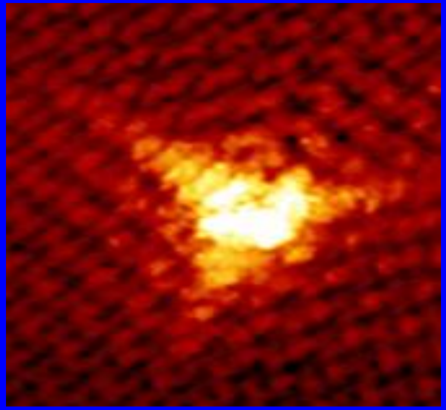
?Is there Kondo Screening in Graphene?

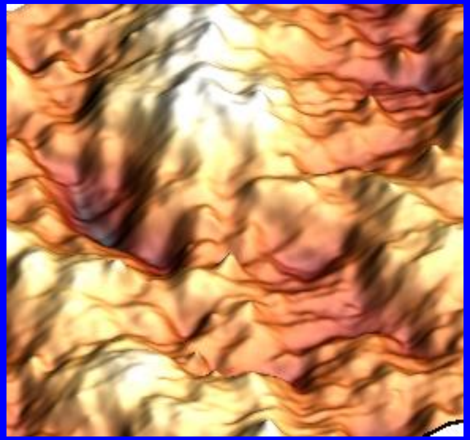
Vacancies in graphene



Eva Y. Andrei

Rutgers University

Vacancy Magnetic moment and Kondo screening



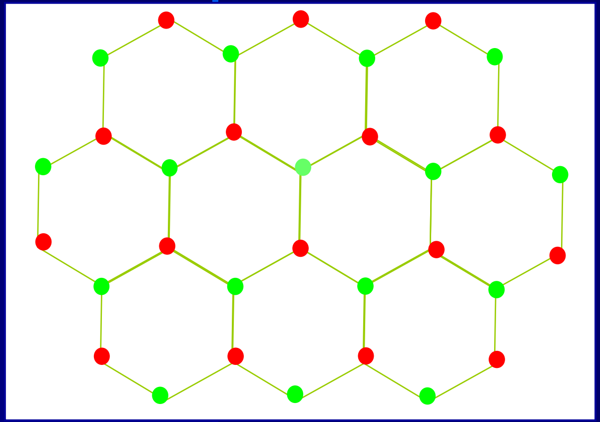
Y Jiang et al Nature Communications 2018
J. Mao et al arXiv:1711.06942 (2017)

D. May et al , Phys. Rev. B 97, 155419 (2018)

THE BATSHEVA DE ROTHSCHILD SEMINAR ON TOPOLOGY MEETS DISORDER AND INTERACTIONS:
PRESENT CHALLENGES, FUTURE PROMISES

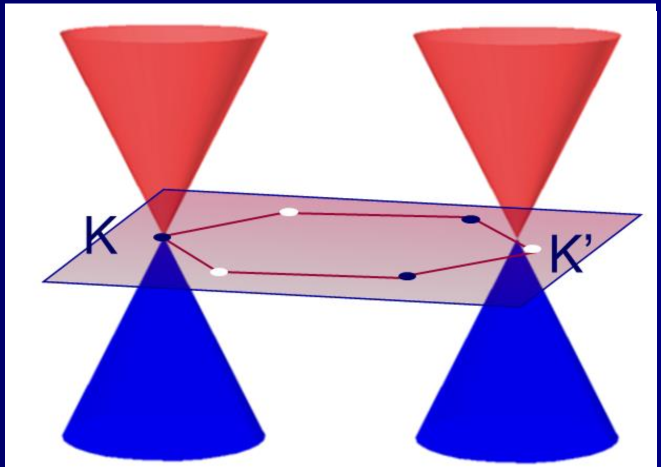
27-31 MAY, 2018
RAMON INN
MITZPE RAMON

Perfect Graphene



sp^2 Carbon

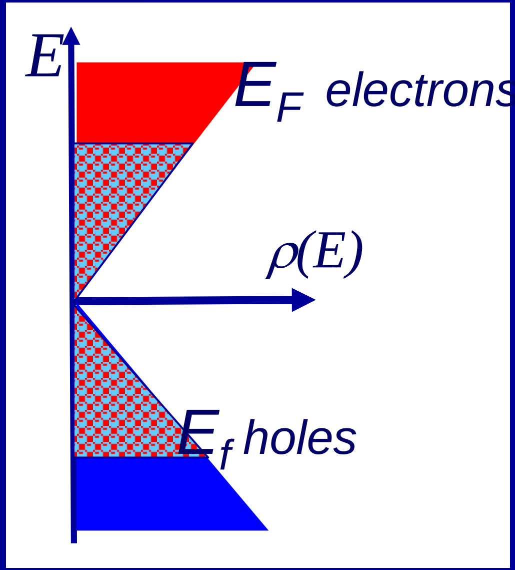
Band structure



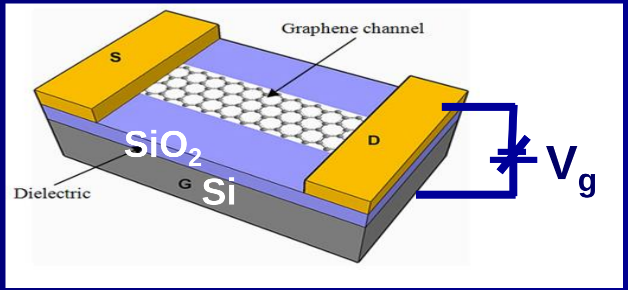
$$E = v_F p$$

Ultra-relativistic
Chiral quasiparticles

Density of states



1V $\mapsto$ 7x10^{10} cm^{-2}



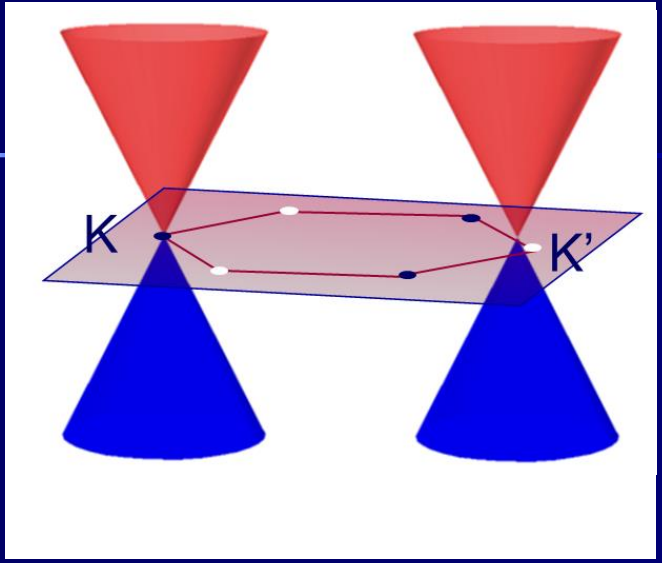
Ingredients:

1. 2D
2. Honeycomb structure
3. Identical atoms

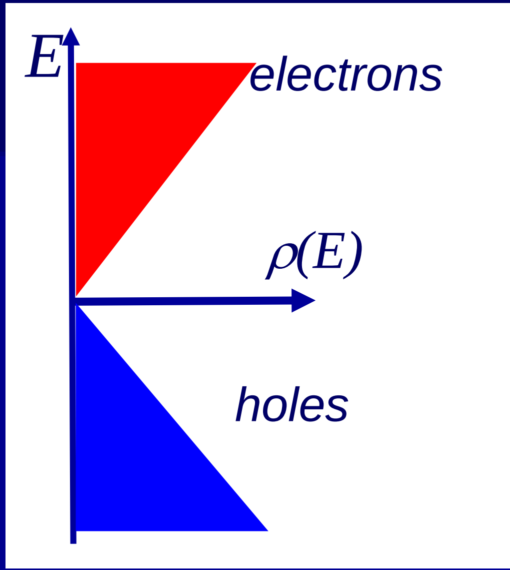
E.Y. Andrei

Perfect Graphene

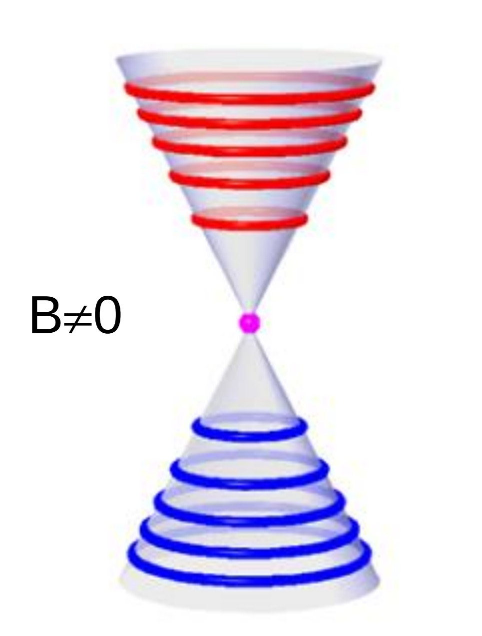
Band structure



Density of states

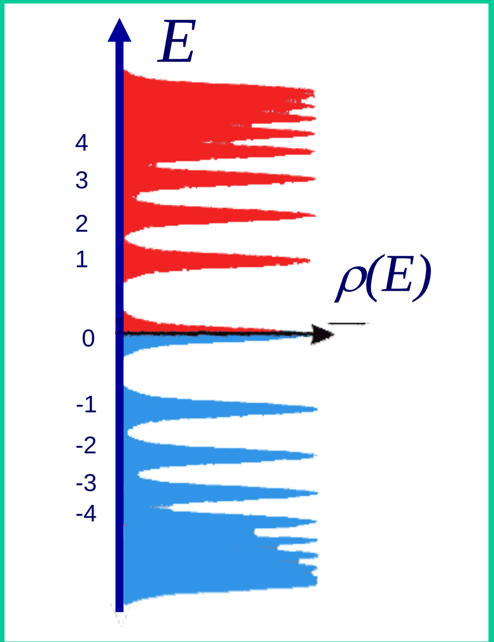


Finite Magnetic field
B>0



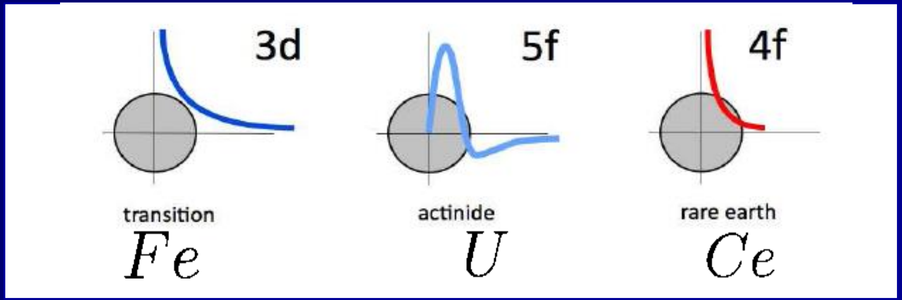
Landau Levels

$$E_N = \pm v_F \sqrt{2e\hbar B|N|} \quad N = 0,1,2..$$



Perfect Graphene

Magnetism: Spin of localized electrons in partially filled inner d or f shell .

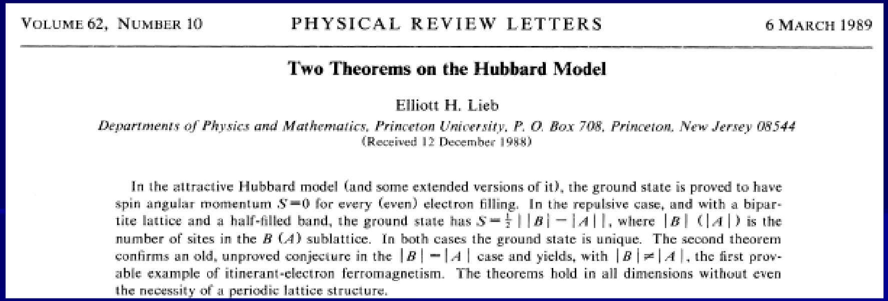


Carbon

- *No d, f electrons*
- *But partially filled p shell*

Graphite, graphene, …, Carbon allotropes
? Non-Magnetic ?

Magnetism and Perfect Graphene


VOLUME 62, NUMBER 10 PHYSICAL REVIEW LETTERS 6 MARCH 1989

Two Theorems on the Hubbard Model

Elliott H. Lieb
Departments of Physics and Mathematics, Princeton University, P. O. Box 708, Princeton, New Jersey 08544
(Received 12 December 1988)

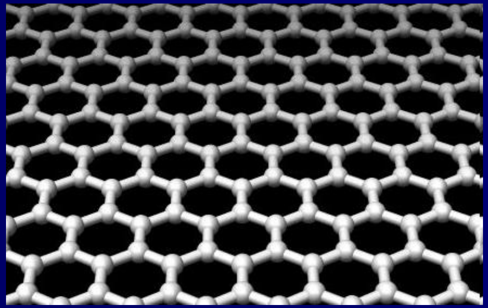
In the attractive Hubbard model (and some extended versions of it), the ground state is proved to have spin angular momentum $S=0$ for every (even) electron filling. In the repulsive case, and with a bipartite lattice and a half-filled band, the ground state has $S=\frac{1}{2}||B|-|A||$, where $|B|$ ($|A|$) is the number of sites in the B (A) sublattice. In both cases the ground state is unique. The second theorem confirms an old, unproved conjecture in the $|B|=|A|$ case and yields, with $|B|\neq|A|$, the first provable example of itinerant-electron ferromagnetism. The theorems hold in all dimensions without even the necessity of a periodic lattice structure.

...repulsive Hubbard model + **bipartite lattice** + **half-filled** band:

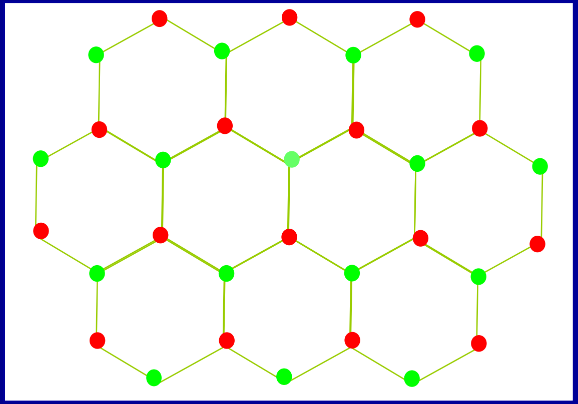
spin of ground state with N_A, N_B populated sites:

$$S = 1/2(N_A - N_B)$$

Pristine graphene (graphite) $N_A = N_B \rightarrow S=0$



Perfect graphene
Non-Magnetic!



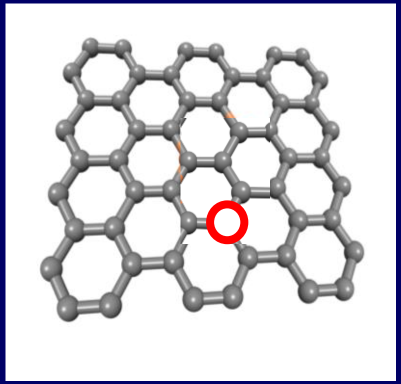
Vacancies $\rightarrow N_A > N_B \mapsto$ magnetic moment

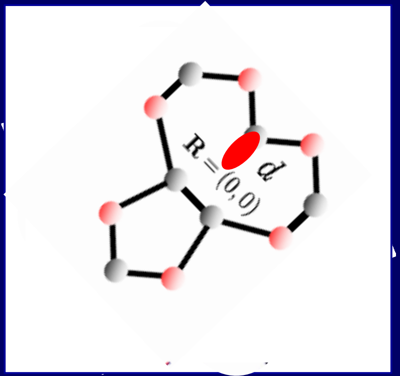
A.H. Castro Neto et al. Solid State Commun. (2009).
T. Wehling,. Phys. Lett. (2009)
O. Yazyev, et al Rep. Prog. (2010).
M. Vojta *et.al*, EPL, 90 (2010) 27006
T. O. Wehling, Phys. Rev. B 81, 115427(2010)
J. O. Sofo, et al Phys. Rev. B 85, 115405 (2012)

E.Y. Andrei

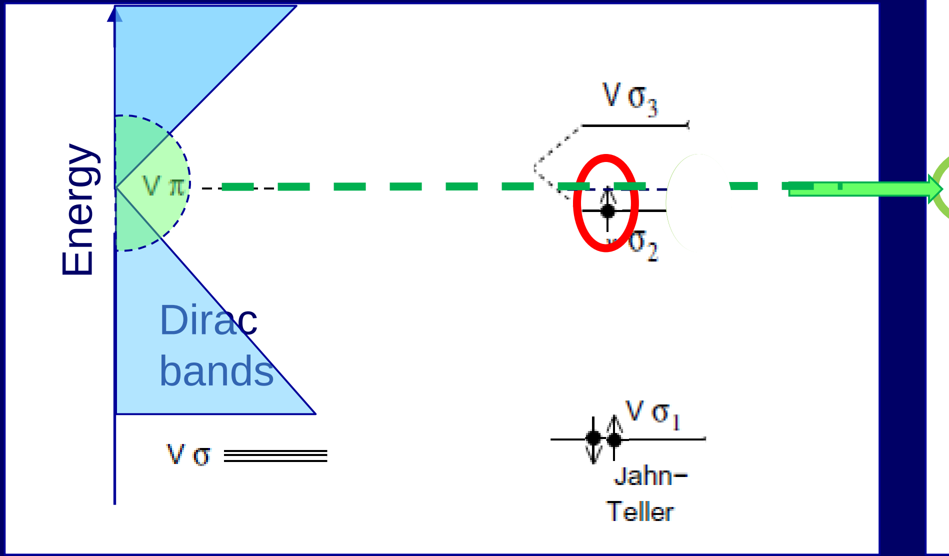
Imperfect Graphene – Vacancy Magnetic Moment

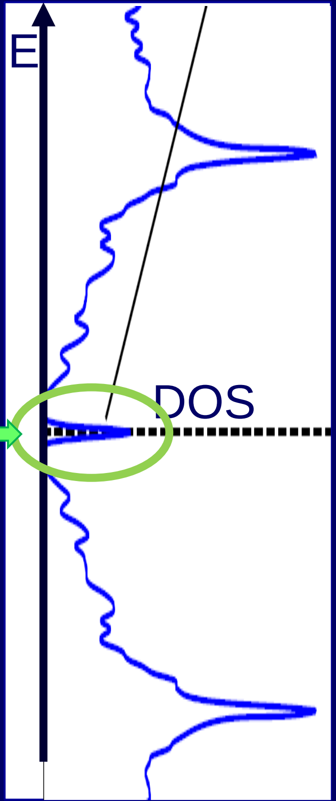
remove
Carbon atom





Yazyev & Helm (2007),
Popovi’c, Nanda, Satpathy (2012)





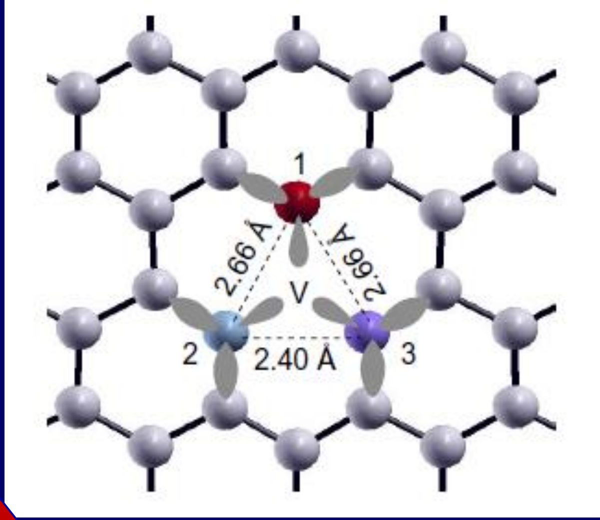
Broken
AB
symmetry

σ Dangling bond $\mapsto$ localized state $\mapsto$ $1\mu_B$

p_z $\mapsto$ quasi-localized state on other sublattice $\mapsto$ ~0.5-$0.7\mu_B$

Zero mode peak at ~Dirac Point

Vacancy Properties



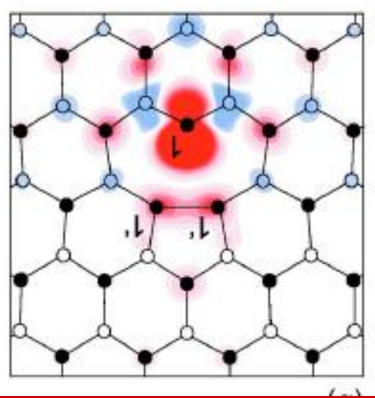
Interaction of ultra-relativistic electron with magnetic moment?

Interaction of ultra-relativistic electron with Point charge ?

Magnetic

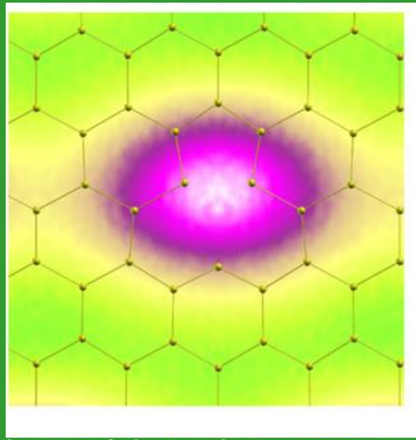
Charge

~ $1.7\mu_B$



Yazyev & Helm (2007)

Charge ~ +1|e|



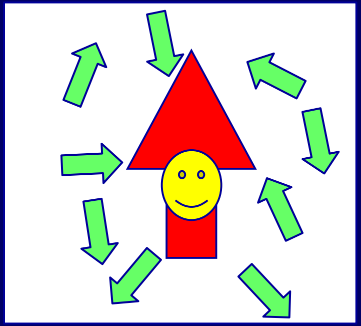
Y Liu et al (2015)
Padmanabhan & Nanda (2016)

Andrei

Kondo Screening of Impurity Moments in Metals

$T>T_K$

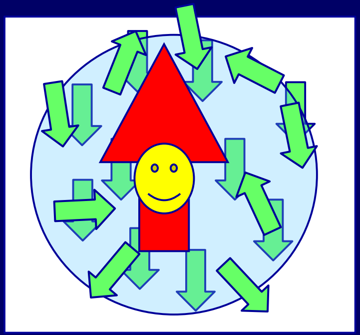
Unscreened



J antiferromagnetic coupling to electron bath

$T<T_K$

Screened



$$T_K \propto \exp(-1/\rho J)$$

ρ ***density of states at*** $\boldsymbol{E_F}$

$\rho(E_F) > 0$, $J>0 \mapsto T_K > 0$

- ❖ Normal metals $\rho(E_F) \sim \textit{finite};\ J \neq 0$ $\mapsto$ $T_K > 0$
- ❖ Insulators $\rho(E_F) = 0$ No Kondo screening

What happens in a pseudogap system?

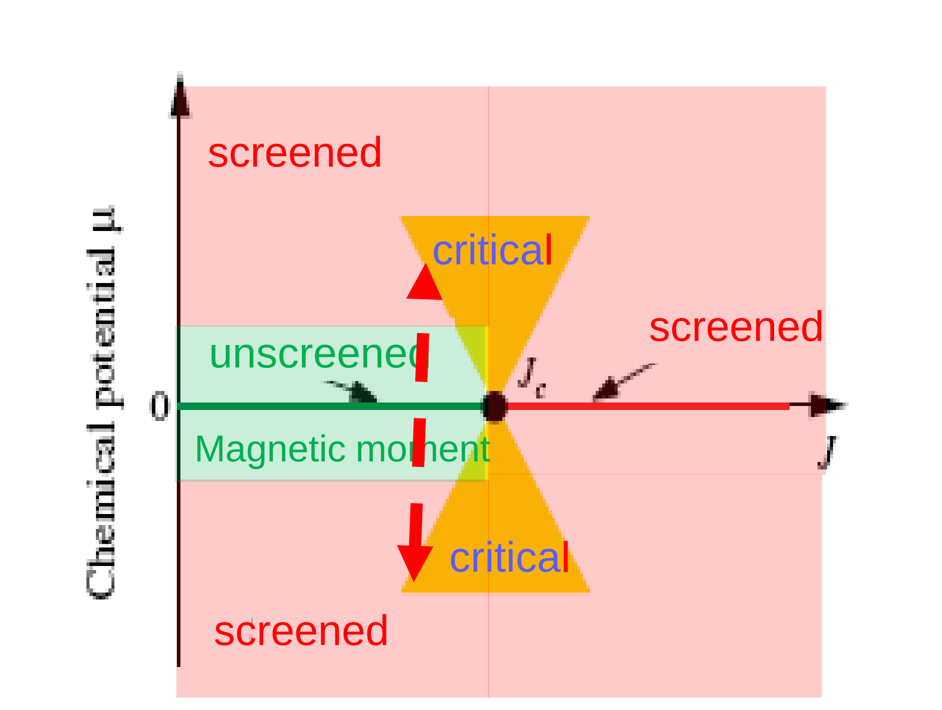
E.Y. Andrei

Kondo Screening in pseudo-gap systems

- Pseudo- gap systems $\rho(E) \propto E^r$ screening suppressed.
  - r = 1 (graphene, high T_c superconductors)

μ~0 (undoped)
- Kondo screening only for J>Jc
- J_c finite only for p-h asymmetry

|μ|>>0 doped
- Normal Kondo screening

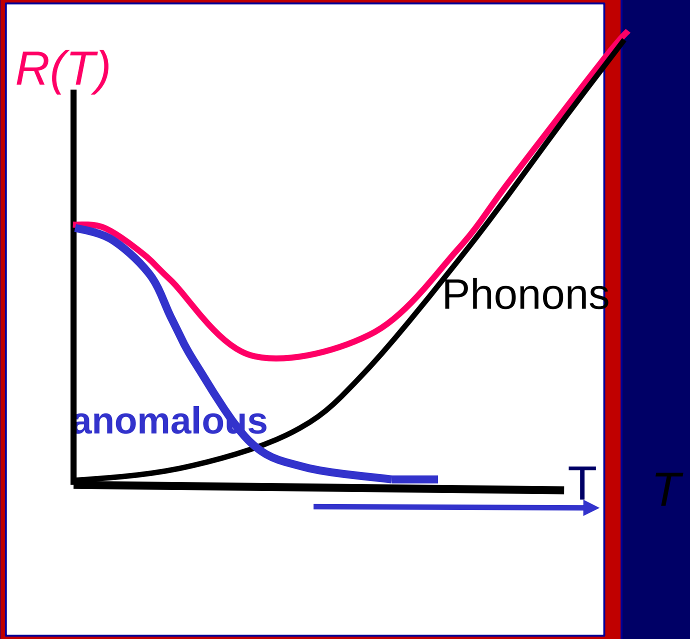


- D. Withoff and E. Fradkin, Phys. Rev. Lett. 64, 1835(1990)
- K. Chen and C. Jayaprakash, J. Phys L491 (1995)
- K. Ingersent, Phys. Rev. B54, 11936 (1996)
- C. Cassanello and E. Fradkin , (1996)
- R. Bulla, T. Pruschke, and A. C. Hewson, (1998)
- Polkovnikov A., Phys. Rev. B, 65 (2002) 064503
- Vojta M. and Fritz L., Phys. Rev. B, 70 (2004) 094502.
- Vojta, Fritz, Bulla EPL (2010)
- PW Lo, GY Guo, F. Anders, arXiv:1402.0040

Electrical tuning of magnetic moment

Kondo Screening Experimental Signatures

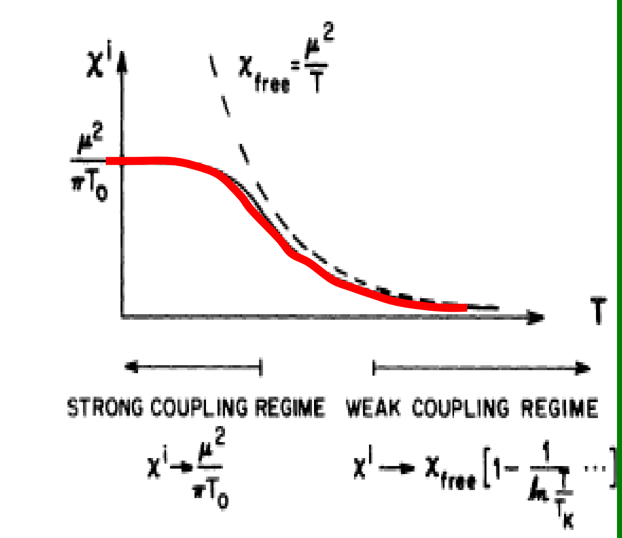
Resistance minimum



- R(T) minimum at T~ T_K
- Logarithmic scaling with T/T_K

Measures:
scattering off Kondo cloud

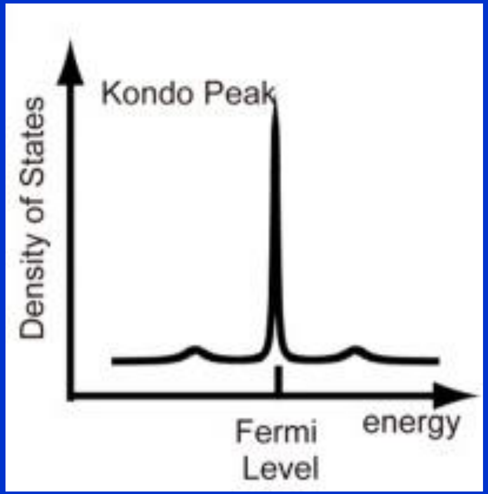
Magnetization saturation



- Low T saturation of χ
- Logarithmic corrections to Curie scale with T/T_K

Measures:
Unscreened moment

DOS – Kondo Peak



- Kondo Peak at E_F
- Low T linewidth Γ

$$k_B T_K \sim \Gamma/2$$

DOS enhancement at E_F

E.Y. Andrei

Is there Kondo screening?

nature physics
LETTERS
PUBLISHED ONLINE: 3 APRIL 2011 | DOI: 10.1038/NPHYS1962

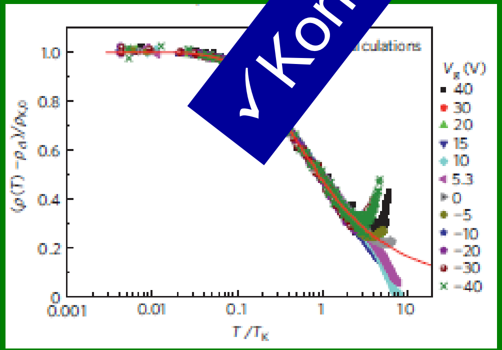
Tunable Kondo effect in graphene with defects

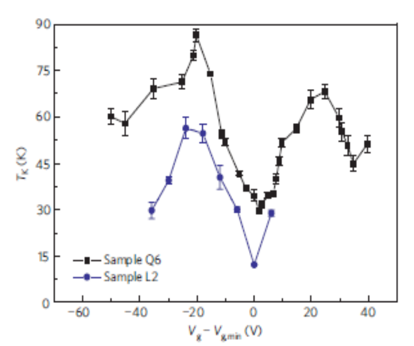
Jian-Hao Chen[1,2†], Liang Li[2], William G. Cullen[1,2], Ellen D. Williams[1,2] and Michael S. Fuhrer[1,2]★

Single layer graphe
He ion irradiation + ...nsport

- R(T) $\mapsto$ Ko... creening
  - T_K ...

✓Kondo screening





nature physics
LETTERS
PUBLISHED ONLINE: 10 JANUARY 2012 | DOI: 10.1038/NPHYS2183

Spin-half paramagnetism in graphene induced by point defects

R. R. Nair[1], M. Sepioni[1], I-Ling Tsai[1], O. Lehtinen[2], J. Keinonen[2], A. V. Krasheninnikov[2,3], T. Thomson[1], A. K. Geim[1] and I. V. Grigorieva[1]★

ARTICLE
Received 12 Mar 2013 | Accepted 15 May 2013 | Published 12 Jun 2013
DOI: 10.1038/ncomms3010

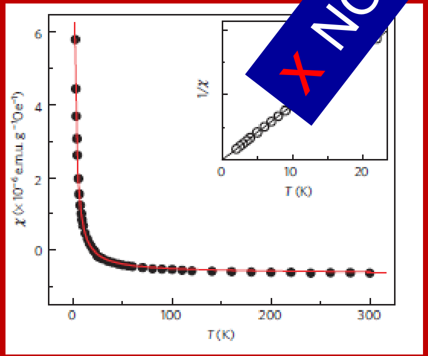
Dual origin of defect magnetism in graph... and its reversible switching by molecul...ng

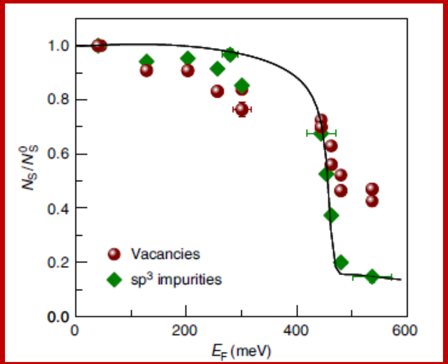
R.R Nair[1], I-L Tsai[1], M. Sepioni[1], O. Lehtinen[2], J. Keinonen[2], A.V Krasheninnikov[2,...] ...eto[4], M.I Katsnelson[5], A.K Geim[1] & I.V Grigorieva[1]

Graphite laminates
proton irradiation + Squid ...netometry

- $\chi(T) \mapsto$ No Kondo ...eening
- Moments unsc...ed at low T
- No full scree... with doping

✗ NO Kondo screening !

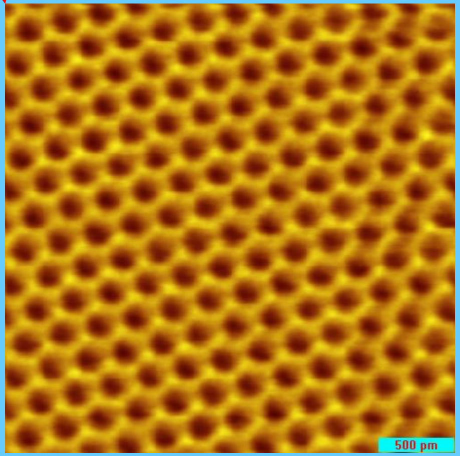




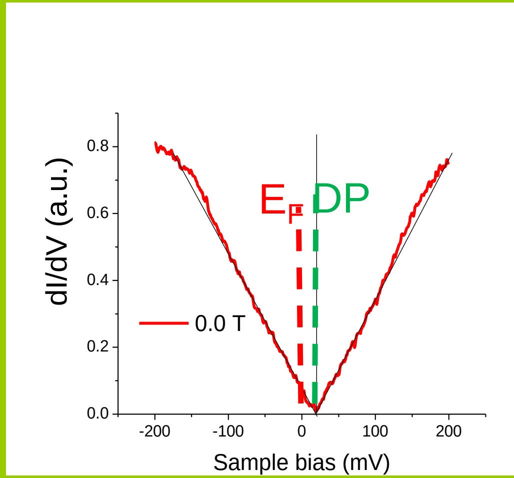
...drei

STM

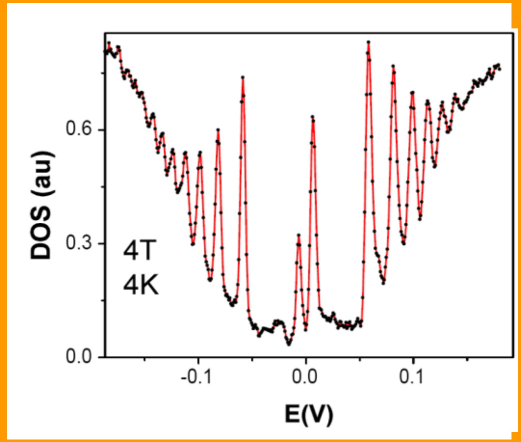
topography



B=0 spectroscopy



B>0 spectroscopy



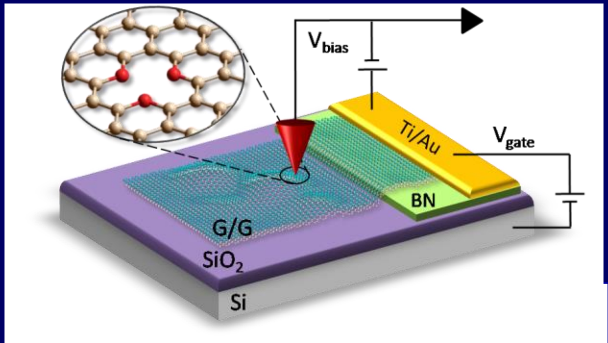
- Local doping

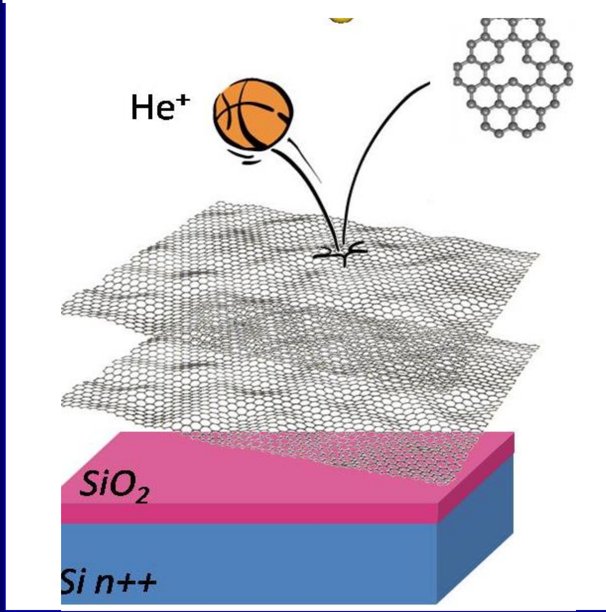
$$E_N = \pm v_F \sqrt{2e\hbar B|N|}$$

- Local Fermi velocity
- Quasiparticle lifetime
- Coupling to substrate

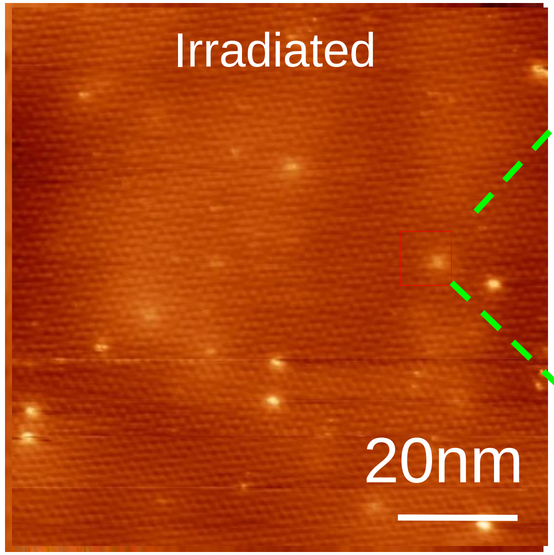
G. Li , E.Y. A - Nature Physics, (2007)
G. Li, A. Luican, E. Y. A., Phys. Rev. Lett (2009)

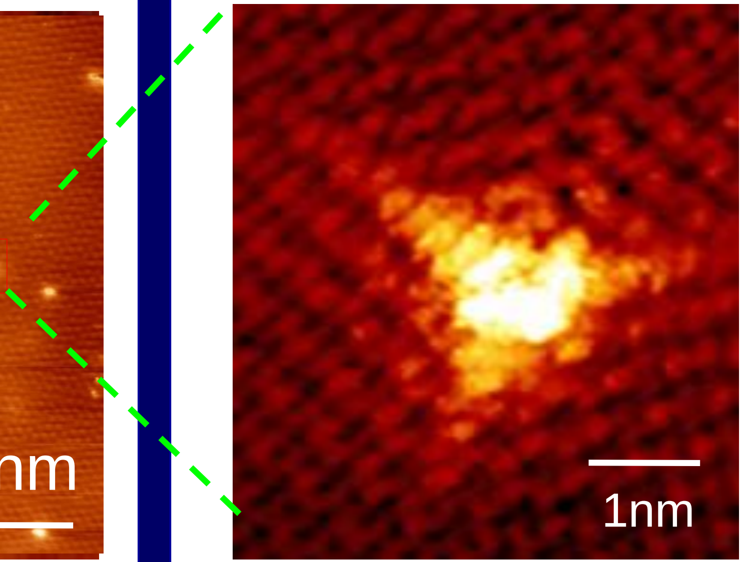
Probing Vacancies with STM/STS





STM Topography

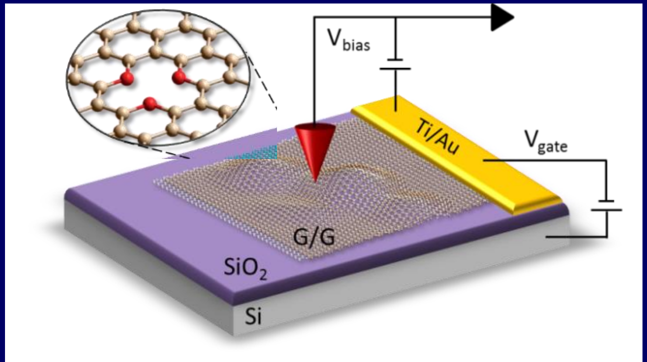


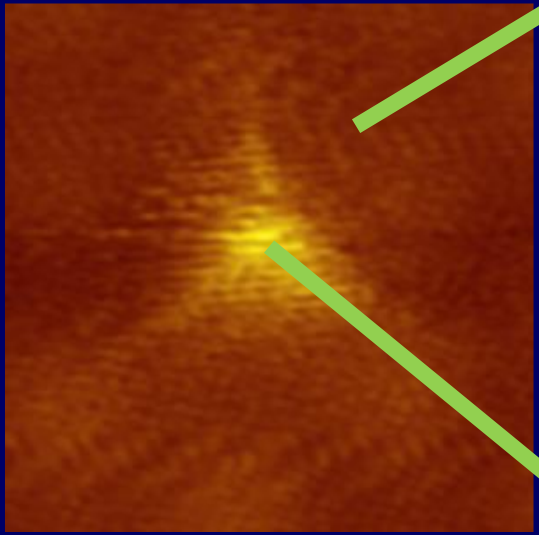


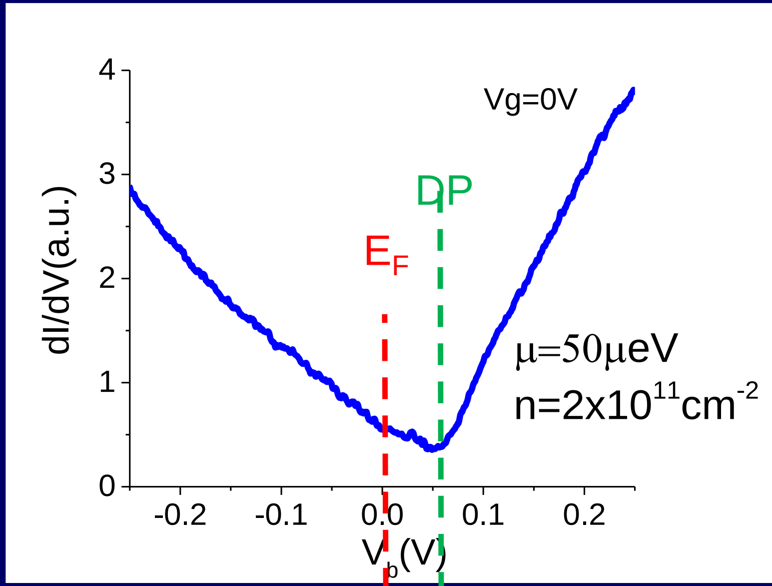
Single atom vacancy ➔ triangular structure.

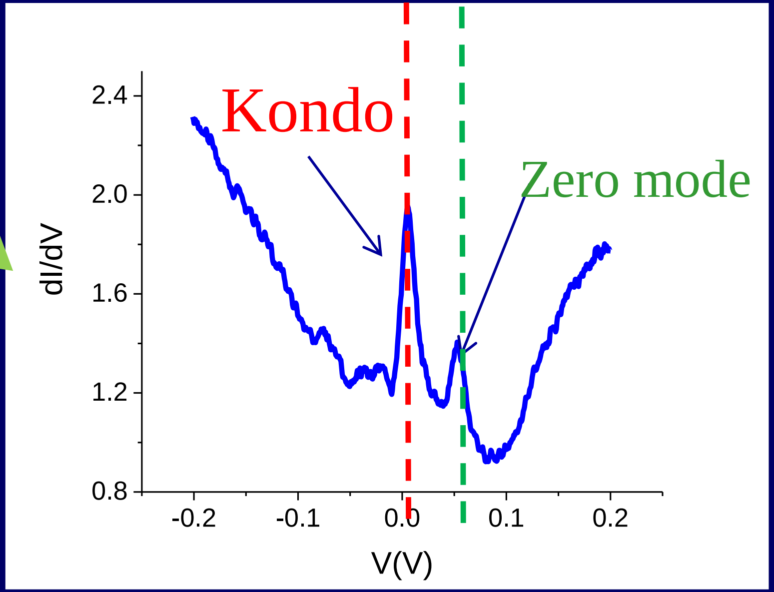
M. M. Ugeda, *et al* PRL 104, 096804 (2010).

STS: DOS





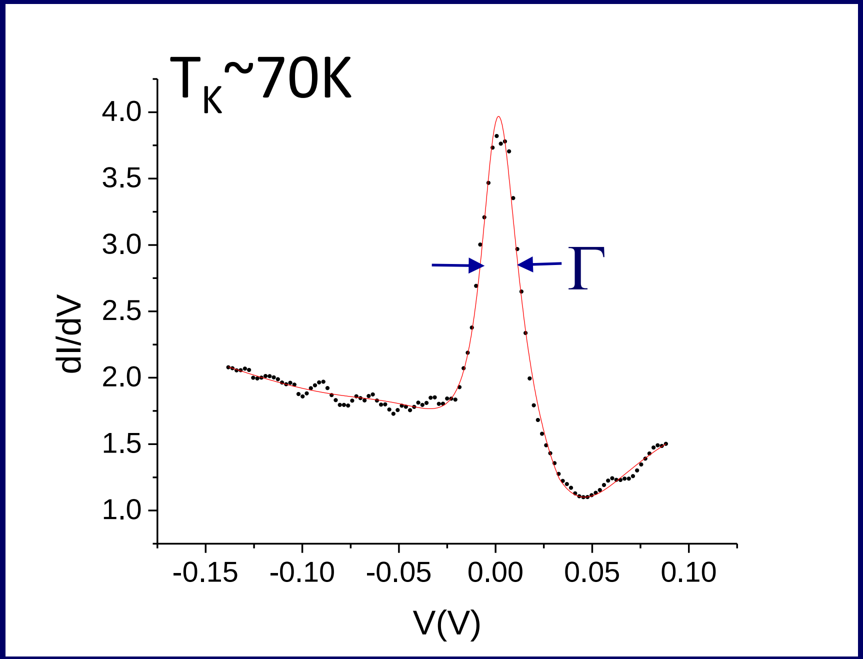


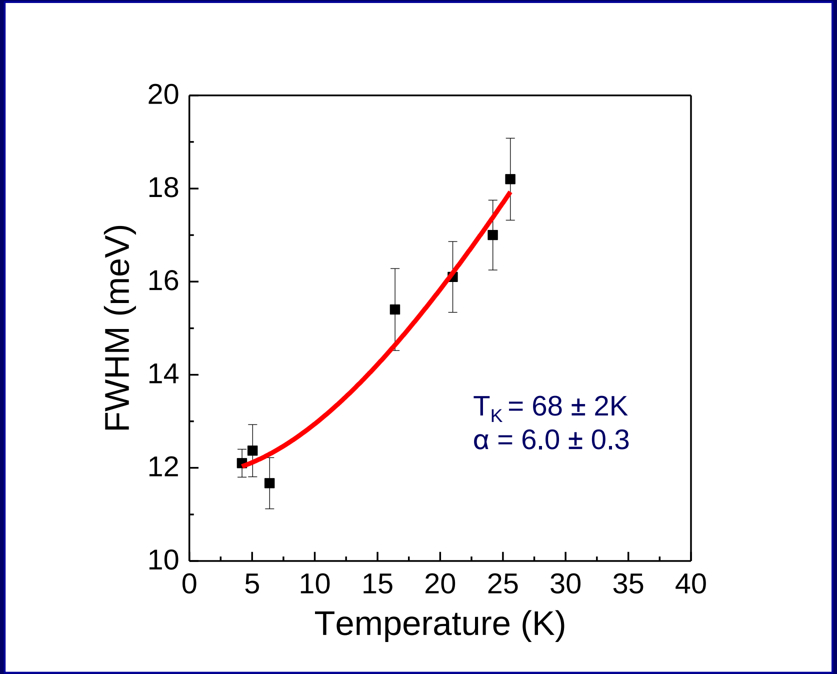


Y Jiang et al
Nature Communications 2018

E.Y. Andrei

Kondo Temperature





Fit to Fano lineshape

$$\frac{dI(V)}{dV} = A\frac{(\varepsilon + q)^2}{1 + \varepsilon^2} + B$$

Fit to T dependence

$$\Gamma = \sqrt{(\alpha k_B T)^2 + (2k_B T_K)^2}$$

$$\varepsilon = \frac{E - \varepsilon_0}{\Gamma/2}$$

$$k_B T_K \sim \Gamma/2$$

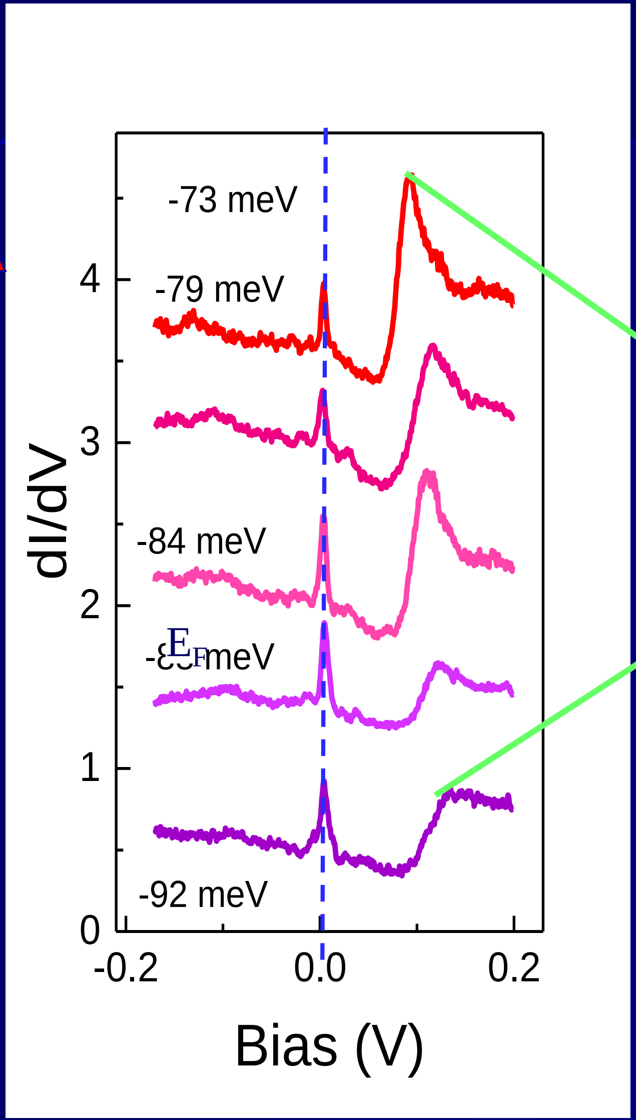
O. Újsághy, et al. Solid State Commun. **117**, 167(2001)
A.S. Zyazin, et al. Synthetic Metals **161**, 591 (2010)
M. Ternes, *et.al.* J. Phys.: Condens. Matter 21, 053001, (2009)

E.Y. Andrei

Gate Dependence

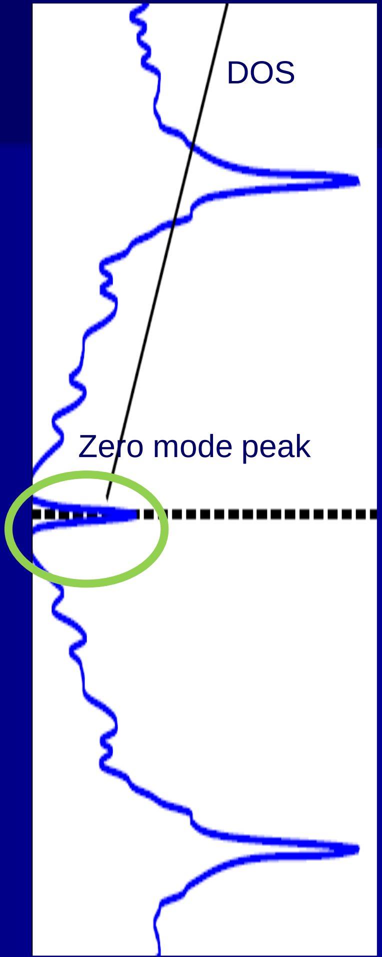
Kondo Peak

Increasing μ



Pinned to E_F

Zero mode

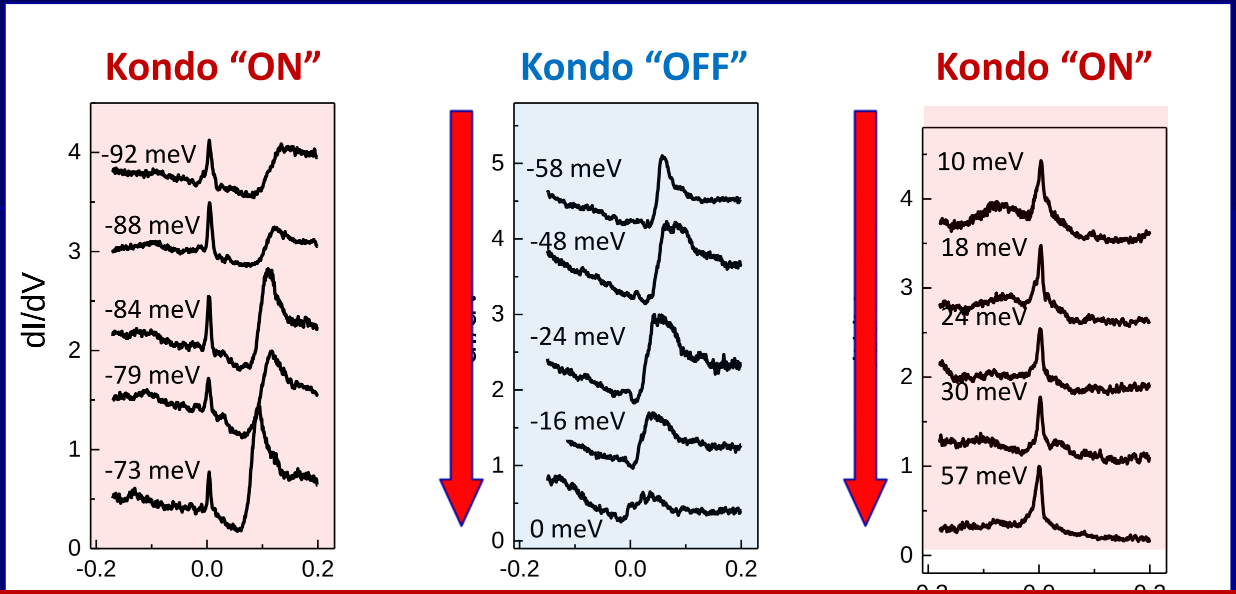


Y Jiang et al
Nature Communications 2018

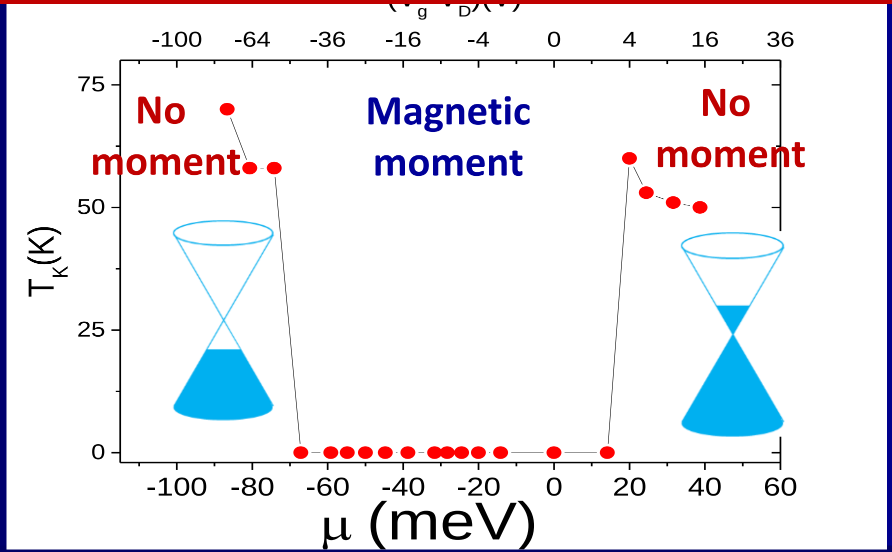
E.Y. Andrei

Reentrant Kondo Screening

Increasing μ



Electrically tuned magnetic moment



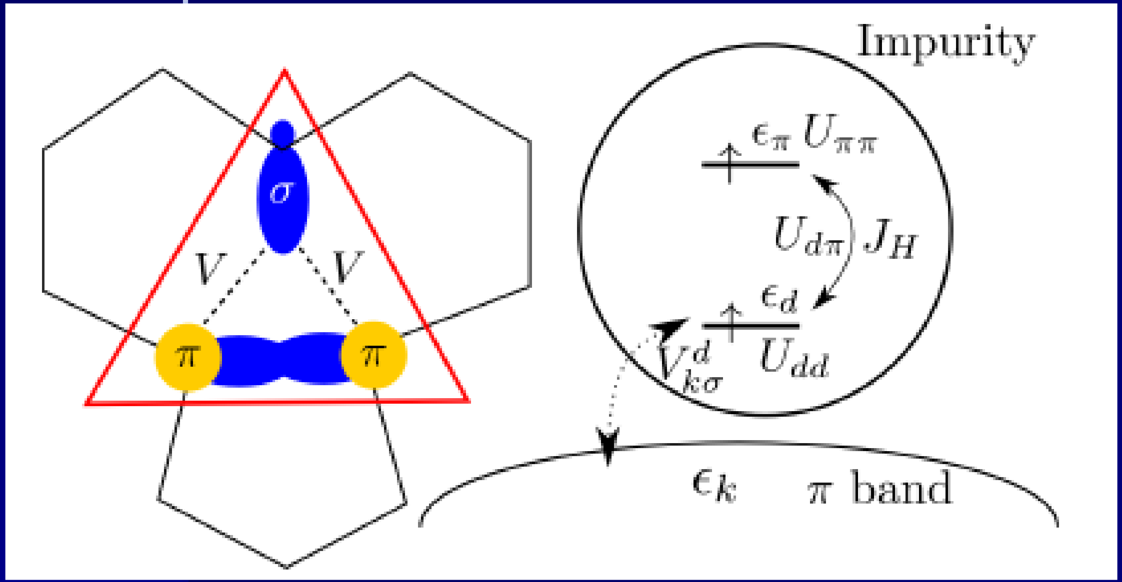
$J<J_c$

Y Jiang et al
Nature Communications 2018

E.Y. Andrei

Model for Kondo screening of vacancy moment

- Anderson impurity model
- Numerical renormalization group calculations

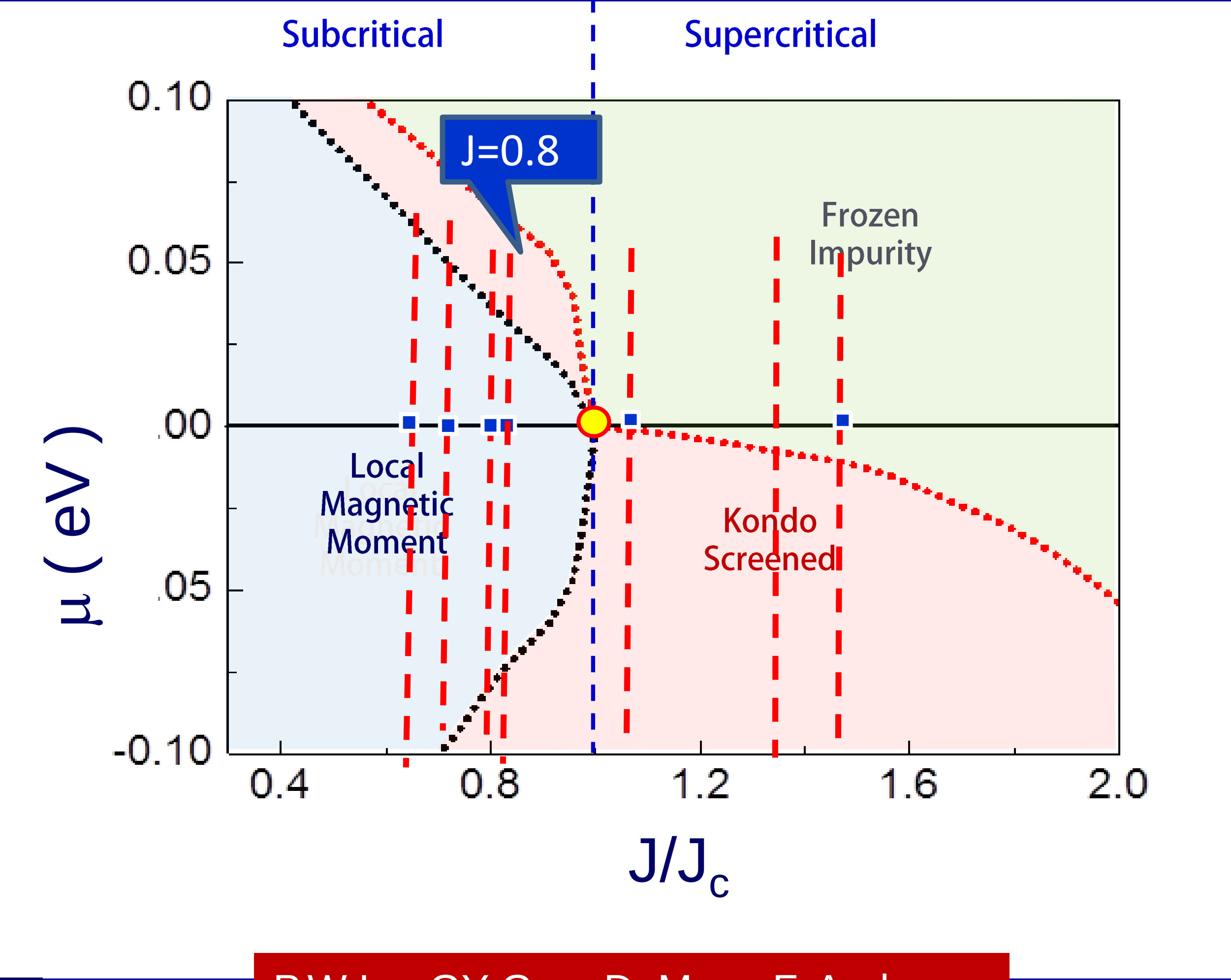


• bare σ-orbital energy	$\varepsilon_d = -1.6eV$
• On site Coulomb	$U_{dd} = 2eV$
• Exchange coupling	$U_{d\pi} = 0.1eV$
• Hund coupling	$J_H \sim -0.35eV$
• Critical coupling	$\Gamma_c = 1.15eV$

$$U_{eff}(\mu) = \begin{cases} U_{dd} & \mu \leq 0 \\ U_{dd} + \min(U_{d\pi}, \alpha\mu) & \mu > 0 \end{cases}$$

Kondo Screening Phase Diagram

Numerical Renormalization Group



Y Jiang et al
Nature Communications 2018

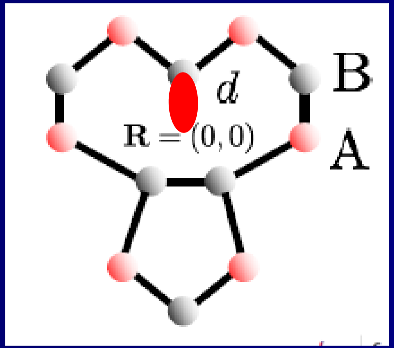
D. May et al
Phys. Rev. B 97, 155419 (2018)

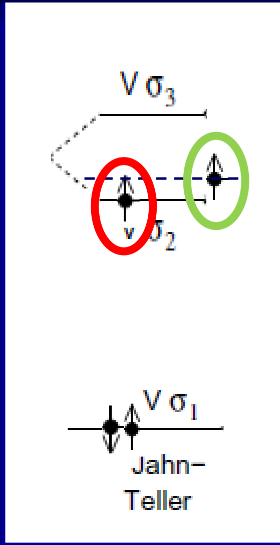
P.W Lo, GY Guo, D. May , F. Anders
Anderson impurity model

E.Y. Andrei

What determines J?

- σ Dangling bond $\mapsto$ localized state $\mapsto$ $1\mu_B$





➢ σ state (in plane) – orthogonal to π conduction electrons $\mapsto$J=0

➢ p_z state – Ferromagnetic coupling $\mapsto$ J=0

J=0 $\mapsto$ NO KONDO SCREENING !!

Hentschel, M. & Guinea, FPhys Rev B **76**, 115407 (200)7
Haase, P., Fuchs, S., Pruschke, T., Ochoa, H. & Guinea, F (2011)
Cazalilla, M. A. I., A.; Guinea, F.; Castro Neto, A. H (2012)

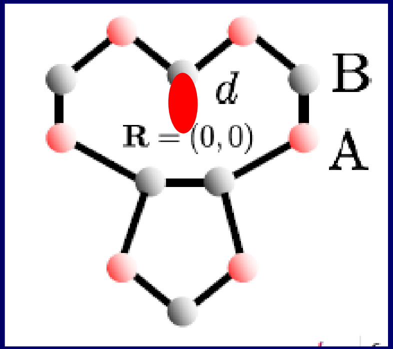
Can J be Finite in Graphene?

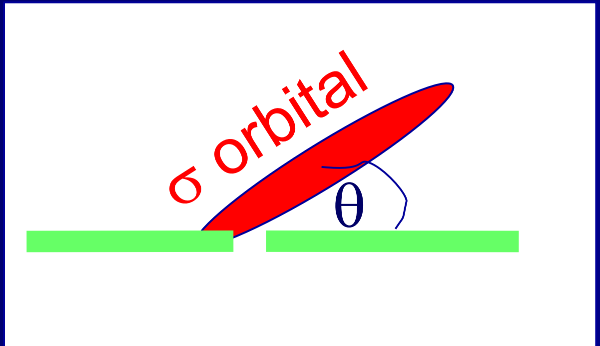
Local Moment Formation and Kondo Effect in Defective Graphene

M. A. Cazalilla,[1,2] A. Iucci,[3] F. Guinea,[4] and A. H. Castro Neto[2]

- Out of plane distortion of dangling bond

$\mapsto$ Finite AF coupling with conduction electrons $\mapsto$ Kondo screening





$J \sim \sin\theta$

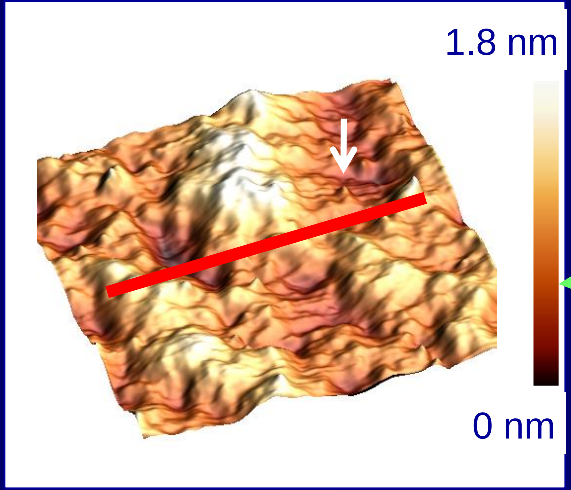
Finite Kondo coupling

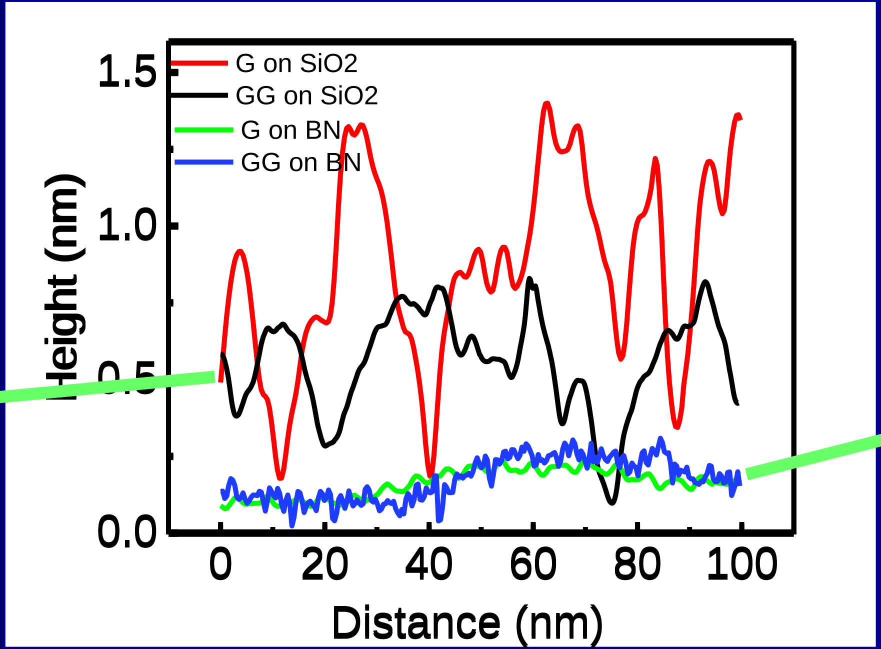
B. R. K. Nanda, M. Sherafati, Z. S. Popovi, and S. Satpathy, New Journal of Physics 14, 083004 (2012).

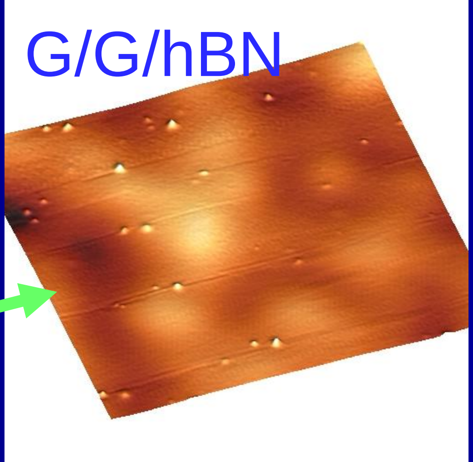
Corrugated Substrate ??

Substrate corrugation and Kondo screening

Substrate Corrugation	G/SiO_2 2nm	$G/G/SiO_2$ 1nm	G/hBN 0.2nm	G/G/hBN 0.2nm
Maximum T_K	T_K~180K	T_K~ 70K	No Kondo	No Kondo
% of screened vacancies	Most	30%	none	none







J depends on Local corrugation

↦ Mechanically controlled magnetism

J. Mao et al
Nature Communications 2018

E.Y. Andrei

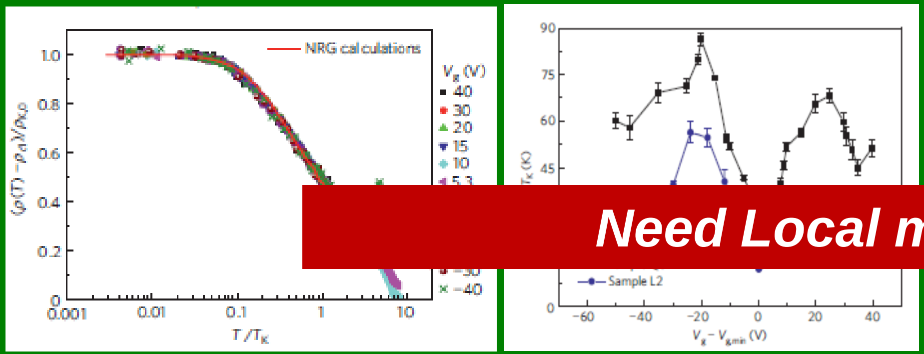
Global Measurements and Conflicting results

nature physics — LETTERS
PUBLISHED ONLINE: 3 APRIL 2011 | DOI: 10.1038/NPHYS1962

Tunable Kondo effect in graphene with defects

Jian-Hao Chen[1,2†], Liang Li[2], William G. Cullen[1,2], Ellen D. Williams[1,2] and Michael S. Fuhrer[1,2]*

- R(T) $\mapsto$ Kondo screening
  - T_K 20-70K

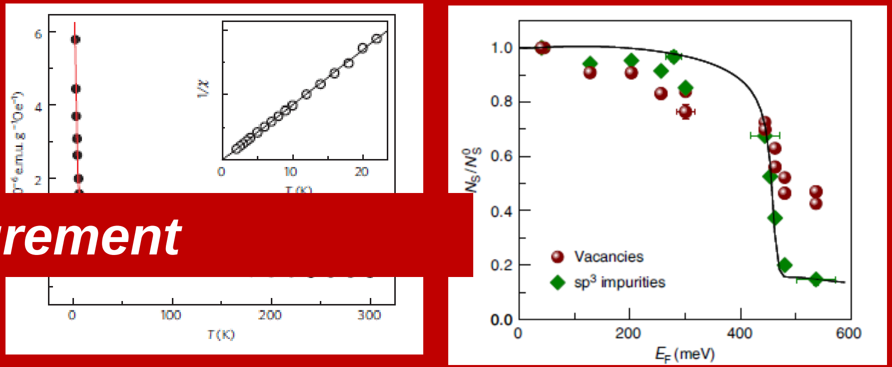


nature physics — LETTERS
PUBLISHED ONLINE: 10 JANUARY 2012 | DOI: 10.1038/NPHYS2183

Spin-half paramagnetism in graphene induced by point defects

R. R. Nair[1], M. Sepioni[1], I-Ling Tsai[1], O. Lehtinen[2], J. Keinonen[2], A. V. Krasheninnikov[2,3], T. Thomson[1], A. K. Geim[1] and I. V. Grigorieva[1]*

- $\chi(T) \mapsto$ No Kondo screening
- Moments unscreened at low T



Need Local measurement

Measures:

Scattering off Kondo cloud

- Sensitive to screened Moments only.

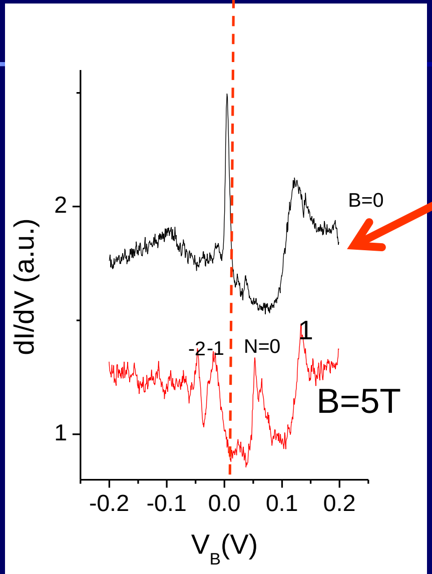
Measures:

Magnetic moments

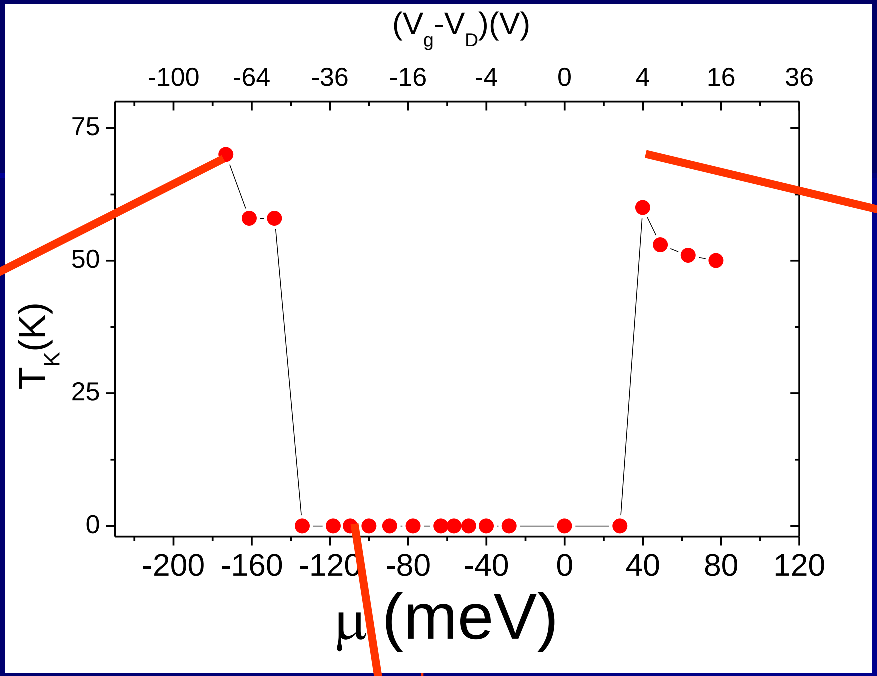
- Sensitive to unscreened Moments only.

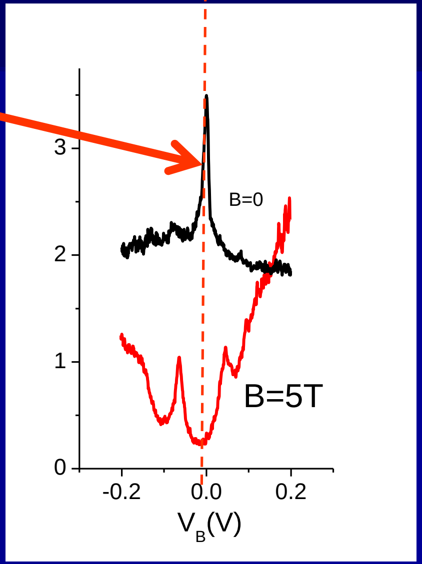
- **Global measurements probe complementary properties**

Magnetic Tuning of Kondo Screening

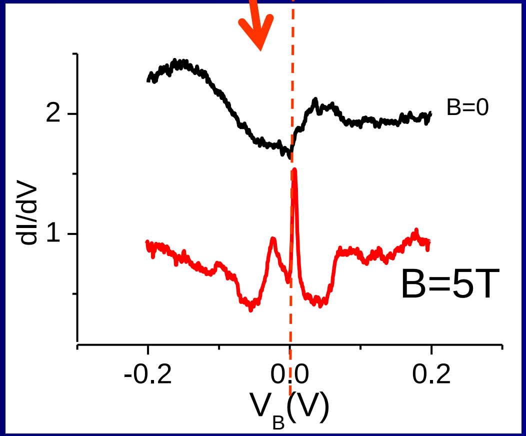


Magnetically Suppressed Kondo screening





Magnetically Suppressed Kondo screening

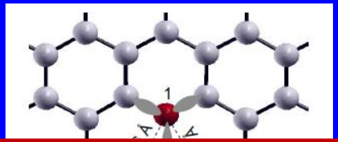


Magnetically induced Kondo screening

E.Y. Andrei

Summary

- Single atom vacancy
  - Magnetic Moment
  - Charge



Efficient way to embed localized moment and charge in graphene

- Kondo screening
- Quantum critical transition
- Control of local moment
  - Electric field
  - Local curvature

Electrically and mechanically controlled magnetism

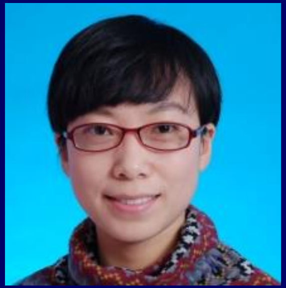
D. May et al Phys. Rev. B 97, 155419 (2018)
Y Jiang et al Nature Communications 2018
J. Mao et al arXiv:1711.06942 (2017)

Theory: (NRG)
D. May, F. Anders
P.W Lo, GY Guo

Substrates: (hBN)
T. Taniguch, K. Watanabe

Guohong Li

Jinhai Mao



Yuhang Jiang