Spin-coupling around a carbon vacancy in graphene

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GrapHEL
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Outline

1. Introduction
   - p_z vacancies
   - Jahn-Teller distorsion
2. Results
   - DFT
   - CASPT2
3. Discussion

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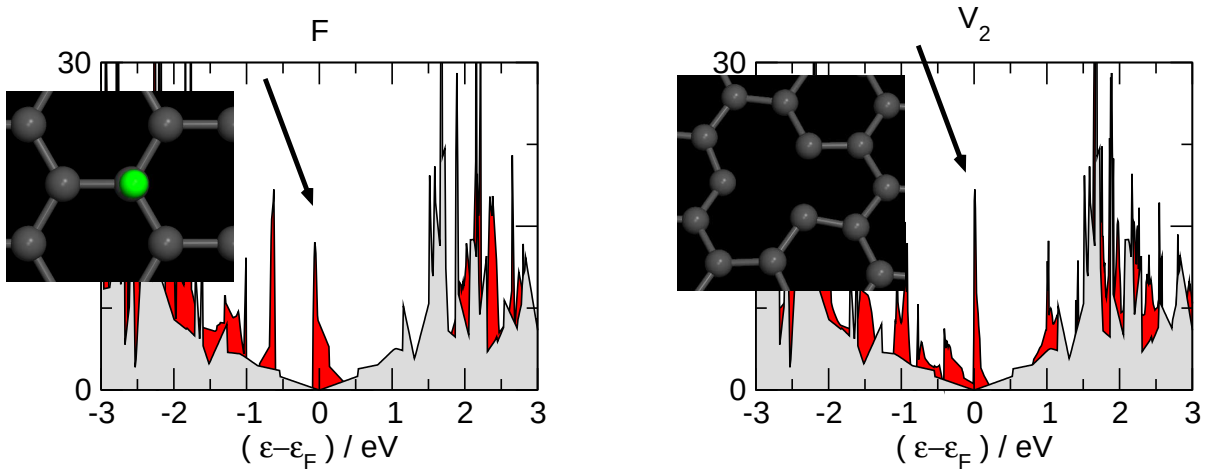
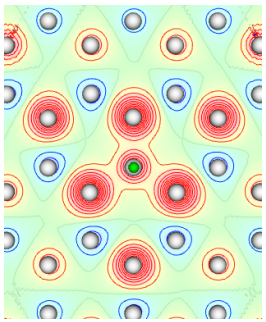
C-vacancies vs. adatoms

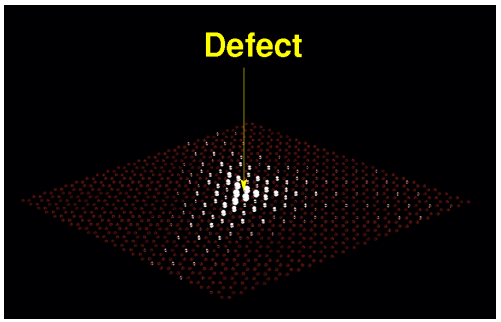


- Covalently bound species (e.g. H, F, OH, CH_3, etc.) and C-vacancies act as "p_z vacancies"
- Sublattice imbalance gives rise to midgap states

See e.g., T. O. Wehling, M. I. Katsnelson and A. I. Lichtenstein, *Phys. Rev. B* **80**, 085428 (2008)

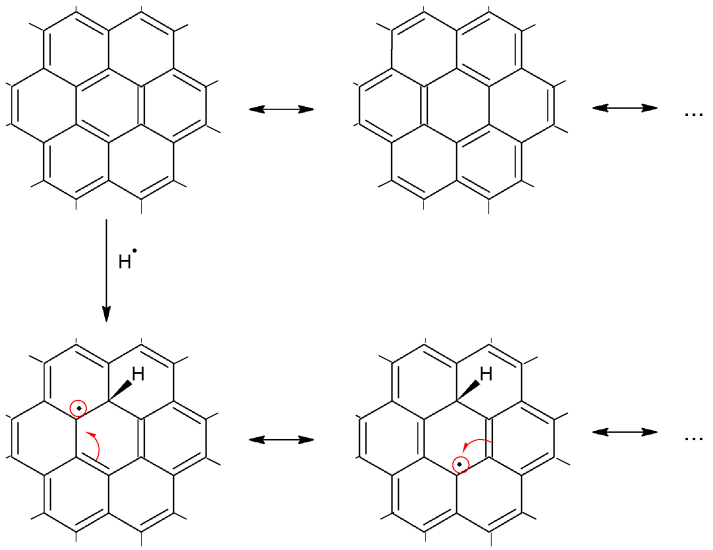
Midgap states





- ψ localizes on majority sites
- $\psi \sim 1/r$
- ψ is singly occupied

V. M. Pereira *et al.*, *Phys. Rev. Lett.* **96**, 036801 (2006); *Phys. Rev. B* **77**, 115109 (2008)

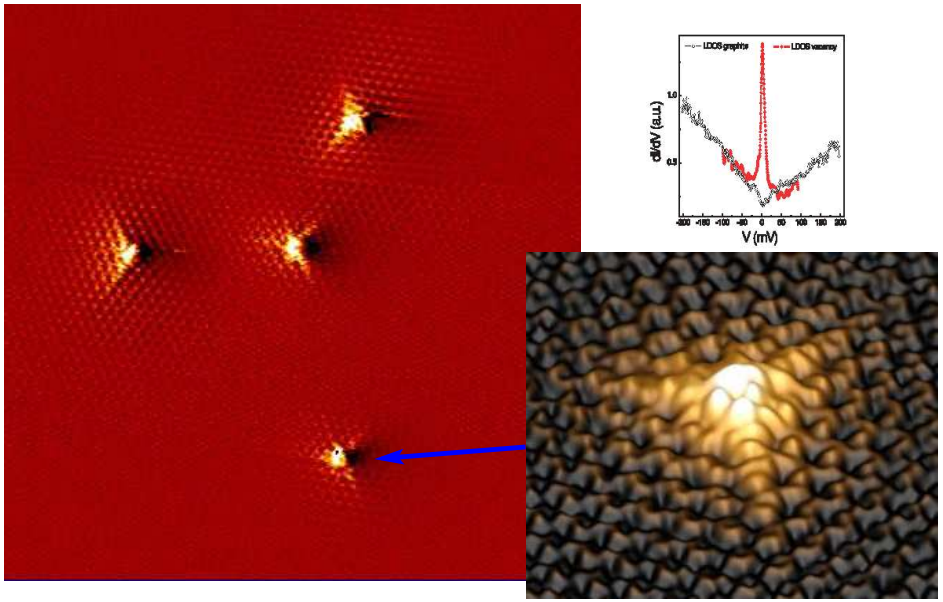


S. Casolo *et al.*, *J .Chem. Phys.* **130**, 054704 (2009); M. Bonfanti *et al.*, *ibid* **135**, 164701 (2012)

$\Rightarrow$ p_z vacancies are spin-1/2 paramagnetic centers

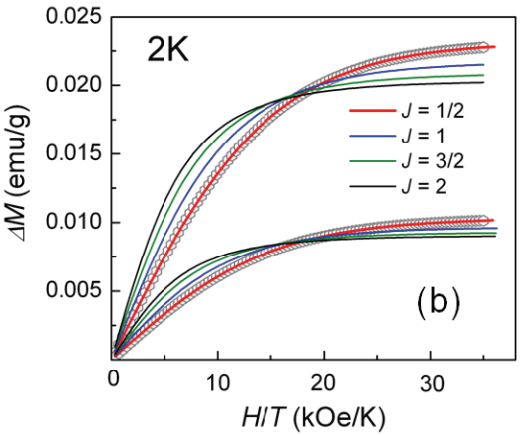
Midgap states

..**midgap state** imaged



M.M. Ugeda *et al.*, *Phys. Rev. Lett.* **104**, 096804 (2010)

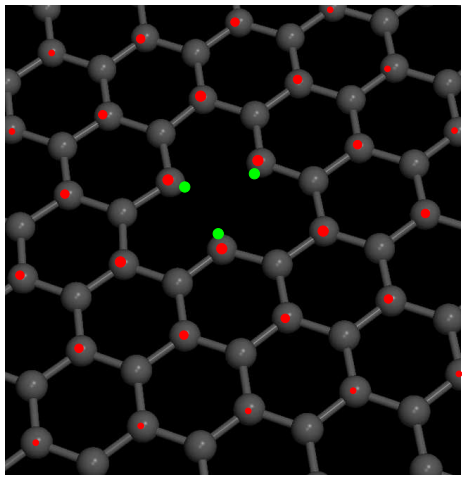
..**spin-$\frac{1}{2}$** paramagnetism measured

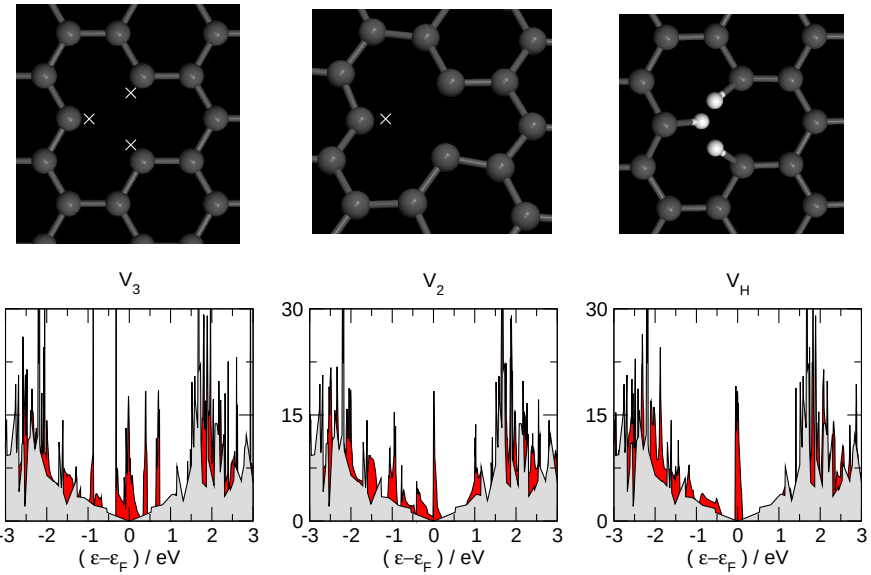


R.R. Nair *et al.*, *Nat. Phys.* **8**, 199 (2012)

π and σ midgap states

- 1 π single-occupied state
- 3 σ dangling bonds (orbitals)



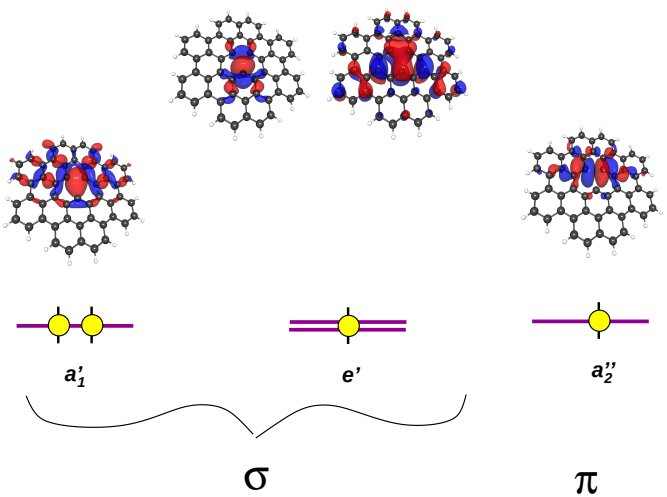


Unrelaxed Relaxed Saturated

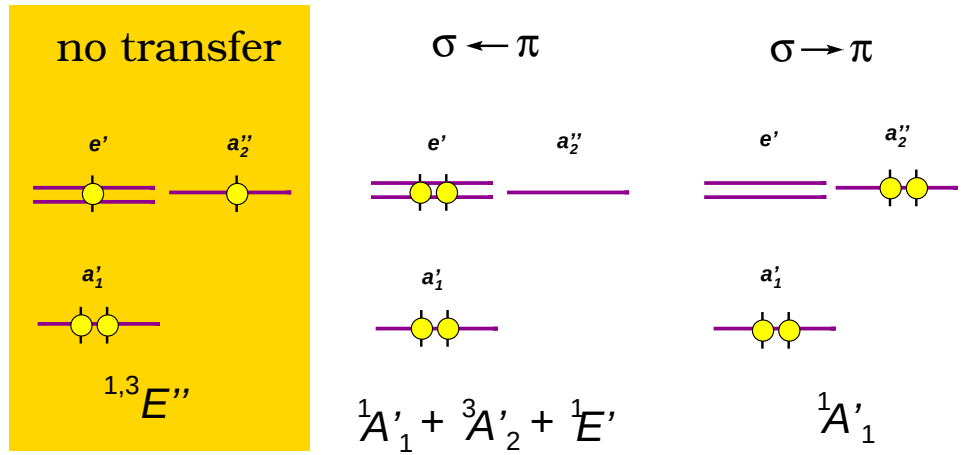
How do the unpaired electrons around the vacancy couple to each other?

π and σ midgap states: local D_{3h} symmetry

No mixing

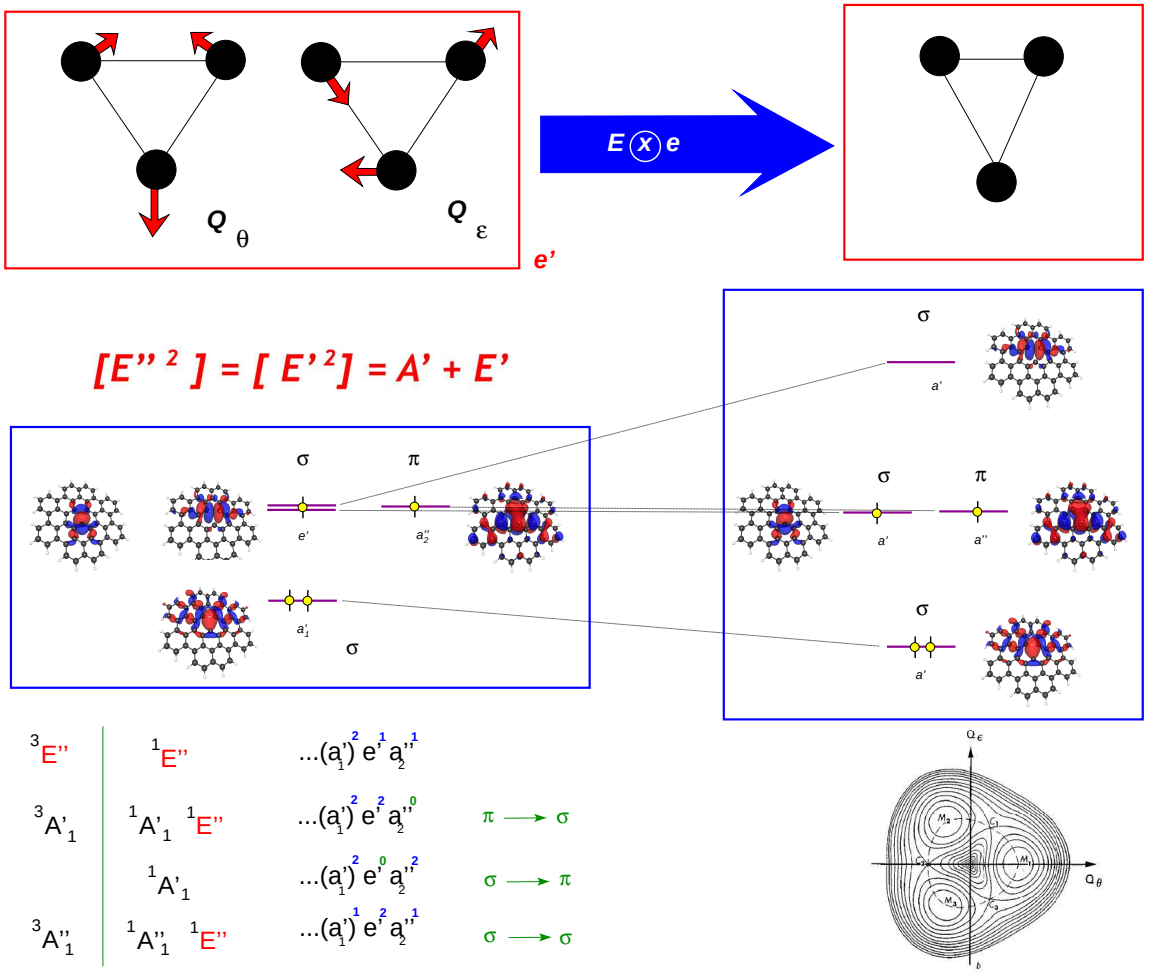


Mixing orbitals: possible scenarios



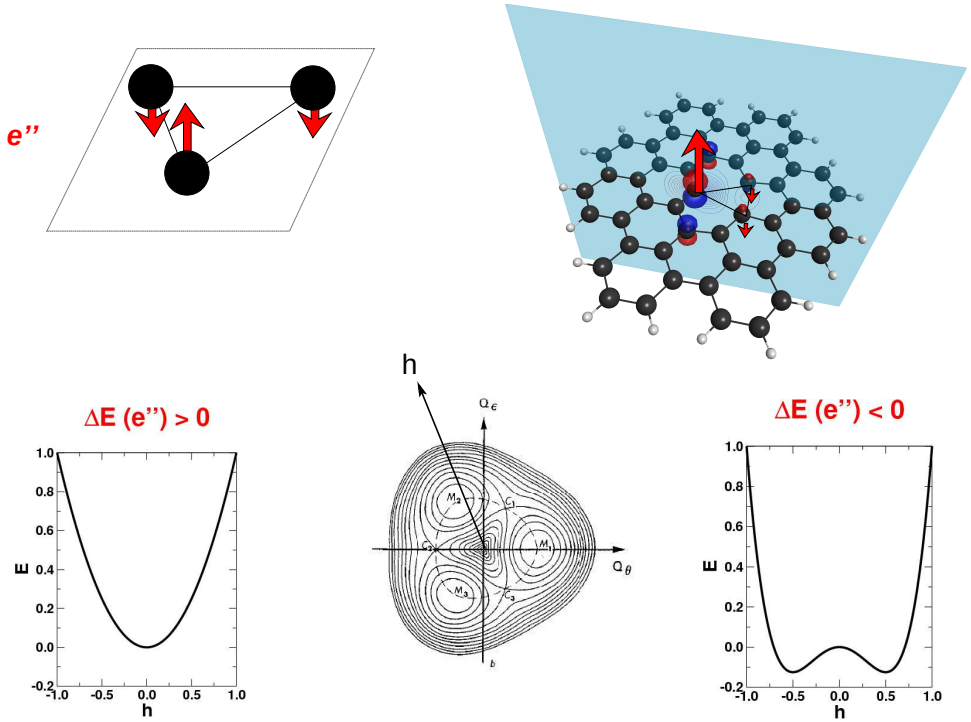
..the ground-state for $S = 0, 1$ is mostly $..(a_1')^2(e')^1(a_2'')^1 \Rightarrow E'$

Standard $E \otimes e$ problem



$E \otimes (e' + e'')$ problem

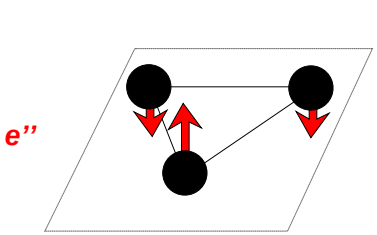
Out-of-plane, E'' vibrations do not lift degeneracy at first order..

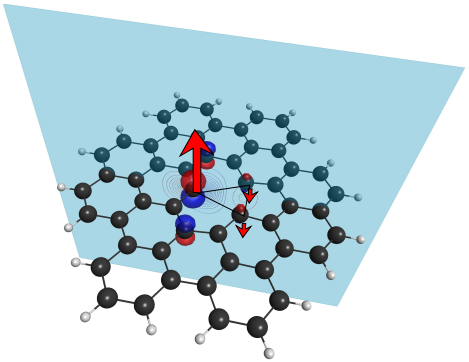


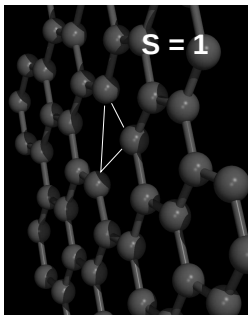
..but give corrections to second order, either positive or negative

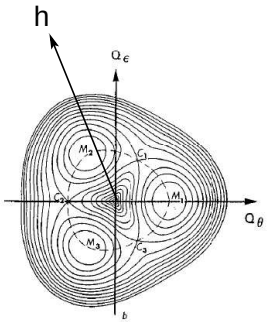
$E \otimes (e' + e'')$ problem

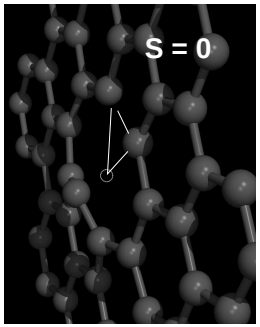
..the sign being different for the two spin species











$\Rightarrow$ Three- *vs.* Six- fold degenerate minima, for $S = 1, 0$

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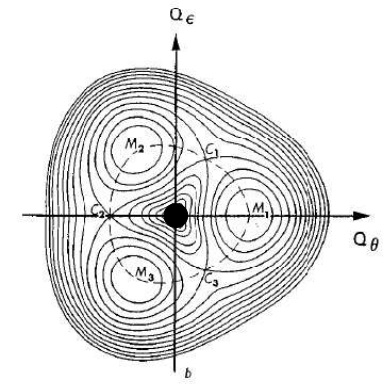
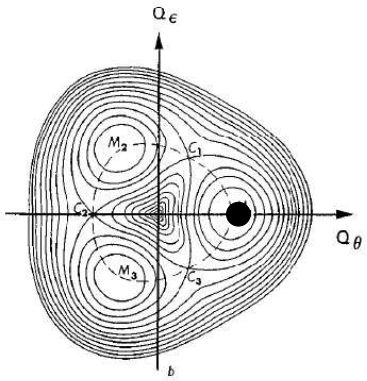
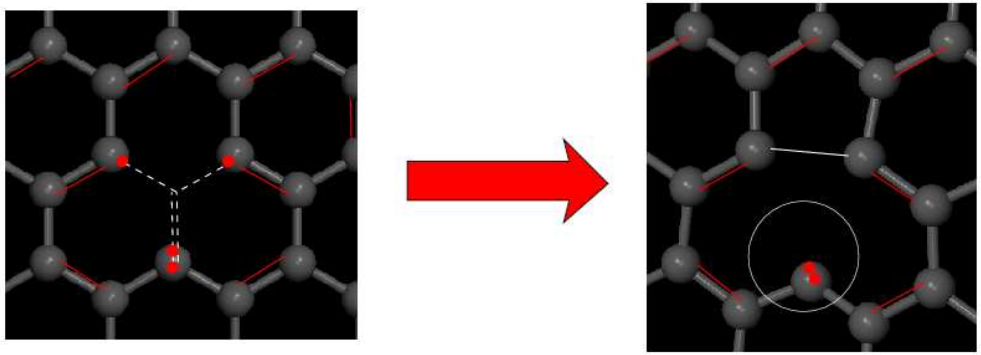
Technicalities

- Supercell approach: **6** $\times$ **6** $\times$ **1**
- **6** $\times$ **6** $\times$ **1** *k*-point mesh
- **PBE** exchange-correlation functional
- **PAW** pseudopotential
- **500 eV** cutoff
- Spin polarized
- Total magnetization constrained to $M_S = 0, 1$ manifold $\Rightarrow$ consistent with the **'molecular character'** of the vacancy-related states

Magnetization relaxed





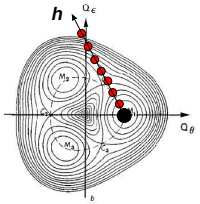


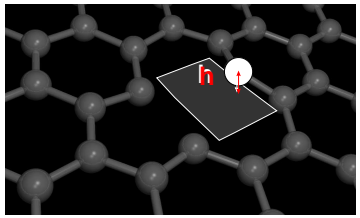
Full geometrical and spin relaxation

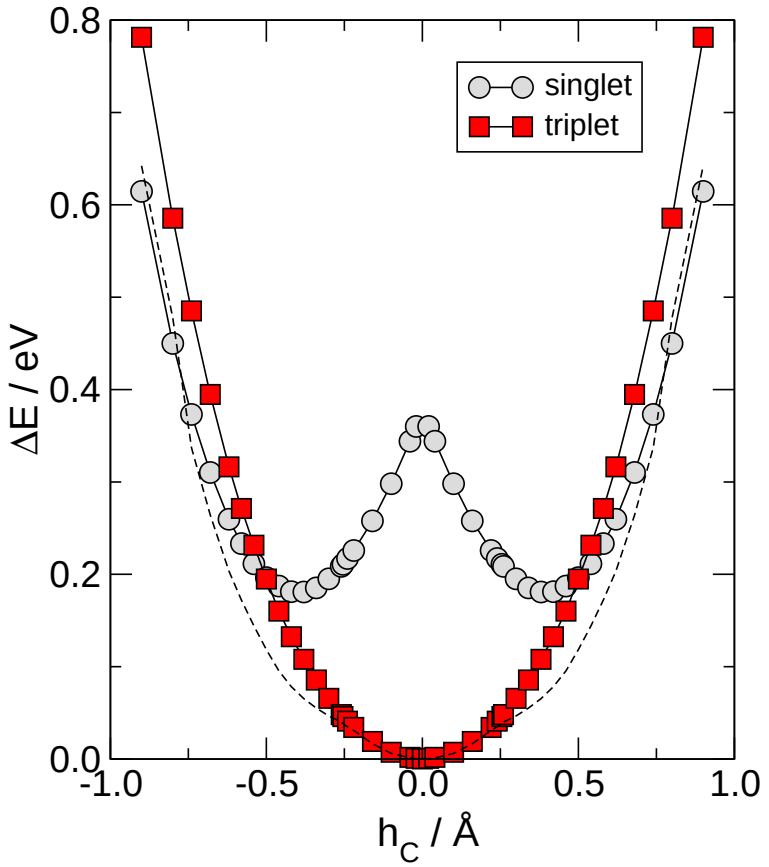
- Planar structure
- $d_{C-C} = 2.01$ Å
- $M \sim 1.6\mu_B$

Magnetization constrained

Partial geometrical relaxation, $M_S = 0, 1$ constrained



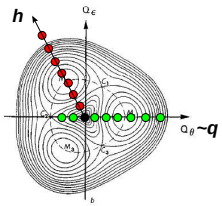


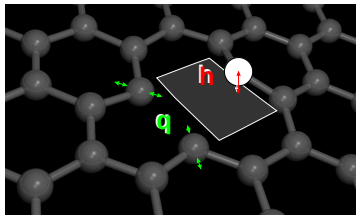


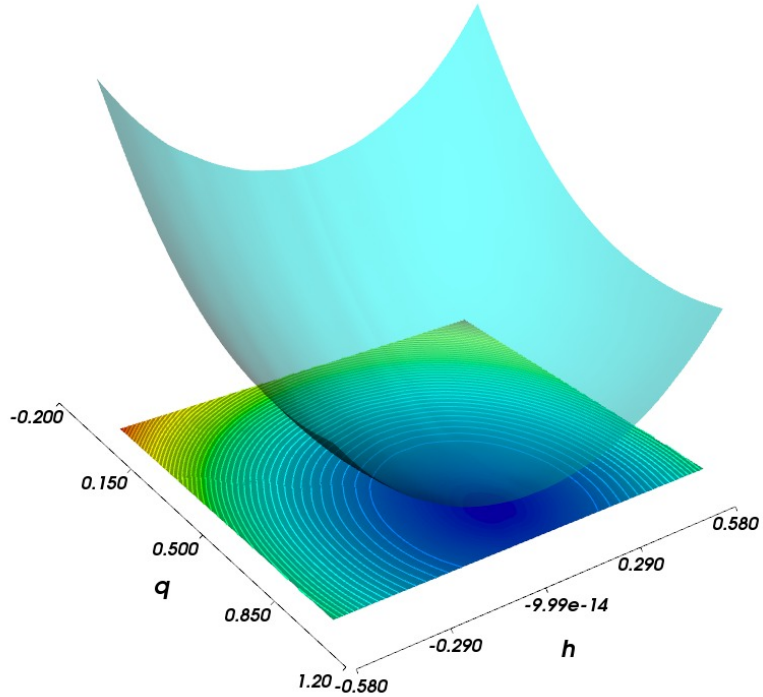
- triplet is stable, $\omega_\perp \sim 200 cm^{-1}$
- singlet is bistable, $\omega_\perp \sim 263 cm^{-1}$
- $S = 1$ is the ground-state up to $h \sim 0.5$ Å

Magnetization constrained

Partial geometrical relaxation,
$M_S = 1$



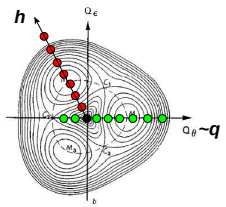


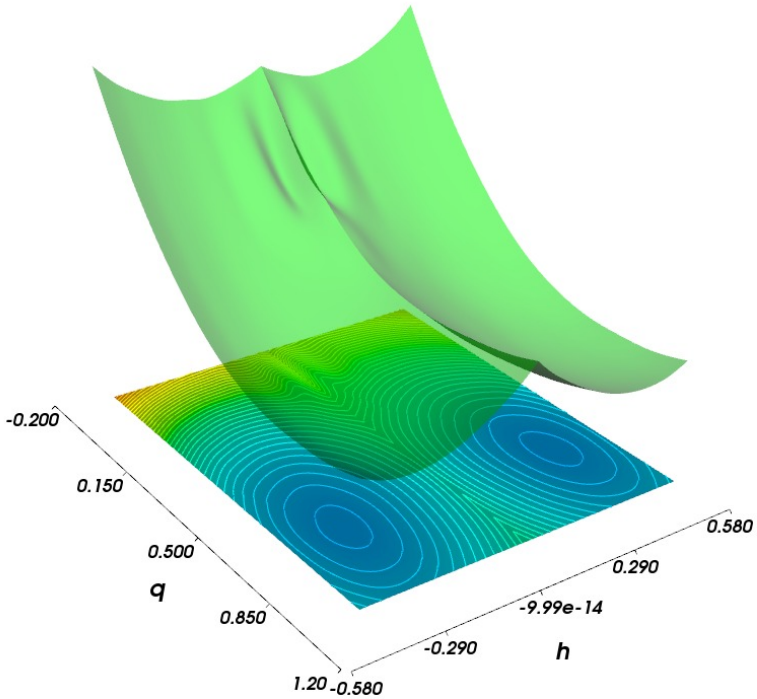


- triplet is stable
- singlet is bistable
- $S = 1$ is the ground-state up to $h \sim 0.5$ Å

Magnetization constrained

Partial geometrical relaxation,
$M_S = 0$

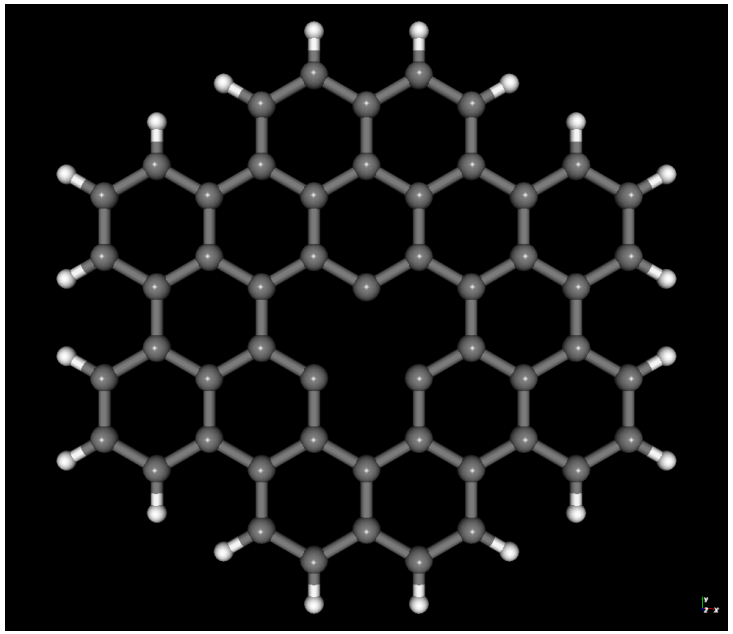




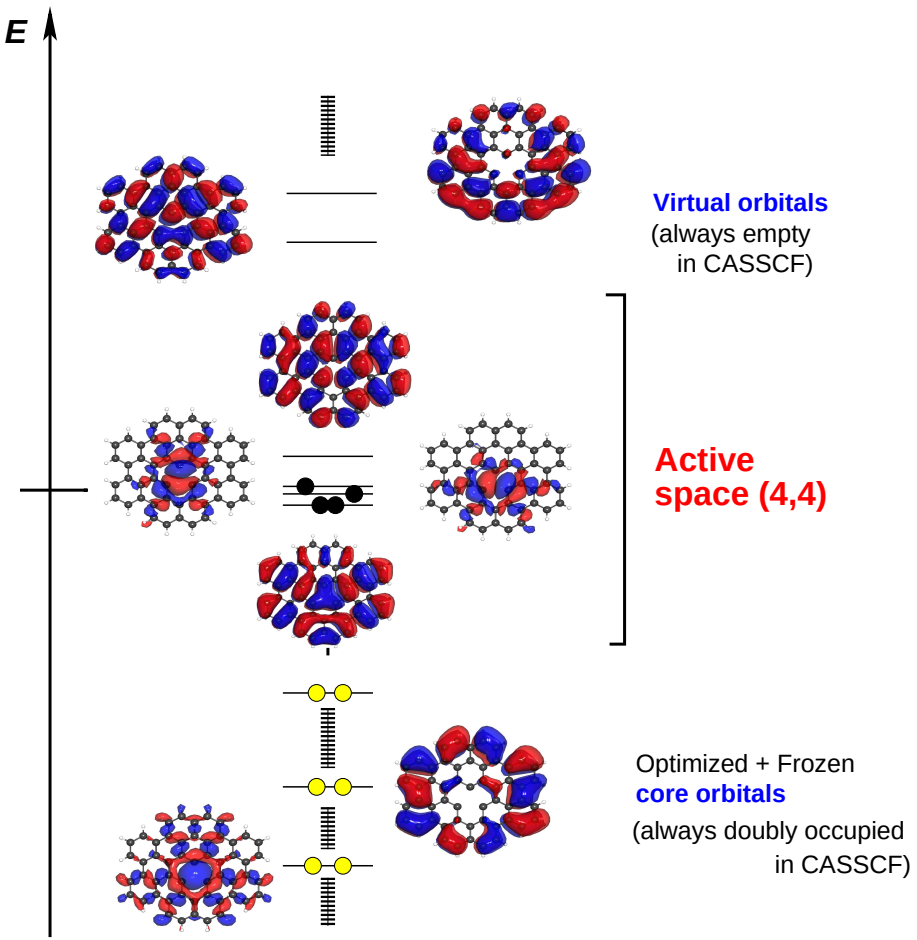
- triplet is stable
- singlet is bistable
- $S = 1$ is the ground-state up to $h \sim 0.5$ Å

Technicalities

- Finite cluster (53 C atoms + 23 H atoms passivating the edges)
- Cluster shape selected in order to avoid ‘edge effects’
- DFT optimized geometries
- Wavefunction-based pertubation theory: CASPT2

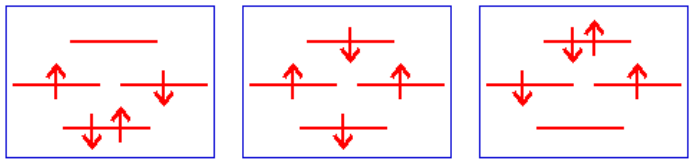


CASPT2 approach



Step 1. multideterminant CASSCF wavefunction: full-CI in the Active Space

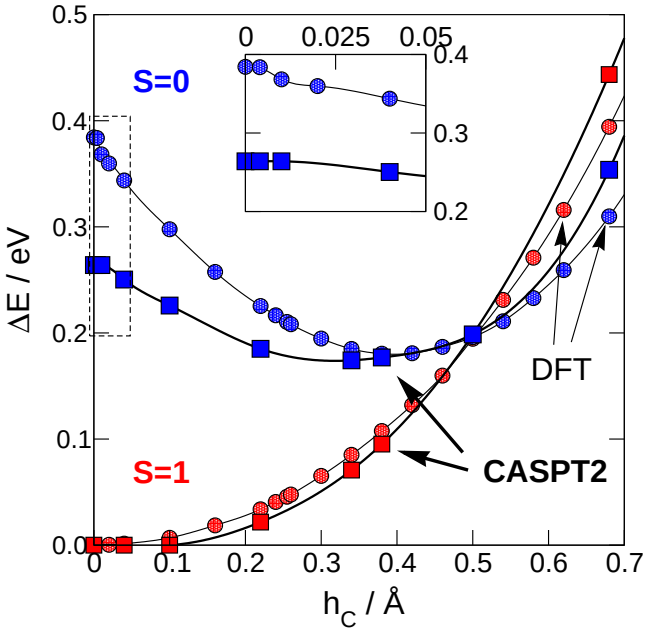
e.g. for the singlet in planar configuration

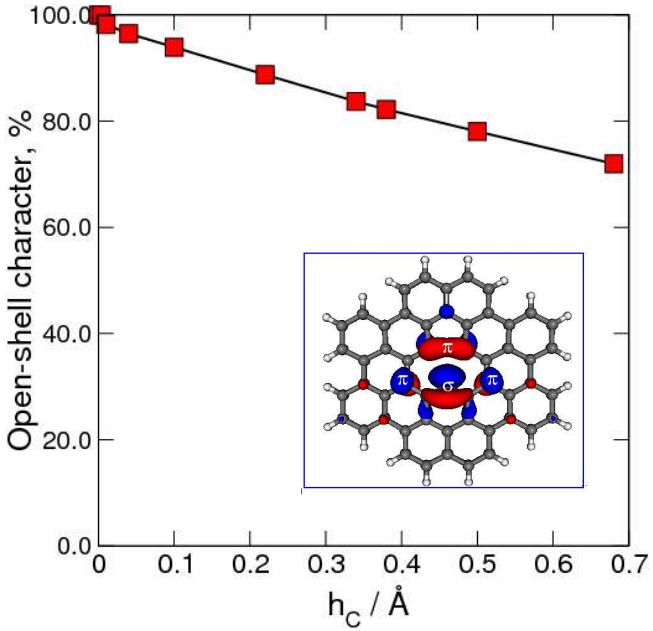


Step 2. build H_0 and compute 2^{nd} order perturbative correction

e.g. include up to double excitations to virtuals

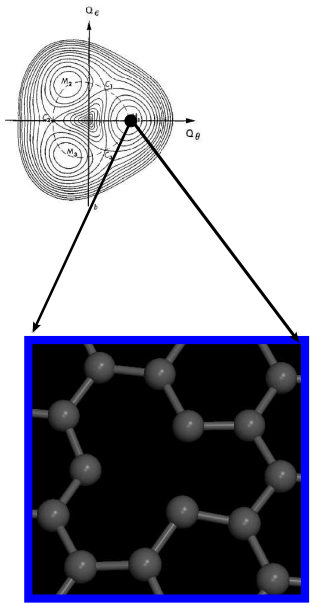
CASPT2 results

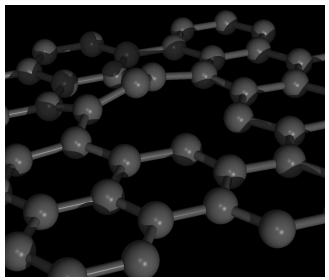


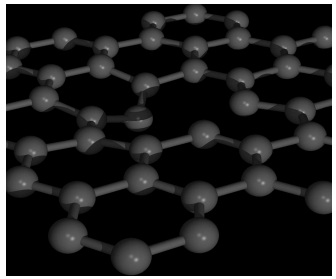


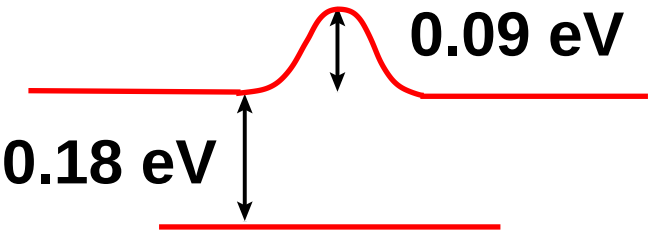
- Magnetization constrained DFT results are reliable
- Accurate energies from CASPT2
- Singlet-state has a dominant open-shell character, $\Psi \propto (\sigma\pi + \pi\sigma)(\alpha\beta - \beta\alpha)$

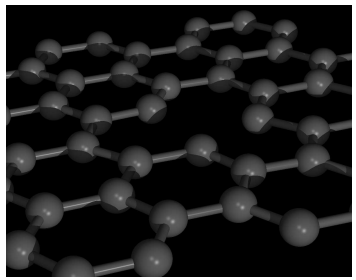
CASPT2 results





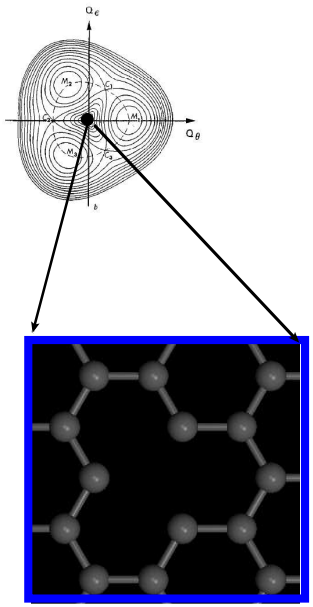


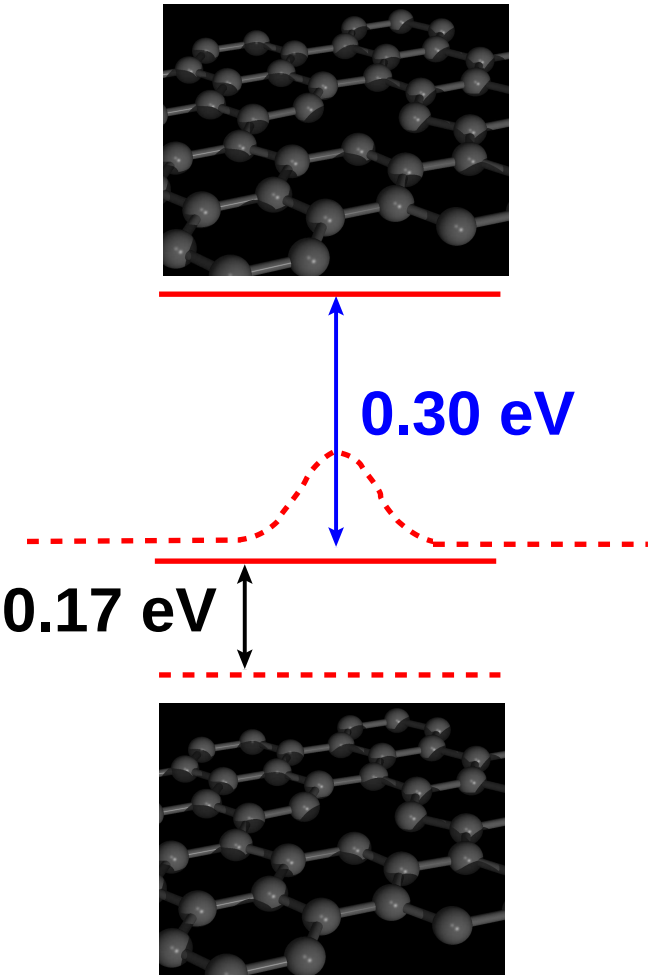




Exchange coupling constant (ground-state minimum):
$\sim$ 0.2 eV

CASPT2 results





Exchange coupling constant (D_{3h}):

$\sim$ 0.3 eV

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Singlet state hardly affects M

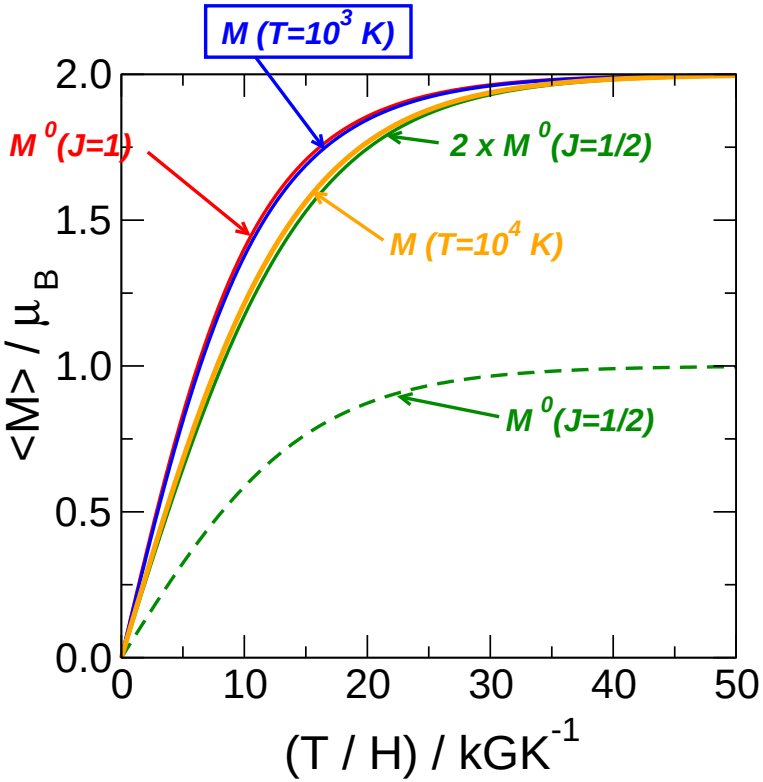
$$\Delta E_n = \mu_B \langle n|L_z + g_0 S_z|n\rangle H + \sum_{n' \neq n} \frac{|\langle n|L_z + g_0 S_z|n'\rangle|^2}{E_n - E_{n'}} H^2 + \frac{e^2}{8mc^2} \langle n|r_\perp^2|n\rangle H^2$$

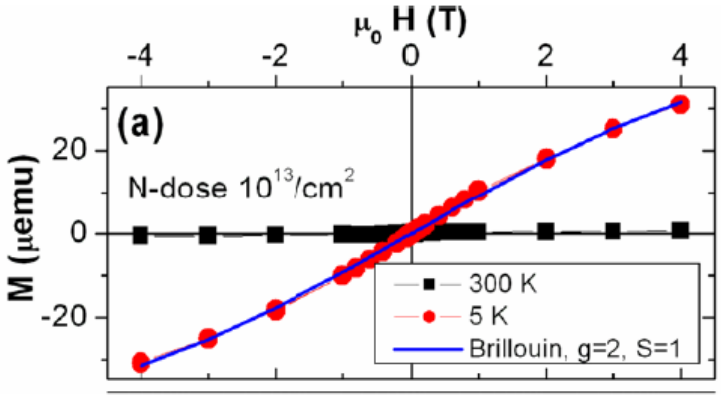
$$M_n = -\frac{\partial E_n}{\partial H} \qquad \langle M \rangle = \sum_n \frac{M_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = -\frac{\partial F}{\partial H}$$

- Angular momentum is quenched ($J = S$), $\gamma = g_0 \mu_B$
- First-order correction to ΔE_n due to $S = 0$ level at energy Δ vanishes
- Only thermal populations are affected,

$$\langle \boldsymbol{M} \rangle = \frac{\boldsymbol{\sinh(\beta\gamma H(J+\frac{1}{2}))}}{\boldsymbol{\sinh(\frac{\beta\gamma H}{2})e^{-\beta\Delta} + \sinh(\beta\gamma H(J+\frac{1}{2}))}} \langle \boldsymbol{M_J^0} \rangle \quad \langle M_J^0 \rangle = \gamma J B_J(\beta\gamma J H)$$

Singlet state hardly affects *M*



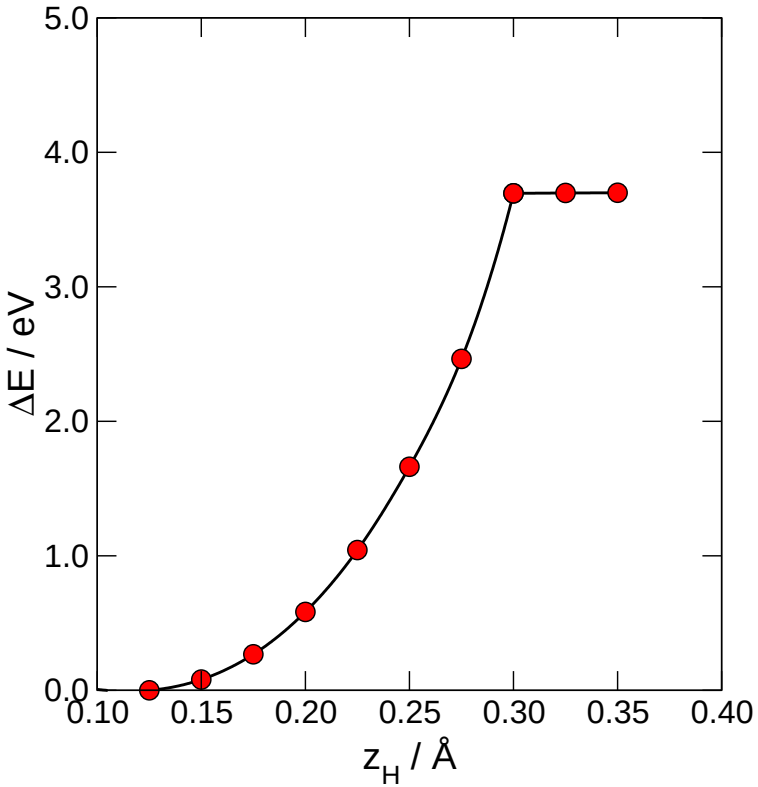


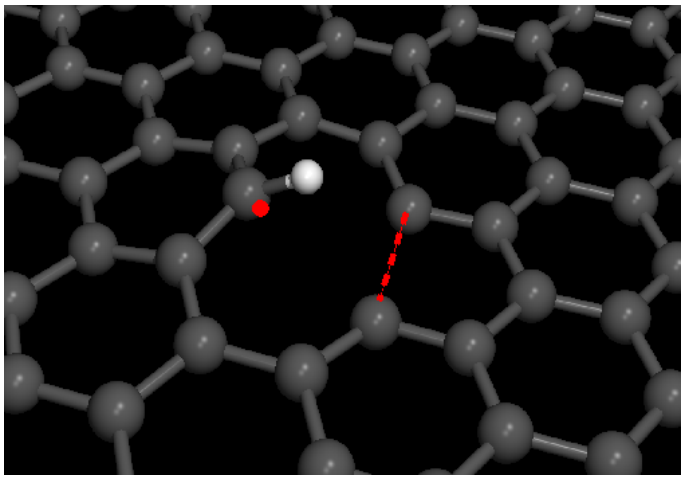
spin-1 paramagnetism in N^+ irradiated FLG

A. Ney *et al.*, *App. Phys. Lett.* **99**, 102504 (2011)

C-vacancy reactivity

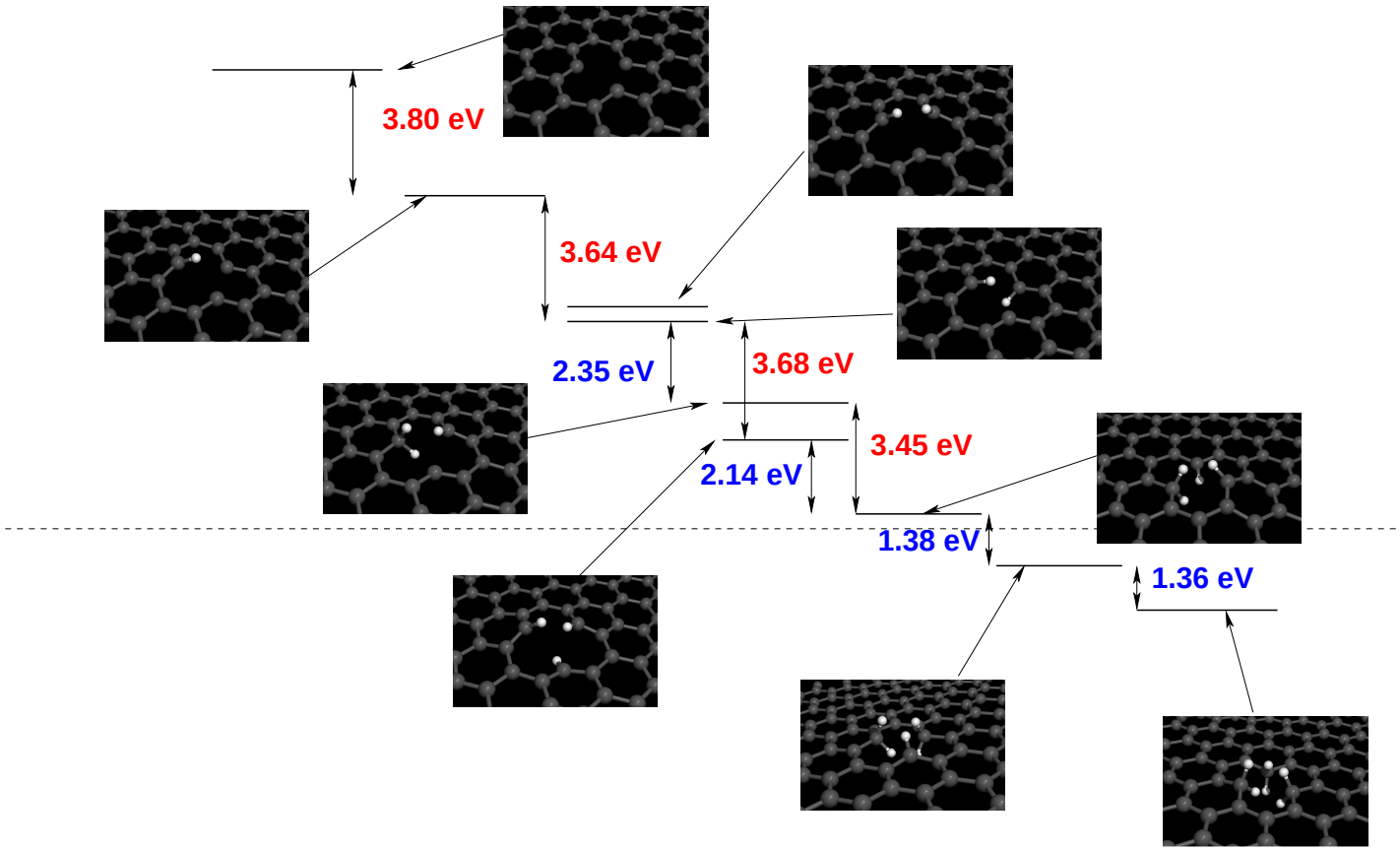
H adsorption on a bare C-vacancy is *energetically* and *kinetically* possible





..a simple (possible) **spin-1/2** paramagnetic species

Hydrogenation



Mono-, **Three-** and **Penta-** hydrogenated vacancies are all **spin-**1/2 species

Summary

- A C-vacancy is more.. than a "p_z vacancy"
- $S = 0, 1$ manifolds have both open shell-character σ^1, π^1
- The singlet is a bistable system potentially useful as solid-state *qubit*
- The bare vacancy is a spin-one paramagnetic species
- Spin-half paramagnetism can be accommodated by chemical bonding to *e.g.* H atoms

Acknowledgements

Marina Casartelli

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+-x:$
C.I.L.E.A
I.S.T.M.

Thank you for your attention!

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