The effect of atomic-scale defects and dopants on Graphene electronic structure

Rocco Martinazzo

Dip. di Chimica-Fisica e Elettrochimica
Universita’ degli Studi di Milano, Milan, Italy

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Outline

1. Introduction
2. Hydrogen adsorption
3. Bandgap engineering

Atomic-scale defects on graphene
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Ionic binding

- DOSs are unchanged except for donor/acceptor levels
- electron / hole doping
- Atomic species are mobile
- Li, Na, K, Cs.. vs Cl, Br, I,..
Covalent binding

- Midgap states show up in the DOSs
- Atomic species are immobile
- H, F, OH, CH$_3$, etc. behave similarly to vacancies

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

See e.g., F. Banhart, J. Kotakoski, A. V. Krasheninnikov, *ACS Nano* 5, 26 (2011)
Vacancies vs adatoms

High-energy $e^-$/ion beams
⇒ *Random* arrangement

Low-energy beams (kinetic control)
⇒ *Clustering* due to preferential sticking
1 Introduction
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Hydrogen chemisorption on graphene

- Sticking is thermally **activated**\(^1,2\)
- Midgap states are generated upon sticking
- Diffusion does **not** occur\(^3,4\)
- Preferential sticking and clustering\(^3,5,6\)

[1] L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
[2] X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)
[3] L. Hornekaer *et al.*, *Phys. Rev. Lett.* **97**, 186102 (2006)
[4] J. C. Meyer *et al.*, *Nature* **454**, 319 (2008)
[5] A. Andree *et al.*, *Chem. Phys. Lett.* **425**, 99 (2006)
[6] L. Hornekaer *et al.*, *Chem. Phys. Lett.* **446**, 237 (2007)
Introduction
Hydrogen adsorption
Bandgap engineering
Summary

Sticking

L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)
Midgap states

..*patterned* spin-density

Atomic-scale defects on graphene
Midgap states

\[ H^{TB} = \sum_{\sigma,ij} (t_{ij} a_{i,\sigma}^\dagger b_{j,\sigma} + t_{ji} b_{j,\sigma}^\dagger a_{i,\sigma}) \]

**Electron-hole symmetry**

\[ b_i \to -b_i \implies h \to -h \]

if \( \epsilon_i \) is eigenvalue and

\[ c_i^\dagger = \sum_i \alpha_i a_i^\dagger + \sum_j \beta_j b_j^\dagger \] eigenvector

\[ \downarrow \]

\[ -\epsilon_i \] is also eigenvalue and

\[ c_i'^\dagger = \sum_i \alpha_i a_i^\dagger - \sum_j \beta_j b_j^\dagger \] is eigenvector

\[ \begin{align*}
    n_A + n_B - 2n_* &= n_* \\
    n_* &
\end{align*} \]
Midgap states

\[ H^{TB} = \sum_{\tau,ij} (t_{ij} a_{i,\tau}^\dagger b_{j,\tau} + t_{ji} b_{j,\tau}^\dagger a_{i,\tau}) \]

**Theorem**

If \( n_A > n_B \) there exist (at least) \( n_I = n_A - n_B \) "midgap states" with vanishing components on B sites.

**Proof.**

\[
\begin{bmatrix}
0 & T^\dagger \\
T & 0
\end{bmatrix}
\begin{bmatrix}
\alpha \\
\beta
\end{bmatrix} =
\begin{bmatrix}
0 \\
0
\end{bmatrix}
\]

with \( T^{n_B \times n_A}( > n_B) \)

\[ \implies T\alpha = 0 \] has \( n_A - n_B \) solutions
Midgap states

$$H^{H_b} = \sum_{\tau,ij} (t_{ij} a_{i,\tau} \dagger b_{j,\tau} + t_{ji} b_{j,\tau} \dagger a_{i,\tau}) + U \sum_i n_{i,\tau} n_{i,-\tau}$$

**Theorem**

If $U > 0$, the ground-state at half-filling has

$$S = |n_A - n_B|/2 = n_i/2$$

**Proof.**

E.H. Lieb, *Phys. Rev. Lett.* **62**, 1201 (1989)

...basically, we can apply **Hund’s rule** to previous result
Midgap states for isolated “defects”

M.M. Ugeda, I. Brihuega, F. Guinea and J.M. Gomez-Rodriguez, *Phys. Rev. Lett.* **104**, 096804 (2010)
Midgap states for isolated “defects”

\[ \psi(x, y, z) \sim 1/r \]

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

Atomic-scale defects on graphene
Dimers

S. Casolo, O.M. Lovvik, R. Martinazzo and G.F. Tantardini, *J. Chem. Phys.* **130** 054704 (2009)
Introduction

Hydrogen adsorption

Bandgap engineering

Summary

Dimers

[1] L. Hornekaer, Z. Sljivancanin, W. Xu, R. Otero, E. Rauls, I. Stensgaard, E. Laegsgaard, B. Hammer and F. Besenbacher. *Phys. Rev. Lett.* **96** 156104 (2006)

[2] A. Andree, M. Le Lay, T. Zecho and J. Kupper, *Chem. Phys. Lett.* **425** 99 (2006)
Clusters

\[ \mu = 1\mu_B \Rightarrow \mu = 2\mu_B \Rightarrow \mu = 3\mu_B \]
Clusters

A\textsubscript{2}B

A\textsubscript{3}

Atomic-scale defects on graphene
Role of edges

- *zig-zag* edge sites have enhanced hydrogen affinity
- geometric effects can be investigated in small graphenes
Role of edges

imbalance `PAHs`

balanced PAHs
Role of edges

imbalance ‘PAHs’

balanced PAHs
Role of edges: graphenic vs edge sites
Role of edges: graphenic vs edge sites
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Band-gap opening

- **Electron confinement**: nanoribbons, (nanotubes), etc.
- **Symmetry breaking**: epitaxial growth, deposition, etc.
- **Symmetry preserving**: “supergraphenes”
Band-gap opening

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**e-h symmetry**

\[ H^{TB} = \sum_{\sigma,ij} (t_{ij} a_{i,\sigma}^{\dagger} b_{j,\sigma} + t_{ji} b_{j,\sigma}^{\dagger} a_{i,\sigma}) \]

**Electron-hole symmetry**

\( b_i \rightarrow -b_i \iff h \rightarrow -h \)

If \( \epsilon_i \) is eigenvalue and
\n\[ c_i^{\dagger} = \sum_i \alpha_i a_i^{\dagger} + \sum_j \beta_j b_j^{\dagger} \] eigenvector

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\(-\epsilon_i\) is also eigenvalue and
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\[ \begin{align*}
&n^* = n_A + n_B - 2n^* \\
&n^* = n^* \\
&n^* = n^* \\
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&n^* = n^* \end{align*} \]
Spatial symmetry

\[ G_0 = D_{6h} \]

\[ G(k) = \{ g \in G_0 | gk = k + G \} \]

\[ \Rightarrow G(K) = D_{3h} \]
Spatial symmetry

$r$-space

$k$-space

\[ G_0 = D_{6h} \]

\[ G(k) = \{ g \in G_0 | g\mathbf{k} = \mathbf{k} + \mathbf{G} \} \]

\[ \Rightarrow G(K) = D_{3h} \]
Spatial symmetry

\[
|A_k\rangle = \frac{1}{\sqrt{N_{BK}}} \sum_{R \in BK} e^{-i k R} |A_R\rangle \\
|B_k\rangle = \frac{1}{\sqrt{N_{BK}}} \sum_{R \in BK} e^{-i k R} |B_R\rangle \\
\langle r | A_R\rangle = \phi_{pz}(r - R)
\]

For \( k = K \) (or \( K' \))

- \( \{|A_k\}, |B_k\rangle \) span the \( E'' \) irrep of \( D_{3h} \)
- Degeneracy is lifted at first order (no \( i \) symmetry in \( D_{3h} \))
Spatial and e-h symmetry

Lemma

*e-h symmetry holds within each kind of symmetry species (A, E, ..)*

Theorem

*For any bipartite lattice at half-filling, if the number of E irreps is odd at a special point, there is a degeneracy at the Fermi level, i.e. \( E_{\text{gap}} = 0 \)*
A simple recipe

- Consider $n \times n$ graphene superlattices (i.e. $G = D_{6h}$): degeneracy is expected at $\Gamma$, $K$
- Introduce $p_z$ vacancies while preserving point symmetry
- Check whether it is possible to turn the number of $E$ irreps to be even both at $\Gamma$ and at $K$
Counting the number of $E$ irreps

$n = 4$

| $\Gamma$ | A          | E          |
|---------|------------|------------|
| $\bar{0}_3$ | $2m^2$     | $2m^2$     |
| $\bar{1}_3$ | $2(3m^2 + 2m + 1)$ | $2(3m^2 + 2m)$ |
| $\bar{2}_3$ | $2(3m^2 + 4m + 2)$ | $2(3m^2 + 4m + 1)$ |

| $K_n$ | A          | E          |
|-------|------------|------------|
| $\bar{0}_3$ | $2m^2$     | $2m^2$     |
| $\bar{1}_3$ | $2m(3m + 2)$ | $2m(3m + 2) + 1$ |
| $\bar{2}_3$ | $2(3m^2 + 4m + 1)$ | $2(3m^2 + 4m + 1) + 1$ |

$\Rightarrow n = 3m + 1, 3m + 2, m \in \mathbb{N}$
An example

(14, 0)-honeycomb
Band-gap opening..

Tight-binding

\[ \epsilon_{\text{gap}}(K) \sim 2t \sqrt{\frac{1.683}{n}} \]

DFT

R. Martinazzo, S. Casolo and G.F. Tantardini, *Phys. Rev. B*, **81** 245420 (2010)
..and Dirac cones

..not only: as degeneracy may still occur at $\epsilon \neq \epsilon_F$

new Dirac points are expected

graphene (4x4)  

(4,0)--honeycomb
..and Dirac cones

..not only: as degeneracy may still occur at $\epsilon \neq \epsilon_F$, new Dirac points are expected.
Antidot superlattices

...the same holds for honeycomb antidots
Antidot superlattices

...the same holds for honeycomb antidots

M. D. Fishbein and M. Drndic, *Appl. Phys. Lett.* **93**, 113107 (2008)

T. Shen *et al.*, *Appl. Phys. Lett.* **93**, 122102 (2008)

J. Bai *et al.*, *Nature Nanotech.* **5**, 190 (2010)
Summary

- Covalently bound species generate midgap species upon bond formation
- Midgap states affect chemical reactivity
- Thermodynamically and kinetically favoured configurations minimize sublattice imbalance
- Symmetry breaking is not necessary to open a gap
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Atomic-scale defects on graphene
Thank you for your attention!