2 dimensional systems (top-down)

graphene

2 dimensional systems (bottom-up)

graphene

Vazquez de Parga et al., PRL (2008)
1 dimensional systems (top-down)

graphene

Melinda Y. Han, Barbaros Oezyilmaz, Yuanbo Zhang, Philip Kim,
1 dimensional systems (bottom-up)

graphene

Chemically Derived, Ultrasmooth Graphene Nanoribbon Semiconductors
Xiaolin Li,† Xinran Wang,† Li Zhang, Sangwon Lee, and Hongjie Dai*
Science Express (2008)
0 dimensional systems (top-down) graphene

0 dimensional systems (bottom-up)

graphene

Vazquez de Parga et al., PRL (2008)
0 dimensional systems (bottom-up)
polycyclic aromatic hydrocarbons (PAH’s)

Benz[d]ovalene

Coronene

Naphthacene

Chrysene

Ovalene

Triphenylene

Corannulene

Anthracene

Pyrene

Benz[a]pyrene

Benz[a]ovalene
0 dimensional systems (bottom-up)
disk-like polycyclic aromatic hydrocarbons (PAH’s)

R = Alkyl, alkylphenyl etc.

Outline

Nanographenes


Vacancies and voids in graphene and graphene ribbons

Outline

Nanographenes


Vacancies and voids in graphene and graphene ribbons

Theoretical description of graphene

\[ \hat{H} = \sum_i \varepsilon_i \hat{n}_i + \sum_{ij} t_{ij} \hat{c}_i^+ \hat{c}_j \]

\[ t_{ij} = t = 2.5 \text{ eV} \text{ if first neighbors} \]

usually \( \varepsilon_i = 0 \)
Electronic structure of graphene
Nanographenes
Nanographenenes

DOS

Energy/t
Nanographenes

Graphene structure

DOS vs. Energy/t
Nanographenes
Understanding the spectra

\[ \hat{P}_A = \sum_{i \in A} \langle i | i \rangle \quad \hat{P}_B = \sum_{j \in B} \langle j | j \rangle \]

\[ \hat{H} \left( \hat{P}_A + \hat{P}_B \right) \phi = E \left( \hat{P}_A + \hat{P}_B \right) \phi \]

\[ \hat{H} \hat{P}_A | \phi \rangle = E \hat{P}_B | \phi \rangle \text{ and } \hat{H} \hat{P}_B | \phi \rangle = E \hat{P}_A | \phi \rangle \]

\[ H \left( \hat{P}_A - \hat{P}_B \right) | \phi \rangle = E \left( \hat{P}_B - \hat{P}_A \right) | \phi \rangle = -E \left( \hat{P}_A - \hat{P}_B \right) | \phi \rangle \]
Understanding the spectra

\[ \hat{P}_A = \sum_{i \in A} |i\rangle\langle i| \quad \hat{P}_B = \sum_{j \in B} |j\rangle\langle j| \]

\[ \hat{H}(\hat{P}_A + \hat{P}_B)\phi = E(\hat{P}_A + \hat{P}_B)\phi \]

\[ \hat{H}\hat{P}_A\phi = E\hat{P}_B\phi \quad \text{and} \quad \hat{H}\hat{P}_B\phi = E\hat{P}_A\phi \]

\[ H(\hat{P}_A - \hat{P}_B)\phi = E(\hat{P}_B - \hat{P}_A)\phi = -E(\hat{P}_A - \hat{P}_B)\phi \]

What if \( N \) odd, e.g., \( N_A - N_B = 1 \)?

At least 1 state with \( E = 0 \)

Let us consider a state with weight only on sites A:

\[ \hat{H}\phi_A = E\phi_A \]

\[ \hat{H}(\hat{P}_A - \hat{P}_B)\phi_A = -E(\hat{P}_A - \hat{P}_B)\phi_A \Rightarrow \hat{H}\phi_A = -E\phi_A \]

\( \implies E = 0 \)
Understanding the spectra

\[ \hat{P}_A = \sum_{i \in A} |i\rangle\langle i| \quad \hat{P}_B = \sum_{j \in B} |j\rangle\langle j| \]

\[ \hat{H}(\hat{P}_A + \hat{P}_B) |\phi\rangle = E(\hat{P}_A + \hat{P}_B) |\phi\rangle \]
\[ \hat{H}\hat{P}_A |\phi\rangle = E\hat{P}_B |\phi\rangle \quad \text{and} \quad \hat{H}\hat{P}_B |\phi\rangle = E\hat{P}_A |\phi\rangle \]
\[ H(\hat{P}_A - \hat{P}_B) |\phi\rangle = E(\hat{P}_B - \hat{P}_A) |\phi\rangle = -E(\hat{P}_A - \hat{P}_B) |\phi\rangle \]

What if \( N \) odd, e.g., \( N_A - N_B = 1 \)?
At least 1 state with \( E = 0 \)
Let us consider a state with weight only on sites A:

\[ \begin{align*}
\hat{H} |\phi\rangle_A &= E |\phi\rangle_A \\
\hat{H}(\hat{P}_A - \hat{P}_B) |\phi\rangle_A &= -E(\hat{P}_A - \hat{P}_B) |\phi\rangle_A \Rightarrow \hat{H} |\phi\rangle_A &= -E |\phi\rangle_A 
\end{align*} \]

\[ \Rightarrow E = 0 \]

What if \( N_A - N_B > 1 \)?
At least \( N_A - N_B \) states with \( E = 0 \) and weight only on sites A

M. Inui, S. A. Trugman, and E. Abrahams
Triangles vs. hexagons
Triangles vs. hexagons

(a) Triangles

(b) Hexagons

(c) Energy vs. n

(d) Energy vs. n

(e) % Edge vs. n

(f) % Edge vs. n
Electron-electron interactions
Electron-electron interactions

Superatomic Hund's rule
Electron-electron interactions

Hubbard model

\[ H = \sum_{i\sigma} \varepsilon_{i\sigma} \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \]

Mean field self-consistent approximation:

\[ H = \sum_{i\sigma} \varepsilon_{i\sigma} \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + U \sum_{i} \left( \langle \hat{n}_{i\uparrow} \rangle \hat{n}_{i\downarrow} + \langle \hat{n}_{i\downarrow} \rangle \hat{n}_{i\uparrow} \right) + \text{cte} \]

Density functional theory
(GAUSSIAN03)

• Kohn-Sham equations (unrestricted)
• GGA (BLYP) approximation to the functional (avoid hybrids, e.g., B3LYP)
• Saturation of dangling bonds with H
DFT vs mean-field Hubbard

Hubbard model
($U=3.85$ eV, $t=2.5$ eV)
Ferromagnetic order
Lieb’s theorem/
Longuet-Higgins conjecture


In the attractive Hubbard model (and some extended versions of it), the ground state is proved to have
spin angular momentum $S=0$ for every (even) electron filling. In the repulsive case, and with a bipar-
tite lattice and a half-filled band, the ground state has $S = \frac{1}{2} |B| - |A|$, where $|B| (|A|)$ is the
number of sites in the $B (A)$ sublattice. In both cases the ground state is unique. The second theorem
confirms an old, unproved conjecture in the $|B| = |A|$ case and yields, with $|B| \neq |A|$, the first prov-
able example of itinerant-electron ferromagnetism. The theorems hold in all dimensions without even
the necessity of a periodic lattice structure.


(1) The number of unpaired electrons present in the ground state is at least as great as the number of
carbon atoms having a deficiency of valence bonds in any principal resonance structure. (2) With a few
special exceptions, these odd electrons are distributed over just those atoms which have a deficiency
of valence bonds in one or more of the principal resonance structures. (3) In singly charged
hydrocarbon anions or cations the ionic charge is located on just those atoms which bear charges in
the various principal resonance structures.
Ferrimagnetic order
Ferrimagnetic order
Outline
Nanographenes


Vacancies and voids in graphene and graphene ribbons

Vacancies = H adsorption

A few words about ribbons
(armchair)

Basic definitions

\( A_{N_A} B_{N_B} \)

Local imbalance charge: \( N_A - N_B = N_I \)

\[
N_{Z}^{\min} = \left| \sum_{\alpha} N_{I}^{+}(\alpha) + \sum_{\beta} N_{I}^{-}(\beta) \right|
\]

\[
N_{Z}^{\max} = \sum_{\alpha} \left| N_{I}^{+}(\alpha) \right| + \sum_{\beta} \left| N_{I}^{-}(\beta) \right|
\]
Basic scenarios

1. $N^\text{min}_Z = N_Z = N^\text{max}_Z$ : All the voids are of the same sign. The coupling between them is always ferromagnetic and the spin of the ground state is $2S = N_Z$. The splitting with smaller spin states will depend on the inter-void coupling.
Basic scenarios

1. \( N_z^{\text{min}} = N_z = N_z^{\text{max}} \): All the voids are of the same sign. The coupling between them is always ferromagnetic and the spin of the ground state is \( 2S = N_z \). The splitting with smaller spin states will depend on the inter-void coupling.

2. \( N_z^{\text{min}} = N_z < N_z^{\text{max}} \): All the voids of different sign are in proximity and interact, yielding a \( 2S = N_z^{\text{min}} \) state. Calculations will be necessary to ascertain the spin texture in these situations.
Basic scenarios

1. $N_{Z}^{\text{min}} = N_{Z} = N_{Z}^{\text{max}}$: All the voids are of the same sign. The coupling between them is always ferromagnetic and the spin of the ground state is $2S = N_{Z}$. The splitting with smaller spin states will depend on the inter-void coupling.

2. $N_{Z}^{\text{min}} = N_{Z} < N_{Z}^{\text{max}}$: All the voids of different sign are in proximity and interact, yielding a $2S = N_{Z}^{\text{min}}$ state. Calculations will be necessary to ascertain the spin texture in these situations.

3. $N_{Z}^{\text{min}} < N_{Z} = N_{Z}^{\text{max}}$: All the voids of different type are separated and uncoupled. The ground state has $2S = N_{Z}^{\text{min}}$, but the spin-flip gap is negligible since there are uncoupled magnetic moments.
Basic scenarios

1. $N^\text{min}_Z = N_Z = N^\text{max}_Z$ : All the voids are of the same sign. The coupling between them is always ferromagnetic and the spin of the ground state is $2S = N_Z$. The splitting with smaller spin states will depend on the inter-void coupling.

2. $N^\text{min}_Z = N_Z < N^\text{max}_Z$ : All the voids of different sign are in proximity and interact, yielding a $2S = N^\text{min}_Z$ state. Calculations will be necessary to ascertain the spin texture in these situations.

3. $N^\text{min}_Z < N_Z = N^\text{max}_Z$ : All the voids of different type are separated and uncoupled. The ground state has $2S = N^\text{min}_Z$, but the spin-flip gap is negligible since there are uncoupled magnetic moments.

4. $N^\text{min}_Z < N_Z < N^\text{max}_Z$ : There are voids of different sign, but some of them are uncoupled and some not. This is the most general case. The ground state has $2S = N^\text{min}_Z$, but, as in the previous case, the spin-flip gap is negligible since there are uncoupled magnetic moments. Calculations will be necessary to ascertain the spin texture in these situations as well.
Single vacancy: A
Single vacancy: A

\[ \Sigma = \sqrt{\sum_i \langle m_i \rangle^2} \]

\[ \eta = \sum_i \left| \phi_v(i) \right|^4 \]
Spin-charge separation

\[ Q = 0 \]

\[ Q = 1 \]
A and $A_2$
Two vacancies

\[ \Sigma_2^{1/2} \Sigma_1 \]

Distance/a

- **A+A, W=7a, U=2eV**
- **A+B, W=7a, U=2eV**
- **A+B, W=13a, U=2eV**
- **A+B, W=13a, U=4eV**

A+A

A+B
Two vacancies: A and B

(no interactions)
Two voids: A$_2$ and B$_2$ (no interactions)
Large voids with $N_i=0$
Two notches
Single vacancy in bulk graphene

\[ \langle R \rangle = \sum_i |r_i - r_0| |\phi_v(i)|^2 \]

\[ M_d^{A(B)} = \sum_{i \in A(B)} |r_i - r_0| \langle m_i \rangle \]

\[ M_d = M_d^A + M_d^B \]
Single vacancy in bulk graphene

\[ \Delta_S (eV) \]

\[ U=4.5eV \]

(a)

Weigh on sites B

(b)

Distance/a
Finite density of vacancies: Compensated graphene ($N_i=0$)
Future work

- Magnetic structure of more generic PAH’s or nanographenes
- Thermal fluctuations: Superparamagnetism
- Stability of open shell structures (radicals)
- Change of properties when deposited on surfaces
- Devices