Spin chemical physics of graphene

E.F. Sheka
Graphene is an allotrope of carbon. Its structure is one-atom-thick planar sheets of sp2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.[1]. The carbon-carbon bond length in graphene is about 0.142 nanometers.[4].


The real miracle of graphene is that it is a union of two entities: the physical and chemical ones, each of which is unique in its own way.

2D graphene crystal

Graphene molecule

2D Solid state theory: close-shell DFT & PBCs

Spin molecular theory of graphene in one of the CI representations

UHF criteria for distinguishing open-shell systems

**Criterion 1:** misalignment of energy

\[ \Delta E^{RU} \geq 0 \quad \Delta E^{RU} = E^R - E^U \]

R-restricted and U-unrestricted solutions

**Criterion 2:** misalignment of squared spin

\[ \Delta \hat{S}^2 \geq 0 \quad \Delta \hat{S}^2 = \hat{S}_U^2 - S(S + 1) \]

**Criterion 3:** appearance of *effectively unpaired electrons* that cause radicalization of the molecule

\[ N_D \neq 0 \]
Table 1. Identifying parameters of the odd electrons correlation in graphene fragments

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Odd electrons in graphene are correlated !!!

E.F.Sheka, Computational strategy for graphene: Insight from odd electrons correlation
Int. J. Quant. Chem. 112, 3076-3090, 2012
Stretching and breaking of carbon chemical bonds lead to $p_z$ (odd) electrons correlation and molecule radicalization.


*Figure 1* $N_D(R)$ graphs related to the dissociation of $\text{C—C}$ (ethane), $\text{C═C}$ (ethylene), $\text{C═C}$ (propyne), and $\text{N═N}$ (dinitrogen) bonds. AM1–UHF calculations.
At laser excitation, the aromatic benzene molecule with delocalized equal C=C bonds of 1.396Å is transformed into two nonaromatic molecules with two types of localized C=C bonds, short and long, of 1.377Å and 1.415Å in both cases. This is the case of the photo stimulated transformation of previously closed-shell molecule into open-shell one.
Experimental evidences of the UHF peculiarities to be real
UHF and higher level of CI theory

Number of unpaired electrons, $e$

Takatsuka (STO-3G)
Takatsuka (UHF-Sheka)

UHF and higher level of CI theory

E. F. Sheka. 2015
Effectively unpaired electrons are a physical reality.
AFM image of pentacene

Olympicene
Science Daily: May 28, 2012

'Chemical portrait'
(RUDN-Moscow, June 1, 2012).
(Top) Constant-height high-resolution AFM image of the zigzag end of a graphene nanoribbon obtained with a CO-terminated tip. White scale bar: 1 nm. (Bottom) ACS map of one of the zigzag ends of the (15, 3) NGr molecule with bare edges. AM1 UHF calculations.

Sheka, E.F. (2016)
Graphene bubbles

Collection of experiments
Graphene, both crystalline and molecular, belongs to open-shell systems.
UHF well suits quantitative description of open-shell molecules
What is absent in routine spinless calculations?

\[ E_{\text{best estimate}} = E_{\text{HF-SCF}} + \Delta E_{\text{correlation}} + \Delta E_{\text{exc}} + \Delta E_{\text{SO}} + \Delta E_{\text{BOC}} + \Delta E_{\text{ZPE}} + \ldots \]

“Different spins – different space” Loewdin’s ideologem, 1957

Only marked contributions mix spins

L.A. Mück. DN dissertation, Mainz 2012
Many-electron systems

\[
\hat{H}_\text{DCB/DCG} = \sum_i \hat{h}_D(i) + \frac{1}{2} \sum_{i \neq j} g_{ij}^{\text{Breit/Gaunt}}
\]

\[
g_{ij}^{\text{Breit}} = -\frac{1}{2r_{ij}} \left[ \hat{a}_i \cdot \hat{a}_j + \frac{(\hat{a}_i \cdot r_{ij})(\hat{a}_j \cdot r_{ij})}{r_{ij}^2} \right]
\]

Implementing within two-electron integral generating codes, the \(H_{\text{DCB/DCG}}\) operator can be transformed into the Dirac-Fock operator that has the same structure as its nonrelativistic UHF analogue.

\[
\hat{f}_{\text{DHF}}(i) \phi(i) = \epsilon_i \phi(i).
\]

Here, \(\phi(i)\) is the four-component-spinor representation of the one-electron state.

**Figure 3.** Spin density distribution over atoms of phenoxy radical (C₆H₅O) calculated by using different formalisms. ⁷¹ (by kind permission of L. Bučinský). \(\Delta S^2\) constitutes 0.6024.

Coherence and conflicts

Chemistry that is consistent with graphene physics expectations

- **Small mass of carbon atoms** that provides the lightest material under ambient conditions;
- **sp² Configuration of the atoms valence electrons** that provides flat 2D structure of condensed benzenoid units;
- **High strength of C–C valence bonds** that provides exclusive mechanical strength:
  - **Frequencies of the C–C stretching vibrations**
    - ethane ~ 1100 cm⁻¹, C–C bond;
    - ethylene ~ 1600 cm⁻¹, C=C bond;
    - acetylene ~ 2200 cm⁻¹, C≡C bond

\[
\text{graphane} \quad Y_{C-C} = \left( \frac{v_{C-C}}{v_{C=C}} \right)^2 \quad Y_{C=C} = (0.50 \div 0.60)Y_{C=C} \quad \text{graphene}
\]

\[
\text{graphyne} \quad Y_{C≡C} = \left( \frac{v_{C≡C}}{v_{C=C}} \right)^2 \quad Y_{C=C} = (1.8 \div 1.9)Y_{C=C} \quad \text{graphene}
\]
Chemistry that is inconsistent with graphene physics expectations

- Radical character of graphene material that provides peculiar chemical properties;

- Collective electronic system of graphene that prevents from localization of its response on any external impact;

- A high propensity to $\text{sp}^2 \rightarrow \text{sp}^3$ transformation of atoms valence electrons that violates flat 2D structure of condensed benzenoid units;

- Molecular nature of graphene magnetism and mechanics that makes the properties size and shape dependent;

- Topochemical character of intermolecular interaction that complicates graphene standing in media.

Morphological patterning of graphene sheets into nanoribbons, nanomeshes, or quantum dots to induce quantum confinement creates the problem of edges.
“Particularly suspect (to me) in the current literature are calculations tinged by chemical and physical unrealism. In this category I would place numerous claims to be able to tune band gaps by creating bizarre (to me) physical defects and chemical decorations of nanoribbons and graphenes.

Roald Hoffmann, 2013

Two-dimensional semiconducting nanostructures based on single graphene sheets with lines of adsorbed hydrogen atoms

Leonid A Chernozatonskii, Pavel B Sorokin, Jochen W Brüning
Spin chemistry of graphene

Atomic chemical susceptibility distribution over atoms of graphene sheet with bare edges

'Chemical portrait' of a graphene sheet

$N_D = 139e$

E.F. Sheka. Computational strategy for graphene: Insight from odd electrons correlation
Conformism of cyclohexanoid units

Chair          Boat          Twist-boat       Stirrup       Arm-chair
Space-extended two-zone chemical platzdarm

\[ n, k \]

![Graph showing PCE, kcal/mol versus \( n, k \)]

- \( E_{\text{step bp}} \)
- \( E_{\text{cpl}} \)
- Basal plane
- \( H_2\)-framing
- \( H_1\)-framing

[Diagram showing chemical structure]
Stepwise hydrogenation of graphene

Bandgap opening in graphene induced by patterned hydrogen adsorption


E.F. Sheka, N.A. Popova.
J. Mol. Mod. 2012, 18, 3751
Many-factor polyderivatization of graphene
“The ripples lead to a small distortion of the carbon–carbon bonds, which leads to changes in the amplitude of the electron hopping between atoms and to the simultaneous appearance of inhomogeneities in the electronic structure. The whiter atoms indicate that the density of occupied electronic states at the Fermi level is higher at the peaks of the ripples”.

Rodolfo Miranda & Amadeo L. Vázquez de Parga
Locally N-doped graphene monolayer by simultaneously using both the *thermal strain engineering* and the *anisotropic surface stress* of Cu substrate.
Electron stimulated desorption of hydrogen atoms from graphene basal plane in the grounds of the graphene writing that patterns the Center for Nanoscale Materials logo and $cnm$ initials with a line width of 5 nm.

Is graphene a topological insulator?
Band structure of graphene. Fermi level is settled at zero. The bands below (above) the Fermi level are related to the valence (conductive) zones. Two pairs of valence/conductive Dirac cones at K and K' points at the Fermi level.
Spin-polarization of Dirac cones band spectra

Spin-polarized band structure and primitive cell of graphitic carbon nitride \( \text{C}_{14}\text{N}_{10} \) (left) and metal-organic framework \( \text{Ni}_{2}\text{C}_{24}\text{S}_{6}\text{H}_{12} \) (right).

Equilibrium structure and the map of local spin distribution of the \( \text{C}_{14}\text{N}_{10}\text{H}_{4} \) molecule; AM1 UHF calculations.


**Sheka, E.F.** (2016)
UHF and the SOC characteristics
Splitting of the spatial and spin degenerate ground state

Orbital energy, eV

(5, 5) graphene

Landé interval rule

$\varepsilon_{50}(j) - \varepsilon_{50}(j-1) = \alpha_{SL}$

$\alpha_{SL} = (2.75 - 5.19) \text{ kcal/mol}$

125 - 236 meV

E.F. Sheka, 2015

**Ferromagnetism in Hydrogenated Graphene Nanopore Arrays**

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²SPINTEC, CEA/CNRS/UJF-Grenoble 1/Grenoble-INP, 38054, Grenoble cedex 9, France
³Department of Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

(Received 4 August 2011)
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Dirac’s cones of continuous graphene film with average grain sizes of 50, 100, and 150 nm at the K point of graphene Brillouin zone obtained by ARPES mapping. Fermi energy is settled to zero.

Structural views and scheme of the molecular magnet Er(trensal). Color code: orange: Er; blue: N; red: O; grey: C; H atoms are omitted for clarity. From left to right: magnetization curves at normal (black) and grazing (red) orientation of magnetic field with respect to the substrate surface.

Experiments evidence that graphene behaves as a topological insulator.
Coherence and conflicts

Я глубоко благодарна моим коллегам и друзьям, совместная работа и плодотворные споры с которыми способствовали выработке нового взгляда на замечательный углерод по имени графен

Наталии Рожковой
Борису Разбирину*
Дмитрию Нельсону
Анатолию Старухину
Надежде Поповой
Ростиславу Андриевскому
Виктору Бендерскому
Леониду Чернозатонскому
Юрию Лозовику
Елене Орленко

Irek Natkaniec
Krystina Natkaniec-Holderna
Kacper Druzbicki
Maria Terranova
James Tour
Masakazu Aono

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Erkki Brandas
Ilya Kaplan
Ottorino Ori
Jacek Karwowski
Thank you for attention
Elena Sheka

Spin chemical physics of graphene

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