Magnetism and Superconductivity in Graphene from Electronic Correlations

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Quantum Matter in Low Dimensions: Opportunities and Challenges

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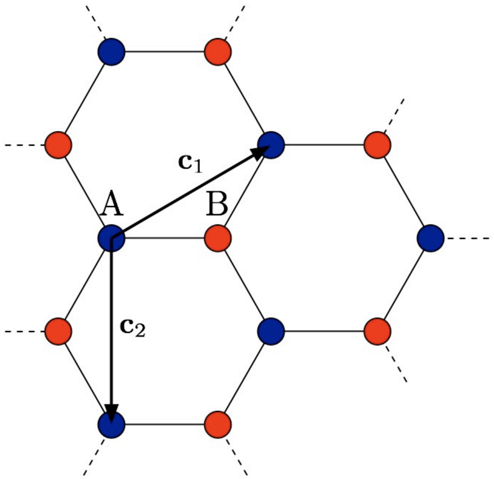
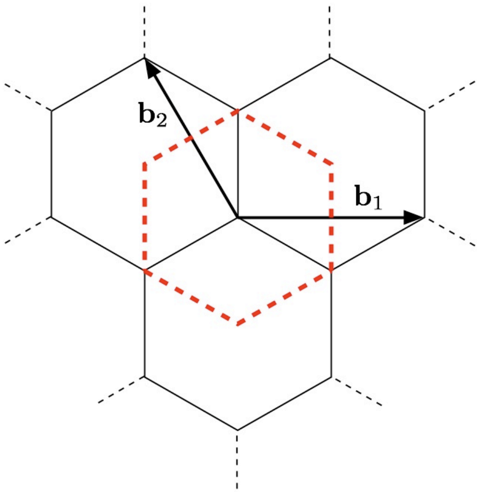
Acknowledgements: Sebastian Doniach (Stanford), Jonas Fransson (Uppsala), Biplab Sanyal (Uppsala)

Free Electron Picture of Graphene

Honeycomb lattice:

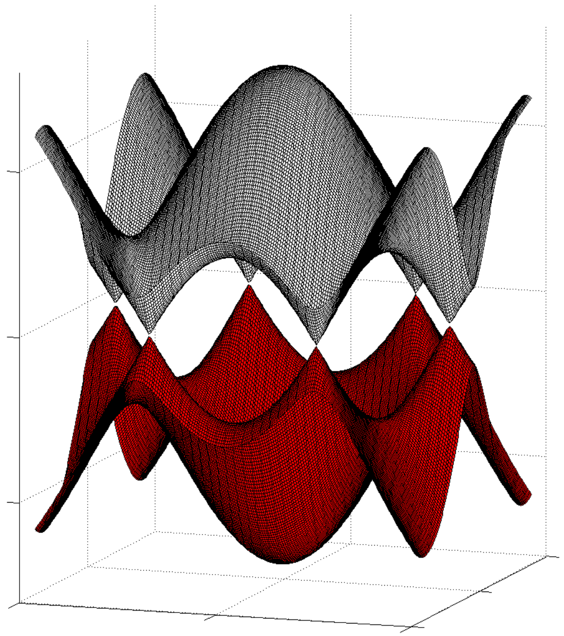


1st BZ:

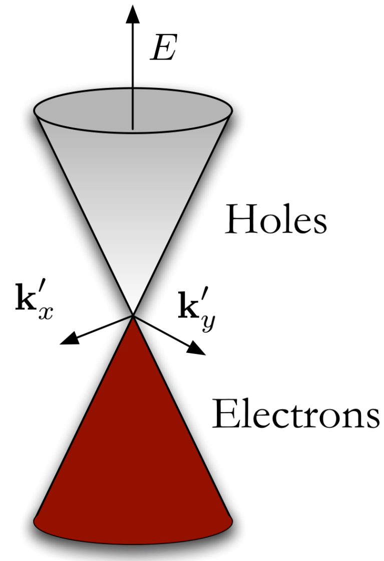


sp^2 hybridization $\Rightarrow$ $1p_z$ orbital per C atom left

Tight-binding with nearest neighbor hopping only:
(Wallace, 1946)



Upper and lower π-band



Massless Dirac Fermions
($c \rightarrow v_F \sim c/300$)

Graphite:
C-C bond distance: 1.42 Å
Interplanar distance: 3.37 Å

Outline

- Evidence for the importance of electronic correlations in graphene
- Modeling electronic correlations
- Mean-field *d*-wave superconductivity in graphene
- Graphene SNS Josephson junctions
- RKKY coupling between magnetic impurities in graphene

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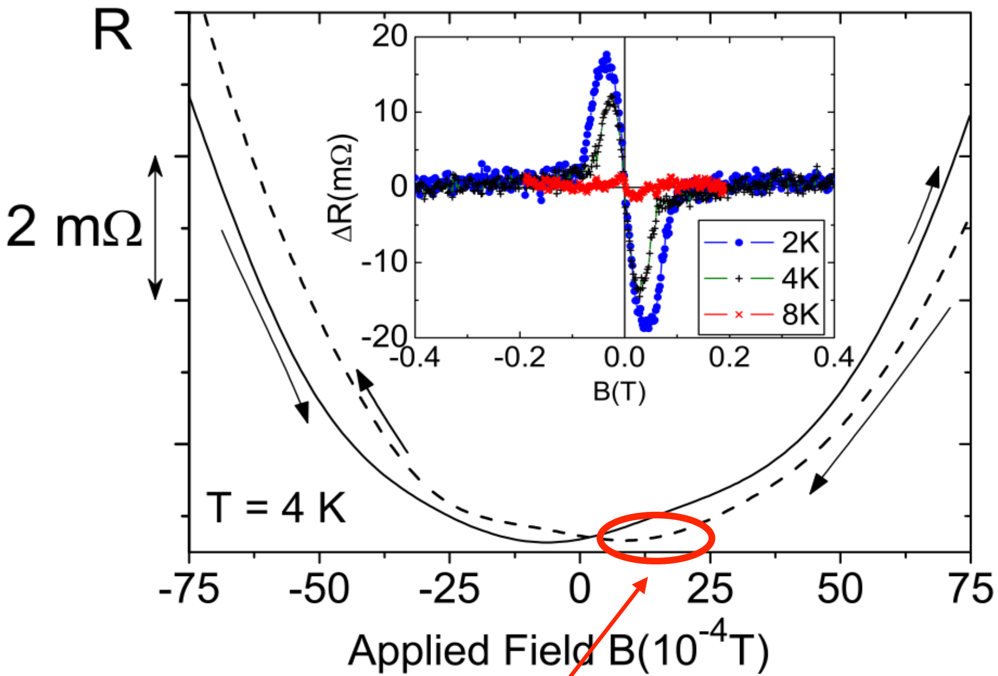
Traces of Superconductivity in Graphite

Magnetoresistance:



[2]

Minima reached for decreasing field at B > 0

- Minima for B < 0:
  - Ferromagnetism (FM)
  - Homogenous superconductor (SC) with pinned vortices
- Minima for B > 0:
  - Granular SC with Josephson coupled grains
    - $T_c \sim 25$ K

Intrinsic granular superconductivity in graphite?

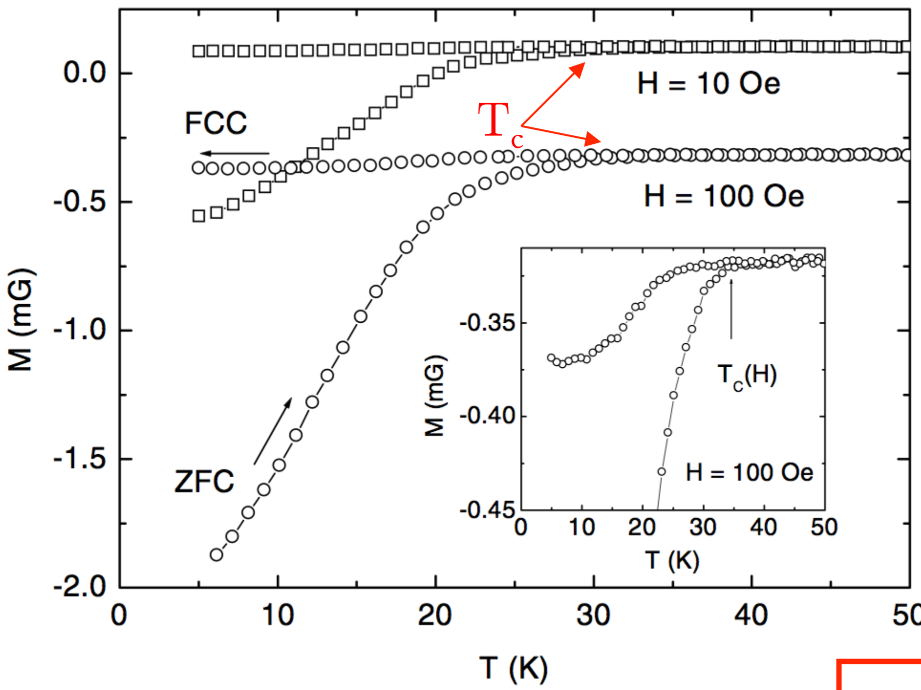
[1]: Esquinazi et al. PRB 78, 134516 (2008)

Graphite-Sulfur Composites

Graphite and sulfur structures are intact

- No additional phases, compounds, or impurities

Superconducting (type-II) behavior:



[1]

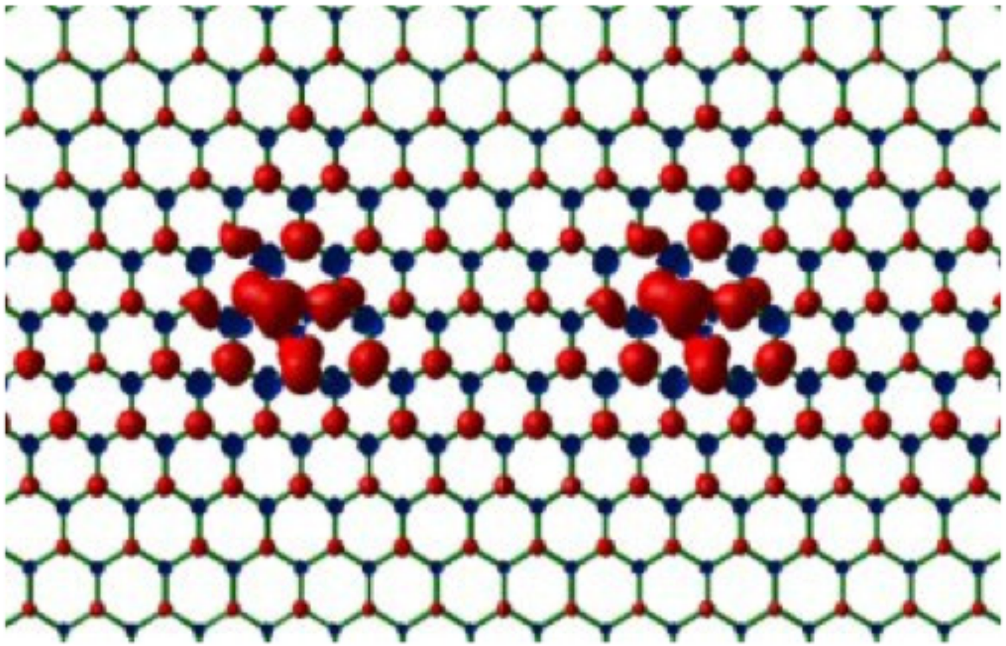
- T_c ~ 10-60 K
- SC located to the graphite planes
- ~ 0.05% of the volume superconducting
  - No bulk SC, no zero resistivity
  - Heat and age sensitive
- SC and FM co-exists

Superconductivity in the graphite sheets, heavily influenced by the sulfur environment

[1]: da Silva et al, PRL 87, 147001 (2001)

Ferromagnetism in Graphene

DFT calculations of spin polarization between two distant magnetic defects on the same sublattice:



[1]

Ferromagnetism at room temperature even for unexpectedly low defect concentrations due to an intrinsic (magnetic) π-band instability

[1]: Pisani et al. New J. Phys. 10, 033002 (2008)

Theoretical Predictions

In comparison to quantum electrodynamics (QED) the fine structure constant $\alpha_g \sim 2$ is very large:

- Expect Coulomb interactions to be very important

- Lattice gauge theory calculations have indicated that Coulomb interactions can cause a semi-metal - insulator transition in graphene [1]

  - 1/r-tail irrelevant coupling, so only short-range interactions are important [2]

[1]: Drut et al. PRL 102, 026802 (2009), [2]: Herbut et al. PRB 80, 075432 (2009)

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Electronic Correlations in Graphene

Electronic correlations should be important in graphite and graphene:

Nearest neighbor hopping t ~ 2.5 eV
On-site repulsion U ~ 6 - 10 eV
} Intermediate coupling regime

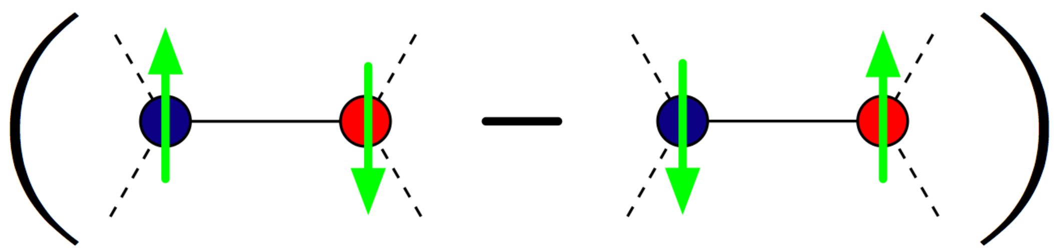
pπ-bonded planar organic molecules:

Nearest neighbor spin-singlet bonds (SB)
encouraged compared to polar configurations
} Pauling's Resonance Valence Bond (RVB) idea

Give good estimates for

Cohesive energy, C-C bond distance, singlet-triplet exciton energy differences etc.

SB =



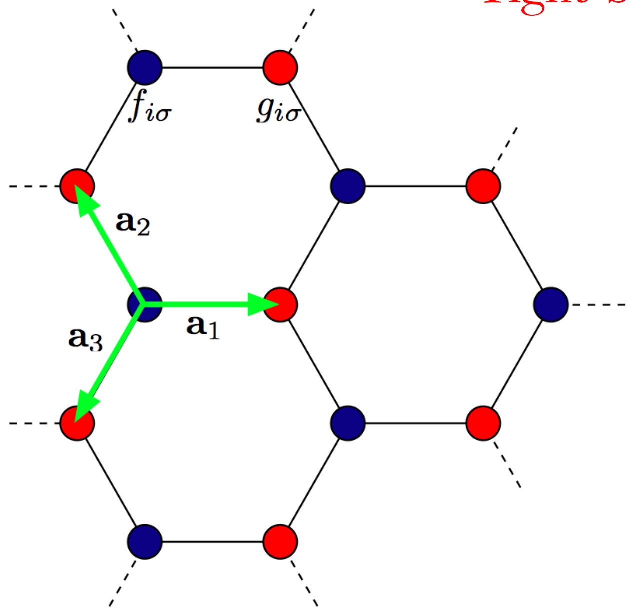
Modeling SB Correlation Effects

G. Baskaran suggested in 2002 a phenomenological model: [1]

$$H = -t \sum_{<i,j>,\sigma} (f^\dagger_{i\sigma} g_{j\sigma} + g^\dagger_{i\sigma} f_{j\sigma}) + \mu \sum_{i,\sigma} (f^\dagger_{i\sigma} f_{i\sigma} + g^\dagger_{i\sigma} g_{i\sigma}) - 2J \sum_{<i,j>} h^\dagger_{ij} h_{ij}$$

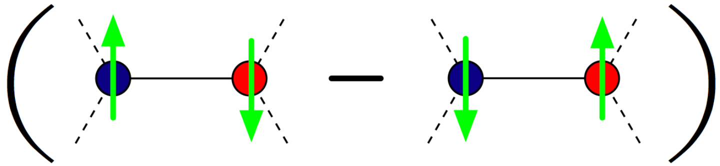
Tight-binding band structure

Favoring singlet bonds (SB)



$$h^\dagger_{ij} = \frac{1}{\sqrt{2}} (f^\dagger_{i\uparrow} g^\dagger_{j\downarrow} - f^\dagger_{i\downarrow} g^\dagger_{j\uparrow})$$

$$h^\dagger_{ij} = \frac{1}{\sqrt{2}}$$



$$\frac{J}{t} \sim 1$$

[1]: Baskaran PRB 65, 212505 (2002)

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Superconducting Mean-Field Treatment

Effective Hamiltonian:

$$H = -t \sum_{<i,j>,\sigma} (f^\dagger_{i\sigma} g_{j\sigma} + g^\dagger_{i\sigma} f_{j\sigma}) + \mu \sum_{i,\sigma} (f^\dagger_{i\sigma} f_{i\sigma} + g^\dagger_{i\sigma} g_{i\sigma}) - 2J \sum_{<i,j>} h^\dagger_{ij} h_{ij}$$

Tight-binding band structure

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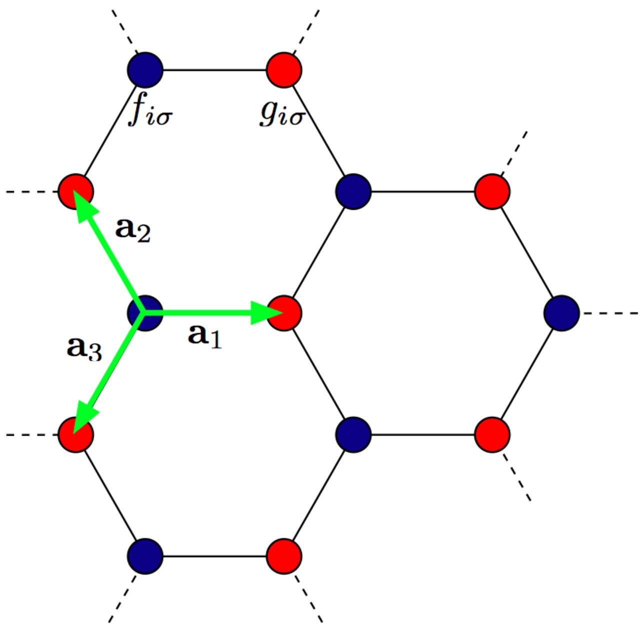


Mean-field order parameter in the Cooper pairing channel:

$$\Delta_{J\mathbf{a}} = \langle h^\dagger_{i,i+\mathbf{a}} \rangle = \langle f^\dagger_{i\uparrow} g^\dagger_{i+\mathbf{a}\downarrow} - f^\dagger_{i\downarrow} g^\dagger_{i+\mathbf{a}\uparrow} \rangle$$

Expectation value of SB pair creation

Black-Schaffer et al. PRB 75, 134512 (2007)

Superconducting Mean-Field Solution

BCS-type self-consistency equation:

Intraband pairing (regular BCS form)

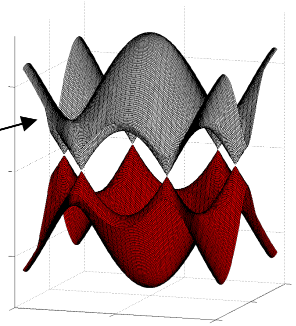
$$\Delta^\dagger_{J\mathbf{a}} = \frac{J}{N}\sum_{\mathbf{k}}\sum_{\mathbf{b}}\Big[\cos(\mathbf{k}\cdot\mathbf{a}-\varphi_{\mathbf{k}})\cos(\mathbf{k}\cdot\mathbf{b}-\varphi_{\mathbf{k}})\left(\frac{\tanh(\beta_c(t\epsilon_{\mathbf{k}}+\mu)/2)}{2(t\epsilon_{\mathbf{k}}+\mu)}+\frac{\tanh(\beta_c(t\epsilon_{\mathbf{k}}-\mu)/2)}{2(t\epsilon_{\mathbf{k}}-\mu)}\right)$$

$$+\sin(\mathbf{k}\cdot\mathbf{a}-\varphi_{\mathbf{k}})\sin(\mathbf{k}\cdot\mathbf{b}-\varphi_{\mathbf{k}})\left(\frac{\sinh(\beta_c\mu)}{2\mu\cosh(\beta_c(t\epsilon_{\mathbf{k}}+\mu)/2)\cosh(\beta_c(t\epsilon_{\mathbf{k}}-\mu)/2)}\right)\Big]\Delta^\dagger_{J\mathbf{b}}$$

$$\alpha_{\mathbf{k}} = \sum_{\mathbf{a}} e^{i\mathbf{k}\cdot\mathbf{a}}$$

$$\epsilon_{\mathbf{k}} = |\alpha_{\mathbf{k}}|$$

$$\varphi_{\mathbf{k}} = \arg(\alpha_{\mathbf{k}})$$



Interband pairing, negligible contribution at low temperatures

3×3 eigenvalue problem for $\mathbf{\Delta}_{Ja} = (\Delta^\dagger_{J\mathbf{a}_1}, \Delta^\dagger_{J\mathbf{a}_2}, \Delta^\dagger_{J\mathbf{a}_3})^T$:

$$\frac{1}{J}\mathbf{\Delta}_{Ja} = \begin{pmatrix} D & B & B \\ B & D & B \\ B & B & D \end{pmatrix}\mathbf{\Delta}_{Ja}$$

D = RHS for a = b
B = RHS for a ≠ b

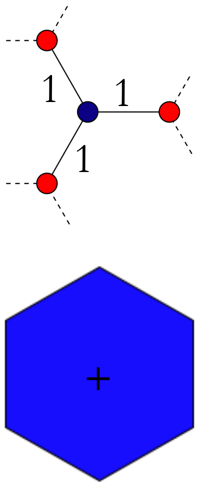
Black-Schaffer et al. PRB 75, 134512 (2007)

Gap Symmetries

s-wave:

- $1/(J/t) = D + 2B$

$\Delta_{Ja} = (1,1,1)$



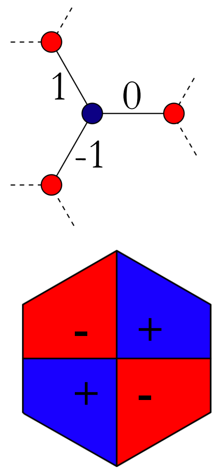
extended *s*-wave ($\Delta_{J\mathbf{k}} \propto |\alpha_\mathbf{k}|$)|

- $\Delta_{J\mathbf{k}} \in A_1$ of D_6

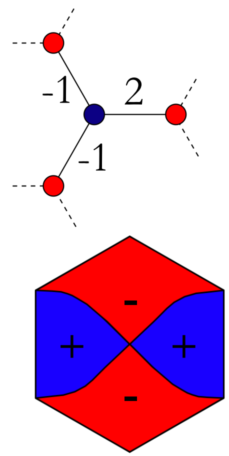
d-waves:

- $1/(J/t) = D - B$

$\Delta_{Ja} = (0,1,-1)$ $\Delta_{Ja} = (2,-1,-1)$



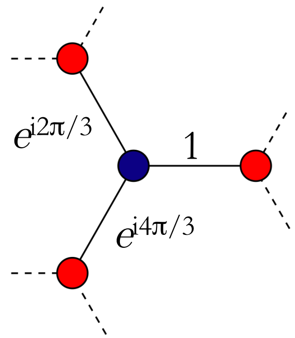
d(xy)-wave



d(x^2-y^2)-wave

- $\Delta_{J\mathbf{k}} \in E_2$ of D_6
- For self-consistency below T_c need $d(x^2-y^2)+id(xy)$

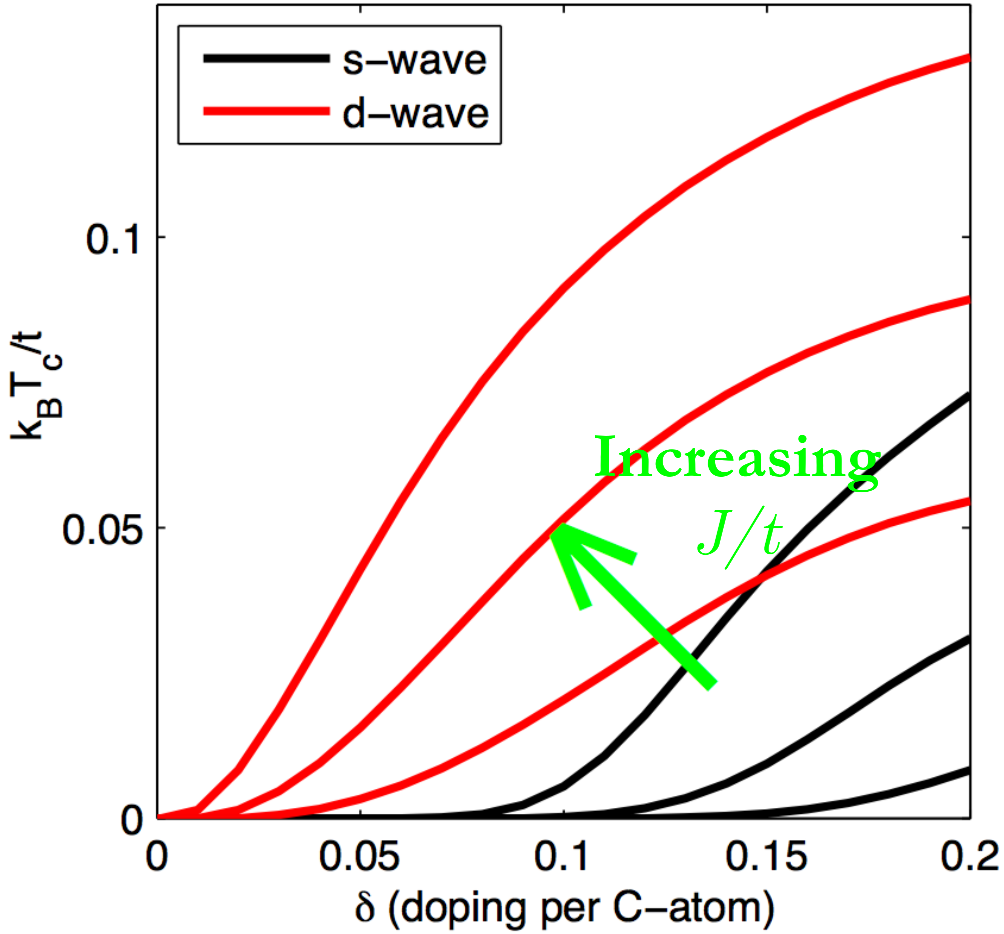
⇒ breaks time-reversal symmetry (FM possible)



Black-Schaffer et al. PRB 75, 134512 (2007)

Mean-Field Results

Transition temperature as a function of doping (δ) for coupling parameters $J/t = 0.8,\ 1.0,\ 1.2$:



Zero doping:

- QCP at $J_c/t = 1.91$
- *s*- and *d*-wave solutions degenerate

Finite doping:

- $T_c(d) >> T_c(s)$ for $0 < \delta < 0.4$

Black-Schaffer et al. PRB 75, 134512 (2007)

Realization of *d*-wave Superconductivity

Need δ ~ 0.01 for T_c(*d*-wave) ~ 10 K:

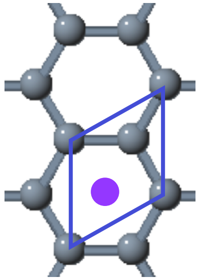
- Doping of a graphene sheet:
  - 3D graphite: δ ~ 10^{-4}
  - Induced doping by gate voltage: δ ~ 0.005
  - Extended defects in graphene might induce self-doping [1]
- Other possibilities:
  - Proximity effect enhancement of SB correlations in a *d*-wave contact graphene SNS Josephson junctions [2]
  - Chemical doping

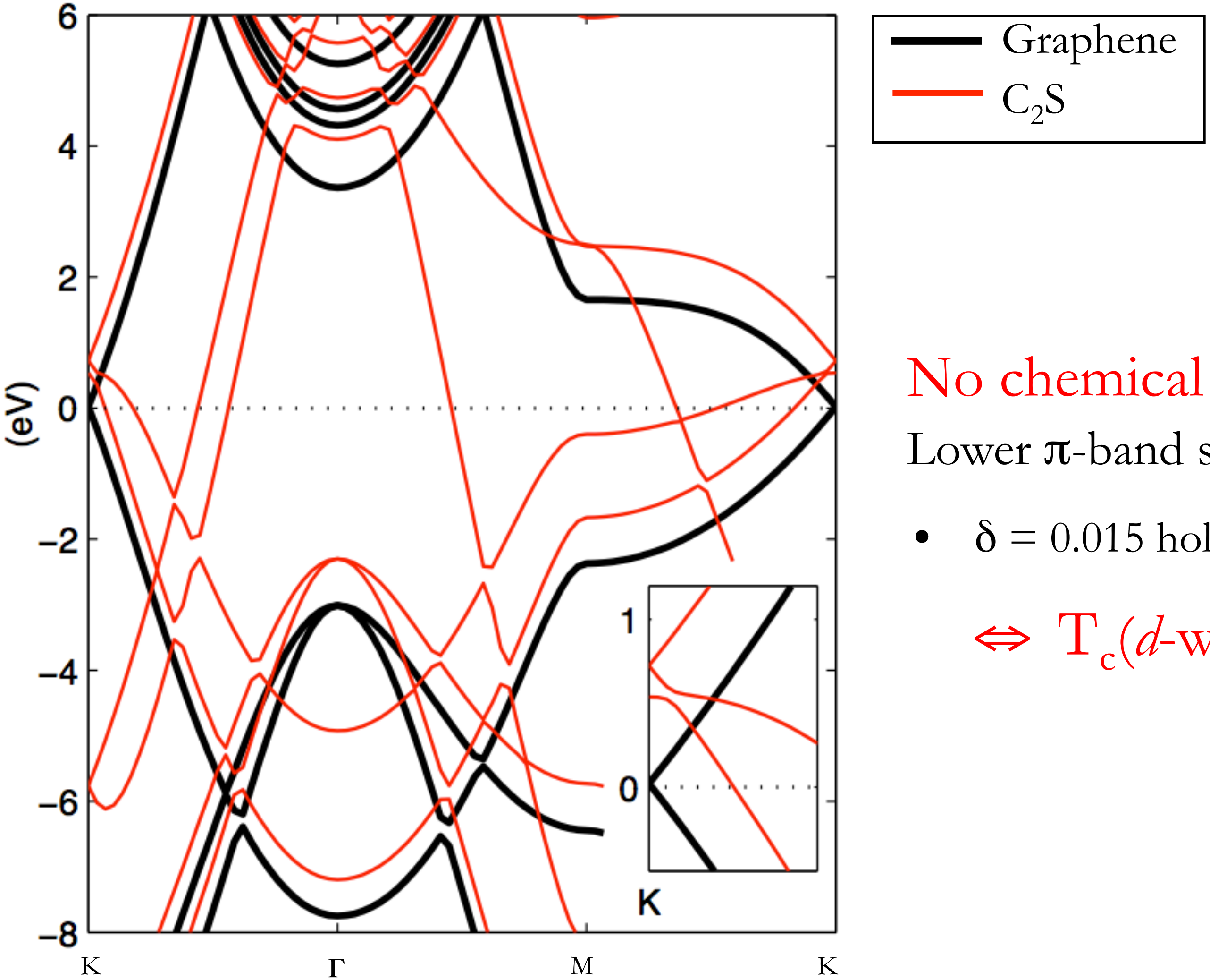
A *d*-wave superconducting state in the interfacial graphite sheets caused by induced doping from sulfur adsorption?

[1]: Peres et al. PRB 73, 125411 (2006), [2]: Black-Schaffer et al. PRB 81, 014517 (2010)

DFT Results

Atomic sulfur on graphene prefers high density adsorption:





No chemical bonds formed

Lower π-band shifts upward ~ 0.7 eV

- δ = 0.015 holes/C-atom

⇔ T_c(*d*-wave) ~ 10 K

Black-Schaffer et al. PRB 75, 134512 (2007)

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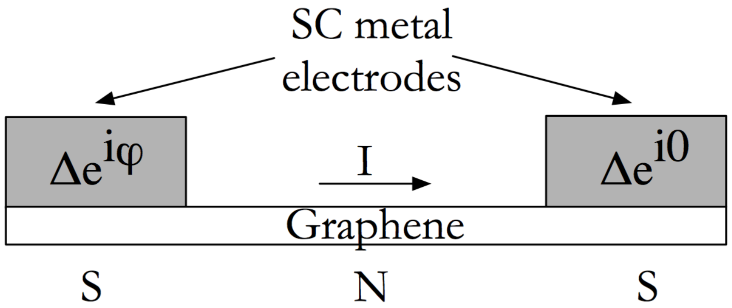
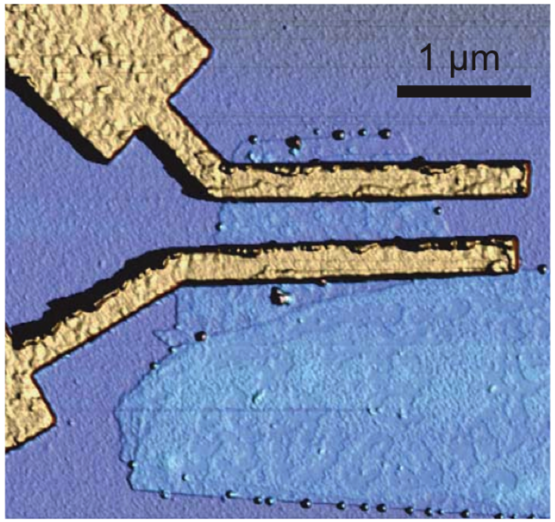
Can an induced superconducting state enhance the intrinsic SB correlations?

- RKKY coupling between magnetic impurities in graphene

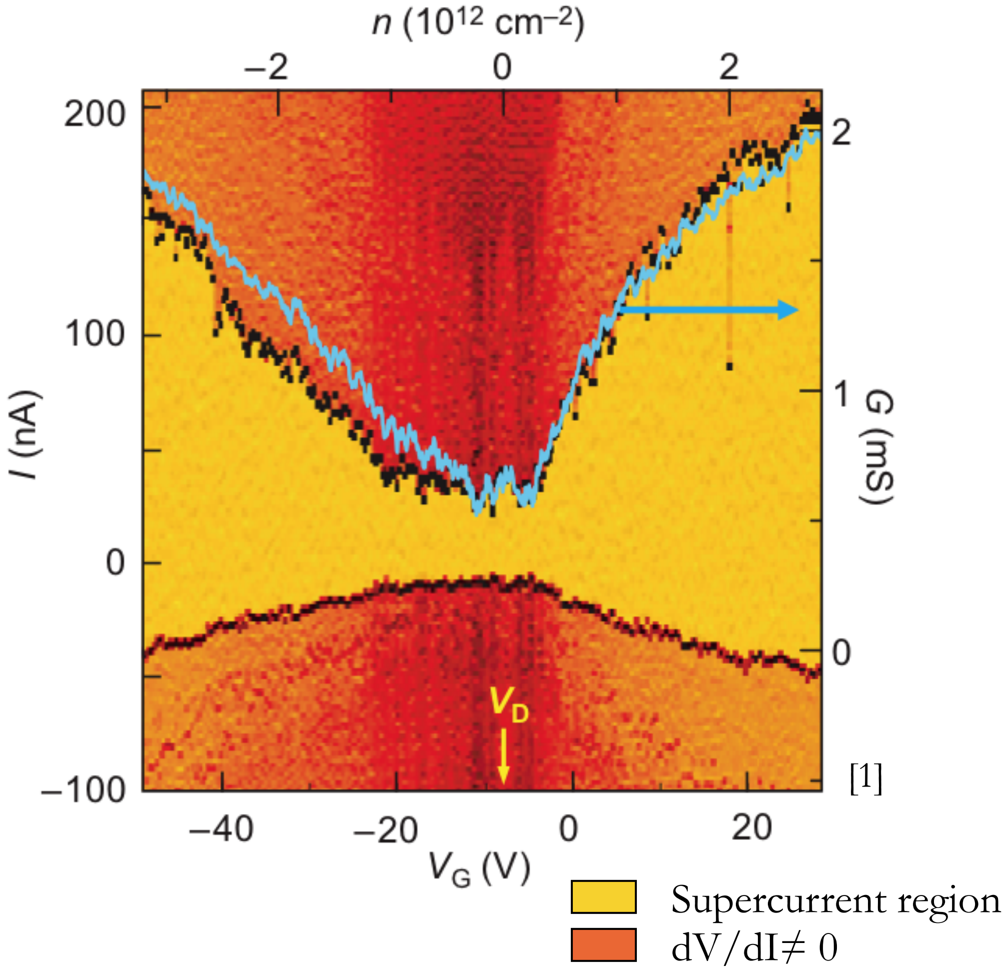
Graphene SNS Josephson Junction

Layout of a graphene SNS Josephson junction:





[1]

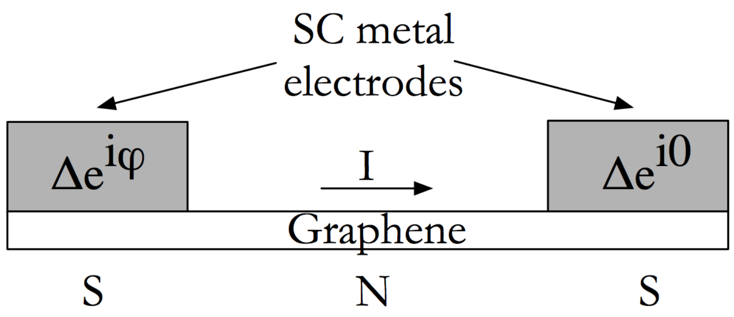


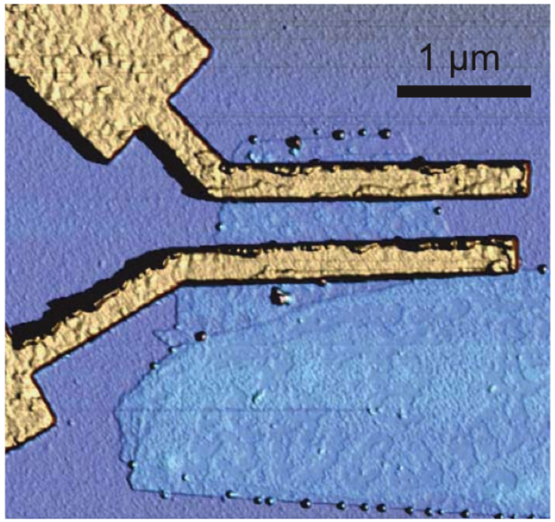
Finite supercurrent measured even at the Dirac point

[1]: Heersche et al. Nature 446, 56 (2007)

Graphene SNS Josephson Junction

Layout of a graphene SNS Josephson junction:





[1]

- Model the effect of the superconducting contacts with
  - Effective pairing potential
  - Heavy doping

- Self-consistently solve the Bogoliubov-de Gennes (BdG) for the tight-binding graphene Hamiltonian

[1]: Heersche et al. Nature 446, 56 (2007)

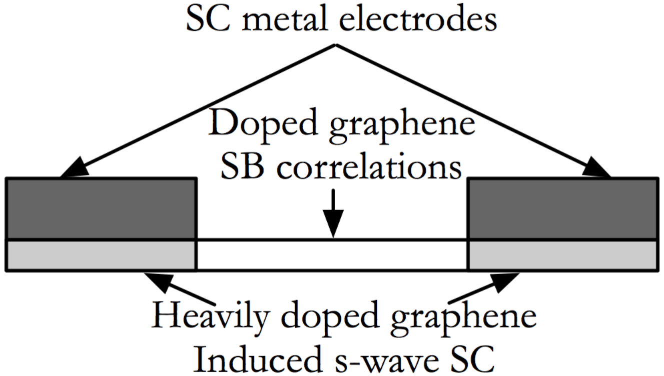
Tight-Binding BdG Formalism

Effective Hamiltonian for conventional, *s*-wave contacts:

$$H_{\text{eff}} = -t \sum_{<i,j>,\sigma} (f^\dagger_{i\sigma} g_{j\sigma} + g^\dagger_{i\sigma} f_{j\sigma}) + \sum_{i,\sigma} \mu(i)(f^\dagger_{i\sigma} f_{i\sigma} + g^\dagger_{i\sigma} g_{i\sigma})$$ } Tight-binding band structure

$$- 2 \sum_{<i,j>} J(i) h^\dagger_{ij} h_{ij}$$ } SB correlations

$$- \sum_i U(i)(n_{fi\uparrow} n_{fi\downarrow} + n_{gi\uparrow} n_{gi\downarrow})$$ } Effective *s*-wave pairing



S	N	S
$U > 0$	$U = 0$	$U > 0$
$J = 0$	$J > 0$	$J = 0$
$\tilde{\mu} \gg 0$	$\tilde{\mu} > 0$	$\tilde{\mu} \gg 0$

Solve self-consistently for

on-site pair amplitude: $\Delta_U(i) = \dfrac{\langle f_{i\downarrow} f_{i\uparrow} + g_{i\downarrow} g_{i\uparrow} \rangle}{2}$

SB pair amplitude: $\Delta_{Ja}(i) = \langle h_{i,i+a} \rangle$

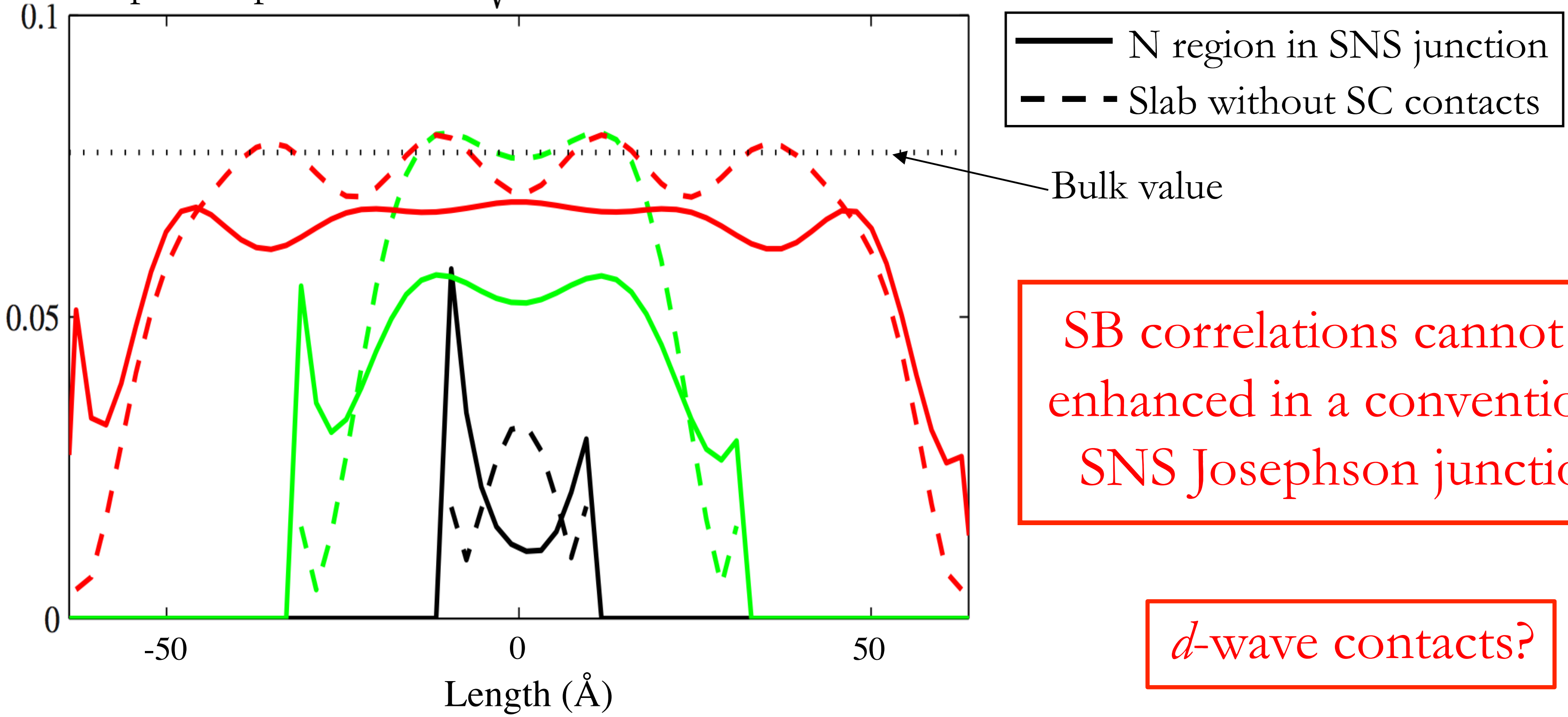
Can the SB correlations be enhanced by *s*-wave superconducting contacts?

Finite Size Suppression

Finite size suppression of superconductivity:

- Larger J (or μ) necessary in N for SC than in the bulk

SB pair amplitude $\Delta_J = \sqrt{|\Delta_{J\mathbf{a}_1}|^2 + |\Delta_{J\mathbf{a}_2}|^2 + |\Delta_{J\mathbf{a}_3}|^2}$



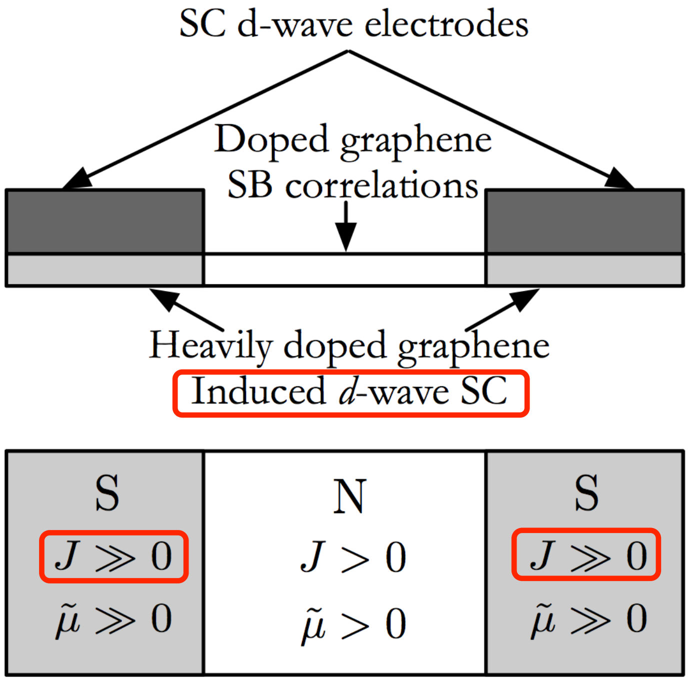
SB correlations cannot be enhanced in a conventional SNS Josephson junction

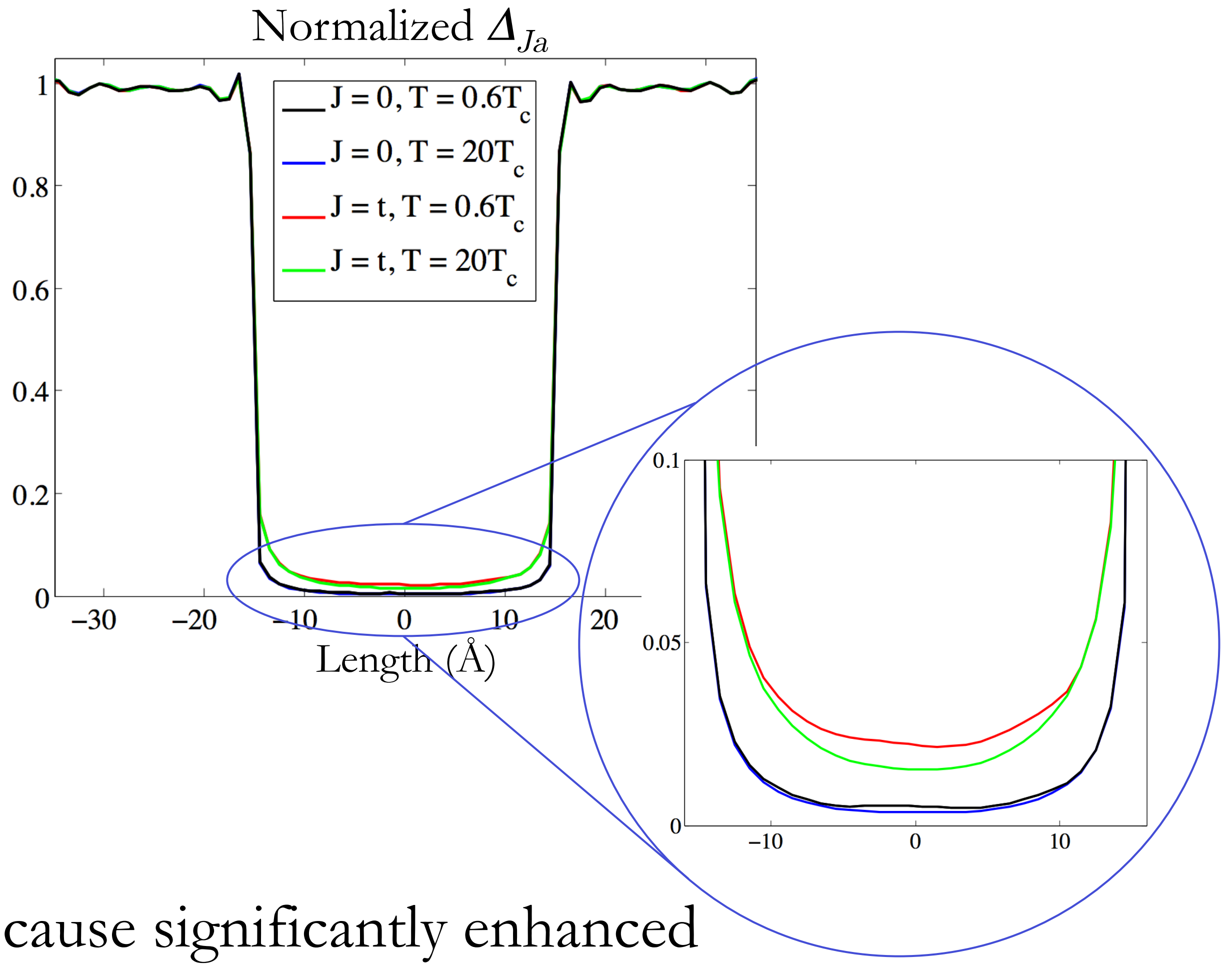
d-wave contacts?

Black-Schaffer et al. PRB 79, 064502 (2009)

d-wave Contacts: Proximity Effect

d-wave contacts: Set J >> 0 and enforce $d(x^2\text{-}y^2)$-symmetry in the S regions





SB correlations cause significantly enhanced proximity effect even for $T >> T_c$(SB)

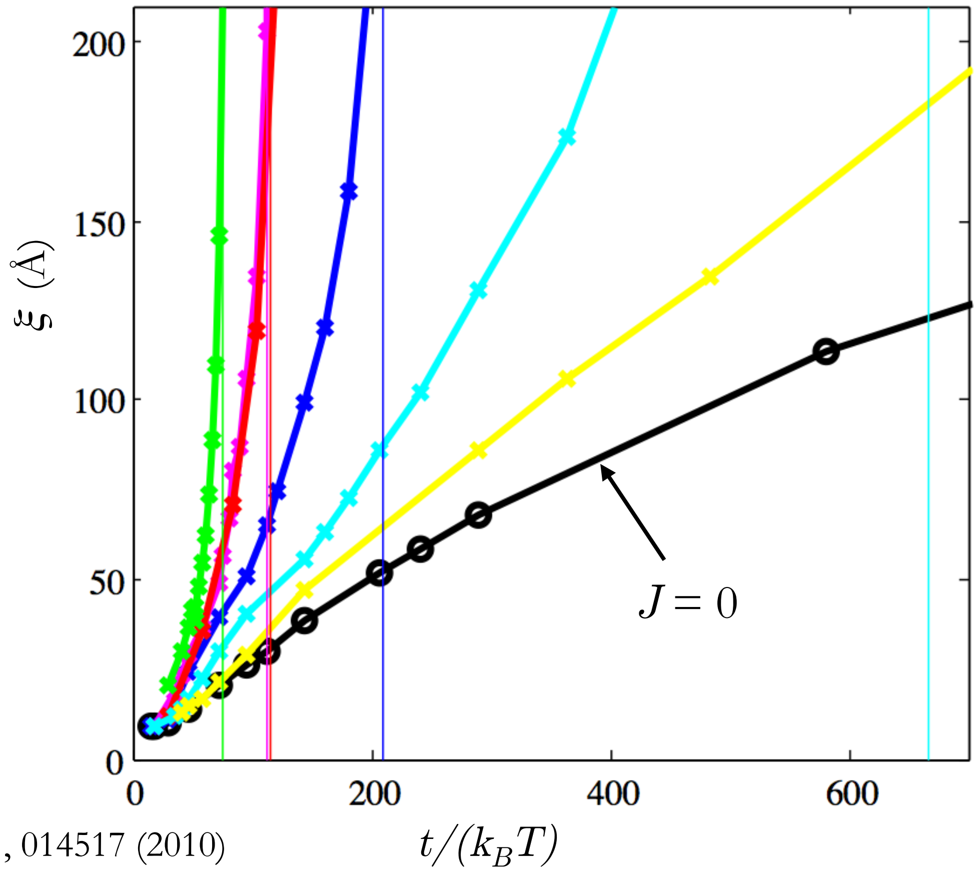
Black-Schaffer et al. PRB 81, 014517 (2010)

d-wave Contacts: Decay Length

The superconducting decay length in N depends on T_c:

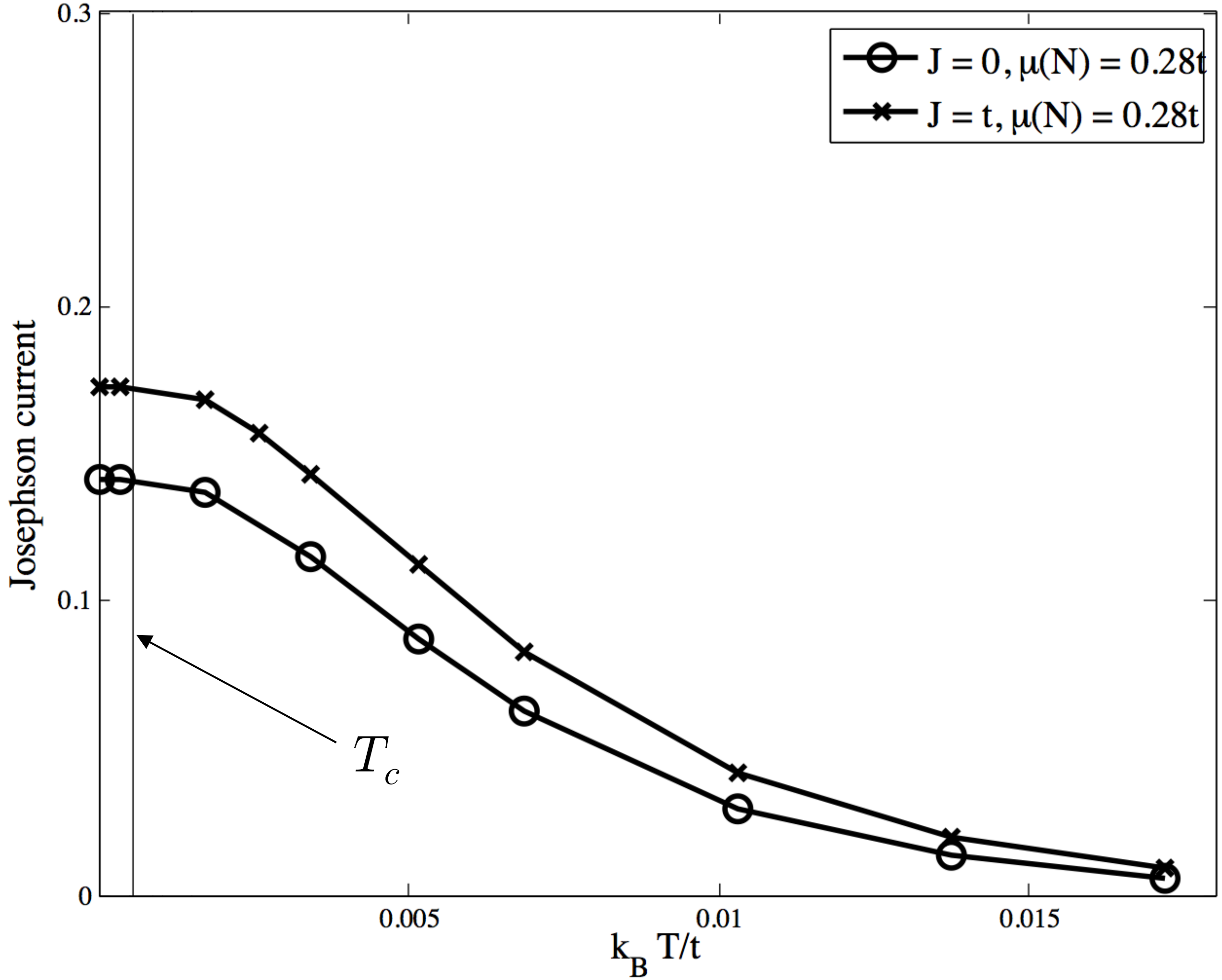
Decay of pair amplitude: $F \propto e^{-x/\xi}$

Decay length: $\xi \propto \dfrac{1}{T - T_c}$



Black-Schaffer et al. PRB 81, 014517 (2010)

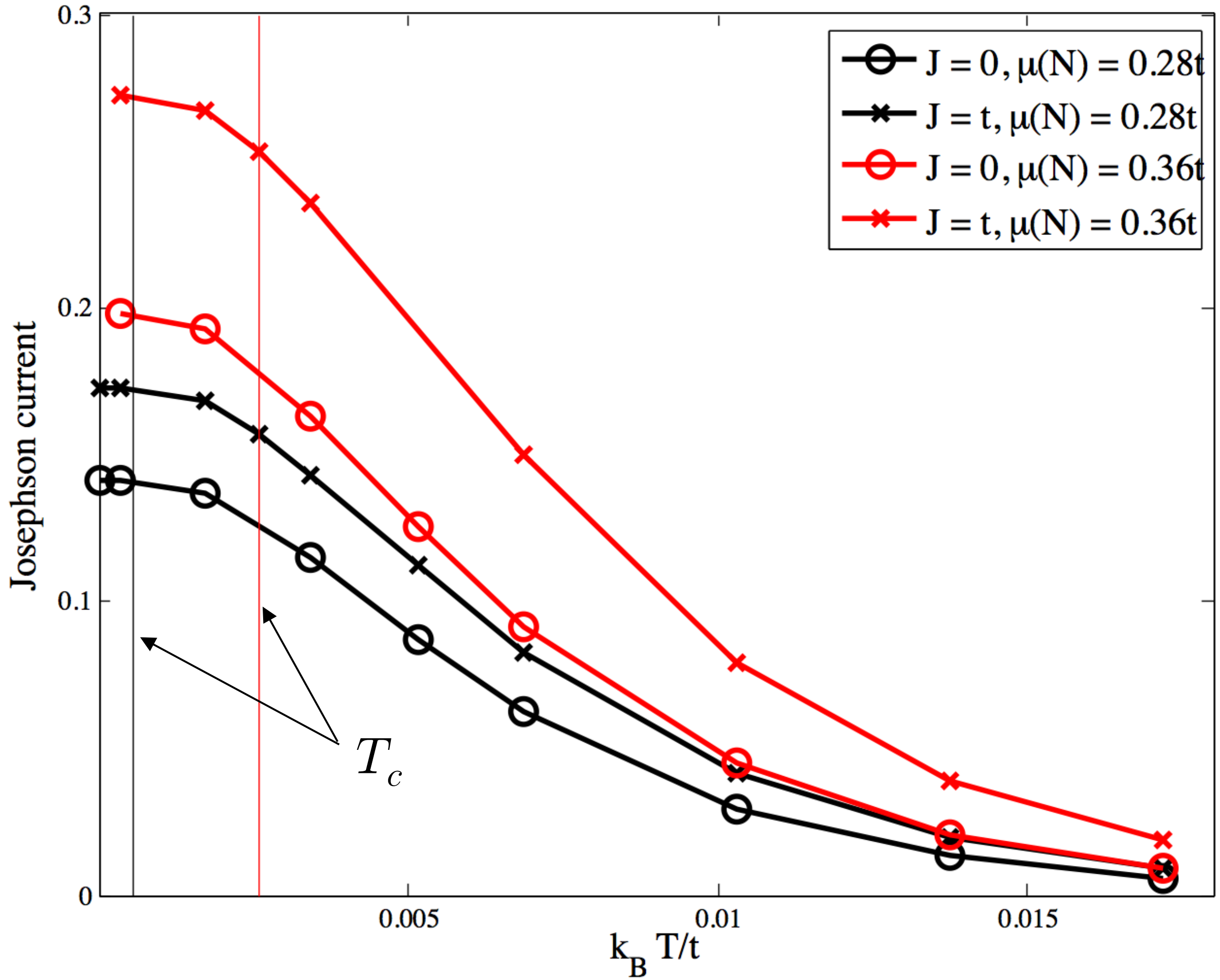
d-wave Contacts: Josephson Current



Enhanced Josephson current even for $T >> T_c$

Black-Schaffer et al. PRB 81, 014517 (2010)

d-wave Contacts: Josephson Current



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SB correlations are also closely related to magnetism;
behavior of magnetic impurities in undoped graphene?

Very weak SC
correlations

Mean-Field Magnetism in Graphene

Effective Hamiltonian (itinerant Heisenberg model):

$$H = -t \sum_{<i,j>,\sigma} (f_{i\sigma}^\dagger g_{j\sigma} + g_{i\sigma}^\dagger f_{j\sigma}) + \mu \sum_{i,\sigma} (f_{i\sigma}^\dagger f_{i\sigma} + g_{i\sigma}^\dagger g_{i\sigma}) - 2J \sum_{<i,j>} h_{ij}^\dagger h_{ij}$$

$\Updownarrow$

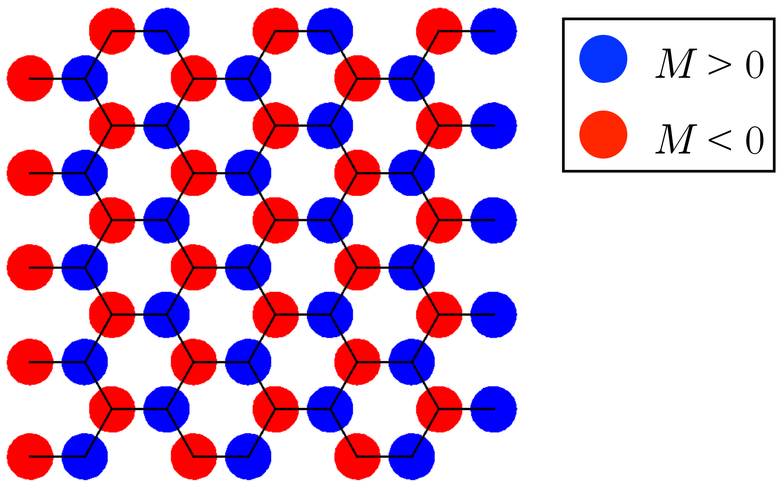
$$J(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} n_i n_j)$$

Mean-field order parameter in the particle-hole (magnetic) channel:

$$M_i = \langle \mathbf{S}_i \rangle = \langle f_{i\uparrow}^\dagger f_{i\uparrow} - f_{i\downarrow}^\dagger f_{i\downarrow} \rangle$$

Expectation value of local spin polarization

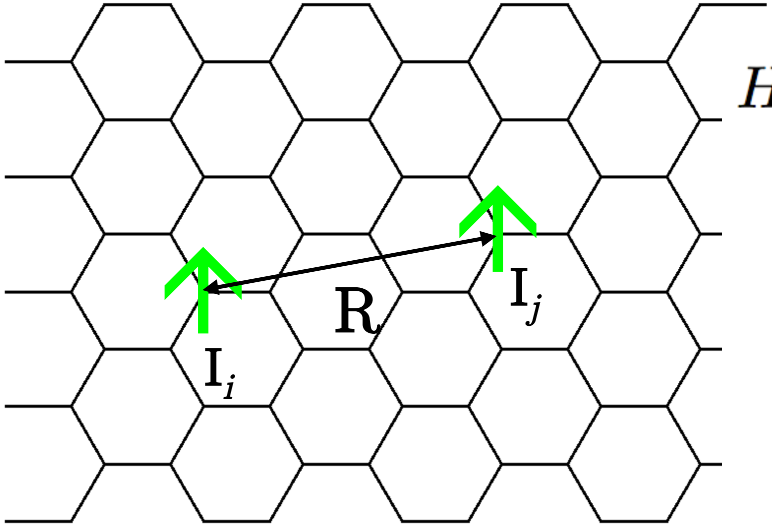
Uniform solution for $J = t$ in undoped graphene:



Zero doping:
AFM for $J > J_c = 0.75t$
No SC

Finite doping:
SC for any J
J_c(AFM) $> 0.75t$

RKKY Coupling in Graphene



$$H_{\mathrm{RKKY}} = -t \sum_{<i,j>,\sigma} (f_{i\sigma}^{\dagger} g_{j\sigma} + g_{i\sigma}^{\dagger} f_{j\sigma})$$ Tight-binding band structure

$$+ J \sum_{<i,j>} \mathbf{S}_i \cdot \mathbf{S}_j$$ SB correlations

$$+ J_k \sum_{i=\mathrm{imp}} \mathbf{I}_i \cdot \mathbf{S}_i$$ Kondo coupling to impurities

Effective coupling J_{RKKY} between two magnetic impurities I_i propagated by the conduction electrons:

$$H_{\mathrm{eff}} = J_{\mathrm{RKKY}}(R)\mathbf{I}_i \cdot \mathbf{I}_j$$

where

$$J_{\mathrm{RKKY}}(R) \propto \chi^0(R, \omega = 0)$$

(static spin susceptibility)

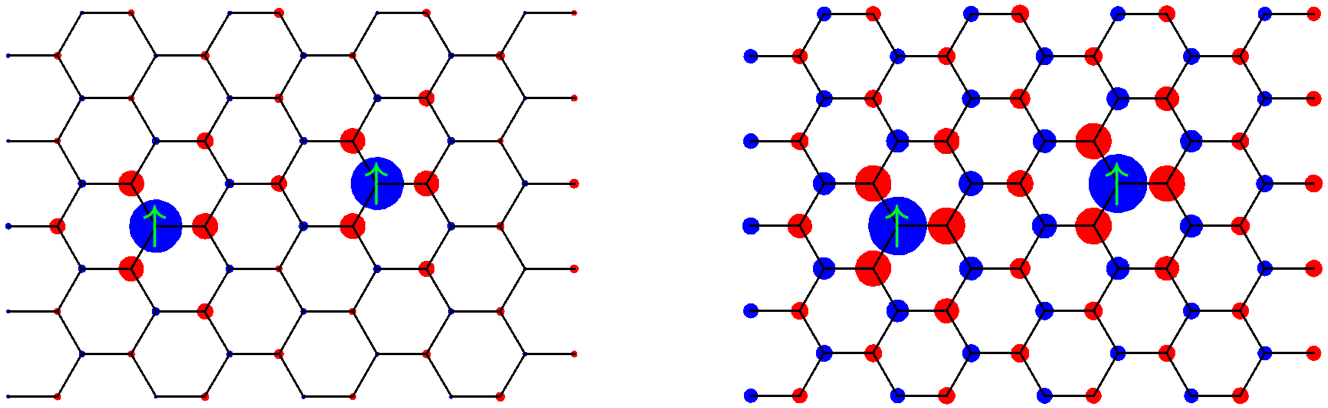
Mean-Field Solution

$$H_{\text{RKKY}} = -t \sum_{<i,j>,\sigma} (f^\dagger_{i\sigma} g_{j\sigma} + g^\dagger_{i\sigma} f_{j\sigma}) + J \sum_{<i,j>} \mathbf{S}_i \cdot \mathbf{S}_j + J_k \sum_{i=\text{imp}} \mathbf{I}_i \cdot \mathbf{S}_i$$

Mean-field solution for $M_i = \langle \mathbf{S}_i \rangle$ with $\begin{cases} \mathbf{I}_i, \mathbf{I}_j = \uparrow, \uparrow & \text{FM} \\ \mathbf{I}_i, \mathbf{I}_j = \uparrow, \downarrow & \text{AFM} \end{cases}$

$$\Rightarrow \quad J_{\text{RKKY}} = \frac{E(\text{FM}) - E(\text{AFM})}{2I^2}$$

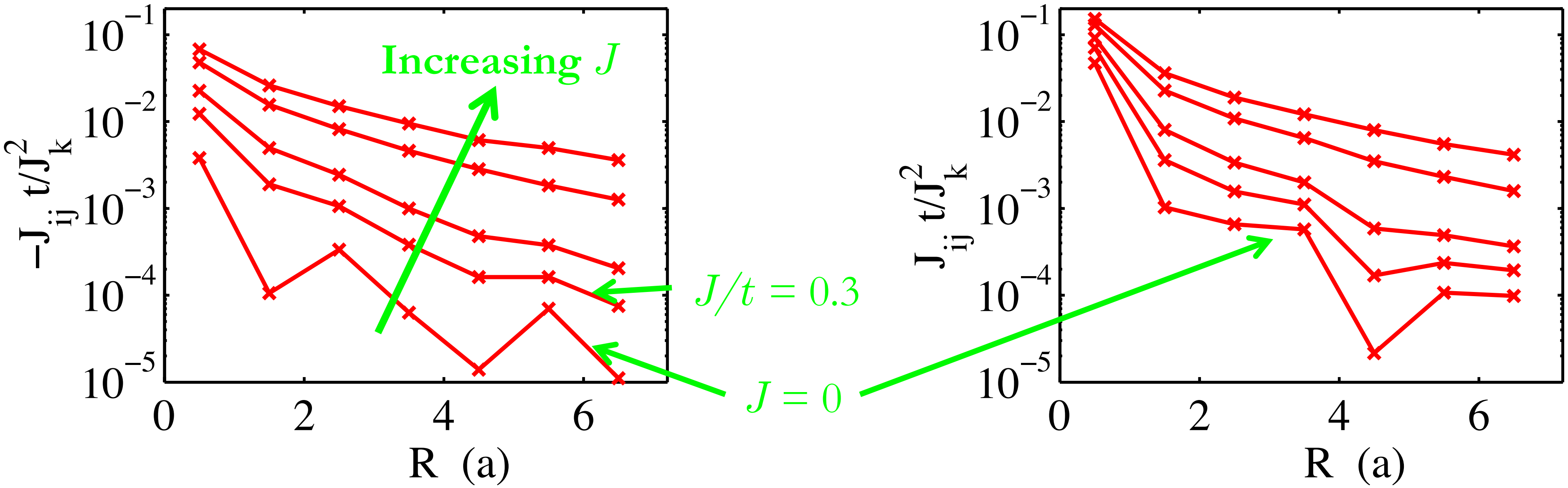
$J = 0$: $J = 0.5t$:



Black-Schaffer PRB 81, 205416 (2010)

RKKY Coupling For Zigzag Impurities

A-A impurities (FM coupling): A-B impurities (AFM coupling):



With increasing J (even for $J << J_c = 0.75t$):

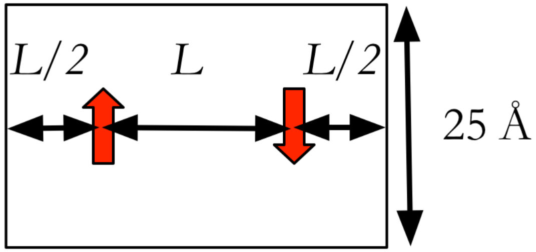
- (1+cos)-type oscillations disappear
- Longer ranged power-law decay
- Lattice details washed out
  (zigzag vs. armchair, A-A vs. A-B impurities etc)

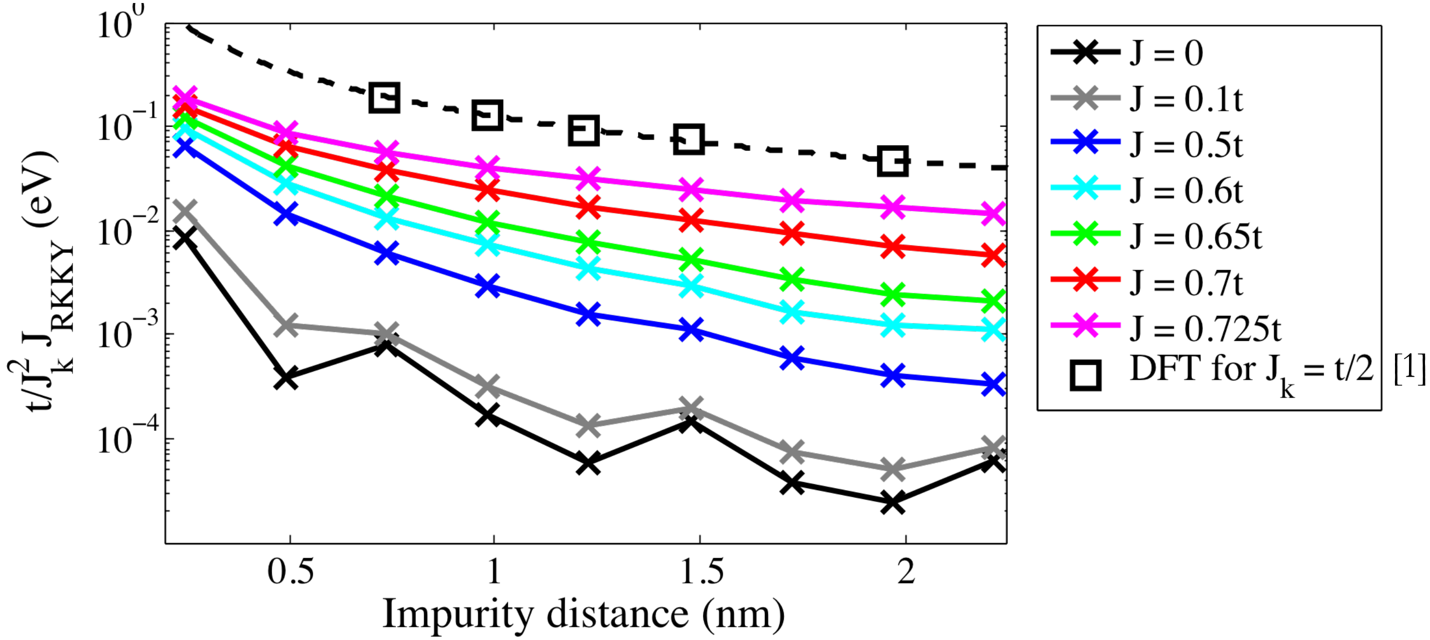
Can we also determine J?

Black-Schaffer PRB (in press)

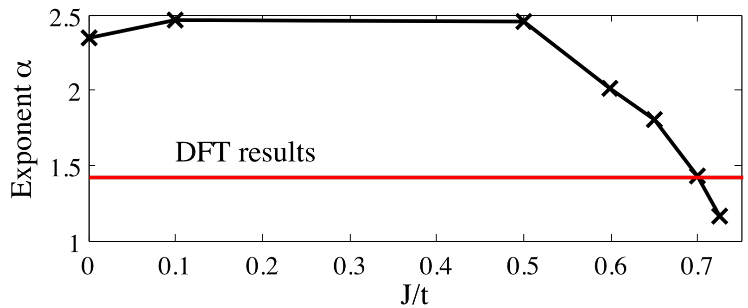
Comparison with DFT Results

Impurity chains:





$$J_{\mathrm{RKKY}} \propto \frac{1}{|\mathbf{R}|^{\alpha}}$$



The SB term captures the DFT result well

$J \sim 0.7t \Rightarrow$ very close to the AFM instability at $J_c = 0.75t$

Black-Schaffer PRB (in press), [1]: Pisani et al. New J. Phys. 10, 033002 (2008)

Summary

Highly doped graphene:

- Nearest-neighbor spin-singlet bond (SB) correlations in graphene lead to a TRSB *d*-wave superconducting state
  - Sulfur adsorption creates a doping level such that $T_c \sim 10$ K
  - The SB correlations are considerably magnified in a *d*-wave contact graphene SNS Josephson junction

Undoped graphene:

- The RKKY coupling between magnetic impurities is significantly enhanced by el-el interactions
  - SB correlations provide a simple way to treat these interaction effects
  - Surprisingly high J, close to the AFM instability

Undoped graphene: close to AFM insulator
Doped graphene: *d*-wave superconductor?