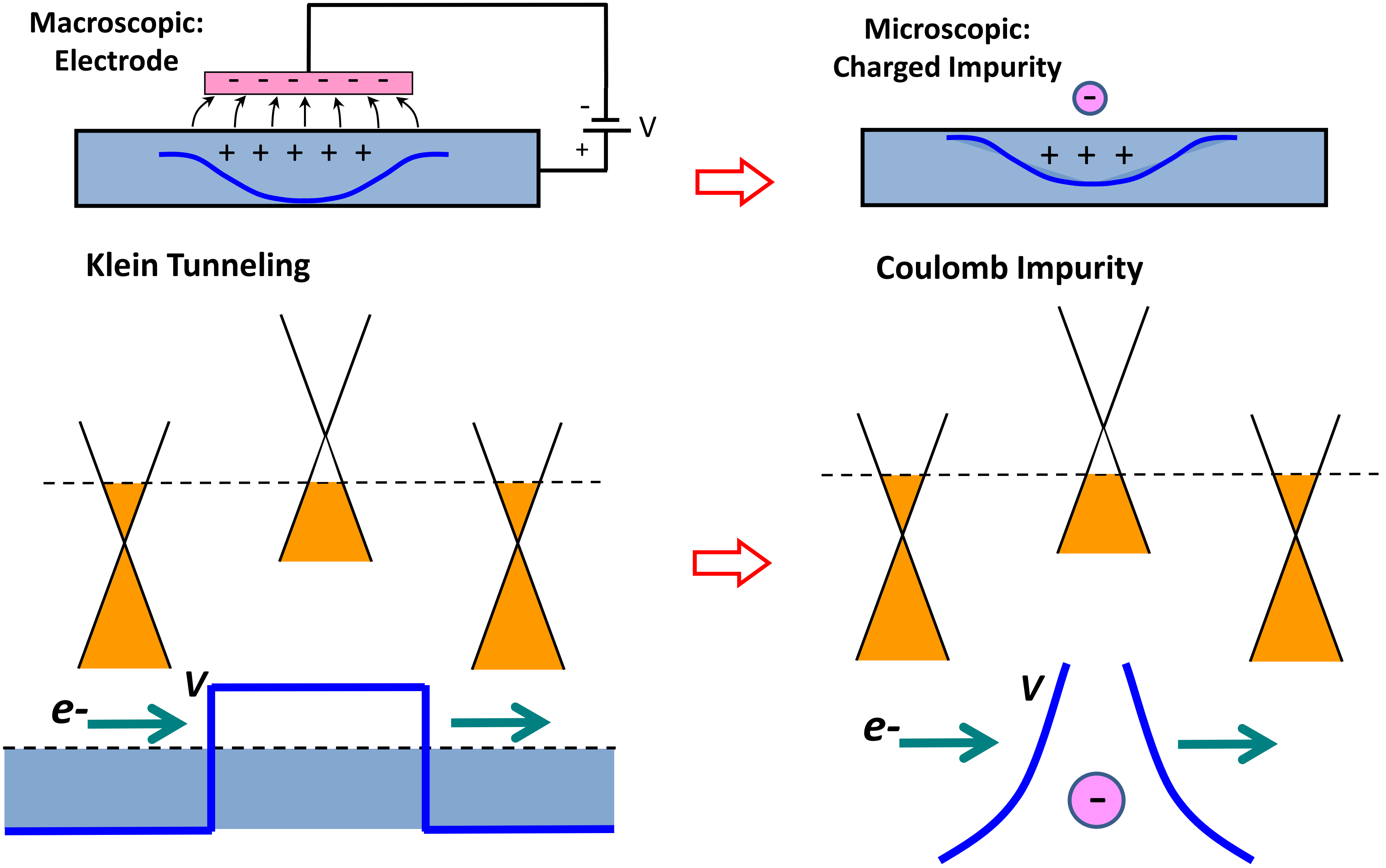
-- Tunable charge centers

(II) Nanoribbon Edge States

-- Controllable edge functionalization

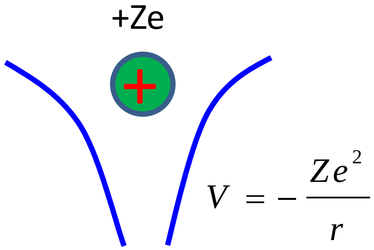


(I) Atomic-scale Gating

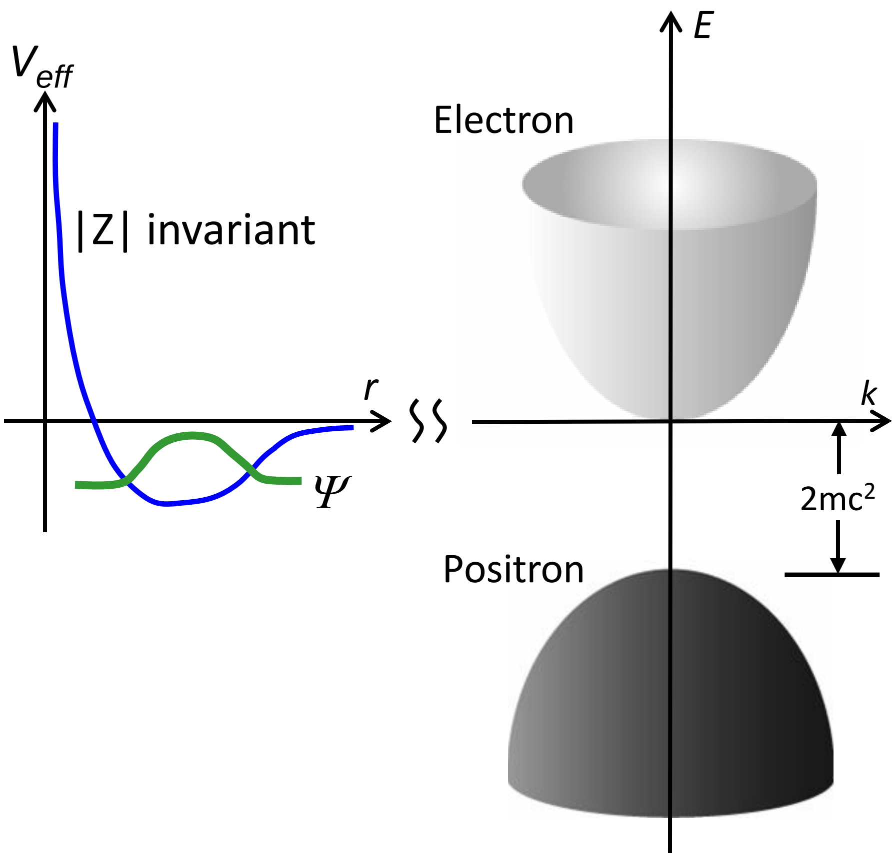


Physics of a Coulomb Impurity

Non-relativistic Case (Hydrogen)



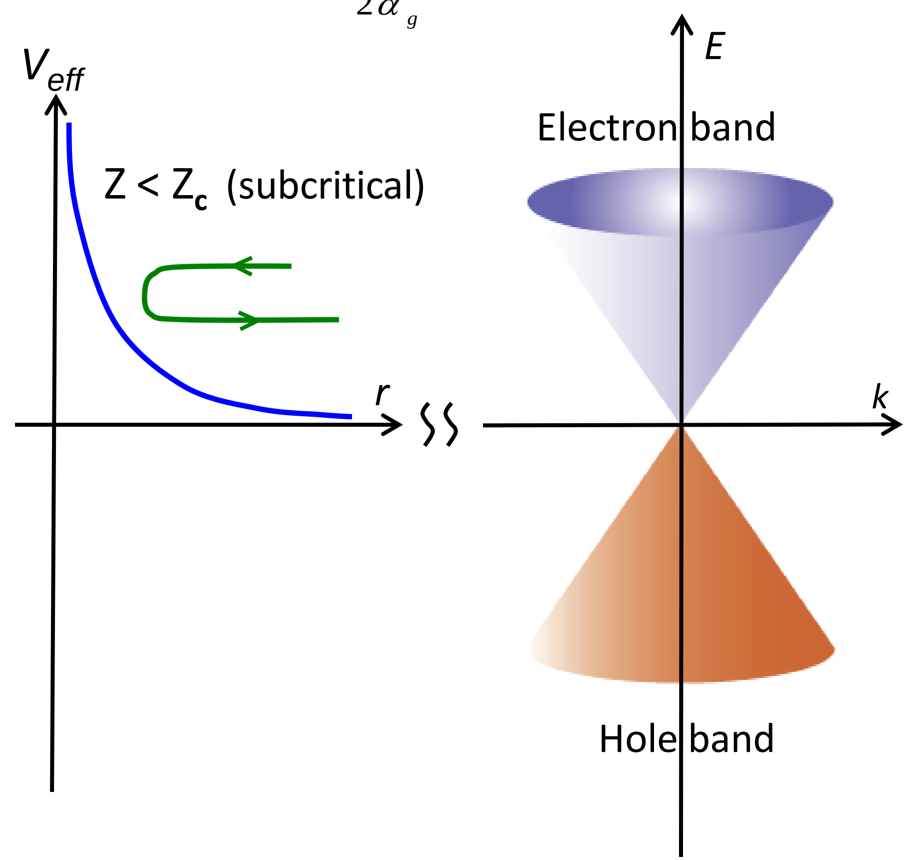
$$E = \frac{P_r^2}{2m} + \underbrace{\frac{L^2}{2mr^2} - \frac{Ze^2}{r}}_{V_{eff}}$$



Ultra-relativistic Case for Graphene

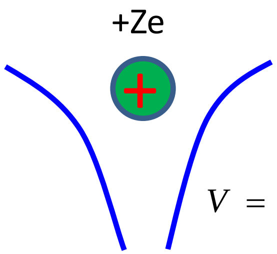
$$E = v_F\, p - \frac{Ze^2}{\varepsilon\, r}$$

Critical Charge: $Z_c = \frac{\varepsilon_g}{2\alpha_g}$



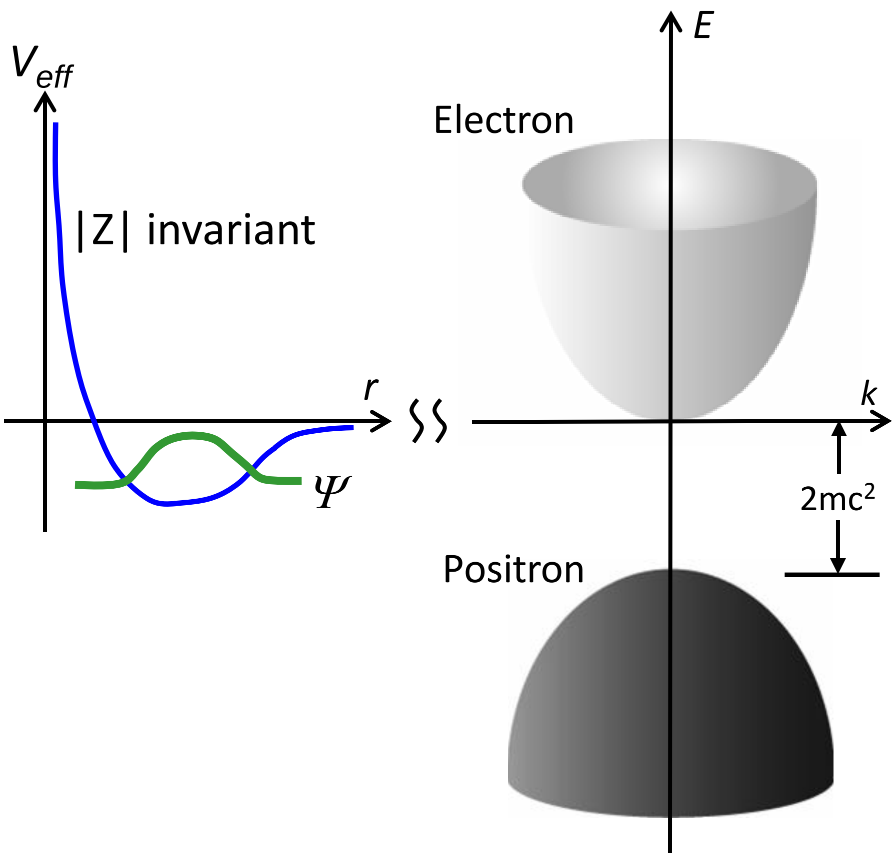
Physics of a Coulomb Impurity

Non-relativistic Case (Hydrogen)



$$V = -\frac{Ze^2}{r}$$

$$E = \frac{P_r^2}{2m} + \underbrace{\frac{L^2}{2mr^2} - \frac{Ze^2}{r}}_{V_{eff}}$$



Ultra-relativistic Case for Graphene

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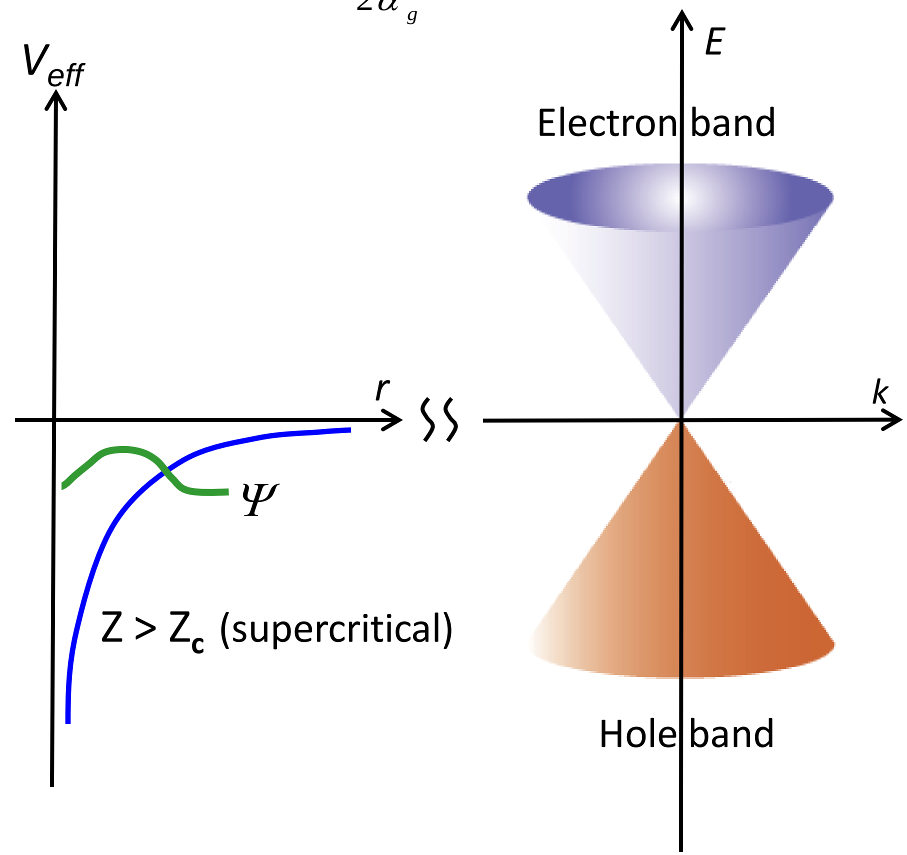
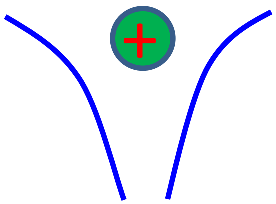


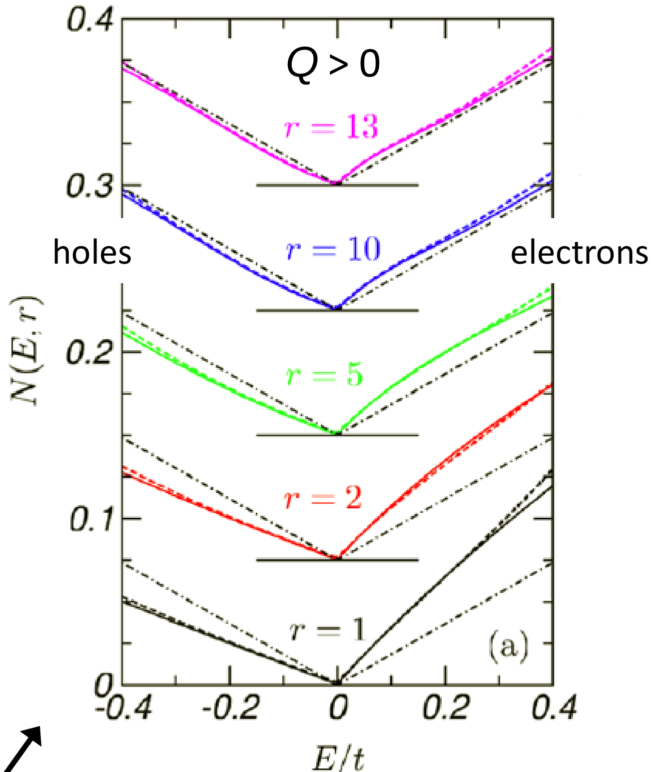
Predicted Behavior for Dirac Fermions Near Coulomb Potential

(Solution to Dirac Equation using a Continuum Model)

Q = + Z |e| > 0

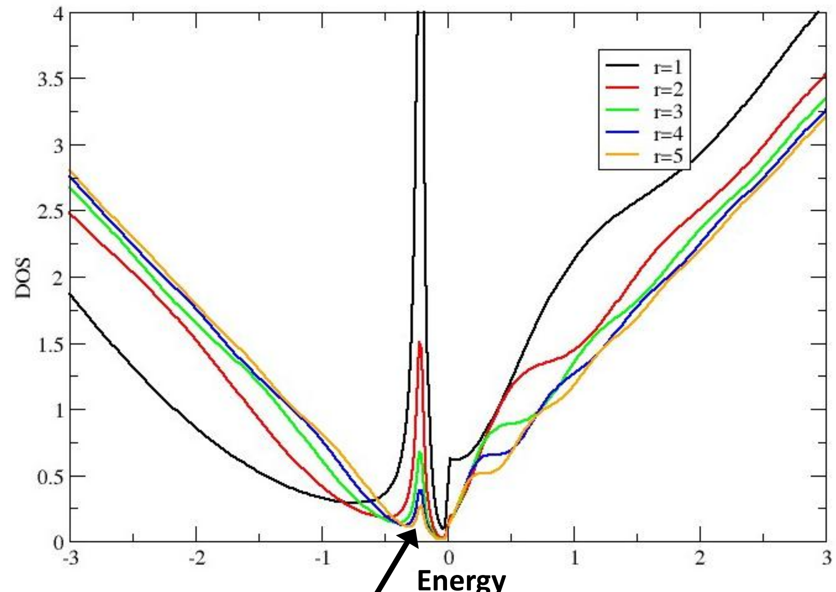


Subcritical ($Z < Z_c$)



Charge asymmetry

Supercritical ($Z > Z_c$)

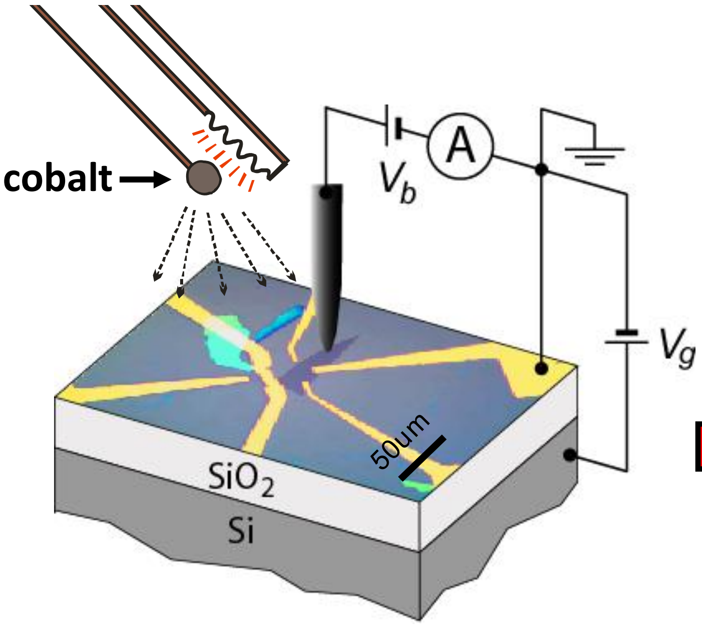


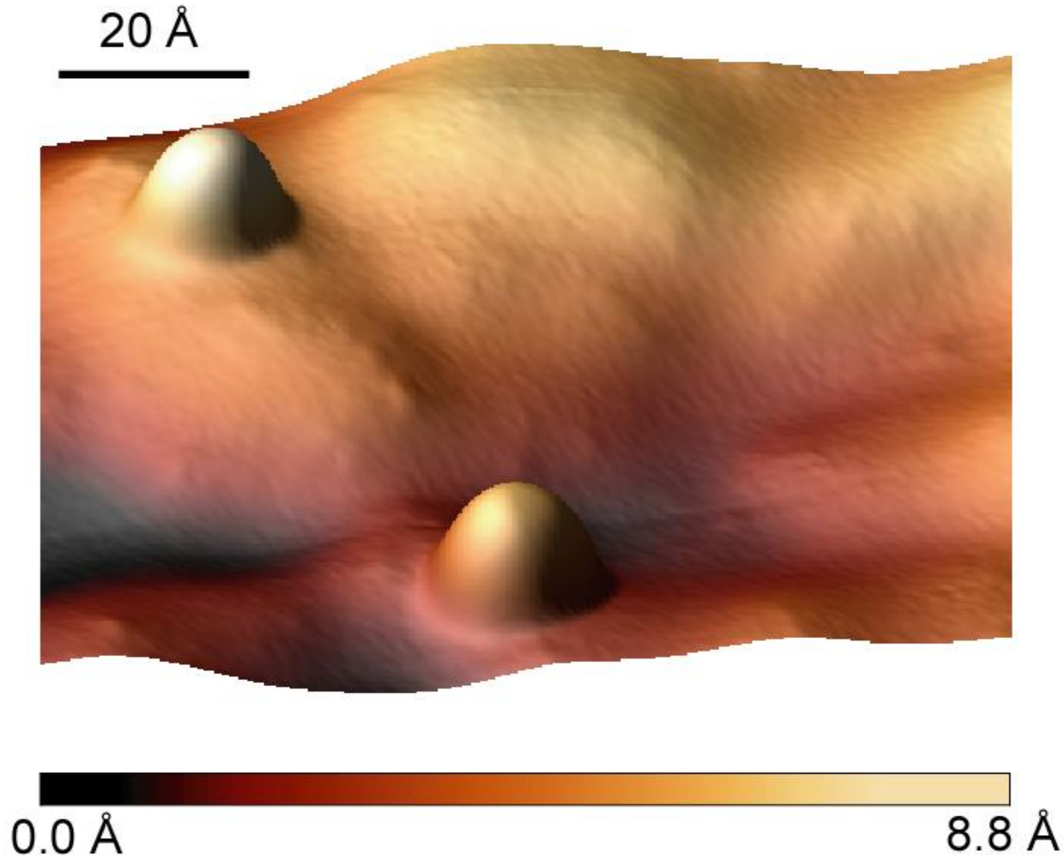
Predicted quasi-bound-states
(atomic collapse states)

Pereira *et al.*, *PRL* **99**, 166802 (2007)

Shytov *et al.*, *PRL* **99**, 246802 (2007)

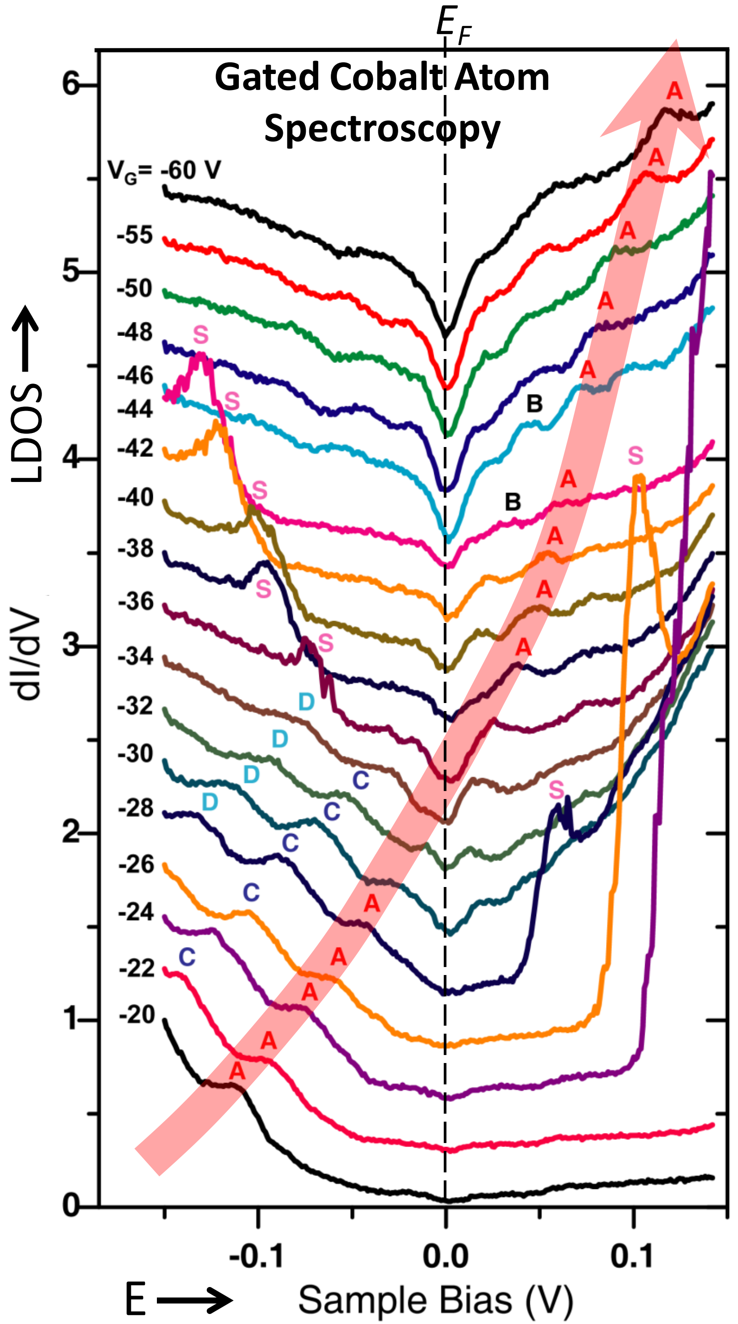
Deposit Cobalt Atoms onto Graphene / SiO_2 Device



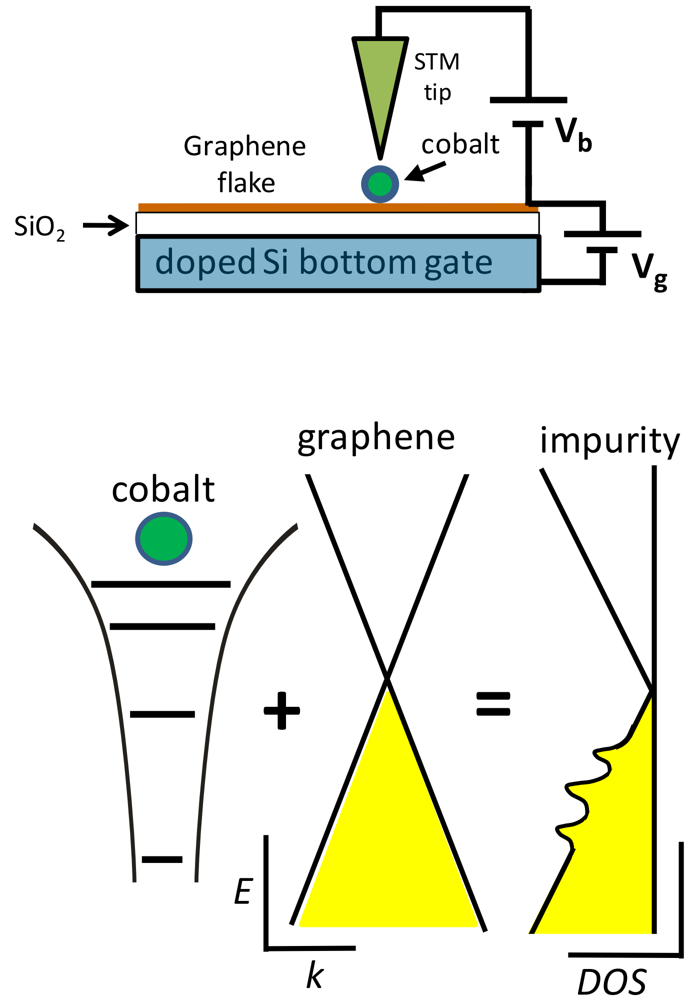


V.W. Brar, et al., *Nature Physics* **7**, 43 (2011)

Spectroscopy at Site of Cobalt Atom on Graphene



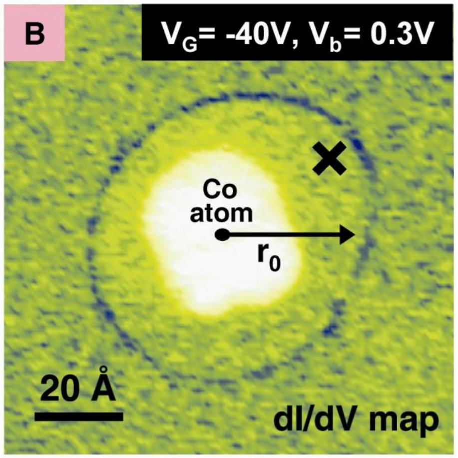
Atomic Resonances, Gate-induced Charging



V.W. Brar, et al., *Nature Physics* **7**, 43 (2011)

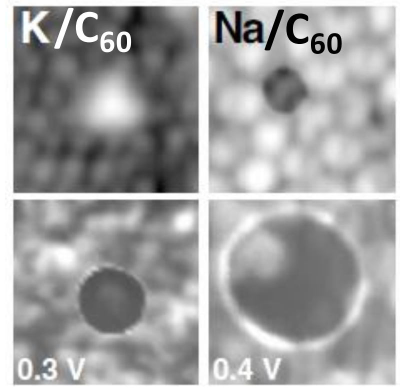
Off-atom Problems: Bi-stability and Inhomogeneity

Charge bi-stability: Co on Graphene

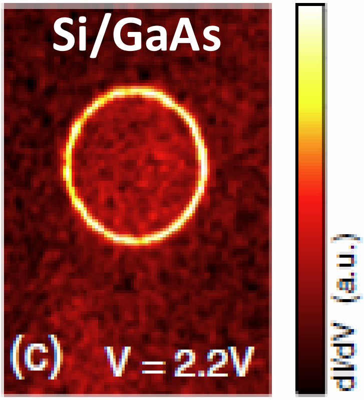


V.W. Brar, et al., *Nat. Phys.* **7**, 43 (2011)

Previous Impurities in Semiconductors

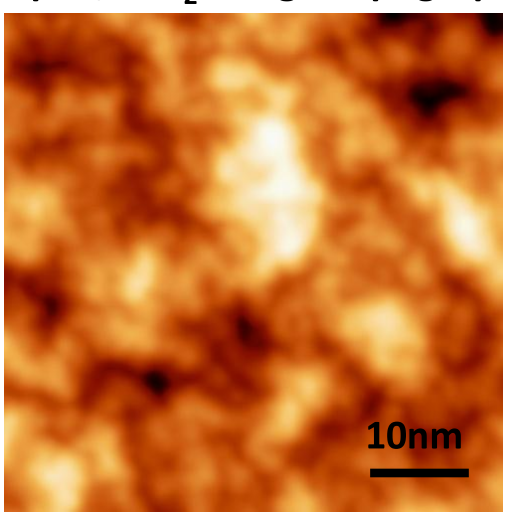


Pradhan, et al., *PRL* **94**, 076801 (2005)

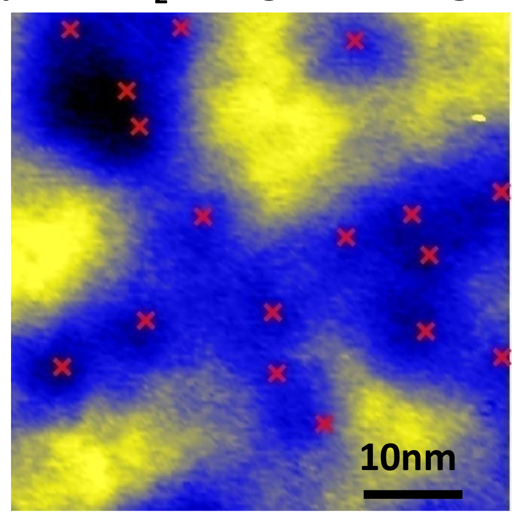


Teichmann, et al., *PRL* **101**, 076103 (2008)

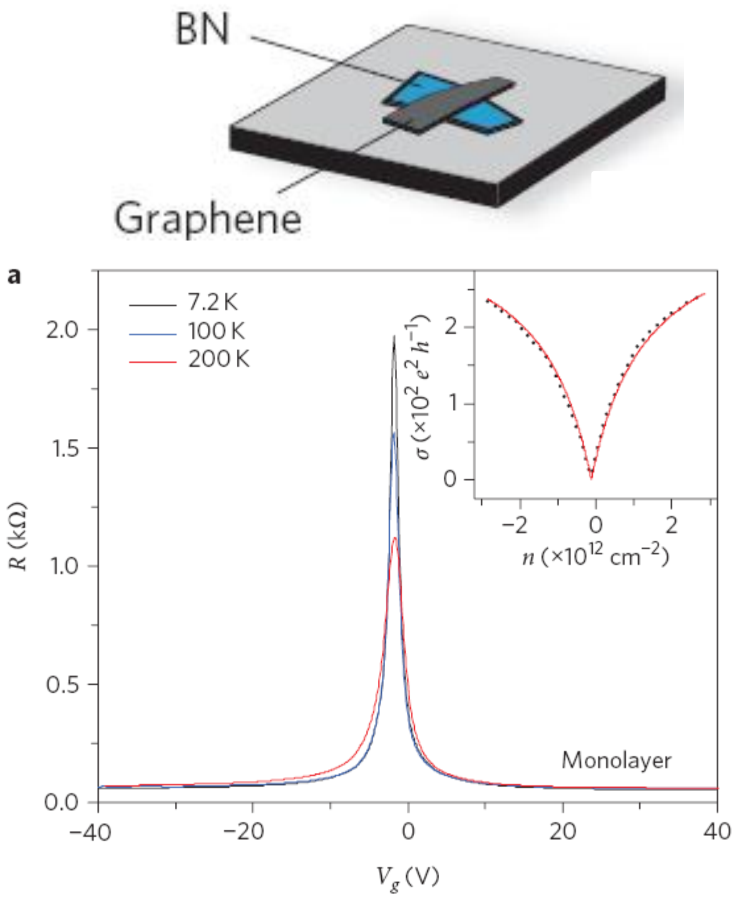
Graph. / SiO_2 Rough Topography



Graph. / SiO_2 Charge Inhomogeneity

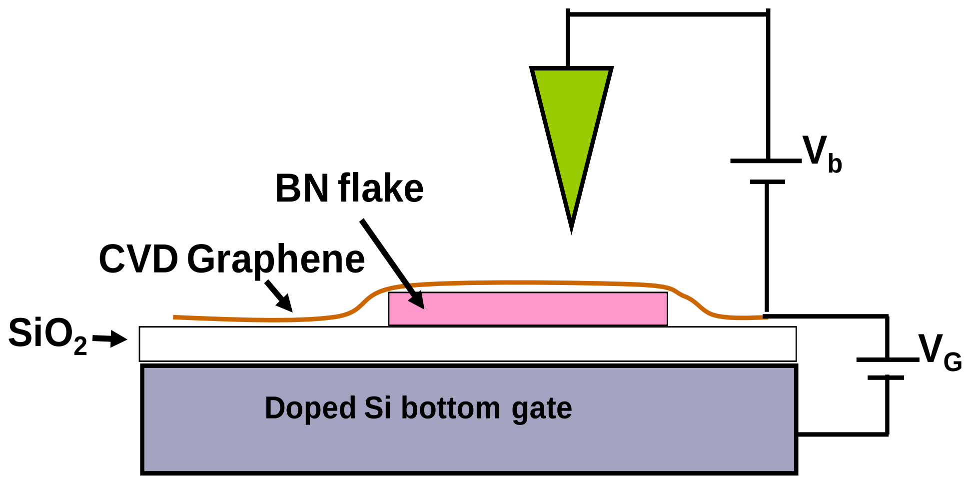


A New Substrate Solves these Problems (BN)



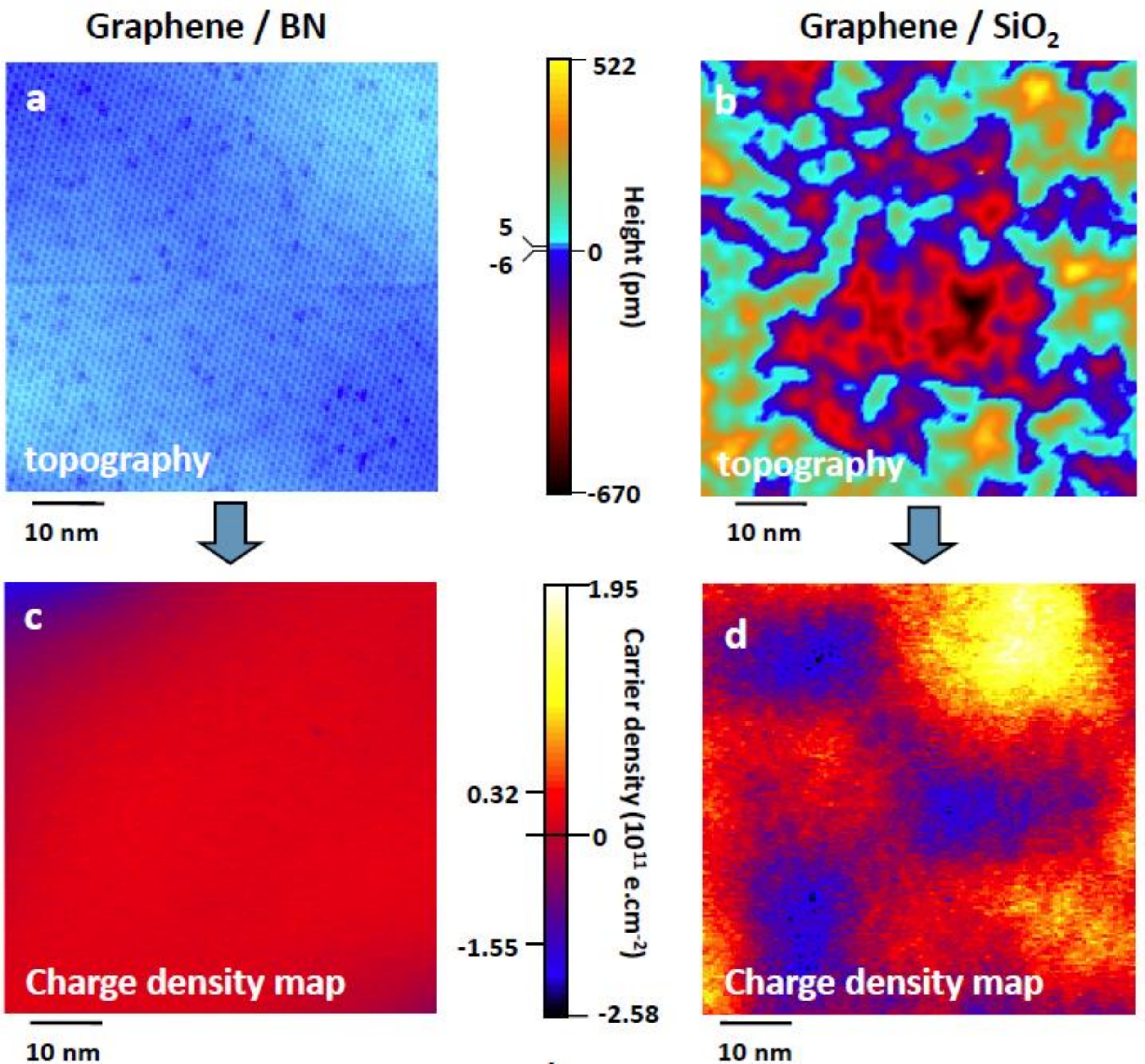
Dean C. R. *et al.*, *Nat Nano* **5**, 722 (2010)

BN substrate in new STM geometry



Crommie, Zettl

Less Inhomogeneity for Graphene on BN

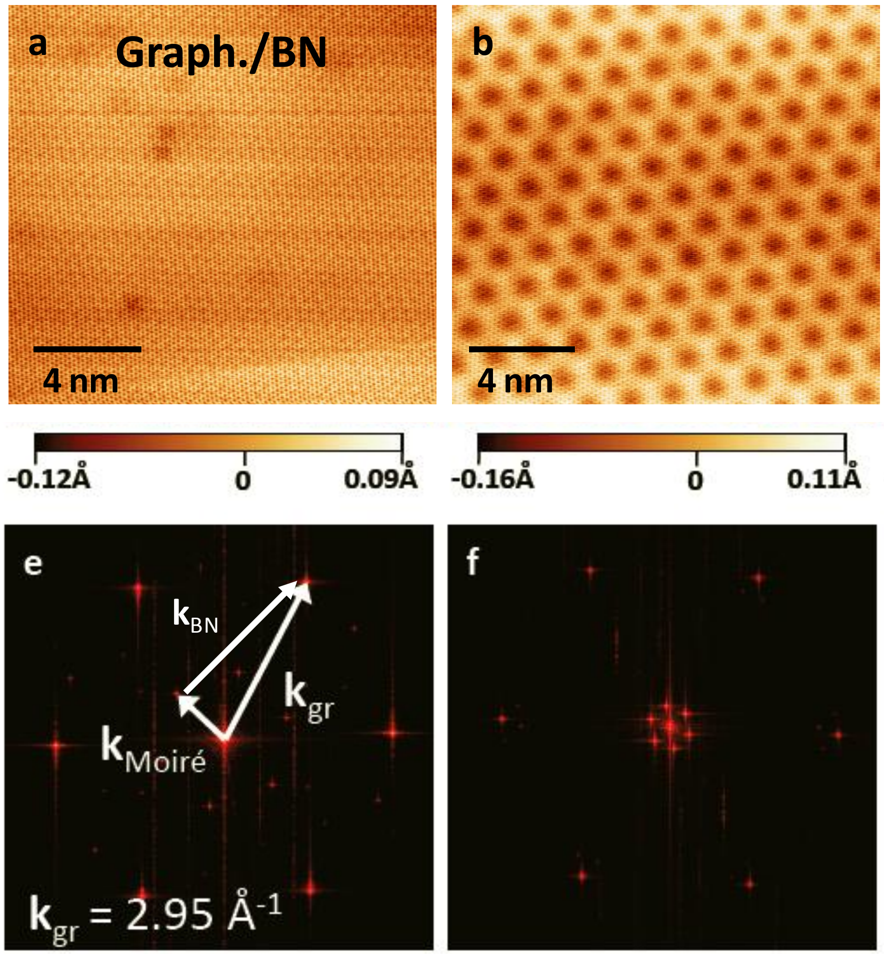


R. Decker, et al., *Nano Letters* **11**, 2291 (2011)

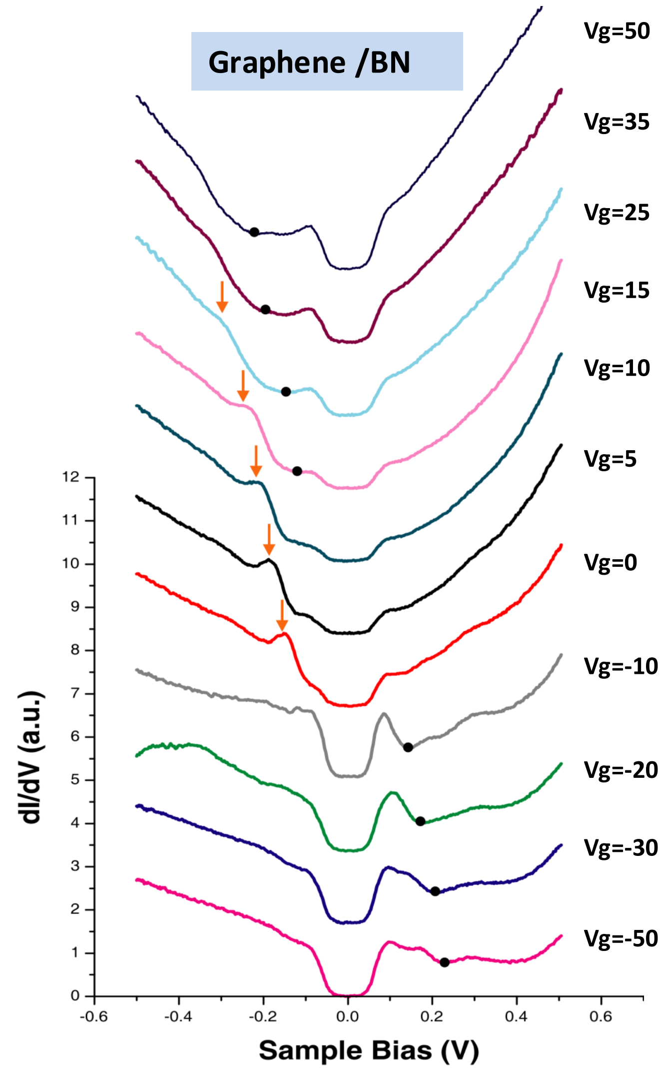
Similar to: J. Xue, et al., *Nature Mat.* **10**, 282 (2011)

Moiré Patterns

$\theta = 21^\circ \pm 1^\circ$ $\theta = 7^\circ \pm 1^\circ$



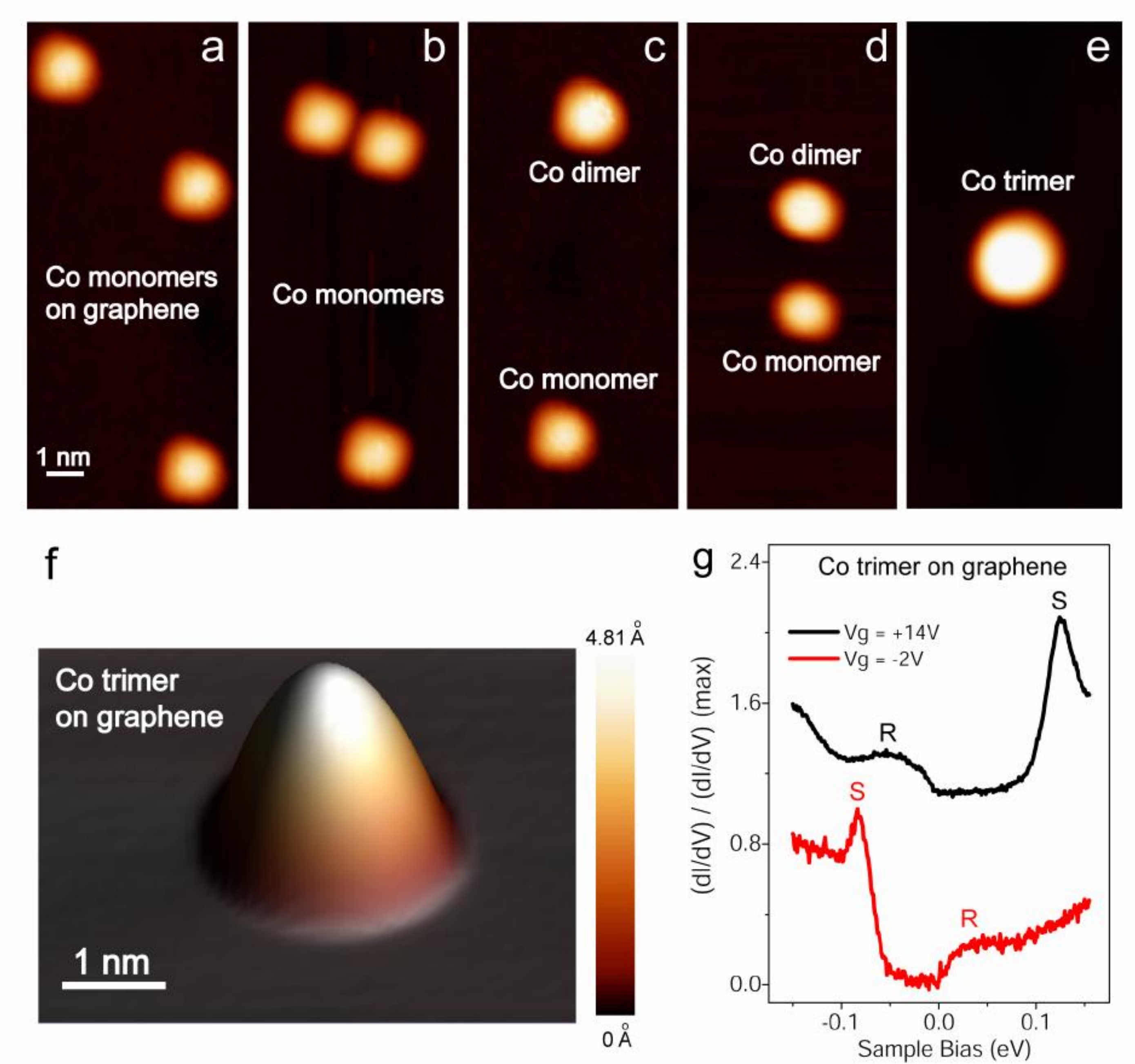
Gate-dependent STM Spect.



R. Decker, et al., *Nano Letters* **11**, 2291 (2011)

General spectral line-shape: V. W. Brar, *et al.*, *PRL* **104**, 036805 (2010)

Atomic Manipulation on Graphene/BN: Co Trimers

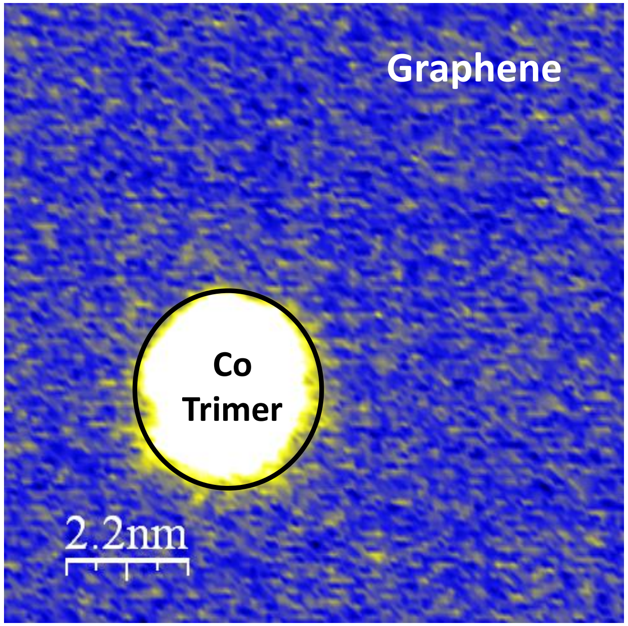


Trimers: no charge bi-stability

Trimers Are Stable, Tunable Charge Centers

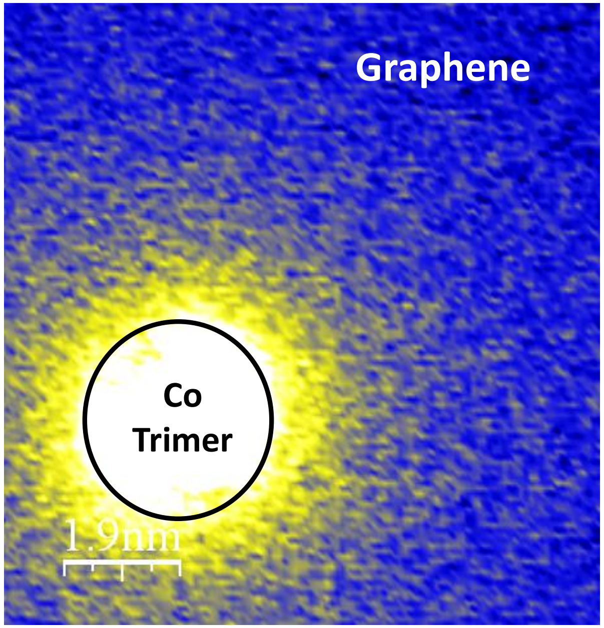
STM dI/dV images

Q = 0 State (uncharged)



V_g = +45V , V_s = +0.3V

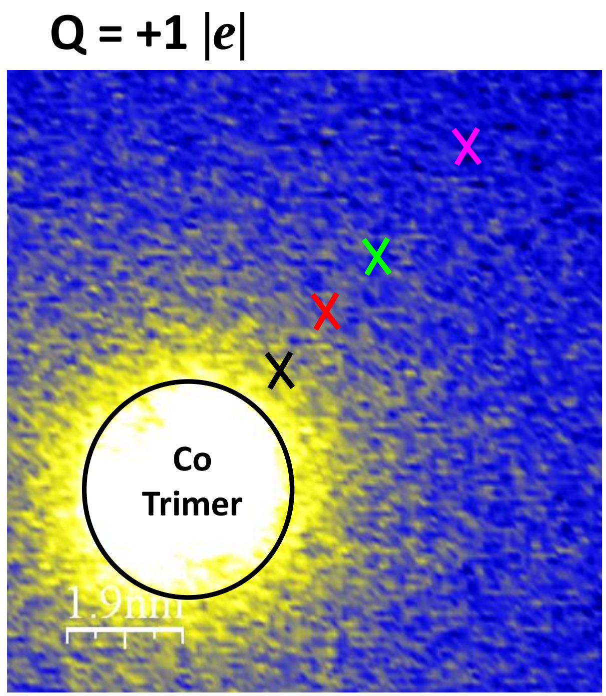
Q = +1 |*e*| State (charged)

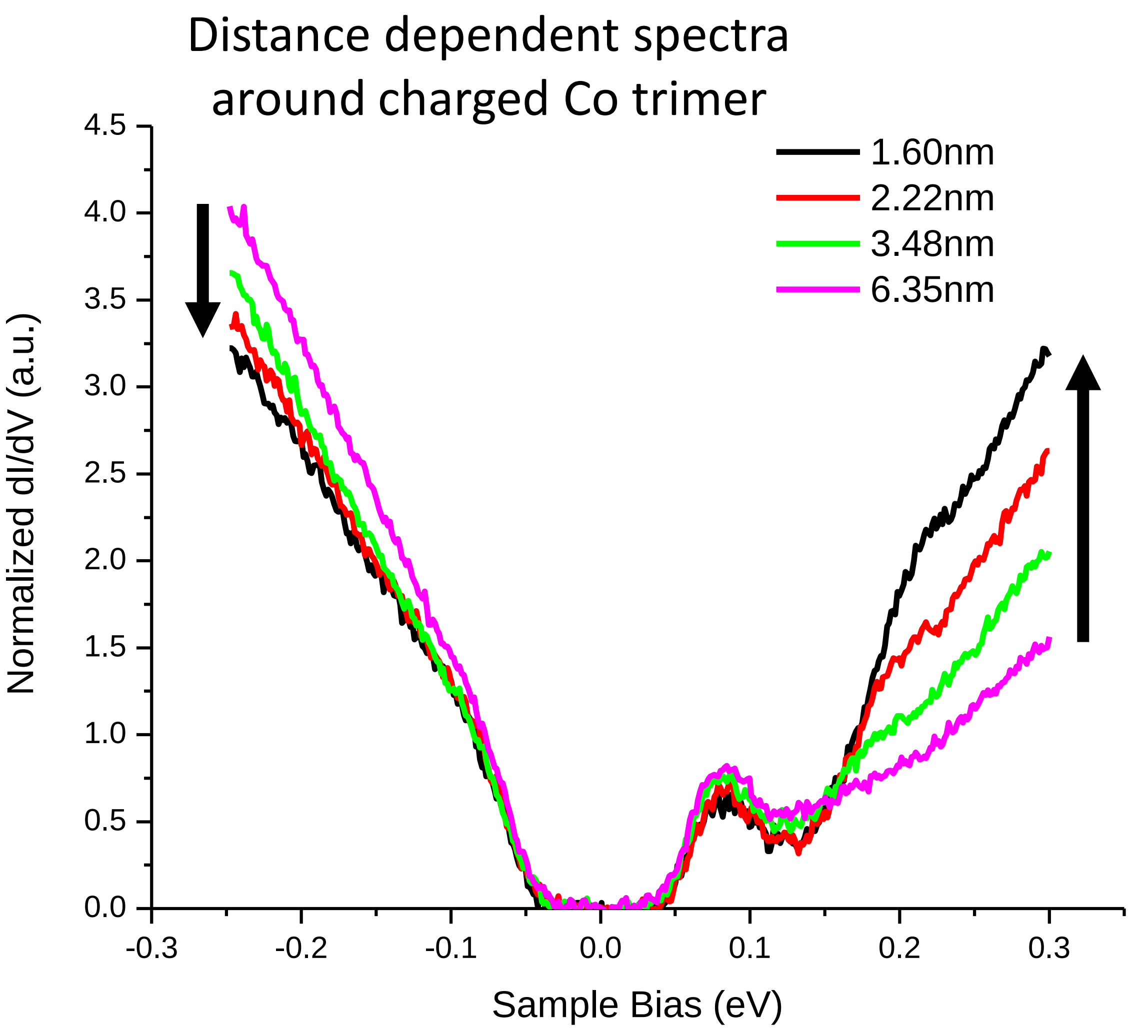


V_g = -20V , V_s = +0.3V

Co Trimer Provides a Stable Charged State

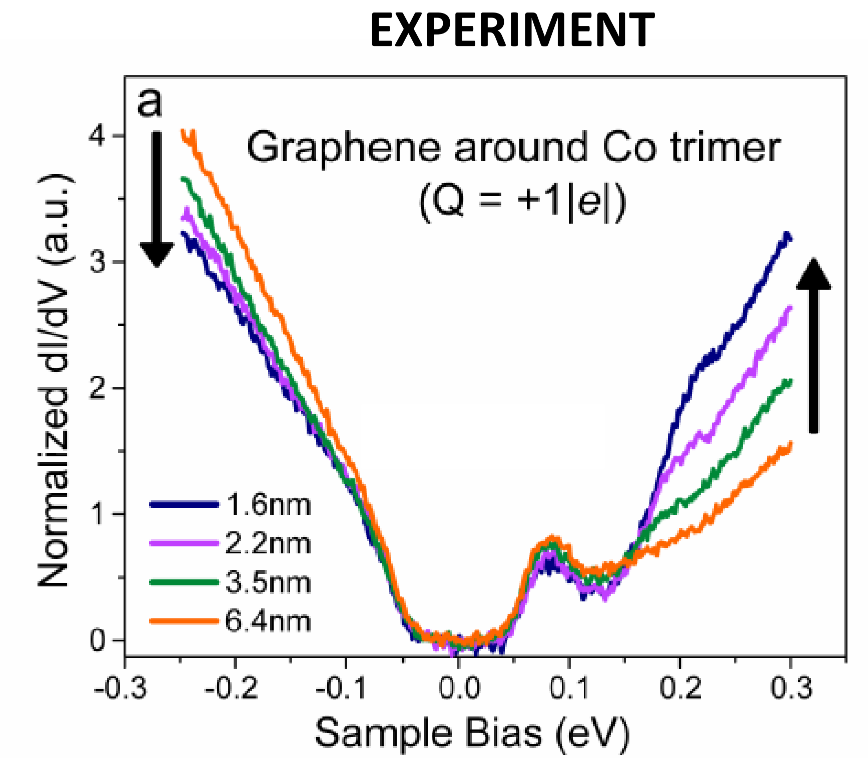
dI/dV Spectra on Graphene around Charged Co Trimer

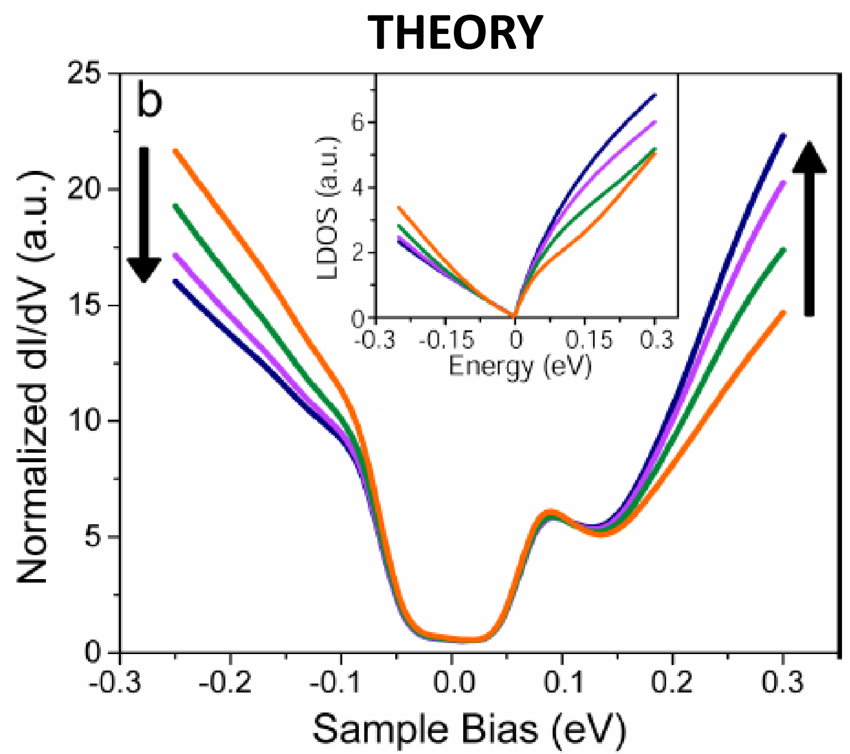




- LDOS Asymmetry
- No Bound-state

Comparing Experiment to Predictions for Dirac Fermions





Interband Dielectric Constant: ε_g = 3.0 ± 1.0

Previous Theory for ε_g :

T. Ando, *J. of the Phys. Soc. of Japan* **75**, 074716 (2006): ε_g **≈ 2**

E. H. Hwang and S. Das Sarma, *PRB* **75**, 205418 (2007): ε_g **≈ 2**

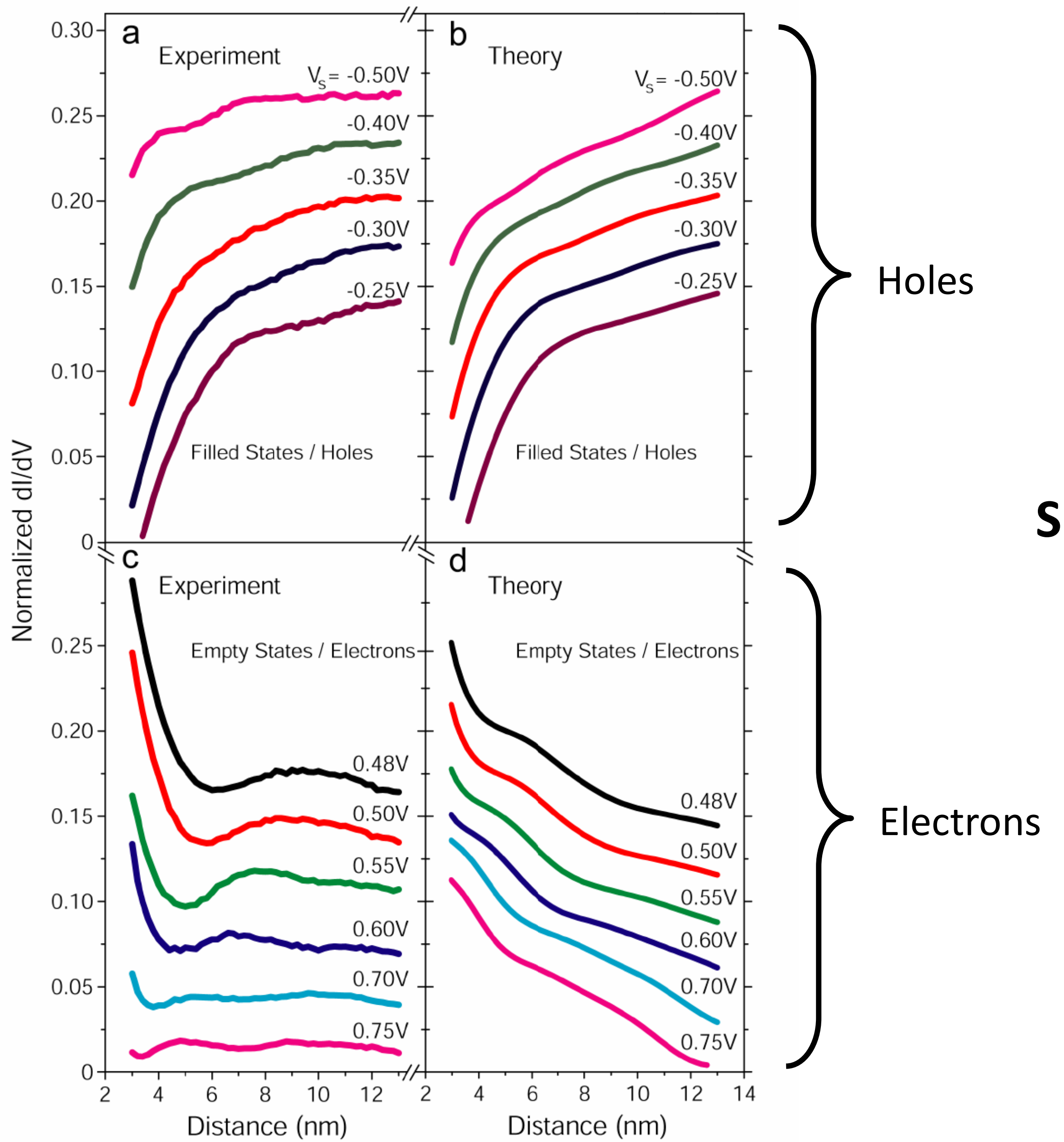
Previous Experiment for ε_g:

D. A. Siegel, et al., *PNAS* **108**, 11365 (2011): ε_g **< 6**

D. C. Elias, et al., *Nat Phys.* ***advance online pub*.** (2011): ε_g **= 2 - 5**

J. P. Reed, et al., *Science* **330**, 805 (2010): ε_g **= 15**

Spatial Dependence Reflects Charge Asymmetry



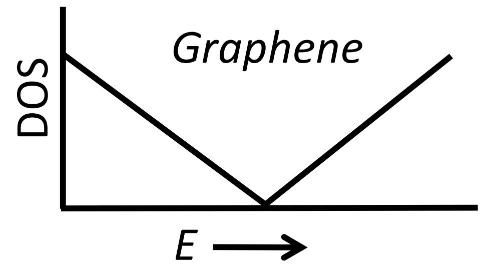
Cobalt Trimer:
Sub-critical Impurity

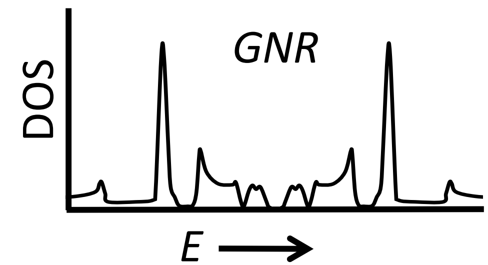
$\varepsilon_g = 3.0 \pm 1.0$

Y. Wang, et al., submitted for publication

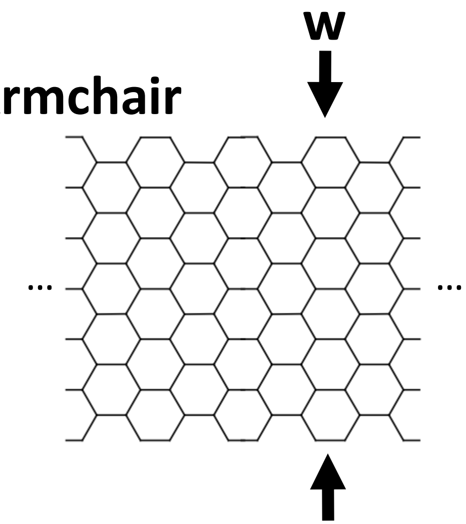
(II) Nanoribbons: Controlling the Edge

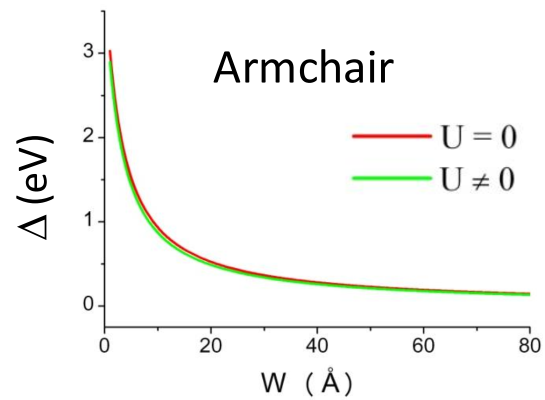
GNRs
- Tunable Gaps
- Edge-states
- Spin





Armchair





M. Fujita, *et al*., *J. Phys. Soc. Jpn* **65**, 1920 (1996)

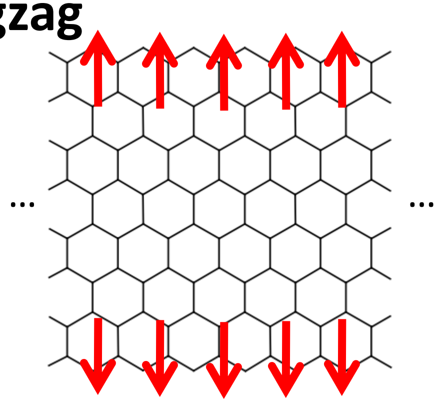
K. Nakada, *et al*., *PRB* **54**, 17954 (1996)

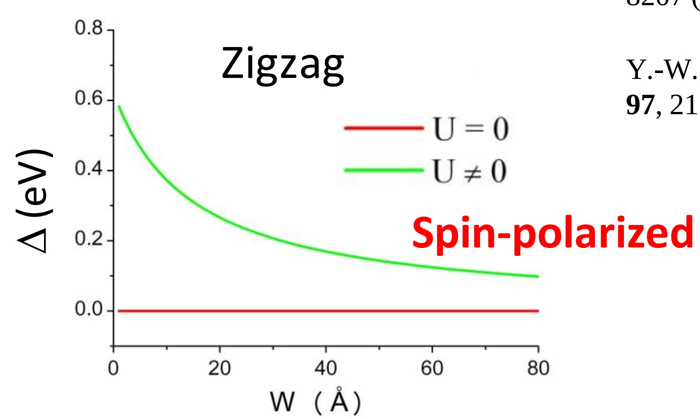
A. Yamashiro *et al*, *Phys.Rev. B* **68**, 193410 (2003)

J. Heyd *et al*, *J. Chem. Phys*. **118**, 8207 (2003)

Y.-W. Son *et al*, *Phys.Rev. Lett*. **97**, 216803 (2006)

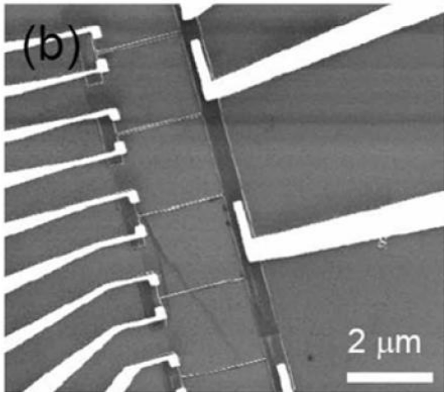
Zigzag





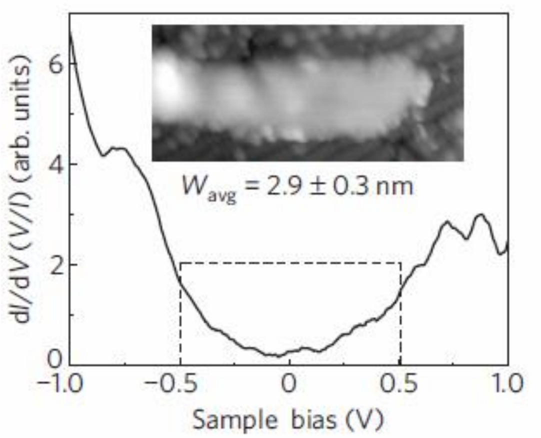
Some Previous Nanoribbon Investigations

Lithography: Transport



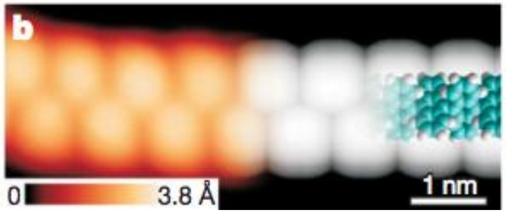
M. Y. Han *et al., PRL* **98**, 206805 (2007)

Graphene platelet on Si(100)



Ritter and Lyding, *Nat. Mat.* **8**, 235 (2009)

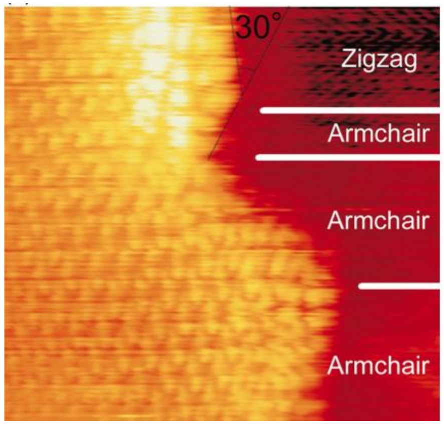
Armchair GNRs grown on Au



Jinming Cao et al., *Nature* **466**, 470 (2010)

Some Previous Edge Investigations

Graphite Step edge



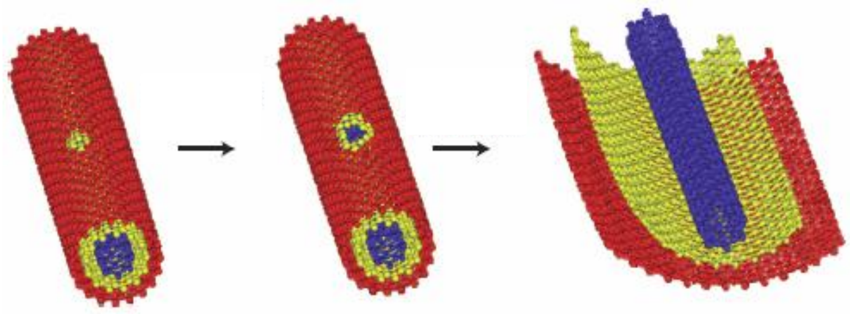
Y. Kobayash *et al.*, *PRB* **71**, 193406 (2005)

Graphene Edges on SiC & Cu

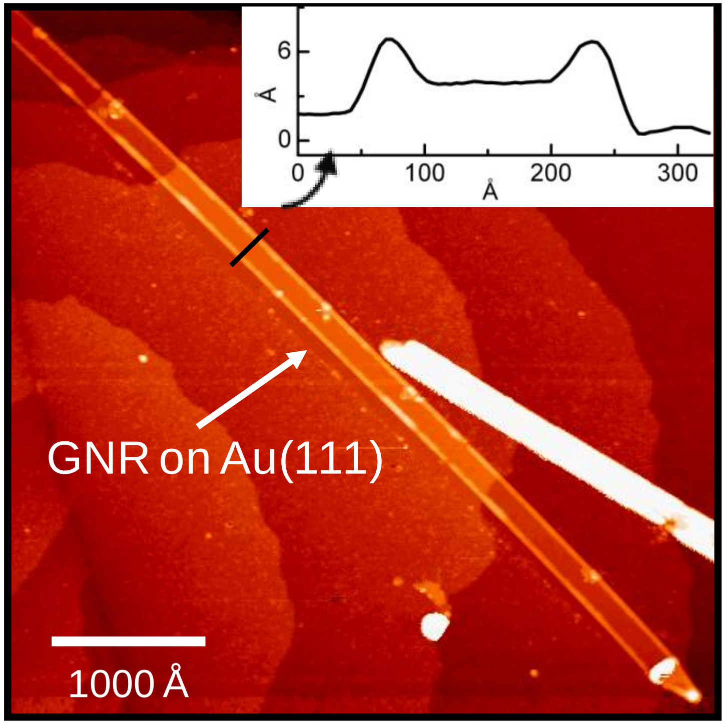
H. Yang, *et al.*, *Nano Lett.* **10**, 943 (2010) }
C. Park, *et al.*, *PNAS*, doi:10.1073 (2011) } SiC

J. Tian, *et al.*, *Nano Lett.* **11**, 3663 (2011) } Cu

GNRs from Unzipped Nanotubes



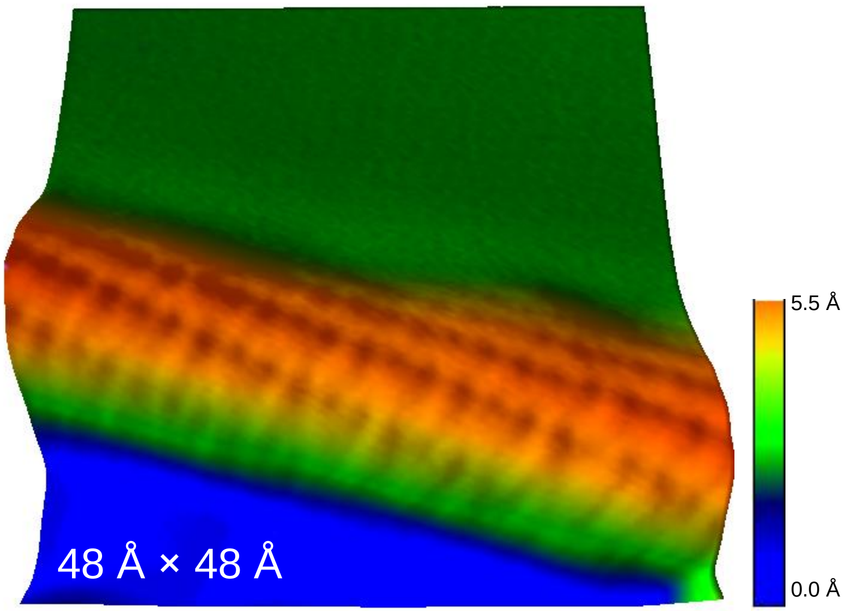
Jiao, et al, *Nat. Nanotechnol* **5**, 321 (2010)

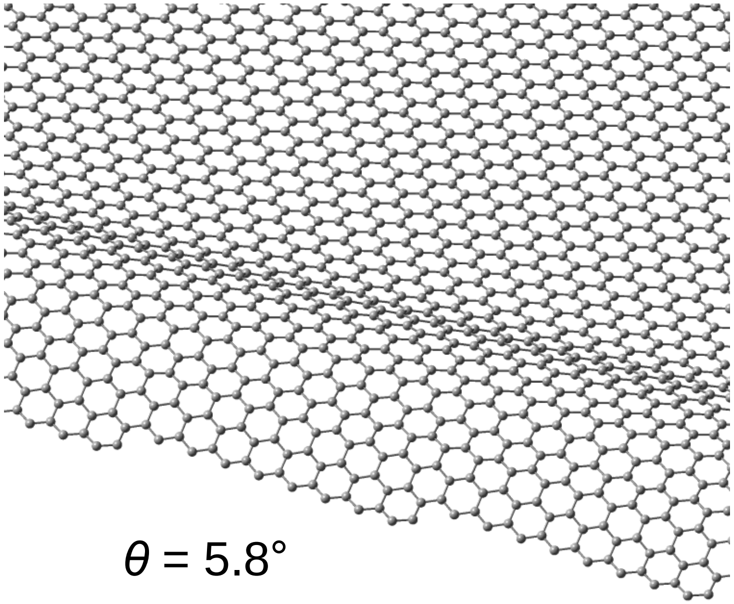


C. Tao, et al., *Nature Physics* **7**, 616 (2011)

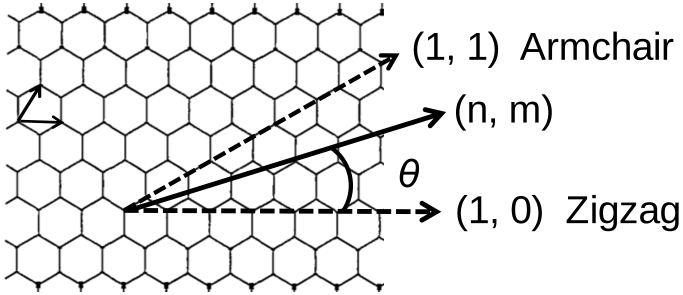
Different Chiralities Observed

Width = 19.8 nm



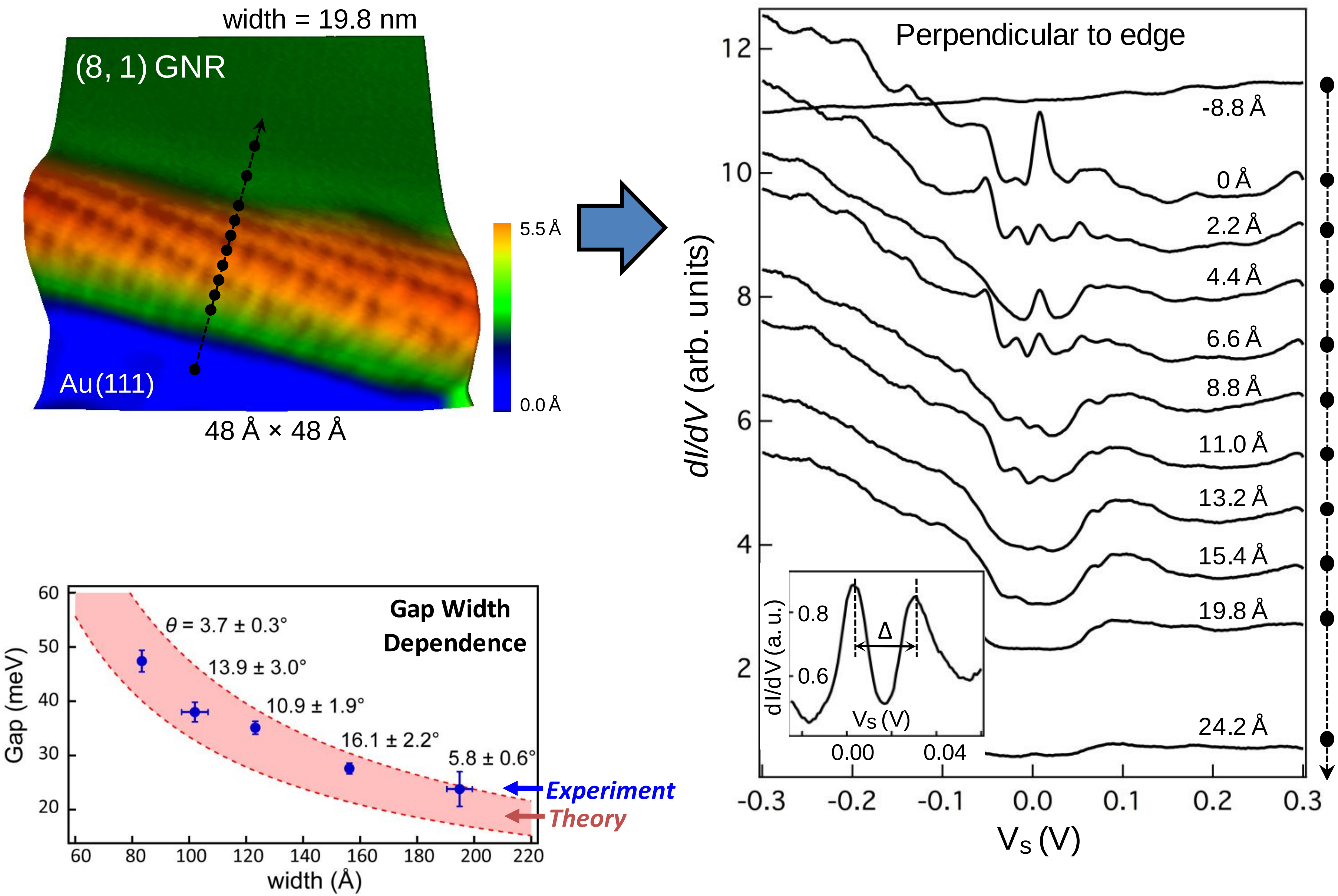


(8, 1) GNR



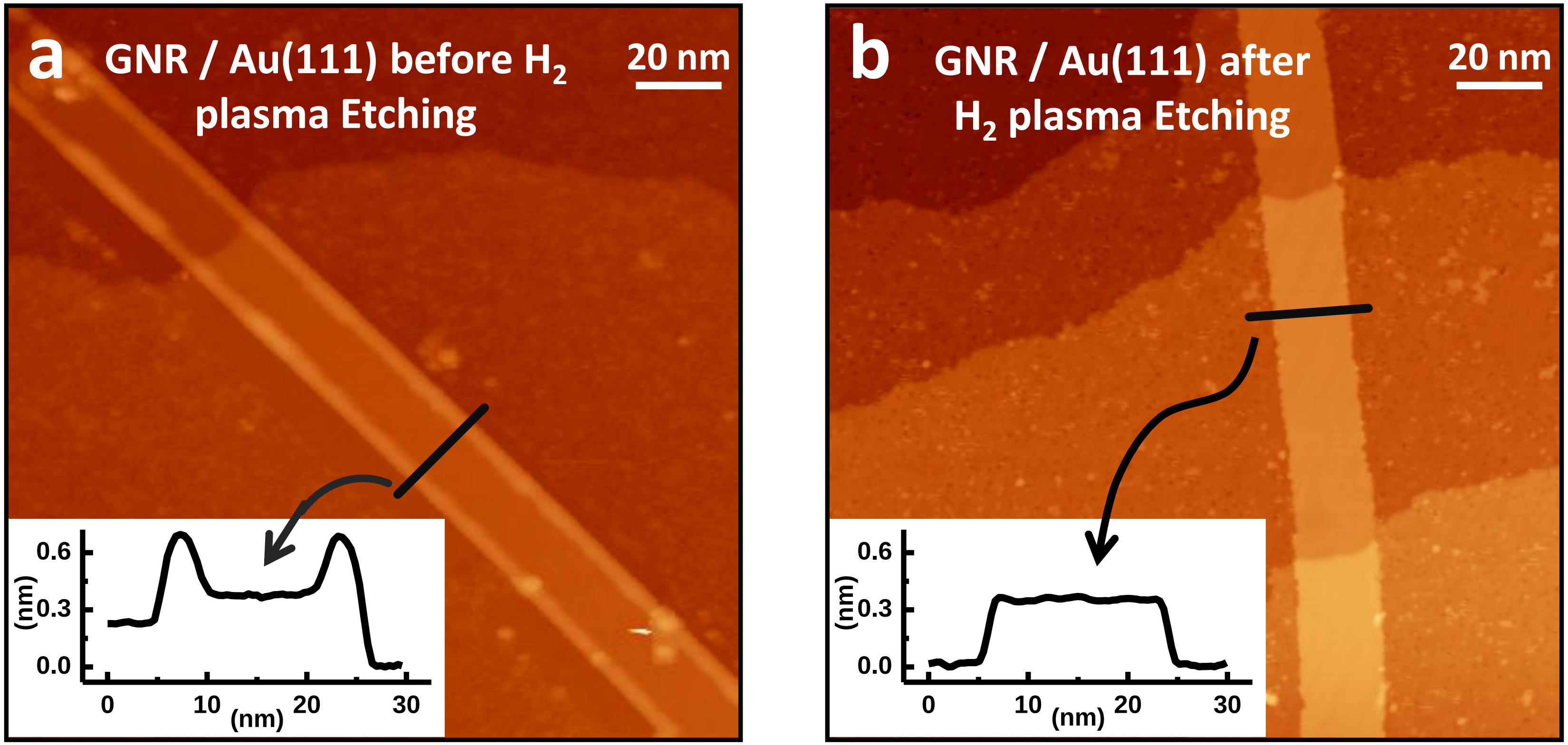
C. Tao, et al., *Nature Physics* **7**, 616 (2011)

STM Spectroscopy of Nanoribbon Edge State



C. Tao, et al., *Nature Physics* **7**, 616 (2011)

Control GNR Edge Through H_2 Plasma Etch

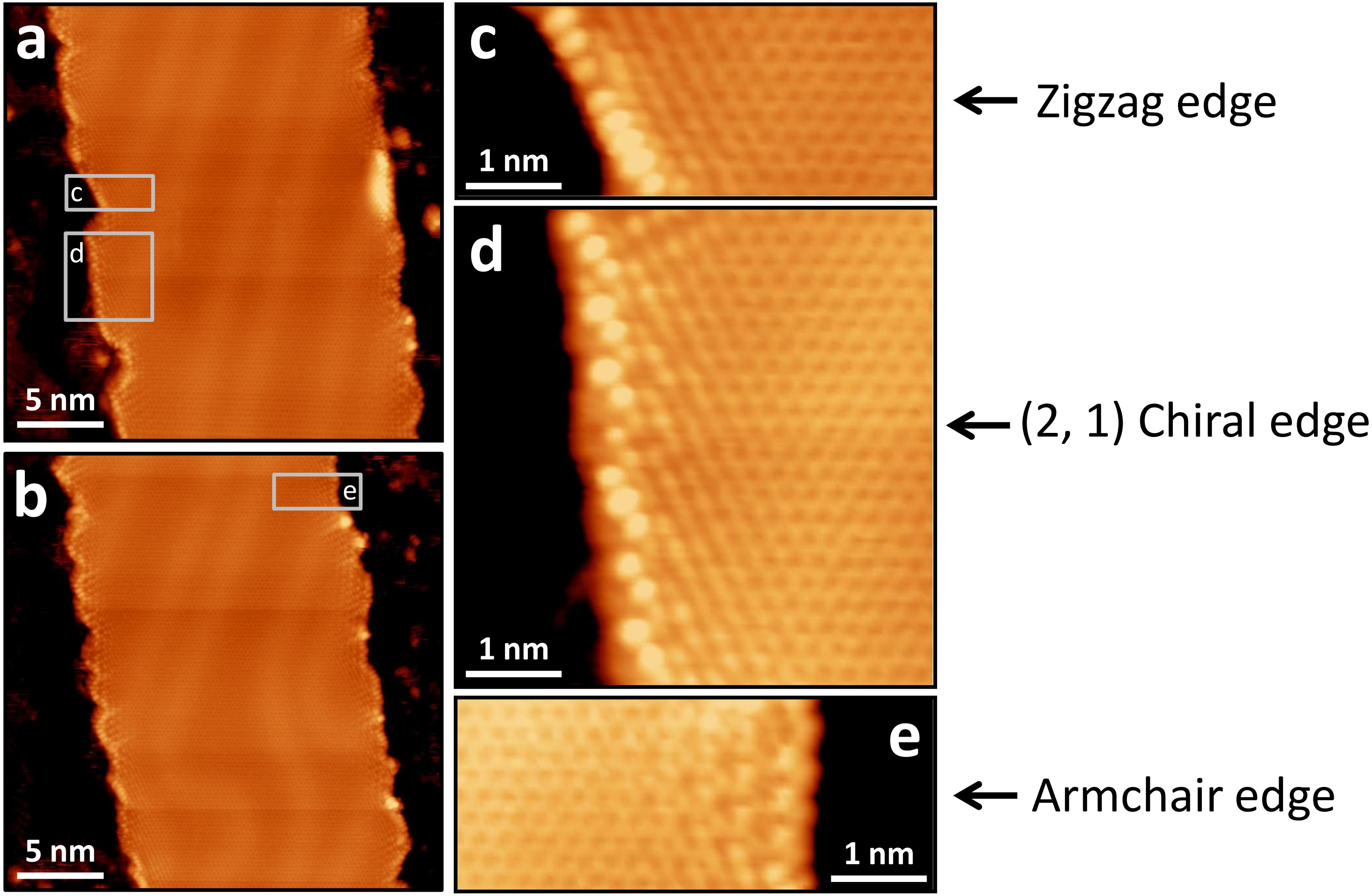


Room temperature STM

Crommie, Dai, Louie, Zettl (unpublished)

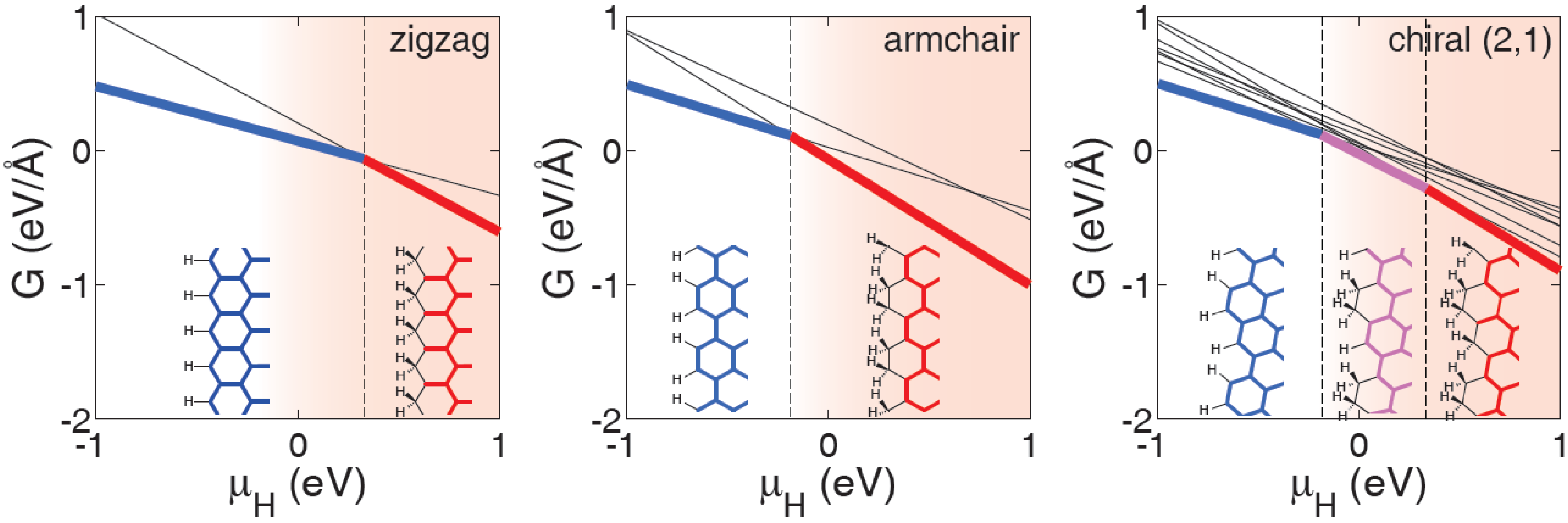
Nano-scale Structure of Edge

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



What is Hydrogen Edge Structure?

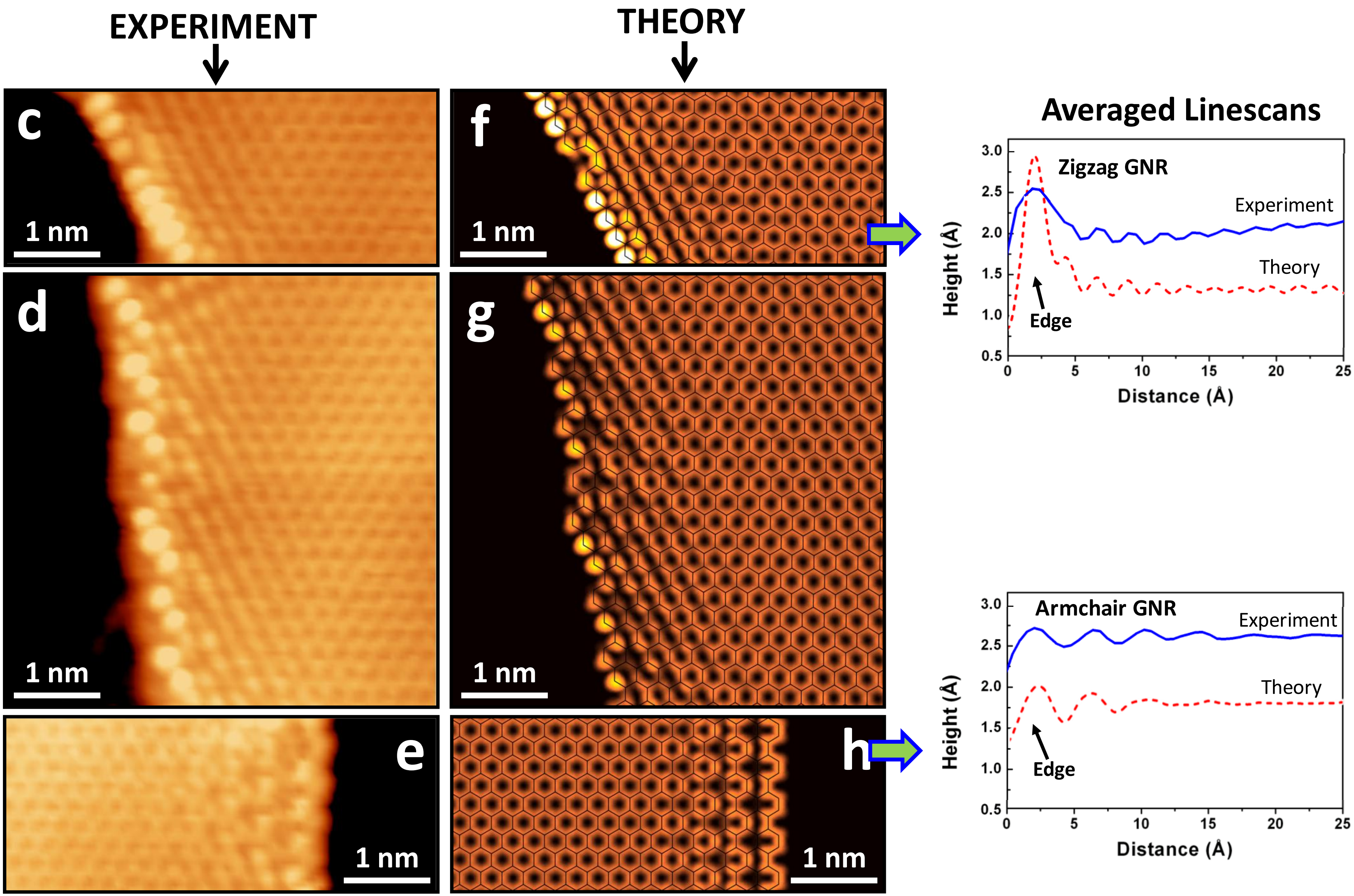
Calculate Thermodynamic Stability of Different Edge Structures



O. Yazyev, S. G. Louie & co-workers

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

Comparing Exp. Edge to Theory w/ Proper *H*-structure



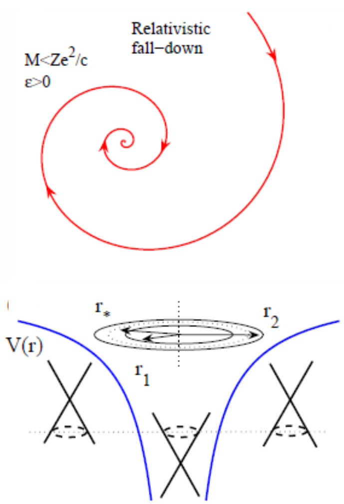
Conclusion

I) Dirac Fermion Screening of Tunable Charge Impurities

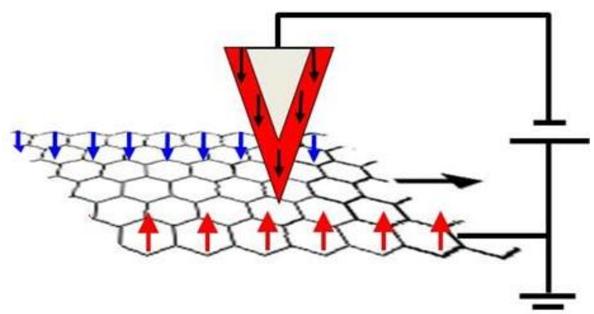
II) Controlling GNR Edges through Chemical Functionalization

Future:

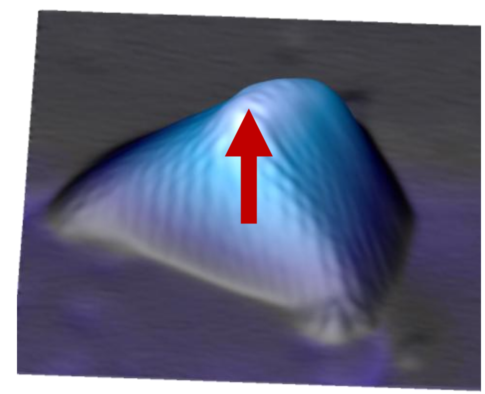
Atomic Collapse



SPSTM of GNRs



Pseudo-field and Spin



Collaborators:

co-PI's: M. F. Crommie, A. Zettl, S. G. Louie, J. M. Tour, H. Dai, L. Levitov

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