Defective graphene, not so bad after all..

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Outline

1. Introduction

2. H atom adsorption energetics
   - Clusters of H atoms

3. Bandgap engineering
   - Superlattices of H atoms and the like
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Hydrogen is the most abundant element of the Universe

H$_2$ is formed on the surface of dust grain

\[ f_{\text{grain}} = \frac{n_{\text{grain}}}{n_H} \sim 10^{-12} \text{ i.e. } \sim 1\% \text{ of ISM mass} \]

Hydrogen-graphite (graphene) is an important model for understanding H$_2$ formation in ISM
Technology

- Hydrogen storage
- Nuclear fusion
- Nanoelectronics, spintronics, nanomagnetism
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The need for understanding adsorption

H on Graphite (Graphene) vs metal substrates

- Chemisorption is thermally activated\(^1,2\)
- Substantial lattice reconstruction upon sticking\(^1,2\)
- Diffusion of chemisorbed H atoms does not occur\(^3\)
- Preferential sticking\(^3\)
- Clustering of H atoms\(^3,4,5\)
- Dimer recombination\(^6\)

Single-H adsorption

Substrate electronic structure

..patterned spin-density
Substrate electronic structure

..patterned spin-density
Substrate electronic structure

Properties of \textit{bipartite} lattices

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

Electron-hole symmetry

\[ b_i \rightarrow -b_i \implies H \rightarrow -H \]

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

\( c_i^{\dagger} \) is eigenvector

\[ \Downarrow \]

\( -\epsilon_i \) is also eigenvalue and
\[ c_i^{\prime\dagger} = \sum_i \alpha_i a_i^{\dagger} - \sum_j \beta_j b_j^{\dagger} \]

\( c_i^{\prime\dagger} \) is eigenvector

\[ n_A + n_B - 2n_* \]

\[ n_* \]
Properties of \textit{bipartite} lattices

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

\textbf{Theorem}

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

\textbf{Proof.}

\[ \begin{bmatrix} 0 & T^\dagger \\ T & 0 \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \] with \( T_{n_B \times n_A} (n_B > n_B) \)

\[ \implies T\alpha = 0 \] has \( n_A - n_B \) solutions
H atom adsorption energetics

Properties of bipartite lattices

\[ H_{Hb} = \sum_{\tau,ij} (t_{ij} a_{i,\tau}^{\dagger} b_{j,\tau} + t_{ji} b_{j,\tau}^{\dagger} a_{i,\tau}) + U \sum_i n_{i,\tau} n_{i,-\tau} \]

Theorem

If \( U > 0 \), the ground-state at half-filling has

\[ S = |n_A - n_B|/2 = n_I/2 \]

Proof.


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

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

![Graphene Dimer Diagram]

\( E_{\text{bind}} / \text{eV} \) for different configurations of dimers in graphene.
H atom adsorption energetics

Dimers


Dimers


(defse@university of milan)
3-atom clusters, etc.

H atom adsorption energetics

Clustering

A\textsubscript{2}B
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Bandgap engineering

Superlattices of H atoms and the like

Basic electronic structure

\[ H \approx -t \sum_{i,\tau} \sum_j a_{\tau i}^\dagger(R_i)b_{\tau}(R_i + \delta_j) + c.c. \]

\[ a_{\tau i} = \frac{1}{\sqrt{N}} \sum_k e^{-ikR_i} a_{\tau}(k) \]

\[ H = -t \sum_{k,\tau} f(k)a_{\tau}(k)b_{\tau}(k) + c.c. \]

\[ H = -t \sum_{k,\tau} \begin{bmatrix} a_{\tau}(k), b_{\tau}(k) \end{bmatrix} \begin{bmatrix} 0 & f(k) \\ f^*(k) & 0 \end{bmatrix} \begin{bmatrix} a_{\tau}(k) \\ b_{\tau}(k) \end{bmatrix} \]
Technology
Device related properties

- **Thickness**: thinnest gate-controlled regions in transistors
- **Mobility**: high-mobility carriers
- **High-field transport**: high saturation velocities
- **Band-gap**: high on-off ratios are not achievable without a bandgap
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Logic applications

\[ n_S = \varepsilon_0 \varepsilon \frac{V_g}{t e} \]

P. Avouris et al., Nat. Mat., 605, 2, (2007)


CNT-FET with ordinary and wrapped around gates
Logic applications

\[ I - V_g \text{ characteristics of a CNT-FET} \]

\[ I = I(V_g, V_{ds}) \text{ GNR-FET} \]
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**

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**Electron-hole symmetry**

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if \( \epsilon_i \) is eigenvalue and
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\[ \begin{align*}
  n_A + n_B - 2n_* \\
  n_*
\end{align*} \]
Spatial symmetry

\[ r\text{-space} \]

\[ k\text{-space} \]

\[ G_0 = D_{6h} \]

\[ G(k) = \{g \in G_0 | gk = k + G\} \Rightarrow G(K) = D_{3h} \]
Spatial symmetry

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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 \( k = K \)

\{ |A_k\rangle, |B_k\rangle \} span the \( E'' \) irrep of \( D_{3h} \)
Spatial symmetry

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\{ |A_k\rangle, |B_k\rangle \} span the \( E'' \) irrep of \( D_{3h} \)
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. \( E_{\text{gap}} = 0 \)

Proof.

Use electron-hole symmetry
A simple recipe

- Consider $nxn$ 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

\[ n = 4 \]

\[ \Gamma: 2A + 2E \quad \Gamma: 2A \quad K: 2A + 2E \quad K: E \]

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

$(14, 0)$-honeycomb

$p_z$ vacancies

2.0 nm
Band-gap opening.

**Tight-binding**

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

**DFT**

..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


..novel transistor?
Summary

Thermodynamically and kinetically favoured H clusters minimize sublattice imbalance.

Defects can be used to open a gap without breaking the substrate symmetry.
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