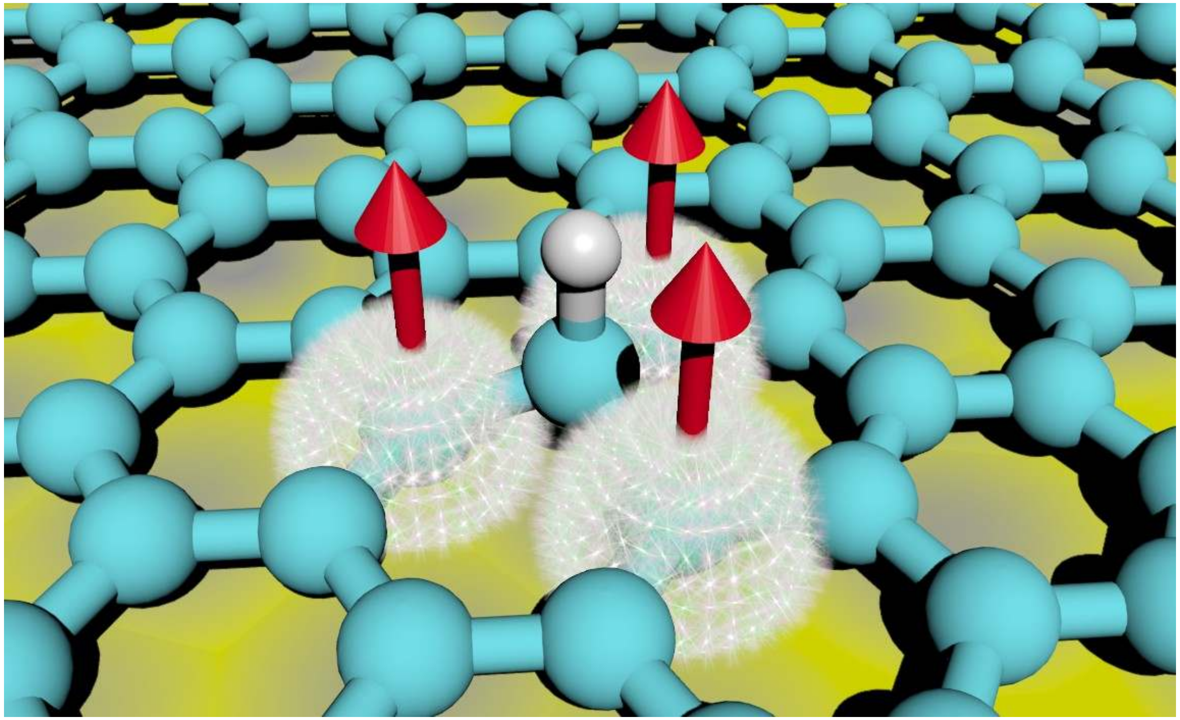
Unconventional Shiba states in hydrogenated graphene

J. L. Lado and J. Fernandez-Rossier

International Iberian Nanotechnology Laboratory, Portugal



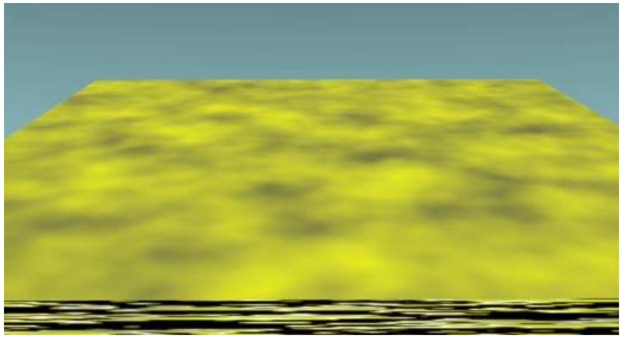
arXiv:1512.05267

22 February 2016

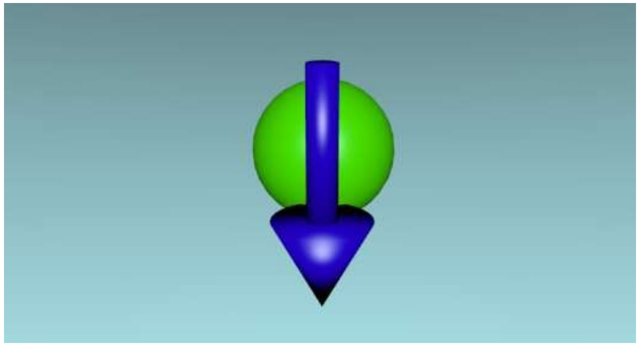
Antagonist electronic orders

Superconductivity ⟷ Magnetism

- Destroyed by magnetic field
- Favors singlet state S=0
- Attractive e-e interaction
- Appears in systems with a large number of atoms



- Stabilized by magnetic field
- Large spin S>0
- Repulsive e-e interaction
- Can appear in a single atom



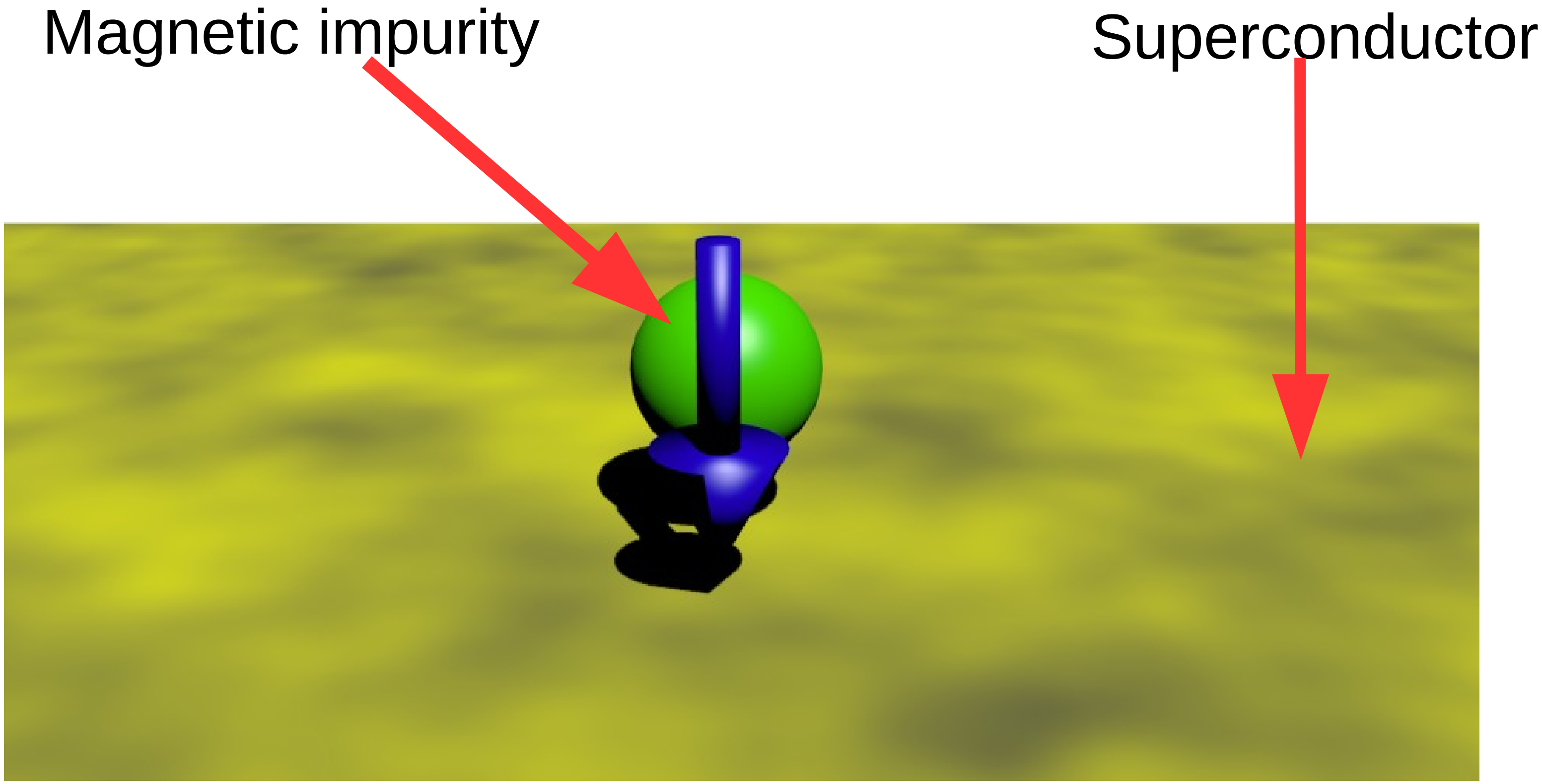
What happens when they coexist?

↓

Ultimate result: Majorana bound states

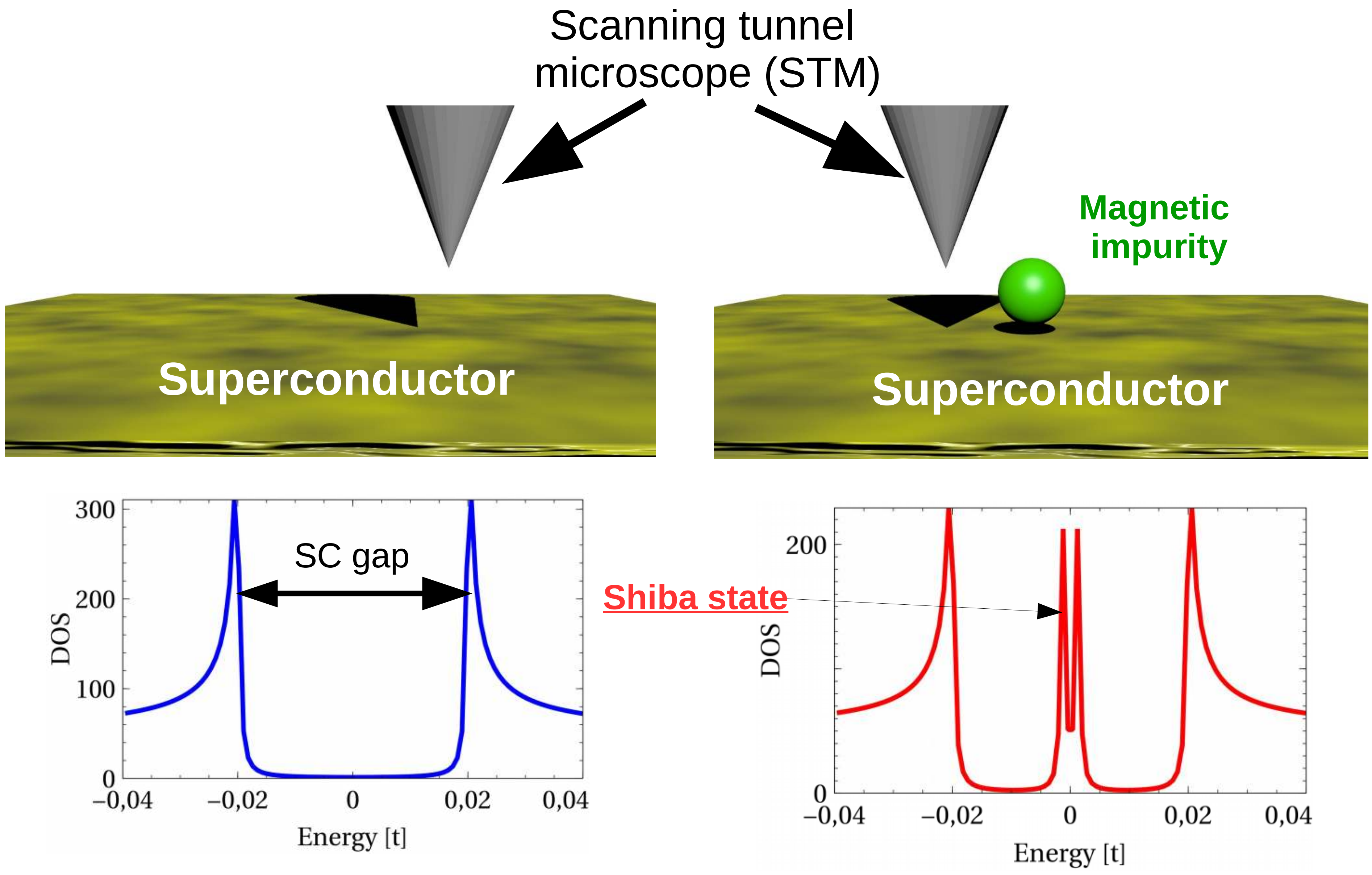
Rev. Mod. Phys. 87, 137 (2015)
Phys. Rev. X 5, 041042 (2015)

Magnetic impurities in a surface

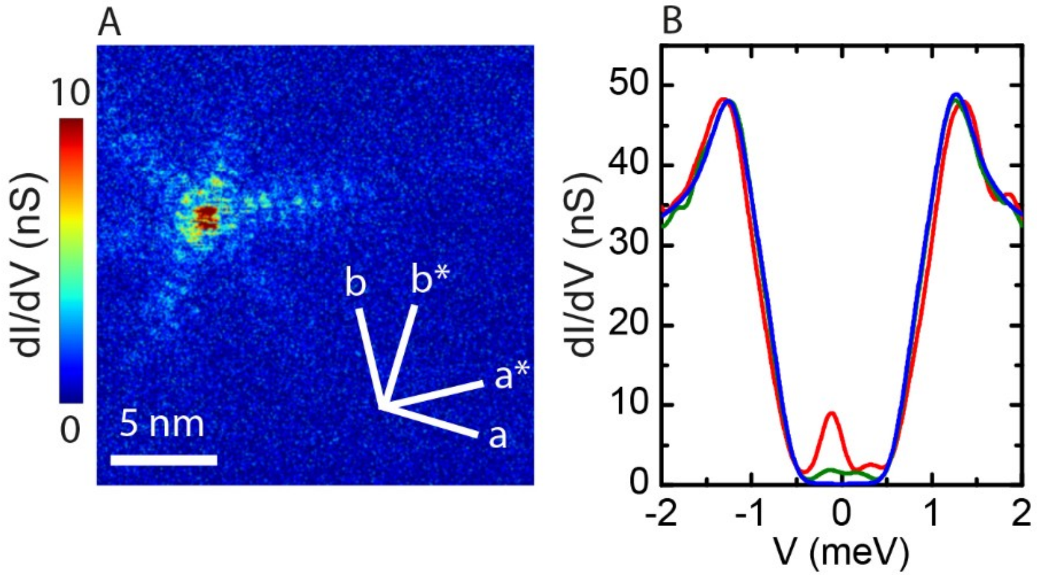


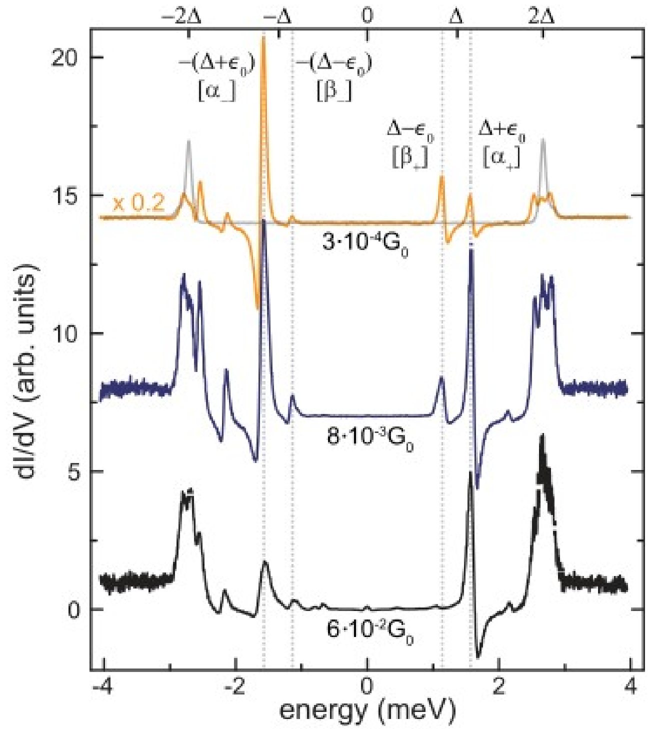
What is the ground state of this system?

Experimental method



Experimental realization





Mn@Pb(111)

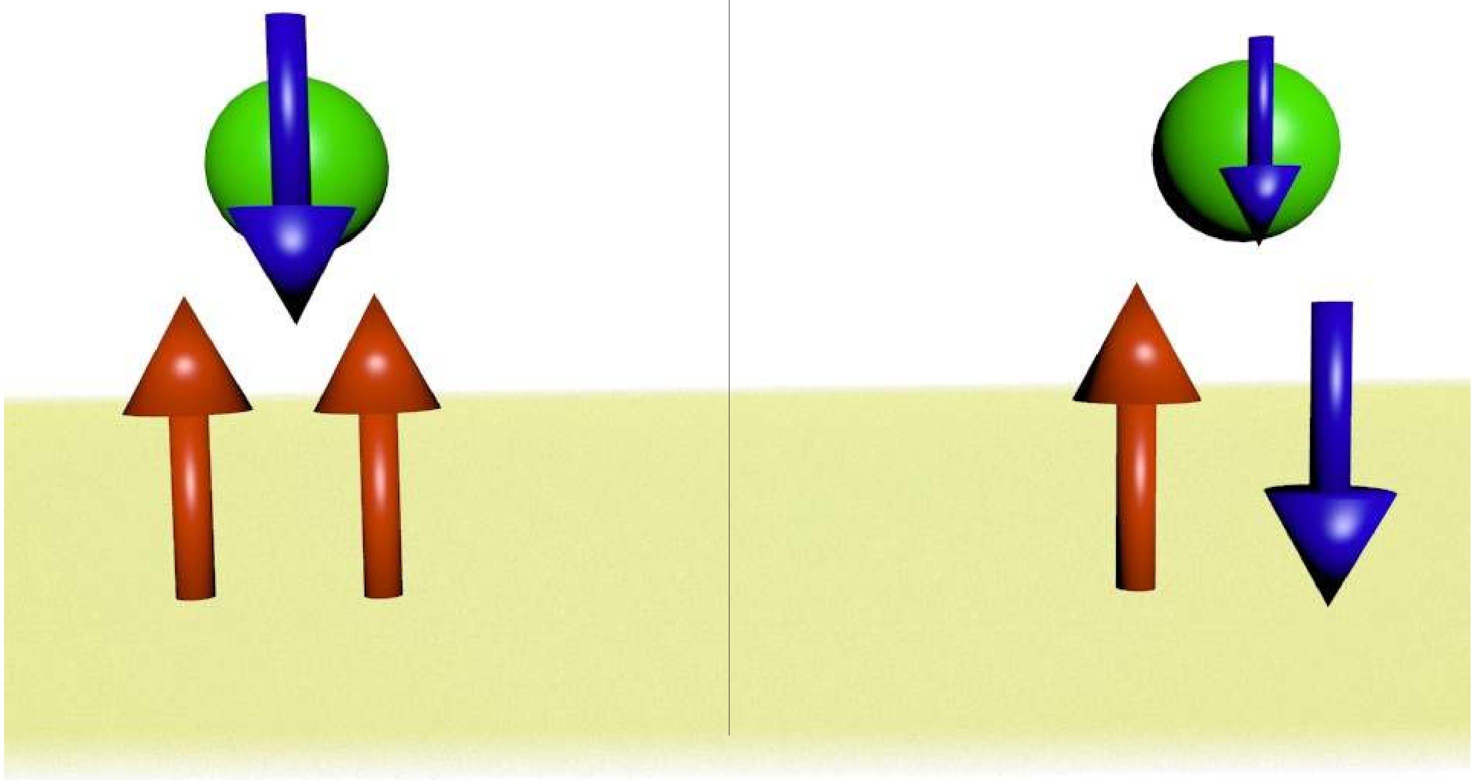
Fe@$NbSe_2$

Nature Physics 11, 1013 (2015)

Phys. Rev. Lett. 115, 087001 (2015)

Magnetism VS superconductivity

Magnetism wins | **Superconductivity wins**



Large J, $S \neq 0$

Parity switching

Small J, $S = 0$

Shiba states, theoretical background

$$H = \epsilon(k) c_k^\dagger c_k + J\delta(r) s_z c_r^\dagger c_r + \Delta \left[c_{\uparrow k} c_{\downarrow -k} + c_{\downarrow -k}^\dagger c_{\uparrow k}^\dagger \right]$$

Kinetic energy

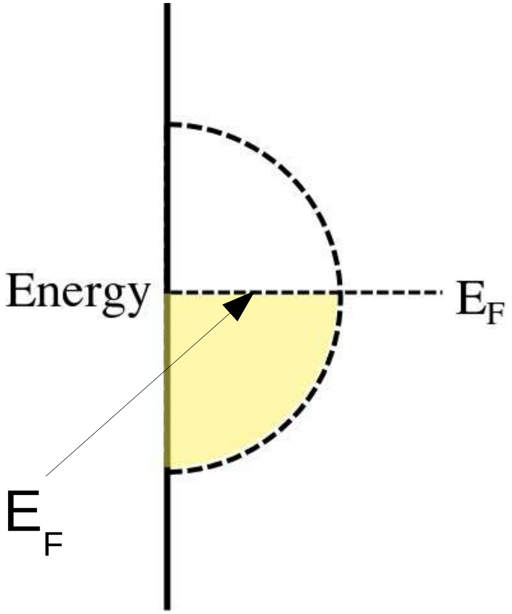
Local exchange

s-wave pairing

Energy of the mid-gap state:

$$E_S = \Delta \frac{1 - (\pi \frac{S}{2} J\rho)^2}{1 + (\pi \frac{S}{2} J\rho)^2}$$

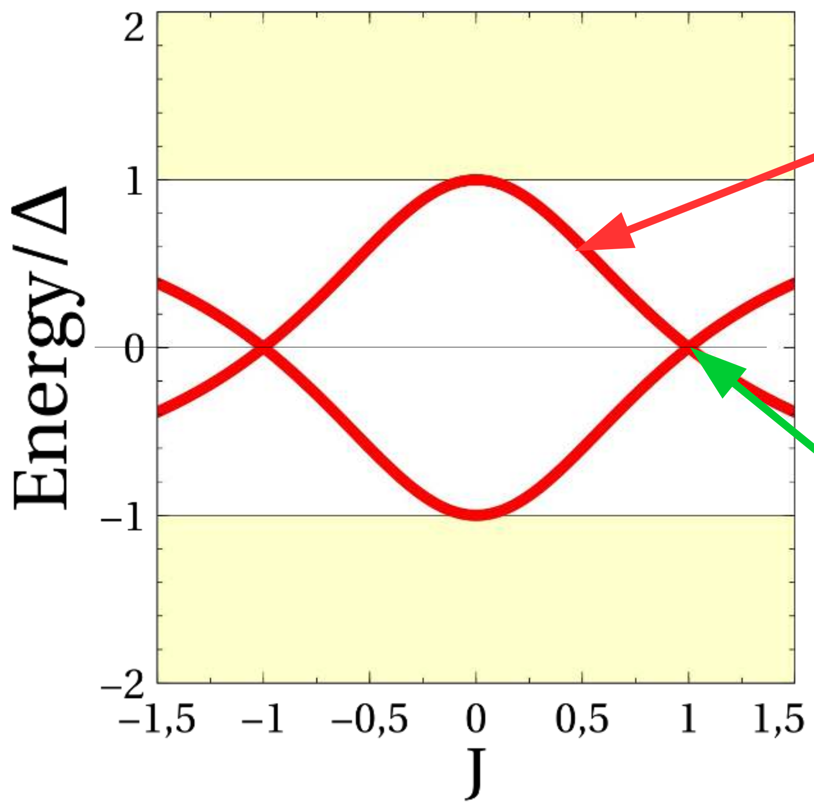
DOS at E_F



Assumptions
- Finite DOS at the Fermi level (normal state)
- Classical spin (acts as a local exchange source)

Rev. Mod. Phys. 78, 373 (2006)

Shiba states, theoretical background



Exchange coupling

Mid-gap Shiba excitation

$$E_S = \Delta \frac{1-(\pi \frac{S}{2} J\rho)^2}{1+(\pi \frac{S}{2} J\rho)^2}$$

Superconducting gap

Parity switching point

$$J_C = \frac{2}{\pi S \rho}$$

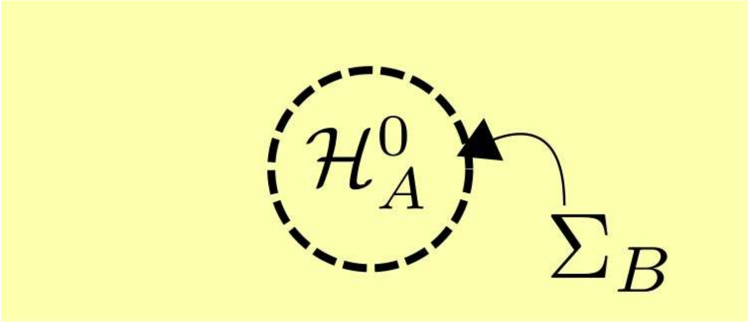
Independent on the superconducting pairing

Rev. Mod. Phys. 78, 373 (2006)

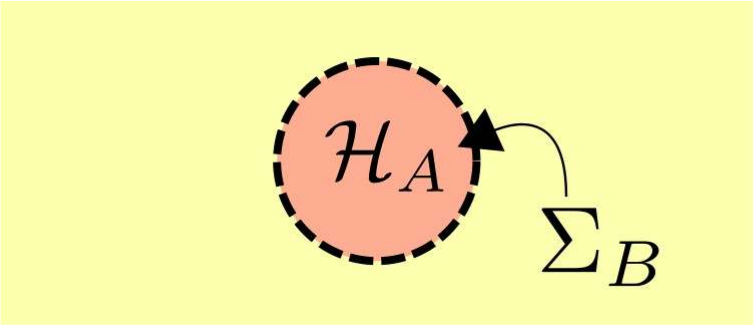
How do we calculate? Embedding technique

Single impurity in an infinite pristine system, Dyson equation

Pristine



Defective



$$\mathcal{G}_A^0 = (\omega - \mathcal{H}_A^0 - \Sigma_B)^{-1}$$

$$\mathcal{G}_A^0 = \sum_k [\omega - H^0(k)]^{-1}$$

Bloch Hamiltonian

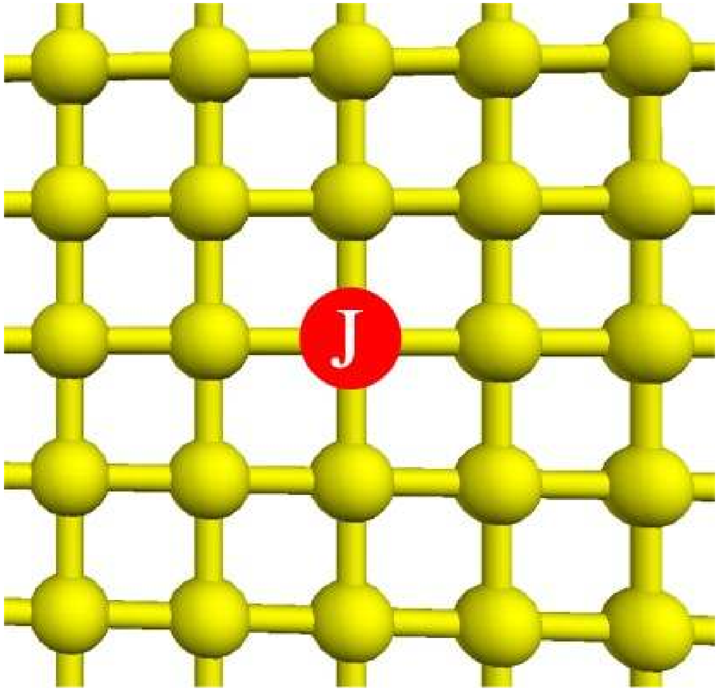
$$\mathcal{G}_A = (\omega - \mathcal{H}_A - \Sigma_B)^{-1}$$

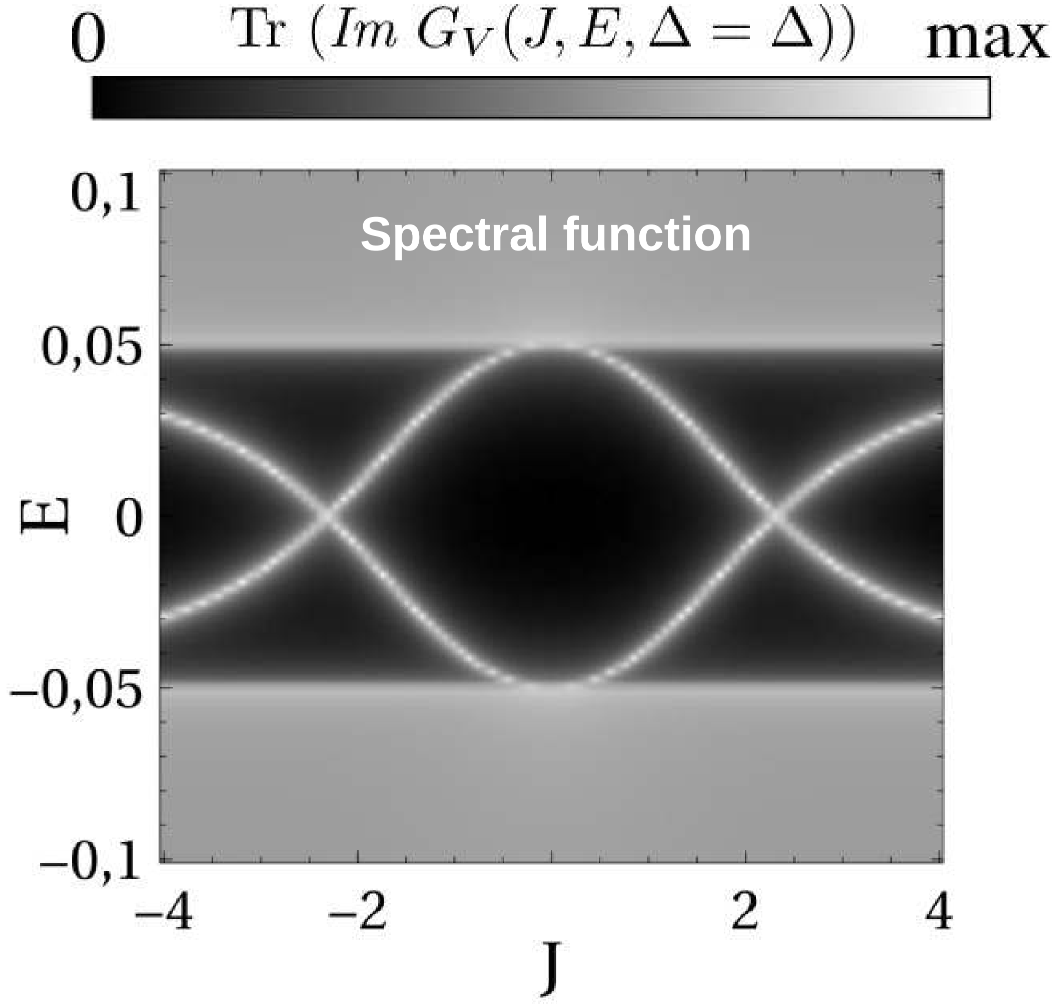
→ **<u>Exact impurity Green function</u>**
→ **<u>No translation invariance</u>**

Requires on the order of 90000 k-points

Considerable speed up using renormalization + adaptive algorithm

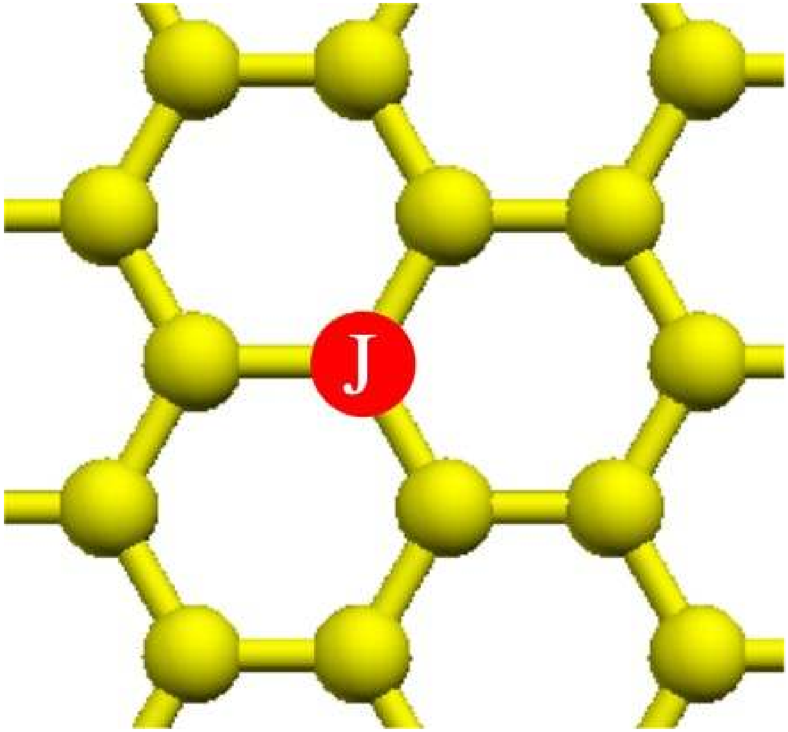
Conventional Shiba state

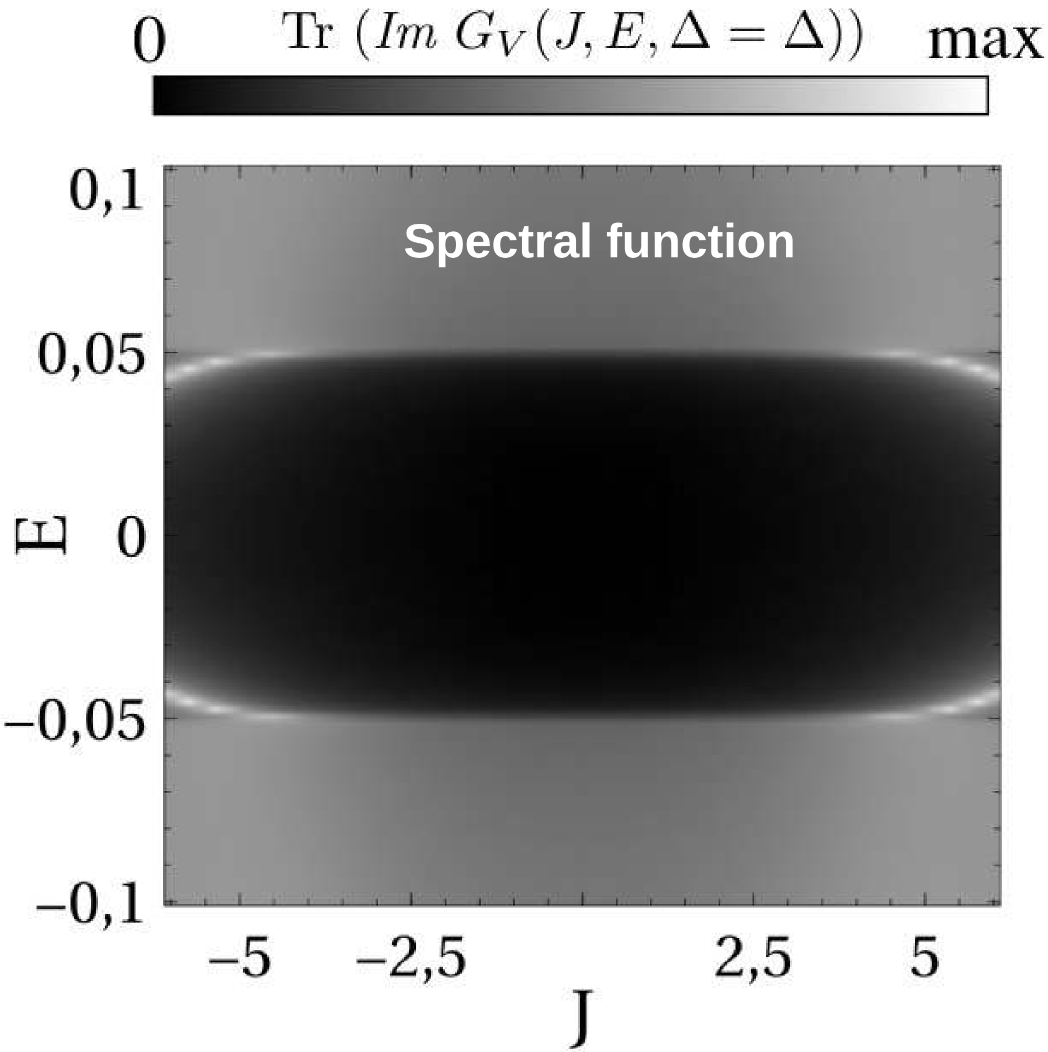




Embedding method recovers the analytical result for conventional Shiba states

Conventional Shiba state in graphene





Embedding method yields **no Shiba states in graphene** at weak coupling

Is there a way around?

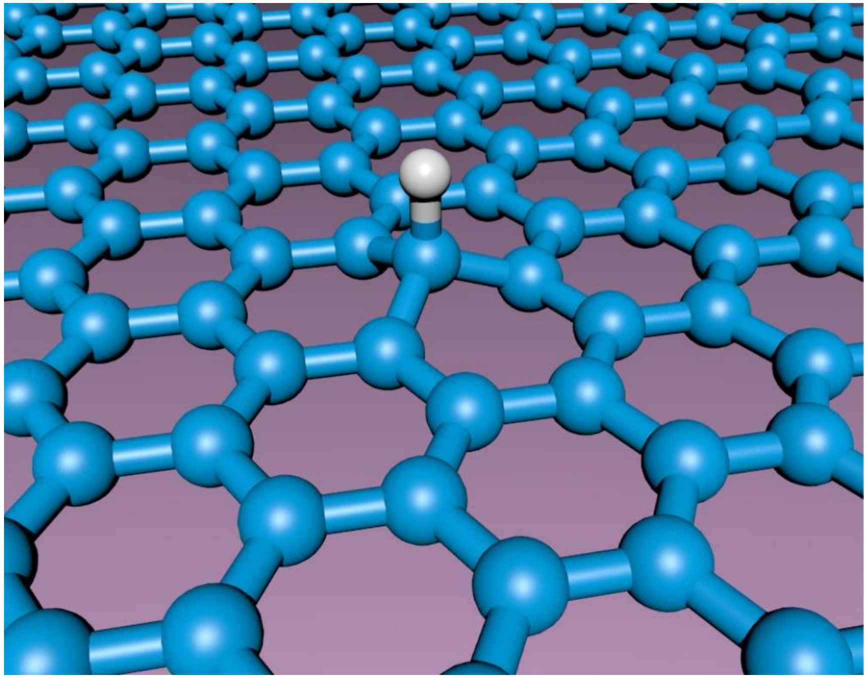
$$E_S = \Delta \frac{1 - (\pi \frac{S}{2} J \rho)^2}{1 + (\pi \frac{S}{2} J \rho)^2}$$

Energy of Shiba bound state

Graphene has zero density of states at the Fermi energy

Can we do something about it?

Single hydrogen on graphene



- Locally enhances DOS close to Fermi energy
- Are expected to induce local paramagnetic moments in carbon

Experimental evidence: Hydrogen atoms have been be manipulated with an STM

H. Gonzalez-Herrera, I. Brihuega et al, SPICE workshop (2015)

Electronic structure of graphene with hydrogen

Hydrogen bonds <u>covalently</u> to the carbon underneath

↓

<u>pz electrons can no longer hop to the orbital of the carbon underneath</u>

Remove site in the honeycomb ↓ *or add infinite on-site potential*

<u>Zero energy state in neighboring carbons shows up</u>

The zero energy state ↓ *becomes singly occupied*

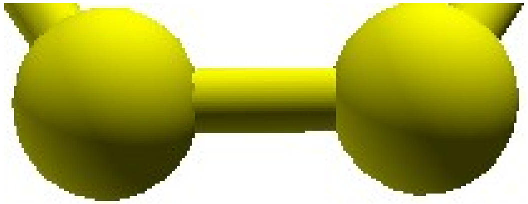
<u>Magnetism in carbon shows up</u>

Minimal Hamiltonian for the system

Minimal model to capture single hydrogenation
in graphene close to a superconductor

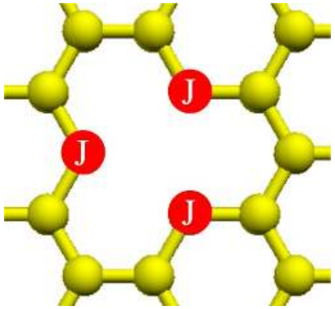
$$H = t \sum_{<i,j>,\sigma} c^\dagger_{j\sigma} c_{i\sigma} + J \sum_{i \in FN} c^\dagger_{\sigma i} \frac{\sigma}{2} c_{i\sigma} + \Delta \sum_i \left[c_{i,\uparrow} c_{i,\downarrow} + c^\dagger_{i,\downarrow} c^\dagger_{i,\uparrow} \right]$$

Nearest neighbor
hopping



p_z hopping

Local exchange



Tunable by doping

Superconducting pairing

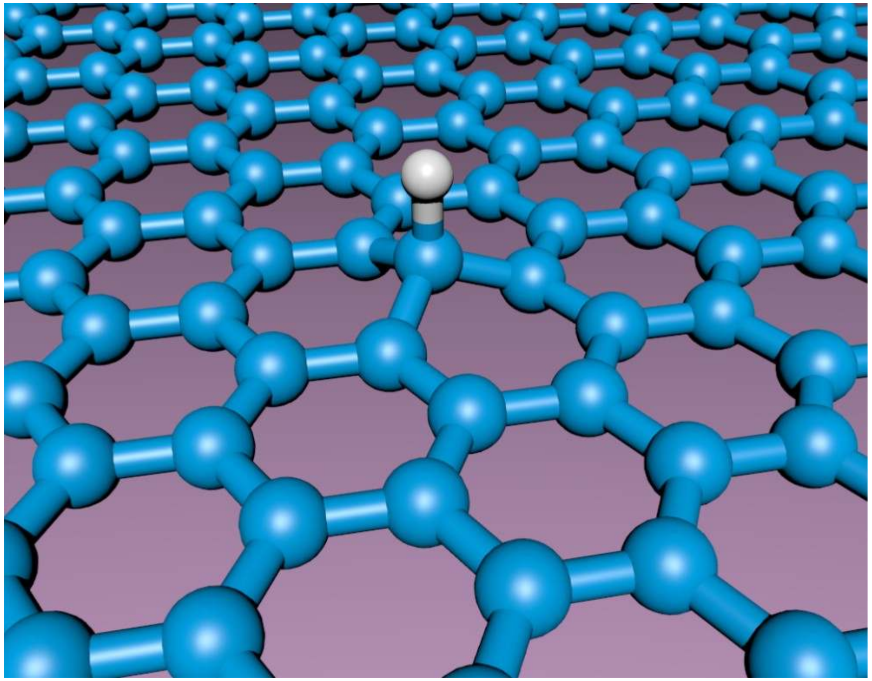
$$\Delta = \langle c_{i,\downarrow} c_{i,\uparrow} \rangle$$

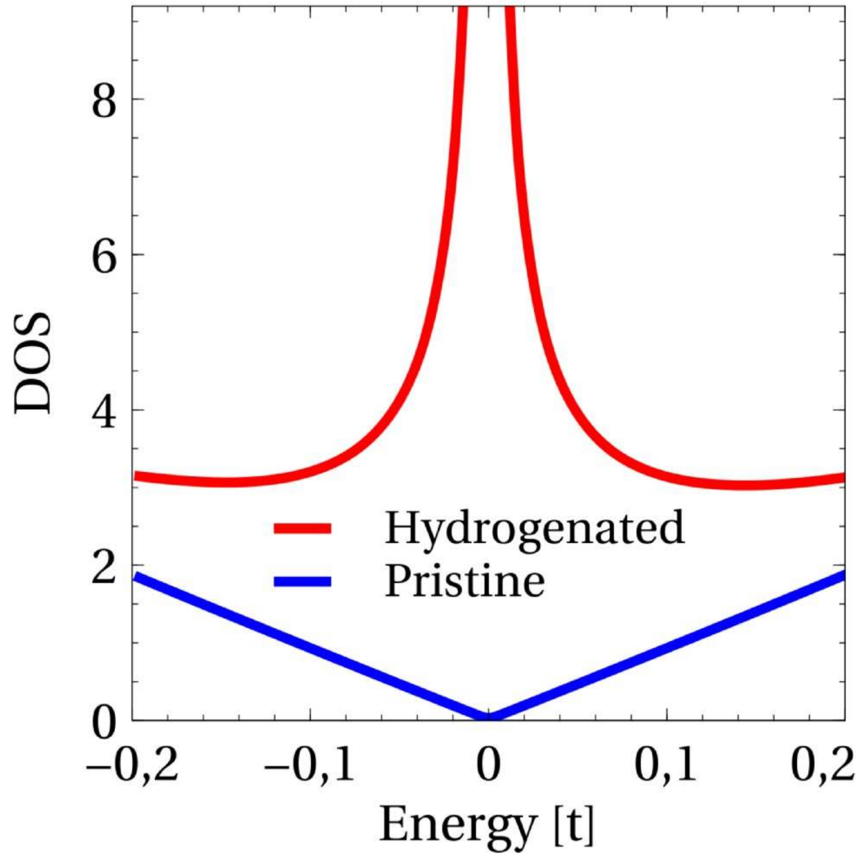
Proximity effect to a SC

Hydrogen is equivalent to a vacancy in a honeycomb lattice in a tight binding model

DOS in chemisorbed hydrogen

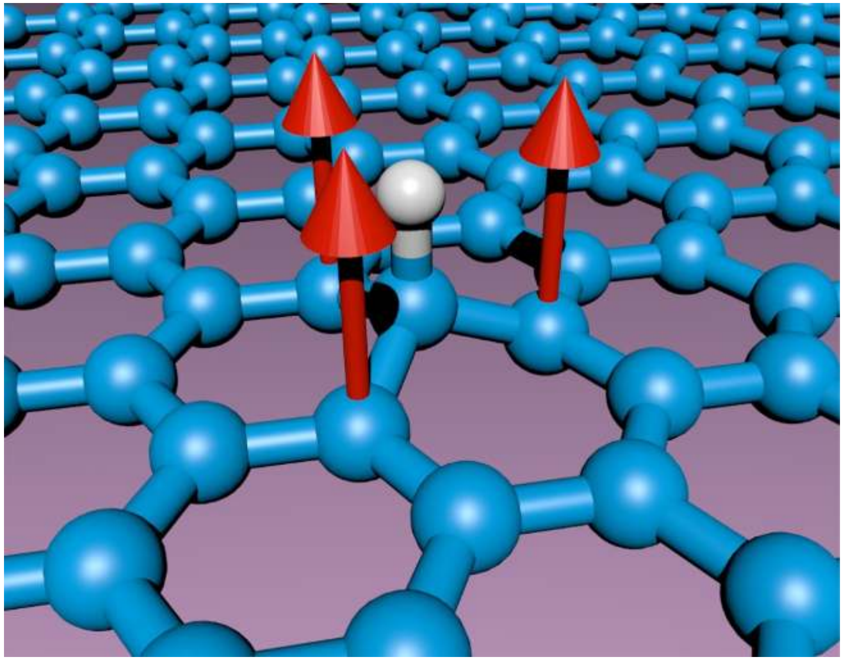
Density of states, non magnetic



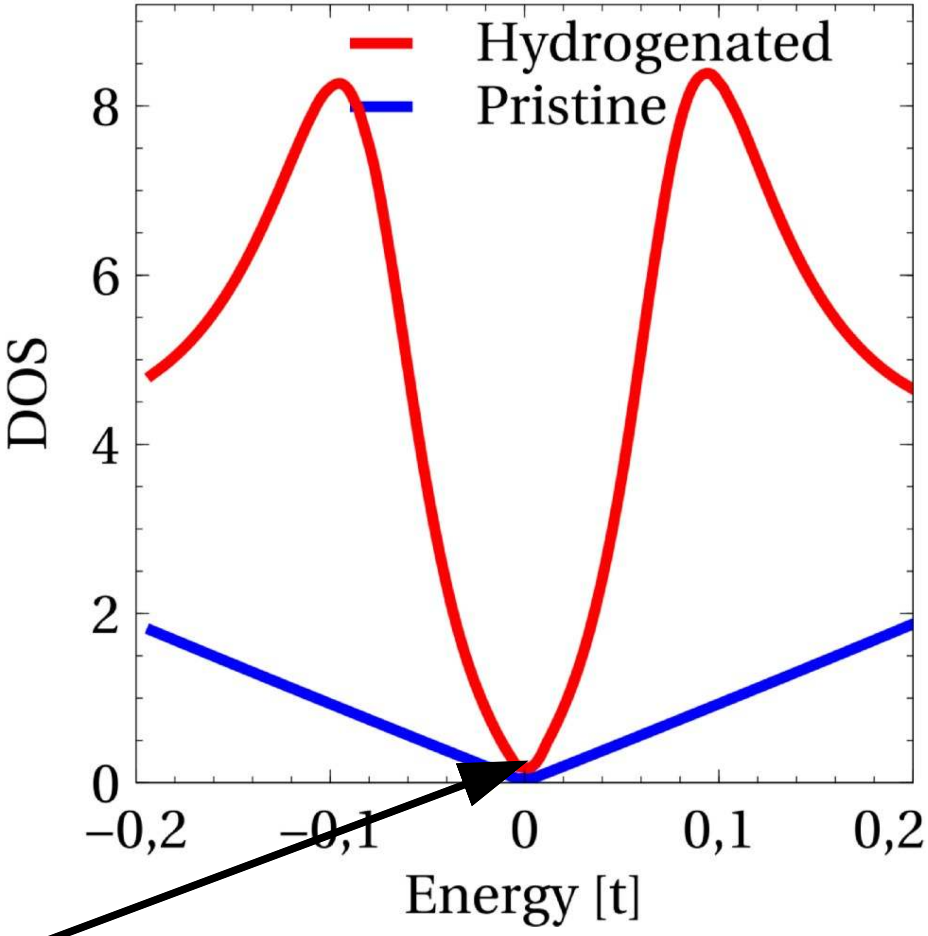


Divergent density of states at the Fermi energy, Stoner instability

Magnetism in chemisorbed hydrogen

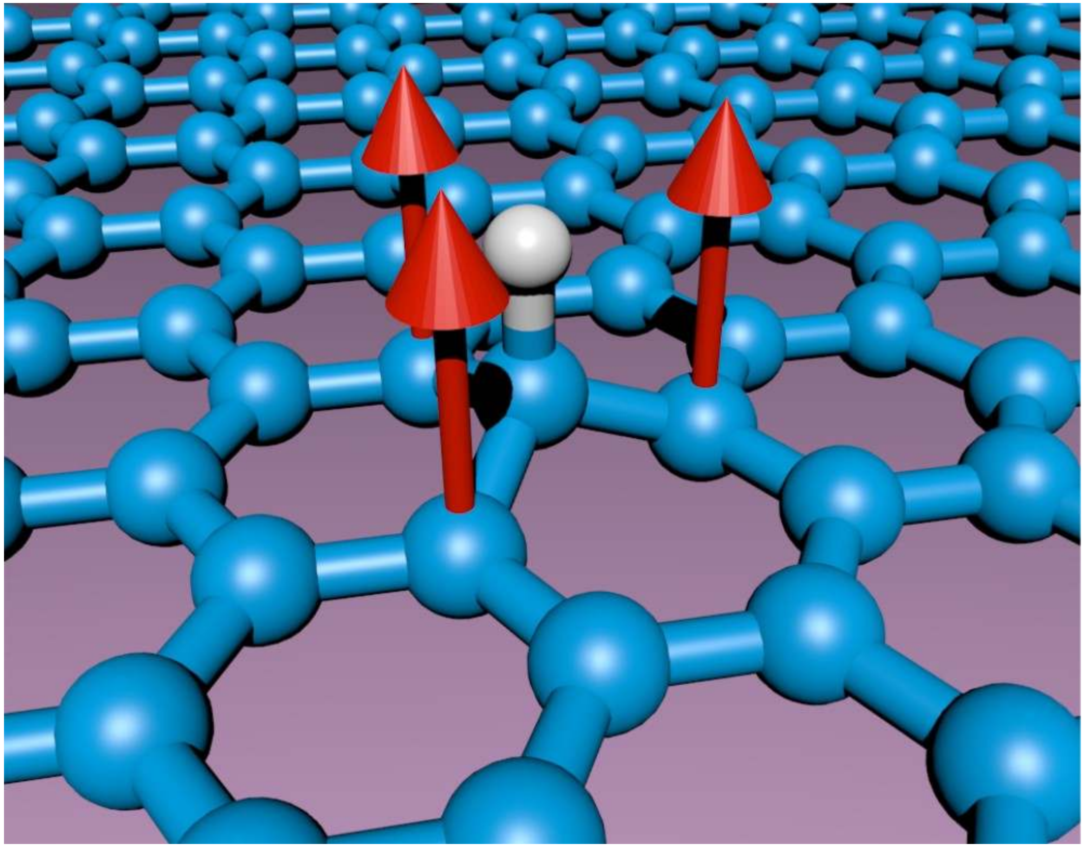


Density of states



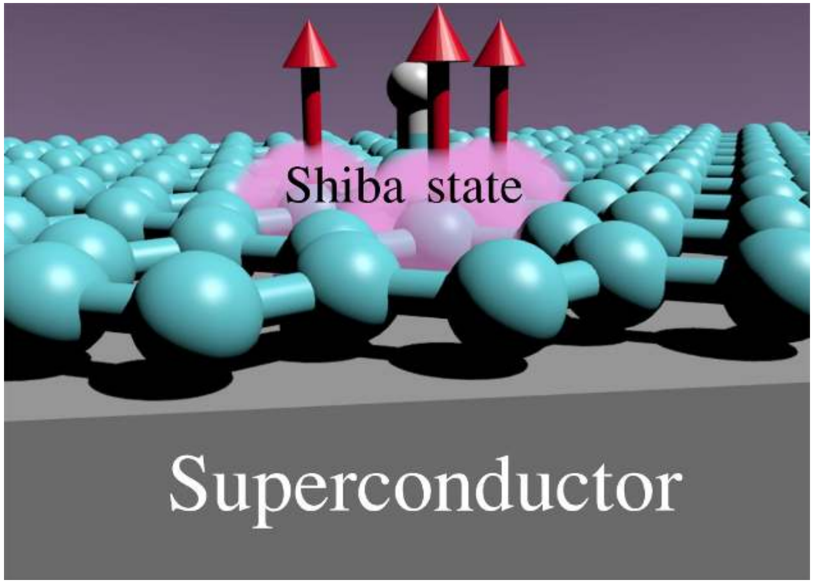
Zero density of states at the Fermi energy

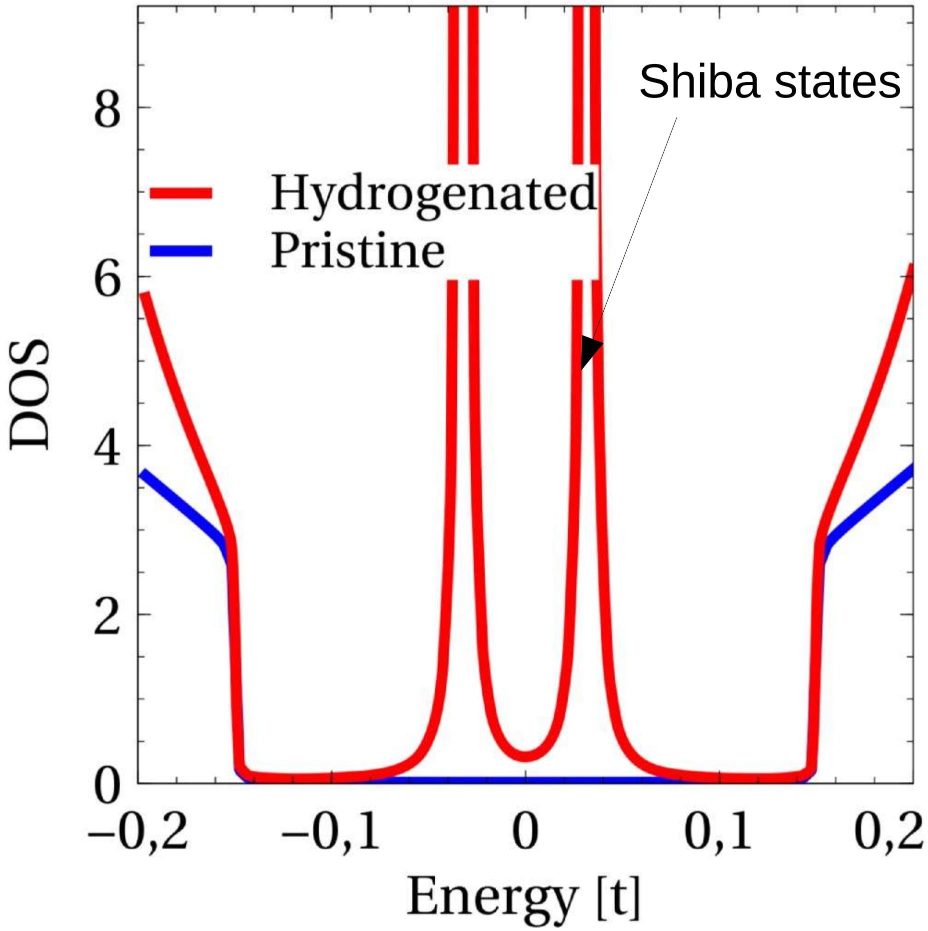
Magnetism in chemisorbed hydrogen



Can this local magnetic moment generate Shiba states?

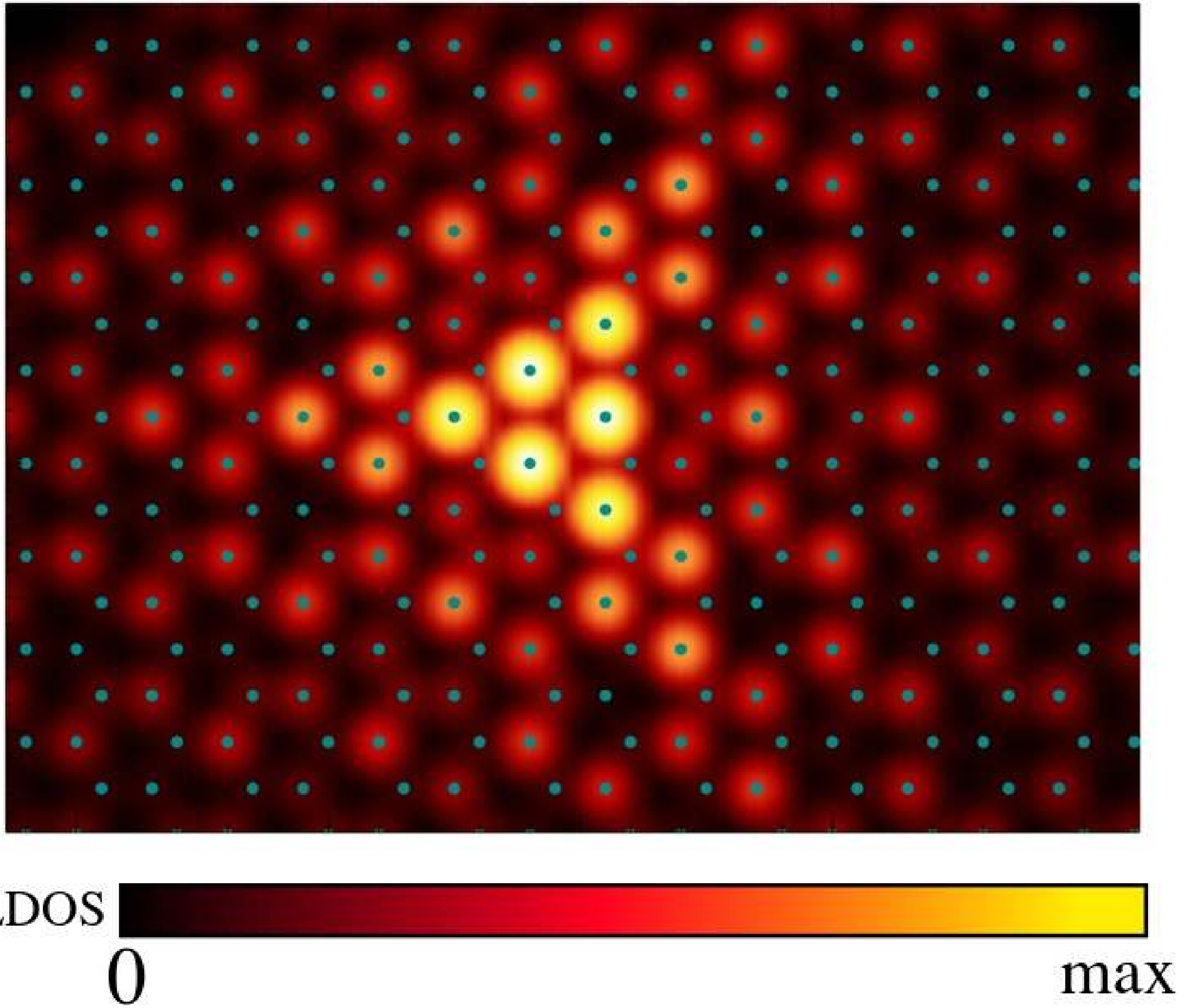
Shiba state in chemisorbed hydrogen





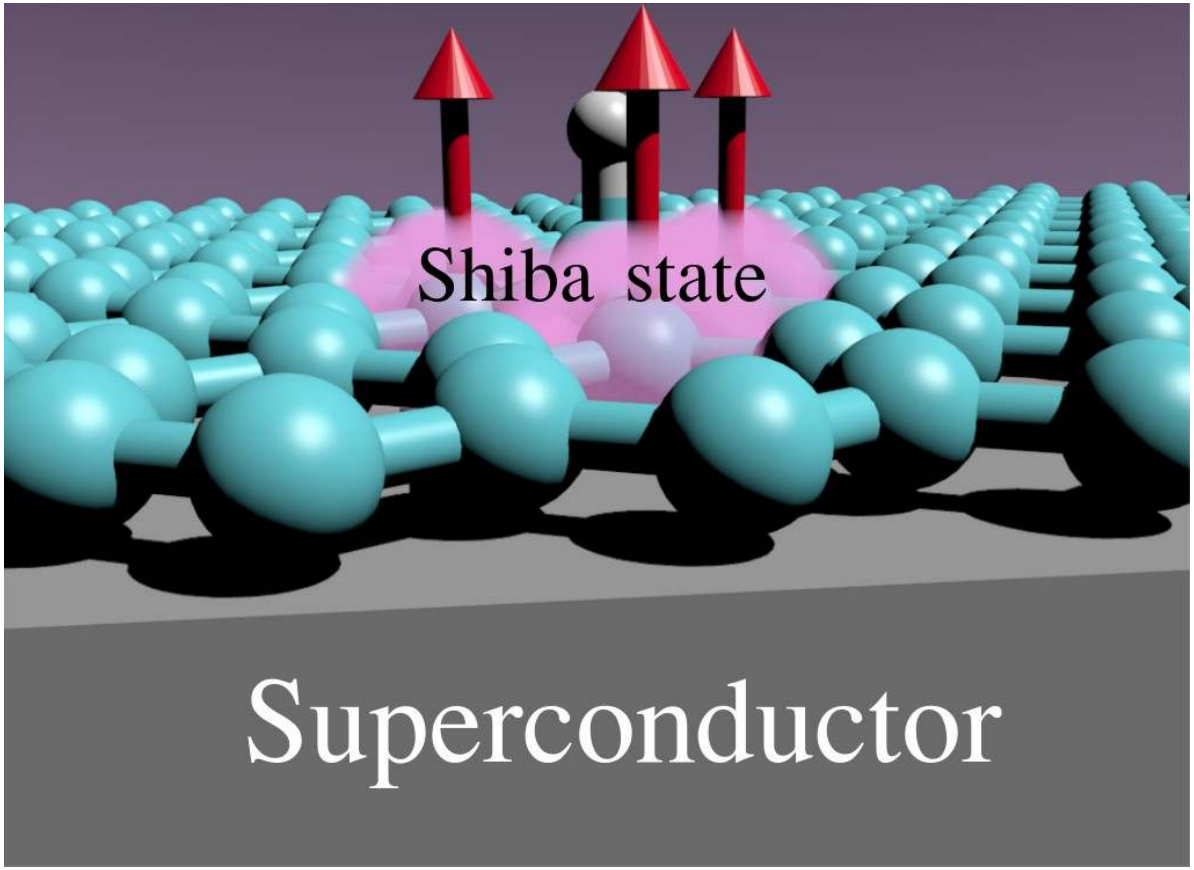
Mid-gap states appear when superconducting pairing is included

Spatial profile of the Shiba state



Shiba state strongly localized close to the hydrogenated site

How different are these Shiba states in comparison with 3d atoms on surfaces?



How do Shibas depend on the exchange?

For conventional Shiba states

$$E_S = \Delta \frac{1-(\pi\frac{S}{2}J\rho)^2}{1+(\pi\frac{S}{2}J\rho)^2}$$

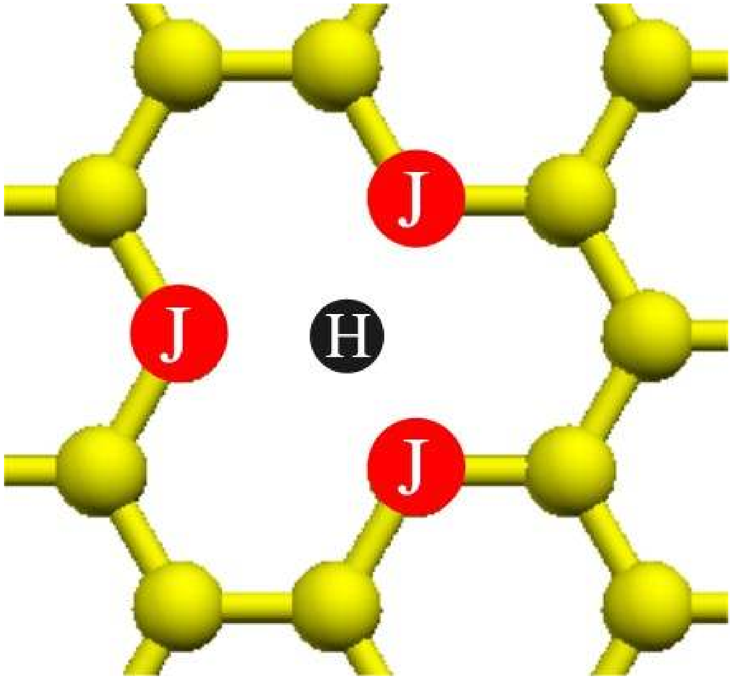
For small J, bound state energy is quadratic in J

$$E_S \approx \Delta(1-2(\pi\frac{S}{2}J\rho)^2)$$

Is this different for Shiba states in graphene?

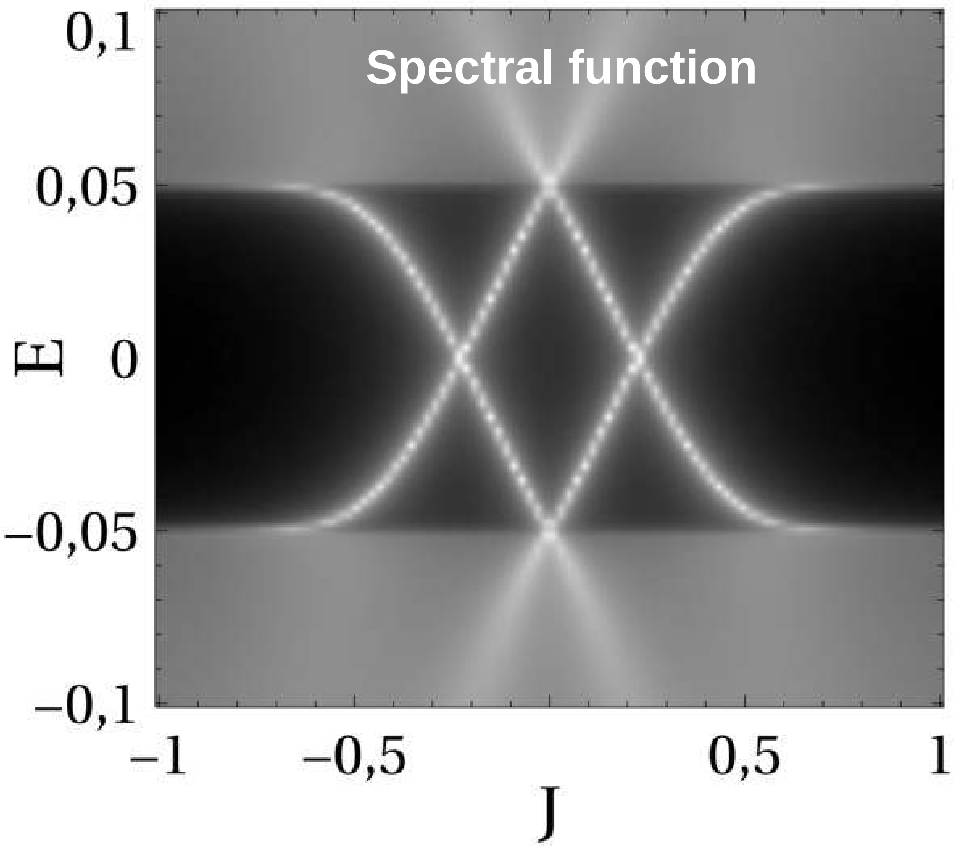
Shiba state in chemisorbed hydrogen

Infinite pristine



Infinite pristine *Infinite pristine*

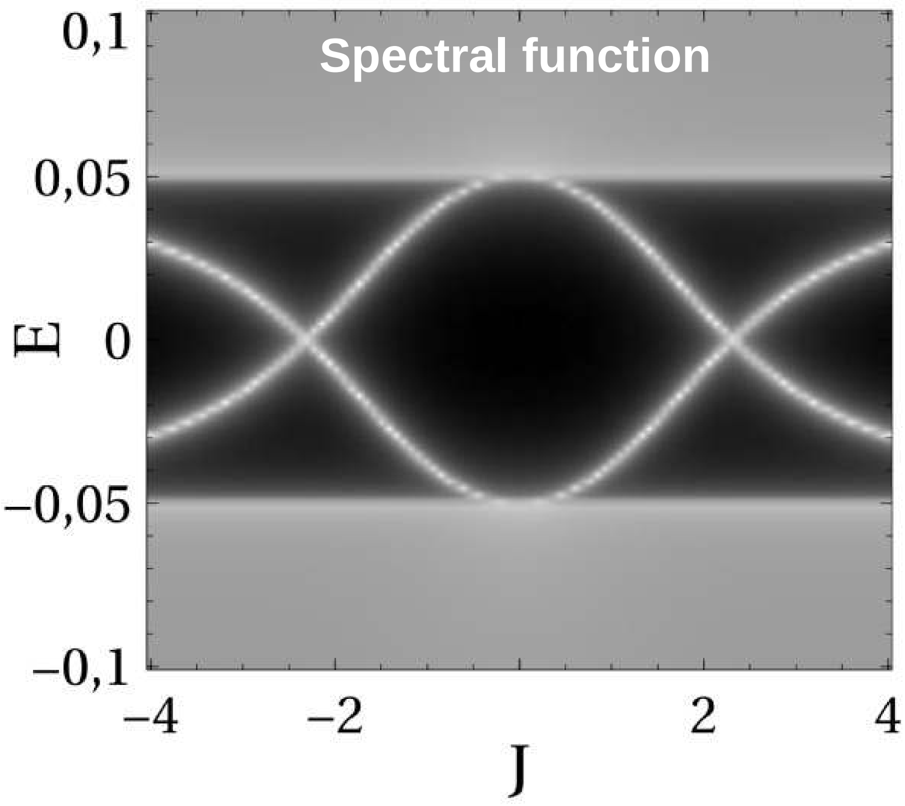
Infinite pristine



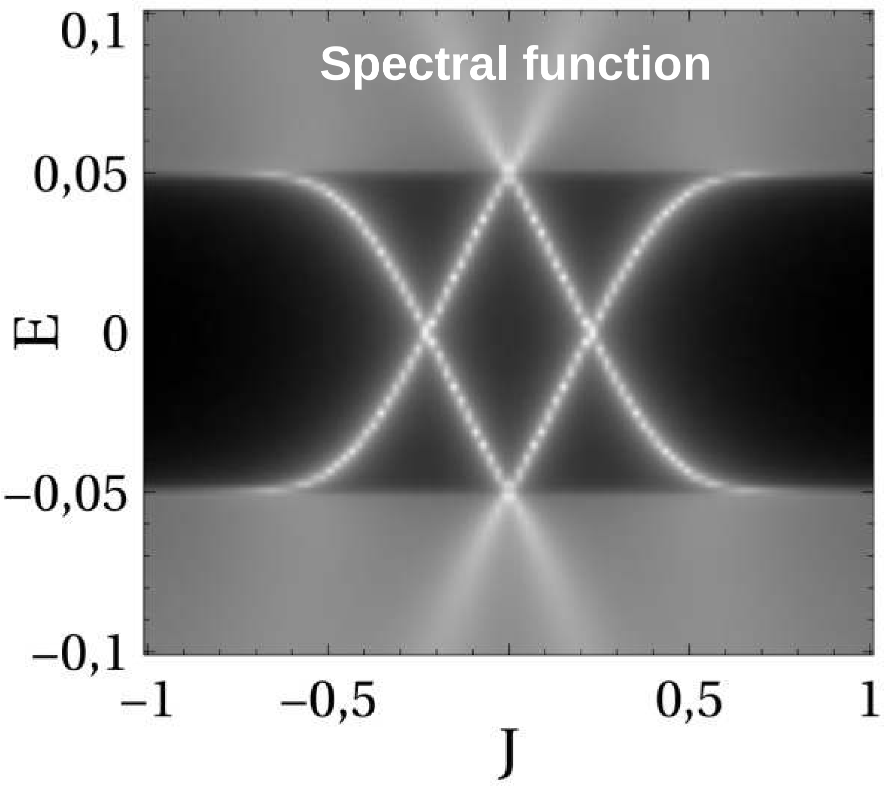
Shiba energy linear in the exchange

Conventional VS unconventional

Conventional Shiba states



Unconventional H-graphene Shiba states



How does the critical exchange depend on pairing?

For conventional Shiba states

$$E_S = \Delta \frac{1 - (\pi \frac{S}{2} J\rho)^2}{1 + (\pi \frac{S}{2} J\rho)^2}$$

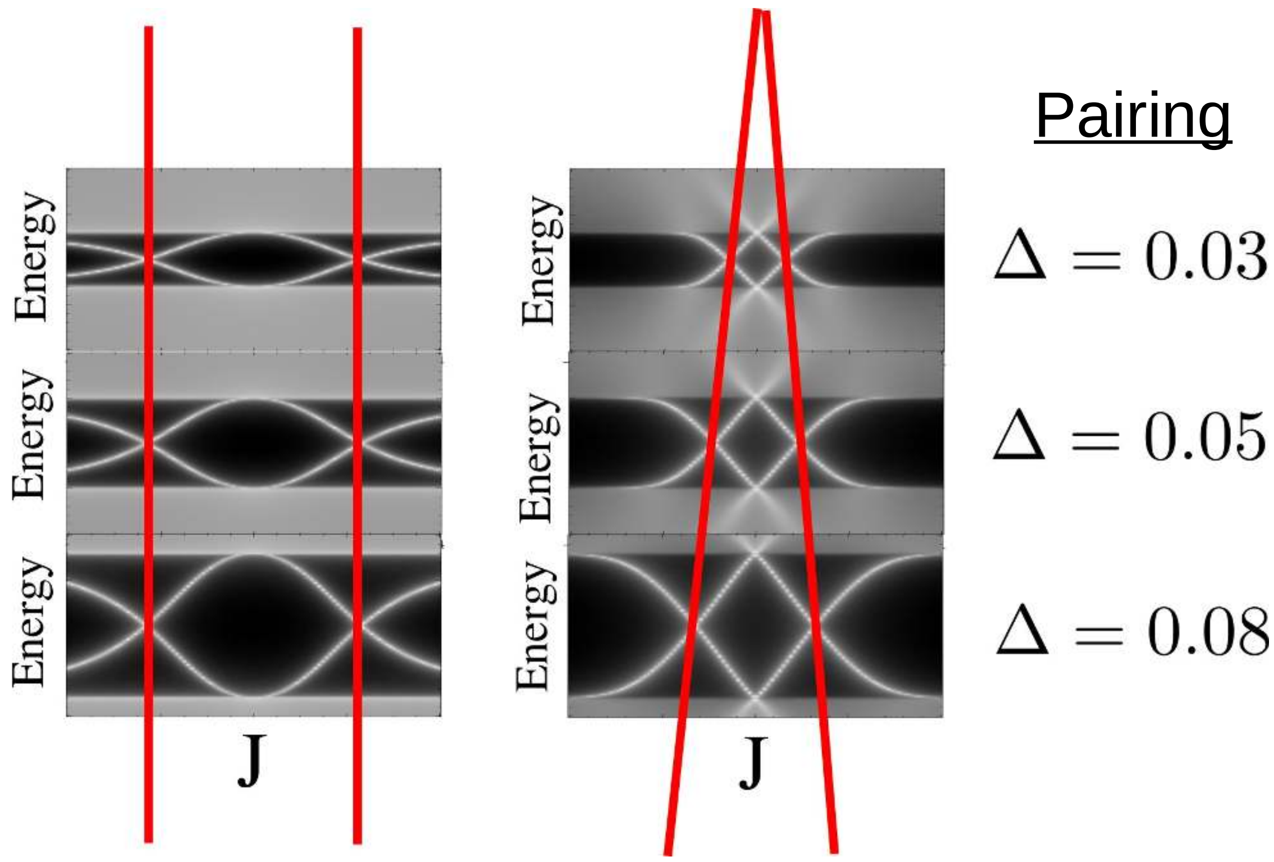
Critical exchange **does not depend** on pairing

$$1 = \pi \frac{S}{2} J_C \rho$$

Is this different for Shiba states in graphene?

Parity switching point

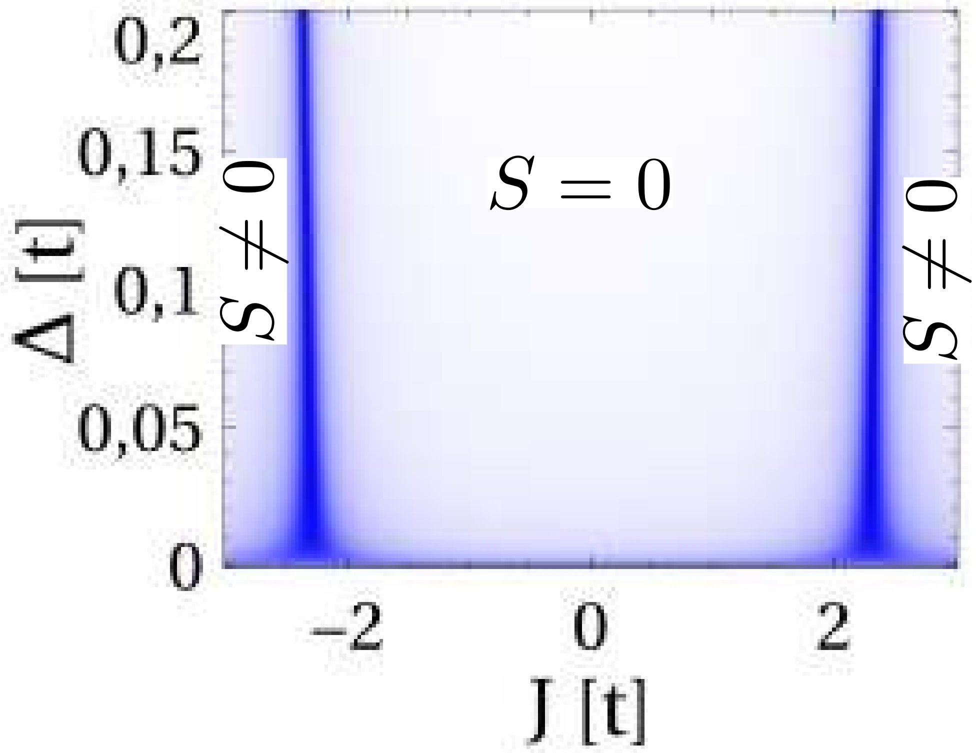
Conventional **Unconventional**



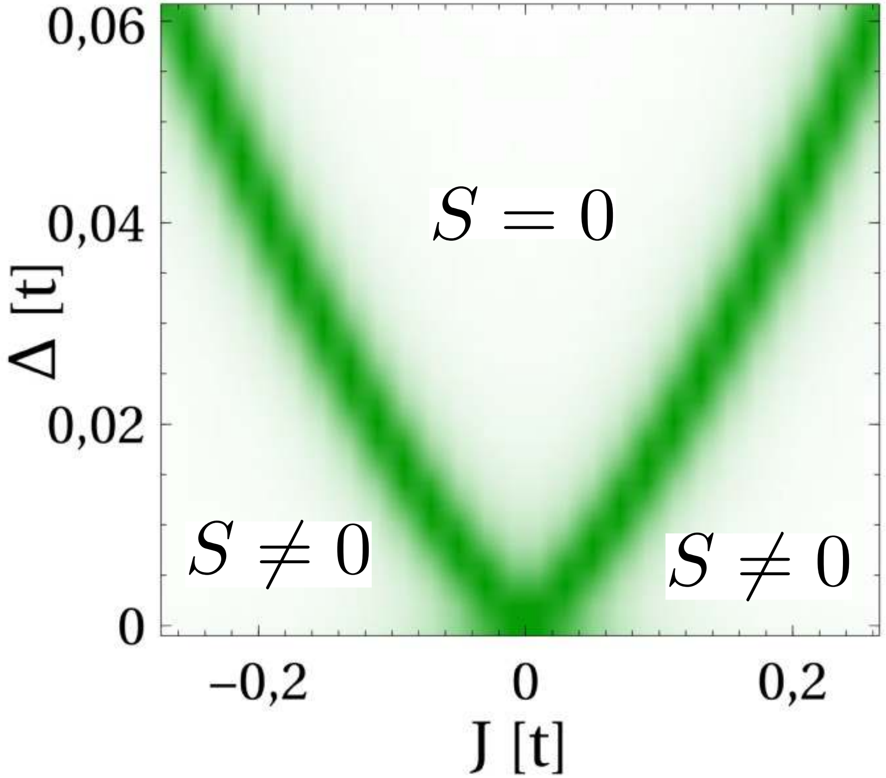
H-Graphene Shibas have a pairing dependent parity switching point

Parity switching point

Conventional Shiba states



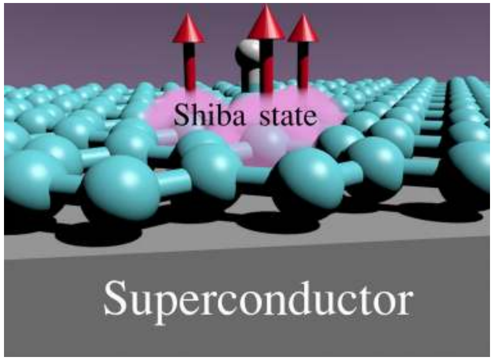
Unconventional H-graphene Shiba states



Pairing dependent critical exchange

What is cool?

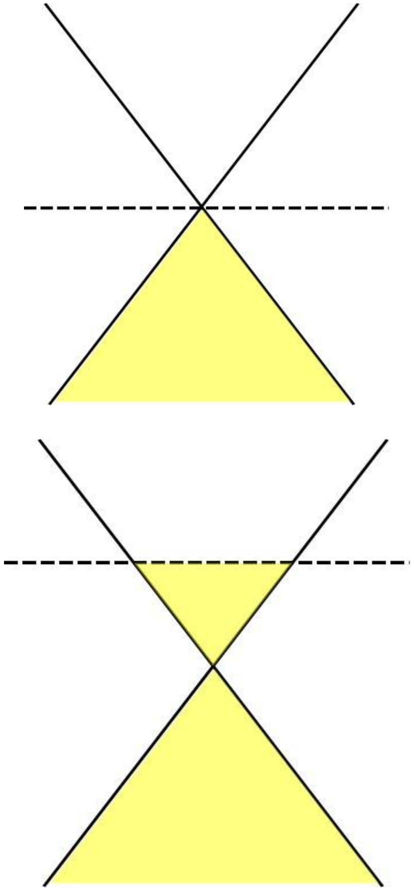
- Shibas without a transition metal
- Shibas with vanishing DOS
- Shibas linear in the exchange coupling
- Exchange tunable with temperature and gating
- Pairing dependent parity switching (T-control)

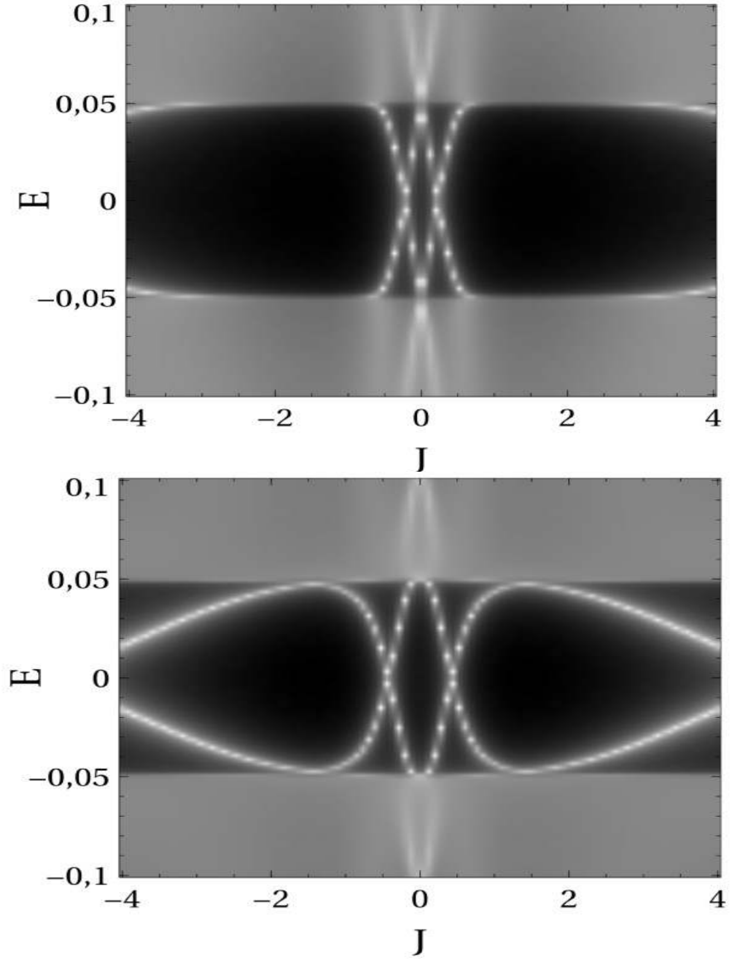


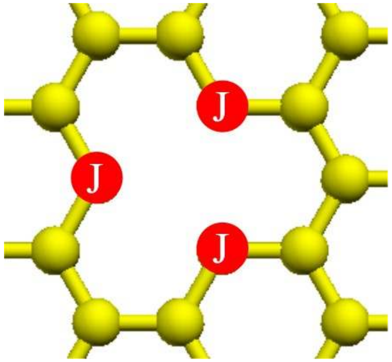
Warning!!

- We are assuming graphene is at half filling
  - Do unconventional Shibas resist doping?

Unconventional Shibas, away from half filling







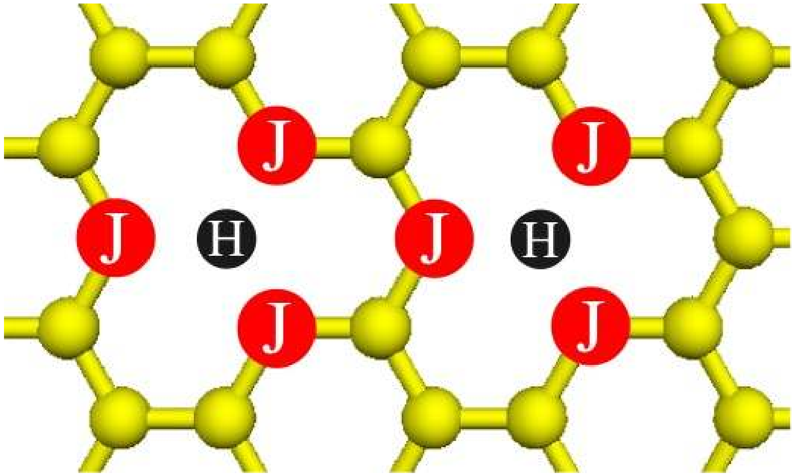
<u>Unconventional states survive in slightly doped graphene</u>

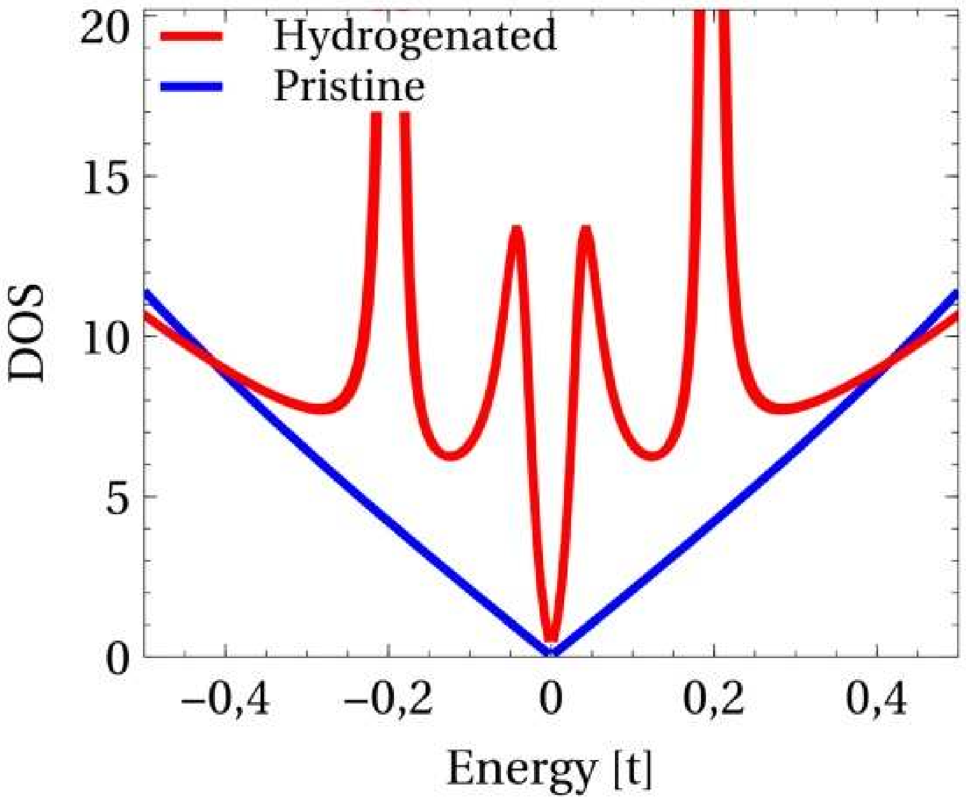
As long as magnetism is not killed!!!

Warning!! (reloaded)

- We are treating a quantum spin classically!!
  - Classical limit becomes more accurate for large S

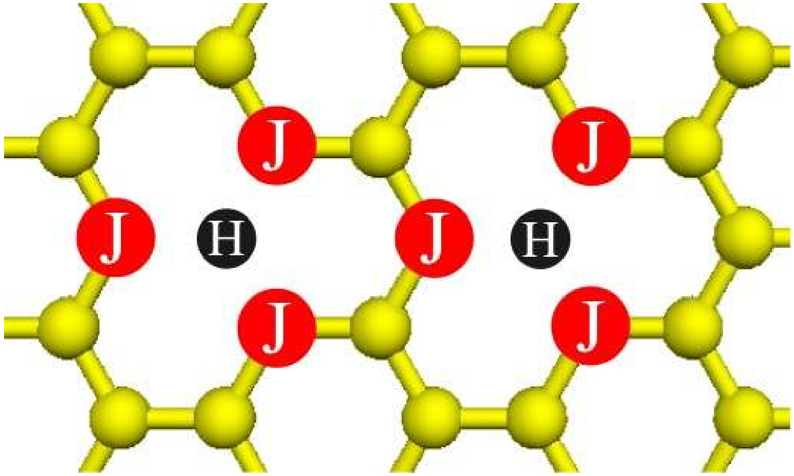
Graphene with two hydrogens: S=1

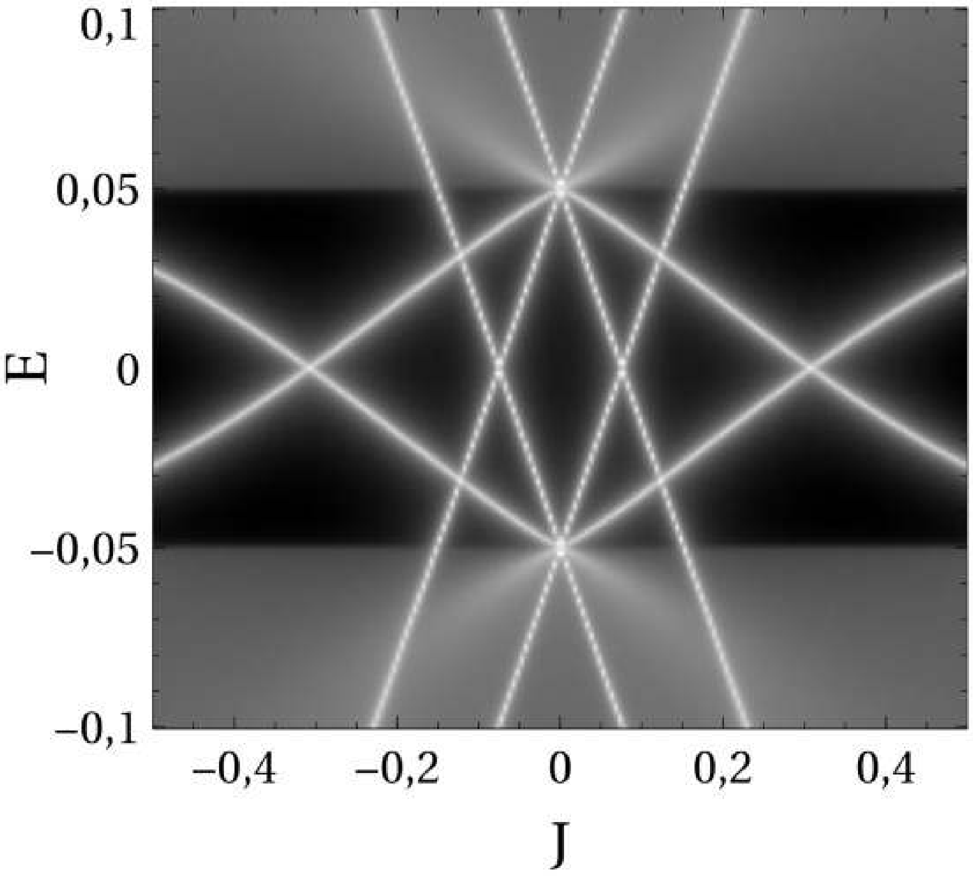




Two peaks appear, DOS is still zero at the Fermi energy

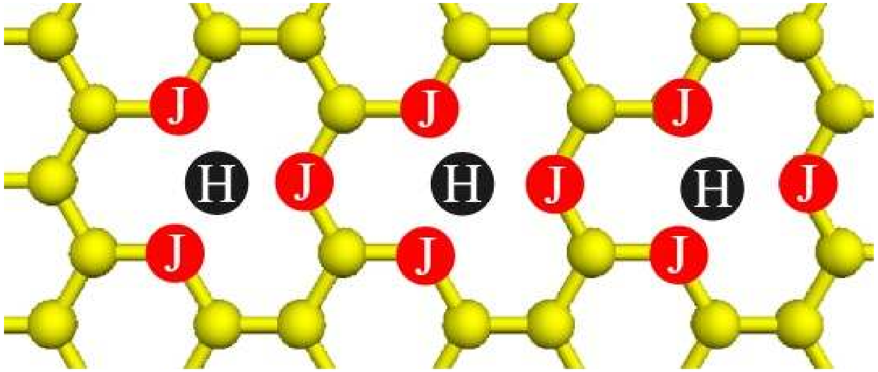
Graphene with two hydrogens: S=1

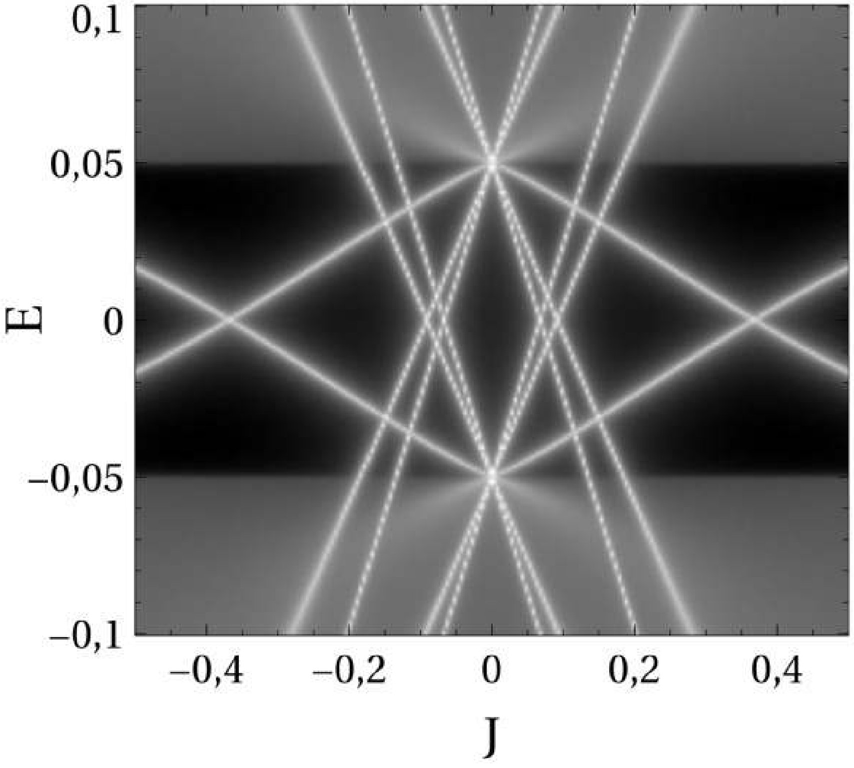




Spectrum linear in the exchange also for two adatoms

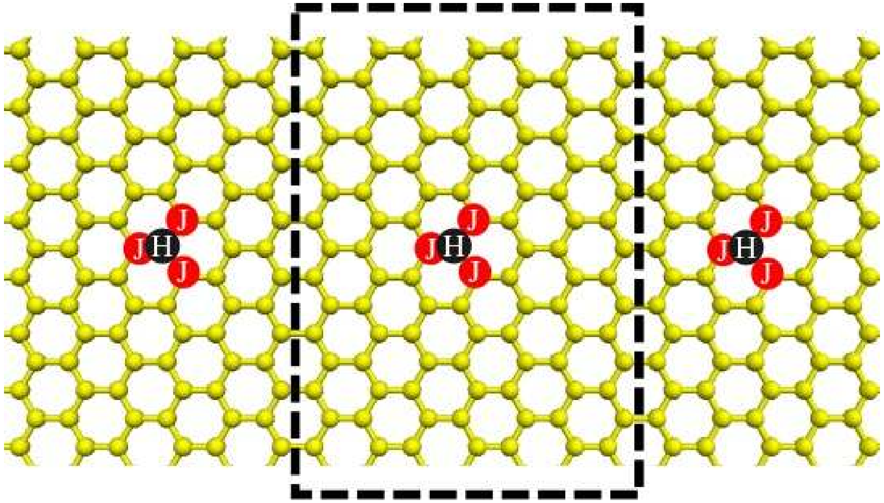
Graphene with three hydrogens: S=3/2

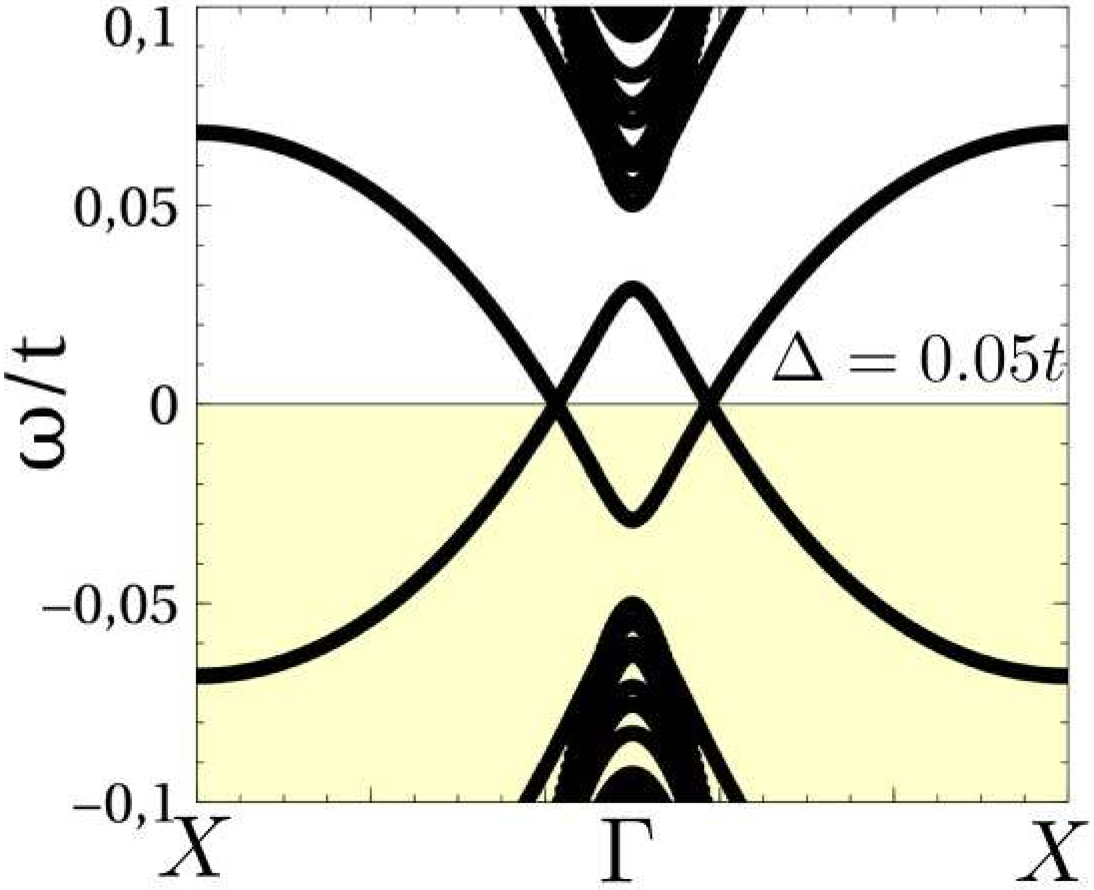




Spectrum linear in the exchange also for three adatoms

Linear hydrogen chain

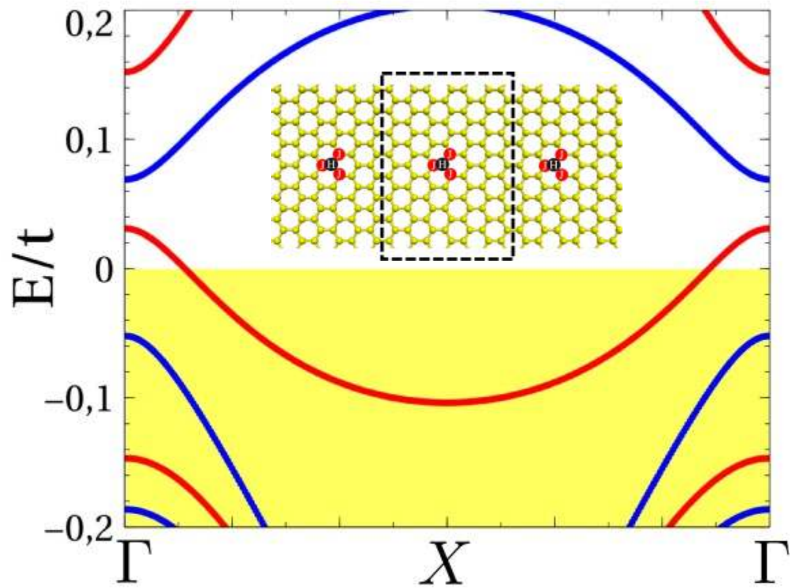




<u>Gapless Shiba band</u>

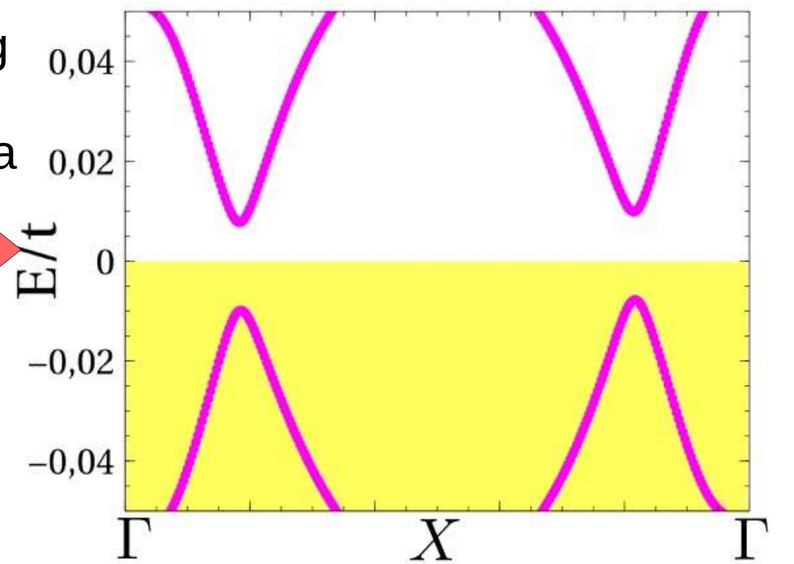
Majorana bound states

Doped ferromagnetic hydrogenated ribbon



1d Topological superconductor

Pairing
+
Rashba



Majorana bound states

Requires spin-coupling, in principle quite weak in graphene...

Summary

- Hydrogen in graphene creates in-gap Shiba states with an unconventional spectrum

Unconventional Shibas as probe of carbon paramagnetism?

Thank you!!

We acknowledge financial support from

Spinograph

Spintronics in Graphene