Minicourse contents:

Lecture 1 (pdf) available at http://www.fmt.if.usp.br/~luisdias

See link on Twitter: @ProfLuisDias

Lecture 1:

- Intro: “More is Different”.
- The Kondo effect: a true “More is Different” phenomenon.
- Wilson’s numerical renormalization group method.

Lecture 2:

- Applications I: Magnetic molecules on surfaces.
- Applications II: Vacancies in graphene.

Application 1:
Magnetic molecules on surfaces
Combining NRG with Ab-initio methods

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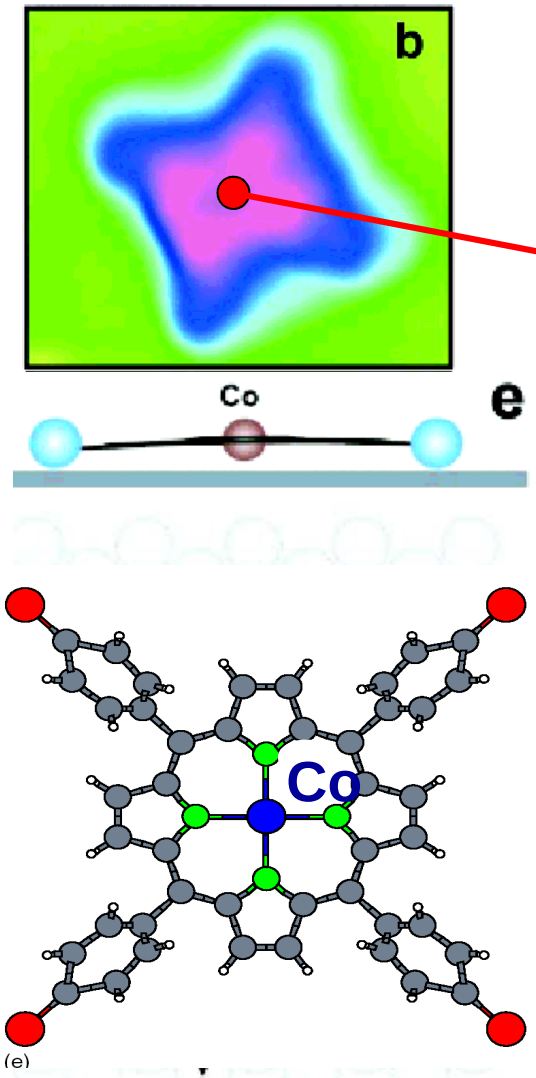
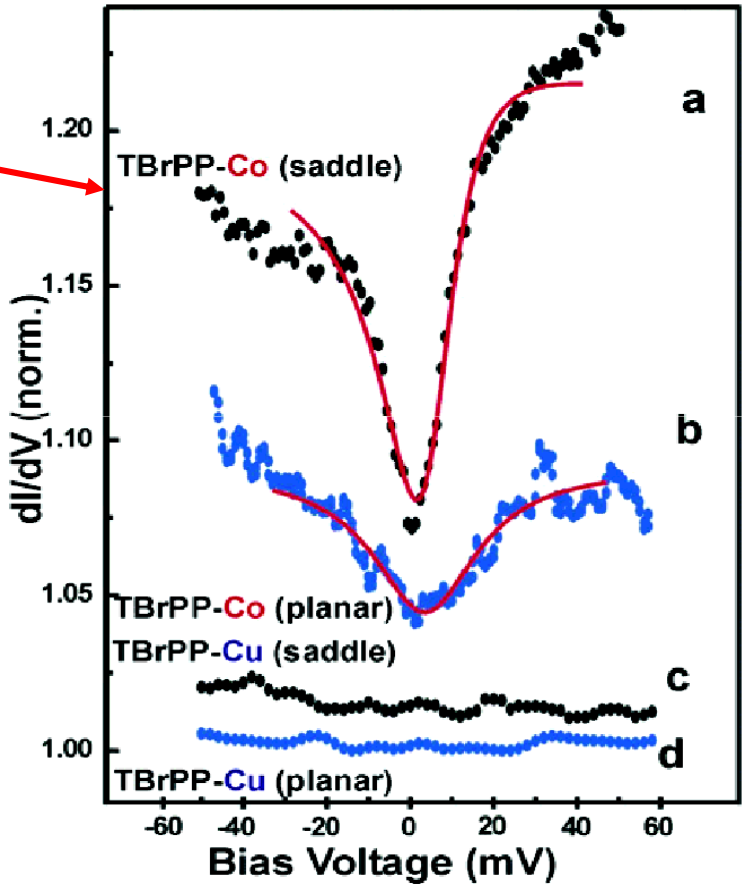
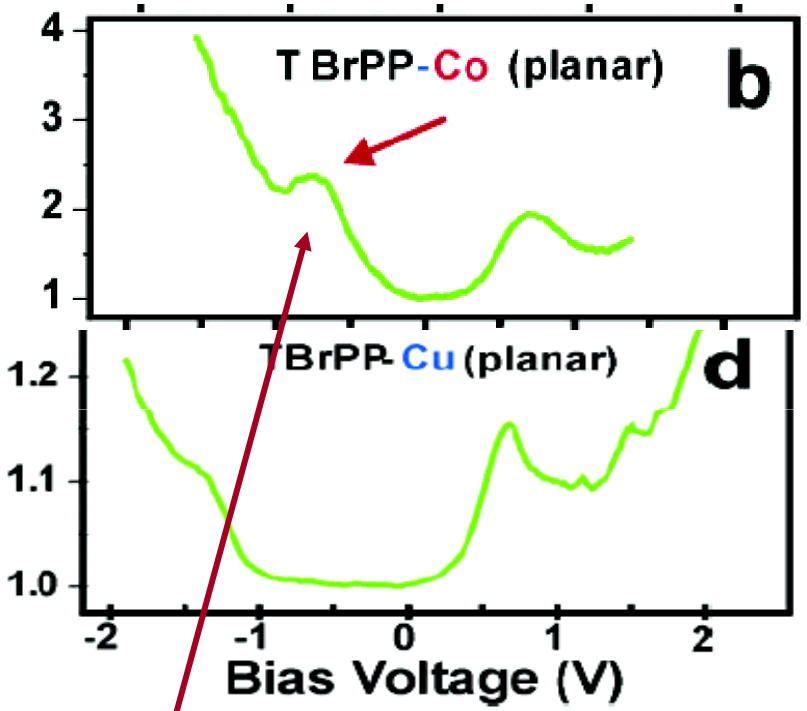
Kondo: Magnetic molecules on surfaces



STM measurements

V. Iancu, A. Deshpande, Saw W. Hla
Nano Lett. **6** 820 (2006)





Co d_{3z2-1} level (at ~-0.7 eV)

Zero-bias dip: Kondo effect. T_K~130-170K

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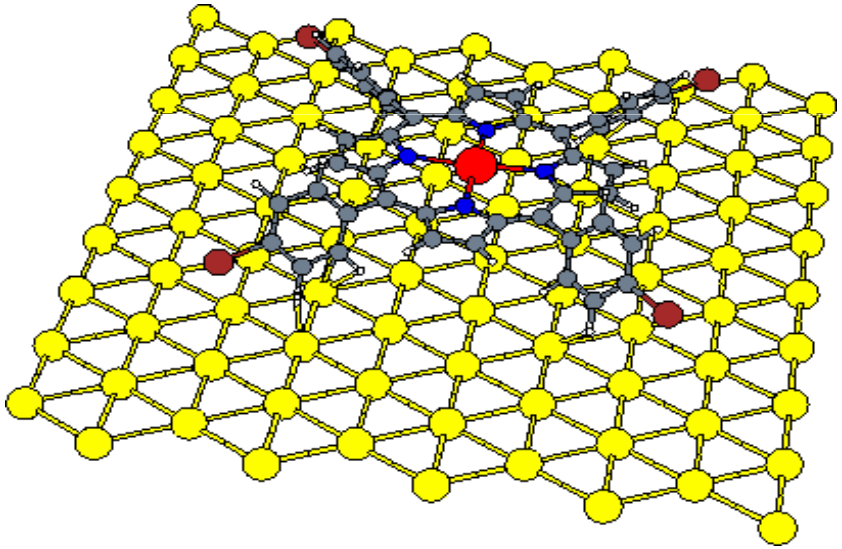
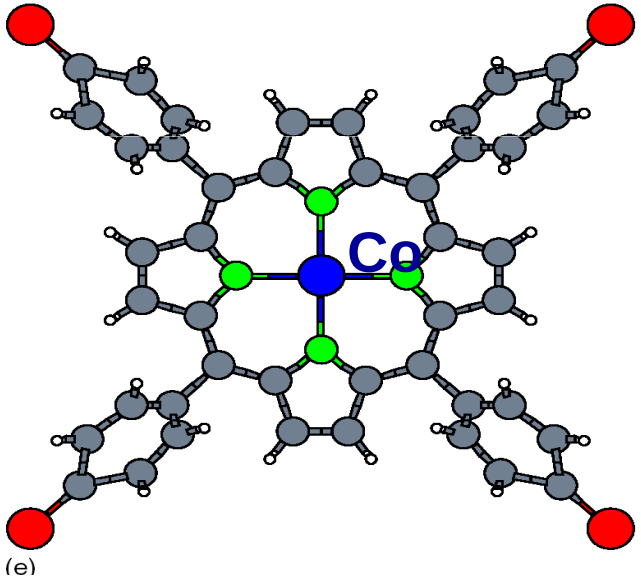
Cobalt Porphyrin molecule on a surface.

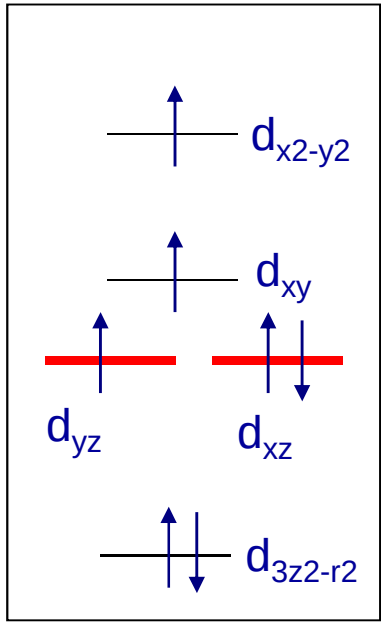
- Molecule: TBrPP-Co ($CoBr_4N_4C_{44}H_{24}$)
- Which microscopic model describes it?
- Naively one might expect S=3/2.

Co atomic configuration: $3d^7$

+ D_{4h} crystalline field:







?

Is the simple “Hund’s rule filling” picture correct?

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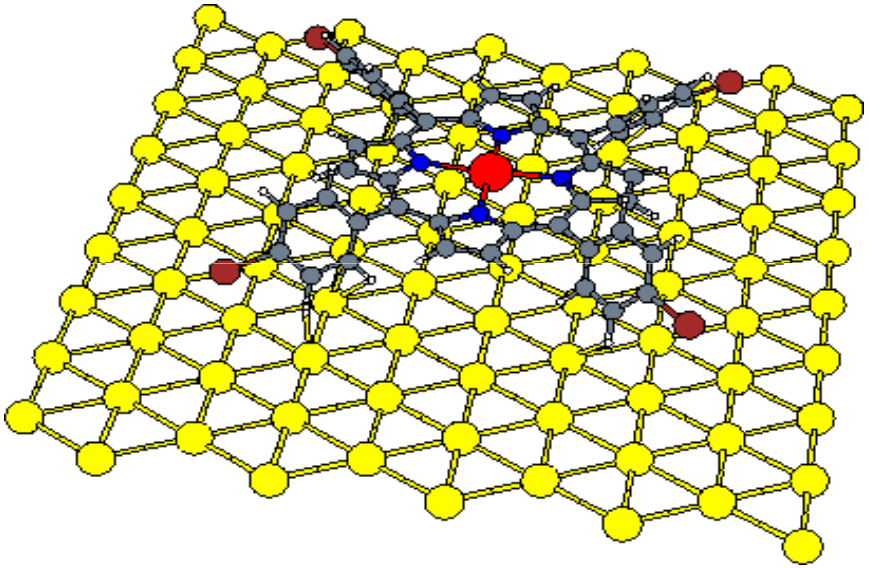
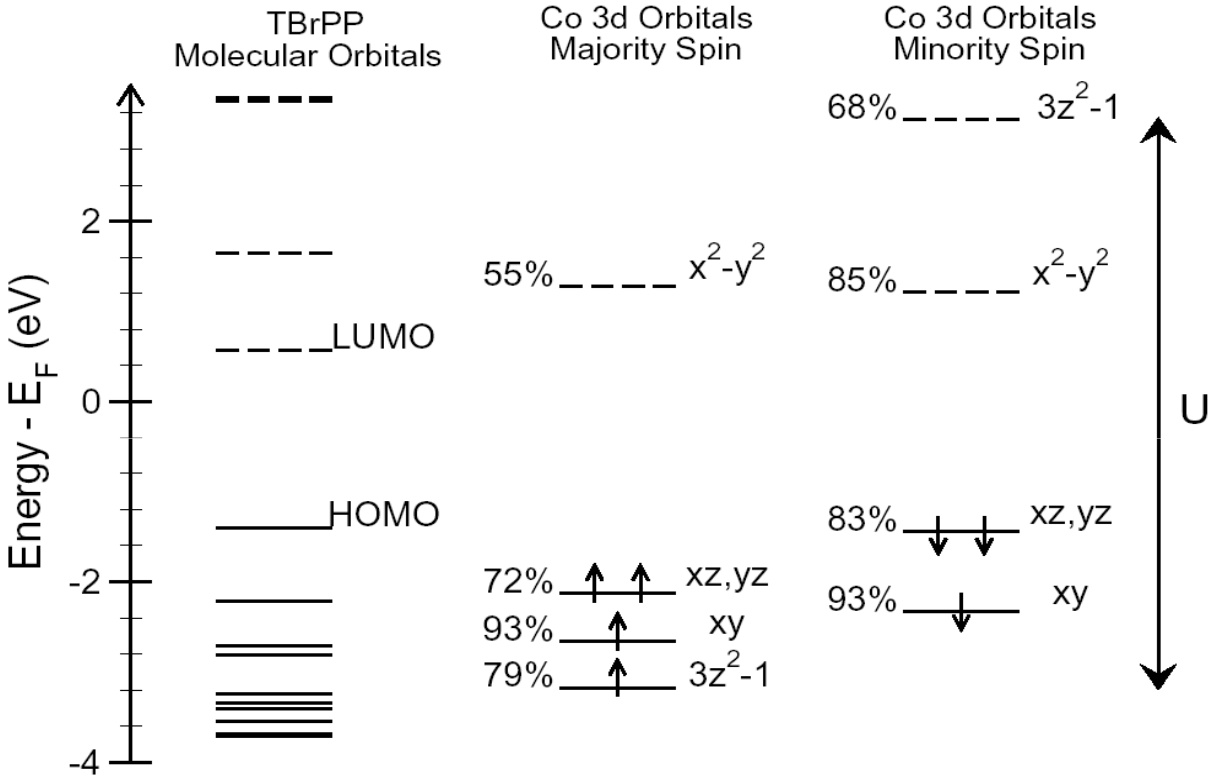
First-principles calculations (GW): hints for a microscopic model.

The answer: not quite!





GW: Molecular levels "Co-like" levels

LDS, M Tiago, S Ulloa, F Reboredo E. Dagotto *PRB* **80** 155443 (2009).

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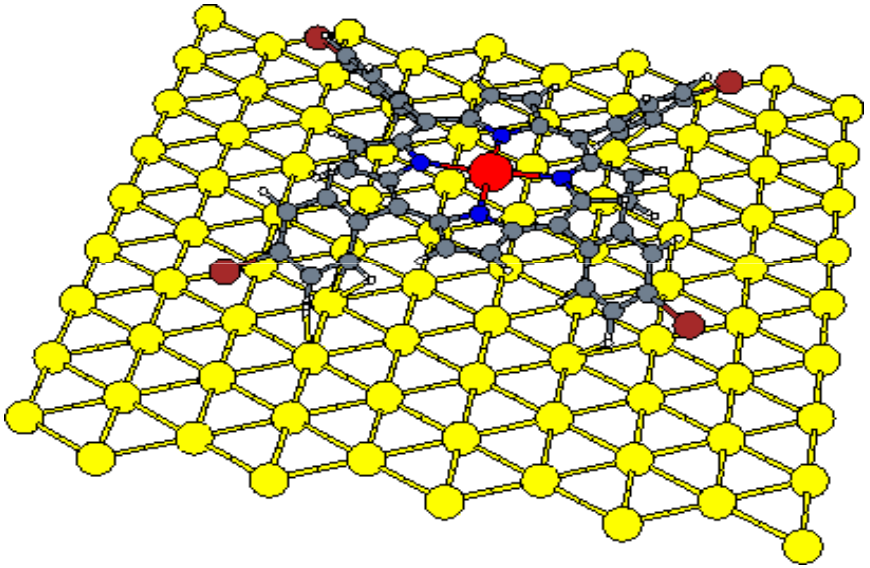
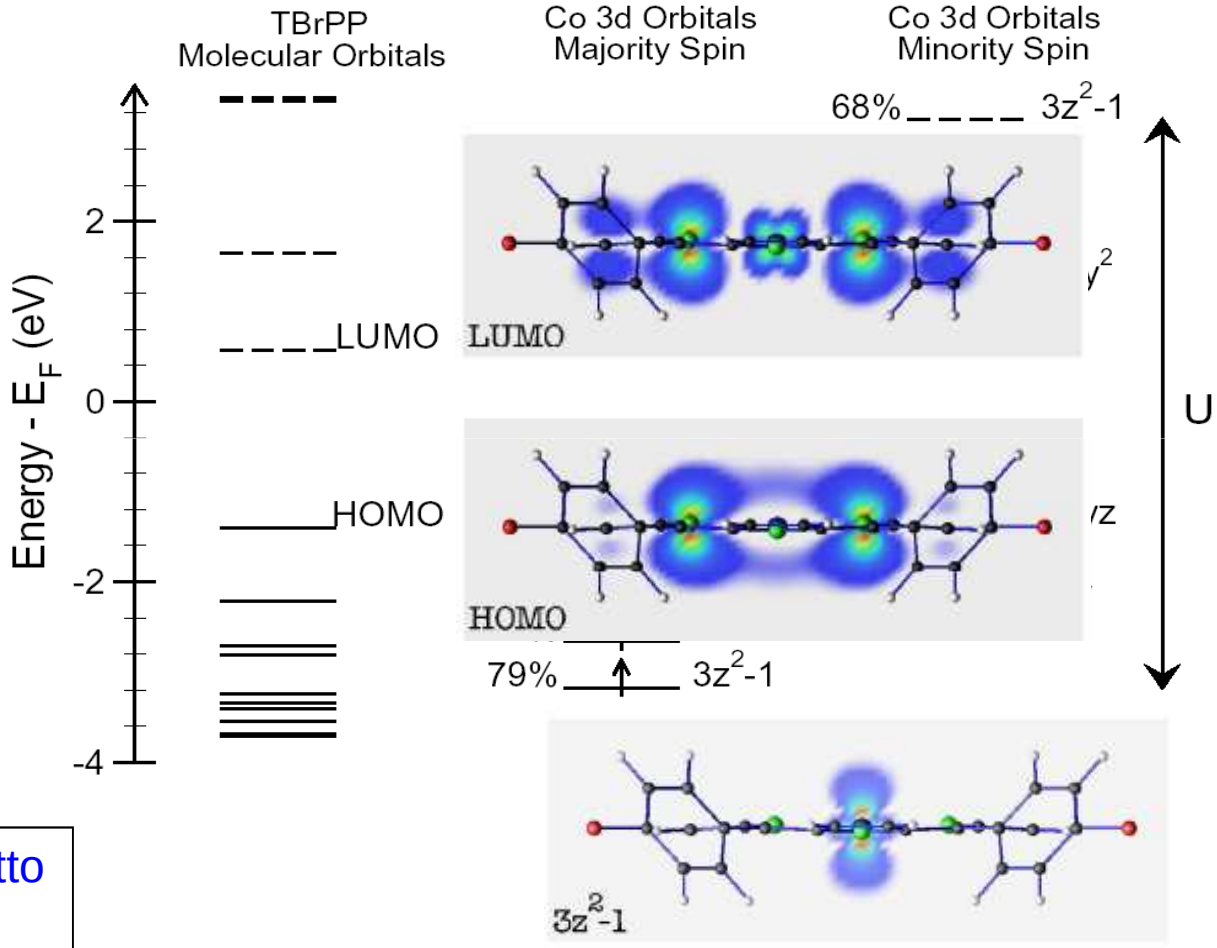
First-principles calculations (GW): hints for a microscopic model.

The answer: not quite!





LDS, M Tiago, S Ulloa, F Reboredo E. Dagotto *PRB* **80** 155443 (2009).

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First-principles calculations (GW): hints for a microscopic model.

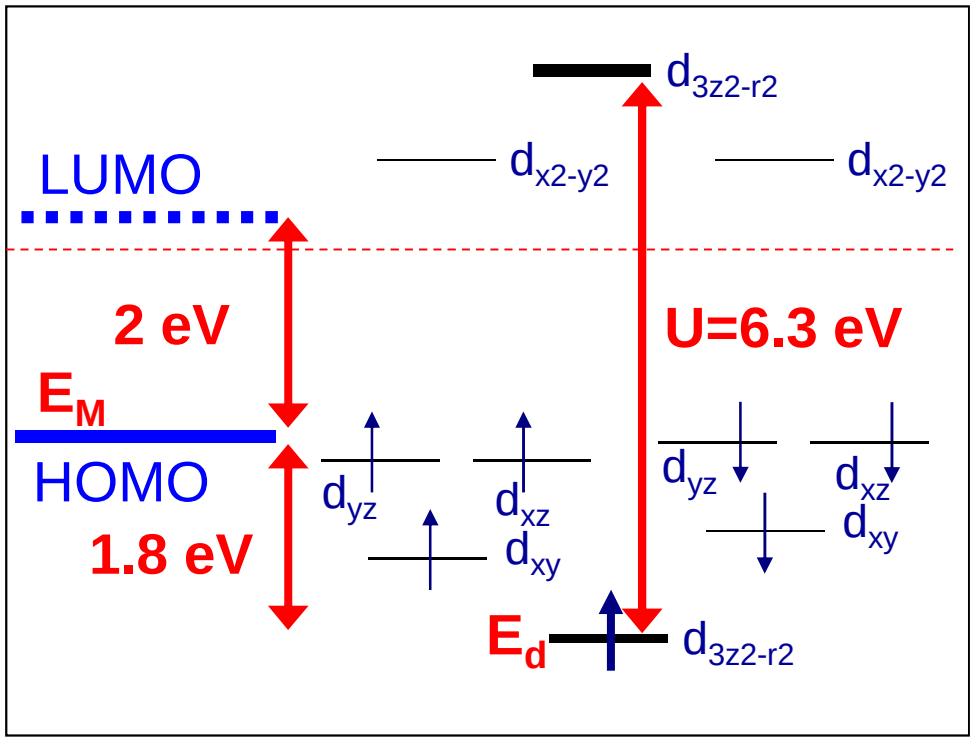
Model: Anderson-like Hamiltonian

$$H = H_{\text{Molecule}} + H_{\text{Mol-Surface}}$$

$$H_{\text{Molecule}} = \sum_{\sigma} E_d \hat{n}_{d\sigma} + U \hat{n}_{d\uparrow} \hat{n}_{d\downarrow} + \sum_{\sigma} E_M \hat{n}_{M\sigma}$$

$$H_{\text{Mol-Surf}} = \sum_{\mathbf{k},\sigma} V_{d\mathbf{k}} c^{\dagger}_{d\sigma} c_{\mathbf{k}\sigma} + \sum_{M\mathbf{k},\sigma} V_{M\mathbf{k}} c^{\dagger}_{M\sigma} c_{\mathbf{k}\sigma} + \text{h.c.}$$

$$V_{d(M)\mathbf{k}} = \langle \phi_{d(M)} | \hat{H} | \psi_{\mathbf{k}} \rangle$$



GW: Molecular levels "Co-like" levels

Not easy to calculate with GW!

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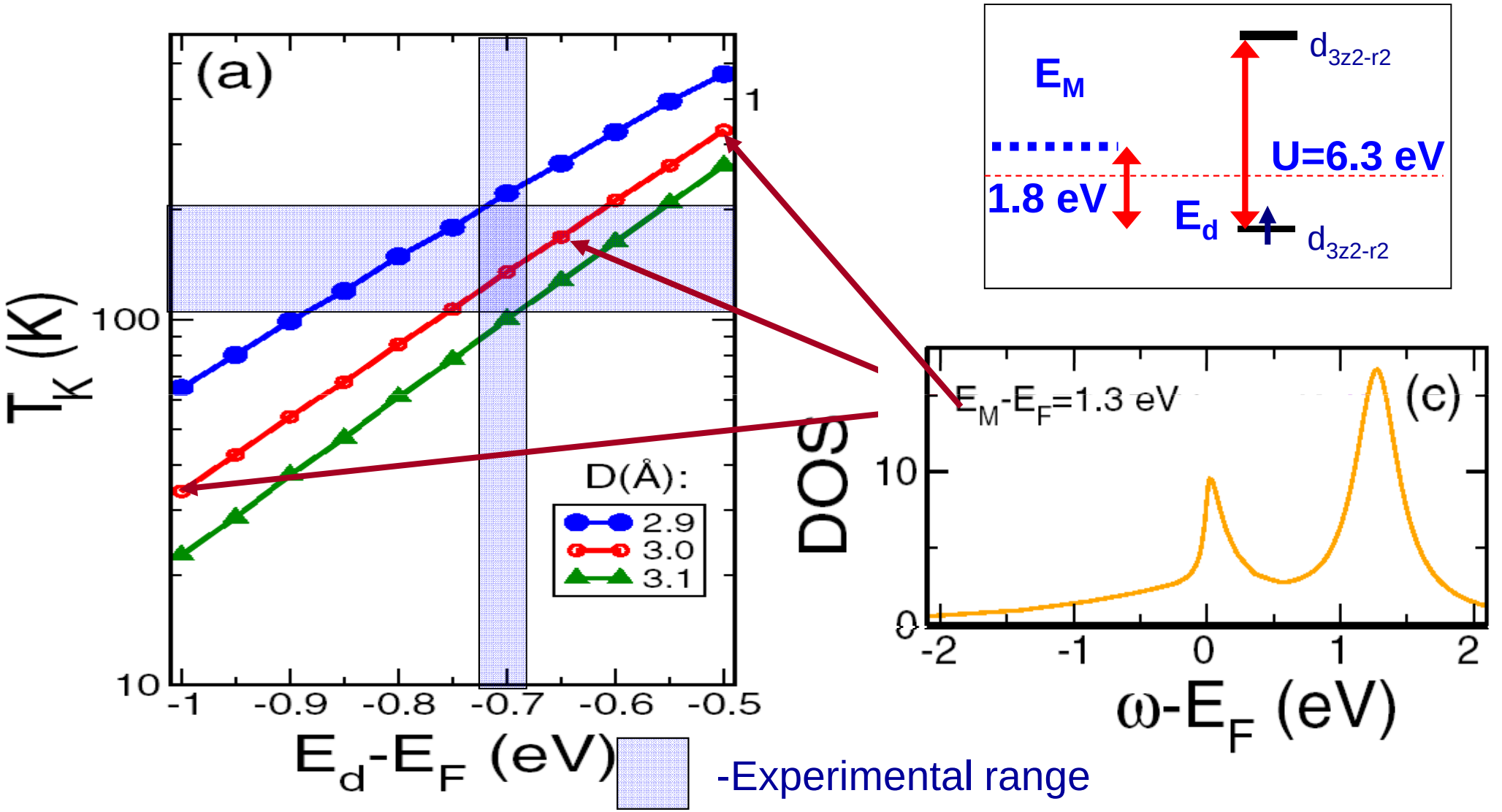
NRG calculations (Kondo temperature).



-Experimental range

LDS, M Tiago, S Ulloa, F Reboredo E. Dagotto *PRB* **80** 155443 (2009).

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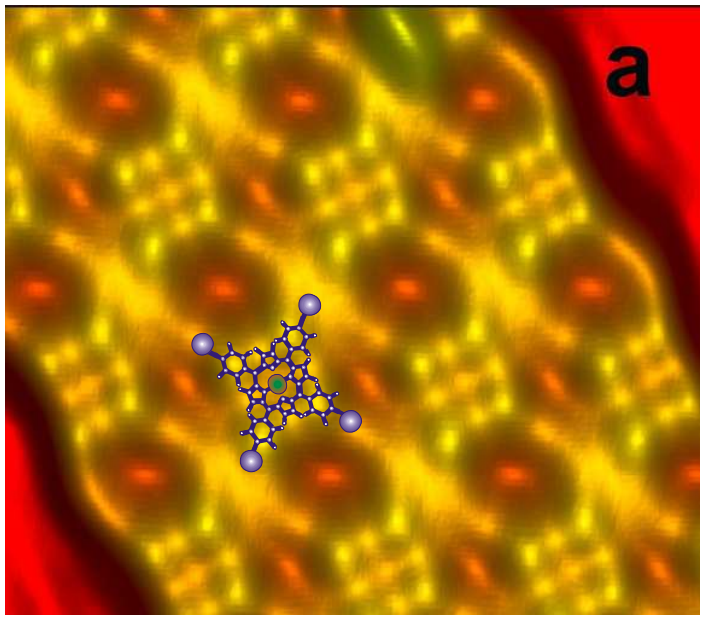
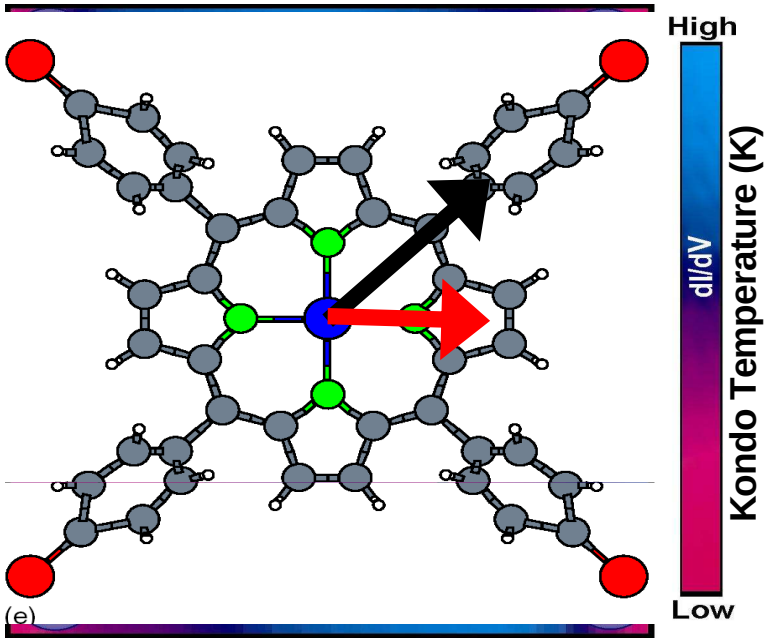
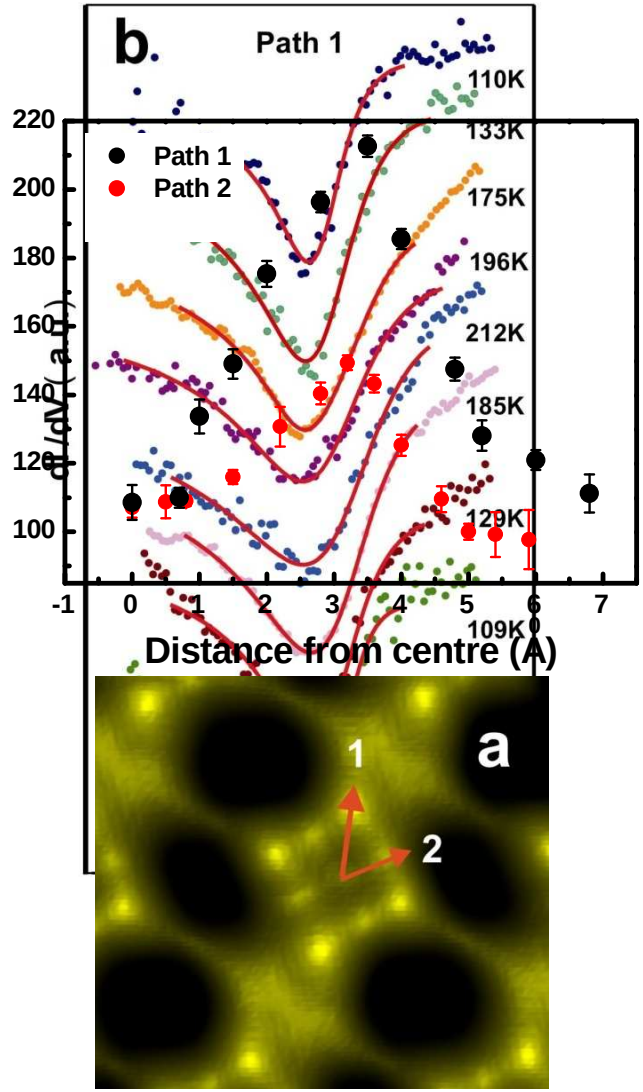
Spatially extended Kondo effect







- Co-porphyrin structures: low-temperature STM dI/dV.
- Kondo resonance found *away* from central Co atom!
- Spatially-dependent Kondo temperature.

UGE Perera, et al. – *PRL* **105** 106601 (2010).

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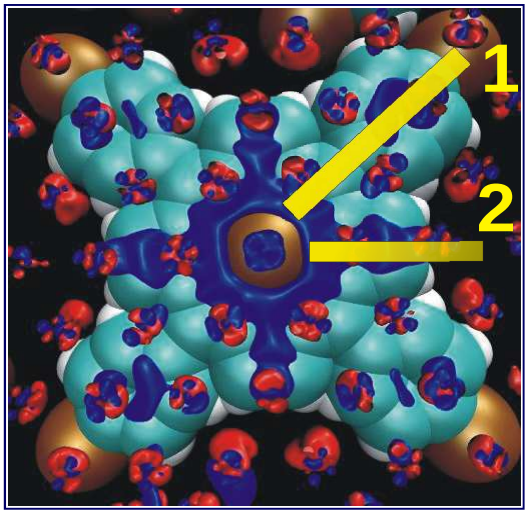
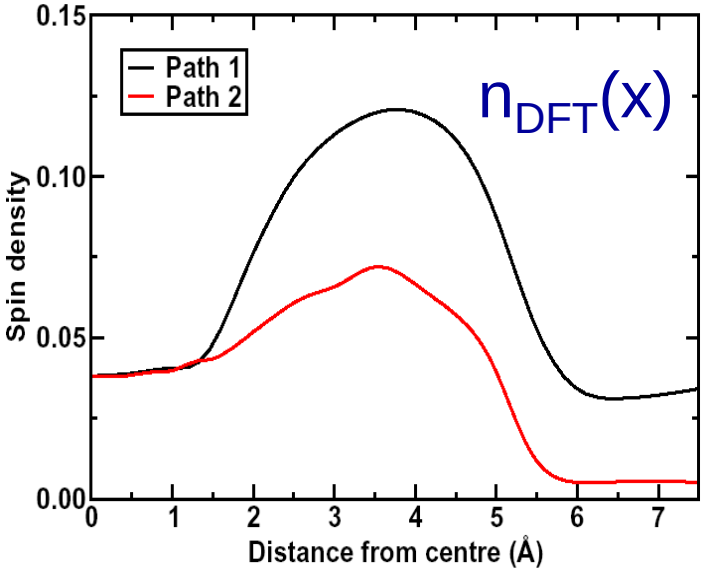
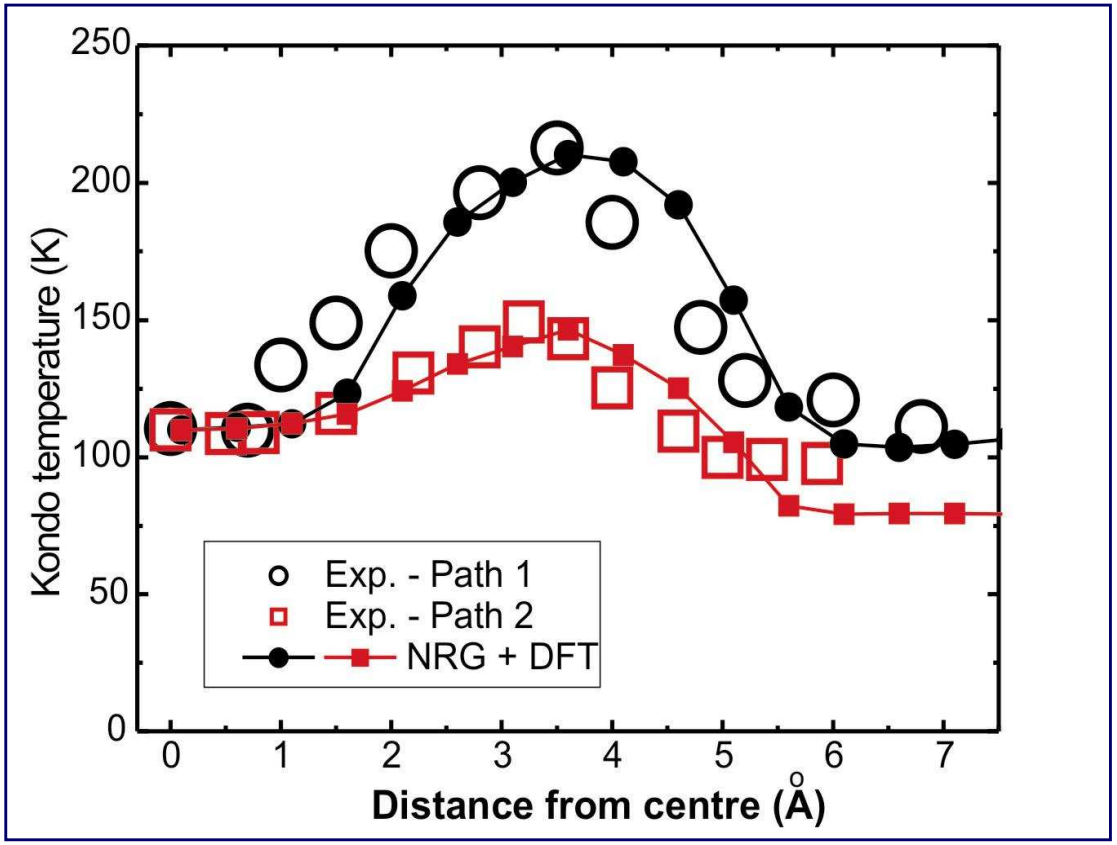
Spatially extended Kondo effect



- DFT calculations: molecular spin density $n_{DFT}(x)$.
- NRG calculations (Kondo model): $J(x) = J_0 + An_{\mathrm{DFT}}(x)$
- Good agreement with experimental data.





UGE Perera, et al. – *PRL* **105** 106601 (2010).

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Application 2:
Kondo effect in graphene.

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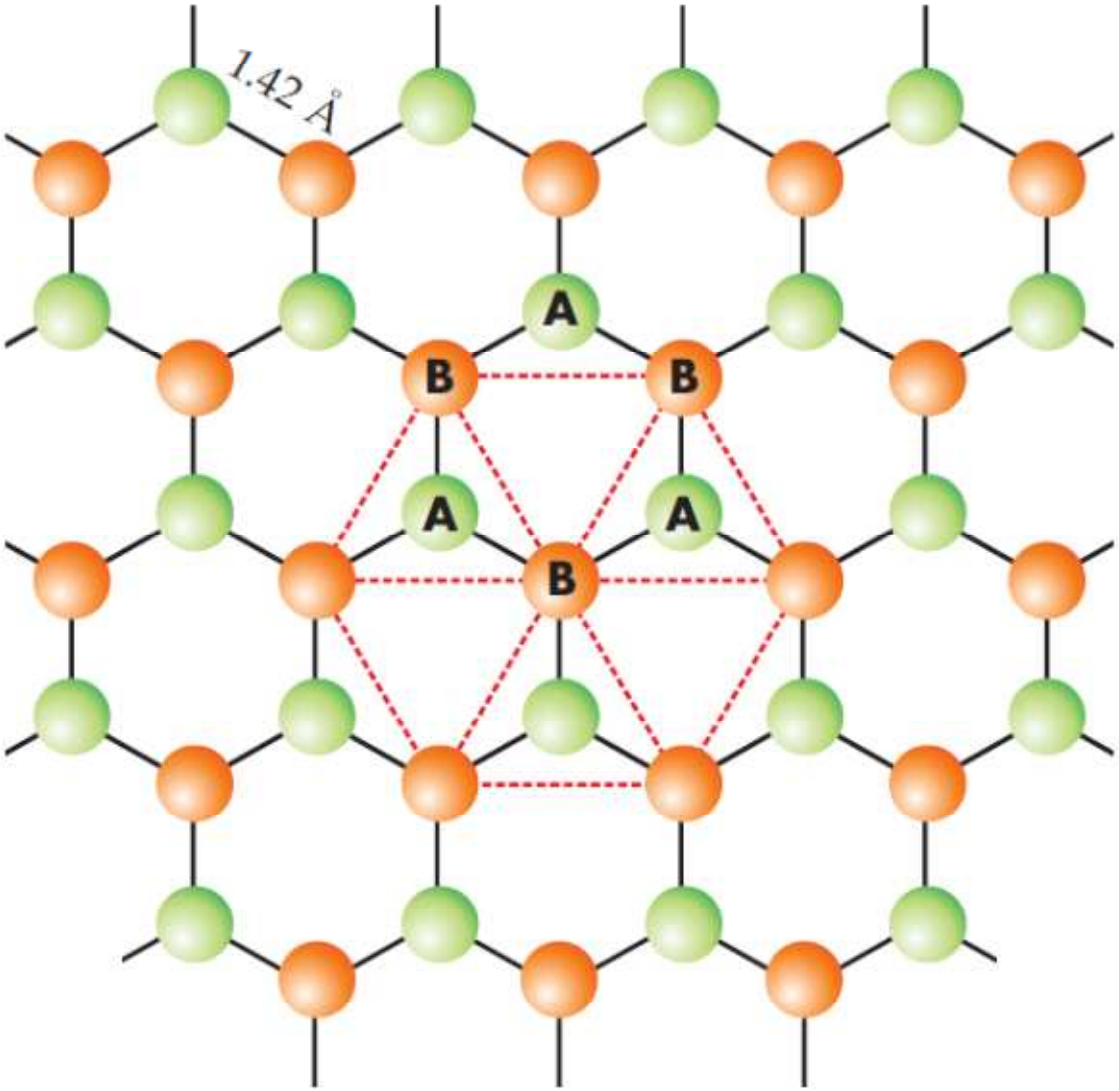
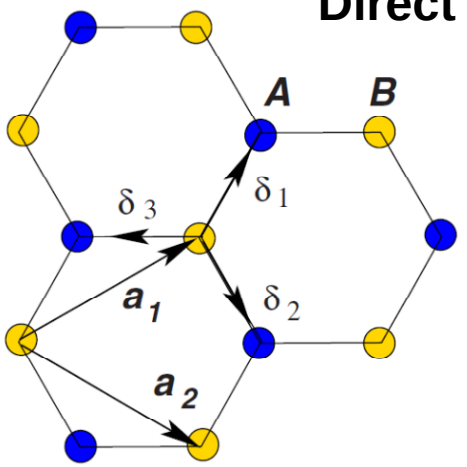
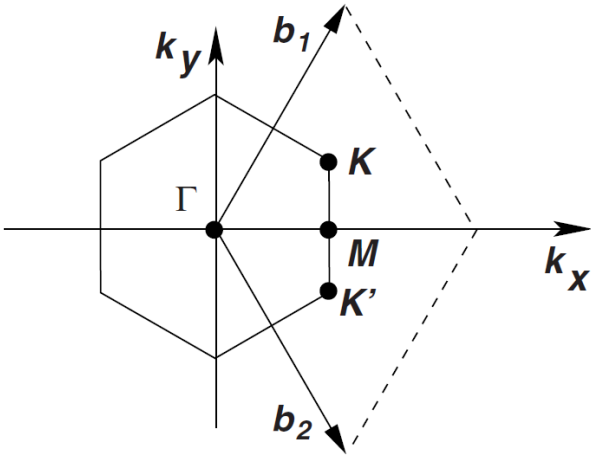
Graphene basics: triangular lattices.



Direct lattice



Reciprocal lattice (k)



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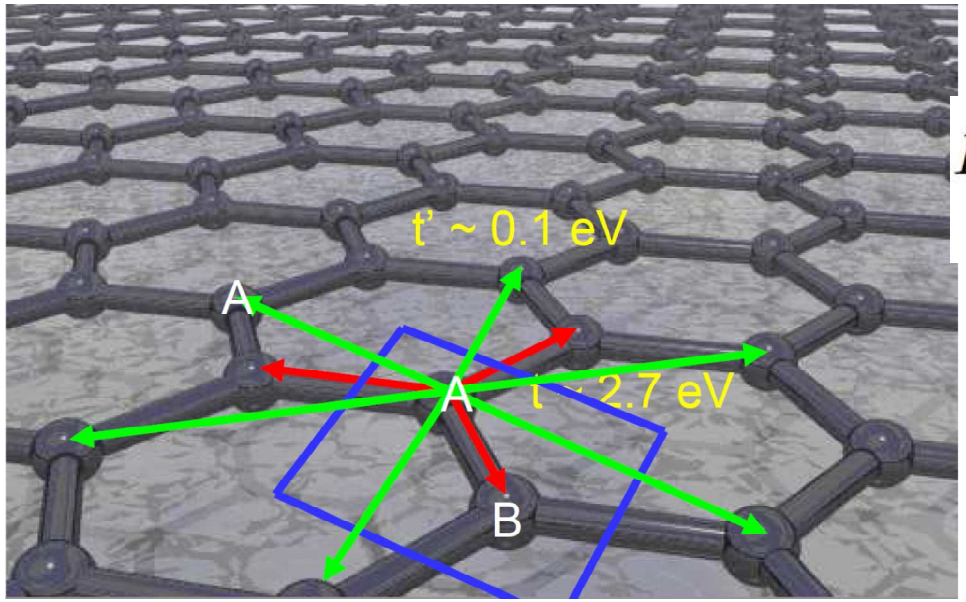
Electronic structure of graphene.



Tight-binding model

$$H = -t \sum_{\langle i,j \rangle, \sigma} \left(a^{\dagger}_{\sigma,i} b_{\sigma,j} + \mathrm{H.c.} \right)$$

$$- t' \sum_{\langle\langle i,j \rangle\rangle, \sigma} \left(a^{\dagger}_{\sigma,i} a_{\sigma,j} + b^{\dagger}_{\sigma,i} b_{\sigma,j} + \mathrm{H.c.} \right)$$

…1st and 2nd neighbours

$$0.02t \leq t' \leq 0.2t$$

Phil R. Wallace

Energy dispersion for graphene (derived in the 40's!)

$$E_{\pm}(\mathbf{k}) = \pm t \sqrt{3 + f(\mathbf{k})} - t' f(\mathbf{k})$$

$$f(\mathbf{k}) = 2\cos(\sqrt{3} k_y a) + 4\cos\left(\frac{\sqrt{3}}{2} k_y a\right) \cos\left(\frac{3}{2} k_x a\right)$$

Wallace, P.R., *Phys. Rev.* **71** 622 (1947)

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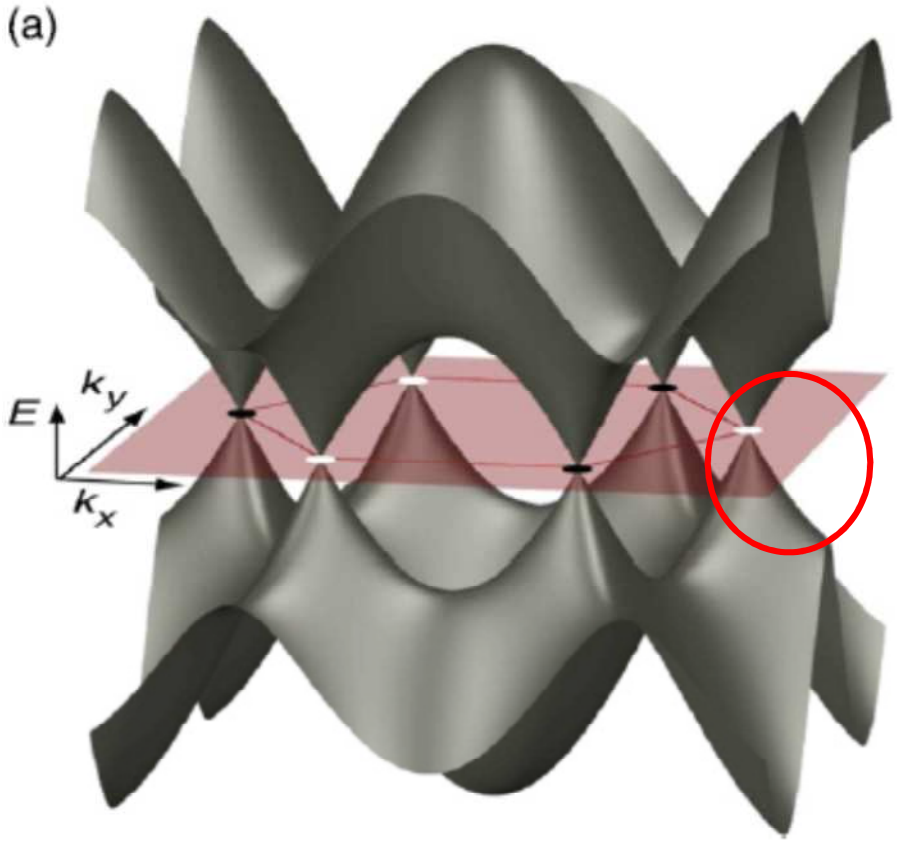
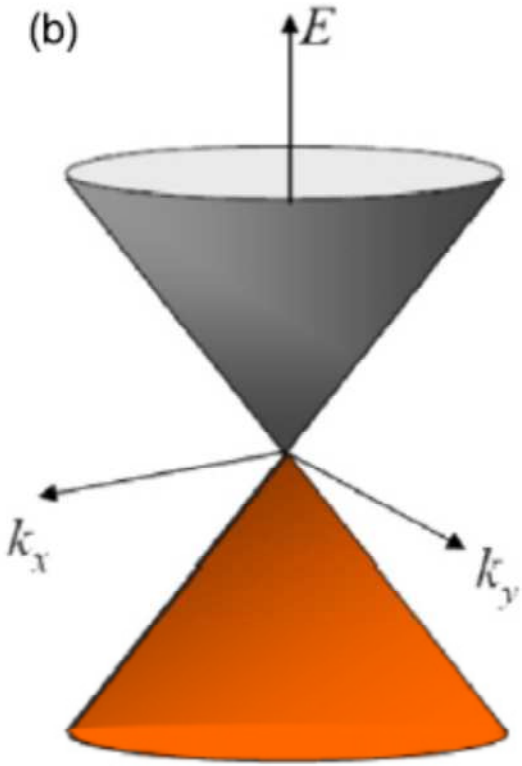
Dirac cones: massless fermions



$$E_{\pm}(\mathbf{k}) = \pm|t|\sqrt{3 + f(\mathbf{k})}$$



$$E_{\pm}(\mathbf{q}) = \pm v_F|\mathbf{q}|$$

Analogy: linear dispersion of massless "relativistic" particles ("E=pc")

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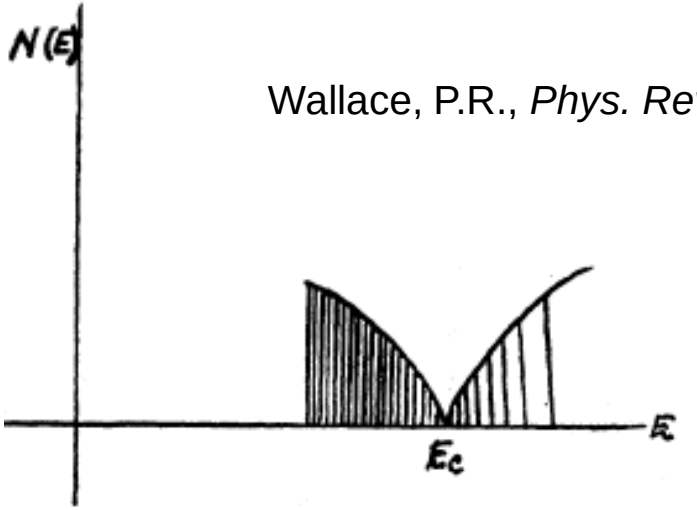
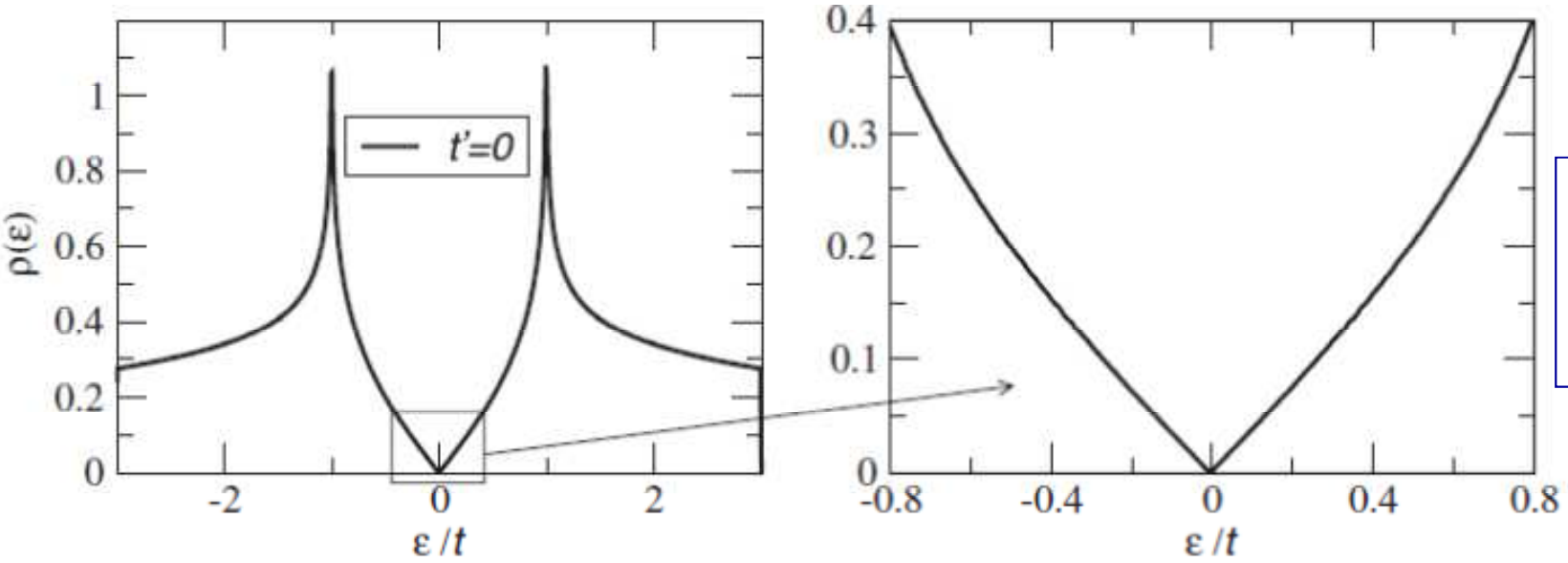
Graphene: density of states



Wallace, P.R., *Phys. Rev.* **71** 622 (1947)

ρ(E) ∝ |E| (*linear*)
Close to the charge neutrality point.



$$\rho(E) = \frac{2A_c}{\pi}\frac{|E|}{v_F^2}$$

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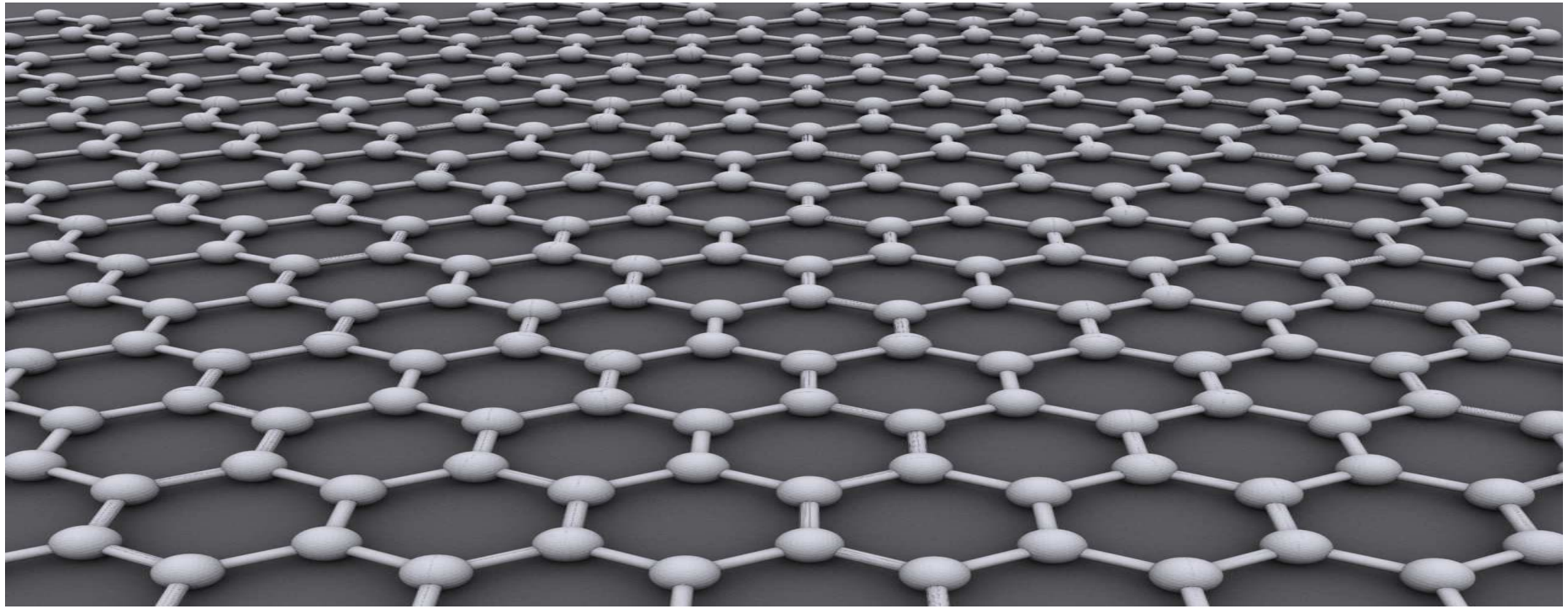
Graphene: How we think it is…

“Ideal” graphene: planar, 2D, ordered, nice…



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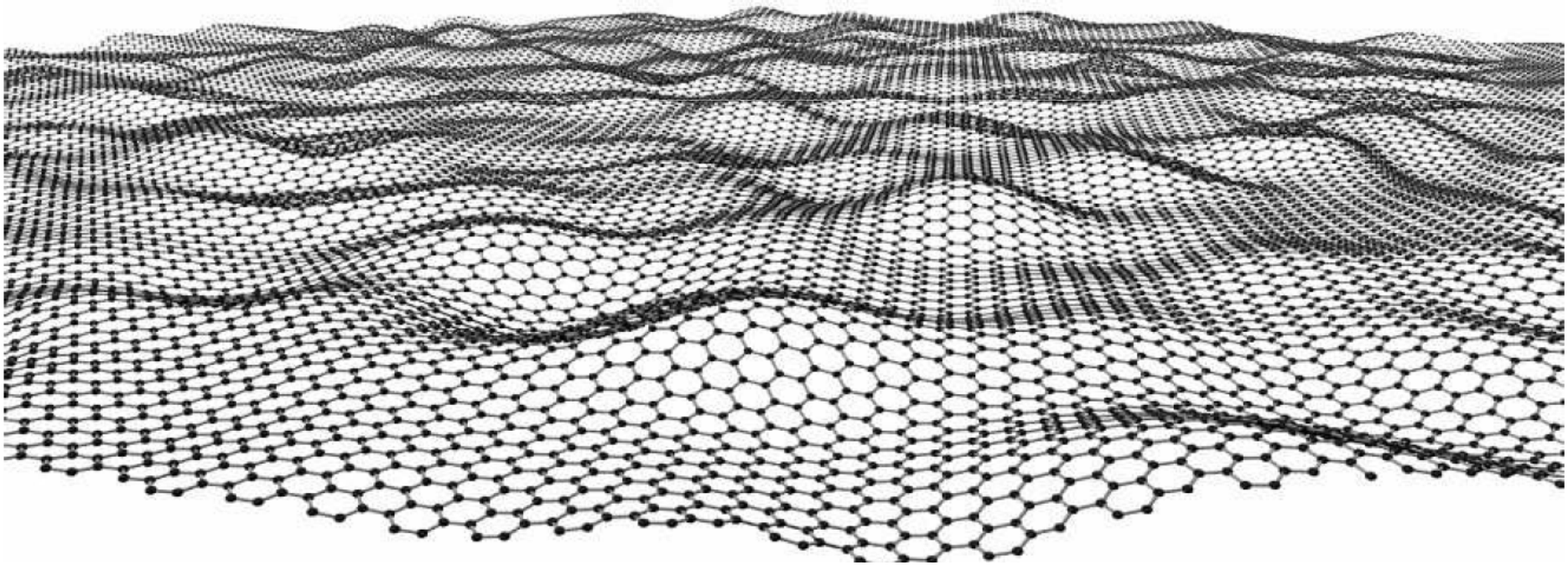
… and how it really is.

… versus “real” graphene: wavy, corrugated, membrane-like.



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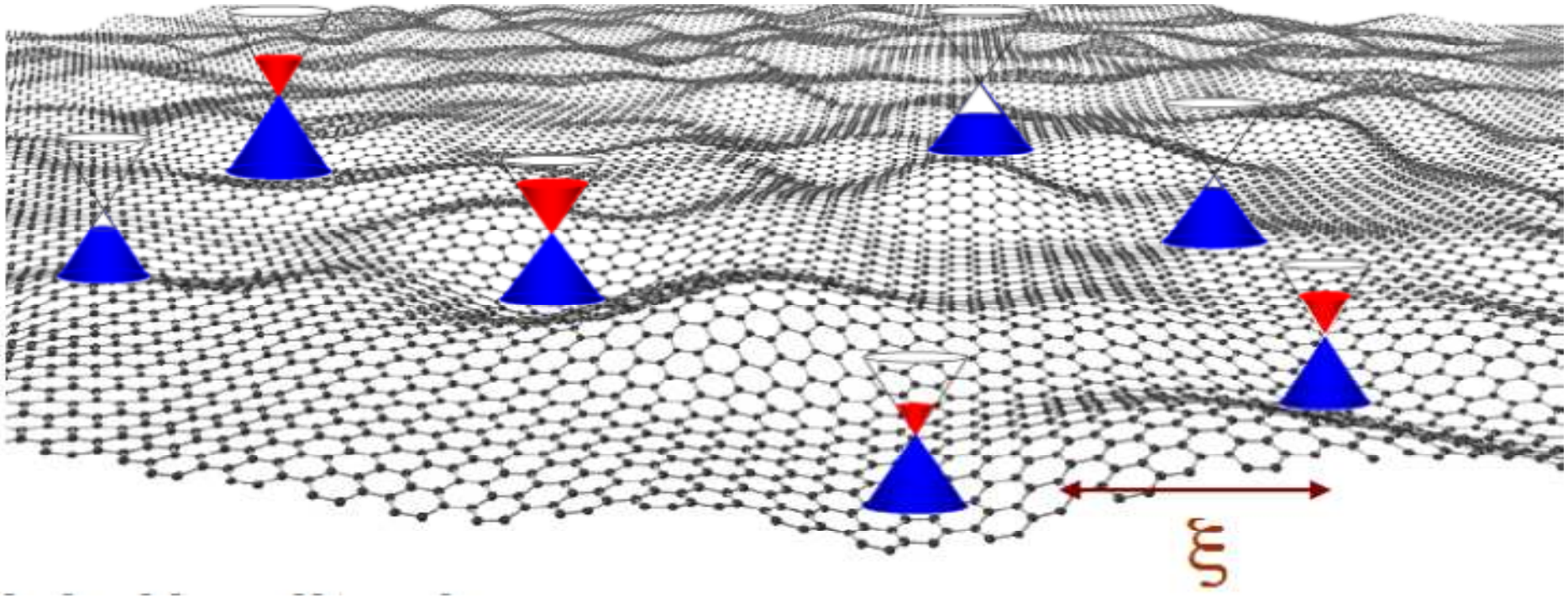
Graphene: “long-range disorder”.

$$U_{\mathrm{dis}}(\boldsymbol{r}_i) = \sum_{j=1}^{N_{\mathrm{imp}}} W_j \, e^{\frac{-(\boldsymbol{r}_i - \boldsymbol{R}_j)^2}{2\xi^2}}$$

Disorder potential



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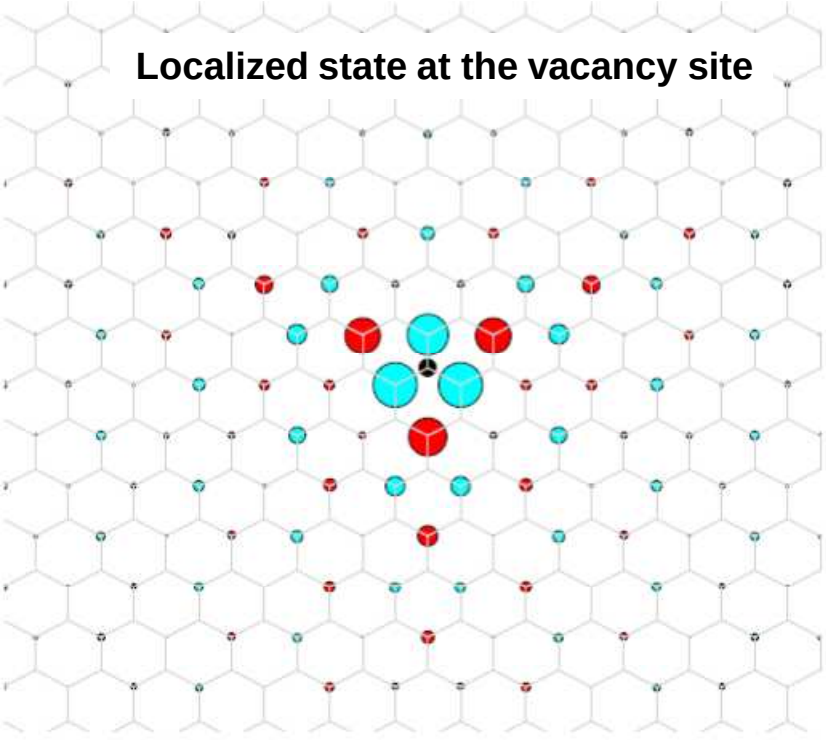
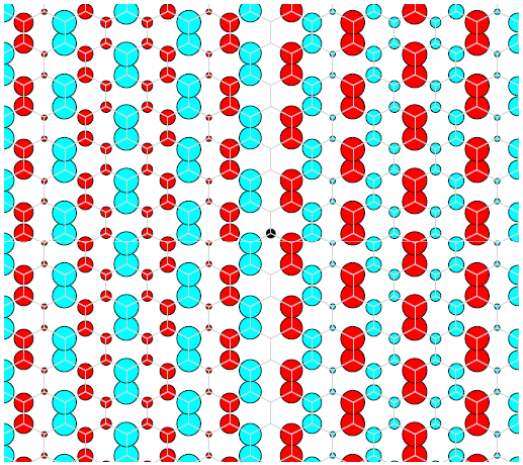
Short-range disorder (vacancies)

Tight-binding calculations: single vacancy leads to midgap state

Localized state at the vacancy site



Typical delocalized state



Vacancy tight-binding model:

$$H_{\rm v} = -t \sum_{\langle i,j \rangle} c_i^\dagger c_j + t \sum_{\langle {\rm v},j \rangle} c_{\rm v}^\dagger c_j + {\rm H.c.}$$

$$H_{\rm v}|\nu\rangle = \begin{cases} \varepsilon_\nu |\nu\rangle & \text{for} \quad \varepsilon \neq 0, \quad |\nu\rangle \text{ is extended,} \\ 0|\nu\rangle & \text{for} \quad \nu = {\rm v}, \quad |{\rm v}\rangle \text{ is localized.} \end{cases}$$

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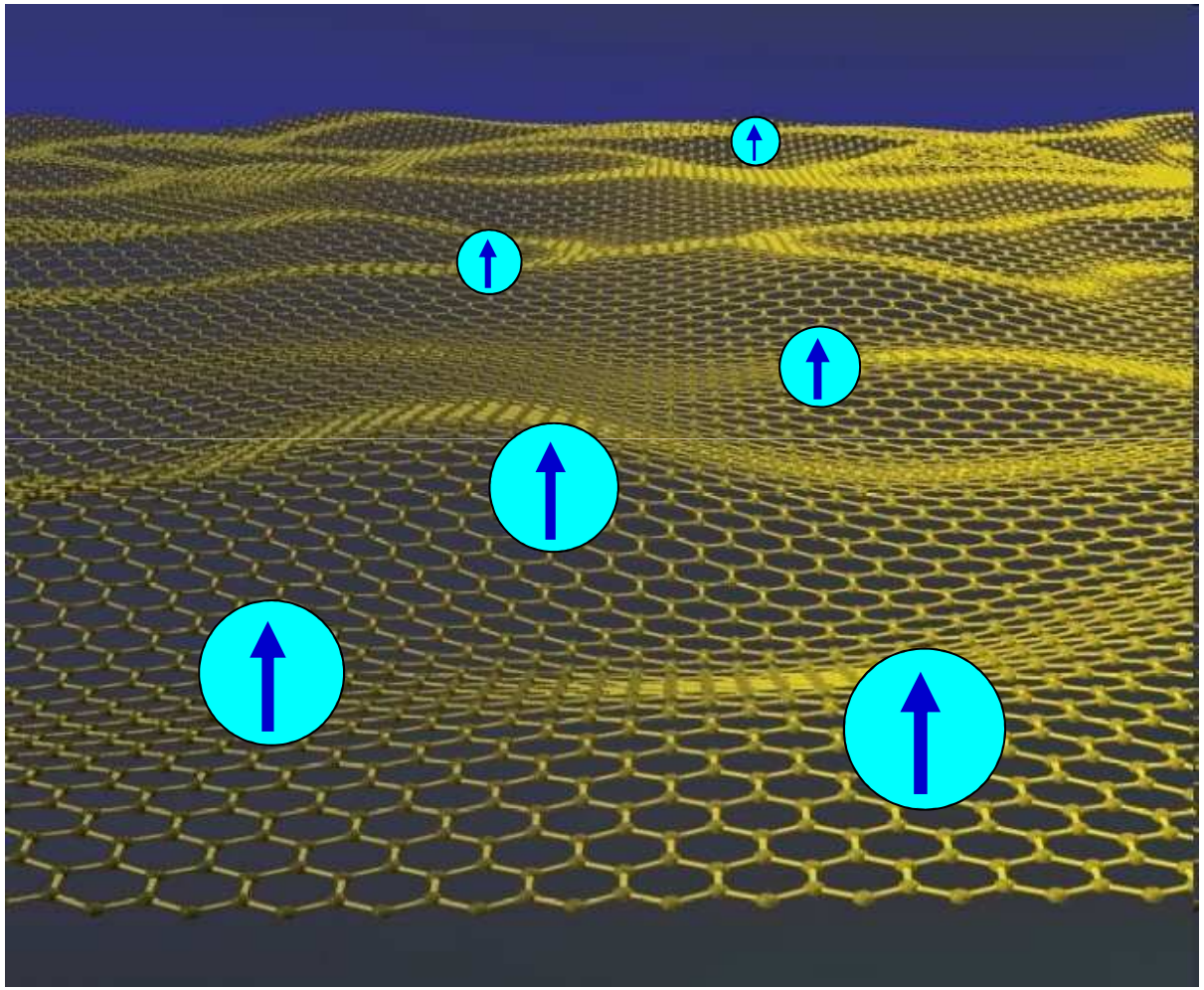
Vacancies = localized spins?



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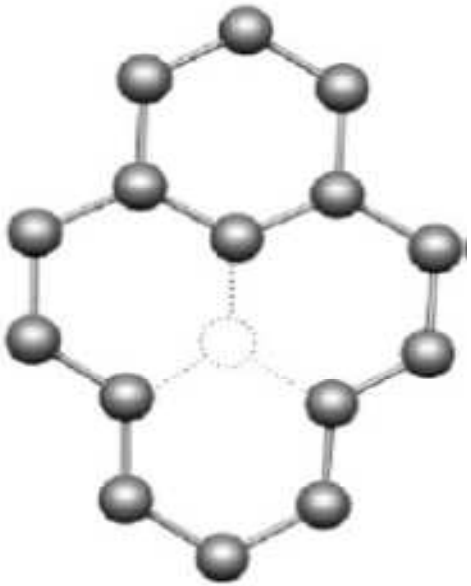
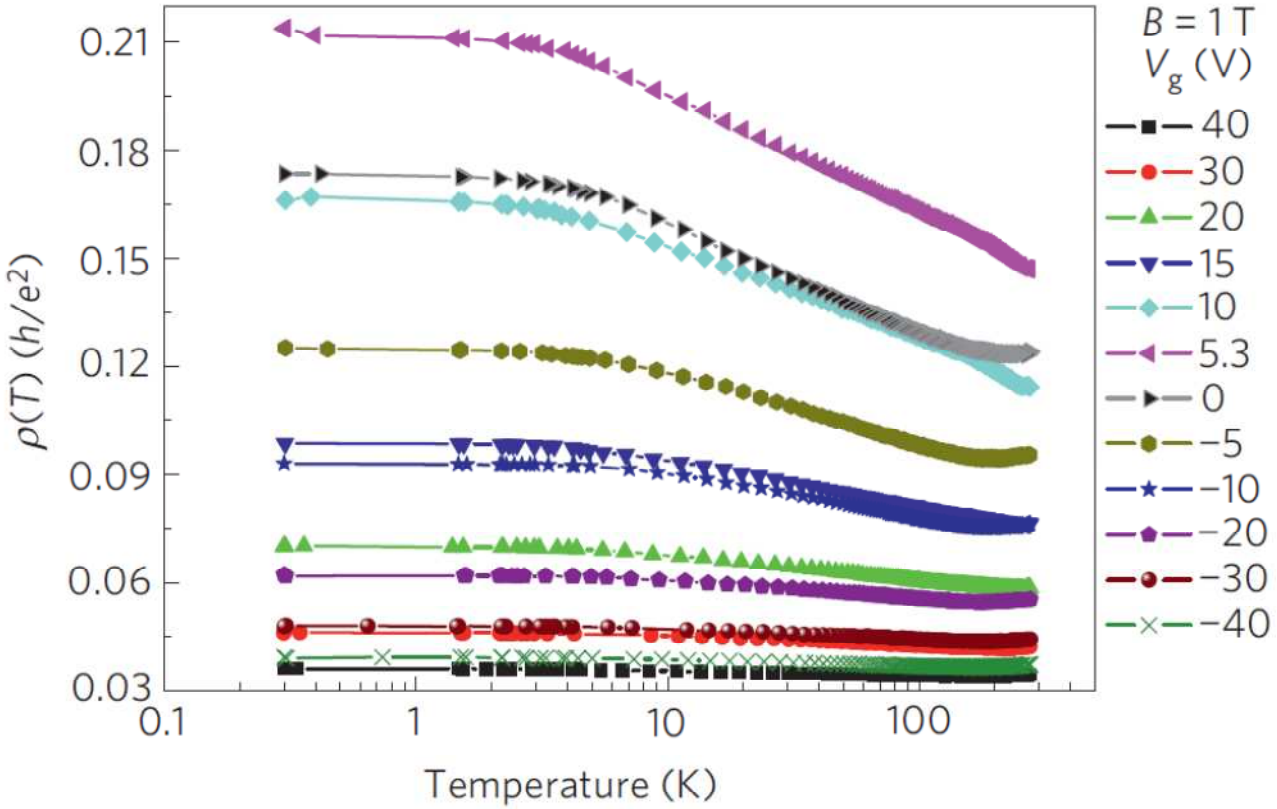
Resistivity ρ(T) in irradiated graphene.





Jian-Hao Chen et al., *Nature Phys.* **7** 535 (2011)

Vacancies (short-range disorder) intentionally caused by irradiation.
Resistivity *increases* at low temperatures !! We have seen that before…

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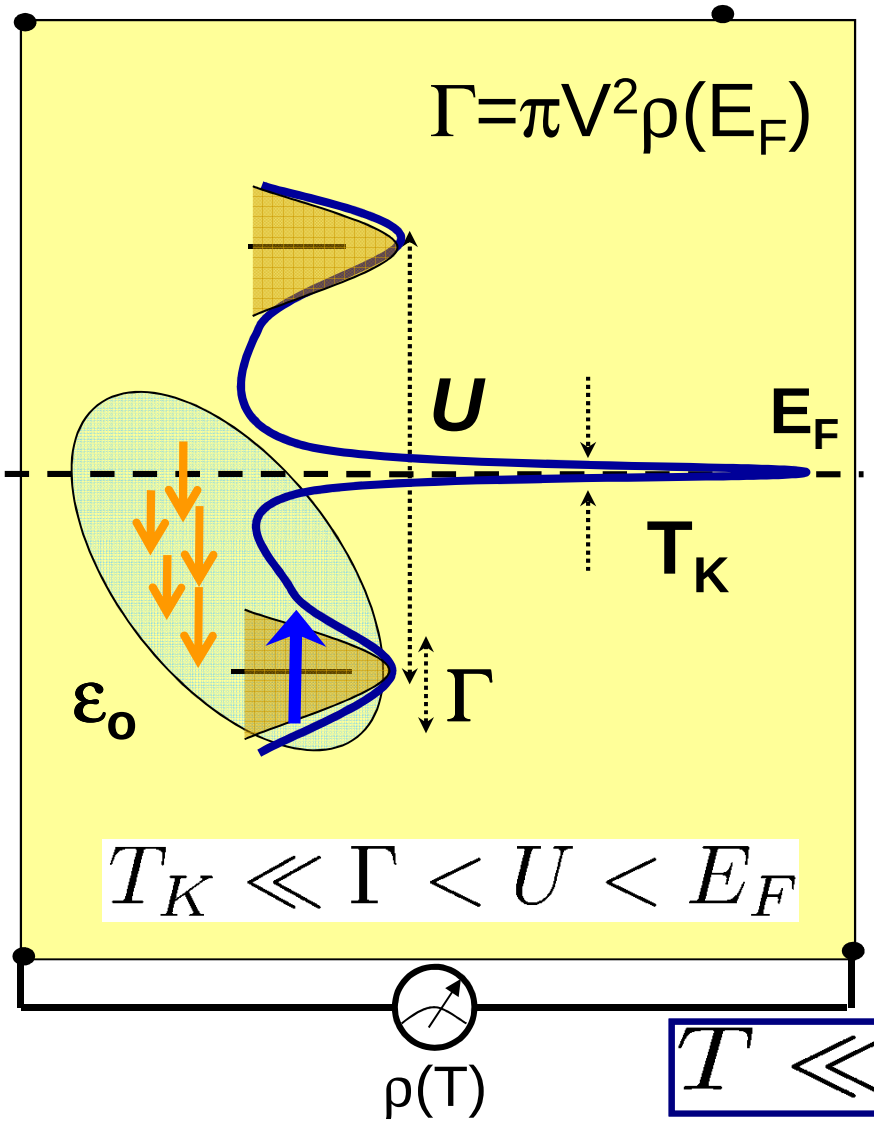
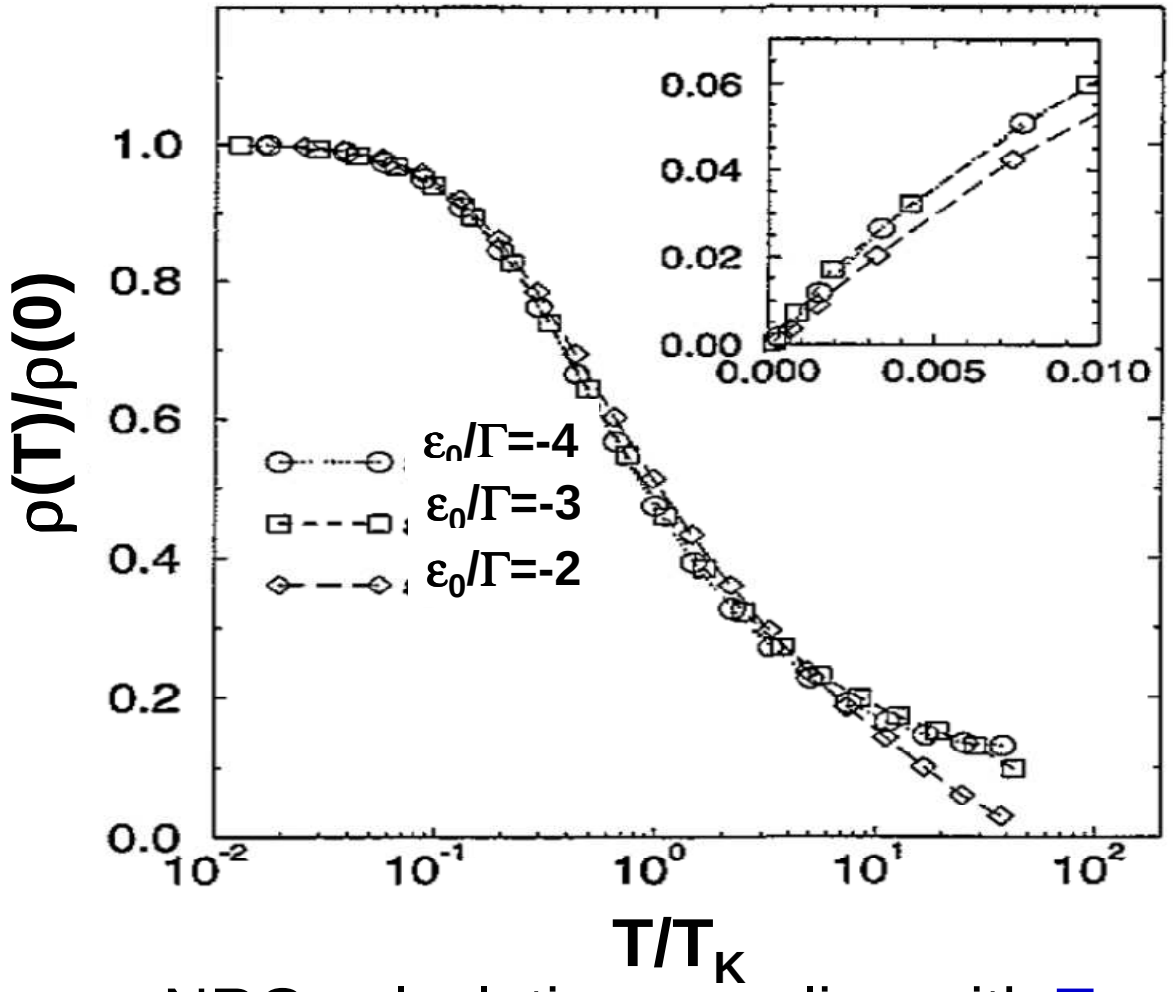
Kondo effect: NRG calculations



$$T_K \ll \Gamma < U < E_F$$

$$T \ll T_K$$



NRG calculations: scaling with T_K

T.A. Costi, et al., *J Phys Cond Mat.***6** 2519 (1994).

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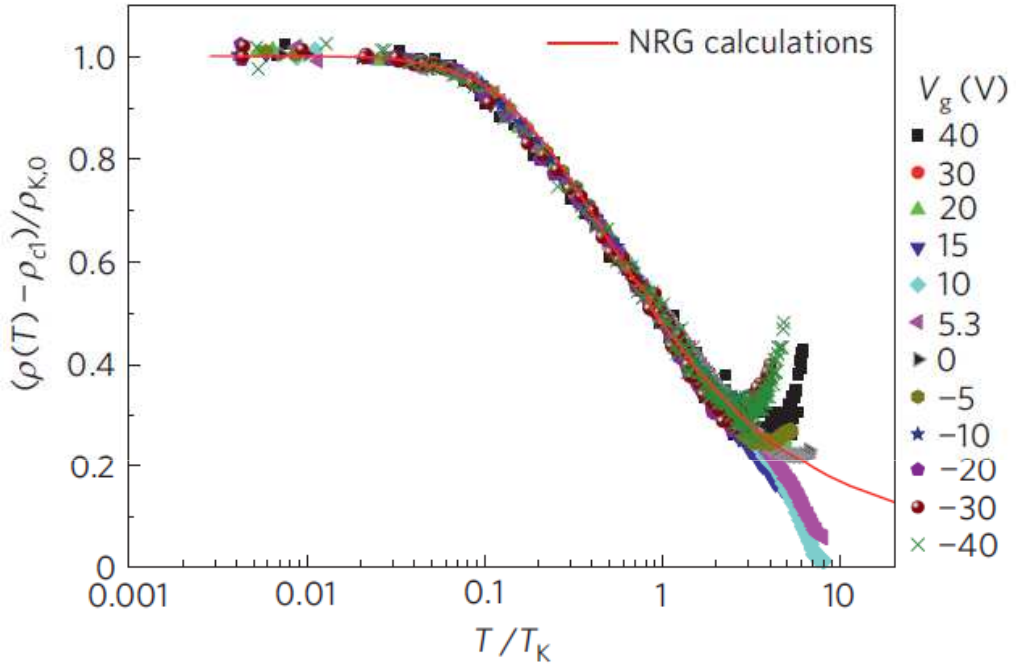
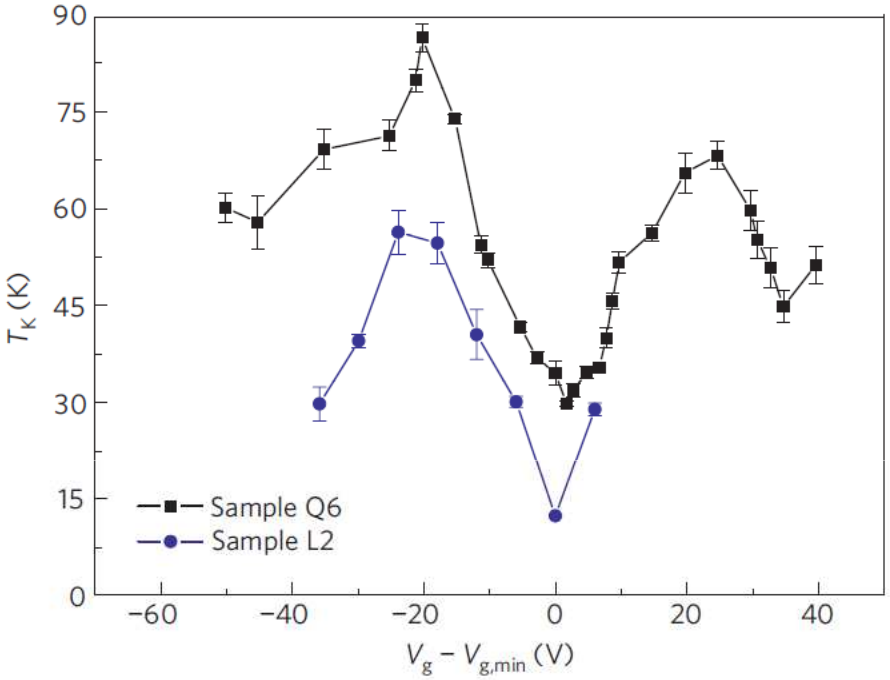
Kondo-like ρ(T) features in irradiated graphene





Jian-Hao Chen et al., *Nature Phys.* **7** 535 (2011)

Resistivity vs Temperature measurements in disordered graphene. Vacancies (short-range disorder) intentionally caused by irradiation. Left: Kondo-like scaling in T/T_K. Right: T_K vs gate voltage.

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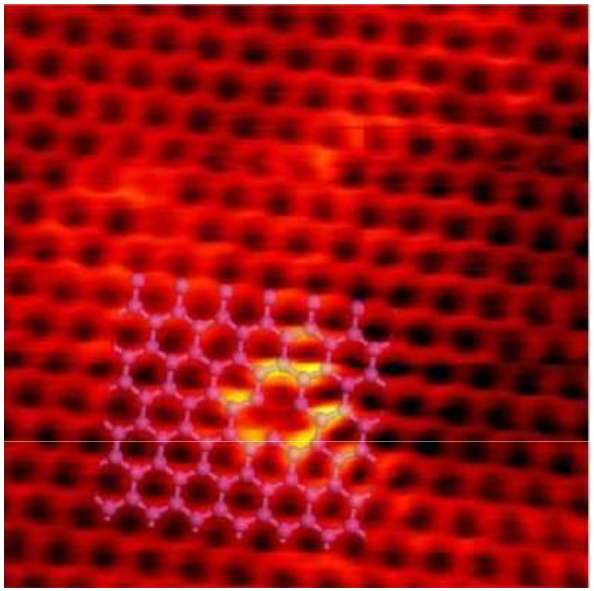
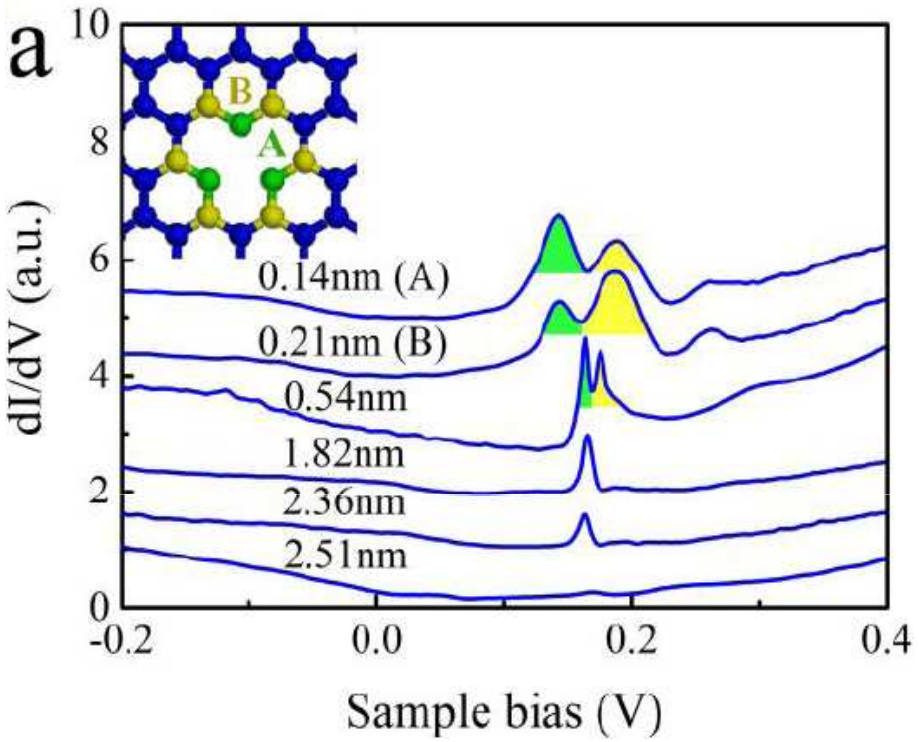
Vacancy magnetism in graphene: STM





Yu Zhang et al., Phys. Rev. Lett. **117**, 166801 (2016)

STS spectra (right) showing Hubbard peaks with U~30 meV.

Our calculations: U~640 meV

V. Miranda, LDS, C.H. Lewenkopf
PRB **94** 075114 (2016) – Editor's Suggestion

Kondo effect in graphene: a few questions.

Where does the localized (magnetic) state come from?

R: Vacancies (=mid-gap states) V. M. Pereira et al., *PRB* **77** 115109 (2008)

How does it couple to the continuous band?

Does this system retain features of an Anderson model coupled to Dirac fermions?

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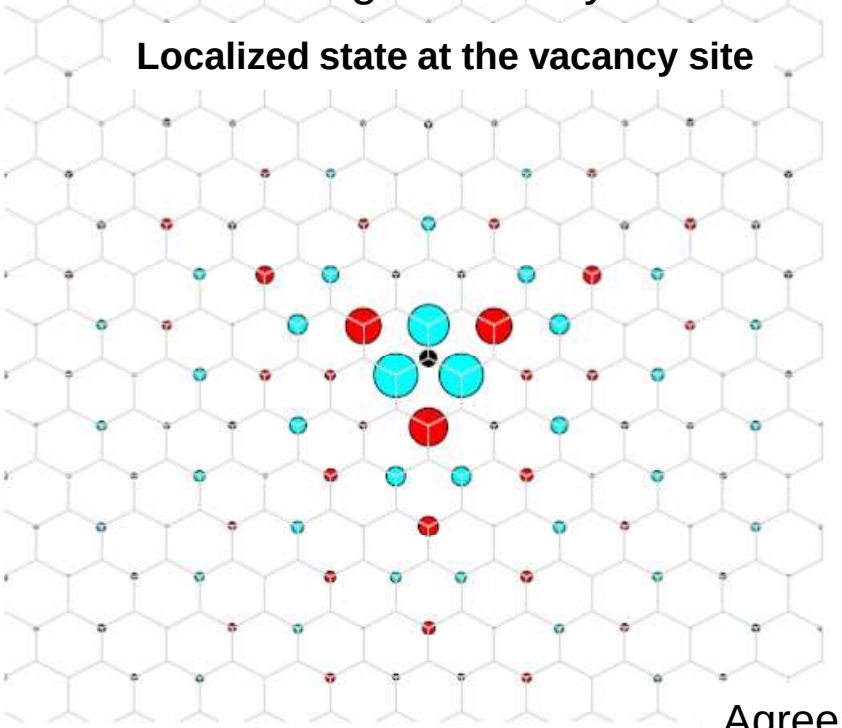
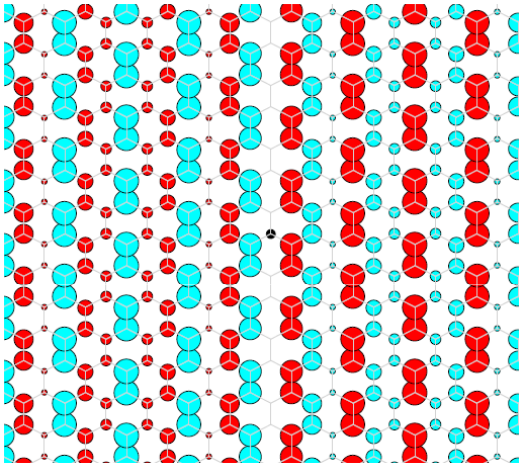
Mid-gap state in the presence of vacancies.

Tight-binding calculations: single vacancy leads to midgap state

Localized state at the vacancy site



Typical delocalized state



Agreement with previous results

V. M. Pereira et al., *PRB* **77** 115109 (2008)

Vacancy tight-binding model:

$$H_{\rm v} = -t \sum_{\langle i,j \rangle} c_i^\dagger c_j + t \sum_{\langle {\rm v},j \rangle} c_{\rm v}^\dagger c_j + {\rm H.c.}$$

$$H_{\rm v}|\nu\rangle = \begin{cases} \varepsilon_\nu |\nu\rangle & \varepsilon_\nu \neq 0, \quad |\nu\rangle \text{ is extended,} \\ 0|{\rm v}\rangle & \varepsilon_{\rm v} = 0, \quad |{\rm v}\rangle \text{ is localized.} \end{cases}$$

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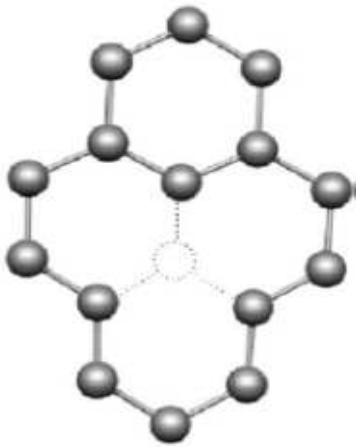
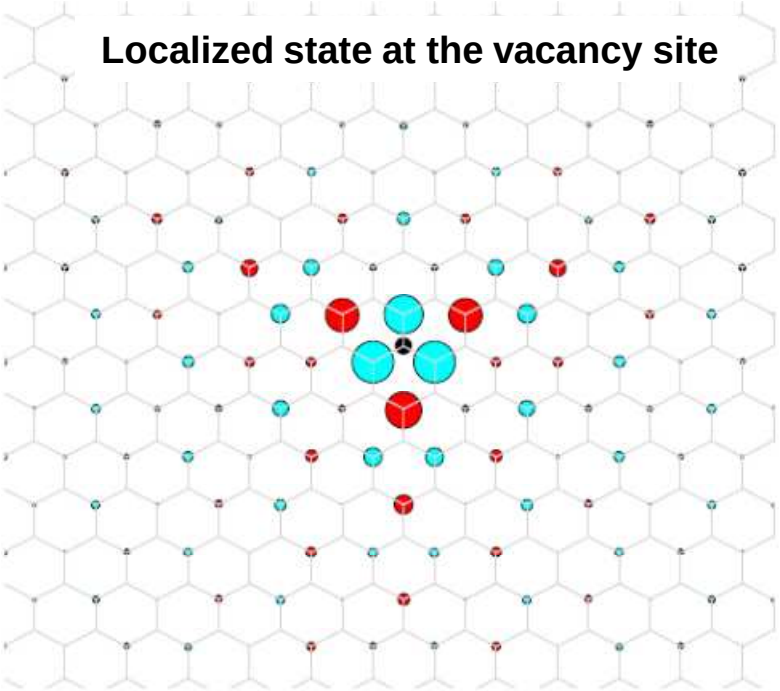
Mid-gap state is not coupled!!

$$H_{\rm v}|\nu\rangle = \begin{cases} \varepsilon_\nu|\nu\rangle \\ 0|{\rm v}\rangle \end{cases}$$

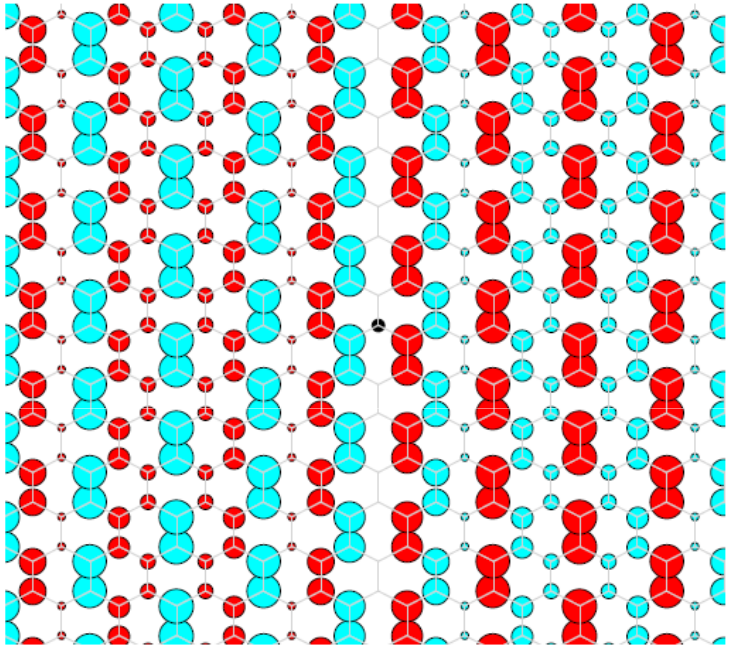


Localized state at the vacancy site



$\varepsilon_{\rm v} = 0, \quad |{\rm v}\rangle$ is localized

Typical delocalized state



$\varepsilon_\nu \neq 0, \quad |\nu\rangle$ is extended

Localized and delocalized states are decoupled:
No Kondo possible.

$$\langle {\rm v}|H_{\rm v}|\nu\rangle = 0 \quad \text{if } {\rm v} \neq \nu \; !$$

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Kondo effect in graphene: a few questions.

Where does the localized (magnetic) state comes from?

R: Vacancies (=mid-gap states) V. M. Pereira et al., *PRB* **77** 115109 (2008)

How does it couple to the continuous band?

R1: Rippling, Jahn-Teller-like distortion M. A. Cazallila et al., arXiv 1207.3135 (2012)

R2: Long-range disorder (this work)

Does this system retain features of an Anderson model coupled to Dirac fermions?

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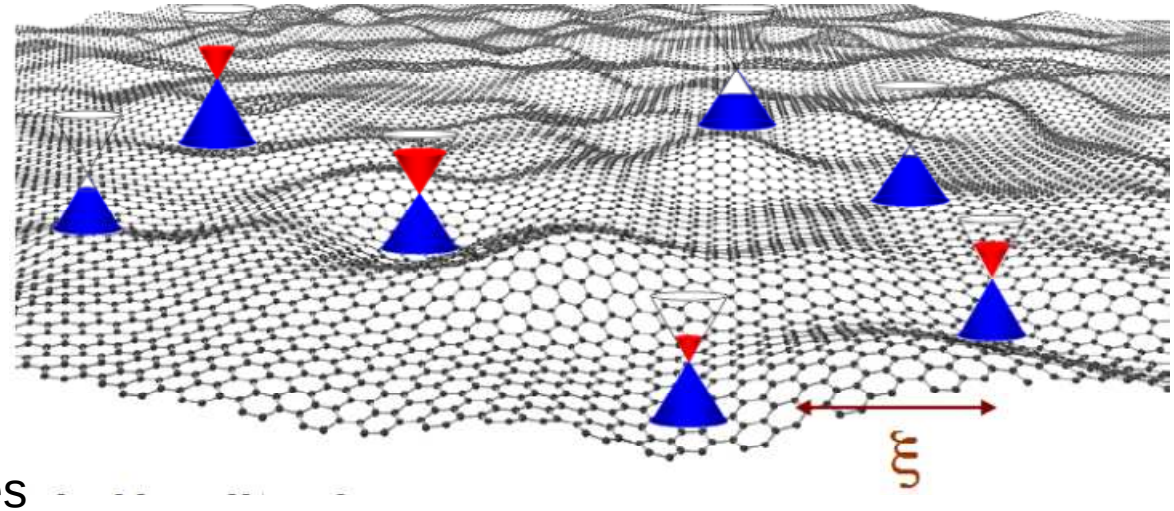
How to couple? Long-range disorder.

How to couple the localized state to the graphene band?

Disorder (weak)

$$U_{\rm dis}(\boldsymbol{r}_i) = \sum_{j=1}^{N_{\rm imp}} W_j \, e^{\frac{-(\boldsymbol{r}_i - \boldsymbol{R}_j)^2}{2\xi^2}}$$



$$H = H_{\rm v} + U_{\rm dis}$$

Our “basis”: localized and extended states

$$H_{\rm v} = -t \sum_{\langle i,j \rangle} c_i^\dagger c_j + t \sum_{\langle {\rm v},j \rangle} c_{\rm v}^\dagger c_j + {\rm H.c.}$$

$$H_{\rm v}|\nu\rangle = \begin{cases} \varepsilon_\mu |\mu\rangle & \text{and} \quad \varepsilon_\mu \neq 0, \quad |\mu\rangle \text{ is extended,} \\ \varepsilon_0 |0\rangle & \text{and} \quad \varepsilon_0 = 0 \quad |0\rangle \text{ is localized.} \end{cases}$$

Projectors:

$$\mathbf{1} = \hat{P} + \hat{Q} \equiv \sum_\mu |\mu\rangle\langle\mu| + |0\rangle\langle 0|$$

$$H = \hat{P}H\hat{P} + \hat{Q}H\hat{P} + \hat{P}H\hat{Q} + \hat{Q}H\hat{Q}$$

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The trick: projecting into different sectors!

How to couple the localized state to the graphene band?

Disorder (weak)

Extended **Coupling** **Localized**

$$H = \hat{P}H\hat{P} + \hat{Q}H\hat{P} + \hat{P}H\hat{Q} + \hat{Q}H\hat{Q}$$

$$\hat{P}H\hat{P} = \sum_{\mu} |\mu\rangle\varepsilon_{\mu}\langle\mu| + \sum_{\mu\mu'} |\mu\rangle\langle\mu|U_{\rm dis}|\mu'\rangle\langle\mu'|$$

Effective band density of states.

$$\rho_{\rm dis}(\omega) = \sum \delta(\omega - \varepsilon_{\beta})$$

$$\hat{Q}H\hat{P} + \text{h.c.} = \sum_{\mu} |0\rangle\langle 0|U_{\rm dis}|\mu\rangle\langle\mu| + \text{h.c.}$$

Coupling to the localized state

$$t_{\beta 0} \equiv \langle\beta|U_{\rm dis}|0\rangle$$

$$\hat{Q}H\hat{Q} = \sum_{\mu} |0\rangle\varepsilon_0\langle 0| + |0\rangle\langle 0|U_{\rm dis}|0\rangle\langle 0| = |0\rangle\varepsilon_0^{\rm dis}\langle 0|$$

Renormalized state energy

$$\varepsilon_0^{\rm dis} \equiv \langle 0|U_{\rm dis}|0\rangle$$

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What about the Hubbard *U*?

Tight-binding (single orbital) contributions to the charging energy of the localized state |0> give:

$$U = e^2 \int d^3r \int d^3r' \frac{\rho_0(r)\rho_0(r')}{|r - r'|}$$

with

$$\rho_0(r) \approx \sum_i |c_i^{(0)}|^2 |\chi_i(r)|^2$$

$$U \equiv U_{\rm diag} + U_{\rm off}$$

$$U_{\rm diag} \sim \frac{U_C}{(\log N_i)^2}$$

"Diagonal"

$$U_{\rm off} \sim e^2 \int d^2r \int d^2r' \frac{|\psi_0(r)|^2 |\psi_0(r')|^2}{|r - r'|}$$

"Off-diagonal"

Our estimates:

$$0.139eV \leq U_{\rm diag} \leq 0.302eV.$$

$$1.859eV \leq U_{\rm off} \leq 3.723eV.$$

In the NRG calculations, we use:

$$U = 0.5D \approx 1.5t = 4.2 \text{ eV}$$

consistent with recent DFT+cRPA calculations

$$U^*/t = 1.6 \pm 0.2$$ M. Schüler et al., *PRL* **111** 036601 (2013)

What about the Hubbard *U*?

Tight-binding (single orbital) contributions to the charging energy of the localized state |0> give:

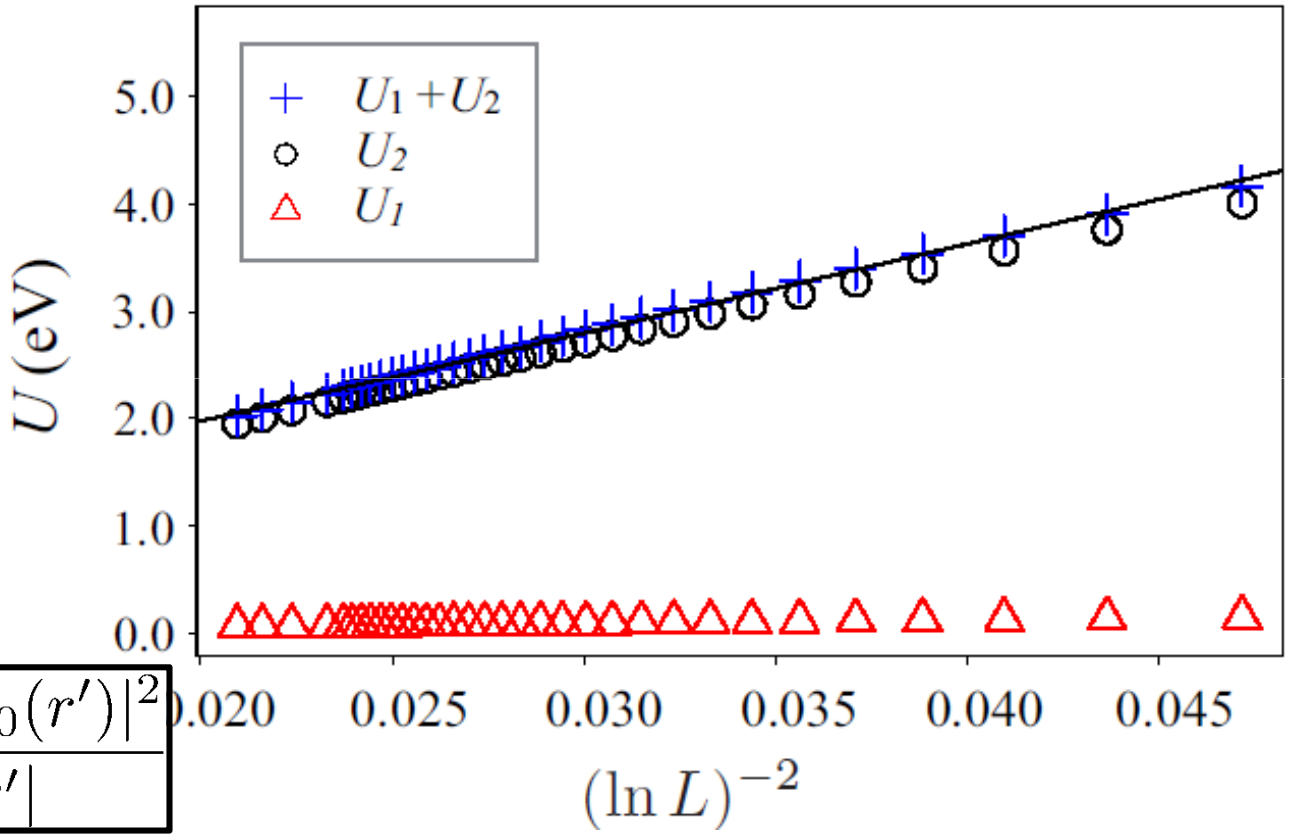
$$U \equiv U_1 + U_2$$

"Diagonal"

$$U_1 \sim \frac{U_C}{(\log N_i)^2}$$

"Off-diagonal"

$$U_2 \sim e^2 \int d^2r \int d^2r' \frac{|\psi_0(r)|^2 |\psi_0(r')|^2}{|r - r'|}$$



V. Miranda, LDS, Caio Lewenkopf PRB **94** 075114 (2016)

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R2: Long-range disorder (this work)

Does this system retain features of an Anderson model coupled to Dirac fermions?

NRG calculations: TB-derived Anderson model

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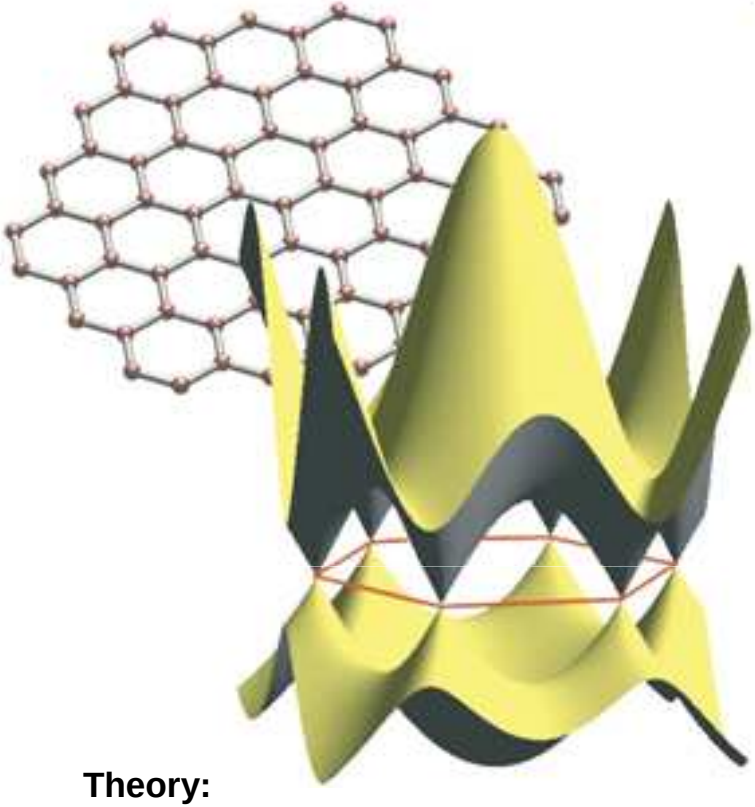
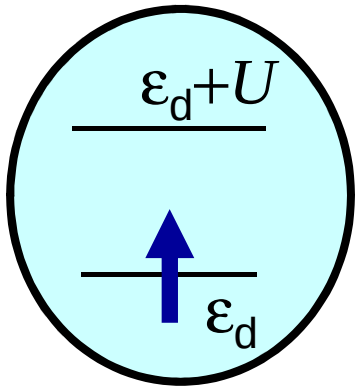
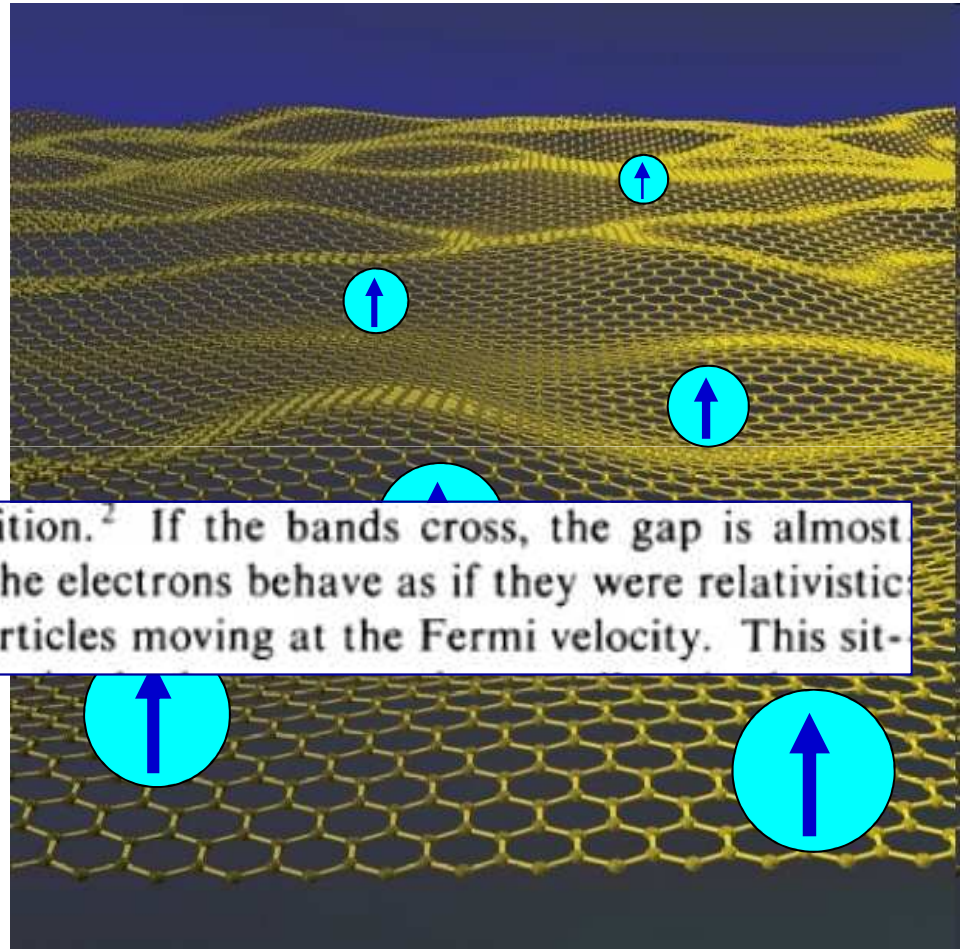
Kondo effect with “massless Dirac Fermions”?



+





cal composition.[2] If the bands cross, the gap is almost linear and the electrons behave as if they were relativistic massless particles moving at the Fermi velocity. This sit-

Theory:

D. Withoff and E. Fradkin, PRL **64** 1835 (1990).
C. Gonzalez-Buxton, K. Ingersent, PRB **57**, 14254 (1998)
P.S. Cornaglia et al. PRL **102** 046801 (2009).
M. Vojta, et al., Europhys. Lett. **90**, 27006 (2010).
Review: L. Fritz and M. Vojta, **arXiv:1208.3113** (2012)

=Quantum phase transition!

Q: Do we see this in our model?

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Long-range disorder model: Hybridization.

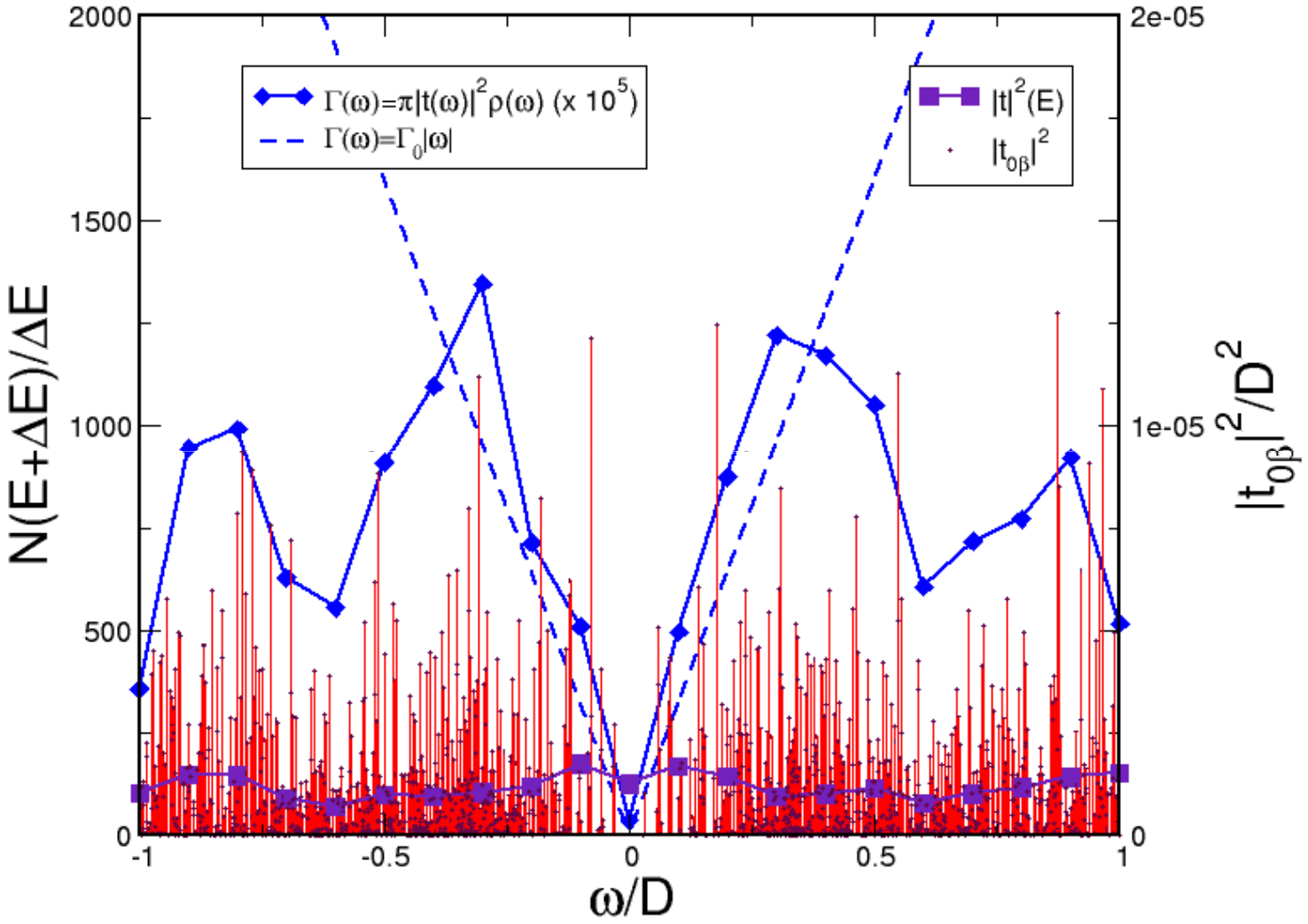
For each realization:

$|t_{0\beta}|^2 \quad \varepsilon_\beta$

$$\Gamma_{\rm dis}(\omega) = \pi |t_\omega|^2 \rho_{\rm dis}(\omega)$$

And also:

$$\varepsilon_0^{\rm dis} \equiv \langle 0|U_{\rm dis}|0\rangle$$



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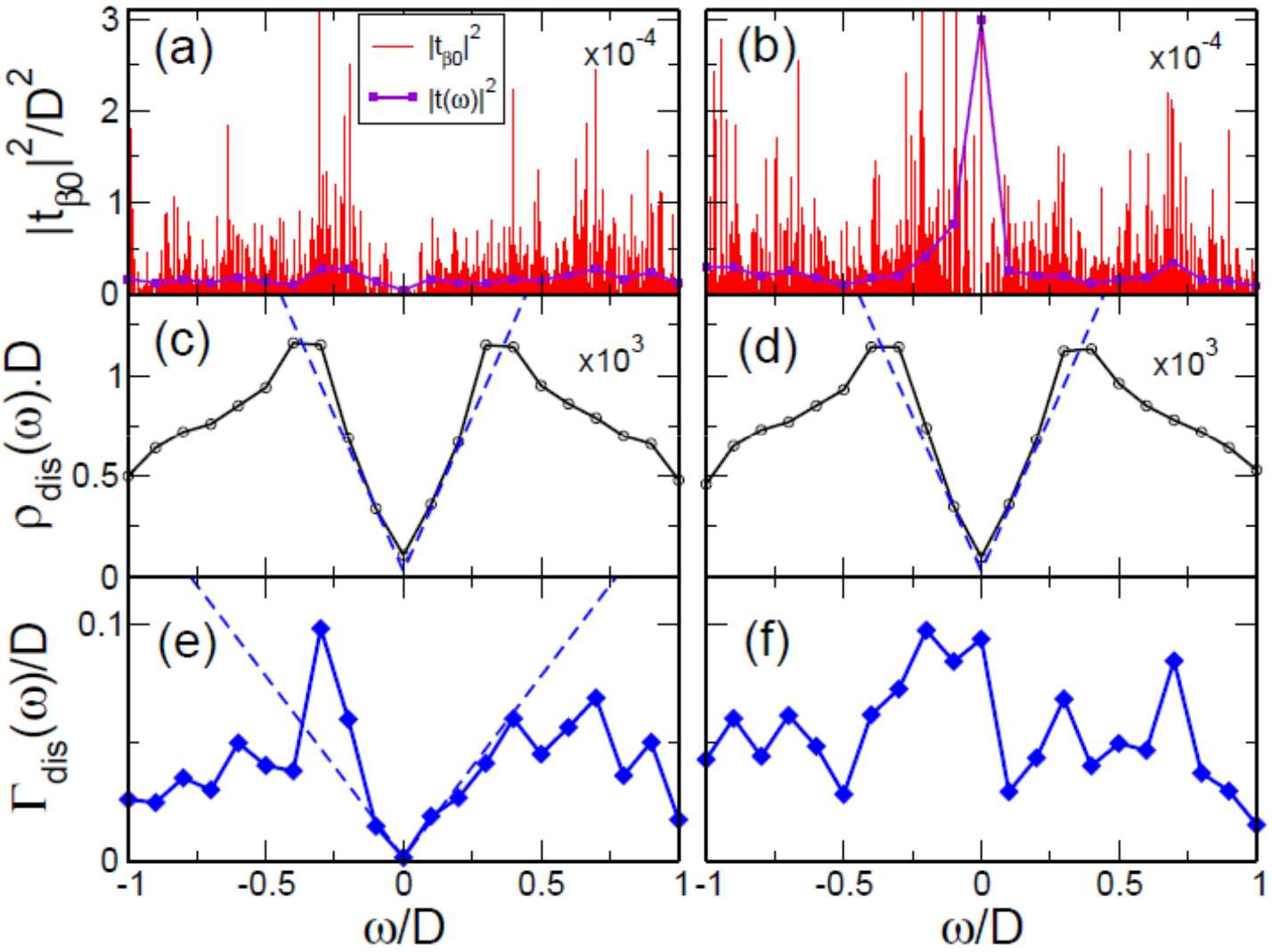

PRB **90** 201101(R) (2014)

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Disorder: model parameters distributions

For each realization:

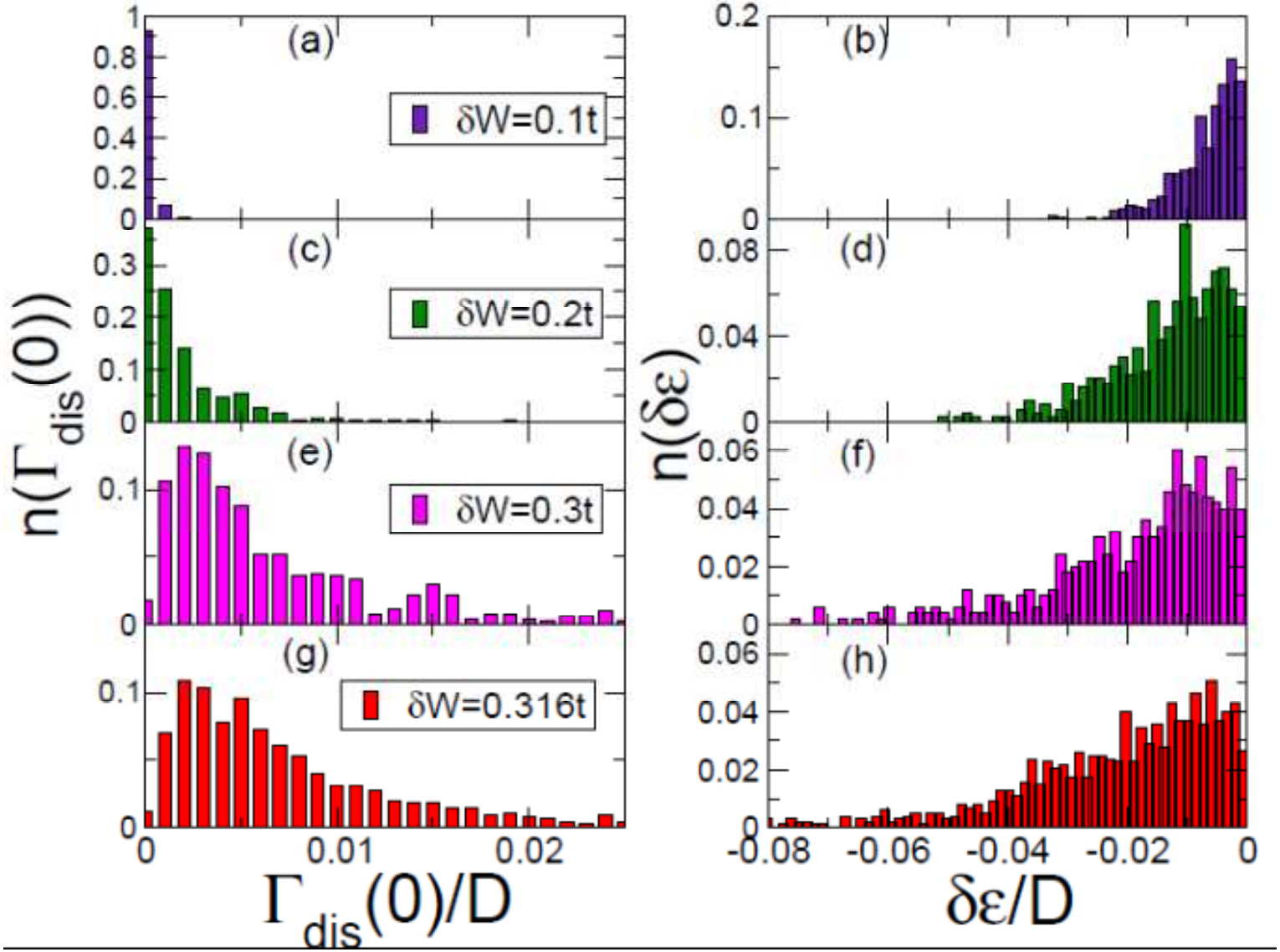
$$|t_{0\beta}|^2 \quad \varepsilon_\beta$$

$$\Gamma_{\rm dis}(\omega) = \pi |t_\omega|^2 \rho_{\rm dis}(\omega)$$

And also:

$$\varepsilon_0^{\rm dis} \equiv \langle 0|U_{\rm dis}|0\rangle$$

$$\delta\varepsilon = \varepsilon_0^{\rm dis} - \mu(V_g)$$



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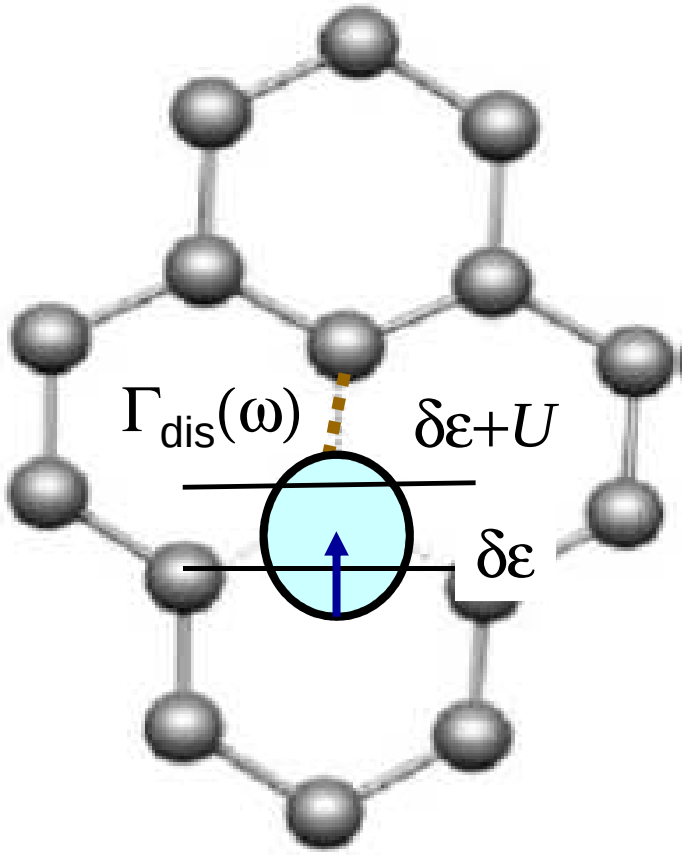
Effective Anderson model: disorder-mediated coupling.



$$H_A = H_{\rm state} + H_{\rm band} + H_{s-b} \text{ where:}$$

$$\begin{aligned}
H_{\rm state} &= \delta\epsilon\, n_{0\sigma} + U n_{0\uparrow} n_{0\downarrow} \qquad \left(\delta\epsilon = \epsilon_0^{\rm dis} - \mu(V_g)\right) \\
H_{\rm band} &= \int_{-D-\Delta\mu}^{D-\Delta\mu} d\omega\; \omega\; c^\dagger_{\omega\sigma} c_{\omega\sigma} \\
H_{s-b} &= \int_{-D-\Delta\mu}^{D-\Delta\mu} d\omega \sqrt{\Gamma_{\rm dis}(\omega)/\pi}\left(c^\dagger_{0\sigma} c_{\omega\sigma} + {\rm H.c.}\right) .
\end{aligned}$$

Anderson model with disorder-mediated coupling.

δε: impurity state energy; $\Gamma_{dis}(\omega)$: hybridization

$\mu(V_g)$: Fermi energy (gate-dependent)

$\mu(0)$: Fermi energy at charge neutrality. ($\Delta\mu=\mu(V_g)-\mu(0)$)

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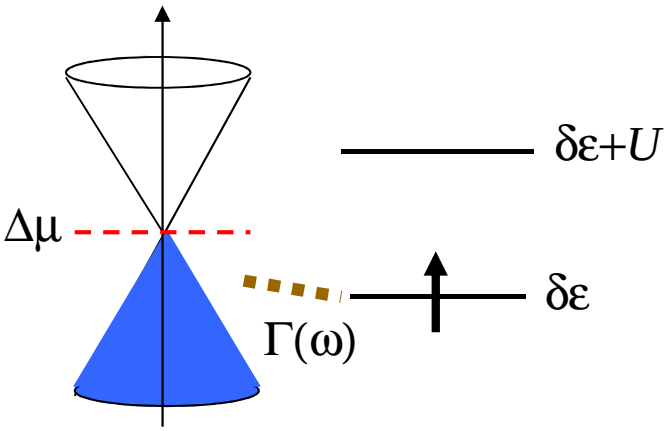
Anderson model + massless Dirac fermions

$\rho(\omega)$: density of states

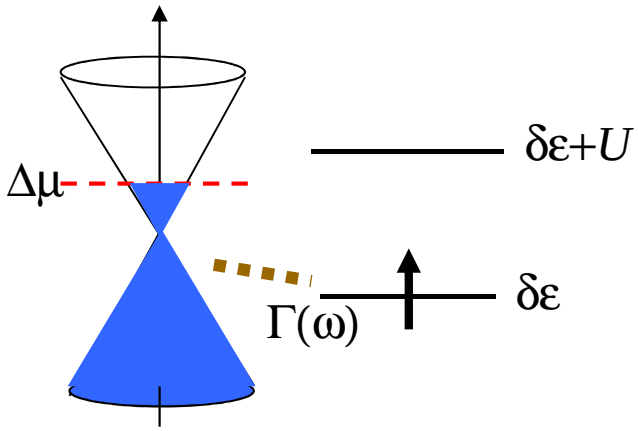
$$\Gamma(\omega) = \pi V^2 \rho(\omega)$$

“Pseudogap” model



$$\Gamma(\omega \to 0) = 0 (\sim |\omega|)$$

“metallic” model



$$\Gamma(\omega \to 0) \neq 0$$

Anderson impurity coupled to a “Dirac band” with linear dispersion.

δε: impurity state energy

$\Delta\mu = \mu(V_g) - \mu(0)$

$\mu(V_g)$: Fermi energy (gate-dependent)

$\mu(0)$: Fermi energy at charge neutrality

Realization of the “pseudogap Anderson model” for V_g=0.

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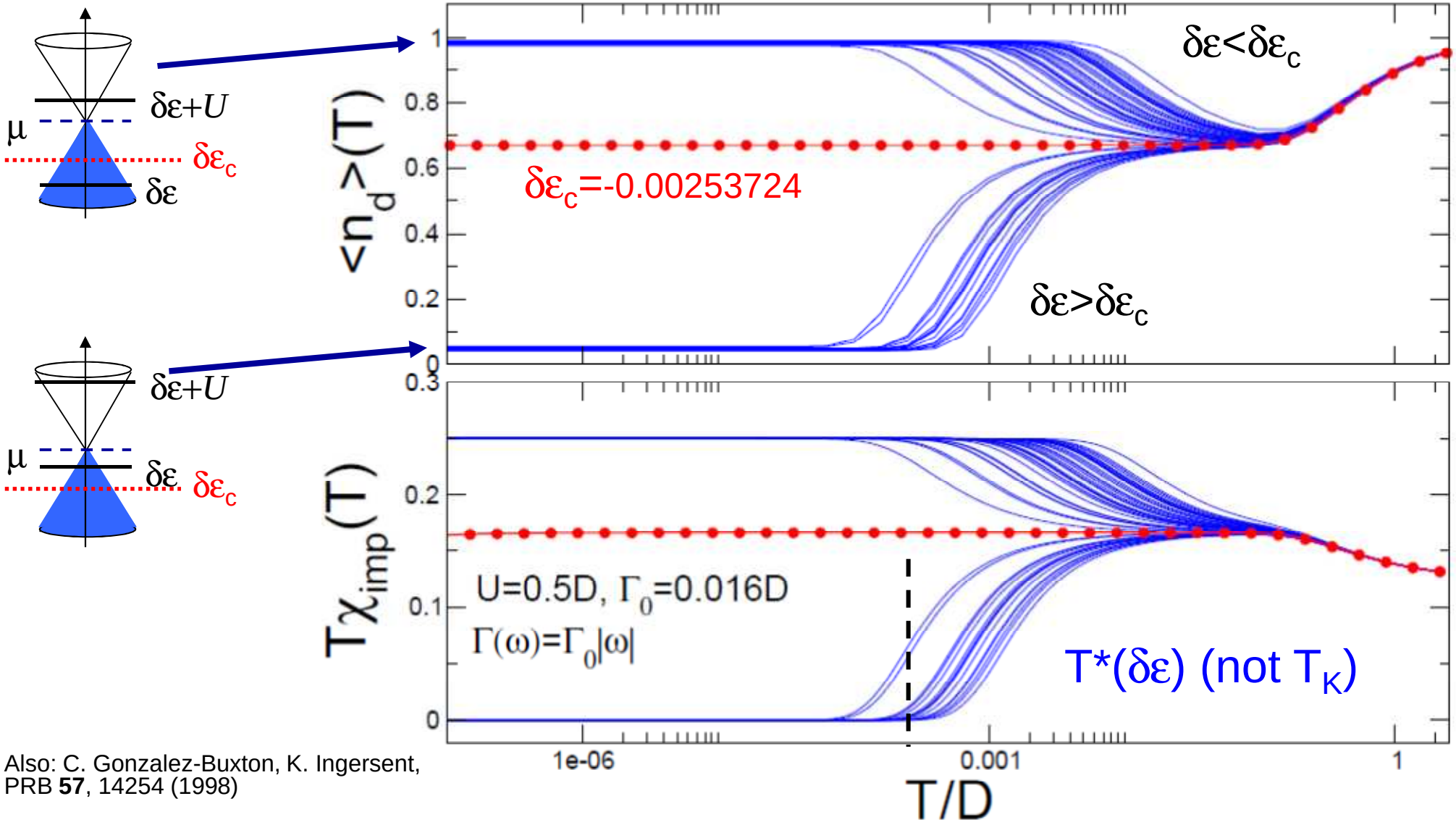
Pseudogap model: quantum phase transition.



Also: C. Gonzalez-Buxton, K. Ingersent, PRB **57**, 14254 (1998)

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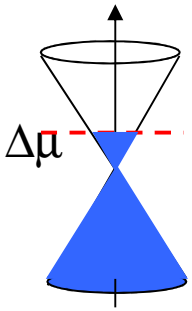
Metallic x Pseudogap: crossover x QPT



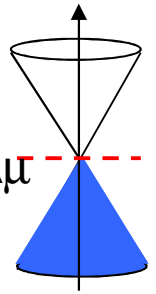
Occupation

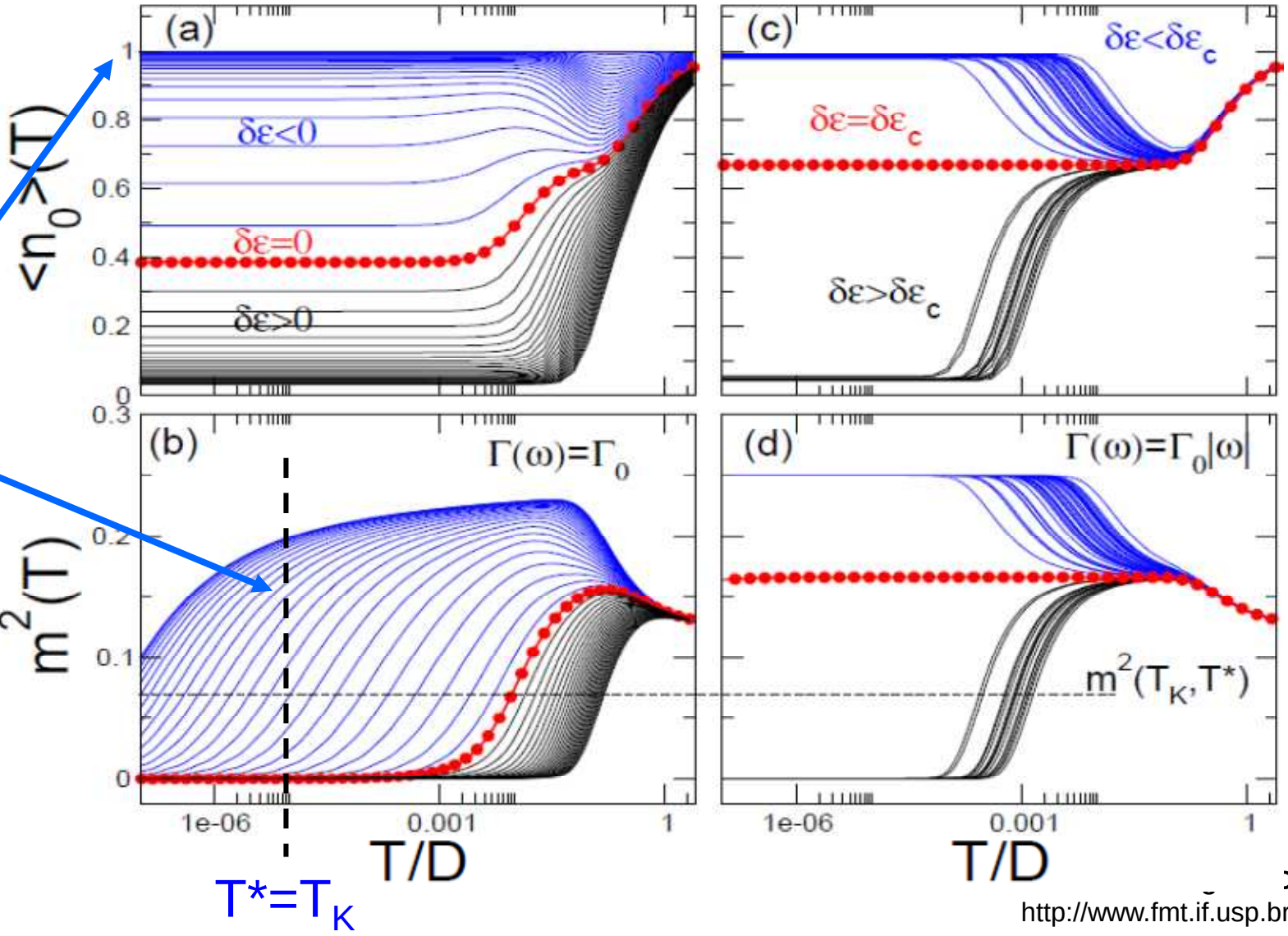
Kondo

Magnetic moment (local)

Metallic ("usual")

Pseudogap





Dias
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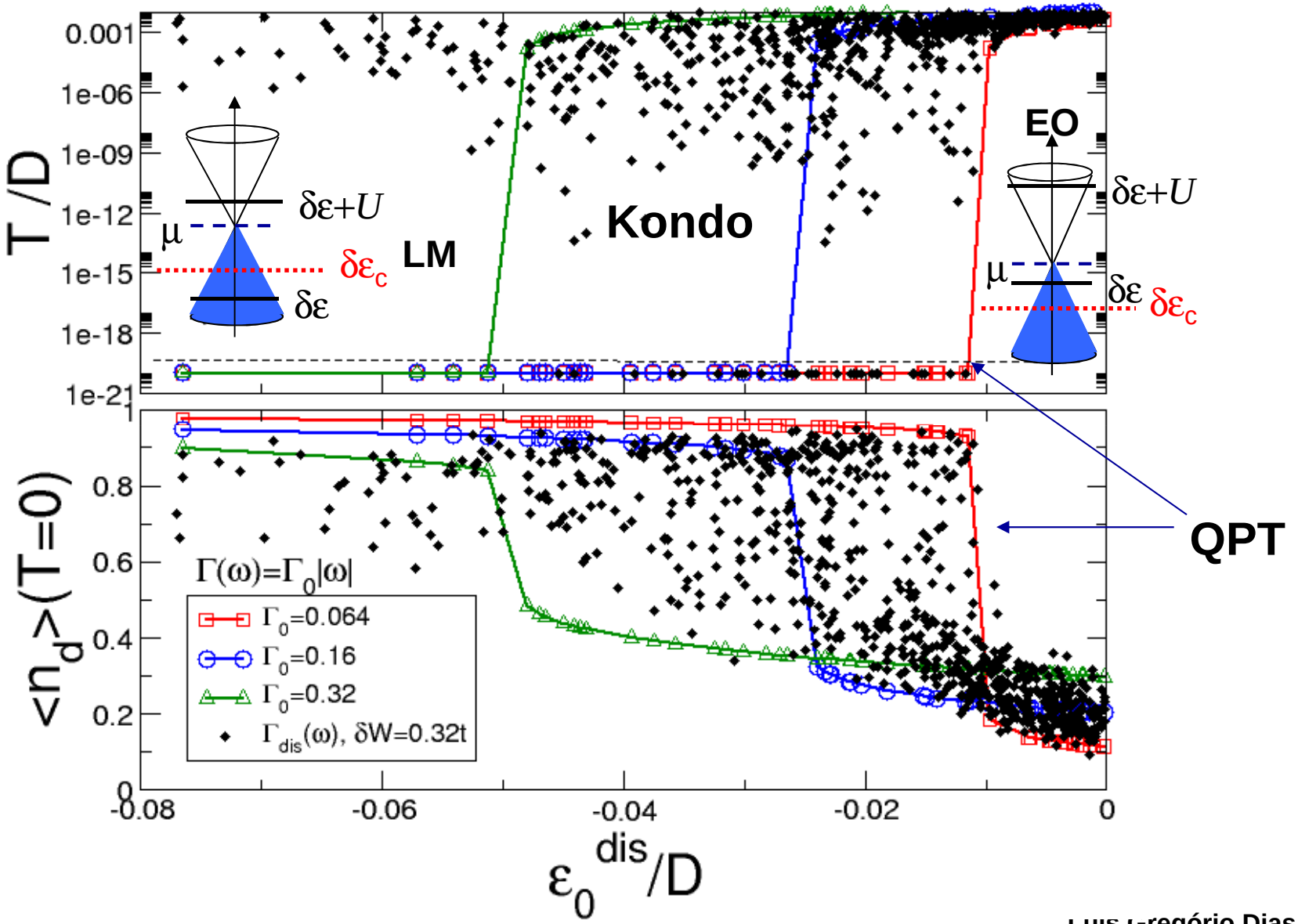
Pseudogap x Disorder: NRG calculations

$\Delta\mu=0$



PRB **90** 201101(R) (2014)

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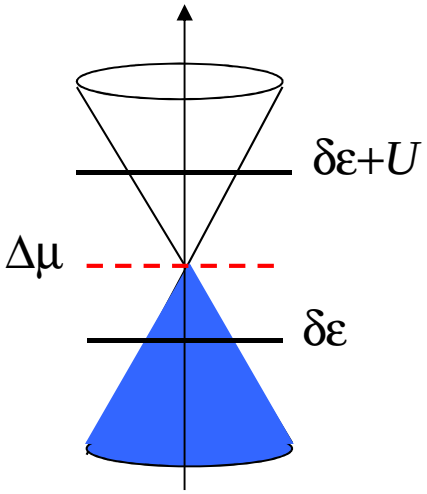
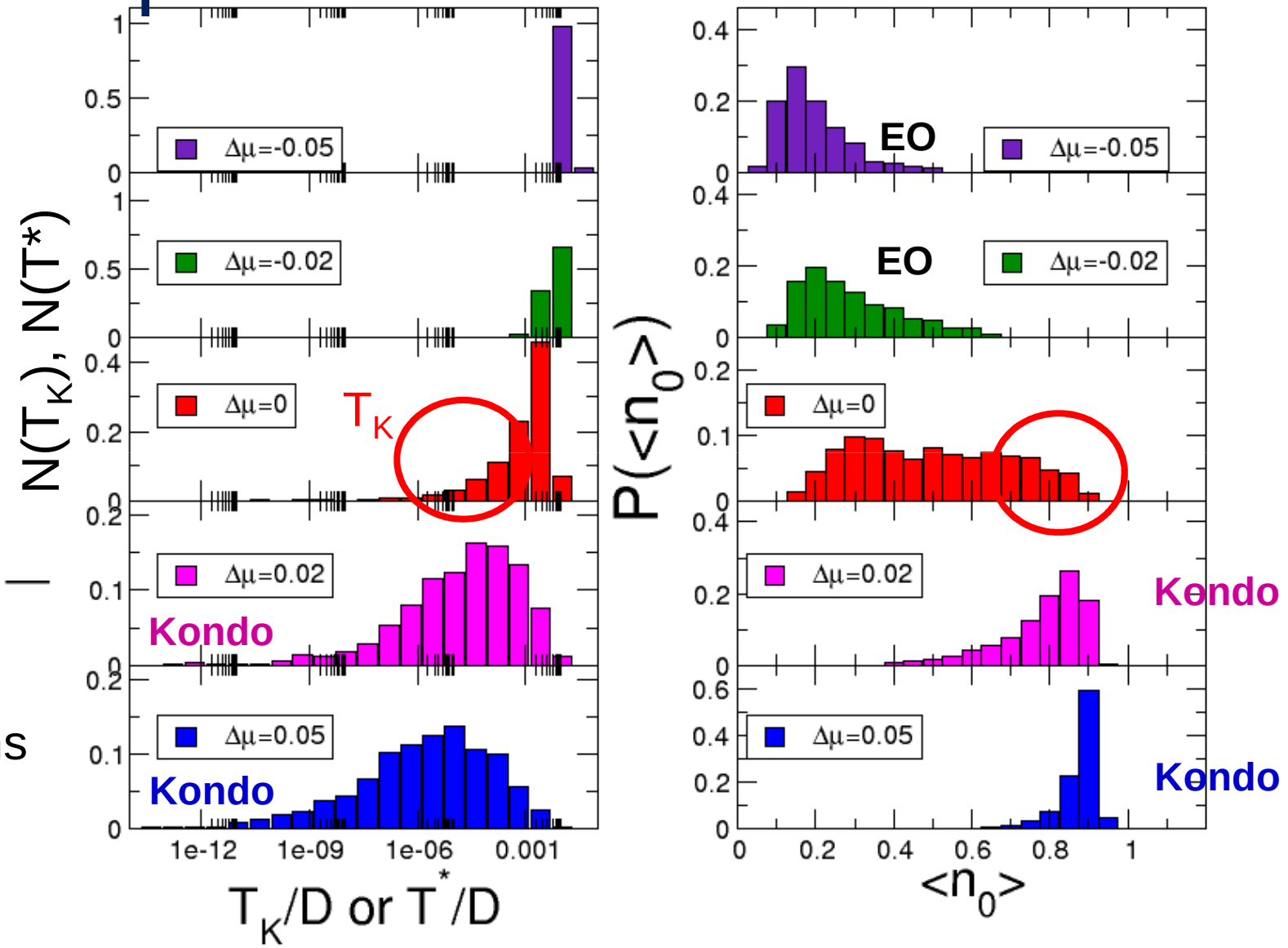
Kondo temperature distributions.

$\Delta\mu=0$



1000 realizations



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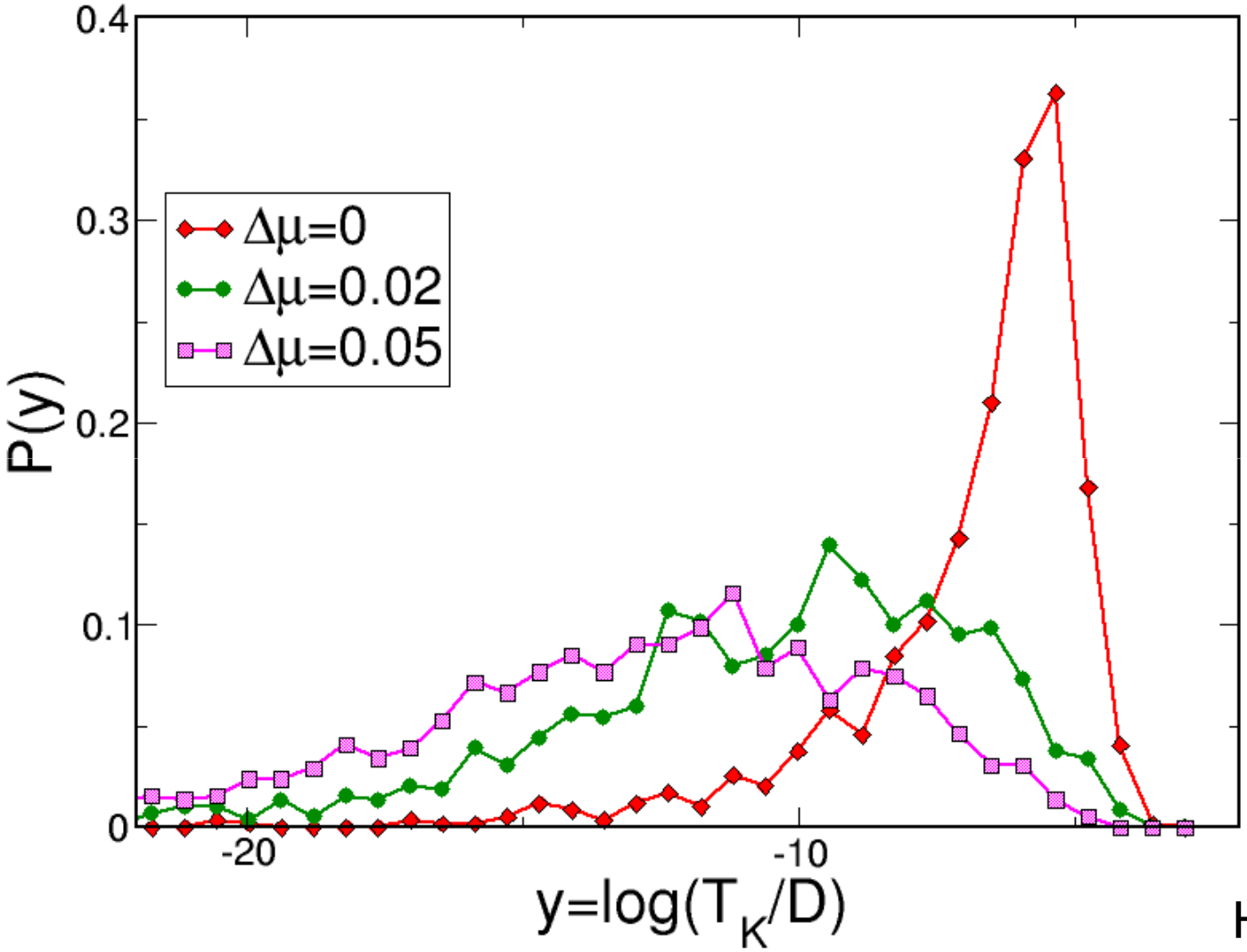
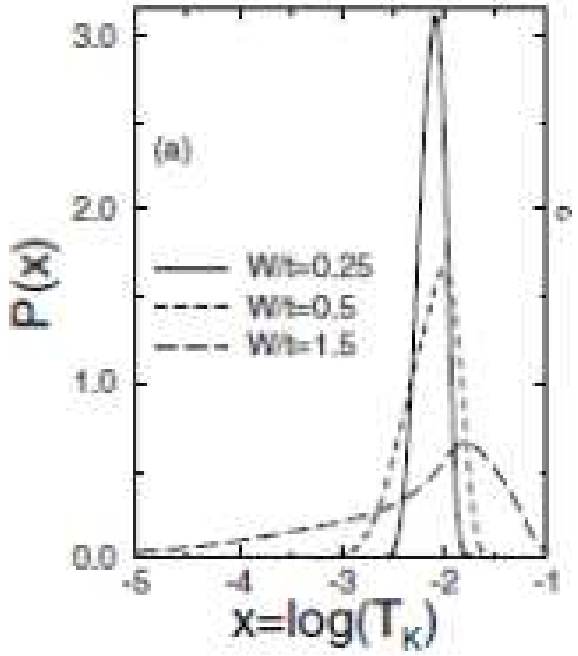
$P(T_K)$ distributions: Griffiths phase.





E. Miranda and V. Dobrosavljevic, *PRL* **86** 264 (2001)

$$P(T_K) \sim T_K^{(\alpha-1)}$$

Hallmark of a “Griffiths phase”

PRB **90** 201101(R) (2014)

In a few words…“More is Different!”

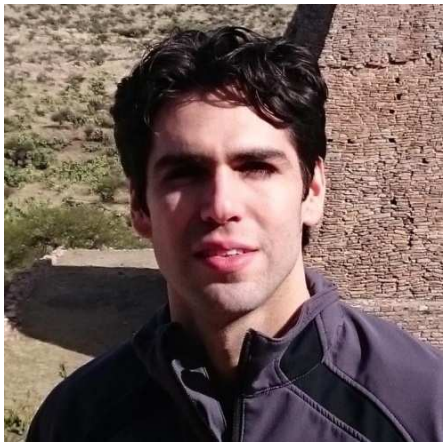
“ The behavior of large and complex aggregates of elementary particles, it turns out, is not to be understood in terms of simple extrapolation of the properties of a few particles.

Instead, at each level of complexity entirely new properties appear and the understanding of the new behaviors requires research which I think is as fundamental in its nature as any other.“

Phillip W. Anderson, “More is different”, *Science* **177** 393 (1972)

Current Group Members

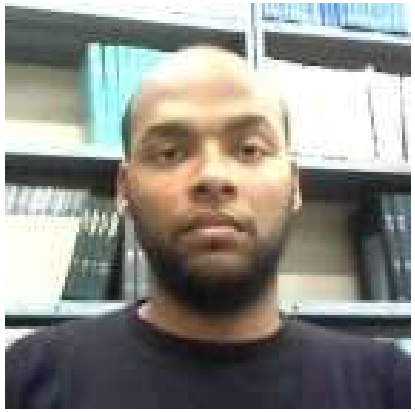
Luis Dias da Silva
Professor



David Ruiz-Tijerina
Post-doc (now at Manchester)

Dimy Nanclares
Graduate student

IF - USP



Marcos Medeiros
Graduate student

Raphael Levy
Graduate student

Acknowledgements

Collaborators on the works presented

Sergio Ulloa (Ohio U,)
Saw Hla (Ohio U. /Argonne)
Gayani Perera (Ohio U.)
Nichola Marzari (MIT)
Heather Kulik (MIT)

Elbio Dagotto (Oak Ridge)
Fernando Reboredo (Oak Ridge)
Murilo Tiago (Oak Ridge)
Caio Lewenkopf (UFF)
Vladimir Miranda (UFF)

FAPESP
CAPES
CNPq
USP PRÓ-REITORIA DE PESQUISA

Support: FAPESP (2016/18495-4); CAPES (PNPD program), CNPq (307107/2013-2 and 449148/2014-9); USP-PRP NAP Q-Nano.